STUDIES ON
DEPOLYMERIZED LIQUID NATURAL RUBBER

Thesis submitted to
The Mahatma Gandhi University
in partial fulfilment of the requirements for the award
of the degree of

DOCTOR OF PHILOSOPHY

Under the Faculty of Science

by

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Dedicated to my parents

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30.5.97

Dr. N.M. MATHEW

Declaration

I hereby declare that the thesis entitled ***Studies on depolymerized liquid natural rubber*** *is a bona fide record of the research work done by me and that no part thereof has been presented earlier for any degree or diploma of any other University.*

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Chapter 1.

INTRODUCTION

1.1. INTRODUCTION

Natural rubber (NR), unlike other similar materials of extensive application is unique in its origin in macromolecular form in rubber tree (*Hevea brasiliensis*). Other elastomers commonly used are derived from petroleum, starting from their respective monomers appearing in fractionating columns. Latex, biosynthesised in the rubber tree, is a mixture of rubber and water with small quantities of stabilizing components and is obtained on tapping. By the method of coagulation, rubber from latex is recovered in almost pure form and processed into sheet, crepe or crumb which form the raw material for various product manufacturing industries. Products are also manufactured from latex compounds by dipping, extrusion, etc. In addition to product manufacture the high molecular weight polymer can be modified to yield other derivatives that find use in many applications like binders, anticorrossive coatings and process aids. The modifications are effected by depolymerization, cyclization, carboxylation, etc. These different forms provide better processability and special properties. In order to expand the area of application of NR modifications of the naturally occurring polymer have become necessary. This study envisages modification of NR into depolymerized liquid NR, evaluation of the properties after modification and various applications of the modified forms.

As an agricultural commodity, NR has several features that make it an important component in tropical agriculture. It is a perennial crop providing income for millions of people in developing countries [1]. As an industrial raw material, despite heavy competition from various synthetic rubbers, NR is the elastomer of choice in many applications from the fact that it possesses certain specific merits.

The role of NR as an environmentally friendly material is also becoming more important. More and more stress is being given to the green image of NR. It is a polymer "which is completely renewable". NR and its lower molecular weight oligomers form molecular precursors for many new materials. Non-rubber materials from the serum are also gaining importance. Method of making fertilizer from the serum has been developed. Possibilities of the serum as a source for biogas generation are also being attempted[2]. Another use is as a fermentation medium[3]. Quebrachitol, an optically active pseudo sugar in the medium, is likely to be a valuable component allowing easy synthesis of various isomers[4].

1.1 Latex

Fresh latex, as it comes from the tree, is a white or slightly yellowish opaque liquid with a specific gravity between 0.974 and 0.976. It is a weak lyophilic system of spherical or pear shaped rubber globules suspended in an aqueous serum. Composition of Hevea latex is given in Table I.1.

Table 1.1. Composition of latex

Component	Percentage
Rubber	30-40
Proteins	2-2.5
Resins	1-2
Sugars	1-1.5
Ash	0.7-0.9
Water	55-60

Fresh latex is slightly alkaline or neutral. It becomes acidic rapidly due to bacterial action, the acids formed neutralizes the negative charge on the rubber particles and the latex gradually gets coagulated on keeping. The normal processing methods avoid the above process of precoagulation. Soon after collection, the latex is cleaned by filtration followed by coagulation using an organic acid such as formic acid, acetic acid or sulphamic acid[5] or by carefully controlled quantity of sulphuric acid[6]. Biological coagulation has been utilized in polybag collection[7].

1.2 Primary processing

NR after primary processing is available in different forms and grades. In India 70 percent of the production is procesed as sheet rubber. The rubber hydrocarbon recovered from the latex is transformed into sheet, crepe or technically specified block rubber. Sheets are dried in smoke houses and are marketed after visual grading. In the case of technically specified block rubber, the larger scale of operation, blending and quality checks assure consistent and guranteed quality. For latex stage manufacture the raw material is concentrated latex, produced by creaming or centrifuging. Field latex that contains 30-35 % dry rubber is concentrated to 50-55 % dry rubber by the use of creaming agents. Separation between water and rubber is effected by centrifugal force generated in a high speed centrifuge for making centrifuged latex. This process is faster and more efficient than creaming.

1.3 Properties

NR is a high molecular weight polymeric substance possessing viscoelastic properties. Structurally it is cis 1,4 polyisoprene. Isoprene is a diene and 1,4 addition leaves a double bond in each of the isoprene units in the polymer. Because of this, NR shows all the reactions of an unsaturated compound. It gives addition compounds with halogens, ozone, hydrogen chloride and several other reactants that combine with olefins. An interesting reaction of NR is its combination with sulphur commonly referred to as vulcanization. This reaction converts the raw rubber into an elastic material. Vulcanized rubber possesses high tensile strength,. hardness and abrasion resistance. Because of the unique combination of these properties, NR finds application in the manufacture of a variety of products.

The main use of NR is in automobile tyres. In developed countries nearly 60% of all the rubber consumed is for automobile tyres and tubes. In heavy duty tyre the major portion of rubber used is NR. Apart from tyres a modern automobile has more than 300 components made out of rubber. Use of rubber in water proofing garments, hoses, footwear, battery box, foam mattress, balloon, toys, etc., are well known. In addition to this, use of NR has been reported in slow release fertilisers by Jeoh and Soong[9], in vibration isolation by Debram[10] and in road making by Lewandowski[11]. A wide range of NR based engineering products have been developed in these fields. Physical properties of raw NR are given in Table I.2.

Table 1.2. Physical properties of NR

Specific gravity	0.92
Refractive index	1.52
Coefficient of cubical expansion	0.00062 per ^{o}C
Cohesive energy density	63.7 cal/cc
Heat of combustion	10,700 cal/g
Thermal conductivity	0.00032 cal/s/cm2/^{o}C
Dielectric constant	2.37
Power factor (1 kHz)	26

1.4 Product manufacture

The raw polymer, NR, having considerable strength, appreciable elasticity and resilience at room temperature is sensitive to high and low temperature and is liable to oxidation to a sticky mass. This factor imposed severe limitations on the usefulness of the material. Today, apart from solution adhesives based on raw rubber, probably the only product used in raw unvulcanized state is the crepe sole for footwear.

NR is usually mixed with different chemicals such as vulcanizing agents, accelerators, activators, fillers, process aids and other ingredients capable of imparting special properties resulting in a vulcanizable rubber compound. Mixing is done on open mill or in internal mixer. The rubber compound is shaped either by pressing in mould cavities or by extrusion or calendering and vulcanized at temperatures above 100^{o}C. For latex stage compounding preparation of chemicals as dispersion or emulsion is the first step. These are added to stabilized latex to form a rubber compound. Shaping into the profiles of the product is achieved by dipping, extrusion, etc., followed by drying and vulcanization. Vulcanization is usually carried out in hot air or boiling water or in autoclave. Product manufacture from latex employs ultra accelerators enabling vulcanization at relatively lower temperature than that used for dry rubber products. However, incorporation of substantial quantity of fillers into a latex compound is difficult and reinforcement by fillers is seldom realised in latex vulcanizates.

Product manufacture from NR starts with the processes of mastication and mixing. Expensive operations are involved in this and the scrap that is left over at the end of the process is not readily recoverable. Automation, computerization and other technical developments could not make any fundamental change in the processing technology. Emergence of new forms of polymers such as thermoplastic rubbers have changed the process eliminating vulcanization. Most of the synthetic rubbers are available in a wide range of molecular weights and forms. NR has limitations in these aspects. Control of the biosynthesis of rubber to obtain desired changes in molecular weight and related parameters is still out of question. Hence, it is imperative that the high molecular weight polymer has to be the starting material for the production of various modified forms. Powdered, liquid, thermoplastic, graft and various other forms of NR are already available and have been enthusiastically received by various product manufacturers.

1.5. Modified forms of NR

NR has been modified in a number of ways in line with several developments that have taken place in the field of synthetic rubbers. These include technically specified rubber, new preservatives for latex and various other new materials from NR. Physical blending with other materials or polymers is commonly referred to as physical modification while direct reaction of the polyisoprene molecule with appropriate reagents results in chemically modified forms. NR was found to be suitable for different types of chemical modification resulting in the production of a number of polymeric materials of very interesting properties. Although many such derivatives lost their significance consequent to the development of totally synthetic counterparts, some are still considered important. The decreasing availability of petroleum based feed stocks and increasing awareness of the importance of renewable and environmentally friendly resources have caused renewed interest in the development of modified forms of NR.

NR can be modified by physical or chemical means and in some cases by a combination of the two. Physical methods involve incorporation of additives that do not chemically react with rubber. Examples are oil extension, blending with other polymers, masterbatching, etc. Although a limited level of chemical reaction may take place between rubber and some of the added materials, the modification in properties is brought about mostly by the physical combination of materials. A chemical modification on the other hand, depends on the chemical reactivity of NR molecule. Being unsaturated, it is highly reactive and many chemical reactions could be carried out on NR resulting in materials having entirely different properties. The most widely practiced chemical reaction on NR is vulcanization. It is an integral part of most of the product manufacturing processes. There are a number of other reactions on NR which yield products with novel properties. These reactions could be broadly divided into three categories:-

1. Intramolecular changes without introduction of a new chemical group.
2. Attachment of a pendant functional groups and
3. Grafting of different polymers at one or more points along the NR molecule.

In a nutshell different modifications which are applied to NR are depicted in Figure 1.1.

1.6. Physical modifications

1.6.1. Superior processing rubber

Superior processing rubber (SP rubber) is an intimate blend of vulcanized and unvulcanized rubbers prepared in the latex stage[12-15]. It is similar to other grades of NR in appearance and physical properties of vulcanizates. The outstanding feature of this rubber is its reduced tendency to recover from deformation. This makes it an ideal material for calendered or extruded products. This rubber is also found to be ideal for blending with synthetic rubbers like EPDM for making extruded products[16]. Compounds prepared from SP rubber show lower die swell, higher viscosity, easier handling and greater resistance to collapse and water marking during open steam cure[17]. It is compounded in a manner similar to ordinary grades of NR. The various advantages of SP rubber could be realized if it contains 20% vulcanized rubber. Therefore, normal grade of SP rubber is prepared with this ratio and is designated as SP 20. However, a more convenient method is to prepare a masterbatch form of SP rubber containing 80% vulcanized and 20% unvulcanized rubber (SP 80). In Malaysia this is available under the trade name PA 80. For the preparation of SP rubber it is necessary to prepare prevulcanized latex. The vulcanizing ingredients are processed into a stable dispersion by ball milling. The proportion of various ingredients to be used for 100 parts of dry rubber is given in Table 1.3. Field latex to be vulcanized is ammoniated to 0.3% and its DRC is determined. Based on the DRC appropriate quantity of the dispersion is added and the latex heated to 80 to 85°C in 1 h under mild stirring. The vulcanized latex is cooled and its total solid content determined. For the preparation of SP 80, the vulcanized latex is first diluted to 20% total solids content and then mixed with fresh field latex of known DRC in the ratio 4:1, the ratio being on total solids of vulcanized latex and DRC of field latex. The blended latex is then sieved through a 60 mesh sieve into a coagulation tank and then immediately coagulated with 5% sulphuric acid. The serum is removed and replaced with fresh water. After soaking for 10 min. the coagulum is passed twice through lightly grooved crepe rolls and the crumbs again soaked in water for 1 h. The washed crumbs are dried in air at 70°C for 4-5 h. SP rubber possesses definite advantages over NR in various processing properties such as die swell, dimensional stability and green strength.

Table 1.3. Recipe for composite dispersion

Sulphur	2.00
Zinc oxide	1.75
Zinc diethyldithiocarbamate	0.20
Mercaptobenzothiazole	0.40
Dispersing agent	0.02
Water	4.85
Total	8.22

1.6.2. Viscosity stabilization

NR on storage encounters the problem of storage hardening due to the inherent carbonyl groups, which are distributed at random along the rubber molecule[18]. The change in hardness is generally more when the viscosity is initially low and is greatly influenced by the relative humidity of storage[19]. Raw rubbers of high hardness require greater mastication time or the use of expensive peptisers to obtain desirable hardness or viscosity. This type of hardening reaction can be almost completely suppressed by adding chemicals such as hydroxylamine or semicarbazide to latex prior to its conversion to dry rubber[20]. Since 5-5' dimethyl 1,3 cyclohexanedione (dimedone), an aldehyde specific reagent, also inhibits storage hardening it is assumed that the carbonyl groups are aldehydes. The minimum effective quantity of the reagent required per million molecular weight provides an indication of aldehyde group content and the figure usually range from 5 to 30. Hydroxylamine added to latex in small quantities is chemically bonded to rubber and inhibits storage hardening. Hydroxylamine being monofunctional preserves the Mooney viscosity of the rubber at the level at which the treatment has been given. Rubber so treated is called constant viscosity (CV) rubber. Hydroxylamine neutral sulphate is now more popular. The recommended dosage is 0.15%. Semicarbazide is preferred over hydroxylamine for light coloured rubbers as the latter has a darkening effect on rubber. Commercially CV rubber is produced within a low viscosity range of 50 to 75 Mooney units and ensures premastication savings to the consumer. In case still lower viscosities are desired, adequate quantities of an inert plasticizer such as nonstaining naphthenic process oil is added to the viscosity stabilized rubber. This type of rubber is termed as low viscosity (LV) rubber.

1.6.3. Oil extended NR (OENR).

Mineral oils have been in use for several years in rubber processing. Oil functions as a plasticizer by improving processability and filler incorporation, or as an extender for cheapening the product. The factor that decides whether an oil functions as a plasticizer or as an extender is its concentration in rubber. Usually when an oil is used in concentrations below 10 phr, it is referred to as a plasticizer or process aid. Above this level, the oil functions as extender for cheapening the product and the resultant mixture is known as oil extended rubber[21]. The concentration of oil for functioning as an extender is in the range of 20 to 40 phr. Extended rubber containing up to 50 phr of oil has been prepared, but then the product is almost a liquid[22]. Different types of oil such as paraffinic, naphthenic and aromatic are used. Each oil imparts specific properties to rubber. This is illustrated in Table 1.4. Oil extension can be carried out in latex or in dry rubber. For latex masterbatching oil is converted into an aqueous emulsion and added to latex at a pH of 8 to 8.5 and then coagulated and processed in the usual manner. Dry mixing can be done either by soaking or by the extrusion method.

Table 1.4. Properties imparted by oil.

Type of oil / Properties	**Paraffinic**	**Naphthenic**	**Aromatic**
Processability	Poor	Superior	Best
Staining	Least	Light	High
Ageing	No effect	No effect	Poor

The following are the advantages and disadvantages of OENR.

Advantages

1. Eliminates premastication
2. Improves resistance to crystallization
3. Gives better skid resistance on icy roads.
4. Cheapens the product.

Disadvantages

1. Shows slightly inferior vulcanizate properties
2. Exhibits cold flow.

1.6.4. Powdering/Granulation

The availability of plastic materials in granular form which could be delivered by container loads and metered automatically in a factory, stimulated technology developments in powdered and granulated rubber. Powdered rubber offers alternative processing routes to those normally used for mixing bale rubber in internal mixers. Lehnen[23] reported saving in mixing time by the use of powdered rubber. By granulating and sieving, powdered rubber having a wide range of particle size can be obtained. Commonly used granulated rubber is in the size range of 4 to 16 nm. Talc is used as the partitioning agent. It is still difficult to say whether the savings in processing on account of powdering/granulation are enough to offset the heavy premium on the modified raw material according to Wheelans[24]. Powdered rubber is prepared by spray and flash drying, particle encapsulation, cryogrinding, etc.

1.6.5. Thermoplastic rubber

Blending of NR with other synthetic rubbers provides added advantages in vulcanizate properties like abrasion resistance and heat build-up[25-27]. Mixing of NR with thermoplastics has resulted in a new range of materials such as thermoplastic NR and NR modified polypropylene. Mixing NR with polyolefines is normally carried out in an internal mixer. By varying the proportion of rubber and olefin, hardness and modulus of the blend can be adjusted. Elastic properties of the blends are improved by crosslinking[28]. Both sulphur and peroxide cure systems are employed. Interfacial adhesion and crosslink density are two important parameters in determining the properties[29]. Additives that provide a useful increase in impact strength usually affect processability adversely. Thermoplastic NRs are prepared by blending NR with other plastics such as polypropylene. These are a new generation polymeric materials with properties intermediate between rubbers and thermoplastics. These combine the properties of rubber with the easy processing character of thermoplastics.

1.7. CHEMICAL MODIFICATIONS

Owing to the presence of carbon-carbon double bonds, NR hydrocarbon may be considered an alkene in terms of reactivity. However, being a long chain molecule, intramolecular reactions involving more than one double bond in the same chain is possible. Cis 1,4 polyisoprene has a carbon atom at the double bond which is more reactive to both free radicals and carbonium ions than 1,4 polybutadiene. The typical addition reactions associated with the double bond suggest that the ultimate hydrogenated, halogenated, hydrohalogenated and isomerised diene polymers would have the same structure[30]. The reactions of diene rubbers which show anti Markonikoff addition, enhanced activity in the presence of peroxides and ultraviolet light, and inhibition by oxygen and chemicals such as hydroquinone, usually indicate that a free radical mechanism is operative.

1.7.1. Grafting

Graft copolymers are prepared by polymerizing monomers such as methyl methacrylate, styrene, acrylonitrile, maleic anhydride and acrylamide in the presence of NR. Grafting of different monomers impart improved properties to NR and the modified product finds use in special applications such as substitutes for high styrene resins in the manufacture of microcellular sheets for footwear, etc[31-33].

1.7.2. Hydrogenation

Hydrogenated NR is only a scientific curiosity, since it has never been produced commercially and may not be on account of the experimental problems usually associated with its preparation. The early processes required either highly purified rubber in dilute solution or the use of high temperatures that caused degradation. Addition hydrogenation requires its catalyst to come in contact with each double bond for the reaction, and thus large amount of catalyst is essential.

Hydrogenation of NR was first reported by Berthalot[34] and there had been a steady stream of research publications on the subject. Work by Pummerer and Burkard[35] and Harris[36] produced hydrorubber $(C_5H_{10})x$ from dilute solutions of purified rubber using platinum black as catalyst. Though only small amounts of hydrogenated rubber were obtained, these experiments showed that the elastic properties were retained along with a relatively high molecular weight. Many papers on diene polymer hydrogenation remained silent on the extent of degradation and cyclization reactions that may accompany the main process although Mango and Lenz[37] reported that cis 1,4 polyisoprene results in an alternating ethylene-propylene copolymer, though there had been little practical value in complete hydrogenation. It is interesting to note that when both gutta percha and balata, the trans forms of NR, are hydrogenated by similar methods, the result is a hydrocarbon rubber of essentially the same properties since the hydrogenation step removes stereo specificity.

Later developments led to the process of using relatively high concentrations of pale crepe rubber, in cyclohexane (2%), to react with hydrogen at 30 to 35 atmospheres, over nickel-kieselguhr catalyst in an autoclave at 200-220°C for 12 h. The fully hydrogenated product was obtained from the reaction mixture by removal of the catalyst by flocculation with glacial acetic acid followed by concentration and precipitation with alcohol. More recently Burfield et al.[38] investigated homogeneous two-component systems based on a variety of nickel and cobalt compounds in combination with triisobutyl aluminium. Complete hydrogenation has been achieved in solution after 1 h at 38°C using this system with nickel 2-ethylhexanoate. More economical methods have been developed, but technique such as spraying provide inadequate reduction owing to the slow diffusion of rubber.

Hydrogenated rubber is colourless and transparent. It is a plastic, elastic waxy solid with the peculiar elastic characteristic of forming threads when stretched. Unfortunately, the limited scale of its preparation so far has precluded the measurement of any technological properties. Fully hydrogenated rubber is chemically inert. It is difficult to vulcanize in conventional manner. Potential area of application is in cable industry, which could utilize its insulation properties. Partially hydrogenated materials still capable of crosslinking by residual unsaturation are of interest for a variety of possible applications including adhesives and rubber-to-metal bonding.

1.7.3. Hydrohalogenation

NR can be modified with hydrogen chloride, bromide, iodide or fluoride to give rubber hydrochloride, hydrobromide, hydroiodide or hydrofluoride respectively. Hydrogen chloride addition is the cheapest and the most feasible while the hydrobromide product is unstable. Hydrogen iodide addition has received only limited attention and hydrogen fluoride is toxic. The main aim of the modification is to reduce chemical activity of rubber by addition to the double bonds as in the case of halogenation[39]. The structure of rubber hydrochloride has been established by Bunn and Garner[40], who confirmed that the addition of hydrogen chloride to polyisoprene obeys Markonikoff's rule with the chlorine atom attaching itself to the carbon possessing least number of hydrogen atoms.

$$-CH2\ -CCH3 =CH\ -CH2\ -\ + HCl\ \text{---->}\ -CH_2\ -CCH_3Cl\ -CH_2\ -CH_2\ -$$

History of hydrohalogenation extents to the work by Weber[41] who produced "rubber hydrochloride" by passing HCl through a solution of NR in chloroform. The reaction is usually carried out by using a solution of NR in benzene. Hydrogen chloride is passed under pressure at 10°C for 6 h. Excess hydrogen chloride is removed by blowing air or by neutralization. The rubber hydrochloride is obtained by precipitation or steam distillation. Chlorine content of the product is 28 to 30%. The product is neither tacky nor brittle. The rubber hydrochloride is a highly crystalline material. It is unaffected by dilute acids and bases at room temperature. Hydrochlorination of NR usually yields a polymer with slightly less than the theoretical chlorine content of 33.5% for complete reaction. NMR studies by Golub and Heller[42] have established that cyclization reaction occurs during hydrohalogenation that accounts for this discrepancy. On the commercial scale, NR hydrochloride is manufactured either by reaction in solution or in a positively charged latex. The polymer is a tough semi-crystalline elastic material. It was being marketed as a raw material for packing film and as a rubber-to-metal adhesive. However, it has become less popular by the advent of plastic films.

Addition of hydrogen bromide to NR was reported by Harries[43] and Hinrichsen et al.[44]. The reaction was similar to that of hydrogen chloride, but the product was relatively unstable owing to the lability of its halogen atom. Hydrogen iodide addition was also carried out. The reaction of NR with hydrogen fluoride has been described by Tom[45]. By suitable selection of solvent and temperature the side reaction of cyclization was considerably reduced to yield a product with 65 to 70% addition. The product was found to have good strength on vulcanization like NR, less swelling in hydrocarbon oils and lower permeability than butyl rubber. The toxicity of hydrogen fluoride combined with its high cost has been economically discouraging.

1.7.4. Chlorination

Chlorinated rubber was one of the first modified forms that has found some real commercial application. During chlorination, substitution and cyclization reactions also occur whether the modification takes place in solution, in latex or in solid rubber. Chlorination can also be done using depolymerized NR[46]. The reaction happens in three different stages according to Bloomfield[47] and Kraus[48]. Completion of the first stage corresponds to 35% chlorine and the material is still rubbery. After the second stage the product contains 57% chlorine, and no unsaturated groups remain. It is a crumb like material and possesses no rubbery properties. Further chlorination yields a product with 65.5% chlorine and is in close agreement with the empirical formula $-C_{10} H_{11} Cl_7-$.

Chlorinated rubber containing approximately 65% chlorine used to be available under the trade name Alloprene (ICI), Parton (Hercules), etc. In India chlorinated rubber is being produced by Rishiroop Polymers under the trade name Chlorub. During the preparation of chlorinated rubber removal of the last traces of solvent used in the process is extremely difficult, hence low density foams can be obtained by heating the commercial products in a press and opening the mould when hot[49].

Chlorinated rubber is a pale cream or off-white thermoplastic powder, non inflammable and highly resistant to chemical attack. It is mainly used in chemical and heat resistant paints and coatings to combat corrosive environment. Chlorinated rubber is dispersed in a suitable solvent and mixed with appropriate plasticizers and pigments. Such paints usually contain 10 to 20% chlorinated rubber and can be applied by brush or spray. In addition to being used to protect wood, steel, cement, etc. from environmental attack, these paints have been applied to chemical equipments as they also posses a degree of abrasion resistance. They have been recommended as traffic paints on roads. Chlorinated NR has also been used in fire retardant applications, adhesives, printing inks, paper coatings and textile finishes. Chlorinated polychloroprene has replaced chlorinated NR to a very great extent.

1.7.5. Isomerization

Cis-trans isomerization of 1,4 polyisoprene has been achieved in the 1950's. A variety of chemicals including selenium, sulphur dioxide and butadiene sulphone were effective isomerization agents. An equilibrium cis content of 45% has been found for all the different methods. Partially isomerized NR has been of some interest as non-crystallizing according to Cunneen and Higgins[50], in view of the rubberiness at low temperature than usually experienced with NR in the vulcanized state. Commercially, however the material has not been able to compete with oil extended or plasticized rubber blends in particular these containing polybutadiene or with synthetic polyisoprene.

1.7.6. Cyclization

There are some evidences to indicate that cyclization was the first chemical modification on NR since it was reported by Bedford and Wilkinson[51] that in 1791 Leonhardi observed that NR treated with sulphuric acid became hard and brittle. Cyclization results in a less elastic product. Flory[52] has calculated that 13.5% of the isoprene units would end up as rings and the final unsaturation should be about 57% of the original. The 3,4 isoprenes have been used by Golub[53] to produce ladder polymers. Cyclized NR has been of some use in providing stiffness to diene rubber vulcanizates without materially increasing the density. It is a competitor for high styrene resins. Further there are a number of elastomers blended with cyclised rubber that possesses this property without the need to add stiffening fillers, are available today.

1.7.7. ENPCAF modification

To some extent, ethyl N-phenylcarbamoylazoformate (ENPCAF) modified NR is only a scientific curiosity like hydrogenated natural rubber. This modification gives an indication of the influence of polar pendant groups on the physical properties of NR[54-57].

The work by Knight et al.[58] indicated that ethyl N-phenylcarbamoyl azoformate might have a practically useful rate of addition to NR and its use as a means of chemically modifying rubber itself has been studied by Barnard et al.[59]. The modification can be carried out either in the latex stage or in dry rubber in an internal mixer or a mill in about 7 m at 110°C or in latex stage in a few hours at 33°C. The addition reaction results in the formation of hydroester pendent groups.

ENPCAF modified NR can be vulcanized with sulphur systems in the normal way. Generally peroxide systems are preferred above 2% to 15% modification. The modification increases glass transition temperature (Tg) of the polymer. In practice the modified rubbers are highly damping compared to NR. In addition, gas permeability and solvent resistance also improve. However, ENPCAF modified NR never became a practical proposition, because of the high costs that would have been involved for the levels of the modification that were required for significant changes in properties.

1.7.8. Maleic derivatives

The interest in the reaction of diene and maleic anhydride was first prompted by Diels Alder reactions occurring between simple conjugated dienes and activated unsaturated compounds, even though the polymer unsaturation in the diene polymer was not conjugated. Bacon and Farmer[60] showed that the reaction between NR and maleic anhydride was accelerated by benzoyl peroxide. Infrared studies have indicated that on reaction of polyisoprene with maleic anhydride there is no loss of unsaturation nor any change in cis-trans ratio. It has been shown by Pinazzi et al.[61] that the reaction can be accelerated by a variety of catalysts such as azodiisobutyronitrile and chlorobromodimethyl hydantoin as well as peroxides. This is clear evidence that the reaction involves a free radical mechanism rather than a specific mechanism involving a peroxide group. The degree of addition (expressed as the number of maleic anhydride units added per 100 polyisoprene units) is usually less than 25. The tendency of the product to gel has been solved by the addition of amines like diethylamine. Addition of maleic anhydride to NR at 22°C was suggested by Le Bras et al.[62]. Over the years there had been some interest in vulcanized maleated polyisoprenes because of their superior solvent resistance, flex cracking resistance and ageing resistance compared to NR vulcanizates. However, due to the ready availability of polymers such as plasticized PVC, ethylene vinylacetate copolymers and the polyurethane rubbers, maleated rubber has not become commercially significant.

1.7.9. Epoxidation

Epoxidation of NR and other unsaturated elastomers is of great interest these days. The reaction was first reported by P~~l~~ummerer and Burkard and later investigated by Roux et al.[63]. Trialkyl ethylenic double bonds of NR are well known to react very readily with peracids to yield epoxide groups. Economy of modifying NR in latex stage with hydrogen peroxide/formic acid has led to this process being extensively studied by Span[64] and Gonovskaya et al.[65]. In spite of their apparent promise, these reactions often led to materials containing products of subsequent ring opening reactions[66-67] and thus provided little interest. Even the introduction of epoxide groups into NR at low level of crosslinking by Colclough[68] in 1962 proved to be a failure owing to lack of reactivity. Due to ring opening side reactions a product of consistent quality was not produced at large. The process carried out under controlled condition at the Malaysian Rubber Producers Research Association was a landmark in the development of this modified form on NR. Gelling[69] established that acid concentration and temperature of epoxidation controlled the extent of secondary ring opening which in turn, substantially affected the properties of the material. Furani~~s~~zation could be avoided and epoxidation of NR became possible with limited undesirable side reactions[70]. The 50, 25, and 10 mol% epoxidised materials have been termed as ENR-50, ENR-25, ENR-10 respectively. Furani~~s~~zed products give leathery, limp vulcanizates. Theoretically any level of epoxidation can be achieved, but practically up to 50% is used. Epoxidation has been shown by ^{13}C NMR to be random with one, two and three adjacent epoxide groups present at levels consistent with those predicted.

ENR can be vulcanized with a normal sulphur formulation used for NR but they possess poor ageing resistance than NR as reported by Gelling and Smith[71]. ENR can be reinforced with silica without coupling agents. In tyre tread ENR gives better wet traction and rolling resistance. It has good resistance to hydrocarbon oils. Epoxidised NRs are reported to have improved solvent resistance, adhesion and also improved resistance to gas permeation. First commercial production of epoxidised NR started in Malaysia in 1989. Conditions for pilot plant production of ENR were optimized by George et al.[72].

1.7.10. Depolymerization

Many polymers are already available in the market in their oligomeric forms. Of the synthetic rubbers that have been offered in liquid or semiliquid forms, liquid silicones and liquid butadiene rubbers have found wide acceptance amounting to 35,000 tonnes and 20,000 tonnes a year respectively in 1990. Synthetic rubber oligomers are readily prepared by controlling the degree of polymerization during the course of production starting from their respective monomers. Unlike other polymers NR is unique in its production from the plant as high molecular weight material and therefore, depolymerization techniques are to be adopted in converting it into the low molecular weight oligomers. However, the mechanical properties of liquid NR vulcanizates are inferior to those of its high molecular weight counterpart. The problem is that a molecular weight low enough to produce a liquid or sufficiently fluid rubber is too low to yield a good crosslinked network on vulcanization. There are too many loose chains or chain ends. As a result they cannot be used as fully satisfactory replacements of solid rubber. Progress in this end demands a chemical breakthrough. Furthermore, the liquid rubbers are currently more expensive than their solid counterparts and their use is restricted to applications in which either the use of liquid form is essential during fabrication, or there are specific technological advantages resulting from its use as an additive in which it replaces existing materials.

1.8. Liquid rubbers

Conventional vulcanized elastomers contain very long molecules connected into a continuous network by means of occasional crosslinks. The flexible and mobile chains provide high extensibility to the vulcanizates. The retractive force following deformation is essentially entropic in origin and depends on the freedom of the chains to undergo easy thermal motion with respect to one another. Hence elastomers are based on polymeric molecules, that at ambient temperatures are far above their glass transition temperature. They are also amorphous (in the unstrained state at least) and are relatively free of polar or bulky side groups.

The molecular weight between crosslinks required to provide a suitable balance between high extensibility, elastic recovery and strength properties is of the order of 10,000. Consequently the molecular weight of the polymer must necessarily be high. Otherwise, the proportion of dangling chain ends which cannot contribute either strength or elasticity will become excessive. In the case of butyl rubber the molecular weight should be as high as 100,000[73]. The term 'liquid' implies easy pourability at ordinary temperatures, and in general, this means a molecular weight in the region of 5,000. Physical properties like strength can be obtained only if the liquid polymer chains are connected end to end, during cure so as to be capable of forming a finished network with a few free ends and with appropriate average chain lengths between the crosslinking sites. Telechelic polymers with terminally reactive end groups have been extensively investigated[74-84]. Such polymers can also be reinforced with carbon black and other fillers. This has been subjected to extensive investigations by Dannenberg[85] and Kraus[86]. Telechelic polymers are capable of providing strong elastomeric products.

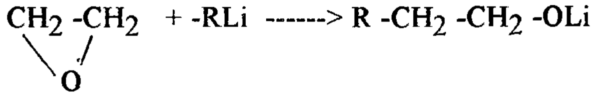
Commercially produced first synthetic elastomer of this kind was polysulphide in 1920's (R--S--S---R'). The curing of the telechelic polymer to form elastic network requires both chain extension and crosslinking mechanisms. Crosslinking is generally carried out by oxidation reaction to form disulphide linkages. Lead oxide is commonly used in formulations to be cured at room temperature. Moisture cure of one component polysulphide sealants is accelerated by the use of organic additives.

Liquid silicones technology also relates to telechelic liquids. The polymers are based, in general, on dichlorodimethyl silane as the prominent monomer. Polymerization occurs via hydrolysis followed by condensation according to the following sequence:-

$$n(CH3)_2\ SiCl_2 + n\ H_2O \text{ ------> } HO[(CH_3)_2\ SiO]_n\ H\ +\ 2n\ HCl$$

Silicones are available in a wide range of properties and molecular weights in both high temperature vulcanizing (HTV) and room temperature vulcanizing (RTV) forms. Polyurethanes containing -NHC(O)O group are also industrially important and are used in continuous foam production, liquid injection moulding, etc.

Terminally active hydroxyterminated polybutadiene is also extensively used. This is prepared by anionic polymerization technique. To form terminal hydroxyl groups, ethylene oxide is added followed by acid hydrolysis.



$$\underset{\diagdown\ O\ \diagup}{CH_2\text{-}CH_2}\ + \text{-}RLi \text{ ------> } R\ \text{-}CH_2\ \text{-}CH_2\ \text{-}OLi$$

$$R\ \text{-}CH2\ \text{-}CH2\ \text{-}OLi\ \ + HX \text{ ------> } R\ \text{-}CH2\ \text{-}CH2\ OH + LiX$$

Commercial development of this technology was developed in United States in 1960's. As with all other terminally reactive polymers, subsequent reactions may be caried out to change the nature of the end groups. For example, it can be esterified with acrylic acid. Curing with esters of phosphoric acid was explored as a possible route to enhance flame resistance [87]. Curing of hydroxyterminated polymers by chelation has been described by Kambara and Aotani [88]. Hydroxy terminated polybutadiene is used as a binder in rocket propellants.

1.9. Economics of chemical modification

Synthesis of NR is determined entirely by the rubber tree. There is yet, no procedure for planned incorporation of monomer units into rubber backbone during the biosynthesis process within the tree. In this respect, NR is at a disadvantage relative to its synthetic competitors, which are frequently the products of carefully manipulated copolymerization process. Therefore, it must rely entirely on modification of the preformed polymer when modified materials are required.

Two major categories of modification are those at low levels that maximize the utility of inherent elastic properties of the polyisoprene backbone (e.g., vulcanization) and those at high levels which cause a major change in fundamental physical behaviour (e.g., formation of ebonite). NR is comparable in price to the more expensive grades of polyethylene (PE) and polypropylene (PP) and emulsion grades of styrene butadiene rubber (SBR). It is significantly cheaper than synthetic polyisoprene (IR), butyl rubber (IIR), ethylene propylene rubber (EPDM) and polychloroprene (CR) and an order of magnitude cheaper than very highly specialised elastomers [89]. The cost of modification added to the cost of raw NR in many cases is below that of the corresponding synthetic materials, making the process viable and worthwhile.

1.10. Degradation and stabilization of polymers

The morphological and chemical changes accompanying the exposure of polymers to elevated temperatures in both inert and oxidizing atmospheres have received great attention in recent years. Polymer stability is generally referred to as the serviceability of the material with respect to one or more physical properties of concern. The polymer may change without loss in weight, without change in spectral behaviour of the substance or in the electrical or mechanical properties and without any observed change in heat content. On the contrary it is far more reasonable to approach the stability of polymer from the opposite extreme, i.e., the ability of the polymer to degrade. When a polymer system (plasticized or pigmented) is exposed to air in an outdoor environment, processes such as oxidation, photolysis, mechanical stresses from expansion and contraction due to variations in temperature, thermal degradation, plasticizer volatilization, photo sensitization, crystallization and potential catalysis of numerous decomposition reactions by pigmenting substances can be envisioned. A few of the above phenomena can be responsible for the deterioration of the sample. Various parameters of interest are change in molecular weight of the substance as a function of temperature, viscosity of depolymerized liquid obtained as a function of temperature, viscosity of the converted material as a function of duration of heating, etc. Viewing the polymer as a liquid, the molecules exist as a group of irregular and free flowing intercoiled chains. A specific polymer molecule is continuously changing its own conformations about each bond capable of rotating with respect to any given site along the chain. It is also changing quite randomly in its relationship to its neighbours in molten phase. The greater the ability of the groups to rotate, the greater will be the entangling and coiling of the polymer system. With respect to such a molecular array, as the chains become less mobile and motions requiring relatively high energy ceases (for example all motions other than those which are quite localized) during cooling, some molecular configuration will be frozen into the system. If due to lack of interaction or short range dipole-dipole interaction, the structure is a random one, the polymer happens to be amorphous. On the other hand, a certain degree of molecular alignment can occur during cooling of the melt with portions of the chains having a uniform relationship with respect to one another in the three dimensional arrangements. The polymer containing such alignment or chains (or coils) can be said to be semicrystalline. The degree of crystallinity depends on the size and number of such areas in the solid polymer mass.

1.10.1. Thermal degradation.

Thermal degradation of polymers can be divided into two general categories according to Conley[90]. The first type, random chain scission, can be visualized as a reaction sequence approximating the reverse of polycondensation. Chain scission occurs at random points along the chain, leaving fragments of relatively high molecular weight (i.e., scission of the high molecular weight chain produces molecules of x and n-x molecular weight where both x and n-x are large compared to monomer units). For all practical purposes it can be assumed that no monomer is liberated and weight loss due to volatile product is nearly negligible. In such a case a scission produces a new molecule. The problem of evaluating the amount of degradation then becomes one of counting the number of polymer molecules.

The second type of degradation process is essentially depolymerization in which monomer units are released from the chain ends. Such a process is viewed as the opposite of the propagation step in addition polymerization. This process is encountered most prevalently with vinyl monomers and cyclic monomers. Theoretically the process is reversible like any chemical reaction. As the temperature is raised, from a kinematic point of view, polymerization rates of monomer and the depolymerization to monomer become equal. In thermodynamic terms the temperature at which this occurs (where the polymer and monomer have equilibrated) is called a ceiling temperature (Tc). Both reactions can occur simultaneously in a polymer chain or any one of them may occur, depending on the temperature, the initiating agent etc.

1.10.2. Oxidative degradation

Action of molecular oxygen can be considered as one of the most important reactions a polymer may undergo when exposed to an oxygen containing atmosphere. The effect of oxygen on polymers under a wide variety of conditions including uses in wire insulation, paint products, automotive products, etc. has been a matter of concern for a very long time.

The generally accepted free radical chain reaction for auto-oxidation of hydrocarbon is

Initiation:

Production of R* or RO2* (by light, heat, decomposition of peroxides, gamma rays, etc

Propagation:

$R^* + O_2$ -----> RO_2^*

$RO_2^* + RH$ -----> $ROOH + R^*$

Termination:

$2R^*$ -----> R--R

$RO_2^* + R^*$ -----> $ROOR$

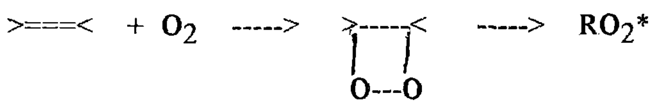
$2RO_2^*$ -----> non-radical products

RH in this scheme denotes the hydrocarbon and H the most labile hydrogen atom.

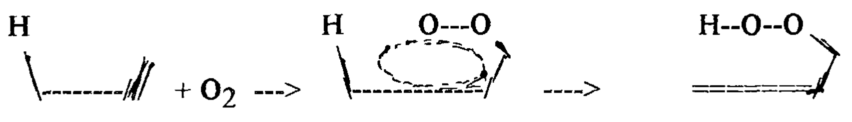
1.10.3. Oxidized rubber

The oxidation process that occurs during normal ageing of NR involves uptake of less than 1% by weight of oxygen. In case of rubber oxidized in the presence of a catalyst the oxygen content may be as high as 15%. In an analysis of NR with 13.3% oxygen content the following levels of oxygen in functional groups have been found: --OH 4%, =CO 0.9%, acid -COOH 0.3%, --OOH 0.06%. The remaining 7.4% of oxygen may be present in epoxy or ether groups.

Direct addition of oxygen to a double bond in the case of NR has been reported by Barnard et al.[91].



Perhalo olefins have been reported to react directly with oxygen to form radicals. Photo sensitized reactions also have been shown not to involve addition of oxygen to a lone double bond. In such cases, however, hydrogen peroxide can be formed directly.



Reactions with oxygen in the excited singlet state gives products similar to those obtained in photosensitized reactions.

1.10.4. Termination

Termination of depolymerization can be categorized into different groups like interaction by peroxy radicals, reaction by alkoxy radicals, unimolecular termination by peroxy radicals and termination by inhibitors.

In liquid phase oxidation reactions generally products formed in the termination reaction are minor and for the same reason chemistry of termination reactions are difficult to establish. Further, this is dependent on the oxygen pressure. At higher oxygen concentrations most of the reactions involve interaction of two peroxy radicals. Variations have been reported at lower pressures of oxygen and different hydrocarbons [92]. Reactions involving alkoxy radicals, directly leading to chain termination reactions are:

2RO* ------> ROOR and

2R' R" CHO -----> R' R" CHOH + R' R" C=O

When alkoxy radicals are produced in reaction that involves peroxy radical, such as epoxidation, the rate determining step will be rather first order. Amines and hindered phenols may react with peroxy radicals to two oxidation chains.

$RO_2^* + IH \text{ -----> } ROOH + I$

$2I^* \text{ ------> }$ non-radical products.

$RO_2^* + I^* \text{ -----> }$ non-radical products.

Various heterolytic reactions are also possible during autooxidations. It is possible, for example, for hydroperoxides to be decomposed to phenols [93], sulphides, amines, acids or bases that produce no initiating radicals.

a) $C_6H_5OH + ROOH \dashrightarrow C_6H_4(OH)_2 + ROH.$

b) $ROOH + R_2S \dashrightarrow ROH + R_2S \dashrightarrow O$

c) $R_3C{-}{-}OOH + H+ \dashrightarrow R_2C{=}O + R{-}OH$

d) $ROOH + OH \dashrightarrow RO_2^- + H_2O$

$RO_2^- + ROOH \dashrightarrow RO^- + ROH + O_2$

Heavy metals may act as inhibitors by converting the peroxy radical in carbonium ion[94]. Furthermore, Russel[95] has reported that hydrocarbons with highly acidic hydrogens that oxidize slowly in organic solvent can be oxidized in basic solution by an electron transfer reaction:-

$$RO_2^* + R^- \dashrightarrow RO_2^- + R^*$$

$$O_2 + R^- \dashrightarrow R^* + O_2^{*-}$$

1.11. Depolymerised NR

Production of well-defined resinous materials from rubber by catalyzed oxidation reactions has been caried out by Stevens and Stevens[96]. They called these "rubbons" and found that certain metallic salts profoundly intensified oxidation and simultaneously reduced the solution viscosity of the rubber to which a small proportion(2.5%) of cobalt linoleate was added. Complete oxidation was effected after 8 h at 80°C. After distilling off the solvent, a clear thick amber material remained whose composition approximated to $(C_5H_8)_2O$. The oxidation yielded a soft elastic material. Further developments made in oxidative degradation of rubber used solutions containing 50% rubber in white spirit, the rubber having been milled with 2.5% cobalt linoleate. These solutions were oxidized under pressure in an autoclave to give rubber resin. Later they found that they could make rubber resins without using a solvent. Rubber resins could be prepared by milling the rubber with oxidation catalysts and exposing a large surface to the atmosphere. The rubber was then heated at 80°C for a short time. Rubbon could be mixed quite satisfactorily with other resins.

Thermal history of solid rubber has been reported by Van Rossem who had at an earlier date concluded that when rubber was heated in air, first of all it is depolymerized or degraded and then oxidized. This opinion was supported by Kohman[97] and Grenquist [98] also who investigated the effect of heating rubber in air and oxygen. From plasticity tests it was concluded that the effect was disaggregation of rubber prior to oxidation. When heated in air at 150°C marked oxidation was observed after 60 minutes, first noticeably as a surface effect that then spread into the entire rubber mass.

1.12. Scope for present work

Processing of rubber compounds still remains a difficult task despite recent progresses in machinery, equipment and automatic process control. The heterogeneous nature of rubber compounds, the strong interactions between various components, the viscous nature of elastomers and poor understanding of the flow behaviour of such complex materials can be attributed to the above. Compounding changes are frequently made in order to meet new specifications for finished products or to compensate for variations in properties and quality of raw materials.

Modifications of polymers have unfolded different schemes that have developed at an unprecedented rate in recent years. Early modifications were rather random work and the molecular structure for the most part was uncertain and imprecise. Later modifications such as grafting, epoxidation, conversion to thermoplastics, etc. have been thoroughly planned with specific targets aimed at. The ability to adapt NR to compete with modern synthetic elastomers is quite a remarkable achievement since they make use of a natural resource material. It will indeed be interesting to see what the future holds for modification of NR in the next decade.

In rubber compounding the viscoelastic material consisting of polymer, filler, etc. has to be processed and formed to shape. Its rheological properties may need to be adjusted by addition of oils, esters, waxes, factice and other substances. To prevent or delay degradation failure of rubber by oxygen, ozone, light, heat and other influences various additives are often used. To make cellular products, to impart flame retardance, to ensure adhesion to textiles and metals, to develop electrical conductivity, etc. special compounding techniques are necessary.

Compounding is done to incorporate the essential ingredients and ancillary substances necessary for vulcanization. By compounding, hardness and modulus of the vulcanized products are adjusted to the required values. Closely associated with these processes is the addition of fillers that impart high tear strength and high abrasion resistance. Wide range of carbon blacks are used for reinforcement. The finer the particle size, the higher the modulus and strength. Certain esters of organic acids or phosphoric acid and high molecular weight alcohols are used as plasticizers in circumstances where petroleum oils may be unsuitable. Plasticizers give polymeric compounds suitable viscosity for processing, aid the incorporation of fillers, give the vulcanizates required stiffness and provide flexibility at lower temperatures. Dibutylphthalate, dioctylphthalate, dibutylphosphate and trixylylphosphate are commonly used. Higher molecular weight polymeric plasticizers show lower volatile loss or loss by extraction. Polymerizable and crosslinkable plasticizers are also used under certain circumstances with various vulcanizing systems. They act as plasticizers and tackifiers contributing to high hardness and stiffness in vulcanizates and increase the state of cure by participating in the crosslinking reaction.

With the increasing use of polymeric materials in civil engineering including residential and public buildings, much stress is being given these days upon reducing fire hazards normally applicable to conventionally used polymers. Flame proofing is the reduction in fire hazards. This is achieved by incorporation of inorganic materials such as antimony trioxide, zinc dust, chlorinated paraffins, etc. It is believed that halogenated paraffins decompose to yield chlorine which immediately forms antimonytrichloride, which in turn, acts as flame retardant. On the other hand zinc borate and phosphorus containing flame retardants are believed to act as crust forming agents.

A wide range of bonding additives, that increase the polar nature of hydrocarbon rubbers, are used to increase adhesion to various substrates. Cobalt based salts, chlorinated NR, etc. are used for this purpose. A number of patented products employing various additives such as chlorinated rubber are available in this connection. Materials with very limited compatibility will bloom to the surface of rubber and act as surface lubricants between metal surface of the processing equipment and the rubber compound. When the process aid exhibits low or medium compatibility the material will act as an internal lubricant improving slippage between 'flow units' of the compound.

In the national scenario of India there had always been a lagging of production behind the demand in the case of NR. With the introduction of new clones and extension of rubber cultivation ~~of more land~~, this difference is reducing[99]. Demand for and production of NR from 1992-93 to 1995-96 are given in Figure 1.2. At this juncture it is worthwhile developing new applications for NR.

Depolymerized liquid NR is a modified form that can be used in a variety of applications. The present study on liquid NR envisages the following aspects.

1. Characterization and viscosity studies on LNR of different molecular weight.
2. Chemical modifications of the depolymerized rubber by phosphorus addition.
3. Applications of LNR as a bulk viscosity modifier in nitrile rubber compounding.
4. Applications of phosphorus modified liquid NR as a flame retardant in NR.
5. Modification of bitumen using LNR as a polymeric additive for enhancement of properties.
6. Stress relaxation of NBR compounds containing LNR.

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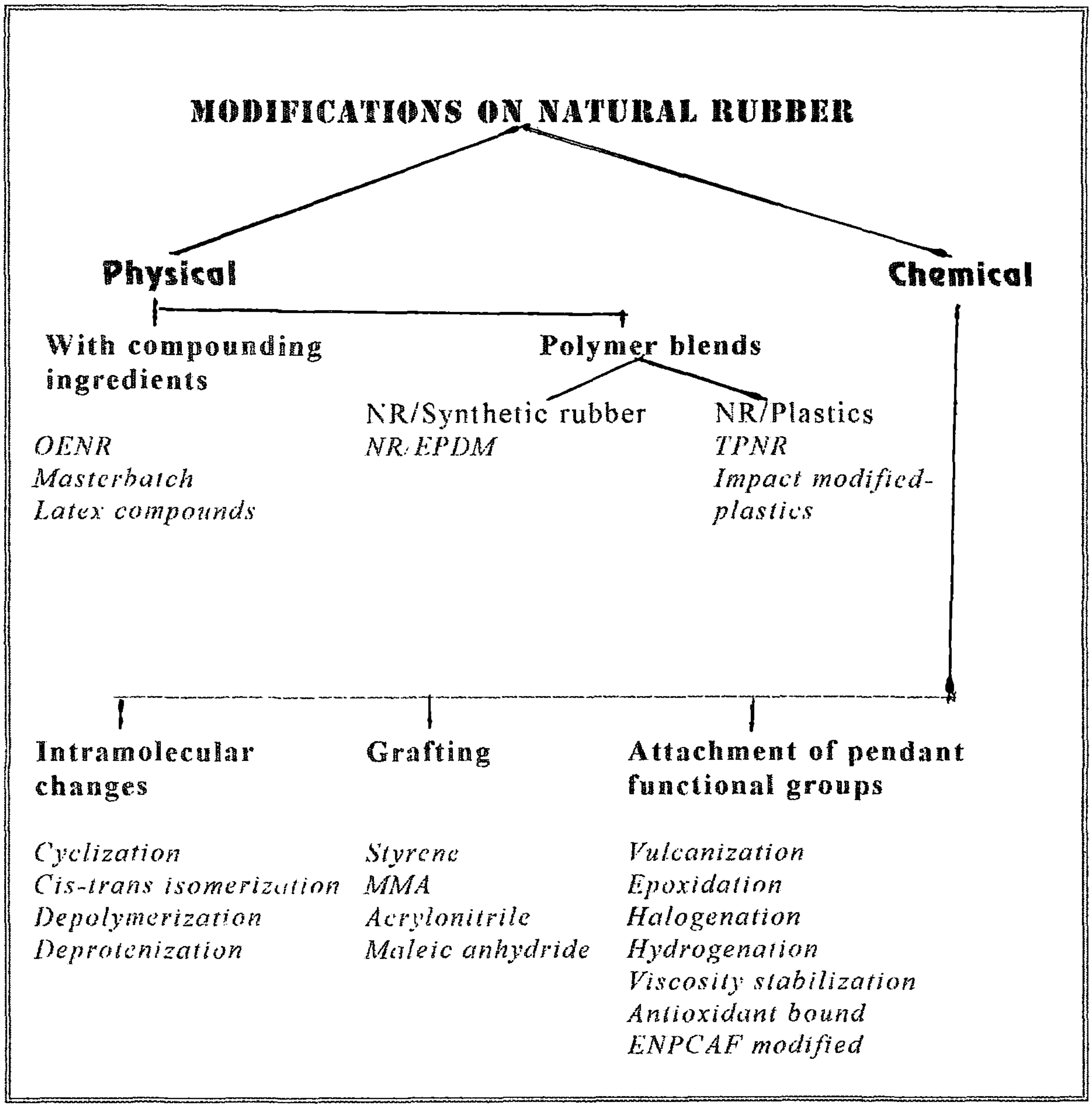

Fig. 1.1 Modifications on NR.

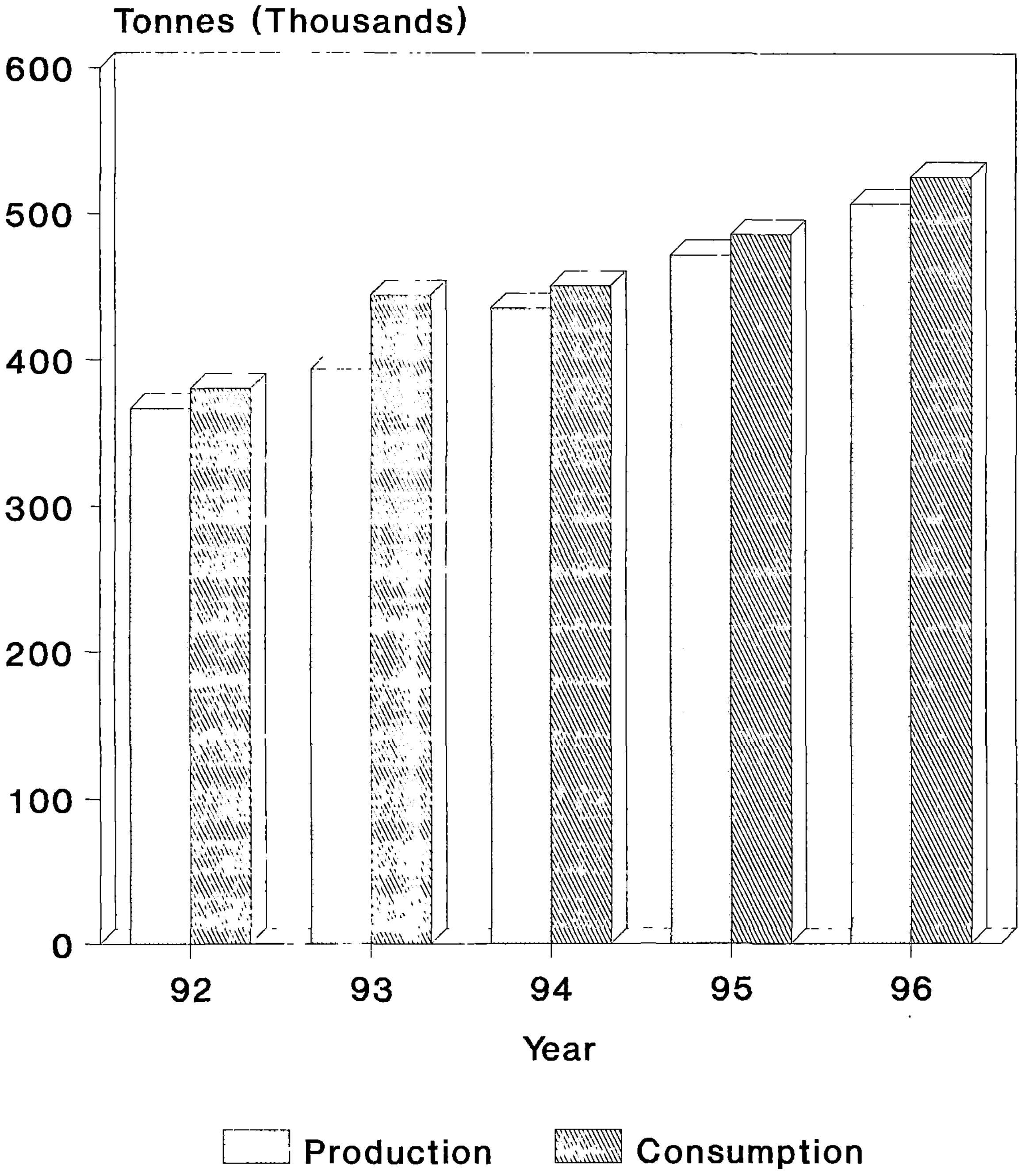

Fig.1.2. Natural rubber in India

Chapter 2.

EXPERIMENTAL TECHNIQUES

2.1. EXPERIMENTAL MATERIALS

2.1.1. Natural rubber

NR used for thermal depolymerization was crumb rubber prepared at the Pilot Crumb Rubber Factory, Rubber Board, Kottayam. The rubber conformed to the Bureau of Indian Standards specifications for ISNR 5 grade. The specification parameters and their limits for ISNR 5 are given in Table 2.1.

Table 2.1. Specifications of ISNR 5 (IS 4588-1986).

Dirt content, % max.	0.05
Volatile matter, % max	0.8
Nitrogen, % max.	0.6
Ash, % max.	0.5
Initial plasticity, Min.	30
Plasticity retention index, Min.	60

Since basic properties such as molecular weight, molecular weight distribution and concentration of non-rubber constituents of NR are being affected by clonal variation, season, use of yield stimulants and methods of preparation[1-2], the same block of NR was used for preparing different samples of depolymerized rubber. For the latex stage depolymerization, centrifuged latex of 60% dry rubber content (DRC) preserved with ammonia was used.

2.1.2. Peptizing agent

Activated pentachlorothiophenol (Renacit 7), supplied by Bayer (India) Ltd. was used as the peptizer. It was incorporated into the dry rubber during mastication on a laboratory two-roll mill.

2.1.3. Nitrile rubber

Butadiene acrylonitrile copolymer of medium acrylonitrile content, Chemaprene N-3309 supplied by Synthetics and Chemicals Ltd., Bareilly was used for the preparation of nitrile rubber compounds. The detailed specifications of this rubber are given in Table 2.2.

Table 2.2. Specifications of nitrile rubber

Volatile matter, % max.	0.75
Ash, % max	1.0
Antioxidants, %	1.0
Bound acrylonitrile content, %	31-35
Mooney viscosity $M_{L(1+4)}$ at 100°C	40-60
Soap, %	0.05

2.1.4. Rubber chemicals

All the chemicals used for the preparation of rubber compounds were of industrial purity.

Accelerator: N-cyclohexyl-2-benzothiazyl sulphenamide, (Vulcacit CZ), was of commercial grade, obtained from Bayer (India) Ltd.

Carbon black: Semi reinforcing black, SRF N-762, supplied by Phillips Carbon Blacks Ltd., Durgapur.

Zinc oxide: Specific gravity 5.5.

Stearic acid: Specific gravity 0.92.

Dibutyl phthalate: Reagent grade.

Sulphur: Elemental sulphur (specific gravity 1.9).

2.1.5. Other chemicals

Dibutylphosphate: ($C_8H_9O_4P$) ($\bar{M}w$ 210.21) of purity greater than 97% manufactured by Fluka A.G. was used for the phosphorus modification reaction on epoxidised liquid NR. Latex stabilizer used for stabilizing the concentrated latex before depolymerization, was Elfapur N 150 manufactured by Akzo Chimie. Chemically it is nonylphenyl ethoxylate. This non-ionic stabilizer was available as 100% paste.

2.2. DEPOLYMERIZATION

2.2.1. Thermal

The apparatus for thermal depolymerization consisted of a vessel that is electrically heated to 250°C. Using a programmable digital temperature controller, the temperature of the vessel was maintained at the desired level within ±1°C. A stirrer, 100 rpm 0.5 HP was used to homogenize the contents of the vessel. The temperature of depolymerization was measured using a glass thermometer inserted into the side jacket of the reaction vessel.

Rubber was masticated on a two-roll mill at a friction ratio of 1:1.25. Uniform mastication was effected on all the samples applying the same weight of the polymer, nip gap and mastication time. The final sheet was milled out at 3mm nip gap. The sheets were cut to pieces and loaded into the depolymerizer and heated to the desired temperature. Stirring was started after the rubber mass has softened. Heating and stirring were continued for a predetermined time and at the end of the process the liquid mass was poured out of the depolymerization vessel.

2.2.2. Chemical

Chemical depolymerization of NR was effected by the action of phenylhydrazine-oxygen redox system in latex stage[3]. The apparatus consisted of a three necked, double jacketed reaction vessel with provisions for stirring, oxygen inlet and an outlet for gases.

Centrifuged latex was deammoniated and stabilized with the non-ionic stabilizer, Elfapur N-150. It was taken in the reaction vessel and phenylhydrazine was added and oxygen bubbled through the system. The reaction was allowed to progress for 24 h. Depolymerized rubber was recovered from the reaction mixture by drying in thin film. It was characterized and used for further modifications.

2.3. COMPOUNDING

The mixes were prepared on a laboratory scale two-roll mill (15 cm x 30 cm) at a friction ratio of 1:1.25. The rubber was masticated, to attain a Wallace rapid plasticity (100°C, 1 cm platen) of about 40, by careful control of temperature, nip gap, time of mastication and uniform cutting operation. The compounding ingredients were added as per ASTM specification D 3182-89[4] in the following order - activators, fillers, plasticizers, accelerators and sulphur. Before the addition of accelerator and sulphur the batch was thoroughly cooled.

After completion of the mixing, the stock was sheeted out and passed six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm. Mixing time and temperature were controlled during the studies. While incorporating sulphur the temperature of the rolls was maintained at 35 to 40°C

2.4. VULCANIZATION

Vulcanization to optimum cure was carried out in a 45 x 45 cm hydraulic press having steam heated platens maintained at a temperature of 150°C and pressure of 45 kg/cm^2 on the mould. Mouldings were cooled quickly in cold water at the end of the curing cycle and stored in cool and dark for 24 h before subsequent physical tests. For samples having thickness more than 6 mm, additional curing time based on the sample thickness was allowed to obtain satisfactory mo$\overset{u}{\wedge}$l~~u~~dings. Optimum cure time was determined by the following equation:-

$$\text{Optimum cure} = 0.9\,(L_f - L_i) + L_i \quad \text{------------(2.1)}$$

where L_f and L_i are maximum and minimum torque respectively.

2.5.VISCOSITY MEASUREMENTS

2.5.1. Low viscosity.

Viscosity of solutions of depolymerized rubber was determined using an Ubbelhode glass viscometer.

2.5.2. Medium viscosity

2.5.2.1. Brookfield viscometer:

For the viscosity measurement on liquid NR a Brookfield viscometer (RVT Model) was used. The samples were conditioned at 38°C before determination of viscosity. Appropriate spindles were chosen to obtain readings within 20 to 80% of the scale and the corresponding multiplication factors were used for calculation of viscosity.

2.5.2.2. Rheomat 30

For the rheological characterization of liquid NR, Rheomat-30, manufactured by Contraves A.G., Switzerland, was used. It is a multi-speed rotational rheometer with a precision measuring system[5]. The instrument has an electronically controlled drive that produces known and selected shear rates. The torque measuring head measures the shear stress required to maintain the shear rate. The drive control system can be programmed to change the rate of shear continuously so that flow behaviour of the material can be plotted automatically as a rheogram (shear stress Vs shear rate). Alternatively the shear rate can be held constant and a plot of viscosity against time can be obtained. One of the four torque ranges given below suiting the viscosity of the sample under investigation was selected.

0 to 4.91 x 10^{-3} Nm (50 cmg)
0 to 9.82 x 10^{-3} Nm (100cmg)
0 to 19.6 x 10^{-3} Nm (200 cmg)
0 to 49.1 x 10^{-3} Nm (500 cmg)

With the built-in program, an ascending shear rate was applied to the sample under investigation. For the measurements with respect to temperature the samples were heated in an air oven and stabilized at that temperature before carrying out the measurements.

2.5.2.3. Haake Rotoviscometer RV 12.

Viscosity studies were also carried out on a rotoviscometer made by Haake, Germany[6]. The equipment consisted of a measuring drive unit, sample cup, sensor system and temperature vessel connected to a constant temperature bath (Fig. 2.1 and 2.2) The drive unit used was M150 with maximum torque 1.47 Nm. Sensors suitable for the test liquid viscosity and shear rates ~~a~~were selected to accommodate the torque values in the measurable range of the viscometer. The sensor system used for the present study was MVI, details of which are given in Figure 2.3.

2.5.3. High viscosity

2.5.3.1.Capillary rheometer

The melt flow properties of high viscous materials were studied using a capillary rheometer attached to a Zwick Universal Testing Machine Model 1474[7]. The barrel was heated using a three zone temperature control system. The difference in temperature between two successive zones of the barrel was kept at 5^oC and the temperature of the lower zone, where capillary is located, was taken as the test temperature.

The moving crosshead of Zwick UTM runs the barrel at a constant speed irrespective of the load on the melt, maintaining constant volumetric flow rate through the capillary (Figure 2.4). The crosshead speed was varied from 0.5 to 500 mm per minute giving shear rates ranging from 3 to 3000 s^{-1} for a capillary L/D ratio = 40. Forces corresponding to specific plunger speeds were recorded on a strip chart recorder. The values were converted to shear stresses.

2.5.3.2. Test procedure

Sample for testing was placed inside the barrel, maintained at the test temperature and was forced down the capillary using a plunger attached to the crosshead. After a warming up period of 3 minutes the melt was extruded through the capillary at preselected speeds of crosshead. The melt height in the barrel before extrusion was kept the same in all experiments and the machine was operated to give 10 different plunger speeds. Each plunger speed was continued until the recorded force was stabilized before changing to next speed. Forces corresponding to specific plunger speeds were recorded. The force and crosshead speed were converted to apparent shear stress (τ) and shear rate (γ) at the wall using the following equations involving the geometry of the capillary and the plunger.

$$\tau_w = F / Ap(lc/dc) \text{ --------------------(2.2)}$$

$$\dot{\gamma}_{wa} = (3n'+1 / 4n') \times 32 Q / \pi dc^3 \text{ ---(2.3)}$$

where F = Force applied at a particular shear rate.

Ap = Cross-sectional area of the plunger,

lc = Length of the capillary,

dc = Diameter of the capillary,

Q = Volumetric flow rate,

n' = Flow behaviour index, defined by d(log τw)/d(log $\dot{\gamma}_{wa}$),

τw = Apparent shear stress at the wall and

$\dot{\gamma}_{wa}$ = Actual shear rate at the wall

n' was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. The shear viscosity (η) was calculated as

$$\eta = \tau / \dot{\gamma}_{wa} \quad \text{--------------------(2.4)}$$

The shear stress at the wall need to be corrected according to Bagley's end correction. This correction factor diminishes as the length to diameter ratio increases and for a capillary having L/D ratio 40, it is assumed that the correction factor is negligible. The following assumptions were also made for the analysis of the data.

1. There is no slip at the capillary wall
2. The fluid is time independent
3. The flow pattern is constant along the capillary
4. The flow is isothermal
5. The material is incompressible and
6. The flow properties are independent of the hydrostatic pressure.

