STUDIES ON THERMOPLASTIC ELASTOMERS
With Special Reference To
NATURAL RUBBER - POLYPROPYLENE BLENDS

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BY
BABY KURIAKOSE

RUBBER TECHNOLOGY CENTRE
INDIAN INSTITUTE OF TECHNOLOGY
KHARAGPUR-721302, INDIA
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an Institute of Technology
RAGPUR 721 302 (INDIA)

ER TECHNOLOGY CENTRE

Gram : Technology Kharagp
Phone : Kharagpur 221-224

Prof. Sadhan K. De
Head of the Centre

Dated..............................

CERTIFICATE

This is to certify that the thesis entitled "Studies on thermoplastic elastomers with special reference to natural rubber-polypropylene blends", which is being submitted by Mr. Baby Kuriakose, for the degree of Doctor of Philosophy, to the Indian Institute of Technology, Kharagpur, is a record of bonafide research work carried out by him under my direct supervision and guidance.

Mr. Kuriakose has worked on this research problem for about three years. In my opinion the thesis has fulfilled the requirements according to the regulations and has reached the standard necessary for submission. The results embodied in the thesis have not been submitted for the award of any other degree or diploma. Seven research papers from this thesis have been published/accepted for publication in International Journals.

Sadhan De

(SADHAN K. DE)
7/1/1985

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(BABY KURIAKOSE)

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The subject matter of the thesis has been presented in seven chapters.

The first chapter consists of a brief [illegible] the earlier work in this field and the scope of the present work.

The experimental techniques and the [illegible] equipment used are described in chapter II.

PREFACE

Thermoplastic elastomers are outgrowing in number and applications day-by-day. But the rheological characteristics under different processing conditions and the mechanism of failure during service of these materials have not been fully understood so far. For optimising the processing conditions and for improveing the service performance, a thorough understanding of the rheological behaviour and the mechanism of failure of the material under various processing and service conditions, is quite essential. In this thesis, the rheological behaviour, nature of deformation and mechanism of failure of thermoplastic elastomers, with special reference to those of thermoplastic natural rubber-polypropylene blends, are discussed.

The subject matter of the thesis has been presented in seven chapters.

The first chapter consists of a brief review of the earlier work in this field and the scope of the present work.

The experimental techniques and the details of the equipments used are described in chapter II.

Chapter III consists of the studies on the melt flow characteristics of thermoplastic NR-PP blends.

The morphology of the blends, its effect on mechanical properties and the mode of failure of the blends under tension, tear and abrasion are discussed in chapter IV of the thesis.

Chapter V contains the results of the studies on the effect of fillers on the technical properties and mechanism of failure of the blends.

The effect of blend ratio and extent of dynamic crosslinking on the dynamic mechanical properties of the blends are discussed in chapter VI of the thesis.

Chapter VII consists of the results of the studies on the melt flow characteristics and mechanism of failure under tension, tear and abrasion of the styrenic block copolymer, thermoplastic polyurethane and thermoplastic 1,2 polybutadiene elastomer.

GLOSSARY OF TERMS

A_P	Cross-sectional area of plunger
CBS	N-cyclohexyl-2-benzothiazole sulphenamide
DCP	Dicumyl peroxide
d_c	Diameter of capillary
d_e	Diameter of extrudate
EPDM	Ethylene propylene diene rubber
EVA	Ethylene vinyl acetate
F	Force on plunger
GR	Guayule rubber
4GT	Tetramethylene terephthalate
HAF	High abrasion furnace
HDPE	High density polyethylene
IR	Isoprene rubber
l_c	Length of capillary
LDPE	Low density polyethylene
NR	Natural Rubber

n'	Flow behaviour index
1,2 PB	Thermoplastic 1,2 polybutadiene
PBR	Polybutadiene rubber
PE	Polyethylene
PP	Polypropylene
PTMEG	Poly (tetramethylene ether) glycol
PTMEGT	Poly (tetramethylene ether) glycol terephthalate
Q	Volume flow rate
rpm	Revolutions per minute
SBS	Styrene-butadiene-styrene block copolymer
SEBS	Styrene-ethylene butylene-styrene block copolymer
SIS	Styrene-isoprene-styrene block copolymer
Tg	Glass transition temperature
Tm	Temperature of melting
TPEs	Thermoplastic elastomers
TMT	Tetramethyl thiuram disulphide
TPU	Thermoplastic polyurethane
UTM	Universal testing machine

Vr	Volume fraction of rubber
%	Per cent
η	Shear viscosity
τ_w	Shear stress at wall
$\dot{\gamma}_w$	Shear rate at wall
$\dot{\gamma}_{w,a}$	Apparent shear rate at wall

CONTENTS

CHAPTER - I

INTRODUCTION

Thermoplastics and elastomers are used in a variety of products that find application in automotive, aeronautical, agricultural, domestic, industrial and medical fields. The large spectrum of application of these two types of materials results from the easy and economic processing characteristics of the thermoplastics and higher extents of recovery and better dimensional stability of the elastomers over a wide range of temperatures. But, both thermoplastics and elastomers [illegible] [illegible] products. Thus, the [illegible] have [illegible] [illegible] stability and dimensional [illegible] at high temperatures. These materials do not withstand [illegible] impacts. On the other hand, elastomers are highly flexible, elastic, [illegible] and resilient, but these materials are [illegible] chemically [illegible], after the shaping operation to attain the [illegible] [illegible]. The shaping and [illegible] processes consume both time and energy. The [illegible]

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The elastic and mechanical properties of vulcanized elastomers are attributed to the presence of chemical crosslinks which unite the polymer chains to form a three dimensional network. In TPEs, this type of network is formed by thermally labile physical forces of attraction between the polymer chains, not through chemical bonds. At elevated temperatures, the thermolabile physical bonds break, allowing the molecules to soften and flow under shear and to be formed like a true thermoplastic material. The TPEs contain rubbery domains and resinous thermoplastic domains. The thermoplasticity results from the melting/transition characteristics of the hard thermoplastic domains, while the elastic properties arise from the rubbery phase.

I.1 TYPES OF THERMOPLASTIC ELASTOMERS :

Since their introduction in the 1960's, TPEs have quickly outgrown speciality markets and have rapidly poliferated both in number and in application. The TPE family now consists of the styrenic block copolymers, thermoplastic polyolefins, thermoplastic polyurethanes, thermoplastic polyesters and a number of emerging and borderline polymers. The first thermoplastic elastomer to be developed was a thermoplastic polyurethane[1,2]. The linear styrene-diene block polymer was introduced in 1965[3]. This was followed by the introduction of radial styrene-diene block polymer[4]. Later, the highly unsaturated diene midblock was replaced by ethylene-butylene blocks to produce thermoplastic styrene-ethylene butylene-styrene block polymer[5].

During the same period, thermoplastic polyolefins which are physical blends of polypropylene (PP) and ethylene propylene diene monomer (EPDM), were patented[6-8]. The process of making thermoplastic elastomer by grafting butyl rubber onto low and high density polyethylene (LDPE and HDPE) was reported by Hartman[9]. Thermoplastic elastomers based on a copolyester i.e. a crystalline polyester and an amorphous long chain polyester random block polymer were developed during 1972-73[10,11]. The latest entry into the commercial TPE market is syndiotactic 1,2 polybutadiene (1,2 PB) with low crystallinity[12], even though a large number of other polymers are reported to behave as thermoplastic elastomers[13-17]. Table I.1 gives the years in which the various types of TPEs were introduced[18].

I.1.1 BASIC REQUIREMENTS :

For the block copolymer to behave as thermoplastic elastomer, it is necessary for the two blocks to be sufficiently dissimilar for phase separation to occur, with one phase being rich in one block having elastomeric characteristics and the second phase rich in a block having the characteristics of a thermoplastic material. The compatibility between the two phases is so low that phase separation occurs even when the difference between the cohesive energy densities is quite small. The point in the chain where the blocks are linked together may be found at or near the interface between the two phases. The elastomeric block should have a glass transition temperature (Tg) below the temperature range in which the material is to be used as a rubber. On the other hand, the thermoplastic segment should have a

Tg or Tm well above the required service temperature range. The elastomeric and thermoplastic segments are often referred to as 'soft' and 'hard' segments respectively. Due to phase separation, the hard segments agglomerate into domains which are dispersed in a continuous soft segment. Each of the domain is therefore a terminal point of several hundred elastomer chains and can be regarded as being a pseudocrosslink. The higher Tg or Tm of the hard segment ensures that the elastomeric polydiene centre block is effectively crosslinked until the temperature is raised high enough to cause the hard domains to soften, dissociate and thus be capable of flow during processing. On cooling, phase separation occurs and the domain structure is regained. The complete reversibility of the interchain forces on dissolution and recovery from solution or on heating and cooling is the fundamental attribute of the thermoplastic elastomers.

The olefinic thermoplastic elastomers are either physical blends of an elastomer with a crystalline polyolefin or graft copolymer of the above two. In these types of TPEs also the presence of hard, glassy or microcrystalline domains of the polyolefin provide stiffness and reinforcement, but some degree of crosslinking of the elastomer phase improves the properties. One important advantage of the olefinic TPEs is that a wide range of properties can easily be attained by varying the composition of the blends.

I.1.2 APPLICATIONS OF TPEs :

The development of the TPEs has narrowed the gap between rubber and plastics processing to a hairline for a host of non-tire rubber products. They are also helping to lure a large number of plastic processers, with their faster extruders and presses, into old and new markets that traditionally the rubber processers have competed for themselves. These materials find applications mainly in those products in which the tensile and set properties are not very critical. The TPEs can be successfully used when neither a rubber nor a plastic will do and at the same time where the properties of both are required. They are also making inroads into the markets previously held by vulcanized rubber products and thermoplastic resins. A comparative evaluation of the properties of conventional rubber vulcanizates with those of thermoplastic elastomers has been made by O'Connor and Fath[19,20]. Automotive parts are an important area for thermoplastic elastomers since these materials are having light weight, flexibility, impact resistance and weather resistance[21-23]. Other applications of TPEs include wire and cables, footwear, adhesives, railpads, sealants, hoses, tubings, sheetings, tarpaulins, gears and flexible couplings[24-30].

I.1.3 ADVANTAGES AND DISADVANTAGES OF TPEs :

The major assets of the TPEs are their easy processability, recyclability and the absence of a vulcanization step to develop strength. The TPEs provide a wide range of service temperatures since the Tg of the soft segment is normally in the range of -50° to -70°C and the Tm of the hard phase is in the range of 100° to 250°C, depending on the type of material used. But the TPEs have higher compression set[31], low rate of recovery after large deformation, higher rate of creep and stress relaxation compared with vulcanized elastomers. The upper limit of service temperature is also a limiting factor for the application of TPEs in many fields.

I.1.4 FUTURE PROSPECTS :

During 1980, when the total consumption of both rubbers and plastics declined, sales of TPEs continued to rise towards a projected world-wide figure of about ½ million tons by 1985[32]. The volume of thermoplastic elastomer is around 4% of the total rubber consumption. However, the TPE consumption grows at a rate of about 6.5 to 10% per year, while that of total rubber increases by 2% per year[33,34]. The styrenic block copolymers comprise the largest volume group of the TPEs and are growing at a rate of 9-10% per year. The polyurethane TPEs have grown at a slower rate. The consumption of polyester and polyolefin TPEs are now growing at a faster rate than the styrenic and polyurethane types. The polyolefin TPEs appear to have the best prospects for an increased rate of growth. They are attractive because they have potentially the lowest cost of all the TPEs. A good number of reviews appeared recently and they indicate the growing importance of the TPEs and the interest shown by the technologists world over[35-42].

I.2 THERMOPLASTIC STYRENIC BLOCK COPOLYMERS :

I.2.1 Structure and Types of Styrenic Blocks : The styrenic block copolymers that behave as thermoplastic elastomers are broadly classified as either A-B-A or $(AB)_n$ type polymers, according to the number and distribution of similar repeat units per molecule. In these, the styrenic blocks always form the hard segments which act as virtual crosslinks by providing junction points for the rubbery chain segments and as reinforcing filler. The soft segment may be polybutadiene rubber (PBR), polyisoprene rubber (IR) or ethylene-butylene blocks (EB). Correspondingly, these block polymers are designated as SBS, SIS and SEBS thermoplastic elastomers respectively. These block polymers may be having a linear or radial structure as shown in figure I.1.

I.2.2 Synthesis of Styrenic Blocks : The styrenic b polymers are synthesised by homogeneous anionic polymeri methods described and reviewed by several authors[43-48]. main feature of this polymerisation system is that sponta terminations are avoided through a judicious choice of th experimental conditions, thereby making it possible to co the block sequence and to achieve narrow molecular weigh tribution. The reaction may be initiated either by a mon functional initiator such as butyl lithium or difunction initiator such as 1,4 dilithio-1,1,4,4 tetraphenyl butan These anionic initiators form carbanions in the presence the monomers and suitable solvents. Such reactive speci possess a long life time and hence are termed as 'living banion'. Depending on the functionality of the initiato either three stage or two stage sequential process may b followed. In the three stage process, polymerisation of styrene monomers is initiated by the addition of monofun anionic initiator. One end of the growing chain consist active anion onto which, additional monomers add to form longer anionic chain. When all the added styrene monome been reacted, the butadiene monomers are added so that m cules of butadiene add onto the still reactive chain. Wh the butadiene molecules have been consumed, additional s monomers are added and the reaction allowed to continue t all the molecules have reacted. With the use of difunct initiators, it is possible to complete the reaction in two stages, i.e. polymerisation of the butadiene monomers, followed by polymerisation of the styrene monomers.

The radial block polymers are prepared by using monofunctional initiation and a subsequent coupling reaction. In this case, the styrene monomers are polymerised first, followed by the butadiene monomers to form a diblock. This diblock is then reactively coupled with other diblocks to form a radial block copolymer. The use of polyfunctional coupling agents such as dimethyl phthalate, phosphorous trichloride, methyl trichlorosilane, hexachlorodisilane, divinyl benzene etc., and the factors affecting the efficiency and degree of the coupling reaction have been discussed by Hsieh[49] and also by Morton[50].

I.2.3 Structure-Property Relations : The properties of styrenic block copolymers depend on the composition, morphology and type of the diene blocks. The polystyrene and polydiene are inherently incompatible, but the critical block molecular weight required for the domain formation in SBS block polymer was found to be greater than those required for phase separation to occur in a simple mixture of the component blocks[51]. Holden et al[52] observed a twenty fold increase in tensile strength when the composition of the SBS block copolymer changed from molecular weight of 6000-8100-6000 to 10000-53000-10000. Morton et al[53] confirmed that useful thermoplastic elastomer could be obtained from SBS block copolymers when the molecular weight of the polystyrene segments is in the range of 10,000 to 20,000 and that of the polydiene is in the range of 40,000 to 80,000. Later work by Kraus et al[54] have shown that it is the length of the polystyrene blocks that exerts a strong influence on the properties of the block polymer rather than the total molecular weight of the block polymer.

The monomer ratio in the block copolymer is an important factor that exerts a significant effect on the properties. Low polystyrene content of the block copolymer produces stress-strain properties similar to those of uncrosslinked conventional rubbers, but as the polystyrene content is increased, the performance approaches to that of crosslinked rubbers. Polystyrene concentrations between 20 and 40% are usually required for getting good elastomeric properties. The morphology of the two-phase system alters by large changes in the polystyrene content. Inversion of continuous phase occurs as the polystyrene content is increased[55]. Detailed studies of the phase morphology in solvent cast films of SBS block copolymer have revealed five fundamental structures as the polystyrene content is increased[56-58].

These five morphological states are :

1) spheres of polystyrene embeded in a continuous polybutadiene phase.

2) cylinders of polystyrene embeded in a continuous polybutadiene phase.

3) alternating lamellae of polystyrene and polybutadiene.

4) cylinders of polybutadiene embeded in a continuous polystyrene phase.

5) spheres of polybutadiene embeded in a continuous polystyrene phase.

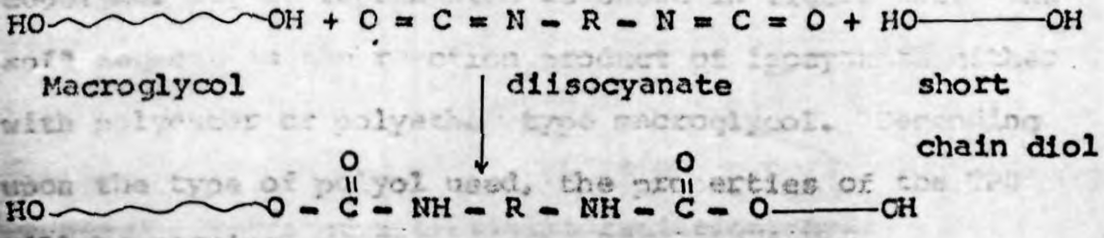
Electron microscopy studies have given futher evidence for the existance of these morphological states[59,60]. Thermodynamic analysis of the formation of the different types of micelle in solution and calculations of the free energy changes required to establish each microstructural form also support the existance of the different morphological states[61-63]. When the polystyrene content is increased, the change from one morphological state to another will not occur instantaneously, but an increasing degree of interconnectivity between the domains will be developed. Electron microscopic observations made by Marker[64] revealed that the thickness of the lamelle is in the range 150A° to 500A°, whereas that of the spherical domains ranges from 100A° to 300A°. It has also been estimated that the size of the spherical hard-segment domains in useful thermoplastic elastomers is about 200A° [65,56]. Controversial observations have been reported on the extent of phase mixing at domain boundaries. Thermodynamic treatments suggest a discrete interface with no intersegmental mixing[63,66,67]. But evidence for the existence of mixed interface or diffuse phase boundaries are also available[68,69].

The nature of the polydiene centre block also affects the properties of the thermoplastic styrenic block copolymers[70]. Both polybutadiene and polyisoprene are useful as the elastomeric segment and in many respects provide similar behaviour. Polyisoprene centre block yields a soft material and shows reduced viscosity relative to polybutadiene[71]. The unsaturation present in the polydiene centre block renders the block copolymer susceptible to attack by oxygen, ozone and U V light. The polybutadiene and polyisoprene centre blocks behave differently on aging, since polybutadiene tends to crosslink and polyisoprene tends to undergo chain scission under the influence of the above mentioned degrading agents. The introduction of ethylene-butylene copolymer midblocks improves the aging, weathering and heat resistance of the thermoplastic styrenic block copolymers considerably.

I.2.4 Compounding : Thermoplastic styrenic block copolymers allow tailoring of physical properties through compounding. Addition of resins such as polystyrene increases the hardness and modulus but the tensile properties are largely unaffected. Paraffinic and naphthenic oils reduce the tensile strength and abrasion resistance but improve the flow characteristics. Blending of polymers such as ethylene vinyl acetate (EVA), EPDM, polychloroprene and polypropylene with SBS block copolymer improves its ozone resistance[72]. Reinforcing fillers such as carbon black and precipitated silica are reported to reduce melt flow and tensile strength at room temperature[73]. But these fillers improve the hot tear and tensile strength. The use of various types of antioxidants and UV stabilizers to improve the aging characteristics of the styrenic block copolymers has been described by Mak et al[74].

I.3 THERMOPLASTIC POLYURETHANE :

I.3.1 Structure and Types : Thermoplastic polyurethane (TPU) is a block copolymer formed by the addition reaction of a diisocyanate with a long chain macroglycol and a short chain glycol which is used as a chain extender. As in the case of the styrenic block copolymers, the thermoplastic elastomer characteristics of TPU results from the presence of soft and hard segments in the block copolymer. The soft flexible chains are formed by the reaction between the isocyanate and macroglycol and the hard segments by the reaction between the isocyanate and the chain extender. The basic reactions involved in the formation of the TPU are given below.



$$HO\sim\sim\sim OH + O=C=N-R-N=C=O + HO-\!\!-\!\!-OH \longrightarrow HO\sim\sim\sim O-\overset{\overset{O}{\|}}{C}-NH-R-NH-\overset{\overset{O}{\|}}{C}-O-\!\!-\!\!-OH$$

The macroglycol usually used in the above reaction is polyethylene adipate, polytetramethylene glycol, polypropylene glycol or polycaprolactone glycol ester. The diisocyanate used is diphenyl methane 4-4'diisocyanate, while the chain extender commonly used is 1,4 butane diol. For getting flexible elastomer chains, the molecular weight of the macroglycol should be in the range 1000 to 3000. It has been postulated that intra and inter segmental hydrogen bonding is responsible for the thermoplastic elastomer characteristics of the TPU[75,76]. But studies using x-ray diffraction[77] and electron microscopy[78] and the evaluation of the dynamic mechanical properties[79] have indicated the presence of domains of highly crystalline regions in the polymer, along with the soft segments. The regions of hard segments have been found to be in the range of 3-100A° in width[78]. The crystalline regions formed by aggregates of the hard segments act as crosslinks at ambient temperature and are realized to contribute significantly to the elastic nature of the TPU. The microphase separation leads to the clustering of the hard segments and the structure of the block copolymer may be represented as shown in figure I.2. The soft segment is the reaction product of isocyanate either with polyester or polyether type macroglycol. Depending upon the type of polyol used, the properties of the TPU will be varying.

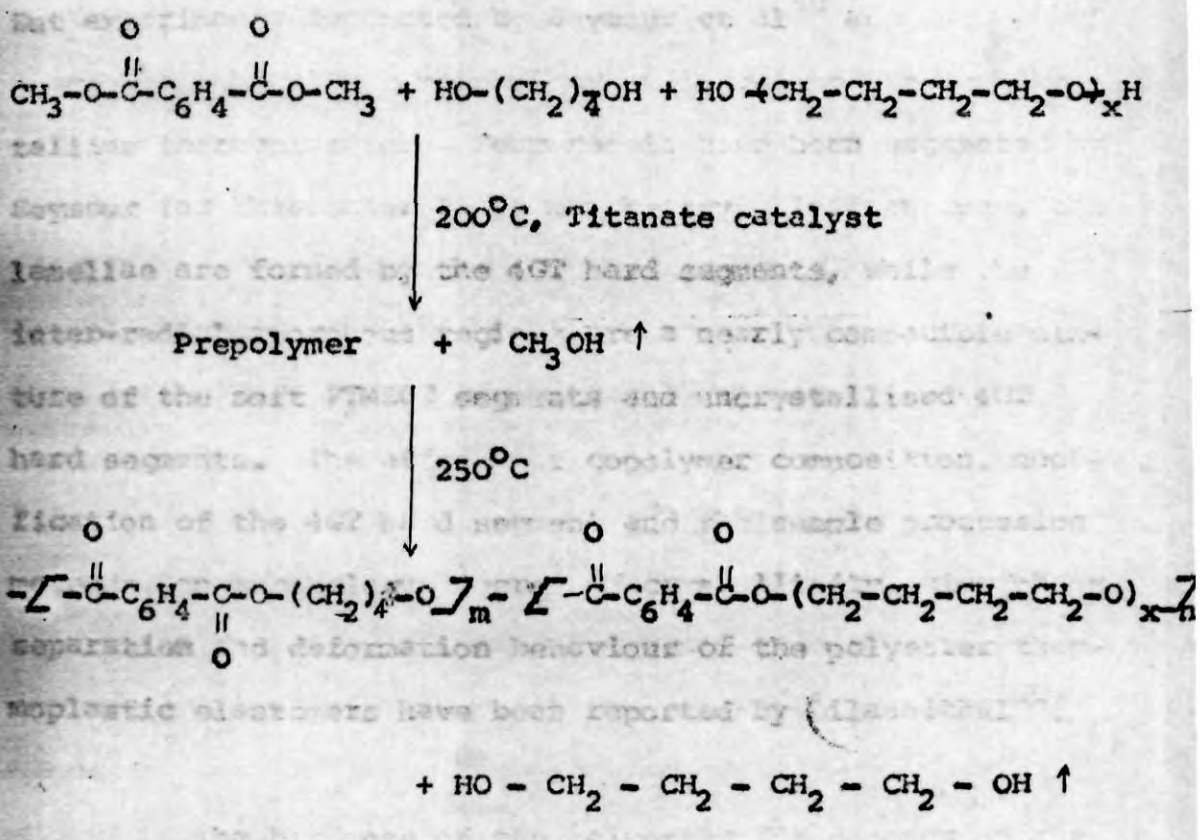
I.3.2 Properties of Thermoplastic Polyurethanes : Thermoplastic polyurethanes have excellent abrasion resistance, load bearing capacity and general toughness. Being polar, these materials also possess good oil resistance. But they have less heat stability and higher set. Polyester based TPU exhibits better abrasion resistance, mechanical properties and oil resistance, but worse hydrolytic stability, heat build-up and low temperature properties than polyether based TPUs[80-81]. The Achilles heel of polyester type TPU is its susceptibility to hydrolytic break down. Among the TPUs based on polyester macroglycol, those produced from a polycaprolactone glycol ester show relatively high resistance to hydrolysis. The hydrolysis reaction can occur at polyester linkage or at the urethane linkage[82,83]. Polycarbodiimide is found to be an effective antihydrolysis stabilizer as it neutralises the carboxylic acid groups which are autocatalysts for the hydrolytic breakdown of the polyester linkage.

TPUs are chemically saturated and hence are less susceptible to ozone attack. But experiments conducted by Wright[84] have revealed that outside exposure deteriorates the material, especially in hot and tropical climates. The failure under the above conditions occurs due to the combined effects of ultraviolet radiation, hydrolytic and microbiological attack. The microbes feed on TPU by excretion of enzymes which catalyse hydrolytic break down. Post curing or annealing of the TPUs improves the tensile strength and decreases creep rate and compression set. Several mechanisms including stress relaxation, crosslinking and rearrangement of the crystalline structures have been put forward to explain the observed increase in properties of TPU after post curing/annealing[85]. The limitations of TPU are poor resistance to strong acids and oxygenated solvents such as ketones.

I.4 POLYESTER THERMOPLASTIC ELASTOMERS :

Polyester thermoplastic elastomers are segmented copolyether esters formed by the melt transesterification of dimethyl terephthalate, a polyalkylene ether glycol and a short chain diol. The formation of long hard segments of crystallisable tetramethylene terephthalate (4 GT) is favoured by stoichiometry and these segments act as crosslinks that bind the soft amorphous polyalkylene ether glycol terephthalate into a network, resembling that of a conventional crosslinked elastomer.

I.4.1 Synthesis of Polyester TPEs : Segmented polyether esters are synthesised by a two step, melt condensation process. Normally, dimethyl terephthalate (T), poly (tetramethylene ether) glycol (PTMEG) and 1,4 butane diol (4G) are used for the manufacture of useful polyester thermoplastic elastomers. The molecular weight of the PTMEG is usually in the range of 600 to 3000. In the first stage, a prepolymer is formed by the transesterification of dimethyl terephthalate with a mixture of PTMEG and a stoichiometric excess of the short chain glycol (50% excess of hydroxyl functionality) in the presence of an ester exchange catalyst (titanate type) at 200°C under atmospheric pressure. The methanol formed is fractionated from the reaction mixture. The polycondensation reaction takes place during the second stage at a temperature of 250°C and reduced pressure. The driving force for the polycondensation reaction depends on the effective removal of 1,4 butane diol from the polymer melt. The resulting condensation products are random block copolymers which consist of crystallisable 4GT hard segments and amorphous, elastomeric polytetramethylene ether terephthalate (PTMEGT). A number average molecular weight in the range 25,000 to 30,000 is required to get optimum physical properties. The reactions involved are given below.



$$CH_3-O-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-O-CH_3 + HO-(CH_2)_4OH + HO-(CH_2-CH_2-CH_2-CH_2-O)_xH$$

$$\xrightarrow{200^{\circ}C,\ \text{Titanate catalyst}}$$

$$\text{Prepolymer} + CH_3OH \uparrow$$

$$\xrightarrow{250^{\circ}C}$$

$$-[-\overset{O}{\overset{\|}{C}}-C_6H_4-\underset{O}{\underset{\|}{C}}-O-(CH_2)_4-O]_m-[-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-O-(CH_2-CH_2-CH_2-CH_2-O)_x]_n$$

$$+ HO-CH_2-CH_2-CH_2-CH_2-OH \uparrow$$

I.4.2 Structure-Property Relations : Two morphological models have been proposed for the structure of segmented polyester copolymer. Cella[86] suggested that continuous and interpenetrating crystalline and amorphous regions exist, where the randomly oriented and interconnected lamellar hard segments serve to anchor the elastomeric portions of the molecule and thus provide physical crosslinking. Using electron micrographs, Cella[87] has shown that the hard phase lamellae is approximately 100A° in thickness, while their length may be upto several thousand Angstroms. The structure suggested by him is schematically shown in figure I.3. But experiments conducted by Seymour et al[88] and Shen et al[89] suggest a spherulitic morphology analogous to the semicrystalline thermoplastics. Four models have been suggested by Seymour for this spherulitic morphology. In each case, the lamellae are formed by the 4GT hard segments, while the inter-radial amorphous regions are a nearly compatible mixture of the soft PTMEGT segments and uncrystallised 4GT hard segments. The effects of copolymer composition, modification of the 4GT hard segment and the sample processing methods, on morphology, degree of crystallinity, microphase separation and deformation behaviour of the polyester thermoplastic elastomers have been reported by Lilaonitkul[90].

The hardness of the polyester TPE depends on the proportion of the hard and soft segments. The softest one (40 shore D) has about 30% 4GT hard segment and the hardest grade (72 shore D) has about 82% hard segments. The melting point, modulus, solubility, resistance to creep and set are largely determined by the nature of the hard segment and its concentration[91]. As the molecular weight of the polyalkylene ether glycol is increased, the 100% modulus passes through a minimum and the tensile strength and elongation at break, a maximum at intermediate molecular weight. The tear strength is high and the resistance to low temperature stiffening poor at lowest PTMEG molecular weight. A molecular weight in the range of 1000 to 2000 was found to give the best balance of properties. The polyester TPEs have better tensile properties at higher temperatures, lower compression set and better chemical resistance compared with TPU of equal hardness. But like TPU, these materials are also susceptible to fungal attack, hydrolysis by moisture and degradation by oxygen and UV radiation.

I.5 POLYOLEFIN THERMOPLASTIC ELASTOMERS :

The polyolefin based thermoplastic elastomers are either physical blends or grafts of a thermoplastic material such as PP and HDPE with an elastomer such as EPDM and natural rubber (NR). These materials are prepared by intensive mixing of the components in an internal mixer at high rates of shear, above the melting point of the polyolefin.

I.5.1 POLYOLEFIN THERMOPLASTIC ELASTOMER GRAFTS : For getting thermoplastic elastomer behaviour, a graft copolymer should have a rubbery component whose Tg is well below room temperature and a hard segment whose Tg or Tm must be higher than the upper limit of service temperature. Crystalline polymers are preferred to glassy ones for the hard blocks since the Tm is usually much sharper and well defined than Tg. Composite materials with natural rubber chemically bonded to a hard polymer such as polymethyl methacrylate or polystyrene were commercially produced long time back[92]. But these materials are not classified as TPEs since the structure of these consists of a small number of very long hard polymer chains attached to the NR backbone in an irregular fashion. A significant portion of the backbone chain may not have any graft chain at all. Thus the basic requirement for getting thermoplastic elastomer characteristics by grafting is that the graft copolymer should have a fairly large number of short hard polymer chains attached to each rubbery backbone.

I.5.1.1 Butyl Rubber - Polyethylene Grafts : Hartman et al[9] were the first to report the synthesis of a thermoplastic elastomer by the grafting method. Butyl rubber was grafted onto LDPE and HDPE using brominated hydroxymethyl phenol. Graft copolymers having compositions of 75:25 and 50:50 polyethylene : butyl rubber were prepared by them. The grafted material retained much of the aging and chemical resistance of polyethylene and could be processed as a thermoplastic. The stress-strain and mechanical properties of these materials are close to those of elastomers. In general, the properties of the grafted TPEs were dependent on both the butyl rubber content and on the type of polyethylene used. The grafted materials containing low density polyethylene were more elastomeric than the high density polyethylene grafts. The limitations of these materials are the amber colour and lack of 'snap back' characteristic of true elastomer.

I.5.1.2 Metalated Polydiene - Polystyrene Grafts : Falk et al[93] reported that polydienes may be metalated under mild reaction conditions to form metalated polymer with no degradation of the polydiene. These metalated dienes can initiate the polymerisation of styrene or α-methyl styrene to form graft copolymers. Graft copolymers of polystyrene and EPDM rubber could also be prepared by this technique. The physical properties of the graft copolymers are functions of melecular weight of the components, graft site level and composition. Products at specific compositions and graft levels are thermoplastic elastomers. Their properties are reported to be comparable to those of SBS block copolymers and they have an advantage of high melt flow characteristics.

I.5.1.3 Polypivalolactone-Elastomer Grafts : Thermoplastic elastomers consisting of elastomeric base polymers grafted with polypivalolactone [poly (2-2 dimethyl propiolactone)] have been described by several authors[94-96]. The elastomeric backbone polymer containing pendent carboxyl or carboxylic acid anhydride groups are reacted with tetrabutyl ammonium hydroxide in a solvating solvent such as tetrahydrofuran. The carboxyl-tetrabutyl ammonium ion pair then initiates the ring opening polymerisation of pivalolactone, forming the grafted copolymer. The morphology of the copolymer consisted of discrete crystallites in a continuous elastomeric phase. The polypivalolactone segments crystallize into discontinuous domains which become points of reinforcement and crosslinking. The EPDM-polypivalolactone grafts were reported to retain a good level of properties even at 100°C. The preparation and properties of polypivalolactone graft copolymers based on elastomeric polyacrylates have been described by Caywood[97].

I.5.1.4 Natural Rubber - Polystyrene Grafts : The usual method to prepare graft copolymer thermoplastic elastomer is to polymerise the hard segment monomer from backbone initiation sites by 'living polymer' techniques. But the high sensitivity of this carbanion propagation method to the non-rubber constituents present in natural rubber precludes the application of this method for the preparation of the thermoplastic natural rubber grafts. Hence scientists at the Malayasian Rubber Producers Research Association, have adopted a different approach for the synthesis of thermoplastic natural rubber - polystyrene grafts[98,99]. This method consists of preparing side chains of the graft copolymer as a separate synthesis and then attaching the prepolymer to the natural rubber backbone through a reactive end group.

The chemical reaction which has been used for the coupling of the prepolymer and the natural rubber backbone is the 'ene' addition of the azodicarboxylate function to an allylic double bond system. The reaction does not rely on the presence of catalysts and is relatively insensitive to the presence of impurities. The preparation of the azodicarboxylate-functional polystyrene has been described by Campbell et al[100]. The azodicarboxylate functional polystyrene having a molecular weight of 7000 to 8000 with one functional group per polymer chain can be reacted with natural rubber either in solution[101] or by direct mixing in an internal mixer[102,99] at high rates of shear and temperature,to produce thermoplastic natural rubber-polystyrene grafts. The basic reaction involved is schematically shown in figures I.4a and I.4b. The azodicarboxylate functional polystyrene is a yellow powder and can be stored for longer periods without the loss of grafting potential. The composition of the graft copolymer, the efficiency of grafting, the molecular weight of the prepolymer etc. are some of the factors that affect the properties of the graft copolymer. A total polystyrene content of 40% and polystyrene molecular weight between 7000 and 8000 were reported to give best balance of processing characteristics and physical properties to the thermoplastic elastomer produced.

I.5.2 POLYOLEFIN THERMOPLASTIC ELASTOMER BLENDS :

The ultimate goal of blending two or more polymers is usually a practical one of achieving materials that are commercially viable, by virtue of having certain properties that cannot be attained by other means or are obtained at lower cost than other means might provide. The preparation of TPEs by blending of polymers is the best example of the application of the above principle. Thus thermoplastic elastomers could be prepared from elastomers which are not thermoplastic and thermoplastics that are not elastomeric, by the process of melt mixing under very high shearing action. Polyolefins such as PP and HDPE, and elastomers such as EPDM and NR are usually used as the blend components. Besides having cost advantages, thermoplastic polyolefin-elastomer blends possess certain definite advantages over other types of TPEs. In these types of blends, the desired properties can be achieved easily by proper selection of the elastomers and plastics components and their ratios in the blend. For example, TPEs having a wide range of hardness could be prepared by adjusting the proportion of the same components of the blend. The range of hardness covered by this type of TPEs is shown in figure I.5.

I.5.2.1 Basic Characteristics of the Components : For getting a wide range of service temperature, the elastomer component of the blend should have a Tg as low as possible and the Tm of the polyolefin should be well above the maximum service temperature of the blend. Elastomers having higher extents of unsaturation are susceptible to degradation during processing and service. In this respect, EPM and EPDM are better than NR or PBR. The Mooney viscosity of the elastomer also affects the processing characteristics and physical properties of the blends. EPDM having a Mooney viscosity in the range of 35 to 100 is reported to be suitable for blending with the polyolefins[103]. Crystalline polyolefins such as PP or HDPE are used as the thermoplastic component of the blends. Isotactic homopolymer and block copolymer PP with melt flow rate between 1 and 20 (230°C, 2.16 kg load) give better balance of processability and physical properties. Higher melt flow rate PP is preferred for making blends requiring more elastomeric characteristics.

Studies conducted by Coran and Patel[104,105] revealed that the properties of the TPE blends depend on the basic characteristics such as critical surface tension for wetting of each components, the weight fraction of crystallinity of the hard phase, the tensile strength of the hard phase and Young's modulus. The difference between the critical surface tension for wetting of the plastic and rubber relates to the interfacial surface energy which controls the size of the particles of one phase dispersed in another. The lower the interfacial tension, the smaller will be the rubber droplets and the finer the dispersion of the rubber particles. The dispersed rubber particles can be considered as flaws in the matrix hard phase. Lower interfacial tension gives smaller rubber particles and hence higher strength. Higher strength due to smaller flaws is the basis of the Griffth equation for material strength[106]. The effect of large surface energy mismatch might also lead to poor adhesion between phases. This could permit cavitation which would interfere with the transfer of recovery stress between the rubber particles and the plastic matrix.

Crystallinity of the polyolefin part of the blend correlates with the stiffness of the uncrosslinked rubber-plastic blends. The effect of crystallinity on the load bearing characteristics of the TPE blend is quite large. Crystallinity might afford a means for rather large deformation in the plastic phase matrix which is the strength member of the composite structure, the deformation being permitted without material failure or fracture. Microcrystalline orientation by yield and draw in the region of a flaw can both dissipate destructive energy and give increased strength in the direction of orientation. The temperature of melting of the crystalline regions determines the maximum service temperature of the thermoplastic elastomer blends.

I.5.2.2 Conditions of Blending : Thermoplastic polyolefin-elastomer blends are usually prepared in an internal mixer under high shearing action. The chamber and the rotors of the internal mixer should be heated to about 100 to 120°C depending upon the type of polyolefin used for preparing the blend. High shearing action during blending builds up heat, which raises the temperature of the mix to the melting point of the polyolefin. Excessive rise in temperature beyond 200°C may cause degradation of the elastomer component such as natural rubber. The elastomer phase of the blend can be crosslinked during blending operation. This process is known as **'dynamic crosslinking'**

Dynamic crosslinking of the elastomer phase is effected by adding crosslinking agents such as peroxide or sulphur in low concentration, after achieving uniform blending of the components. The blending should be continued for some more time so as to get uniform distribution of the crosslinked rubber particles. Antioxidants and process aids, if required can be added before the blend is dumped from the mixer. The hot blend is then sheeted out through a two-roll mill. Elliott[107] has described a process for the continuous production of the thermoplastic natural rubber - polypropylene blends. This is achieved through a combination of an internal mixer and an extruder and by adjusting the batch frequency and extruder throughput.

I.5.2.3 <u>Morphology of the Blends</u> : In two phase polymer blends, it has been established that the phase in highest concentration tends to become a continuous phase when both polymers are of a similar viscosity at the temperature and shear rate of mixing. But at similar concentrations, the polymer with the lower viscosity tends to become the continuous phase[108]. This morphology is common with all heterogeneous polymer blends of two mutually incompatible components. Most of the polyolefin-elastomer blends also show similar morphological features. The main physical factors that control the final morphology of the blends are component ratio, their intrinsic melt viscosity, rate of shear during melt mixing and the presence of other ingradients such as lubricants, extenders and fillers. Studies conducted by Porter et al[109] using phase contrast microscopy on EPDM-PP blends revealed that the elastomer phase forms the dispersed phase at lower concentrations. The size of the dispersed particles was in the range of 0.5 to 5.0 microns. He has also shown that the dispersed particles of rubber undergo deformation under high shear stress that occurs during extrusion and injection moulding of the uncrosslinked thermoplastic elastomer blends. Kresge[110] has reported that in EPM-PP blends, the PP forms a continuous phase even in compositions of 15:85 PP:EPM. Due to higher proportion, EPM also forms a continuous phase, giving a structure having two interpenetrating continuous phases resembling an open-celled sponge with intercommunicating voids filled up with EPM. This type of phase structure results, due to the lower melt viscosity of the polyolefin and higher proportion of the elastomer phase. The morphology of the dynamically crosslinked thermoplastic elastomer blends has not been well understood. However, it is expected that the dispersed elastomer phase in dynamically crosslinked blends may be having a finer particle size and more uniform distribution. This is because, the migration and reagglomeration of the dispersed rubber particles that occur in uncrosslinked blends are restricted in dynamically crosslinked blends as observed by Dao[111].

I.5.2.4 Effect of Dynamic Crosslinking : It was Gessler[112] who introduced the term **'dynamic crosslinking'** for the process of curing the elastomer phase while it is being melt mixed with a thermoplastic resin. Later, Fisher[6, 113] observed that dynamic crosslinking of the elastomer phase improved the physical properties of the blends, especially those pertinent to the elastomeric characteristics. Usually peroxides are recommended as the crosslinking agent, but Coran and Patel [104] have shown that other crosslinking systems are also equally good. Dynamic crosslinking of the elastomer phase improves properties such as tension and compression set, hardness, tensile strength and elongation at break of the TPE blends. Dynamic crosslinking was reported to be helpful in retaining the stiffness of the blend especially at higher temperatures[114]. Elliott[115] has reported that in harder blends, dynamic crosslinking contributes little or not at all to the physical properties and may damage the environmental resistance. The thermoplastic behaviour of the blends is retained even after crosslinking of the rubber phase because the crosslinked rubber remains dispersed in the continuous PP matrix as very small particles.

I.5.2.5 Effect of Compounding Ingredients : Carbon black and other fillers, which act as true reinforcing agents of cured rubbers, do not play any prominent role in improving the strength of the thermoplastic elastomer blends, apart from a general stiffening of the compound and reducing the mould shrinkage[116]. But Zoo[117] has reported that use of precipitated silica improves the abrasion resistance and tensile and tear strength. Fillers generally reduce the elongation at break and the flow characteristics of the blends. Addition of plasticizers improves flexibility. Addition of antioxidants are reported to improve the aging and weather resistance of the TPE blends[74]. For maximum protection, a combination of phenolic or amine antioxidant and a UV absorber is recommended.

I.5.2.6 Melt Flow Characteristics : One of the most important advantages of the TPEs is that these materials can be processed just like the thermoplastics. Hence a reliable knowledge of the rheological characteristics of the blends overa a wide range of shear rate or stress and temperature is of paramount importance in predicting the flow characteristics during processing. Olefinic TPEs have a relatively high melt viscosity compared with that of other thermoplastic materials. This characteristic necessitates the use of higher processing temperatures and pressures during the fabrication of these materials into useful products. These materials exhibit highly non-Newtonian flow behaviour and the melt viscosities are highly sensitive to rate of shear. The melt viscosities are less sensitive to temperature variations above the melting point of the polyolefin. This helps to maintain uniform properties despite fluctuations in processing machine temperature. But, this restricts the use of higher temperatures for reducing the melt viscosity, which is desirable in certain processing operations.

In the case of EPM-PP blends, Porter[109] has observed that when the blend is flowing, the dispersed elements are elongated at the entrance of the capillary under the action of the longitudinal velocity gradient. The deformation and consequent breakdown of the dispersed domains is accompanied by a competetive process of coalescence which is facilitated by the narrowing and the turbulance of the stream at the capillary entrance. If the extrusion rate is sufficiently low to assure a laminar flow, before the exit from the capillary, deformation process of the dispersed component becomes predominant and brings about fine, uniform structures highly elongated in the extrusion direction. As the extrusion rate is increased, the higher values of shear stress facilitate the breakdown process of the dispersed elements oriented in the flow direction and thus producing telescopic structures for blends of intermediate compositions.

Goettler et al[118] have shown that the olefinic thermoplastic vulcanizates behave like highly filled fluids during flow. The dynamically crosslinked blends give lower extrudate swell compared with the uncrosslinked blends. The viscosity follows the power law model over a wide range of shear rate and temperature. The lower die swell is expected to simplify the die design and extrusion sizing. Scanning electron microscopy studies of the extrudates of thermoplastic guayule rubber (GR)-HDPE blends[119] have revealed that at higher shear rates, the size of the GR domains is decreased as it was observed in the case of EPM-PP blends. The viscosity decreased with increase in HDPE content. But the viscosity of the blends was found to be a non-additive function of the viscosity of the components and it was always lower than that predicted by simple linear additivity. The formation of a sheath and core type configuration during extrusion, with the component of lower viscosity forming the sheath, was suggested as one of the reasons for this non-linear additivity of the viscosity of the thermoplastic elastomer blends.

I.6 MISCELLANEOUS THERMOPLASTIC ELASTOMERS :

A large number of materials other than those described in the previous sections also show thermoplastic elastomer characteristics. But many of them are not yet produced on a commercial scale. Materials such as ethylene-vinyl acetate, 1,2 polybutadiene are produced commercially in limited quantities. Various types of ionic thermoplastic elastomers, polysiloxane based TPEs, silicone-polyethylene grafts etc. are also being tried in this field.

I.6.1 Ethylene-Vinyl Acetate Copolymer : Ethylene and vinyl acetate can copolymerise to give polymers having a wide range of composition ratios. But copolymers having 10 to 40% vinyl acetate content only, come under thermoplastic elastomer grade. Higher vinyl acetate content reduces the crystallinity of the polyethylene and the material becomes completely amorphous. Another factor affecting the properties of the copolymer is molecular weight. An increase in molecular weight increases the viscosity, softening point, impact strength, tensile strength and resistance to chemicals. Compared to polyethylene, these materials have better flexibility, toughness and clarity, but have lower dielectric properties, chemical resistance and heat resistance.

I.6.2 **Ionic Thermoplastic Elastomers** : Ionically bonded TPEs are copolymers primarily composed of ethylene molecules with a small amount of a second monomer which contains carboxylic acid groups. When this material is blended with metal oxides or salts, ionic crosslinks are formed, which are strong at normal room temperature but which disappear on heating. The second monomer used is either acrylic acid or methacrylic acid and the quantity of these groups in the copolymer varies from 2 to 10%. The use of monovalent salts to neutralise these carboxylated rubbers apparently gives rise to a modest ionic crosslinks at ambient temperatures but, if heated to 100°C, this structure is dissociated. Use of divalent metal salts gives a network that is considerably stronger. Ionomers such as zinc sulfonated EPDM also show the thermoplastic elastomer characteristics, due to the presence of metal sulfonate groups which are temperature dependent. High temperature and shear dissociate the ionic bonds, thus making it easy for processing by extrusion and injection moulding techniques. The disadvantages of these types of TPEs are higher compression set, higher stress relaxation and limited upper use temperature range.

I.6.3 **Polysiloxane Based Thermoplastic Elastomer** : Block copolymers consisting of short blocks of polystyrene and polydimethyl siloxane behave as TPEs having good low temperature flexibility, excellent electrical properties and weather resistance. In these types of TPEs, the hard and soft segments alternate six to eight times, unlike the SBS triblocks. The hard segments should have a molecular weight of 4000 to 15,000 to get good balance of processing and physical properties. The styrene content usually ranges from 20 to 50%. Use of α-methyl styrene blocks in place of polystyrene provides better tensile properties at a given temperature. Block copolymers having an elastomer block of polydimethyl siloxane and a hard block composed of poly (bisphenol A carbonate) also show TPE characteristics. Polycarbonate contents in these materials range from 35 to 50%. Depending on the polycarbonate content, the properties of the block copolymer change widely. Block copolymers based on a polysulfone hard block and a siloxane soft block are also having the properties of thermoplastic elastomers.

I.6.4 Thermoplastic 1,2 Polybutadiene Elastomer : Polybutadiene having 1,2 content greater than 90% and crystallinity in the range 15 to 25% behaves as a thermoplastic elastomer. This material is prepared by solution polymerisation using Zieglar-type catalyst system. Thermoplastic 1,2 polybutadiene is having a softening point of 80-90°C and is more flexible than LDPE. It can be sulphur vulcanized and is having very good ozone and weather resistance. The film prepared from this material is having better transparency, higher gas permeability, high tear resistance and coefficient of friction compared to those of LDPE and EVA.

Most of the [illegible] been concentrated [illegible] evaluation of the physical properties of these materials. For improving the service performance of any material, a thorough understanding of the mechanism of failure of the material under different conditions of service is quite essential. The major fields of application of TPEs are mechanical moulded goods and footwear, wherein factors such as flexing, tear and wear are the main criteria leading to failure of the product. Examination of the failure surfaces of rubber vulcanizates, plastic materials and epoxy resins using scanning electron microscope had provided valuable information on the mechanism of failure and the mechanism of toughening of plastics by elastomer particles[120-124]. But the mechanism of failure of TPEs has received little attention so far. Since these materials are being used in new fields of application, [illegible] studies on the mechanism of failure shall be [illegible] ing towards the development of new products [illegible] and also for the modification of the TPEs to [illegible] service conditions.

1.7 SCOPE OF THE PRESENT WORK :

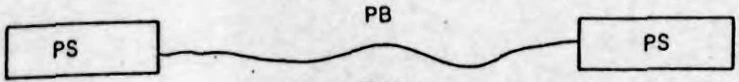
From the foregoing discussion, it is clear that most of the previous work on thermoplastic elastomers have been concentrated on the method of preparation and evaluation of the physical properties of these materials. For improving the service performance of any material, a thorough understanding of the mechanism of failure of the material under different conditions of service is quite essential. The major fields of application of the TPEs are mechanical moulded goods and footwear, wherein factors such as flexing, tear and wear are the main criteria leading to failure of the product. Examination of the failure surfaces of rubber vulcanizates, plastic materials and epoxy resins using scanning electron microscope had provided valuable information on the mechanism of failure and the mechanism of toughening of plastics by elastomer particles[120-124]. But the mechanism of failure of TPEs has received little attention so far. Since these materials are being tried for new fields of application day by day, studies on the mechnism of failure shall be highly rewarding towards the development of new products from the TPEs and also for the modification of the TPEs to meet rigorous service conditions.

One of the important advantages of the TPEs over the conventional elastomers is that these materials can be processed just like the thermoplastics. To take full advantage of this characteristic of the TPEs, it is essential that the processing conditions selected and the equipment used should be standardised to give maximum output. This can be achieved only through an understanding of the melt flow behaviour of the material under different conditions of temperature and rate of shear. So far, no systematic study on TPEs has been conducted.

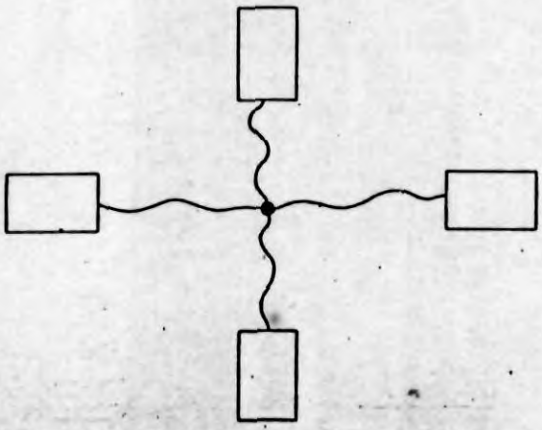
The performance of polymer blends under static and dynamic conditions shall depend on the morphology of the blends. In the case of TPEs which form a two-phase structure, the factors affecting the performance under dynamic conditions have not been fully evaluated, even though some studies on the dynamic mechanical properties of styrenic block copolymers have been reported[125,126]. The morphology-property relations of thermoplastic elastomer blends are also not well understood so far. This thesis presents the results of the investigations on the above aspects of the thermoplastic elastomers. Emphasis has been given for the studies on thermoplastic elastomers from natural rubber-polypropylene blends, since both the components are indigenously available and these types of blends are expected to become the leading ones among thermoplastic elastomers in future.

Table I.1 YEAR OF COMMERCIALISATION OF TPEs

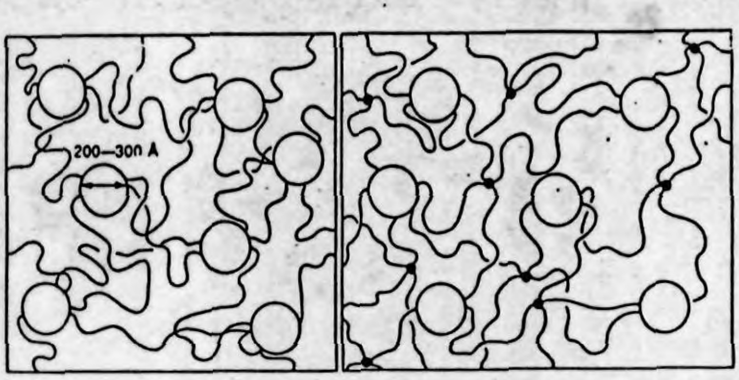
Sl. No.	Type	Year	Company
1.	Thermoplastic Polyurethane Elastomer	1958	Bayer AG
2.	Styrene-Butadiene-Styrene/ Styrene-Isoprene-Styrene Block Copolymer	1965	Shell Chemicals
3.	Styrene-Butadiene-Styrene and Styrene-Isoprene-Styrene Radial Blocks	1968	Phyllips Petroleum Company.
4.	Styrene-Ethylene Butylene-Styrene Block Copolymer	1972	Shell Chemicals
5.	Polyolefins-Elastomers Blends	1972	Uniroyal
6.	Polyester Block Copolymer	1972	Du Pont
7.	1,2 Polybutadiene	1975	Japanese Synthetic Rubber Company



Linear SBS type



Radial (tetrachain) SBS type



Linear type Radial type

FIG.I.1 SCHEMATIC REPRESENTATION OF SBS BLOCK COPOLYMERS.

