STUDIES ON HDPE/LLDPE BLENDS

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Mr.Philip Kurian under my supervision and guidance. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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I certify that the corrections suggested by the examiner have been incorporated by the candidate

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DECLARATION

I hereby declare that the thesis entitled **"STUDIES ON HDPE/LLDPE BLENDS"** is the original work carried out by me under the supervision of Dr.K.E.George, Reader, Dept. of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022 and no part of this thesis has been presented for any other degree from any other institution.

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PHILIP KURIAN

CONTENTS

Chapter 1

INTRODUCTION

Studies on the future of plastics production and the associated occurrence of wastes originating from these products have shown that, by the year 2000, plastics will account for more than 30% of the volume of controlled waste dumps. In view of the fact that most plastics require at least 300 years before starting to decompose and that capacity of controlled waste dumps will be exhausted in the near future, it is vital to seek a new technical solution. The need for a rapid solution has arisen due to the following reasons.

1. The increase in price of basic raw materials for the manufacture of polymers.

2. The very low percentage use of plastic wastes.

3. The limited capacity for storing plastics wastes at dumps.

4. The disposal of plastics wastes by combustion is very expensive and requires a complicated and expensive system for controlling the combustion process. Such a system must include a thermal process which does not produce dioxines, furanes or other chemicals which add

to environmental problems such as acid rain and deterioration of ozone layer.

These factors point towards recycling of plastics as the only solution to the problem of handling plastic wastes. The present method of recycling sorted and mostly clean plastics cannot be expected to handle the ever increasing problem of plastics wastes. Hence, new methods should be aimed at recycling of unsorted plastics wastes.

On the basis of analysis, the average composition of the mixed plastics waste can be something like 60-70% polyolefins (HDPE, LDPE, LLDPE and PP), 15-25% PVC and the remaining PS and other types of plastics. Thus polyolefin blends form a major part of all plastics wastes. The present study on polyolefin blends was undertaken to gain a realistic understanding of the problems of recycling of unsorted plastics wastes. Further, polyolefin blends are widely used for optimising the properties and processability of individual components and a detailed study of such blends will be very rewarding.

POLYMER BLENDS

Polymer blends are mixtures of structurally different homopolymers, co-polymers, terpolymers and the like. The copolymers, terpolymers etc., may be random, alternating, graft or block type. Given the economical and technical uncertainities associated with synthesising new polymeric materials, the development of polymer mixtures to achieve a desired combination of properties has obvious attractions.

One of the major areas of studies on polymer blends is the dependence of the mechanical properties on composition. This is due to the fact these complex systems exhibit a behaviour that does not simply follow the sum of the properties of the components. The mechanical properties depend on a number of factors, the most important one being the miscibility of the components. Polymer blends can be homogeneous (miscible) or heterogeneous (multiphase).

MISCIBILITY

Most of the polymer blends form heterogeneous systems which in a few cases present good characteristics. In particular, the size domains of the dispersed phase, its dispersibility and its interfacial interactions control the physical properties of the polymer blends.[1-3] The heterogenity can exist in amorphous, crystalline or both phases.[4]

In general, miscible polymer blends will phase separate on increasing the temperature or molecular weight of the resins.[5,6]

Many polymer pairs are known to be miscible or partially miscible, and many have become commercially important. The criteria for polymer/polymer miscibility are embodied by the equation for the free energy of mixing,

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

where ΔG_m is the change in Gibbs free energy, ΔH_m the change in enthalpy, ΔS_m the change in entropy upon mixing and T the absolute temperature. The necessary condition for miscibility is that $\Delta G_m < 0$. The combinatorial entropy of mixing depends on the number of molecules present[7] according to,

$$\Delta S_m/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2$$

where n_1 and n_2 represent the number of molecules and ϕ_1 and ϕ_2 represent the corresponding mole fractions of the components. Therefore, when the molar mass gets large the number of molecules becomes small, and the combinatorial entropy of mixing becomes negligibly small. Hence, two polymers can be expected to be miscible only when there is a very close match in cohesive energy density or in specific interactions, which produce a favourable enthalpy of mixing.

CLASSIFICATION OF POLYMER BLENDS

Polymer blends may be classified based on the method of preparation given in Fig.1.1.

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

Frequently during such a process one tries to compatibilise the blend by shear/temperature grafting with or without radical initiators or by addition of compatibilisers. Such mixtures are referred as polymer alloys. The distinction between polymer blends (PB) and polymer alloys (PA) is quantitative and refers to the extent of interpenetration of domains.

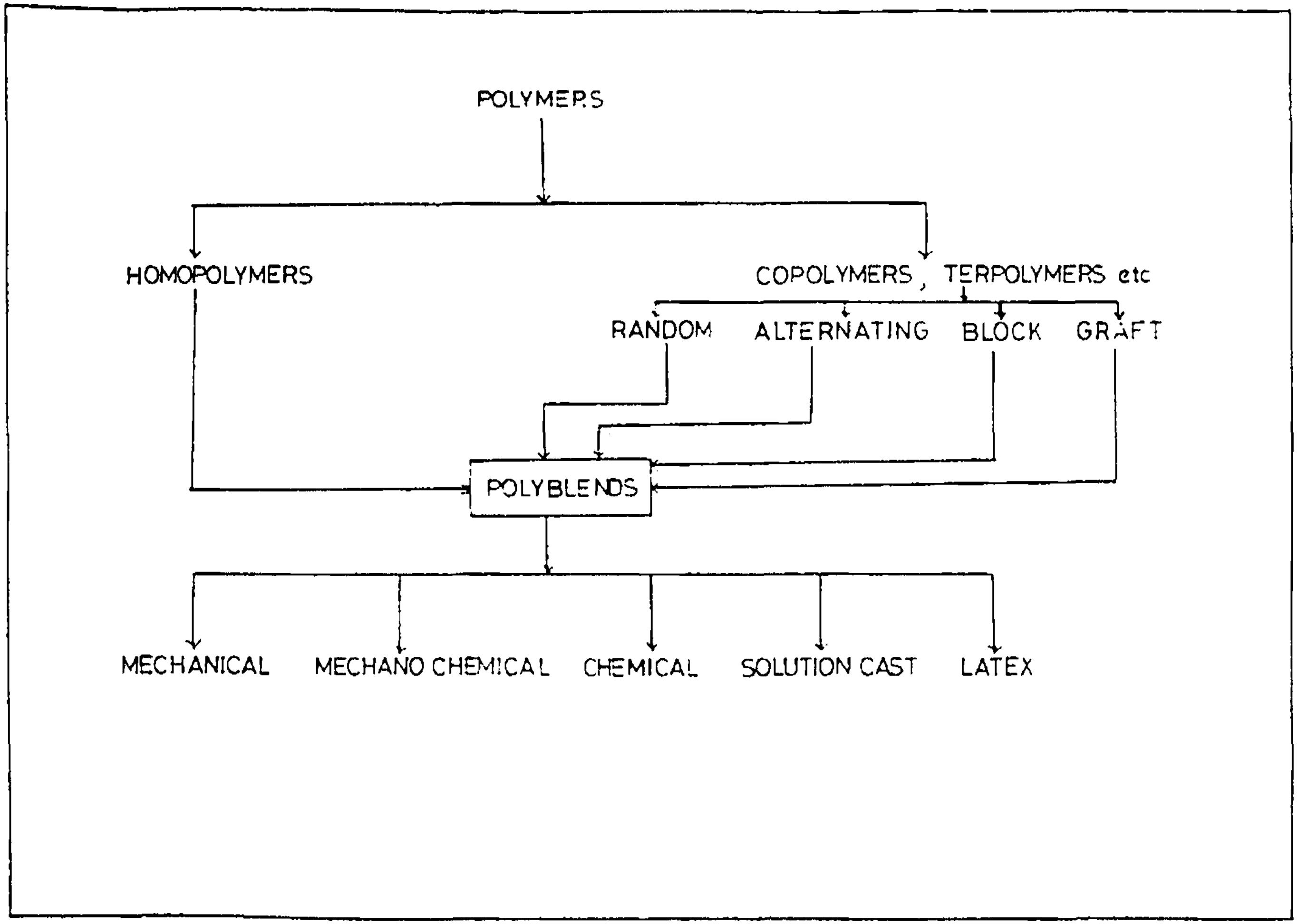

FIG.1.1 CLASSIFICATION OF POLYMER BLENDS BASED ON METHODS OF PREPARATION.

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 system.[8]

The following definitions are assigned for the various classes of polymer blends:[9]

Polymer blends (PB): the all inclusive term for any mixture of homopolymers and copolymers.

Homologous polymer blends: a subclass of PB limited to mixtures of chemically identical polymers differing in molar mass.

Polymer alloys (PA): a subclass of PB reserved for polymer mixtures with stabilized morphologies.

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

Immiscible polymer blends: a subclass of PB referring to those blends that exhibit two or more phases at all compositions and temperature.

Partially miscible polymer blends: a subclass of PB including those blends that exhibit a 'window' of miscibility ie., only at certain concentrations and temperature.

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 subclass 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.

PHYSICAL AND MECHANICAL PROPERTIES OF POLYMER BLENDS

The physical properties such as T_g, density, refractive index, dielectric constant, thermal conductivity heat capacity, thermodynamic properties, elastic modulus and viscosity of miscible blends vary smoothly with composition, and can be described by the equation,

$$P = P_1\phi_1 + P_2\phi_2 + I\phi_1\phi_2$$

where P is the property of interest, ϕ is the composition and I is the interaction term, which can be positive, zero or negative.[10]

when $I > 0$, the property is synergistic,

$I = 0$, the property is additive

$I < 0$, the property is non-synergistic

The properties of the polymer blends as a function of composition is given in Fig.1.2. Properties of heterogeneous blends are more difficult to predict. The property depends on additional factors such as shape and orientation of the dispersed phase, nature of the interface etc.

POLYETHYLENE BLENDS

Copolymerisation of ethylene and α-olefins has led to a new polyolefin known as linear low density polyethylene (LLDPE). The structure of LLDPE along with the structures of other commercial polyethylene viz., low density polyethylene (LDPE) and high density polyethylene (HDPE) is given in Fig.1.3. While LLDPE resembles LDPE in density, it is a linear polyethylene containing short side chains and resembles HDPE in structure.

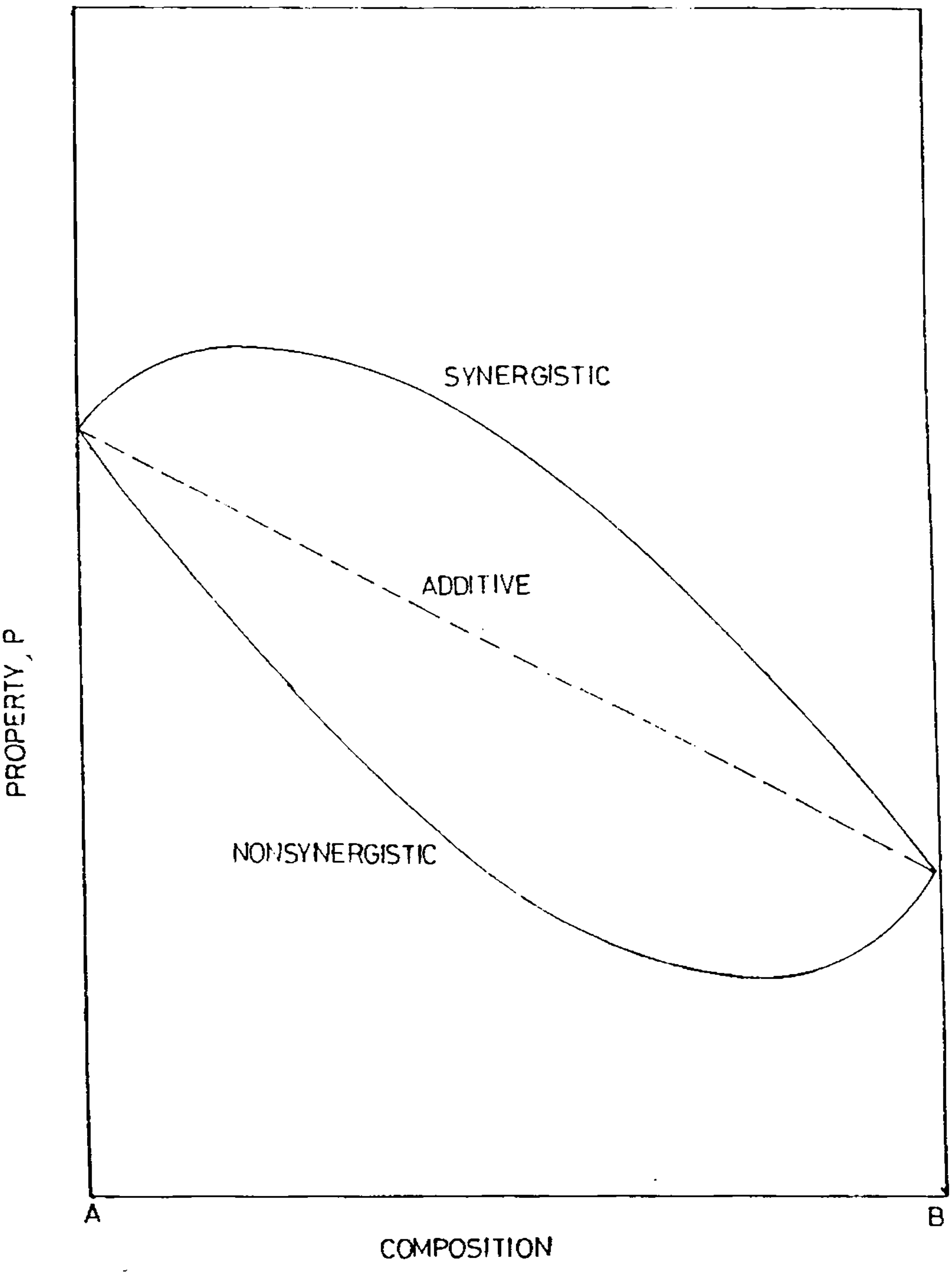

FIG.1.2 PROPERTIES OF POLYMER BLENDS AS A FUNCTION OF COMPOSITION.

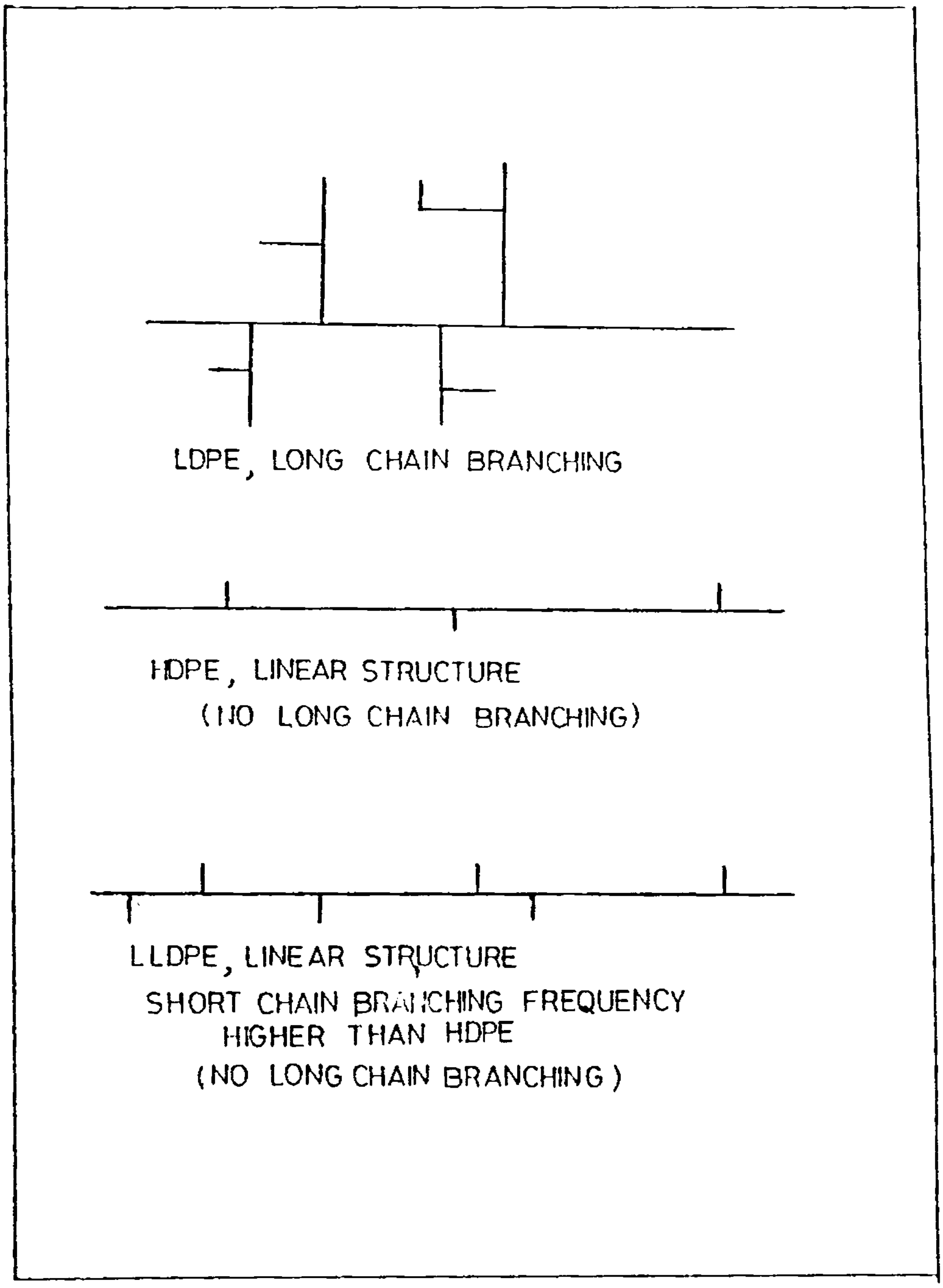

FIG.1.3 STRUCTURE OF LDPE, HDPE and LLDPE.

In recent years blends of various polyolefins have received more and more attention for two main reasons. The first is that polyolefins form most of the plastic wastes and their recycling lead to mixtures without separation.[11] The second is that the blends lead to new materials with improved processing and mechanical properties for specific purposes.[1,2,12] The advantages obtained by blending are improvement in impact strength, environmental stress cracking, optical properties, crystallisation rate, low temperature impact strength, rheological properties and overall mechanical behaviour.[13]

Some of the polyethylene blends have become commercially important and certain properties of the blends are better than those of the parent polymers. Unfortunately, sometimes failure results from poor mechanical properties as a consequence of incompatibility.[14-18] In low density polyethylene (LDPE)/isotactic polypropylene (PP) blends tensile properties are different from the generally observed behaviour.[19] This was related to the morphological features induced in the material by the mixing procedure adopted. The influence of mixing parameters on mechanical properties of LDPE/PP blends was reported by Rizzo.[20]

Several studies have been performed in order to investigate the mechanical properties of polyethylene blends.[21-30] For HDPE/LDPE blends, the results are somehow contradictory, both a severe incompatibility[25] and semi-compatibility[26] as seen from the elongation at break have been reported. For semicompatible blends the mechanical properties of the blends are intermediate between those of the homopolymers.

Densities measured for incompatible blends have been reported to agree with values calculated from the simple additivity relation given by the euation.[15,31]

$$1/\rho_b = w_1/\rho_1 + w_2/\rho_2$$

where ρ_b is the density of the blend, ρ_1 and ρ_2 are the densities and w_1 and w_2 the corresponding weight fractions of the components.

The density of compatible blends may be upto 5% higher than the additive values. The increase in density or negative excess volume of mixing observed for compatible blends is indicative of strong intermolecular interactions favouring better packing between molecules.

Polyethylenes are generally crystalline. The closer packing of molecules causes an increased density. The decreased intermolecular distance will increase the secondary forces holding the chain together and increase the value of properties such as tensile strength, stiffness and softening point.

Linear low density polyethylene (LLDPE) has acquired great commercial importance because of its superior mechanical behaviour compared to low density polyethylene (LDPE) and high density polyethylene (HDPE).[32] LLDPE being a comparatively new material there is considerable interest in its blends with LDPE or HDPE. Blends of LDPE and LLDPE are now regarded as excellent materials for film manufacture because they combine the processability of LDPE and the good mechanical properties and environmental stress cracking resistance of LLDPE.[33-35]

The low production cost of LLDPE is also one of the factors in its commercial success. However, despite the advantages of pure LLDPE, blending it with other polyethylenes is a common practice in industry. The reasons include:

1. The higher viscous and less shear sensitive melt properties of LLDPE.

2. The physical and mechanical properties of the blends can fill the gap existing among various pure polyethylenes.

3. Financial incentives.

4. Polyethylene blends occur in plastics wastes and is of interest in recycling of mixed plastics wastes.

Of the three polyethylenes (HDPE, LLDPE and LDPE), HDPE possesses the maximum strength and melting temperature while LLDPE has the highest impact strength. HDPE also has the highest stiffness, but it is considered the most difficult in processing.[36,37]

While many studies have been undertaken on LDPE/LLDPE and HDPE/LDPE blends, only very few studies are reported on HDPE/LLDPE blends. However, it is reported that a blend of HDPE and LLDPE exhibits a crystallisation exotherm of a single peak which indicates that it is a compatible system,[38] making the study of these blends most interesting.

The rheology of polyethylene melts has been extensively studied[15,39-49] but the rheology of LLDPE is less known.[50-63] Sometimes LLDPE is sold in blends with other polyolefins or EVA.[64] The rheology of LLDPE blends were studied by Utracki et al.[65-71] The molecular characteristics and the steady state and the dynamic shear behaviour of LLDPE blended with LDPE and different grades of LLDPE are reported in the literature.[21-23]

MODIFICATION OF POLYETHYLENE BLENDS

The properties of polyethylene and hence their blends can be modified by adding certain additives or by employing certain modification processes.

Controlled crosslinking of polyolefins has been found to improve creep, tensile properties, mechanical stability at higher temperatures etc.[72,73] Since crosslinking of polyolefin blends can generate interpenetrating polymer networks, it may improve the properties of the blends. Crosslinking is generally achieved by chemical means or by radiation. Radiation crosslinking is found to affect crystallinity less severely[74] and radiation crosslinking in the presence of a sensibilising agent[75] is suggested as an attractive means of obtaining improvement in properties associated with crosslinking without adversly affecting the mechanical properties.[76]

The mechanical properties of the incompatible polymer blends can be improved by the use of solid phase dispersants.[77] Since both HDPE and LLDPE are crystalline polymers, rubbery modifiers improve properties such as toughness, stress crack resistance and environmental stress crack resistance of the blends.

Mineral fillers are frequently used to increase the heat distortion temperature, rigidity and tear resistance of PE and PP matrices. Particulate fillers are added to polymers for a variety of purposes. For example, to enhance mechanical properties, dimensional stability, to control opacity, barrier properties and the like.[78-81] The performance of filled plastics is not defined by composition alone, the condition of the interface between the polymer and additive being a very important variable.[82,83] Particulate fillers are often surface modified to control interfacial conditions within the composite.[84]

OBJECTIVES AND SCOPE OF THE PRESENT STUDY

Following the introduction of linear low density polyethylene (LLDPE) in 1977 interest became focussed on the modification of other polyolefins with LLDPE. The similarity in structure of HDPE and LLDPE makes them ideal components for blending and thus generating a spectrum of new polymer materials.

The present study on HDPE/LLDPE blends was undertaken with the following objectives.

1. To characterise the physical, mechanical and processing behaviour of HDPE/LLDPE blends.

2. To investigate methods of improving the physical and mechanical properties of the blends so as to make them more useful.

3. To study the effect of elastomeric impact modifiers in the blends.

4. To explore the possible use of fillers in the blends for economic advantage.

In the present study, selected grades of HDPE and LLDPE are proposed to be melt mixed over the entire composition range and the mechanical and rheological properties are proposed to be evaluated.

Several modifications are proposed to be done for improving the performance of HDPE/LLDPE blends. A low level of crosslinking in polyethylene that does not affect processing leads to structural modifications that affects its properties significantly. In this study, HDPE/LLDPE blends are proposed to be crosslinked to a low level by chemical means and by irradiation. The mechanical and rheological properties of the modified HDPE/LLDPE blends are proposed to be studied in detail.

Low concentrations of elastomers such as natural rubber (NR), butyl rubber (IIR), ethylene propylene diene rubber (EPDM) and styrene isoprene styrene (SIS) thermoplastic elastomer are proposed to be tried as impact and environmental stress crack modifiers in HDPE/LLDPE blends.

The effect of adding fine particle fillers to HDPE/LLDPE blends on their mechanical properties is also proposed to be evaluated. It is also proposed to study the effect of dispersing them unevenly between the polymeric components.

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Chapter 2

MATERIALS AND EXPERIMENTAL PROCEDURES

POLYMERS

Commercially available polymer grades were used without any modifications. The important characteristics of the materials are as follows:

High Density Polyethylene (HDPE)

The HDPE grade used for the study was GA 7260 (PIL, Bombay) with a density of 0.957 g/cm^3 and an MFI of 5.2 g/10 min. The crystalline melting point of the grade was determined by differential scanning calorimetry as 132°C (Table 4.3).

Linear Low Density Polyethylene (LLDPE)

Two grades of LLDPE were used for the study.

1. LADENE 218 W (supplied by IPCL, Baroda) which had a density of 0.92 g/cm^3 and an MFI of 2 g/10 min. The crystalline melting point of the sample was determined by DSC as 122°C (Table 4.3).

2. LADENE 118 W (supplied by IPCL, Baroda) which had a density of 0.92 g/cm^3 and an MFI of 10 g/10 min.

Natural Rubber (NR)

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

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

Ethylene Propylene-diene Rubber (EPDM)

EPDM was JSR EP 33 with an ethylene content 33 mole %, diene content 1 mole % and a mooney viscosity [ML (1+4), 100°C] of 52.

Butyl Rubber (IIR)

IIR was Exxon 065 with 0.8 mole % unsaturation and a mooney viscosity [ML (1+8), 100°C] of 50.

Styrene Isoprene Styrene (SIS) Thermoplastic Rubber

SIS was Kraton D 1107 (Supplied by Shell Chemical Company) with an MFI of 9 g/10 min. and a styrene/isoprene ratio of 14/86.

ADDITIVES

Dicumyl Peroxide (DCP)

DCP was bis-(α - α' dimethylbenzyl) peroxide supplied by Merck.

Calcium Carbonate

Calcium carbonate was ground whiting with particle size below 30 nm.

Precipitated Silica

Silica was HISIL 235 (hydrated silica) with a particle size of 20-25 nm and surface area 150 m^2/g.

Carbon Black

Carbon black was General Purpose Furnace (GPF) Black (Supplied by M/s.Philips Carbon Black Company) with a particle size of 50-60 nm and a surface area 40 m^2/g.

Stearic Acid

Stearic acid was commercial grade.

Solvents

Toluene was analytical grade supplied by Merck.

EXPERIMENTAL METHODS

Blending of Polymers

Brabender plasticorder model PL 3S was used for the blending. Brabender plasticorder, a type of torque rheometer, has been widely used for polymer blending, processability studies of polymers and evaluation of the rheological properties of the polymer melts.[1,2] The torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material being mixed or flowing under preselected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 40 cc for the model used. Mixing or shearing of the material in the mixing chamber is done by two horizontal rotors with protrusions. The resistance generated by the material is made available with the help of a dynamometer. 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 silicone oil. The temperature can be varied upto 300°C.

Thermocouple with a temperature recorder is used for control and measurement of temperature. Different types of rotors can be employed depending upon the nature of the polymers.

The rotors can be easily mounted and dismounted due to 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 material can be charged into the mixing chamber to obtain a plastogram (torque-time curve). For blending, the appropriate constituents in the form of pellets were accurately weighed and tumbled to achieve a good mix. These blends were then fed to the Brabender plasticorder with roller mixing heads. The mixing parameters (temperature, time of mixing and rpm) were selected as follows. The temperature (150°C) was selected as the minimum temperature above the crystalline melting point of both polymers at which they fully homogenised.

The time and rpm of mixing (10 minutes, 30 rpm) were set to obtain a uniform torque value and a maximum tensile strength in the minimum possible time.

Preparation of Test Sheets

Sheets of 120x120x3 mm size were prepared at 200°C by compression moulding in an electrically heated press with provision for water cooling under pressure.

A 450 x 450 mm platen hydraulic press with precision temperature control (temperature tolerance ± 1°C) was used for the moulding. The moulding pressure could be varied upto 5000 kg/cm^2.

Gamma Irradiation

Irradiation was done by ^{60}Co γ-rays using a gamma chamber model 900 supplied by M/s.Bhabha Atomic Research Centre, Bombay. It offers an irradiation volume of approximately 1000 cc. The unit essentially consists of the following components.

(a) Source cage
(b) Biological sheild for the source
(c) Central drawer incorporating the sample chamber
(d) Drive system
(e) Control panel
(f) External cabinet

The main features of the chambers are shown in Fig.2.1.

The source cage holds the radiation source pencils vertically and symmetrically distributed along its

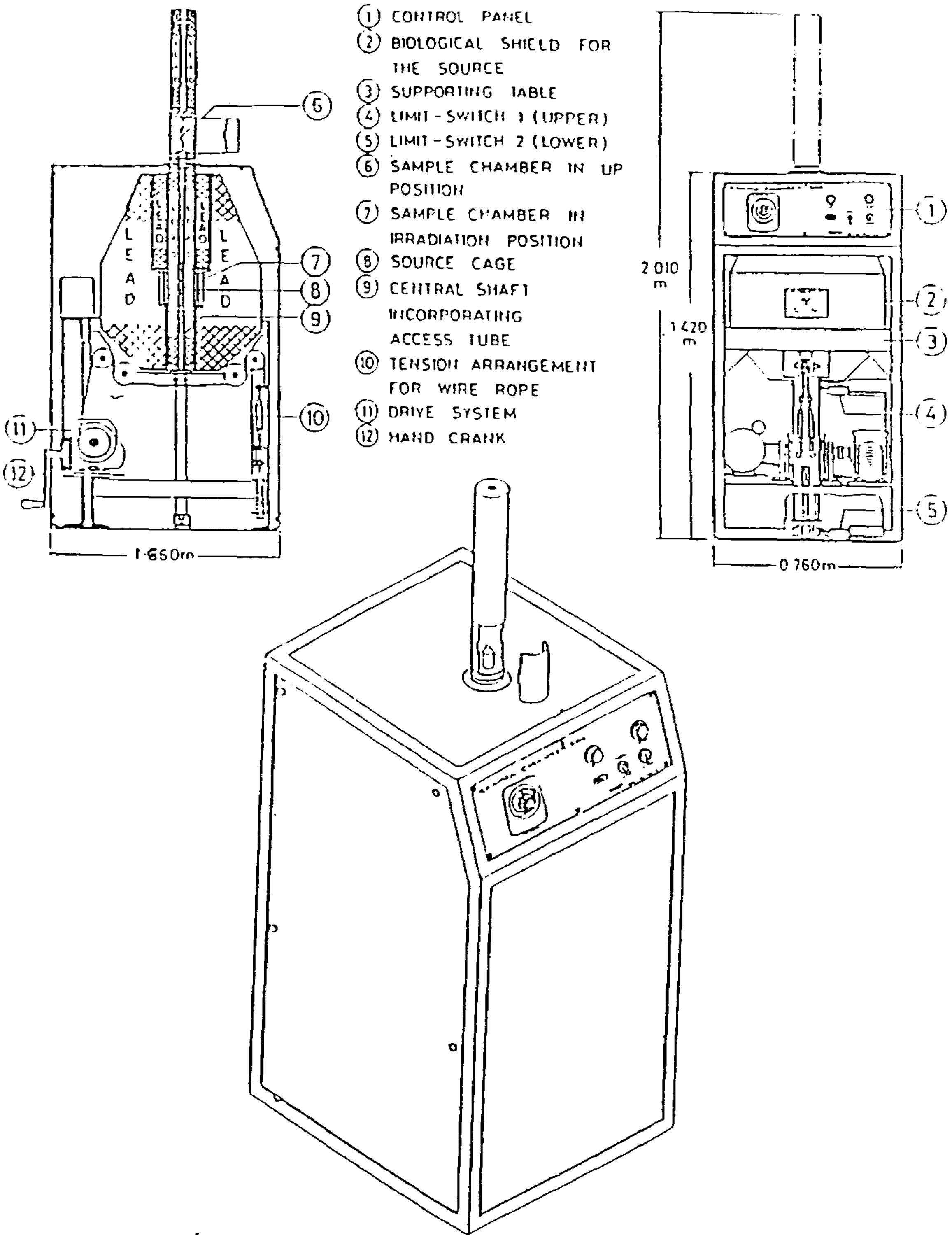

FIG.2.1 SCHEMATIC DIAGRAM OF A GAMMA CHAMBER.

periphery. The cage can hold a maximum of 24 pencils containing ^{60}Co in the form of pellets or aluminium clad slugs.

The biological shield is a lead filled steel container and surrounds the source cage. It consists of two parts, main outer shield and an inner removal plug. The radiation source is housed in the main outer shield.

The central drawer is one long cylinder consisting of two cylindrical stainless steel clad lead shields with the sample chamber fitted in between them. The sample chamber is 10 cm diameter, 14 cm in height and made of stainless steel. The central drawer is raised or lowered by a wire rope passing over a system of pulleys and wound on a drum by a geared motor. This enables the sample chamber to be moved up or down as is required. For irradiation the drawer is lowered until the sample chamber reaches the centre of the source cage. For loading or unloading of sample the drawer is raised. Control panel allows the smooth functioning of the equipment. The radiation is emitted at the rate of 1 M rad/hr.

Evaluation of Mechanical Properties

Tensile Tests

Stress-strain properties were measured in tension by stretching the specimens at a uniform rate and simultaneously measuring the force on the specimen. Uniaxial tensile stress-strain data at 25°C and 50% relative humidity were obtained according to the procedure outlined in ASTM standard D-638. Dumbbell shaped specimens (ASTM Type IV) were tested in a Zwick UTM model 1445 at a constant cross head speed of 50 mm/min. Elongation was measured on these dumbbell specimens using a strain gauge extensometer.