2.5.3.3. Extrudate swell

Extrudate swell was expressed as ratio of the diameter of the extrudate to that of the capillary used. The extrudate emerging from the capillary was collected without deformation. The diameter of the extrudate was measured, after 24 h rest period, using a WILD stereo microscope model M650 at several points on the extrudate. The average value of 10 readings was taken as diameter of the extrudate. For each sample the extrudate swell was calculated at different shear rates as (d_e/d_c) where d_e is the diameter of the extrudate and d_c is the diameter of the capillary.

2.6. THERMAL ANALYSIS

Thermal analysis was carried out using a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA).

2.6.1. Differential scanning calorimeter

Direct calorimetric measurements, characterization and analysis of thermal properties of the samples were made using a Perkin Elmer 7 series differential scanning calorimeter. Sub-ambient operation was carried out by cooling the specimen and the specimen holder with liquid nitrogen. Exactly weighed (about 5 mg) of sample was used for the studies. Samples were encapsulated in standard aluminium pans with holes and covers and sealed by crimping. For purging the sample holders pure dry nitrogen gas (99.99%) was used. The inlet gas pressure was adjusted at 2 kg/cm^2 to attain a flow rate of about 25 ml per minute. Scanning rate was 10^{o}C per minute.

2.6.2. Thermogravimetry

A Perkin Elmer make thermogravimetric analyzer was used for the studies. It is a computer controlled instrument that permits the measurement of weight changes in the sample material as a function of temperature or time. It is programmed from an initial to final temperature and measures the weight change resulting from chemical reaction, decomposition, solvent and water evolution, curie point transitions and oxidation of the sample materials. The temperature is scanned at a linear rate. The instrument supplied by Perkin Elmer had two major components, an ultrasensitive micro balance and a furnace element. The balance is sensitive to 0.1 microgram and the furnace could be heated from ambient to 1000^{o}C at rates of 0.1 to 200^{o}C per minute. For purging the sample holder, gases commonly used are oxygen, air (a mixture of 80% nitrogen and 20% oxygen) or nitrogen so as to study the oxidation, burning and thermal stability of the materials. The purge gas flows directly over the sample. The recommended flow rate of the sample purge was kept less than the flow rate of the balance purge at all times.

2.7. LIMITING OXYGEN INDEX

The above test was carried out using a Limiting Oxygen Index (LOI) apparatus manufactured by Appareillage Industrial et Scientifique Company, France[8]. Both oxygen and nitrogen were connected to the equipment through pressure regulators (about 2 bars). The flow of gases was regulated at 17 litres per minute by adjusting the flow speed to 4 cms per minute on the glass tube.

Test specimens of 70 to 150 mm long, 6.5 mm wide and 3 mm thick were cut from vulcanized sheets and clamped in the specimen holder vertically in the approximate centre of the column with the top of the specimen at least 100 mm below the top of the open column

A concentration of oxygen in the mixture was selected and the flow valves were adjusted so as to read the set oxygen concentration. The test chamber was purged with the mixture for 30 seconds and the specimen was ignited with the ignition flame so that it was well lit and the entire top was burning. Subsequent trials were carried out with new specimens and changed concentrations of oxygen. The level of oxygen flow was adjusted to the minimum at which the specimen burned for 3 minutes or more than 30 mm length whichever is earlier. The test specimen was changed after each trial and the test continued until reaching the minimum oxygen concentration with a precision of at least 0.2 %.

2.8. PHYSICAL TEST METHODS

2.8.1. Modulus, Tensile strength and Elongation at break

These three parameters were determined according to ASTM D 412-92[9], using dumb bell specimens. The test specimens were punched out from moulded sheets using the C-type die, along the mill grain direction. The thickness of the specimen within the gauge length of the test specimen was measured using a dial gauge of accuracy 0.001mm. The specimens were tested on a Zwick Universal Testing Machine (UTM) model 1474 at ambient temperature and at a crosshead speed of 500 mm per minute. The elongation at break, modulus and tensile strength were obtained as a print out.

2.8.2. Tear resistance

Tear resistance of the samples was tested as per ASTM-D-624-81[10], using unnicked 90° angle test specimens that were punched out from moulded sheets, along the mill grain direction. This test was also carried out on a Zwick UTM, at a crosshead speed of 500 mm per minute. The tear strength was reported in kN/m.

2.8.3. Hardness

Hardness of the samples was measured according to ASTM D-2240-81[11] using a Shore A type durometer which employed a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after firm contact between the indentor and the sample, the recordings immediately after establishment of firm contact were taken.

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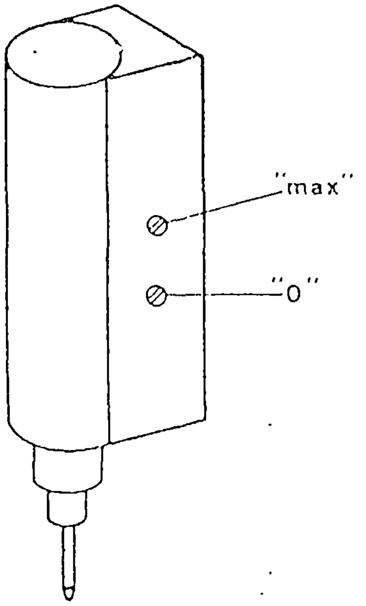


Figure 2.1. Drive unit of Haake viscometer

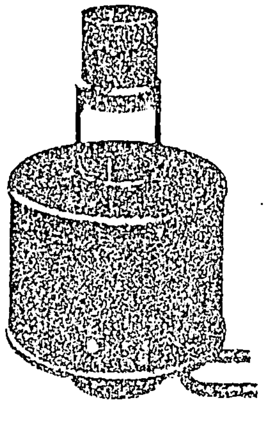
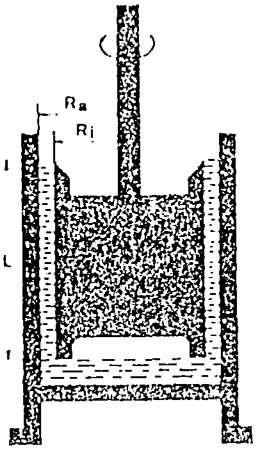
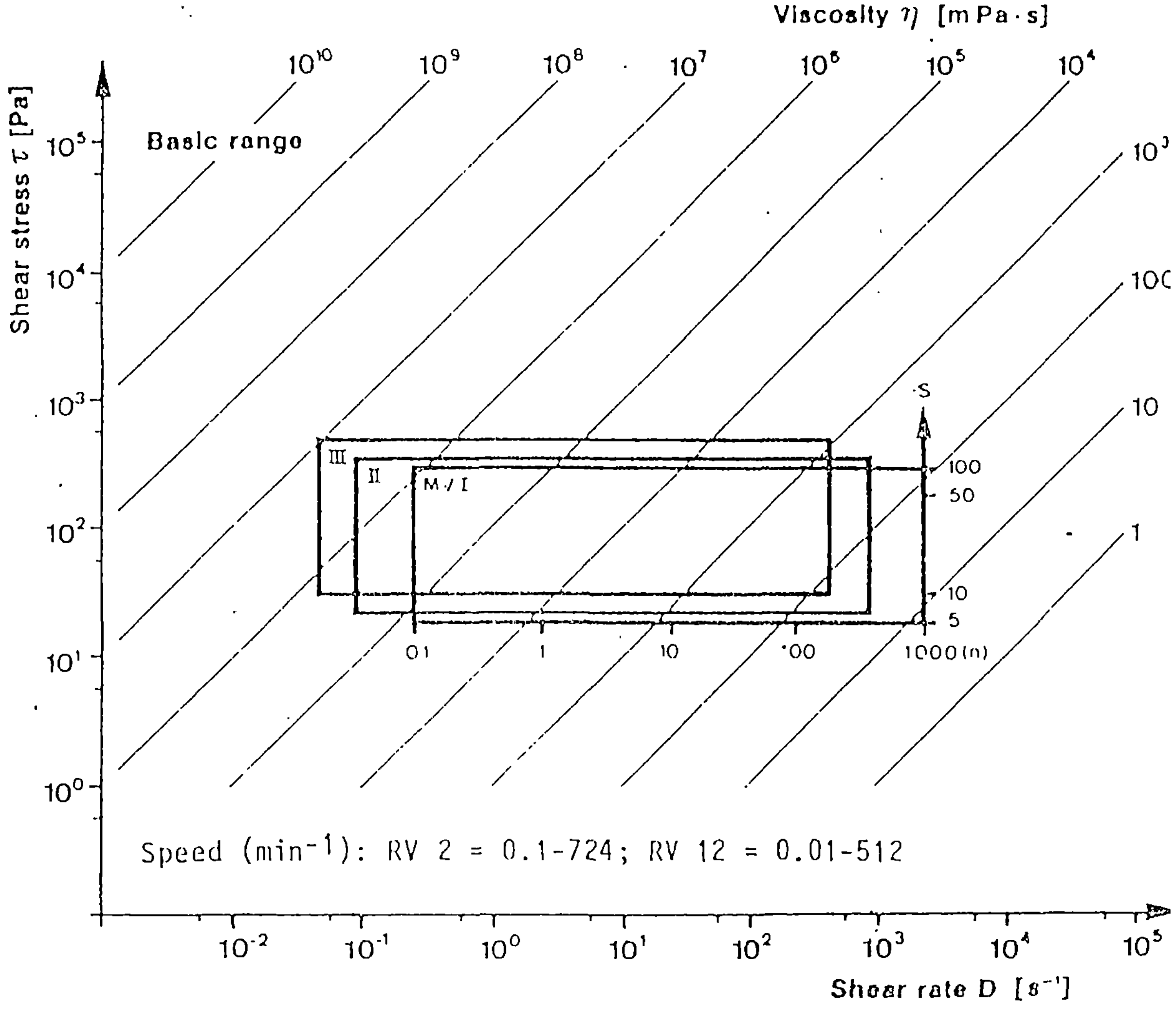


Figure 2.2. Temperature vessel



Calculation factors for MV1

A (Pa/scale grad.)	3.22
M (min/s)	2.34
G (mPa.s/scale grad. min.	1374



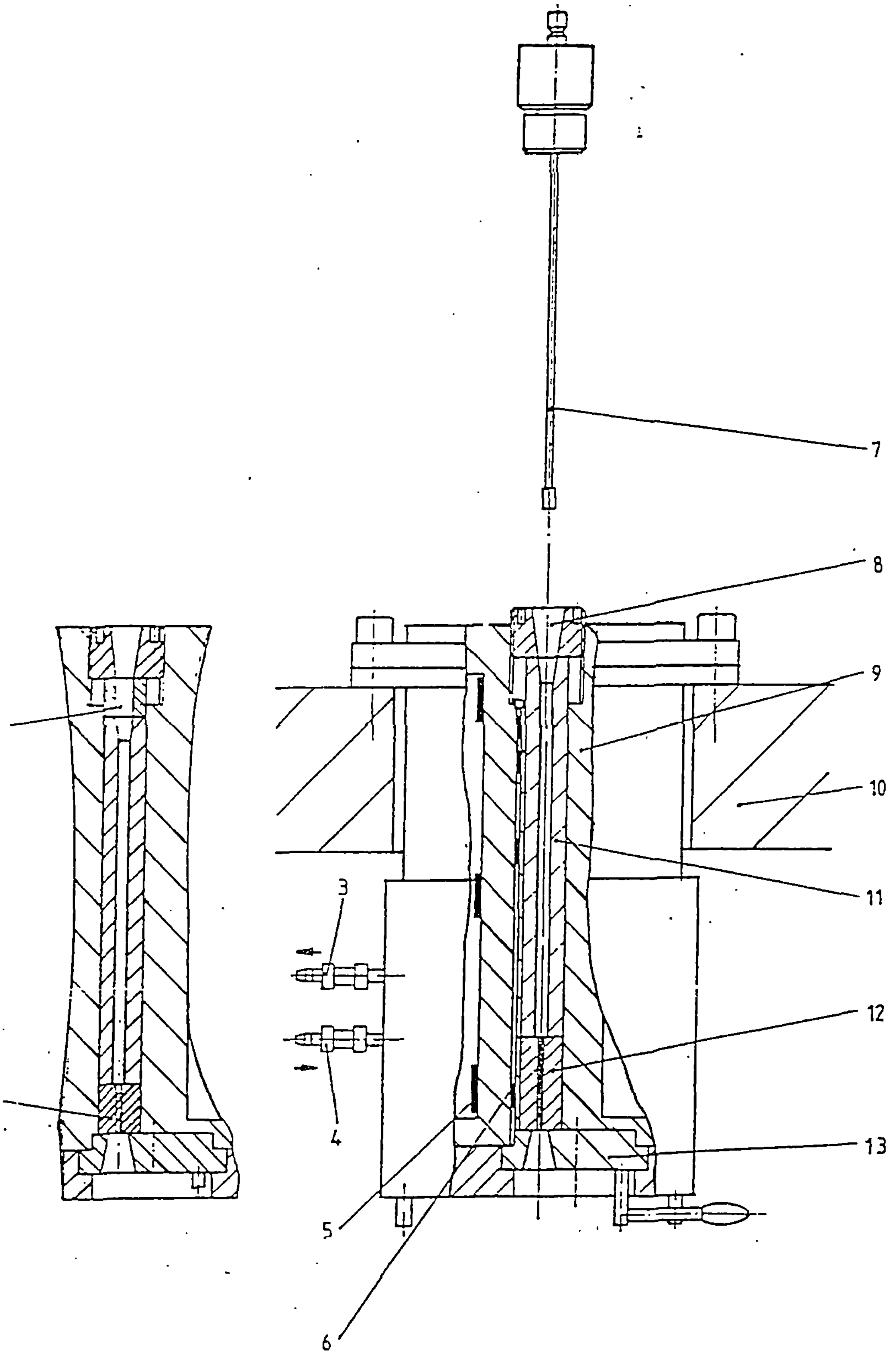


Figure 2.4. Capillary extrusion assembly

1. Jet compensation ring 2. Jet 3. Coolant outlet 4. Coolant inlet 5. Wrap-around heating system
6. Measuring or regulating sensor 7. Plunger unit 8. Threaded ring 9. Heating body 10. Cross-head of the Universal testing machine 11. Testing channel 12. Jet 13. Jet cover plate.

Chapter 3.

CHARACTERIZATION AND RHEOLOGICAL STUDIES ON LIQUID NATURAL RUBBER

The results of this chapter have been published in the Journal of Applied Polymer Science, Vol. 55, 723-731 (1995)

3.1. INTRODUCTION

3.1.1. Viscosity

Ideal solids deform elastically. The energy of deformation is fully recovered when the stresses are removed. Ideal fluids such as liquids and gases deform irreversibly or they flow. Energy of deformation is dissipated into fluids as heat. It cannot be recovered by releasing the stresses. Real solids deform irreversibly under stress, i.e they creep. Solids can be subjected to both tensile and shear stresses while fluids can only be sheared. Young's modulus in a solid defines its resistance to deformation. The resistance of a fluid to irreversible position change of its volume elements is called viscosity. Natural rubber shows such rheological behaviour that it is neither liquid nor solid and is known as viscoelastic.

The viscosity of a liquid may depend upon five independent parameters.

$$\eta = f\,(S, T, P, D, t) \qquad \text{-------(3.1)}$$

where

S = shear stress
T = temperature
P = pressure
D = shear rate
t = time.

Particulate or molecular alignments allow particles or molecules slip past each other and this shows up as reduced viscosity. Viscosity spectrum of materials is given in Table 3.1.

Table 3.1. Viscosity spectrum

Viscosity scale, cps	Typical materials
$> 10^{22}$	Quartz
10^{22}	Limestone
10^{20}	Crown glass
10^{18}	Concrete
10^{16}	PMM resin
10^{14}	Glucose
10^{12}	Lead
10^{10}	Ice crystal, PTFE
10^{8}	Cheese, NR
10^{6}	Butter, Bitumen
10^{4}	PE melt, acrylic resin
10^{2}	Honey
10^{0}	Blood, Water
10^{-2}	Liquid oxygen
10^{-4}	Common gases, Liquid hydrogen
10^{-6}	Hydrogen gas
10^{-8}	
10^{-10}	
10^{-12}	Liquid helium

3.1.2. Coaxial cylinder viscometers

Figure 3.1. is the sketch of a coaxial cylinder viscometer. Rheological parameters are calculated as:

Shear stress $\tau = M / 2\pi R^2 h$ -------------------------------- (3.2)

Shear rate at the bob $DRb = 2\omega / (1 - Rb^2 / Rc^2)$ --------- (3.3)

Shear rate at the cup $DRc = 2\omega / (Rc^2 / Rb^2 - 1)$ --------- (3.4)

Average shear rate = $(DRb + DRc) / 2$ ------------- (3.5)

where

Rb = Radius of the bob

Rc = Radius of the cup

ω = Angular velocity of the bob = 2π N/60.

N = Number of revolutions per minute

h = Height of the bob

Vmax = Velocity of the bob

Vo = Velocity of the cup

M = Torque

τ = Shear stress

D = Shear rate

η = Viscosity

These equations are derived by assuming Newtonian flow behaviour. Also, the velocity gradient is assumed to be straight line between the maximum velocity Vm and Vo. Shaded area in Figure 3.1. represents the error in assuming the linear relationship for rate of shear. The error is small if the gap is narrow. For best results, Rb / Rc shall lie between 1.0 and 1.1.

Since the top and bottom surfaces of the rotor are not taken into account in the mathematical interpretation of the results, an error can creep in. This is maintained by suitably shaping the top and bottom surfaces of the rotor.

3.1.3. Wiesenberg effect (Normal stress effect)

This is the tendency of viscoelastic fluids to flow in a direction normal to the direction of the shear stress. It is due to this effect that certain fluids climb up the spindle in a rotational viscometer. Because of this normal stress effect, material will try to leave the gap, thus changing the height of the gap.

3.1.4. Temperature effect

When material is caused to flow, energy is degraded into frictional heat, and the temperature of the material tends to rise. When viscosity is more, temperature rise will be appreciable. This temperature rise may give rise to hysteresis loops which will be mistaken for thixotropic effect.

3.1.5. Particle size effect

When a rotational viscometer is used to measure viscosity of suspensions which contain particles greater than a few microns, there will be slippage at the wall and the particles are not mechanically carried around the rotating member. In such cases, grooved cups and bobs may help. In suspensions, the gap size should be of the order of 10 to 100 times the diameter of the large particle in the suspension

3.2. EXPERIMENTAL

3.2.1. Depolymerization

Depolymerization of NR has been effected in a number of ways[1-3]. For this study it was prepared by the combined action of mechanical and thermal energies aided by a peptizer, activated pentachlorothiophenol. For the thermal depolymerization, conditions suggested by Claramma et al.[4] were chosen to produce LNR samples of a wide range of viscosity and, in turn, wide range of molecular weight. Liquid elastomers are used in a number of applications such as moisture resistant sealants for filling voids, self adhesive tapes, binder for grinding wheels, rocket propellants, etc according to Hardman and Lang[5]

Improvements in flow properties are imparted to rubber compounds by incorporating LNR[6-7]. In applications of LNR such as castings, the property of most importance is its flowability and pourability. Rheology of elastomers is affected by the viscoelastic character common to all polymeric materials. In addition, the morphology of compounds, resulting from elastomer-filler interactions, has a significant effect on the flow mechanism and induces different types of behaviour. Good flow properties result in less defects and fewer rejects in the end products.

In the present study, viscosity measurements were carried out on a series of LNR samples of different molecular weight using a rotational type viscometer, Rheomat 30, that could record a continuous plot of shear rate against shear stress. The measurements were made at different temperatures.

3. 2. 2. Rheomat 30

For the measurement of viscosity, the viscometer used was Rheomat 30 from Contraves A.G., Switzerland. The equipment was capable of measuring shear stresses explicitly over a wide range of shear rate. It is a multispeed rotational viscometer with a precision measuring system.

3. 2. 3. LNR

Fundamentally LNR differs from other liquid elastomers in the method of preparation. It is produced by the depolymerization of the naturally occurring high molecular weight polymer. For the preparation of LNR two routes are normally adopted, one starting from dry rubber and the other directly from the latex. Latex stage depolymerization[9] has gained global interest with the installation of the liquid natural plant at Bimbreso, Ivory Coast, under UNIDO assistance. The plant has been designed to produce LNR starting from latex using phenyl hydrazine-oxygen redox system. The samples used in this study were prepared by thermal depolymerization.

3. 2. 4. Temperature stabilization.

Viscosity is greatly affected by temperature. So the measurements are to be carried out at known temperature. The sample to be measured was taken in the cup of the instrument, heated to test temperature and allowed to stand for 30 min in an air oven. The rotating bob was attached to the measuring head after temperature stabilization.

LNR samples were prepared by thermal depolymerization of ISNR-5. The parameters such as temperature, duration of heating, peptizer dosage, etc. were chosen to obtain LNR samples of viscosities in the low, medium and high ranges. The samples were identified based on their viscosity measured using a Brookfield viscometer (model RVT, spindle 6.5 rpm) at 38^{o}C. Five samples, having viscosities over a wide range, were selected for the studies and the details are given in Table 3.2.

Table 3.2. Brookfield viscosity of LNR samples.

Sample	Brookfield viscosity at 38°C, mPas.
LNR1	52,000
LNR2	70,000
LNR3	1,12,000
LNR4	2,68.000
LNR5	4,92,000

These samples were also characterized by NMR and IR spectroscopy. ^1H NMR spectra were taken on a Bruker 400 MHz instrument. IR spectra were obtained with a Perkin Elmer 16 PC spectrometer with a thin film on KBr cell. Gel permeation chromatographic studies were carried out using a Waters GPC fitted with a Polymer Laboratory's gel 10 microns mixed 600 x 7.5 mm column and two detectors (UV and refractometer). Measurements were performed at 25°C with tetrahydrofuran as solvent (throughput 0.5 ml/min.). Calibration curve was established with standard polystyrene samples and polystyrene data were calculated as suggested by Subramaniam[10].

$$\text{Log Mpi} = 0.093 + 0.950 \log \text{Mps} \qquad \text{-------------} \quad (3.6)$$

where Mpi is the molecular weight of cis-polyisoprene and Mps is the molecular weight of polystyrene.

3.3. RESULTS AND DISCUSSION

The samples were characterized for their physical and chemical properties.

3.3.1. Properties

The depolymerized LNR samples in the viscosity range of 52,000 cps to 3,92,000 cps at 38°C were pourable liquids. Figure 3.2. gives a comparison of the NMR spectra of LNR 1. The spectrum appeared with three chemical shifts of protons, (methyl) at 1.54 ppm, (methylene) at 2.00 ppm and (ethyl) at 5.1 ppm typical of cis 1,4 polyisoprene. Infra-red spectra of the compounds also looked similar. The spectrum obtained for LNR1 with maximum depolymerization is given in Figure 3.3. This indicated occurrence of limited extent of side reactions during the depolymerization process. Table 3.3. gives the physical and chemical properties of LNR 1.

Table 3.3. Properties of LNR.

Specific gravity at 25°C	0.92
Colour	Light brown in thin films
Ash content (%)	0.6
Volatile matter (%)	0.1
Iodine value	305

Brown colour of the sample was due to the formation of small quantities of char during thermal depolymerization. Iodine value measured on the sample was 305, lower than that of raw natural rubber (322). The Table 3.4. gives the number and weight average molecular weights of the samples.

Table 3.4. Molecular weight of LNR samples.

Sample	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$
LNR 1	3918	30900	7.89
LNR 2	5113	32490	6.35
LNR 3	5920	44210	7.46
LNR 4	6461	54420	8.42
LNR 5	8474	72960	8.61

Polydispersity ($\overline{Mw}/\overline{Mn}$) of different LNR samples are also given in the table. The molecular weight distribution values ranging from 6.35 to 8.61 showed relatively large distribution range. A comparison of gel permeation chromatograms is given in Figure 3.4.

3.3.2. Viscosity studies

The parameters subjected to investigation with respect to the rheological properties of LNR were the shear rate, shear stress, temperature and molecular weight.

3.3.2.1. Shear rate - shear stress relationship

The shear rate-shear stress relationship for the samples at $50^{o}C$ is compared in Figure 3.5. It gives a plot of logarithm of shear rate ($\dot{\gamma}$) Vs shear stress (τ). With increase in shear rate, shear stress increases linearly for all the samples. As the slopes of the lines are close to 1 it can be inferred that the samples behave almost Newtonian. The mathematical expression relating shear stress (τ) and shear rate ($\dot{\gamma}$) for Newtonian liquids is given by the power law equation

$$\eta = K \gamma^n \qquad \text{---------} \quad (3.7)$$

where K is the consistency factor and n is the flow behaviour index. It can be noticed that the value of n is around 1 for low molecular weight samples. The high molecular weight sample exhibits more pseudoplastic behaviour as is evidenced by the lower values of n. This may be attributed to the fact that at high temperatures, the inter particle or intermolecular interactions will be weak and therefore, the molecules of the high molecular weight samples will be oriented in the direction of shear (Figure 3.6). In general with the decrease in molecular weight the Newtonian behaviour increases. Figure 3.7. gives the pseudoplasticity index at different temperatures.

3.3.2.2. *Effect of shear rate on viscosity*

Effects of shear rate on viscosity at 20°C for different LNR samples are given in Figure 3.8. In the case of LNR 1, 2 and 3 as the viscosity is independent of shear rate, the samples exhibit perfect Newtonian behaviour. In the case of high molecular weight samples, LNR 4 and LNR 5, a marginal reduction in viscosity with increasing shear rate is observed which may be attributed to the effect of molecular orientation. In liquid polymers of high molecular weight the molecules are substantially entangled giving rise to non-Newtonian behaviour. The elastic nature of the samples were evident from the normal stress effect as shown in Figure 3.9. In the case of low molecular weight liquid polymers the entanglement between molecules is low that coupling is a weak phenomenon.

3.3.2.3. *Effect of molecular weight on viscosity*

Figure 3.10. is a plot of viscosity Vs weight average molecular weight of LNR samples at 50 and 80°C. In both the cases the viscosity increases with increase in molecular weight. This is due to the fact that as the molecular weight increases the

entanglements and interaction between polymer chains also increase. It is interesting to note that the increase in viscosity with molecular weight is more pronounced at low temperatures. At high temperatures the intermolecular interaction decreases. This minimizes the effect of molecular weight on viscosity.

3.3.2.4. *Effect of temperature on viscosity*

Viscosities of the samples at different temperatures were plotted at shear rates 0.397 S^{-1} and are given in Figure 3.11. In all the cases viscosity decreased with increase in temperature. However, due to increased thermal motion and free volume the viscosity difference among samples showed variation. Curves for different samples showed greater divergence at high temperatures indicating that the low molecular weight materials became more fluidy than the high molecular weight samples. Thus the viscosity range widens at higher temperatures. This may be attributed to the free Brownian movement of low molecular weight polymer chains under the influence of thermal energy. In the case of high molecular weight samples the extra chain length restricts the molecular motion. A comparison of viscosities for different samples shows that the reduction in viscosity is around 100 fold for a rise in temperature through 120°C. Thus warming of LNR makes it possible to flow even high viscosity samples which are difficult to handle at room temperature. Variation of flow properties with temperature is of interest in engineering applications. Viscosity at elevated temperatures is governed by the equation

$$\eta = A\ e\text{-}E/RT \qquad \text{----------------(8)}$$

where

E is the activation energy of flow

and T the absolute temperature.

The activation energy of flow at a particular shear rate can be calculated from the slope of the curve obtained by plotting log η Vs 1/T. A plot of the above parameter was made at shear rate of 0.997 S^{-1} and is given in Figure 3.12. The slopes of the lines were calculated and the activation energy of flow was determined. The activation energy values of different samples are given in Table 4.4. The activation energy marginally increases with increase in molecular weight of the samples.

Table 3.4. Activation energy of flow

Sample	Activation energy, kCals/mol
LNR 1	1176
LNR 2	1209
LNR 3	1262
LNR 4	1331
LNR 5	1368

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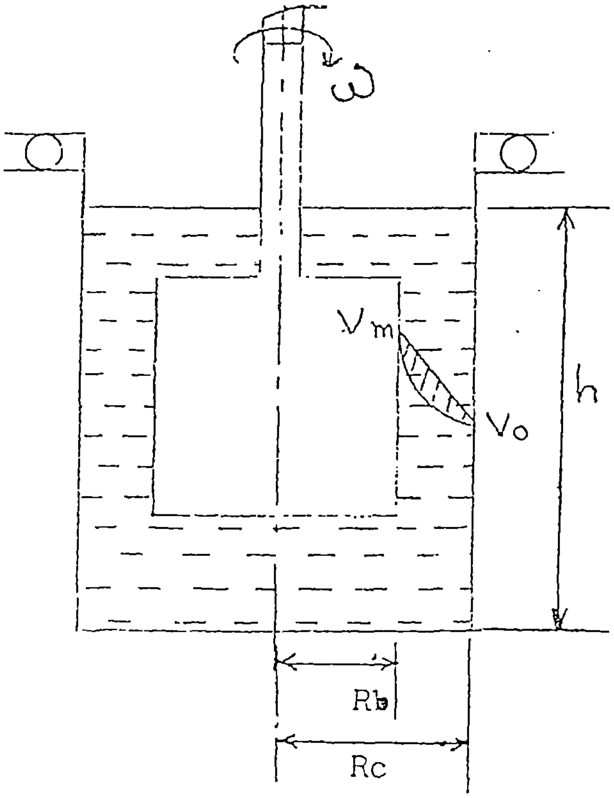


Fig. 3.1. Sketch of coaxial cylinder viscometer

Rb = Radius of the bob, **Rc** Radius of the cup, **h** = Height of the bob,

ω = Angular velocity of the bob = 2π N/60, **Vm** = Velocity of the bob and

Vo = Velocity of the cup

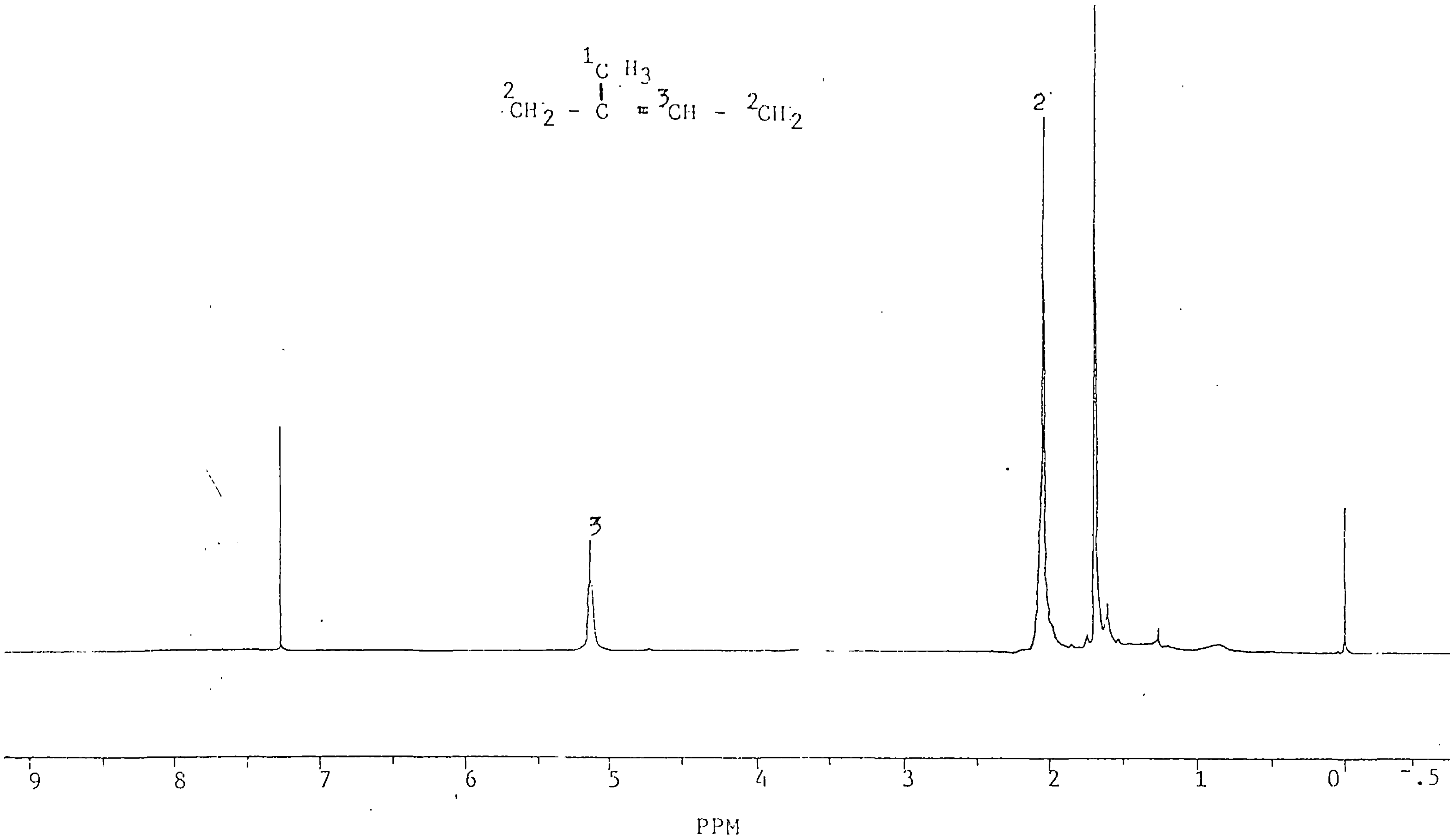


Fig. 3.2. ^{1}H NMR spectrum of LNR1.

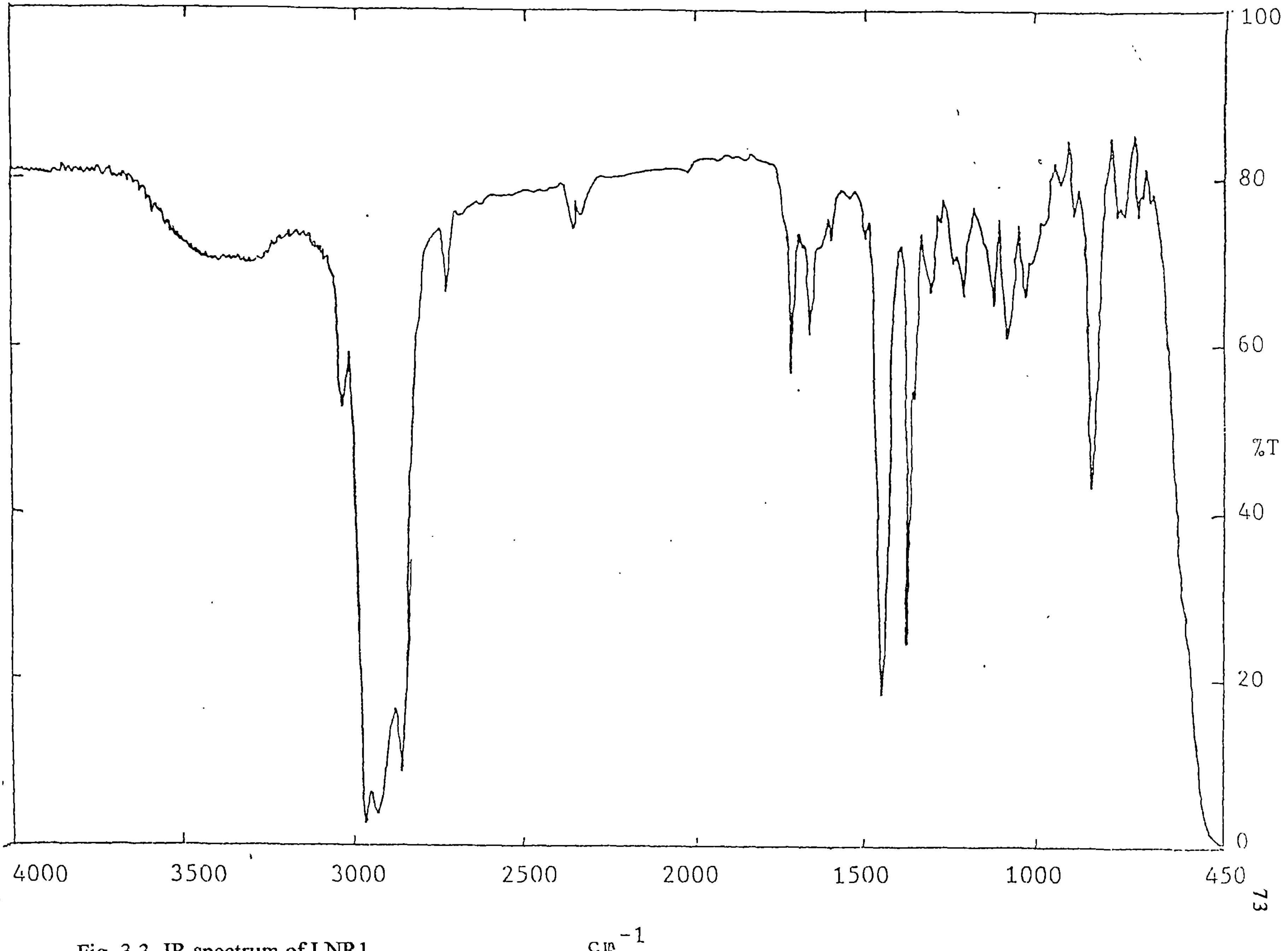


Fig. 3.3. IR spectrum of LNR1

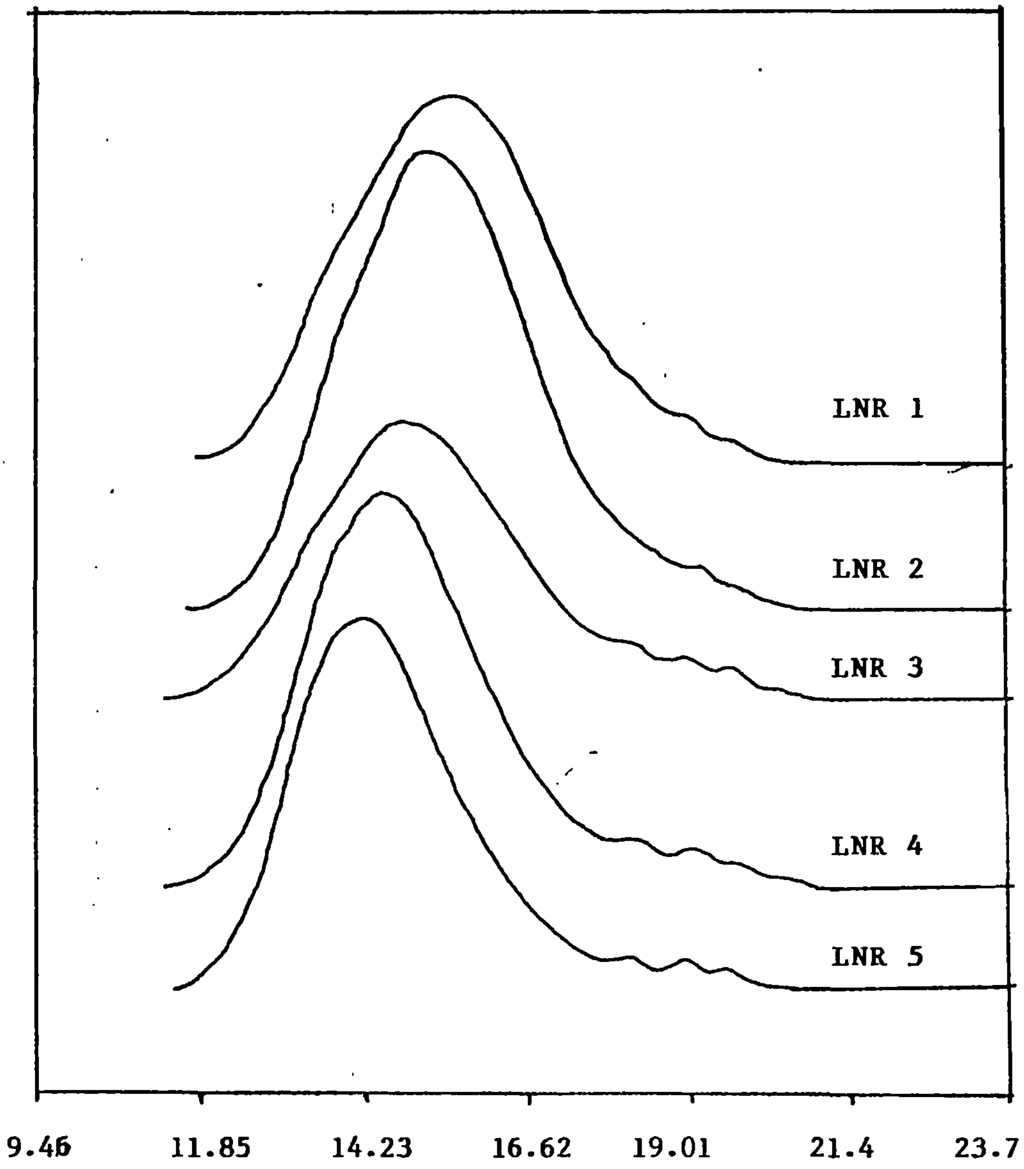


Fig. 3.4. GPC of LNR samples

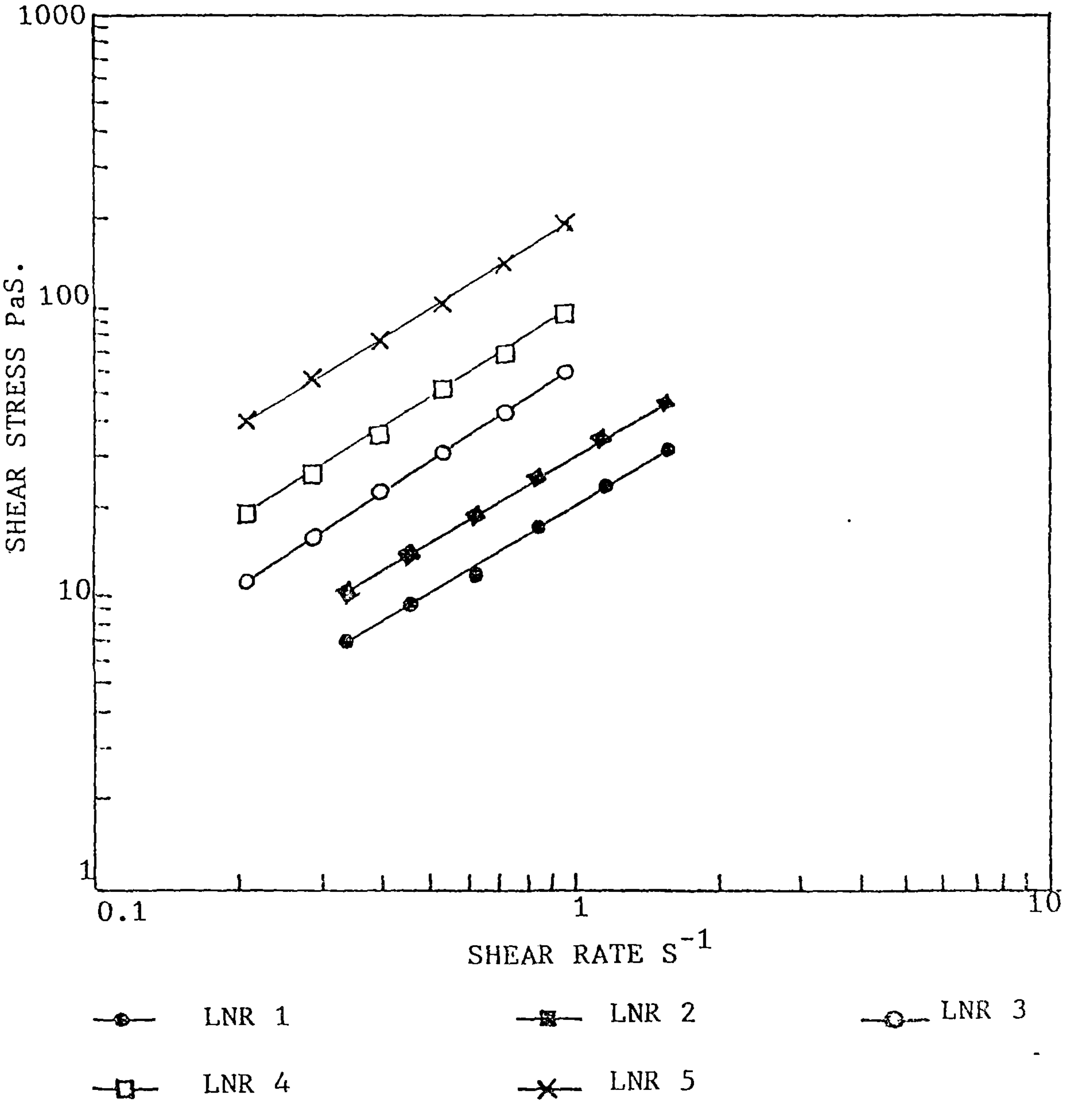


Fig. 3.5. Plots of shear rate vs shear stress

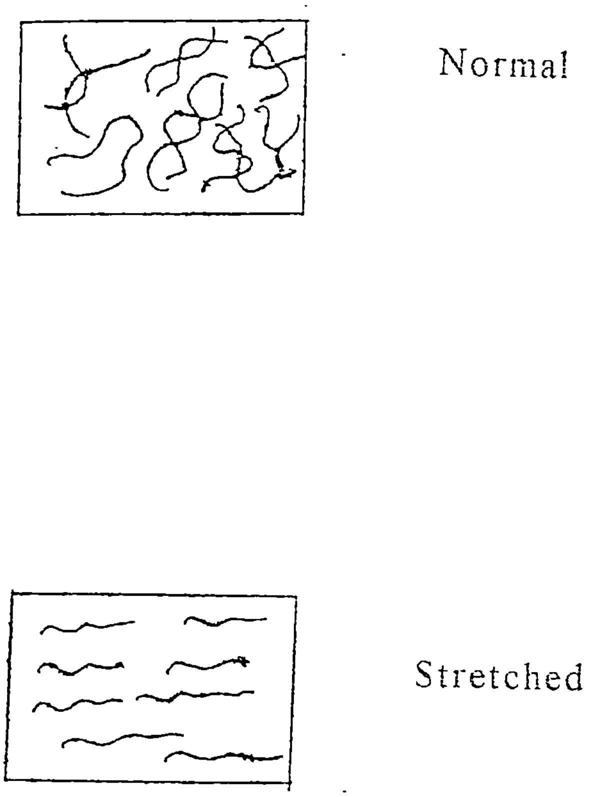


Fig. 3.6. Orientation of structure on shearing

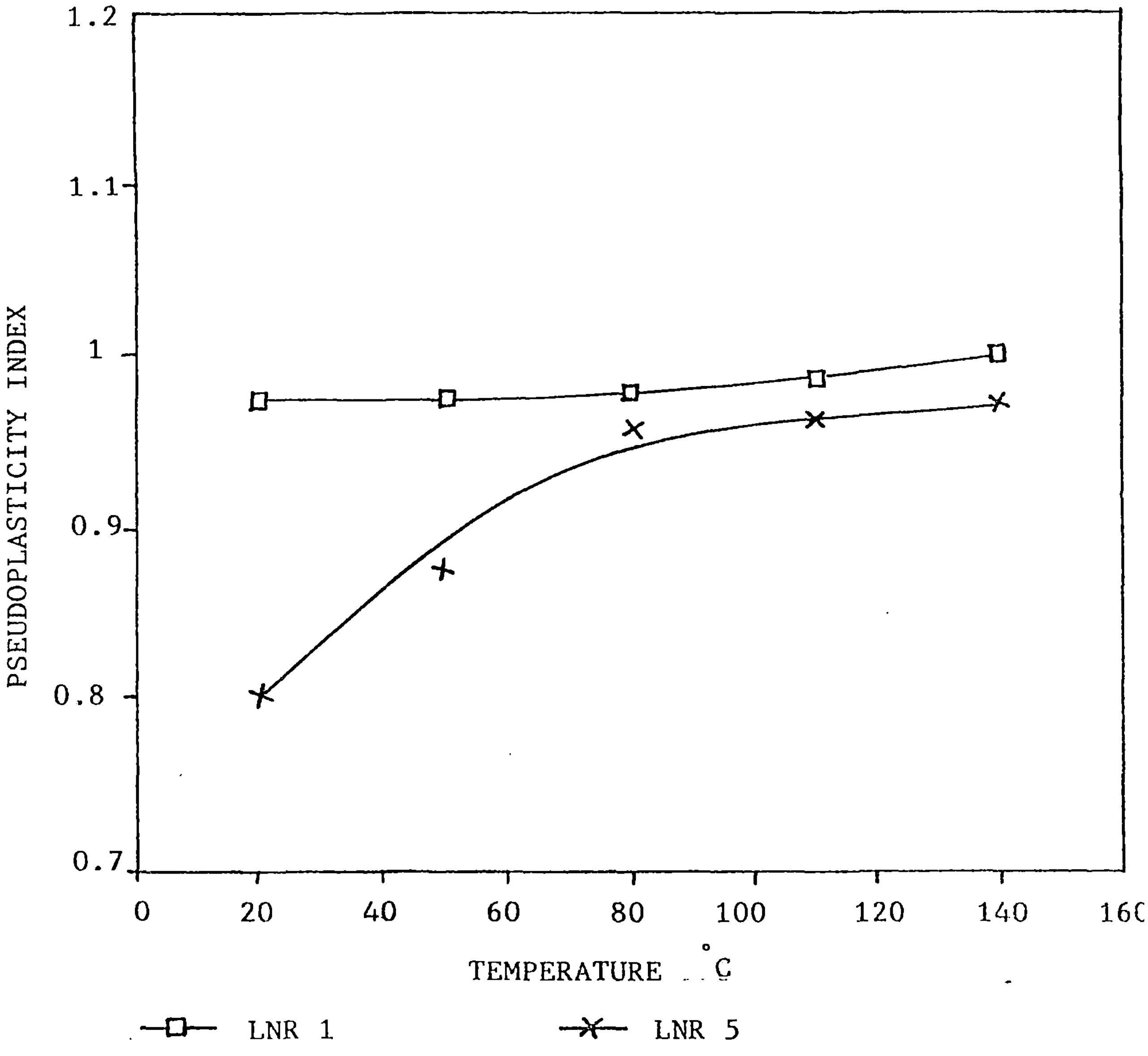


Fig. 3.7. Temperature vs pseudoplasticity index

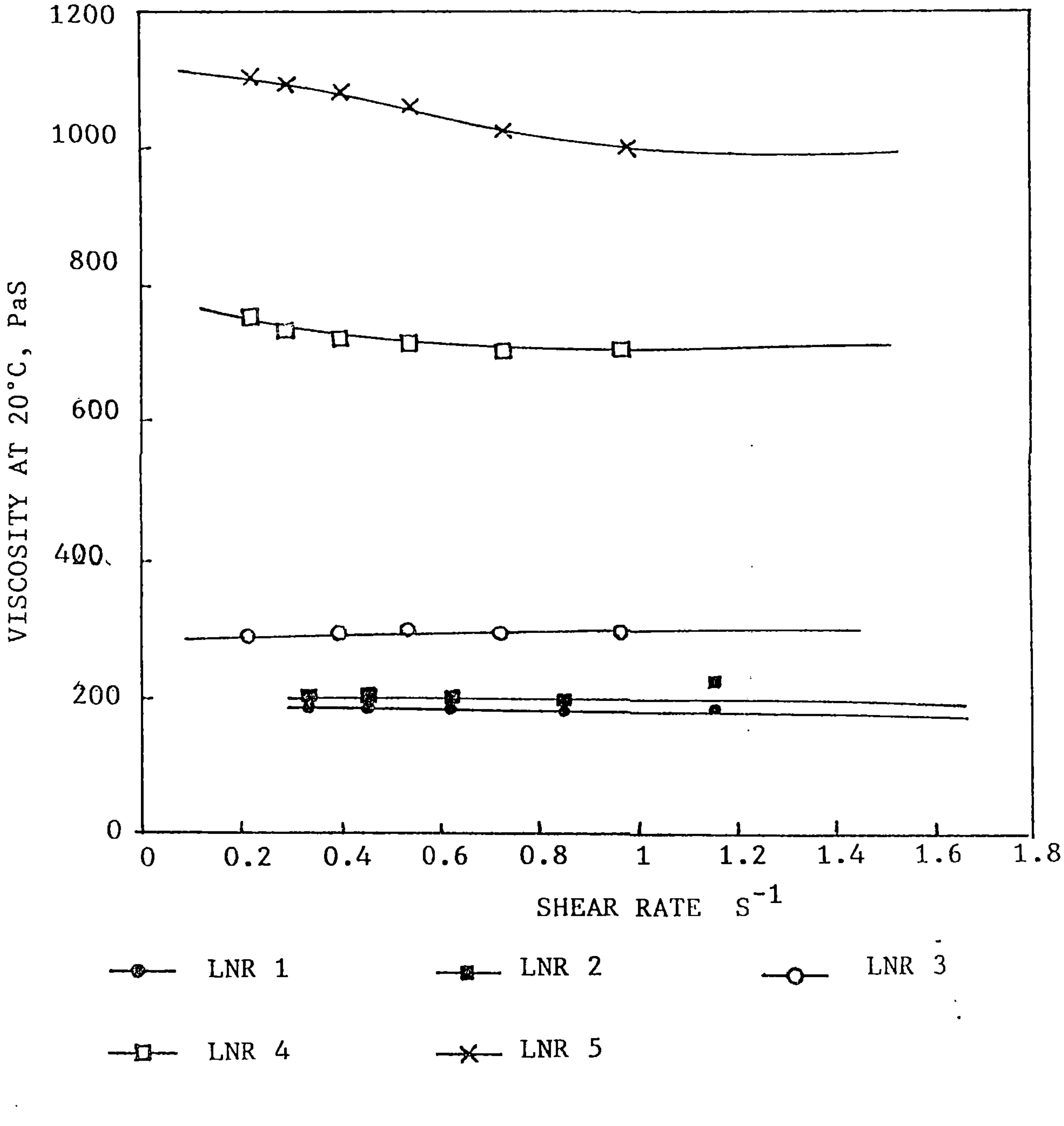
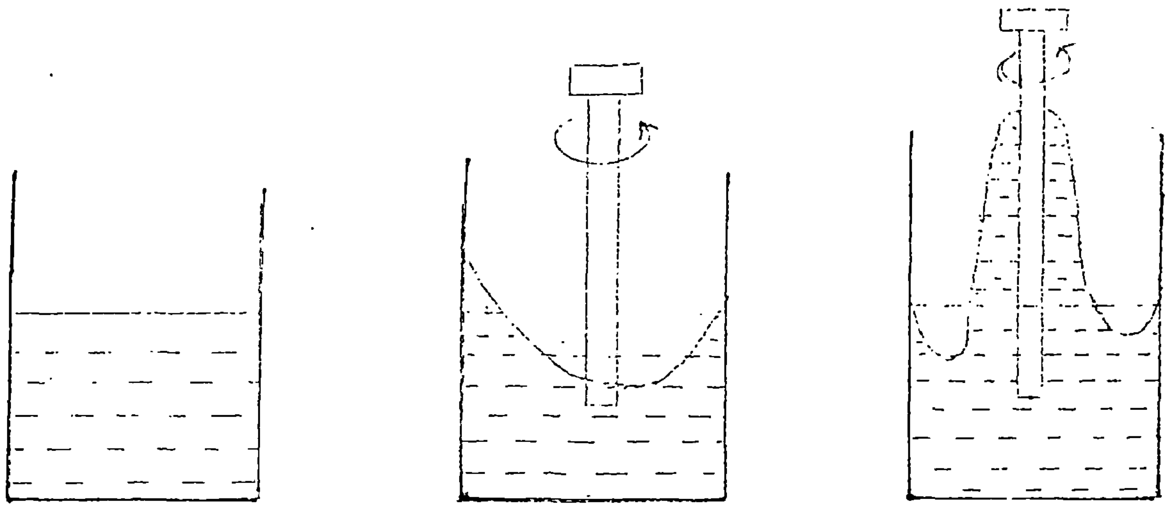


Fig. 3.8. Shear rate vs viscosity at 20°C



(Liquid at rest) (Viscous) (Elastic) LNR

Fig. 3.9. Normal stress effect

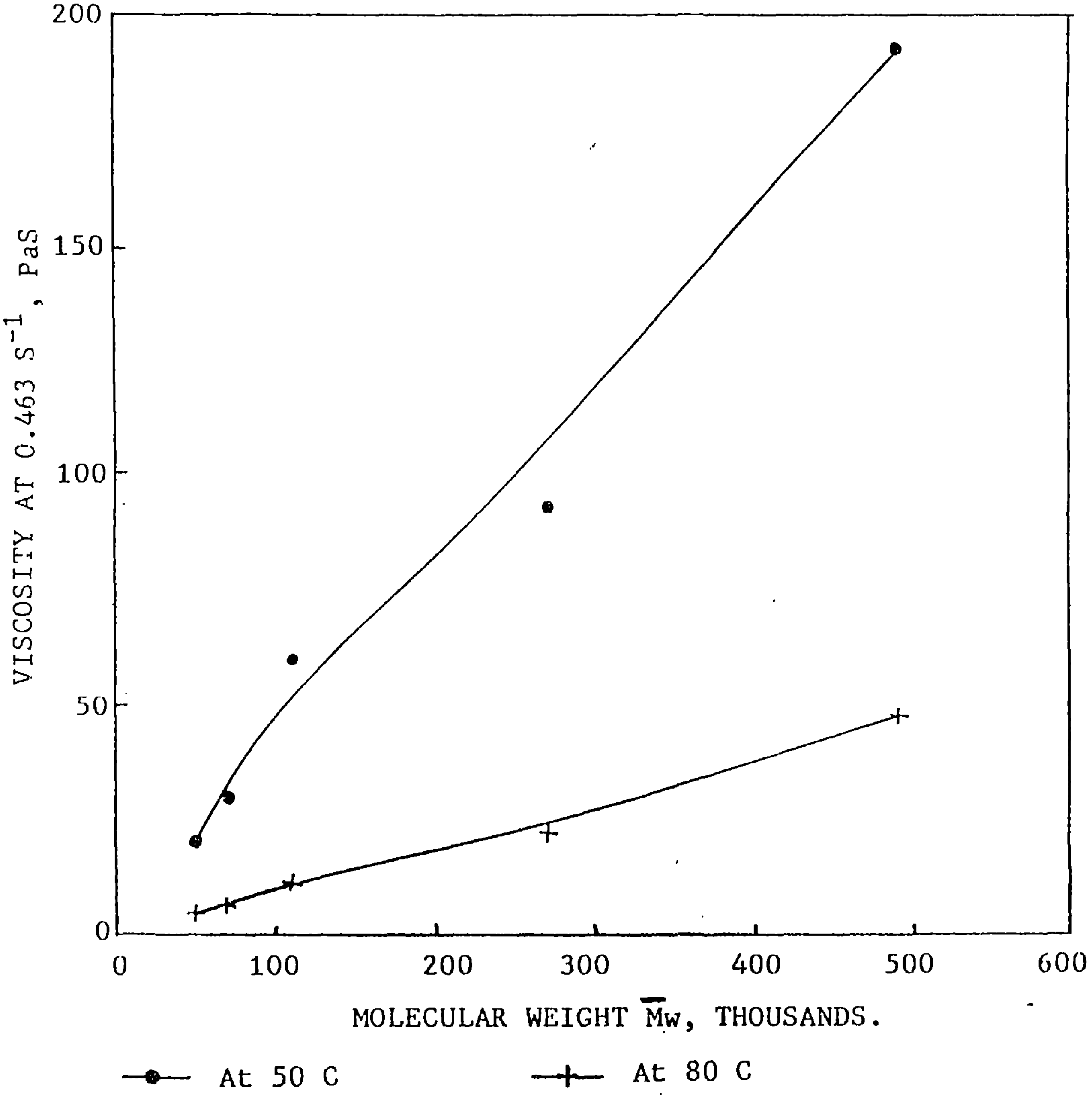


Fig. 3.10. Molecular weight vs viscosity

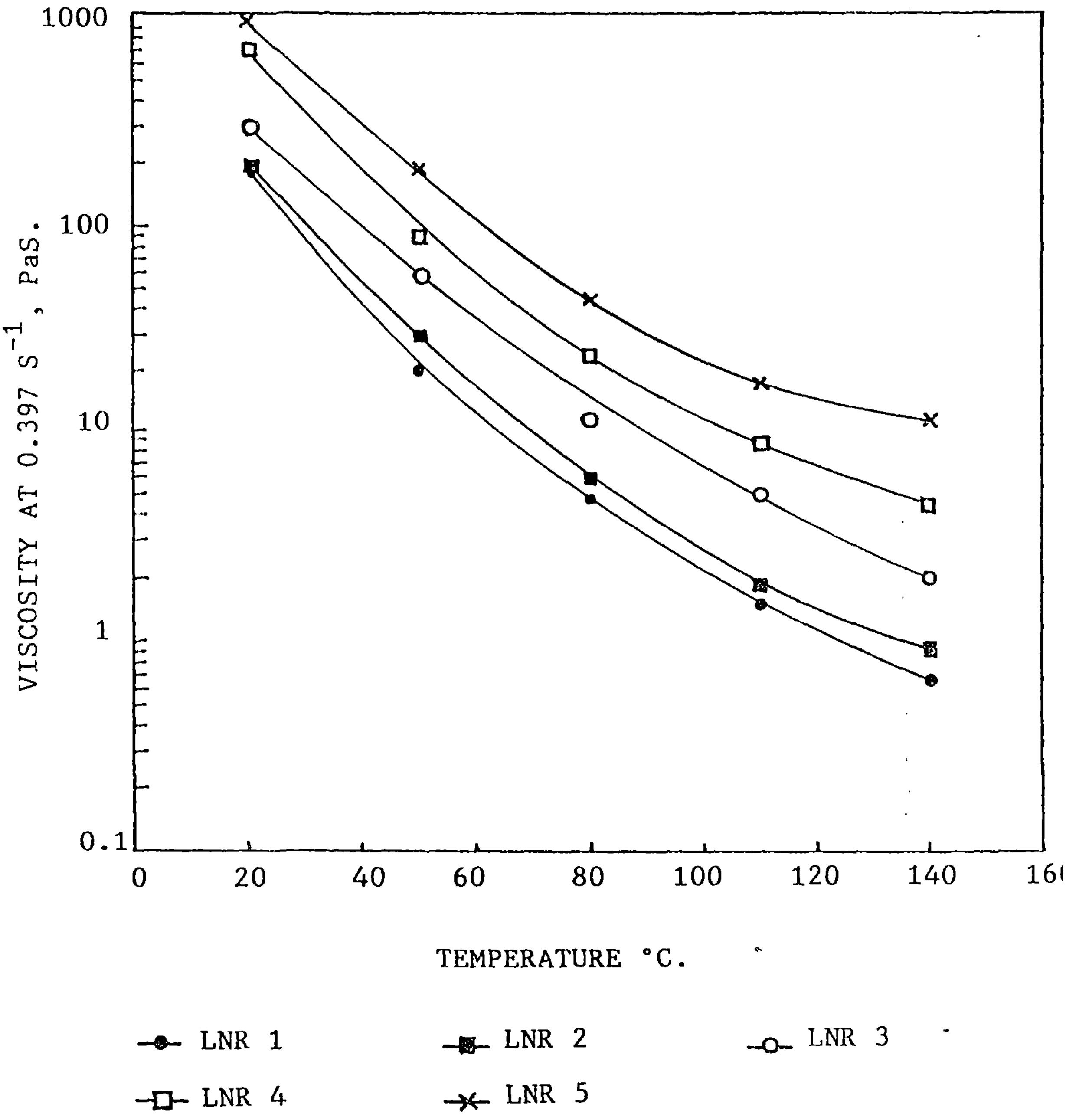


Fig. 3.11. Effect of temperature on viscosity

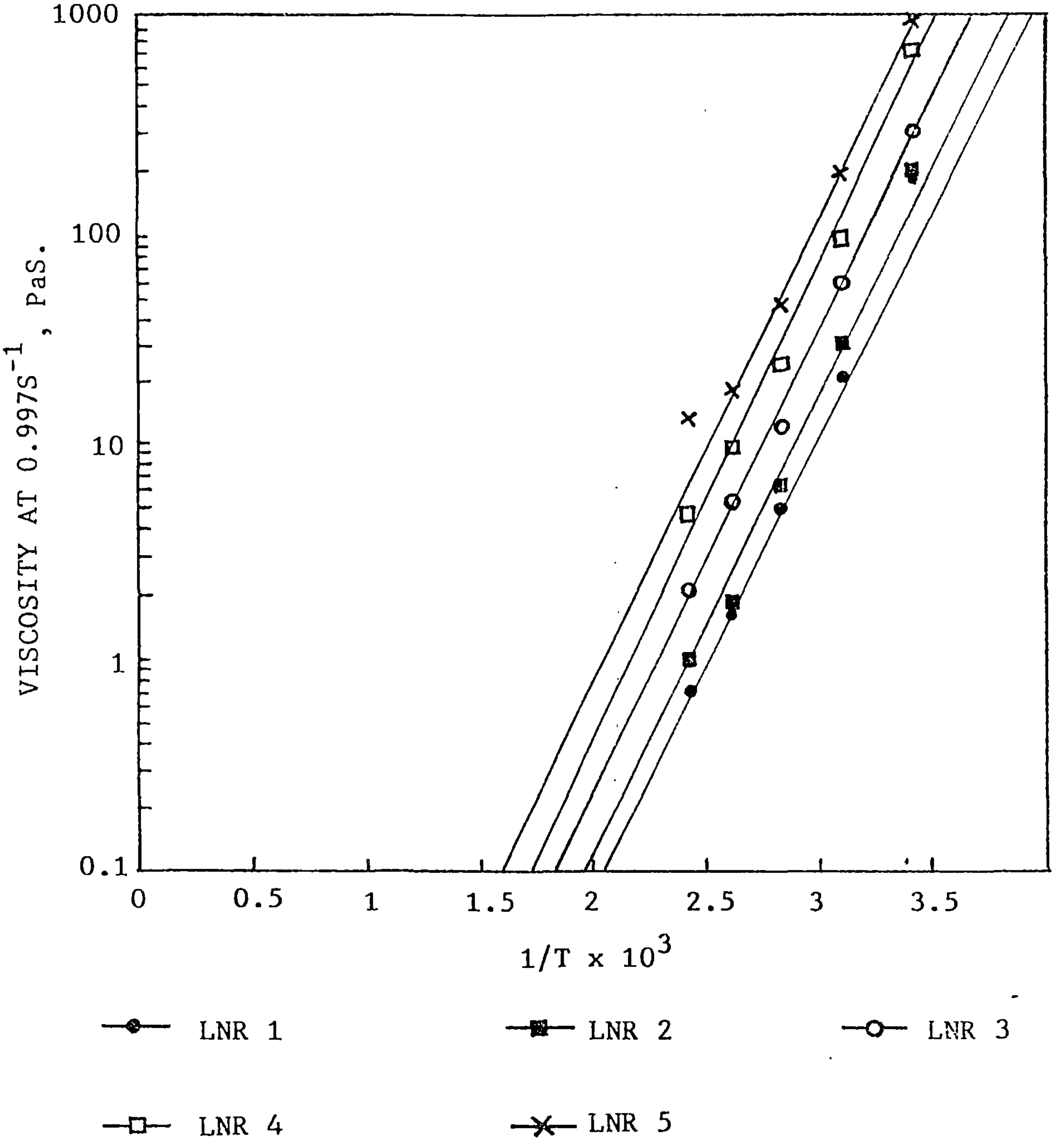


Fig. 3.12. 1/T vs viscosity

Chapter 4

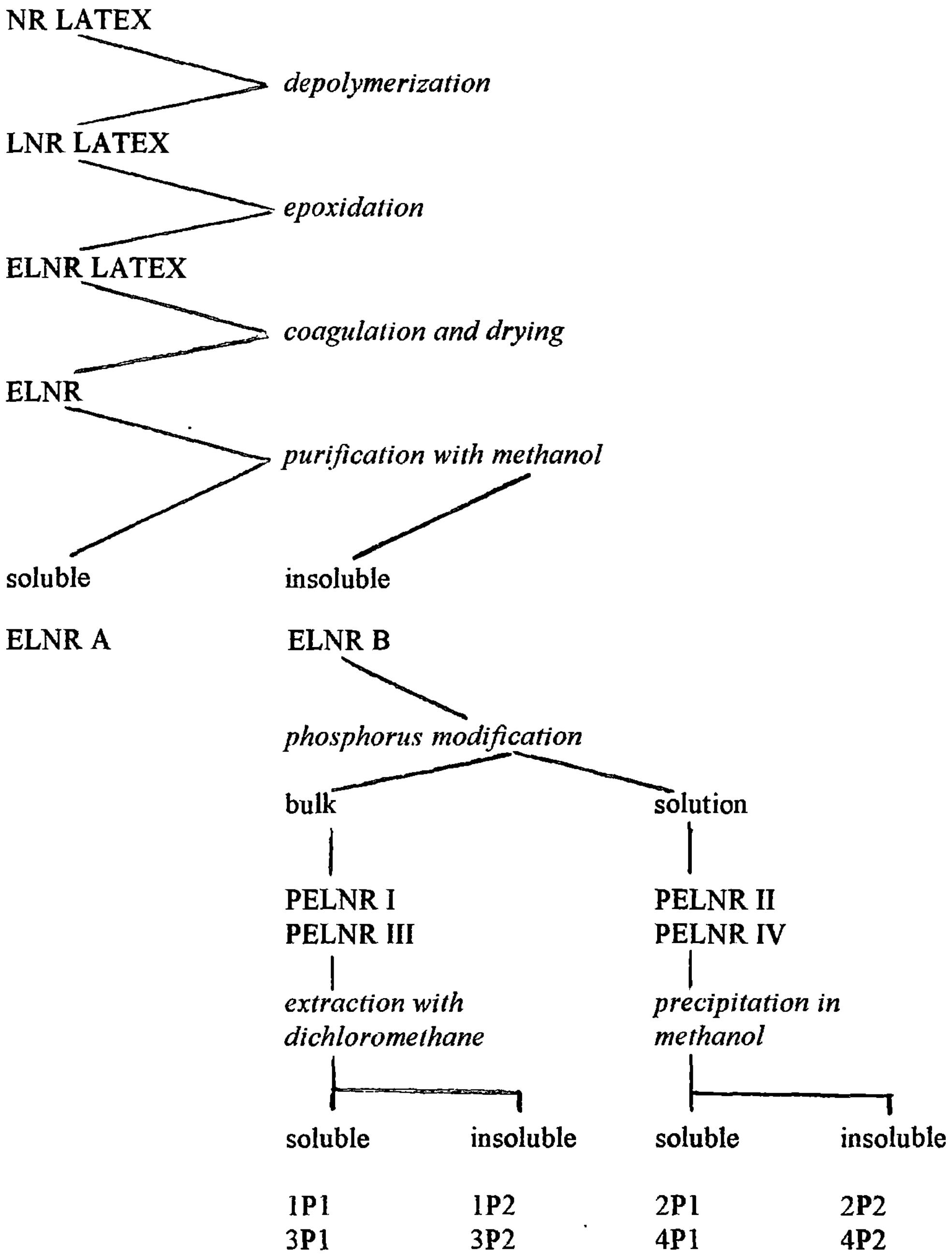
CHEMICAL MODIFICATION BY PHOSPHORUS ADDITION

The results of this chapter have been published in the Journal of Applied Polymer Science Vol. 52, 1309 - 1316 (1994).