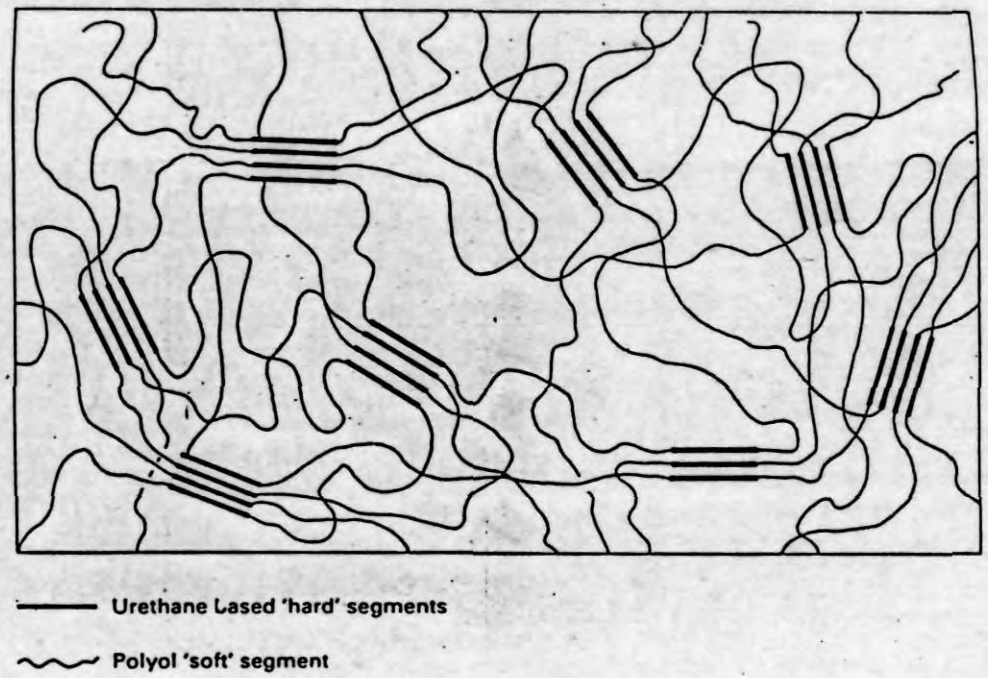


FIG.I.2 *Schematic representation of thermoplastic urethane morphology*

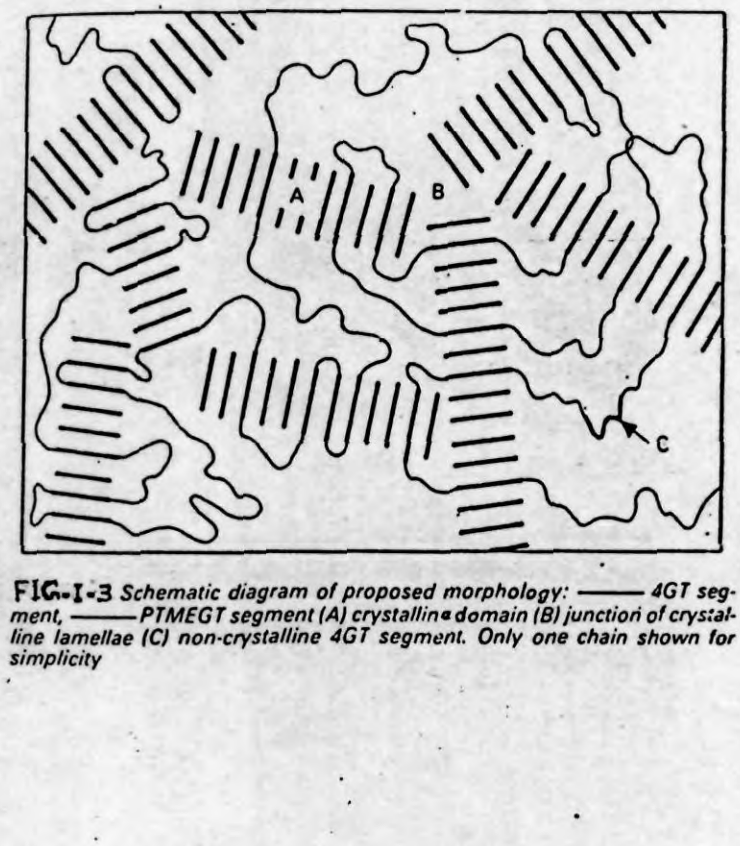


FIG-I-3 *Schematic diagram of proposed morphology: ——— 4GT segment, ———PTMEGT segment (A) crystalline domain (B) junction of crystalline lamellae (C) non-crystalline 4GT segment. Only one chain shown for simplicity*

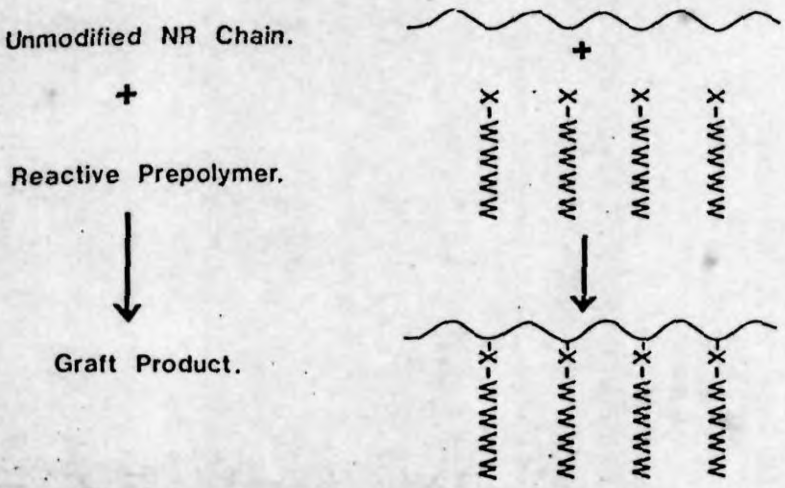


FIG.I.4a method of grafting using reactive prepolymer.

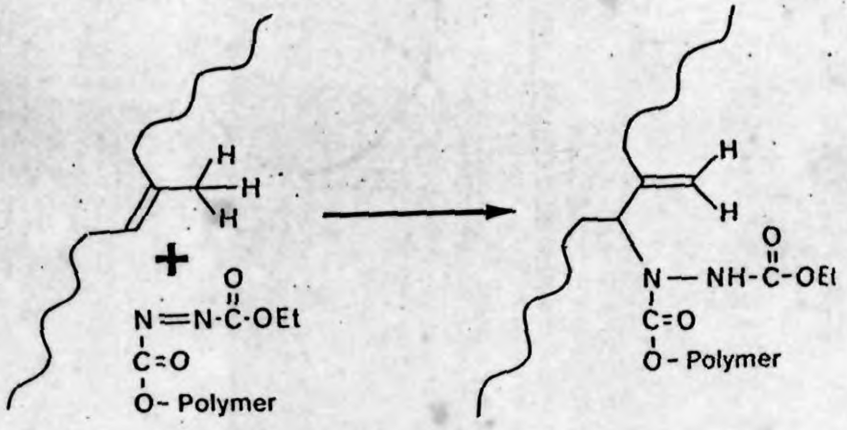


FIG.I.4b 'ene' addition of the azodicarboxylate end group of the reactive prepolymer group to an allylic double bond system.

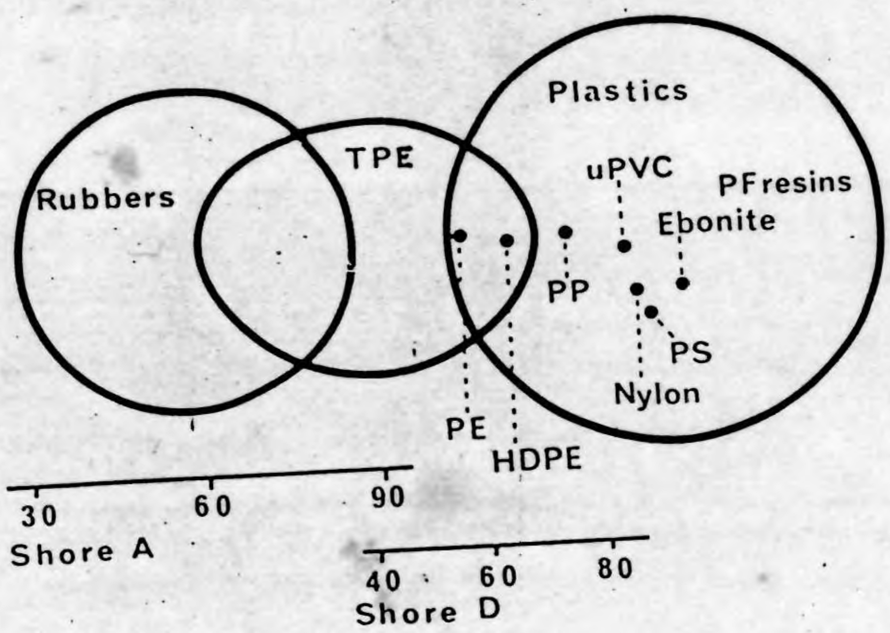


FIG.I.5 Hardness range of TPE, rubbers and plastics.

CHAPTER - II

The details of the materials used and the experi-
chniques adopted in the present investigation are
this chapter.

EXPERIMENTAL TECHNIQUES

MATERIALS USED :

Natural Rubber : The natural rubber used was
ber, was obtained from the Rubber Research Institute
Kottayam. This [illegible] [illegible] the Indian [illegible]-
[illegible] [illegible] [illegible] [illegible] rubber.
tion parameters and their limits for the [illegible]
ural rubber are given in table II.1. Since the
perties such as molecular weight, molecular weight
on and the presence of non-rubber constituents of
bber [illegible]

The details of the materials used and the experimental techniques adopted in the present investigation are given in this chapter.

II.1 MATERIALS USED :

II.1.1 Natural Rubber : The natural rubber used was crumb rubber, as obtained from the Rubber Research Institute of India, Kottayam. This rubber satisfied the Indian standard specifications for ISNR-5 grade natural rubber. The specification parameters and their limits for the ISNR-5 grade natural rubber are given in table II.1. Since the basic properties such as molecular weight, molecular weight distribution and the contents of non-rubber constituents of natural rubber are affected by clonal variation, season, use of yield stimulants and methods of preparation[127,128] rubber from the same lot has been used in a particular experiment.

II.1.2 Polypropylene : The polypropylene used was isotactic polypropylene, Koylene MO030, as obtained from the Indian Petrochemicals Corporation Limited, Vadodara. The properties of Koylene MO030 are given in table II.2.

The basic characteristics of the natural rubber and the polypropylene used in the present investigation are given in table II.3.

II.1.3 Styrene-Butadiene-Styrene Block Copolymer : SBS block copolymer having styrene/butadiene ratio 48/52 and containing about 10% by weight amorphous silica (Kraton D 5152), was received from M/s. Shell Chemical Company, U.S.A.

II.1.4 Styrene-Isoprene-Styrene Block Copolymer : SIS block copolymer having styrene/isoprene ratio 14/86 (Kraton D 1107), was received from M/s. Shell Chemical Company, U.S.A.

II.1.5 Thermoplastic Polyurethane Elastomer : Aromatic ester type thermoplastic polyurethane elastomer (Estane 5715), manufactured by M/s. B.F. Goodrich Company, U.S.A. was received from M/s. Bengal Waterproof Works Ltd., Calcutta.

II.1.6 1,2-polybutadiene : Thermoplastic 1,2-polybutadiene elastomer having 1,2-content about 90% and degree of crystallinity 25% (JSR RB820) manufactured by M/s. Japanese Synthetic Rubber Company, Japan, was received from M/s. Bengal Waterproof Works Ltd., Calcutta.

II.1.7 Rubber Chemicals : Accelerators N-cyclohexyl-2-benzothiazole sulphenamide and tetramethylthiuram disulphide, were commercial grades obtained from M/s. Indian Explosives Ltd., Rishra. Dicumyl peroxide containing 40% active ingredient was obtained from M/s. Bengal Waterproof Works Ltd., Calcutta.

II.1.8 Fillers : High abrasion furnace black (N330) was supplied by M/s. Phillips Carbon Blacks Ltd., Durgapur and precipitated silica, Vulcasil-S, was obtained from M/s. Modi Rubber Ltd., Modipuram.

II.1.9 Other Chemicals : Zinc oxide ($\rho = 5.5$), stearic acid ($\rho = 0.92$) and elemental sulphur ($\rho = 1.9$) used in the present study were chemically pure grade.

II.1.10 Special Chemicals : The silane coupling agent used was Si-69, [Bis (triethoxysilylpropyl) tetrasulphide] obtained from M/s. Modi Rubber Limited, Modipuram.

II.1.11 Solvents : Benzene and toluene used were of analytical grade.

II.2 PREPARATION OF THE BLENDS :

II.2.1 Composition of the Blends : The composition of the thermoplastic PP-NR blends prepared for evaluation under the present study are given in table II.4. The PP:NR ratio has been varied from 70:30 to 30:70, since the blends in this range are expected to behave as thermoplastic elastomers. For comparison, the pure components have also been evaluated wherever required. In those blends in which the effect of HAF black has been evaluated, the black was loaded at 50 parts per hundred parts of natural rubber and in the case of silica filler, only 20 parts per hundred rubber was used. The dosage of silane coupling agent was 5% by weight of silica filler.

II.2.2 Cure Systems : The dosage of curing systems has been selected as shown in table II.4, so that only low extent of crosslinking was effected in the rubber phase and also the vulcanization process during blending could be completed within two to three minutes. The cure systems were heat resistant and hence were stable during further processing at higher temperatures. The rheographs presented in figure II.1 illustrate the above features of the selected cure systems. Different extents of degree of crosslinking could not be obtained using a single cure system since higher dosages of DCP affected the physical properties and higher sulphur dosses affected the processability. All the ingredients except DCP have been added in masterbatch form, so as to get uniform distribution of the ingredients.

II.2.3 Designation of the Blends : The blend ratios are designated by A, B, C, D, E, F and G. Letters U, D, M and S which follow denote the curing system. Blends containing HAF black, silica or silane coupling agent are denoted by letters H, Si and X respectively, after the letter indicating the cure system. Thus, blend BMSiX indicates that the blend ratio is 70:30 PP:NR, the curing system used is a mixed one and that the blend contains 20 phr silica and a silane coupling agent at a loading of 5% by weight of silica filler.

II.2.4 Blending Process : Blends of NR and PP were prepared in a Brabender Plasti-corder, model PLE 330, using a cam-type mixer with a rotor speed of 80 rpm and mixer chamber temperature set at 180°C. This equipment was having facilities to record the torque generated and the stock temperature, continuously throughout the mixing cycle. PP was melted in the mixer for one minute and then NR was added and the mix was allowed to blend for four minutes. At the end of five minutes, curatives were added and the mixing continued for three more minutes. For the uncrosslinked blends also, the total blending time was kept the same as that for the dynamically crosslinked blends. The blend was taken out from the Plasti-corder and passed through a laboratory mill at 2.0 mm nip setting. The sheeted material was cut into small pieces and again mixed in the Plasti-corder at 180°C for one minute and then finally sheeted out through the mill, while the blend is still hot. This second blending step was found to be necessary for getting uniform dispersion of the ingredients. In the case of blends containing DCP and sulphur, DCP was added after four minutes blending of NR and PP and the blending continued for one minute after adding DCP. Next, other ingredients were added. Typical plastographs obtained from this type of blending are shown in figure II.2.

II.2.5 <u>Melting of Commercial TPEs</u> : The pellet form of the SBS, SIS, TPU and 1,2PB were melted in the Plasti-corder at 180°C, for four minutes, at a rotor speed of 80 rpm. The molten mass was then sheeted out through a laboratory mill at 2.0 mm nip setting.

II.2.6 Moulding of Test samples : The sheeted out sample was compression moulded in an eletrically heated hydraulic press at 200°C for three minutes, to get sheets of 15 x 15 x 0.2 cm size. Test samples for abrasion resistance test and for the evaluation of dynamic mechanical properties were directly moulded out. The mould used was provided with bolts and nuts so that the material inside could be held under pressure even after taking out the mould from the press. After completing the moulding time, the sample, still under compression, was immediately cooled by plunging the mould in cold water. This treatment was adopted to avoid the possible degradation of the natural rubber phase under high temperature exposure for longer periods. Aluminium foils were used between the mould surfaces and the sample, to reduce shrink marks on the sheets.

II.3 PHYSICAL TEST METHODS :

For the tests described below, at least three specimens per sample were tested for each property and the mean values are reported.

II.3.1 Modulus, Tensile Strength and Elongation at Break :

In the present work, these tests were carried out according to ASTM D 412-80 test method, using dumbbell shaped test pieces. The test pieces were punched out from the moulded sheets using C-type die, along the mill grain direction of the sheets. The thickness of the narrow portion of the specimen was measured using a bench thickness gauge. The specimens were tested in an Instron Universal Testing Machine (UTM), model 1195, at 25 ± 2°C and at a cross-head speed of 500 mm per minute. The elongation at break was measured using an extensiometer attached to the UTM. The load and the elongation at break were recorded on a strip chart recorder. The machine used was having a sensitivity of 0.5% of the full scale load. From the recorded load, the stress was calculated based on the original cross-sectional area of the test specimen. The modulus and tensile strength are reported in MPa and the elongation at break in percentage of original length.

II.3.2 Tear Resistance : The tear resistance of the samples was tested as per ASTM D 624-81 test method, using unnicked 90° angle test specimens which were punched out from the moulded sheets, along the mill grain direction. This test was also carried out in the Instron UTM, at a cross-head speed of 500 mm per minute and at 25 ± 2°C. The tear strength values are reported in kN/m.

II.3.3 Hardness : The hardness of the samples was measured as per ASTM D 2240-81 test method using a Shore A-type Durometer, which employs a calibrated spring to provide the indenting force. Since the hardness readings decreased with time after firm contact between the indentor and the sample, the readings were taken immediately after the establishment of firm contact.

II.3.4 Abrasion Resistance : The abrasion resistance of the samples was tested using a Du Pont Abrader. In this machine, two test pieces, each having 2 cm square surface, are simultaneously held against an abrasive paper disc which rotates at a speed of 40 rpm. The normal load on the samples was 3.26 kg and the silicon carbide abrasive paper used for the test was of grain size 320. The samples were abraded for 10 min after an initial conditioning period of 5 min. Separate abrasive discs were used for each sample. The Abrasion loss of the samples was calculated and expressed as volume loss in cm^3h^{-1}.

II.3.5 Tension Set : Tension set is described as the extension remaining after a specimen has been stretched and allowed to retract in a specified manner, expressed as a percentage of the original length. The test was conducted as per ASTM D 412-80 test method. Dumbbell shaped test pieces were used for this test. Bench marks were given at the narrow portion of the dumbbell at one inch apart (lo). The test piece was then clamped on the grips of the Instron UTM and stretched to 100% elongation within 15 sec. It was held in that position for 10 min and quickly released without allowing it to snap back. The sample was allowed to rest for 10 min and the distance between the bench marks measured (l). The tension set is calculated as

$$\left(\frac{l - lo}{lo} \right) \times 100 \qquad II.0$$

II.3.6 Flexural Modulus : The flexural modulus was tested as per ASTM D 790-71 test method. A three point loading system, utilizing centre loading on a supported beam, was used for carrying out the test. The radius of the loading nose was 3.2 mm so as to avoid excessive indentation directly under the loading nose. The test specimens were die-cut from the moulded sheets of about 2.5 mm thickness. The breadth and length of the specimens used were 25 mm and 60 mm respectively. The support span was 40 mm and the test was conducted at 25 ± 2°C. The load was applied on the sample using the moving cross-head of the Instron UTM and the rate of cross-head motion was 1.0 mm per minute. From the load-deflection curves that were recorded on the chart, the flexural modulus was calculated using the following equation.

$$S = \frac{3PL}{2bd^2} \qquad \text{II.1}$$

where,
S = Stress at mid span, N/m^2
p = Load at any point on the load-deflection curve, N.
L = Support span, m.
b = Width of the beam tested, m.
d = Depth of the beam tested, m.

II.3.7 Tensile Impact Energy : The tensile impact energy to break the sample was determined as per DIN 53448 test method. The energy utilised to break a test specimen in this method is delivered by a single swing of a calibrated pendulum of a standarised tension-impact machine. The machine used in the present investigations was a Ceast 6545/000 model tensile impact tester. The principle involved in this test is to measure the energy, to fracture by strock in tension, in the form of the kinetic energy extracted from the pendulum of the impact machine, in the process of breaking the specimen. Short dumbbell shaped samples of 2.0 mm thickness were used in the present study as the extension of the sample during testing is comparatively low in this type of specimens. The pendulum used could deliver an energy of 7.5 J and the speed of travel was 3.7 m sec^{-1}. One end of the test specimen was gripped by a fixed chuck of such a size and shape that the falling pendulum passes unhindered down past the fixed chuck but was firmly arrested by the larger chuck which simply grips the other end of the specimen. The tensile impact energy of the specimen could be directly read from the instrument, at the instant of impact of the pendulum on the large chuck that holds the free end of the specimen and it is expressed as J/m.

II.4 DYNAMIC MECHANICAL PROPERTIES :

The dynamic mechanical properties of the thermoplastic NR-PP blends were measured using a Rheovibron DDV IIIC. A schematic diagram of the instrument is given in figure II.3a. The extension modulus and loss angle under sinusoidal deformation at various frequencies and amplitudes can be determined using this equipment. The environmental chamber allows the testing to be carried out at a very wide range of temperatures. Yielding of the sample, as shown in figure II.3b, occurs in the holder clamps. Corrections for this were made in the calculations as per the method suggested by Morawski[129]. Moulded samples of dimensions 7 x 1 x 0.5 cm where used for testing. The samples were tested at a strain amplitude of 0.0025 cm and at a frequency of 35 Hz. The heating rate of the samples was 1°C rise in temperature per minute. The complex modulus E* was calculated using the following equation.

$$E^* = \frac{(L + \Delta L) \times 10^{12}}{8 \times S \times A\,(D - K)} \ \text{dynes/cm}^2 \qquad \text{II.2}$$

where, E^* = Dynamic complex modulus

L = Length of the sample between the clamps

ΔL = Oscillating displacement

S = Cross-sectional area of the sample

A = Amplitude factor

D = Value of dynamic force dial

K = Error constant.

Parameters A, D and δ (loss angle) can be directly read using the instrument.

The storage modulus E' and loss modulus E" are obtained from E* and δ using the following equations.

$$E'' = E^* \sin\delta \qquad \text{II.3}$$

$$E' = E^* \cos\delta \qquad \text{II}\cdot 4$$

The loss tangent, $\tan\delta = E''/E'$, indicates the damping characteristics of the material.

II.5 MELT FLOW STUDIES :

II.5.1 Equipment Details : The melt flow studies were carried out using a capillary rheometer MCR 3210 attached to an Instron UTM, model 1195. The extrusion assembly consists of a barrel, made of hardened steel mounted on a special support, underneath the moving cross-head of the Instron UTM. A hardened steel plunger, which is accurately ground to fit inside the barrel, is driven by the moving cross-head of the machine. The plunger is held to the load cell extension with the help of a latch assembly. The barrel is mounted on a ball and socket system on the support, so that the system will be self-aligning. The capillary is inserted at the bottom of the barrel and is locked using a clamping nut. The capillary is made of tungston carbide material. A teflon O-ring around the capillary prevents leakage of the material through the gap between the barrel and the capillary. An O-ring and a split ring were also used on the plunger so that the combination acted as a piston seal. The barrel was heated electrically using a three zone temperature control system. The difference between the successive temperature zones in the barrel was kept at 5°C and the temperature of the lower zone, where the capillary is located, is taken as the test temperature. The details of the capillary are shown in figure II.4.

The moving cross-head of the Instron UTM runs the plunger at a constant speed irrespective of the load on the melt, maintaining constant volumetric flow rate through the capillary. Using the Instron machine, the cross-head speed can be veried from 0.5 mm/min to 500 mm/min, giving a shear rate range of 3 sec^{-1} to 3000 sec^{-1} for a capillary of L/D = 40. Forces corresponding to specific plunger speeds were recorded on a strip chart recorder. This was then converted into the shear stress.

II.5.2 <u>Test Procedure</u> : Sample for testing was placed inside the barrel which was maintained at the test temperature. The sample was forced down to the capillary using the plunger attached to the moving cross-head. After a warming up period of five minutes, the melt was extruded through the capillary at pre-selected speeds of the cross-head. The melt height in the barrel before extrusion was kept the same in all the experiments and the machine was operated to give ten five different plunger speeds from lower to higher speeds, with a single charge of the material.

Each plunger speed was continued until the recorded force was stabilized, before changing to the next speed. Forces corresponding to specific plunger speeds were recorded. The force and cross-head speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at wall by using the following equations involving the geometry of the capillary and the plunger.

$$\tau_w = \frac{F}{4 A_p (l_c / d_c)} \qquad \text{II.5}$$

$$\dot{\gamma}_w = \left(\frac{3 n' + 1}{4 n'} \right) \times \frac{32 Q}{\pi d_c^3} \qquad \text{II.6}$$

where, F = Force applied at a particular shear rate

A_p = Cross-sectional area of the plunger

l_c = Length of the capillary

d_c = Diameter of the capillary

Q = Volume flow rate

n' = Flow behaviour index, defined by $d(\log \tau_w) / d(\log \dot{\gamma}_{w.a})$

$\dot{\gamma}_{w.a}$ = Apparent wall shear rate.

n' was determined by regression analysis of the values of τ_w

and $\dot{\gamma}_{w.a}$ obtained from the experimental data. The statistical analysis of the data indicated that the coefficient of determination of the system was beyond 0.95. The shear viscosity η was calculated as $\eta = \tau_w / \dot{\gamma}_w$.

It was shown earlier that the shear stress at wall need be corrected for end corrections as suggested by Bagley[130]. But this end correction factor diminishes as the length to diameter ratio increases and for a capillary having l/d ratio of 40, ~~It~~ it is assumed that the correction factor is negligible. The capillary used in the present investigations was having l/d of 40. The following assumptions were also made for the analysis of the data :

a) the flow is parallel to the axis,

b) the velocity of any fluid element is a function of radius only, giving axial symmetry,

c) the fluid is incompressible,

d) the fluid velocity is zero at the wall, i.e. there is no slip at the wall,

e) all energy is consumed within the capillary and the flow is isothermal.

II.5.3 Extrudate Swell : Extrudate swell was expressed as the ratio of the diameter of the extrudate to that of the capillary used. The extrudate emerging out from the capillary was collected without any deformation. The diameter of the extrudate was measured after 24 hours rest period, using Olympus stereo-binocular microscope, model VB454, at several points on the extrudate. The average value of five readings was taken as the diameter (d_e) of the extrudate and the swelling index was calculated as d_e/d_c where d_c is the diameter of the capillary. For each blend, the extrudate swell at three different shear rates was determined.

II.6 DETERMINATION OF VOLUME FRACTION OF RUBBER :

The volume fraction of rubber, Vr, in the solvent swollen samples of rubber vulcanizates GD, GM and GS and that of the blends FD, FM and FS which contained higher proportion of the elastomer phase was determined by using the equilibrium swelling method. Samples of approximately 10 mm diameter and 2.5 mm thickness were punched out from the central portion of the moulded sheets and allowed to swell in thiophene-free benzene containing 0.5 per cent phenyl-β-naphthylamine at 35 ± 0.1°C in boiling tubes, kept immersed in a thermostatically controlled water bath. Swollen samples were taken out after 1,2,3,5,9,14,24,36 and 48 hours of immersion in benzene and the surfaces blotted with filter paper and quickly weighed in stoppered weighing bottles. It was observed that 48 hours were required in most of the cases to attain equilibrium swelling. Samples were then dried in an air oven set at 70°C, for 24 hours and then in vacuum. The dried samples were weighed accurately, after cooling in a desiccator. Duplicate readings were taken for each sample. The Vr values calculated using the method reported by Ellis and Welding[131]. The equations used for calculating the Vr values are given below.

$$V_r = \frac{(D - FT)\,\rho_r^{-1}}{(D-FT)\,\rho_r^{-1} + A_o\,\rho_s^{-1}} \qquad \text{II.7}$$

where, T = Initial weight of the test specimen,

D = Deswollen weight of the test specimen,

F = The weight fraction insoluble components,

A_o = Weight of the absorbed solvent, corrected for swelling increment,

ρ_r = Density of rubber,

ρ_s = Density of solvent.

From the experimental data, the value of Ao can easily be calculated as described below.

The weight of the solvent absorbed at any time 't' is given by :

$Wt = \frac{St - T}{T}$, where St is the swollen weight of the sample at time 't'. If the equilibrium time is taken as 'x' hours, the percentage increment d_x after 'x' hours is calculated from the equation,

$$d_x = \frac{100\ (Wx - Wo)}{Wo} \qquad \text{II.8}$$

where, Wo is the weight of the solvent absorbed per gram of the sample in the absence of swelling increment. Wo is obtained from a plot of W_t against $t^{\frac{1}{2}}$, by extrapolating the straight line to zero time. The value of Ao is then given by

$$Ao = A_x \left(1 - \frac{d_x}{100}\right) \qquad \text{II.9}$$

where, A_x is the weight of the solvent absorbed after 'x' hours immersion, and is equal to $(S_x - D)$. S_x is the swollen weight of the sample after 'x' hours.

II.7 MORPHOLOGY STUDY :

For studying the morphology of the blends, the rubber phase of the uncrosslinked blends was extracted using toluene. Moulded samples of the blends were cut using a Bright Cryostat Microtom, after cooling the samples to below $-80^{o}C$, using liquid nitrogen. The microtomed edge of the sample was kept immersed in toluene at $35 \pm 1^{o}C$, for seven days. The solvent was changed after every 6 hours. After seven days of immersion, the sample was dried in an air oven at $40 \pm 1^{o}C$. The extracted edge of the sample was examined under a Philips 500 model, scanning electron microscope.

II.8 SCANNING ELECTRON MICROSCOPY STUDIES :

Scanning electron microscopy (SEM) has been successfully used for studying the failure surfaces of rubber composites[132-138]. It has also been found to be a valuable tool in studying the phase morphology of high impact strength blends of PP and EPDM[139,140]. In using the SEM, the sample preparation is quite simple, unlike in other microscopes and it presents a physical picture of the fracture surfaces under investigation. But care should be taken to keep the sample undisturbed, in dust-free atmosphere after failure. Due to non-conducting nature of the rubber and plastics surfaces, the fracture surfaces shall be coated with a conducting material such as gold or copper.

II.8.1 Principle of the SEM : The principle of the working of the SEM is shown in figure II.5. Electrons from an emission source or filament are accelerated by voltage usually in the range of 1 to 30 KV and are directed down to the centre of an electron-optical column consisting of two to three magnetic lenses. These lenses cause a fine electron beam to be focussed onto the specimen surface. Scanning coils placed before the final lens cause the electron spot to be scanned across the specimen surface in the form of a square raster, similar to that of a television screen. The currents passing through the scanning coils are made to pass through the corresponding deflection coils of a cathode ray tube, so as to produce a similar but larger raster on the viewing screen in a synchronous manner.

The electron beam incident on the specimen surface causes various phenomena, of which the emission of secondary electrons is used in SEM. The emitted electrons strike the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. The time for the emission and collection of the secondary electrons is negligibly small compared with the time for the scanning of the incident electron beam across specimen surface. Hence there is a one-to-one correspondance between the number of secondary electrons collected from any particular point of the specimen surface and the brightness of the analogous point on the screen, and thus an image of the surface is progressively built up on the screen.

In SEM, the image magnification is determined solely by the ratio of the sizes of the rasters on the screen and on the specimen surface. In order to increase the magnification, it is only necessary to reduce the currents in the SEM scanning coils. As a consequence of this, it is easy to obtain high magnifications in SEM, while for very low magnifications of 10X, it would be necessary to scan a specimen, approximately 10 mm across and this presents difficulties because of the large deflection angles required.

II.8.2 Scanning the Fracture Surfaces : The SEM observations reported in the present investigations were made using a Philips 500 model scanning electron microscope. The fracture surfaces of the samples were carefully cut out from the failed test pieces without disturbing the surface. These surfaces were then sputter coated with gold within 24 hours of testing. The SEM observations were made as early as possible, but not later than one week, after gold coating.. The tilt was kept 0° in all cases, unless specified otherwise. The gold coated samples were kept only in desiccators before the SEM observations were made. Earlier studies have shown that storage of fractured specimens for one week before gold coating and upto a period of one month after gold coating does not alter the fracture surface topography as observed in SEM. The shapes of the test specimens, directions of the applied force and abrassion and the portions from where the surfaces have been cut out for SEM observations are shown in figure II.6 .

TABLE II.1 SPECIFICATIONS FOR ISNR-5 GRADE NATURAL RUBBER

Parameters	Limit
Dirt Content (% by Mass, Max.)	0.05
Volatile Matter (% by Mass, Max.)	1.0
Nitrogen Content (% by Mass, Max.)	0.7
Ash Content (% by Mass, Max.)	0.6
Initial Plasticity (Po, Min.)	30
Plasticity Retention Index (PRI, Min.)	60

TABLE II.2 PROPERTIES OF KOYLENE MO030

Property	Test Method	Value
Melt Flow Index (g/10 min)	ASTM D 1238	10.0
Melting Point (°C)	-	165-170
Vicat Softening Point (°C)	ASTM D 1525	152
Brittle Point (°C)	ASTM D 746	5
Density at 23°C (g/cm^3)	ASTM D 1505	0.905
Hardness, Rockwell (R. Scale)	ASTM D 785/B	72

TABLE II.3 CHARACTERISTICS OF BASE POLYMERS

Property		NR	PP
Molecular Weight	$\bar{M}n$	-	1,06,000
	$\bar{M}w$	7,80,000	5,30,000
Molecular Weight Distribution	$\bar{M}w/\bar{M}n$	-	5·0
Intrinsic Viscosity (Benzene , 30 °C, dl / g)	$[\eta]$	4·45	-
Melt Flow Index (230 °C , 2·16 Kg)	MFI	-	10·0
Wallace Plasticity	Po	59·0	-

TABLE II.4 COMPOSITION OF THE BLENDS

Ingredients	A	B	C	D	E	F	G
PP[a]	100	70	60	50	40	30	–
NR[b]	–	30	40	50	60	70	100
Curatives [c]	–	U, D, S, M	U,D,S,M	U,D,S,M	U,D,S,M	U,D,S,M	D,S,M
HAF Black [d]	–	H	–	H	–	H	–
Silica [e]	–	–	–	–	–	Si	–
Silane Coupling Agent [f]	–	–	–	–	–	X	–

[a] Isotactic polypropylene

[b] Natural rubber, INSR 5 grade

[c] U Blends without curative

D Blends containing 1·0 phr 40% DCP based on rubber phase only

M Blends containing 1·0 phr. 40% DCP. ZnO 5·0. St.Acid 2·0. CBS 1·0, TMTD 1·25, and S 0·15 phr.

S Blends containing ZnO 5·0, St. Acid 2·0, CBS 2·0, TMTD 2·5 and S 0·30 phr.

[d] H Blends containing 50 phr. HAF black

[e] Si Blends containing 20 phr. silica (vulcasil S)

[f] X Blends containing (5 % by weight of silica) silane coupling agent (Si - 69)

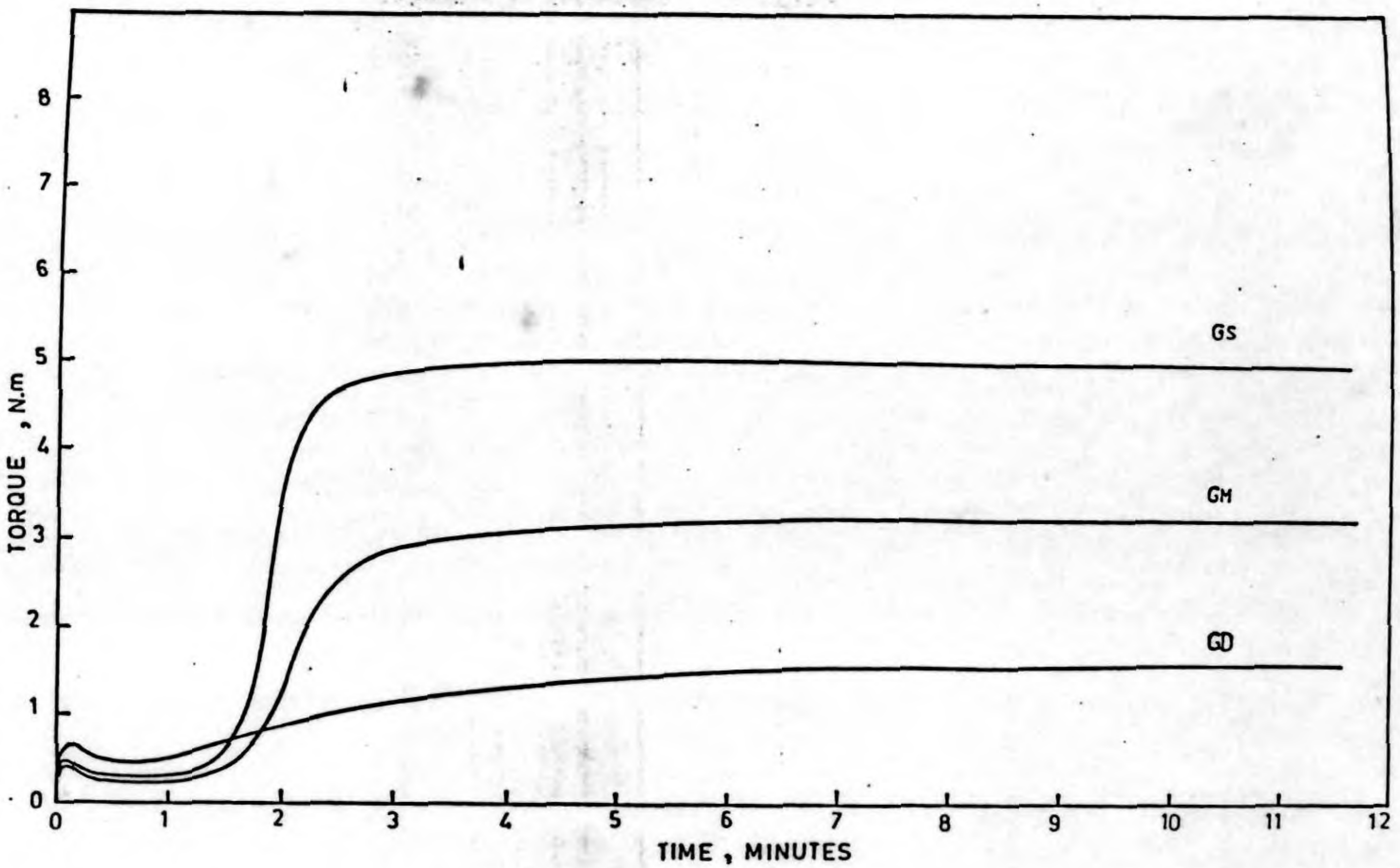


FIG.II.1 RHEOGRAPHS OF RUBBER COMPOUNDS

2

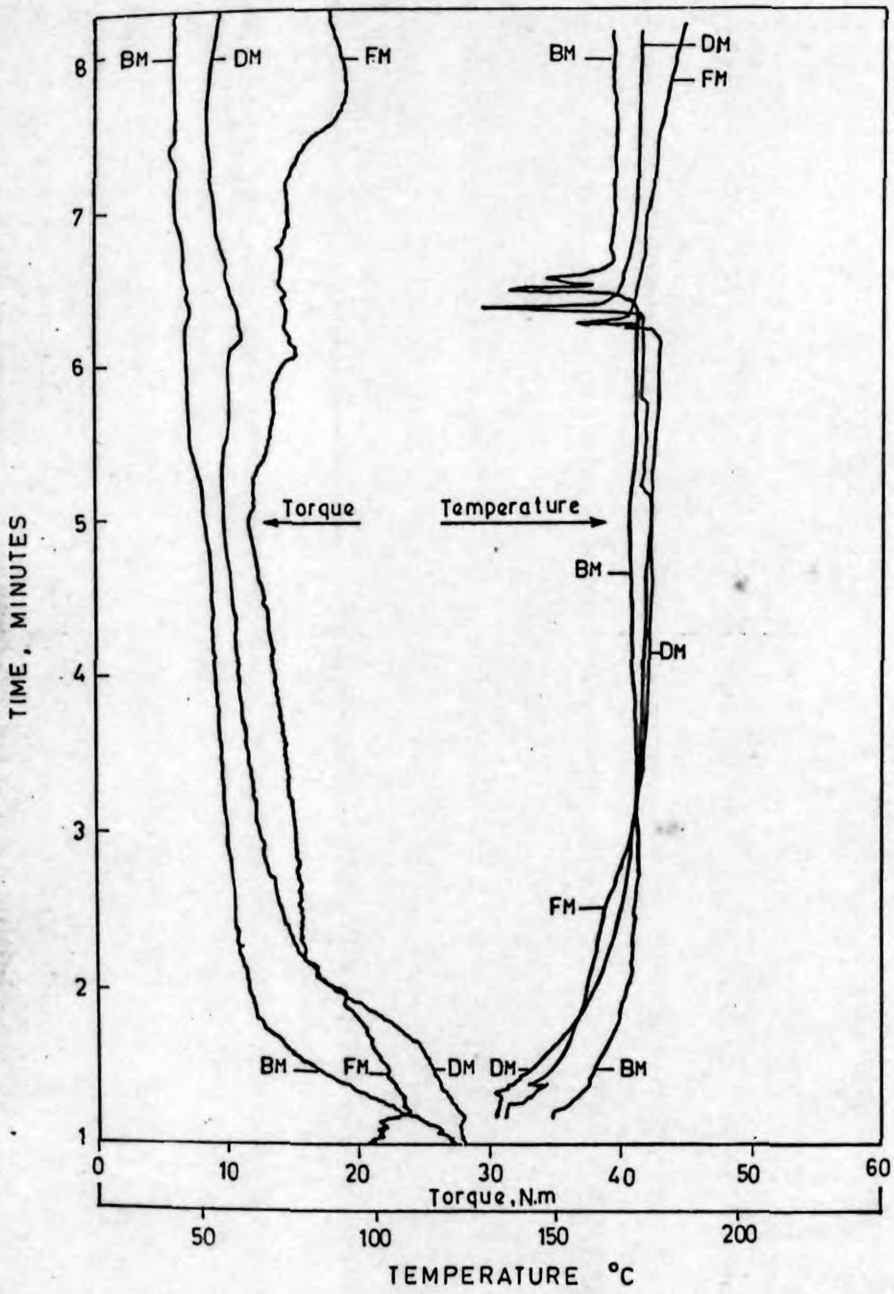


FIG.II.2 PLASTOGRAPHS OF BLENDS BM, DM AND FM

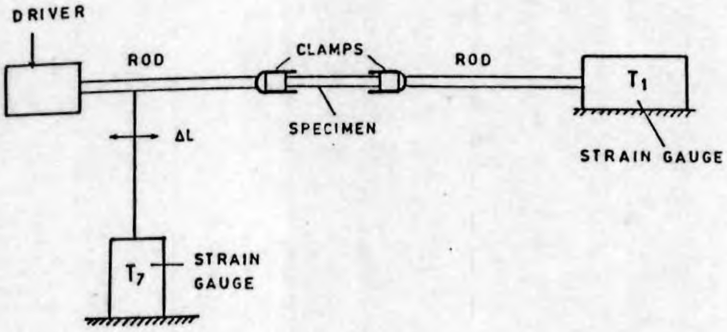


FIG.II. 3a SCHEMATIC OF RHEOVIBRON

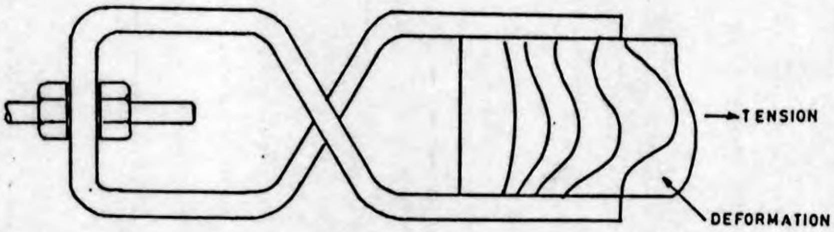
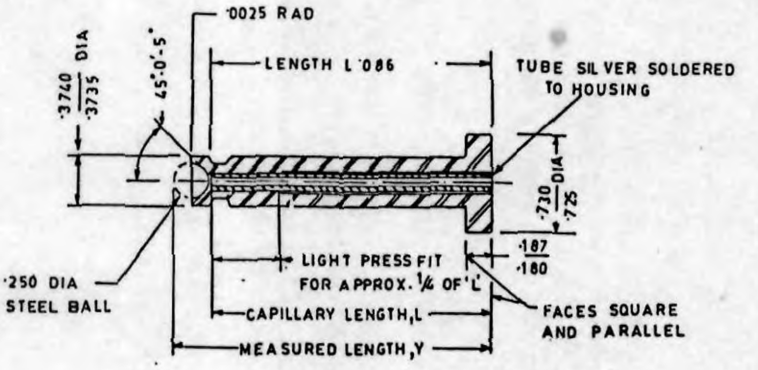


FIG.II. 3b YIELDING OF CLAMPED SPECIMEN



$L = 2{\cdot}0066 \pm 0{\cdot}0001$ IN

CAPILLARY DIA = $0{\cdot}0495 \pm 0{\cdot}005$ IN

FIG.II.4 TYPICAL CAPILLARY DETAILS

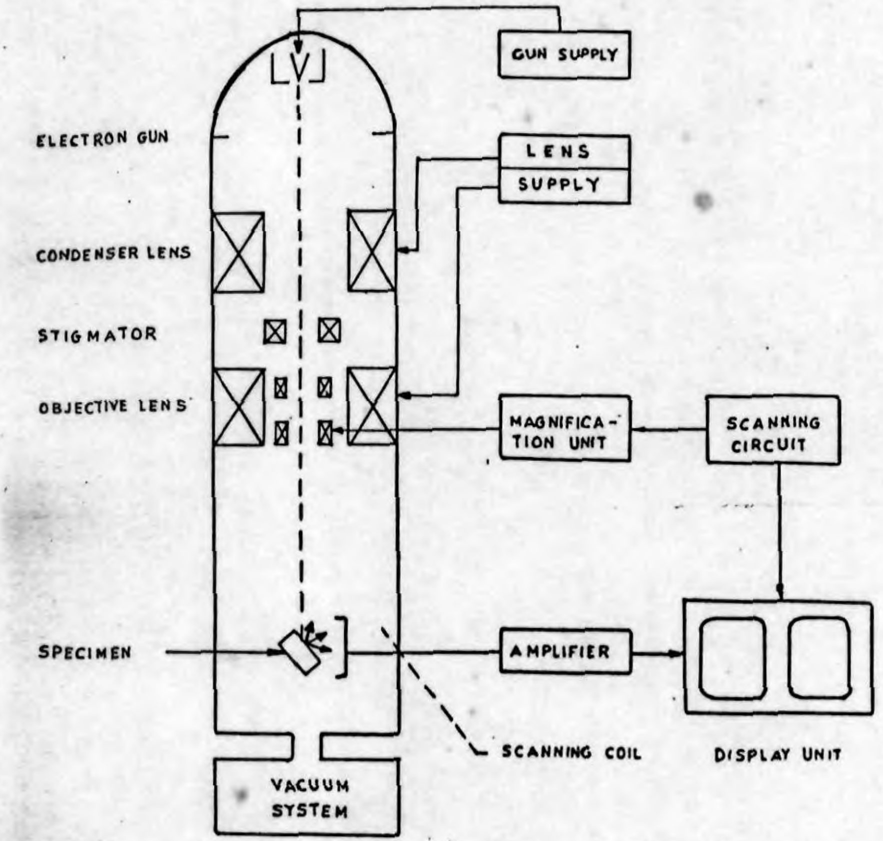


FIG.II.5 SIMPLIFIED BLOCK DIAGRAM OF AN SEM.

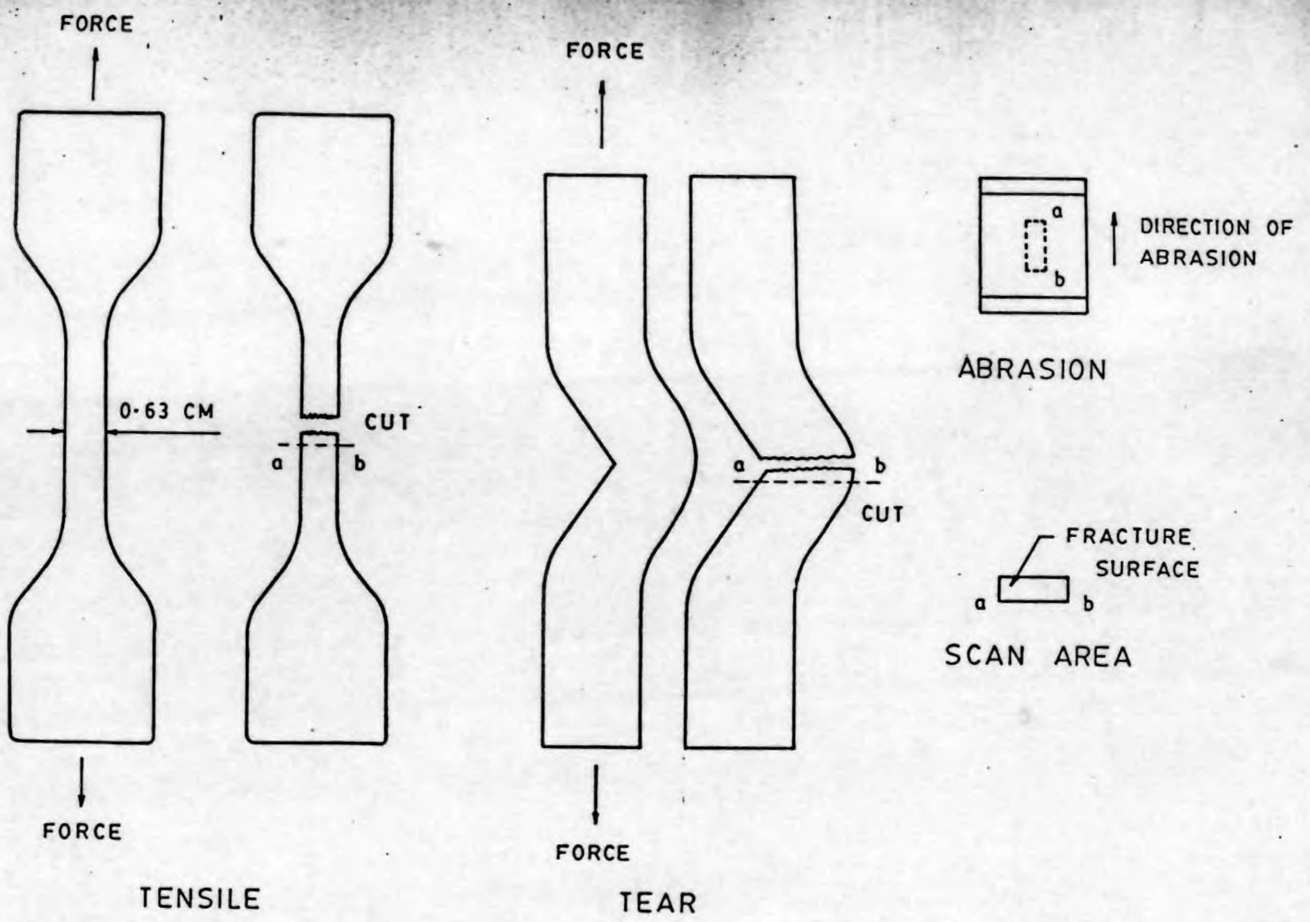


FIG.II.6 SAMPLES FOR TENSILE, TEAR AND ABRASION TESTS, FRACTURE SURFACE AND SCAN AREA

PART - I

STUDIES ON THERMOPLASTIC NATURAL RUBBER-POLYPROPYLENE BLENDS

CHAPTER - III

STUDIES ON THE MELT FLOW CHARACTERISTICS OF THERMOPLASTIC NATURAL RUBBER-POLYPROPYLENE BLENDS

Part of the results included in this chapter have been published in POLYMER ENGINEERING AND SCIENCE, 25, 630 (1985).

The processing behaviour of polymers is essentially influenced by their rheological properties. This is the reason why now-a-days the viscosity function of a polymer i.e., the shear viscosity as a function of shear rate/shear stress and temperature, becomes more and more important in trying to optimise the processing operations and in designing processing equipment such as extruders and the dies required for various products. For example, the shape of an extruded product depends not only on the dimensions of the die but also on the rate of shear and temperature at which it is extruded and on the extent of elastic swell of the material. Hence a large number of indepth studies have been conducted on the rheological behaviour of elastomers and their blends, rubber modified thermoplastic melts and blends of thermoplastic materials, by different research groups[141-148]. The effects of crosslinked particles, carbon black and non-black fillers on the flow properties of polymer melts have also been studied[149-152]. Numerous studies on the factors affecting the die swell, melt fracture and deformation of extrudates have been conducted to optimise the production processes for manufacturing articles free from defects[153-157]. But only a limited number of studies have been reported on the processing characteristics of thermoplastic elastomer blends, even though one of the important advantages of these materials is their easy and economic processability[109,118,

This chapter of the thesis presents the results of the studies conducted for assessing the melt flow behaviour of thermoplastic elastomers prepared from natural rubber-polypropylene blends. The effects of blend ratio, extent of dynamic crosslinking, temperature and shear stress/shear rate on melt viscosity, flow behaviour index, die swell and melt fracture of the blends have been studied.

Among the compositions of the blends given in table II.4, blends B, D and F were selected for the melt flow studies, since it is expected that the behaviour of the other blends could be predicted from the results of these blends. Uncrosslinked and dynamically crosslinked blends containing various extents of crosslinking of the elastomer phase were used for this study. The extent of crosslinking was assessed by measuring Vr values as described in section II.6. The Vr values of the natural rubber gum vulcanizates containing the same level of curatives, and vulcanized at the same conditions of temperature and time as those of the blends, were 0.07, 0.13 and 0.17 respectively for the DCP (blend GD), mixed (blend GM) and sulphur (blend GS) cured samples. This indicated that the extents of crosslinking was in the order, sulphur cure > mixed cure > DCP cure for the vulcanization systems selected. The corresponding Vr values for the blends FD, FM and FS were 0.12, 0.21 and 0.25 respectively. The higher Vr values of the blends compared with those of the rubber vulcanizates may be due to the restriction imposed by the crystalline PP phase for the swelling.

The melt flow characteristics were evaluated in the temperature range of 180°C to 210°C since the processing temperatures of these materials are in this range. The shear rates of testing covered a wide range from 3.0 sec^{-1} to 3000.0 sec^{-1}, so as to simulate the processing conditions such as compression moulding (shear rate, 10 sec^{-1}) and injection moulding (shear rate, 10^3 sec^{-1}).

III.1 EFFECT OF BLEND RATIO AND SHEAR STRESS ON VISCOSITY :

Figure III.1 shows the effect of blend ratio and shear stress on viscosity of the thermoplastic PP-NR blends at 210°C. At lower shear stresses, the viscosity of the blend increased with increase in proportion of rubber in the blend. The viscosity decreased with increase in shear stress showing pseudoplastic flow behaviour of the blends and at high shear stresses (2×10^7 Pa), the difference between the viscosity of the blends containing various proportions of PP and NR is only marginal. At lower shear stresses, the viscosity of fresh PP pellets is higher than that of 30:70 NR:PP blend (BU). Thermal degradation and the corresponding decrease in melt viscosity of PP has been reported by White et al[158]. Melting and mixing of PP in the Plasti-corder at 180°C for 8 minutes degraded the PP in the blend and reduced its viscosity. This is evident from the lower viscosity of the PP which has been melted and sheared in the Plasti-corder for 8 minutes at 180°C and 80 rpm, compared with that of fresh PP pellets. Since the difference between the viscosity of the blends containing various proportions of the elastomer phase and that of PP is low at high shear stresses, it is clear that these blends can be processed just like thermoplastic PP at higher shear stress.

III.2 EFFECT OF DYNAMIC CROSSLINKING AND SHEAR STRESS ON VISCOSITY :

The effect of shear stress on viscosity of the 30:70 NR:PP blends containing rubber particles having different extents of crosslinking is shown in figure III.2. At lower shear stresses the viscosity of the blends increased with increase in degree of crosslinking of the rubber phase. At higher shear stresses also, the trend is the same, even though the differences in viscosities of the blends having different extents of crosslinking of the rubber phase is only marginal. Blend BU showed lower viscosity at lower shear stresses and higher viscosity at higher shear stresses than the blends containing crosslinked rubber particles (BD, BM and BS). Since the dispersed rubber phase is having higher viscosity than the continuous PP phase (figure III.1), the continuous phase experiences the same deformation in all the blends whereas, the deformation undergone by the dispersed phase depends on its melt viscosity[109].

It has been reported that the uncrosslinked rubber particles in polypropylene-elastomer blends are bigger in size and are highly deformable[118] and that these particles are broken down into smaller ones under high shear rates[119], as observed in other heterogeneous blends[159]. Crosslinking of the elastomer phase increased its viscosity and decreased the deformation of the dispersed particles as indicated by the increase in Brabender mixing torque values (at 180°C, 80 rpm rotor speed) from 5.5 Nm for the uncrosslinked blend (BU) to 8.0 Nm for the sulphur crosslinked blend (BS). Considering the above details, the changes in morphology of the blend B containing uncrosslinked and crosslinked rubber particles, under low and high shear stress conditions, may by represented as depicted in figure III.3. This phenomenon has been confirmed by SEM studies in the case of extrudates of natural rubber-polyethylene blends under similar conditions[160]. The uncrosslinked rubber particles in the blend are elongated at the entrance of the capillary and are broken down into smaller particles whereas, the crosslinked particles which are less deformable, retains the morphology of the blend even at high shear stresses. Thus the observed difference in viscosities of the uncrosslinked blend BU and crosslinked blends BD, BM, and BS at low and high shear stresses is due to the change in morphology of the uncrosslinked blend under high shear stress conditions.

