

STUDIES ON THERMOPLASTIC ELASTOMERS WITH SPECIAL REFERENCE TO TRIBLOCK COPOLYMERS AND NBR/PVC BLENDS

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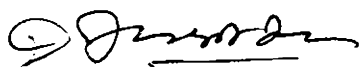
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AUGUST 1992

CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Miss Ivy Mathew 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 "STUDIES ON THERMOPLASTIC ELASTOMERS WITH SPECIAL REFERENCE TO TRIBLOCK COPOLYMERS AND NBR/PVC BLENDS" is the original work carried out by me under the supervision of Prof. (Dr.) D. Joseph Francis, Head of the 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 USED IN THIS THESIS

TPE	Thermoplastic elastomer
TPU	Thermoplastic polyurethane
SBS	Styrene-butadiene-styrene
SIS	Styrene-isoprene-styrene
SEBS	Styrene-ethylene butylene-styrene
PVC	Poly(vinyl chloride)
EVA	Ethylene vinyl acetate
NBR	Acrylonitrile butadiene rubber
EB	Ethylene butylene
ZnO	Zinc oxide
MgO	Magnesium oxide
TBLS	Tribasic lead sulphate
DCP	Dicumyl peroxide
DBP	Dibutyl phthalate
SP	Styrenated phenol
T_g	Glass transition temperature
ΔG_m	Free energy change of mixing
ΔH_m	Enthalpy change of mixing
ΔS_m	Entropy change of mixing
T_m	Melting temperature
SEM	Scanning electron microscopy

IR	Infrared
HAF	High Abrasion Furnace
phr	Parts per hundred rubber/resin
rpm	Revolutions per minute
T	Absolute temperature
$\tau_{w\text{app}}$	Apparent shear stress at the wall
$\dot{\gamma}_{w\text{app}}$	Apparent shear rate at the wall
η_{app}	Apparent viscosity
τ_w	True shear stress at the wall
$\dot{\gamma}_w$	True shear rate at the wall
γ_R	Recoverable shear strain
η	Viscosity
ΔP	Pressure drop across the capillary
P_c	Bagley correction factor
R	Radius of the capillary die
L	Length of the capillary die
D	Diameter of the capillary die
D_e	Diameter of the extrudate
M	Torque
S	Revolutions per minute of the Brabender rotor
n	Power law index
Q	Volumetric flow rate
E	Activation energy for viscous flow
R	Gas constant

ASTM	American Society for Testing and Materials
UTM	Universal testing machine
MFI	Melt flow index
ML(1+4) at at 100°C	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of 4 minutes at 100° C
M gm	Meter gram
Nm	Newton meter

Chapter 1

INTRODUCTION

INTRODUCTION

Thermoplastic elastomers (TPEs), the most dynamic segment of the entire elastomer industry, which straddle the gap between plastics and elastomers, as the name implies, denote a spectrum of materials having the properties of vulcanizates, but with significant processing savings.¹⁻⁴ The versatile chemistry involved allows a wide range of properties for each type.^{5,6} As a result, they compete not only with other elastomers and plastics, but also with natural materials such as metal and leather. While they have the mechanical properties of vulcanized elastomers eg., good strength, elongation, resilience, abrasion resistance and flex resistance, their distinctive plus over other elastomers lies in their thermoplasticity. This results in a variety of economic advantages. Processing without the need for post curing means shorter cycle times, greater throughput, less scrap and lower operating costs. These are some of the operating economies which facilitated the growth of thermoplastic elastomers which are having a commercial history of only three decades.

A new class of high performance thermoplastic elastomers was opened up by the introduction of polyurethane

thermoplastic elastomers.⁷⁻⁹ Formed by a simple polyaddition reaction,¹⁰ the polyurethanes proved to be very versatile. Today thermoplastic polyurethane elastomers (TPU) play an important role within the rapidly growing family of thermoplastic elastomers.

Thermoplastic elastomers offer a variety of practical advantages over conventional thermoset rubbers.^{11,12} Most thermoplastic elastomers require little or no compounding. The processing steps are fewer and also simple. Recycling of the scrap material is possible. Better quality control as well as lower energy consumption during processing result in a mature and remarkable growth in the field of thermoplastic elastomers.

The performance properties of thermoplastic elastomers are derived from their chemistry and morphology. In thermoplastic elastomers, the polymer system itself provides the reinforcement, which is provided by carbon black in thermoset articles.¹¹ Chemical composition and morphology provide a rational convenient means of categorizing the existing commercial thermoplastic elastomers. Presently six categories of commercial thermoplastic elastomers are available.¹³

1. Styrenic block copolymers
2. Rubber-polyolefin blends
3. Elastomeric alloys
4. Thermoplastic polyurethanes
5. Thermoplastic copolyesters
6. Thermoplastic polyamides.

The cost and performance of these categories of thermoplastic elastomers increase in the order styrenics, polyolefin blends, elastomeric alloys, polyurethanes, copolyesters, polyamides.

BLOCK COPOLYMERS BASED ON STYRENE

Of the various types of thermoplastic elastomers those based on triblock copolymers of polystyrene and polydienes are the largest and one of the earliest to be investigated.^{12,26} They have the basic structure poly(styrene-b-butadiene-b-styrene) (SEBS) or poly(styrene-b-isoprene-b-styrene) (SIS). The one with a hydrogenated central diene block has the structure poly(styrene-b-ethylene-butylene-b-styrene) (SEBS). The most important feature of this structure is that they are phase separated systems, quite unlike the corresponding random copolymers.

The history of styrene based thermoplastic elastomers started some 25 years back, and has found

application for general mouldings, shoe soles, modifying agents for plastics and as base materials for adhesives and bonding agents.¹⁴ These materials are not only leaders in the field in comparison with the various other types of thermoplastic elastomers, but they are also highly regarded in the industry as important production materials.

Polystyrene/polydiene block copolymers differ from ordinary plastics and conventional rubbers in that they have a triple block copolymer (tele-block-copolymer) structure consisting of polystyrene terminal block-rubber central block-polystyrene terminal block. This unique structure gives rise to some very useful properties. Fig.1.1 shows the structures of SBS, SIS and SEBS.

These thermoplastic elastomers have properties similar to those of a vulcanized rubber at normal temperatures in that they stretch when put under tension and return to their original form when released. As shown in Fig.1.2 the terminal blocks are segregated in these products since the polystyrene end blocks are incompatible with the central rubber block and form so called polystyrene domains.

Thus they are phase separated systems--one of the uniqueness of thermoplastic elastomers--having two glass

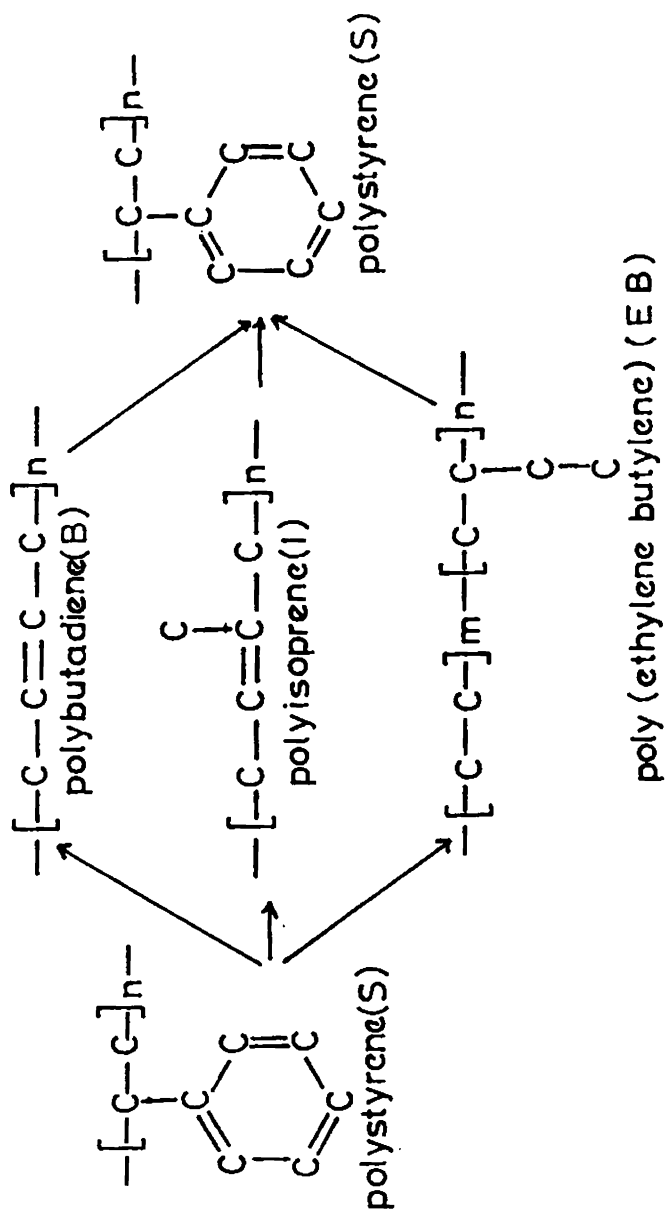


Fig.1.1 Structure of SIS, SBS and SEBS

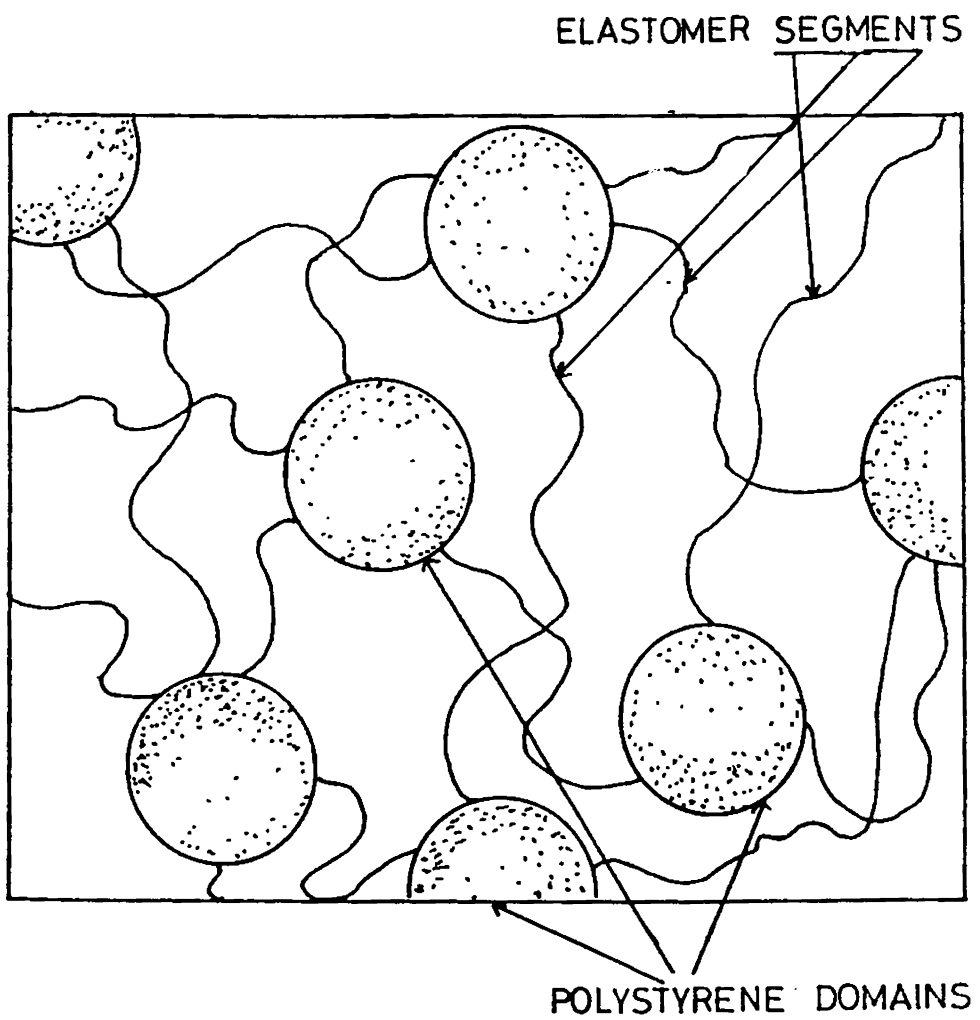


Fig.1.2 Diagrammatic representation of the two phase behaviour of a triblock thermoplastic elastomer.

transition temperatures (T_g) characteristic of respective homopolymers whereas the equivalent random copolymers have a single intermediate T_g .¹⁵⁻¹⁸ This means that in styrenic thermoplastic elastomers, at room temperature, the polystyrene phase is strong and rigid while the polydiene phase is soft and elastomeric.

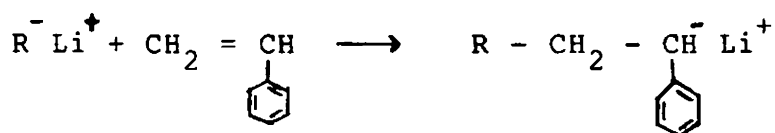
Block copolymers demonstrate a number of unique properties as a result of morphological features which are unique to such systems. The unique features are the result of phase separation of the incompatible block components being restricted to a microscopic scale. The resulting microphases have dimensions of the order of the dimensions of the constituent polymer molecule and the microphases often develop a highly organized domain morphology. Such microphase separation in block copolymers was clearly established by Sadron et al.¹⁹ The existence of a form of phase separation between block components is not surprising since the dissimilar block components--as homopolymers--are typically incompatible with one another as a result of positive heat of mixing or as a result of crystallization of one or both components.

The thermodynamically stable state of a simple mixture of two incompatible homopolymers is the gross

separation of the components from one another so as to limit their interfacial contact, and with the phase sizes being limited only by the amount of the components present. Incompatibility still exists when such homopolymers are joined to form a block copolymer, and each would like to segregate itself from the other. However, the fact that they are joined together, restricts their segregation to microscopic dimensions ie., to microphases having dimensions of the order of the molecular sizes of the blocks. In addition, the equilibrium morphological state of the microphases will be a highly organised domain structure. Thus, there is a fundamental difference between phase separation in a system of incompatible homopolymers and that in a corresponding block copolymer system.

METHOD OF PREPARATION OF BLOCK COPOLYMERS

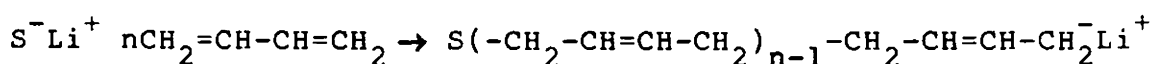
Typically the poly(styrene-b-elastomer-b-styrene) materials are made by anionic polymerization²⁰⁻²² using an alkyl-lithium initiator (R-Li). This first reacts with styrene monomer.



The product now acts as an initiator for further polymerization,



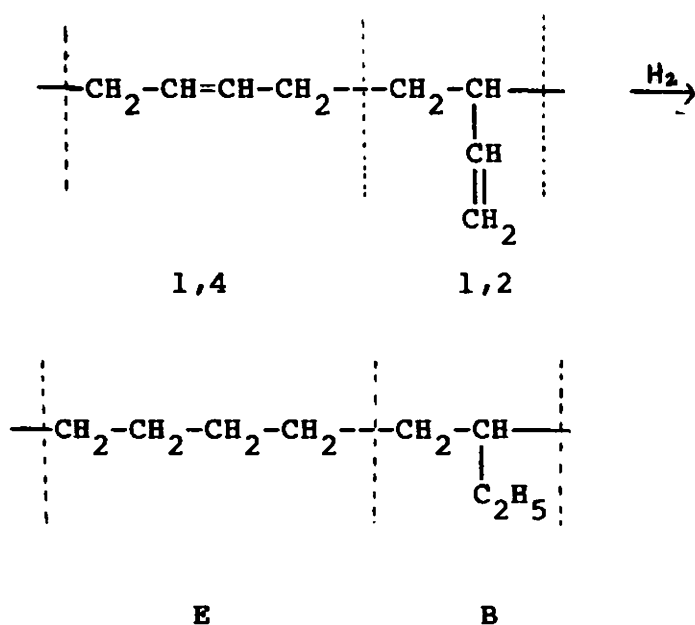
This product (denoted S^-Li^+) has been termed a living polymer because it can initiate further polymerization. If a second monomer, such as butadiene, is added, the following reaction occurs,



This reaction product (denoted $\text{S-B}^-\text{Li}^+$) can then initiate a further reaction with added styrene monomer to give $\text{S-B-S}^-\text{Li}^+$, which in turn can be reacted with an alcohol, R-OH , to give $\text{S-B-SH} + \text{LiOR}$.

There are only three common monomers--styrene, butadiene and isoprene--that are easy to polymerize using this process. So only two poly(styrene-b-elastomer-b-styrene) block copolymers are directly produced on a commercial scale. These are SBS and SIS. In both cases the

elastomer segments contain one double bond per molecule of original monomer. These bonds are quite reactive and limit the stability of the product. To improve stability, microstructure modifiers are added and as a result, the polybutadiene mid segment is produced as a random mixture of two structural forms, the 1,4 and 1,2 isomers. On hydrogenation, these isomers give a polymer that is essentially a copolymer of ethylene and butylene (EB). The SEBS block copolymers produced in this way have excellent resistance to degradation.



MISCIBILITY IN BLOCK COPOLYMERS

For mixtures of two substances, complete miscibility requires that the free energy of mixing (ΔG_m) be favourable ie., it should be negative^{23,24}. Conversely if

ΔG_m is positive, phase separation will occur, and in the case of the block copolymers, domains will be formed. This free energy can be expressed as,

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where ΔH_m and ΔS_m are the enthalpy and entropy of mixing, respectively, and T is the absolute temperature. For styrenic thermoplastic elastomers, ΔH_m is positive (because there are no strongly interacting groups) and will increase as the structures of the two polymers forming the segments become less alike. T and ΔS_m will always be positive and $-T\Delta S_m$ will always be negative. However, this term will approach zero as the molecular weights of the segments become large and/or as T decreases. Thus we can expect domain formation to be favoured by,

1. A high degree of structural difference between the segments
2. High segmental molecular weight
3. Low temperature.

The theory of domain formation has been extensively developed using this approach.²⁵⁻²⁹

HARD AND SOFT SEGMENTS IN BLOCK COPOLYMERS

The hard and soft segments of the block copolymers determine most of the properties of these copolymers. While the elastomer segments control many of the properties of the block copolymers, the hard segments determine the upper service temperatures. The double bond associated with polybutadiene and isoprene segments in SIS and SBS are the points of chemical attack and limit the thermal and oxidative stability whereas the saturated SEBS block copolymers are more stable.

FACTORS AFFECTING PROPERTIES OF BLOCK COPOLYMERS

The fundamental variables which affect the polymer physical properties are,³⁰

1. Elastomer and hard segment type
2. Glass transition temperature of hard and soft segments
3. Molecular weight
4. Composition of hard and soft segments.
5. Morphology
6. Interphase adhesion.

Compared to homopolymers of similar molecular weight, the melt viscosities of styrene block copolymers are

very high, because of the two phase domain structure. In contrast, if the styrene content is held constant, the total molecular weight has little or no effect on the modulus of the material at ambient temperatures.

The effect of various factors on the morphology of these two phase systems has been studied both theoretically and experimentally. As the polystyrene content is increased, starting from spheres, the morphologies change to cylinders and then lamellae. Beyond 50% styrene content, there is apparently a phase inversion with polystyrene forming a continuous phase and elastomer dispersion assuming different shapes.

When the T_g of the hard segments imposed service temperature limitations, a substitution of polystyrene with high T_g plastic segments yielded excellent results, providing a strong confirmation that the plastic domains are the principal stress bearers, whereas the T_g of the elastomer segments show no strong dependences on the properties.³⁰

The hard phase which separates from the soft, rubbery matrix form domains which have the dimensions of

reinforcing fillers in rubber. Studies have shown that there is a strong influence of the filler-elastomer interphase adhesion on the properties of the material.

RHEOLOGY OF TRIBLOCK COPOLYMERS

For a number of reasons rheological measurements are often the method of choice for the characterization of polymers produced from new monomers, or of polymers made from known monomers by new processes.^{31,32} The most important reasons are:

1. Laboratory characterization: Rheological tests are useful for comparing the properties of materials, for determining their structure, and for estimating their potential usefulness.
2. Processing: Typical applications are in the selection of resins for a given process, the optimization of formulations and diagnosis and solution of processing problems.
3. Quality control: Both resin manufacturers and users need to ensure that properties critical for a processing and/or end use are maintained within acceptable limits.

The strong dependence of rheological properties on the unique multiphase morphology and physical properties of triblock copolymers and the relative ease of making rheological measurements are the particular reasons for using rheological measurements as part of the present investigation.

The phase separated block copolymers are considered as immiscible blends, with added constraint that the blend components are joined chemically. A few studies on these polymers have shown that these block copolymers exhibit unusual melt rheological properties at very low shear rates and high temperature.³³⁻³⁸ But there have been relatively very few studies in the area of melt rheology of these block copolymers.

Triblock copolymers in which two phases co-exist are of increasing commercial importance and their rheological behaviour differs from that of homogeneous melts, as do those of melts containing rigid fillers, because the flow field is affected by the presence of a second phase. An understanding of the dependence of viscosity on shear rate, temperature and molecular parameters can provide valuable processing information. The capillary flow method used in the investigation is particularly worthy of

study since it is basically the most useful method of studying flow properties at the normally high shear rates used in polymer processing.

ELASTOMER--THERMOPLASTIC BLENDS AS THERMOPLASTIC ELASTOMERS

A considerable amount of research has been done over the last several years with a view to obtain new polymeric materials with enhanced properties for specific applications or a better combination of different properties.³⁹⁻⁴² In recent years elastomer-thermoplastic blends have become technologically useful as thermoplastic elastomers.⁴³⁻⁴⁸

THERMOPLASTIC ELASTOMERS FROM PVC

Thermoplastic elastomers based on mixtures of thermoplastics and elastomers came into commercial prominence long ago. A number of thermoplastic elastomers from elastomers and poly(vinyl chloride) (PVC) are reported such as nitrile elastomer with PVC, polyesters with PVC, ethylene copolymers with PVC, etc.⁴⁹⁻⁵¹

Barlow, Paul and coworkers found that PVC formed compatible blends with several different aliphatic

polyesters such as poly(butylene adipate) and immiscible mixtures with other aliphatic and aromatic polyesters such as poly(ethylene adipate) and poly(ethylene orthophthalate).^{50,52} They concluded that there was an optimum density of ester groups in the polymer chain for achieving maximum interaction with PVC. A series of aliphatic polyesters having methylene to carboxyl ratios ranging from 2 to 14 in their repeat units were examined for miscibility with PVC.⁵² At high end of the range, phase separation caused by a lower critical solution temperature occurs at progressively lower temperature as the methylene to carboxyl ratio increases beyond 10.

Ethylene vinyl acetate (EVA) and PVC form another group of thermoplastic elastomers from PVC. With increasing vinyl acetate content, they form compatible blends that are clear and transparent.^{51,53,54}

MISCIBILITY IN THERMOPLASTIC ELASTOMERS DERIVED FROM ELASTOMERS AND PLASTICS

The most basic question when considering a polymer blend, is the miscibility of the components as governed by the laws of thermodynamics. While the block copolymers are considered to be immiscible blends which are joined

chemically, thermoplastic elastomers derived from elastomer-plastic blends are either miscible or immiscible. According to the law of thermodynamics, ΔG_m , the free energy of mixing must be negative to obtain a miscible blend.

The entropy of mixing (ΔS_m) of two polymers is dramatically smaller than that for two low molecular weight compounds. The enthalpy of mixing ΔH_m on the other hand, is often a positive quantity or at best zero. In such cases immiscibility results when polymers are mixed. Consequently, the number of known miscible blends is relatively small. If, however, there exist specific interactions such as ion dipole interactions, H-bond interactions between functional groups, the heat of mixing ΔH_m becomes negative and the resulting system is miscible. In other words miscibility depends on the degree of interaction between polymer components.^{55,56} This thermodynamic criterion of component interaction is different from, though often confused with, the technological criterion of 'compatibility'. Materials may be termed compatible if fine dispersions can be obtained by, for example, intensive shear mixing processes. Unless they are also thermodynamically miscible, however, then phase separation and similar morphological changes will occur with time, and these may be

reflected in significant property changes of the material. There is little doubt that miscibility strongly affects the morphology of the interface in a multicomponent system. Recent works from this source indicates that the miscibility of blend components may also determine the sensitivity of blend properties (eg., ultimate tensiles) to variations in the preparation and the use history of the material.^{57,58} In other words, such effects as the shear refinability of polymer blends may correlate with the miscibility concept. Analogous to the documented importance of interaction concepts to the mechanical and physical properties displayed by polymer blends, it seems possible that the dispersion behaviour and the processing of polymer blends may also depend on component miscibility or compatibility.^{59,60} In this terms, seeking information on the conditions of mixing to achieve a degree of dispersion in a blend and also the viscoelastic properties of polymer blends become important factors.

The degree of dispersion attained during mixing under different shearing conditions may distort the size distribution of the component polymers and hence the properties of the blend.

RHEOLOGY OF TWO PHASE MELTS OF THERMOPLASTIC ELASTOMERS

Flow characterization of polymer blends become an important criterion which determines the miscibility or compatibility.⁶¹⁻⁶⁴ But interpretation of rheological data is complicated both by the inherently complex non-Newtonian flow characteristics of most polymers involved in blends and by the blend morphology. The latter factor is a variable dependant on processing conditions and, apparently, on component interaction. Not surprisingly, attempts to rationalize blend viscosity data have been largely empirical to date and have been only partly successful.^{65,66}

Shear flow properties in polymer melts of thermoplastic elastomers are not quite different from those of thermoplastics. These behave like rubbers at ambient temperatures but if sufficiently heated they become thermoplastic and flow.

MODIFICATION IN THERMOPLASTIC/ELASTOMER BLENDS

The ideal elastomer-plastic blend comprises finely divided elastomer particles dispersed in a relatively small amount of plastic. The favourable morphology should remain during the processing of the material into parts and also in

use. Because of these requirements for the ideal case, the usual methods for preparing elastomer-plastic blends by melt mixing, solution blending etc. are not sufficient.

The best way to produce thermoplastic elastomeric compositions comprising vulcanized elastomer particles in melt processable plastic matrices is by the method called dynamic vulcanization. Dynamic vulcanization is a route to new thermoplastic elastomers which have properties as good or better than those of block copolymers. It imparts to the blends, improvements in permanent set, ultimate mechanical properties, fatigue resistance, oil resistance, thermoplastic fabricability, technological compatibilization etc.⁶⁷⁻⁷⁰

In addition to dynamic vulcanization, property modification can be achieved by addition of a variety of low molecular weight chemicals through reactions such as grafting, co-crosslinking etc. Liu et al.⁷¹, Mori and Nakamura^{72,73} have studied modification of a series of blends and polymers. The continuous nature of the phases obtained as a result of these modifications can lead to efficient force/stress transfer between the component phases.

METHODS OF PREPARATION

Most commercially available thermoplastic elastomers from elastomer/plastic blends are prepared by mechanical means either on an open roll mill, in an extruder or in a suitable internal mixer. The processing temperature must be well above the glass transition temperature (T_g) of each constituent for mixtures of amorphous polymers and above the melting temperature (T_m) of mixtures containing semicrystalline polymers.

Blends can also be prepared by dissolving the constituent polymers in a common solvent and the resulting solution then film casted to form the solution cast thermoplastic elastomer blend. A melt method can be used for compounding and pelletising the solution cast TPE blends.

The elastomer phase can be kept unvulcanized or vulcanized under intensive shear by adding crosslinking agents to give a fine dispersion of the crosslinked elastomer in the hard thermoplastic. This latter process known as dynamic vulcanization gives the products better resistance to deformation at high temperatures.

BLENDS OF NITRILE ELASTOMERS WITH PVC

Elastomeric copolymers of acrylonitrile and 1,3 butadiene (nitrile elastomers or NBR) have been blended with PVC to achieve a number of purposes.⁷⁴⁻⁷⁶ Small amounts of nitrile elastomer in PVC can be used to improve the impact strength of rigid PVC compositions. Small amounts of PVC can be added to nitrile elastomers before vulcanization to improve the ozone resistance of vulcanizates. Blends of comparable amounts of nitrile elastomer and PVC can be used as thermoplastic elastomer or can be vulcanized to form thermoset elastomers.⁶

PVC has assumed a leading position among plastics because of its economic and design advantages. It is a material of choice due to lower cost, greater availability or improved performance. It is a versatile polymer used in flexible, semirigid or rigid form. PVC resin is so amenable to widespread property modification that it accounts for the number one position in overall product volume and number of applications.^{77,78}

The choice of butadiene-acrylonitrile rubber as the soft segment of NBR/PVC thermoplastic elastomer arises mainly from the polarity of this rubber, which can produce

compatible and semicompatible blends with PVC according to the acrylonitrile content of the rubber. Butadiene acrylonitrile rubber is a highly oil resistant rubber. The use of nitrile elastomers as plasticizer for PVC resulted in blends with excellent resistance to swelling. The use of precrosslinked and powdered nitrile elastomer which is effective in reducing the elastic memory or nerve of NBR/PVC blends which will act as an efficient plasticizer for PVC was reported.⁷⁹ Some studies on NBR/PVC blends have been reported on the effect of acrylonitrile content on properties, phase behaviour, compatibility etc.⁷⁹⁻⁸²

MORPHOLOGY OF THERMOPLASTIC ELASTOMERS

Scanning Electron Microscopy (SEM) was used almost exclusively, for different types of studies in various fields such as biological, medical metallurgical studies etc. SEM is now extensively used in polymer fields also in adhesives, filled polymers, short fibre reinforced plastics, coatings, fracture studies etc.

Fracture in polymer has been the subject of a number of SEM studies. The fatigue fracture surfaces of polyethylene and poly(vinyl chloride) have been studied by White and Teh⁸³ and they have observed that the appearance

of fracture surfaces reflects to a large extent the microstructure and properties of materials used. The fracture surfaces of extrudates of polyethylene/poly(vinyl chloride) blends, fracture surface morphology and phase relationships of polystyrene/poly(methyl methacrylate) systems etc. were studied by various scientists.^{83,84}

SEM has also been used in studies such as surface characteristics of fillers, extent of rubber-filler interaction, short fibre-reinforced rubber composites etc.^{85,86} When parts fail in mechanical products the fracture surface of the broken part provides important clues to the cause of the breakdown. Lewis and co-workers have combined autoradiography with electron microscopy to identify accurately the phases in two component elastomer blends.⁸⁷

SEM studies in thermoplastic elastomers have also become important recently.^{88,89} However, there have been only a few systematic investigations on the failure analysis fracture surface studies, morphological studies etc. in thermoplastic elastomers. SEM studies on NR/PE thermoplastic elastomers have been reported.⁸⁸

OBJECTIVES AND SCOPE OF THE PRESENT STUDY

Thermoplastic elastomers are a relatively new class of materials which compete with thermoset rubbers in some areas and thermoplastic materials in other areas. The main thrust of the present investigation is a comparative study on commercially available triblock styrene thermoplastic elastomers and those derived from blends of acrylonitrile-butadiene rubber and poly(vinyl chloride). The styrene-based thermoplastic elastomers are gaining acceptance as a replacement for both natural and synthetic rubber in many applications. TPEs based on blends of elastomers and plastics is the fastest growing segment of the broad class of thermoplastic elastomers. Broad applicability and simple technology of production are the attractive features of this class of TPEs. NBR/PVC thermoplastic elastomers were selected for this investigation due to the versatility of PVC, its number one position, low cost, ability to be compounded into various flexible and rigid form with good physical and chemical and weathering properties etc., which will be passed over to PVC blends especially NBR/PVC blends which are known to form miscible systems.⁴³

The mechanical properties and rheology of both styrene and NBR/PVC thermoplastic elastomers are proposed

to be studied in detail so as to compare the two phase behaviour of these materials in the solid phase and in the melt. Morphology of these TPEs is also proposed to be investigated.

NBR/PVC blends have scope for further improvement in properties by use of interface modifiers. The effect of such modifiers is also proposed to be investigated.

The objectives of the study are:

1. To characterise the mechanical and rheological properties of typical thermoplastic elastomers belonging to triblock copolymers and elastomer/plastic blends.
2. To compare the elastic recovery behaviour of these thermoplastic elastomers with that of vulcanized elastomers.
3. To investigate the possible use of modifiers in NBR/PVC blends to improve their mechanical behaviour.
4. To examine the morphology of the different TPEs to correlate it with the strength and type of failure.

The thesis is divided into the following chapters.

Chapter 1 Introduction

Chapter 2 Experimental Techniques

Chapter 3 Mechanical and Rheological behaviour of Polystyrene/Polydiene Block Copolymers

Chapter 4 Mechanical and Rheological behaviour of Thermoplastic Elastomers derived from NBR/PVC blends

Chapter 5 Modification of Thermoplastic Elastomers derived from NBR/PVC Blends

Chapter 6 Summary and Conclusions

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Chapter 2

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

Materials used and the experimental procedures adopted for the present investigations are given in this chapter.

MATERIALS

Polymers

1) Styrene-Isoprene-Styrene

Styrene-isoprene-styrene (SIS) used in the study was Kraton D 1107 supplied by Shell Chemical Company. It had the following specifications:

Melt flow index - 9 (g/10 min)

Styrene/rubber ratio - 14/86

2) Styrene-butadiene-styrene

Styrene-butadiene-styrene (SBS) used was Kraton D 1102 supplied by Shell Chemical Company. It had the following specifications:

Melt flow index - 6 (g/10 min)

Styrene/rubber ratio - 30/70

3) Styrene-ethylene-butylene-styrene

Styrene-ethylene-butylene-styrene (SEBS) used was Kraton G 1652 supplied by Shell Chemical Company. The specifications of the sample are:

Specific gravity - 0.91

Styrene/rubber ratio - 29/71

4) Butadiene-acrylonitrile rubber

Butadiene-acrylonitrile (nitrile or NBR) rubbers used in the study were the following grades:

(i) Acrylonitrile content : 42%

Mooney viscosity : 50
[ML(1+4) at 100°C]

(ii) Acrylonitrile content : 33%

Mooney viscosity : 40.9
[ML(1+4) at 100°C]

The rubbers were obtained from Synthetics and Chemicals Ltd., Bareilly.

5) Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) used was extrusion grade

suspension polymer in powder form with a K value of 67. The resin was obtained from IPCL, Baroda.

Polymer additives

6) Zinc oxide

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

Specific gravity - 5.57

Zinc oxide content - 98%

Acidity - 0.4% max.

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

7) Magnesium oxide

Magnesium oxide (MgO) used in the study was commercial grade calcined light magnesia with a specific gravity of 3.6.

8) Stearic acid

Stearic acid having the following specifications was supplied by Godrej Soaps (P) Ltd., Bombay:

Melting point - 50-69°C

Acid number - 185-210

Iodine number - 9.5% max.

Specific gravity - 0.85 ± 0.01

Ash content - 0.1% max.

9) Tribasic lead sulphate

Tribasic lead sulphate ($3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$) (TBLS) used was commercial grade with a specific gravity of 7.0.

10) Irgastab A 70

Irgastab A 70 (Amino crotonate) was used in this study as a metal free stabilizer for PVC.

11) Dicumyl peroxide

Dicumyl peroxide (DCP) used as a crosslinking agent in this study was crystals with following specifications:

Purity - 99%

Density - $1.02 \text{ (g/cm}^3\text{)}$

Recommended processing temperature - $160\text{--}200^\circ\text{C}$

12) Modifiers

Acrylic acid, Maleic anhydride and acrylamide used as modifiers were of commercial grade.

13) Vulkanox 4010 NA

Vulkanox 4010 NA (N phenyl N' isopropyl phenylene diamine) used as antioxidant was supplied by Bayer Chemicals, Bombay. It had the following specifications:

Specific gravity - 1.17

Melting point - 75°C

14) Vulkanox SP

Vulkanox SP (styrenated phenol) used as an antioxidant was supplied by Bayer Chemicals, Bombay.

15) Carbon black

Carbon black used as a filler in this study was high abrasion furnace black (HAF N 330). It was supplied by M/s. Carbon and Chemicals (India) Ltd., Kochi. It had the following specifications:

Iodine adsorption - 80 mg/g

DBP absorption - 105 cm³/100 g

Mean particle diameter - 32 nm

16) Silica

Silica used as a filler in this study was hydrated precipitated silica of commercial grade.

Solvents used in the study (toluene, methyl ethyl ketone) were of analytical grade.

EXPERIMENTAL PROCEDURE

Mixing and homogenization using a mixing mill

Mixing and homogenization of NBR and PVC along with the heat stabilizer for PVC were done on a laboratory size two roll mill (15x33 cm) at a friction ratio of 1:1.25. The elastomer was allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained between 30 and 50°C during mastication. After the nerve disappeared, PVC powder and the heat stabilizers were added. The band was properly cut from both sides to improve the homogeneity of the compound. After mixing, the compound was further homogenized by passing endwise through the nip gap for two to three times and finally sheeted out.

Melt mixing using Brabender Plasticorder

A Brabender Plasticorder (torque rheometer model PL3S) was used for the melt mixing of the polymers and blends. This instrument manufactured by M/s. Brabender OHG Duisburg, Germany has been widely used for measuring processability

of polymers, rheological properties of polymer melts, for blending of polymers, modelling processes such as extrusion etc.^{1-4,6}

The Brabender torque rheometer is essentially a device for measuring torque generated due to the resistance of a material during mastication or flow under pre-selected conditions of shear and temperature. A jacketed mixing chamber with a volume capacity of 40 cc is the heart of the Plasticorder. The torque required for mixing or shearing of the material 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. Different measuring ranges of torque from 0-1000 metergrams, 0-2500 metergrams and 0-5000 metergrams as minimum, intermediate and maximum span respectively can be set by means of a lever and weight arrangement.

The mixing or shearing of the polymers in the mixing chamber is done by two rotors rotating in opposite directions. The speed control of the rotors (range 0-150 rpm) is done by means of a D.C. thyristor controlled drive. Different types of rotors can be employed depending upon the type

of polymers used. The rotors can be easily mounted due to the simple fastening and coupling system.

The temperature of the mixing chamber is controlled by circulating hot silicone oil. The temperature can be set at any value upto 300°C. Stock temperature thermocouple coupled with a temperature recorder is used for temperature measurement.

Once test conditions have been decided (rotor type, rpm and temperature) and set, sufficient time should be given for the temperature to attain the set value and to become steady. Then the materials can be charged into the mixing chamber to obtain a torque-time curve or a plastogram. A typical plasticorder torque-time curve for a crosslinkable compound is shown in Fig.2.1. The following data can be taken from the torque-time curve:

MB = Minimum torque

MX = Maximum torque

TV = Scorch time [Time to attain MV units of torque increase above minimum torque]

TR = cure time [Time to attain 90% of maximum torque]

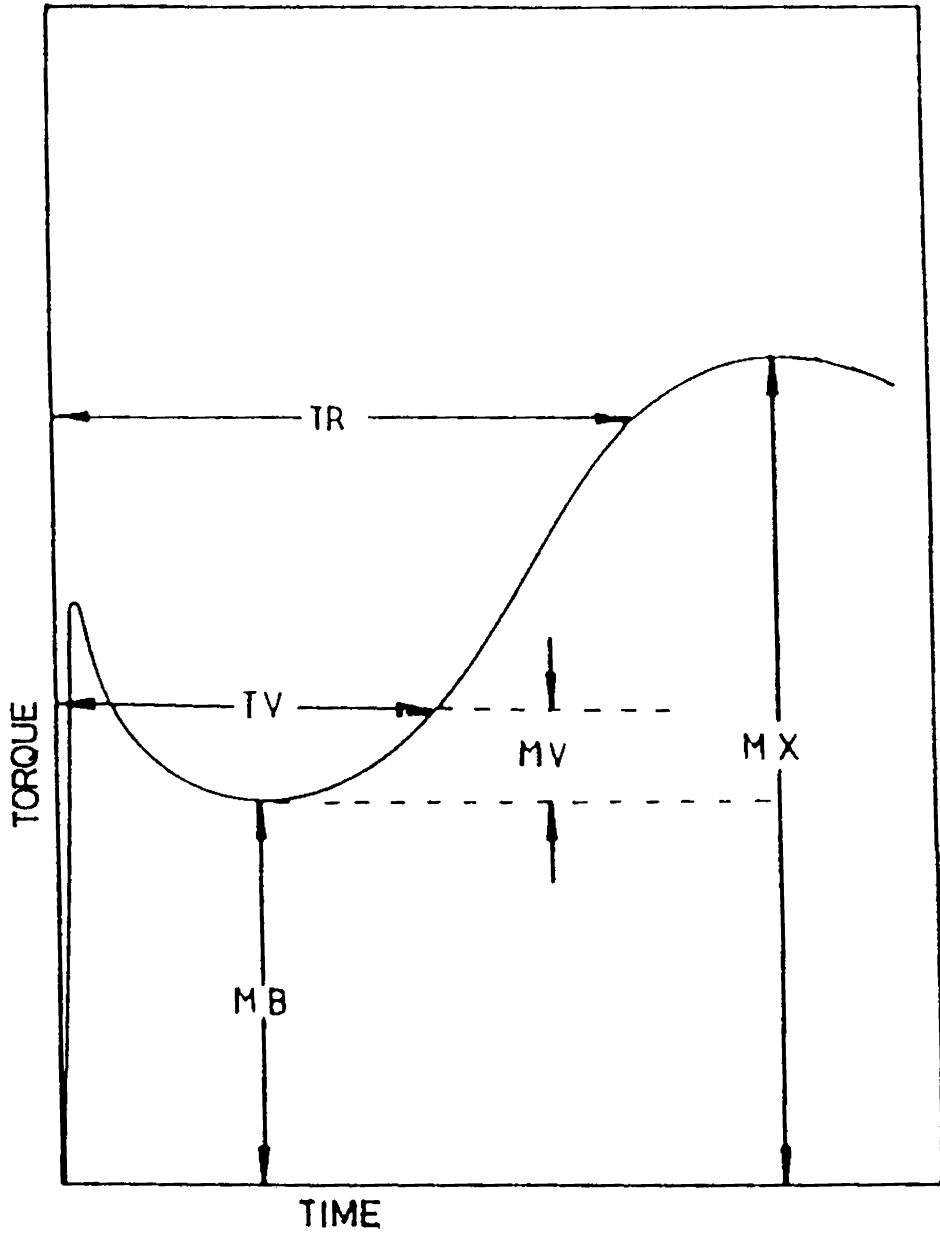


Fig.2.1 - A typical Brabender plasticorder torque-time curve for a crosslinkable compound

Rheological Evaluation of Polymer Melts by Brabender Plasticorder

Brabender plasticorder was also used to study the rheological behaviour of polymer melts under processing conditions. The instrument imparts a very complex shearing motion to the polymer and consequently the data obtainable from the Brabender can be related more specifically to processing operations such as extrusion or milling. Another advantage of the system is that due to the complex shearing, the polymer melts at a comparatively lower temperature. Hence rheological data can be taken at a lower temperature that would be employed in other rheometers. However, only the lower shear rate range can be covered in this instrument.⁴

The relation obtainable from the plasticorder in the form

$$M = CS^a$$

where

M = torque

S = rpm (revolutions per minute) and

C and a are constants

closely resembles the familiar power law behaviour^{5,6}

$$\tau = K\dot{\gamma}^n$$

and hence can be used for the calculation of rheological parameters such as power law index 'n'.

Also [torque/rpm] of the Brabender plasticorder represents viscosity and hence activation energy for viscous flow can be measured from log (torque/rpm) vs. $1/T$ plots where T is the absolute temperature.⁴

Rheological Evaluation of Polymer Melts using a Capillary Rheometer

Melt rheological measurements were also made using a capillary rheometer (Göttfert viscotester 1500). Capillary rheometer allows to cover the shear rate range of practical polymer processing.⁷ The test sample is melted in a thermostated barrel and is extruded through a capillary die of particular length to diameter (L/D) ratio. Capillaries most often used have a circular or slit shaped cross section. By fixing a constant volumetric output as Q , the pressure drop ΔP required for maintaining the flow along the capillary is measured. From these quantities, the apparent shear rate ($\dot{\gamma}_{w_app}$) at the wall were calculated from Poiseuille law for steady, fully developed capillary flow using the expressions

$$\dot{\gamma}_{w_app} = \frac{4Q}{\pi R^3} \text{ s}^{-1}$$

$$\tau_{w_app} = \frac{\Delta P}{2} \frac{R}{L} \text{ N/m}^2$$

where R and L are the radius and length of the capillary die.

The apparent viscosity at each shear rate was calculated according to the equation,

$$\eta_{app} = \tau_{wapp} / \dot{\gamma}_{wapp}$$

The data so obtained is usually corrected for several factors. Though a series of corrections is appropriate to derive the absolute or the true viscosity, two important corrections, Rabinowitsch⁸ and Bagley⁹ corrections are generally recommended.

Bagley correction

The Bagley correction separates inlet and outlet pressure losses from ΔP . This is demonstrated schematically in Fig.2.2. As can be seen from this diagram, part of the pressure P measured in front of the capillary is used to deform the melt to enter the capillary will be stored as elastic deformation energy within the melt. At the outlet of the capillary, part of this deformation energy that has not yet released within the capillary will be relaxed again giving rise to a swelling of the extrudate. However, die swelling of the extrudate is also influenced

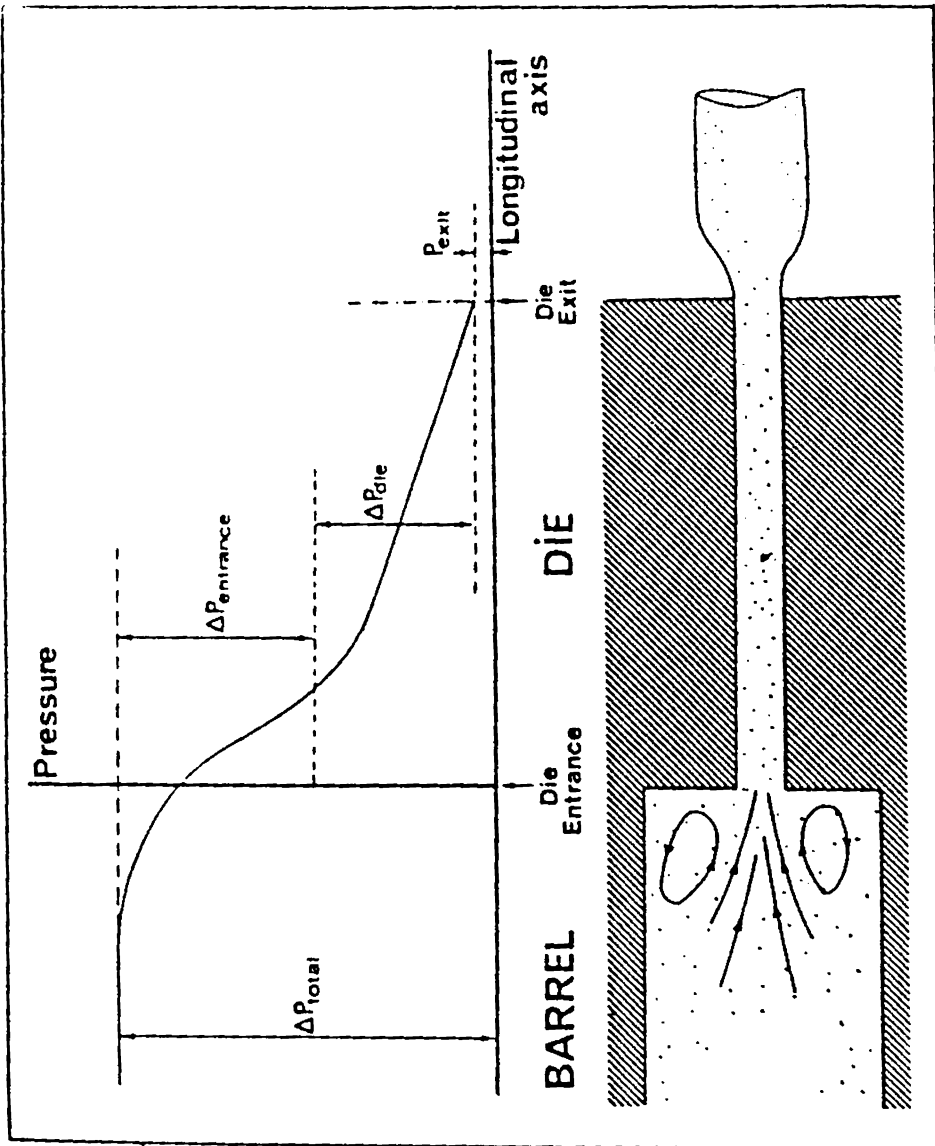


Fig.2.2.2 Pressure profile in a capillary rheometer.

by normal stresses being produced by the shear formation of the melt flowing through the capillary.