The ultimate tensile strength (TS) of the sample was measured as the force measured by the load cell at the time of break divided by the original cross sectional area of the sample at the point of minimum cross section.

$$\text{Ultimate tensile strength} = \frac{\text{Force (N)}}{\text{Cross Sectional Area (mm}^2\text{)}}$$

The elongation at break (EB%) of the sample was measured in terms of its initial length L_o and final length L_1 as,

$$\text{EB \%} = \frac{L_1 - L_o}{L_o} \times 100$$

The modulus of elasticity was determined as the rate of the stress to corresponding strain below the proportional limit.

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 and other defects.

Wear Resistance

The wear resistance of the samples was measured on a Zwick abrader according to ASTM D 1242 (1988). The test specimen in the form of a disc (50 mm dia and about 6 mm thick) was abraded using number 240 emery paper, with the abrader under 10 N load.

Environmental Stress Crack Resistance

The environmental stress crack (ESC) resistance of polyethylene blends was determined as per ASTM D 1693 (1980).

Environmental stress cracking is the failure in surface initiated brittle fracture of polymer specimen or a part under polyaxial stress in contact with a medium in the absence of which fracture does not occur under the same conditions of load. Combinations of external and/or internal stresses may be involved and the sensitising medium may be gas, liquid, semisolid or solid. The test piece was bent into 'U' shape held in a metal channel and exposed to the aggressive environment at elevated temperature, at 50°C and examined at intervals for failure. Ten replicate test pieces were used and the duration of the test was 168 hours. The time for 5 out of the 10 specimen to fail is reported. The test piece is a strip 38 mm long and 13 mm wide, in which a controlled cut (imperfection) is made with a blade. The stress crack failure is defined as 'any crack visible to the observer with normal eye sight'. The extension of the controlled imperfection is not considered as failure.

Density

The densities of the polymer samples were measured as per 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,

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

Rheological Evaluation Using Capillary Rheometer

For evaluating the rheological characteristics of the blends, a Goettfert capillary viscometer model 1500 was used. A schematic diagram of the capillary rheometer is shown in Fig.2.2. The flow patterns in the capillary is presented in Fig.2.3. The dies used for the study had a diameter of 1 mm and L/D ratio 10, 20 and 30. The Newtonian shear rates used in this study varied from about 20 S^{-1} to 3500 S^{-1}. The apparent shear stress at the wall was determined from the equation,

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

where, ΔP includes the pressure drop at the capillary entrance plus the pressure drop along a capillary of length L and radius R. The apparent shear rate at the wall was calculated from,

$$\gamma_{w_{app}} = 4Q/\pi R^3$$

where, Q is the volumetric flow rate through a capillary of radius R. From the shear stress and shear rate the apparent viscosity was determined as,

$$\eta = \tau_{w_{app}}/\gamma_{w_{app}}$$

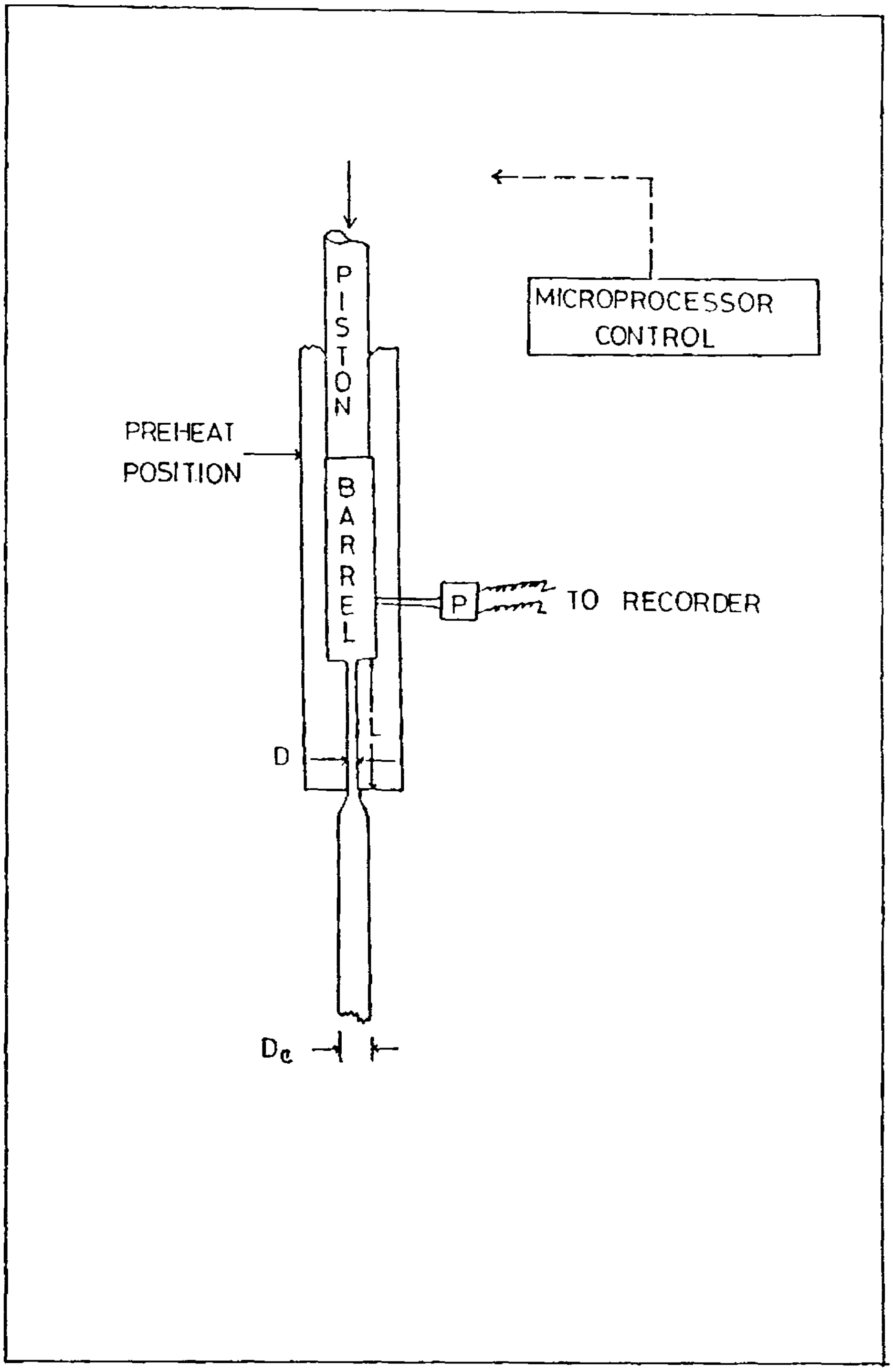

FIG.2.2 SCHEMATIC DIAGRAM OF A CAPILLARY RHEOMETER.

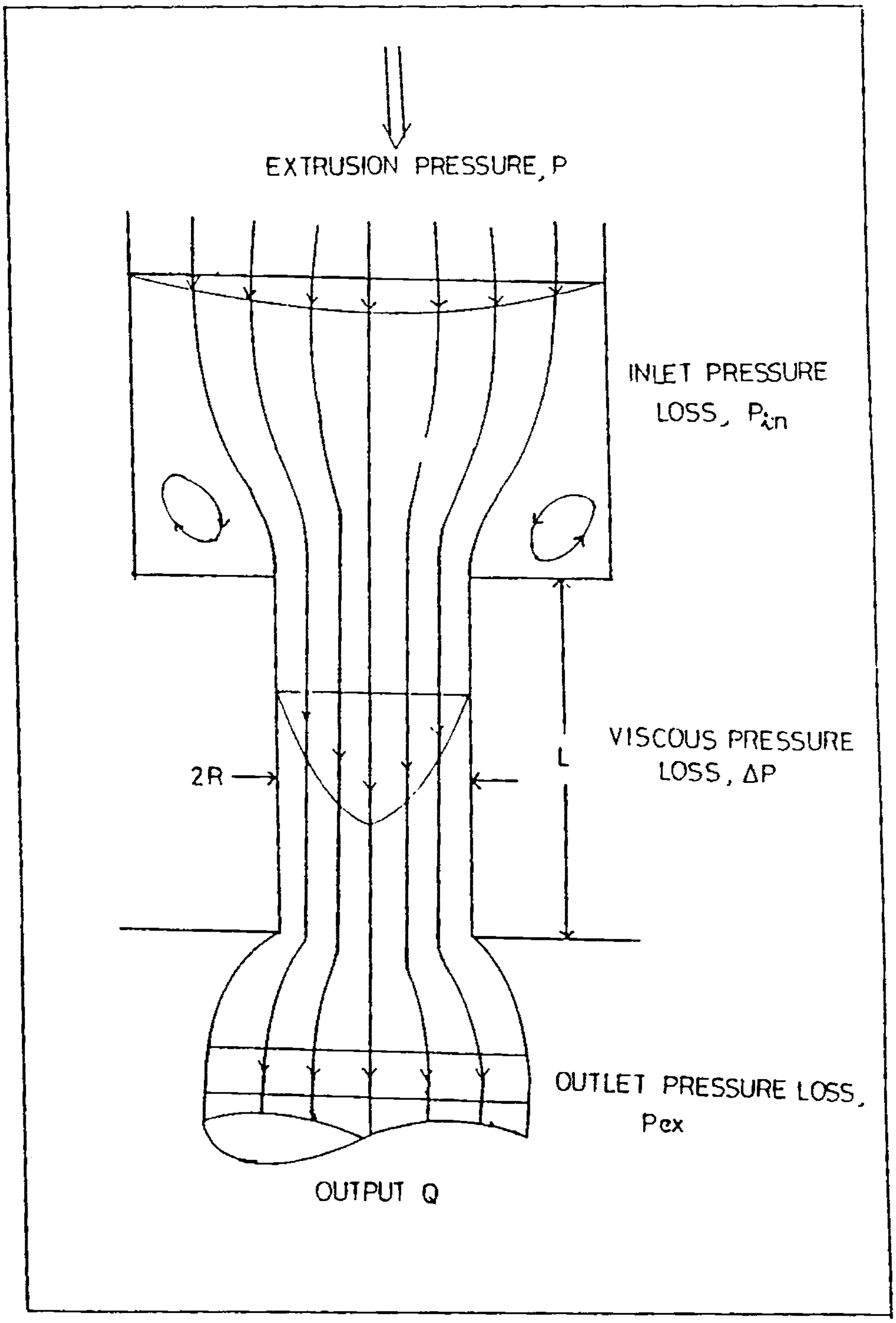

FIG.2.3 THE FLOW PATTERNS IN THE CAPILLARY VISCOMETER.

The power law exponent (n) of the Ostwald de Waale model[3,4] was calculated from,

$$\tau = K(\gamma)^n$$

The temperature dependence of the viscosity was calculated from the activation energy E for viscous flow from an Arrhenius type expression.

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

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

Corrections Employed in Capillary Rheometer

For capillary rheometry, a series of corrections is appropriate to determine the true shear viscosity.[5] Generally the most important correction is that due to 'end effect'. This effect is negligible when the die used has a large ratio of length (L) to diameter (D). The end effect can be eliminated by using two or more dies of the same diameter but different lengths[6] if the pressure drop over a finite length (ΔP) is plotted versus L/D for the same shear rate in each die. The Bagley plot so obtained should be linear and the intercept at L/D = 0 determines the end correction factor or Bagley correction factor (P_c). The true shear stress at the capillary wall (τ_w) can then be calculated, by using the expression,

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

Polymer melts show non-Newtonian behaviour and so the apparent shear rates may be corrected by the degree of non-Newtonian behaviour (Rabinowitsch correction) by using the slope of the flow curve[8] as,

$$\gamma_w = \left(\frac{3n + 1}{4n}\right) \gamma_{w_{app}}$$

Melt Elasticity Measurements

Melt elasticity of the melts was measured from their die swell behaviour.

Die Swell

The die swell is related to the elasticity and first normal stress difference of polymer melts.[9] The first normal stress coefficient and the first normal stress difference are used to describe the elastic component of the visco-elastic flow behaviour of polymer melts.

Elasticity of the melt results in the expansion of the polymer on its exit from the die. The extrudate swell ratio D_e/D, where D_e and D are diameters of the extrudate and die respectively is a direct measure of melt elasticity.

Recoverable Shear Strain (γ_R)

Bogue and White[10,11] suggested the use of recoverable shear strain, γ_R for describing and distinguishing the fluid elasticity of different visco-elastic materials as a function of shear stress. γ_R was calculated from the relation,[12]

$$\gamma_R = (\tau_{11} - \tau_{22})/2\,\tau_{w_{app}}$$

where the first normal stress difference,

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

Apparent Shear Modulus (G)

The apparent shear modulus (G) of the polymer melts was calculated from the following relation,[12]

$$G = \tau_{w_{app}} / \gamma_R$$

Rheological Evaluation Using Brabender Plasticorder

The Brabender plasticorder was also used to study the rheological behaviour of HDPE/LLDPE blends. The instrument imparts a very complex shearing motion to the polymer and subsequently the data cannot be taken as fundamental rheological properties. However, the design of the mixing head of the plasticorder is similar to that of an internal mixer, and hence the behaviour of the melt in actual processing can be studied. Another advantage is that due to complex shearing, the polymer melts at comparatively lower temperature. The relationship obtainable from the rotor torque and rotor speed was shown to be similar to the usual power law expression[13] as,

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

where, M is the torque, n the power law index, C(n) a function weakly dependant on n, K a constant and S rotor speed.

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

The energy required to plasticize a polymer over a period of time at a given temperature and shear may be calculated from the area under the torque-time curve at that temperature for the specified period of time. The energy W may be calculated using the formula,

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

where n is the number of revolutions per minute of rotor, t_1 the initial time, t_2 the final time and M the torque in Nm.

Gel Content Measurement

The gel content of the crosslinked samples was measured as per ASTM D 2765-84 by extracting the soluble component in hot toluene for 12 hrs using a soxlet assembly and drying in a vacuum oven set at 70°C for 24 hrs. About 0.5 gm of each sample was 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 12 hrs, dried in vacuum and the gel fraction was calculated from the initial and final sample weights.

Differential Scanning Calorimetry (DSC)

DSC thermograms were taken on a Perkin-Elmer DSC-7 model at a heating/cooling rate 10°C/minute under nitrogen atmosphere as per ASTM D 3417 (1988). DSC yields peaks relating to endothermic and exothermic transitions, and show changes in heat capacity. The DSC method also yields quantitative information relating to enthalpic changes in the polymer.[14-16]

The DSC method uses a servosystem to supply energy at varying rate to the sample and the reference, so that the temperature of the two stay equal. The DSC output plots energy supplied against average temperature. By this method the area under the peak can be directly related to the enthalpic changes quantitatively.

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Chapter 3

MECHANICAL AND RHEOLOGICAL EVALUATION OF HDPE/LLDPE BLENDS

Polyethylene blends have become commercially important for optimising the mechanical properties and processability of individual members. Linear low density polyethylene (LLDPE) has better mechanical properties than LDPE. It has a higher tensile strength, elongation at break and also has higher resistance to puncture and tearing. One of the draw backs of LLDPE is that it has poorer fluidity in the molten state than LDPE. The viscosity of molten LLDPE is about 50% higher than molten LDPE with the same MFI value. As a consequence of the greater viscosity of LLDPE in the molten state it is necessary to carry out processing of the polymer at a higher temperature, using extruder with a modified design. However, the processing problem of LLDPE can be minimised by blending with LDPE or HDPE.

Hence blends of LDPE and LLDPE are now regarded as excellent materials for film manufacture because they combine the processability of LDPE and the good mechanical and environmental cracking resistance of LLDPE.[1-3] While many studies have been undertaken on LDPE/LLDPE and HDPE/LDPE blends, only very few studies are reported on HDPE/LLDPE blends. However, it is reported that a blend of HDPE and LLDPE exhibited a crystallisation exotherm of a single peak which indicates that it is a compatible system.[4]

1. EVALUATION OF MECHANICAL PROPERTIES OF BLENDS OF HDPE AND LLDPE

Experimental

HDPE was blended with two selected grades of LLDPE such that one of them had a higher melt viscosity than HDPE (LLDPE 1) while the other had a lower melt viscosity (LLDPE 2). The polymer blends were prepared in the weight ratios 80/20, 60/40, 40/60 and 20/80. The appropriate constituents in the form of pellets were accurately weighed and then tumbled to achieve a good mix. These blends were then extruded in a laboratory extruder having a screw length to diameter (L/D) of 20:1 attached to a Brabender plasticorder at a die temperature of 220°C and pelletised. This process was repeated again for better homogeneity.

Sheets of 120x120x3 mm size were prepared at 200°C by compression moulding. Test specimens for tensile tests were cut from the moulded sheets with dimensions according to the standard specifications.

Tensile stress-strain data were obtained at 25°C and 50% relative humidity as per the ASTM standard D-638.

Dumbbell specimens (ASTM type IV) were tested in the Zwick UTM at a constant crosshead speed of 50 mm/min.

Results and Discussion

The tensile stress-strain behaviour of the HDPE/ LLDPE 1 blends is shown in Fig.3.1. LLDPE has a lower yield stress than HDPE, but a much higher elongation at break. The very high elongation at break of LLDPE 1 is due to its stable necking behaviour. In the case of LLDPE 1, an increase in the neck occurs as a result of the transfer of material from the wider part of the specimen, while in the case of HDPE it occurs by deformation of the already transformed material. The necking behaviour of HDPE and LLDPE 1 is schematically shown in Fig.3.2. The tensile properties of the blends vary smoothly between those of the parent polymers. The obvious effects of adding LLDPE to the blends are to lower the yield stress and increase the elongation at break. The strain hardening during plastic flow is similar for both the polymers and the blends.

Fig.3.3 shows the stress-strain curves of HDPE/ LLDPE 2 blends. LLDPE 2 has a lower yield stress and elongation at break than HDPE. Obviously, the low

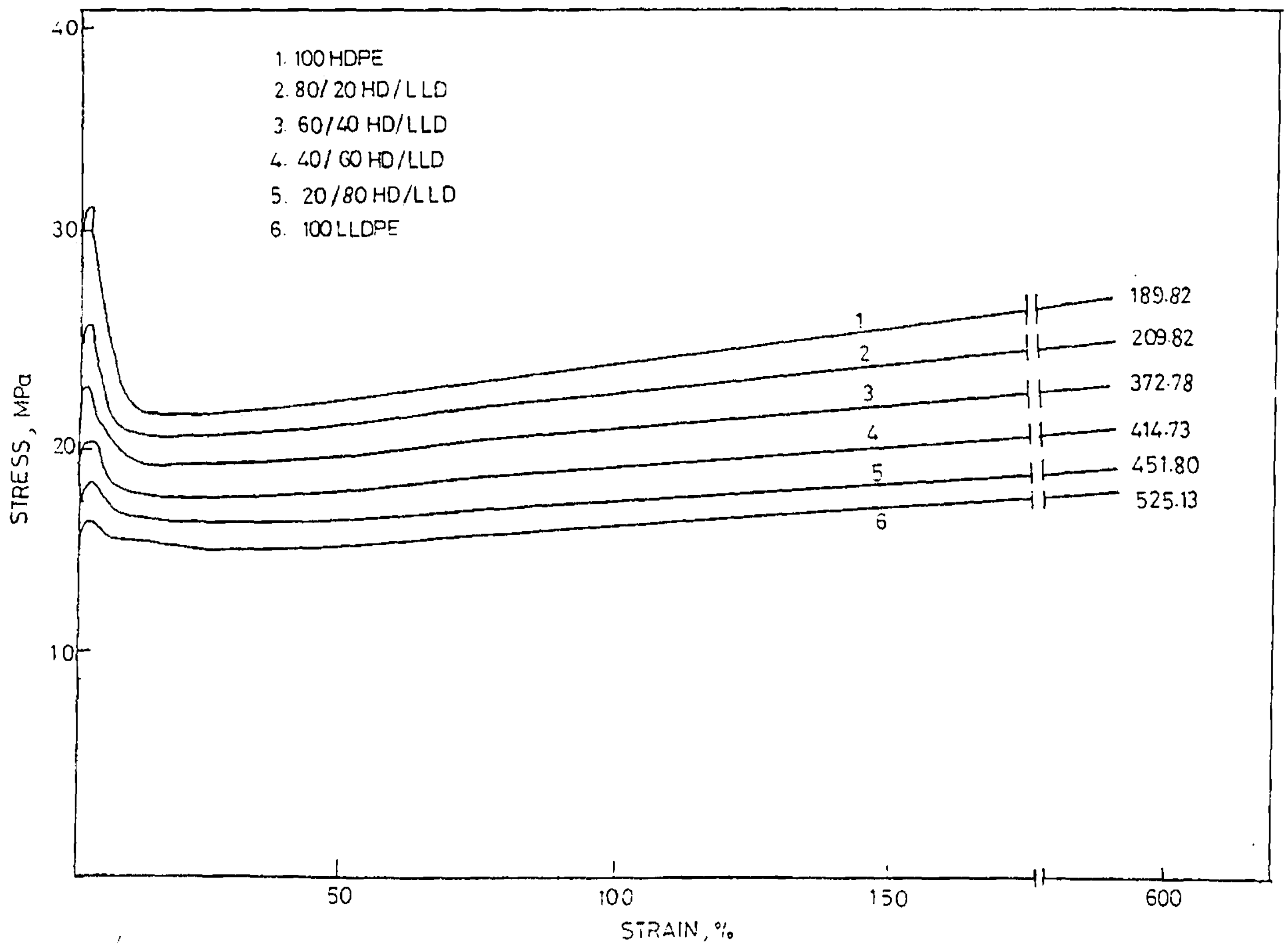

FIG.3.1 STRESS-STRAIN BEHAVIOUR OF HDPE/LLDPE 1 BLENDS.

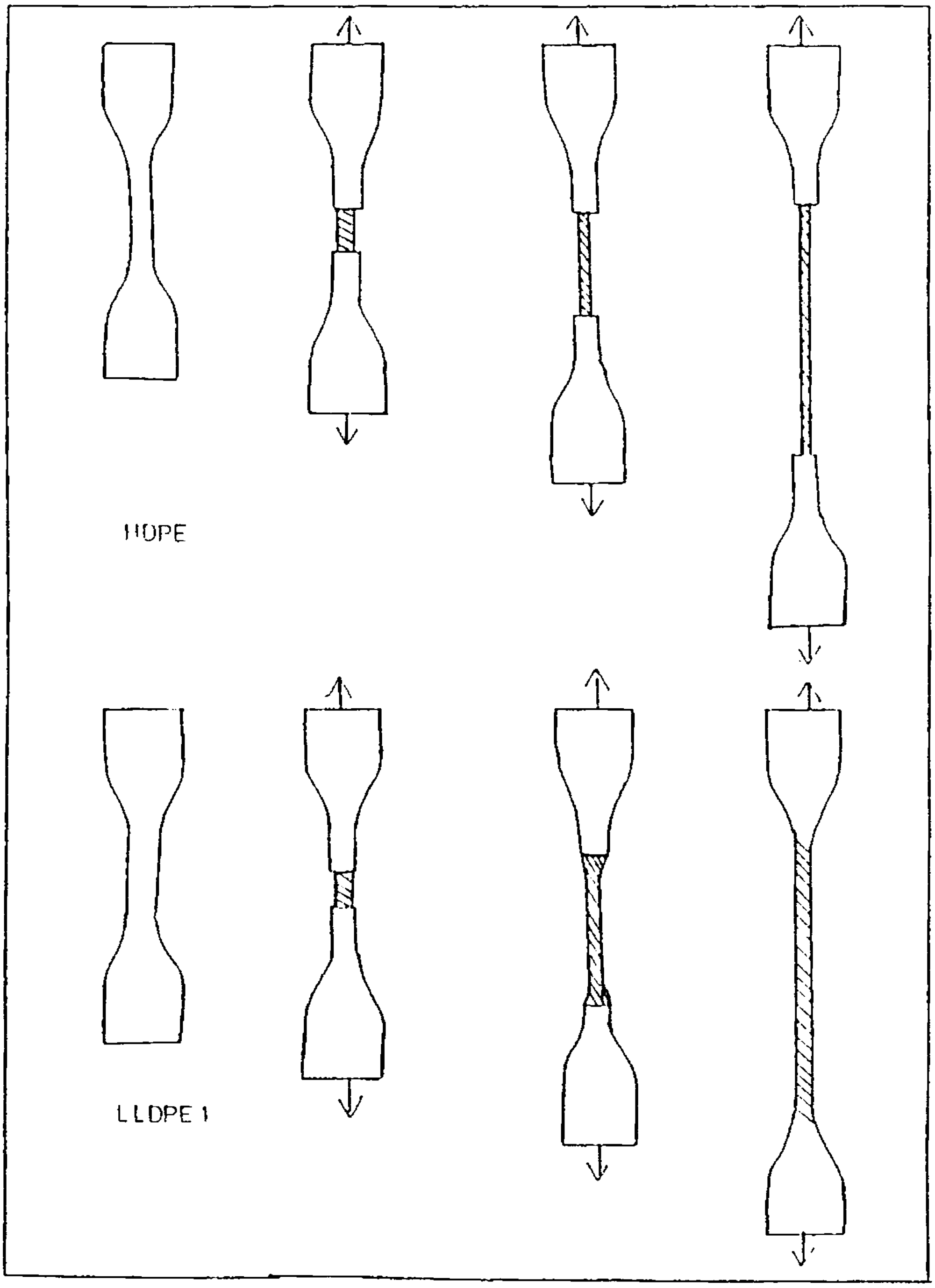

FIG.3.2 SCHEMATIC DIAGRAM OF THE NECKING BEHAVIOUR OF HDPE AND LLDPE 1.

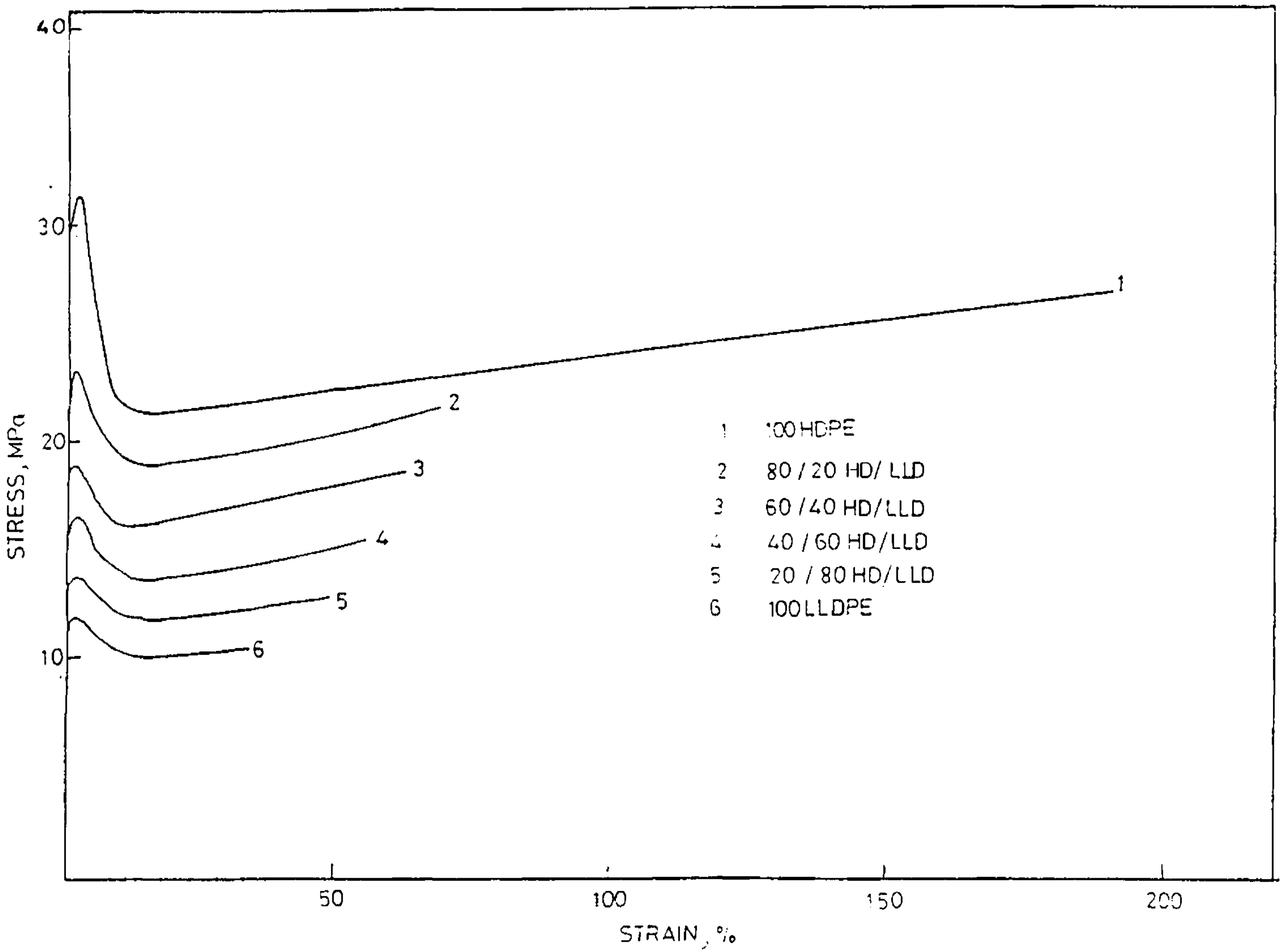

FIG.3.3 STRESS-STRAIN BEHAVIOUR OF HDPE/LLDPE 2 BLENDS.

molecular weight sample cannot support a stable neck. However, in this case also the properties of the blends vary smoothly between those of the parent polymers, HDPE and LLDPE 2.

The tensile behaviour of the HDPE/LLDPE 1 and HDPE/LLDPE 2 suggests that the blends exhibit sufficient compatibility between HDPE and LLDPE in the solid phase, irrespective of the different grades chosen. The ability to co-crystallise may be a strong driving force for the miscibility of these blends.[5]

2. EVALUATION OF THE RHEOLOGICAL PROPERTIES OF HDPE/LLDPE BLENDS USING CAPILLARY RHEOMETER

HDPE/LLDPE blends were prepared in the weight ratios 80/20, 60/40, 40/60 and 20/80 using Brabender plasticorder. For evaluating the rheological characteristics of the blends, a Goettfert capillary viscometer model 1500 with capillary dies of 1 mm diameter and lengths of 10, 20 and 30 mm were used. These three different capillaries were used to evaluate the Bagley end corrections. The Newtonian shear rates used in this study varied from about 20 S^{-1} to 3500 S^{-1} and the temperatures employed were 160, 170 and 180°C.

Figs.3.4 and 3.5 show the variation of apparent viscosity with apparent shear rate of HDPE/LLDPE 1 and HDPE/LLDPE 2 blends. These flow curves are identical indicating their strong non-Newtonian behaviour. The flow curves converge at the high shear rate area, indicating improved compatibility. All the flow curves could be approximated by straight lines and hence described the Ostwald-de Waale power law relation.

Figs.3.6 and 3.7 show curves of apparent shear viscosity versus composition, obtained by cross plotting the flow curves at a particular shear rate. Also plotted in the figures are viscosities of the blends predicted from viscosities of parent polymers, calculated from simple additivity rules.[6] Conformity to these simple mixing rules is considered to result from miscibility in the melt.[7] In both cases, the experimental values are very close to the predicted values with only minor positive deviation, which have also been shown to imply miscibility. These figures thus suggest that HDPE/LLDPE blends are also compatible in the melt. This is obviously due to the similarities in the structure of HDPE and LLDPE, both possessing regular short branches.

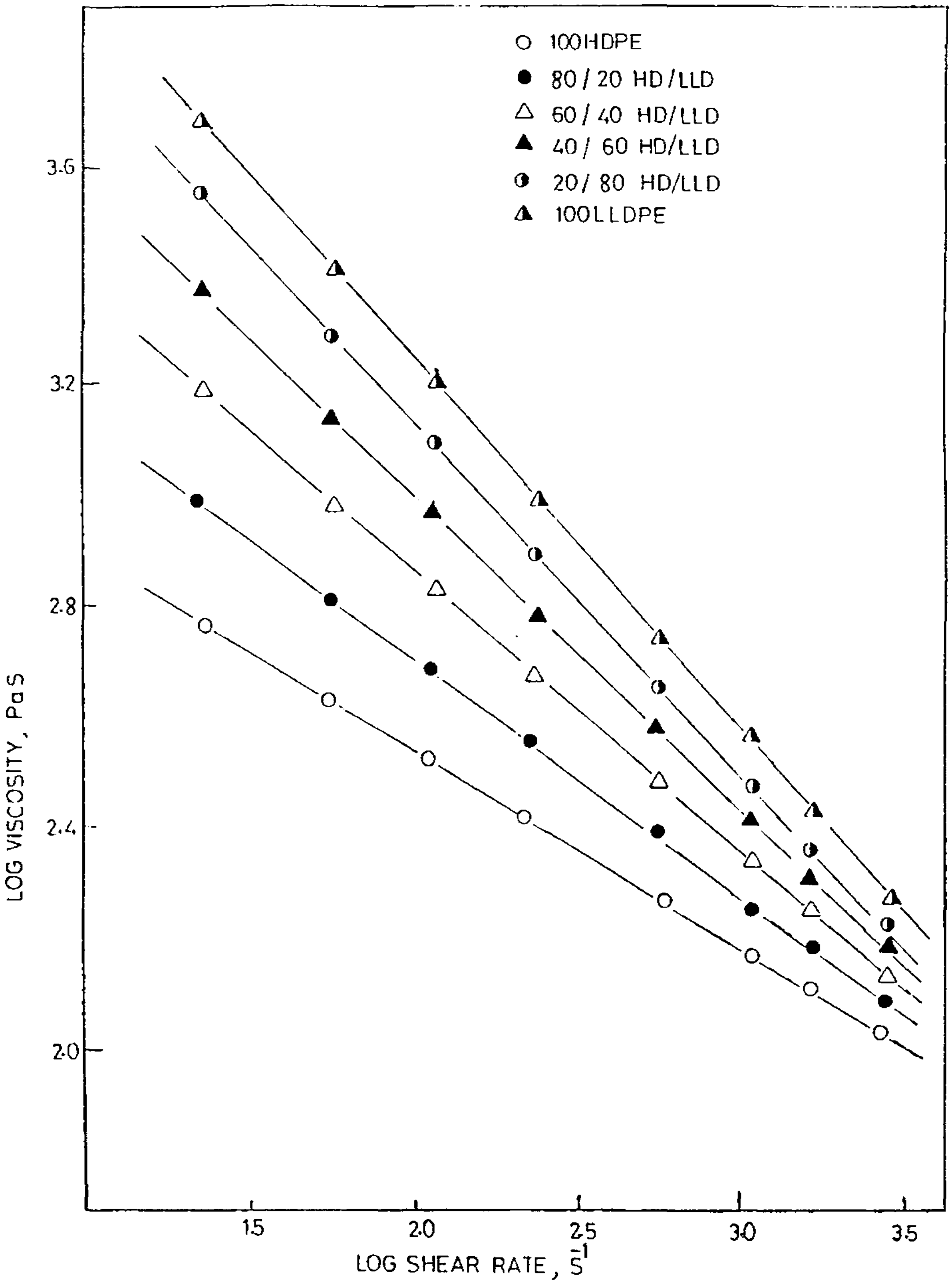

FIG.3.4 VISCOSITY Vs. SHEAR RATE CURVES OF HDPE/LLDPE 1 BLENDS AT 160°C.