The DCP cured 30:70 NR:PP blend (BD) showed lower viscosity compared with that of blends, BU, BM and BS. It has been reported that DCP degrades PP at elevated temperature and that this effect is more prominent at higher proportions of PP in NR-PP blends, as evidenced by increase in melt flow index values of these blends[107]. Thus the lower viscosity of the blend BD can be attributed to the degradative effect of DCP on PP at high temperature of blending.

In the 50:50 NR:PP blend, there was a sharp increase in viscosity with crosslinking at lower shear stresses and blends DM and DS showed yield stresses (figure III.4). Münstedt[149] has reported that in rubber modified styrene-acrylonitrile and poly (vinyl chloride) the viscosity increase at lower shear stresses is due to structure build-up of rubber particles and that the viscosity increase is more pronounced at higher concentration and smaller size of the rubber particles. At higher extents of crosslinking, the smaller size of the mixed and sulphur cured rubber particles in blends DM and DS, compared with that of uncrosslinked and slightly crosslinked blends, form some sort of structure build-up inside the system, which leads to yield stress and increase in viscosity at low shear stresses of these blends. The degradative effect of DCP on PP was evident from the lower viscosity of the blend DD at higher shear stress. In 70:30 NR:PP blends (figure III.5), the observed differences in viscosities of the blends FU, FD, FM and FS were proportional to the degree of crosslinking of the rubber phase. The viscosities of the blends FU and FD were comparable and the blends FM and FS also showed the same trend at lower shear stresses, unlike the viscosities of the blends in the D series, which showed a wide difference (figure III.4). The degradative effect of DCP on PP which has been observed in blends BD and DD was not prominent in blend FD. It was also seen that the effect of extent of crosslinking on viscosity was less pronounced for the blends in F series at higher shear stresses unlike that observed for the blends in D series. At this blend ratio, both rubber and plastic components from continuous phases due to higher proportion of the rubber phase and lower viscosity of the plastic phase and the crosslinking agents have their action mainly on the rubber phase. At higher shear rates, the effect of crosslinking of the rubber phase on viscosity is not prominent as the blends attain a sheath and core like structure and the plastic phase forms a lubricating layer at the capillary wall during extrusion.

III.3 EFFECT OF TEMPERATURE AND SHEAR RATE ON VISCOSITY :

Effect of temperature on viscosity of the blends in

B series, at three different shear rates, is shown in figure III.6. At all shear rates, the viscosity decreased with increase in temperature from 180°C to 200°C and the decrease was more sharp for the blends BS, BM and BD which contained the crosslinked rubber particles. The change in viscosity of the blends above 200°C was only marginal. For blend BU, at higher shear rates, there was an increase in viscosity at temperature above 190°C and this effect was more prominent at shear rate 3000 sec^{-1}. This shows that temperature also accelerated the reduction of the size of the uncrosslinked rubber particles during extrusion at high shear rates. The change in viscosity with increase in temperature was comparatively less for PP. In the case of blends in D series, the viscosity decreased with increase in temperature at all shear rates for blends DM and DS. But blends DU and DD showed slight increase in viscosity at lower shear rates, at temperatures above 200°C (figure III.7). This is due to the fact that at higher temperature, the lower viscosity of the continuous plastic phase preserved the structure build-up by the rubber particles, at lower shear rates. For the blends in F series also, increase in temperature reduced the viscosity of the blends at all shear rates, except in the case of blend FD which shows slight increase in viscosity at higher shear rates (figure III.8).

III.4 EFFECT OF SHEAR RATE AND DYNAMIC CROSSLINKING ON DIE SWELL :

Figure III.9 shows the die swell values of the NR:PP blends containing different crosslinking systems, at three different shear rates. In general, die swell increased with increase in shear rate and this effect was more prominent in uncrosslinked blends than in crosslinked ones. Increasing the rubber content in the blend decreased the die swell of the uncrosslinked blends but for blends containing crosslinked rubber phase, die swell depends on shear rate and degree of crosslinking of the rubber phase. At lower shear rate, DCP cure showed decrease in die swell with increase of rubber content in the blend. But at shear rates of 300 sec^{-1} and 3000 sec^{-1} this system showed minimum swell for the 50:50 blend. The mixed cure system showed slight decrease in swell at shear rates of 30 sec^{-1} and 300 sec^{-1} with increase in rubber content, but at shear rate of 3000 sec^{-1}, showed maximum swell for the 50:50 blend. At 30 sec^{-1} shear rate, sulphur curing system showed increase in die swell with increase of rubber content in the blend. But at higher shear rates, this system showed maximum swell for the 50:50 blend. These observations show that the extrudate swell depends not only on shear rate but also on blend ratio and degree of crosslinking of the rubber phase, due to the difference in size, structure and deformability of the rubber particles in different blend ratios.

III.5 EFFECT OF TEMPERATURE AND DYNAMIC CROSSLINKING ON FLOW BEHAVIOUR INDEX :

The effects of temperature and degree of crosslinking of the rubber phase on n' values are presented by histograms in figure III.10. For the 30:70 NR:PP blends, at 210°C the n' values decreased with increase in extent of crosslinking of the rubber phase. At 200°C blend BS showed slightly higher value for n' than that for BM. Similarly at 190°C blend BD showed slightly higher value than blend BU. Blend BS showed maximum value for n' at 200°C whereas for blends BU, BD and BM, n' values were maximum at 210°C. In 50:50 NR:PP blends, the n' values decreased with increase in degree of crosslinking and this trend is shown at all the three temperatures. For these blends, a tendency to form maximum value for n' at 200°C was also observed. In the case of blends in F series, no regular change in n' values with increase in temperature or crosslink density of the rubber phase was observed except for blend FS which showed gradual decrease in n' value with increase in temperature. Blends FU and FM showed minimum values at 200°C.

III.6 EFFECT OF DYNAMIC CROSSLINKING ON MELT FRACTURE :

Figure III.11 shows that the deformation of the extrudate is increased with increase in shear rate, both for the uncrosslinked and crosslinked blends. Increasing the rubber content in the blend beyond 30% increased the melt fracture of the extrudates as the elastic response increased with increase in proportion of the rubber phase. At higher shear rates the distortion of the extrudates decreased with increase in crosslink density of the rubber phase. DCP cured blends showed higher deformation and the sulphur cured blends gave least deformation at all blend ratios. This is due to less deformation and quick recovery of the rubber particles containing higher degree of crosslinking.

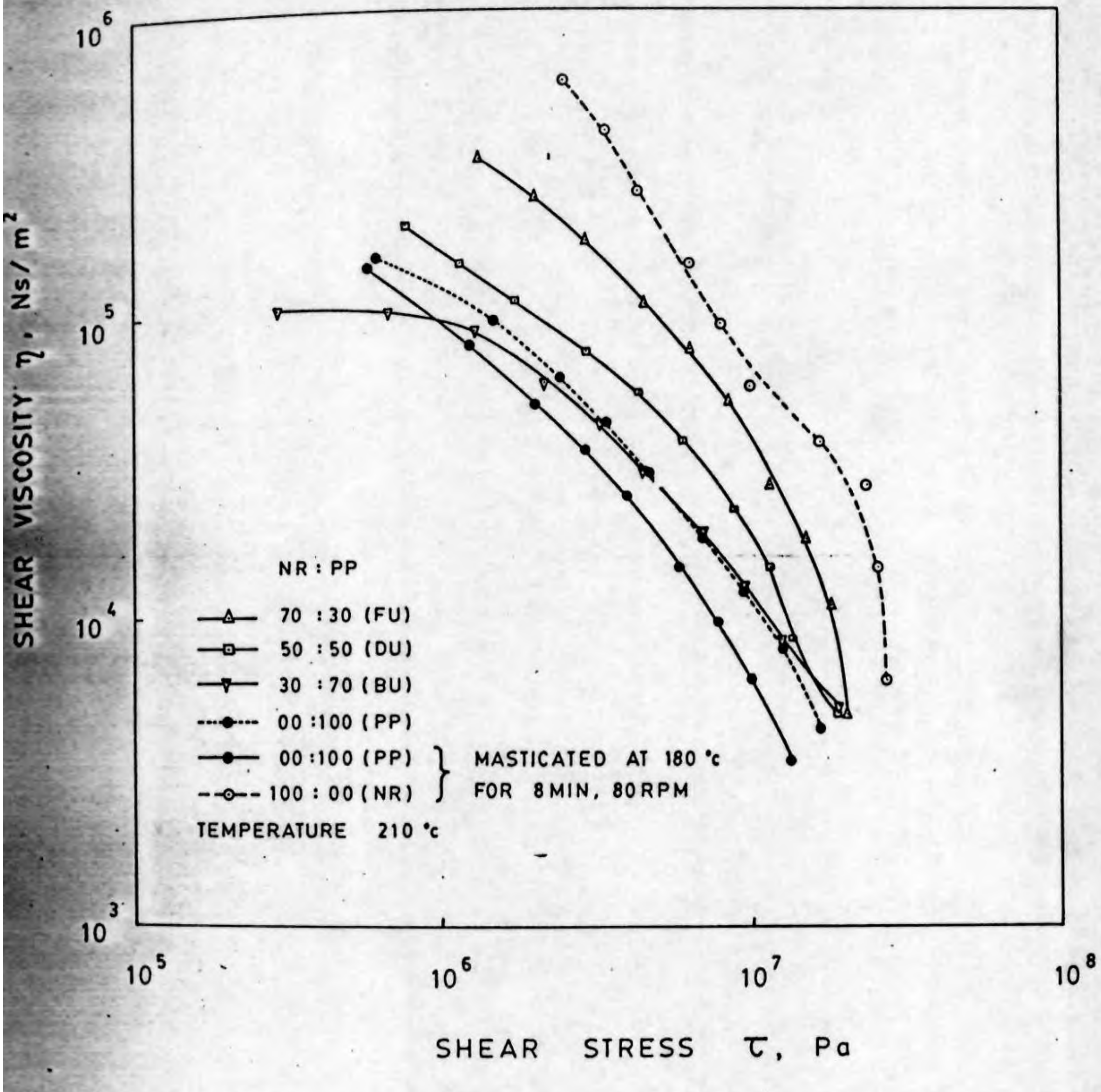


FIG. III.1 VISCOSITY-SHEAR STRESS PLOTS SHOWING EFFECT OF BLEND RATIO

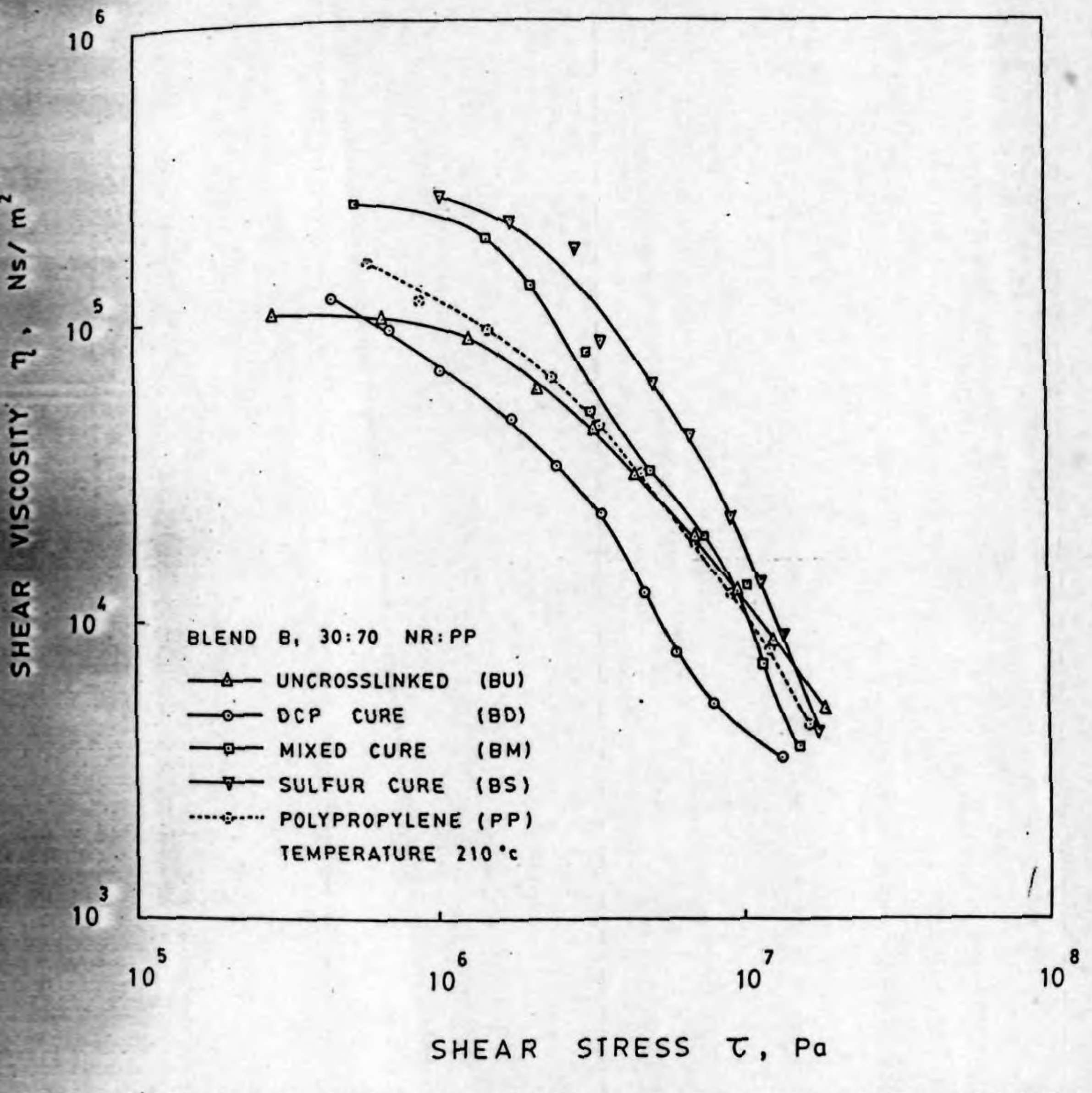


FIG. III.2 VISCOSITY-SHEAR STRESS PLOTS SHOWING EFFECT OF DYNAMIC CROSSLINKING IN BLEND B

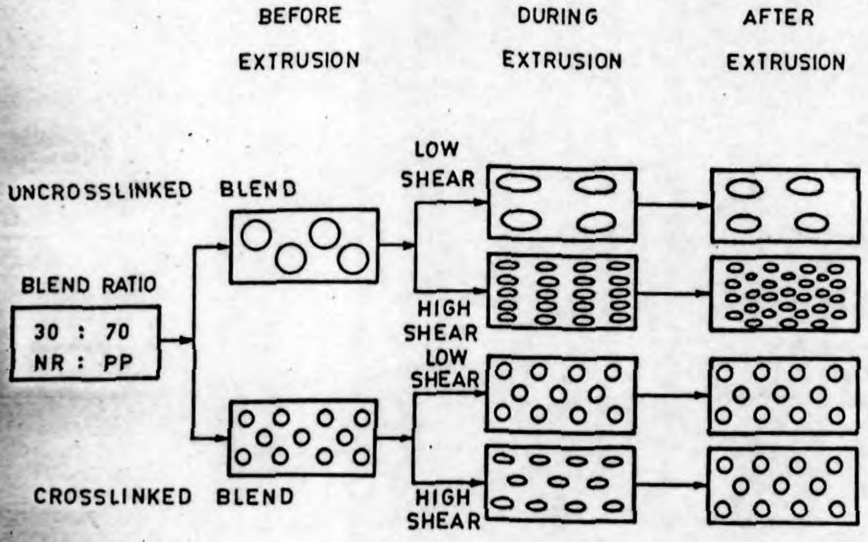


FIG. III.3 REPRESENTATION OF POSSIBLE MORPHOLOGY CHANGE DURING EXTRUSION OF BLEND B

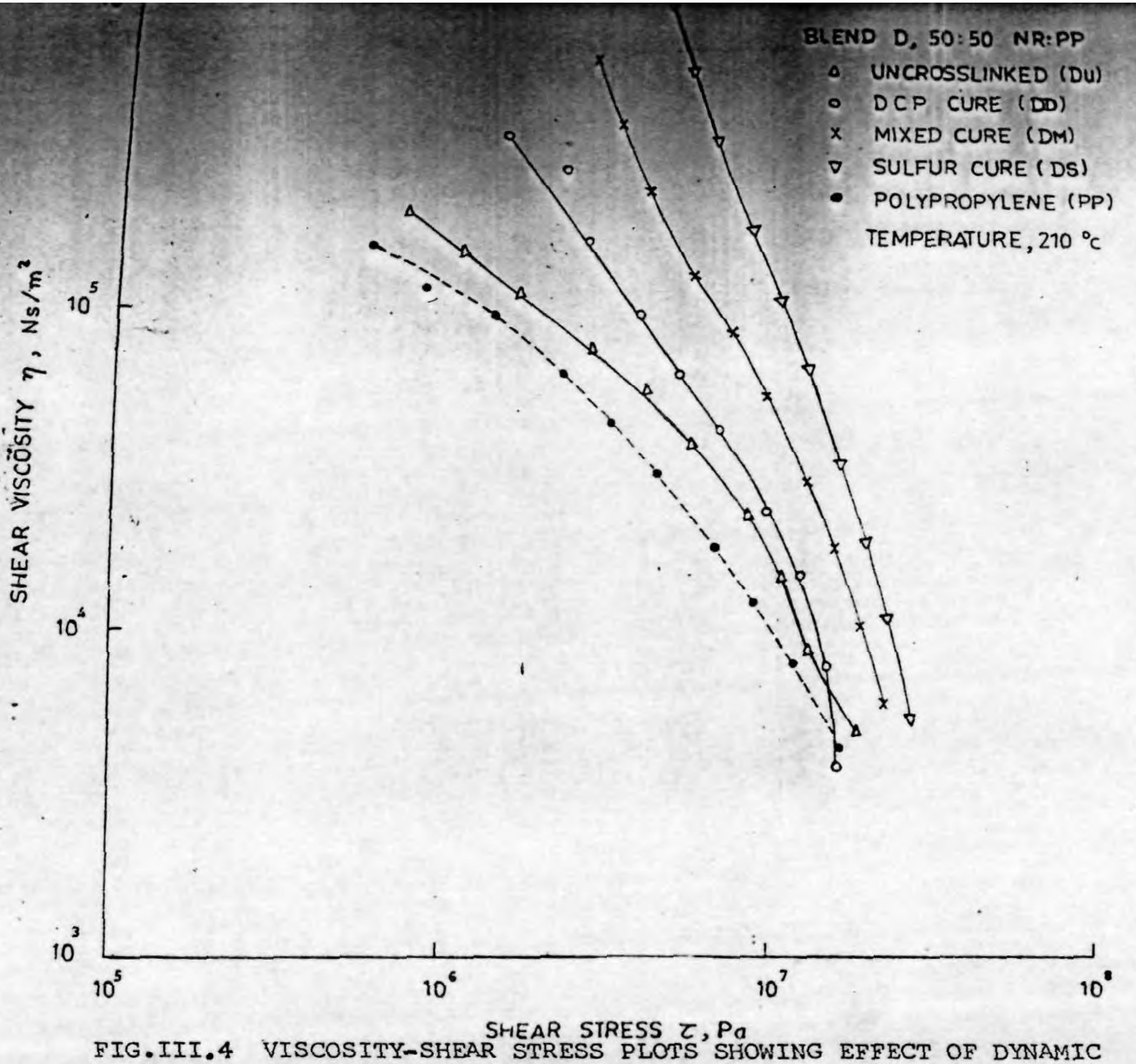


FIG.III.4 VISCOSITY-SHEAR STRESS PLOTS SHOWING EFFECT OF DYNAMIC CROSSLINKING IN BLEND D

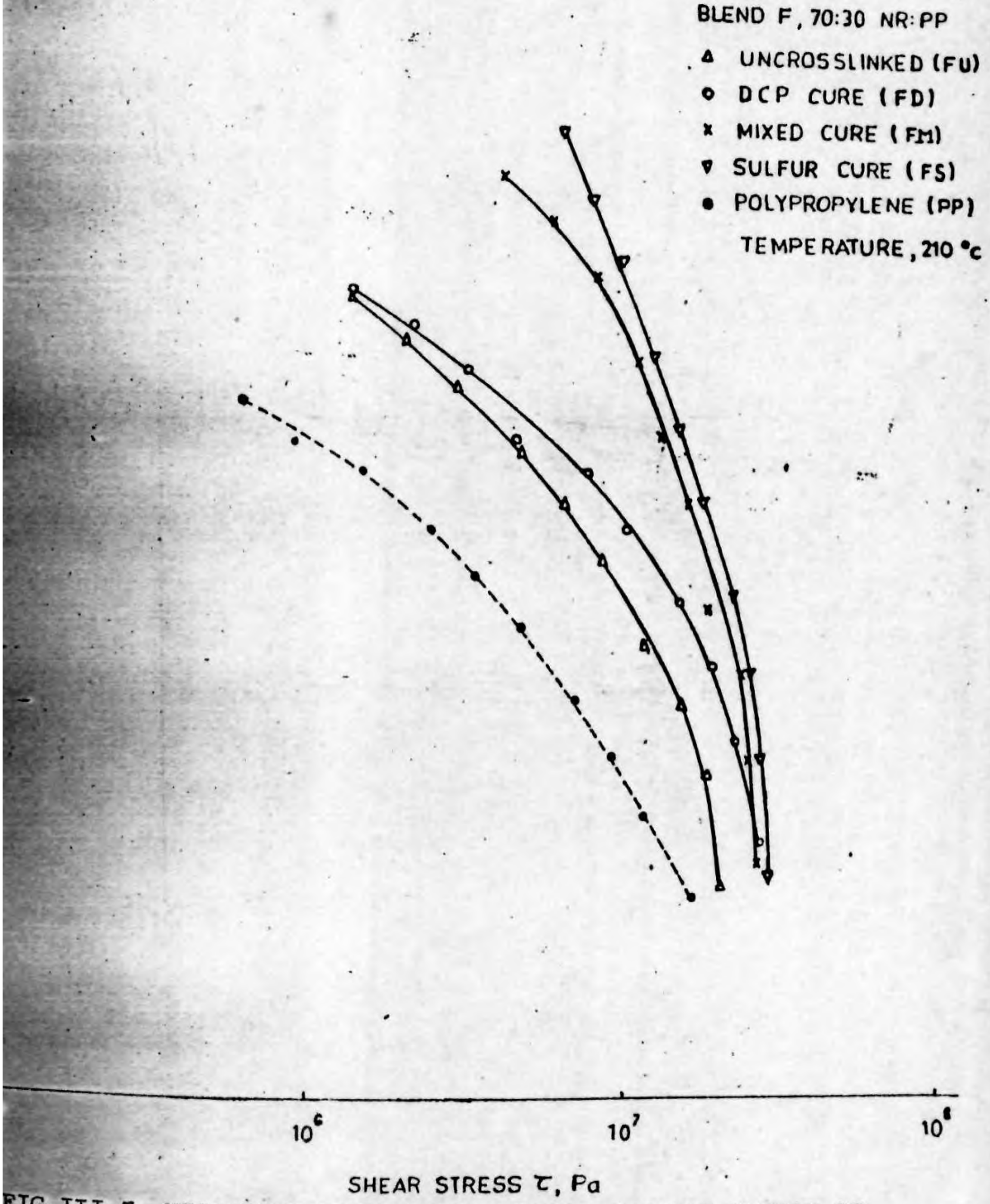


FIG.III.5 VISCOSITY-SHEAR STRESS PLOTS SHOWING EFFECT OF DYNAMIC CROSSLINKING IN BLEND F

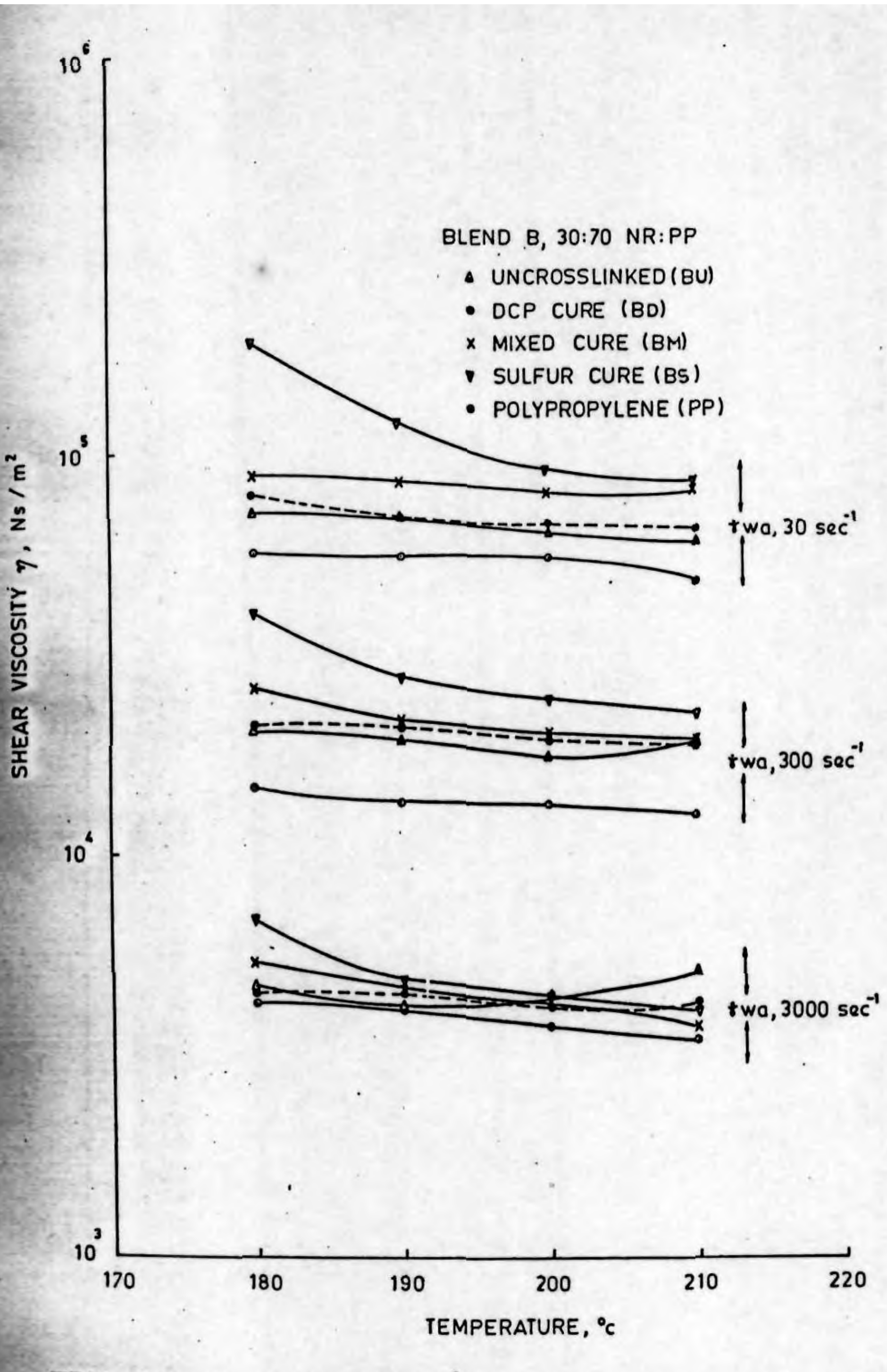


FIG. III.6 EFFECT OF TEMPERATURE AND SHEAR RATE ON VISCOSITY OF BLEND B

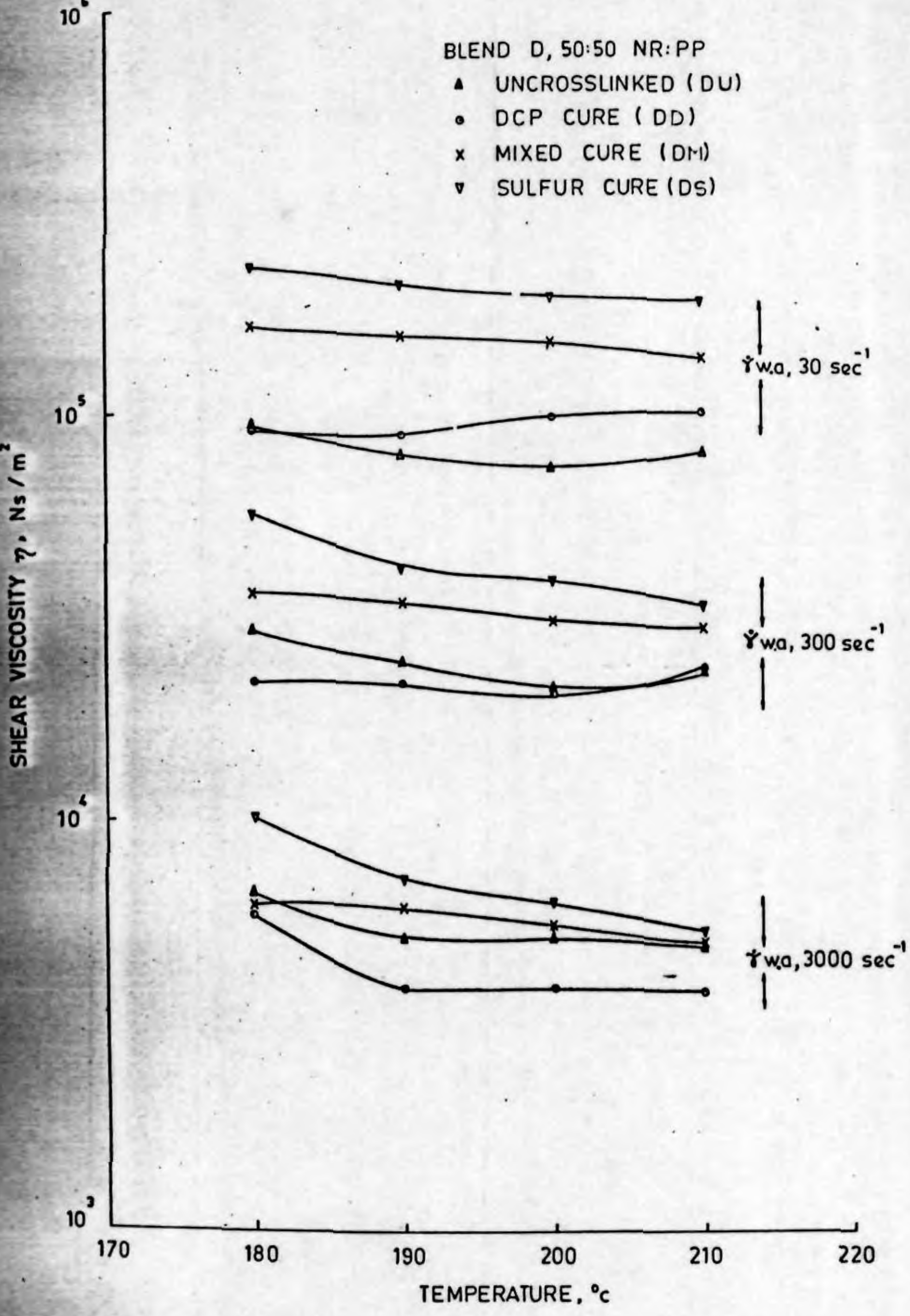


FIG.III.7 EFFECT OF TEMPERATURE AND SHEAR RATE ON VISCOSITY OF BLEND D

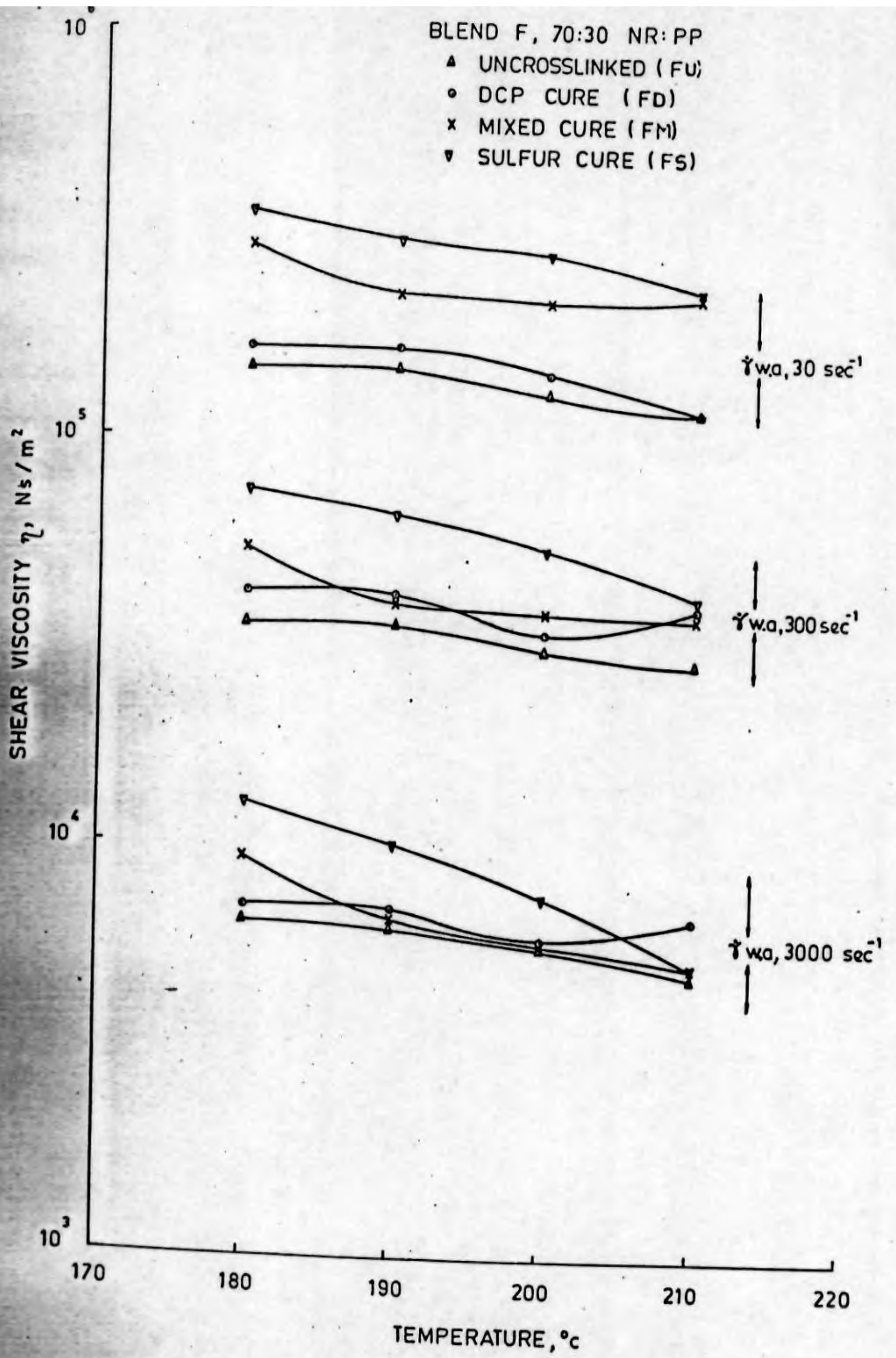


FIG.III.8 EFFECT OF TEMPERATURE AND SHEAR RATE ON VISCOSITY OF BLEND F

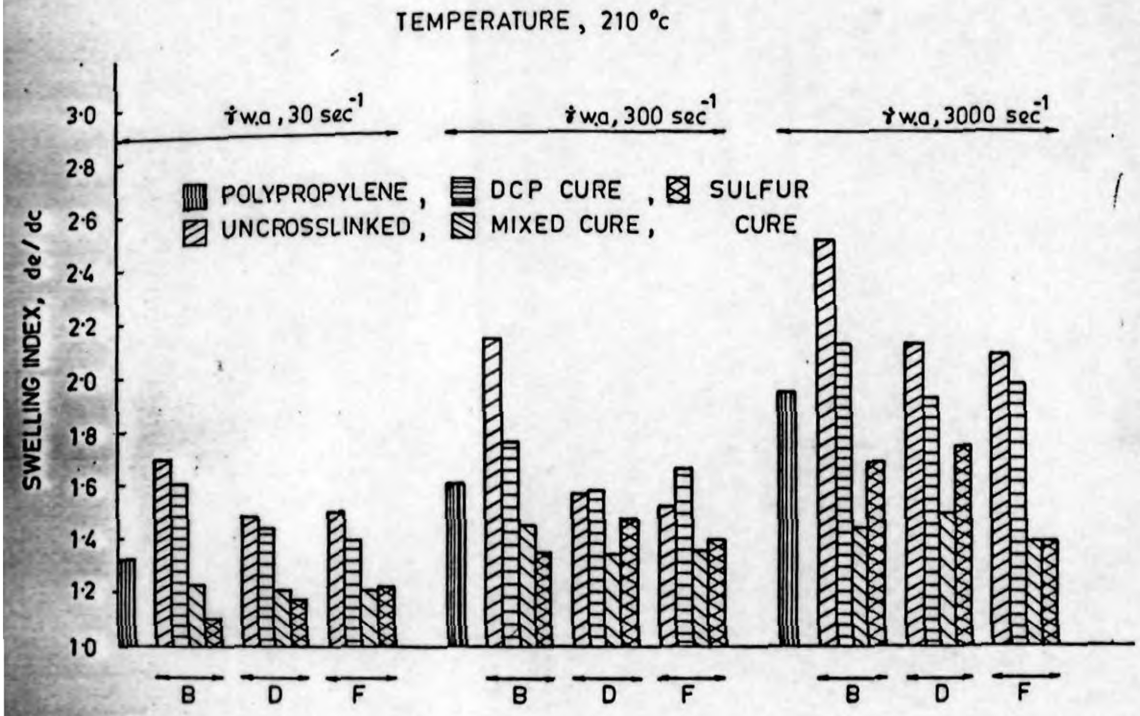


FIG.III.9 EFFECT OF BLEND RATIO, DYNAMIC CROSSLINKING AND SHEAR RATE ON DIE SWELL

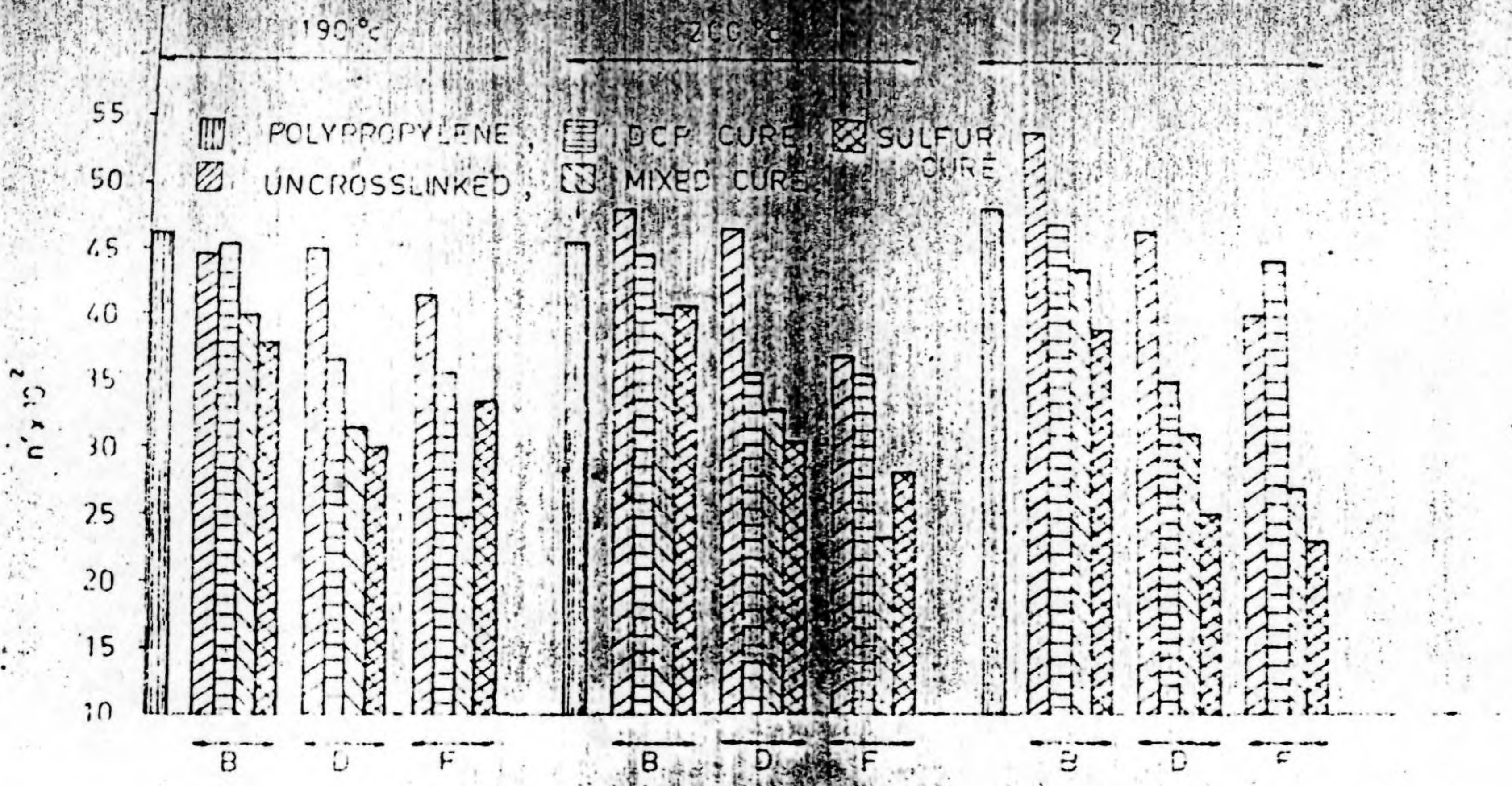


FIG.III.10 EFFECT OF BLEND RATIO AND DYNAMIC CROSSLINKING ON n'

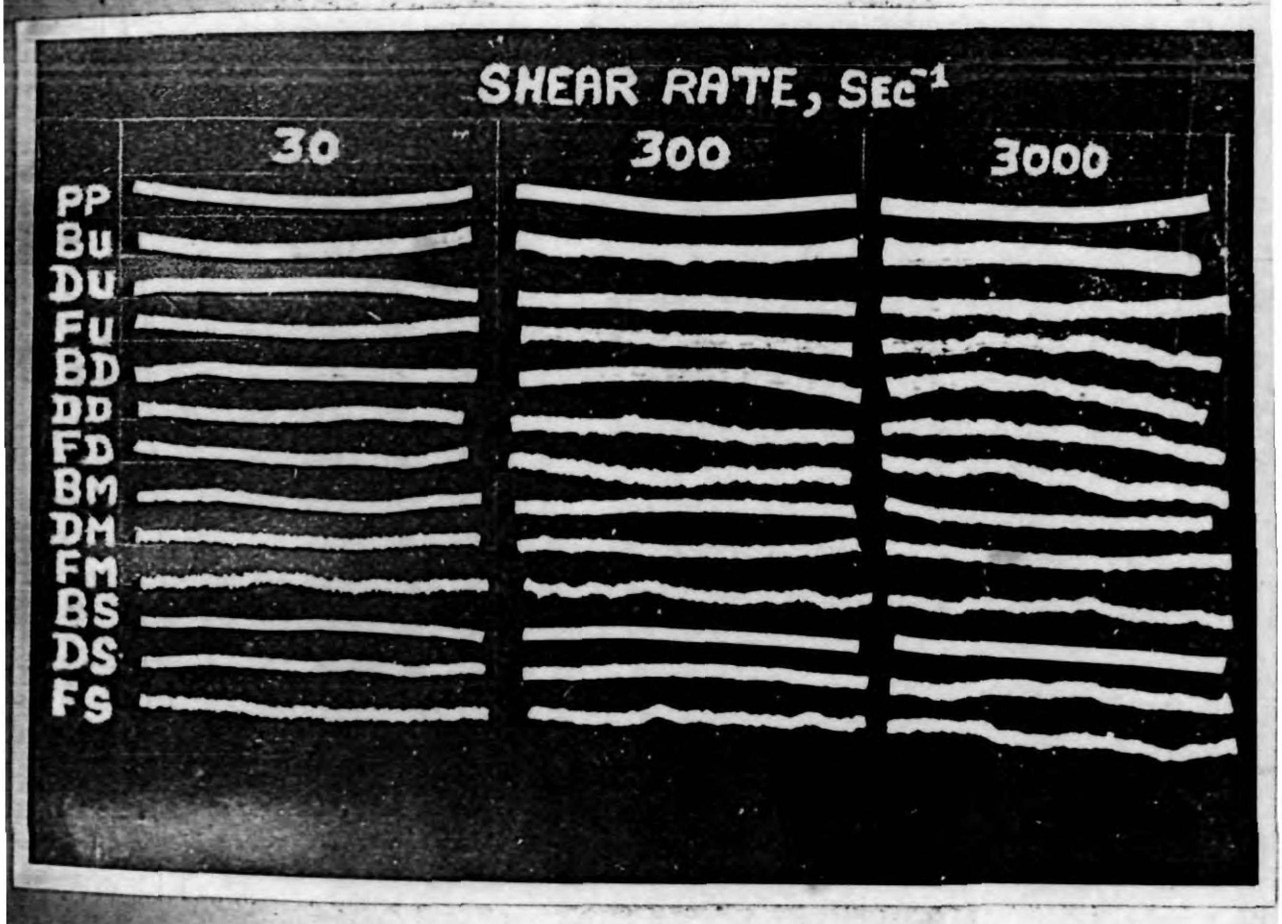


FIG.III.11 EFFECT OF SHEAR RATE AND DYNAMIC CROSSLINKING ON DEFORMATION OF EXTRUDATES

CHAPTER - IV

EFFECT OF BLEND RATIO AND DYNAMIC CROSSLINKING ON

PART A : MORPHOLOGY
PART B : MECHANICAL PROPERTIES
PART C : MODE OF FAILURE UNDER TENSILE FRACTURE
PART D : MODE OF FAILURE UNDER TEAR FRACTURE
PART E : MODE OF FAILURE UNDER ABRATION

OF THERMOPLASTIC NATURAL RUBBER-POLYPROPYLENE BLENDS

Parts of the results in this chapter have been published in the following journals :

1) MATERIALS CHEMISTRY AND PHYSICS, 12, 137 (1985)
2) JOURNAL OF MATERIALS SCIENCE LETTERS, 4, 455 (1985)

Thermoplastic elastomer blends possess an additional advantage over the other types of TPEs in that a wide range of properties can easily be obtained by varying the composition of the blends. Dynamic crosslinking of the elastomer phase was reported to improve the physical properties further[6,104,112,113]. A clear understanding of the range of physical properties and the mode of failure under the application of load is essential for selecting the correct grade of the thermoplastic elastomer blend for a particular application.

This chapter of the thesis consists of the results of a systematic study conducted on the effect of blend ratio and extent of dynamic crosslinking on the mechanical properties and mode of failure under tensile and tear fracture and abrasion of thermoplastic NR-PP blends. This chapter is divided into five parts.

In part A of this chapter, the changes in morphology of the blends with change in composition are discussed. Part B contains the results of the studies on the effect of blend ratio and extent of crosslinking on the mechanical properties of the blends. In part C, the mechanism of failure of the blends under tensile fracture is discussed. The mechanism of failure under tear fracture is given in part D and the mode of abrasion of the blends is discussed in part E of this chapter.

CHAPTER IV A

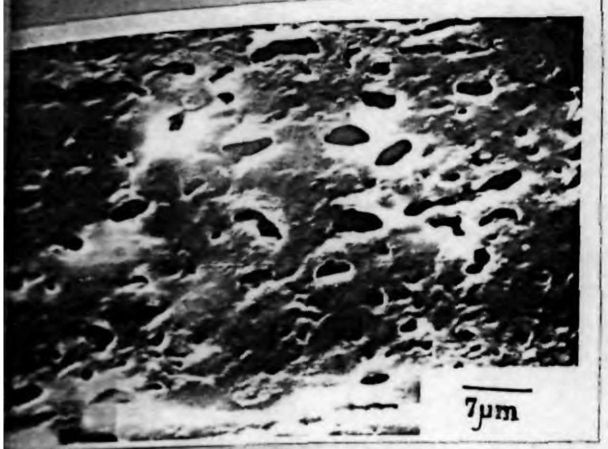
MORPHOLOGY OF THE THERMOPLASTIC NR-PP BLENDS

The morphology of the blends of two mutually incompatible polymers depends on several factors such as composition of the blends, intrinsic viscosity of the components, rate of shear during blending and temperature. As a general rule, the component having higher viscosity or lower proportion in the blend forms the dispersed phase, while the continuous phase consists of the component having higher proportion or lower viscosity. But depending on the relative proportion and viscosity of the components, a structure having two interpenetrating continuous phases, is also possible.

The natural rubber used in the present study was having a higher molecular weight and higher melt viscosity compared with that of PP (table II.3 and figure III.1). The variations in morphology of the uncrosslinked blends with change in composition of the blends are discussed in this part of chapter IV. The composition of the blends varied from 70:30 PP:NR to 30:70 PP:NR. The details of the procedure for studying the morphology are given in section II.7.

The scanning electron micrographs of the microtomed edges of the blends BU, CU, DU, EU and FU from which the rubber phase has been extracted out using toluene, are shown in figure IV.A.1 to IV.A.5 respectively. In these figures, the black regions represent the rubber phase which has been extracted out. From figure IV.A.1, it is evident that the rubber phase remained as dispersed particles in the PP matrix in blend BU. As the rubber content is increased, the number and size of the dispersed rubber particles have increased, as observed from figure IV.A.2 of blend CU. The dispersed particles in this blend are having more deformed shape than the particles in blend BU. In 50:50 NR:PP blend, the boundary layers of the PP phase separating the dispersed rubber particles have narrowed down and the rubber phase also tends to form a continuous phase, as observed from figure IV.A.3 of blend DU. The larger particle size and more continuous nature of the rubber phase compared with those of blends BU and CU may be attributed to the diffusion and reagglomeration of the dispersed rubber particles under various processing condition. The average size of the dispersed particles has increased from about 3μm to 10μm as the composition of the blend was changed from 30:70 NR:PP to 60:40 NR:PP, as seen from the scale of magnification in the micrographs. Figure IV.A.4 of blend EU shows that the rubber phase becomes almost continuous at the 60:40 blend ratio of the NR and PP, as evidenced by the fibrils, formed by the broken layers of PP, seen in the photograph. The micrograph of the 70:30 NR:PP blend (figure IV.A.5) shows continuous layers of dark regions of the NR phase, which are interconnected by white layers of PP. Thus in blends EU and FU both NR and PP exist as continuous phases due to the higher proportion of the NR phase and lower melt viscosity of the PP phase.

In the dynamically crosslinked blends SEM studies on morphology was not possible, because the crosslinked rubber phase could not be extracted. But it is expected that the size of the dispersed rubber particles is much smaller than that of the uncrosslinked blends. There are two main reasons for this. In first place, the mixing torque of the dynamically crosslinked blends is higher than that of the uncrosslinked blends (table IV.B.1) and these blends show higher viscosity (figure III.2). Better shearing action at higher viscosity produces smaller particle size of the dispersed phase, with round or ellipsoidal shapes. Secondly, as the rubber particles are already vulcanized, change in morphology of the system, due to diffusion and recombination of the dispersed particles is unlikely, as that occurs in the case of uncrosslinked



IG.IV.A.1 SEM PHOTOGRAPH OF
END BU, AFTER EXTRACTION OF
E RUBBER PHASE

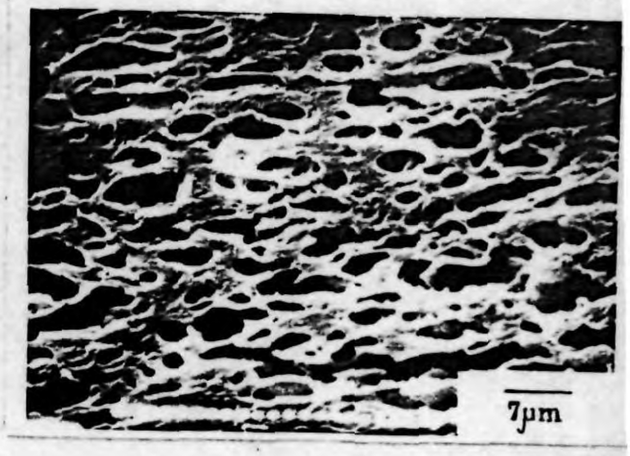


FIG.IV.A.2 SEM PHOTOGRAPH OF
BLEND CU, AFTER EXTRACTION OF
THE RUBBER PHASE

G.IV.A.3 SEM PHOTOGRAPH OF
END DU, AFTER EXTRACTION OF
E RUBBER PHASE

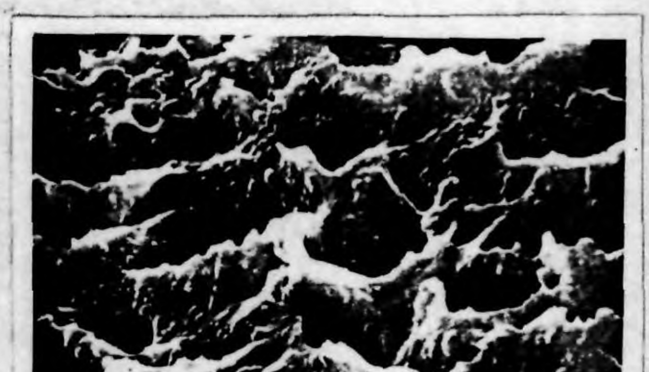


FIG.IV.A.4 SEM PHOTOGRAPH OF
BLEND EU, AFTER EXTRACTION OF
THE RUBBER PHASE

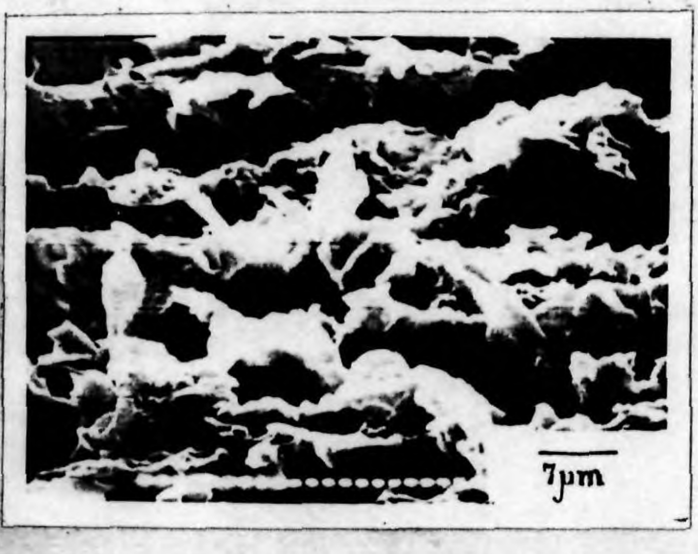


FIG.IV.A.5 SEM PHOTOGRAPH OF BLEND FU, AFTER EXTRACTION OF THE RUBBER PHASE

CHAPTER IV B

EFFECT OF BLEND RATIO AND DYNAMIC CROSSLINKING ON THE MECHANICAL PROPERTIES OF NR-PP BLENDS

The blend ratios and details of the curing systems used are given in table II.4. The extent of crosslinking was in the order sulphur cure > mixed cure > DCP cure, as discussed in section III.1. The properties of the blends are given in table IV.B.1.

IV.B.1 Mixing Torque : The torque values reported in table IV.B.1 are those recorded in the Brabender Plasticorder at the time of dumping the blends after the scheduled time. These values indicate the processability of the blends under a shear rate equivalent to that developed during blending the components in the Plasti-corder. In both uncrosslinked and dynamically crosslinked blends, the mixing torque increased with increase in proportion of the rubber phase. As the extent of dynamic crosslinking is increased the mixing torque increased, irrespective of the proportion of NR and PP in the blends. But, this effect was more pronounced in blends containing higher proportion of the elastomer phase. This is because, the crosslinking agent has its action mainly on the rubber phase, as reported by Coran and Patel[114]. This indicated that more energy is required for processing the blends containing higher proportion of the elastomer phase and higher extent of crosslinking.

