STUDIES ON LDPE/LLDPE BLENDS

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MARCH 1992

... to strive

to seek

to find &

not to yield

CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Mr.Daniel Abraham 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 LDPE/LLDPE BLENDS" is the original work carried out by me under the supervision of Prof.(Dr). D.Joseph Francis, Professor and Head, 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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CONTENTS

LIST OF ABBREVIATIONS USED IN THIS THESIS

Polymers

LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
HDPE	High density polyethylene
PP	Polypropylene
SBS	Styrene-butadiene-styrene
SIS	Styrene-isoprene-styrene
IIR (Butyl)	Isoprene-isobutylene rubber
NR	Natural rubber
EPDM	Ethylene-propylene-diene rubber
SEBS	Styrene-ethylene-butylene-styrene

Other abbreviations

DCP	Dicumyl peroxide
SPD	Solid phase dispersant
ISNR	Indian standard natural rubber
ASTM	American Society for Testing and Materials
µm	Micrometer
rpm	Revolutions per minute
phr	Parts per hundred rubber/resin
Tg	Glass transition temperature

Tm	Melting temperature
T	Temperature
T_R	Reference temperature
δ	Solubility parameter
ϕ	Volume fraction
ML(1+4) at 100℃	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of 4 minutes at 100℃
MFI	Melt flow index
ΔG_m	Free energy change of mixing
ΔH_m	Enthalpy change of mixing
ΔS_m	Entropy change of mixing
ΔE	Energy change of vaporisation
W	Energy required for plasticisation
$P_{c'}$	Property of the blend
η	Viscosity
$\tau_{w_{app}}$	Apparent shear stress at the wall
$\dot{\gamma}_{w_{app}}$	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	Bagley correction factor
P	Corrected pressure
L	Length of capillary die
R	Radius of the capillary die

Q	Volumetric flow rate
a_T	Shift factor
n	Power law index
E_a	Activation energy
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
MPa	Mega Pascal
kJ/mole	Kilo Joules/mole
K	Consistency index
Nm	Newton meter
Mw	Molecular weight
G	Molar attraction constant
PB	Polymer blends
PDB	Positive deviation blends
NDB	Negative deviation blends
PNDB	Positive negative deviation blends
IPN	Interpenetrating polymer network
V	Molar Volume
UTM	Universal Testing Machine
L_0	Initial gauge length of the dumbell specimen
L_1	Final gauge length of the dumbell specimen

B	Swelling ratio
P_0	Initial plasticity
PRI	Plasticity retention index
S^{-1}	Per second
E_b	Elongation at break

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Chapter 1

INTRODUCTION

INTRODUCTION

A considerable amount of research has been done over the last several years with a view to obtaining new polymeric materials with enhanced properties for specific applications or a better combination of different properties. After the syntheses of polymers from new monomers had been largely explored, efforts were focussed on multiphase polymeric systems that have two or more distinct phases such as block or graft copolymers, composites, polymer blends and interpenetrating networks.[1-5] Much attention is currently being devoted to the simplest route for combining outstanding properties of different existing polymers, that is, the formation of polymer blends.[6-28] Although an increasing number of miscible blends is reported in the literature,[29] most polymer pairs are nonetheless immiscible, thus leading to heterophase polymer blends.[30,31]

Polymer Blends

The following definitions are assigned to the commonly used terms.[32]

- Polymer Blends (PB): the all inclusive term for any mixture of homopolymers or copolymers.

- Homologous Polymer Blends: a sub-class of PB limited to mixtures of chemically identical polymers differing in molar mass.

- Polymer Alloys: a sub-class of PB reserved for polymer mixtures with stabilised morphologies.

- Miscible Polymer Blends: a class of PB referring to those blends which exhibit single phase behaviour.

- Immiscible Polymer Blends: a sub-class of PB referring to those blends that exhibit two or more phases at all compositions and temperatures.

- Partially Miscible Polymer Blends: a sub-class of PB including those blends that exhibit a 'window' of miscibility, ie., are miscible only at some concentrations and temperatures.

- Compatible Polymer Blends: a utilitarian term, indicating commercially useful materials, a mixture of polymers without strong repulsive forces that is homogeneous to the eye.

- Interpenetrating Polymer Network (IPN): a sub-class of PB reserved for mixtures of two polymers where both components form continuous phases and at least one is synthesised or crosslinked in the presence of the other.

Miscibility in Polymer Blends

The most basic question when considering a polymer blend concerns the miscibility as governed by the law of thermodynamics. According to this law, for two polymers to be miscible the free energy of mixing ΔG_m must be negative, ie.,

$$\Delta G_m = \Delta H_m - T \Delta S_m \tag{1.1}$$

where, ΔH_m is the heat of mixing and
ΔS_m is the entropy of mixing.

The combinatorial entropy of mixing ΔS_m of two polymers is dramatically smaller than that for two low molecular weight compounds. The enthalpy of mixing ΔH_m, on the other hand, is often a positive quantity or at best zero. In such cases immiscibility results when polymers are mixed. Consequently the number of known miscible blends is relatively small.[33] If however, there exist specific interactions (ion-dipole interactions, H-bonds) between the components, the heat of mixing ΔH_m becomes negative and the resulting system is miscible. In other words, miscibility depends on the degree of interaction between polymer components.[34-39]

The concept of solubility parameter, a measure of the attractive forces between molecules, is used as an aid in comparing the relative compatibility of polymers.[30] It is based on the principle that molecules of two different species will be able to coexist if the force of attraction between different molecules is greater than the force of attraction between like molecules of either species.

The energy of vaporisation per unit weight is a measure of the forces of attraction holding molecules together. The energy of vaporisation per unit volume is known as the cohesive energy density and its square root is known as the solubility parameter. .

$$\delta = (\Delta E/V)^{\frac{1}{2}}$$

$$= \left(\frac{H - RT}{Mw/D}\right)^{\frac{1}{2}} \qquad (1.2)$$

where, E is the energy of vaporisation
V is the molar volume
R is the gas constant
T is the temperature
M_w is the molecular weight and
D is the density.

Solubility parameter δ can also be calculated from a list of molar attraction constant, G for various parts of the molecule, which on addition gives δ from the relation,

$$\delta = \frac{D\Sigma G}{M_w} \tag{1.3}$$

where, D is the density
M_w is the molecular weight

δ values calculated in this way help in predicting compatibility.

Methods of Preparation

Polyblends are mixtures of structurally different homopolymers, copolymers, terpolymers and the like. The copolymers, terpolymers etc., may be random, alternating, graft or block type. Fig.1.1 gives a classification of polyblends in terms of their method of preparation.

Most commercial blends are prepared by mechanical means either on an open roll mill, in an extruder or in a suitable internal mixer. The processing temperature must be well above the glass transition temperature (T_g) of each constituent for mixtures of amorphous polymers and above the melting temperature (T_m) of mixtures containing semicrystalline polymers, whichever is higher.

Depending on the state of thermal stability of the polymers being mixed, the high processing shear could initiate degradation, resulting in free radicals. If the free radicals react with the other structurally different polymers present, resulting in true chemical graft or block copolymer, the mixture is referred to as a mechanochemical blend.

A chemical polyblend is made by in situ polymerisation and crosslinking of the constituent polymers, giving an interpenetrating crosslinked polymer network of structurally different polymers.

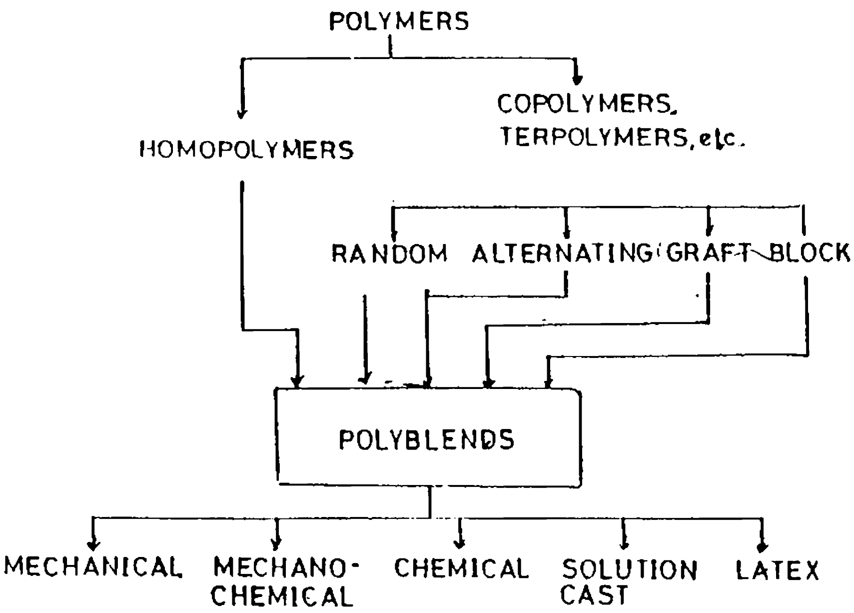


Fig.1.1: Classification of blends based on the method of preparation

Solution cast polyblends are prepared by dissolving the constituent polymers in a common solvent in such a way that the solutions have about the same viscosity. These solutions are mixed thoroughly and the resulting solution can be film cast to form the solution cast polyblend. A melt processing method can be used for compounding and pelletising the solution cast polyblends.

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.

Rheology of Polymer Blends

Considering the fact that most industrial scale preparations of polymer blends are carried out by mixing of polymer melts, studies on their rheological properties are of paramount importance. In most cases, the blend products have properties imposed by the morphology, created by a particular combination of the thermal and deformational history.

Classification of Polymer Blends

From the rheological point of view, the blends are classified into three groups, those where viscosity shows positive deviation from the log-additivity rule, (PDB) those where the opposite effect is observed (NDB), and the remaining mixed behaviour systems (PNDB).[40] To PDB belong the miscible blends and those with strong inter-domain interactions. To NDB belong those where the interactions are weak. To PNDB belong the blends in which there is a concentration dependent transition of structure. The melt flow of polyethylenes and their blends has been reviewed by Plochocki[41-43] and Utracki.[44,45]

Modification of Polymer Blends

One of the reasons for the differences in performance of different resins of the same chemical type is the interface. The most frequent method of modification of this zone is the introduction of a compatibiliser, its presence not only decreases the variability of blend performance but also improves it.

There exist two general routes to compatibility.[46]

i) By adding a third component (compatibiliser) capable of specific interactions and/or chemical reactions with the blend constituents. Block and graft copolymers and a variety of low molecular weight reactive chemicals fall under this category.

The choice of a block or graft copolymer as compatibiliser is based on the miscibility or reactivity of its segments with at least one of the blend components. The influence of these copolymers referred to as 'interfacial agents' has been related to their tendency to be preferentially located at the interface between phases and to the capability of their individual segments to penetrate into the phase to which they are chemically identical or similar.[47] On the other hand reactive chemicals such as co-crosslinking agents do not necessarily act at the interface although they meet the above definition of compatibiliser.

ii) By blending suitably functionalised polymers capable of enhanced specific interactions and/or chemical reactions. Functionalisation can be carried out in solution or in a suitable internal mixer,[48] and may involve the formation of block or graft copolymers, halogenation, sulfonation, hydroperoxide formation etc. The in situ formed compatibilisers have segments that are chemically identical to those in the respective unreacted homopolymers and are thought to be located preferentially at the interface, thus they may be considered equivalent to the block or graft copolymers that are added separately.

Physical and Mechanical Properties

In a multiphase polymeric system, a property P_c, depends on an average of the properties of the constituents, usually weighed in terms of volume fraction (ϕ).[49,50]

$$P_c = \phi_A f(P_A) + \phi_B f(P_B) \qquad (1.4)$$

The precise form of the equation depends on the particular system, the interactions between the components and on the compatibility.

In the case of miscible systems that are homogeneous the mixtures will be essentially transparent with a single phase and a sharp T_g. In such a case the above equation may be written in the following semiempirical form,

$$P_{C'} = \phi_A P_A + \phi_B P_B + I\phi_A \phi_B \qquad (1.5)$$

where I is an interaction parameter which can be positive, zero or negative as shown in Fig.1.2. When I is positive the property is synergistic, when I is zero the property is additive and when I is negative the property is nonsynergistic.

Equation (1.5) describes in particular, variation with composition of such properties as glass transition temperature, density, refractive index, dielectric constant, thermal conductivity, heat capacity, thermodynamic properties, elastic moduli, viscosity of liquid mixtures and surface tension. Most polymer mixtures are immiscible and the properties of these heterogeneous blends are difficult to predict. Many of

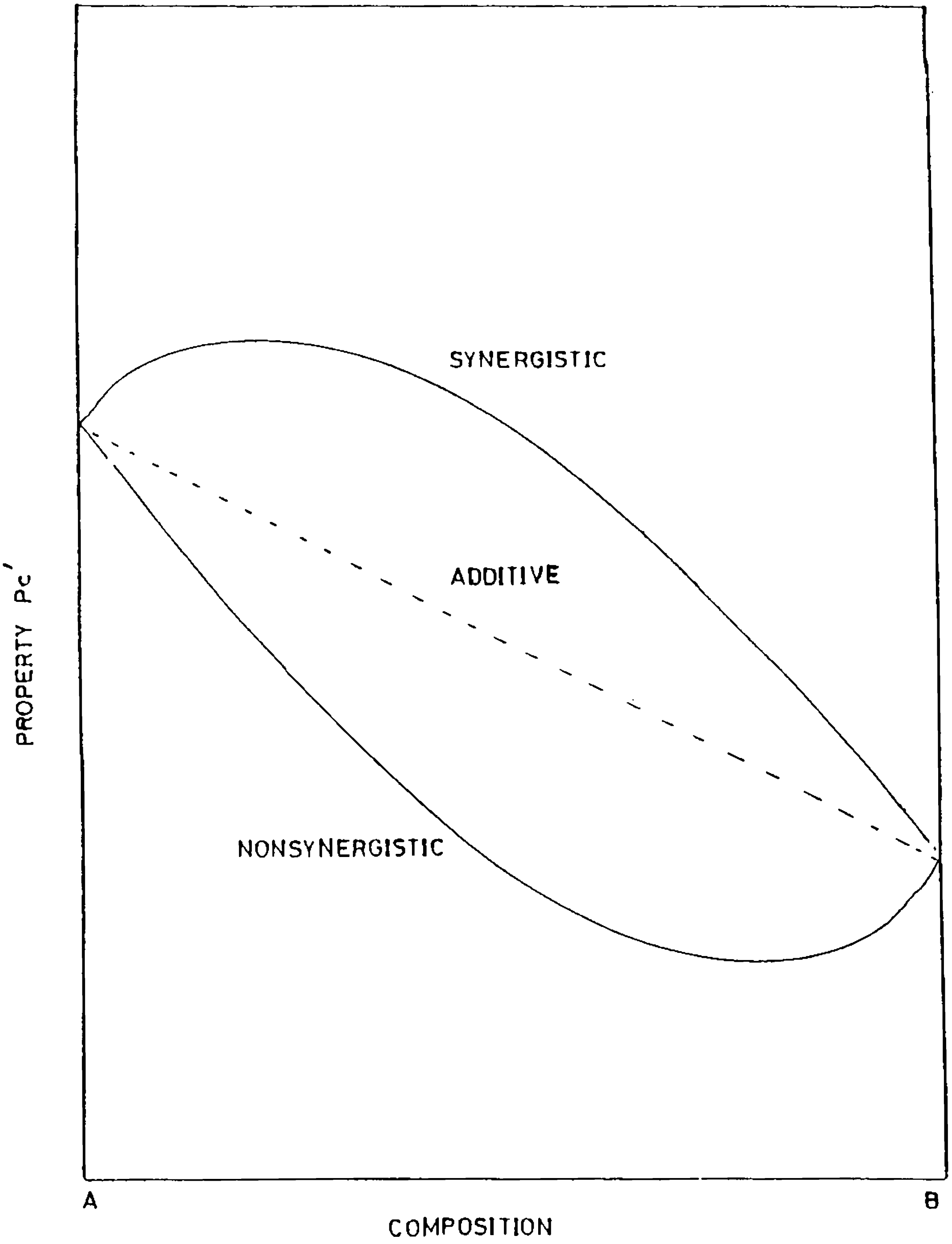


Fig.1.2: Properties of polymer blends as a function of composition

the equation proposed to account for the behaviour of heterogeneous blends can be expressed by the relation,[51,52]

$$\frac{P_{C'}}{P_A} = \frac{1 + AB\,\emptyset_B}{1 + B\,\psi\,\emptyset_B} \qquad (1.6)$$

where P_A is the property of the continuous matrix. $A > 0$ depends on the shape and orientation of the dispersed phase and the nature of the interface, B is a function of A, P_A & P_B and ψ is a reduced concentration term which is a function of the maximum packing volume fraction of the dispersed phase. This semi-empirical rule of mixing is obeyed by many physical properties such as moduli, impact strength, thermal and oxidative resistance, flame retardance, domain morphology, thermal expansivity thermal conductivity, compressibility and refractive index. Properties of all polymer blends and the heterogeneous ones in particular, strongly depend on the thermodynamic and rheological properties of the ingredient resins, the method and extent of mixing and processing. These factors taken together define the morphology of the final product and therefore its ultimate properties and performance. These correlations are presented schematically in Fig.1.3.

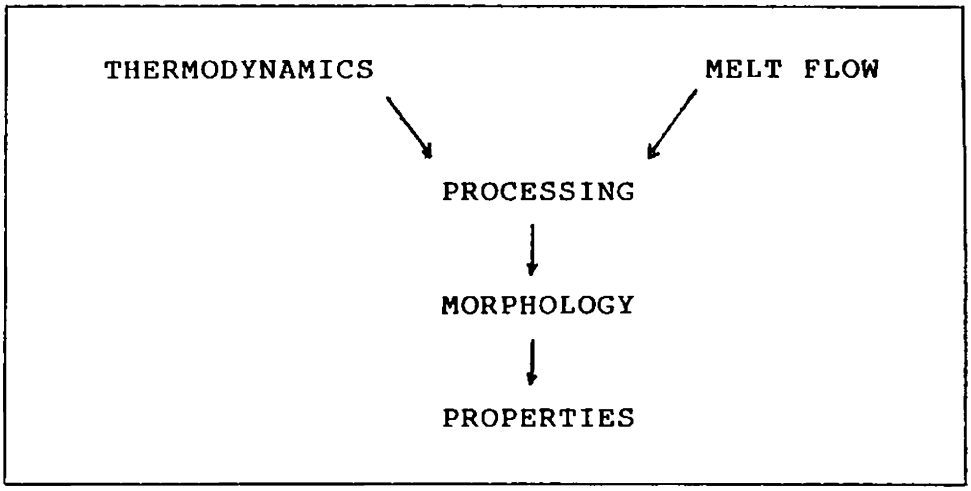


Fig.1.3: Factors affecting the properties of a polymer blend

Polyethylene Blends

Many thousands of tons of plastics are produced yearly all over the world. Among these materials polyethylene plays a very important role as the most extensively used product. Since their discovery in 1933 there has been a continuous rise in consumption to the present level of 25 million tons per annum or 42% of all plastics.[53] This extended period of growth originates in continuous development and modification of these resins, resulting from a widening range of polymerization techniques.

The history of polyethylene can be divided into three periods.

1. The initial period characterised by predominance of the radical polymerization of ethylene C_2 at high temperature and pressure.

2. Development of coordination copolymerization of C_2 monomer with other α-olefines.

3. Development of polymer blending technology.

Discoveries in the laboratories of Ziegler and Natta in the early 1950's caused a revolution in polymer and organometallic chemistry.[54-57] Natta discovered that Ziegler catalysts containing highly ordered transition metal salts in a low valence state (eg., $TiCl_3$, VCl_3) polymerise α-olefines to crystalline stereoisomeric polymers. This discovery led to the commercialisation of high density polyethylene (HDPE), which had to be toughened by copolymerization with butene C_4. What followed next was the development of a new class of polymers called the linear low density polyethylene (LLDPE), by Du Pont, Canada in the late 1950s. The polymer was prepared by coordination polymerisation in solution of ethylene with 10 to 20 mol per cent of C_4, C_6 or C_8 comonomers. In 1979 Union Carbide patented the gas phase coordination polymerization process.

The impact of this new technology on the plastics industry has not only made LLDPE popular around the world but also led to an ingress of blending methods for obtaining new polymers with a range of properties for specific end use applications.

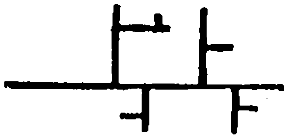
Structure of LLDPE

If LDPE is pictured as a highly branched molecule with branches of varying lengths and HDPE as a linear molecule with relatively few or no branches, then LLDPE can be described as molecules having a linear configuration with many short side-chains all of uniform length.[58]

A comparison of the structures[59] of LDPE, LLDPE and HDPE is shown in Fig.1.4

Table 1.1 reports a comparison among the physical, mechanical and application characteristics of LDPE and LLDPE.

The main positive features of LLDPE in comparison to LDPE may be deduced from Table 1.1 as follows:



LDPE
LONG CHAIN BRANCHING

HDPE
LINEAR STRUCTURE

LLDPE
SHORTCHAIN BRANCHING FREQUENCY
HIGHER THAN FOR HDPE

Fig.1.4: Structures of LDPE, HDPE and LLDPE

Table 1.1: Comparison among typical characteristics of LDPE and LLDPE used in Blown Films

Characteristics	LDPE	LLDPE
MFI (g/10 min.)	1.6-2.2	0.8-1.2
Density (g/cm^3)	0.920	0.918
Melting temperature (°C)	110	125-130
Crystallinity (%)	60-65	65-70
Maximum stretch ratio at 190°C	120-160	800-1000
Processability	Good	Fair
Impact strength:		
Longitudinal* (J/cm)	6	25
Transverse* (J/cm)	25	40

* Determined according to ASTM test methods on films of 30 µm thickness (1:1.6 blow ratio) for LDPE and LLDPE.

a) Heat resistance considerably higher

b) Higher crystallinity and consequently a greater degree of stiffness

c) Excellent stretchability which permits thinner films to be obtained

d) Higher and better balanced impact resistance properties.

On the other hand the high melt viscosity of LLDPE associated with its long regular molecular chains makes processability difficult. Many extruders now running LDPE have insufficient torque capability to run LLDPE. Furthermore melt fracture may also occur due to high shear stress in the die. The best solution to this problem is to mix LLDPE with conventional LDPE. The resulting blends combine the good mechanical properties of LLDPE and processing properties of LDPE.

Objectives and Scope of this Work

Polyolefine blends have been extensively studied with a view to improving the properties and processability of the homopolymers involved. The benefits claimed include, for example, improvement in impact strength, environmental stress cracking, optical properties, crystallisation rate, low temperature impact strength, rheological properties and overall mechanical behaviour. A further reason for the study of such blends is that mixtures of such polymers often occur in plastics scrap and waste and affect the possible reuse of such low cost material.

With the introduction of LLDPE, the polyolefine industry is poised for another leap. Its sufficient compatibility with conventional polyethylene (HDPE and LDPE) enables the formation of blown films and other products consisting of a combination of various types of polyethylene in the form of blends and/or composite multilayer structures. Of these, it is the blends of LDPE and LLDPE which are likely to become the most useful especially for the manufacture of blown films. LLDPE gives a greater degree of stiffness and higher tensile strength compared to LDPE and also has a more regular crystalline structure, higher melting point and better fracture resistance at low temperature. This provides the opportunity for improving the performance of LDPE with

LLDPE. If the mechanical and rheological properties of these blends are clearly understood, it can revolutionise the blown film industry. It was with this aim that the present study on LDPE/LLDPE blends was undertaken.

In the present study, the mechanical properties of the blends of various grades of LDPE and LLDPE are proposed to be studied. The rheological and processing properties of the blends are also proposed to be studied in detail. At high shear rates encountered in the processing equipments, the viscosity of LLDPE is considerably greater compared to LDPE and this can cause difficulties in the forming of film at the die exit, and also in the drawing of the films uniformly from the die. Investigation on the rheological properties will answer the question whether conventional processing machines used for LDPE itself can be used for processing of LDPE/LLDPE blends or whether any modification is necessary.

In order to improve the mechanical and processing behaviour of polymers they are sometimes crosslinked by addition of organic peroxides. Creep and tensile properties, mechanical stability at high temperature and ductile–brittle failure can be improved by introducing a low level of crosslinking. However, no such studies have been reported so far on polyolefine blends.

Mechanical and rheological behaviour of chemically crosslinked LDPE/LLDPE blends are also proposed to be investigated. Studies on the processing and rheological behaviour of two phase blends is a challenging field. Conventional equipments like a capillary rheometer may not reveal the behaviour of the melt under complex shearing conditions encountered in actual processing operations. Shear and temperature can be varied over a wide range in a Brabender Plasticorder. Rheological evaluation of LDPE/LLDPE blends have also been done using the Brabender plasticorder.

The effect of modifiers in improving the mechanical behaviour of the blends is also proposed to be investigated. Since both LDPE and LLDPE are crystalline polymers, rubbery modifiers may be able to improve properties such as toughness, stress crack resistance etc. of the blends.

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Chapter 2

MATERIALS AND EXPERIMENTAL PROCEDURE

MATERIALS AND EXPERIMENTAL PROCEDURE

MATERIALS

The materials used were commercially available polymers with the following characteristics:

Low density polyethylene (LDPE)

Indothene FS 300 was supplied by IPCL, Baroda, density (g/cm^3) = 0.922, melt flow index (g/10 min) = 6.

Linear low density polyethylene (LLDPE)

Ladene 218 W was supplied by IPCL, Baroda, density (g/cm^3) = 0.918, melt flow index (g/10 min) = 2.

Natural rubber (NR)

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

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

Ethylene-propylene-diene rubber (EPDM)

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

Butyl rubber

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

Thermoplastic elastomers

Styrene-isoprene-styrene (SIS): Kraton D 1107 was supplied by Shell Chemical Company, melt flow index (g/10 min) = 9; styrene/rubber ratio : 14/86.

Styrene-butadiene-styrene (SBS): Kraton D 1102 was supplied by Shell Chemical Company, melt flow index (g/10 min) = 6; styrene/rubber ratio : 30/70.

Styrene -ethylene-butylene-styrene (SEBS): Kraton G 1652 was supplied by Shell Chemical Company, styrene/rubber ratio 29/71.

Additive

Dicumyl peroxide (DCP): bis-(α,α'-dimethyl-benzyl) peroxide was supplied by Merck.

Solvents used

Methanol and toluene were of analytical grade.

EXPERIMENTAL

Rheological Evaluation using a Brabender Plasticorder

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

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

The Brabender plasticorder is used to study the rheological behaviour of polymer blends. The instrument imparts a very complex shearing motion to the polymer and consequently the data cannot be taken as fundamental rheological properties. However, the nature of shear in the plasticorder is similar to that encountered in practical processing operations such as extrusion or milling. Another advantage is that due to complex shearing the polymer melts at a comparatively lower temperature and hence rheological data could be obtained at a comparable shear and temperature that would be employed in actual processing. Blyler and Daane[3] observed that the power law relationship between rotor torque and rotor speed is reminiscent of the power law relationship often found between shear stress and shear rate and with a few assumptions derived the equation,

$$M = C(n)KS^n$$

where, M is the torque

n the power law index

C(n) a function weakly dependent on n

K a constant and

S rotor speed

The slope of the plot of log M vs log S gives the power law index n.

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 10^4 S^{-1} with good reproducibility. In this study the rheological properties of polymer blends were measured using a Göttfert Viscotester model 1500 in accordance with ASTM D 3835-79.

In capillary rheometry (Fig.2.1) the polymer to be tested is first of all melted in a thermostated barrel and then extruded through a capillary of circular cross-section. The volumetric output Q is set and the pressure drop ΔP along the capillary is measured. From the measured values of ΔP the viscosity functions such as apparent shear stress, apparent shear rate and apparent viscosity are calculated from Poiseuille law for steady flow according to the following equations:

$$\text{Apparent shear stress } \tau_{w_{app}} = \frac{\Delta P}{2.L/R} (\text{MPa})$$

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

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

where, ΔP is the pressure drop across the capillary (MPa)

Q is the volumetric flow rate (mm^3/sec)

R is the capillary radius (mm)

L is the capillary length (mm).