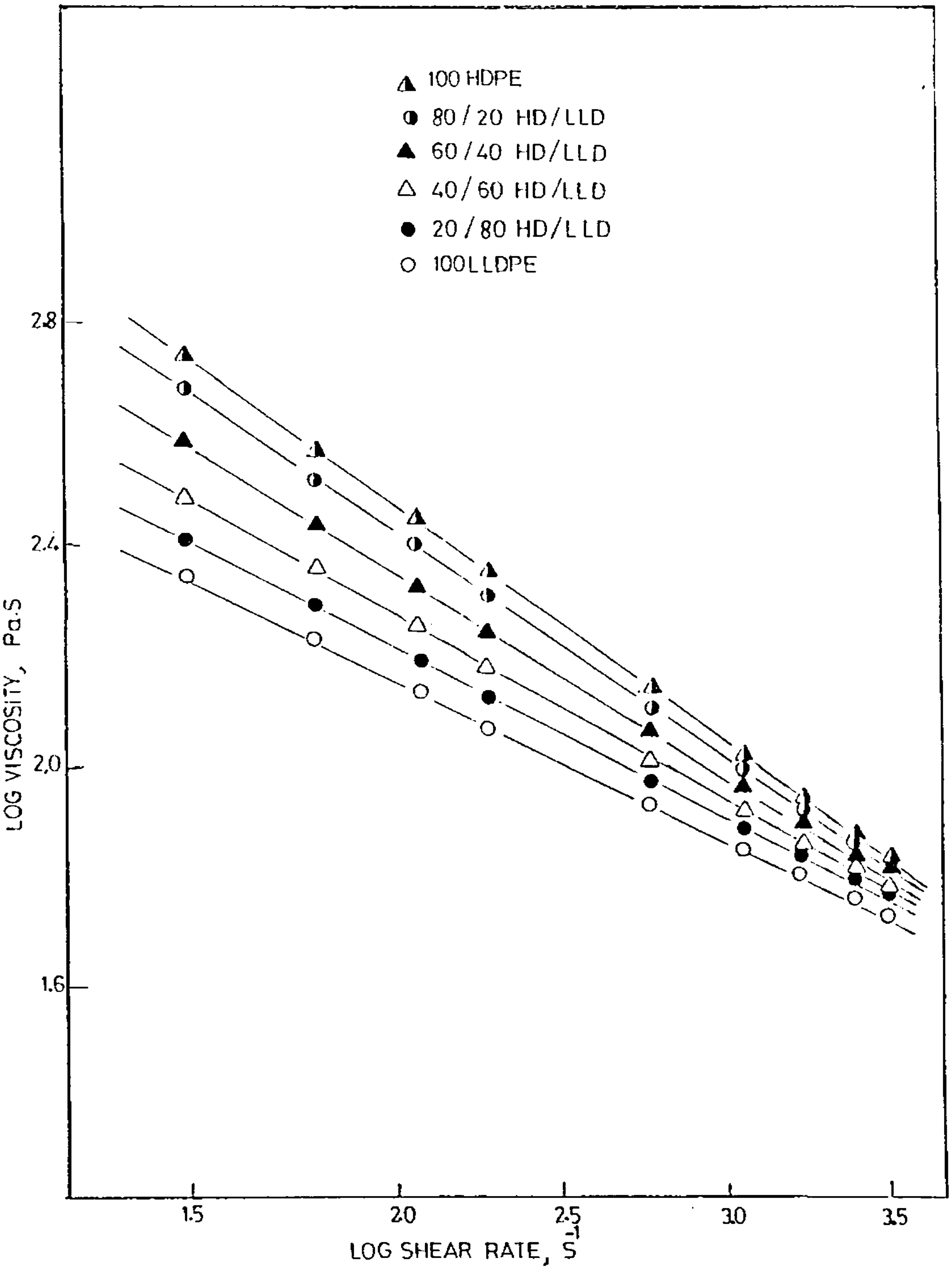

FIG.3.5 VISCOSITY Vs. SHEAR RATE CURVES OF HDPE/LLDPE 2 BLENDS AT 160°C.

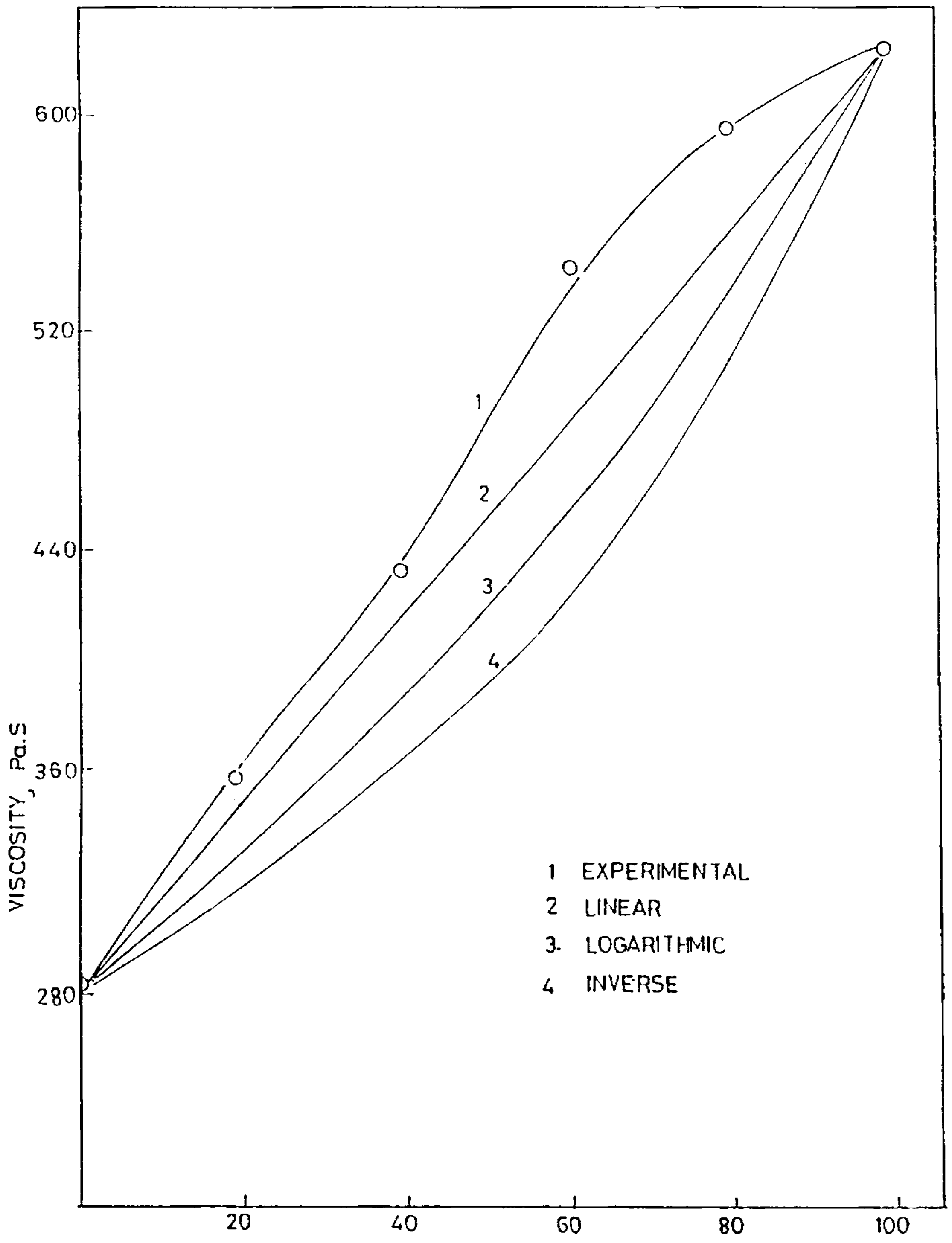

FIG.3.6 VARIATION OF VISCOSITY OF HDPE/LLDPE 1 BLENDS WITH COMPOSITION (SHEAR RATE 57.6 S^{-1}, TEMPERATURE 160°C.).

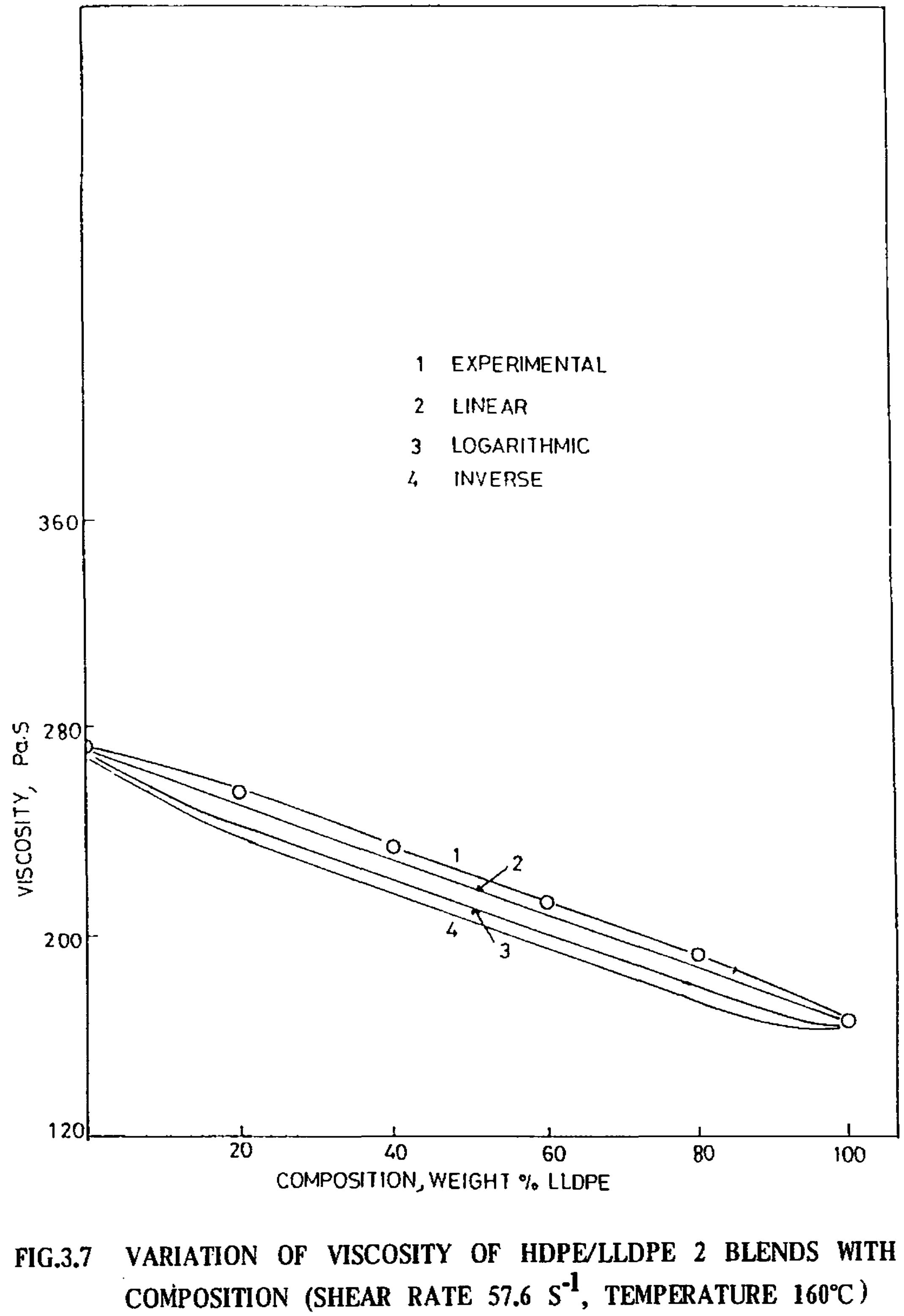

FIG.3.7 VARIATION OF VISCOSITY OF HDPE/LLDPE 2 BLENDS WITH COMPOSITION (SHEAR RATE 57.6 S^{-1}, TEMPERATURE 160°C)

The flow curves of the blends are replotted in Figs.3.8 and 3.9 and the power law exponents of the blends calculated from the curves are shown in Table 3.1. It can be observed that LLDPE 1 is more non-Newtonian than HDPE while LLDPE 2 is less non-Newtonian than HDPE. Since structure of HDPE and LLDPE have close similarities, the most important factor contributing to the non-Newtonian behaviour may be the average molecular weight of the polymers. The usual behaviour of the polymers is to become more non-Newtonian with increase in the molecular weight. The power law exponent for the blends also varies smoothly between those of the parent polymers indicating compatibility of the polymers in the melt.

The slope of the log η vs. 1/T plot is proportional to an apparent energy of activation for viscous flow. Figs. 3.10 and 3.11 are such plots of HDPE/LLDPE 1 and HDPE/LLDPE 2 blends. The activation energies calculated for the various blends are shown in Table 3.1.

The activation energy for flow for low viscosity material is generally smaller than that for high viscosity system. But the behaviour of these blends displays a very interesting phenomenon. LLDPE 1 having a higher viscosity

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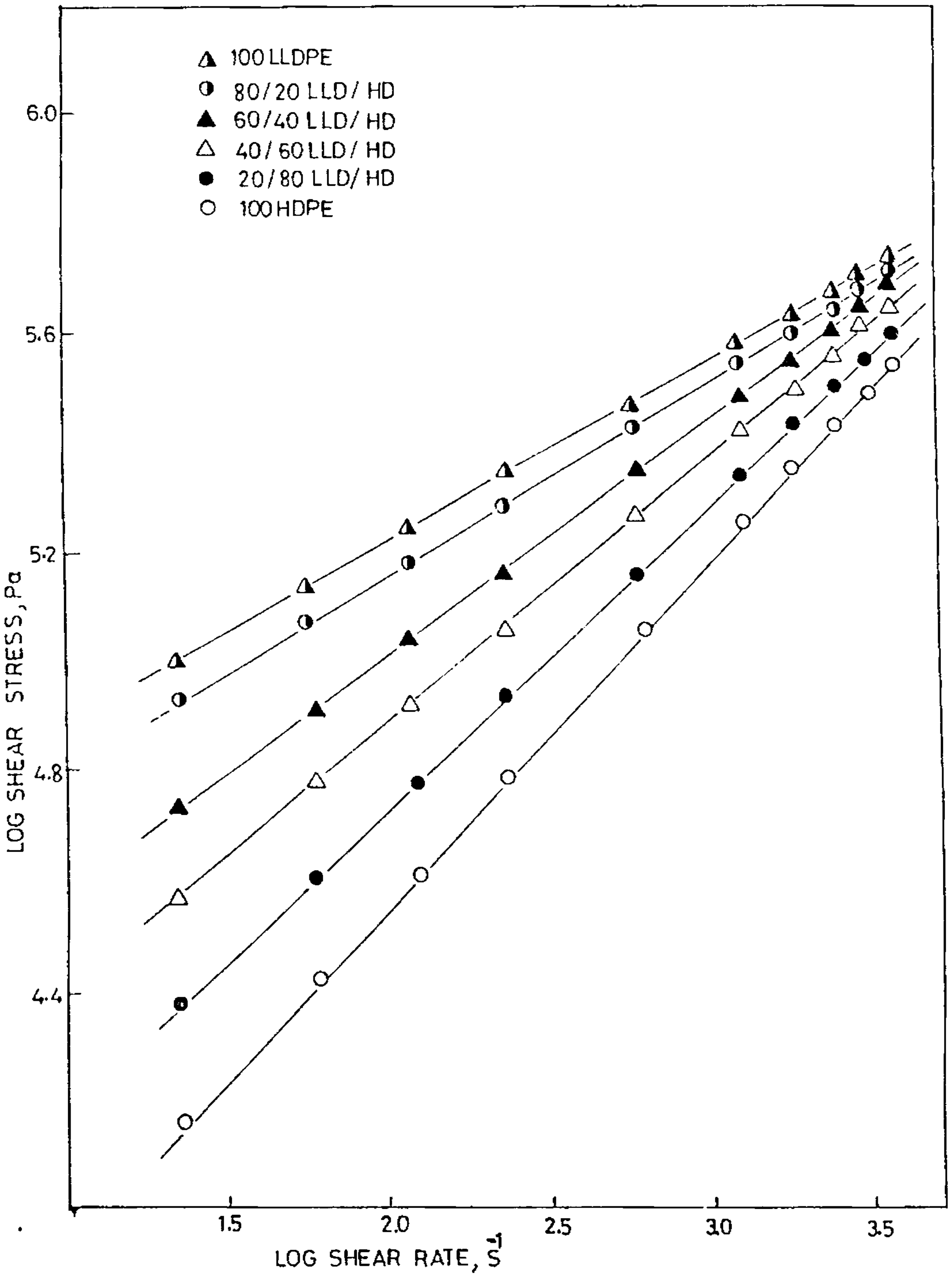

FIG.3.8 FLOW CURVES OF HDPE/LLDPE 1 BLENDS AT 160°C.

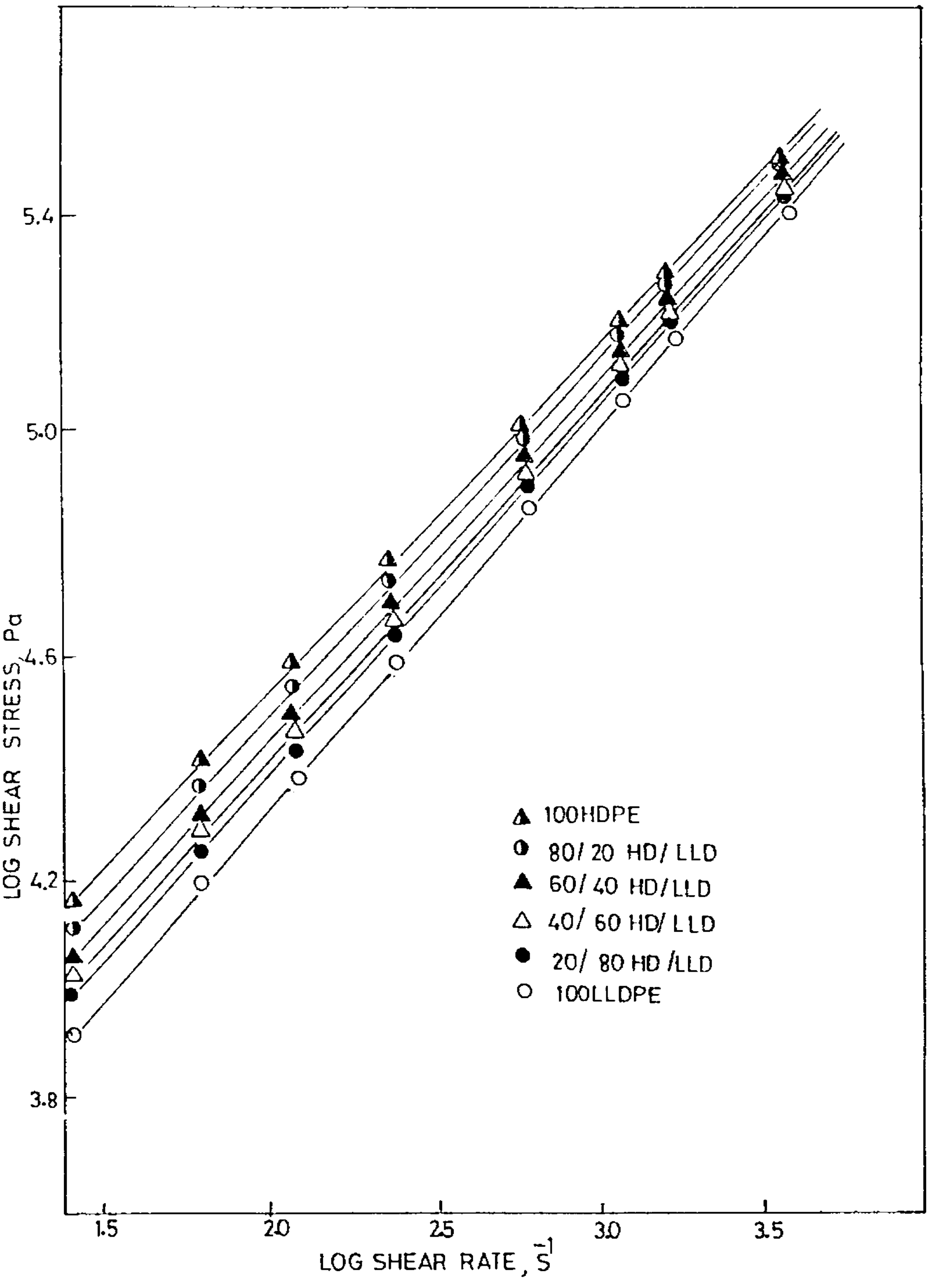

FIG.3.9 FLOW CURVES OF HDPE/LLDPE 2 BLENDS AT 160°C.

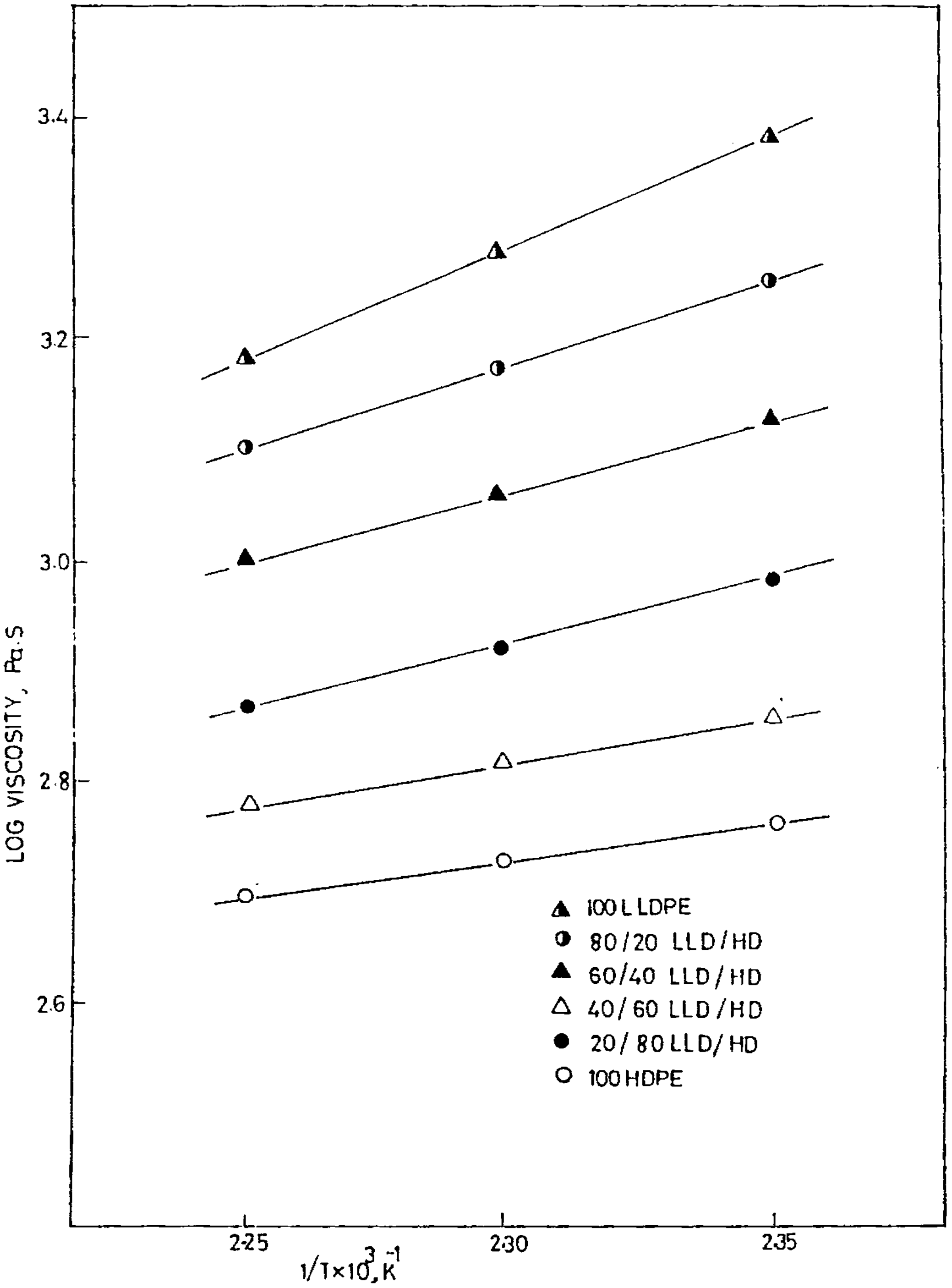

FIG.3.10 VISCOSITY Vs. 1/T CURVES OF HDPE/LLDPE 1 BLENDS (SHEAR RATE 115.2 S^{-1}).

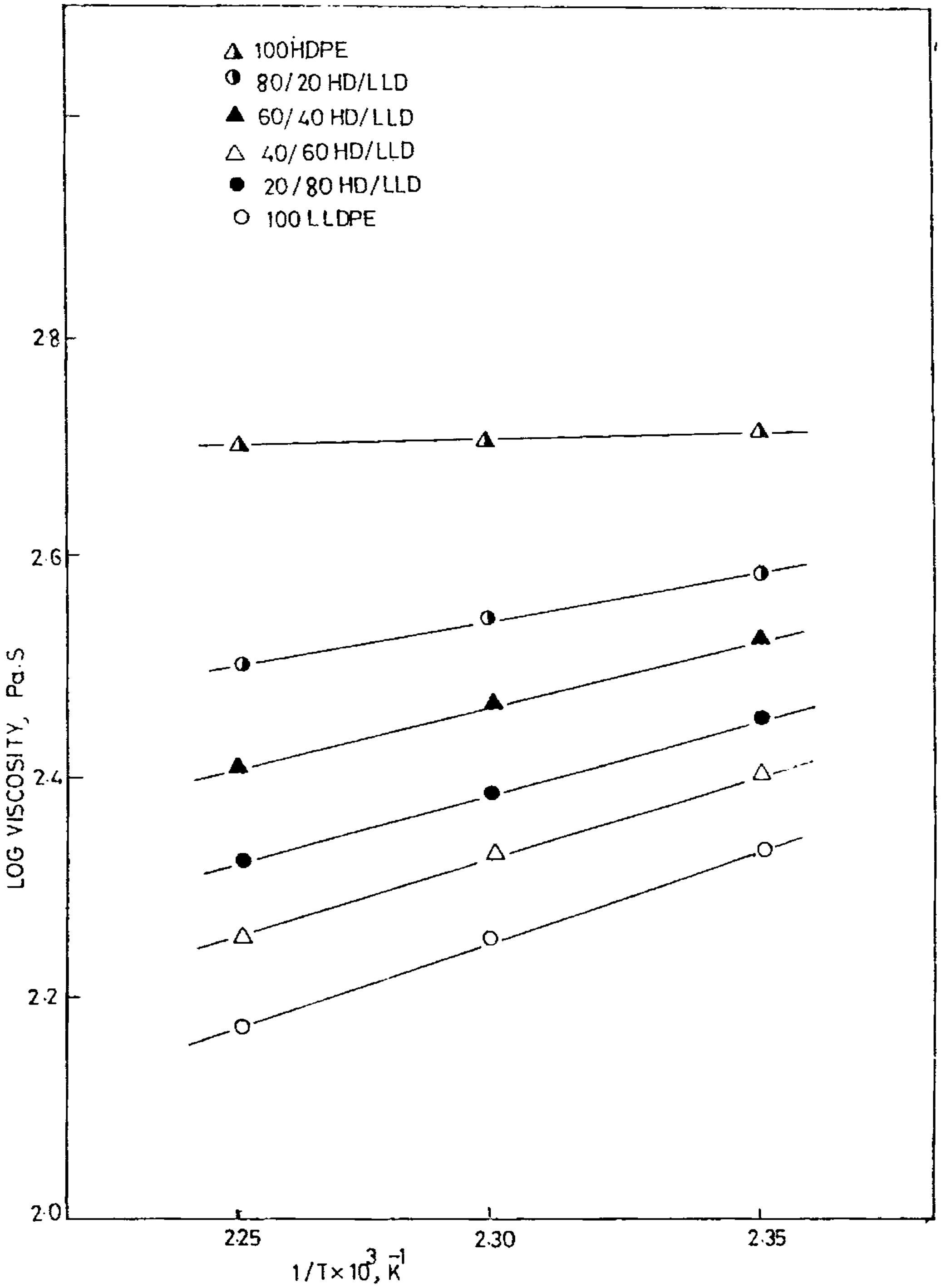

FIG.3.11 VISCOSITY Vs. 1/T CURVES OF HDPE/LLDPE 2 BLENDS (SHEAR RATE 115.2 S^{-1}).

Table 3.1 Dependence of non-Newtonian behaviour and activation energy on blend composition

LLDPE (wt. %)		Power law exponent (n)	Activation energy (kJ/mol)
HDPE/ LLDPE 1	0	0.65	14.5
	20	0.60	12.5
	40	0.54	10.7
	60	0.48	10.4
	80	0.42	9.7
	100	0.36	8.6
HDPE/ LLDPE 2	0	0.65	14.5
	20	0.60	15.1
	40	0.67	16.2
	60	0.68	18.4
	80	0.69	21.0
	100	0.70	22.0

than HDPE, shows a slightly lower activation energy than HDPE and LLDPE 2, which has a much lower viscosity than HDPE and LLDPE 1 shows a higher activation energy. This may imply that LLDPE does possess a certain amount of crystallinity in the melt. The degree of crystallinity may be higher for the lower molecular weight LLDPE due to its increased mobility and ability to pack into ordered regions. Such crystallisation effects have been observed for polypropylene melts.[9]

Bagley Correction Factor (P_c)

Bagley correction factor, P_c for HDPE/LLDPE 1 blends was evaluated from the flow data recorded with three different dies of L/D ratio 10, 20 and 30. Bagley plots, ΔP as a function of L/D for HDPE/LLDPE blends at various composition are quite linear (Fig.3.12). This linearity of Bagley plot confirms the absence of slippage at the capillary wall and at the interface boundaries where the slippage is believed[10] to cause curvature in the Bagley plot.

The true shear stress at the wall, τ_w was calculated by applying Bagley correction factor. Variation of Bagley correction factor as a function of blend composi-

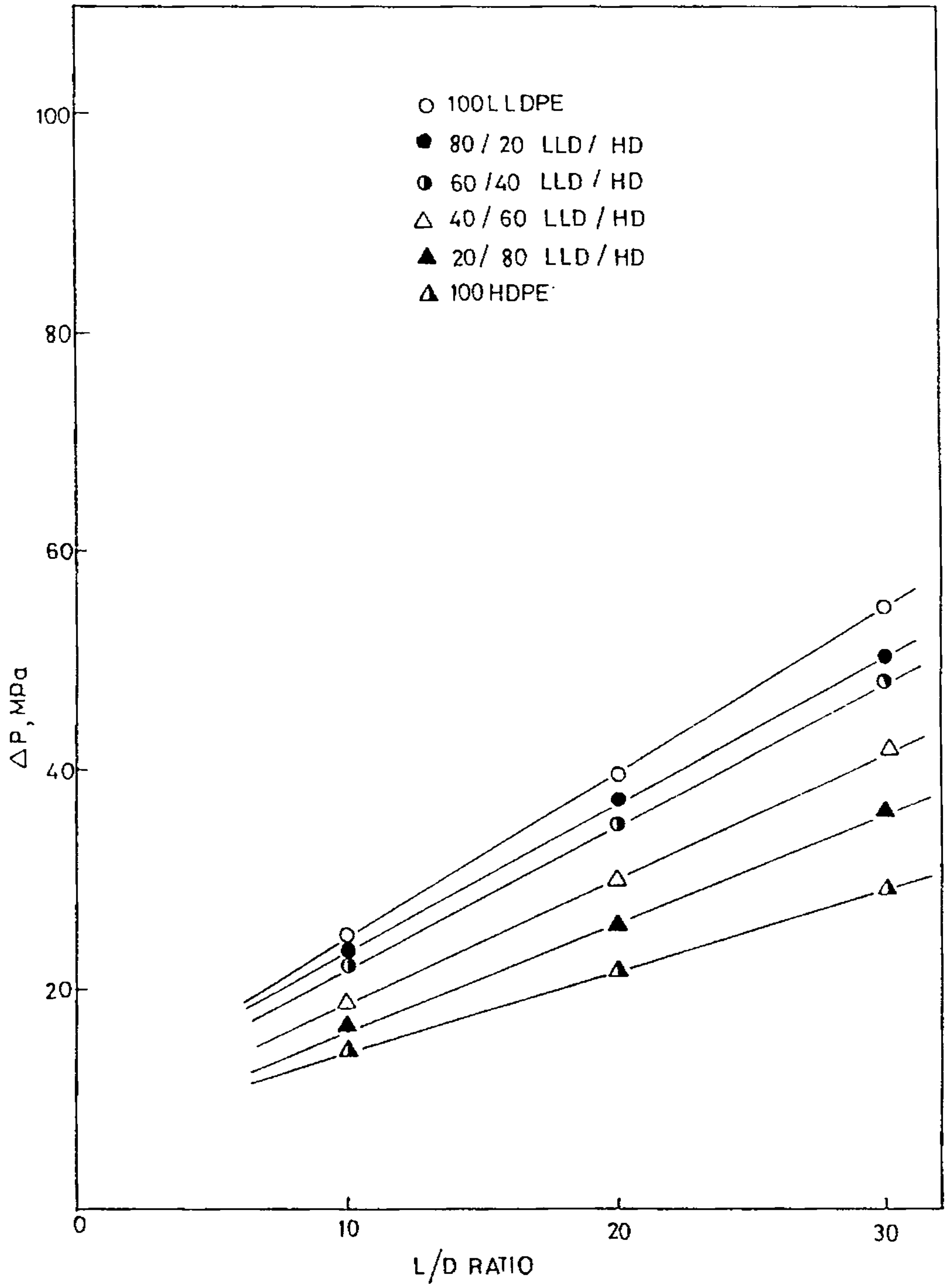

FIG.3.12 VARIATION OF PRESSURE DROP, ΔP, WITH L/D RATIO OF THE CAPILLARY FOR HDPE/LLDPE 1 BLENDS (SHEAR RATE 115.2 S^{-1}, TEMPERATURE 160 °C).