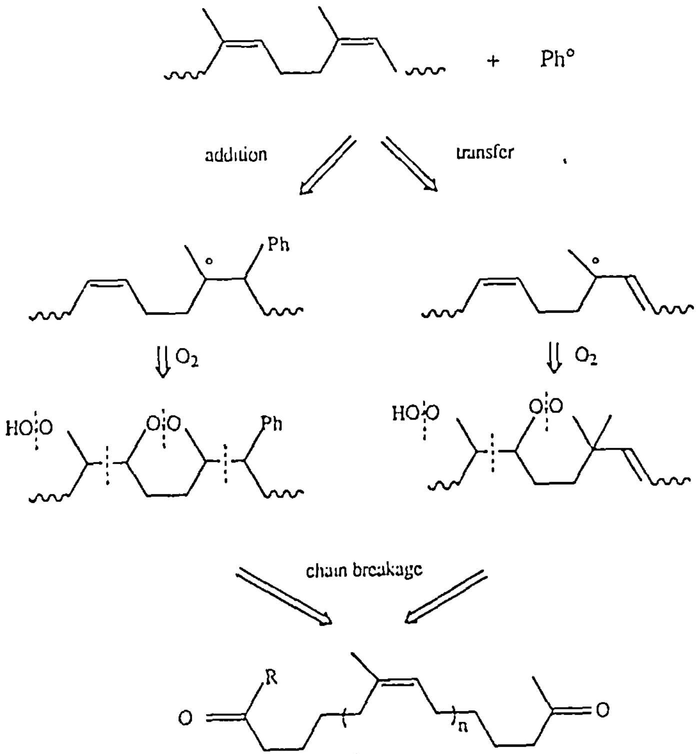
4.1. INTRODUCTION

Modification of liquid natural rubber was attempted through chemical reactions such as epoxidation and phosphorus addition. These modified forms find use in various specialized applications[1]. Epoxidised rubber improves adhesion of rubber compounds to various substrates. Phosphorus modification was attempted with a view to find application in fire retardant formulations because of the advantage of reduced emission of toxic combustion products of phosphorus containing flame retardant materials, over their chlorine containing counterparts. Easy dissolution of low molecular weight rubber can be taken as an advantage in the preparation of various other forms[2]. Natural rubber contains substantial quantity of gel which makes dissolution of rubber in solvent, a time consuming process. In addition, the concentration of rubber has to be limited to less than 3 to 5 per cent to ensure a free flowing solution. In the present case natural rubber was depolymerized in the latex stage by the action of phenyl hydrazine-oxygen redox system[3], and the depolymerized latex was epoxidised by performic acid, formed *in-situ* by the reaction between formic acid and hydrogen peroxide[4]. The epoxidised liquid natural rubber (ELNR) was dried as a thin film. The ELNR was purified by solvent extraction and phosphorus addition was carried out by the action of dibutyl phosphate in bulk and also in solution . The scheme of the process is given below.

Scheme of work



LNR used in this study was produced in latex phase, through the combined action of phenylhydrazine and atmospheric oxygen. Phenylhydrazine with oxygen in air gives phenyl radicals which attack the isoprene chain by addition and transfer reactions. Oxygen is grafted on to the macromolecular radical to form peroxy group, which causes scission of the polymer chain leading to smaller molecules.

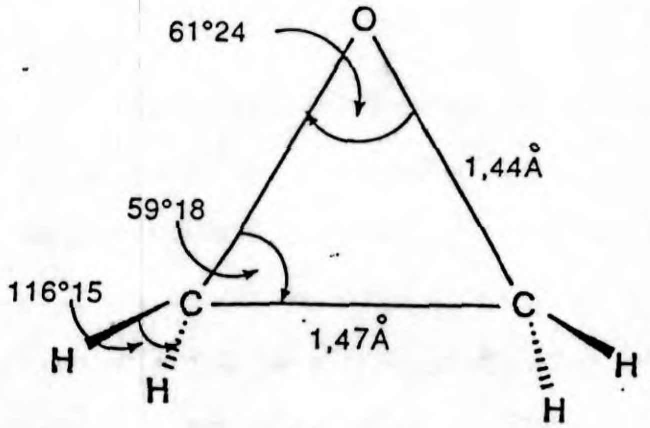


Depolymarization reaction

In addition to the main reaction of depolymerization, side reactions are also possible in the presence of excess phenyl hydrazine which can react with carbonyl groups leading to phenyl hydrazones.

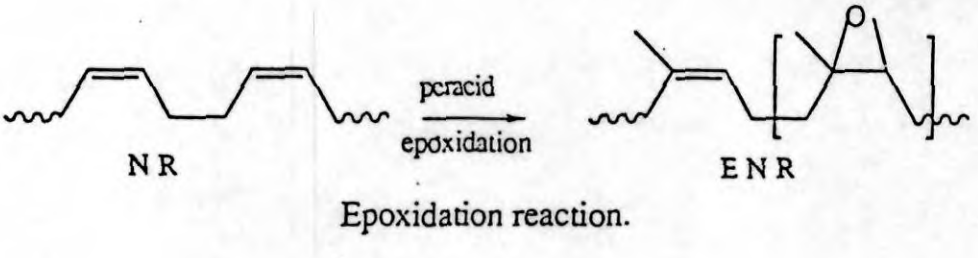
Epoxidation reaction

Epoxidised natural rubber (ENR) is a chemically modified form of natural rubber which has been commercially established now. It has many salient features like strain induced crystallization, improved adhesion, reduced gas permeation, resistance to hydrocarbon oils, etc. The reaction of natural rubber and other unsaturated polymers with epoxidation reagents are well documented. Epoxidised polymers are derivatives of ethylene oxide.



Ethylene oxide

Epoxidation is carried out by reacting NR with a peroxyacid, generally performic acid or peracetic acid. By employing suitable conditions for the reaction, it is possible to epoxidise natural rubber to varying degrees from soft rubbery polymer to hard thermoplastic material. With the escalation of petroleum prices the interest in chemical modification of natural rubber to provide a number of polymer derivatives has increased. New attractive routes in latex phase involving relatively low cost reagents have also been attempted.



Epoxidation reaction.

Epoxidation to different mole percent epoxide levels is possible by selecting suitable concentrations of peracid.

Side reactions

Studies carried out by different workers have revealed that epoxidation of natural rubber latex with peroxy acid leads to the formation of secondary ring opened products influenced by the acid concentration and temperature. Two types of ring opened products have been isolated. At low levels of epoxidation the product is normally a diol. For higher levels of modification, as the number of epoxide groups increases, five member cyclic ether becomes the major product. Furanisation is another type of reaction. Oxidation products that contain ring opened structures have reduced solubility due to crosslinking reaction that follows the epoxidation reaction.

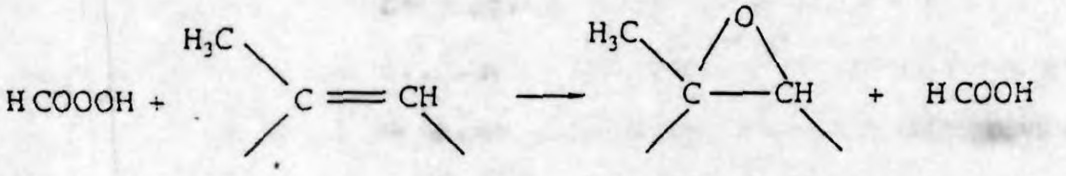
Chemically epoxidation of rubbers is a stereo specific process and the ENR is cis 1,4 polyisoprene with epoxide groups randomly distributed along the polymer backbone. The rate of the reaction is governed by the substituents on the double bond. The ease and positioning of the ring opening epoxides is also controlled by neighbouring groups influenced by electronic and steric factors. Temperature and pH are two important parameters governing the nature of the reaction of rubber with peracids. At low pH and high temperatures, major products are derived from secondary ring opening reactions. So, for the epoxidation of NR, suitable conditions are chosen. The nature of ring opened products depends on the degree of epoxidation. At low modification levels majority of the epoxide groups are isolated due to random reaction, and the major products expected are hydroxy acetals, diols, intermolecular ethers, etc. while at higher levels of crosslinking, cyclic ethers etc., are produced. The extent of epoxidation chosen was 25%. Mild reaction conditions were so employed to minimise secondary reaction products.

.2. Preparation of ELNR

The reaction mixture containing the depolymerized rubber in latex form was diluted to bring down its DRC. This reduction in DRC helps to reduce the extent of side reactions that an happen during the course of the reaction. Formic acid was poured into the reactor and the ontents were stirred well. Adequate quantity of hydrogen peroxide to achieve the desired evel of epoxidation was added into the reactor. Stirring was continued and the temperature was maintained at 60°C. Epoxidation of NR with peracetic acid is a second order reaction. Hydrogen peroxide reacts with formic acid to form performic acid that reacts with the ydrocarbon. The first reaction is endothermic while the second is exothermic.

Formic acid generated during the course of the reaction is recycled. The reaction was llowed to continue for 24 h. The reaction mixture was transferred to a beaker and neutralized with sodium hydroxide. The latex was destabilized and the polymer was separated, washed with water and dried at 110°C.

$$H_2O_2 + HCOOH \rightleftharpoons HCOOOH + H_2O$$



Epoxidation of NR with formic acid-hydrogen peroxide system.

3. Purification

The epoxidised liquid polymer was first purified by extraction with dichloromethane nd then by precipitation with methanol. Small amounts of side reaction products formed uring the epoxidation reaction were also characterized. Crosslinked products exhibited reduced solubility and hence little extractability. Precipitation of the polymer with methanol was expected to free it from relatively more polar fractions containing hydroxyl groups with increased solubility in methanol.

The epoxidised polymer mass was taken into a filter paper cone, inserted in a soxhlet extraction apparatus and extracted with distilling dichloromethane, for 24 h. The polymer was extracted almost completely leaving behind traces (0.7 % by weight) of solid residue on the paper cone. The extract containing the polymer in dichloromethane was partially evaporated and slowly poured into methyl alcohol, agitated vigorously using a magnetic stirrer. The polymer separated and the liquid was allowed to stand undisturbed for distinct separation of the layers. The methyl alcohol phase was decanted and the polymer dissolved in dichloromethane was reprecipitated in methanol. It was then dried on a rotavapor and finally in vacuum desiccator at 40^{o}C (ELNR B). The methanol phase was evaporated and was designated as ELNR A. These two fractions were characterized by different analytical techniques.

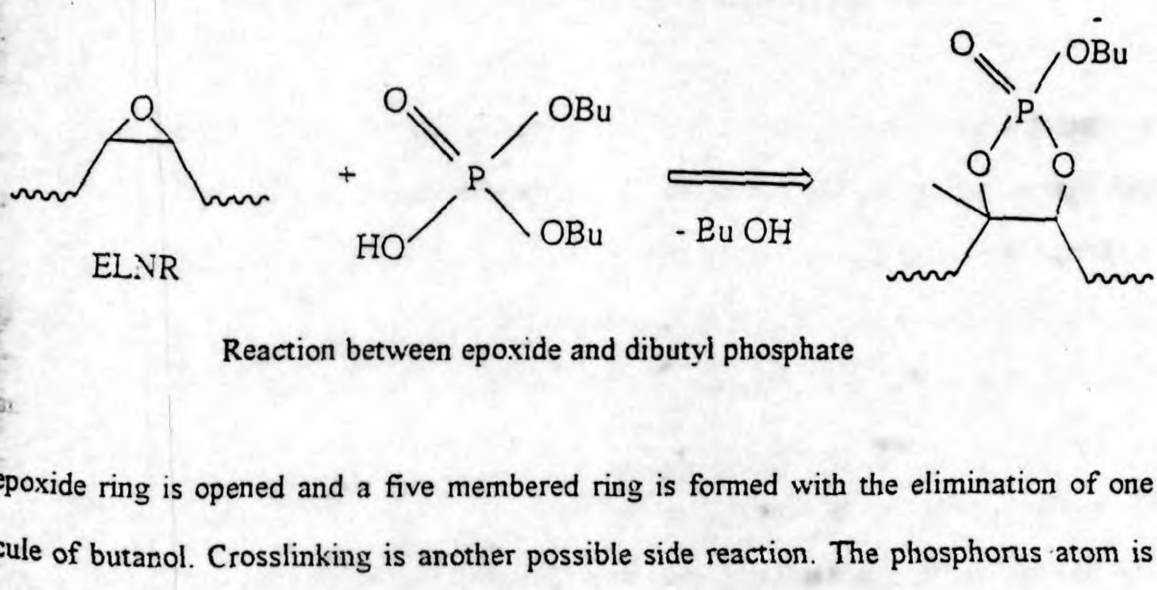
4.4. Phosphorus modification

Possibilities of improving fire resistance properties of polymers by incorporating halogen, phosphorus and/or metal have been subjected to extensive studies[5,6]. Phosphorus containing polymers are increasingly becoming popular over their halogen counterparts as they give out less toxic combustion products. Thermostability and flame retardancy of polyamide phosphate esters were reported by Kannan et al.[7]. Polymers based on phosphorus containing compounds are expensive and have, therefore, not attained much commercial significance.

Modification of conventional polymers with small amount of phosphorus monomers or oligomers to impart flame retardancy on its own or to improve other products has become commercially significant. Phosphorus in the presence of catalysts such as iodine, sulphur, odium, etc. is converted as red phosphorus at 270 to 400°C, a stable non-toxic form. This akes it a useful additive. To prevent decomposition to the toxic and highly inflammable hite form, red phosphorus stabilized with additives is added to thermoset resins[8]. Sulphur s used as a vulcanizing agent in natural rubber formulations and in the present study it is xpected to play the dual role of vulcanizing agent as well as phosphorus stabilizer.

Phosphorus is believed to act as a flame retardant by a variety of mechanisms. robably the most important is its ability to increase markedly the conversion of organic atter to char during burning, and thus to decrease the formation of flammable carbon ontaining gases. The char also helps to protect the substrate from burning interfering with ccess to oxygen and heat according to Sanders[9].

Fixing of phosphorus on natural rubber backbone, is effected by the reaction between poxidised liquid natural rubber and dibutyl phosphate. The anticipated reaction between LNR and dibutyl phosphate is as follows.



Reaction between epoxide and dibutyl phosphate

he epoxide ring is opened and a five membered ring is formed with the elimination of one olecule of butanol. Crosslinking is another possible side reaction. The phosphorus atom is xed on to the polymer in either case. The quantity of dibutyl phosphate required for mplete reaction with 1 g of ELNR was calculated as follows.

If n is the % epoxidation and N the number of units in 1g of ELNR

weight of 100 units = 100 x 68 + n x 16

N = 100/(6800+16n)

for 25% epoxidation N = 0.013888

quantity of epoxide units in 1g = N x n/100 = 3.47 x 10-3 mols

or

0.729g of dibutyl phosphate.

The reaction between dibutyl phosphate and ELNR was carried out by two methods, in bulk and in solution. For the reaction in bulk, the required amount of ELNR and stoichiometric quantity of dibutyl phosphate were taken in a corning glass reactor with a cover suitable for attaching a water condenser and a mechanical stirrer. The mixture were stirred well and the temperature of the bath raised to 100^{o}C. Stirring and refluxing were continued for 24 h. The mixture was then transferred to a filter paper cone and extracted with dichloromethane in a soxhlet extraction apparatus for 8 h. The extract was evaporated, dried and designated as 1P1 and the insoluble solid mass left on the filter paper as 1P2.

For conducting the reaction in solution medium, ELNR was dissolved in toluene in a round bottomed flask and stoichiometric quantity of dibutyl phosphate was added. The mixture was stirred well using a magnetic stirrer and heated in the oil bath to 100^{o}C for 24 h under reflux. The resulting homogeneous solution was slowly poured into well agitated methanol so that the polymer got precipitated. It was collected, dried on a rotavapor slowly, and finally under vacuum. The methanol fraction was dried and designated as 2P1 and the separated polymer as 2P2. Two other reactions 3P and 4P were also carried out applying the same conditions and the polymers after modification were purified and designated as 3P2 and 4P2 respectively. All the above samples were subjected to chemical analysis.

4.5. Results and discussion

LNR:

Figure 4.1 shows the ^1H NMR spectrum of LNR. The resonances at 1.69, 2.05 and 5.10 ppm correspond to cis -CH3-C= , CH2-C= and -C=CH- respectively. Figure 4.2 shows the ^{13}C NMR spectrum of LNR. Five different peaks at 24, 26, 33, 126 and 136 ppm were obtained corresponding to five different states of carbon atoms of the C_5H_8 cis units. the carbon atoms are identified as 1, 2, 3, 4 and 5 in the figure.

The infra-red spectrum of depolymerized rubber is given in Figure 4.3. Absorption bands at 830 cm^{-1} is due to C=C cis, at 1830 cm^{-1} due to CH_3, at 1450 cm^{-1} due to CH_2 bending and at 1660 cm^{-1} due to C=C stretching. The weak peak at 1700 cm^{-1} indicated the formation of small amounts of carbonyl groups during the depolymerization process. A broad but small peak was observed in the range of 3400 to 3500 cm^{-1} due to probable presence of -OH and -NH groups in depolymerized rubber. The number average and weight average molecular weights were measured by GPC technique and the results are

$$\overline{Mn} = 7982$$

$$\overline{Mw} = 21060$$

$$\overline{Mw}/\overline{Mn} = 2.64$$

The viscometric average molecular weight $\overline{Mv}$ was determined using an Ubbelhode glass viscometer (0.58 mm diameter capillary) at 25 ^oC. LNR dissolved in toluene was used for the viscosity measurements. The values of K and coefficient of the Mark-Houwinck equation used are $5.02x10^{-5}$ (dl/g) and 0.667 respectively. The $\overline{Mv}$ of LNR sample was 10,000.

[illegible]

A quantitative analysis of epoxide groups was made utilizing the ^{1}H NMR spectrum by comparison of the integral values corresponding to the proton on the carbon-carbon double bonds with epoxide oxygen. Figure 4.4. gives the ^{1}H NMR spectrum of ELNR. The level of epoxidation was calculated from the integrals of the peaks corresponding to olefinic bond at 2.25 and epoxy bond at 2.7, in this case $6/(18+6) = 0.25$ or 25%. In addition to the olefinic protons at 5.1 ppm and epoxy group linked proton at 2.7 ppm, the spectrum revealed protons corresponding to methyl groups at 1.7 (unsaturated units) and epoxide units at 1.3.

A small peak corresponding to the furanisation of epoxide linkages was observed at 3.7 ppm. Hence the spectrum was enlarged in the range 2.5 to 5.4 ppm (Figure 4.5.) and it was found that this reaction has proceeded only to a very small extent.

Figure 4.6. shows the ^{13}C NMR spectrum of ELNR. Peak assignments corresponding to different carbon atoms in the isoprene structure are also given in the figure.

Infra-red spectra of the compound (Figure 4.7) shows absorption peaks at 870 and 1240 cm^{-1} corresponding to the double bonds and epoxide groups respectively. The peak at 1600 cm^{-1} corresponding to carbonyl group appears weak. Another weak but enlarged peak at 3500 cm^{-1} is indicative of the presence of traces of -OH and -NH groups.

On purification of epoxidised liquid natural rubber two fractions were obtained. Percentage by weight of the two fractions, extent of epoxidation and results of gel permeation chromatographic analysis are given in Table 4.1.

Table 4.1. Properties of ELNR

Sample	% by weight	% epoxidation	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$
ELNR	100	25	6562	20300	4.47
ELNR A	33.7	29	3554	13500	3.80
ELNR B	65.6	23	7623	27860	3.65

The low molecular weight fraction indicated a higher level of epoxidation. Latex stage epoxidations are two phase systems and, therefore, heterogeneous. The homogeneity in size of the molecules present in latex also can influence the end products. The size of rubber particles in latex varies from 0.02 to 2 micrometer and, therefore the size difference exhibited by different particles are 100 fold. A higher rate of epoxidation than the diffusion rate of peroxy carboxylic acid into the rubber particle can lead to a heterogeneous product. At higher epoxidation in particular the interior of the particles may be at a lower level of epoxidation while the surface may be 100% epoxidised. The level of heterogeneity varies according to the size of the particle.

Figure 4.7. also compares the infra-red absorption spectra of ELNR before and after purification. The spectra of methanol soluble fraction showed more pronounced peaks at 1700 cm^{-1} pertaining to carbonyl groups and at 3500 cm^{-1} due to -OH groups and -NH groups. The reduction in the respective peaks observed in ELNR B is indicative of the relatively higher purity of the precipitated portion. Figures 4.8 and 4.9 are the ^{1}H NMR spectra of ELNR A and ELNR B respectively. Peak at 3.6 was smaller in the case of ELNR B indicating comparatively smaller amounts of furanised product present after purification.

Phosphorus modified polymer:

Results of chemical analysis of the modified polymers showed that the phosphorus content of the samples were consistently different for the preparations in bulk and in solution. The former retained a higher percentage of phosphorus. Higher value of phosphorus content observed for the product prepared in bulk than in solution may be due to retention of small quantities of unreacted dibutyl phosphate in the highly crosslinked mass even after extraction with dichloromethane. Chemical analysis of the polymers was carried out and the results are given in Table 4.2.

Table 4.2. Results of elemental analysis

Phosphorus modified polymer	C%	H%	0%	P%
1P2	64.54	9.42	16.30	6.7
2P2	69.53	9.40	13.75	5.21
3P2	67.45	9.58	16.21	6.66
4P2	68.74	9.60	14.88	5.58

The products 1P2 and 3P2 were prepared by the same method, reaction in bulk and their phosphorus content obtained on chemical analysis were close to each other supporting the repeatability of the reaction. So is the case of 2P2 and 4P2 prepared in solution.

Figure 4.10. shows the ^{1}H NMR spectrum of the soluble portion extracted with dichloromethane from the reaction products in bulk (1P1). Assignments of atoms corresponding to different peaks are also given. A weak peak appearing at 1.2 is due to the presence of methyl corresponding to the opened epoxide ring. Two small peaks at 2.1 and 5.1

were also observed corresponding to hydrogen atoms attached to epoxide ring and C=C. This is due to the presence of small quantities of unreacted ELNR.

^{1}H NMR spectrum of the methanol soluble fraction from the solution reaction products (2P1) is given in Figure 4.11. Weak peaks at 5.1 and 2.1 due to LNR units were more pronounced than in the case of bulk reaction products. This may be attributed to the more efficient purification of the solution reaction product by precipitation than by soxhlet extraction in the case of the bulk reaction product. The reaction in solution medium being slower might also have a contribution to the residual quantity of the reactants.

Figure 4.12. shows the ^{1}H NMR spectrum of the methanol insoluble portion of the solution reaction products (2P2). Peaks corresponding to $-CH_2$, $-CH_3$ and C=CH hydrogen atoms are prominent in the figure indicative of the presence of unsaturated cis 1,4 polyisoprene units. Small peaks were observed corresponding to the butyl group, $-CH_3$ at 1.0 ppm, $-CH_2$ at 1.4 ppm and $-OCH_2$ at 3.8 ppm. Addition of dibutyl phosphate is characterized by a signal which appears between 4.1 and 4.2 ppm which corresponds to -CH in the β position of the phosphorus atom.

Figures 4.13. and 4.14. are the ^{13}C NMR spectra of portions extracted with dichloromethane (1P1) and methanol soluble fraction (2P1) respectively. Peaks are explained under LNR in Figure 4.2. Figure 4.15. is the ^{13}C NMR spectrum of the purified polymer from the reaction in solution (2P2). Peaks correspond to the carbon atoms in the polyisoprene units.

Figure 4.16. gives the ^{31}P NMR spectrum of dibutyl phosphate. ^{31}P NMR spectrum of 1P1 and 2P1 are given in Figures 4.17. and 4.18. respectively. These figures indicated the presence of dibutyl phosphate in the extract (peak at 1.81 ppm). The peak at 16 ppm was

small and revealed the presence of only very small quantities of the phosphorus polymer in the extract. Figure 4.19. is the ^{31}P NMR spectrum of the modified polymer (2P2). Three different peaks close to each other were observed at 15 ppm corresponding to three different states of phosphorus in the modified compound.

DSC plots of the modified polymers in bulk (3P2) and in solution (4P2) are given in Figure 4.20. Tg values recorded were -34.41°C for 3P2 and -18.31°C for 4P2. The shift in Tg may be due to different extents of crosslinking. The curves indicate that the method in which the reaction is carried out influenced the end product.

Figure 4.21. , 4.22. and 4.23. are the TGA thermograms for the samples in nitrogen, air and oxygen respectively. For both the samples weight changes were noticed in three different stages. Reduction in weight around 200°C may be due to the liberation of volatile material owing to the elimination reaction or labile bond scission, that at 400°C may be attributed to the decomposition of hydrocarbons and that at 600°C upwards, due to the burning of char. The slope of the third change was more pronounced in the presence of oxygen due to faster oxidation of the charred mass.

References:

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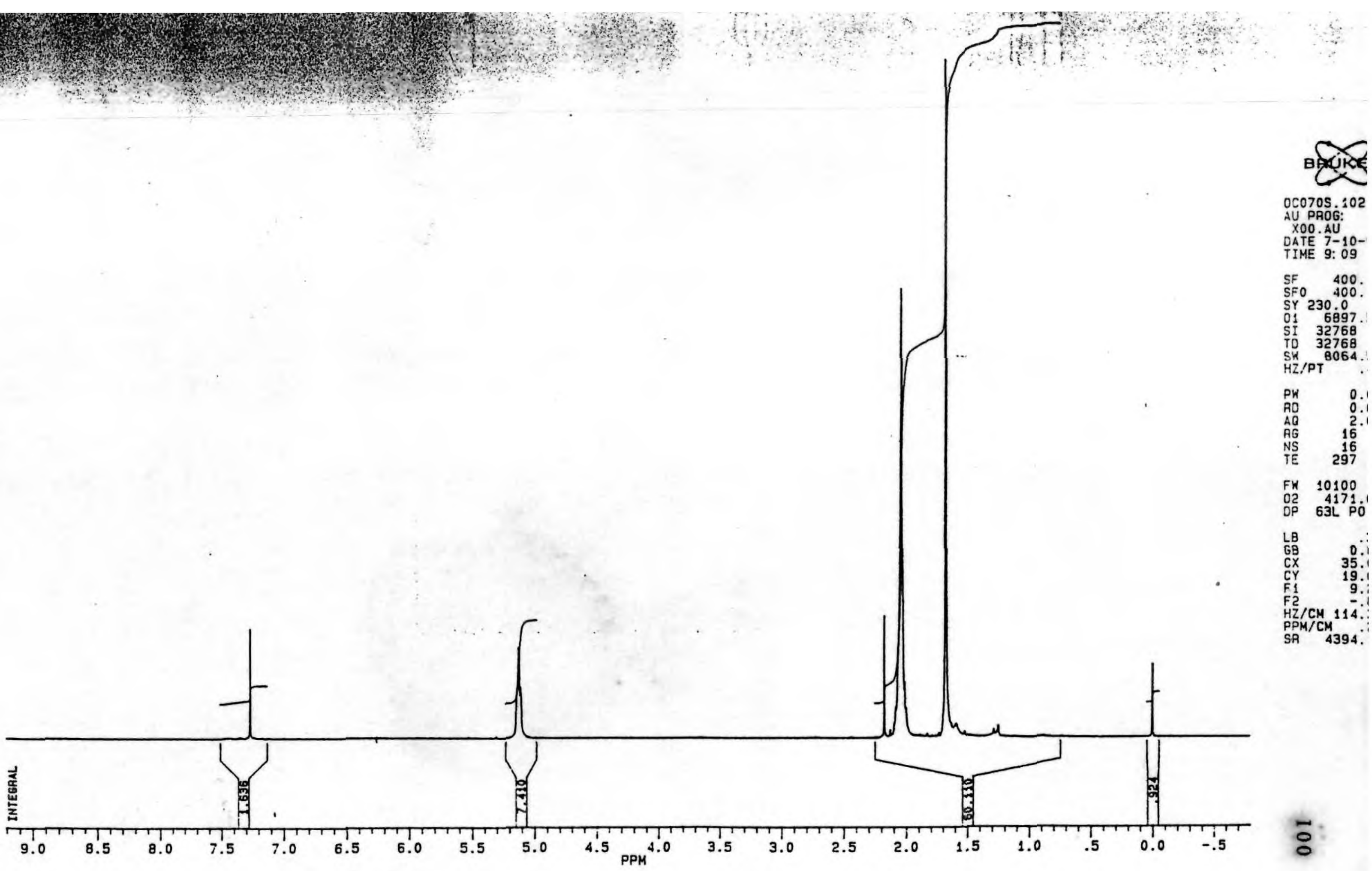


Fig. 4.1. ^{1}H NMR spectrum of LNR

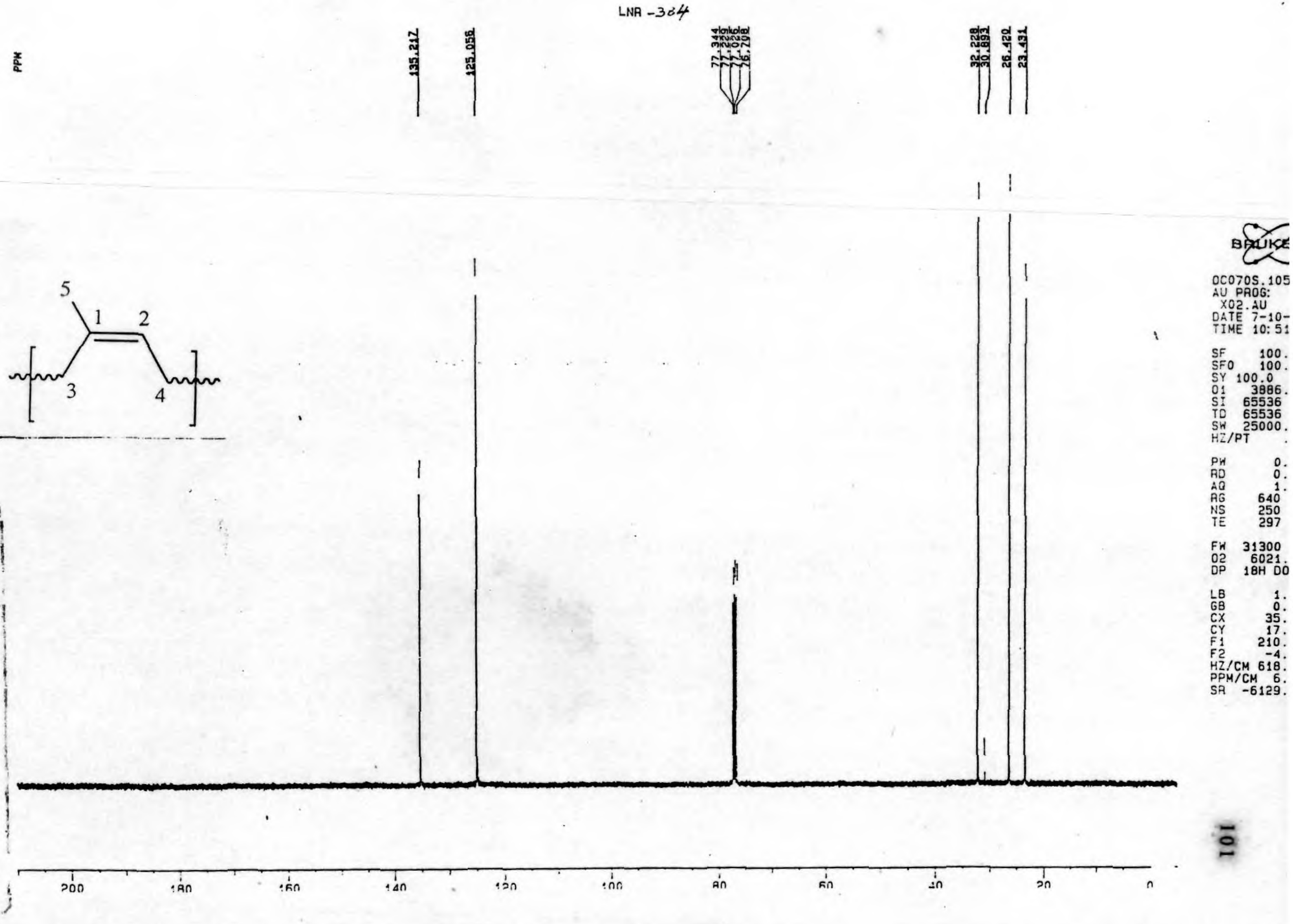


Fig. 4.2 ^{13}C NMR spectrum of LNR

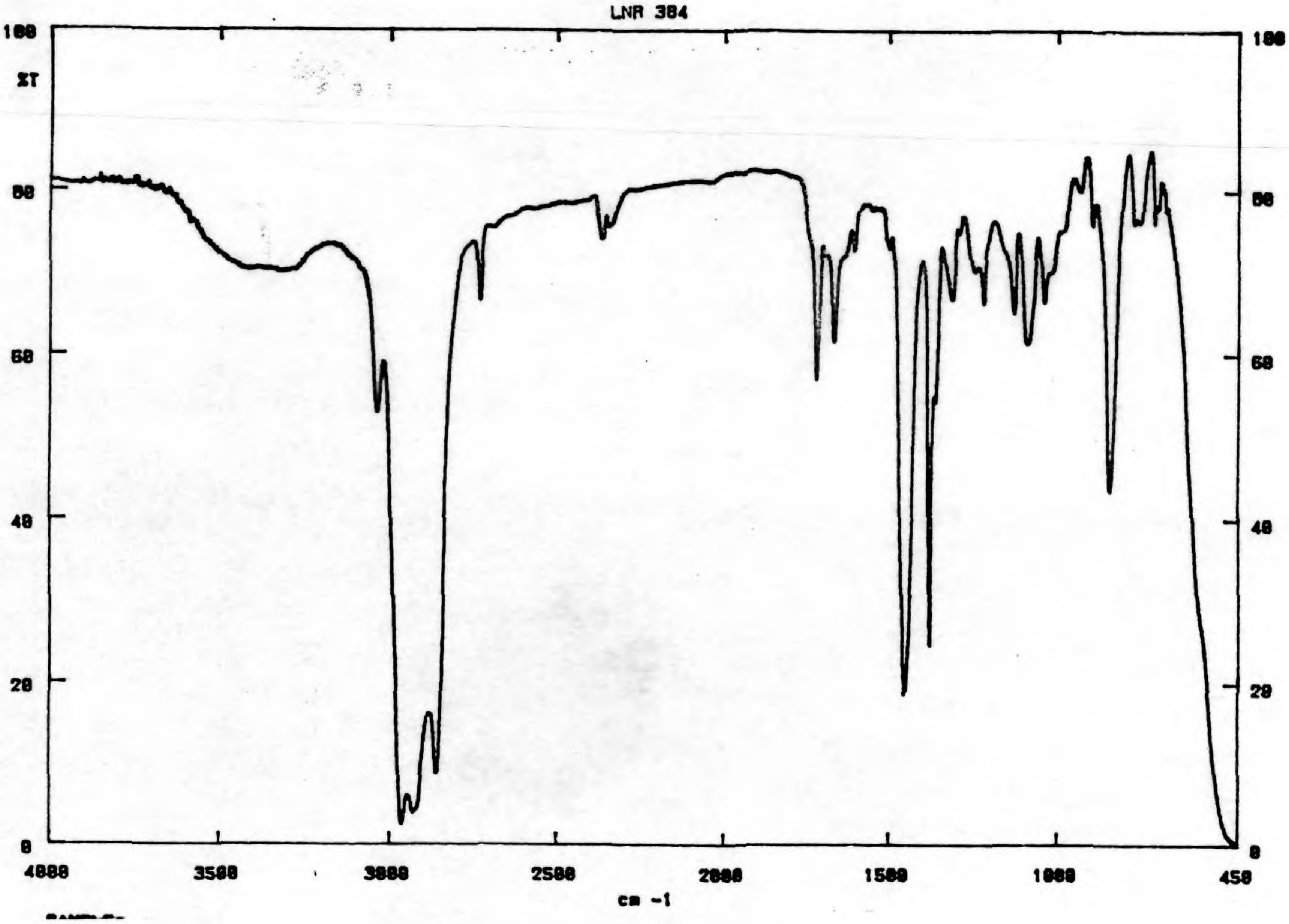
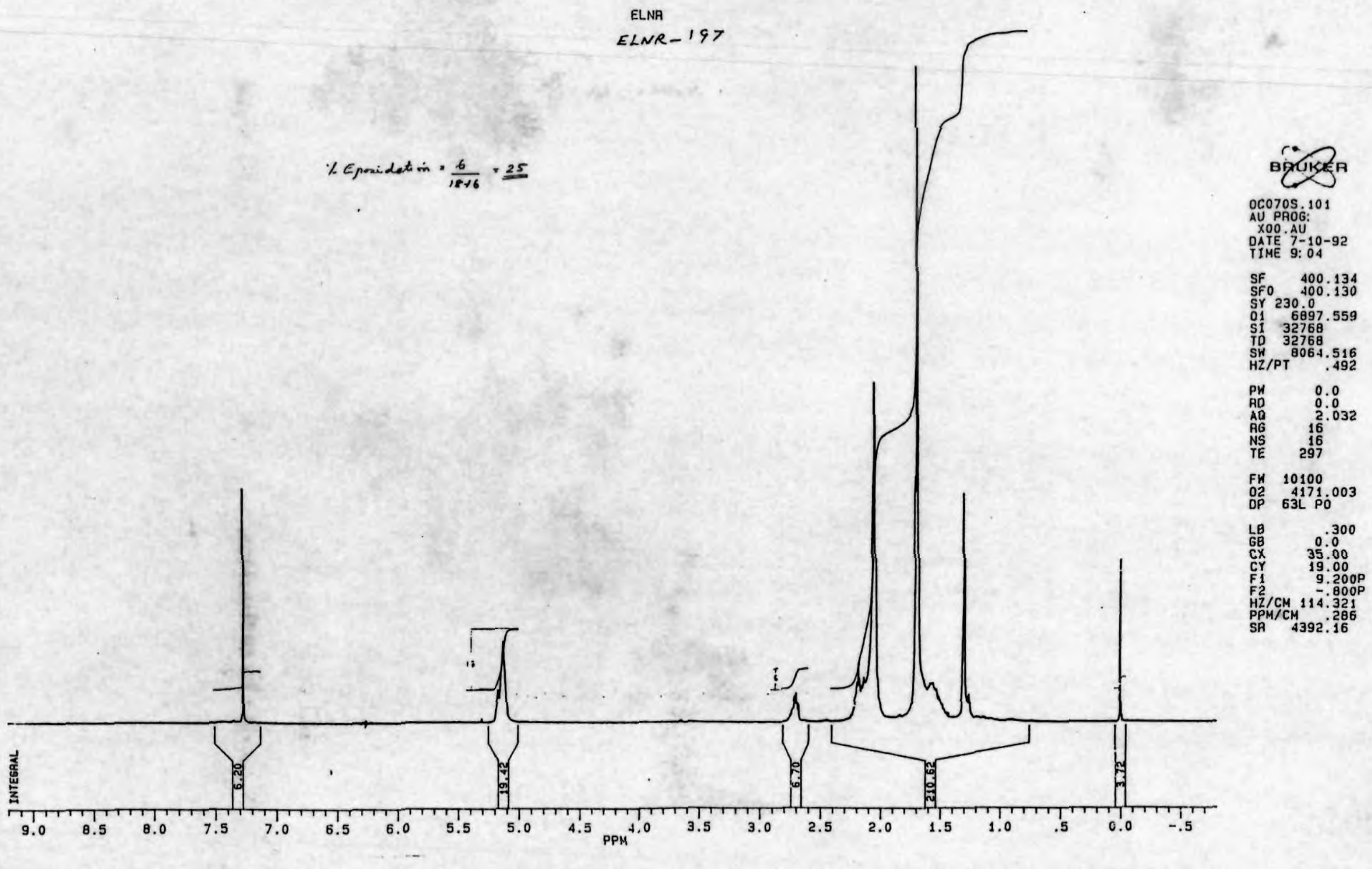


Fig. 4.3. IR spectrum of LNR

N°8420



ELNR-197

% Epoxidation = $\frac{6}{18+6} = \underline{\underline{25}}$

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Fig. 4.4. ^{1}H NMR spectrum of ELNR

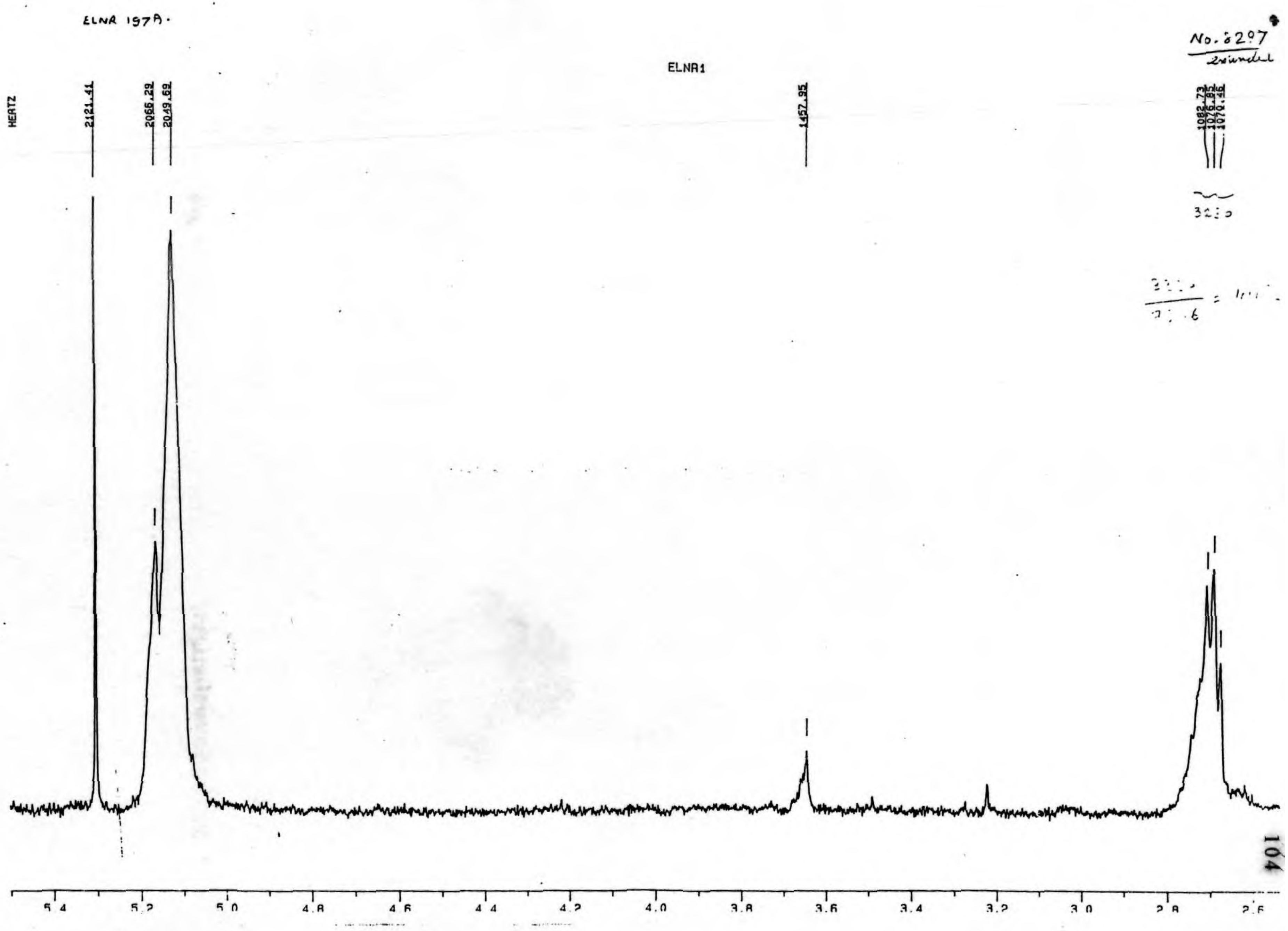


Fig. 4.5. ^{1}H NMR spectrum of ELNR enlarged

No. 8425

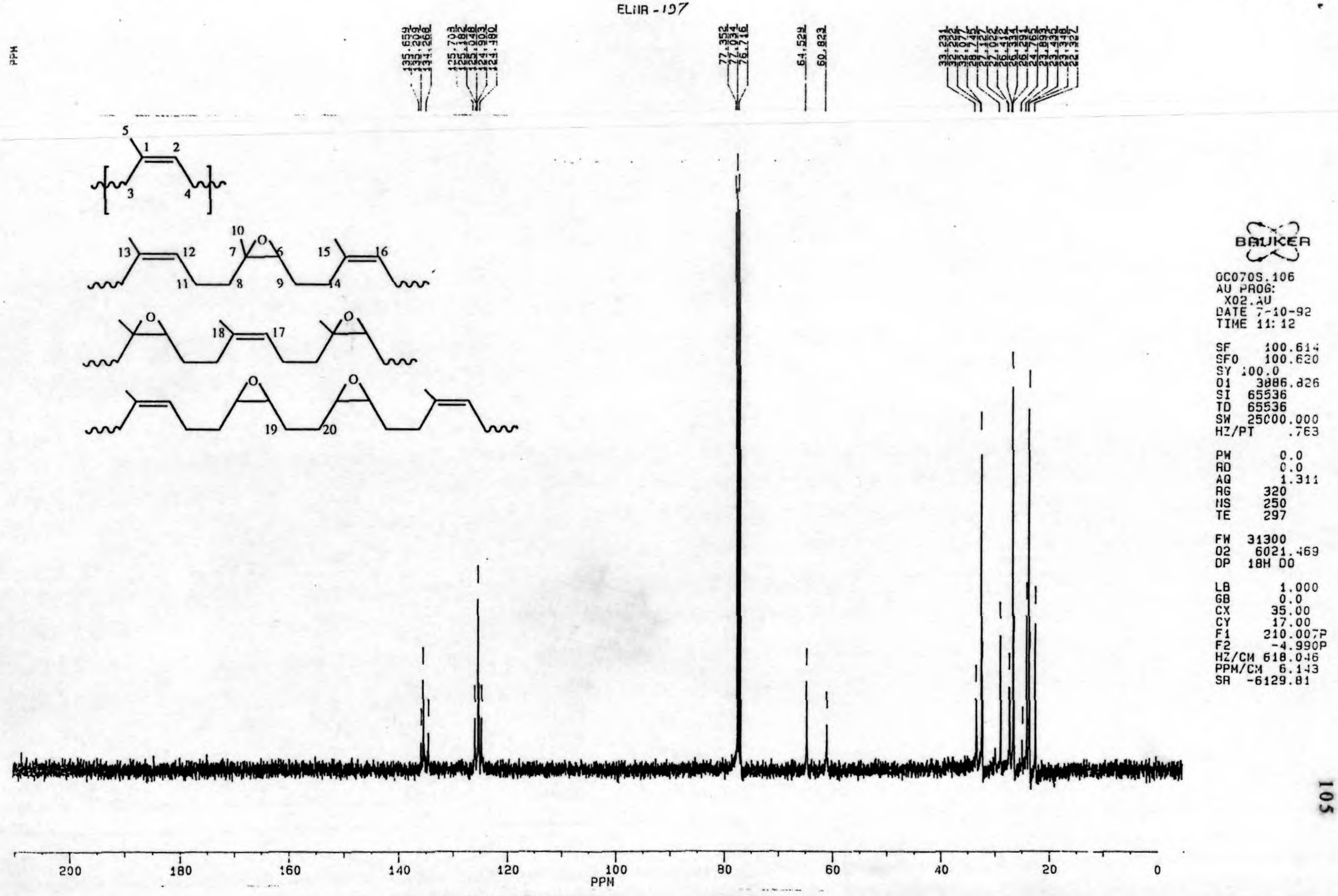
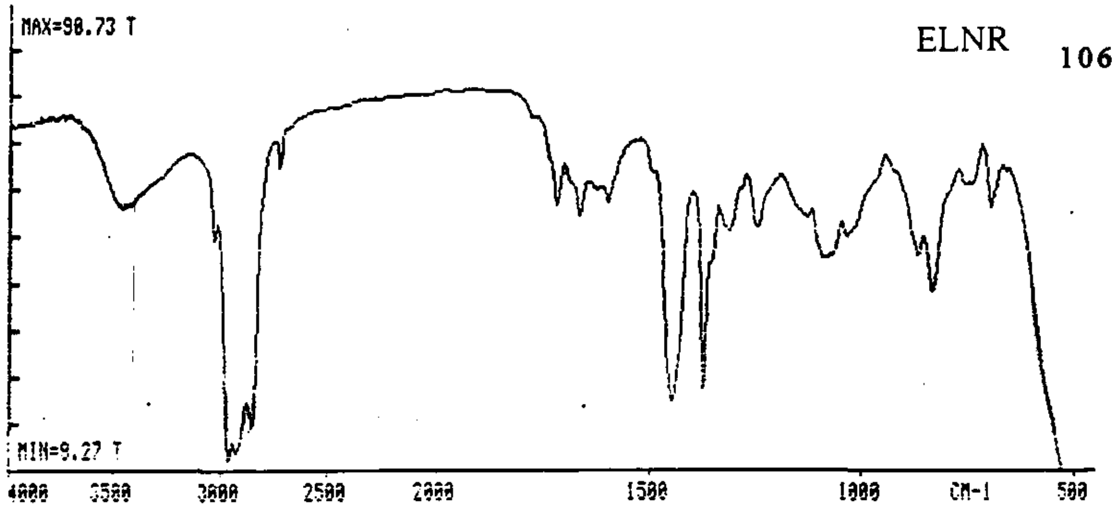
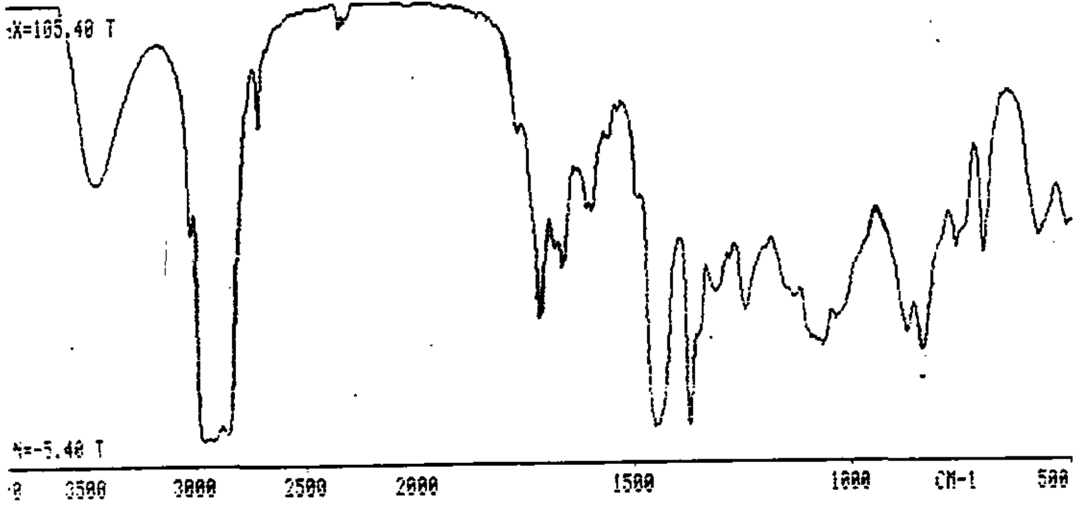


Fig. 4.6 ^{13}C NMR spectrum of ELNR

ELNR



ELNR A



ELNR B

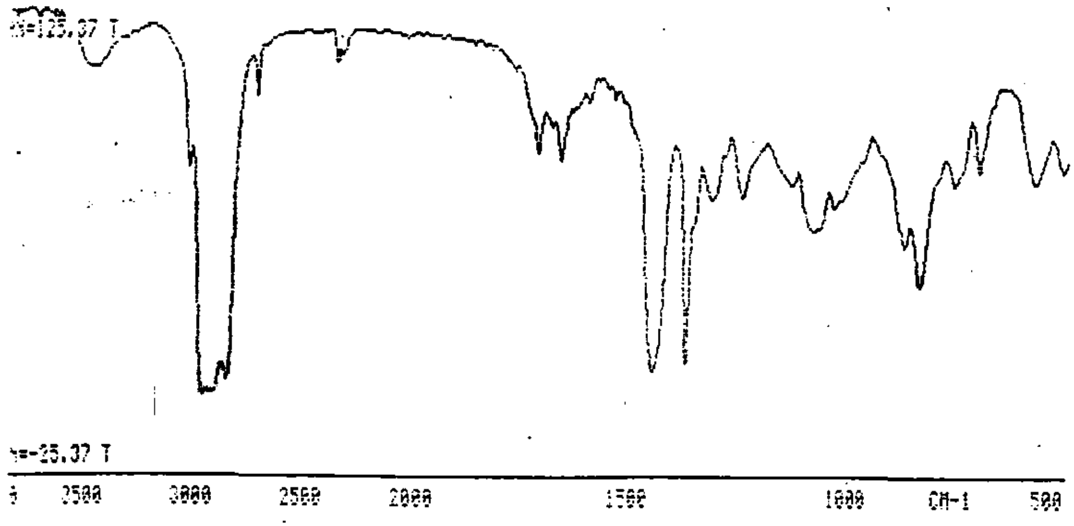


Fig. 4.7. IR spectra . of ELNR and separated fractions.

