COVULCANIZATION OF ELASTOMER BLENDS WITH SPECIAL REFERENCE TO NR/IIR AND NR/EPDM BLENDS

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Miss N. Suma under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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DECLARATION

I hereby declare that the thesis entitled "COVULCANIZATION OF ELASTOMER BLENDS WITH SPECIAL REFERENCE TO NR/IIR AND NR/EPDM BLENDS" is the original work carried out by me under the supervision of Dr.Rani Joseph, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022, and no part of this thesis has been presented for any other degree from any other institution.

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LIST OF ABBREVIATIONS

Polymers

NR	Natural rubber
IIR	Isobutylene-isoprene rubber or Butyl rubber
EPDM	Ethylene-propylene-diene rubber
BR	Polybutadiene rubber
CR	Polychloroprene rubber
IR	Polyisoprene rubber
SBR	Styrene-butadiene rubber
NBR	Acrylonitrile-butadiene rubber
RR	Rubber Reclaim

Additives

ZnO	Zinc oxide
MBTS	Dibenzthiazyl disulphide
MBT	Mercapto benzthiazole
TMTD	Tetramethyl thiuram disulphide
BP	Benzoyl peroxide
DCP	Dicumyl peroxide
MAH	Maleic anhydride
HAF black	High abrasion furnace black

Other abbreviations

ISNR	Indian standard natural rubber
ASTM	American Society for Testing and Materials
rpm	Revolutions per minute
phr	Parts per hundred rubber
P_0	Initial plasticity
PRI	Plasticity retention index
T_g	Glass transition temperature
T	Temperature
ML(1+4) at 100℃	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of four minutes at 100℃
ΔG	Free energy change of mixing
ΔH	Enthalpy change of mixing
ΔS	Entropy change of mixing
ΔE	Internal energy change of mixing
R	Gas constant
E	Activation energy
n	Power law index
M	Torque
S	Revolutions per minute of the Brabender rotor
IR	Infra red
Nm	Newton meter
DBP	Dibutyl phthalate

VGC	Viscosity gravity constant
V_r	Volume fraction of rubber network
V_{ro}	Value of V_r for filled vulcanizates
M_c	Number average molecular weight of rubber chains between crosslinks
χ	Polymer-solvent interaction parameter
V_s	Molar volume of solvent
ρ_r	Density of rubber
ρ_s	Density of solvent
PDMS	Poly(dimethyl siloxane)

Chapter 1

INTRODUCTION

Elastomer blends are of central importance to the rubber industry. Almost all vulcanized rubbers in industrial and transportation applications are used as blends. Moreover, the science and technology of elastomer blends is advancing at a rapid rate. One of the main advantages of elastomer blends is the great regulatable variability of their properties despite the limited number of initial components. The blending technology has long been widely used in rubber industry. Compounding with blends of two or more elastomers is an attractive method for attaining properties not available in a single elastomer.[1-20]

POLYMER BLENDS

In recent years, research and development activities in the field of polymer science and technology have been concentrated more on the modification of existing polymeric materials rather than on synthesising new polymers. The easiest method to develop polymer compositions having the required properties involves physical blending of two or more polymers. All materials attract interest on the basis of their property-processing-cost-performance relationship. The most important concept in polymer blends is additivity of properties. By this we mean that when a polymer is mixed with another polymer, the resulting blend has a property which is the weighed average of the properties of the individual polymers. Modulus is one of such properties that is expected to obey some additivity relationship.[21] For blends the weighing functions of the composition will be sensitive to the morphology. A very intriguing possibility, although less frequently observed, is synergism in property, such as tensile strength, when the blend has a better property than those of the components. The success of a new material depends on several factors such as combination of properties and cost dilution. For example, when we blend a high thermal resistant polymer having poor processability with another polymer having good processability and poor thermal stability, the resulting blend may be useful for certain applications for which both the individual polymers are unsuitable. Similarly, when a costlier polymer is blended with a cheaper one it may reduce the properties to a level still acceptable for a particular application. At the same time it will bring the cost of the blend to a range which is competitive in the market. Thus blending is an attractive means to engineer a material so that the user does not have to pay for more than he needs. This is the most important driving force for developing products from elastomer blends.

Since the driving force for development of polymer blends is generally some combination of economics and blend performance or properties, knowledge of the rules of mixtures for blend properties is of critical interest. These rules will again depend on the state of miscibility of the blend. The properties of miscible blends will follow relationships that are functions of composition and to some extent the degree of interaction between the blend components.[22,23] Immiscible blend properties will depend on the phase morphology and phase interaction as well as composition. There are many possible properties of interest such as mechanical, thermal, electrical and chemical.

A wide range of properties can be achieved by blending which includes mechanical, electrical and chemical properties along with processability. Compatibility is the fundamental property, deciding the practical utility of a polymer blend.[24-26] In polymer blends the property (P) depends on average properties of the constituents and can be described by the following equation:

$$P = P_1C_1 + P_2C_2 + IP_1P_2$$

where, P is the property of the blend, P_1 and P_2 the properties of the isolated components and C_1 and C_2 the respective concentrations of the constituents. I is an interaction parameter which can be positive, zero or negative as shown in Fig.1.1. When I is positive the property is synergistic, when I is zero the property is additive and when I is negative the property is non-synergistic.

The most important factor governing the ultimate properties of a polymer blend is intermolecular bonding force between the molecules. The low interaction at the interface is responsible for its tendency towards phase separation under various conditions (stress, blend ratio and temperature). The poor adhesion between the molecules at the interface in a heterogeneous system does not allow efficient transfer of stress across the interface leading to premature failure under stress. Though many immiscible systems form useful products and are being successfully commercialised, the applicability of such polymer blends is limited because of the inferior macroscopic properties. So

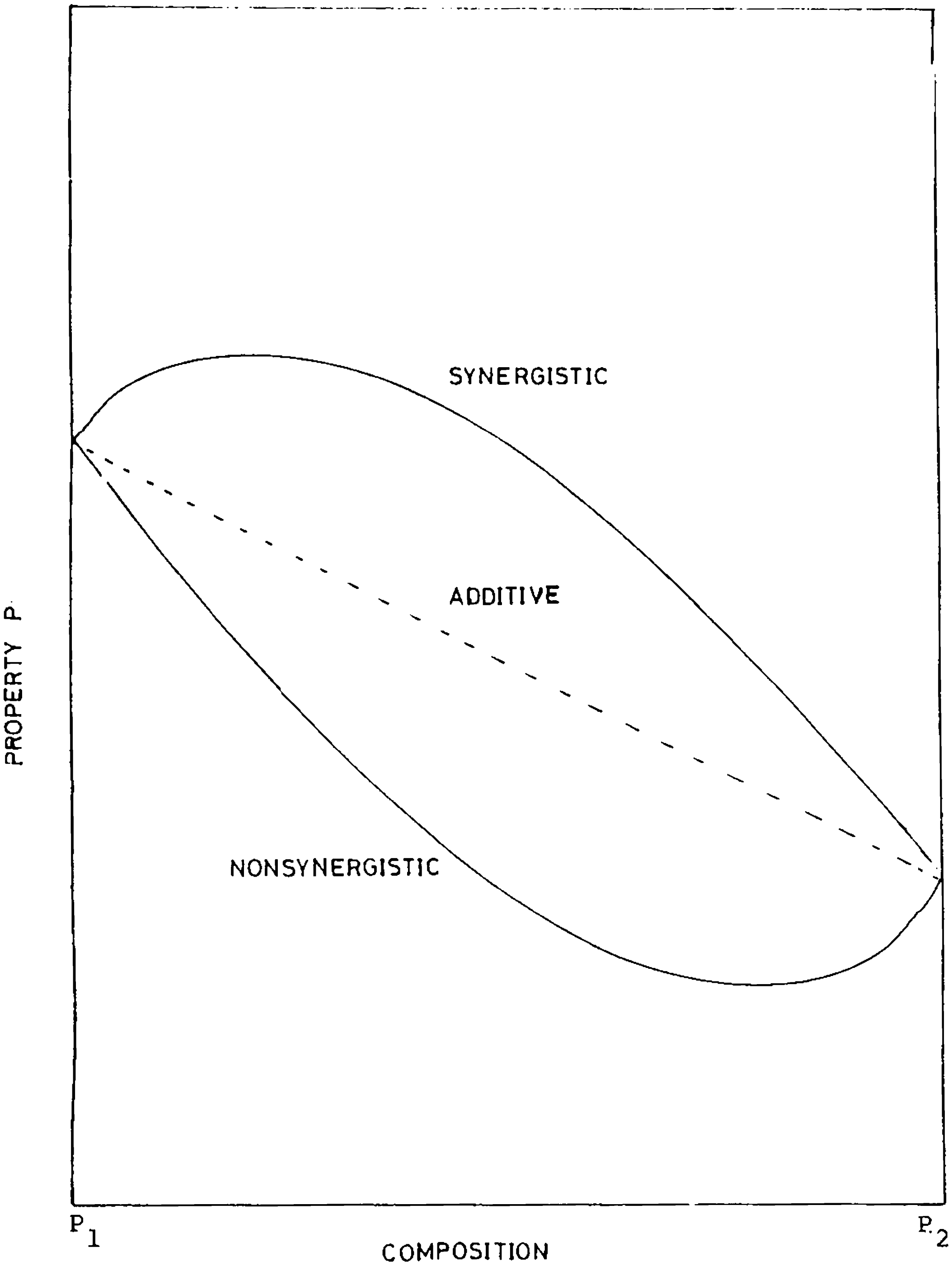

Fig.1.1: Variation of property with composition for a binary polymer blend

successful blending of incompatible polymer systems is gaining increasing importance both in the academic and industrial field.

ELASTOMER BLENDS

The great variety of commercially available elastomers offer a myriad of opportunities for blending. Each elastomer may have particularly desirable qualities in practical use in certain areas of application, but less desirable in other areas. For instance, polybutadiene rubber (BR) has excellent abrasion resistance, but poor processability and poor resistance to wet slip (slipping on a wet road) in tire treads. On the other hand, styrene-butadiene rubber (SBR) has excellent processability and an acceptable resistance to wet slip, but lower abrasion resistance compared to BR. Blends of BR and SBR will produce an elastomer matrix with more desirable properties for automotive tire treads than either of the constituents. Ethylene-propylene-diene modified rubber (EPDM) is added to elastomer formulations for improved oil acceptance and ozone resistance; Acrylonitrile-butadiene rubber (NBR) for improved oil resistance; Polychloroprene rubber (CR) for improved flame resistance; BR for improved low temperature flexibility; Butyl rubber (IIR) for improved gas impermeability etc.[27] Besides these blends, the important synthetic rubbers are frequently blended with natural rubber (NR) or with synthetic polyisoprene rubber (IR). In general, the rubber used in practical application is frequently a blend of elastomers.

BLENDING METHODS

There are several methods of forming elastomer blends such as mixing of melts, mixing of solutions, mixing of latices, partial block or graft copolymerization and synthesis of interpenetrating networks (IPNS).[28]

Mixing of polymer melts is the most common industrial method of preparing polymer blends. The main advantage of this method is the fact that no additives (eg., solvents) need to be removed from the product. The disadvantages are the high energy demands of mixing, very viscous polymer melts and the possibilities of macromolecular changes (degradation, crosslinking, chemical decomposition) at high temperatures and stresses. The strong dependence of material morphology and properties on mixing conditions can be both an advantage and a disadvantage. The problem in this case is that the rheology of molten polymer systems is very complex and it is very difficult to forecast the structure of the material from a knowledge of the mixing conditions.

Mixing of polymer solutions is in practice mainly used for coatings, because it allows rapid and easy mixing of the components at low energy costs, leads to simple applications at normal temperatures and neither causes degradative colour changes nor premature crosslinking reactions. From the point of view of the preparation of solid polymer blends, however, this method requires removal of the solvent (by evaporation, precipitation of the polymeric components and filtration) which usually leads to phase separation and hence poorly controlled heterogeneity in the product. Furthermore, the use of solvents implies problems connected with their price, toxicity, flammability, pollution and the economics of the whole process. Usually, only laboratory samples of solid polymer blends are prepared by this method. However, the use of a common solvent is particularly important in the cases of polymers miscible at room temperature (ie., in the solid phase) but immiscible in the melt.[21]

Mixing of latices is a suitable method of obtaining polymer blends, with a heterogeneity of the order of micrometers, without organic solvents and because of the low viscosity of the latices, without high energy costs in the mixing stage. Water removal requires somewhat higher energy requirements (evaporation or coagulation of the latex). The greatest limitation of this method is that the components have to be available in the form of mutually miscible latices which tend to contain a significant amount of impurities. Furthermore, it is usually necessary to finish mixing of the product in the melt stage. Even so, the energy saving resulting from mixing the components as latices is usually so great that this method of preparation of polymer blends is economically attractive, and hence a common industrial method.

Partial block and graft copolymerisation means that block or graft copolymerisation is carried out in such a way that its products are mainly homopolymers (or statistical copolymers), but sufficient block or graft copolymer is produced to ensure good adhesion between otherwise incompatible components. Products of this process are suitable for further mixing (in the latex or melt form) with the same or different homopolymers or copolymers.

Synthesis of mutually interpenetrating networks is done as follows. Usually one of the polymers is prepared first and crosslinked. The resulting polymer network is then allowed to swell to a gel in the second monomer. Finally, the second monomer is polymerised and crosslinked. In this way a second polymer network is created, completely interwoven with the first.

PROPERTIES OF ELASTOMER BLENDS

Elastomer blends, in general, display inferior mechanical properties compared to the average property of the components. The inferior properties displayed by cured elastomer blends is due to the incompatibility of the constituents on a molecular scale since the mechanical behaviour of the blend is likewise related to phase structure. It is apparent that the mechanical properties of a cured elastomer will be a function of the processing methods used in both blend formation and moulding conditions. Several investigators[29,30] have examined the morphology under electron microscopes but little scientific work has been done to establish the factors which are important in determining the mechanical properties of such blends. The variables of a blend system can be divided into two categories: direct and indirect variables[31] (Table 1.1). The direct variables can be further subdivided into those which are important because the poor component properties depend on them and those that are unique to the

Table 1.1: Blend variables

A. DIRECT VARIABLES (FUNDAMENTAL)

1. Glass transition temperature
2. Molecular weight
3. Crosslink density
4. Compositions (Proportions)
5. Morphology
6. Interfacial adhesion
7. Relative stiffness

B. INDIRECT VARIABLES (PROCESSING)

1. Mixing conditions (time, temperature, torque)
2. Annealing
3. Irradiation dose or crosslinking agent

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blend systems. The direct variables are the fundamental ones and can be controlled by the indirect or processing variables.

The first three fundamental variables are those that also affect the pure components. They are the glass transition temperature (T_g), the molecular weight and crosslink density of the components. Among the rubbery materials a higher T_g or molecular weight generally increases toughness for a given crosslink density.[32] In addition, it is well known that the mechanical properties of elastomers depend very strongly on crosslink density.[33] Specifically, the energy required to rupture an elastomer in simple tension generally passes through a maximum as a function of crosslink density.

The remaining four direct variables are unique to blends. The properties obviously depend on the properties of each component in the blend. In addition, the morphology of the blend may be important. One rubber may form the continuous phase while the other is dispersed phase or a cocontinuous structure when both phases are continuous may exist. Also various sizes and shapes of the dispersed particles are possible.

The interfacial adhesion between the two phases may determine the path that a growing crack takes in a deformed rubber blend and also determines the extent to which stresses can be transferred between the matrix and particle phases. If interfacial adhesion is sufficiently low, small cavities may be opened up between the dispersed domains and the matrix when the blend is stressed. Thus the interfacial adhesion plays a key role in determining the mechanical properties. The relative stiffness between the two phases is a function of the molecular weight, T_g and rate of crosslinking (and scission if it occurs) of the two rubber phases. The micro-deformation of the blend particles will depend in part on this property. It is found in many composites that the relative stiffness also affects the mechanical properties.

Three processing variables are listed in Table 1.1. The morphology of the blend depends upon the conditions under which the rubbers are mixed. Two methods have been used in literature: (1) Solutions of rubbers are stirred together, then dried or precipitated; (2) The bulk rubbers are comasticated in a Brabender or similar high shearing mixer. Most investigators have used the latter method. With this technique, the mixing time, temperature, and/or speed can be varied to obtain different morphologies. Another means of changing the morphology is by annealing after mixing. This can cause an increase in dispersed particle size or phase inversion.

REINFORCEMENT OF ELASTOMER BLENDS

All synthetic rubbers in practical applications need fillers for reinforcement and although polymer chemistry has progressed to the point where many polymers can be tailor-made with special properties, there is still a need for fillers. The term 'reinforcement' refers to an improvement in end use performance of the vulcanizate associated with an increase in modulus and in the so called ultimate properties like tensile strength and tear strength, fatigue life, abrasion resistance etc. The filler distribution in elastomer blends has some inherent special characteristics. Polymers are usually not miscible and blends consist of microdispersions of one in the other or of intermingled microregions of both often having dimensions around 0.1 to 1.5 microns. With elastomer blends that consist of a mixture of two phases it is difficult to partition a filler, and particularly carbon black, uniformly between the two phases. The factors that dominate the partitioning of carbon black are the degree of saturation of the polymers, their viscosities and their polarities, the method of mixing etc.[34] The affinities of carbon black for various elastomers are shown below and as a general rule the following order can be recognised.[35]

BR > SBR > CR > NBR > NR > EPDM > IR

High ←———— Affinity ←———— Low

When the filler is added to a binary elastomer blend it goes to the less viscous polymer and when the viscosity becomes equal to that of the highly viscous polymer it would be taken up by both the polymers. So, often the low viscosity polymer gets highly loaded. A typical example is the blending of NR and BR. Hess, Scott and Callan[35] showed evidence that the best mechanical properties of the blend were obtained when the BR contained the larger proportion of reinforcing carbon black as determined by electron microscopic techniques. If black was mixed into a previously prepared 50/50 blend of NR and BR, the black would be preferentially incorporated in the NR.

The explanation of this phenomenon is probably that during the mixing of the preblend with filler, the soft polymer will penetrate the voids between black particles first so that there will be a higher concentration of black in the softer rubber. Because of the uptake of filler, the viscosity of the softer rubber increases until it nearly matches that of the higher viscosity rubber, after which the second polymer participates in the black penetration at about the same rate so that the viscosity of the two phases is roughly the same. The other effect, which is that better properties are found when the polybutadiene phase contains the larger proportion of black, is due to the fact that BR as a gum vulcanizate is weak and needs carbon black for reinforcement whereas NR by itself is already strong. It has the built-in reinforcement of its crystallites which fulfill a similar function as a reinforcing filler.

It appears that in elastomer blends the sequence of blending and carbon black addition are of utmost importance for the distribution of the black in the blend, which in turn, largely determines the physical properties of the vulcanizates.[36-44] Thus, Sircar et al.[45] noticed that a Francis Shaw intermixed black masterbatch cut back with the same or with a second elastomer is characterised by a lower modulus, hardness, abrasion resistance and flexometer heat generation and by a higher elongation and rebound value than when the black is added to the elastomer blend. Unvulcanized letdown compounds have lower viscosities than directly mixed blends. It is therefore important in reinforcing elastomer blends with carbon blacks to determine those mixing procedures which yield optimum physical properties of the vulcanizates.

CRITICAL FACTORS IN THE DEVELOPMENT AND APPLICATION OF ELASTOMER BLENDS

There are technological problems which are frequently the result of some type of mutual incompatibility which can exist between dissimilar elastomers. Three types of incompatibility have generally been noted; incompatibility due to viscosity mismatch, thermodynamic incompatibility and incompatibility due to cure rate mismatch.

1. Viscosity mismatch

This prevents or greatly delays the formation of intimate blends.[46,47] If only viscosity mismatch derived incompatibility is encountered, one can greatly improve the blending process and in some cases even the quality of the blend by adjusting extender-oil and filler concentrations in the dissimilar elastomers and by adjusting the individual raw polymer viscosities so that, through much of the mixing process, the effective viscosities of the phases will no longer be mismatched. Otherwise, rather large 'chunks' of the more viscous blend component will tend to 'float around' and remain very coarsely dispersed in the more fluid material.

2. Thermodynamic incompatibility

This sort of incompatibility prevents mixing on molecular scale.[48,49] Thermodynamic incompatibility of polymer blends is governed by the well known Gibbs free energy relation,

$$\Delta G = \Delta H - T\Delta S$$

where, ΔG is the change in free energy of mixing,

ΔH change in enthalpy of mixing,

ΔS change in entropy of mixing and

T the absolute temperature.

Microscopic miscibility occurs only when ΔG is negative. Since in the case of long chain polymers the contribution of the entropy of mixing ΔS is negative and very small, the enthalpy of mixing, ΔH becomes the deciding factor. In the case of purely dispersive forces, ΔH is always positive consequently,high molecular weight systems with this type of interaction are rarely miscible. Miscibility drops significantly with growing chain length if, however, there exist so-called 'specific interactions' (eg., ion-dipole interactions, hydrogen bonds) between the components, then ΔH can be negative and the polymers can become miscible.

3. Cure rate mismatch

Cure rate mismatch occurs as a result of solubility and diffusion differences of compounding ingredients in elastomer blends.[50-53] F.X.Guillamond[54] has determined the solubility of curatives in various rubbers by the method of equivalent solvents. The results are given in Table 1.2.

Table 1.2: Solubility of accelerators at 153°C

Materials	Solubility at 153°C, phr		
	SBR	EPDM	BR
S	17.3	10.7	16.8
MBT	5.2	1.1	2.4
TMTD	14.3	5.0	4.9

J.B.Gardiner[55,56] has demonstrated that diffusion of common vulcanizing ingredients such as sulphur, TMTD, MBTS and DOTG occurs from compounded low unsaturation rubbers, such as IIR and EPDM, to uncompounded high unsaturation rubbers, such as NR and SBR; and also to be a lesser extent from compounded high unsaturation rubbers to uncompounded low unsaturation rubbers. Migration is observed to commence in a very short time (eg., 3 sec at 307°F), indicating that a diffusion gradient may be produced between dissimilar elastomers considerably before significant vulcanization occurs. Since the solubility of the common curatives is greater in high unsaturation elastomers than in low unsaturation elastomers, migration from the latter to the former may be inevitable, even when concentrations are equal initially.[55] Such migration will be accentuated by higher curative reaction rates in the high diene-elastomers, causing excess material to be drawn from the adjacent phases and associated with over and under cure.[56,7] In such circumstances vulcanizate properties may not approach the levels attainable by either of the elastomers alone. Attention to mixing schedules and masterbatching procedures has been demonstrated to offer advantages in certain instances, according to vulcanization recipes and individual accelerator influence.[57] Also vulcanizing systems which function independently of polymer unsaturation have been suggested to permit the development of higher mechanical performance in elastomer combinations of differing unsaturation.[58]

PROCESSING CHARACTERISTICS OF ELASTOMER BLENDS

One of the most important problems in the rubber industry is the behaviour of unvulcanized elastomers and compounds as they are processed in mixing and shaping equipment. Efficient production of rubber products requires that fillers be easily incorporated into gum elastomers and the resulting rubber compounds be readily and reproducibly extruded or calendered. The rheological and stress-deformation properties of the elastomer or compound probably represent the most important single factor for these determine the resistance to deformation and the necessary power consumption to impose a flow. There are four important ways in which, studies on the flow behaviour of polymers can be of value.

1. Most processing techniques involve some form of directed flow of polymer solutions or melts. Therefore processing defects can be identified and thus the conditions can be adjusted to minimise the defect.

2. The design of process and equipment by deriving qualitative and to some extent quantitative relations between such factors as output, power consumption, machine dimensions, material properties and operational variables such as temperature and pressure can be done.

3. The best polymer which can be used under a given set of circumstances can be selected.

4. Flow of polymer solutions plays an important role in the identification and characterisation of their molecular structure.

Processing of rubbers involves those operations that come between the initial mastication of rubbers and the vulcanization of the otherwise finished article, that is operations of mixing, calendering, frictioning, extrusion, moulding etc. In all these cases rheological properties are predominant than any other properties.[59-65]

A fascinating variety of methods and instruments have been devised to measure viscosity and other flow properties of liquids in all cases.[66] Nearly all viscometric systems fall into two classes, those in which flow is caused by a difference in pressure from one part of the liquid to another and those in which flow is caused by controlled relative motion of the confining solid boundaries of the liquid. In the first class are the capillary types, in the second are the rotational types.

For a more accurate determination of the processability of a material testing devices were developed whose operating principles are identical with those of processing devices. One example is the Brabender plasticorder.

Blending of rubbers is often utilized to obtain a better processing material. This improvement may consist of lowering of stock viscosity, or producing a material that is less prone to fracture or crumbling when subjected to flow. The elastic behaviour, and the related phenomena of die swell and shrinkage can also be altered by blending. Generally it is expected that the processing behaviour of the blend will be intermediate between that of the components. However, polymer blends sometimes display anomalous rheological properties. The viscosity of a blend may exhibit minima or maxima as a function of the composition. Very complex dependencies on composition have been observed.

The morphology of a blend can rearrange in order to accomodate the applied stresses. The principle of minimum energy dissipation underlies the often encountered sheath/core configuration. Since in the vicinity of a wall of the containing vessel the velocity gradient tends to be highest, while at the core of a flowing polymeric material there is often plug flow, the lower viscosity component will tend to accumulate towards the surface of the polymer mass. The result is a blend viscosity which can be low as that of the lower viscosity component. Incorporation of a few per cent of EPDM to a fluroelastomer or of PDMS to SBR was found to significantly reduce steady state viscosities. This can be attributed to the lower viscosity, lubricious component taking up residence at the interface, giving rise to lubricating layer and perhaps some interfacial slippage. In short, the processability behaviour of elastomer blends can be quite complex and hence needs careful investigation

RUBBER RECLAIM FOR DEVELOPING ELASTOMER BLENDS

Developments in the rubber reclaiming industry are closely related to those in the rubber industry in general. The vulcanized rubber produced by the latter becomes in time the raw material used by the former. The machinery used in the production of reclaim, and the reclaiming processes used today, are for the major part still the same as used before. The object of reclaiming vulcanized scrap is still the same, ie., the breakdown (depolymerisation) of the scrap to a plastic state which will permit reuse of it in the current rubber processing machinery for the manufacture of new goods. This breakdown is achieved by the application of energy.

The high degree of cure obtained by modern vulcanization techniques, use of antioxidants, and reinforcing fillers which induce strong surface forces, have greatly enhanced the resistance to thermal plasticization of vulcanizates. This has necessitated the adoption of a more intense degree of reclaim process for regenerating vulcanized rubber. It involves degradation of the vulcanizate structure, induced by chemical and thermal means, followed by mechanical working, after the removal of the constructive fabrics, extraneous matter etc. However, many attempts have been made to reclaim rubber without the use of heat.[67] The reclaim obtained in such cases is quite different from the usual reclaimed rubber. They are drier (less internal tack) and have poor milling properties.

The chemistry of reclaiming is complex. Reclaiming is not exactly devulcanization. The combined sulphur still present after reclaiming is an evidence for this. Vulcanized rubber molecule is depolymerised by chain scission.[68] The oxygen probably in the form of peroxides, developed during the use of the article and partly during the grinding operation, facilitates reclaiming.[69,70] This is inferred from the fact that new tyres (factory rejects) do not reclaim well.

Butyl rubber, has been reclaimed for a number of years. The reclaim carries the parent polymer's properties in regard to ozone and weather resistance. The amount of unsaturation in the reclaim polymer lies between ½ and 1 per cent. Its air retention is equivalent to the virgin polymer and its retention of physical properties is high. In addition to this, butyl reclaim shows a reasonably high modulus and good resistance towards deformation under load and under heat. Hence there is good scope for using butyl reclaim for developing blends with elastomers such as natural rubber for upgrading properties of NR economically.

OBJECTIVES AND SCOPE OF THE PRESENT STUDY

An important consideration in obtaining acceptable vulcanizate properties in a rubber blend is the development of a satisfactory network structure in each of the phases. During mixing curatives more often make first contact with the lower viscosity phase. But later, curative migration can occur due to the higher solubility of sulphur in unsaturated elastomers and the greater affinity of many accelerators for more polar rubbers which lead to significant difference in crosslink density of the phases of the rubber blends. In addition, if the rate of vulcanization varies considerably between the elastomers blended, depletion of the curatives in the faster curing component can cause curative migration and worsen the cure balance. Obviously the problems encountered with curative imbalance are particularly significant when the components of the blends are dissimilar such as blends of NR/IIR and NR/EPDM due to the large difference in the unsaturation of the components. When such blends are tried for new applications, a detailed study on all aspects concerning the preparation, properties etc. are to be made. Usually, the components for blending are selected considering the properties required and the compatibility of the components with respect to molecular and vulcanization characteristics. NR possesses excellent physical properties. However, its resistance to ageing and ozone attack is poor which preclude its application in many critical areas. IIR and EPDM possess heat, oxygen, ozone and weather resistance. Hence the blends of NR and IIR and NR and EPDM may possess the good mechanical properties of NR and the good heat, oxygen, ozone and weather resistance of IIR and EPDM. While the latter has been found to be experimentally true, the mechanical properties of the blends are far below the average mechanical properties of the blends. The aim of the present work has been to improve the mechanical behaviour of NR/IIR and NR/EPDM blends by minimising their viscosity mismatch, thermodynamic incompatibility and cure rate imbalance.

Attempts have been made to attain satisfactory network structures in each of the phases of a rubber blend by minimising the cure rate imbalance by employing methods such as grafting of accelerators to the slow curing rubber, chemically bonding the crosslinking agents to the rubber in which it has lower solubility, functionalisation of the slow curing rubber, masterbatching of the curing agents to the slow curing rubber etc. Functionalisation of the slow curing constituents of NR/IIR and NR/EPDM blends is tried using novel reagents as the first part of this study. However, the crux of the present study is a more direct approach to attaining a covulcanized state in NR/IIR and NR/EPDM blends: Precuring the slow curing rubber (IIR or EPDM) to a low level when it can still blend with NR and then to do the final curing after blending with NR. The precuring is also likely to minimise the viscosity mismatch. Since a low level of residual crosslink density is likely to be present in reclaimed rubbers, blending heat resistant reclaimed rubber such as butyl reclaim with NR may also have the same effect of precuring IIR, and then blending with NR. Hence use of IIR reclaim for developing blends with NR is also proposed to be investigated in this study.

The main objectives of the present investigations are:

1. Upgrade the heat, oxygen, ozone and weather resistance of NR to make it suitable for more demanding applications.

2. Improve the mechanical properties of NR/IIR and NR/EPDM blends by reducing the technological problems in their blending such as viscosity mismatch, thermodynamic incompatibility and cure rate imbalance.

3. Characterise the processing behaviour of such modified blends.

4. Bring down the cost of NR/IIR and NR/EPDM blends.

This thesis is divided into the following chapters.

Chapter 1: Introduction

Chapter 2: Experimental techniques

Chapter 3: Carboxylation of IIR and EPDM for improving the mechanical properties of NR/IIR and NR/EPDM blends

Chapter 4:

Part I: Precuring of IIR and EPDM for improving the mechanical properties of NR/IIR and NR/EPDM blends

Part II: Investigation of the processability of NR/IIR and NR/EPDM blends using a torque rheometer

Chapter 5: Utilisation of IIR tube reclaim for developing NR/IIR blends

Chapter 6: Summary and conclusions.

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Chapter 2

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigations are given in this chapter.

ELASTOMERS

1. Natural Rubber (NR)

ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam. The Indian Standard specifications for this grade of rubber are given below:

Parameters	Limit
Dirt content, % by mass, Max.	0.05
Volatile matter, % by mass, Max.	1.00
Nitrogen, % by mass, Max.	0.70
Ash, % by mass, Max.	0.60
Initial plasticity, P_o Min.	30.00
Plasticity retention index (PRI) Min.	60.00

2. Isobutylene-isoprene Rubber or Butyl Rubber (IIR)

IIR used was Exxon 065, 0.8 mol per cent unsaturation, Mooney viscosity [ML(1+8), 100°C] : 50.

3. Ethylene-propylene-diene Rubber (EPDM)

EPDM rubber used was JSR EP 33, Mooney viscosity [ML (1+4), 100°C] : 52.

4. Isobutylene-isoprene Rubber Tube Reclaim

Isobutylene-isoprene rubber tube reclaim was supplied by Elgi Rubber Products Ltd., Coimbatore.

COMPOUNDING ADDITIVES

1. Zinc Oxide

Zinc oxide (ZnO) was supplied by M/s.Meta Zinc Ltd., Bombay. It had the specifications given below:

Specific gravity - 5.5

Zinc oxide content - 98%

Acidity - 0.4% max.

Heat loss (2 hrs at 100°C) - 0.5% max.

2. Stearic Acid

Stearic acid used in the study was supplied by Godrej Soaps (Pvt.) Ltd., Bombay and had the following specifications:

Melting point - 50-69°C

Acid number - 185-210

Iodine number	- 9.5 max.
Specific gravity	- 0.85 ± 0.01
Ash	- 0.1% max.

3. Dibenzthiazyl Disulphide (MBTS)

Dibenzthiazyl disulphide was supplied by Bayer Chemicals, Bombay. It had the following specifications.

Specific gravity	- 1.34
Melting point	- 165°C

4. Tetramethyl Thiuram Disulphide (TMTD)

Tetramethyl thiuram disulphide used was supplied by Polyolefins Industries Ltd., Bombay. It had the following specifications:

Melting point	- 136°C
Specific gravity	- 1.4

5. Sulphur

Sulphur was supplied by Standard Chemical Company (Pvt.) Ltd., Madras and had the following specifications:

Specific gravity	- 2.05
Acidity	- 0.01% max.
Ash	- 0.01% max.
Solubility in CS_2	- 98% max.

6. High Abrasion Furnace Black (HAF N-330)

High abrasion furnace black (HAF) was supplied by M/s.Carbon and Chemicals (India) Ltd., Kochi. It had the following specifications:

Iodine adsorption	-	80 mg/g
DBP absorption	-	105 cm^3/100 g
Mean particle diameter	-	32 nm

7. Naphthenic Oil

Naphthenic oil was supplied by M/s.Hindustan Petroleum Ltd. It had the following specifications:

Colour - light coloured oil

Viscosity gravity constant (VGC) - 0.85-0.9

8. Mercapto Benzthiazole (MBT)

Mercapto benzthiazole having the following specifications was supplied by Bayer Chemicals, Bombay.

Specific gravity	-	1.45-1.52
Melting point	-	160-180°C

OTHER ADDITIVES

Dicumyl peroxide (DCP), benzoyl peroxide (BP) hexamethylene diamine, potassium hydroxide, potassium iodide, starch, sodium thiosulphate and potassium dichromate used were of analytical grade.

SOLVENTS

Solvents used in the study (toluene, chloroform, con. hydrochloric acid, iodine monochloride, isopropanol, methanol, ethylene glycol, cyclohexane and acetic acid) were of analytical grade.

EXPERIMENTAL METHODS

1. Mixing and Homogenization

a) Using the mixing mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15x33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip (0.002x100)". Then it was given 2 passes through the nip of (0.002x10)" and allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained at 70±5°C during the mastication. After the nerve had disappeared, the compounding ingredients were added as per ASTM D 3184 (1980) and ASTM D 3182 (1982) in the order activators, fillers, accelerators and curing agents. Before the addition of accelerators and sulphur the batch was thoroughly cooled.

After completion of the mixing the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm. For the preparation of compounds of elastomer blends, NR was masticated to the Mooney viscosity level of the synthetic rubber and then the other additives were added as described above unless otherwise specified.

b) Using Francis Shaw Intermix

Masterbatching and carboxylation was done in a Francis Shaw intermix model (KO MK3) with a working volume of 1 litre. It is a batch mixer, capable of mixing materials in a short period of time. The heart of the intermix is the mixing chamber which contains two rotors of unique design. Materials to be mixed are fed into the intermix at the top. The rotors are driven by an electric motor. Drive is transmitted from motors through a set of reduction gears. Pressure is applied on the stock from the top by a plunger or ram. The discharge door is at the bottom.

2. Cure Characteristics

a) Using Goettfert elastograph

The cure characteristics of the elastomers and elastomer blends were determined using a Goettfert elastograph model 67.85. It is a microprocessor controlled rotorless curemeter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity which is oscillated through a small deformation angle (±0.2°). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half. A typical elastograph cure curve is shown in Fig.2.1 and the following data can be taken from the torque-time curve.

i) Minimum torque: Torque obtained by the mix after homogenizing at the test temperature before the onset of cure.

ii) Maximum torque: This is the torque recorded after the curing of the mix is completed.

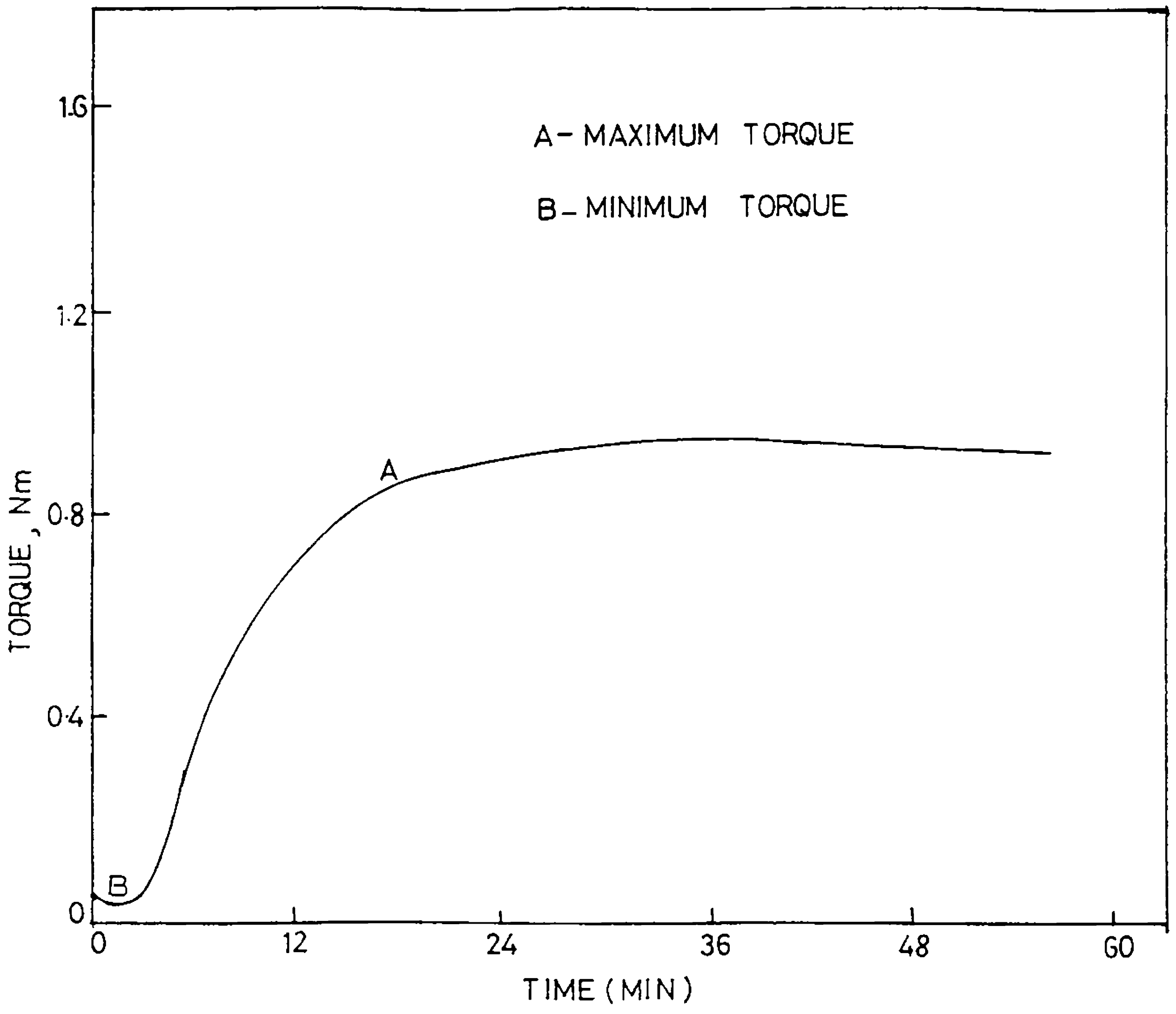

Fig.2.1: A typical cure curve of a rubber compound from Elastograph

iii) Scorch time: This is the time taken for 2 units rise (0.02 Nm) above the minimum torque (about 10% vulcanization).

iv) Optimum cure time: This is the time taken for attaining 90% of the maximum torque.

v) Cure rate: Cure rate was determined from the following equation,

$$\text{Cure rate (Nm/min)} = \frac{L_{max} - L_{min}}{t_{90} - t_2}$$

where, L_{max} and L_{min} are the maximum and minimum torque respectively and t_{90} and t_2 the times corresponding to the optimum cure time and scorch time respectively.