A straight line relationship on a log-log plot indicates that the variables $\tau_{w_{app}}$, $\dot{\gamma}_{w_{app}}$ can be related by the following power law equation,

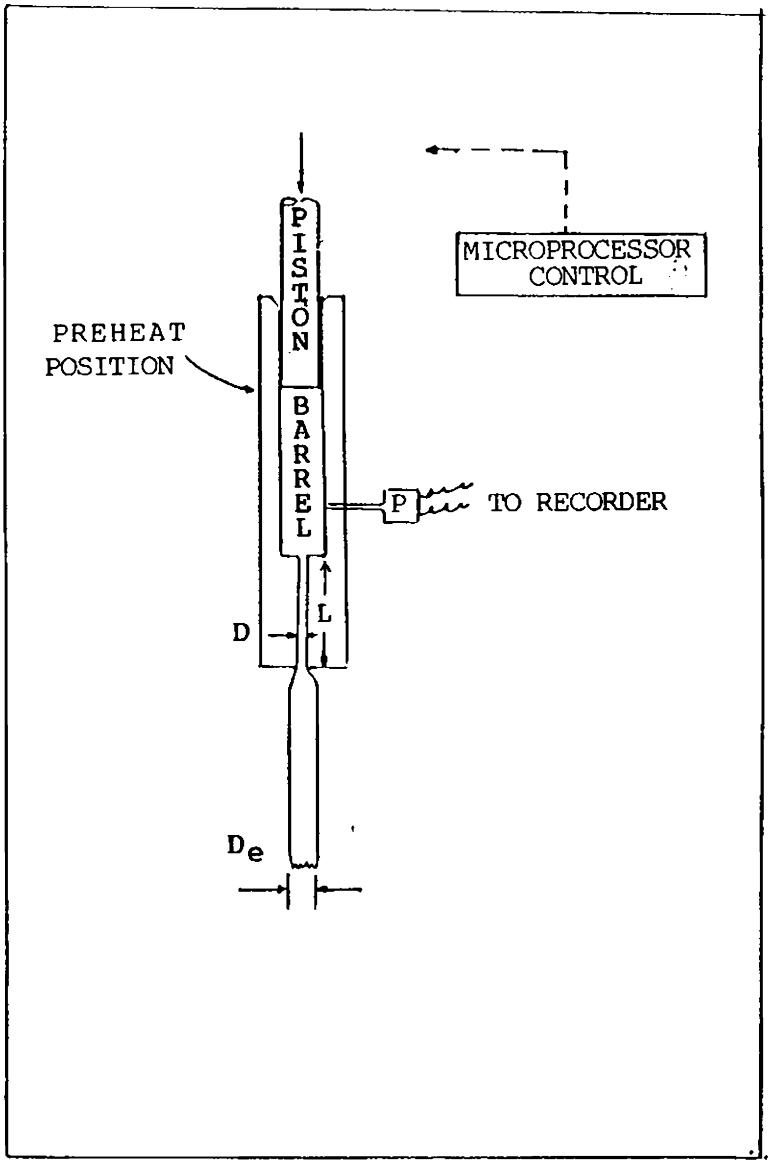


Fig.2.1: Schematic diagram of a capillary rheometer

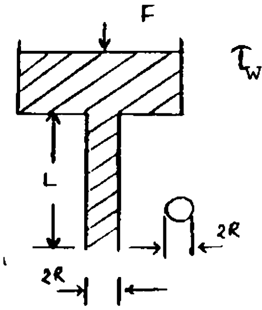
$$\tau_{w_{app}} = K \dot{\gamma}^{n}_{w_{app}}$$

where, K is the consistency index

n is the power law index.

This law is often referred to as the power law of Ostwald and de Waele.[4,5] The power law index n indicates how rapidly the viscosity decreases with shear rate. For pseudoplastic fluids the power law index ranges from 1 to 0. When the power law index is unity, the fluid is Newtonian and the consistency index becomes the Newtonian viscosity. The power law index indicates the degree of non-Newtonian behaviour. The apparent viscosity data are corrected in order to get the absolute viscosity data of the material under test. The most important corrections according to Bagley and Rabinowitsch are given in Table 2.1.

Table 2.1: Important corrections employed in a capillary rheometer

Capillary geometry	Shear stress at wall	Shear rate	Most important corrections
	$\tau_{w_{app}} = \frac{\Delta P}{2.L/R}$	$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3}$	Bagley correction $P = \Delta P - P_c$ Rabinowitsch correction $\dot{\gamma}_w = \frac{(3n+1)}{4n} \dot{\gamma}_{w_{app}}$

Bagley correction

With the Bagley correction inlet and outlet pressure losses are separated that are included if pressure ΔP measured in front of a circular capillary is used as pressure drop along the capillary to calculate the wall shear stress (τ_w).

This is demonstrated schematically in Fig.2.2 by the flow lines of the melt entering and leaving the capillary.

As can be seen from this diagram part of the pressure ΔP measured in front of the capillary is used to deform the melt to enter the capillary and is stored as elastic deformation energy within the melt. At the outlet of the capillary part of this deformation energy that has not yet relaxed within the capillary will be released again giving rise to a swelling of the extrudate. However, swelling of the extrudate is also influenced by normal stresses being produced by the shear deformation of the melt flowing through the capillary.

To separate the elastic inlet and outlet pressure losses from the real viscous pressure drop along

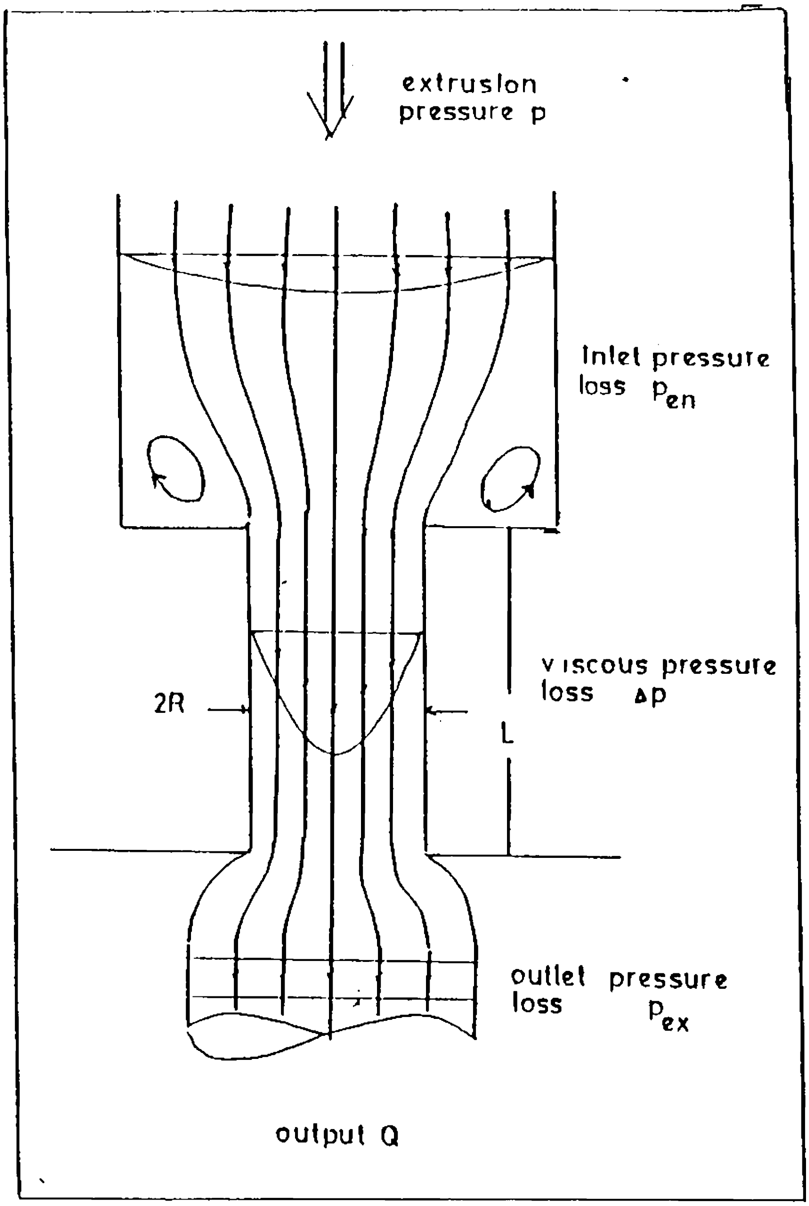


Fig.2.2: Flowlines and velocity fields inside and outside of a round hole die

the capillary with the Bagley correction,[6] ΔP is measured at constant volumetric outputs with a minimum of three capillaries of a constant diameter but different lengths. The measured values of ΔP is then plotted versus L/R to give a so called Bagley plot. Linearisation and extrapolation of this curve to L/R = 0 gives the Bagley correction term 'P_c' to be subtracted from ΔP measured.

Corrected shear stress is then given by $\tau_w = \dfrac{\Delta P - P_c}{2.L/R}$

where, ΔP is the pressure drop along the capillary

P_c is the Bagley correction term.

Rabinowitsch correction[7,8]

Rabinowitsch correction takes into account that the equation given in Table 2.1 to calculate apparent shear rate holds only for Newtonian fluids with a shear rate independent viscosity but does not hold for non-Newtonian fluids like polymer melts. These apparent shear rates are corrected by the degree of non-Newtonian behaviour by using the slope of the flow curve.

Melt elasticity measurements

One of the characteristics of polymers is that their rheological behaviour has a dual nature; ie., they combine the features of elastic solids and viscous liquids. Most polymeric materials at some stage in their responses display both these characteristics and are described as viscoelastic. The elastic flow component of the melt has the effect that a pure shear deformation of a melt which gives rise to an orientation of the macromolecules in flow direction also generate normal stress differences within the melt. These normal stresses are the cause of unusually high inlet and outlet pressure losses and of swelling effects at changes in cross sections of flow passages.

The measurement of entrance pressure loss P_c is a useful rheological parameter directly related to the elastic component of the melt. The most obvious elastic effect during capillary extrusion is post extrusion swelling.

Melt Flow Index Measurement

An extrusion plastometer was used for measuring the melt flow index of polymer melts (ASTM D 1238). The rate of extrusion through a die of specified length and diameter was measured under prescribed conditions of temperature, load, and piston position in the barrel as a function of time. Melt index is calculated and reported as g/10 min. This index is inversely related to molecular weight.

Activation Energy for Viscous Flow

The activation energy has considerable practical importance because it expresses the viscosity/ temperature dependence of a material subjected to flow. It is an operationally defined quantity that relates viscosity to temperature by the relation,

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

where, Ea is the activation energy
A is a constant
R is the gas constant and
T is the absolute temperature.

Compression Moulding of Test Sheets

The test specimens were prepared using a hydraulic press with heated platens working at various temperatures and pressures. The test specimen was placed in an open cavity, compressed under high pressure when the material softened and flowed within the mould cavity. The moulding was then ejected and allowed to cool.

Mechanical Properties

Mechanical properties are the total of properties determining the response of bodies to external mechanical influences, manifested in the ability of the bodies to develop reversible and irreversible deformations and to resist failure. The basic characteristics of mechanical properties of solids is usually determined by a test resulting in various deformation versus stress dependencies such as stress-strain diagrams. Examination of such dependencies readily brings out characteristics of elasticity, plasticity and strength.

Stress-strain measurements

Stress-strain measurements are generally made in tension by stretching the specimen at a uniform rate and simultaneously measuring the force on the specimen. The most popular instrument used in stress-strain measurements is a Universal Testing Machine. This instrument is essentially a device in which a sample is clamped between grips or jaws which are pulled at constant strain rates. The stress on the sample is followed with load cells.

The ultimate tensile strength of the sample is given by the force measured by the load cell divided by the cross sectional area of the sample,

$$\text{Ultimate tensile strength} = \frac{\text{Force (kg)}}{\text{Cross sectional area (cm}^2\text{)}}$$

The elongation at break of the sample is measured in terms of its initial length L_o and final length L_1 as,

$$\text{Percentage elongation} = \frac{L_1 - L_o}{L_o} \times 100$$

Dumbell shaped specimens (specimen dimensions are according to ASTM 412/75, Type C) were cut from sheets of the materials. The cross sectional area of the specimens at the point of minimum cross-section was measured using a micrometer. The experiments were carried out in a Zwick UTM model 1445. The dumbell shaped specimens were held in pneumatic grips and then pulled at a uniform crosshead speed of 50 mm/min. till it failed. The load versus crosshead movement is recorded on a chart which runs at a definite speed. The ultimate tensile strength and percentage of elongation at break were calculated from the load at break and the extension.

Density

The densities of the polymer samples were estimated by the method of displacement of liquid

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

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

Hardness

Hardness was measured according to ASTM D 2240 using a Zwick hardness tester of the Shore D scale. The specimens were at least 3 mm thick with a surface free of scratches or other defects which could lead to errors.

Wear resistance

For determination of wear resistance, specimens in the form of discs (50 mm diameter and about 3 mm thick) were abraded using no.240 emery paper, with a Zwick Abrader with 0.5 kg load.

Gel Content Measurement

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

Morphology Studies

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

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Chapter 3

RHEOLOGICAL CHARACTERISATION OF BLENDS OF LDPE AND LLDPE

RHEOLOGICAL CHARACTERISATION OF BLENDS OF LDPE AND LLDPE

Polyethylene blends have been studied extensively for improving the properties and processability of homopolymers involved. The flow behaviour of melts of polyethylene blends is a critical factor in determining the usefulness of a given blend or in determining the conditions under which the material is formed into a finished product. The most classical experiment for a thermoplastic resin is to determine the flow curve ie., shear stress versus shear rate or apparent viscosity versus shear stress or shear rate. This flow curve can be obtained with a capillary viscometer in the shear rate range 10 to 10^4 S^{-1}. However, for calculating parameters such as extruder power consumption for laboratory experiment, it will be more appropriate to use a processing equipment itself for calculating such functions. In this study, the rheological evaluation of LDPE/LLDPE blends was carried out by using a Brabender plasticorder and a capillary rheometer.

Linear low density polyethylene has acquired great commercial importance because of its superior mechanical behaviour compared to low density polyethylene.[1] Blends of LDPE and LLDPE are now considered as excellent materials for film manufacture because they combine the processability of LDPE and the good mechanical properties of LLDPE.[2-4] Studies on the rheological and mechanical behaviour of this new class of blends are few.[5-23] Papers published on this subject indicate that while the mechanical properties of the blends generally vary smoothly and proportionately between the constituent polymers, the melt flow properties present a complex picture.[5,8,12]

I. RHEOLOGICAL EVALUATION OF BLENDS OF LDPE AND LLDPE USING A TORQUE RHEOMETER

Blend Preparation

The polymer blends were prepared by melt mixing in the Brabender plasticorder model PL 3S equipped with roller mixing heads. Simultaneous loading technique was employed. The mixing conditions were 140°C, 30 rpm and 10 minutes. After this time a constant torque was recorded for all the blends. The pure polymers were also subjected to the same procedure in order to make the data comparable to those of the blends. The investigated compositions of the blends were 0, 25, 50, 75 and 100 weight per cent LDPE. Rheological measurements in shear flow were also carried out for each blend and pure polymers using the plasticorder.

Results and Discussion

Fig.3.1 shows the equilibrium torque values as a function of blend composition for various rpm of the rotors. The torque values may be taken to be proportional to the viscosity of the system at the temperature and shear rate involved. In each case the viscosity of the melt decreases with increase in LDPE content. This indicates that the processability of the blends improve progressively with increase in composition of LDPE. From a practical point of view the lower values of effective viscosity make it possible to bring down the processing temperatures thereby leading to a reduction in energy required for production. The same type of behaviour is observed also at higher shear rates.

The viscosity of the blends are between those of the pure polymers. The blend viscosity is found to obey the logarithmic additivity rule.[12]

$$\log \eta_{mix} = w_1 \log \eta_1 + w_2 \log \eta_2 \qquad (3.1)$$

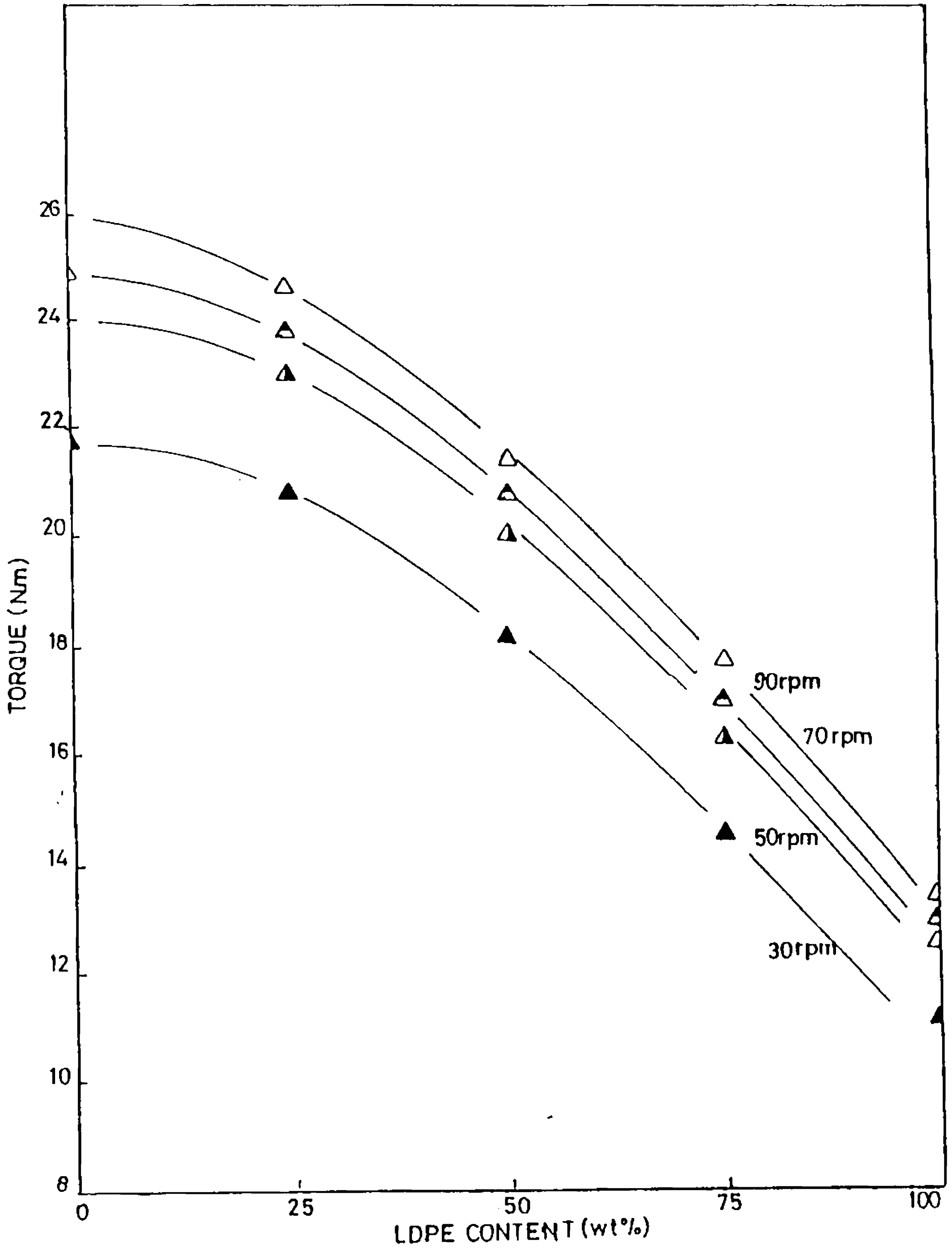


Fig.3.1: Torque as a function of blend composition at various rpms

where w_1 and w_2 are the weight fractions and η_1 and η_2 are the viscosities of the corresponding constituents in the mixture. This might indicate partial miscibility in the melt.

Fig.3.2 shows the variation of torque with blend composition at various temperatures and a fixed shear rate. In each case viscosity decreases with increase in temperature as expected. The influence of temperature on viscosity may be determined with the help of a shift factor a_T defined as:

$$a_T = \frac{\eta_T}{\eta_{T_R}} \qquad (3.2)$$

where T_R is the reference temperature.

The shift factors for the pure polymers and the blends are found to be similar.

Blyler and Daane[24] observed that the power law relationship between rotor torque and rotor speed is reminiscent of the power law relationship often found between shear stress and shear rate and with a few assumptions they derived the expression,

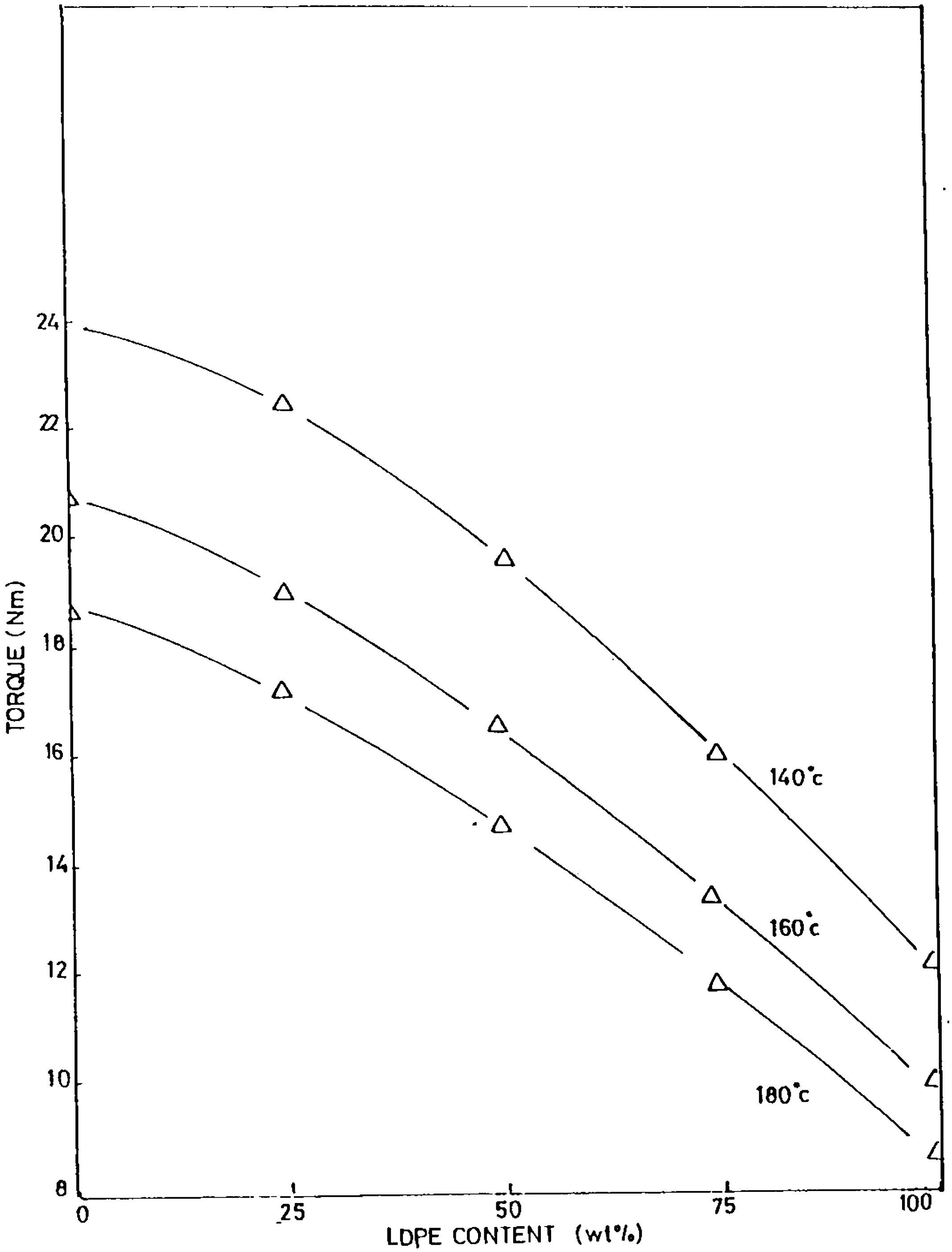


Fig.3.2: Torque as a function of blend composition at various temperatures

$$M = C(n)K\ S^n \tag{3.3}$$

where M is the torque

n the power law index

C(n) a function weakly dependent on n

K a constant in the power law shear stress/shear rate relationship and

S the rotor speed.

The slope of the plot of log M vs log S gives the power law index 'n'.

Fig.3.3 shows the plot of log M vs log S for various compositions of the blend. The family of straight lines obtained is parallel showing that the power law indices for the parent polymers and their blends are more or less the same.

The parameter K in the above equation depends on temperature and often has an Arrhenius type dependence ascribed to it such as,

$$K = k_o \exp(E_a/RT) \tag{3.4}$$

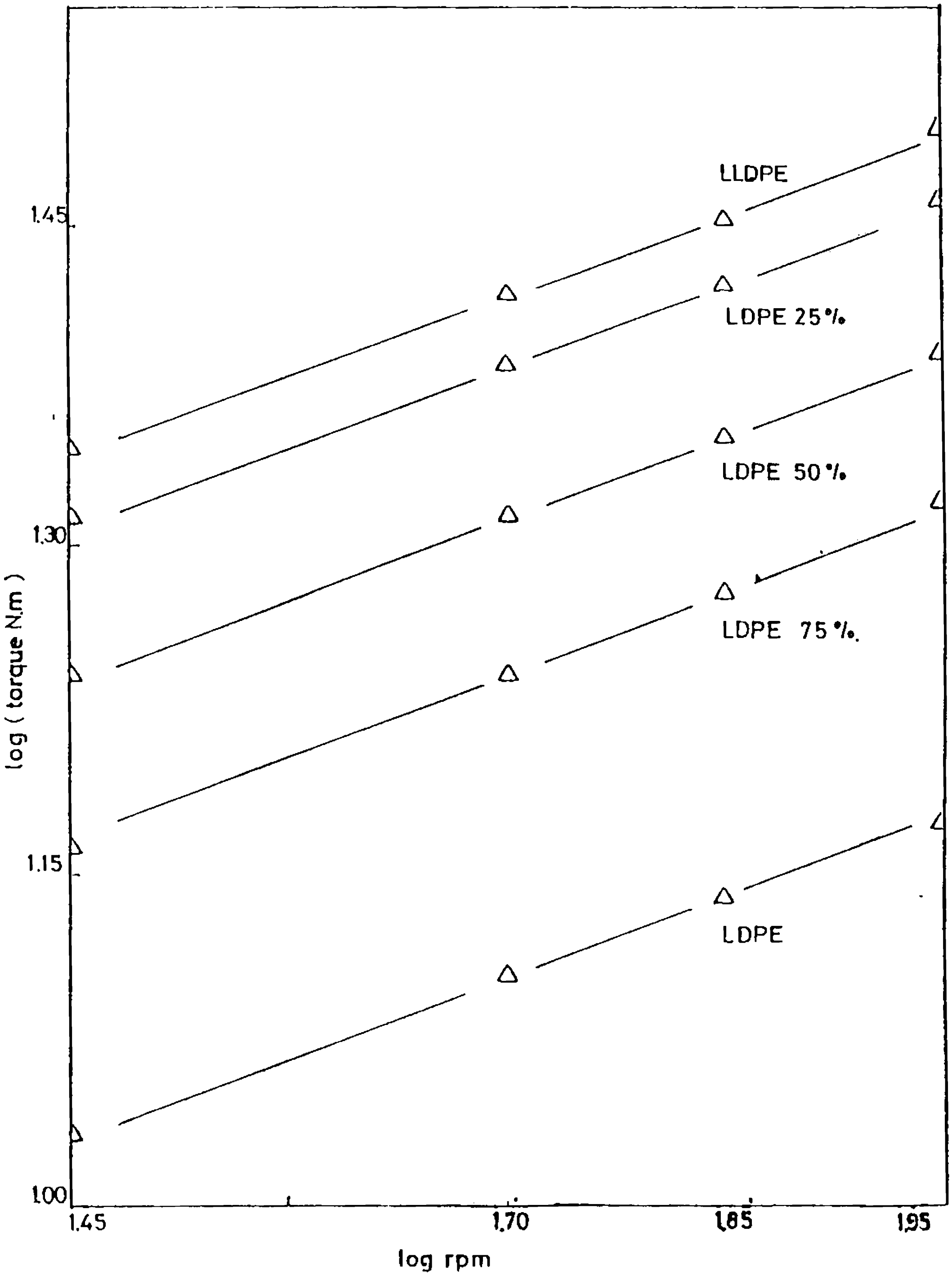


Fig.3.3: Shear dependence of torque values for LDPE/LLDPE blends

where, E_a is the flow activation energy

R the gas constant and

k_o a coefficient.

The slope of the plot of log torque vs the reciprocal of absolute temperature is proportional to an apparent energy of activation for viscous flow.[25] The linear plots shown in Fig.3.4 confirm Arrhenius type behaviour. The increase in flow activation energy with increase in LLDPE content may be observed from the progressive increase in the slope of the lines with increase in composition of LLDPE. This is in conformity with an earlier observation that blends rich in LLDPE require higher energy for processing.

Yet another way of calculating the energy required to plasticise a polymer for a period of time at a given temperature is to calculate the area under the torque-time curve at a preset temperature for the specified period of time. The energy W may be calculated using the formula at a given temperature and shear rate,[26]

$$W = 2\pi n \int_{t_1}^{t_2} M.dt \qquad (3.5)$$

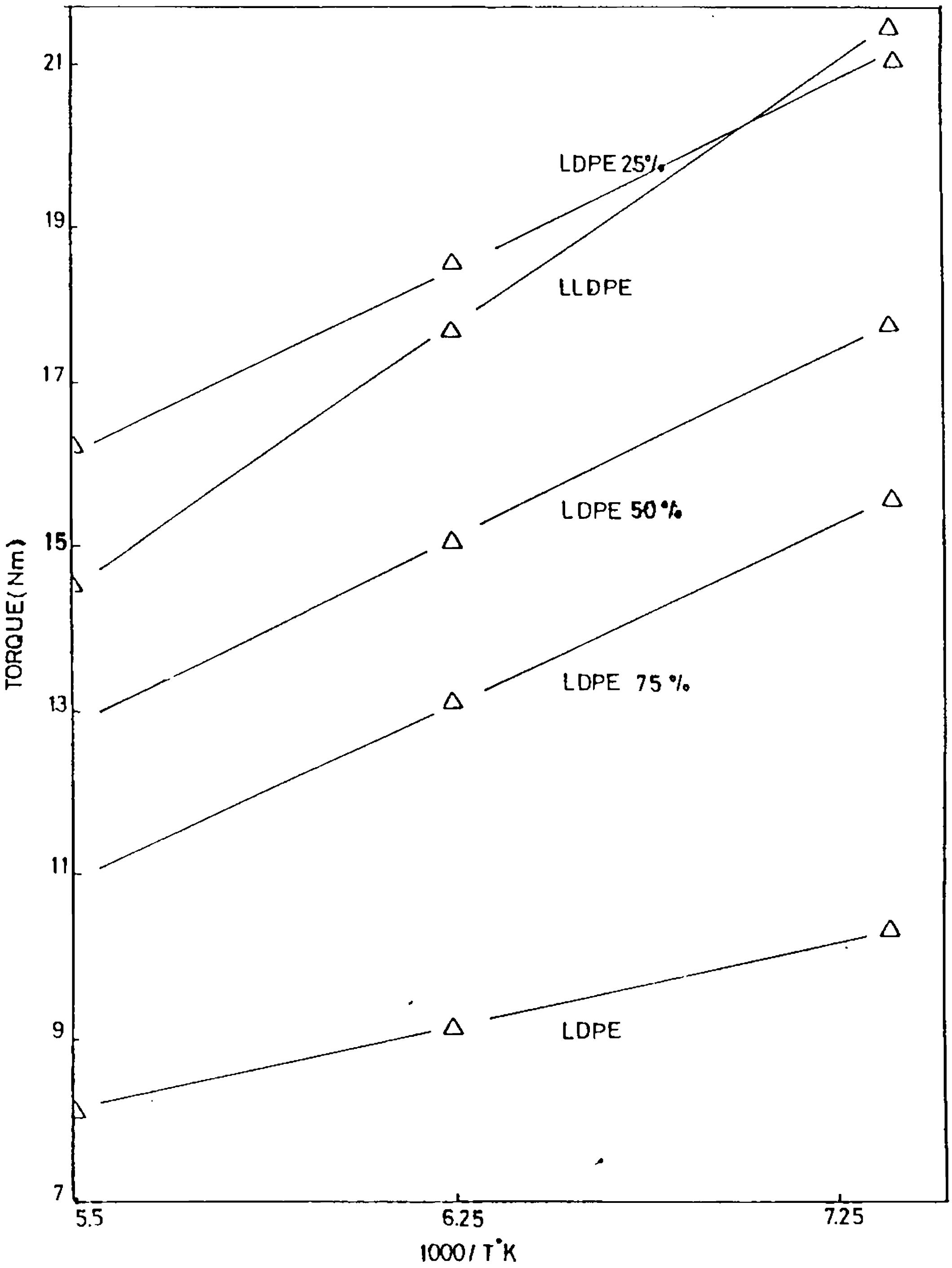


Fig.3.4: Temperature dependence of torque values for LDPE/LLDPE blends

where, n is the number of revolutions of the rotor(min^{-1})

t_1 the initial time

t_2 the final time and

M the torque in Nm

The values calculated for the pure polymers and blends for 15 minutes run on the plasticorder at 140°C are shown in Table 3.1.