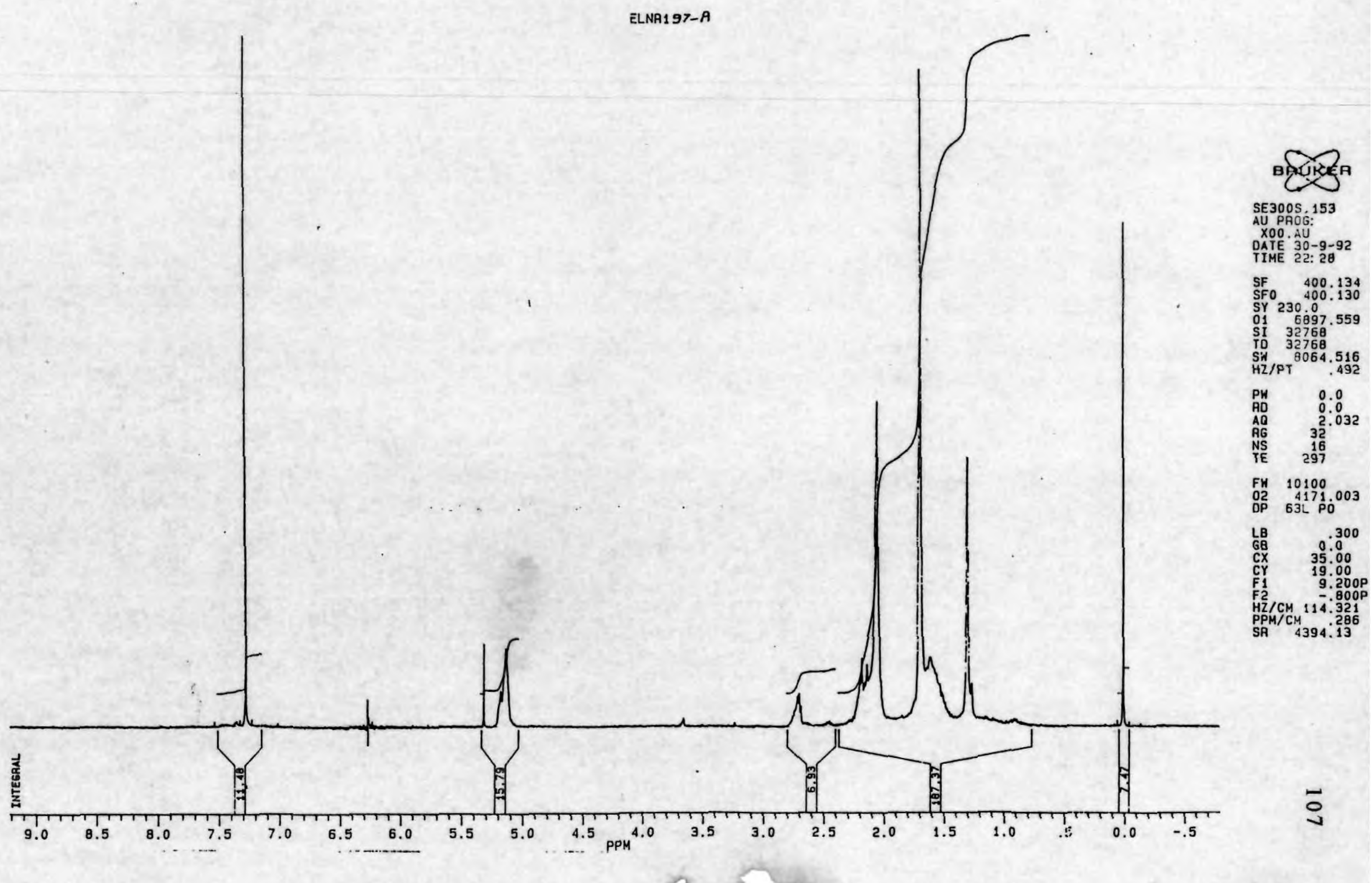


Fig. 4.8. ^{1}H NMR spectrum of ELNR A

N 8296

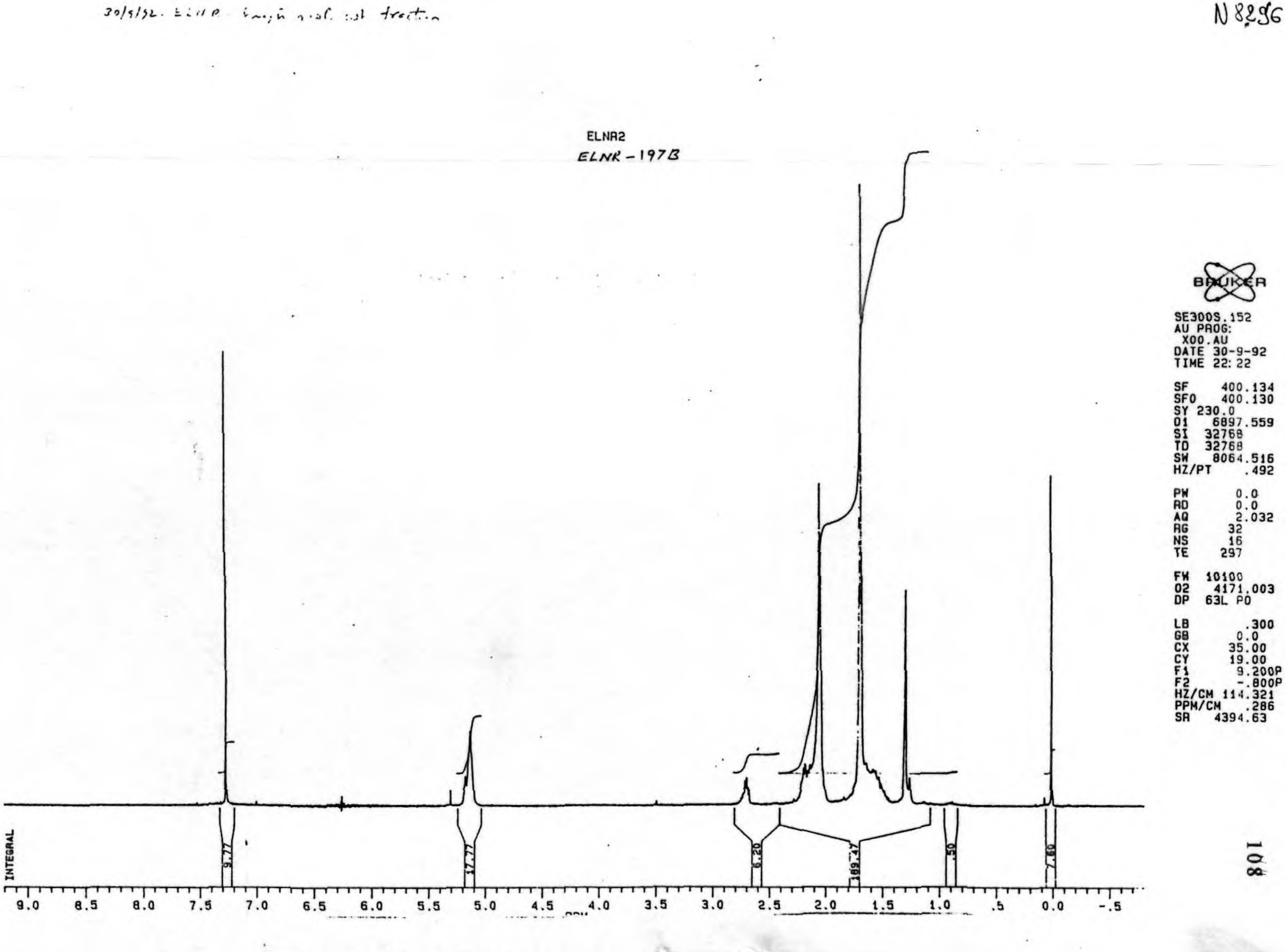


Fig. 4.9. ^{1}H NMR spectrum of ELNR B

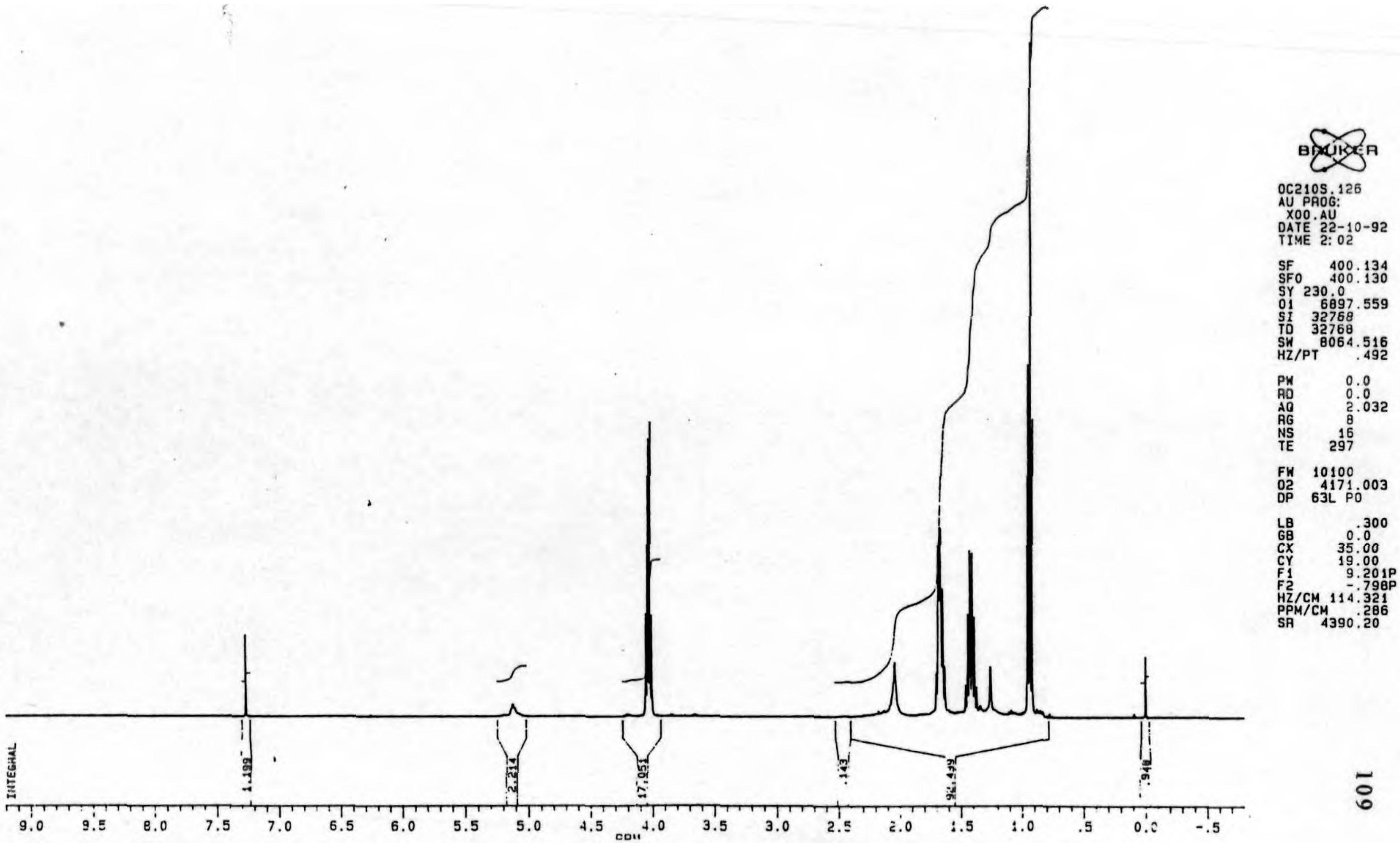


Fig. 4.10. ^{1}H NMR spectrum of dichloromethane extract (1P1)

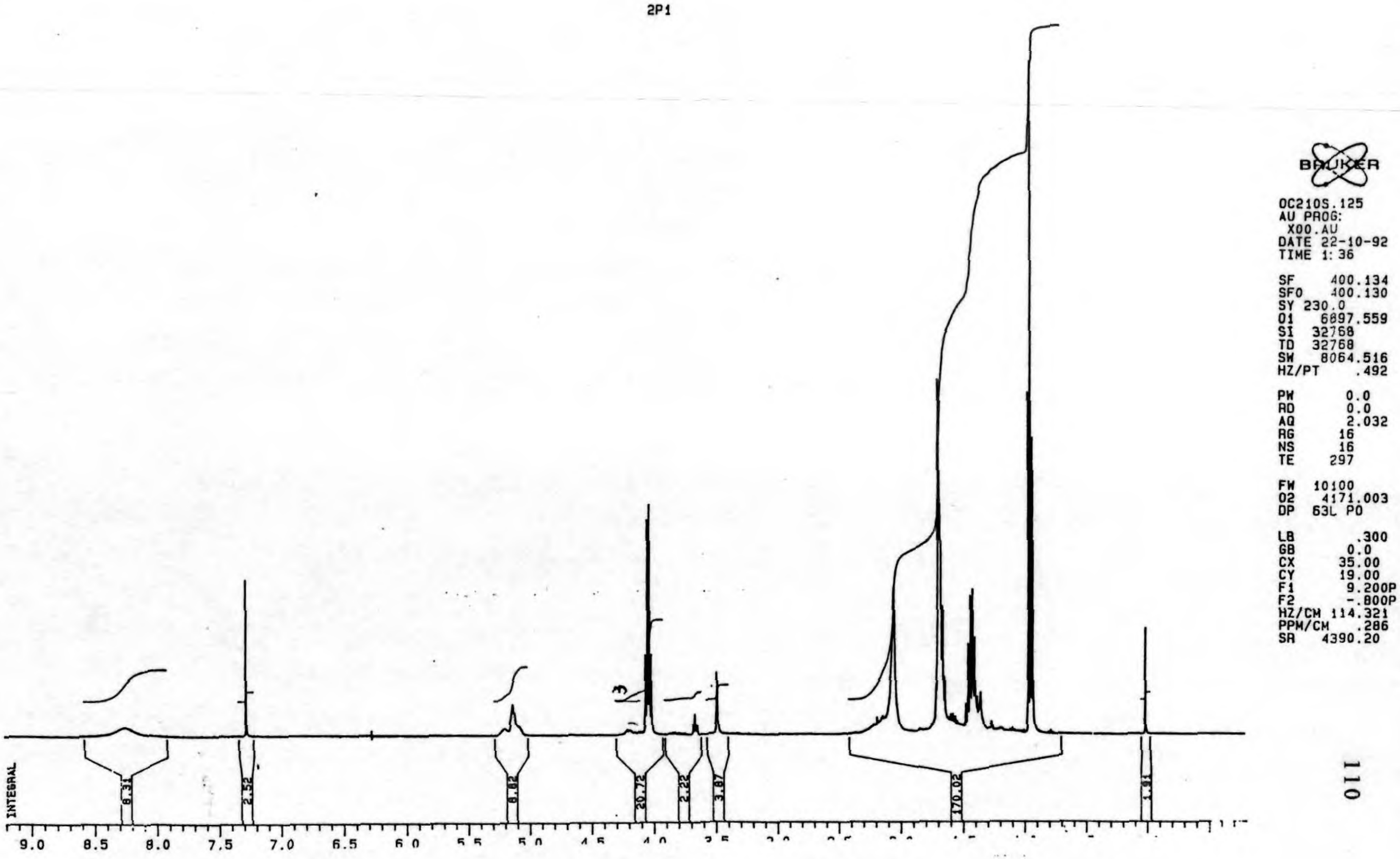


Fig. 4.11. ^{1}H NMR spectrum of methanol solubles (2P1)

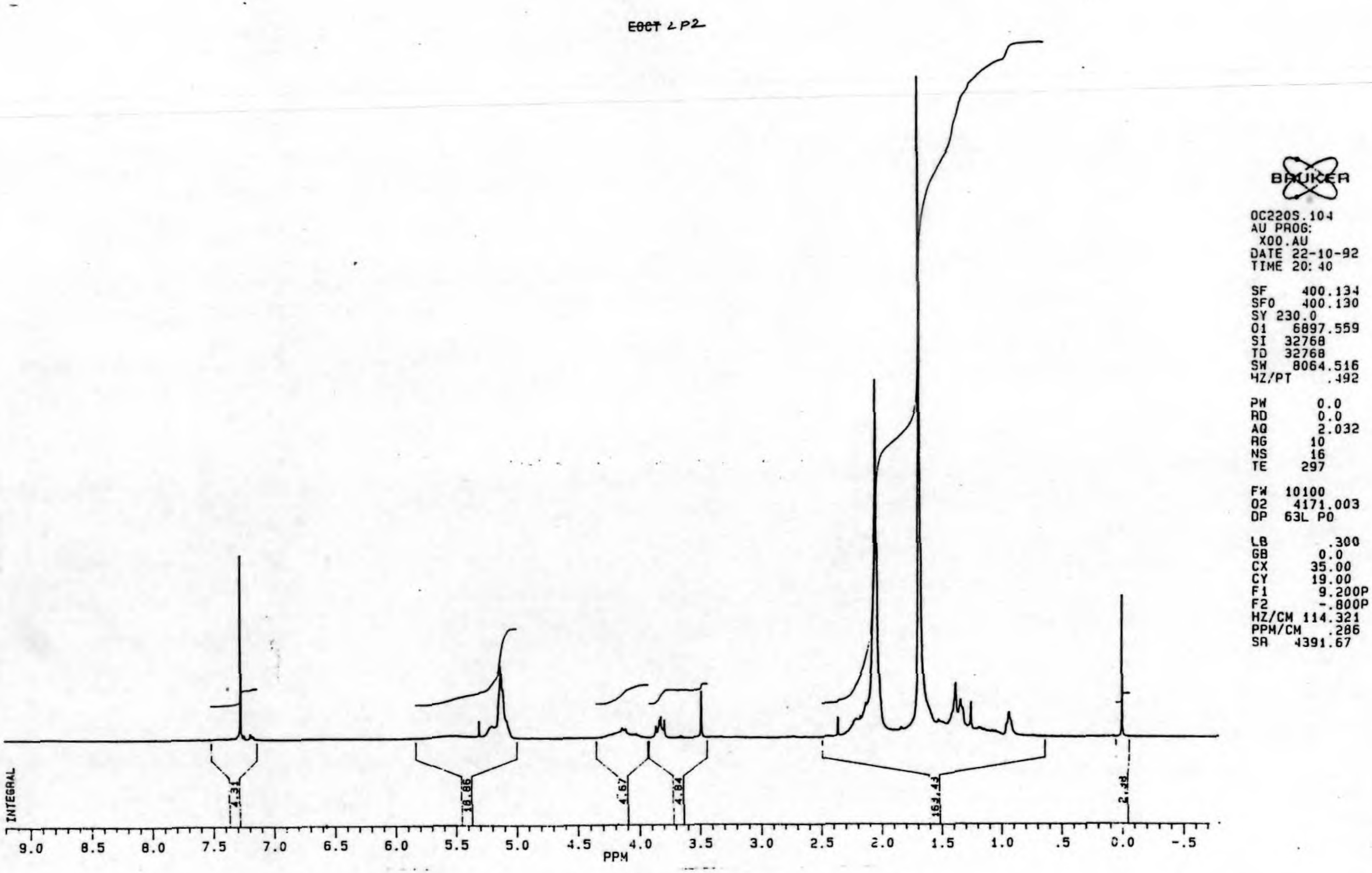


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Fig. 4.12. ^{1}H NMR spectrum of phosphorus modified polymer (2P2)

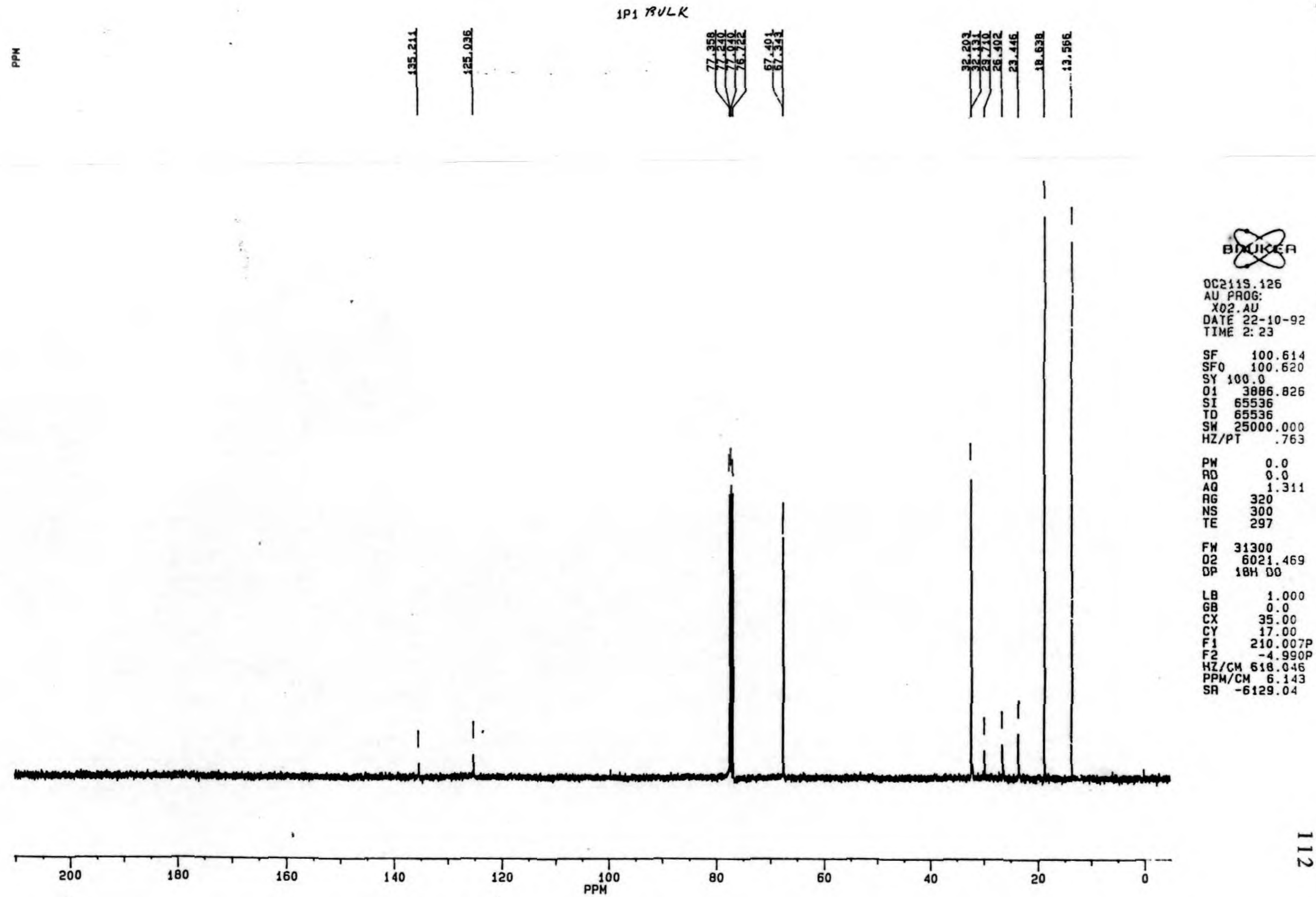


Fig. 4.13. ^{13}C NMR spectrum of dichloromethane extract (1P1)

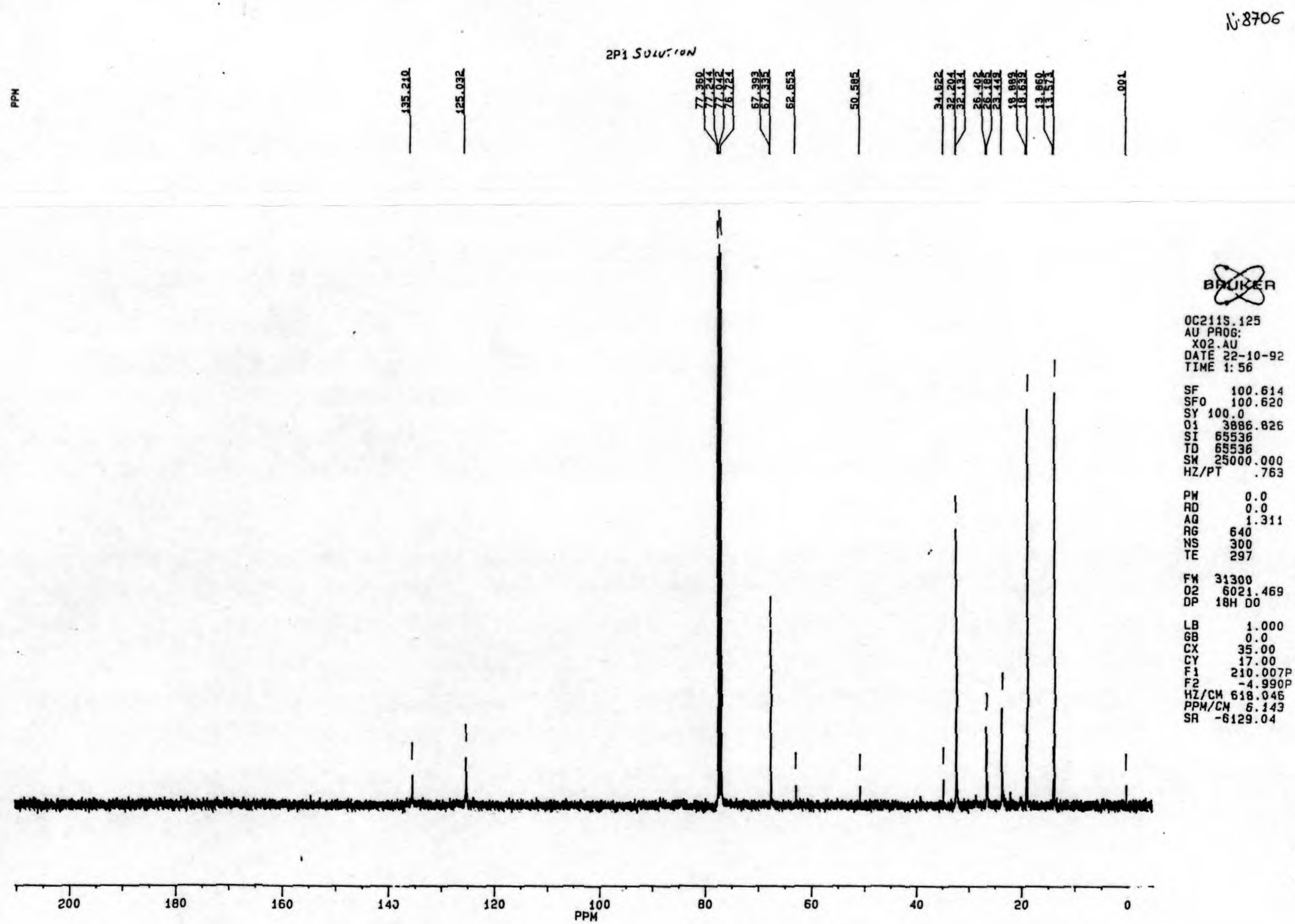


Fig. 4.14. ^{13}C NMR spectrum of methanol solubles (2P1)

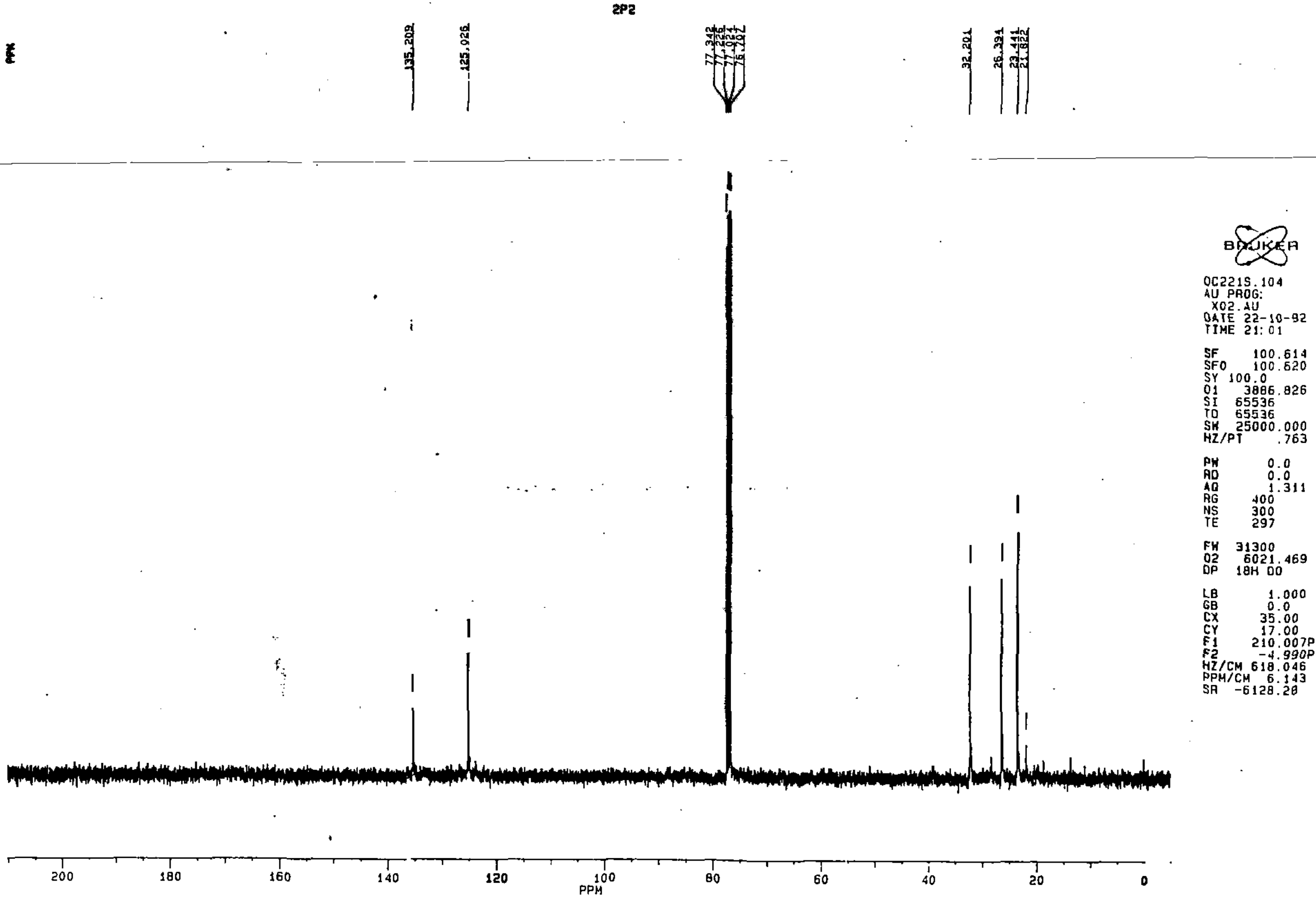


Fig. 4.15. ^{13}C NMR spectrum of phosphorus modified polymer.

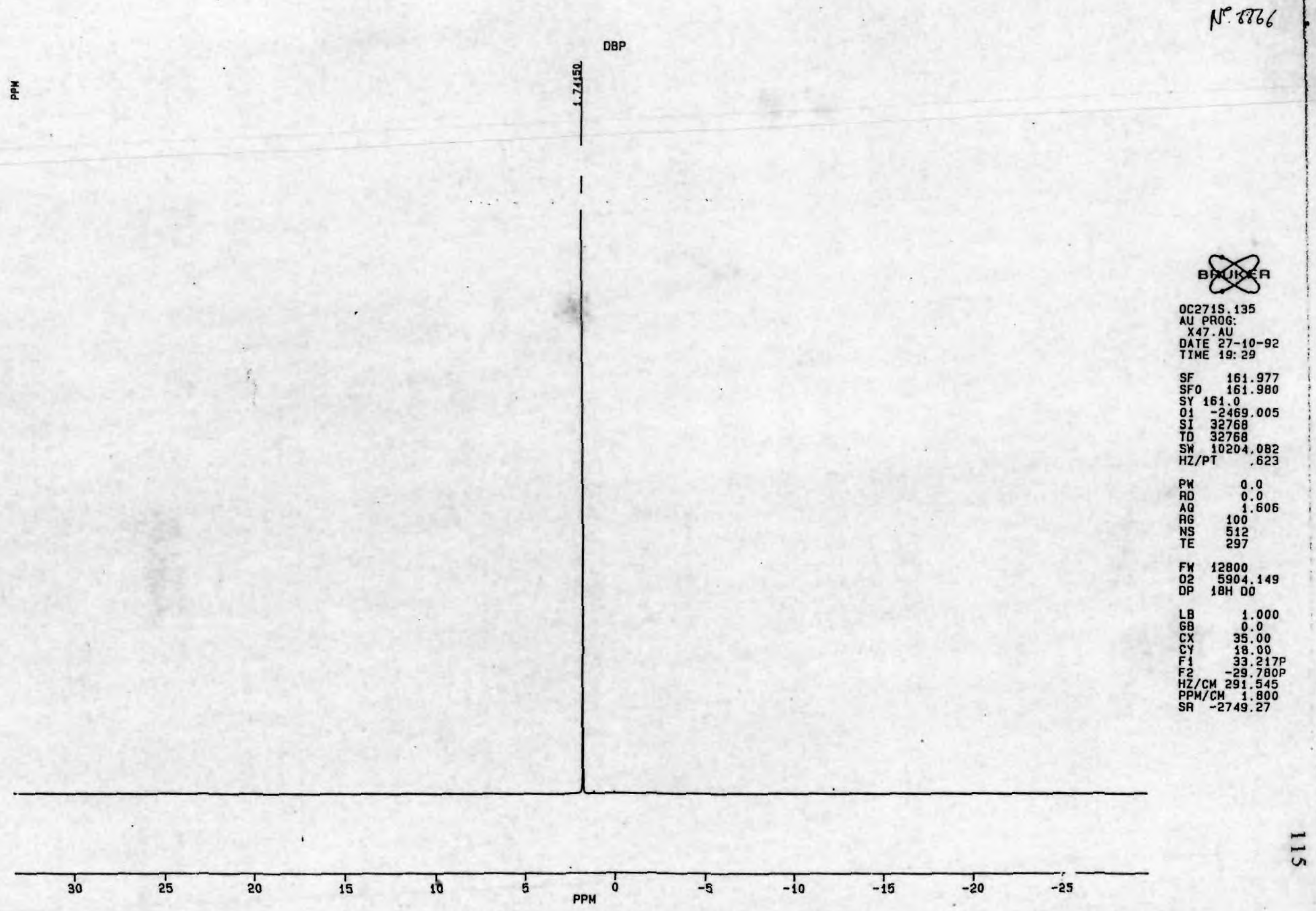


Fig. 4.16. ^{31}P NMR spectrum of dibutylphosphate

N°8776

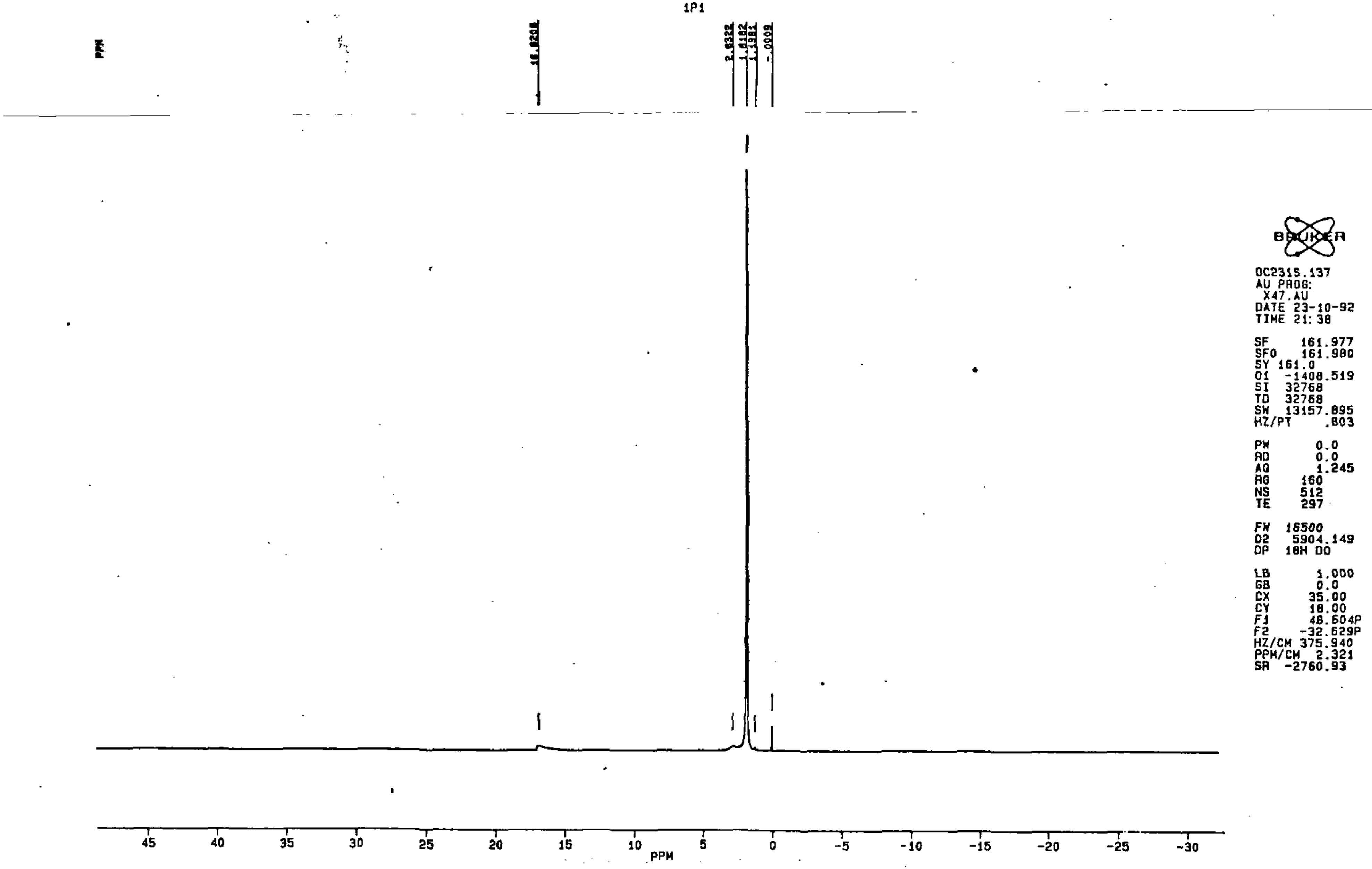


Fig. 4.17. ^{31}P NMR spectrum of dichloromethane extract (1P1)

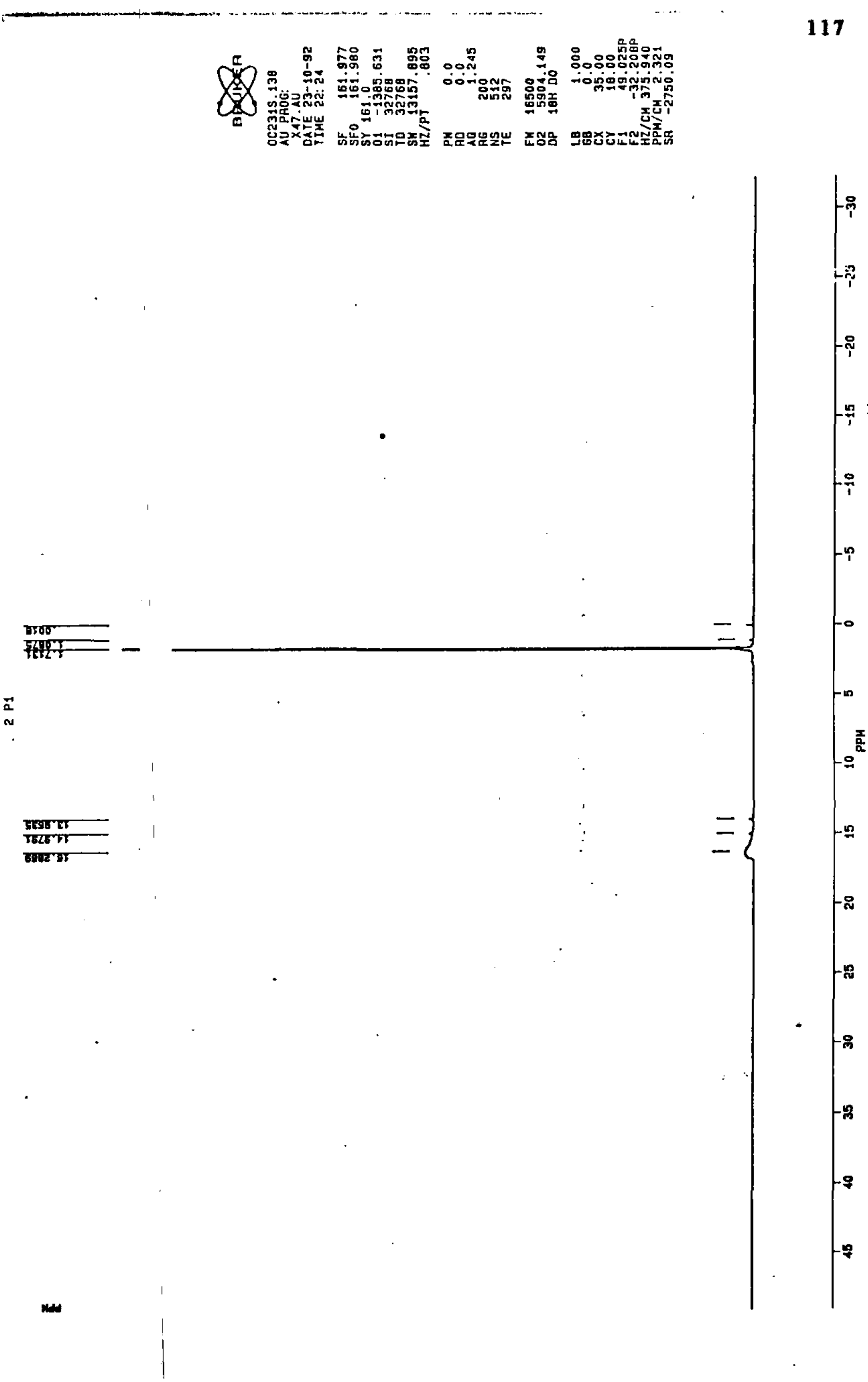


Fig. 4.18. ^{31}P NMR spectrum of methanol solubles

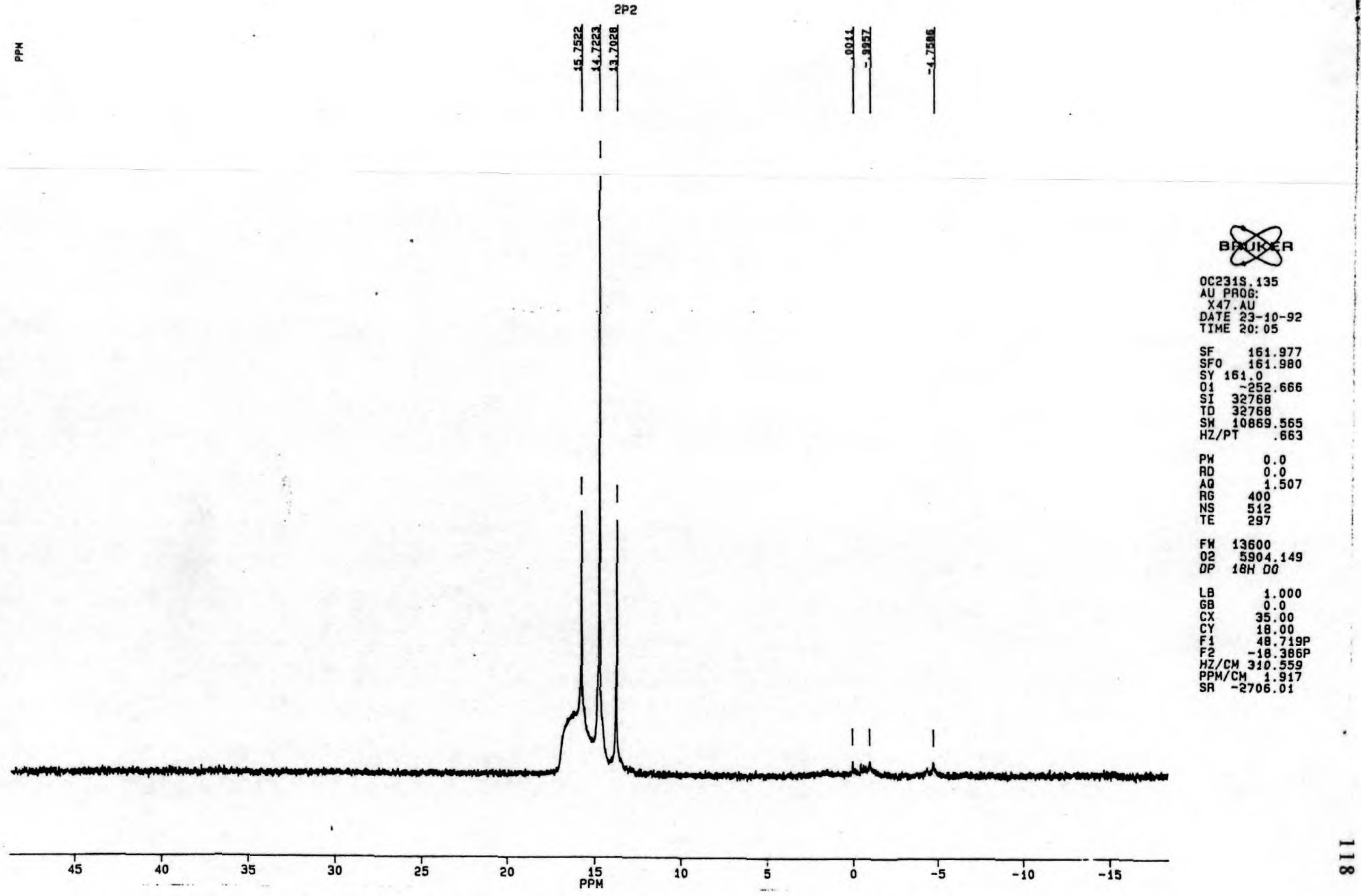
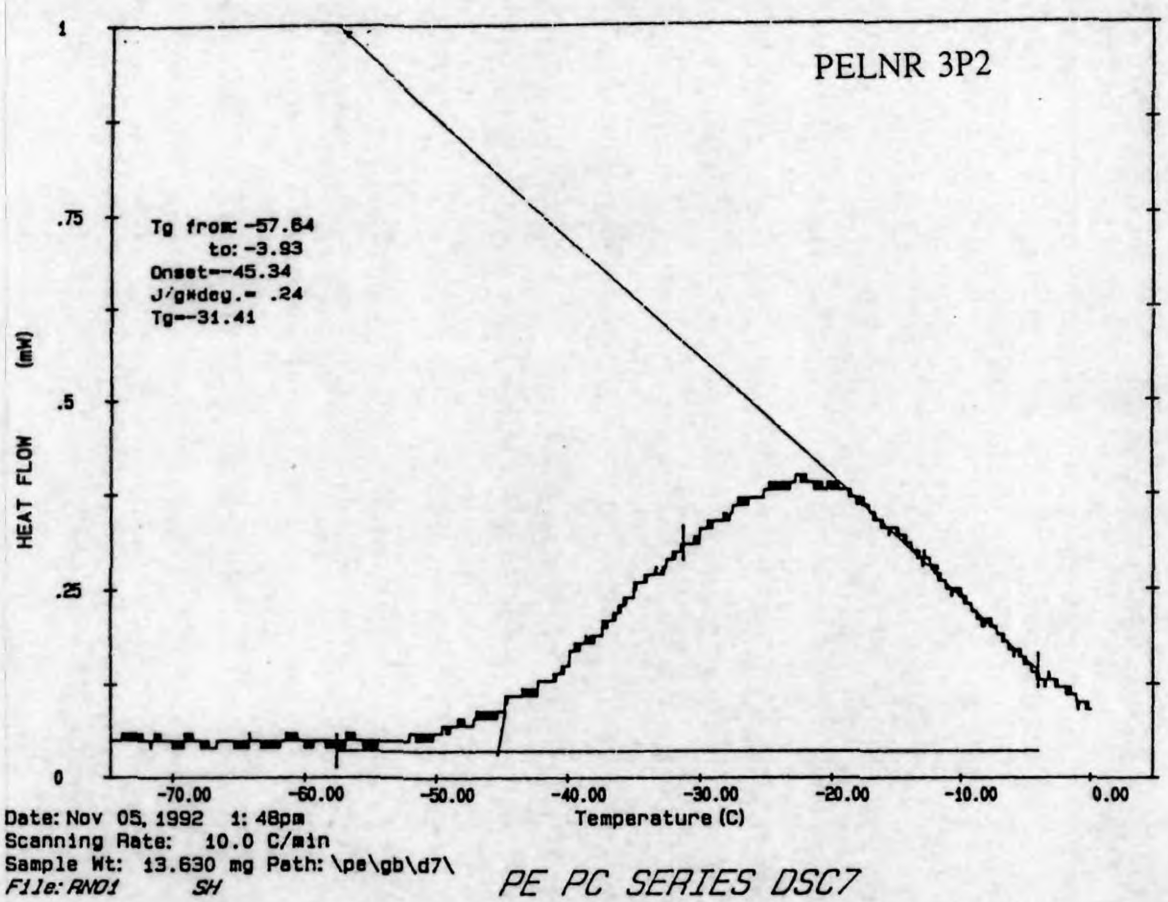


Fig. 4.19. ^{31}P NMR spectrum of phosphorus modified polymer (2P2)



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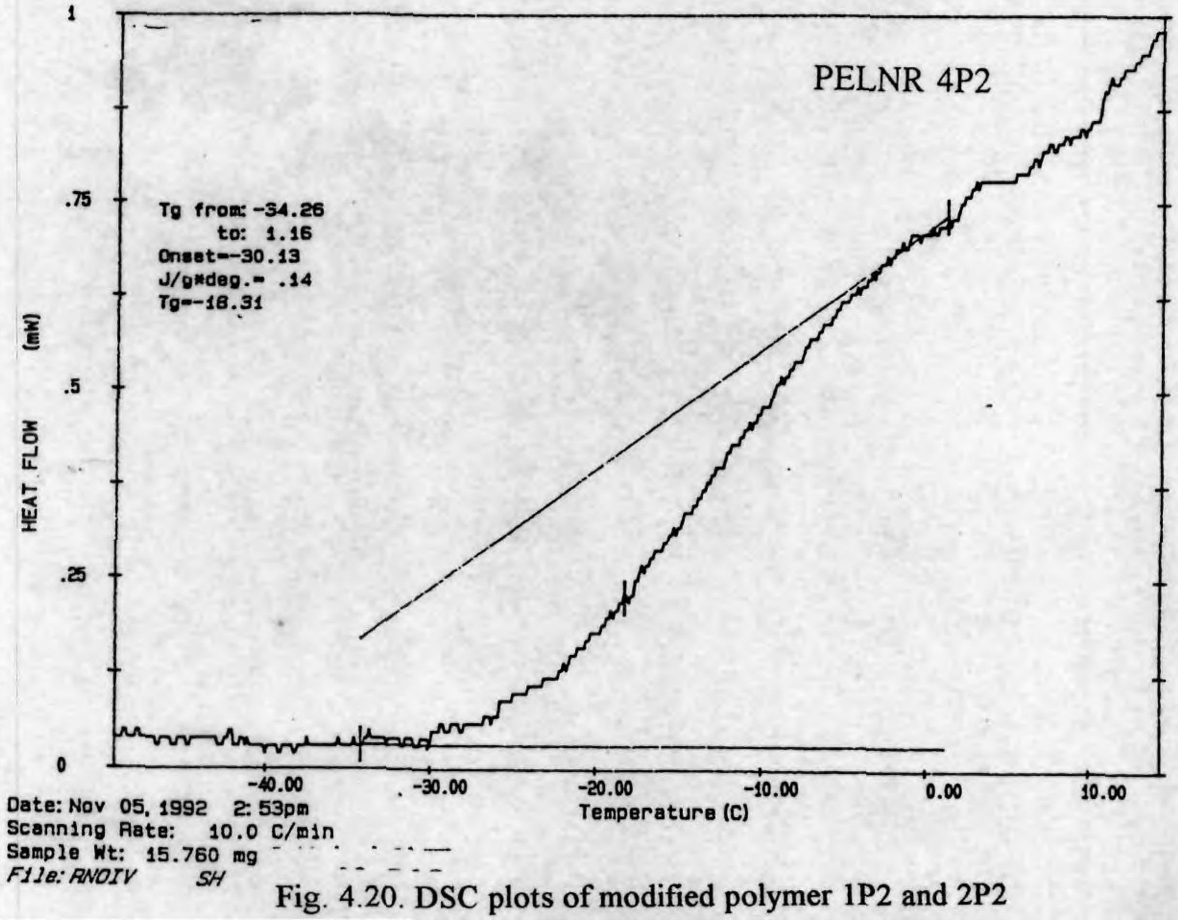

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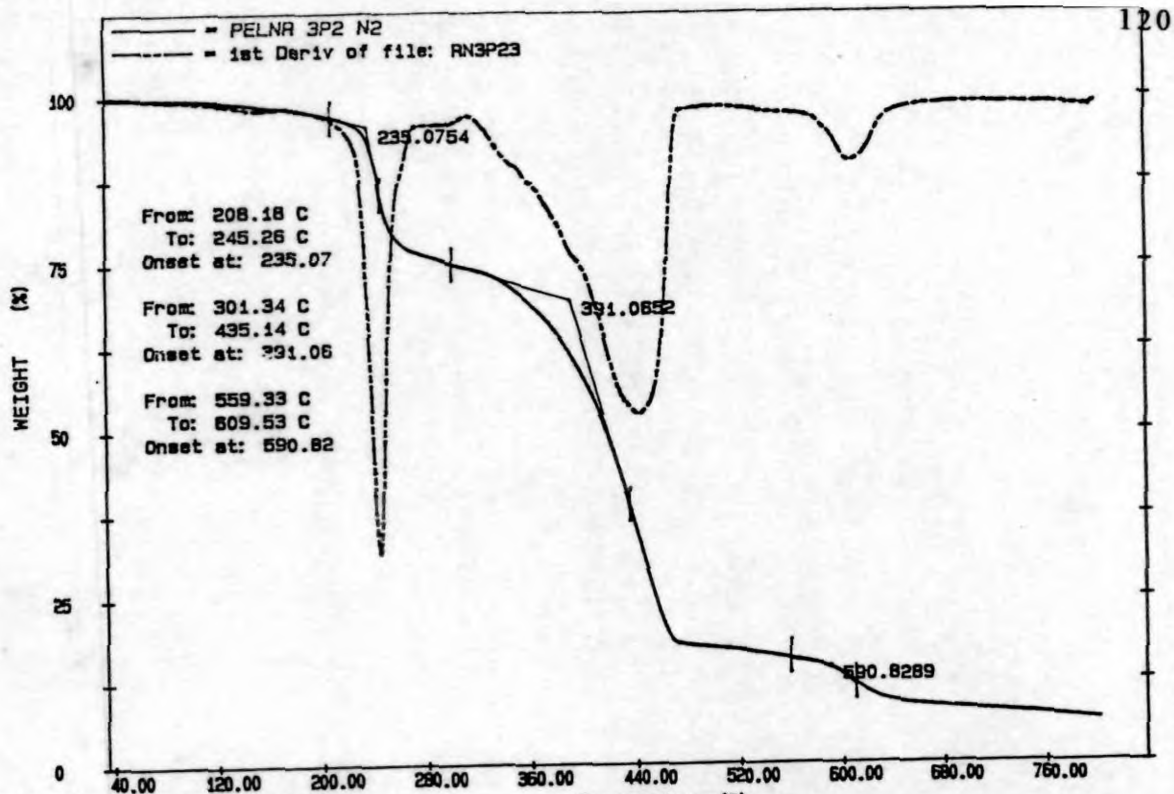
Fig. 4.20. DSC plots of modified polymer 1P2 and 2P2



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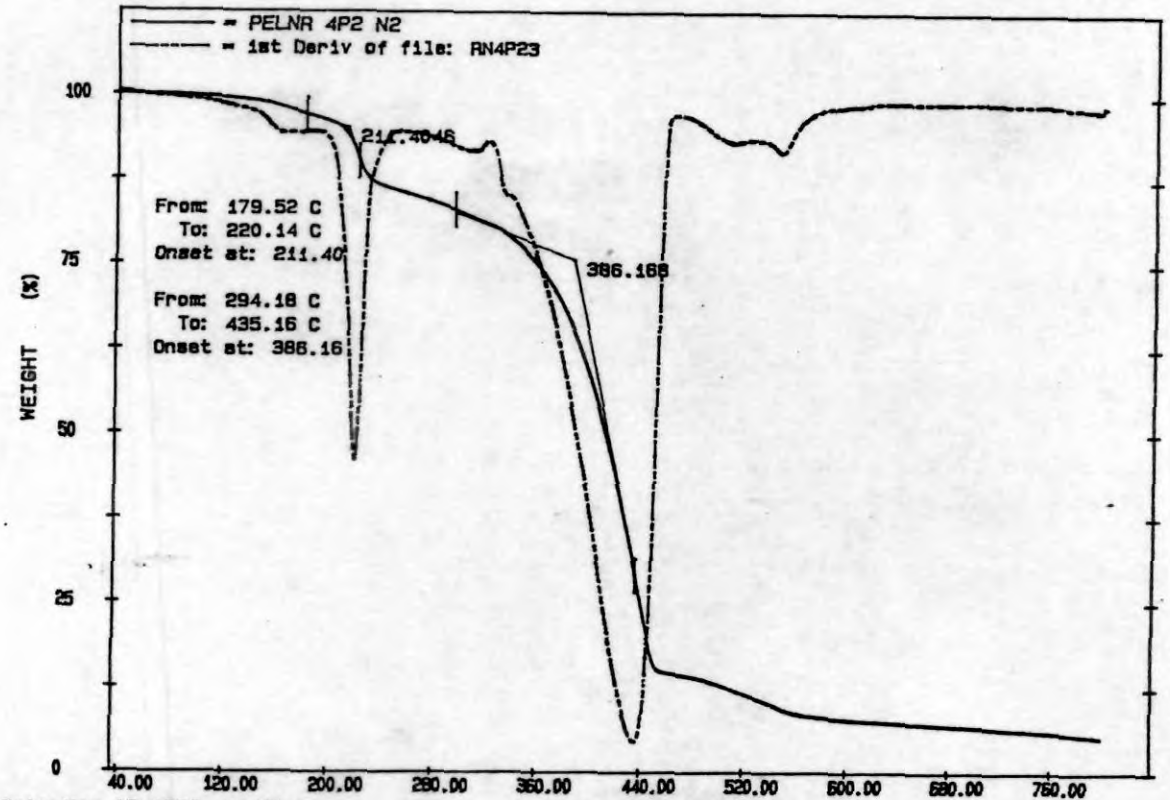

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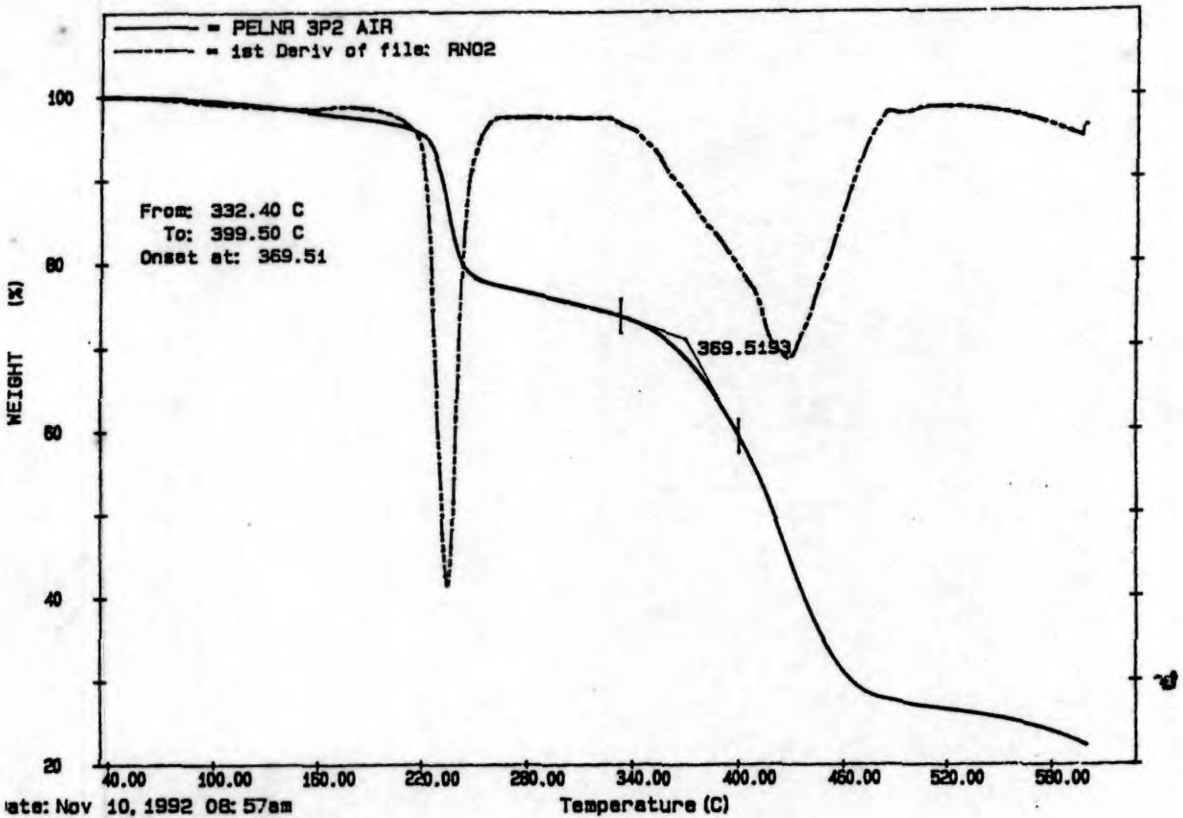
Fig. 4.21. TGA curves of the modified polymers in nitrogen



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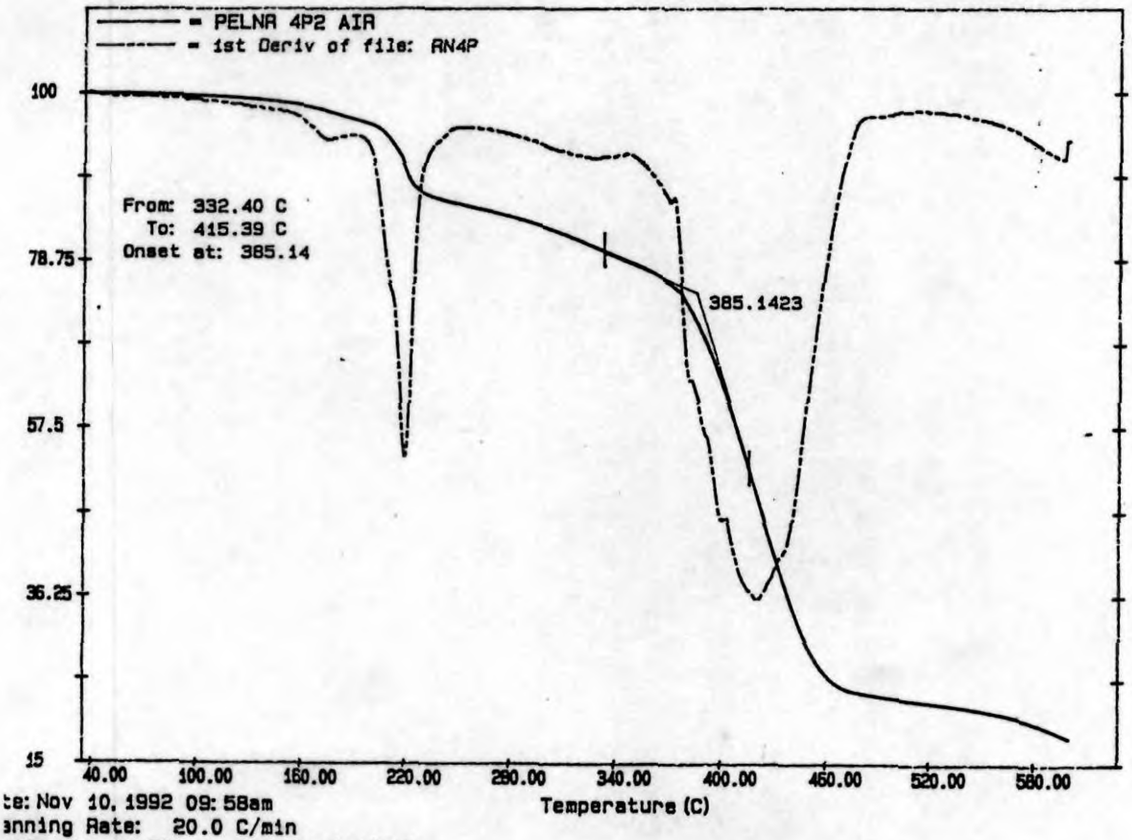

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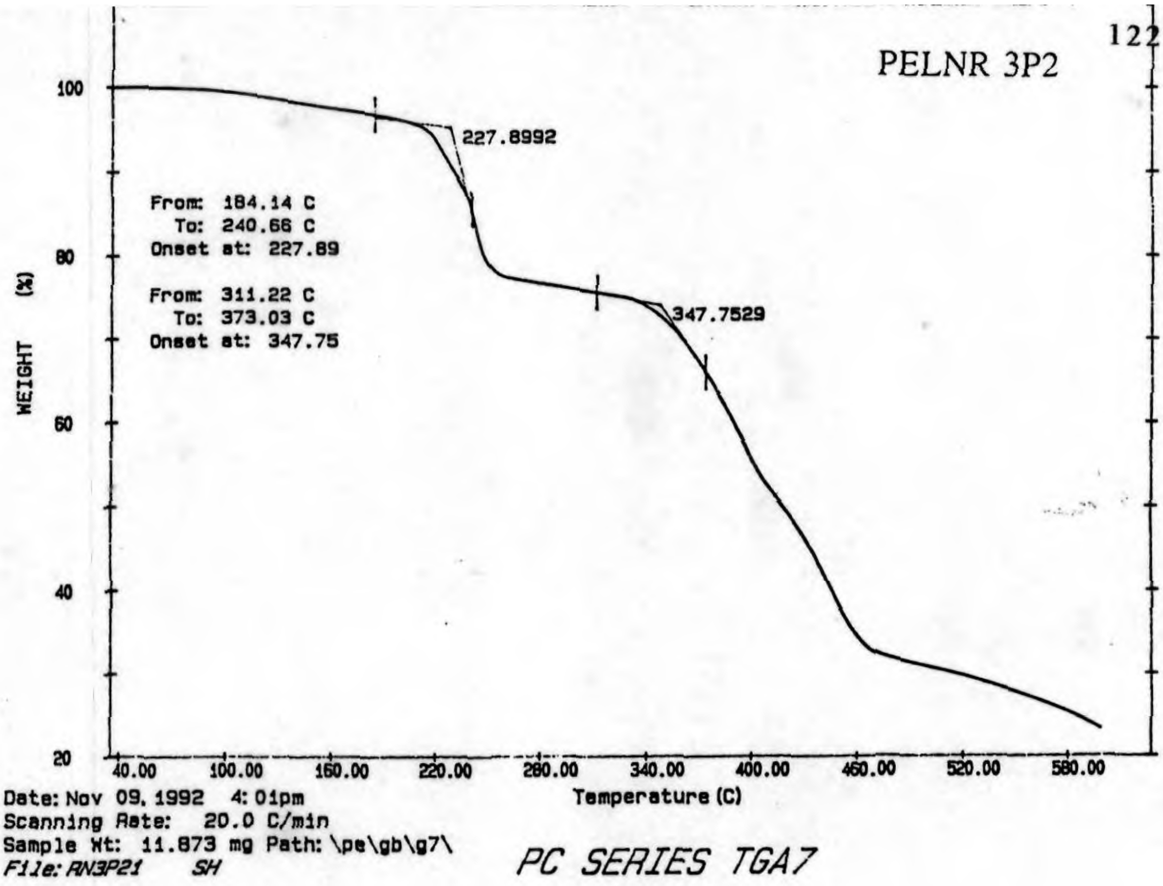
Fig. 4.22. TGA curves of the modified polymers in air



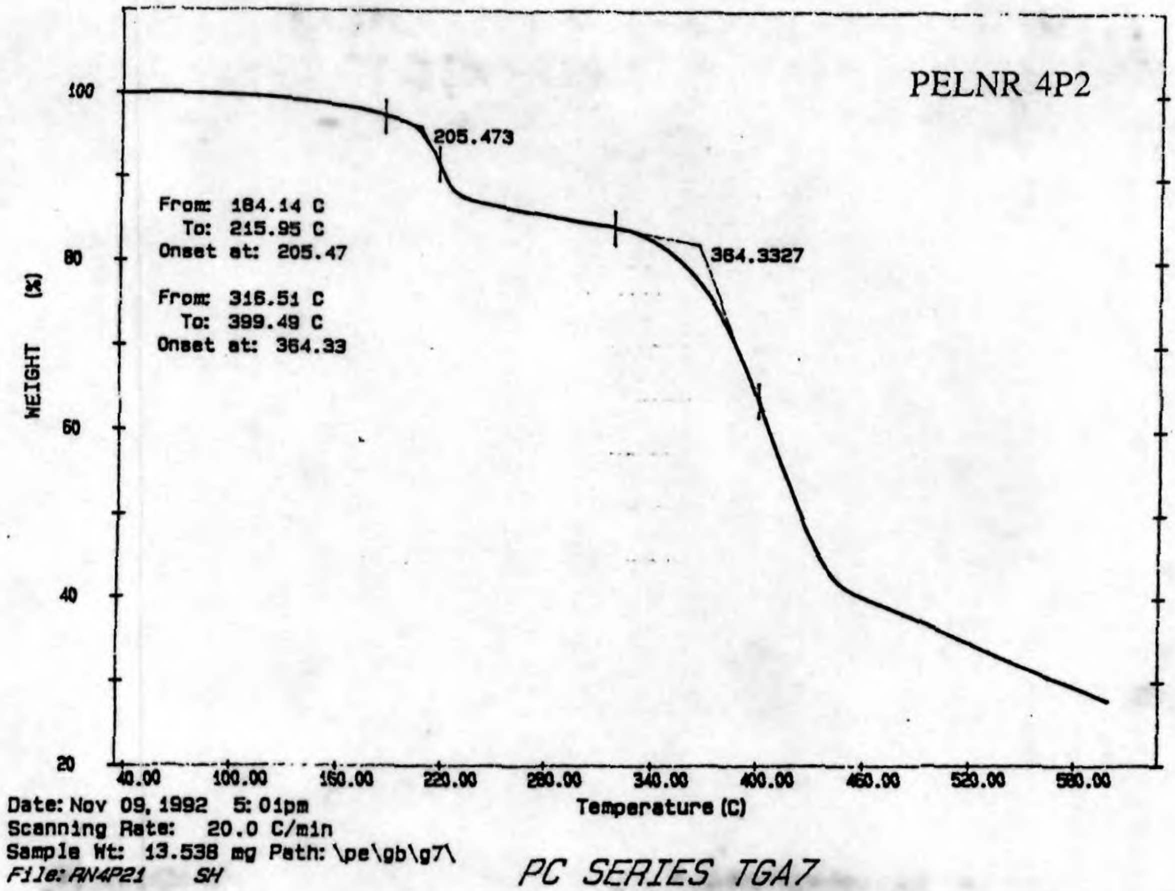


Fig. 4.23. TGA curves of the modified polymers in oxygen

Chapter 5.

LIQUID NATURAL RUBBER AS A VISCOSITY MODIFIER IN NITRILE RUBBER PROCESSING

5.1. INTRODUCTION

Oligomers are used as process aids in various rubber and plastic formulations. Advantages derived over conventional oil and ester type plasticizers are their easier addition, improvement in properties for oil resistant applications where the plasticizer is not to be leached by the surrounding oil medium, enhancement of physical properties due to their polymeric nature, better processability etc. Heterogeneous nature of rubber compounds, the strong interaction between the various components, viscoelastic nature of elastomers and poor understanding of flow behaviour of such complex materials make the processing of rubber compounds complex. Changes in the recipe are often made either in order to meet new specifications for finished products or to compensate for variations in properties or quality of raw materials. Improvement in rubber processing has become necessary because of the need for high performance rubber formulations and for competetiveness in order to face introduction of new materials like thermoplastic elastomers. Modification in bulk viscosity of compounds results in improved processability leading to fewer rejects, reduction in energy consumption, efficient shaping and higher output.

Nitrile rubber is generally difficult to process due to high viscosity of the compounds. The use of low molecular weight polymers in rubber compounding has been reported by Eric[1] and Hashimoto[2]. Compounding nitrile rubber with furfuryl alcohol as a plasticizer has been reported by Magrupov et al.[3].Thermally depolymerized natural rubber has been studied as a reactive plasticizer in nitrile rubber by Nair et al.[4]. Use of latex stage depolymerized natural rubber, prepared using phenyl hydrazine redox system, as a bulk viscosity modifier in rubber compounding has been reported by Le Blanc et al.[5]. This chapter discusses further work on plasticization of nitrile rubber using liquid natural rubber produced by thermal depolymerization.

5.2. EXPERIMENTAL

5.2.1.Materials.

A liquid natural rubber sample in the medium viscosity range prepared by thermal depolymerization, was used for plasticizing nitrile rubber. The physical properties of the LNR are given in Table 5.1.

Table 5.1. Properties of LNR.

Brookfield Viscosity, cps at 38°C	1,12,000
$\overline{\mathrm{Mw}}$	44210
$\overline{\mathrm{Mn}}$	5929
Polydispersity Index	7.48

Nitrile rubber of medium acrylonitrile content (grade N-339) manufactured by Synthetics and Chemicals, Bareilly, India was used for the preparation of the compounds. Specification parameters of the rubber are given in Table 5.2.

Table 5.2 Properties of NBR

Volatile matter, %	0.75
Ash, %	1.0
Soap, %	0.05
Antioxidant, %	1.0
Bound ACN content, %	33
Mooney viscosity, ML(1+4) at 100°C	50

Laboratory grade N-dibutyl phthalate was used. Other chemicals used were of industrial purity.

5.2.2. Preparation of compounds

The formulations are based on cyclohexyl benzthiazyl sulphenamide (CBS)- sulphur cure system. A gum recipe was selected so as to observe the changes uninfluenced by filler. Mixing was done on a laboratory scale two-roll mill with a friction ratio of 1: 1.25. A compound containing no plasticizer was taken as control. Plasticizer content in the range of 0 to 25 phr was investigated. Formulations of the mixes are given in Table 5.3.

Table 5 3 Formulations of mixes, phr.

Compound	C	L5	L10	L15	L20	L25	D5	D10	D15	D20	D25
NBR	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	3	3	3	3	3	3	3	3	3	3	3
LNR	-	5	10	15	20	25	-	-	-	-	-
Dibutyl phthalate	-	-	-	-	-	-	5	10	15	20	25
Accelerator CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5		1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

5.2.3. Testing

For the determination of cure time an oscillating disc rheometer was used. Mooney viscosity of the compounds was determined using a SPRI Mooney viscometer. A capillary rheometer attached to a Zwick UTM model 1474 was used for the rheological measurements. Various dimensions of the capillary are given in Table 5.4.

Table 5.4. Physical dimensions of capillary rheometer

Diameter of capillary, mm.	1.27
Length of capillary, mm.	50.08
Diameter of plunger, mm.	15.99
Diameter of cylinder, mm.	16.00

The sample for testing was placed in the barrel which was maintained at the test temperature. The sample was forced down the capillary using the plunger attached to the fixed crosshead. After a warming up period of 3 minutes the melt was extruded through the capillary at preselected speeds of crosshead. The melt height in the barrel before extrusion was kept the same in all experiments and the machine was operated to give ten different plunger speeds. 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 the crosshead speeds were converted into corresponding apparent shear stress (τ_w) and the shear rate (γ_w) at the wall by using the following equations involving the geometry of the capillary and plunger.

$$\tau_w = F/4Ap\ (lc/dc) \quad \text{------------------ ------} \quad (5.1)$$

$$\dot{\gamma}_w = [(3n' + 1)/4n']\ 32\ Q/\pi\ dc^3 \quad \text{-------------} \quad (5.2)$$

where F is the force applied at a particular shear rate

Ap is the crosssectional area of the plunger

lc is the length of the capillary

Q is the volumetric flow rate

n is flow behaviour index defined by d (log γ_w) / d (log γ_{wa})

$\dot{\gamma}_{wa}$ is the apparent shear rate at the wall

$\dot{\gamma}_w$ is the actual shear rate at the wall

dc is the diameter of the capillary

n was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. The shear viscosity η was calculated as

$$\eta = \tau_w / \dot{\gamma}_w \quad \text{------------------} \quad (5.3)$$

Melt viscosity of the compounds were also calculated at shear rate 333 S^{-1} and 120°C. The principal normal stress difference $\tau_{11} - \tau_{12}$ was calculated from the formula

$$\tau_{11} - \tau_{12} = 2 \times \tau_w [2 (de/dc)^6 - 2]^{1/2} \quad \text{--------} \quad (5.4)$$

where τ_w is the shear stress at the wall

de is the diameter of the extrudate and

dc is the diameter of the capillary

Recoverable elastic shear stress was calculated from the formula

$$SR = (\tau_{11} - \tau_{12}) / 2 \tau_w \quad \text{--------------------} \quad (5.5)$$

Elastic shear modulus was also calculated using the equation

$$G = \tau_w / SR \quad \text{------------------------} \quad (5.6)$$

The extrudates were collected at selected shear rates and their diameters determined using an optical microscope. Die swell values were calculated from the formula

$$\text{Die swell (\%)} = [(de - dc) / de] \times 100 \quad \text{-----------} \quad (5.7)$$

where de is the diameter of the extrudate and

dc is the diameter of the capillary

Free vibration method on a Yerzely Oscillograph has been used for measuring the important engineering properties of the vulcanizates. Static modulus (I) has been determined from the slope of the loading curve. Resilience (YR) has been expressed in percent, determined as the average computed from the second and third half cycles.

$$YR (\%) = [(CD/BC) + (DE/CD)] \times 50 \text{ -------- } (5.8)$$

where BC is the vertical distance of the first half cycle of the damped sinusoidal wave,

CD is the vertical distance of the down stroke of the second cycle and

DE is the vertical distance of the upstroke of the second cycle.