The elastograph microprocessor evaluates the vulcanization curve and prints out these data after each measurement.

b) Using Monsanto rheometer

The Monsanto rheometer used in the study for determining the curing behaviour of rubber compounds was model R 100. In this instrument the rubber compound is contained in a cylindrical cavity 50x10 mm and has embedded in it a biconical rotor of diameter 37 mm which is oscillated sinusoidally through a small arc amplitude (1 to 3 degree). The cavity and the specimen are maintained to within ±0.5°C and the force required to oscillate the disc is measured. The torque-time curve (vulcanization curve) of the rheometer is similar to that of the elastograph and all the relevant data could be taken accordingly.

3. Moulding of Test Specimens

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding on a single day light, electrically heated press having 30x30 cm platens at a pressure of 120 kg/cm^2 on the mould. The rubber compounds were vulcanized upto their respective optimum cure times at 150°C unless otherwise specified. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hours and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set, abrasion resistance etc.) additional curing time based on the sample thickness was given to obtain satisfactory mouldings.

4. Physical Test Methods

At least five specimens per sample were tested for each property as follows and mean values are reported.

a) Tensile stress-strain behaviour

Tensile properties of the elastomer blends were determined according to ASTM D 412 (1980) using dumbell specimens on a Zwick universal testing machine model 1445. All the tests were carried out at 28±2°C. Samples were punched out from compression moulded sheets using a dumbell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by the two grips, the upper grip of which was fixed. The rate of separation of the power actuated lower grip was fixed at 500 mm/min. for elastomeric specimens. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

b) Tear resistance

This test was carried out as per ASTM D 624 (1981) using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on a Zwick universal testing machine. The speed of extension was 500 mm/min and the test temperature 28±2°C.

c) Hardness

The hardness (Shore A) of the moulded samples was tested using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981). The tests were performed on mechanically unstressed samples of 300 mm diameter and minimum 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimens.

d) Compression set

The samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 100°C. After the heating period, the samples were taken out, cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set (\%)} = \frac{t_o - t_1}{t_o - t_s} \times 100$$

where, t_o and t_1 are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used. The procedure used was ASTM D 395 (1982) (method B).

e) Abrasion resistance

The abrasion resistance of the samples was tested using a DIN Abrader. Sample having a diameter of 6±0.2 mm and a thickness of 6 to 10 mm, was kept on a rotating sample holder and 10 N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece getting abraded away by its travel through 42 m on a standard abrasive surface. The abrasion loss was calculated as follows:

$$V = \Delta m/\rho$$

where, m = mass loss, ρ = density of the sample and v = abrasion loss.

f) Rebound resilience

Dunlop tripsometer (BS 903, Part 22, 1950) was used to measure rebound resilience. The sample was held in position by applying vacuum. It was conditioned by striking the indentor six times. The temperature of the specimen holder and the sample was kept constant at 35°C. Rebound resilience was calculated as follows:

$$\text{Rebound resilience (\%)} = \frac{1 - \cos \Theta_2}{1 - \cos \Theta_1} \times 100$$

where, Θ_1 and Θ_2 are the initial and final rebound angles respectively, Θ_1 was 45° in all cases.

g) Ageing Studies

Dumbell samples for evaluation of physical properties were prepared and kept in an air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break, modulus etc., were measured after ageing. The percentage retention of these properties was evaluated for assessing the effect of ageing. The procedure given in ASTM D 573 was followed.

h) Density

The densities of the polymer samples were estimated by the method of displacement of liquid (ASTM D 792). In this method the weight of the specimen in air was first noted and then the specimen was immersed in a liquid and its loss of weight in liquid was determined. The density is given by,

$$\text{Density} = \frac{\text{Weight of specimen in air x density of the liquid}}{\text{Weight loss of specimen in liquid}}$$

5. Rheological Evaluation Using a Brabender Plasticorder

Brabender plasticorder (torque rheometer) has been widely used for measuring processability of polymers, rheological properties of polymer melts, blending of polymers etc.[1,2] The torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material to mastication or flow under preselected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 40 cc for the model used (PL 3S) Mixing or shearing of the material in the mixing chamber is done by two horizontal rotors with protrusions. The resistance which is put up by the test material against the rotating rotors in the mixing chamber is made visible with the help of a dynamometer balance. The dynamometer is attached to a precise mechanical measuring system which indicates and records the torque. A D.C thyrister controlled drive is used for speed control of the rotors (0 to 150 rpm range). The temperature of the mixing chamber is controlled by circulating hot oil. The temperature can be varied upto 300°C. Stock temperature thermocouple with a temperature recorder is used for temperature measurement. Different types of rotors can be employed depending upon the nature of the polymers.

The rotors can be easily mounted and dismounted due to the simple fastening and coupling system. Once test conditions (rotor type, rpm and temperature) are set, sufficient time should be given for the temperature to attain the set value and become steady. Subsequently, the materials can be charged into the mixing chamber to obtain a torque-time curve or a plastogram.

The Brabender plasticorder was used to evaluate the rheological behaviour of polymer blends in this study. The nature of shear in the plasticorder is similar to that encountered in practical processing operations such as extrusion or milling. Blyler and Daane[3] observed that the power law relationship between rotor torque and rotor speed is reminiscent of the power law relationship often found between shear stress and shear rate and with a few assumptions derived the equation,

$$M = C(n)\, KS^{n}$$

where, M is the torque

n the power law index
C(n) a function weakly dependent on n
K a constant and
S the rotor speed.

The slope of the plot of log M versus log S gives the power law index. Also torque/rpm of the Brabender plasticorder represents viscosity and the activation energy for viscous flow can be measured from it if log (torque/rpm) is plotted against 1/T. The activation energy at constant rpm obtained by this procedure should correspond to the flow activation energy at constant shear rate.

6. Morphology Studies

a) Using optical microscope

The morphology of polymer blends was investigated using an optical microscope (Versamet-2, Union 7596). For optical microscopy a compression set test piece was cut to a convenient size and mounted on a microscope slide. Photographs were taken at a magnification of 330.

b) Scanning electron microscope

Scanning electron microscope (JEOL JSM 35C) was used to investigate the morphology of fractured surfaces.[4-6] In this technique an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors and magnified. An image of the investigated microscopic region of the specimen is thus photographed.

If the specimen under investigation is not a good conductor, it should be coated with a thin layer of conducting material like platinum or gold. This is done by placing the specimen in a high vacuum evaporator and vaporizing the conducting material held in a tungsten basket (vacuum dispersion).

The SEM observations reported in the present investigation were made on the fracture surface of tensile test specimen. The fractured surfaces of the samples were carefully cut out without disturbing the surface. These surfaces were then sputter coated with gold within 24 hours of testing. The SEM observations were made within one weak after gold coating. The gold coated samples were kept in desiccator before the SEM observations were made.

7. Chemical Test Methods

a) Determination of chemical crosslink density

The concentration of chemical crosslinks was estimated from the equillibrium swelling data as follows:

Samples of approximately 1 cm diameter, 0.20 cm thickness and 0.20 gm weight were punched out from the central portion of the vulcanizate and allowed to swell in solvent (toluene). The swollen sample was taken out of the solvent after 24 hours and weighed. Solvent was then removed in vacuum and the sample weighed again.

The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding[7] from the following equation,

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_o\rho_s^{-1}}$$

where, T = weight of the test specimen

D = Deswollen weight of the test specimen

F = weight fraction of insoluble components

A_o = weight of the absorbed solvent corrected for the swelling increment

ρ_r = density of the rubber

ρ_s = density of solvent.

The value of ρ_r and ρ_s taken were

ρ_r(NR) = 0.921 g/cm^3

ρ_r(IIR) = 0.917 g/cm^3

ρ_r(EPDM) = 0.860 g/cm^3

ρ_s(Toluene) = 0.886 g/cm^3

In the case of vulcanizates containing HAF black, the values of V_r obtained as above, were converted into V_{ro}, (the value of V_r in the absence of the black) by means of the following equation which was derived by Porter.[8]

$$V_{ro}/V_r = 0.56\, e^{-Z} + 0.44$$

where, Z = weight fraction of filler.

The crosslink density ($1/2M_c$) was then determined from V_{ro} using the Flory-Rehner equation,

$$1/2M_c = \frac{-\left[\ln(1-V_{ro}) + V_{ro} + \chi V_{ro}^2\right]}{2\rho_r V_s (V_{ro})^{1/3}}$$

where, V_s = molar volume of solvent

V_s(toluene) = 106.2 cc/mol and

χ = parameter characteristic of interaction between rubber and solvent

Values of parameter χ taken for calculations were the following:[9,10]

For NR-Toluene = 0.420

IIR-Toluene = 0.557

EPDM-Toluene = 0.490

b) Determination of gm equivalent of carboxyl groups

The principle of this method is based on the reaction of carboxyl group attached to the rubber with potassium hydroxide and the excess potassium hydroxide is titrated against hydrochloric acid.

Two per cent solutions of the samples were prepared in cyclohexane. 50 ml of the solution was mixed with 5 ml of ethanolic potassium hydroxide (0.5 N) in an R.B. flask and refluxed for 1½ hours. After cooling it was titrated against isopropanolic hydrochloric acid (0.25 N) using phenolphthalein as indicator.

A blank run was taken without sample. Gram equivalent of carboxyl groups was calculated as follows:

$$\text{Acid number (A)} = \frac{(x-y) \times N \times 56.1}{W}$$

where, x = volume of hydrochloric acid consumed in the blank in cc y = volume of hydrochloric acid consumed in each experiment in cc

N = normality of potassium hydroxide solution and

W = weight of the sample taken.

$$\text{Maleic anhydride percentage (M)} = \frac{A \times E_W}{2 \times 561}$$

where, E_W = equivalent weight of maleic anhydride.

$$\text{Gram equivalent of carboxyl group per 100 gm rubber} = \frac{M \times 100}{E_W \times W}$$

c) <u>Determination of iodine value</u>

0.2 gm of sample was dissolved in 25 ml chloroform in a 500 ml conical flask. 20 ml of 0.1 N solution of iodine monochloride in glacial acetic acid was added. It was then stoppered and allowed to stand in darkness for 30 minutes. After that 100 ml 10% potassium iodide solution was added. The resultant 2 phase solution was titrated against thiosulphate using starch as indicator. Iodine value was calculated as,

$$\text{Iodine value} = \frac{(V_1 - V_2) \times 12.69 \times n}{m}$$

where, n = normality of thio

m = weight of polymer sample

V_2 and V_1 = volume of thio for the sample and blank.

d) Thin layer chromatography

Thin layer chromatography was done using silica gel (Kieselgel G Merck) with methanol as the solvent.

e) Infrared spectroscopy

IR spectra given in the investigations were taken in a Beckmann infrared spectrophotometer. Different functional groups and structural features in the molecule absorb electromagnetic radiations at characteristic frequencies.[11] Absorption at 1800 cm^{-1} was made use of in this study because it is appropriate for carbonyl group determination.

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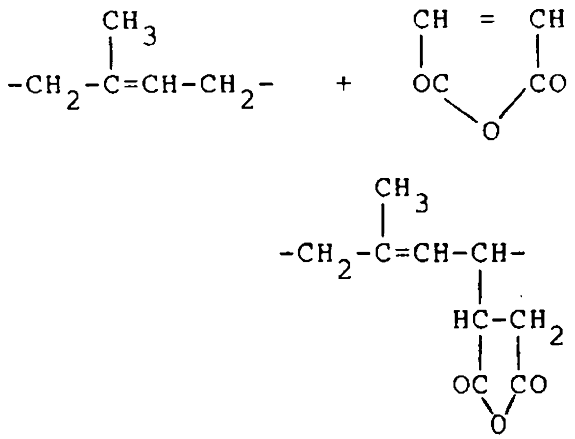
Chapter 3

CARBOXYLATION OF IIR AND EPDM FOR IMPROVING THE MECHANICAL PROPERTIES OF NR/IIR AND NR/EPDM BLENDS

NR/IIR and NR/EPDM blends are commercially important particularly as a means of improving the ageing resistance of NR without losing much of its mechanical properties.[1] However, these blends usually display poor mechanical properties, mainly due to the difference between the reactivities of elastomers with curatives and/or due to the difference between solubilities of curatives in the elastomers.[2]

One way of reducing the problem of cure rate incompatibility in these blends is to functionalise the slow curing rubber (IIR in NR/IIR and EPDM in NR/EPDM blends). For example, carboxylic acid groups can be incorporated into these elastomers either by copolymerising with monobasic acids like acrylic acid or methacrylic acid or by treatment with maleic acid or maleic anhydride at high temperature in presence of a promoter.[3-13]

The reaction between maleic anhydride (MAH) and rubber has been studied in solution, by milling and by heating in the solid phase.[14-16] The most probable product formed between rubber and MAH is,[17]



Thus the modification process gives rise to molecules of rubbers which have pendant succinic anhydride groups. These groups, in the presence of metal oxides, become the junctures of an ionomeric network, possibly by the formation of ion-cluster crosslinks.[18,19] These carboxylic elastomers can also be crosslinked with sulphur in the presence of accelerators by means of the double bonds. It has been reported that mixed crosslinking systems containing both ionic and sulphur crosslinks give vulcanizates with improved mechanical properties.[20,21]

In this study IIR and EPDM rubbers are functionalised by using MAH, and then blended with NR to improve the performance of NR/IIR and NR/EPDM blends. Improvement in mechanical behaviour is likely due to the fact that functionalised IIR and EPDM can be ionically crosslinked by the action of zinc oxide. Thus an ionic crosslink network can be formed in the IIR or EPDM phase which is not competitive with NR unlike the accelerated sulphur vulcanization system which reacts rapidly with NR compared to IIR or EPDM. Carboxylated IIR/NR and carboxylated EPDM/NR blends will be referred to as modified blends whereas unmodified IIR/NR and unmodified EPDM/NR blends as conventional blends.

EXPERIMENTAL

Modification of IIR and EPDM by Carboxylation

Maleic anhydride and a promoter were added to IIR or EPDM in a Brabender plasticorder model PL 3S employed with roller mixing heads rotating at 60 rpm. The various promoters used for the study were MBT, MBTS, DCP and BP. 5 phr ZnO was added to the modified samples to facilitate ionic crosslinking and 2 phr stearic acid as a lubricant on a laboratory mixing mill. Thermal stability of the ionic crosslinks likely to be formed was evaluated by taking the cure curves of these compounds at different temperatures from 40 to 160°C on a Goettfert elastograph. A substantial curing was observed for MAH modified samples in which MBT was used as the promoter. Curing was not observed with promoters other than MBT, which clearly demonstrates the superiority of MBT among the promoters tried. So further studies were done with MBT as promoter. Other curing aids such as hexamethylene-diamine and ethylene glycol were also tried in place of zinc oxide. But curing was not observed at any temperature.

Inorder to optimise the concentration of MAH and MBT for efficient cabroxylation, the carbonyl groups attached to the rubber at varying concentration of MAH and MBT were calculated volumetrically.[22] Keeping the amount of MBT at a constant level (0.4 phr) MAH concentration was varied from 2 to 10 phr. In each case the number of gram equivalents of carbonyl group attached was estimated. The concentration of MBT was then varied from 0.2 to 0.8 phr at a fixed maleic anhydride (4 phr) level. The number of gram equivalents of carbonyl group attached was again estimated. Inorder to study the effect of temperature on carboxylation the temperature of the mixing chamber was varied from 170 to 210°C. The samples taken at different temperatures were mixed with ZnO and stearic acid and the cure curves of the compounds were taken at 50°C to compare the extent of carboxylation.

The IR spectra of the carboxylated rubbers were taken after removing the unreacted maleic anhydride by washing with water. Thin layer chromatographic technique was used to confirm the absence of free maleic anhydride in the carboxylated rubbers. Iodine values of the carboxylated rubbers were also determined and compared with those of the unmodified IIR and EPDM samples.

Determination of Mechanical Properties of Modified IIR/NR and Modified EPDM/NR Blends

The carboxylated IIR and EPDM samples were then blended with NR over the whole composition range as follows. Masterbatches of IIR and EPDM with 50 parts of HAF black were taken in a Francis Shaw intermix. Maleic anhydride and MBT were added along with black to one of the batches. The formulations employed are shown in Table 3.1. The intermix was set at a temperature of 80°C. After mixing it reached upto 190°C. Mixing was carried out for 10 minutes and then the batch was dumped off.

These masterbatches were blended with NR on a laboratory mixing mill. The curatives and other compounding ingredients were also added on the mill. Formulationsof the mixes are shown in Tables 3.2 and 3.3. The optimum cure

Table 3.1: Formulations of conventional and carboxylated IIR and EPDM masterbatches

Materials	BATCH No.			
	1	2	3	4
IIR	600	600	--	--
EPDM	--	--	600	600
Carbon black (HAF N-330)	300	300	300	300
Naphthenic oil	48	48	48	48
MAH	--	24	--	24
MBT	--	2.4	--	2.4

NR	100	—	—	90	90	80	80	70	70	60	60	50	50	40	40	30	30	20	20	10	10
IIR	—	100	—	10	—	20	—	30	—	40	—	50	—	60	—	70	—	80	—	90	—
IIR (modified)	—	—	100	—	10	—	20	—	30	—	40	—	50	—	60	—	70	—	80	—	90
Zinc oxide	5.0	4.0	8.0	4.9	5.3	4.8	5.6	4.7	5.9	4.6	6.2	4.5	6.5	4.4	6.8	4.3	7.1	4.2	7.4	4.1	7.7
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
MBTS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0.0	1.0	1.0	0.1	0.1	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.3	0.8	0.9	0.9
Carbon black (HAF N-330)	50	—	—	45	45	40	40	35	35	30	30	25	25	20	20	15	15	10	10	5	5
Naphthenic oil	8.0	—	—	7.2	7.2	6.4	6.4	5.6	5.6	4.8	4.8	4.0	4.0	3.2	3.2	2.4	2.4	1.6	1.6	0.8	0.8
Sulphur	2.5	1.5	1.5	2.4	2.4	2.3	2.3	2.2	2.2	2.1	2.1	2.0	2.0	1.9	1.9	1.8	1.8	1.7	1.7	1.6	1.6

Table 3.2: Formulations of conventional and modified NR/IIR blends

NR	100	—	—	90	90	80	80	70	70	60	60	50	50	40	40	30	30	20	20	10	10
EPDM	—	100	—	10	—	20	—	30	—	40	—	50	—	60	—	70	—	80	—	90	—
EPDM (modified)	—	—	100	—	10	—	20	—	30	—	40	—	50	—	60	—	70	—	80	—	90
Zinc oxide	5.0	4.0	8.0	4.9	5.3	4.8	5.6	4.7	5.9	4.6	6.2	4.5	6.5	4.4	6.5	4.3	7.1	4.2	7.4	4.1	7.7
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
MBTS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0.0	1.0	1.0	0.1	0.1	0.2	0.2	0.3	0.3	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9
Carbon black (HAF N-330)	50	—	—	45	45	40	40	35	35	30	30	25	25	20	20	15	15	10	10	5	5
Naphthenic oil	8.0	—	—	7.2	7.2	6.4	6.4	5.6	5.6	4.8	4.8	4.0	4.0	3.2	3.2	2.4	2.4	1.6	1.6	0.8	0.8
Sulphur	2.5	1.5	1.5	2.4	2.4	2.3	2.3	2.2	2.2	2.1	2.1	2.0	2.0	1.9	1.9	1.8	1.8	1.7	1.7	1.6	1.6

Table 3.3: Formulations of conventional and modified NR/EPDM blends

times of the compounds were determined on a Goettfert elastograph at 150°C. The compounds were then vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press at 150°C. Dumbell shaped tensile test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were measured on a Zwick universal testing machine. The ageing resistance of the vulcanizates was studied after ageing the vulcanizates for 24 h at 100°C in a laboratory air oven. The swelling measurements were done in toluene.

RESULTS AND DISCUSSION

Carboxylation of IIR and EPDM

Fig.3.1 shows the cure curves of the carboxylated IIR and EPDM rubbers with MBT as promoter to which zinc oxide had been added. Curing was observed for the compounds only below 50°C which is obviously due to the lack of thermal stability of the ionic crosslinks at high temperature. Fig.3.2 shows the amount of carbonyl group attached to the polymer chain as a function of the amount of maleic anhydride keeping the amount of MBT at a constant level (0.4 phr). It is observed that the amount of carbonyl group increases with increase in the MAH concentration upto about

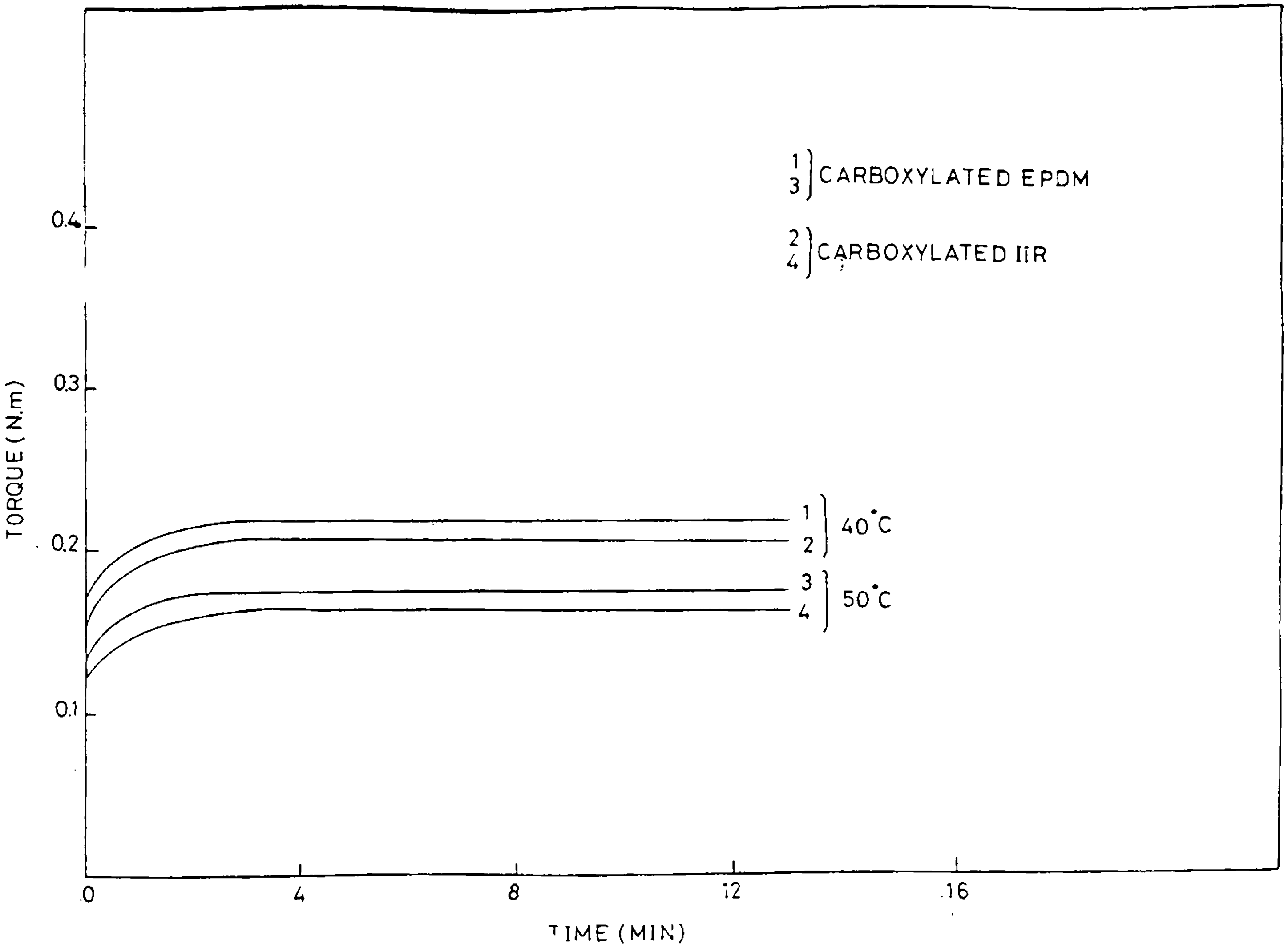


Fig.3.1: Cure curves of the carboxylated IIR and EPDM

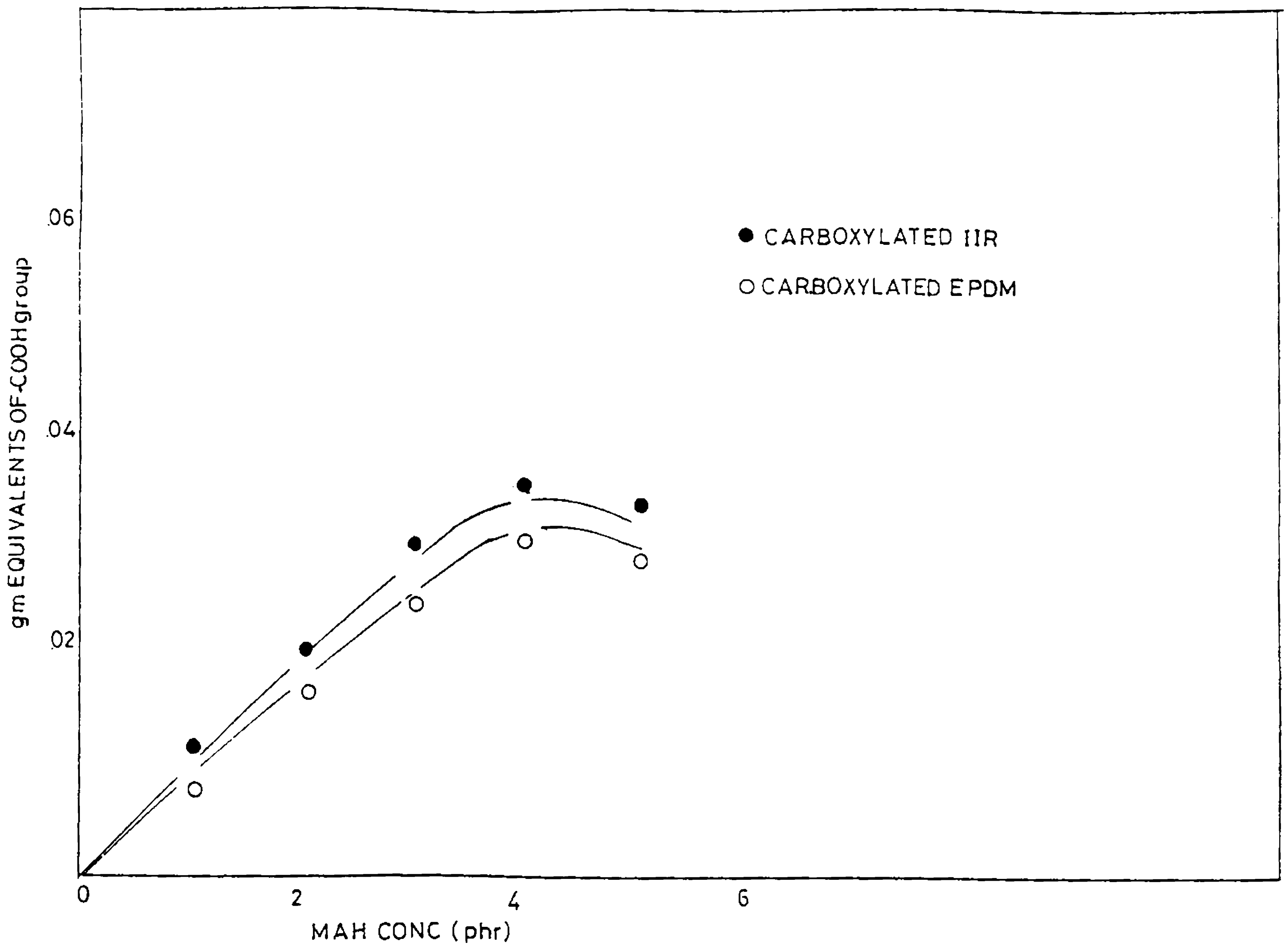


Fig.3.2: Effect of MAH concentration on carboxylation of IIR and EPDM

4 phr and thereafter remains more or less the same. The amount of carbonyl group attached as a function of the amount of MBT keeping the concentration of MAH at a constant level (4 phr) is shown in Fig.3.3. The effect of temperature on carboxylation is shown in Fig.3.4. The maximum torque, a measure of crosslink density, increases with mixing temperature upto about 190°C and thereafter levels of. Hence it may be assumed that a mixing temperature of 190°C is optimum. Thus for efficient carboxylation optimum concentration of MAH and MBT were taken as 4 phr and 0.4 phr and temperature as 190°C.

The carboxylation was further confirmed from IR studies. A peak at 1800 cm^{-1} (Fig.3.5) indicates the presence of -COOH group.[23] It may be observed that the intensity of the peak increase upto a level of 4 phr MAH and thereafter remains more or less the same. Table 3.4 shows the iodine values of the modified rubbers along with those

Table 3.4: Iodine values of IIR and EPDM

Rubber	Iodine values
IIR	10.5
IIR (Carboxylated)	8.79
EPDM	16.96
EPDM (Carboxylated)	15.07

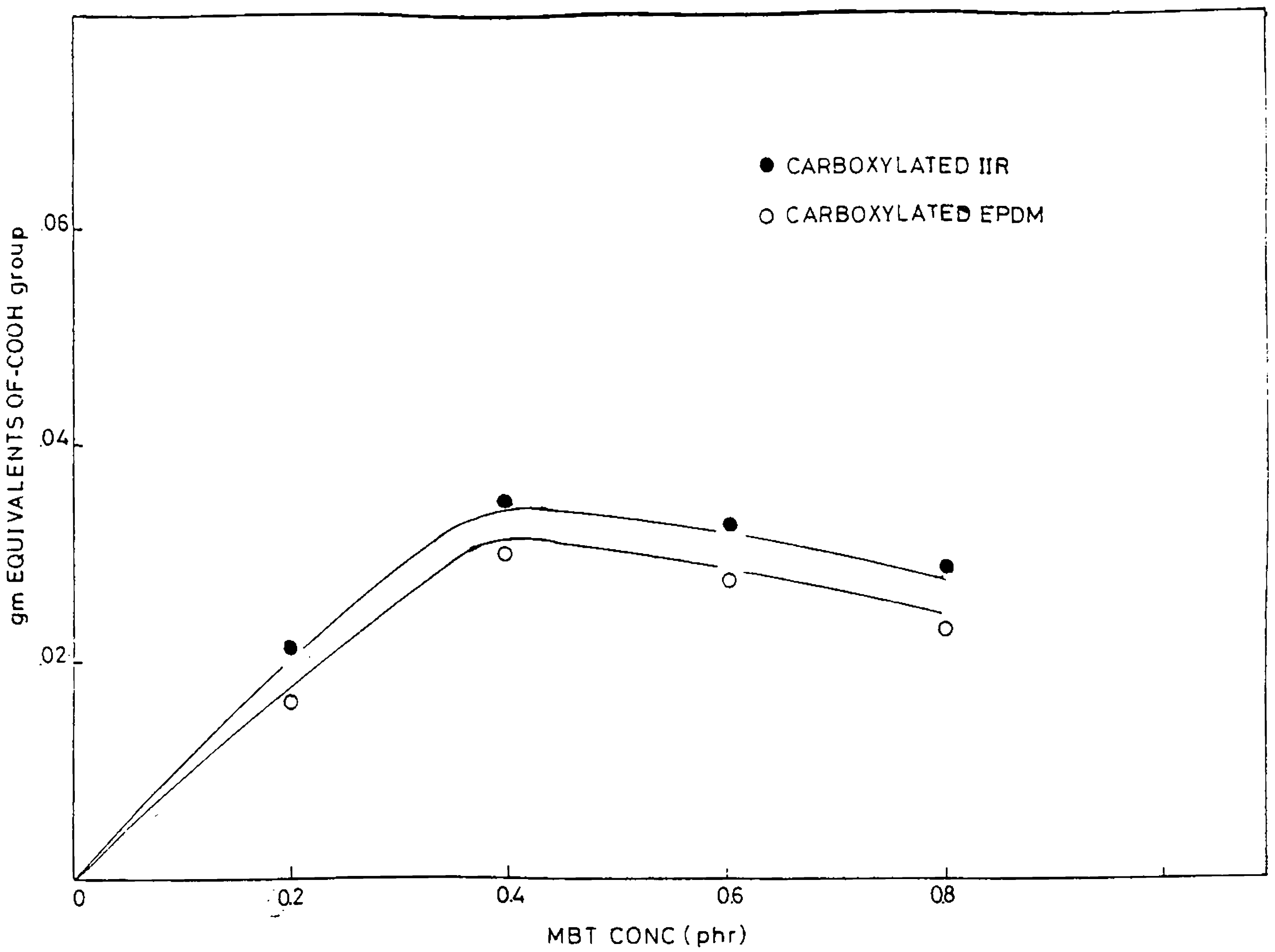


Fig.3.3: Effect of MBT concentration on carboxylation of IIR and EPDM

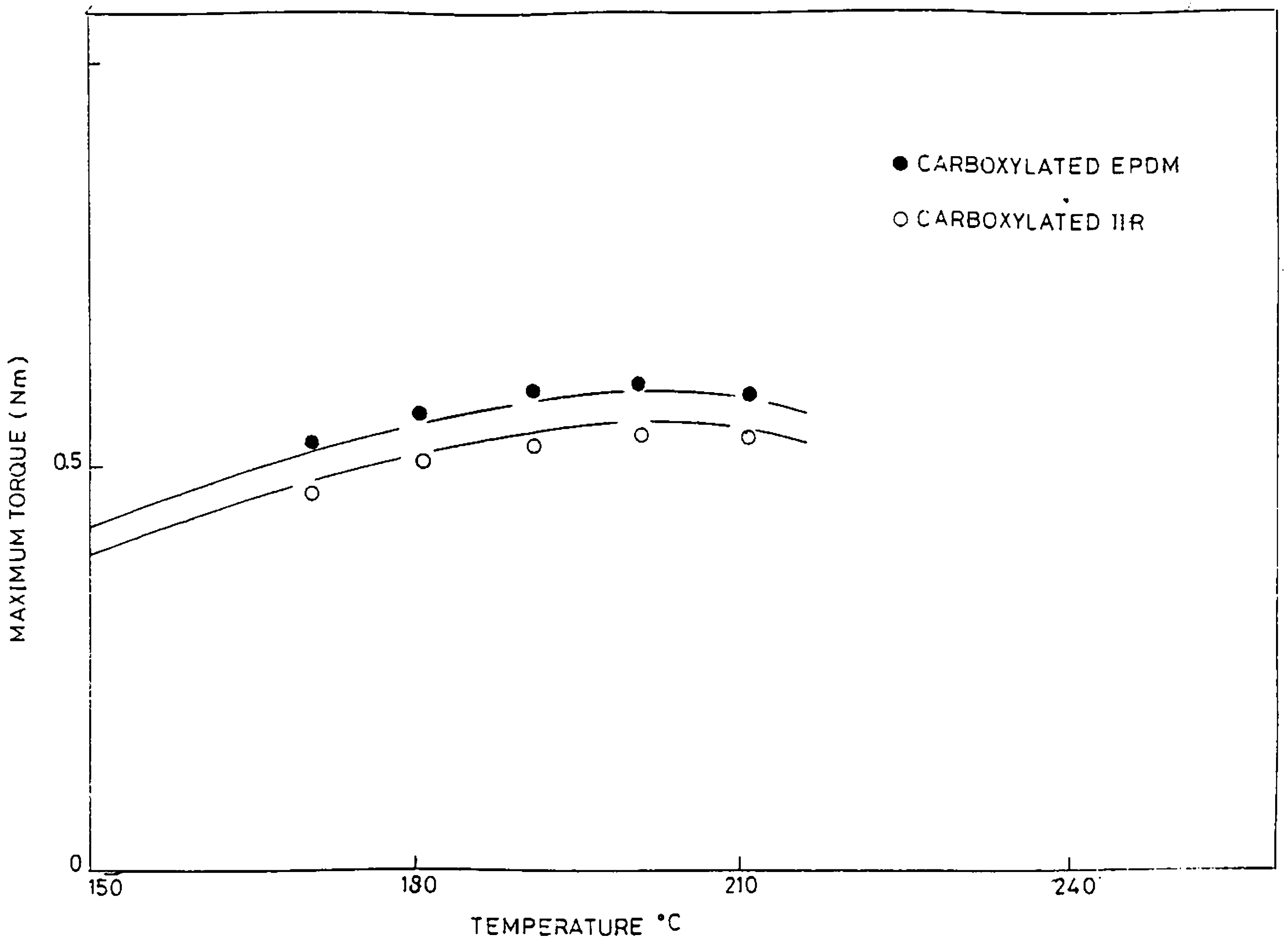


Fig.3.4: Effect of temperature on carboxylation of IIR and EPDM

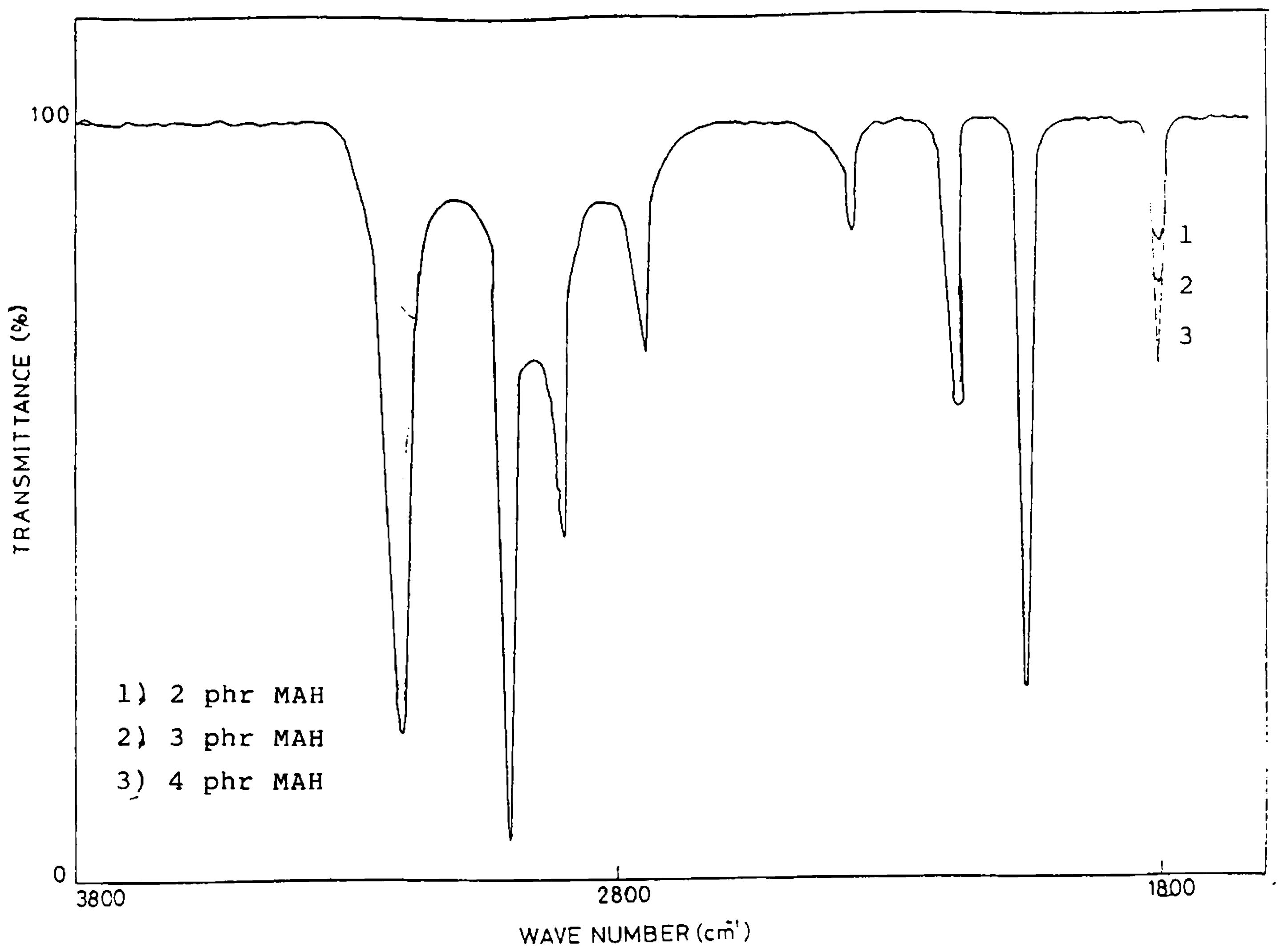


Fig.3.5: IR spectrum of carboxylated EPDM

of the conventional rubbers. There is only a slight change in iodine values of the conventional and modified rubbers. So it may be assumed that MAH molecules are attached to IIR and EPDM as pendant succinic anhydride groups.