IV.B.2 Tensile Properties : Polypropylene, containing no rubber phase, showed highest tensile strength and lowest elongation at break. Increase of rubber content decreased the tensile strength and 100% modulus but increased the elongation at break. The strength of the NR-PP blends depends on the strength of the PP matrix, which in turn is dependent upon the extent of crystallinity. Martuscelli et al[161,162] have shown that the spherulite growth of isotactic polypropylene in blends with rubbers is disturbed by the presence of the rubber phase. Hence the observed drop in tensile strength of the blends with increase in rubber content may be due to the reason explained above. Dynamic crosslinking of the elastomer phase increased the tensile properties of the thermoplastic NR-PP blends and in blends containing higher proportion of the elastomer phase, the increase was proportional to the extent of crosslinking. But in blends having a higher proportion of the PP phase, dynamic crosslinking using DCP did not show any improvement in tensile properties. This is because of the degradation action of DCP on the PP matrix in addition to its crosslinking effect on the rubber phase.

IV.B.3 Stress-Strain Curves : The stress-strain curves given in figure IV.B.1 show that the uncrosslinked blends undergo plastic type deformation, under tension. With increase in PP content yielding increased and blends CU and BU showed yielding with drawing. But dynamic crosslinking of the elastomer phase, changed the deformation behaviour from plastic to elastic type, as seen from the stress-strain curves of blends FS to BS. The extent of crosslinking also had a profound influence on the shape of the stress-strain curve. This is shown in figure IV.B.2. At higher rubber contents, the uncrosslinked blend (FU) showed plastic type deformation. Dynamic crosslinking changed its nature to elastic type (FD) and as the extent of dynamic crosslinking is increased, the stress-strain curve of this blend (FS) resembled to that of a vulcanized elastomer.

IV.B.4 Tear Strength : The tear strength of the blends decreased with increase in proportion of the rubber phase. But the dynamically crosslinked blends showed higher tear strength than the corresponding uncrosslinked blends. The degradation effect of DCP on the blends containing higher proportions of PP is clearly evident from the lower tear strength values of the DCP cured blends compared with those of the uncrosslinked blends. The load-time plots for the tearing process (figure IV.A.3) indicated that the rate of propagation of the tear is slowed down with increase in the proportion of the elastomer phase, even though the tear strength is reduced.

IV.B.5 Hardness : The hardness values decreased with increase in the proportion of the elastomer phase in the blend. But dynamic crosslinking increased the hardness and the increase was proportional to the extent of crosslinking of the elastomer phase. The increase in hardness values with extent of crosslinking was more prominent in blends D, E and F which contained higher proportions of the elastomer phase. This is because the crosslinking agent has its action mainly on the rubber phase, which tends to form a continuous phase of the blend at these blend ratios.

IV.B.6 Flexural Modulus : The flexural modulus decreased with increase in rubber content of the NR-PP blends. But dynamic crosslinking did not show any regular pattern of increase or decrease of flexural modulus with extent of crosslinking. In all the cases, the uncrosslinked blends showed higher flexural modulus values compared to the dynamically crosslinked blends. This is because, the smaller size of the crosslinked particles was more effective in reducing the spherulite growth of the PP as reported by Martuscelli[161].

IV.B.7 <u>Tension Set</u> : The uncrosslinked blends showed very high set values which exceeded even the limit of 50% that is fixed for classifying the materials as elastomers. But dynamic crosslinking reduced the set values considerably and even the blend BS which contained the highest proportion of PP showed a value less than 50%. This is due to a change in deformation behaviour of blends from plastic to elastic type, when the elastomer phase is crosslinked, as explained in section IV.A.3.

IV.B.8 <u>Tensile Impact Energy</u> : The tensile impact energy increased with increase in rubber content of the blends. Dynamic crosslinking of the elastomer phase increased the tensile impact energy considerably and this effect was more prominent in blends containing higher proportion of PP. The dynamically crosslinked blend BS showed almost double the value of impact energy compared to the uncrosslinked blend BU. In the uncrosslinked blends, the dispersed rubber particles are bigger in size and less uniformly distributed than the rubber particles in dynamically crosslinked blends[118]. In dynamically crosslinked blends, better shearing action during blending makes the particles smaller in size and uniformly distributed[103]. These particles do not reagglomerate through diffusion and form bigger particles unlike the uncrosslinked rubber particles[111]. The principle of toughening of the thermoplastic materials by using elastomer particles is that the impact energy may be dissipated through controlled deformation of the matrix by providing a large number of stress concentrations or crazes[163]. This is achieved through smaller particle size and uniform distribution of the dispersed rubber particles. The above discussion explains the higher tensile impact energy of the dynamically crosslinked blends compared to that of the uncrosslinked blends.

Sample Number	Mixing Torque (Nm)	100 % Moduluss (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Tear Strength (kN/m)	Hard-ness (Shore A)	Flexural Modulus (MPa)	Tension Set (%)	Tensile Impact Energy (J/m)
A	5.5	-	23.7	5	126.0	100	970	-	475
BU	5.5	-	15.0	90	100.5	90	701	-	1379
BD	6.5	-	15.0	70	86.0	93	562	-	-
BM	6.0	15.1	15.2	170	101.6	94	573	-	-
BS	8.0	-	15.4	55	115.2	95	638	48	2853
CU	6.5	12.6	12.6	100	78.2	89	532	78	1938
CD	8.0	11.8	11.8	120	71.2	92	487	-	-
CM	7.5	11.3	14.2	395	80.1	93	374	-	-
CS	12.0	13.3	14.3	190	100.0	94	444	39	3459
DU	7.5	8.9	8.9	100	54.9	86	286	88	2581
DD	10.5	7.5	9.1	200	54.1	91	241	-	-
DM	8.5	9.1	12.0	375	70.1	93	218	-	-
DS	14.0	10.2	12.3	230	93.1	94	260	31	3702
EU	9.0	5.3	5.3	130	36.1	84	193	75	2308
ED	14.0	5.4	7.4	230	46.2	84	120	-	-
EM	14.5	6.5	12.0	405	65.0	90	115	-	-
ES	21.0	8.0	12.1	220	73.8	91	127	22	3717
FU	10.0	1.7	2.4	180	22.1	81	35	63	3069
FD	16.0	3.3	5.1	310	27.2	84	28	-	-
FM	18.5	3.7	8.3	315	38.0	86	39	-	-
FS	22.5	5.3	9.2	270	44.4	89	54	11	3271

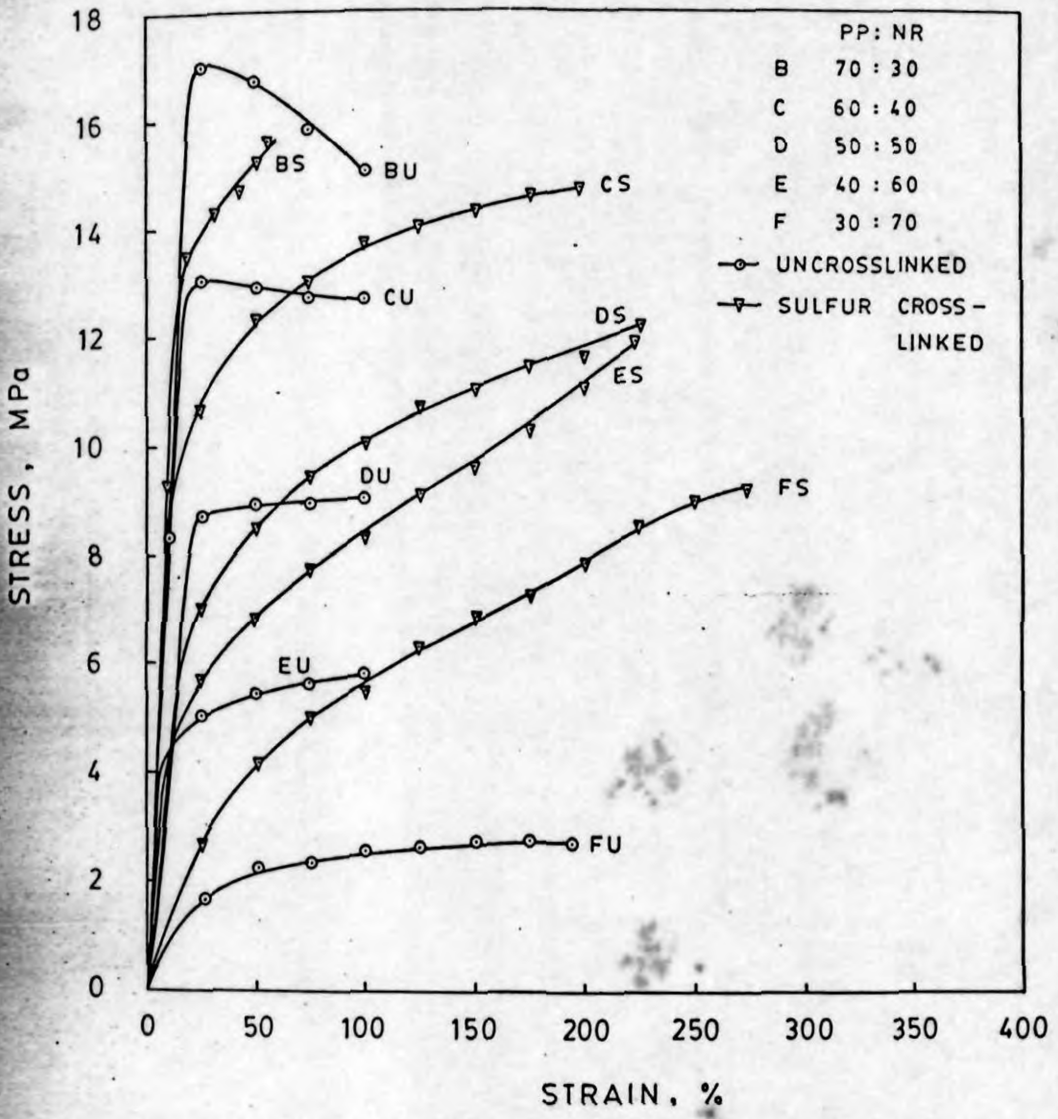


FIG.IV.B.1 STRESS-STRAIN CURVES OF NR-PP BLENDS

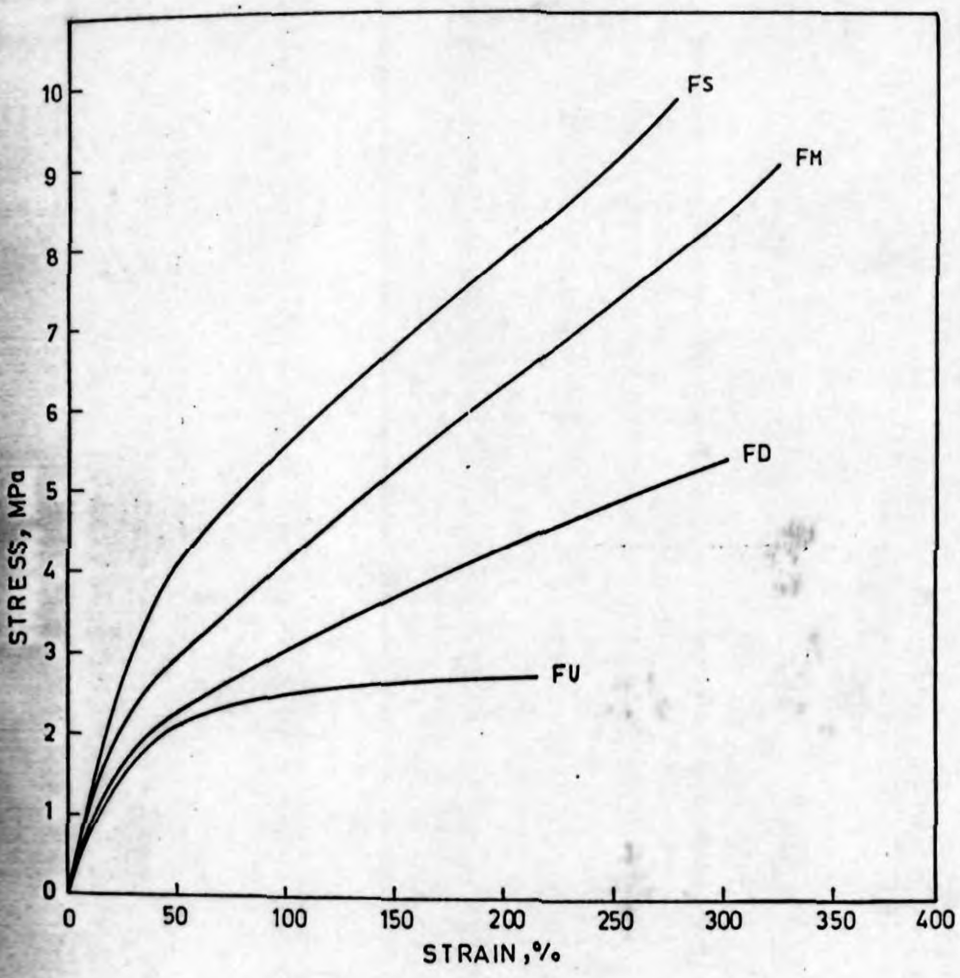


FIG.IV.B.2 STRESS-STRAIN CURVES OF F SHOWING EFFECT OF CROSSLINKING

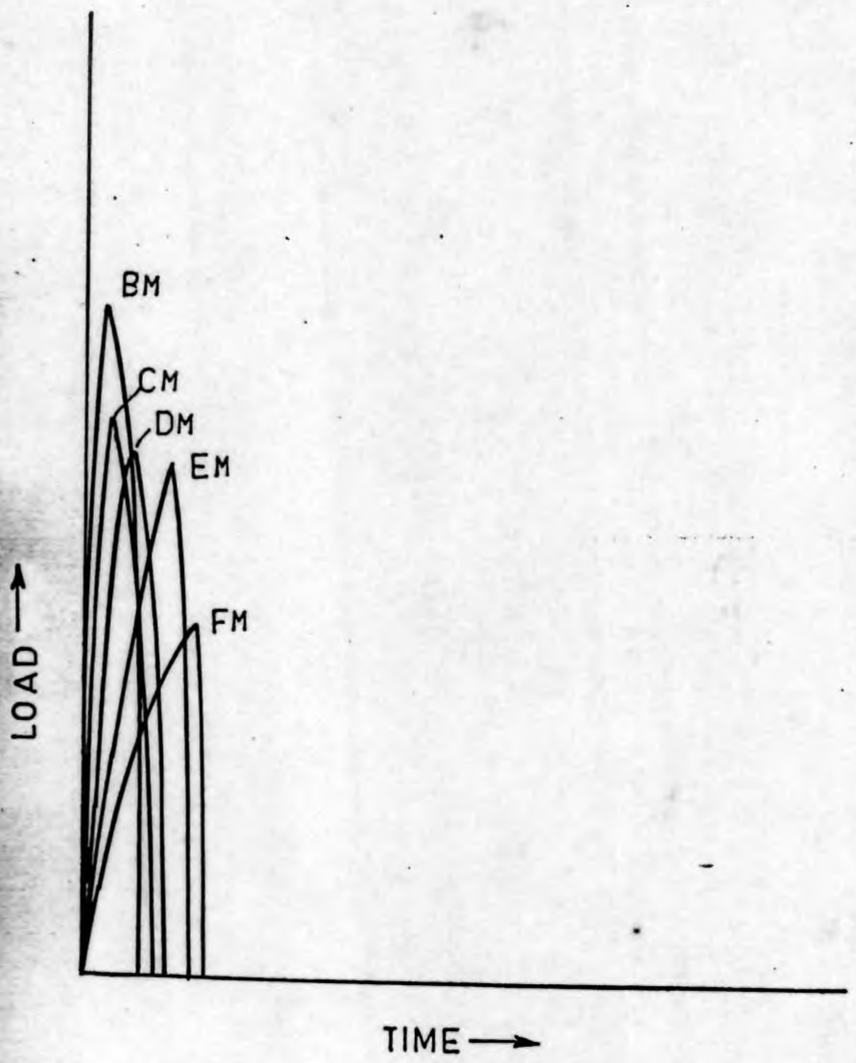


FIG.IV.B.3 LOAD-TEAR PLOTS, SHOWING EFFECT OF BLEND RATIO

CHAPTER IV C

EFFECT OF BLEND RATIO AND DYNAMIC CROSSLINKING ON THE MODE OF TENSILE FAILURE

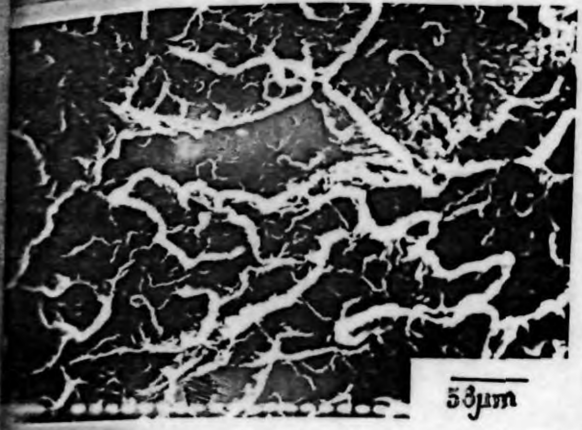
It has been observed earlier[110] that PP undergoes brittle type fracture which proceeds through craze formation. Presence of rubber in the plastic phase changes the fracture mode from brittle to ductile. The fracture, other than craze formation, takes place by shear yielding at higher proportions of rubber. The rubbery phase acts as stress concentrator and initiates shear bands. The molecular orientation within the shear zones is approximately parallel to the applied stress and forms shear bands normal to the stress.

The mechanical properties and the stress-strain curves described in the previous section this chapter have shown that dynamic crosslinking changes the deformation behaviour of the blends from ductile to elastic type. The SEM studies described in this section substantiate the above observations with the help of tensile fractographs.

Figure IV.C.1 is the fractograph of tensile fracture of PP. The failure is of brittle nature as evidenced by the presence of multidirectional cracks in different planes. Addition of NR to PP changed the fracture mode from brittle to ductile type. In the case of uncrosslinked 70:30 PP:NR blend (BU) tensile fracture surface showed fibrils of rubber mass which flowed normal to the direction of application of stress (figure IV.C.2). Increasing the proportion of rubber in the blend (DU) reduced the brittleness, made the fracture surface smooth, caused matrix flow and the appearance of microdimples (figure IV.C.3). Occurrence of voids in the fractograph may correspond to the plastic phase detachment under high elongation. Further increase of rubber content (FU) showed ductile failure with elongated dimple structure (figure IV.C.4). The rupture is apparently initiated by the formation of cavity due to drawing of the plastic phase from plastic-rubber matrix during testing.

Crosslinking of the elastomer phase in the blend restricts the matrix flow under stress. In the case of blends of low rubber content, the dispersed rubber particles act as craze initiator and arrestor during rupture under stress[164-166]. But at higher proportions of rubber in the blend, the rubber also tends to form a continuous phase and the blends show different tensile fracture modes.

Dynamic crosslinking of the elastomer phase in 30:70 NR:PP blend provides smaller size and more uniform dispersion of the elastomer particles which are more effective in craze initiation and in restricting matrix flow. This is evident from the tensile fractograph of blend BS (figure IV.C.5). The fractograph showed one main fracture line and many secondary fracture paths. The absence of large flow of the matrix and fibrils on the fracture surface indicated that the deformation behaviour has changed from ductile to elastic type. This was shown in the stress-strain curves given in figure IV.B.1 also. In the case of 50:50 blend (DS) no separate fracture path was observed on the fractograph but restricted flow of the matrix can be seen in figure IV.C.6 when compared with figure IV.C.3 of the uncrosslinked blend. For the dynamically crosslinked 70:30 NR:PP blend (FS) the rubber phase becomes less deformable and quickly recovering, due to crosslinking. Since the rubber also formed a continuous phase due to higher proportion in the blend, the fracture proceeds by shearing action. This is evident from the fractograph of FS shown in figure IV.C.7, which contained fracture paths in different planes. The absence of any elongated dimple and signs of residual deformation indicated that this blend has undergone elastic type deformation during tensile rupture.



G.IV.C.1 TENSILE FRACTOGRAPH OF PP; BRITTLE FAILURE

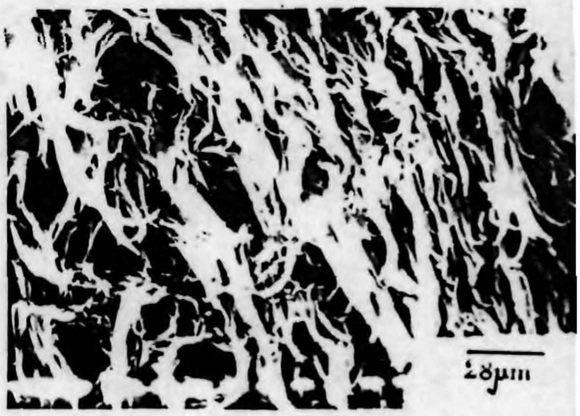


FIG.IV.C.2 TENSILE FRACTOGRAPH OF BLEND BU; DUCTILE FAILURE

FIG.IV.C.3 TENSILE FRACTOGRAPH OF BLEND DU; MATRIX FLOW AND MICRODIMPLES

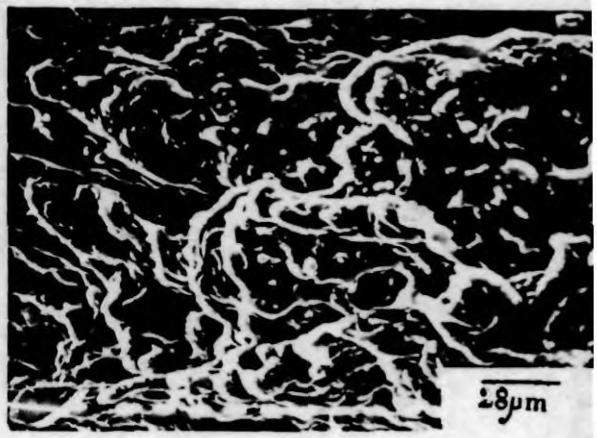
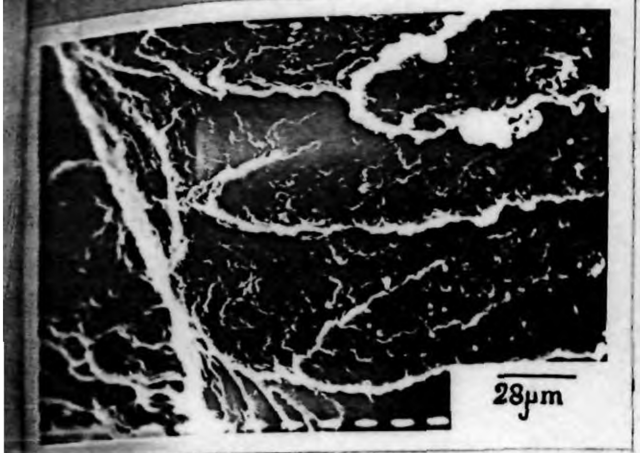


FIG.IV.C.4 TENSILE FRACTOGRAPH OF BLEND FU; DUCTILE FAILURE WITH ELONGATED DIMPLES



IG.IV.C.5 TENSILE FRACTOGRAPH
F BLEND BS; MAIN FRACTURE PATH
D SECONDARY FRACTURE LINES

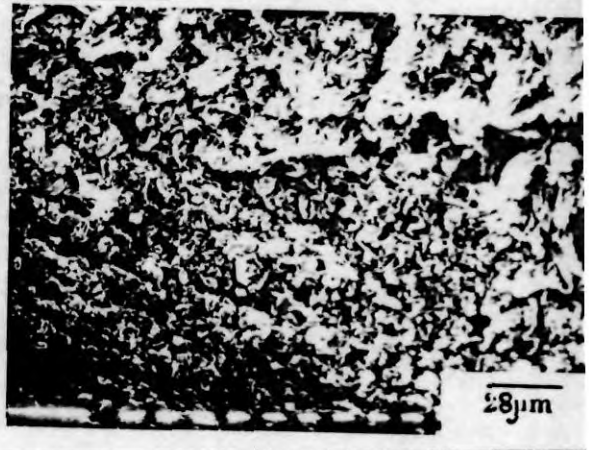


FIG.IV.C.6 TENSILE FRACTOGRAPH
OF BLEND DS; SMOOTH SURFACE AND
RESTRICTED FLOW OF MATRIX

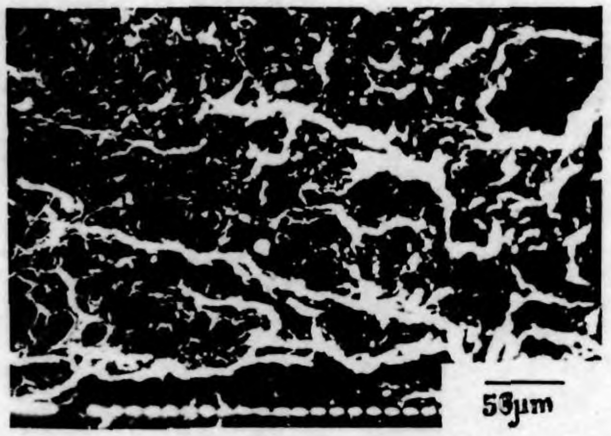


FIG.IV.C.7 TENSILE FRACTOGRAPH OF
BLEND FS; SMOOTH PROPAGATION OF
FRACTURE PATH AND SHEAR PLANES

CHAPTER IV D

EFFECT OF BLEND RATIO AND DYNAMIC CROSSLINKING ON THE MODE OF TEAR FAILURE

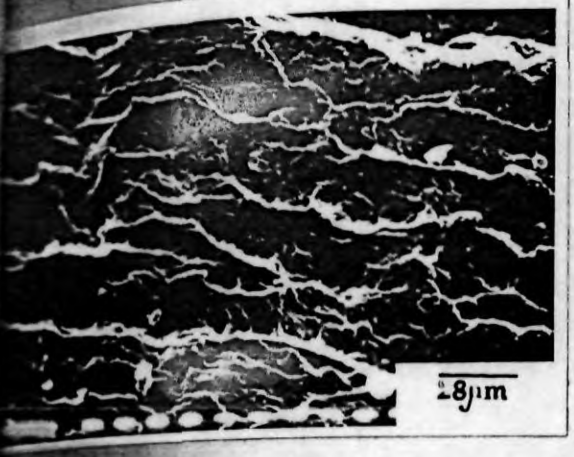
In rubber modified thermoplastics, the principal effect of the elastomer phase in the fracture process is to allow the energy to be dissipated into a relatively large volume of the material at the tip of the crack. This is more effectively accomplished by smaller particle size and uniform dispersion of the elastomer phase in the plastic matrix.

At higher proportion of PP in the blend, the rubber phase remains as dispersed particles. In uncrosslinked blends, the molecular entanglements in the rubber particles, are unable to prevent rapid flow and fracture, in response to an applied stress. This results in lower tear strength of the uncrosslinked blends.

Crosslinking of the elastomer phase during blending results in finer particles size and uniform dispersion of the elastomer phase. During tearing, the rubber particles which bridge the growing crack stretch to very large strains before failing. The tearing strain of a rubber particle increases as its size is reduced[123]. Crosslinking of the elastomer phase allows the rubber particles to reach higher strains and at the same time confers mechanical strength to the particles. Thus, the higher tear strength of the dynamically crosslinked blends compared with that of the uncrosslinked blends is due to smaller particle size, higher elongation and mechanical strength of the dispersed particles. In blends having higher rubber contents, both the polymers form continuous phases, due to higher proportion of the elastomer phase and lower viscosity of the plastic phase. As the rubber also tends to form continuous phase, crosslinking of the elastomer phase increases the tear strength of the blends containing higher proportion of the elastomer phase.

Scanning electron microscopic examination of the tear fracture surfaces of the blends supports the above views. Figure IV.D.1 shows the tear fracture surface of PP. The presence of several parallel fracture bands in different planes revealed the brittle nature of the failure. Figure IV.D.2 shows the fracture surface of the uncrosslinked 70:30 PP:NR blend. It indicated the initiation of the parabolic fracture pattern which is propagated concentrically as the tear advanced. The fibrils on the surface along the direction of propagation of the crack indicated high extent of deformation and ductile nature of the failure. Increasing the rubber content in the blend increased the continuity of the rubber phase and the fracture surface of the 50:50 PP:NR blend (figure IV.D.3) and that of the 30:70 PP:NR blend (figure IV.D.4) showed smooth tear path with rough surface.

Dynamic crosslinking of the elastomer phase in the 70:30 PP:NR blend reduced the particle size and improved the dispersion of the rubber phase. The resistance to high deformation of the crosslinked particles restricted the flow under stress, as shown by the presence of many short rounded tear lines on the fracture surface (figure IV.D.5). In 50:50 PP:NR blend, crosslinking of the elastomer phase gave a broad tear path (figure IV.D.6) as the rubber phase also tends to form a continuous phase. In 30:70 PP:NR blends, both plastic and rubber phases exist as continuous interpenetrating two-phase system[110] and dynamic crosslinking reduced the deformation of the rubber phase. Under the applied stress, a series of discontinuous cracks are formed (figure IV.D.7) on the surface due to less deformation of the rubber phase and weak interaction between the two phases.



.IV.D.1 TEAR FRACTOGRAPH OF
BRITTLE FRACTURE

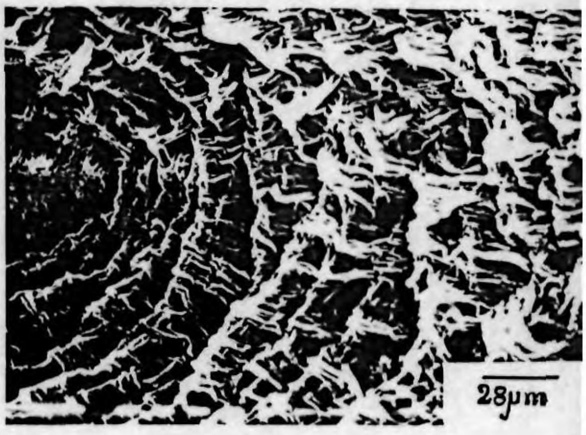
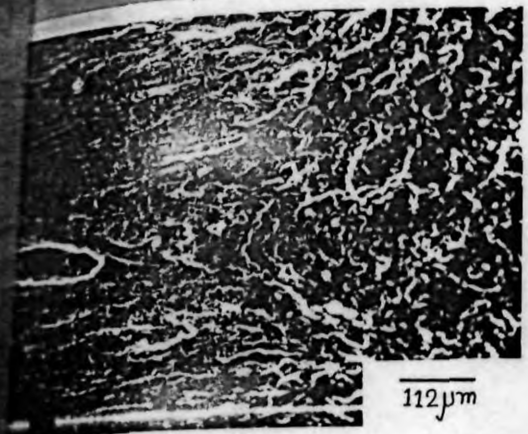


FIG.IV.D.2 TEAR FRACTOGRAPH OF
BLEND BU; PARABOLIC CRACK
INITIATION AND FIBRIL

G.IV.D.3 TEAR FRACTOGRAPH OF
END DU; SMOOTH TEAR PATH AND
UGH SURFACE

FIG.IV.D.4 TEAR FRACTOGRAPH OF
BLEND FU; SMOOTH, CONTINUOUS
TEAR PATH AND ROUGH SURFACE



IV.D.5 TEAR FRACTOGRAPH OF
D BS; SHORT ROUNDED TEAR
S

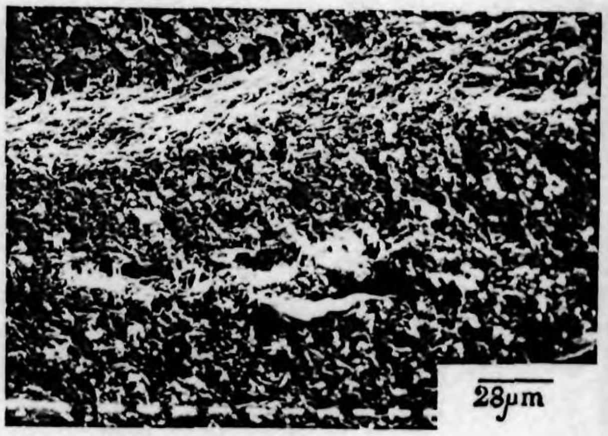


FIG.IV.D.6 TEAR FRACTOGRAPH OF
BLEND DS; BROAD CONTINUOUS
TEAR PATH

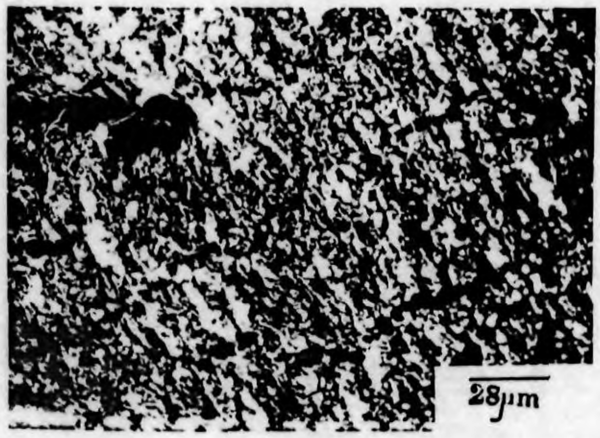


FIG.IV.D.7 TEAR FRACTOGRAPH OF
BLEND FS; SMOOTH SURFACE WITH
CRACKS

CHAPTER IV E

EFFECT OF BLEND RATIO AND DYNAMIC CROSSLINKING ON THE MODE OF ABRASION FAILURE

Abrasion of elastomers involves complex processes such as microcutting and tearing, crack growth, fatigue and thermal and oxidative degradation. Depending on the type of polymer and conditions of abrasion, any one of the above factors may play a prominent role in the failure of the sample by abrasion. Schallamach[167-170] was the first to study the patterns developed on abraded surface of the elastomers. Southern and Thomas[171] have found that formation of abrasion pattern is followed by crack growth, which plays an importent role in material removal from the abraded surface. The different types of wear associated with the abrasion of various polymers have been described by Reznikovskii and Brodskii[172]. The main three types of wear of highly elastic materials are fatigue wear, abrasive wear and wear by means of roll formation out of which, the last two types are more severe than fatigue wear. The wear of thermoplastic is abrasive in its type, which results from microcutting by solid projections on the surface of the abrasive. The abrasive wear is characterised by longitudinal furrows on the surface. The frictional wear of elastomer is characterised by vertical ridge formation and subsequent removal of the ridges during the course of abrasion. Thus the patterns appearing on the abraded surface are indicative of the type of wear and help to understand the mechanism of abrasion.

In this part of chapter IV, the effects of blend ratio and dynamic crosslinking of the elastomer phase, on the abrasion resistance of thermoplastic NR-PP blends are discussed. Scanning electron microscopic observations of the abraded surfaces were made to elucidate the mechanism of abrasion of the blends.

Figure IV.E.1 is a plot of abrasion loss against the proportion of NR and PP in the blend for the uncrosslinked and dynamically crosslinked blends. It can be observed that the abrasion loss increased with increase in proportion of the rubber phase, both for the uncrosslinked and dynamically crosslinked blends. The uncrosslinked blends BU and CU showed higher abrasion resistance than the dynamically crosslinked blends BS and CS. But at higher proportions of the elastomer phase this trend is reversed and the crosslinked blends showed better abrasion resistance compared with the uncrosslinked blends (DS > DU; ES > EU and FS > FU). Dynamic vulcanization decreases the size of the dispersed rubber particles and thereby improves the strength of the matrix through better distribution of the applied stress. But crosslinking reduces the adhesion between the dispersed particles and the matrix. These two factors act in opposite directions for blends containing higher proportions of PP. Since the abrasion process involves several parameters such as microcutting, tearing, cut growth and fatigue, which are also dependent on both these opposing factors, the net effect is a reduction in resistance to abrasion of the dynamically crosslinked blends, in which the rubber phase remained as finely dispersed particles. For those blends in which the rubber phase also formed a continuous phase (E and F) dynamic crosslinking improved the matrix strength because, crosslinking imparts high strength to the rubber phase. As the abrasion resistance is dependent upon the resistance of the matrix towards cutting and tearing action and crack growth, dynamic crosslinking increases the abrasion resistance of the blends containing higher proportions of the rubber phase. More than 100% increase in tensile and tear resistance of the blends EU and FU (table IV.B.1) through dynamic crosslinking, compared with less than 10% increase in properties of blend BU, supports the above view.

Scanning electron microscopic observations of the abraded surfaces of the blends also showed that there is a change in the mode of abrasion, as the rubber also formed a continuous phase. The abraded surfaces of blends BU and CU (figures IV.E.2 and IV.E.3 respectively) showed deep grooves horizontal to the direction of abrasion, which are characteristics of abrasive type wear for thermoplastic materials[173,174]. For the 50:50 blend (DU) the abraded surface showed less intense grooves (figure IV.E.4) compared to those of BU and CU. The abraded surface of blend FU was comparatively smooth even though it also showed the appearance of horizontal grooves, to a lesser extent (figure IV.E.5).

In the dynamically crosslinked blends, the abraded surfaces of BS and CS (figure IV.E.6 and figure IV.E.7 respectively) showed characteristics similar to those of blends BU and CU. The grooves in these cases were deeper than those of the uncrosslinked blends. In the case of blend DS (figure IV.E.8), the abraded surface contained only small number of shallow grooves. But, in the case of blend FS, which contained the largest proportion of the elastomer phase, a tendency to form vertical ridges was observed (figure IV.E.9). This was characteristic of frictional type wear and similar to that observed for the blends of natural rubber and polybutadiene rubber[175]. The above observations confirm that

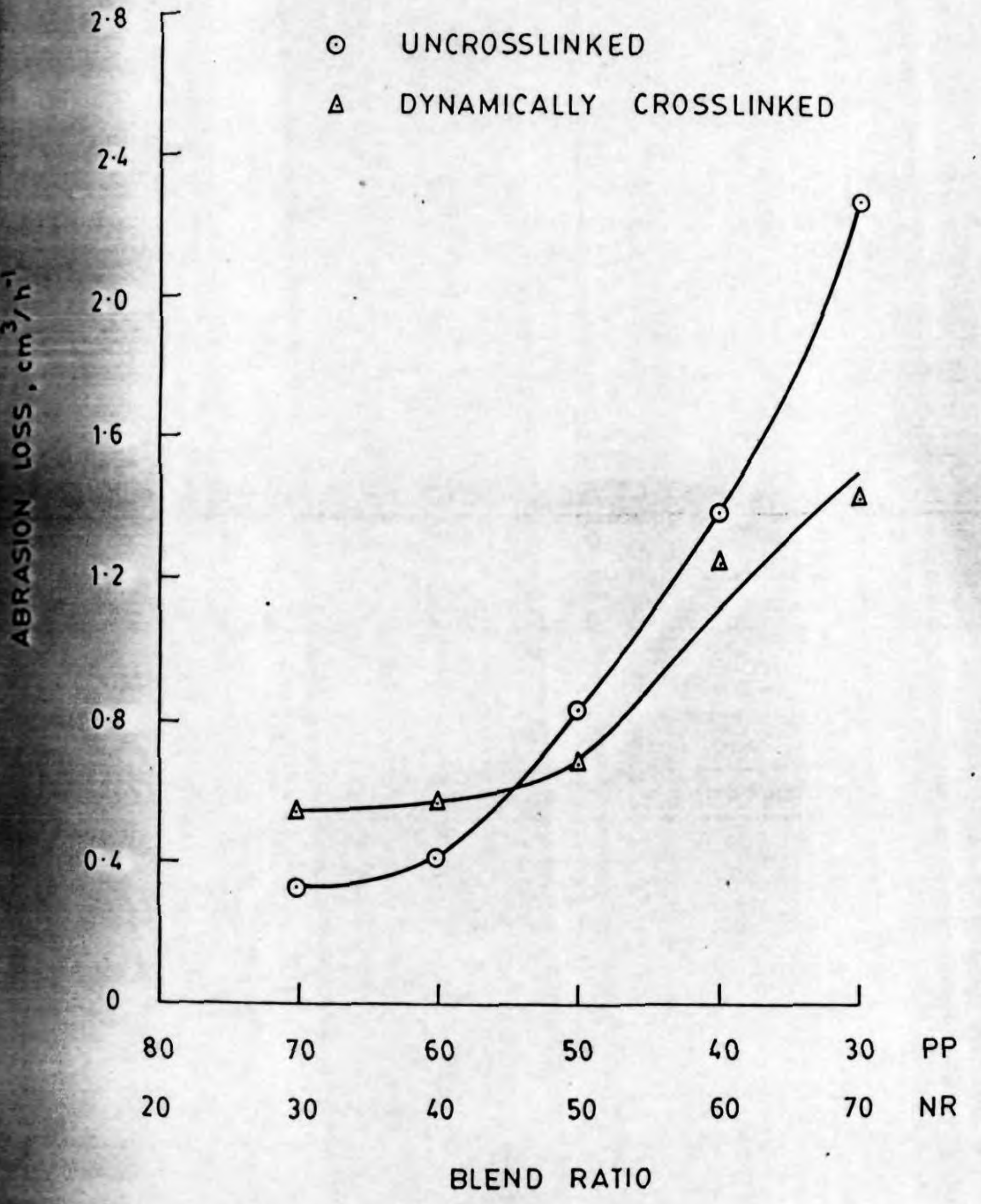
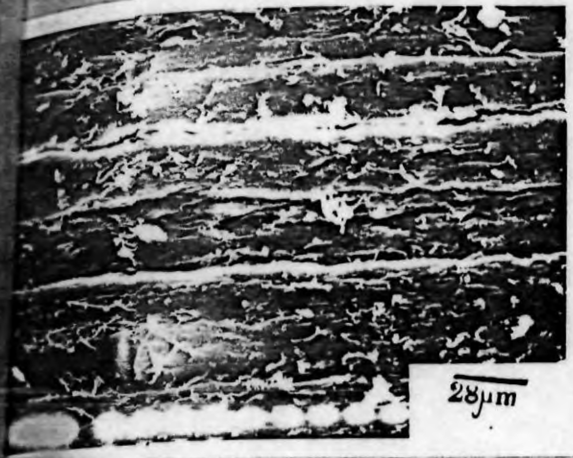


FIG. IV.E.1 EFFECT OF BLEND RATIO AND DYNAMIC CROSSLINKING ON ABRASION LOSS



G.IV.E.2 SEM PHOTOGRAPH OF
RADED SURFACE OF BLEND BU;
EP HORIZONTAL GROOVES AND
BRIS

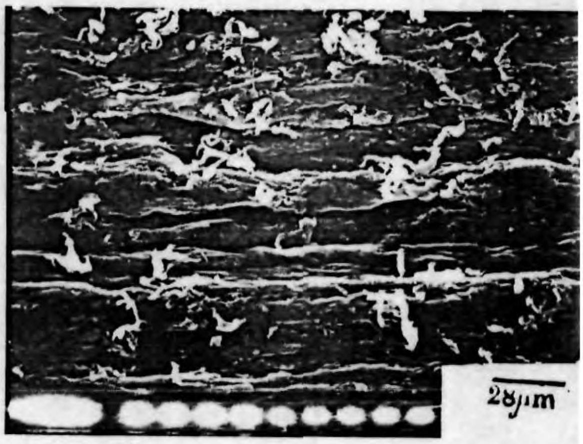


FIG.IV.E.3 SEM PHOTOGRAPH OF
ABRADED SURFACE OF BLEND CU;
DEEP HORIZONTAL GROOVES AND
DEBRIS

IG.IV.E.4 SEM PHOTOGRAPH OF
ABRADED SURFACE OF BLEND DU;
SHALLOW GROOVES AND ROUGH
SURFACE

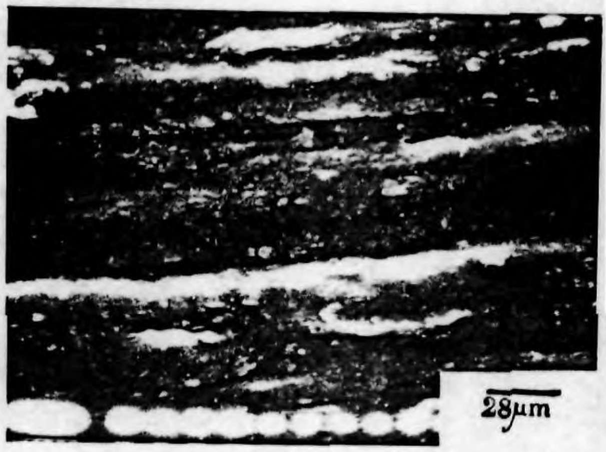
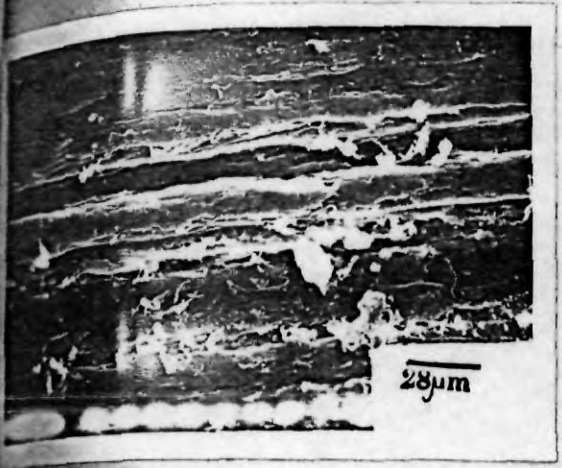


FIG.IV.E.5 SEM PHOTOGRAPH OF
ABRADED SURFACE OF BLEND FU;
SMOOTH SURFACE AND SHALLOW,
HORIZONTAL GROOVES



IG.IV.E.6 SEM PHOTOGRAPH OF
BRADED SURFACE OF BLEND BS;
EEP HORIZONTAL GROOVES AND
EBRIS

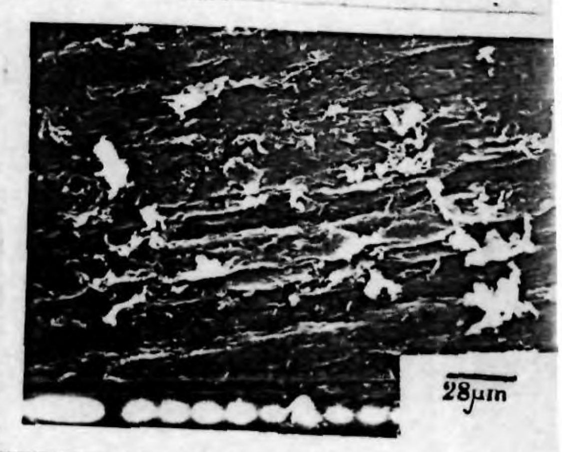


FIG.IV.E.7 SEM PHOTOGRAPH OF
ABRADED SURFACE OF BLEND CS;
DEEP HORIZONTAL GROOVES AND
DEBRIS

FIG.IV.E.8 SEM PHOTOGRAPH OF
ABRADED SURFACE OF BLEND DS;
HALLOW GROOVES

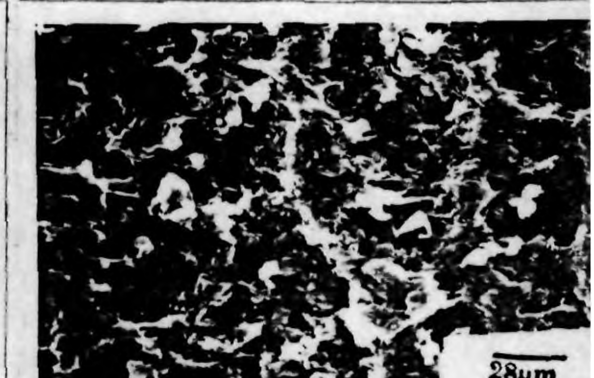


FIG.IV.E.9 SEM PHOTOGRAPH OF
ABRADED SURFACE OF BLEND FS;
ROUGH SURFACE AND VERTICAL
RIDGES

CHAPTER - V

STUDIES ON THE EFFECT OF FILLERS ON TENSILE, TEAR AND WEAR PROPERTIES OF THERMOPLASTIC NATURAL RUBBER - POLYPROPYLENE BLENDS

Part of the results included in this chapter have been accepted for publication in INTERNATIONAL JOURNAL OF POLYMERIC MATERIALS

Fillers are generally incorporated in rubber compounds for reinforcement as well as for reducing the cost. In thermoplastic elastomers of the styrenic block type, fillers and plasticizers are commonly used to optimise processing characteristics, physical properties and economic factors[73]. But in thermoplastic elastomer blends, use of fillers is seldom practised and only a limited number of studies have been conducted to explore the possibilities of using fillers in these types of blends[176,107,117]. In this chapter of the thesis, the results of the studies on the effects of high abrasion furnace (HAF) black, precipitated silica and a silane coupling agent on the properties of thermoplastic NR-PP blends, are presented.

The formulations of the blends are given in table II.4. Earlier studies have shown that addition of HAF black affected the processability[107]. Hence in the present study, we chose a mixed cure system, which showed better processability, but comparable physical properties of the sulphur cured blends (table IV.A.1). Since the effect of HAF black was found to be more prominent in blend F, the effect of silica was studied using this blend (70:30 NR:PP) only. The fillers were added in masterbatch form. Scanning electron microscopic studies of the fracture surfaces were conducted to explain the observed changes in physical properties.

V.1 Effect of HAF black : The properties of the HAF black filled thermoplastic elastomer blends are given in table V.1. Addition of carbon black increased the mixing torque of the blends containing higher proportion of the elastomer phase, which in turn reduces their processability at the shear rate of blending. But, for the blends containing a higher proportion of the PP phase, no effect on the mixing torque was observed.

Carbon black increased the 100% modulus, tensile and tear strength of the blends. But the elongation at break was reduced in all cases. On the above mentioned properties of the blends, the effect of HAF black was similar to its effect on these properties of conventional rubber vulcanizates. The effect of HAF black was more prominent in blends containing higher proportion of the elastomer phase, since the rubber phase also tends to form a continuous phase at higher proportions. The effect of HAF black on hardness was negligibly small.

It was suggested that the partition of filler in the blend is such that it preferentially gets distributed in the rubber phase[177]. This has the effect of both stiffening the rubber phase and increasing the proportion of it in the compositions. These effects act in opposite directions on stiffness of the composition as a whole. The effects largely cancel out and the effect of filler on stiffness or hardness is minimised. Since the black has good reinforcing effect on the rubber phase, the blends containing higher proportions of the rubber phase showed improvement in properties. These points are more clearly evident from the SEM fractographs of the HAF black filled blends, under tensil and tear failure.

Figure V.1 is the tensile fractograph of HAF black filled 70:30 PP:NR thermoplastic blend (BMH). The fracture surface showed dimples with cracks. Scattered black agglomerates are also observed on the surface. In HAF black filled 50:50 blend (DMH) the fracture surface showed increased number of cracks (figure V.2) and the surface is smooth showing planer separation under stress. The rubber particles in the matrix bridge the matrix crack and are stretched between the opened crack as the crack advances, as observed earlier by Kunz-Douglass and co-workers[123] for epoxy-rubber particulate composites. But at a higher proportion of rubber in the blend (FMH), the fracture characteristics were similar to black filled NR (figure V.3). Shear band and cavities were visible on the surface and cracks were also present. The fracture in this case may be due to failure of rubber phase, rather than phase separation due to weak interaction between the HAF filled rubber and the plastics phase.

Figure V.4 shows the tear fracture surface of blend BMH. Aggregates of carbon particles, rough surface and cavities due to the separation of the pulled up plastic phase showed weak interaction between the black filled rubber phase and polypropylene. Increase of rubber content in the blend (DMH) increased the number of cavities and tiny cracks were also formed on the surface (figure V.5). But high rubber content black filled blend (FMH) had a smooth fracture surface with scattered, rounded tear lines (figure V.6), which were similar to those observed on the tear fracture surface of black filled rubber vulcanizates[134]. Thus, in this blend, the fracture has proceeded through the rubber phase which formed the major constituent of the blend.

V.2 Effect of Precipitated Silica : The physical properties of the 70:30 NR:PP blend containing silica and silane coupling agent are given in table V.2. For comparison, the properties of the unfilled blends are also provided in the table. Addition of silica increased the mixing torque of the dynamically crosslinked blends both in presence and absence of the silane coupling agent (Si-69). But, for the uncrosslinked blend, no increase in mixing torque was observed.

V.2.1 Tensile Properties : The 100% modulus of the uncrosslinked blend was increased by the addition of silica, but the blend FUSiX containing Si-69 showed lower modulus compared with FUSi. In all the dynamically crosslinked blend the increase in modulus was negligibly small. Blends FUSi and FUSiX showed an unusual increase in elongation at break, whereas all the dynamically crosslinked blends showed a decrease in elongation at break, by the addition of silica filler. The tensile strength of the uncrosslinked blend FU was improved by the addition of silica filler and the silane coupling agent but blend FUSiX showed lower tensile strength than FUSi. In the case of dynamically crosslinked blends, the improvement in tensile strength with addition of silica was negligibly small and for the blend FSSi it was lower than that of FS. At higher extents of crosslinking, blends FMSiX and FSSiX showed better tensile strength and hardness compared with those of FMSi and FSSi respectively.

The observed anomaly in the action of silica and silane coupling agent on the uncrosslinked and dynamically crosslinked blends can be explained as follows. In the uncrosslinked blend (FU), addition of silica improves the tensile strength (FUSi > FU) due to the stiffness imparted by the silica filler to the rubber which formed a continuous phase of the blend. But in dynamically crosslinked blends, the effect of silica filler on tensile strength was less prominent and even reduced the strength in the case of blends containing higher extents of crosslinking. This is due to the retarding effect of silica on the rate of vulcanization of the rubber phase. The Vr values were 0.120, 0.210 and 0.249 for the blends FD, FM and FS respectively, whereas those of the silica filled blends were 0.117, 0.153 and 0.203 for the blends FDSi, FMSi and FSSi respectively. Since the rubber also formed a continuous phase in the blend, the extent of vulcanization affects the strength of the matrix considerably.

The improvement of tensile properties of silica filled rubber compound by the addition of Si-69 is achieved due to chemical interaction of the filler with the rubber matrix through the coupling agent[178]. The above interaction occurs most effectively in presence of a crosslinking agent and is dependent upon the type of coupling agent and the curing agent[179]. In uncrosslinked silica filled blend, Si-69 acts in two ways. It increases the stiffness and strength of the rubber phase through better rubber-filler interaction by chemical bond formation. But this weakens the plastic phase - rubber adhesion and hence reduces the strength of the blend. In sulphur cured silica filled blends, chemical interaction of the coupling agent with the reactive groups on the filler and the rubber phase results in interfacial wetting and adhesion of the filler and helps to improve the dispersion by preventing the reflocculation of the filler. This also reduces the affinity of the filler towards the adsorption of the curing systems, which in turn reduces the retardation effect of the filler on the rate of vulcanization. The Vr values of the blends containing the coupling agent were 0.142, 0.187 and 0.224 respectively for FDSiX, FMSiX and FSSiX. These values were higher than those of the blends which contained no coupling agent. The net effect is an improvement in tensile strength of the blends containing the coupling agent and having higher extents of crosslinking.

This is further supported by SEM studies of the fracture surfaces.

Figure V.7 is the tensile fractograph of blend FUSi. It showed a smooth surface with dispersed silica particles and restricted flow of the matrix. Figure V.8 is the tensile fractograph of the blend FUSiX which contained the coupling agent. Better adhesion of the filler particles to the matrix and rough surface can be observed. The holes and roughness are due to the detachment of the plastic phase. Dynamic crosslinking of the elastomer phase further increases the stiffness of the rubber phase and the fracture proceeds by shearing action in the case of blends FSSi and FSSiX (figures V.9 and V.10 respectively). But the fracture surface of blend FSSiX showed more roughness and better adhesion of the filler particles. The tensile strength of this blend is slightly higher than that of FSSi.

V.2.2 <u>Tear Strength</u> : Addition of silica filler improved the tear strength of the blends and the effect was more prominent in uncrosslinked and DCP cured blends. Addition of silane coupling agent further enhanced the tear strength of the blends containing mixed and sulphur curing systems. Figure V.11 shows that addition of silane coupling agent adversely affected the tear energy of the uncrosslinked blend and did not affect the DCP cured blend, but increased the tear energy of the blends dynamically crosslinked by sulphur and sulphur plus DCP. The role of the crosslinking system on interfacial wetting and adhesion of the filler to the rubber phase through the coupling aagent, in improving the tear strength, was edivent from the fact that the increase in tear strength of the DCP cured blend containing coupling agent was negligibly small due to lack of reactivity of the coupling agent in this cure system[179]. The blend without curing agent also showed no improvement in tear strength with the addition of Si-69.

