MODIFICATION OF POLYETHYLENES BY REACTIVE EXTRUSION

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Certificate

*This is to certify that this thesis entitled "**Modification of Polyethylenes by Reactive Extrusion**" is an authentic record of the research work carried out by **Mrs. Sheela kumari Isac** under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.*

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DECLARATION

*I hereby declare that the thesis entitled "**Modification of Polyethylenes by Reactive Extrusion**" is an authentic record of the research work carried out by me under the supervision of **Dr. K.E. George,** Head of the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682 022, and no part of the work reported in this thesis has been presented for any other degree from any other institution.*

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SHEELAKUMARI ISAC

LIST OF ABBREVIATIONS

POLYMERS

DCP	Dicumyl peroxide
EP	Ethylene propylene copolymer
GMA	Glycidyl methacrylate
LDPE	Low density polyethylene
LLDPE	Linear low density Polyethylene
MA	Maleic anhydride
PP	Polypropylene
PPE	Polyphenylene ether
PS	Polystyrene
SEBS	Styrene/ethylene – butylene/styrene copolymer
TAC	Triallyl cyanurate

Other Abbreviations

δ	The clearance space
α,β	Collections of machine design parameters
η	The fluid viscosity
ϕ	The helix angle
θ	Volume fraction / residence time
A, B	Collection of terms from the full force balance equation for solids conveying
ASTM	American society for testing and materials
D	Diameter of the capillary die / Diameter of the screw
De	Diameter of the extrudate

$\frac{dp}{dL}$	The pressure gradient
Ea	Activation energy
e	The flight width
EB	Elongation at break
FTIR	Fourier transform infrared
H	The channel depth
Hp	The power requirement
k	Consistency index
l	Characteristic length
L	The effective screw length / barrel length
l_0	Microspcopic dimension associated with the tube radius
MPa	Mega pascal
MRE	Microscopic reaction environment
n	Power law index
N	The screw speed
Nm	Newton meter
ΔP	Overall pressure drop along the screw
P	Pressure
Phr	Parts per hundred resin
Q	Total output
Qd	Drag flow
Ql	Leakage flow
Qp	Pressure flow
R	Capillary radius
Re	Reynold's number

rpm	Revolutions per minute
SSE	Single screw extruder
UTM	Universal testing machine
Z	The lead length
τw_{app}	Apparent shear stress at the wall
γw_{app}	Apparent shear rate at the wall
η_{app}	Apparent viscosity

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CHAPTER 1

INTRODUCTION

INTRODUCTION

One of the main reasons for the widespread use of polymers over other engineering materials like metals, ceramics etc is their easy processability ie, polymeric materials can be easily converted into products. Extrusion and injection moulding are the most widely used processing techniques. Extrusion is also the basis of many other processing techniques. Fundamentally the process of extrusion consists of converting a suitable raw material into a product of specific cross section by forcing the softened material through an orifice or die under controlled conditions. Among the products manufactured by extrusion are pipe, rod, film, sheet, fibre, unlimited number of shapes or profiles and other continuous products.

In certain processing applications, the commercially available polymers are not always optimum in terms of processability and mechanical properties. So polymers, in particular polyolefines, are modified by peroxides, halogens or by grafting techniques to improve mechanical/ thermal stability.[1-5] The conventional method of modification and subsequent processing is a two step process. But in reactive extrusion, both modification and processing are done simultaneously and hence this technique is gaining importance now days.

Over the past decade, the growth of research and development interest in polymer extrusion has been guided by the facts that plastics can no longer be considered as cheap materials and that better quality is required in extruded products. Thus, there is considerable interest in computer aided manufacture which could be one of the most significant new technologies affecting polymer extrusion in this decade.

1.1. PRINCIPLES OF SINGLE SCREW EXTRUSION

The single screw extruder is the most important type of extruder used in the polymer industry. Its key advantages are relatively low cost, straight forward design, ruggedness and reliability, and favourable performance /cost ratio. Many different materials are formed through an extrusion process; metals, clays, ceramics, food stuffs etc. Extruders uniquely can handle high viscosity polymers. They can melt, pump, mix, compound and devolatilize them, and have been doing so since the beginning of the polymer industry early. The single screw extruder is thus highly suitable for continuously processing a wide range of synthetic thermoplastic polymers into an equally wide range of finished products.[6-9]

Materials can be extruded in the molten state or in the solid state. Fundamentally, the screw extrusion machine consists of a screw of special form rotating in a heated barrel or cylinder in which a feed opening is placed radially or tangentially at one end and an orifice or die axially at the other. A restriction in the form of a breaker plate is sometimes placed between the end of the screw and the extruding die in order to assist build up of a pressure gradient along the screw.

The basic operation of a single screw extruder is rather straight forward. Material enters from the feed hopper. Generally, the feed material flows by gravity from the feed hopper down into the extruder barrel. As the material falls down in the extruder barrel, it is situated in the annular space between the extruder screw and barrel, and further bounded by the passive and active flanks of the screw flight, the screw channel. The barrel is stationary and the screw is rotating. As a result, frictional force will act on the material, both on the barrel as well as on the screw surface. These frictional forces are responsible for the forward transport of the material, at least as long as the material is in the solid state.

As the polymer flows through the die, it adopts the shape of the flow channel of the die. Thus, as the polymer leaves the die, its shape will more or less correspond to the cross sectional shape of the final portion of the die flow channel. Since the die exerts a resistance to flow, a pressure is required to force the material through the die. The die head pressure is determined by the shape of the die, the temperature of the polymer melt, the flow rate through the die and the rheological properties of the polymer melt. The die head pressure is caused by the die, by the flow process taking place in the die flow channel. The screw is usually bored throughout or for some part of its length, so that it may be fluid cooled or heated, according to the requirements of the feed material.

1.1.1. Extruder screw

The extruder screw is the heart of the machine. Everything revolves around the extruder screw, literally and figuratively. Extruder screws as a general rule employ simple-start flights although two or even more starts are sometimes used. The alteration of flight depth to obtain a compression on the material as it moves towards the die is standard practice on most screws and is either carried out progressively throughout the length of the screw, or in stages or by a combination of both methods. The deliberate reduction of the volumetric capacity of the screw channel or channels is necessary in order to accommodate the reduction in volume of the material as it becomes fluid and homogenous and to apply compression to the material so that the channel is completely filled.

If the screw is considered solely as a means of conveying the material, then the diameter and length are major factors in determining its volumetric capacity and hence the quantity of feed material can handle. These two functions remains important controls of capacity irrespective of screw design. The length and diameter have a second important influence in that they affect the rate at which heat is transferred from the barrel walls to the material, and this in turn affects the amount of heat generated by friction and shear, the energy input and the power to through put ratio. Different thermoplastic materials require different processing conditions, so that maximum screw efficiency for every material with one design of screw is not possible.

The proper design of the geometry of the extruder screw is of crucial importance to the proper functioning of the extruder. One of the important requirements for screw design is that the screws have sufficient mechanical strength to withstand the stresses imposed by the conveying process in the extruder. The important factors are the following.

a) Pitch of the screw thread

The pitch and helix angle of the flight is, in conjunction with the peripheral speed, one of the major factors determining the output of the machine. It also influences to a marked degree the amount of shear applied to the material and the frictional heat generated thereby. The depth of the flight also affects the amount of heat generated by shear and the transfer of heat to the material by direct contact with the barrel.

b) Helix angle

One of the mysteries surrounding the extruder screw design, is the apparent sanctity of the 'square' helix angle. The competing requirements are a steep angle to resist back pressure flow and a shallow angle to provide the least tortuous path for drag flow. The universally accepted normal helix angle is 17.66°.

c) Residence time

Residence time is the period of time polymeric materials actually spend in the extruder. It can be used to analyse the mixing process, the chance of degradation and process design in an extruder.[10-13] Other factors being constant, the residence time in the screw is proportional to its effective length and inversely proportional to speed or output. Thus factors dependent on residence time such as melting, heat transfer, heating between melting and final temperatures, distributive mixing and reduction of solid particles and temperature variations in the melt pumping section will be similarly influenced and a longer screw will tend to offset limitations occurring with increased speed.

The maximum residence time is, of course, equal to the available hold up divided by the volumetric throughput rate. If the extruder is running starved, the residence time θ is essentially independent of degree of fill, and for a barrel length L is approximately $\theta = 2L/ZN$. The lead length Z may range from 0.25 to 1.5 D. N is the screw speed. D is the screw diameter.

d) Speed of the screw

The peripheral speed of the screw is an important variable in the performance of an extruder, not only in the movement of material but also in establishing the amount of heat generated by friction. The output of an extruder does not necessarily increase in direct proportion to the increase in screw speed or power input. An economical speed which gives maximum output per unit of power input therefore is used as the operating speed.

1.1.2. Functional zones in an extruder

a) Feed zone

The purpose of the feed zone is to pick up the cold material from the hopper and to feed it to the compression zone. Feed materials differ widely in their physical form and supplied as free running fine powders, regular cubes, random cut chips with a percentage of fines, or even as small cylinders or spheres. It has been found by experiment that the helix angle most suitable for one form of material is not necessarily the best for another. Also the coefficient of friction varies considerably according to the form of the feed material as well as its nature. The ideal helix angle for this zone would be 45° with a hypothetical coefficient of friction between the screw and material equal to 0.

The performance of the feed zone of the screw has a marked influence on the output of the machine but the influence of the helix angle in other zones of the screw has a smaller effect. On the other hand it is equally important to ensure that the supply of material from the feed zone is not too great to overrun the metering zone. A pronounced departure from this balance either way will result in surging or pulsation so that it is necessary to exercise reasonable care in the selection of a compression ratio to suit the bulk factor of the feed material.[14-23] Compression ratio is the ratio of the volume of one screw flight in the feed zone to the volume of a flight in the metering zone. The frictional properties between the material and the bore, and between the material and the screw in the feed section, is maintained by cooling water in the screw.

b) Compression zone

The compression zone or transition zone of a screw is probably the most difficult part to define and can be formed by the gradual increase of the root diameter of the screw thread until the diameter of the metering section is reached. This zone must be designed not only to compact the material by removing the occluded air but also to improve its thermal conductivity. Moreover, this zone conforms to the rate of melting and change of volume as the material passes from the solid to the viscous state. Furthermore, during its passage through the compression zone the material should become sufficiently viscous and deformable to be able to absorb energy from shear so that it may be heated and mixed uniformly throughout its mass. The melt viscosity and heat transfer both change within a short or long length of screw depending on the melt characteristics of the material and the feed stock at this stage consists of a continually changing suspension of solid particles in a molten matrix. [24-32] The most common method of achieving a compression ratio on an extruder screw is to decrease the depth of flight over a certain distance and so effect either a gradual or a rapid reduction in the cross sectional area of the screw flight. The position of the transition point along the length of the screw is believed to have a considerable influence on the quality of the extrudate.

c) Metering zone

The metering zone is the final part of the screw and acts rather as a metering pump from which the molten plastic material is delivered to the die system at constant volume and pressure. The mechanisms of drag flow, pressure flow, and leakage flow may be envisaged as operating in the metering zone and the interaction of the variables of this part of the screw and die system was extensively studied.[33-40] The desirable depth of metering zone on a screw is closely related to the mean viscosity of the material passing through the section.

Investigations showed that pressure drop could be overcome by increasing the metering zone length and decreasing the transition length. A better mixing and higher output could also be obtained. The channel depth of the metering zone needed to be increased to prevent over-heating of the material.

1.1.3. Flow mechanism

a) Conveying

Solids conveying may limit the output of an extruder. In solid conveying action at least three process are involved.

1. Flow in the hopper or feed pipe
2. Filling of the screw channel from the feed throat
3. Conveying by the screw from the open feed section into the closed barrel and compaction in the latter.

When the material sticks to the screw only and slips on the barrel the screw and the material would simply rotate as a solid cylinder and there would be no transport. When the material resists rotation in the barrel and slips on the screw, it will tend to be transported axially, like a normal, deep channelled, solid conveying Archimedian screw.

b) Melting

Analysis of polymer behaviour during melting was based on screw push-out experiments.[41-52] As the polymer is conveyed along the screw, a thin film softens and melts at the barrel wall. This is usually by means of conducted heat from the barrel heaters, but could be frictional. The screw scrapes off the melted film as it rotates. The molten polymer moves down the front face of the flight to the core and then sweeps up again to establish a rotary motion in front of the leading edge of the flight. Other solid granules or parts of the compacted slug of polymer are swept into the forming 'melt pool'. The process is progressive until all the polymer is melted.

1.1.4. Analysis of flow

a) Drag flow

In practice, there is friction with both screw and barrel, and this leads to the principal transport mechanism, drag flow. This is literally the dragging along by the screw of the melt as a result of the frictional forces. The drag flow is equivalent to the viscous drag between stationary and moving plates separated by a viscous medium. It constitutes the output component for the extruder.