Table 3.2 Variation of Bagley correction factor with blend composition at various shear rates.

Shear rate S^{-1}	Blend composition wt % of LLDPE					
	0	20	40	60	80	100
20	4	4.5	5	5.5	5.7	6
115	4	7.5	8.1	8.7	9.2	10
575	8	8.9	10.2	11.3	13	14
1730	9	10	12.1	14.3	16.5	18
2880	12	14.3	16.8	18.3	20.6	22
3450	13	15.5	18.6	21.3	23.8	25

tion at various shear rates is shown in Table 3.2. Similarly the Rabinowitsch correction was applied using values of n determined from flow curves, to obtain true shear rate γ_w.

Flow curves in terms of corrected values of shear stress and shear rate for HDPE, LLDPE and HDPE/LLDPE blends at various compositions are shown in Fig.3.13. Flow curves of the blends are in between the flow curves of the pure HDPE and LLDPE.

The power law exponent n obtained from the corrected flow curves (Fig.3.13) are given in Table 3.3.

Table 3.3: Corrected values of power law exponent for HDPE/LLDPE blends

LLDPE (wt %)	0	20	40	60	80	100
Power law exponent, n	0.61	0.57	0.50	0.44	0.39	0.28

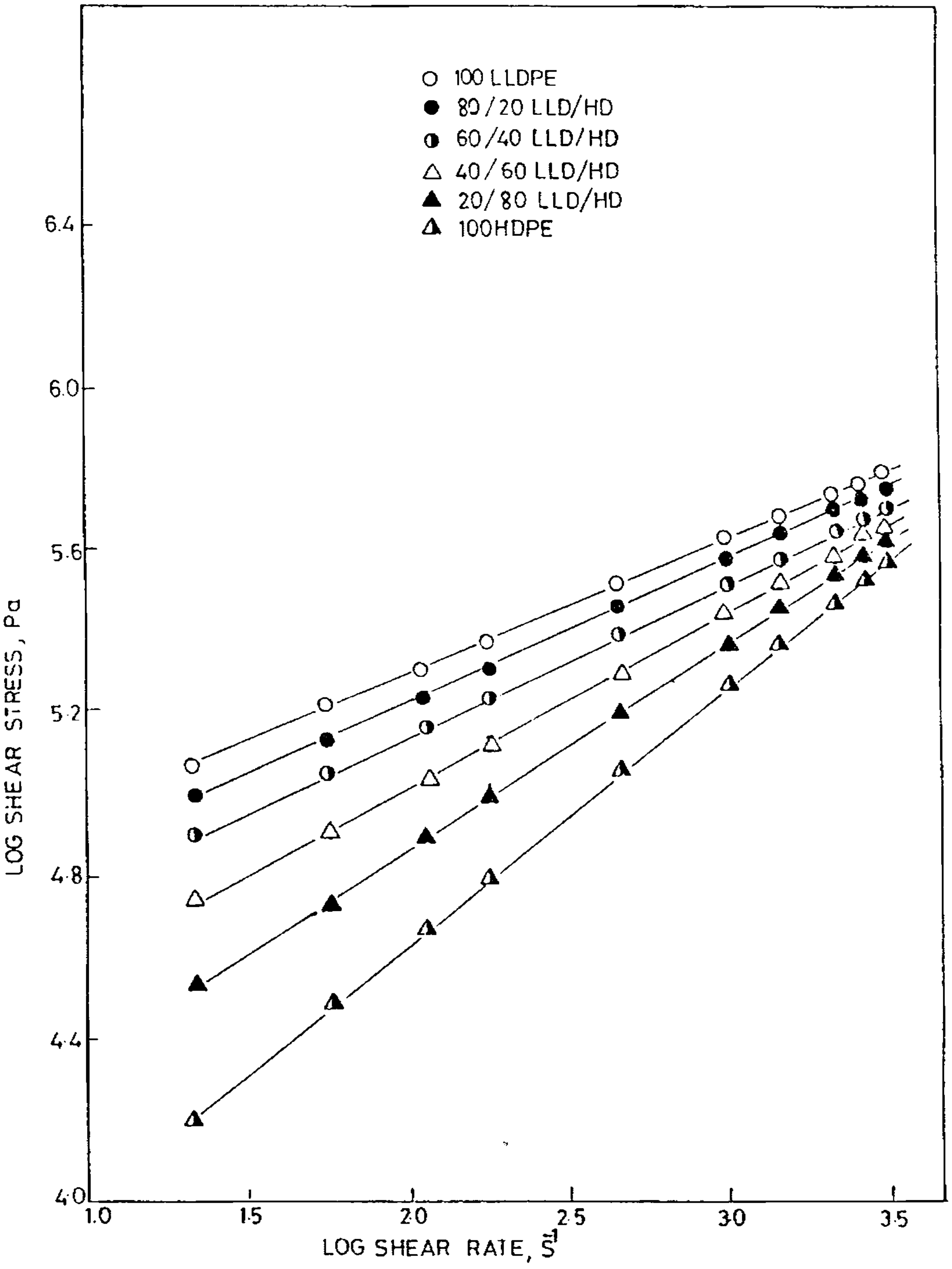

FIG.3.13 CORRECTED FLOW CURVES OF HDPE/LLDPE 1 BLENDS AT 160°C.

Melt Elasticity

Elasticity of the melt results in the expansion of the polymer on its exit from the die. Variation of extrudate die swell with blend composition at various shear rates is shown in Fig.3.14.

The recoverable shear strain calculated from the die swell values is shown in Fig.3.15. Recoverable shear strain increases with increasing shear rates as expected. It also increases with LLDPE content, obviously due to higher elastic nature of LLDPE. The reduction in melt elasticity of LLDPE with addition of HDPE may be advantageously used in processing.[11-13]

Fig.3.16 shows the apparent shear modulus versus blend composition curves of HDPE/LLDPE blends at various shear rates. The shear modulus decreases with increasing shear rate as expected. It increases and goes to a maximum and thereafter decreases with increasing LLDPE content.

3. RHEOLOGICAL EVALUATION OF BLENDS OF HDPE AND LLDPE USING A TORQUE RHEOMETER

The polymer blends were prepared by melt mixing in a Brabender plasticorder model PL 3S equipped with roller

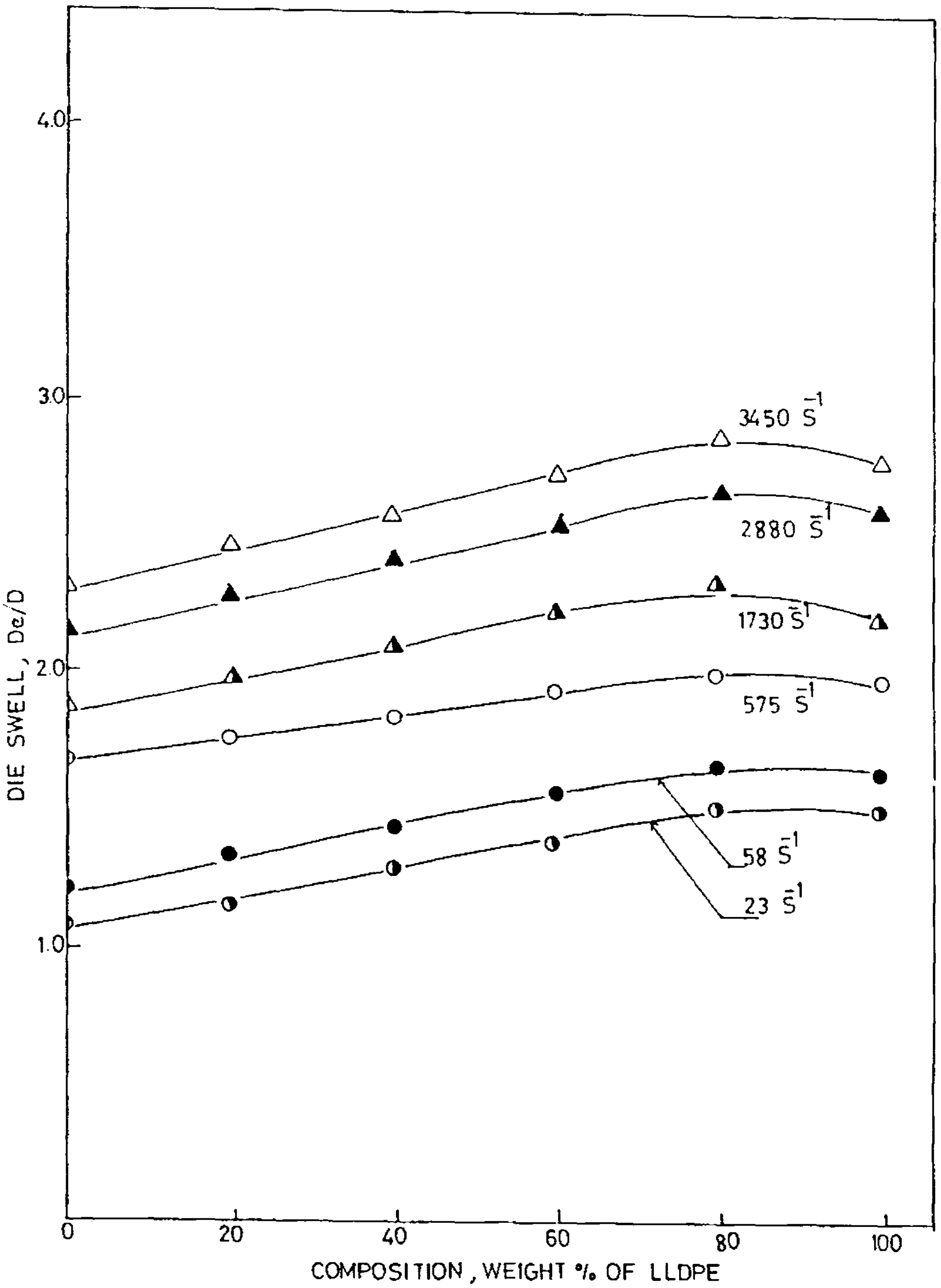

FIG.3.14 VARIATION OF EXTRUDATE DIE SWELL WITH BLEND COMPOSITION AT VARIOUS SHEAR RATES FOR HDPE/LLDPE 1 BLENDS AT 170°C.

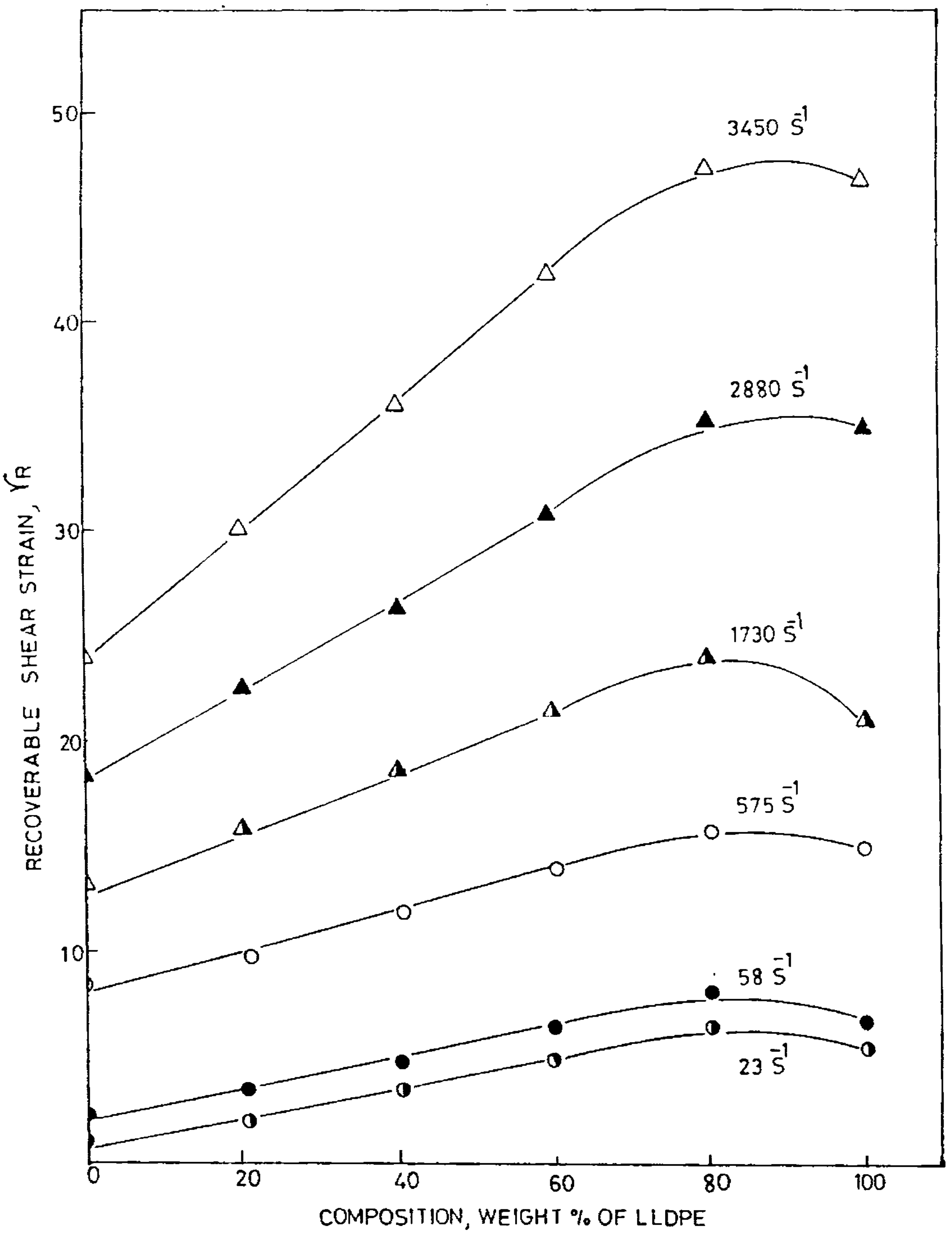

FIG.3.15 VARIATION OF RECOVERABLE SHEAR STRAIN WITH BLEND COMPOSITION AT VARIOUS SHEAR RATES FOR HDPE/LLDPE 1 BLENDS AT 170°C.

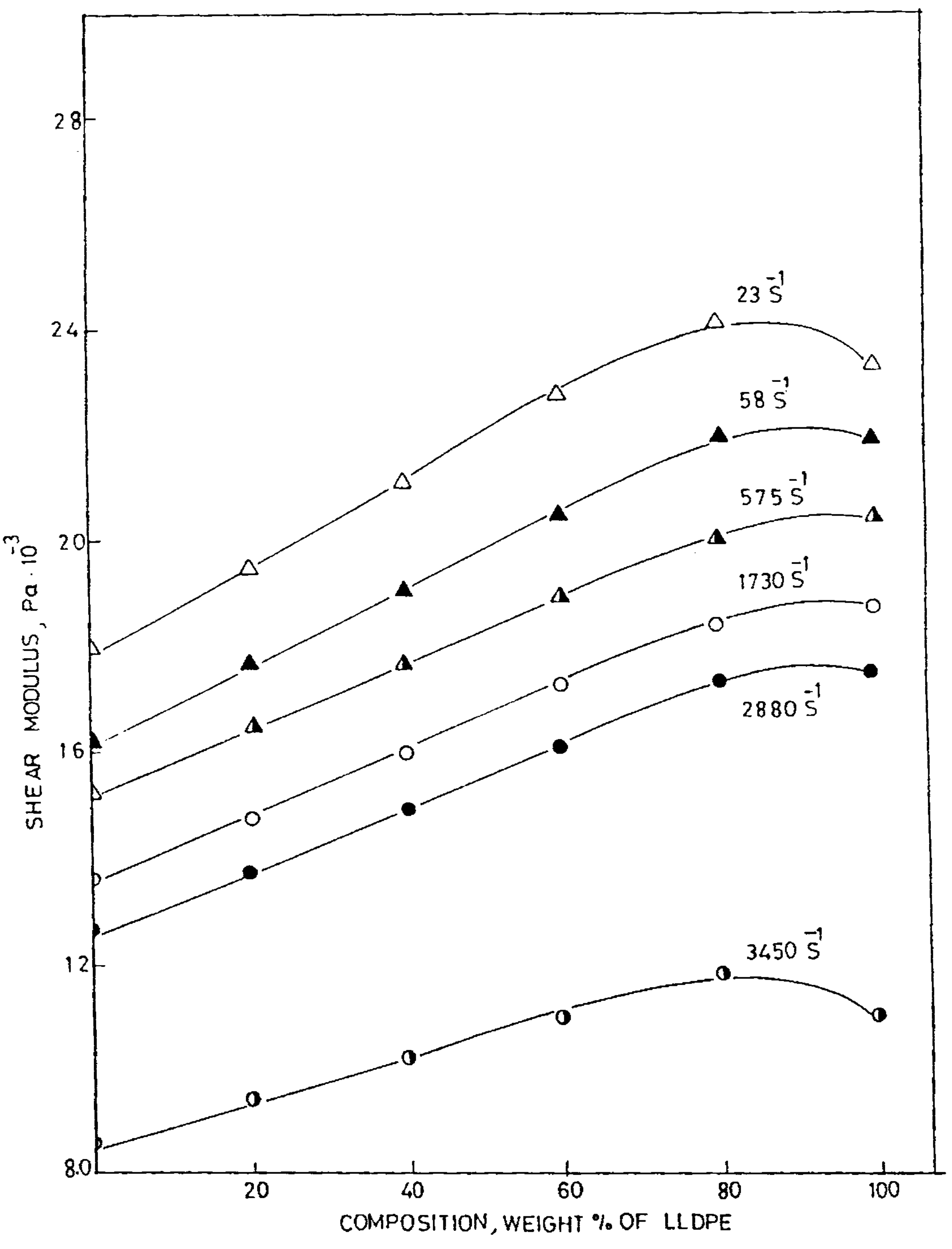

FIG.3.16 VARIATION OF SHEAR MODULUS WITH BLEND COMPOSITION AT VARIOUS SHEAR RATES FOR HDPE/LLDPE 1 BLENDS AT 170°C.

mixing heads and a rotor speed of 30 rpm and temperature of 150°C. Rheological measurements in shear flow were also carried out for each blend and pure polymers using the same plasticorder.

Fig.3.17 shows the equilibrium torque values as a function of blend composition for various rpm of the rotors. The torque values are proportional to the viscosity of the system. The torque increases with increase in LLDPE 1 content and increases with rpm (higher shear rates). The viscosity of the blends are between those of the pure polymers.

Fig.3.18 shows the variation of torque with blend composition at various temperatures and at a fixed shear rate (rpm). In each case the viscosity decreases with increase in temperature as expected.

The power law relationship between the rotor torque (M) and rotor speed (S) resembles the power law relationship between shear stress and shear rate and hence the slope of the curve log M vs. log S gives the power law index n.

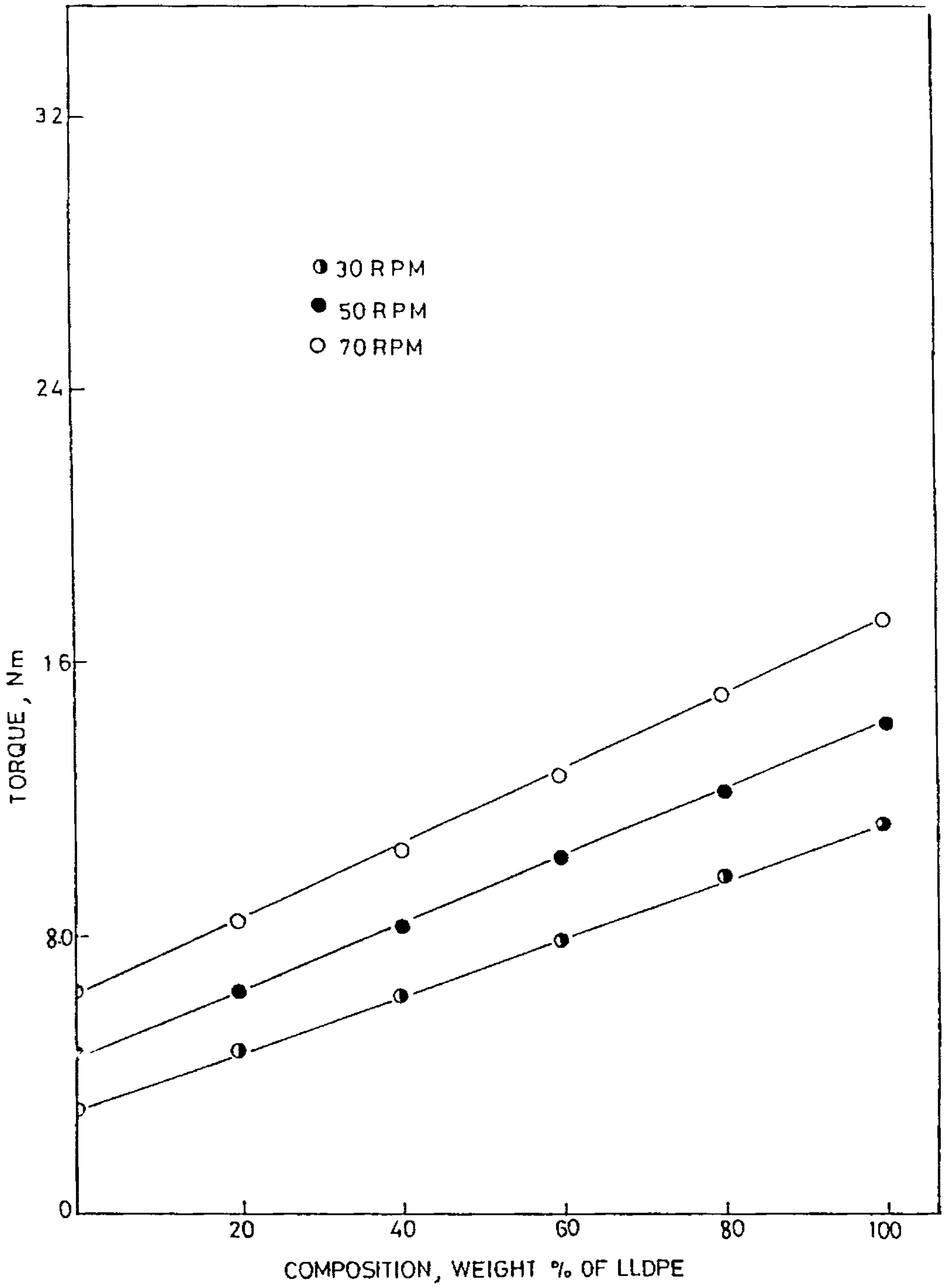

FIG.3.17 VARIATION OF EQUILIBRIUM TORQUE VALUES WITH BLEND COMPOSITION AT VARIOUS RPM AT 170°C.

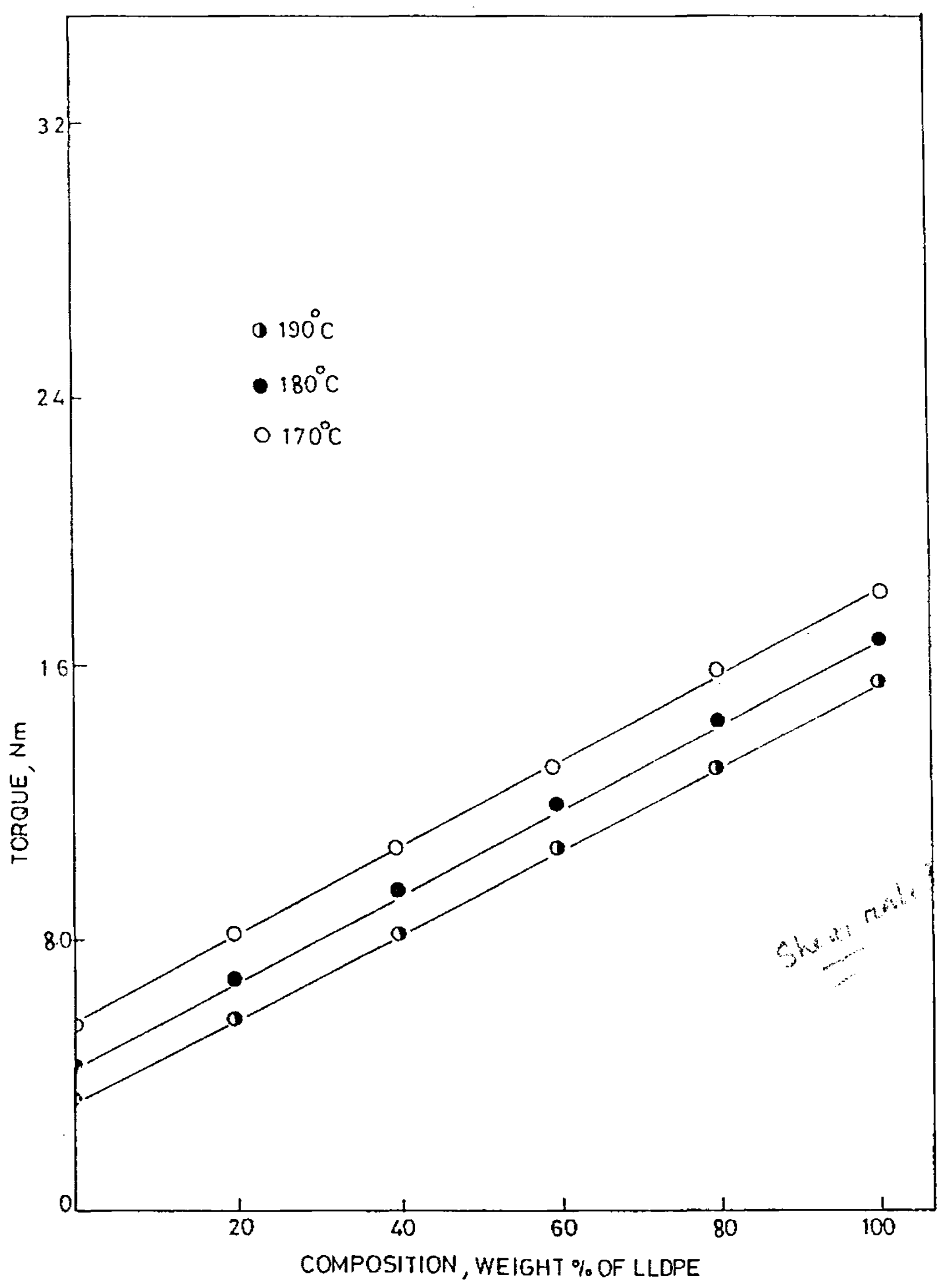

FIG.3.18 VARIATION OF TORQUE WITH BLEND COMPOSITION AT VARIOUS TEMPERATURES (70 RPM).

Fig.3.19 shows the log M versus log S plot for various composition of the blend. The parallel straight lines in this figure indicate that the power law indices for the parent polymers and their blends are more or less the same.

Fig.3.20 shows the log torque versus reciprocal of absolute temperature (1/T) for the HDPE/LLDPE 1 blends. The slopes of the linear plots is proportional to the apparent energy of activation,[14] which confirms the Arrhenius type behaviour. This confirms the earlier observation that LLDPE rich blends requires higher energy for processing than HDPE rich blends.

The energy required to plasticize the material was calculated from the torque-time curve at a particular temperature for a specified period of time. The values calculated for the blends and pure polymers at 150°C for 15 minutes are shown in Table 3.4.

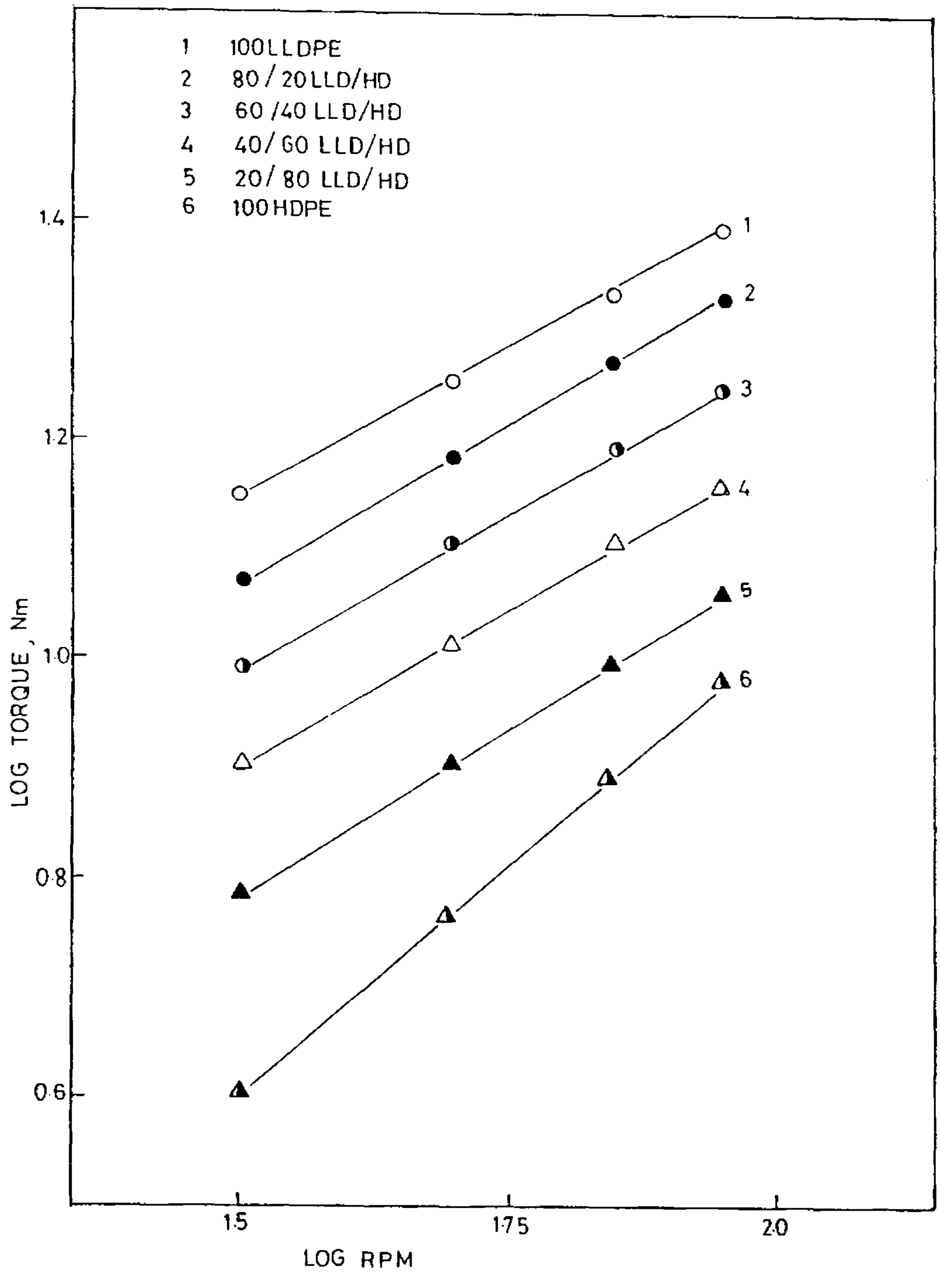

FIG.3.19 VARIATION OF LOG TORQUE WITH LOG RPM FOR HDPE/LLDPE 1 BLENDS.

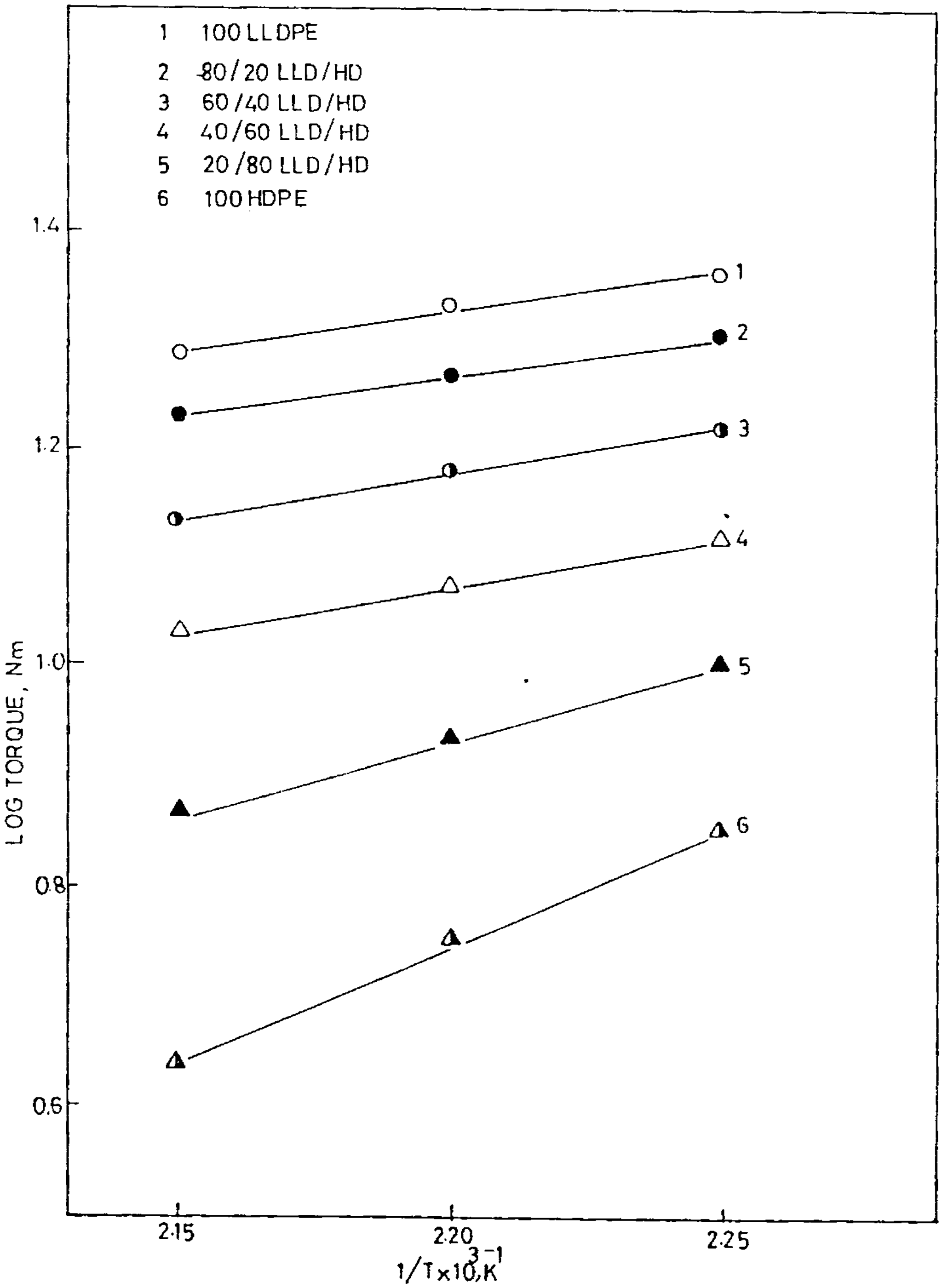

FIG.2.20 VARIATION OF LOG TORQUE WITH TEMPERATURE FOR HDPE/LLDPE 1 BLENDS.