To separate this elastic inlet and outlet pressure losses from real viscous pressure drop along the capillary with the Bagley correction ΔP is measured at constant volumetric outputs with a minimum of three capillaries of a constant diameter but different lengths. Measured values of P is then plotted against L/R as shown schematically in Fig.2.3 to give a so called Bagley plot.⁹ Linearisation and extrapolation of this curve to $L/R = 0$ gives the Bagley correction term ' P_c ' to be subtracted from ΔP measured. Corrected shear stress is then given by,

$$\tau_w = \frac{\Delta P - P_c}{2} \frac{R}{L}$$

Rabinowitsch correction

Rabinowitsch correction takes into account the fact that the equation

$$\dot{\gamma}_{w_{app}} = \frac{4Q}{\pi R^3}$$

to calculate apparent shear rate hold only for Newtonian fluids with shear rate independent viscosity but does not

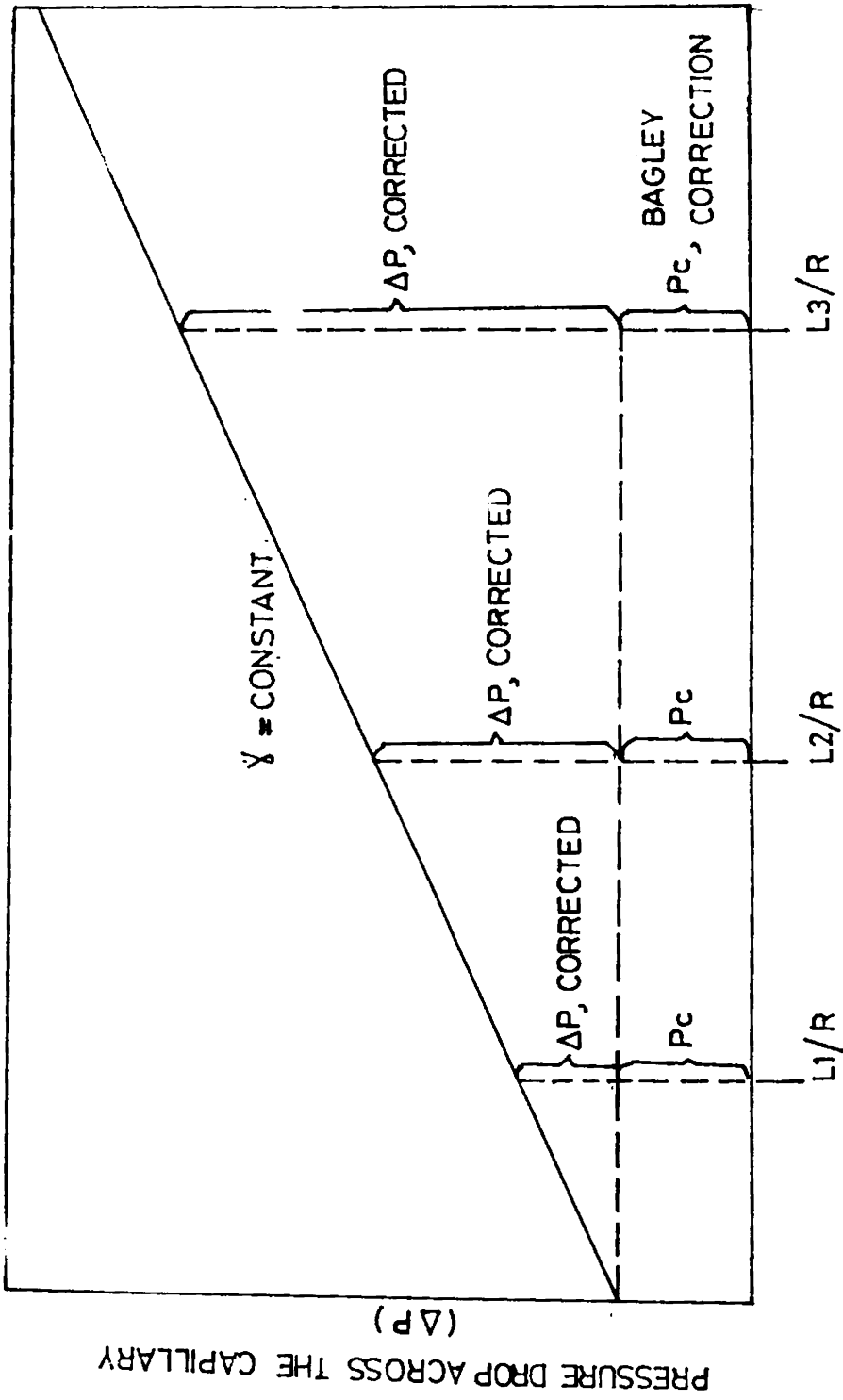


Fig.2.3 Schematic representation of Bagley correction

hold for non-Newtonian fluids like polymer melts. These apparent shear rates can be corrected by the degree of deviation from Newtonian behaviour by using the slope of the flow curve using the equation

$$\dot{\gamma}_w = [(3n+1)/4n] \dot{\gamma}_{wapp}$$

where

$$\dot{\gamma}_w = \text{true or absolute shear rate at the wall}$$

n = power law index taken as the slope of the straight lines from τ_{wapp} vs. $\dot{\gamma}_{wapp}$ plot at various points.

Degree of deviation from Newtonian behaviour

A straight line relationship on a log-log plot between τ_{wapp} and $\dot{\gamma}_{wapp}$ indicates that these variables can be related by a power law equation.

$$\tau_{wapp} = K \cdot \dot{\gamma}_{wapp}^n$$

which is referred to as the power law of Ostwald and de Waele^{4,10,11} where,

K is the consistency index and n is the power law index.

The power law index (n) indicates how rapidly the viscosity decreases with shear rate. For pseudoplastic fluids the power law index ranges from 1 to 0. When the power law index is unity, the fluid is Newtonian and the consistency index becomes the Newtonian viscosity. The power law index was used in this study to describe the degree of non-Newtonian behaviour.

Activation energy for viscous flow

The activation energy has considerable practical importance because it expresses the viscosity (η) - temperature (T) dependence of a material subjected to flow. η can be related to T using an Arrhenius type equation, by

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

where

E is the activation energy for viscous flow

and

R the gas constant.

Melt elasticity measurements

Polymers are viscoelastic in nature ie., they are partly viscous and partly elastic in the molten state.

They combine the features of elastic solids and viscous liquids. The relative contributions of these two components to the overall flow behaviour of the material are characteristic for the respective polymer.

The elastic flow component has the effect that a pure shear deformation of a melt which gives rise to an orientation of the macromolecules in the flow direction also generates normal stress differences within the melt. These normal stresses give rise to high inlet and outlet pressure losses and to swelling effects in cross sections of flow passages and in extreme cases to other undesirable flow phenomena.

The extrudate swell ratio D_e/D , where D_e and D are the diameter of the extrudate and the die respectively is a direct measure of the melt elasticity.¹²

Bogue and White¹³ suggested use of the parameter recoverable shear strain Υ_R for describing and distinguishing the fluid elasticity of different viscoelastic fluids as a function of shear stress. Υ_R was calculated from the expression

$$\Upsilon_R = 2[(D_e/D)^6 - 2]^{\frac{1}{2}}$$

which is derived from the Tanner's equation¹⁴ which correlates the dependence of extrudate swell ratio and normal stress functions by the relation

$$\tau_{11} - \tau_{22} = 2\tau_{w_{app}} [2(D_e/D)^6 - 2)]^{\frac{1}{2}}.$$

In the present study, the extrudates emerging from the capillary die were collected at various shear rates taking care to avoid any deformation. The diameter of the extrudate was measured at various points and the extrudate swell ratio D_e/D was determined as a measure of the melt elasticity.

Observation of extrudate surface roughness

The extrudate from capillary rheometer may provide useful visual evidence of non-laminar flow or surface imperfections. The extrudate appearance may be used to assess the quality of flow behaviour during processing and also to obtain evidence of rupture behaviour and the shear rate at which flow instabilities commence.

Melt flow index measurement

Melt flow index of polymers was measured according

to ASTM D 1238 using an extrusion plastometer. The rate of extrusion through a die of specified length and diameter was measured under prescribed conditions of temperature and load on the piston in the barrel.

Melt flow index was reported as the number of grams of polymer extruded in a time period of 10 min (g/10 min).

Mooney viscosity measurements

The Mooney viscosities of the raw rubbers were measured on the Mooney viscometer which is designed for measuring the shearing viscosity of rubber and rubber like materials by a disc rotating (2 rev/min) in a cylindrical cavity set at 100°C and filled with rubber under test. In running a viscosity test the sample was allowed to warm up for one minute after the platens were closed and the motor was then started. Reading after 4 minutes was reported as the Mooney viscosity of rubber [ML(1+4) at 100°C]. The procedure according to ASTM D 1646 (1981) was followed.

Compression moulding of test samples

The test samples for determining the physical properties were prepared in standard moulds by compression

moulding in an electrically heated hydraulic press, compressed under a pressure of 45 kg/cm^2 for a predetermined moulding time. Compression moulded sheets were then cooled in air. The sheets were stored in a cool dark place for 24 hours and were used for subsequent physical tests. Test samples were punched out of these sheets by standard dies.

Physical Test Methods

Tensile stress-strain measurements

Tensile tests were carried out according to ASTM D 412 (1980) using a Zwick universal testing machine model 1445. Dumbell specimens for testing were punched from moulded sheets parallel to the grain direction using a dumbell die (C type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight on the grips of the machine, the upper grip of which being fixed. Different types of grips were used according to the test materials. The rate of separation of the power actuated lower grip was fixed at 500 mm/min. for rubbers and 50 mm/min. for plastics. The computer attached to the machine calculates the tensile strength, elongation at break and stress at a particular elongation (modulus) and prints out these data after each testing.

Hysteresis Measurements

One of the main indices which determines the service life of rubber articles is the hysteresis loss. The cyclic loading/unloading tests were carried out on a Zwick universal testing machine model 1445 with dumbbell specimens. The test specimen was held tight by two grips, the upper grip of which was fixed. The specimen was stretched and released at a selected constant rate by the movement of the lower grip either between two force values or two extension values. The number of loading/unloading cycles as well as the interval between the loading cycles can be varied. The stress-strain curve for each loading/unloading cycle is drawn by the plotter and relevant data are also printed out. The hysteresis loss was calculated from the area measured under the extension and retraction curves. Set values were taken as the change in length after 5 cycles.

Hardness

The hardness (shore A or D) 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. Readings were taken after 10 seconds of the indentation after firm contact had been established with the specimens.

Compression set

The samples (1.25 cm thick and 2.8 cm diameter) in duplicate were compressed to constant deflection of 25% and were kept in an air oven for 22 hrs at 70°C. After the heating period, the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated using the equation,

$$\text{Compression set (\%)} = \frac{t_0 - t_1}{t_0 - t_s} \times 100$$

where t_0 and t_1 are the initial and final thickness of the specimen and t_s is the thickness of the spacer bar used.

Determination of gel content

Gel content was determined by extraction in boiling methyl ethyl ketone for eight hours. Small quantities of each sample approximately 0.3 gm were weighed and placed in a 15x15 mm envelope made from 120 gauge stainless steel woven mesh. The sample in the container envelope was immersed in refluxing methyl ethyl ketone for 5 minutes, dried under vacuum for 16 hours at 110°C, removed from

the container and reweighed. Gel fraction was determined by dividing the final sample weight by the initial sample weight.

Swelling studies

Samples of approximately 1 cm diameter, 0.25 cm thickness and 0.30 gm weight were punched out from the central portion of the compression moulded sheets, weighed and allowed to swell in excess of the respective solvents at laboratory temperature ($30 \pm 2^\circ\text{C}$) for the specified period of time. Then the samples were taken out, quickly dried with a filter paper and weighed. The percentage increase in weight was calculated. The procedure given in ASTM 471 (1983) was followed.

Infrared spectroscopy

Infrared (IR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm^{-1} by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are indication of the bond strengths and structural geometry in the molecule. Absorption at around

1700 cm^{-1} was made use of in this study because it is appropriate for carbonyl group determination.^{15,16}

The IR spectra given in this investigation were taken in KBr pellets using a Perkin Elmer model 983.

Scanning electron microscopy

In scanning electron microscopy, electrons are focused by either electrostatic or electromagnetic lenses. The final lens (objective) controls the focal point of the beam, and the first lens (condenser) controls the size of the electron beam being focused. All must operate in a vacuum and a better vacuum results in better electron source stability and longer life.

To obtain the maximum vacuum from the system it is necessary to keep it clean. The specimen changes the illuminating electron beam, adding information. The specimen, in effect, separates the monochromatic illuminating beam into a number of separate energy levels, each of which can be detected by with suitable detectors.

Specimen surface topography is usually seen by secondary electrons, those very low energy electrons that can penetrate only a small amount of material and thus

originate very close to the surface. Because of their very low energy, these electrons can be strongly influenced by electric field of the Faraday cage of the secondary electron collector. The signals monitored by detectors are magnified. An image of the investigated microscopic region of the specimen is thus photographed.

The SEM observations reported in the present investigation were made using JEOL JSM 35C model scanning electron microscope on the tensile fracture surfaces. The fracture surface was kept in a desiccator to keep it away from dust. Then the fracture surface was coated with a conducting material like gold, due to the nonconducting nature of the polymer surface. This was done by placing the specimen in a high vacuum evaporator and vapourizing the conducting material held in a tungsten basket (vacuum dispersion). The fracture surfaces were carefully cut from the failed test specimens and were sputter coated with gold within 24 hours of testing. The SEM observations were made within one week after gold coating. The fractured surfaces were kept in desiccators before and after gold coating till SEM observations were made.

Optical microscopy

The morphology of polymer blends was investigated

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

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Chapter 3

MECHANICAL AND RHEOLOGICAL BEHAVIOUR OF POLYSTYRENE/POLYDIENE BLOCK COPOLYMERS

MECHANICAL AND RHEOLOGICAL BEHAVIOUR OF
POLYSTYRENE/POLYDIENE BLOCK COPOLYMERS

Of the various classes of thermoplastic elastomers, those based on triblock copolymers of polystyrene/polydienes or polystyrene/hydrogenated polydienes are the largest and one of the earliest to be investigated.¹ The styrenic thermoplastic elastomers represent a class of materials introduced during 1965. They have many of the physical properties of vulcanized rubbers such as softness, flexibility, resilience but are processed as thermoplastics.^{2,3} Styrenic thermoplastic elastomers have the basic structure Poly(styrene-b-butadiene-b-styrene) (SBS), poly(styrene-b-isoprene-b-styrene) (SIS) or the one with a hydrogenated central ethylene-butylene (EB) block poly(styrene-b-ethylene-butylene-b-styrene) (SEBS). The most important feature of this structure is that they are phase separated systems.⁴⁻⁷ They have multiphase compositions in which the phases are chemically bonded by block copolymerization. At least one phase is a styrenic polymer that is hard at room temperature but becomes fluid when the polymer is heated, whereas another phase is a softer material that is rubber like at room temperature.

Styrenic thermoplastic elastomers are characterized by phase separated structures quite unlike the corresponding random copolymers in which the two phases polystyrene and polydiene retain many of the properties of the respective homopolymers. For example, such block copolymers have two glass transition temperatures (T_g) characteristic of the respective homopolymers whereas the equivalent random copolymers have a single intermediate T_g . While the incompatibility between the styrene and butadiene blocks have been identified as beneficial as far as the physical properties are concerned it has been shown to influence the processability adversely.⁸

The physico-mechanical properties of the styrenic block copolymers arise from the selection of the terminal and centre blocks. The terminal hard segments determine the upper service temperature while the elastomer segment control many of the properties such as thermal and oxidative stability, elastic nature etc.

Hysteresis loss under repeated deformation is of great importance with materials showing both thermoplastic and elastomeric behaviour. These studies are important since the elastomeric property of these materials can be demon-

strated more dramatically in a hysteresis curve than in a stress-strain curve.

1. Mechanical Properties of SIS, SBS and SEBS

Experimental

Commercially available SBS, SIS and SEBS were used for the present investigation. All the samples were further stabilized by 1% amine type antioxidant (Vulkanox 4010 NA) since it was found to be more efficient than phenolic types by Brabender dynamic stability test. Melting and homogenization of SIS and SBS were done at 150°C and SEBS at 200°C on a Brabender plasticorder model PL3S at 30 rpm. The homogenized material was compression moulded at the corresponding melting temperatures in an electrically heated laboratory hydraulic press. The mould was then water cooled and the compression moulded sheets taken out. After 24 hours, dumbbell shaped test pieces were punched out of this sheet using standard die.

Tensile testing of the test pieces was done on a Zwick Universal testing machine model 1445 at 25°C and at a crosshead speed of 500 mm/min.

Hysteresis studies were also done on the Universal testing machine at a crosshead speed of 50 mm/min and at a strain level of 50%. Hysteresis loss was determined by measuring the area under extension and retraction curves.

Results and Discussion

Fig.3.1 shows the stress-strain curves of the tri-block copolymers. SIS having a styrene content of only 14% gives typically a rubber like elongation curve whereas SBS and SEBS having higher styrene content give plastic deformation to some extent. SEBS shows an inflection point or knee and has the maximum tensile strength among the three thermoplastic elastomers. SBS shows a sharp yield point indicating a close similarity in behaviour with plastics. Table 3.1 shows the tensile strength, elongation at break, hardness and specific gravity of these thermoplastic elastomers. The ultimate values are comparable to the properties of vulcanized rubbers.

Hysteresis loss for the three thermoplastic elastomers at 50% strain is shown in Fig.3.2. The nature of the hysteresis loops is different for each polymer. SBS exhibits highest hysteresis loss compared to the other two, when the applied strain is beyond the yield point. The retraction curves for all the polymers do not reach the

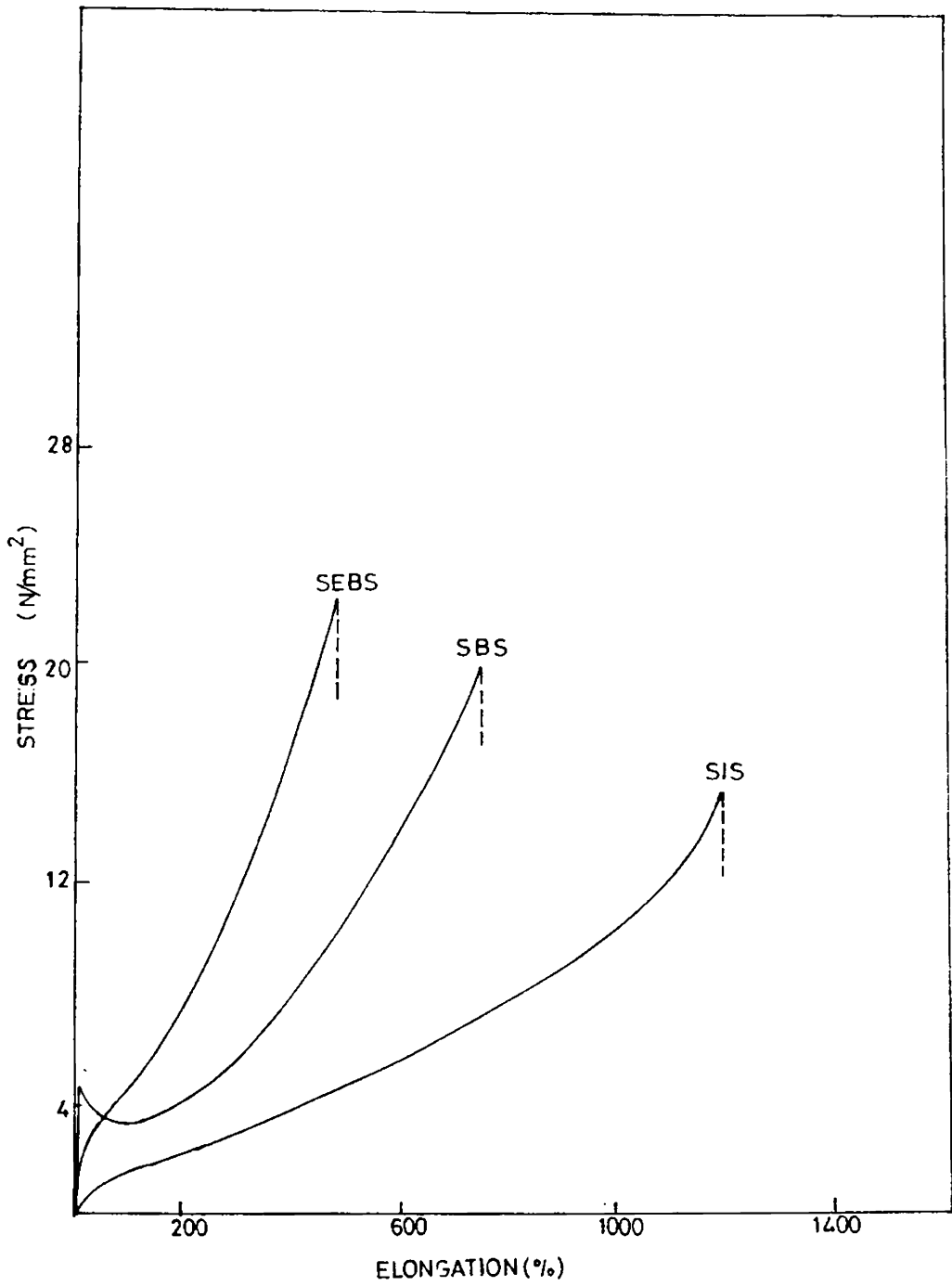


Fig.3.1 Tensile stress-strain curves of SIS, SBS and SEBS.

Table 3.1 Physical properties of triblock thermoplastic elastomers

Polymer	Specific gravity	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
SIS	0.92	15.5	1200	40
SBS	0.94	18.3	800	68
SEBS	0.91	22	500	72

Table 3.2 Hysteresis behaviour of triblock thermoplastic elastomers

Polymer	Hysteresis loss (J) at		
	I cycle	II cycle	III cycle
SIS	0.544	0.294	0.252
SBS	0.744	0.256	0.168
SEBS	0.298	0.10	0.084

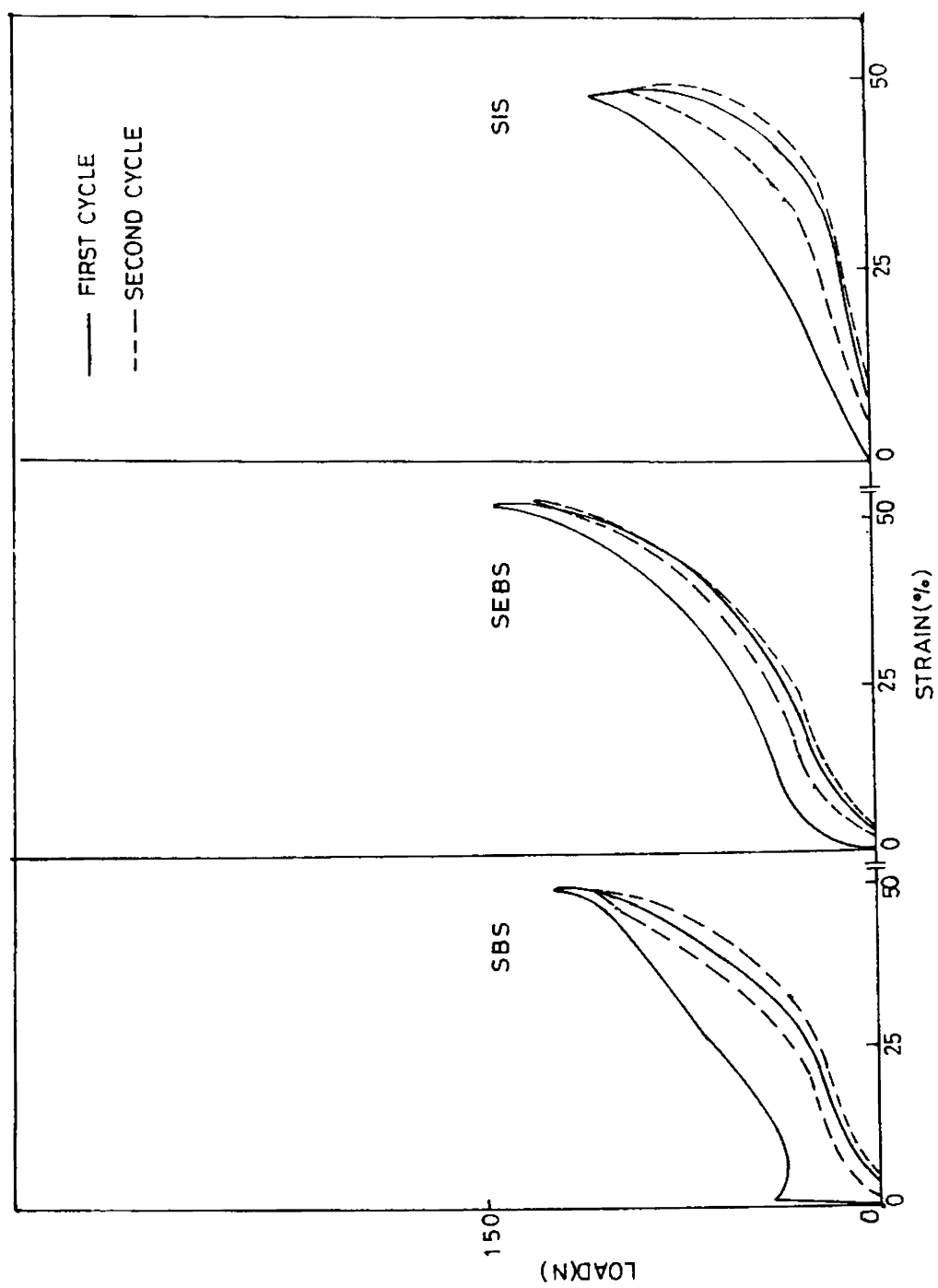


Fig.3.2 Hysteresis curves of SIS, SBS and SEBS at 50% strain level

starting point indicating some plastic deformation. The hysteresis losses during the first three cycles are given in Table 3.2.

2. Rheological Behaviour of SBS and SIS

A striking feature of styrenic thermoplastic elastomers is their very high melt viscosities.^{4,9} The incompatibility between the styrene and the elastomer phase leads to higher melt viscosities in styrenic thermoplastic elastomers. While the incompatibility between the hard and soft segments has been identified as beneficial for good physical properties, it influences the processability adversely. Melt viscosity increases with the degree of incompatibility as seen from the behaviour of SEBS thermoplastic elastomer¹⁰.

The melt viscosities of SBS and SIS block copolymers are found to be much higher than those of either polybutadiene, polyisoprene or random copolymers of styrene and butadiene of equivalent molecular weights.^{11,12} There have been only very few systematic studies in characterizing the rheological behaviour of these thermoplastic elastomers. The behaviour of these materials under different shear and temperatures have been reported as highly non-Newtonian¹¹⁻¹³ and even Newtonian.¹⁴

The complex nature of the melt seems to stem from the persistence of a two phase structure in the melt. This study on SBS and SIS thermoplastic elastomers have been taken up with the intention of throwing more light on their rheological behaviour.

Experimental

Melt rheological measurements were made using a capillary rheometer (Göttfert Viscotester 1500) using a capillary die of circular cross section (L/D ratio 30mm/1 mm) and flat at the entrance region and also using a Brabender plasticorder model PL3S equipped with roller mixing heads at different temperatures and shear rates.

Results and Discussion

Shear stresses and shear rates at the wall were calculated using the expression for Newtonian flow in cylindrical capillaries

$$\tau_w = \frac{\Delta P \cdot R}{2L} \quad \text{and}$$

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3}$$

where ΔP is the pressure drop across the capillary of radius

R and length L. The apparent viscosity at each shear rate was calculated according to the equation

$$\eta = \tau_w / \dot{\gamma}_w$$

The power law exponent (n) was calculated using the relation

$$\tau_w = K.(\dot{\gamma}_w)^n$$

where K is a constant.

The temperature dependence of the viscosity was expressed in terms of an Arrhenius equation

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

where E is the activation energy for viscous flow, R the gas constant, T the absolute temperature and A is a constant. The activation energy was calculated from plots of η vs. $1/T$.

The Brabender plasticorder (torque rheometer) has also been used to study the rheological behaviour of polymer

melts under processing conditions.¹⁵⁻¹⁷ It was shown that the relationship obtainable from this instrument

$$M = Cs^a$$

where M is the torque, S, the rpm (revolutions per minute) and C and a are constants, resembles the familiar power law behaviour¹⁶⁻¹⁸

$$\tau = K\dot{\gamma}^n$$

and hence could be used for calculation of the power law index n.

Fig.3.3 shows the variation of viscosity with shear rate of SBS in the range of shear rates generally encountered in most polymer processing operations. The figure clearly shows the highly non-Newtonian behaviour of the melts. As expected, the curve lowers with increasing temperature which is a general feature of polymer melts due to the increased mobility of the polymer molecules at higher temperatures. The viscosities increase as the shear is decreased and apparently approach infinite values at low shear rates, particularly at lower temperatures. This could be attributed to the existence of a two phase structure in the melt.

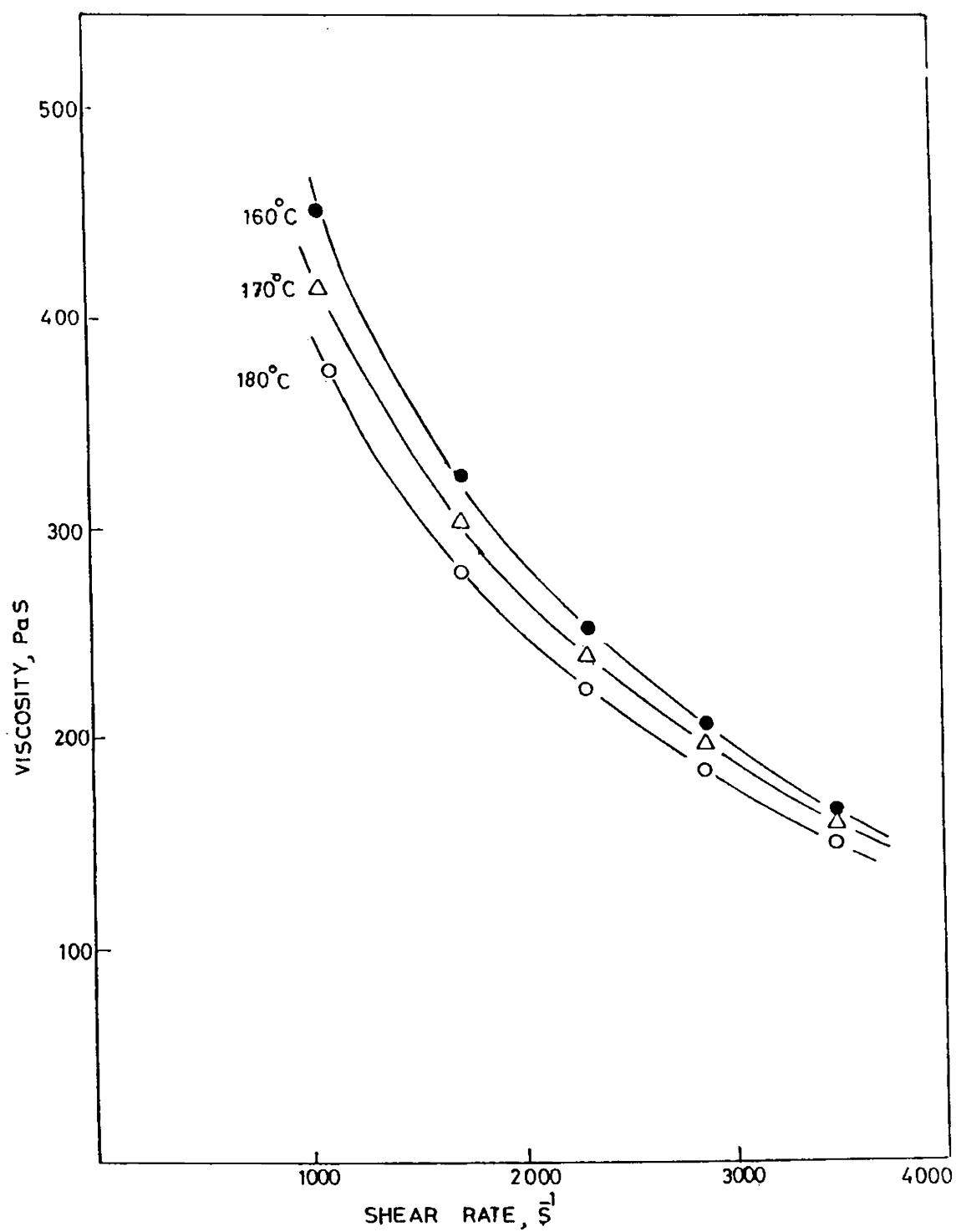


Fig.3.3 Variation of viscosity with shear rate of SBS at different temperatures.

Fig.3.4 shows the plot of shear stress versus shear rate of SBS at 160 and 180°C. It is interesting to note that each curve can be represented as two straight lines. The two straight lines may represent distinct flow behaviour. The initial straight line may be the flow region where polystyrene domains act as reinforcing filler in the rubber matrix. The flow involves the transfer of hard blocks through the polydiene phase. This additional energy required for flow accounts for the higher melt viscosities. The slope of the initial line, the power law index, when this type of flow prevails is comparable to the value of filled rubbers.^{19,20}

At higher shear rates the behaviour becomes more non-Newtonian and the power law index values are comparable to that of raw rubbers.^{19,20} With increase in temperature, the critical shear rate at which the flow transition occurs shifts to lower values and both the flow regimes tend to become more Newtonian as evidenced by the increase in power law index in both cases. It is likely that the critical shear rate at which the flow transition takes place, further comes down and the first flow regime may be completely absent at higher temperatures. Thereafter, the flow may become nearly Newtonian as indicated by the increase in the power law

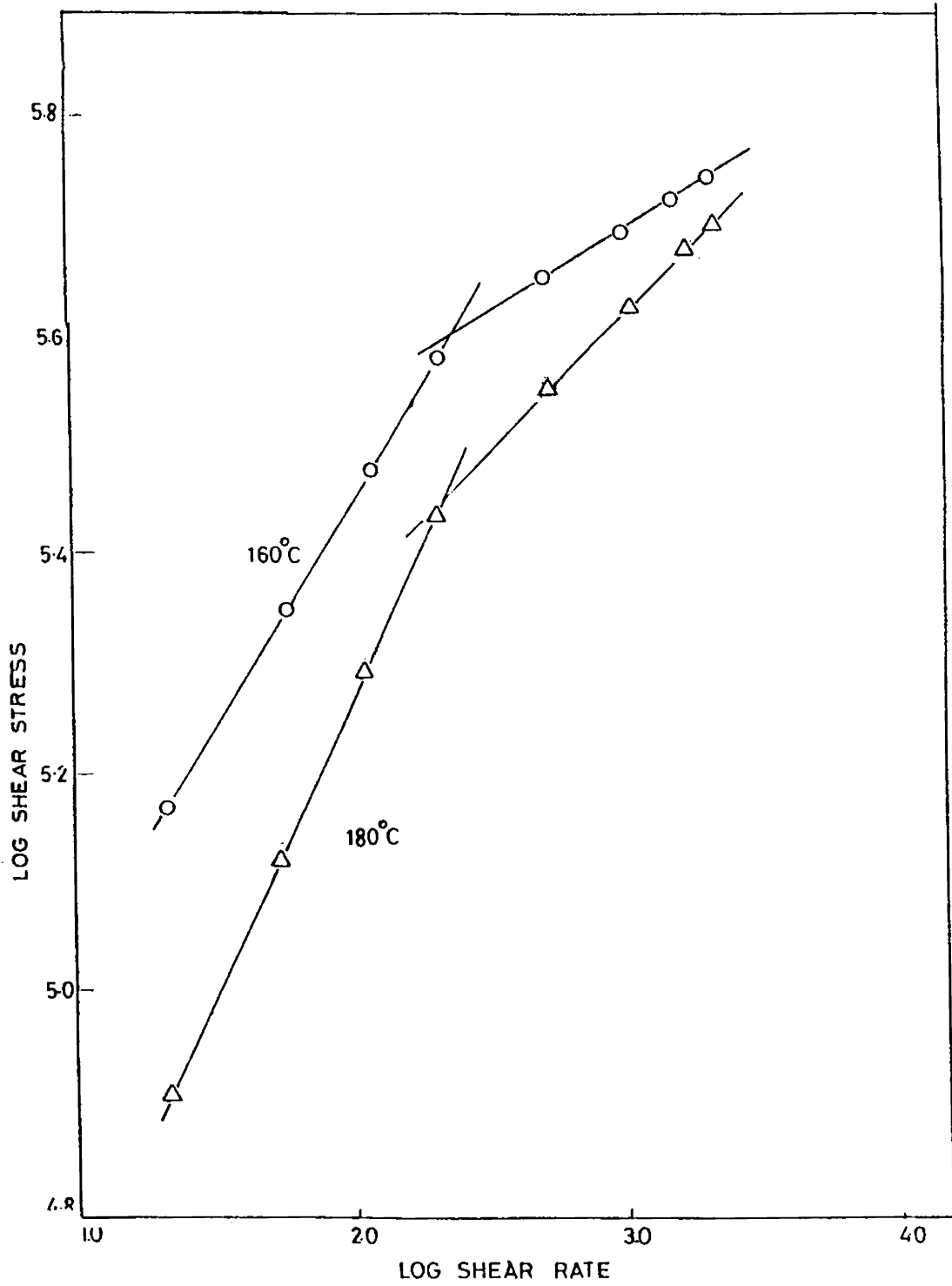


Fig.3.4 Plot of shear stress vs. shear rate of SBS at 160°C and 180°C.

exponent with increase in temperature. This might be the reason for a near Newtonian behaviour at high temperature.²¹ The power law indices calculated from the slopes of the straight lines are shown in Table 3.3.

Fig.3.5 shows the variation of viscosity with absolute temperature. The straight lines obtained indicate Arrhenius type behaviour and from the slopes activation energies may be determined. The activation energy of viscous flow is found to decrease with increase in shear rate (Table 3.4). This is probably due to the large reduction in viscosity with increase in shear rate.

The rheological data of SBS obtained from the Brabender plasticorder are shown in Figs.3.6-3.8. As expected torque/rpm representing viscosity decreases with increase in temperature and shear rate (rpm) (Fig.3.6). The variation of shear stress (torque) with shear rate (rpm) is shown in Fig.3.7. Eventhough only low ranges of shear rates could be investigated in this equipment, data are available at lower temperatures compared to those of the capillary rheometer. The data show the behaviour of the melts as more non-Newtonian compared to their behaviour

Table 3.3 Power law indices for SBS and SIS

CAPILLARY RHEOMETER				BRABENDER PLASTICORDER		
Polymer	Temp. °C	Flow Indices		Polymer	Temp. °C	Flow Index
		Lower shear	Upper shear			
SBS	160	0.48	0.16		130	0.08
	170	0.50	0.19	SBS	140	0.09
	180	0.64	0.24		150	0.11
SIS	160	0.41	0.10		130	0.11
	170	0.45	0.12	SIS	140	0.12
	180	0.50	0.16		150	0.13

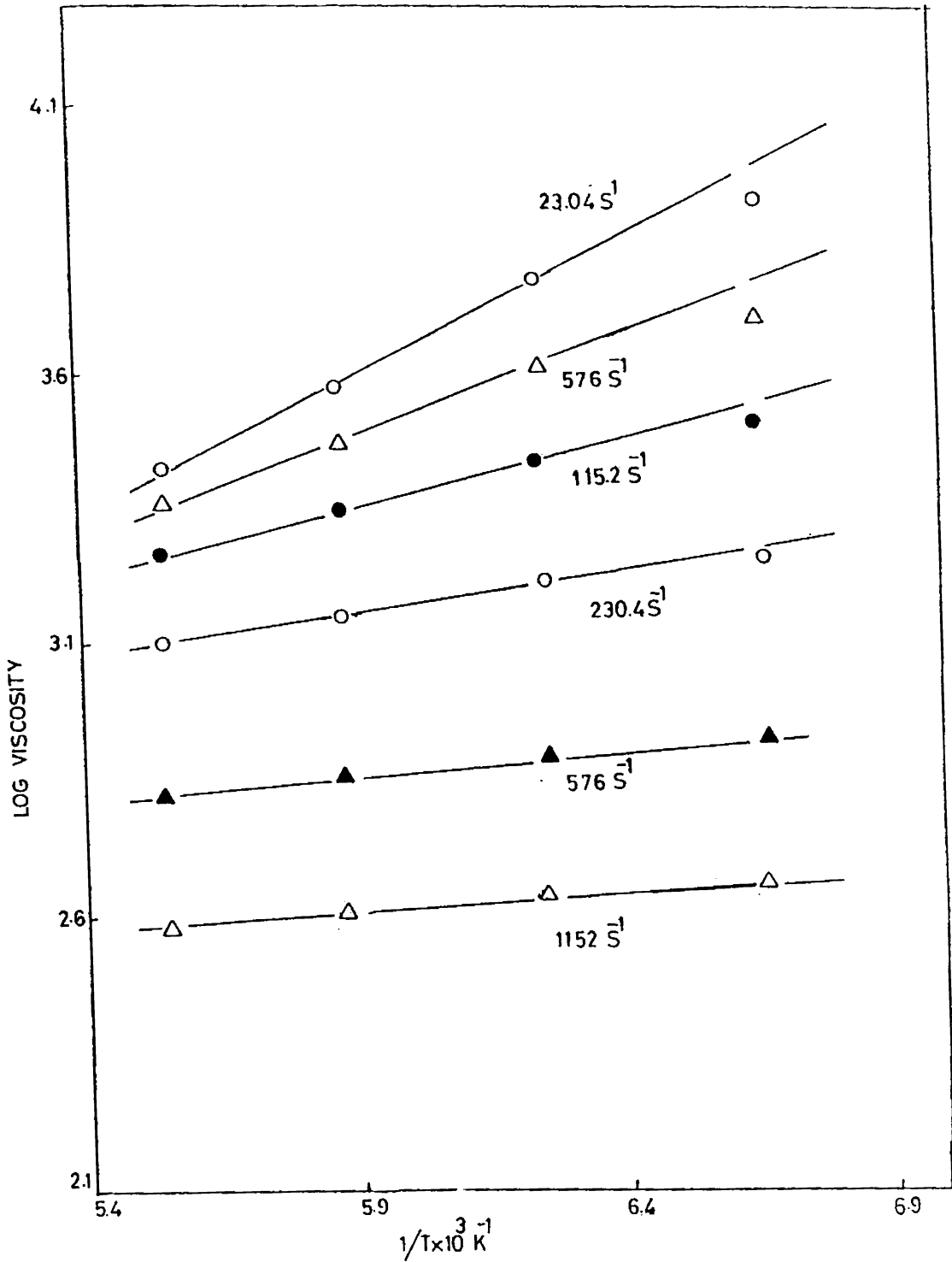


Fig.3.5 Variation of viscosity with reciprocal absolute temperature of SBS at various shear rates.

Table 3.4 Activation energy of viscous flow for SBS and SIS

Polymer	Capillary Rheometer		Brabender Plasticorder	
	Shear rate (s^{-1})	Activation energy KJ mole^{-1}	RPM	Activation energy KJ mole^{-1}
SBS	23	4.4	30	13.8
	57	3.43	40	9.7
	115	2.3	50	9.2
	230	1.2	60	8.9
	576	0.83		
	1152	0.4		
SIS	23	3.4	30	10.3
	57	2.5	40	8.5
	115	2.2	50	6.9
	230	2.1	60	5.2
	576	1.9		
	1152	0.9		

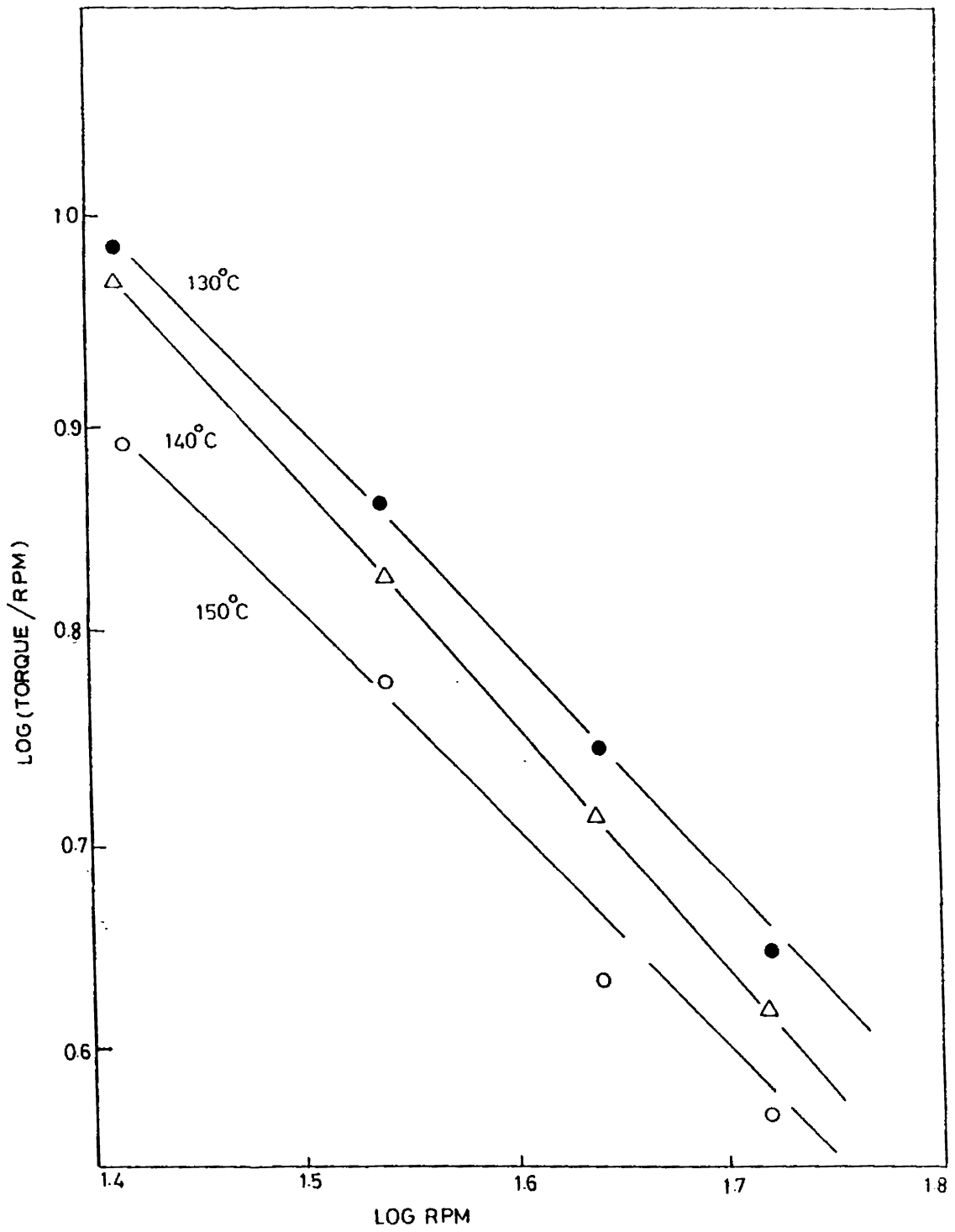


Fig.3.6 Variation of torque/rpm with rpm of SBS at different temperatures.