Drag flow $Qd = \frac{1}{2} \pi^2 D^2 NH \sin\varphi \, \mathrm{Cos}\varphi$

Where,

D is the screw diameter

N the screw speed

H the channel depth and

φ the Helix angle.

b) Pressure flow

Pressure flow is caused by the pressure gradient along the screw. There is high gradient along the screw. There is high pressure at the output end, low at the feed end and this pressure gradient opposes the drag flow.[53-60] It is important to note that there is no actual flow resulting from the pressure, only an opposition.

$$\text{Pressure flow } Qp = \frac{\pi DH^3 \mathrm{Sin}^2\varphi}{12\eta} \frac{dp}{dL}$$

Where,

D is the screw diameter

H the channel depth

φ the helix angle

η the fluid viscosity and

$\frac{dp}{dL}$ the pressure gradient

c) Leakage flow

The final component in the flow pattern is leak flow or leakage flow. It is the flow into the finite space between screw and barrel, through which material can leak backwards. This is also a pressure-driven flow and ofcourse it opposes the drag flow.

$$\text{Leakage flow } Q_l = \frac{\pi^2 D^2 E \delta^3 \tan\varphi \, \Delta P}{12 \eta e L}$$

Where,

D is the screw diameter

E	the factor for eccentricity of the screw
δ	the clearance space
φ	the helix angle
ΔP	the overall pressure drop along the screw
η	the fluid viscosity
e	the flight width, and
L	the effective screw length

The theoretical calculation of leakage flow for both pressure and drag flow effects has also been developed by Mohr, Mallouk and Booy,[61] who considered the flow across the flight lands in a direction at right angles to the axis of the screw.

d) Total flow and output

If the material is compressible, the total output of the extruder is given by the sum of the drag flow Qd, the pressure flow Qp and the leakage flow Ql .

Total output of the extruder, $Q = Qd - Qp - Ql$

Since both Qp and Ql will have opposite signs to Qd

However leakage flow is very small compared with drag flow and pressure flow and may be neglected in finding the total flow. So the output Q is obtained by summing the expressions for drag flow and pressure flow.

$$\text{Ie, } Q = Qd + Qp = 1/2\pi^2 D^2 NH \sin\varphi\cos\varphi - \frac{\pi D H^3 \sin^2\varphi P}{12\eta L}$$

For a given extruder L, D, H and Q are all fixed. Thus on simplification,

$$Q = \alpha N - (\beta P/\eta)$$

So the practical variables influencing the output of the extruder are:

The screw speed N

The head pressure P

The melt viscosity η

1.1.5. Heat and power requirement

One of the main functions of an extruder is to raise the temperature of the feed material usually from ambient to a temperature at which it can flow and suitably form to a desired shape. It is therefore, necessary to supply heat energy to the material. Power must be supplied to the screw in order to turn it against the frictional and viscous resistance of the material in the screw flights. It will be readily appreciated that those two energy mechanisms are closely interrelated since an alteration in the rate of supply of one will produce a change in the other. Conventional melt flow theories are available for determination of screw power for normal extrusion operations [62-64] and the total screw power requirements can be estimated by the methods given by Mohr etal and Gore and McKelvey. Conventional melt flow theories are available for determination of screw power for normal extrusion operations.[65-66]

The power absorbed by the screw can be considered to be used for applying shear to the material and for applying pressure to it. The square of the channel size is proportional to the necessary residence time for homogeneity and quality. For optimum design, Carley suggests the use of a simplified equation for calculating the power requirement.

$$Hp = 6\times10^{-4}\, Q\Delta P$$

1.1.6. Mixing

The attainment of proper mixing is undoubtedly the single most important consideration when specifying or designing an extruder reactor. A uniform composition may be obtained by a proper laminar mixing of the polymer. Mixing consists of two processes viz., one is the dispersion of the particles of the material being processed (ie, dispersive mixing) and the other is their uniform distribution throughout their entire volume (ie, distributive mixing). Non-uniform composition (insufficient mixing) leads inevitably to poor properties, and poor external appearance of the product as well as to non-uniform distribution of its properties.

Dispersive mixing during the extrusion process consists of overcoming the cohesion of particles of the material and takes place due to shear stress in the surrounding fluid. On the other hand distributive mixing consists of changing the difference in composition of the material in various places and is affected by a relative motion of components.

Selecting the optimum mixing configuration depends upon the nature of the feed streams (solid, liquid, melt or gas) and the specific mixing requirements. For the purposes of analysis, we focus our attention on a small element called a microscopic reaction environment (MRE), having a characteristic dimension l. MRE could be a dispersed solid particle, a liquid droplet, a blob of melt or a gas bubble, soluble or insoluble in the surrounding continuous medium or it could be an imaginary region within the continuous phase.

In most situations, the process of mixing the MRE with its surroundings involves two elementary steps; reducing its size from some initial dimension ($l_0 \longrightarrow l$) as much as required, and distributing the resulting fragments in space as uniformly as possible. For turbulent flow fields, l can be associated with the dimensions of a turbulent microscopic eddy and related to Reynolds number

$$l_0/l = f(Re)$$

Where l_0 is a macroscopic dimension associated with the origin of the turbulent field, such as tube radius, the material used, but also on the efficiency of the die.

1.1.7. Extruder die

The quality of an extruded product, depends not only on the extruder and the material used, but also on the efficiency of the die. The objective of an extrusion die is to distribute the polymer melt in the flow channel such that the material exits from the die with a uniform velocity. The pressure required to force the melt through the die is called die head pressure.[67-70] The variables that affect the die head pressure and hence the key factors in the practical die design are:

1. The geometry of the flow channel in the die
2. The rheological properties of the polymer melt
3. The temperature distribution in the polymer melt
4. The flow rate through the die
5. Product geometry

Generally, the size (cross sectional area) of the extrudate is determined by controlling the screw speed relative to the line speed. Inaddition to the die land /orifice thickness ratio, the surface finish, the compound lubrication, the filler loading, the construction of the die upstream of the land and the system of product sizing to be used are to be mentioned for the proper die design. The breaker plate/screen pack before the die ensures pressure in the screw of the extruder, thus enabling the material to be worked and sheared and to be properly homogenized. The back- pressure due to the die land restriction is relied upon to compact the material downstream of the breaker plate into one homogenous stream.

Extrusion dies may be attached to the extruder in three different ways according to the requirements of the complete extrusion process of which they form part. These three systems are known as straight-through, cross head and offset respectively, depending on the direction of the resulting extrusion and take off relative to the direction of melt feed from the extruder.

Straight through dies are obviously those dies whose axes are arranged to be in line with the direction of supply of melt. These dies are commonly used for the extrusion of pipe, rod, profiles and sheet. A predominant and distinguishing characteristic of straight through die systems is that some form of spider mandrel support assembly is essential in the production of tubular extrusions.

Crosshead dies are arranged with their axes at an angle to their feed supply. Dies of this form are generally used for the production of insulated wires, cables and continuous filaments. An outstanding advantage of crosshead type die assemblies is that by this means it is possible to have ready access to the upstream end of the die mandrel so that heating or cooling is easily effected.

Offset dies have been developed from crossheads to combine the advantages of this form of side-feed die assembly with those of the straight through type. Offset dies are popular for the production of pipe where the lack of a spider and also the ease of applying temperature control to the mandrel do much to improve the quality of the product.

1.1.8. Extrudate swell

A well-known and typical phenomenon in polymer melt extrusion is the swelling of the extrudate as it leaves the die. This is sometimes referred to as die swell; however, it is not the die but the polymer that swells. The elasticity of the polymer melt is largely responsible for the swelling of the extrudate upon leaving the die. This is primarily due to the elastic recovery of the deformation that the polymer was exposed to in the die. The elastic recovery is time dependent. A die with a short land length will have a large amount of swelling, while a long land length will reduce the amount of swelling.

In inelastic fluid, the mechanism of extrudate swell is not an elastic recovery of prior deformation. The swelling is caused by a significant rearrangement of the velocity profile as the polymer leaves the die. The velocity profile changes from an approximately parabolic velocity profile in the die to a straight velocity profile a short distance away from the die.

One of the main problems with extrudate swell is that it is generally not uniformly distributed over the extrudate. This means that some areas of the extrudate swell more than others. The wall shear rate in the corner is relatively low, while the highest shear rate occurs at the middle of the wall. Therefore, the elastic recovery in the middle will be larger than the elastic recovery at the corners. A good die designer must anticipate the amount of uneven swelling and design the flow channel accordingly. The amount of swelling is very much dependent on the nature of the material.

1.2. THE MULTI-SCREW EXTRUDERS

Extruders employing two or more screws which may or may not have intermeshing flights are also available. The presence of further screws in the same barrel and the wide range of combinations and individual designs which may be used considerably influences the characteristics of the machine, although many of the fundamental requirements obviously remain unchanged. During the later half of the nineteenth century, multi-screw extruders were experimented for the processing of ceramics, soap, waxes, and food stuffs. The use of the multi-screw principle for thermoplastics, is believed to have originated in Italy. In late 1930s Roberto Colombo of Turin produced a successful two screw arrangement, in which the screws intermeshed and formed a positive pump. In multi- screw extruders, the feed section is the same as on a standard single screw extruder. However, the mixing section of the extruder looks considerably different. In the planetary roller section of the extruder, six or more planetary screws, evenly spaced, revolve around the circumference of the main screw. In the planetary screw section, the main screw is referred to as the sun screw. The planetary screws intermesh with the sun screw and the barrel. Thus, heat sensitive compounds can be processed with a minimum of degradation.

1.2.1. The twin screw extruder

There is a variety of twin screw extruders with vast differences in design, principle of operation and field of application.[71-83] A twin screw extruder is a machine with two Archmedian screws. It acts as positive displacement pumps with little dependence on friction and this is the main reason for their choice for heat sensitive materials.

Based on the geometrical configuration of the twin screw extruders, they are classified into intermeshing and non intermeshing extruders. They are further classified as counter rotating, co-rotating and coaxial extruders. Counter rotating machines, if conjugated may have no passage at all for material to move around the screws, it must move axially towards the die end. Likewise co-rotating machines will have no passage around each screw and only a small and tortuous one round both, also leading to positive axial flow. Also because of the positive pumping action, the rate of feed is not critical in maintaining output pressure.

1.2.2. Comparison between the characteristics of multi screw and single screw machines

From a comparison of the equations it appears that the multi screw machine is the least sensitive to die variations and its output would remain fairly constant for a given screw speed over a wide range of die apparatus.

The plot of output against screw speed for a multi-screw machine tends to a straight line much more closely than for the single screw machine. For the multi screw extruder the volumetric efficiency of the screw is fairly high, and is almost independent of pressure. In the case of the single screw machine, on the other hand, volumetric efficiencies are always low and are highly pressure dependent.

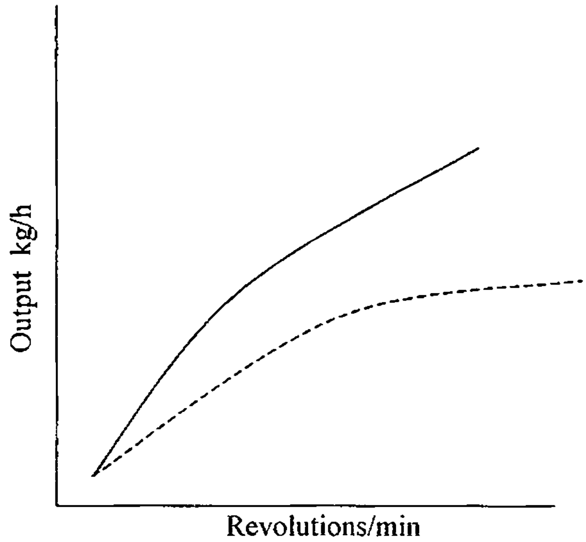

Fig 1.1 The plot of output against screw speed for multi screw machine and single screw machine.

The power requirement for a given output is

$$Z = \frac{A}{B^2} \quad Q^2$$

Where,

Z is the power requirement

Q the extruder delivery

From this equation it may be seen that the power is proportional to the square of the extruder delivery and since energy appears in the material as heat, the extruder becomes hotter as the screw speed increases, provided sufficient power is available to turn the screw. In the case of multi screw machines, because of the deep screw flights the power requirements are relatively low and the greater part of the heating is effected by conduction from barrel heaters. The material heating and, therefore, the allowable rate of throughput is thus time dependent and there exists for all multi-screw machines a definite upper speed limit which depends on the thermal properties of the material being extruded.

The mixing obtainable in multi-screws must be very limited because of the positive forwarding obtained in such machines. It is obvious that because of their more complicated construction, multi-screw machines will generally be more costly than a single screw extruder of comparable output. Another important limitation of multi-screw systems results from the geometry of the adaptor section of the barrel, which renders effective streamlining of this zone extremely difficult.

Multi-screw machines will accept difficult feed materials more readily than will single screws, and will forward such materials to the die with less supervision of processing conditions.