The cure curves of conventional and modified IIR and EPDM compounds are shown in Figs.3.6 and 3.7. The curing behaviour of both the conventional and modified rubbers is similar which indicates that there is no cure retardation due to the carboxylation of these rubbers. There is only a slight difference between the cure times of the conventional and modified rubbers. The maximum torque is almost the same in both cases. Cure characteristics are given in Table 3.5. Table 3.6 shows the swelling ratio of the conventional and modified samples. This further shows that carboxylation does not adversely affect the curing behaviour or the crosslink density in IIR and EPDM.

Mechanical Properties of the Conventional and Modified NR/IIR and NR/EPDM Blends

Tables 3.5, 3.7 and 3.8 show the cure characteristics of the compounds determined at a temperature of 150°C. From the table it is clear that in the conventional

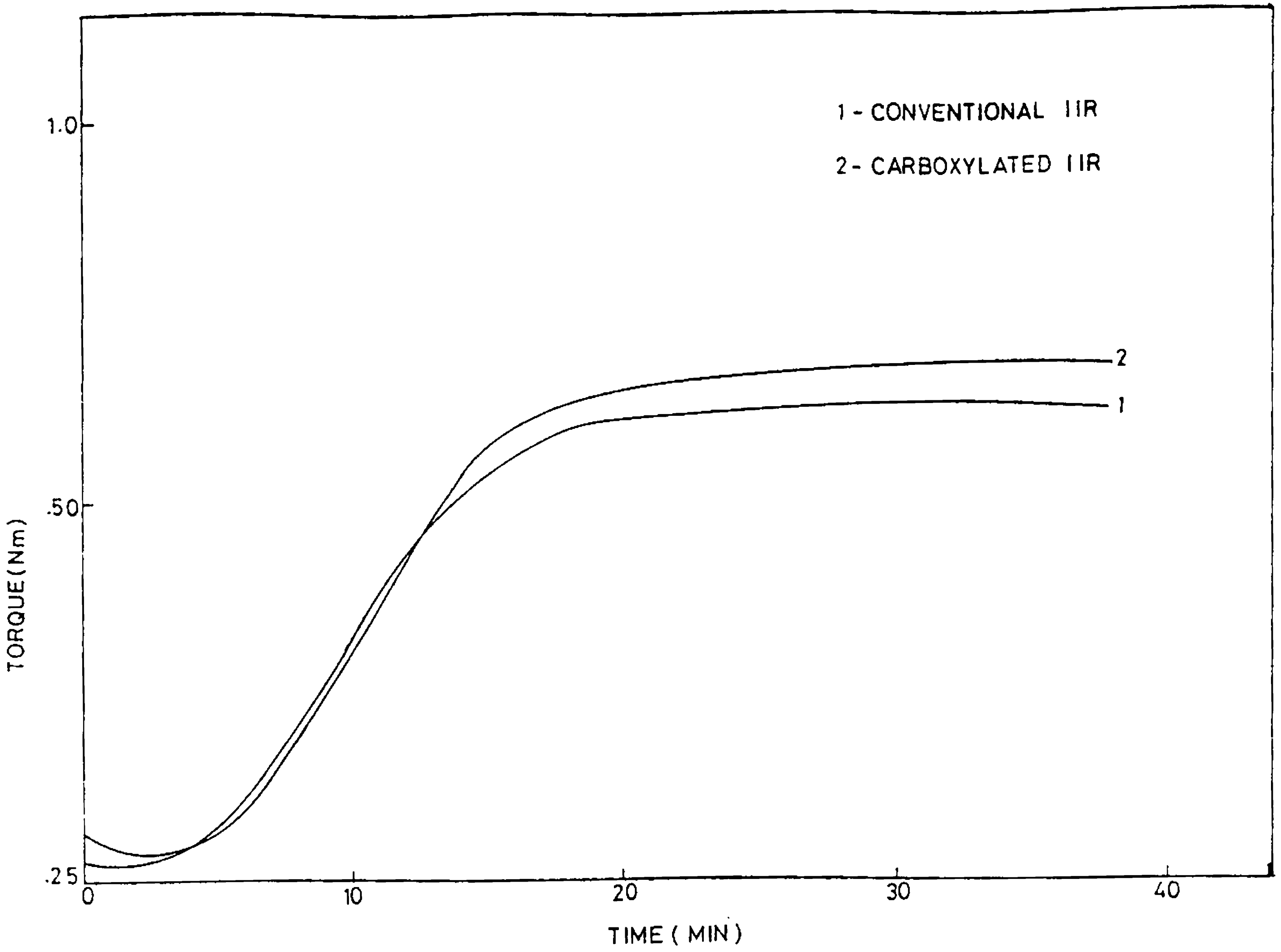


Fig.3.6: Cure curves of conventional and carboxylated IIR

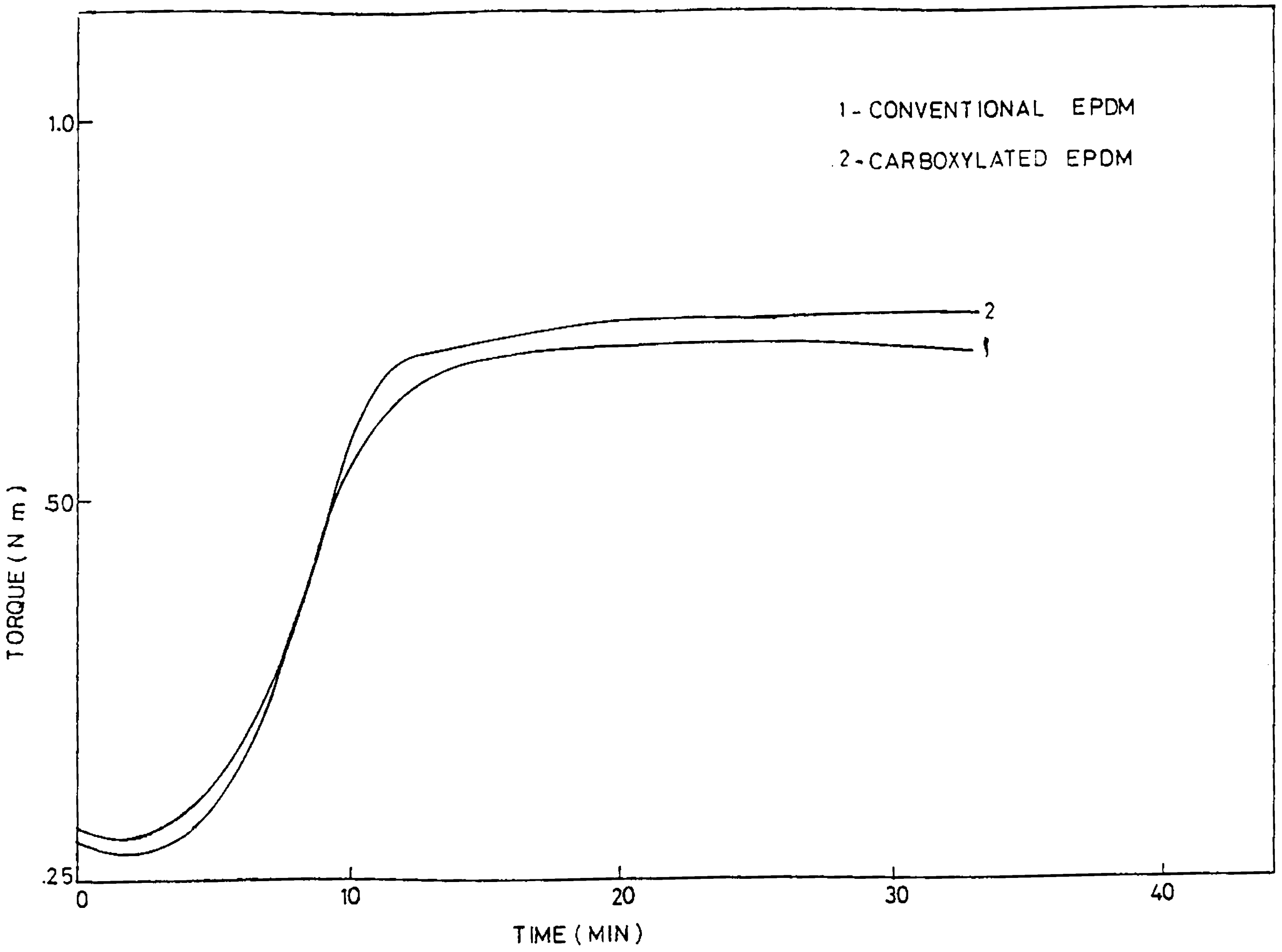


Fig.3.7: Cure curves of conventional and carboxylated EPDM

Table 3.5: Cure characteristics of IIR, EPDM and NR

Rubber	Cure time 150°C (Min.)	Scorch time (Min.)	Min.torque (Nm)	Max.torque (Nm)
IIR	15	3.6	0.02	0.62
IIR (carboxylated)	16	3.8	0.04	0.69
EPDM	11	3.2	0.02	0.70
EPDM (carboxylated)	12	3.6	0.05	0.75
NR	8	2.8	0.02	0.29

Table 3.6: Swelling ratios of IIR and EPDM

Rubber	Swelling ratios $\left(\frac{\text{Swollen wt. - initial wt.}}{\text{initial wt.}}\right)$
IIR	1.90
IIR (carboxylated)	1.96
EPDM	1.83
EPDM (carboxylated)	2.00

Table 3.7: Cure characteristics of NR/IIR blends

Stock NR/IIR	CONVENTIONAL				MODIFIED			
	Cure time 150°C (Min.)	Scorch time (Min.)	Min. torque (Nm)	Max. torque (Nm)	Cure time 150°C (Min.)	Scorch time (Min.)	Min. torque (Nm)	Max. torque (Nm)
90/10	8	2.7	0.02	0.32	9	2.8	0.02	0.33
80/20	6	2.6	0.03	0.34	8	2.8	0.04	0.35
70/30	4.7	2.6	0.03	0.35	6	2.7	0.04	0.36
60/40	5.5	2.5	0.04	0.34	7	2.7	0.05	0.36
50/50	7	2.7	0.05	0.37	8.5	2.9	0.06	0.38
40/60	8	2.8	0.05	0.40	9	3.0	0.07	0.41
30/70	9	3.1	0.06	0.43	9.5	3.2	0.08	0.45
20/80	11	3.2	0.07	0.46	11.5	3.3	0.09	0.49
10/90	12	3.4	0.07	0.50	13	3.6	0.10	0.50

Table 3.8: Cure characteristics of NR/EPDM blends

Stock NR/EPDM	CONVENTIONAL				MODIFIED			
	Cure time 150°C (Min.)	Scorch time (Min.)	Min. troque (Nm)	Max. torque (Nm)	Cure time 150°C (Min.)	Scorch time (Min.)	Min. torque (Nm)	Max. torque (Nm)
90/10	7	2.6	0.03	0.32	7	2.7	0.03	0.35
80/20	6	2.4	0.04	0.37	6.25	2.5	0.04	0.39
70/30	5.5	2.3	0.04	0.42	7	2.4	0.05	0.47
60/40	5.5	2.2	0.05	0.45	7	2.3	0.06	0.47
50/50	6	2.5	0.05	0.51	7.50	2.5	0.06	0.54
40/60	7	2.6	0.06	0.55	8	2.7	0.07	0.58
30/70	8	2.6	0.07	0.59	8.5	2.7	0.08	0.62
20/80	8.5	2.8	0.08	0.61	9.5	2.9	0.09	0.66
10/90	9.5	3	0.08	0.62	9.5	3.2	0.1	0.70

blends NR takes the major share of curatives and gets overcured. But in the case of modified blends the situation is different. The chemical modification of IIR and EPDM makes them more polar, reduces curative migration and reduces solubility difference of curatives which helps to attain a covulcanized state. Thus the modified blends show longer cure times compared to the conventional ones. This is an indication of cocuring of both the phases. Scorch safety is not affected by the chemical treatment. The minimum torque is greater in case of maleic anhydride treated blends. This may be due to the fact that the ionic crosslink network forms quite rapidly by the action of zinc oxide on the succinic anhydride groups. It shows that the elevated temperatures required for accelerated sulphur vulcanization are not necessarily required for the formation of the ionic network. The maximum torque is also higher in the modified blends. This again suggests that a network is formed by the action of zinc oxide on the maleic anhydride modified rubbers. This, ofcourse, is in addition to the network which is formed in the blend due to the accelerated sulphur vulcanization.

Fig.3.8 shows the tensile strengths of the modified NR/IIR blend compared with those of conventional NR/IIR

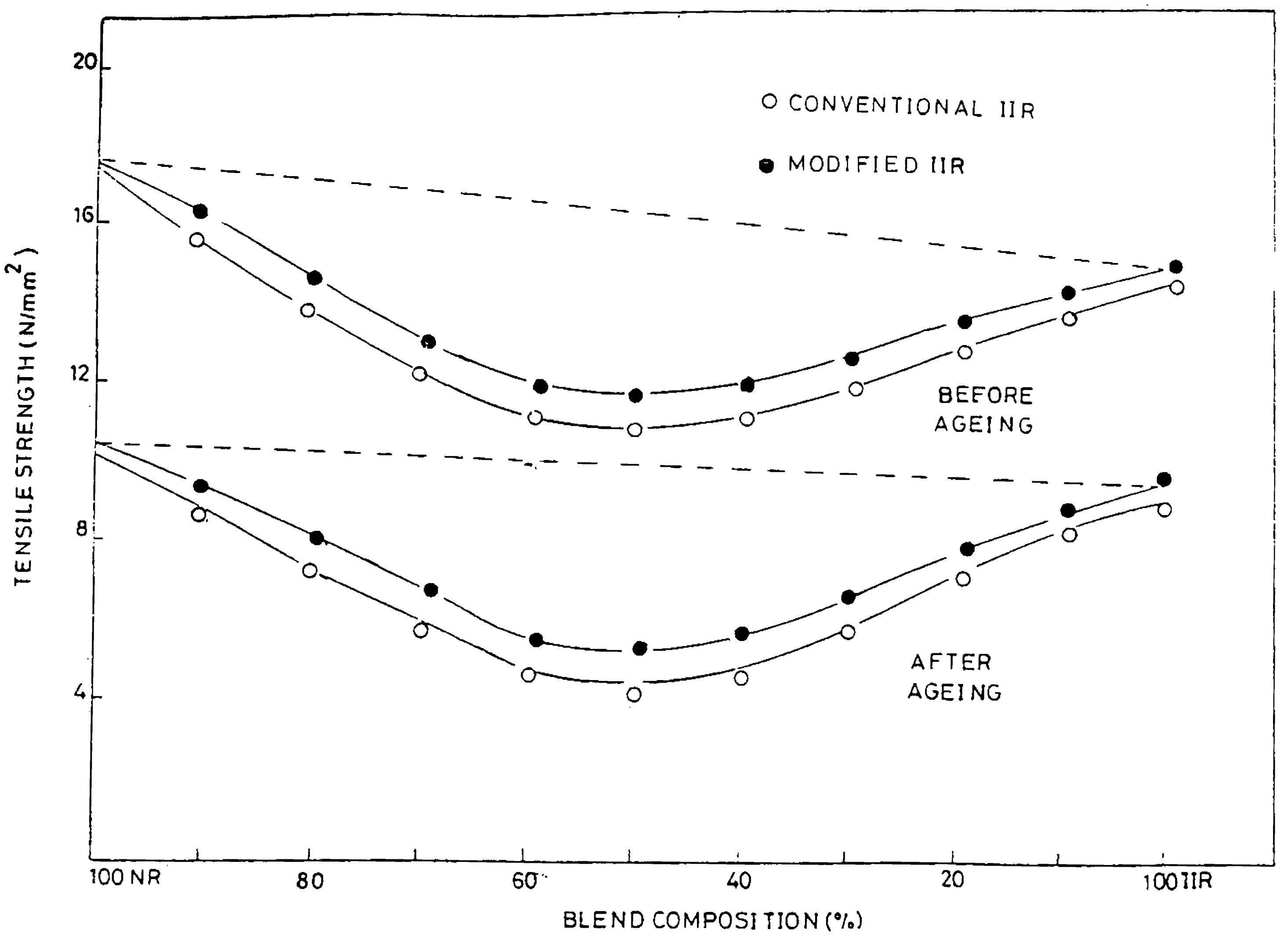


Fig.3.8: Variation of tensile strength with blend composition of NR/IIR blends

blends of different compositions. When the IIR phase is not modified, the tensile strengths obtained deviate much from the linear combination of the individual strengths, indicating poor cocrosslinking. However, when IIR phase is modified, the behaviour is closerto the linear rule, which might be due to the formation of optimum crosslink densities in both the phases. This in turn may be due to the reduction in the migration of the curatives and due to the contribution of ionic crosslinks in the IIR phase. The tensile strength of the blends after ageing are also shown in the figure. The ageing resistance of the blends improve with increase in the IIR concentration. The carboxylation does not seem to affect the ageing resistance. Fig.3.9 shows the tensile strengths of the modified NR/EPDM blends in comparison to the conventional blends. Here also the modified blends show superior strength compared to the conventional blends. The ageing resistance of the blends is also similar to those of the NR/IIR blends and ageing resistance improves with increase in the EPDM content. Fig.3.10 shows the elongation at break of the modified and conventional NR/IIR blends before and after ageing. In the conventional blends NR gets a higher proportion of the curing agents resulting in overcure. The improved EB in the

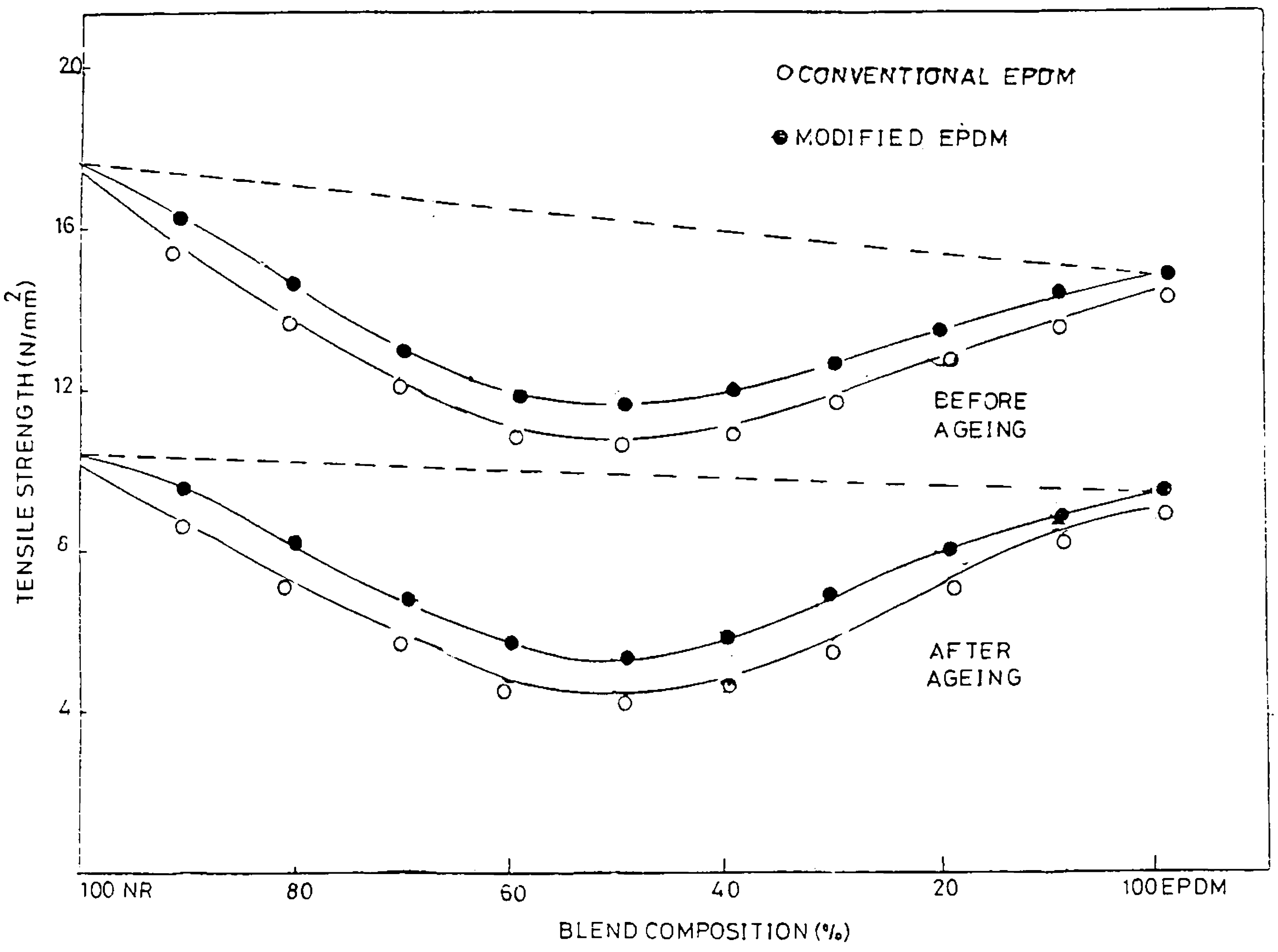


Fig.3.9: Variation of tensile strength with blend composition of NR/EPDM blends

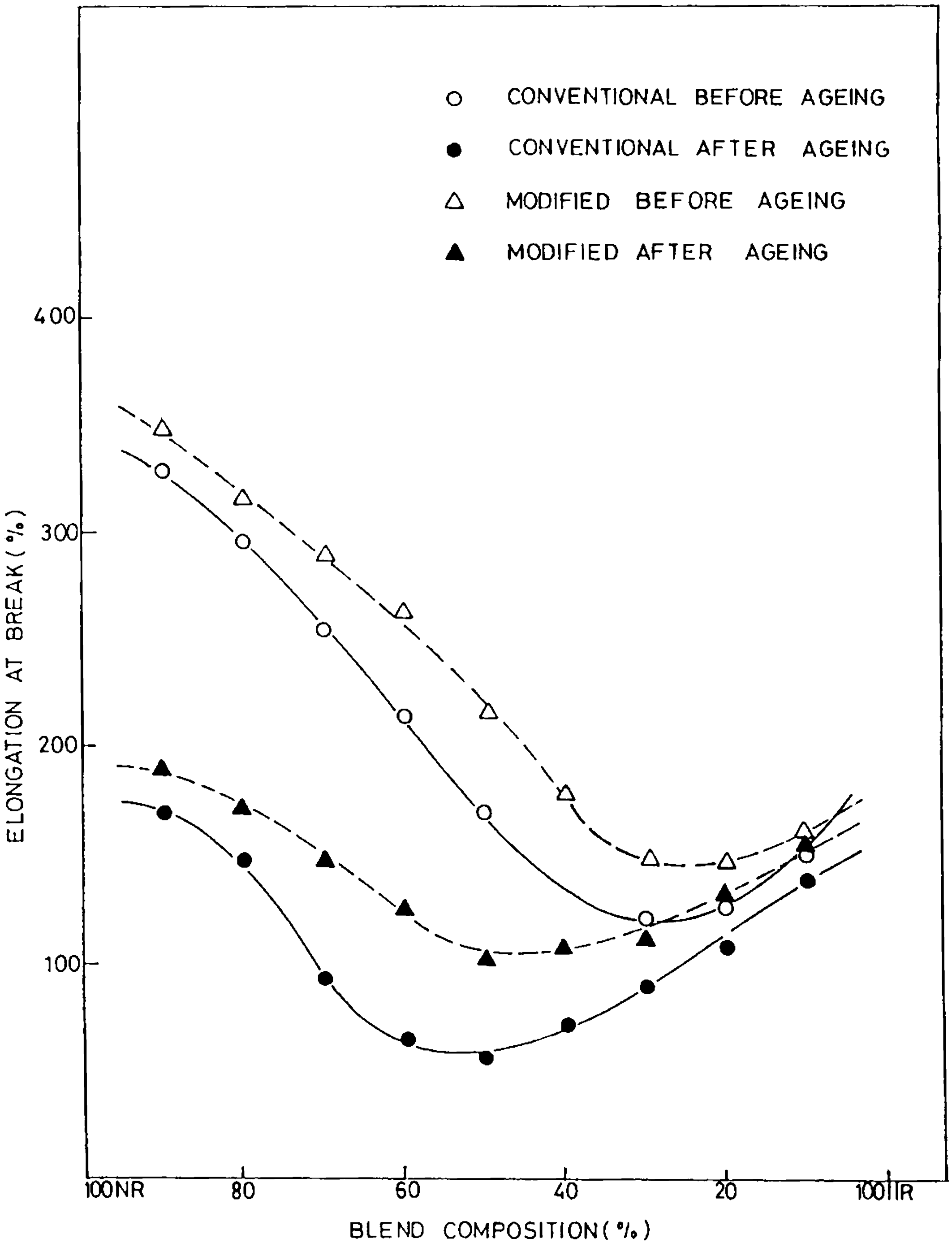


Fig.3.10: Variation of elongation at break with blend composition of NR/IIR blends

case of modified NR/IIR blends points towards optimum crosslink densities in both NR and IIR phases. Similar trends are shown by NR/EPDM blends too (Fig.3.11).

Fig.3.12 gives the modulus at 100% elongation for NR/IIR blends before and after ageing. The reduction in modulus as a result of modification may be due to the absence of overcuring in the NR phase. The variation of modulus with ageing is similar both in the case of conventional and modified blends. The behaviour of NR/EPDM blends before and after ageing is also similar (Fig.3.13).

CONCLUSIONS

1. IIR and EPDM rubber can be carboxylated by maleic anhydride treatment. MBT can act as an efficient promoter for this modification.

2. The carboxylation of IIR and EPDM rubber can improve the mechanical properties of their blends with NR by producing an improved covulcanized state.

3. The ionic crosslinks formed due to carboxylation are stable only below 50°C. However, they probably reinforce normal sulphur crosslinks at ambient temperature and hence improve the mechanical properties.

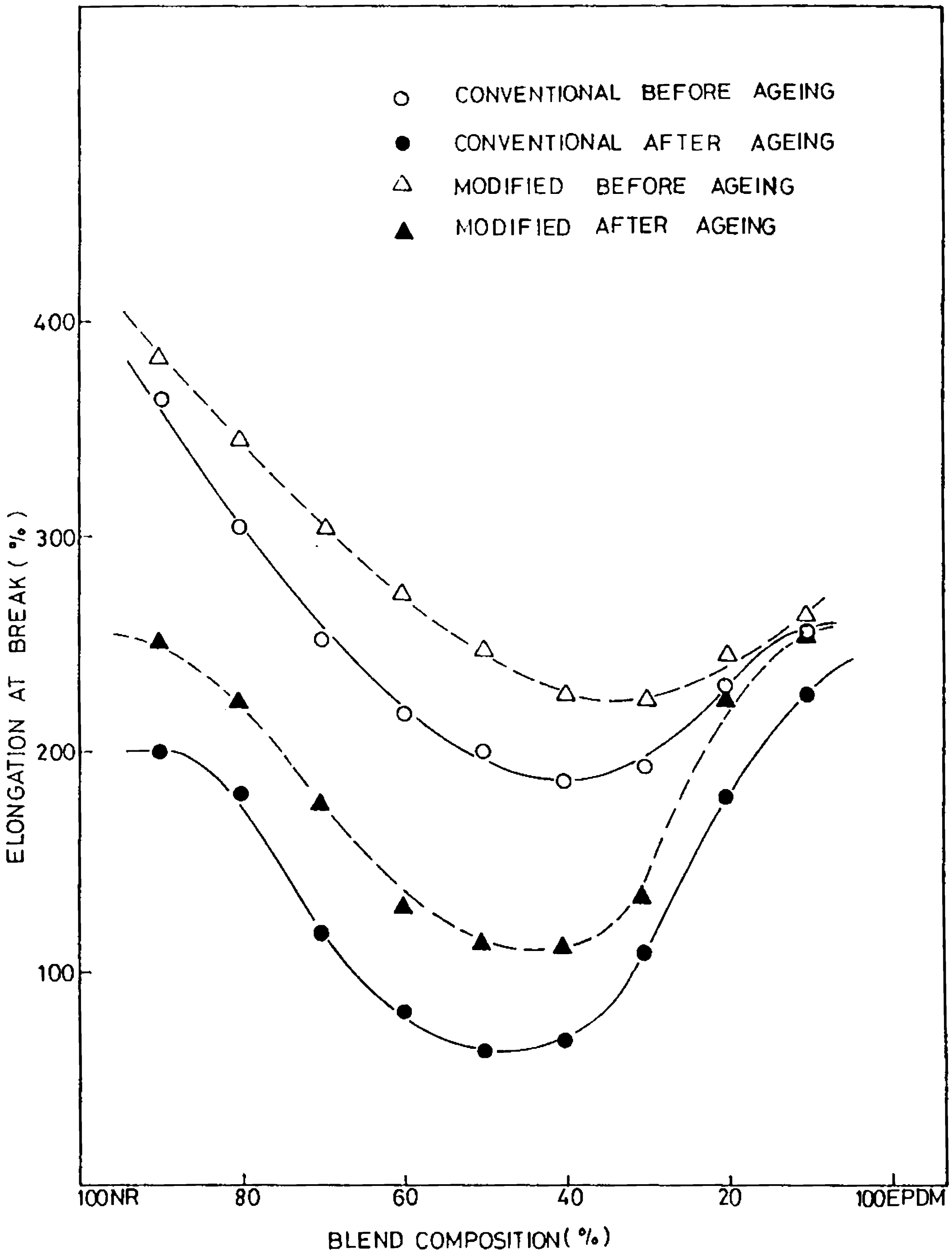


Fig.3.11: Variation of elongation at break with blend composition of NR/EPDM blends

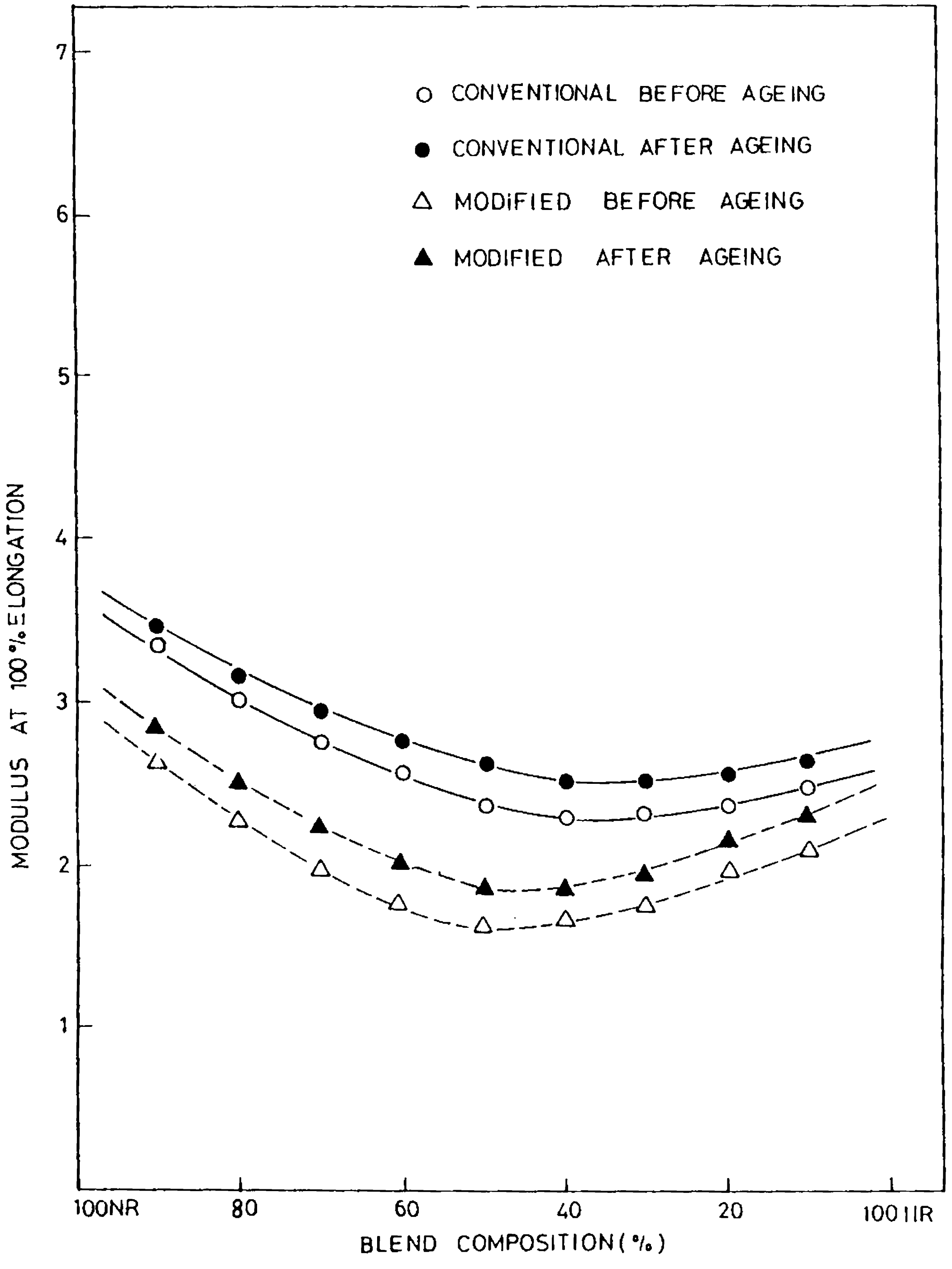


Fig.3.12: Variation of modulus with blend composition of NR/IIR blends

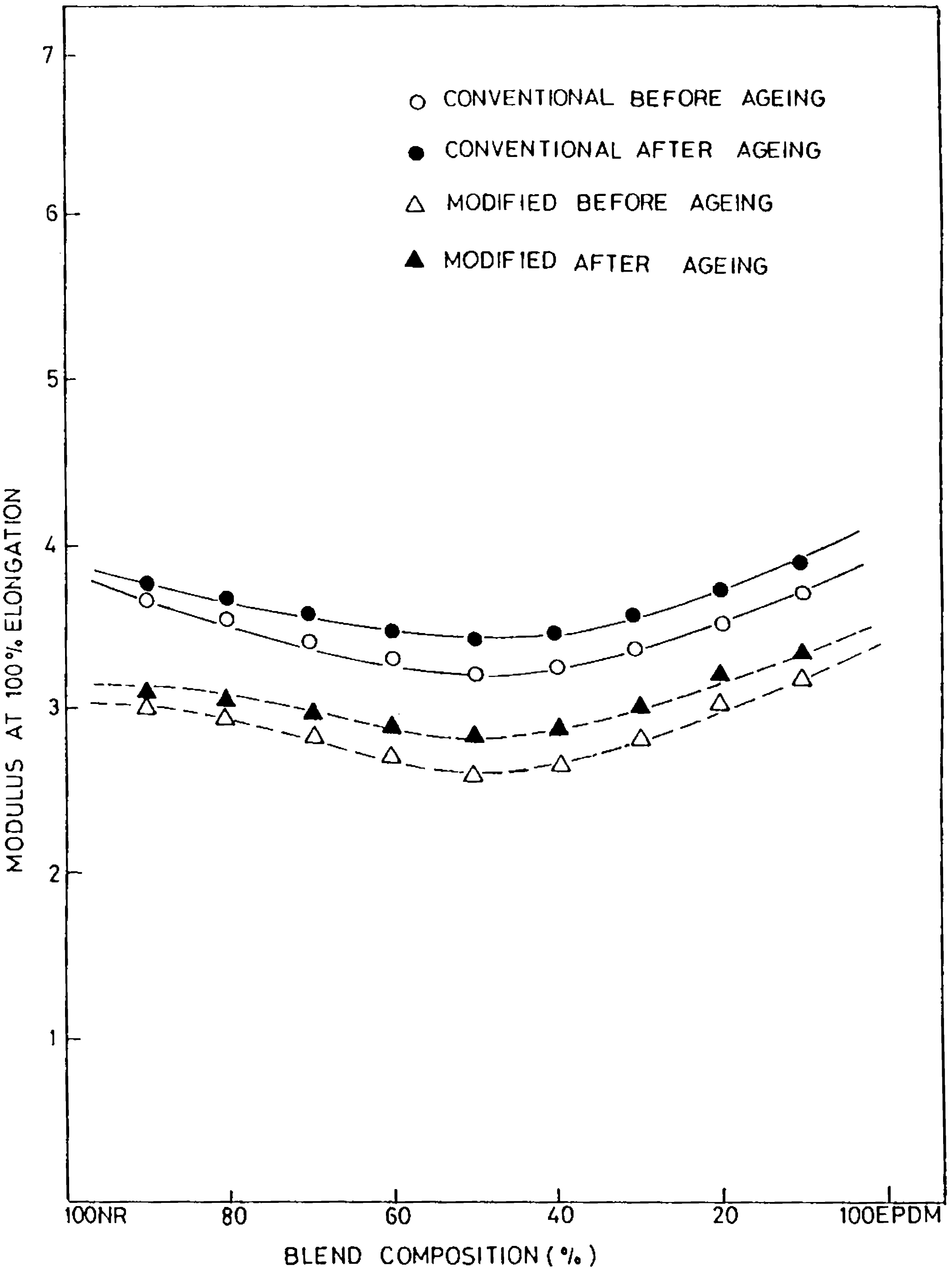


Fig.3.13: Variation of modulus with blend composition of NR/EPDM blends

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Chapter 4

Part I: PRECURING OF IIR AND EPDM FOR IMPROVING THE MECHANICAL PROPERTIES OF NR/IIR AND NR/EPDM BLENDS

NR possesses excellent physical properties and good processing characteristics. But its resistance to heat, oxygen and ozone is not good and hence it is not employed in demanding applications. Blending with IIR or EPDM is a very attractive way of improving the resistance of NR to heat, oxygen and ozone if moderate mechanical properties can be achieved.[1,2] But NR/IIR and NR/EPDM blends usually show inferior mechanical properties compared to the average properties of the constituent elastomers. The main reason for this deterioration in mechanical properties is that both rubbers do not get cured to their optimum crosslink densities or attain a covulcanized state during vulcanization. In this chapter, the effect of precuring the slower curing rubber (IIR in NR/IIR and EPDM in NR/EPDM blends) as a possible route to attain optimum crosslink densities in both the phases of NR/IIR and NR/EPDM blends is reported.

EXPERIMENTAL

Determination of Optimum Precuring Levels

The optimum level of precuring that has to be given to the IIR or EPDM phase was determined from the variation of tensile properties of blends of NR/IIR and NR/EPDM with variation of precuring. IIR and EPDM compounds were prepared on a laboratory mixing mill (6"x12") according to ASTM D 3182 (1982) as per formulations given in Table 4.1. These compounds were sheeted out in the mixing mill at a thickness of about 3 mm and then precured for different times at different temperatures varying from 120 to 160°C in a laboratory air oven. The crosslink densities of the precured IIR and EPDM rubbers were evaluated by the extent of their swelling in toluene.[3,4] The precured compounds were then blended with masticated NR in various compositions on the mill and then compounding ingredients for NR were added. The compounds were then vulcanized upto the respective optimum cure times and the tensile properties of the vulcanizates were determined.

Mechanical Properties of NR/IIR and NR/EPDM Blends

IIR and EPDM rubbers, precured upto the optimum levels, were blended with masticated NR at various percentages. The compounding ingredients required for NR were then added. The optimum cure times were determined on a Goettfert elastograph model 67.85 as per ASTM D 1646 (1981). The compounds were then vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press

Table 4.1: Formulations of NR, IIR and EPDM

Natural rubber	100.0	--	--
Isobutylene-isoprene rubber	--	100.0	--
Ethylene-propylene-diene rubber	--	--	100.0
Zinc oxide	5.0	4.0	4.0
Stearic acid	2.0	2.0	2.0
MBTS	0.6	0.6	0.6
TMTD	0.2	1.0	1.0
Carbon black (HAF N-330)	50.0	50.0	50.0
Naphthenic oil	8.0	8.0	8.0
Sulphur	2.5	1.5	1.5

at 150°C. Dumbell shaped tensile test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties were measured on a Zwick universal testing machine model 1445 using a cross head speed of 500 mm/min. as per ASTM D 412-80.

Angular test specimens were punched out of the compression moulded sheets and tear resistance of the blends was measured on a Zwick universal testing machine according to ASTM D 624. Samples for abrasion resistance, compression set, hardness and resilience were moulded and tested as per relevant ASTM standards. The ageing resistance of the vulcanizates was studied after ageing the samples at 100°C for 24 hours in a laboratory air oven.

Samples of dimensions 6.25 mm thickness and 18 mm diameter were moulded and kept in toluene for 48 hours and the photographs of the swollen samples were taken.

Morphology Studies

Morphology of the tensile fracture surfaces of conventional and modified blends was studied using scanning electron microscope. An optical microscope was used to investigate the surface morphology of the above blends.

