STUDIES ON PVC BLENDS WITH SPECIAL REFERENCE TO PVC/CR AND PVC/LLDPE BLENDS

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Miss Jayamma Francis 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 PVC BLENDS WITH SPECIAL REFERENCE TO PVC/CR AND PVC/LLDPE BLENDS" is the original work carried out by me under the supervision of Dr.K.E. George, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022, and no part of this thesis has been presented for any other degree from any other institution.

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JAYAMMA FRANCIS.

CONTENTS

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LIST OF ABBREVIATIONS USED IN THIS THESIS

Polymers

PVC	Poly(vinyl chloride)
PE	Polyethylene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
HDPE	High density polyethylene
PP	Polypropylene
PS	Polystyrene
PMMA	Poly(methyl methacrylate)
ABS	Acrylonitrile-butadiene-styrene
MBS	Methyl methacrylate-butadiene-styrene
EVA	Ethylene-vinyl acetate
CPE	Chlorinated polyethylene
SBS	Styrene-butadiene–styrene
SIS	Styrene-isoprene-styrene
SEBS	Styrene-ethylene-butylene-styrene
SAN	Styrene-acrylonitrile
POM	Poly(oxy methylene)
NR	Natural rubber
NBR	Acrylonitrile-butadiene rubber
SBR	Styrene-butadiene rubber
ESEBS	Epoxidised styrene-ethylene-butylene-styrene

CR	Polychloroprene rubber
EPDM	Ethylene-propylene-diene rubber
BR	Polybutadiene rubber
ENR	Epoxidised natural rubber

Additives

S	Sulphur
TMTD	Tetra methyl thiuram disulphide
CBS	N-cyclohexyl-2-benzthiazyl sulphenamide
IPPD	Isopropyl p-phenylene diamine
ZnO	Zinc oxide
MgO	Magnesium oxide
TBLS	Tribasic lead sulphate
DCP	Dicumyl peroxide
NA-22	Ethylene thiourea
$SnCl_2$	Stannous chloride

Other abbreviations

ISNR	Indian standard natural rubber
ASTM	American Society for Testing and Materials
μm	Micrometer
rpm	Revolutions per minute
phr	Parts per hundred rubber/resin
LOI	Limiting oxygen index

Tg	Glass transition temperature
T	Temperature
δ	Solubility parameter
ϕ	Volume fraction
ML(1+4) 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.
MFI	Melt flow index
ΔG_m	Free energy change of mixing
ΔH_m	Enthalpy change of mixing
ΔS_m	Entropy change of mixing
ΔE_m	Internal energy change of mixing
η	Viscosity
τ_{wapp}	Apparent shear stress at the wall
γ_{wapp}	Apparent shear rate at the wall
τ_w	True shear stress at the wall
$\dot{\gamma}_w$	True shear rate at the wall
ΔP	Pressure drop
P_c	Entrance pressure loss
L	Length of capillary die
R	Radius of the capillary die
Q	Volumetric flow rate
n	Power law index
E	Activation energy
R	Gas constant

D_e	Diameter of the extrudate
D	Diameter of the capillary die
γ_R	Recoverable shear strain
M	Torque
S	Revolutions per minute of the Brabender rotor
Mg	Meter gram
Mrad	Mega rad
MPa	Mega Pascal
IR	Infra red
K	Consistency index
Nm	Newton meter

Chapter 1

INTRODUCTION

INTRODUCTION

Development of new molecules and chemical modifications of existing ones have been the most common ways of facing new challenges for polymeric materials. These routes have become increasingly complex and expensive over the years and thus alternative ones have become more interesting and attractive. Polymer blending is one such approach that is presently in a state of rapid scientific and commercial development. The reduced probability of finding new, inexpensive and wide utility homopolymers led to the blending technology as one of the fastest growing segments of polymer technology. The increasing range of application makes polymer blending more attractive.[1-6] The rapid development and commercialisation of polymer blends is due to their

quick modification of performance,

higher performance at reasonable price,

ability to extend the performance of expensive resins

and potential for recycling of plastic wastes.

BASIC THEORY OF BLENDING

A successful polymer blend is a cost effective mixture of two or more polymers with a better combination of different properties. Depending upon the polymer miscibility, the blends can be classified as miscible, partially miscible and immiscible, or in a technological sense as compatible, semicompatible and incompatible. An ideal blend is one which is homogeneous and behaves like a single component system. A large number of compatible polymer blends and alloys have been investigated and successfully commercialised.[5-9] Alloys are a class of polymer blends in which a large interpenetration of domains is secured by physical and/or chemical means. Although the terms alloys and blends are often used synonymously, they differ in the level of thermodynamic compatibilities and resulting properties. On the high end of the compatibility spectrum are the alloys. Alloys give a tighter, denser molecular structure than blends.

The structure and stability of polymer blends depends primarily on the miscibility of polymers used in its preparation. Miscibility is governed by the Gibbs free energy of mixing (ΔG_m). The thermodynamic condition for obtaining miscible blend is that the free energy of mixing must be negative

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

where ΔH_m is the change in enthalpy, ΔS_m the change in entropy upon mixing and T, the absolute temperature. Since the entropy term is negligible for polymers, the heat of mixing ΔH_m is the key factor deciding the polymer-polymer miscibility. In the case of purely dispersive forces ΔH_m is always positive. Consequently, high molecular weight systems with this type of interaction are rarely miscible. Miscibility drops significantly with growing chain length. If however, there exist so called specific interactions (ion-dipole interactions, hydrogen bonds) between the components, then ΔH_m can be negative and the polymers can become miscible. Or, in otherwords, miscibility depends upon the degrees of interaction among the polymer components.[7-14] From the standpoint of selecting polymer blends, a quantitative means of predicting the affinities of polymer pairs in terms of easily measured properties of the components would be desirable. One possibility is through the use of solubility parameter δ , which has proved useful in the study of the dissolution and swelling of polymers in low molecular weight liquids.[15] Compilation of the solubility parameters of the polymers is available.[16] For nonpolar liquids the internal energy change upon solution is given by $\Delta E = \emptyset_1\emptyset_2(\delta_1-\delta_2)^2$(cal/cc of solution) where $\emptyset$s are volume fractions of the components. Realising that amorphous polymers are essentially liquids and assuming that the volume change upon mixing is negligible this is an expression for the change in enthalpy on solution since $\Delta E = \Delta H$ for constant volume, constant pressure process. This equation always results in a positive ΔH, indicating that for nonpolar high polymers, where the $T\Delta S$ term is small, true solution will not occur unless the δ s are almost perfectly matched.

Most of the polymer pairs are thermodynamically unfavourable to form homogeneous mixtures and mixing them leads to multiphase systems. Inorder to achieve a homogeneous or a compatible blend, it is necessary to choose polymer components capable of specific interactions among them leading to negative heats of mixing.

The usual miscibility criterion is the measurement of glass transition temperature T_g. Miscible polymers are considered to be those which give a blend with a single glass transition temperature dependent on the composition of the blend. Polymers, which in a blend, exhibit two or more T_gs, corresponding to the glass transition temperatures of the individual components are considered to be immiscible.[10,17]

METHODS OF PRODUCING POLYMER BLENDS

The simplest and most direct method is mechanical blending. This may be accomplished on two roll mill or in internal mixers , eg., Banbury. The nature of the resulting dispersion depends on the length of mixing, the shear field in equipment, temperature, rheological properties of the component polymers etc. Also there is a possibility of chemical effects produced by the milling operation.

When the individual components can be obtained in latex form, they may be conveniently combined by blending the latices. The polymer is then recovered by coagulation or spray drying. This method results in an intimate, uniform dispersion. However, one drawback is the difficulty in completely removing the nonpolymer material (emulsifier etc.) present in the latices.

Mixing of polymer solutions is in practice mainly used for coatings, because it allows rapid and easy mixing of the components at low energy costs, leads to simple applications at normal temperatures and neither causes degradative colour changes nor premature crosslinking reactions. But, for the preparation of the solid polymer blends, this method requires removal of the solvent, which usually leads to phase separation. Furthermore, the use of solvents implies problems connected with their price, toxicity, flammability, pollution and the economics of the whole process. Usually only laboratory samples of solid polymer blends are prepared by this method.

Blends may also be prepared by dissolving a polymer in the monomer of the other component and then polymerising the second component. This may result in appreciable grafting of the polymer in addition to good dispersion.

PROPERTIES OF POLYMER BLENDS

A wide range of properties can be achieved by blending which includes mechanical, electrical and chemical properties along with processability. Compatibility is the fundamental property deciding the practical utility of a polymer blend.[1,11,18] Polymer blends can be described by the following equation:

$$P = P_1C_1 + P_2C_2 + I\ P_1P_2$$

where P is the property value of the blend, P_1 and P_2 the properties of the isolated components and C_1 and C_2 the respective concentrations of the constituents. I is a term for the system which defines the level of synergism created by the combination of the two components.

For $I > 0$ the property is synergistic
$I = 0$ the property is additive
$I < 0$ the property is nonsynergistic.

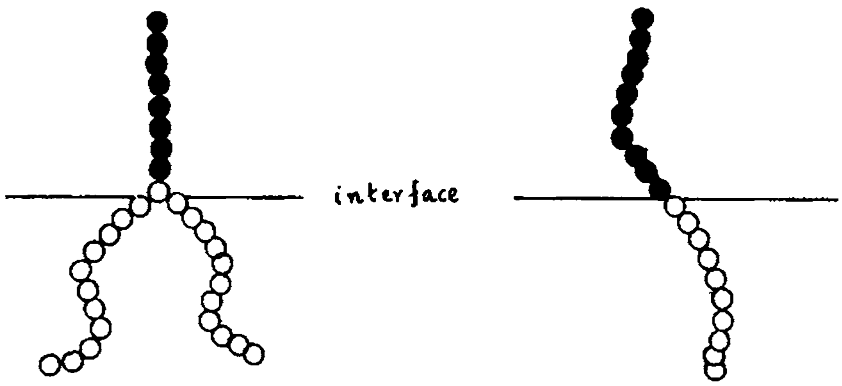
The most important factor governing the ultimate properties of a polymer blend is the intermolecular bonding force between the molecules. The low interaction at the interface is responsible for its tendency towards phase separation under various conditions (stress, blend ratio and temperature). The poor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

INTERFACE MODIFICATION IN POLYMER BLENDS

The performance of a polymer blend is dependent upon the strength of the interface. It is possible to make a polymer blend compatible so that the resultant properties may be more synergestic and the blend becomes more homogeneous. Modification of polymer blend can be achieved by a variety of ways.[18,19]

By Addition of a Polymeric Compatibiliser

The incorporation of block, graft or random copolymers whose chemical structures are identical with the blend components is found to promote miscibility. Such compatibilisers are able to make specific interactions with each of the blend components.[20-24] Di or triblock copolymers of styrene and butadiene have been found to be more useful in this way to act as interfacial agents in blends of polyolefine/polystyrene (PS) mixtures. Diblocks are more efficient interfacial agents than triblock or graft copolymers.[25-27] Ethylene-propylene-diene rubber (EPDM) and poly (methyl methacrylate) (PMMA) can be made more or less compatible by adding EPDM-g-MMA copolymer.[28] The compatibilising or emulsifying action of certain solid phase dispersants in poly (vinyl chloride) (PVC)/Polyethylene (PE) and PVC/PS blends has been reported earlier.[29-34] Boutevin et al.[35] investigated P(E-g-MMA) copolymers as a compatibiliser to low density polyethylene (LDPE)/PVC blends. They found values of tensile strength to be almost double compared to those of homopolymer mixtures. Statistical copolymers have also been found to be useful to a limited extent as in the case of ethylene-propylene rubber compatibilising polypropylene (PP) and high density polyethylene (HDPE).[36-39] The compatibilisers can be either added separately or may be formed in situ during blending.



Compatibilising action of a block or graft copolymer

By Blending Functionalised Polymers

Chemical modification of polymers is a common means of improving properties of the polymer blends. Blending of polymers containing carboxyl and epoxy groups has been reported as a promising way to promote interfacial strength.[18,40-42] The reactive blending of such functionalised polymers is followed by the in situ formation of compatibilising interchain polymers. Carboxyl terminated butadiene/acrylonitrile rubber (NBR) has been utilised for the successful blending with epoxies. Polypropylene can be functionalised to link with functionalised NBR during melt mixing.[21] As a result, improved ultimate properties are achieved by making the polymer blend less incompatible.

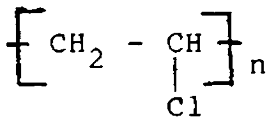
By Addition of Low Molecular Weight Materials

A veriety of low molecular weight chemicals can also act as modifiers or compatibilisers through reactions such as grafting, crosslinking, co-crosslinking etc. Recently,grafting of maleic anhydride on LDPE followed by blending with PS was investigated by Liu et al.[41] as a possible means for improving the compatibility. The addition of some polyfunctional monomers in presence of peroxide was reported to be effective in blends of PVC with polyethylene.[43,44] Mori and Nakamura studied the effect of co-crosslinking by triazine trithiols on the property modification for a series of blends.[45-47] Examples of the class include PVC/NBR, PVC/CR and PVC/EPDM.

The continuous nature of the phases as a result of such interface modifications leads to efficient force/stress transfer between the component phases.

PVC BASED POLYMER BLENDS

Poly(vinyl chloride) (PVC) is a versatile polymer, used in flexible, semirigid and rigid forms. In world wide plastic production it is second only to polyolefines. The rapid expansion and consumption of PVC is due to lower cost, greater availability, good mechanical properties and diversity of its properties.[48-50] It is mainly produced by the polymerisation of vinyl chloride by suspension method. The structure of PVC is,



$$\left[CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} \right]_n$$

Although PVC has many desirable properties, it has two shortcomings in commercial applications: poor processability and poor impact strength. Common ways of overcoming poor processability are to mix with plasticizers or to increase the processing temperature. There are associated disadvantages since by the former method, it is not possible to obtain high impact strength because of antiplasticizing effect and by the latter method there is a risk of thermal degradation. Also low molecular weight plasticizers of PVC have a tendency to leach out on ageing. These problems can be solved successfully by the addition of small amounts of polymeric modifiers/plasticizers to yield polymer blends.[51-53] Hence polymeric plasticizers like chlorinated polyethylene (CPE), ethylene-vinyl acetate (EVA), acrylonitrile-butadiene rubber (NBR), polyether-ester block copolymer (Hytrel) etc. are being used.[54-57] PVC behaves generally as an electron acceptor and thus should interact strongly with electron donors. In fact, it is said that of all polymers studied to date, PVC is the most miscible with structurally different homopolymers and copolymers. A lot of work has been done on the compatibility of PVC with various polymeric plasticizers.[58,59] Combining nonpolar elastomers with PVC is one of the promising methods of increasing the oil, petrol and fire resistance of the vulcanizates based on them.[60] Majority of the PVC systems show multiphase behaviour. Yet, they are used in several applications. The mechanical properties of such blends are far inferior to those expected. This is probably due to the low level of compatibility between the polymers and also the insufficient fusion characteristics of PVC particles. Deak et al.[61] studied the effect of small quantities of additives on the properties of rigid PVC and PVC modified with other polymers.

BLENDS OF ELASTOMERS WITH PVC

One of the most prominent needs for PVC in application end use is permanent plasticization. A very important and commercially significant blend is that of NBR and PVC.[62-65] NBR acts as a permanent plasticizer for PVC and at the same time PVC improves the ozone, thermal ageing and chemical resistance of NBR. PVC/NBR blends are used in applications such as wire and cable insulation, O-rings and oil seals, printing roll covers, gaskets, fuel hose covers, shoe soles, anti static floor tiles etc. The amount and type of vulcanising system has a great effect on the properties of the blends. The effect of non-conventional vulcanising system for property modification of PVC/NBR blends was investigated. P-nitrosophenyl amine plays the role of a modifier and aids the vulcanisation of the blend in presence of sulphur (S) and TMTD.[66] More recently modification of NBR/PVC blends was studied using natural rubber (NR), polybutadiene rubber (BR) and styrene-butadiene rubber (SBR).[67] Co-crosslinking is found to be an effective means of improving the mechanical properties of the blends. Triazine trithiols can be used effectively as a co-crosslinking agent for PVC/CR, PVC/NBR and PVC/EPDM blends.[45-47] Blending of SBR with PVC results in a marked improvement in the impact strength of PVC.[68] The effect of addition of a third component on the mechanical properties, compatibility and morphologies of the PVC blends with SBR and BR was investigated.[69] NBR is found to be a good compatibiliser for PVC/SBR and PVC/BR blends. Properties of PVC/EPDM blends modified with CPE were also investigated.[70] The mechanical, rheological and morphological studies of PVC/Epoxidised natural rubber (ENR) have shown that higher levels of epoxidation makes NR to be more compatible with PVC.[71,72] Mixing with PVC is found to be an effective method for the property modification and cost reduction of high priced speciality rubbers like polysulphide and chloroprene rubber (CR).[73,74]

BLENDS OF OTHER PLASTICS WITH PVC

The impact resistance of PVC can also be improved by introduction of polymeric modifiers in particular acrylonitrile-butadiene-styrene (ABS) or methyl methacrylate-butadiene-styrene (MBS) plastics. The toughness and processability of ABS combines with the flame resistance of PVC in PVC/ABS blends. The miscibility of the system depends upon the acrylonitrile content in ABS. PVC/ABS and PVC/MBS blends are noted for their good dimensional stability. PVC/ABS blends have been utilised for interior truck panels, communication relays, electrical housings, appliance housings, television housings etc.[75] The impact modification of PVC by CPE has been reported earlier. CPE also acts as a permanent plasticizer for PVC.[76] Recently, compatibilisation of PVC/CPE blends with epoxidised NR has been studied by Stathis and coworkers.[77] The effectiveness of epoxidised hydrocarbons to produce compatible polymers were reported by several research groups.[33] Epoxidised SBS was found to be a typical example for improving the compatibility of PVC/PS systems. PVC/PMMA blends combine the heat resistance of PMMA with chemical and flame resistance of PVC in some applications.[78] The main application of this blend is in mass transit vehicles. Paul and Barlow[79] studied the miscibility behaviour of PVC/styrene-acrylonitrile (SAN) copolymers. NBR is found to be useful for the compatibilisation of poly vinylidene-fluoride co-vinyl chloride/PVC blends. The effect of some solid phase dispersants on the mechanical performance of the immiscible PVC/PE blends was studied as a means for reutilisation of these plastic wastes.[29,32,80] Functionalised polyolefine/PVC blends are used for the development of low halogen and non-halogen, fire resistant, low smoke cable sheathing compound.[81] PVC/PE combinations are also used for the preparation of thermofoamable blisters.[82] Mixtures of acrylic terpolymer with PVC are used for preparing adhesive sealent compositions with improved properties and enhanced outdoor resistance.[83] The processability of PVC can be improved by the addition of EVA, CPE, Hytrel etc.[54-57,84]

COMMERCIAL PVC BLENDS

Mixing of PVC with various types of polar and non-polar polymers changes the properties of PVC, so significantly that the application spectrum of this polymer is continuously increasing. The commercially important blends of PVC and their properties are given in Table 1.1.[1]

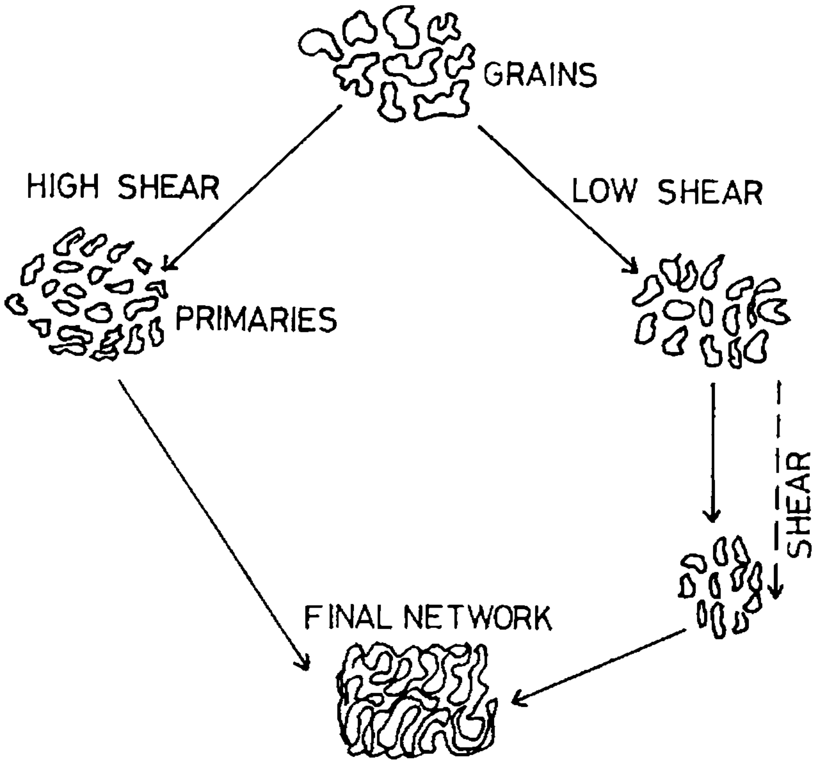
Table 1.1

No.	Additive	Improved property
1.	ABS; MBS	Impact resistance, hardness, tensile strength, distortion temperature.
2.	Acrylics	Impact resistance, transparency, chemical resistance, oil resistance, mouldability.
3.	Poly(caprolactone)	Plasticization, mouldability, impact resistance.
4.	SAN	Low temperature toughness, processability, dimensional stability.
5.	Poly(imide)	Transparency, high distortion temperature, impact resistance.
6.	Poly(urethanes)	Plasticization, tensile strength, impact resistance, low temperature toughness.
7.	Nitrile rubber	Plasticization, toughness.
8.	EVA	Plasticization, toughness, adhesiveness.
9.	Chlorinated PE	Processability.

10.	Poly(vinyl chloride-g-ethyl-acrylate)	Impact resistance, thermal stability, processability.
11.	PE + CPE	Ductility, elongation, low temperature toughness
12.	PB	Toughness, weatherability.
13.	Hytrel	Low temperature toughness, plasticization.
14.	PVC/EVA copolymer	Processability, mechanical properties.
15.	Chlorinated POM	Processability, plasticization.

FUSION OF RIGID PVC

PVC differs from other widely used plastics like PE, PS, PP in that the polymer has a distinct structure. Suspension PVC consists of grains of about 100 µm size. Inside these grains, smaller primary particles of about 1 µm size are found partly agglomerated to larger units. This hierarchial structure of PVC has to be destroyed in order to get a thermoplastic melt necessary for processing rigid PVC.[85] Fusion involves the loss of identity of grains and primary particles of PVC which is highly dependant upon both shear and thermal history of PVC.



Fusion mechanism of PVC

The processing behaviour and end use properties of PVC are strongly influenced by the degree of fusion.[85-89]

RHEOLOGY OF PVC BLENDS

The rheological properties of polymer melts have been studied extensively over the past decade. These studies have concentrated on pure polymer systems. Recently rheological properties of polymer mixtures are also being studied due to the great practical use of such mixtures. Investigation of the rheological properties of the mixtures will make it possible to assess their behaviour during manufacture into article. Moreover, the rheological properties of mixtures help gaining insight into the structure of polymer melts.[89-91] In regard to two phase flow of molten polymers, rheology should clearly be known to rationally design processing devices and to smoothly operate equipments which handle two phase systems. One of the most fundamental requirements is to determine the rheological properties of a given two phase system in terms of viscosities and elasticities of individual components, composition ratio and melt temperature. Rheology of PVC blends is particularly important due to the fusion behaviour of PVC.[90-93] The mechanical strength of PVC blends is critically dependant upon the fusion state of PVC and hence study of the processing characteristics of PVC blends is of great importance.

OBJECTIVES AND SCOPE OF THE PRESENT WORK

The present investigation is mainly on PVC blends. PVC resins surpass every class of polymers in world wide commercial importance, both in diversity of applications and in total tonnage of finished products. The factors responsible for PVC's number one position are low cost and ability to be compounded into various flexible and rigid forms with good physical, chemical and weathering properties. In addition, PVC has broad processability including calendering, extrusion, moulding (injection, compression, rotational, blow) fluid (solution, latex, organosol, plastisol) coating and impregnation.[64]

PVC formulations contain varying amounts of the following ingradients in order to give the polymer the desired processing and end use characteristics.

Plasticizers
Polymeric modifiers
Fillers
Heat stabilisers
Lubricants
Colourants
Light stabilisers
Blowing agents
Flame retardants.

The present study is mainly in the area of solid polymeric modifiers for PVC. The first part of the study is on PVC/Elastomer blends. Polymeric modifiers can be classified into four categories: those that plasticize, increase impact strength, increase heat distortion temperature and improve processability. The property modification is highly dependent upon the miscibility of the modifying polymer with PVC. By far the wide range of polymeric modifiers for PVC fall into the broad category that can be classified as partially miscible. A broad range of properties may be obtained depending upon the degree of miscibility. These polymers can increase the rate of fusion of PVC powder leading to a more rapid formation of a homogeneous melt having higher melt strength. The present study on the blends of PVC with elastomers was undertaken with a dual purpose of improving the fusion behaviour and melt strength of PVC along with imparting special properties to the elastomers. Effect of compatibilizers in improving the mechanical and processing behaviour of PVC/Elastomer blends is a major part of the study.

The second part of the study is on PVC/Linear low density polyethylene (LLDPE) blends. The study was selected mainly as a possible means of reprocessing mixed scrap or waste plastics, since PVC and polyethylene form a sizable fraction of such wastes.[94] Their lack of biodegradability is generating new problems owing to their large space requirements and the possible damage to the environment by the various materials contained in them. The best solution to reducing waste, according to many scientists, is a combination that includes bio-degradable plastics and plastic recycling. However, by 2002 bio-degradable plastics are expected to account for only three per cent of all plastic packaging waste and hence there is very good scope for polymer recycling in the years to come.

Recycling by reprocessing of plastic waste is a major solution to the problem.[31,80] However, blends of mixed scrap or waste plastics usually have very poor ductility and toughness, a situation which renders their practical use difficult. This problem generally exists because the ingradients of most polymer blends are grossily incompatible and separate into individual phases. Application of mechanical stress usually results in interfacial failure.[2,4,7] It has been shown that mechanical properties of the blends of incompatible polymers can be significantly improved by addition of agents which improve interfacial adhesion. The most common compatibilisers are block, graft or random copolymers, co-solubilisers enhancing interpenetration of resin domains, co-reactants or catalysts enhancing chemical reaction between the resins and modifiers or additives enhancing the specific interactions.[1]

Co-crosslinking of the polymers is also a special means of achieving miscibility.[43,44] Several of these methods are investigated as possible means of improving the mechanical behaviour of PVC/LLDPE blends.

This thesis is divided into five chapters.

Chapter 1 : Introduction

Chapter 2 : Experimental Techniques

Chapter 3 : Studies on Poly(Vinyl Chloride)/Elastomer Blends

Chapter 4 : Studies on Poly(Vinyl Chloride)/Linear Low Density Polyethylene Blends

Chapter 5 : Summary and Conclusions

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Chapter 2

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

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

MATERIALS

Polymers

1. Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) used was extrusion grade since it is easy to achieve a better fusion state with this grade. PVC-1 was suspension polymer as powder with a K value of 65. PVC-2 was also suspension polymer as powder with a K value of 67. Both grades were supplied by IPCL, Baroda.

2. Linear low density polyethylene

Two grades of linear low density polyethylene (LLDPE) were used. LLDPE-1 was Ladene 218 W with a melt index (g/10 min) of 2 and density 0.918 (g/cm^3). The other grade of LLDPE was Ladene 118 W with a melt index (g/10 min) of 1.0 and density 0.918 (g/cm^3). Both grades were obtained from IPCL, Baroda.

3. Natural rubber

Natural rubber (NR) used was solid block rubber ISNR-5 grade obtained from Rubber Research Institute of India, Kottayam. The Mooney viscosity [ML(1+4) at 100°C] of the rubber was 85.3.

4. Acrylonitrile-butadiene rubber

Acrylonitrile-butadiene rubber (NBR) was obtained from Synthetics and Chemicals Ltd., Bareilly. The rubber had an acrylonitrile content of 33% and a Mooney viscosity [ML(1+4) at 100°C] of 40.9.

5. Polychloroprene rubber

Polychloroprene rubber (CR) used in this study was W type with a Mooney viscosity [ML(1+4) at 100°C] of 47. The rubber was supplied by Du Pont, USA.

6. Styrene-butadiene rubber

Styrene-butadiene rubber (SBR) had a styrene content of 23.5% and a Mooney viscosity [ML(1+4) at 100°C] of 49.2. The rubber was obtained from Synthetics and Chemicals Ltd., Bareilly.

7. Ethylene-propylene-diene rubber

Ethylene-propylene-diene rubber (EPDM) used was JSR EP.33 and had a Mooney viscosity [ML(1+4) at 100°C] of 52.

8. Chlorinated polyethylene

Chlorinated polyethylenes (CPE) used in this study were the following grades.

a) CPE-1 Chlorine content - 38% ;
Mooney viscosity [ML(1+4) at 120°C] - 51

b) CPE-2 Chlorine content - 41% ;
Mooney viscosity [ML(1+4) at 120°C] - 74

c) CPE-3 Chlorine content - 35% ;
Mooney viscosity [ML(1+4) at 120°C] - 87.

All the three grades were obtained from Hoechst, Germany.

9. Hytrel

A polyether-ester block copolymer (40 D) obtained from Du Pont, USA, which is composed of hard crystalline segments and soft elastomeric segments.

10. Ethylene-vinyl acetate

Ethylene-vinyl acetate (EVA) copolymer used in this study had a vinyl acetate content of 30% and melt flow index MFl(190/5) = 200. It was supplied by Poly Olefins Industries Ltd., Bombay.

Polymer Additives

1. Tribasic lead sulphate (stabiliser)

Tri basic lead sulphate (TBLS) used was commercial grade with a specific gravity of 7.0.

2. Irgastab A 70 (stabiliser)

Amino crotonate (Irgastab A 70) used in this study was a metal free stabiliser.

3. Dicumyl peroxide (crosslinking agent)

Dicumyl peroxide (DCP) used was crystal with purity 99% and density 1.02(gm/cm^3). The recommended processing temperature of the material is 160-200°C.

4. Phenolic resin

Phenolic resins used in the study were the following grades:

Phenolic resin-1: Powder, containing hexamine (9%)

Phenolic resin-2: Yellow, clear lumps, containing methylol (11%)

Both resins were obtained from Indian Plastics, Bombay.

5. Other additives

P-phenylene diamine, acrylic acid, maleic anhydride and stannous chloride were commercial grades.

6. Zinc oxide

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

Specific gravity	: 5.5
Zinc oxide content	: 98%
Acidity	: 0.4% max.
Heat loss (2 hrs. at 100°C)	: 0.5% max.

7. Stearic acid

Stearic acid used in the study had the following specifications:

Melting point	: 50-69°C
Acid number	: 185-210

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

It was supplied by Godrej Soap (Pvt.) Ltd., Bombay.

8. Tetra methyl thiuram disulphide

Tetra methyl thiuram disulphide (TMTD) used was supplied by Poly Olefines Industries Ltd., Bombay having the following specifications:

Melting point : 136°C
Specific gravity : 1.40

9. N-cyclo hexyl-2-benzthiazyl sulphenamide

N-cyclo hexyl-2-benzthiazyl sulphenamide (CBS) was supplied by Poly Olefines Industries Ltd., Bombay and had the following specifications:

Ash : 0.5% max.
Moisture : 0.5% max.
Specific gravity : 1.27

10. Sulphur

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

Specific gravity : 2.05

Acidity : 0.01% max.

Ash : 0.10% max.

Solubility in CS_2 : 98% max.

11. Magnesium oxide

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

12. Isopropyl p-phenylene-diamine

Isopropyl p-phenylene-diamine (IPPD) was commercial grade supplied by Poly Olefines Industries Ltd., Bombay. It had the following specifications:

Ash : 0.5% max.

Specific gravity : 1.13

13. Ethylene thio urea

Ethylene thio urea (NA-22) was commercial grade supplied by Alkali and Chemical Corporation of India Ltd., Rishra.

14. ASTM reference oil

ASTM reference oil 3 which conformed to the specification given in ASTM D 471 (1983) was used.

15. Solvents

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

EXPERIMENTAL METHODS

1. Brabender Studies

A Brabender plasticorder (torque rheometer) model PL 3S was used for various investigations. It is a device for measuring the torque during processing under pre-selected conditions of shear and temperature. The mixing chamber (40 cc capacity) which is the central part of the machine is heated by oil circulating thermostat heating tanks. The mixer temperature can be adjusted with the contact thermometer in the heating tank. High temperature silicone oil is used as heating tank liquid and the temperature on the mixer can be varied upto 300°C. The measuring head is equipped with a stock temperature thermocouple coupled with a temperature recorder for temperature measurement. The mixing or shearing of the material in the mixing chamber is done by two rotors. Various types of rotors can be used, depending upon the nature of the polymers. A speed controlled DC drive thyristor allows the rotor speed adjustment between 0 to 150 rpm. The measurement is based on the fact that the resistance which is put up by the material against the rotors in the chamber is made visible as a means of viscosity in the dynamometer. The torque is plotted continuously against time. Torque upto 20,000 meter grams can be measured by the torque-rheometer.

In the present study, Brabender plasticorder was used for blending different polymers, to study the fusion behaviour and thermal stability of PVC compounds, and to assess the processability of PVC blends.

a) Blend preparation

Polymer blends were prepared in the Brabender plasticorder equipped with roller mixing heads according to ASTM D 3184 (1980) and 3182 (1982). Blending parammeters were selected based on torque-temperature data of the individual components and the particular blend. The basic principle followed in every blending was to ensure the melting (fusion) of the polymers and the compatibiliser (if any) at the minimum possible temperature to keep polymer degradations to minimum.

b) Fusion studies

Fusion testing of PVC compounds was done in the Brabender plasticorder[1,2] as per ASTM D 2538-69. A typical Brabender torque-time curve (fusion curve) for PVC or PVC blend is shown in Fig.2.1. The following relevant data can be taken from the torque-time curve. Point A is the fusion peak, Period B is the portion of the curve referred to as equilibrium. At this period in the processing curve, the melt is homogeneous and in a melt state for fabrication to take place. Point C is defined as the onset of crosslinking or degradation and determines the ultimate stability of the compound. This point is defined by the intersection of the slope of the upturning torque and the equilibrium torque. Stability time is the difference between the degradation time (Point C) and fusion time (Point A).

c) Thermal stability tests

Dynamic thermal stability

The simultaneous action of mechanical shearing and temperature stimulates the degradation process in the processing machine. It is well known that the degradation of PVC is followed by HCl elimination which accelerates further degradation catalytically. The degree of

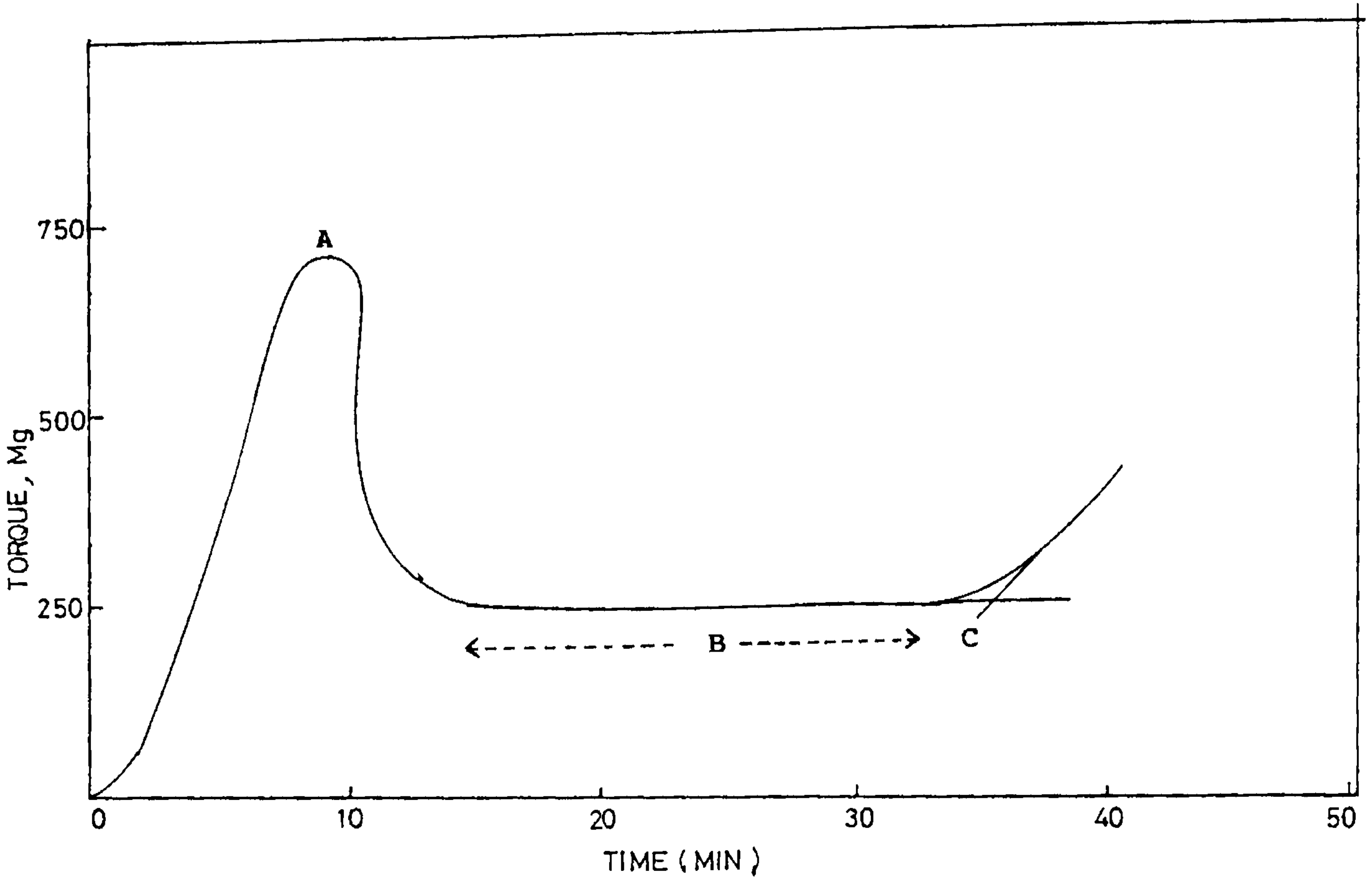

Fig.2.1: A typical Brabender torque-time curve (fusion curve)

degradation is indirectly measured by the increase in torque.[3-5] The development of colour in the material during the processing is an indication of the extent of PVC degradation. The dynamic thermal stability of PVC compounds is assessed by noting the stability time and the colour change at periodical intervals as per ASTM D 2538. The degree or the order of colour change is noted as follows:[6]

0. Clear
1. Very slight change
2. Slight yellow tinge
3. Pale yellow
4. Yellow
5. Faint tinge of red
6. Pale red
7. Red
8. Deep red
9. Very deep red
10. Dark black

Static thermal stability

The static thermal stability of PVC in presence of compatibilisers was determined by keeping the test samples in an air oven at a particular temperature suitable for the particular composition.[3-6] As in the case of the dynamic test, the extent of degradation can be assessed by the colour development. The static thermal stability was assessed in terms of heating time to reach a certain level of degradation (colour) as per ASTM D 2115 (1974).

d) Processability of PVC blends

The Brabender plasticorder has also been used to study the processing behaviour of polymer melts.[7] The instrument imparts a very complex shearing motion to the polymer and consequently the data obtainable from the instrument cannot be taken as fundamental rheological properties. However, the nature of the shear in the Brabender is similar to that in the actual processing operations such as extrusion or milling and has practical relevance. Another advantage of the system is that due to the complex shearing, the polymer melts at a comparatively lower temperature than the corresponding melting temperature in a capillary rheometer and hence the rheological data can be obtained at comparable shear and temperature that would be employed in the actual processing. However, only the lower shear rate range can be studied using the instrument. It has shown that the relationship obtainable from the Brabender plasticorder in the form,

$$M = C.S^a$$

where M is the torque, S the rpm, and C and a are constants, closely resembles the power law behaviour,[8]

$$\eta = K(\dot{\gamma})^n$$

and hence the Brabender data can be used for calculation of the power law index 'n'. Also torque/rpm of the Brabender plasticorder represents viscosity and the activation energy for viscous flow can be measured from the Brabender Plasticorder from log M vs 1/T plots at different revolutions per minute.[9] The activation energy at constant rpm obtained by this procedure should correspond to the flow activation energy at constant shear rate.

2. Cure Characteristics

The cure characteristics of the elastomers and elastomer blends were determined using a Goettfert Elastograph model 67.85. It is a microprocessor controlled rotorless curemeter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of defined size is kept in the lower half of the cavity which is oscillated through a small deformation angle (± 0.2°). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half. A typical elastograph cure curve is shown in Fig.2.2 and the following data can be taken from the torque-time curve.

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

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

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

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

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

3. Moulding of Test Sheets

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

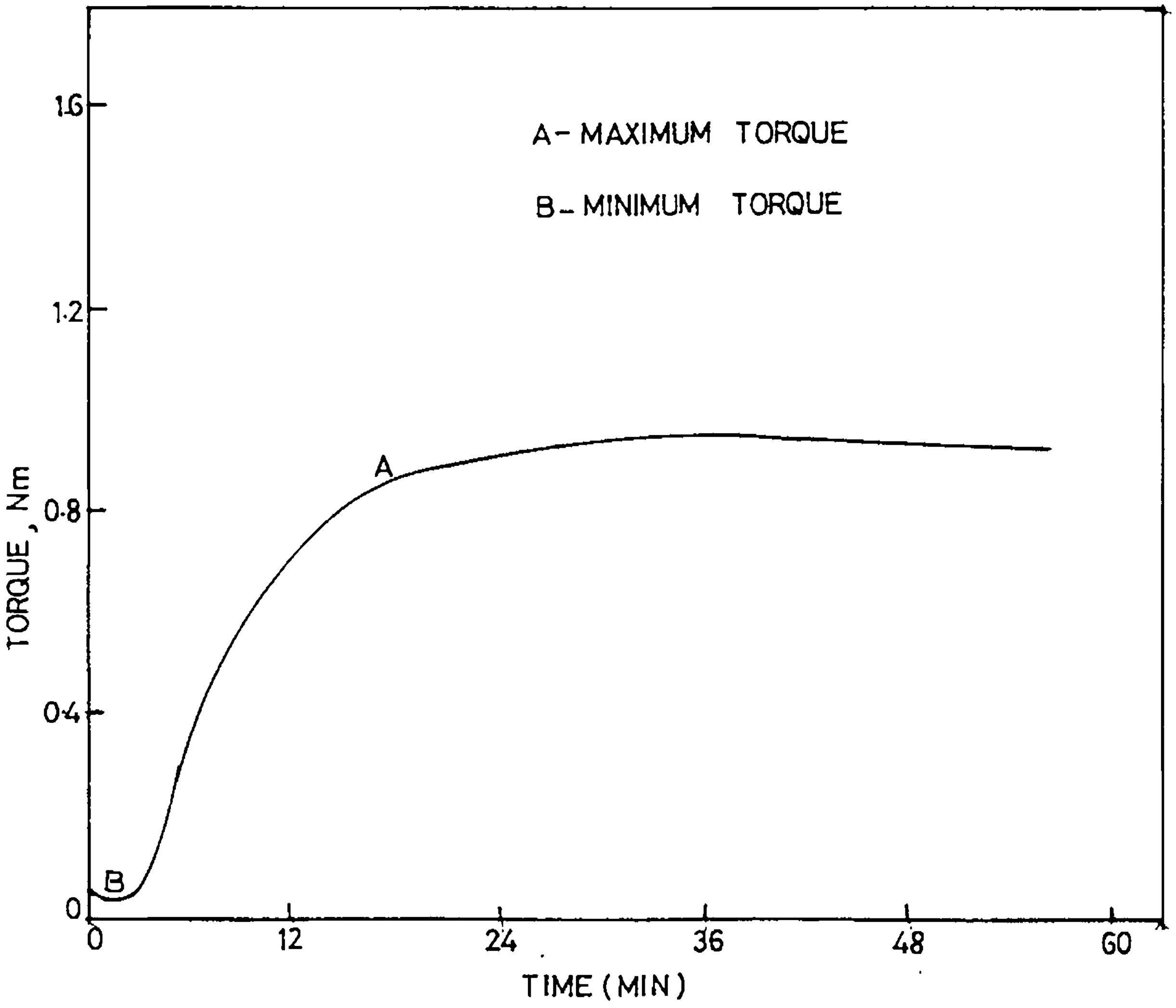

Fig.2.2: A typical Elastograph cure curve

moulding on a single day light electrically heated press having 30x30 cm platens at a pressure of 120 kg/cm^2 on the mould, upto the optimum cure time. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hours and were used for subsequent physical tests. For compression moulding of thermoplastics, specially designed moulds with provision for cooling under pressure were used. In the case of thermoplastics, moulding temperature and time were determined by trial and error methods according to ASTM D 3182 (1982).

4. Physical Test Methods

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

a) Tensile stress--strain behaviour

Tensile properties of the elastomer blends were determined according to ASTM D 412 (1980) using dumbell specimens on a Zwick universal testing machine model 1445. All the tests were carried out at 28 ± 2°C. Samples were punched out from compression moulded sheets using a dumbell die (C-type). The thickness of the narrow portion was measured by a bench thickness gauge. The sample was held tight by the two grips, the upper grip of which was fixed. The rate of separation of the power actuated lower grip was fixed at 500 mm/min. for elastomeric specimens. The tensile properties of the thermoplastic blends were determined according to ASTM D 638 on the Zwick universal testing machine using a cross head speed of 50 mm/min. The tensile strength, elongation at break and modulus are evaluated and printed out after each measurement by the microprocessor.

b) Hardness measurements

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

5. Limiting Oxygen Index Measurement

The relative flammability of PVC blends was measured by the limiting oxygen index method according to

ASTM D 2863-74. Limiting oxygen index is the minimum concentration of oxygen expressed as volume per cent, in a mixture of oxygen and nitrogen that will just support combustion of a material initially at room temperature. The test specimen of desired dimension is kept vertically in the test column. The flow rates are set so that the desired initial concentration of oxygen is flowing through the column. The top of the specimen is then exposed to the ignition flame. The procedure is then repeated with gradually increasing the oxygen flow rate so that the specimen is well lighted at a particular concentration of oxygen. The limiting oxygen index (LOI) is calculated according to the equation,

$$\mathrm{LOI} = \frac{100 \times O_2}{O_2 + N_2}$$

where O_2 = volumetric flow of oxygen mm^3/s at the concentration when the specimen is ignited and N_2 = corresponding volumetric flow of nitrogen mm^3/s.