Natural frequency was determined by counting the convenient number of complete cycles, measuring the horizontal distance JK traversed by these number of cycles, X, along the central axis. The frequency was calculated for the drum of 37.5 cms circumference and 4 rpm rotation, using the equation

$$f(Hz) = X / JK \text{ ------------------ } (5.9)$$

The loss factor was calculated according to the method suggested by Scott[6] from the formula

$$A_3 / A_2 = e^{-1/2\, \pi \tan \delta} \qquad (5.10)$$

where

A_3 and A_2 are the amplitudes of the third and second vibrations and $\tan \delta$ is the loss factor.

5.3. RESULTS AND DISCUSSION

5.3.1. Cure characteristics

Table 5.5 shows the processing parameters of the nitrile rubber compounds. Scorch time of the compounds indicated that the increased addition of plasticizers to nitrile rubber compounds has only little effect on cure.

Table 5.5 Properties of compounds

Compound	Scorch time, min.	Cure time, min.	Mooney viscosity
C	5.25	21.5	38
L5	5.25	24.0	32
L10	5.50	22.5	28
L15	6.75	23.0	20
L20	7.00	22.5	15
L25	7.00	25.0	10
D5	5.25	19.5	33
D10	5.50	23.0	25
D15	5.75	22.0	21
D20	6.00	22.0	18
D25	6.00	19.5	15

Slightly higher cure times were recorded on the rheometer for the LNR containing compounds. Figure 5.1 shows the rheographs of compounds plasticized with 10 and 20 phr of DBP and LNR in comparison with the unplasticized stock. The torque showed a steady decrease with increased loading of the plasticizers. On comparing DBP and LNR the latter showed more reduction of torque especially at higher loadings.

Mooney viscosity of the compounds are also given in Table 5.5. From the data it is inferred that addition of the plasticizers decreased the Mooney viscosity of compounds. The higher the quantity of the plasticizer, the higher the reduction. Between the plasticizers the influence was more pronounced for LNR at higher loading.

5.3.2. CAPILLARY RHEOMETRIC STUDIES.

5.3.2.1. Shear stress vs shear rate

Shear stress values at different shear rates for the compounds containing LNR and DBP plasticizers and the control compound were measured at 90°C. The results are given in Figure 5.2. In general the shear stress values at all shear rates were the highest for the control compound. This was due to the absence of any plasticizer that enhanced flow behaviour. The lowest values were recorded for the compounds containing LNR indicating an effective plasticizing action. With increasing shear rate the shear stress values also increased steadily. A comparison of LNR and DBP showed that at all shear rates LNR containing compounds exhibited lower shear stress than the corresponding DBP compounds. Comparison of the shear stresses at different shear rates indicated a shear thinning trend of the compounds. This indicates pseudoplastic behaviour. The random ground state structure is progressively broken down with increase in shear rate and a shear oriented structure is formed which offer reduced resistance to the force field. Pseudoplastic nature represents the behaviour of a fluid which when subjected to a shear rate from zero upwards shows a convex curvature with respect to the shear rate axis. This can be represented by the power law equation

$$\tau \ \alpha \ \gamma^{n} \qquad \text{-------------} \qquad (5.11)$$

where n is the flow behaviour index.

5.3.2.2. Influence of shear rate on viscosity

Effect of shear rate on viscosity of the compounds containing 15 phr of LNR, DBP and the control are shown in Figure 5.3. The viscosity at low shear rates were the highest for the unplasticized compound followed by DBP and LNR. As the shear rate increased drop in viscosity was noticed in all the cases. The pseudoplastic nature of the compounds can be attributed to the structured state of entanglement density at zero shear rate being progressively destroyed upon increasing shear. LNR containing compound showed the minimum viscosity. This indicates that LNR acts as an effective lubricant between the molecules of nitrile rubber and is an efficient viscosity modifier.

5.3.2.3. *Effect on flow index*

Figure 3.4 shows the change in flow index with increasing plasticizer content. In general the flow index was higher for LNR compounds at all loadings. In fact the values increase linearly with LNR content. In the case of DBP increase in the value of flow index was nominal indicative of little impact of the plasticizer on the pseudoplastic flow behaviour of the compounds. LNR containing compounds revealed that plasticizer loading has more profound effect on the flow behaviour. For materials with pseudoplastic behaviour the value of n in the equation 5.11 should be below unity. When high shear rates are operating on a polymer melt the chain segments of the polymer molecules are aligned along the streamlines, thus increasing flowability. Presence of LNR also influences these orientations and contributes towards the flow behaviour.

5.3.2.4. Influence of temperature.

Figure 5.5 on its Y1 axis shows the flow behaviour index of the compounds containing 15 parts each of LNR and DBP as a function of temperature. With increase in temperature the flow index increased in both the cases. A consistent reduction in viscosity values was also observed with temperature. At all temperatures the DBP compounds showed higher viscosities. A small levelling off trend was observed at elevated temperatures which was more prominent for LNR compounds. Increase in temperature increases the brownian motion in polymeric liquids and soft solid materials and the free volume. Increase in molecular mobility enhances the flow behaviour. Viscosity temperature relations are governed by the Arrhenius equation

$$\eta = A\, e^{-E/RT} \quad \text{------------} \qquad (5.12)$$

where E is the activation energy of flow and T the absolute temperature. In order to obtain the activation energy log viscosity was plotted against 1/T at shear rate 333 S^{-1} (Figure 5.6). The slope of the lines were calculated and the activation energy values of LNR and DBP were found to be 1128 and 846 kcals/mol, respectively. Dependence of flow properties on temperature is of interest. Temperature is an effective means of controlling melt viscosity in processing operations. A control on thermal energy is also required to save the polymer from degradation due to excessive heat and to provide long life to products.

5.3.2.5. Die swell

The die swell values of the compounds with varying loading of the plasticizers from 0 to 20 phr at different shear rates are given in Figure 5.7. The temperature at which the extrudates were collected was 120°C. It has been observed that die swell values decreased with increasing shear rate. Similar trend was observed with the plasticizer loading also. On comparing the plasticizers the LNR containing compounds exhibited lower die swell than the corresponding DBP compounds. At higher shear rates the dimensional stability of LNR containing compounds was remarkably better. The surface finish of the extrudates were also good (Figure 5.8).

5.3.2.6. Effect of shear rate on melt elasticity

Melt elasticity of the compounds were calculated from the extrusion parameters at shear rates 333 S^{-1} and at temperature 120°C. The results are depicted in Figure 5.9. The principal normal stress difference $\tau 11$ - $\tau 12$ decreased with increased loading of the plasticizer. The primary or principal normal stress difference of viscoelastic liquids represents a combination of elastic and viscous effects. A remarkable difference in the values of τ_{11} - τ_{12} with increase in plasticizer content indicated the influence of plasticizer loading on the viscosity of compounds. Recoverable elastic stress showed a decreasing trend with increasing plasticizer content. Minor inflections in the values of shear modulus G were also observed.

5.3.2.7. Vulcanizate properties

Stress strain properties of the vulcanizates containing plasticizers loaded at different levels were measured and are given in Figure 5.10. Modulus values of the compounds at 300% elongation showed a decreasing trend with increase in plasticizer content. Tensile strength of the compounds showed a marginal reduction on addition of both the plasticizers at 5 to 10 phr levels but remained constant thereafter. Elongation at break showed a decreasing trend initially (5 to 10 phr) followed by an increase. LNR at high loadings showed higher elongation values, attributable to the polymeric nature of the plasticizer. In agreement with the general concept on plasticizer both LNR and DBP made the rubber compounds softer with increasing plasticizer content. However, this decrease was less for LNR indicative of its use in making relatively harder vulcanizates.

Dynamic mechanical properties determined by using a Yerzely Oscillograph are given in Figure 5.11. Yerzely resilience values were in general higher for LNR containing compounds than DBP containing compounds. This may be attributed to the polymeric nature of LNR which is not applicable in the case of DBP. Correspondingly higher values of loss factor were recorded for the DBP compounds than the LNR compounds. The fundamental frequency of the samples were comparable, within minor experimental fluctuations. The static modulus showed a slightly decreasing trend with increasing plasticizer content.

5.3.2.8. Evaluation of superposition shift factor

The experimental flow curves for log γ_w vs τ_w at temperatures 90 to 120°C were constructed for the nitrile rubber compounds. The method of superposition has been done by the arbitrary choice of a reference temperature. The values of superposition shift factors were obtained by choosing shear rate values at 100 and 1000 s^{-1} on the reference temperature flow curve and shifting the corresponding points (constant shear rate) on the flow curves for other temperatures to coincide with these shear stress. The values of a_T were calculated from the following equation

$$a_T = \tau\ (\text{ref}) \,/\, \tau\ (\text{T})\ (\text{constant}\ \gamma w) \quad \text{----------} \quad (5.13)$$

where a_T is the shift factor, τ(ref) is the shear stress at reference temperature and τ (T) (constant) is the shear stress at a particular temperature.

The average value of shift factors for the compounds were calculated[7] and are plotted as a function of temperature in Figure 5.12. Using the appropriate average values of the shift factors the master flow curve at 90°C was constructed and is given in Figure 5.13. The shear rate-temperature superposition method can be used for predicting the viscosities of the polymer melts at any required temperature by determining the viscosity at a reference temperature.

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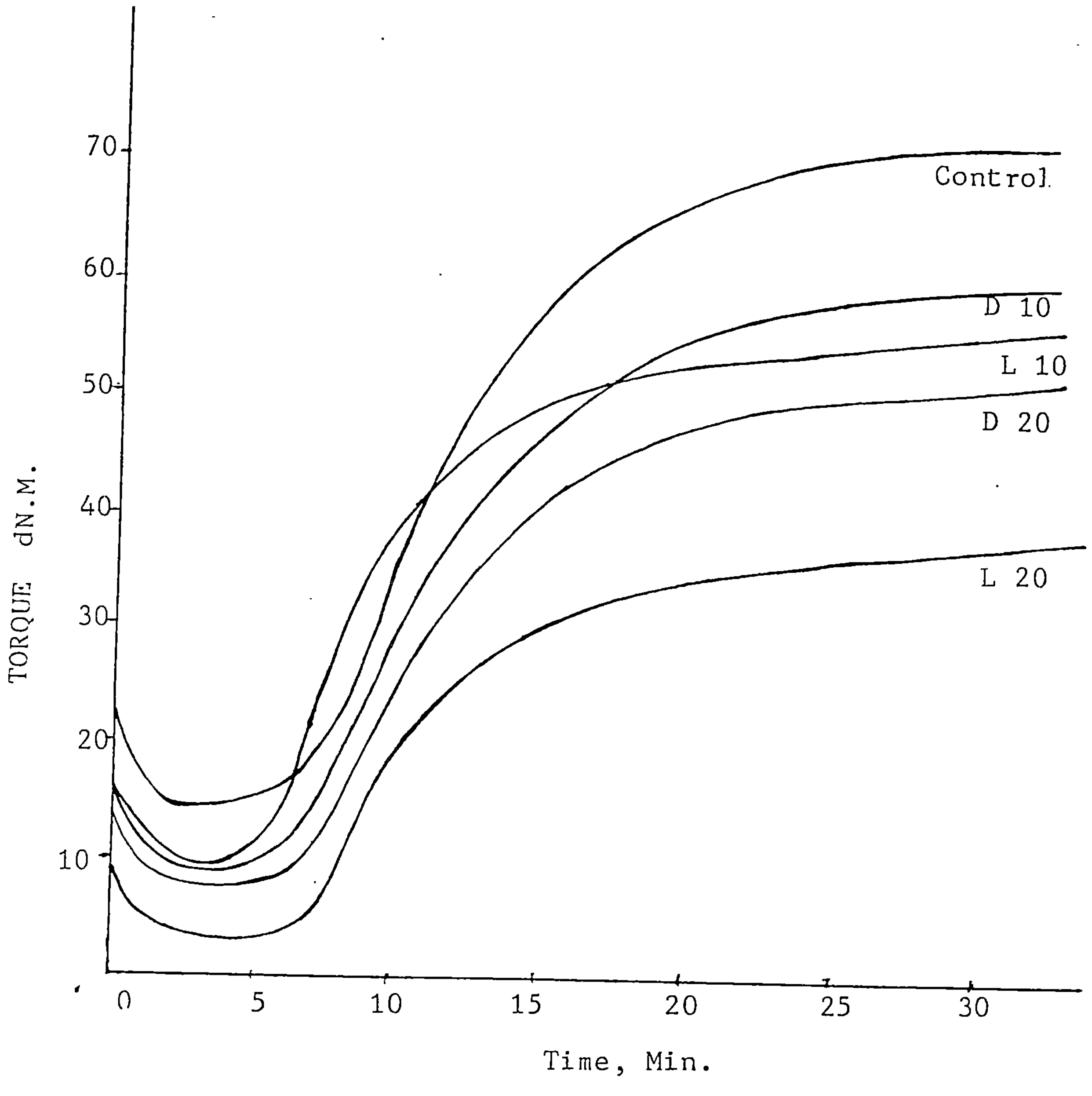

Fig. 5.1. Effect of plasticizers on cure.

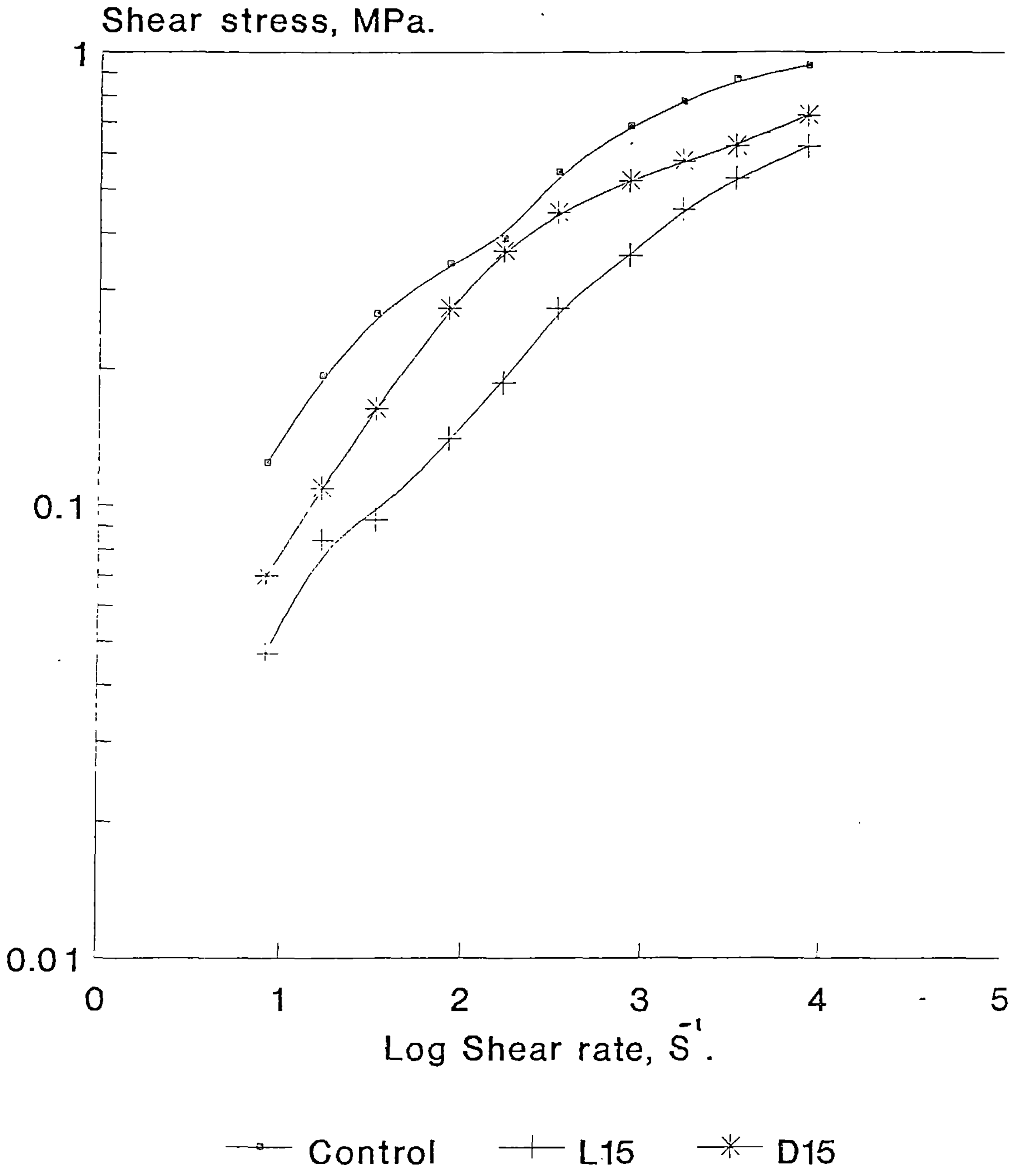

Fig. 5.2. Shear stress vs shear rate at 90°C

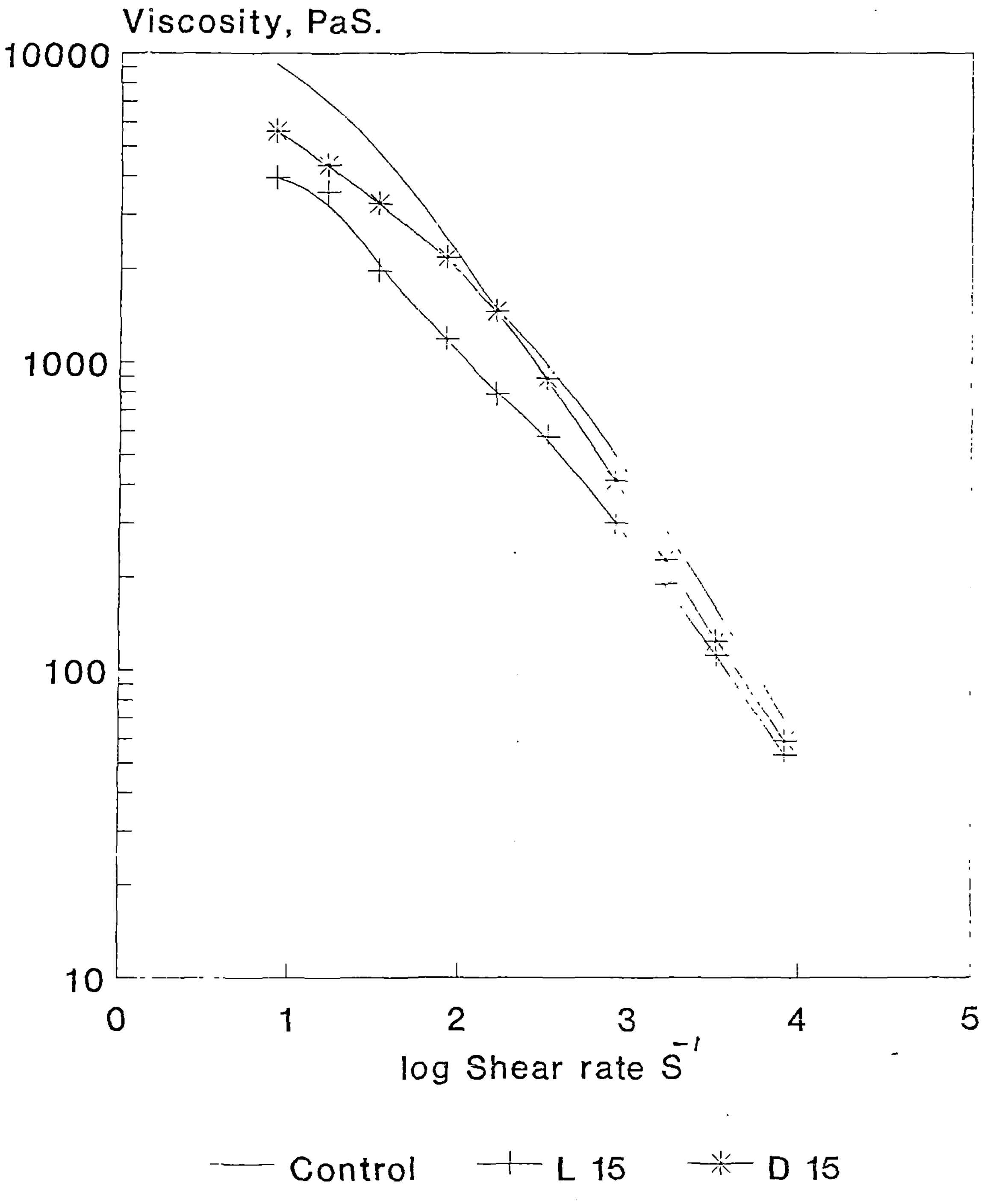

Fig. 5.3. Viscosity vs shear rate at 90°C

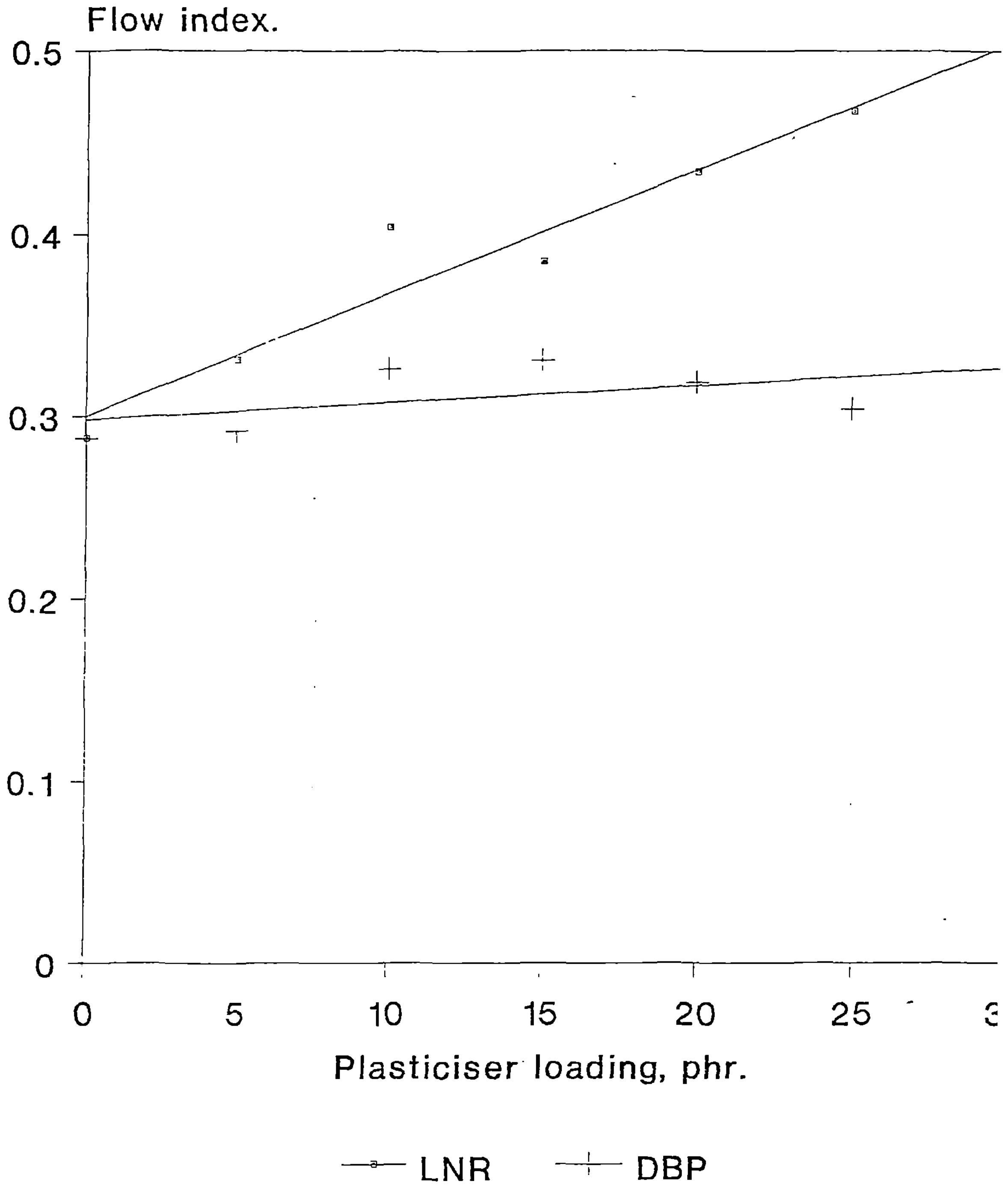

Fig. 5.4. Influence of plasticizer on flow index

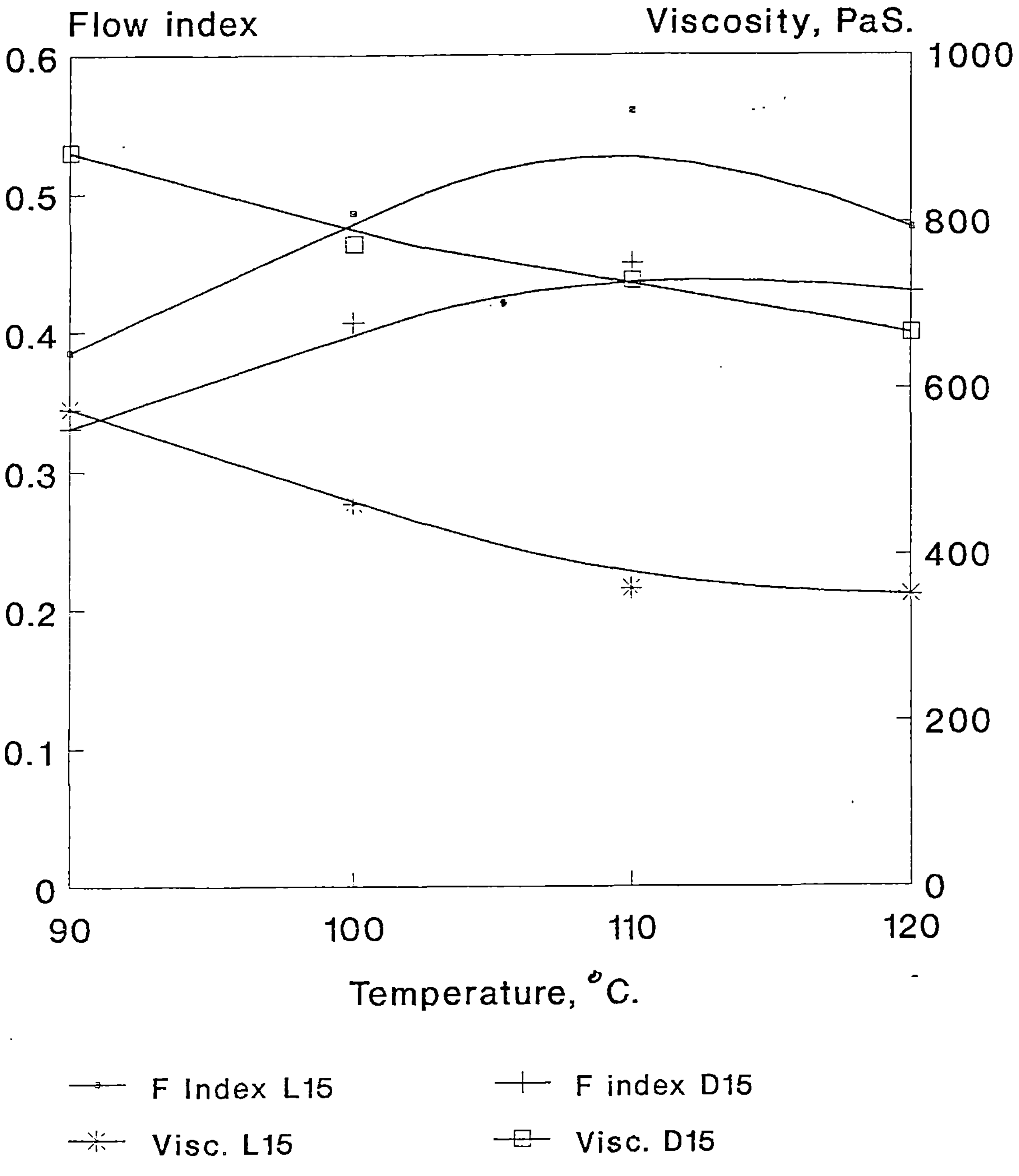

Fig. 5,5. Temperature vs viscosity and flow index

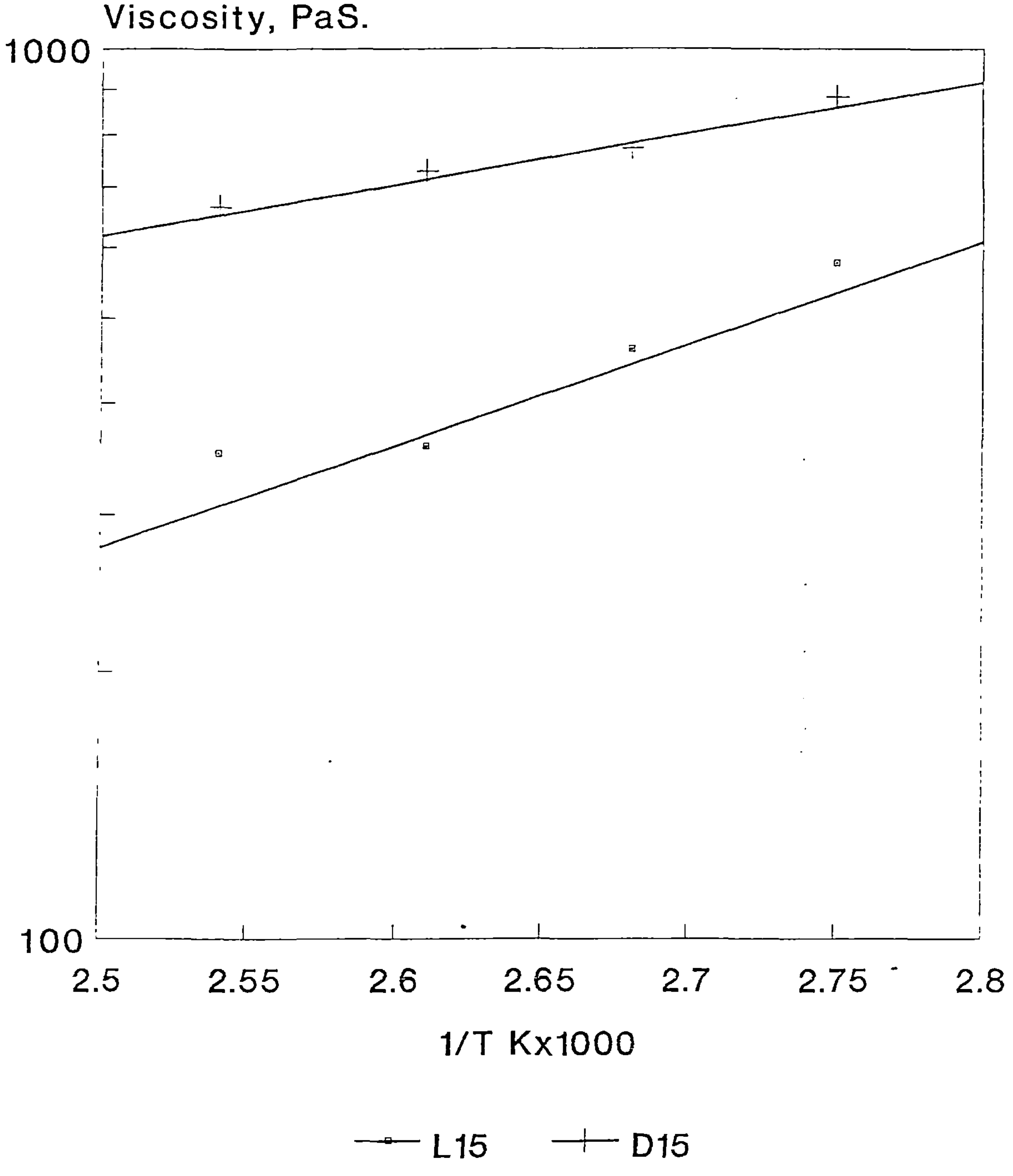

Fig. 5.6. Log viscosity vs 1/T

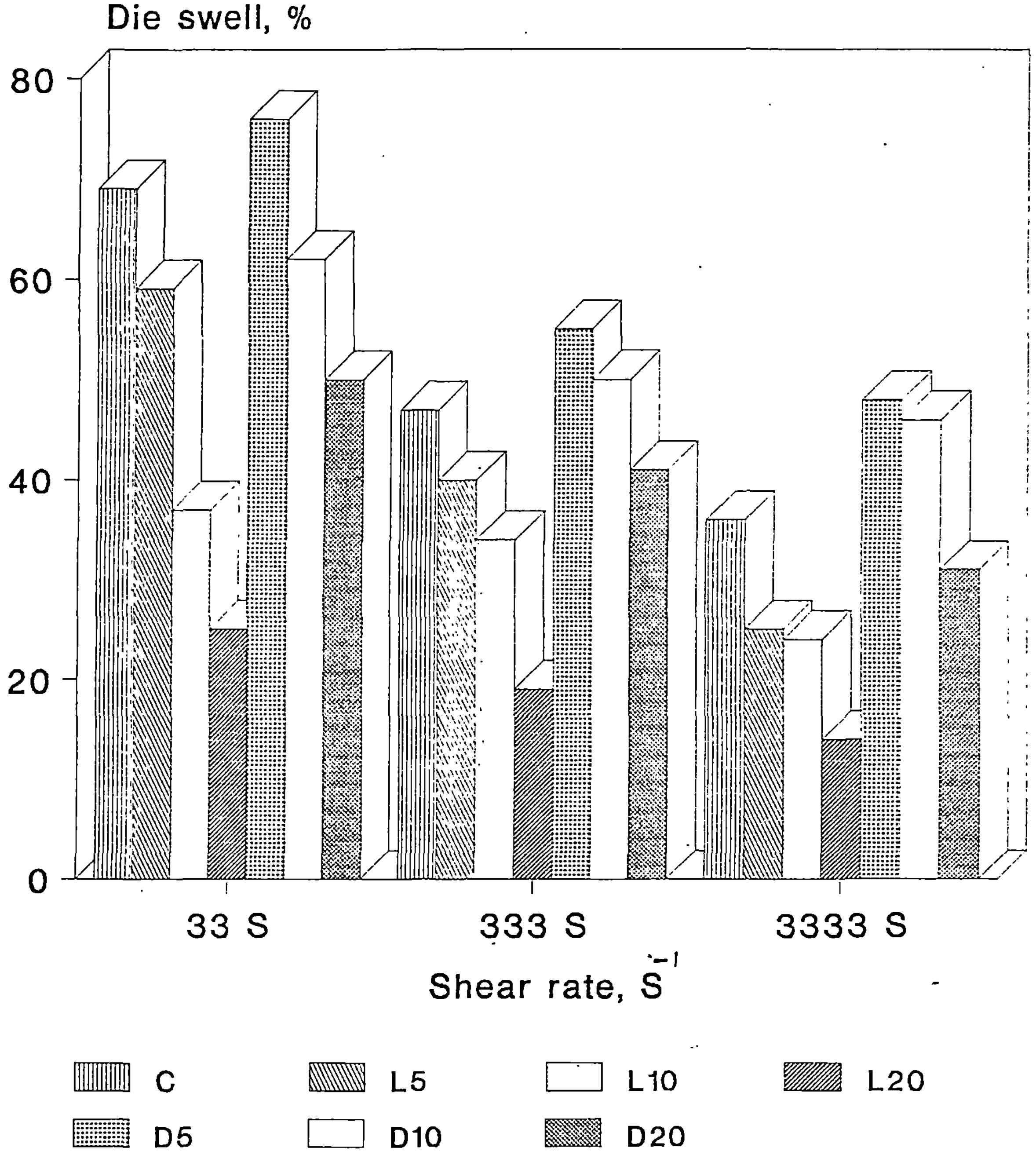

Fig. 5.7. Die swell (%) at 120°C

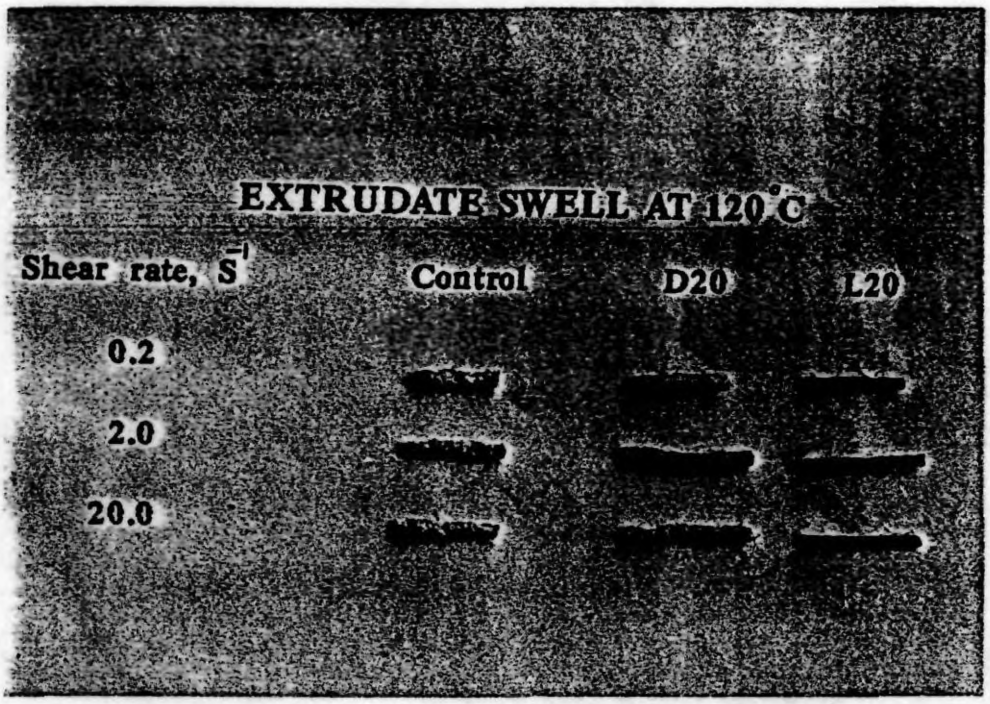

Fig. 5.8. Photograph of extrudates

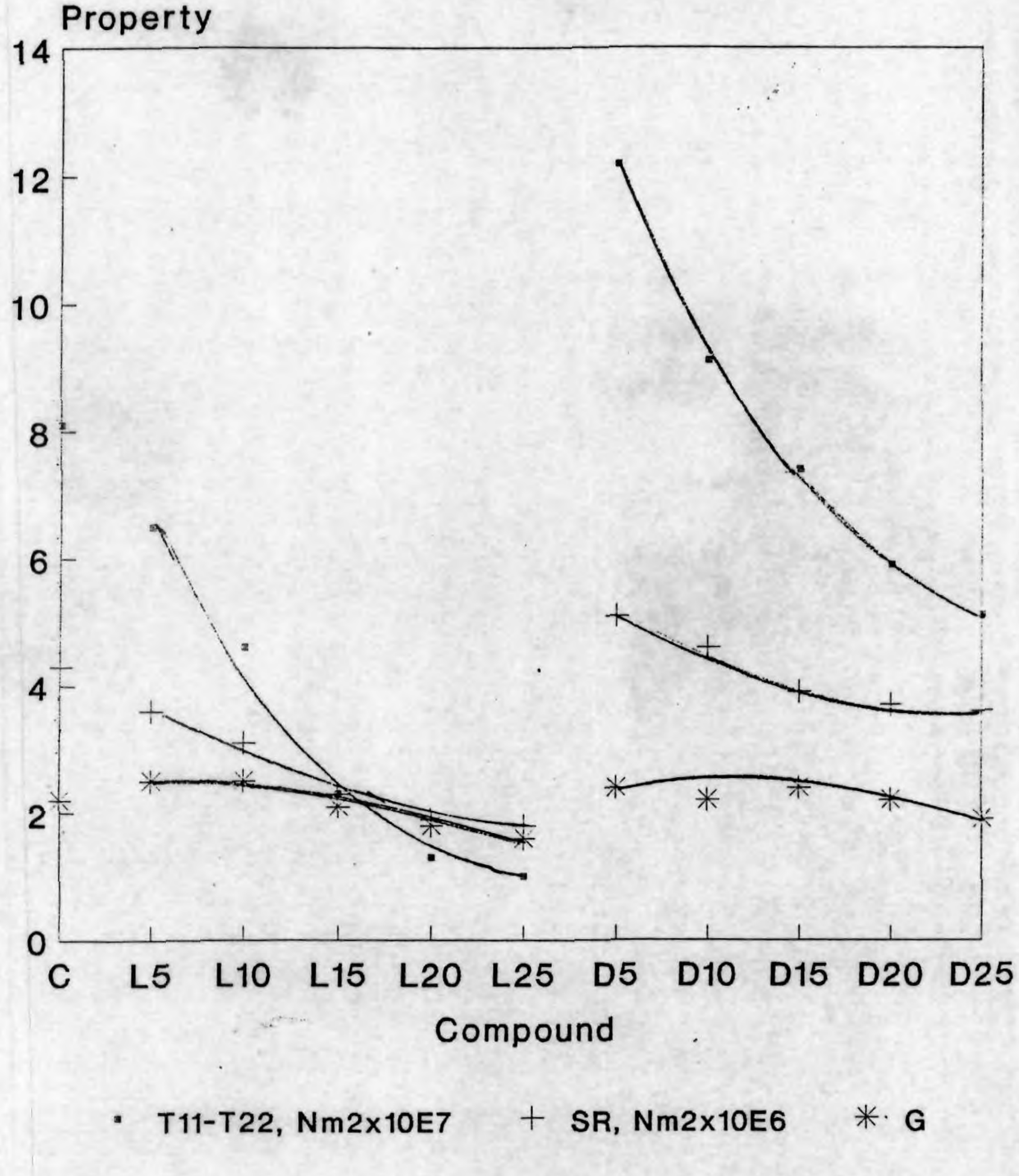

Fig. 5.9. Melt elasticity at 333 s^{-1} and 120°C

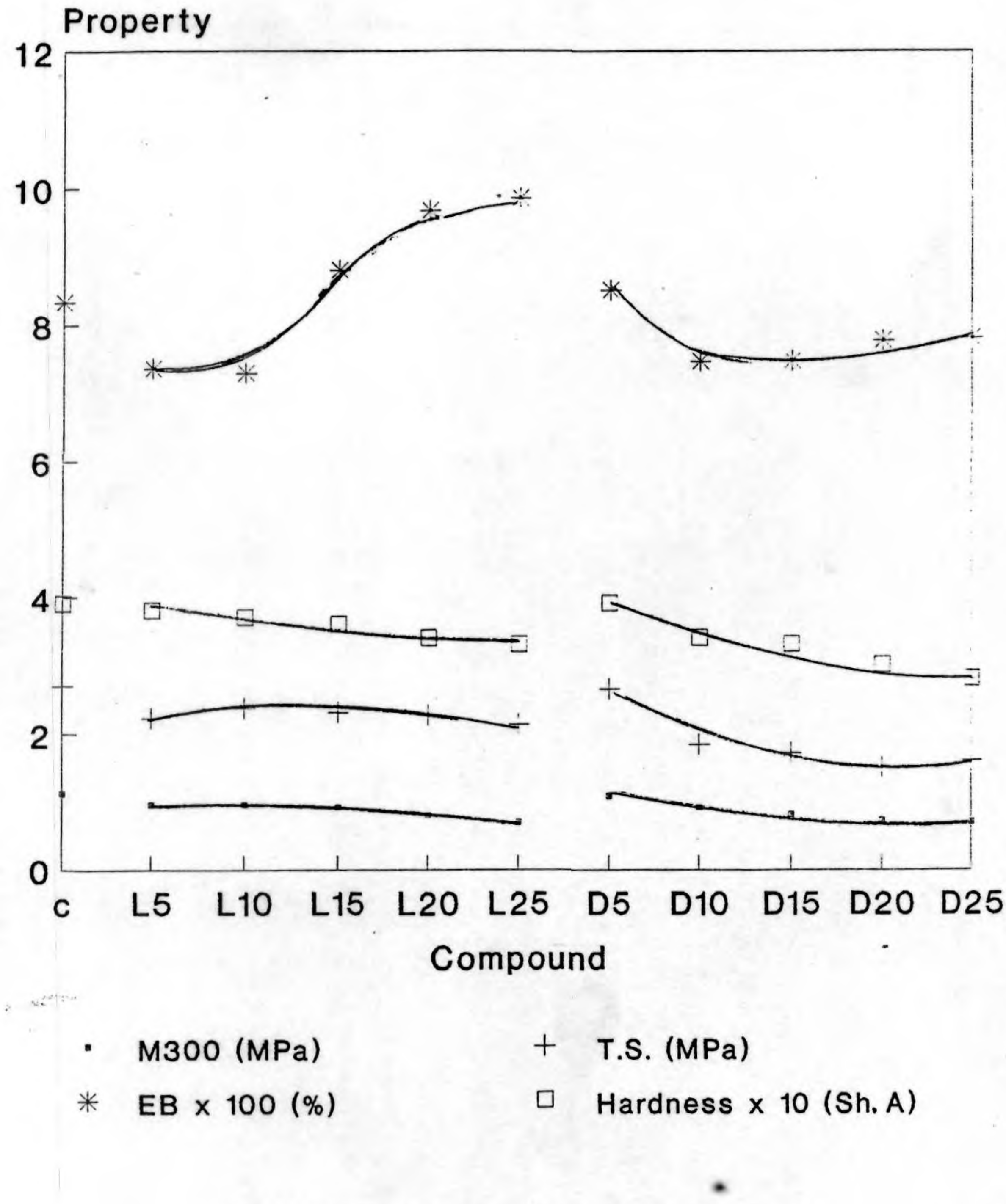

Fig. 5.10. Physical properties of vulcanizates

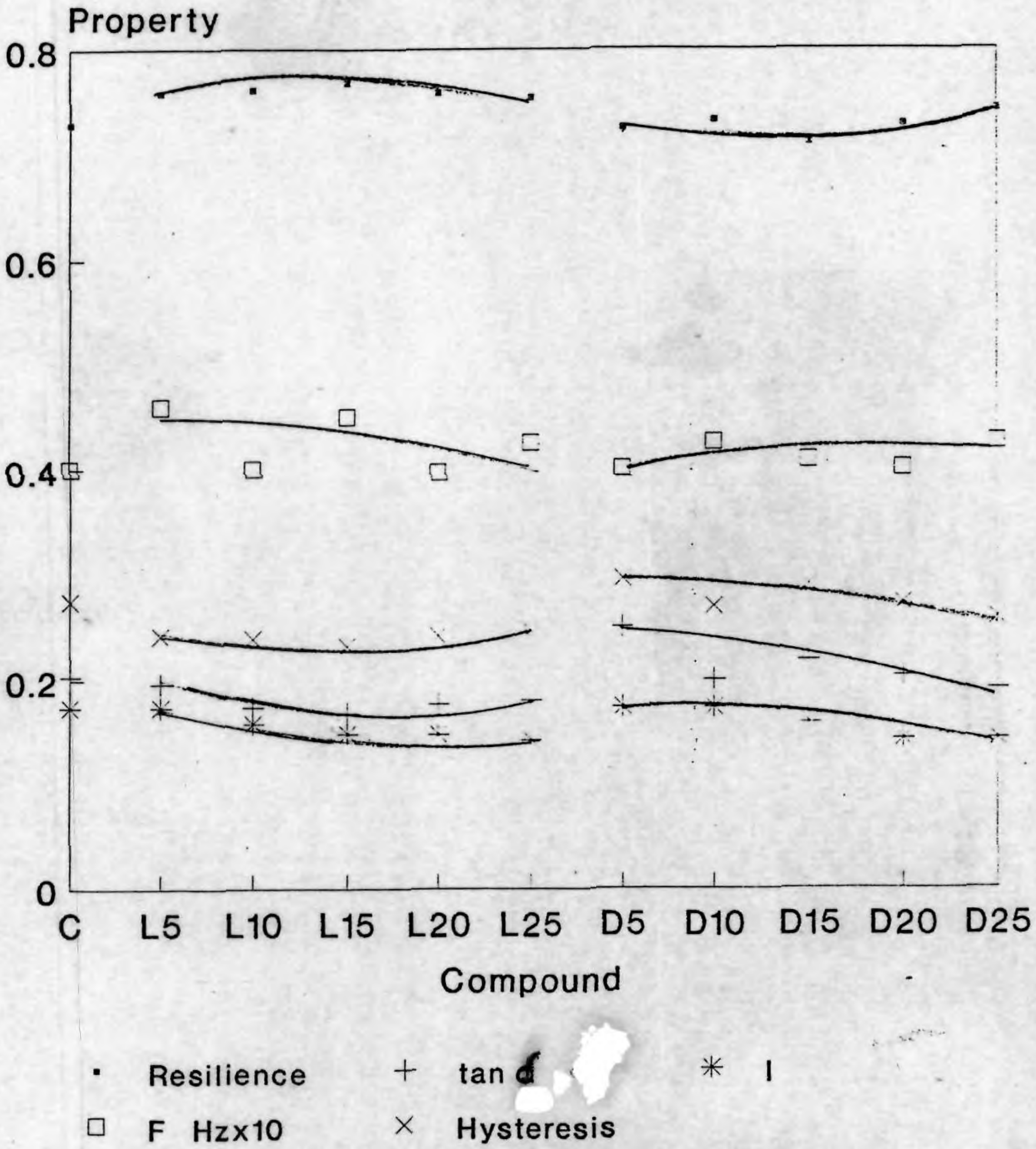

Fig. 5.11. Dynamic properties of vulcanizates

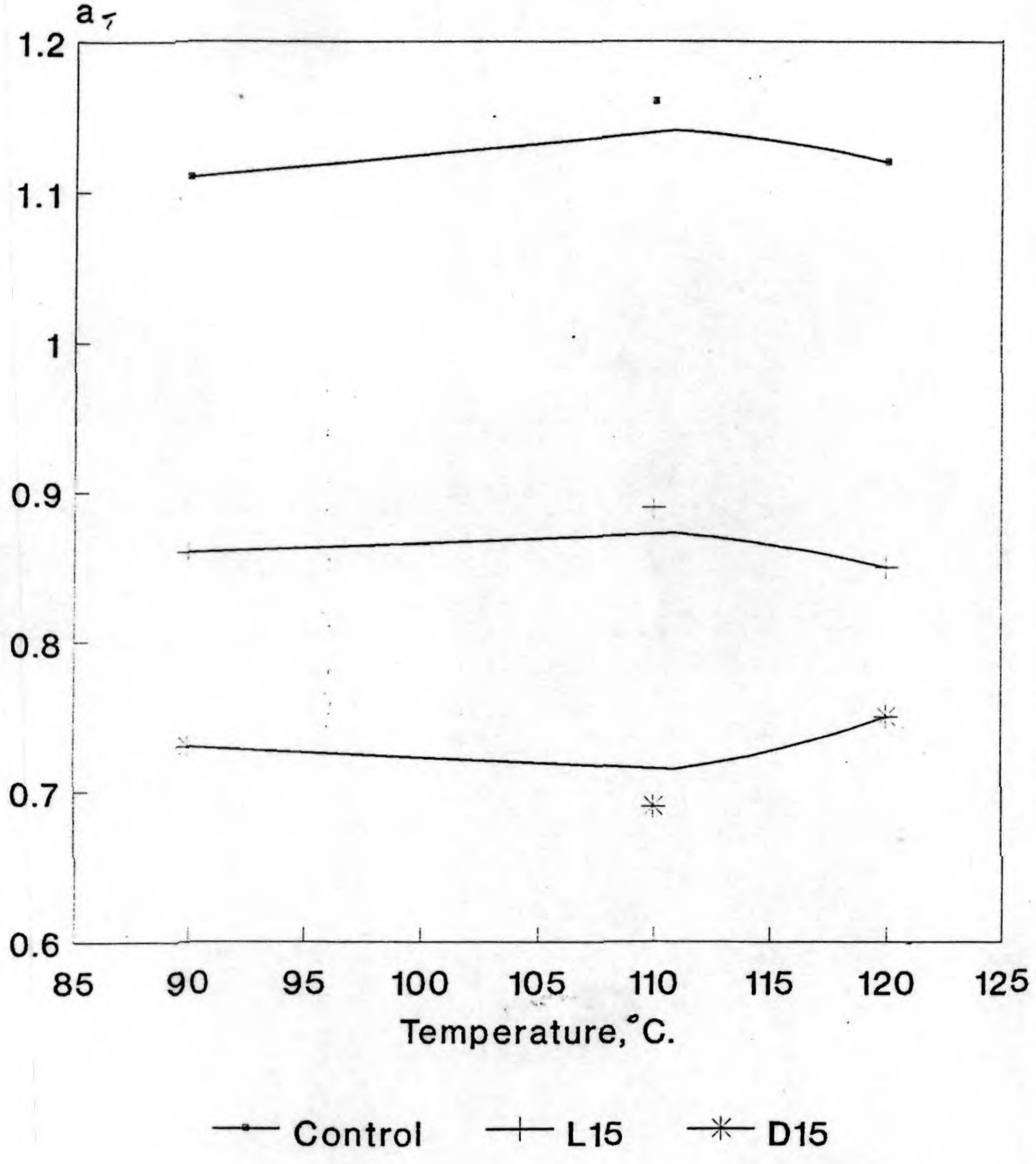

Fig. 5.12. aT vs temperature

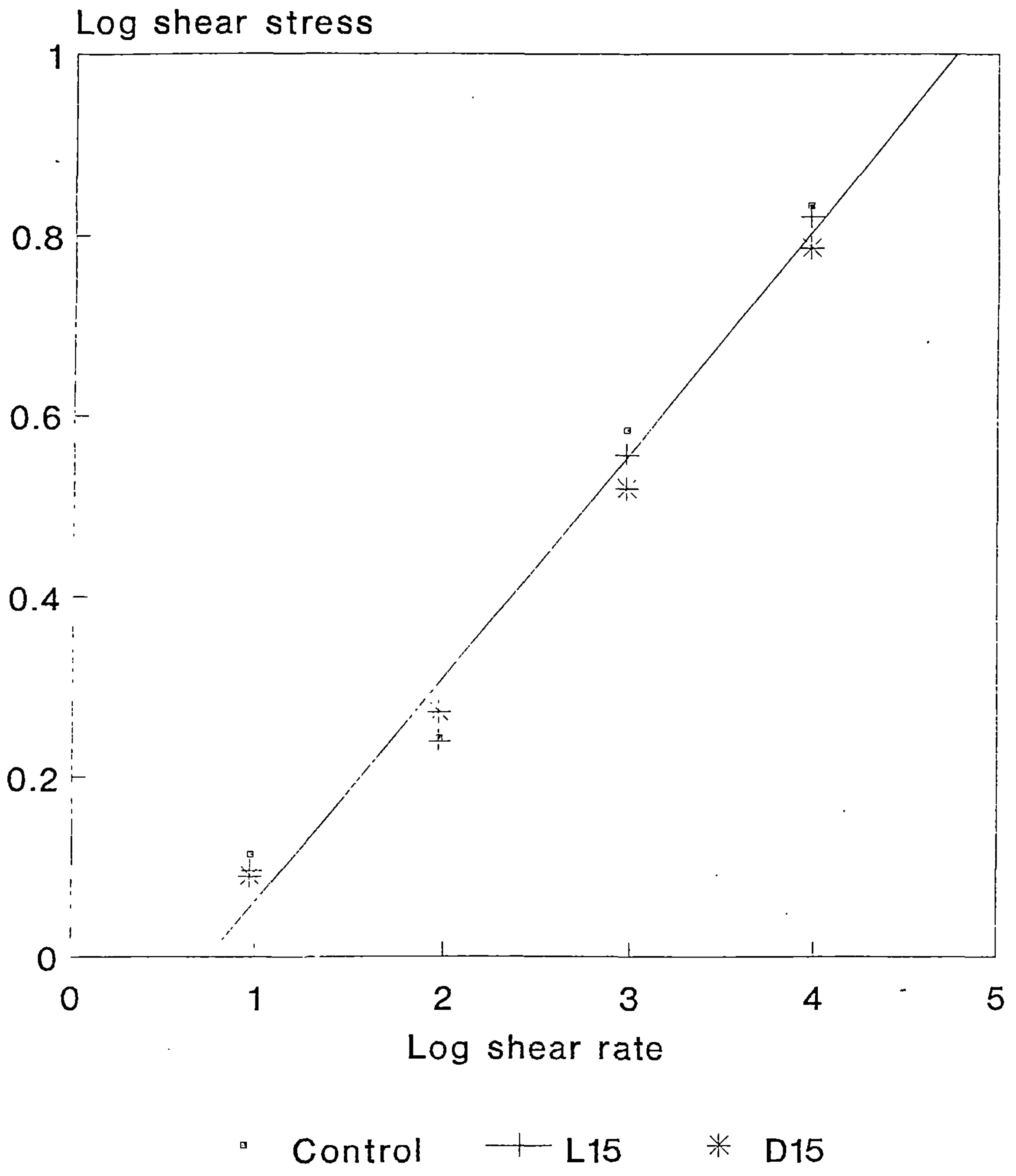

Fig. 5.13. Superposition master curve.

Chapter 6.

STRESS RELAXATION IN NITRILE RUBBER COMPOUNDS CONTAINING LIQUID NATURAL RUBBER

6.1. INTRODUCTION

Rubber composites are prepared incorporating various types of plasticizers to modify their behaviour with respect to processability[1] and vulcanizate properties like hardness, modulus[2], extractability[3] etc. Relaxation of stresses is also influenced by the nature of plasticizer present in a rubber vulcanizate. Stress relaxation measurements in simple extension on polyacetal-polyurethane blends were carried out at 30°C by Kumar et al.[4]. Stress relaxation behaviour of Kevlar fibre reinforced thermoplastic polyurethane has been reported by Kutty and Nando[5]. Similar studies were conducted on jute fibre reinforced nitrile rubber composites by Bhagawan et al.[6].

Vulcanized rubbers subjected to constant deformation undergo a marked relaxation of stress. Low temperature deformation is due to slow attainment of equilibrium in a viscous medium[6] whereas high temperature relaxation is caused by chemical reaction of various kinds that lead to scission of the network chains or crosslinks[7]. The present investigation describes relaxation, creep and recovery in unfilled vulcanizates under moderate deformations. Effect of the two plasticizers, dibutylphthalate and liquid natural rubber are discussed under similar loading conditions. At lower elongations the functional relaxation process is mainly due to molecular rearrangements and is a reversible phenomenon within the elastic limits. The mechanism was directly dependant on the viscoelastic contribution of the polymer influenced by the plasticizer.

Stress relaxation measurements in tension have been made on nitrile rubber vulcanizates containing liquid natural rubber. The effect of strain level, influence of plasticizer content, effect of prestretching and effect of ageing have been studied over a period extending to four decades.

6.2.EXPERIMENTAL

6.2.1. Materials

Nitrile rubber of medium acrylonitrile content, Chemaprene N-339, a product from Synthetics and Chemicals, Bereilly, India was used for the study. Plasticizer, dibutylphthalate was of laboratory reagent grade. The other chemicals used were of industrial purity. Liquid natural rubber used for compounding was prepared by thermal depolymerization starting from ISNR 5. Molecular weight $\bar{M}w$ of the LNR sample was about 45,000.

6.2.2. Compounding

For the preparation of the compounds, a cure system was selected as shown in the formulations given in Table 6.1 so that the resulting compounds had sufficient scorch and cure times.

Table 6.1. Formulations of mixes

Compound	C	L5	L10	L15	D5	D10	D15
NBR	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5
Stearic acid	3	3	3	3	3	3	3
LNR	-	5	10	15	-	-	-
DBP	-	-	-	-	5	10	15
Accelerator CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

The compounds were prepared on a laboratory two-roll mill (15 cm x 30 cm) with a friction ratio of 1: 1.25. NBR was first masticated to attain a Wallace rapid plasticity of around 40. The compounding ingredients were added in the order sulphur, activator, plasticizer and accelerator. Before the addition of accelerator the batch was thoroughly cooled. Vulcanization to optimum cure was carried out in a 45cm x 45 cm hydraulic press, having steam heated platens, at a pressure of 45 kg/cm^2 on the mould. Optimum cure time at 150°C was determined by a Monsanto rheometer R-100.

6.2.3. Stress-strain measurements.

Stress-strain measurements were carried out on a universal testing machine model 1474 from Zwick Gmbh, Germany. The dumb-bell shaped test specimens were prepared by punching out with a die, from standard compression moulded test sheets of about 2mm thickness. The test specimens were held on the testing machine with the help of clamps operated by air pressure. These devices prevent slippage by maintaining a constant clamping pressure even though the sample is subjected to some plastic deformation due to their pressure. The properties were measured on three selected formulations containing 5, 10, 15 phr of the plasticizers and also on the control compound. Four different tests were used to determine the rate of stress relaxation at ambient temperature.

a) at 300% elongation
2) at 50% elongation
3) after prestretching.
4) after ageing at 100°C for 24 h.

The samples were stretched to 200% elongation for 60 sec. The stress was completely released and the sample was allowed to recover for 60 sec. Both stretching and releasing were done at a test speed of 500 mm/min. Then the stress relaxation measurements were done on the test specimens.

It has been observed by Gent[8] that numerical rate of creep C and stress relaxation S at a given extension e are related in the following way.

$$C = \alpha\, S \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.1)$$

where

$$\alpha = (\sigma / e) / (d\sigma - de)_t \ldots\ldots\ldots\ldots (6.2)$$

σ is the stress corresponding to the extension e, $(d\sigma - de)_t$ is the slope of stress relaxation curves. The factor α relating to S and C may thus be calculated from the stress-extension relation. The tensile relaxation modulus is given by

$$Et = f(t)\, Lo / (A\, \Delta L) \ldots\ldots\ldots\ldots\ldots\ldots (6.3)$$

where f(t) is the force as a function of time, Lo is the sample gauge length and ΔL is the total sample extension and a is the crosssectional area. According to the theory of rubber elasticity the behaviour of soft crosslinked polymers is Hookean in shear up to substantial strains, but the force displacement relation is nonlinear. This may be expressed as

$$F = (E\, Ao/3)\, [L/Lo - (Lo/L)^2\,] \ldots\ldots\ldots (6.4)$$

where Ao and Lo are the initial area and length respectively, E is the Young's modulus defined for small strains and it is assumed that AoLo = AL. However, for strains of the order of 50% e must be expressed as a function of L/Lo and equation 6.4 becomes

$$F = E\, Ao\, Lo/L\, [\Delta L\, (L^2 + LLo + Lo^2) / 2(L^3 + Lo^3)] \ldots\ldots (6.5)$$

If this result can be assumed to apply the time dependant force as well, the tensile relaxation modulus is given by

$$E(t) = f(t)\, (1 / A\Delta L)\, [(2L^3 + Lo^3) / L^2 + LLo + Lo^2) \ldots\ldots (6.6)$$

where a is the crosssectional area after the sample has been strained. The assumption that L = Lo, or the deformation is small, requires equation 6.3 to equation 6.6 so that the latter is a good approximation for small deformations. Hence,

$$Et = f(t)\, (L / \Delta L) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6.7)$$

at higher strains the difficulty of calculating the modulus is often avoided by plotting the quantity of f(t)/fo where fo is the initially applied force.

6.3. RESULTS AND DISCUSSION

6.3.1. Cure

Addition of both the plasticizers, LNR and DBP contributed only small changes to the cure process. Figure 6.1 shows the plot of cure times for the NBR compounds plasticized to different extents. Optimum time for attaining 90% cure as determined by an oscillating disc rheometer was found to increase on addition of both the plasticizers at 5 phr level. At higher loadings a slightly decreasing trend was noticed. However, the deviations were small.

6.3.2. Modulus

Incorporation of the plasticizers was found to decrease the modulus values of the NBR compounds. The modulus values at 100 and 200% elongations were plotted against plasticizer content and are given in Figure 6.2. The general trend is the modulus to decrease with increasing plasticizer content. But, as the LNR content increased the decline in modulus was less. This difference between the two plasticizers may be attributed to the high molecular weight of LNR and establishment of additional crosslinks, which is not possible in the case of DBP.

6.3.3. Elongation at break

A comparison of LNR and DBP with respect to elongation is given in Figure 6.3. At lower loadings of LNR, EB was found to be lower than that of the corresponding DBP compounds. DBP being a less viscous, free flowing liquid, might be enhancing molecular uncoiling on applying tensile force and increase the elongation to relieve internal stresses, before the rupture takes place. At loadings higher than 10 phr, the elongation was higher for LNR. This may be attributed to the polymeric nature of LNR and the crosslinks established in the same.

6.3.4. Stress relaxation

Plots of σ/σ_0 against log t were made for the samples at the stretched condition (σo is obtained from the maximum load at t=0 when the desired strain is reached and σ is the stress at subsequent times, t). The decay in stress was found to proceed approximately in proportion to the logarithm of the period spent in the deformed state. The slopes of the lines are conveniently measured as the progress in stress relaxation. The relaxation was found to be more or less proportional to the logarithm of time. It became slower than a linear relation would suggest at longer times. An approximately linear relation could be fitted to the experimental points over limited ranges and corresponding straight lines were plotted. The slopes of the lines were calculated and their intersections also were noted. The percentage of the slopes were also calculated.

6.3.4.1. Relaxation at 200% strain

Relaxation tests carried out at 200% strain revealed that the decay in stress was at a rapid rate which subsequently stabilized. Figure 6.4 and 6.5 are the plots of σ/σ_0 vs log time for the DBP and LNR compounds respectively. Early part of the relaxation plots were not considered as the time interval between two successive readings made in this region was too small to provide precise observations. The lower slope in this region may be due to the contribution of viscous elements in the polymer hindering molecular movements. Excluding this section the curve consisted of two regions of different slopes. The slopes and the intercepts of the lines are given in Table 6.2. From the slopes it can be inferred that compounds showed the behaviour of general composites with a higher slope in the beginning due to a faster decrease in stress level followed by a lower slope, indicative of sluggish response. Stress decay was more prominent for LNR compounds which attained σ/σ_0 values less than 0.75 in 10,000 seconds whereas the corresponding values were above 0.8 for the DBP compounds. In the case of LNR the stress relaxation curves were comparatively close to each other, indicating that lower is the influence of loading of LNR in the relaxation characteristics. Figure 6.6 gives a comparison of compounds containing 15 phr of the plasticizers. Relaxation in DBP compounds were comparable to that of the control compound that contained none of the plasticizers while the LNR compounds exhibited much faster relaxation. This may be attributed to the polymeric contribution of liquid natural rubber.

