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MORPHOLOGY AND ABRASION PATTERN OF THERMOPLASTIC POLYPROPYLENE—NATURAL RUBBER BLENDS

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Thermoplastic elastomers prepared by melt mixing of isotactic - polypropylene (PP) and natural rubber (NR) were evaluated for abrasion resistance. The morphology of the blends and the patterns developed on the abraded surfaces of the test samples were studied using a scanning electron microscope. The morphology of the blends was found to change from that of a dispersed phase of natural rubber to that of a continuous phase when the NR : PP ratio was changed from 30 : 70 to 60 : 40. Correspondingly, a change in the mode of abrasion of the blends from abrasive type with horizontal groove patterns to frictional type with vertical ridge patterns on the abraded surface was observed for these blends. This change in the pattern of abrasion was prominent in dynamically crosslinked blends compared with the uncrosslinked ones.

Key words — Thermoplastic elastomer, Polypropylene, Natural rubber, Morphology, Abrasion, Dynamic crosslinking, Wear, Blends.

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INTRODUCTION

Thermoplastic elastomers (TPEs) are replacing polyolefins and conventional elastomers from many of their respective fields of application, since the TPEs possess the easy processing characteristics of thermoplastics and the physical properties of vulcanized elastomers (Reed, 1984). Several reviews and research papers have already appeared describing the different types of TPEs and their applications (Mullins, 1978; West and Cooper, 1978; Walker, 1979; Thorn, 1980; Brydson, 1982; Coran, 1988). TPEs prepared by physical blending of thermoplastic polyolefins and elastomers have the advantage that the desired properties can be tailored without difficulty by proper selection of the polyolefin and the elastomer components and their blend ratios. The effects of blend ratios and dynamic crosslinking of the elastomer phase on the physical properties, rheological behaviour, dynamic, mechanical properties and mode of failure under tensile and tear fracture of thermoplastics-elastomer blends have been studied by different research groups (Campbell *et al*, 1978; Coran and Patel, 1980, 1981; Ramos-De Valle, 1982; Goettler *et al*, 1982; Kuriakose and De, 1985a, 1985b, 1986; Kuriakose *et al*, 1985). But only a limited number of studies have been reported on morphology-property relations of thermoplastics-elastomer blends (Danesi and Porter, 1978; Yang *et al*, 1984; Dao, 1984). In this paper the results of studies on the morphology and abrasion pattern of thermoplastic elastomers, prepared from blends of polypropylene and natural rubber, are reported.

EXPERIMENTAL

MATERIALS

Natural rubber (NR) used for the study was ISNR 5 and the isotactic polypropylene (PP) was Koylene M0030, obtained from Indian Petrochemicals Corporation Limited Vadodara. The basic characteristics of NR and PP are given in Table 1. All the other chemicals used were of commercial grade. The composition of the blends used in this study is given in Table 2. The dynamically crosslinked blends also contained zinc oxide, stearic acid, N - cyclohexyl benzothiazyl sulphenamide (CBS), tetramethyl thiuram disulphide (TMTD) and sulphur, at 5.0, 2.0, 2.0, 2.5 and 0.3 phr, respectively, based on the rubber phase only. The uncrosslinked blends are denoted by BU, CU, DU, EU and FU while the dynamically crosslinked blends are denoted by BS, CS, DS, ES and FS, respectively.

Table 1. **Characteristics of the base polymers**

Characteristics		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
Wallace plasticity	Po	59	..
Melt Flow Index (230°C, 2.16 Kg)	MFI	..	10.0
Brittle point, °C		..	5

Table 2. **Composition of the blends**

Blend	B	C	D	E	F
Polypropylene	70	60	50	40	30
Natural rubber	30	40	50	60	70
State of cure*	U,S	U,S	U,S	U,S	U,S

*U - Uncrosslinked
S - Dynamically crosslinked

BLENDING AND MOULDING

The blends were prepared in a Brabender plasticorder, model PLE 330, using a cam-type mixer at a temperature of 180°C and a rotor speed of 80 rpm. The blending time was seven minutes. In the case of the dynamically crosslinked blends, the curatives were added at the end of five minutes and the blending continued for another two minutes. At the end of seven minutes, the blend was taken out and sheeted in a laboratory mill, at 2.0 mm nip setting. It was then cut into small pieces and remixed in the plasticorder for one minute and finally sheeted out to ensure uniform dispersion of ingredients. The test specimens were compression moulded at 200°C in a specially designed mould so that the mould could be cooled immediately after the moulding time of two minutes, keeping the sample still under compression. Testing was carried out after 24 hours of moulding the specimens.