6. Chemical/Swelling Resistance Determination

Chemical/swelling resistance of the samples was determined according to ASTM D 471. Samples of desired dimensions were punched out from the compression moulded sheets, weighed and kept in respective chemicals at laboratory temperature for the specified period of time. The samples were taken out, quickly dried with a filter paper and weighed. The percentage change in weight was calculated.

7. Rheological Evaluation using a Capillary Rheometer

Capillary rheometer is widely used for determining the rheological properties of polymer melts since they cover a shear rate range of interest in practical processing upto (10,000 S^{-1}) with good reproducibility. In this study, the rheological properties of polymers and polymer blends were measured using a Goettfert viscotester model 1500 as per ASTM D 3835-79.

Apparent shear stress at the wall and shear rate at the wall were calculated from Poiseuille law for steady, fully developed capillary flow.

Apparent shear stress at the wall $(\tau_{w_{app}}) = (\frac{\Delta P}{L})\frac{R}{2}$ (N/m^2)

Apparent shear rate at the wall $(\dot{\gamma}_{w_{app}}) = \frac{4Q}{\pi R^3}$ (S^{-1})

Apparent viscosity $(\eta) = \frac{\tau_{w_{app}}}{\dot{\gamma}_{w_{app}}}$

where ΔP is the pressure drop (N/m^2)

Q is the volume flow rate (m^3/S)

R is the capillary radius (m)

L is the capillary length (m)

A straight line relationship between $\tau_{w_{app}}$ and $\dot{\gamma}_{w_{app}}$ on a log-log plot indicates that the variables can be related by a power law equation $\tau_{w_{app}} = K.\dot{\gamma}_{w_{app}}^{\;n}$ where K is the consistency index and n the power law index. This law is often referred to as the power law of Ostwald and de Waele.[9-11] The power law index (n) indicates how rapidly the viscosity varies 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 powerlaw index indicates the degree of non-Newtonian behaviour.

A series of corrections is appropriate to derive the true viscosity to account for factors such as,

1. Non-Newtonian behaviour of melts (Rabinowitsch correction)
2. Ends pressure drop (Bagley correction)
3. Reservoir and friction losses

4. Slip at the die wall
5. Influence of pressure on viscosity
6. Influence of pressure on volume
7. Influence of heat generation
8. Influence of decomposition on temperature
9. Modification of the material due to work in the die.

These corrections themselves are subject to many errors and therefore should be used with caution. Corrections for the first two are generally recommended.

Because the polymer melts are in general non-Newtonian it is necessary to correct the apparent shear rate. Rabinowitsch[12] and Mooney[13] derived the relationship between true shear rate ($\dot{\gamma}_w$) and apparent shear rate ($\dot{\gamma}_{w_{app}}$) as,

$$\dot{\gamma}_w = \frac{\dot{\gamma}_{w_{app}}}{4} \left(3 + \frac{d \ln \dot{\gamma}_{w_{app}}}{d \ln \tau_{w_{app}}}\right)$$

$\dfrac{d \ln \dot{\gamma}_{w_{app}}}{d \ln \tau_{w_{app}}}$ can be taken as the slope of the curve (n) of $\tau_{w_{app}}$ and $\dot{\gamma}_{w_{app}}$ at various points.

Bagley[14] observed that a plot of pressure drop vs die length to radius ratio at a fixed wall shear rate gives a straight line with an intercept such that the shear stress in capillary flow is more correctly

$$\tau_w = \left(\frac{\Delta P - P_c}{L}\right)\frac{R}{2}$$

where P_c is the pressure drop at the die entrance (Fig.2.3).

The entrance pressure drop may be ideally determined by using dies of several lengths.

The true viscosity may then be determined as,

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

The measurement of entrance pressure loss (P_c) is itself a useful rheological parameter since P_c is directly related to the elastic properties of the melt. The most obvious elastic effect during capillary extrusion is post-extrusion swelling.

a) <u>Melt elasticity measurements</u>

Polymers are partly viscous and partly elastic. In the molten state, polymers are primarily viscous but

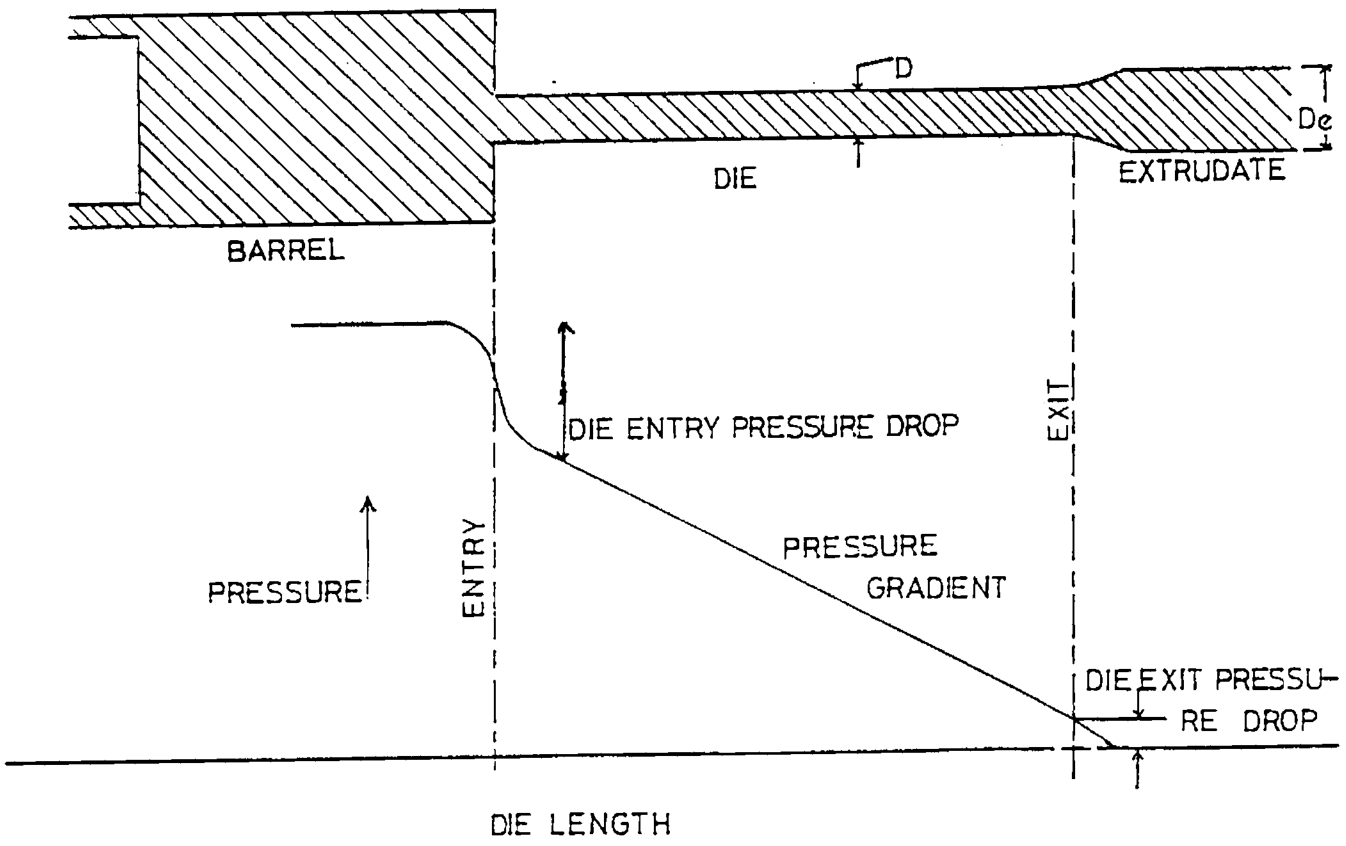

Fig.2.3: Schematic diagram of the capillary rheometer and the pressure drop across the die

will be elastic to some extent. This behaviour is generally referred to as visco elastic behaviour. High polymeric liquids show pronounced elastic properties during flow. The normal stress built up in such materials can exceed shear stresses by a larger order of magnitude and cause losses of pressure at the inlet and outlet of the capillary, extrudate swell and in extreme cases other undesirable flow phenomena.

The extrudate swell ratio, $\frac{D_e}{D}$ where D_e and D are the diameter of the extrudate and the die respectively is a direct measure of the melt elasticity. Extrudate swelling of two phase blends is composed of two parts (i) matrix swell and (ii) form recovery of dispersed drops. Bogue and White[15] suggested the 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 can be calculated from the expression,

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

γ_R increases with increasing shear stress.

The measurement of extrudate swell ratio is correlated with normal stress functions according to the Tanner's equation.[16]

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

In the present investigations the extrudate emerging from the capillary was collected taking care to avoid any deformation The diameter of the extrudate was measured at various points and the extrudate swell ratio was measured.

b) Observation of extrudate appearence

The extrudate from capillary rheometer may provide useful visual evidence of non-laminar flow or surface imperfections. The extrudate appearence 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.

c) Activation energy for viscous flow

The viscosity of a polymer decreases as the temperature increases. Over a small region of temperature variation, the temperature dependence of viscosity can be represented by the equation,

$$\eta_{app} = A.\exp^{E/RT}$$

where A is a constant, E the activation energy, R the gas constant and T the absolute temperature. A plot of η_{app} against 1/T gives an Arrhenius plot.

d) Melt index measurements

The melt index tester is a simple capillary rheometer. The piston is driven down by placing a weight on top of it.

The melt index is the number of grams of polymer extruded in a time period of 10 minutes at a specified temperature. The measurement procedure is described in ASTM D 1238. This index is generally used for characterization of polyolefines.

e) 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 given in ASTM D 1646 (1981) was followed.

8. Infrared Spectroscopy

IR spectra given in this investigation were taken in a Beckmann Infrared spectrophotometer. Different functional groups and structural features in the molecule absorb electro-magnetic radiations at characteristic frequencies. Absorption at 1700 cm^{-1} was made use of in this study because it is appropriate for carboxyl group determination.

9. Radiation Studies

Test samples (2 ± 0.2 mm thick) were irradiated with Gamma-rays from a ^{60}Co source in a Gamma chamber. The samples were irradiated for different radiation doses at a dose rate of 0.157 Mrad/h in air at room temperature. The mechanical properties were measured before and after irradiation.

10. Polymer to Metal Bond Strength Measurement

Adhesive strength of polymer samples with metals was measured using a Zwick universal testing machine. The metal specimens were cleaned with emery paper, and then degreased. The adherends were obtained by hot pressing the polymer sample, kept in between two metal sheets at 180°C for 3 minutes in a laboratory hydraulic press at a pressure of 120 kg/cm^2. After removal of pressure and cooling to room temperature, peel resistance of the joint was determined. Peel strength was assessed from the resistance to peeling of a 25 mm strip, the angle of peeling being 180° at 50 mm/min test speed. The reported values of peel force (N/mm) represent the mean from measurements of 4 strips.

11. Morphology Studies

The morphology of polymer blends was investigated using an optical microscope (Versamet-2 Union 7596).

For optical microscopy a compression set test piece was cut to a convenient size and mounted on a microscope slide. Photographs were taken at a magnification of 330.

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Chapter 3

STUDIES ON POLY(VINYL CHLORIDE)/ELASTOMER BLENDS

STUDIES ON POLY(VINYL CHLORIDE)/ELASTOMER BLENDS

Blends of several elastomers with PVC have been developed to achieve a number of purposes. Modifying polar and nonpolar elastomers with PVC is one of the promising methods of improving the oil, petrol, ozone and fire resistance of the vulcanizates based on them.[1,2] One of the commercially important and miscible polymer blends is that of NBR and PVC. The primary purpose of such blends is to provide NBR having enhanced ozone resistance. However, PVC also serves to reinforce the rubber. Modulus, hardness and abrasion resistance increase with increasing PVC content.[3,4] Tensile strength also frequently increases with PVC content while elongation decreases. When PVC is modified with NBR, it serves as a polymeric plasticizer and improves the toughness of PVC.[5-8]

PVC/CR BLENDS

Polychloroprene rubber (CR) and poly(vinyl chloride) (PVC) both possess excellent oil resistance, chemical resistance, weather resistance and non-flammability. Hence modifying CR with PVC would be an excellent way of improving its mechanical strength without losing any of the useful properties of CR. PVC is generally used as a cheap plastic material whereas CR is used as a comparatively high priced special rubber. Hence blends of CR and PVC can be advantageously used to replace CR in many applications.[9,10]

However, it has not been possible to achieve a marked improvement in the physico-mechanical properties of the vulcanizates based on CR when modified with PVC. Blends of such immiscible polymers have complex property relationships that are rarely additive. The poor mechanical behaviour of the phase separated blends is usually the consequence of inadequate adhesion between the phases that does not allow efficient transfer of stress across the interface.[11-13] Mechanical properties would be nearly additive if the interfacial zone is strengthened. Suitably chosen additives are used to reduce the interfacial tension and in this way the blend can be brought into more wider applications. Block and graft copolymers have been found to be the most useful in modifying the interface or to act as compatibilising agents.[14-17] Statistical copolymers have also been found to be useful to a limited extent as in the case of ethylene-propylene rubber (EPR) compatibilizing polypropylene and high density polyethylene.[18-21] In the present study, an attempt is made to modify PVC/CR blends so as to improve their mechanical behaviour. The main thrust of the work is the use of selected compatibilisers in blends of PVC and CR. The materials tried as compatibilisers are block and random copolymers of the following types:

Hytrel - A polyether-ester block copolymer
NBR - Acrylonitrile-butadiene rubber
EVA - Ethylene-vinyl acetate copolymer
SIS - Styrene-isoprene-styrene block copolymer
SBS - Styrene-butadiene-styrene block copolymer
SEBS - Styrene-ethylene-butylene-styrene block copolymer.

FUSION STUDIES

Since the fusion state of PVC is a critical factor in determining the mechanical strength of PVC blends, the efficiency of the various compatibilisers was first compared based on their ability to modify the fusion behaviour of PVC/CR blends. The addition of a true compatibiliser decreases the fusion time and thereby improves the processability. A common method of investigating the fusion process is to subject the material to an appropriate shear and temperature in a Brabender mixer and then to monitor the torque as a function of time.[6,22] By this mechanical and thermal treatment all primary particles of PVC are destroyed resulting in an apparently homogeneous state which can be observed from the torque-time curve.

Experimental

Fusion characteristics of a 50/50 PVC/CR blend with and without various polymeric modifiers were studied at two temperatures 150°C and 170°C in a Brabender plasticorder using roller mixers at 30 rpm speed. The fusion time of each blend is given in Table 3.1.

Results and Discussion

It can be observed that the time required to fuse the PVC compound (fusion time) is significantly reduced by EVA, Hytrel and NBR which are common plasticizers of PVC. The other additives give only little or no reduction in the fusion time. Hence these three additives EVA, Hytrel and NBR were selected as modifiers /compatibilisers for further studies.

Table 3.1: Fusion time of 50/50 PVC/CR in the presence of various modifiers

PVC/CR blend	rpm	Temperature (°C)	Fusion time (minutes)
Unmodified	30	150	12.0
EVA modified	30	150	7.0
Hytrel modified	30	150	7.5
NBR modified	30	150	7.0
SIS modified	30	150	10.5
SBS modified	30	150	10.0
SEBS modified	30	150	9.5
Unmodified	30	170	8.0
EVA modified	30	170	5.5
Hytrel modified	30	170	6.0
NBR modified	30	170	6.5
SIS modified	30	170	7.0
SBS modified	30	170	7.5
SEBS modified	30	170	8.0

A faster fusion also lowers the demands on the PVC stabiliser and results in more stable PVC compounds. It is confirmed by static and dynamic thermal stability tests.

THERMAL STABILITY OF PVC IN PRESENCE OF MODIFIERS

The main outward manifestations of thermal degradation of PVC are the evolution of hydrogen chloride and the development of colour. It is widely accepted that the cleavage of HCl is accompanied by polyene sequence formation and crosslinking.[23,24] As a result the polymer discolours from light yellow to dark brown and almost black in severe case. In this study the thermal stability of PVC in presence of the modifiers is investigated.

Experimental

In the dynamic thermal stability tests[25-27] 40 gm of 50/50 PVC/modifier blends without any stabiliser for PVC were worked at 170°C and 30 rpm in the Brabender plasticorder mixer for 20 minutes and the torque-time curves were taken. Also, the sequence of colour development for each of the above compounds during the test run was visually observed at every 3 minutes.

In the static thermal stability test[25-27] the PVC/modifier blends were made into sheets of standard size and kept in an air oven at 180°C for a period of 100 minutes. The colour change was noted at every 10 minutes.

Results and Discussion

Fig.3.1 shows the Brabender torque-time curves of the 50/50 PVC/modifier blends. The initial unstable part may be the period of homogenisation. The period over which the constant torque level continues (stability time) may be taken as a measure of the efficiency of the stabilising system. It is found that these modifiers improve the stability time and reduce the degradation tendency of PVC considerably. The stability time is found to be least when NBR is used as the modifier, maximum in the case of EVA and that for Hytrel being in between those of NBR and EVA.

Table 3.2 shows the colour development in the PVC/modifier blends during the dynamic thermal stability test and Table 3.3 during the static thermal stability test. An examination of the colour changes occuring during the dynamic test run shows that the maximum colour development

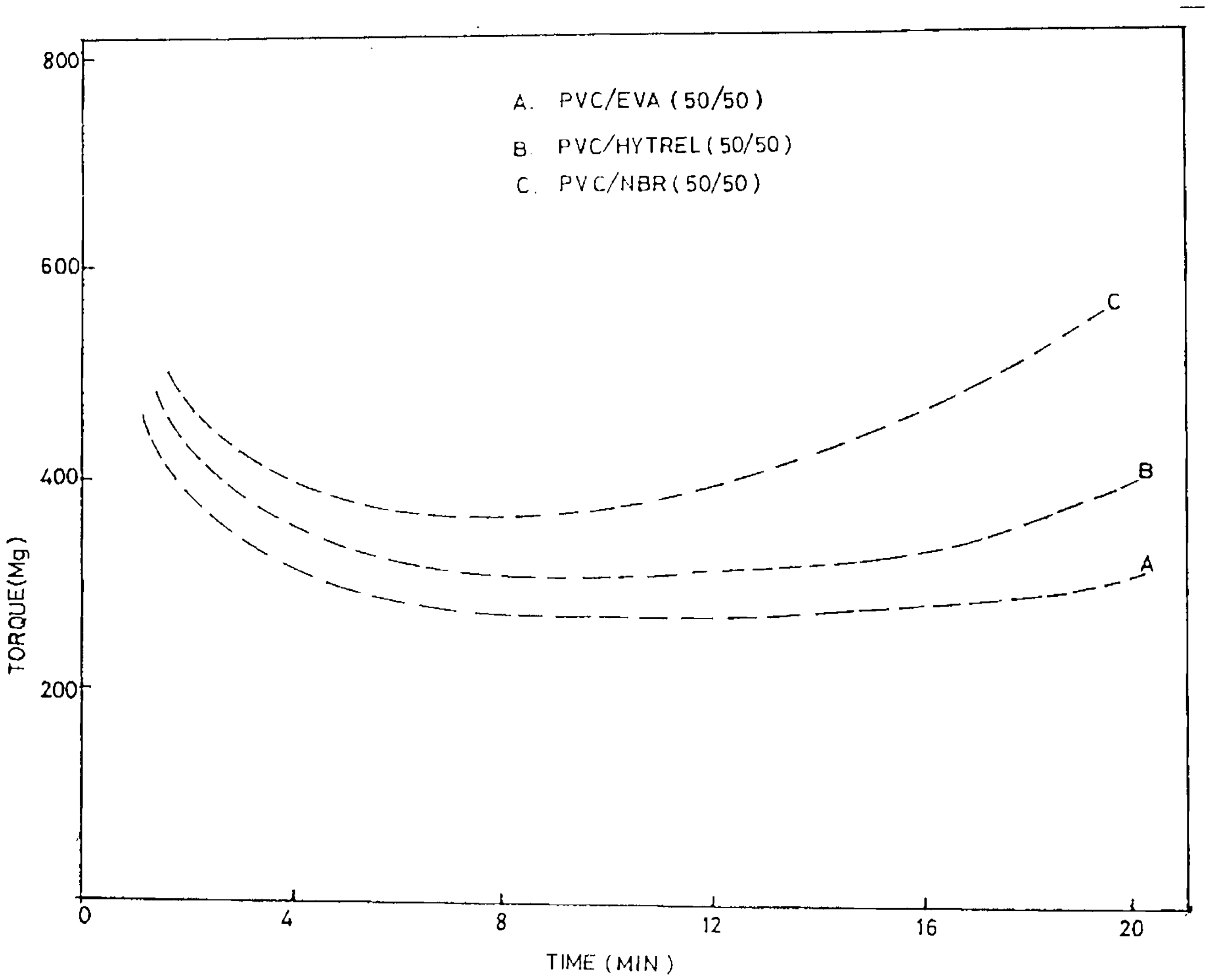


Fig.3.1: Brabender torque-time curves of 50/50 PVC/modifier blends

Table 3.2: Sequence of colour change during dynamic thermal stability tests—50/50 PVC/modifier blends

Time in minutes	0		6	9	12	15	18	21
PVC/EVA	0	0	1	1	3	4	6	6
PVC/Hytrel	0	1	3	5	6	8	9	10
PVC/NBR	0	1	4	5	7	9	10	10

Degree of colour development over the scale 0-10

0 - colourless ; 10 - black

Table 3.3: Sequence of colour change during static thermal stability test—50/50 PVC/modifier blends.

Time in minutes	10	20	30	40	50	60	70	80	90	100
PVC/EVA	1	2	3	5	6	6	6	7	8	8
PVC/Hytrel	4	5	5	6	7	8	8	9	10	10
PVC/NBR	3	4	5	7	8	8	9	10	10	10

Degree of colour development over the scale 0-10

0 - colourless ; 10 - black

occurs when NBR is used. In the case of EVA modified blend the discolouration occurs very slowly. The results of the static thermal stability tests confirm the results obtained from the dynamic thermal tests.

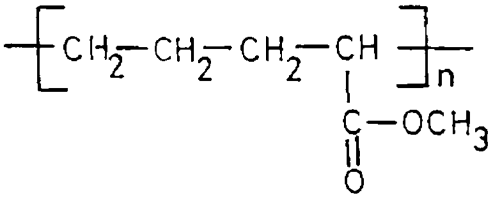
HYTREL, EVA AND NBR AS MODIFIERS FOR PVC/ELASTOMER BLENDS

Ternary blends are gaining an important share in the field of property diversification of polymer blends. These systems offer the possibility of extending the list of miscible or mechanically compatible blends. Theoretically their study offers the possibility to explore the important principles governing the compatibilization of immiscible or nearly miscible blends.

In this study, Hytrel, EVA and NBR are tried as modifiers for different PVC/Elastomer blends. The chemical structure of the modifiers are shown in Fig.3.2.

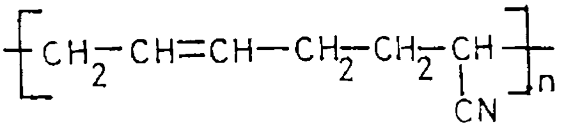
Experimental

The blends were prepared in the Brabender plasticorder. The formulations employed with each polymer are shown in Table 3.4.



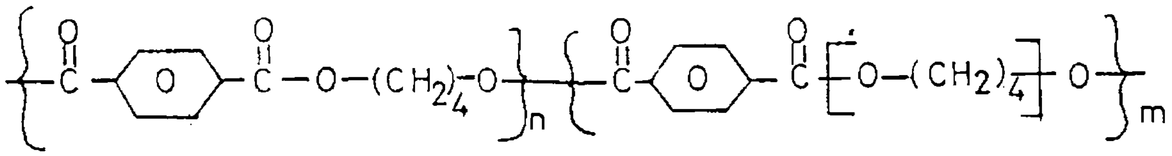
$$-\!\!\left[CH_2-CH_2-CH_2-\underset{\displaystyle \underset{\displaystyle \overset{\|}{O}}{C}-OCH_3}{\underset{|}{CH}} \right]_n\!\!-$$

EVA



$$-\!\!\left[CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}} \right]_n\!\!-$$

NBR



Hytrel

Fig.3.2: Structure of EVA, NBR and Hytrel

Table 3.4: Formulations of individual polymer compounds

	NBR	NR	SBR	EPDM	CR	PVC
Polymer	100	100	100	100	100	100
ZnO	4.0	4.0	4.0	4.0	5.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
Sulphur	1.5	2.5	2.2	2.0	--	--
CBS	1.5	0.6	0.8	1.2	--	--
TMTD	0.5	--	0.2	1.0	--	--
IPPD	1.0	1.0	1.0	1.0	1.0	--
MgO	--	--	--	--	4.0	4.0
NA 22*	--	--	--	--	0.5	--

* NA-22 is ethylene thio urea, a common accelerator used in poly chloroprene compounds.

The PVC content of the blends was varied from 0-50% of the total polymer, since beyond this level it is difficult to process the blend under the test conditions. The elastomer was added first, then the compatibiliser and finally PVC. This sequence permitted the use of low temperatures of blending and hence polymer degradations were kept to minimum. PVC stabilisers were added along with PVC but the additives for the elastomers were added after the preparation of the base polymer blend. MgO/ZnO/stearic acid system was used as the heat stabiliser for PVC, since it does not affect the elastomer adversely.[28,29] Sulphur curing was employed for SBR, EPDM and NR while MgO/ZnO curing was employed for CR. The compatibiliser concentration was kept at 10% of the total polymer in every case since this level was found to be a good compromise. The compatibilisers were added without any additives.

The cure curves of the blends were taken at 170°C on a Goettfert elastograph. The compounds were vulcanized upto their optimum cure times in a laboratory hydraulic press, at the same temperature. The mechanical properties of the vulcanizates were determined on a Zwick universal testing machine. The swelling behaviour of the vulcanizates was determined by keeping the vulcanizates in the respective solvents.

Results and Discussion

Fig.3.3 shows the cure curves of the 50/50 blends of CR and PVC modified with NBR, EVA and Hytrel along with that of CR alone and the unmodified blend. It can be observed that the presence of PVC and the modifiers does not affect the curing of CR. Also, there seems to be no scorching of the mixtures during blending.

Fig.3.4 shows the effect of adding compatibilisers on the tensile strength of PVC/CR blends in comparison to an ideal linear relationship given by the relation $P = X_1P_1 + X_2P_2$ where P is the tensile strength of the blend, X_1 and X_2 are the weight fractions of CR and PVC and P_1 and P_2 their individual tensile strengths. All the three modifiers are found to introduce some compatibilising action in PVC/CR blends. This shows that they are able to bring about some adhesion between CR and PVC and/or reduce the interfacial tension.[14] Among the three modifiers added, NBR seems to be the best, since the curve of the blend modified by NBR is closer to the linear curve than those of the others.

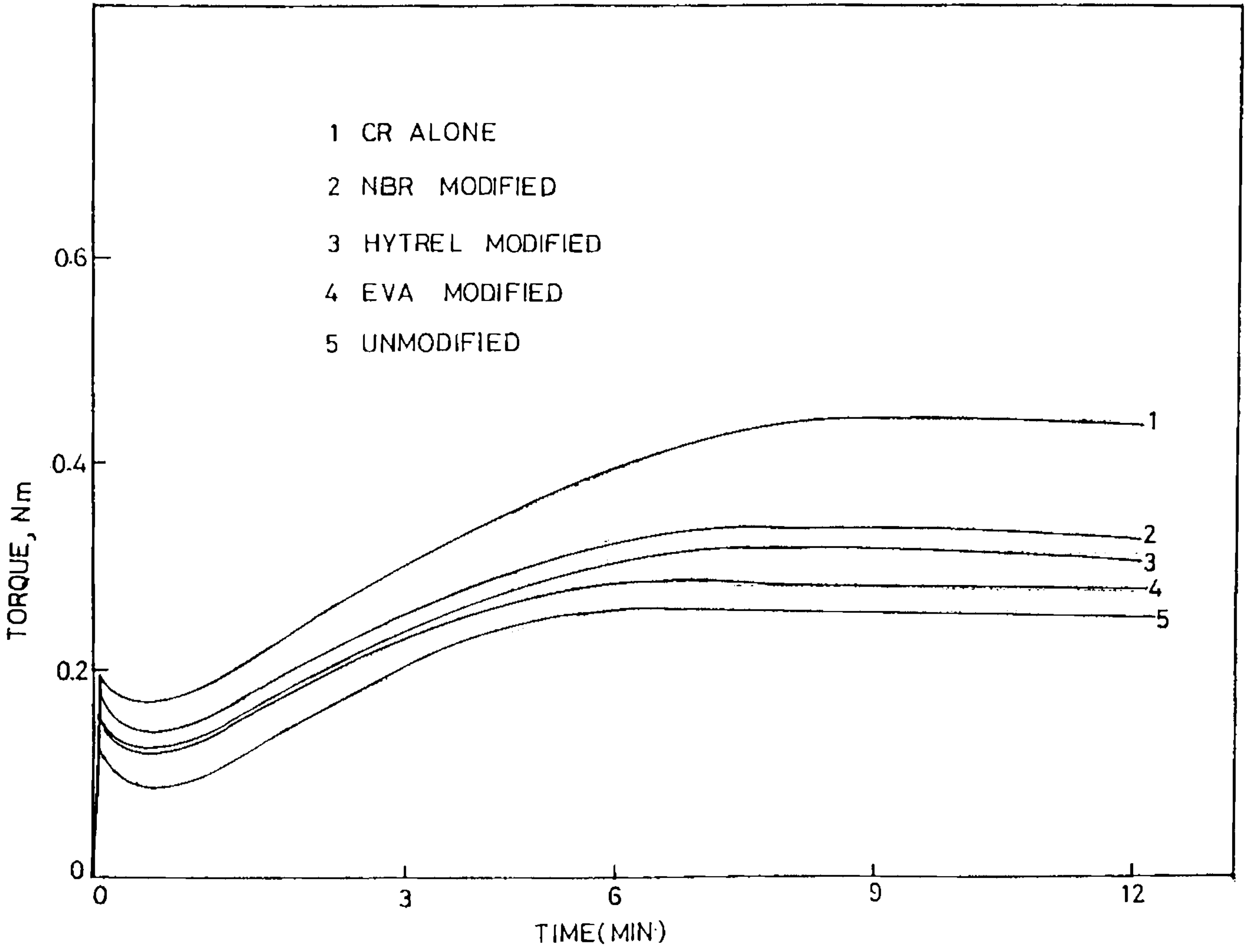


Fig.3.3: Cure curves of 50/50 PVC/CR blends

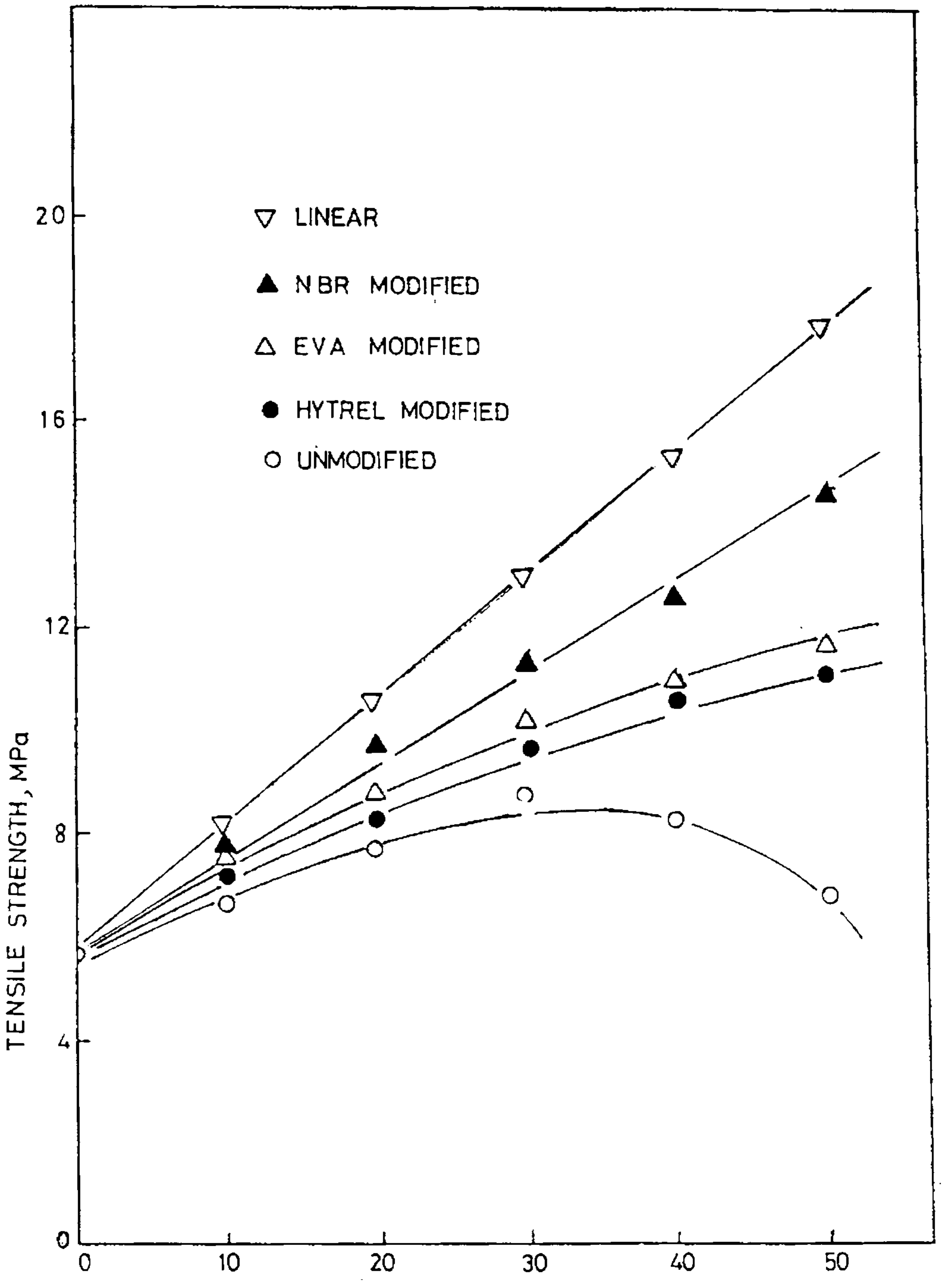


Fig.3.4: Variation of tensile strength of PVC/CR blends with PVC content

Fig.3.5 shows the modulus (stress at 50% elongation) values of modified and unmodified PVC/CR blends. The behaviour is similar to that observed in the case of the tensile strength; NBR producing maximum improvement followed by EVA and Hytrel.

Hardness of the unmodified and modified PVC/CR blends is given in Table 3.5. The hardness of the blends increases with PVC content as expected. Modification makes little or no improvement in the hardness of the PVC/CR blends.

Table 3.5: Variation of hardness of the PVC/CR blends with blend composition.

Percentage composition of PVC : CR	Unmodified	Hytrel modified	EVA modified	NBR modified
0 : 100	40.6	42.3	41.6	40.8
20 : 80	46.4	52.3	54.8	54.5
40 : 60	67.6	56.8	66.6	56.2
50 : 50	72.4	71.6	72.0	74.2

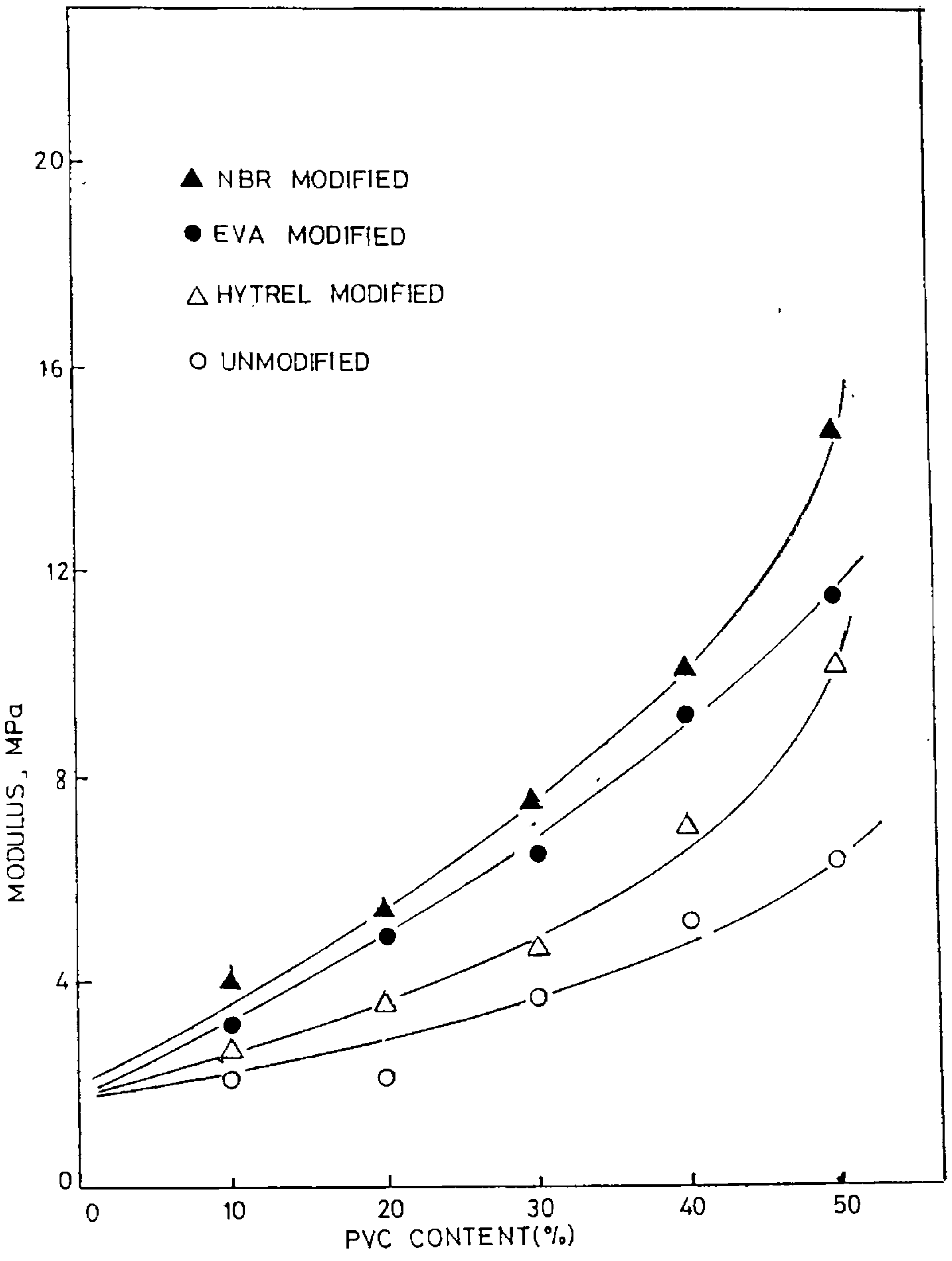


Fig.3.5: Variation of modulus of PVC/CR blends with PVC content

As possible applications for the PVC/CR blends, their swelling behaviour in some common solvents and their flammability characteristics as indicated by limiting oxygen index values are compared in Table 3.6. It can be observed that PVC/CR blends offer significant advantage over the commercially available PVC/NBR blends in the areas of swelling resistance and resistance to flammability.

Mechanism of Modification

In the case of NBR, the polar acrylonitrile and the nonpolar butadiene may be compatibilising the domains at the interface giving good mechanical compatibility. The polarity of vinyl acetate and the nonpolarity of ethylene may be contributing to the compatibilising action of EVA. In the case of Hytrel, the interaction between the carbonyl group of the Hytrel and the α-hydrogen of the PVC and CR are also likely to contribute to compatibility in addition to the similar solubility parameters.[12]

Another reason for the compatibilising action in the case of PVC blends may be the modification of the fusion behaviour of PVC. Fig.3.6 shows the fusion behaviour of 50/50 blends of PVC/NBR, PVC/EVA and

Table 3.6: Comparison of properties of PVC/CR and PVC/NBR blends

Property		percentage composition of PVC	PVC/CR BLEND				PVC/NBR blend
			Unmodified	EVA mofified	Hytrel modified	NBR modified	
Oxygen index		0	34.0	33.0	33.0	33.5	19.0
		20	36.5	35.0	33.5	33.0	20.8
		40	43.0	38.5	38.0	39.0	25.0
		50	44.0	40.0	41.0	39.5	28.5
Swelling index (% increase in weight in 7 days)	ASTM Oil No.3	0	2.7	2.7	2.7	2.5	1.2
		20	2.2	2.6	2.3	2.2	1.2
		40	1.8	2.2	2.1	2.0	1.7
		50	1.8	2.2	1.9	1.8	1.8
	Toluene	0	240.0	242.0	241.0	239.8	249.0
		20	206.1	212.1	202.3	182.6	226.1
		40	148.2	181.3	178.4	140.9	189.0
		50	142.1	168.2	137.6	139.0	164.1
	Acetic acid	0	46.1	45.9	46.8	44.0	49.0
		20	32.9	40.0	38.2	32.3	45.6
		40	25.3	27.6	29.6	18.1	32.8
		50	24.8	19.2	20.1	15.0	23.1
	Methyl ethyl ketone	0	61.2	62.6	61.6	61.2	197.2
		20	98.6	86.4	64.0	92.3	184.8
		40	100.0	110.2	97.8	112.3	144.8
		50	104.1	111.6	117.7	113.4	116.6

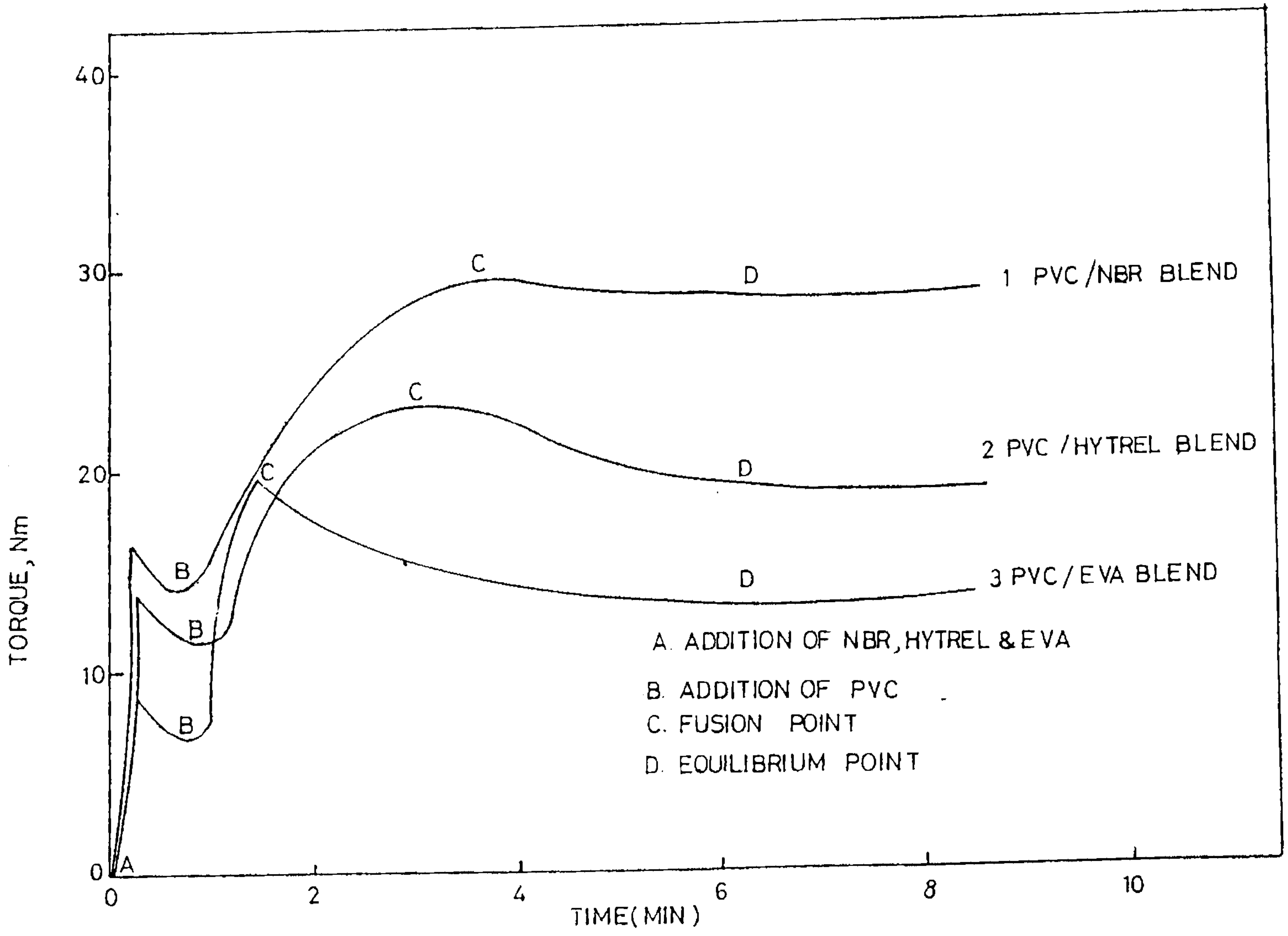


Fig.3.6: Fusion behaviour of 50/50 blends of PVC/NBR, PVC/EVA and PVC/Hytrel blends

PVC/Hytrel. At the maximum torque (fusion point) most of the primary particles are likely to be fused together, but are still distinguishable. After the fusion point the melt temperature increases significantly causing a reduction in the melt viscosity and torque. At this point the particulate structure starts to disappear. The temperature continues to rise and the viscosity decreases until they level out to relatively constant value. At this equilibrium point all primary particles may have disappeared and a continuous melt is formed. It can be observed from the figure that the fusion behaviour of PVC is more uniform and rapid in presence of EVA, followed by Hytrel and NBR. In the case of PVC/NBR blend, a larger increase in torque is observed (B-C) when PVC is added. This may be taken as an evidence for a strong interaction between the polymers.[6] Fig.3.7 shows the fusion behaviour of 50/50 PVC/CR blends modified with NBR, EVA and Hytrel. It can be observed that almost the same trend as in Fig.3.6 is followed in this case also even at this low concentrations of EVA, Hytrel and NBR. From the foregoing it may be reasoned that the modifying action of NBR, Hytrel and EVA on PVC/CR blends stems from two factors: (1) reduction in the interfacial tension between CR and PVC (2) improvement in the fusion behaviour of PVC.