Table 3.4: Variation of energy required for plasticization with blend composition

Property	Blend composition (wt % of LLDPE)					
	0	20	40	60	80	100
Energy required for plasticization (kJ)	64	70	75	80	86	92

Conclusions

1. HDPE and LLDPE are sufficiently miscible in the solid phase as well as in the melt to take advantage of the attractive properties of both.

2. If the LLDPE used is of sufficiently higher molecular weight to support a stable necking behaviour, it enhances the toughness of HDPE with only slight decrease in yield stress.

3. If the LLDPE added is of low molecular weight, it improves the miscibility of the polymers in the melt. However, the mechanical properties are inferior.

4. Irrespective of the viscosity of LLDPE, it shows a higher activation energy than HDPE. This suggests that under the influence of high stress LLDPE melts may crystallise to a low degree, resulting in enhanced resistance to flow.

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Chapter 4

CHEMICAL AND RADIATION CROSSLINKING OF HDPE/LLDPE BLENDS

In certain processing application, the available polyethylene resins, are not always optimum in terms of processability or mechanical properties of finished product. A low level of crosslinking in polyethylene that does not affect processing leads to structural modifications that affect its properties significantly.[1-6] Crosslinking leads to elevation in melting point, improvement in stress crack resistance and solvent resistance etc.[7-9] Crosslinking can be carried out either by irradiation with high energy radiation or by the use of chemical crosslinking agents. In this study HDPE/LLDPE blends are crosslinked to a low level by using dicumyl peroxide and by using gamma radiation.

1. EFFECT OF CONTROLLED CROSSLINKING ON THE MECHANICAL AND RHEOLOGICAL PROPERTIES OF HDPE/LLDPE BLENDS

Experimental

HDPE and LLDPE 1 were selected for this study due to their good mechanical properties. The polymer mixture was fed as a dry blend of virgin pellets to the hopper of a Brabender extruder. This extruder has an L/D ratio of 20 and the screw had a compression ratio of 3/1. The screw speed was 30 rpm. The extruder heater zones were set at 200°C and the die temperature at 220°C. The polymer output was extruded as thin film into a water quench bath. Samples for testing were compression moulded from these films by pressing into sheet at 180°C using an electrically heated laboratory hydraulic press with provision for water cooling under pressure. Dumbbell specimens for tensile tests were punched from these sheets and tested according to ASTM D 638. The stretching rate was 50 mm/min. and temperature of testing 25°C.

Dicumyl peroxide (DCP) at a concentration of 0.5 or 1.0% of the total weight of the polymers was employed as the crosslinking agent. DCP was added to the Brabender plasticorder hopper along with the polymers and the samples for tensile testing were prepared as described above.

The rheological measurements were made with a Goettfert capillary rheometer using a die of 1 mm dia and a length/diameter ratio of 30. The shear stress (τ) and shear rate (γ) were calculated from Newtonian expressions and the viscosity (η) as their ratio (τ/γ).

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

Results and Discussion

Figs.4.1 shows the Brabender torque curves of HDPE/LLDPE blends with and without DCP. Of the two

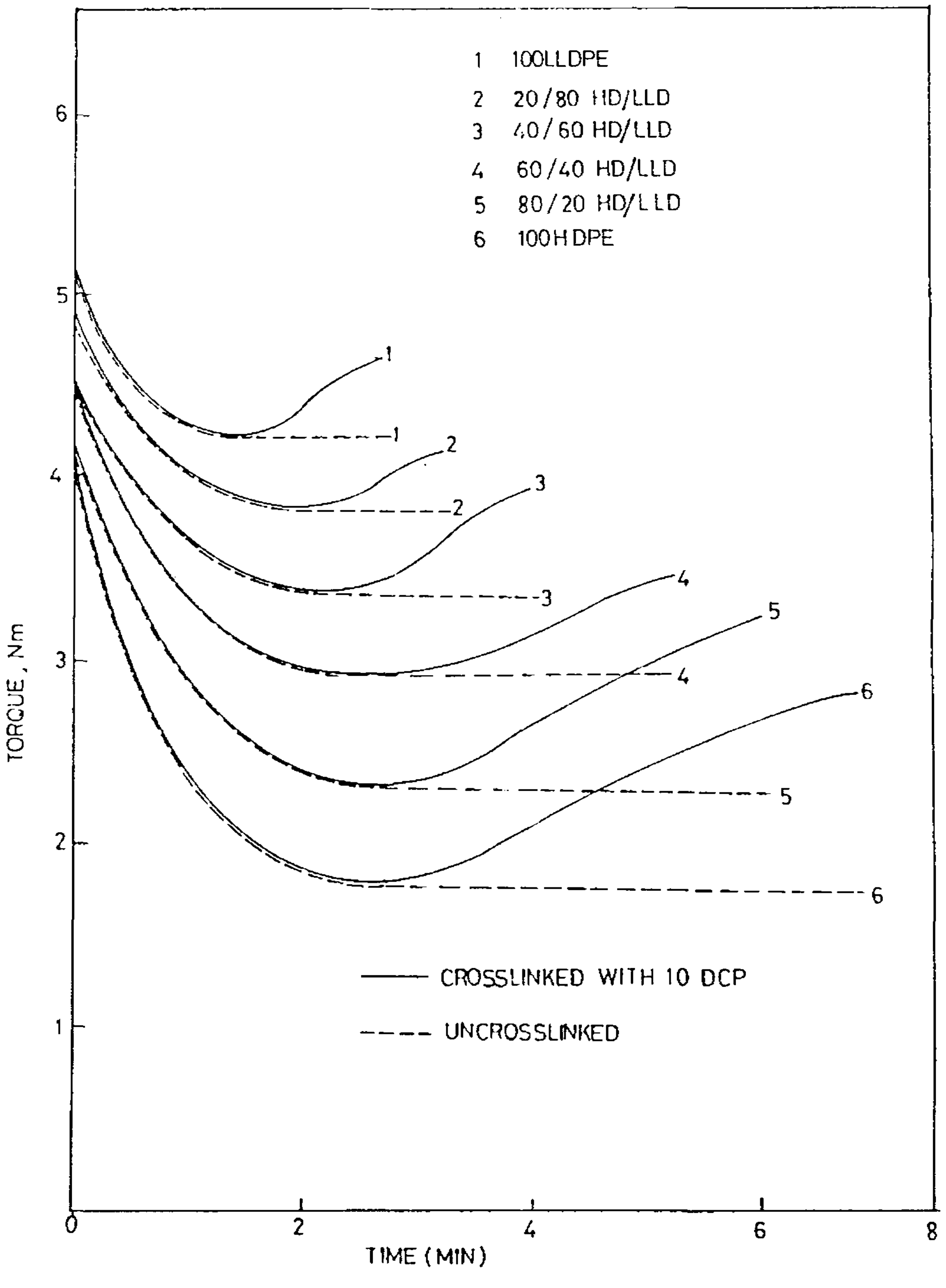

FIG.4.1 BRABENDER TORQUE CURVES OF HDPE/LLDPE BLENDS WITH AND WITHOUT DCP (1.0 WEIGHT % DCP).

polymers, LLDPE shows a greater tendency for crosslinking initially as shown by the fast increase in torque. This effect is probably due to the larger number of tertiary carbons and lower crystallinity in LLDPE compared to HDPE. However, the extent of crosslinking is larger for HDPE as indicated by the larger increase in torque. The low crosslinking efficiency of peroxide in LLDPE may be due to the preponderance of chain scission relative to crosslinking.[10] The optimum time required for crosslinking for various blends was determined from Brabender torque curves.

Fig.4.2 shows the tensile stress-strain curves of HDPE/LLDPE blends. In all cases, crosslinking increases the modulus, yield stress and breaking stress with only marginal decrease in the breaking strain. These results show that the crosslinked matrix is capable of supporting a greater stress, as expected. It may also be inferred that a low level of crosslinking does not seriously affect the crystallinity in these blends. Probably the small number of crosslinks act as initiators for crystallization.[11] HDPE rich blends show a greater change in yield stress, compared to the uncrosslinked matrix. This difference is probably due to the greater degree of crosslinking in such matrices as seen from the Brabender torque studies.

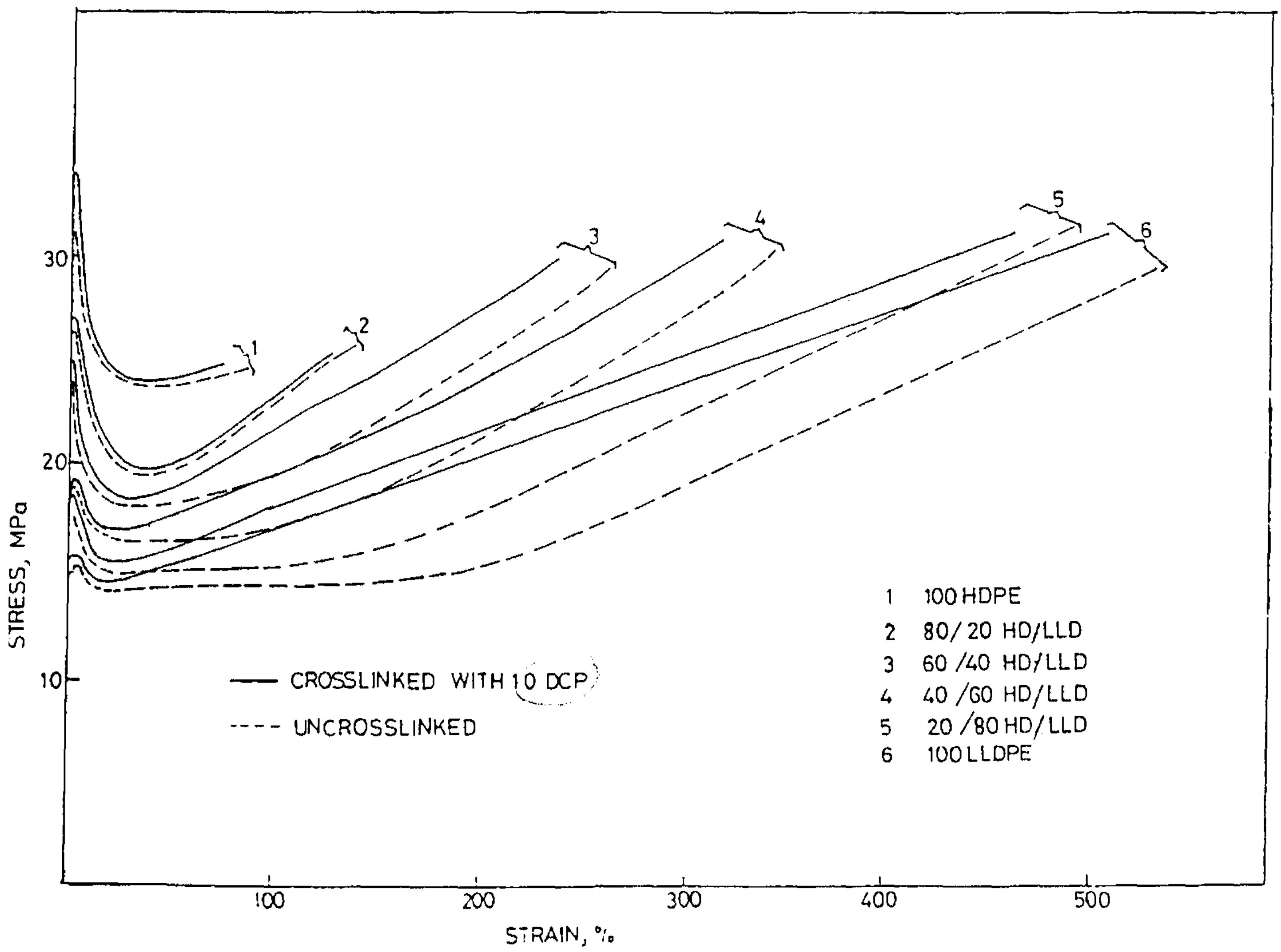

FIG.4.2 STRESS-STRAIN CURVES OF UNCROSSLINKED AND CROSSLINKED HDPE/LLDPE BLENDS.

Fig.4.3 shows the variation of gel content and physical properties such as 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 and hardness decrease and abrasion resistance increases with crosslinking. Gel content increases with HDPE content indicating that the HDPE phase forms a relatively more dense network structure than LLDPE phase. The decrease in density and hardness of crosslinked blends may be due to looser packing of the crosslinked molecules resulting from the reduced crystallinity.

In order to evaluate the processing characteristics of these crosslinked polymers, their rheological properties were compared with those of the uncrosslinked polymers. Degree of crosslinking increases the viscosity of the blends as shown in Fig.4.4. A larger increase is observed for HDPE rich blends as expected. As the dependence of viscosity on composition is essentially linear, one may suggest that substantial changes in the structure of the melts do not takes place over the entire composition range.[12] At higher shear rates, the variation of viscosity with blend composition and crosslinking becomes minimal. As the closeness of the rheological

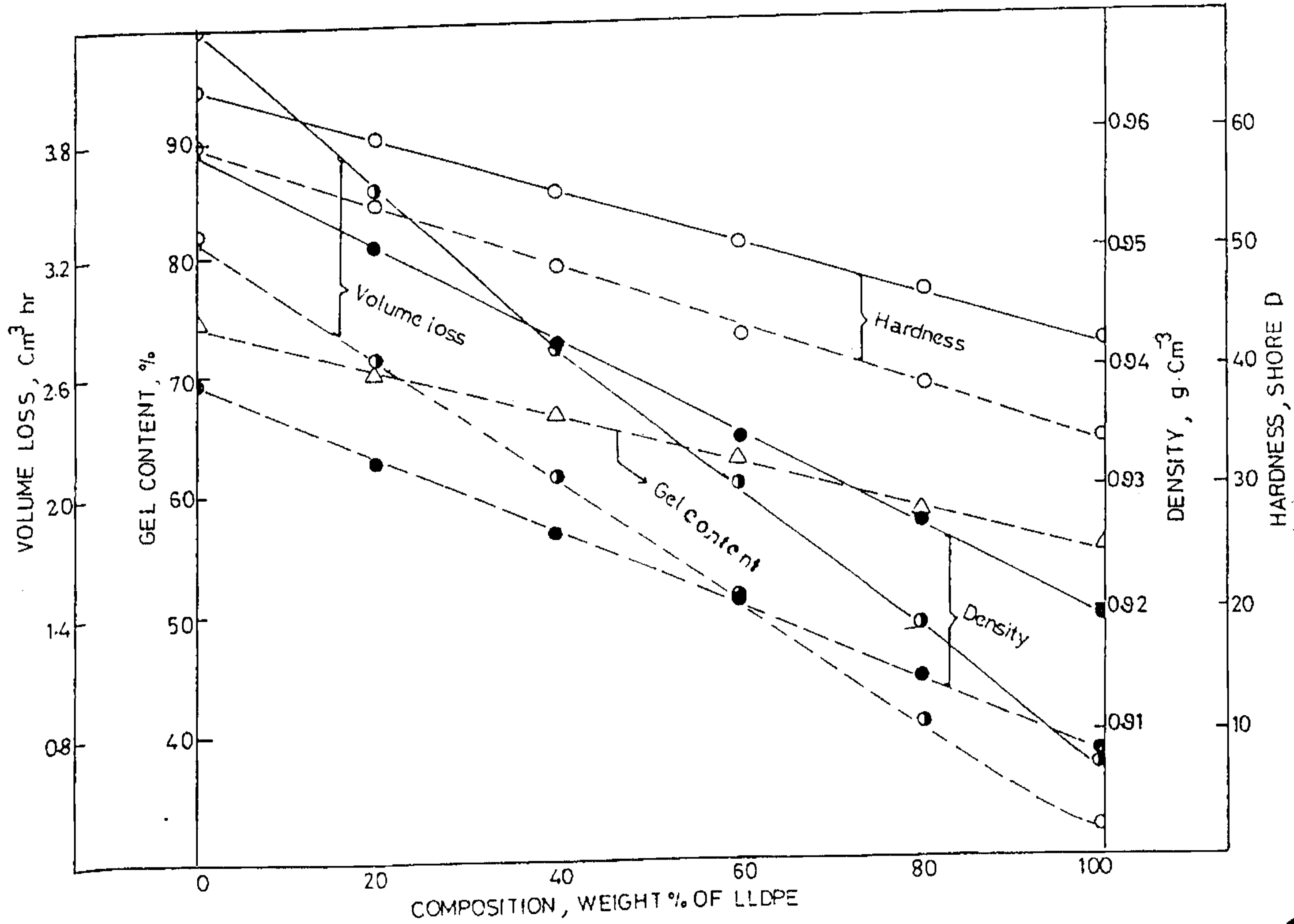

FIG.4.3 VARIATION OF GEL CONTENT AND PHYSICAL PROPERTIES OF HDPE/LLDPE BLENDS WITH COMPOSITION: SOLID LINE -- UNCROSSLINKED; DOTTED LINE - CROSSLINKED WITH 1.0 DCP.

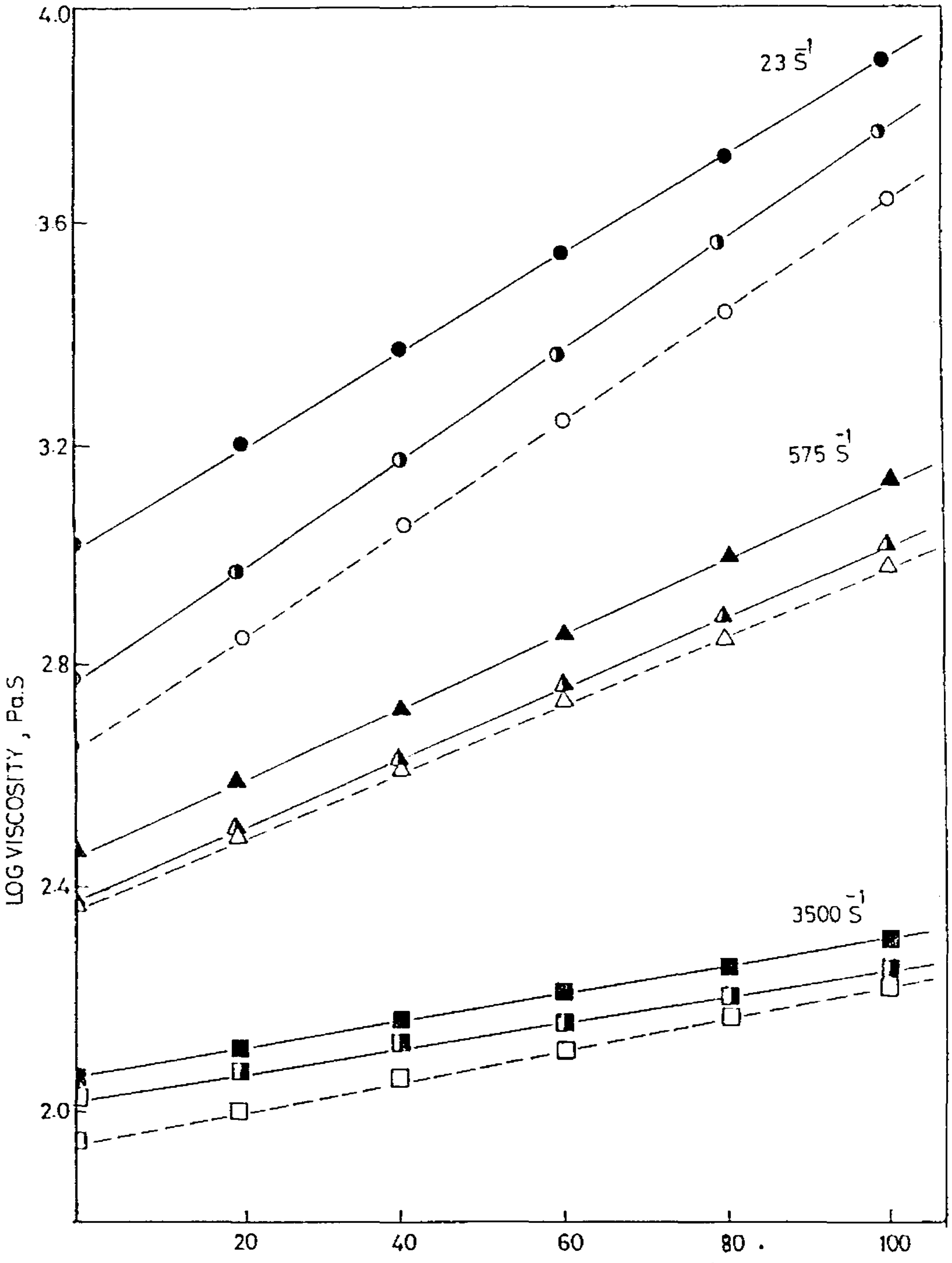

FIG.4.4 VARIATION OF VISCOSITY OF HDPE/LLDPE BLENDS WITH COMPOSITION AT VARIOUS SHEAR RATES: UNSHADED - UNCROSSLINKED; HALF SHADED - CROSSLINKED WITH 0.5 DCP; FULL SHADED - CROSSLINKED WITH 1.0 DCP.

properties of the melt ensures a higher degree of homogeneity it may be comparatively easy to process such blends at higher shear rates.

The flow curves of the blends using 0.5 and 1% DCP concentrations are given in Figs.4.5 and 4.6. At higher shear rates, the influences of the composition of the blends and crosslinking on the flow curves diminish in both cases. The derived values of the power law index are shown in Table 4.1. They increase marginally with crosslinking showing that the melt becomes slightly more Newtonian. This effect may be due to the less freedom available to the molecules in the crosslinked state to orient themselves in the shear direction and to exhibit the usual non-Newtonian behaviour.

The variation of viscosity of the blends with temperatures is found to be minimal (Fig.4.7). The temperature dependence of viscosity could be expressed by the activation energy for viscous flow (Table 4.1). The activation energy is found to increase with increase in the degree of crosslinking, as expected. A larger increase is again observed for HDPE rich blends because of the larger extent of crosslinking.

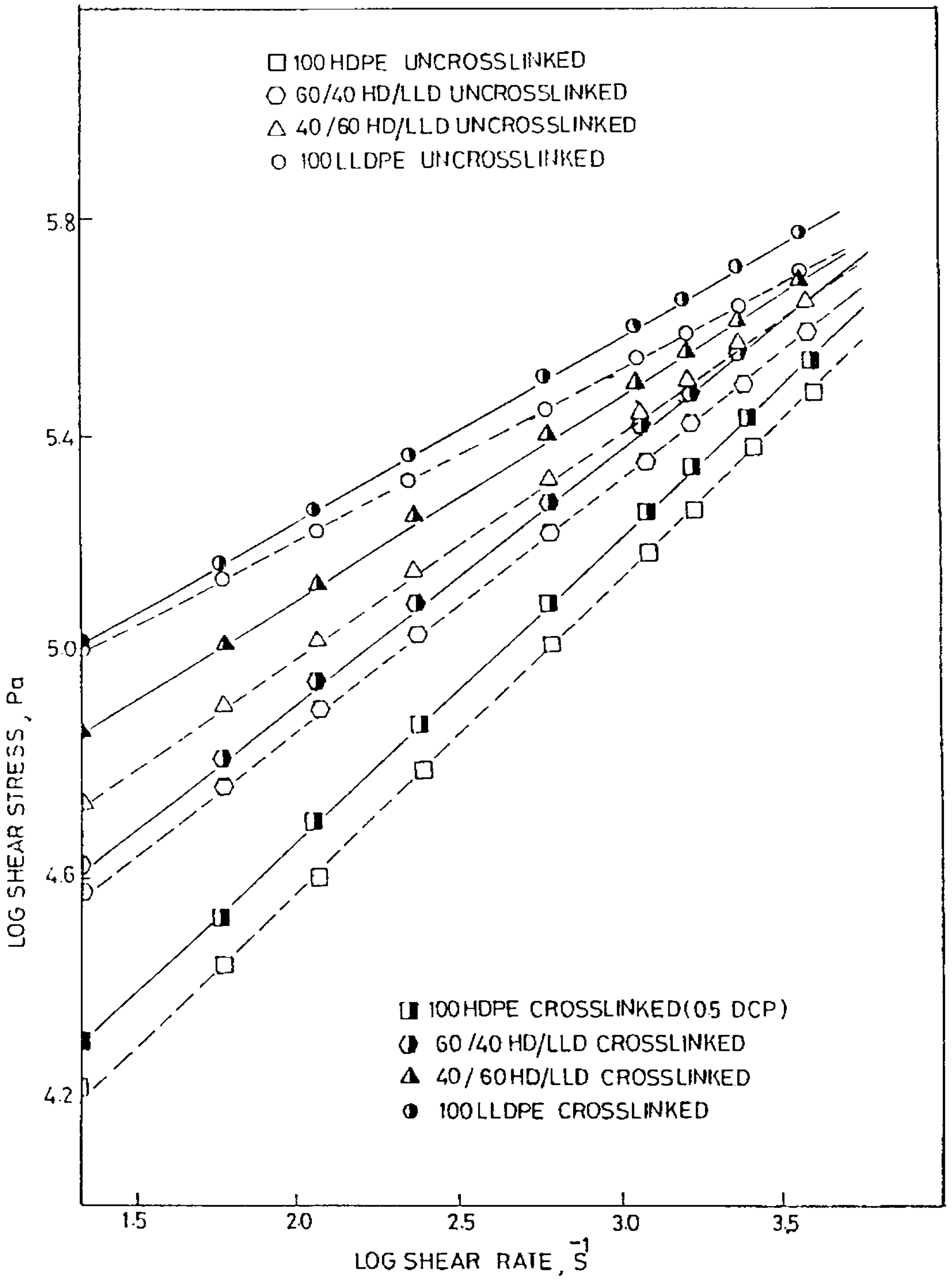

FIG.4.5 FLOW CURVES OF UNCROSSLINKED AND CROSSLINKED HDPE/LLDPE BLENDS (0.5 DCP).

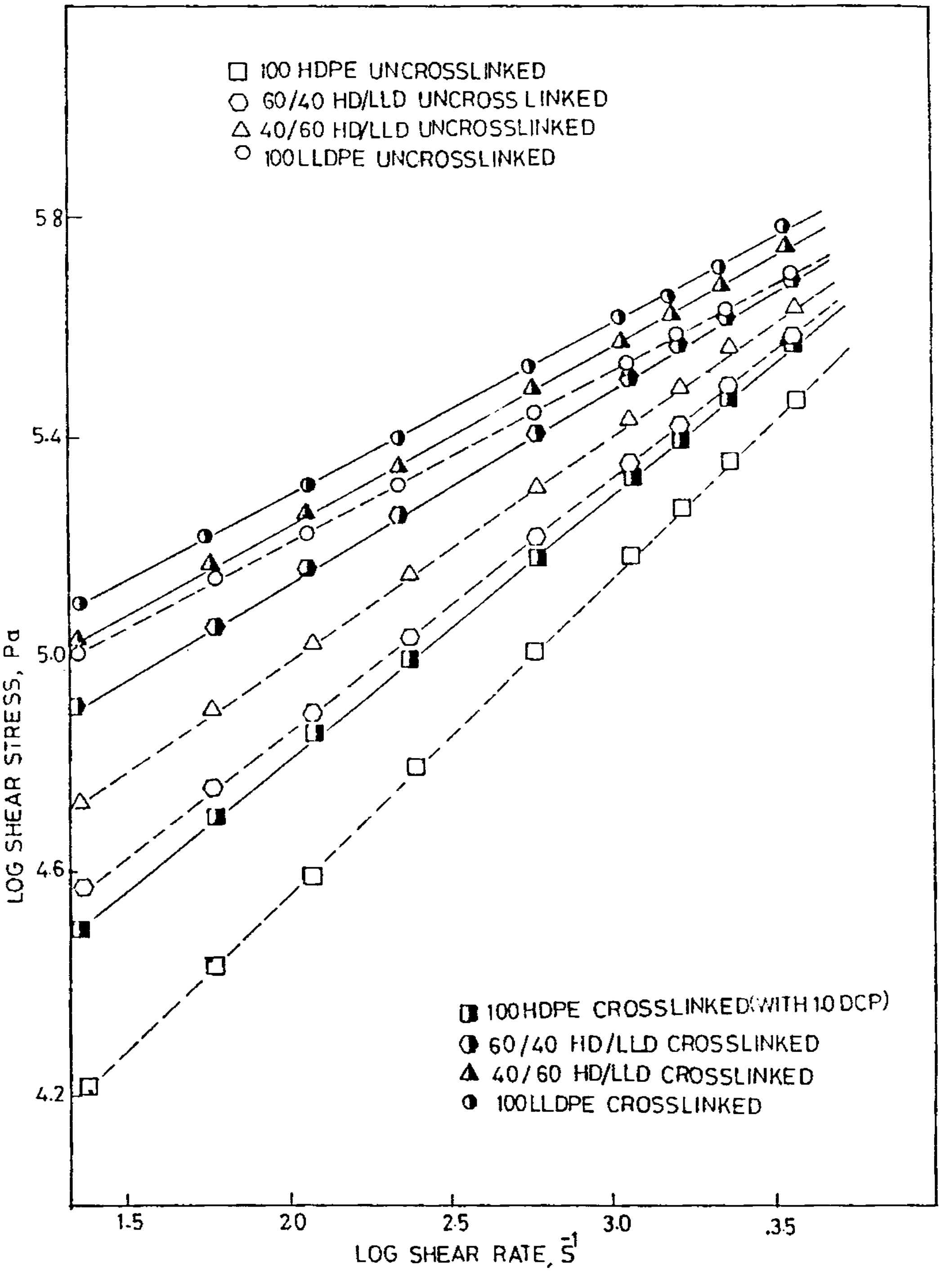

FIG.4.6 FLOW CURVES OF UNCROSSLINKED AND CROSSLINKED HDPE/LLDPE BLENDS (1.0 DCP).

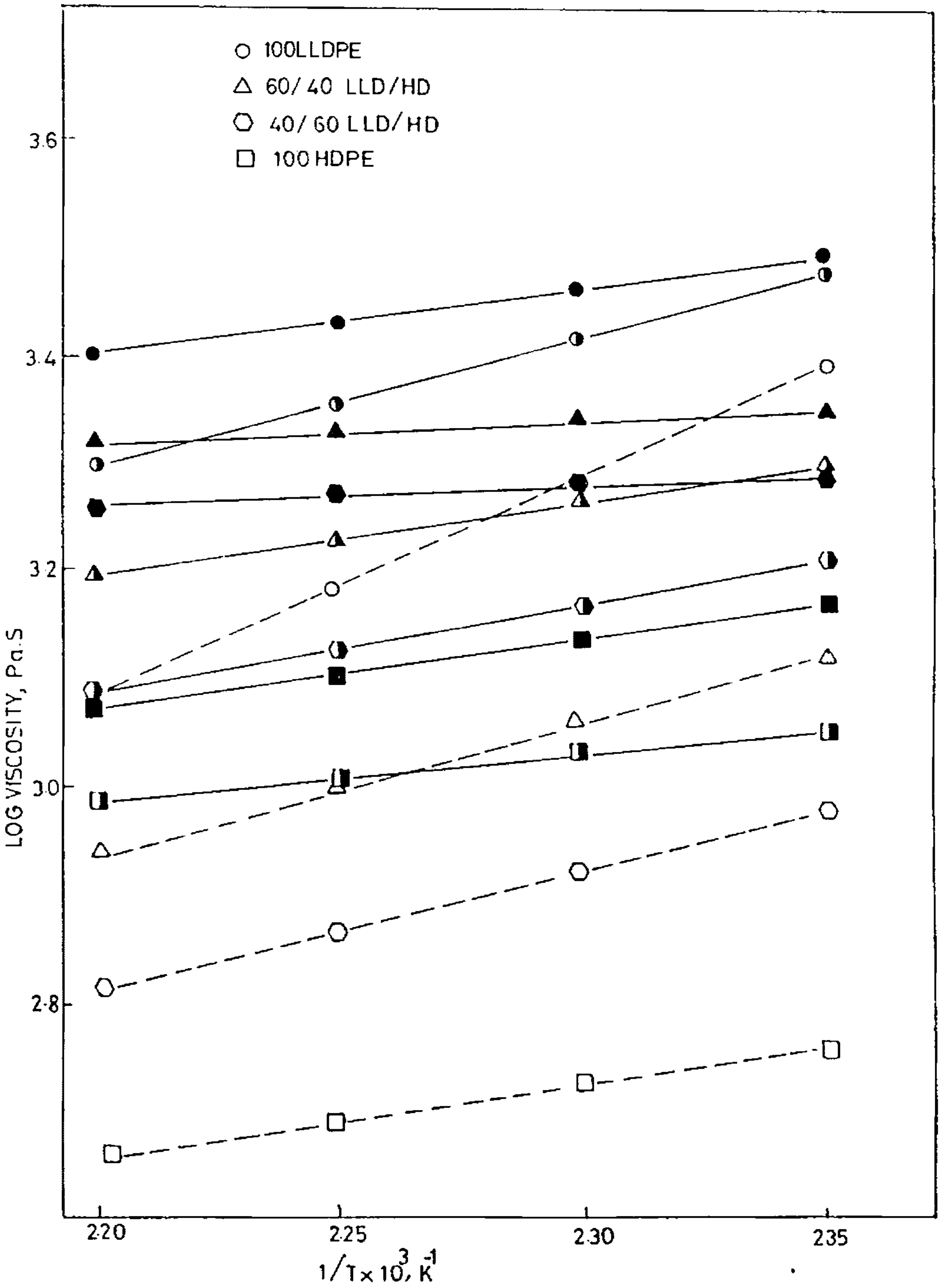

FIG.4.7 VISCOSITY Vs. 1/T CURVES OF HDPE/LLDPE BLENDS: UNSHADED - UNCROSSLINKED; HALF SHADED - CROSSLINKED WITH 0.5 DCP; FULL SHADED - CROSSLINKED WITH 1.0 DCP.