Table 3.1: Dependence of energy required for plasticisation with blend composition

Property	Blend composition (% LDPE)				
	0	25	50	75	100
Energy required for plasticisation (kJ)	92	86	66	60	46

Conclusions

1. The study shows that by proper selection of LDPE and LLDPE grades a very useful blend system could be developed.

2. The blends provide a range of properties intermediate between those of the pure polymers.

3. The torque required to process the blend increases progressively with increase in composition of LLDPE.

4. The blends may be used to produce films with improved properties under conventional LDPE processing conditions.

II. RHEOLOGICAL EVALUATION OF BLENDS OF LDPE AND LLDPE USING A CAPILLARY RHEOMETER

Blend Preparation

The blends were prepared by melt mixing in a Brabender plasticorder model PL 3S at 160°C and 30 rpm for about 20 minutes. The pure polymers were also subjected to the same procedure in order to make the data comparable to those of the blends. The investigated compositions were 0, 20, 40, 60, 80 and 100 weight per cent respectively of LLDPE.

Rheological Investigation

A complete rheological investigation was performed on each blend with the aid of a capillary rheometer (Göttfert Viscotester model 1500) over a wide range of shear rates (25 to 1500 S^{-1}) at 160, 180 and 200°C. Three different capillaries were used in order to evaluate the entrance and exit effects. The diameter was always 1 mm and the length to diameter ratios were 10, 20 and 30 mm.

Results and Discussion

Flow curves

From volumetric flow rates at various applied pressures, values of apparent shear stress at wall, $(\tau_w)_{app}$, and apparent shear rate $(\dot{\gamma}_w)_{app}$ were calculated using the following expression.[27]

$$(\tau_w)_{app} = \frac{\Delta P}{2.L/R} \qquad (3.6)$$

$$(\dot{\gamma}_w)_{app} = \frac{4Q}{\pi R^3} \qquad (3.7)$$

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

From the log $(\tau_w)_{app}$ vs log $(\dot{\gamma}_w)_{app}$ plots (shown Fig.3.5) values of power law exponent n were calculated in accordance with the following power law:

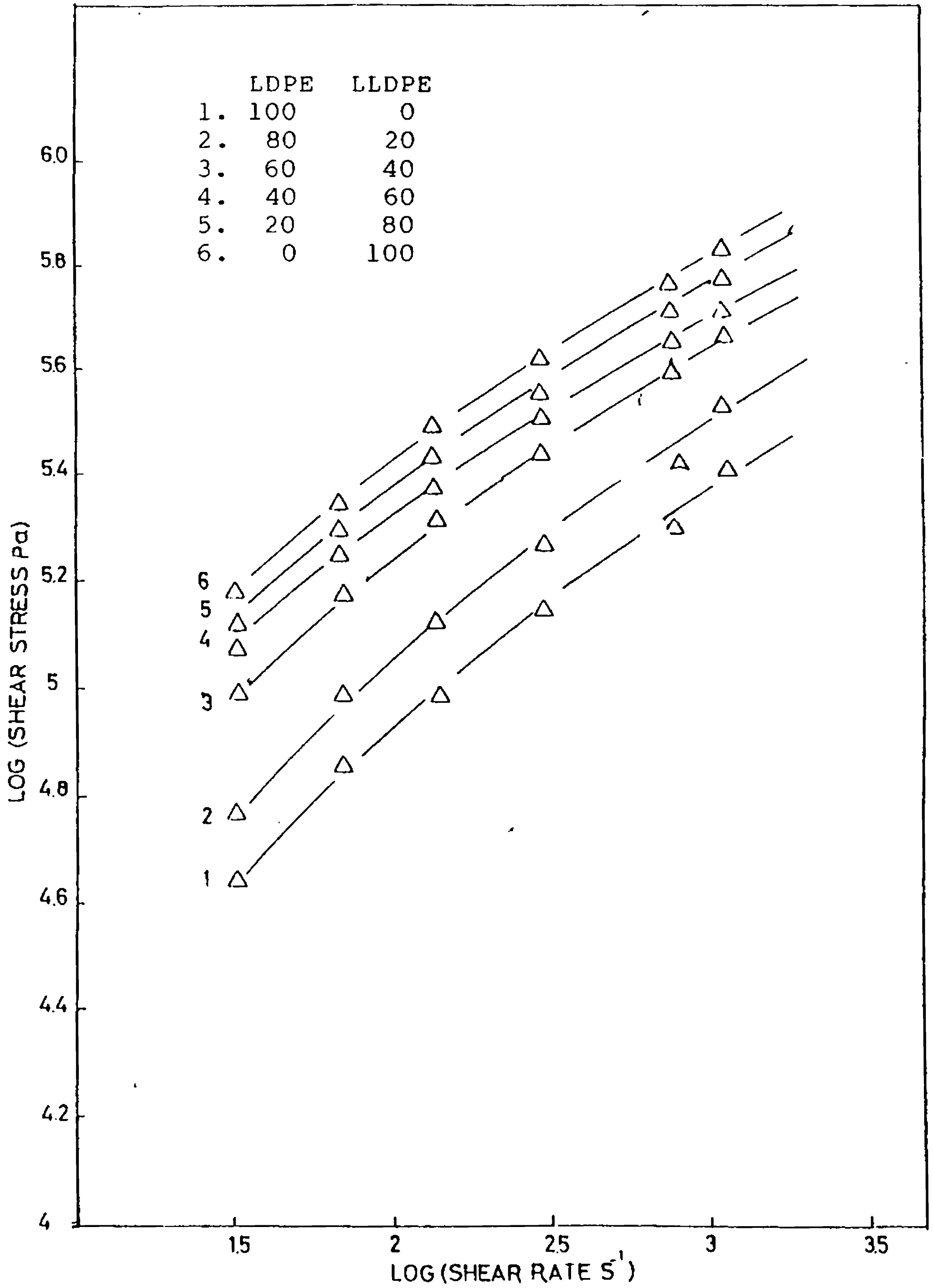


Fig.3.5: Apparent shear stress as a function of apparent shear rate for LDPE/LLDPE blends at 180°C

$$(\tau_w)_{app} = K(\dot{\gamma}_{w_{app}})^n \qquad (3.8)$$

where K is a constant. Values of n, shown in Table 3.2, are much smaller than unity, implying a strong pseudoplastic character of the melt of these binary blends. It can also be seen that the flow behaviour of the blends does not reflect the large differences in the viscosity of the individual components.

Table 3.2: Values of power law exponent for LDPE/LLDPE blends

Shear rate (S^{-1})	3×10^2					
LLDPE content (wt.%)	0	20	40	60	80	100
n [eq.(3.8)]	0.44	0.47	0.49	0.42	0.42	0.41
n' [eq.(3.11)]	0.36	0.38	0.34	0.32	0.32	0.31

Rabinowitsch correction was applied using values of n determined from eq.(3.8), to obtain true shear rate $\dot{\gamma}_w$ according to the following expression.[27]

$$\dot{\gamma}_w = [(3n+1)/4n]\dot{\gamma}_{w_{app}} \qquad (3.9)$$

Similarly, true shear stress at wall τ_w was calculated by applying Bagley correction according to the following expression.[27]

$$\tau_w = \frac{\Delta P - P_c}{2.L/R} \qquad (3.10)$$

where the Bagley correction factor P_c was evaluated from the flow data recorded with three different dies of L/R varying from 20 to 60. Bagley plots, ΔP as a function of L/R for LDPE/LLDPE blend at various compositions, are quite linear as shown in Fig.3.6. This linearity of Bagley plot confirms the absence of slippage at the capillary wall and at the interface boundaries where the slippage is believed[28] to cause curvature in Bagley plot.

Variation of ΔP with log $\dot{\gamma}_w$, shown in Fig.3.7 is quite linear over the entire range of measurements for the blend at various compositions as well as the blend components. The slope of the lines increases gradually with increase in LLDPE content, at relatively low rates of shear and rapidly at relatively high rates of shear. Increase of slope implies greater difficulty to flow or higher viscosity, due to the occurrence of elongational flow. The observed increase of slope with the increase

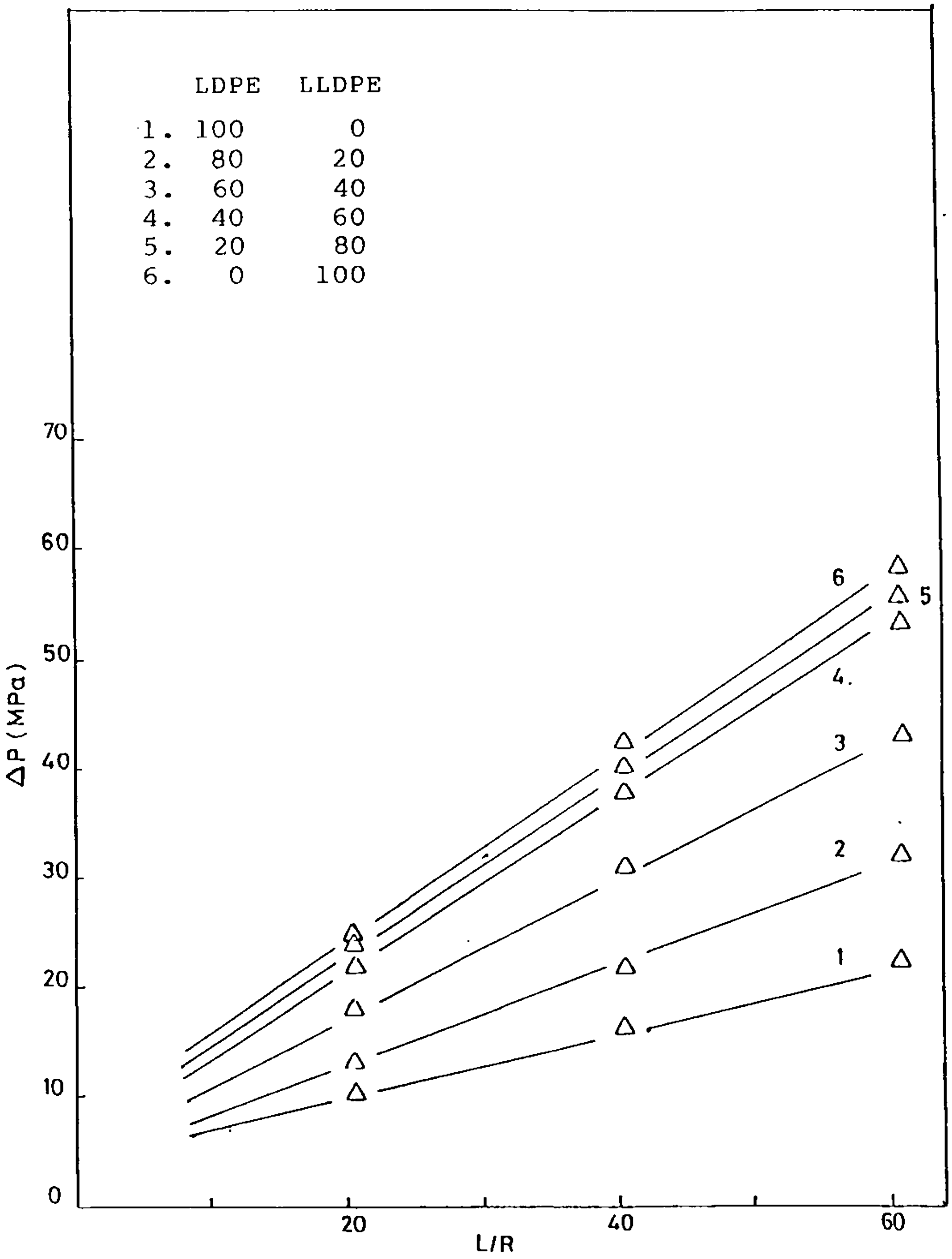


Fig.3.6: Variation of pressure drop ΔP with L/R ratio of the capillary for LDPE/LLDPE blends at a fixed shear rate (10^2 s^{-1})

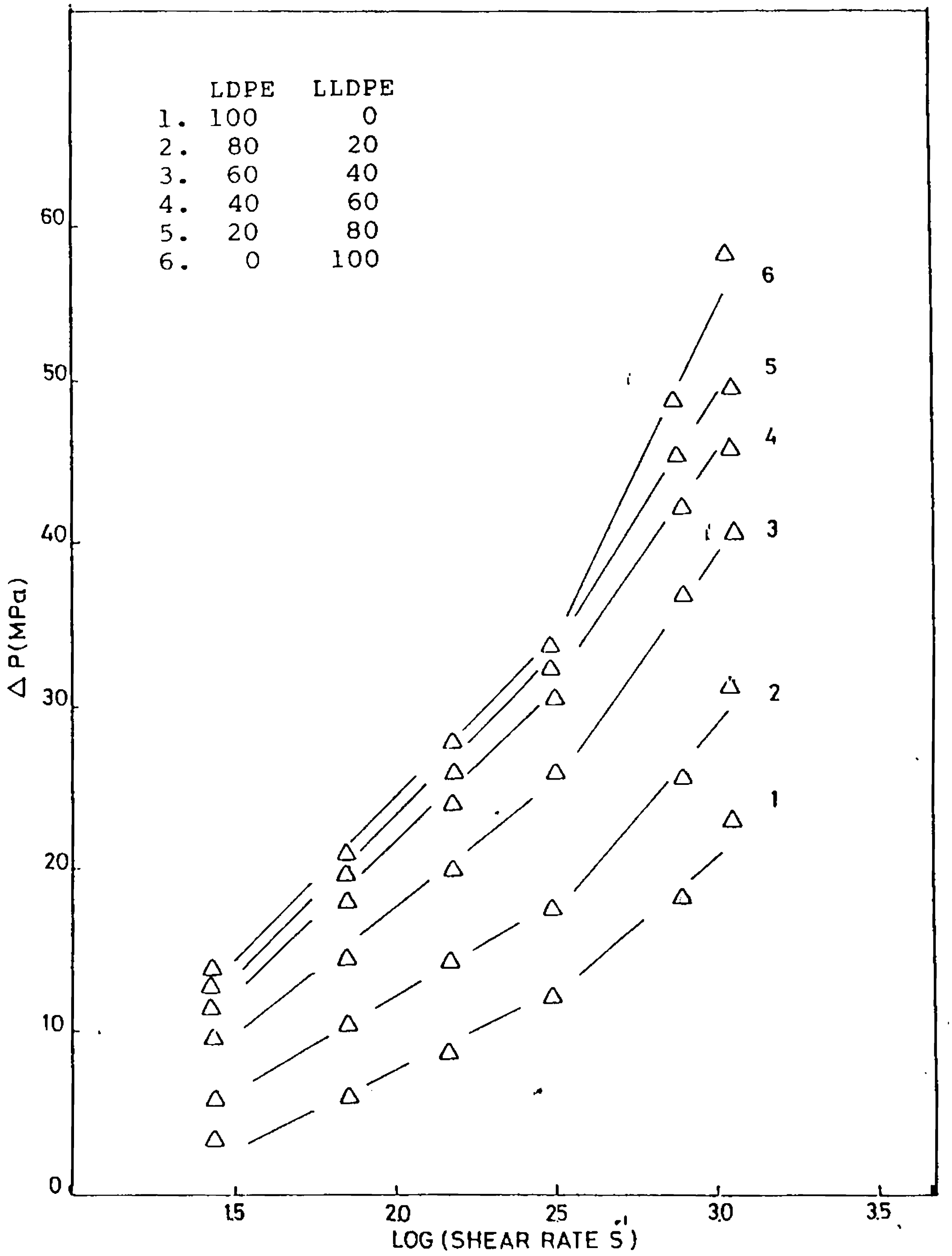


Fig.3.7: Variation of pressure drop ΔP with shear rate at 180°C (L/R = 60) for LDPE/LLDPE blends

of shear rate supports this view, since the elongational flow predominates at higher shear rates. The two step variation of slope in the case of the blends might correspond to the onset of elongational flow of the two components (LDPE and LLDPE) of the blend.

Variation of ΔP as a function of blend composition at a constant shear rate is shown in Fig.3.8. The value of ΔP increases gradually with LLDPE content.

Flow curves in terms of corrected values of shear stress and shear rate are presented in Fig.3.9 for the LDPE/LLDPE blend at various blend compositions. Data on pure LDPE and LLDPE resins are also included in Fig.3.9 to illustrate the behaviour of the blend in comparison with its two components. Viscosity of LLDPE is higher than that of LDPE. Flow curves for the blend at various compositions lie in between the flow curves of LDPE and LLDPE.

Variation of melt viscosity with blend composition at various shear rates (Fig.3.10) shows a

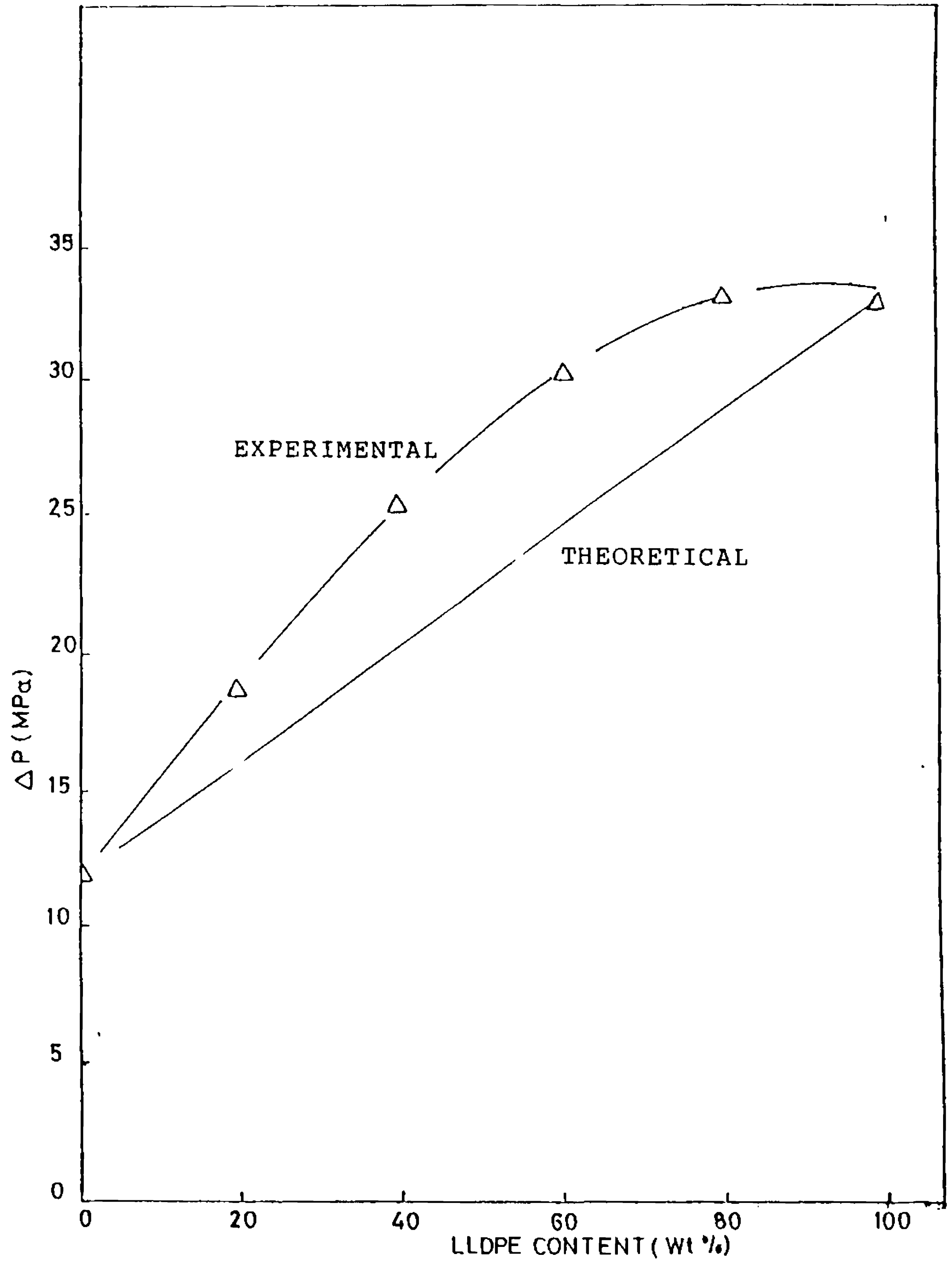


Fig.3.8: Variation of pressure drop ΔP with blend composition of LDPE/LLDPE blends at 180°C, (L/R = 60) and shear rate 10^2 S^{-1}

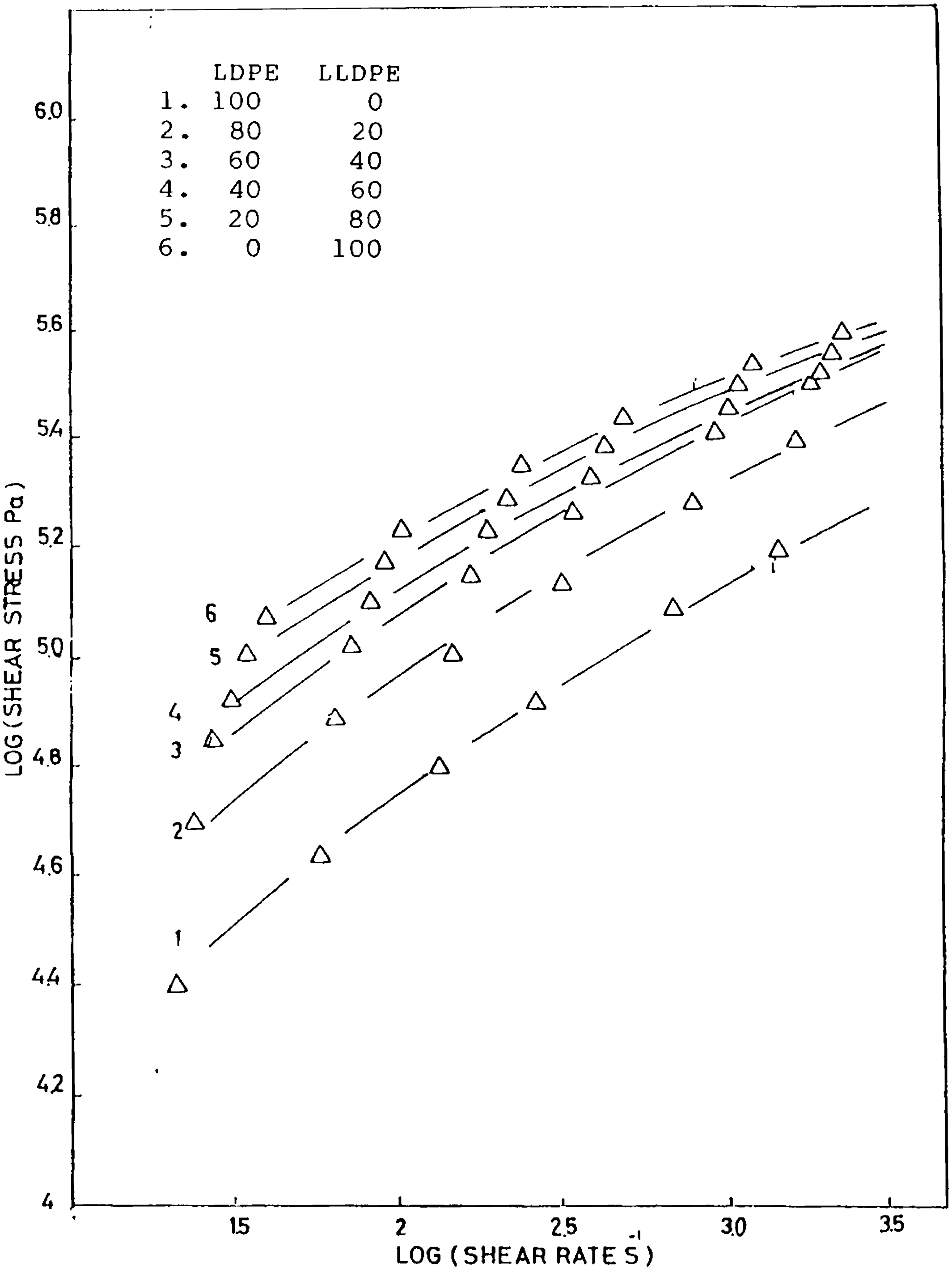


Fig.3.9: Flow curves in terms of shear stress as a function of shear rate of LDPE/LLDPE blends at 180°C

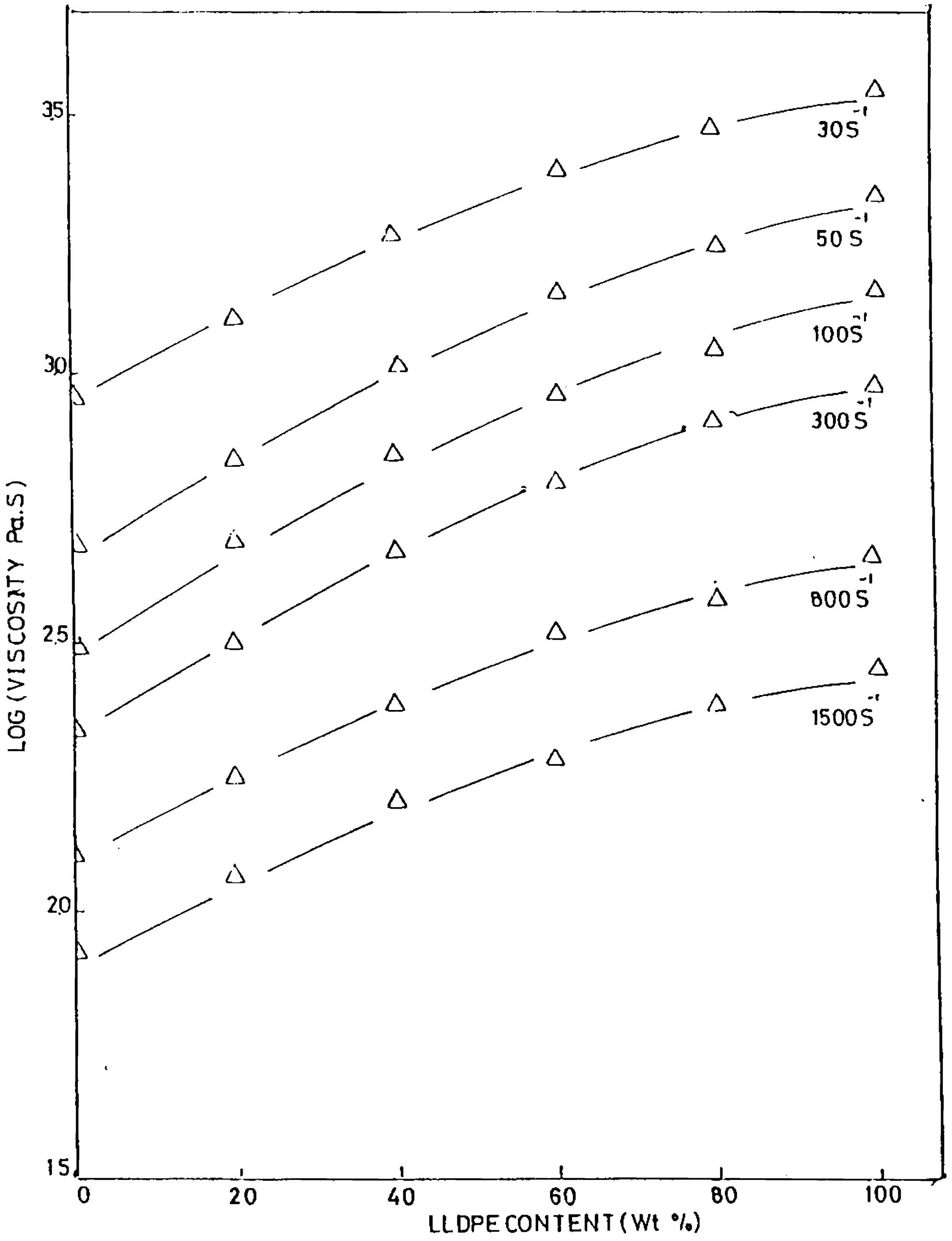


Fig.3.10: Variation of melt viscosity with blend composition at 180°C for LDPE/LLDPE blends

'positive deviation' with respect to linear extrapolation between LDPE and LLDPE extremes. This indicates stronger interface interaction in accordance with Utracki's[29] definition of a positive deviation blend.