Table 6.2. Percentage change of stress with time at 200% strain

Compound	First slope	Second slope	Intersection
Control	19.7	12.9	3.0
5D	19.4	13.1	3.0
10D	18.2	14.2	3.0
!5D	19.4	14.3	3.0
5L	24.9	20.6	2.9
10L	24.9	18.9	2.9
15L	23.1	21.4	2.9

6.3.4.2. Relaxation at 50% strain

Studies at 50% strain revealed relatively stable values from the beginning of the plots. The strain being less the stress values were lower. Figures 6.7 and 6.8 show the progress in relaxation of DBP and LNR compounds respectively. The relaxation trends of the compounds were similar and the σ/σ_0 values were close to each other for DBP compounds. In the case of LNR the trends were the same but the extent to which relaxation was taking place vividly differed. The extent of relaxation had a direct bearing on the plasticizer content. Figure 6.9 gives a comparison of the relaxation processes with respect to the plasticizer content. The slope and intercepts are given in Table 6.3. The control and the DBP compounds exhibited comparable relaxation rates while for LNR it was much higher. The equilibrium conformation of the polymer molecules changes when a force is applied. The new conformation is characteristic of the state of the molecule under the influence of the applied force. The transformation from one conformation to another is not instantaneous, but proceeds at a finite rate that depends on the height of the barrier to free rotation. The lubricity theory of plasticizers considers the plasticizer as a lubricant for molecular chains in polymers enhancing the flow behaviour. It has been found that at test strains of 200 and 50% LNR acted as a lubricant for easy movement of the chain segments and, in effect, relaxation at a faster rate was observed.

Table 6.3. Percentage change of stress with time at 50% strain.

Compound	First slope	Second slope	Intersection
Control	25.7	15.7	1.9
5D	21.4	14.3	2.5
10D	21.4	15.7	2.5
!5D	22.9	14.3	2.5
5L	25.7	14.3	2.0
10L	22.9	18.6	2.0
15L	24.3	18.6	2.0

6.3.4.3. Prestretching

Stress relaxation curves for the compounds were plotted after prestretching. In the case of DBP (Figure 6.10) loading of the plasticizer showed only little influence. A comparison with Figure 6.7 shows that relaxation after prestretching was slightly less in magnitude as indicated by the σ/σ_0 valuess at 10,000 seconds. Figure 6.11 shows the change in stress ratio with time for the LNR compounds after stretching. A decreasing gradation was observed in the stress relaxation property with increasing plasticizer content. Figure 6.12 is a comparison of the plasticizers after stretching. Distinct difference was noticed for the control and DBP compounds. After an initial relaxation, up to log t = 1.5, the control compound had a low rate of relaxation while the compound 15D showed a higher and 15L still higher relaxation. Due to lack of chain mobility the control compound contained the stress whereas the other compounds, in presence of the plasticizers, released the stress by making molecular rearrangements even in weak force fields.

6.3.5. Effect of ageing

Effect of ageing with respect to stress relaxation are given in Figures 6.13 to 6.15. Contribution of ageing at 100°C for 24 h was nor significant in the NBR vulcanizates. Addition of plasticizers also had little impact as is revealed by Figures 6.13 for LNR and 6.14 for DBP. It can also be found from a comparison of the properties of the control, 15L and 15D after ageing (Figure 6.15) and before ageing (Figure 6.9) that the contribution of the plasticizers to ageing was not significant.

6.3.6. Permanent set

Permanent set of the samples were determined after the test at 50% elongation. Gauge length was marked on the specimens before starting the experiment and the lengths were again measured at 30 seconds and 24 h after the experiment to determine the extent of permanent set the samples have undergone. The elongations were calculated as percentage of original length. Elongation of samples measured after 30 seconds of releasing the stress are given in Table 6.2.

Table 6.4. Percentage elongation of samples after 30 seconds.

Process	Control	L5	L10	L15	D5	D10	D15
Normal	5	7	16	20	10	10	13
After ageing	10	13	16	20	10	10	13
Prestretched	7	7	13	20	10	13	13

Control compound and D5 had comparable elongation. An increase in elongation was observed with those compounds containing higher amounts of plasticizer. Elongations measured after 24 h of relieving stresses revealed that the residual effect was negligible and the samples have undergone extension within their elastic limits.

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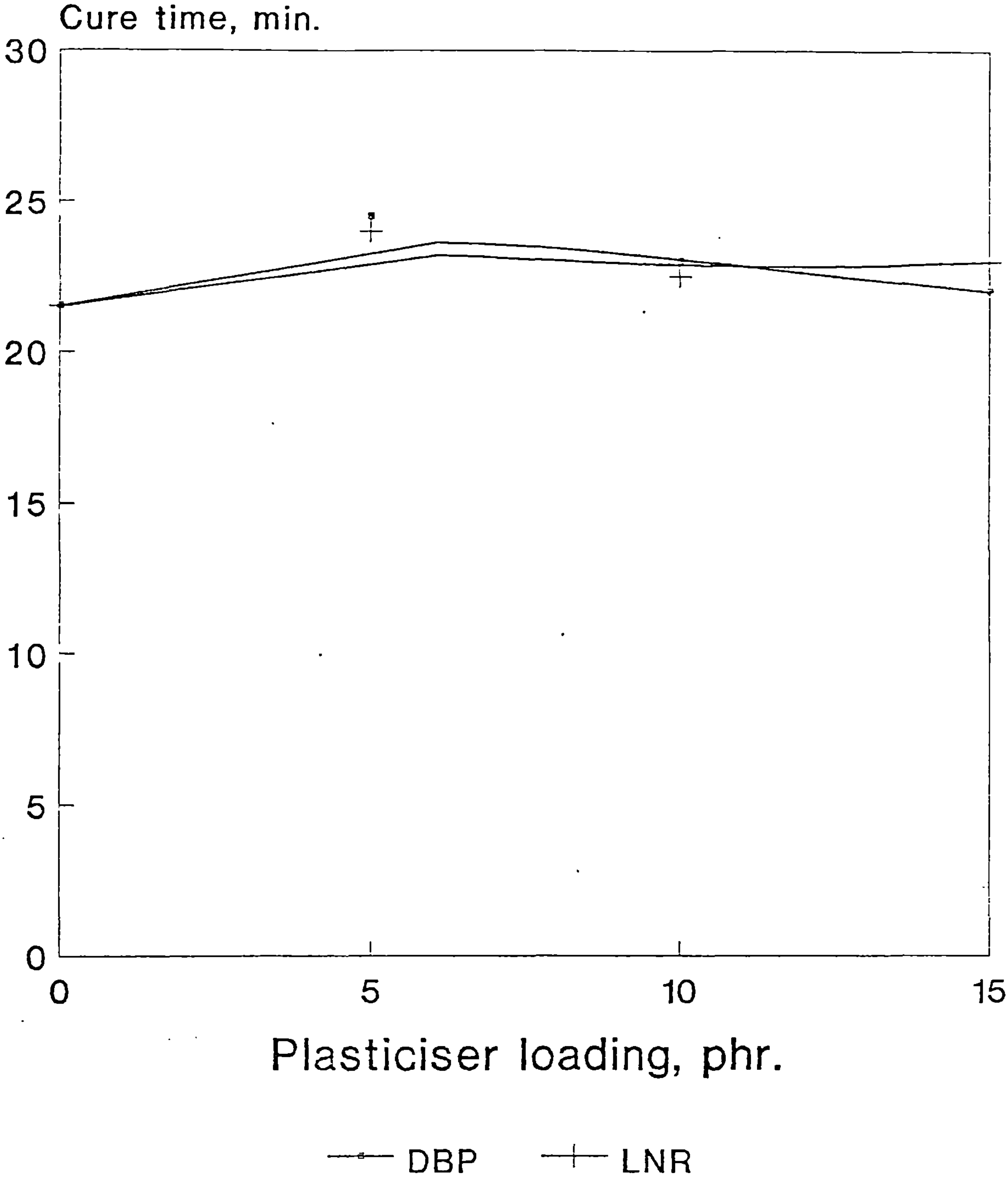

Fig.6.1. Effect of plasticizer on cure

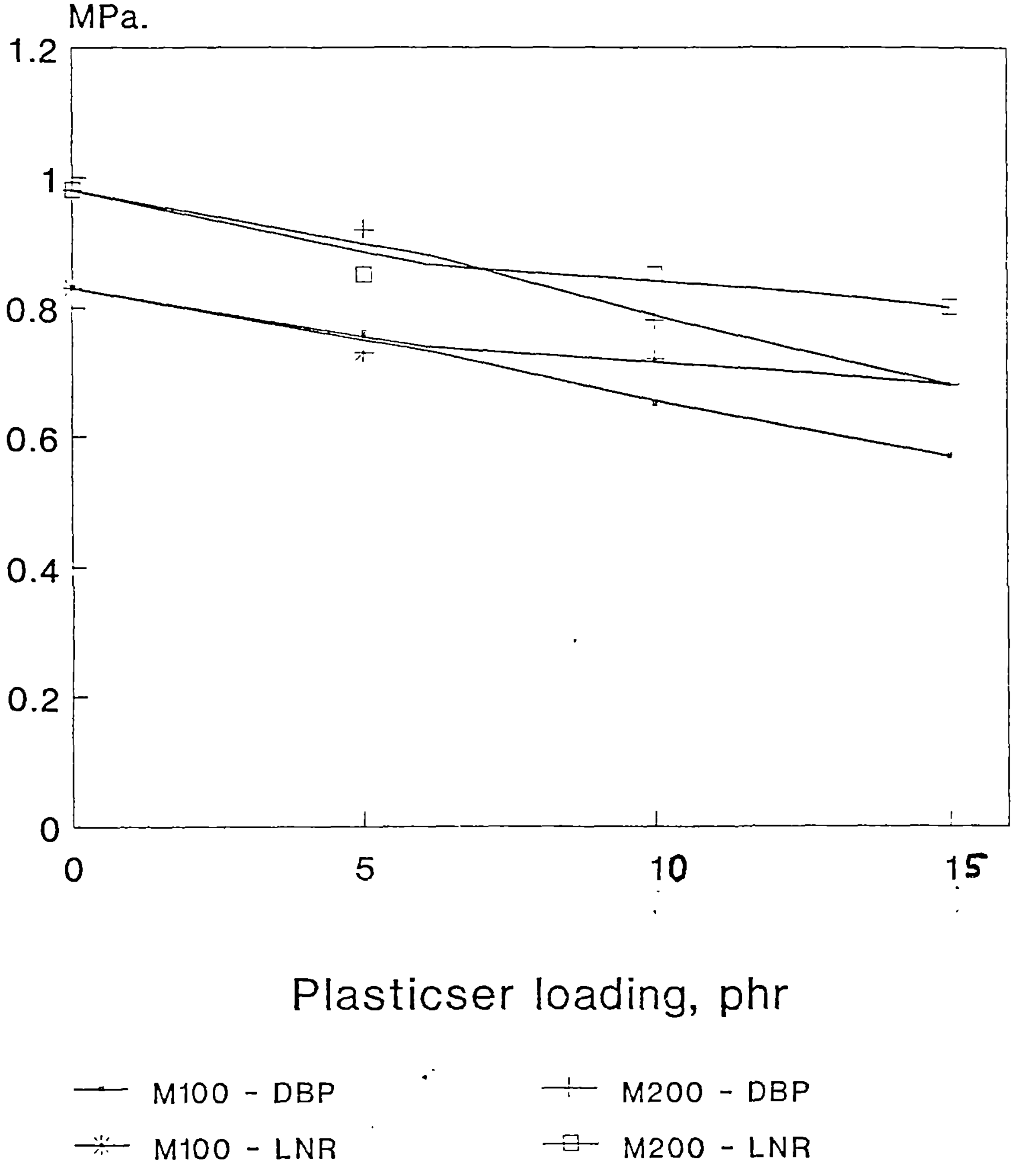

Fig.6.2. Effect of plasticizer on modulus

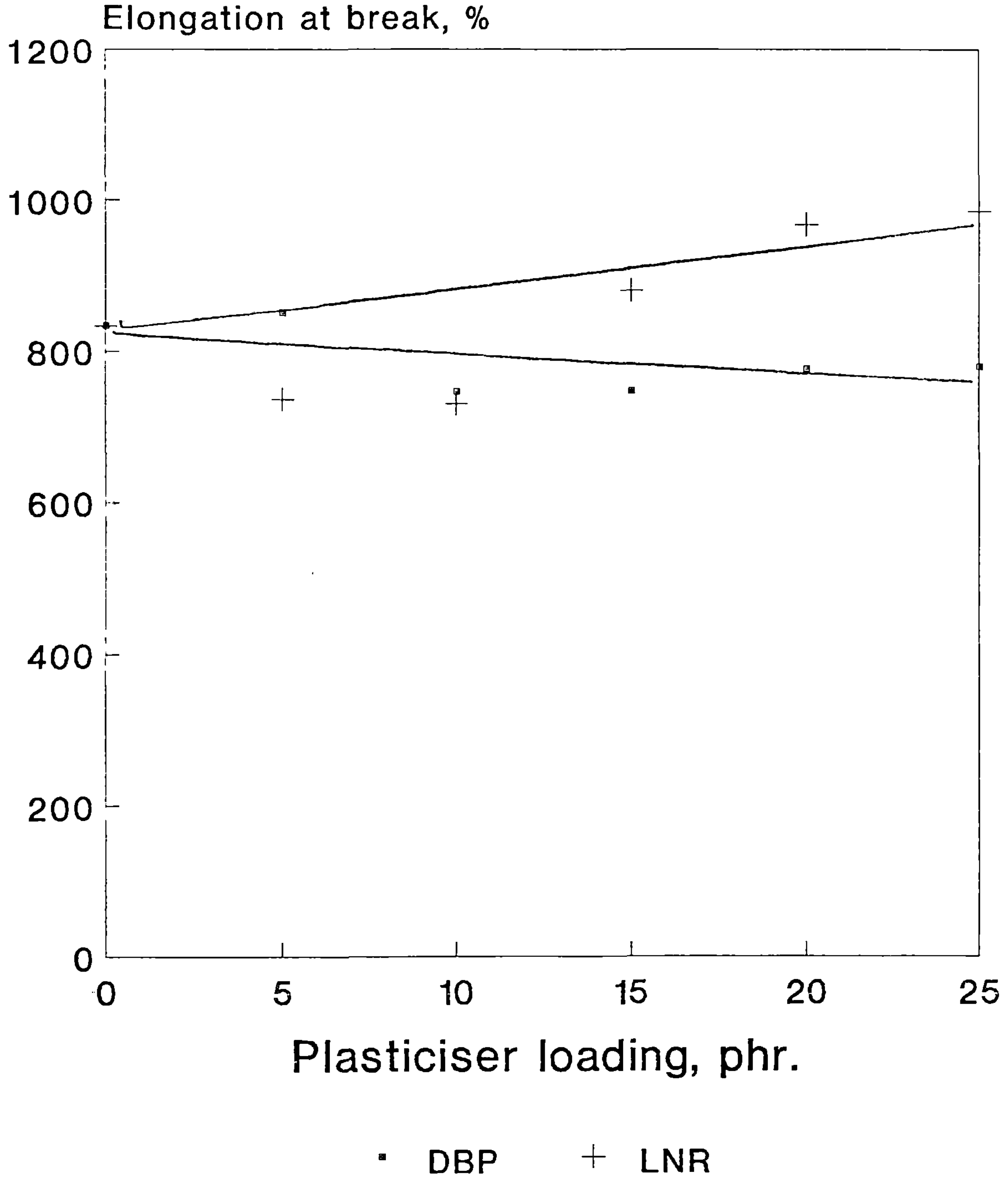

Fig.6.3. Effect of plasticizer on elongation at break

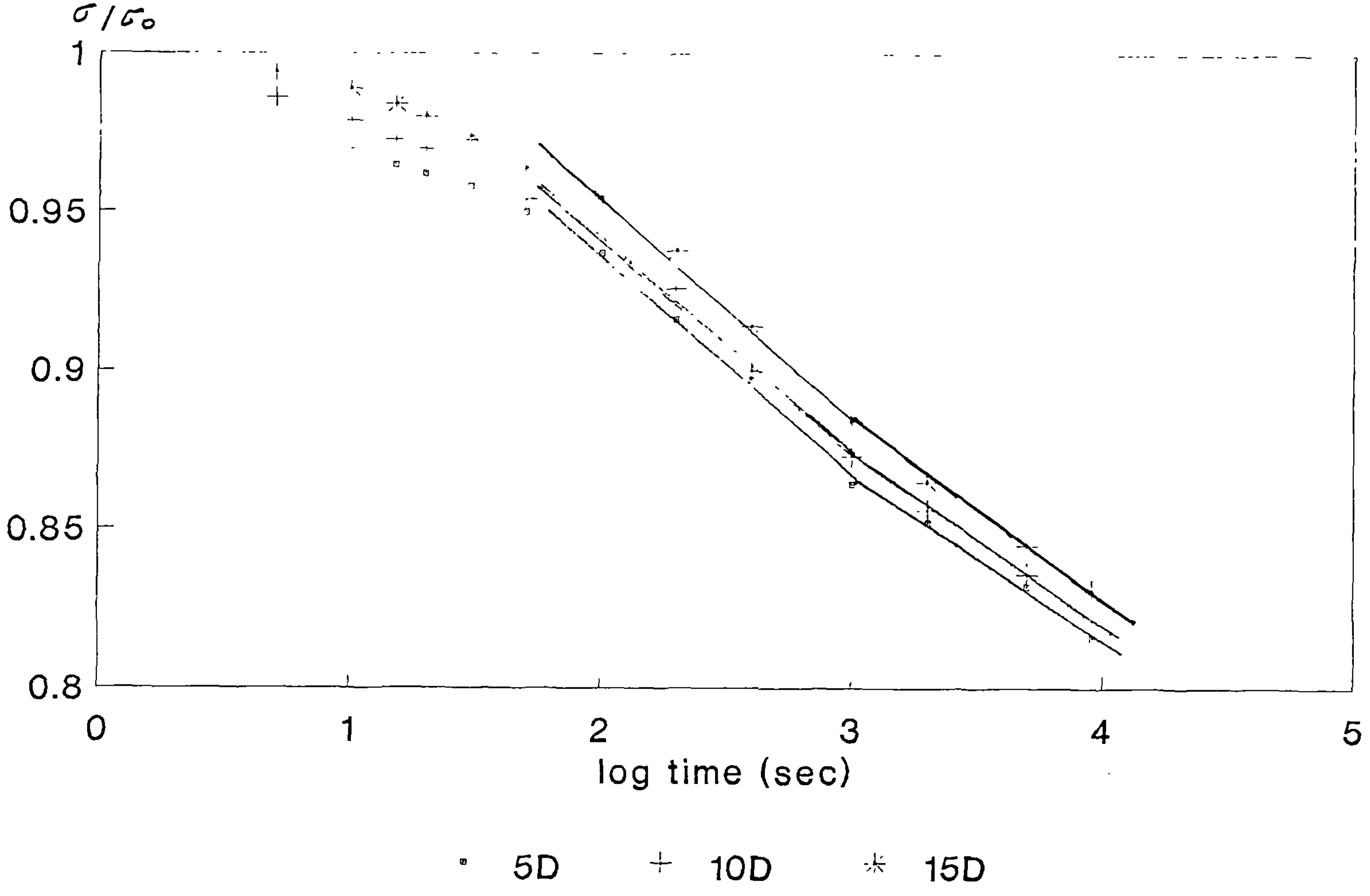

Fig.6.4. Stress relaxation of DBP compounds at 200% elongation.

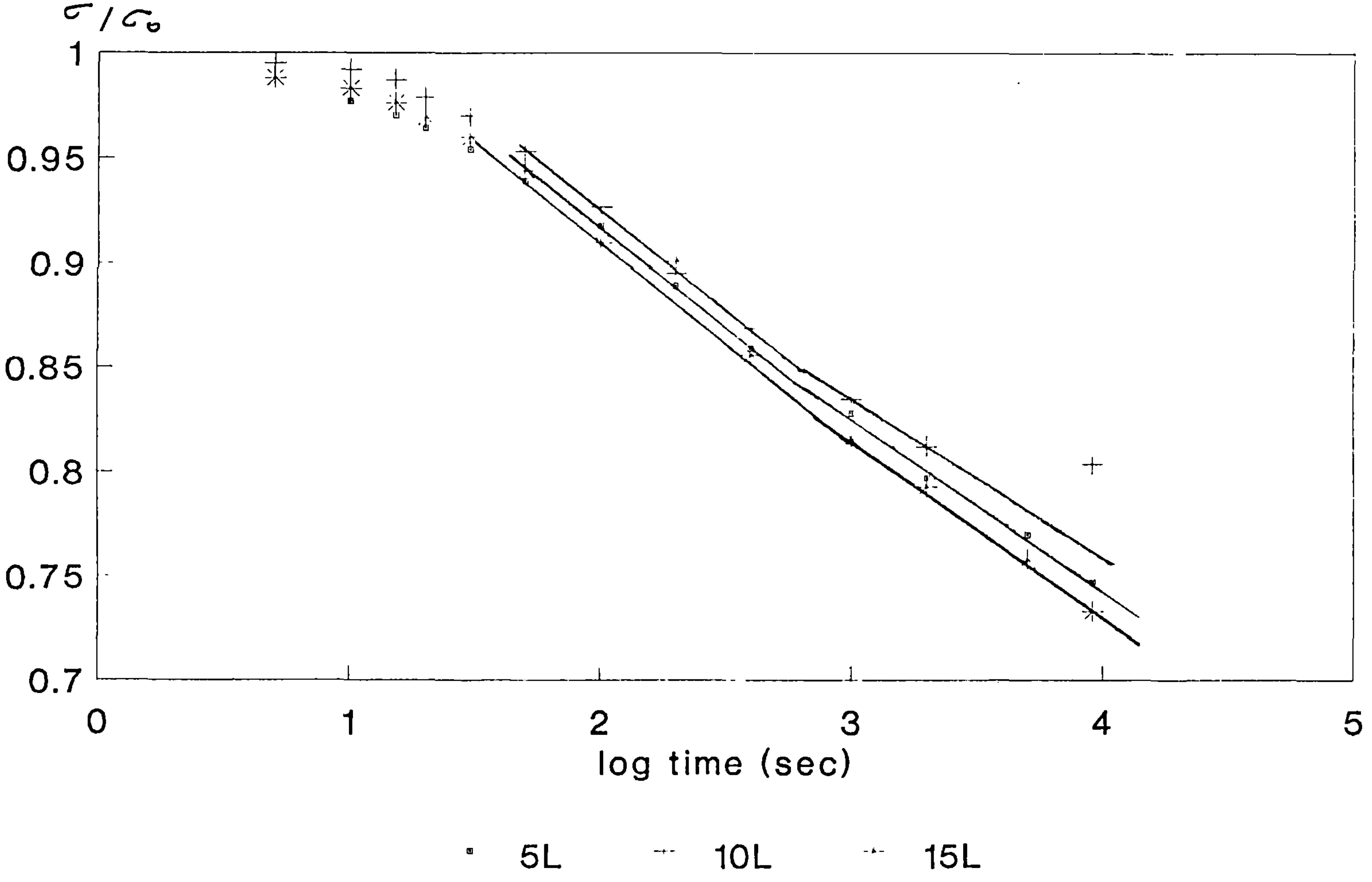

Fig.6.5. Stress relaxation of LNR compounds at 200% elongation.

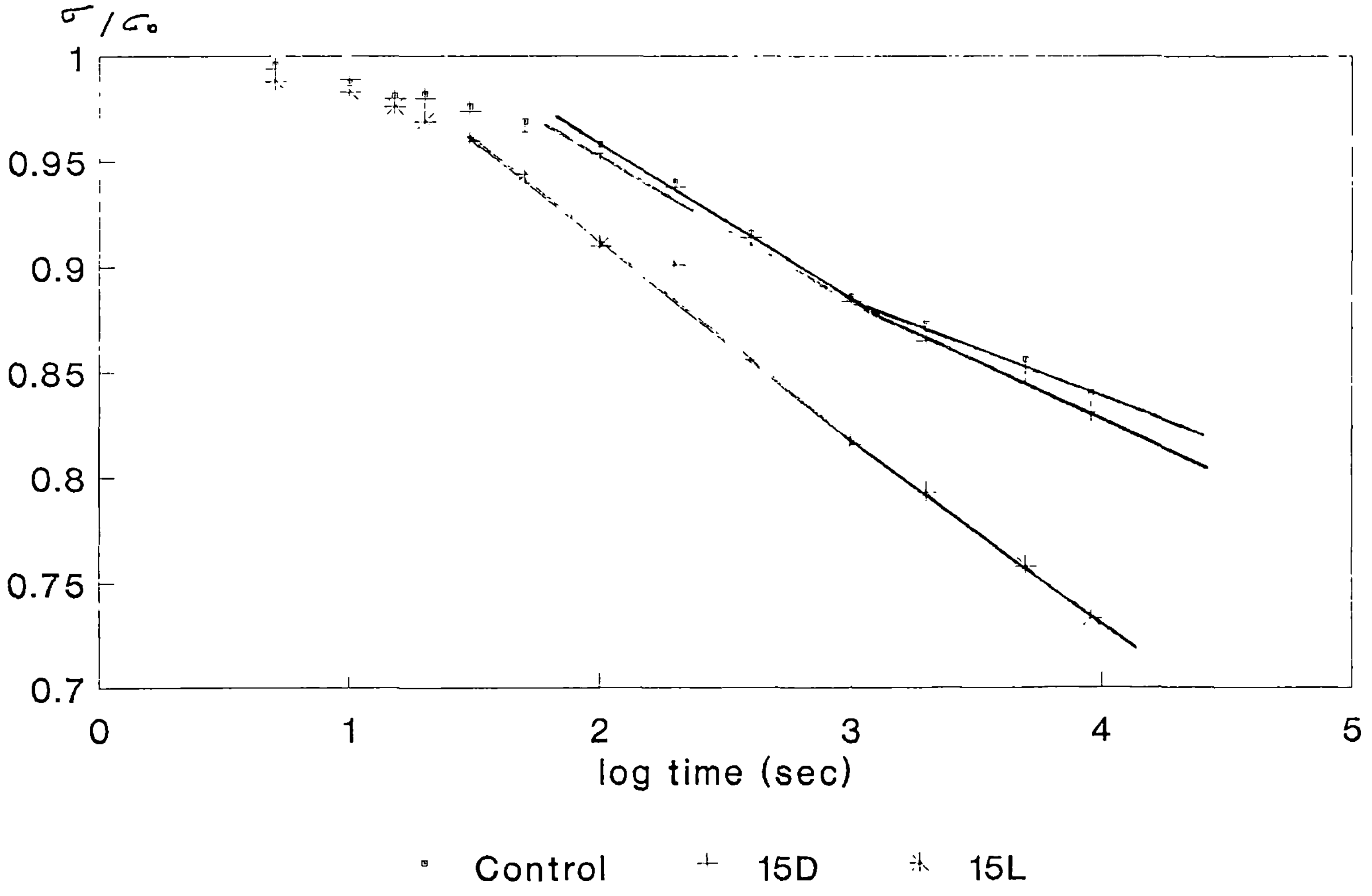

Fig.6.6. Effect of plasticizer on relaxation at 200% elongation.

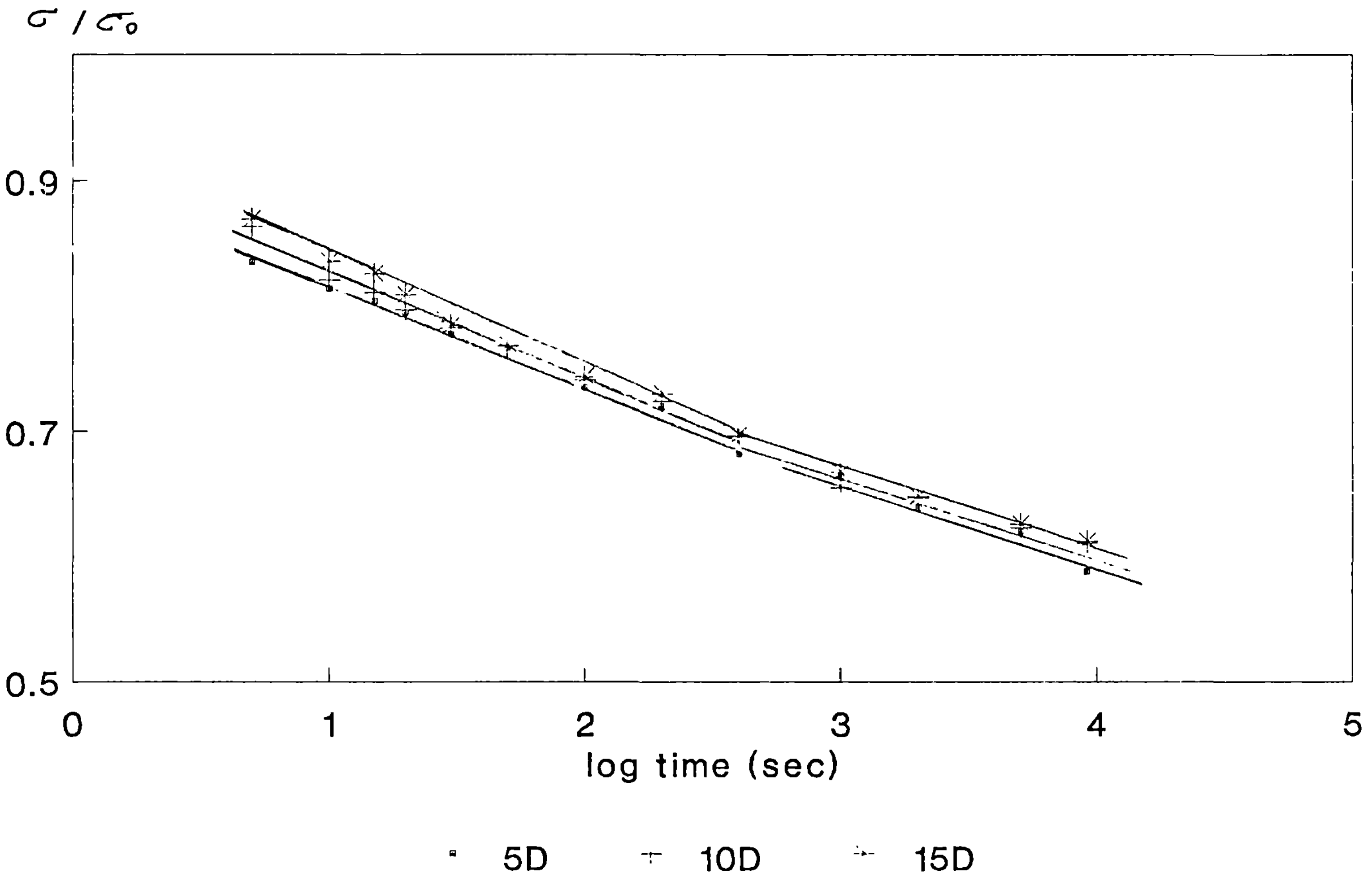

Fig.6.7. Stress relaxation of DBP compounds at 50% elongation.

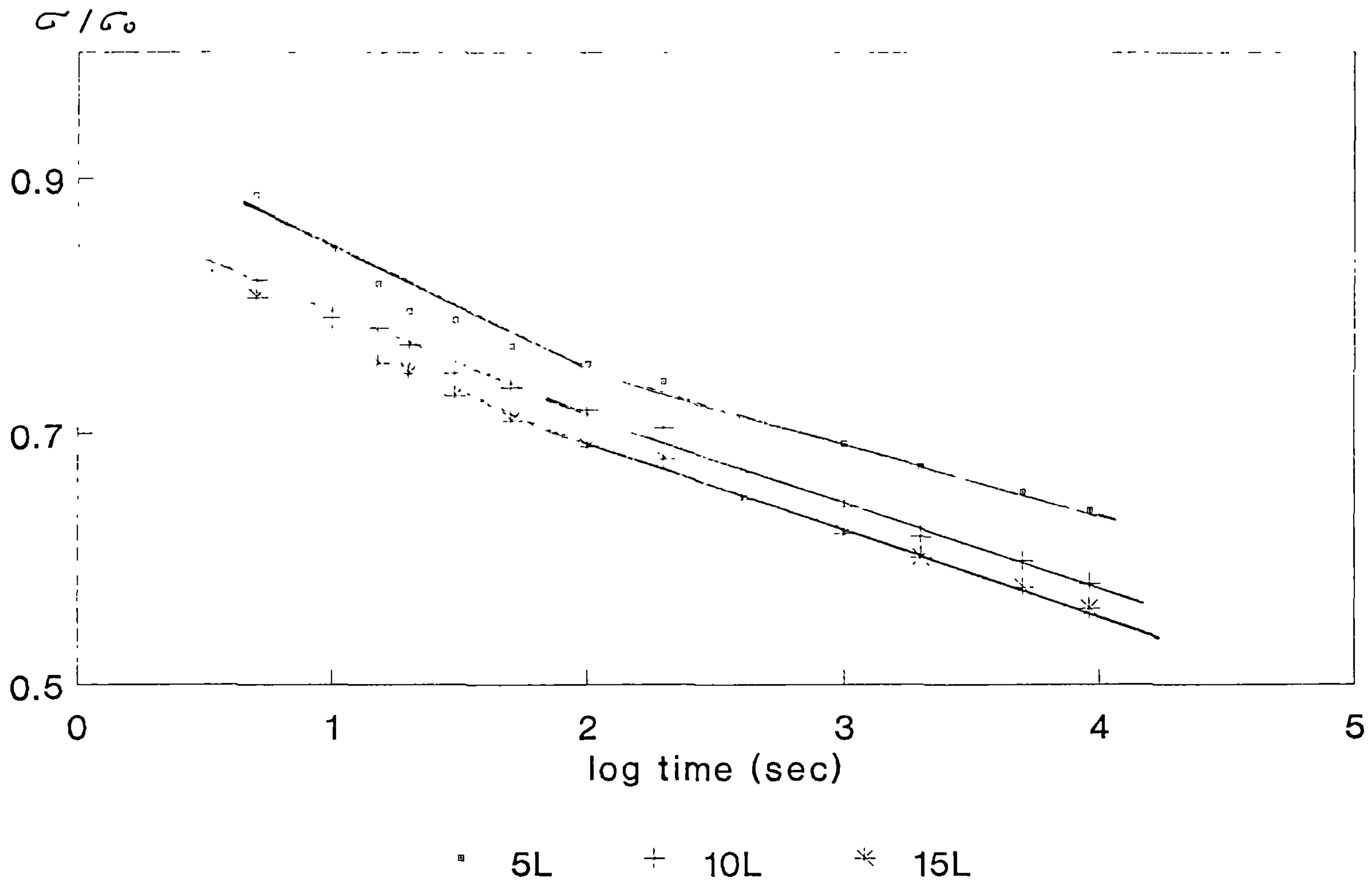

Fig.6.8. Stress relaxation of LNR compounds at 50% elongation.

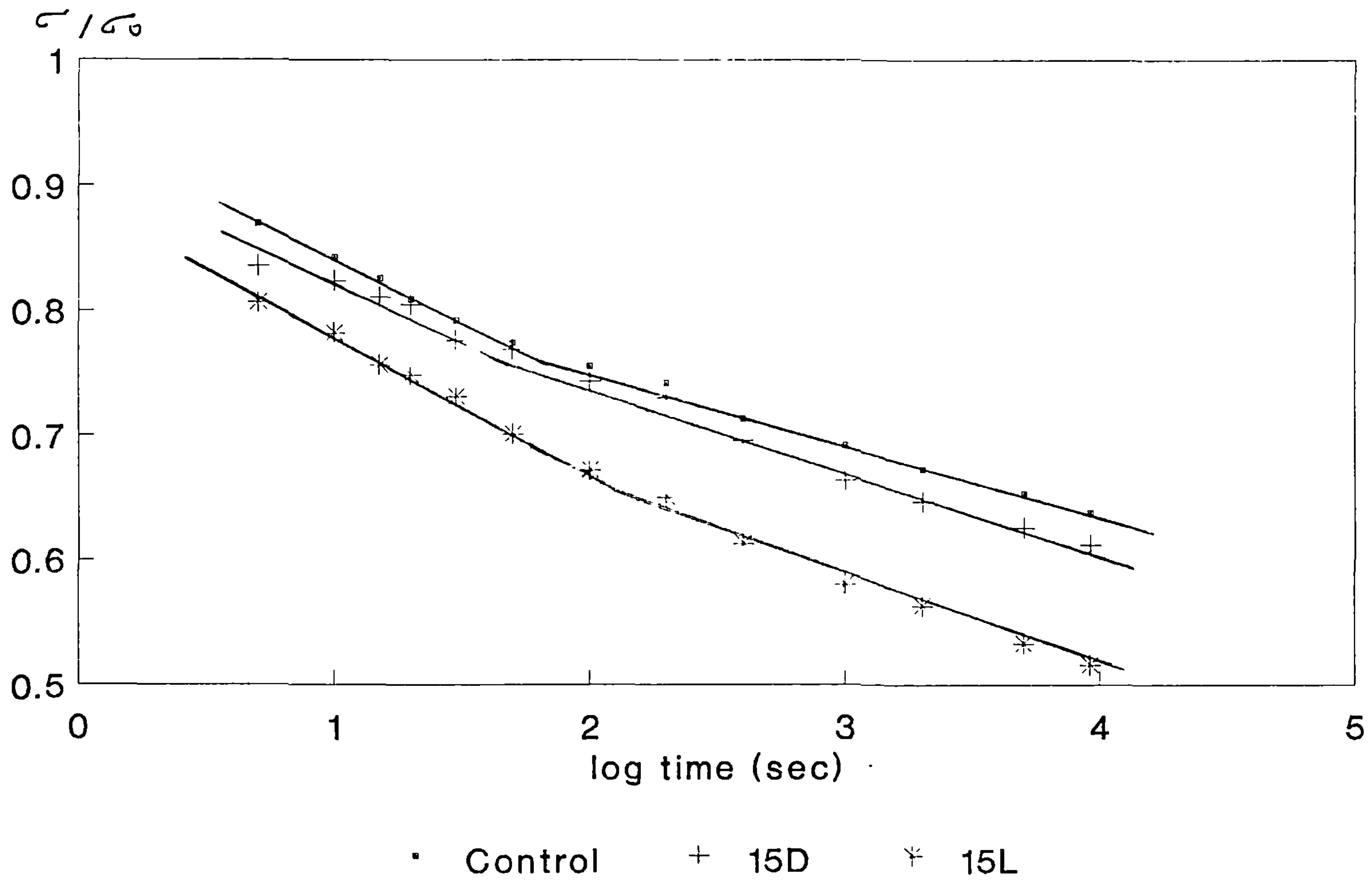

Fig.6.9. Effect of plasticizer on relaxation at 50% elongation.

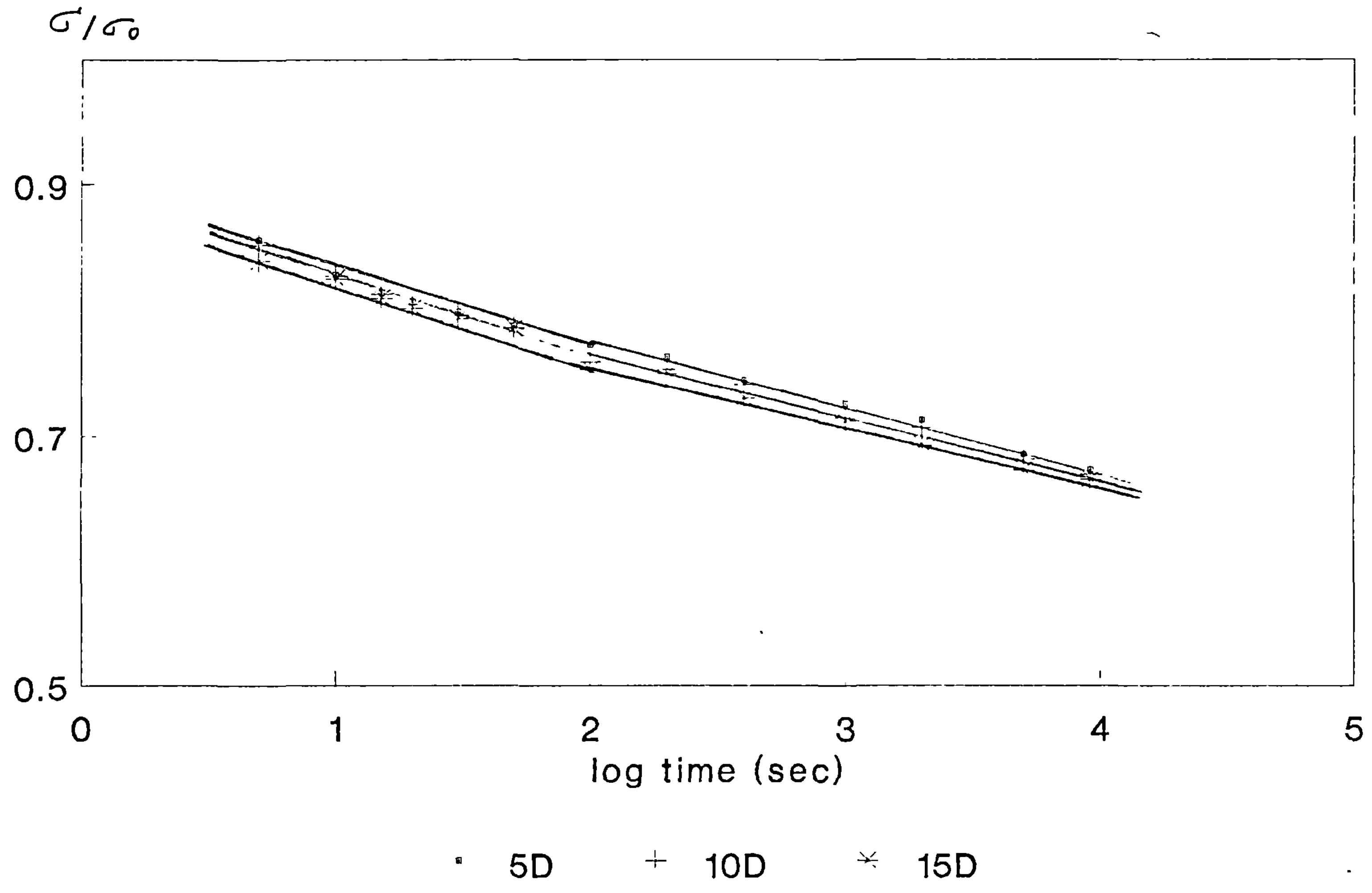

Fig.6.10. Relaxation after prestretching in DBP compounds at 50% elongation.

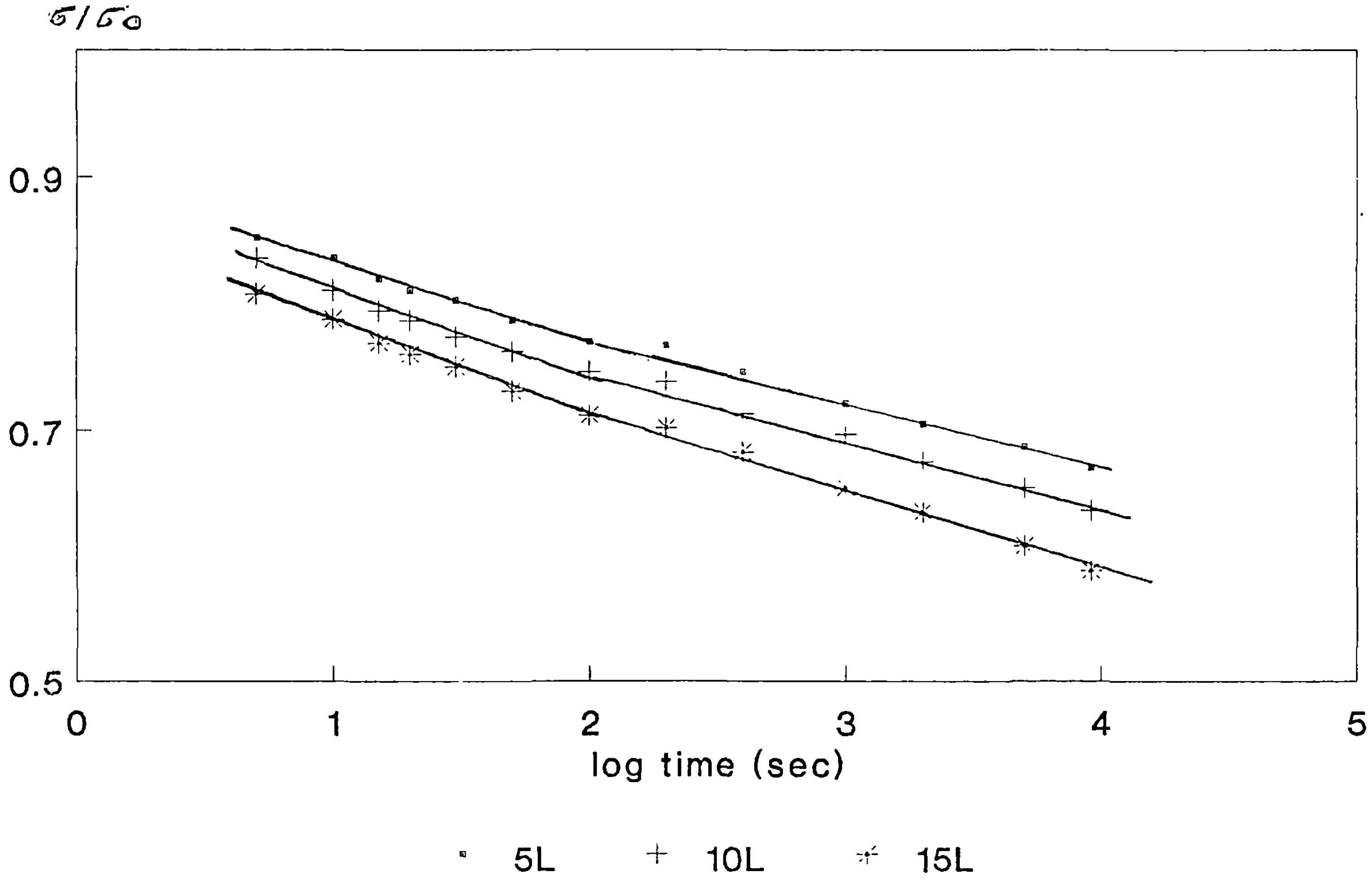

Fig.6.11. Relaxation after prestretching in LNR compounds at 50% elongation.

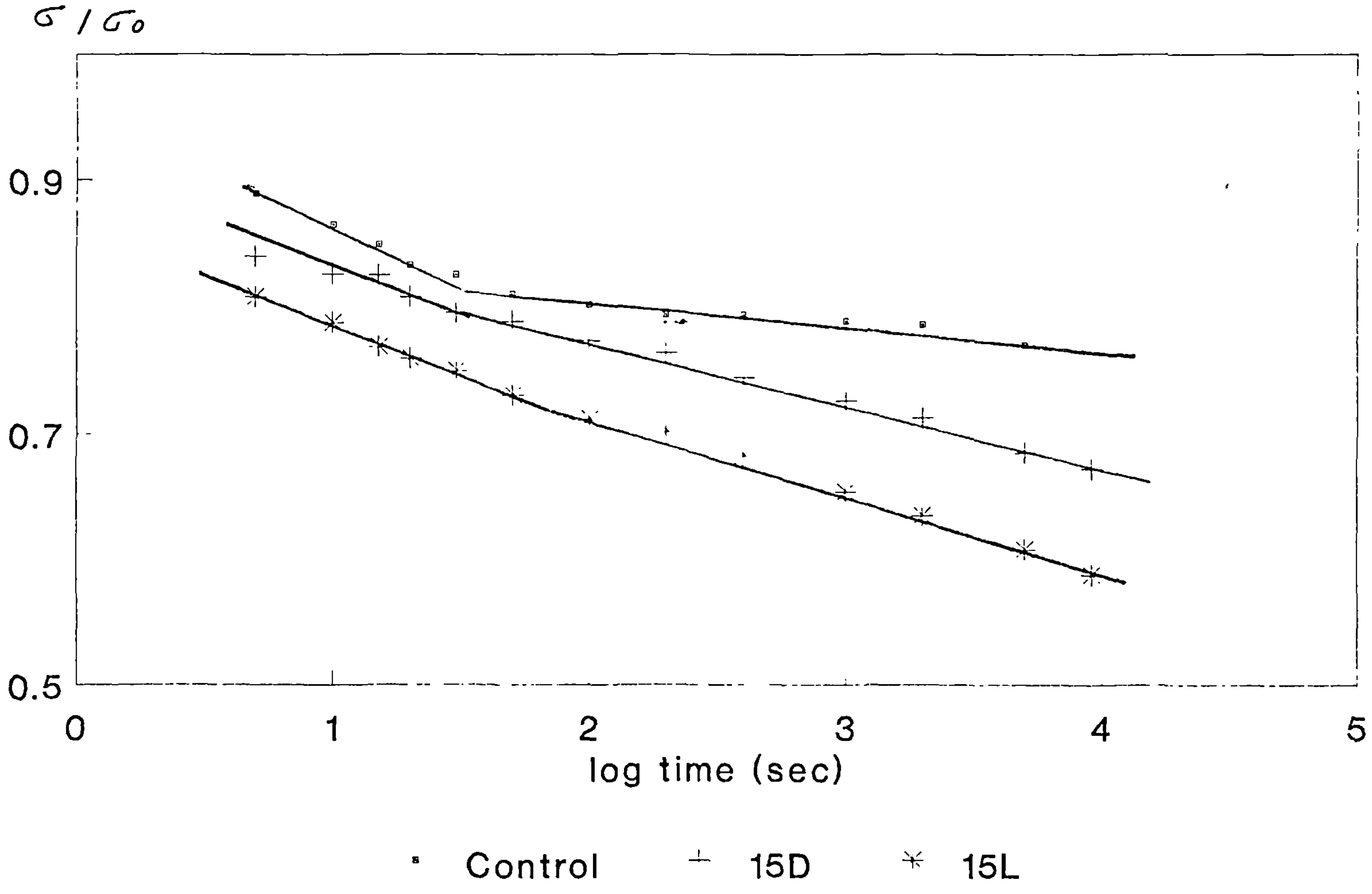

Fig.6.12. Effect of plasticizer content after prestretching

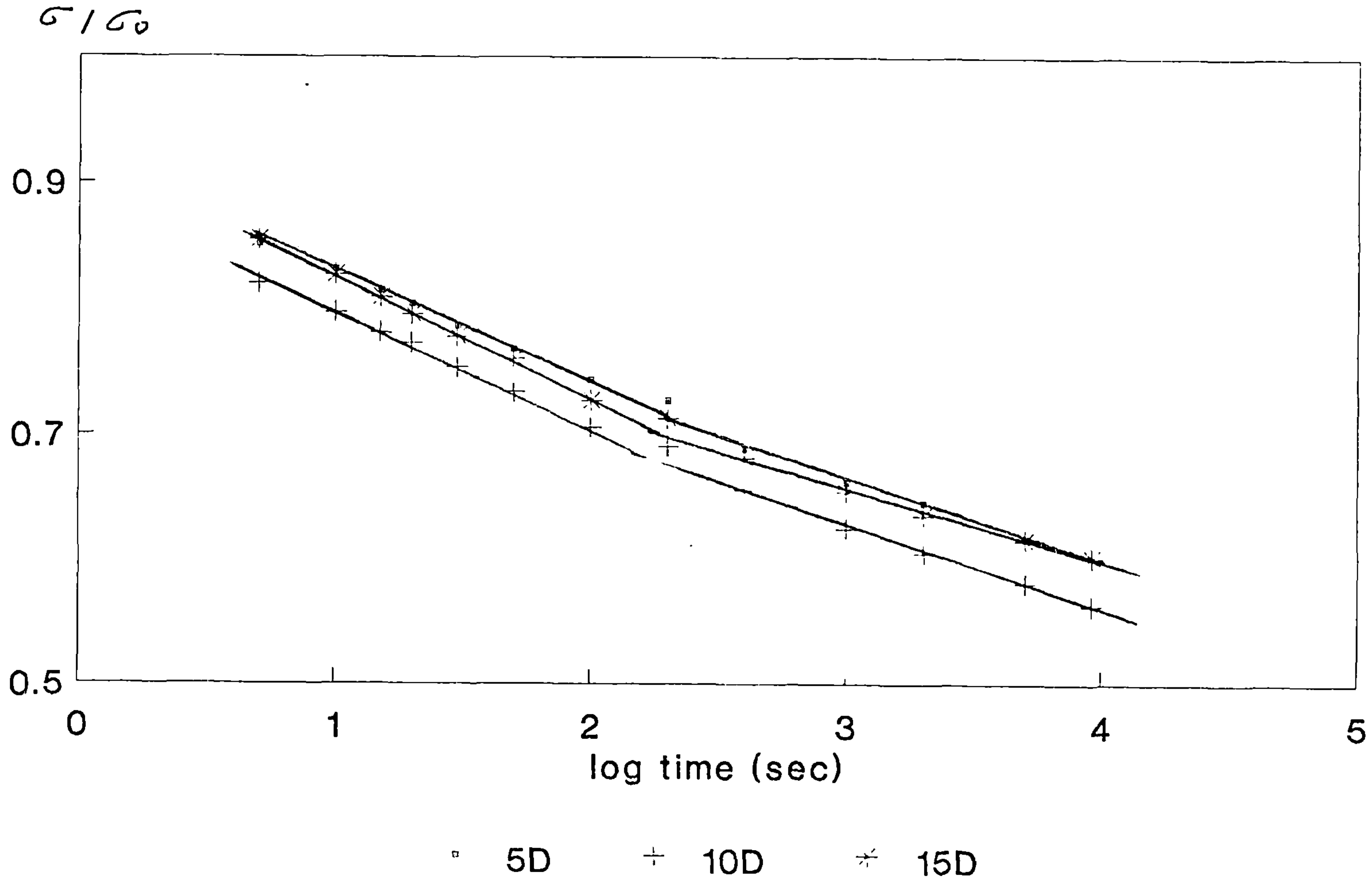

Fig.6.13. Relaxation after ageing in DBP compounds.

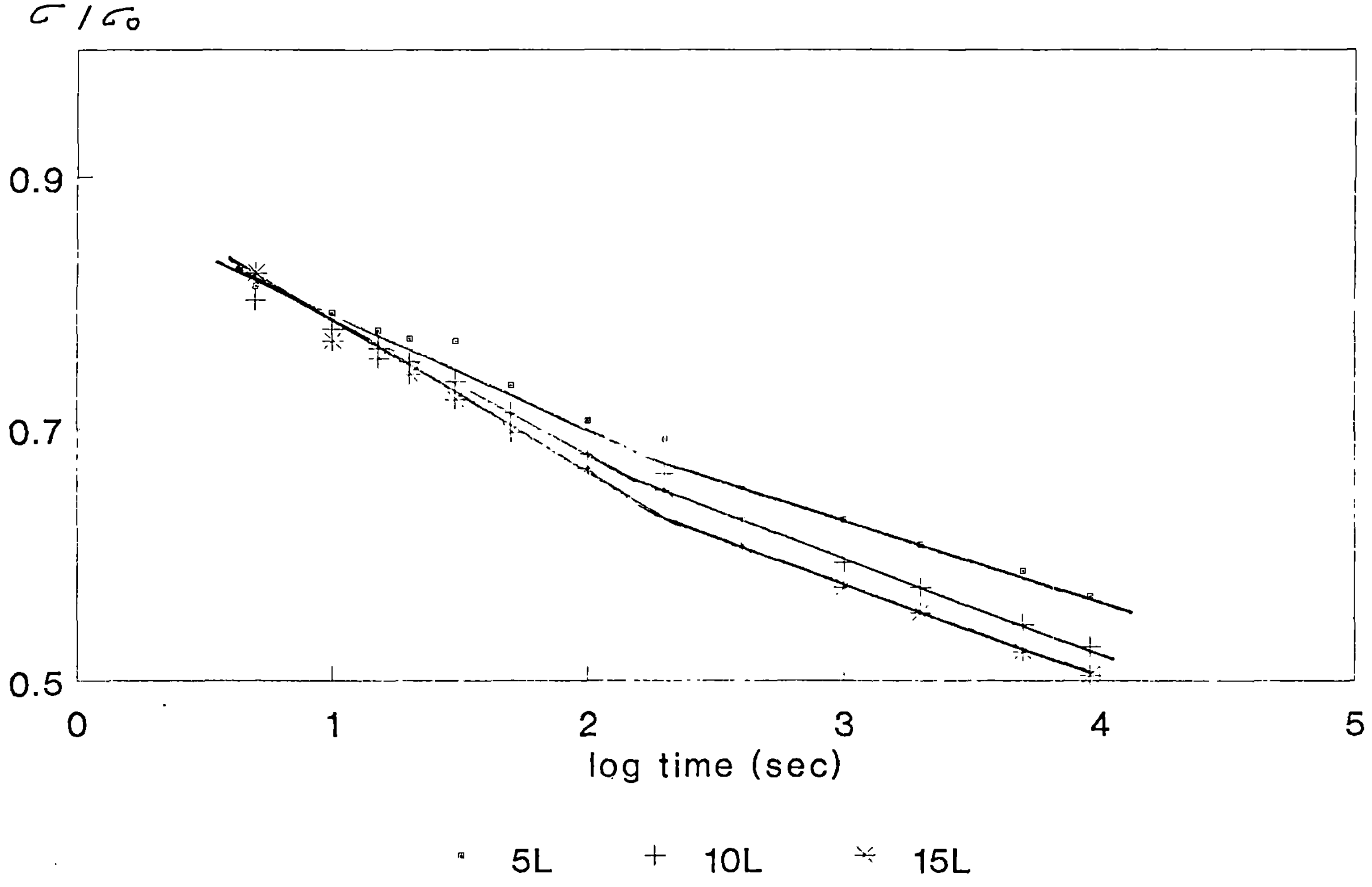

Fig.6.14. Relaxation after ageing in LNR compounds

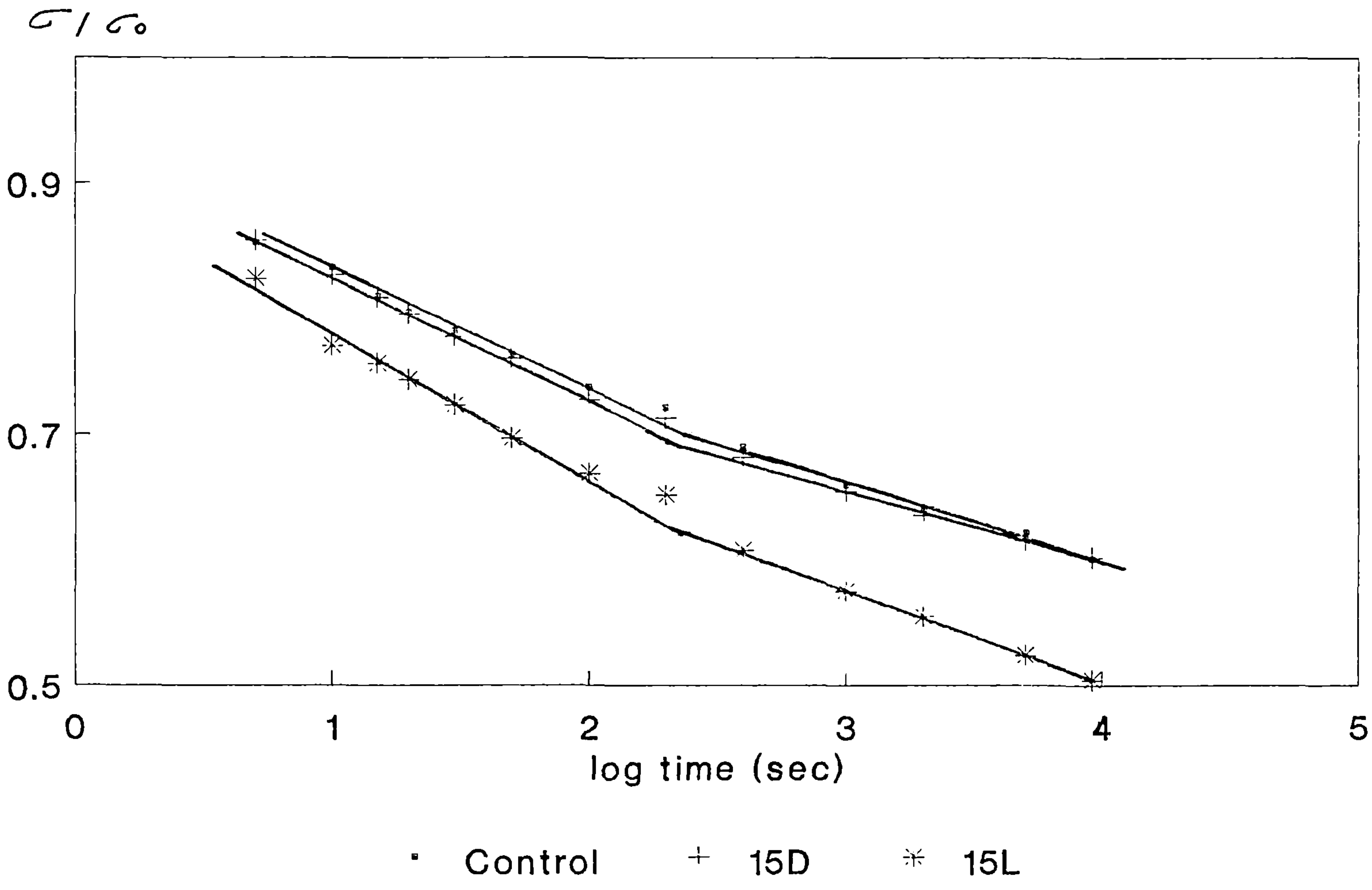

Fig.6.15. Effect of plasticizer content after ageing.

Chapter 7.

PHYSICAL AND RHEOLOGICAL CHARACTERISTICS OF LIQUID NATURAL RUBBER MODIFIED BITUMEN

he results of this chapter have been communicated to the Journal of Applied Polymer Science.

7.1. INTRODUCTION

Bitumen by itself has become inadequate in many applications due to changed perception and working environment. Traffic factors have increased with respect to both load and volume. Higher pressures are employed for tyres and higher costs demand construction of thinner pavements. Bitumen based coatings are used in a number of anticorrossive applications. Composites based on bitumen are used for water-proofing buildings. It is also used for sealing joints of underground cables. Hence, modification of bitumen by different techniques has become a topic of interest. Modification using polymers is a widening area due to the viscoelastic contribution of the polymer to the bitumen properties. The changes are aimed at addressing major problems such as high temperature permanent deformation, load associated fatigue cracking, low temperature thermal cracking, etc. Ageing is the hardening of bitumen over time and temperature. Polymers have been found to reduce hardening, moisture susceptibility and improve adhesion of the binder to aggregates. Use of rubber by a French bitumen company for laying pavements as early as in 1902 has been documented[1]. Most bitumen binders were classified by viscosity graded system. The viscosities at 60 and at 135°C are important to the application and use of bitumen binders. The viscosity graded system has been replaced by the penetration system in the sixties[2]. Other tests used to characterize bitumen binders are ring and ball softening point [3].

Modification with rubber permits bitumen, even of low quality to acquire attractive properties. This makes it possible to lay down suitable road paving, using relatively inexpensive bitumen. NR is a potential candidate among various polymers for blending with bitumen. It is one of the polymers with which bitumen modification has been successfully carried out. Addition of NR to bitumen has been attempted in different ways. One of the earliest methods is the addition of latex, stabilized with alkali, to molten bitumen under vigorous stirring. Water evaporates and NR gets mixed with the bitumen[4]. Addition of rubber in powder form has also been attempted. These include rubber powder from the rejections of various dry rubber and latex products[5-6].

NR latex is the most effective additive to bitumen, but difficulties arise due to its water content. Vulcanized and lightly vulcanized powders are convenient to use. Smoked sheet or crepe rubber can be used, by masticating and dispersing in fluxing oil. The present investigation is a study on the addition of NR, in liquid form, for imparting desirable properties on bitumen binders and encapsulating materials. The process of polymer addition has been made easy by simple melt blending on account of the easy miscibility of LNR and bitumen. The mixing process is rather simpler than latex addition as little precaution is needed to prevent lump formation, fall in temperature due to water, frothing due to evaporation, etc. This method can be easily adopted as one of the unit operations in a petrochemical complex to manufacture modified bitumen. Stabilizing agents incorporated into the latex can also be dispensed with. Further, NR in the latex form is a premium grade whereas depolymerized rubber can be prepared starting even from scrap rubber which is considered inferior for many automotive/ engineering applications.

Polymer modification of commercially available bitumen has been attempted by the incorporation of LNR of medium viscosity. Both soft and blown bitumens were studied. Physical and rheological characteristics of the samples were investigated. Improvement in physical properties such as shear strength and ductility in the case of blown bitumen and resistance to flow in the case of soft bitumen were observed. It was also found that as a result of addition of LNR the activation energy of flow increases in the case of soft bitumen and decreases in the case of blown bitumen.

7.2. MATERIALS AND METHODS

7.2.1. Bitumen

Two types of bitumen, normal and blown, were used. The soft bitumen, 80-100 grade, was a product of Cochin Refineries Ltd., Cochin. Blown bitumen was of 5 grade, on the penetration scale, supplied by Bituminex Ltd, Ambalamugal. It was prepared by removing the volatile fragments like gas oils by heating to 300 - 350°C and also by the application of vacuum for 3 to 4 h.

7.2.2. Liquid natural rubber

The LNR was of medium viscosity grade with Brookfield viscosity 1,60,000 mPa.s. It was prepared starting from ISNR 5 by thermal depolymerization technique as suggested by Claramma et al.[7].

7.2.3. Preparation of samples

Table 7.1. Formulation of blends.

Sample no.	% of bitumen	% of blown bitumen	Liquid natural rubber
B0	100	Nil	Nil
B5	95	Nil	5
B10	90	Nil	10
B20	80	Nil	20
B30	70	Nil	30
BB0	Nil	100	Nil
BB5	Nil	95	5
BB10	Nil	90	10
BB20	Nil	80	20
BB30	Nil	70	30

LNR was incorporated into bitumen by melt blending. The bitumen was first heated to easily flowable consistency and LNR was added slowly with stirring and was homogenized properly. Formulations of the blends are given in Table 7.1.

7.2.4. Viscosity measurements

For the measurement of viscosity of the soft bitumen samples a Haake rotational viscometer was used. The sensor system used was MV1. The viscosity of the blown bitumen samples were measured on a capillary rheometer attached to a Zwick UTM. Viscosity was measured over a range of temperature and shear rate to study the flow behaviour on modification of bitumen with LNR.