Table 4.1 Power law index and activation energy of cross-linked HDPE/LLDPE blends

	Composition, wt. % of LLDPE	Uncross-linked	Cross-linked with 0.5 DCP	Cross-linked with 1.0 DCP
Power law exponent, n	0	0.56	0.57	0.50
	20	0.52	0.54	0.55
	40	0.46	0.49	0.50
	60	0.42	0.44	0.45
	80	0.37	0.40	0.42
	100	0.32	0.35	0.37
Activation energy kJ/mol	0	14.5	15.5	17.4
	20	12.5	13.4	13.9
	40	10.7	11.8	13.2
	60	10.4	11.0	12.2
	80	9.7	10.7	11.3
	100	8.6	9.3	9.7

Conclusions

The study shows that a low degree of crosslinking, not affecting processing, can be introduced in HDPE/LLDPE blends for improving the mechanical behaviour. Since the thermal stability and dimensional stability of such crosslinked polymers would be superior to those of the uncrosslinked polymers, such blends could be used in more demanding applications. Melt rheological characteristics of these blends indicate that such low levels of crosslinking do not adversely affect processing, especially at higher shear rates.

2. RADIATION CROSSLINKING OF HDPE/LLDPE BLENDS IN PRESENCE OF DICUMYL PEROXIDE

Radiation crosslinking in presence of a peroxide such as dicumyl peroxide as a sensibilising agent is suggested as an attractive means of obtaining improvement in properties associated with crosslinking without adversely affecting the mechanical properties.[13,14] In this study the effect of radiation crosslinking of HDPE/LLDPE blends on their mechanical properties is investigated.

Experimental

The blends of HDPE and LLDPE were prepared by melt mixing in an extruder attached to a Brabender plasticorder. The extruder has an L/D ratio of 20 and the compression ratio of the screw was 3:1. The screw speed was 30 rpm. The extruder heater zones was set at 140°C and the die temperature at 150°C. The polymer mixtures were added as dry blend of virgin pellets to the hopper of the Brabender plasticorder. DCP was also added to the hopper.

Samples for irradiation were compression moulded at 150°C in a steam heated laboratory hydraulic press for 5 minutes. Gamma radiation was done in a Gamma chamber model GC 900 using ^{60}Co source at room temperature. The irradiation dosage was 1 Mrad/hr.

The gel fraction of the irradiated test pieces was measured as per ASTM D 2765. Dumbbell specimens for tensile tests were punched out from the compression moulded sheets and tested at a cross head speed of 50 mm/min. at 25°C on a Zwick UTM as per ASTM D 638. The wear resistance of the samples was measured as per ASTM D 1242 (1988) using a Zwick abrader. DSC thermograms were taken on a Perkin-

Elmer DSC-7 model at a heating/cooling rate of 10°C/min. under nitrogen atmosphere as per ASTM D 3417 (1988).

Results and Discussion

Fig.4.8 shows the variation of gel content of HDPE with irradiation dosages with peroxide concentration upto 2.5 wt. percentage. The crosslinking is obviously not very effective without DCP. There is a continuous increase of the gel content with increase in peroxide concentration and irradiation dosages (Table 4.2). Very similar curves were obtained with LLDPE and HDPE/LLDPE blends of different concentrations. The crosslinking behaviour seems to be similar which may be due to the similarity in the structure of the two polyethylenes. However, for the same DCP concentration and irradiation dosage HDPE is found to have slightly higher gel content than LLDPE. This shows that HDPE phase has slightly higher crosslinking density than that of LLDPE.

Fig.4.9 illustrates the fusion endotherm of HDPE, LLDPE and 50/50 HDPE/LLDPE blends. In all the cases, only a single peak is observed. However, this may not be a sufficient reason for cocrystallisation or miscibility since a fairly high heating rate was employed.[15,16] The

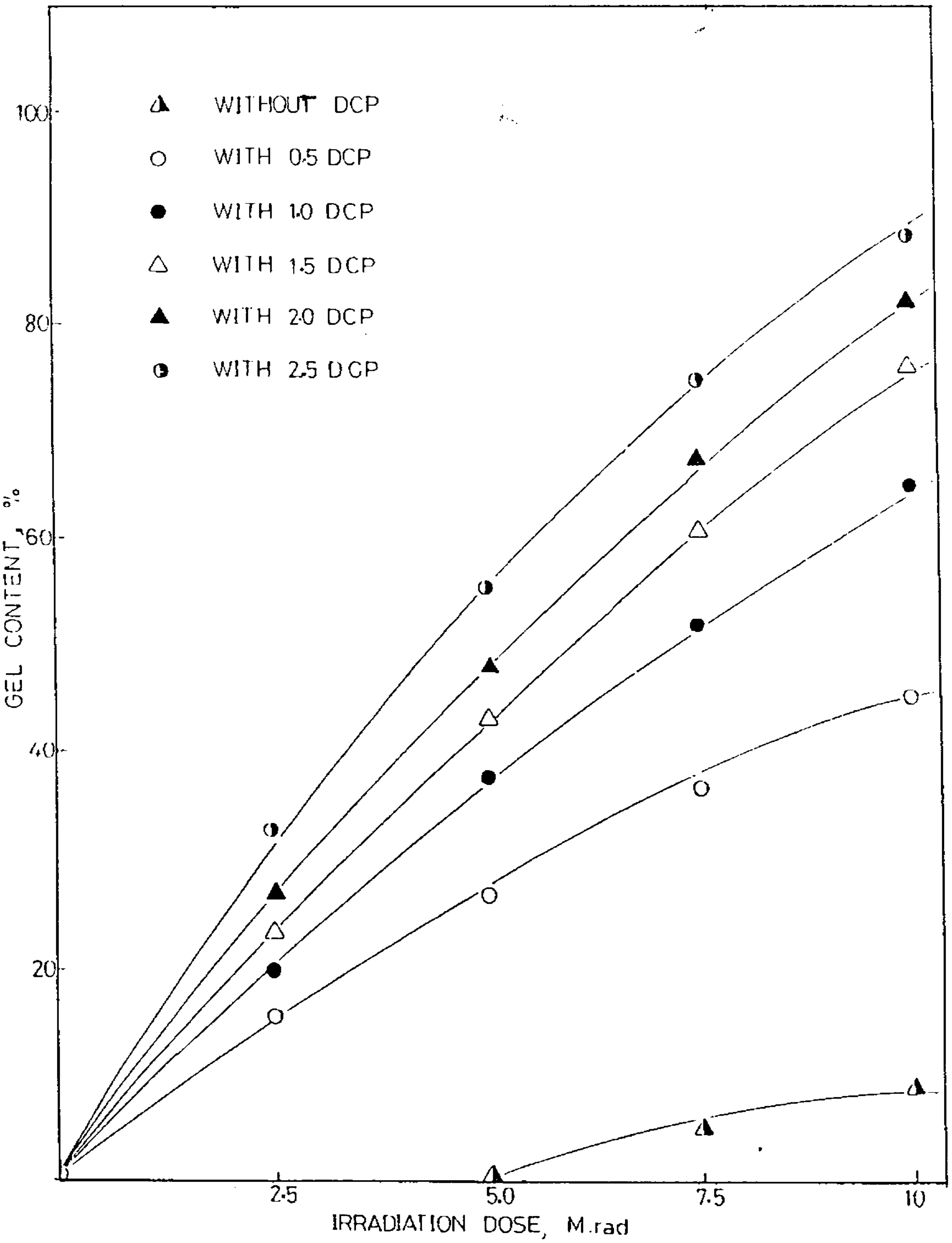

FIG.4.8 VARIATION OF GEL CONTENT OF HDPE WITH IRRADIATION DOSE.

Table 4.2: Variation of gel content (%) with radiation dosage and DCP concentration in HDPE/LLDPE blends

Composition wt % of LLDPE	DCP Concentration (wt %)																			
	0.5				1.0				1.5				2.0				2.5			
Radiation dose, Mrad	2.5	5	7.5	10	2.5	5	7.5	10	2.5	5	7.5	10	2.5	5	7.5	10	2.5	5	7.5	10
0	17	25	37	42	20	35	52	63	23	42	63	77	36	58	75	81	42	67	75	88
25	17	23	36	40	19	34	51	60	24	41	62	74	36	55	73	81	41	66	72	87
50	16	21	33	39	17	33	48	59	22	40	60	71	34	52	72	79	39	63	70	85
75	15	21	30	37	16	31	47	58	20	37	57	68	33	49	68	78	39	61	68	83
100	14	19	28	36	16	29	45	55	19	35	54	65	32	46	66	75	37	58	67	82

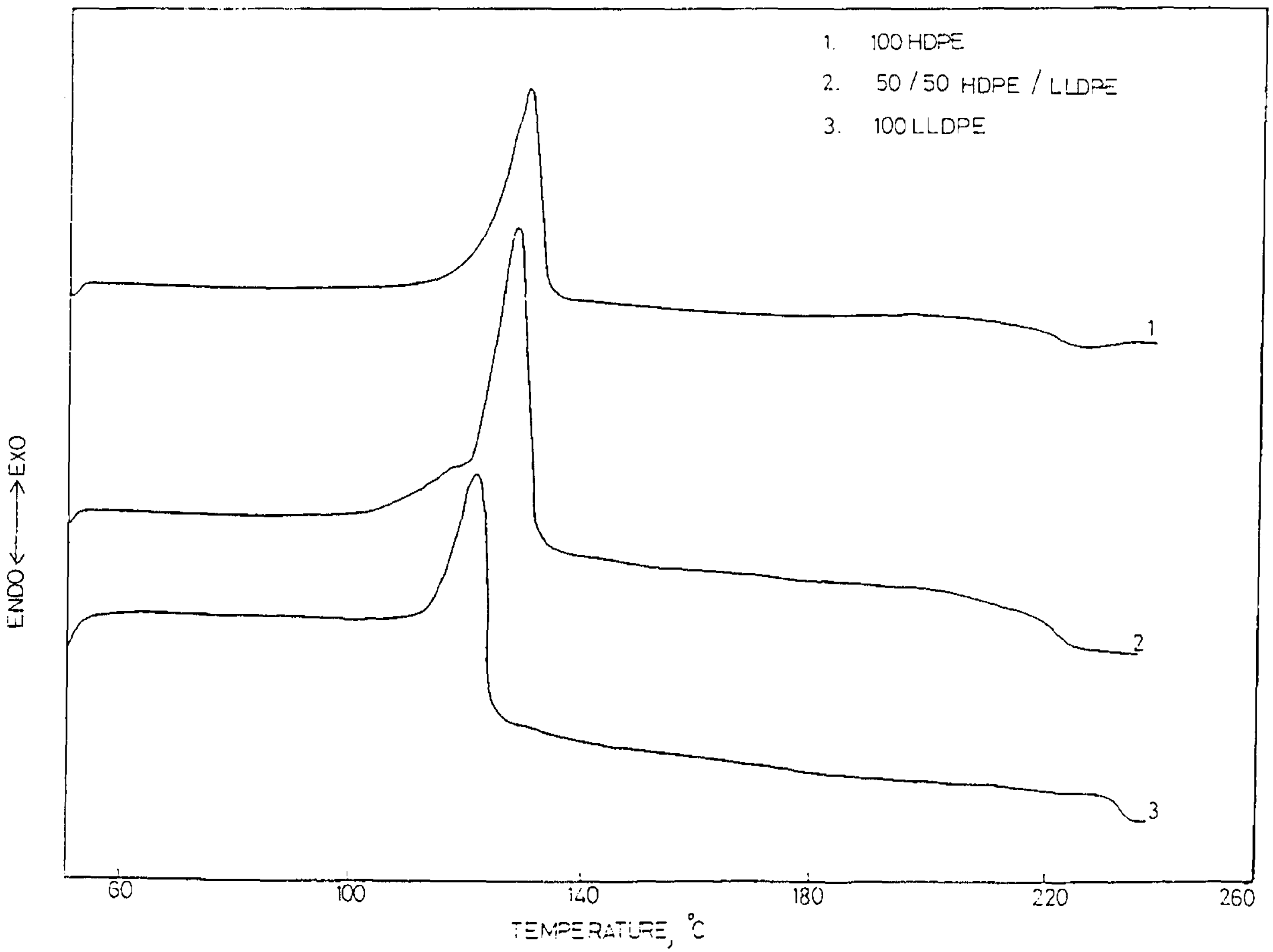

FIG.4.9 FUSION ENDOTHERMS OF HDPE, LLDPE AND 50/50 HDPE/LLDPE BLEND.

relative amount of crystallinity in the different samples can be measured from the heat required to melt the crystalline portion of the polymers or from the area under the curve (Table 4.3). These values indicate that HDPE is more crystalline than LLDPE and the crystallinity in the 50/50 blend is in between those of HDPE and LLDPE.

Fig.4.10 shows the DSC thermograms of DCP cross-linked HDPE, LLDPE and 50/50 HDPE/LLDPE blends. It may be observed that crystallinity of the polymer is sharply reduced during chemical crosslinking (Table 4.2) whereas during gamma radiation, the crystallinity of the polymer is not severely affected (Fig.4.11 and Table 4.3). This may be mainly due to two reasons: (1) Radiation crosslinking takes place predominantly in the non-crystalline region and (2) DCP acts as initiators for crystallisation[11].

Fig.4.12 shows the tensile stress-strain curves of irradiated (10 Mrad) HDPE, LLDPE and their 50/50 blends with different amounts of DCP. The yield strength and tensile strength are found to increase with DCP concentration in all cases with marginal decrease in modulus and elongation at break. One striking difference is in the case of LLDPE with 2.5 wt % of DCP. The sharp reduction in

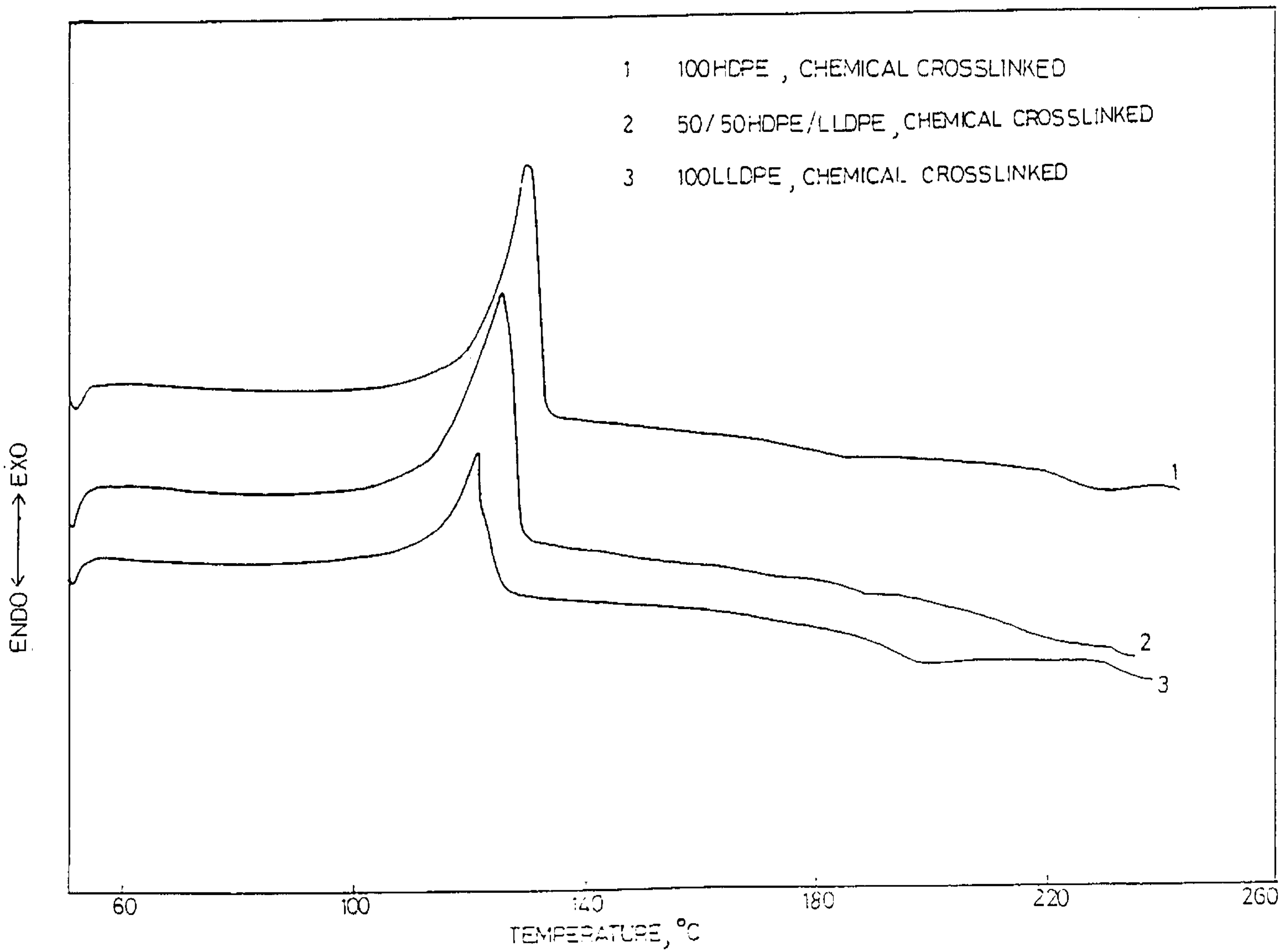

FIG.4.10 FUSION ENDOTHERMS OF DCP CROSSLINKED HDPE, LLDPE AND 50/50 HDPE/LLDPE BLEND.

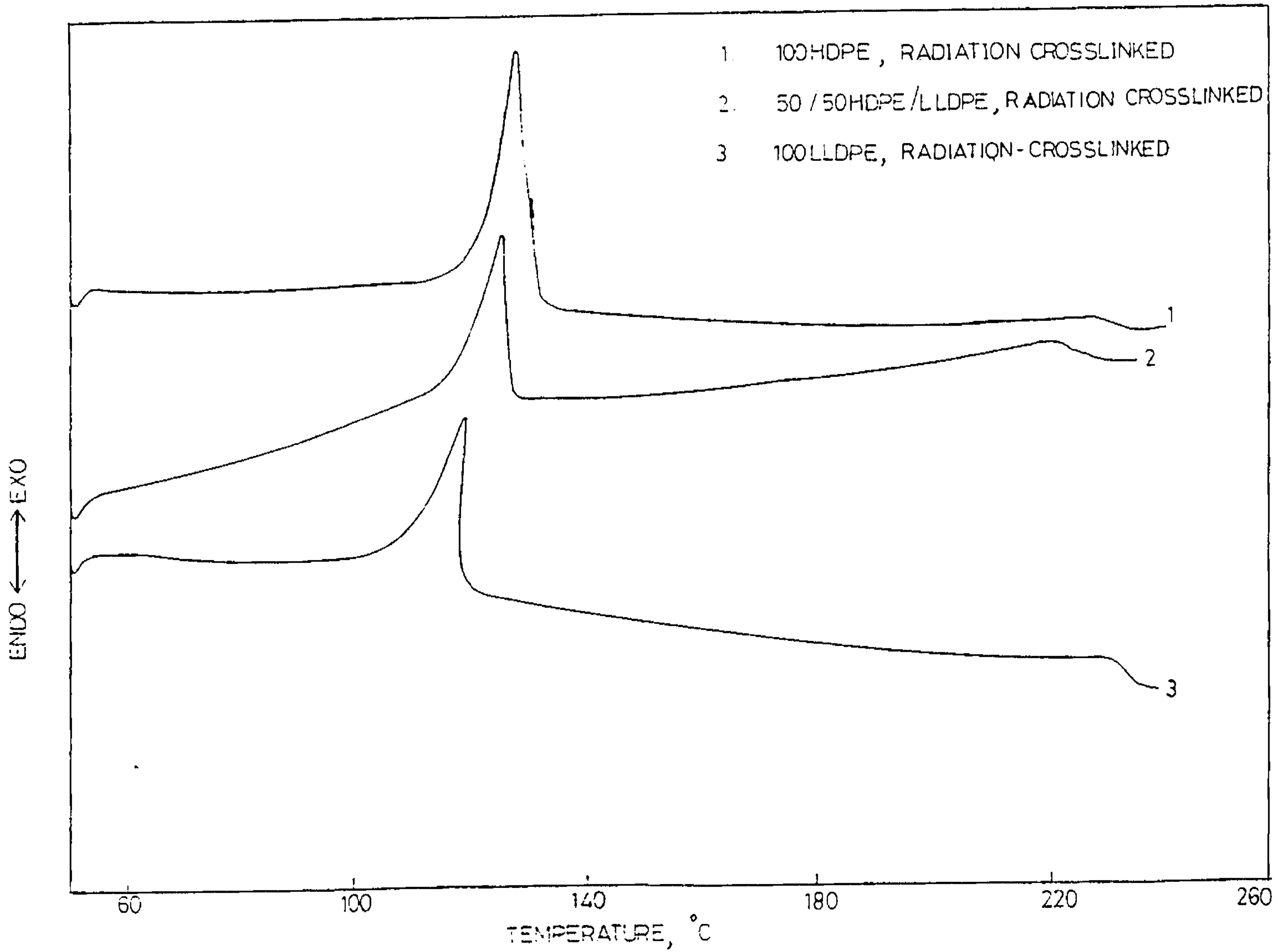

FIG.4.11 FUSION ENDOTHERMS OF RADIATION CROSSLINKED HDPE, LLDPE AND 50/50 HDPE/LLDPE BLEND.

Table 4.3: DSC data for pure polymers, crosslinked polymers and blends

HDPE/LLDPE	DCP concentration	T_m °C	ΔH, cal/gm
100/0	0	132	38.9
50/50	0	130	26.8
0/100	0	122	26.3
* 100/0	1.0	131	23.4
50/50	1.0	125	20.8
0/100	1.0	124	20.5
**100/0	1.0	129	37.8
50/50	1.0	126	28.2
0/100	1.0	121	25.7

* Chemical crosslinked

** Radiation crosslinked

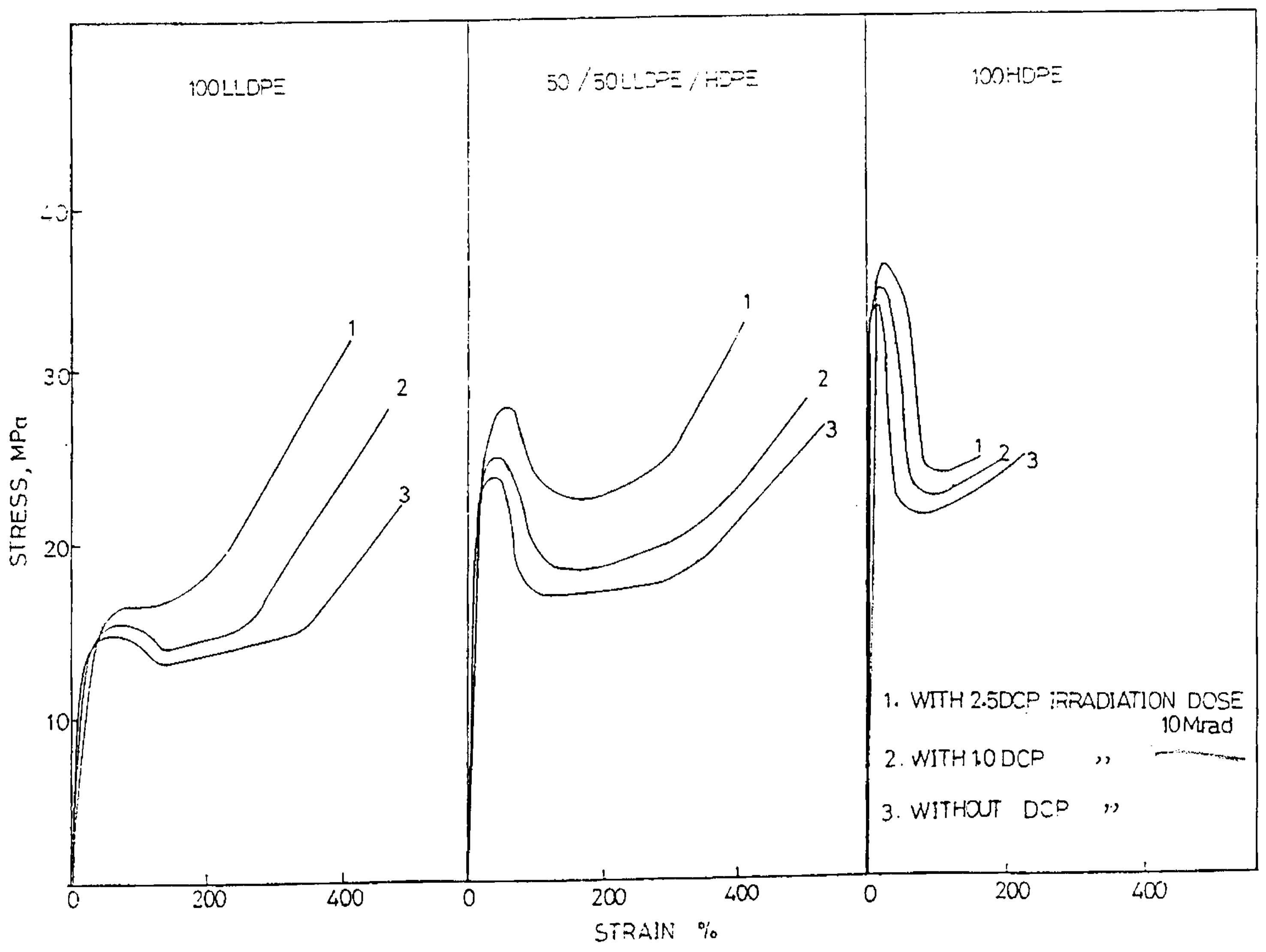

FIG.4.12 TENSILE STRESS – STRAIN CURVES OF IRRADIATED HDPE, LLDPE AND 50/50 HDPE/LLDPE BLEND.

stress at yield is not observed in this case. This is obviously because of the stable necking behaviour of the polymer is absent in this case, indicating notable changes in structure with radiation crosslinking.

Figs.4.13 and 4.14 show the variation of modulus and yield stress with gamma radiation in blends containing 2.5 wt % of DCP. While modulus decreases, yield stress steadily increases with irradiation dosages for all compositions.

Figs.4.15 and 4.16 show the abrasion loss of HDPE and LLDPE with increase in radiation dosage and DCP content. The abrasion resistance of the blends is found to improve with increase in radiation dosage and DCP content as expected. The abrasion resistance of the blends is found to be in between those of HDPE and LLDPE (Table 4.4). The resistance is found to be higher for HDPE and HDPE rich blends. This again supports our earlier proposition that HDPE phase gets crosslinked more than that of LLDPE.

Conclusion

Gamma radiation of HDPE, LLDPE and their blends in presence of DCP is found not to affect the crystallinity of

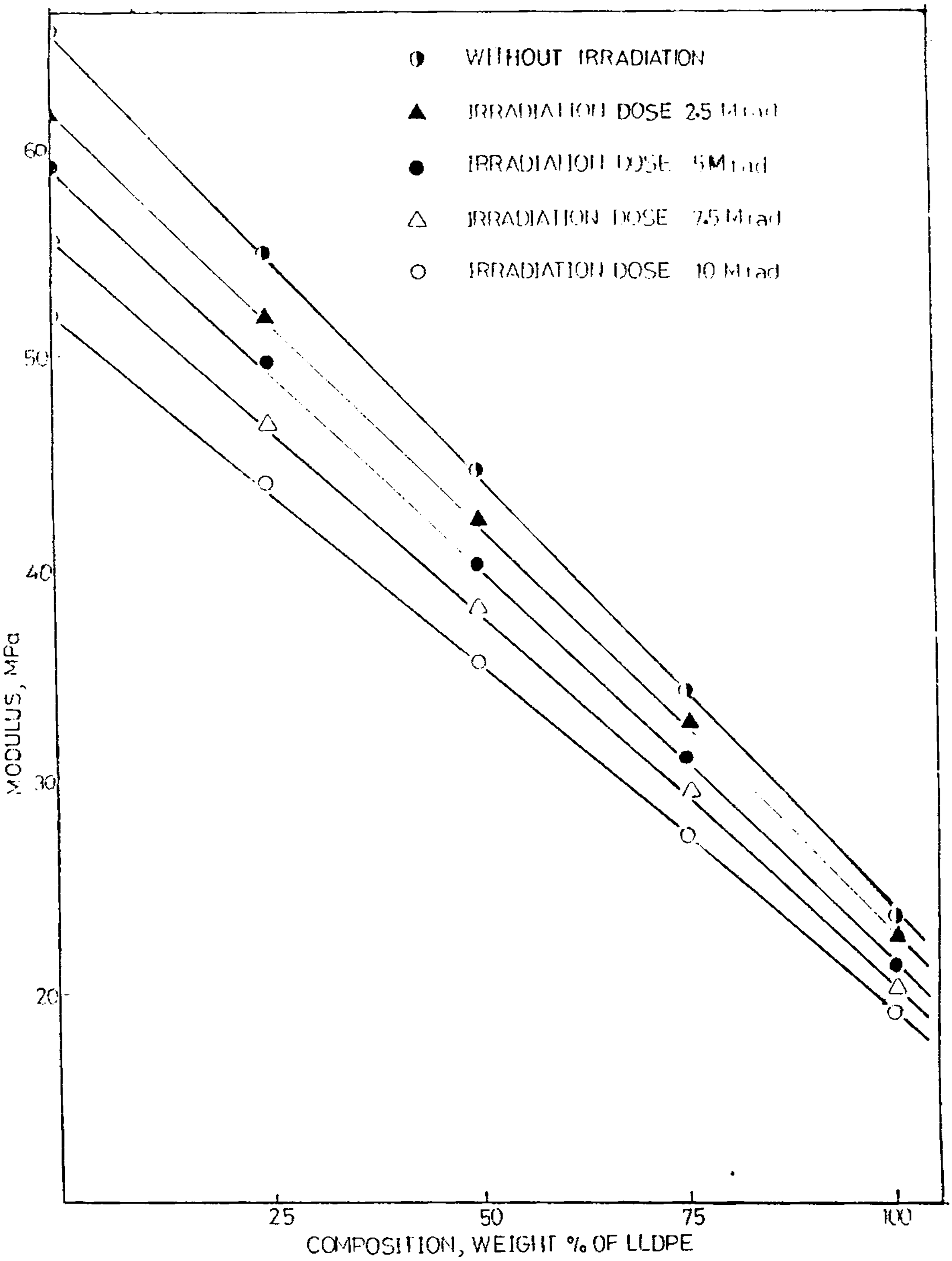

FIG.4.13 VARIATION OF MODULUS OF HDPE/LLDPE BLENDS WITH COMPOSITION.

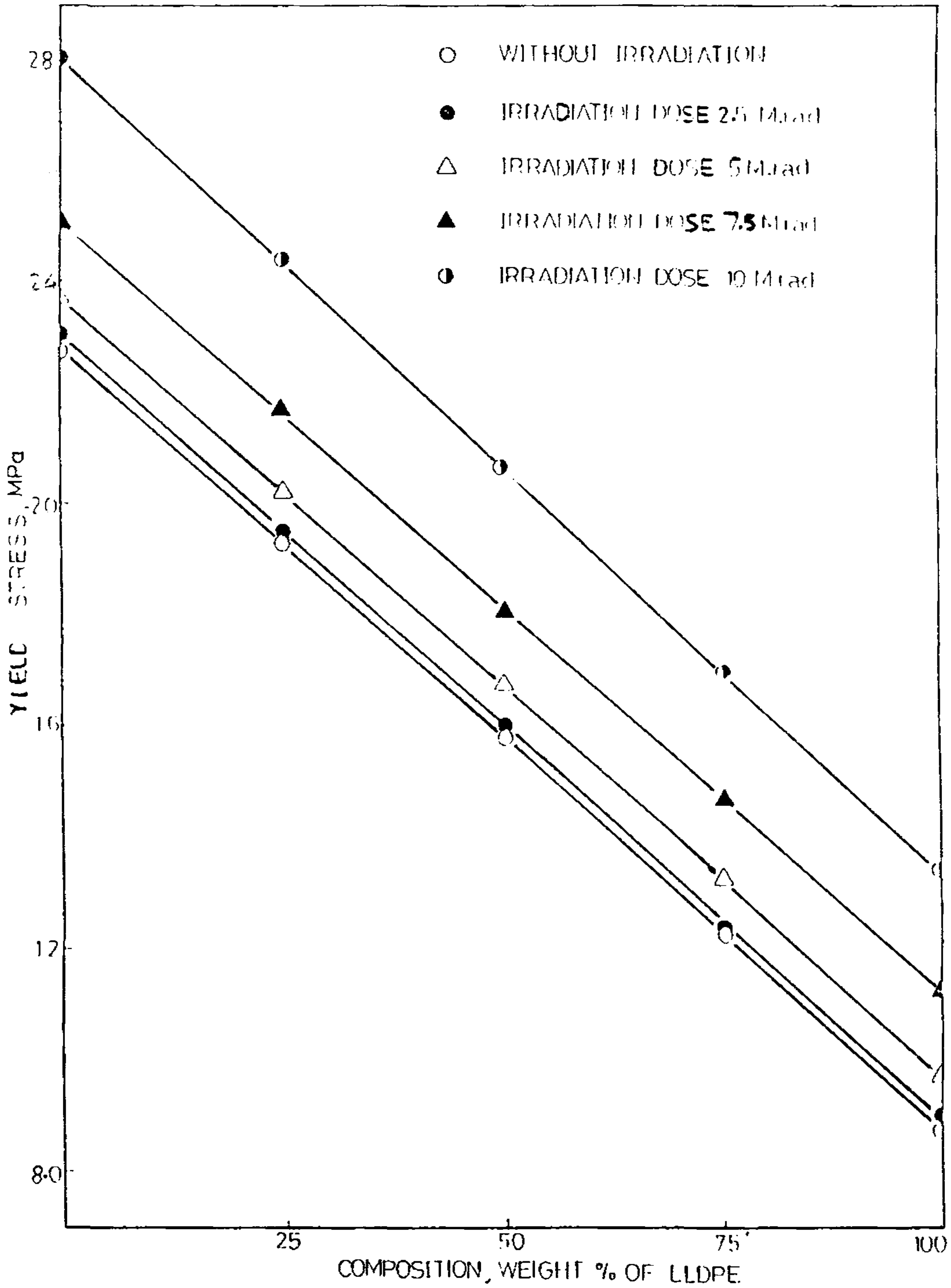

FIG.4.14 VARIATION OF YIELD STRESS OF HDPE/LLDPE BLENDS WITH COMPOSITION.