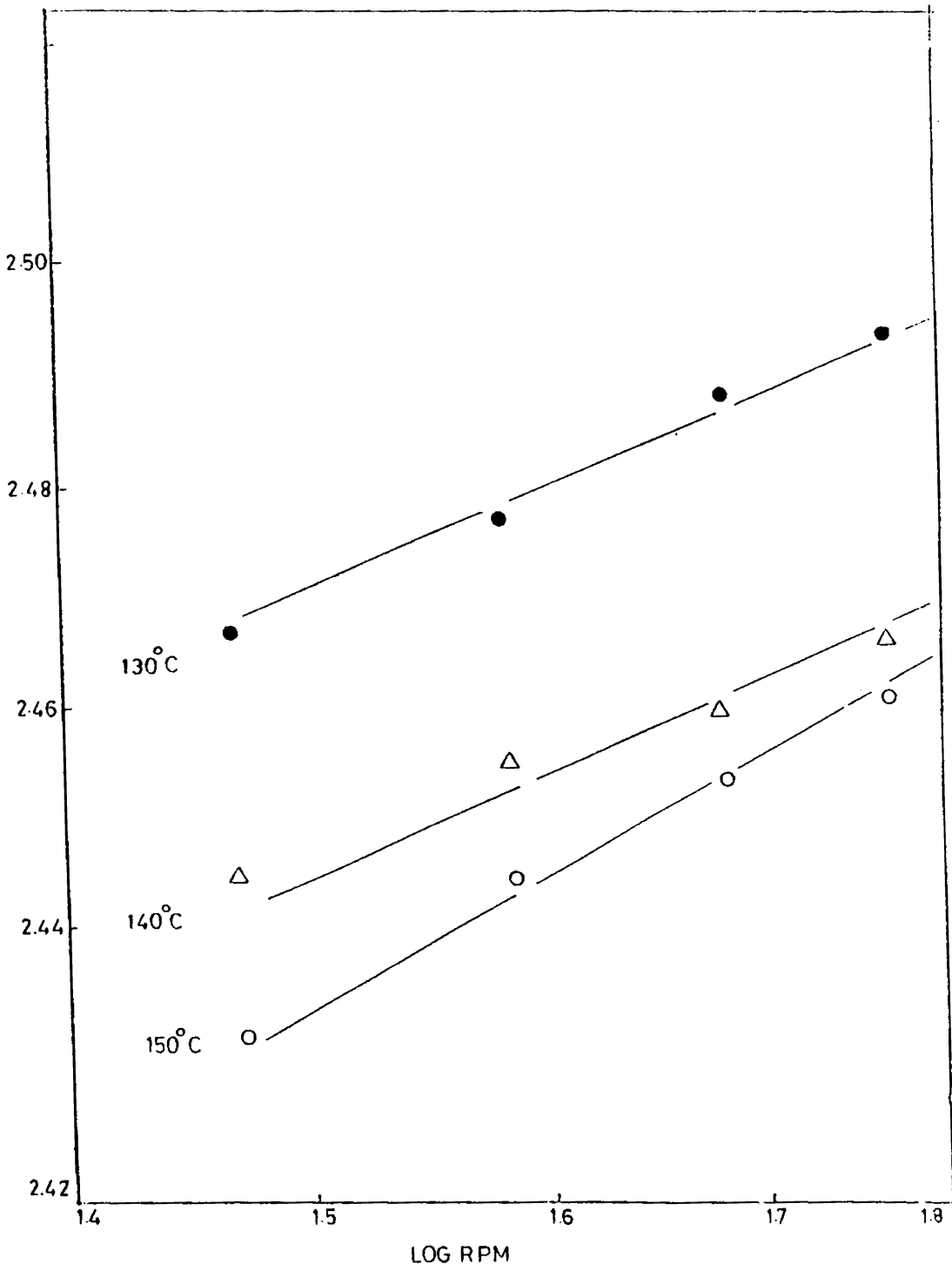


Fig.3.7 Variation of torque with rpm of SBS at different temperatures.

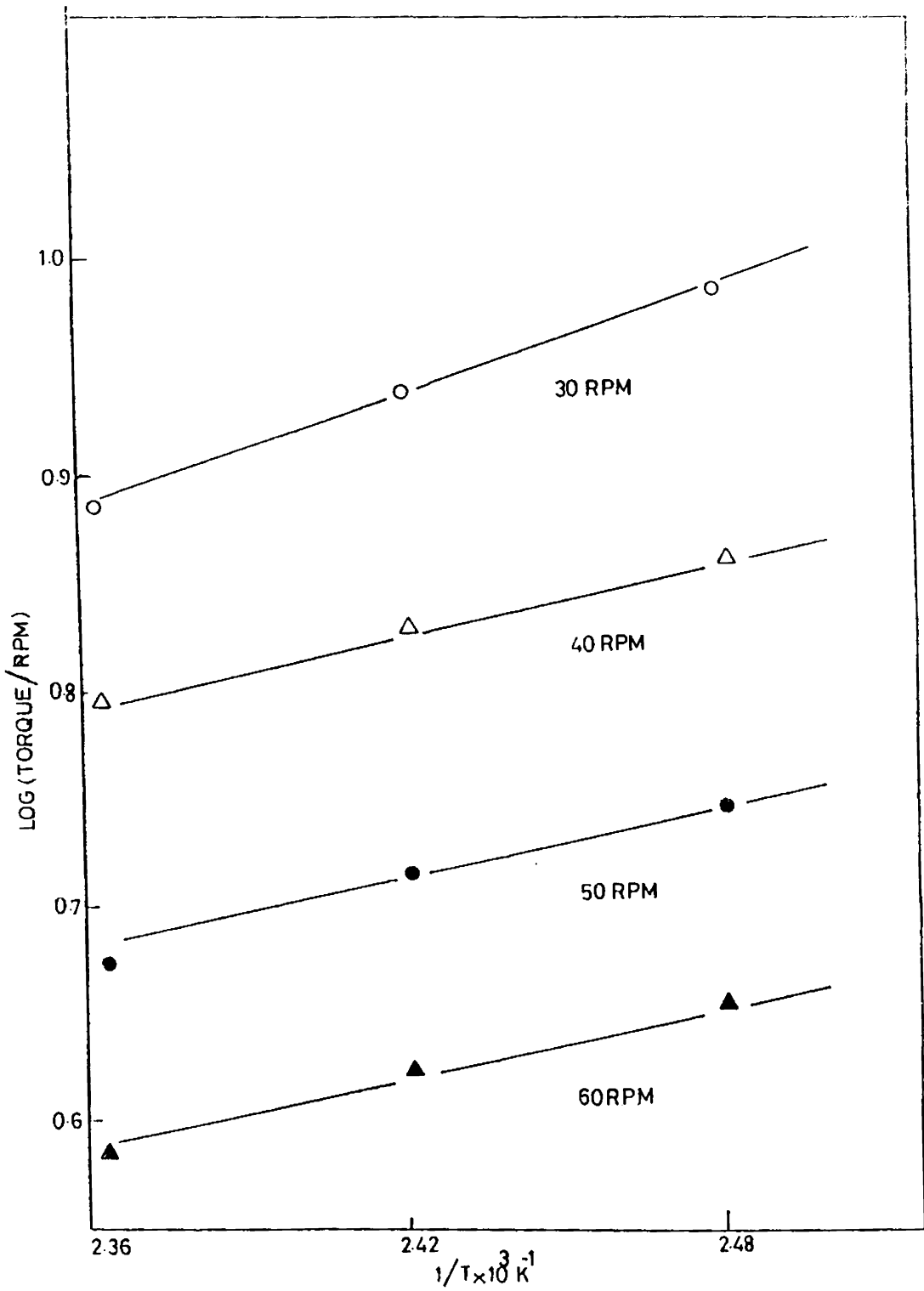


Fig.3.8 Variation of torque/rpm with reciprocal absolute temperature of SBS at different rpms.

in the capillary rheometer. However, these data cannot be fully taken as representing the rheological behaviour of the melts, since chances of oxidative degradation are much more in the Brabender plasticorder. Also, the shear rate is not uniform throughout the mixing chamber and the stability of temperature at the set value is poor. The flow indices calculated from the Brabender data (Fig.3.7 and Table 3.3) are lower than the values obtained for capillary rheometer. The activation energies (Fig.3.8 and Table 3.4) calculated from the Brabender plasticorder show the same trend of variation as the values obtained from the capillary rheometer. But the values are larger than those obtained from the capillary. This is probably due to the lower temperatures to which they belong and other factors which are relevant to this instrument already mentioned.

Figs.3.9-3.11 show the rheological behaviour of SIS obtained from the capillary rheometer. The variation of viscosity with shear rate (Fig.3.9) closely resembles the behaviour of SBS. From Fig.3.10 it can be observed that the flow curves of SIS also can be approximated by two straight lines characterizing two distinct flow behaviour. The behaviour at lower shear rate is less non-Newtonian than that at high shear rates as shown by the values of the power law exponents (Table 3.3). The activation

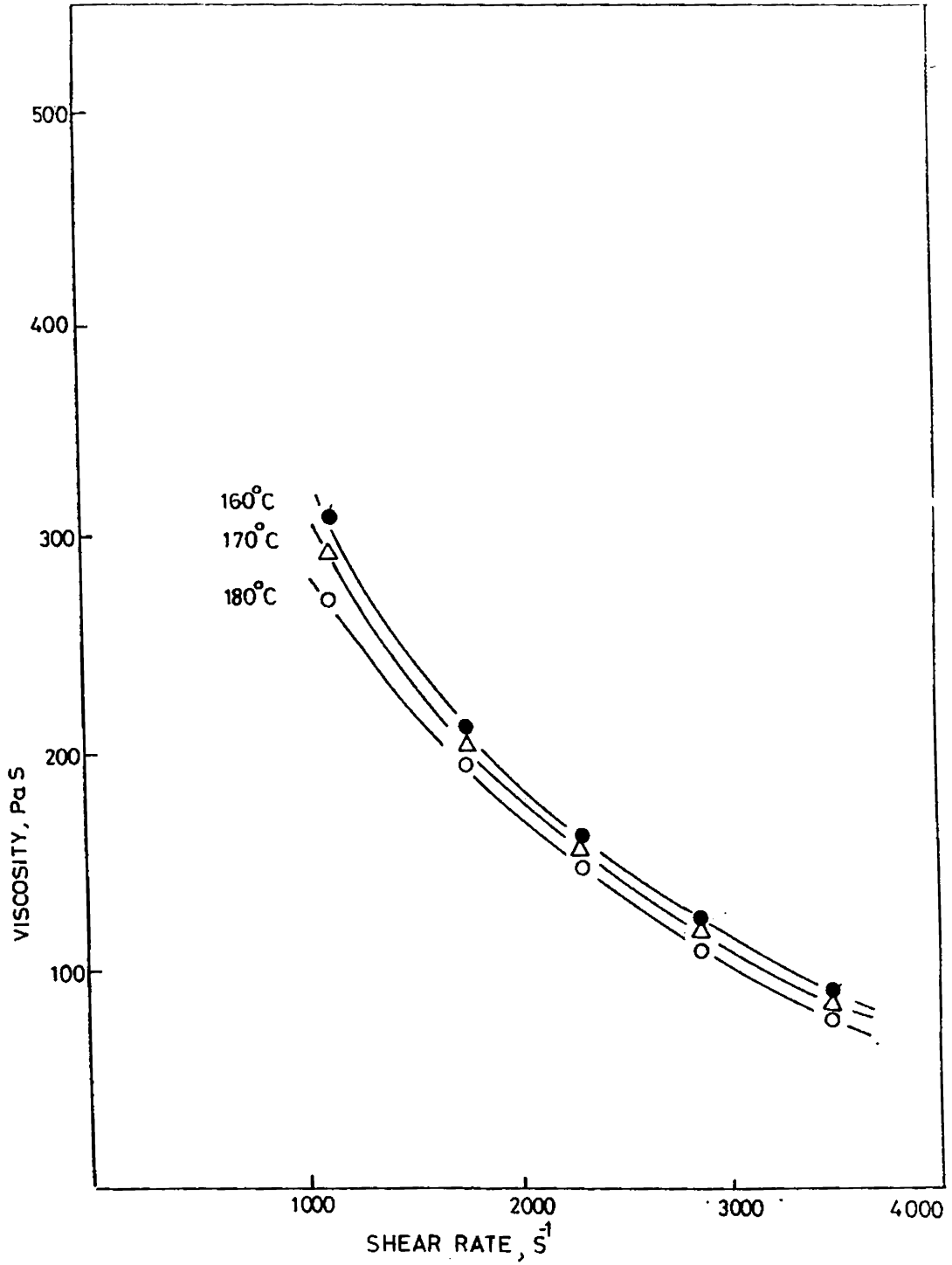


Fig.3.9 Variation of viscosity with shear rate of SIS at different temperatures

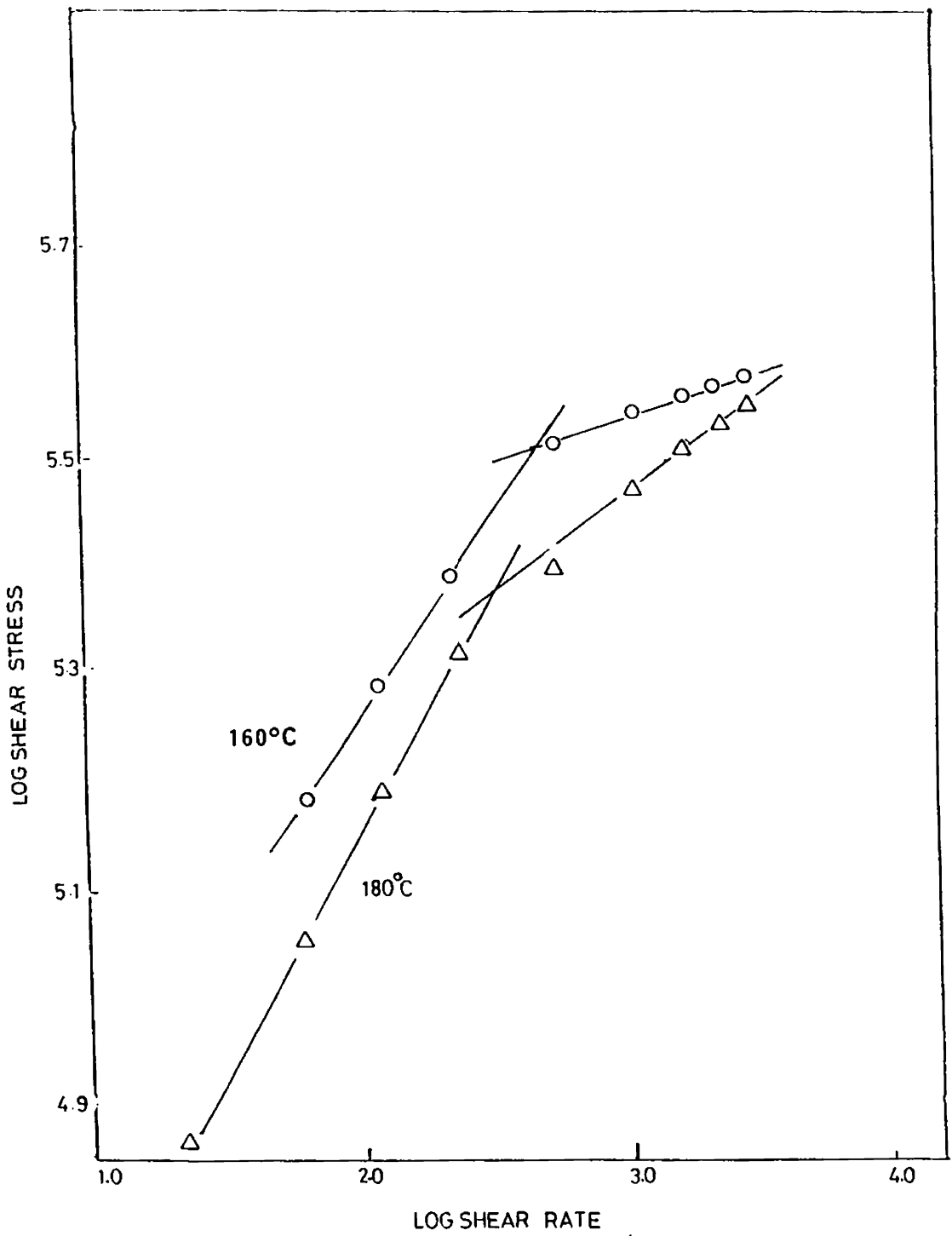


Fig.3.10 Variation of shear stress with shear rate of SIS at different temperatures.

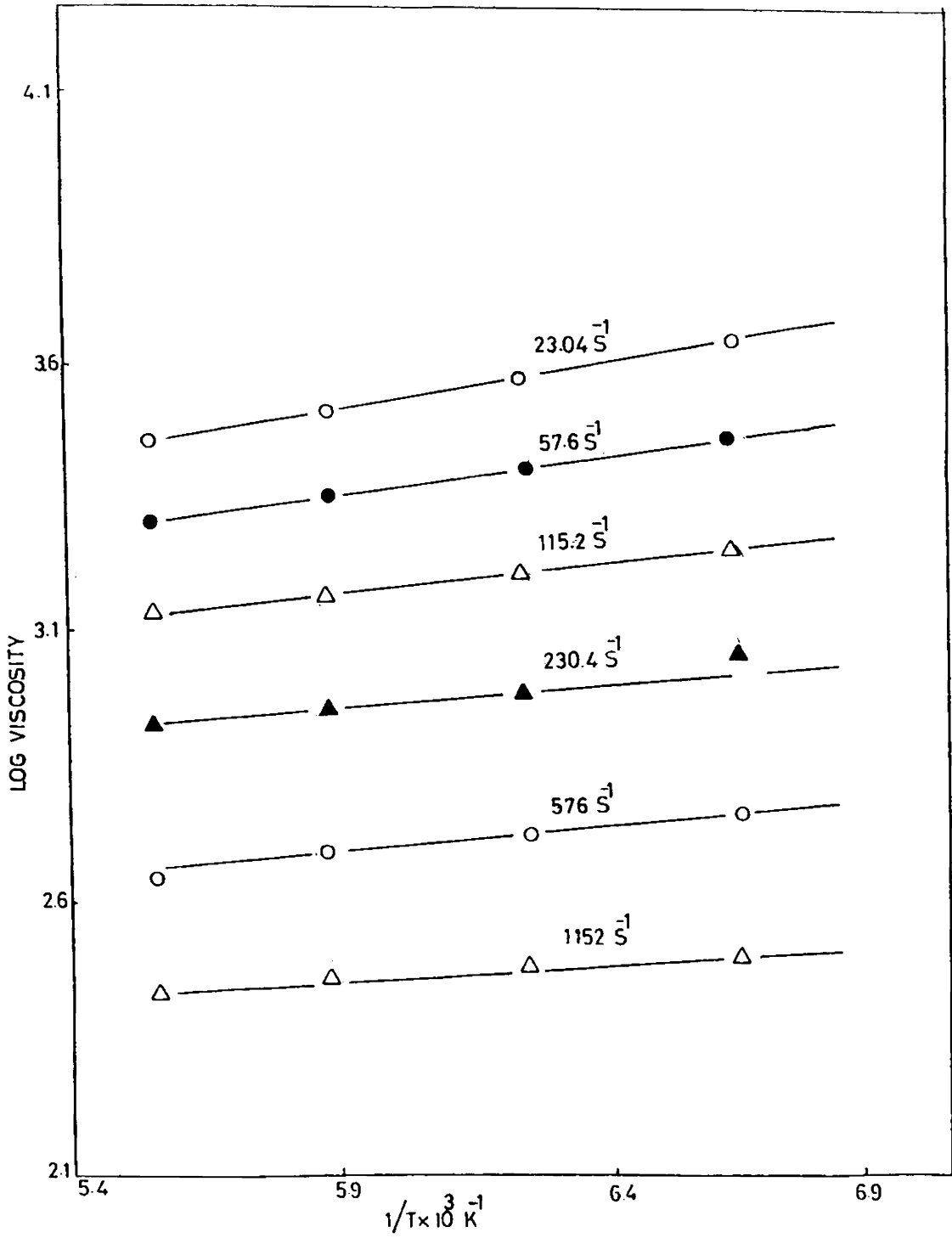


Fig.3.11 Variation of viscosity with reciprocal absolute temperature of SIS at different shear rates.

energy of flow is comparable to that of SBS and decrease with increase in shear rate (Fig.3.11 and Table 3.4).

Figs.3.12-3.14 show the rheological behaviour of SIS from Brabender plasticorder. Fig.3.12 represents the variation of viscosity with shear rate and Fig.3.13 the variation of shear stress with shear rate. The power law indices calculated from Fig.3.13 are given in Table 3.3. Fig.3.14 permits the calculation of activation energies of viscous flow. As in the case of SBS, the rheological data obtained from the Brabender plasticorder do not agree well with those obtained from the capillary rheometer.

3. Viscous and elastic behaviour of SEBS triblock copolymer

Excellent resistance to creep and compression set, high tensile and tear strength are some of the factors²² which differentiate SEBS saturated triblock copolymers from their unsaturated counterparts, SBS and SIS. Because of their excellence in mechanical properties and heat resistance it is important to study the processing behaviour of these TPEs. The viscous and elastic behaviour of these TPEs are described in this section.

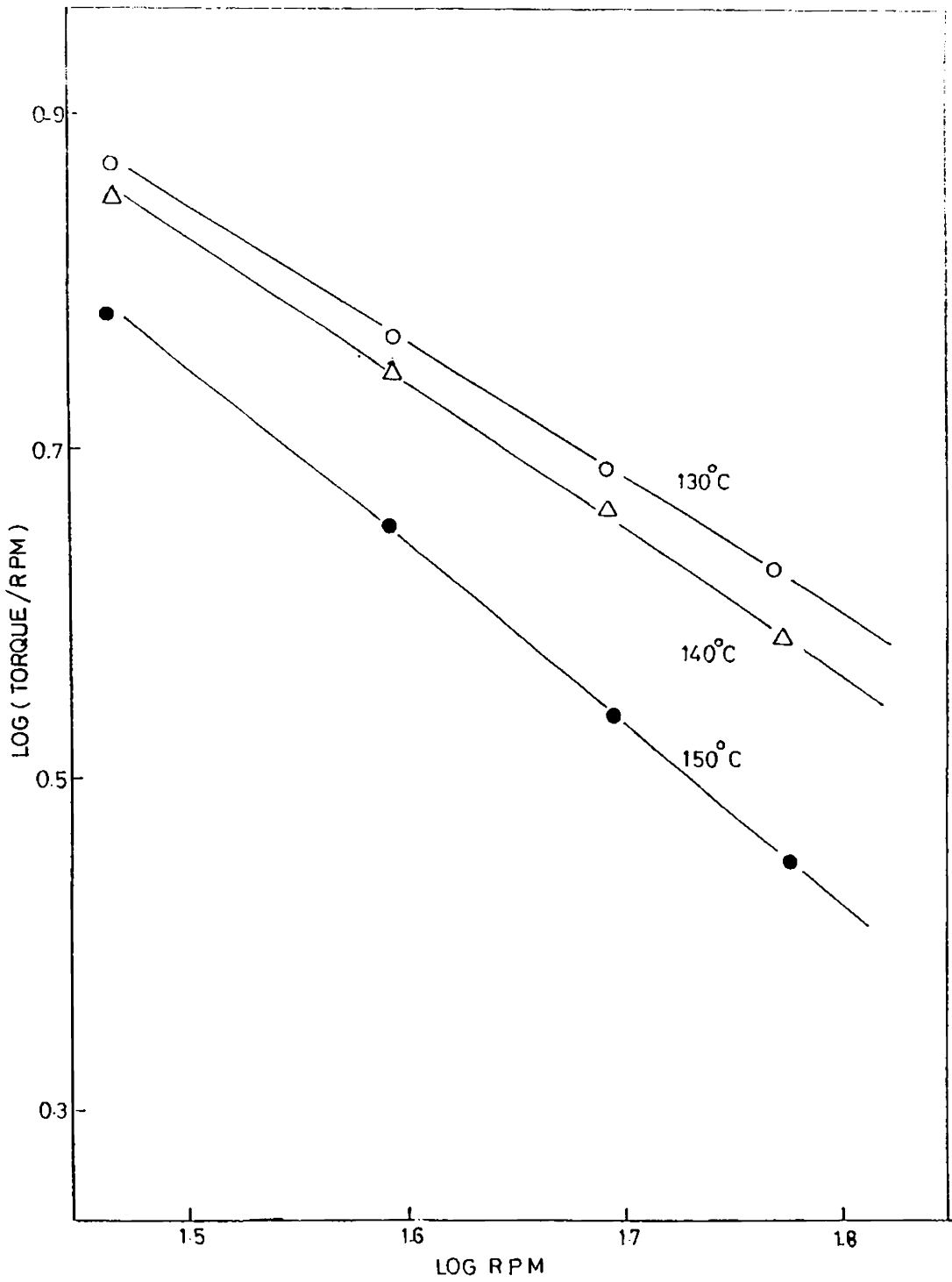


Fig.3.12 Variation of torque/rpm with rpm of SIS at different temperatures.

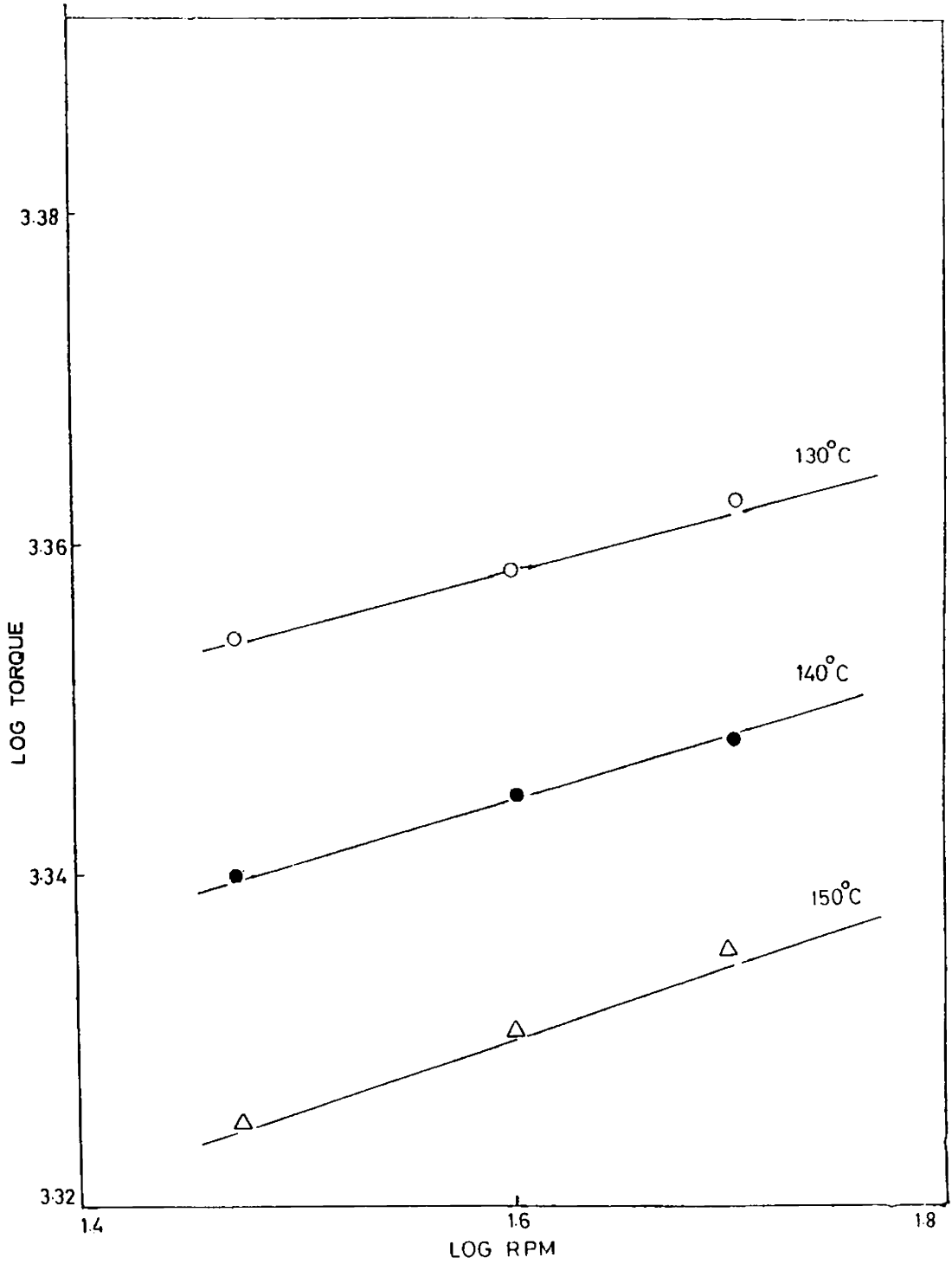


Fig.3.13 Variation of torque with rpm of SIS at different temperatures.

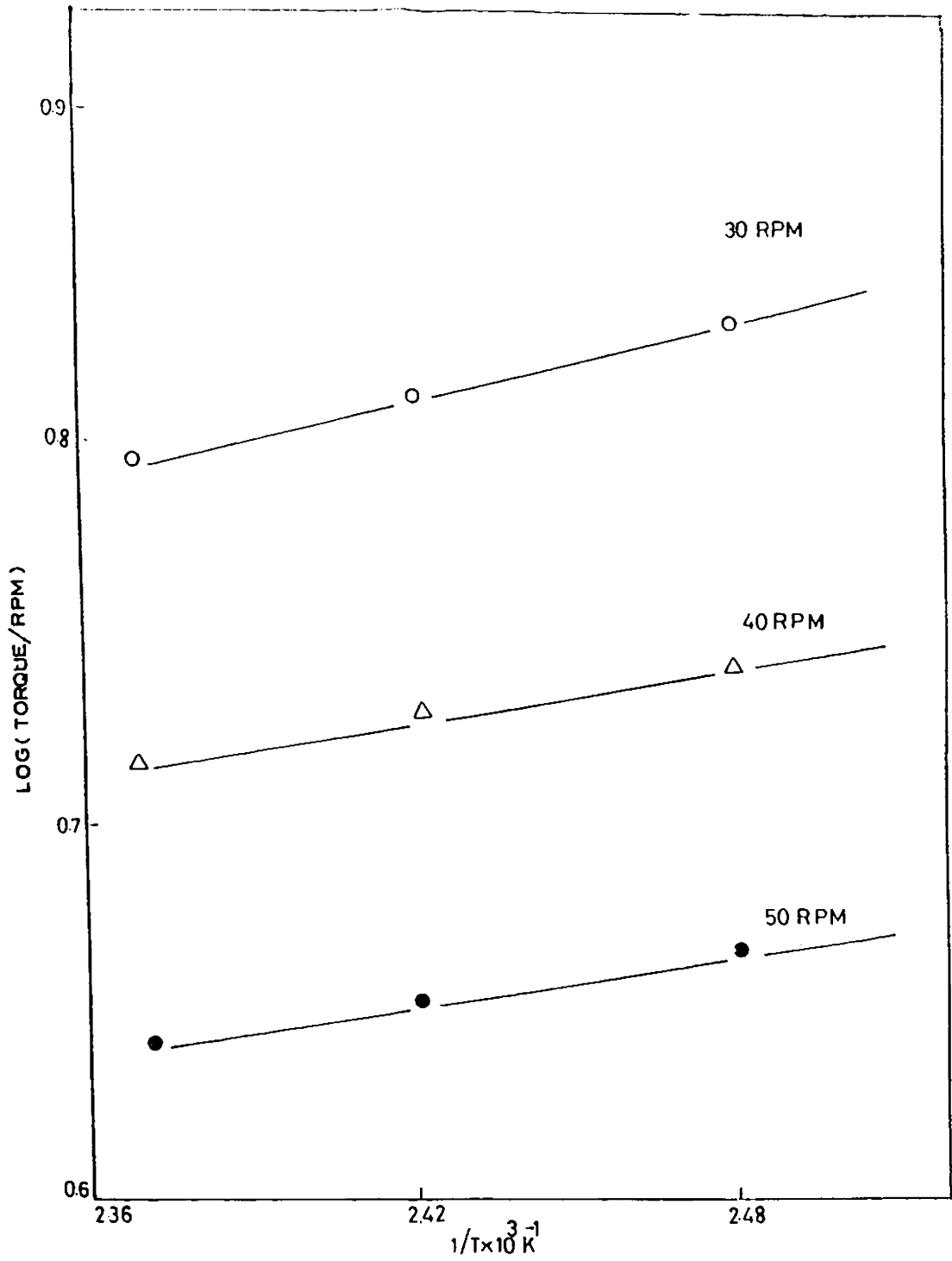


Fig.3.14 Variation of torque/rpm. with reciprocal absolute temperature of SIS at different rpms.



Experimental

Viscous and elastic properties of SEBS triblock copolymer were measured on a capillary rheometer (Göttfert Viscotester 1500) using capillary dies of circular cross sections with L/R ratios 60, 40 and 20 at different shear rates and temperatures varying over a range of 20-3000 s⁻¹ and 200-250°C respectively.

From volumetric flow rates at various applied pressures, values of apparent shear stress at wall (τ_{wapp}), apparent shear rate ($\dot{\gamma}_{wapp}$) and apparent viscosity (η_{app}) were calculated.

From the log τ_{wapp} vs. log $\dot{\gamma}_{wapp}$ plots, values of power law exponent 'n' were calculated.

Rabinowitsch correction was applied using values of 'n' to obtain true shear rate ($\dot{\gamma}_w$) according to the following expression.²³

$$\dot{\gamma}_w = [(3n+1)/4n] \dot{\gamma}_{wapp}$$

Bagley correction²⁴ was applied to obtain true shear stress at wall (τ_w) from the expression

$$\tau_w = \frac{\Delta P - P_c}{L} \frac{R}{2}$$

where the entrance pressure loss P_c was evaluated from plots of ΔP vs. L/R values.

The true viscosity was then calculated using the expression

$$\eta = \tau_w / \dot{\gamma}_w$$

The entrance pressure loss P_c was also taken as an index of the elasticity of the melts. Elasticity of the melts was also measured from the die swell ratio D_e/D where D_e is the diameter of the extrudate and D that of the die.²⁵ Extrudates emerging from the capillary die were collected carefully at different shear rates and diameter was measured after 24 hours. The extrudate surface at various shear rates was photographed to look for surface roughness.

Results and discussion

Fig.3.15 shows the variation of viscosity of SEBS with shear rate. The melt shows a strong non-Newtonian behaviour similar to the behaviour of SIS or SBS. The viscosities increase as the shear is decreased and apparently approach infinite values at low shear rates particularly at low temperatures which may be attributed to the existence of two phase structure.

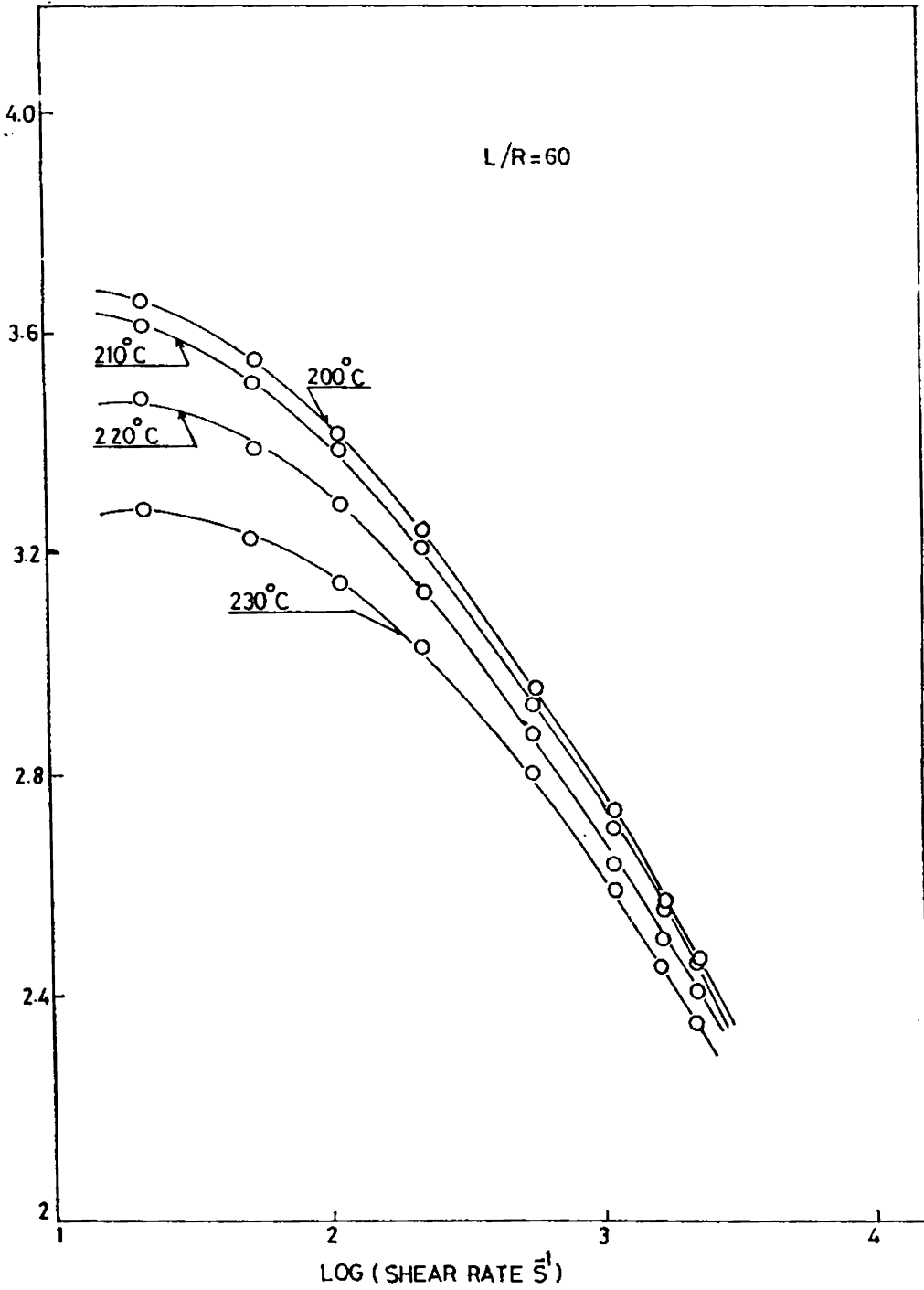


Fig.3.15 Variation of viscosity with shear rate of SEBS at different temperatures.

Fig.3.16 shows the plot of shear stress versus shear rate of SEBS at 220°C and 240°C. Here also, the curve can be represented as two straight lines. The slope of the initial line, the power law index, is comparable to the value of filled rubbers. The behaviour becomes more non-Newtonian at higher shear rates at all temperatures and the power law index values are comparable to that of raw rubbers. The transfer of polystyrene domains during flow through highly associated EB blocks require additional energy and this accounts for the higher melt viscosities of SEBS than SBS and SIS. As the shear rate is increased, the polystyrene domains also get destroyed due to high shearing and the behaviour becomes similar to raw elastomers. The shear rate at which the flow transition takes place is termed as critical shear rate. As the temperature is increased, the critical shear rate shifts to lower values and both the flow regimes tend to become more Newtonian. The power law indices calculated from the slopes of the straight lines and the shear rate at which the flow transition occurs at 220°C, 230°C and 240°C are shown in Table 3.5.

Variation of viscosity with reciprocal absolute temperature is shown in Fig.3.17. The straight lines indicate Arrhenius type behaviour and the activation energies

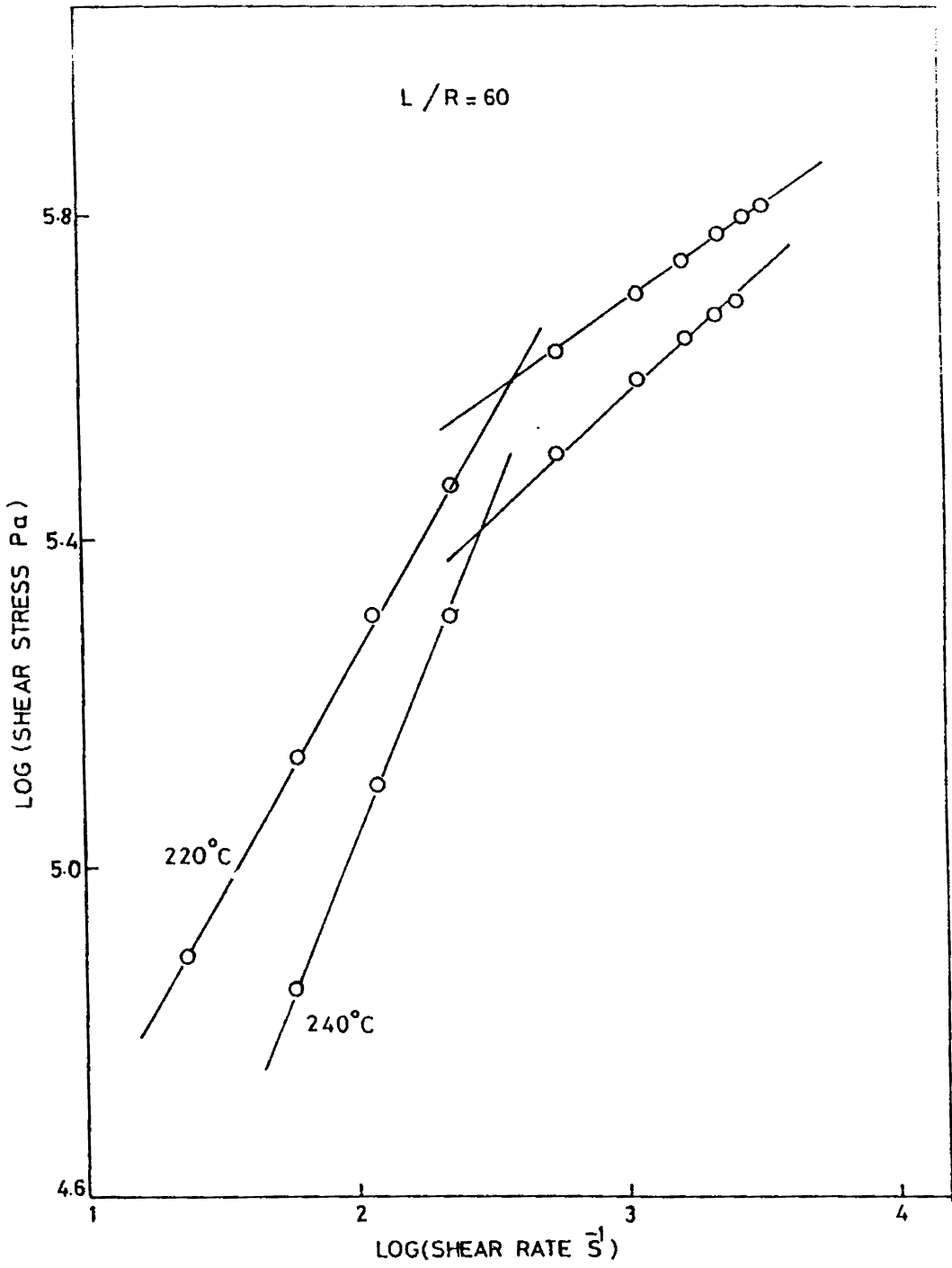


Fig.3.16 Variation of shear stress versus shear rate of SEBS.

Table 3.5 Power law indices for SEBS

Temperature (°C)	Power law index values at		Critical shear rate for the flow transition (s ⁻¹)
	Lower shear rate region	Upper shear rate region	
220	0.57	0.22	416
230	0.61	0.26	363
240	0.66	0.33	302

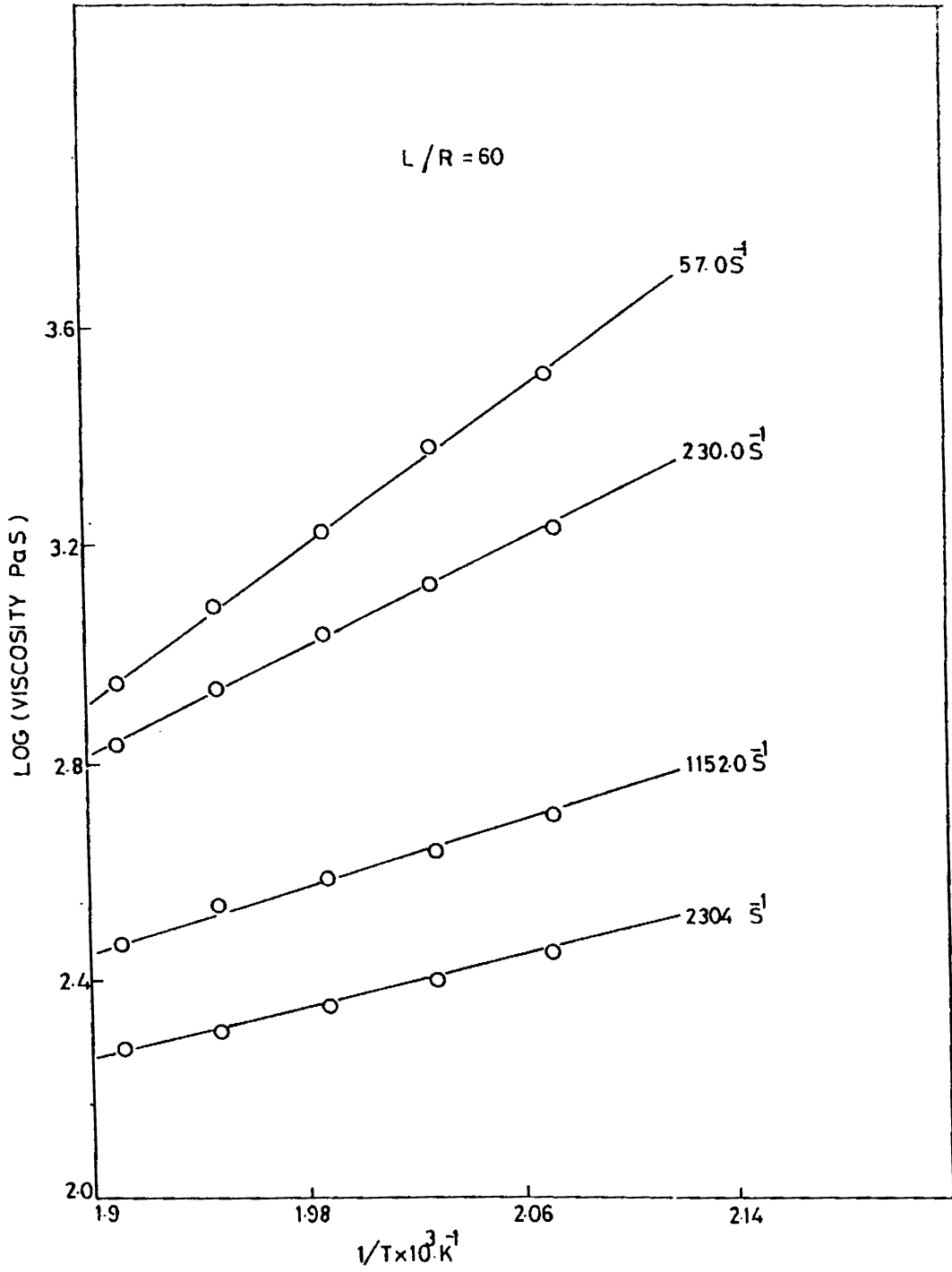


Fig.3.17 Variation of viscosity with reciprocal absolute temperature of SEBS.

calculated from the slopes of the straight lines are given in Table 3.6. Activation energy of viscous flow is found to decrease with increase in shear rate, probably due to reduction in viscosity with increase in shear rate. Compared to other diene triblock copolymers, activation energy of viscous flow for SEBS is very high. This may be due to the high entanglement density of the EB blocks, sharp phase separation and strongly associated styrene/domain structure.