RESULTS AND DISCUSSION

Figs.4.1 and 4.2 show the variation in tensile strength of a 50/50 NR/IIR and NR/EPDM blend with precuring time at various temperatures. At every temperature, tensile strength initially increases with the amount of precuring reaches a maximum and decreases thereafter. The precuring level at which the tensile strength of the blend is maximum was taken as the optimum. For attaining maximum tensile strength different times are required at different temperatures in both cases. At lower temperatures more time is required for attaining the optimum precuring level than at higher temperatures as expected. Table 4.2 shows the optimum precuring time and the corresponding tensile strength at different temperatures for 50/50 NR/IIR and NR/EPDM blends in comparison to the tensile strength of the 50/50 NR/IIR and NR/EPDM blends in which no precuring was given (conventional blends). Maximum tensile strength is not affected much by the temperature of precuring in the range of temperature investigated. Ageing resistance of the blends is also not affected by the precuring temperature. So for further studies precuring of the IIR and EPDM phases were done upto the optimum level at 140°C.

Figs.4.3 and 4.4 show the variation in tensile strength of a 50/50 NR/IIR and NR/EPDM blend with amount

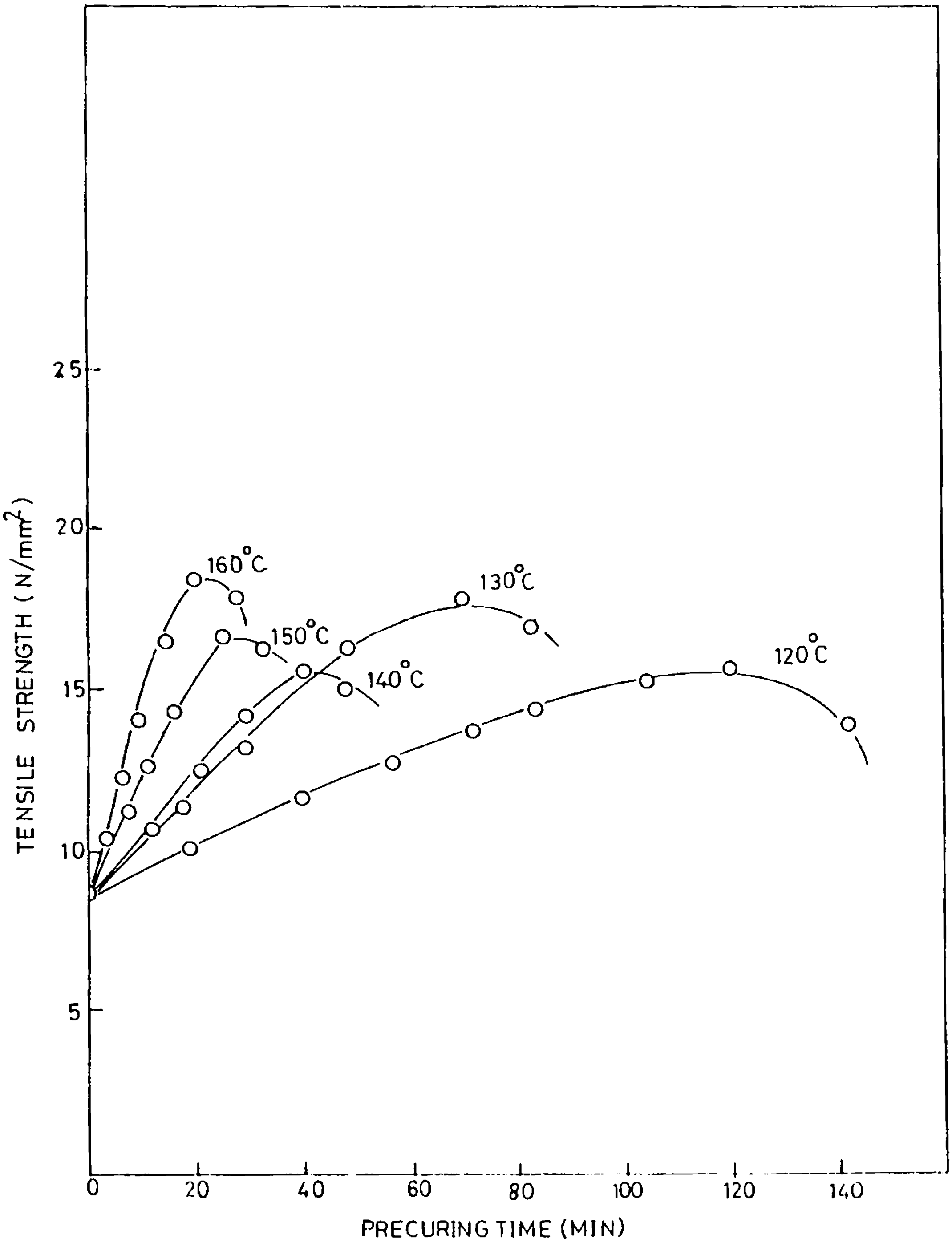


Fig.4.1: Variation of tensile strength of 50/50 NR/IIR blend with precuring time at various temperatures

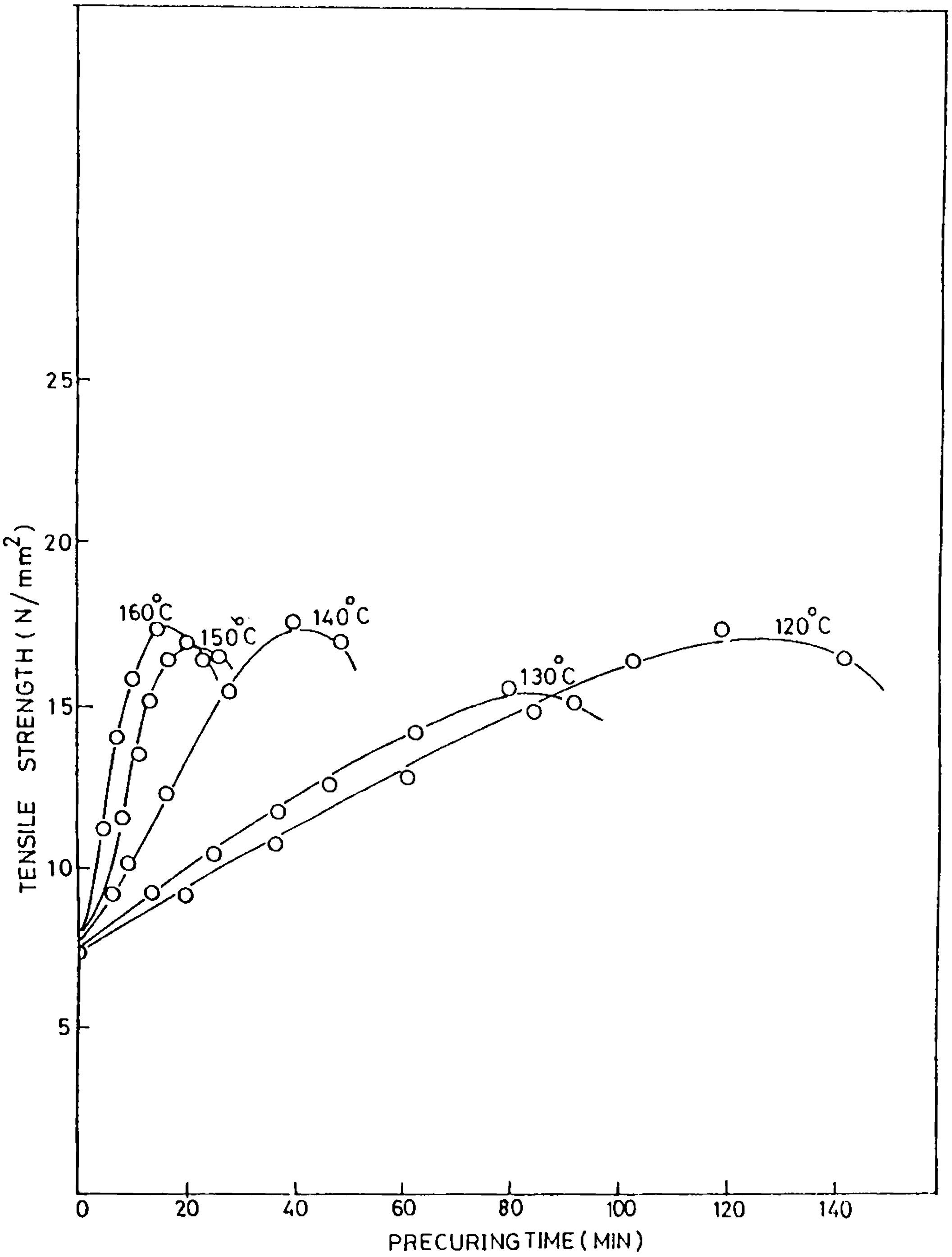


Fig.4.2: Variation of tensile strength of 50/50 NR/EPDM blend with precuring time at various temperatures

Table 4.2: Optimum precuring time and tensile strength of 50/50 NR/IIR and NR/EPDM blends as a function of the precure temperature

	Temperature of precuring (°C)	Time (Min.)	Tensile strength (N/mm^2)	Tensile retention after aging at 100°C for 24 hrs (%)
50/50 NR/IIR BLEND	--	--	8.60	86
	120	120	15.64	61
	130	70	17.91	60
	140	40	15.61	63
	150	25	16.63	60
	160	20	17.34	61
50/50 NR/EPDM BLEND	--	--	7.51	86
	120	120	16.52	72
	130	80	15.65	75
	140	40	17.70	72
	150	20	17.01	74
	160	15	17.40	75

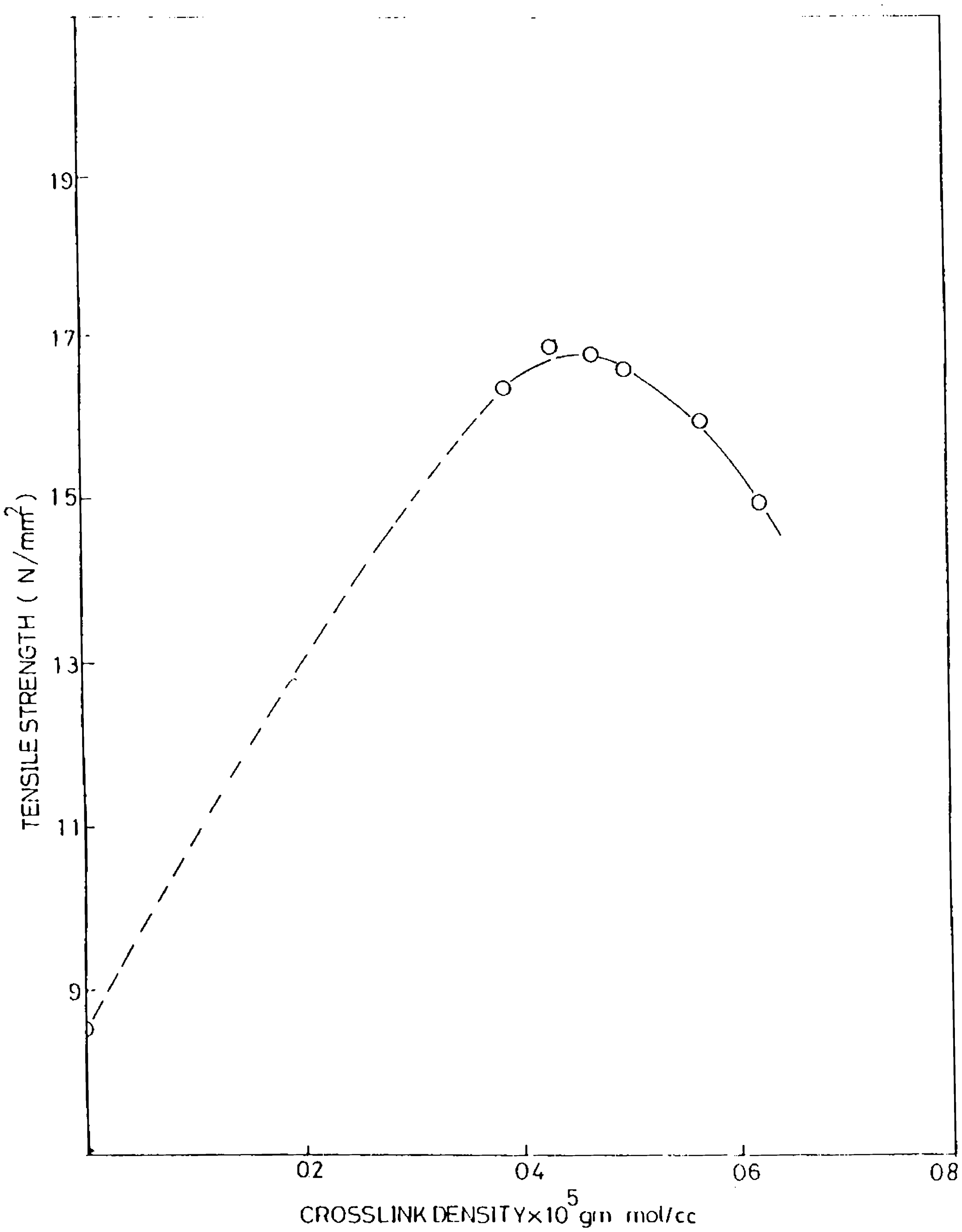


Fig.4.3: Variation of tensile strength of 50/50 NR/IIR blend with precuring crosslink density of IIR rubber

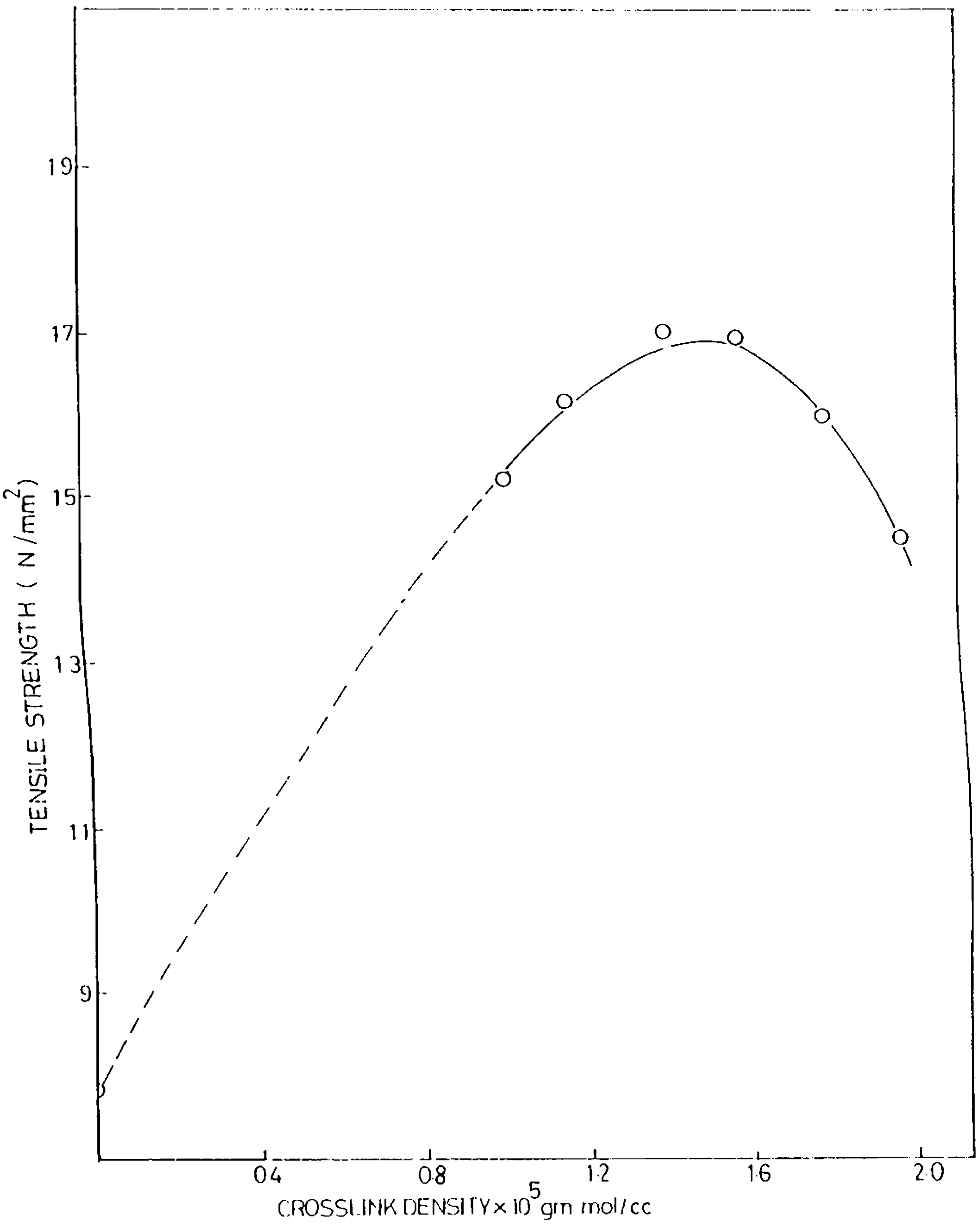


Fig.4.4: Variation of tensile strength of 50/50 NR/EPDM blend with precuring crosslink density of EPDM rubber

of precuring in the IIR or EPDM rubbers. As shown earlier, tensile strength initially increases with the amount of precuring, reaches a maximum and decreases thereafter. In the case of NR/IIR blend maximum tensile strength is observed at a precuring crosslink density of 0.4311×10^{-5} gm mol/cc in the IIR phase and in the case of NR/EPDM blends, when the crosslink density of precured EPDM is 1.427×10^{-5} gm mol/cc. Similar curves were obtained for other blend compositions but maximum tensile strength was observed at slightly different crosslink densities. This shows that there is an optimum crosslink density to which the IIR or EPDM rubber should be precured to attain maximum advantage in mechanical properties of their blends with NR, but develops inhomogeneity in the blends thereafter. Plots of optimum precuring crosslink density that has to be given in IIR and EPDM for developing maximum strength in NR/IIR and NR/EPDM blends with blend composition are given in Figs.4.5 and 4.6. From the figures it is clear that as percentage of IIR or EPDM increases in the blend the precuring crosslink density required to attain maximum mechanical properties decreases. Figs.4.7 and 4.8 show the corresponding optimum precuring time at 140°C as a function of blend composition for NR/IIR and NR/EPDM blends. As expected the precuring time decreases with increase in IIR or EPDM content. This

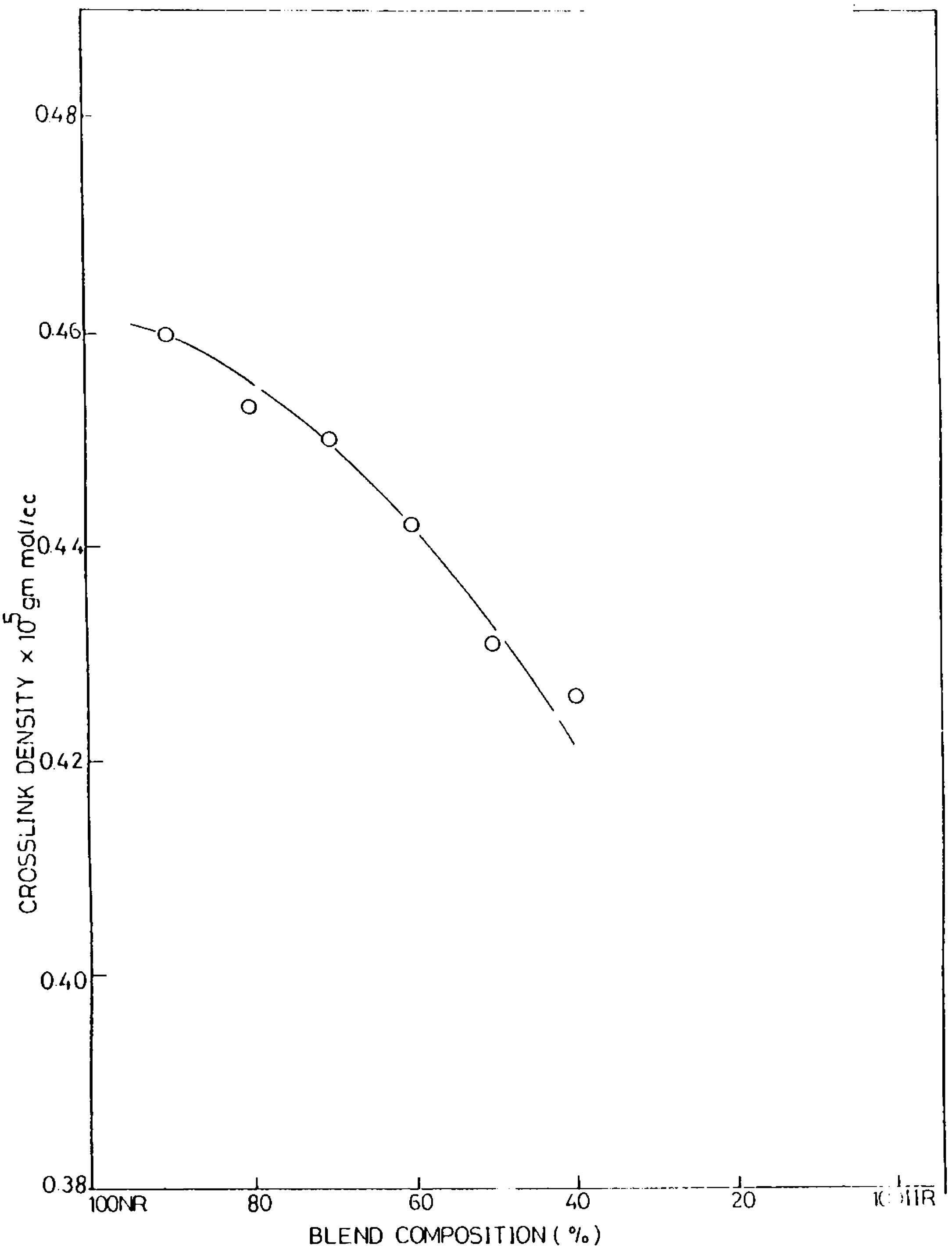


Fig.4.5: Variation of optimum precuring crosslink density in IIR phase with blend composition of NR/IIR blends

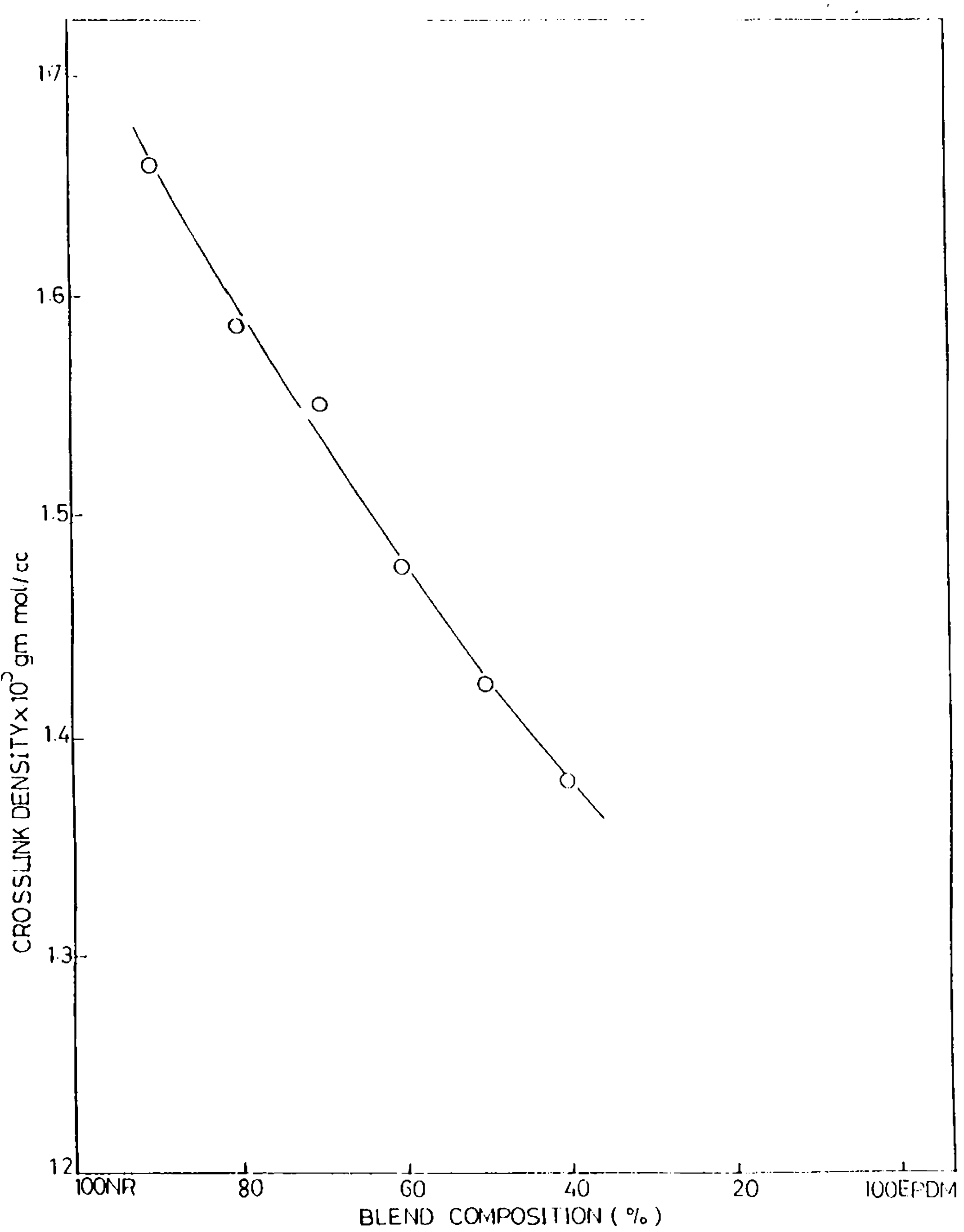


Fig.4.6: Variation of optimum precuring crosslink density in EPDM phase with blend composition of NR/EPDM blends

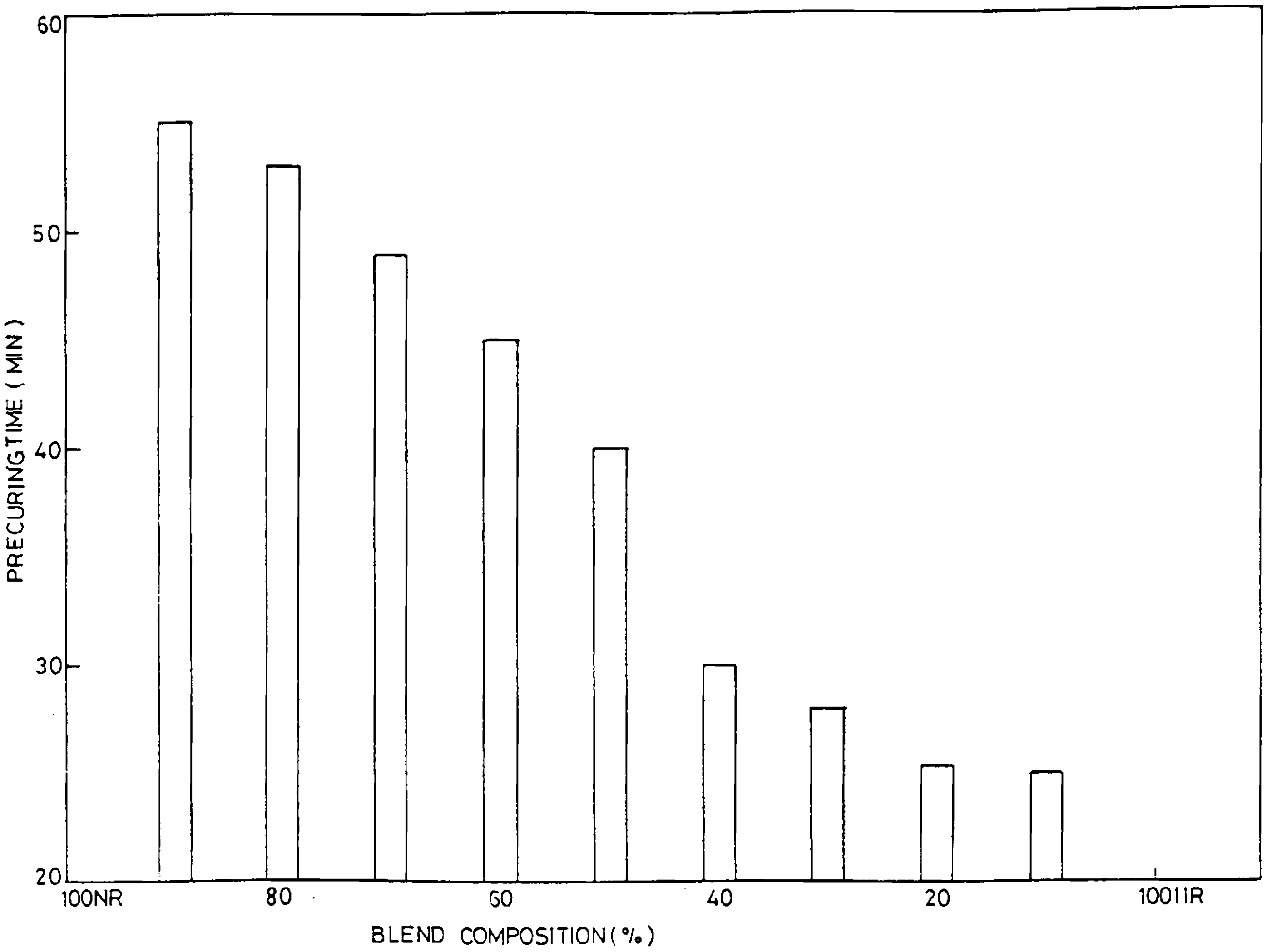


Fig.4.7: Variation of optimum precuring time with blend composition of NR/IIR blends

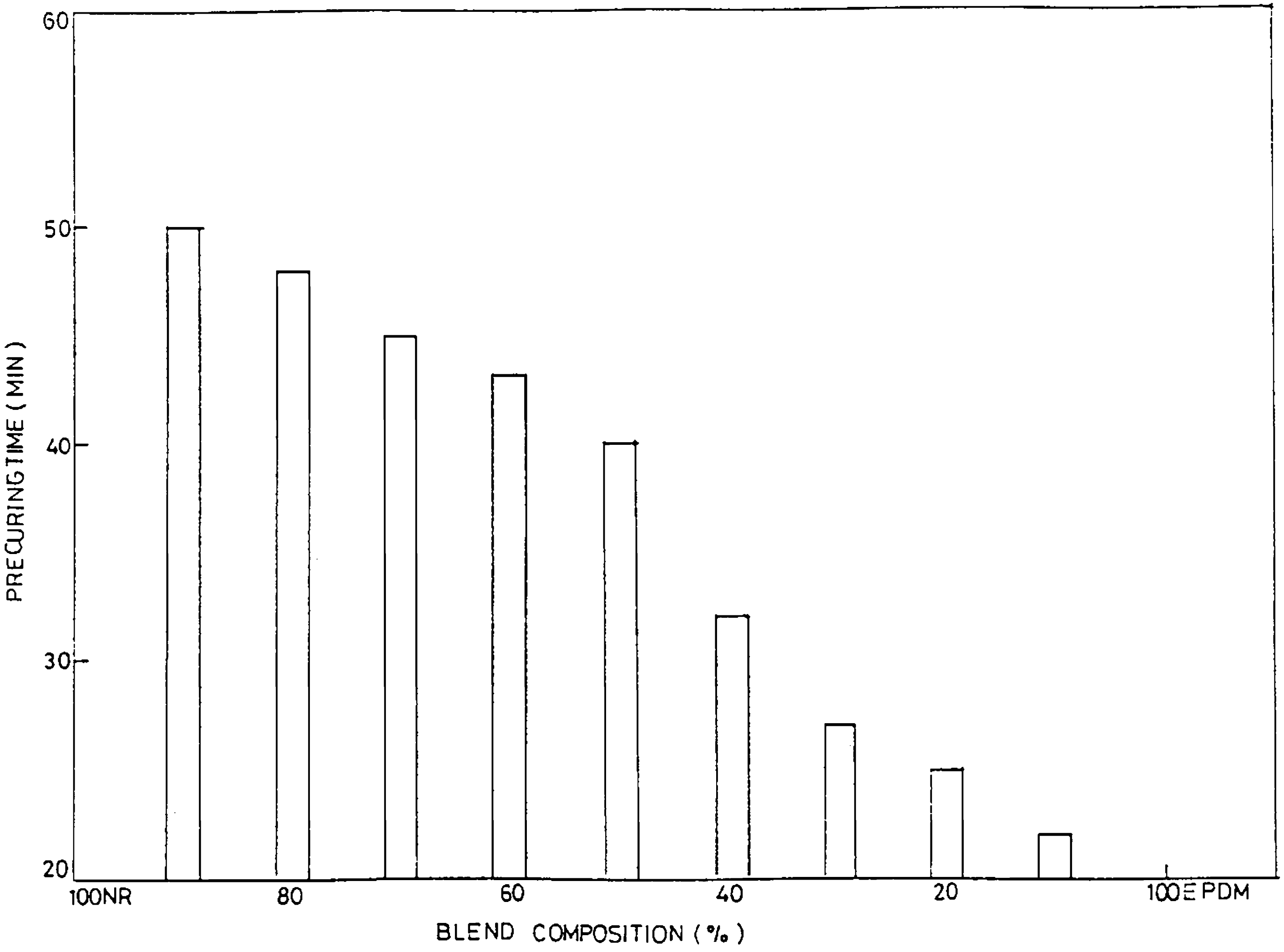


Fig.4.8: Variation of optimum precuring time with blend composition of NR/EPDM blends

behaviour throws light on the cocrosslinking of the blends. For developing good mechanical strength, optimum levels of crosslinking may be necessary in both the elastomer phases and in the interface. The optimum level of crosslinking in IIR or EPDM is thus a compromise between the degree of crosslinking in these phases and in the interface with NR. When IIR or EPDM forms the continuous phase, the optimum crosslink density in them has to be low in order to form a homogeneous blend with NR. The precuring in the IIR or EPDM phase also possibly reduces the migration of the curing agents out of them into the NR phase.

The cure characteristics of the NR/IIR and NR/EPDM blends are shown in Tables 4.3 and 4.4. Cure curves of selected compositions are given in Figs.4.9 to 4.12. In the blends when NR forms the major constituent the curing is slightly slower in the modified blends than in their corresponding conventional counterparts. Since the curing behaviour is likely to be more influenced by the major constituent, this may mean that NR is not able to take an unproportionally higher share of the curing agents in the modified blends unlike in the case of the conventional blends. This reasoning is supported by the slightly faster curing of the modified blends than their corresponding

Table 4.3: Cure characteristics of NR/IIR blends

NR	IIR	CONVENTIONAL		MODIFIED	
		Cure time at 160°C (Min.)	Scorch time (Min.)	Cure time at 160°C (Min.)	Scorch time (Min.)
100	--	4.0	1.4	--	--
--	100	20.0	2.0	--	--
90	10	2.5	1.4	3.0	1.5
80	20	2.5	1.35	3.0	1.4
70	30	2.5	0.85	3.5	1.2
60	40	2.5	0.85	3.5	1.1
50	50	3.0	0.5	3.5	0.75
40	60	4.5	0.8	4.0	0.8
30	70	5.5	1.1	5.0	1.2
20	80	6.5	1.5	6.0	1.7
10	90	7.0	1.8	6.0	1.9

Table 4.4: Cure characteristics of NR/EPDM blends

		CONVENTIONAL		MODIFIED	
NR	EPDM	Cure time at 160°C (Min.)	Scorch time (Min.)	Cure time at 160°C (Min.)	Scorch time (Min.)
100	--	4.0	1.4	--	--
--	100	9.0	1.7	--	--
90	10	2.0	1.5	2.5	1.6
80	20	2.5	1.5	3.0	1.6
70	30	2.5	1.3	3.0	1.4
60	40	2.5	1.2	3.5	1.4
50	50	2.5	1.0	4.0	1.2
40	60	4.0	1.2	4.0	1.5
30	70	4.8	1.3	4.0	1.5
20	80	5.5	1.4	5.0	1.6
10	90	6.0	1.6	5.0	1.7