1.3. REACTIVE EXTRUSION

Reactive extrusion has been the subject of vigorous research activity in recent years, both in industry and academy and has resulted in numerous commercial processes and products. The primary reason for the success of reactive extrusion is the extruder's unique stability as a vehicle for carrying out chemical reactions in the bulk phase, to produce value added, speciality polymers, through chemical modification of existing polymers.[84-96] The extruder is an ideal reactor for polymer modification in that it serves as a pressure vessel equipped for intensive mixing, shear, control of temperature, control of residence time, venting of by-product and transport of molten polymer through the various sections of the extruder, each serving as a mini-reactor. Further, reactive extrusion is economically attractive since the extrusion and processing are done in a single stage. The combination of chemical reaction and polymer processing, in general, remains a rich potential source for further development of new and novel products and processes.

Chemical reactions on polymers, or to form polymers, have historically been done in diluted systems, avoiding the problem of high viscosity. As the extrusion technology has improved in recent years, it is recognised that the application of extruders could be extended into reactions.

If we compare a reaction done in an extruder, to one done in solvent or diluent, the advantages are :

1. Elimination of the energy of recovery of the diluent.
2. Absence of emissions from the solvent or diluent.
3. Large savings in the plant space.

Since the solvent/diluent usually comprises 5-20 times the weight of the desired polymer product, the magnitude of the above potential advantages is very large. There are technical advantages as well, because the extruder can be made to be a plug flow reactor.

The comparative advantages of the extruder as a chemical rector are the following.

1. Nearly plug flow reactor conditions
2. Multi-staging capability
3. Uses of drag flow to convey and mix high viscosity polymer
4. Wide ranges of pressure and temperature

1.3.1. Types of reactions performed by reactive extrusion

The types of chemical reactions which have been performed by reactive extrusion may be conveniently divided into six categories as described in table 1.1.

Table 1.1 Types of chemical reactions performed by reactive extrusion

Type	Description
A. Bulk Polymerisation	Preparation of high molecular weight polymer from monomer or low molecular weight prepolymer, or from mixture of monomers or monomer and prepolymer.
B. Graft Reaction	Formation of grafted polymer or copolymer from reaction of polymer and monomer.
C. Interchain Copolymer Formation	Reaction of two or more polymers to form random, graft or block copolymer either through ionic or covalent bonds.
D. Coupling/Crosslinking Reactions	Reaction of polymer with poly functional coupling or branching agent to build molecular weight by chainextension or branching.
E. Controlled Degradation	Controlled molecular weight degradation of high molecular weight polymer or controlled degradation to monomer.
F. Functionalization	Introduction of functional groups into polymer backbone, end group or side chain.

A. Bulk Polymerisation

In bulk polymerisation a monomer or a mixture of monomers is converted to high molecular weight polymer with little or no solvent dilution. Extruder reactors have been designed which handle pure monomer as feed or which take low viscosity pre-polymer to high viscosity. Bulk polymerisation in an extruder has been considered in general review articles by Mack and Mack and Herter[71] and in more specialised articles on engineering aspects by Meyuhas et.al. and Lindt. For maximum rate of reaction and most economical operation bulk polymerisation is carried out at the highest possible temperature. More efficient heat transfer and shorter extruder residence time is possible using twin screw extruders with intermeshing, self-wiping screws.[97-110]

Two types of bulk polymerisation have been performed in extruder reactors (1) condensation polymerisation and (2) addition polymerisation.

1. Condensation polymerisation

Condensation polymers can arise through a repeated condensation process of two distinct monomers to give high molecular weight polymer and a low molecular weight by-product such as water or a low bailing alcohol. To ensure high conversion to product, the reaction equilibrium must be optimised by efficient removal of low molecular weight by-product. Extruder reactors for condensation polymerisation typically provide for vacuum venting at one or more barrel segments to remove volatile by-product. An example is use of an alpha, omega aminocrboxylic acid to form polyamide with water as side product.

Takekoshi and Kochanowski, Banucci and Mellinger and Schmidt and Lovgren have described condensation of bisphenol. A dianhydride with different aromatic diamines to give polyetherimides using an extruder reactor.

Polyesters have been synthesised in extruder reactors from low molecular weight prepolymer. Melamine-formaldehyde prepolymer has been synthesized by Streetman in a single screw extruder reactor at 130°C.

2. Addition polymerization

The synthesis of addition polymers by bulk polymerisation in an extruder is often done with vacuum venting to remove unreacted monomer. The polymerising reaction mixture may be cooled by volatilisation of the inert material, which may be removed through vacuum venting at an appropriate extruder barrel segment.

Examples of addition polymerisation are synthesis of polyurethanes and polyurethane ureas in extruder reactors. As these reactions proceed by step-growth polymerisation, often the reactants are fed to the extruder as melts or liquids. Reischl combined toluene disocyanate distillation residues with 34.6% diethylene glycol in a 53mm corotating twin screw extruder at 165°C with 1-2 minute residence time. The polyurethane product could be moulded into board with or without woodchip filler. Polyamide synthesis in extruder reactors by ring opening polymerisation of lactams has been reported. Illing polymerised lactams such as caprolactam in a twin screw extruder equipped with corotating, intermeshing screws.

B. Graft Reactions

Grafting in an extruder reactor involves reaction of a molten polymer with a monomer or mixture of monomers capable of forming grafts to the polymer backbone. Depending upon the individual reactivities and mole ratios of monomer and polymer, the initiator level, the processing temperature, and other factors, the graft chain length may be different. An example is functionalization of polyolefines through grafting with maleic anhydride.

Grafting of vinylsilanes to polyolefine substrates in the presence of peroxide is the most common example of a graft reaction performed in extruder reactors. Reviews summarising aspects of the various grafting and crosslinking processes have been published by scott and Humphries, Bloor, Munteanu and cartasegna.[111-119]

Grafting of acrylic acid and its analogues to polyolefines such as polyethylene and polypropylene has been disclosed by a number of workers. Polypropylene, polyethylene or mixtures have been grafted with acrylic acid, n-butyl methacrylate or lauryl methacrylate using DCP in a 60mm extruder reactor at 180°C. Grafting of acrylic acid to polypropylene or polystyrene or poly (4-methyl pentene-1) under apparently similar conditions has been reported by Ide and Sasaki in connection with improving adhesion of the polymers for use in laminates or glass-reinforced blends. Zeitler et.al have grafted ethyl vinyl acetate with acrylic acid in the presence of radical initiator. Grafting of methacrylic acid to natural rubber by a mechanochemical process has been described by Shuttleworth and Watson.[120] Johnson et.al have grafted polyphenylene ether with acrylate derivatives in extruder reactors.

Jones and Nowak[121] have grafted styrene to polyethylene in a reactive extrusion process. One of the most common subjects of reactive extrusion patents and referred publications is grafting of maleic anhydride and its analogues such as fumaric acid, itaconic acid, citraconic acid etc.

C. Interchain Copolymer Formation

Interchain copolymer formation may be defined as reaction of two or more polymers to form copolymer. Interchain copolymer formation through chain cleavage followed by recombination has been reported as a method for making random and/or block copolymers by reactive extrusion but there are only a small number of examples which produce useful materials. In the majority of cases interchain copolymer formation involves combination of reactive groups of one polymer with reactive groups on a second polymer to form a block or graft copolymer with molecular weight roughly equal to the sum of that of the two homopolymers. Ionic crosslinks are usually thermally reversible which may limit the usefulness of blends containing them in certain commercial applications.[122-127]

Casale and Porter[128] have published reviews on mechanochemical generation of radicals by chain scission of addition polymers during extrusion under high shear and recombination of these radicals to form block and graft copolymers. Block copolymers have been formed in extruder reactors through reaction between functionalised end groups of two different polymers. Since the probability of two end groups reacting within typical extruder residence time is low, highly reactive functionality is necessary and sometimes low molecular weight polymers with high concentrations of end groups are employed.

Many commercial nylon products are two phase blends which are toughened by the presence of a dispersed polyolefine containing phase with lower modulus than the nylon matrix. Extrusion of nylon with anhydride or acid functionalised polyolefine may form atleast some nylon- polyolefine copolymer which acts as compatibilizing agent leading to stabilized nylon-polyolefine blends with excellent physical properties.

Ethylene vinyl acetate/GMA copolymer has been reacted with an equal weight of styrene maleic anhydride copolymer at 200°C in a twin screw kneader extruder to give 42% grafted styrene copolymer by selective solvent extraction. Blends of this copolymer with PPE/PS gave improved mechanical properties compared to blends without the copolymer.

Graft copolymers have also been made in which the graft linkage between polymers in an ionic bond instead of a covalent bond. Impact modified blends of PPE could be prepared with ionomeric polyolefines or polysiloxanes if an ionomeric PPE or PS was present as compatibilizing agent and both zinc stearate and triphenyl phosphate were added as plasticizers. Brown and McFay[129] formed a graft copolymer by co extrusion of the zinc salt of solphonated polystyrene with an EP rubber functionalised with phosphonate ester groups.

D. Coupling/Crosslinking Reactions

Coupling reactions involve reaction of a single polymer with a condensing agent, a polyfunctional coupling agent, or a crosslinking agent to build molecular weight by chain extension or branching or to build melt viscosity by crosslinking. Suitable polymers have end groups or side chains capable of reacting with the condensing, coupling or crosslinking agent. Examples of the use of condensing agents in reactive extrusion include viscosity building in nylon 6,6 by co extrusion with an alkyl Phosphonic acid.

Polyamides have been chain extended by reactive extrusion with diisocyanates by Nelb et al. Early work by Gregorian showed that polyethylene could be crosslinked through melt reaction with peroxide in a Brabender plastograph. Christensen and Voss achieved crosslinking of polyphenylene sulphide by reactive extrusion in the presence of air.[130-136]

Crosslinking of carboxylic acid groups on ethylene/n-butyl acrylate/ methacrylic acid copolymer has been achieved by co extrusion with aluminium salts. Coupling reactions have also been mediated through silane crosslinkng. For example the end groups of nylon 12 or nylon 6 have been capped by reactive extrusion with 1-isocyanato-3-triethoxy silyl propane.[137] Saito et al grafted styrene- butadiene- styrene block copolymer with MA followed by crosslinking with metal hydroxide.

E. Controlled Degradation

Controlled degradation of polymers in extruder reactors generally involves lowering of molecular weight to meet some specific product performance criterion or in the case of biological polymers, degrading to release valuable low molecular weight species.

Castagna et al have degraded PP in the presence of peroxide and air in an extruder. Fritz[138] and Stohrer studied peroxide-initiated PP degradation in a twin screw extruder. Mueller-Tamm et al have degraded polyisobutylene by extrusion with a specific antioxidant to prevent carbon black formation.

Biological polymers have been subjected to controlled degradation in extruder reactors. Waste sawdust or paper pulp has been partially degraded to glucose monomer in an extruder by Rugg and Brenher. Den Otter converted coal to a mixture of fluid hydrocarbons by reaction with hydrogen under pressure in a SSE. Fulger et al. treated coffee extraction residue consisting of 70% moisture with 0.5-2.0wt% sulphuric acid in two single screw extruders in series at 107-200°C to produce a solution of mannan oligomer.

F. Polymer Functionalisation and Functional Group Modification

Reactive extrusion has been used to introduce a variety of functional groups into polymers and to modify existing functional groups. The most sophisticated example of polymer functionalisation performed in an extruder reactor is chlorination or bromination of polyolefines developed by workers at Exxon. Newman and Kowalski, Boocock and white used sulfur trioxide/trimethylamine complex to sulphonate polyolefines.[139-142]

Udding introduced carboxylic acid groups into SEBS by melt reaction with 3-azidosulfonyl benzoic acid. Trialkoxy silane arylsulfonyl azides have been used to introduce crosslinkable silane functionality into polymers. Lambla and Barnabeo[143] has described conversion of polymer-bound cyclic anhydride groups to imide groups by reaction at 180°C in an SSE with ammonia which had been pre saturated into the polymer at high pressure. Pendant ester groups on ethylene-vinyl acetate copolymer have been hydrolysed under controlled conditions in extruder reactors. Scott and co workers have shown that certain thiol-containing stabilizers can become covalently bound to polymers during melt processing. Mijangoes et al. studied the reaction of PVC in the melt with sodium benzenethiolate. Reactions were performed in a Brabender mixer at 160°C and 40 rpm.

1.3.2. Applications of reactive extrusion

The polyethylenes are probably the most widely used of all plastic materials and a high proportion of their applications result from the extrusion process. The most important usage for low density polyethylene is in the packaging industry, where it is extruded into tubular and flat film in both and standard and shrinkable varieties for wrapping an immense variety of product and in the case of high density, high molecular weight materials, into tissue paper film and bags for the retail food trades. Polyethylene is also extrusion laminated to paper, metal foils, cellophane and other substrates to give composite packaging media where the properties of each material are combined. Extruded polyethylenes are also widely used as low dielectric- loss material for wire and cable insulation. Extruded pipe and tubing from the various grades of polyethylene are also widely used.

The thermoplastics extrusion industry can be considered in a general way is being divided into two large groups, viz, the cable makers and the specialist extrusion firms. The specialist extrusion firms, founded their branch of the industry on the new materials and have grown with the increasing availability and types of new extrudable resins, and with the development of new applications for them.[144-150] The important factors, such as greater resistance to weathering, outstanding electrical properties and excellent extrudability etc have had such an effect on the cable industry that today the manufacture of insulated wires and cables is in volume one of the most important uses for polyethylene and plasticised PVC.