The SEM observations of the tear fracture surfaces of the blends supported these views. The tear fractographs of the uncrosslinked blend (FUSiX) showed rough surface and ductile failure with dimples and pores (figure V.12). Dynamic crosslinking of the elastomer phase with DCP (blend FDSiX) reduced the deformation of the elastomer phase giving smooth fracture surface with fracture path (figure V.13). The fracture surface of the blend FMSiX was similar to FDSiX, but stretching of the matrix along the fracture path was visible due to better rubber-filler interaction (figure V.14). The fracture surface of the sulphur cured blend containing silica and coupling agent (blend FSSiX) showed similar characteristics with subsidiary fracture paths. The stretching of the rubber phase along the fracture path can also be observed in this case (figure V.15).

V.2.3 Abrasion Resistance : The abrasion resistance of the unfilled blends increased with increase in extent of dynamic crosslinking of the elastomer phase (FS > FM > FD > FU). Silica filler improved the abrasion resistance of the NR-PP blends and the effect was more prominent in uncrosslinked and DCP cured blends (FUSi > FU, FDSi > FD, FMSi > FM, FSSi > FS). Addition of silane coupling agent improved the abrasion resistance of the blends containing sulphur and sulphur-DCP mixed curing systems (FSSiX > FSSi and FMSiX > FMSi). In the uncrosslinked and DCP cured blends (FUSiX and FDSiX) silane coupling agent adversely affected the abrasion resistance. These observations are similar to the trend in tear strength of these blends and may be explained in the following way. During abrasion, small particles are formed on the surface by microtearing of the matrix. The number and size of such particles and their removal from the matrix depend mainly on the tear strength of the matrix, apart from other factors like frictional force[121]. These particles coalasce to form ridges on the surface, aligned at right angle to the direction of abrasion[180]. Finer particles form finer ridges and the height and spacing of the ridges increase with the intensity of wear. The SEM photomicrograph of the abraded surface of the blend FDSiX showed thick and widely spaced ridges (figure V.16) revealing poor resistance to abrasion of the blend containing DCP cure system In the case of blend FMSiX the abraded surface showed sma ridges interconnected by elongated rubber matrix (figure V.17). The abraded surface of the blend FSSiX showed no tendency towards ridge formation (figure V.18). The abrasion resistance of the blends increased in the order, blend FSSiX $>$ FMSiX $>$ FDSiX. It can also bee seen that the tear strength of these blends follows a similar trend (table V.2).

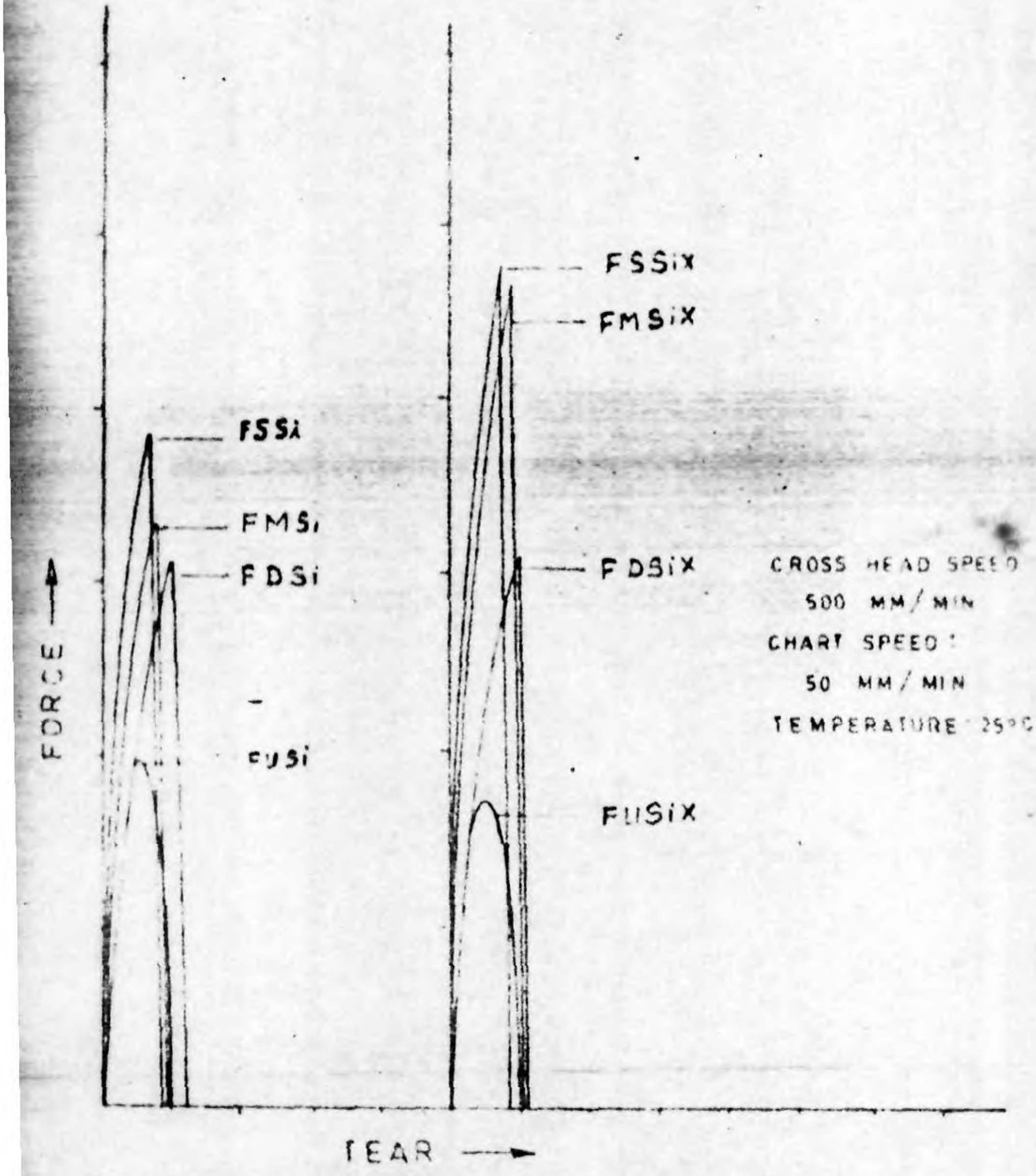
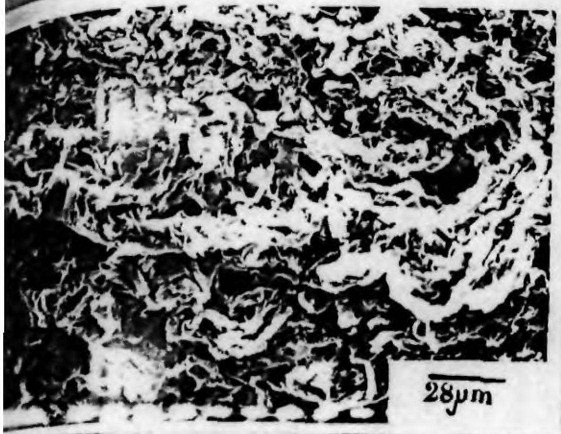


FIG.V. 11 LOAD-TEAR PLOTS SHOWING EFFECT OF SILANE COUPLING AGENT



.V.12 TEAR FRACTOGRAPH OF
D FUSiX; ROUGH SURFACE,
DIMPLES AND PORES

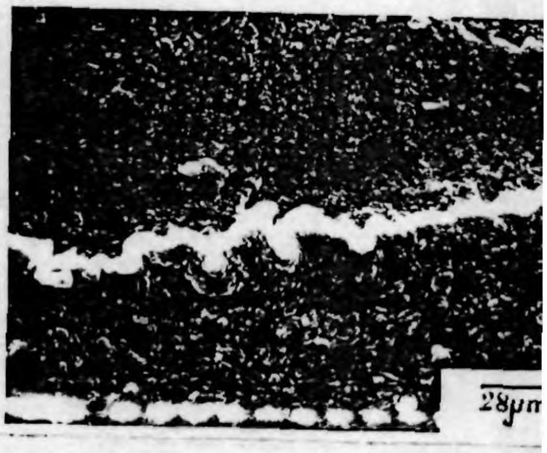
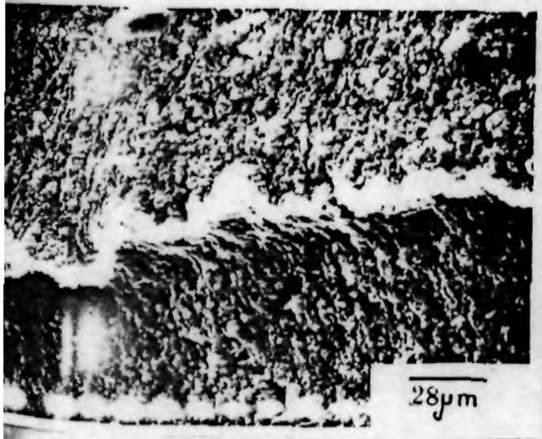


FIG.V.13 TEAR FRACTOGRAPH OF BLEND FDSiX; SMOOTH SURFACE AND CONTINUOUS FRACTURE PATH



V.14 TEAR FRACTOGRAPH OF
D FMSiX; SMOOTH, CONTI-
S FRACTURE PATH AND
TCHING OF MATRIX

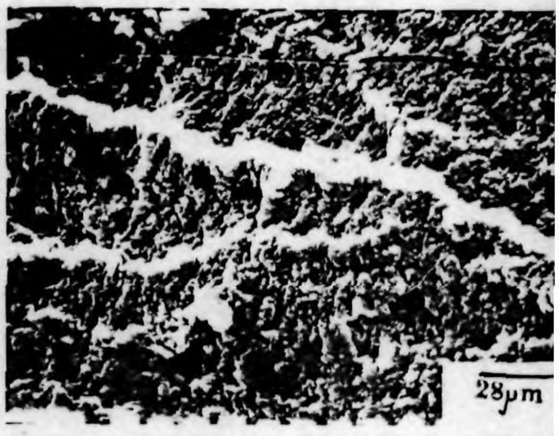
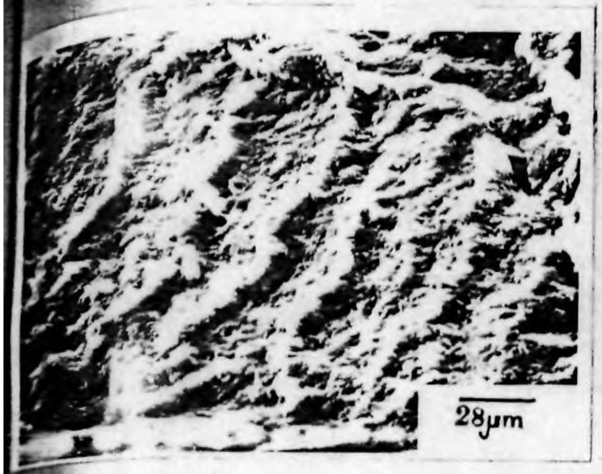


FIG.V.15 TEAR FRACTOGRAPH OF BLEND FSSiX; MAIN FRACTURE PATH WITH SUBSIDIARY TEAR LINES



IG.V.16 SEM PHOTOGRAPH OF
BRADED SURFACE OF BLEND FDSiX;
DELY SPACED VERTICAL RIDGES

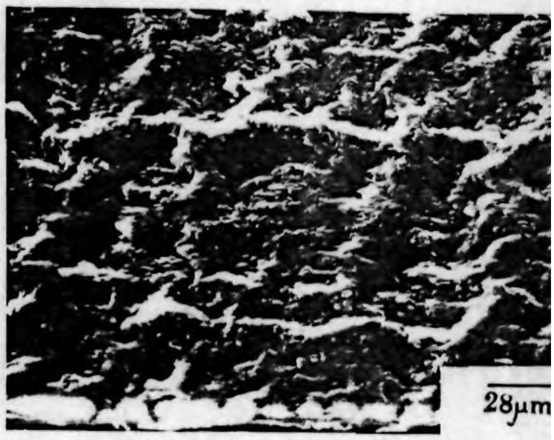


FIG.V.17 SEM PHOTOGRAPH OF
ABRADED SURFACE OF BLEND FMSiX;
SMALL VERTICAL RIDGES INTERa
CONNECTED BY ELONGATED RUBBER
MATRIX

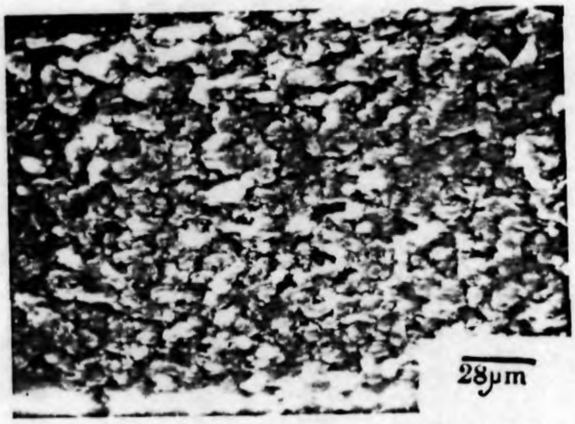


FIG.V.18 SEM PHOTOGRAPH OF ABRADED
SURFACE OF BLEND FSSiX; ROUGH
SURFACE WITH NO RIDGES

CHAPTER - VI

DYNAMIC MECHANICAL PROPERTIES OF THERMOPLASTIC NATURAL RUBBER - POLYPROPYLENE BLENDS

The results included in this chapter have been accepted for publication in JOURNAL OF APPLIED POLYMER SCIENCE

Dynamic mechanical properties describe the responses of materials to periodically varying strains or stresses and are usually measured as functions of frequency or temperature. For small sinusoidally varying strains or stresses, the responses are sinusoidally varying stresses or strains respectively. The storage modulus obtained from these measurements accounts for the elastic energy stored and recovered in cyclic deformation. The loss modulus is a measure of energy dissipated as heat and the loss tangent (tan δ) indicates the damping characteristics of the material.

The thermoplastic elastomers are used in a number of mechanical moulded goods, but the lower maximum service temperature of the TPEs precludes their use in many other

VI.1 Effects of Blend Ratio : The changes in E', E" and tan δ_E of the blends BU, DU and FU with increase in temperature are shown in figure VI.1. The storage modulus and loss modulus decreased with increase in temperature and proportion of the elastomer phase in the blend. The loss tangent values initially decreased and then increased with increase in temperature. The increase in tan δ_E and decrease in moduli were quite remarkable when the proportion of rubber phase in the blend exceeded 50%. In blend BU, the rubber phase remained as dispersed particles in the PP matrix and as the rubber content was increased to 50%, the rubber phase also showed a tendency to form a continuous phase. In 70:30 NR:PP blend, both the phases existed as continuous phases as discussed in chapter IV.... When the elastomer phase becomes continuous in nature, this phase contributes a major share in the viscous deformation since the molecules are in the uncrosslinked state. This resulted in progressive decrease in storage modulus and increase in loss tangent values from blend BU to FU. The initial decrease in tan δ_E values of the blends is due to a transition in the state of PP which has a brittle point of 0°C. This is evident from figure VI.6 also.

VI.2 Effects of Crosslinking : The effects of crosslinking of the elastomer phase in 30:70 NR:PP blend on E', E" and tan δ_E are shown in figure VI.2. The storage modulus and loss modulus decreased with increase in temperature and the decrease in loss modulus was more prominent in the uncrosslinked blend (BU) than in the crosslinked blends. The effect of extent of crosslinking of the elastomer phase on E' and E" was not prominent in the 30:70 NR:PP blend. The degradative action of DCP on PP, in addition to its crosslinking action on the dispersed NR phase, was evident from the lower storage modulus and higher loss tangent values of the blends BM and BD compared to those of BS and BU. The loss tangent values of the dynamically crosslinked blends increased with increase in temperature beyond 40°C, whereas that of the uncrosslinked blend (BU) showed an increase in tan δ_E only beyond 70°C. Above this temperature the tan δ_E values of the dynamically crosslinked blends were higher than that of blend BU. This is due to weak interaction between the crosslinked rubber particles and the PP matrix, which increases the hysteresis. But, this trend is reversed in the 50:50 NR:PP blend and the dynamically crosslinked blend (BS) showed lower tan δ_E values than blend BU at all temperatures (figure VI.3). The loss modulus was higher for the uncrosslinked blend and the storage modulus did not show any change due to dynamic crosslinking. This is because the rubber phase also tends to form a continuous phase and dynamic crosslinking increases the elasticity of the dispersed phase. But higher E' and lower tan δ_E values of the blend DU compared with those of DM and DD showed that the degradative effect of DCP on PP dominated over its crosslinking action on the rubber phase. The effects of extent of crosslinking of the elastomer phase on E', E" and tan δ_E were clearly observable in 70:30 NR:PP blend (figure VI.4). The storage modulus increased steadily with extent of crosslinking (FS > FM > FD > FU) and the increase was proportional to the degree of crosslinking of the elastomer phase. The loss tangent values decreased with extent of crosslinking of the elastomer phase and the effect of temperature was less prominent as the degree of crosslinking increased. It is well known[191] that the effect of any modification in one of the homopolymers of a polymer blend will tend to show up more clearly when that particular component becomes continuous or the dominent phase than when it is the discontinuous phase. At higher proportions of the elastomer phase, the crosslinking agent, especially the sulphur cure system, has its action mainly on the elastomer phase[114]. The effect of crosslinking agents on E' and tan δ_E was quite remarkable in 70:30 NR:PP blend, since the rubber phase also became continuous in this blend. Thus, crosslinking of this phase leads to higher extents of recoverable deformation under cyclic straining of the blends, resulting in lower tan δ_E and higher E' values with higher extents of crosslinking.

VI.3 **Effects of Reinforcing Fillers** : The effect of reinforcing fillers, HAF black and silica, on the dynamic mechanical properties of 70:30 NR:PP blend containing mixed cure system are shown figures VI.5 and VI.6. Both HAF black and silica filled blends showed higher E' and E" values than the unfilled blend. The peaks in E" and tan δ_E values and the sharp decrease in E' values in the temperature range of -50°C indicated the glass transition state of the NR phase. In the tan δ_E versus temperature plot (figure VI.6) another peak can be observed in the temperature range of +10°C. This is due to the transition in the PP phase which has a brittle point of +5°C. The presence of two peaks in this plot indicated the existence of two separate phases in the 70:30 NR:PP blend. The two phases may be existing as an interpenetrating network system, due to higher proportion of the NR phase and lower melt viscosity of the PP phase.

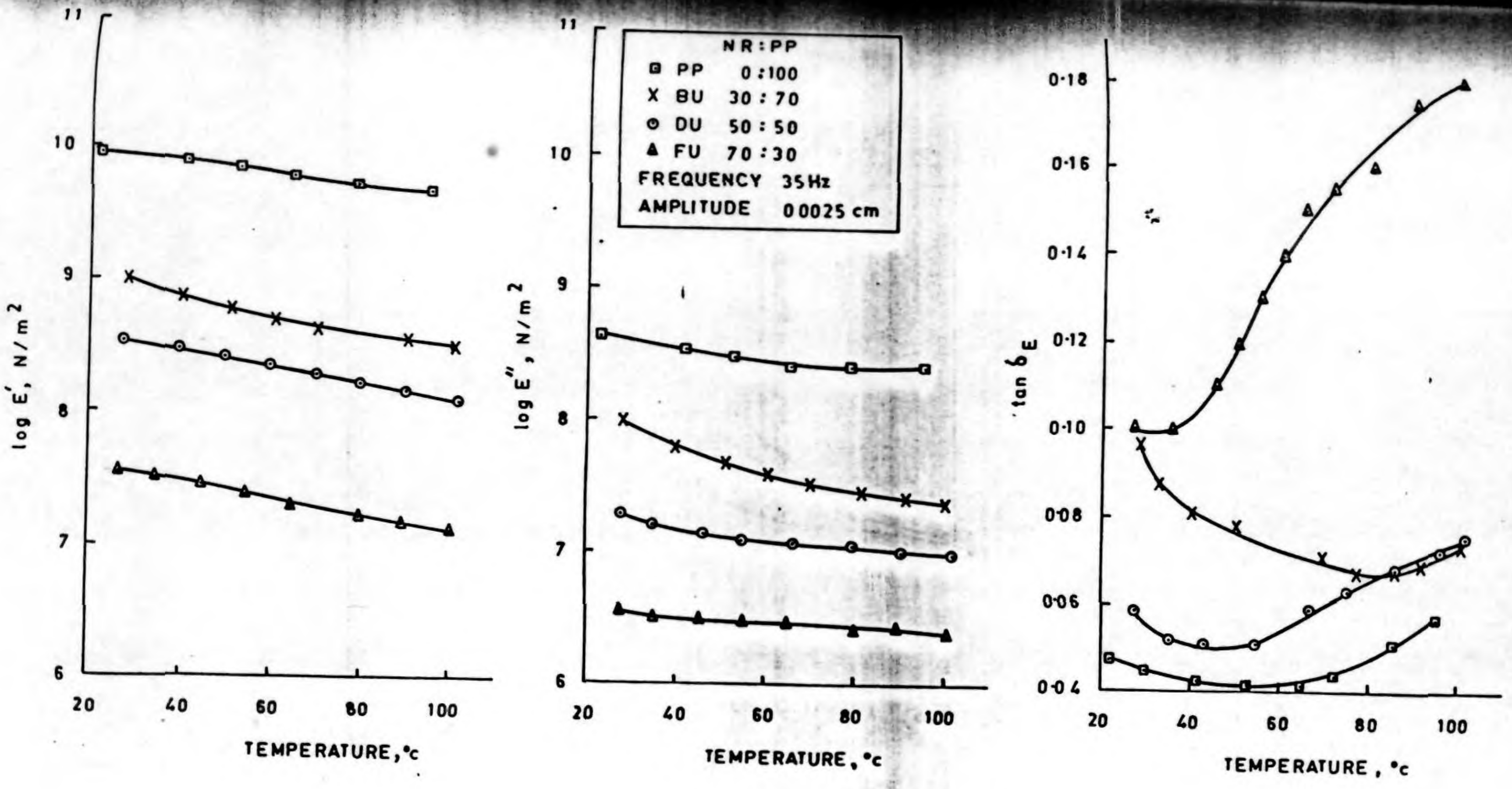


FIG. VI·1 EFFECT OF BLEND RATIO ON E', E'' AND tan δ_E OF NR:PP BLENDS

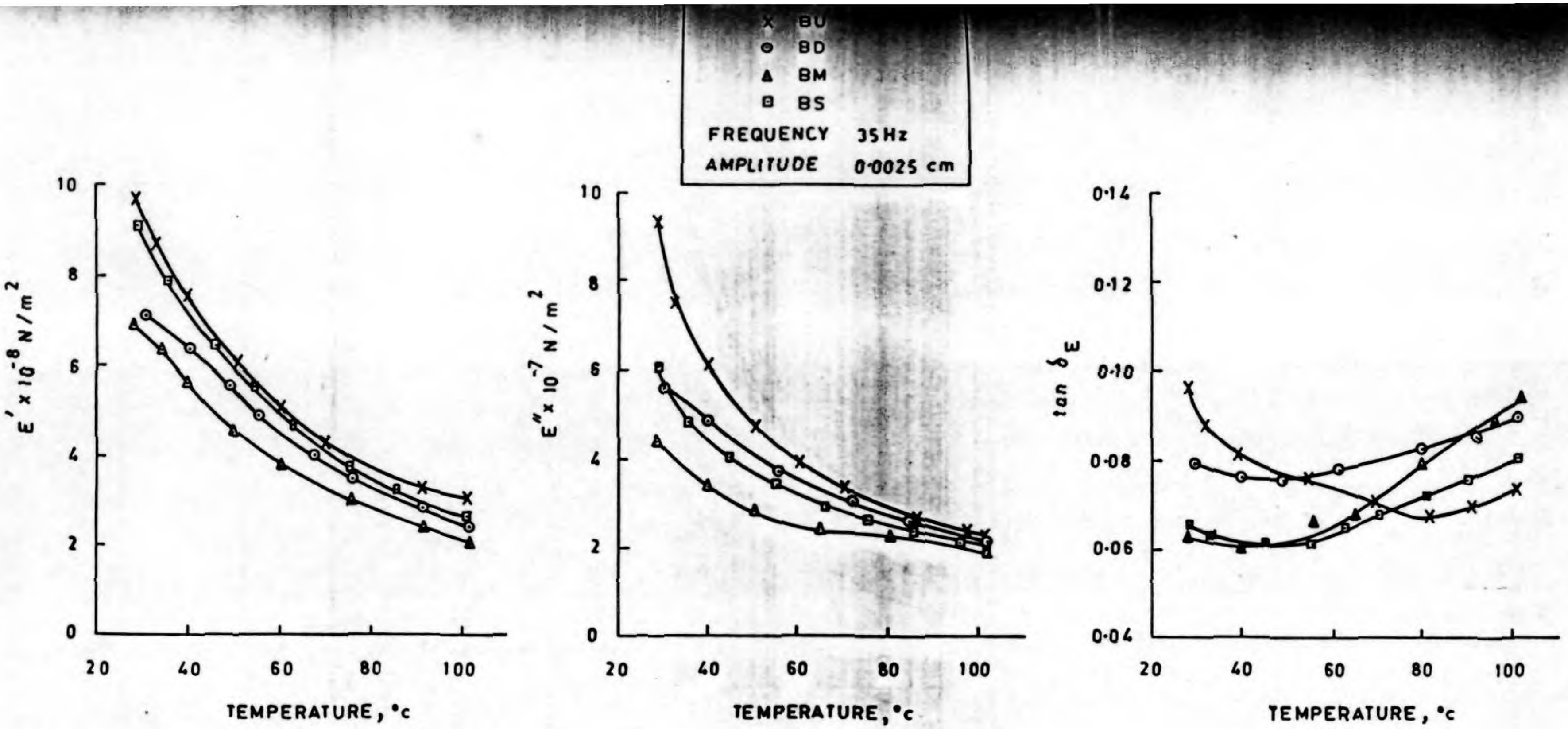


FIG. VI · 2 EFFECT OF DYNAMIC CROSSLING ON E', E'' AND tan δ_E OF 30:70 NR:PP BLENDS

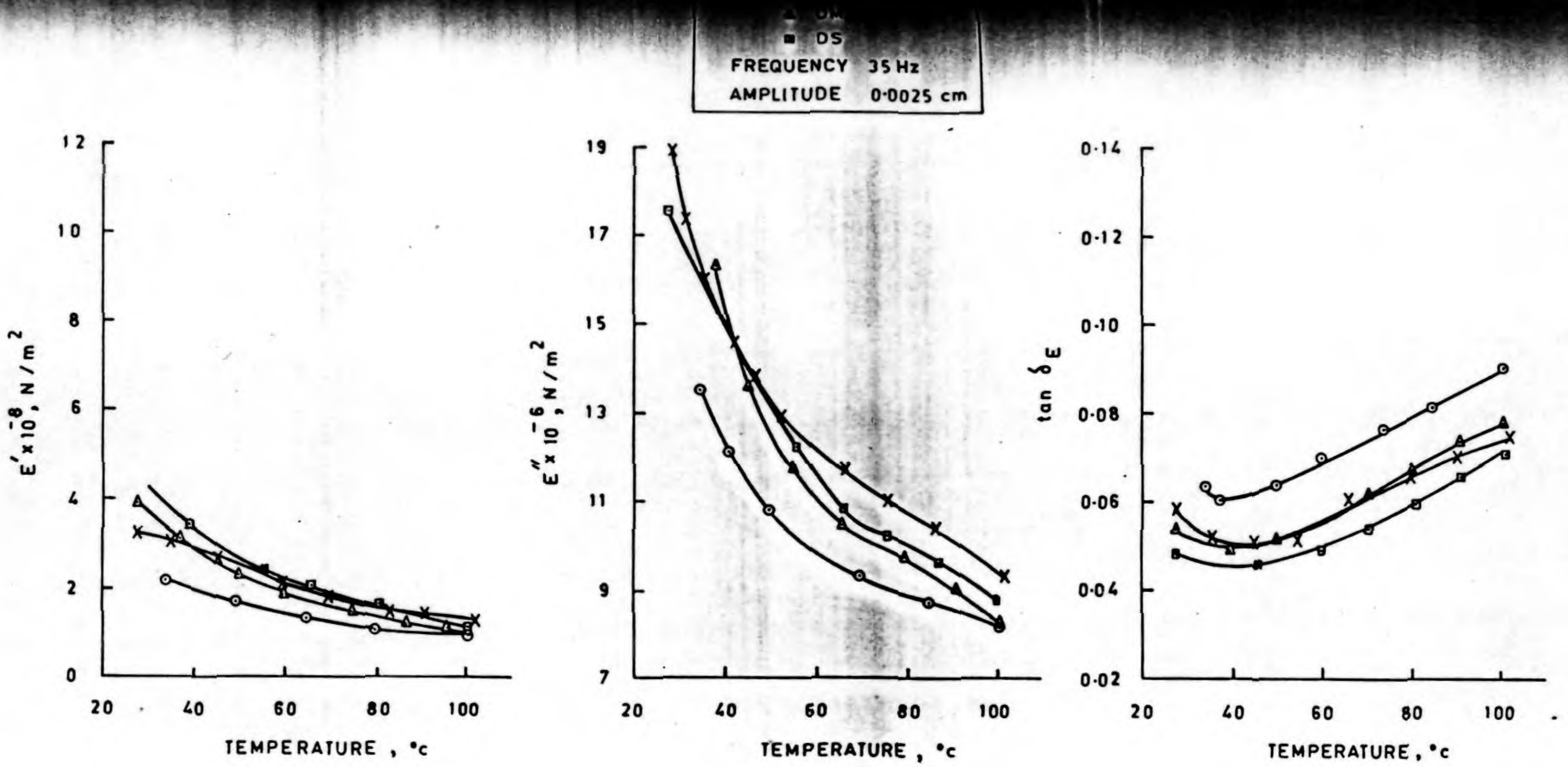


FIG. VI·3 EFFECT OF DYNAMIC CROSSLINKING ON E', E'', AND tan δ_E OF 50:50 NR:PP BLENDS

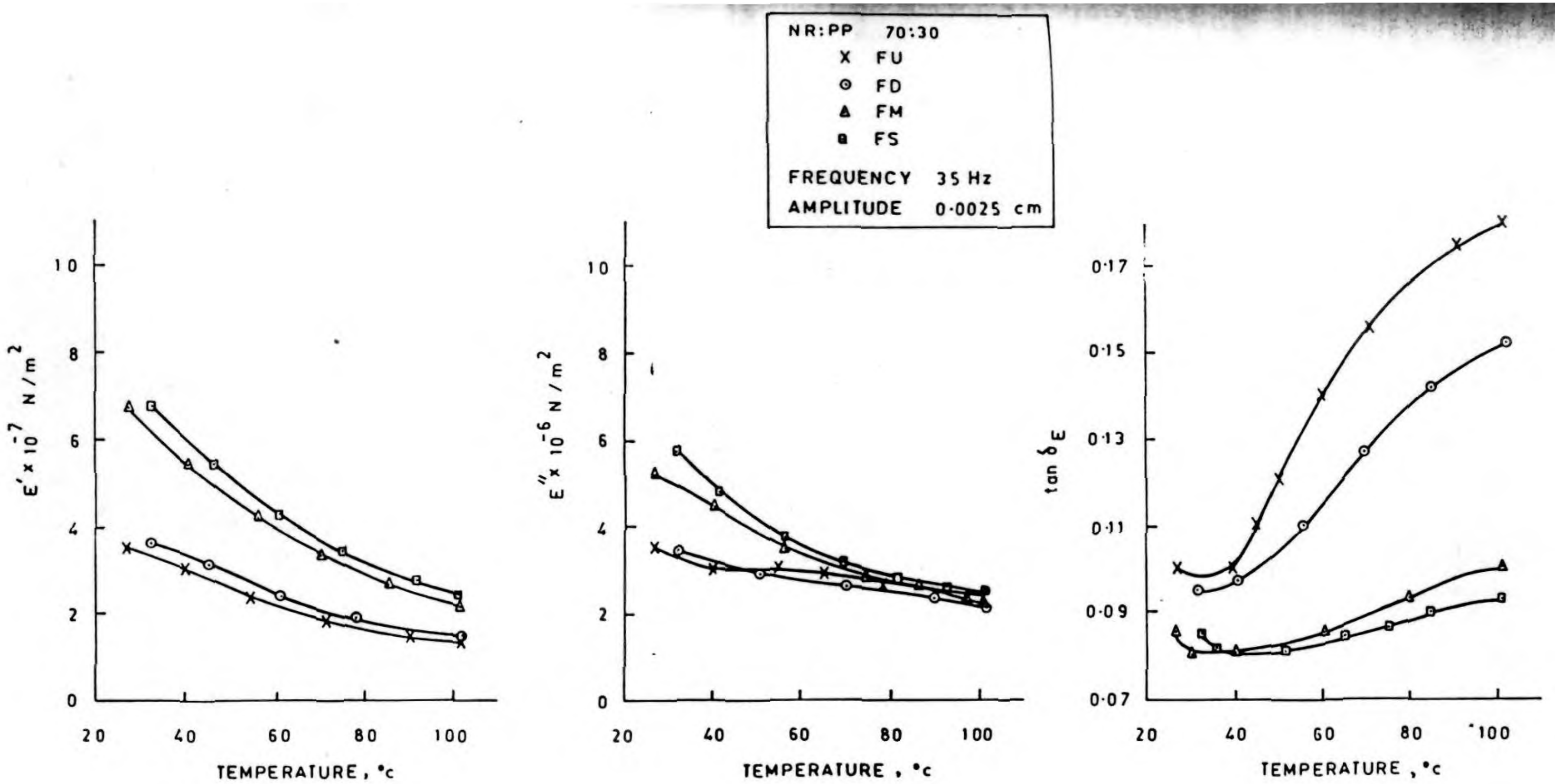


FIG. VI·4 EFFECT OF DYNAMIC CROSSLINKING ON E', E'' AND $\tan \delta_E$ OF 70:30 NR:PP BLENDS

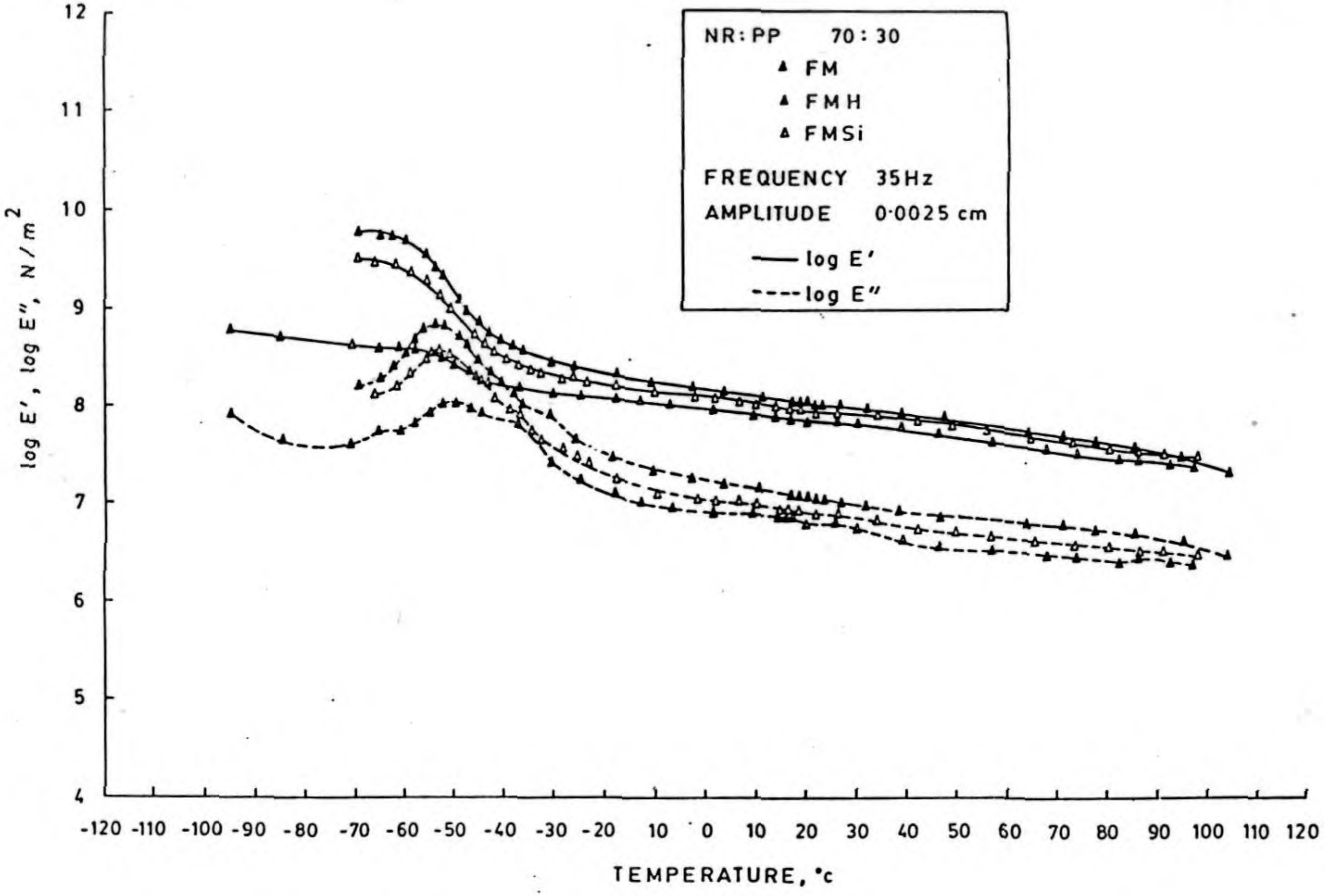


FIG.VI.5 Effect of HAF black and silica fillers on E' and E'' of 70:30 NR:PP blends

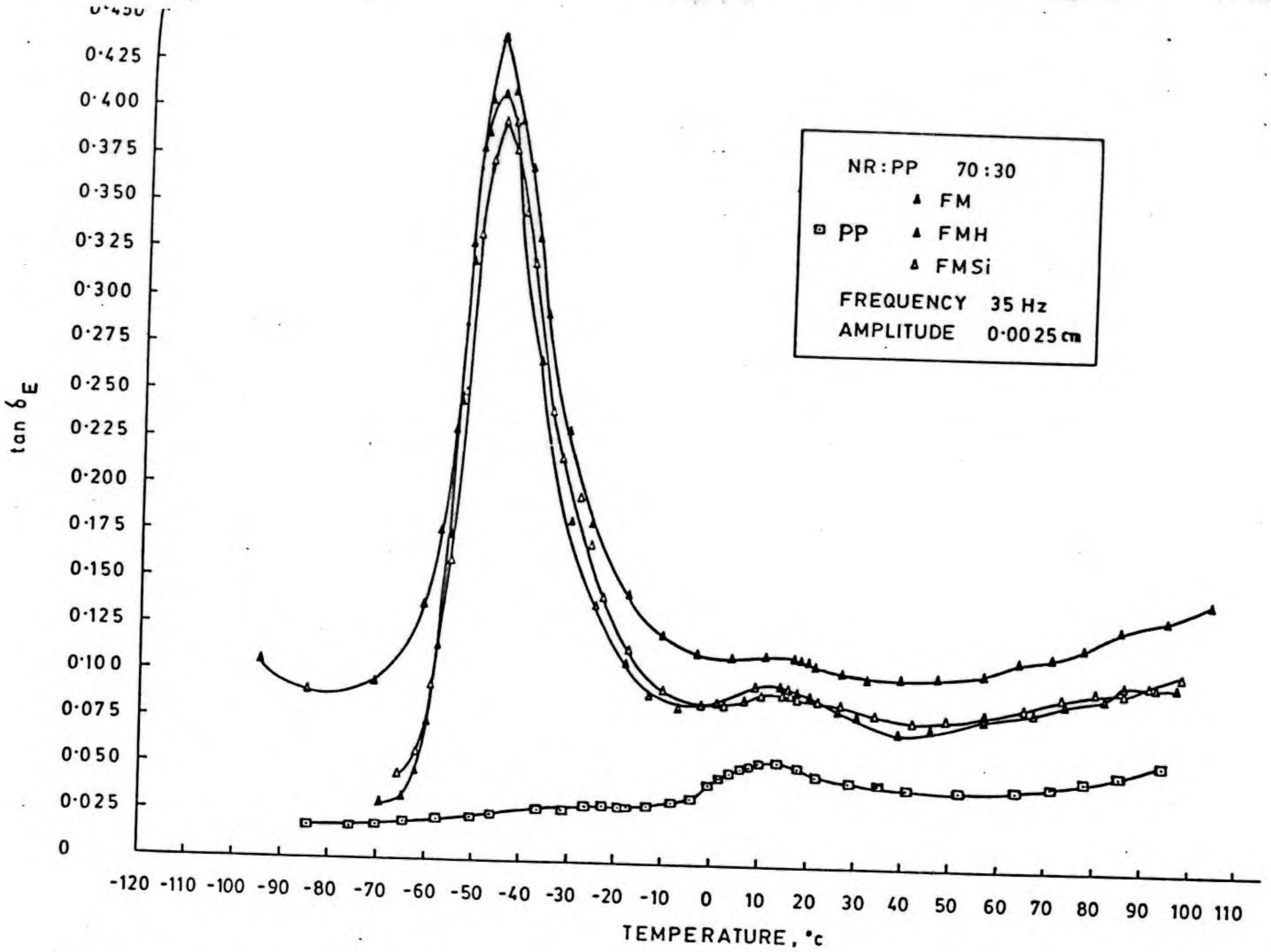


FIG.VI.6 Effect of HAF black and silica fillers on tan δ_E of 70:30 NR:PP

PART - II

STUDIES ON THE RHEOLOGICAL BEHAVIOUR AND TENSION, TEAR AND ABRASION FAILURE OF STYRENE-BUTADIENE-STYRENE COPOLYMER, STYRENE-ISOPRENE-STYRENE COPOLYMER, THERMOPLASTIC POLYURETHANE AND 1,2 POLYBUTADIENE -

CHAPTER - VII

STUDIES ON STYRENE-BUTADIENE-STYRENE COPOLYMER, STYRENE-ISOPRENE-STYRENE COPOLYMER, THERMOPLASTIC POLYURETHANE AND 1,2 POLYBUTADIENE

PART A - RHEOLOGICAL BEHAVIOUR

PART B - MODE OF FAILURE UNDER TENSION, TEAR AND ABRASION

The results of the studies included in this chapter have been published in the following journals:

1) JOURNAL OF MATERIALS SCIENCE, 20, 1864 (1985)
2) KAUTSCHUK GUMMI KUNSTSTOFFE, 37, 1044 (1984)

CHAPTER VII - A

STUDIES ON THE RHEOLOGICAL BEHAVIOUR OF SBS BLOCK COPOLYMER, SIS BLOCK COPOLYMER, THERMOPLASTIC POLYURETHANE AND 1,2 POLYBUTADIENE

The four commercial thermoplastic elastomers selected for the investigations are styrene-butadiene-styrene block copolymer, KRATON D 5152 (K5); styrene-isoprene-styrene block copolymer, KRATON D 1107 (K1); thermoplastic polyurethane elastomer, ESTANE 5715 (PU); and thermoplastic 1,2 polybutadiene, JSR RB 820 (PB). The details of the above TPEs are discussed in section II.1, which is summarised in table VII.A.1. These materials belong to different classes of TPEs and a comparative evaluation of the rheological behaviour of these materials are presented in this part of chapter VII.

Due to the growing importance of thermoplastic elastomers, the rheological characteristics of thermoplastic block copolymers and those of thermoplastics-elastomer blends have been studied extensively. Kraus and co-workers[54] have reported the influence of molecular weight and length of the block sequences on the rheological characteristics of random and block copolymers of butadiene and styrene and showed that as the length of the block sequences became sufficiently large, the blocks segregated to form a two-phase system and that some of the associations of the poly-styrene segments persisted even at temperatures well above the glass transition temperature of polystyrene. This multiphase morphology of the block copolymers at various temperatures has been reported to be the reason for the high sensitivity to shear conditions of block copolymers of styrene and butadiene[52]. Arnold and Meier[192] showed that the dynamic viscosities of styrene-butadiene-styrene block copolymers continuously increased with decreasing deformation rate. It was explained that this behaviour is due to the interplay of processes tending to disrupt and reform the network and domain systems in the block copolymer, under different extents of deformation. Chung and Gale[193] have reported that the changes in viscoelastic properties of SBS block copolymer with temperature is due to a phase transition resulting in a homogeneous morphology at higher temperatures and extent of deformation. Gouinlock and Porter[194] observed that the non-Newtonian characteristics of SBS block copolymer at low temperatures, change to Newtonian responses at about 142°C. Above 142°C, the polystyrene blocks, existing in dispersed domains at lower temperatures, were shown to exceed a critical degree of compatibility with the continuous polybutadiene phase. A similar transition was reported by Pico and Williams[195] in plasticized SBS block copolymer and attributed this reaction to an accompanying morphological transition. This was further confirmed by a detailed study by Chung and Lim[196]. The effect of shear rate and temperature on shear viscosity, die swell and extrudate deformation of thermoplastic polyurethane, 1,2 polybutadiene, styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers are discussed in the present investigations.

VII.A.1 <u>Effect of Shear Rate on Viscosity</u> : The viscosity-shear rate plots of the samples at 180°C are given in figure VII.A.1. Between the two styrenic block copolymers (K1 and K5), sample K1 showed higher viscosity at all shear rates since it contained lower proportion of polystyrene segments (table VII.A.1). The viscosity of both the samples decreased with increase in shear rate, indicating pseudoplastic behaviour. The decrease in viscosity of these samples was faster above a shear rate of 10^2 sec^{-1}. In the case of sample K5, a sharp increase in viscosity was observed in the shear rate region of 10^1 sec^{-1}. It has been reported earlier that polymer melts containing fine particle silica and carbon black show yield stress, which increased with decreasing particle size of the filler[151,197]. Similar observations have been reported for acrylonitrile-butadiene-styrene and acrylonitrile-butadiene-acrylic ester copolymers containing dispersed rubber particles[149]. The occurrence of yield stress in these cases was atributed to the presence of 'structure build-up' or gel formation due to the inter-particle forces existing among the dispersed particles. Sample K5 contained about 10% by weight of fine particle silica filler. Thus, the sharp increase in viscosity of the sample K5 below a shear rate of 10^1 sec^{-1} is due to the structure build-up by the silica particles. This gel structure has to be broken before the system can flow. The viscosity of the samples PB and PU showed gradual decrease with increase in shear rate. At lower shear rate PB showed higher viscosity but at higher shear rates, the viscosity of PU was higher than that of PB. This indicated that the viscosity of PU is less sensitive to shear than that of PB and that PU shows more Newtonian flow characteristics at lower shear rates than PB.

VII.A.2 Effect of Temperature and Shear Rate on Viscosity :

The combined effects of temperature and shear rate on viscosity of the TPE samples are shown in figure VII.A.2. The viscosity of the styrenic block copolymers (K1 and K5) decreased with increase in temperature and shear rate. At higher shear rates the viscosity of the sample K5 showed a sharp decrease, in the temperature 190-200°C. For both these samples, the change in viscosity with increase in temperature was negligibly small, beyond 200°C. The multiphase morphology of block copolymers at temperatures above the crystalline melting point or glass transition temperature of the thermoplastic segment has been reported by several authors[54,192,193]. Gouinlock and Porter[194] have shown that in SBS block copolymer melts, the polystyrene blocks existing in dispersed domains at lower temperatures, exceed a critical degree of compatibility with the continuous polybutadiene phase, at a temperature of 142°C. With increasing temperature, a continuous increase in miscibility would be expected, resulting in complete disappearance of the polystyrene phase first, followed by the polybutadiene phase and forming a completely homogeneous melt. The nature of the viscosity-temperature plots of the samples K1 and K5 at three different shear rates indicated that complete miscibility of the two segments of these copolymers may be occuring at a temperature of about 200°C. The viscosity of the PU sample reduced drastically with increase in temperature. PU showed less sensitivity to shear rates at 210°C compared with other TPE samples. This indicated that PU shows more Newtonian characteristics at higher temperatures. The flow behaviour index values (n') given in the table VII.A.2, further confirmed this concept. The n' values increased with increase in temperature and reached unity at about 210°C.

The viscosity of PB sample showed an increase with increase in temperature and this effect was found to be more pronounced at lower shear rate than at higher shear rates. It has been reported that 1,2 polybutadiene undergoes crosslinking reaction at higher temperatures[198]. Thus, the increase in viscosity of PB sample is due to the effect of crosslinking of the polymer at higher temperatures. At lower shear rates, the polymer gets more residence time in the capillary to undergo crosslinking reaction. Hence the effect of temperature, in increasing the viscosity of the polymer, was more pronounced at lower shear rates.

VII.A.3 Flow Behaviour Index, Die Swell and Extrudate Deformation Characteristics : Table VII.A.2 shows the effect of temperature on flow behaviour index and that of shear rate on die swell, at 180°C, of the TPEs. SBS block copolymer (K5) showed regular decrease in n' value with increase in temperature whereas the SIS block copolymer (K1) showed an initial increase in n' value at 190°C, which decreased with further increase in temperature. Similar trend of decreasing values of n' with increase in temperature has been reported for olefin based thermoplastic vulcanizates[118]. The decrease in n' values of the thermoplastic 1,2 polybutadiene sample is due to crosslinking of the polymer, the extent of which increased with increase in temperature. PU showed increase in n' values with increase in temperature and at 210°C, the value of n' was almost equal to unity. This indicated that PU tends to show Newtonian characteristics at about 210°C. This behaviour may be due to the morphological transition from a multiphase structure to a single phase system, as reported in the case of a SBS block copolymer by Chung and Gale[193].

For all the TPEs included in this study, the extrudate swell increased with increase in shear rate, except for PB which showed less swell at a shear rate of 3000 sec^{-1}. This unusual behaviour of PB is due to lower extent of crosslinking of the sample at higher shear rate, as explained earlier. The higher die swell values of PB compared with that of other TPEs is due to higher extent of elastic response attained by this polymer due to crosslinking of the chains at higher temperature. At lower shear rate, PU and K1 samples showed swell indices less than unity. This may be due to drawing out of the extrudate due to gravity, at this very low rate of shear. Sample K1 which contained higher proportion of the elastomer phase showed higher swell values at higher shear rates compared to sample K5.

The deformation of the extrudates shown in figure VII.A.3 indicated that there is little deformation for the extrudates of sample K5 and PU. Sample K1 which contained higher proportion of elastomer segments showed high deformation with increase in rate of shear. The lower deformation characteristic shown by sample K5 at all shear rates is due to the combined effects of higher proportion of polystyrene content and the presence of fine particle silica filler which reduced the die swell. Thermoplastic 1,2 polybutadiene showed higher distortion at lower shear rates than that at higher rate of shear due to higher elastic response of the sample resulting from higher extent of crosslinking at lower shear rates.

LE VII.A.1 DETAILS OF THE THERMOPLASTIC ELASTOMERS USED

Chemical Name	Description
1,2 Polybutadiene	Thermoplastic 1,2 polybutadiene elastomer having 1,2 content greater than 90% and degree of crystallinity 25%. JSR RB 820, manufactured by Japanese Synthetic Rubber Company, Japan.
Styrene-Butadiene-Styrene Block Copolymer	SBS block copolymer having styrene/butadiene ratio 48/52 and containing about 10% by wt. amorphous silica. KRATON D5152, manufactured by Shell Chemical Company, U.S.A.
Styrene-Isoprene-Styrene Block Copolymer	SIS block copolymer having styrene/isoprene ratio 14/86. KRATON D1107, manufactured by Shell Chemical Company, U.S.A.
Thermoplastic Polyurethane Elastomer	Aromatic ester type thermoplastic polyurethane elastomer. ESTANE 5715 manufactured by B.F. Goodrich Company, U.S.A.

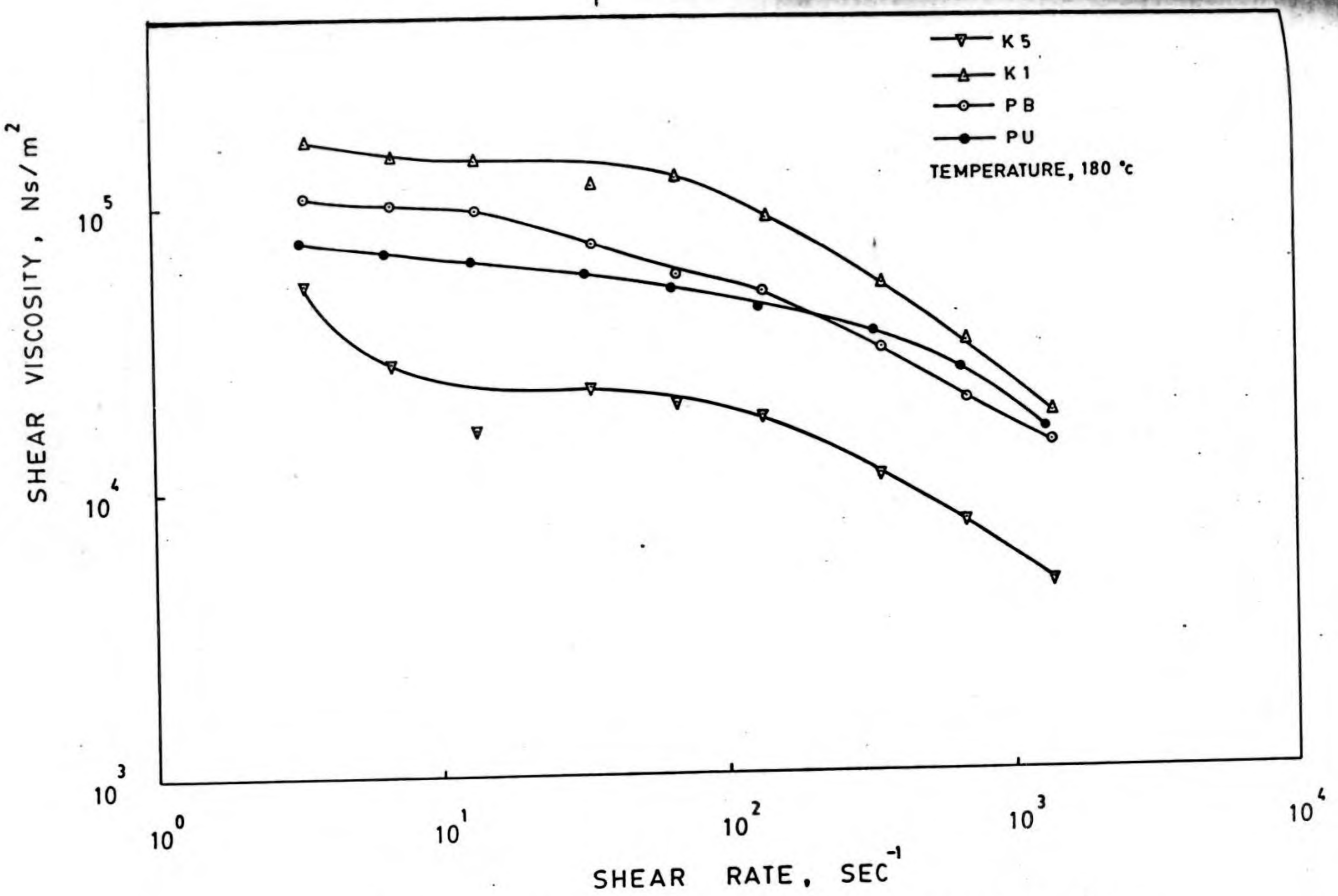


FIG.VII.A.1 VISCOSITY-SHEAR RATE PLOTS AT 180°C.