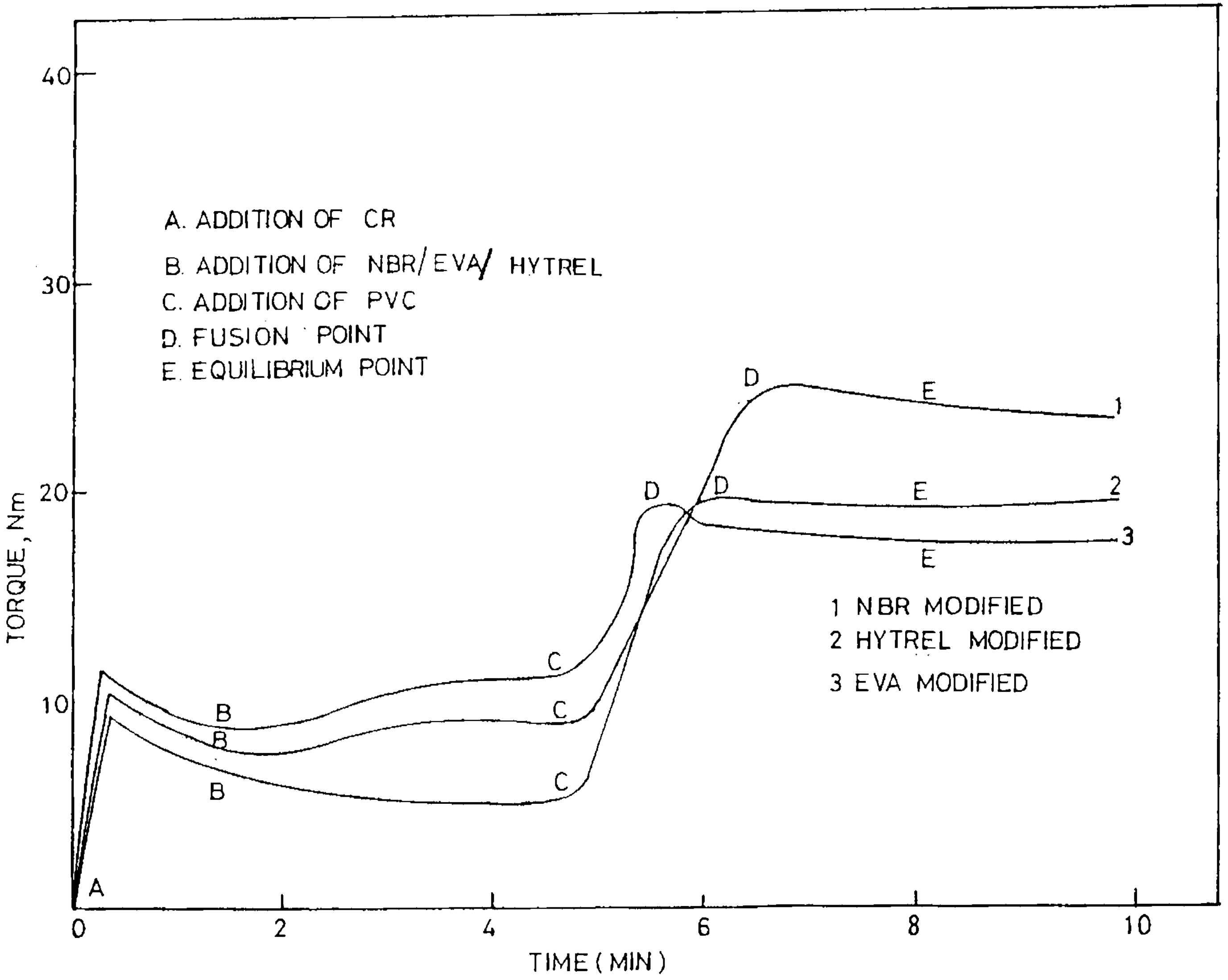


Fig.3.7: Fusion behaviour of 50/50 PVC/CR blends modified with NBR, Hytrel and EVA

To verify the effect of the fusion behaviour of PVC, Hytrel and EVA were tried as modifiers in PVC/NBR blends. Fig.3.8 shows the tensile strength of unmodified and modified PVC/NBR blends. It is observed that Hytrel and EVA are able to bring about some improvement in the strength of PVC/NBR blends. This may be solely due to the modification of the fusion characteristics of PVC by them since NBR was found to have stronger interactions with PVC than Hytrel or EVA.

Thermoplastic Elastomers from CR and PVC

Blends of comparable amounts of elastomers and PVC can be used as thermoplastic elastomers or vulcanised to form thermoset elastomers.[30] The tensile properties of the 50/50 PVC/CR blend and modified blends are given without vulcanising the rubber phase in Table 3.7. The blend was also reprocessed in the Brabender plasticorder and found to have comparable tensile properties after reprocessing.

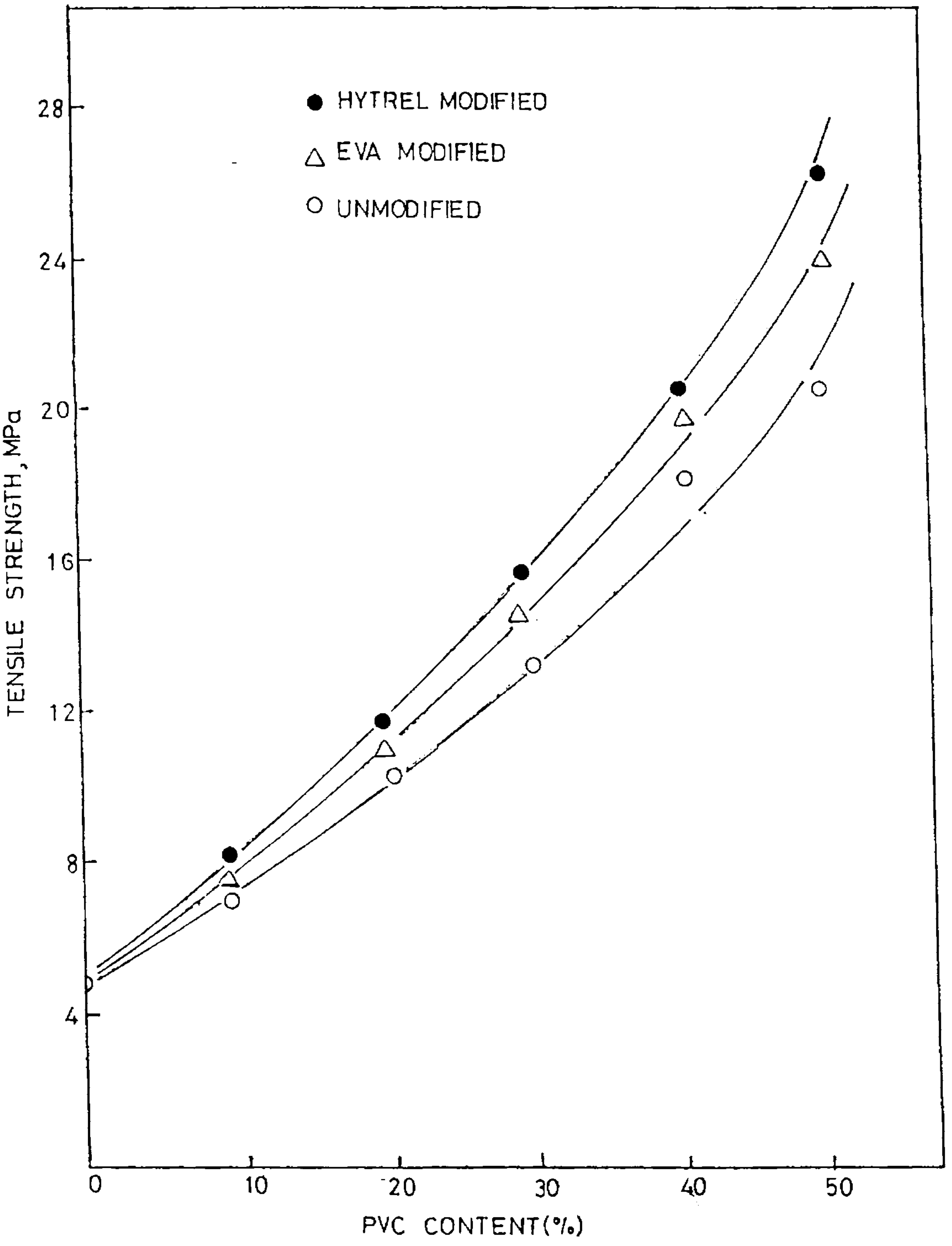


Fig.3.8: Variation of tensile strength of PVC/NBR blends with PVC content

Table 3.7: Tensile properties of 50/50 PVC/CR blends (Rubber phase unvulcanised).

	Tensile Strength in(MPa)	Elongation at break(%)
Unmodified	5.2	78.0
EVA modified	8.9	91.4
Hytrel modified	8.2	96.1
NBR modified	9.6	129.6

THE EFFECT OF MODIFIERS ON THE MECHANICAL PROPERTIES OF PVC WITH OTHER ELASTOMERS

Since EVA, Hytrel and NBR were found to be effective modifiers in PVC/CR blends, they were also tried as modifiers in blends of PVC with other elastomers.

PVC/SBR Blends

Fig.3.9 shows the variation of tensile strength of PVC/SBR blends with and without modifiers. Though the modifiers reduce the fusion time, they are able to make only marginal improvements in the tensile properties.

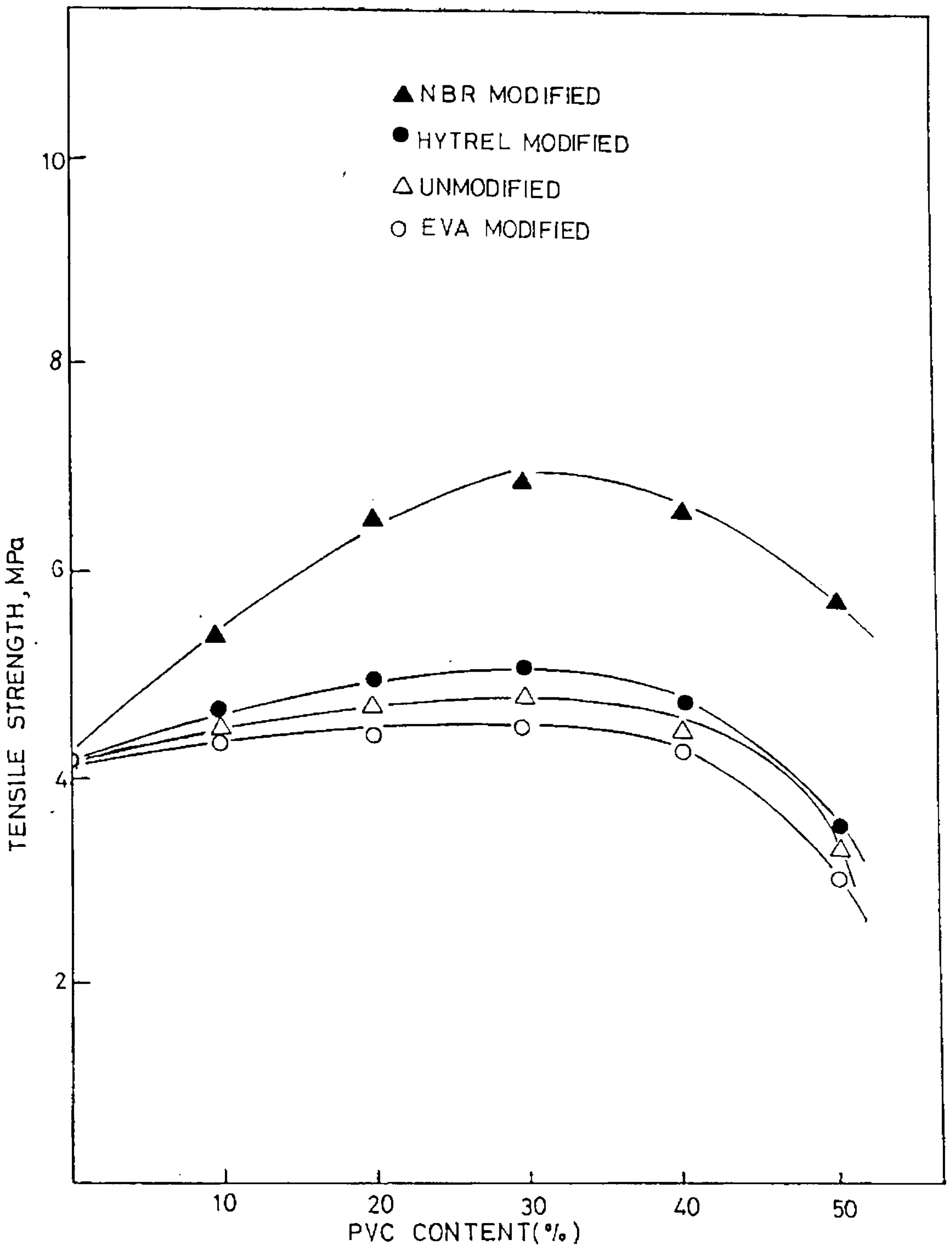


Fig.3.9: Variation of tensile strength of PVC/SBR blends with PVC content

PVC/EPDM Blends

The effect of modifiers on the mechanical properties in this case is also similar to that on PVC/SBR blends (Fig.3.10). Only marginal improvements occur by modification.

PVC/NR Blends

Fig.3.11 shows the variation of tensile strength of PVC/NR blends with PVC content. Modification by EVA, Hytrel and NBR makes no improvement in the case of PVC/NR blends. This shows that there is little interfacial modification in this case. Further, the state of fusion of PVC particles also may not have improved in this case. In the case of NR, the high strength results from the ability of the elastomer to crystallize under high strains. The addition of PVC brings down the strains, evidently limiting the strength to a lower value.

RHEOLOGICAL EVALUATION OF THE PVC BLENDS

Since improvement in the fusion state of PVC is considered as one of the mechanisms by which EVA, Hytrel and NBR work, it will be worthwhile to examine the rheological behaviour of the blends of modifiers with PVC,

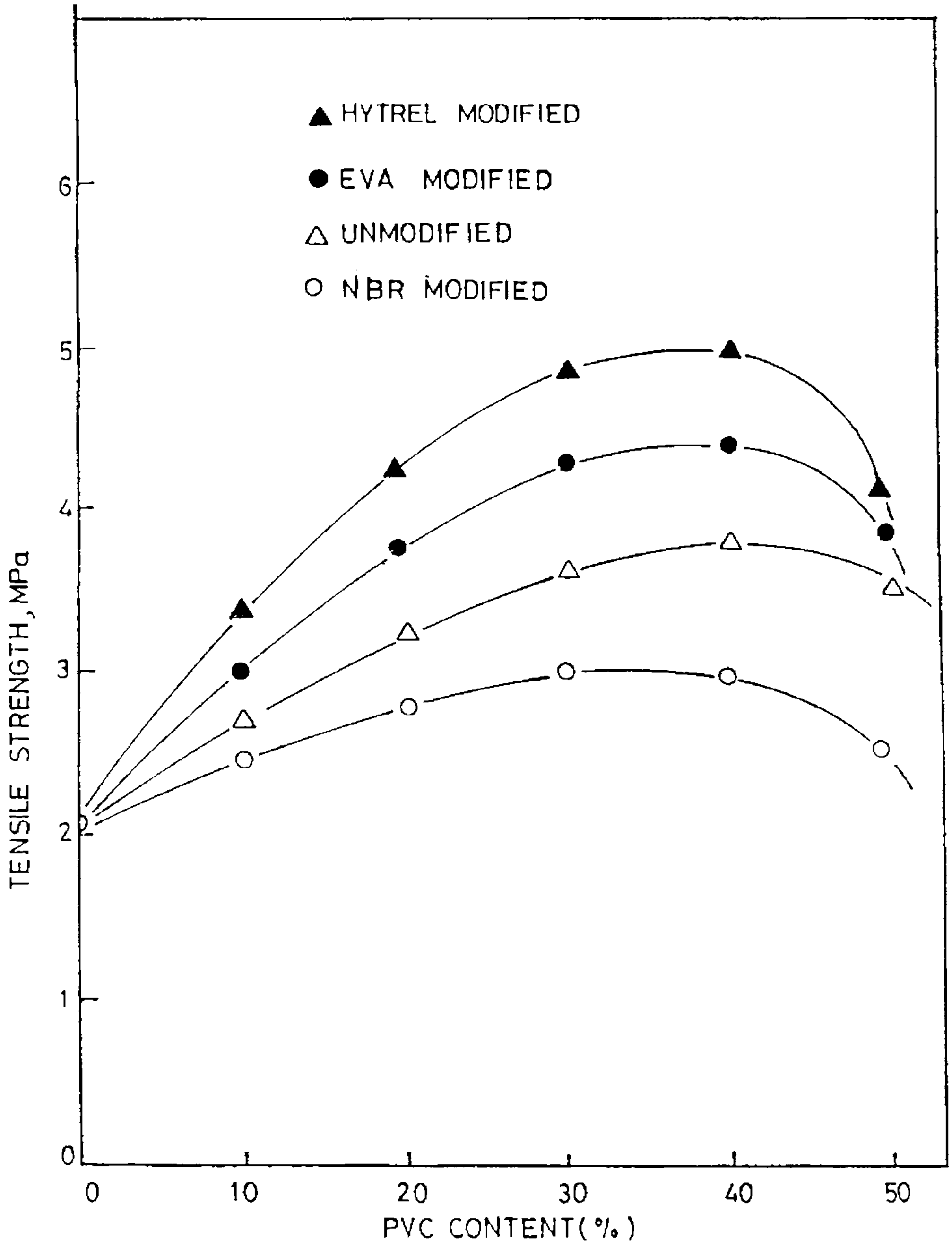


Fig.3.10: Variation of tensile strength of PVC/EPDM blends with PVC content

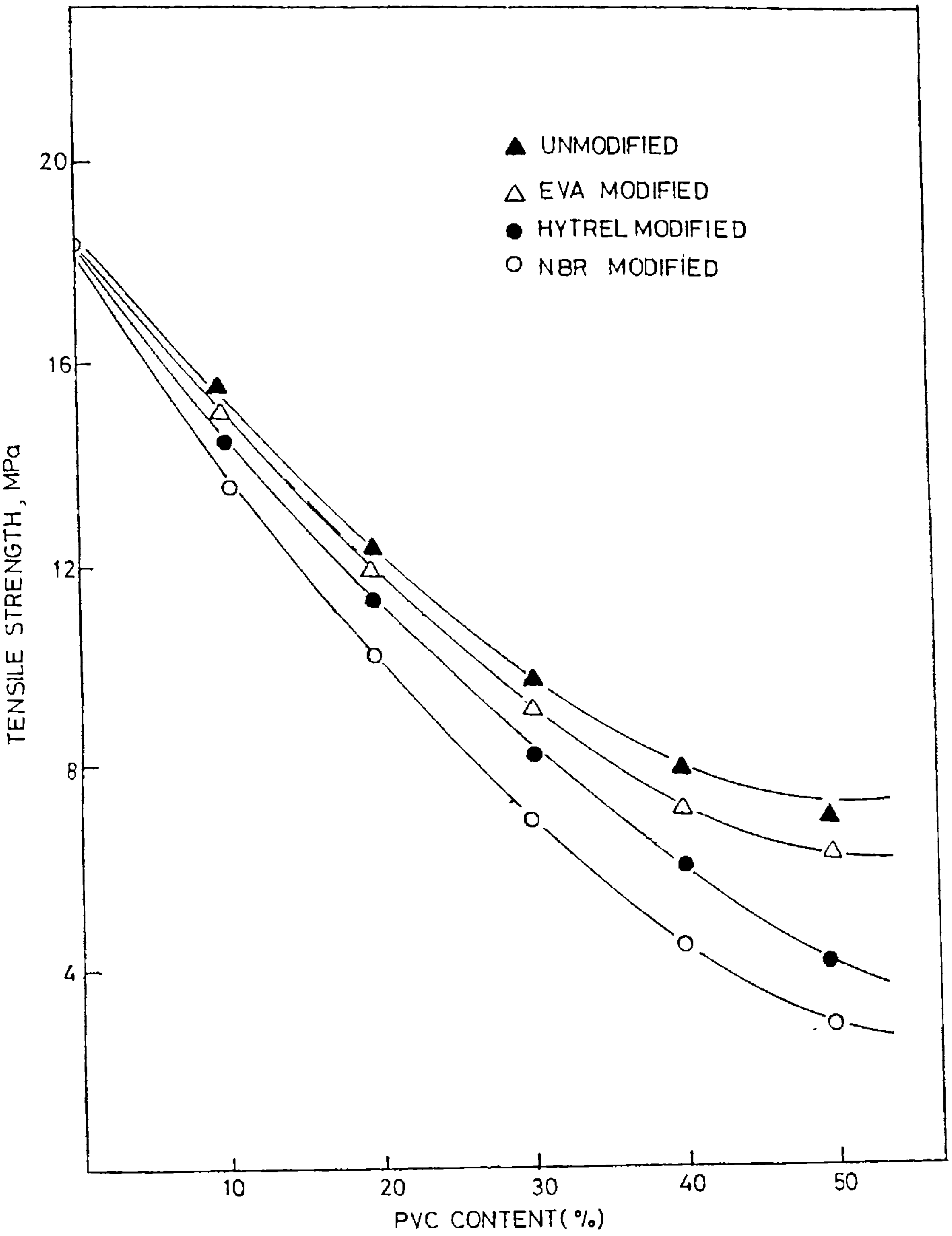


Fig.3.11: Variation of tensile strength of PVC/NR blends with PVC content

since it provides a means of gaining insight into the structure of the polymer melt.[31] It is well known that physical properties of polymer products are not only dependant on the properties of the raw materials but also on the processing conditions. In the course of various processing techniques, polymer melts will be subjected to varying shear and elongational deformations. Determination of rheological functions at comparable shear and temperatures used in actual processing will throw light on the processing behaviour.[32,33]

Experimental

Polymer blends were prepared on the Brabender plasticorder. Mixing conditions were 30 rpm and 170°C. Initially, Hytrel, EVA or NBR was charged into the mixer and then PVC along with its heat stabiliser (4 phr TBLS) was added. A mixing time of 7 minutes was provided during which the torque stabilised to a constant value in all cases. The amount of PVC in the blends was varied from 0 to 50% by weight of the polymers. After mixing, the blends were sheeted out by passing on a laboratory mixing mill and then granulated on a laboratory extruder attached to the Brabender plasticorder. Melt rheological properties were measured on a capillary rheometer

(Goettfert viscotester 1500) using a capillary die of circular cross section (length 30 mm and diameter 1 mm) and also on the Brabender plasticorder at different shear rates at 160°C, 170°C and 180°C.

From volumetric flow rates at various applied pressures, values of apparent shear stress at wall ($\tau_{w_{app}}$), apparent shear rate ($\dot{\gamma}_{w_{app}}$), and apparent viscosity (η_{app}) were calculated using the following expressions,

$$\tau_{w_{app}} = \frac{\Delta P}{L}\,\frac{R}{2}$$

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

$$\eta_{app} = \frac{\tau_{w_{app}}}{\dot{\gamma}_{w_{app}}}$$

where ΔP is the pressure difference between entrance and exit regions of the capillary die, Q the volumetric flow rate, and L and R the length and radius of the die respectively.

From the log $\tau_{w_{app}}$ vs log $\dot{\gamma}_{w_{app}}$ plots, values of power law exponent n were calculated in accordence with the following power law,

$$\tau_{w_{app}} = K(\dot{\gamma}_{w_{app}})^n$$

where K is a constant.

Rabinowitsch correction was applied using values of n to obtain true shear rate $\dot{\gamma}_w$ according to the following expression.[34]

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

Similarly the true shearstressat wall τ_w was calculated by applying Bagley correction according to the following expression.[35]

$$\tau_w = \left(\frac{\Delta P - P_c}{L}\right) \frac{R}{2}$$

where the entrance pressure loss (P_c) was evaluated from the flow data recorded with 3 different dies of L/R values 20, 40 and 60. The true viscosity was calculated as,

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

The rheological characterisation of the blends was also done using the Brabender plasticorder.[36] The torque was considered proportional to shear stress, speed of rotation of the rotors to shear rate, and torque/rpm to viscosity. The activation energy was measured by plotting log (torque/rpm) against 1/T.

Results and Discussion

Fig.3.12 shows the flow curves of the PVC/EVA blend. The slope of the curve (n) was calculated at different points on the curve. Bagley plots of ΔP as a function of L/R for PVC/EVA blends at various shear rates are shown in Fig.3.13. Then the true shear rate $\dot{\gamma}_w$ and true shear stress τ_w were calculated by applying the appropriate corrections. The influence of Rabinowitsch/ Bagley correction on the viscosity curve is demonstrated in Fig.3.14, where apparent viscosity and corrected or true viscosity are plotted against shear rate. As can be seen from the figure, the true viscosity curve is slightly displaced from the apparent viscosity curve. However, the nature of the curves remains more or less the same in both cases. Since all the experiments in the present study were done using a capillary die of fairly high L/R ratio (60), end effects may be negligibly small and hence $\tau_{w_{app}}$ may be close to the true shear stress at the wall.[37,38] Also since the present evaluations are of a comparative nature the apparent values of τ_w and $\dot{\gamma}_w$ are reported for further studies.

Fig.3.15 shows the variation of viscosity with shear rate of Hytrel and PVC/Hytrel blends, measured by

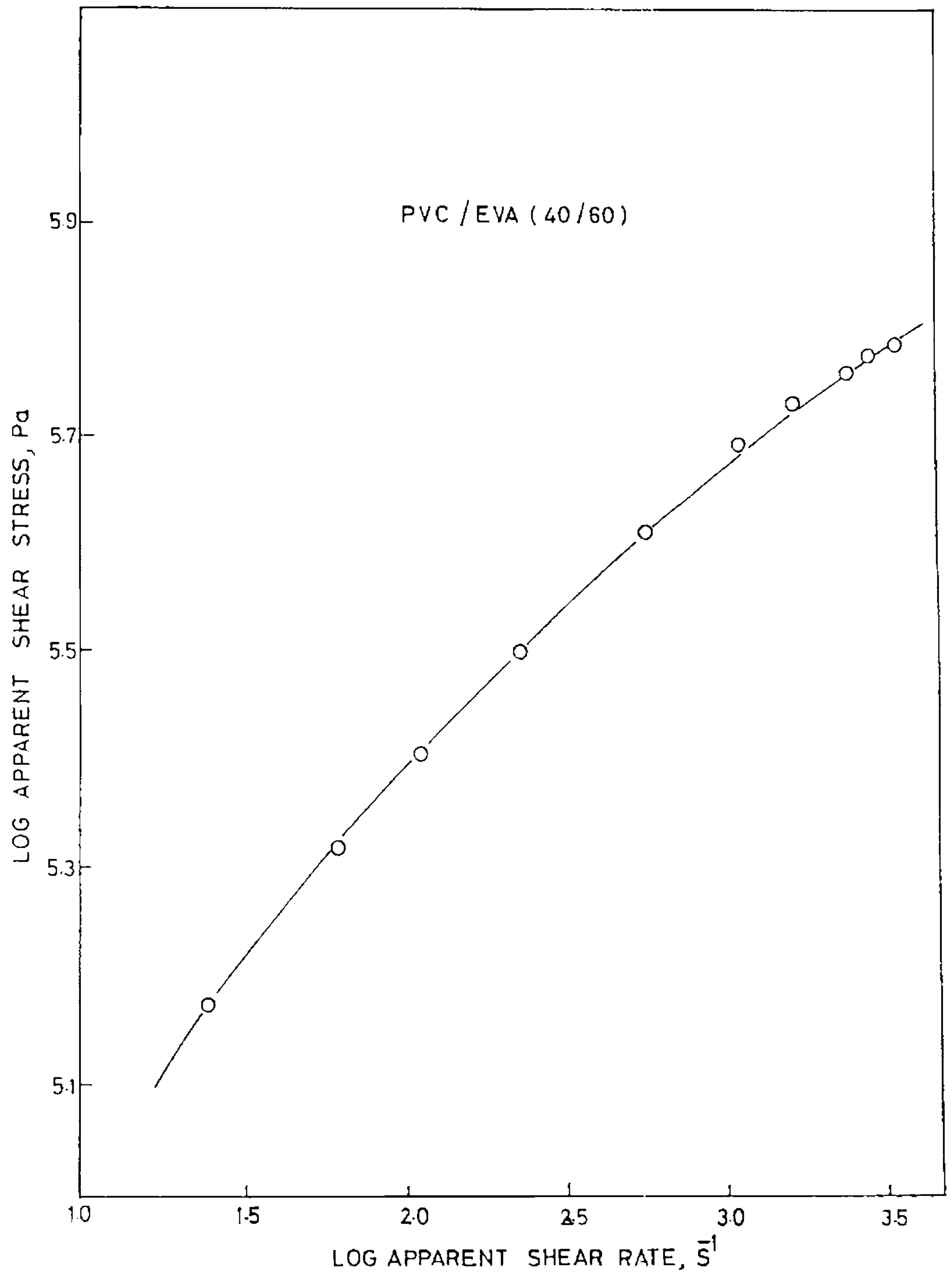


Fig.3.12: Shear stress—shear rate curve (flow curve) of the 40/60 PVC/EVA blend

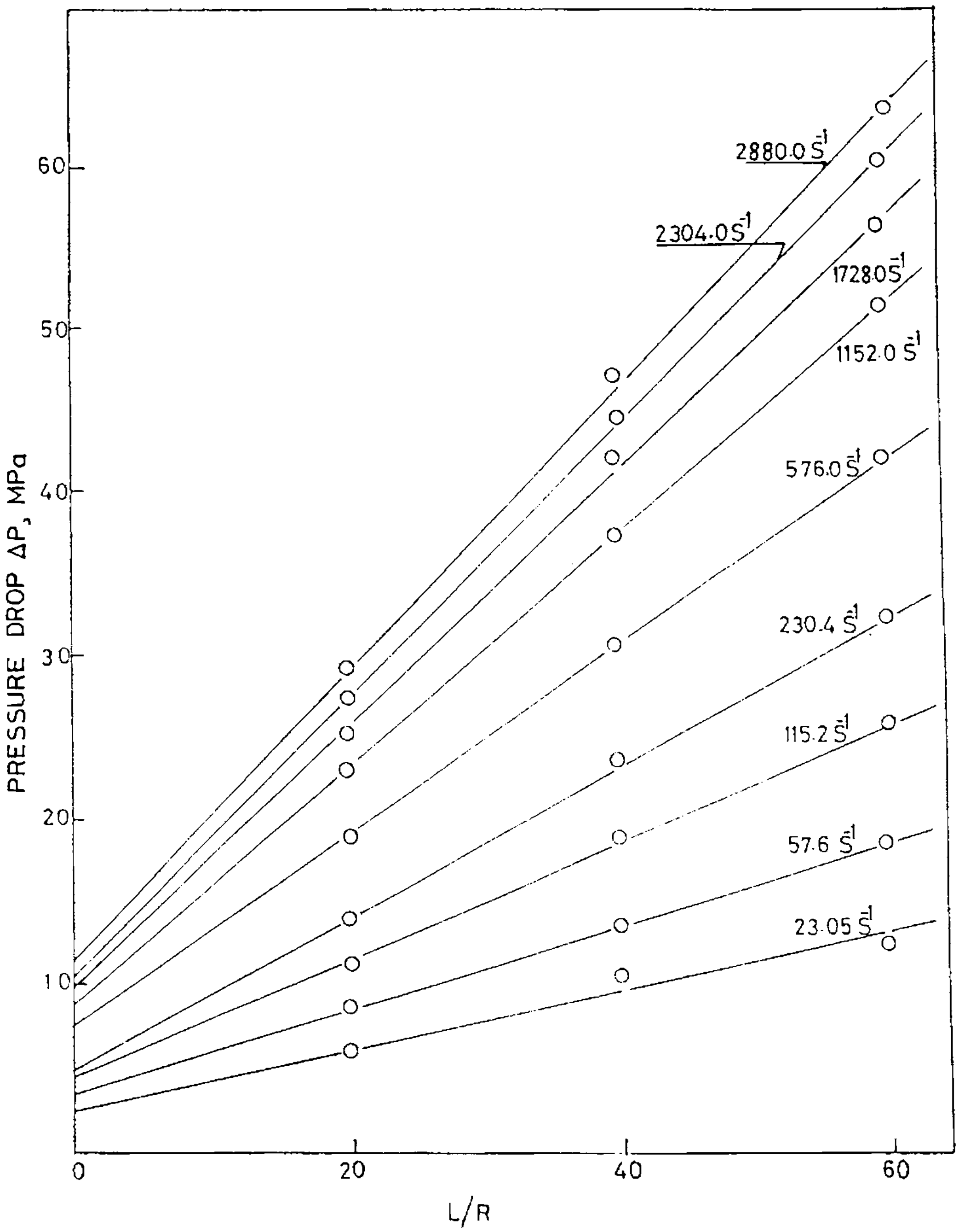


Fig.3.13: Bagley plot of 40/60 PVC/EVA blend at various shear rates

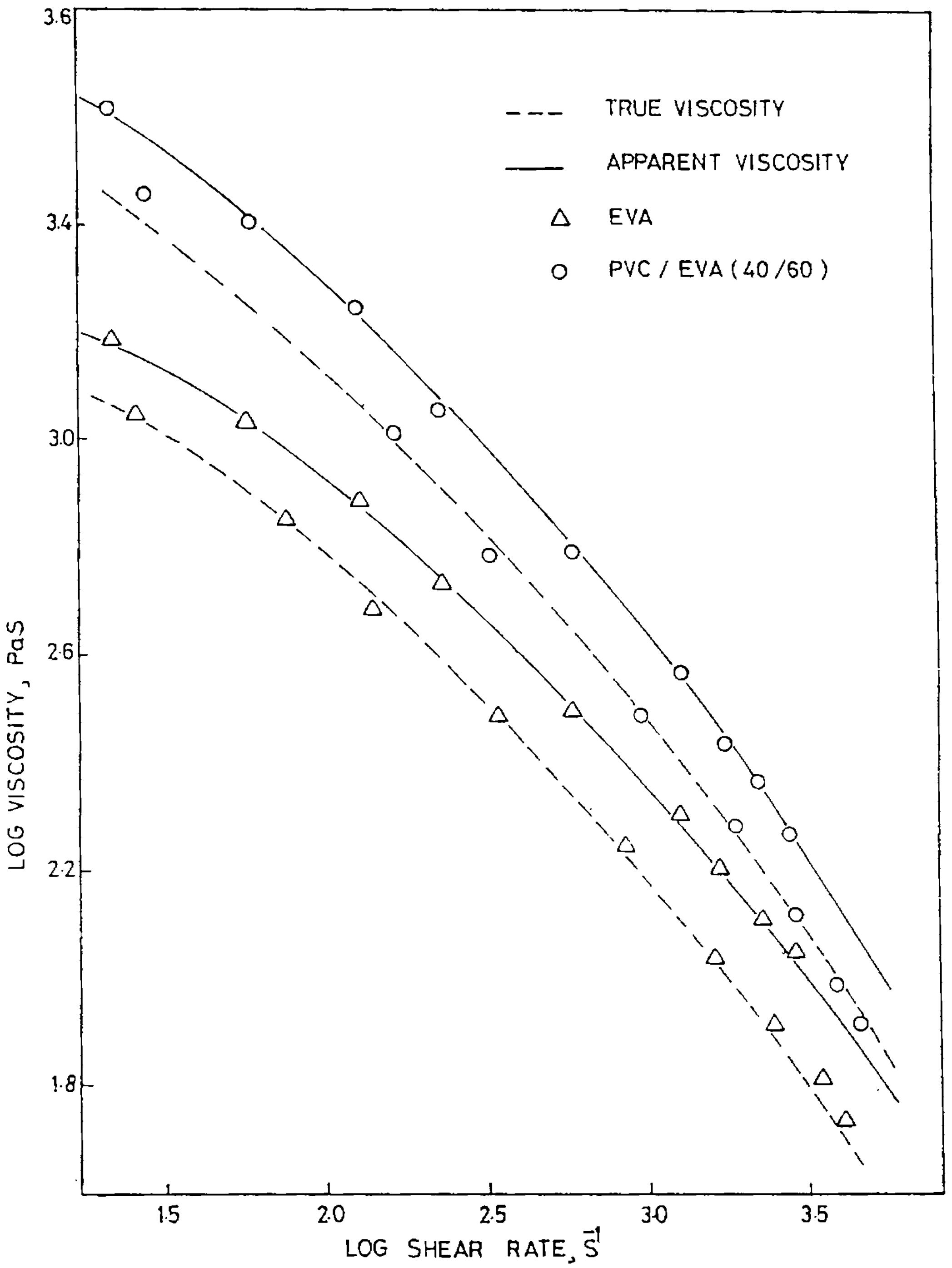


Fig.3.14: Comparison of apparent and true viscosity with shear rate for PVC/EVA blend

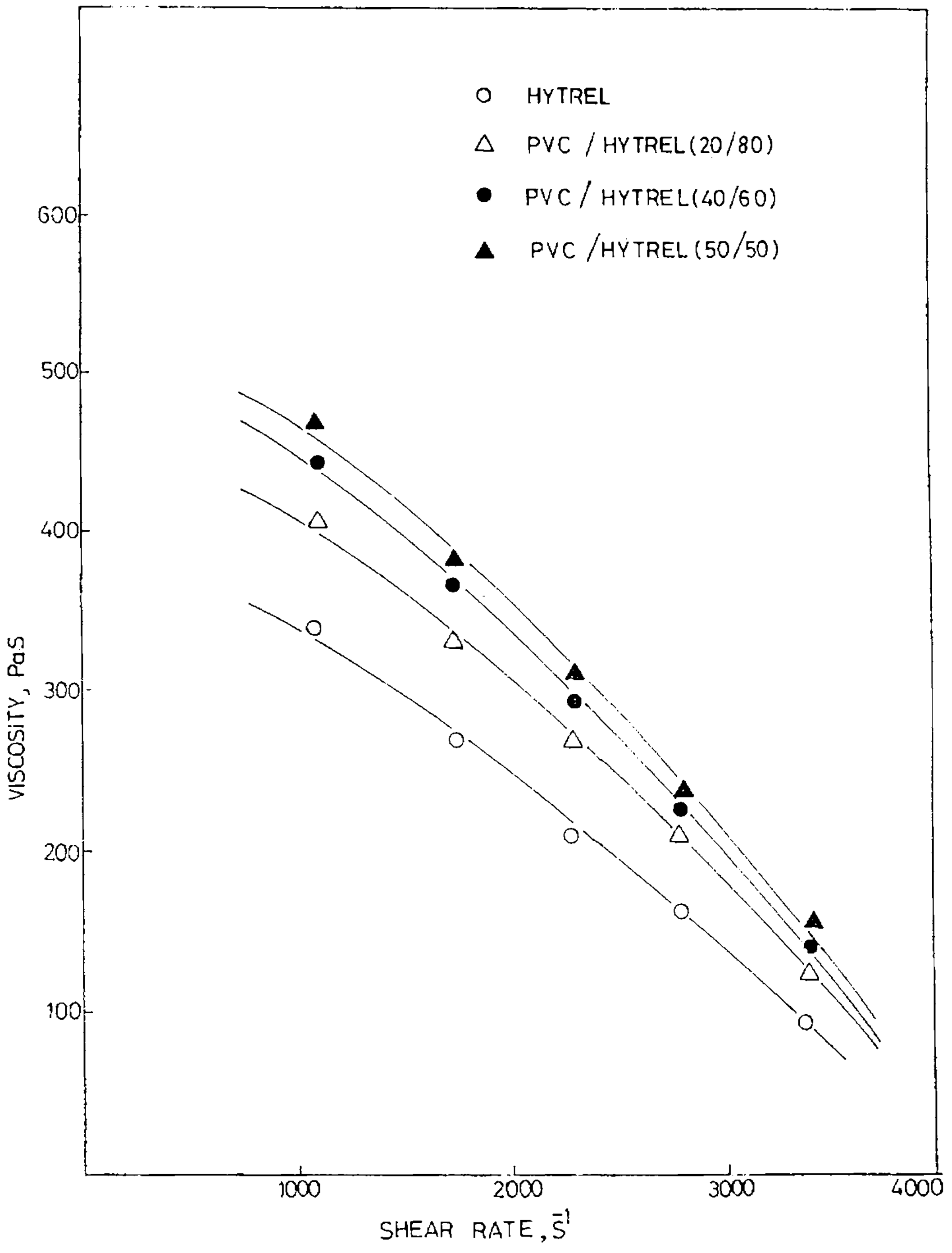


Fig.3.15: Variation of viscosity with shear rate of PVC/Hytrel blends at 170°C

the capillary rheometer (only the higher shear region is shown since the linear axis cannot accommodate the complete range). It can be observed that with increase in Hytrel content the viscosity of the blend decreases which means that Hytrel acts as a lubricant or plasticizer for PVC. This behaviour has been observed for other polymeric modifiers for PVC.[38,39] PVC particles fuse together faster in presence of plasticizers and hence this may be one of the ways in which Hytrel improves the mechanical properties of the PVC blends since an improvement in the fusion state leads to increased strength. Figs.3.16 and 3.17 show the viscosity-shear rate plots of PVC/EVA and PVC/NBR blends. These blends also exhibit almost the same behaviour as those of PVC/Hytrel blends showing an effective decrease in overall viscosity with increase in the concentrations of EVA or NBR. Another notable observation from Figs.3.15 to 3.17 is that these three modifiers make the behaviour of PVC less non-Newtonian. This is expected since rigid PVC melts are characterised by high viscosity and high pseudo plasticity.[40] The melt behaviour of the blends becomes more and more pseudo-plastic with increase in PVC content. But with the progressive addition of the modifiers a Newtonian behaviour seems to develop at least in the low shear rate

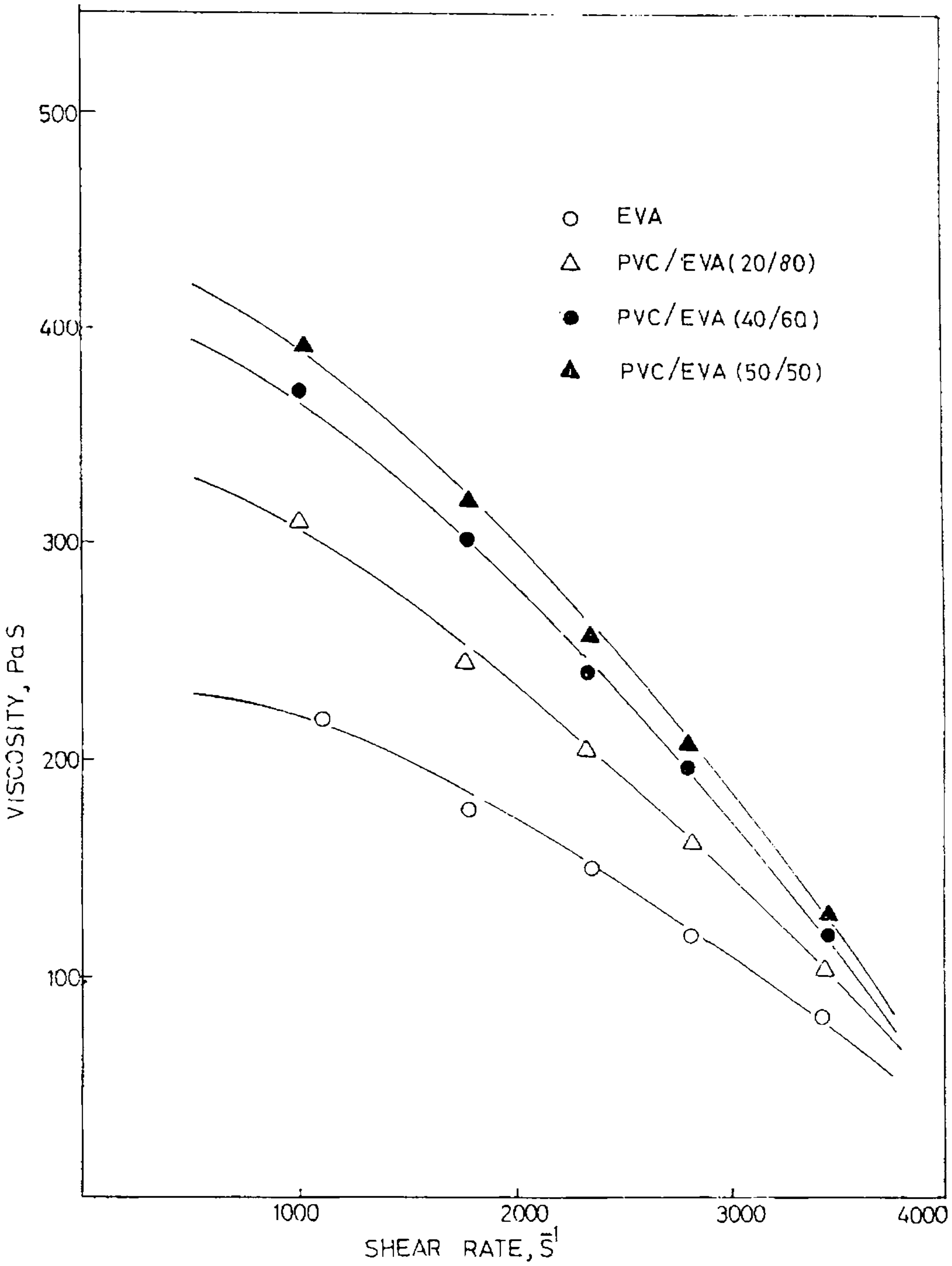


Fig.3.16: Variation of viscosity with shear rate of PVC/EVA blends at 170°C

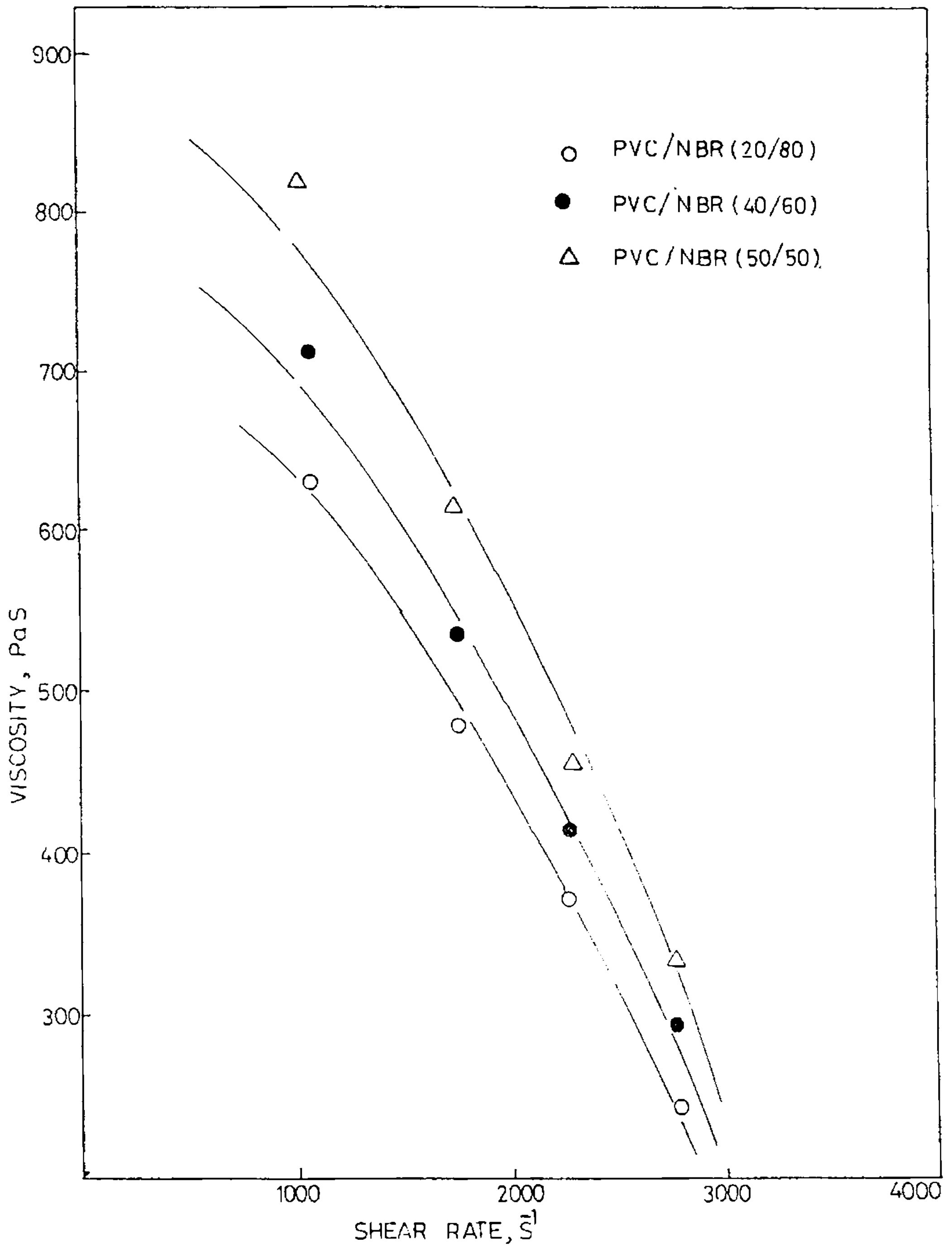


Fig.3.17: Variation of viscosity with shear rate of PVC/NBR blends

region. Since rigid PVC melts, are characterised by high viscosity and high pseudoplasticity, it follows that these polyblends can be processed at lower temperatures and shear rates as compared to PVC alone.[38,40,41]