The power law fitting these flow curves (Fig.3.9) may be written as follows:

$$\tau_w = K(\dot{\gamma}_w)^{n'} \tag{3.11}$$

where K' and n' are used to distinguish them from K and n of eq.(3.8). These corrected values of power law exponent n' shown in Table 3.2 are slightly smaller than the values of n corresponding to eq.(3.8). Furthermore the flow behaviour of blends does not reflect large differences in the viscosity of the individual components.

Melt viscosity

Melt viscosity data of the blend at various compositions are presented in Figs.3.11 and 3.12 as the variations of melt viscosity ($\eta = \tau_w/\dot{\gamma}_w$) with shear rate and shear stress. At any given shear rate or shear stress melt viscosity is lowest for LDPE and increases

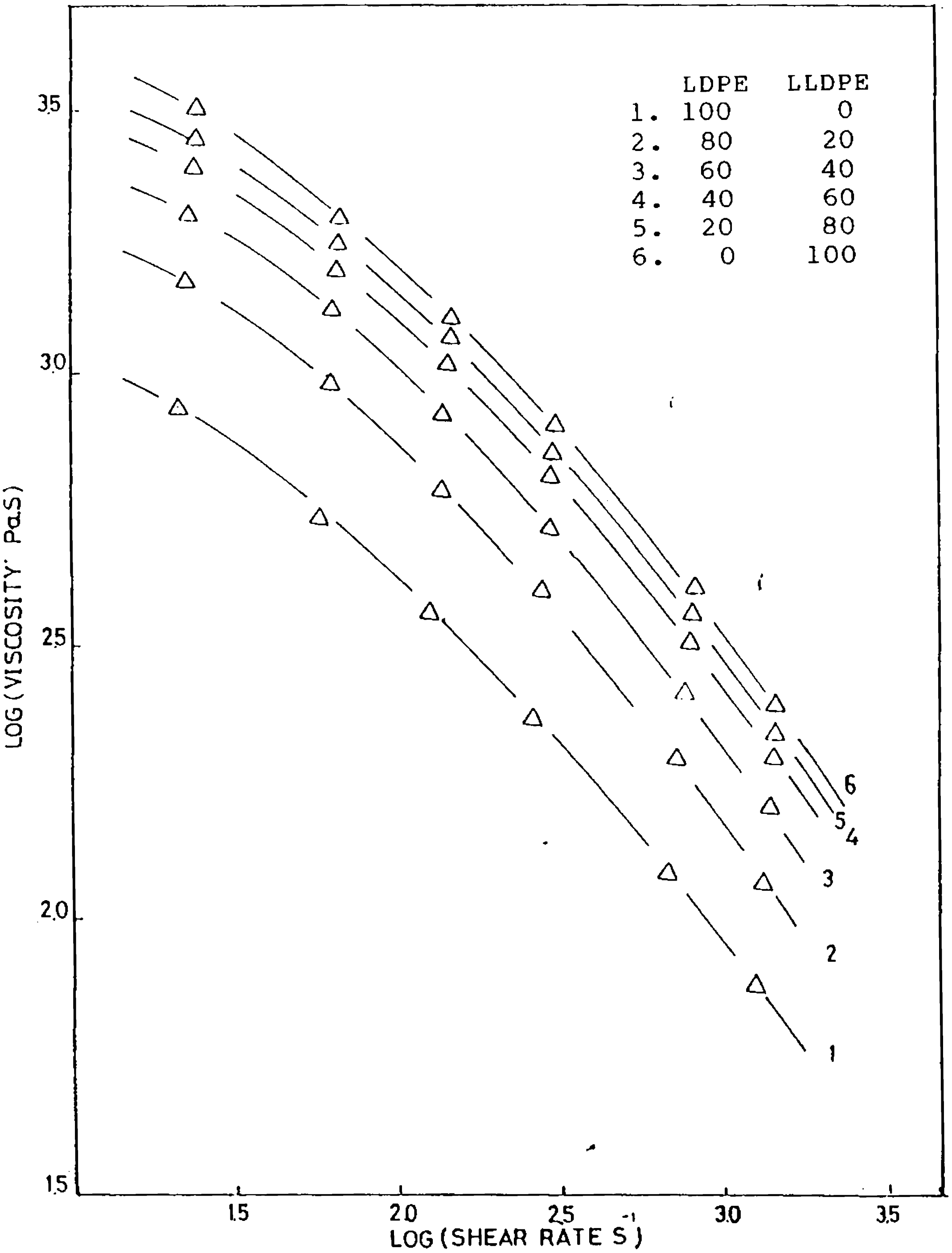


Fig.3.11: Variation of melt viscosity with shear rate at 180°C for LDPE/LLDPE blends

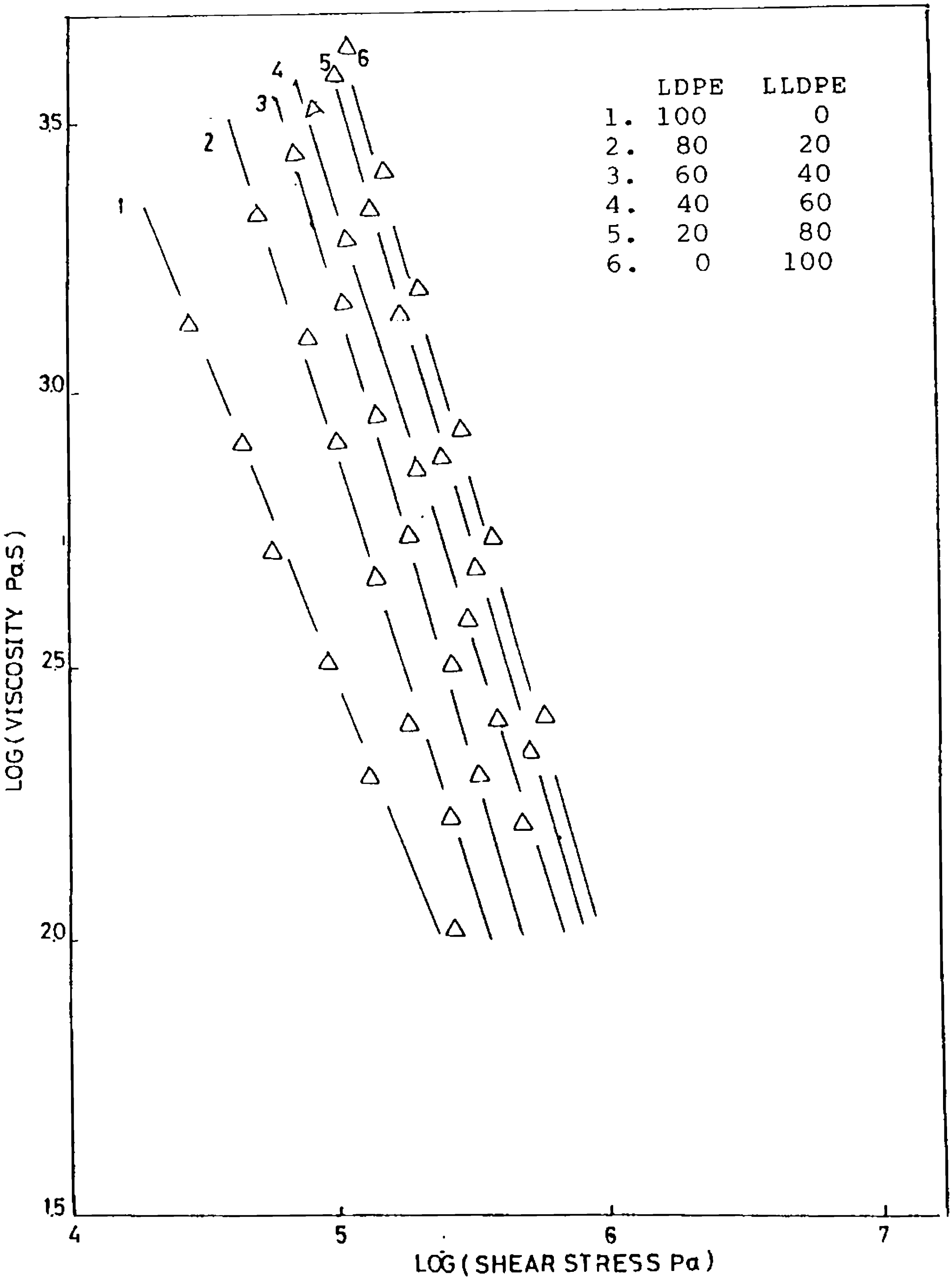


Fig.3.12: Variation of melt viscosity with shear stress at 180°C for LDPE/LLDPE blends

smoothly with LLDPE content. Decrease of melt viscosity with increasing shear stress is linear for all the compositions of the blend. These linear variations are consistent with the following power law relationships:

$$\eta = A \tau_w^{a} \tag{3.12}$$

$$\eta = B \dot{\gamma}_w^{b} \tag{3.13}$$

Activation energy for viscous flow

Variation of viscosity with reciprocal of absolute temperature for the blend at various compositions and a fixed shear rate (10^2 s^{-1}) is shown in Fig.3.13. The slope of the lines is proportional to an apparent energy of activation for viscous flow. The family of straight lines is parallel for all compositions of the blend indicating that the activation energy is more or less the same.

Elastic Parameters

Bagley correction factor P_c

Variation of Bagley correction factor P_c, as a function of blend composition at various shear rates is shown in Fig.3.14. P_c value increases with increasing

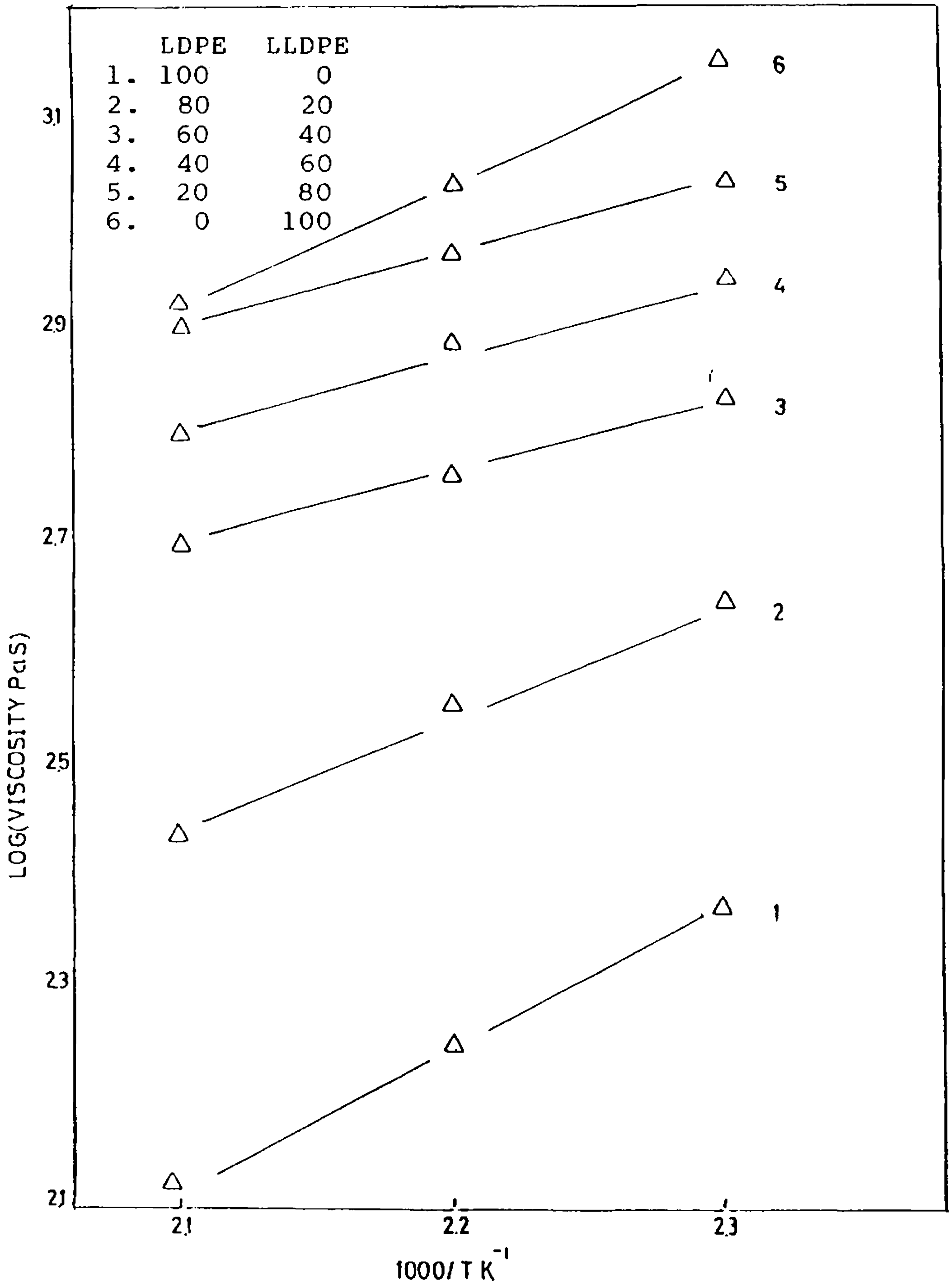


Fig.3.13: Variation of melt viscosity with reciprocal absolute temperature of LDPE/LLDPE blends at a fixed shear rate (10^2 S^{-1})

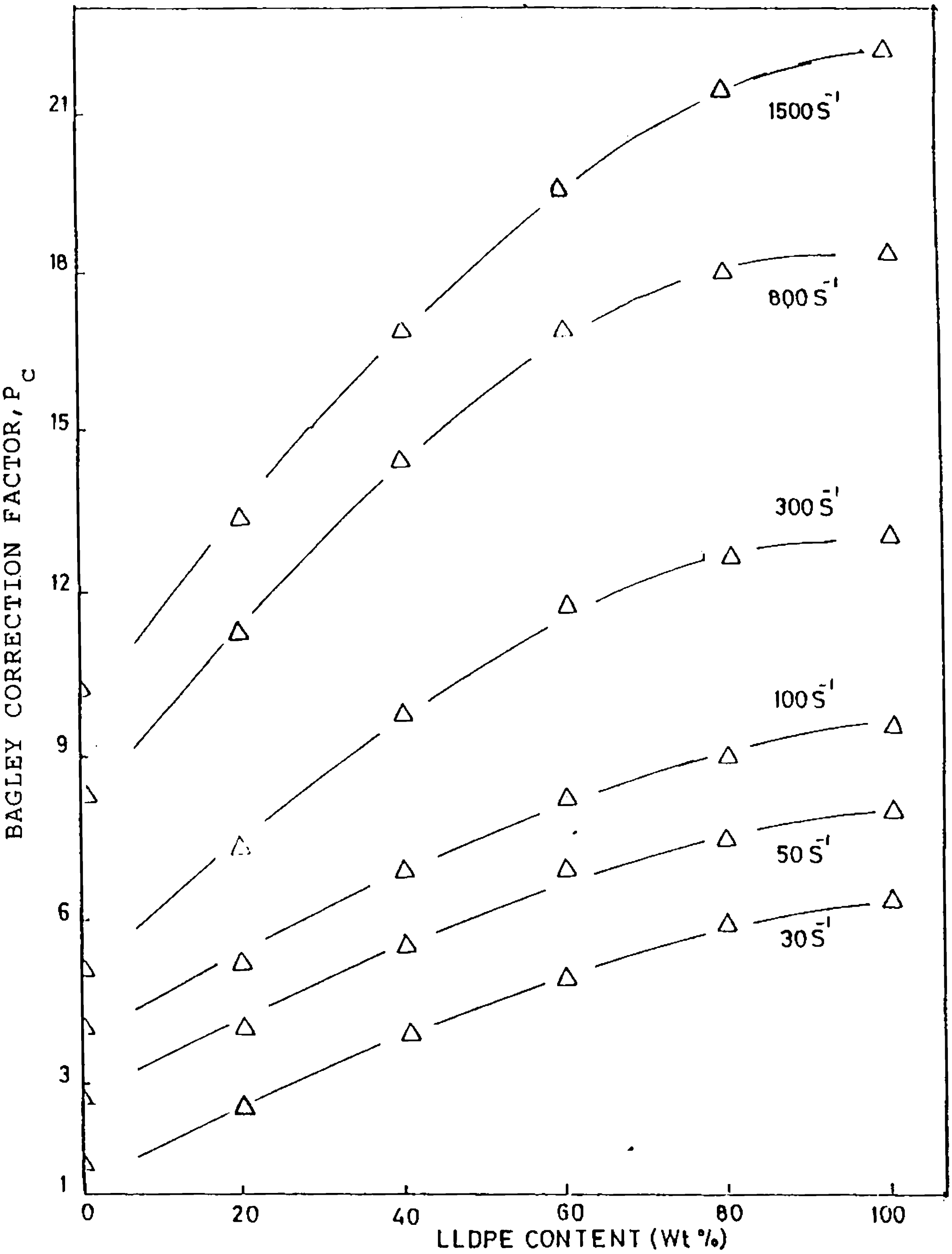


Fig.3.14: Variation of Bagley correction factor P_c as a function of blend composition at various shear rates

shear rates at all compositions of the blend. At relatively low rates of shear, P_c value increases gradually with increase in LLDPE content and rapidly at relatively high shears. This effect may be attributed to the fact that at high shear rates, the normal stresses built up in the polymer by flow exceed the shear stresses by a larger order of magnitude and cause losses of pressure at the inlets and outlets of the capillaries and in extreme cases melt fracture and other mostly undesirable flow phenomena.

Melt elasticity

Elasticity of the melt results in expansion of the polymer fluid on its exit from the die. The extrudate swell ratio D_e/D, where D_e and D are diameters of the extrudate and the die, respectively, is a direct measure of melt elasticity. As a function of blend composition, extrudate swell(B)is shown in Fig.3.15. All the blends show larger B values than those of the constituent polymers. Bogue and White[30,31] suggested use of the parameter recoverable shear strain, γ_R, for describing and distinguishing the fluid elasticity of different viscoelastic fluids as a function of shear stress. γ_R was calculated from the expression,[32]

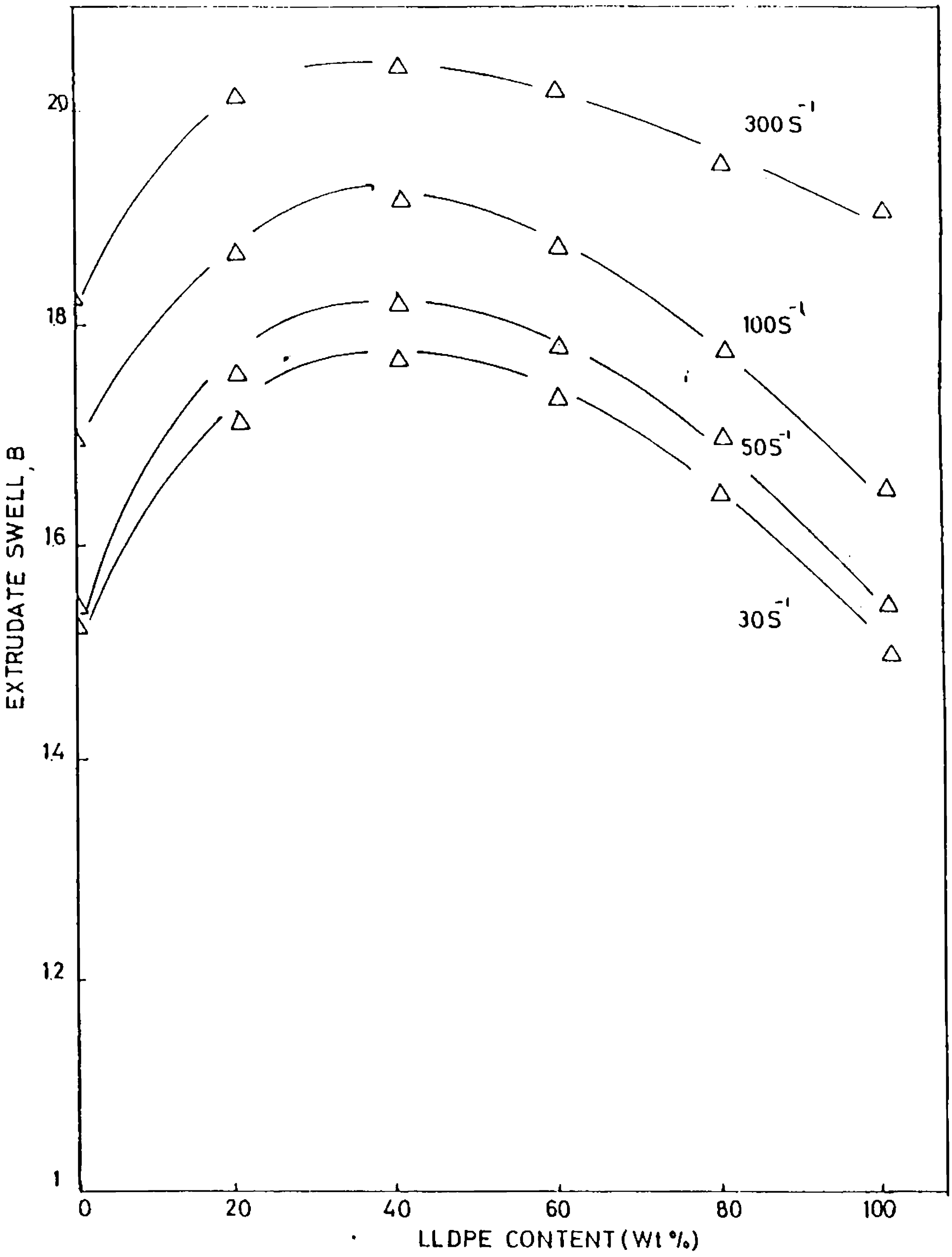


Fig.3.15: Variation of extrudate swell (B) with blend composition of LDPE/LLDPE blends at 180°C, at various shear rates

$$\gamma_R = 2[(D_e/D)^6 - 2]^{\frac{1}{2}} \quad . \qquad (3.14)$$

As shown in Fig.3.16 γ_R increases with LLDPE content and then decreases at relatively low rates of shear. At high rates of shear (8×10^2 S^{-1}) γ_R increases rapidly with increase in LLDPE. Pure LLDPE has the highest value of γ_R which decreases substantially on blending with LDPE. The reduction of melt elasticity of LLDPE on blending with LDPE is a useful gain in property relevant to processing, since extrudate distortion tendency reduces with decreasing melt elasticity[33-35] thus enabling the processing at higher shear rates without loss of surface smoothness of the product.

Melt fracture

Another important feature in plastics processability is flow instability or 'melt fracture', which shows with surface roughness of the material when extruded at a certain critical output rate. Fig.3.17 illustrates the instabilities of the blends extruded at 180°C by the capillary rheometer at a shear rate of 8×10^2 S^{-1}. Melt fracture phenomena occur through mechanisms which are not satisfactorily known, although their occurrence seems to be strictly related to the elastic component of the polymer.

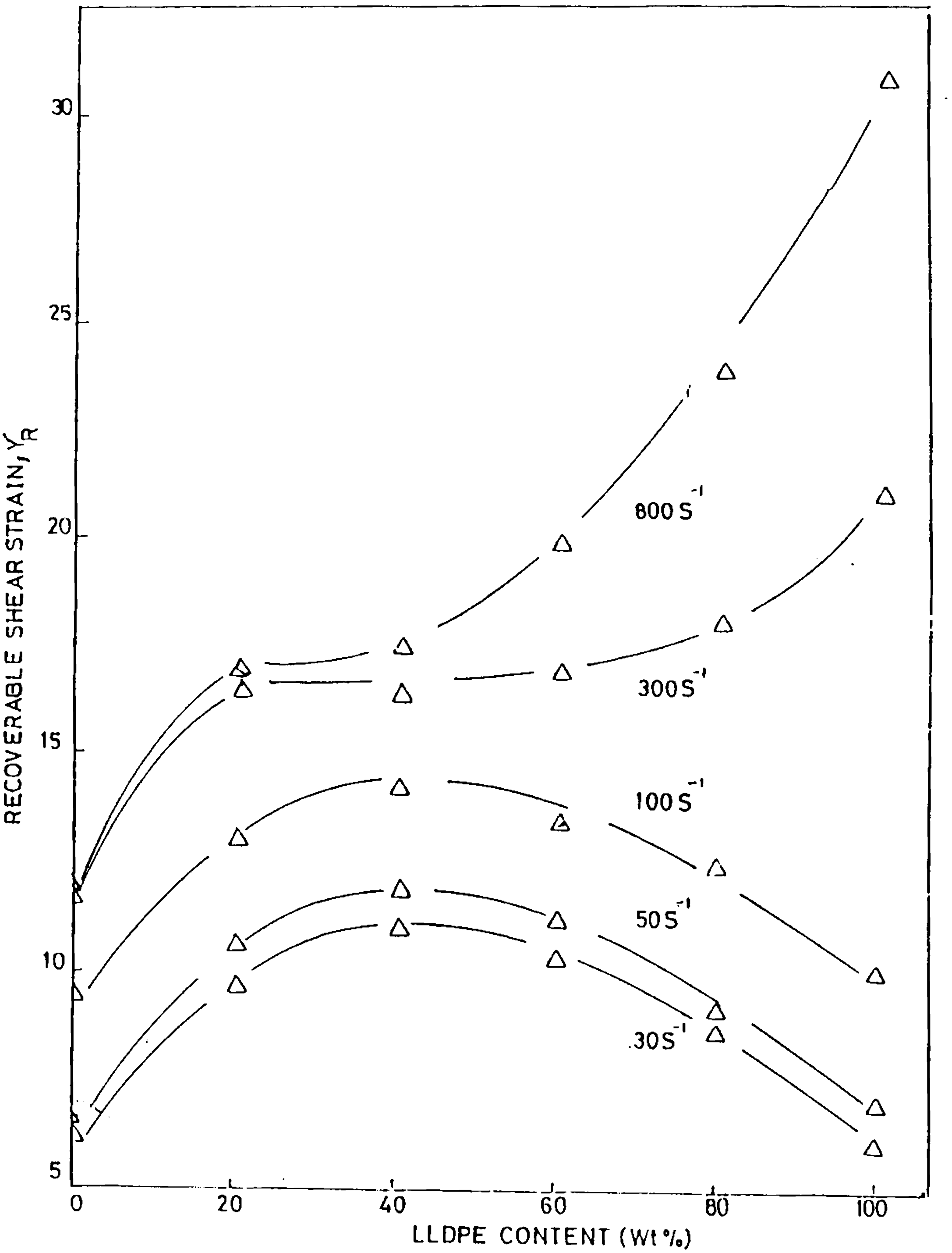
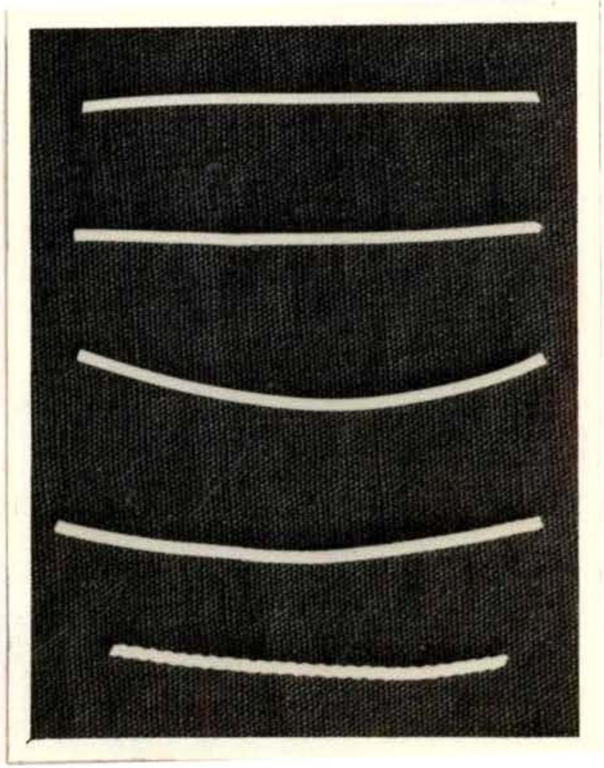


Fig.3.16: Variation of recoverable shear strain with blend composition of LDPE/LLDPE blends at 180°C, at various shear rates



Blend composition	
LDPE	LLDPE
100	0
80	20
50	50
20	80
0	100

Fig.3.17 Variation of extrudate morphology with blend composition at a shear rate of 576.0 S^{-1}

Conclusions

1. Melt viscosity of LDPE/LLDPE blends shows positive deviation from the log additivity rule indicating strong interface interaction resulting in sufficient compatibility in the melt.

2. The pseudoplasticity of the blends does not show large differences from those of the individual components.

3. The melt elasticity of LDPE/LLDPE blend decreases with the increase in composition of LDPE.

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Chapter 4

MODIFICATION OF LDPE/LLDPE BLENDS USING DICUMYL PEROXIDE

MODIFICATION OF LDPE/LLDPE BLENDS USING DICUMYL PEROXIDE

Polyethylene derives its mechanical properties from a crystalline morphology. The loss of this crystal structure with increasing temperature limits material serviceability. Crosslinking is a means of modifying the base structure of polyethylene after polymerisation. This can be accomplished either by irradiation with high energy electron beams or through the use of chemical crosslinking additives. Chemical crosslinking is accomplished by incorporating organic peroxides, such as dicumyl peroxide, into the matrix of polyethylene and subsequently activating the peroxide to connect the polymer chains into a three dimensional network. This modification in structure induces many changes in its properties. Many authors have studied these changes reporting comparable or contradictory results.[1-28]

Deviations have been attributed to the variety of PE types used and to the diversification of cross-linking processes (ie., radiation or chemical technique). The various polyethylene types are characterised by density (the magnitude depending directly on crystallinity) as well as by the melt flow index (MFI) which is a rather crude indicator of average molecular weight. These parameters are critical for the subsequent behaviour and the changes caused by crosslinking. For example a highly crystalline polyethylene sample crosslinked chemically is expected to reveal a drastic reduction of crystallinity and severe changes in properties affected by that parameter. On the other hand radiation induced crosslinking does not affect the crystalline phase of the polymer so that the changes in such a case should be of a different character.