ABRASION TESTING

Abrasion resistance of the samples was tested in a Du Pont abrader as per IS 3400 part III 1965, 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 minutes after an initial conditioning period of three minutes. Abrasion loss of the samples was calculated from the weight loss and expressed as the volume loss in cm^3h^{-1}, using the specific gravity values of the samples.

MORPHOLOGY

The morphological studies were conducted using the uncrosslinked blends only. The moulded samples were cut using a rotary retracting microtome after cooling the samples at –80°C to –90°C so as to avoid any deformation of the rubber phase during cutting. The cut edge of the sample was kept immersed in toluene at 40°C for seven days for removing the rubber phase. The solvent was changed after every 12 h. The solvent extracted samples were dried at 40°C for 24 h and used for scanning electron microscopic (SEM) observations.

SEM OBSERVATIONS

A Philips 500 model scanning electron microscope was used for making observations on the surface of the samples. The microtomed and toluene extracted surface of the sample/the abraded surface of the test piece was sputter coated with gold before loading into the SEM. The tilt was kept at 30° and observations made. The microphotographs of the surface were taken at appropriate magnifications.

RESULTS AND DISCUSSION

MORPHOLOGY OF THE BLENDS

The morphology of two mutually incompatible polymers depends on several factors such as composition of the blends, melt viscosity of the components, rate of shear during blending and temperature of blending. As a general rule, the component having higher viscosity and/or lower proportion in the blend forms the dispersed phase, while the continuous phase consists of the component having higher proportion and/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 scanning electron micrographs of the microtomed surface of the blends BU, CU, DU, EU and FU from which the rubber phase has been extracted using toluene, are shown in Figs. 1 to 5, respectively. In these figures the black regions represent the rubber phase which has been extracted. From Fig. 1 it is evident that the rubber phase remained as dispersed particles in the PP matrix in the blend BU. As the rubber content is increased the number and size of the dispersed rubber particles have increased, as observed from Fig. 2 of the blend CU. The dispersed particles in this blend are more deformed than the particles in BU. In the 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 Fig. 3 of DU. The larger particle size and the more continuous nature of the rubber phase compared with those of the blends BU and CU may be attributed to the diffusion and reagglomeration of the dispersed rubber particles under various processing conditions. The average size of the dispersed particles has increased from about 3 μm to 10 μm as the composition of the blend is changed from 30:70 NR:PP to 60:40 as seen from the micrographs. Figure 4 of EU shows that the size of the rubber particles becomes much larger at the 60:40 NR:PP ratio and that the PP layer has narrowed down as evidenced by the fibrils formed by the broken layers of PP. The micrograph of the 70:30 NR:PP blend (Fig. 5) shows layers of dark regions of the NR phase, which are interconnected by white layers of PP. Thus in the blends EU and FU both NR and PP exist as continuous phases due to the higher proportion of the NR phase and the lower melt viscosity of the PP phase.

SEM studies on morphology were not possible in the dynamically crosslinked blends, because the crosslinked rubber phase could not be removed by extraction. But it is expected that the size of the dispersed rubber particles is much smaller than that of the uncrosslinked blends. This is because, in dynamically crosslinked blends

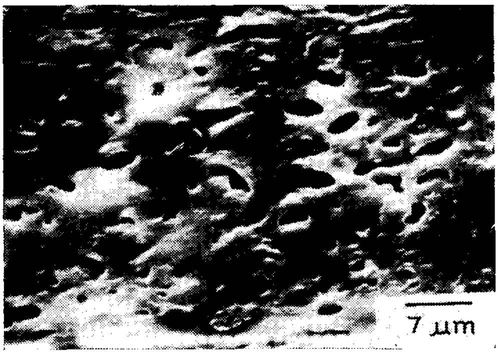

Fig. 1. SEM of blend BU after extraction of the rubber phase.

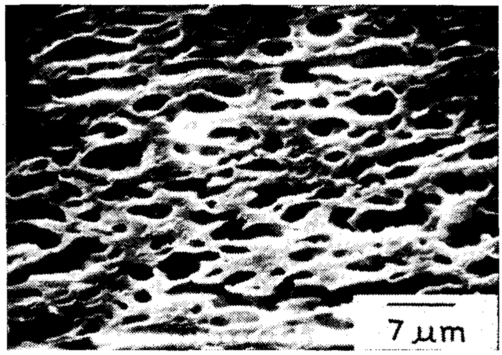

Fig. 2. SEM of blend CU after extraction of the rubber phase.