Fig.3.18 shows plots of log (shear stress) vs log (shear rate) for Hytrel and for PVC/Hytrel blends at 170°C. The curve for Hytrel could not be approximated by a single straight line which makes approximation to a single power law relationship difficult. However, the curve could be approximated as two straight lines with different slopes and these two straight lines may be associated with two flow mechanisms. Blends of Hytrel with PVC also exhibit a similar behaviour. But in this case the flow mechanisms indicated by the two straight lines may have direct relation to the fusion of PVC particles. In the region of low shear rates the straight lines are fairly parallel to the initial straight line shown by Hytrel. This may imply that at low shear rates, capillary flow can occur without the individual particles of PVC being destroyed.[40] For a given composition of PVC/Hytrel blend and at a particular temperature there seems to be a particular shear rate above which domain interfaces are obliterated and conventional intermolecular

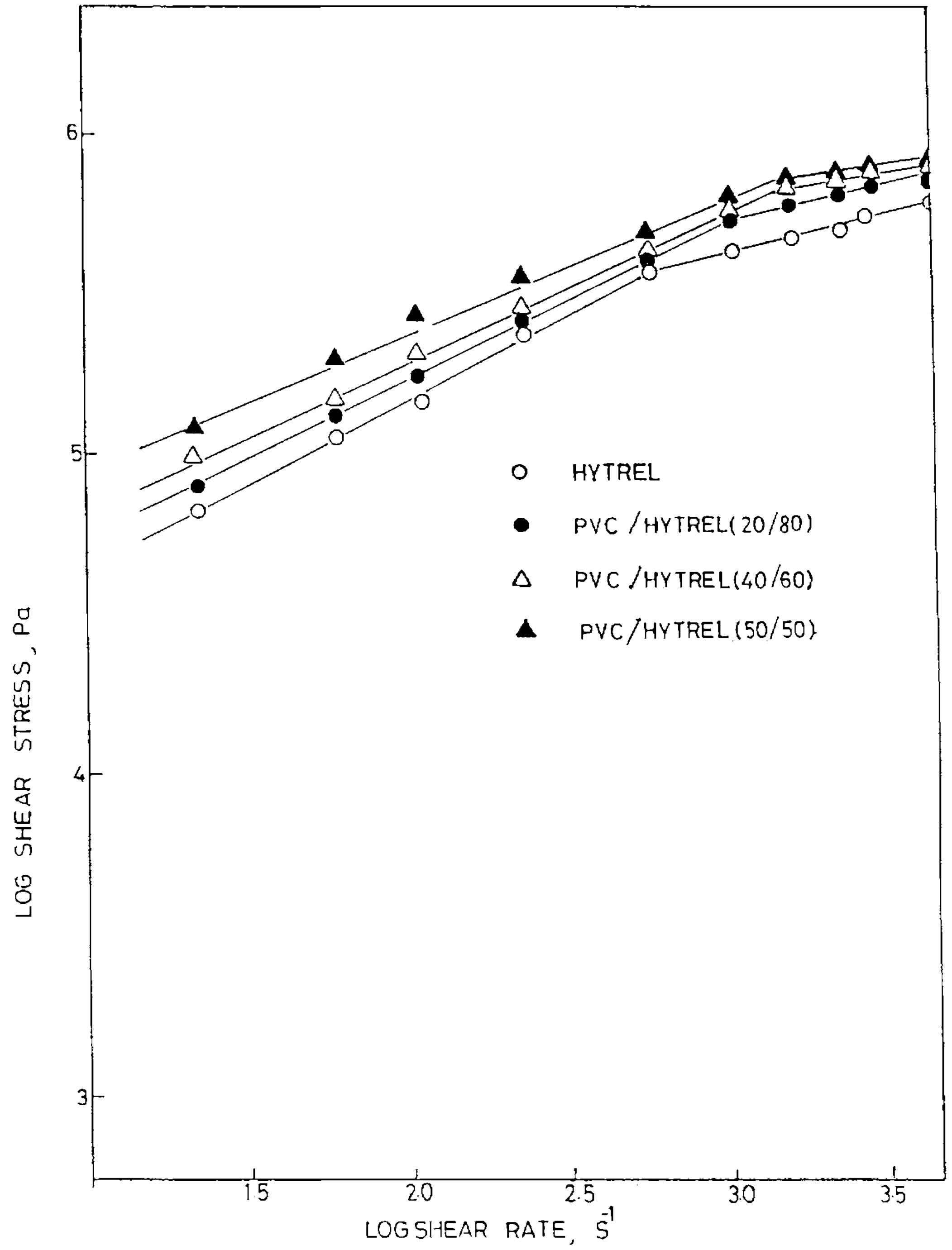


Fig.3.18: Shear stress—shear rate curves of PVC/Hytrel blends

flow occurs. In the case of PVC/Hytrel blends the upper straight lines show highly non-Newtonian behaviour as in the case of rigid PVC melts. The critical shear rate at which the transition occurs shifts to higher and higher values with increase in PVC content, as expected. However, complete fusion of PVC particles may not be taking place at higher PVC concentrations since the critical shear rates are close to each other. This incomplete fusion of PVC particles has been shown as one of the reasons for the inferior mechanical properties of PVC blends.[42] Figs.3.19 and 3.20 show the shear stress--shear rate plots of PVC/EVA and PVC/NBR blends respectively. The linearity of the EVA curve over the entire range studied confirms the validity of a single power law relationship. However, with the addition of PVC, the behaviour becomes similar to that of PVC/Hytrel blends, a mildly non-Newtonian initial behaviour at low shear rates and then a strongly non-Newtonian behaviour after a critical shear rate, the value of which is decided by the composition and temperature. As before the straight line at low shear rates may represent the flow behaviour of the blend when primary particle structure of PVC is not destroyed and the straight line at high shear rates when the particle structure is destroyed. Almost

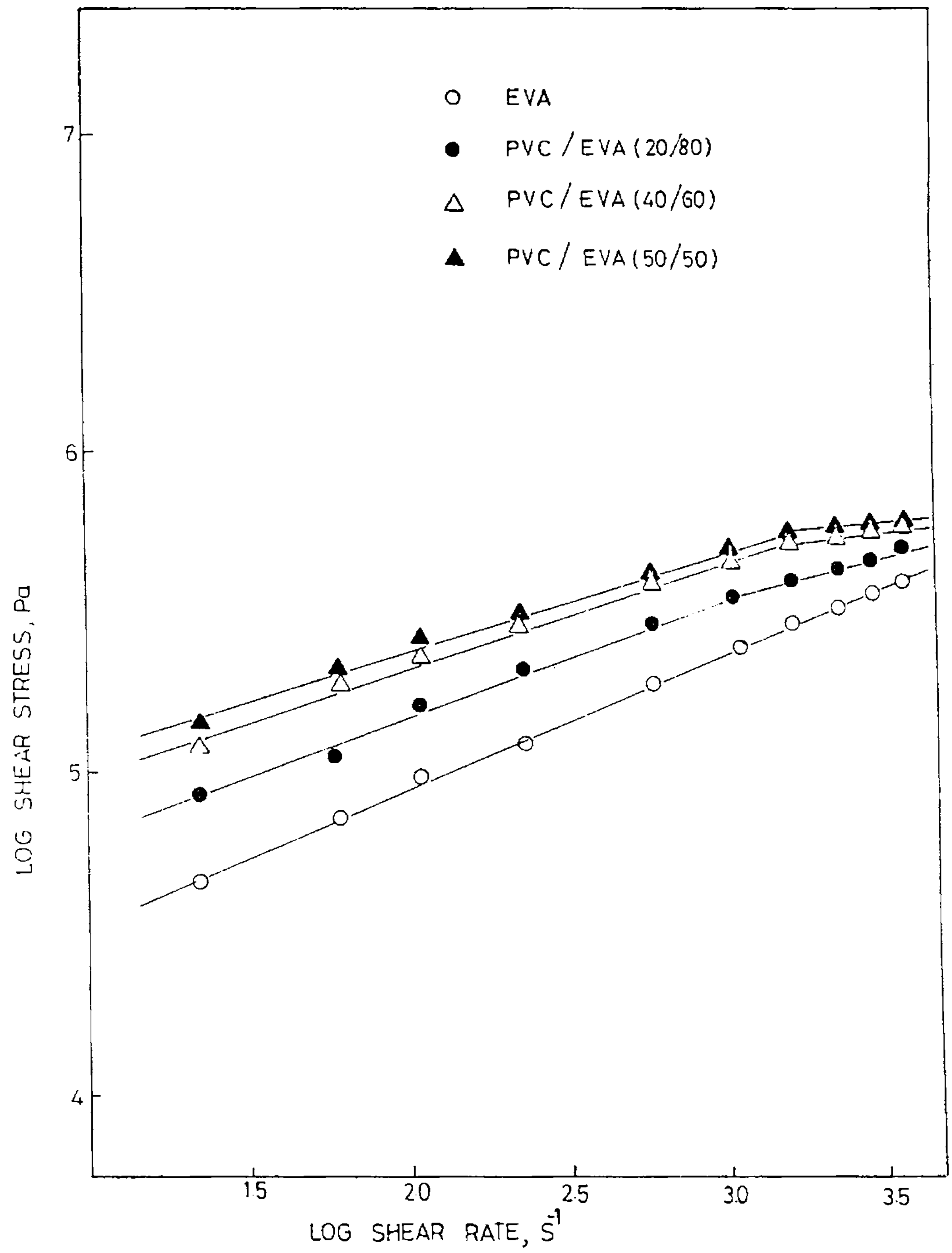


Fig.3.19: Shear stress—shear rate curves of PVC/EVA blends at 170°C

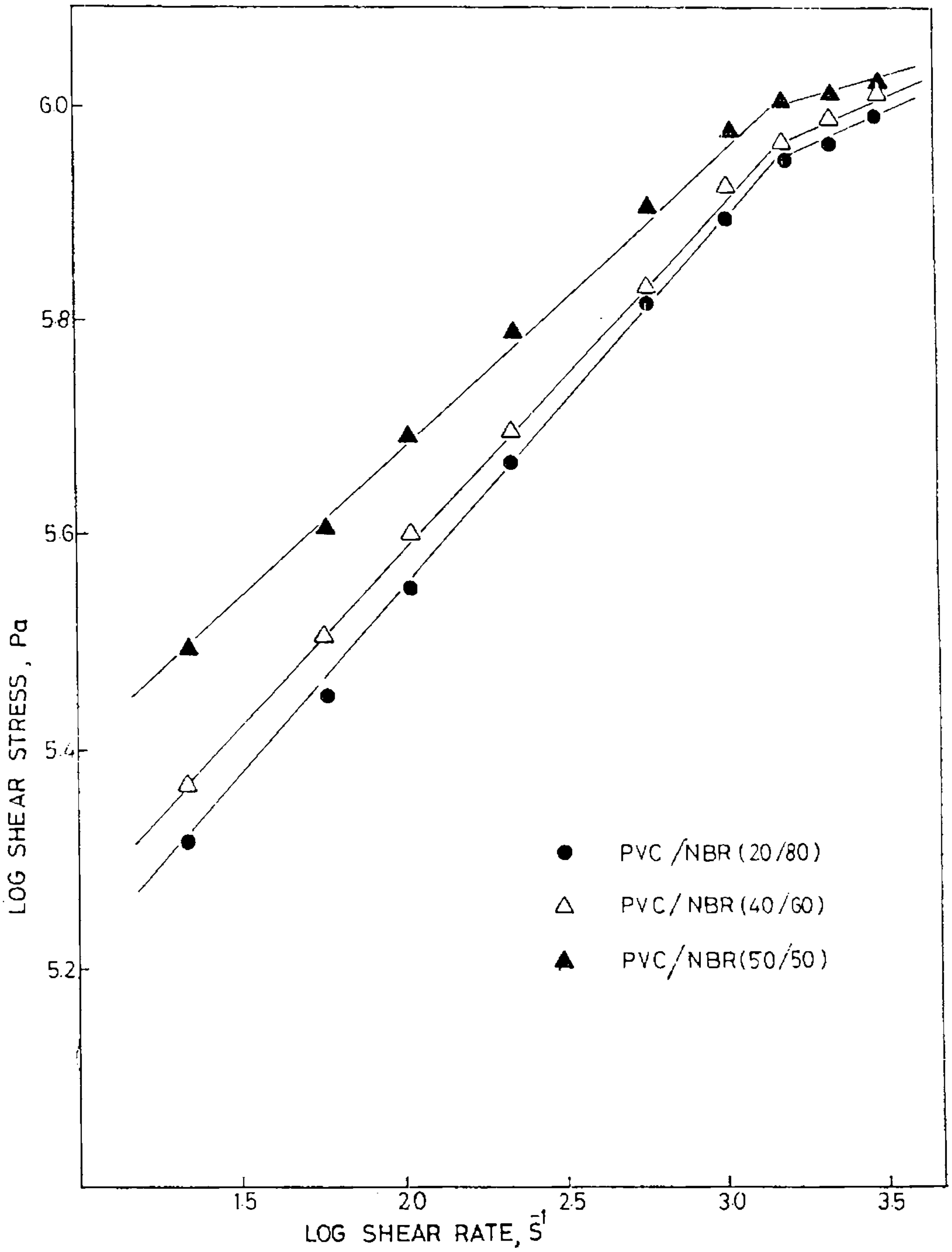


Fig.3.20: Shear stress—shear rate curves of PVC/NBR blends at 170°C

the same behaviour is exhibited by PVC/NBR blends also. We could not report the behaviour of NBR alone since the capillary rheometer, could not handle the high viscosity of NBR alone. The power law indices, a measure of the pseudoplastic behaviour, calculated as the slopes of the straight lines below and above the critical shear rates from Figs.3.18 to 3.20 are shown in Table 3.8.

The temperature dependence of the viscosity of the polymer blends can be expressed by the flow activation energy calculated from the Arrhenius type equation,

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

where E is the activation energy for viscous flow, R the gas constant, T the absolute temperature and A is a constant. Since the flow behaviour is dependant upon shear rate and temperature, a plot of viscosity vs temperature may also reveal the two flow mechanisms shown by shear stress vs. shear rate plots, provided the data are taken over a broad spectrum of temperatures.[31,40] However, the data were taken only at three temperatures in the present study and the double flow behaviour obviously will not be revealed. However, if the plot of η vs 1/T

Table 3.8: Power law index values of PVC blends at 170°C

Percentage composition of PVC:Modifier	CAPILLARY VISCOMETER						Torque Rheometer		
	PVC/Hytrel		PVC/EVA		PVC/NBR				
	Below critical shear rate	After critical shear rate	Below critical shear rate	After critical shear rate	Below critical shear rate	After critical shear rate	PVC/ Hytrel	PVC/ EVA	PVC/ NBR
0 : 100	0.56	0.34	0.42	0.42	--	--	0.27	0.28	0.21
20 : 80	0.50	0.30	0.36	0.20	0.44	0.18	0.22	0.26	0.18
30 : 70	0.48	0.27	0.32	0.18	0.40	0.16	0.18	0.24	0.15
40 : 60	0.45	0.26	0.30	0.16	0.38	0.11	0.15	0.21	0.13
50 : 50	0.39	0.22	0.30	0.14	0.28	0.07	0.13	0.18	0.12

for a particular blend is drawn for a wide range of shear rates, the critical shear rate at which the flow mechanism changes can be observed. Fig.3.21 shows the variation of viscosity with absolute temperature at different shear rates for a 30/70 PVC/Hytrel blend. The activation energy of viscous flow calculated from these straight lines is shown in Table 3.9.

It can be observed that the flow activation energy remains more or less the same with marginal changes when the shear rate varies from 23.0 S^{-1} to 576.0 S^{-1}. After that there is a sharp decrease in the flow activation energy and thereafter remains more or less the same again. This shows that the critical shear rate for the blend is around 576.0 S^{-1}. The sharp reduction in the flow activation energy beyond this critical shear rate is obviously due to the highly non-Newtonian behaviour introduced due to the fusion of PVC particles.[31] The table also shows the flow activation energies of 30/70 blends of PVC/EVA and PVC/NBR. In these cases also the shear rate at which the flow transition occurs can be observed. Fig.3.22 shows the effect of blend ratio on the activation energy of PVC/Hytrel blends. The activation energy of PVC/modifier blends at 23.0 S^{-1} shear rate is

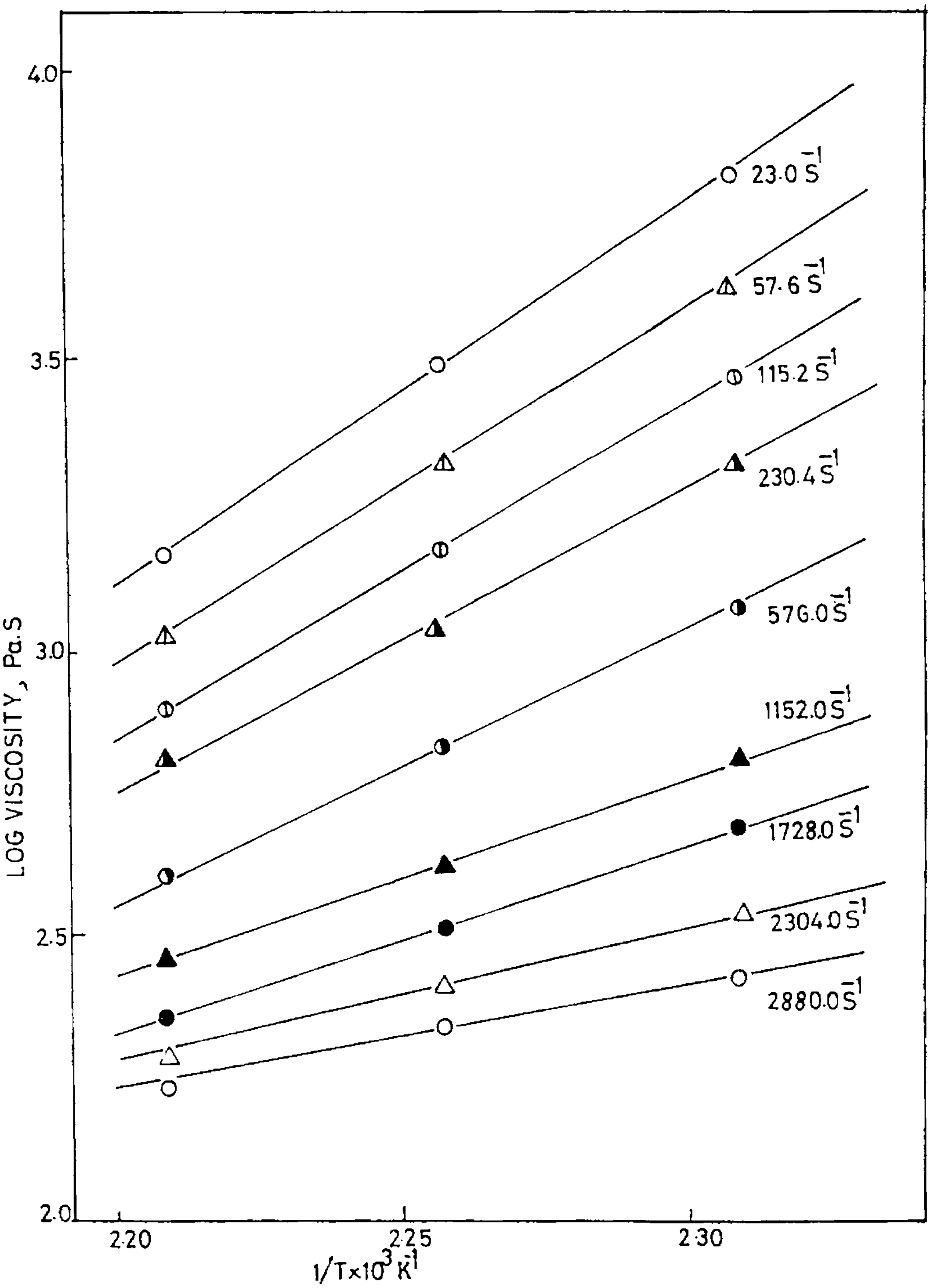


Fig.3.21: Variation of viscosity with temperature at different shear rates for a 30/70 PVC/Hytrel blend

Table 3.9: Variation of activation energy of PVC blends with shear rate

Apparent shear rate (s^{-1})	Flow activation energy kJ/mole		
	PVC/Hytrel (30/70)	PVC/EVA (30/70)	PVC/NBR (30/70)
23.0	131.5	38.3	50.3
57.6	123.8	33.5	47.8
115.2	123.8	33.5	47.8
230.4	112.5	31.9	40.2
576.0	101.4	28.7	38.2
1152.0	57.4	28.7	20.1
1728.0	57.4	15.1	19.1
2304.0	47.8	14.9	18.2
2880.0	40.2	9.5	14.3

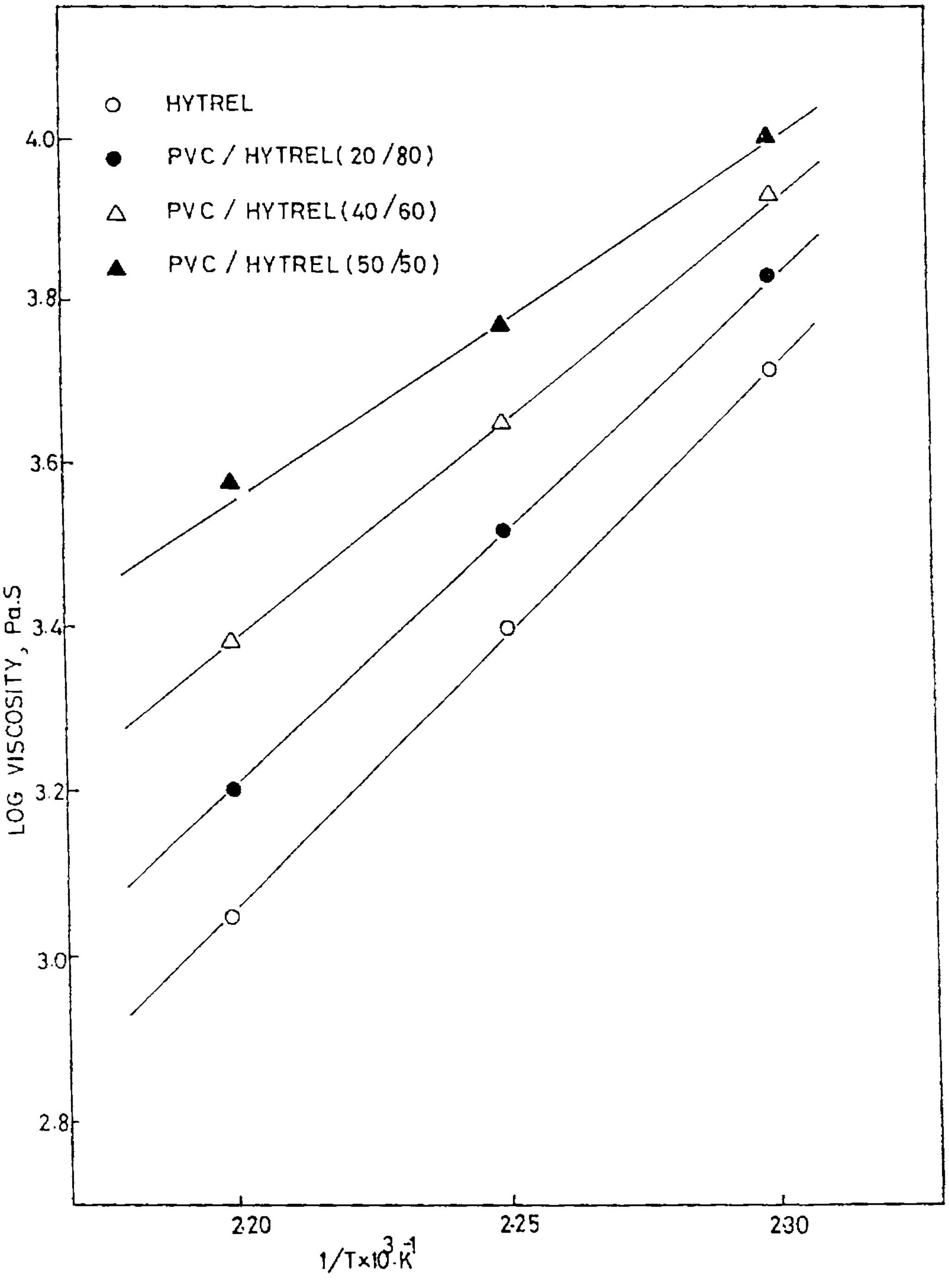


Fig.3.22: Variation of viscosity with temperature for PVC/Hytrel blends with (PVC content) (at a shear rate of 23.0 S^{-1})

given in Table 3.10. It can be observed from the table that the flow activation energy decreases with increase of PVC content.

Table 3.10: Variation of activation energy of PVC blends with blend composition.

Percentage composition of PVC : Modifier	Flow activation energies at 23.0 S^{-1} shear rate (kJ/mole)		
	PVC/Hytrel	PVC/EVA	PVC/NBR
0 : 100	145.8	50.6	--
20 : 80	135.4	47.9	56.39
40 : 60	109.5	35.3	47.8
50 : 50	94.8	31.9	42.5

Rheological Functions using the Brabender Plasticorder

Fig.3.23 shows the variation of torque/rpm vs rpm for PVC/Hytrel blends at 170°C in the Brabender plasticorder. As in the case of capillary rheometer torque/rpm, representing viscosity, decreases with increase in rpm which represents shear rate. It is interesting to note that even though the shear rates involved are not high, the behaviour is strongly non-Newtonian and the flow

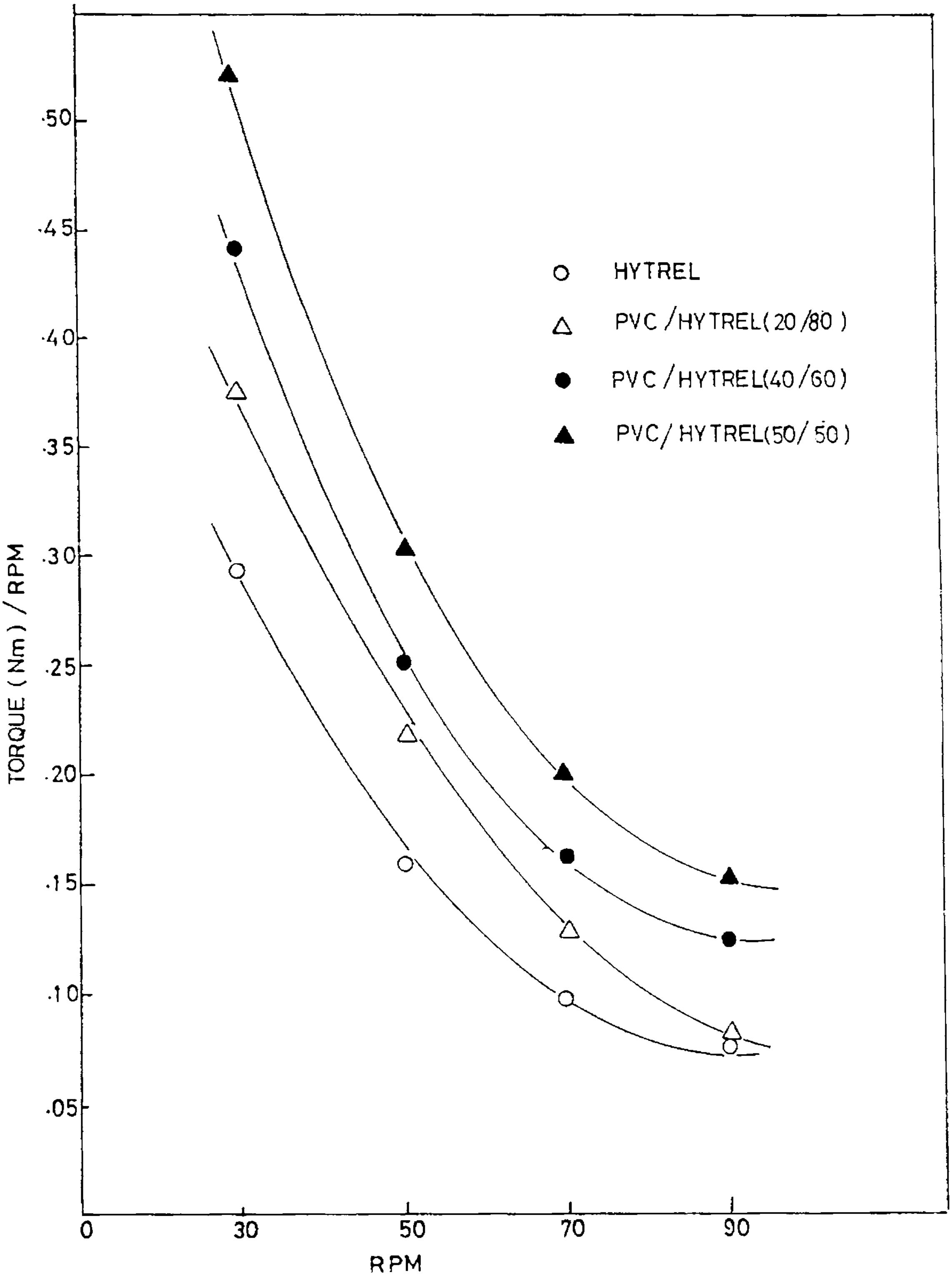


Fig.3.23: Variation of Brabender torque/rpm vs rpm for PVC/Hytrel blends at 170°C

behaviour corresponds to that observed above the critical shear rate in the capillary rheometer.[43] However this behaviour cannot be fully taken as representing the rheological behaviour of the blends due to lack of uniformity in shear and temperature in the Brabender plasticorder. The large initial drop in torque in each case is probably due to the mechanical degradations occuring in the melt resulting from the complex shearing and also due to oxidative degradations to which this instrument is more susceptible. There is no sign of zero shear viscosity in any case. This further shows that the Brabender plasticorder is not efficient in describing the rheological behaviour of such two phase melts. The same behaviour is observed for PVC/EVA (Fig.3.24) and PVC/NBR (Fig.3.25) blends.

Fig.3.26 shows the variation of log torque vs log rpm for PVC/Hytrel blends at 170°C. The behaviour of each blend can be approximated by a straight line, probably since only a small range of shear rates is covered in this instrument. The slope of the lines represents the value of the power law index. Unlike the behaviour of the melt in the capillary rheometer the melt behaviour is highly non-Newtonian even at the low shear

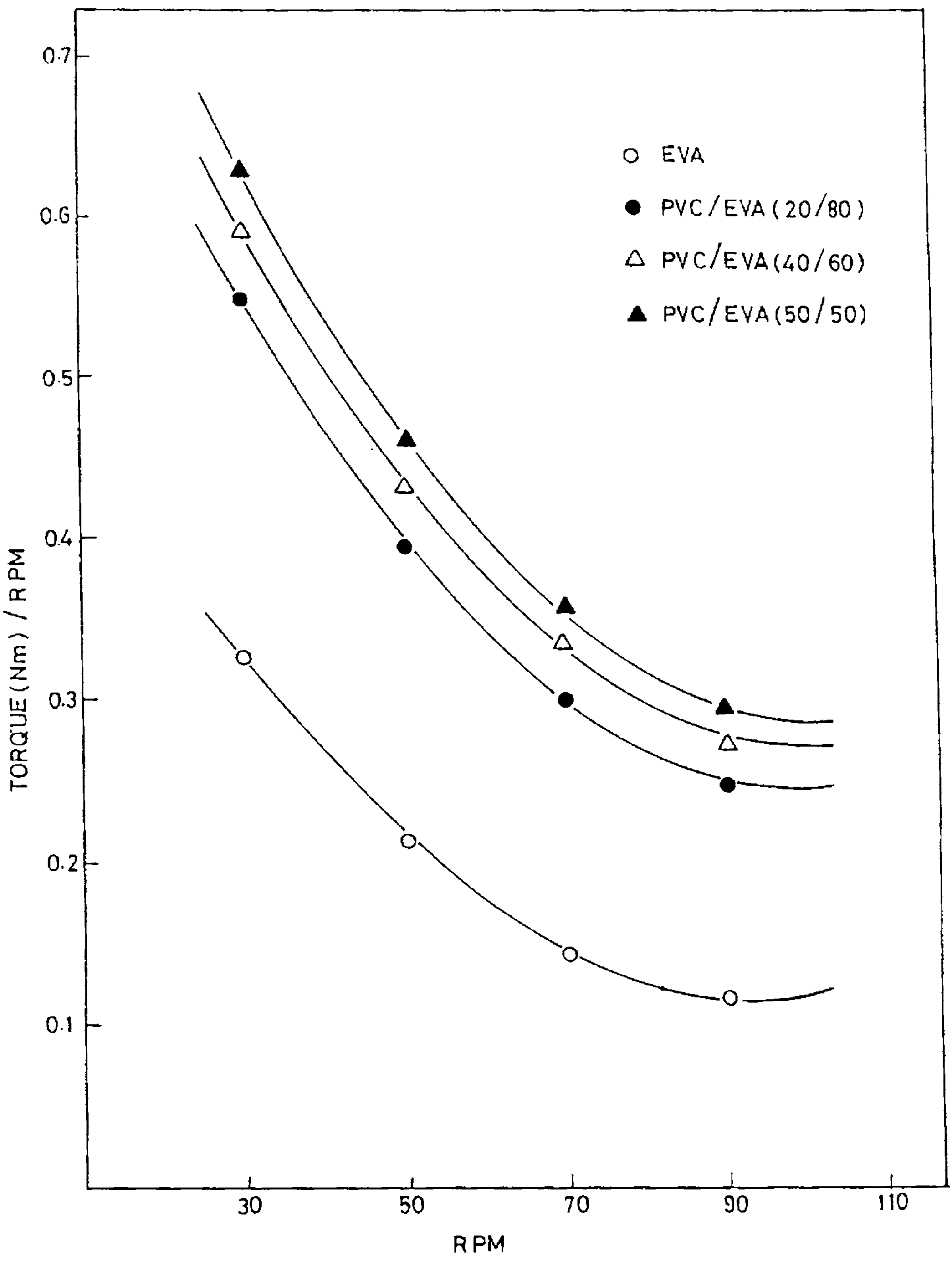


Fig.3.24: Variation of Brabender torque/rpm vs. rpm for PVC/EVA blends at 170°C

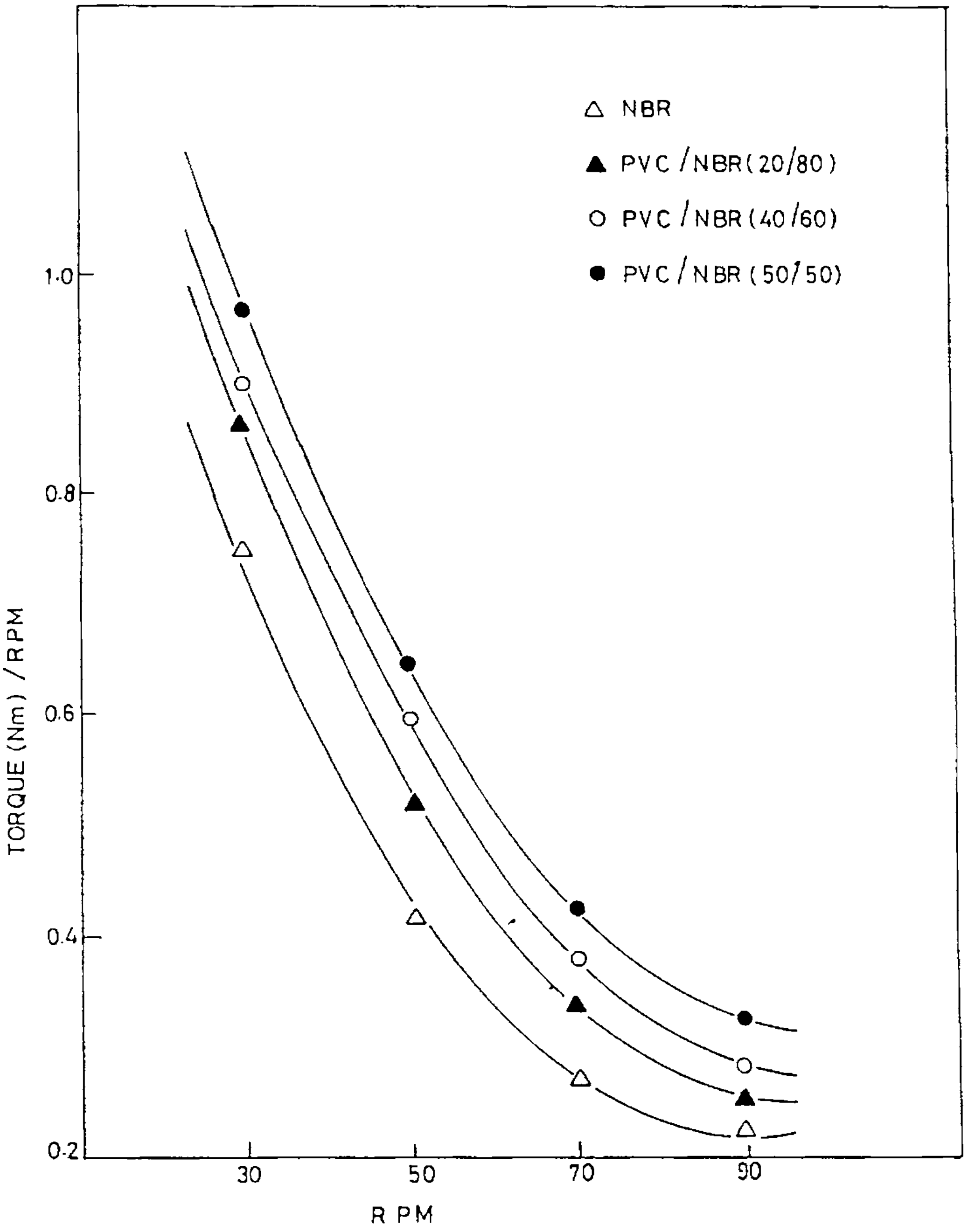


Fig.3.25: Variation of Brabender torque/rpm vs rpm for PVC/NBR blends at 170°C

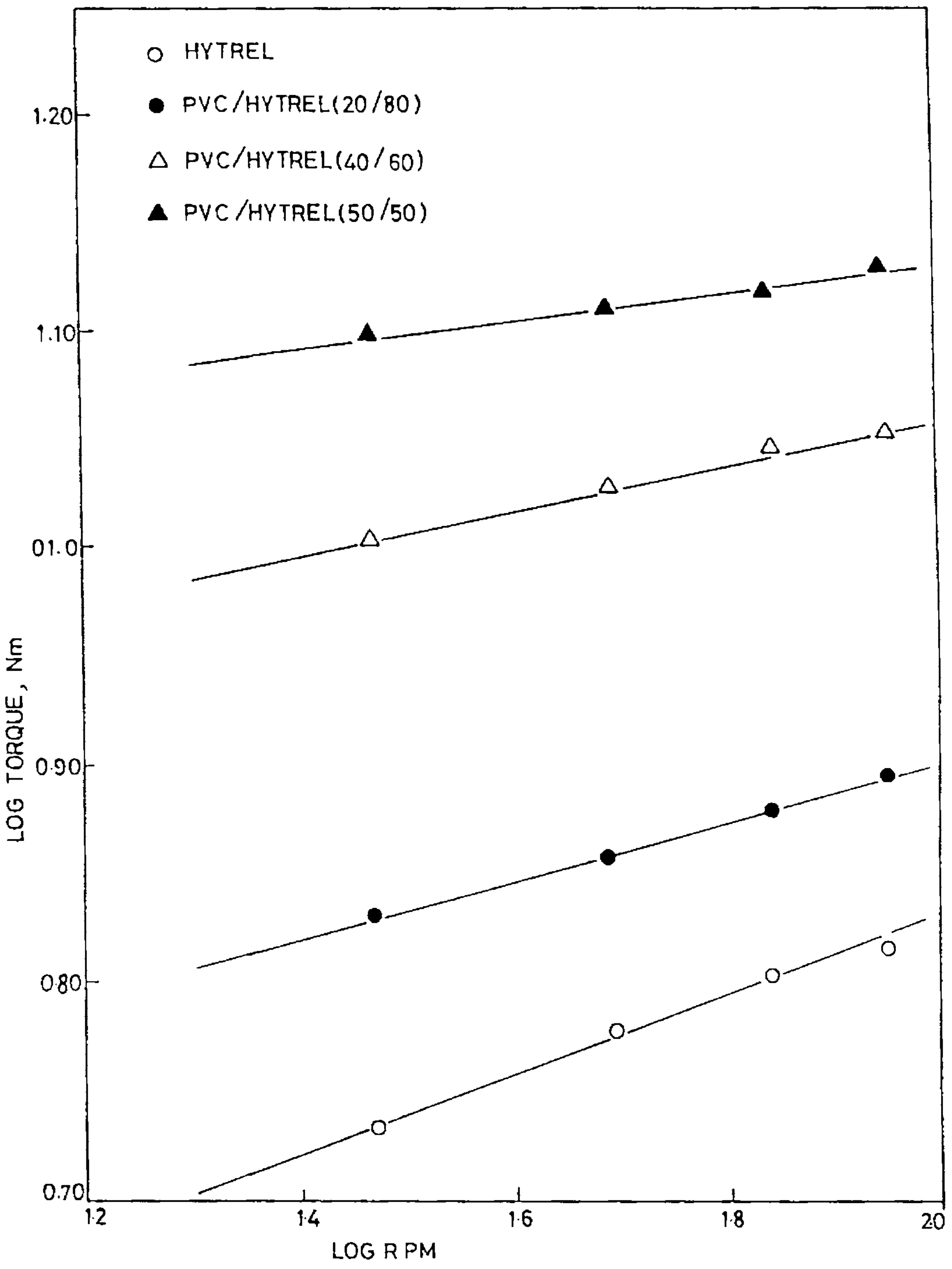


Fig.3.26: Brabender torque-rpm curves for PVC/Hytrel blends at 170°C

rates encountered. This again shows the inefficiency of the Brabender plasticorder in describing the rheological behaviour of the complex melts used in the present study. The same behaviour is observed for PVC/EVA and PVC/NBR blends also. The power law indices calculated from the figures for the blends are given in Table 3.8.

Fig.3.27 shows the variation of log torque/rpm vs reciprocal absolute temperatures for PVC/Hytrel blends at a particular rpm. As observed from the capillary rheometer data the activation energy decreases with increase in PVC content.

From the foregoing discussions it is clear that a Brabender plasticorder is not suitable for evaluating the rheological functions of a complex two phase melt due to the following reasons:

1. only a small range of shear rates is covered
2. lack of uniformity of shear and temperature
3. more susceptible to oxidative degradations.

Elastic Behaviour of the Blends

The elastic nature of the melts was determined from the entrance pressure loss P_c and extrudate swell ratio D_e/D.