7.2.5. Lap shear test

Lap shear test was used to determine the room temperature cohesive strength of modified bitumen and also to study the thickening process[8]. Two aluminium strips, 1mm thick, were overlapped by 2.5 cm and firmly bonded together with a drop of molten bitumen. The test pieces were held in position with alligator clips until ready for testing. The samples were bonded together as shown in Figure 7.1 and tested after 24 h conditioning. The test was carried out on a Zwick universal testing machine with the crosshead travelling at 5 mm per minute.

7.2.6. Softening point

This test was carried out as per IS 1205 - 1958. A ring and ball softening point apparatus was used.

7.2.7. Ductility

Ductility of the samples was determined according to the test specified in IS 1208 -1958. The method consists of measuring the distance in centimetre to which a briquette specimen of the material elongates before breaking, when its two ends are pulled apart at a rate of 50 mm per minute at 27 ± 0.5°C.

7.2.8. Penetration

Standard penetration tests were conducted as per IS 1204 - 1958 on samples in a container having depth greater than 15 mm. A needle thoroughly cleaned with benzene was used. The test was conducted at 25°C applying 100 g load for 5 seconds and the depth measured and expressed in 1/100th of a centimetre.

7.3.RESULTS AND DISCUSSION

7.3.1. Liquid natural rubber.

For the modification of bitumen a LNR sample in the medium viscosity range was chosen in order to have a compromise between ease of blending and strength characteristics. The physical strength of NR decreases on depolymerization and the low molecular weight samples exhibit more viscous rather than elastic properties. On the other hand more viscous LNR samples are difficult to mix with other liquids. Hence, an LNR of optimum molecular weight has to be chosen to optimize between processability and properties of the resultant compounds [9]. The molecular weight details of the LNR sample are given in Table 7.2. Figure 7.2 is the GPC chromatogram of the sample.

Table 7.2. Properties of LNR

$\overline{Mn}$	5,057
$\overline{Mw}$	33,360
$\overline{Mw}/\overline{Mn}$	6.598
Brookfield viscosity, mPa.s.	1,60,000

A wide range in the elution time of the polymer molecules indicated a broad molecular weight distribution. This is also evidenced from the polydispersity index.

7.3.2. Softening point

The observations are given in Table 7.3. The softening points were found to be in the range 29 to 53°C for soft, and 96 to 110°C for blown bitumen. On addition of small quantities of LNR to soft bitumen, the softening point increased. But around 10 parts, this property showed a reversing trend and at 30 parts loading, the softening point was much lower than that of the unmodified bitumen. For the blown bitumen samples also, a steady increase in softening point was observed with a maximum value around 10 parts. However, the subsequent decrease was not prominent as in the case of soft bitumen. Sample containing 30 parts of LNR had a higher softening point than the unmodified bitumen. Softening point is a measure of the resistance to cold flow. Hence, addition of LNR increases the service temperature of bitumen for different applications.

Table 7.3. Tests on bitumen as per BIS

Sample no.	Softening point, °C	Ductility, at 27°C, cm.	Penetration at 25°C.
B0	43	>150	80
B5	44	92	85
B10	53	26	119
B20	39	25	260
B30	29	25	340
BB0	96	3	5
BB5	107	3	5
BB10	110	4	18
BB20	105	3	30
BB30	100	3	40

7.3.3. Ductility

Ductility of the samples, measured at 27°C on the soft bitumen samples, showed a continuously decreasing trend with increasing concentration of LNR. Ductility is the ability of a material to yield to tensile strains without collapsing. Bitumen is a thermoplastic material and is often subjected to variable mechanical reactions. The properties are affected by the conditions of loading and by the presence of solvents remaining from distillation or purposely added. Mechanical resistance to deformation and mode of failure are influenced by the low molecular weight materials. Much of the low molecular weight substances having been removed during the process of preparation, the blown bitumen appeared less ductile. Presence of NR was found to make the soft bitumen sample is less ductile. In the case of blown bitumen a slight improvement was noticed with 10 parts of LNR (Table 7.3).

7.3.4. Penetration

The penetration tests on the samples were done at 25°C and the values are given in Table 7.3. The values are found to increase with increasing loading of LNR. Penetration gives an indication about the resistance of the material to indentation. The test revealed that the samples were rendered softer by LNR at 25°C. In the case of BB0 and BB5 no difference was noticed but at higher loadings, an increasing trend prevailed. Thus LNR was found to soften the samples at low temperatures and reduce temperature susceptibility at high temperatures.

7.3.5. Lap shear

Figure 7.3 shows the results of lap shear test. In both the soft and hard samples, an appreciable increase was noticed in the force for shear failure on incorporation of LNR. Peak strength was noticed around 10 parts of LNR in soft bitumen and 5 parts of LNR in hard bitumen. The shear test in the present case has led to breakage within the material rather than pealing of the bitumen from the substrate and so the values directly reflect the strength of the samples. Any sign of cleavage of the material from the substrate was not visible. The blown bitumen samples were brittle and therefore, a slow test speed of 5 mm per minute was used.

7.3.6. Viscosity studies

7.3.6.1. Effect of shear rate

Figure 7.4 shows the plot of shear stress values of the soft bitumen samples at different shear rates measured at 100°C. In general the viscosity values showed an increasing trend with increasing shear rate. Among the different compounds, at low shear rates the values were in a close range, but at high shear rates B10 showed the highest shear stress value. Figure 7.5 shows the corresponding values for the blown bitumen samples. Shear stress increased with increasing shear rates. The rate was high initially and decreased gradually. The downward curvature of the shear stress-shear rate curve may be attributed to the pseudoplastic nature of the composite. An upward trend in the shear stress values of BB5 over the other samples showed that the addition of small quantities of LNR increased the resistance to flow. Addition of larger quantities of LNR caused decline in the stress values. The viscoelastic behaviour of bitumen are governed by both solid and continuous phases[10]. Asphaltenes are suspended in a colloidal manner within a matrix which contains a variety of chemical compounds like resins. Addition of large amounts of LNR increases the proportion of soft continuous phase and enhances the flow behaviour. Particularly at high shear rates a shear stress stabilizing trend was noticed, most prominently for BB0, the Bingham plastic behaviour of bitumen. The compound with 30 parts of LNR appeared closer to Newtonian in behaviour.

7.3.6.2. Effect of temperature

Temperature dependence of the soft bitumen samples at an arbitrary shear rate, 15 s^{-1} is presented in Figure 7.6. All samples showed a decrease of viscosity with increase in temperature. At all temperatures the shear stress values were the highest for the sample containing 20 parts of LNR. The general trend was that shear stress increased from B0 to B20 and then declined. For the sample BB30 with 30 parts of LNR a steady decrease in shear stress with increase in temperature was noticed, but the stress values were the lowest. For samples with low LNR content the rate of reduction in viscosity was higher at low temperatures as was evidenced by the slope of the curve. Figure 7.7 shows the corresponding values for blown bitumen samples. A gradual decrease in stress values was observed for the samples on increasing LNR content. The slope of the curves in the low temperature region was found to decrease with increasing LNR/bitumen ratio. Higher quantities of LNR rendered the bitumen too soft at low temperatures.

7.3.6.3. Effect of temperature on viscosity

Figures 7.8 and 7.9 are the plots of viscosity on logarithmic scale vs reciprocal of temperatures expressed on the absolute scale. Activation energy of flow has been calculated from the slope of the lines. The viscosity at higher temperature obeys the Arrhenius equation

$$\eta = A\, e^{-E/RT} \qquad \text{---------------(7.1)}$$

where E is the activation energy of flow and T the absolute temperature. The activation energy values are given in Table 7.4.

Table 7.4. Activation energy of flow.

Sample	Activation energy, kCals/mol
B0	24.75
B10	25.79
B30	36.38
BB0	2892
BB10	2573
BB30	1438

For soft bitumen the slope of the lines increases with increase in LNR content indicating that the activation energy increases with increasing LNR content. The observation in the case of blown bitumen was on the contrary. With increasing LNR content the activation energy was found to decrease considerably. Bitumen is a complex mixture consisting of asphaltenes predominant in high molecular weight fractions surrounded by several substances of different chemical structure with varying functionalities from polar aromatic to nonpolar aliphatic[11]. Due to their presence in soft bitumen, swelling of the added polymer is likely to cause increase in viscosity. With the blown bitumen samples during the process of blowing or oxidation most of the low molecular weight fractions are removed. As a result the influence of the polymer might be less.

7.3.6.4. Evaluation of superposition shift factor

The experimental flow curves for log γ_w vs τ_w were plotted at temperatures 70, 80, 90 and 100°C for the compounds BB0, BB5 and BB10. The method of superposition has been done by arbitrarily choosing 80°C as the reference temperature. The values of superposition shift factors were obtained by choosing log shear rates 2, 2.5, 3 and 3.5 s^{-1} on the reference temperature flow curve and shifting the corresponding points (constant shear rate) on the flow curve for other temperatures to coincide with the shear stresses. The values of the shift factors were calculated from the equation

$$a_T = \tau_w(\text{ref}) / \tau(T) \ (\text{constant } \gamma_w) \qquad \ldots\ldots\ldots\ldots(7.2)$$

where a_T is the shift factor, τ_w(ref) is the shear stress at reference temperature and $\tau(T)$ (constant γ_w) is the shear stress at a particular temperature. The average values of shift factors were calculated[12] and are plotted in Figure 7.10. Using the appropriate average values of the shift factors a master flow curve at 90°C was constructed and is given in Figure 7. 11. The shear rate temperature superposition method is a useful tool in predicting the viscosities of polymer melts at any required temperature by determining the viscosity at a reference temperature.

7.3.7. Effect of LNR content

Figure 7.12 represents the change in the shear stress of soft bitumen compounds with LNR content. The values were recorded at 100°C. At lower loadings and lower shear rates the values were almost steady. In general the stress values showed an increasing trend with increasing loading of LNR. Dissolution of LNR in low molecular weight components of bitumen can cause thickening and hence, can lead to high shear rates needed to maintain the same flow rate. Figure 7.13 shows the corresponding parameters for blown bitumen. In this case a general decrease in shear force was observed with increasing LNR content. This may be due to the volumetric contribution of LNR which has a significantly low viscosity than blown bitumen at 100°C. Figures 7.14 and 7.15 give the influence of LNR loading on viscosity at different temperatures of the soft and blown bitumen respectively. As is evident from Figure 7.14, the viscosity of the compounds increased up to 20 parts loading and subsequently decreased. The increase in viscosity could be attributed to the dissolution of LNR and the subsequent thickening. Decrease in viscosity above 20 parts may be due to limiting solubility and existence of free LNR in the mixture. On the other hand a gradually decreasing trend in viscosity was observed with increasing LNR content in blown bitumen irrespective of the loading. Considerable reduction was noticed above 10 parts.

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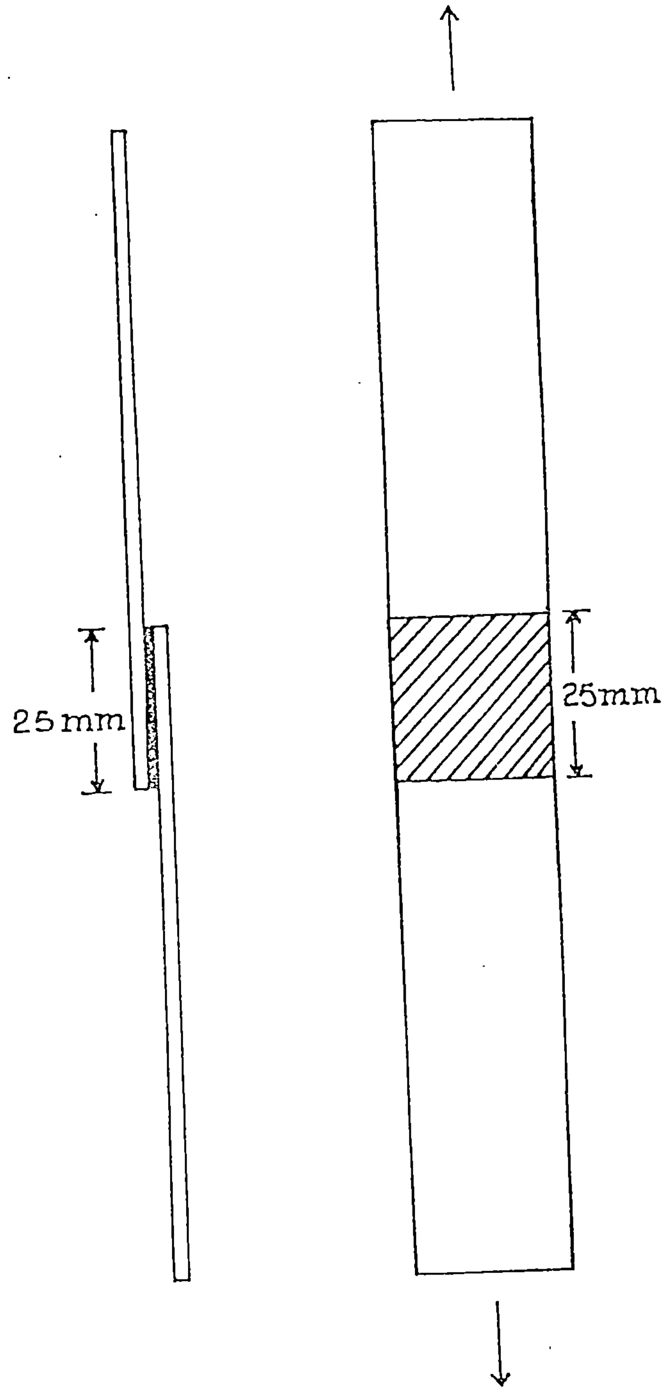

Fig. 7.1. Test samples for lap shear test

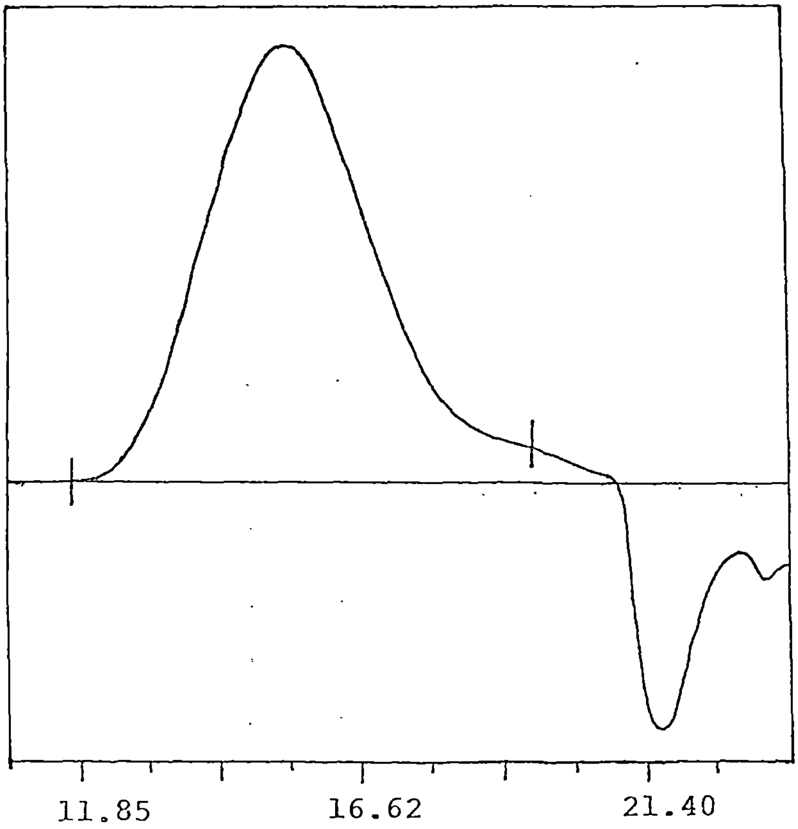

Fig. 7.2. GPC Chromatogram of LNR sample

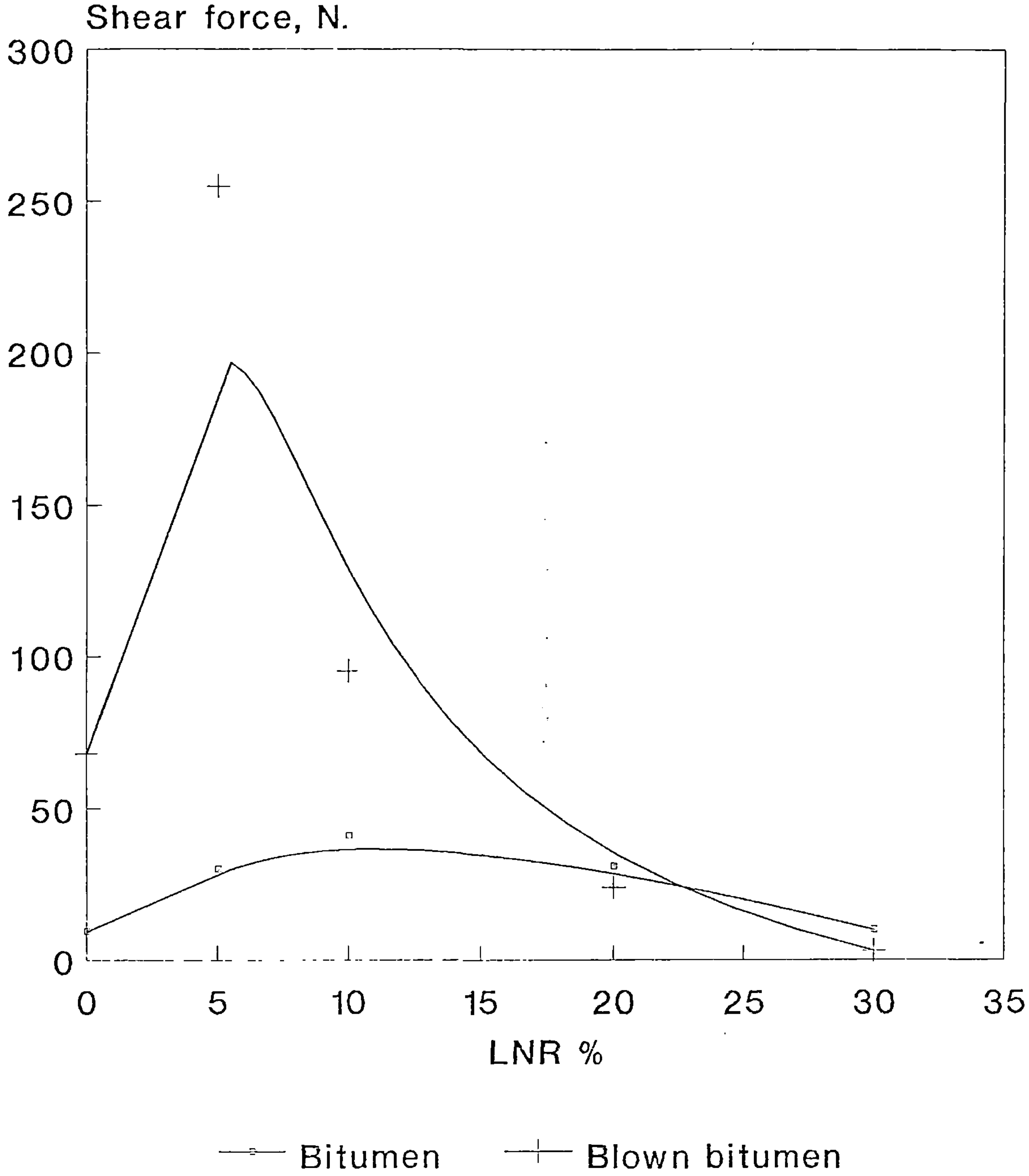

Fig. 7.3. Influence of LNR on shear strength

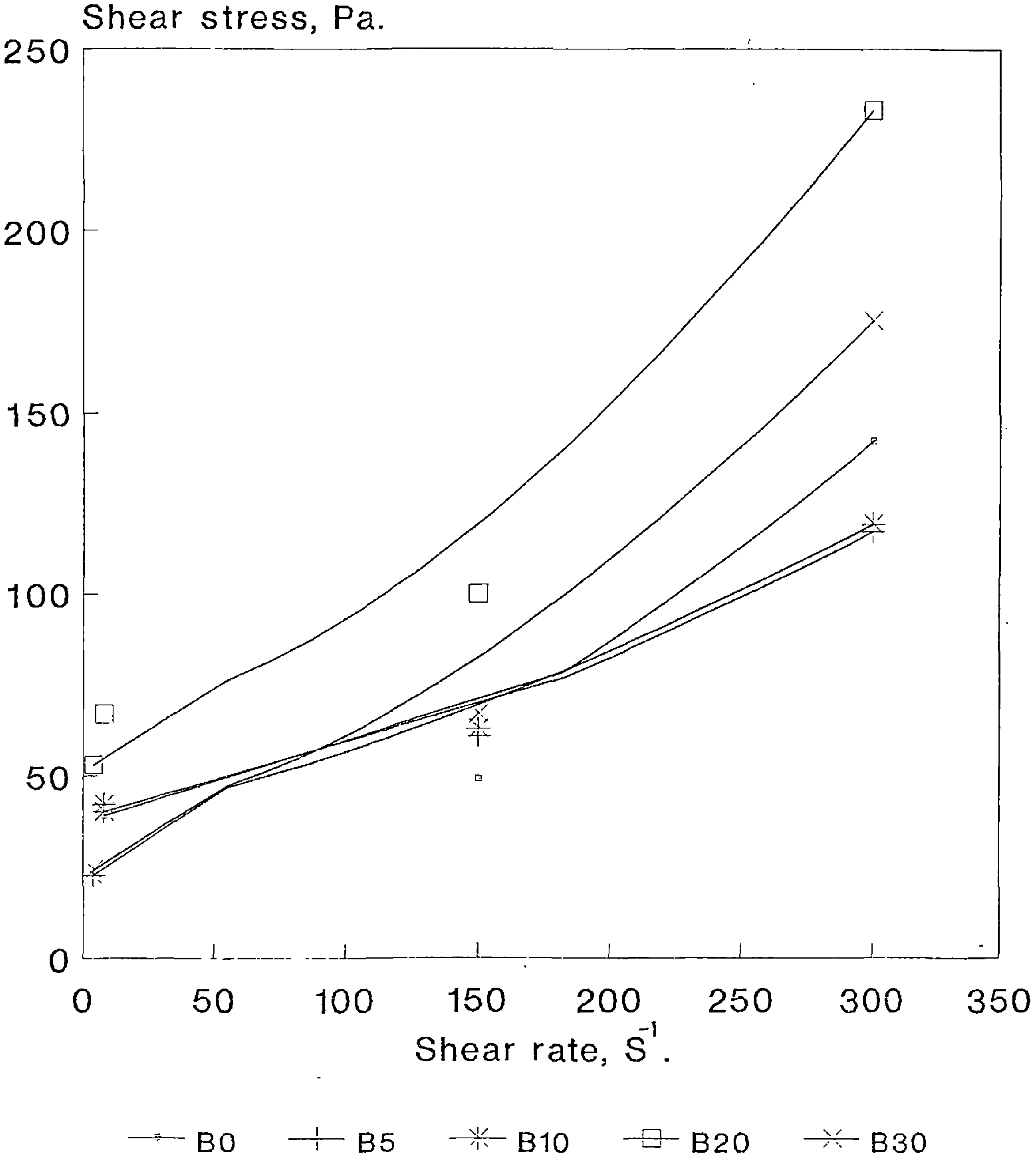

Fig. 7.4. Shear stress vs shear rate at 100 °C (B)

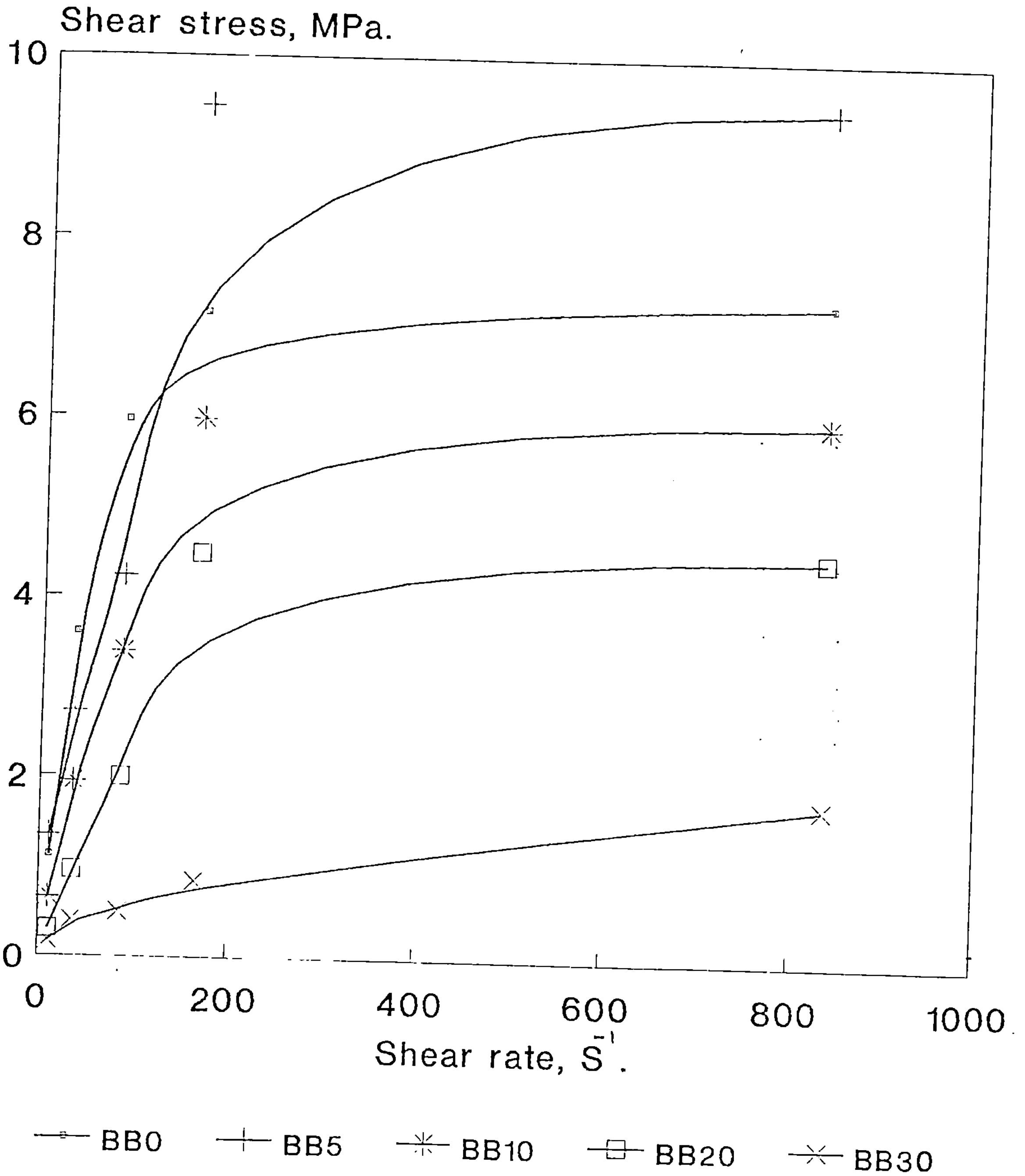

Fig. 7.5. Shear stress vs shear rate at 100 °C (BB)

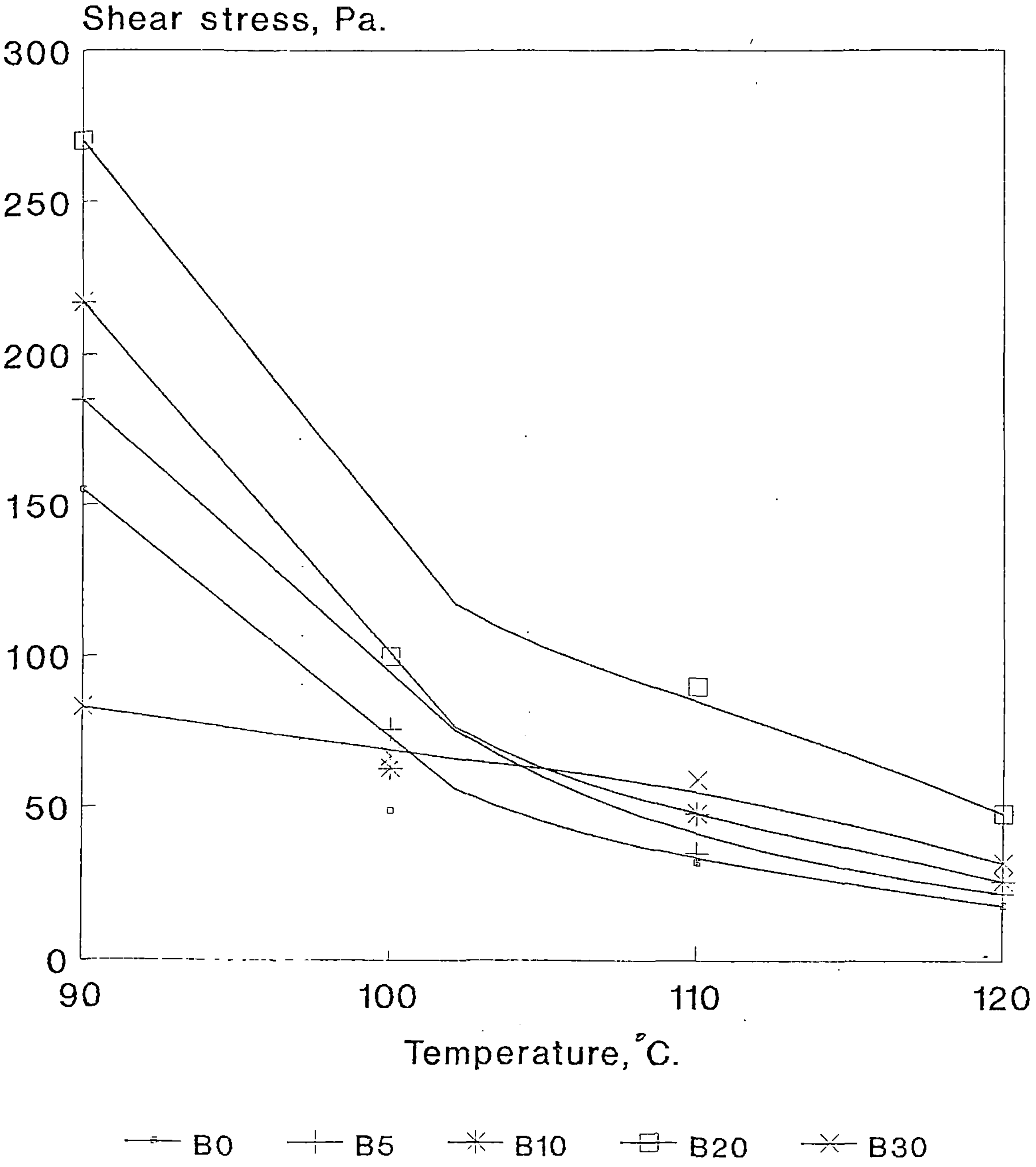

Fig. 7.6. Shear stress vs temperature at 15 s^{-1} (B)

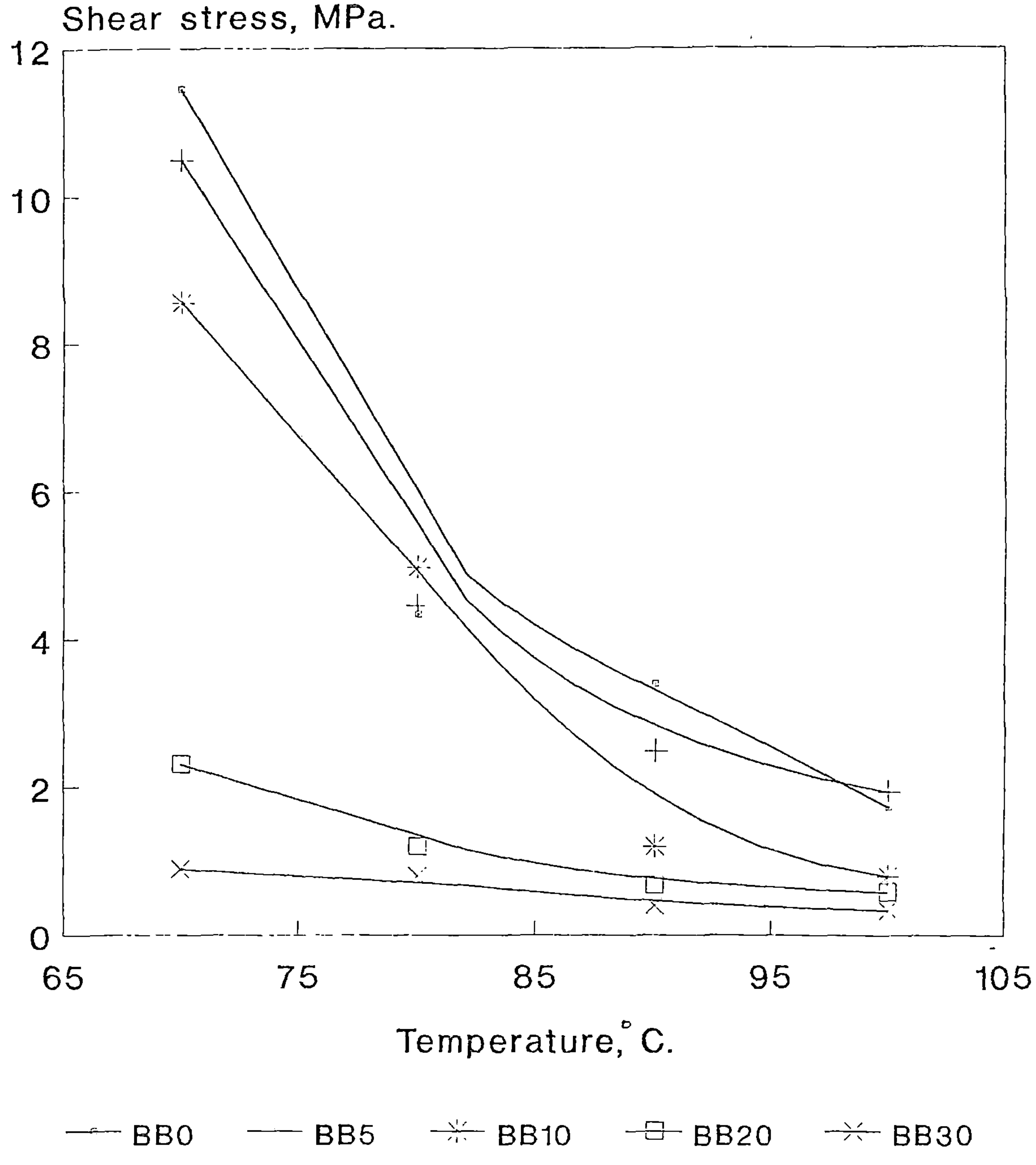

Fig. 7.7. Shear stress vs temperature at 16.6 s^{-1} (BB)

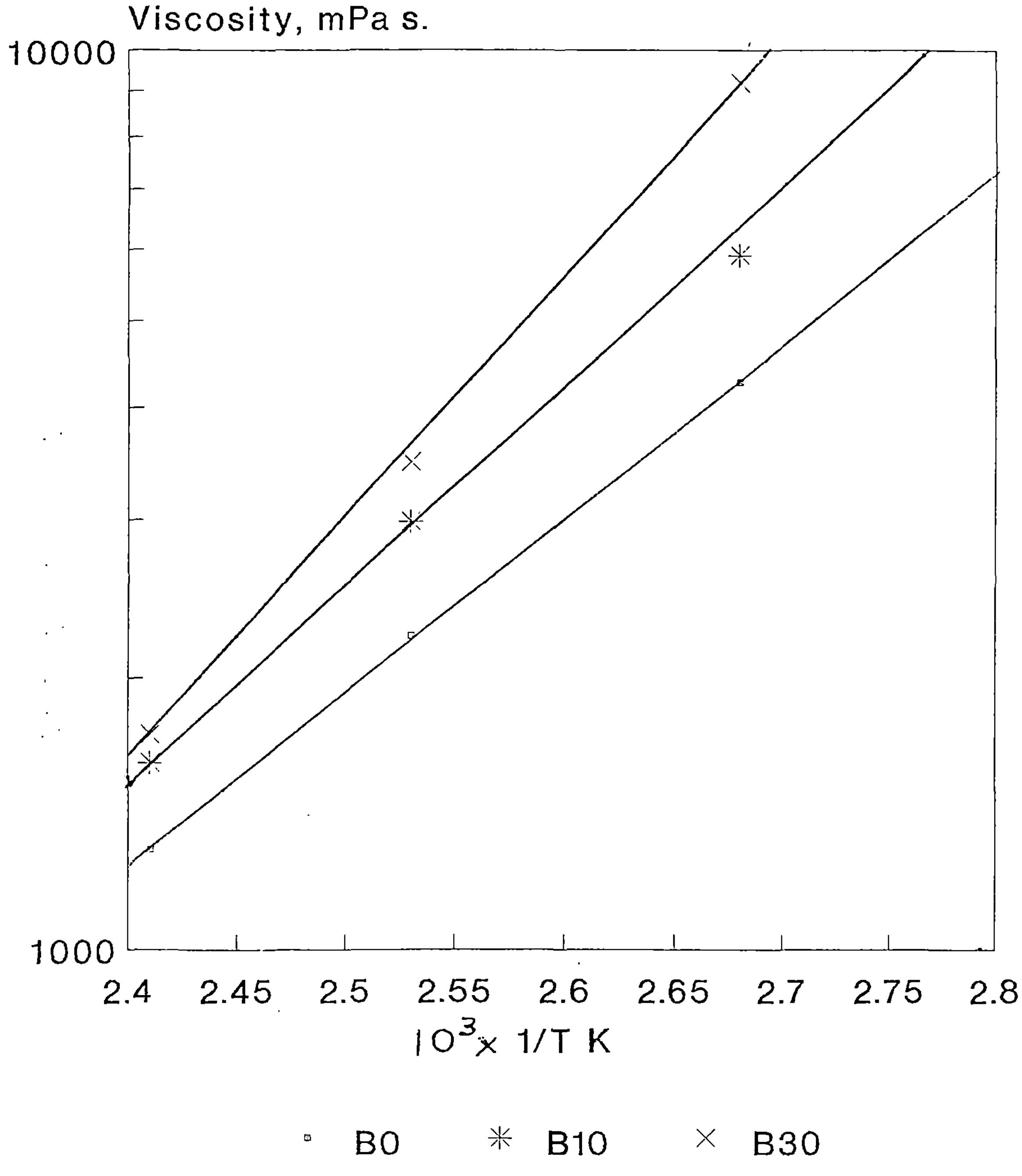

Fig. 7.8. Viscosity vs 1/T K (B)

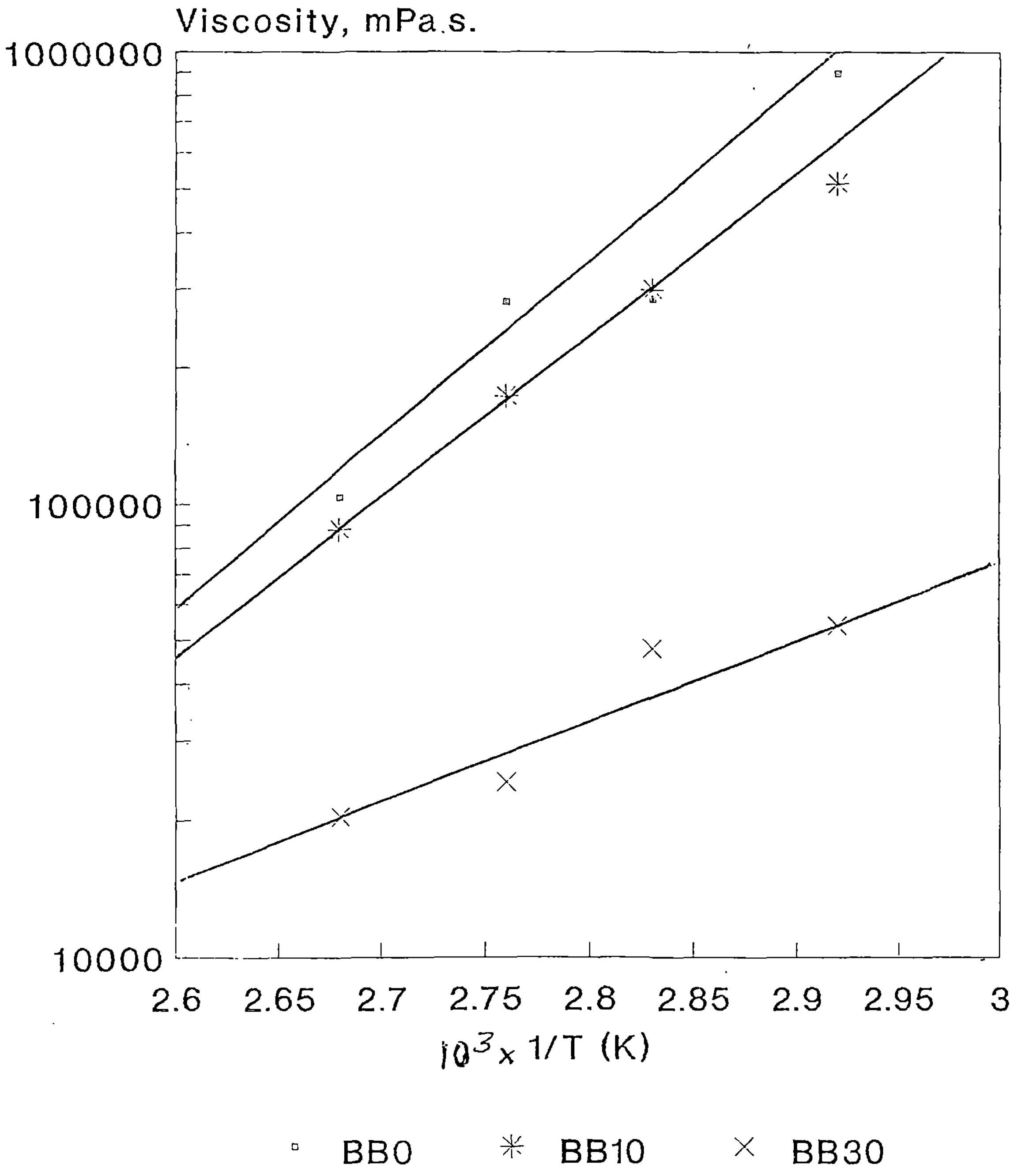

Fig. 7.9. viscosity vs 1/T K (BB)

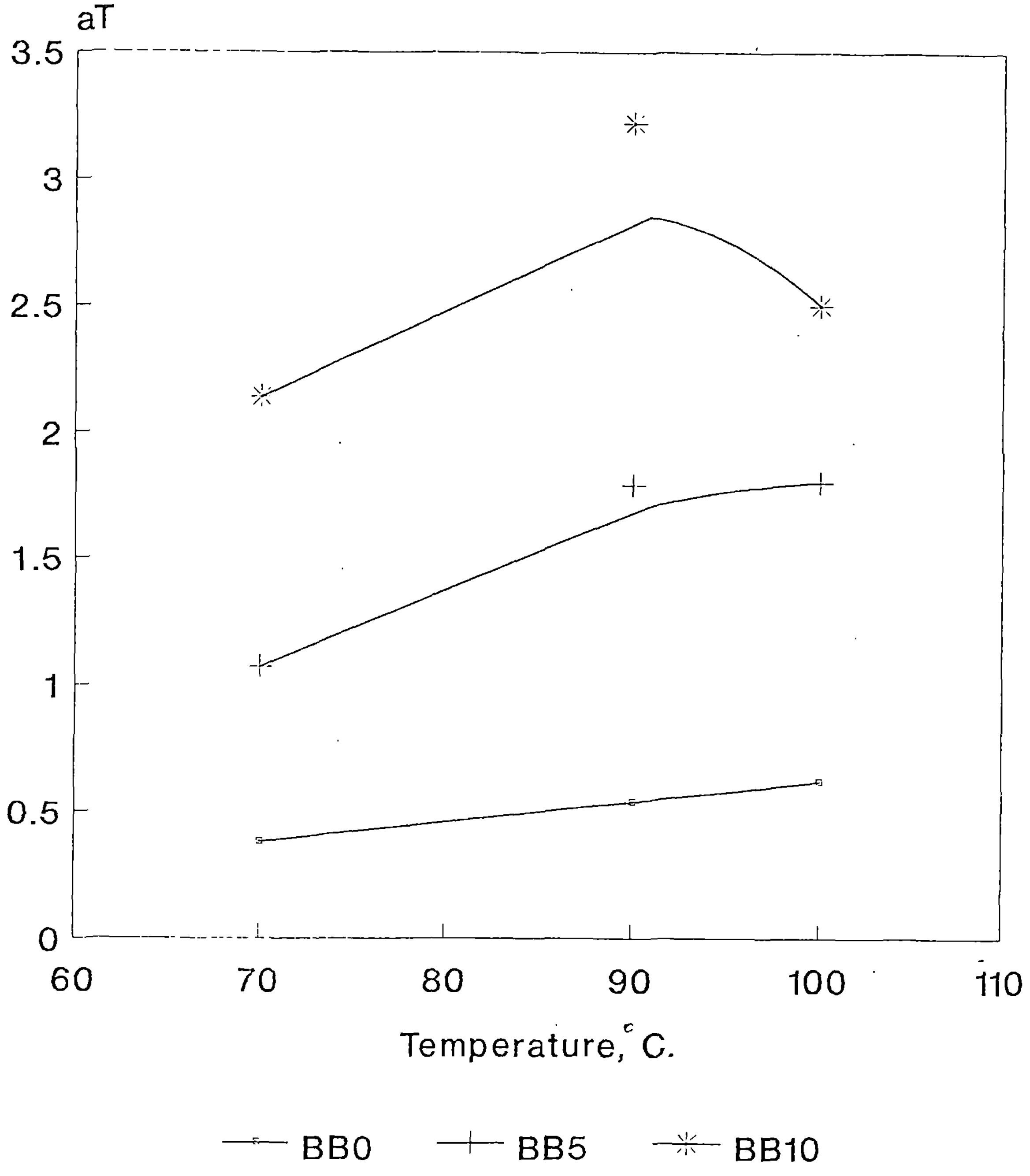

Fig. 7.10. Shift factor vs temperature

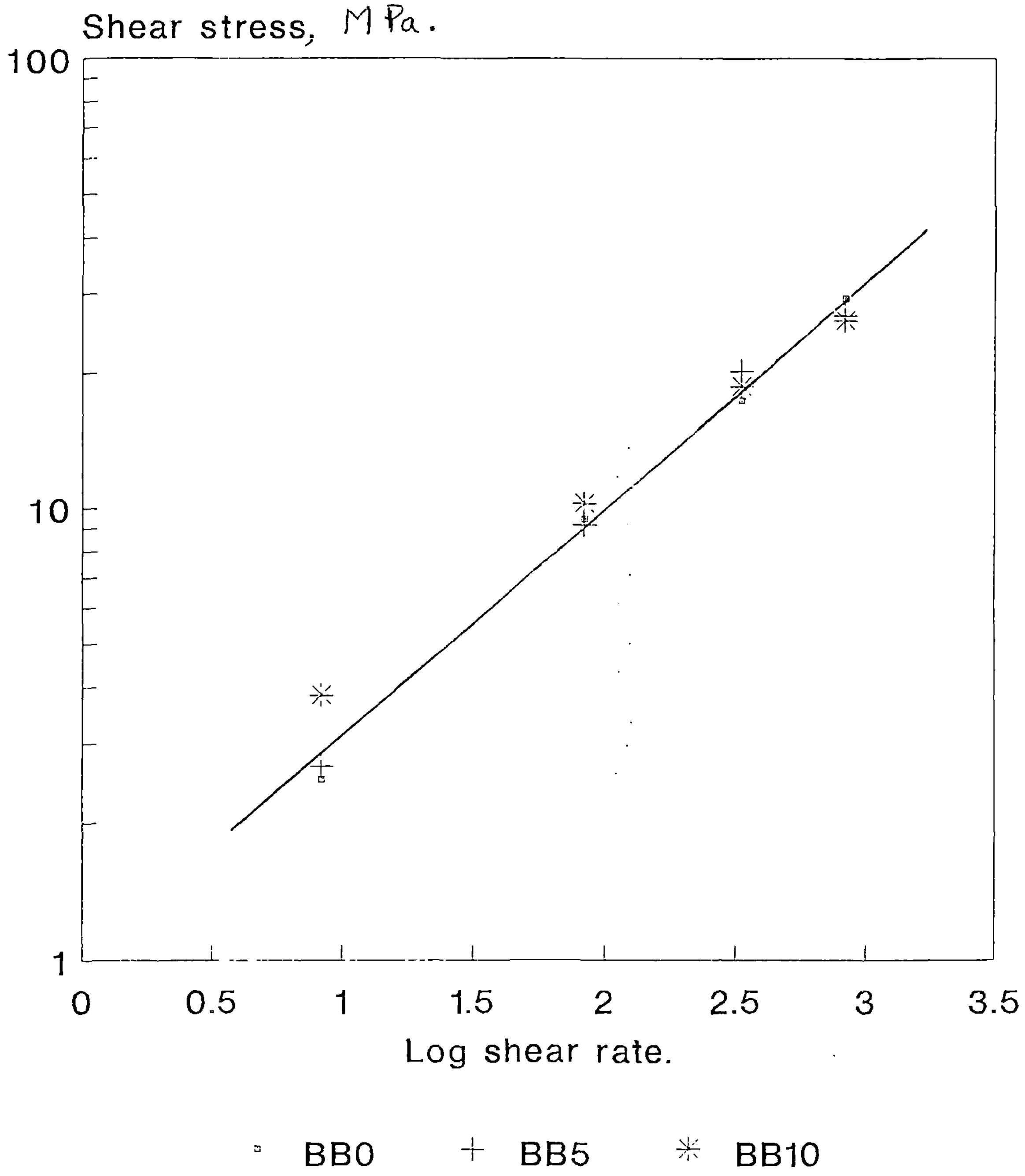

Fig. 7.11. Suerposition maser curve

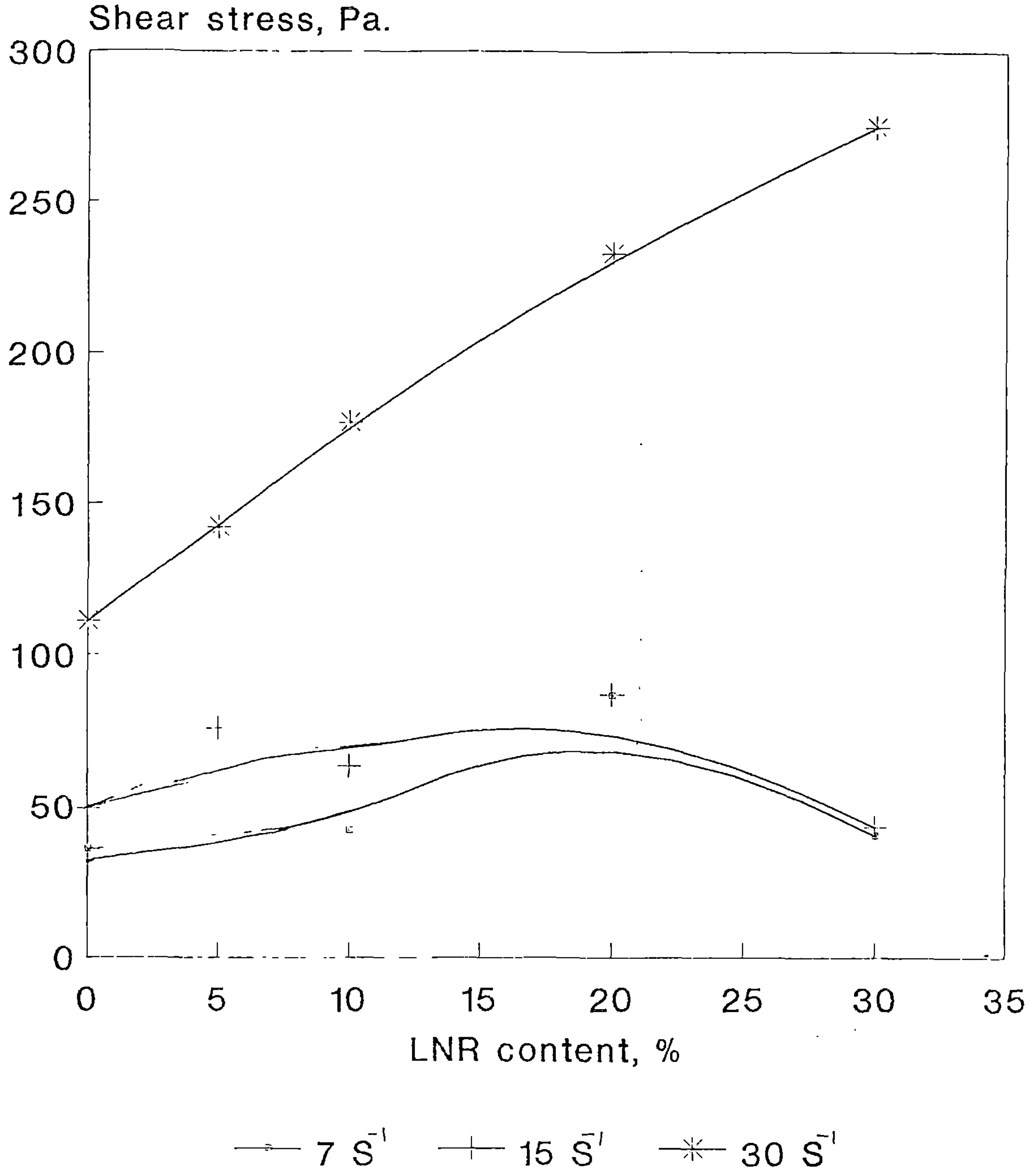

Fig. 7.12. Effect of LNR on shear stress at 100 °C (B)

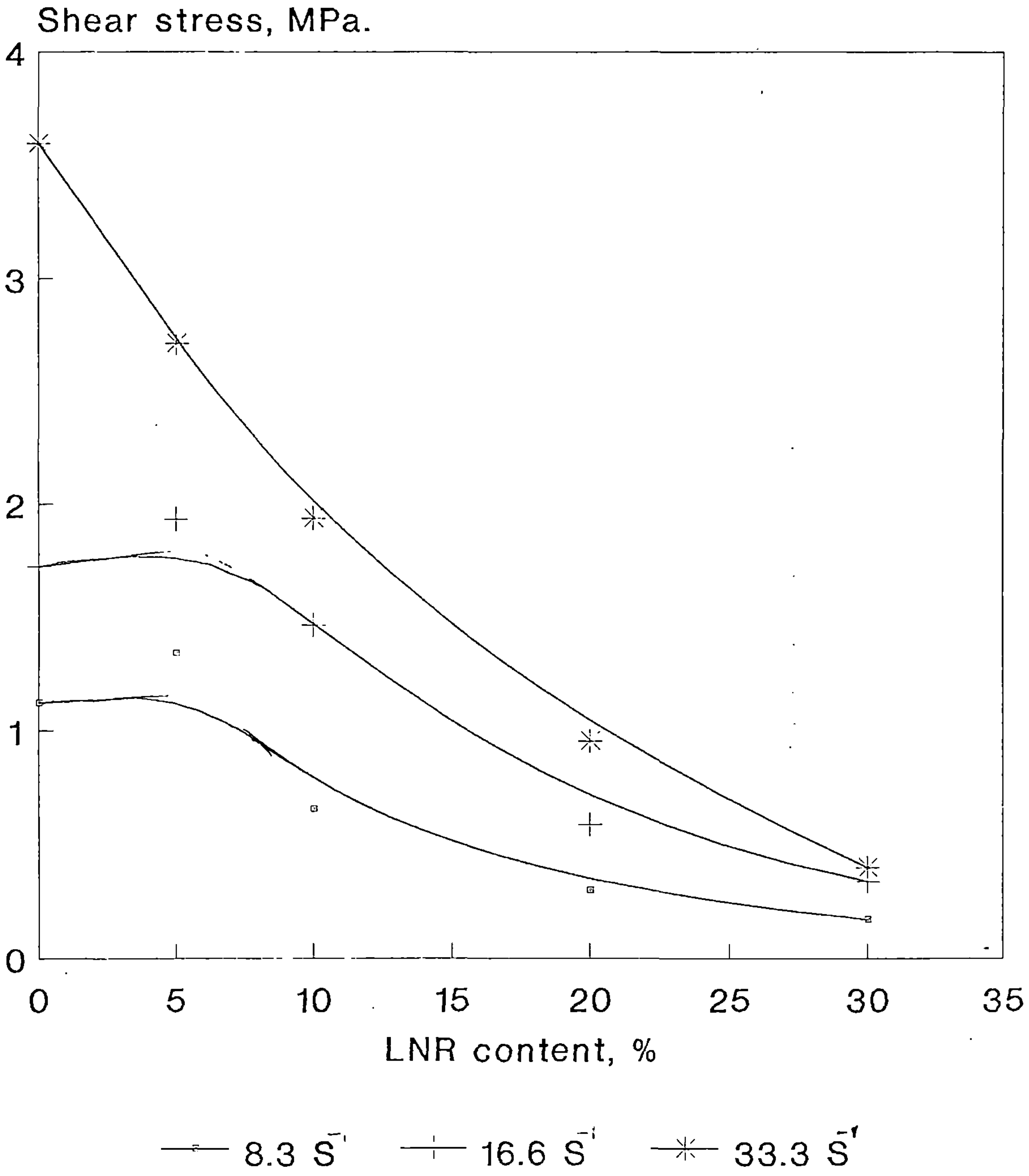

Fig. 7.13. Effect of LNR on shear stress at 100 °C (BB)

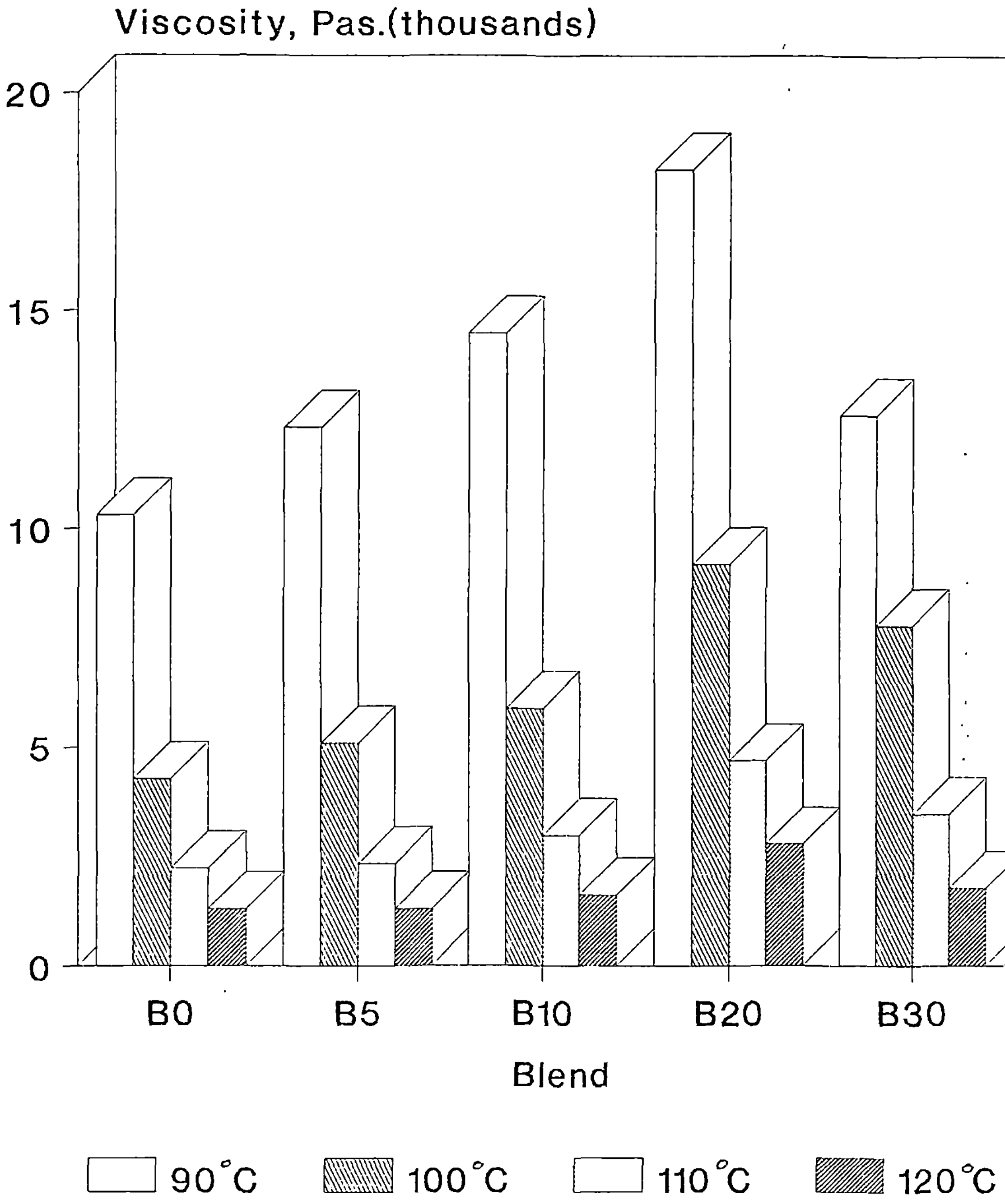

Fig. 7.14. Effect of LNR on Viscosity of soft bitumen (15 s-1)

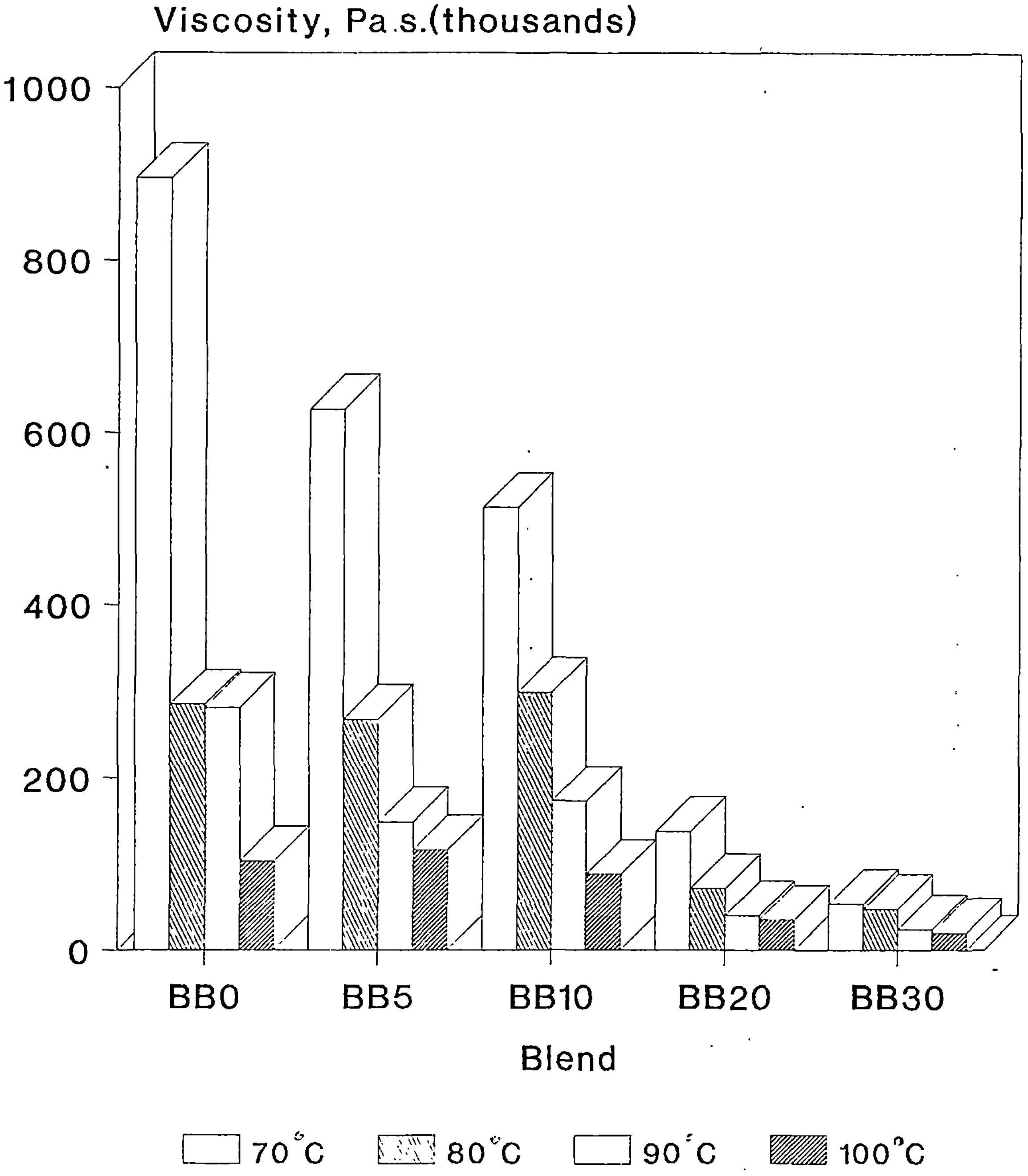

Fig. 7.15. Effect of LNR on viscosity of blown bitumen (16.6 s-1)

Chapter 8.

FLAMMABILITY AND THERMAL PROPERTIES OF PHOSPHORUS MODIFIED LIQUID NATURAL RUBBER

he results of this chapter have been published in the Journal of Applied Polymer Science,

ol. 52, 1309-1316 (1994)

8.1. INTRODUCTION

Polymeric materials are today a part and parcel of everyday life. The risk and damage incurred by fire in which polymers are involved are great, considering modern way of construction of multistorey buildings for various functions, the use of modern means of transportation etc. All these involve the risk of high rate of occupancy and difficulty in speedy evacuation of people from the zone, if critical situation arises. Rubber and plastic components are generally prone to high rates of flammability and propagation of flame being derived from hydrocarbons. Unlike thermoplastics, rubber compounds are composites containing a variety of ingredients like curing agents, fillers, process aids and special additives capable of imparting certain specific properties. Selection and addition of a new material into the system is to be carefully carried out so as to have minimum changes to other properties.

8.1.1. Flammability

Combustion is a fast reduction-oxidation process usually accompanied by flame and light. Combustion of standard polymeric materials is considered as a reaction between the combustible polymeric compound and atmospheric oxygen. The polymer is in the condensed state and the oxidant is a gas. The reaction is in between substances in different phases and therefore, heterogeneous. Such reactions take place on the condensed phase. The dynamics of heterogeneous reactions depend on the rate of supply of the gaseous reactant to the surface and removal of reaction products from the surface. Depending on whether the rate of oxygen supply is lower than the reaction of oxygen with the polymer compound, the heterogeneous reaction is either activation or diffusion controlled.