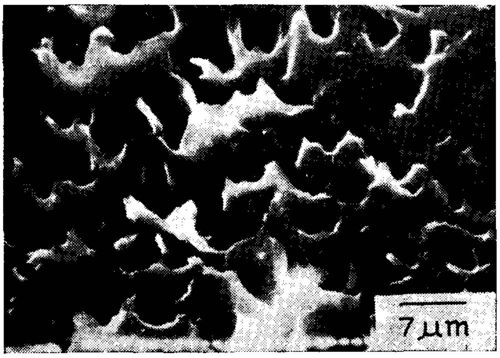

Fig. 3. SEM of blend DU after extraction of the rubber phase.

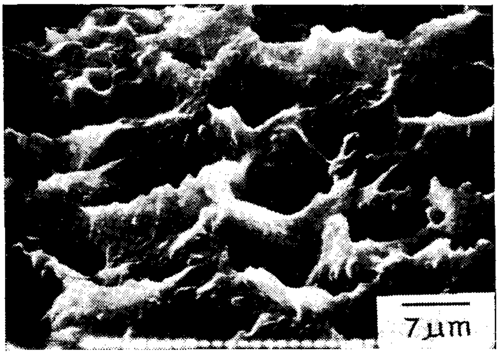

Fig. 4. SEM of blend EU after extraction of the rubber phase.

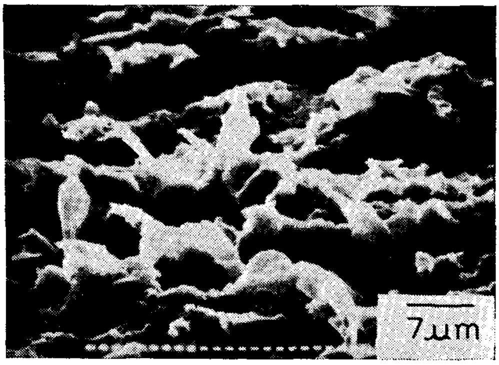

Fig. 5. SEM of blend FU after extraction of the rubber phase.

the rubber particles which are already vulcanized, cannot diffuse and recombine to form larger particles as that occurs in the case of the uncrosslinked blends.

ABRASION OF THE BLENDS

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 or more of the above factors may play a prominent role in the failure of the sample by abrasion. Schallamach (1952, 1968, 1971) and Southern and Thomas (1979) showed that patterns developed on the abraded surface are indicative of the mechanism of abrasion of elastomers. The main types of wear of highly elastic materials are fatigue wear, abrasive wear and wear by roll formation, of which the latter two are more severe. The wear of thermoplastics is abrasive in type, which results from micro-cutting by solid projections on the surface of the abrasive. Abrasive wear is characterised by longitudinal furrows on the surface. Frictional wear 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.

Abrasion loss against the proportion of NR and PP in the blend for the uncrosslinked and the dynamically crosslinked blends is represented in Fig 6. It can be observed that abrasion loss increased with increase in the proportion of the rubber phase, both for the uncrosslinked and the dynamically crosslinked blends. The uncrosslinked blends BU and CU showed higher abrasion resistance than the dynamically crosslinked blends BS and CS. But as the proportion of rubber in the blend is increased this trend is reversed and the crosslinked blends showed better abrasion resistance compared to 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 abrasion resistance in 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

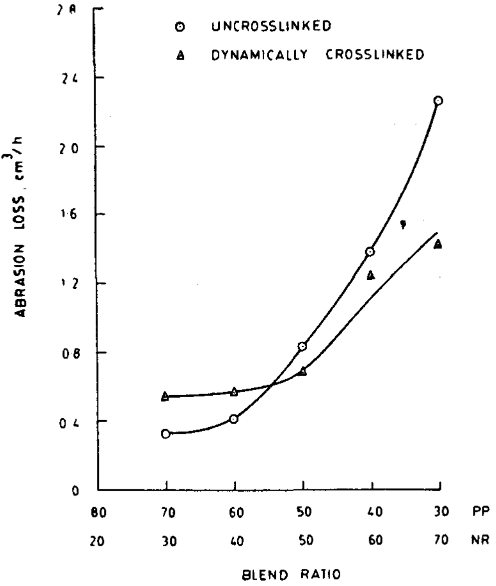

Fig. 6. Effect of blend ratio and dynamic crosslinking on abrasion loss of NR/PP blends.

phase (E and F) dynamic crosslinking improved the matrix strength because crsosslinking 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 abrasion resistance of the blends containing higher proportions of rubber. Results reported earlier (Kuriakose and De, 1985a) showed that there was more than 100 per cent increase in tensile strength and tear resistance of the blends EU and FU through dynamic crosslinking, compared with less than 10 per cent increase in the properties of blend BU. This supports the above view.