In the present study LDPE, LLDPE and their blends have been crosslinked with dicumyl peroxide and the properties studied as a function of the gel content. This correlation is expected to give a clearer picture of the structure-property interrelations.

I. EFFECT OF CONTROLLED CROSSLINKING ON THE PHYSICAL, MECHANICAL AND RHEOLOGICAL PROPERTIES OF LDPE/LLDPE BLENDS

Blend Preparation

The blends of LDPE and LLDPE were prepared in a Brabender Plasticorder model PL 3S equipped with a mixing head of 40 cc capacity. The working conditions were 160°C, 30 rpm and 40 gm sample weight. Mixing time was kept constant at 15 minutes for the uncrosslinked blends. For crosslinked blends the mixing time varied with blend composition as shown in Fig.4.1. The samples were then moulded as plaques in a hydraulic press with heated platens. The moulding conditions varied (see Table 4.1) because the thermoplastic character of the samples varied over a wide range. The specimens for tests were cut from the plaques.

Characterisation and Testing

Gel content was determined by extraction in refluxing toluene. Small quantities of each sample (approximately 0.3 gm) were weighed and placed in a 15x15 mm envelope made of stainless steel woven mesh. The sample in the container envelope was immersed in refluxing toluene for 8 hours, washed in acetone for 5 minutes, dried under vacuum for 16 hours at 100°C, removed from the container and reweighed. The gel fraction was obtained by dividing the final sample weight by the initial sample weight. The density measurements were performed according to ASTM D 792.

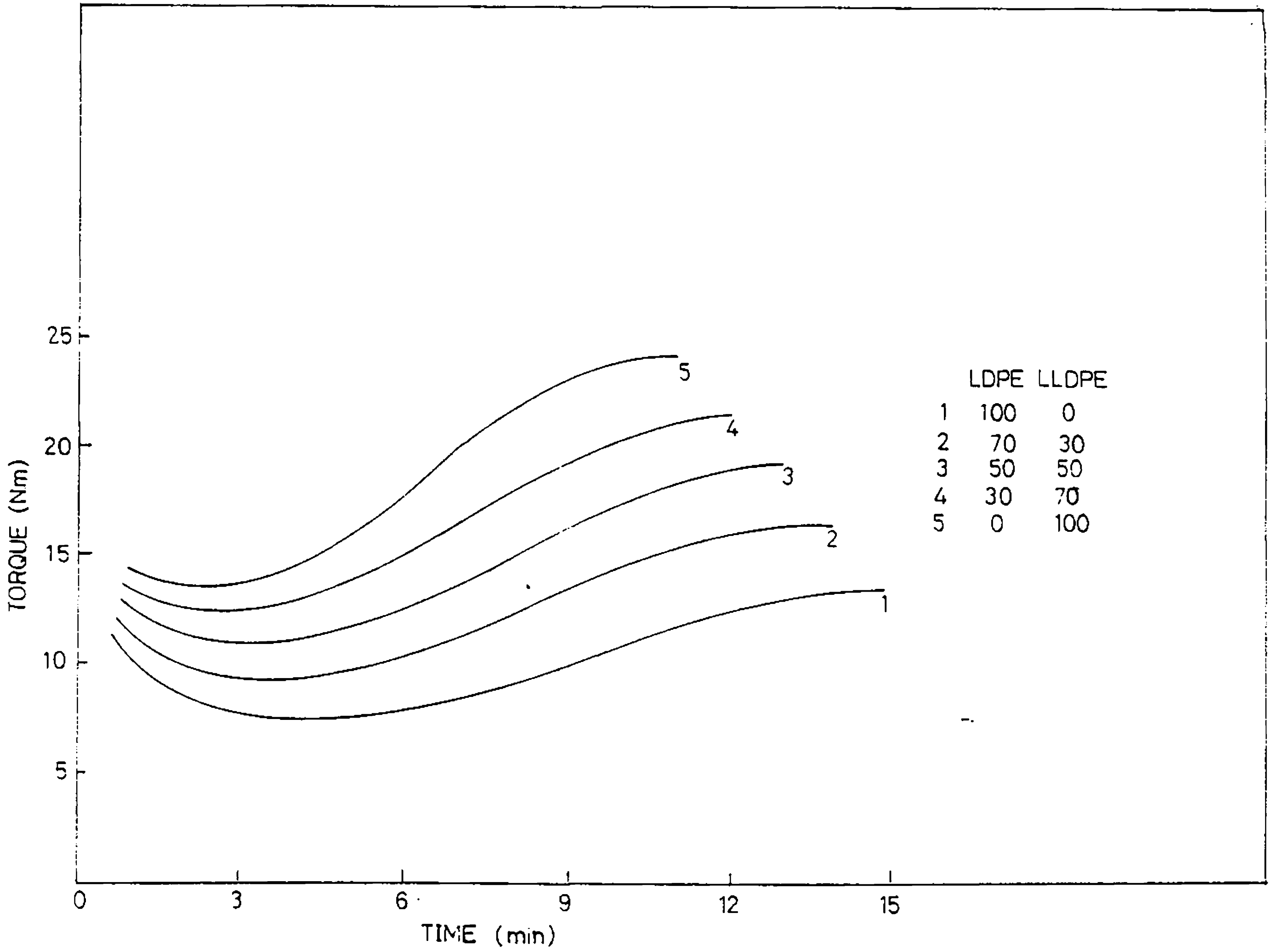

Fig.4.1: Torque as a function of mixing time of crosslinking for LDPE/LLDPE blends

Table 4.1: Moulding conditions for LDPE/LLDPE blends

Blend Composition		DCP	Temperature	Pressure	Time
LDPE	LLDPE	(phr)	(°C)	(atm.)	(min.)
100	0	0	125-130	10	10
100	0	1	145-150	40	15
70	30	0	125-130	10	10
70	30	1	155-160	45	15
50	50	0	135-140	10	10
50	50	1	175-180	50	20
30	70	0	140-150	10	10
30	70	1	185-190	50	25
0	100	0	140-150	10	10
0	100	1	195-200	50	30

Hardness was measured according to ASTM D 2240 using a Zwick Durometer of the shore D scale. The specimens were at least 3 mm thick with a surface free of scratches or other defects.

For determination of wear resistance, specimens in the form of discs (50 mm diameter and about 3 mm thick) were abraded with a Zwick abrader using a no.240 emery paper and 0.5 kg load. The mechanical properties were examined according to ASTM D 638 using a Zwick Universal testing machine model 1445 working at room temperature.

Melt rheological properties were evaluated on a capillary rheometer (Göttfert Viscotester model 1500) using a capillary die of circular cross section (length 30 mm and diameter 1 mm) over a wide range of shear rates at 160, 180 and 200°C.

Apparent shear stress and apparent shear rate at the wall was calculated using the expressions for Newtonian flow in cylindrical capillaries using the following equations:

$$\text{Apparent shear stress } \tau_{w_{app}} = \frac{\Delta PR}{2L}$$

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

where, ΔP is the pressure drop along the capillary of radius R and length L and is given by the force F per unit plunger cross sectional area. Q is the volumetric flow rate through the capillary.

Since all the experiments were performed using a capillary of fairly high L/R ratio, end effects may be quite small and hence apparent shear stress may be close to the true shear stress at the wall. The true shear rate at the wall may be calculated by correcting the expression for the apparent shear rate for the non-Newtonian character of flow. However, since the present evaluations are of a comparative nature, the apparent shear rates calculated directly from the above equation were employed.

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

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

Values of power law exponent (n) of the Ostwald de Waele model was calculated from the relation,

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

where K is constant.

The temperature dependence of viscosity, was calculated from the activation energy E_a for viscous flow using an Arrhenius type expression,

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

where, E_a is the activation energy
R is the gas constant
T the absolute temperature and
A a constant

The activation energy was calculated from plots of η versus the reciprocal of absolute temperature.

Results and Discussion

Fig.4.1 shows the value of Brabender torque as a function of mixing time of crosslinking for LDPE/LLDPE blends.

LLDPE and LLDPE rich blends undergo a faster rate of reaction and a higher degree of crosslinking. This effect may be attributed to the large number of tertiary carbon atoms in LLDPE than in LDPE.

Fig.4.2 shows the stress-strain behaviour of crosslinked and uncrosslinked LDPE/LLDPE blends. The stress-strain behaviour of the crosslinked blends closely resemble each other to those of the uncrosslinked blends (nos.2, 3 and 4). This may be due to the better compatibility of the blends resulting from the introduction of crosslinks between the chains.

Fig.4.3 shows the variation of tensile strength of the uncrosslinked and crosslinked blends with composition. All the compositions show a moderate increase in tensile strength on crosslinking while the increase is more pronounced in the case of LDPE and LDPE rich blends.

Fig.4.4 shows the variation of yield stress and elongation at break of the blends with composition. The very high elongation at break of LLDPE is due to its stable necking behaviour. The elongation at break increases for LDPE and LDPE rich blends while it

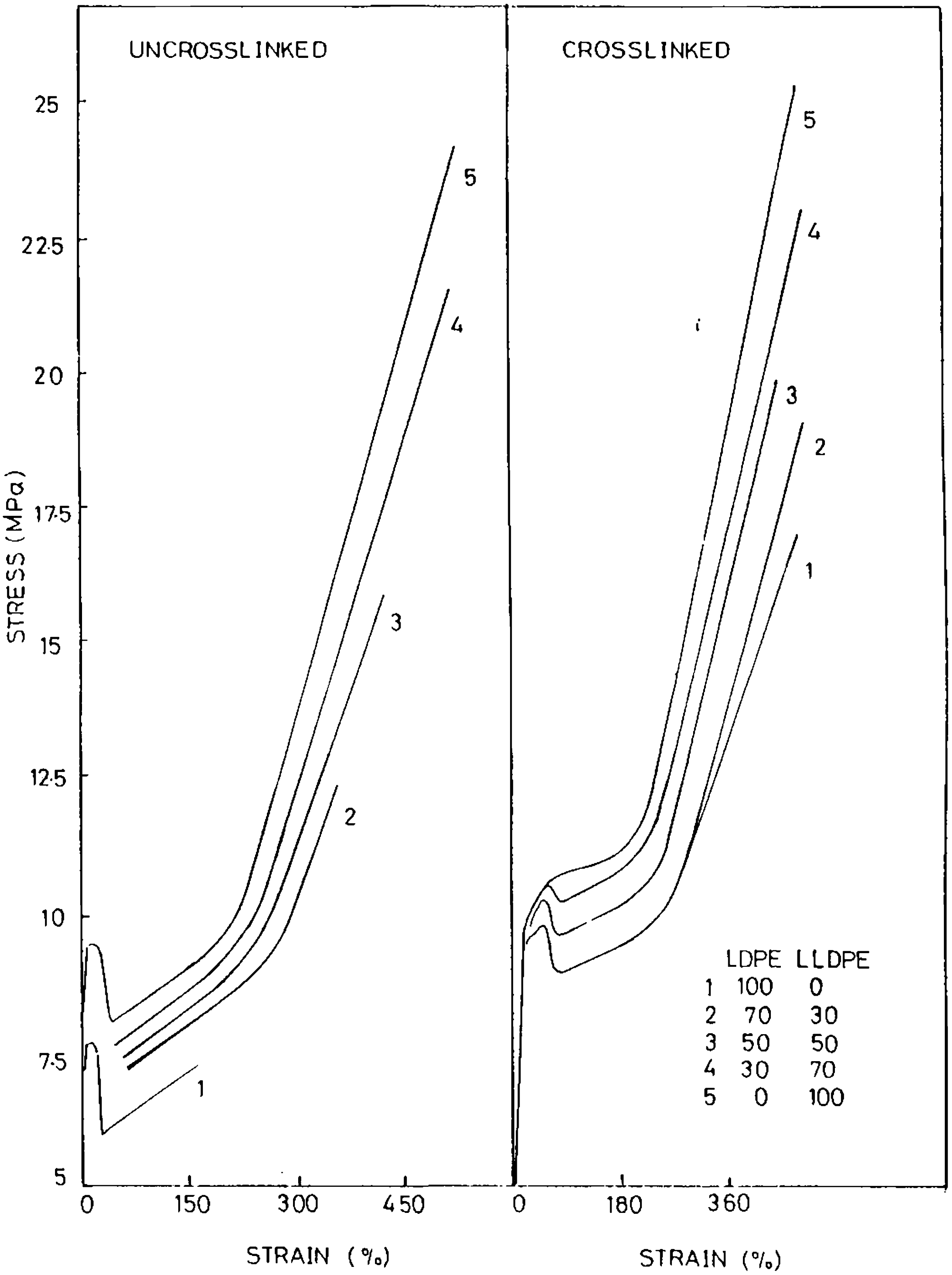

Fig.4.2: Stress-strain curves of uncrosslinked and crosslinked LDPE/LLDPE blends

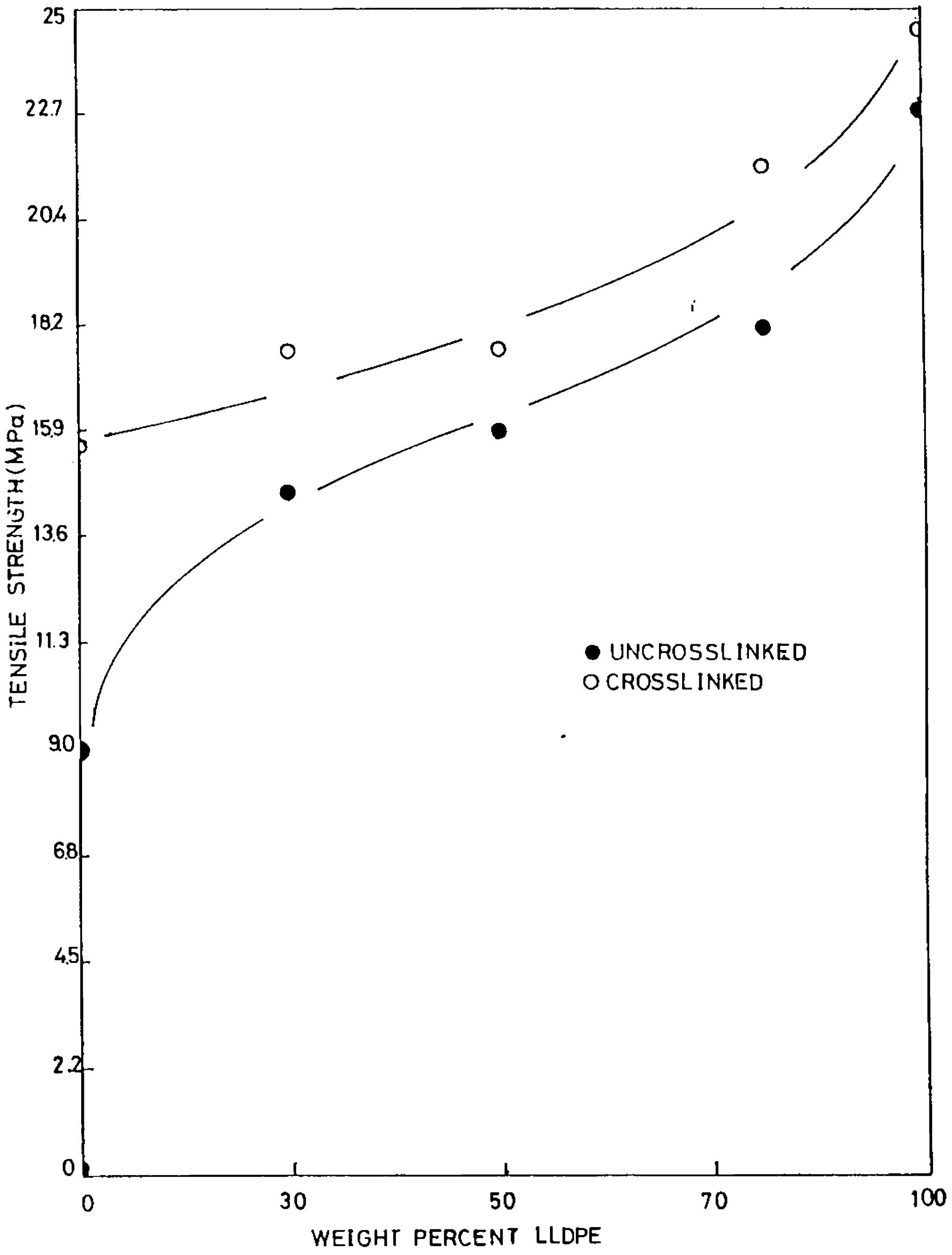

Fig.4.3: Variation of tensile strength of uncrosslinked and crosslinked LDPE/LLDPE blends with composition

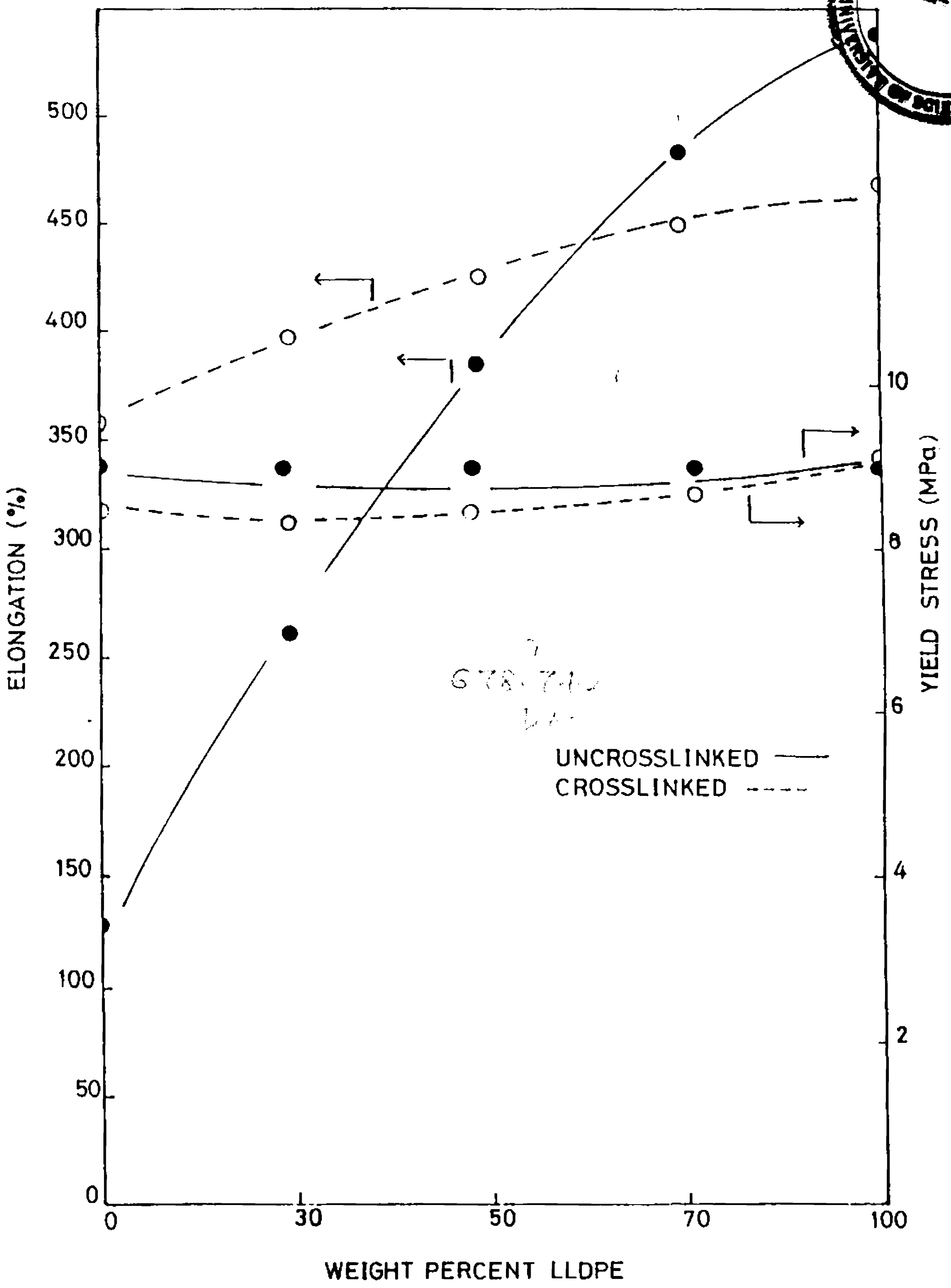

Fig.4.4: Variation of yield stress and elongation at break of uncrosslinked and crosslinked LDPE/LLDPE blends with composition

decreases for LLDPE and LLDPE rich blends on crosslinking. This may be attributed to the degree of crosslinking which is relatively low for LDPE and increases with LLDPE content. On the whole the large variation in the elongation at break is reduced to a smooth pattern from one end of the spectrum to the other. This observation may be taken to be a proof for the better compatibility of the crosslinked blends. On treatment with DCP the yield stress remains more or less the same. This indicates that the mechanical behaviour is not significantly affected on crosslinking. It is likely that crosslinking affects the inherent crystallinity and makes up for the loss in stiffness.

Fig.4.5 shows the variation of viscosity with blend composition at different shear rates. In the case of uncrosslinked blends, slight positive deviation from the logarithmic additivity rule is observed. This might indicate that the blends are fairly compatible in the melt. In the case of crosslinked blends viscosity is higher than the viscosity of the corresponding uncrosslinked blends which is obviously due to the introduction of crosslinks between the chains. The positive deviation in this case increases with LLDPE content. This is in conformity with the earlier observation that the LLDPE phase gets more crosslinked than LDPE.

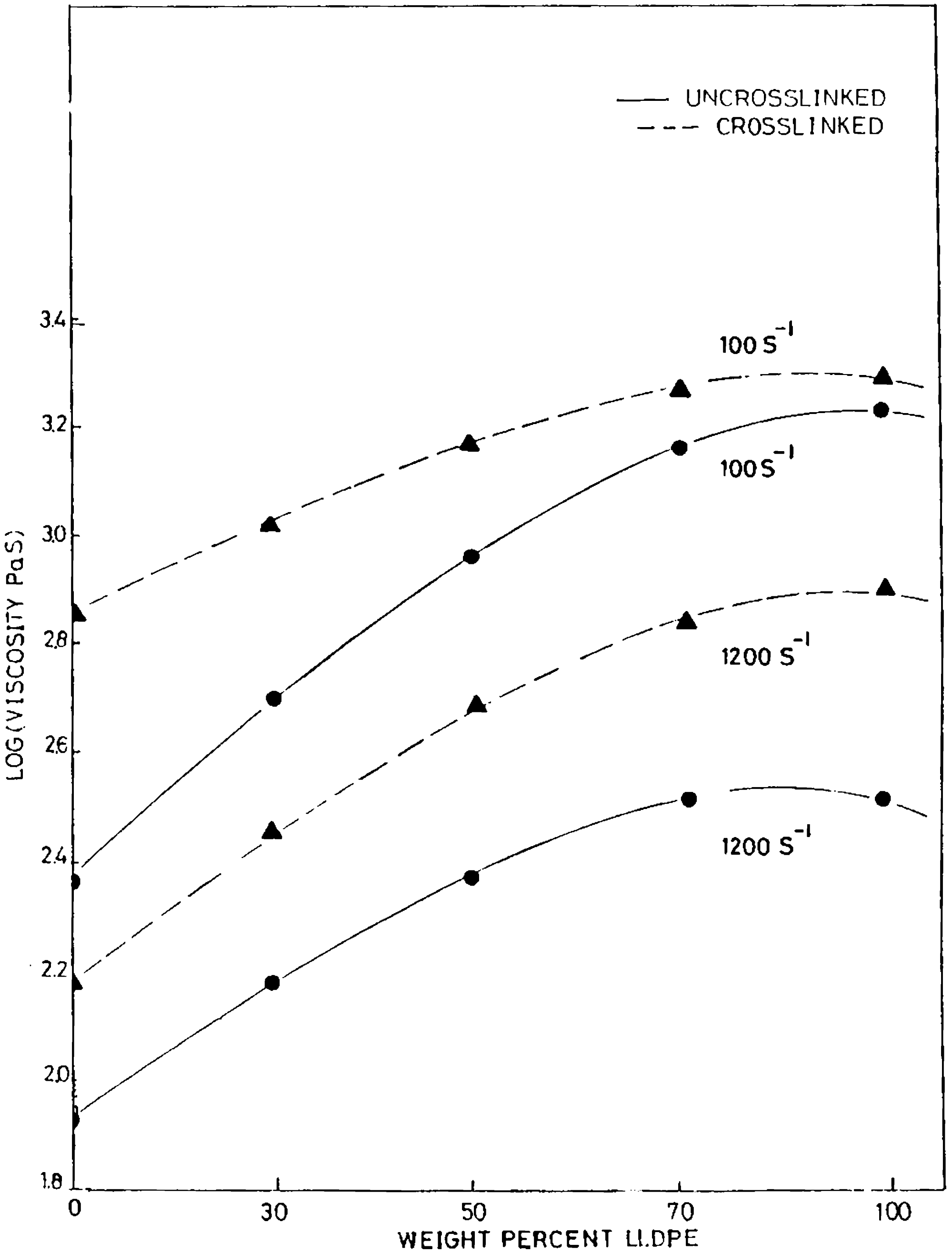

Fig.4.5: Variation of viscosity of uncrosslinked and crosslinked LDPE/LLDPE blends with composition

Figs.4.6 and 4.7 show the flow curves of the uncrosslinked and crosslinked blends. For a given shear rate, the crosslinked blends show a higher stress than the corresponding uncrosslinked blends as expected. However, the flow curves of both uncrosslinked and crosslinked blends follow the same pattern and the flow index values calculated from the curves by regression analysis are almost identical. This indicates that the non-Newtonian nature of the blends is more or less unchanged on crosslinking. The crowding of the flow curves in Fig.4.7 might indicate better compatibility of the crosslinked blends in the melt.

Figs.4.8 and 4.9 show the variation of viscosity with temperature of the uncrosslinked and crosslinked blends. The slope of these lines is proportional to an activation energy for viscous flow. The activation energy of the blends is shown in Table 4.2. As expected, the crosslinked blends show marginally higher activation energy. Activation energy gradually increases with LLDPE content on crosslinking. This again is likely to be due to the higher crosslink density in LLDPE than in LDPE.