Fig.3.18 shows Bagley plots (variation of ΔP as a function of L/R ratios) of SEBS at 200°C. The linearity of Bagley plot confirms the absence of slippage at the capillary wall, otherwise slippage will cause curvature in the Bagley plot.²⁶

Variation of end correction factor P_c against log shear rate are shown in Fig.3.19. The increase in P_c with shear is gradual at lower shear rates whereas a sharp variation occurs at higher shear. This may mean that elastic effects sharply increase with shear rates and may dominate the viscous effects at higher shear rates.

Effect, of shear rate on die swell ratio which is a direct measure of melt elasticity is shown in Fig.3.20. The die swell ratio increases with increase in shear rate

Table 3.6 Activation energy of viscous flow for SEBS

Capillary shear rate (s^{-1})	Activation energy (KJ mole^{-1})
60	68.4
230	44.6
1150	26.5
2300	24.0

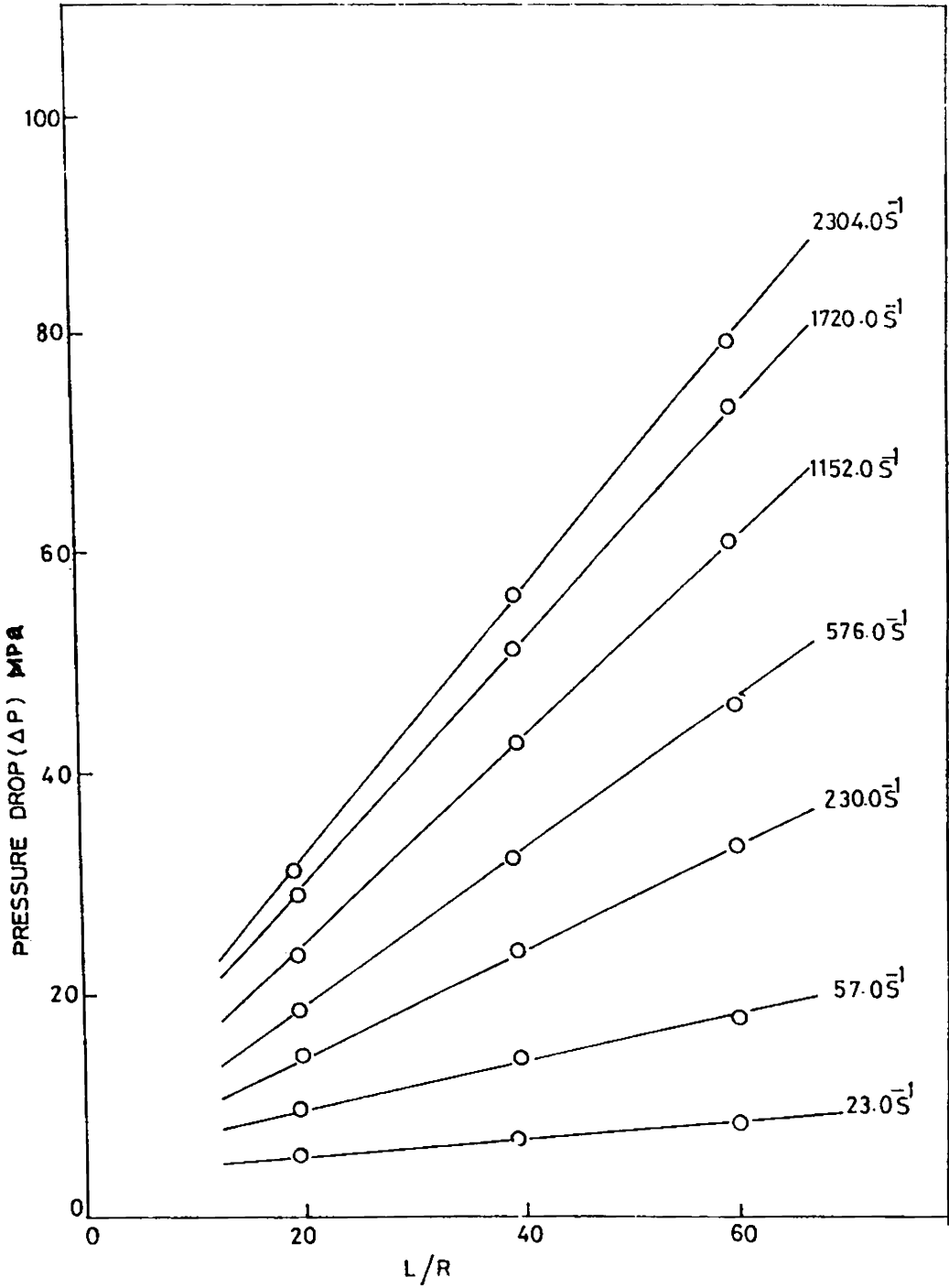


Fig.3.18 Variation of ΔP as a function of L/R ratios for SEBS at 200°C .

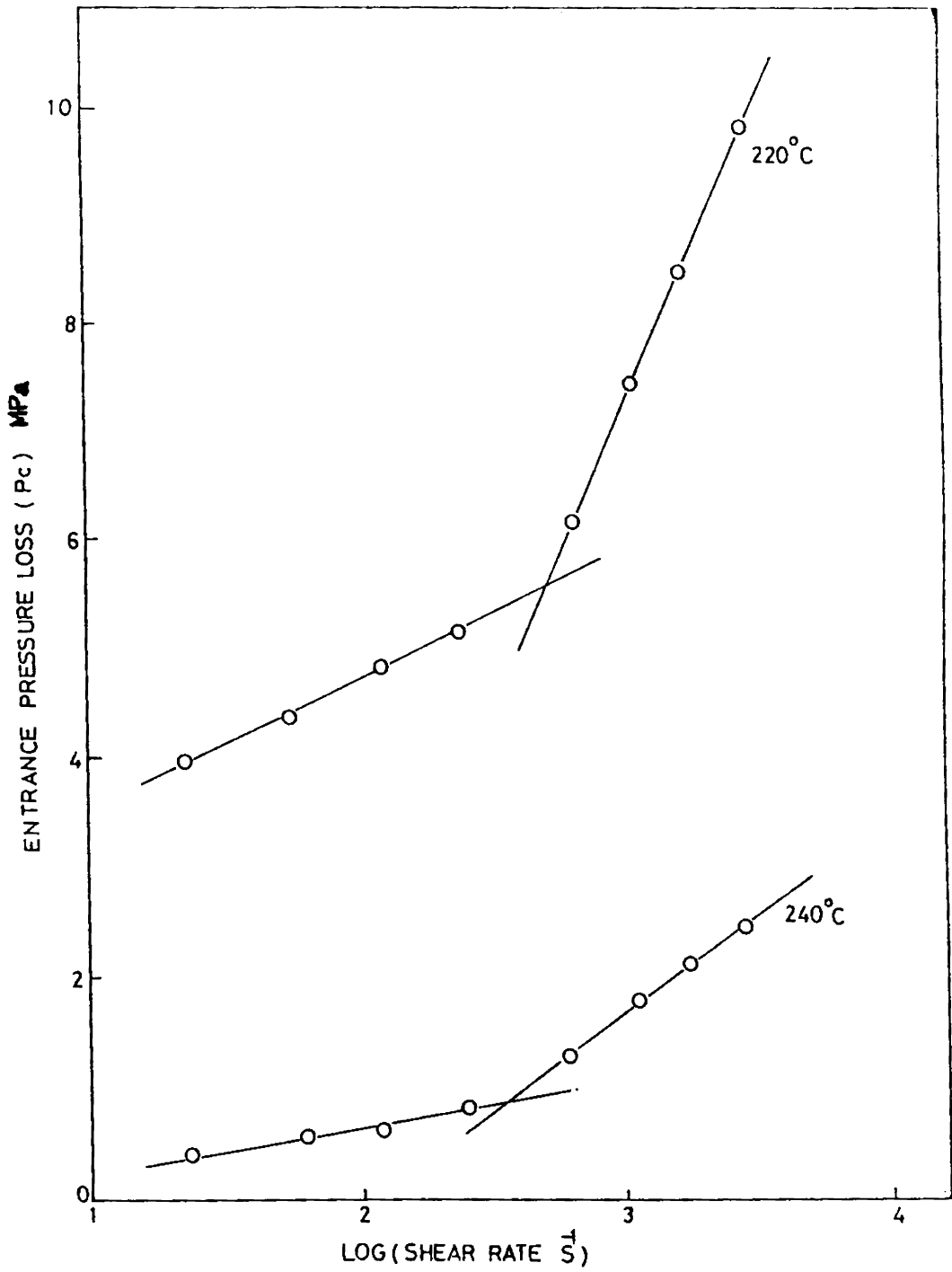


Fig.3.19 Variation of entrance pressure loss, P_c with shear rate of SEBS.

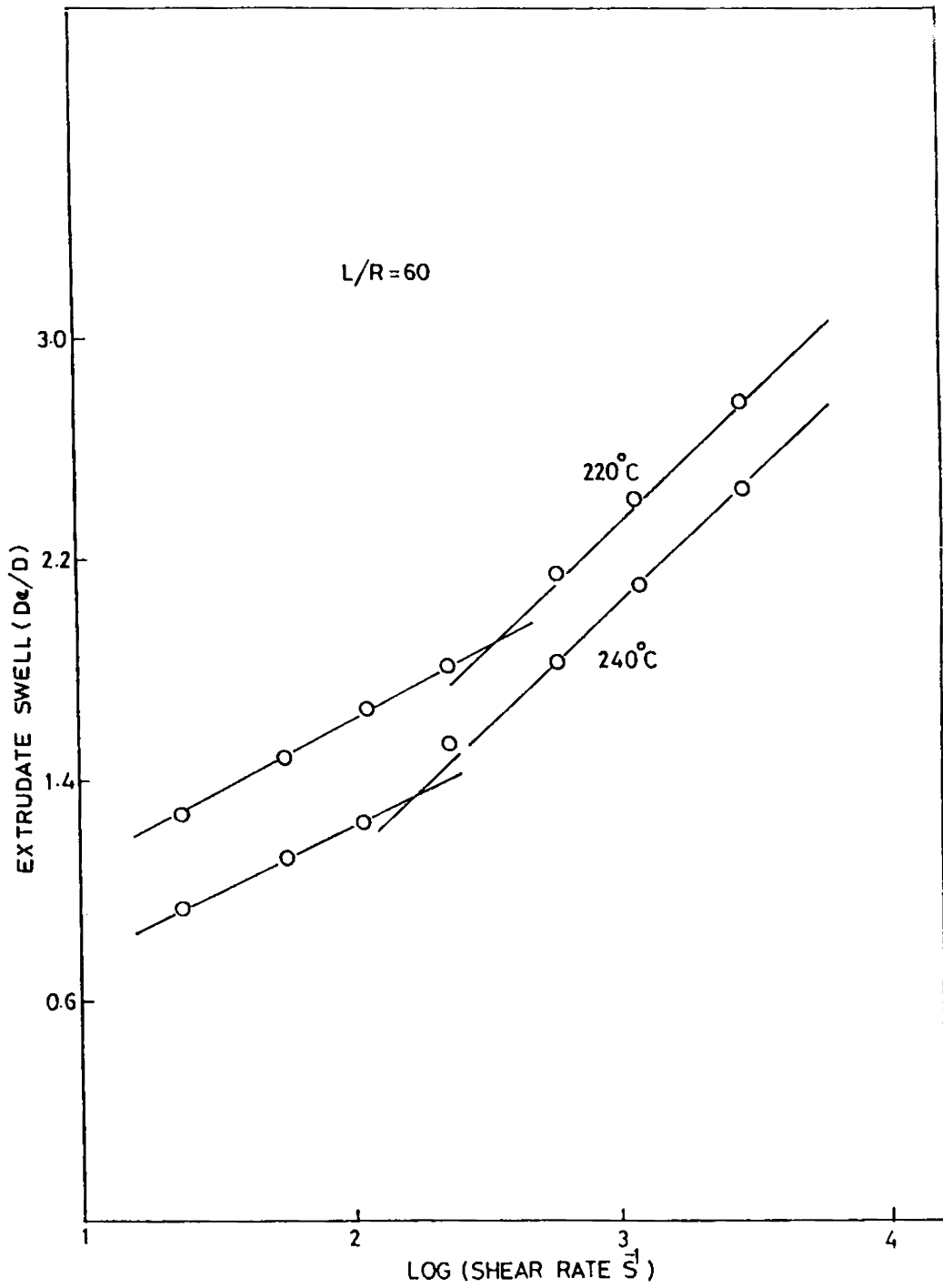


Fig.3.20 Effect of shear rate on die swell ratio of SEBS

as expected whereas it decreases with increase in temperature. Bogue and White²⁷ suggested use of the parameter recoverable shear strain, γ_R , for describing and distinguishing the fluid elasticity of different viscoelastic fluids as a function of shear stress. γ_R was calculated and is given in Fig.3.21. The two step variation of recoverable shear strain at lower temperatures gradually diminishes as the temperature increases. This marks the elongational flow of the matrix and the deformation and breaking up of the dispersed polystyrene phase.

Fig.3.22 shows the variation of extrudate swell ratio with L/R ratio of capillary die. As expected, the melt elasticity behaviour of the triblock copolymer decreases with increase in length of the capillary die.

Flow curves in terms of corrected values of shear stress and shear rate are presented in Fig.3.23. Variation of viscosity is nonlinear and the corrected viscosity is slightly lower than that of the apparent viscosity. The difference is negligible at high shear rates.

Another important factor in processability is flow instability or melt fracture^{28,29} which shows surface roughness of the material when extruded at certain critical output

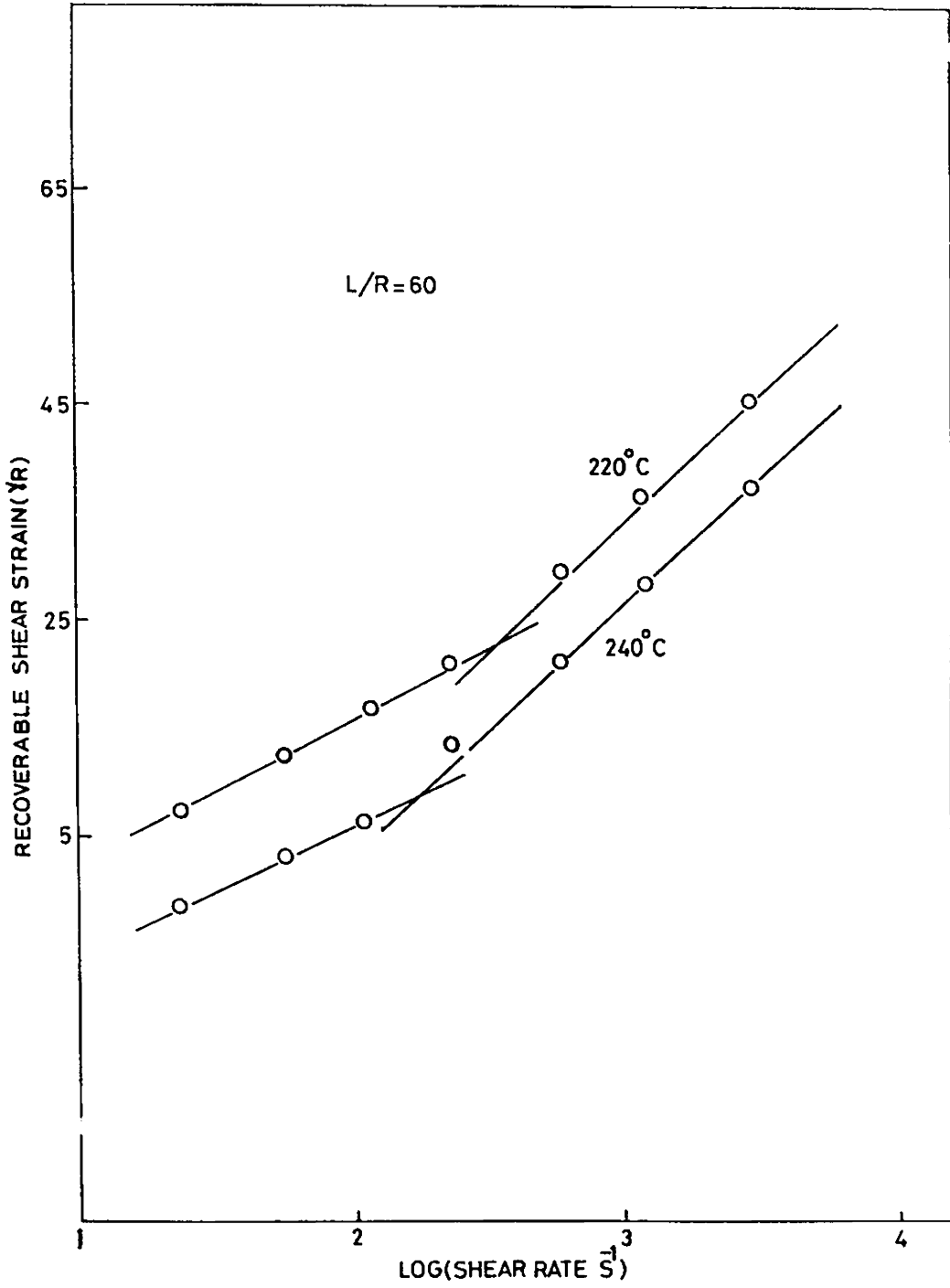


Fig.3.21 Effect of shear rate on recoverable shear strain of SEBS.

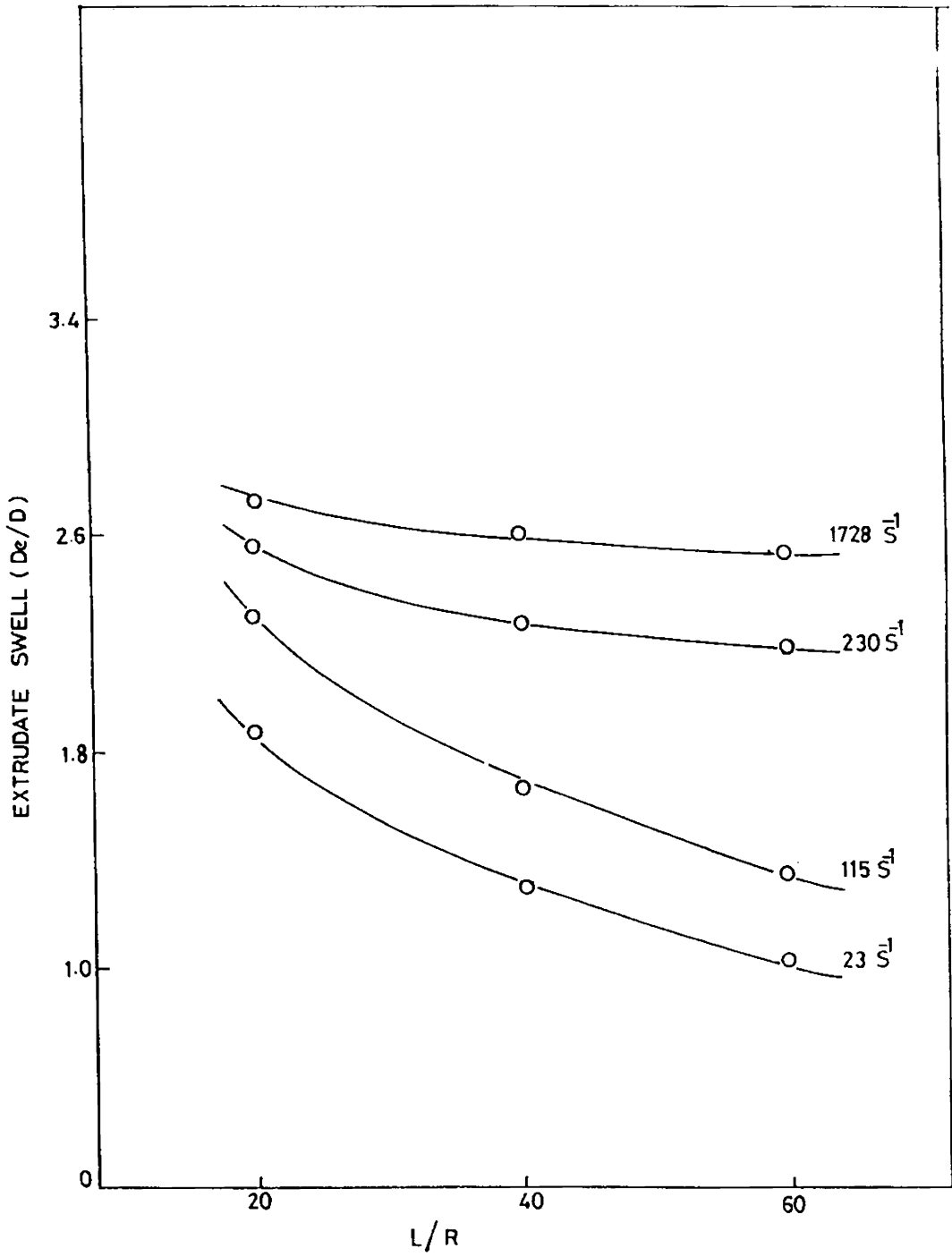


Fig.3.22 Variation of extrudate swell ratio with L/R ratio for SEBS.

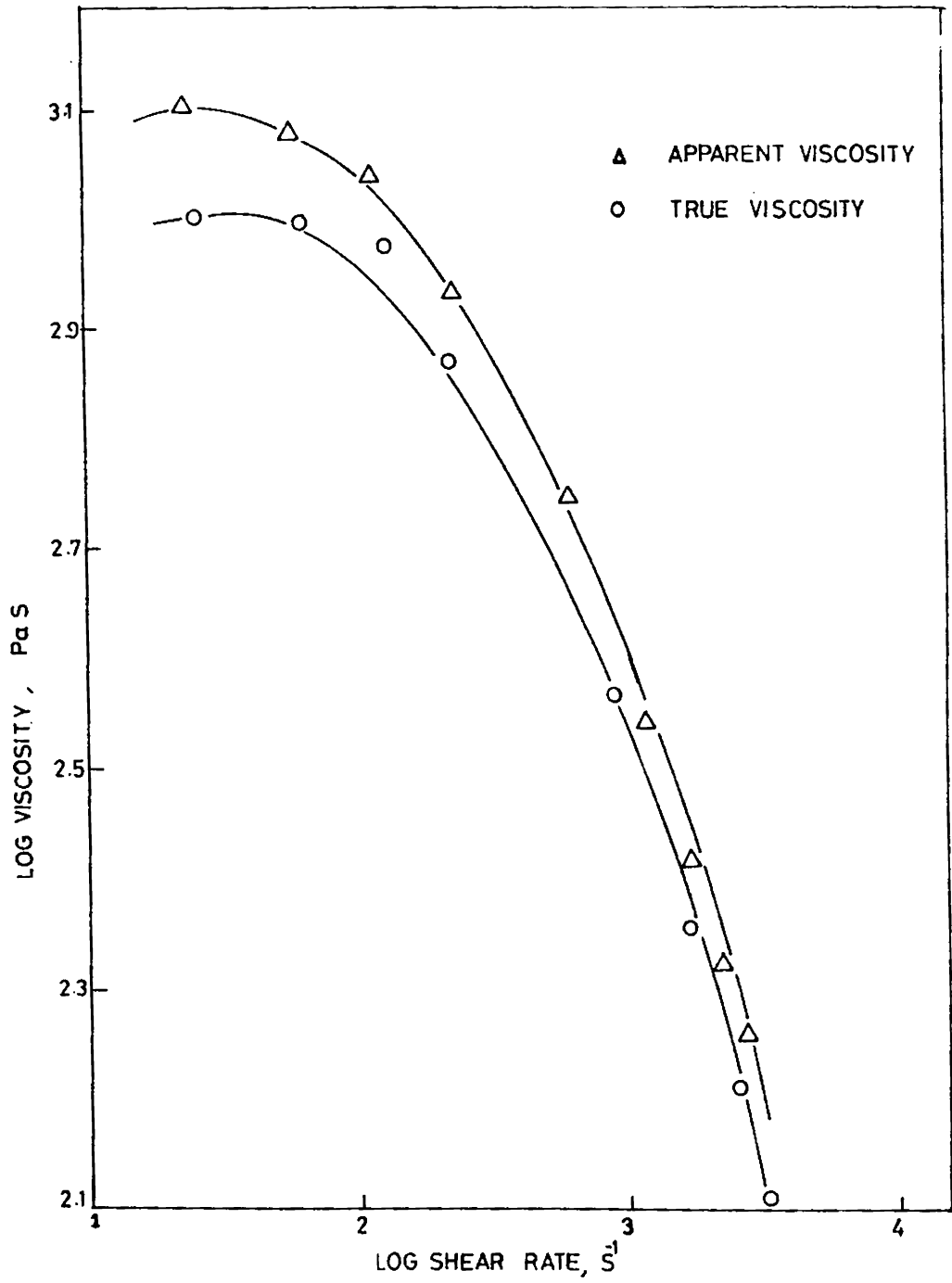


Fig.3.23 Flow curves in terms of corrected values of shear stress and shear rate of SEBS.

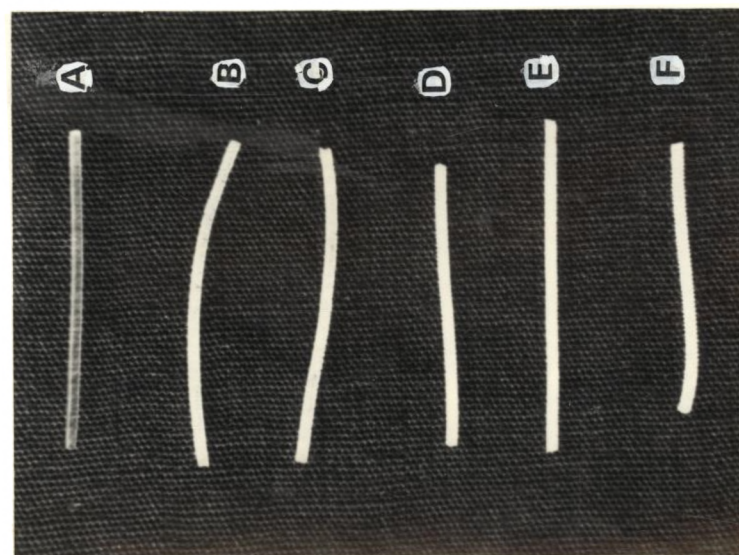
rate. Melt fracture phenomena occur through mechanisms which are not satisfactorily known, although their occurrence seems to be strictly related to the elastic components of the polymer.

Photographs of the extrudates are presented in Figs.3.24 and 3.25 as typical examples of the observed effect of temperature and shear rate on the distortion of extrudate surface of SEBS. For any given temperature, extrudate surface roughness was found to increase with increasing shear rate. A decrease in melt elasticity at higher temperature decreases the surface roughness as seen from Fig.3.25.

Conclusions

1. The ultimate properties such as tensile strength and elongation at break of the triblock copolymers SBS, SIS and SEBS are similar to those of vulcanized rubbers. But the stress-strain curve of SBS shows yield point indicating similarity with the behaviour of plastics. This behaviour is further exemplified in the hysteresis behaviour where SBS shows maximum hysteresis loss.
2. SBS, SIS and SEBS exist as phase separated systems in the melt and they exhibit two distinct flow behaviour depending upon the temperature and shear rate. Their elastic behaviour is also derived from their two phase structure.

Shear rate (s^{-1})



A	23.0
B	57.0
C	230.0
D	576.0
E	1152.0
F	2304.0

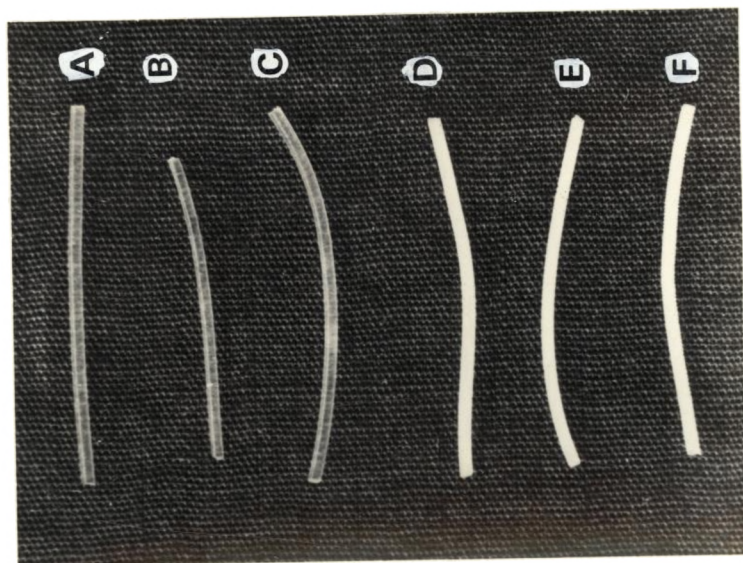


Fig.3.24: at 210°C

Fig.3.25: at 250°C

Extrudate photographs of SEBS at various shear rates.

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Chapter 4

MECHANICAL AND RHEOLOGICAL BEHAVIOUR OF THERMOPLASTIC ELASTOMERS DERIVED FROM NBR/PVC BLENDS

MECHANICAL AND RHEOLOGICAL BEHAVIOUR OF THERMOPLASTIC
ELASTOMERS DERIVED FROM NBR/PVC BLENDS

The great variety of commercially available elastomers and thermoplastics offers a myriad of opportunities for blending. Blending of polymers for property improvement or for economic advantage has gained considerable importance in the field of polymer science.¹⁻³ One of the key requirements for forming successful blends is miscibility of the constituent components.

Blends may generally fall into the following categories depending upon the relative amounts of elastomers and plastics.²⁻⁵

1. Elastomers modified with thermoplastics
2. Thermoplastics modified with elastomers
3. Thermoplastic elastomers.

One of the earliest blends employed to generate all the above classes of materials is that of poly(vinyl chloride) (PVC) and butadiene-acrylonitrile copolymer (NBR). The primary purpose of modifying NBR with PVC is to obtain

NBR having enhanced ozone resistance. However, PVC also serves to reinforce the rubber. In the case of PVC modified with NBR, NBR acts as permanent plasticizer for PVC. When NBR/PVC blends have both the constituents in roughly equal proportions a third family of polymers known as thermoplastic elastomers (TPEs) is formed. These thermoplastic elastomers can be processed like plastics but possess rubber like properties. A low level of crosslinking can also be introduced into the rubber phase either by a dynamic method or by a static one whichever is feasible.^{5,6} Vulcanization of the rubber phase will improve the properties of the TPE at elevated temperatures. It would be interesting to observe the mechanical and rheological properties of NBR/PVC blends when the system forms the three different classes of materials. The present investigation reports the mechanical and rheological properties of NBR/PVC blends over a composition range when they traverse the spectrum of elastomers, plastics and thermoplastic elastomers.

1. Mechanical properties of NBR/PVC blends

Experimental

NBR/PVC blends with PVC content ranging from 30 wt. per cent to 70 wt. per cent were prepared for the present studies. Initial blending of NBR [Acrylonitrile content 42%] and PVC was done in a laboratory mixing mill.

After banding NBR in the roll, PVC along with its heat stabilizer, TBLS (5 parts per hundred parts of PVC), was added. Melt mixing of the blends was done in a Brabender plasticorder equipped with roller mixing heads. A mixing time of 5 min. was employed at a temperature of 170°C. In all the cases the torque stabilized to a constant value by this time. The blends were then pressed into sheets of 2 mm thickness in an electrically heated laboratory hydraulic press at 170°C for 3 min. The mould was taken out and cooled in water and then the sheet taken out of the mould. Dumbell shaped test pieces for mechanical testing were punched out from these sheets. Dynamically cured blends were prepared by adding dicumyl peroxide (0.3 phr of the total polymer weight as the crosslinking agent along with PVC and its heat stabilizer on the mixing mill and following the same procedure given above.

Tensile properties of the blends were evaluated in a Zwick universal testing machine at the crosshead speed of 500 mm/min. The hysteresis behaviour of the blends was also evaluated in the UTM at a speed of 50 mm/min. at strain levels upto 100% for 5 cycles.

The effect of blend ratio and dynamic crosslinking on the morphology of the fractured surfaces of NBR/PVC

blends was studied using an optical microscope (Versamet-2, Union 7596) and a scanning electron microscope (JEOL JSM-35C).

Results and discussion

Fig.4.1 shows the stress-strain curves of NBR/PVC blends. When the PVC content is high (80%) the sample shows brittle failure with very low elongation. The blend with 70% PVC shows the behaviour of an impact modified plastic material which shows yielding and moderate elongation at break. When NBR content is very high (70% or 80%) the modulus is very low and the blends display very high elongation at break without yielding which is typical elastomer behaviour. The intermediate blend compositions (40%, 50% and 60% PVC) may be taken to represent the behaviour of thermoplastic elastomers which do not exhibit yielding or plastic deformation. These samples take higher loads at lower extensions, possibly due to the deformation in the continuous rigid PVC phase, then typical elastic behaviour with high elongation at lower loads. This suggests the existence of plastic and rubber phases in a co-continuous state in these blends.

Fig.4.2 shows the stress-strain curves of

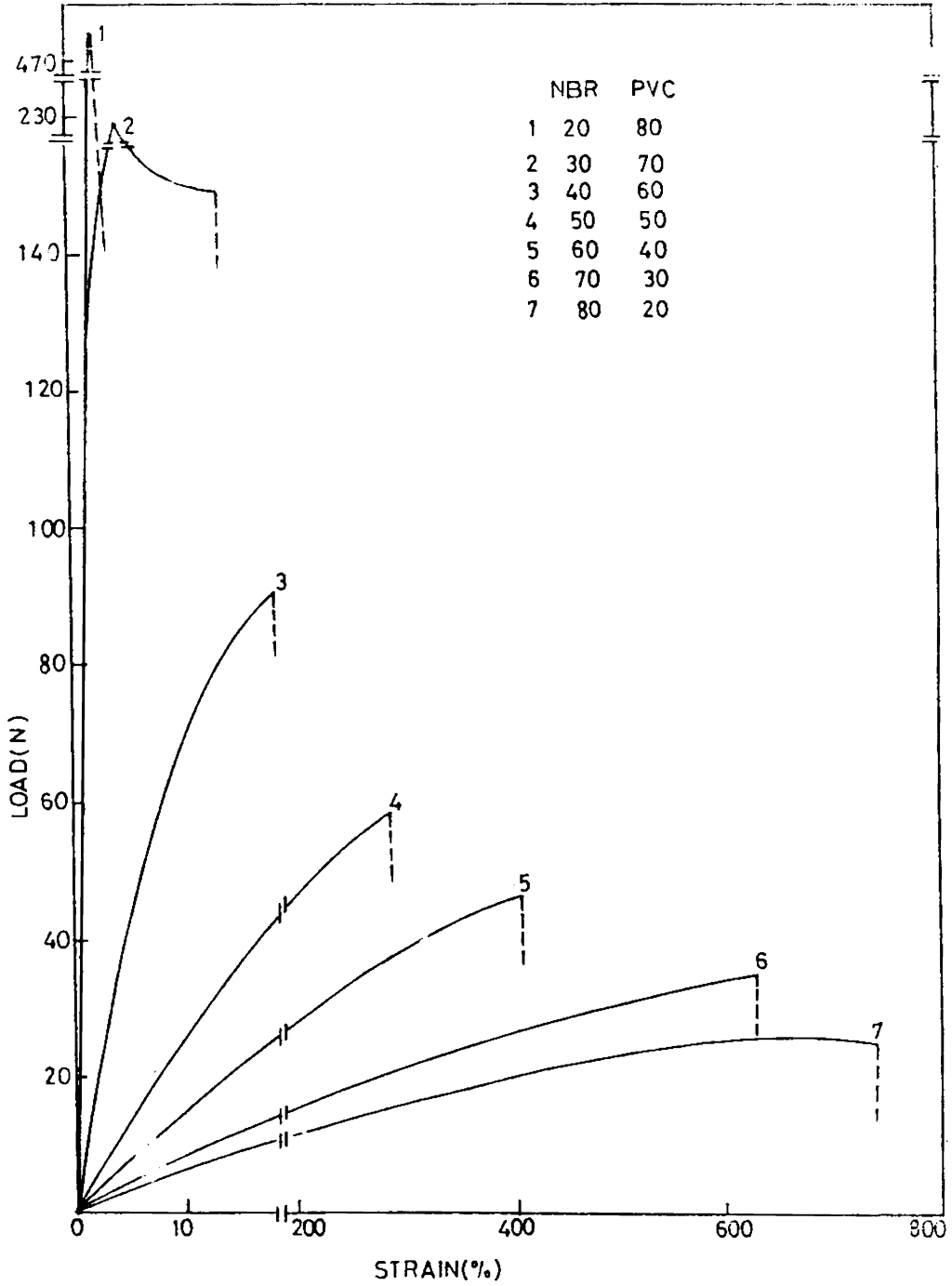


Fig.4.1 Tensile stress-strain curves of uncured NBR/PVC blends

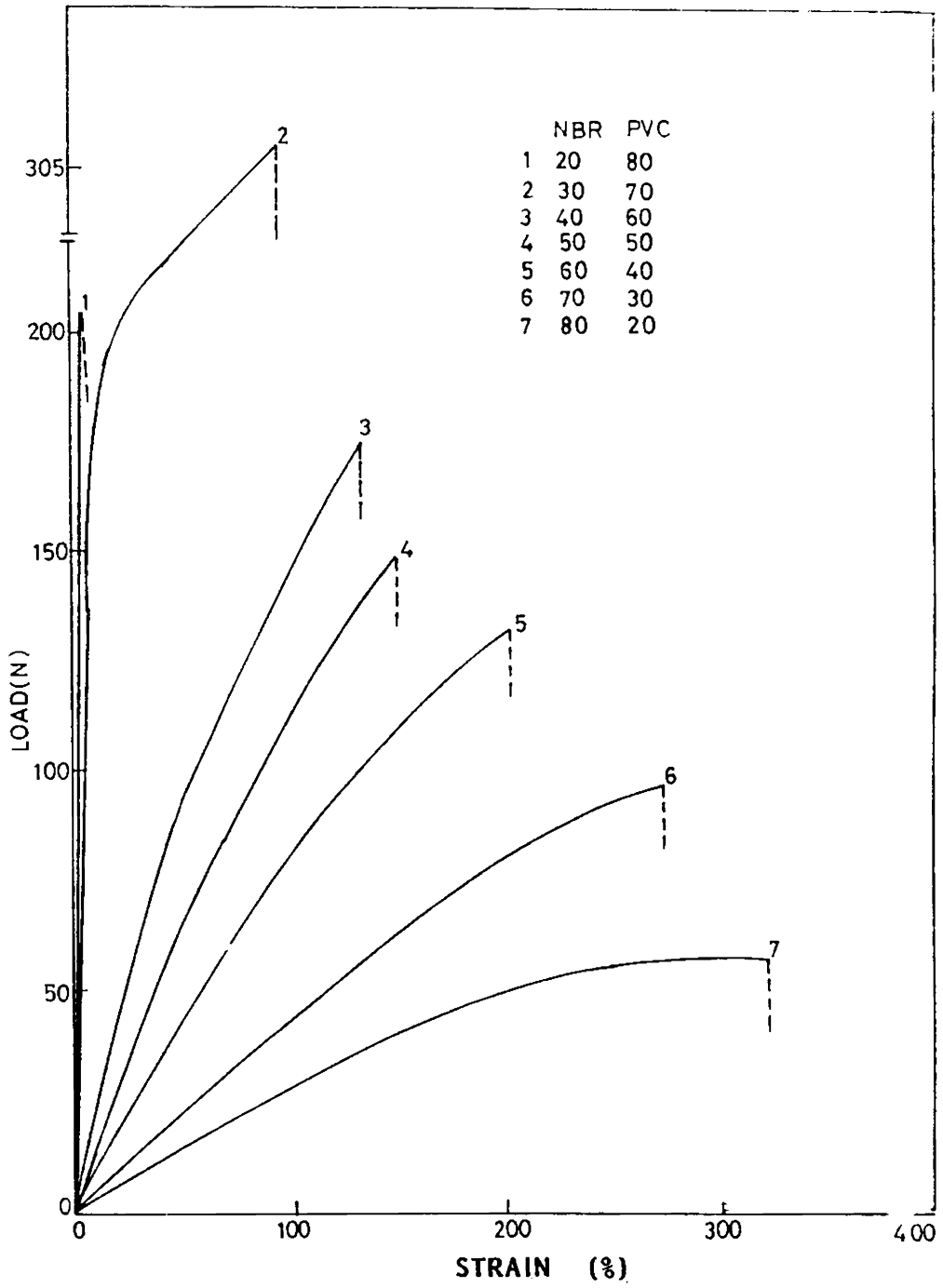


Fig.4.2 Tensile stress-strain curves of curved NBR/PVC blends

dynamically cured blends of NBR and PVC. Blends with 80% and 70% PVC exhibit yielding and plastic deformation similar to their uncrosslinked compositions. However, introduction of crosslinks reduces the yield stress and plastic deformation in these plastic rich blends. The other blends exhibit predominantly elastic deformation without any yielding. The crosslinks in these blends contribute towards increasing the modulus of the blends, while the crosslinks in plastic rich blends interfere with deformation of the plastic phase, thereby leading to a decrease in yield stress.

Figs.4.3, 4.4 and 4.5 show variations in tensile strength, elongation at break and modulus at 100% elongation of the cured and uncured blends with blend composition. As the PVC content increases, the tensile strength increases uniformly for all the compositions (Fig.4.3). The thermoplastic elastomeric compositions exhibit a property varying in between that of plastic rich and rubber rich compositions. The elongation at break of the blends decreases with increase in PVC content as expected. Crosslinking further reduces elongation at break. Modulus steadily improves with increase in PVC content. The improvement is more pronounced in the case of PVC rich blends. Crosslinking increases the moduli of all compositions as expected.

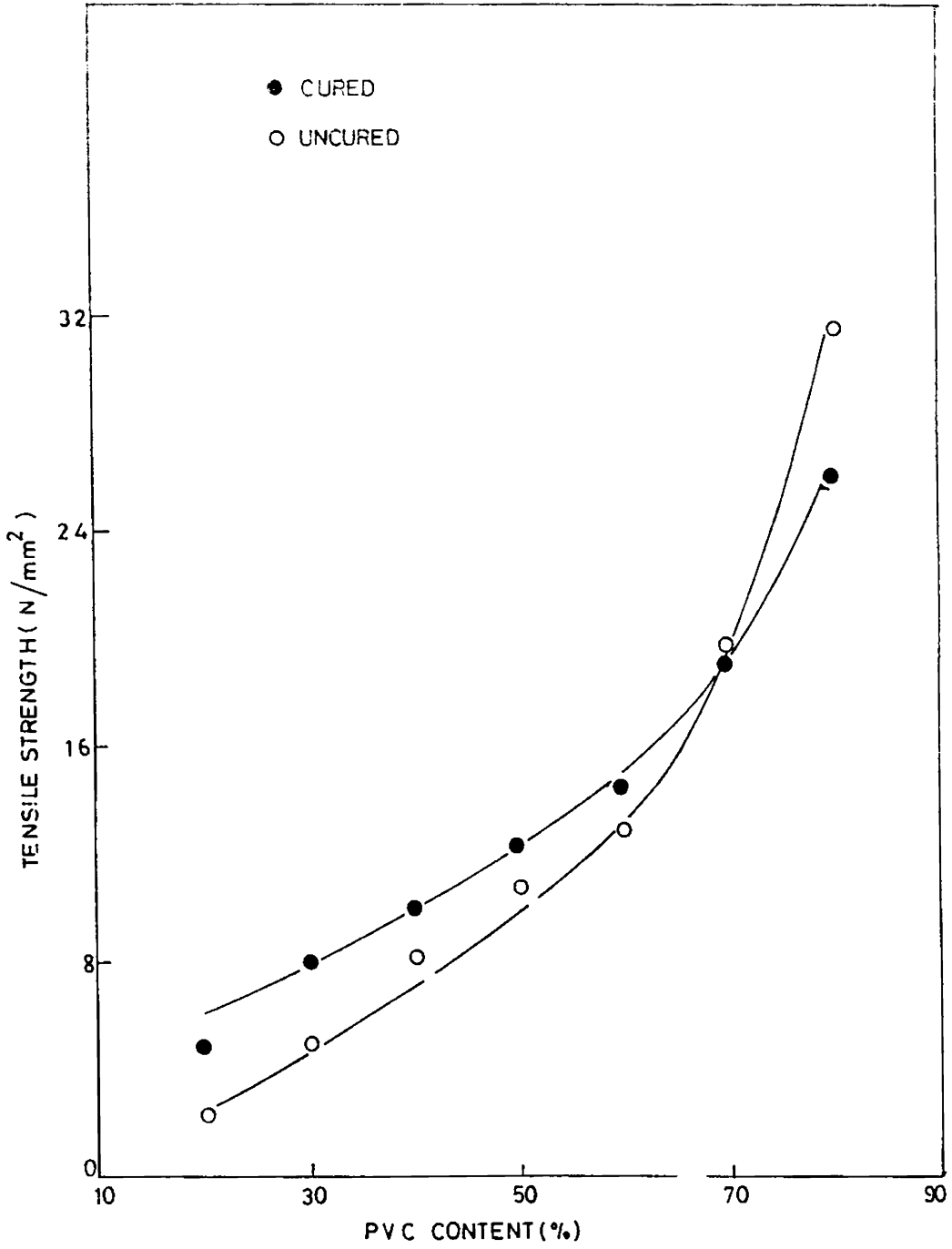


Fig.4.3 Variation of tensile strength with blend composition of NBR/PVC blends

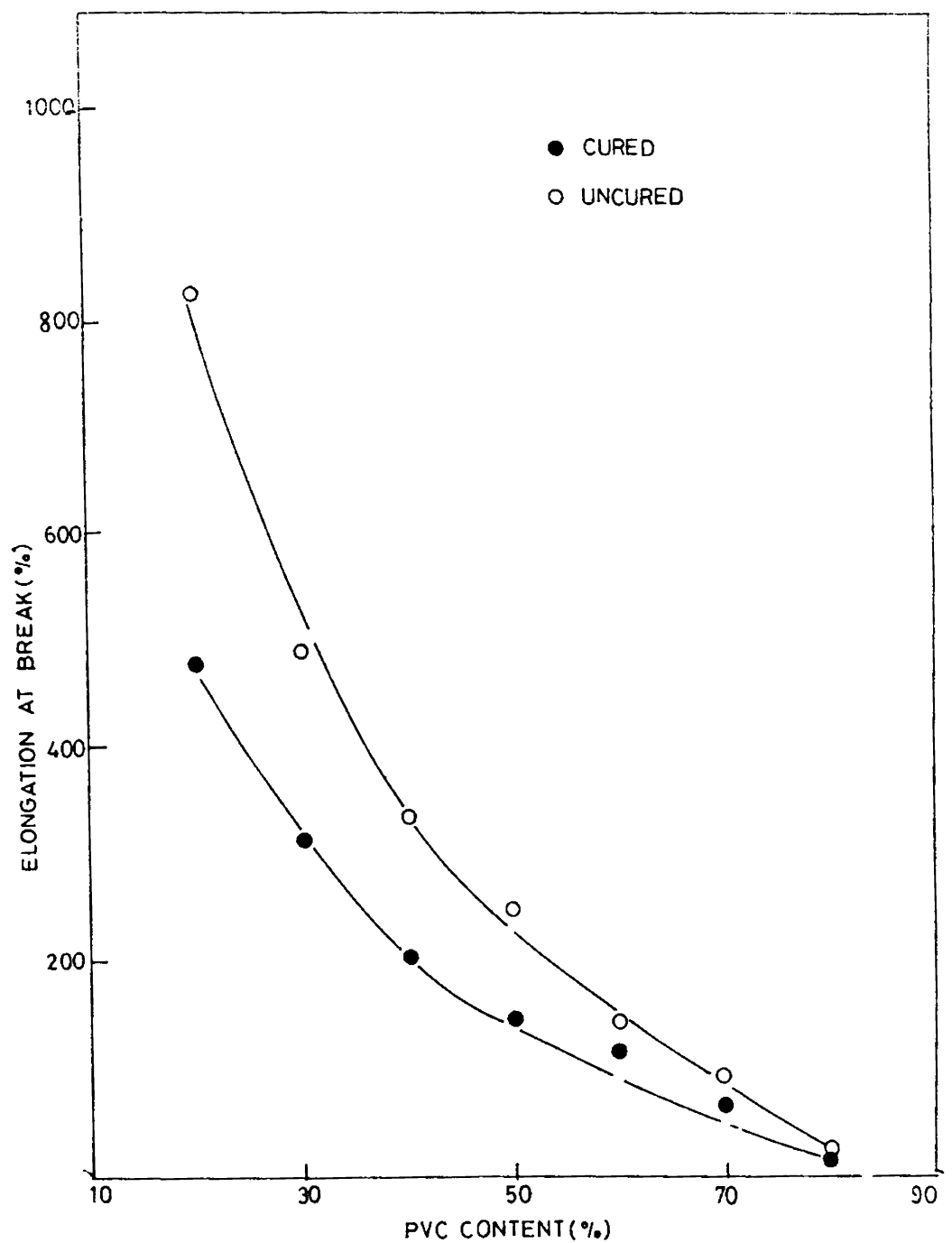


Fig.4.4 Variation of elongation at break with blend composition of NBR/PVC blends.