Scanning electron microscopic observations of the abraded surface of the blends also showed that there is a change in the mode of abrasion as rubber also formed a continuous phase. The abraded surfaces of BU and CU (Fig. 7 and 8, respectively) showed deep grooves parallel to the direction of abrasion, which are characteristic of abrasive wear for thermoplastic materials (Ratner, 1967; Engel *et al*, 1981). For the 50:50 blend (DU) the abraded surface showed less intense grooves (Fig. 9) compared to those of BU and CU. The abraded surface of FU was comparatively smooth even though it also showed parallel grooves which were not pronounced (Fig. 10).

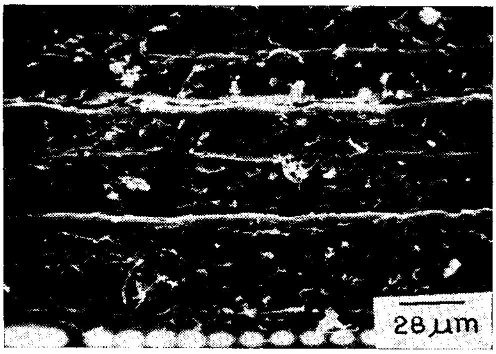

Fig. 7. SEM of abraded surface of blend BU.

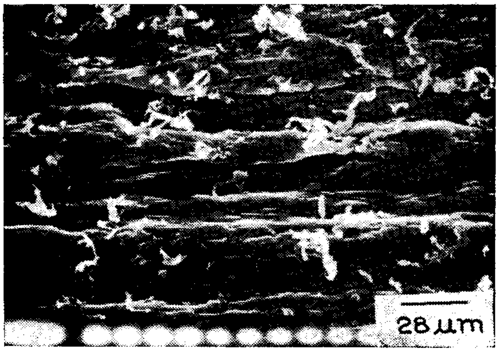

Fig. 8. SEM of abraded surface of blend CU.

Fig. 9. SEM of abraded surface of blend DU.

Fig. 10. SEM of abraded surface of blend FU.

In the dynamically crosslinked blends, the abraded surfaces of BS and CS (Figs. 11 and 12, 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 DS (Fig. 13), the abraded surface contained only a small number of shallow grooves. But in the case of FS, which contained the largest proportion of rubber, a tendency to form vertical ridges was observed (Fig. 14). This is characteristic of frictional wear and similar to that observed for the blends of natural rubber and polybutadiene rubber (Mathew and De, 1983). The above observations confirm that there is a change in the mechanism of abrasion of NR:PP blends with increase in the proportion of the elastomer and that this change from abrasive wear to frictional wear occurred when the morphology of the blend changed from a dispersed phase to a continuous phase of NR in the blend. This effect was quite remarkable in dynamically crosslinked blends than in the uncrosslinked blends.

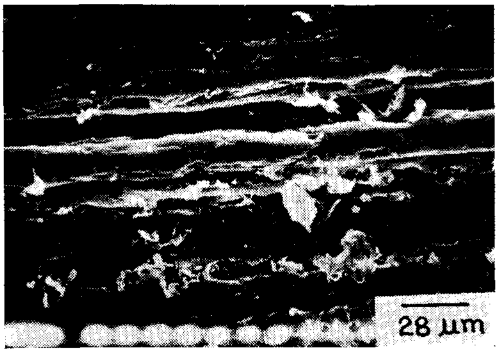

Fig. 11. SEM of abraded surface of blend BS.

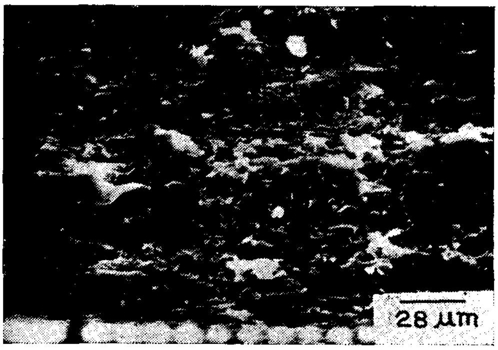

Fig. 12. SEM of abraded surface of blend CS.

Fig. 13. SEM of abraded surface of blend DS.

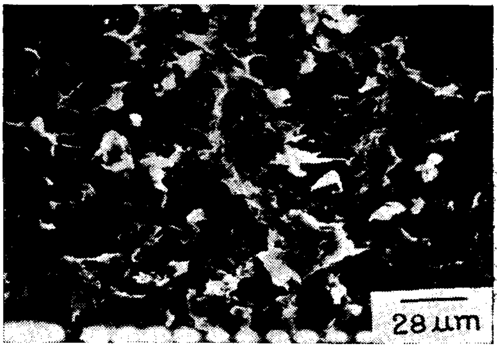

Fig. 14. SEM of abraded surface of blend FS.

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