Fig.4.10 shows the variation of gel content, the value of mixing torque and physical properties such as

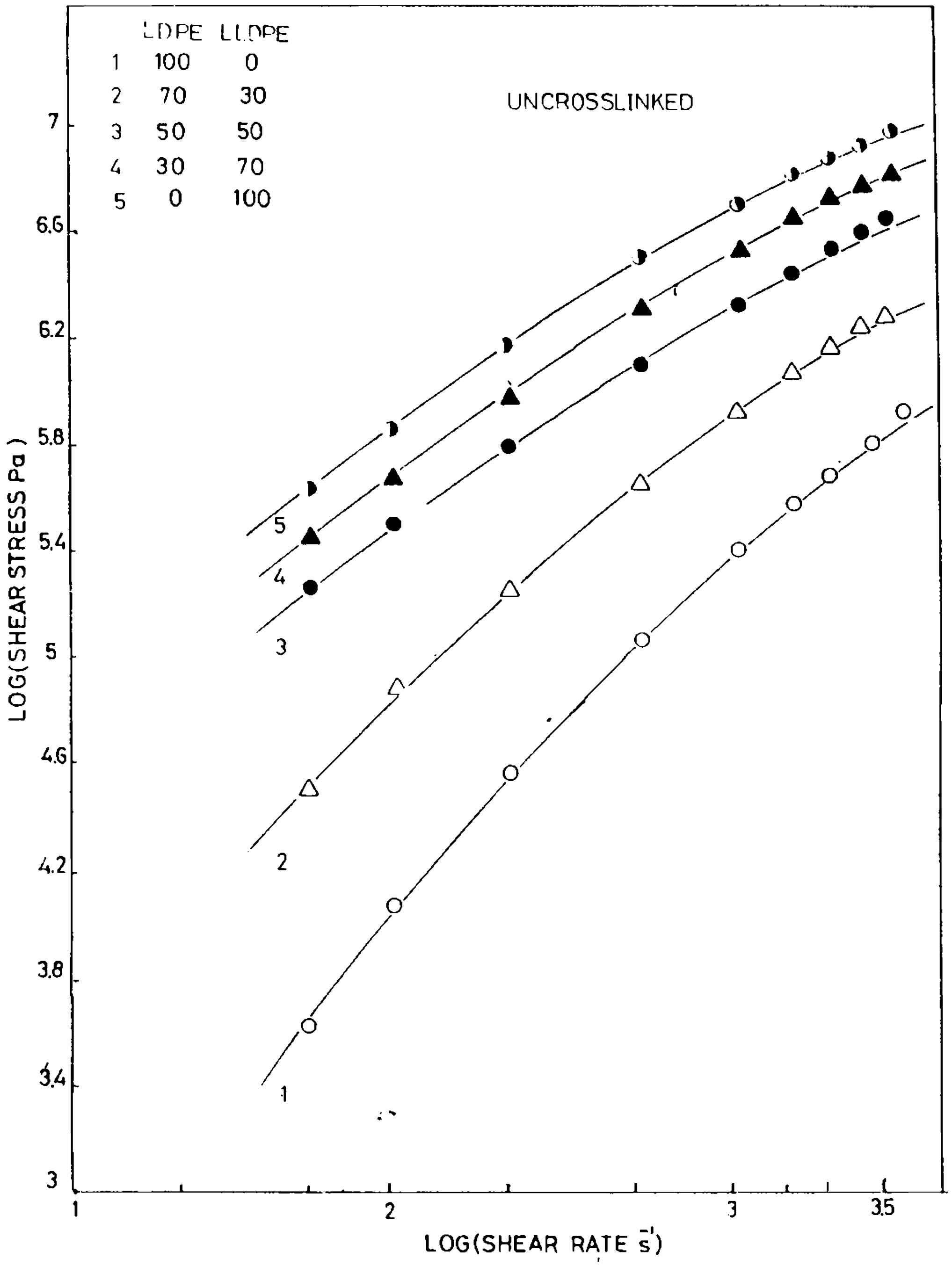

Fig.4.6: Flow curves of uncrosslinked LDPE/LLDPE blends with composition

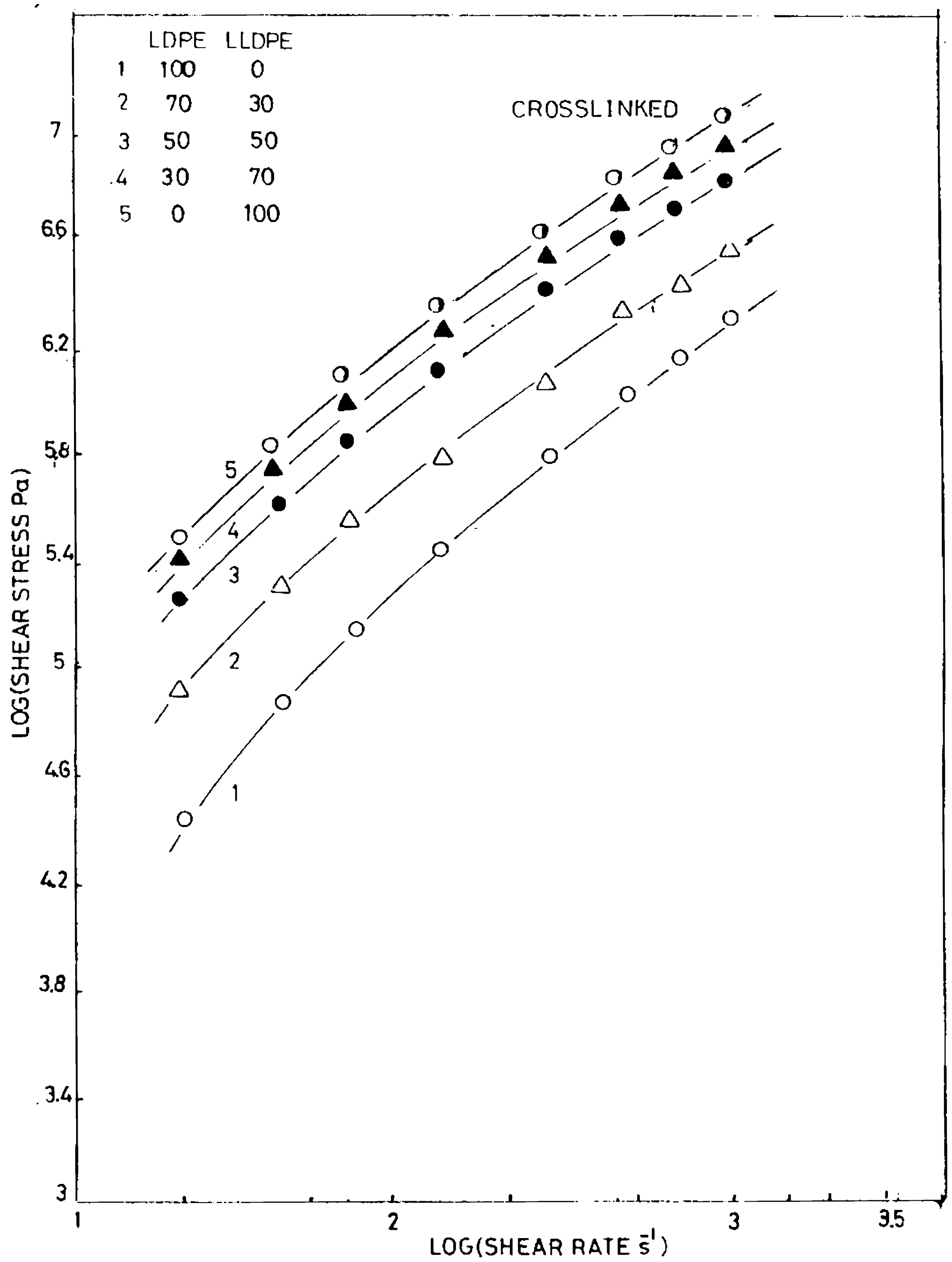

Fig.4.7: Flow curves of crosslinked LDPE/LLDPE blends with composition

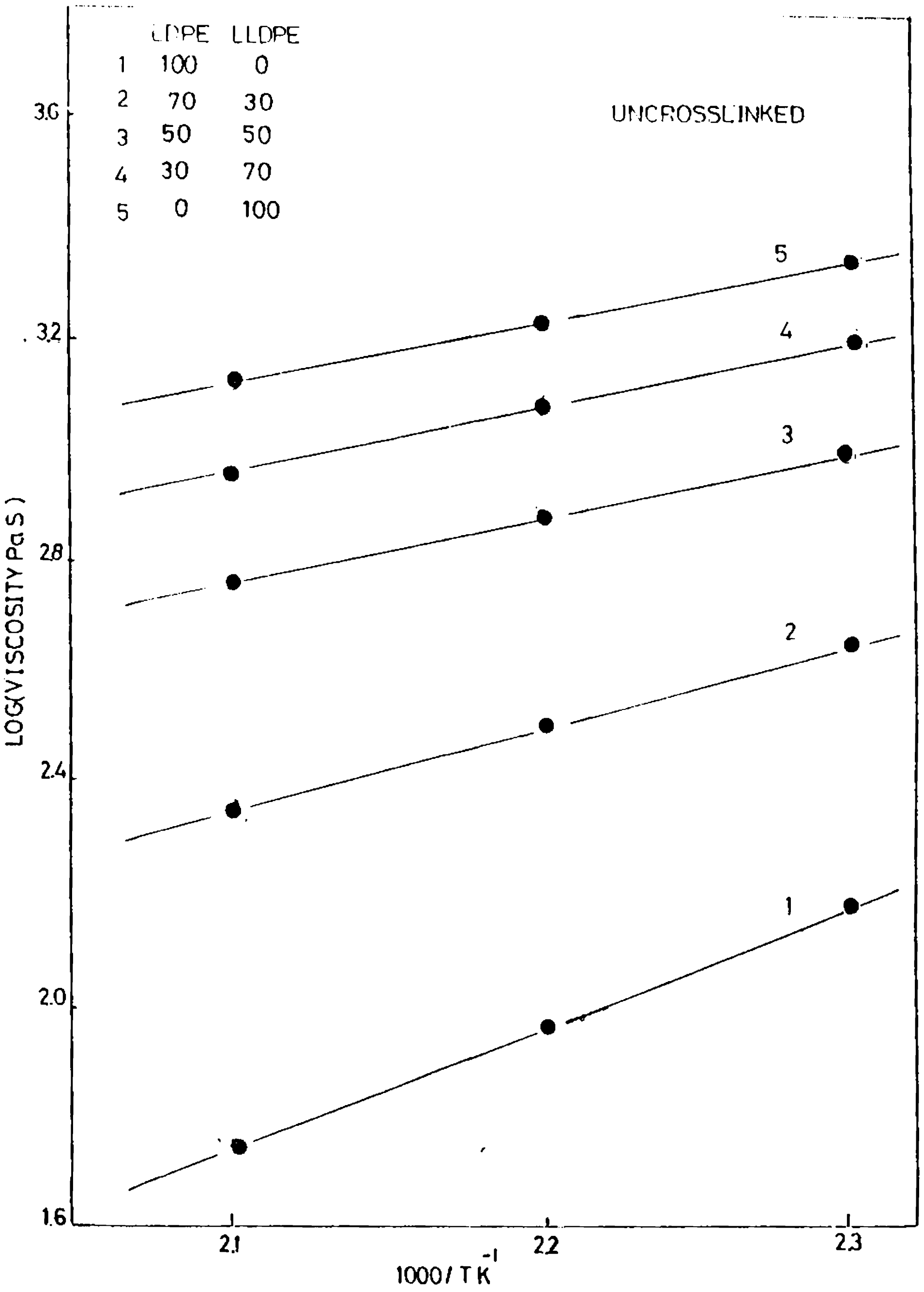

Fig.4.8: Variation of viscosity with temperature of uncrosslinked LDPE/LLDPE blends

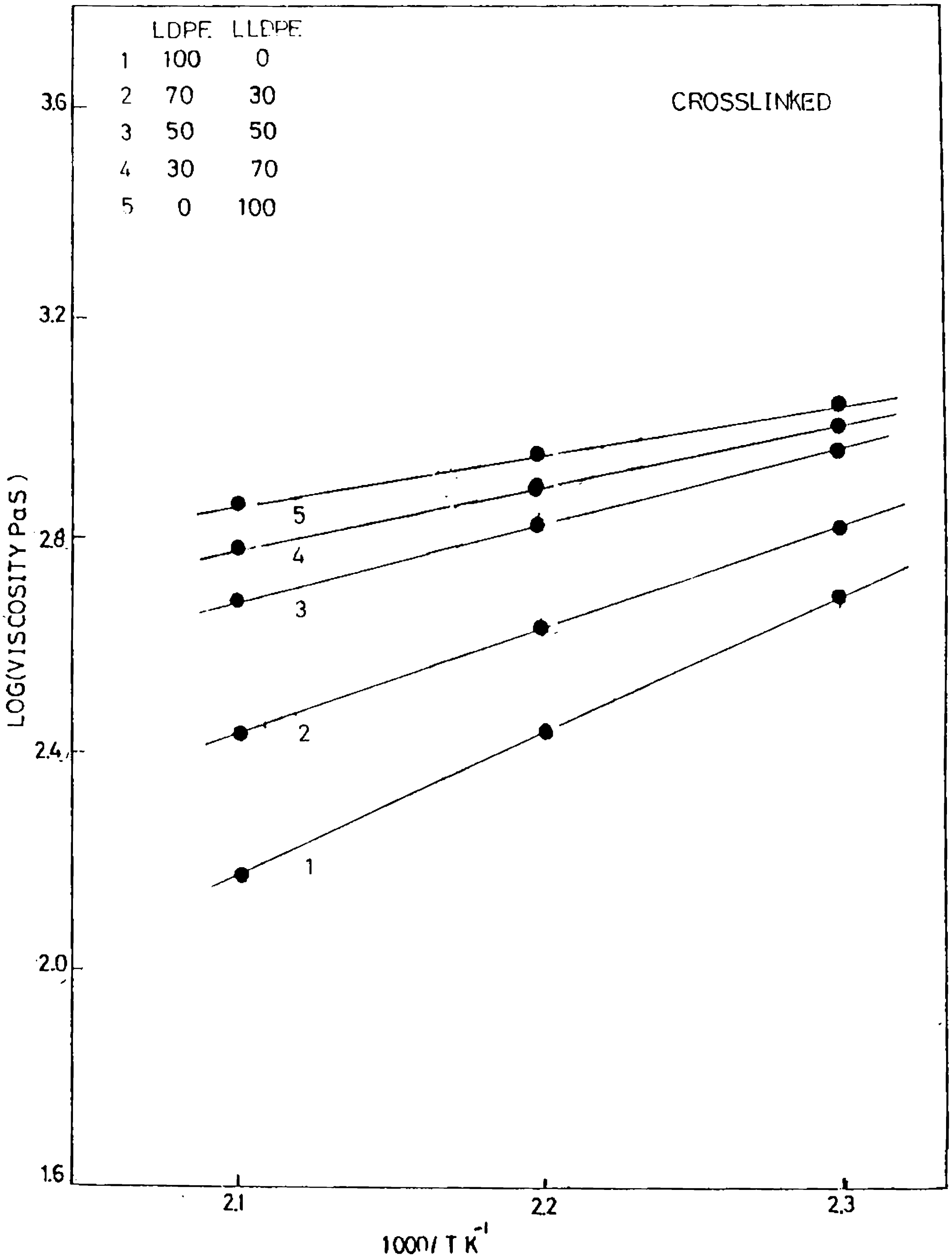

Fig.4.9: Variation of viscosity with temperature of crosslinked LDPE/LLDPE blends

Table 4.2: Dependence of activation energy with composition of uncrosslinked and crosslinked blends

Blend Composition		DCP (phr)	Activation energy (kJ mol^{-1})
LDPE	LLDPE		
100	0	0	11.96
100	0	1	11.29
70	30	0	11.96
70	30	1	11.41
50	50	0	12.40
50	50	1	14.95
30	70	0	16.50
30	70	1	17.60
0	100	0	23.90
0	100	1	25.08

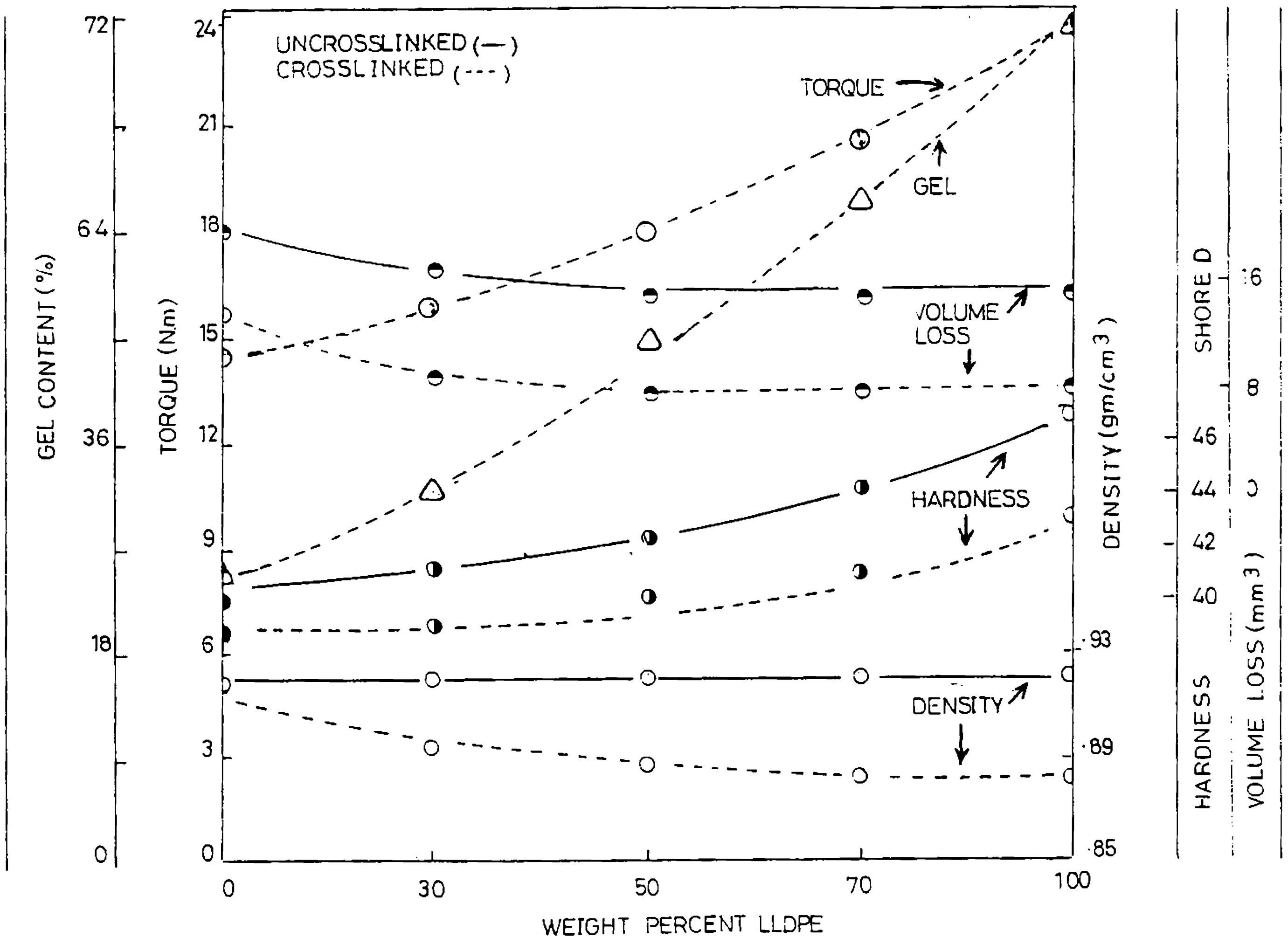

Fig.4.10: Variation of gel content, torque and physical properties of LDPE/LLDPE blends with composition

density, hardness and volume loss on abrasion of the crosslinked blends. Density, hardness and volume loss of the uncrosslinked blends are also shown for comparison. Density decreases with the increase in LLDPE content in the case of crosslinked blends while it remains unchanged more or less in the case of uncrosslinked blends. The decrease in density with increase in LLDPE content in the case of crosslinked blends may be attributed to the level of crosslinking which is relatively low for LDPE and increases with increase in LLDPE content. Hardness, a related property, follows the same trend. Wear resistance improves on crosslinking as expected. Gel content which relates to the three dimensional network structure increases with LLDPE content indicating that the LLDPE phase forms a relatively more dense network structure. As a consequence the value of the mixing torque increases with LLDPE content.

A comparison of the morphological features of unmodified and modified 50/50 blend is shown in Fig.4.11 and 4.12. It may be observed from the optical micrograph that DCP modification results in a more regular and homogeneous distribution of the individual components in the blend.

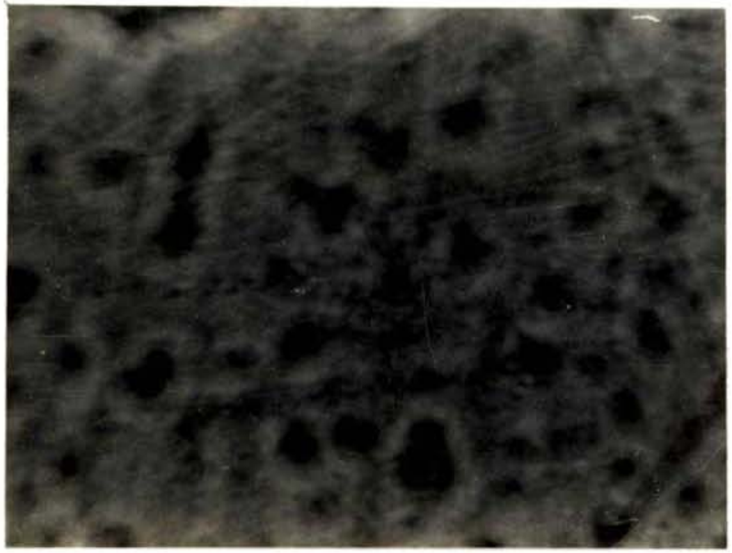

Fig.4.11 Uncrosslinked

Fig.4.12 DCP Crosslinked

Optical microscope photographs of the 50/50 LDPE/LLDPE blend

Conclusions

1. Modification of the blends with dicumyl peroxide at a concentration of 1 phr introduces crosslinks between the long chain molecules.

2. The level of crosslinking increases with LLDPE content indicating that the LLDPE phase forms a relatively more dense network structure.

3. Crosslinking improves the compatibility of the blends and increases the melt viscosity.

4. The mechanical properties of the crosslinked blends are more uniform compared to the uncrosslinked blends.

5. The physical properties controlled by the crystallinity of the polymer, such as density, hardness and volume loss on abrasion, decrease on crosslinking.

II. EFFECT OF GEL CONTENT ON THE PHYSICAL, MECHANICAL AND RHEOLOGICAL PROPERTIES OF LDPE/LLDPE BLENDS

Experimental

Materials

Two types of polyethylenes in powder form were used. The low density grade had a density of 0.922 g/cm^3 and MFI of 6, the values for the linear low density type were 0.922 g/cm^3 and 2 g/10 min. respectively. Dicumyl peroxide (DCP) Merck, bis-(α,α'-dimethyl benzyl) peroxide was used as crosslinking agent at concentrations of 0.5 to 2 phr. The two series of crosslinked samples with their gel contents are shown in Table 4.3.

Table 4.3: Gel content of crosslinked PE samples

DCP (phr)	LDPE Gel content (%)	LDPE/LLDPE (75/25) Gel content (%)
0.0	0	0
0.5	10	17
1.0	24	33
1.5	36	49
2.0	70	77

Preparation of PE powder

150 gm of PE was dissolved in 1000 ml toluene at 90°C and the solution added to 3 lit. of methanol under thorough stirring. The resulting precipitate was collected by filtering and washed twice with 1000 ml methanol. After washing, the PE slurry was dried in an air circulating oven at 50°C to give the PE powder.

Preparation of crosslinked PE blend

For preparation of crosslinked PE, a one step process was used. Premixed PE powder and DCP were transferred to a Brabender Plasticorder mixing head of 40 cc capacity working at 160°C, 30 rpm and 40 gm sample weight mixed for 15 minutes. The use of plasticorder offers the advantage of recording the mixing torque during mixing of the molten resin with peroxide thus giving a first indication of the crosslinking reaction. The samples were then moulded as plaques in a hydraulic press with heated platens, the moulding conditions varied (Table 4.4) because the thermoplastic character of the samples varied over a wide range. Specimens prepared from crosslinked PE by compression moulding were tested to determine their tensile strength

Table 4.4: Moulding conditions for LDPE, LDPE/LLDPE (75/25) crosslinked samples

DCP (phr)	Temperature (°C)	Pressure (atm.)	Time (min.)
0.0	125-130	10	10
0.5	125-130	25	15
1.0	145-150	30	15
1.5	150-155	35	15
2.0	150-160	40	15

according to ASTM D 638. Gel content was determined for each of the samples from extraction in boiling toluene for 8 hours.

Results and Discussion

Rheological investigation

The value of mixing torque (peak value) as a function of DCP concentration is shown in Fig.4.13 for LDPE and mixed polyethylene. In each case the value of mixing torque increases with increasing peroxide concentration. For mixed PE which presents a higher melt

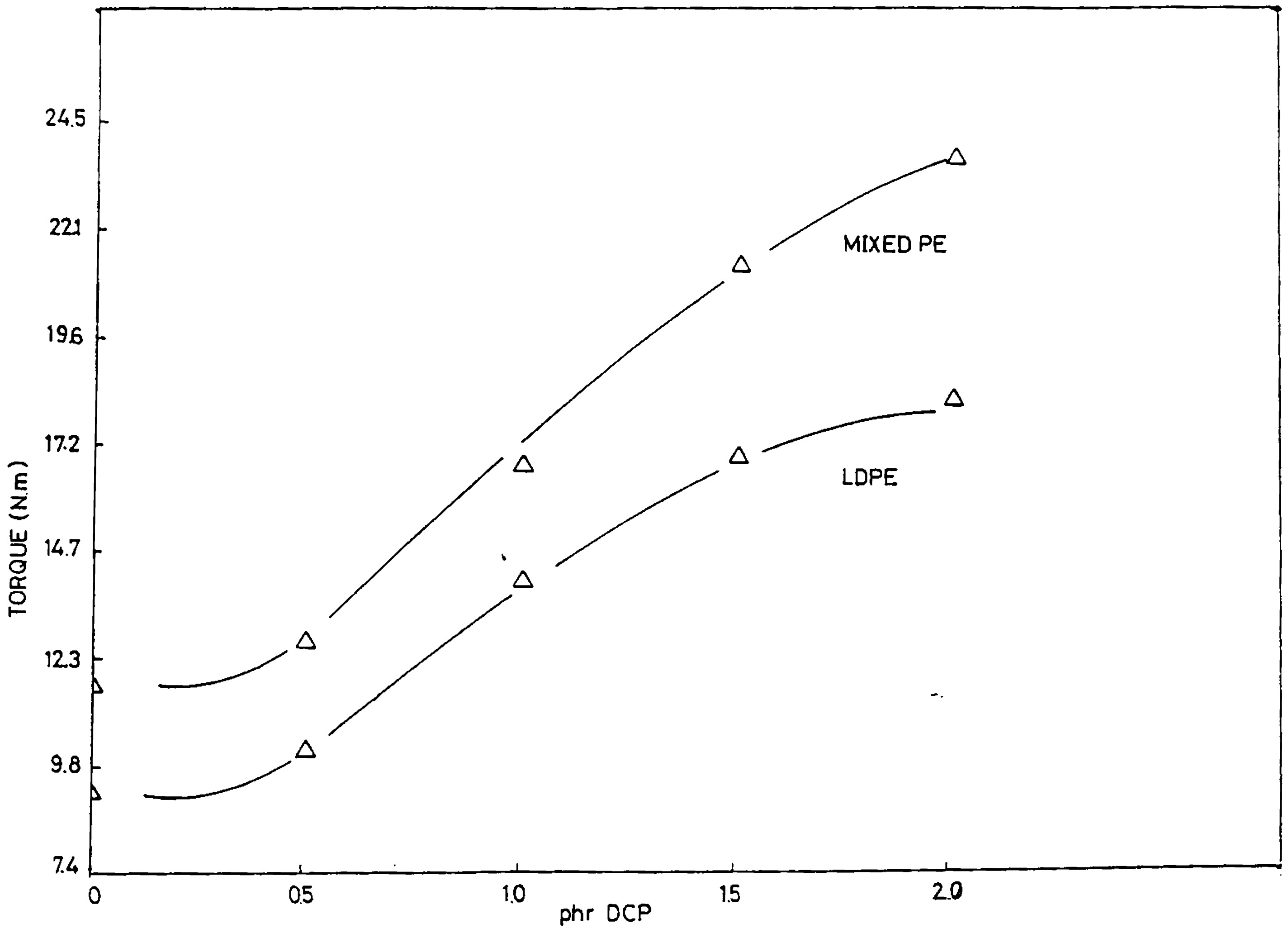

Fig.4.13: Torque as a function of DCP concentration of LDPE and mixed PE [LDPE/LLDPE (75/25)]

viscosity, the rate of increase is higher compared to LDPE. This effect may be attributed to the more number of tertiary carbon atoms in LLDPE.

The value of mixing torque as a function of reaction temperature for LDPE and mixed PE is shown in Figs.4.14 and 4.15. In each case torque increases with increase in temperature, the rate of increase being relatively higher for mixed polyethylene.