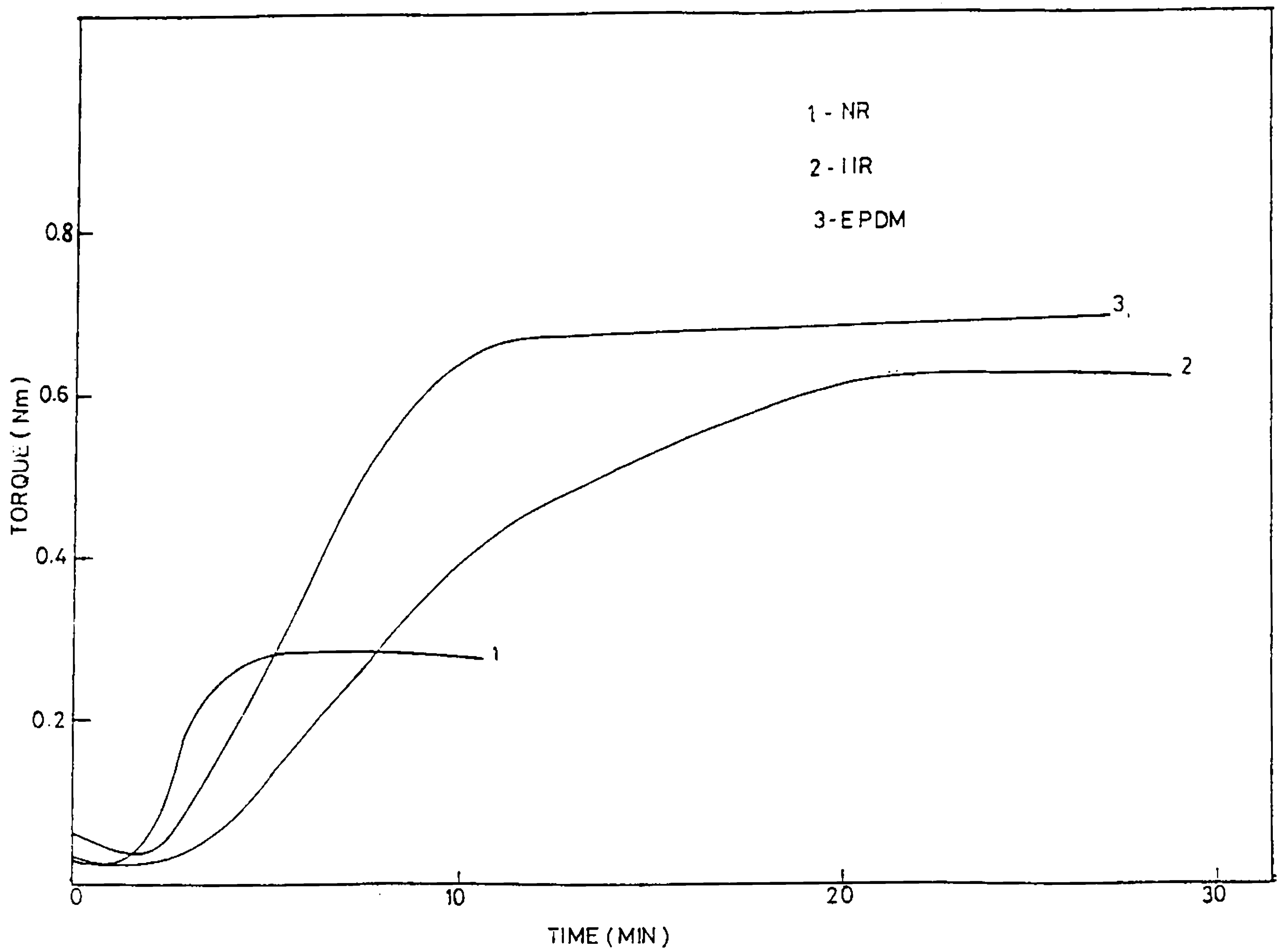


Fig.4.9: Cure curves of NR, IIR and EPDM

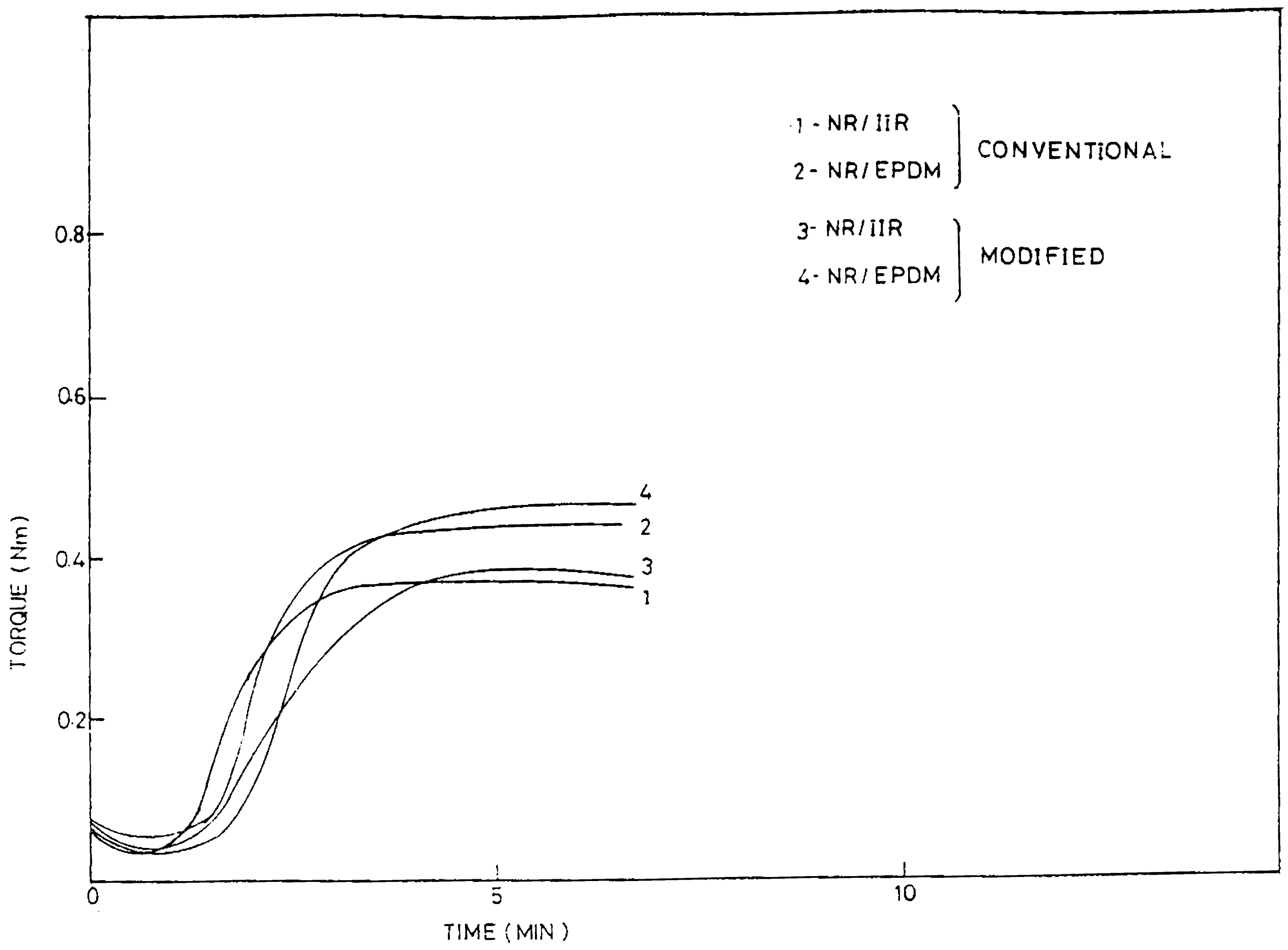


Fig.4.10: Cure curves of 70/30 NR/IIR and 70/30 NR/EPDM blends

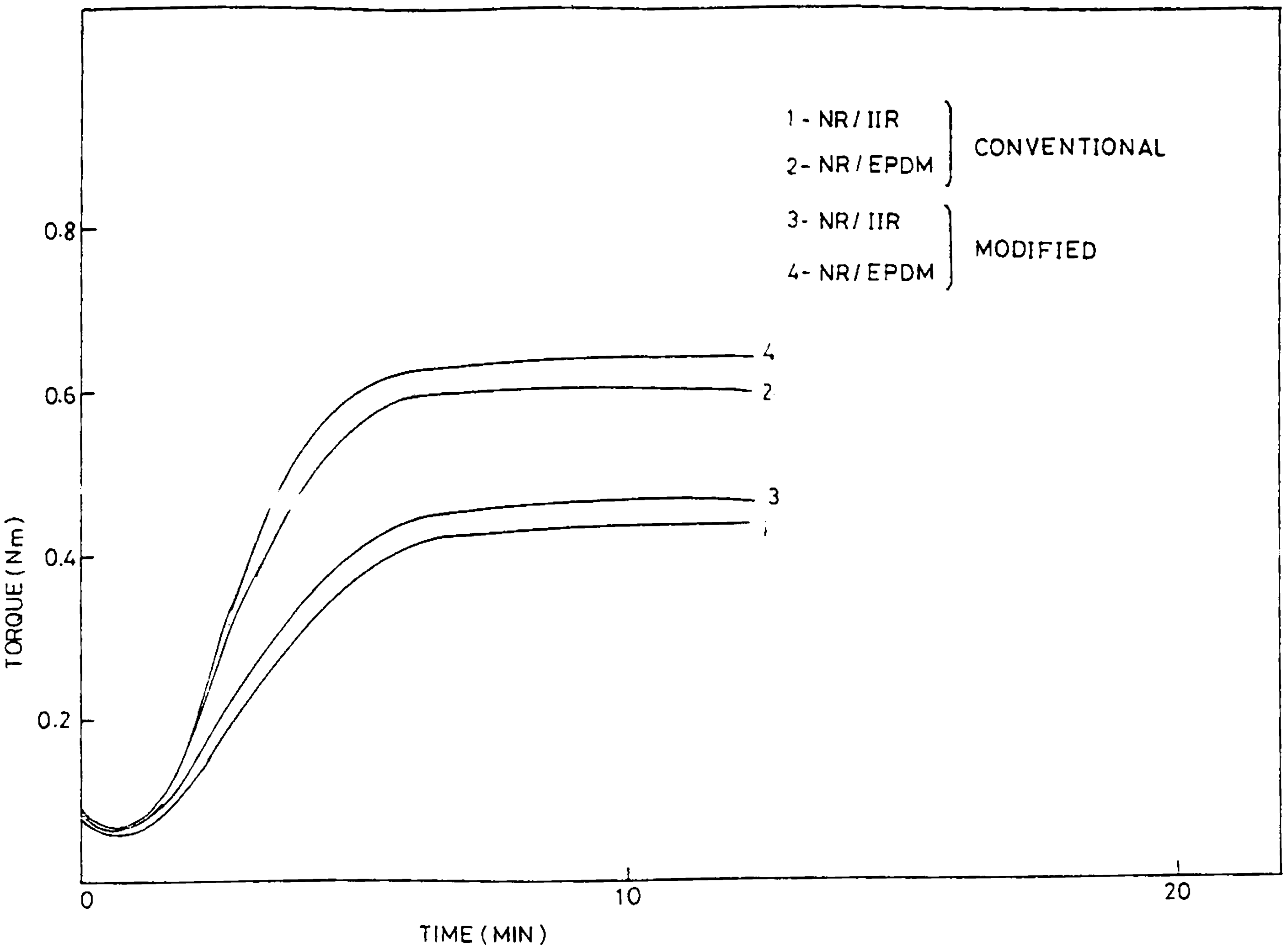


Fig.4.12: Cure curves of 30/70 NR/IIR and 30/70 NR/EPDM blends

conventional blends where IIR or EPDM forms the major constituent. The scorch safety of the modified compounds does not seem to be affected by the precuring step.

Fig.4.13 shows the variation in tensile strength of modified NR/IIR blends with composition in comparison to that of conventional NR/IIR blends. The modified blends show much better tensile strength compared to the conventional blends. The ageing resistance is also found to be superior for the modified blends. Fig.4.14 shows the variation of tensile strength of the modified and conventional NR/EPDM blends, which also shows a behaviour similar to that of NR/IIR blends.

Fig.4.15 shows the elongation at break (EB) of the modified and conventional NR/IIR blends. Modified blends show higher EB compared to the conventional blends before and after ageing as in the case of tensile strength. In the conventional curing of the blends, NR gets a higher proportion of the curing agents resulting in overcure. The improved EB in the case of modified NR/IIR blends points towards optimum crosslink densities in both NR and IIR phases. Similar trends are shown by NR/EPDM blends too (Fig.4.16).

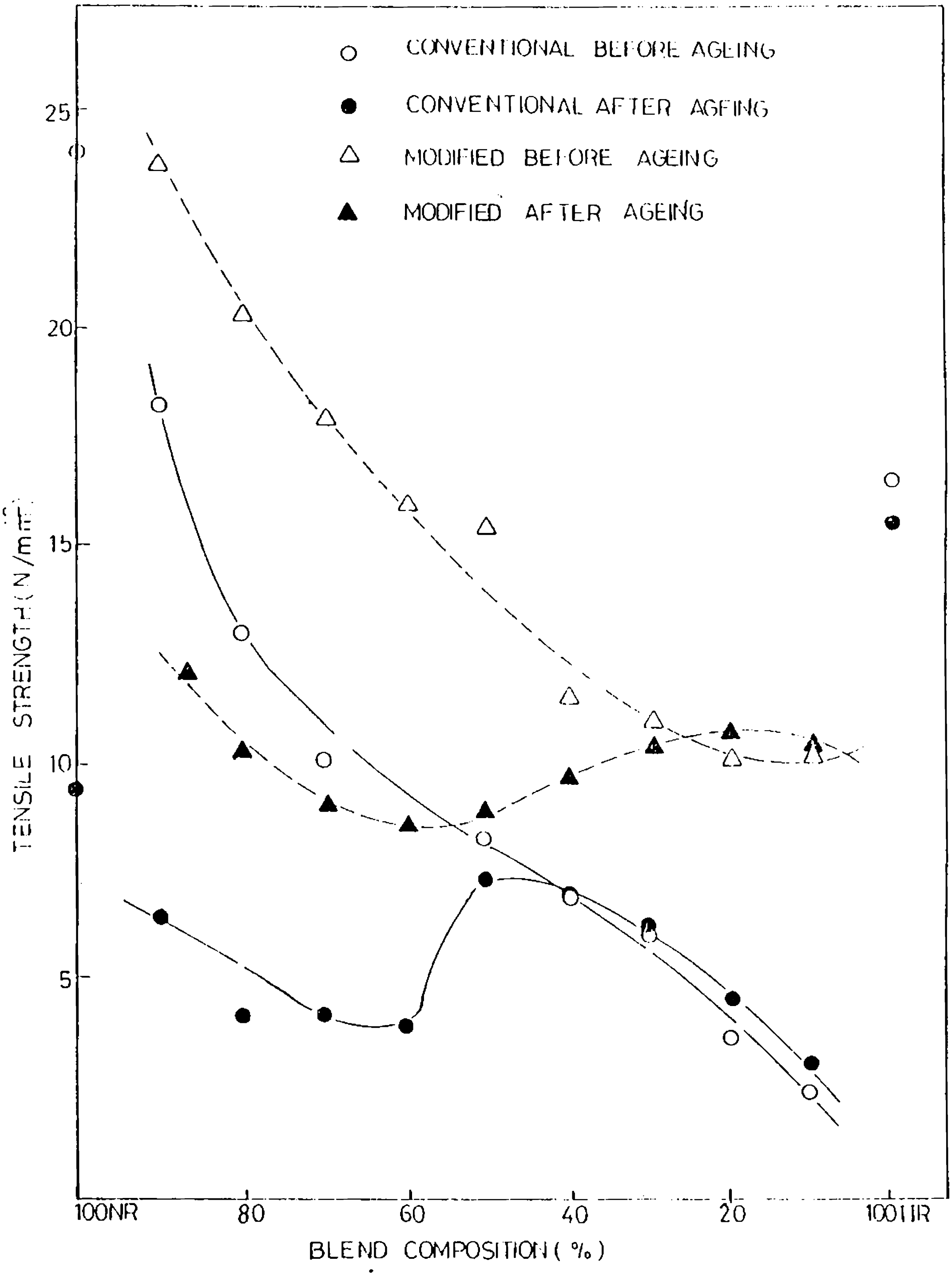


Fig.4.13: Variation of tensile strength with blend composition of NR/IIR blends

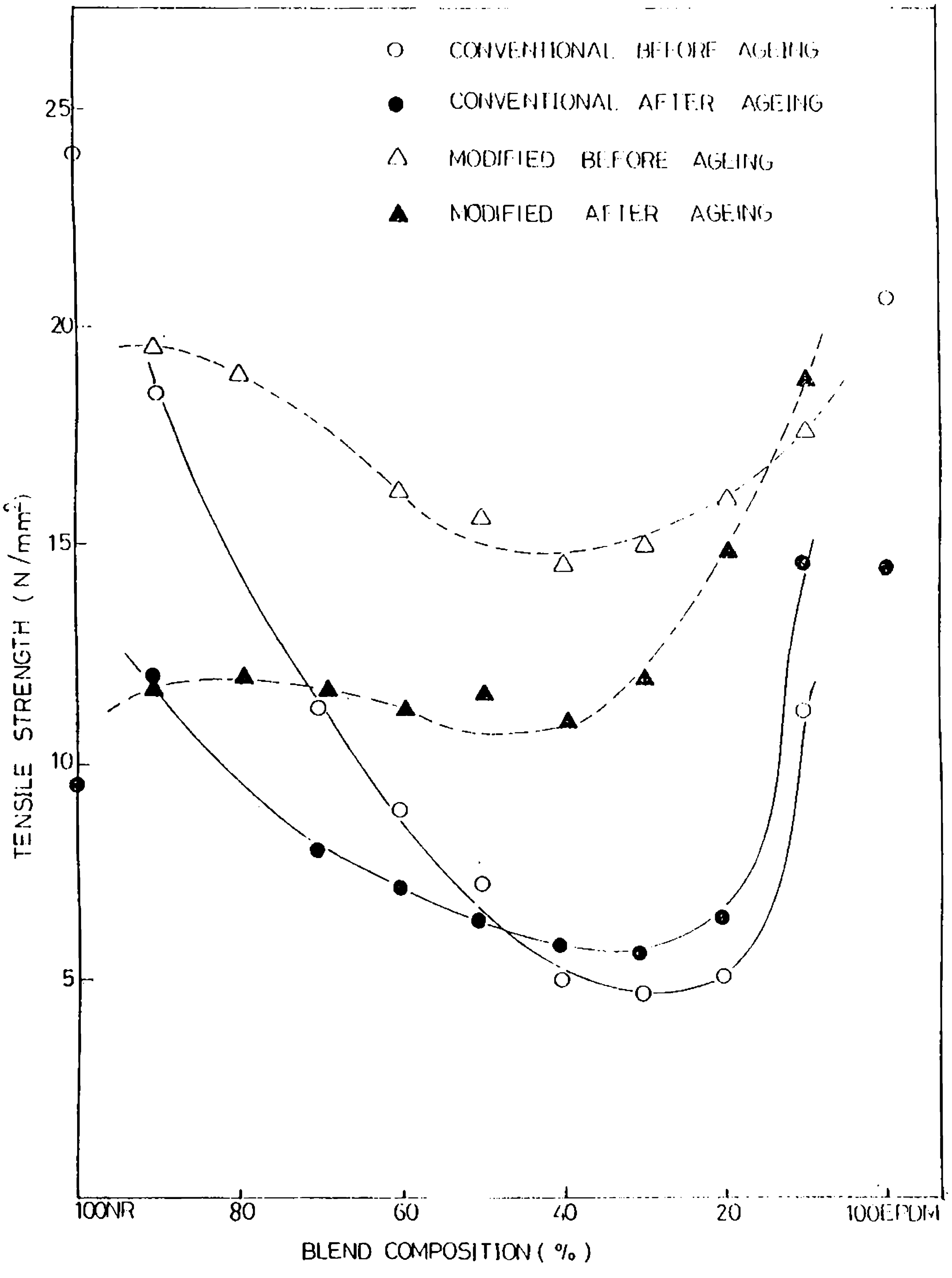


Fig.4.14: Variation of tensile strength with blend composition of NR/EPDM blends

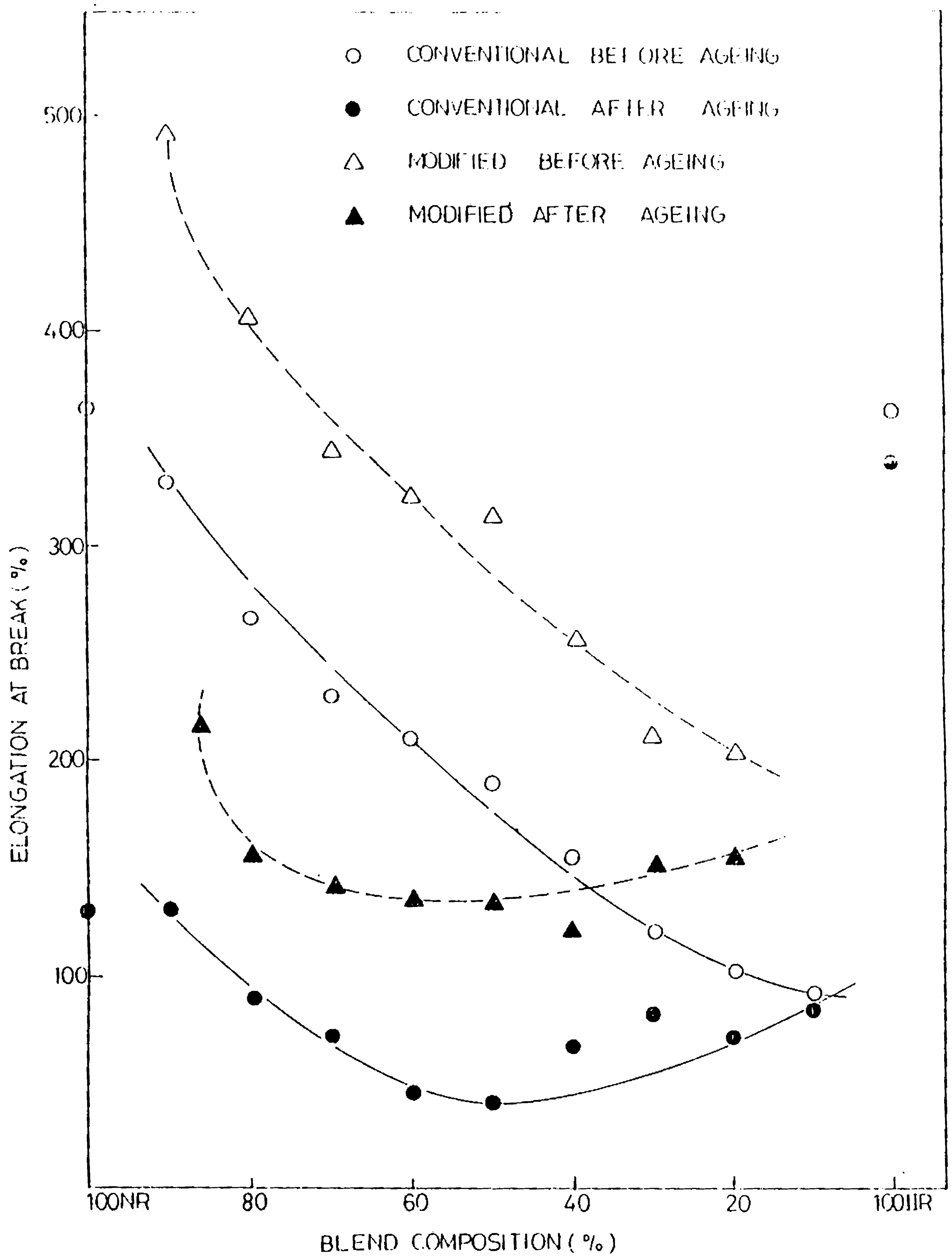


Fig.4.15: Variation of elongation at break with blend composition of NR/IIR blends

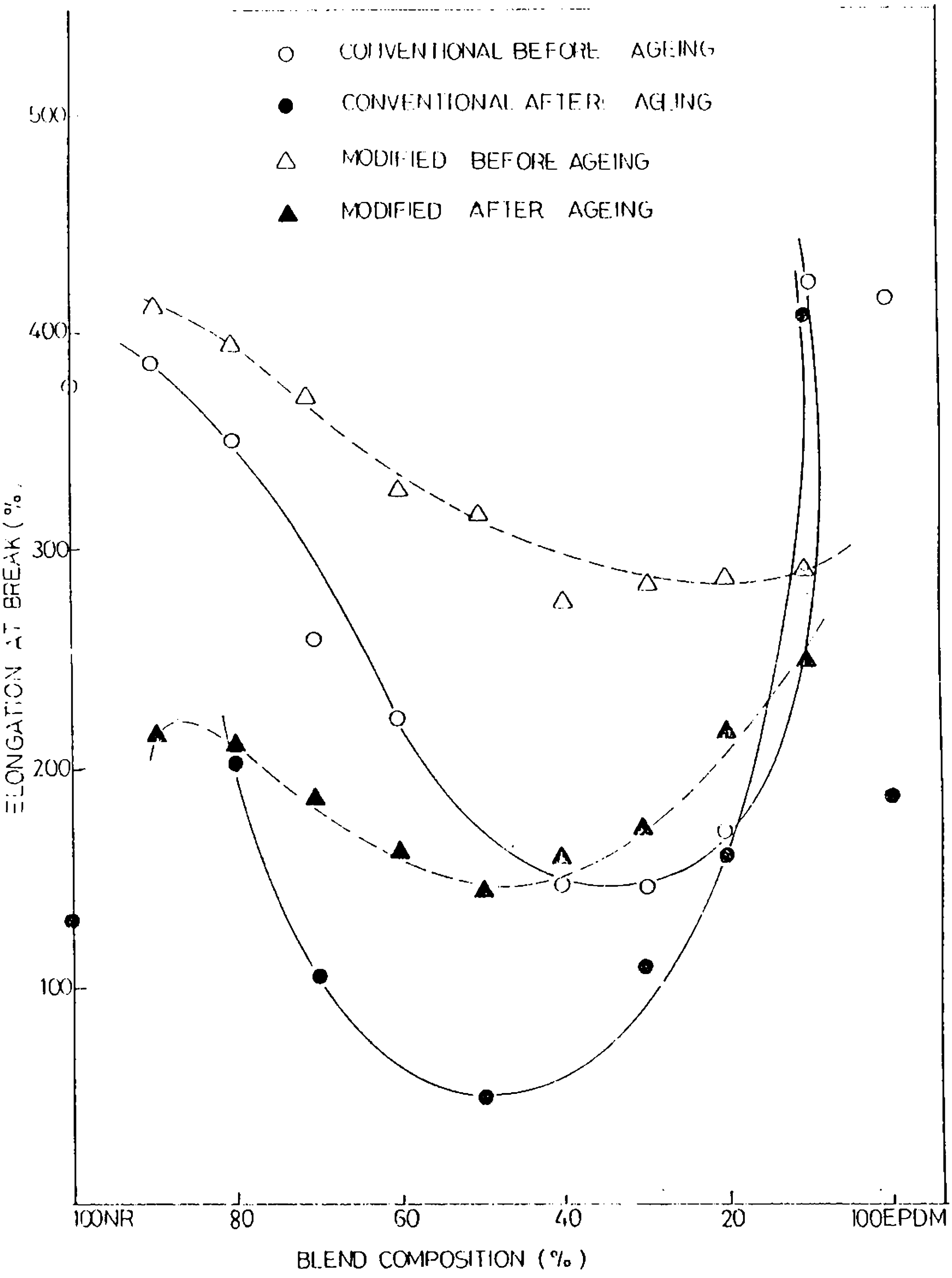


Fig. 4.16: Variation of elongation at break with blend composition of NR/EPDM blends

The variation of tear strength with blend composition for modified and conventional NR/IIR and NR/EPDM blends is shown in Fig.4.17. The modified blends show better tear strength as well. The tear strength improvement with modification is even more pronounced than that of the tensile strength since the tear strength is more sensitive to optimum crosslink densities in both rubbers.[5]

Hardness, compression set and abrasion resistance of the modified and conventional NR/IIR and NR/EPDM blends are shown in Tables 4.5 and 4.6. The results are comparable for the modified and conventional blends. The crosslink densities of the modified and conventional compounds are also shown in the Tables. When NR is the continuous phase the conventional blends show a higher crosslink density which is obviously more influenced by NR. But when IIR or EPDM is the larger constituent, the modified blends show higher crosslink density than their conventional counterparts. These values reflect the crosslink density in the IIR or EPDM phase. Since NR, IIR and EPDM swell in similar solvents, it was not possible to measure the crosslink densities of the different phases separately.[6]

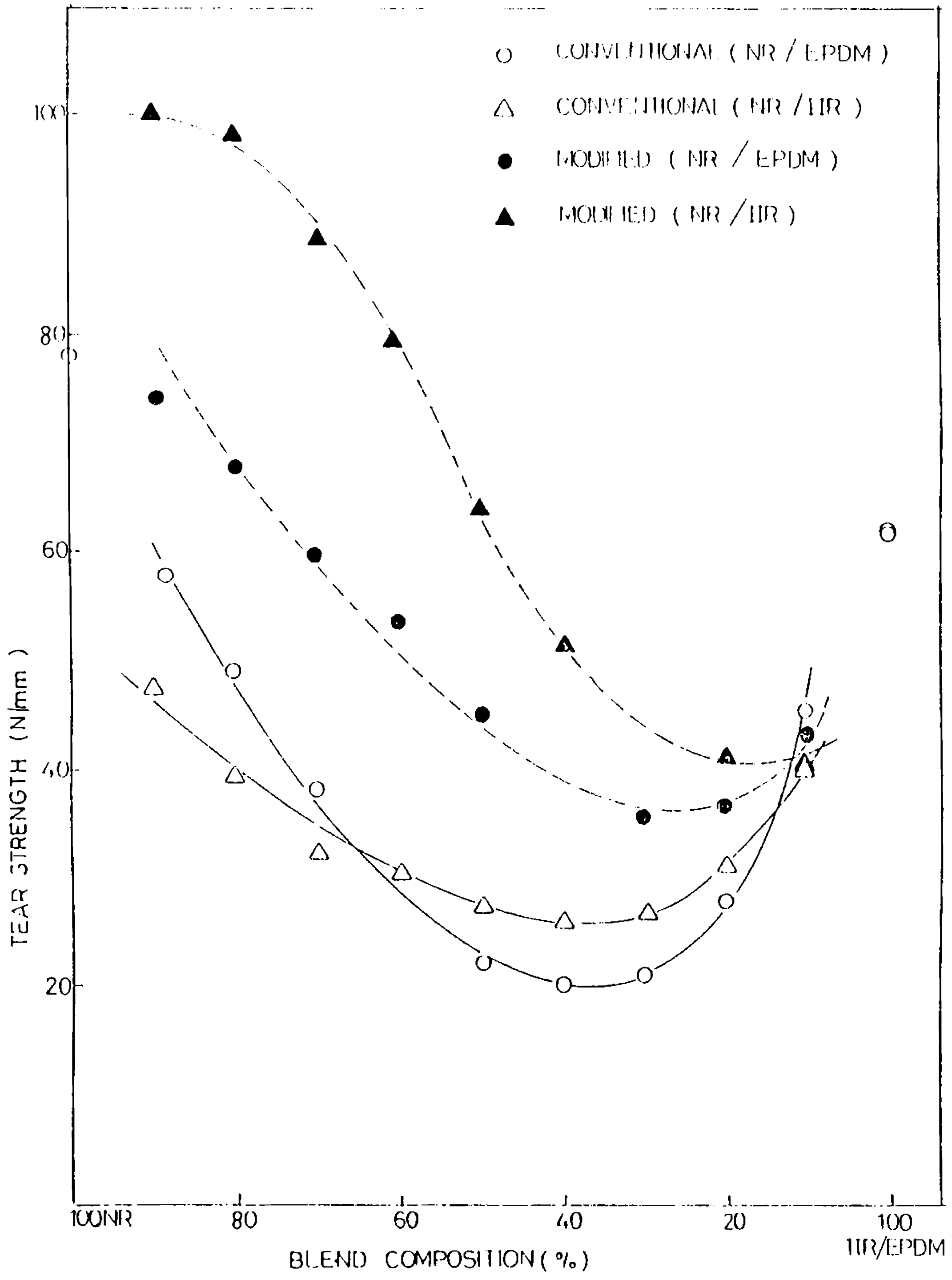


Fig.4.17: Variation of tear strength with blend composition of NR/IIR and NR/EPDM blends

Table 4.5: Properties of NR/IIR vulcanizates

		CONVENTIONAL				MODIFIED			
NR	IRR	Hardness (Shore A units)	Abrasion resistance (cc/hr)	Compression set (%)	Crosslink density x10^5 (gm mol/cc)	Hardness (Shore A units)	Abrasion resistance (cc/hr)	Compression set (%)	Crosslink density x10^5 (gm mol/cc)
100	--	62	6.00	39.0	5.20	--	--	--	--
--	100	55	9.13	62.3	1.43	--	--	--	--
90	10	64	4.86	60.0	4.12	60	5.00	60.0	3.72
80	20	72	5.41	53.0	5.18	65	5.45	59.9	3.26
70	30	72	6.01	54.6	5.95	64	5.57	56.0	4.30
60	40	74	6.18	59.4	4.93	65	6.88	52.4	4.32
50	50	69	5.86	55.8	3.15	65	6.88	52.4	4.13
40	60	69	4.60	51.8	1.68	64	3.88	35.2	3.84
30	70	70	5.81	53.9	0.90	65	3.65	31.7	2.01
20	80	67	8.65	60.4	0.19	67	3.87	31.0	2.61
10	90	63	8.93	64.3	0.18	66	6.06	30.7	0.85

Table 4.6: Properties of NR/EPDM vulcanizates

NR	EPDM	CONVENTIONAL				MODIFIED			
		Hardness (Shore A units)	Abrasion resistance (cc/hr)	Compression set (%)	Crosslink density x 10^5 (gm mol/cc)	Hardness (Shore A units)	Abrasion resistance (cc/hr)	Compression set (%)	Crosslink density x 10^5 (gm mol/cc)
100	--	62	6.00	39.0	5.20	--	--	--	--
--	100	67	6.27	56.8	4.20	--	--	--	--
90	10	70	6.27	77.8	5.22	65	5.18	60.2	5.21
80	20	60	6.55	68.6	5.25	70	6.27	60.0	5.21
70	30	70	7.09	64.6	5.26	66	6.55	63.0	5.25
60	40	64	6.55	63.2	5.28	73	6.27	53.8	5.27
50	50	67	6.48	73.2	5.29	65	6.30	55.6	5.28
40	60	70	4.72	47.1	1.92	70	2.70	32.7	4.70
30	70	71	4.72	50.3	2.00	68	3.00	28.12	4.73
20	80	70	3.27	36.5	1.52	68	2.48	24.87	3.90
10	90	70	2.00	38.1	1.69	68	2.00	29.05	4.83

The variation in modulus of the blends also follows a similar pattern (Figs.4.18 and 4.19). When NR is the major constituent, the conventional blends show a higher modulus than the modified blends. However, when IIR or EPDM forms the major constituent, the difference in modulus is found to be marginal. This behaviour is expected since the modulus is directly proportional to the crosslink density. The variation of rebound resilience also follows a similar pattern (Fig.4.20).

Fig.4.21 shows the photographs of the swollen samples of modified and conventional blends of NR/IIR (50/50). This clearly shows that there is no proper interface bonding in the conventional blends due to the lack of a good amount of interface crosslinks. Also the swelling ratio is high compared to modified blends probably due to the very low crosslink densities in the interface and IIR phase. In the modified blends the swelling ratio is comparatively less which is obviously due to higher crosslink densities in the interface and IIR phase. Fig.4.22 shows the photographs of the swollen samples of modified and conventional blends of NR/EPDM (50/50), which are also similar to the NR/IIR blends.

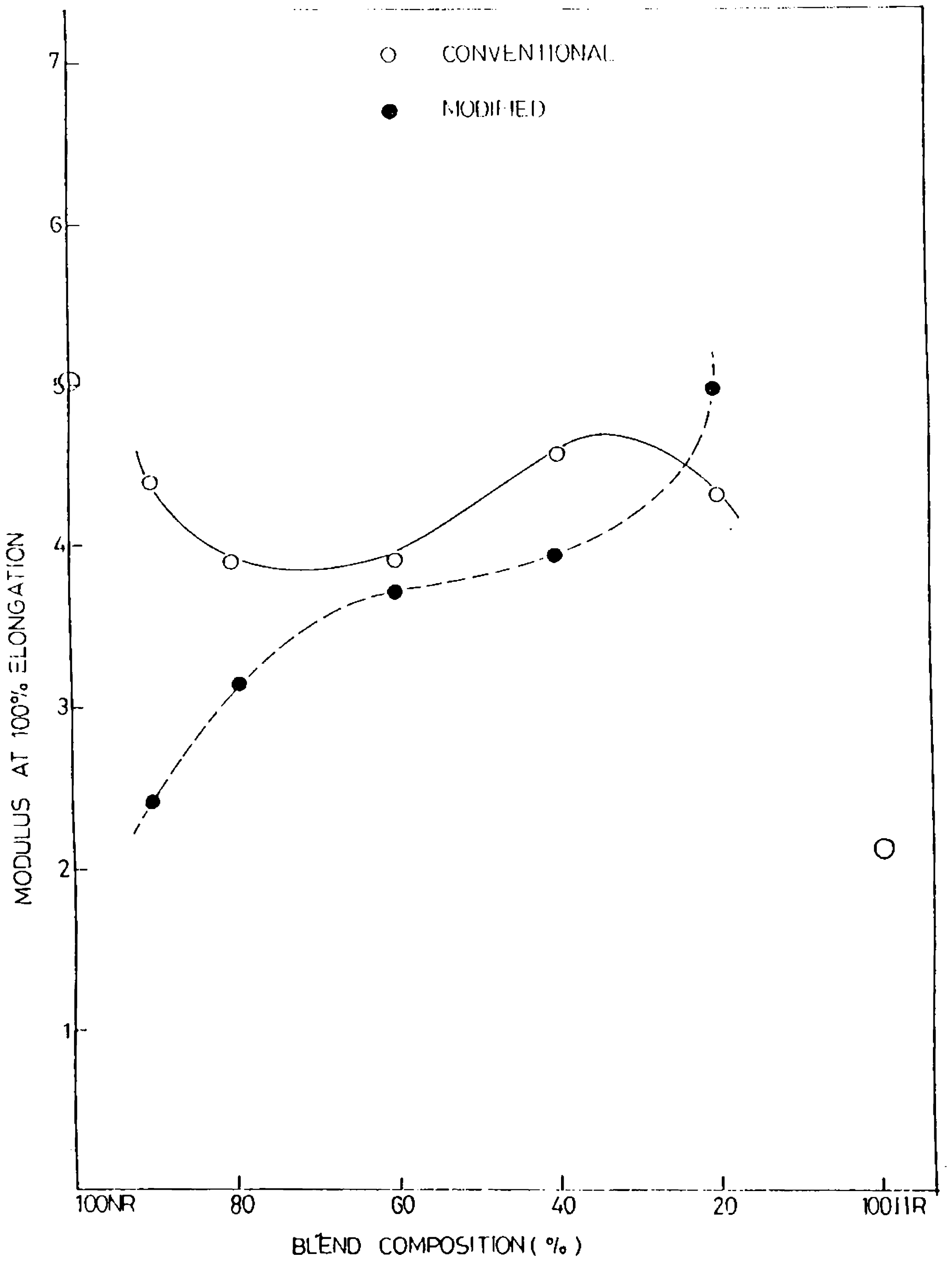


Fig.4.18: Variation of modulus with blend composition of NR/IIR blends

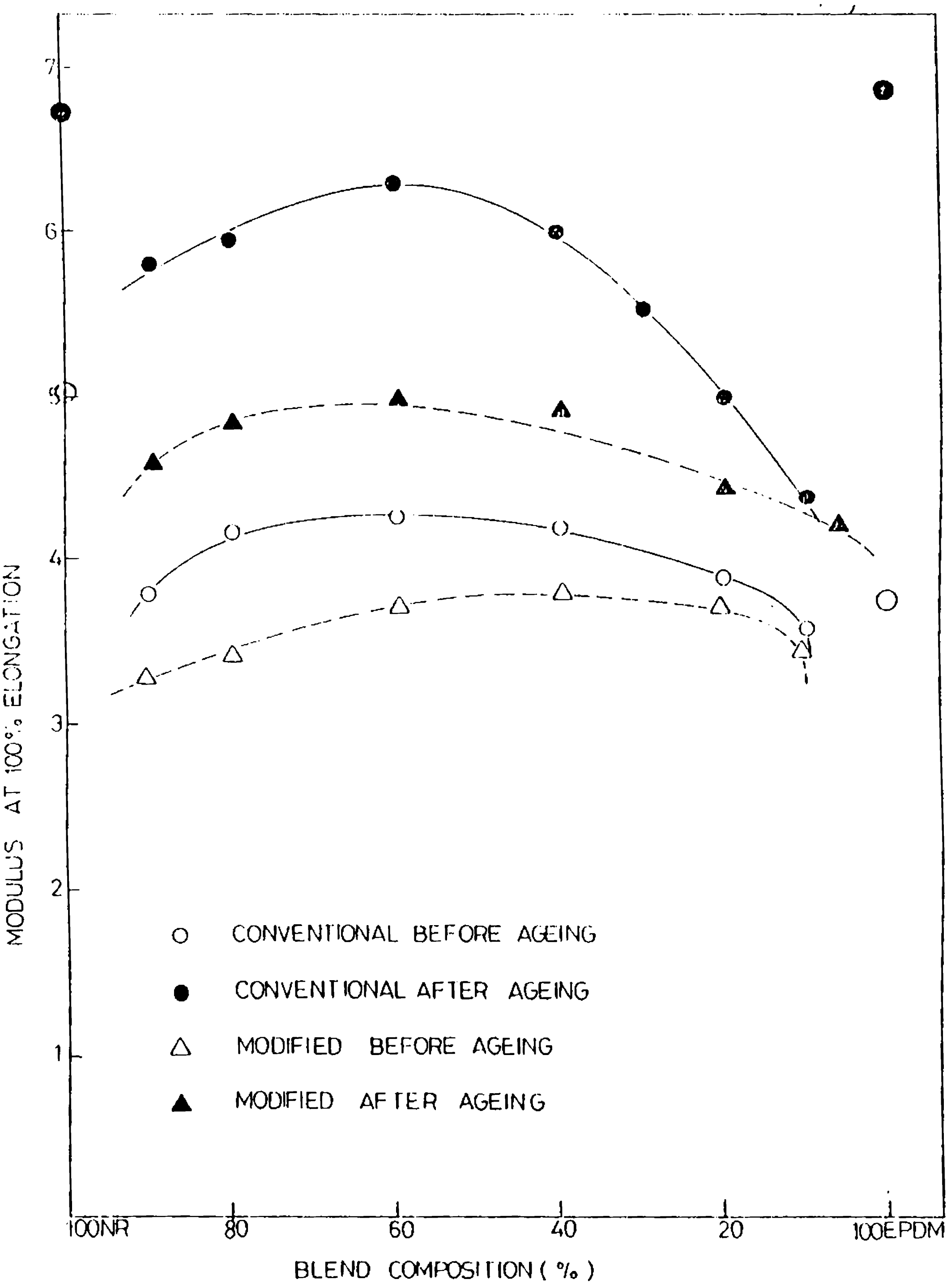


Fig.4.19: Variation of modulus with blend composition of NR/EPDM blends

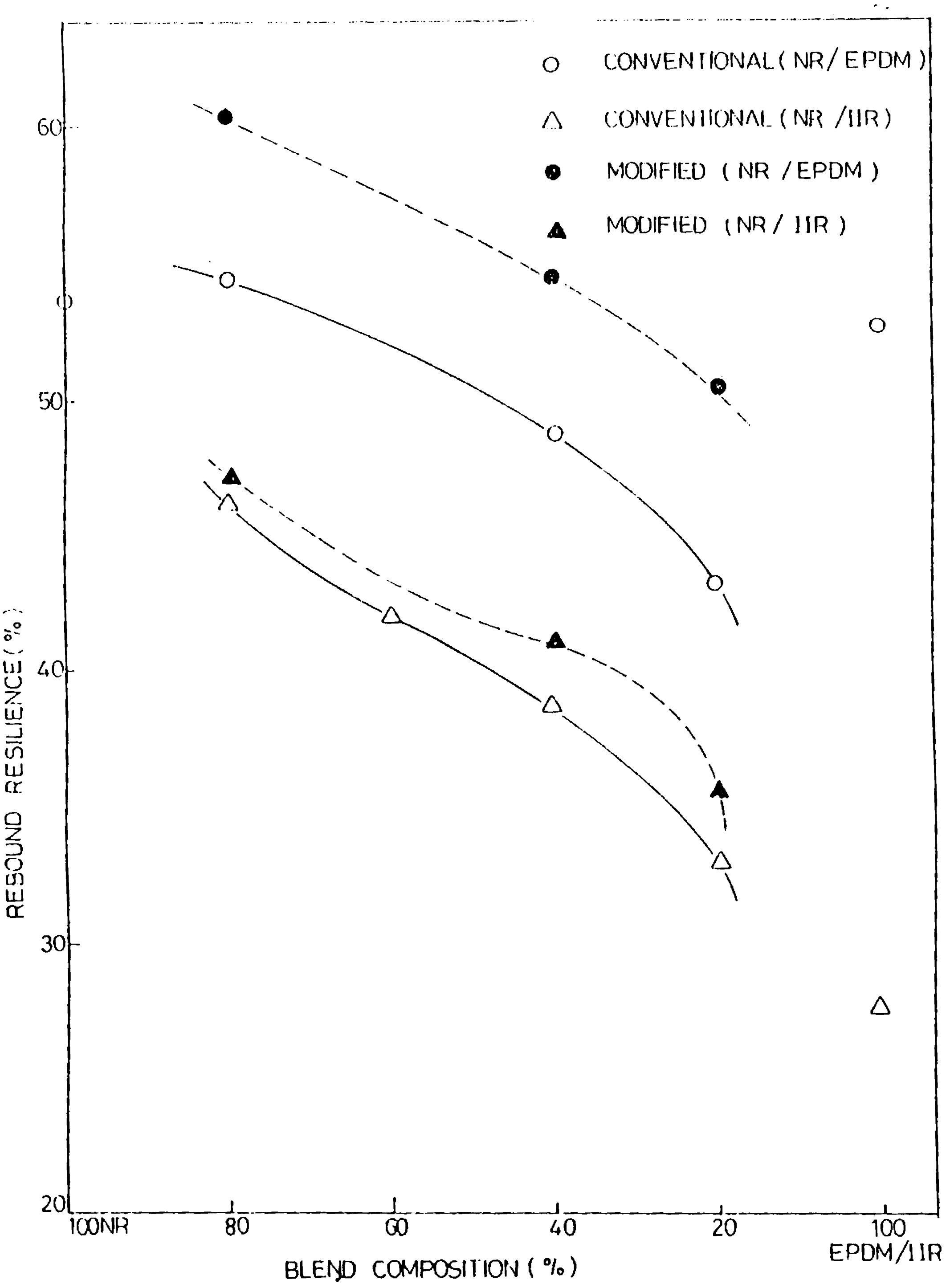
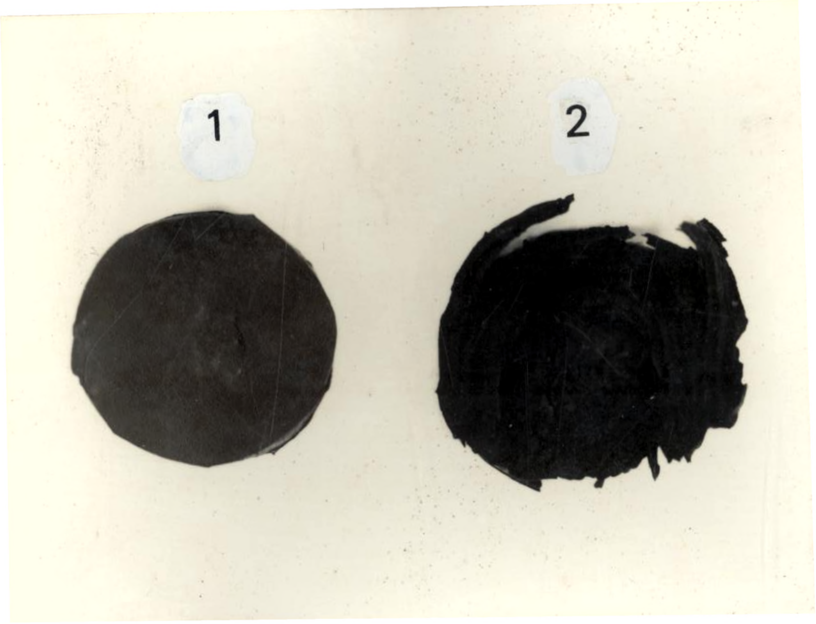