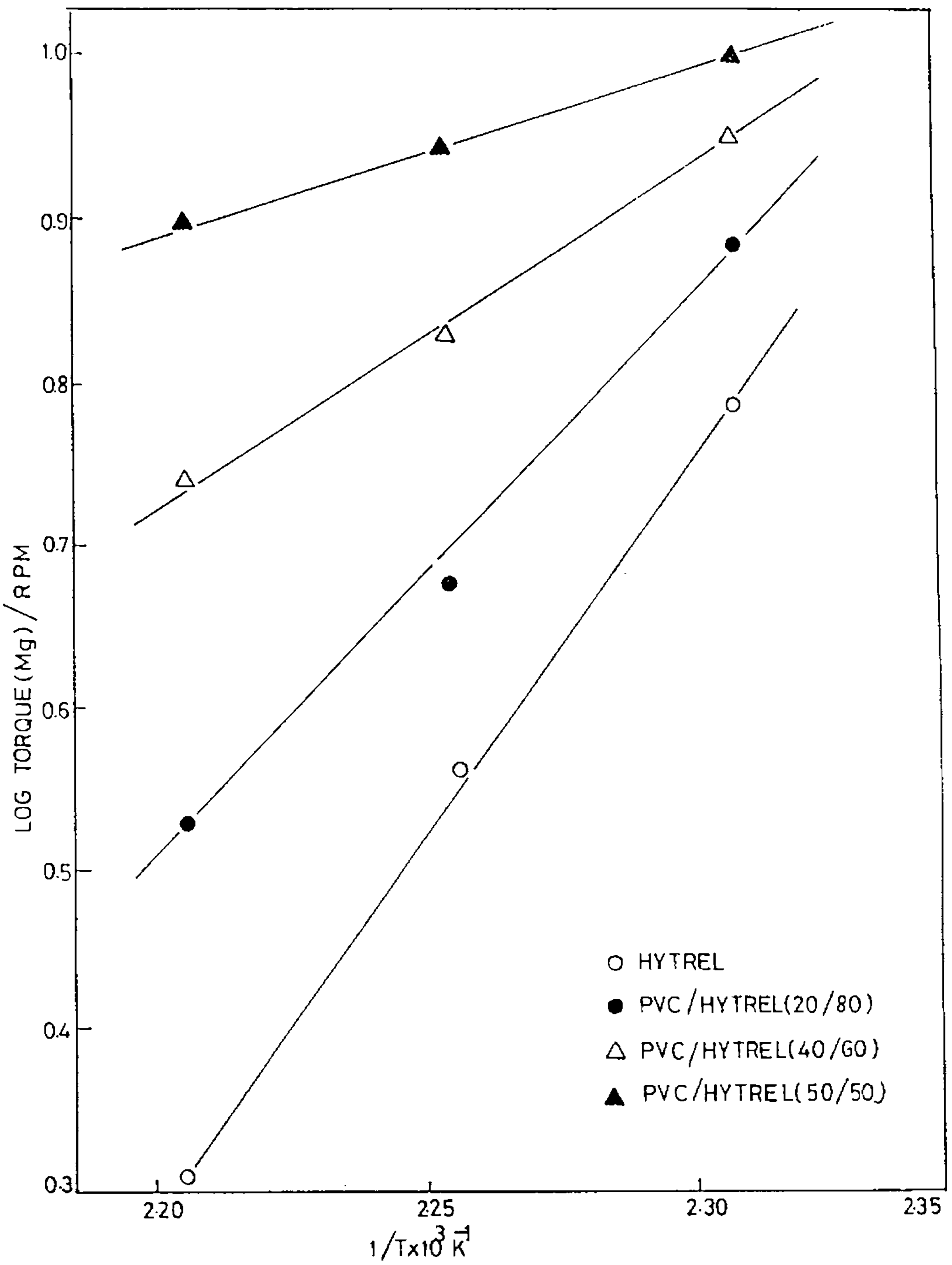


Fig.3.27: Variation of Brabender torque/rpm with temperature for PVC/Hytrel blends at 30 rpm

Experimental

Melt elasticity parameters were evaluated at 170°C. The entrance pressure losses (P_c) for the blends were determined from Bagley plots. Pressure drop (ΔP) was measured at constant shear rates with three capillaries of constant radius (0.5 mm) but different lengths (10 mm, 20 mm and 30 mm). The measured values of ΔP were plotted against L/R. Linearisation and extrapolation of these curvesto L/R = 0 gave the entrance pressure loss (P_c).

The extrudate swell ratio was measured as the ratio of the extrudate diameter (D_e) to the capillary diameter (D).

Results and Discussion

Fig.3.28 shows the Bagley plot of 50/50 PVC/Hytrel blend at various shear rates. The entrance pressure losses P_c at various shear rates were determined from this plots. Similarly entrance pressure losses were calculated for PVC/EVA and PVC/NBR blends. The variation of entrance pressure loss with shear rate for PVC/Hytrel blends is shown in Fig.3.29. The pressure loss is strongly dependent upon the shear rate, as expected. The

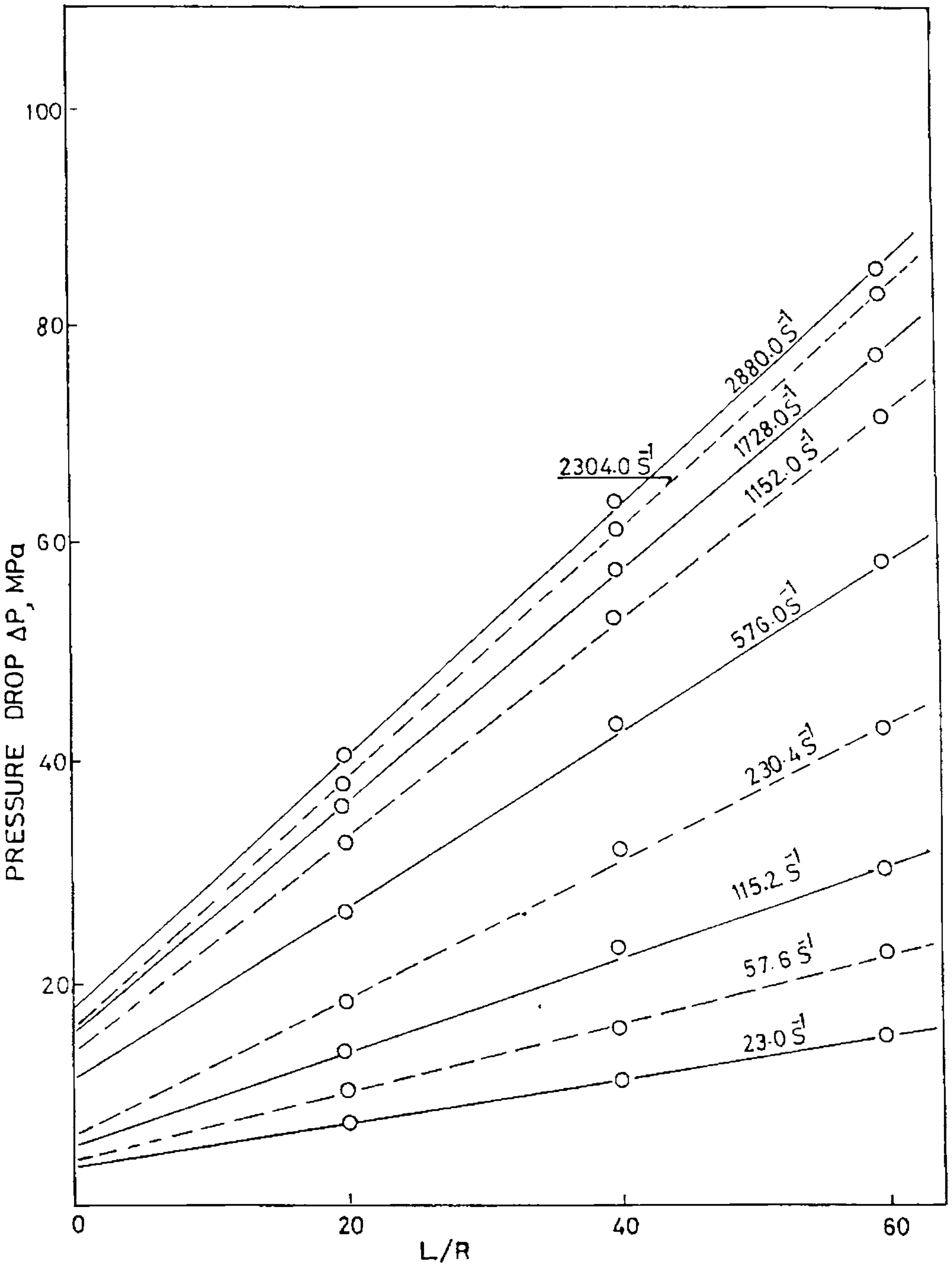


Fig.3.28: Bagley plot of (50/50) PVC/Hytrel blends at various shear rates

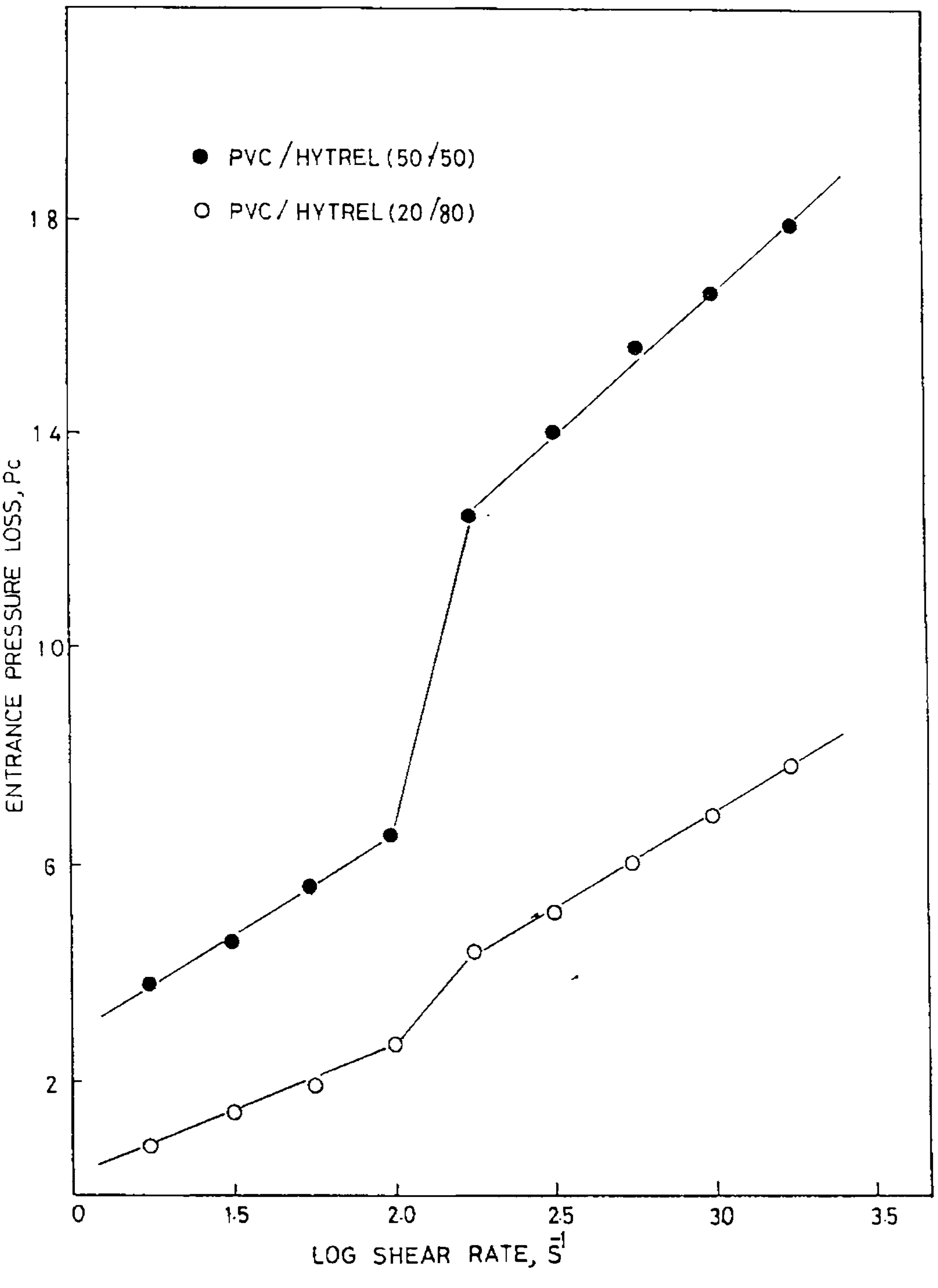


Fig.3.29: Variation of entrance pressure loss with shear rate for PVC/Hytrel blends at 170°C

pressure loss is found to vary smoothly and mildly between the shear rates 23.0 S^{-1} and 230.0 S^{-1}. After this, there is a large increase in pressure loss and thereafter there is only a mild variation. The transition may be the region at which large scale fusion of PVC particles takes place. This is similar to the flow mechanisms shown by PVC blends (Fig.3.18). Similar variation in entrance pressure loss is observed for PVC/EVA (Fig.3.30) and PVC/NBR blends.

Fig.3.31 shows the variation of entrance pressure loss with PVC content for PVC/Hytrel blends. In the low shear region the elastic effects are found to increase with PVC content upto about 40% PVC and thereafter decrease. However, this decrease in the elastic effects with PVC content probably results from the improper fusion of PVC particles, since at higher shear rates, the elastic effects again increase with PVC content. This is in conformity with earlier observations. Similar behaviour is shown by PVC/EVA (Fig.3.32) and PVC/NBR blends.

Figs.3.33 and 3.34 show the variation of extrudate swell ratio with blend composition at different

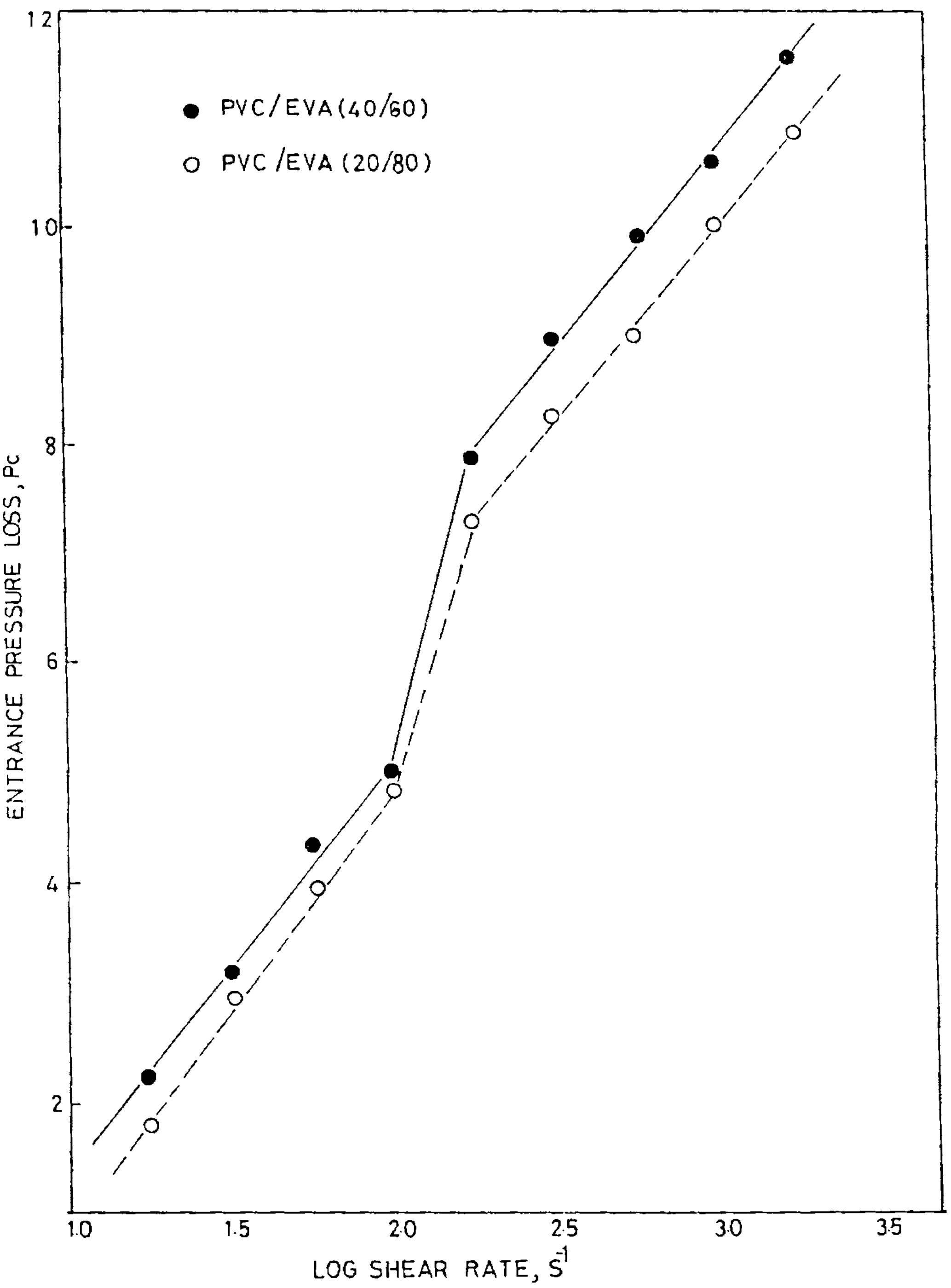


Fig.3.30: Variation of entrance pressure loss with shear rates for PVC/EVA blends at 170°C

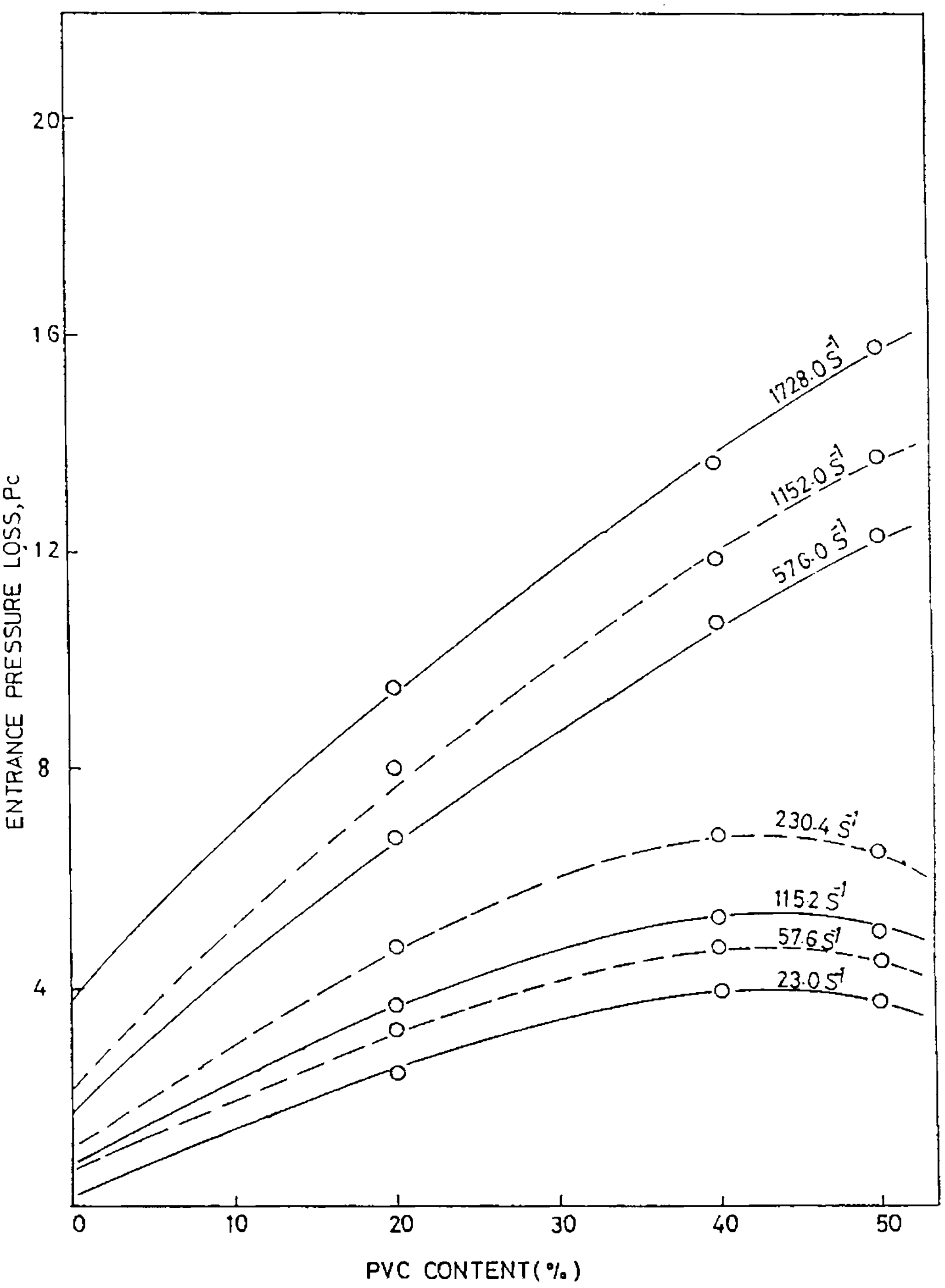


Fig.3.31: Variation of entrance pressure loss with composition for PVC/Hytrel blends at different shear rates

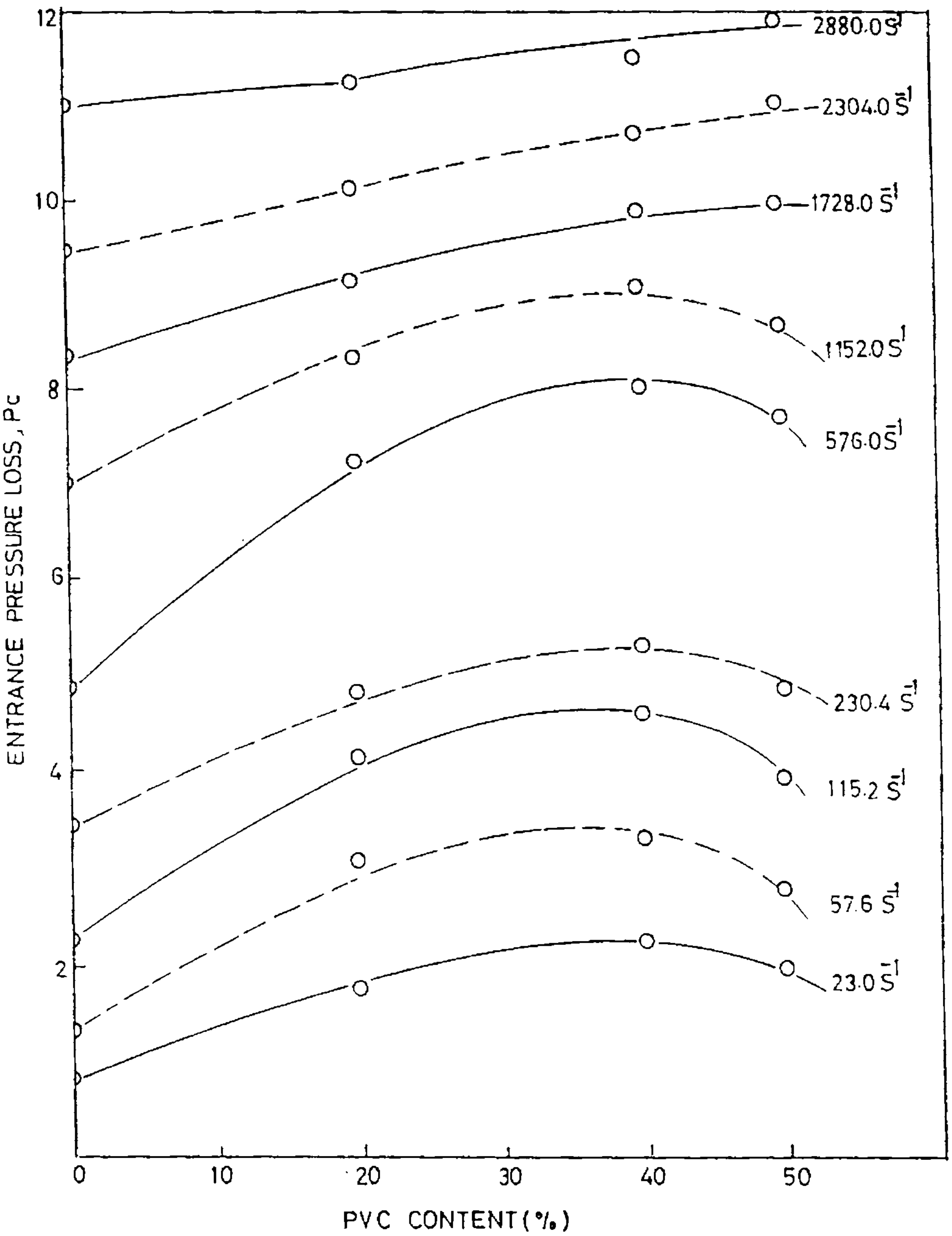


Fig.3.32: Variation of entrance pressure loss with blend composition for PVC/EVA blends at different shear rates

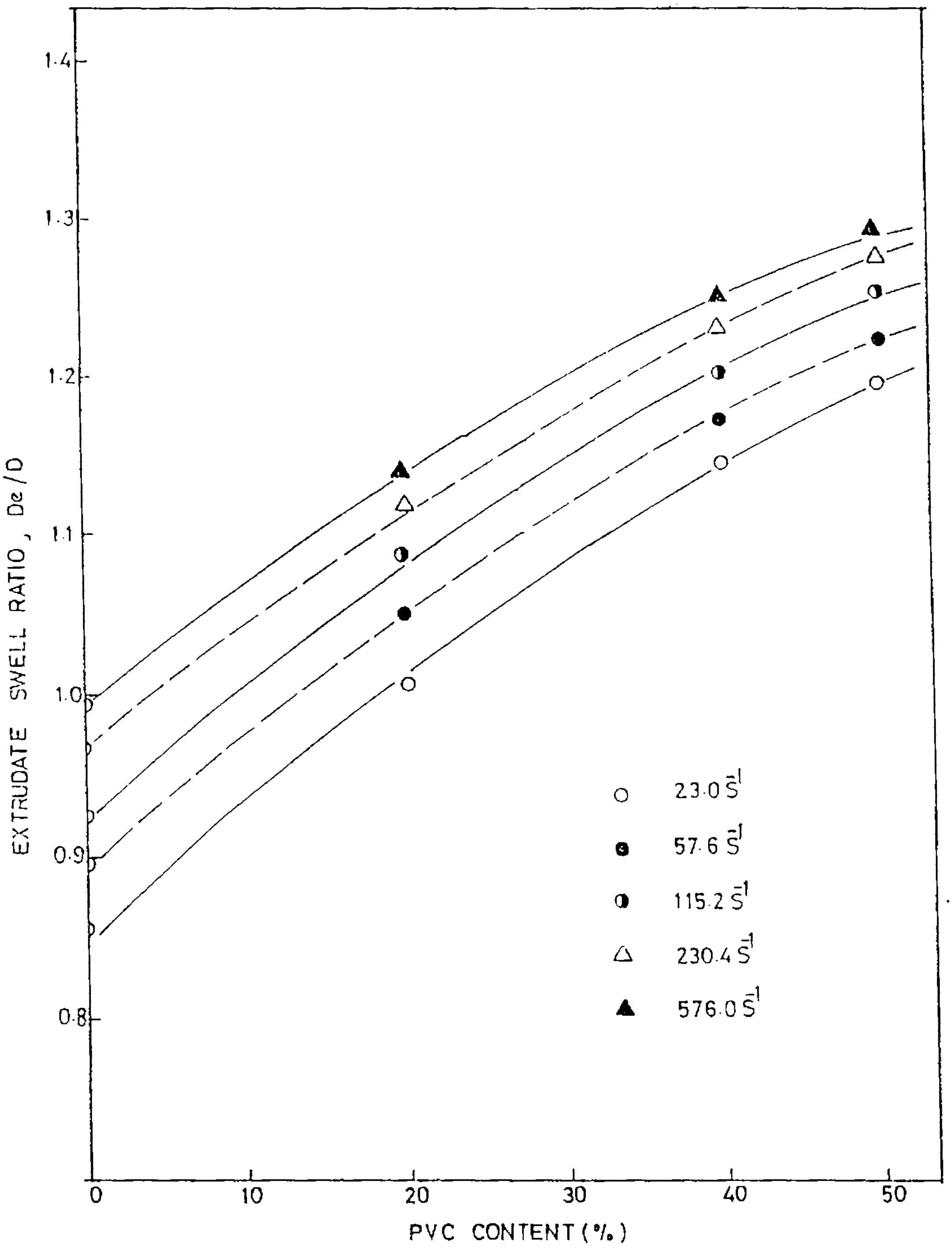


Fig.3.33: Variation of extrudate swell ratio with blend composition for PVC/Hytrel blends at different shear rates

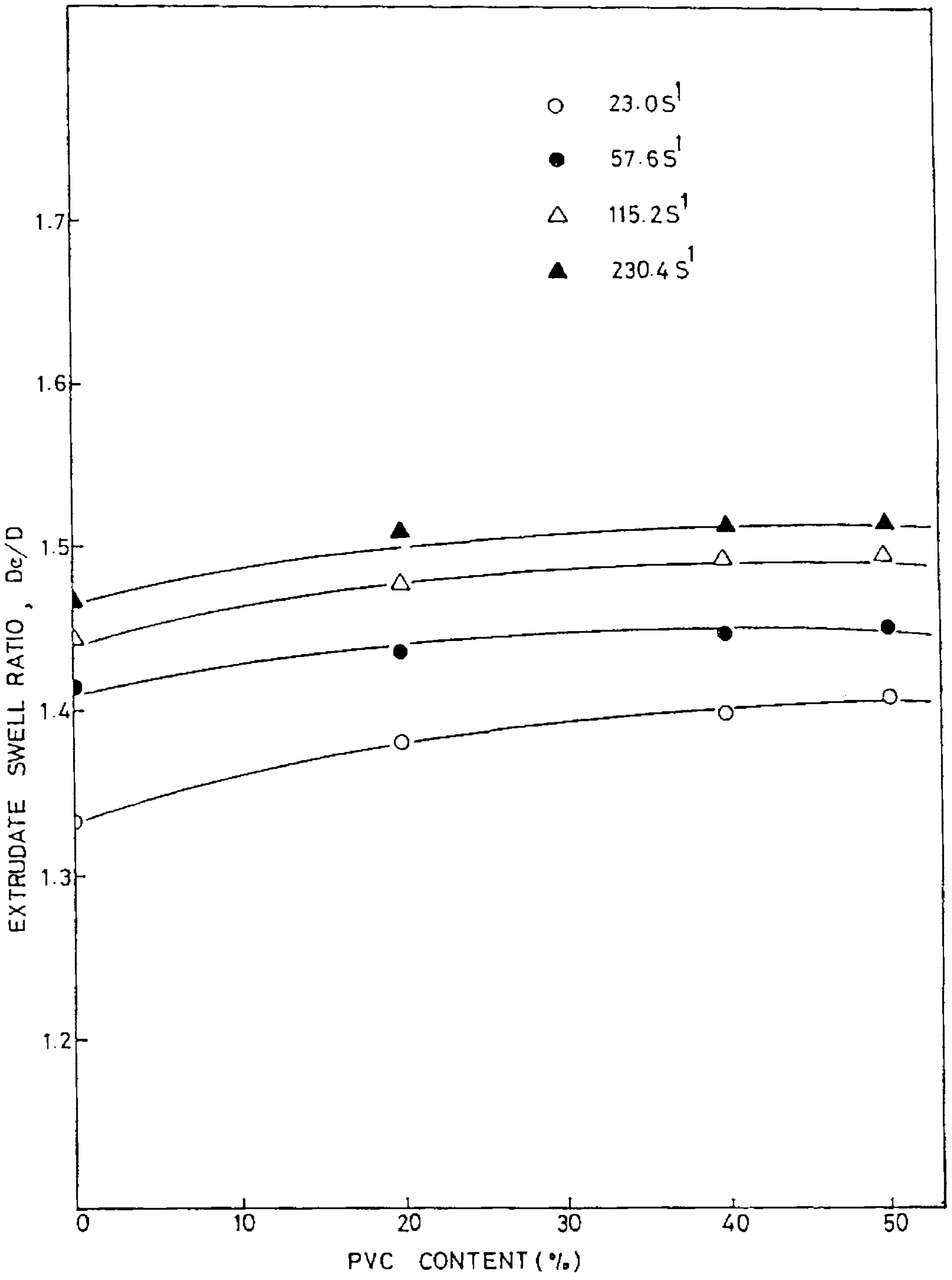


Fig.3.34: Variation of extrudate swell ratio with blend composition for PVC/EVA blends at different shear rates

shear rates for PVC/Hytrel and PVC/EVA blends. Extrudate swell increases with shear rate in all cases as expected. As in the case of the entrance pressure loss, the die swell ratio also increases with PVC content. This further confirms the higher elastic nature of PVC in melts compared to Hytrel, EVA and NBR. The higher elastic recovery of PVC compared to other polymeric additives such as Hytrel and epoxidized natural rubber has already been reported.[44,45]

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Chapter 4

STUDIES ON POLY(VINYL CHLORIDE)/LINEAR LOW DENSITY POLYETHYLENE BLENDS

STUDIES ON POLY(VINYL CHLORIDE)/LINEAR LOW DENSITY POLYETHYLENE BLENDS

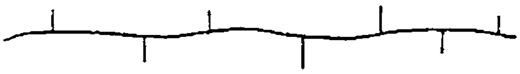
The widespread development of plastics and plastic products all over the world has also brought it with a huge problem. Plastics, today form a sizable fraction of solid wastes, a large portion of which are commodity plastics. Their lack of biodegradability is generating new problems such as lack of landfill sites, growing water and land surface litter etc. Recycling by reprocessing of plastic waste is a solution to the major problem created by the plastic consumer society. This method of reutilisation of solid plastic waste is used as a base for producing secondary products, lowering energy costs, and reducing environmental pollution. Also the increase in the price of polymeric raw materials is making the recycling of consumer waste to secondary products attractive. Polyethylene is a major component of the plastic waste. Eighty per cent of the polyethylene waste is contaminated with other polymers like polypropylene, polystyrene, poly(vinyl chloride) etc.[1-3] However, separating these polymers and then recycling them individually, introduces an addition costly step in the reprocessing route. Instead, reprocessing of the mixed plastic waste is becoming more popular in view of the economic benefits.

Several researchers have studied the blends of low density polyethylene (LDPE) with polystyrene (PS), high density polyethylene (HDPE) and polypropylene[4,5] (PP). Mikkonen et al.[2] studied the rheological, morphological and mechanical properties of the LDPE/plasticised PVC blends. The PVC/PE blend is now utilised in several applications like blister packaging, low halogen-low smoke fire resistant electric cable sheathing etc.[6,7] Many of the problems associated with recycling of mixed plastic wastes are identifiable in the processing/reprocessing of PVC/PE mixtures. Processing of the PVC/PE mixtures is not likely to yield products with the expected mechanical properties because of the poor adhesion of the phases due to the thermodynamic incompatibility.[8-10] In literature, various methods have been suggested for the reactive compatibilisation of such immiscible blends for demanding applications. The mechanical properties and the technical performance of the immiscible blends would be more nearly additive if the interfacial zone is strengthened. One way to do this is to add interfacially active agents to the immiscible mixture.[8,10] Thus the interfacial energy between the immiscible phases is reduced ensuring a finer dispersion upon mixing and higher stability against phase separation. Most common types of compatibilisers are[11]

1. block, graft or random copolymers
2. co-solubilisers enhancing the interpenetration of resin domains
3. co-reactors, catalysts enhancing chemical reaction between the resins
4. modifications or additives enhancing specific interactions.

In the present study an attempt is made to modify the immiscible PVC/PE blend by various methods listed above. The polyethylene selected for the study is the newest member of the polyolefine family viz., linear low density polyethylene (LLDPE), since it is fast replacing low density polyethylene (LDPE) in many applications. LLDPE has a greater degree of stiffness and higher tensile strength than LDPE and also has a more regular crystalline structure, higher melting point and a better fracture resistance at low temperature. Coupled with these attractive properties is the low pressure manufacturing advantage of LLDPE compared to the high pressure technique employed for LDPE. While LDPE is manufactured by high pressure process in which polymerization occurs by a radical mechanism, LLDPE is produced by low pressure process with Ziegler-Natta or Phillips catalysts in the presence of sufficient amounts of olefinic comonomers. Although with respect to its density LLDPE is a low density polyethylene from the point of view of its structure it is a linear polyethylene containing short side chains.[12]

LDPE with branched chains



LLDPE with short side chains

CHLORINATED POLYETHYLENE (CPE) AS A MODIFIER FOR PVC/LLDPE BLENDS

Block and graft copolymers with the segments or blocks chemically identical or similar to the components of the blend have been found to be the most useful to act as compatibilising agents. Since vinyl chloride can only be polymerised by a radical mechanism, production of block copolymers of PVC is difficult and a constitutive block miscible with PVC is the only alternative method.[13] Chlorinated polyethylene, a block like polymer with segmented structure, has been suggested as a compatibiliser for HDPE/PVC and PS/PVC mixtures.[14] Bataille et al.[15] have studied the influence of CPE, EVA etc. on the physical and processing properties of LDPE/PVC mixtures. Also the ability of block chlorinated polyethylene to improve the ductility of blends of LDPE and PVC has previously been reported by Locke and Paul.[16] Hence in the present study, CPE is selected as the modifier for PVC/LLDPE blends. In PVC blends, the improvement in the fusion state of PVC is found to be one of the mechanisms by which the modifiers act (previous chapter). Hence PVC-1 with a lower molecular weight was chosen for modification by CPE since it is easier to achieve a better fusion state with a PVC grade of lower K value.

Experimental

Polymer blends were prepared on a Brabender plasticorder equipped with roller blades. Mixing conditions were 170°C and 30 rpm. LLDPE was added first, then CPE and finally PVC along with its heat stabiliser (4 phr tribasic lead sulphate). Samples were prepared by compression moulding at 180°C for 3 minutes. The tensile properties of the blends were determined according to ASTM D 638 on a Zwick universal testing machine using a cross head speed of 50 mm/min.

Results and Discussion

Fig.4.1 shows the effect of adding CPE (10 parts per 100 parts of PVC and LLDPE) on the tensile properties of PVC-1/LLDPE-1 and PVC-1/LLDPE-2 blends. The tensile properties of the unmodified PVC/LLDPE blends are far below the expected average values of tensile strength. This result is probably due to the incompatibility of the constituents resulting from large differences in the polarity and crystallinity, and hence their incapability to combine the properties of the constituent polymers. A second reason specific to this blend might be the state of fusion of PVC particles in the blend, since it has a

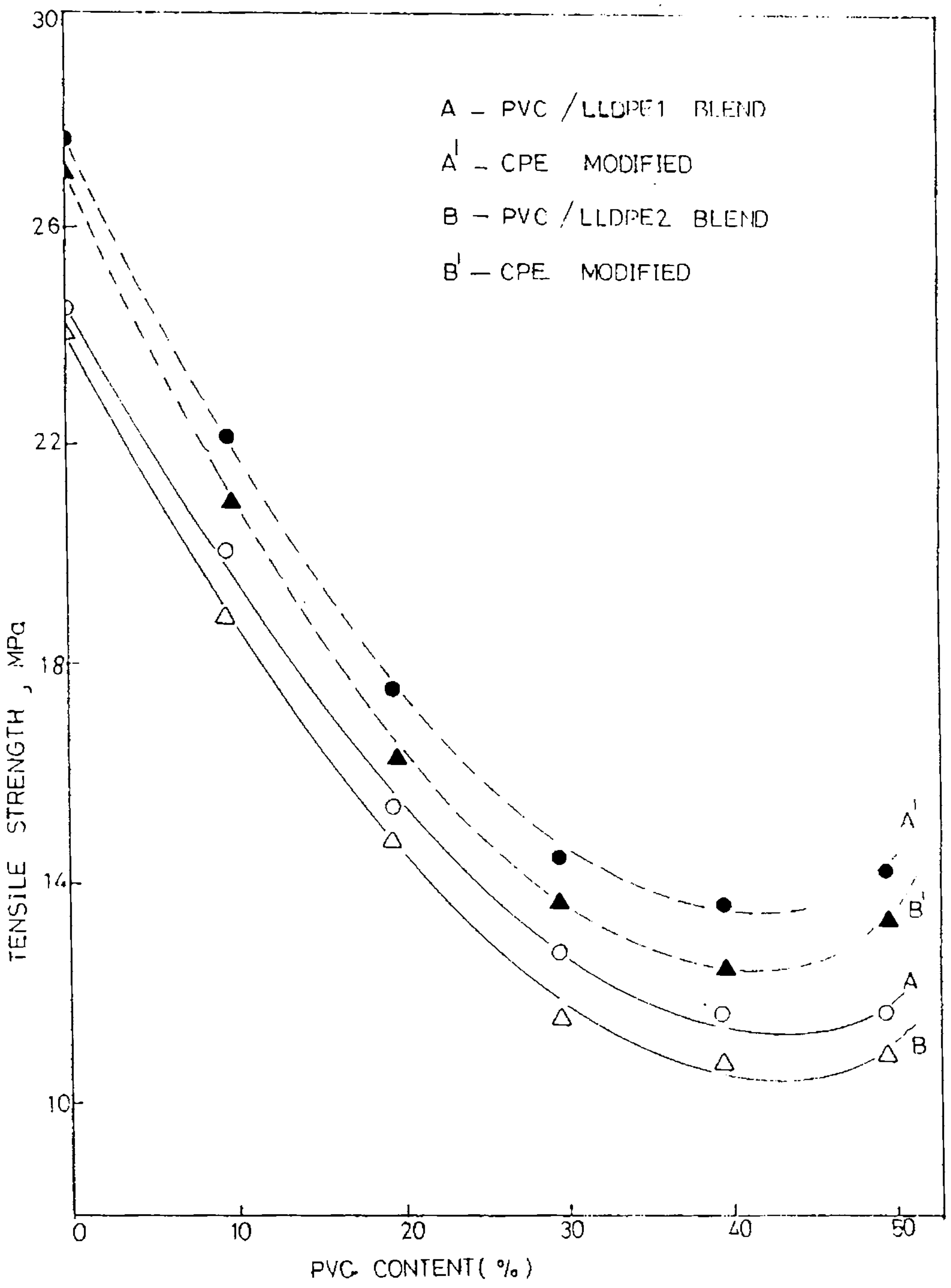


Fig.4.1: Effect of CPE modification on the tensile strength of PVC/LLDPE blends

distinct structure of primary particles different from other commodity plastics such as polyethylene or polystyrene.[17-20] PVC-1/LLDPE-1 shows marginally better strength than PVC-1/LLDPE-2 blends. This might be due to the better molecular weight/viscosity matching of the PVC-1 and LLDPE-1 grades than that of PVC-1 and LLDPE-2 blends. Also it seems to be more sensitive to the addition of CPE. Hence further studies on CPE modification have been done on PVC-1/LLDPE-1 blends.

The effect of three grades of CPE (all grades added at a concentration of 10 parts per 100 parts of PVC and LLDPE) in improving the tensile strength of PVC/LLDPE blends is shown in Fig.4.2. While all the three grades are successful in bringing about some improvement in the strength, CPE-1 is the best showing that it has the ideal molecular weight/viscosity characteristics to emulsify the PVC/LLDPE blends. Hence CPE-1 was chosen for further studies.

Fig.4.3 shows the effect of the variation of CPE content on the tensile strength and elongation at break of 50/50 PVC/LLDPE blends. It is found that increasing the

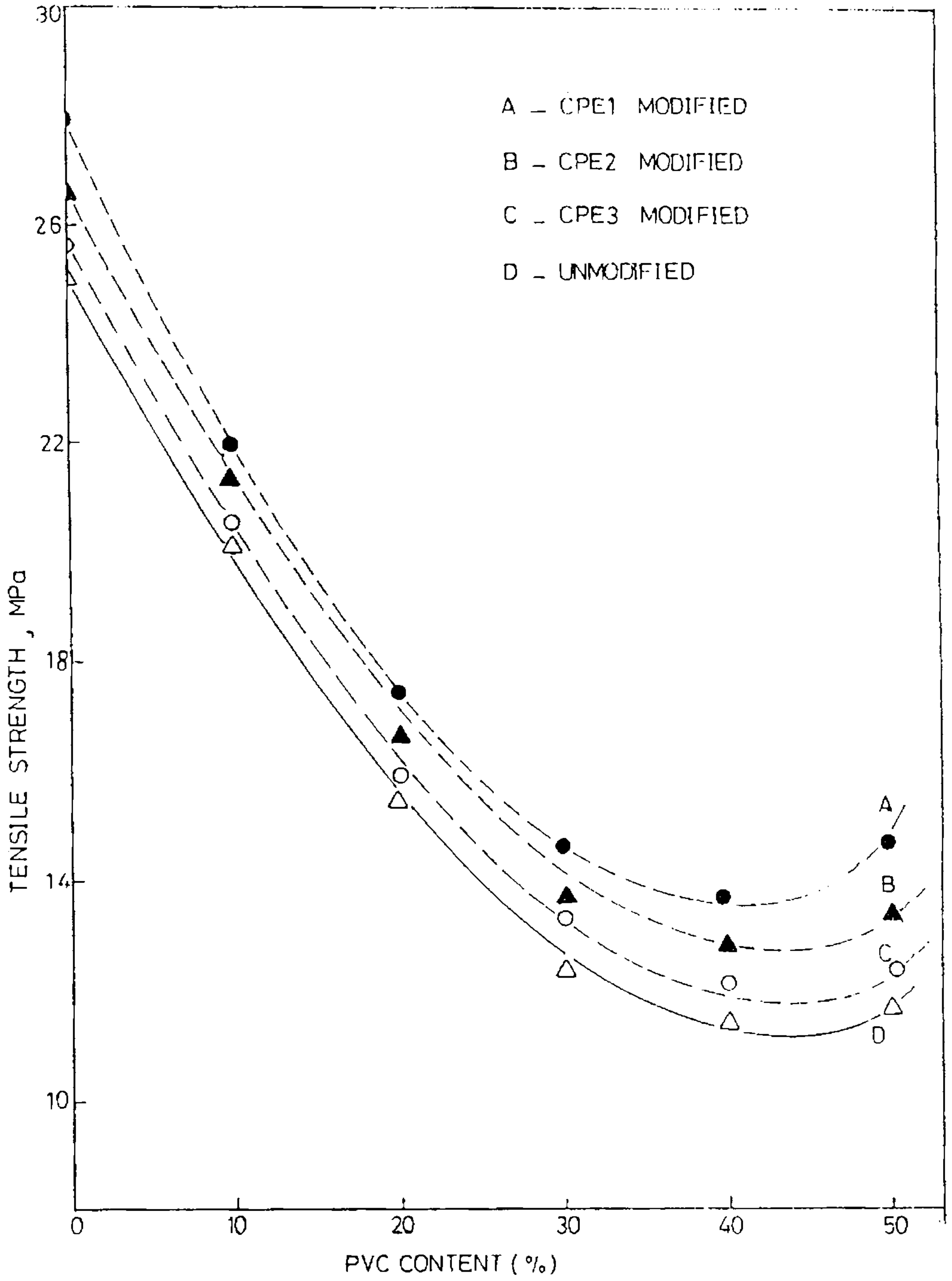


Fig.4.2: Effect of different types of CPE on the tensile strength of PVC/LLDPE blends

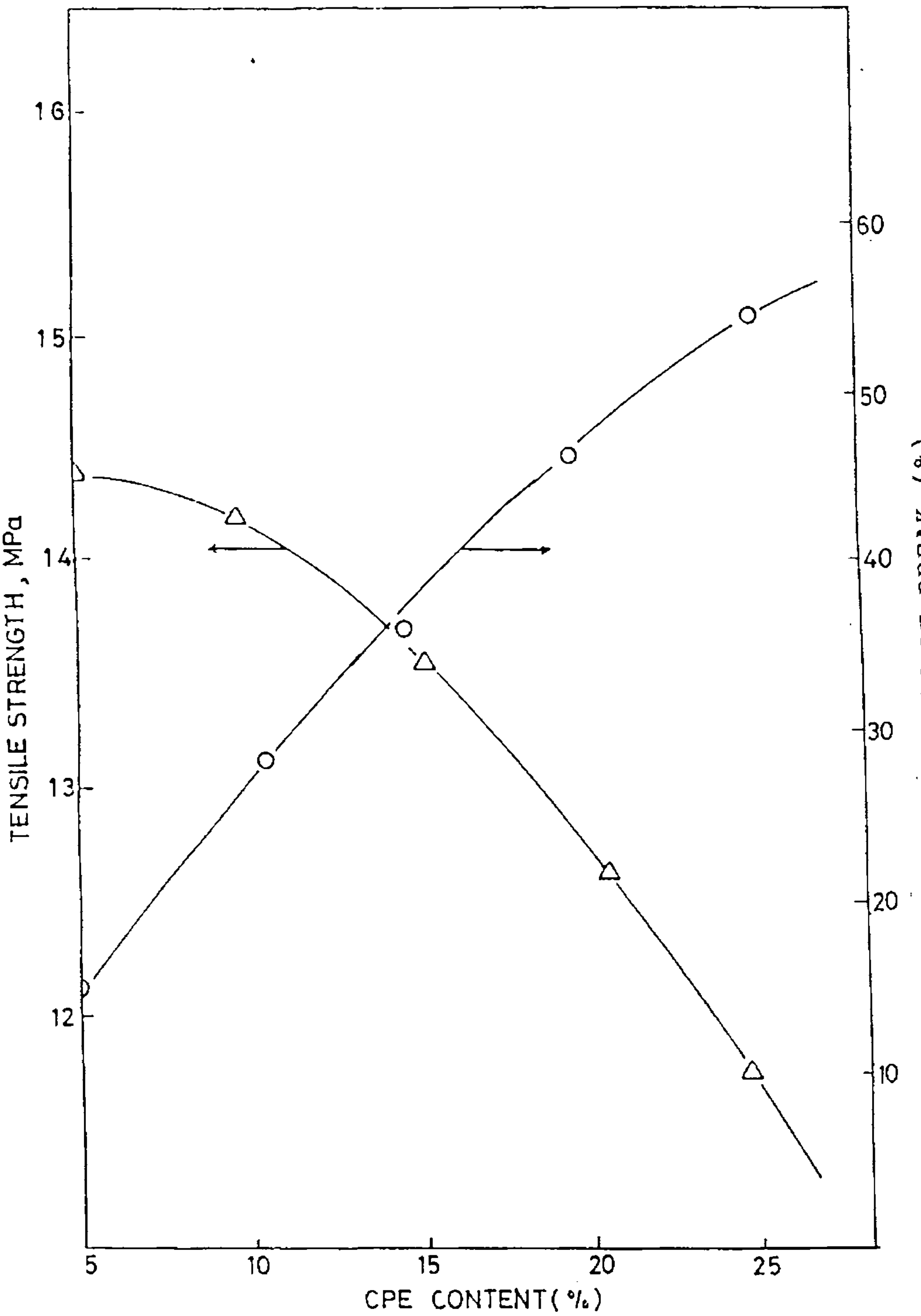


Fig.4.3: Variation of tensile strength and elongation at break of 50/50 PVC/LLDPE blend with CPE content

amount of CPE steadily improves the elongation at break of the blends while the tensile strength falls. A compromise has to struck for overall improvement in mechanical properties. Ten per cent by weight of the total polymer is taken as the optimum CPE concentration since the tensile strength does not start falling sharply at this concentration. CPE concentration was fixed at this level for further studies.