Thus it seems that the present trend in the extrusion industry is for the custom extrusion firms to develop specific products in response to customer demand or as a result of their own search for novel products. Such a trend is a valuable one as it results in the development of the most economic production methods, giving lower prices and, therefore, the wider application of extruded thermoplastics. The process of reactive processing permits the preparation of functionalised polymers, including copolymers containing carboxyl groups which cannot be made directly by the polymerisation process, and opens up significant possibilities for the creation of new speciality and engineering plastics. The crosslinking initiated improvement of the heat resistance indicate extended property profiles and new application fields for polyethylene, ie, bellows for the automotive industry, electro conductive films with good thermal qualities or gaskets with high-dimensional stability.

1.4. SCOPE AND OBJECTIVES OF THE WORK

While reactive extrusion is economically attractive, the completion of the reaction along with the processing is a major challenge. The main objective of the study was to optimise the reactive extrusion conditions in the conventional modification processes of polyethylenes. The specific objectives of the work are:

1. To find the optimum conditions of peroxide modification, silane grafting, and maleic anhydride grafting, in the case of LDPE, LLDPE, and their blends.
2. To perform the actual reactive extrusion in a laboratory extruder using the optimum parameters.
3. To study the mechanical/thermal behaviour of the modified polymers in comparison to the original polymers.
4. To find the effect of modification on the processability of the polymers.

The thesis is divided into the following chapters:

Chapter 1	Introduction
Chapter 2	Experimental techniques
Chapter 3	Peroxide modification of polyethylenes
Chapter 4	Silane grafting of polyethylenes
Chapter 5	Maleic anhydride grafting of polyethylenes
Chapter 6	Summary and conclusions

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

The details of the experimental procedures adopted in the present investigations are given in this chapter.

1. MATERIALS

Low density polyethylene (LDPE)

Indothene 24FSO40 was supplied by IPCL, Baroda. It had a density of $0.922 g/cm^3$ and melt flow index 4g/10min.

Linear low density polyethylene (LLDPE)

Indothene LL20FSO10 was supplied by IPCL, Baroda. It had a density of $0.92 g/cm^3$ and melt flow index 1.0g/10 min.

Dicumyl peroxide(DCP)

DCP used was commercial grade with 40% activity.

Triallyl cyanurate(TAC)

TAC used was commercial grade.

Silane-Si-69

Bis(3-(triethoxy silyl)propyl) tetrasulphide

Yellow liquid of p H 7-8.

2. EXPERIMENTAL PROCEDURE

2.1. EXTRUSION USING A BRABENDER PLASTICORDER

Brabender Plasticorder (torque rheometer) has been widely used for measuring processability of polymers, rheological properties of polymer melts, blending of polymers etc. The torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material to mastication or flow under selected 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 which is put up by the test material against the rotating rotors in the mixing chamber is made visible with the help of a dynamometer balance. The dynamometer is attached to a precise mechanical measuring system which indicates and records the torque. A DC thyrister controlled drive is used for speed control of the rotors(0 to 150 rpm range).The temperature of the mixing chamber is controlled by circulating hot oil. The temperature can be varied up to 300°C. Stock temperature thermocouple with a temperature recorder is used for temperature measurement. Different types of rotors can be easily mounted and dismounted due to the simple fastening and coupling system. Once test conditions (rotor type, rpm and temperature) are set, sufficient time was given for the temperature to attain the set value and become steady. Subsequently the materials were charged into the mixing chamber to obtain a torque time curve or a plastogram.

2.2. EXTRUSION ON A LABORATORY EXTRUDER

The basic extruder on which reactive extrusion studies were done was a laboratory extruder attached to a Brabender Plasticorder model PL 2000.Brabender Plasticorder is a computerised torque rheometer system used for testing thermoplastics, thermosets and elastomers [1-3].The measuring instruments are built according to the modular system and the measuring heads such as mixers, extruder etc can be interchanged within a short time. Production processes like mixing, mastication, extrusion etc can thus be simulated in a laboratory scale and followed by measurement.

The Plasticorder PL 2000 consists of a dynamometer unit, a data transfer interface and a computer. The dynamometer unit consists of the Brabender torque dynamometer with electronic speed control with tacho generator feed back, stepless speed adjustment and digital speed display. The designed speed can be adjusted either manually at the dynamometer unit or can be fed via the computer.

Brabender however uses measuring extruders and die heads, which are optimised for the individual experiments. Swell behaviour, surface quality melt fracture, feeding characteristics, feeding rate measurements and many other criteria can be evaluated. Iron constantan thermocouples are provided to sense the melt temperature at the different regions of the screw and at the die .A “servocar” strip chart was used to record these temperatures. Carrying out reactions with polymeric materials whose viscosities are typically in the 10 to 10000 Pas range is generally possible in extruders . Extruders offer such attractive features which can be advantageously utilised when it is used as a reactor.

2.3. FTIR SPECTRA

FTIR spectra of the compression moulded films were taken in Nicolet Avatar 360 ESP FTIR, spectrometer, after extraction in boiling toluene for 8 hours.

2.4. RHEOLOGICAL EVALUATION USING A CAPILLARY RHEOMETER

Capillary rheometer is widely used for determining the rheological properties of polymer melts since they cover a shear rate range of interest in practical processing upto 10^4 S^{-1} with good reproducibility. In this study the rheological properties of polymers were measured using a Gottfert viscotester model 1500 in accordance with ASTM D 3835-79.

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

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

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

Apparent viscosity $\eta_{app} = \frac{\tau w_{app}}{\gamma w_{app}}$

where,

Δp is the pressure drop across the capillary (MPa)

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

R the capillary radius (mm)

L the capillary length (mm)

A straight line relationship on a log-log plot indicates that the variables τw_{app}, γw_{app} can be related by the following power law equation,

$$\tau w_{app} = k \gamma^n w_{app}$$

where,

k is the consistency index

n the power law index

This law is often referred to as the power law of Ostwald and de Waele.[4-6] The power law index n indicates how rapidly the viscosity decreases with shear rate. For pseudoplastic fluids the power law index ranges from 0 to 1. When the power law index is unity, the fluid is Newtonian and the consistency index becomes Newtonian viscosity. Hence the power law index indicates the degree of non-Newtonian behaviour of the fluid while the consistency index denotes the viscosity of the fluid.

2.4.1. Melt elasticity measurements

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

The extrudate swell ratio De/D, where De and D are diameters of the extrudate and the die, respectively, is a direct measure of melt elasticity. The extrudate emerging from the capillary was collected and the diameter of the extrudate was measured at various points. The extrudate swell ratio was calculatted as the ratio of the diameter of the extrudate De to the diameter of the capillary die D.

2.4.2. Activation energy for viscous flow

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

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

Where,

Ea is the activation energy

A constant

R the gas constant and

T the absolute temperature

Activation energy can be calculated at a constant shear rate or at a constant shear stress.

2.5. COMPRESSION MOULDING OF TEST SHEETS

The test specimens were prepared using an electrically heated press with 30x30cm platens at a pressure of 120 kg/cm^2 on the mould. The compound was homogenised in the Brabender mixer and sheeted out in a two roll mill. It was then placed in the mould cavity and compressed under high pressure and the pre set temperature, so the material softened and flowed inside the mould cavity [7-10]. The temperature of moulding was fixed at 150° C when not specified. The mould could be kept closed by bolting under pressure so that it could be taken out when hot and water cooled.

2.6. TENSILE STRESS-STRAIN BEHAVIOUR

Tensile properties of the specimen were determined accordingly to ASTM D 638 using dumb- bell specimens on a Zwick universal testing machine and placed in a 15x15 mm envelope made from 120 mesh stainless steel cloth. The sample was then placed in the soxhlet extractor and immersed in refluxing toluene for 8hrs,dried under vacuum at 150°C and cooled in a desiccator before weighing. The specimen was dried to constant weight. Gel fraction was obtained by dividing the final sample weight by the initial sample weight.

2.9. THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermogravimetric analysis of the samples was done using a Du-Pont-2000 thermogravimetric analyser. About 10 mg of the sample was taken in a platinum crucible and the experiment was done in air atmosphere at a heating rate of 10°C/minute. The weight loss of the sample was taken and then plotted against temperature.

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CHAPTER 3

PEROXIDE MODIFICATION OF POLYETHYLENES

PEROXIDE MODIFICATION OF POLYETHYLENES

3.1. INTRODUCTION

Blends of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) are widely used for making films. LLDPE has a greater degree of stiffness and better strength than LDPE, a more regular crystalline structure, higher melting point and better fracture resistance. However, the shear viscosity of LLDPE is usually greater compared to LDPE causing difficulties in the formation of films. Addition of small amounts of LDPE to LLDPE results in reduced haze and better bubble stability. LDPE/LLDPE films can be made in thinner gages than that of LDPE alone with acceptable properties in conventional extruders employed for LDPE alone.[1-5]

Polyolefines are sometimes modified with organic peroxides to alter their processability and mechanical properties.[6-7] These peroxides can either induce crosslinking or initiate chain scission which leads to many changes in the properties of the polymer. A highly crystalline polyethylene sample crosslinked chemically is expected to reveal a drastic reduction in crystallinity and severe changes in properties affected by that parameter. On the other hand radiation induced crosslinking does not affect the crystalline phase of the polymer.

Crosslinking of polyethylene with peroxides is accomplished as follows:

1. A first order chemical reaction for thermal decomposition of the peroxide to produce peroxy radicals.
2. Peroxy radical interaction and abstraction of hydrogen atoms from the polymer chain, resulting in a free radical site on the polymer chain.
3. Coupling of two free radical sites to form a C-C crosslink.

The better stability and lower volatility of the peroxide enables it to be incorporated into the polyethylene in a practical processing operation such as mixing and extrusion or moulding. By crosslinking, thermoplastic polyethylene is converted to a thermoset material extending its usefulness at higher temperatures. This improvement in properties has led to a broadening of the scope of application for the polymer, particularly in the wire and cable industry.[8-14]

High temperature peroxide crosslinking of polyethylene is now a well established technology in production lines of cable insulation, foams, rotational moulding, piping and electrically conductive compounds.[15-20] Thermoplastic can also be crosslinked by irradiation in air or under vacuum, at ambient temperatures.[21-30] The peroxide and irradiation crosslinking methods produce carbon–carbon crosslinks which convert the thermoplastic polyethylene into a thermosetting material distinguished by its high environmental stress crack resistance and creep resistance. An additional advantage of crosslinked polyethylene is its ability to absorb high loadings of fillers (reinforcing, electrically conductive and fire retardents), contrary to the thermoplastic polymer which becomes brittle and unusable upon the addition of fillers. The service temperature of crosslinked polyethylene can be extended to significantly higher temperatures than of thermoplastic polyethylene. For example, an important application of peroxide crosslinked polyethylene is in hot water piping installations where the combination of high temperatures and pressures has caused failure of thermoplastic polyethylene and polypropylene.[31-38]

It is known that the effectiveness of the chemical three-dimensional stucturisation of polyethylenes can be increased by the use of coagents. The literature contains information on the use for this purpose of compounds with various functional groups in reactions of chemical and radiation crosslinking of elastomers and polymers.[39-50] Radical processes occurring in their presence lead to the formation of a three dimensional network, the links in which are different from the usual C-C links and confer special properties on the polymer materials. Thus coagents not only improve the effectiveness of the crosslinking reactions but also improve the properties of the final products. Depending on the type of coagent employed, different degrees of crosslinking can be obtained on these polymers.

The optimum conditions for peroxide crosslinking of low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and their blends were determined on a torque rheometer and then actual extrusion was performed using these conditions. We also studied the influence of the coagent, triallyl cyanurate (TAC) on the crosslinking of LDPE in the presence of dicumyl peroxide (DCP). When crosslinking is carried out in the presence of TAC, a hydrogen atom which is readily separated from the polymer chain attaches to one of the three allyl groups, as a result of which a grafted C-C unit is formed. If this process takes place between the same molecule of TAC and another polymer chain, a crosslinking unit is formed. This unit also contains a fragment of the coagent. Using a controlled opening of the double bonds of the TAC, it is possible to achieve a store of allyl groups which can be used for further crosslinking. A change in the mechanical properties may be due to the effect of the characteristics of different shapes of the skeleton structure formed.

3.2. EXPERIMENTAL

Reactive extrusion

Conditions for reactive extrusion were first determined on a Brabender plasticorder mixer model PL3S equipped with roller type rotors, having a capacity of 40g.Changes in torque obtained are a measure of the changes in the melt viscosity of the polymer. Different mixing conditions were generated by varying the temperature and rpm. Dicumyl peroxide (DCP) at concentrations of 0.5, 1.0 and 1.5% of the total weight of the polymers was employed as the crosslinking agent. DCP was added along with the polymers. The dosage of triallyl cyanurate used as the coagent was varied from 0.25 to 1% of the amount of the polymers. Reactive extrusion was done on a laboratory general purpose plastic extruder attached to a Brabender plasticorder model PL 2000 with an L/D ratio of 25 and a compression ratio of 2 and fitted with a ribbon die. The temperatures of the barrel and the die, rpm of the screw and DCP and TAC concentrations were fixed as per the results obtained from the mixer.