Fig.4.20: Variation of rebound resilience with blend composition of NR/IIR and NR/EPDM blends

1 - Modified, 2 - Conventional

Fig.4.21 Photographs of swollen samples of 50/50 NR/IIR blend



1 - Modified, 2 - Conventional

Fig.4.22 Photographs of swollen samples of 50/50 NR/EPDM blend

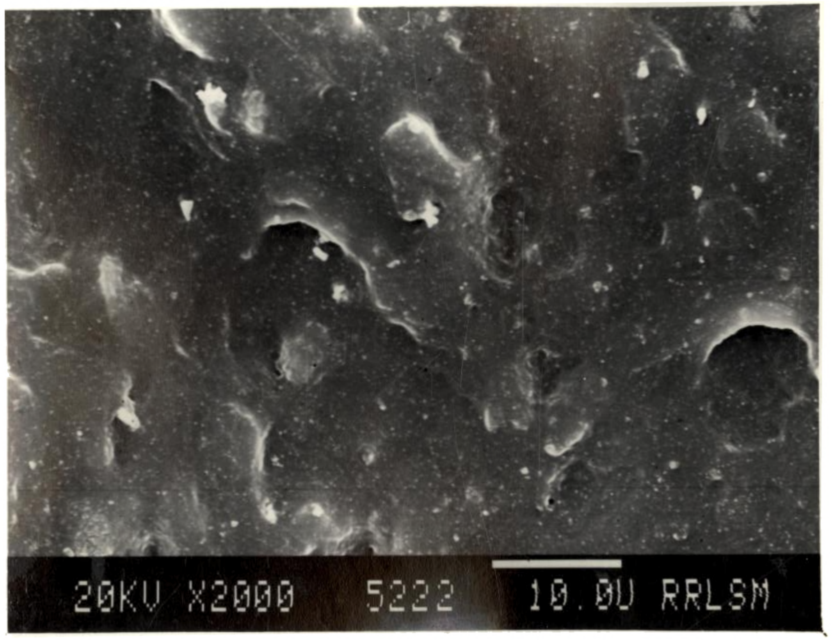


Fig.4.23 Modified

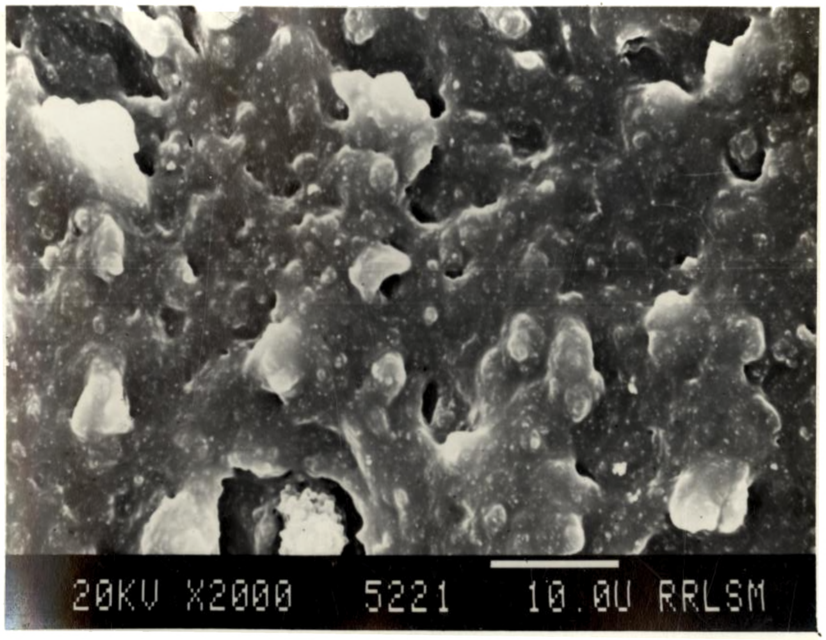


Fig.4.24 Conventional

SEM photographs of the tensile fracture surface of 50/50 NR/IIR blends

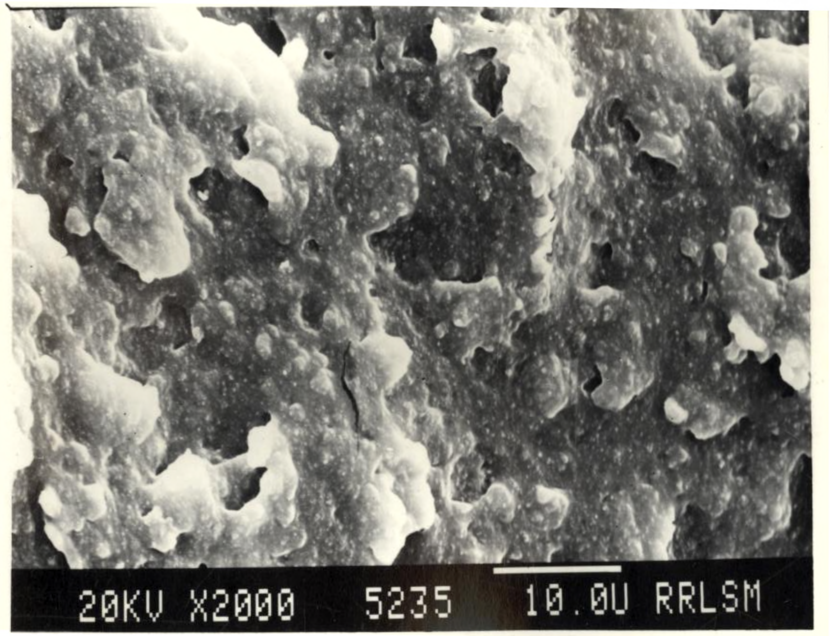


Fig.4.25 Modified

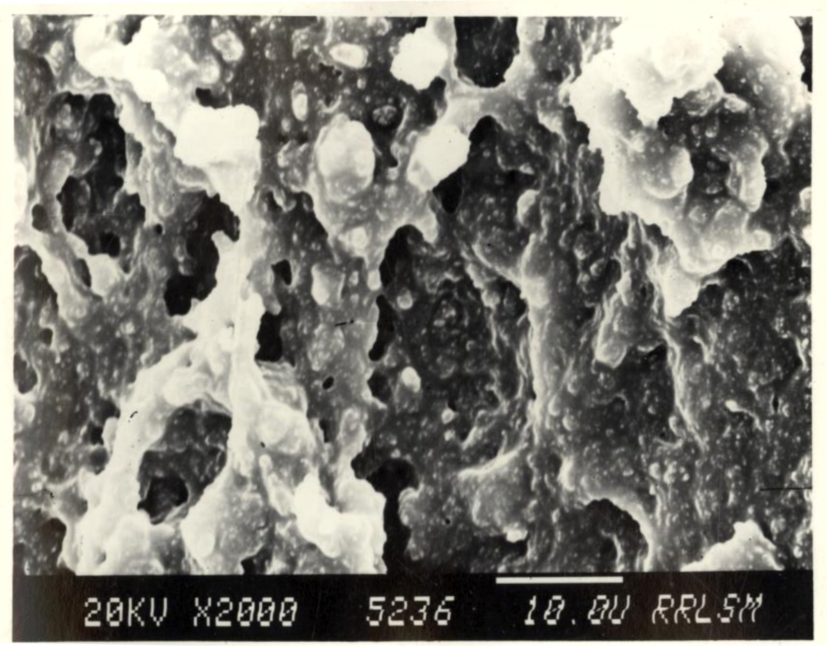


Fig.4.26 Conventional

SEM photographs of the tensile fracture surface of 20/80 NR/IIR blends

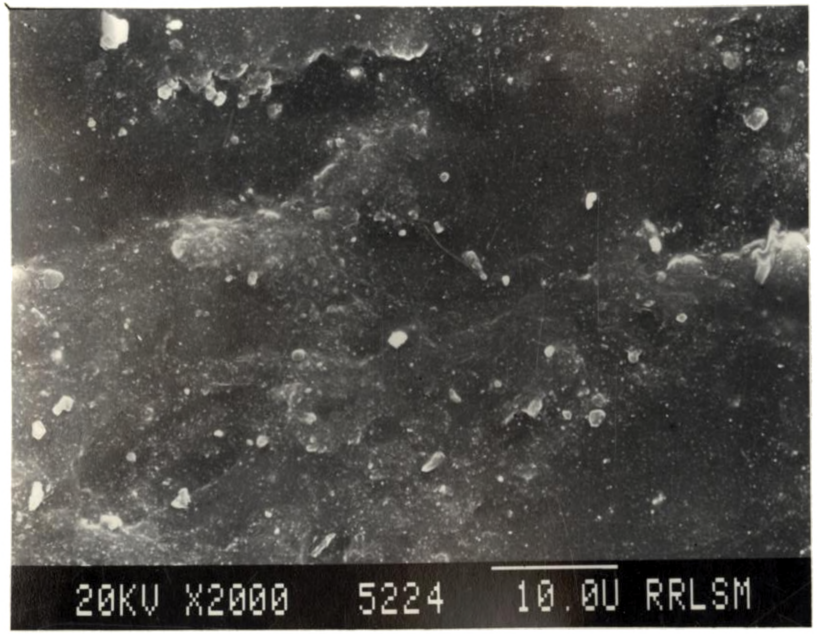


Fig.4.27 Modified

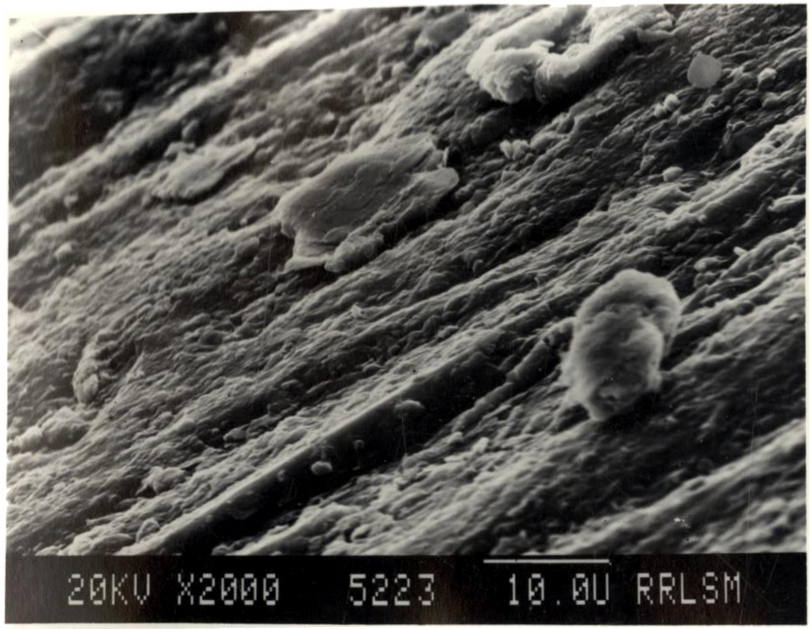


Fig.4.28 Conventional

SEM photographs of the tensile fracture surface of 50/50 NR/EPDM blends

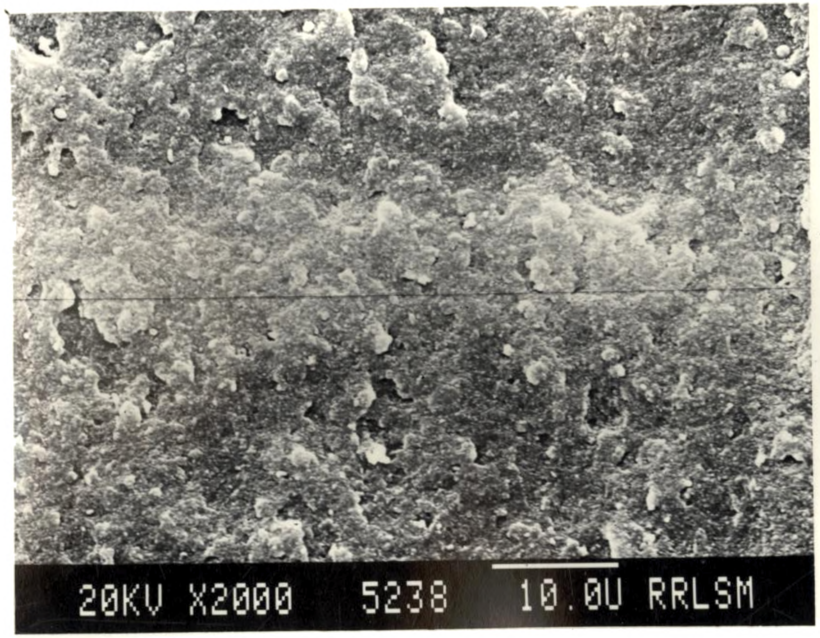


Fig.4.29 Modified

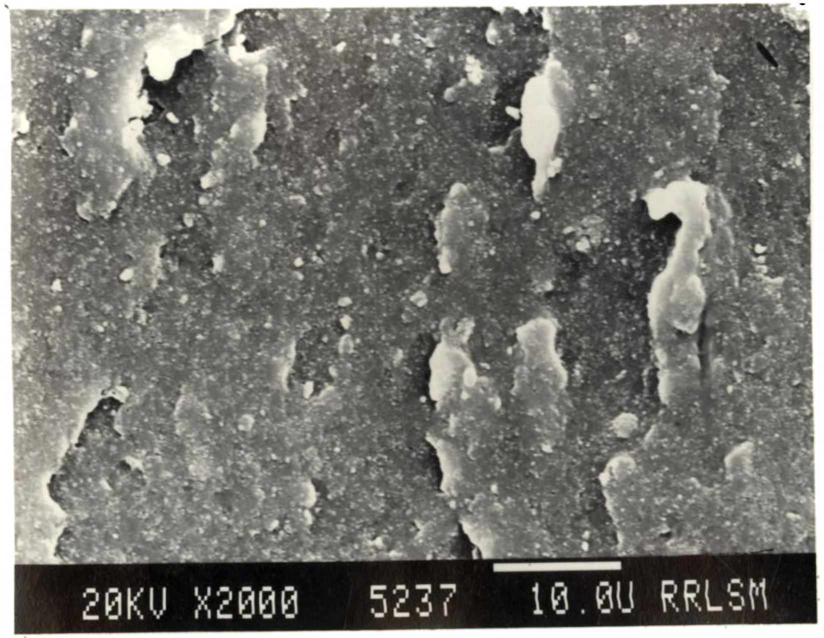


Fig.4.30 Conventional

SEM photographs of the tensile fracture surface of 80/20 NR/EPDM blends

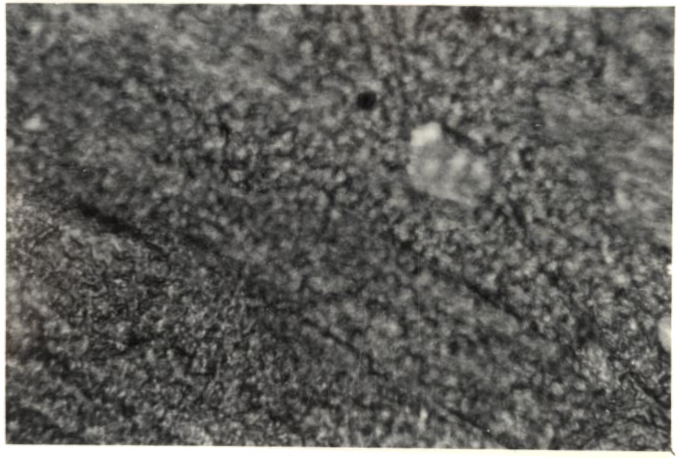


Fig. 4.31 Modified

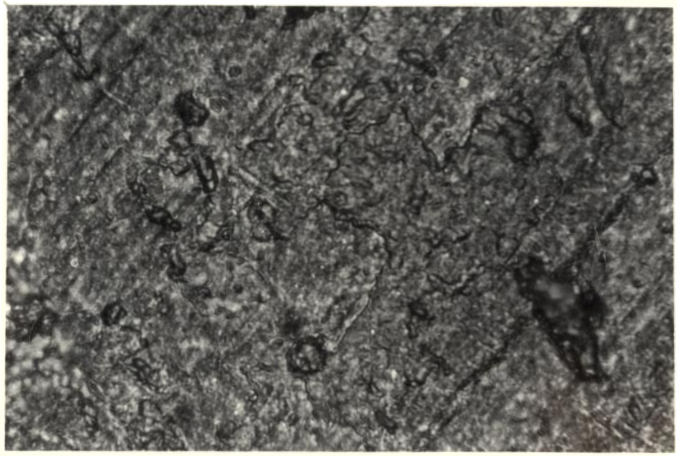


Fig. 4.32 Conventional

Optical microscope photographs of 70/30 NR/IIR blends

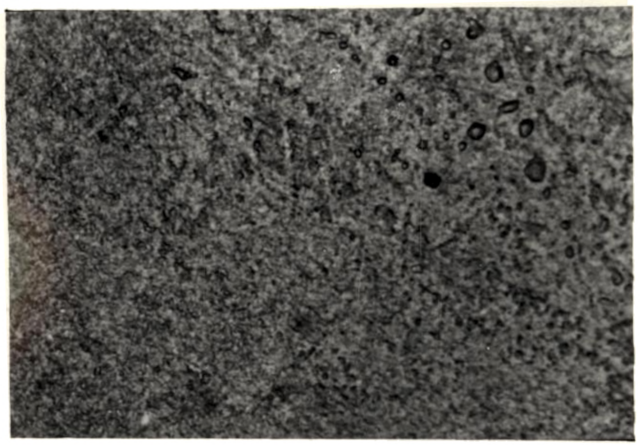


Fig.4.33 Modified

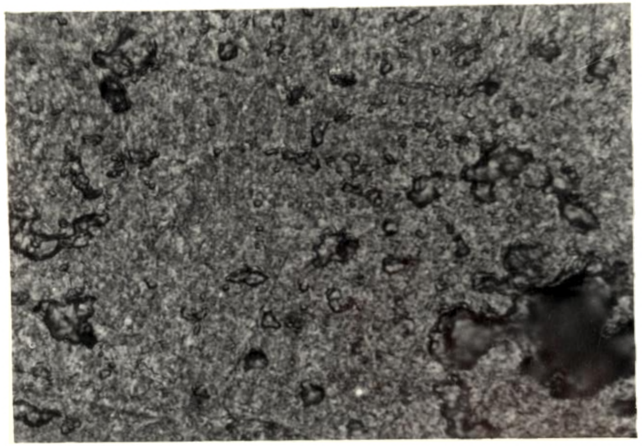


Fig.4.34 Conventional

Optical microscope photographs of 50/50 NR/IIR blends

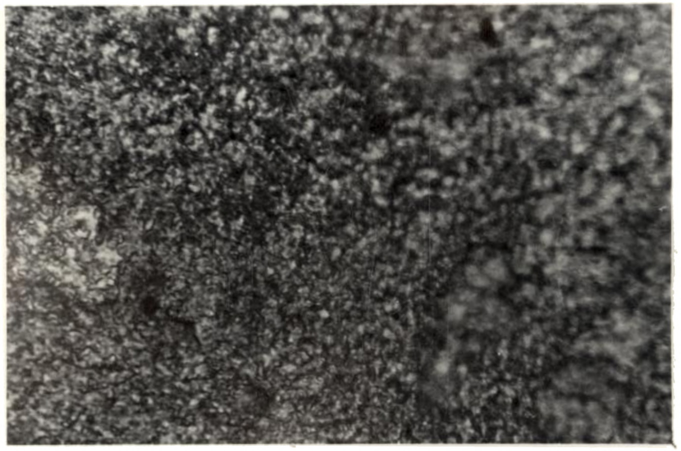


Fig.4.35 Modified

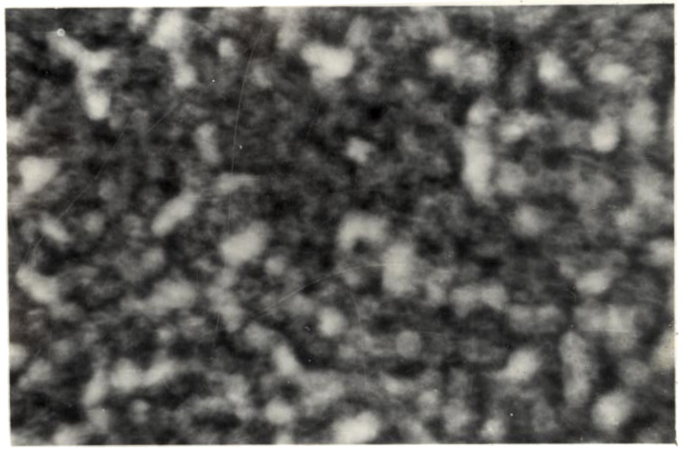


Fig.4.36 Conventional

Optical microscope photographs of 30/70 NR/IIR blends

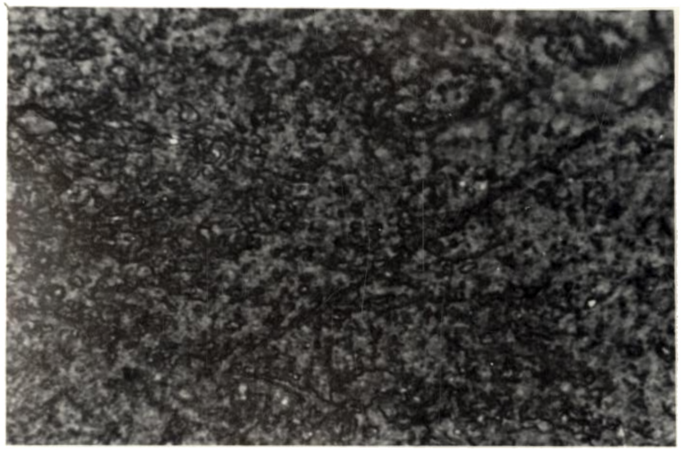


Fig.4.37 Modified

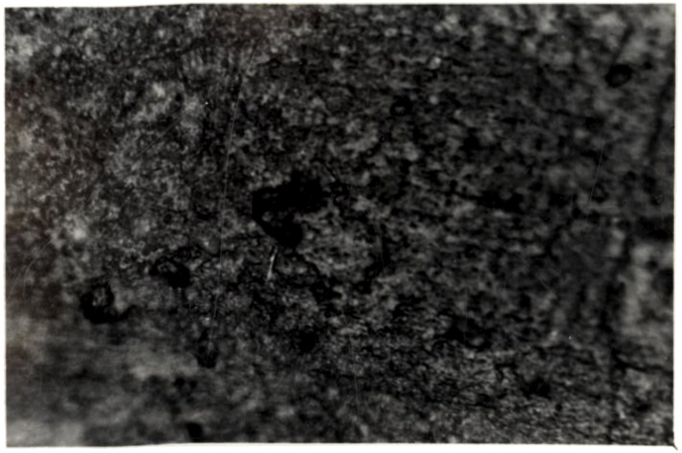


Fig.4.38 Conventional

Optical microscope photographs of 80/20 NR/EPDM blends

Fig.4.39 Modified

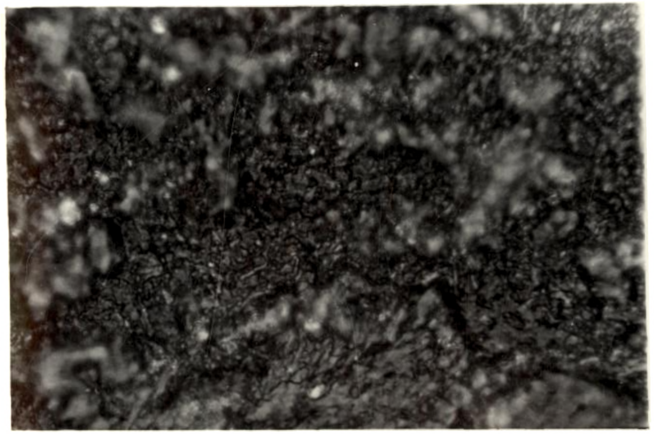


Fig.4.40 Conventional

Optical microscope photographs of 50/50 NR/EPDM blends

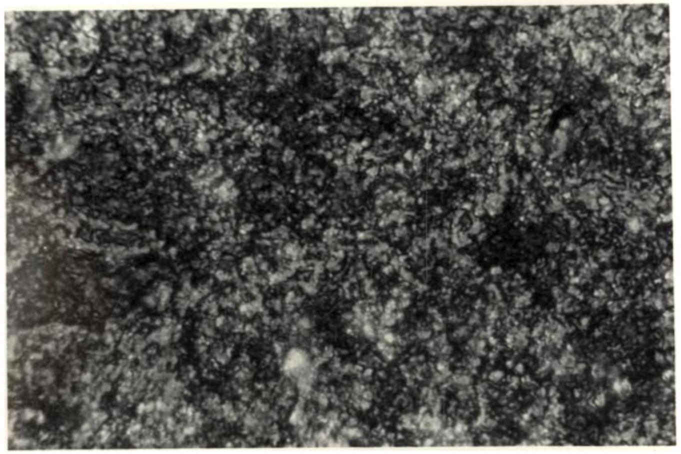


Fig.4.41 Modified

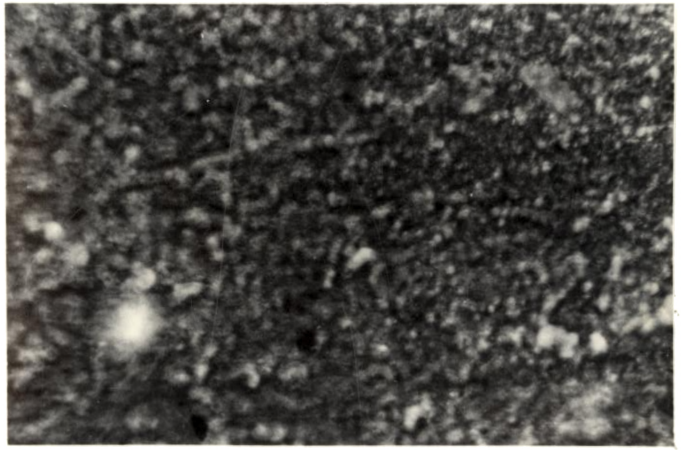


Fig.4.42 Conventional

Optical microscope photographs of 20/80 NR/EPDM blends

CONCLUSIONS

1. A low degree of precuring in the IIR phase in NR/IIR blends and in the EPDM phase in NR/EPDM blends is found to be an attractive means of achieving cocrosslinked state in these blends.

2. Mechanical properties which are influenced by the crosslink densities in both the phases and in the interface are remarkably improved by precuring.

3. The processing safety is not adversely affected by precuring.

4. Precuring helps to improve the compatibility of NR/IIR and NR/EPDM blends.

Part II: INVESTIGATION OF THE PROCESSABILITY OF NR/IIR AND NR/EPDM BLENDS USING A TORQUE-RHEOMETER

Melt flow behaviour of polymers is of great importance in optimising the processing parameters. The concept of 'processability' of a rubber mix is closely related to its plasticity or its elastic recovery during shaping. According to the ASTM standard[7], processability is the relative ease with which a raw rubber or mix is shaped in the processing equipment. Almost all large tonnage rubber compounds today comprise blends of two or more elastomers. A large number of indepth studies have been reported on the melt flow behaviour of elastomers and their blends.[8-16]

The rubber industry operates with devices imparting shear stresses and shear rates over a wide range. Therefore the viscosity of a polymer as a function of shear rate and temperature is very important. To be able to investigate the processability of a material, laboratory conditions must simulate operating conditions as closely as possible. For determining the processability of a material, testing devices were developed whose operating principles are identical with those of operational devices, a common example being the Brabender plasticorder.[17-21] The processability of modified NR/IIR and NR/EPDM blends is compared with their conventional counterparts on a Brabender plasticorder in this part of the study.

EXPERIMENTAL

The various elastomer compounds and the blend compounds used in this study (Tables 4.7 and 4.8) were prepared on a two roll mixing mill. Processability studies of the above compounds were done on a Brabender plasticorder at different temperatures and rotational speeds of the rotors (rpms) and the dependence of viscosity of the mixes on the shear rate and temperature was evaluated keeping 15 minutes as the mixing time.

RESULTS AND DISCUSSION

It was shown that the relationship obtainable from a Brabender plasticorder, $M = CS^a$ (where M is the torque, S the rpm and c and a are constants), closely resembles the familiar power law behaviour and hence can be used for calculation of the power law index.[19] In the above equation 'a' represents the power law index. Also torque/rpm represents viscosity and the activation energy can be

Table 4.7: Formulations of NR/IIR blends

Materials	Designation of the blends							
	1	2	3	4	5	6	7	8
NR	100	--	75	75	50	50	25	25
IIR	--	100	25	--	50	--	75	--
IIR (Modified)	--	--	--	25	--	50	--	75
ZnO	5.0	4.0	4.75	3.75	4.5	2.5	4.25	1.25
Stearic acid	2.0	2.0	2.0	1.5	2.0	1.0	2.00	0.50
MBTS	0.6	0.6	0.6	0.45	0.6	0.3	0.60	0.15
TMTD	0.2	1.0	0.4	0.15	0.6	0.1	0.80	0.05
Carbon black (HAF N-330)	50	50	50	37.5	50	25	50	12.50
Naphthenic oil	8.0	8.0	8.0	6.0	8.0	4.0	8.00	2.00
Sulphur	2.5	1.5	2.25	1.88	2.0	1.25	1.75	0.63

Table 4.8: Formulations of NR/EPDM blends

Materials	Designation of the blends							
	1'	2'	3'	4'	5'	6'	7'	8'
NR	100	--	75	75	50	50	25	25
EPDM	--	100	25	--	50	--	75	--
EPDM (Modified)	--	--	--	25	--	50	--	75
ZnO	5.0	4.0	4.75	3.75	4.5	2.5	4.25	1.25
Stearic acid	2.0	2.0	2.0	1.5	2.0	1.0	2.0	0.5
MBTS	0.6	0.6	0.6	0.45	0.6	0.3	0.6	0.15
TMTD	0.2	1.0	0.4	0.15	0.6	0.1	0.8	0.05
Carbon black (HAF N-330)	50	50	50	37.5	50	25	50	12.5
Naphthenic oil	8.0	8.0	8.0	6.0	8.0	4.0	8.0	2.0
Sulphur	2.5	1.5	2.25	1.88	2.0	1.25	1.75	0.63

measured from torque rheometer data if log(torque/rpm) is plotted against 1/T, using the expression,

$$\eta = Ae^{E/RT}$$

where E is the activation energy for viscous flow,

R the gas constant

T the absolute temperature and

A is a constant.

Fig.4.43 shows the variation of viscosity of NR/IIR blends with shear rate. The viscosity is strongly dependent on the shear rate as expected. The flow curves of modified IIR rich blends are close to that of IIR alone. For NR rich blends the location of the flow curve is close to that of NR. As temperature increases the shear dependence of viscosity becomes weaker. Change in viscosity of NR/EPDM blends with shear rate is given in Fig.4.44. As evidenced from the figure, flow curves for the NR/EPDM blends are located in a region bounded by the flow curves of the individual rubbers and with the increase in the concentration of a rubber the flow curve approaches the flow curve of that rubber. As in the case of NR/IIR blends, the shear dependence of viscosity is found to weaken with

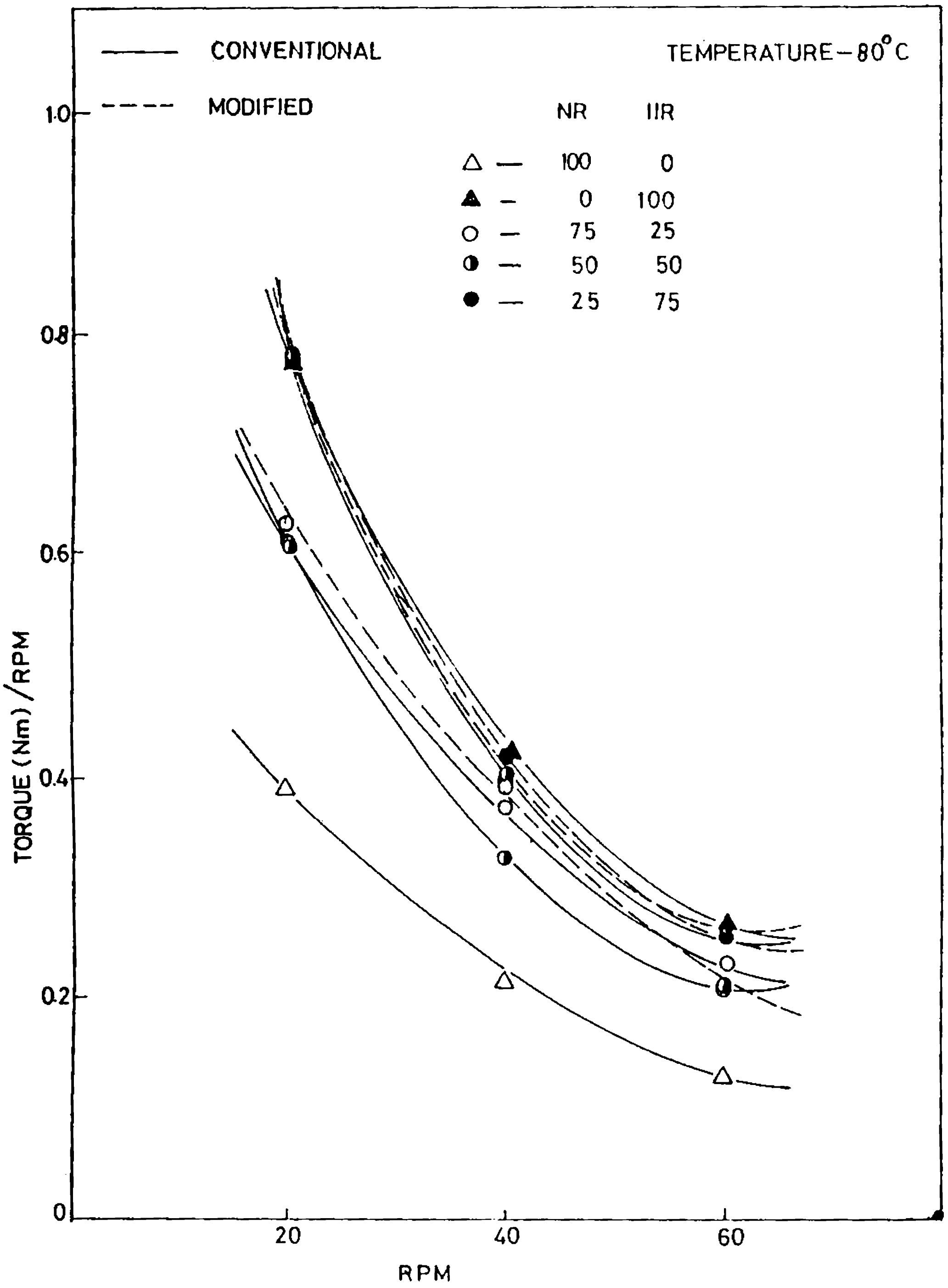


Fig.4.43: Variation of viscosity (torque/rpm) with shear rate (rpm) for NR/IIR blends at 80°C

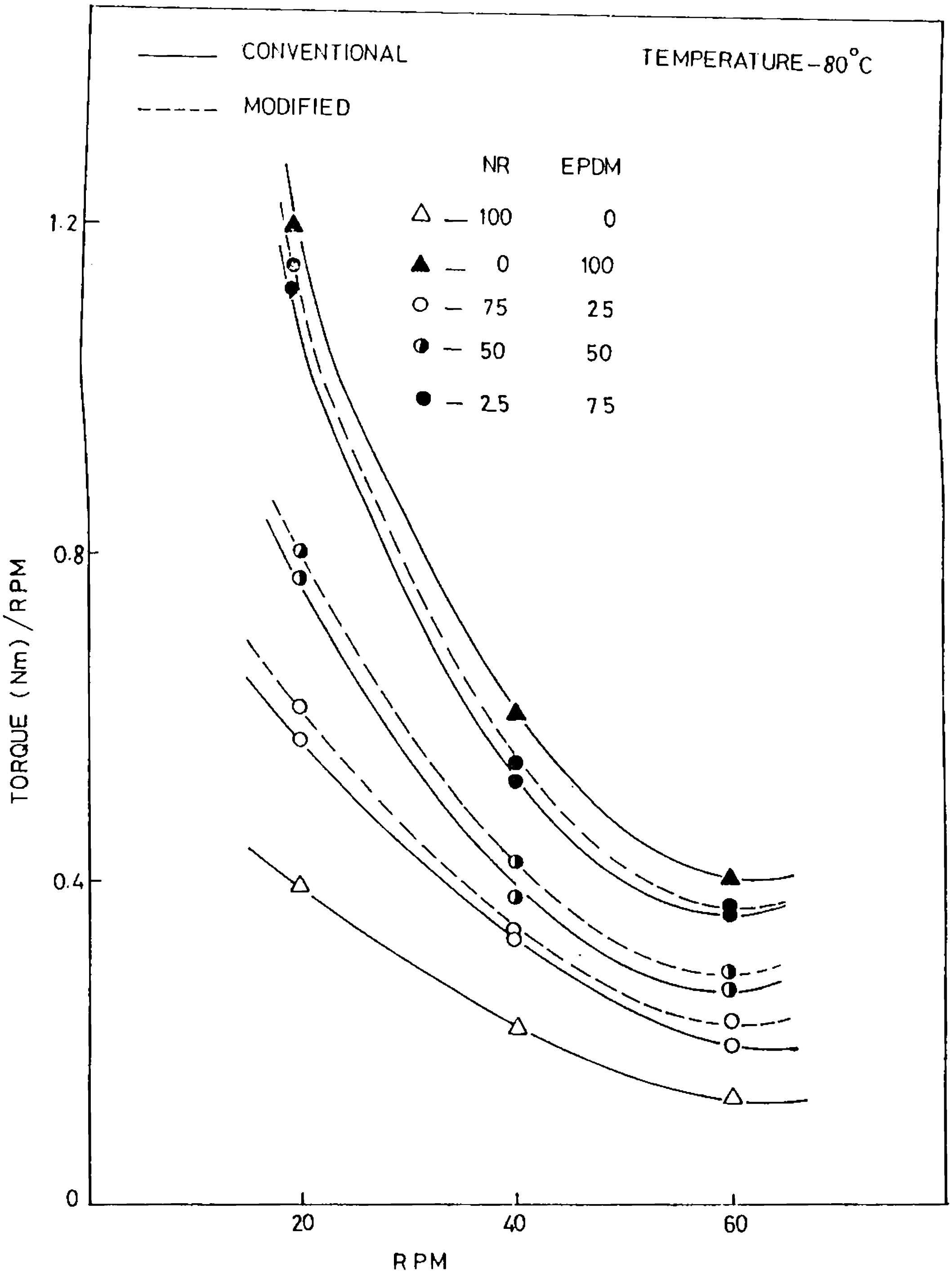


Fig.4.44: Variation of viscosity (torque/rpm) with shear rate (rpm) for NR/EPDM blends at 80°C

increase in temperature. The power law index values calculated from the plots of torque versus rpm (Figs.4.45 and 4.46) curves, are shown in Tables 4.9 and 4.10. The extent of non-Newtonian behaviour can be understood from these values. Both the conventional and modified blends are highly pseudoplastic in nature.