Morphological Studies

The morphology of the blends was investigated using an optical microscope. The surface morphology of the blends observed with the optical microscope at a magnification of 330 is shown in Figs.4.4 to 4.7. As is evident from the photographs the morphology of the different systems varies with composition. CPE modification makes a more regular and homogeneous distribution of the dispersed phase of the PVC/LLDPE blends. All the morphological observations are in accordance with the tensile properties of these blends. The CPE modified blends show improved mechanical strength because of the better co-continuous nature of the phases permitting stress transfer of the components across the interface.

Fig.4.4 20/80 PVC/LLDPE blend
(unmodified)

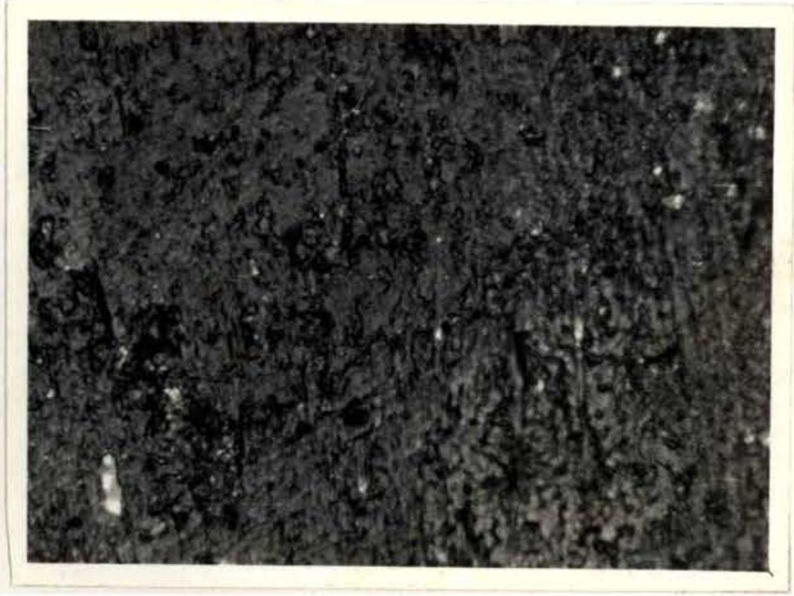


Fig.4.5 20/80 PVC/LLDPE blend
(CPE modified)

Optical microscope photographs of the PVC/LLDPE blends

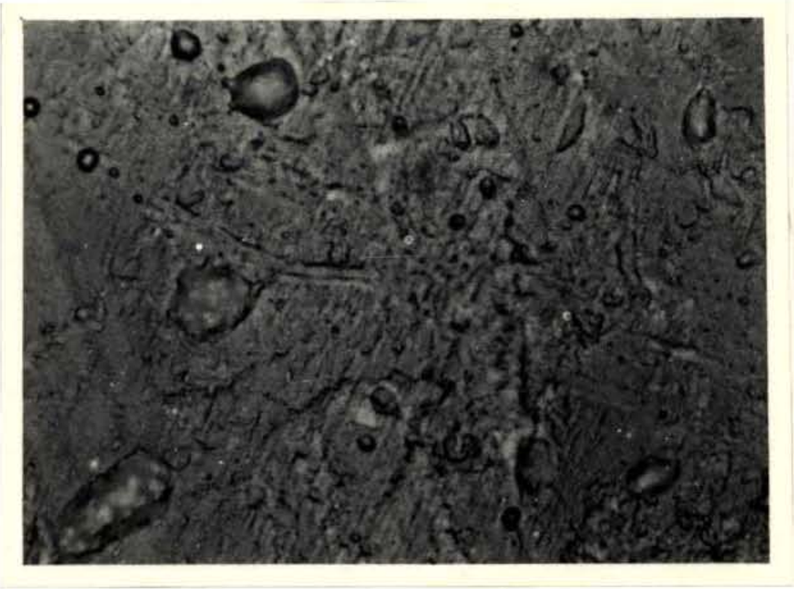


Fig.4.6 40/60 PVC/LLDPE blend (unmodified)

Fig.4.7 40/60 PVC/LLDPE blend (CPE modified)

Optical microscope photographs of the PVC/LLDPE blends

Processability Studies

Investigation of the rheological properties of the mixtures was done to assess their behaviour during melt processing. Moreover, the rheological properties of the mixtures permit the study of the structure of the melts.[21-24] The effect of CPE on the melt viscosity and melt elasticity of PVC/LLDPE blends is investigated.

Experimental

Melt rheological properties were measured on a capillary rheometer (Goettfert visco-tester 1500) using a capillary die of circular cross section (length 30 mm diameter 1 mm) over a wide range of shear rates at 160, 170, 180 and 200°C. Apparent viscosities and shear rates were calculated according to Hagen-Poiseuille law. The true values of shear stress, shear rate and viscosity were calculated by correcting the apparent values. The true shear rate ($\dot{\gamma}_w$) was calculated by applying the Rabinowitsch correction according to the equation.[23]

$$\dot{\gamma}_w = \left(\frac{3n + 1}{4n}\right) \dot{\gamma}_{w_{app}}$$

where the 'n' values were determined as the slopes of the shear stress-shear rate flow curves at different points.

Similarly Bagley correction was applied for correcting the shear stress.[28] The pressure drops ΔP for three different dies of length/radius ratios 20, 40, 60 were measured for each shear rate, and plotted. The intercept at L/R = 0 was taken as the entrance pressure loss (P_c) for that shear rate. Then the true shear stress was calculated from the expression,

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

The true viscosity was calculated according to the equation,

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

Results and Discussion

Fig.4.8 gives a comparison of apparent and true viscosities against shear rate for 40/60 PVC/LLDPE blend. The true viscosity values are only slightly displaced from the apparent values probably because the apparent values were taken with a capillary of fairly high L/R ratio (60). Also since the evaluations in the present study are of a comparative nature, Bagley and Rabinowitsch corrections were not employed for further rheological studies.

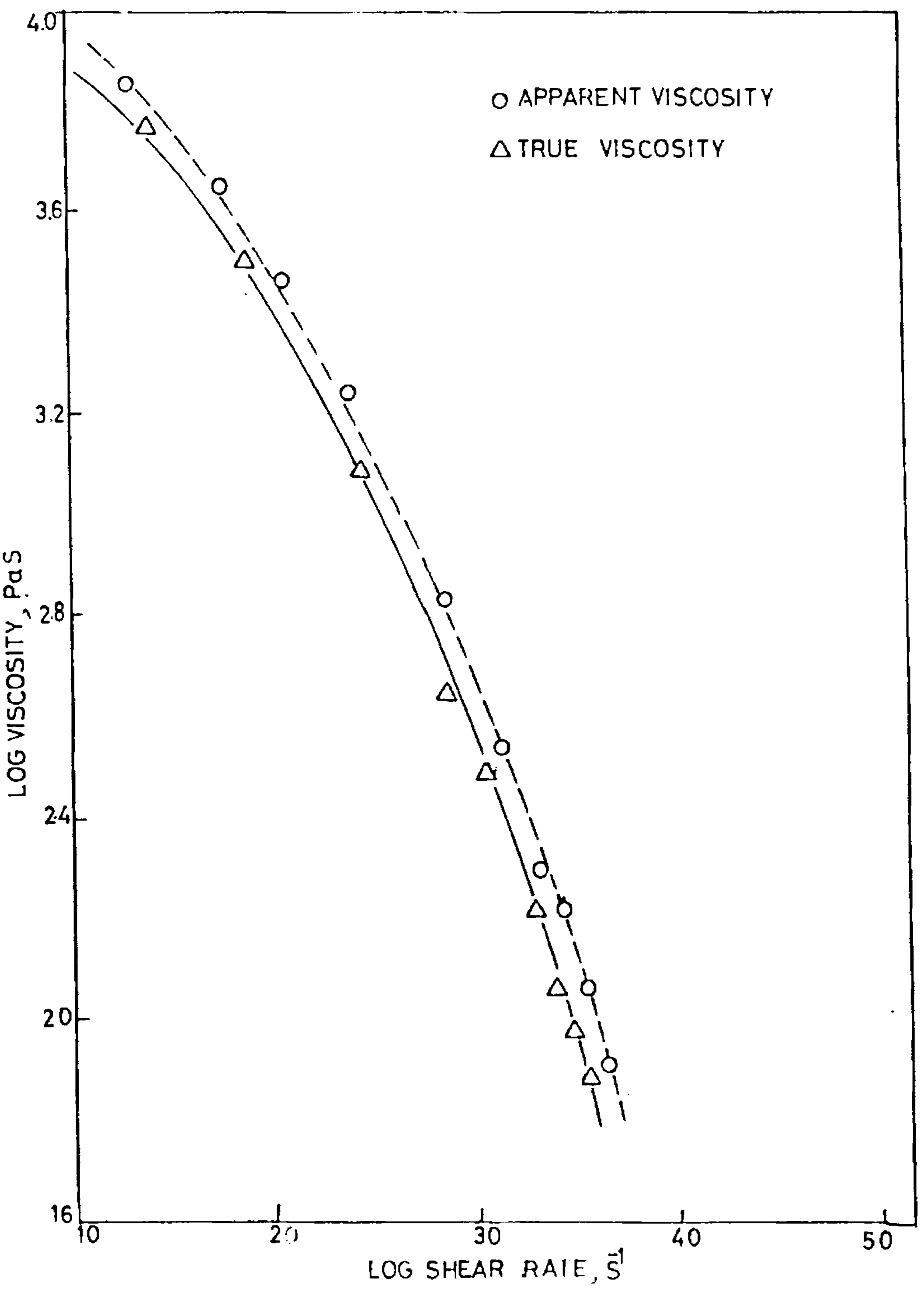


Fig.4.8: Comparison of apparent and true viscosities with shear rate (curves) for 40/60 PVC/LLDPE blend

Fig.4.9 shows the variation of viscosity (η) of the blends with blend composition at 170°C, at different shear rates. Since the dependence of viscosity on composition is essentially linear at low and high shear, it may be concluded that there is no substantial change in the structure of the melt for the composition range studied. At higher shear rates, the straight lines becomes almost parallel to the X-axis obviously because of the higher pseudoplasticity of PVC. When CPE is added it enhances the viscosity of the system, particularly at lower shear rates. This effect may be due to the interactions which contribute towards increasing the strength of the blends. At higher shear rates, this effect is not so pronounced suggesting that better properties can be obtained by mechanical compatibilisation of the blends at high shear. Large increase in torque values is also observed for a CPE modified PVC/LLDPE blend compared to unmodified PVC/LLDPE blend during Brabender shear mixing (Fig.4.10). This result also suggests strong interactions among the constituents at low rates of shear.[25,26] Figs.4.11 and 4.12 show the viscosity-shear rate curves of PVC/LLDPE and CPE modified PVC/LLDPE blends. The strong non-Newtonian behaviour of the blends at higher shear rates is evident from these figures.

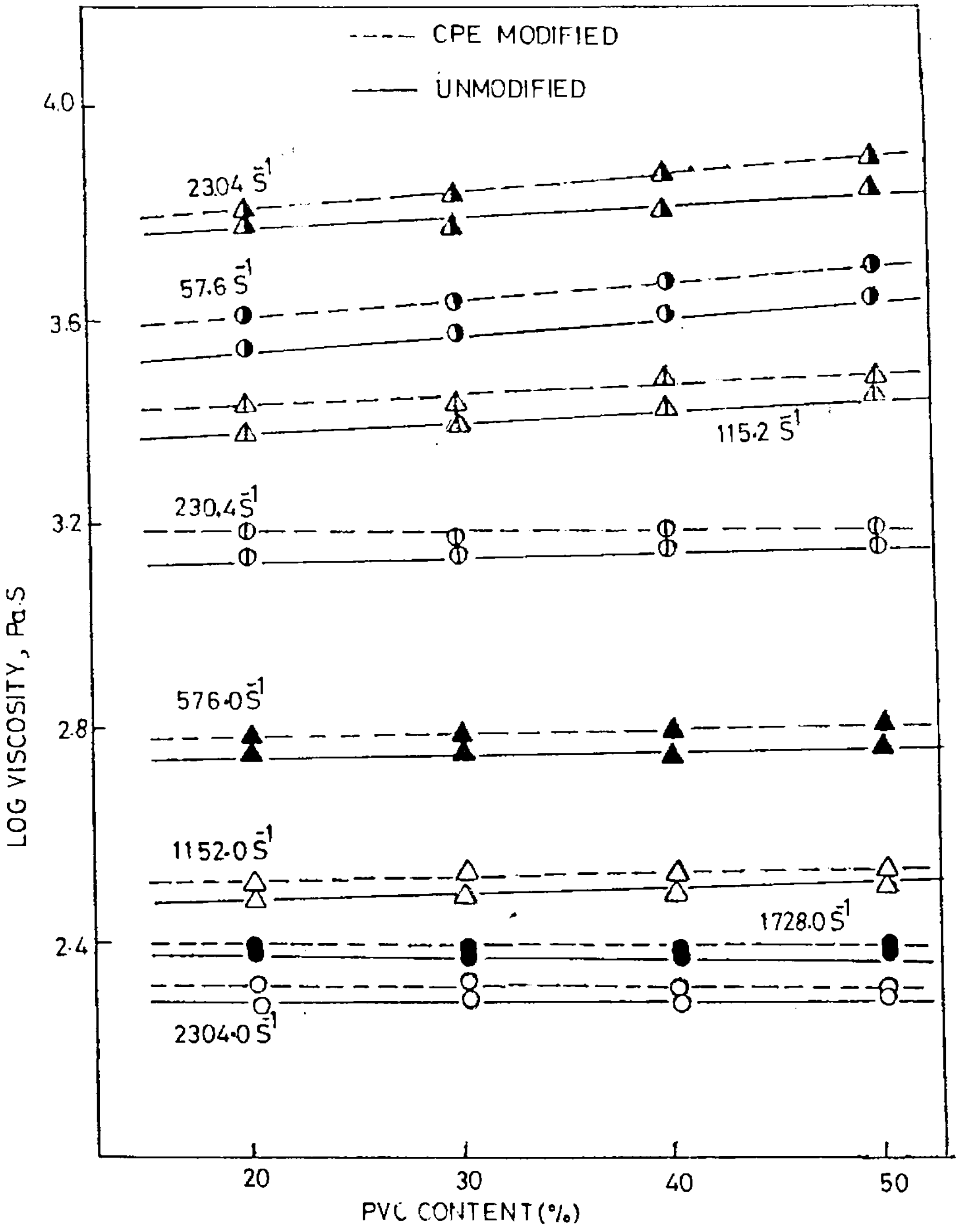


Fig.4.9: Viscosity of the PVC/LLDPE blend as a function of composition at different shear rates at 170°C

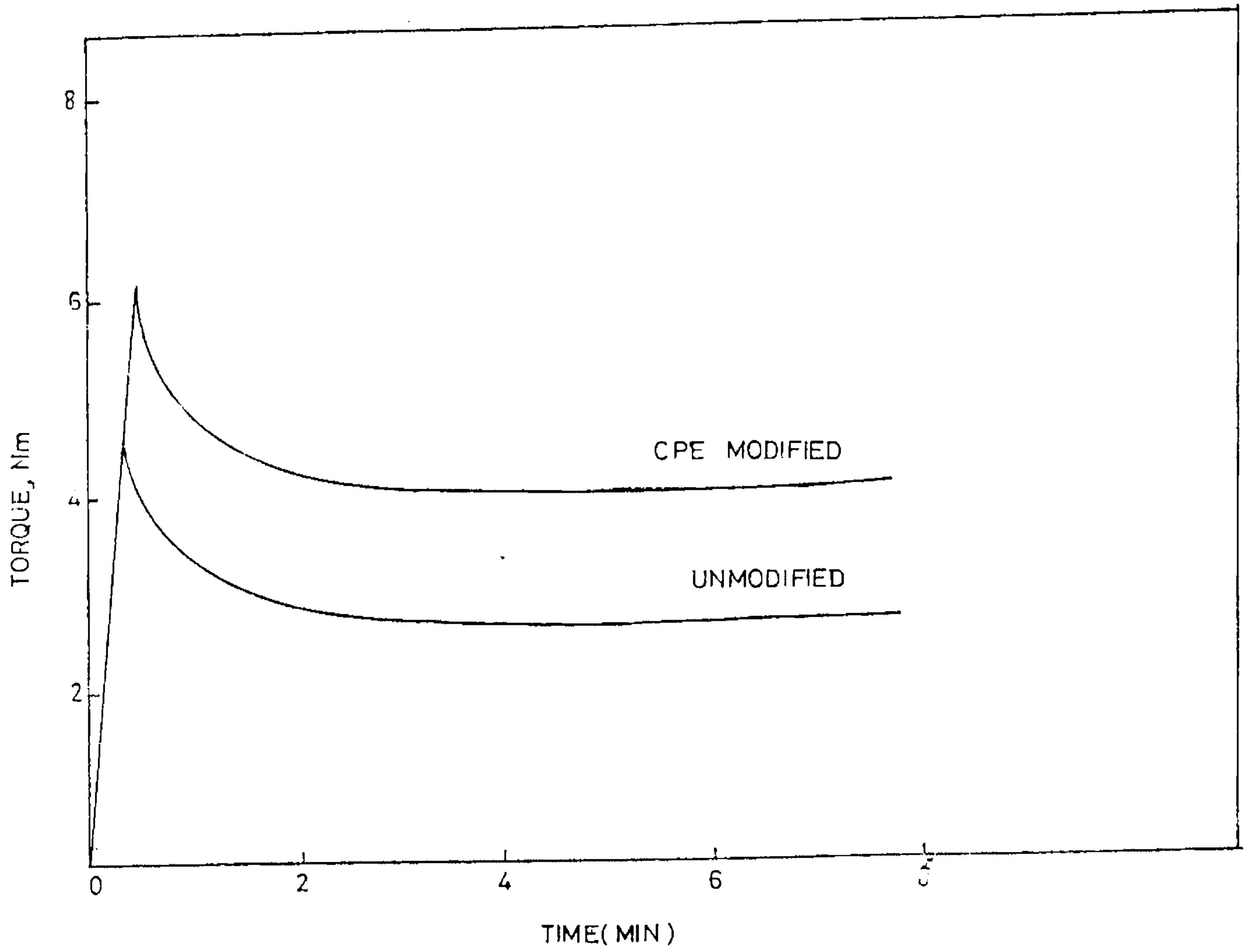


Fig.4.10: Torque curves of the CPE modified and unmodified 50/50 PVC/LLDPE blends

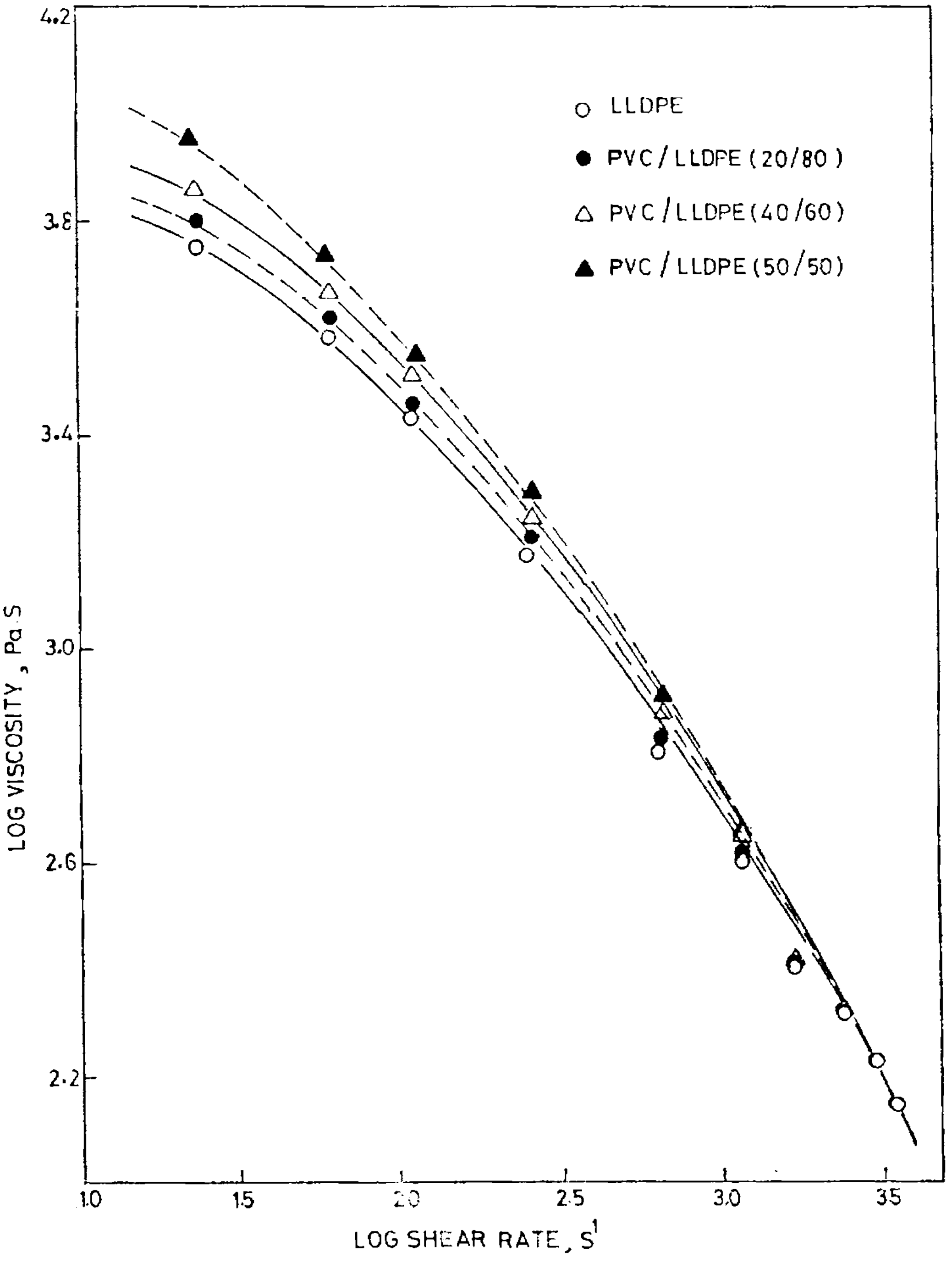


Fig.4.11: Viscosity-shear rate curves of PVC/LLDPE blends at 170°C

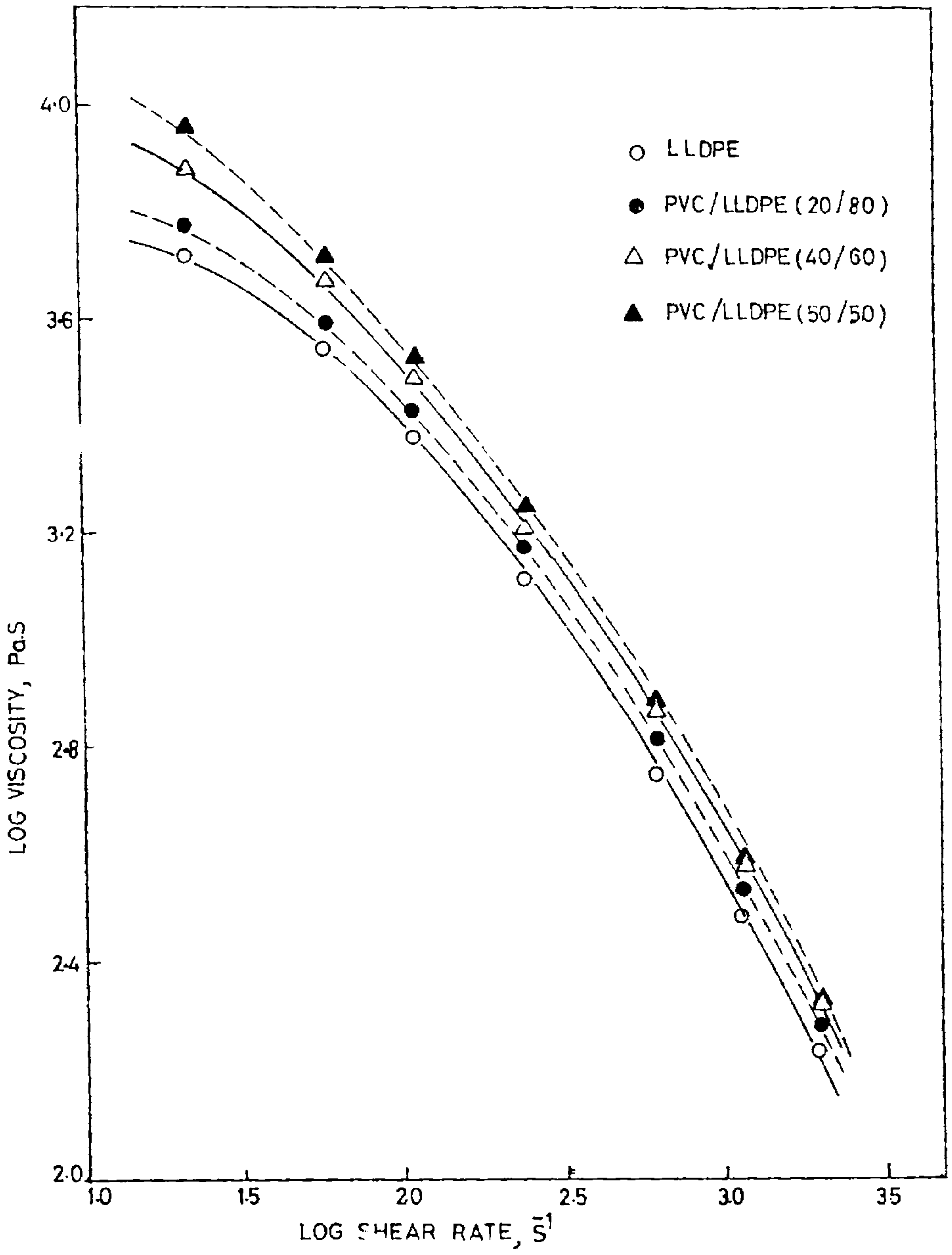


Fig.4.12: Viscosity-shear rate curves of CPE modified PVC/LLDPE blends at 170°C

Fig.4.13 shows the flow curves of typical blends at 170°C. It is interesting to note that the flow curves of the unmodified and modified blends show some distinctive features. The unmodified blend curve can be approximated as three straight lines. These straight lines may indicate different polymer melt structures and the fusion of PVC particles may be the key factor in deciding the melt structure. The initial straight line may indicate a flow behaviour where PVC particles remain largely unfused, while the intermediate region, a region of shear where most of the fusion takes place, and the final straight line may be the normal melt behaviour of the blends. The intermediate region is not so pronounced and may be absent for CPE modified blends supporting the earlier proposition that CPE improves the fusion behaviour of PVC particles. This effect can be further observed from Fig.4.14 which is a plot of log η vs 1/T for a 20% PVC blend at different shear rates. The slopes of these curves are proportional to an apparent activation energy for viscous flow. The activation energy has considerable practical importance because it expresses the temperature dependence of viscosity of the material. The activation energies calculated from the slopes of the lines are shown in Table 4.1. The lower activation energies obtained from

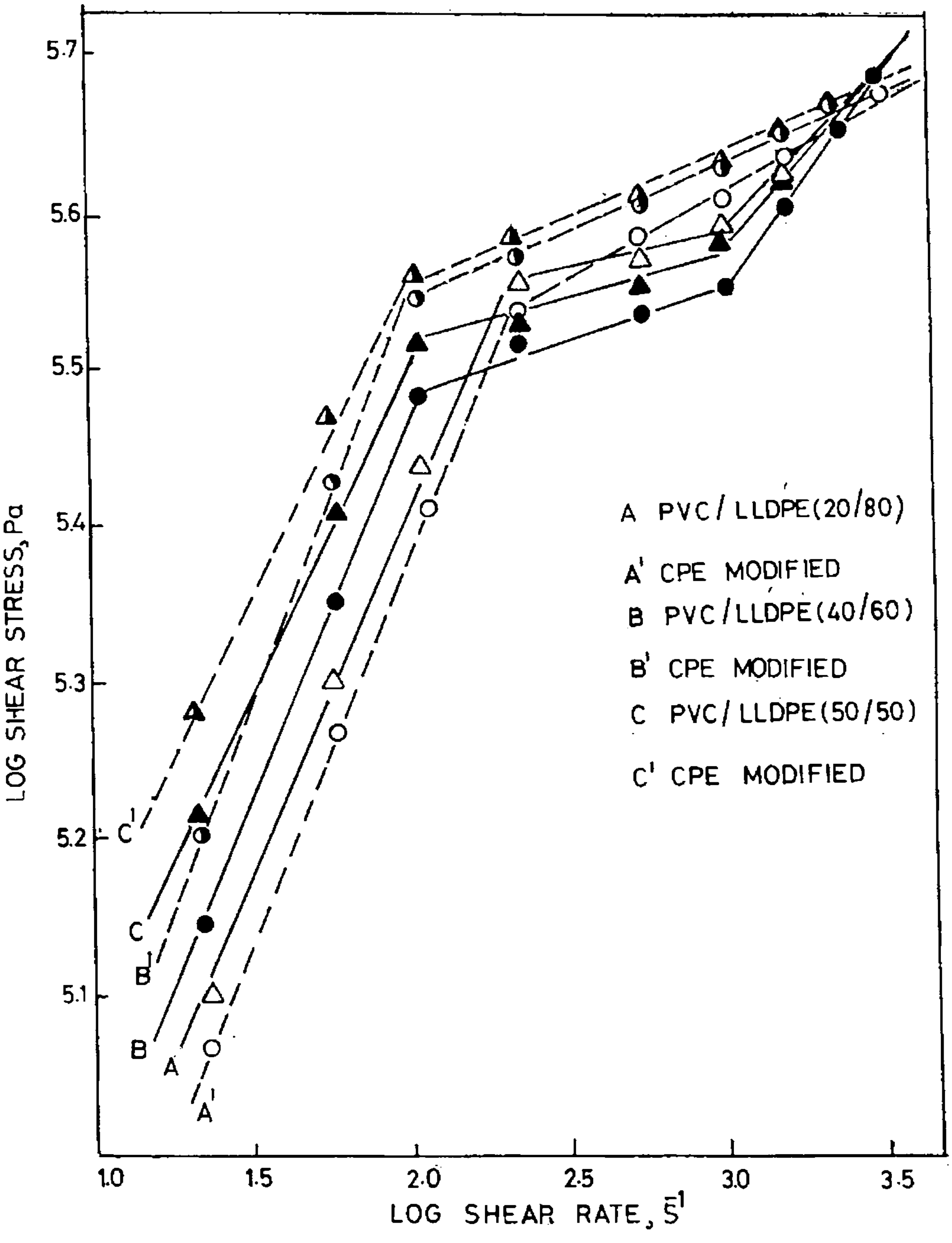


Fig.4.13: Shear stress--shear rate curves of modified and unmodified PVC/LLDPE blends at 170°C

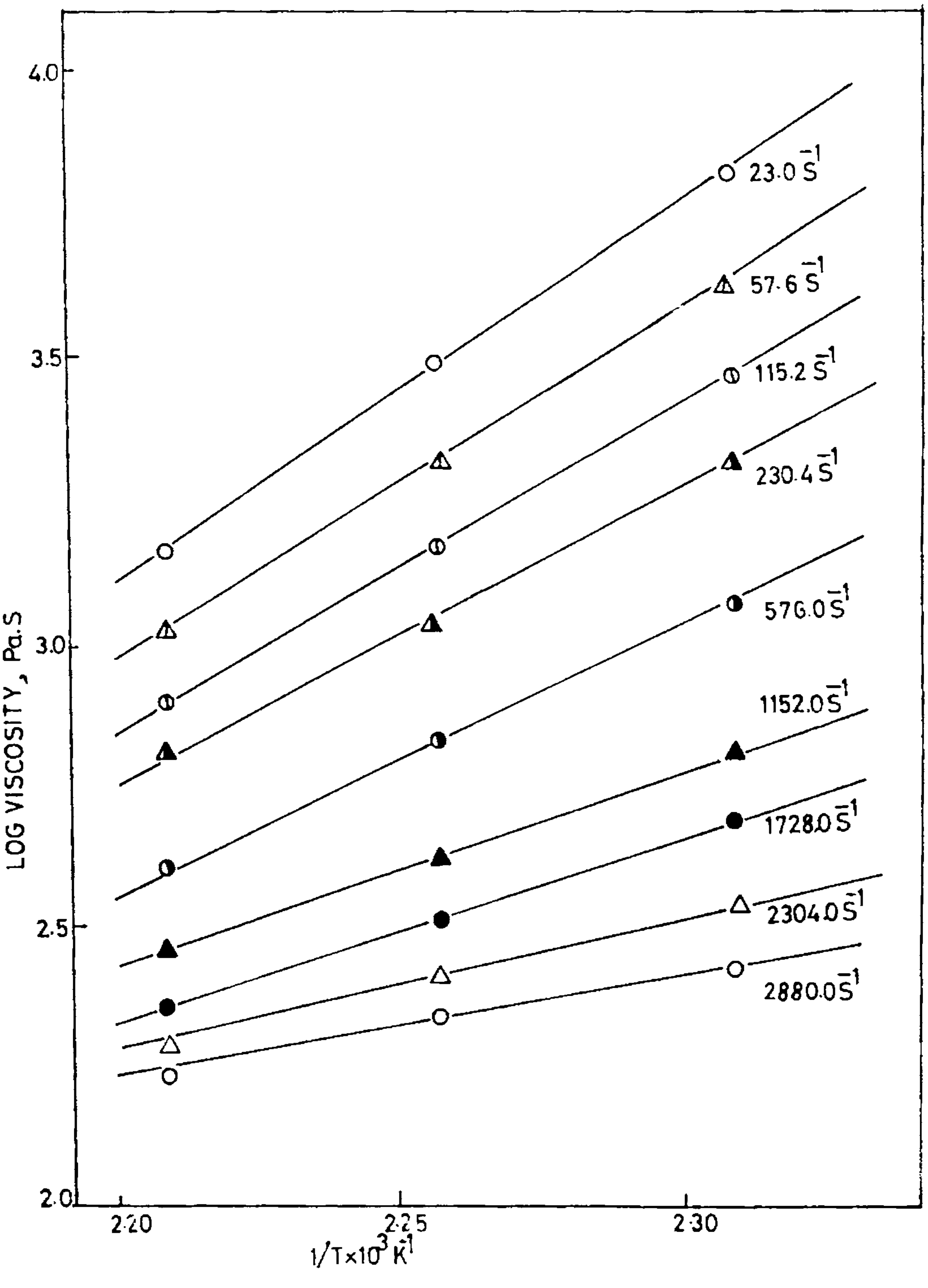


Fig.4.14: Variation of viscosity with temperature of 20/80 PVC/LLDPE blend at different shear rates

Table 4.1: Variation of flow activation energies of PVC/LLDPE blends with shear rate

Shear rate s^{-1}	20 per cent PVC/LLDPE blend	
	Unmodified kJ/mole	CPE modified kJ/mole
23.0	22.4	19.3
57.6	19.3	15.2
115.2	16.9	14.4
230.4	14.4	11.5
576.0	10.9	6.3
1152.0	9.1	5.8
1728.0	8.6	5.5
2304.0	8.3	5.3

CPE modified blends show that CPE is an active flow improver. Further, it seems that, for each blend at a particular temperature, there is a particular shear, which exhibits a transition from one melt structure to other.

Figs.4.15 and 4.16 show the plots of log viscosity vs 1/T for the PVC/LLDPE and CPE modified PVC/LLDPE blends at a particular shear rate. The activation energies calculated from the slopes of the straight lines are shown in Table 4.2. It can be observed

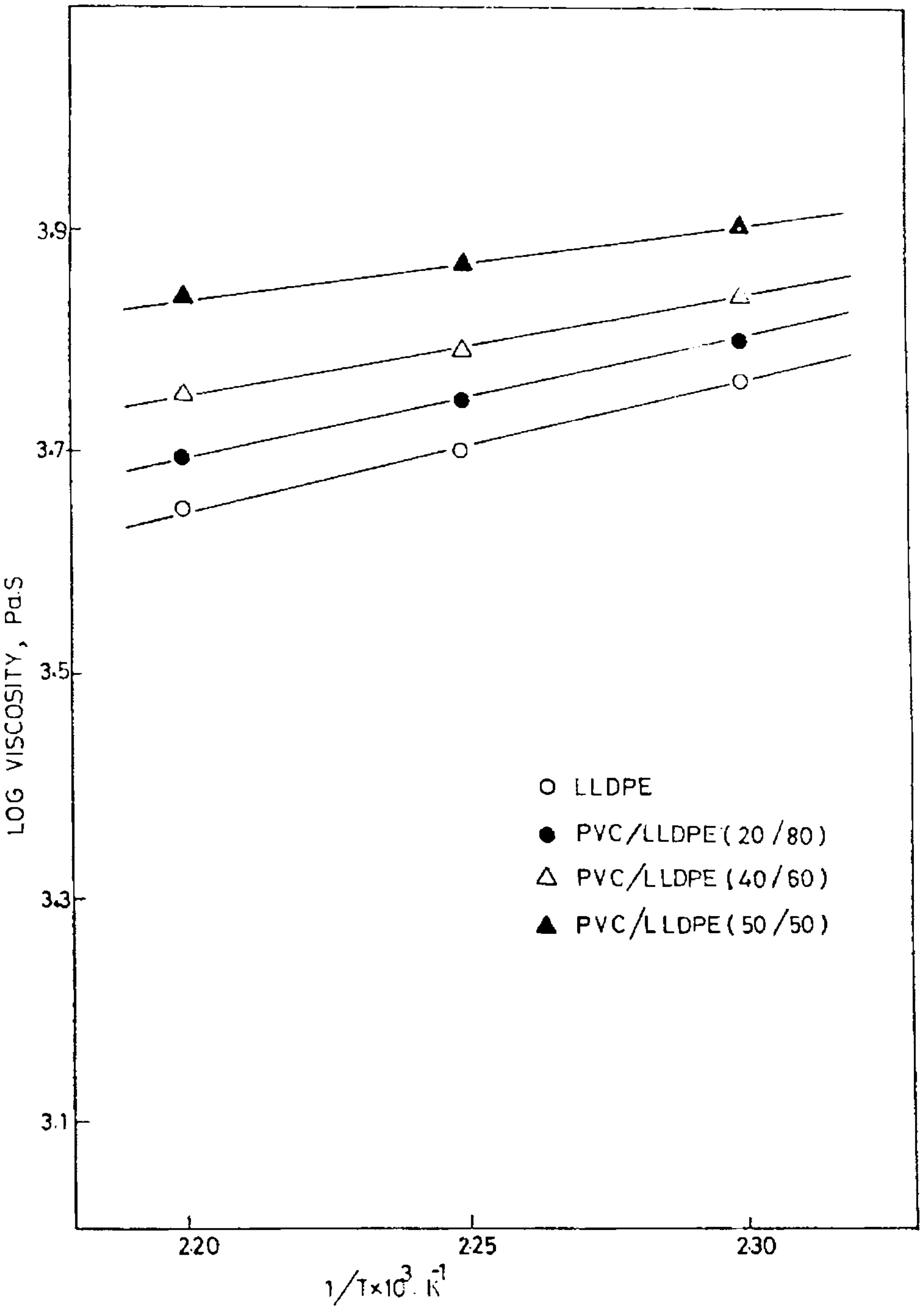


Fig.4.15: Variation of viscosity with temperature of PVC/LLDPE blends with blend composition at a shear rate of 23.0 S^{-1}

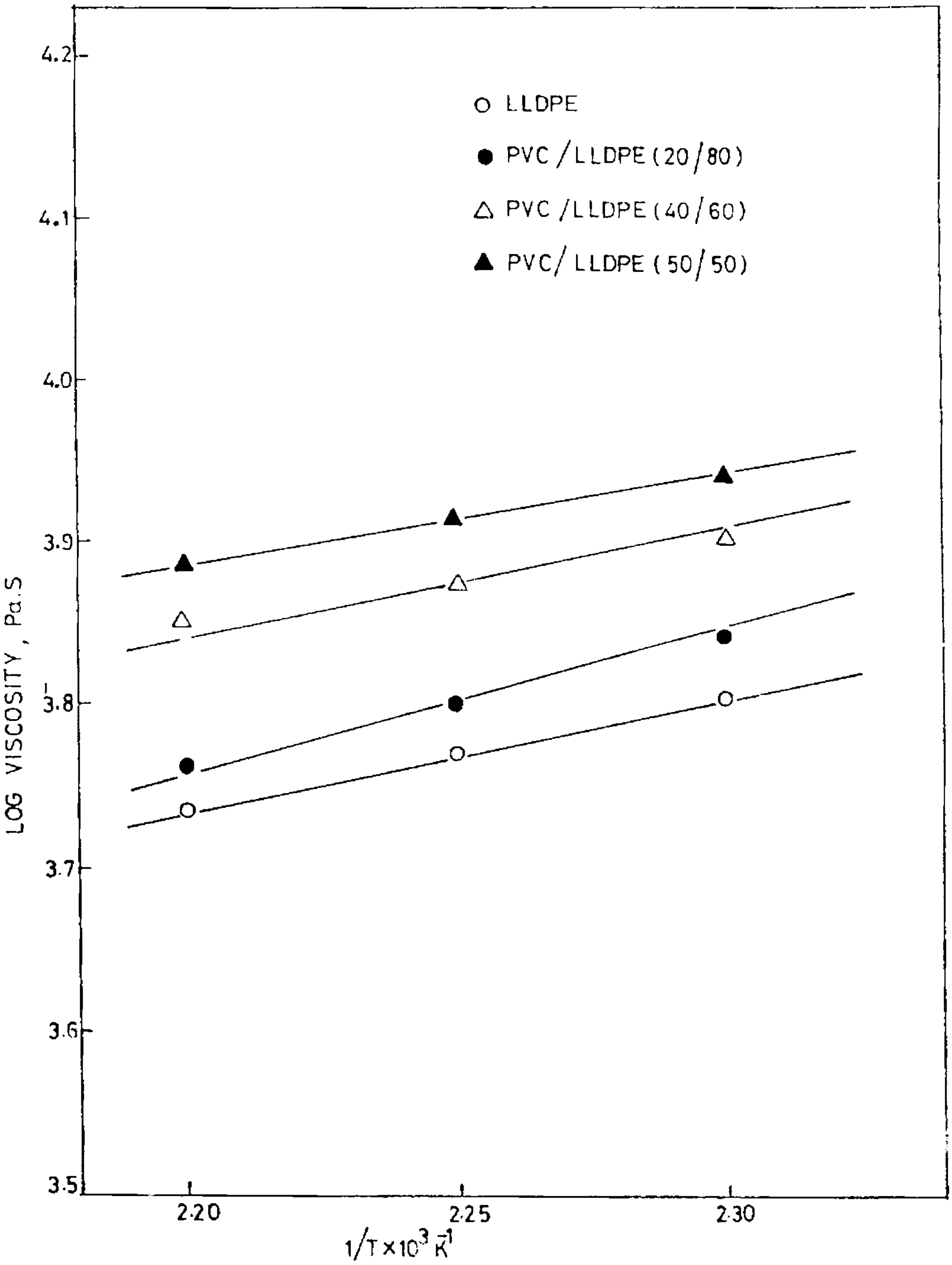


Fig.4.16: Variation of viscosity with temperature of CPE modified PVC/LLDPE blends with blend composition at a shear rate of 23.0 S^{-1}

Table 4.2: Variation of activation energy of the PVC/LLDPE blends with blend composition

Percentage composition of PVC : LLDPE	Activation energy at a shear rate of 23.0 S^{-1}	
	Unmodified kJ/mole	CPE modified kJ/mole
0 : 100	23.94	19.15
20 : 80	19.14	17.23
40 : 60	17.42	15.11
50 : 50	13.40	10.44

that, the flow activation energy decreases with increase in PVC content. Also, CPE modification reduces the flow activation energy of the blends, in all the cases.