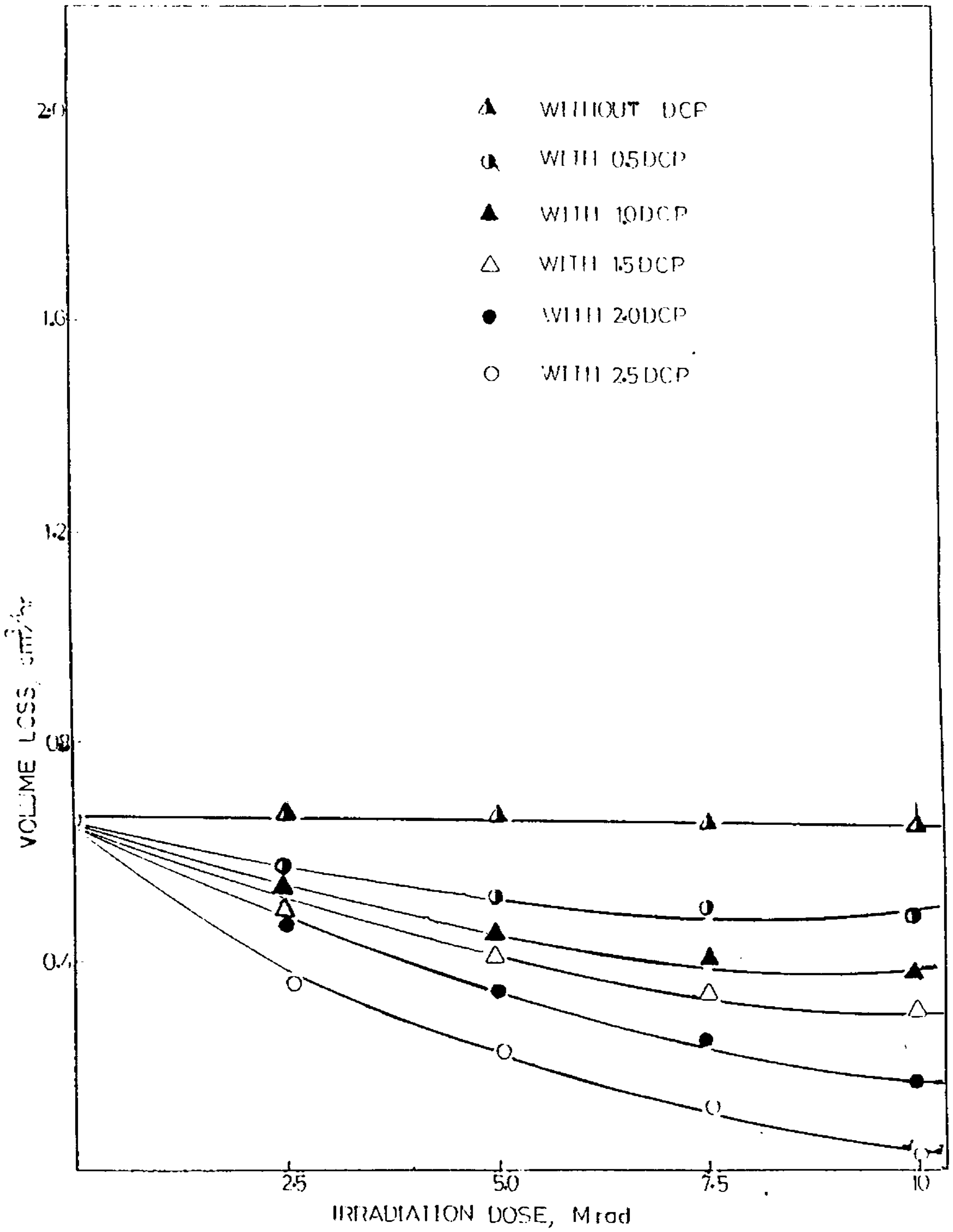

FIG.4.15 VARIATION OF ABRASION LOSS OF HDPE WITH IRRADIATION DOSE.

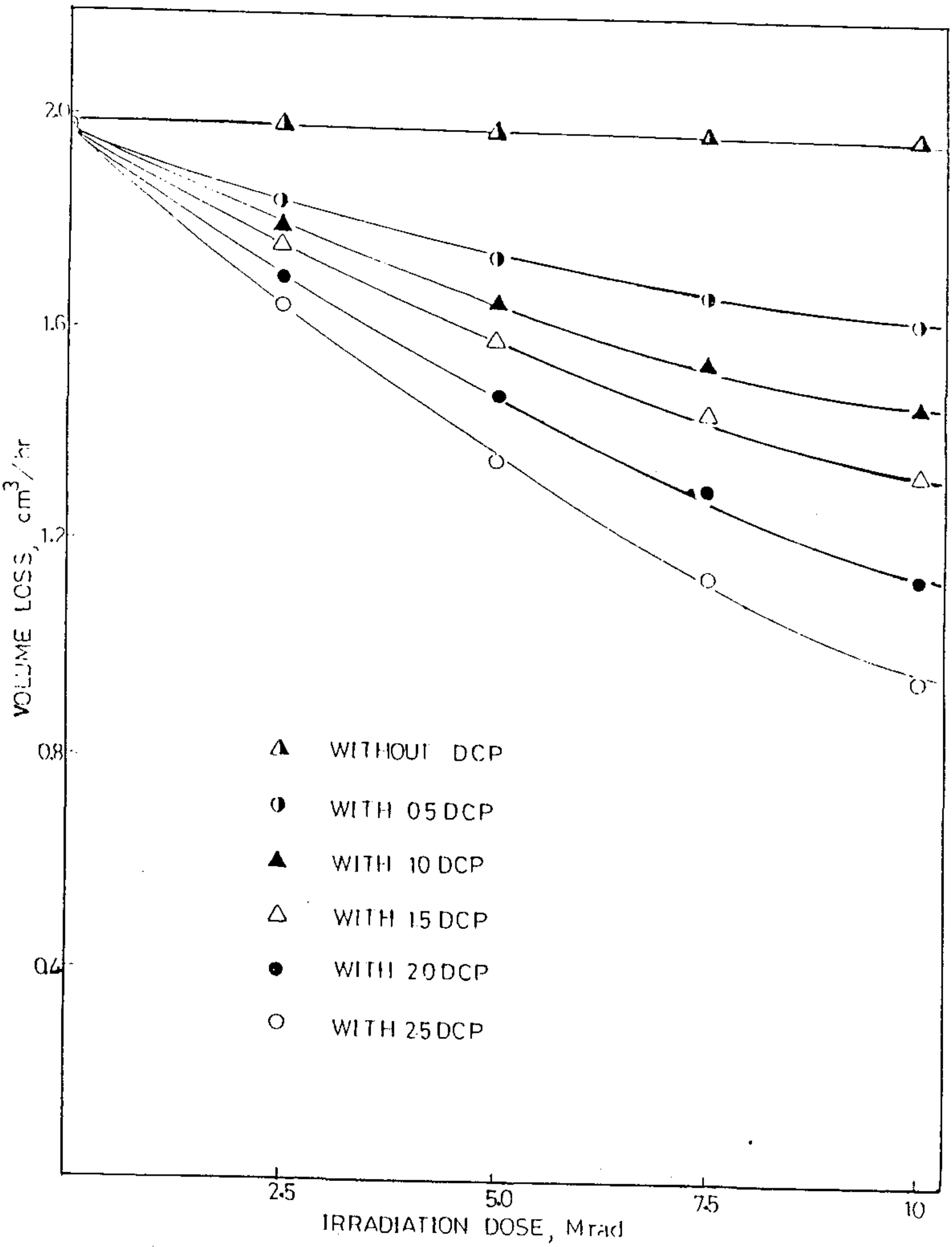

FIG.4.16 VARIATION OF ABRASION LOSS OF LLDPE WITH IRRADIATION DOSE.

Table 4.4: Variation of volume loss (cm^3/hr) on abrasion with irradiation dosage and DCP concentration in HDPE/LLDPE blends

	DCP Concentration (wt %)																			
	0.5				1.0				1.5				2.0				2.5			
Composition wt % of HDPE / Radiation dose, Mrad	2.5	5	7.5	10	2.5	5	7.5	10	2.5	5	7.5	10	2.5	5	7.5	10	2.5	5	7.5	10
0	1.85	1.74	1.68	1.64	1.8	1.66	1.55	1.48	1.75	1.57	1.45	1.34	1.7	1.48	1.3	1.15	1.65	1.38	1.15	0.96
25	1.78	1.64	1.52	1.42	1.73	1.55	1.4	1.27	1.66	1.42	1.2	1.02	1.58	1.34	1.1	0.9	1.55	1.21	0.91	0.7
50	1.38	1.3	1.07	1.05	1.3	0.98	0.88	0.8	1.06	0.9	0.75	0.63	1.01	0.8	0.61	0.45	0.97	0.51	0.45	0.26
75	0.6	0.55	0.55	0.54	0.55	0.52	0.48	0.47	0.53	0.47	0.44	0.4	0.51	0.45	0.38	0.36	0.5	0.4	0.31	0.25
100	0.57	0.51	0.49	0.48	0.53	0.45	0.4	0.38	0.49	0.41	0.34	0.3	0.45	0.34	0.25	0.18	0.35	0.23	0.12	0.05

the polymers seriously and hence radiation induced cross-linking improves the tensile strength, yield stress and abrasion resistance.

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Chapter 5

MODIFICATION OF HDPE/LLDPE BLENDS USING ELASTOMERS AND FILLERS

1. EFFECT OF ELASTOMERIC MODIFIERS ON HDPE/LLDPE BLENDS

Improvement in impact resistance of brittle thermoplastics by elastomers has been in commercial practice for about 50 years now, one of the most classical examples being impact resistant polystyrene. Eventhough polyolefins may be regarded as rubber reinforced thermoplastics because they comprise crystalline and amorphous (rubbery) regions, elastomers have been added to improve impact resistance and environmental stress crack resistance of polyolefins.

A number of papers have reported on the behaviour of the blends based on high density polyethylene (HDPE), polypropylene (PP) and various ethylene propylene elastomers (EPM and EPDM).[1-12] The low temperature impact resistance of PP can be improved by rubber toughening[7] which may also employ combinations including HDPE.[12]

Although many rubbery materials show varying compatibility with polyethylene the elastomeric materials used in commercial compounds are polyisobutylene (PIB) and Butyl rubber (IIR). PIB was originally used as a plasticiser for polyethylene but was later found also to improve the environmental stress cracking resistance. 10%

of PIB in polyethylene gives a compound resistant to stress cracking as assessed by the severe BTL test. It has been shown that the higher the molecular weight of PIB, the greater the beneficial effect. PIB may or may not increase the fluidity (ease of flow) of polyethylene, this depending on the molecular weight of the two polymers. Because of its lower cost butyl rubber is preferred to PIB.

Polyethylene is sometimes blended with ethylene propylene rubber upto 20% in blown film applications. In the present study low concentrations of elastomers such as natural rubber (NR), butyl rubber (IIR), ethylene propylene rubber (EPDM) and a thermoplastic elastomer, styrene-isoprene-styrene (SIS) are tried as impact and environmental stress crack modifiers in HDPE/LLDPE blends.

Experimental

The blends of HDPE, LLDPE 1 and elastomers were prepared in a Brabender plasticorder model PL 3S equipped with a roller mixing head at 150°C, and 50 rpm for 10 minutes. Sheets of 2 mm thick were formed from the blends by compression moulding at 160°C for 2 minutes using a mould having provision for water cooling under pressure.

Tensile properties were determined using a Zwick UTM model 1445 using a crosshead speed of 50 mm per minute at room temperature.

Environmental stress crack resistance of the samples was measured as per ASTM D 1693 (1980) at 50°C using 25% pot. oleate and 25% sulphuric acid as sensitising media.

Results and Discussion

Fig.5.1 shows the tensile strength of 50/50 HDPE/LLDPE blends as a function of elastomer content. From the figure it may be observed that the tensile strength values decrease with increasing elastomer levels. Of the various elastomers tried butyl rubber and ethylene propylene rubber seem to be the best, the reduction in tensile strength in these cases being less compared to natural rubber and styrene-isoprene-styrene rubber.

Elongation at break as a function of elastomer content is shown in Fig.5.2. The elongation at break increases with increasing elastomer content as expected. This will probably result in an improvement of impact strength by the addition of elastomers.

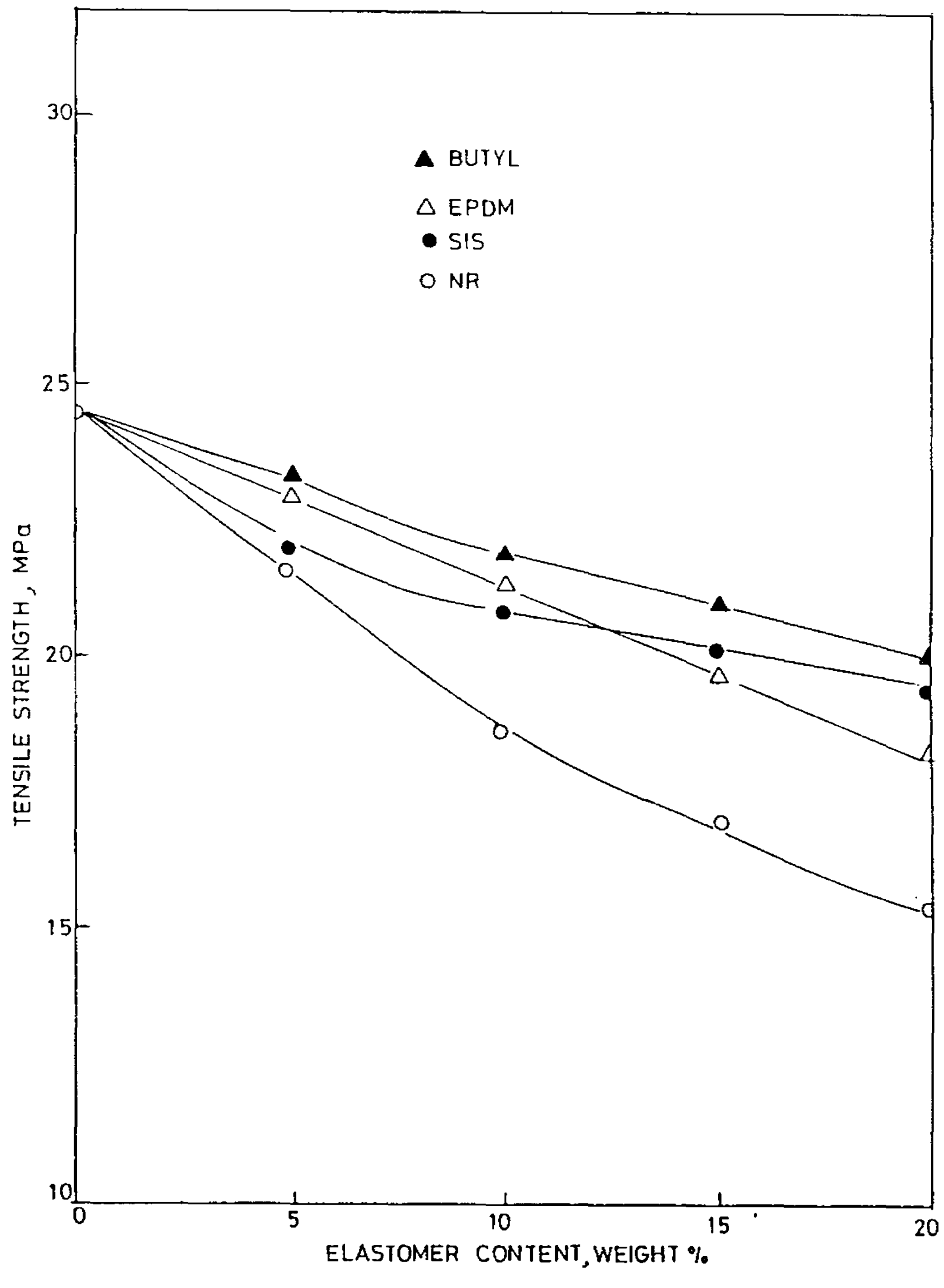

FIG.5.1 VARIATION OF TENSILE STRENGTH OF 50/50 HDPE/LLDPE BLEND WITH ELASTOMER CONTENT.

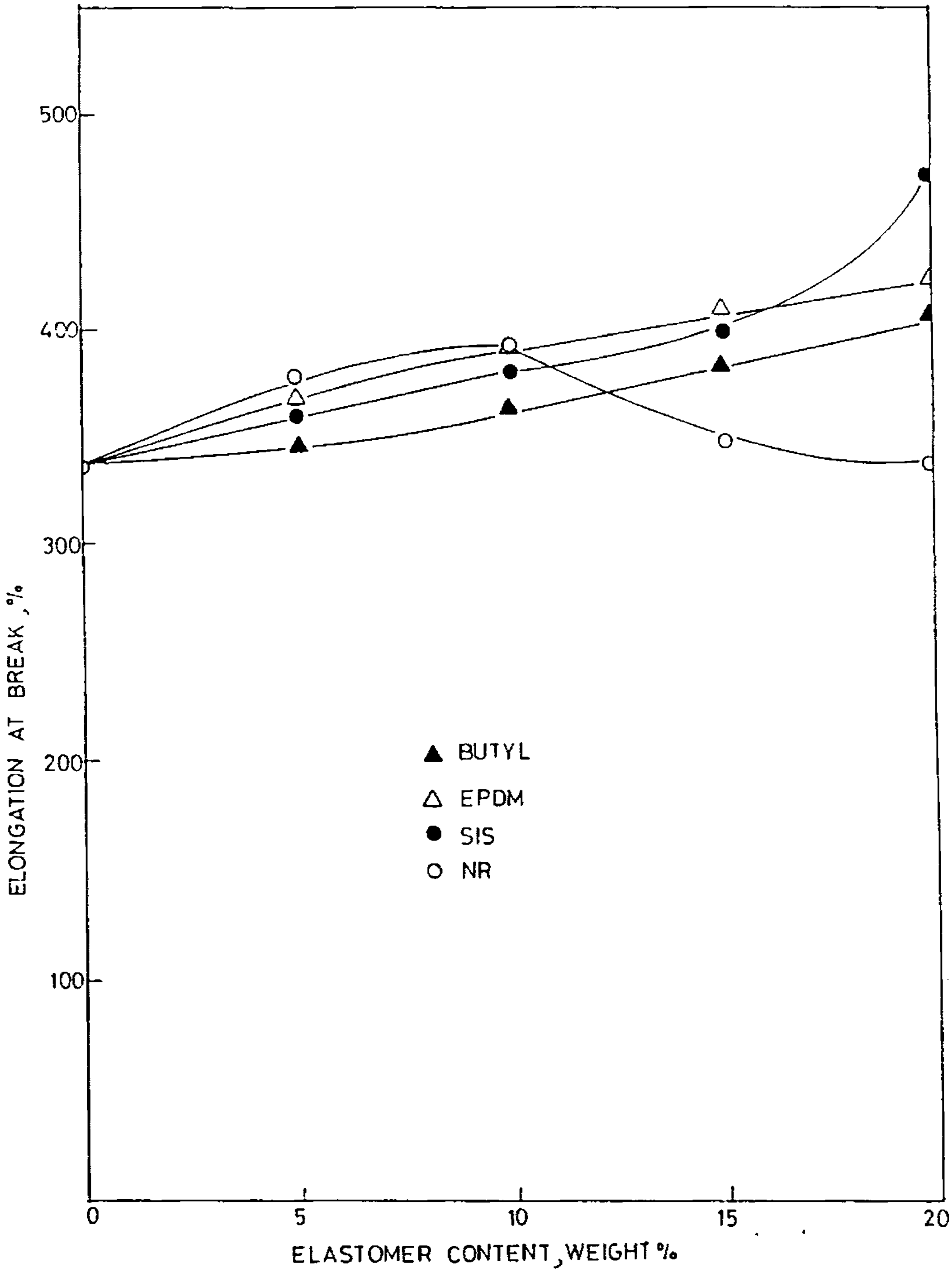

FIG.5.2 VARIATION OF ELONGATION AT BREAK OF 50/50 HDPE/LLDPE WITH ELASTOMER CONTENT.

Fig.5.3 shows the yield stress as a function of elastomer concentration for the blend. This property exhibits an almost linear decrease with increase in elastomer content.

Modulus of the blends as a function of elastomer concentration is shown in Fig.5.4. Addition of elastomer reduces the modulus almost linearly.

The effect of elastomer concentration on the mechanical properties of HDPE, LLDPE and the complete range of their blends is shown in Tables 5.1, 5.2, 5.3 and 5.4. From these tables it is found that in the case of butyl rubber and EPDM, modulus, yield stress and tensile strength decrease only marginally.

Fig.5.5 shows the environmental stress crack (ESC) values of HDPE as a function of the elastomeric modifier concentration. ESC values increase with the elastomer concentration. From Figs.5.5 and 5.6 it can be observed that the environmental stress cracking is more in 25% H_2SO_4 than in 25% pot. oleate (soap). For blends with 25 or more weight % of LLDPE no crack was observed even after seven

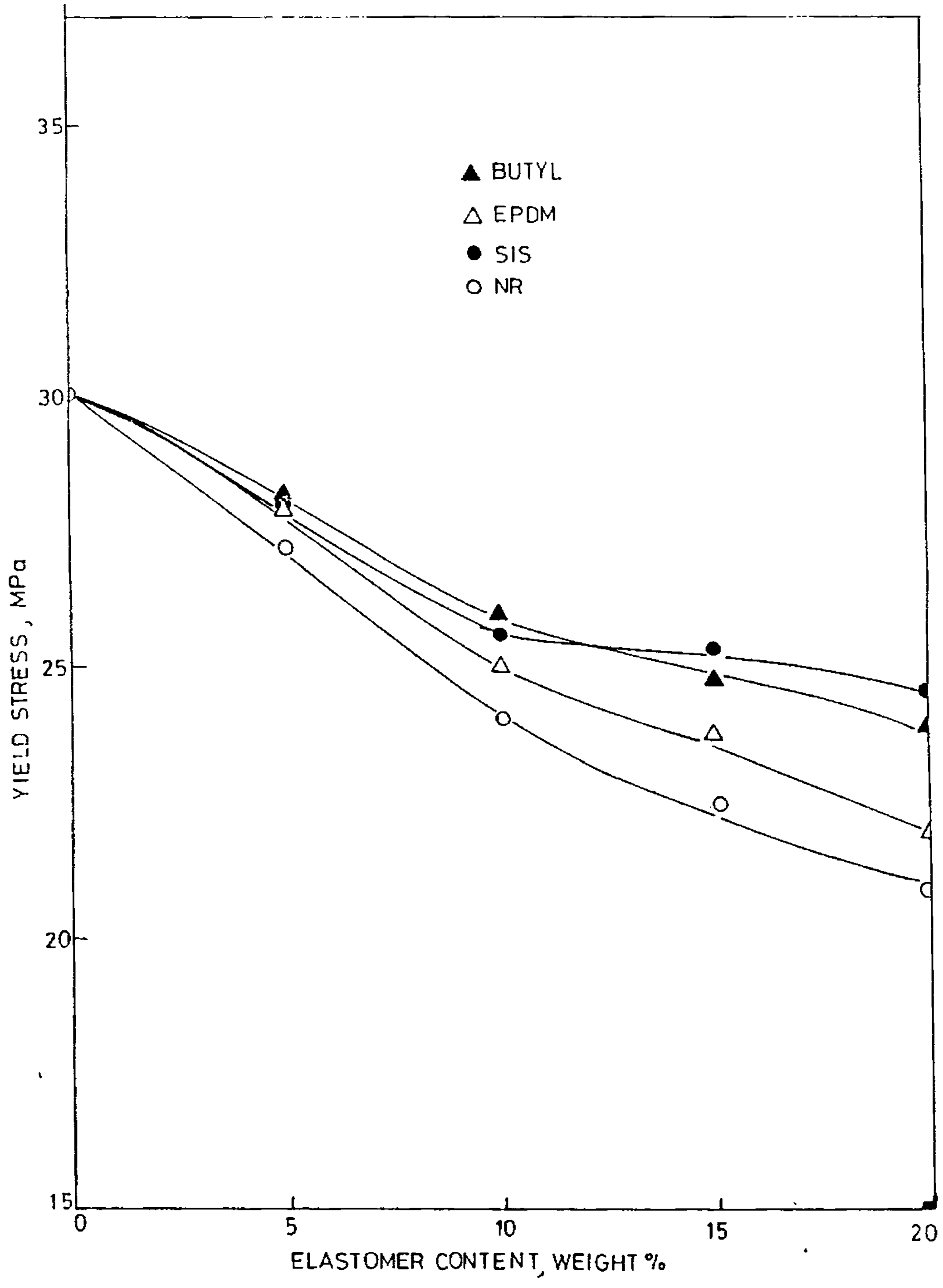

FIG.5.3 VARIATION OF YIELD STRESS OF 50/50 HDPE/LLDPE BLEND WITH ELASTOMER CONTENT.

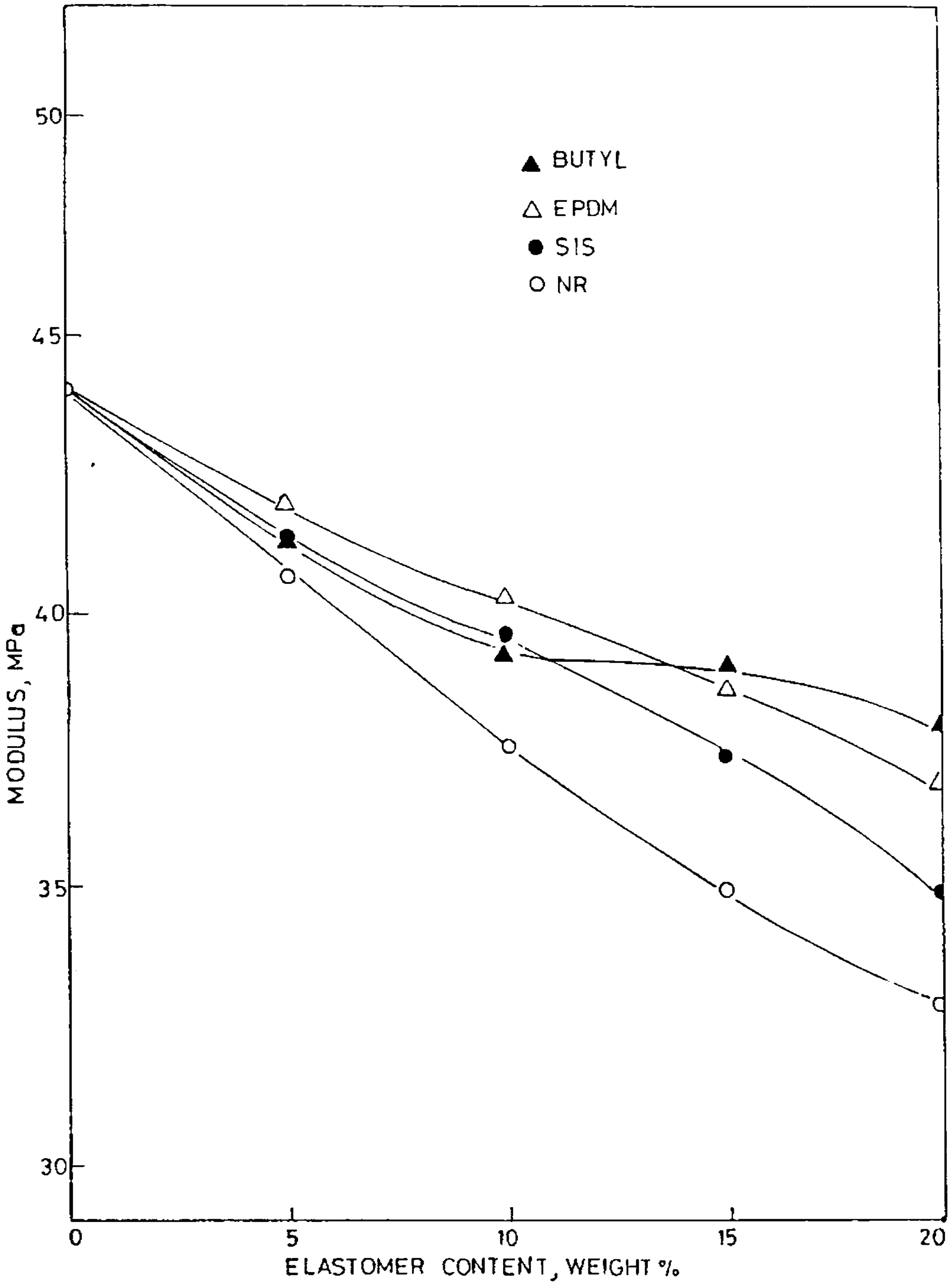

FIG.5.4 VARIATION OF MODULUS OF 50/50 HDPE/LLDPE BLEND WITH ELASTOMER CONTENT.

Table 5.1: Effect of Natural rubber content on the mechanical properties of HDPE/LLDPE blends

LLDPE wt. %	Natural Rubber wt %																			
	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20
	Tensile strength, MPa					Elongation at break, %					Yield stress, MPa					Modulus, MPa				
0	26.5	23	22	20.8	20.4	25	30	32	36	40	35	32	28	26.5	25	65	63	58	54	50
25	25.2	22.1	21.3	20.5	19.7	200	225	235	250	260	33	30	26.2	24.6	23	55	53	51	46	44
50	24.5	21.8	21	20.3	19.5	337	372	387	350	330	30	27.2	24	22.5	21	44	43	39	35	33
75	24.3	22	21	20	19	437	440	460	475	500	27	24.2	21	19.8	18.4	32.5	31	29	28	26
100	24	22	21	20	19	525	540	550	560	575	23	20.5	18	61.5	15	22.5	22	21	19	18

Table 5.2: Effect of SIS content on the mechanical properties of HDPE/LLDPE blends

LLDPE wt. %	Styrene Isoprene Styrene wt. %																			
	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20
	Tensile Strength, MPa					Elongation at break, %					Yield stress, MPa					Modulus, MPa				
0	26.5	25	22.4	21	19.6	25	28	30	33	37	35	34	32.8	32	30.9	65	62	59	55	52.5
25	25.2	23.8	21.5	20.2	19.1	200	212	225	250	275	33	31.3	30	29	27.4	55	52	50	46	45
50	24.5	23	21.3	19.8	18.5	337	360	378	400	470	30	28	27	25.4	23.6	44	42.5	40	37.5	35
75	24.3	22.3	20.4	19.5	18.8	437	470	490	505	525	27	24.4	23	21	19.5	33	32.5	31	29	27.5
100	24.2	22.	20.5	19.8	19.1	525	560	575	600	630	23	20	18	16.5	14.4	22	22.5	21	20	19

Table 5.3: Effect of EPDM content on the mechanical properties of HDPE/LLDPE blends

LLDPE wt. %	Ethylene propylene diene rubber wt. %																			
	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20
	Tensile strength, MPa					Elongation at break, %					Yield stress, MPa					Modulus, MPa				
0	26.5	23.4	21	20.8	20.5	25	28	30	32	35	35	33.6	31.5	30	28	65	62	60	56	52
25	25.2	22	20.6	20.5	20	200	210	230	255	310	33	31	28.5	26.5	24.7	55	53	51	49	47
50	24.5	22	21	20.3	19.5	337	375	387	411	425	30	27.8	25	24	22.1	44	42	38	36	35
75	24.3	20.9	20.7	20	19.3	437	460	475	500	535	27	24	21	19	17.8	32.5	31	30.5	29	29
100	24.2	22	21.8	19.2	18.5	525	535	550	575	625	23	19	17	15.6	14.5	22.5	22	21	21	20

Table 5.4: Effect of butyl rubber content on the mechanical properties of HDPE/LLDPE blends

LLDPE wt. %	Butyl rubber wt. %																			
	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20
	Tensile strength, MPa					Elongation at break, %					Yield stress, MPa					Modulus, MPa				
0	26.5	25.2	24.8	24	23	25	27	29	30	30	35	32	30	28	27	65	62	59	56	54
25	25.2	24.1	23.6	22.7	22	200	230	260	275	300	33	30	29	27	26	55	52.5	51	48	46
50	24.5	23.5	22	21	20	337	342	360	382	405	30	28.2	26	25	24	44	41.5	39.2	39	38
75	24.3	22.1	21.6	20.8	20	437	450	470	500	520	27	25	22	20.5	20	32.5	31	30.5	29.5	28
100	24.2	21.8	20.8	20.2	19.8	525	535	550	580	600	23	21	20.5	19	18	22.5	22	21	20.5	20

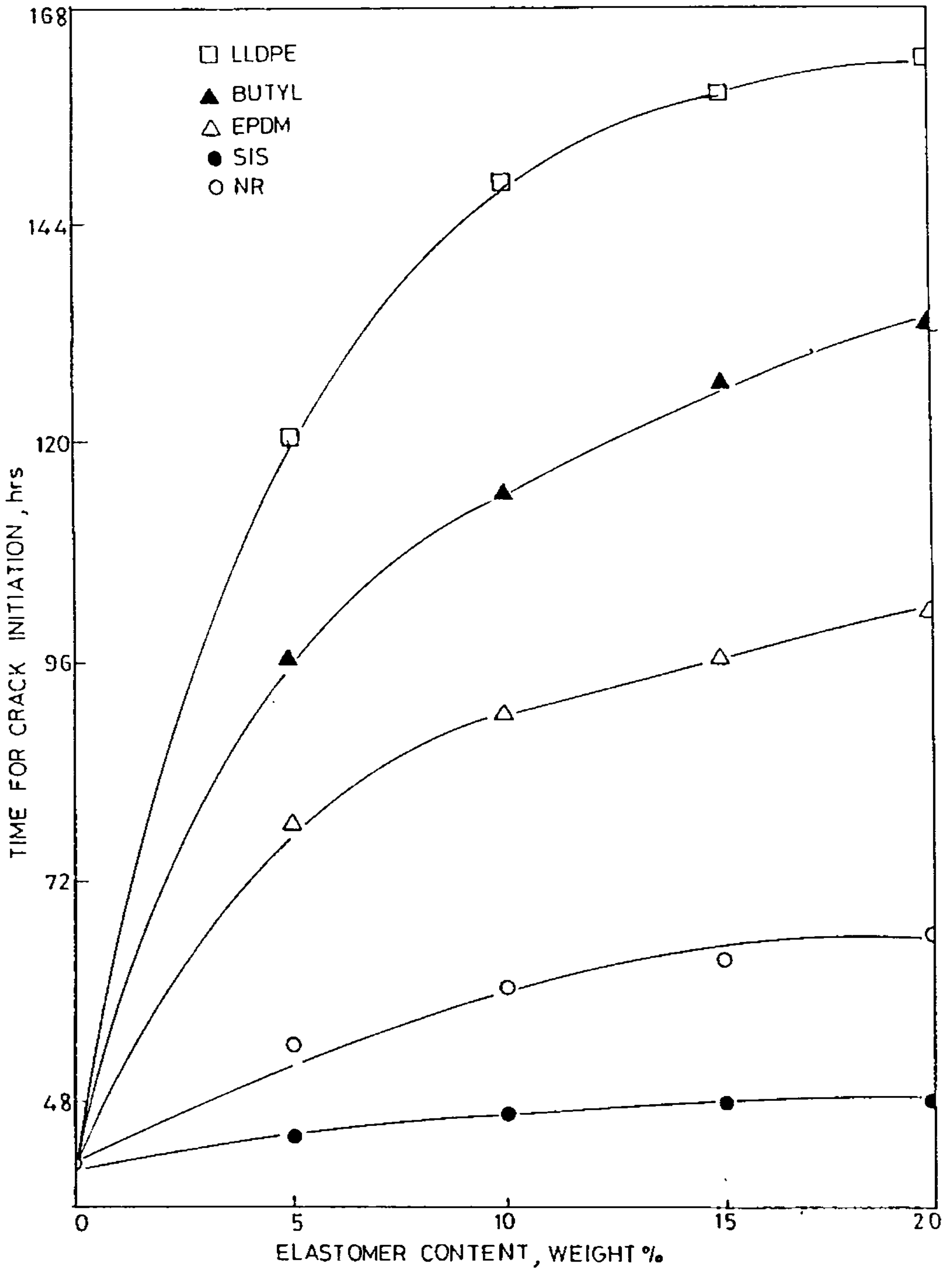

FIG.5.5 VARIATION OF ENVIRONMENTAL STRESS CRACK RESISTANCE OF HDPE WITH ELASTOMER CONTENT [MEDIUM – 25% POTASSIUM OLEATE AT 50°C].