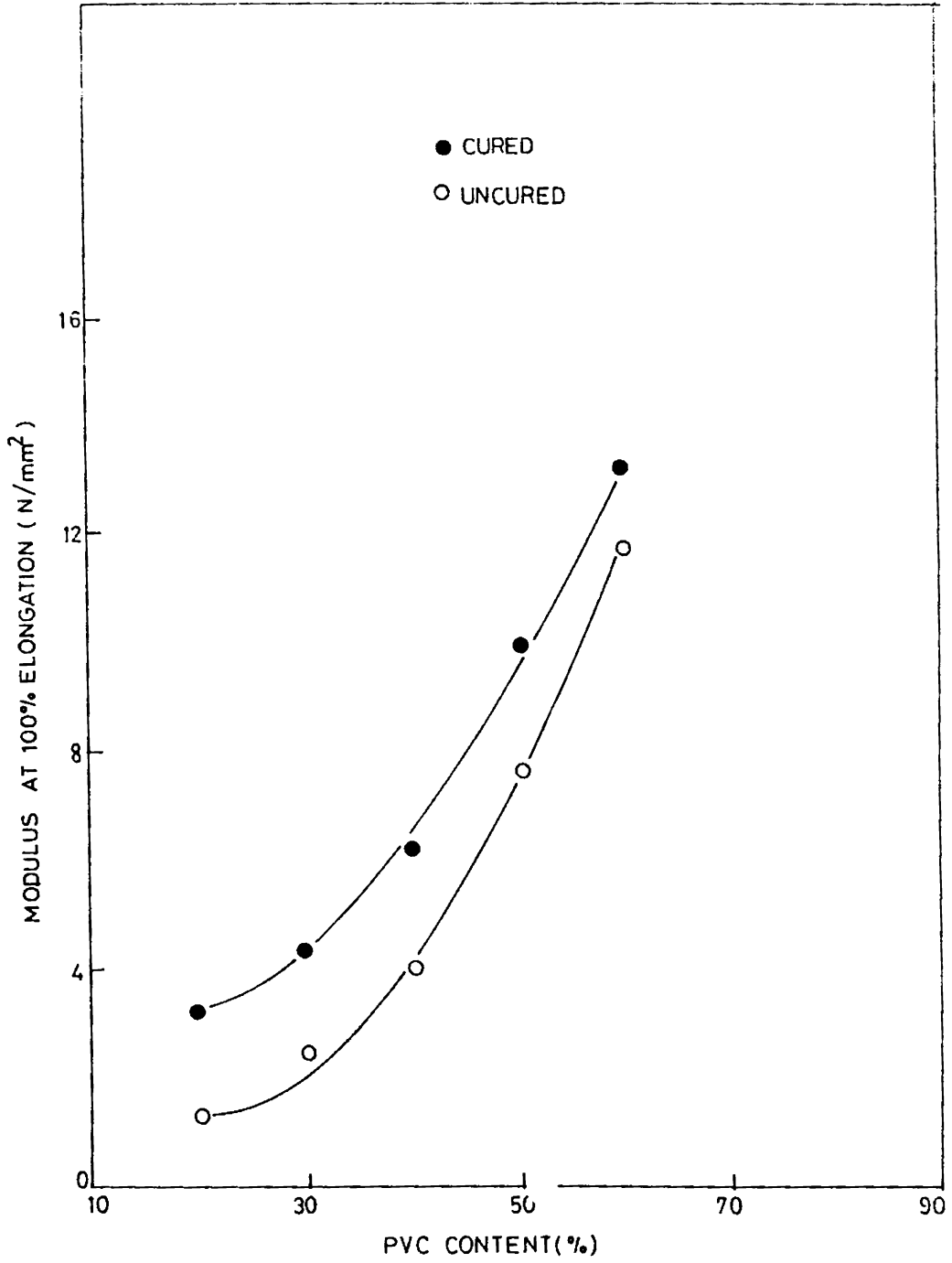


Fig.4.5 Variation of modulus with blend composition of NBR/PVC blends.

Variation in hardness of the blends (cured and uncured) are given in Fig.4.6. The higher hardness of the PVC phase increases the hardness of the blends with increase in PVC content. While the crosslinking imparts a higher hardness to the rubbery blends, the deterioration in the property for plastic rich blends may be due to some degradation of the PVC phase at the temperature and/or shear. The hardness of the thermoplastic elastomeric compositions ranges between 25-50 shore D.

Variation of compression set values of NBR/PVC blends (cured and uncured) with blend composition measured under constant load conditions is shown in Fig.4.7. NBR/PVC thermoplastic elastomers exhibits good load bearing abilities leading to lower compression set values. Cross-linking helps to reduce the compression set.

Effect of fillers on the tensile strength and elongation at break of the thermoplastic elastomeric compositions is shown in Fig.4.8. Reinforcing effect is better in the case of carbon black than silica. Both the fillers reduce elongation at break of the blends due to the rigidity imparted to the polymer matrix by the addition of filler.

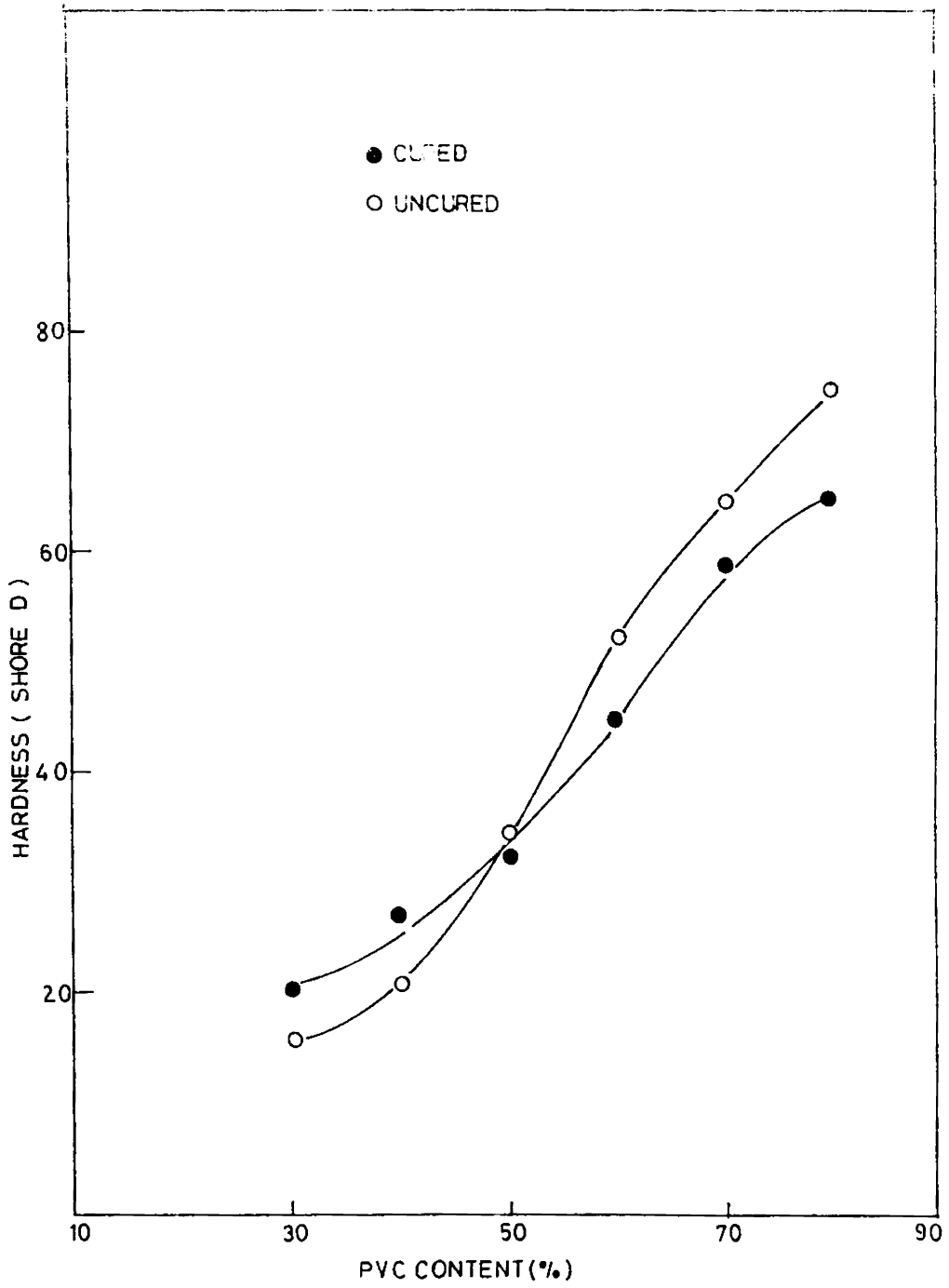


Fig.4.6 Variation of hardness with blend composition of NBR/PVC blends.

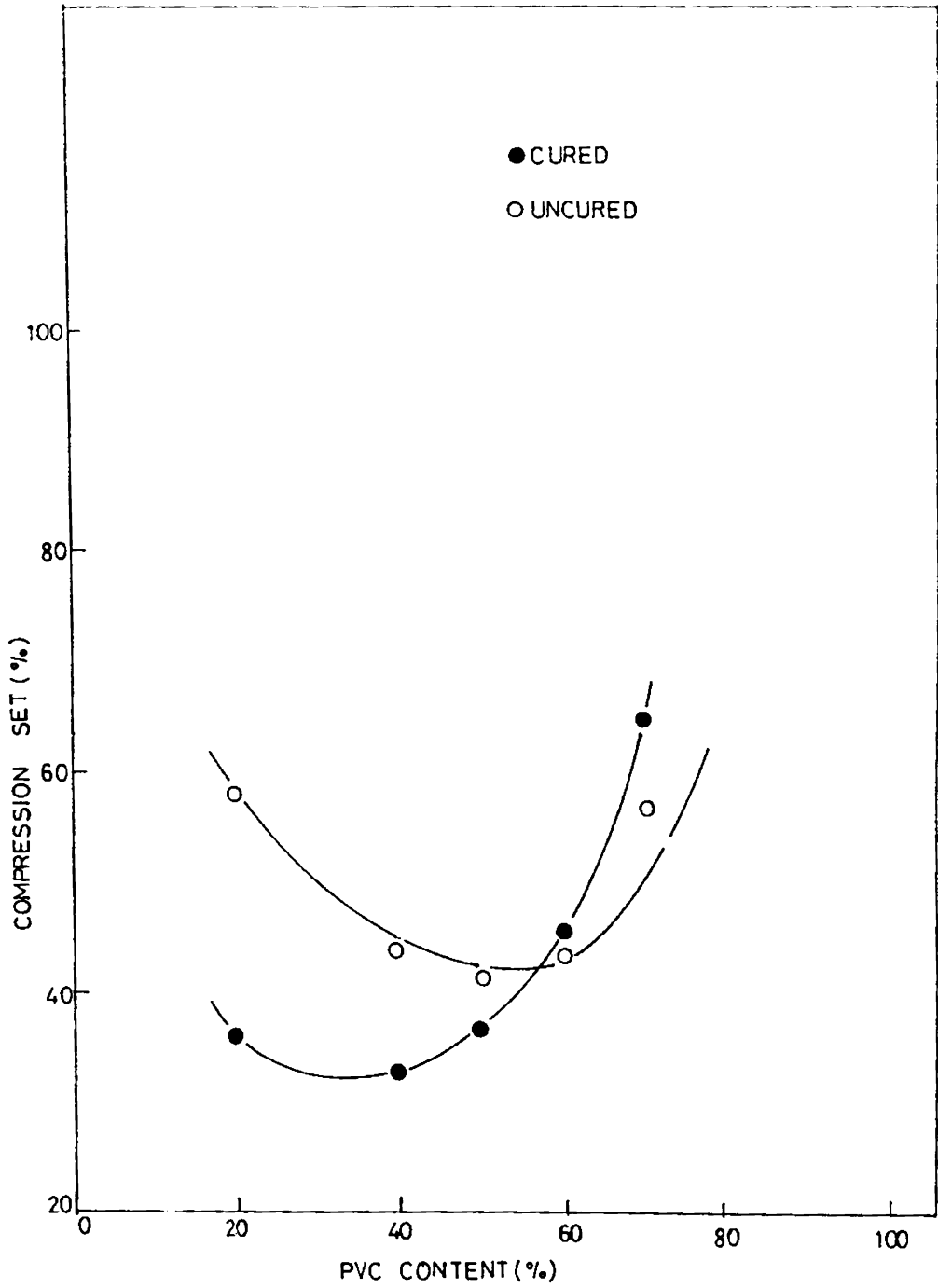


Fig.4.7 Variation of compression set with blend composition of NBR/PVC blends

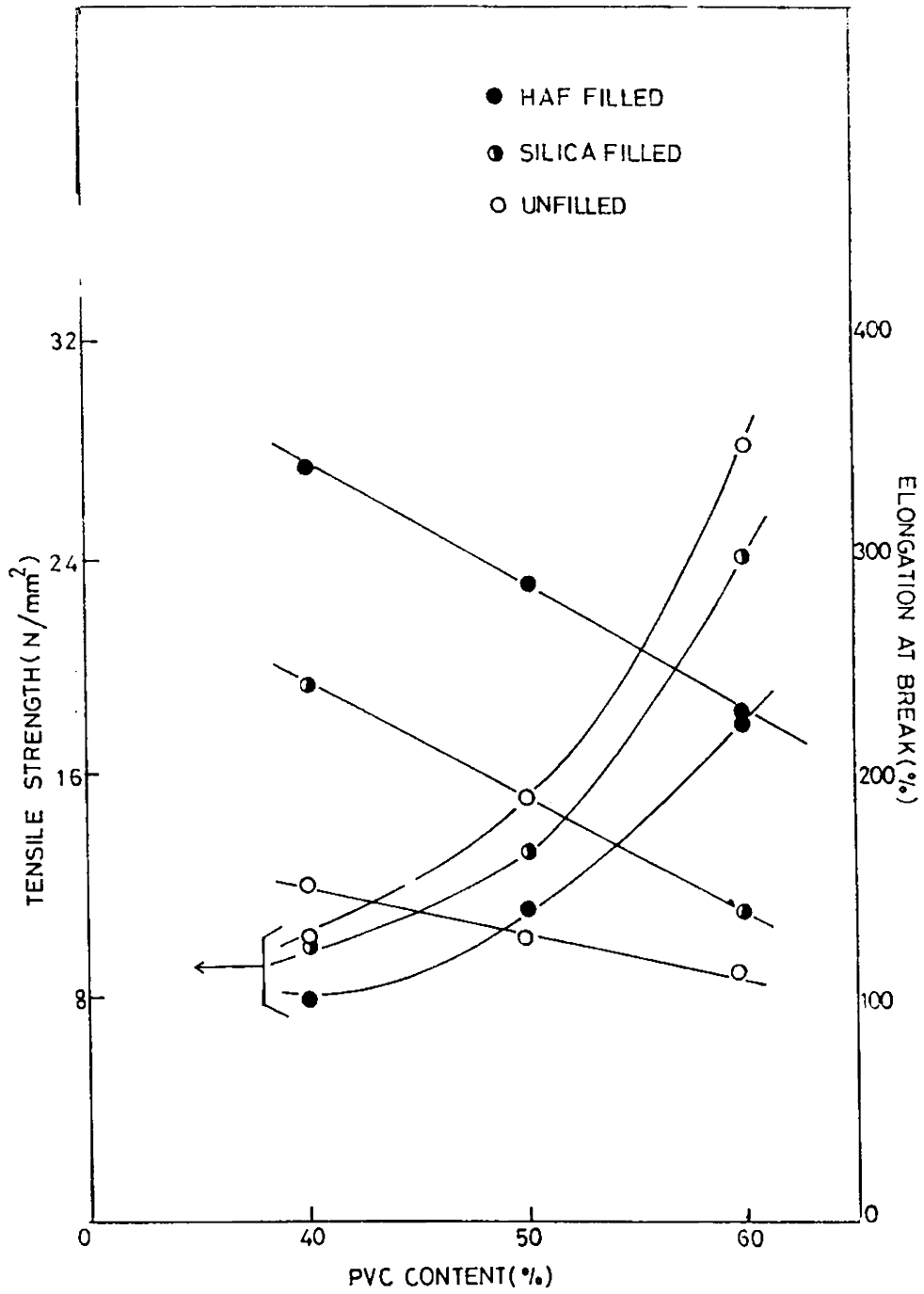


Fig.4.8 Effect of fillers on the tensile strength and elongation at break of NBR/PVC blends

Fig.4.9 shows the effect of various PVC stabilizers on the strength and elongation of NBR/PVC blends. It shows that TBLS is the most efficient stabilizer for PVC in NBR/PVC blends compared to MgO/ZnO/Stearic acid system and Irgastab 70A. However, Irgastab 70A gives clear and highly transparent blends.

Swelling studies (Fig.4.10) of NBR/PVC blends in ASTM oil No.3 (which conformed to the specifications given in ASTM D 471, 1983) shows that the thermoplastic elastomer blends exhibit very good oil resistance.

Thermoplastic elastomers are used frequently wherever they can suitably replace conventional materials. The ability to be recycled, their ease of processing, good physical and mechanical properties have drawn the attention of many designers in recent years. While their technical properties have been extensively studied,⁷⁻¹⁰ relatively very few attempts have been made to study their behaviour under cyclic loading/unloading conditions, in particular, those related to the energy stored and dissipated during a complete cyclic process. Several related studies have been made in this field for different rubbers evaluating direct relationship between the total energy at break and the work done on stretching.¹¹⁻¹⁴

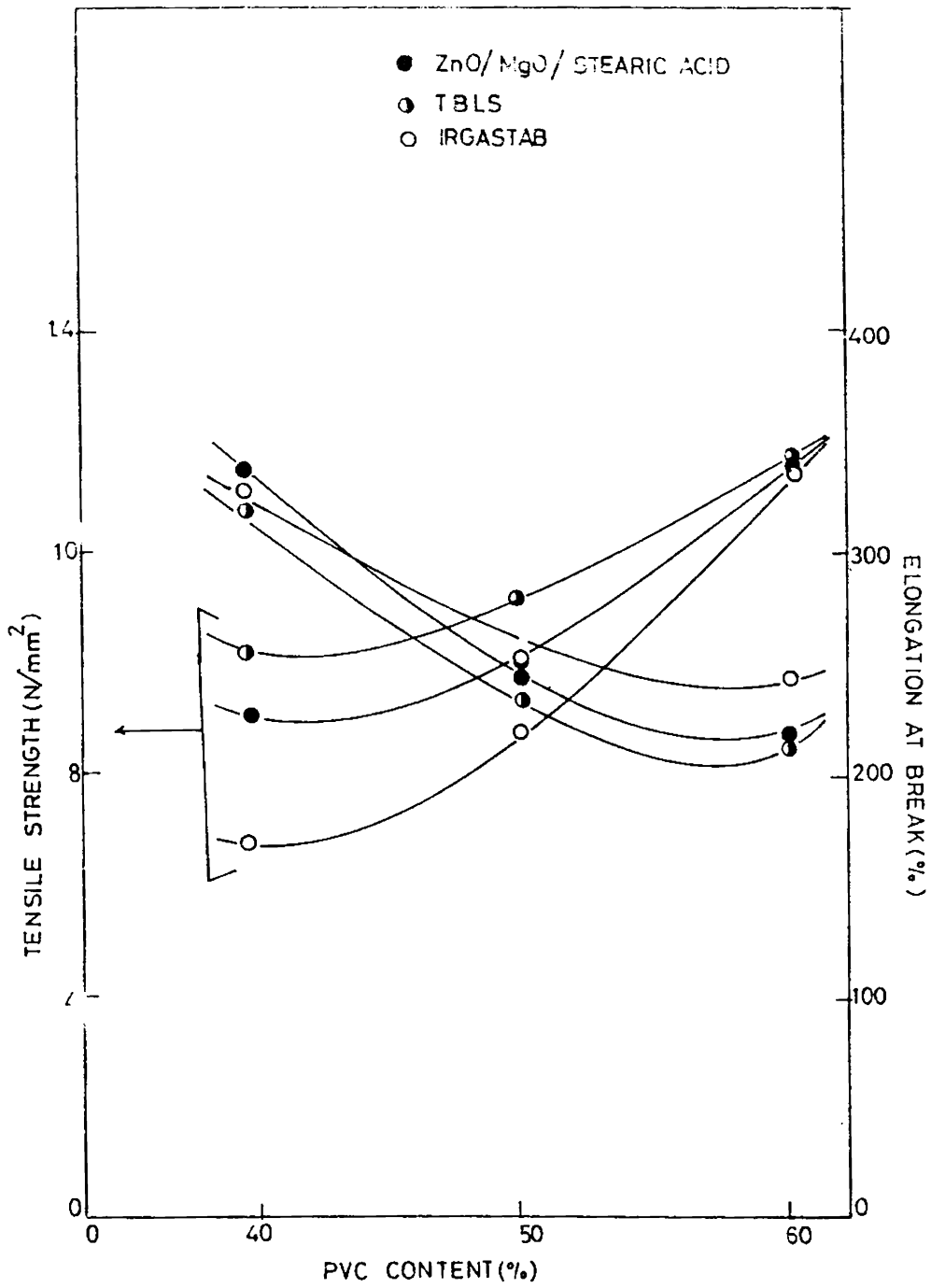


Fig.4.9 Effect of PVC stabilizers on the tensile strength and elongation at break of NBR/PVC blends

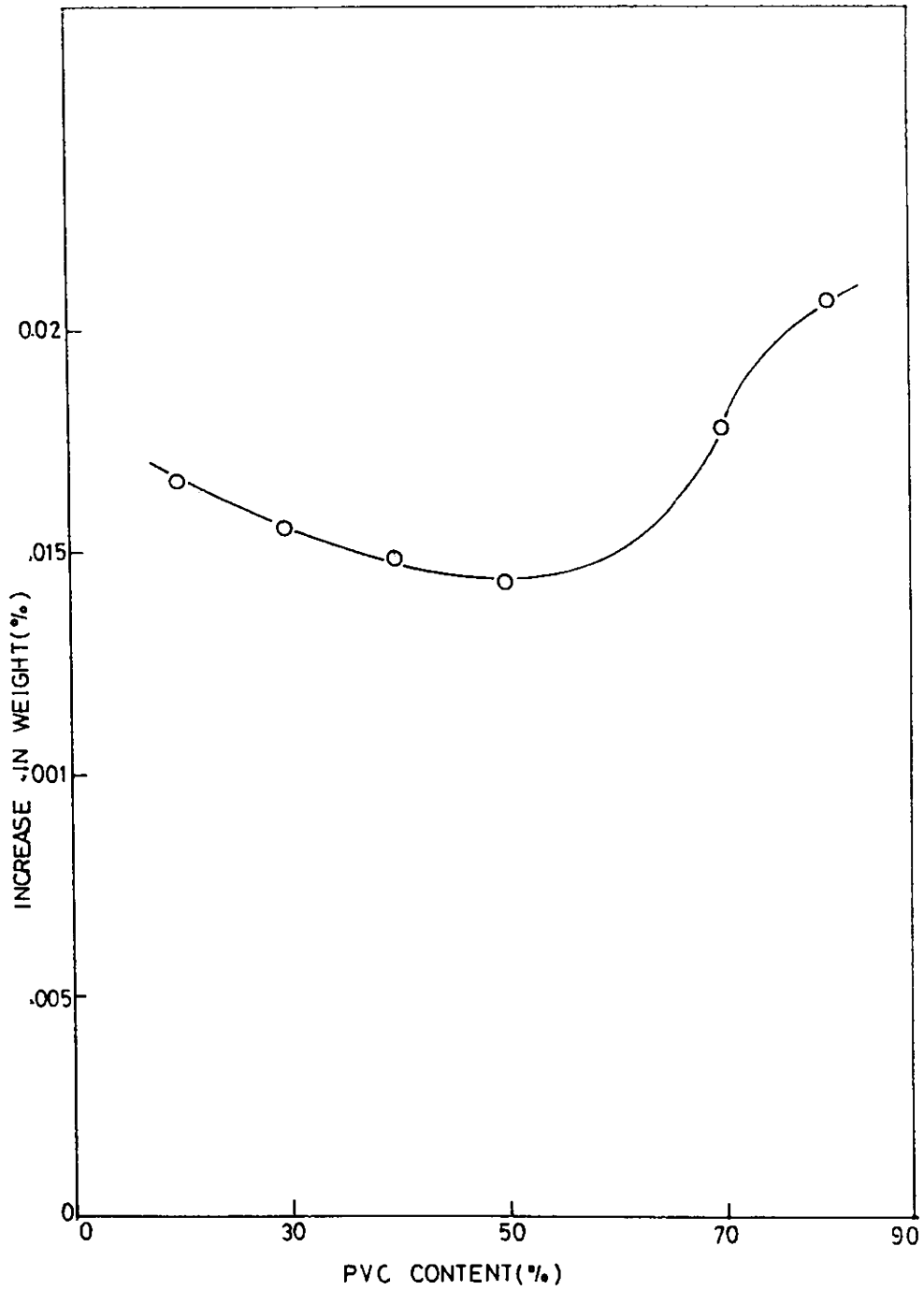


Fig.4.10 Variation of increase in weight after swelling in oil with blend composition of uncured NBR/PVC blends

Figs.4.11 and 4.12 show the hysteresis curves for the blend compositions during first and second cycles. It is clear from these figures that the magnitude of energy dissipated during the cyclic process varies with change in blend composition. There is a pronounced difference in the nature of the hysteresis curves obtained for plastic rich and rubber rich blends. The differences arise mainly due to changes in the continuous rigid phase (80% and 70% PVC) and the rubbery phase (80% and 70% NBR) in the respective blends. The plastic blends show high irrecoverable plastic deformation due to yielding especially at higher strain levels where the curves do not reach the starting point upon retraction. The behaviour of the thermoplastic elastomeric compositions is in between that of the plastic rich and rubber rich blends.

Fig.4.13 shows the effect of a small amount (0.3 phr) of dicumyl peroxide introduced into the system where it increases the stability by forming stable C-C crosslinks, thereby enhancing the elastic behaviour of the blends and reducing the hysteresis loss. The reduction in the area under the hysteresis loops (70/30, 50/50 and 30/70 NBR/PVC blends) further indicates that crosslinking decreases the breakdown of the bonds considerably by redistribution of the stresses.

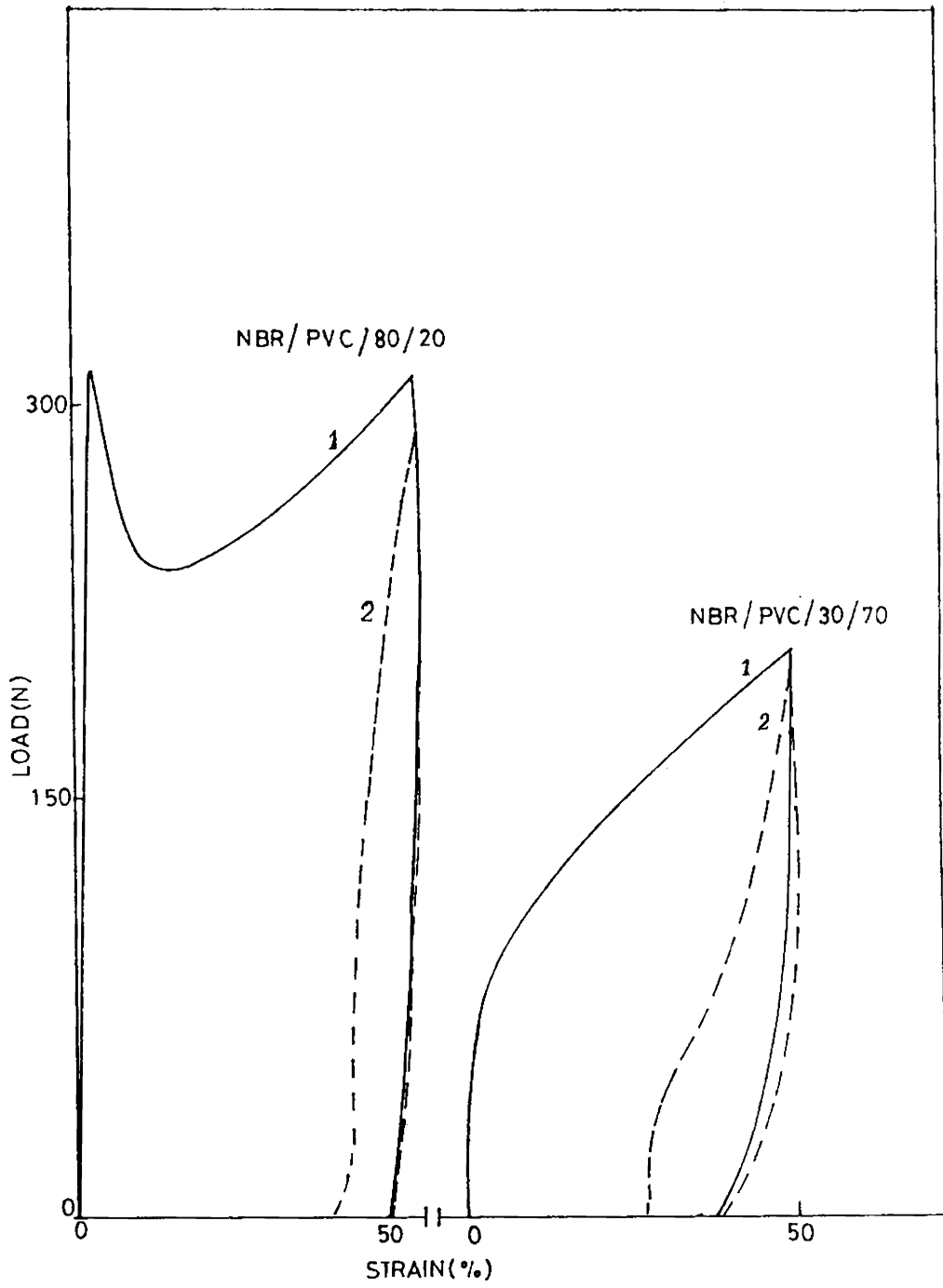


Fig.4.11 Hysteresis curves of uncured NBR/PVC blends

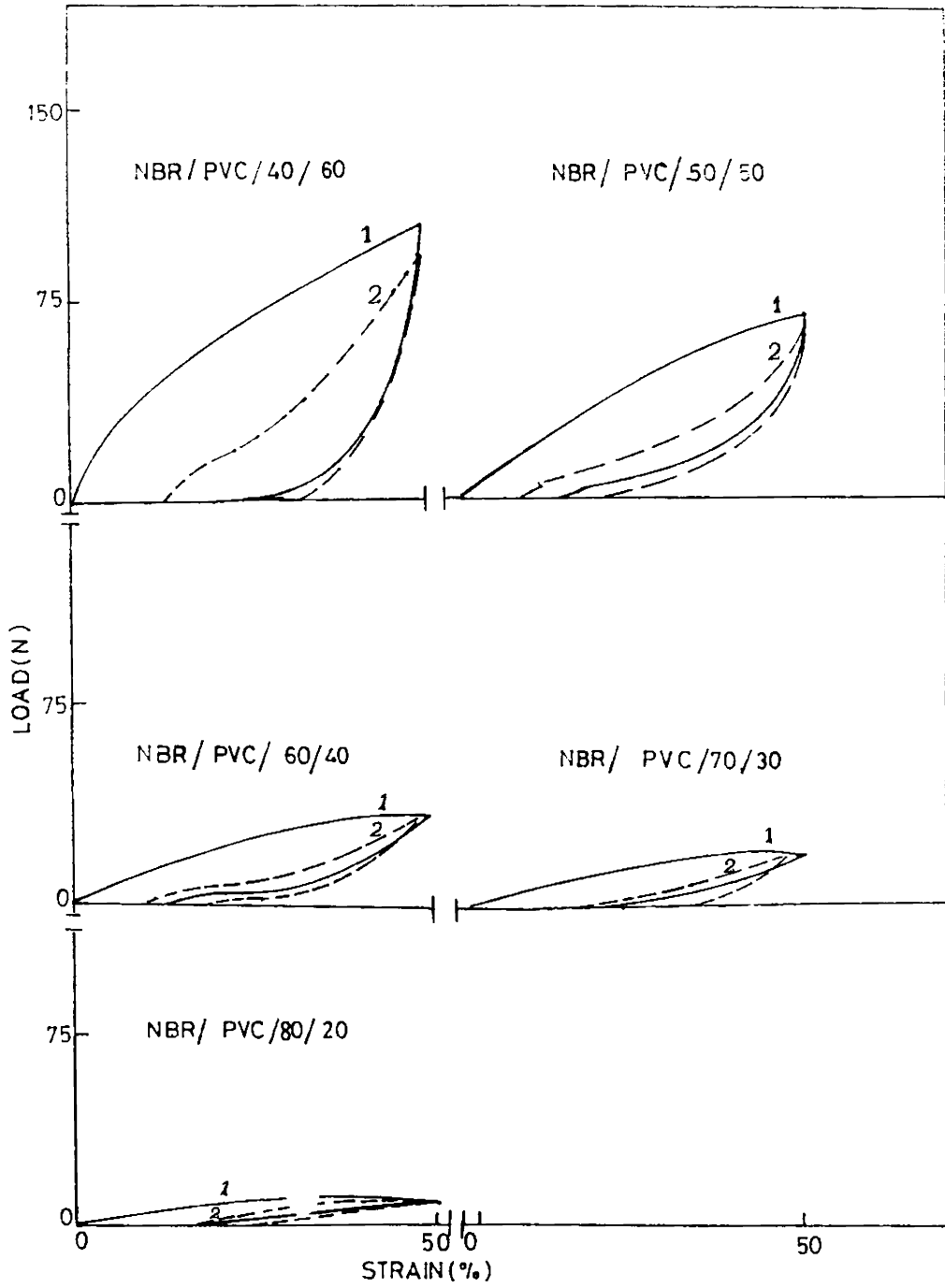


Fig.4.12 Hysteresis curves of uncured NBR/PVC blends

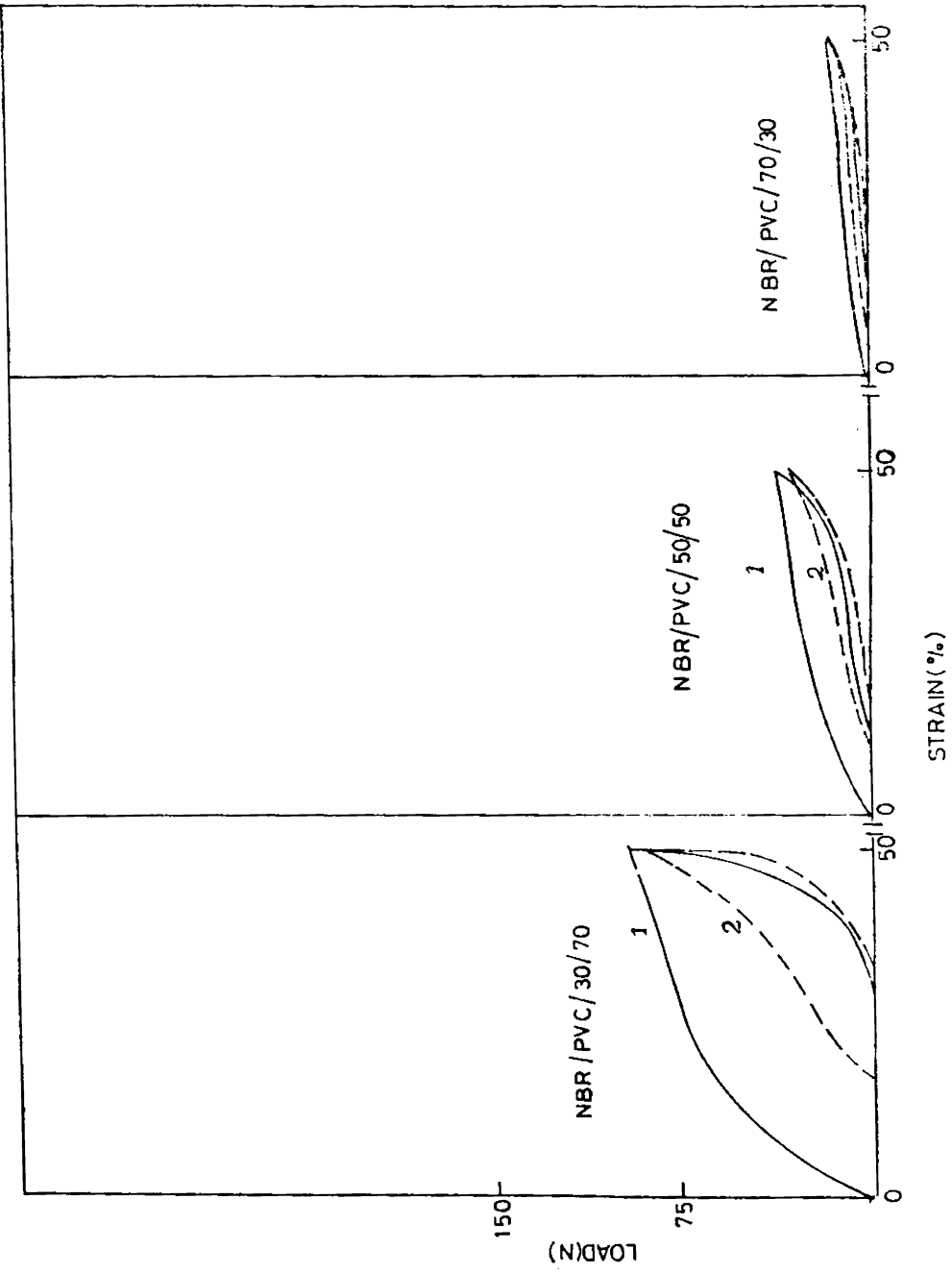


Fig.4.13 Hysteresis curves of cured NBR/PVC blends

Fig.4.14 shows the variation of hysteresis loss calculated in joules with blend composition for the cured and uncured blends at a strain level of 50%. The hysteresis loss (taken for the first cycle) decreases with increase in rubber phase. When the rigid PVC phase in the plastic rich blends contributes much to the hysteresis loss by plastic deformation and yielding of that phase, a decrease in the PVC content reduces hysteresis loss considerably at the other end of the composition spectrum.

Fig.4.15 shows variation in hysteresis loss with strain level, for the cured and uncured blends for a 50/50 blend. It is seen that the hysteresis increases with increase in strain level. At 100% strain the blends exhibit high hysteresis, whereas energy dissipation at 10% strain is negligibly small. Increase in hysteresis at high strain levels may be probably due to the additional energy dissipation mechanisms such as the motion of the dispersed phase, chain slippage or breakage and dewetting at these strains.

Fig.4.16 shows the variation of hysteresis loss with change in number of deformation cycles. It is observed that the energy loss during first deformation cycle is very high compared to the other cycles. The curves show

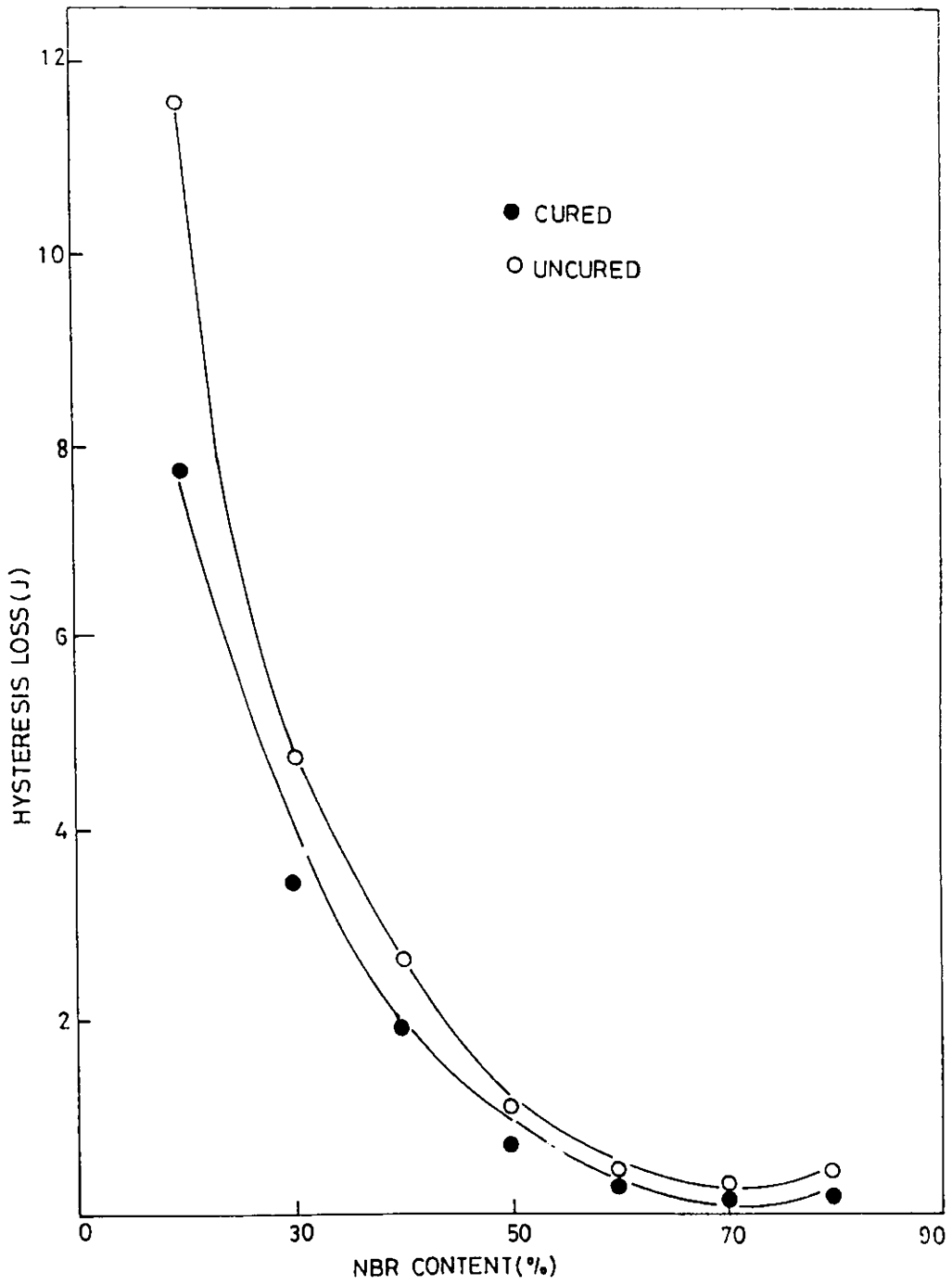


Fig.4.14 Variation of hysteresis loss with blend composition of NBR/PVC blends.