3.3. RESULTS AND DISCUSSION

On addition of LDPE and DCP to the Brabender mixer, the torque rises due to melting / crosslinking, reaches a maximum value and then stabilises at a lower value.

Fig.3.1 shows a typical torque vs time graph obtained from the Brabender mixer for 50/50 LDPE/LLDPE blend containing 1% DCP at 140^0C. The torque rises initially due to melting / crosslinking of the polymer, reaches a maximum and then decreases and stabilises. The maximum and/or stabilised torque attained may give indication of the extent of melting and crosslinking of the polymer. The extent of melting/ crosslinking was assessed both from the maximum and stabilised torques.

Fig3.2 shows the variation of maximum torque with temperature for LDPE, LLDPE and their blend with and without DCP and TAC. 140°C registers the highest torque for all the combinations. This is probably due to better crosslinking efficiency at this temperature at the conditions employed.

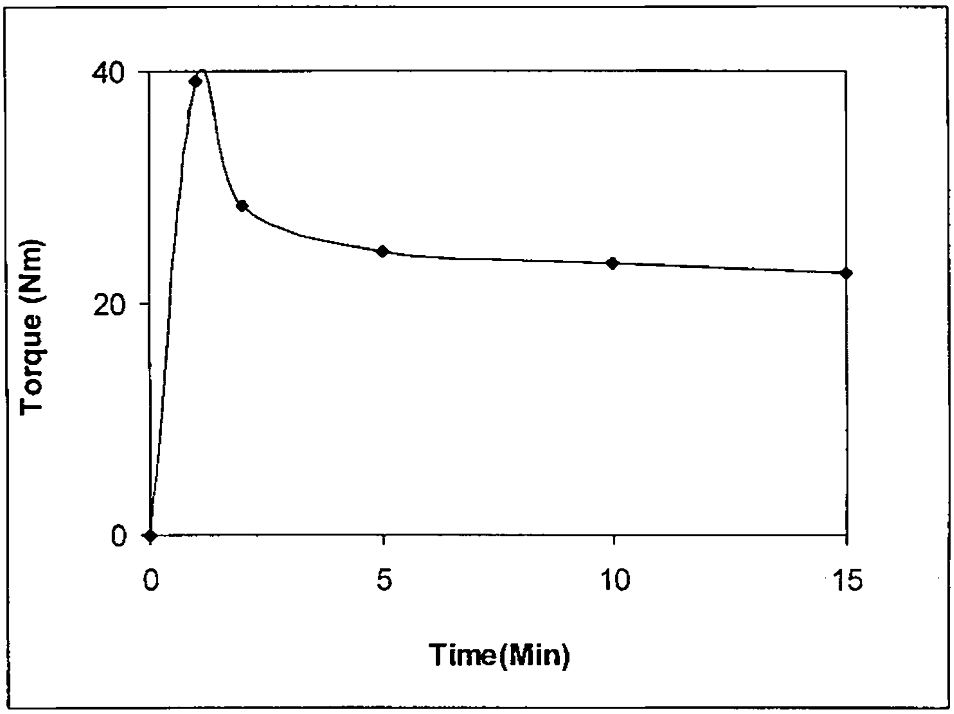

Fig 3.1 Variation of torque with time for LDPE/LLDPE blend at 140° C

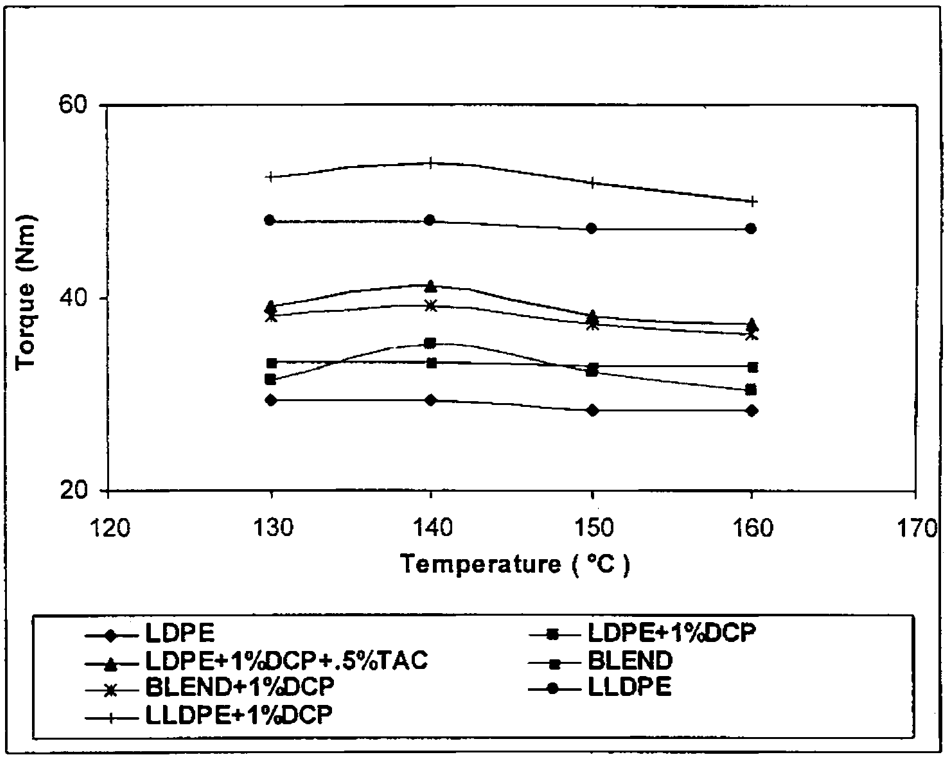

Fig 3.2 Variation of maximum torque with temperature

Fig 3.3 shows the variation of stabilised torque with mixer temperature. For pure polymer without any DCP the torque is almost parallel to the x-axis as expected. The increase in the torque for the compositions containing DCP is obviously due to crosslinking. Since 140°C again registers the maximum torque for DCP modified LDPE, LLDPE and their blend, this temperature was chosen as optimum for DCP modification in the case of these polymers. LLDPE and its blend show a higher degree of crosslinking than that of LDPE. This may be due to larger number of tertiary carbon atoms in LLDPE than LDPE[14]. On addition of coagent TAC, the torque has increased, indicating the efficiency of coagent (TAC) for DCP modification. Fig3.4 shows the variation of stabilised torque of LLDPE with DCP content at 140°C. The stabilised torque increases with DCP content, reaches a maximum and then decreases indicating there is an optimum DCP concentration. Maximum torque is observed for 1% DCP[8]. The same behaviour was observed in the case of LDPE and LDPE/LLDPE blend at different temperatures. So 1% DCP was chosen as the optimum concentration. The optimum dosage of TAC was found by varying the concentration from 0 to 1% keeping the DCP concentration 1%. The optimum concentration of TAC was found to be 0.5% (Fig 3.5).

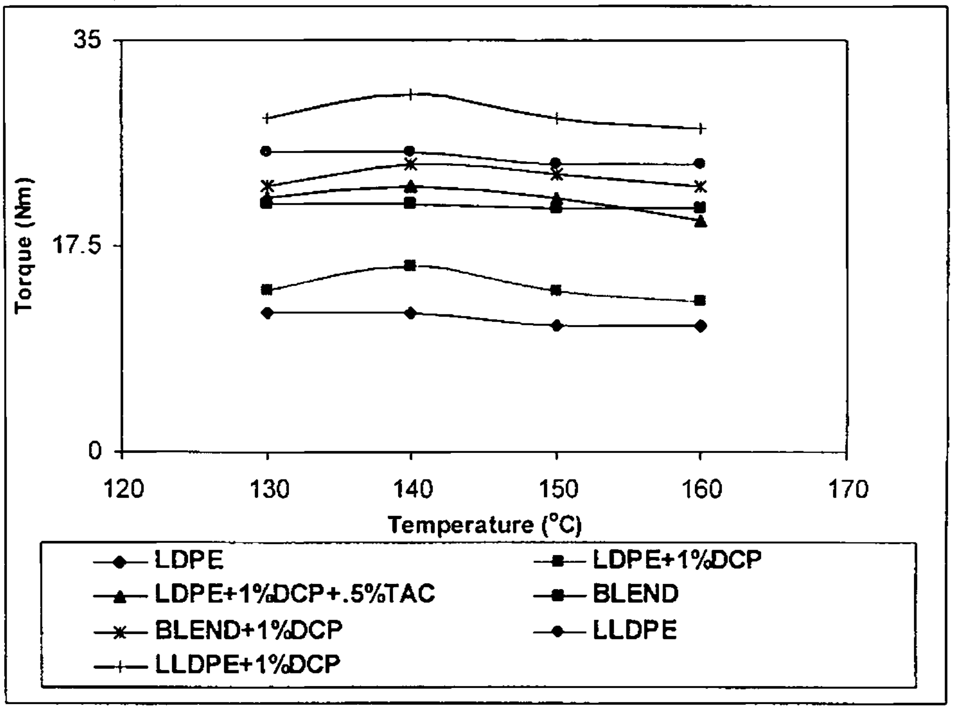

Fig 3.3 Variation of stabilised torque with temperature

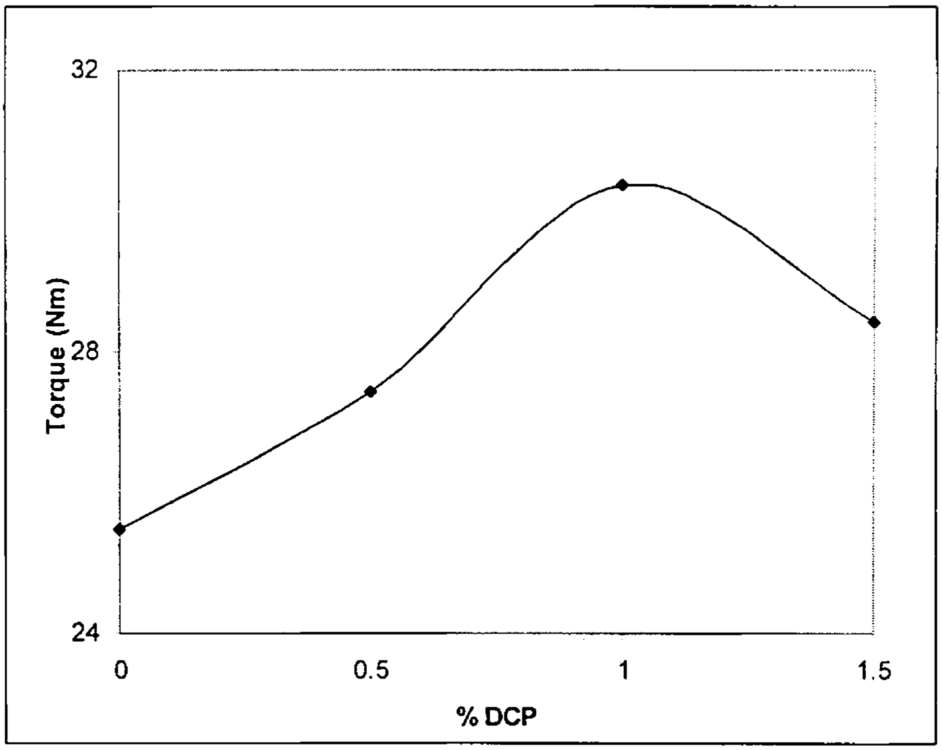

Fig 3.4 Variation of stabilised torque of LLDPE with DCP content at 140° C

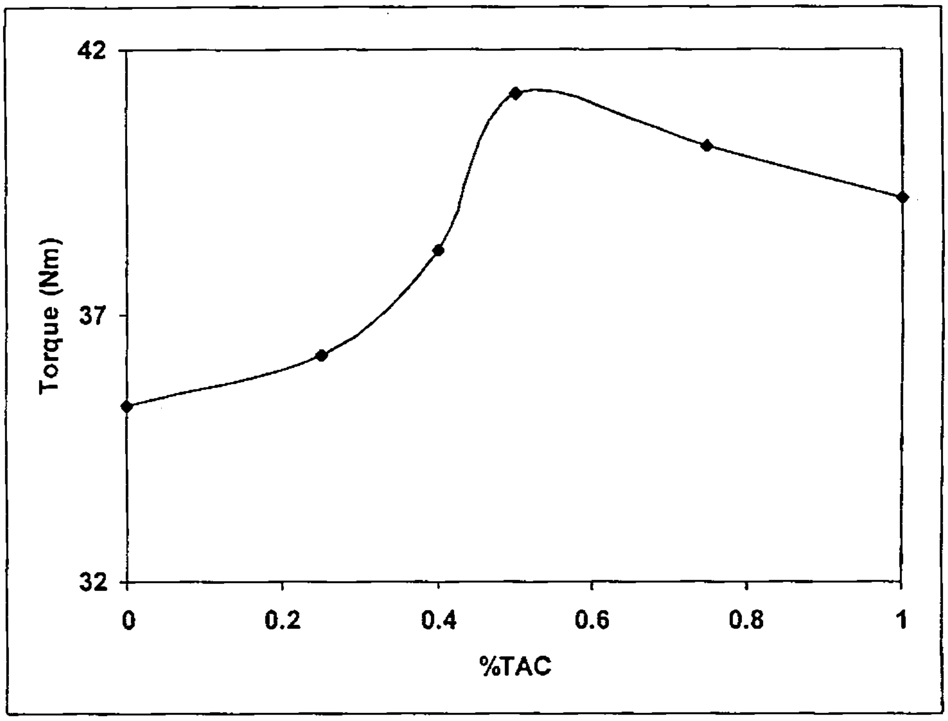

Fig 3.5 Variation of maximum torque with TAC content for modified LDPE at 140° C

The variation of torque values on addition of different percentages of TAC is given in table 3.1.