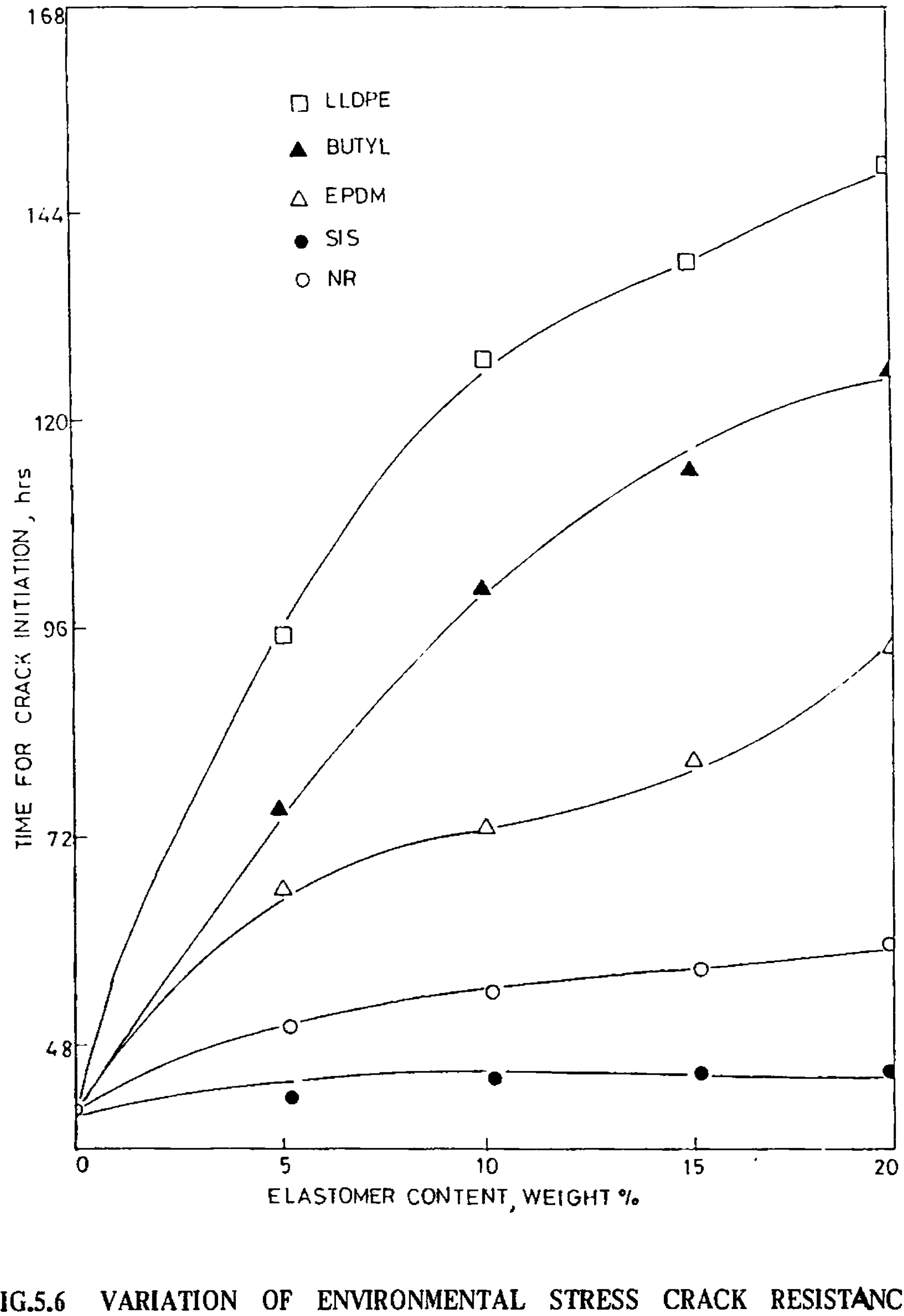

FIG.5.6 VARIATION OF ENVIRONMENTAL STRESS CRACK RESISTANCE OF HDPE WITH ELASTOMER CONTENT [MEDIUM 25% SULPHURIC ACID AT 50°C].

days (168 hrs) exposure in 25% pot. oleate or 25% H_2SO_4. This shows the superiority of LLDPE to environmental stress cracking compared to HDPE.

Conclusions

1. Among the various elastomers used as modifiers butyl rubber is found to be the best for improving the environmental stress crack resistance and improving elongation at break.

2. The optimum levels of the modifiers is found to be between 5-10 wt % of HDPE and LLDPE taken together.

3. Blends of HDPE and LLDPE with LLDPE concentration of above 25% have very good resistance to environmental stress cracking.

2. MECHANICAL PROPERTIES OF FILLED HDPE/LLDPE BLENDS

Although polyethylene and its blends can be, and indeed often is, used without additives a number of them may be blended into the polymer for various reasons. In polymer blends, fine particle fillers may be dispersed unevenly between the polymeric components which can influence the mechanical properties of the blends.

Fillers, the important constituent of many plastic materials, are rarely used with polyethylene since they interfere with the crystallinity of the polymer and often give brittle products of low ductility. Compounds with increased rigidity and tensile strength compared to unfilled polymer may be obtained by using titanate or silane coupling agents along with nonblack fillers. Microwave plasma discharges were also used to modify the filler surfaces.[13] The effect of filler particle shape and surface treatment on yield stress of PP filled with calcium carbonate was studied.[14] Fillers improve the stiffness and heat deformation resistance of sheetings, injection moulded products etc.

In the present study surface treated calcium carbonate, silica and GPF blacks were employed as a means to improve the stiffness and yield stress of a blend containing equal parts of HDPE and LLDPE.

Experimental

The polymers were first melt mixed in a Brabender plasticorder at 160°C for 5 minutes at 50 rpm rotor speed. Then the filler was added at 20 rpm (2 minutes) and finally dispersed for 8 minutes at 50 rpm. Sheets of 2 mm thick were pressed at 160°C between aluminium foils at 140 kg/cm^2 for 3 minutes and then cooled under pressure to 60°C by water circulation.

The tensile measurements were performed using a Zwick UTM model 1445 at a crosshead speed of 50 mm per minute. For the high rate tension test a cross head speed of 200 mm per minute was used. The area under the stress-strain curve in the high rate tension test is reported as a measure of the toughness of the material.

Results and Discussion

Fig.5.7 shows the tensile strength of the blend as a function of filler loading. The tensile strength decreases with addition of 5 phr of filler. This may be due to interference in crystallinity by the addition of fillers. After the initial decrease the tensile strength values gradually increase with filler loading. This may be due to the stiffening action of the fillers.

Fig.5.8 shows the elongation at break as a function of filler loading. Except in the case of GPF black EB decreases with increase in filler loading. For GPF black filled blend, EB increases upto 5 phr level and then

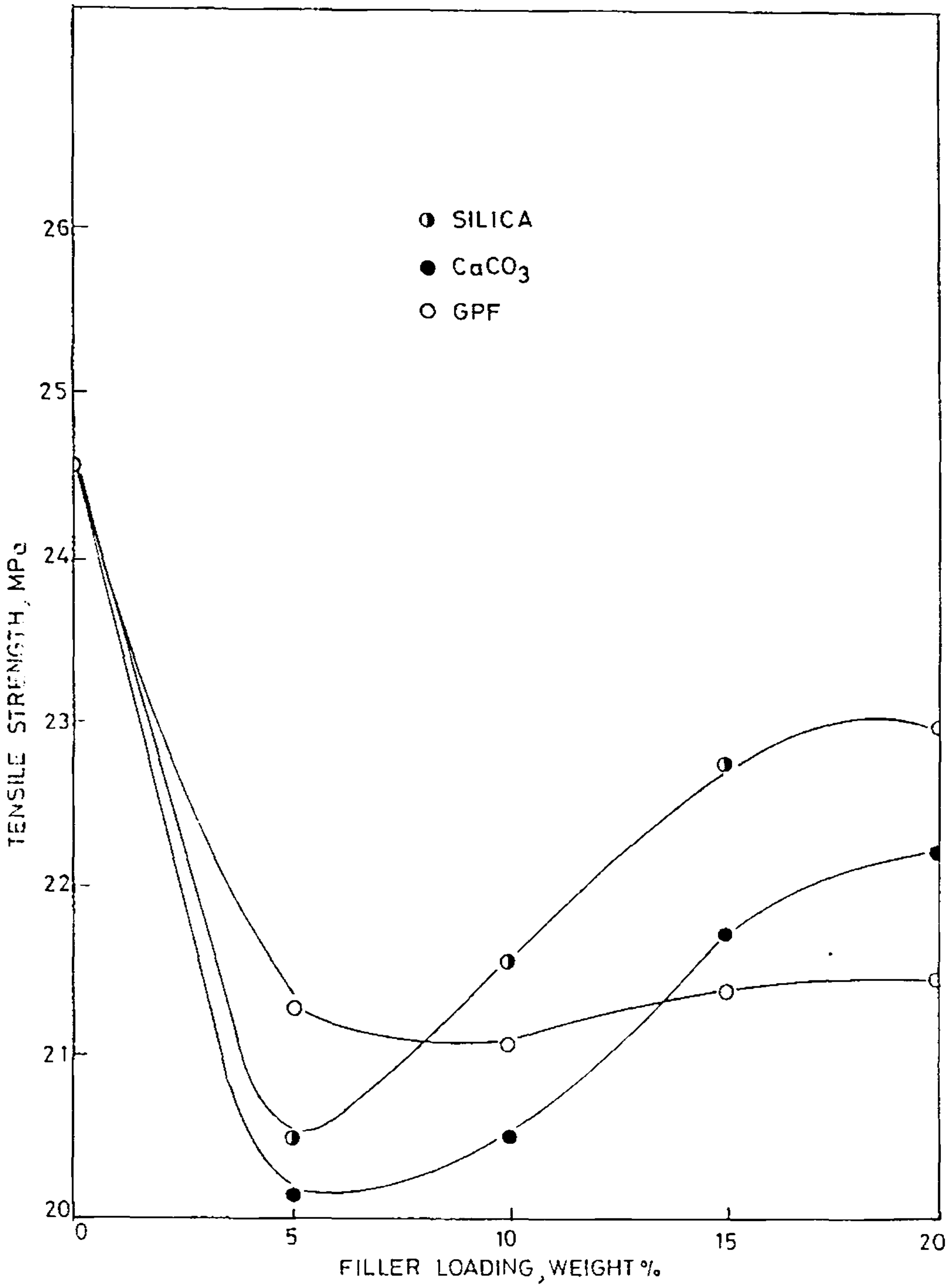

FIG.5.7 VARIATION OF TENSILE STRENGTH OF 50/50 HDPE/LLDPE BLEND WITH FILLER LOADING.

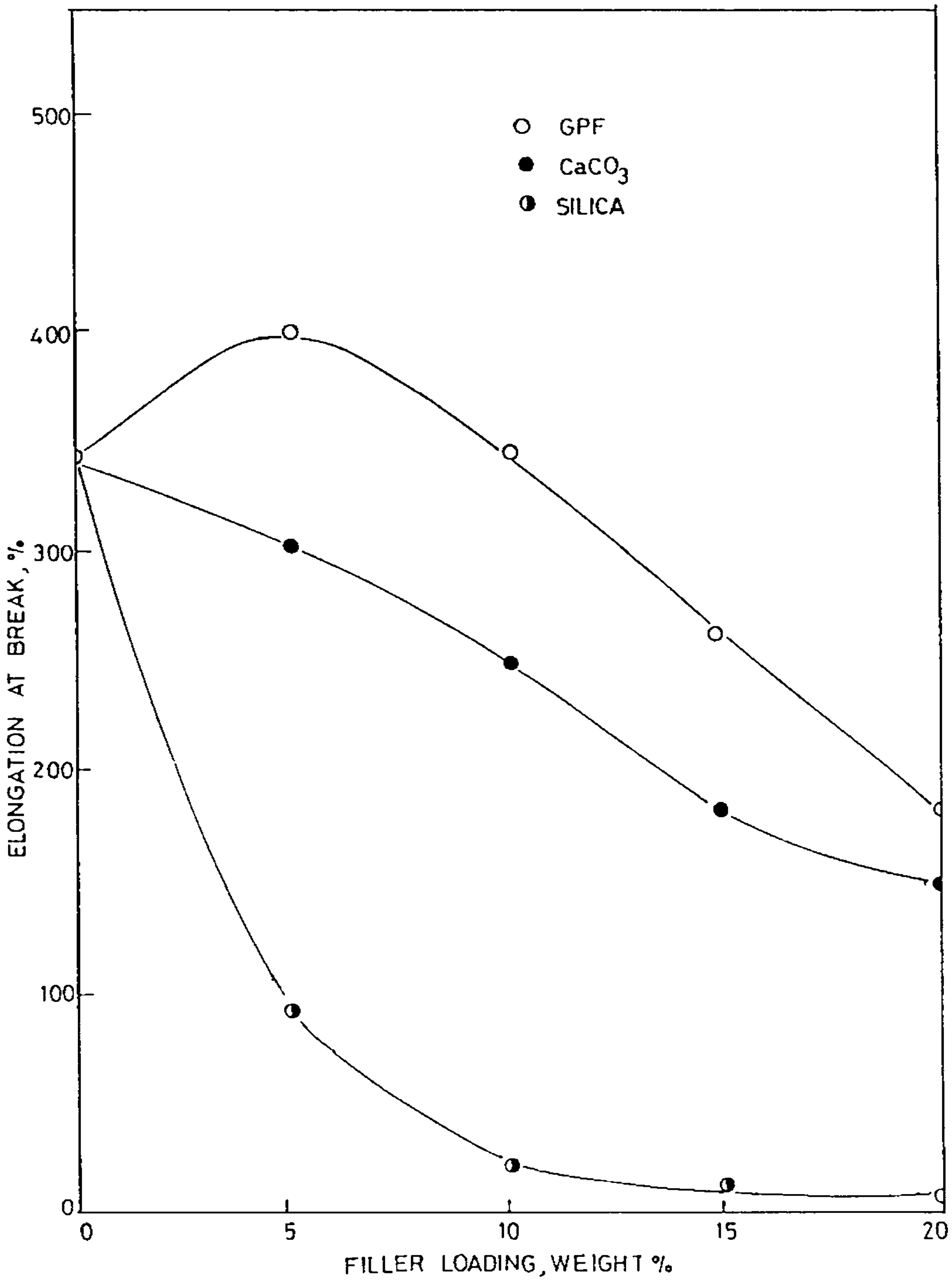

FIG.5.8 VARIATION OF ELONGATION AT BREAK OF 50/50 HDPE/LLDPE BLEND WITH FILLER LOADING.

decreases. The sharp decrease in EB values for silica filled blends may be due to the poor interfacial adhesion between silica and the polymers.

Modulus increases almost linearly with filler loading (Fig.5.9). The yield stress of the blends as a function of filler concentration is shown in Fig.5.10. The tensile yield stress decreases with increase in filler loading. A number of factors may be contributing to this effect.[15] Filler reduces the effective cross section of the matrix in the loaded polymer blend. This leads to an increase in internal stress, at any given external loading, compared with the unfilled matrix. Stress concentration caused by the filler also contributes to the internal stress. Microplastic deformations occur around particles which facilitate damage of the material at lower external load, compared with the unfilled blend. As a consequence of the different expansion coefficients, thermally induced internal stresses occur around the filler particles. This contributes to an increase of the dewetting stress. The dewetting stress for sufficiently small particles is greater than the stress necessary for crazing or occurrence of shear bands. At constant temperature and strain rate the decrease of yield stress is inversely proportional to

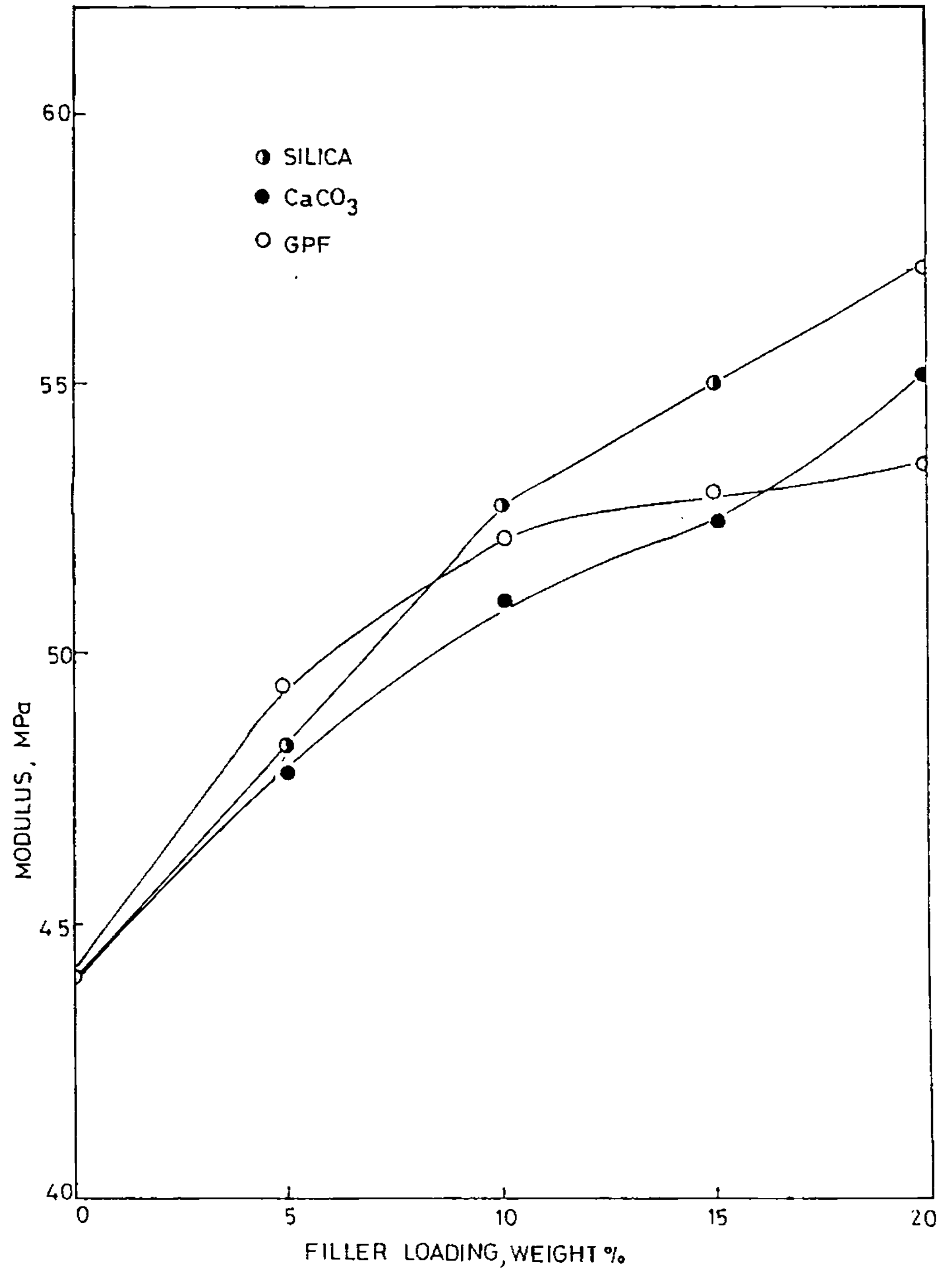

FIG.5.9 VARIATION OF MODULUS OF 50/50 HDPE/LLDPE BLEND WITH FILLER LOADING.

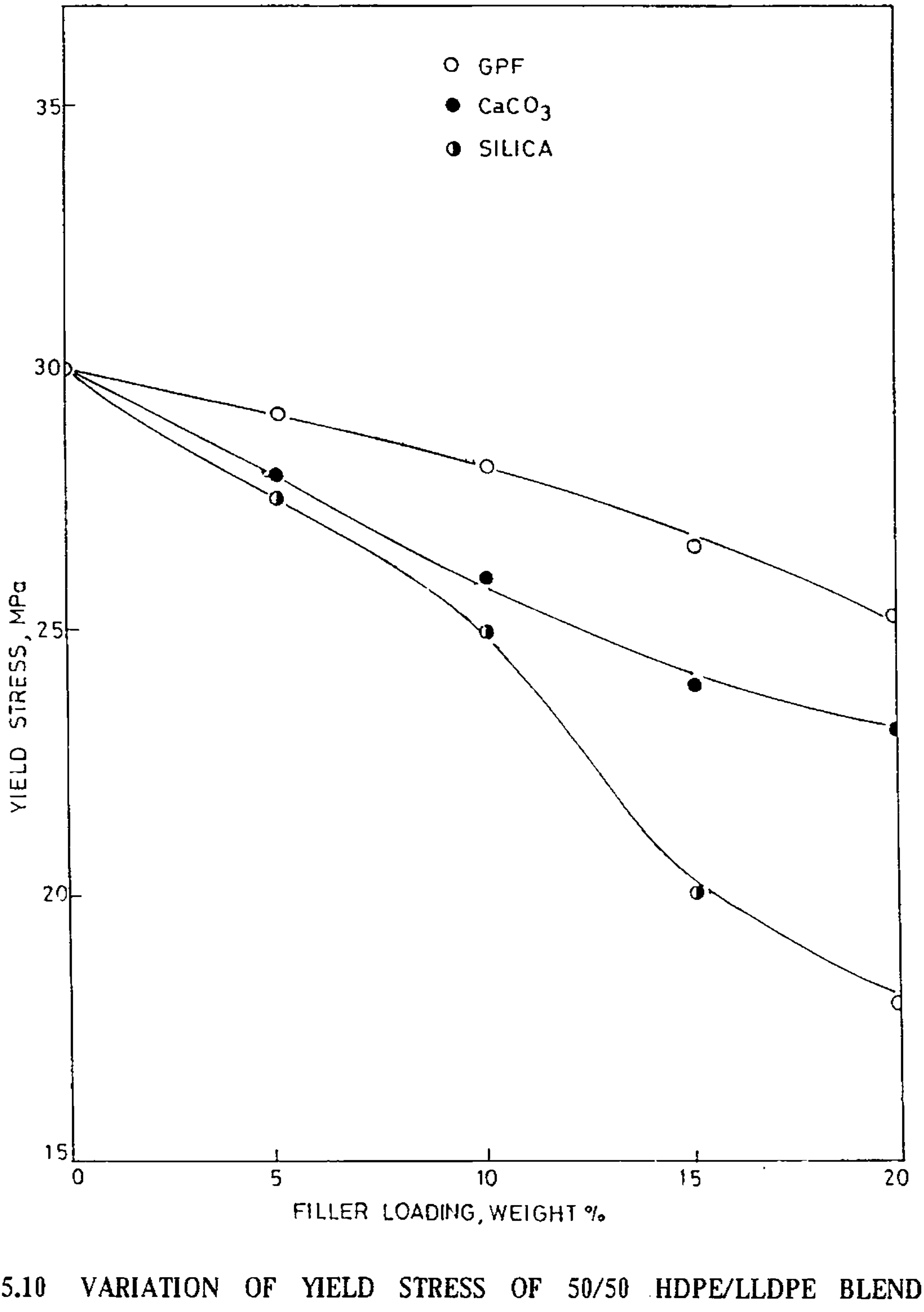

FIG.5.10 VARIATION OF YIELD STRESS OF 50/50 HDPE/LLDPE BLEND WITH FILLER LOADING.

the square root of the particle radius. The same phenomenon was observed in the case of PP/$CaCO_3$ composition also.[16,17] The degree of iterfacial adhesion also affects the yield stress.

The effect of filler loading on the toughness, hardness and mixing torque of HDPE/LLDPE blend is given in Table 5.5. From the table it can be observed that addition of calcium carbonate and carbon black does not increase the mixing torque appreciably while addition of silica increases the mixing torque and thus affects the processability.

Conclusion

A low level of fillers such as calcium carbonate, silica or carbon black may be incorporated in HDPE/LLDPE blends for cost reduction without seriously affecting the mechanical properties. The modulus and hardness of the blend improve upon filler loading.

Table 5.5 Properties of 50/50 HDPE/LLDPE blend as a function of filler concentration

Filler	Filler loading (wt. %)	Area under the stress-strain curve (mm^2)	Uniform mixing torque (Nm)	Hardness (Shore D units)
Silica	0	8280	3.14	50
	5	1869	3.24	52
	10	450	3.33	54
	15	285	3.72	56
	20	120	4.12	60
Calcium carbonate	5	10400	3.14	51
	10	7780	3.14	51
	15	5635	3.19	53
	20	3810	3.19	55
Carbon black	5	6021	3.14	51
	10	5128	3.24	52
	15	3936	3.33	54
	20	3328	3.43	56

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Chapter 6

SUMMARY AND CONCLUSIONS

Blends of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) were prepared to generate a spectrum of polymers bridging the gap between the mechanical and processing properties of the homopolymers.

The solid phase mechanical behaviour and the melt rheology of HDPE/LLDPE blends are described in chapter 3. The mechanical properties of the blends are in between those of the parent polymers. The properties are in direct proportion to the composition which shows that the blends can be prepared in any desired composition to take advantage of the higher strength and stiffness of HDPE and the higher impact strength of LLDPE. The HDPE/LLDPE melt is strongly non-Newtonian as their precursors. The flow curves could be approximated by straight lines when plotted on log-log scale in the range of shear rates studied and hence could be represented by Ostwald de Waale power law relation. Since the chemical structures of HDPE and LLDPE closely resemble each other, the most important factor promoting the non-Newtonian behaviour is the length of the polymer chain or the molecular weight. The power law index of the blends is in between those of the constituent HDPE and LLDPE. The temperature dependence of viscosity of the blends was measured in terms of an apparent energy of activation for viscous flow. Irrespective of the viscosity, LLDPE shows a higher activation energy which may be due to a low degree of crystallinity in the melt as in the case of polypropylene. Melt elasticity behaviour was described in terms of Bagley correction factor (P_c), and die swell. The melt elasticity of HDPE could be reduced by addition of LLDPE and hence the processing of the blend could be easier than that of HDPE alone. The rheological measurements were also made using a torque rheometer and found to follow the same pattern as obtained from the capillary rheometer.

Chapter 4 describes the modification of HDPE/LLDPE blend by introduction of a low level of crosslinking by using both chemical and radiation methods so as to improve their application spectrum. Dicumyl peroxide was used as the crosslinking agent in chemical crosslinking. The extent of crosslinking was measured by gel content of matrix and properties such as hardness, abrasion loss improved with crosslinking. Crosslinking also improves modulus, yield stress and breaking stress with only marginal decrease in breaking strain. Due to the high elongation of LLDPE, the reduction in this property may not affect the performance of the blends and hence crosslinking could be advantageously used to capitalise on the improvement in mechanical properties and others such as improvement in temperature resistance, creep resistance etc. Another advantage of crosslinking is that the variation of mechanical properties with composition becomes more uniform indicating that the solid phase compatibility has improved and that the crosslinked blends represent an altogether new class of material. Improved uniformity in rheological behaviour was also observed, eventhough the melt viscosity was marginally higher. The power law index, activation energy of viscous flow etc., are also slightly higher for crosslinked blends/polymers.

Radiation crosslinking of the blends was done in a Gamma chamber using dicumyl peroxide as a sensibilising agent in this case. DSC studies showed that radiation crosslinking affected the crystallinity only less severely than chemical crosslinking. Hence this technique can be employed advantageously to improve the thermal and dimensional stability of the blends without seriously affecting the stiffness.

Chapter 5 describes modification of HDPE/LLDPE blends with elastomers and fillers. Elastomers such as natural rubber, butyl rubber, ethylene propylene rubber and a thermoplastic elastomer (styrene-isoprene-styrene) were tried as impact and environmental stress crack modifiers in HDPE/LLDPE blends. Of the various elastomers tried butyl rubber was found to be the best modifier. It was found that a low concentration of fillers can also be incorporated in the HDPE/LLDPE matrix for cost reduction or improvement in modulus and hardness.

LIST OF PUBLICATIONS FROM THIS WORK

1. Studies on PE-HD/PE-LLD blends, Die Angewandte Makromolekulare Chemie, 193, 39-49 (1991).

2. Melt viscosity and melt elasticity of HDPE/LLDPE blends, International Journal of Polymeric Materials (Communicated).

3. Effect of controlled crosslinking on the mechanical and rheological properties of HDPE/LLDPE blends, European Polymer Journal, 28(1), 113-116 (1992).

4. Radiation crosslinking of HDPE/LLDPE blends in presence of dicumyl peroxide, Journal of Elastomers and Plastics (in Press).

5. Effect of Elastomeric modifiers on the mechanical properties of HDPE/LLDPE blends, Kautschuk Gummi Kunststoffe (in Press).

LIST OF ABBREVIATIONS

Polymers

EPDM	Ethylene propylene diene rubber
EVA	Ethylene vinyl acetate
HDPE	High density polyethylene
IIR	Isobutylene isoprene rubber (Butyl rubber)
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
NR	Natural rubber
PIB	Polyisobutylene
PP	Polypropylene
SIS	Styrene isoprene styrene

Other Abbreviations

ASTM	American Society for Testing Materials
BIS	Bureau of Indian Standards
BTL	Bell Telephone Laboratory
JSR	Japan synthetic rubber
ISNR	Indian standard natural rubber
IPCL	Indian Petrochemical Corporation Ltd,
PIL	Polyolefin Industries Ltd.
RRII	Rubber Research Institute of India
DCP	Dicumyl peroxide

DSC	Differential Scanning Calorimetry
D	Diameter of the capillary die
De	Diameter of the extrudate
E	Activation energy
EB	Elongation at break
ESC	Environmental stress crack
G	Apparent shear modulus
kJ/mol	Kilo Joules/mole
L	Length of the capillary die
L_o	Initial gauge length of the dumbbell specimen
L_1	Final gauge length of the dumbbell specimen
M	Torque
MFI	Melt flow index
ML(1+4)100°C	Mooney viscosity determined at 100°C using large rotor after a dwell time of one minute and rotor run for 4 minutes
M_w	Molecular weight
MPa	Mega pascal
n	Power law index
Nm	Newton meter
nm	Nano meter
P	Corrected pressure
P_c	Bagley correction factor
PB	Polymer blends

PA	Polymer alloys
PDB	Positive deviation blends
NDB	Negative deviation blends
PNDB	Positive negative deviation blends
IPN	Interpenetrating polymer network
phr	Parts per hundred rubber/resin
P_o	Initial plasticity
PRI	Plasticity retention index
Q	Volumetric flow rate
R	Radius of the capillary die
rpm	Revolutions per minute
S	Revolutions per minute of the Brabender rotor
S^{-1}	Per second
TS	Tensile strength
T	Temperature (absolute)
T_g	Glass transition temperature
T_m	Melting temperature
UTM	Universal testing machine
W	Energy required for plasticisation

LIST OF SYMBOLS

$\gamma_{w_{app}}$	Apparent shear rate at the wall
γ_{w}	True shear rate at the wall
γ_{R}	Recoverable shear strain
$\tau_{w_{app}}$	Apparent shear stress at the wall
τ_{w}	True shear stress at the wall
ΔP	Pressure drop
ΔG_{m}	Free energy change of mixing
ΔH_{m}	Enthalpy change of mixing
ΔS_{m}	Entropy change of mixing
η	Viscosity
ϕ	Volume fraction
μm	Micrometer
ρ	Density

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