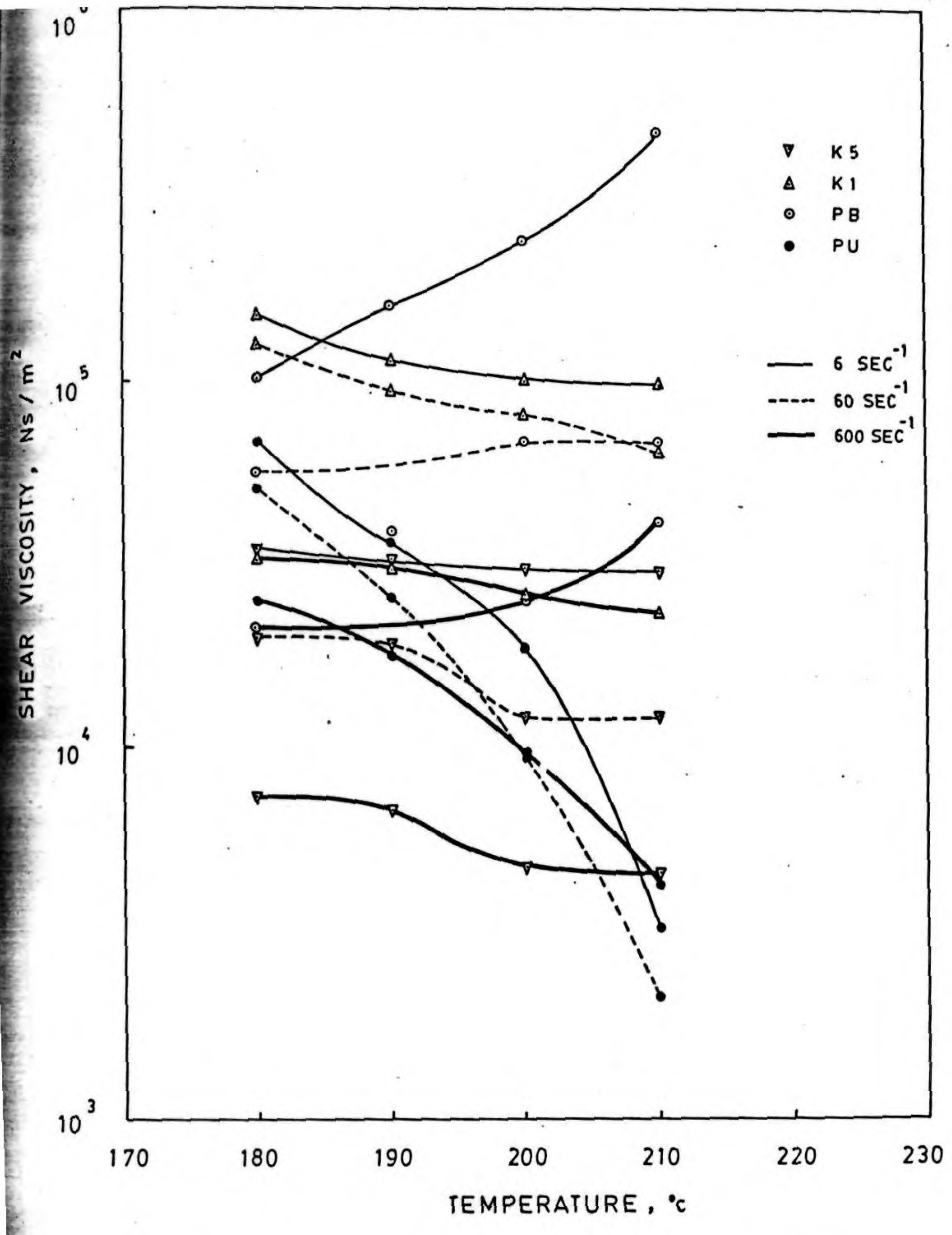


FIG.VII.A.2 VISCOSITY-TEMPERATURE PLOTS

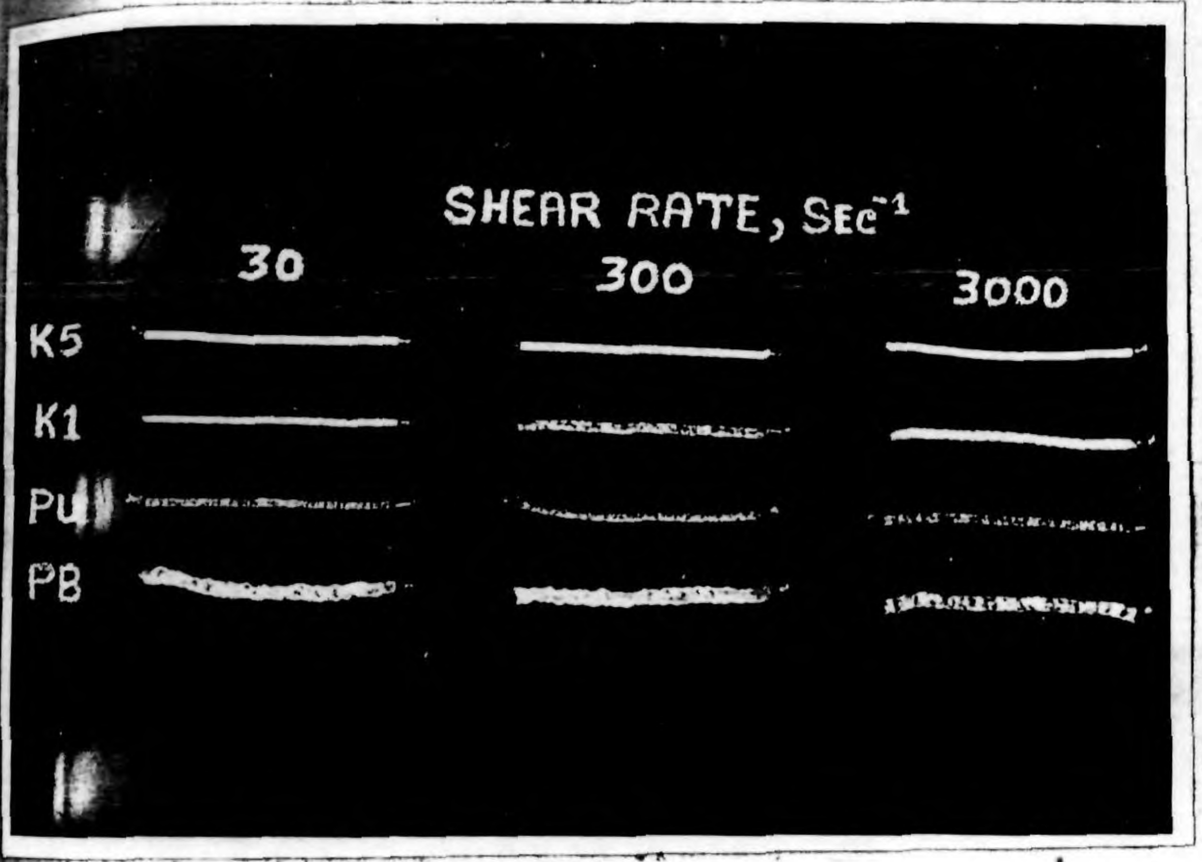


FIG.VII.A.3 EFFECT OF SHEAR RATE ON DEFORMATION OF EXTRUDATES

CHAPTER VII - B

STUDIES ON THE MODE OF FAILURE UNDER TENSION, TEAR AND ABRASION OF STYRENE-BUTADIENE-STYRENE COPOLYMER, STYRENE-ISOPRENE-STYRENE COPOLYMER, THERMOPLASTIC POLYURETHANE AND 1,2 POLYBUTADIENE

Thermoplastic elastomers are finding applications in a number of mechanical moulded goods, which undergo different types of deformation during service. Since the elastic characteristics of TPEs result from various physical forces of attraction, the type of deformation of these materials, leading to failure under the application of load, will vary depending on the nature and proportion of the hard and soft regions present in the material. Examination of the failure surfaces can provide valuable information about the factors leading to failure and the type of failure. In this part of chapter VII, an attempt has been made to understand the failure mechanism of the styrenic block copolymers, 1,2 polybutadiene and thermoplastic polyurethane elastomer by scanning electron microscopic examination of the failure surfaces under tensile and tear fracture and abrasion.

VII.B.1 Technical Properties : Table VII.B.1 gives the technical properties of the TPEs. Since the materials evaluated are manufactured for specific end uses, direct comparison of the technical properties may not be relevant. But these materials represent each class of thermoplastic elastomer and show certain distinct properties. Thus thermoplastic polyurethane (PU) is characterised by its high resistance to abrasion, whereas thermoplastic 1,2 polybutadiene (PB) shows higher tear strength and styrene-isoprene-styrene block copolymer (K1) provides highest elongation. The abrasion resistance of K1 could not be tested as the samples chipped out during one minute run of the test, probably due to its very poor resistance to cutting and tearing action compared to that of styrene-butadiene-styrene block copolymer (K5). The comparative data on physical properties are used for explaining the mechanism of different types of failure of these samples.

The stress-strain curves (figure VII.B.1) clearly show that the deformation nature of the four TPEs under an applied load in tension, is quite different from one another. At low strains (<300 %) PU showed a stress-strain curve similar to that of vulcanized elastomers whereas, at higher strains, there is a sharp increase in stress, probably due to the orientation of the hard segments in the direction of the applied stress. This behaviour is typical of the ester-type thermoplastic polyurethanes[199,200]. PB showed a stress-strain relation that is intermediate between that of plastic and rubber[198]. At lower strains ($< 100\%$), there is a tendency to yield, but this is not so prominent as in the case of thermoplastics. At higher elongations, the stress gradually increased with strain and this portion of the curve was similar to that of elastomers. The stress-strain behaviour of K5 was almost similar to that of gum vulcanizates of noncrystallizable rubbers. K1 showed very low modulus values at low strains and behaved like elastomers containing very low extent of crosslinking. But at higher strains ($> 800\%$), there was a sharp increase in modulus which may be due to the combined effect of orientation of the hard polystyrene segments and strain induced crystallization of the polyisoprene segments of the block copolymer[201]. Towards the breaking point, the sample yielded and then broke with no definite neck formation. The scanning electron microscopic studies of the tensile, tear and abrasion failure surfaces provide more information on the mode of deformation of these materials under the application of load.

VII.B.2 Tensile Failure : The tensile fracture surfaces of the TPEs shown in figures VII.B.2 to VII.B.8, reveal that these materials vary in their deformation characteristics under an applied load. The tensile fracture surface (figure VII.B.2) of PU, which has the highest tensile strength among the four TPEs studied, showed elastic type deformation of the sample under tensile stress, evidence for which is a broad continuous fracture path and less residual deformation, indicated by the absence of peaks or fibrils on the surface. The foldings on the surface adjacent to the fracture path indicated the high extent of elastic deformation undergone by the matrix before failure. The nature of the stress-strain curve of the sample also supported the above views.

The tensile stress in homogeneous materials may be relieved by the formation of crazes which have semicircular or circular boundaries. The crazes opened-up during tensile failure are characterised by a central normal stress zone with curved boundaries and an adjacent tear zone[174]. The tensile fracture surface of PB showed these features. Figure VII.B.3 showed the central stress zone with circular boundaries. The V-shaped foldings adjacent to the central zone (figure VII.B.4) indicated the tear zone which further propagated the crack. A network of channels was also observed inside the central stress zone (figure VII.B.5). Thus in PB the fracture was initiated by craze formation and propagated by tear fracture. Craze formation before failure is characteristic of rubber modified thermoplastics[163]. The fractographs and the stress-strain curve indicated that the deformation behaviour of PB under an applied load in tension is in between that of rubber and thermoplastics. The fracture surface of K1 showed a smooth fracture path with peaks due to pulling up of the material before failure (figure VII.B.6). The foldings, lips and fibrils on the surface (figure VII.B.7) showed high extent of deformation of the matrix and indicated ductile nature of the failure. The stress-strain curve of this sample also showed ductile nature of failure as indicated by yielding with no definite neck formation (figure VII.B.1). Sample K5 contained approximately equal proportion of polystyrene and polybutadiene segments in the block copolymer and the polystyrene segments remained as laminar domains in the matrix. It also contained plasticizers and small quantity of filler. Under the application of tensile stress, shear deformation between the two segments took place and the fracture proceeded by shearing action. This was clearly indicated by the tensile fractograph of K5 (figure VII.B.8) which showed discontinuous fracture paths in different planes.

VII.B.3 <u>Tear Failure</u> : The resistance to tearing of the elastomers depends on the process by which stress dissipation near the tip of the growing crack takes place. This may be accomplished by several processes such as slippage or breakage of crosslinks or chain entanglements, deviating or arresting of the growing crack by filler particles, etc.[134]. The process of stress dissipation may be understood by careful examination of the tear fracture surfaces. Figure VII.B.9 showed that the tear fracture in PB has proceeded through stick-slip process due to the presence of crystalline regions in the matrix. The presence of branched tear path, vertical striations on the surface and the stick-slip tear path indicate the high energy expended for the propagation of the tear. The peaks appearing as pulled up wavy crests (figure VII.B.10) showed the high extent of stretching that has taken place before failure. Thus, the high tear strength of PB (table VII.B.1) compared with that of the other TPEs is due to higher extent of stress dissipation through the various processes described above. The tear fracture surface of TPU showed a broad tear path and vertical striations (figure VII.B.11). The tear strength of TPU was less than that of PB but greater than that of K5. The fracture surface of K5 (figure VII.B.12) did not contain any continuous tear path, which indicated laminar tearing between the hard and soft segments. Small rounded tear lines seen on the fracture surface may be due to the deflection of tear path by the silica particles present in the sample. This sample showed higher tear strength than K1. K1 contained about 14% by weight of hard segment which remained as spherical domains, in the bulk of the soft segment. The tear fractograph of this sample (figure VII.B.13) showed a smooth surface and a continuous tear path with irregular foldings. The tear strength of K1 was poor, which is in line with the continuous tear path observed on the fracture surface. Similar observations have been reported in the tear failure of resin cured carboxylated nitrile rubber[202].

VII.B.4 Abrasion Failure : Abrasion resistance of elastomers depends mainly on factors such as strength of the matrix, resistance to thermo-oxidative degradation, crack growth resistance under dynamic conditions etc., apart from other factors such as frictional force and nature of the abrasive. The nature of definite patterns appearing on the abraded surface has been shown to be indicative of the mechanism of abrasion of elastomers[133,120]. The abraded surface of PU showed well defined ridge pattern at right angles to the direction of abrasion (figure VII.B.14). The absence of any lumpy mass and the presence of small particles on the surface indicated that these ridges are highly resistant to deformation (figure VII.B.15). Low ridge height and close spacing of the ridges are indications of high resistance to abrasion[203]. The formation of the ridges by microtearing and subsequent removal of the material from the surface depend on the tensile strength, tear and cut growth resistance of the matrix[121]. Thus the inherent strength properties of PU account for its high resistance to abrasion. The abraded surface of PB also showed ridge patterns (figure VII.B.16). But in this case, the ridges were less closely spaced and the channels between the ridges were bridged by elongated fibrils (figure VII.B.17). PB which has high tear strength and elongation at break (table VII.B.1) has undergone high deformation and the torn surfaces were stretched to high elongation before the material was removed from the surface. This sample showed lower abrasion resistance than PU, but higher than that of K5. The abraded surface of K5 showed highly deformed ridges (figure VII.B.18). The material removal in roll form can also be seen on the surface. This sample was less resistant to the frictional forces of abrasion, due to its very low tensile strength and tear resistance, which account for its lower resistance to abrasion.

LE VII.B.1 PHYSICAL PROPERTIES OF THE THERMOPLASTIC ELASTOMERS

ber	Modulus 300% (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Tear Strength (kN m^{-1})	Abrasion Loss (cm^{3} h^{-1}
(TPU)	6.0	400	16.1	37.9	0.120
(1,2 PB)	6.0	745	9.1	59.1	1.188
(SBS)	2.8	520	4.2	17.4	4.786
(SIS)	0.34	1450	11.1	10.1	a

a could not be tested as the sample chipped out after one minute.

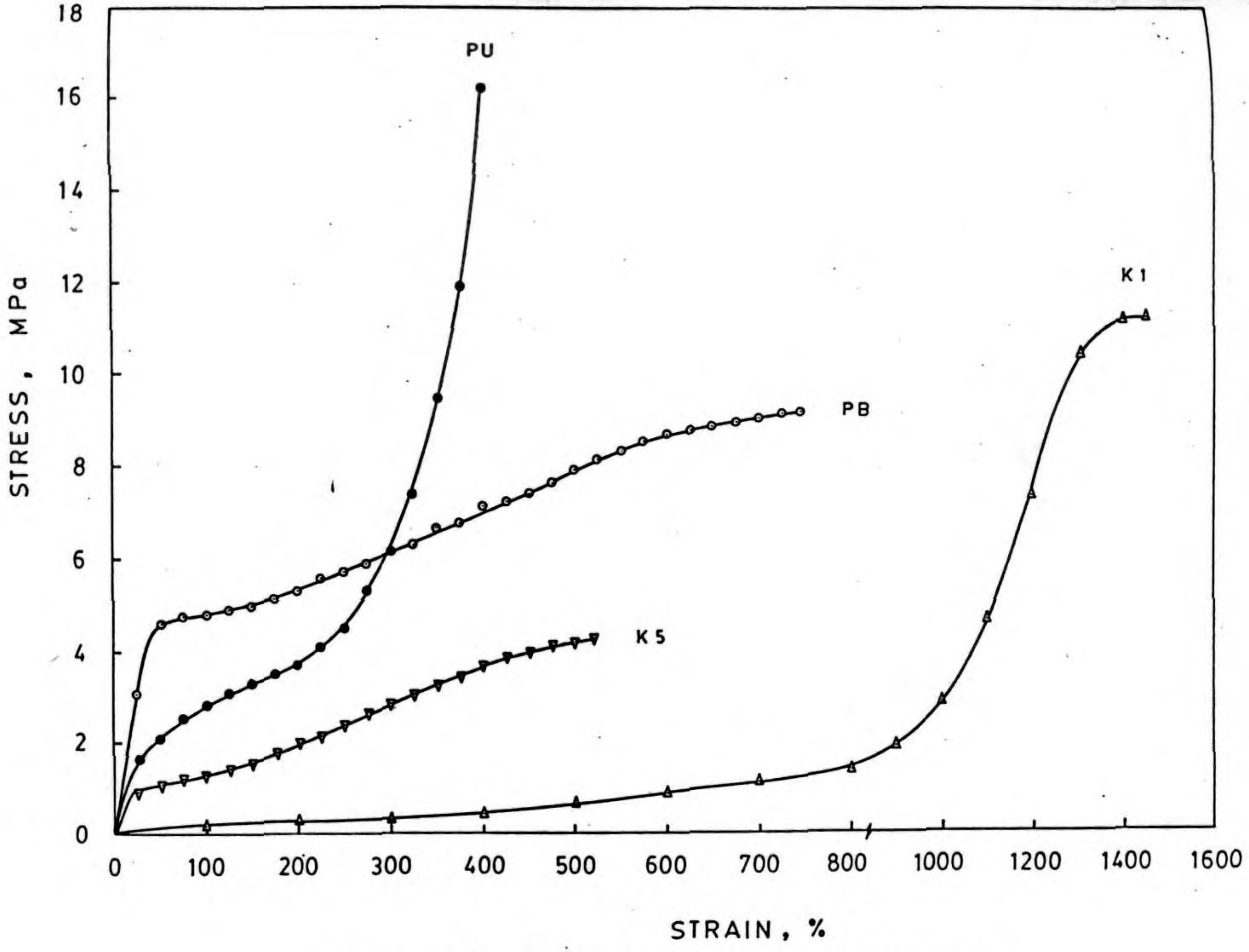


FIG.VII.B.1 STRESS-STRAIN CURVES OF TPEs

G.VII.B.2 TENSILE FRACTURE
FACE OF PU; BROAD FRACTURE

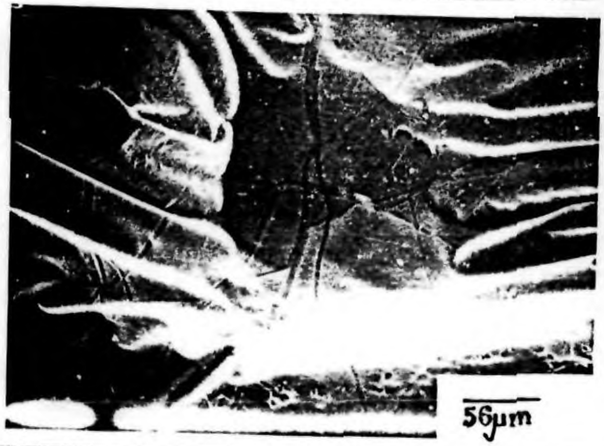
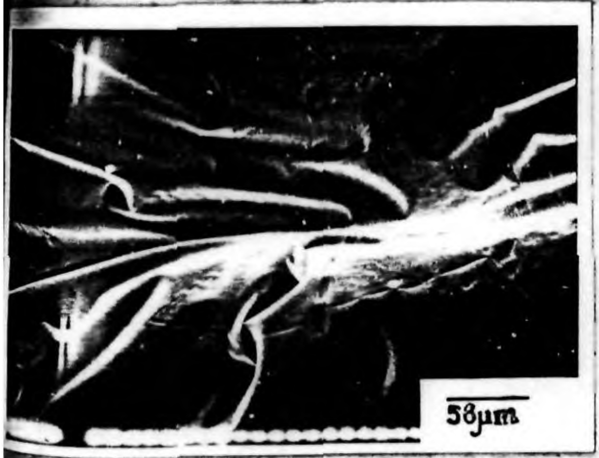
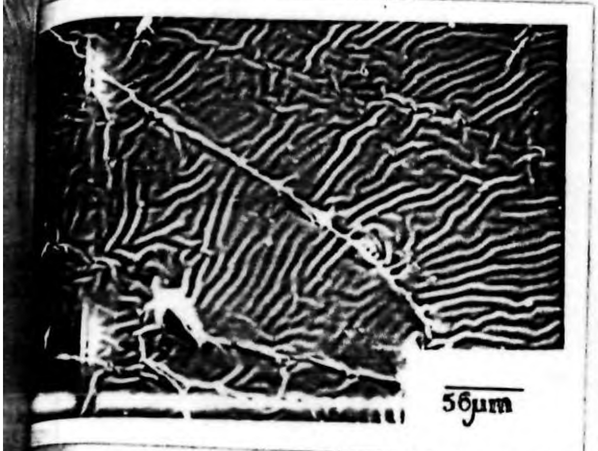


FIG.VII.B.3 TENSILE FRACTOGRAPH
OF PB; OPENED UP CRAZE



IG.VII.B.4 V-SHAPED FOLDINGS IN
E TEAR ZONE OF THE CRAZE IN
NSILE FAILURE OF PB

FIG.VII.B.5 NETWORK OF CHANNELS
INSIDE THE CENTRAL STRESS ZONE
IN TENSILE FAILURE OF PB



G.VII.B.6 TENSILE FRACTOGRAPH
K1; SMOOTH FRACTURE PATH
LDINGS

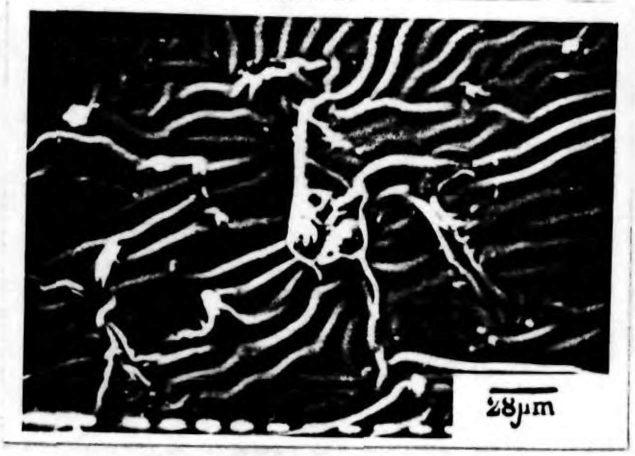
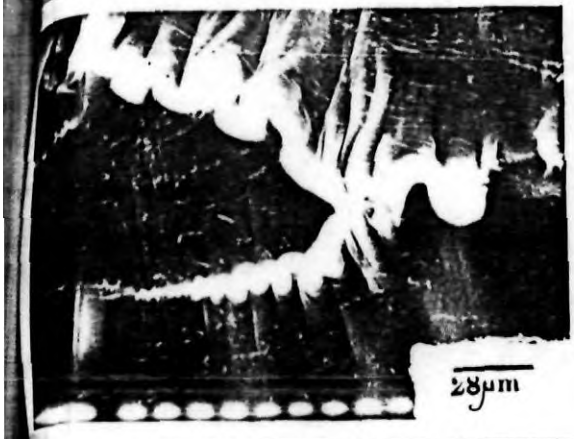


FIG.VII.B.7 FOLDINGS, LIPS AND FIBRILS ON THE TENSILE FAILURE SURFACE OF K1

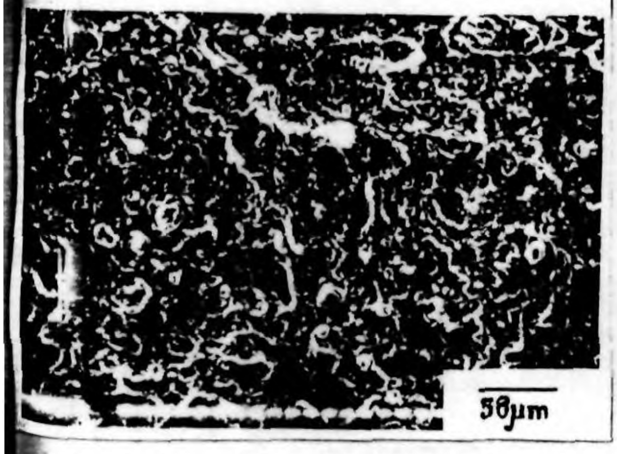
IG.VII.B.8 TENSILE FRACTOGRAPH
K5; DISCONTINUOUS FRACTURE
ATHS IN DIFFERENT PLANES

FIG.VII.B.9 TEAR FRACTOGRAPH OF PB; STICK-SLIP FRACTURE PATH, BRANCHED TEAR LINE AND VERTICAL STRIATIONS



G.VII.B.10 PULLED-UP WAVY
ESTS ON THE TEAR FAILURE
RFACE OF PB

FIG.VII.B.11 TEAR FRACTOGRAPH
OF PU; BROAD CONTINUOUS TEAR
LINE WITH VERTICAL STRIATIONS



G.VII.B.12 TEAR FRACTOGRAPH
F K5; SMALL NUMBER OF SHORT
UNDED TEAR LINES

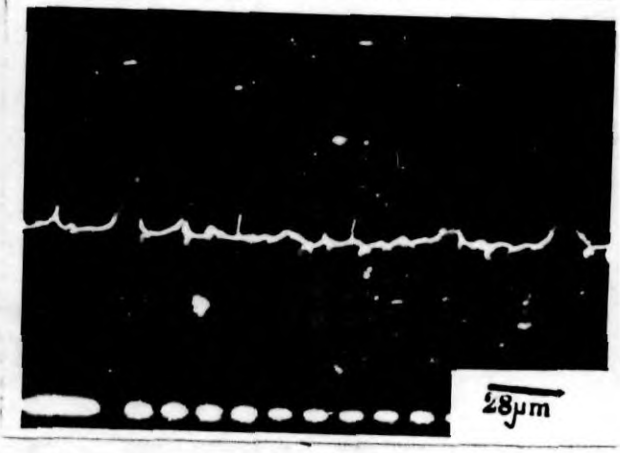
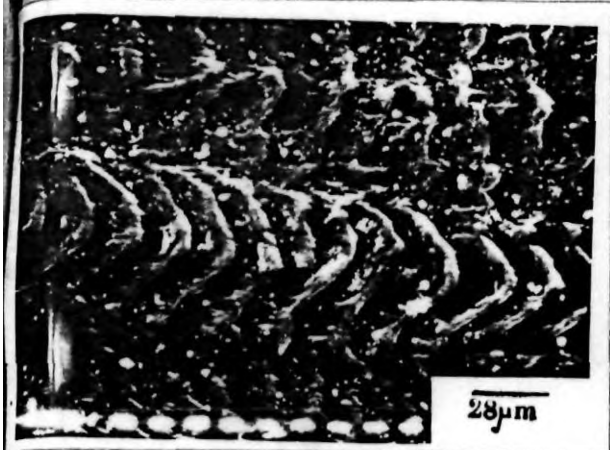
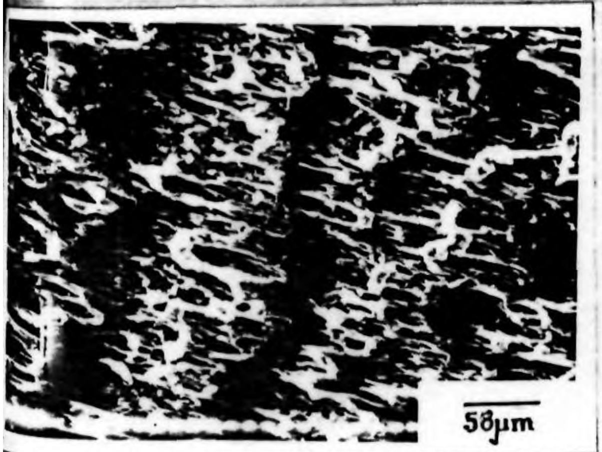


FIG.VII.B.13 TEAR FRACTOGRAPH
OF K1; CONTINUOUS TEAR LINE
WITH IRREGULAR FOLDINGS



IG.VII.B.14 SEM PHOTOGRAPH OF BRADED SURFACE OF PU; CLOSELY PACED VERTICAL RIDGES

FIG.VII.B.15 ENLARGED PICTURE OF THE VERTICAL RIDGES AND ABRADED PARTICLES OF PU



IG.VII.B.16 SEM PHOTOGRAPH OF BRADED SURFACE OF PB; WIDELY PACED RIDGES

FIG.VII.B.17 BRIDGING OF THE RIDGES BY ELONGATED FIBRILS OF PB

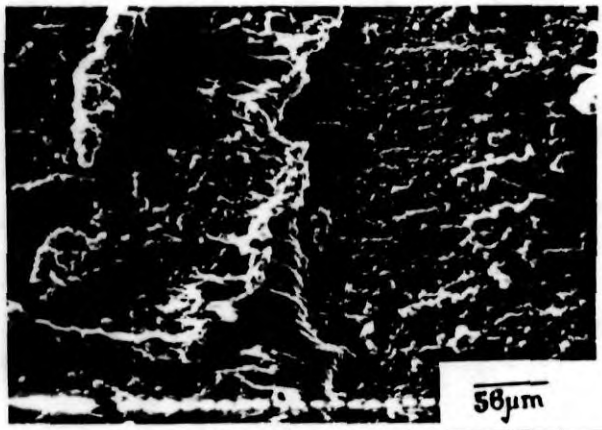


FIG.VII.B.18 SEM PHOTOGRAPH OF ABRADED SURFACE OF K5; HIGHLY DEFORMED RIDGES AND ROLL FORM OF THE MATERIAL REMOVED

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Thermoplastic elastomers (TPEs) are either block copolymers containing soft and hard segments or physical blends or grafts of a hard thermoplastic material and a soft rubbery polymer. These materials are having the processing characteristics of thermoplastics and technical properties of vulcanized elastomers. The thermoplastic characteristics of the TPEs arise from the physical forces of attraction between the crystalline segments of the hard phase, whereas the elastomeric properties result from presence of flexible chains of soft segments, which are linked by the hard segments. At higher temperature, the hard segments get softened, allowing the material to be processed like a thermoplastic. The processing characteristics and technical properties of the TPEs will be dependent upon the chemical nature and proportion of soft and hard segments in the copolymer/blend.

The data presented in this thesis consist of the results of a systematic study conducted on the rheological behaviour and mode of failure under tension, tear and abrasion of thermoplastic elastomers. Emphasis has been given for the studies of natural rubber-polypropylene blends. Other TPEs evaluated are SBS and SIS block copolymers, thermoplastic polyurethane elastomer and thermoplastic 1,2 polybutadiene elastomer. The thesis consists of seven chapters and is divided into two parts. In part I, the effects of blend ratio and extent of dynamic crosslinking of the elastomer phase, on the melt flow characteristics and technical properties of NR-PP blends have been studied. The morphology of the blends, dynamic mechanical properties and the mode of failure under tension, tear and abrasion have also been studied. The effect of carbon black and silica fillers on the above properties have been evaluated and those results are also included in this part. Part II of the thesis consists of a comparative evaluation of four different types of commercially available thermoplastic elastomers, with a view to understanding the rheological behaviour and mode of failure under tension, tear, abrasion of these materials.

The first chapter contains the review of the work done earlier in the field of thermoplastic elastomers and the scope of the present work. The development of different types of TPEs, their structure-property relations, studies on the factors affecting the processing characteristics and physical properties, advantages and disadvantages, and applications of TPEs have been discussed in this chapter.

The second chapter consists of a detailed account of the experimental procedures adopted for the preparation of the blends and the test samples. Description of the testing procedures and the details of the equipments used for testing are also included in this chapter.

The results of the studies on the melt flow characteristics of the thermoplastic NR-PP blends are discussed in the third chapter of the thesis. The effects of blend ratio, extent of dynamic crosslinking and temperature on viscosity, flow behaviour index, die swell and melt fracture of NR-PP blends have been evaluated. The proportion of the rubber phase in the blend and the extent of dynamic crosslinking were found to have a profound influence on the melt viscosity of the blends at lower shear stresses. But at higher shear stresses, the effect of blend ratio on viscosity was comparatively low for the uncrosslinked blends than that for the dynamically crosslinked blends. At lower shear stresses, the viscosity of the blends increased with increase in degree of crosslinking of the elastomer phase but at higher shear stresses, the effect of crosslinking was found to vary depending on the ratio of PP and NR in the blend. Dicumyl peroxide was found to lower the viscosity of the blends containing higher proportion of the PP phase due to its degradative action on the PP molecules. A change in morphology of the uncrosslinked blend, containing dispersed rubber particles was expected to occur during extrusion, at high shear rates. Dynamic crosslinking of the elastomer phase reduced the die swell and melt fracture of the extrudates, the extent of which was dependent on both blend ratio and degree of crosslinking.

The fourth chapter consists of the results of the studies on morphology, mechanical properties and mode of failure under tension, tear and abrasion of the thermoplastic NR-PP blends. The effect of blend ratio and dynamic crosslinking on the above properties were evaluated. The morphology studies of the blends showed that the rubber phase remained as dispersed particles in the PP matrix at lower proportions but as the proportion of the rubber is increased beyond 50%, this phase also formed a continuous phase of the blend. The 70:30 NR:PP blend was found to exist as an interpenetrating two-phase system looking like a sea sponge. This morphology change greatly influenced the physical properties of the blends. The effect of dynamic crosslinking on the mechanical properties became more prominent as the continuity of the elastomer phase increased. Scanning electron microscopic studies of the failure surfaces of the blends showed that addition of NR changed the brittle fracture of PP to a ductile type and dynamic crosslinking of the elastomer phase changed the deformation behaviour of the blends from plastic to elastic type. The mode of abrasion of the samples changed from abrasive type to frictional type and this change was more prominent in dynamically crosslinked blends than in the uncrosslinked blends.

The effects of high abrasion furnace black, precipitated silica and a silane coupling agenet on the physical properties of NR-PP blends containing different proportions of the base polymers are discussed in the fifth chapter. HAF black increased the modulus, tensile strength and tear strength of the blends, whereas, the elongation at break was decreased. The effect of HAF black was prominent in blends containing higher proportions of the elastomer phase and the action of HAF black was similar to its action on rubber vulcanizates. Addition of silica increased the technical properties of the uncrosslinked and DCP cured 70:30 NR:PP blends. In those blends which had higher extents of crosslinking, the effect of silica was more pronounced in presence of a silane coupling agent. Addition of silane coupling agent was found to adversely affect the properties of the uncrosslinked and DCP cured blends.

The sixth chapter contains the results of the studies on the dynamic mechanical properties of the thermoplastic NR-PP blends, with special reference to the effects of blend ratio, extent of dynamic crosslinking and addition of HAF black and silica on storage modulus, loss modulus and loss tangent at different temperatures. Increasing the proportion of the elastomer phase reduced the storage modulus and increased the loss tangent values of the blends. The improvement in storage modulus and decrease in loss tangent values were quite remarkable with increase in extent of crosslinking of the elastomer phase, for those blends which contained a higher proportion of the elastomer phase, The degradation effect of DCP on PP was reflected more clearly in the dynamic mechanical properties of those blends which contained higher proportion of the PP phase. Both HAF and silica filled blends showed higher storage modulus and loss modulus values than the unfilled blends.

Part II of the thesis forms the seventh chapter. It consists of the results of the studies on the rheological properties and mode of failure of four different types of commercial thermoplastic elastomers, under tension, tear and abrasion. Thermoplastic polyurethane elastomer showed better Newtonian flow characteristics than SBS, SIS and 1,2 polybutadiene at 210°C. For the SBS and SIS block copolymers, complete miscibility of the hard and soft segments was found to occur at 200°C. Thermoplastic 1,2 polybutadiene showed higher viscosity at higher temperatures due to cross-linking of the polymer chains. The changes in shear viscosity, flow behaviour index, extrudate swell and distortion of the extrudates showed evidences for these transitions in the above thermoplastic elastomer melts. Under tension, the thermoplastic polyurethane undergoes elastic type deformation and failure whereas in 1,2 polybutadiene the failure was initiated by craze formation and propagated by tear failure. The SIS block polymer showed ductile type failure, whereas in SBS block polymer the fracture occured by shearing action. The surfaces of the above four thermoplastic elastomers after tear fracture and abrasion showed well defined fracture patterns which could be correlated with the strength of the materials.

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LIST OF PUBLICATIONS FROM THE PRESENT WORK

1. Scanning electron microscopy studies on tensile failure of thermoplastic elastomers from polypropylene-natural rubber blends.

   Mater. Chem. Phys., 12, 157 (1985).

2. Scanning electron microscopy studies on tear failure of thermoplastic elastomers from polypropylene-natural rubber blends.

   J. Mater. Sci. Letters, 4 (4), 455 (1985).

3. Tear and wear resistance of silica filled thermoplastic polypropylene-natural rubber blend.

   Inter. J. Polym. Mater., (In press).

4. Studies on melt flow behaviour of thermoplastic elastomers from polypropylene-natural rubber blends.

   Polym. Eng. Sci., 25 (10), 630 (1985).

5. Dynamic mechanical properties of thermoplastic elastomers from polypropylene-natural rubber blend.

   J. Appl. Polym. Sci. (In press).

6. Scanning electron microscopy studies on tensile, tear and abrasion failure of thermoplastic elastomers.

   J. Mater. Sci., 20 (5), 1864 (1985).

Studies on the Melt Flow Behavior of Thermoplastic Elastomers from Polypropylene—Natural Rubber Blends

BABY KURIAKOSE *and* S. K. DE

Rubber Technology Centre
Indian Institute of Technology
Kharagpur 721302
West Bengal, India

The melt flow behavior of thermoplastic polypropylene-natural rubber blends has been evaluated with specific reference to the effects of blend ratio, extent of dynamic crosslinking of the rubber phase and temperature, on viscosity, flow behavior index, and deformation of the extrudate. The proportion of rubber in the blend and the extent of dynamic crosslinking of the rubber phase were found to have profound influence on the viscosity of the blends at lower shear stresses. But at higher shear stresses, the effect of blend ratio on viscosity was comparatively less for the uncrosslinked blends than that for the crosslinked blends. At lower shear stress, the viscosity of the blend increased with increase in degree of crosslinking but at higher shear stress, the effect of crosslinking on viscosity was found to vary depending on the ratio of the plastic and rubber components in the blend. The deformation of the extrudates was also very much dependent on both blend ratio and degree of crosslinking.

INTRODUCTION

ermoplastic elastomers combine the excellent
rocessing characteristics of the thermoplastic
rials at higher temperatures and a wide range
ysical properties of elastomers at service tem-
tures (1–4). The materials prepared by melt
g of a thermoplastic material and an elastomer
r high shearing action, have gained consider-
attention due to the simpler method of prep-
on and easy attainment of the desired physical
erties (5). It has been further shown that ad-
n of small quantities of crosslinking agent dur-
he mixing operation improves the final prop-
s, mildly affecting the processing behavior (6–
This process is known as dynamic crosslinking.
these materials can be processed in the same
as the thermoplastics, melt flow studies of
noplastic elastomers have become important
timizing the processing conditions, and in de-
ping new processing equipment and the dies
ssary for the production of various types of
ded and injection molded products.

e rheological behavior of polymer blends and
of polymers containing gel and crosslinked
cles have been studied by different research
ps (13–21). The effects of rubber particles,
on black and non-black fillers on the flow prop-
s of polymer melts have also been studied (22–
Various factors affecting the die swell, melt
fracture, and deformation of extrudates have been reported by several authors (26–30). Studies on the rheological behavior of thermoplastic block copolymers (31–34), metal sulfonated ethylene propylene terpolymers (35), and those of the blends of a thermoplastic polyolefin and an elastomer (36–38), have become the subject of recent interest due to the growing importance of the thermoplastic elastomers. In this paper, we report on the results of the melt flow studies on dynamically crosslinked thermoplastic elastomers from natural rubber (NR)-polypropylene (PP) blends. The effects of blend ratio, extent of dynamic crosslinking and temperature, on viscosity, flow behavior index, and melt fracture of the extrudate have been studied.

EXPERIMENTAL

Base Materials Used

The NR used for this study was Indian Standard Natural Rubber, ISNR 5 grade, conforming to IS 4588-1977 specifications. PP used in the present study was isotactic polypropylene (Koylene M0030 of Indian Petrochemicals Corporation Ltd.). The characteristics of the above two base materials are given in *Table 1.*

Preparation of the Blends

Formulations of the blends are given in *Table 2.* The blend ratios are denoted by letters B, D, and

Table 1. Characteristics of NR and PP

Property	NR	PP
Molecular Weight $\bar{M}_n$	—	1,06,000
Molecular Weight $\bar{M}_w$	7,80,000	5,30,000
Molecular Weight Distribution $\bar{M}_w/\bar{M}_n$	—	5.0
Intrinsic Viscosity (Benzene, 30°C; dl/g) $[\eta]$	4.45	—
Melt Flow Index (230°C and 2.16 kg) MFI	—	10.0
Wallace Plasticity P_o	59.0	—

Table 2. Composition of the NR-PP Blends

Components	B	D	F
Natural Rubber[a]	30	50	70
Polypropylene[b]	70	50	30
Curing systems[c]	U, D, M, S	U, D, M, S	U, D, M, S

[a] Crumb rubber ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam, Kerala, 686 009.

[b] Koylene M0030 received from M/s Indian Petrochemical Corporation Ltd., Vadodara, Gujrat.

[c] U Uncrosslinked system.
D Dicumyl peroxide (DCP) cure system (40 percent DCP, 1.0 phr level, based on rubber phase only).
S Sulfur cure system (zinc oxide 5.0, stearic acid 2.0, N-cyclohexyl benzothiazyl sulphenamide (CBS) 2.0, tetra-methyl thiuram disulphide (TMTD) 2.5, and sulfur 0.30 phr, based on rubber phase only).
M Mixed cure system (40 percent DCP 1.0, zinc oxide 5.0, stearic acid 2.0, CBS 1.0, TMTD 1.25, and sulfur 0.15 phr, based on rubber phase only).

F. The suffixes U, D, M, and S denote the blends without any curative, that containing dicumyl peroxide (DCP), mixed and sulfur cure systems, respectively. Thus, the blend B_M means NR:PP as 30:70 with mixed crosslinking system. The blend ratios were selected to represent thermoplastic elastomer ranges of the polyolefin-elastomer blends. Blends of NR and PP were prepared in a Brabender Plasti-corder model PLE 330, using a cam-type mixer with a rotor speed of 80 rpm and the mixer chamber temperature set at 180°C. PP was melted in the mixer for one min. and then NR was added and the blend was allowed to mix for four mins. At the end of five mins., curatives were added and the mixing continued for three more mins. The blend was taken out and sheeted through a laboratory mill at 2.0 mm nip setting. The sheeted material was cut into small pieces and again mixed in the Plasti-corder at 180°C for one min. and then finally sheeted out in the mill so as to get uniform dispersion of the ingredients. Except DCP, all the ingredients were added as masterbatches. For blends containing mixed cure system, DCP was added after four mins. blending of PP and NR and then the mixing continued for one min. Other ingredients were added after this step. Specimens of dimensions 5.0 by 5.0 by 2.5 mm were cut from the sheets and used for the melt flow measurements.

Melt Flow Measurements

The melt flow measurements were carried out using a capillary rheometer MCR 3210 attached to an Instron Universal Testing Machine model 1195 and a capillary of length to diameter ratio (l_c/d_c) 40 with an angle of entry of 90°. Sample for testing was placed inside the barrel of the extrusion assem-

plunger attached to the moving crosshead. Af warming up period of five mins. the melt wa truded through the capillary at pre-selected sp of the crosshead which varied from 0.5 to 5 mm per min. The melt height in the barrel be extrusion was kept the same in all the experim and the machine was operated to give five diffe plunger speeds from lower to higher speed, w single charge of the material. Forces correspon to specific plunger speeds were recorded usi strip chart recorder assembly. The force and c head speed were converted into apparent s stress (τ_w) and shear rate ($\dot{\gamma}_w$) at wall by using following equations involving the geometry o capillary and the plunger:

$$\tau_w = \frac{F}{4\, A_P(l_c/d_c)}$$

$$\dot{\gamma}_w = \left(\frac{3\,n' + 1}{4\,n'}\right) \times \frac{32\,Q}{\pi d_c^3}$$

where, 'F' is the force applied at a particular sh rate, 'A_P' is the cross-sectional area of the plun 'l_c', the length of the capillary, and 'd_c' the diam of the capillary. 'Q', the volume flow rate calculated from the velocity of crosshead and ameter of the plunger. n' is the flow behavior in defined by $n' = d(\log \tau_w)/d(\log \dot{\gamma}_{w \cdot a})$ and determined by regression analysis of the value τ_w and $\dot{\gamma}_{w \cdot a}$ obtained from the experimental d $\dot{\gamma}_{w \cdot a}$ is the apparent wall shear rate calculate $32Q/\pi d_c^3$. The shear viscosity η was calculated f τ_w and $\dot{\gamma}_w$.

RESULTS AND DISCUSSIONS

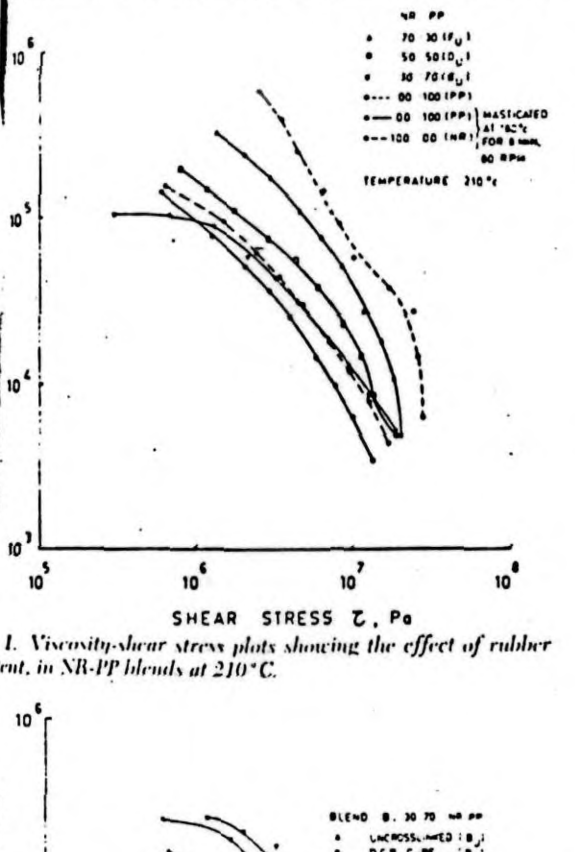
Our earlier studies (39, 40) on the physical p erties and tensile and tear failure of these ble showed that the physical properties of the ble were improved with increase in degree of crossl ing of the rubber phase. The degree of crosslin of the rubber phase in the blend was in the or sulfur cure > mixed cure > DCP cure, as measu by the V_r values (volume fraction of rubber in solvent swollen sample of rubber vulcanizates c taining the same level of curatives), which w 0.07, 0.13, and 0.17 respectively for DCP, mi and sulfur cured samples.

Effect of Blend Ratio and Shear Stress on Viscosity

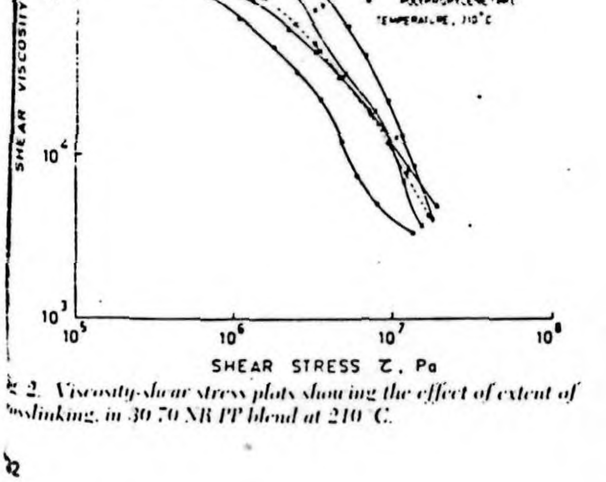
Figure 1 shows the effect of blend ratio and sh *stress on viscosity of the thermoplastic* PP- blends. At lower shear stresses, the viscosity of t blend increases with increase in proportion of ru ber in the blend. The viscosity decreases with crease in shear stress and at high shear stres (2×10^7 Pa), the difference between the visco of the blends containing various proportions of and NR is only marginal. At lower shear stress the viscosity of fresh PP pellets is higher than t of 30:70 NR:PP blend (B_U). Thermal degradati and the corresponding decrease in melt viscosity PP had been reported by White, *et al* (41). Melti ins. degraded the PP in the blend and reduced iscosity. This is evident from the lower viscosity he PP which has been melted and sheared in plasti-corder for 8 mins. at 180°C and 80 rpm, pared with that of fresh PP pellets. However, zero shear viscosity shown by blend B_U at lower ar stress remains unexplained.

ct of Dynamic Crosslinking and Shear Stress Viscosity

he effect of shear stress on viscosity of the 30:70 PP blends containing rubber particles having rent extents of crosslinking is shown in *Fig. 2.* lower shear stresses, the viscosity of the blends eases with increase in degree of crosslinking of rubber phase. At higher shear stresses also, the d *is the same, even though the differences in* osities of the blends having different extent of crosslinking of the rubber phase is only marginal. Blend B_U shows lower viscosity at lower shear stresses and higher viscosity at higher shear stresses than the blends containing crosslinked rubber particles (B_D, B_M, and B_S). *Since the dispersed rubber* phase is having higher viscosity than the continuous PP phase (*Fig. 1*), the continuous phase experiences the same deformation in all the blends whereas, the *deformation undergone by the dispersed phase* depends on its melt viscosity (36). It has been reported that the uncrosslinked rubber particles in polypropylene-elastomer blends are bigger in size and highly deformable (38) and that these particles are broken down into smaller ones under high shear rates (37), as observed in other heterogeneous blends (42). Crosslinking of the elastomer phase increases its viscosity and decreases the deformation of the dispersed particles as indicated by the increase in Brabender mixing torque values (at 180°C, 80 rpm rotor speed) from 5.5 Nm for the *uncrosslinked blend (B_U) to 8.0 Nm for the sulfur* crosslinked blend (B_S). Considering the above details, the changes in morphology of the blend B containing uncrosslinked and crosslinked rubber particles, under low and high shear stress conditions, may be represented as dipicted in *Fig. 3*. The uncrosslinked rubber particles in the blend are elongated at the entrance of the capillary and are broken down into smaller particles whereas, the crosslinked particles which are less deformable, retain the morphology of the blend even at high shear stresses. Thus, the observed difference in viscosities of the uncrosslinked blend B_U and crosslinked blends B_D, B_M, and B_S at low and high shear stresses is due to the change in morphology of the uncrosslinked blend under high shear stress conditions. The DCP cured 30:70 NR:PP blend (B_D) *shows lower viscosity compared with that of blends* B_U, B_M, and B_S. It has been reported that DCP degrades PP at elevated temperature and that this effect is more prominent at higher proportions of PP in NR-PP blends, as evidenced by increase in melt flow index values of these blends (7). Thus the lower viscosity of the blend B_D can be attributed to the degradative effect of DCP on PP at high temperature of blending.



1. *Viscosity-shear stress plots showing the effect of rubber tent, in NR-PP blends at 210°C.*



2. *Viscosity-shear stress plots showing the effect of extent of sslinking, in 30 70 NR PP blend at 210°C.*

In the 50:50 NR:PP blend, there is a sharp increase in viscosity with crosslinking at lower shear stresses and blends D_M and D_S show yield stresses (*Fig. 4*). Münstedt (22) has reported that in rubber

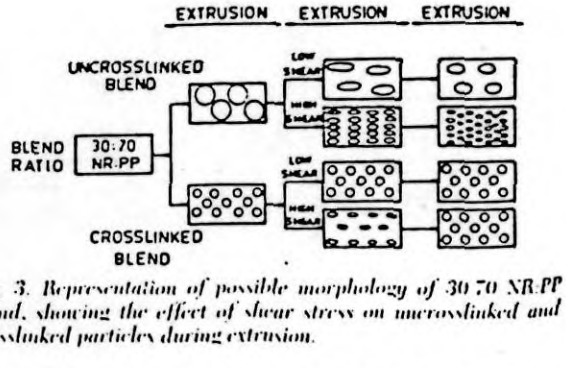


Fig. 3. Representation of possible morphology of 30 70 NR:PP blend, showing the effect of shear stress on uncrosslinked and crosslinked particles during extrusion.

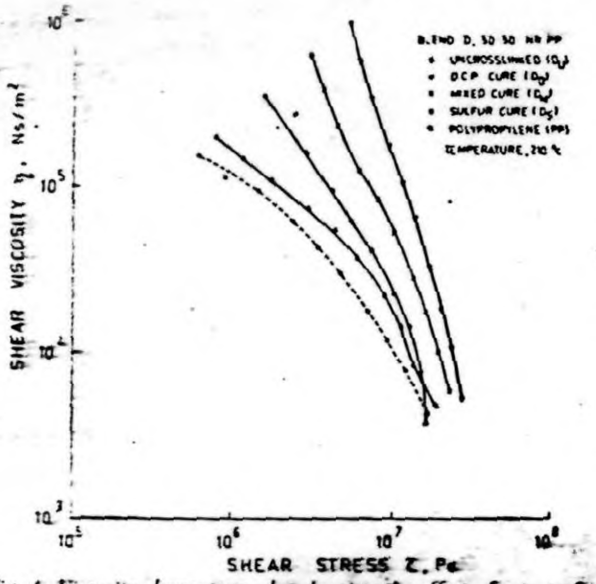


Fig. 4. Viscosity-shear stress plot showing the effect of extent of crosslinking in 50:50 NR:PP blend at 210°C.

modified styrene-acrylonitrile and poly(vinyl chloride) the viscosity increase in lower shear stresses is due to structure build-up of rubber particles and that the viscosity increase is more pronounced at higher concentration and smaller size of the rubber particles. At higher extents of crosslinking, the smaller size of the mixed and sulfur cured rubber particles in blends D_M and D_S, compared with that of uncrosslinked and slightly crosslinked blends, form some sort of structure build-up inside the system, which leads to yield stress in these blends. The degradative effect of DCP on PP is evident from the lower viscosity of the blend D_D at higher shear stress. In 70:30 NR:PP blends (*Fig. 5*), the observed differences in viscosities of the blends F_U, F_D, F_M, and F_S are proportional to the degree of crosslinking of the rubber phase. The viscosities of the blends F_U and F_D are comparable and the blends F_M and F_S also show the same trend at lower shear stresses, unlike the viscosities of the blends in the D series, which show wide difference (*Fig. 4*). The degradative effect of DCP on PP which has been observed in blends B_D and D_D is not prominent in blend F_D. It is also seen that the effect of extent of crosslinking on viscosity is less pronounced for the blends in F series at higher shear stresses unlike that observed for the blends in D series.