The time for maximum torque for LDPE and mixed PE processed at 160°C is shown in Table 4.5

Table 4.5: Time for maximum torque of LDPE and mixed PE at 160°C

Sample	DCP (phr)	Time (min.)
LDPE	1.0	15
	1.5	14
	2.0	13
LDPE/LLDPE (75/25)	1.0	13
	1.5	12
	2.0	11

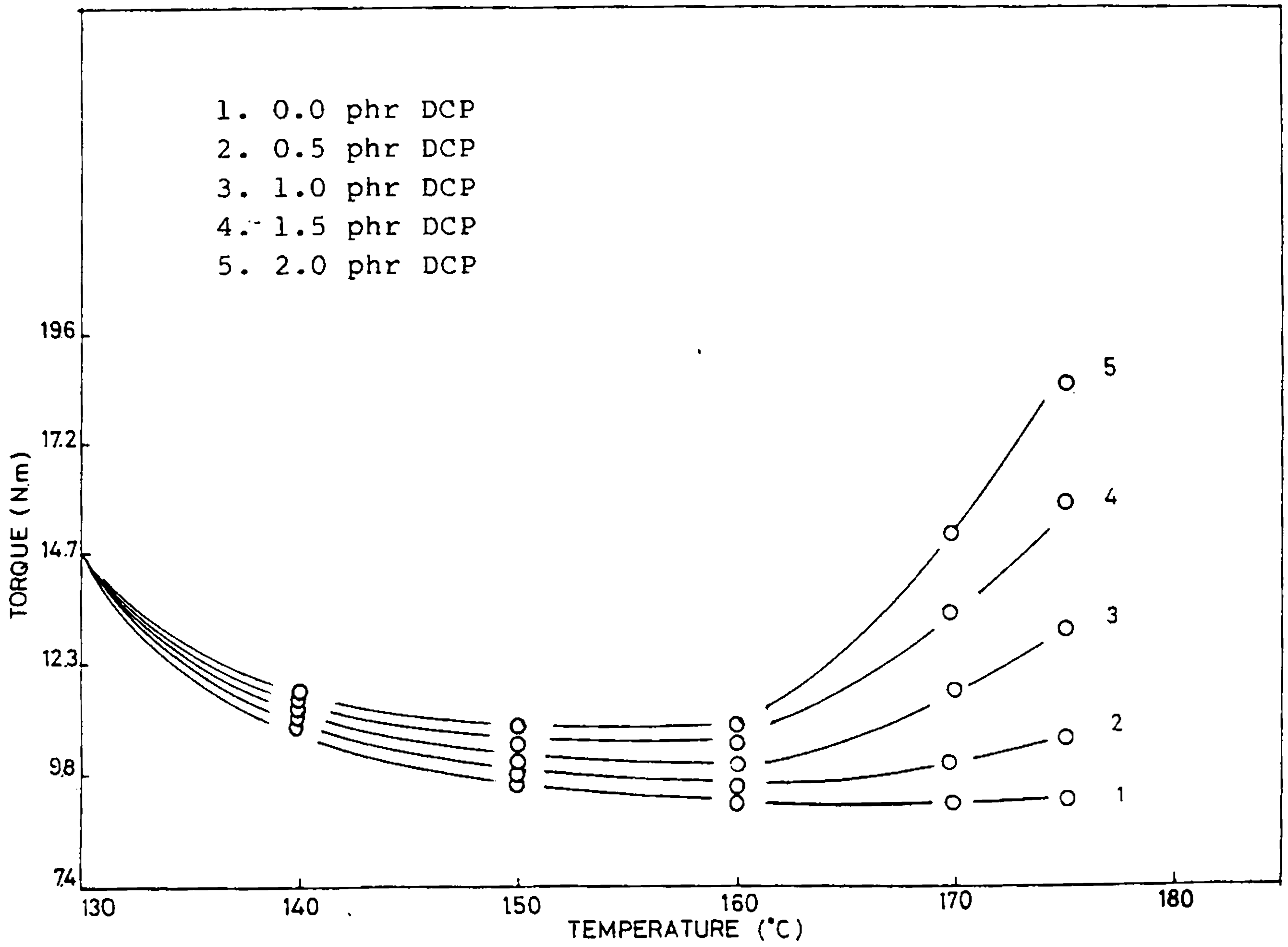

Fig.4.14: Torque as a function of temperature of LDPE

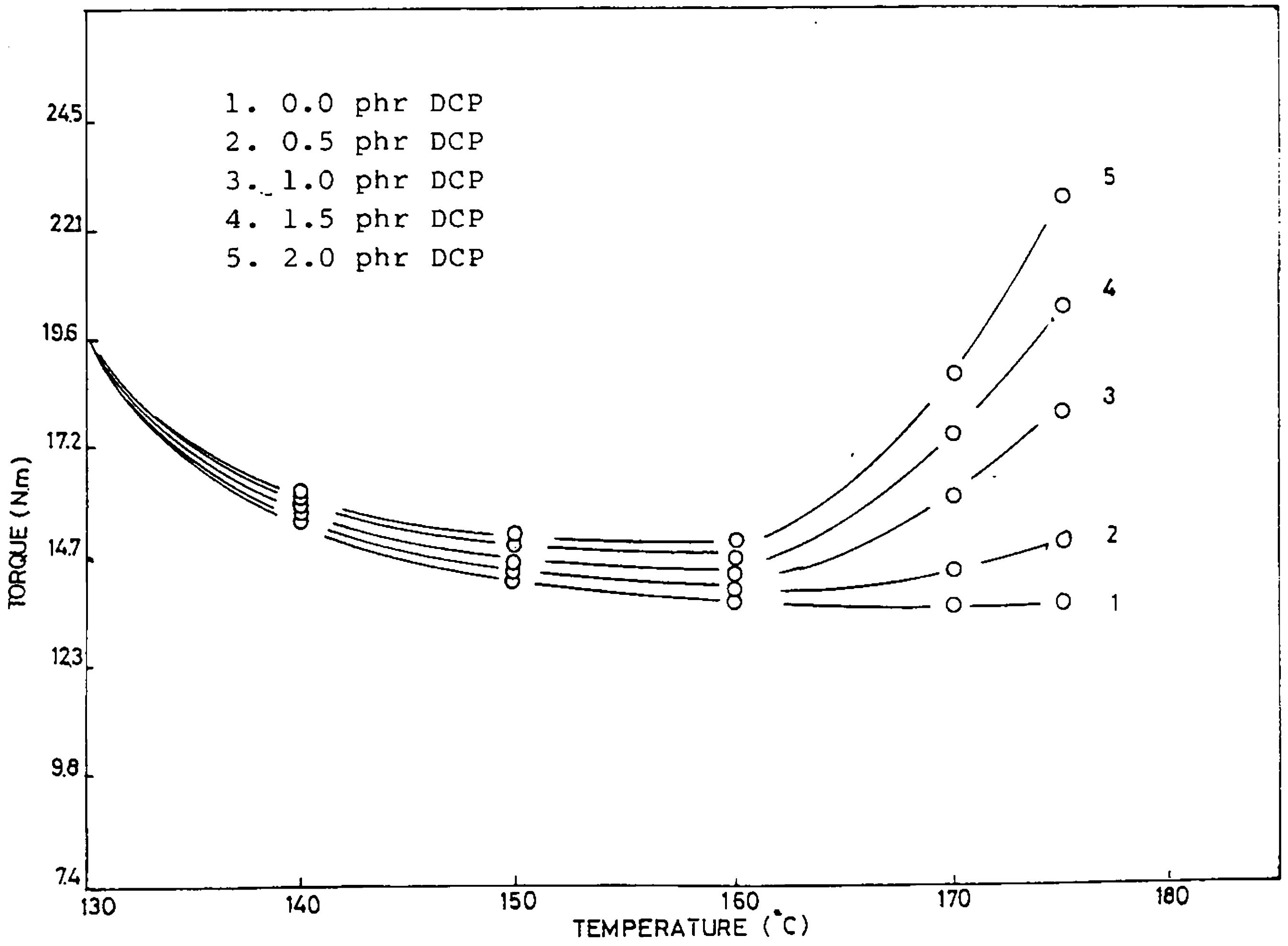

Fig.4.15: Torque as a function of temperature of mixed PE [LDPE/LLDPE (75/25)]

A decrease in peak time with peroxide concentration can be observed for both LDPE and mixed PE. Furthermore, mixed PE undergoes a faster rate of reaction than LDPE.

Analytical determination of gel content

The characterisation of the samples prepared was carried out by determination of gel content. The results for LDPE and mixed PE are plotted against gel content in Fig.4.16. As the curves indicate, there is a continuous increase in gel content with increase in DCP concentration. When the processing time increases, the gel content is reduced considerably for the same peroxide concentration (Fig.4.17). This fact is possibly due to mastication which occurs simultaneously with crosslinking reaction in the plasticorder mixing head. This process leads to chain scissions and subsequently lowers the gel content. For the same reason higher peroxide concentrations are effective, since it propagates crosslinking reaction in a further stage after network destruction.

Mechanical properties

The results obtained from tensile strength measurements at room temperature for LDPE and mixed PE

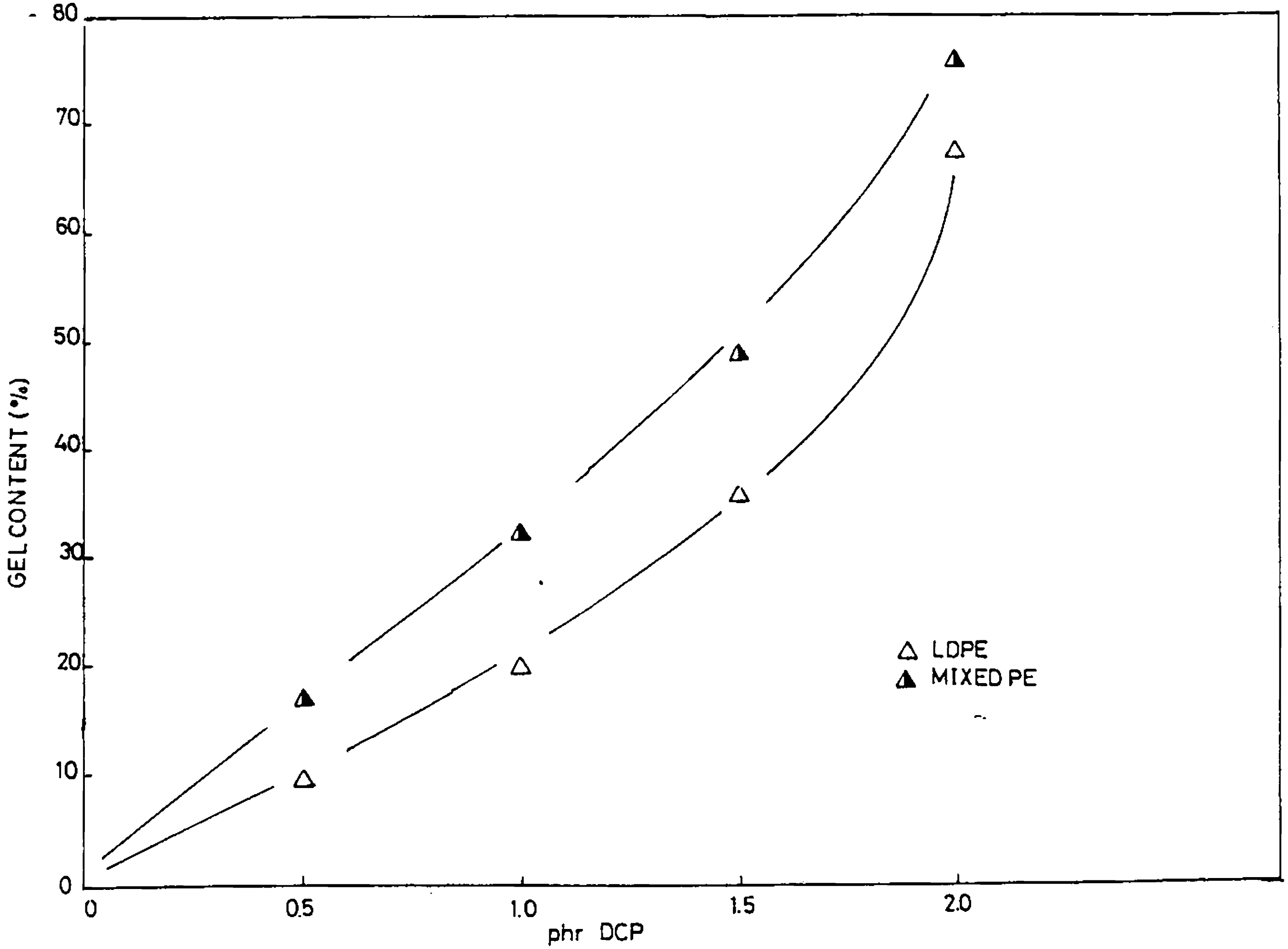

Fig.4.16: Gel content as a function of DCP concentration of LDPE and mixed PE [LDPE/LLDPE (75/25)]

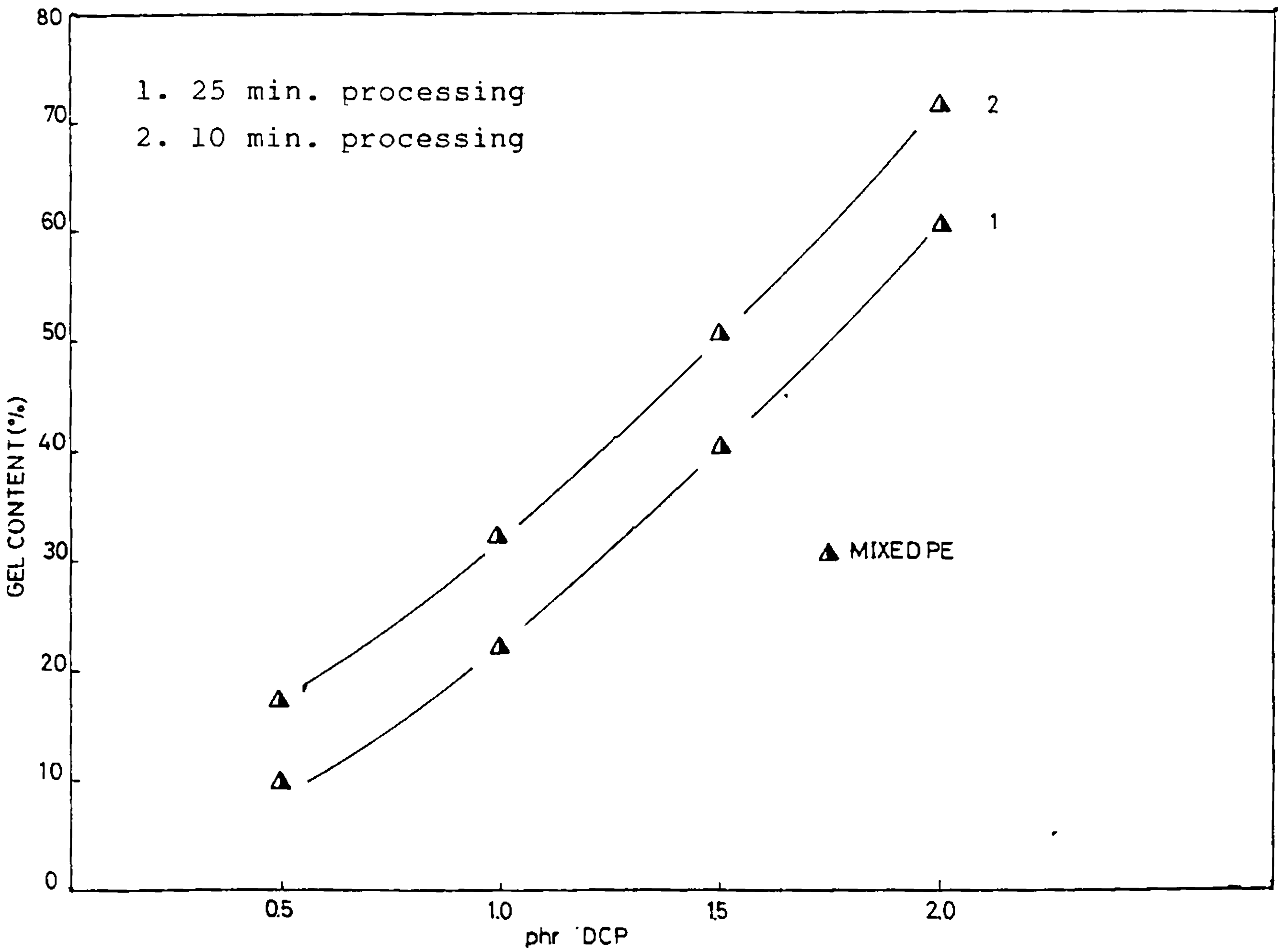

Fig.4.17: Gel content as a function of DCP concentration of LDPE and mixed PE [LDPE/LLDPE (75/25)] processed at 160°C

correlated with gel content measurements are shown in Table 4.6 and Fig.4.18. As the curves indicate, for low gel content, there is little effect concerning the tensile strength for both LDPE and mixed PE. The effect is stronger for gel values above 30% where the tensile strength is observed to increase continuously with gel content. Furthermore tensile strength values of mixed PE are much higher compared to LDPE.

The results obtained from the measurements of elongation at break for LDPE and mixed PE of various gel contents are shown in Table 4.6 and Fig.4.19. As the curves indicate, within the limits of experimental conditions followed, there is a linear decrease in elongation with gel content for mixed PE. For LDPE on the other hand elongation at break increases at low values of gel content (30%) and thereafter decreases.

The effect of gel content on the moduli of elasticity is shown in Table 4.6 and Fig.4.20. A decrease in modulus can be observed reaching a limiting value for gel above 50% for both LDPE and mixed PE, the values being correspondingly higher for mixed PE.

Table 4.6: Effect of gel content on tensile properties

Sample	Gel content (%)	Tensile Strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
LDPE	0	9.0	100	51
	10	9.4	185	46
	24	10.2	225	41
	36	10.8	197	35
	70	11.0	130	31
LDPE/LLDPE (75/25)	0	13.0	350	57
	17	13.0	350	52
	33	13.8	260	42
	49	13.8	260	42
	77	15.6	230	36

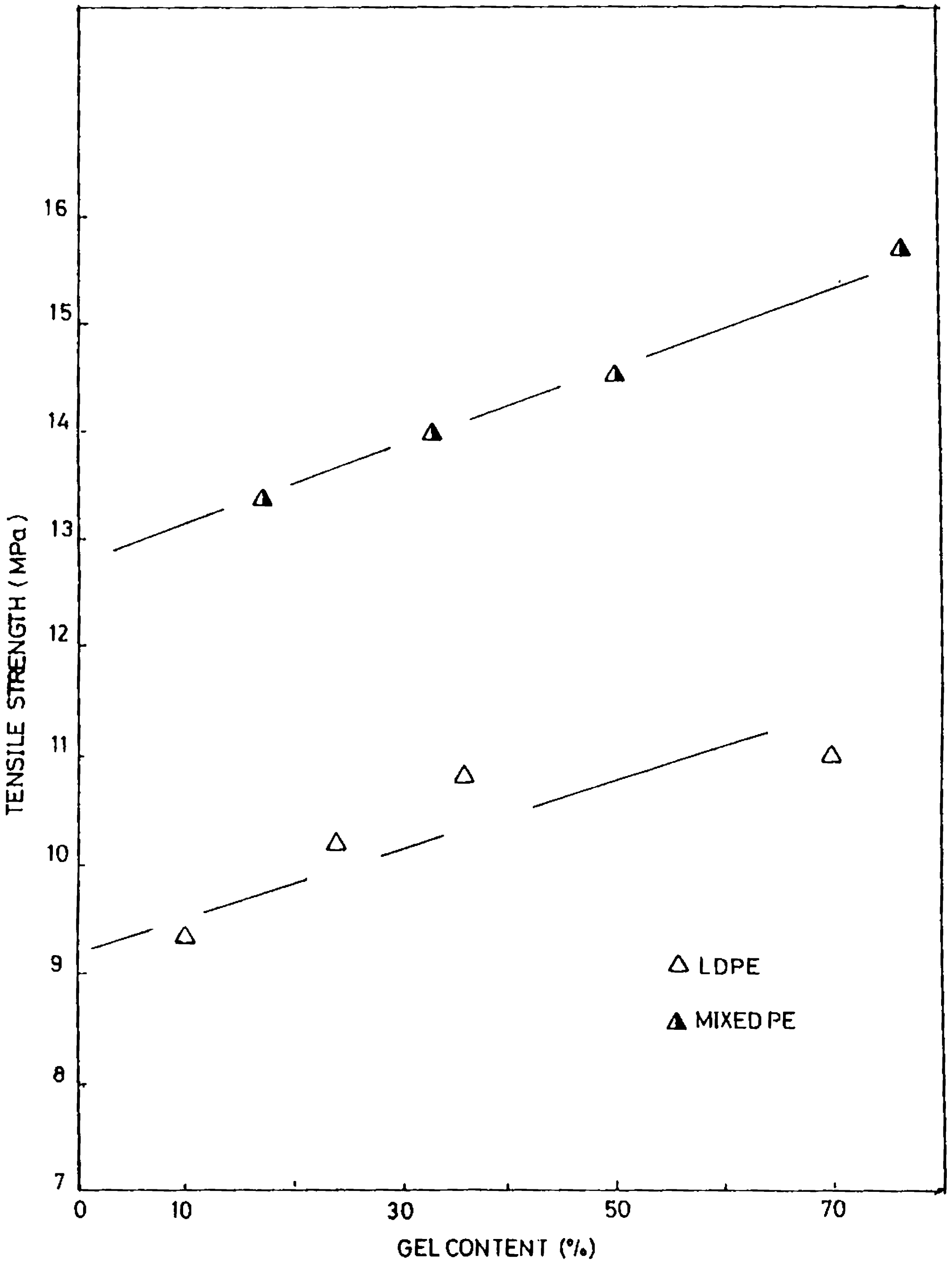

Fig.4.18: Correlation of tensile strength with gel content of LDPE and mixed PE [LDPE/LLDPE (75/25)]

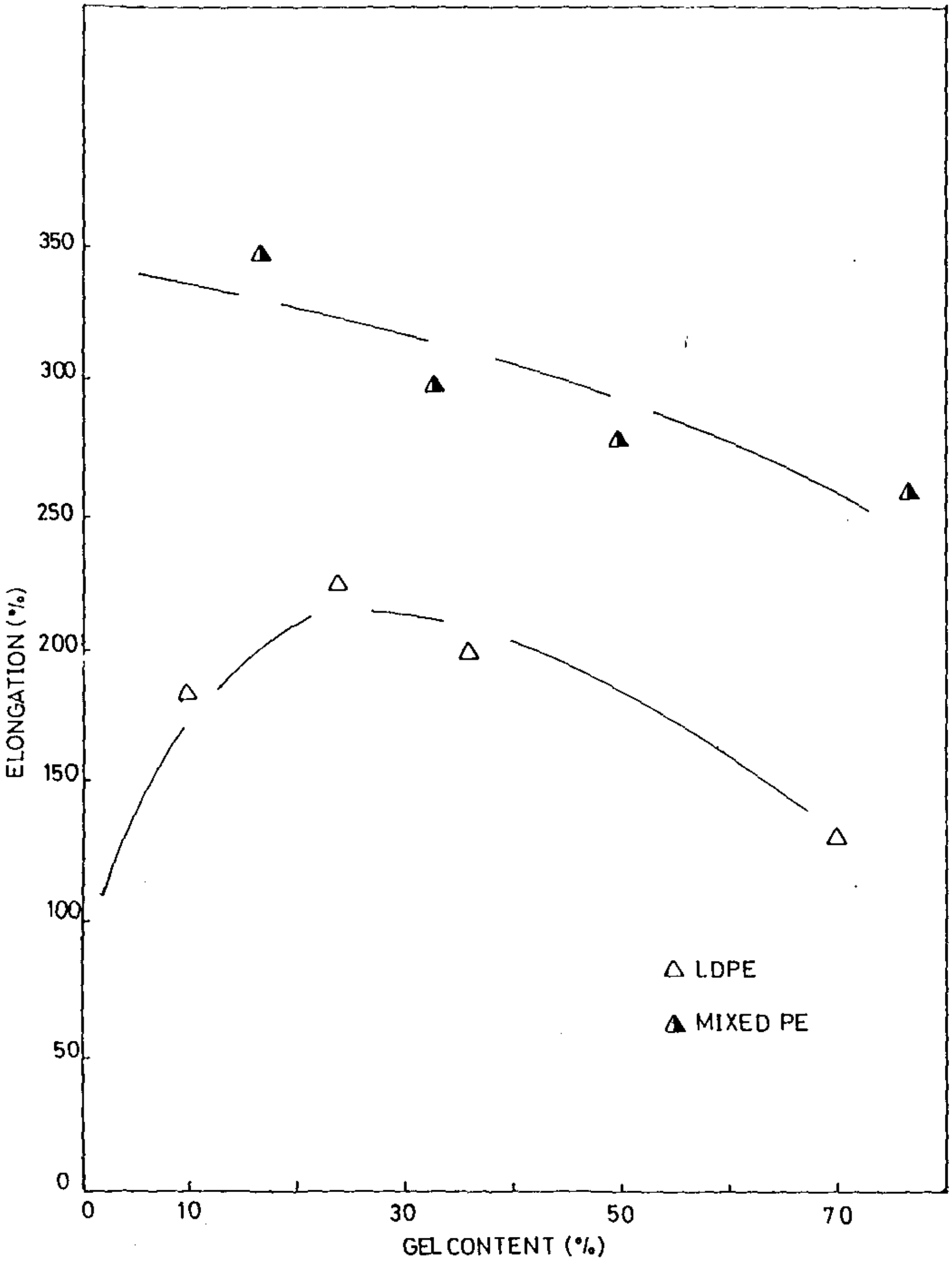

Fig.4.19: Elongation at break as a function of gel content of LDPE and mixed PE [LDPE/LLDPE (75/25)]

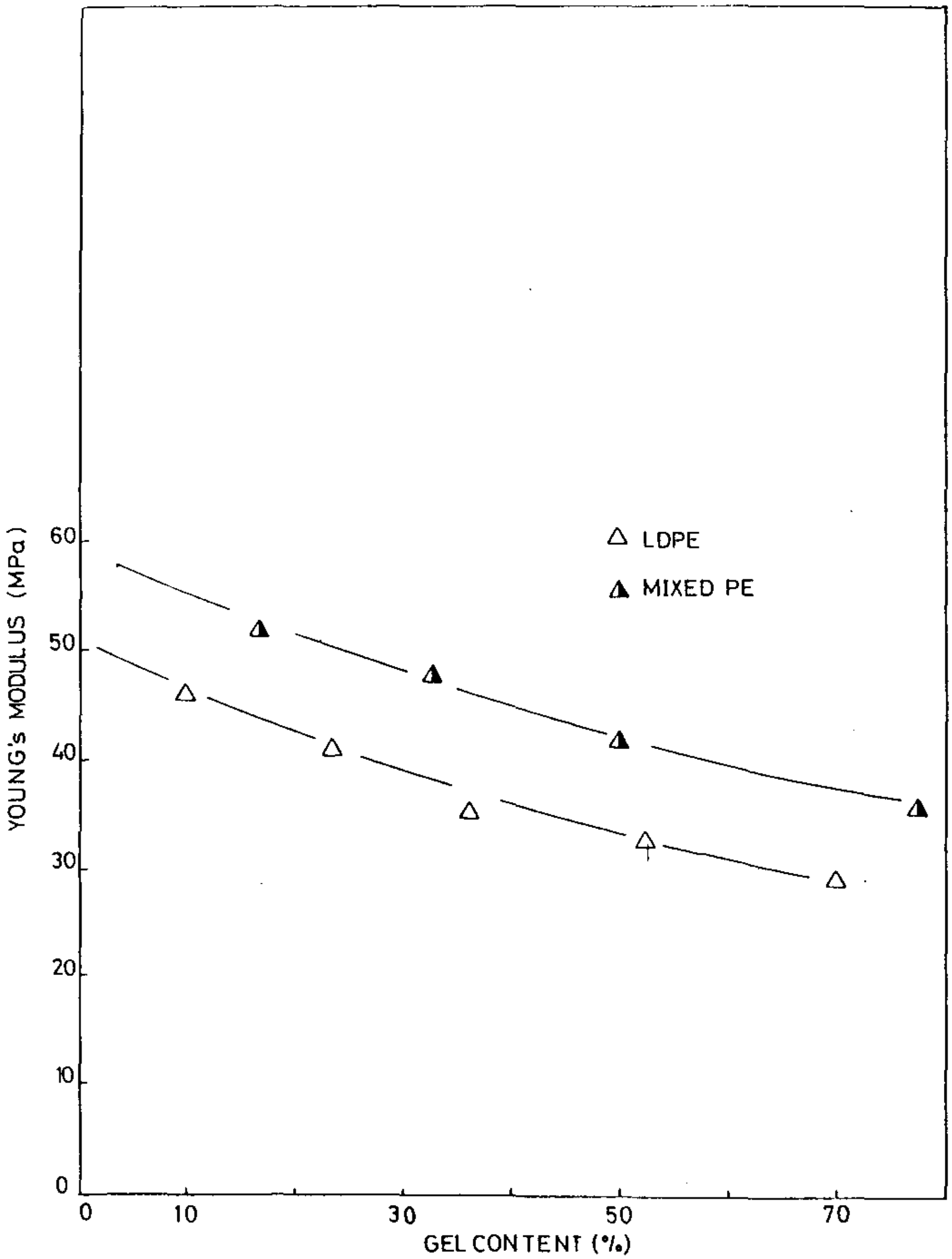

Fig.4.20: Correlation of modulus of elasticity with gel content of LDPE and mixed PE [LDPE/LLDPE (75/25)]

Table 4.7: Effect of gel content on mixing torque and physical properties

Sample	Gel content (%)	Max.torque (Mg)	Density (gm/cm^3)	Hardness shore D	Volume loss (mm^3)
LDPE	0	180	0.920	41	26
	10	200	0.920	40	24
	24	300	0.910	39	20
	36	320	0.906	37	12
	70	370	0.906	37	12
LDPE/LLDPE (75/25)	0	260	0.921	43	20
	17	260	0.921	42	18
	33	350	0.911	41	13
	49	440	0.908	41	8
	77	480	0.908	40	8

Finally, the effect of gel content on mixing torque and physical properties such as density, hardness and volume loss is presented in Table 4.7.

The densities of both LDPE and mixed PE decrease continuously with gel content. This behaviour can be attributed to reduction of crystallinity in both series of samples because of network formation. The interconnection of polymer chains by crosslinking restricts their mobility so that the arrangement is very difficult. Nevertheless the network itself corresponds to a more dense structure than the amorphous phase. Thus network formation and crystallinity reduction are competitive factors and as is evident, the second factor dominates in both cases leading to decrease in density. The changes in hardness with gel content show behaviour similar to that for density. The explanation is essentially the same as that given previously in connection with changes in density. Volume loss on abrasion improves on crosslinking as expected.

Conclusions

1. The use of polyethylene in powder form ensures homogeneity in crosslinking.

2. A relatively small amount of LLDPE (25 weight per cent) incorporated into LDPE (mixed PE) increases the rate and extent of crosslinking.

3. Mixed PE provides good processability with satisfactory product properties.

4. The tensile properties of mixed PE are significantly higher compared to LDPE.

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Chapter 5

EFFECT OF POLYMERIC MODIFIERS (SOLID PHASE DISPERSANTS) ON THE MECHANICAL PROPERTIES OF 50/50 LDPE/LLDPE BLEND

EFFECT OF POLYMERIC MODIFIERS (SOLID PHASE DISPERSANTS) ON THE MECHANICAL PROPERTIES OF 50/50 LDPE/LLDPE BLEND

Blends of polyolefines have attracted wide attention during recent years. The reason for the study of such blends is to find new materials combining the beneficial mechanical and processing properties of the components.

A number of recent papers have reported on the behaviour of the blends, which can be formed from combinations of high density polyethylene (HDPE), polypropylene (PP) and various ethylene-propylene elastomers.[1-15] A part of this interest stems from the need to improve the impact resistance of PP especially at low temperature, through rubber toughening,[6] which may also employ combinations including HDPE.[11] A general motivation stems, however, from the fundamental interest in the possibilities offered by physical blending for achieving tailored or unique behaviour.

In the present study a broad range of elastomeric additives were employed as a means to improve the ductility and toughness of a blend containing equal parts of LDPE and LLDPE.

Materials

The modifiers [solid phase dispersants (SPDs)] employed for property improvement in LDPE/LLDPE blends are elastomers (NR, EPDM, Butyl) and thermoplastic elastomers (SIS, SBS, SEBS).

Experimental

Sample preparation and testing

A binary mixture of 50/50 blend was batch mixed in the melt state using a Brabender plasticorder at 150°C for 8-10 minutes at a rotor speed of 30 rpm. After mixing, the molten mass was transferred to a compression mould with platens set at 160°C where sheets were pressed. Sheets 2 mm thick were formed and stamped into specimens conforming to ASTM D 638 for tensile testing. The sheets were formed by using a laboratory hydraulic press. The sheets were cooled in the mould by quenching by cooling water, circulated through the platens of the press. Tensile tests were carried out on a Zwick Tensile Tester (model 1445) using a cross head speed of 5 cm per min. at room temperature.