Table 3.1 Variation of torque with TAC content

Material: LDPE+1%DCP, Temperature :140°C, RPM-60

Time (minutes)	Torque (Nm)				
	.25%TAC	.4%TAC	.5%TAC	.75%TAC	1%TAC
1	36.26	38.22	41.16	40.18	39.2
2	15.68	16.66	17.64	16.66	15.68
5	13.72	14.7	16.66	15.68	14.7
10	13.72	14.7	16.66	15.68	14.7
15	13.72	14.7	16.66	15.68	14.7

To study the correlation between the mixing parameters for DCP modification with those of the extrusion parameters reactive modification of polyethylenes and their blend was done on a laboratory extruder at different temperatures and rpms at different DCP concentrations. The tensile properties of the extruded film were measured. Fig3.6 shows the variation of tensile strength with temperature of extrusion for LDPE, LLDPE and their 50/50 blend at 60 rpm. Maximum tensile strength is obtained at 140°C as in the case of the mixer showing that this temperature is the optimum for DCP modification at the conditions employed. The extrusion behaviour also shows that the results obtained from the mixer can be employed for fixing the extrusion characteristics. Fig3.7 shows the variation of tensile strength with rpm in the case of 50/50 blend with 1% DCP at 140°C. A maximum value of tensile strength is obtained at 60 rpm. This shows that the shear rate/ residence time under these conditions give the best choice for DCP modification. Fig3.8 shows the variation of elongation at break (EB) with temperature, in the case of unmodified and DCP modified, LDPE, LLDPE and their blend. It is found that the EB values decreased on DCP modification as expected.

Fig3.9 shows the variation of EB with %DCP in the case of DCP modified LDPE, LLDPE and their blend at 140° C. The decrease in the EB values with the DCP content may be due to crosslinking.

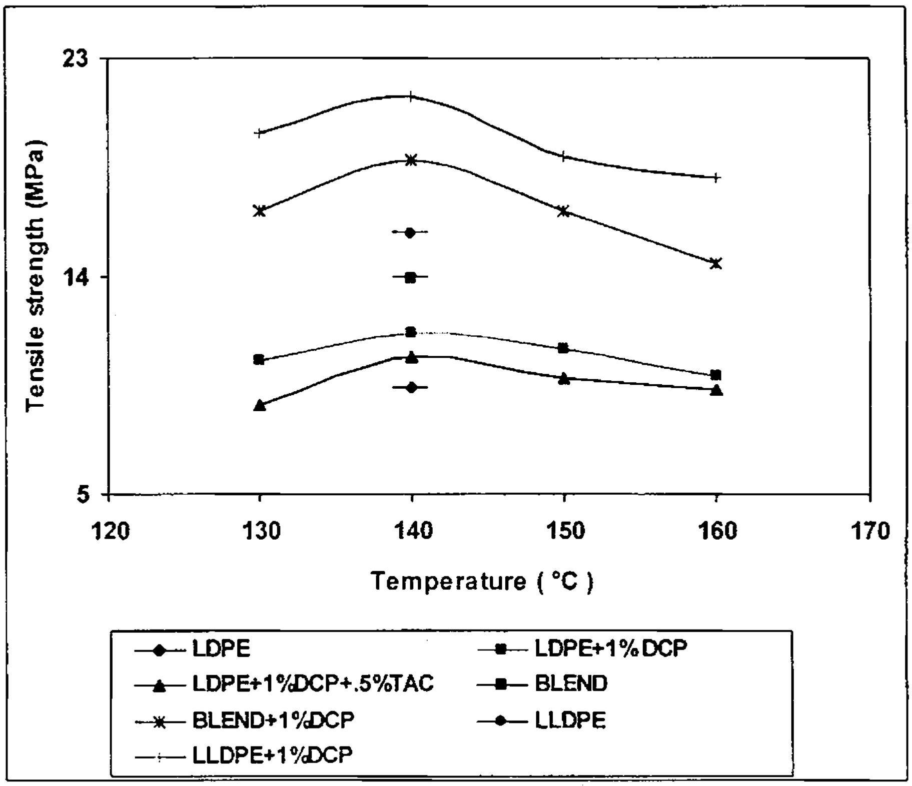

Fig 3.6 Variation of tensile strength with temperature of extrusion

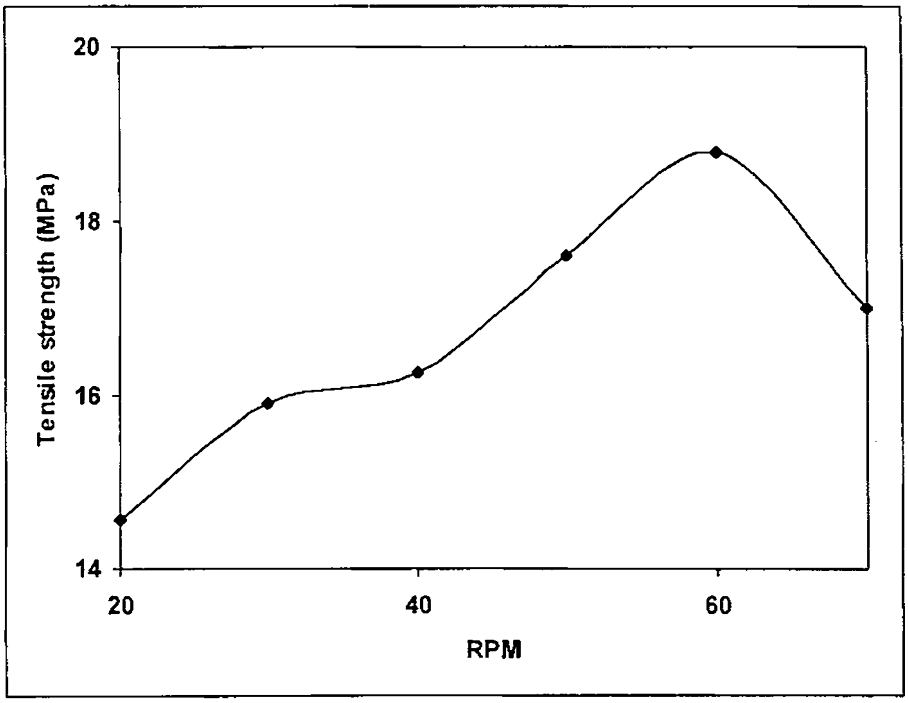

Fig 3.7 Variation of tensile strength with rpm for modified LDPE/LLDPE blend at 140° C

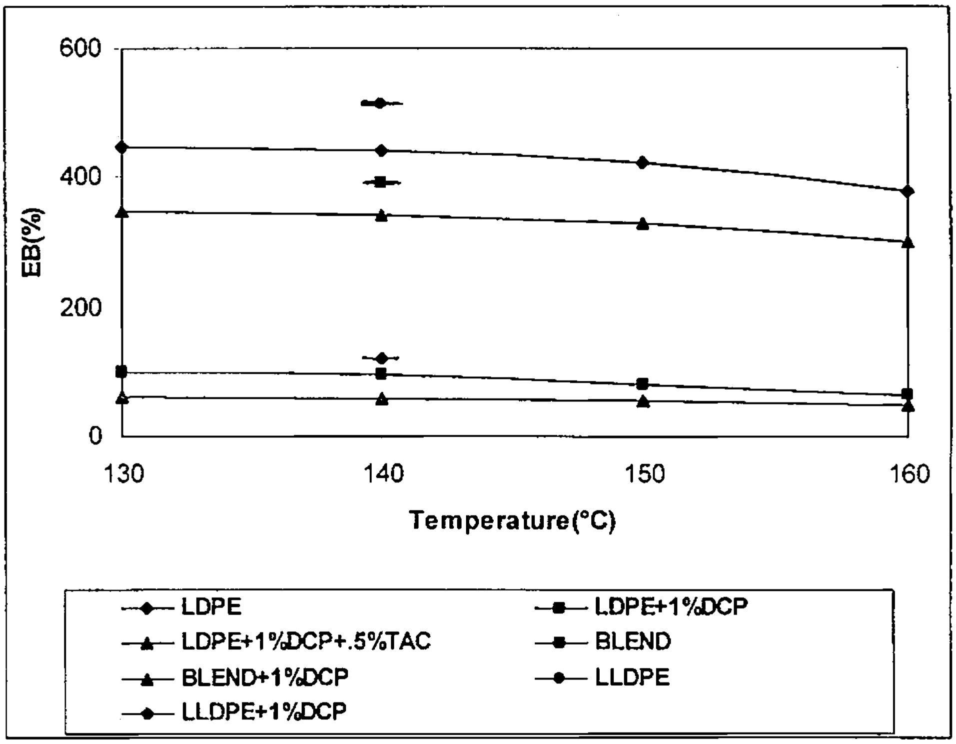

Fig 3.8 Variation of EB with temperature

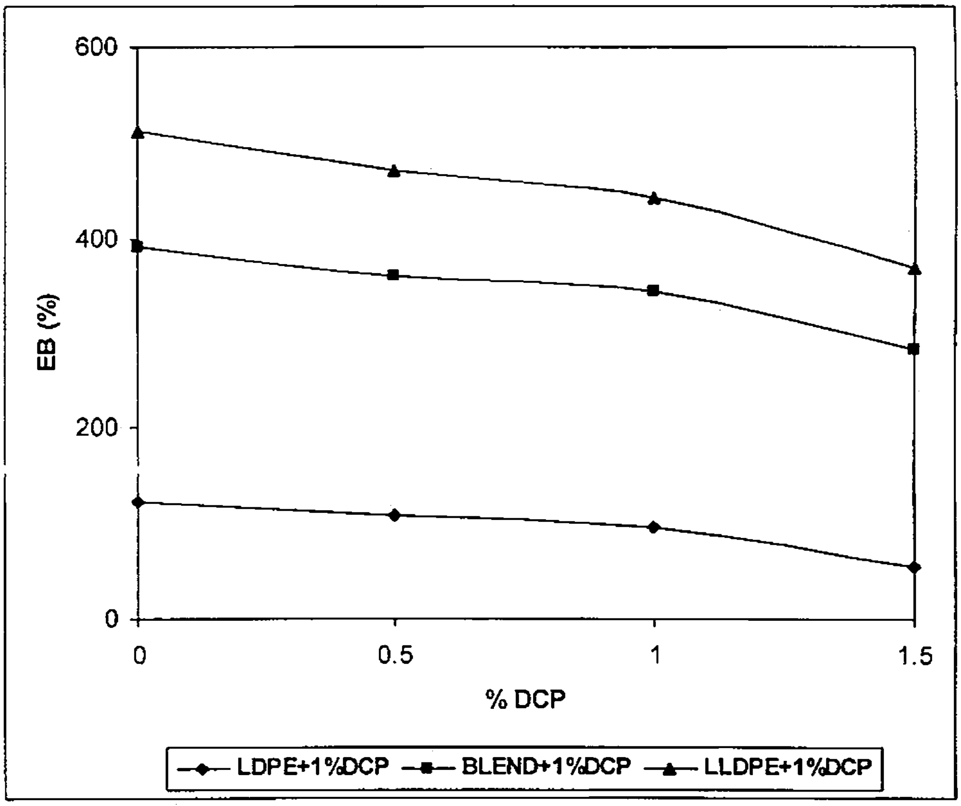

Fig 3.9 Variation of EB with DCP content at 140° C

The FTIR spectra of pure polymers and DCP modified polymers were taken. Figs 3.10&11 show the FTIR spectrum of blend and DCP modified blend. The IR spectrum of DCP modified polymers do not show much variation as expected. The grafting of TAC on the polymer chain was confirmed by FTIR spectrum. The absorption at 1112 cm^{-1} is characteristic of C-O stretching vibrations. The absorption at 1565 cm^{-1} is characteristic of C-N stretching vibrations and allyl group.