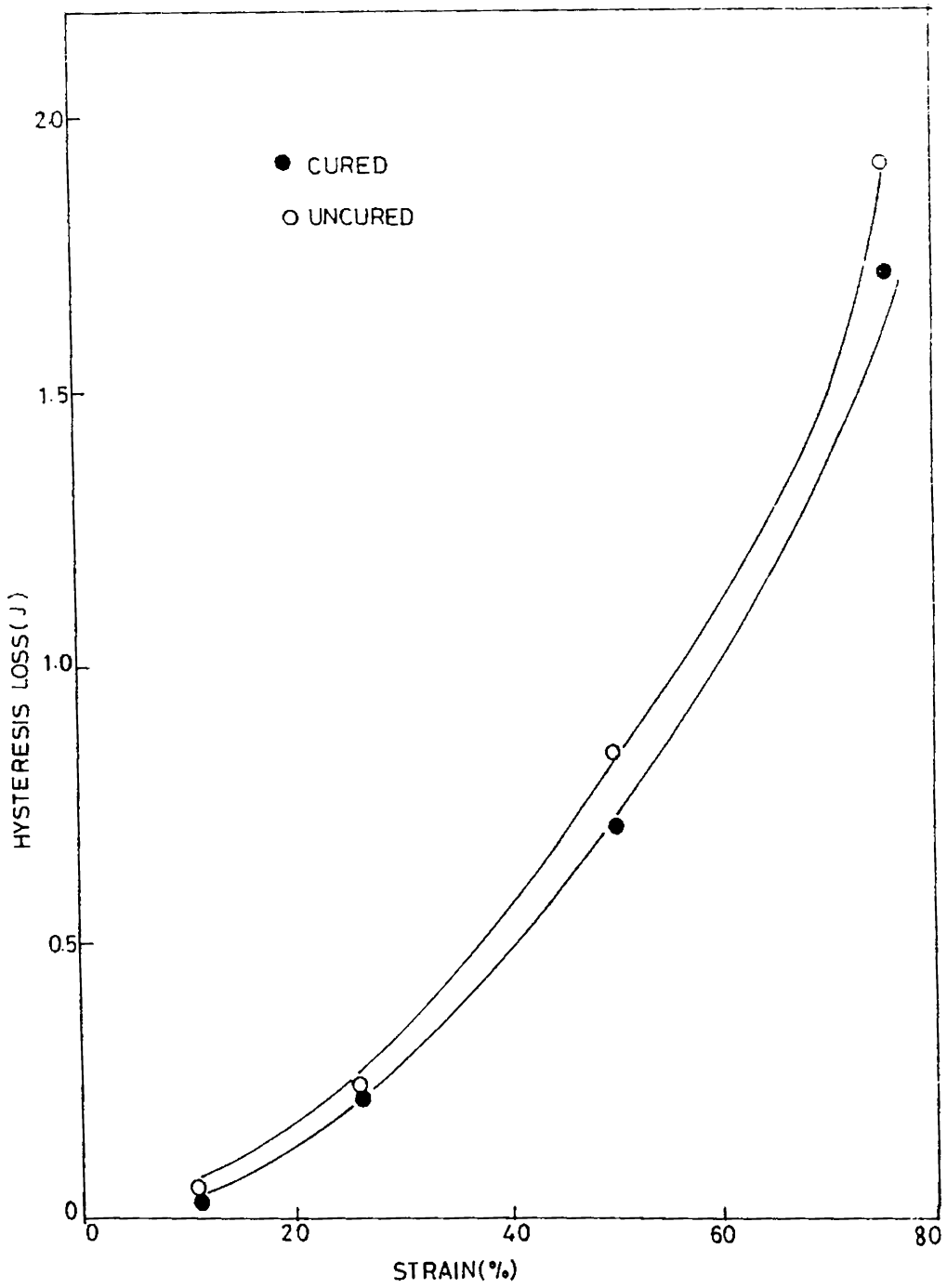


Fig.4.15 Variation of hysteresis loss at different strain levels for 50/50 NBR/PVC blend.

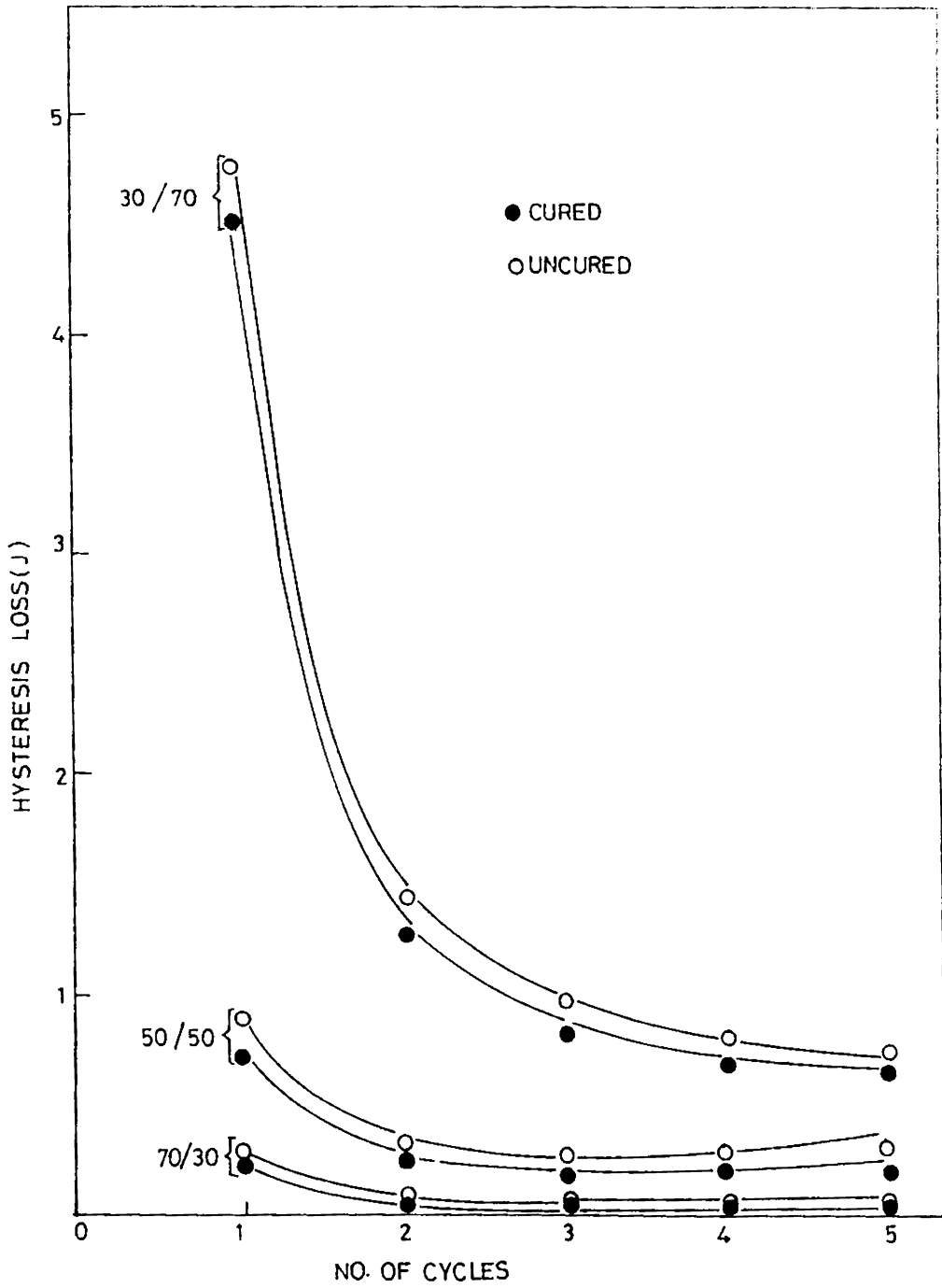


Fig.4.16 Variation of hysteresis loss with number of cycles for NBR/PVC blends at 50% strain.

levelling effect after some cycles. It is further observed that the change in hysteresis loss between cycles is most pronounced in plastic rich blends due to deformations in the PVC phase.

The set values for the thermoplastic elastomeric compositions are shown in Figs.4.17, 4.18 and 4.19. The variation in set values after 5 deformation cycles for the cured and uncured blends is plotted against strain levels. The cured blends show considerable reduction in set values especially at high strain levels due to the elastic behaviour acquired by crosslinking. It can be seen that NBR/PVC blends exhibit reversible deformations at very low strain levels (10%) but significant irreversible deformations at higher strain levels.

Figs.4.20-4.25 show optical microscope photographs of 70/30, 50/50 and 30/70 NBR/PVC blends (cured and uncured). It is seen from the photographs that crosslinking increases the uniformity in the dispersion of blend components.

Figs.4.26-4.28 show SEM photographs of 70/30, 50/50 and 30/70 uncured NBR/PVC blends. The change in the

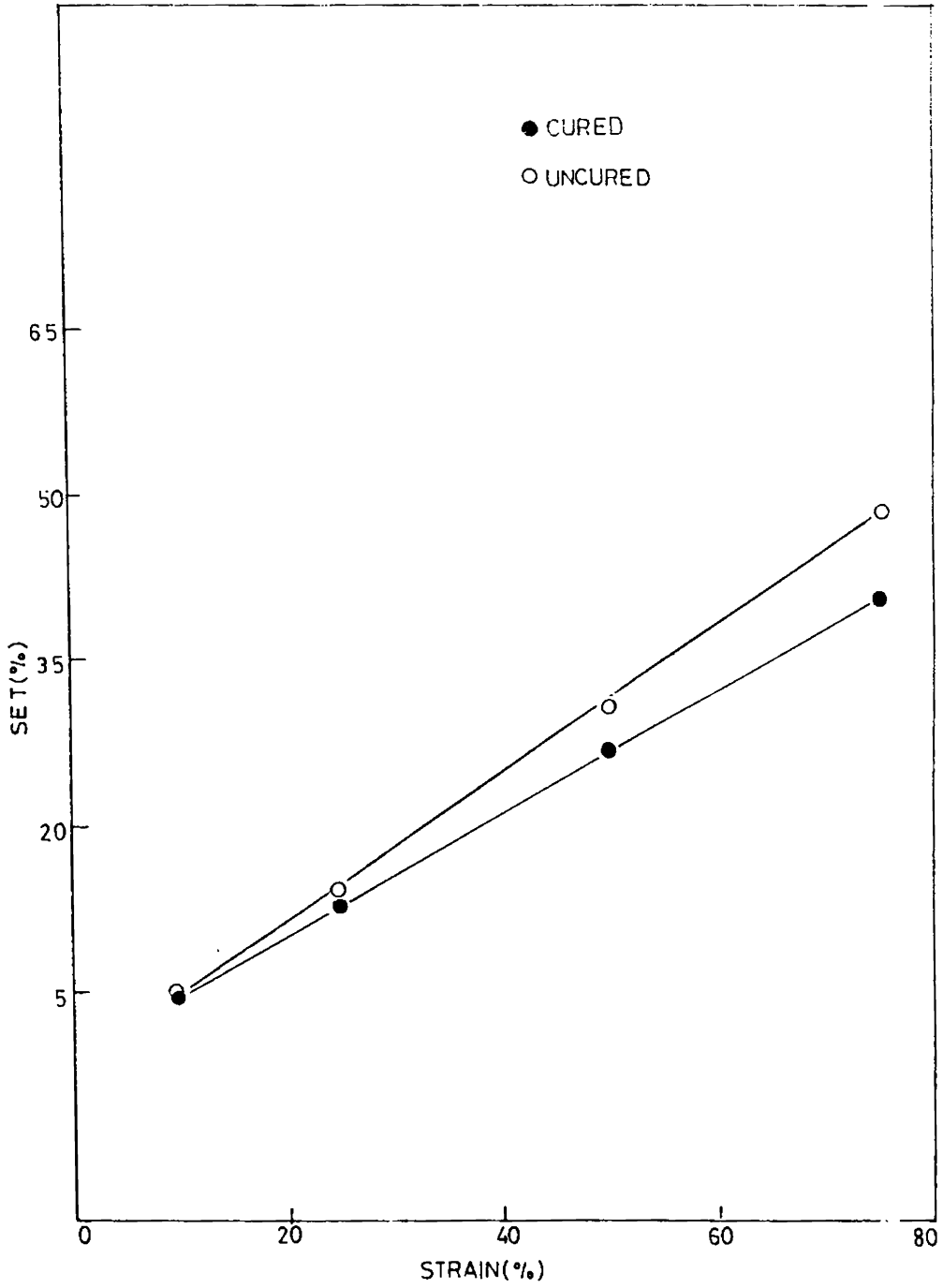


Fig.4.17 Set values after 5 hysteresis cycles at various strain levels for 40/60 NBR/PVC blend.

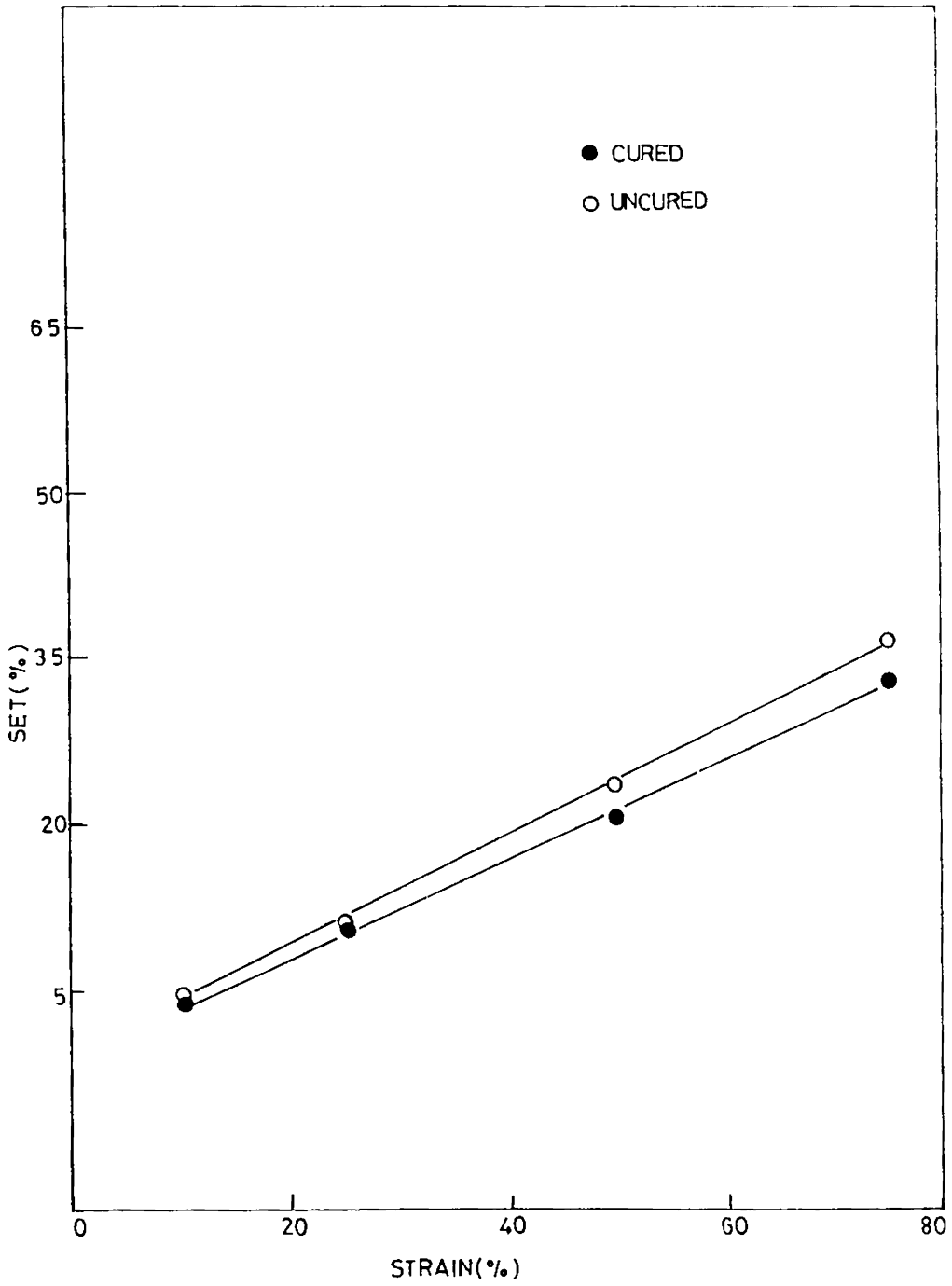


Fig.4.18 Set values after 5 hysteresis cycles at various strain level for 50/50 NBR/PVC blend.

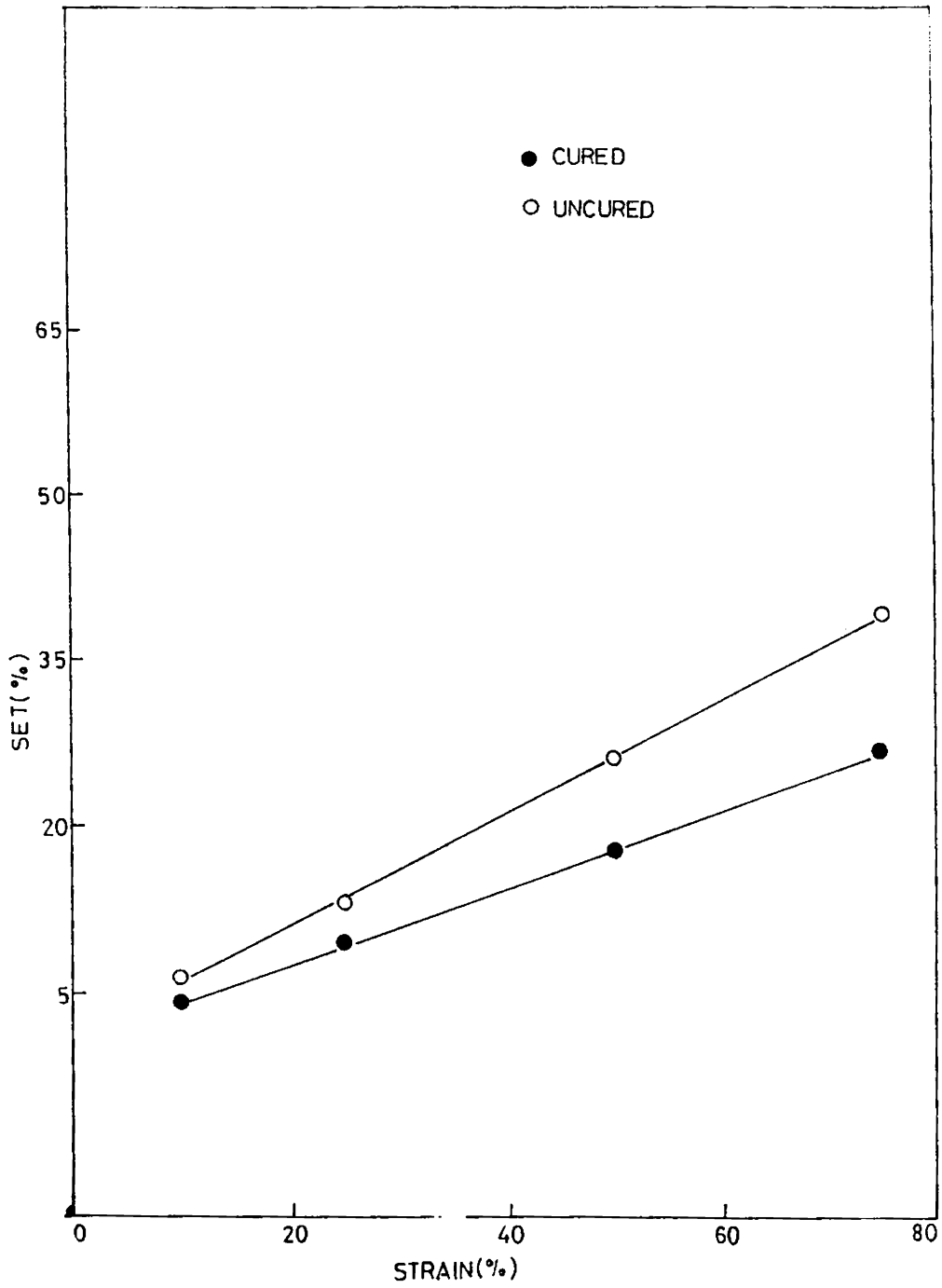


Fig.4.19 Set values after 5 hysteresis cycles at various strain levels for 60/40 NBR/PVC blend.

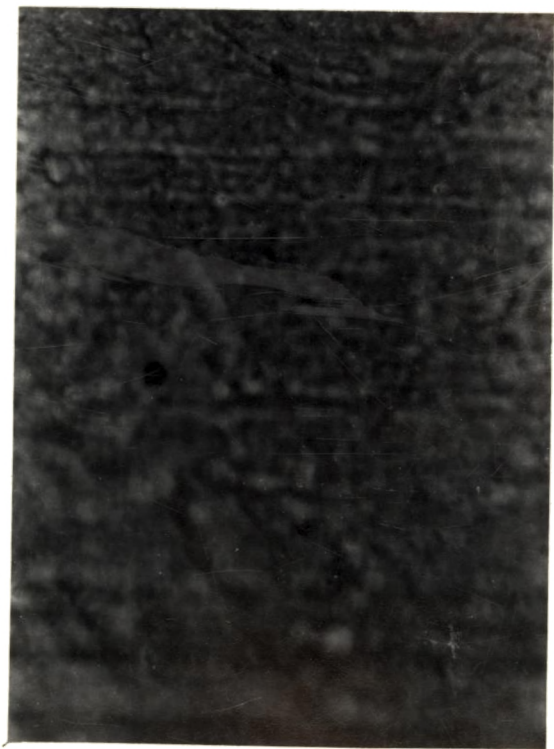


Fig.4.20 DCP cured

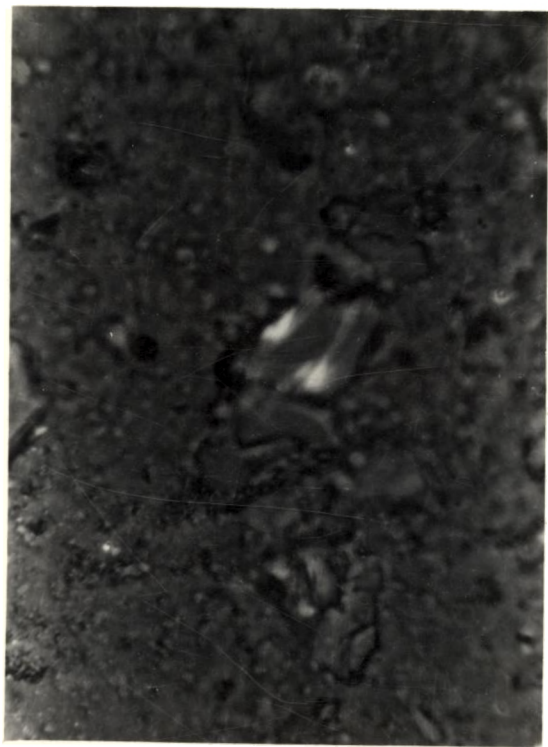


Fig.4.21 uncured

Optical microscope photographs of 70/30 NBR/PVC blends

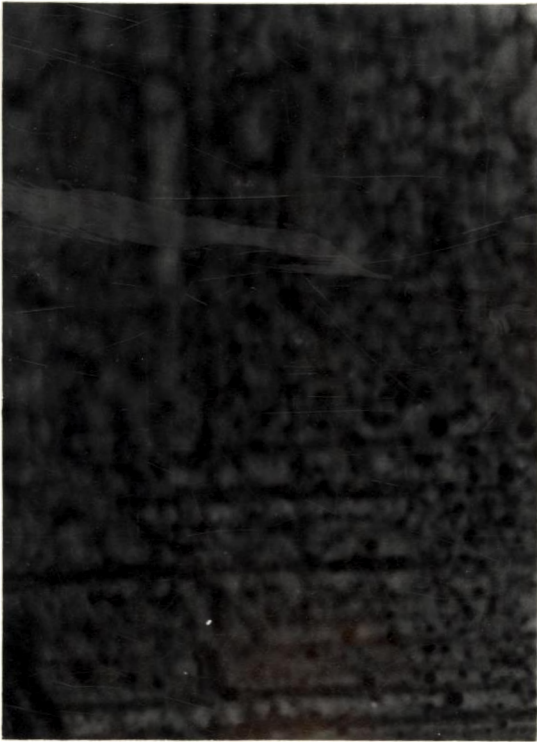


Fig.4. 22 DCP cured

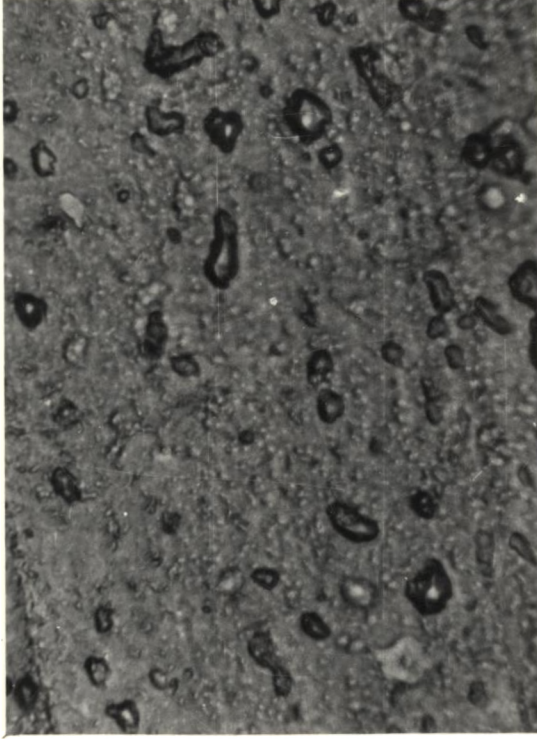


Fig.4.23 Uncured

Optical microscope photographs of 50/50 NBR/PVC blends

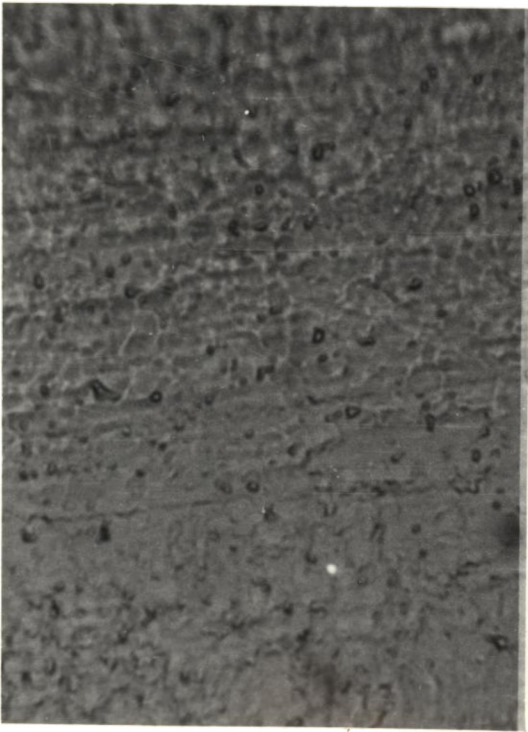


Fig.4.4.24 DCP cured

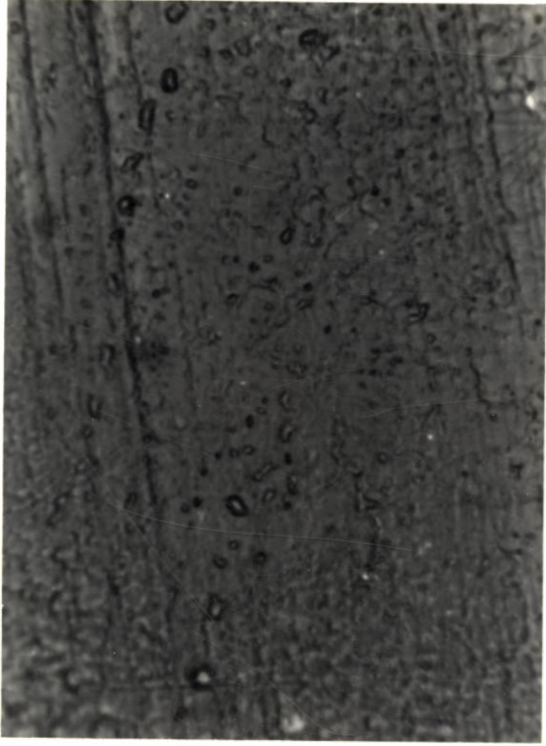


Fig.4.4.25 Uncured

Optical microscope photographs of 30/70 NBR/PVC blends

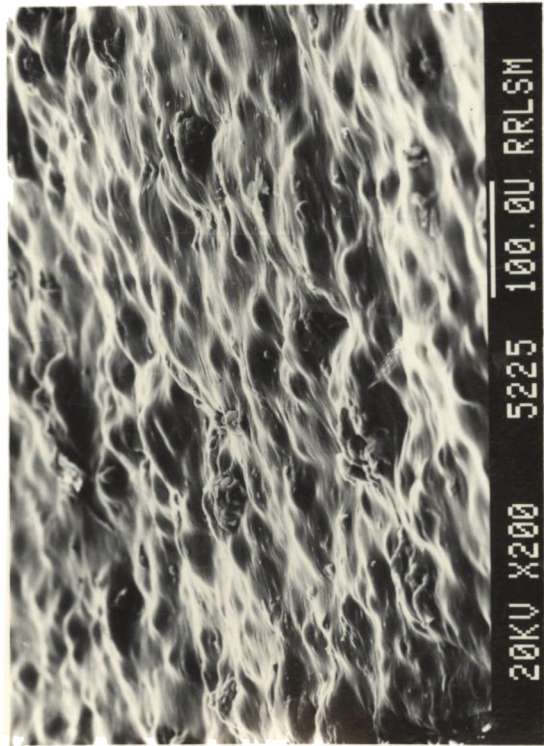


Fig.4.26 70/30 uncured

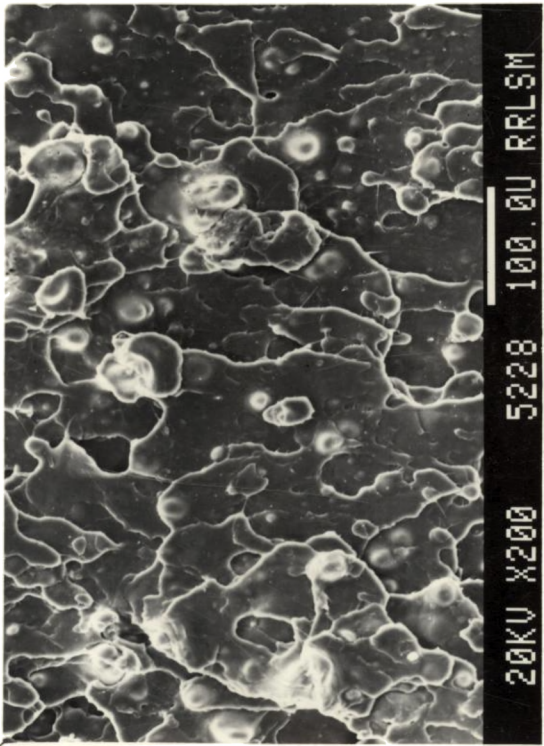


Fig.4.27 50/50 uncured

SEM photographs of the tensile fracture surface of NBR/PVC blends

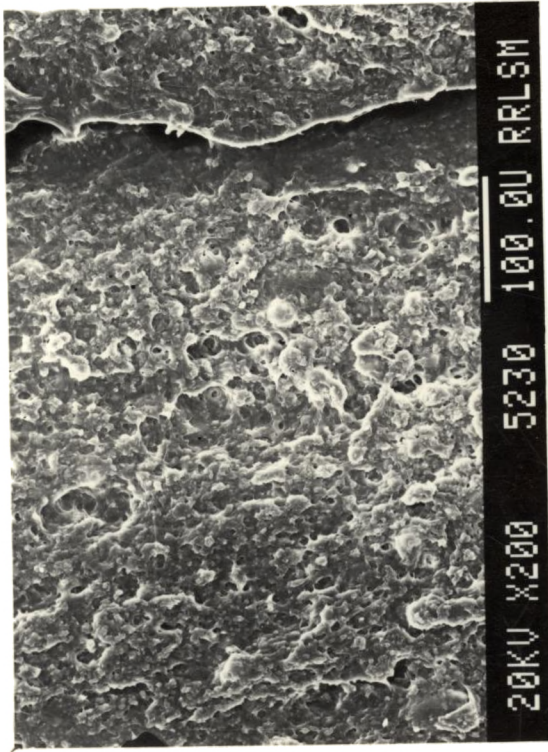


Fig.4.28 30/70 Uncured

SEM photograph of the tensile fracture surface of NBR/PVC blend

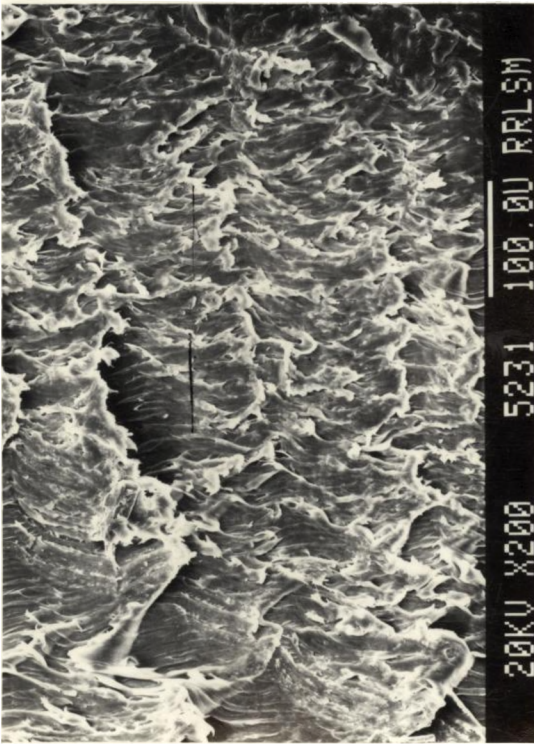


Fig.4.29 30/70 DCP cured

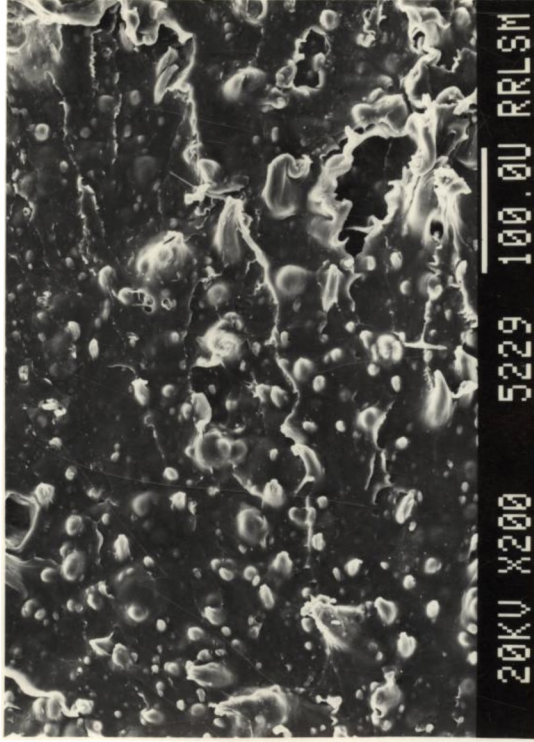


Fig.4.30 50/50 DCP cured

SEM photographs of the tensile fracture surface of NBR/PVC blends

affecting the die swell, melt fracture and deformation of extrudates have been reported.¹⁹ Studies on the rheological behaviour of thermoplastic block copolymers²⁰, those of blends of thermoplastics and rubbers²¹ etc. have become the subject of interest due to the growing importance of thermoplastic elastomers. The present study describes the flow behaviour of thermoplastic elastomers derived from NBR and PVC using a capillary rheometer and a Brabender plasticorder.

Experimental

NBR/PVC blends with PVC content ranging from 30 wt. per cent to 70 wt. per cent were prepared by melt mixing in a Brabender plasticorder model PL3S at 170°C and at 30 rpm, with 5 phr TBLS (of the wt. of PVC) added as heat stabilizer for PVC. The mix from the Brabender was sheeted on a mill while it was hot and then pelletized for further studies.

Melt rheological properties of the uncured blends were measured on a capillary rheometer (Göttfert Viscotester 1500) using a capillary die of circular cross section (length 20 mm and diameter 1 mm) at different shear rates at 180°C and 190°C.

Melt rheological properties of the cured and uncured blends were also evaluated on a Brabender plastimeter at 30, 40 and 50 rpms and at temperatures 130, 140 and 150°C.

Results and discussion

Shear stress and shear rate were calculated using the expression for Newtonian flow in cylindrical capillaries (given in Chapter 3) and from this, apparent viscosity was calculated. Power law index was calculated as the slopes of the straight lines of the shear stress vs. shear rate curve.

Figs.4.31 and 4.32 show the variation of viscosity with shear rate of 30/70, 50/50 and 70/30 NBR/PVC blends at 180 and 190°C respectively. The blends show non-Newtonian behaviour at the temperatures ie., the viscosities increase with decrease in shear. It is further observed that, with increase in NBR content, the viscosity of the blend decreases which means that NBR is acting as a plasticizer especially in the rubber rich blends. PVC rich blend (70% PVC) is characterized by high viscosity among the three compositions, whereas the melt behaviour of the blends with plastic and rubber phase in continuous state is less

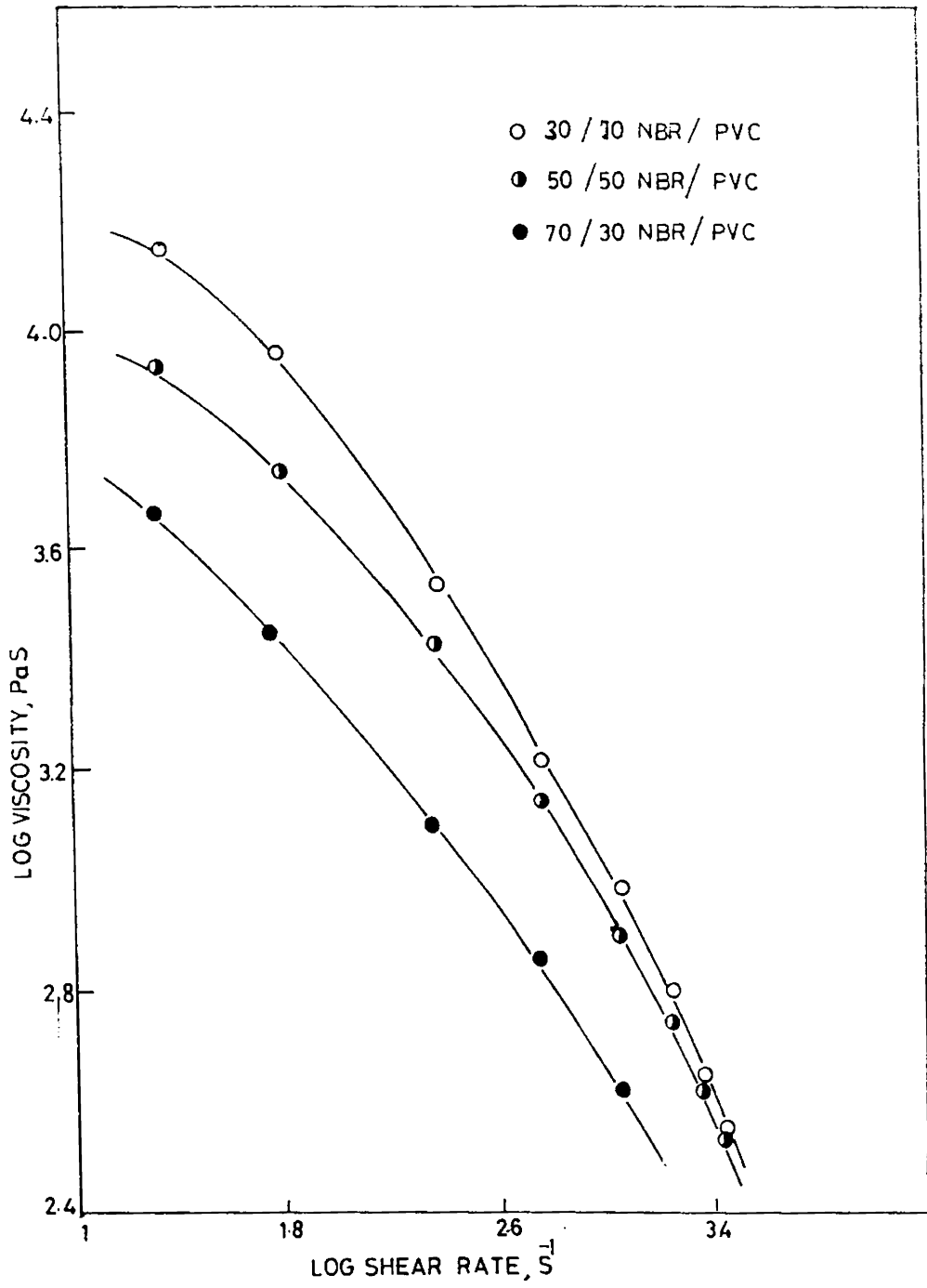


Fig.4.31 Variation of viscosity with shear rate for NBR/PVC blends at 180°C.

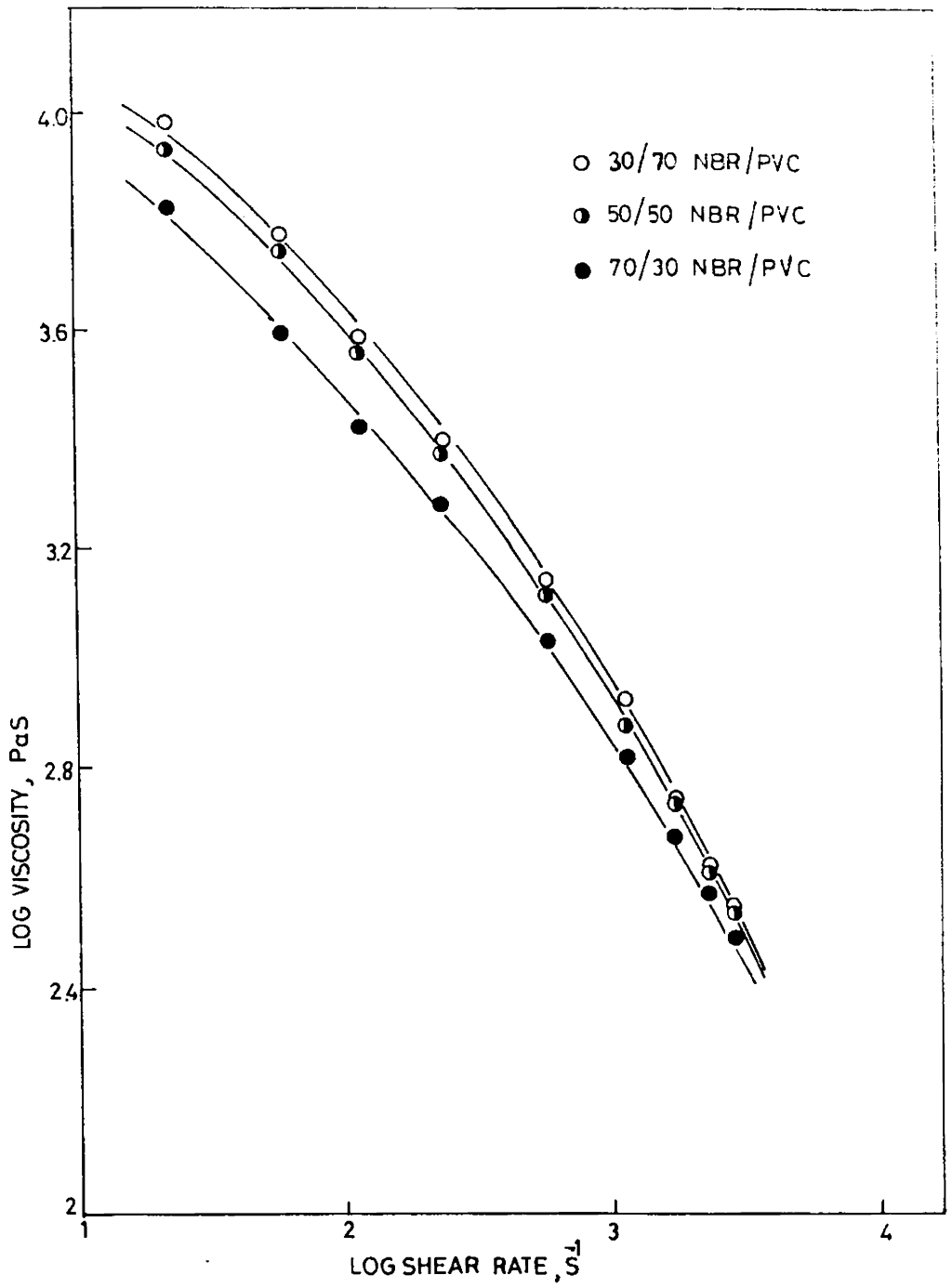


Fig.4.32 Variation of viscosity with shear rate for NBR/PVC blends at 190°C.

non-Newtonian and hence such blends can be processed at lower temperatures and shear rates compared to plastic rich blends.

Fig.4.33 shows plots of \log (shear stress) vs. \log (shear rate) for the blends at 180°C. As in the case of triblock polymers, the curves could not be represented by a single straight line, but only as two straight lines. The two straight lines may be representing different flow mechanisms of the blends as in the case of triblock copolymers. The initial mild Newtonian behaviour may be the behaviour of NBR, where the PVC phase remains mostly in the unfused state. The second strongly non-Newtonian behaviour may be the flow behaviour of the blends, after large scale fusion of PVC particles take place. The slopes of the straight lines taken as the power law index are given in Table 4.1. There is a critical shear rate region for each blend where the flow transition takes place and this critical shear rate transition shifts to higher and higher values with increase in PVC content. As one of the polymer becomes dominant over the other, the straight lines tend to become one where the rheological behaviour can be represented by a single power law relationship. Thus the blends exhibit a mildly non-Newtonian initial behaviour at

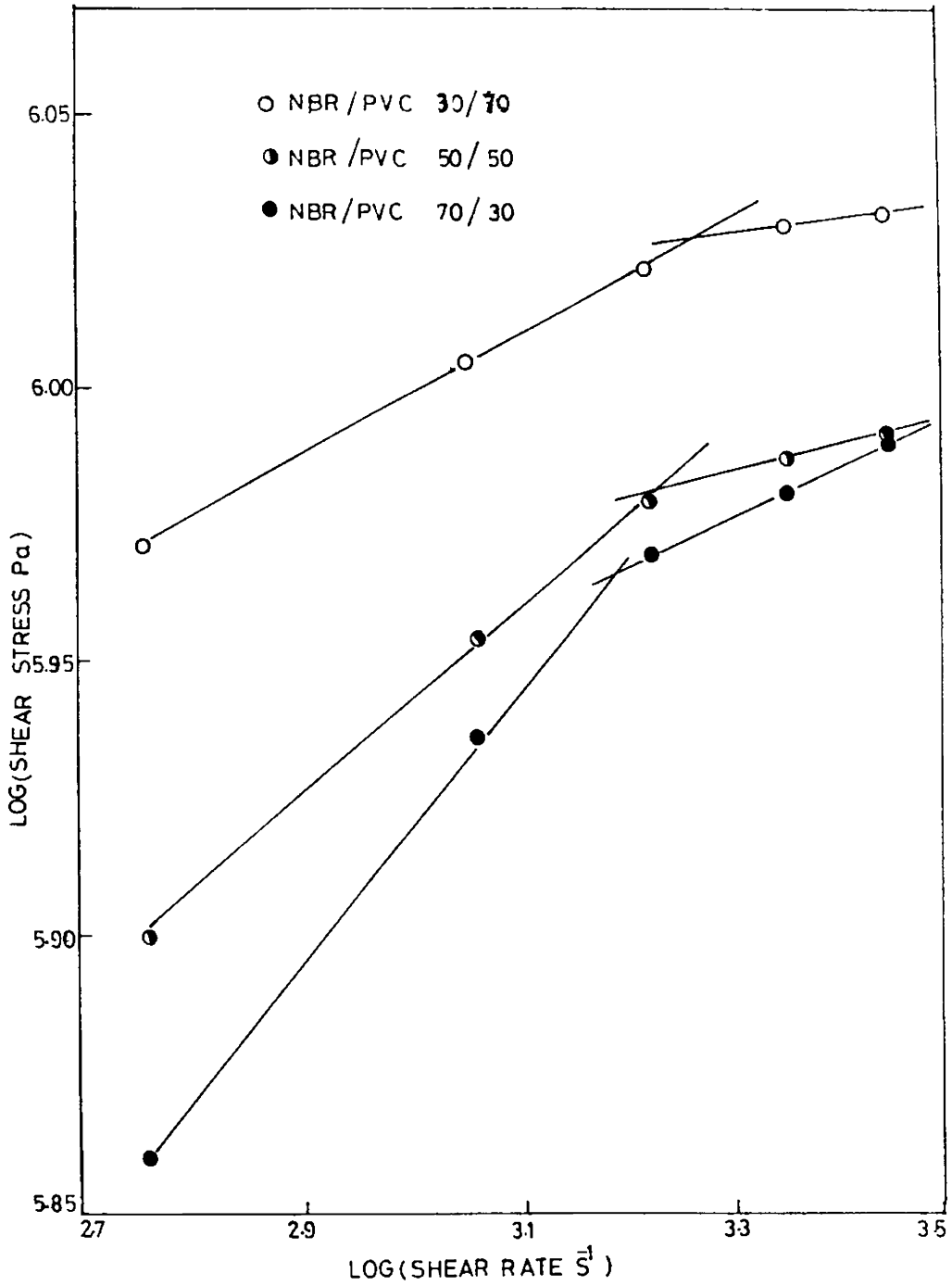


Fig.4.33 Variation of shear stress with shear rate of uncured NBR/PVC blends

Table 4.1 Flow index values of NBR/PVC blends at 180°C
using a capillary rheometer

Percentage of PVC	Flow index values		Critical shear rate (s^{-1})
	Below critical shear rate	After critical shear rate	
30	0.23	0.089	1.5×10^3
50	0.171	0.058	1.6×10^3
70	0.114	0.026	1.9×10^3

low shear rates where the PVC particular structure is not destroyed to any appreciable extent, then a strongly non-Newtonian behaviour after a critical shear rate where the particular structure is destroyed.