Effect of Temperature and Dynamic Crosslinking on Flow Behavior Index

The effects of temperature and degree of crosslinking of the rubber phase on *n′* values are presented by histograms in *Fig. 6*. For the 30:70 NR:PP blends, at 210°C the *n′* values decrease with increase in extent of crosslinking of the rubber phase. At 200°C blend B_S shows slightly higher values for *n′* than that for B_M. Similarly at 190°C blend B_D shows slightly higher value than blend B_U. Blend B_S shows maximum value for *n′* at 200°C whereas for blends B_U, B_D, and B_M, *n′* values are maximum at 210°C. In 50:50 NR:PP blends, the *n′* values decrease with increase in degree of crosslinking and

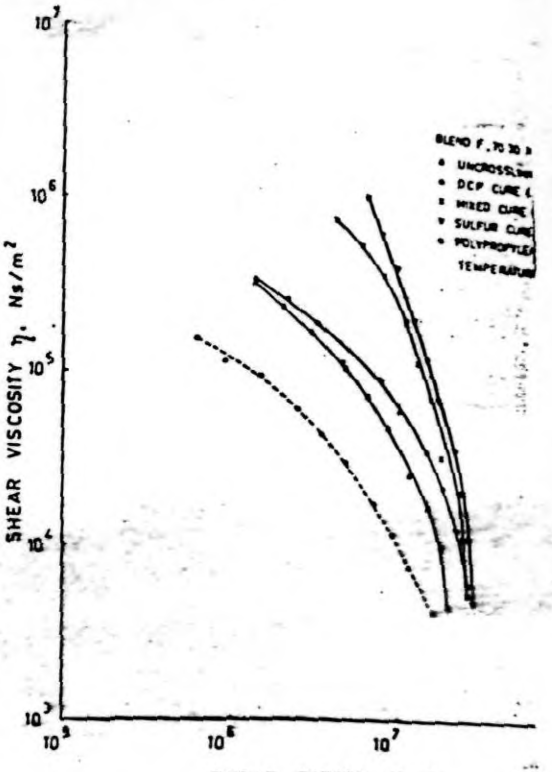


Fig. 5. Viscosity-shear stress plot showing the effect of exten crosslinking in 70:30 NR:PP blend at 210°C.

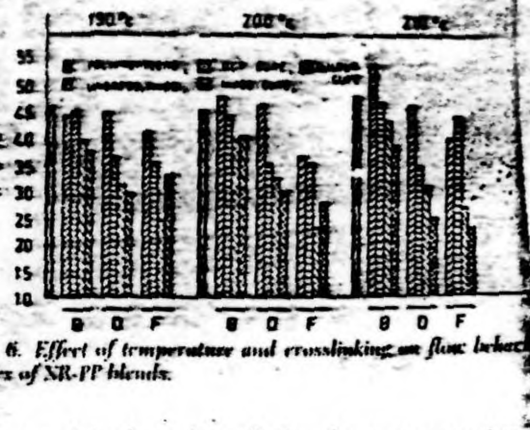
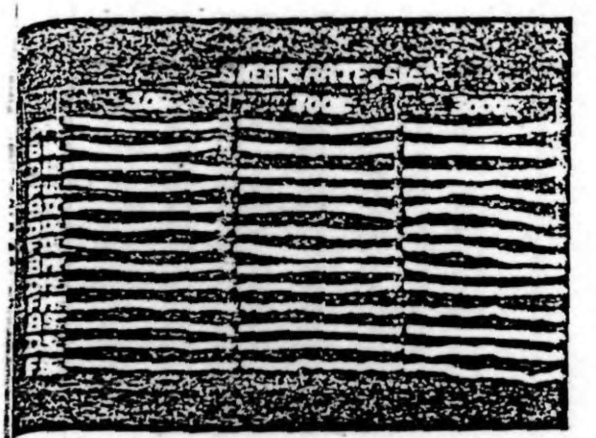


Fig. 6. Effect of temperature and crosslinking on flow behav index of NR-PP blends.

this trend is shown at all the three temperature For these blends, a tendency to form maximu value for *n′* at 200°C is also observed. In the ca of blends in F series, no regular change in *n′* value with increase in temperature or crosslink density the rubber phase is observed except for blend F which shows gradual decrease in *n′* value wit increase in temperature. Blends F_U and F_M showe minimum values at 200°C.

Effect of Dynamic Crosslinking on Melt Fracture

Figure 7 shows that the deformation of the extru date is increased with increase in shear rate, bot for the uncrosslinked and crosslinked blends. In creasing the rubber content in the blend beyond 30 percent increases the melt fracture of the ex trudates as the elastic response increases with in crease in proportion of the rubber phase. At higher shear rates the distortion of the extrudates de



g. 7. *Effect of extent of crosslinking on distortion of extrudates NR-PP blends at 210°C.*

reases with increase in crosslink density of the ubber phase. DCP cured blends show higher deformation and the sulfur cured blends give least deformation at all blend ratios. This is due to less deformation and quick recovery of the rubber particles containing higher degree of crosslinking.

CONCLUSIONS

The following conclusions can be drawn from the present study:

1. In thermoplastic PP-NR blends, the increase in viscosity with increase in rubber content is predominant only at lower shear stresses.

2. Dynamic vulcanization of the elastomer phase increases the viscosity of the blends, the extent of which depends on the degree of crosslinking of the rubber phase.

3. The effect of dynamic vulcanization on viscosity of the blends depends also on the blend ratio.

4. Crosslinking of the elastomer phase reduces the distortion of the extrudates at higher shear stresses.

5. Dynamically vulcanized thermoplastic PP-NR blends can be processed by extrusion and injection molding techniques as the viscosity at higher shear stresses is low.

NOMENCLATURE

NR = Natural Rubber
ISNR = Indian Standard Natural Rubber
PP = Isotactic polypropylene
DCP = Dicumyl peroxide, 40 percent active ingredient
V_r = Volume fraction of rubber in vulcanizate swollen in benzene at 35°C for 48 h
rpm = Revolutions per minute
phr = Parts per hundred rubber
l_c = Length of capillary (mm)
d_c = Diameter of capillary (mm)
d_e = Diameter of extrudate (mm.)
A_p = Cross-sectional area of the plunger (mm^2)
F = Extrusion force (N)
Q = Volume flow rate
n' = Flow behavior index, defined by $d(\log \tau_w)/d(\log \dot{\gamma}_{w,a})$
τ_w = Apparent shear stress at wall (Pa)
$\dot{\gamma}_w$ = Shear rate at wall (s^{-1})
$\dot{\gamma}_{w,a}$ = Apparent shear rate at wall (s^{-1})
η = Shear viscosity (Ns/m^2)

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NNING ELECTRON MICROSCOPY STUDIES ON TENSILE FAILURE OF THERMOASTIC ELASTOMERS FROM POLYPROPYLENE-NATURAL RUBBER BLENDS

BY KURIAKOSE, S.K. CHAKRABORTY and S.K. DE

bber Technology Centre, Indian Institute of Technology,
aragpur 721302, West Bengal (India)

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STRACT

The tensile properties of thermoplastic polypropylene [PP]-tural rubber [NR]blends have been evaluated with special referen- to the effect of blend ratios and dynamic cross-linking of the astomer phase. The effects of silica filler and silane coupling ent on the tensile properties of the 30:70 PP:NR blend have also en studied. Analysis of the stress-strain curves and scanning ectron microscopic examination of the tensile fracture surfaces the blends have been used to correlate the test results on nsile properties.

TRODUCTION

Thermoplastic elastomers are materials having the characteris-cs of thermoplastics at processing temperatures and those of astomers at service temperatures. This unique combination of the operties of vulcanized rubber and the easy processability of astics enabled thermoplastic elastomers to bridge the gap between nventional elastomers and thermoplastics. Among the different pes of thermoplastic elastomers, those prepared by physical blend-g of an elastomer and a thermoplastic material in an internal xer under high speed mixing, at temperatures above the melting int of the plastic, have certain definite advantages. In these pes of blends, the desired properties can easily be achieved by oper selection of the elastomer and plastic components and their tios in the blend.

During the period from 1960 to 1975, a large number of patents elastomer-thermoplastics blends, especially those on ethylene-

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propylene rubber [EPM] , ethylene-propylenediene rubber [EPDM] and polypropylene [PP] were issued [1-3]. Considerable improvement in properties of EPDM-PP thermoplastic blends, by partial cross-linking of the elastomer phase during blending ('dynamic cross-linking') was reported by Fisher [4]. Recent developments in thermoplastic elastomers have been reviewed by several authors [5-7]. Thermoplastic blends of EPDM and polyolefin dynamically cured during blending was reported by Fisher [8]. Campbell, Elliott and Wheelans [9]have described the method of preparation, injection moulding conditions and physical properties of a range of natural rubber NR - PP and NR - polyethylene [PE] thermoplastic blends. Elliott [10] has compared the properties of thermoplastic NR - PP and NR - HDPE blends with those of commercial thermoplastics like styrene-butadiene-styrene block copolymer, thermoplastic polyurethane etc., in applications such as automotive components. Recently Coran and co-workers [11-15] have studied EPDM - PP, nitrile rubber nylon and many other elastomer-thermoplastics compositions and attempted to correlate the physical properties of the blends with the fundamental characteristics of the elastomer and thermoplastics components of the blends. Ramos-De Valle and Ramirez [16] have reported the mechanical properties of guayule rubber - HDPE thermoplastic blends and the rheological behaviour of the blends was further studied by Ramos-De Valle [17]. O'Connor and Fath [18] have studied the technical properties of dynamically vulcanized thermoplastic elastomers in comparison with those of conventional vulcanizates of EPDM, polychloroprene and chlorosulphonated polyethylene. The use of fine particle silica at lower loadings has been reported to improve the physical properties and reduce the shrinkage of thermoplastic elastomer blends containing a higher proportion of elastomer phase [19, 20]. Silane coupling agents have been reported to enhance the physical properties of silica and china clay filled rubber compounds [21-29].

In this paper, we report the results of our studies on thermoplastic NR - PP blends with special reference to the effect of dynamic cross-linking of the elastomer phase on the tensile properties of the blends. The effects of blend ratios, silica filler and that of the silane coupling agent on the tensile properties have also been studied. Tensile fracture surfaces of the blends have been analysed by scanning electron microscopy [SEM]. SEM has been successfully used to study tensile fracture surfaces of rubber vulcanizates and rubber-fibre composites [30-33].

PERIMENTAL

Formulations of the mixes used are given in Table I. The blend tios are denoted by the letters A, B, C, D, E and F. Letters U d S denote the blends without any curative and that containing a lphur cure system, respectively. Blends containing silica and a lane coupling agent are denoted by Si and X respectively. Thus, end F S Si X denotes 70:30 NR:PP blend with a sulphur curing stem, containing silica and silane coupling agent .

ble I. Formulations of the Blends

end	A	B	C	D	E	F
lypropylene[a]	100	70	60	50	40	30
tural Rubber[b]	-	30	40	50	60	70
rative[c]	-	U,S	U,S	U,S	U,S	U,S
ller[d]	-	-	-	-	-	Si
upling Agent[e]	-	-	-	-	-	X

[a] Isotactic polypropylene, Koylene M0030, obtained from Indian Petrochemicals Corporation Limited, Vadodara, Gujarat.

[b] Crumb rubber, ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam, Kerala 686009.

[c] U, Blends without curative.

S, Blends containing zinc oxide 5.0, stearic acid 2.0, CBS 2.0, TMTD 2.50 and sulphur 0.30 phr., based on rubber phase only.

[d] Precipitated silica, vulcasil S, obtained from Modi Rubber Ltd., Modipuram - 20 phr loading based on rubber phase only.

[e] Bis [triethoxysilylpropyl] tetrasulphide, Si-69, obtained from Modi Rubber Ltd., Modipuram - 5% by weight of silica filler.

Blends of NR and PP were prepared in a Brabender Plasti-corder del PLE 330, using a cam-type mixer with a rotor speed of 80 rpm d the mixer chamber temperature set at 180°C. PP was melted in e mixer for 1 min and then NR was added and the mix was allowed blend for 4 min. At the end of 5 min, curatives were added as ster batches and the mixing continued for 3 more min. The mix s then taken out and sheeted through a laboratory mill at 2.0 mm p setting. The sheeted material was cut into small pieces and ain mixed in the Plasti-corder at 180°C for 1 min and then final- sheeted out in the mill. This second mixing step was found to be necessary to get uniform dispersion of the ingredients. In the case of silica filled blends, a master batch of the silica in NR was prepared first and this was added to PP and blended for 4 min. The sheeted out stock was compression moulded in an electrically heated hydraulic press at 200°C for 3 min. The mould used was provided with bolts and nuts so that the material inside could be held under pressure even after taking out the mould from the press. At the end of the moulding time, the sample, still under compression, was immediately cooled by plunging the mould into cold water.

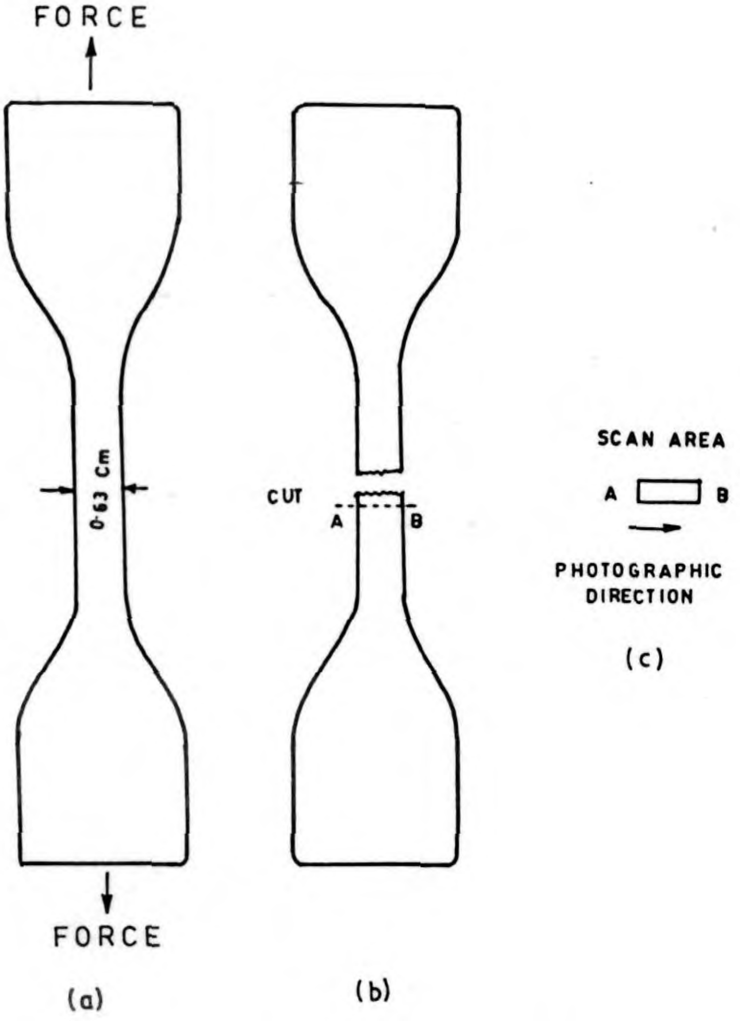


Fig. 1. Tensile test specimen and scan area for SEM observations.

uminium foils were used between the mould surfaces to reduce rink marks on the sheets. Tensile testing of the samples was ne at 25°C as per ASTM D 412-80 test method at a cross head speed 500 mm per min using an Instron Universal Testing Machine odel 1195 .

The SEM observations of the tensile rupture surfaces were made ing a Philips 500 model scanning electron microscope. The frac-re surfaces of the test samples were carefully cut out from one the failed test pieces without touching the surfaces and then utter coated with gold within 24 h of testing. Tensile rupture ecimens were stored in a desiccator before and after gold coat-g until the SEM observations were made, in order to avoid conta-nation. The tilt was kept at 0° and the orientation of the otographs was kept the same in all cases. Fig. 1a, 1b and 1c ow details of test specimen, scan area and photographic direct-n. Thermoplastic elastomer blends of NR and PP in the ratios :70, 50:50 and 70:30, respectively, were chosen for the SEM udy.

SULTS AND DISCUSSION

Table II gives the physical properties of the thermoplastic PP- blends. The Brabender mixing torque increases with an increase the proportion of the elastomer phase in the blend. Cross-link-g of the elastomer phase further increases the torque values and e effect is more prominent in blends containing a higher propor-on of the elastomer phase. Addition of silica does not increase e torque in uncross-linked blend, but in cross-linked blends the crease is quite remarkable. This indicates that processing of e blends becomes difficult and requires more energy as the rubber ntent increases.

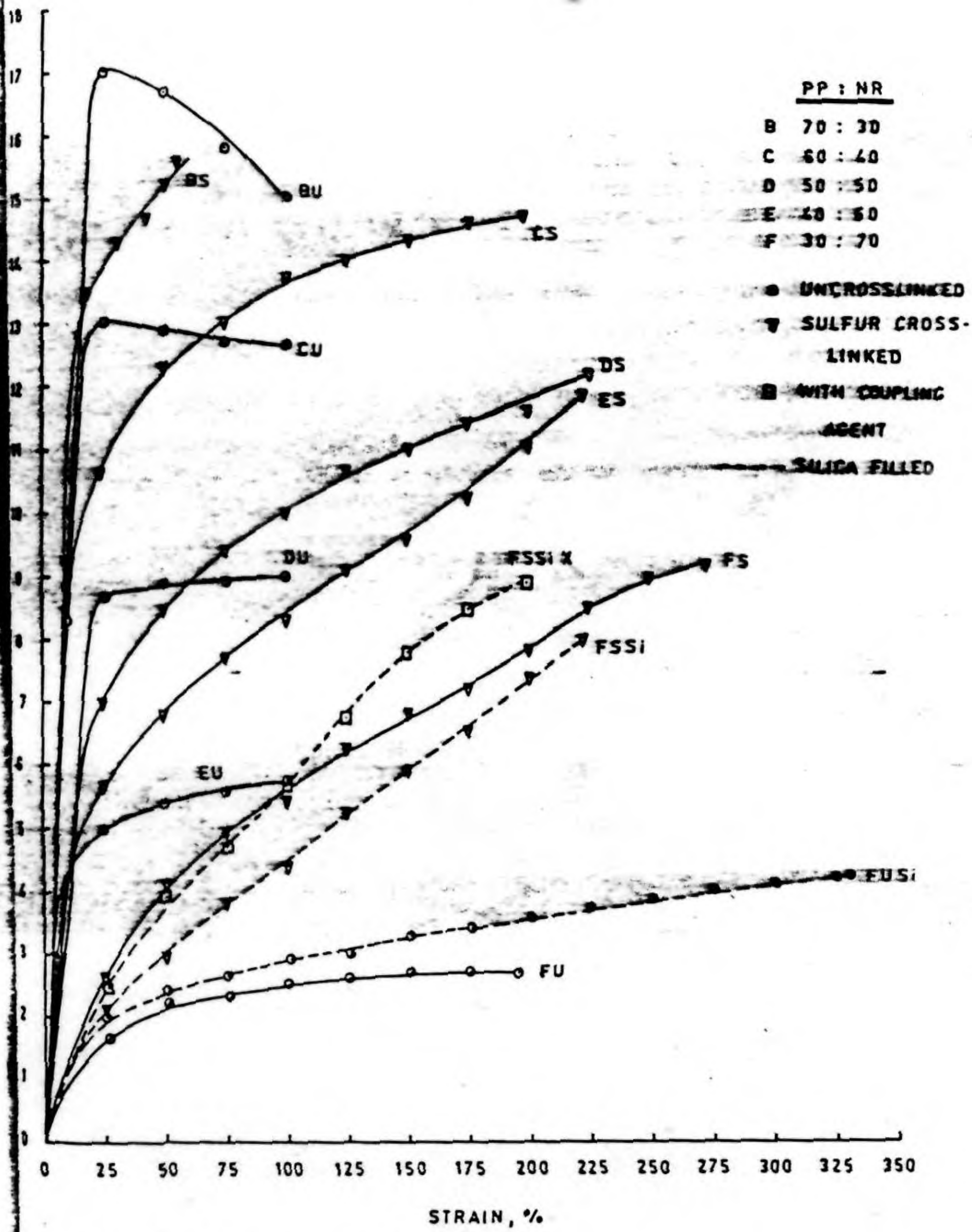
The tensile strength of the blends decreases and the elongation break increases with an increase in the rubber content of the ends, both in uncross-linked and cross-linked blends. In blends ntaining a higher proportion of PP, the elastomer phase remains dispersed particles. Smaller size and uniform dispersion of the spersed phase improve the tensile properties of the blends [11]. namic cross-linking of the elastomer phase during blending creases the viscosity of the blends, as seen from the increase Brabender mixing torque values [Table II]. At higher viscosity tter shearing action during blending leads to finer size and more uniform dispersion of the elastomer phase in the PP matrix [34]. Thus the increase in tensile strength with cross-linking of the elastomer phase of the blends containing a higher proportion of p is due to smaller particle size and more uniform dispersion of th rubber phase, compared with that in the uncross-linked blends. A the proportion of the rubber content is increased, the rubber pha also tends to form a continuous phase and both plastic and rubber phases exist as an interpenetrating two-phase system, looking lik a sea sponge structure, due to the higher proportion of the elast mer phase and the lower viscosity of the plastic phase [35]. As the cross-linking agent has its action only on the rubber phase [1: and since the elastomer phase tends to form a continuous phase, the tensile strength and elongation at break of the blends are increased with cross-linking of the elastomer phase and the effect becomes more prominent at a higher proportion of the elastomer phase in the blend.

Table II. Properties of the Blends

Sample number	Mixing torque after 8 min, Nm	Modulus 100%, MPa	Tensile strength, MPa	Elongation at break,%
A	5.5	—	23.7	5.0
BU	5.5	—	15.0	90.0
BS	8.0	—	15.4	55.0
CU	6.5	12.6	12.6	100.0
CS	12.0	13.4	14.3	190.0
DU	7.5	8.9	8.9	100.0
DS	14.0	10.2	12.3	230.0
EU	9.0	5.3	5.3	130.0
ES	21.0	8.0	12.1	220.0
FU	10.0	1.7	2.4	180.0
FUSi	9.5	3.1	4.4	275.0
FUSiX	9.5	2.3	3.2	300.0
FS	22.5	5.3	9.2	270.0
FSSi	32.0	4.2	8.0	220.0
FSSiX	32.0	5.5	8.9	200.0

Addition of silica filler improves the tensile properties of the uncross-linked 70:30 NR:PP blend and decreases those of the sulphur cured blend. A similar trend has also been reported in carbon black filled NR-PP/HDPE blends [9]. Addition of a silane coupling agent reduces the tensile strength of the uncross-linked silica filled blend, whereas that of the sulphur cured silica filled blend is increased. The decrease in tensile strength of the uncross-linked blend is due to a lack of reactivity of the

lane coupling agent with the filler and the matrix in the sence of a proper curing system [23]. In sulphur cured blends, emical interaction of the coupling agent with the filler and the trix results in better interfacial wetting and adhesion of the ller, and helps to improve the dispersion and to prevent refloc-
lation of the dispersed filler particles. This leads to an provement of the tensile strength of the cross-linked blend.



2. Stress-strain curves of NR-PP blends.

Stress-strain curves of the blends given in Fig. 2 show that the uncross-linked blends containing a higher proportion of the rubber phase undergo plastic type deformation, giving no further increase in stress after the initial increase, with an increase in strain. Blends containing a higher proportion of PP show plastic deformation with yielding. But cross-linking of the elastomer phase changes the nature of the stress-strain curves to that of rubber vulcanizates. At lower strains, the sulphur cured - silica filled blend shows lower modulus, but at higher strains the blend containing a silane coupling agent shows higher modulus values. Scanning electron microscopic observations of the failure surfaces of the blends further illustrate the deformation behaviour of these blends.

Fig. 3 shows the tensile fractograph of PP. The failure is of a brittle nature with multi-directional cracks. Addition of NR to PP changes the fracture mode from brittle to ductile type. Fig. 4, 5 and 6 show the tensile fractograph of the uncross-linked 70:30, 50:50 and 30:70 PP:NR blends, respectively. Fig. 4 shows fibrils on the surface, indicating high deformation before failure. As the rubber content in the blend is increased, the brittle nature is further reduced and the fracture surface of the 50:50 blend [Fig. 5] shows higher flow of the matrix. In the 30:70 PP:NR blend, the rubber phase also becomes continuous in nature and the fracture surface [Fig. 6] shows ductile failure with elongated dimple structure. Dynamic cross-linking of the elastomer phase in the 70:30 PP:NR blend gives smaller particle size and more uniform dispersio of the elastomer phase in PP. The smaller size and cross-linked

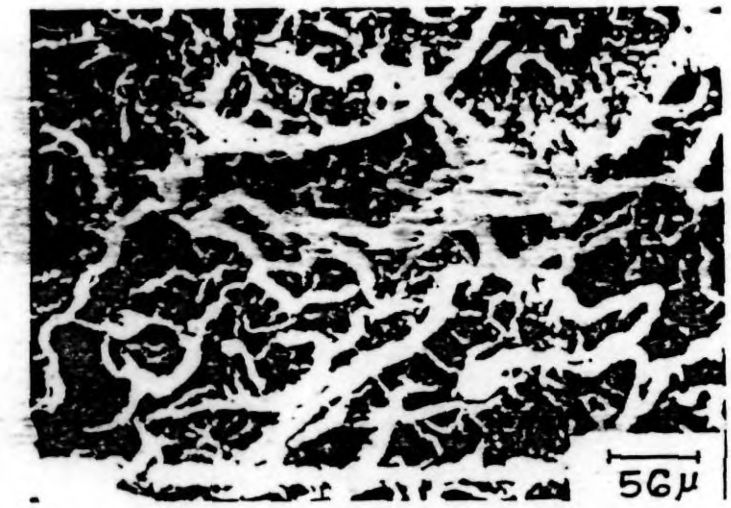
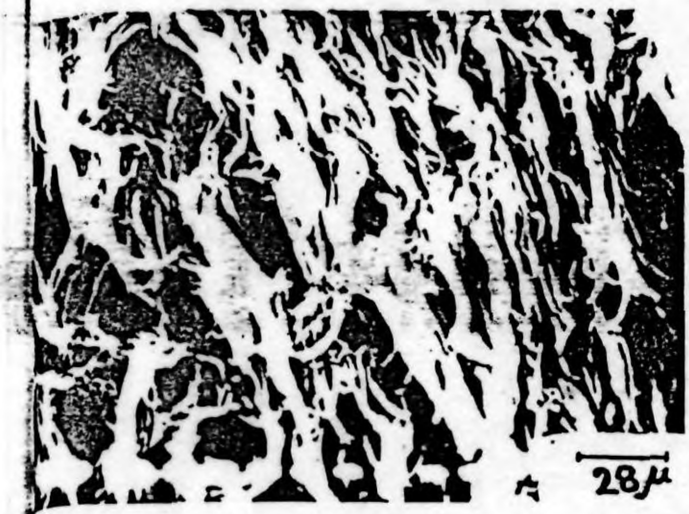
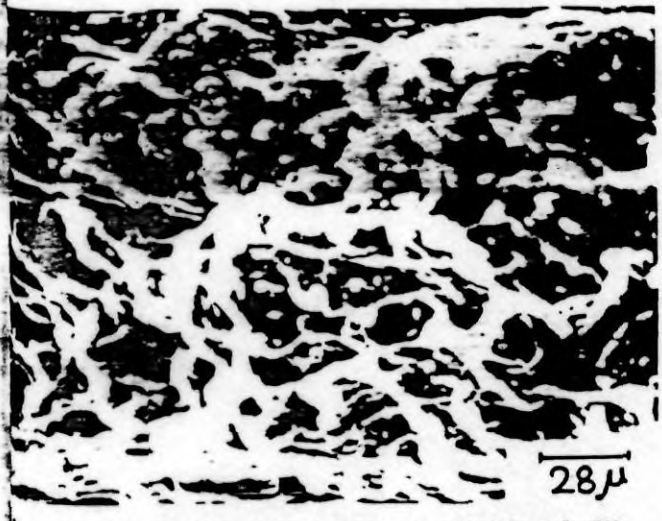


Fig. 3. Tensile fractograph of polypropylene.



ig. 4. Tensile fractograph of blend BU.

ig. 5. Tensile fractograph of blend DU.



ig. 6. Tensile fractograph of blend FU.

Fig. 7. Tensile fractograph of blend BS.

Fig. 8. Tensile fractograph of blend DS.

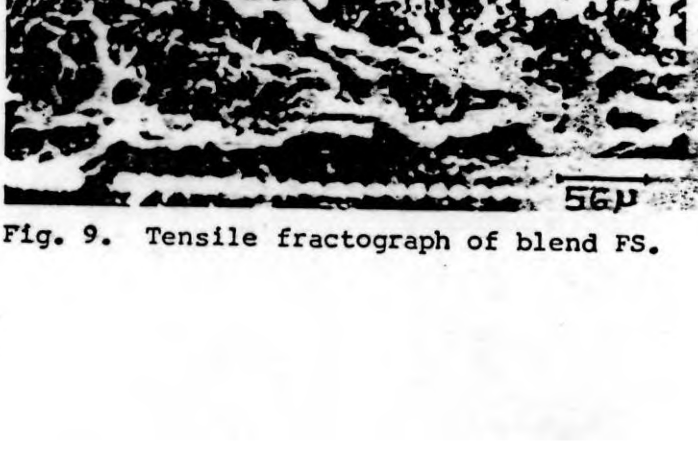
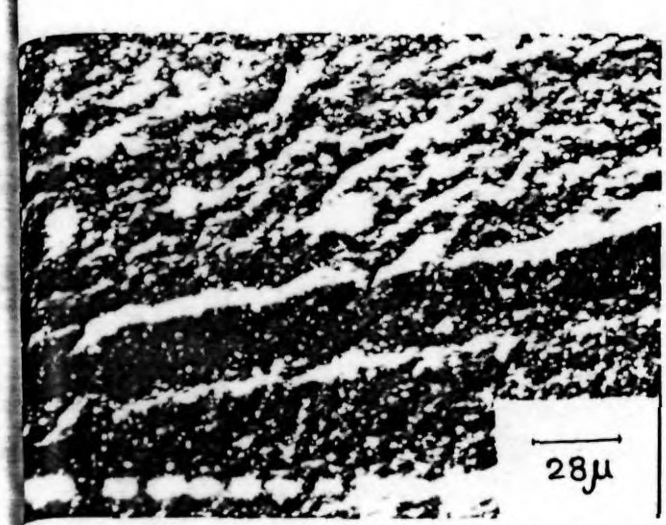
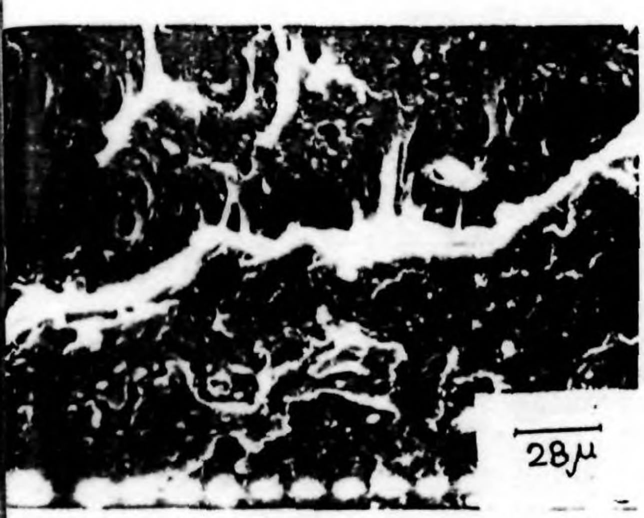


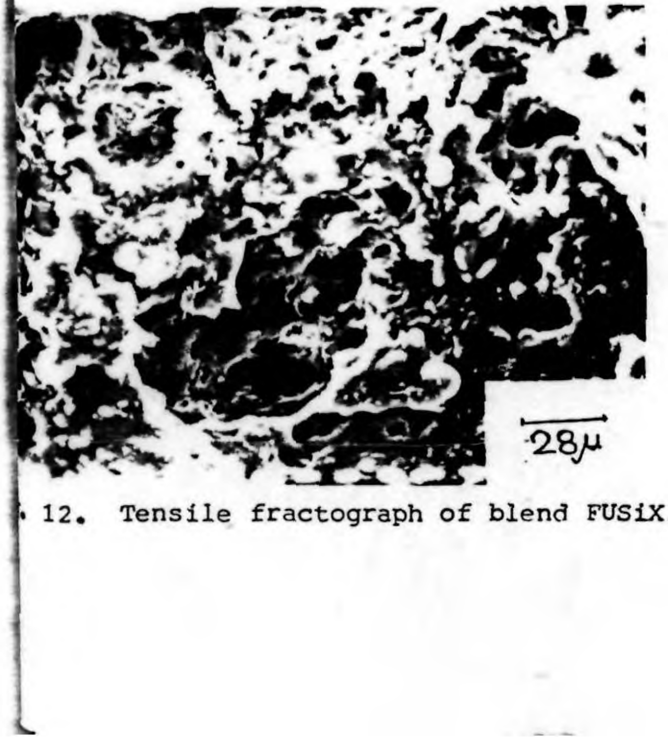
Fig. 9. Tensile fractograph of blend FS.



g. 10. Tensile fractograph of blend FUSi.



. 11. Tensile fractograph of blend FSSi.



. 12. Tensile fractograph of blend FUSiX.

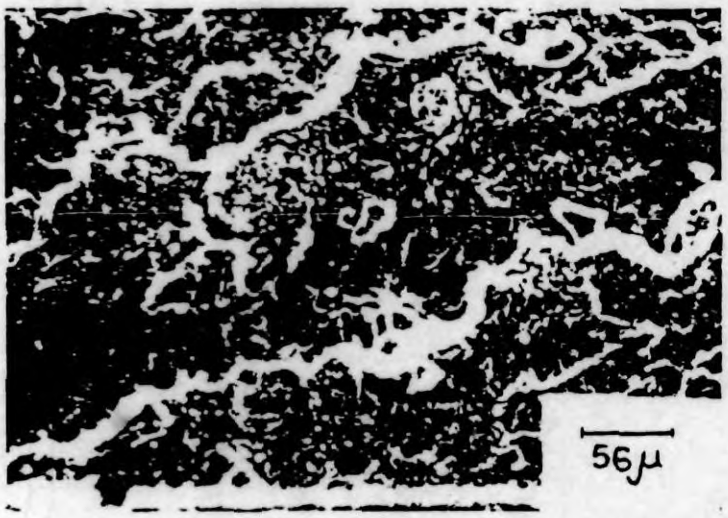


Fig. 13. Tensile fractograph of blend FSSiX.

nature make the dispersed particles more effective in craze initiation and in restricting matrix flow. This is evident from the fractograph [Fig. 7] of the cross-linked 70:30 PP:NR blend. The fracture surface of BS shows one main fracture line and many secondary fracture paths attached to it. In the case of the 50:50 blend [Fig. 8], no separate fracture path is visible and the fracture surface shows restricted flow of the matrix due to cross-linking of the elastomer phase. In the 30:70 PP:NR blend, the rubber phase becomes less deformable due to cross-linking. Since the rubber phase also forms a continuous phase, the fracture proceeds by shearing action. This is evident from the fracture surface of the blend [Fig. 9] which shows fracture paths in different planes. The fracture surface of the uncrosslinked-silica filled 30:70 PP:NR blend [Fig. 10] shows a smooth surface with dispersed silica particles. The flow of the rubber matrix in this case is restricted compared with that of the unfilled blend [Fig. 6] due to higher modulus of the silica filled blend. Due to cross-linking of the elastomer phase, in the case of blend F S Si, the fracture proceeds by shearing action, as evident from Fig. 11. Addition of a coupling agent improves the interfacial wetting and adhesion of the silica filler to the matrix. Since chemical interaction occurs only in the presence of a suitable cross-linking agent, the fracture surface of the uncross-linked-silica filled blend containing a silane coupling agent [Fig. 12] shows a rough surface due to the removal of the partially bonded silica particles along with the matrix, during the fracture process. In the silica filled blend containing a coupling agent and a sulphur curing system, chemical teraction of silica with the matrix through the coupling agent creases the modulus of the blend and the fracture proceeds by ing action. The strength properties and the fracture surface ig. 13]of this blend are comparable to those of the unfilled-lphur cured 30:70 PP:NR blend [Fig. 9].

NCLUSIONS

The tensile strength of the thermoplastic PP-NR blends decreases th an increase in the proportion of the elastomer, both in cross-linked and cross-linked blends. Dynamic cross-linking of e elastomer phase increases the tensile strength of the blends d this effect is more prominent in the blends containing a higher oportion of the elastomer phase. Addition of rubber changes the ittle fracture of the polypropylene to a ductile type and cross-nking of the elastomer phase changes the deformation behaviour the blends from plastic to elastic type. A silane coupling ent helps to keep up the tensile properties of the blends, where ne particle silica filler is used in blends containing a higher oportion of the elastomer phase.

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Scanning electron microscopy studies on tear failure of thermoplastic elastomers from polypropylene — natural rubber blends

BABY KURIAKOSE, S. K. DE
Rubber Technology Centre, Indian Institute of Technology, Kharagpur, West Bengal 721 302, India

Thermoplastic elastomers are becoming increasingly popular since they combine the processing advantages of thermoplastics and physical properties of elastomers. Reviews and research publications on the preparation, properties and applications of thermoplastics–elastomers blends have appeared recently [1–11]. The major area of application of this type of material is in footwear [12], where processes such as abrasion, flexing, and tear are the prominent factors, leading to failure of the product. The mechanism of tear fracture or rubber vulcanizates has been studied in detail by several research groups [13, 14]. The role of rubber particles in the mechanism of tear propagation in rubber modified thermoplastics and thermosets has also been reported [15–18]. Scanning electron microscopy (SEM) has been found to be a valuable tool in studying the fracture mechanism of rubber vulcanizates and rubber based composites [19–22]. In this paper, we have studied the effects of blend ratios and the influence of dynamic crosslinking of the elastomer phase on the tear strength of thermoplastic polypropylene (PP)–natural rubber (NR) blends. The nature of tear fracture of these blends has been studied by using SEM.

Thermoplastic PP–NR blends were prepared in a Brabender Plasticorder at 180° C and the blends were moulded in an electrically heated hydraulic press at 200° C to get sheets of 15.0 × 15.0 × 0.2 cm size. Detailed mixing and moulding procedures have already been reported [23]. The formulations of the mixes are given in Table I. From the moulded sheets, test samples (unnicked 90° angle test pieces) were punched out along the mill grain direction, for tear testing. The tear strengths of the samples were determined as per ASTM D 624-81 test method, at a crosshead speed of 500 mm min^{-1}, using an Instron Universal Testing Machine (model 1195). The tear strength values of the samples are given in Table II. The tear fracture surfaces were examined under SEM using a Philips 500 model scanning electron microscope. Fig. 1 shows the details of the test specimen and scan area of the fracture surface.

In rubber modified thermoplastics, the principal effect of the elastomer phase in the fracture process is to allow the energy to be dissipated into a relatively large volume of the material at the tip of the crack. This is more effectively accomplished by a smaller particle size and uniform dispersion of the elastomer phase in the plastic matrix. From Table II, it is seen that the tear strength of the thermoplastic PP–NR blends decreases, both in uncrosslinked and dynamically crosslinked blends, with an increase in the proportion of the elastomer phase. Dynamic crosslinking of the elastomer phase gives higher tear strength values compared

TABLE I Formulations of the mixes

	Mix					
	A	B	C	D	E	F
Polypropylene[a]	100	70	60	50	40	30
Natural rubber[b]	–	30	40	50	60	70
Curatives[c]	–	U, S	U, S	U, S	U, S	U, S

[a] Koylene M0030, obtained from Indian Petrochemicals Corporation Limited, Vadodara, Gujarat.
[b] Crumb rubber, ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam, Kerala.
[c] U, Blends without any curative. S, Blends containing zinc oxide 5.0; stearic acid 2.0; CBS 2.0; TMTD 2.5 and sulphur 0.30 phr, based on rubber phase only (sulphur cure system).

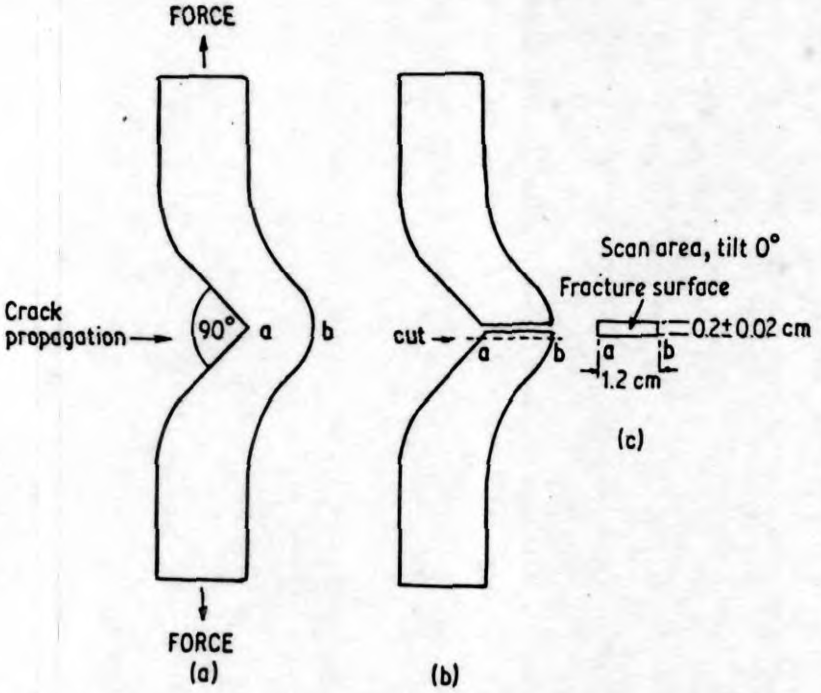

Figure 1 90° angle tear test specimen, fracture surface and scan area.

with those of the uncrosslinked blends and this effect is more prominent in blends containing a higher proportion of the elastomer phase. At higher proportions of PP in the blend, the rubber phase remains as dispersed particles. In uncrosslinked blends, the molecular entanglements in the rubber particles alone are unable to prevent rapid flow and fracture, in response to an applied stress. This results in the lower tear strength of the uncrosslinked blends. Crosslinking of the elastomer phase during blending increases the viscosity of the system. A better shearing action at higher viscosities results in a finer particle size and uniform dispersion of the elastomer phase [24]. During tearing, the rubber particles which bridge the growing crack, stretch to very large strains before failing. The tearing strain of a rubber particle increases as its size is reduced [18]. Crosslinking of the elastomer phase allows the rubber particles to reach higher strains and at the same time confers mechanical strength to the particles. Thus, the higher tear strength of the dynamically crosslinked blends compared with that of the uncrosslinked blends is due to a smaller particle size, higher elongation and mechanical strength of the dispersed particles. In blends having higher rubber content, both the polymers form continuous phases, due to the higher proportion of the elastomer phase and the lower viscosity of the plastic phase. As the rubber phase also tends to form a continuous phase, crosslinking of the elastomer phase increases the tear strength of the blends containing a higher proportion of the elastomer phase.

Scanning electron microscopic examination of the tear fracture surfaces of the blends supports the above views. Fig. 2 shows the tear fracture surface of PP. The presence of several parallel fracture bands in different planes reveals the brittle nature of the failure. Fig. 3 shows the fracture surface of the uncrosslinked 70:30 PP–NR blends. It indicates the initiation of the parabolic fracture pattern which is propagated concentrically as the tear advances. The fibrils on the surface along the direction of propagation of the crack indicate the high extent of deformation and the ductile nature of the failure. Increasing the rubber content in the blend increases the continuity of the rubber phase and the fracture surface of the 50:50 PP–NR blend (Fig. 4) and

TABLE II Tear strength of NR–PP thermoplastic blends (kN m^{-1})

	System					
	A	B	C	D	E	F
Uncrosslinked	126.0	100.5	78.2	54.9	36.1	22.1
Dynamically crosslinked	–	115.2	100.0	93.1	73.8	44.4

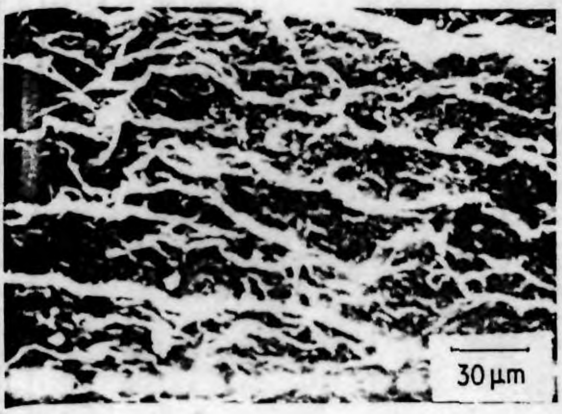

Figure 2 Tear fractograph of PP, brittle failure.

Figure 5 Tear fractograph of blend FU, smooth, continuous tear path and rough surface.

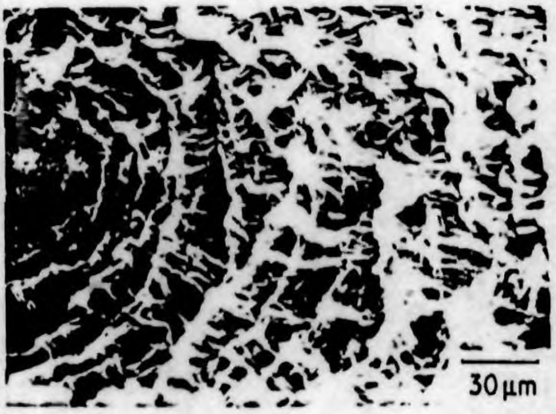

Figure 3 Tear fractograph of blend BU, parabolic crack initiation and fibrils.

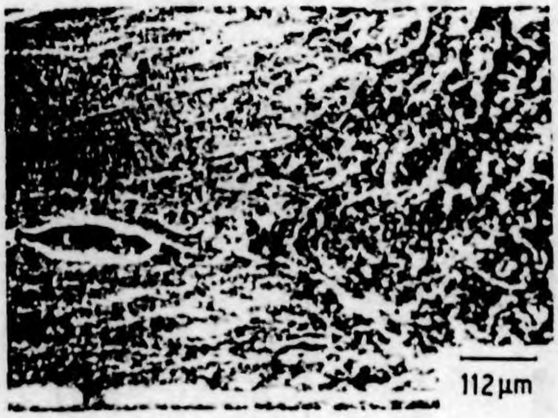

Figure 6 Tear fractograph of blend BS, short rounded tear lines.

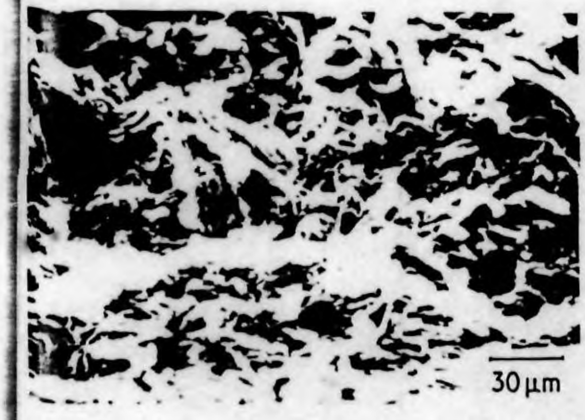

Figure 4 Tear fractograph of blend DU, smooth tear path and rough surface.

Figure 7 Tear fractograph of blend DS, broad continuous tear path.

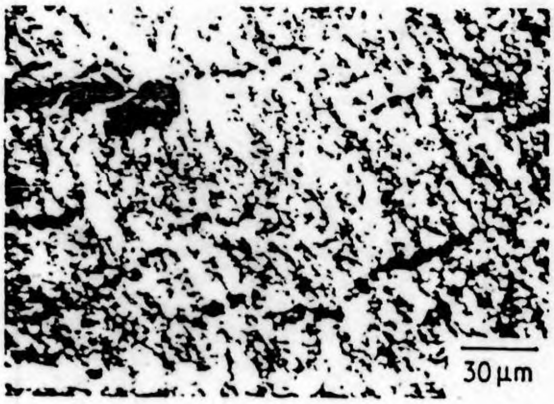

Figure 8 Tear fractograph of blend FS, smooth surface with cracks.

that of the 30:70 PP–NR blend (Fig. 5) both show a smooth tear path with a rough surface. Dynamic crosslinking of the elastomer phase in the 70:30 PP–NR blend reduces the particle size and improves the dispersion of the rubber phase. The resistance to high deformation of the crosslinked particles restricts the flow under stress, as shown by the presence of many short rounded tear lines on the fracture surface (Fig. 6). In the 50:50 PP–NR blend, crosslinking of the elastomer phase gives a broad tear path (Fig. 7) as the rubber phase also tends to form a continuous phase. In the 30:70 PP–NR blends, both the plastic and rubber phases exist as a continuous interpenetrating two-phase system [25] and dynamic crosslinking reduces the deformation of the rubber phase. Under the applied stress, a series of discontinuous cracks are formed (Fig. 8) on the surface due to less deformation of the rubber phase and the weak interaction between the two phases.

The present study shows that the tear strength of thermoplastic polypropylene–natural rubber blends decreases with increase in rubber content in the blend but dynamic crosslinking of the elastomer phase gives higher tear strength values as compared with those of the uncrosslinked blends. Scanning electron microscopic examination of the tear fracture surfaces indicates that brittle fracture of polypropylene is changed to a ductile type with the addition of natural rubber and crosslinking of the elastomer phase changes the high deformation nature of the blends (plastic type flow) to restricted flow (elastic type), under tear fracture.

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Tear and Wear Resistance of Silica Filled Thermoplastic Polypropylene—Natural Rubber Blend

BABY KURIAKOSE and **S. K. DE**

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, West Bengal, India

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The tear and wear resistance of silica filled thermoplastic polypropylene-natural rubber blend were found to increase with extent of dynamic crosslinking of the elastomer phase. Addition of silane coupling agent causes improvement in the failure properties of blends containing sulfur and sulfur-dicumyl peroxide (DCP) mixed vulcanizing systems and not in DCP containing blend. Scanning electron photomicrographs of the failure surfaces of the blends throw light on the mode of their failure.

INTRODUCTION

Thermoplastic elastomers combine the excellent processing characteristics of the thermoplastic materials at higher temperatures and a wide range of physical properties of elastomers at service temperatures.[1-3]. The blends prepared by melt mixing of a crystalline thermoplastic material and an elastomer under high shearing action, have gained considerable attention due to the simple method of preparation and easy attainment of the desired physical properties by varying the blend ratios.[4] It has been further shown that addition of small quantities of crosslinking agent during the mixing operation improves the final properties without affecting the processing behaviour.[5-9] This process is known as dynamic crosslinking. The physical properties of the blend depend on the extent of dynamic crosslinking and on the presence of reinforcing carbon black filler particularly when the blend consists of higher proportion of rubber phase than the plastic phase.[10,11]

One of the major applications of the thermoplastic elastomers is in footwear wherein the use of fine particle silica at lower loadings has been reported to improve the physical properties and reduce the shrinkage of the thermoplastic elastomer blends.[12-13] The use of silane coupling agents in enhancing the physical properties of the silica and clay filled rubber vulcanizates has also been reported.[14-22] In this paper we report the results of our studies on the effects of dynamic crosslinking of the elastomer phase and use of bis [triethoxysilylpropyl] tetrasulfide, abbreviated as Si-69, on the tear and abrasion resistance of silica filled 70:30 natural rubber [NR]:polypropylene [PP] thermoplastic elastomer blend. In order to correlate the observations on strength properties, the failure surfaces of the test samples have been analysed by scanning electron microscopy [SEM].

EXPERIMENTAL

Preparation of the blends

Formulations of the mixes used are given in Table I. The blends containing no filler, those containing silica and those containing silica and coupling agent are denoted by the letters *A*, *B* and *C* respectively. The suffixes *U*, *D*, *M* and *S* denote blends without curing agent and those containing dicumyl peroxide [DCP], mixed cure [DCP and sulfur] and sulfur cure systems respectively. Thus, the blend C_M denotes 70:30 NR:PP blend containing silica and coupling agent and having mixed cure system. Blends of NR and PP were prepared in a Brabender Plasti-corder model PLE 330, using a cam type mixer with a rotor speed of 80 rpm and mixer chamber temperature set at 180°C. PP was melted in the mixer for one minute and then NR was added and the mix was allowed to blend for four minutes. In the case of blends containing silica alone and that with coupling agent, master-batches of the ingredients in NR were prepared first and then the masterbatch was blended with PP. At the end of five minutes curatives were added and the mixing was continued for three more minutes. The mix was taken out and sheeted through a laboratory mill at 2.00 mm nip setting. The sheeted material was again mixed in the Plasti-corder at 180°C for one minute and then finally sheeted out in the mill so as to get uniform dispersion of the ingredients. In the case of mixed cure system, DCP was added after five minutes and allowed to blend for one minute. All the other ingredients were added after this step. The sheeted out stock was compression moulded at 200°C for three minutes in specially designed moulds so that the mould with the sample inside could be cooled immediately after the moulding time, keeping the sample still under compression.

TABLE I

Formulations of the blends

Ingredients	A	B	C
Natural Rubber[a]	70	70	70
Polypropylene[b]	30	30	30
Silica[c]	—	14	14
Coupling Agent[d]	—	—	0.70
Curatives[e]	*UDMS*	*UDMS*	*UDMS*

[a] Crumb rubber, ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam, Kerala.

[b] Isotactic polypropylene, Koylene M0030, obtained from Indian Petrochemicals Limited, Vadodara, Gujarat.

[c] Precipitated Silica, Vulcasil S, obtained from Modi Rubber Limited, Modipuram.

[d] Si-69, Bis (Triethoxysilylpropyl) tetrasulfide, obtained from Modi Rubber Limited, Modipuram.

[e] *U*, Blends without any curative. *D*, Blends containing 2.0 phr 40% dicumyl peroxide, based on rubber phase only (DCP cure). *M*, Blends containing 1.0 phr 40% dicumyl peroxide and zinc oxide 5.0; stearic acid 2.0; CBS 1.0; TMTD 1.25 and sulfur 0.15 phr based on rubber phase only (mixed cure). *S*, Blends containing zinc oxide 5.0; stearic acid 2.0; CBS 2.0; TMTD 2.5 and sulfur 0.30 phr based on rubber phase only (sulfur cure).

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Physical testing of the sample

Tear strength of the samples was determined as per ASTM D 624-81 test method, using unnicked 90° angle test pieces cut along the

TABLE II

Properties of the blends

Parameter	Uncrosslinked			D C P Cure			Mixed Cure			Sulfur Cure		
	A_U	B_U	C_U	A_D	B_D	C_D	A_M	B_M	C_M	A_S	B_S	C_S
Brabender mixing torque, Nm	10.0	9.5	9.5	16.0	19.0	17.5	18.5	18.0	21.5	22.5	32.0	32.0
V, of swollen blend*	—	—	—	0.1203 (0.0732)	0.1166	0.1415	0.2097 (0.1358)	0.1525	0.1874	0.2491 (0.1717)	0.2030	0.2242
Tear strength, kn/m	22.1	27.2	24.0	27.2	41.4	42.4	38.0	42.2	60.6	44.4	48.8	66.0
Abrasion loss, cc/h	2.263	1.806	2.113	1.823	1.531	1.805	1.602	1.510	1.465	1.410	1.375	1.233

* Values in brackets correspond to 100% NR gum vulcanizates

mill grain direction, at a crosshead speed of 500 mm per minute in Instron Universal Testing Machine [model 1195]. The abrasion test was carried out using Du Pont abrader on samples of dimension 2 cm square 1 cm thick. The test results obtained are given in Table II. Figure 1 shows the force-tear charts of the silica filled blends with and without coupling agent tested at a crosshead speed of 500 mm per minute and chart speed of 50 mm per minute.