Fig 3.12 shows the variation of viscosity at different shear rates, at 170°C, in the case of LDPE, DCP modified LDPE and coagent (TAC) modified LDPE. An increase in viscosity is obtained on DCP addition as expected. The increase in viscosity is due to the introduction of crosslinks between the chains. However, the increase in viscosity is only marginal and hence may not affect the processability. The increase in viscosity is much pronounced in the case of coagent (TAC) modified LDPE. Fig3.13 shows the variation of viscosity at different shear rates, at 170° C, in the case of blend, LLDPE, DCP modified blend and LLDPE. Here also DCP addition shows increase in viscosity. Fig3.14 shows the variation of gel content with mixing temperature for LDPE. Maximum value of gel content is obtained at 140°C confirming that maximum crosslinking occurs at this temperature.

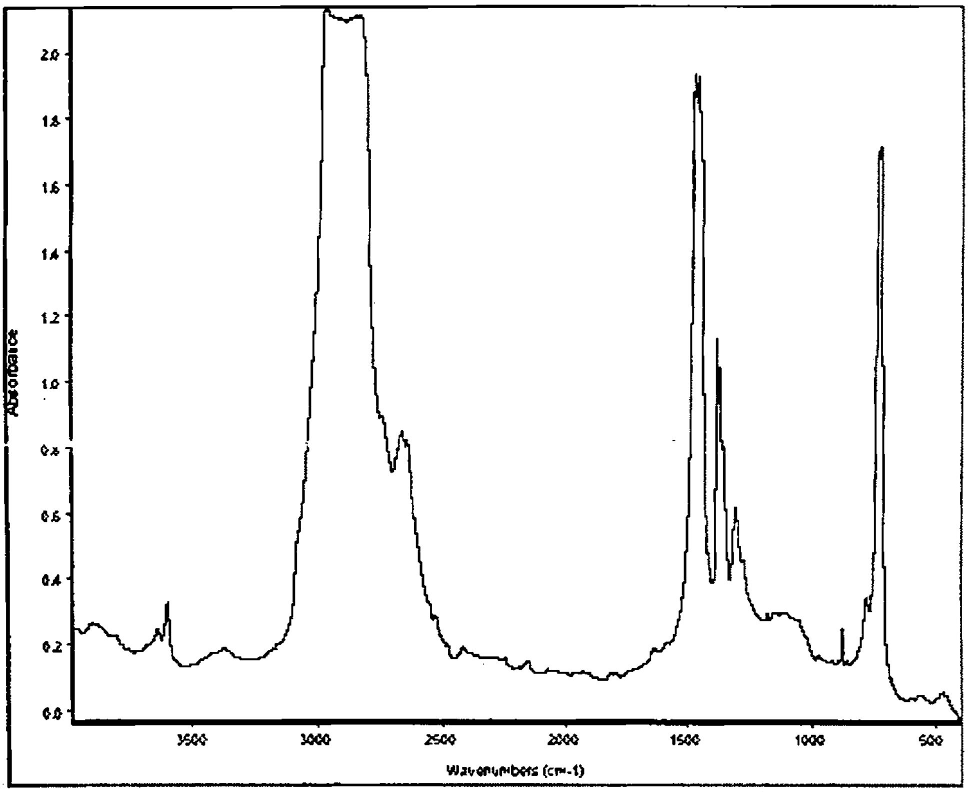

Fig 3.10 FTIR spectrum of blend

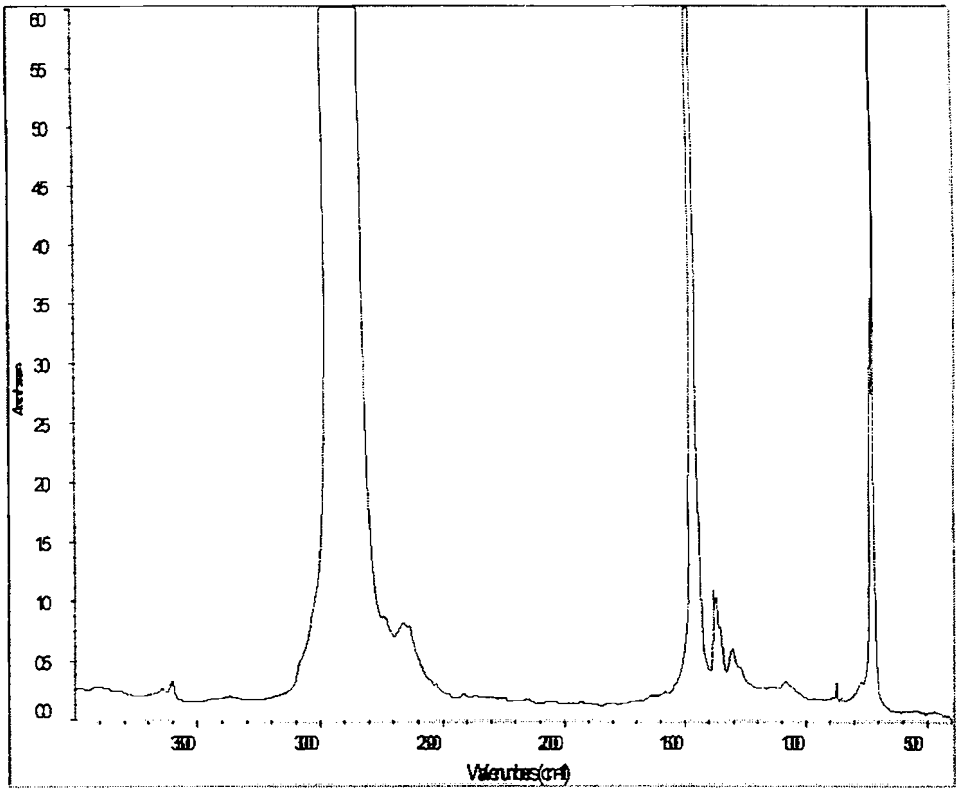

Fig 3.11 FTIR spectrum of DCP modified blend

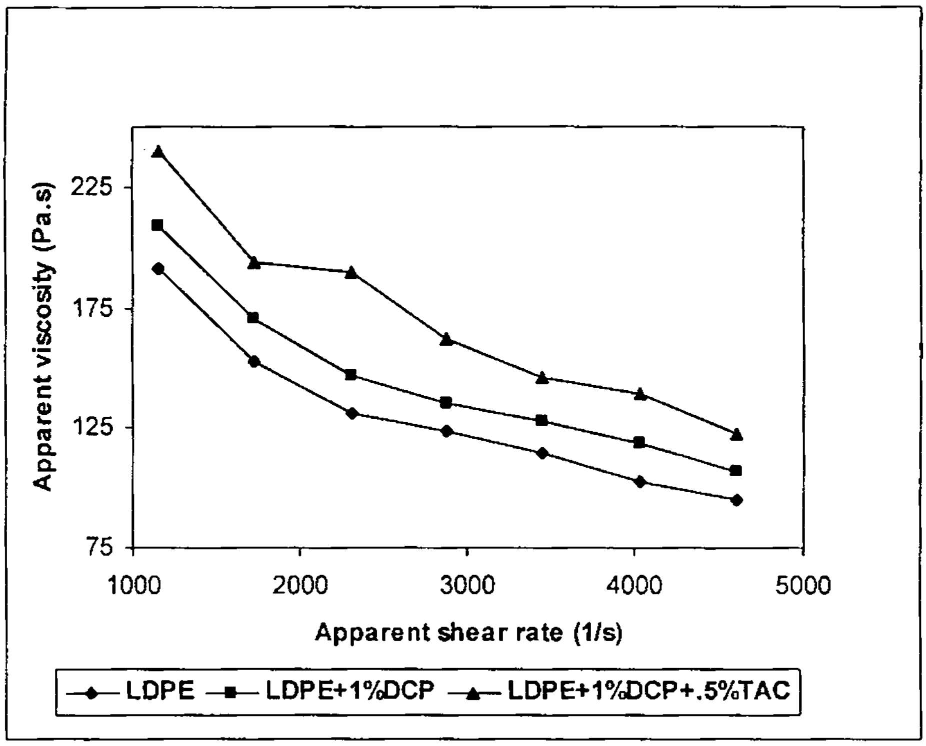

Fig 3.12 Flow curves of unmodified and modified LDPE

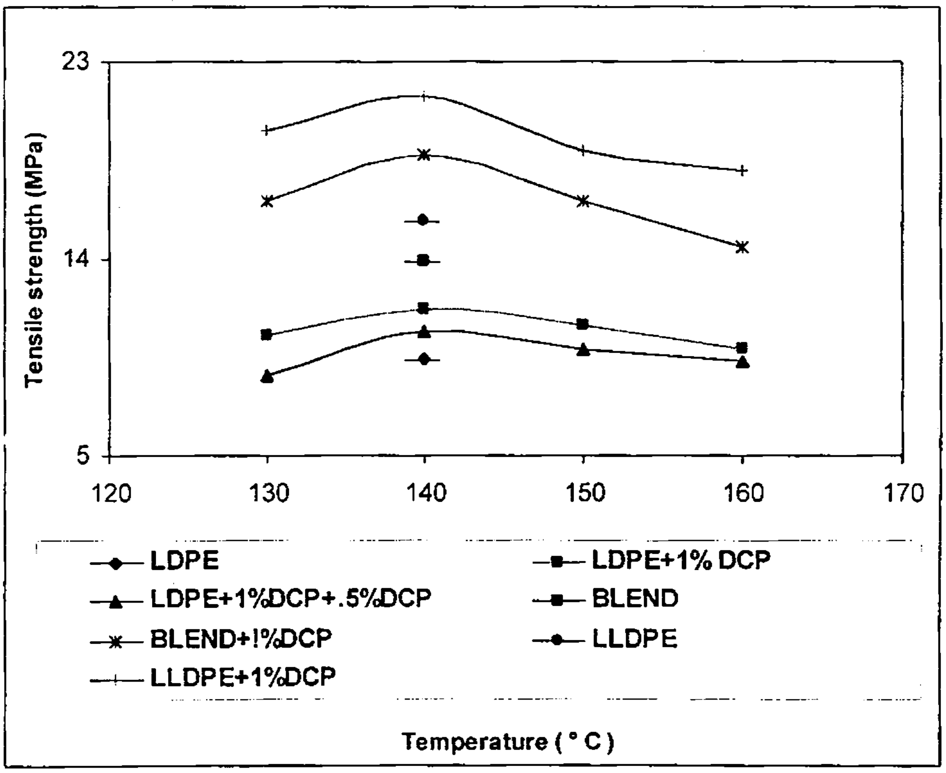

Fig 3.13 Flow curves of unmodified and modified blend and LLDPE

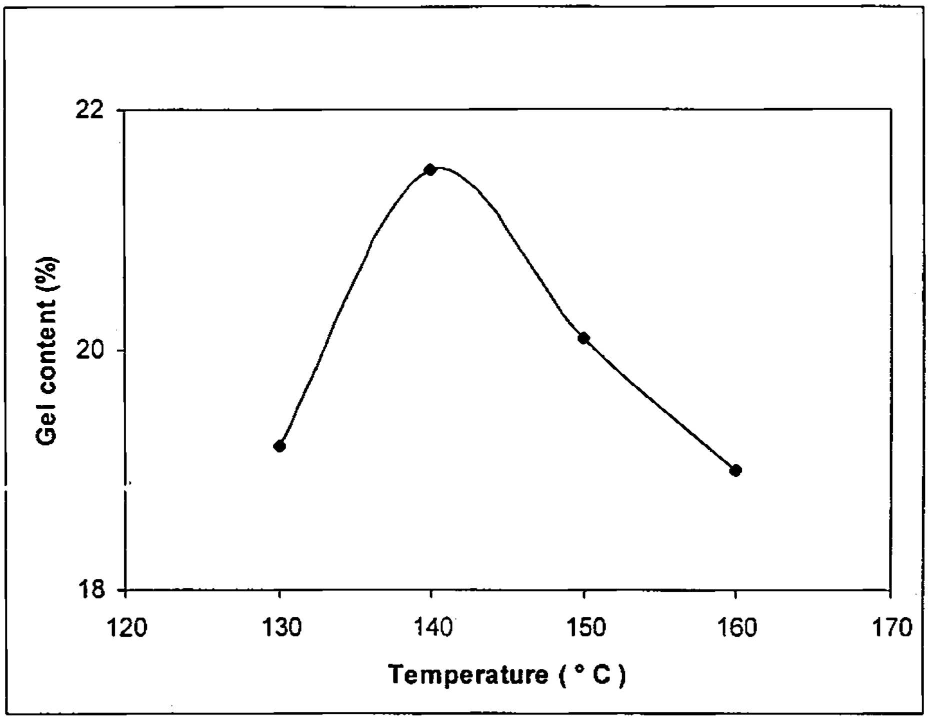

Fig 3.14 Variation of gel content with mixing temperature for modified LDPE

The gel content of LDPE is compared with that of LLDPE and 50/50 LDPE/LLDPE blend in table3.2.

Table3.2 Gel content values at 140° C

Material	Gel Content (%)
LDPE + 1 % DCP	21.5
LDPE + 1%DCP +. 5% TAC	25.6
BLEND + 1% DCP	24.4
LLDPE + 1% DCP	26.2

LLDPE has a higher crosslink density than LDPE. Gel content, which relates to the three dimensional network structure, increases with LLDPE content, indicating that the LLDPE phase forms a relatively denser network structure. Addition of the coagent is found to improve the crosslink density.