Melt Elasticity

The melt elasticity of the blends was measured from the extrudate swell ratio, D_e/D.[22,24,27] The extrudate emerging from the capillary was collected and the diameter of the extrudate was measured at various points. The extrudate swell ratio was calculated as the ratio of the diameter of the extrudate D_e to the diameter of the capillary die D.

A plot of extrudate swell ratio vs blend composition of PVC/LLDPE blend at constant shear rate is presented in Fig.4.17. It can be seen from the figure that the value of D_e/D increases with the shear rate. This is expected because the recoverable elastic energy built up in the melt while flowing in the capillary increases as shear rate is increased. The figure also reveals that, for every value of shear rate, the extrudate swell of the blends decreases with PVC content. Similar decrease in extrudate swell ratio with increase of PVC content, has been reported by earlier workers in other PVC blends.[2,27] The plots of extrudate swell ratio as a function of blend composition at constant shear rate for CPE modified blend is shown in Fig.4.18. It is found that CPE modification does not make any significant change in the extrudate swell behaviour of the blends.

Flow instabilities associated with shearing flow often cause the polymer melt extrudates to have surface deformations or irregularities. A smooth extrudate can be obtained upto a certain critical shear rate but beyond this shear rate, surface roughness occurs. The roughness increases as the shear rate increases and in some cases

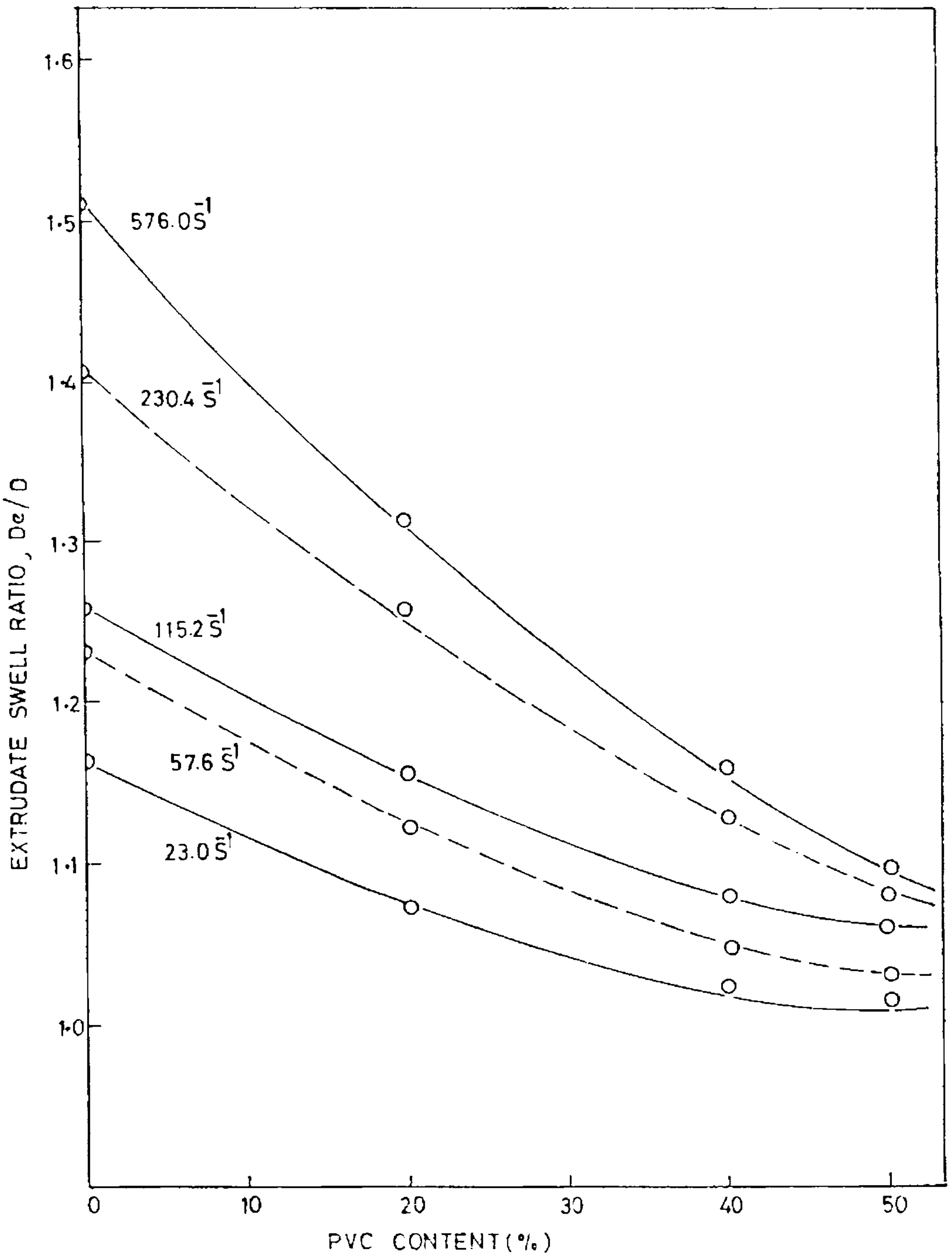


Fig.4.17: Variation of extrudate swell ratio with blend composition of PVC/LLDPE blends at different shear rates

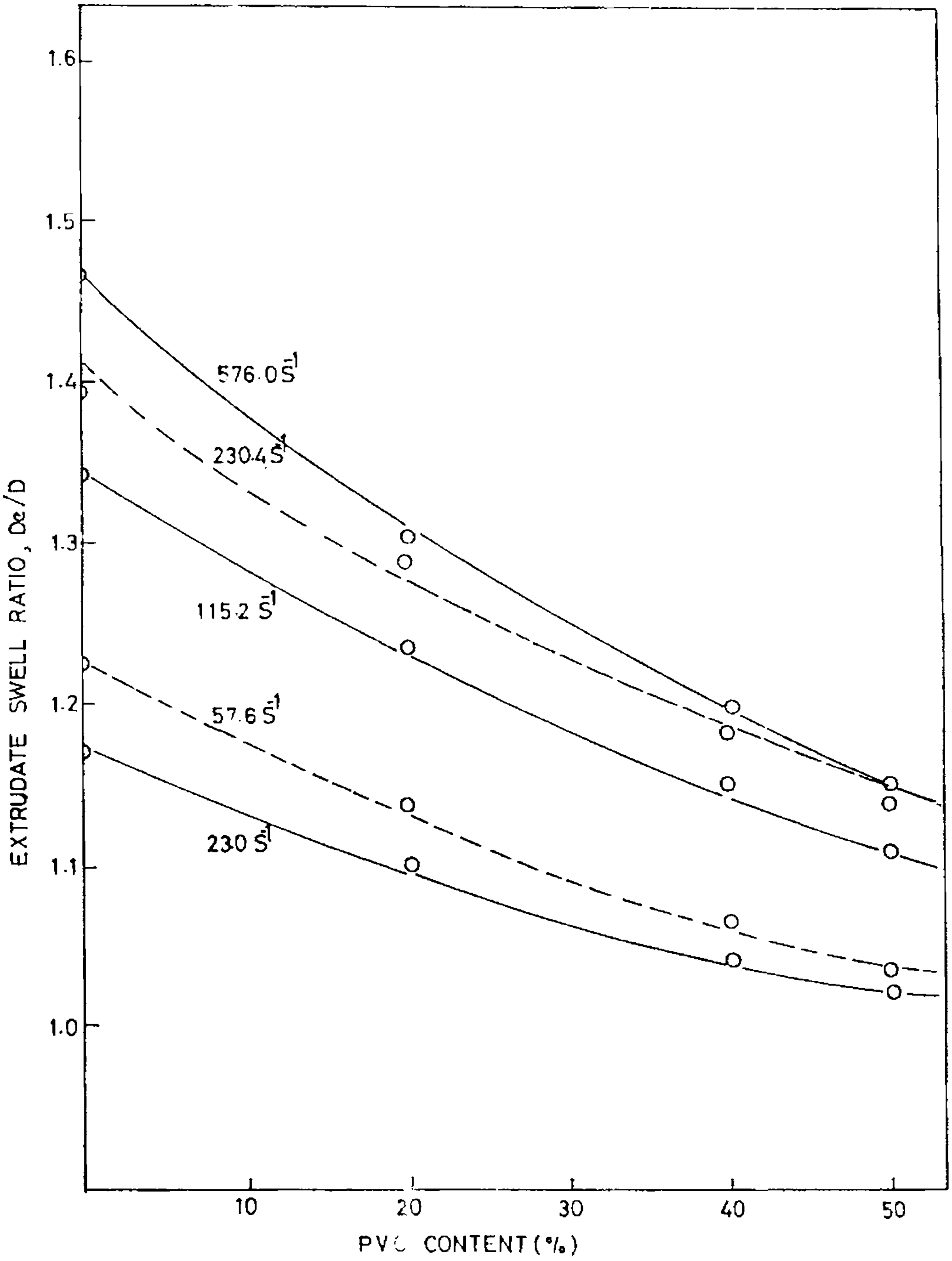


Fig.4.18: Variation of extrudate swell ratio with blend composition of CPE modified PVC/LLDPE blends at different shear rates

the extrudate fractures completely and is called melt fracture.[24] The origin of the melt fracture is due to the excessive elastic energy stored during the flow.

The surface characteristics of the extrudates of the blends are shown in Figs.4.19 to 4.26. Figs.4.19 and 4.20 show the extrudate photographs of the 20/80 and 40/60 PVC/LLDPE blends at various shear rates. The surface roughness of these blends is first observed at a shear rate of 576 S^{-1} and 1152 S^{-1} respectively. The photographs of the extrudates of CPE modified blends are given in Figs.4.21 and 4.22. In this case also the surface roughness starts only at the corresponding shear rates of the unmodified blends and hence CPE modification does not seem to affect processing as far as the surface characteristics are considered.

Figs.4.23 and 4.24 show the extrudate photographs of the unmodified and CPE modified LLDPE. The surface roughness develops at a fairly low shear rate of 115.2 S^{-1}. Figs.4.25 and 4.26 show the effect of adding PVC to LLDPE on the surface characteristics of the latter at a shear rate of 576.0 S^{-1}. Surface roughness disappears with the progressive addition of PVC. This shows that

Fig.4.19 20/80 PVC/LLDPE (unmodified)

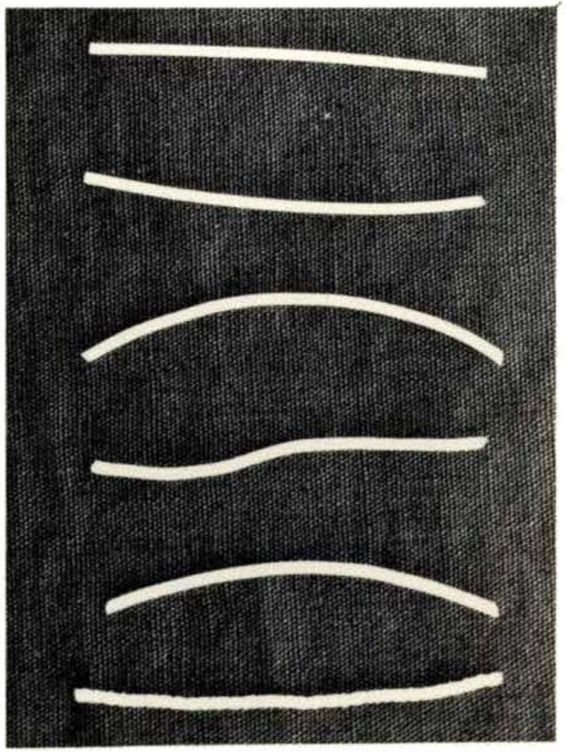


Fig.4.20 40/60 PVC/LLDPE (unmodified)

Photographs of the extrudates of PVC/LLDPE blends at various shear rates

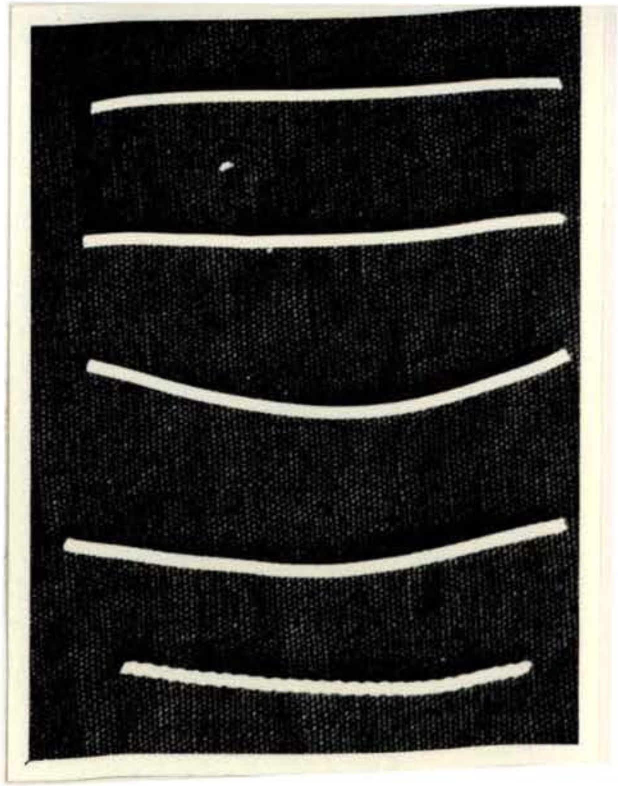


Fig.4.21 20/80 PVC/LLDPE
(CPE modified)

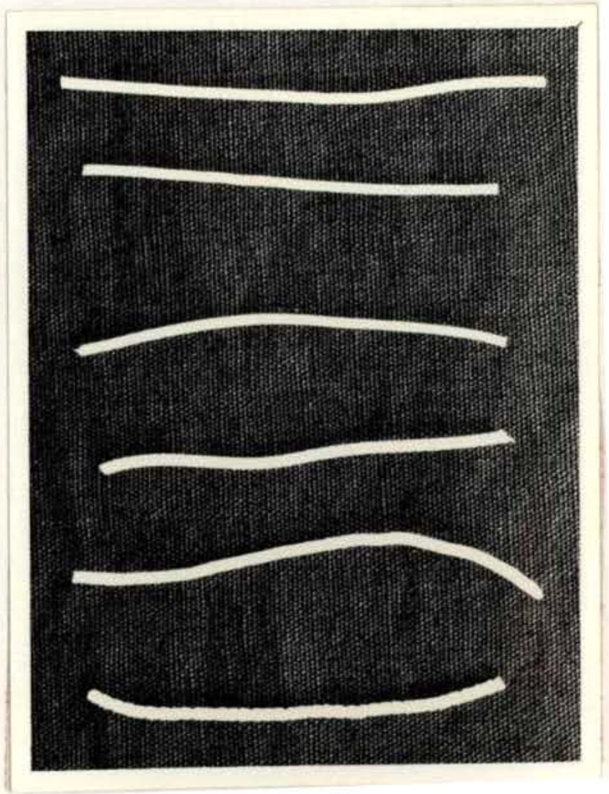


Fig.4.22 40/60 PVC/LLDPE
(CPE modified)

Photographs of the extrudates of PVC/LLDPE blends at various shear rates

Shear rate (S^{-1})

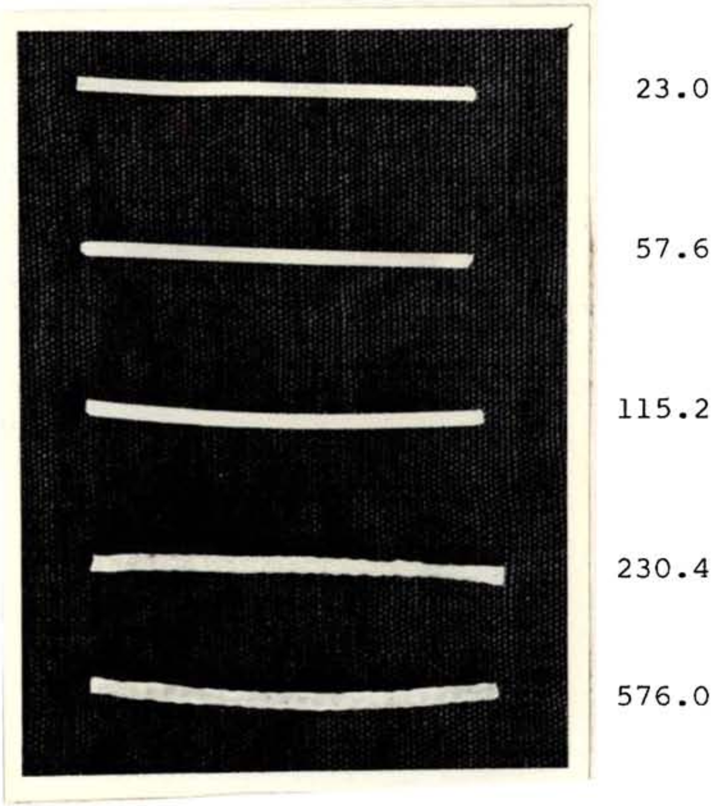


Fig.4.23 LLDPE (unmodified)

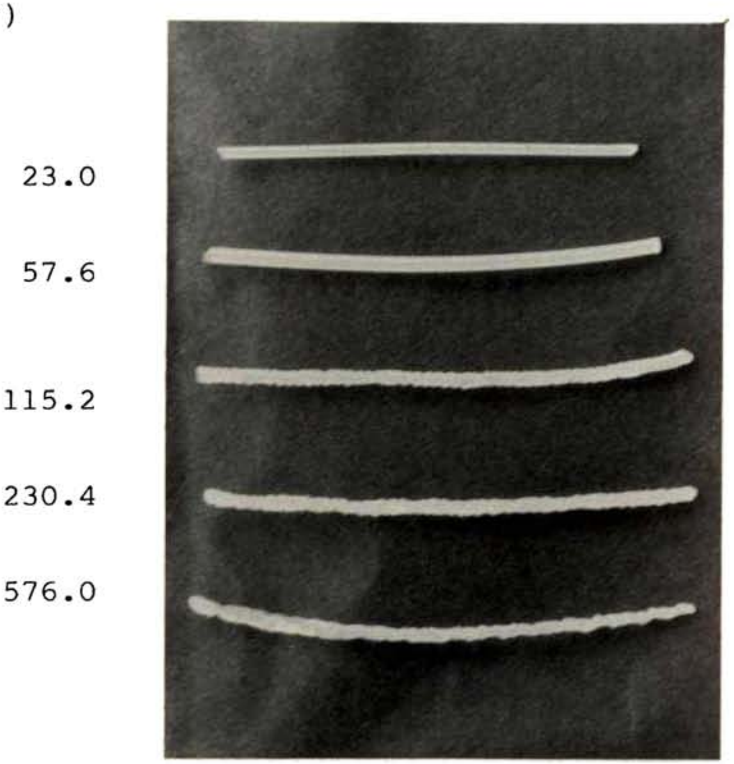
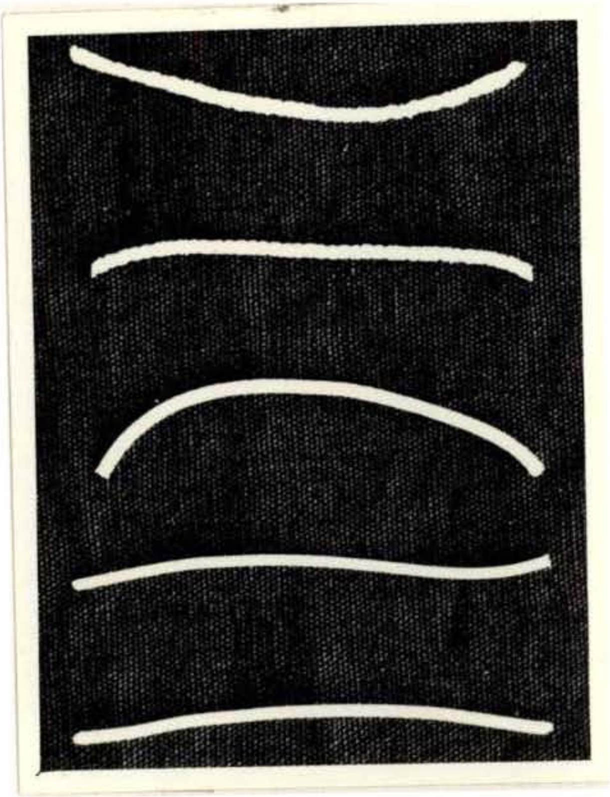


Fig.4.24 LLDPE (CPE modified)

Photographs of the extrudates of LLDPE at various shear rates



Percentage composition
of PVC:LLDPE

PVC	LLDPE
0	100
20	80
30	70
40	60
50	50

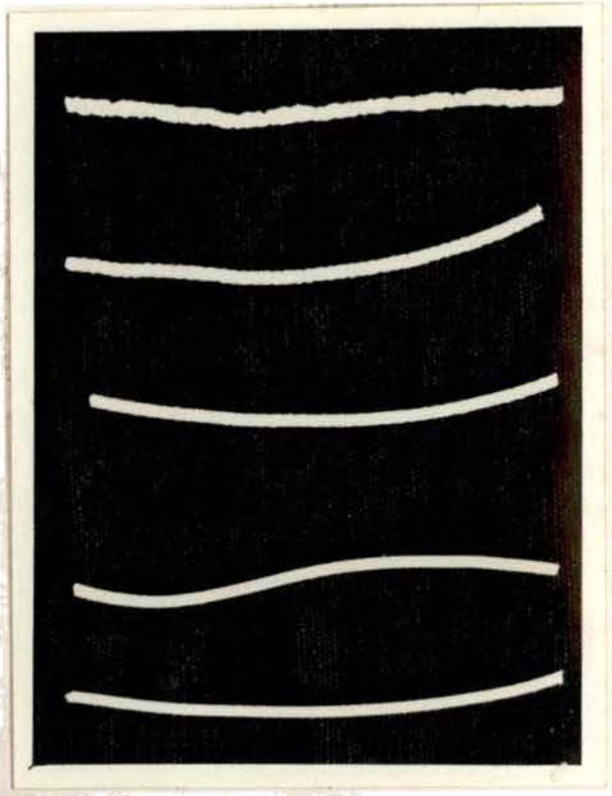


Fig.4.25 Unmodified

Fig.4.26 CPE modified

Photographs of the extrudates of PVC/LLDPE blends at a shear rate of 576.0 S^{-1}

elastic nature of the melts of the PVC/LLDPE is reduced by the addition of PVC. This behaviour is in conformity with the die swell characteristics of PVC/LLDPE blends.

MODIFICATION OF PVC/LLDPE BLENDS BY CO-CROSSLINKING USING DCP

Crosslinking of polymers improves their mechanical stability at high temperature, creep and tensile properties. Polyolefines are sometimes modified with organic peroxides to alter their processability and mechanical properties.[29,30] It is known that the effectiveness of the chemical crosslinking of polyolefines can be increased by the use of co-agents. Various radical initiators, amines etc., can act as co-reactants/co-agents which enhance the chemical reaction between the resins.[29] The use of such co-agents is of great importance in the case of polymers containing tertiary carbon atoms in the chain. The ability of organic peroxides to function as crosslinking agent for PVC also has been described earlier.[30-33] If two polymers which are incompatible can be co-crosslinked, it may be possible to achieve better properties and better technical performance. The literature contains information about the improvement in physico-mechanical properties of immiscible polymer blends through co-crosslinking.[34,35] Nakamura et al.[36] studied the effect of partial co-crosslinking on the mechanical properties of PVC/PE blend. In this study the effect of modifying PVC/LLDPE blends by dicumyl peroxide is reported, since such modification is likely to introduce some co-crosslinking in PVC/LLDPE blends, it may improve the compatibility, mechanical behaviour, thermal resistance, creep resistance, solvent resistance etc., of the blends.

Experimental

Polymer blends were prepared on a Brabender plasticorder. Mixing conditions were 160°C and 30 rpm. LLDPE was added first, then PVC with its heat stabiliser(s) and finally DCP was added. Three different stabilisers viz., Tribasic lead sulphate (4 parts per 100 parts of PVC ie., 4 phr), Irgastab A 70 (4 phr), ZnO (4 phr)/MgO (4 phr)/stearic acid (3 phr) were used in this study. Test samples were prepared by compression moulding at 180°C for 3 minutes. The tensile properties of the blends were determined on a Zwick universal testing machine using a cross head speed of 50 mm/min.

Results and Discussion

For determining the effect of co-crosslinking, the higher molecular weight polymers (PVC-2 and LLDPE-1) were used. Fig.4.27 shows the Brabender torque curves of the 30/70 PVC/LLDPE blend. A large increase in torque value is obtained upon DCP addition. It shows that DCP introduces some crosslinking in the matrix. When the samples for tensile testing were prepared, mixing was done at 160°C to prevent crosslinking during mixing permitting it to occur during compression moulding done at 180°C. Another observation from the figure is that there is a pronounced increase in the band width of the torque curve at the end of mixing in the case of DCP modified blends. This may be due to the higher crosslink density at the end of mixing.

It is well known that crosslinking changes the stress-strain behaviour of the polymers. Fig.4.28 shows the tensile stress-strain curves of an unmodified and DCP modified 20/80 PVC/LLDPE blend containing different PVC stabilisers. All the blends show some improvement in the yield strength with modification by DCP which shows that the matrix has become stronger by the crosslinking and from the better compatibility resulting from it.

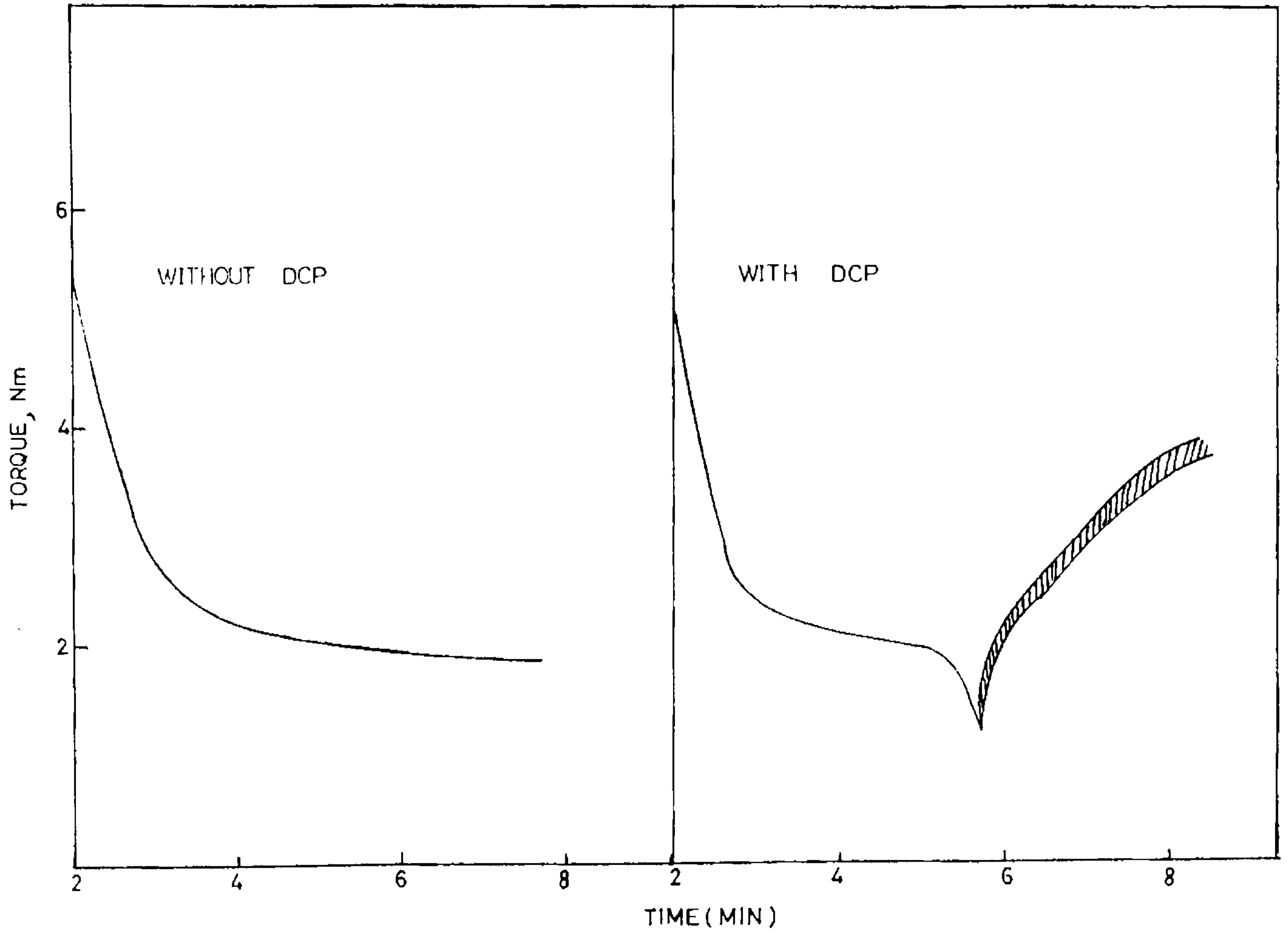


Fig.4.27: Brabender torque curves of the unmodified and DCP modified PVC/LLDPE blend (30/70) at 180°C

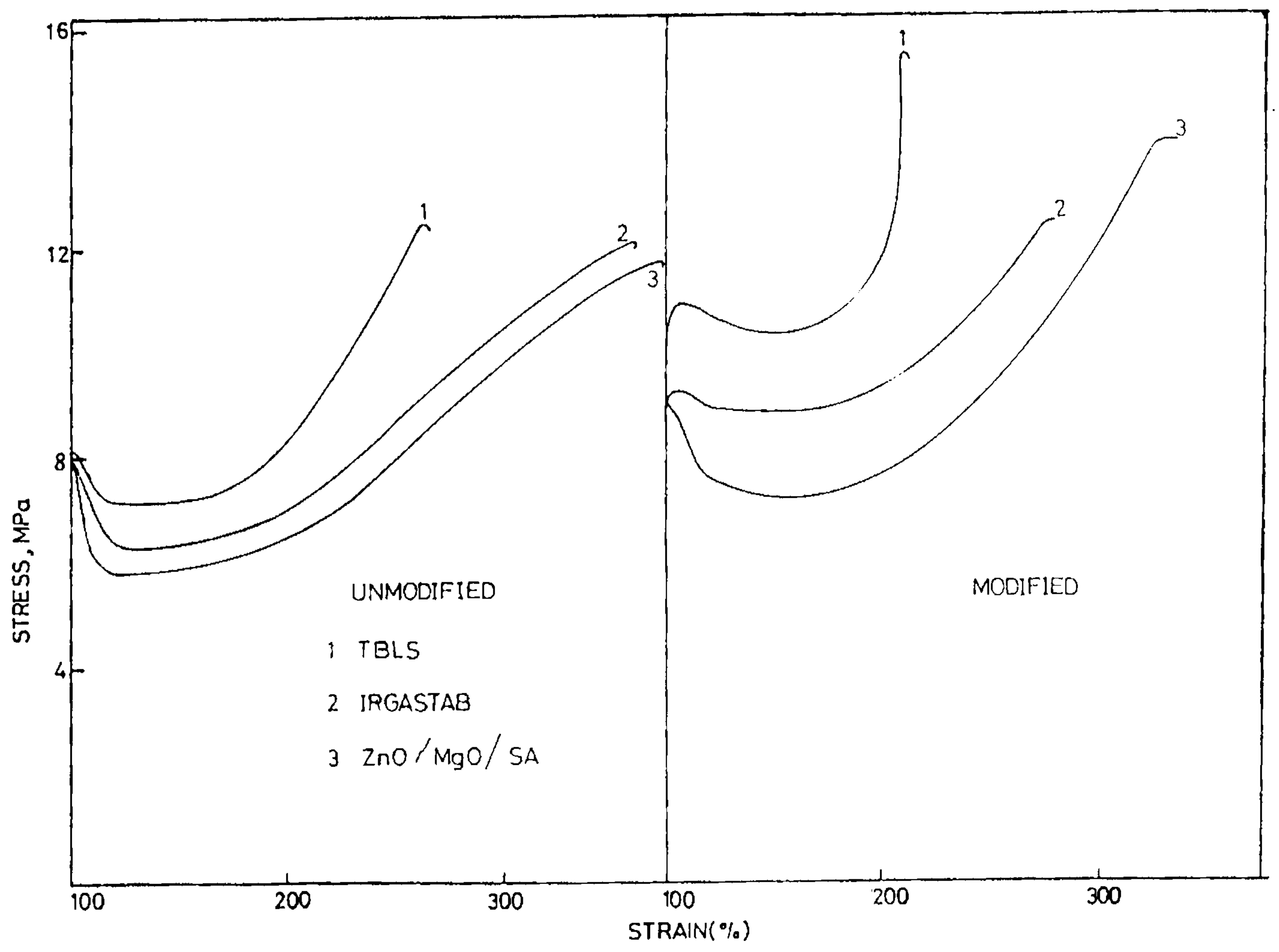


Fig.4.28: Stress-strain curves of an unmodified and DCP modified PVC/LLDPE (20/80) blend containing different stabilisers

Since organic peroxides are also likely to introduce degradative reactions in the polymer, the mechanical behaviour of the samples containing three different PVC stabilisers is compared in Fig.4.28. Eventhough TBLS is staining and shows maximum colour development, it shows maximum strength. Irgastab A 70 (amino crotonate) being metal free shows least colour development, but lower mechanical strength compared to TBLS.[37] This is probably due to the plasticising action of this liquid stabiliser. MgO/ZnO/stearic acid stabilised mixture also develops colour. It shows the lowest yield strength and maximum elongation at break. This is likely to be due to a lower crosslink density in the matrix resulting from a higher loading of the stabiliser.

The effect of various levels of DCP on the tensile strength of PVC/LLDPE blends is shown in Fig.4.29. The blend having 0.5 phr DCP does not show any significant improvement in tensile properties. The blend which has 1.5 phr DCP exhibits much better mechanical properties, but colour development is very pronounced. So an optimum concentration of DCP may be taken as 1 part per 100 parts of PVC and LLDPE.

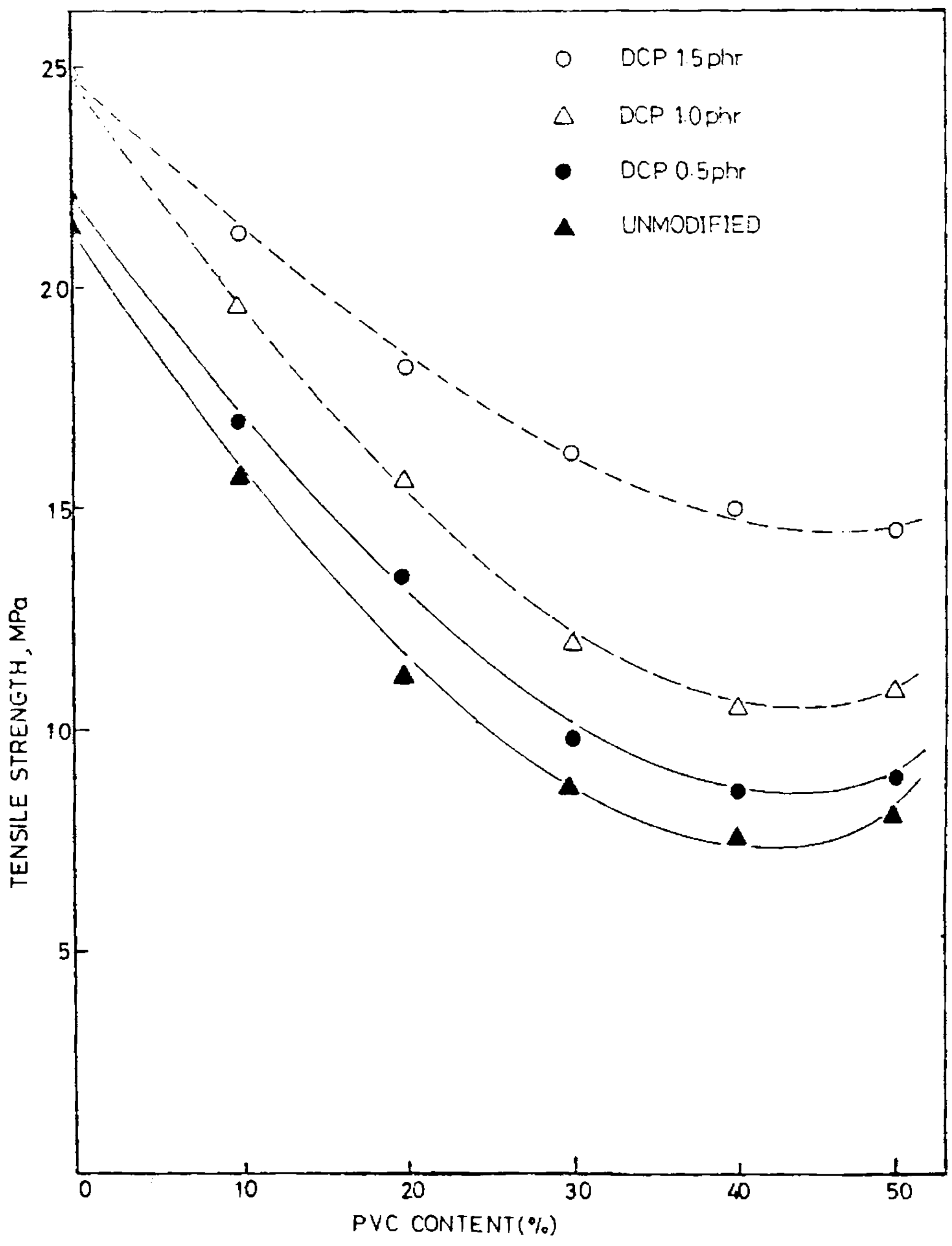


Fig.4.29: Tensile strength of PVC/LLDPE blend as a function of composition—Effect of DCP concentration

RADIATION MODIFICATION

When polymers are irradiated, chemical compounds are created which in turn lead to permanent changes in certain properties. The absorption of radiant energy can cause the breakdown of the chemical bonds. Breakage of the bond gives rise to free radicals which crosslink with other radicals. Consequences of the irradiation of polymers are not only the formation of crosslinks but also molecular breakdown due to breakage of the main chain. As a result, irradiation can lead to improvement (crosslinking) or degradation (breakdown) of the properties of the material.[38,39] The chemical structure of the polymer and the radiation conditions decide the dominating reaction. The properties of both PVC and PE can be modified by high energy radiation.[40,41] Since such modifications are likely to introduce some co-crosslinking in the PVC/PE blend, it may improve the compatibility and other properties of the blend. Further, while chemical crosslinking is known to affect crystallinity of the matrix and hence may adversely affect the mechanical behaviour, radiation crosslinking is found to affect crystallinity only less severely.[42]

Experimental

Polymer blends were prepared on the Brabender plasticorder. Mixing conditions were 160°C and 30 rpm. LLDPE was added first, then PVC with its heat stabiliser and finally 1 phr DCP was added as accelerator. Test samples were moulded at 160°C for 3 minutes to minimise DCP induced crosslinking. Then such samples were subjected to gamma radiation of different dosages. Tensile properties were determined on a Zwick universal testing machine using a cross head speed of 50 mm/min.

Results and Discussion

Radiation modification of PVC/LLDPE blends was done by subjecting the blends to various radiation dosages. Table 4.3 shows the variation of tensile properties and colour development of the unmodified and radiation modified blends of 30/70 PVC/LLDPE blends with radiation dosage. As in the case of DCP modification, higher dosages give rise to degradations leading to colour development. An irradiation dosage of about 3 Mrads is found to be an optimum giving rise to some crosslinking in the matrix without serious degradation. Fig.4.30 gives a

Table 4.3: Variation of 30/70 PVC/LLDPE blend properties with radiation dosages

Property	Unmodified	3 Mrad	6 Mrad	15 Mrad
Tensile strength (Mpa)	8.8	11.9	10.3	11.0
Elongation (%)	248	315	250	107
Colour	Colourless	Colourless	Light yellow	Reddish brown

comparison of chemical and radiation modification of PVC/LLDPE blends. From the figure DCP modification is seen to be more effective in improving the mechanical properties in addition to being less expensive.

CHEMICAL MODIFICATION

Functionalisation or chemical modification of the polymers is another common means of improving the physical and mechanical properties of the blends.[43-45] The chemical modification of polymers continues to be an active field of research as evidenced by the number of recent publications on this topic. The compatibilisation of incompatible polymer blends via chemical modification involves, functionalisation of one polymer to chemically

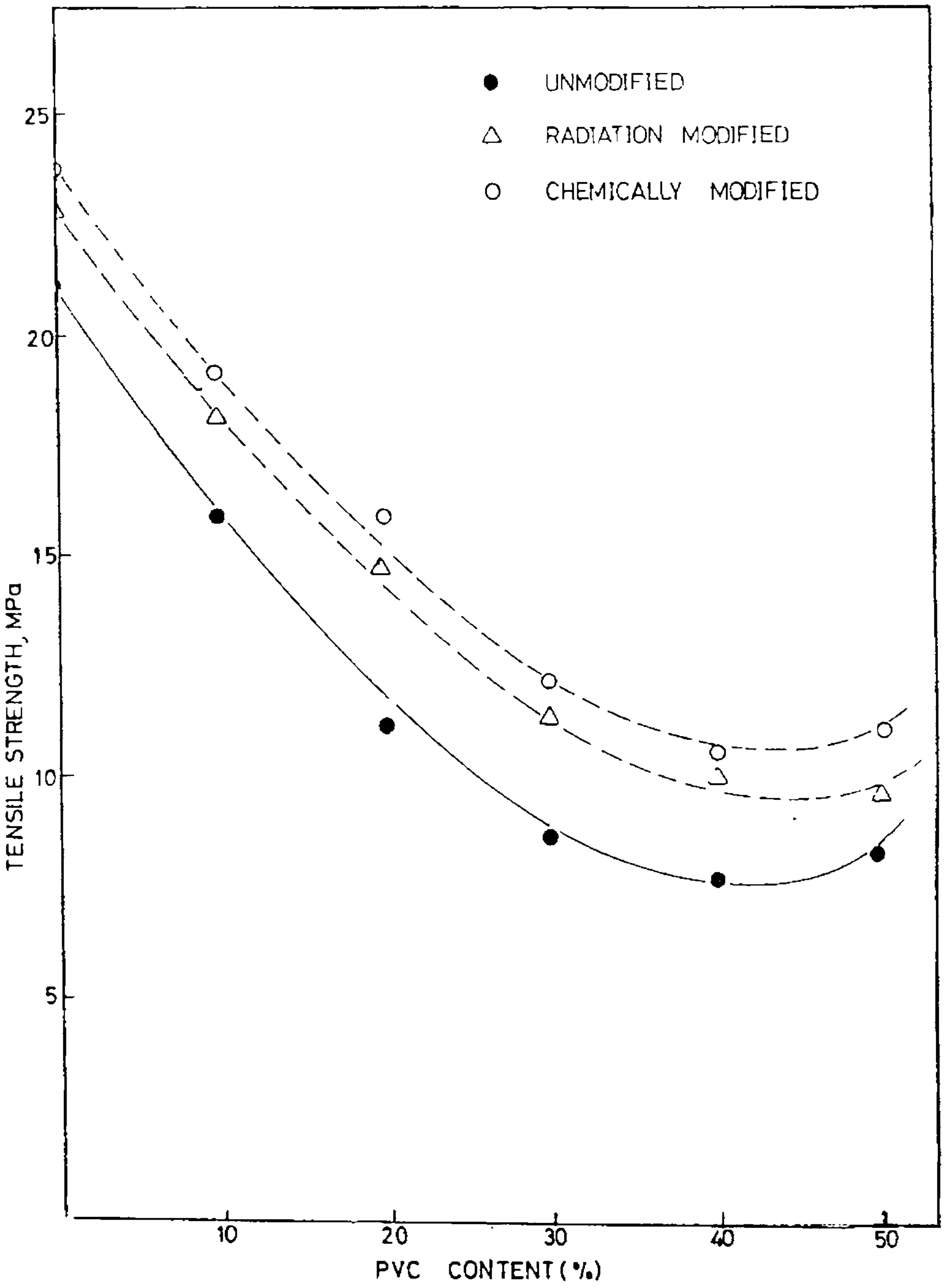


Fig.4.30: Tensile strength of PVC/LLDPE blend as a function of composition--Comparison of chemical&radiation modification

link with the molecules of another type of polymer. For example, PP can be functionalised to chemically link with NBR during melt mixing.[43] Good mechanical properties are generally obtained from the linkages formed between the molecules of the two polymers. The compatibility enhancement in polyolefine/styrene maleic anhydride via polar interactions was recently reported by Simmons et al.[46] In this study acrylic acid, maleic anhydride, phenolic resin and P-phenylene diamine are used for the chemical modification of PVC/LLDPE blends. Dicumyl peroxide is used as a sensibilizing agent in the case of acrylic acid and maleic anhydride.[41]

Experimental

PVC/LLDPE blends of various compositions (PVC content varied from 0 to 50% of the total polymer weight) were prepared on the Brabender plasticorder. The level of modifiers and stabilisers used for a 20/80 PVC/LLDPE blend is shown in Table 4.4 as an example.