Results and Discussion

Mechanical properties

Stress-strain tests were done at room temperature. Initial modulus, maximum stress and elongation at break were recorded. The results were based on samples of unmodified LDPE/LLDPE 1:1 blend and blends modified with thermoplastic elastomers (SIS, SBS, SEBS) and elastomers (NR, EPDM, Butyl) as shown in Table 5.1.

Addition of SPDs reduces the modulus to some extent. However, the maximum stress level is marginally affected and the elongation at break is remarkably increased.

Yield stress values of the binary blend is shown in Figs.5.1 and 5.2 as a function of SPD content. The lowering of moduli with SPD content as shown in Table 5.1 is followed by a decrease in the corresponding values of yield stress. As shown in Figs.5.1 and 5.2, the blend exhibits an almost linear decrease with increase in SPD content.

Tensile strength values of the binary blend is shown in Figs.5.3 and 5.4 as a function of SPD content. From the figures it may be observed that for each modifier there is an optimum level (5 phr) at which the blend shows superior tensile properties compared to the unmodified blend.

Table 5.1: Stress-strain properties of LDPE/LLDPE blend with polymeric modifiers as solid phase dispersants

	LDPE/LLDPE 50/50 unmodified blend	Solid Phase Dispersants - 5 phr					
		SIS	SBS	SEBS	NR	EPDM	Butyl
Initial Modulus (MPa)	56	51	54	54	43	48	48
Maximum stress (Mpa)	16	16	18.5	17.5	16	15.6	16
Elongation at break (%)	410	460	500	440	460	470	470

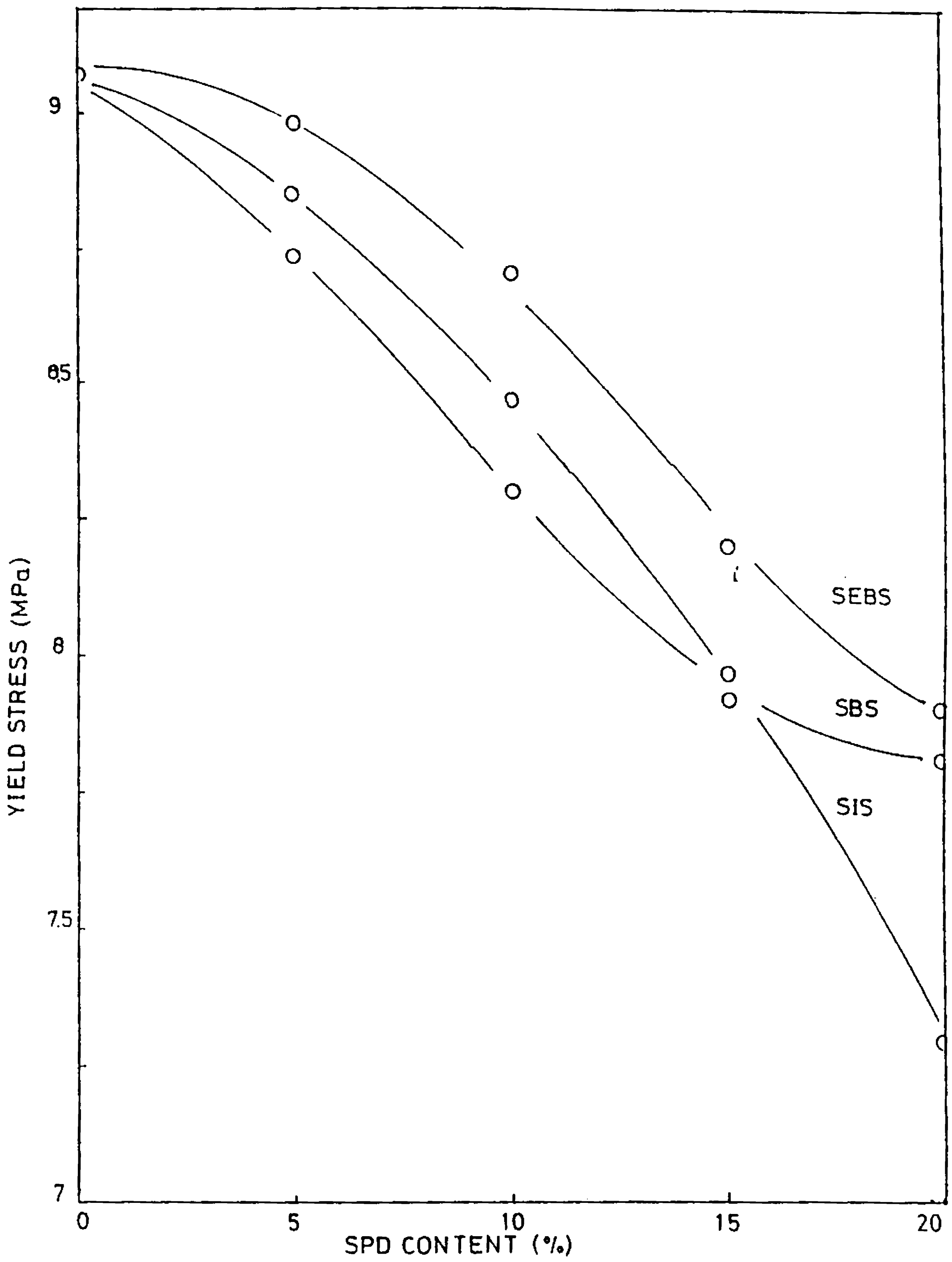

Fig.5.1: Yield stress values of the binary blend as a function of SPD content (SIS, SBS, SEBS)

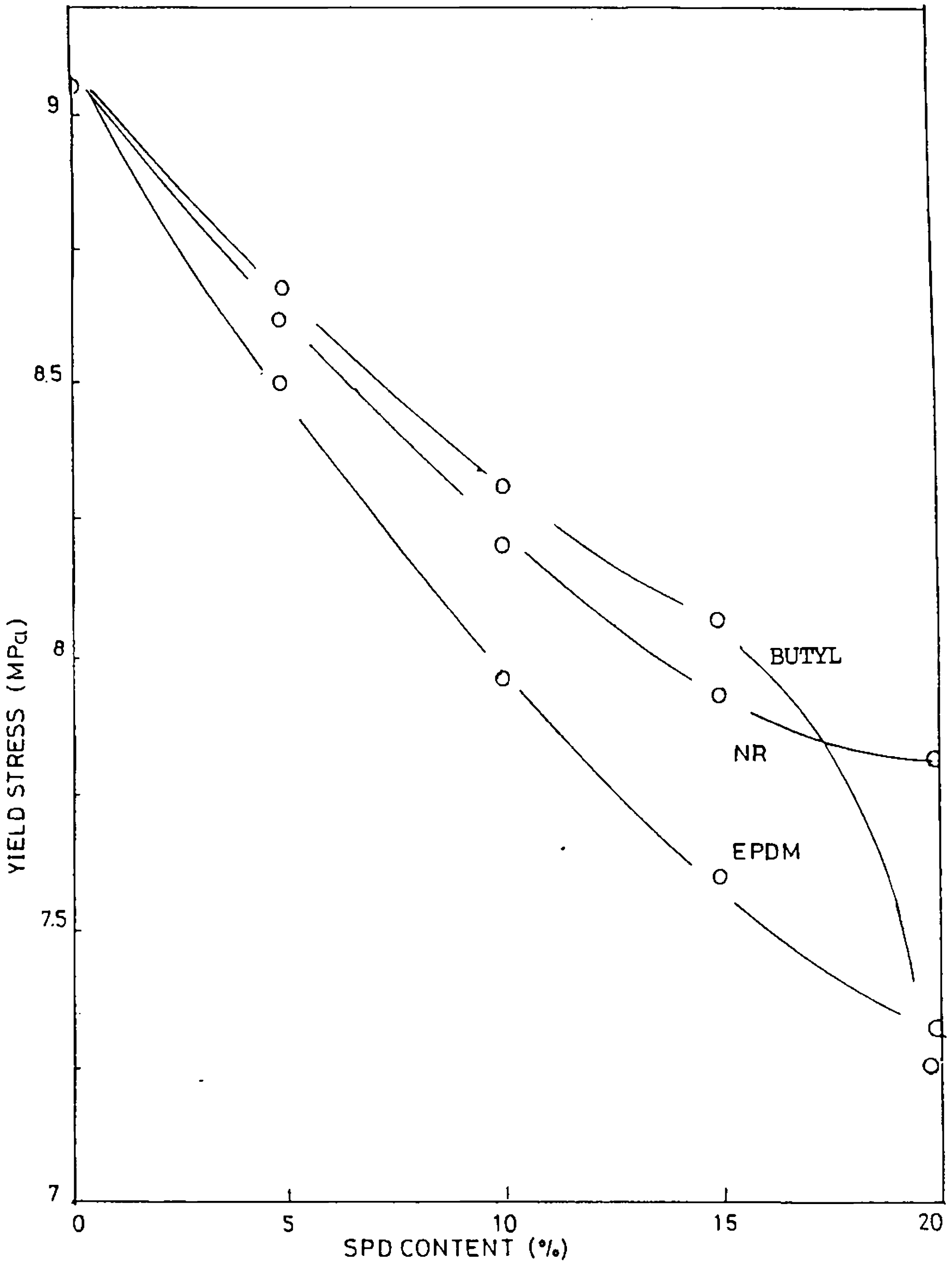

Fig.5.2: Yield stress values of the binary blend as a function of SPD content (NR, EDPM, Butyl)

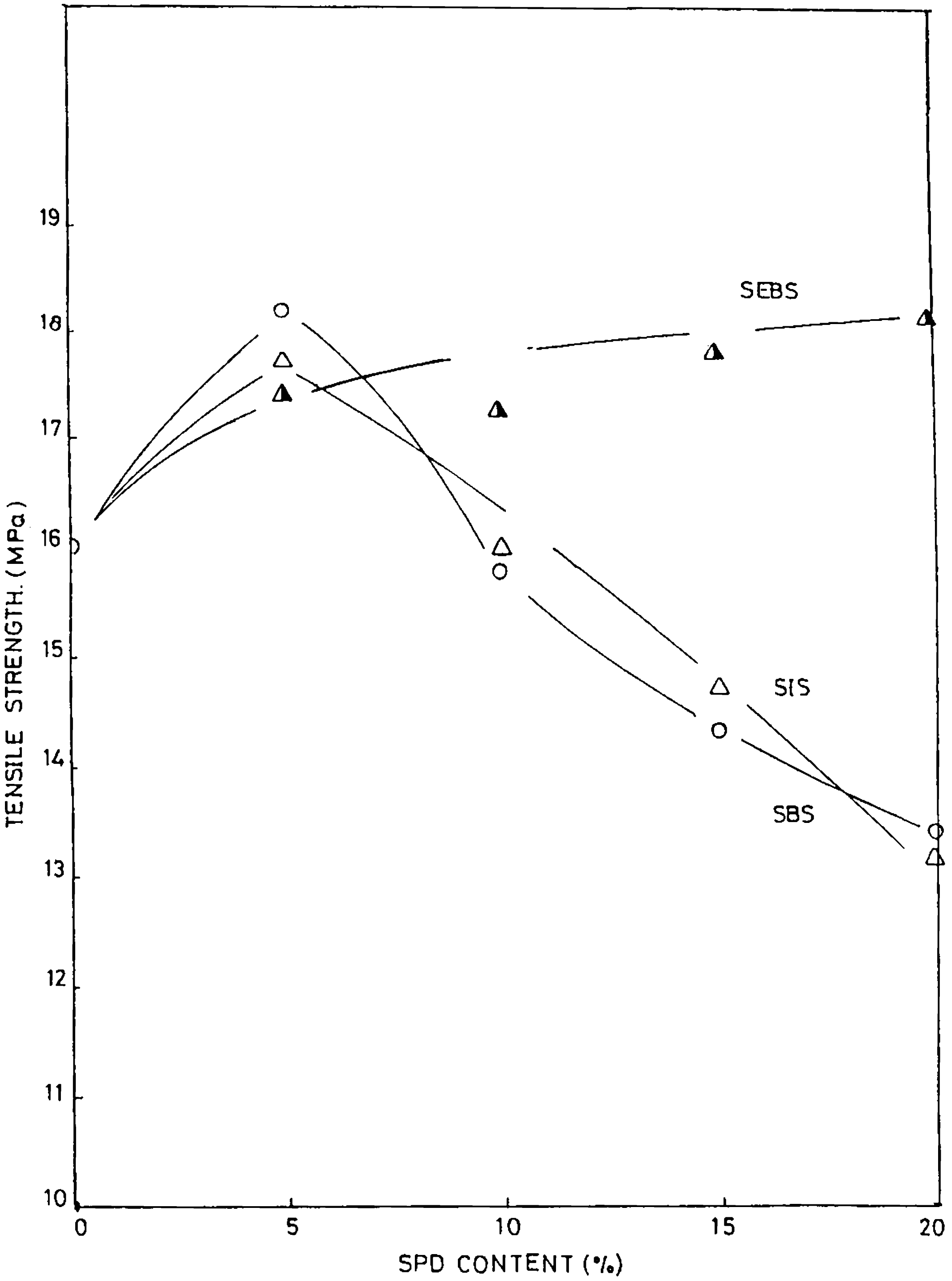

Fig.5.3: Tensile strength values of the binary blend as a function of SPD content (SIS, SBS, SEBS)

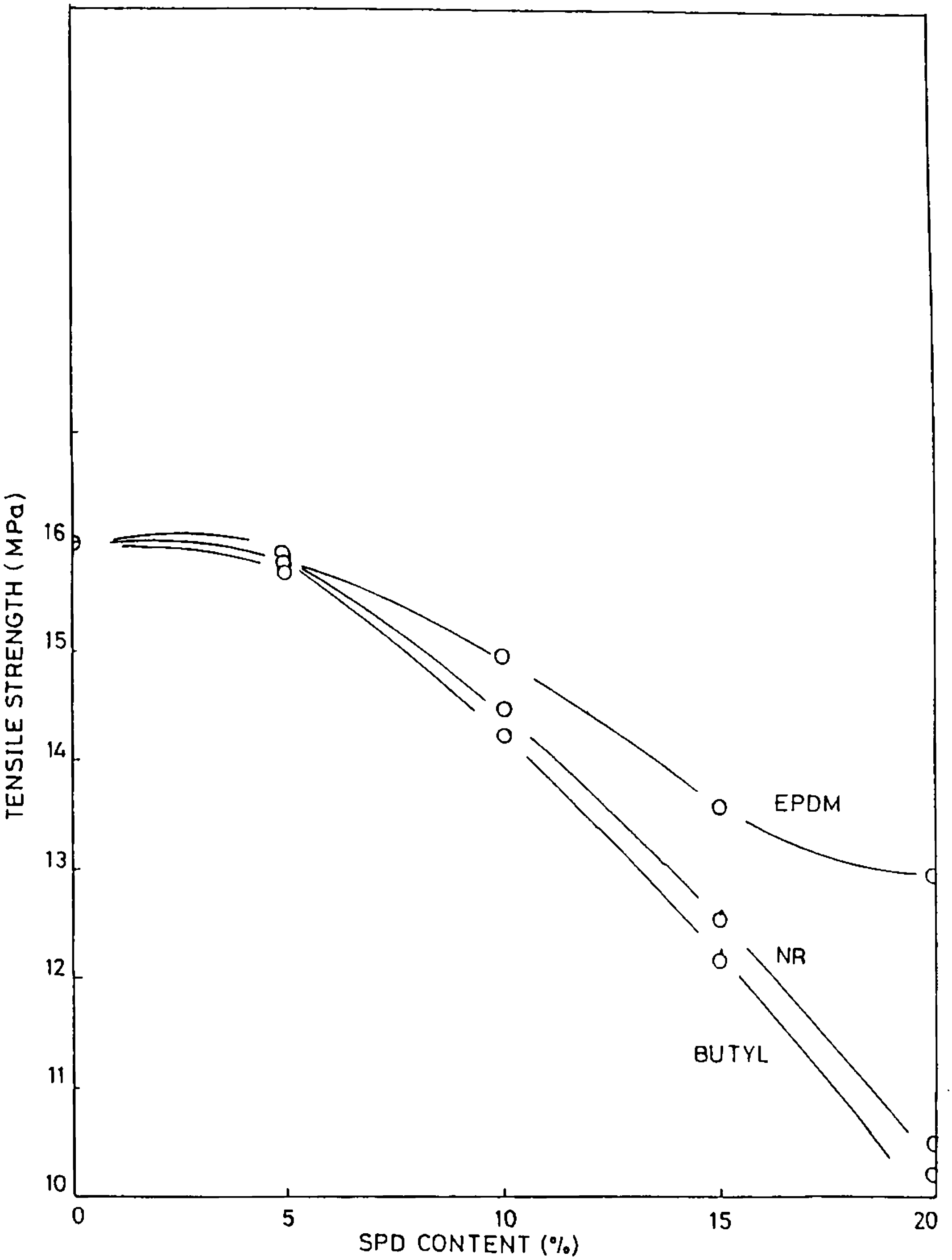

Fig.5.4: Tensile strength values of the binary blend as a function of SPD content (NR, EPDM, Butyl)

Elongation at break values of the binary blend is shown in Figs.5.5 and 5.6 as a function of SPD content. Addition of SPDs to a level of 5 phr improves toughness of the binary mixture considerably. Among the thermoplastic elastomers, the behaviour of styrene-ethylene-butylene-styrene (SEBS) in the blend is significant (Fig.5.5). The considerable increase in the value of E_b may be attributed to the ability of the ethylene butylene segments to interact at interface, thereby increasing the interfacial adhesion between the two phases of the binary mixture.

On the other hand among the SPDs of the class of elastomers the behaviour of EPDM in the blend is more pronounced in view of the presence of similar structural units in both the terpolymer and in the components of the blend (Fig.5.6). Although it is not believed that the ethylene and propylene units are present to a major extent as blocks the present evidence indicates compatibility of EPDM with both phases. The fact that EPDM increases the toughness and impact resistance of a 1:1 blend of LDPE and LLDPE suggests that as in the case of other impact modified polymers[16], rubber remains as an energy absorbing interface between the two phases of the binary mixture.

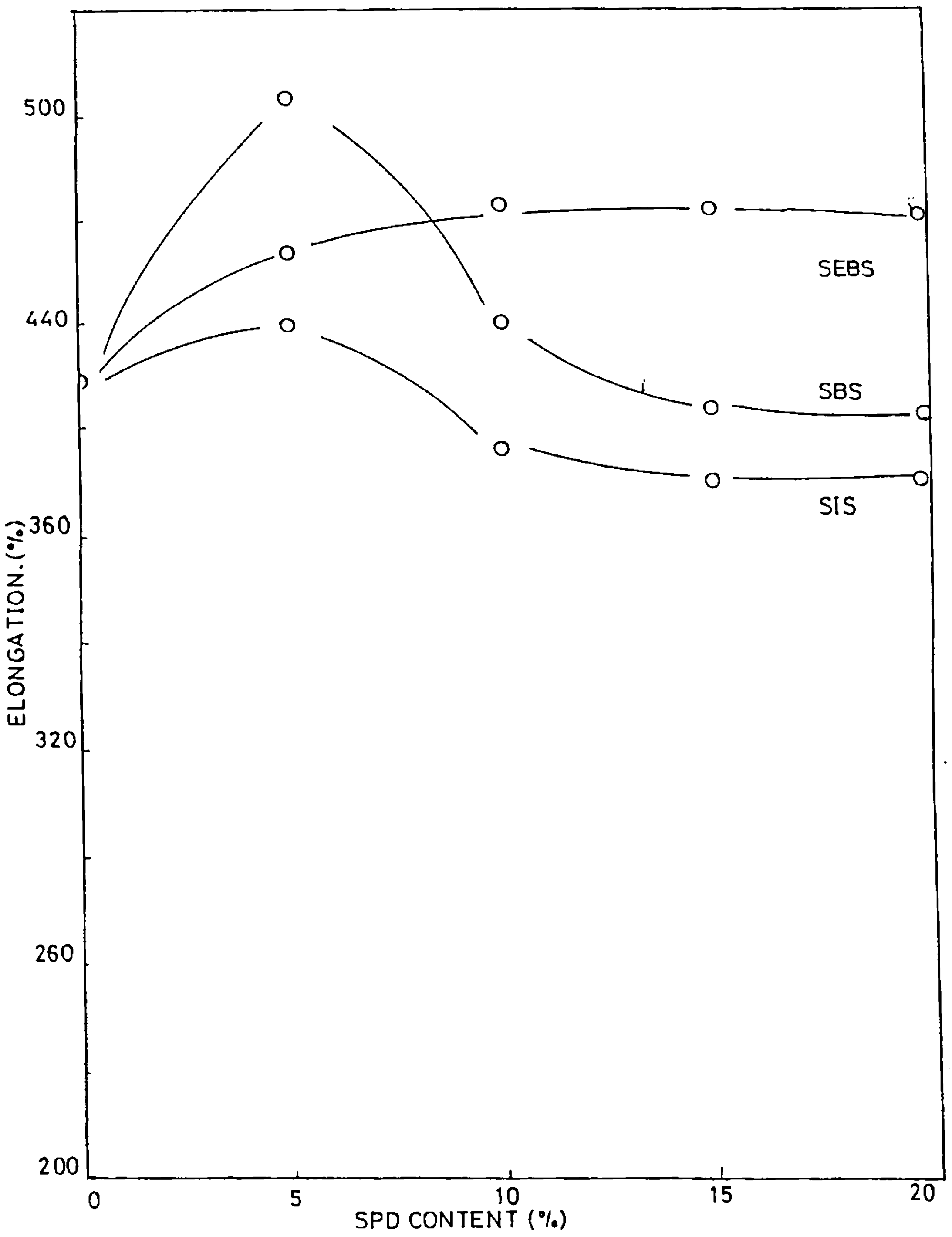

Fig.5.5: Elongation at break values of the binary blend as a function of SPD content (SIS, SBS, SEBS)

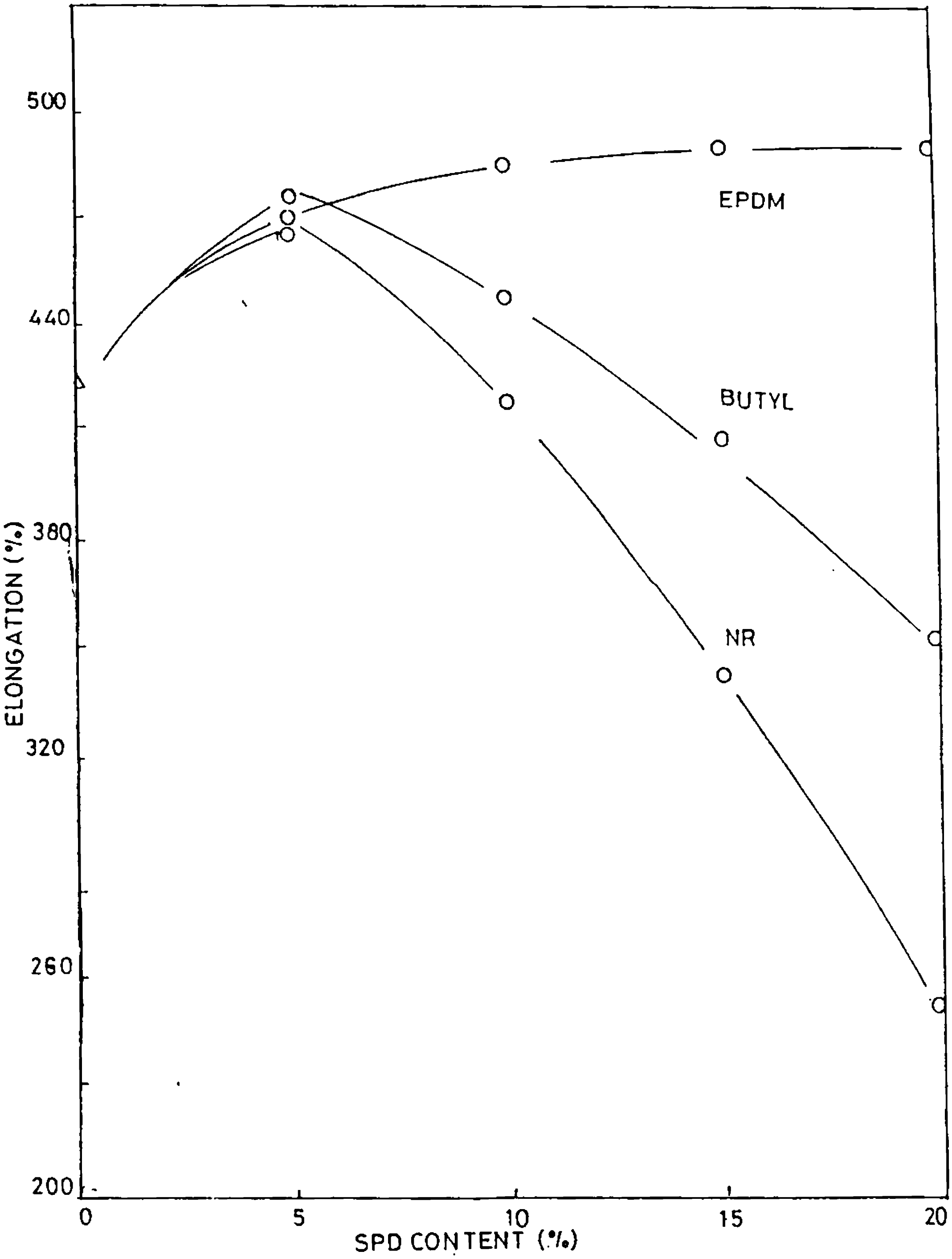

Fig.5.6: Elongation at break values of the binary blend as a function of SPD content (NR, EPDM, Butyl)

A comparison of the morphological features of unmodified and SEBS modified 50/50 blend is shown in Fig.4.11 and Fig.5.7. It may be observed from the optical micrograph that SEBS modification results in a more regular and homogeneous distribution of the individual components in the blend.

Conclusions

1. Among the various elastomers and thermoplastic elastomers, used as modifiers EPDM and SEBS were found to be the best as evidenced by the improvement in elongation at break value.

2. The optimum concentration of the various modifiers was found to be about 5 phr.

Fig.5.7 Optical microscope photograph of the 50/50 LDPE/LLDPE blend - SEBS modified

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Chapter 6

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Blends of polyethylene are widely used for optimising the properties and processability of individual polymers. This study on low density polyethylene/linear low density polyethylene blends has been undertaken because of their commercial importance. Mechanical properties of LLDPE are superior to those of LDPE, while LDPE surpasses LLDPE in processability. Hence blending LDPE and LLDPE would be an excellent means of generating a spectrum of polymers with useful properties.

Rheological evaluation of the blends was done using a capillary rheometer and a Brabender torque rheometer. Flow curves (shear stress vs shear rate) of the blends were generated using the capillary rheometer. The power law index values were also calculated. Corrections of rheological functions as per Rabinowitsch and Bagley were made to generate the true flow curves. The temperature dependence of viscosity was evaluated from the activation energy for viscous flow. The elastic effects of the blends were evaluated from the Bagley pressure correction and the dieswell values. The extrudate surface characteristics of the blends were also investigated. In most cases the rheological functions varied smoothly between the values of the constituent polymers indicating that the polymers could be mixed in any proportion for optimising the processing behaviour. LLDPE shows higher melt viscosity, pseudoplasticity index, melt elasticity and higher tendency for surface irregularities indicating that addition of LDPE to LLDPE is a good means of improving its processability.

The rheological evaluation of the blends was also done in Brabender torque rheometer. In this case the torque recorded by the rheometer was taken to be proportional to shear stress, rpm of the rotors as proportional to shear rate and torque/rpm as proportional to the viscosity. While the rheological data obtained from the torque rheometer was generally in agreement with those obtained from the capillary rheometer, it facilitated additional calculations such as energy required for plasticisation.

The mechanical properties of the LDPE/LLDPE blends also showed a clear pattern, the properties improving with LLDPE content. This further shows that blends of LDPE/LLDPE can be advantageously used depending upon the specific requirements. Modification of the blends with dicumyl peroxide was found to be a promising method for improving the compatibility of LDPE/LLDPE blends further, since the dominating reaction upon modification was found to be that of crosslinking. The DCP modified blends showed improved properties such as higher abrasion resistance, higher solvent resistance etc. at the expense of marginal decrease in the mechanical modulus. This is obviously due to the loss in crystallinity of the blends on modification with DCP. DCP modification also enhances the melt viscosity.

A promising method for improving the toughness and stress crack resistance of the blends was found to be addition of elastomeric modifiers such as EPDM and SEBS. SEBS was found to be the best modifier in improving the elongation at break of the 50/50 blends remarkably without any deterioration in the tensile strength.

LIST OF PUBLICATIONS FROM THIS WORK

1. Rheological Characterization of Blends of Low Density with Linear Low Density Polyethylene using a Torque Rheometer, European Polymer Journal, 26 (2) 197 (1990).

2. Studies on LDPE/LLDPE Blends, Die Angewandte Makromolekulare Chemie (in press).

3. Melt Rheology of LDPE/LLDPE Blends, Journal of Elastomers and Plastics (communicated).

4. Melt Viscosity and Melt Elasticity of LDPE/LLDPE Blends, International Journal of Polymeric Materials (communicated).

5. Effect of Gel Content on the Physical, Mechanical and Rheological Properties of LDPE/LLDPE Blends, Journal of Applied Polymer Science (communicated).

6. Effect of Controlled Crosslinking on the Mechanical and Rheological Properties of LDPE/LLDPE Blends--Paper presented at the National Conference on Advances in Polymer Technology, February 1991.