Fig.4.47 gives the variation of viscosity of NR/IIR blends with composition. The modified blends exhibit a positive deviation with composition whereas the conventional blends exhibit a negative deviation. This may be due to the strong interface interaction at the boundary layer upon modification. This is particularly true for IIR rich blends. Fig.4.48 shows the ,variation of viscosity of NR/EPDM blends with composition. With increase in EPDM content the viscosity increases, but does not exceed that of EPDM alone. There is a slight increase in viscosity as a result of modification in all cases.

Fig.4.49 permits the calculation of activation energies of viscous flow for NR/IIR blends. Inorder to understand the influence of temperature on viscosity of the blends at a particular shear rate, Arrhenius plots at constant rpms were made. In this figure, logarithm of

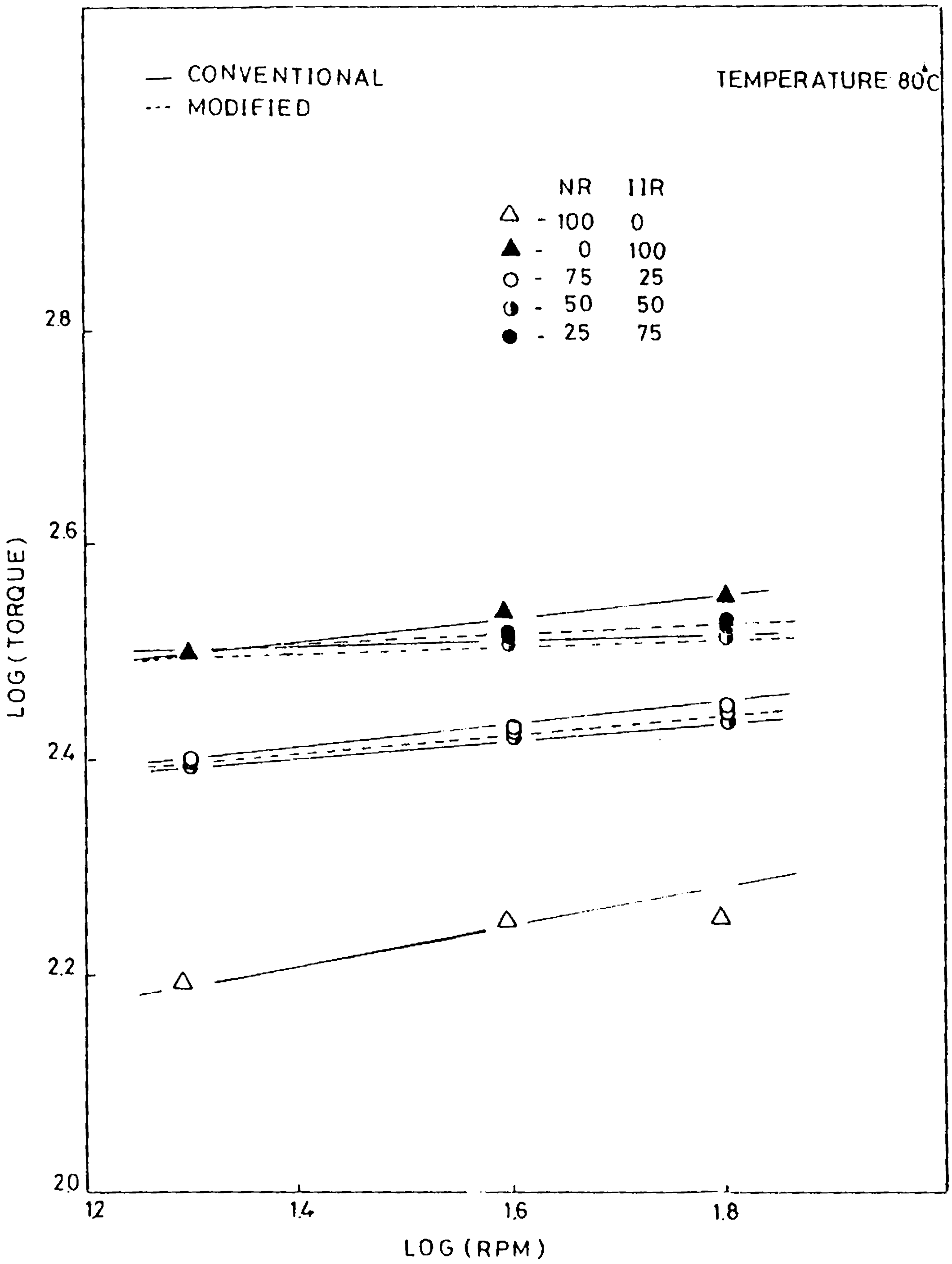


Fig.4.45: Variation of torque with rpm for NR/IIR blends at 80°

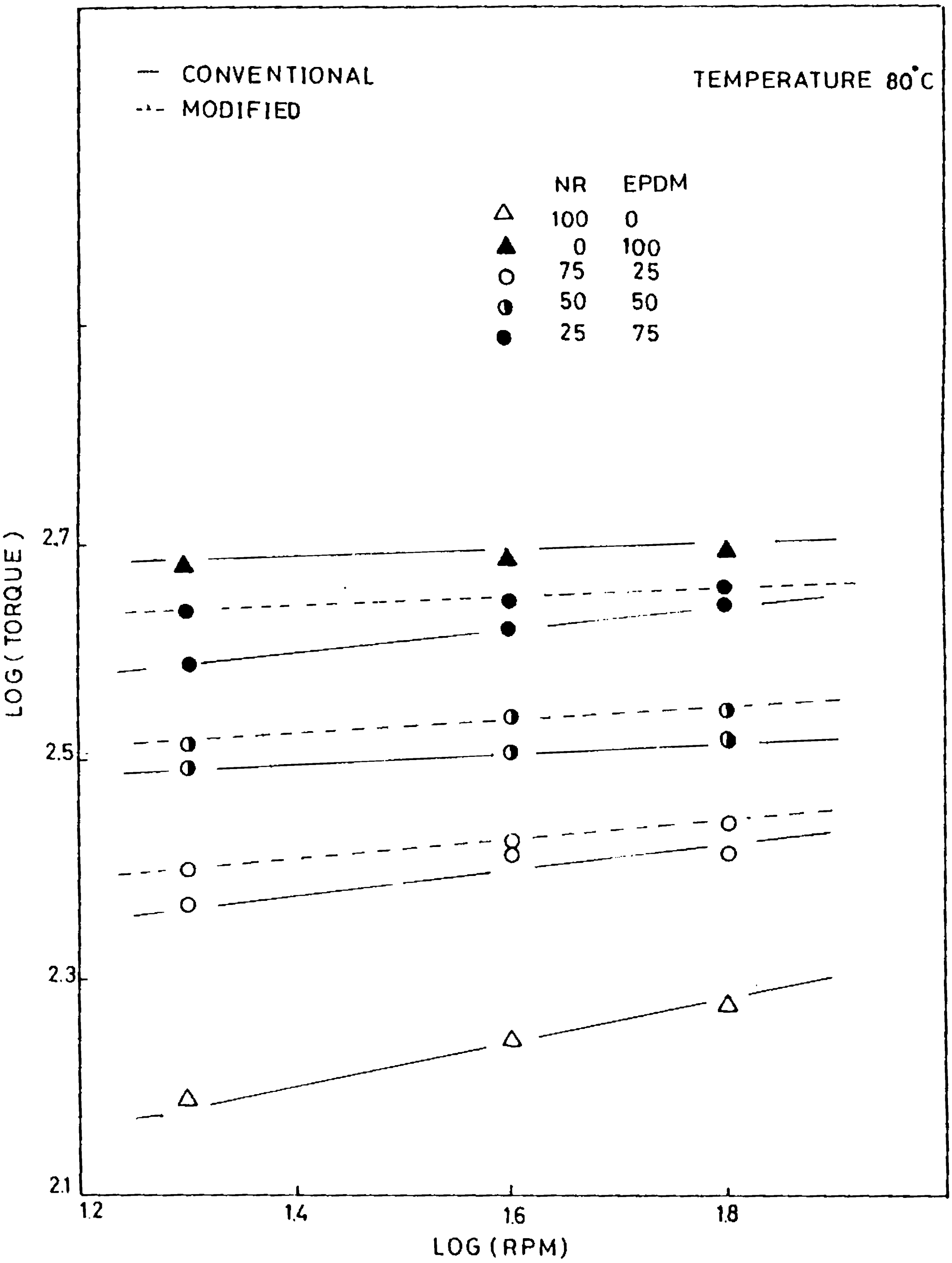


Fig.4.46: Variation of torque with rpm for NR/EPDM blends at 80°C

Table 4.9: Power law index for NR/IIR blends

Blend composition (percentage of IIR)	Power law index at a temperature of		
	80°C	100°C	120°C
0	0.22	0.40	0.57
100	0.01	0.08	0.20
25	0.10	0.25	0.27
25 (Modified)	0.11	0.21	0.20
50	0.08	0.11	0.12
50 (Modified)	0.04	0.13	0.11
75	0.05	0.10	0.24
75 (Modified)	0.03	0.13	0.14

Table 4.10: Power law index for NR/EPDM blends

Blend composition (percentage of EPDM)	Power law index at a temperature of		
	80°C	100°C	120°C
0	0.22	0.40	0.57
100	0.13	0.12	0.21
25	0.15	0.19	0.31
25 (Modified)	0.10	0.19	0.28
50	0.08	0.15	0.20
50 (Modified)	0.08	0.15	0.17
75	0.10	0.17	0.20
75 (Modified)	0.05	0.20	0.17

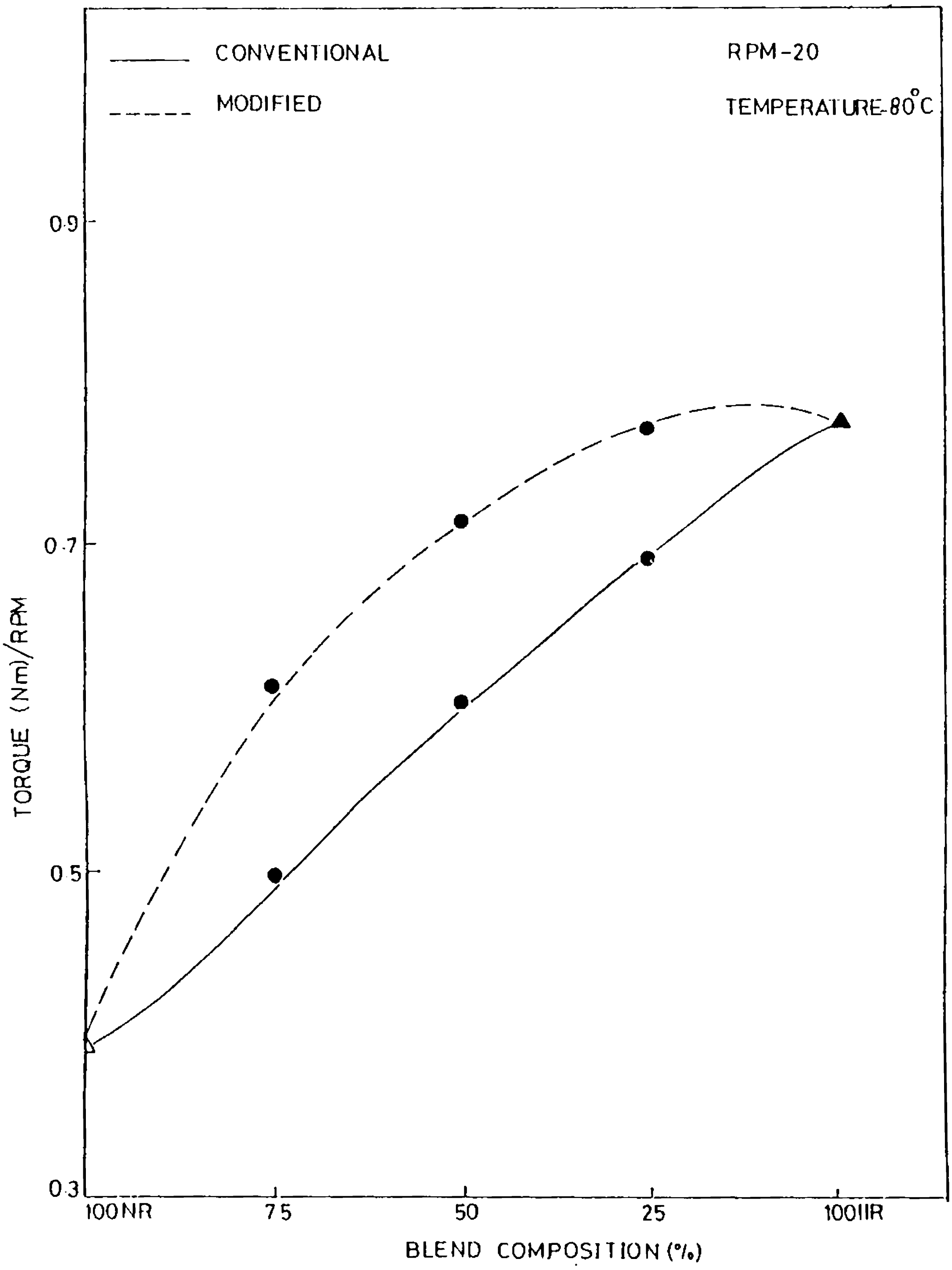


Fig.4.47: Variation of viscosity (torque/rpm) with composition of NR/IIR blends

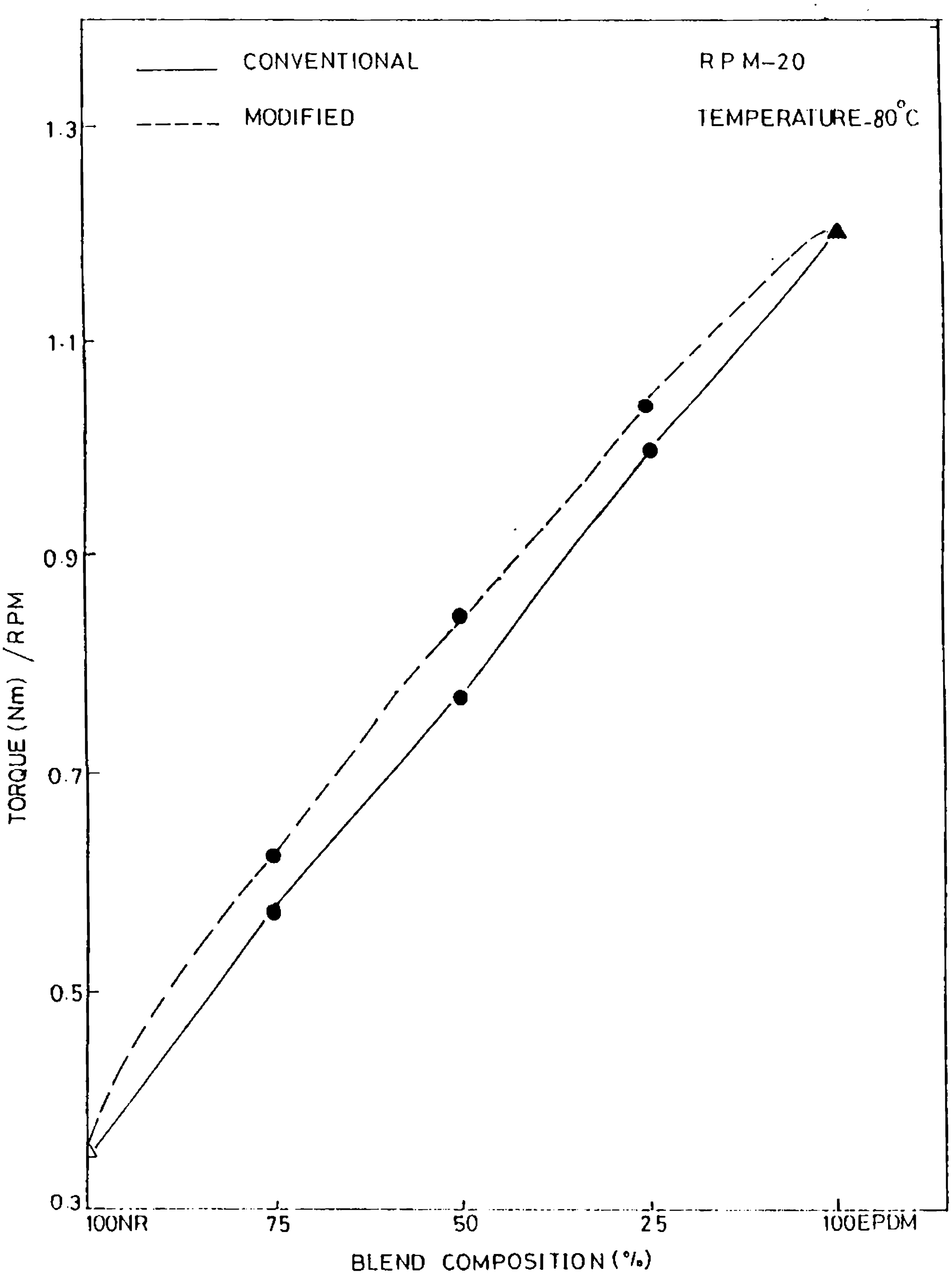


Fig.4.48: Variation of viscosity (torque/rpm) with composition of NR/EPDM blends

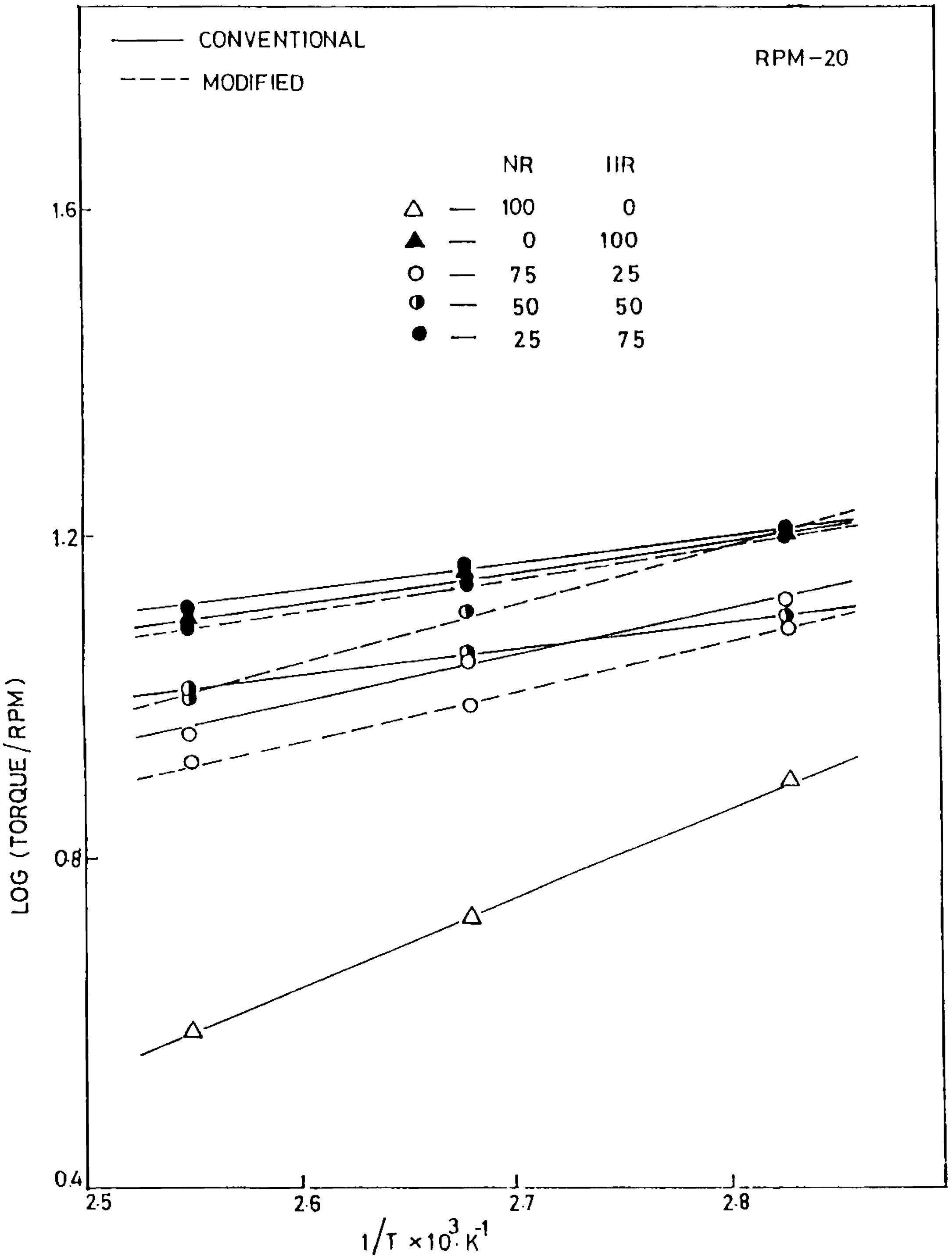


Fig.4.49: Variation of viscosity (torque/rpm) with temperature for NR/IIR blends

viscosity is plotted as a function of reciprocal temperature. The activation energy (E) of flow, calculated from the slope of these lines is given in Table 4.11. It provides valuable information on the sensitivity of the material towards the change in temperature. The higher the activation energy, the more temperature sensitive the material will be. NR has a higher activation energy compared to IIR. Consequently, NR rich blends show higher activation energies. However, all the blends have an activation energy intermediate between those of the components. But in the case of 50/50 blends, the activation energy is higher as a result of modification. It may be due to the strong interface interactions at boundary layer. The temperature dependence of viscosity for NR/EPDM blends is given in Fig.4.50. Table 4.12 shows the activation energies calculated from this figure, which are comparable with those of the NR/IIR blends. The 50/50 NR/EPDM blend has a very low value. It may be due to the fact that at this composition, a cocontinuous phase of both rubbers occurs and easy slippage of the molecules is possible. In most cases the activation energies of the modified blends are less than those of the conventional blends.

Table 4.11: Activation energy of viscous flow for NR/IIR blends

Blend composition (percentage of IIR)	Activation energy (kJ mol^{-1}) at various rpms		
	20	40	60
0	8.87	7.65	5.54
100	3.14	2.67	1.78
25	7.43	3.80	3.18
25 (Modified)	4.84	3.09	2.60
50	2.29	1.94	1.44
50 (Modified)	6.08	3.18	1.78
75	3.57	2.40	1.44
75 (Modified)	2.88	2.34	1.44

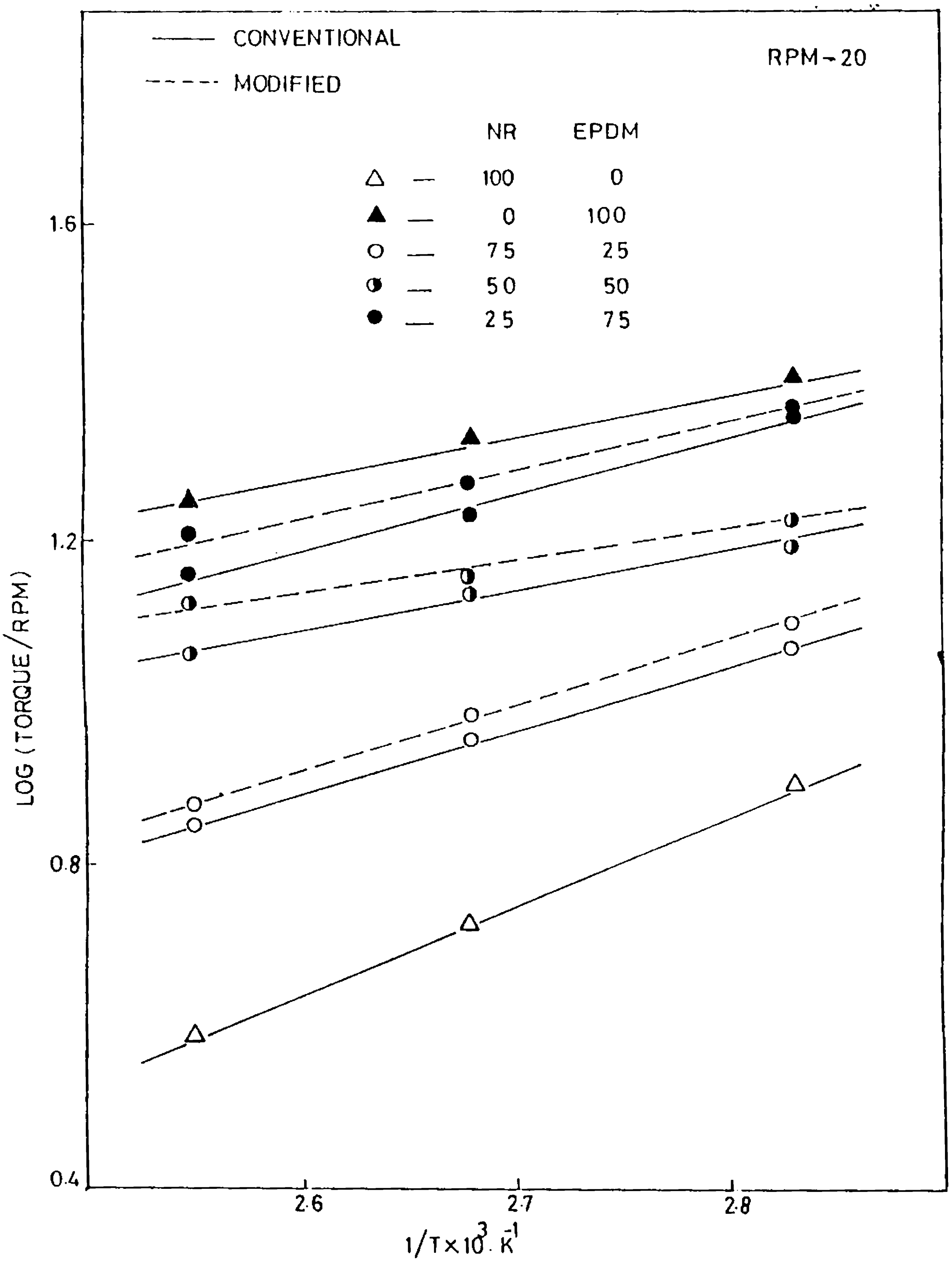


Fig.4.50: Variation of viscosity (torque/rpm) with temperature of NR/EPDM blends

Table 4.12: Activation energy of viscous flow for NR/EPDM blends

Blend composition (percentage of EPDM)	Activation energy ($kJ\ mol^{-1}$) at various rpms		
	20	40	60
0	8.87	7.65	5.54
100	4.59	2.53	1.77
25	6.82	5.33	3.86
25 (Modified)	7.00	4.93	4.16
50	4.43	2.22	1.08
50 (Modified)	3.70	1.62	0.79
75	6.05	2.70	2.60
75 (Modified)	5.12	2.27	2.29

CONCLUSIONS

1. The study shows that melts of NR/IIR and NR/EPDM blends are highly pseudoplastic.

2. The processability characteristics of the modified NR/IIR and NR/EPDM blends are similar to those of the conventional blends.

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Chapter 5

UTILISATION OF IIR TUBE RECLAIM FOR DEVELOPING NR/IIR BLENDS

Reclaim is the type of degraded rubber with unique properties and it is prepared from waste or worn-out rubber products. Reclaiming process imparts the necessary degree of plasticity to vulcanized rubber and thereby enables it to be blended with natural or synthetic rubber. Utilisation of waste is almost as old as rubber manufacturing since it offers processing as well as economic advantages.[1] The utilisation of scrap materials is an important factor in the expansion of the raw materials base of industry, the reduction of demand for primary raw materials and economization of financial resources.

Standard methods of utilisation of polymer scrap may be divided into various groups[2] (Fig.5.1).

In the last few years considerable work has been done on reuse of scrap polymeric materials.[3-10] Acetta and Vergnaud,[11,12] have studied vulcanization of scrap rubber powder with vulcanizing agents under normal conditions of temperature, time and pressure without adding

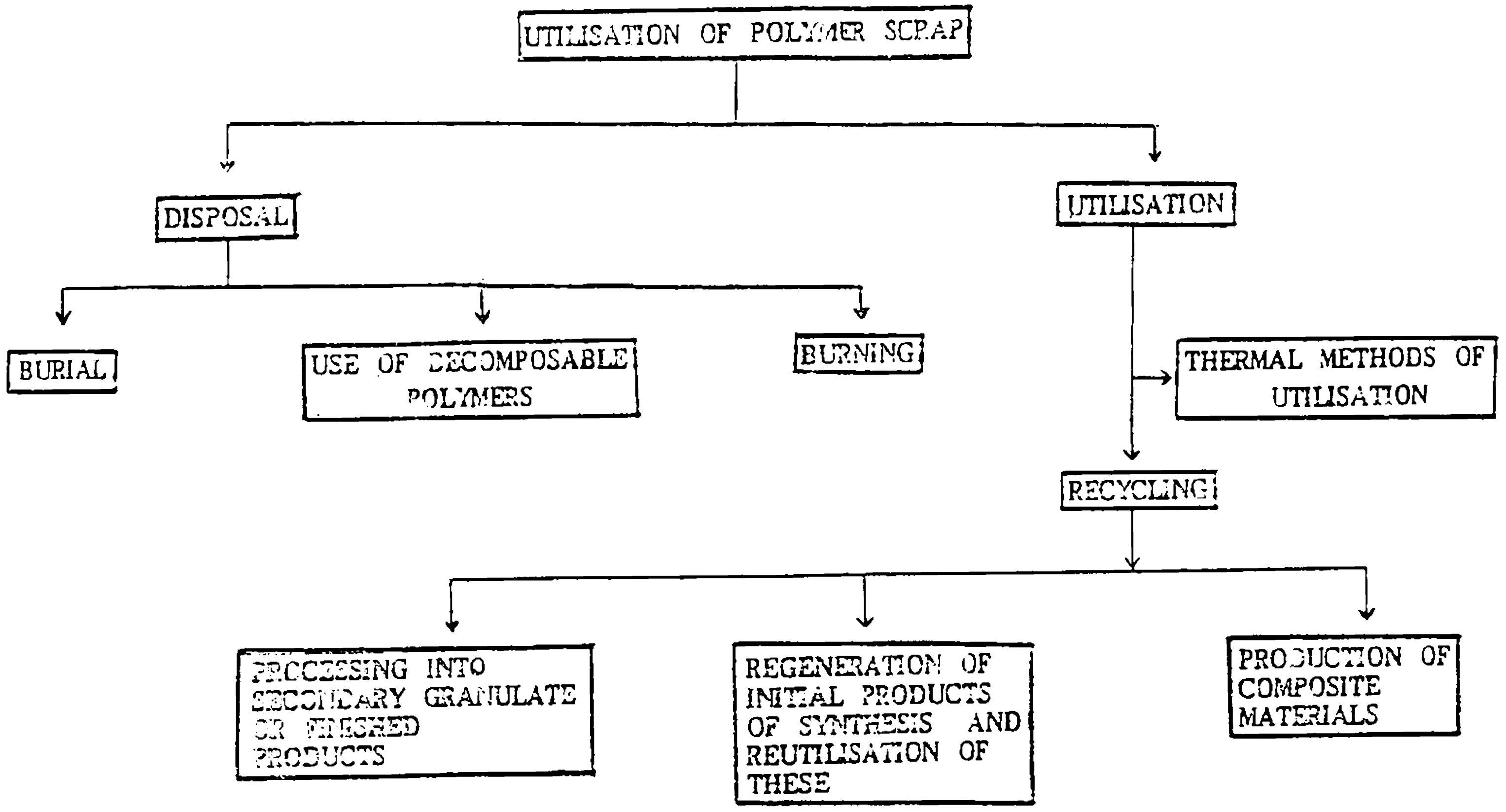

Fig.5.1 METHODS OF UTILISATION OF POLYMER SCRAP

fresh raw rubber. De and coworkers[13,14] have studied vulcanization of reclaimed rubber (RR) and NR/RR blends. Studies by Kretic et al.[15] showed that there is a significant drop in tensile strength even at low levels of scrap rubber in the mix.

In this chapter, the effect of addition of isobutylene-isoprene rubber (IIR) tube reclaim in natural rubber compounds at various levels and the flow behaviour of these compounds using a torque rheometer are reported.

EXPERIMENTAL

Natural rubber compounds containing various levels of IIR reclaim (hereafter referred to as reclaimed rubber--RR) were prepared on a laboratory mixing mill (6"x12") according to ASTM D 3182 (1982) as per formulations given in Table 5.1. Cure characteristics of these compounds were determined using a Monsanto rheometer model R 100. The compounds were then vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press at 150°C. Dumbell shaped tensile test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties were then measured on a

Table 5.1: Formulations of NR/RR blends

Mix	A	B	C	D	E	F
NR	100	90	80	70	60	50
RR	--	20	40	60	80	100
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
MBTS	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0.2	0.2	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5
Carbon black (HAF N-330)	40	40	40	40	40	40
Naphthenic oil	8.0	8.0	8.0	8.0	8.0	8.0

Zwick universal testing machine as per ASTM D 412. Angular test pieces were punched out of the compression moulded sheets and tear resistance was measured on a Zwick universal testing machine according to ASTM D 624. Samples for abrasion resistance, compression set and hardness were moulded and tested as per relevant ASTM standards.

The ageing resistance of the vulcanizates was studied after ageing the samples at 100°C for 24 hours in a laboratory air oven.

Processability of the rubber compounds was evaluated at different temperatures (80, 100 and 120°C) and at different shear rates (20, 40 and 60 rpms) on a Brabender plasticorder model PL 3S.

RESULTS AND DISCUSSION

The cure curves of the blends obtained from Monsanto rheometer are shown in Figs.5.2 and 5.3. The cure characteristics calculated from these curves are shown in Table 5.2. The cure characteristics of the blends indicate that an increase in reclaimed rubber content decreases the scorch time, decreases the optimum cure time, increases the cure rate and reduces reversion. The reduced scorch time

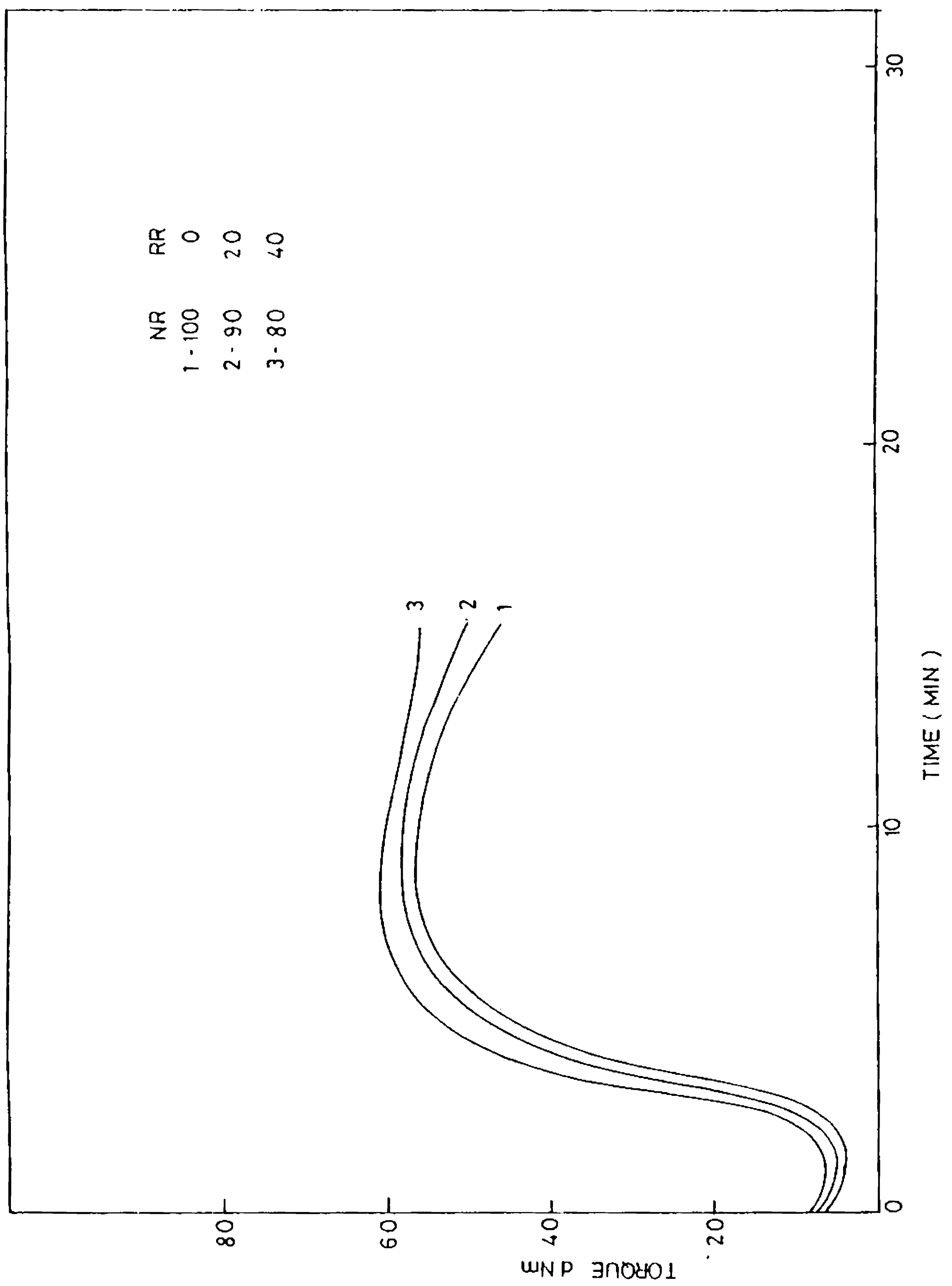

Fig.5.2: Cure curves of NR/RR blends

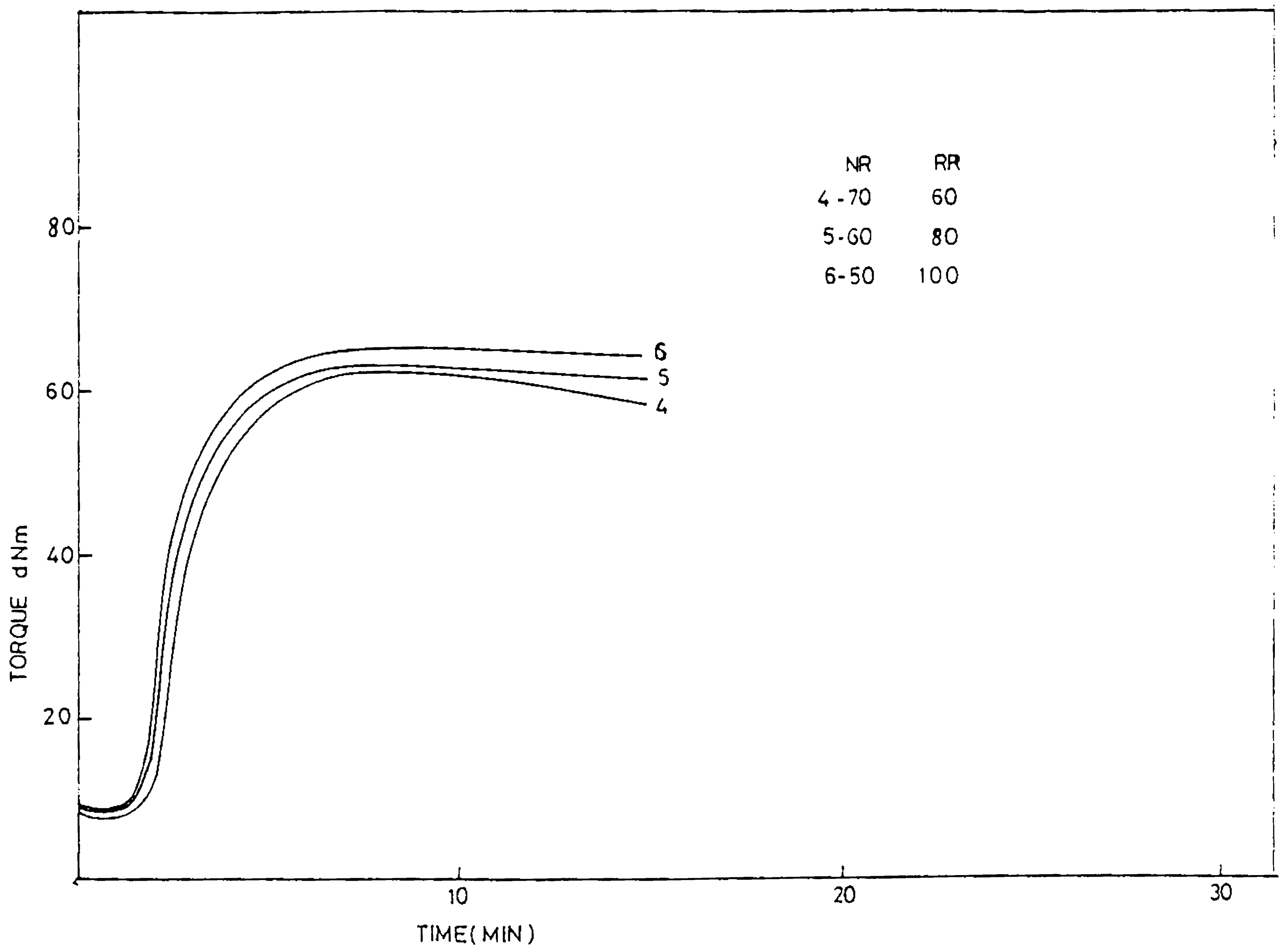

Fig.5.3: Cure curves of NR/RR blends

Table 5.2: Cure characteristics of NR/RR blends

Mix	Percentage of rubber reclaim					
	0	10	20	30	40	50
Scorch time, min.	2.25	2.25	2.00	2.00	1.75	1.70
Optimum cure time, min.	5.00	5.00	4.75	4.75	4.00	3.50
Cure rate (d.Nm/min.)	18.6	21.8	23.3	25.2	27.0	28.7
Maximum torque, d.Nm	56	58	60	62	63	65
Reversion, number of units dropped in 5 min.	2.5	2.0	1.75	1.50	0.75	Nil

may be due to the unreacted/released curatives in RR. This may also be the reason for the high cure rate and low cure time. Excellent heat resistance of IIR may be the reason for the reduction in the reversion of the mixes. Maximum torque, which is a measure of the modulus, increases with the addition of reclaimed rubber.