The interdependence between blend melt viscosity and component interaction is presented in Fig.4.34. The results show the composition dependence of apparent melt viscosity for NBR/PVC blends, at three different shear rates. The melt viscosities at given rates of shear may be represented by simple logarithmic additivity rule.²² The deviation from the additivity rule for these blends are noted to be positive. The magnitude of this deviation decreases somewhat with increasing shear rate.

Fig.4.35 shows the temperature rise due to shear heating (ΔT) in the Brabender plasticorder for a 50/50 NBR/PVC blend where,

$$\Delta T = T_{\text{melt}} - T_{\text{apparatus}}$$

A steady state of shear heating rate was reached in each case after about 12-14 min. The shear heating was found to depend on the shearing rate (rpm) and at higher rpm the

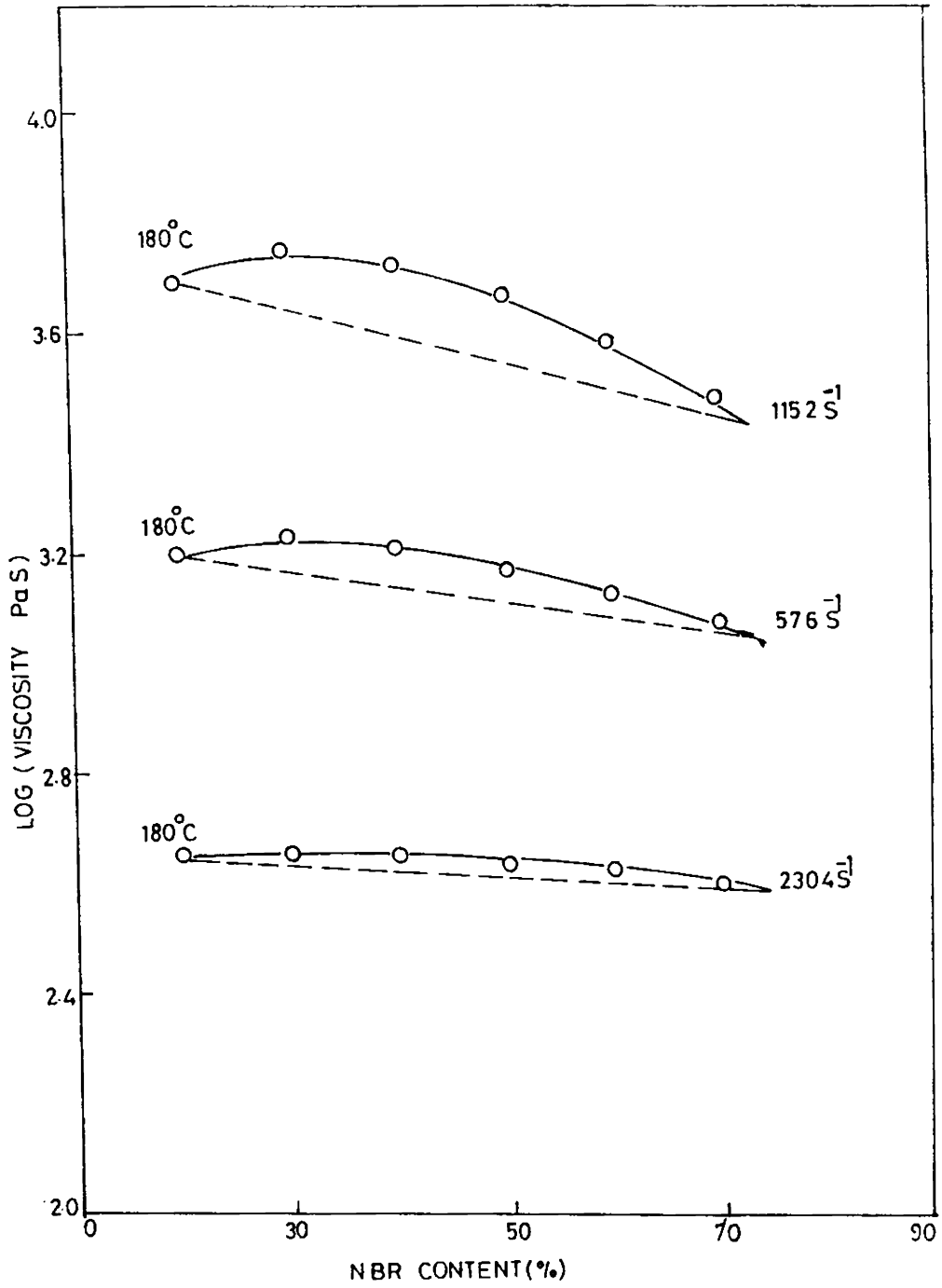


Fig.4.34 Variation of viscosity with blend composition of uncured NBR/PVC blends

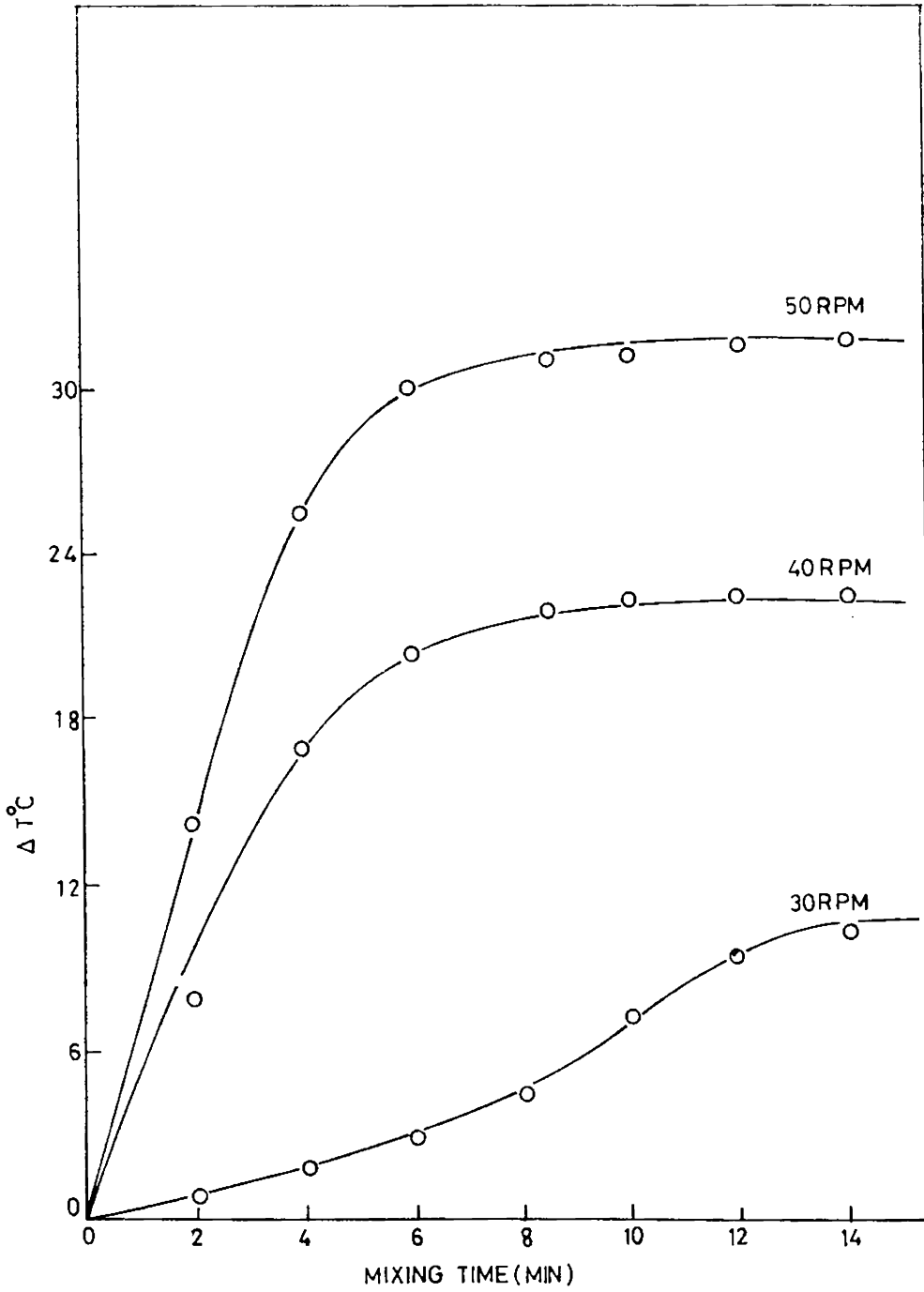


Fig.4.35 Temperature rise due to shear heating in a Brabender plasticorder for 50/50 NBR/PVC blend.

onset of stabilized temperature shifted to lower mixing times. The increase in shear heating over the nominal apparatus temperature is directly proportional to the apparent viscosity under shear conditions. Since ΔT was found to depend on the shearing rate, ΔT could also be conveniently expressed as a function of the total energy expended in the mixing process by the equation,²²

$$E = 2\pi n \int_0^t M dt$$

where E = energy input at a given time t and at an rpm n .

Figs.4.36 and 4.37 show the variation of viscosity with shear rate and temperature of 50/50 and 60/40 NBR/PVC blends (cured and uncured). As expected, torque/rpm representing viscosity decreases with increase in temperature and shear rate (rpm). The cured and uncured blends in both cases show the same type of viscosity variations, but the cured blends show higher viscosity. The differences seem to be quite marked resulting from enhanced frictional resistance introduced due to crosslinking as chains are not deformed easily by the shearing action of the mixer.

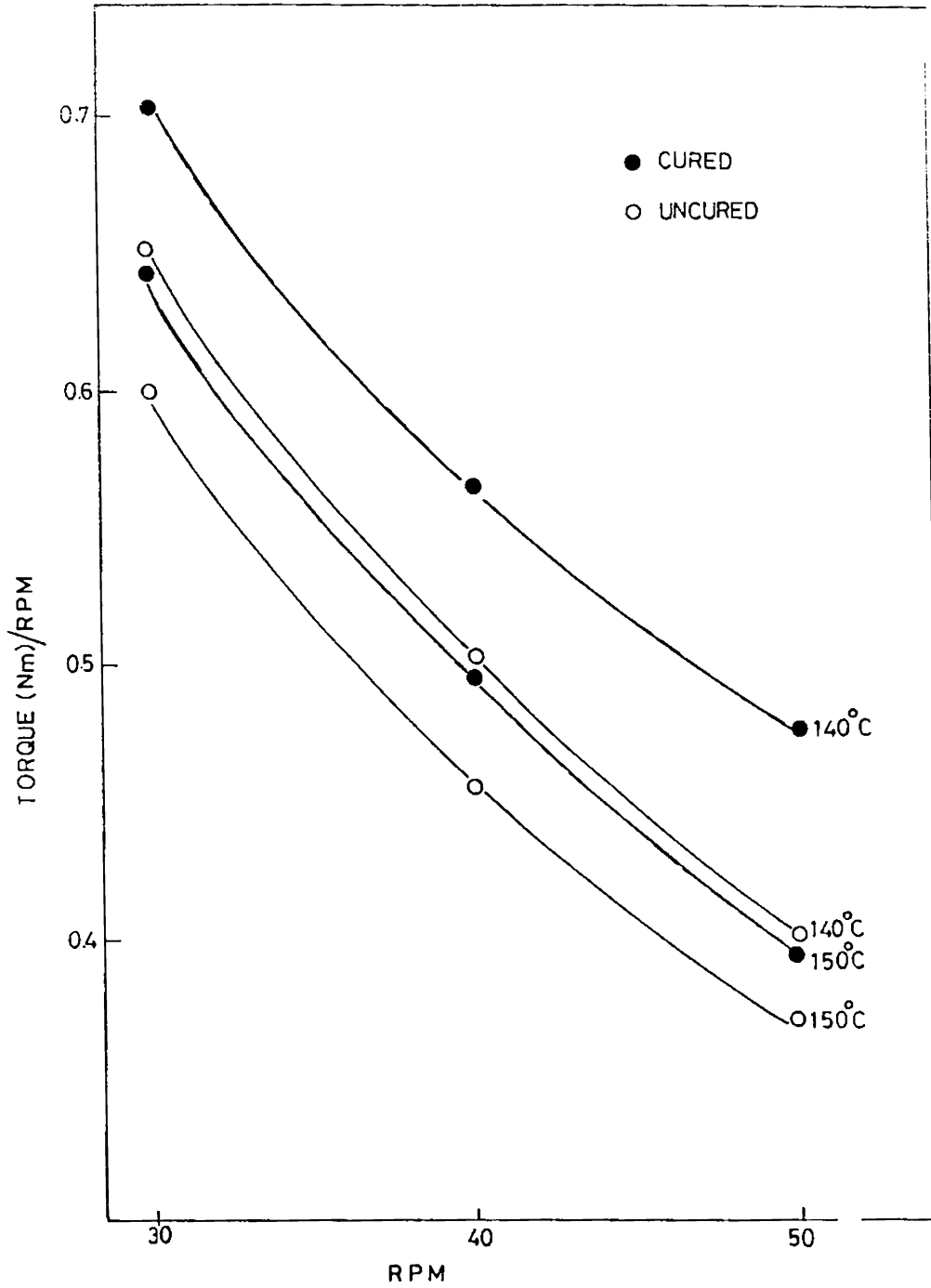


Fig.4.36 Variation of torque/rpm with rpm at different temperatures for 50/50 NBR/PVC blend.

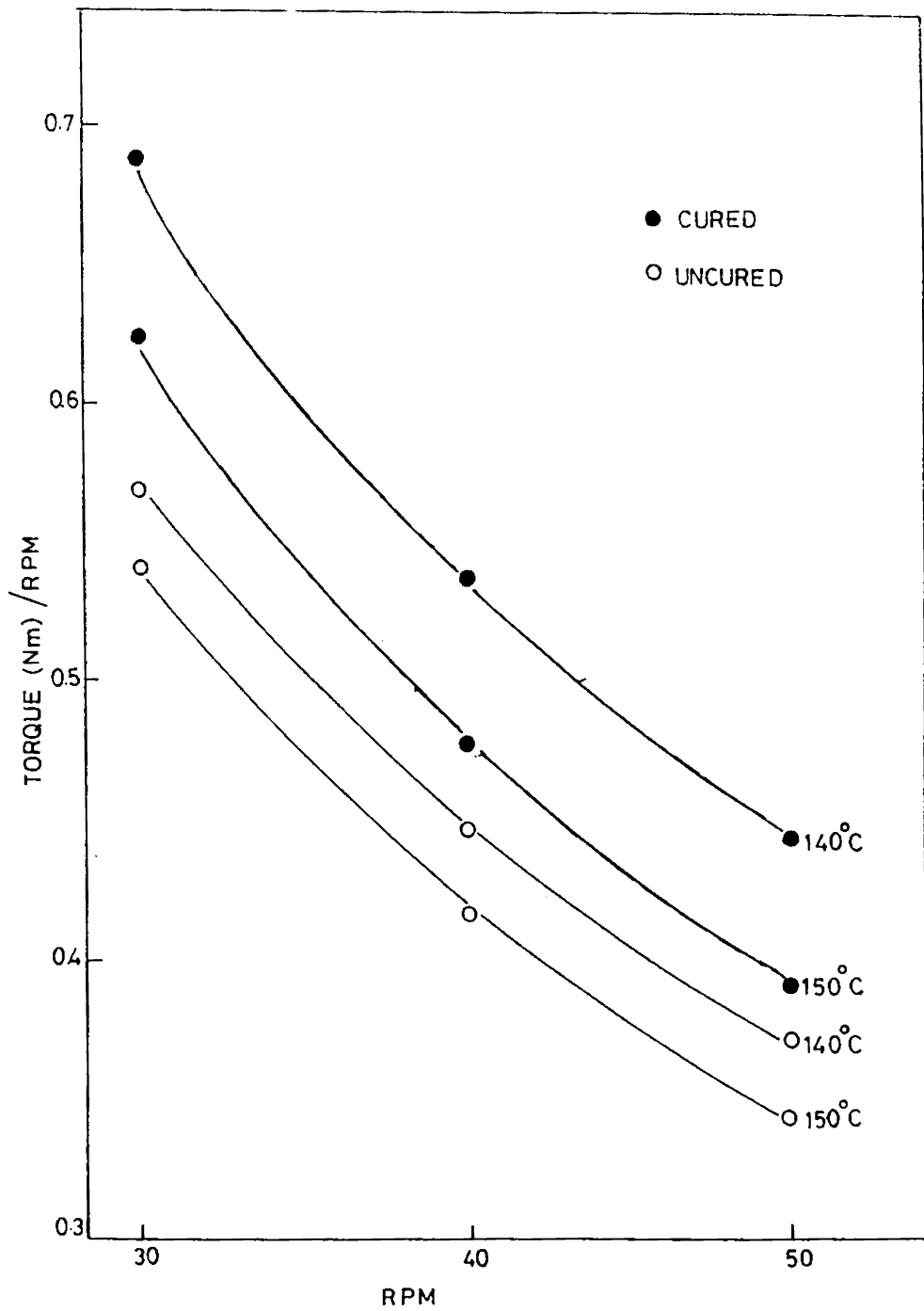


Fig.4.37 Variation of torque/rpm with rpm of 60/40 NBR/PVC blend at various temperatures.

Fig.4.38 shows the variation in viscosity with the blend composition. As the PVC content of the blend increases from 40 to 60%, there is a gradual increase in the viscosity at all the temperatures. The increase in viscosity arises due to the higher viscosity of the PVC phase. The effective decrease in overall viscosity with increase in the concentration of NBR may be due to the plasticization effect of NBR on PVC which also makes the behaviour of PVC less non-Newtonian.

Figs.4.39 and 4.40 show shear stress (torque) vs. shear rate (rpm) plots of 50/50 and 60/40 NBR/PVC blends at 140 and 150°C. The data show the behaviour of the melts as highly non-Newtonian. Unlike the behaviour in the capillary rheometer, the blends could be represented by a single power law index due to the lower temperature and shear to which they are exposed in a Brabender plasticorder. Hence the flow transition could not be represented for these blends using this equipment. The power law indices are given in Table 4.2. The cured blends show a less non-Newtonian behaviour compared to that of the uncured blends.

Figs.4.41 and 4.42 show the variation of torque/rpm vs. reciprocal absolute temperature for 50/50

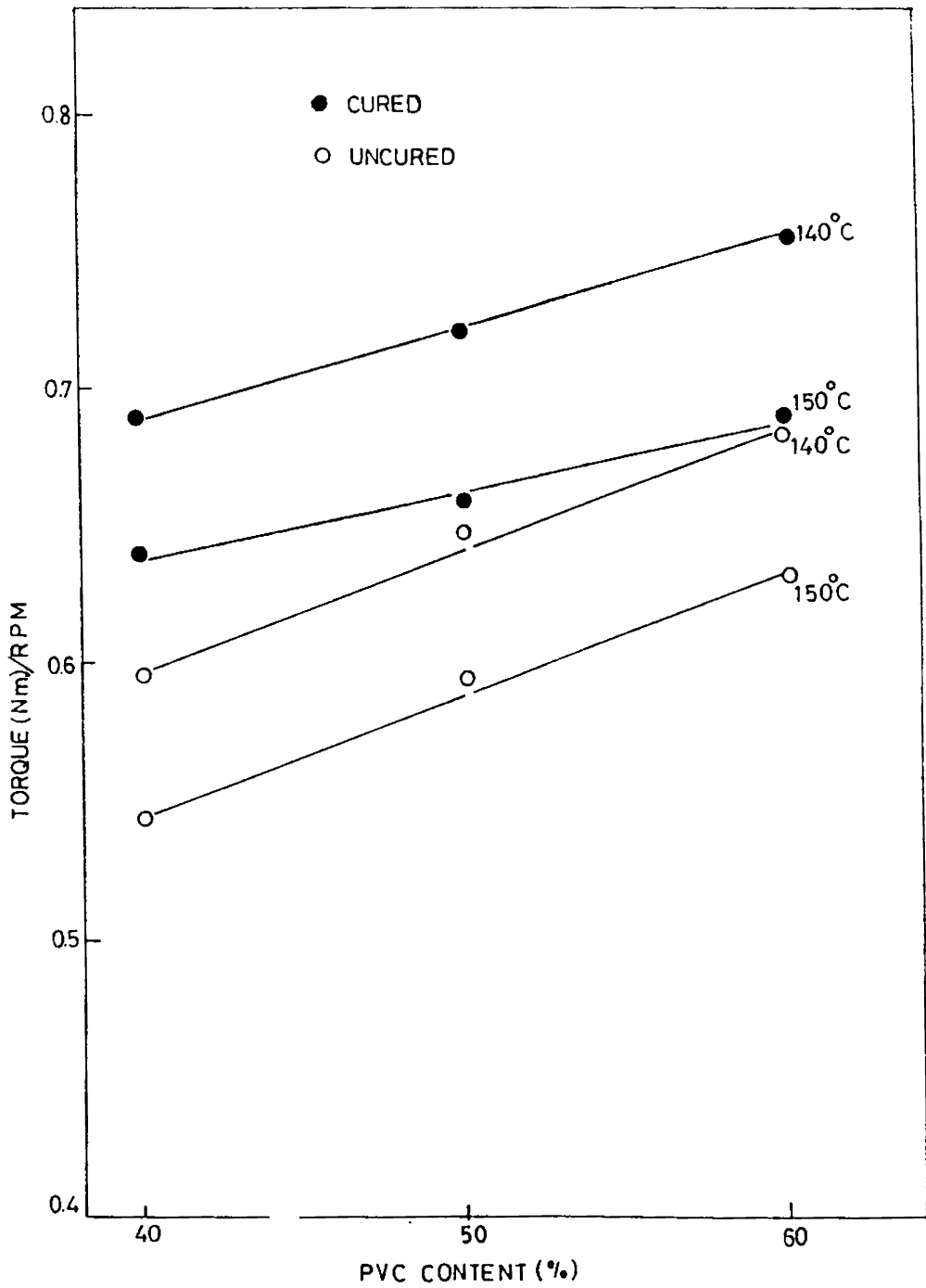


Fig.4.38 Variation of torque/rpm with blend composition of NBR/PVC blends at various temperatures.

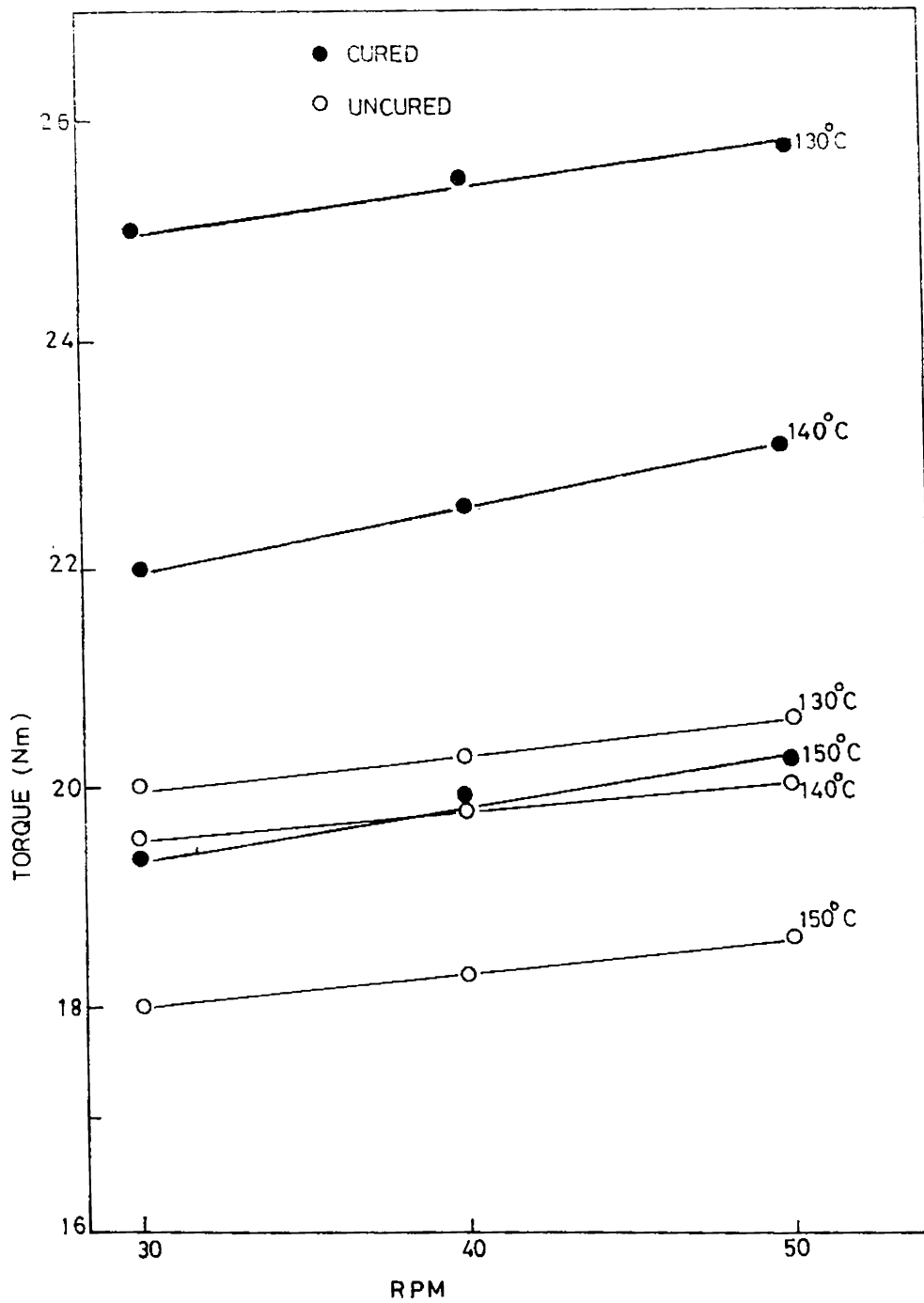


Fig.4.39 Variation of torque with rpm at different temperatures for 50/50 NBR/PVC blend.

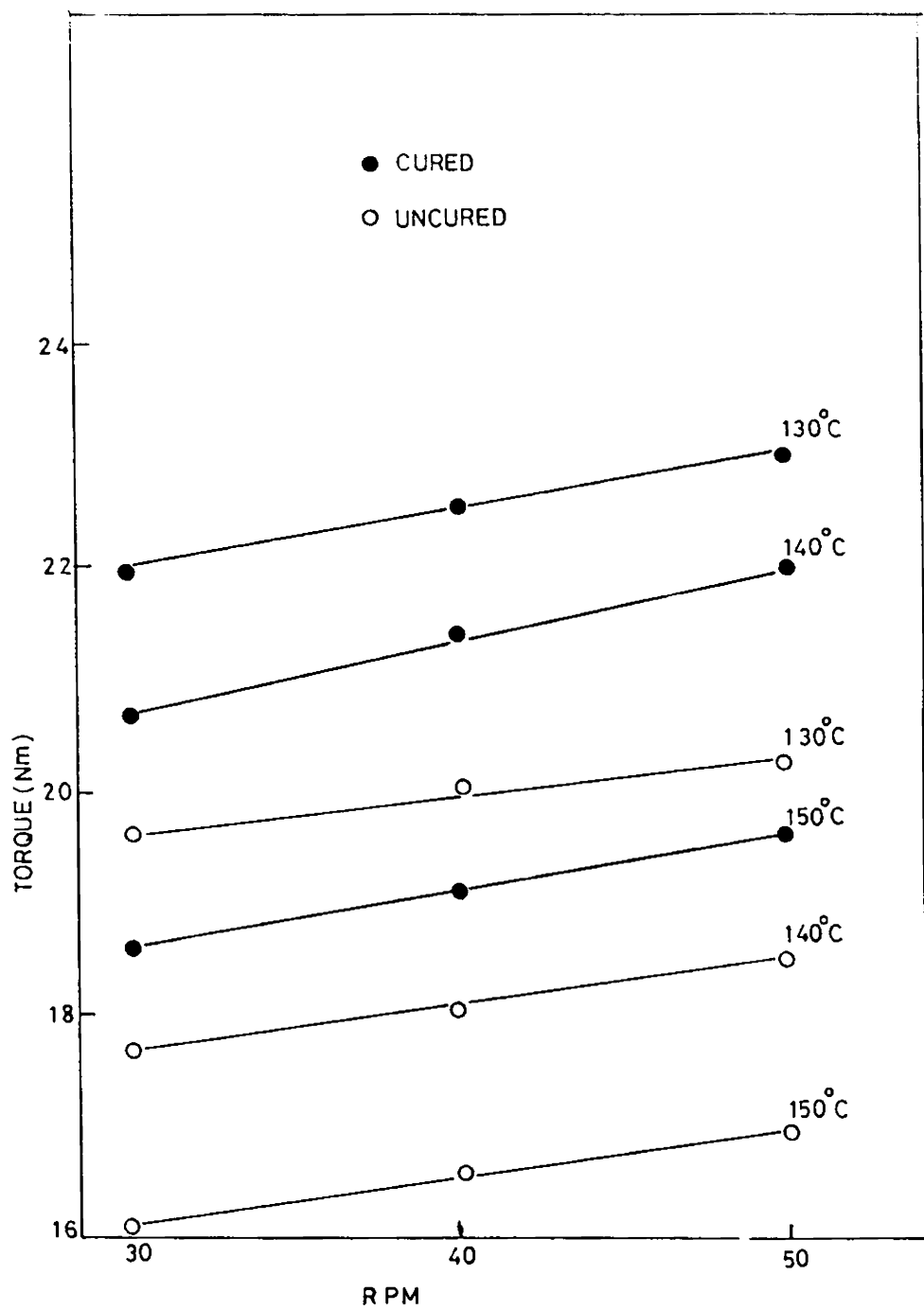


Fig.4.40 Variation of torque with rpm at different temperatures for 60/40 NBR/PVC blend.

Table 4.2 Flow index values of NBR/PVC blends using a
Brabender plasticorder

PVC content (%)	Tempe- rature (°C)	Flow index values of	
		Cured blends	Uncured blends
50	130	0.0502	0.023
	140	0.0528	0.0251
	150	0.054	0.027
40	130	0.0428	0.0317
	140	0.0442	0.037
	150	0.0502	0.043

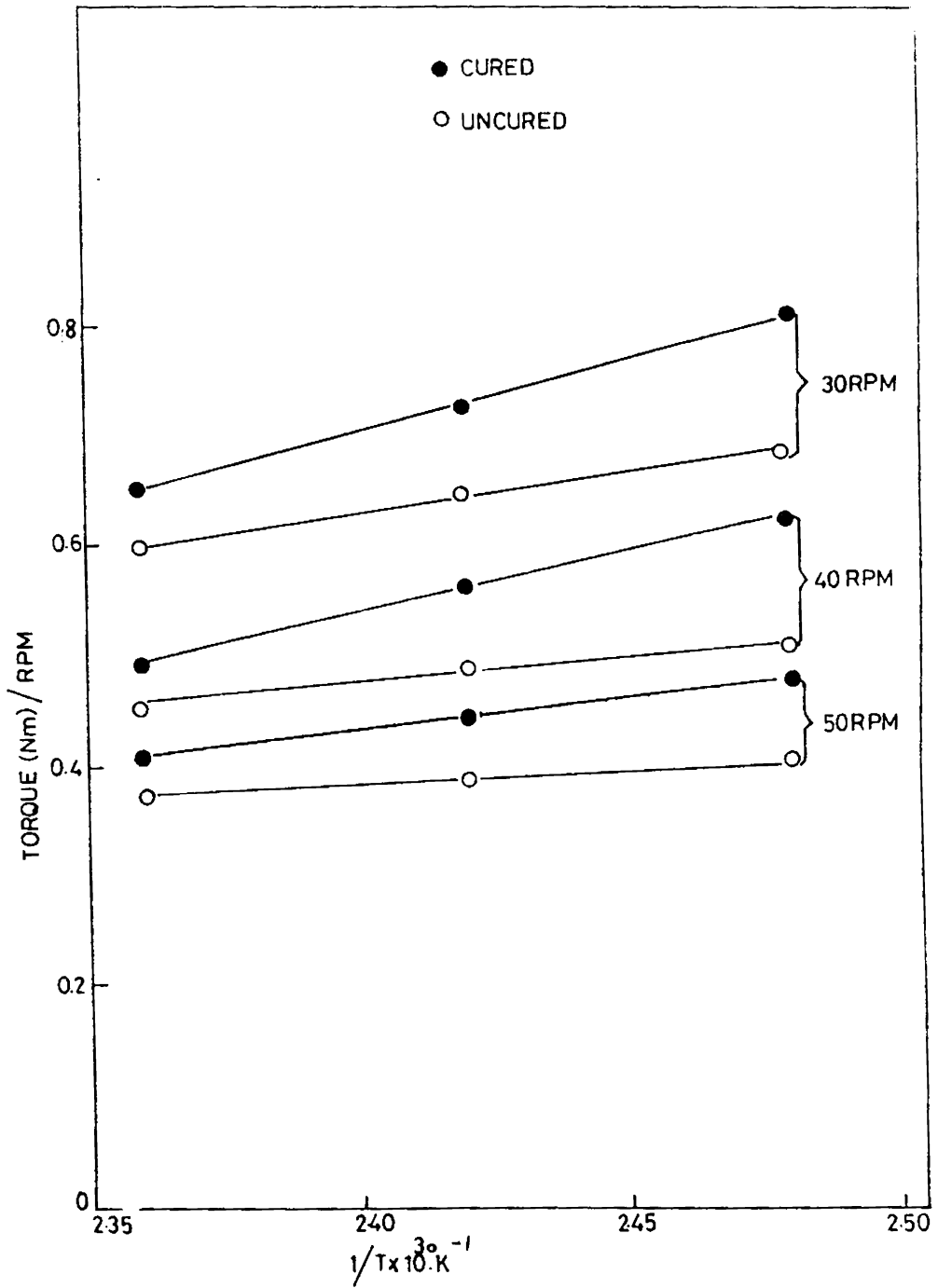


Fig.4.41 Variation of torque/rpm with reciprocal absolute temperature for 50/50 NBR/PVC blend at various rpms.

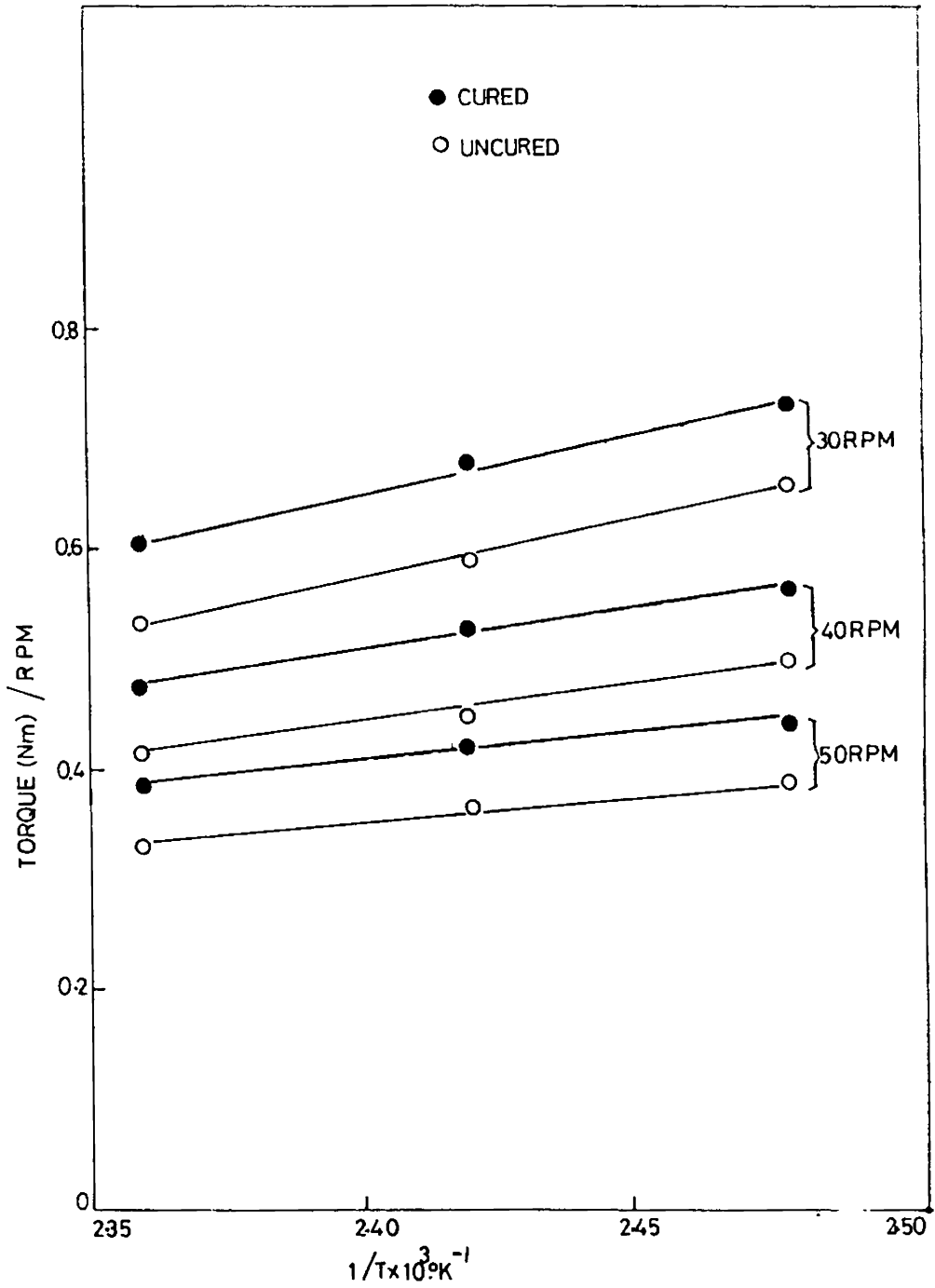


Fig.4.42 Variation of torque/rpm with reciprocal absolute temperature for 60/40 NBR/PVC blend at various rpms.

and 60/40 NBR/PVC blends. The temperature dependence of the viscosity of the blends can be expressed by the flow activation energy calculated from the Arrhenius type equation

$$\eta = A e^{E/RT}$$

The flow activation energies calculated from the slopes of the straight lines are given in Table 4.3. The activation energy of viscous flow is found to decrease with increase in shear rate, obviously due to the highly non-Newtonian behaviour arising from the fusion of PVC particles.²³ It is also observed from the table that the flow activation energy decreases with increase in PVC content at higher shear rates which may be due to the increase in fusion of PVC particles.

CONCLUSIONS

1. Thermoplastic elastomers derived from NBR and PVC show good mechanical properties varying between those of plastic rich and rubber rich NBR/PVC blends.
2. Dynamic crosslinking imparts improvement in tensile strength, elongation at break, modulus etc. It reduces the hysteresis loss and set values.
3. Thermoplastic elastomer NBR/PVC blends exhibit two phase behaviour in the melt and are highly non-Newtonian.

Table 4.3 Flow activation energies for NBR/PVC blends in a Brabender plasticorder

PVC content (%)	rpm	Flow activation energies of (KJ/mole)	
		Cured blends	Uncured blends
50	30	7.9	5.32
	40	3.754	2.659
	50	3.545	1.60
40	30	8.0	7.09
	40	5.318	4.909
	50	3.98	2.45

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Chapter 5

MODIFICATION OF THERMOPLASTIC ELASTOMERS DERIVED FROM NBR/PVC BLENDS

MODIFICATION OF THERMOPLASTIC ELASTOMERS DERIVED FROM
NBR/PVC BLENDS

INTRODUCTION

The chemical modification of polymers has taken its place alongside copolymerization and blending as a common means of altering and optimizing the physical and mechanical properties of macromolecules.¹⁻⁴ Recent advances in reactive polymer processing provide a new way to achieve compatibilization which is done by modifying a polymer with suitable chemical functions to make it reactive towards the components of the alloy. In addition to improving the physical and mechanical properties, functionalization or chemical modification also offers flexibility in tailoring polymer properties for specific applications, reductions in equipment investments etc. Consequently, reactive polymer processing has received increasing attention among polymer scientists and engineers. Several reactive melt processing studies have been reported by several researchers.⁵⁻¹²

For the peroxide initiated functionalization of polyolefins in the molten state, it is generally observed

that crosslinking or chain scission may occur simultaneously with the grafting. For polyethylene, the dominant side reaction is crosslinking, while for polypropylene the dominant side reaction is chain scission. In the case of ethylene-propylene rubber, both crosslinking and chain scission may be important.⁵⁻¹² As the interfacial properties are expectedly improved with grafting of the polar moiety, side reactions such as crosslinking and chain scission may certainly alter the processing characteristics of the functionalized polymer. The present investigation was undertaken to study the effect of modifiers such as maleic anhydride, acrylic acid and acrylamide on NBR/PVC thermoplastic elastomers in presence of dicumyl peroxide. The reaction of the thermoplastic elastomer blend in the melt stage with the above mentioned modifiers in the presence of free radical precursor results in the appendage of individual modifier functional units onto the polymer backbone, accompanied by crosslinking.

EXPERIMENTAL

50/50 NBR/PVC blend was used for the study. Formulations of the mixes are given in Table 5.1.

Table 5.1 Recipe for the 50/50 NBR/PVC blend

PVC and stabilizer

PVC = 20 g (50% of total polymer)

TBLS = 1 g (5 parts per 100 parts of PVC)

Rubber

NBR = 20 g (Acrylonitrile content 33% with Mooney viscosity [ML(1+4) at 100°C] - 40.6)

Modifiers

Acrylic acid, maleic anhydride and acrylamide in the following levels were used.

1. 0.04 g - 0.1 parts per 100 parts of PVC and
NBR (0.1 phr)
2. 0.4 g - (1 phr)
3. 1.2 g - (3 phr)
4. 2 g - (5 phr)

0.12 g (0.3 phr) of DCP was added as free radical initiator for all blend compositions.

BLEND PREPARATION

NBR and PVC along with its heat stabilizer were first homogenized in a two roll mill at 30-50°C. The homogenized material was then melt mixed in a Brabender plasticorder equipped with roller mixers at a speed of 30 rpm. Temperature of the chamber was set at 150°C, but the actual temperature raised to 170-175°C during mixing due to shear heating. When a constant mixing torque was obtained, DCP along with the modifier(s) was added. The mixing was continued for few more minutes.

The materials from the mixing chamber was then pressed in a hydraulic press at 170°C for 3 minutes. Then the mould was taken out, water cooled and the sheet taken out. Dumbell shaped specimens were punched out from the sheets for further testing.

INFRARED SPECTROSCOPY

The reaction products were washed, dried and then pressed at 150°C into thin films from which Infrared spectra were taken using a Beckmann Infrared Spectrophotometer.

GEL CONTENT MEASUREMENTS

Gel content of the reaction products was determined by means of a typical extraction procedure of

refluxing in boiling methyl ethyl ketone for 8 hrs. Small quantities of each sample, approximately 0.3 gm, were weighed and placed in a 15x15 mm envelope made from 120 gauge stainless steel woven mesh. The sample in the container envelope was immersed in refluxing methyl ethyl ketone for 5 minutes, dried under vacuum for 16 hrs at 110°C, removed from the container and weighed. Gel fraction was obtained by dividing the final sample weight by the initial sample weight.

SCANNING ELECTRON MICROSCOPIC STUDIES

Scanning electron microscopy has been used to study the characteristics of the fracture surfaces of the grafted NBR/PVC thermoplastic elastomer blends. The SEM observations reported in the present investigation were made on a JEOL JSM 35C scanning electron microscope on the fracture surface of tensile test specimens. These fracture surfaces were sputter coated with gold within 24 hours of testing.

RESULTS AND DISCUSSION

Fig.5.1 shows representative torque curves of NBR/PVC thermoplastic elastomer blend in presence of modifiers.

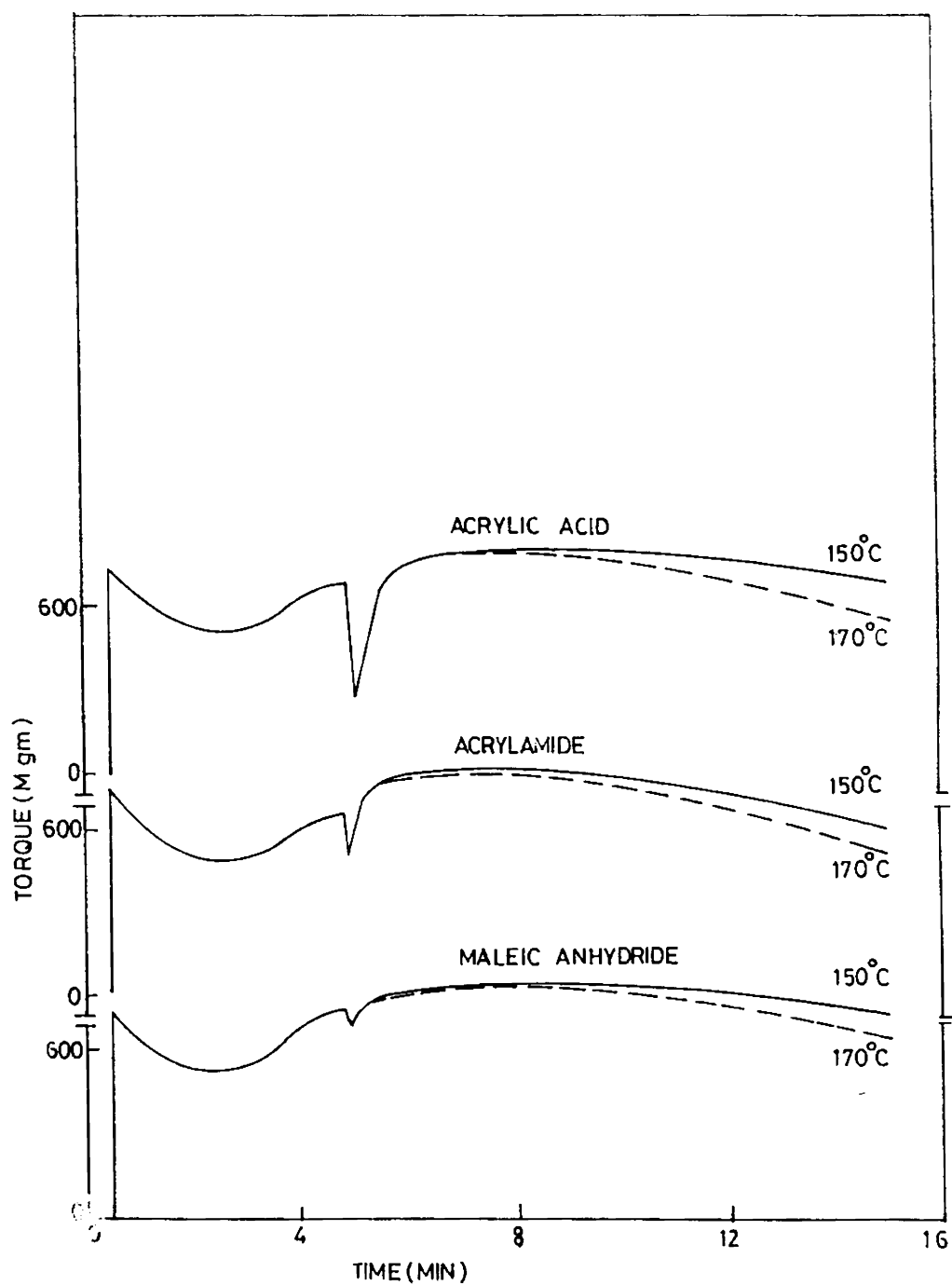


Fig.5.1 Brabender torque-time curves for 50/50 NBR/PVC blend in presence of various modifiers.