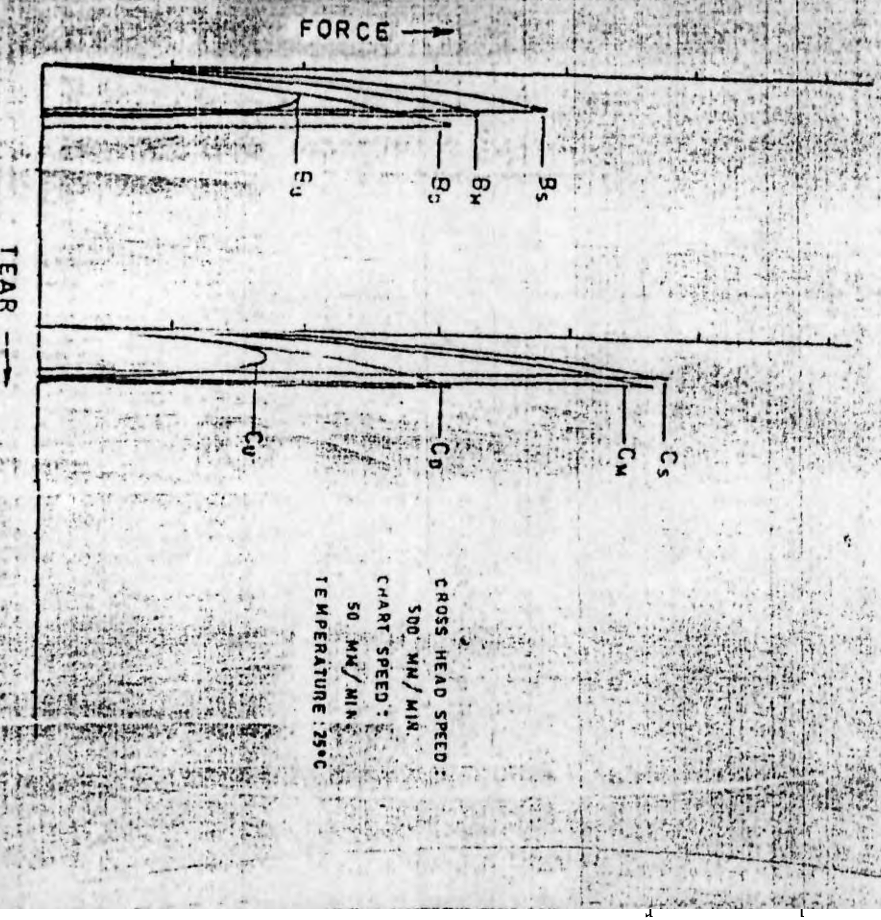

FIGURE 1 Force-tear curves for silica filled blends with and without coupling agent.

Scanning electron microscopic studies

The SEM observations of the failure surfaces in tear and abrasion tests were made using Philips 500 model scanning electron microscope. The fracture surfaces of the test samples were carefully cut out from one of the failed test pieces without touching the surfaces and then sputter coated with gold within 24 hours of testing. The specimens were stored in a desiccator before and after gold coating until the SEM observations were made. Figure 2 shows the details of the test specimen and scan area of the failed surfaces.

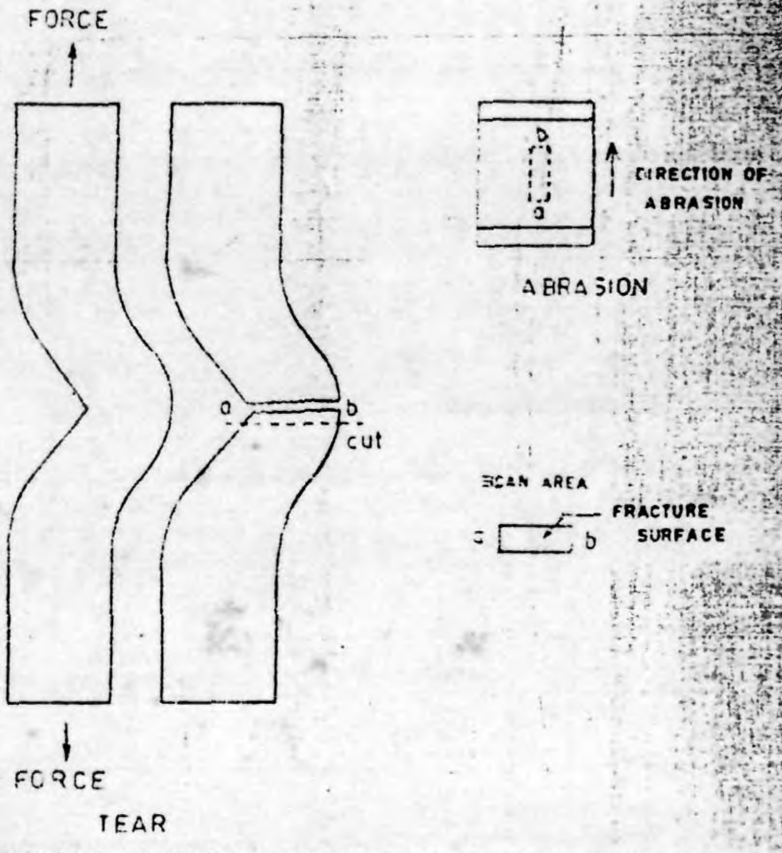

FIGURE 2 Samples for tear and abrasion tests, showing the fracture surface and scan area.

RESULTS AND DISCUSSIONS

The physical properties of the thermoplastic elastomer blends depend mainly on factors like continuity of the phase, size of the dispersed particles and extent of dynamic cross-linking of the elastomer phase. At 70:30 NR:PP ratio, both NR and PP form continuous phases leading to an inter-penetrating two-phase system, looking like a sea sponge structure, due to higher proportion of the rubber phase and lower viscosity of the plastic phase.[23] The extent of crosslinking of the elastomer phase in the blends of present investigation was in the order, sulfur cure > mixed > DCP cure, as measured by V_r values [volume fraction of rubber in the solvent swollen sample] of the natural rubber vulcanizates containing the same level of curatives and extent of curing as that in the blend. The V_r values were 0.0732, 0.1358 and 0.1717 respectively for DCP, mixed and sulfur cured rubber vulcanizates and the corresponding values for the blends were 0.1203, 0.2097 and 0.2490 respectively for A_D, A_M and A_S. The higher V_r value of the blends compared with those of the rubber vulcanizates is due to the restriction imposed by the crystalline PP for swelling. The blends containing silica filler show lower V_r values compared with those of the corresponding unfilled blends [Table II—$B_D < A_D$, $B_M < A_M$, $B_S < A_S$] due to the retarding effect of silica filler on rate of vulcanization of the rubber phase. The silica filled blends containing silane coupling agent show higher V_r values compared with those of the corresponding silica filled blends without coupling agent [$C_D > B_D$, $C_M > B_M$, $C_S > B_S$]. This is due to the interaction of the coupling agent with the reactive groups on the silica filler and thereby reducing the retardation effect of the silica on the vulcanization rate. Similar observations had been reported earlier for silica filled EPDM and NR vulcanizates.[22,28,29] Among the different dynamically crosslinked blends containing silica filler, B_M and C_M which contain mixed cure system have lower Brabender mixing torque values. This shows better processing characteristics of the blends containing mixed cure system.

Tear strength

The tear strength values of the 70:30 NR:PP blends given in Table II show that dynamic crosslinking of the elastomer phase improves the tear strength of the blends remarkably, and that the increase is *proportional to the extent of crosslinking.* Tear strength is in the order $A_U > A_D > A_M > A_S$. Dynamic crosslinking of the elastomer phase increases the viscosity of the system as seen from the increase in Brabender mixing torque values [Table II]. At higher viscosity, better shearing action during blending leads to finer particle size and more uniform dispersion of the rubber phase in the PP matrix.[24] During tearing, the rubber particles which bridge the growing crack stretch to very large strains before failing. The tearing strain of a rubber particle increases as its size is reduced.[25] Thus the increase in tear strength with extent of crosslinking of the elastomer phase is due to smaller size and higher elongation of the crosslinked particles.

Addition of silica filler improves the tear strength of the blends and the effect is more prominent in uncrosslinked and DCP cured blends. Addition of silane coupling agent further enhances the tear strength of the blends containing mixed and sulfur curing systems. Figure 1 shows that addition of silane coupling agent adversely affects the tear energy of the uncrosslinked blend and does not affect the DCP cured blend but increases the tear energy of the blends dynamically crosslinked by sulfur and sulfur plus DCP. The role of interfacial wetting and adhesion of the filler to the rubber phase through the coupling agent in improving the tear strength is evident from the fact that the increase in tear strength of the DCP cured blend containing coupling agent is negligibly small due to lack of reactivity of the coupling agent in this cure system.[16] The blend without curing agent also shows no improvement in tear strength with the addition of Si-69.

The SEM observations of the tear fracture surfaces of the blends support these views. The tear fractograph of the uncrosslinked blend

FIGURE 3 Tear fractograph of blend C_U—ductile failure, rough surface, with dimples and pores.

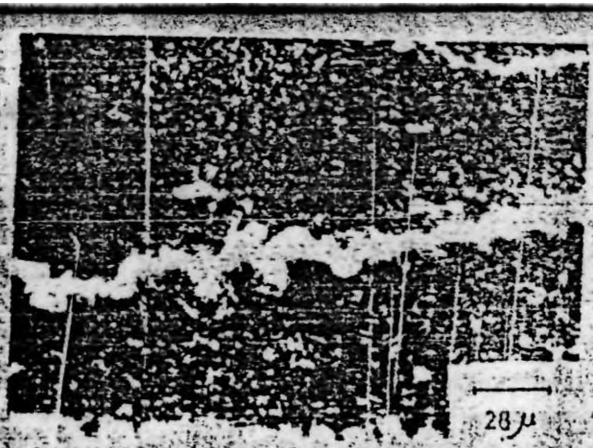

FIGURE 4. Tear fractograph of blend C_D—smooth surface and fracture path.

FIGURE 5. Tear fractograph of blend C_M—smooth surface and stretching of the matrix towards the fracture path.

FIGURE 6 Tear fractograph of blend C_S—stretching of the matrix and subsidiary tear paths

[C_U] shows rough surface and ductile failure with dimples and pores [Figure 3]. Dynamic crosslinking of the elastomer phase with DCP [blend C_D] reduced the deformation of the elastomer phase giving smooth fracture surface with fracture path [Figure 4]. The fracture surface of the blend C_M is similar to C_D but stretching of the matrix along the fracture path is visible due to better rubber-filler interaction [Figure 5]. The fracture surface of the sulfur cured blend containing silica and coupling agent [blend C_S] shows similar characteristics with subsidiary fracture paths. The stretching of the rubber phase along the fracture paths can also be observed in this case [Figure 6].

Abrasion resistance

The abrasion resistance of the unfilled blends increases with increase in extent of dynamic crosslinking of the elastomer phase [$A_S > A_M > A_D > A_U$]. Silica filler improves the abrasion resistance of the NR-PP blends and the effect is more prominent in uncrosslinked and DCP cured blends [$B_U > A_U, B_D > A_D, B_M > A_M, B_S > A_S$]. Addition of silane coupling agent improves the abrasion resistance of the blends containing sulfur and sulfur-DCP mixed curing systems [$C_S > B_S$ and $C_M > B_M$]. In the uncrosslinked and DCP cured blends [C_U and C_D] silane coupling agent adversely affects the abrasion resistance. These observations are similar to the trend in tear strength of these blends and may be explained in the following way. During abrasion, small particles are formed on the surface by microtearing of the matrix. The number and size of such particles and their removal from the matrix depend mainly on the tear

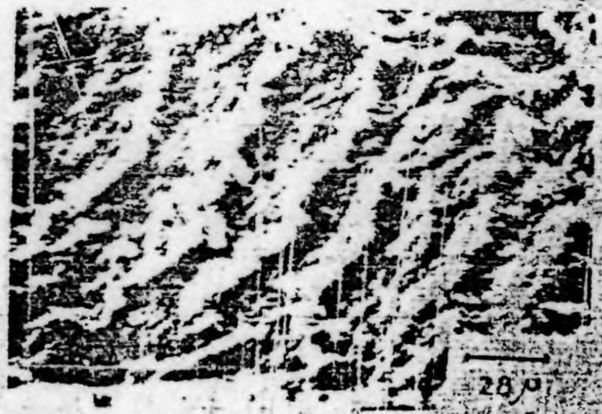

FIGURE 7 Abraded surface of blend C_D—thick and widely spaced ridges perpendicular to the direction of abrasion

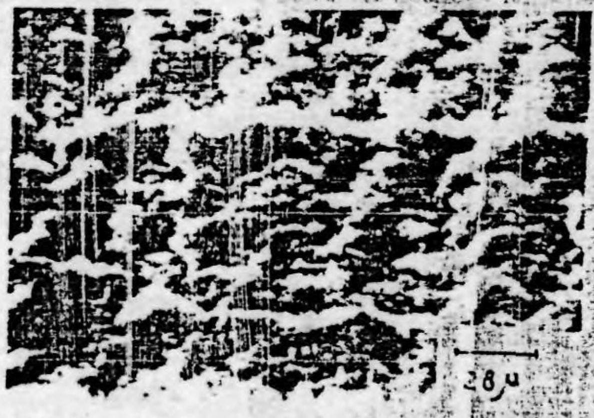

FIGURE 8. Abraded surface of blend C_M—small ridges interconnected by elongated rubber matrix.

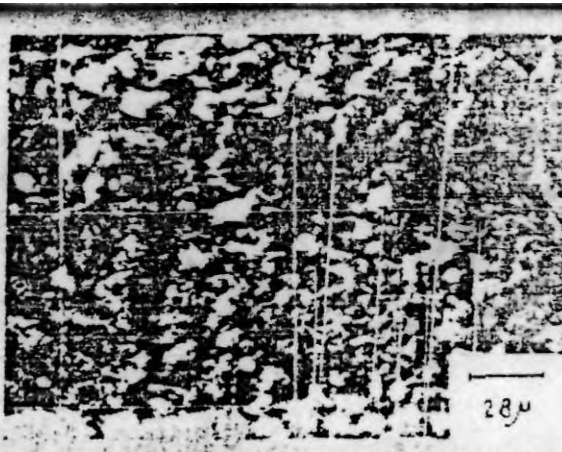

FIGURE 9. Abraded surface of blend C_S—without ridges

strength of the matrix, apart from other factors like frictional force.[26] These particles coalesce to form ridges on the surface, aligned at right angle to the direction of abrasion.[27] Finer particles form finer ridges and the height and spacing of the ridges increase with the intensity of wear. The SEM photomicrograph of the abraded surface of the blend C_D shows thick and widely spaced ridges [Figure 7] revealing the poor resistance to abrasion of the blend containing DCP cure system. In the case of blend C_M the abraded surface shows small ridges interconnected by elongated rubber matrix [Figure 8]. The abraded surface of the blend C_S shows no tendency towards ridge formation [Figure 9]. The abrasion resistance of the blends increase in the order, blend $C_S > C_M > C_D$. It can also be seen that the tear strength of these blends follow similar trend [Table II].

CONCLUSIONS

The tear strength of the 70:30 natural rubber:polypropylene thermoplastic blend is increased by dynamic crosslinking of the elastomer phase and the increase is proportional to the extent of crosslinking. Addition of silica filler improves the tear strength of the blends and addition of bis[triethoxysilylpropyl] tetrasulfide, Si-69, further enhances the tear strength of the silica filled blends. Effect of silica filler is prominent in uncrosslinked and DCP-crosslinked systems. Effect of coupling agent is prominent in blends with sulfur and sulfur-DCP mixed vulcanizing systems. The abrasion resistance of different blends follow similar trend as the tear resistance.

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udies on the Rheological Behaviour of Four Thermoplastic astomers

B. Kuriakose, Kharagpur, West Bengal (India)

ntroduction

rmoplastic elastomers (TPEs), as the name indicates, w the characteristics of thermoplastics and those of anized elastomers depending on temperature. These erials may be block copolymers consisting of a hard moplastic segment and a soft rubbery segment or ds of a crystalline polyolefin and an elastomer or may uch polymers which have specific stereo-regular struc- and controlled extent of crystallinity [1, 2]. Elastomers ch contain thermolabile crosslinks are also classified PEs. One of the important advantages of TPEs is that can be processed like thermoplastic materials, at tem- atures above the crystalline melting point or glass sition temperature of the thermoplastic component of system, by extrusion or injection molding techniques. importance of rheological studies in predicting the behaviour of polymer systems at high temperature and ar conditions of extrusion and injection molding pro- ses has been described by several authors [3 – 5]. The uence of filler and rubber particles on the processing racteristics of thermoplastics melts has been studied etail [6 – 8]. Due to the growing importance of TPEs, the ological characteristics of thermoplastic block copoly- s and those of thermoplastics elastomer blends have been studied extensively [9 – 14]. *Kraus* and co-work- [15] have reported the influence of molecular weight length of the block sequences on the rheological char- eristics of random and block copolymers of butadiene styrene and showed that as the length of the block uences became sufficiently large, the blocks seg- ated to form a two-phase system and that some of the ociations of the polystyrene segments persisted even at peratures well above the glass transition temperature olystyrene. This multiphase morphology of the block olymers at various temperatures has been reported to the reason for the high sensitivity to shear conditions of k copolymers of styrene and butadiene [16]. *Arnold and ier* [17] showed that the dynamic viscosities of styrene- adiene-styrene [S-B-S] block copolymers continuously eased with decreasing deformation rate. It was ex- ined that this behaviour is due to the interplay of pro- ses tending to disrupt and reform the network and do- n systems in the block copolymer, under different ex- ts of deformation. *Chung and Gale* [18] have reported the changes in viscoelastic properties of S-B-S block olymer with temperature is due to a phase transition re- ing in a homogeneous morphology at higher tempera- s and extent of deformations. *Gouinlock and Porter* [19] erved that the non-Newtonian characteristics of S-B-S k copolymer at low temperatures change to Newtonian onses at about 142 °C. Above 142 °C, the polystyrene ks, existing in dispersed domains at lower tempera- s, were shown to exceed a critical degree of compatibil- with the continuous polybutadiene phase. A similar sition was reported by *Pico and Williams* [20] in plas- zed S-B-S block copolymer and attributed this transition an accompanying morphological transition. This was her confirmed by a detailed study by *Chung and Lim* . In this paper we report our observations on the effect of shear rate and temperature on shear viscosity, die swell and extrudate deformation of four commercially available TPEs namely, polyurethane, 1,2-polybutadiene, styrene-butadiene-styrene, and styrene-isoprene-styrene block copolymers.

2 Experimental

2.1 Rheological Measurements

Details of the commercial TPEs used in the present study are given in *Table 1*. The rheological measurements were carried out using a capillary rheometer MCR 3210 attached to an Instron Universal Testing Machine model 1195. A capillary of length to diameter ratio [l_c/d_c] 40, with an angle of entry of 90° was used for this study so as to minimize the capillary end effects. The test temperature was controlled within ± 0,5 °C using a thermocouple attached to a three action current adjusting type control unit. The test samples were placed inside the barrel of the extrusion assembly and forced down to the capillary with the plunger attached to the moving crosshead. After a warming up period of 3 min, the melt was extruded through the capillary at pre-selected speeds of the crosshead which varied from 0,5 – 200,0 mm/min. The melt height in the barrel before extrusion was kept the same in all the experiments and the machine was operated to give five different plunger speeds from lower to higher speed, with a single charge of the material. Force corresponding to different plunger speeds was recorded using a strip chart recorder assembly. The force and crosshead speed were converted into shear stress τ_w and shear rate $\dot{\gamma}_w$ at wall respectively, using the following equations involving the geometry of the capillary and the plunger –

$$\tau_w = \frac{F}{4 \cdot A_P} \cdot \frac{d_c}{l_c}$$

$$\dot{\gamma}_w = \frac{(3\,n' + 1)}{4\,n'} \cdot \frac{32\,Q}{\pi\, d_c^3}$$

where F is the force applied at a particular shear rate. A_P is the cross-sectional area of the plunger, l_c the length of the capillary and d_c the diameter of the capillary. Q the volume

Table 1. **Details of the TPEs used**

Code number	Chemical name	Description
PB	1,2-polybutadiene	Thermoplastic 1,2-polybutadiene elastomer having 1,2-content >90 % and degree of crystallinity 25 %. JSR RB 820, manufactured by Japanese Synthetic Rubber Company, Japan
K5	Styrene-butadiene-styrene block copolymer	S-B-S block copolymer having styrene/butadiene ratio 48/52 and containing about 10 % by wt. amorphous silica. KRATON D5152, manufactured by Shell Chemical Company, USA
K1	Styrene-isoprene-styrene block copolymer	S-I-S block copolymer having styrene/isoprene ratio 14/86. KRATON D1107, manufactured by Shell Chemical Company, USA
PU	Thermoplastic polyurethane elastomer	Aromatic ester type thermoplastic polyurethane elastomer. ESTANE 5715, manufactured by B.F. Goodrich Company, USA

flow rate, was calculated from the velocity of the crosshead and diameter of the plunger. n′ is the flow behaviour index defined by $n' = d \log \tau_w / d \log \dot{\gamma}_{w.a}$ and was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{w.a}$ obtained from the experimental data. $\dot{\gamma}_{w.a}$ is the apparent wall shear rate calculated as $32\,Q/\pi\, d^3_c$. The shear viscosity η was calculated from τ_w and $\dot{\gamma}_w$.

2.2 Swell measurements

The extrudate emerging out from the capillary was collected, taking maximum care to avoid any further deformation. The diameter of the extrudate was measured at several points using an Olympus stereo-binocular microscope, model VB 454, after a relaxation period of 24 h. The average value of five readings was taken as the diameter d_e of the extrudate. The swelling index was calculated as the ratio of the diameter of the extrudate to that of the capillary d_e/d_c.

3 Results and discussions

3.1 Effect of shear rate on viscosity

The viscosity-shear rate plots of the samples at 180 °C are given in *Figure 1*. Between the two styrenic block copolymers K1 and K5, the sample K1 showed a higher viscosity at all shear rates since it contained a lower proportion of polystyrene segments (Table 1). The viscosity of both the samples decreased with increase in shear rate, indicating pseudoplastic behaviour. The decrease in viscosity of these samples was faster above a shear rate of $10^2\ s^{-1}$. In the case of sample K5, a sharp increase in viscosity was observed in the shear rate region of $10^1\ s^{-1}$. It has been reported earlier that polymer melts containing fine particle silica and carbon black show yield stress, which increased with decreasing particle size of the filler [6, 7]. Similar observations have been reported for acrylonitrile-butadiene-styrene and acrylonitrile-butadiene-acrylic ester copolymers containing dispersed rubber particles [8]. The occurrence of yield stress in these cases was attributed to the presence of "structure build-up" or gel formation due to the inter-particle forces existing among the dispersed particles. The sample K5 contained about 10 % by weight of fine particle silica filler. Thus, the sharp increase in viscosity of the sample K5 below a shear rate of $10^1\ s^{-1}$ is due to the structure build-up by the silica particles. This gel structure has to be broken before the system can flow. T viscosity of the samples PB and PU showed gradual crease with increase in shear rate. At lower shear rates P showed higher viscosity but at higher shear rates, viscosity of PU was higher than that of PB. This indicat that the viscosity of PU is less sensitive to shear than th of PB and that PU shows more Newtonian flow charact istics at lower shear rates than PB.

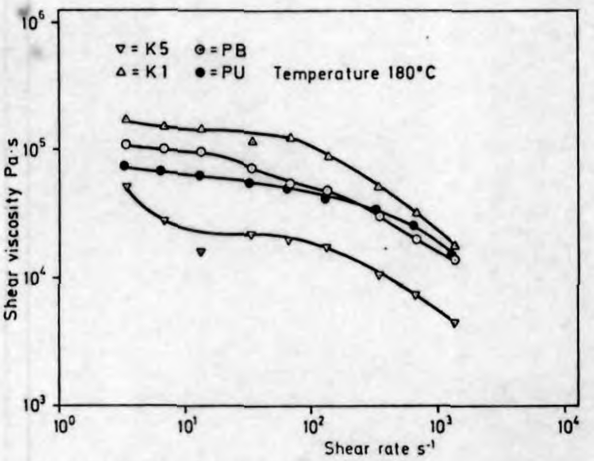

Figure 1. Viscosity-shear rate plots at 180 °C

3.2 Effect of temperature and shear rate on viscosity

The combined effects of temperature and shear rate on t viscosity of the TPE samples are shown in *Figure 2*. T viscosity of the styrenic block copolymers (K1 and K5) d creased with increase in temperature and shear rate. higher shear rates the viscosity of the sample K5 showed sharp decrease, in the temperature range 190 – 200 °C. F both these samples, the change in viscosity with increas in temperature was negligibly small, beyond 200 °C. T multiphase morphology of block copolymers at tempe tures above the crystalline melting point or glass transiti temperature of the thermoplastic segment has been ported by several authors [15, 17, 18]. Gouinlock and Por [19] have shown that in S-B-S block copolymer melts, t polystyrene blocks existing in dispersed domains at low temperatures, exceed a critical degree of compatibil with the continuous polybutadiene phase, at a temperatu

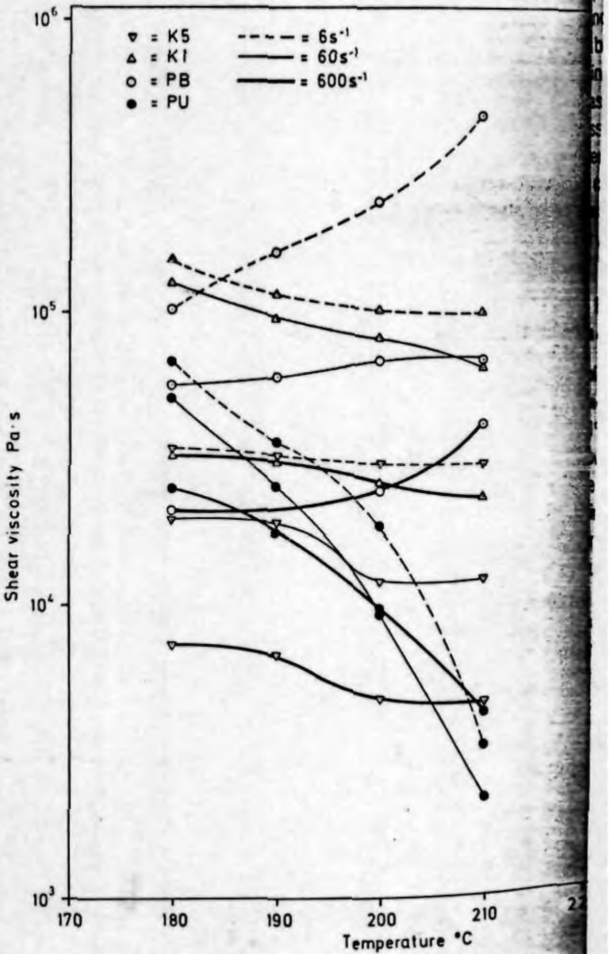

Figure 2. Viscosity-temperature plots at shear rates of 6,60
600 s^{-1}

142 °C. With increasing temperature, a continuous in- ase in miscibility would be expected, resulting in a com- te disappearance of the polystyrene phase first, fol- ed by the polybutadiene phase both forming a com- tely homogeneous melt. The nature of the viscosity-tem- ature plots of the samples K1 and K5 at three different ar rates indicated that complete miscibility of the two ments of these copolymers may be occurring at a tem- ature of about 200 °C. The viscosity of the PU sample re- ed drastically with increase in temperature. PU showed s sensitivity to shear rates at 210 °C compared with er TPE samples. This indicated that PU shows more tonian characteristics at higher temperatures. The behaviour index values n′ given in *Table 2* further con- ed this concept. The n′ values increased with increase emperature and reached unity at about 210 °C.

e 2. **Flow behaviour index and die swell values of TPEs**

e ber	Flow behaviour index n′ at temperature in °C				Die swell d_e/d_c at 180 °C for shear rates in s^{-1}		
	180	190	200	210	30	300	3000
	0,6785	0,6300	0,5783	0,5599	1,010	1,047	1,139
	0,6484	0,7265	0,7011	0,6832	0,962	1,304	1,371
	0,6586	0,5304	0,4585	0,4272	1,821	1,863	1,805
	0,7653	0,8371	0,8434	1,0090	0,947	1,018	1,227

viscosity of the PB sample increased with increase in perature and this effect was found to be more pro- nced at lower shear rate than at higher shear rates. It been reported that 1,2-polybutadiene undergoes cross- ing reactions at higher temperatures [22]. Thus, the in- se in viscosity of the PB sample is due to the effect of sslinking of the polymer at higher temperatures. At er shear rates, the polymer gets more residence time in capillary to undergo crosslinking reaction. Hence the ct of temperature in increasing the viscosity of the poly- was more pronounced at lower shear rates.

Flow behaviour index, die swell and extrudate deforma- n characteristics

le 2 shows the effect of temperature on the flow be- iour index and that of shear rate on the die swell, at °C, of the TPEs. The S-B-S block copolymer (sample K5) wed a regular decrease in n′ with increasing tempera- e whereas the S-I-S block copolymer (sample K1) showed initial increase in n′ at 190 °C, which decreased with fur- increase in temperature. A similar trend of decreasing ues of n′ with increase in temperature has been reported olefin based thermoplastic vulcanizates [13]. The de- ase in n′ values of the thermoplastic 1,2-polybutadiene nple is due to crosslinking of the polymer, the extent of ich increases with increase in temperature. PU showed ease in n′ values with increase in temperature and at °C, the value of n′ was almost equal to unity. This in- ated that PU tends to show Newtonian characteristics about 210 °C. This behaviour may be due to the mor- logical transition from a multiphase structure to a gle phase system, as reported in the case of a S-B-S ck copolymer by Chung and Gale [18].

all the TPEs included in this study, the extrudate swell eased with increase in shear rate, except for PB which wed less die swell at a shear rate of 3000 s^{-1}. This un- ual behaviour of PB is due to lower extent of crosslinking of the sample at higher shear rate, as explained earlier. The higher die swell values of PB compared with that of other TPEs is due to a higher extent of elastic response attained by this polymer due to crosslinking of the chains at higher temperature. At lower shear rate, PU and K1 samples showed die swell indices less than unity. This may be due to drawing out of the extrudate due to gravity, at this very low rate of shear. Sample K1 which contained higher proportion of the elastomer phase showed higher swell values at higher shear rates compared to sample K5.

The deformation of the extrudates shown in *Figure 3* indicated that there is little deformation for the extrudates of sample K5 and PU. Sample K1 which contained higher proportion of elastomer segments showed high deformation with increase in rate of shear. The lower deformation characteristic shown by sample K5 at all shear rates is due to the combined effects of a higher proportion of polystyrene content and the presence of fine particle silica filler which reduced the die swell. Thermoplastic 1,2-polybutadiene showed higher distortion at lower shear rates due to higher elastic response of the sample resulting from a higher extent of crosslinking at lower shear rates.

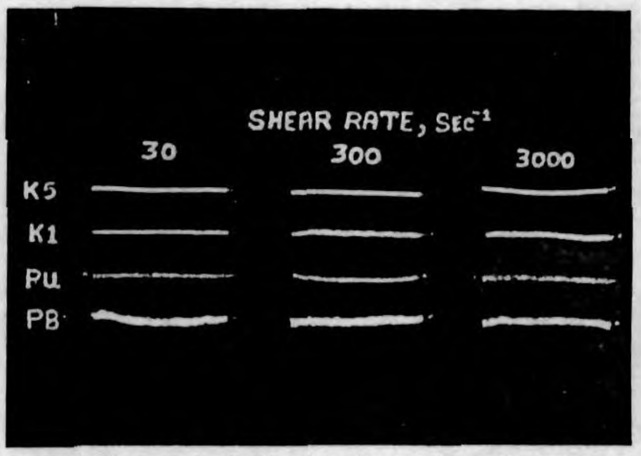

Figure 3. Photograph showing the effect of shear rate on the extrudate deformation, at 180 °C

4 Conclusions

Evaluation of the rheological characteristics of TPEs of different classes namely, styrene-butadiene-styrene, styrene-isoprene-styrene, thermoplastic polyurethane and 1,2-polybutadiene reveals that thermoplastic polyurethane tends to show Newtonian behaviour at about 210 °C whereas the styrenic block copolymers show complete miscibility of the two phase system at about 200 °C. 1,2-polybutadiene undergoes crosslinking of the polymer chains at higher temperature. The changes in shear viscosity, flow behaviour index, extrudate swell and distortion of the extrudates show evidence for the above transitions in the thermoplastic elastomer melts.

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The address of the author:
Baby Kuriakose, Indian Institute of Technology, Rubber Technology Centre, Kharagpur 721302, India.

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nning electron microscopy studies ensile, tear and abrasion failure of moplastic elastomers

KURIAKOSE, S. K. DE
Technology Centre, Indian Institute of Technology, Kharagpur, West Bengal
India

ile strength, tear resistance and abrasion resistance of four different types of
cial thermoplastic elastomers have been studied and their fracture surfaces
d by scanning electron microscopy. Thermoplastic polyurethane (TPU) showed
eformation under tensile fracture, whereas in 1,2 polybutadiene (1,2 PB) the
was initiated by craze formation and propagated by tear failure. Styrene–
–styrene block copolymer (K1107) showed ductile type failure whereas in
-butadiene–styrene block copolymer containing a higher proportion of styrene
a filler (K5152), the fracture occurred by shearing action. The tear failure
of the thermoplastic elastomers showed different fracture patterns which could
lated with the tear strength of the materials. The tear fracture surface of 1,2 PB
stick–slip tear lines and that of TPU had a broad tear path with vertical striations.
cture surfaces of K5152 and K1107 had the characteristics of laminar tearing and
rupted continuous tearing processes, respectively. The abrasion resistance of the
s was in the order TPU > 1,2 PB > K5152, which was manifested through the type
patterns formed on the abraded surfaces. Abraded surfaces of TPU, 1,2 PB and
showed closely spaced stable ridges, widely spaced ridges bridged by elongated
nd highly deformed ridges, respectively.

oduction

plastic elastomers (TPEs) are a relatively
ss of materials which combine the pro-
advantages of thermoplastics and the
l properties of vulcanized rubbers. These
ls may be block copolymers consisting of a
ermoplastic segment and a soft rubbery
t or blends of a crystalline polyolefin and
omer or may be those polymers which have
stereoregular structure and controlled
of crystalllinity. Elastomers which contain
labile crosslinks are also classified as
plastic elastomers. The processing charac-
s, physical properties, applications and
nic advantages of TPEs have been reviewed
eral authors [1–9]. The major fields of
tion of these materials are in mechanical moulded goods and footwear, wherein factors such as flexing, tear and wear are the main criteria leading to failure of the product. The mechanism of failure of TPEs has received little attention so far. The failure of rubber vulcanizates and that of rubber-based composites have been studied by scanning electron microscopic (SEM) examination of the failure surfaces [10–15]. SEM has also been found to be a valuable tool in studying the mechanism of toughening of plastics and epoxy resins by elastomer particles [16–18]. Recently, SEM has been used in explaining the effect of basic components of the blends on the physical properties of dynamically crosslinked thermoplastic elastomer blends [19–23]. In this paper we report the results of our SEM observations on the nature of tensile, tear and abrasion failure of some

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LE I Details of the thermoplastic elastomers used

name	Chemical name	Description
PB	1,2 Polybutadiene	Thermoplastic 1,2 polybutadiene elastomer having 1,2 content greater than 90% and degree of crystallinity 25%. JSR RB 820, manufactured by Japanese Synthetic Rubber Company
52	Styrene–butadiene–styrene block copolymer	S–B–S block copolymer having styrene/butadiene ratio 48/52 and containing about 10% by weight amorphous silica. KRATON K5152, manufactured by Shell Chemical Company, USA
107	Styrene–isoprene–styrene block copolymer	S–I–S block copolymer having styrene/isoprene ratio 14/86. KRATON D-1107, manufactured by Shell Chemical Company, USA
T	Thermoplastic polyurethane	Ester type thermoplastic Polyurethane. Estane 5715 elastomer, manufactured by B. F. Goodrich Company

mmercially available thermoplastic elastomers, mely, polyurethane, 1,2 polybutadiene, yrene–butadiene–styrene and styrene–oprene–styrene block copolymers.

. Experimental procedure

.1. Preparation of the test samples

he details of the TPEs used in the present study e given in Table I. The pellet or flake form of the PE was melted in a Brabender Plasti-corder odel PLE 330, for about 4 min, using a cam-type ixer with a rotor speed of 80 rpm and chamber mperature set at 180° C. The molten material as sheeted out through a laboratory mill at 5 mm nip setting. The sheeted out stock was mpression moulded at 180°C for 3 min in ecially designed moulds so that the mould with e sample inside could be cooled immediately ter moulding, keeping the sample still under mpression. Samples for tensile and tear tests ere punched out along the mill grain direction om the moulded sheets of 15 cm × 15 cm × 2 cm size and test pieces of dimensions 2 cm quare, 1 cm thick were directly moulded for the brasion test.

.2. Physical testing of the samples

ensile testing of the samples was done at 25°C s in ASTM D412-80 test method using dumb-bell haped test pieces, at a crosshead speed of 500 mm nin^{-1} using an Instron Universal Testing Machine model 1195). The tear strength of the samples vas determined as in ASTM D624-81 test method sing unnicked 90° angle test pieces. The tear test vas carried out at the same conditions of temperature and crosshead speed as described for the tensile test. The abrasion resistance of the samples was tested in a Du Pont abrader using silicon carbide abrasive paper of grain size 320. The speed of rotation of the abrasive disc was 40 rpm and the normal load was 3.26 kg. The samples were abraded for 10 min after an initial conditioning period of 5 min. The abrasion loss of the samples was calculated and expressed as volume loss in $\text{cm}^3\,\text{h}^{-1}$. The hardness values decreased with time after firm contact between the indentor and the sample, especially for TPU and 1,2 PB. Hence the hardness values were measured after 1 and 5 sec of firm contact, according to ASTM D 2240-81 test method.

2.3. Scanning electron microscopic observation.

The SEM observations of the failure surfaces were made using a Philips 500 model scanning electron microscope. The failure surface of the test samples were carefully cut out from one of the test pieces without touching the surfaces and then sputter coated with gold within 24 h of testing. The specimens were stored in a desiccator before and after gold coating until the SEM observations were made, in order to avoid contamination. The tilt was kept at 0° in all cases. Fig. 1 shows the details of test specimen, failure surface and scan area of the tensile, tear and abrasion test samples.

3. Results and discussion

3.1. Technical properties

Table II gives the technical properties of the TPEs. Since the materials evaluated are manufactured for

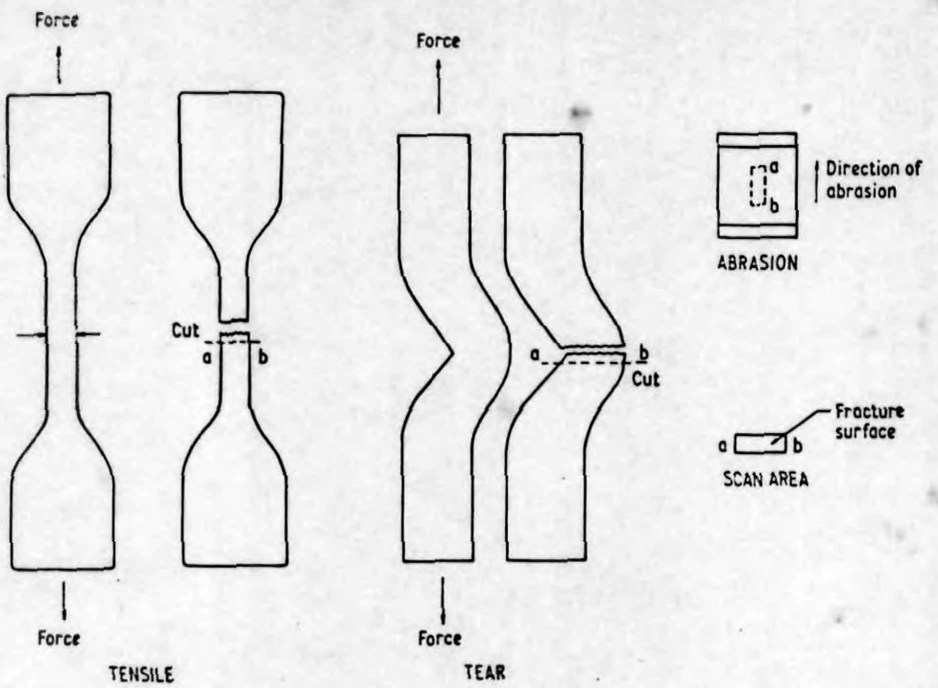


Figure 1 Samples for tensile, tear and abrasion tests, fracture surface and scan area.

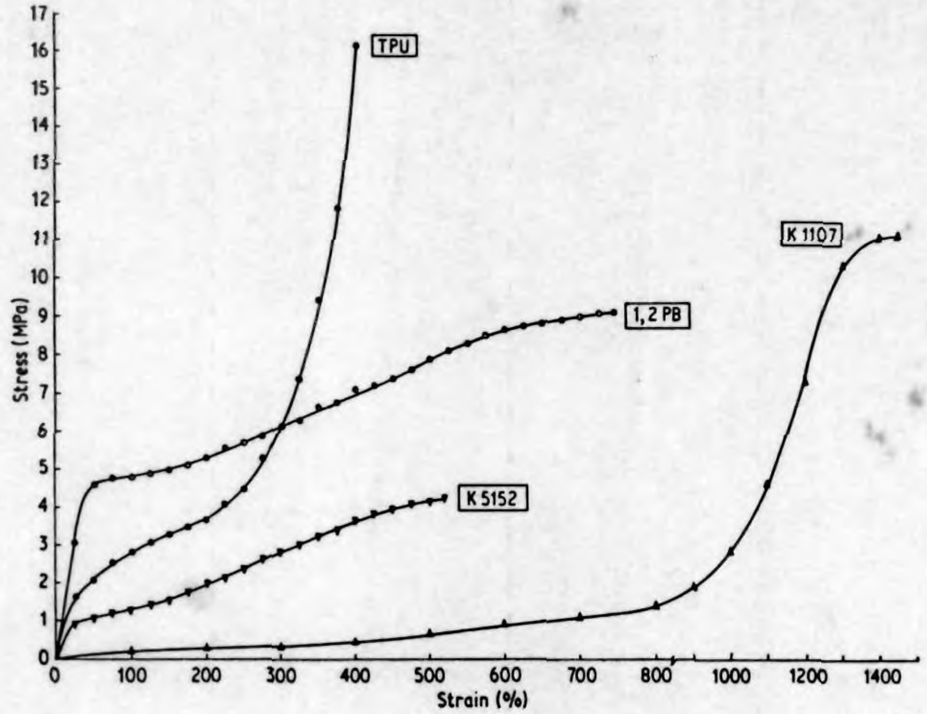
specific end uses, direct comparison of the technical properties may not be relevant. But these materials represent each class of thermoplastic elastomer and show certain distinct properties. Thus, TPU is characterized by its high resistance to abrasion, whereas 1,2 PB shows higher tear strength and K1107 provides highest elongation. The abrasion resistance of K1107 could not be tested as the samples chipped out during a 1 min run of the test, probably due to its very poor resistance to cutting and tearing action. The comparative data on physical properties are used for explaining the mechanism of different types of failure of these samples.

The stress–strain curves (Fig. 2) clearly show that the deformation nature of the four TPEs under an applied load in tension, is quite different from one another. At low strains (< 300%), TPU shows a stress–strain curve similar to that of vulcanized elastomers whereas, at higher strains there is a sharp increase in stress, probably due to the orientation of the hard segments in the direction of the applied stress. This behaviour is typical of ester type thermoplastic polyurethanes [24, 25]. 1,2 PB shows a stress–strain relation that is intermediate between that of plastic and rubber [26]. At lower strains (< 100%), there is a tendency to show yielding, but this is not so prominent as in the case of thermoplastics. At higher elongations, the stress gradually increases with strain and this portion of the curve is similar to that of elastomers. The stress–strain behaviour of K5152 is almost similar to that of gum vulcanizates of noncrystallizable rubbers. K1107 shows very low modulus values at low strains and behaves like elastomers containing a very low extent of crosslinking. But at higher strains (> 800%), there is a sharp increase in modulus

TABLE II Physical properties of the thermoplastic elastomers

Rubber	Hardness (Shore A)		Modulus 300%	Elongation at break	Tensile strength	Tear strength	Abrasion loss
	1s	5s	(MPa)	(%)	(MPa)	(kN m^{-1})	(cm^3 h^{-1})
TPU	86	75	6.0	400	16.1	37.9	0.120
1,2 PB	92	90	6.0	745	9.1	59.1	1.188
K5152	45	45	2.8	520	4.2	17.4	4.786
K1107	35	35	0.34	1450	11.1	10.1	*

*Could not be tested as the sample chipped out after 1 min.



ure 2 Stress–strain curves of TPEs.

ich may be due to the combined effect of entation of the hard polystyrene segments and ain-induced crystallization of the polyisoprene gments of the block copolymer [27]. Towards e breaking point, the sample yielded and then oke with no definite neck formation.

.2. Fractographs

.2.1. Tensile failure

he tensile fracture surfaces of the different types f TPEs shown in Figs. 3 to 9 reveal that these aterials vary in their deformation characteristics nder an applied load. The tensile fracture surface (Fig. 3) of TPU, which has the highest te strength among the four TPEs studied, sh elastic type deformation of the sample u tensile stress, evidence for which is a br continuous fracture path and less residual de mation, indicated by the absence of peaks fibrils on the surface. The foldings on the sur adjacent to the fracture path indicate the l extent of elastic deformation undergone by matrix before failure. The nature of the str strain curve of the sample also supports the ab views.

The tensile stress in homogenous materials be relieved by the formation of crazes which

igure 3 Tensile fracture surface of TPU, broad fracture path.

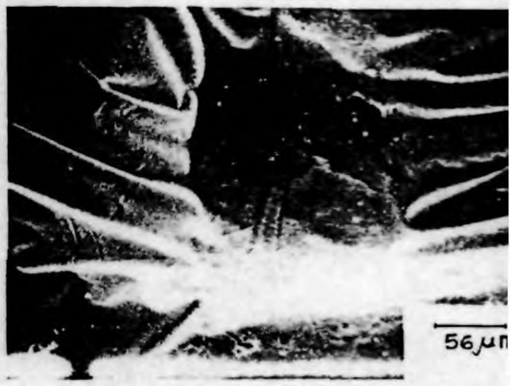


Figure 4 Opened-up craze in tensile failure of 1,2 PB.

Figure 5 V-shaped foldings in the tear zone of the opened-up craze in tensile failure of 1,2 PB.

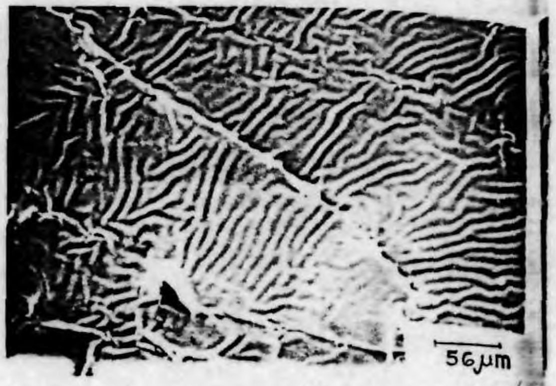


Figure 7 Smooth fracture path with foldings in tensile failure of K1107.

semicircular or circular boundaries. The crazes opened up during tensile failure are characterized by a central normal stress zone with curved boundaries and an adjacnet tear zone [28]. The tensile fracture surface of 1,2 PB shows these features. Fig. 4 shows the central stress zone with circular boundaries. The V-shaped foldings adjacent to the central zone (Fig. 5) indicate the tear zone which further propagated the crack. A network of channels is also observed inside the central stress zone (Fig. 6). Thus in 1,2 PB the fracture is initiated by craze formation and propagated by tear fracture. Craze formation before failure is characteristic of rubber modified thermoplastics [29]. The fractographs and the stress–strain curve indicate that the deformation behaviour of 1,2 PB under an applied load in tension is in between that of rubber and thermoplastics. The fracture surface of K1107 shows a smooth fracture path with peaks due to pulling up of the material before failure (Fig. 7). The foldings, lips and fibrils on the surface (Fig. 8) show a high extent of deformation of the matrix and indicate the ductile nature of the failure. The stress–strain curve of this sample also shows the ductile nature of failure as indicated by yielding with no definite neck formation (Fig. 2). Sample K5152 contains approximately equal proportions of polystyrene and polybutadiene segments in the block copolymer and the polystyrene segments remain as laminar domains in the matrix. It also contains plasticizers and a small quantity of filler. Under the application of tensile stress, shear deformation between the two segments takes place and the fracture proceeds by shearing action. This is clearly indicated by the tensile fractograph of K5152 (Fig. 9) which shows discontinuous fracture paths in different planes.

3.2.2. Tear failure

The resistance to tearing of the elastomers depends on the process by which stress dissipation near the tip of the growing crack takes place. This may be accomplished by several processes

Figure 6 Network of channels inside the central stress zone in tensile failure of 1,2 PB.

Figure 8 Foldings, lips and fibrils on the tensile failure surface of K1107.

ure 9 Discontinuous fracture paths in different planes the tensile failure surface of K5152.

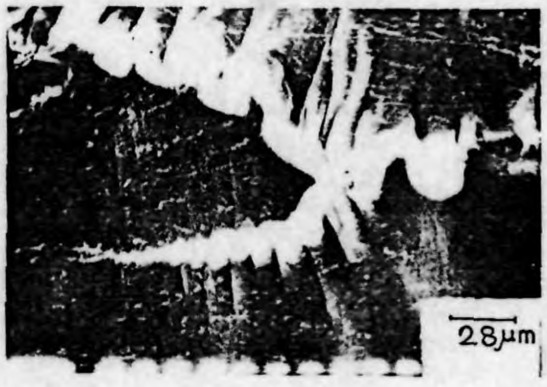
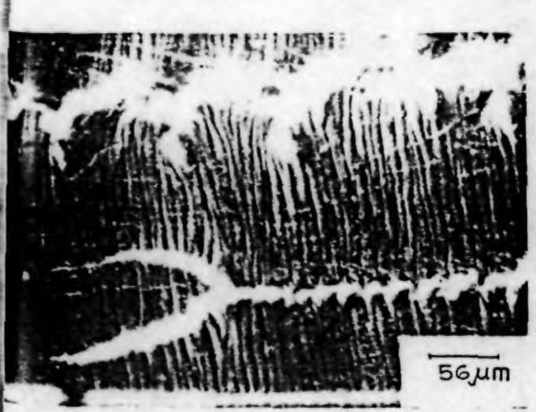


Figure 11 Pulled-up wavy crests on the tear failure surface of 1,2 PB.

ch as slippage or breakage of crosslinks or chain tanglements, deviating or arresting of the owing crack by filler particles, etc. [12]. The ocess of stress dissipation may be understood by reful examination of the tear fracture surfaces. g. 10 shows that the tear fracture in 1,2 PB has oceeded through a stick–slip process due to the esence of crystalline regions in the matrix. The esence of a branched tear path, vertical striations n the surface and the stick–slip tear path indicate e high energy expended for the propagation of e tear. The peaks appearing as pulled up wavy *ests (Fig. 11) show the high extent of stretching* at has taken place before failure. Thus, the high ar strength of 1,2 PB (Table II) compared with at of the other TPEs is due to the higher extent f stress dissipation through the various processes escribed above. The tear fracture surface of TPU ows a broad tear path and vertical striations Fig. 12). The tear strength of TPU is less than at of 1,2 PB but greater than that of K5152. The fracture surface of K5152 (Fig. 13) does not contain any continuous tear path, which indicates laminar tearing between the hard and soft segments. Small rounded tear lines seen on the fracture surface may be due to the deflection of the tear path by the silica particles present in the sample. This sample shows a higher tear strength than K1107. K1107 contains about 14% by weight of hard segment which remains as spherical domains in the bulk of the soft segment. The tear fractograph of this sample (Fig. 14) shows a smooth surface and a continuous tear path with irregular foldings. The *tear strength of K1107 is poor, which is in line* with the continuous tear path observed on the fracture surface. Similar observations have been reported in the tear failure of resin-cured carboxylated nitrile rubber [30].

3.2.3. Abrasion failure

Abrasion resistance of elastomers depends mainly on factors such as strength of the matrix,



igure 10 Stick–slip fracture path, branched tear line and rtical striations on the tear failure surface of 1,2 PB.

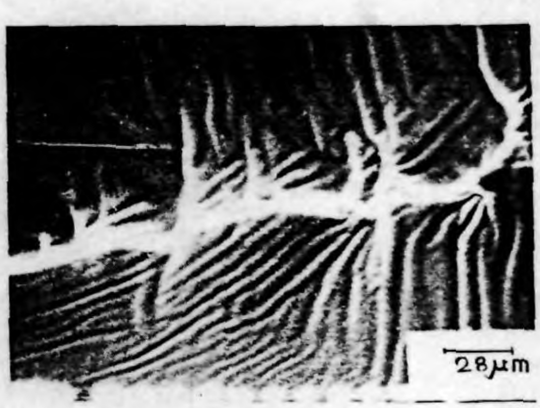


Figure 12 Broad continuous tear line with vertical striations on the tear failure surface of TPU.

Figure 13 Small number of short rounded tear lines on the tear failure surface of K5152.

Figure 16 Enlarged picture of the vertical ridges showi abraded particles and stable nature of the ridges of TPU.

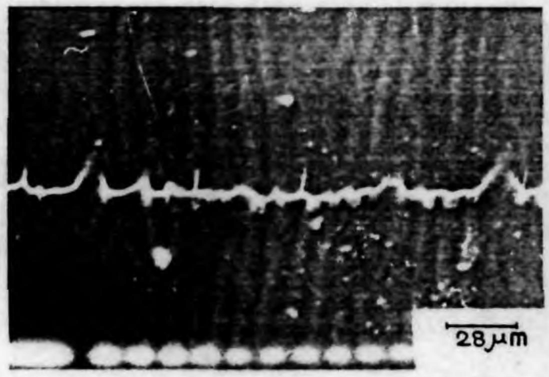


Figure 14 Continuous tear line with irregular foldings on the tear failure surface of K1107.

Figure 17 Widely spaced ridges on the abraded surface of 1,2 PB.

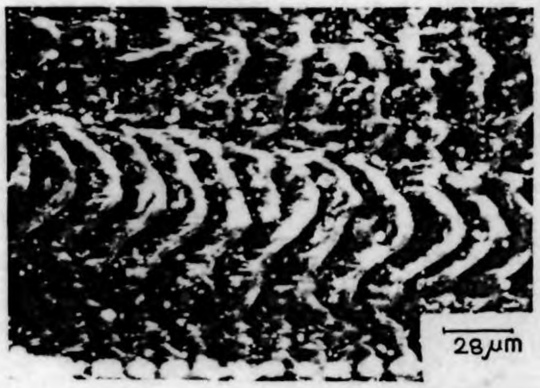
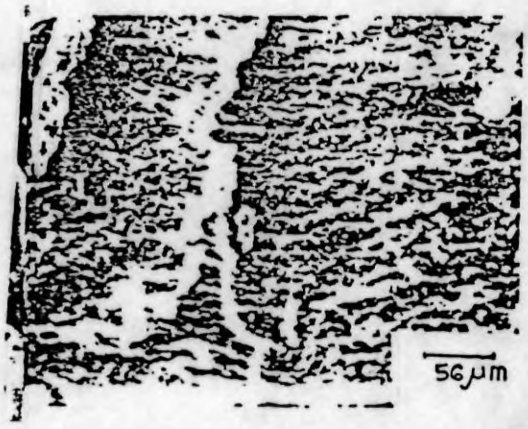


Figure 15 Closely spaced vertical ridges on the abraded surface of TPU.

Figure 18 Bridging of the ridges by elongated fibrils on the abraded surface of 1,2 PB.



re 19 Highly deformed ridges and roll form of the rial removed on the abraded surface of K5152.

stance to thermo-oxidative degradation, crack th resistance under dynamic conditions etc, t from other factors such as frictional force the nature of the abrasive. The nature of nite patterns appearing on the abraded surface been shown to be indicative of the mechanism abrasion of elastomers [11, 15]. The abraded ace of TPU shows a well-defined ridge pattern right angles to the direction of abrasion (Fig. The absence of any lumpy mass and the ence of small particles on the surface indicate these ridges are highly resistant to defor- tion (Fig. 16). Low ridge height and close cing of the ridges are indications of high resist- e to abrasion [31]. The formation of the ridges microtearing and subsequent removal of the aterial from the surface depend on the tensile ength, tear and cut growth resistance of the atrix [32]. Thus the inherent strength properties TPU account for its high resistance to abrasion. e abraded surface of 1,2 PB also shows ridge tterns (Fig. 17). But in this case, the ridges are s closely spaced and the channels between the ges are bridged by elongated fibrils (Fig. 18). 2 PB which has a high tear strength and elongation break (Table II) undergoes high deformation d the torn surfaces are stretched to high ongation before the material is removed from the rface. This sample shows a lower abrasion resist- ce than TPU but higher than that of K5152. The braded surface of K5152 shows highly deformed ges (Fig. 19). The material removal in roll form n also be seen on the surface. This sample is less sistant to the frictional forces of abrasion, due its very low tensile strength and tear resistance, hich account for its lower resistance to abrasion 33].

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