Fig.5.4 shows the tensile and tear strength of the blends. There is a significant drop in tensile and tear strength even at low levels of reclaimed rubber. Elongation at break and modulus at 100% elongation of the blends are shown in Fig.5.5. The introduction of RR leads to an increase in the modulus and reduction in the elongation at break of the vulcanizates.

Fig.5.6 shows the retention in tensile strength and modulus on thermal ageing at 100°C for 24 hours with different levels of reclaimed rubber. The very poor ageing resistance of NR can be seen from the figure. But the ageing resistance steadily improves with increase in the levels of RR. The retention in modulus also improves with RR content (Fig.5.6). Fig.5.7 shows the compression set of the blends. The compression set decreases with the addition of RR. Fig.5.8 shows the hardness and abrasion resistance

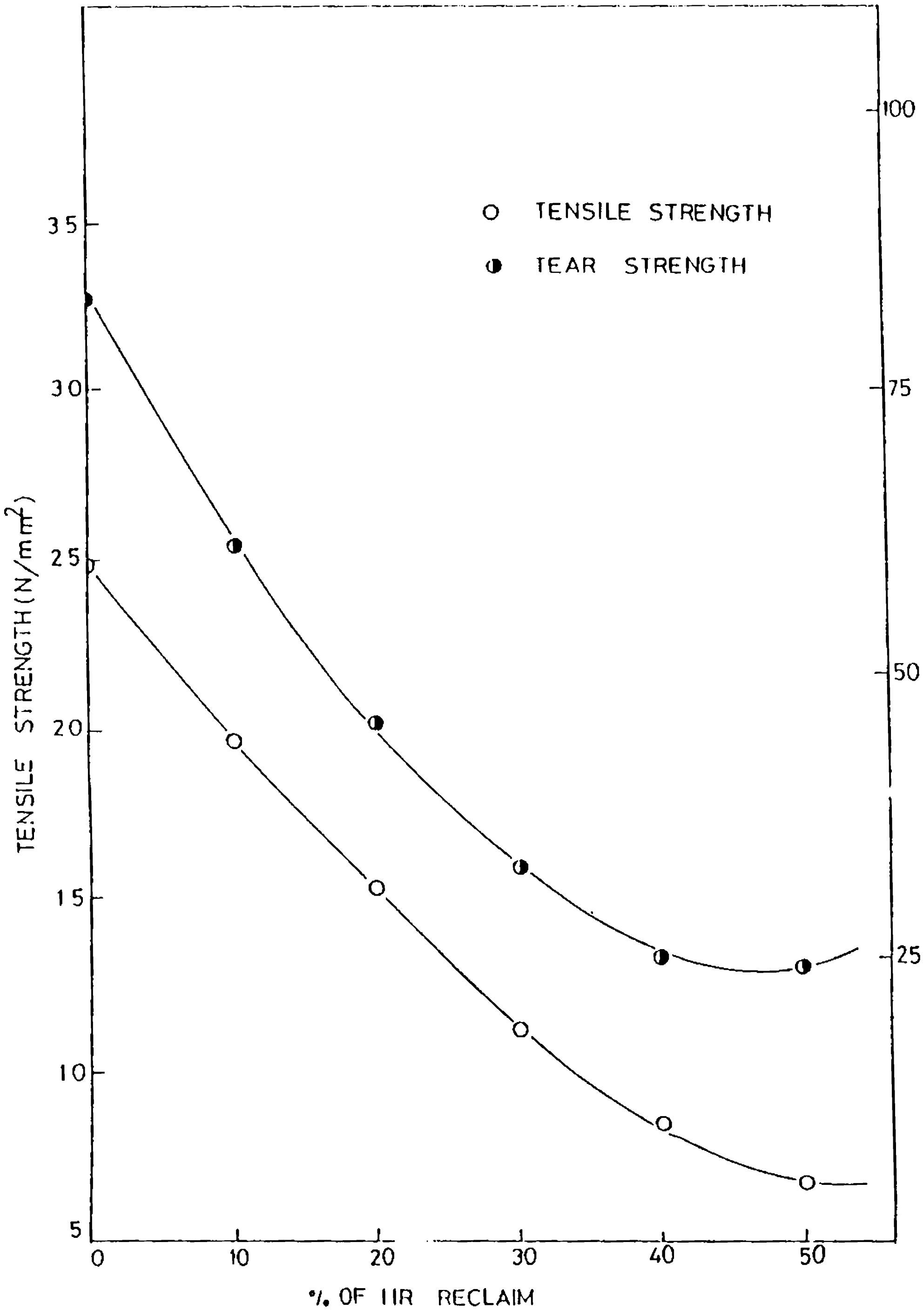

Fig.5.4: Variation of tensile strength and tear strength of NR with RR content

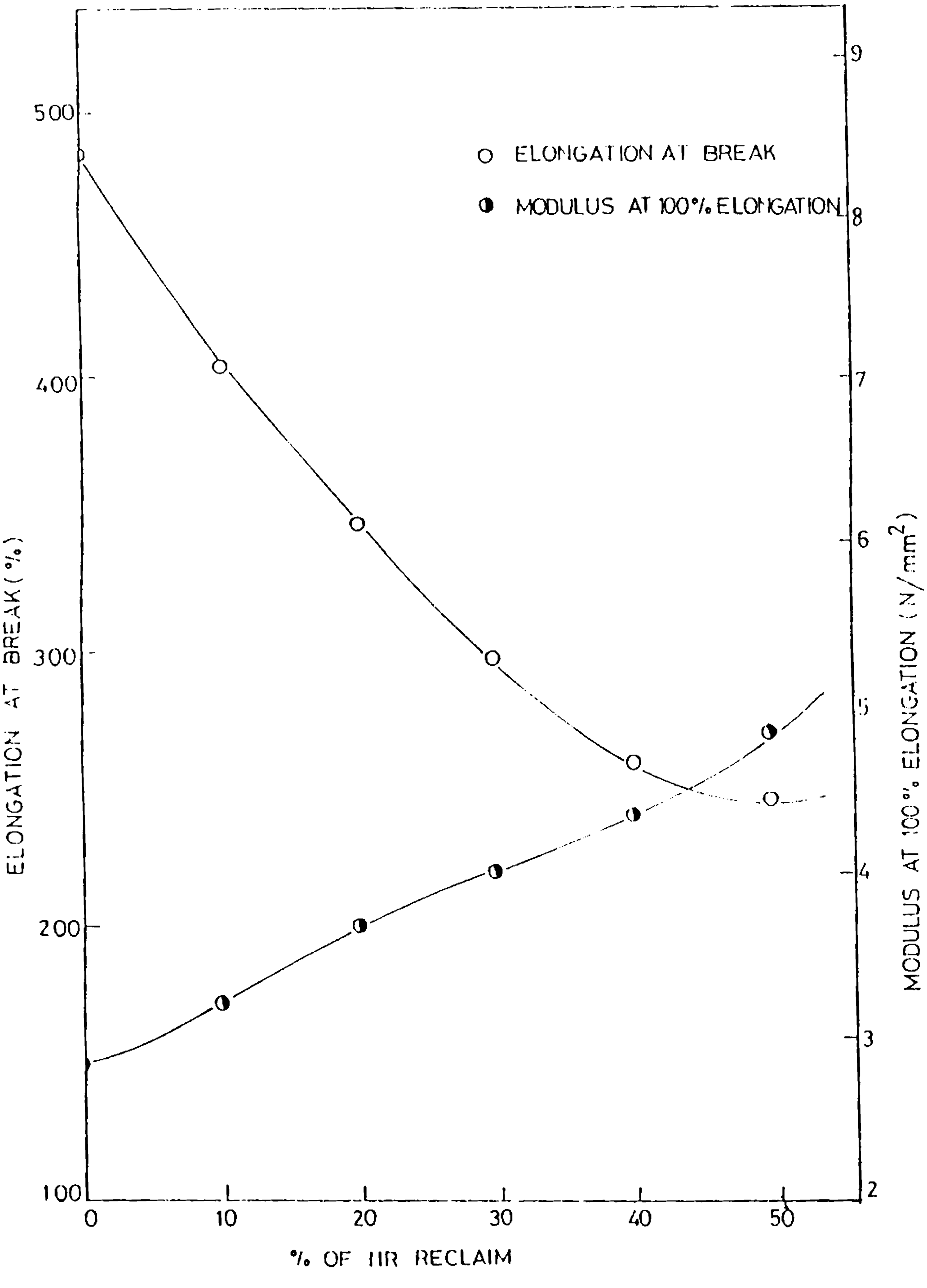

Fig.5.5: Variation of elongation at break and modulus of NR with RR content

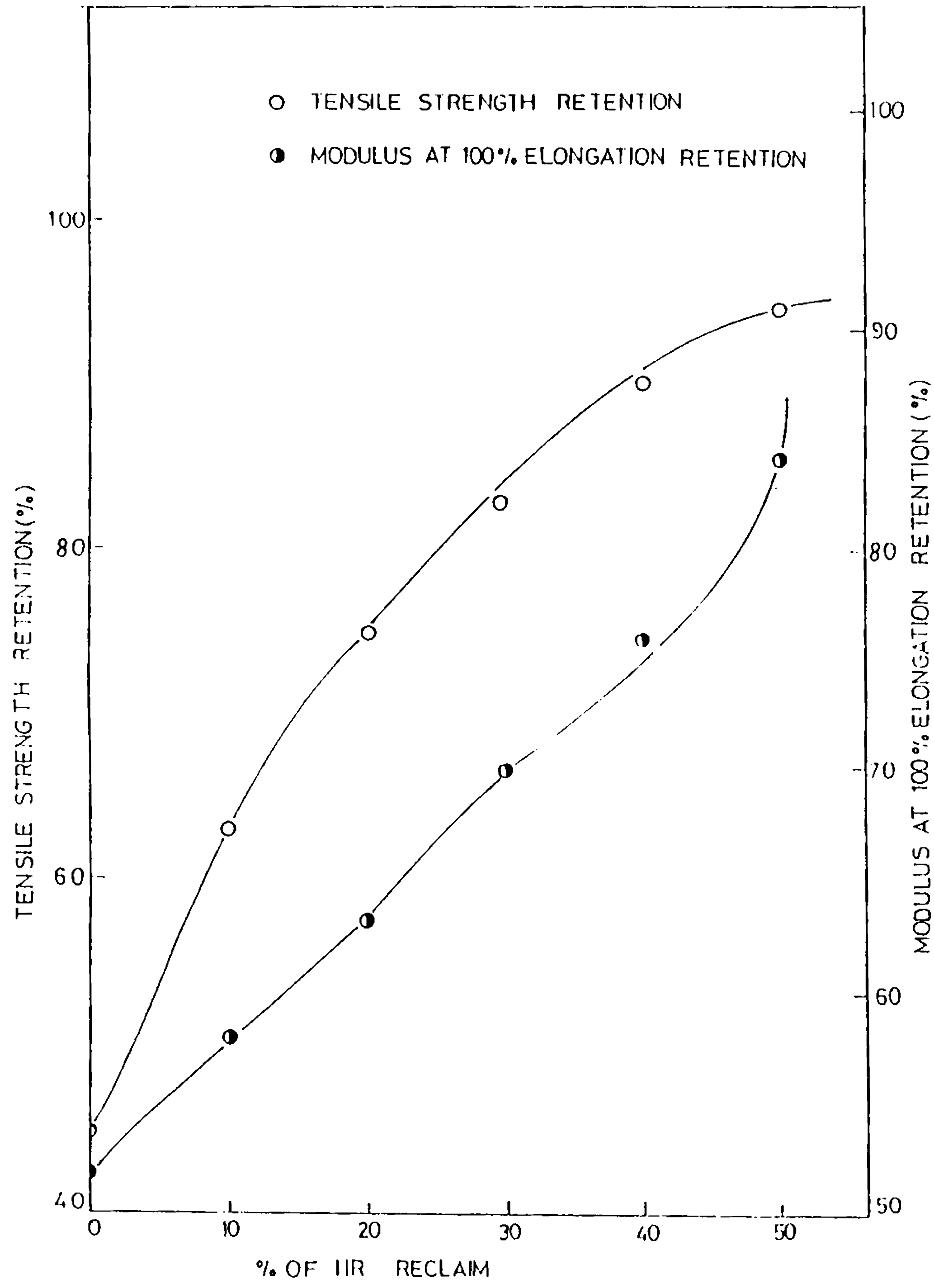

Fig.5.6: Variation of tensile strength retention and modulus retention of NR with RR content

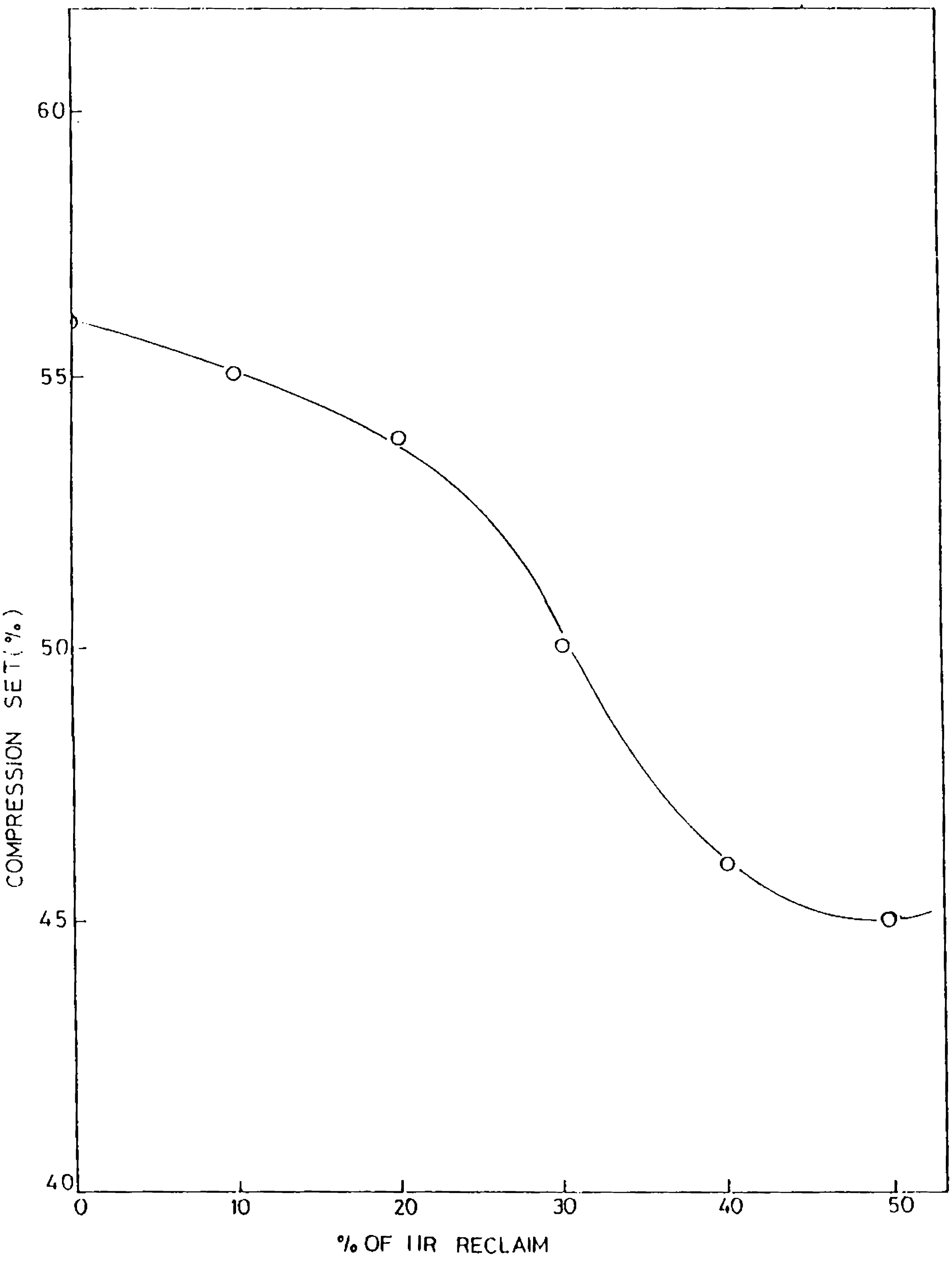

Fig.5.7: Variation of compression set of NR with RR content

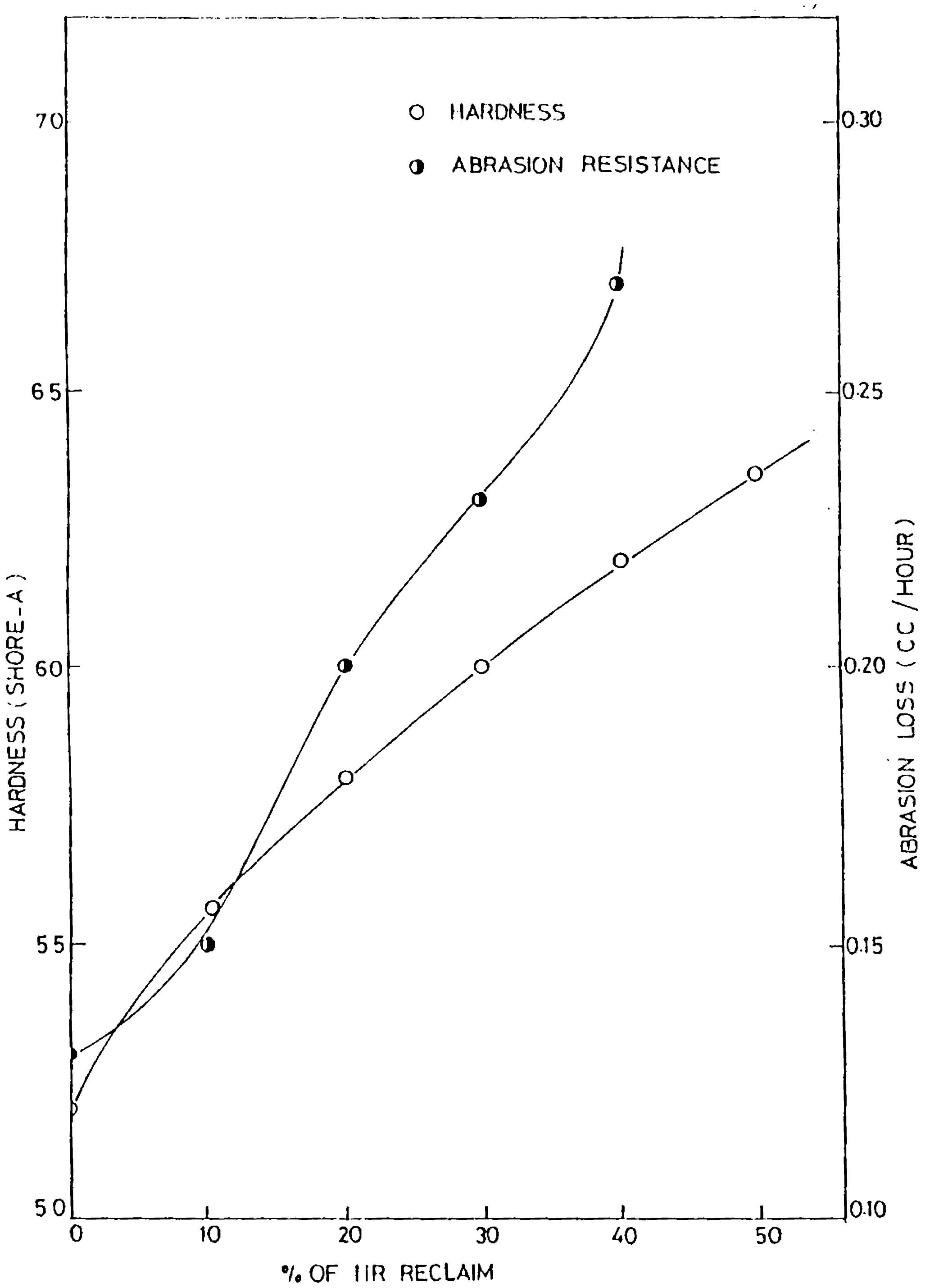

Fig.5.8: Variation of hardness and abrasion loss of NR with RR content

of the blends. With the addition of RR, hardness increases but abrasion resistance decreases. From the mechanical properties, it seems that about 10 to 20% of RR may be added to NR without much deterioration in mechanical properties.

The processability studies were done on two compositions: NR with 10% RR and NR with 20% RR. Fig.5.9 illustrates the effect of viscosity of the blends with shear rate at a temperature of 80°C. As expected, the blends are highly pseudoplastic. It may also be observed that the addition of RR upto 20% does not change the viscosity of NR significantly. Fig.5.10 shows the variation of torque with rpm at different temperature (80, 100 and 120°C). The power law index was calculated as the slope of the log(torque) vs. log(rpm) lines.[16,17] Variation of power law index with temperature for the blends is shown in Table 5.3. The value of the power law index increases with increase in temperature and with the level of RR, which means that the blends become more Newtonian as expected.

Torque/rpm can represent viscosity and the activation energy can be measured from torque rheometer data, if log(torque/rpm) is plotted against 1/T.[18] Fig.5.11 shows the effect of viscosity on temperature at different

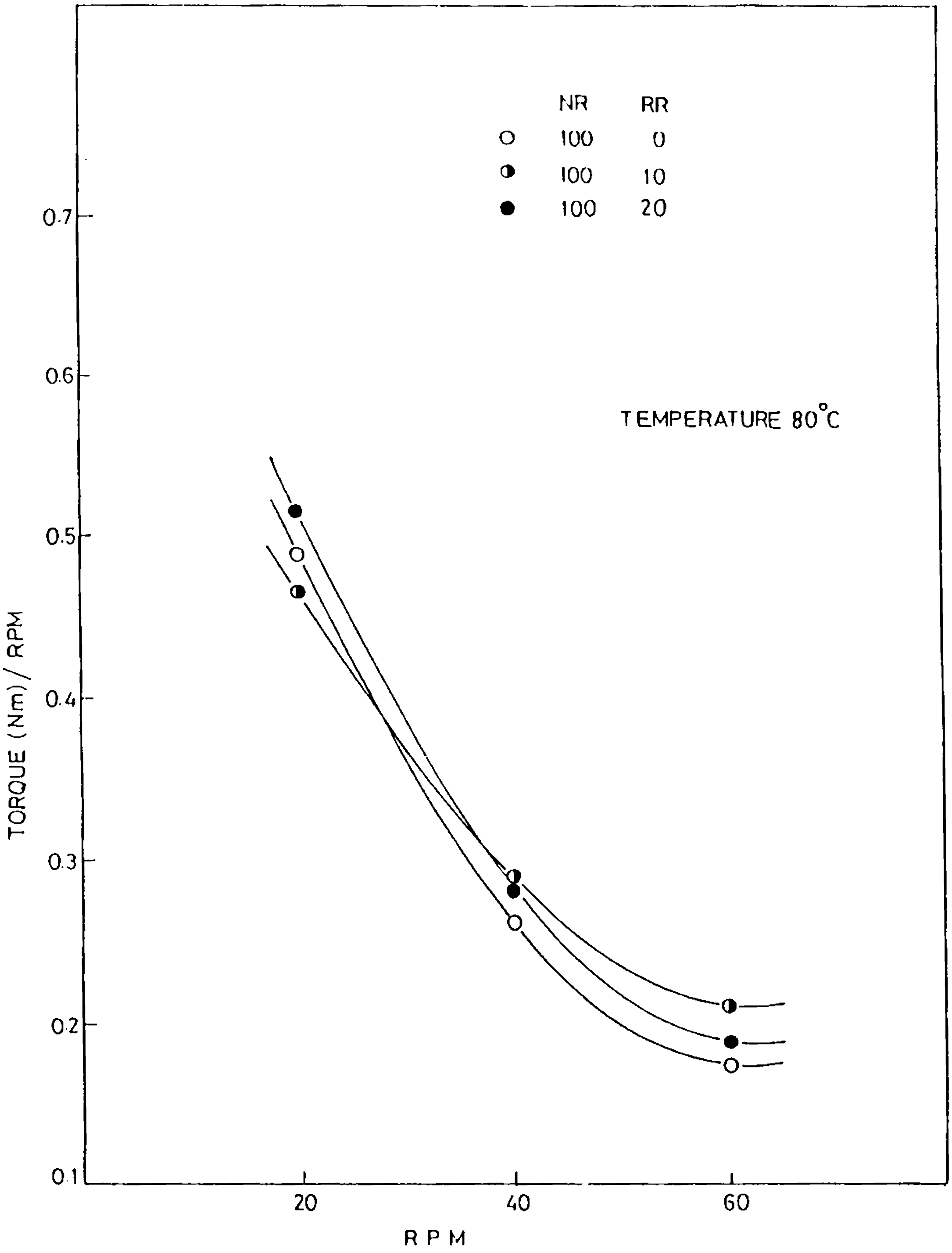

Fig.5.9 Variation of viscosity (torque/rpm) with shear rate (rpm) for NR/RR blends at 80°C

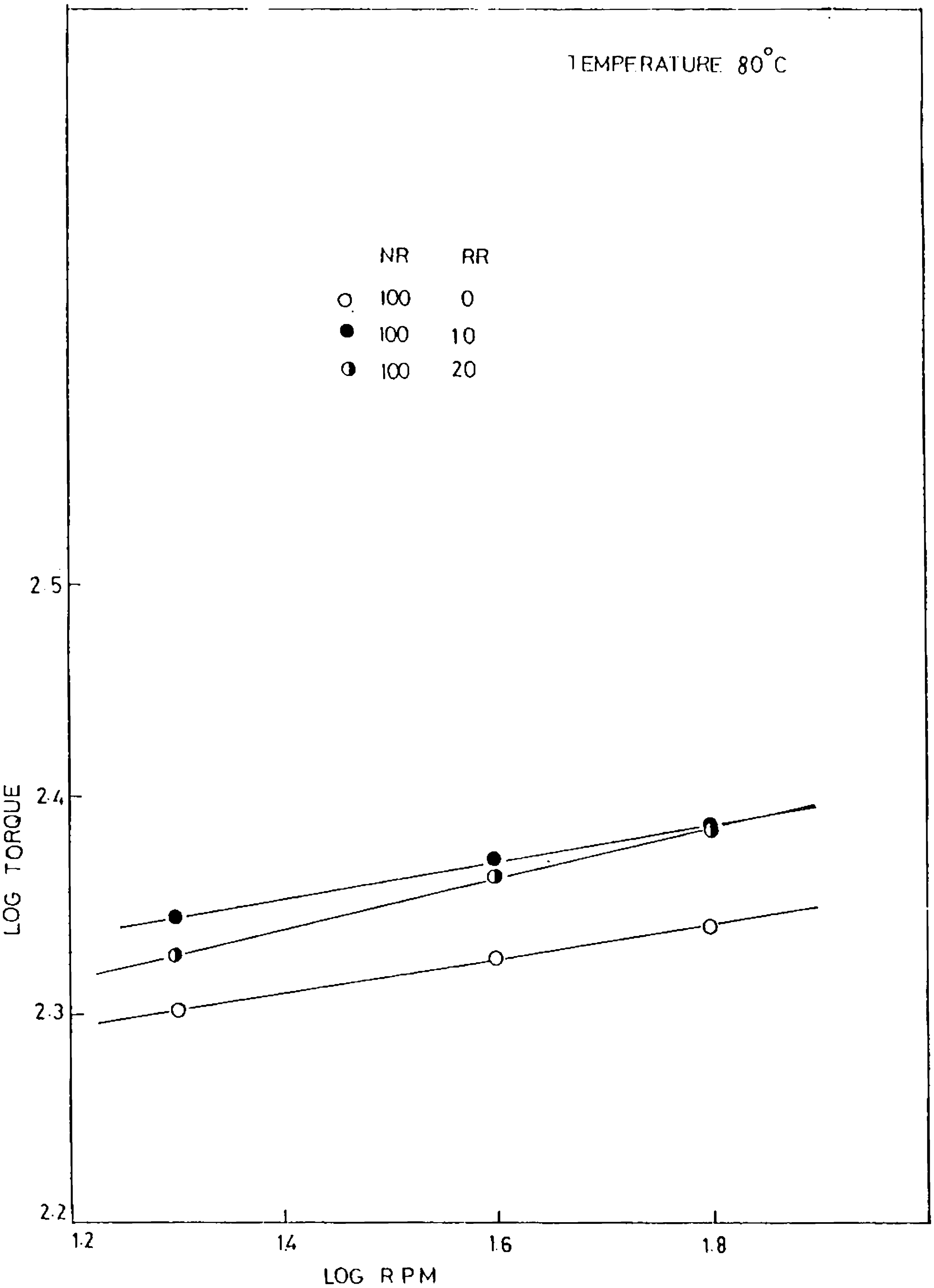

Fig.5.10: Variation of torque with rpm for NR/RR blends at 80°C

Table 5.3: Power law index for NR/RR blends

Percentage of rubber reclaim	Power law index at		
	80°C	100°C	120°C
0	0.07	0.09	0.13
10	0.08	0.09	0.19
20	0.13	0.22	0.25

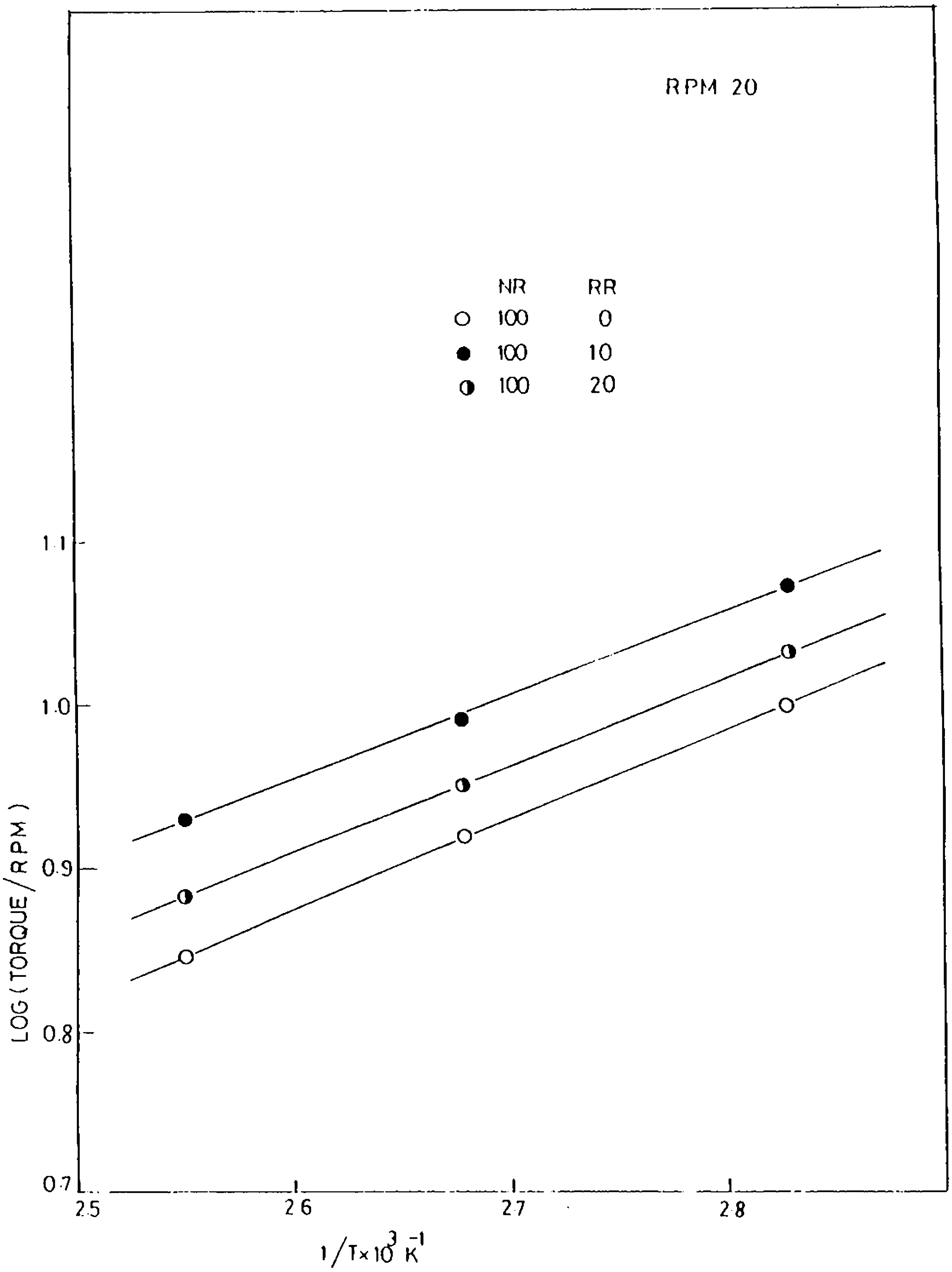

Fig.5.11: Variation of viscosity (torque/rpm) with temperature for NR/RR blends

rpms (20, 40 and 60). The activation energy of flow calculated from the slope of the lines is given in Table 5.4. From the table it is clear that the activation energy decreases with progressive addition of RR.

CONCLUSIONS

1. Upto 20% of IIR reclaim can be added to NR without serious deterioration in mechanical properties.

2. The heat ageing resistance of NR can be improved by addition of IIR reclaim.

3. The processability of NR is not seriously affected by addition of IIR reclaim upto 20%.

Table 5.4: Activation energy of viscous flow for NR/IIR blends

Percentage of rubber reclaim	Activation energy (kJ/mol^{-1}) at		
	20 rpm	40 rpm	60 rpm
0	4.74	2.76	1.58
10	4.16	2.21	1.11
20	4.07	2.21	1.10

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Chapter 6

SUMMARY AND CONCLUSIONS

Several methods have been suggested in this thesis to improve the mechanical properties of commercially available NR/EPDM blends and to develop useful blends of NR and IIR. All the methods were directed at developing a satisfactory network structure in each of the phases and at the interface.

First method investigated was carboxylation of the slower curing phase viz., IIR in NR/IIR blends and EPDM in NR/EPDM blends. Carboxylation was done by grafting maleic anhydride to IIR and EPDM in presence of a promoter. MBT was found to be the most efficient promoter among the many promoters tried. Conditions for carboxylation were optimised. Carboxylation possibly slows down the migration of curatives from IIR or EPDM to NR and hence it was possible to improve the mechanical properties of NR/IIR and NR/EPDM blends over conventional NR/IIR and NR/EPDM blends. The improvement in mechanical properties due to carboxylation was found to arise from a second factor too: formation of ionic crosslinks, which do not compete with NR, in IIR or

EPDM in addition to sulphur crosslinks. The heat ageing resistance of such modified NR/IIR and NR/EPDM blends was found to be superior to the conventional blends.

Second method investigated was precuring of the IIR or EPDM phases to a low level so that optimum crosslink densities develop in both elastomer phases and interface of NR/IIR and NR/EPDM blends after final curing. For this the following blending sequence was adopted: IIR or EPDM was first compounded, a low level of precuring was given to it, then the precured elastomer was blended with NR and the compounding ingredients for NR added, and finally curing of the compound was done. The optimum crosslink density to which IIR or EPDM has to be precured to develop maximum tensile strength in the complete composition range of NR/IIR and NR/EPDM blends was determined. Mechanical properties of the precured IIR/NR and precured EPDM/NR blends were compared with those of conventional IIR/NR and EPDM/NR blends. Considering the attractive properties of NR/IIR and NR/EPDM blends, precuring IIR or EPDM before blending with NR is found to be a very promising method to develop these blends. Also, this is a very promising route for upgrading natural rubber, which was one of the main objectives of this work.

Third method investigated in the line of precuring the slower curing rubber was to use reclaim of speciality rubbers like IIR, which probably has a low level of crosslink density, to modify NR. It was found that NR could be loaded upto 20% with IIR reclaim without serious deterioration in mechanical properties. Considering the improvements in the ageing resistance, modulus and processing behaviour with addition of reclaimed rubber, this may be a promising method for effectively using an otherwise waste product.

LIST OF PUBLICATIONS

1. Improved compatibility of NR/Butyl and NR/EPDM blends by carboxylating Butyl and EPDM, Kautschuk Gummi. Kunststoffe, 43(12) 1095 (1990).

2. Improved mechanical properties of NR/EPDM and NR/Butyl blends by precuring EPDM and Butyl, Journal of Applied Polymer Science (In press).

3. Cure compatibilisation of NR/Butyl and NR/EPDM blends, Paper presented at the National Conference on Advances in Polymer Technology, Kochi, February 1991.

4. Improved compatibility of NR/Butyl and NR/EPDM blends by precuring Butyl and EPDM, Paper presented at the International Natural Rubber Conference, Bangalore, February 1992.

5. Investigation of the processability of NR/IIR and NR/EPDM blends using a Torque rheometer, International Journal of Polymeric Materials (communicated).

6. Studies on NR/IIR reclaim blends, European Polymer Journal (Communicated).

Figs.4.23 and 4.24 show SEM photographs of the tensile fracture surfaces of modified and conventional NR/IIR blends (50/50). The modified blend has a smooth and homogeneous surface showing better compatibility compared to the rough pattern in the conventional blend. For 20/80 NR/IIR blends (both for modified and conventional) (Fig.4.25 and 4.26) there is not much difference in surface patterns. This is expected since the improvement obtained in tensile strength is also not very high for this blend ratio. Figs.4.27 and 4.28 show the tensile fracture surfaces of modified and conventional NR/EPDM blends (50/50). Here also an increased homogeneity is observed in the modified blends. A similar behaviour is shown by the modified and conventional 80/20 NR/EPDM blends also (Figs.4.29 and 4.30).

Figs.4.31 to 4.36 show the optical photographs of the surfaces of modified and conventional NR/IIR blends of various compositions (70/30, 50/50 and 30/70). In all cases the modified blends show a more homogeneous surface with smaller particle size compared to the corresponding conventional blends. Figs.4.37 to 4.42 are the optical photographs of the surfaces of modified and conventional NR/EPDM blends of various compositions (80/20, 50/50 and 20/80). As in the case of NR/IIR blends, the modified blends have a more homogeneous surface than the corresponding conventional blends.