Functionalisation

a) Acrylic acid/maleic anhydride

PVC with its heat stabiliser (2.5 phr tribasic lead sulphate) was melt mixed with LLDPE at a temperature

Table 4.4: Recipe for the 20/80 PVC/LLDPE blend

PVC and Stabiliser

PVC = 8 g (20% of total polymer)

TBLS = 0.2 g (2.5 parts per 100 parts of PVC)

Polyethylene

LLDPE = 32 g

Modifiers

a) Acrylic acid = 1.2 g (3 parts per 100 parts of PVC and LLDPE (3phr))

DCP = 0.08 g (0.2 phr)

b) Maleic anhydride = 1.2 g (3 phr)

DCP = 0.08 g (0.2 phr)

c) P-phenylenediamine = 1.2 g (3 phr)

d) Phenolic resin-1 = 1.2 g (3 phr)

$SnCl_2$ = 0.16 g (0.4 phr)

MgO = 0.003 g (0.07 phr)

e) Phenolic resin-2 = 1.2 g (3 phr)

$SnCl_2$ = 0.16 g (0.4 phr)

MgO = 0.003 g (0.07 phr)

of 150°C and 30 rpm. After 2 minutes, DCP (0.2 phr) was added as the free radical precursor, and then acrylic acid or maleic anhydride (3 phr) was added. Mixing was continued for another 3 minutes.

b) Phenolic resin modification

Mixing was done at a temperature of 180°C and 30 rpm. After melt mixing of PVC and LLDPE, phenolic resin was added along with $SnCl_2$ as the accelerator. After 3 min. MgO was added to neutralise the free acid. The total mixing time was 8 min.

c) P-phenylene diamine modification

The mixing conditions were 180°C and 30 rpm. P-phenylene diamine (3 phr) was added after the melt mixing of PVC and LLDPE. The mixing was continued until the torque reached a steady value.

The test samples were prepared by compression moulding at 180°C for 3 min. in a laboratory hydraulic press. Tensile properties were determined on a Zwick universal testing machine using a cross head speed of 50 mm/min.

Results and Discussion

Fig.4.31 shows the Brabender torque curves of the unmodified and acrylic acid modified PVC/LLDPE (40/60) blends at 180°C. A large increase in torque occurs with the addition of acrylic acid along with DCP (0.2 phr). The increase in torque (viscosity) is probably due to 1) co-crosslinking of the polymers in presence of carboxylic acid and/or 2) grafting of carboxylic acid on to the polymer chains. Since DCP concentration was low, the grafting of carboxylic acid is probably the dominating reaction.[47,49]

The mixing temperature seems to be very critical for successful chemical modifications. When the mixer temperature is < 180°C the torque curves of the acrylic acid modified blends resemble those of the unmodified blends without any significant increase in torque values (Fig.4.32). Hence for preparing test pieces of the modified blends, mixing was done at 150°C and then compression moulding at 180°C for sufficient time for the modifying action to take place.

The preferred site for the grafting is possibly the tertiary carbon atom of LLDPE and the carbon atom to

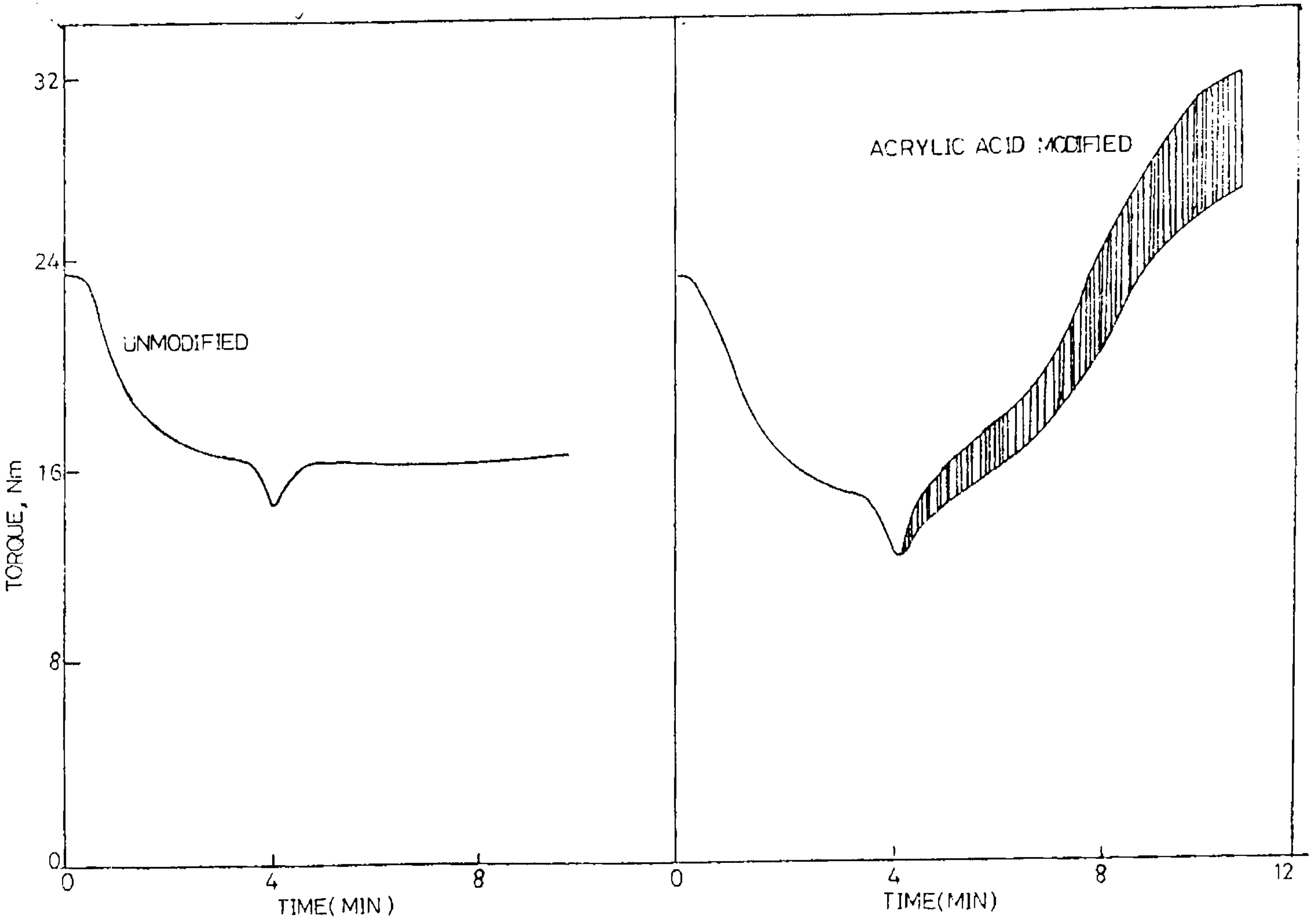


Fig.4.31: Brabender torque-curves of the 40/60 PVC/LLDPE blend at 180°C

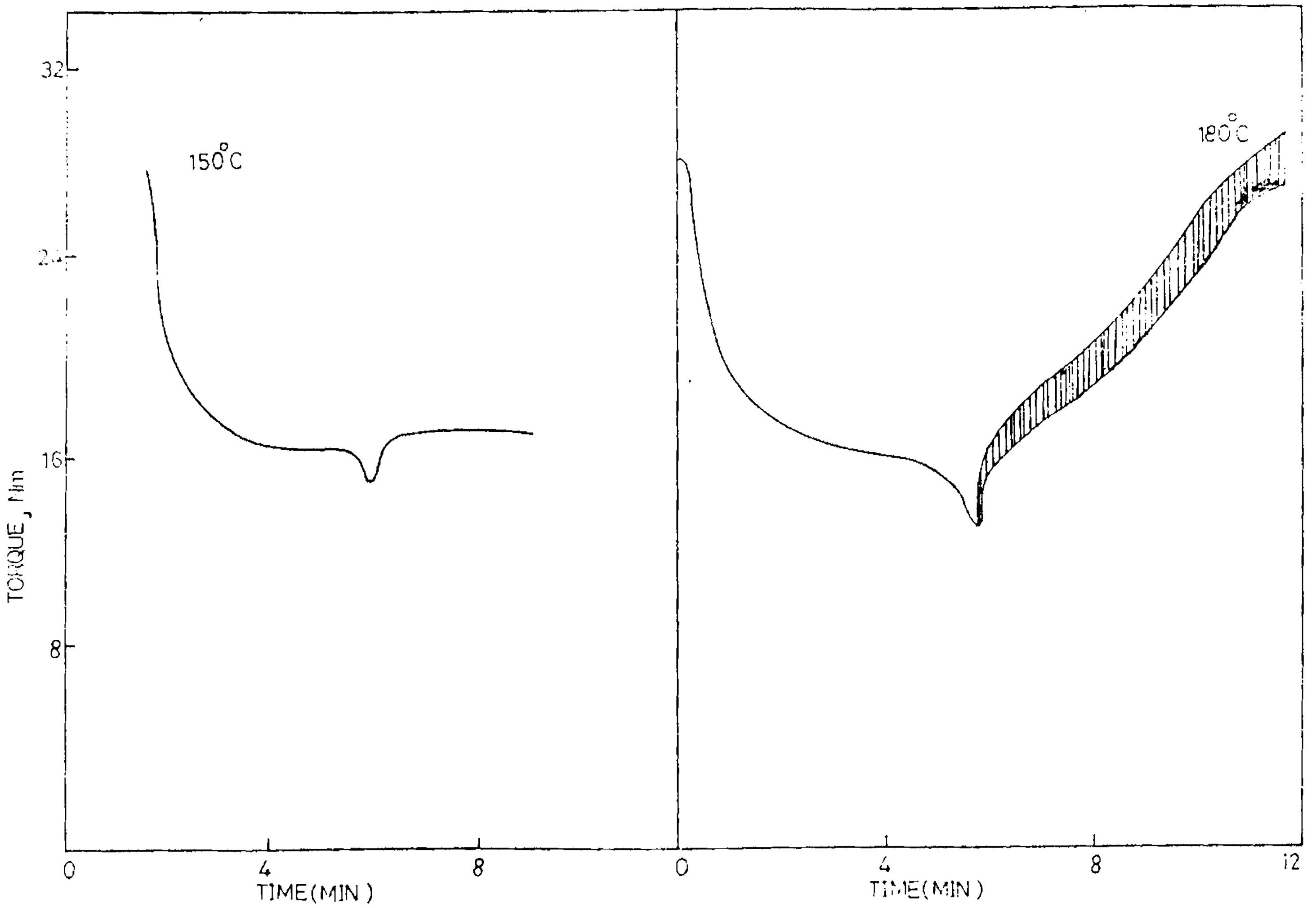


Fig.4.32: Brabender torque-curves of the acrylic acid modified 30/70 PVC/LLDPE blend at 150°C and 180°C

which the chlorine atom is attached in PVC. Grafting can give rise to strong interaction between the phases. Another observation is that, with increase of PVC content, there is a pronounced increase in the bandwidth of the torque curve at the end of mixing (Fig.4.33). Similar behaviour was also observed when LLDPE alone was crosslinked with various concentrations of DCP. Hence it may be concluded that the increase in the bandwidth of the curve is due to higher crosslink density and that PVC is more susceptible to crosslinking and modification than LLDPE.

The acrylic acid grafting on the polymer chains was confirmed by IR spectra. IR spectra of the modified blends (excess carboxylic acid free) were taken with a Beckman Infrared spectrophotometer. Fig.4.34 shows the IR spectra of unmodified, acrylic acid modified and acrylic acid--DCP modified LLDPE. It shows that acrylic acid grafting occurs only in the presence of DCP. The band at 1730 cm^{-1} shows the presence of $\rangle C{=}O$ groups. The IR spectrum of 30/70 PVC/LLDPE blend also shows acrylic acid grafting (Fig.4.35).

The variation of tensile strength with composition for the unmodified and carboxylic acid modified

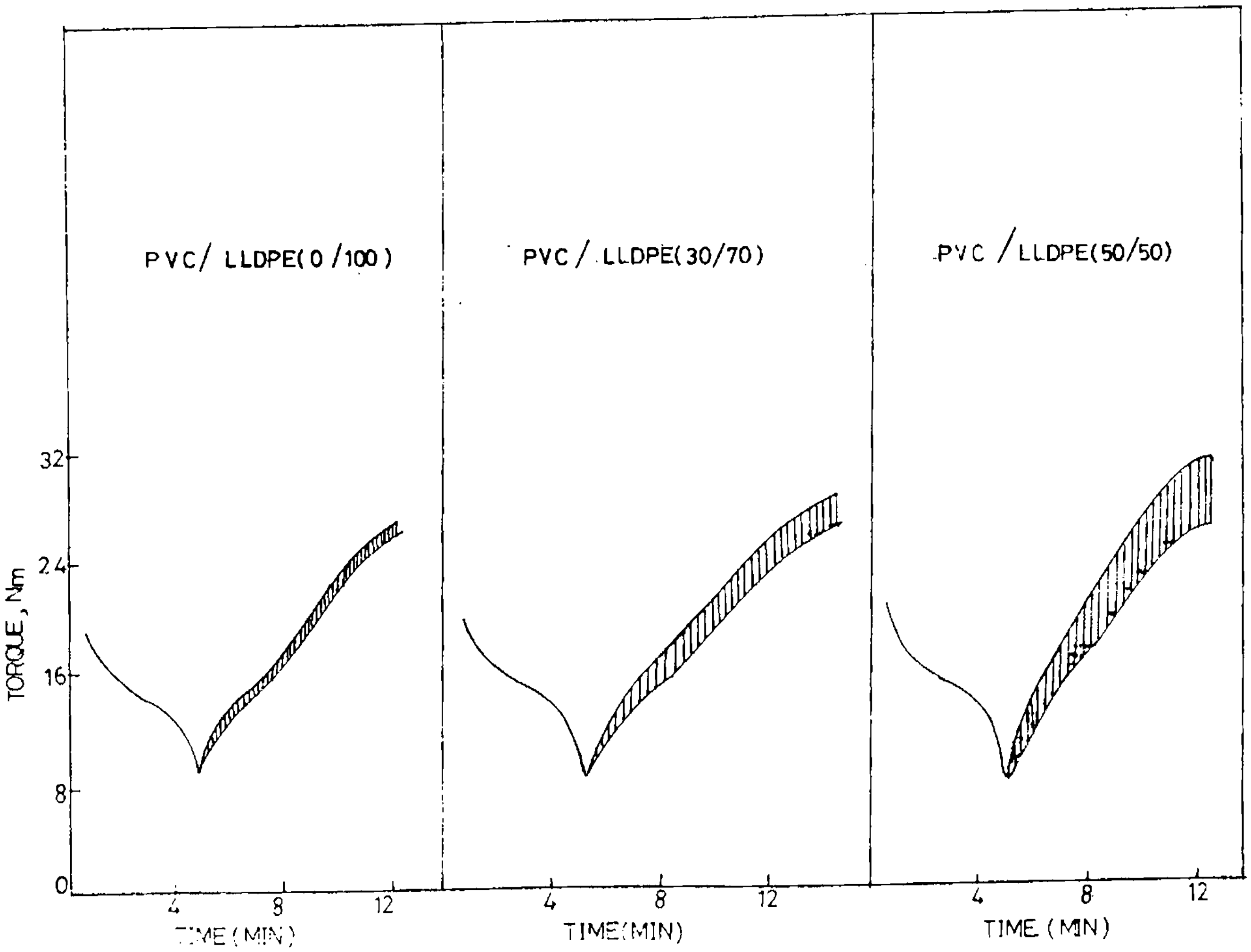


Fig.4.33: Variation in the nature of the Brabender torque with PVC content

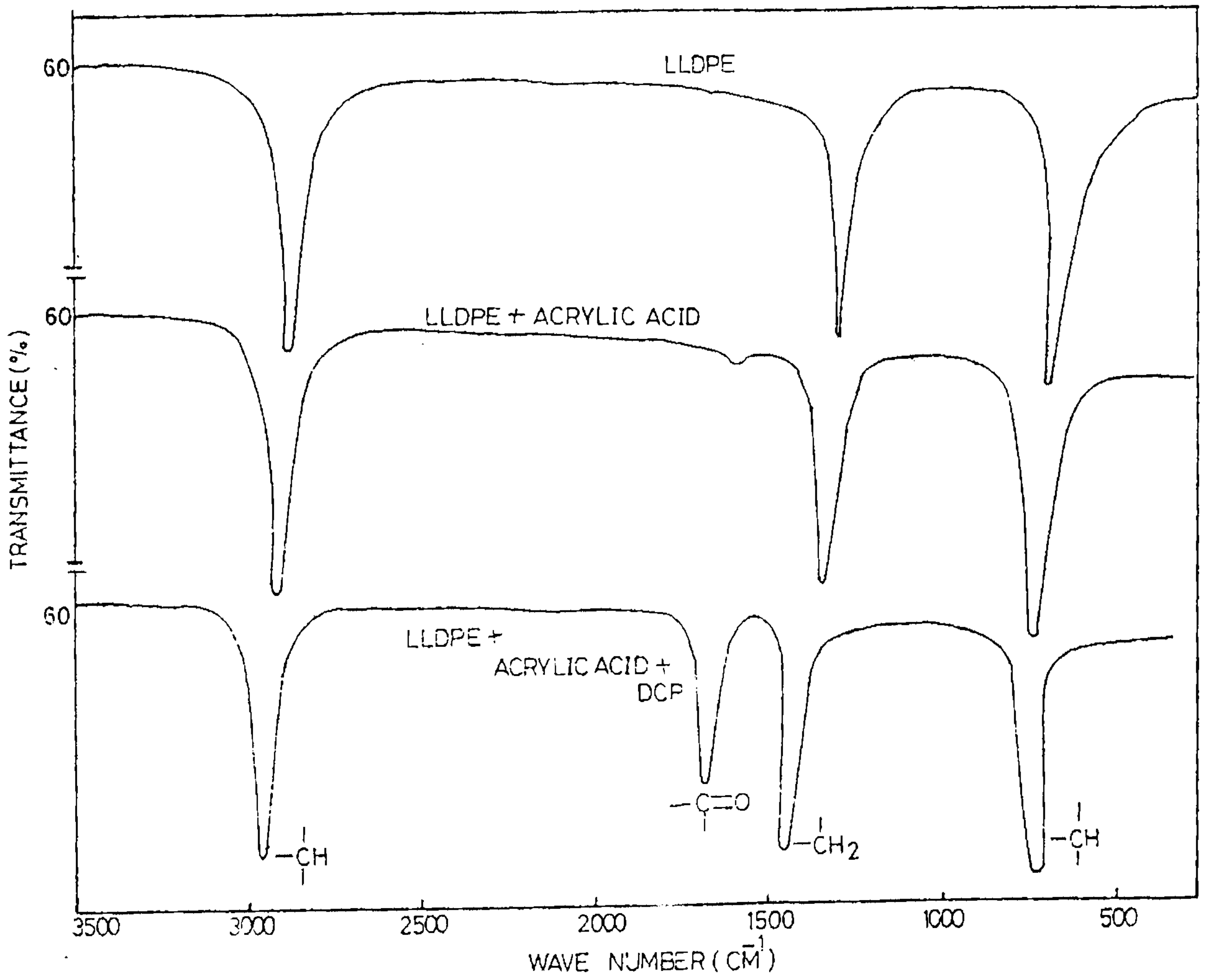


Fig.4.34: IR spectra of unmodified and modified LLDPE

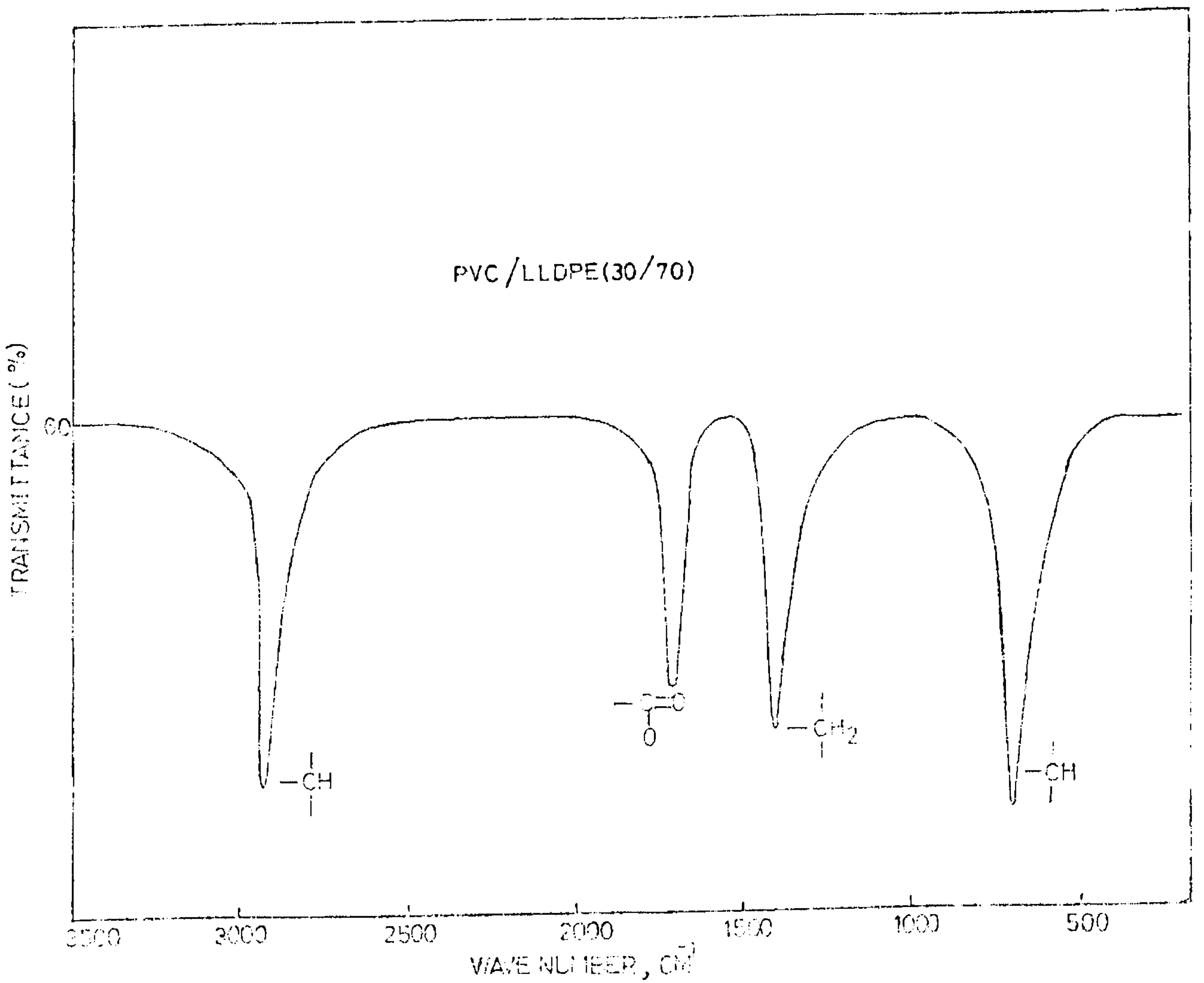


Fig.4.35: IR spectrum of acrylic acid-DCP modified 30/70 PVC/LLDPE blend

PVC/LLDPE blends is shown in Fig.4.36. Good improvement in tensile strength is found to result from the chemical modification. Fig.4.37 shows the variation in the yield stress. It is also found that increasing the concentrations of acrylic acid/maleic anhydride or DCP does not result in further improvement in properties. Chemical modification is found to vary the stress-strain behaviour substantially (Fig.4.38).

Fig.4.39 gives the effect of chemical modifications using phenolic resin and P-phenylene diamine on the tensile strength of PVC/LLDPE blends. The ability of phenolic resin to improve the ultimate properties of PE or PP blend with NBR has previously been reported. Both types of phenolic resins (high methylol type and resin containing hexamine) were used for the technological compatibilisation. Even though these modifications result in marginal improvements, it is not comparable with the improvement obtained with carboxylation.

CARBOXYLIC ACID MODIFIED PVC/LLDPE BLEND AS AN ADHESIVE

Earlier studies show that the introduction of some polar groups can increase the adhesive bond strength of polyolefines to various materials especially metals.

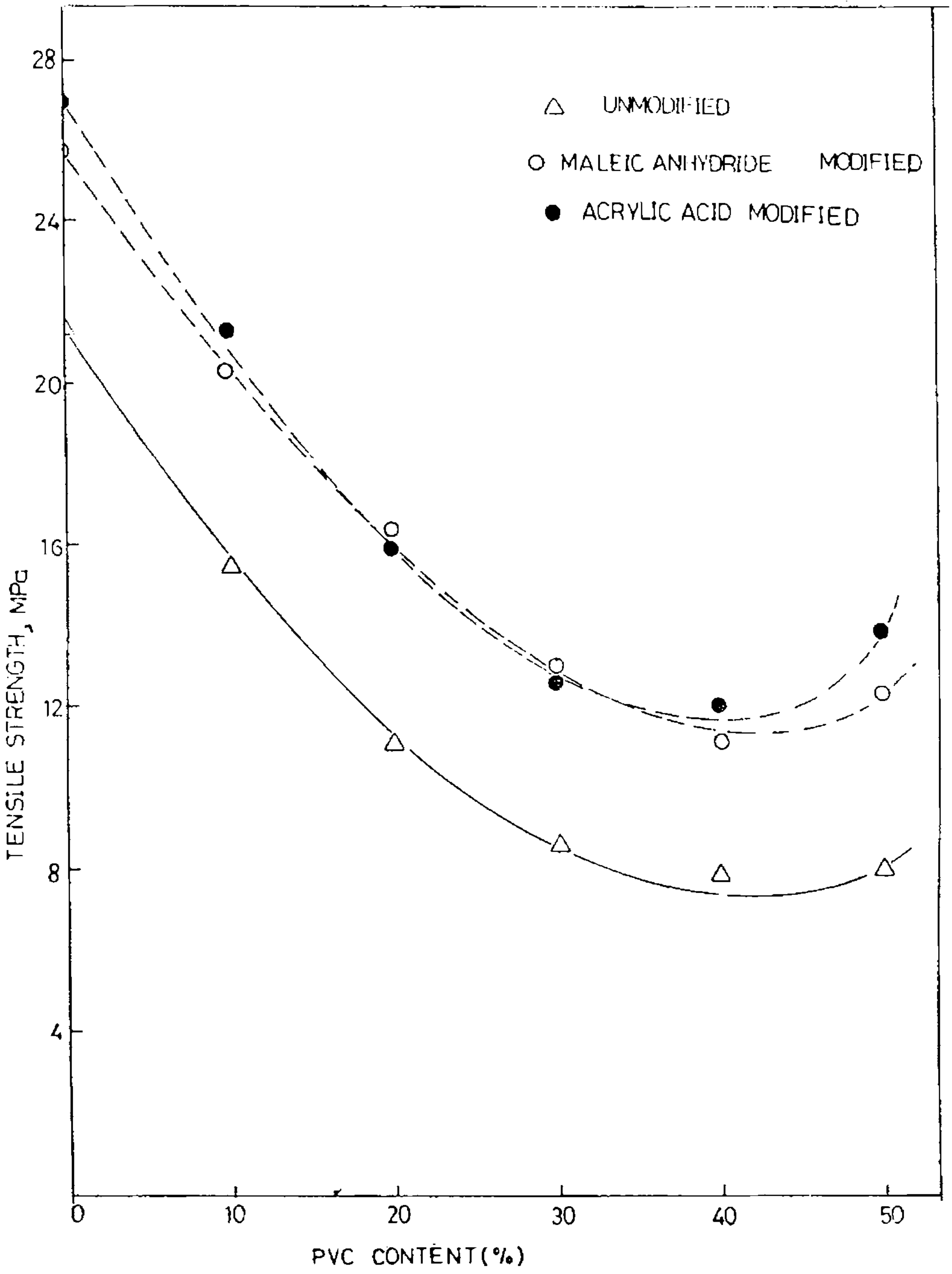


Fig.4.36: Variation of tensile strength with composition for the unmodified and carboxylic acid modified PVC/LLDPE blends

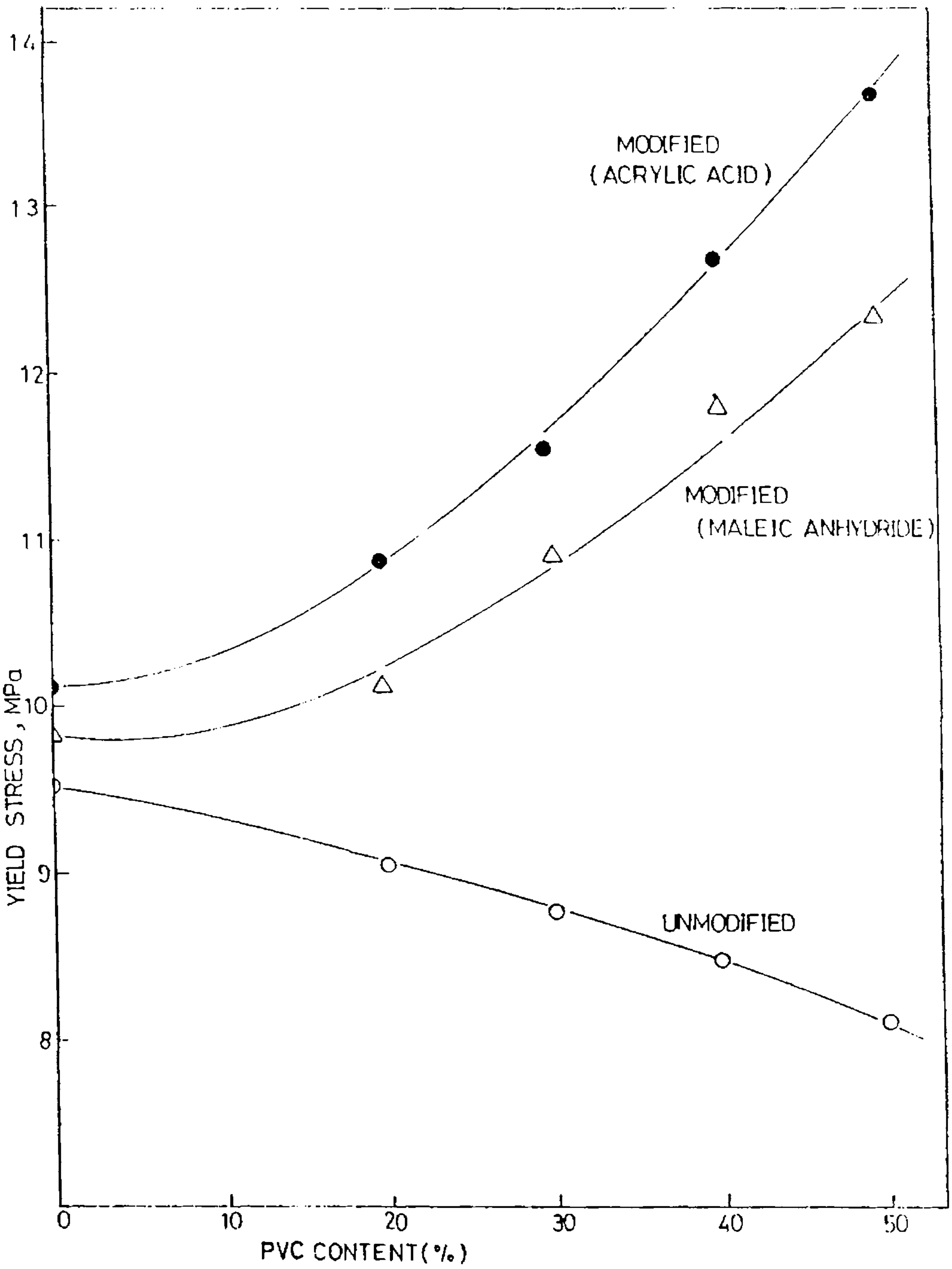


Fig.4.37: Variation of yield stress with composition of PVC/LLDPE blends

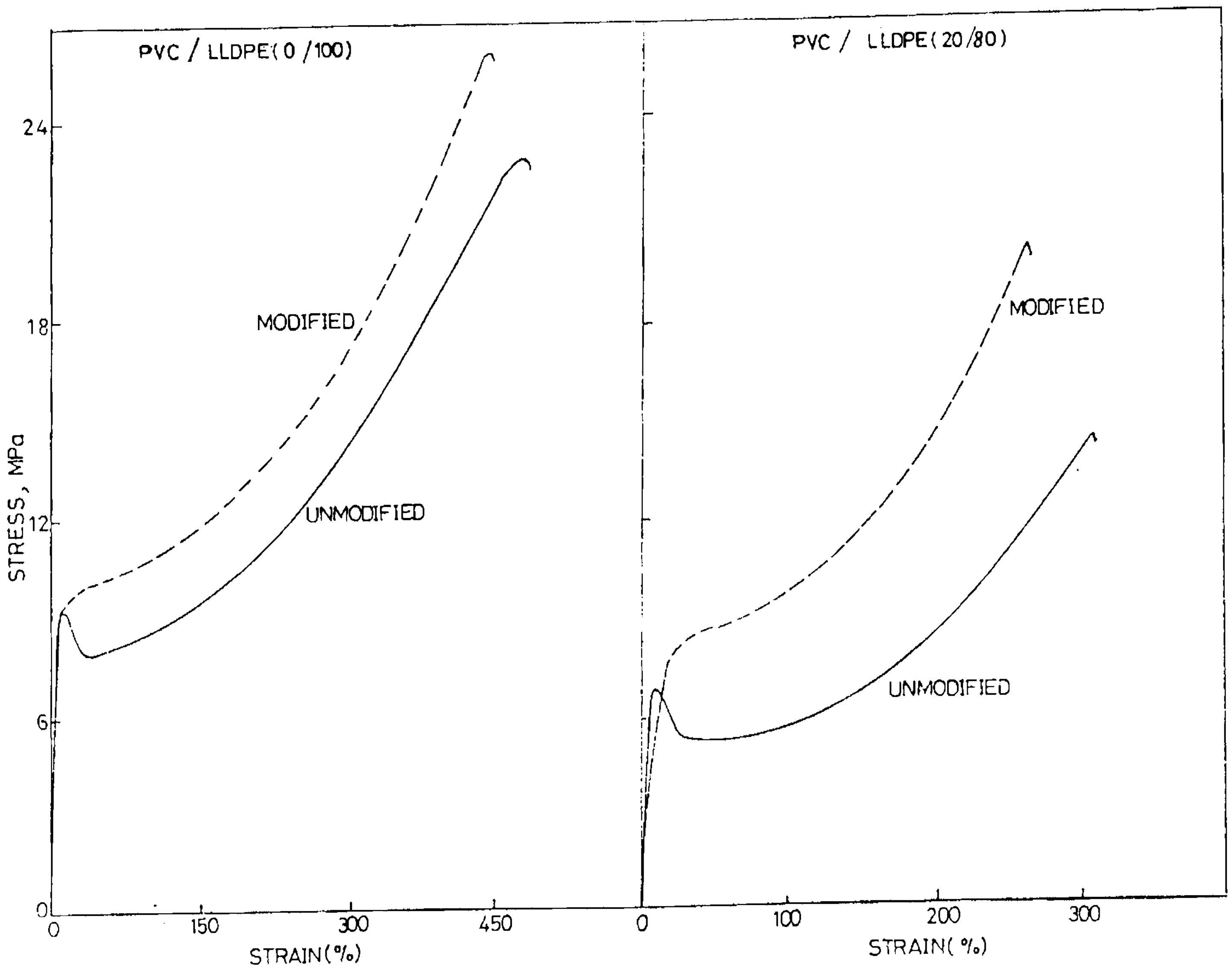


Fig.4.38: Stress-strain curves of LLDPE and 20/80 PVC/LLDPE blend

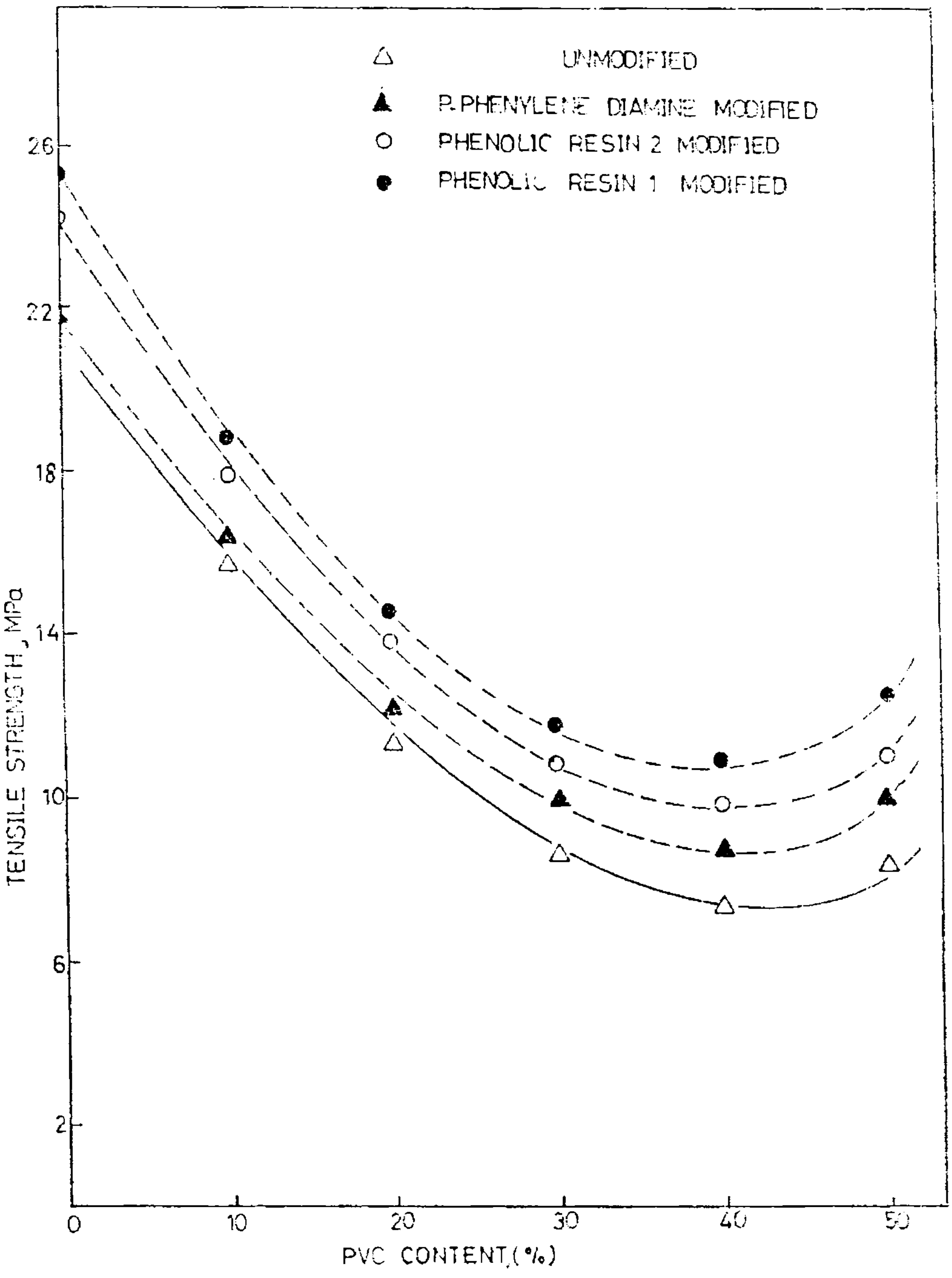


Fig.4.39: Variation of tensile strength with composition of PVC/LLDPE blends

Ethylene copolymers with polar groups were found to have such adhesive properties. The polarity of the groups on the polymer chain is utilised to support adhesion to various materials.[12] Hjertberg et al.[48] have studied the effect of various functional groups on the adhesion capability of polyolefine to metals. They found that carboxylic acid is very effective in increasing the adhesion between the polyethylene and metal. In this study acrylic acid and maleic anhydride modified PVC/LLDPE blend, is investigated for its adhesive properties with metals.

Experimental

Thin metal sheets (steel and aluminium) were cleaned with emery paper and then degreased. Then the sheet metal and the polymer were pressed together in a laboratory hydraulic press at 180°C for 3 min at 120 kg/cm^2 pressure. Then the metal/polymer sample was taken out of the hydraulic press, cooled to room temperature and the peel resistance (adhesive bond strength) of the joint was determined. The adhesive bond strengths between metal and modified polymer blends were assessed from the resistance to peeling of a 25 mm strip polymer sample from the metal surface, angle of peeling being 180° at 50 mm/min test speed.

Results and Discussion

PVC/LLDPE blends are found to show good adhesive properties to metals such as steel and aluminium. The bond strength is found to be much superior in the presence of PVC. This result confirms our earlier observation that chemical modification of the PVC/LLDPE blend is more efficient than that of LLDPE alone. The peel strength of the carboxylic acid modified LLDPE and its blend with PVC is given in Table 4.5.

Table 4.5: Variation of peel strength of the carboxylic acid modified PVC/LLDPE blends with blend composition

Percentage composition of PVC : LLDPE	PEEL RESISTANCE (N/mm)			
	Acrylic acid treated		Maleic anhydride treated	
	Steel	Aluminium	Steel	Aluminium
0 : 100	8.90	6.62	5.24	3.48
20 : 80	9.82	8.25	5.86	4.47
30 : 70	15.34	10.81	6.26	4.71
40 : 60	12.00	10.12	5.50	4.41
50 : 50	11.68	7.37	3.51	2.82

The peel strength of the modified PVC/LLDPE blends is found to improve steadily with PVC content but, when the PVC content exceeds 30% of the total weight, the strength of the polymer matrix is not sufficient to support the high bond strength. It is found that the introduction of polar functional groups to PVC/LLDPE blend increases adhesion and blend compatibility which makes them suitable for sophisticated end uses in place of more expensive polymers.

The water and temperature resistance of the adhesive bond is important when its practical utility is considered. To assess the water resistance of the adhesive bond the specimens were immersed in boiling water. The resistance to boiling water is shown in Table 4.6.

The boiling water resistance of the adhesive bond for acrylic acid modified LLDPE alone is not very high but the modified PVC/LLDPE blends show very good resistance even after 50 hrs of immersion in boiling water. This observation is also in conformity with the earlier observation that the presence of PVC increases the

Table 4.6: Hot water resistance of the PVC/LLDPE—metal bond strength

Blend composition percentage PVC : LLDPE	Initial peel strength (N/mm)	Peel strength (N/mm) after 50 hrs of immersion in hot water
0 : 100	6.62	--
20 : 80	8.25	5.62
30 : 70	10.80	5.31
40 : 60	10.10	4.62
50 : 50	7.37	4.28

adhesive bond strength. The chemical resistance of the acrylic acid modified blends was determined by keeping it in the respective chemicals at ambient temperature for one week. The percentage increase in weight of the acrylic acid modified blends in oil, toluene and concentrated HNO_3 is given in Table 4.7.

Table 4.7: Chemical resistance of the acrylic acid modified PVC/LLDPE blends

Percentage composition of PVC : LLDPE	PERCENTAGE INCREASE IN WEIGHT				
	At room temp. for 7 days			At 70°C for 24 hrs	
	Oil	Toluene	Con.HNO_3	Oil	H_2O
0 : 100	5.0	21.4	3.3	30.6	1.4
20 : 80	2.7	28.6	2.6	30.0	1.6
30 : 70	2.4	25.6	2.4	17.1	2.1
40 : 60	1.0	23.8	3.2	14.3	1.6
50 : 50	1.3	25.0	3.8	13.1	2.1

The blends are found to have good chemical resistance in these media. The blends also possess good dimensional stability in hot oil and hot water.

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Chapter 5

SUMMARY AND CONCLUSIONS

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Several elastomers were modified with PVC, the most notable among these being polychloroprene rubber (CR). Modification of CR with PVC was found to improve oil, petrol, ozone and fire resistance of CR. However, the mechanical properties of PVC/CR blends were far below the average properties of CR and PVC. Hytrel, EVA and NBR were found to be effective compatibilisers for improving the mechanical behaviour of PVC/CR blends.[1,6] The modified PVC/CR blends can replace CR in critical applications requiring superior chemical resistance, flame resistance and ageing resistance.

In order to study the mechanism of modification by Hytrel, EVA and NBR, the melt rheological properties of these modifiers and their blends with PVC were evaluated. It was found that all the three modifiers reduce the viscosity and non-Newtonian behaviour of PVC showing that these modifiers make the flow of PVC easier and more uniform. The flow curves (shear stress vs. shear rate curves) of PVC/Hytrel, PVC/EVA and PVC/NBR were found to display a uniform pattern. Each of them could be represented by two straight lines, each straight line representing a particular flow behaviour. The initial straight line represents largely the behaviour of the modifier alone when the PVC particles remain unfused to any great extent and the second straight line represents the true flow behaviour of the melts of the blends when the PVC is mostly in the molten state. There is a critical shear rate, which is a function of the blend composition and the temperature, at which transition from the first flow behaviour to the second one occurs. Hence the modifying action of Hytrel, EVA or NBR on PVC blends was concluded to be due to the following:[2]

1. Plasticising action on PVC which makes fusion of PVC particles faster and/or at a lower temperature.

2. Making the flow of PVC smoother and easier, enabling more efficient blending with the other constituent.

3. Lowering of the critical shear rate for a particular composition and temperature at which fusion of PVC particles occurs.

The second part of the study on PVC/LLDPE blends was motivated by the rising volume of polymeric materials to be found in industrial and muncipal wastes. PVC and polyethylene constitute about 50 per cent of all polymer wastes and hence recycling PVC/PE blends will give some guidelines as to how the ever increasing problem of pollution by non-biodegradable polymers can be mitigated. Chlorinated polyethylene was found to be a very useful additive for PVC/LLDPE mixtures for improving both the mechanical and processing properties of the blends.[3,5]

Co-crosslinking of the PVC/LLDPE blends was found to be another promising method for improving the physical and mechanical properties. Modification by chemical means (by using an organic peroxide) and by irradiation (by using gamma radiation) was found to improve the strength and stiffness of the matrix since the dominating reaction in both cases was that of co-crosslinking. It was also observed that the degradations in the blends during the course of such crosslinking can be minimised by using certain stabilisers which thus impart good colour flexibility to the blends.

Functionalisation or chemical modification of polymers was found to be another way of improving the mechanical properties of PVC/LLDPE blends.[4] Modification by acrylic acid and maleic anhydride in presence of dicumyl peroxide was found to be useful in improving the compatibility of the blends. The improvement was found to be mainly due to the grafting of carboxylic acid to the polymer chains and the grafting was found to be more effective in PVC/LLDPE blends than in pure LLDPE.

The grafting of acrylic acid or maleic anhydride to the polymers was also found to improve their adhesion with various materials. Acrylic acid and maleic anhydride modified PVC/LLDPE blends displayed very good bonding with metals like aluminium and steel. The bond was found to be much stronger in presence of PVC compared to LLDPE alone.

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