8.1.2. Ignition phenomena.

Combustion is always preceded by a situation promoting its origination. Essentially this unsteady process called ignition arises from conditions in the system which causes self acceleration of oxidation. This may be caused by progressive accumulation of heat or by active particles initiating a chain of oxidation reactions. Heat generation is the dominant factor responsible for polymer ignition. Heat build-up depends on the heat exchange between the reactants and the environment. Heat build-up rate is proportional to the oxidation rate which increases exponentially with temperature[1] according to the Arrhenius law

$$q = H\,Ko\,\exp(-E/RT)\,Yox \quad \text{-------------} \qquad (8.1)$$

where q is the amount of heat produced per unit surface area per unit time, H is the enthalpy of reaction, Ko the pre-exponential factor, Yox the concentration of the oxidant and E the activation energy. The heat removal q_L is proportional to the temperature difference between the reaction zone (T) and the ambient medium ($T\alpha$) to which heat is transferred.

$$qL = \alpha\,(T - T\alpha) \quad \text{----------------------} \qquad (8.2)$$

where α is the coefficient of heat transfer. Choice of ignition criterion is one of the most difficult problems in the study of ignition in condensed systems. Transition to steady combustion is an asymptotical process and the moment of ignition is mathematically an indeterminate value.

8.1.3. Propagation

Most of the theoretical work reported have actually been concerned with the flame propagation behaviour as function of thermophysical and physical characteristics of the polymer material and environment (pressure, temperature, oxygen concentration, sample orientation, shape and size etc.) The mechanism of heat transfer from combustion zone to "fresh" layer of the polymer is important in quantitative measure of combustion propagation in space. The linear velocity of combustion propagation (v) may be represented in terms of ignition temperature concept (T_{ign}) by the fundamental formula

$$q_v H = q_s \quad \text{-------------} \quad (8.3)$$

where H is the difference in fuel enthalpies at the ignition and initial temperature. $H = C_p (T_{ign} - T_o)$ and q_s the heat flux transferred from the reaction zone to a fresh surface with initial temperature T_o. As oxygen concentration (in a $O_2 + N_2$ mixture) increases, the flame temperature increases. This causes an increase in heat flux to the polymer surface and flame speed rate. It has been found that the combustion velocity depends on thermal effects, kinetic parameters of exothermic oxidation reaction, and on the rate of oxygen supply to the surface of the condensed phase. Hence, the incoming oxidant flow velocity and oxygen concentration in the flow are important. The thicker the layer of combustible material, the lower the propagation rate of a heterogeneous combustion process.

8.1.4. Extinction of polymer combustion

The investigations of critical conditions of polymer combustion is important in the theory of flame retarding as well as for practical reduction of flammability of materials, for fire prevention and extinction. Combustion is an integral process and critical conditions of combustion are closely associated to the ratio of heat transfer to and from the leading zone of combustion reaction. Three important parameters in this process are chemical reaction, mass transfer and heat transfer. Various external factors such as temperature, pressure, environment, oxidant flow rate, etc. affect primarily the rates of the above three parameters. The extinction of combustion occurs in the range where the rate of chemical reaction and transport process are commensurate or the latter becomes much lower than the former. The extinction limit is sensitive to environmental variations.

8.1.5. Phosphorus containing flame retardants

Phosphorus modified polymers are gaining importance in the use of flame retardant applications due to less toxic combustion products. Polymers based principally on phosphorus containing components are expensive and have, therefore, not attained much commercial significance. On the other hand, the modification of conventional polymers with small amounts of phosphorus comonomers or oligomers to impart flame retardancy or to improve flame retardancy has become commercially significant[2-6].

8.2. EXPERIMENTAL

The phosphorus modified liquid natural rubber was incorporated in a natural rubber formulation to study its effect on the properties of the compounds. Preparation of gum compounds without incorporation of filler for this study was difficult because of the excessive tackiness of the mixes containing ELNR and the phosphorus modified polymer. The filler used was HAF black. Influence of the modified polymer was studied by comparing the properties of the compounds that contained LNR, ELNR, and PELNR (phosphorus modified polymer). Phosphorus modified polymer prepared in bulk and in solution were used. A compound containing ELNR and dibutylphosphate added at the time of mill mixing, anticipating the reaction to happen at the time of vulcanization, was also prepared. A control compound without any additive was also prepared for comparison.

Formulations of the mixes are given in Table 8.1. The dosage of the additives were so chosen that the phosphorus content in the resultant vulcanizates was 1 percent. To achieve the above phosphorus content 13.3 phr of PELNR was added to the mix. Mix F contains ELNR and dibutylphosphate in stoichiometric quantities for the reaction and to provide one percent phosphorus content.

Table 8.2 Formulations of mixes.

Compound	A	B	C	D	E	F
Natural rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
High abrasion furnace black	35	35	35	35	35	35
N-tertiarybutyl 2-benzthiazole sulphenamide	0.7	0.7	0.7	0.7	0.7	0.7
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25
LNR	-	13.3	-	-	-	-
ELNR	-	-	13.3	-	-	13.3
PELNR (bulk)	-	-	-	25	-	-
PELNR (solution)	-	-	-	-	25	-
Dibutyl phosphate	-	-	-	-	-	11.3

8.3. RESULTS AND DISCUSSION

8.3.1. Properties of compounds

The processing parameters of the compounds are given in Table 8.2. The Mooney viscosity values showed a reducing trend with LNR and ELNR compounds in comparison with the control compound A. This may be attributed to their plasticising action. Similar effect was not noticed with compounds D and F while E showed a much higher viscosity. Epoxidation appears to have caused minor decrease in the plasticising action of LNR. The phosphorus modified compound had little influence on plasticity. The Mooney viscosities of the compounds were high indicating that phosphorus modification of ELNR remarkably reduces the plasticising action. With respect to cure characteristics, LNR and ELNR compounds were close to the control compound A, while a slowing down in the curing times was observed in the case of phosphorus modified LNR containing compounds. The retarding action was prominent for E but comparatively smaller for the compounds D and F. The cure rate index of the compound was considerably low. This may be due to the higher retarding effect of the solution modified polymer. Reduction was observed in the values of maximum torque. The rate of crosslinking of E was lowered as evidenced by the cure rate index values. The Tg values of the compound obtained from DSC measurements were in a close range.

Table 8.2. Properties of compounds

Properties	**A**	**B**	**C**	**D**	**E**	**F**
Mooney viscosity, $ML_{(1+4)}$ at 100 °C	34	26	28	39	58	37
Scorch time, t_{s2} at 150°C, min.	10	10.75	11.75	12	35	9
Cure time t_{90} at 150°C, min.	30.5	28.5	28.5	65	85	46
Max. torque, dNm	79	65	62	37	30	49
Cure rate index	86	85	86	68	16	57
Tg, °C	-61.8	-60.9	-62.3	-61.8	-61.7	-61.7

8.3.2. Vulcanizate properties

The vulcanizate properties of the compounds are given in Table 8.3. A general decrease in tensile strength was observed in the case of compounds containing the phosphorus modified polymers, with a maximum reduction for the compound E.

Table 8.3. Vulcanizate properties.

Properties	A	B	C	D	E	F
Tensile strength, MPa	30.0	28.1	27.1	11.8	7.16	13.2
Elongation at break, %	527	600	590	514	473	472
Modulus at 100% elongation, MPa	2.01	1.68	1.81	1.55	1.56	2.10
Modulus at 200% elongation, MPa	4.53	3.86	3.95	3.38	2.62	3.95
Modulus at 300% elongation, MPa	8.94	7.63	7.47	5.46	4.11	6.51
Hardness, Shore A	59	57	58	57	58	61
Tear strength, N/mm	65.5	61.0	76.8	35.5	25.6	35.0

Among the phosphorus modified compounds, F showed the highest value. Remarkable changes were not observed in the case of elongation values. So is the case with modulus at 100, 200 and 300 percent elongations. Hardness, Shore A measured on the samples are in the range of 57 to 61, the highest being for the compound F with the reactants added on the mixing mill. This may be due to the more effective establishment of crosslinks by the phosphorus atoms and polymer molecules during the course of reaction *in-situ*. In the case of compound C containing ELNR, a remarkable improvement in tear strength was observed.

8.3.3. Thermogravimetric studies

Analysis of the samples was conducted in standard air and oxygen. Figures 8.1. to 8.6. show the thermograms of the compounds A to F respectively in air. The measurements of weight loss as a function of temperature or time represents the thermal stability of materials. Compounds in air suffered a remarkable weight loss in the temperature range 300 to 400°C. This may be attributed to the burning of hydrocarbon and formation of charred mass. A further reduction due to burning of char was noticed in the temperature range of 650 to 700°C. In presence of oxygen also two transitions are recorded and the corresponding thermograms are given in Figures 8.7. to 8.12. In the oxygen environment, the transitions were sharp and were noticed at 375 and 500°C for compounds without phosphorus. For phosphorus containing compounds the transition at 375°C was the same but the second change was found at 575°C. This showed the improvement imparted by the phosphorus modified polymer. Various chemical agents (gas phase inhibitors) are available for retarding polymer combustion. Halogen containing compounds used as flame retardants either decompose in the condensed phase or evaporarate and decay in the gas phase. Introduction of phosphorus-containing fragments into polymeric molecules affect the decomposition process to a high degree. The phosphorus-containing compounds affect combustion both in condensed and gas phase. The flame retardancy effect is due to its activity in the condensed phase[7]. Though TGA studies predict thermal stability of materials, physical properties like mechanical strength need to be related to weight loss data[8-10] before predictions are made regarding stability and service life of components. Halogen compounds are believed to function as flame retardants in the vapour phase of the flame zone of a burning polymer by inhibiting radical propagation while phosphorus compounds are believed to function in the condensed or plastic phase by forming a surface char or glass[11]. The delayed burning of char in the case of compounds D, E and F is in agreement with this.

8.3.4. Burning behaviour

The flammablity behaviours of the samples were studied by measuring the time of burning in oxidants with varying oxygen content using a Limiting Oxygen Index apparatus. The results are given in Table 8.4. Burning properties of the compounds A, B and C without phosphorus were comparable. However, a small increase in burning time for LNR and ELNR compounds was noticed.

Table 8.4. Burning time of the samples, sec.

% of oxygen	A	B	C	D	E	F
21	80	84.5	86	102	101	103
19.5	102	106	108	138	137	139
19	123	125	128	180	175	178
18.5	164	166	170	187	190	195
18	180	190	192	230	225	230
17.5	217	219	218	270	280	extinguished

The compounds D, E and F with phosphorus showed similar burning behaviour. the differences in burning times noticed between phosphorus containing and the phosphorus free compounds were significant and showed the same trend at all levels of oxygen percentage. Figure 8.13. shows the flame length of the compounds at various concentrations of oxygen. The test was conducted from 21 to 17.5 percent of oxygen where the sample F was found self extinguishing. In general it could be inferred that phosphorus modification of LNR decreased the flammability of the compounds. LNR and ELNR compounds had comparable properties with that of the control compound. The modified polymers formed in solution and *in-situ* were found superior.

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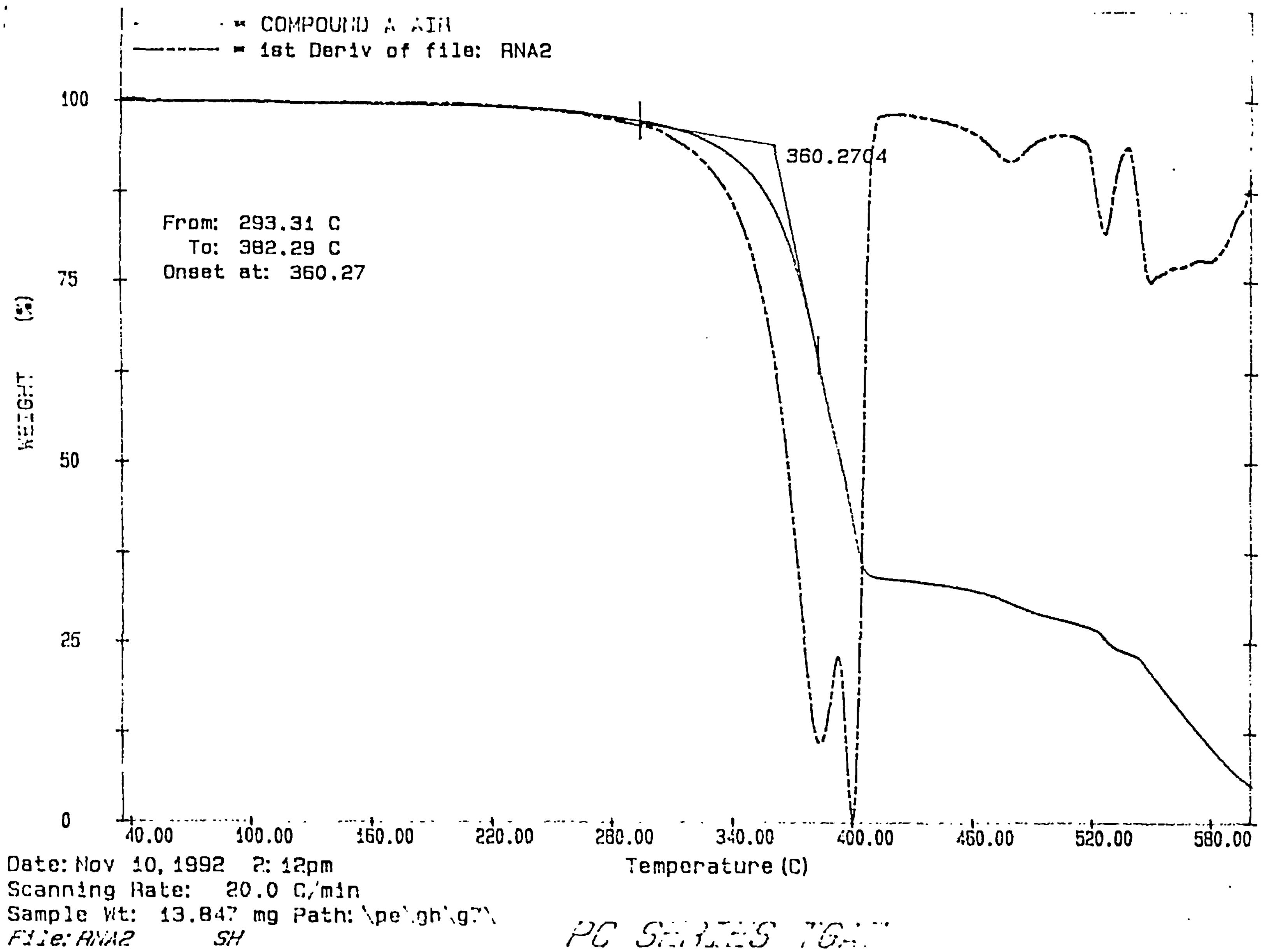

Fig. 8.1. TGA Thermogram of compound A in air.

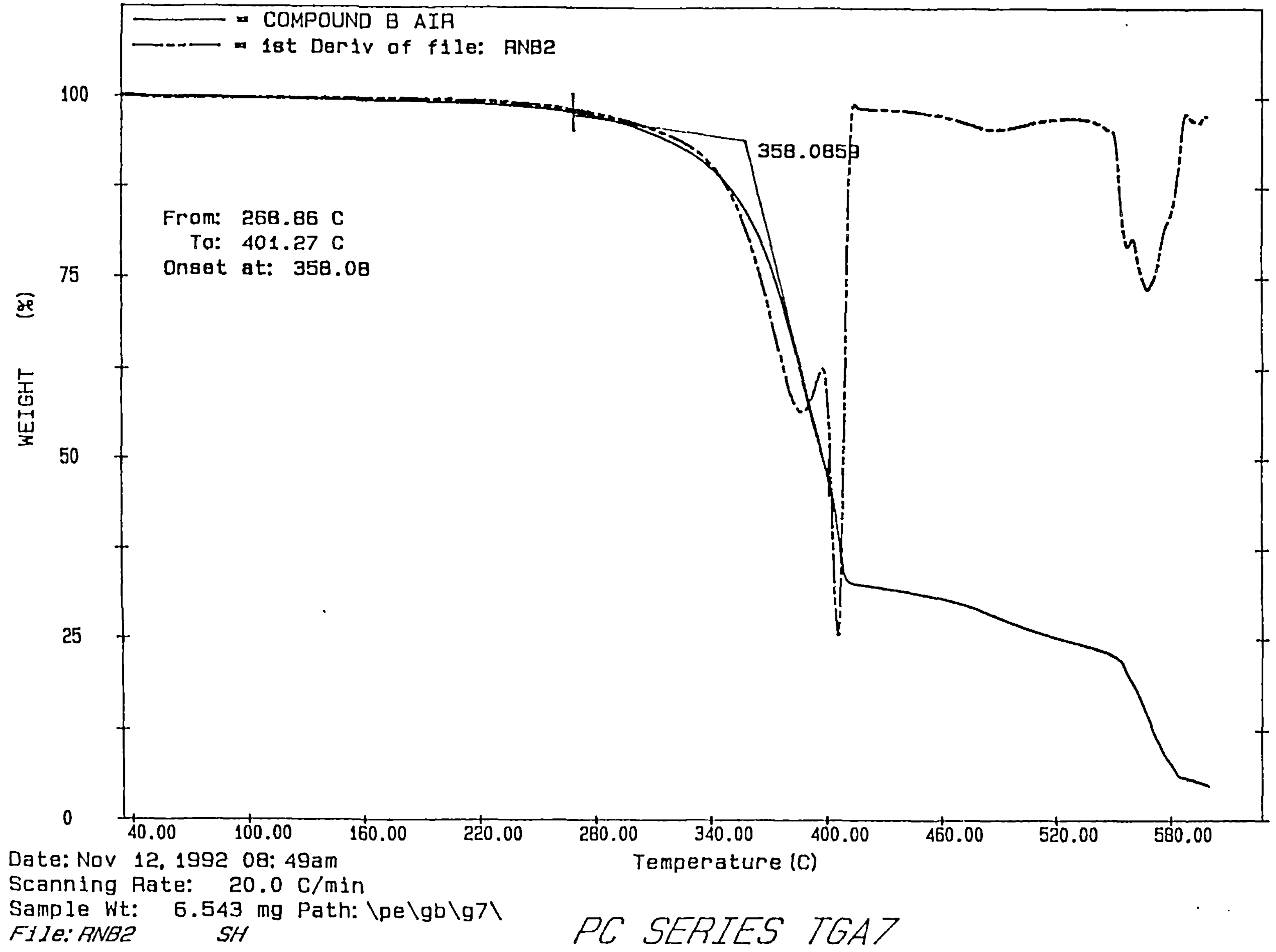

Fig. 8.2. TGA Thermogram of compound B in air.

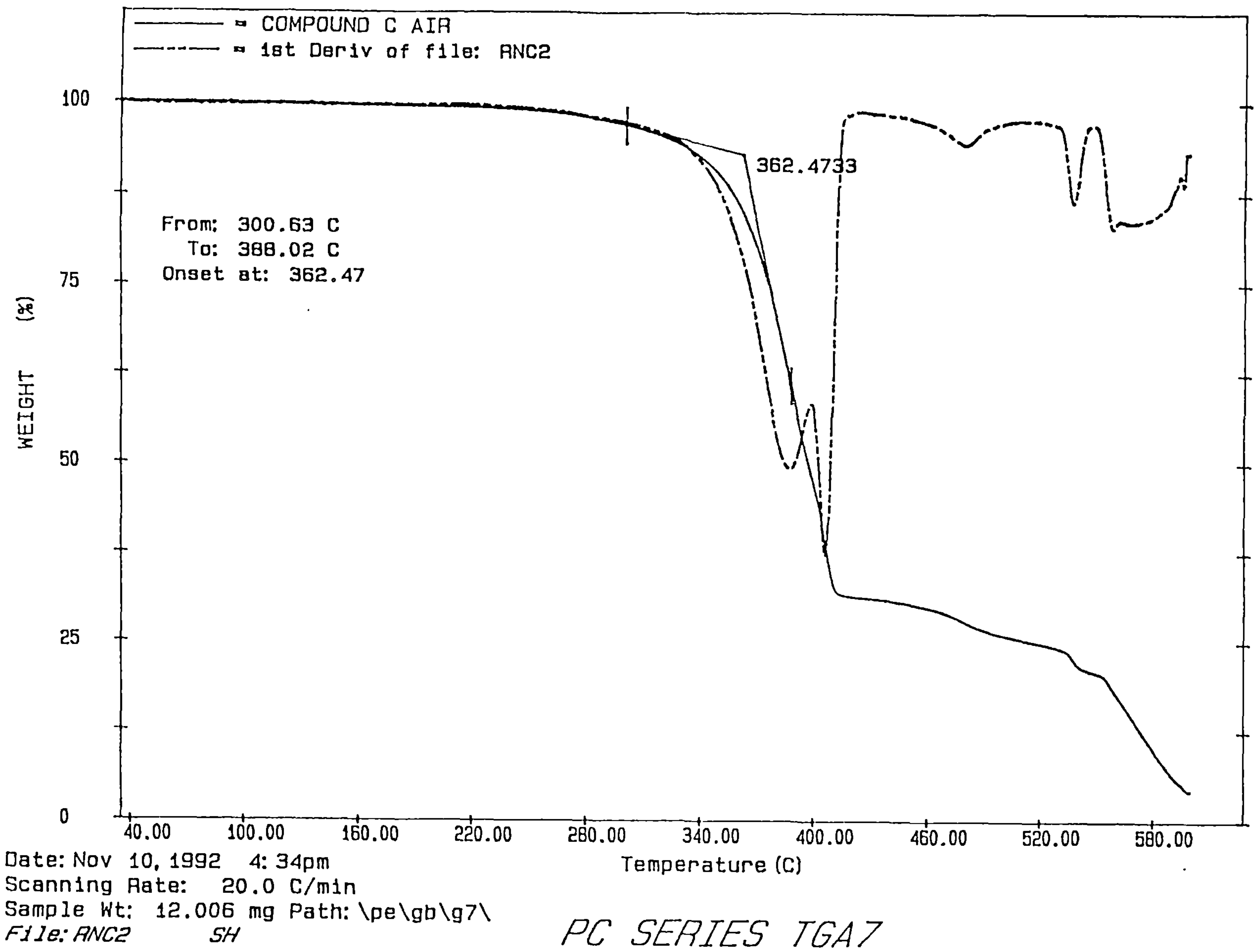

Fig. 8.3. TGA Thermogram of compound C in air.

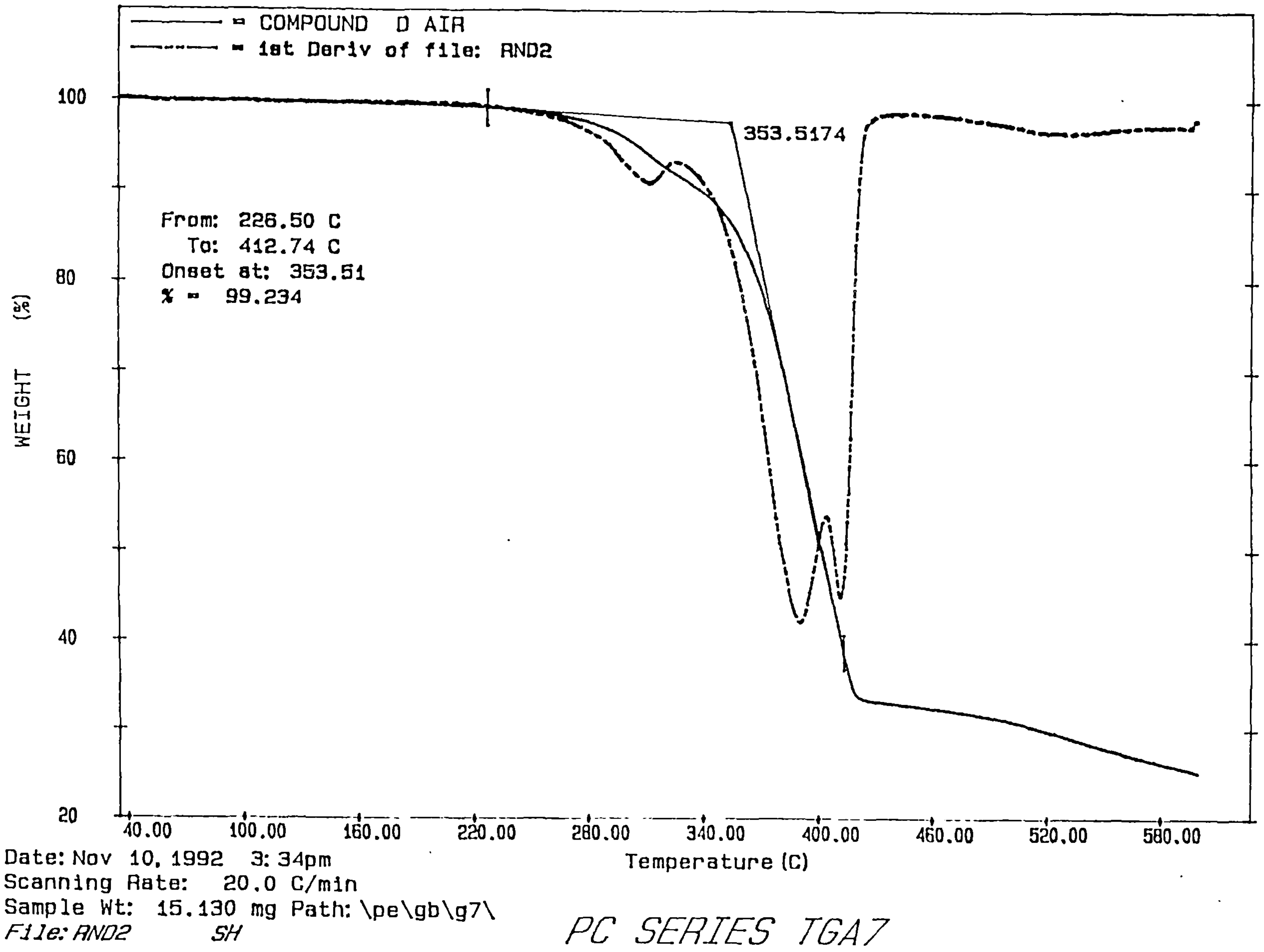

Fig. 8.4. TGA Thermogram of compound D in air.

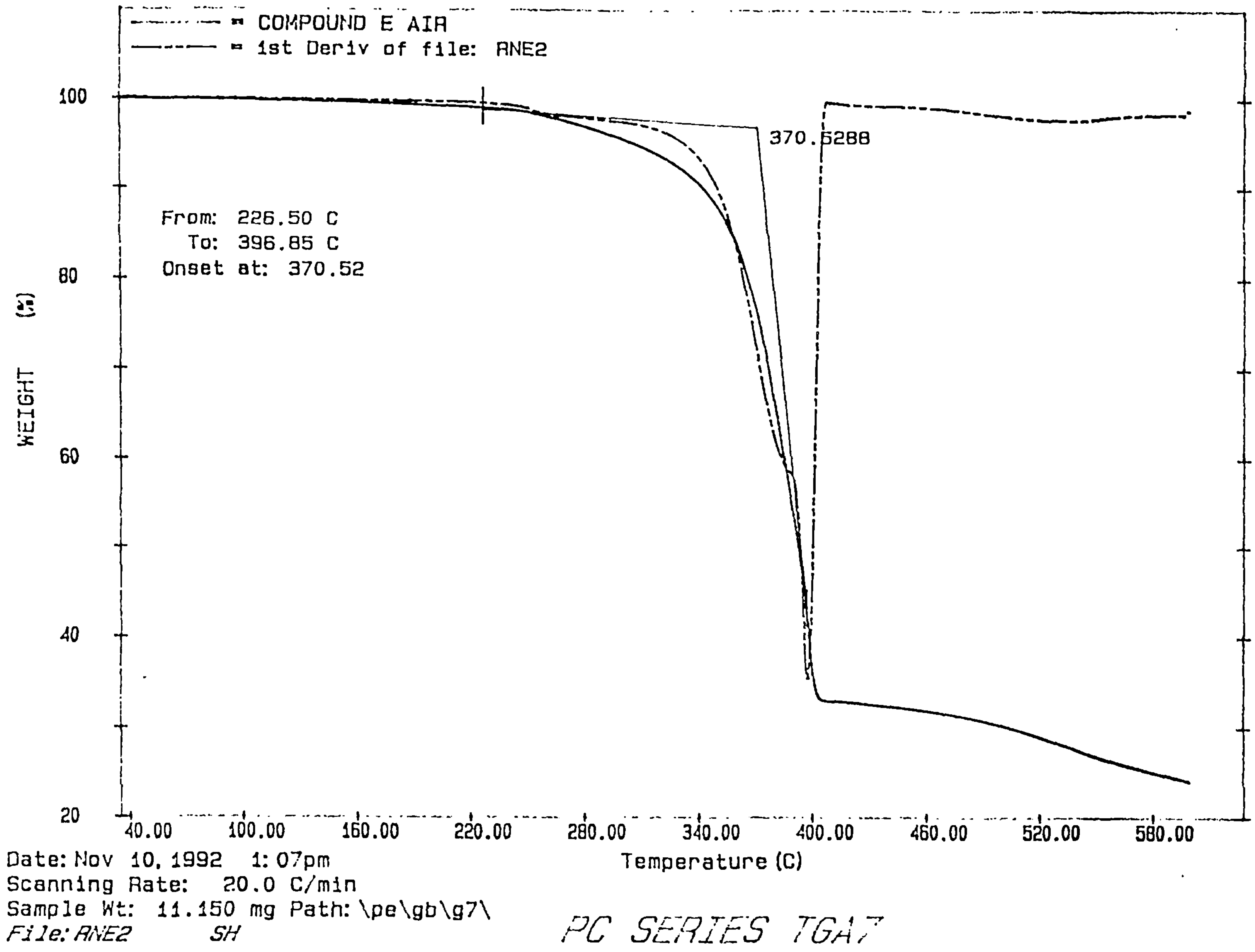

Fig. 8.5. TGA Thermogram of compound E in air.

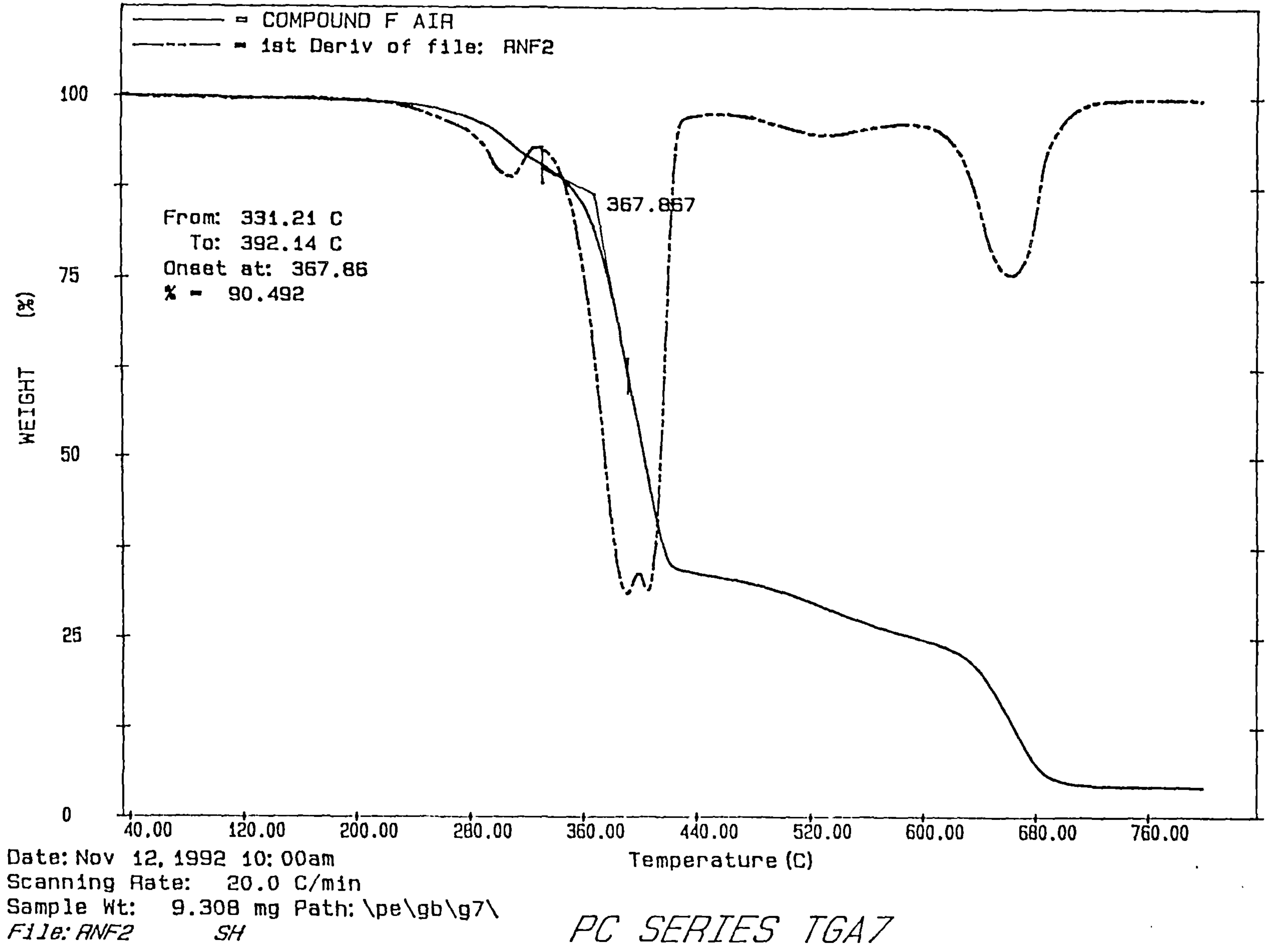

Fig. 8.6. TGA Thermogram of compound F in air.

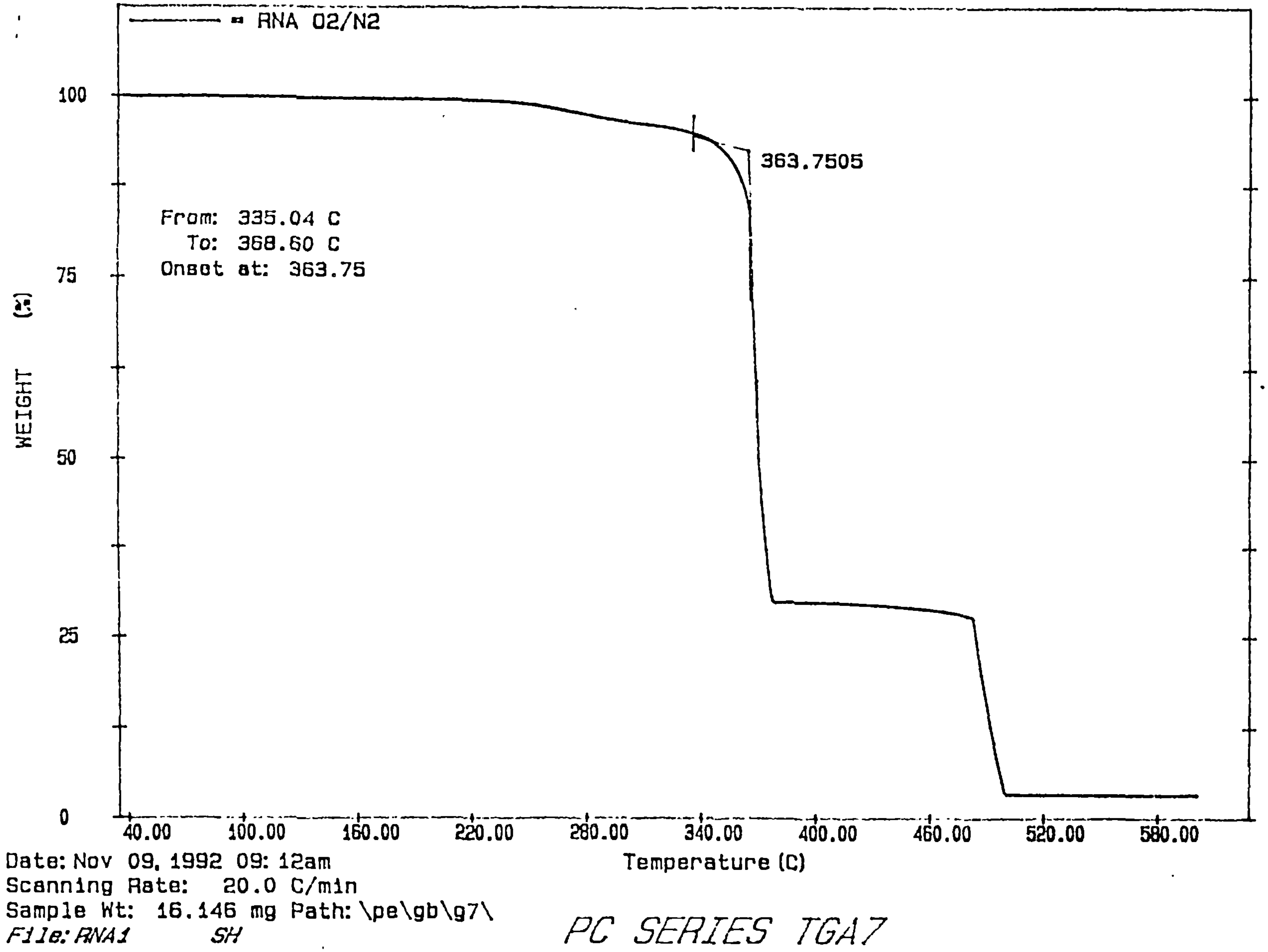

Fig. 8.7. TGA Thermogram of compound A in oxygen.

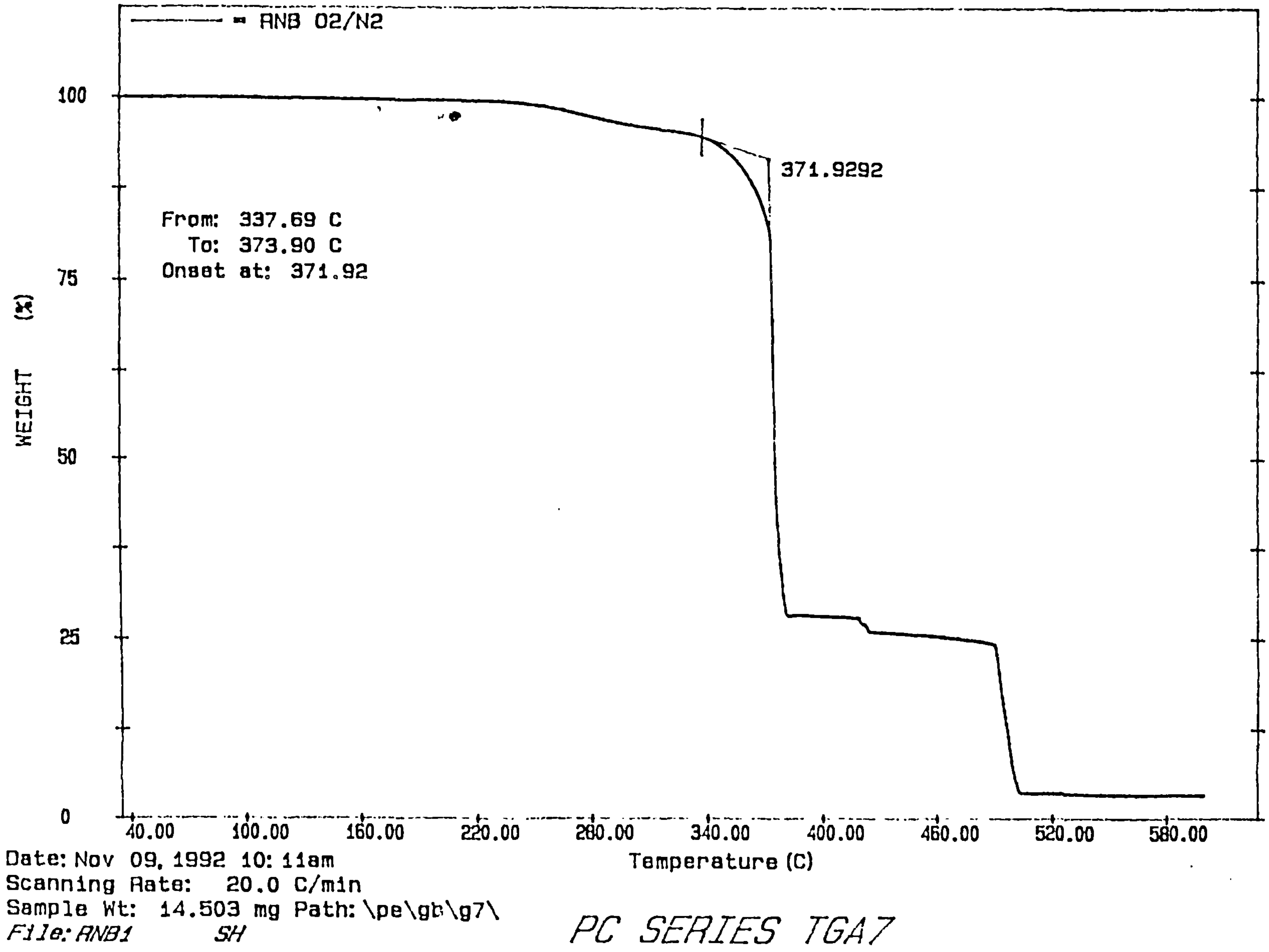

Fig. 8.8. TGA Thermogram of compound B in oxygen.

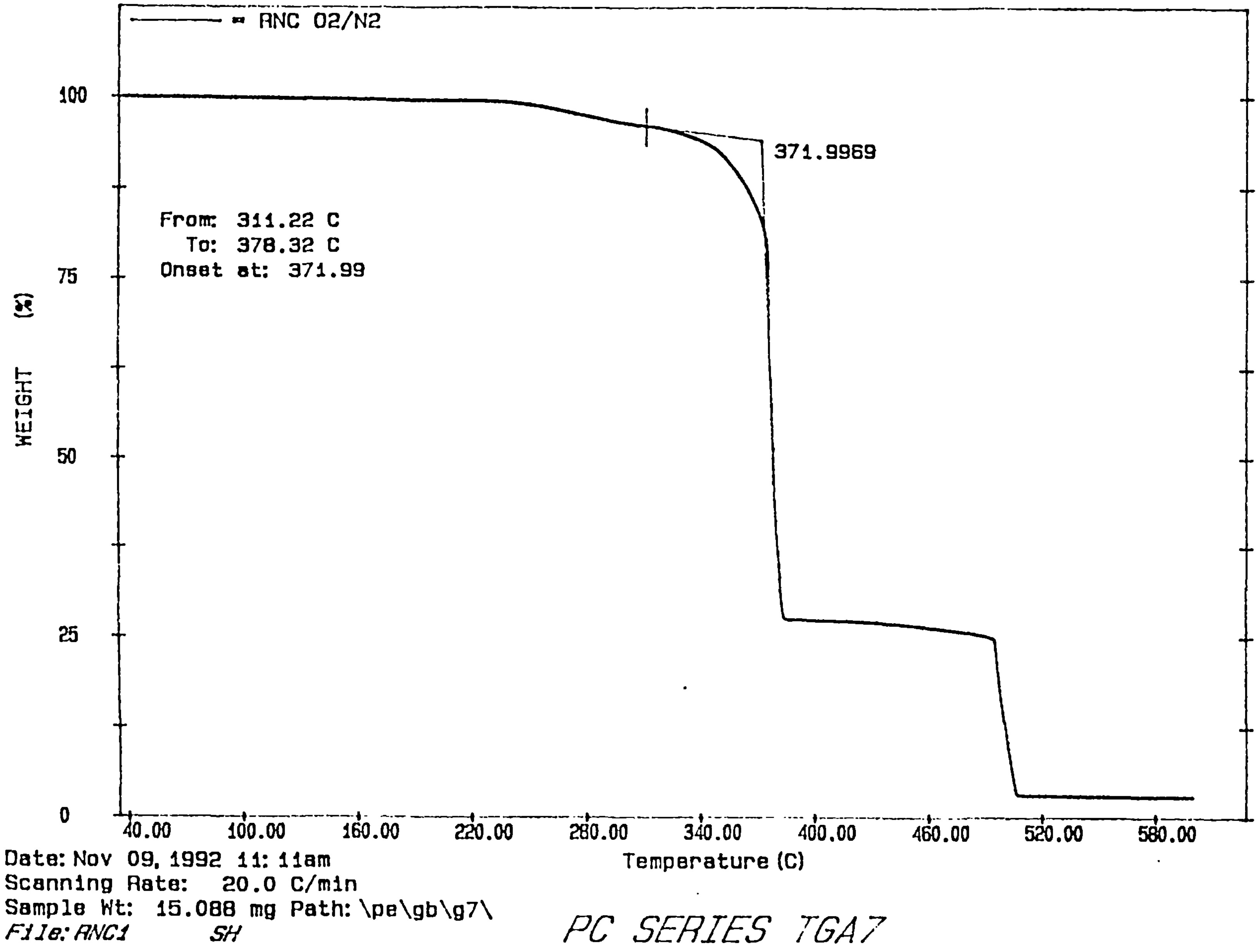

Fig. 8.9. TGA Thermogram of compound C in oxygen.

exp.

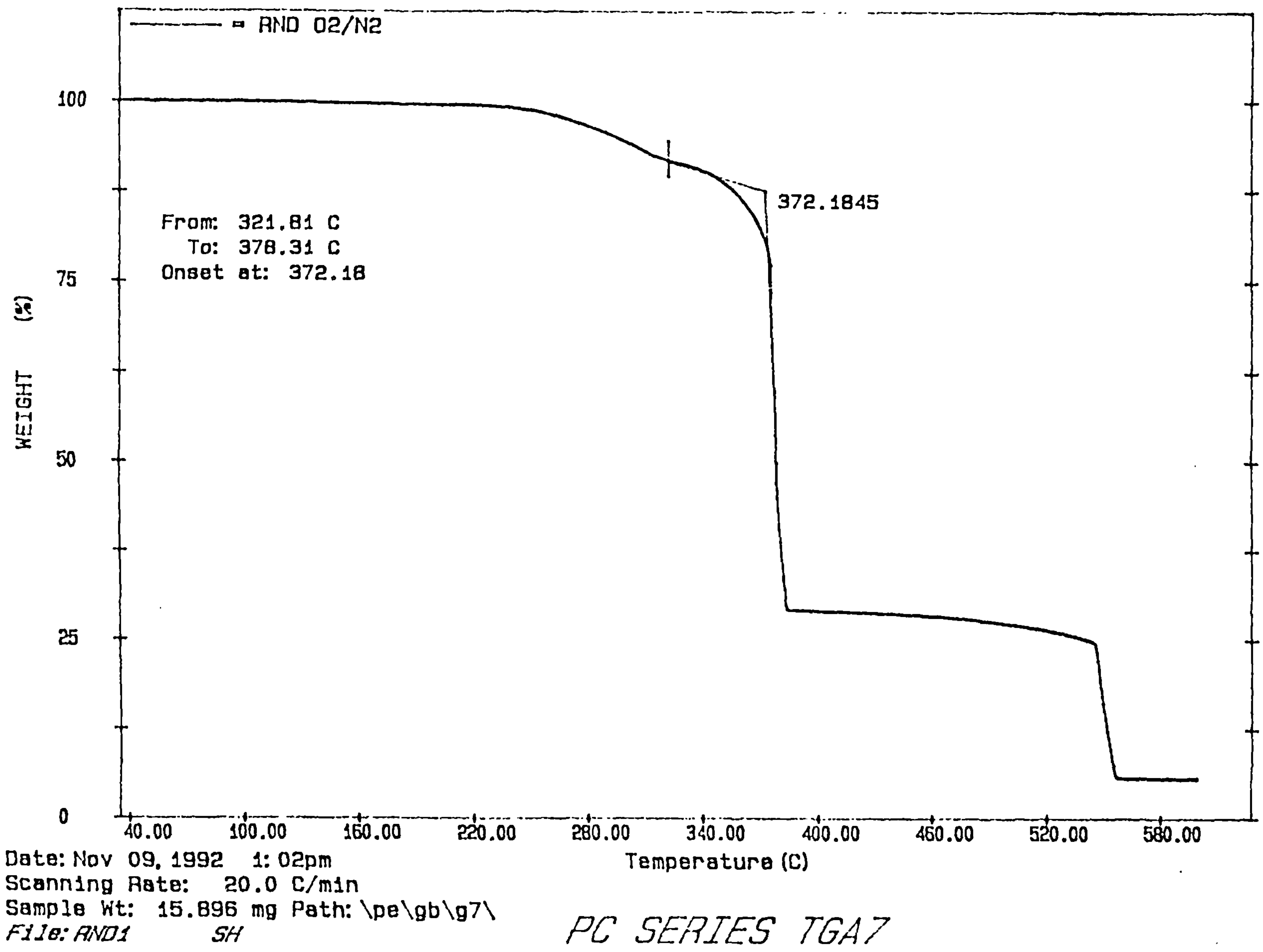

Fig. 8.10. TGA Thermogram of compound D in oxygen

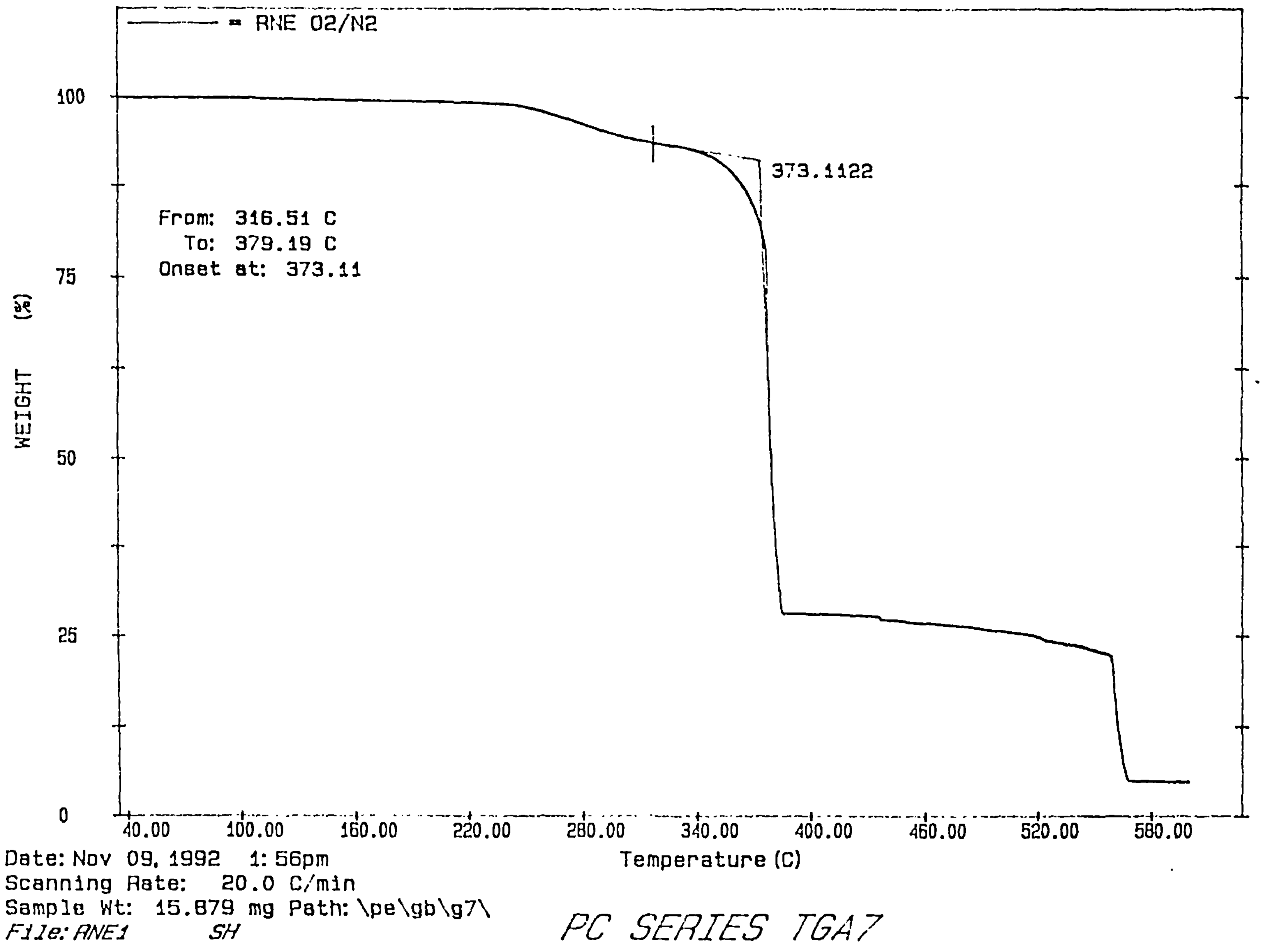

Fig. 8.11. TGA Thermogram of compound E in oxygen.

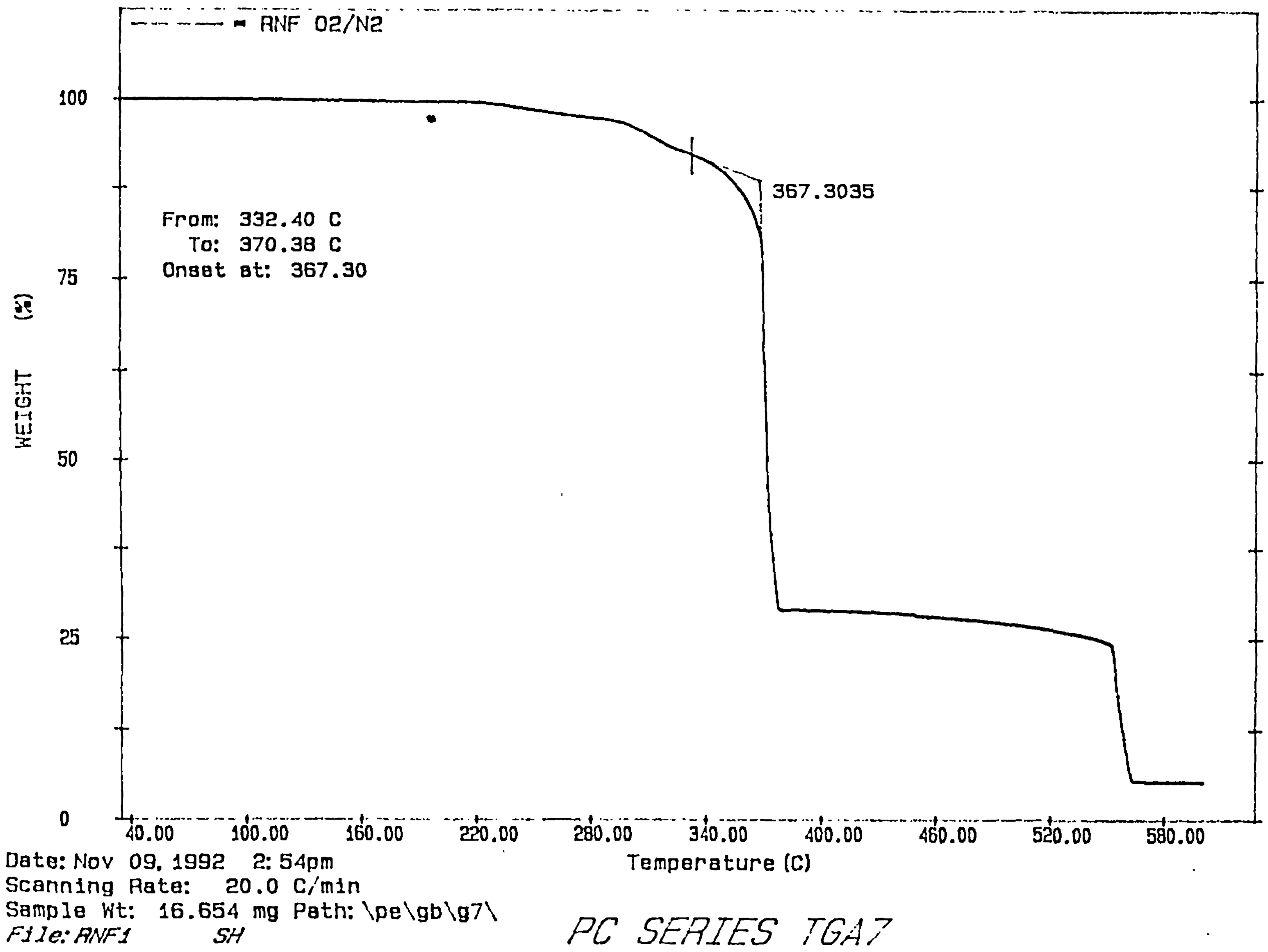

Fig. 8.12. TGA Thermogram of compound F in oxygen.

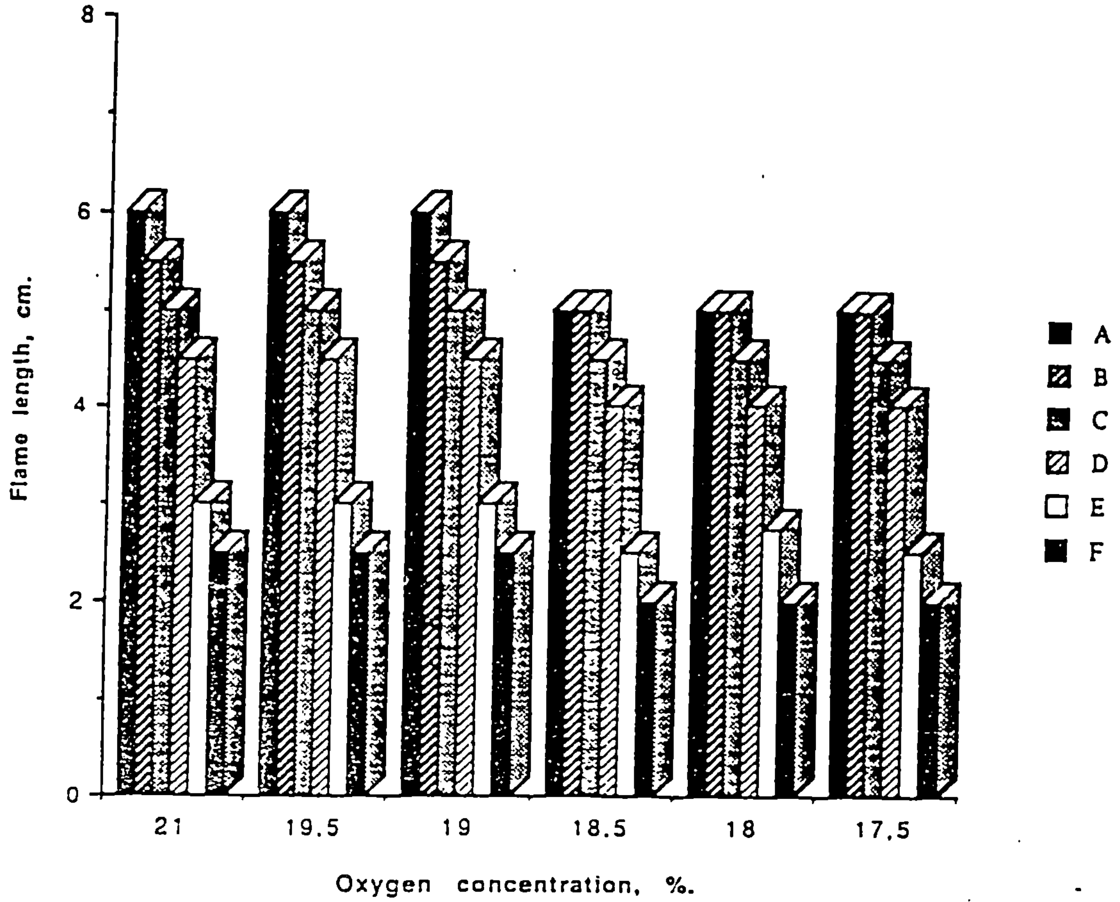

Fig 8.13. Flame length for different concentrations of oxygen.

Chapter 9.

SUMMARY
CONCLUSION AND SCOPE FOR FUTURE WORK

9.1. Summary

This study envisages modification of natural rubber into depolymerized liquid natural rubber. Depolymerizing conditions such as extent of mastication, peptizer dosage, temperature and duration of heating influence the molecular weight, molecular weight distribution, viscosity and colour. By controlling the above parameters different samples of liquid natural rubber with a wide depolymerization range have been prepared. These samples were graded according to the viscosity as determined by a Brookfield viscometer at 38°C.

The present work was on LNR samples. Their physical properties, molecular weights, molecular weight distribution, and flow behaviour were tested. They were also characterized by Infra-red and NMR spectroscopy. Chemical modification on LNR was attempted to impart special properties. Phosphorus addition on NR backbone was done by depolymerization of NR followed by *in situ* epoxidation and phosphorus addition by the reaction between the epoxide and dibutylphosphate. The modified LNR was characterized by chemical analysis and spectroscopic studies. LNR was used as a process aid-cum-viscosity modifier in nitrile rubber compounds. NBR compounds containing different weight percentage of LNR were prepared. The physical and rheological properties were analysed. The effect of LNR on stress relaxation in nitrile rubber was also studied. Vulcanizates containing different weight percentage of LNR were used. The properties were compared with compounds containing dibutylphthalate. The effect of strain level, LNR loading, prestrain, etc. on stress relaxation were assessed. Investigation on LNR for improving the properties of bitumen was also carried out. Depolymerized rubber was added to bitumen in different concentrations and the properties were studied with special reference to their flow behaviour. The influence of phosphorus modified LNR on processing and vulcanizate properties was studied in a natural rubber formulation. The flammability of the vulcanizates was also studied at different concentrations of oxygen.

9.2. CONCLUSIONS

Thermal depolymerization of natural rubber yielded liquid natural rubber. Product of desired viscosity could be obtained by controlling the conditions of depolymerization such as time of mastication, time of heating and temperature of depolymerization. Thermal depolymerization resulted in samples with broad molecular weight distribution. Polydispersity was around 8 as against 3 for chemically depolymerized samples. The present investigations indicated that flow behaviour of liquid natural rubber is influenced by shear rate, temperature and molecular weight. The low molecular weight samples exhibited Newtonian behaviour. High molecular weight samples showed pseudoplastic tendency especially at low temperatures and shear rates. Increase in temperature caused significant reduction in viscosity for LNR samples in general. Activation energy of flow was only marginally influenced by molecular weight of the samples and showed an increasing trend with increasing molecular weight.

Epoxidised liquid natural rubber could be produced by reacting liquid natural rubber with performic acid, formed *in situ* by the reaction between formic acid and hydrogen peroxide. By reacting epoxisdised liquid natural rubber with dibutyl phosphate it has been possible to chemically modify the polymer further. By using 25% ELNR it is possible to fix about 6% of phosphorus on the polymer. The reaction carried out in bulk and in solution resulted in products with different Tg values probably due to varying crosslink levels. Chemical analysis of the modified polymers prepared by two sets of reactions under identical conditions revealed repeatability of the reactions in bulk and in solution. Incorporation of the phosphorus modified polymer in a natural rubber formulation decreased the flammability behaviour of vulcanizates. Influence of the modified polymer on curing and vulcanizate properties of the compounds was also studied. Phosphorus addition can also be carried out by mixing ELNR and dibutyl phosphate at the time of mixing the rubber compounds. This was found to result in equally good flame retardance with relatively better processing and mechanical properties.

The effect of liquid natural rubber in a nitrile rubber gum recipe was studied in comparison with dibutyl phthalate, the popular ester type plasticizer used in nitrile rubber. Cure characteristics of the compounds were comparable. In the rheograph LNR at higher loading showed lower torque values than DBP. Studies on shear stress-shear rate relations using a capillary rheometer showed that both DBP and LNR decreased compound viscosities with increased loading. LNR compounds showed lower stress values than DBP compounds at equal shear rates. Flow measurements at different temperatures showed higher values of activation energy of flow for LNR compounds. Both sets of compounds exhibited pseudoplastic behaviour. As far as the vulcanizate properties are concerned LNR imparted a slight increase in elongation and hardness and decrease in tensile strength. Morphological studies revealed structural similarity. Small improvement in resilience was also noticed in the case of LNR. In general, LNR was found to be an effective plasticizer and good process aid in nitrile rubber compounding.

Stress relaxation studies on NBR vulcanizates containing liquid natural rubber revealed that the decay in stress increased approximately in proportion to the logarithm of the period under stress. The ratio of initial stress to the stress at any time t ($\sigma/\sigma o$) was plotted against log t. An approximately linear relation with two different slopes could be fitted to the experimental points over the range of time in seconds extending to four decades. The slope of the lines were calculated and their intercepts determined. Relaxation of DBP compounds were comparable to that of the control compound. The decay of stress in LNR compounds were higher than those of DBP. Samples tested at 200% strain level revealed that DBP imparted little contribution to relaxation while increased rates were observed with LNR at higher loading. At lower strain (50% elongation) the relaxation trends were similar for all the compounds while more separation was seen in the case of LNR compounds. At 50% elongation also, the values of σ/σ_0 decreased with time, for both the plasticizers. This effect was lower for the DBP compounds after prestretching. Ageing studies at 100°C for 24 h imparted little influence on stress relaxation. Permanent set after the release of tension was more for the highly plasticized compounds.

Polymer modification of bitumen was studied using LNR of molecular weight ($\bar{M}w$) around 33,000. Effect of LNR on soft bitumen as well as blown bitumen was studied. Increase in softening point was observed by the addition of 5 to 10 parts of LNR. Ductility decreased in the case of soft bitumen while some improvements were noticed in the case of blown bitumen at 10 parts loading. Penetration values consistently decreased in both the cases. Resistance to shear increased on addition of LNR and was maximum in the region of 5 to 10 parts of rubber. It was also observed that shear stress for all the bitumen samples increased with increasing shear rate. For soft bitumen, temperature dependence on viscosity was prominent up to 100°C and subsequently marginal. Maximum viscosity resulted on addition of 20 parts of LNR. Activation energy of flow of soft bitumen increased while that of blown bitumen decreased on addition of LNR.

Phosphorus as a flame retardant in natural rubber was investigated. Phosphorus was fixed on to the NR backbone by the reaction between epoxidised liquid natural rubber and dibutyl phosphate. The modified polymer was incorporated into a HAF black filled natural rubber to contain 1% phosphorus. The cure time was found to increase by the addition of the phosphorus modified polymer prepared in solution. The product formed in bulk and *in situ* resulted in comparatively better processing and vulcanizate properties. Thermogravimetric studies conducted in standard air and oxygen revealed improvements in flame retardance on addition of phosphorus during the second stage of oxidative degradation namely the burning of char. The function of phosphorus as a flame retardant in the condensed phase of forming a surface char has been concluded. The flammability of the materials were assessed by studying the samples in a Limiting Oxygen Index apparatus. Improvement in flame resistance, over the compounds without phosphorus, was evident from the oxygen index values and length of flame.

9.3. SCOPE FOR FUTURE WORK

Depolymerization of NR to liquid natural rubber has been a topic of interest in view of the increasing applications involving liquid rubbers and the status of LNR as a renewable material. Applications such as water-proofing compounds, cable joints, adhesives, binders for various applications, cast rubber products, etc are making this liquid polymer important. This work has been done on various fundamental aspects of LNR such as flow behaviour, viscosity modification, chemical modification and improvement in technological properties and the work opens up scope for elaborate studies on various applications mentioned above.

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Research experiene

Primary processing of natural rubber including drying of the crop by using firew electricity and solar energy.

Chemical modification of natural rubber for value addition and use in applicat requiring special properties like improved flame retardancy, oil resistance, mechan properties etc.

Studies on blends of natural rubber with other rubbers for improving the prope and increasing the area of applications.

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