These torque curves are characterised by an early sharp peak due to material loading, following by a plateau region of nearly constant mixing torque due to melt mixing of NBR and PVC. A drop in the torque value after 5 minutes indicates the torque reduction due to modifier addition, where the modifiers act as a lubricant at the point of addition. The observed constant mixing torques after modifier addition clearly shows the absence of grafting in the presence of modifier alone at all temperatures.

The representative IR spectrum obtained for the blend/modifier pair is given in Fig.5.2. Absence of characteristic absorption of $>C=O$ group near 1700 cm^{-1} confirms that grafting has not taken place in the presence of modifiers alone.

With DCP as the sole additive at 150°C , the mixing torque shows no significant change even after 10 minutes of mixing (Fig.5.3). The torque values remain in the range of 640-650 M gm. This indicates that the extent of cross-linking at this temperature and shear must have been limited.

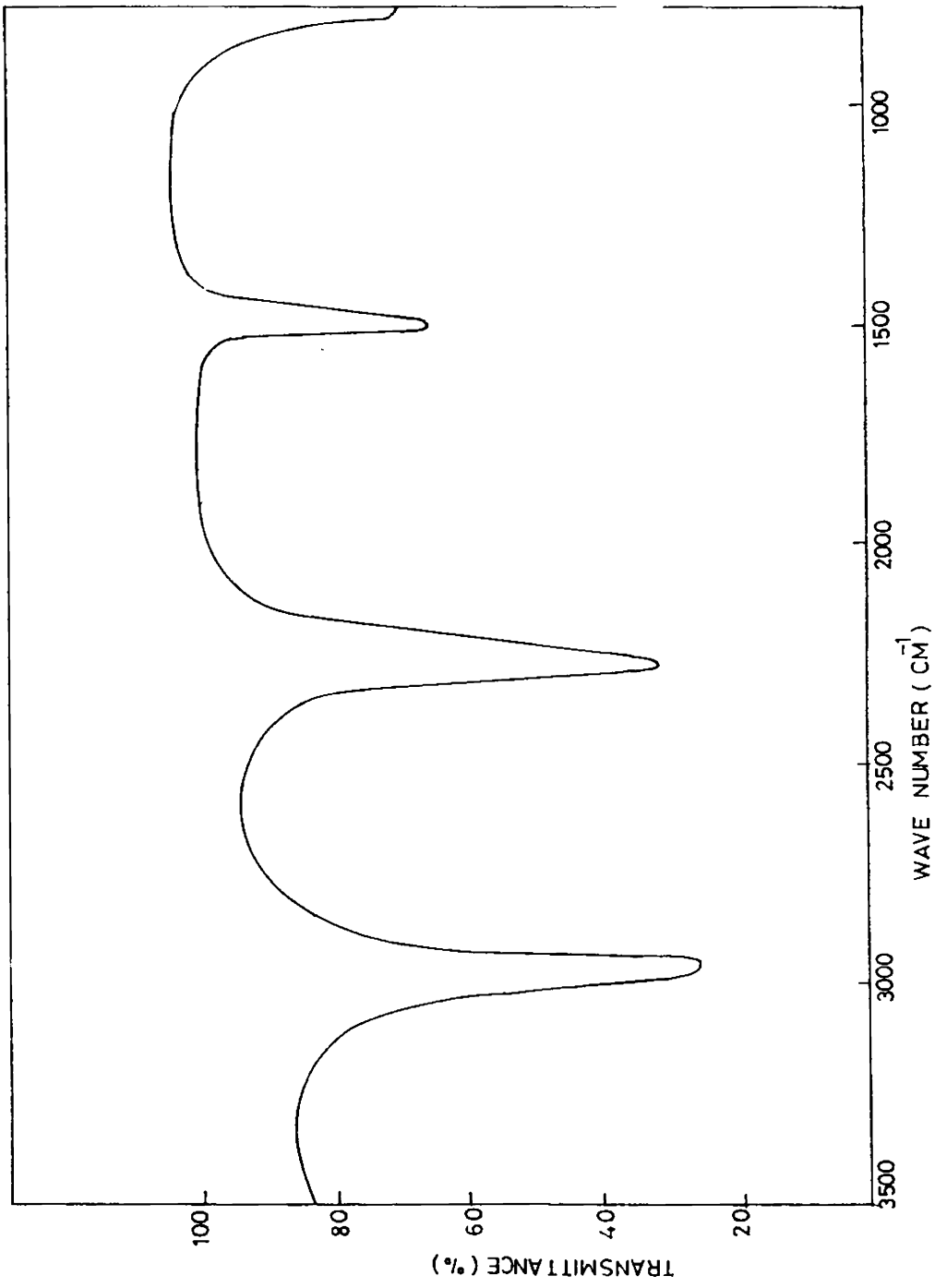


Fig.5.2 IR spectrum of 50/50 NBR/PVC blend in presence of maleic anhydride

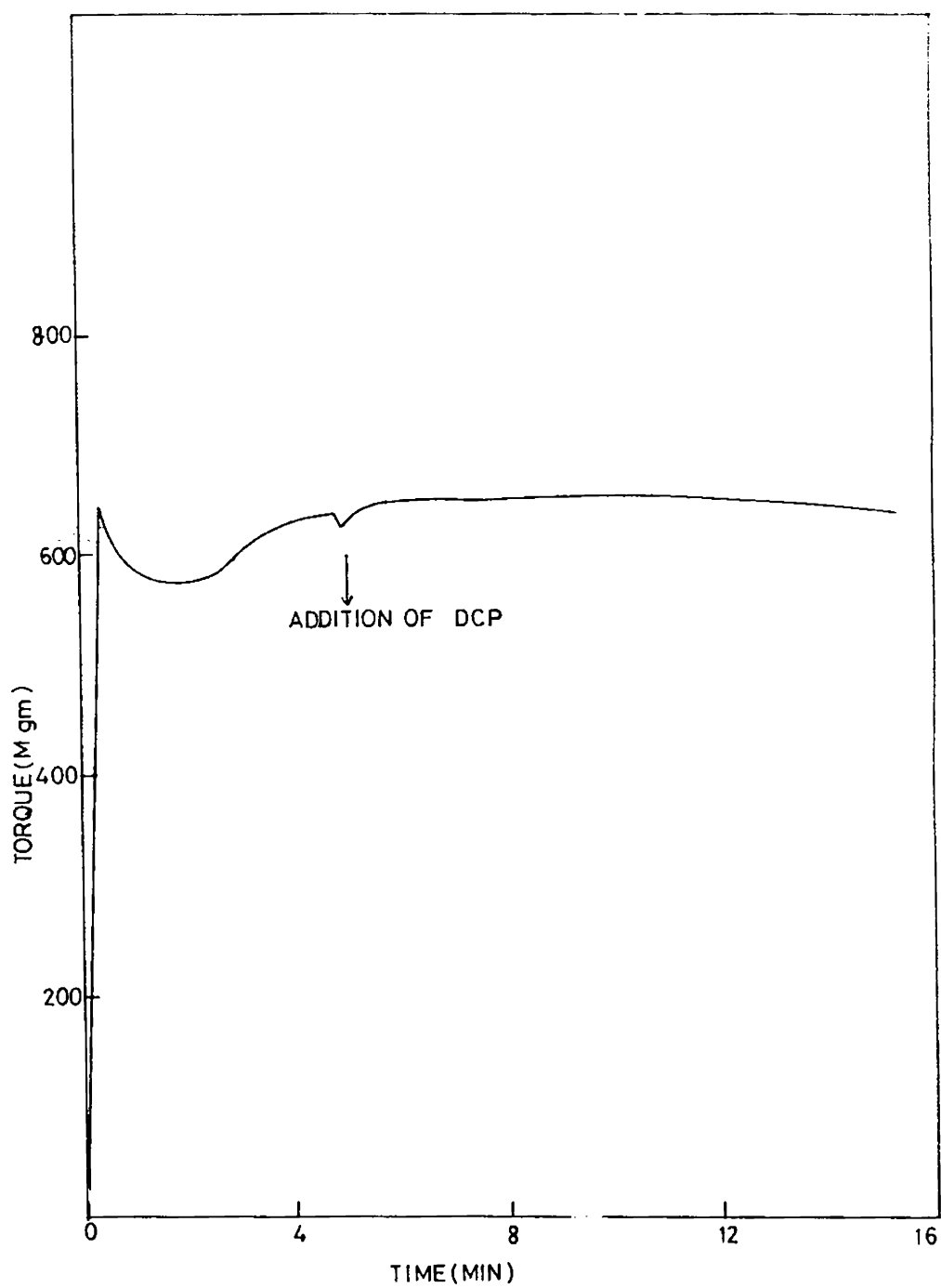


Fig.5.3 Brabender torque-time curve for 50/50 NBR/PVC blend in presence of DCP.

As demonstrated in Figs.5.4, 5.5 and 5.6 use of modifiers in presence of DCP at 150°C resulted in a rise in the torque curve after the addition of modifier/DCP system. The height of the resulting peak increases with increase in modifier content. The final torque value, however, varies as the type of modifier changes. The emergence of a broad cure peak here implies that the presence of modifiers kinetically enhances the crosslinking of the blend with DCP resulted in grafting of the polar $>C=O$ groups within the network. However, a decrease in mixing torque after the maximum in Figs.5.5 and 5.6 suggests scission of the crosslinked chains after some period of time. This may be attributed to shear induced scission or competing degradation reaction taking place at this temperature and shear in the presence of acrylic acid and acrylamide modifiers. Thus under the given DCP loading, significant grafting of maleic anhydride, acrylic acid and acrylamide to polymer chains occurs resulting in improved mechanical properties.

Representative IR spectrum of the blend grafted with acrylic acid, is given in Fig.5.7. Strong characteristic absorptions are observed at 1760 cm^{-1} for acrylic acid indicating the presence of symmetric carbonyl stretching absorptions in these blends with significant

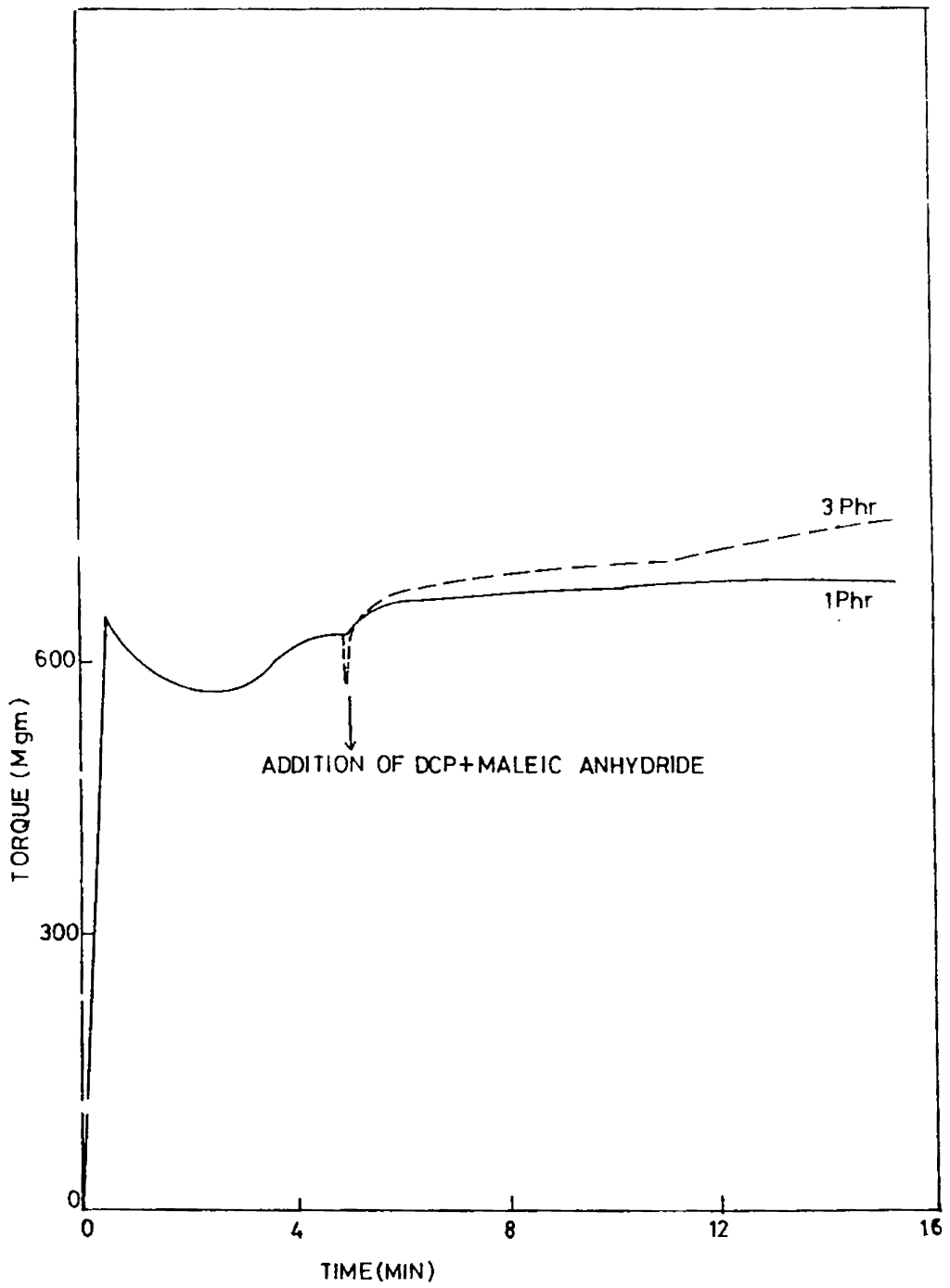


Fig.5.4 Brabender torque-time curve for 50/50 NBR/PVC blend in presence of DCP and maleic anhydride at 150°C

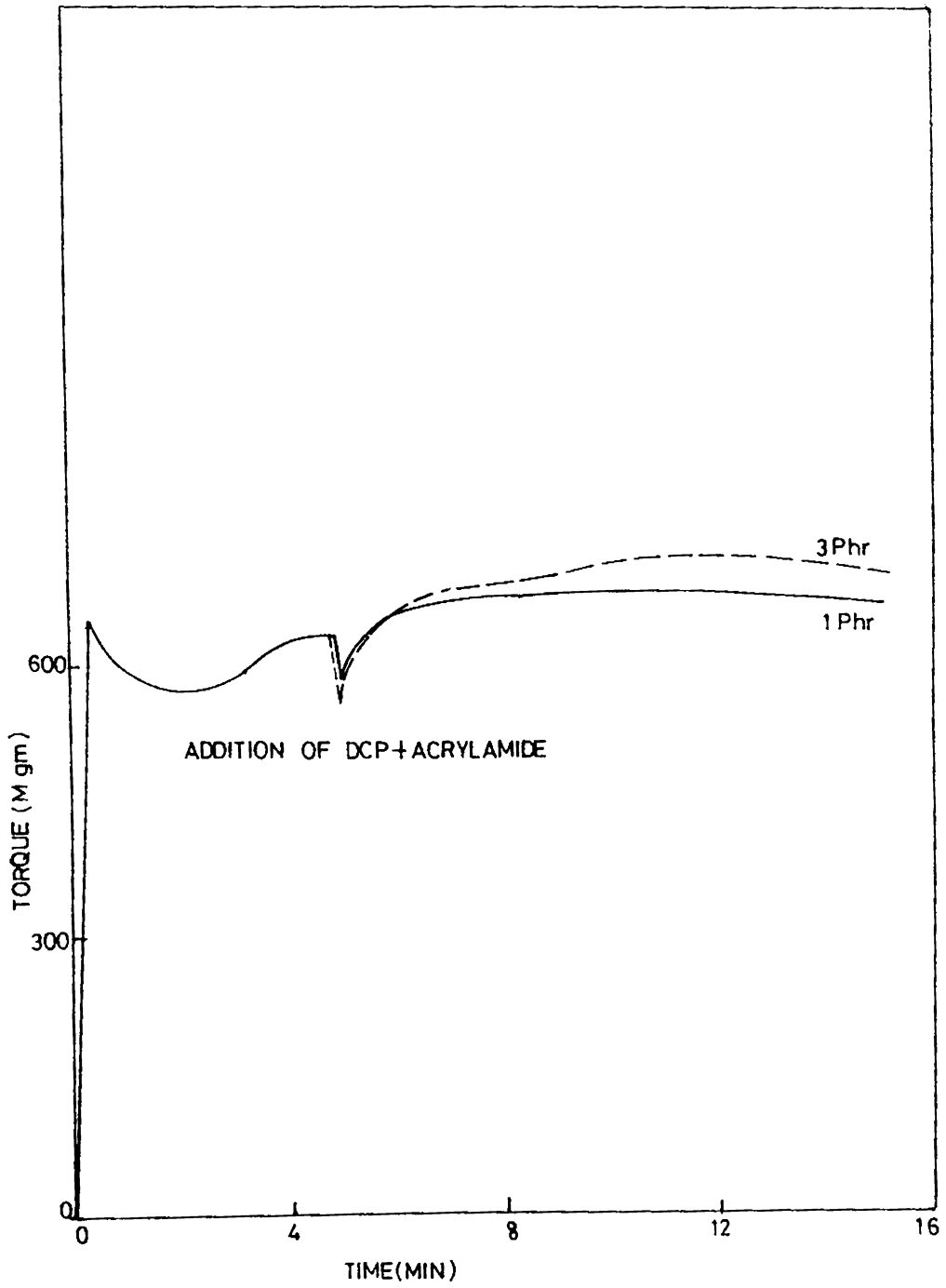


Fig.5.5 Brabender torque-time curve for 50/50 NBR/PVC blend in presence of DCP and Acrylamide at 150°C

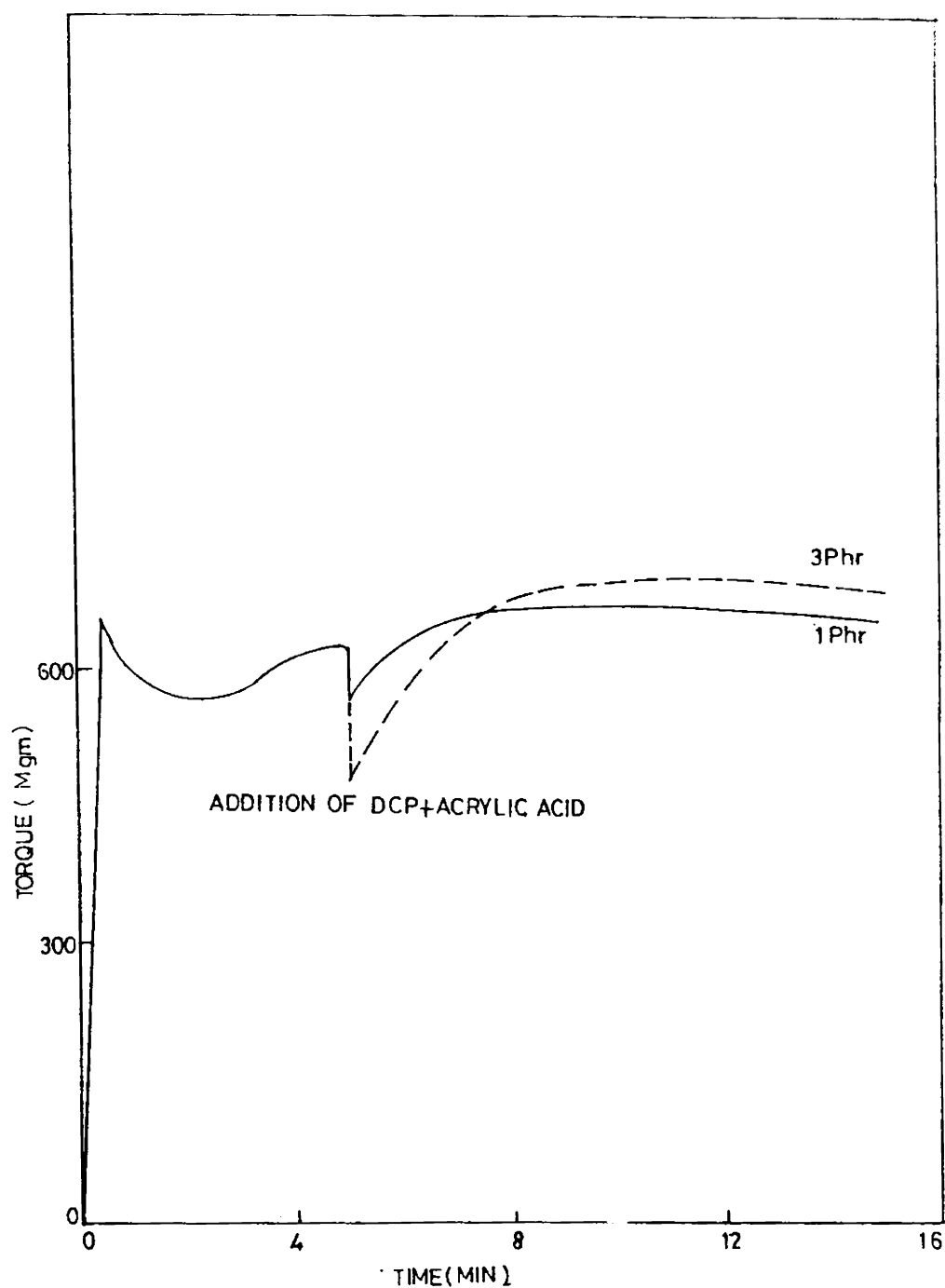


Fig.5.6 Brabender torque-time curve for 50/50 NBR/PVC blend in presence of DCP and acrylic acid at 150°C

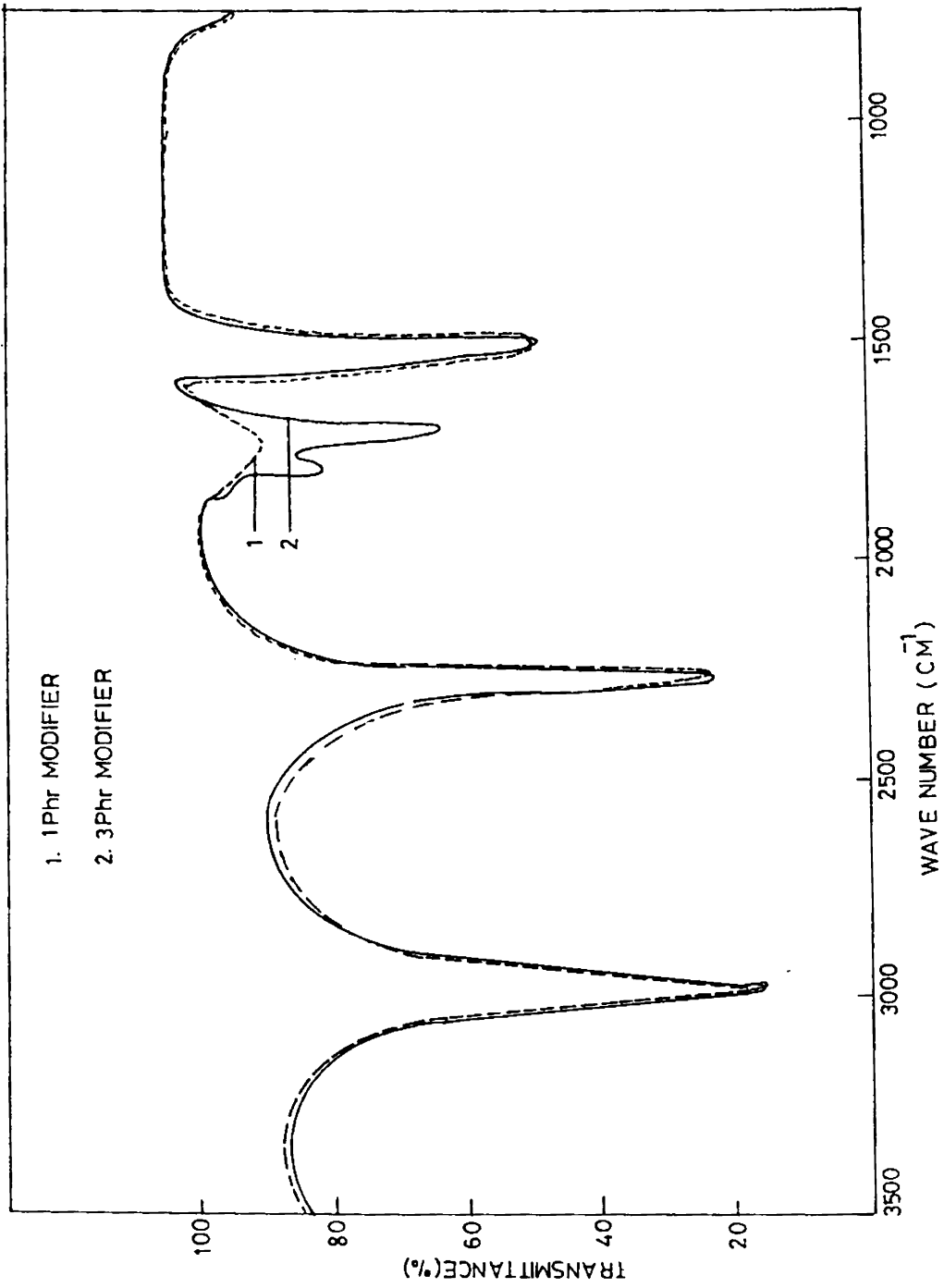


Fig.5.7 IR spectrum of 50/50 NBR/PVC blend in presence of DCP and acrylic acid.

grafting of the modifiers onto the polymer. The width of the absorption peak is shown to be increased with increase in the modifier level.

Results of gel content measurement support this finding. Table 5.2 gives percentage increase in gel fraction values with increase in modifier loading. The gel fractions of the reaction products increase with increase in addition of modifiers.

Table 5.2 Percentage increase in gel content due to grafting

Modifiers	Modifier level (phr)			
	0.1	1	3	5
Maleic anhydride	0.4	0.533	0.96	1.495
Acrylamide	0.32	0.425	0.815	0.9
Acrylic acid	0.35	0.39	0.63	0.7

Fig.5.8 shows the variation of tensile strength with levels of the grafted blends at a constant DCP loading. At a fixed level of DCP, the number of $>C=O$ groups increases appreciably with increase in modifier levels upto 3 phr additions in all cases, whereas acrylic acid and acrylamide grafted blends show some deterioration in properties after that level. The enhancement in tensile strength may be due to the increased polarity arising due to the incorporation of carbonyl groups in the polymer, in addition to the nitrile and chlorine groups, which enhances the interfacial adhesion between the component polymers.

Elongation at break values of the grafted blends are given in Fig.5.9. While an increase in the modifier level increases the tensile strength, a significant reduction in breaking elongation values is observed. The observed effect can be attributed to the fact that as the concentration of modifier increases, there is substantial grafting, which leads to orientation difficulties and the interaction of the grafted groups.

Fig.5.10 shows the modulus of elasticity of the grafted thermoplastic elastomer blends. Analysis of the

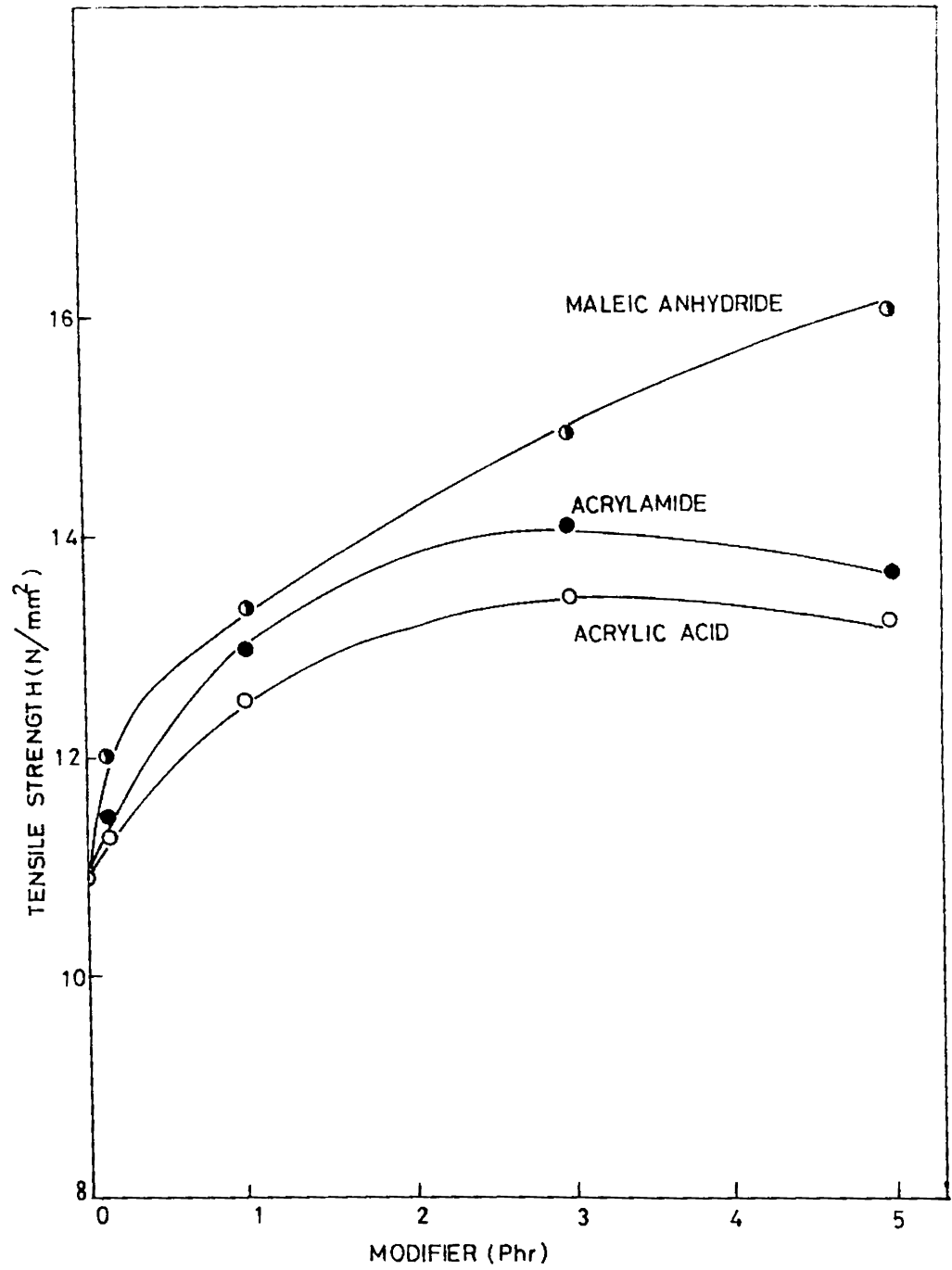


Fig.5.8 Effect of modifiers on the tensile strength of 50/50 NBR/PVC blend.

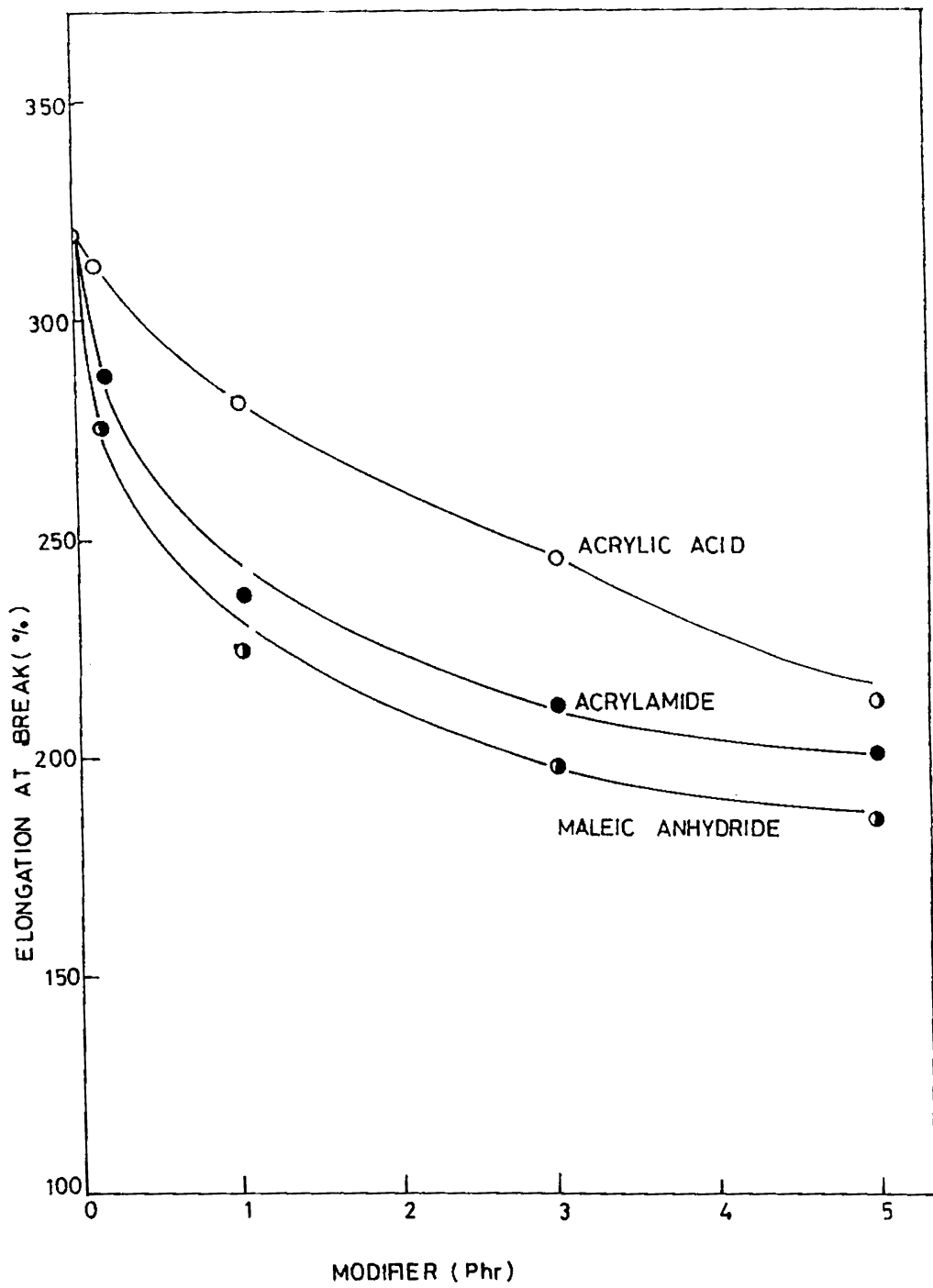


Fig.5.9 Effect of modifiers on the elongation at break of 50/50 NBR/PVC blend.

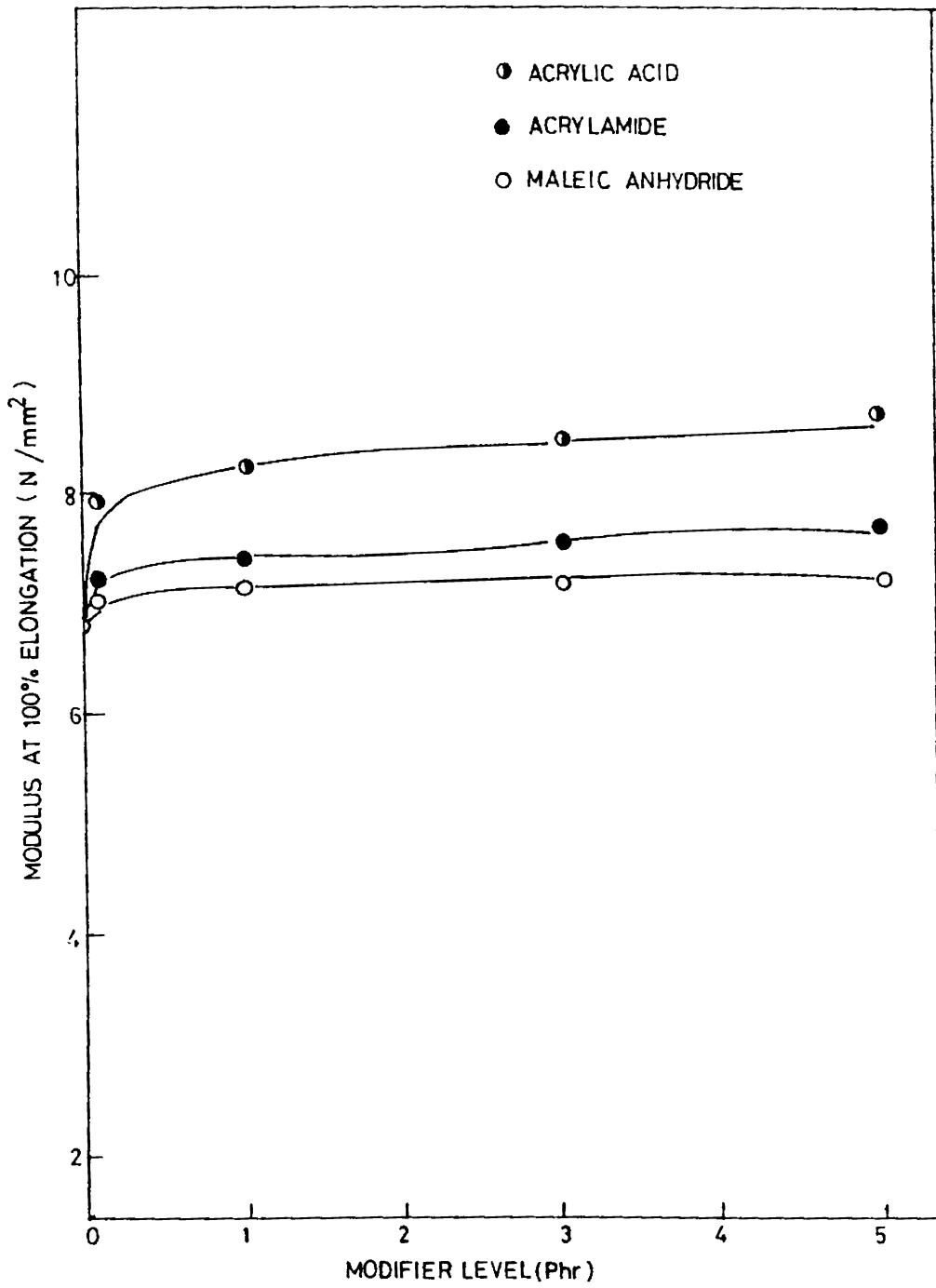


Fig.5.10 Effect of modifiers on the modulus of 50/50 NBR/PVC blend

obtained data indicates an increase in modulus value with increase in extent of grafting due to increase in cross-linking in presence of modifiers.

MORPHOLOGY STUDIES USING SCANNING ELECTRON MICROSCOPE

The tensile fracture surfaces of modified NBR/PVC blends are shown in Figs.5.11-5.13 (fracture surface of unmodified blend was shown in Fig.4.27 (Chapter 4). The obvious differences in the fine structure of the modified blends from the unmodified blend may mainly be due to grafting of the blends in presence of dicumyl peroxide radical initiator. The distribution of globular formations seen in Fig.4.27 becomes more uniform with the addition of modifiers. The granular structure is more prominent in Fig.5.11 (maleic anhydride modified) and this observation is in agreement with the tensile strength of the blend. Figs.5.12 and 5.13 are acrylamide and acrylic acid modified systems respectively. The modified systems having improved mechanical properties than the corresponding unmodified blend have a better co-continuous nature of the phases permitting direct load transfer of the components. The co-continuity of the matrix in the case of modified system is a result of improved adhesion.

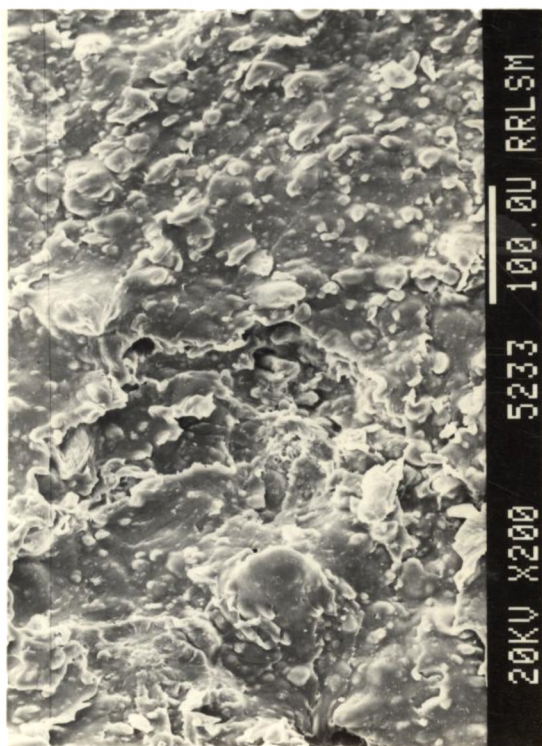


Fig.5.11 Maleic anhydride modified

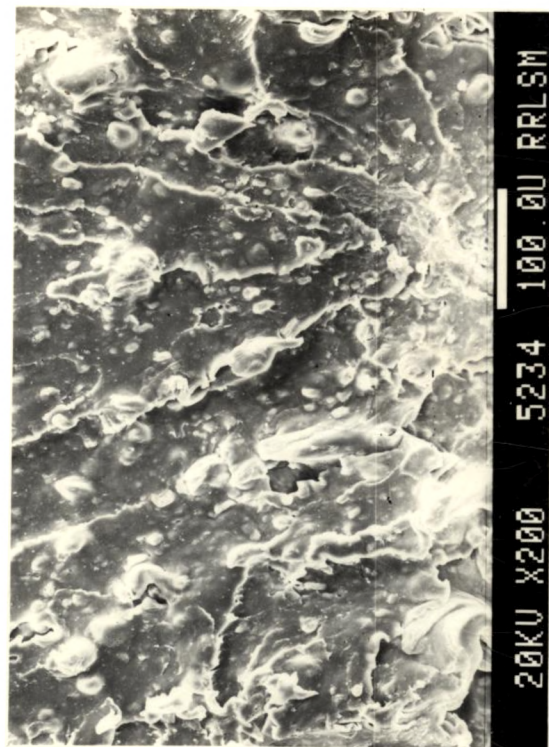


Fig.5.12 Acrylic acid modified

SEM photographs of the tensile fracture surface of 50/50 NBR/PVC blend

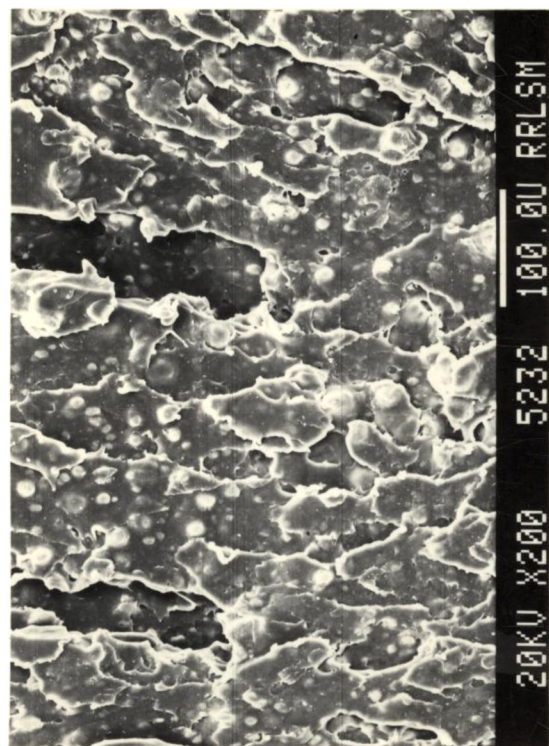


Fig.5.13 Acrylamide modified

SEM photograph of the tensile fracture surface of 50/50 NBR/PVC blend

CONCLUSIONS

Modification of NBR/PVC blends by maleic anhydride, acrylic acid and acrylamide in presence of dicumyl peroxide is found to be useful in improving the compatibility of the blends. The improvement was found to be mainly due to the grafting of $>C=O$ groups to the polymer chains. The modified blends exhibit improved mechanical properties.

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Chapter 6

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Mechanical and rheological behaviour of thermoplastic elastomers based on triblock copolymers viz., SBS, SIS and SEBS were compared with those derived from blends of thermoplastics and elastomers viz., PVC and NBR. The stress-strain behaviour of both these classes of thermoplastic elastomers was more or less similar to that of elastomers. However, certain members of these classes, such as SBS in the triblock polymers and NBR/PVC blends containing fairly high proportions of PVC, show yielding phenomena. Such members also show higher hysteresis loss, showing some deviations from the mechanical behaviour of elastomers.

The peculiar rheological behaviour of both these classes of thermoplastic elastomers stems from the fact that the two phase behaviour of these materials persist even in the melt under normal conditions of processing. Single phase melt flow is achieved only under very high temperature and/or shear which eventually leads to substantial degradations. This means that the two phase behaviour of the melts should normally be taken care of under normal processing operations. Thus SBS, SIS and SEBS

exhibit two distinct flow behaviour depending upon the shear and/or temperature to which they are exposed. The critical factor here is whether the polystyrene domains are destroyed or not. The same two phase melt behaviour is shown by NBR/PVC blends, too, the critical factor in this case being the fusion of PVC particles. The melt elasticity parameters of the two classes of TPEs were also found to exhibit a close similarity with viscosity characteristics. Due to the complex nature of melts, instruments such as Brabender plasticorder in which uniformity of shear and temperature are difficult to achieve may not give a very good rheological representation of such thermoplastic elastomers. For studying the flow transition, a wide range of shear rates is required which is usually not achieved with precision in a Brabender plasticorder.

Of the two classes of thermoplastic elastomers, the one derived from elastomer/plastic blends has slight edge over the triblock copolymers, in the comparative ease with which the properties can be modified over a very wide range by adjusting the composition, characteristics of individual polymers, use of interfacial additives, use of

chemical modifiers, co-crosslinking etc. However, the homogeneity of the blends is dependant upon the processing history which requires close control if uniformity in properties is to be achieved.

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LIST OF PUBLICATIONS FROM THE WORK

1. Rheological behaviour of thermoplastic elastomers
Kautschuk Gummi Kunststoffe, **44**, 450 (1991).
2. Viscous and elastic behaviour of SEBS triblock copolymers
Rubber Chemistry and Technology (Communicated).
3. Modification of thermoplastic elastomers derived from NBR/PVC blends
Journal of Elastomers and Plastics (Communicated).
4. Melt rheology of thermoplastic elastomers derived from NBR/PVC
blends
International Journal of Polymeric Materials (Communicated).
5. Hysteresis behaviour of NBR/PVC blends
European Polymer Journal (Communicated).