Figs3.15-17 show the extrudate swell ratio vs shear rate of unmodified and DCP modified LDPE, LLDPE and their blend. It can be seen from the figures that the extrudate swell ratio (De/D) increases with the shear rate. This is expected because the recoverable elastic energy built up in the melt while flowing in the capillary increases as shear rate is increased. The figures also reveal that the extrudate swell ratio increases on DCP modification. The increase in swell ratio may be due to the marginal reduction in crystallinity resulting from crosslinking.

Figs3.18-20 show the variation of viscosity with shear rate at different temperatures of the crosslinked LDPE, LLDPE and their blend. The viscosity decreases with increase in temperature as expected.

The variation of log viscosity with reciprocal of absolute temperature at various shear rates of the uncrosslinked and crosslinked LDPE, LLDPE and their blend are shown in figures 3.21-26.The slope of these lines is proportional to the activation energy for viscous flow.

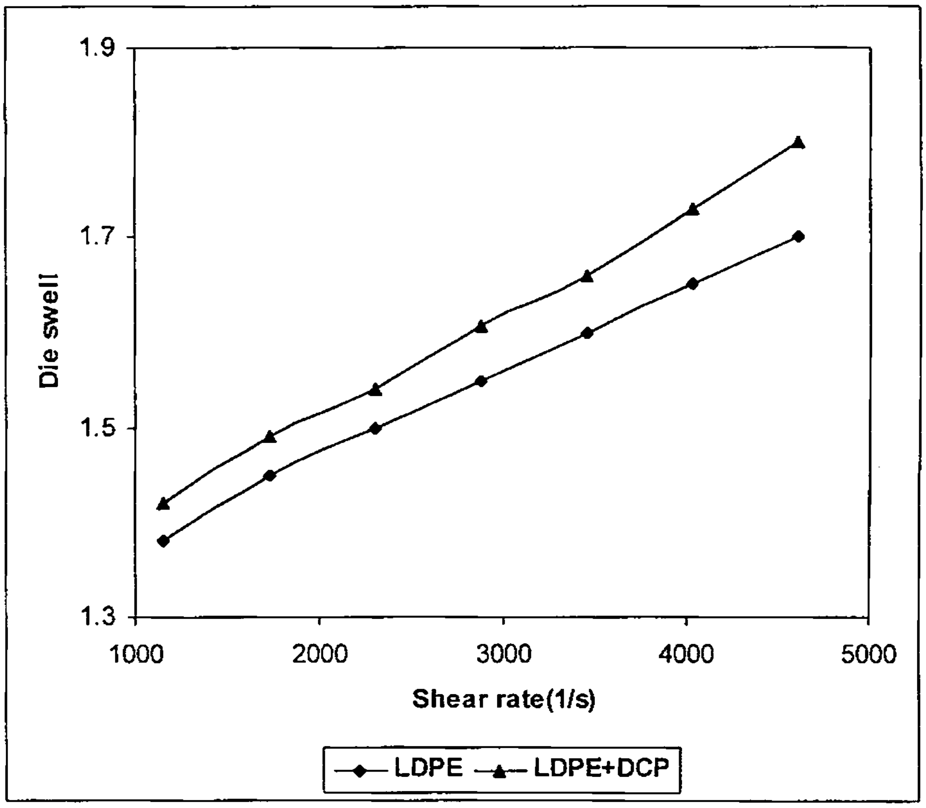

Fig 3.15 Variation of extrudate swell ratio with shear rate

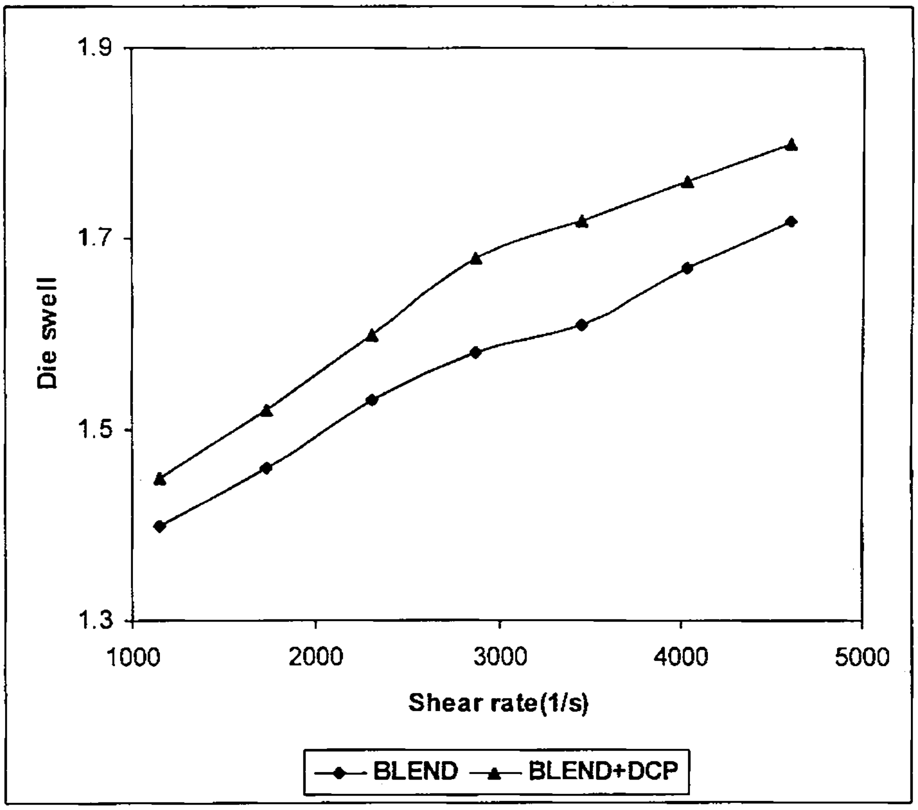

Fig 3.16 Variation of extrudate swell ratio with shear rate

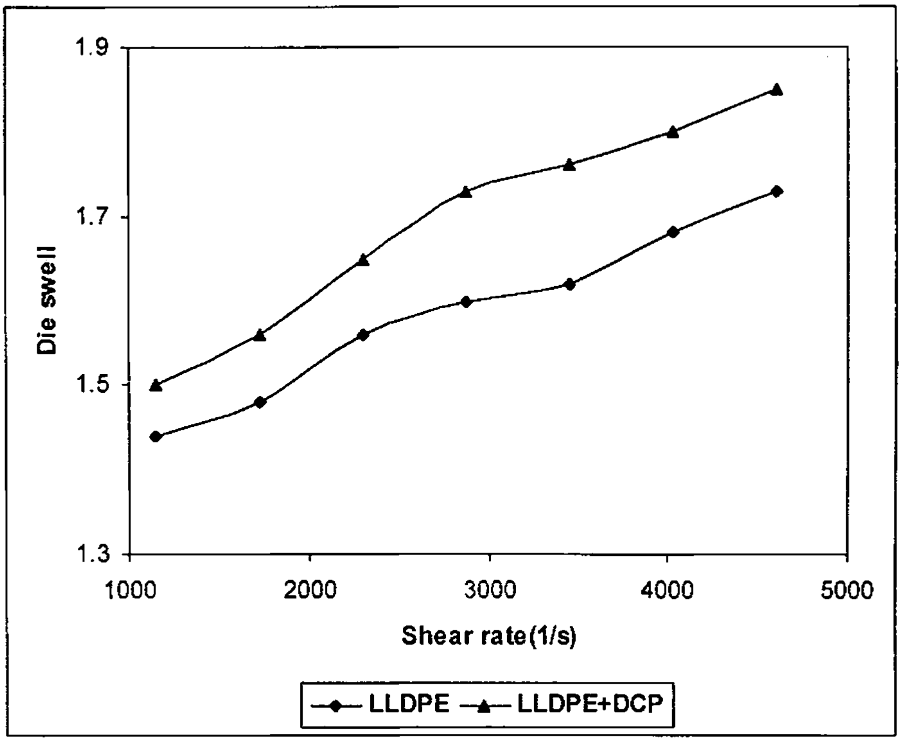

Fig 3.17 Variation of extrudate swell ratio with shear rate

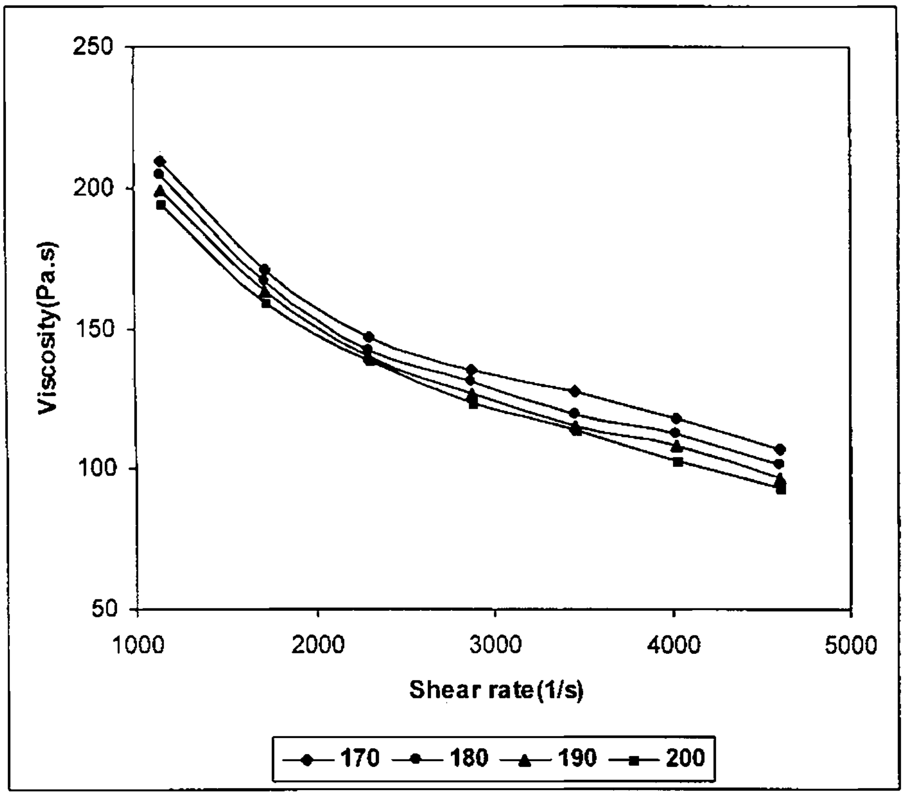

Fig 3.18 Variation of viscosity with shear rate at different temperatures for modified LDPE

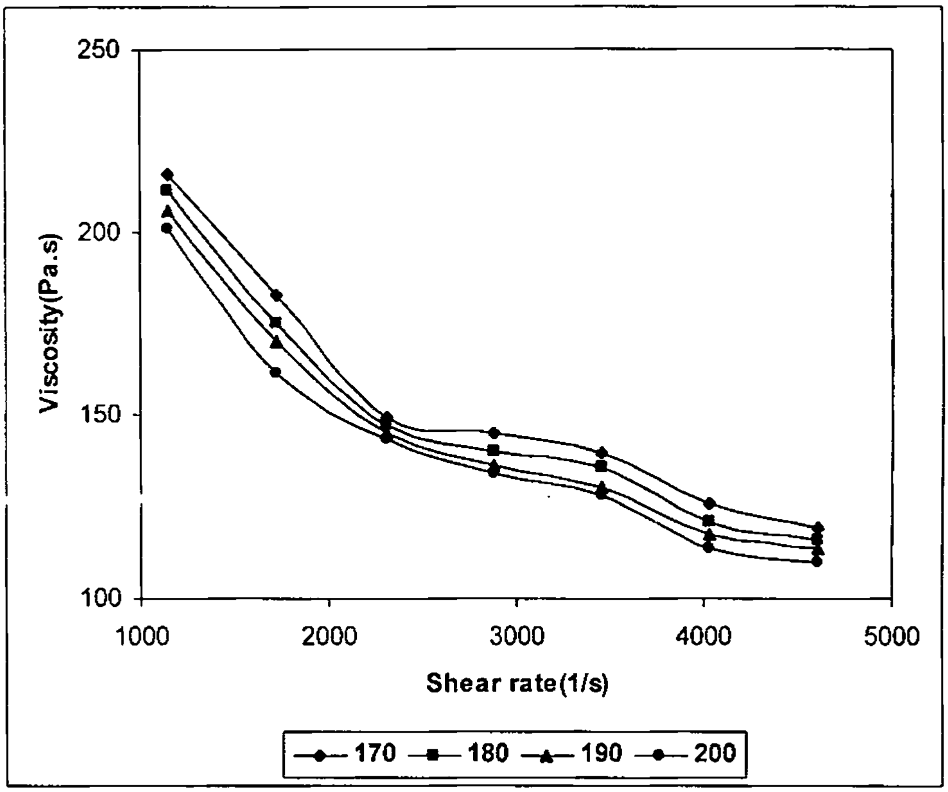

Fig 3.19 Variation of viscosity with shear rate at different temperatures for modified blend

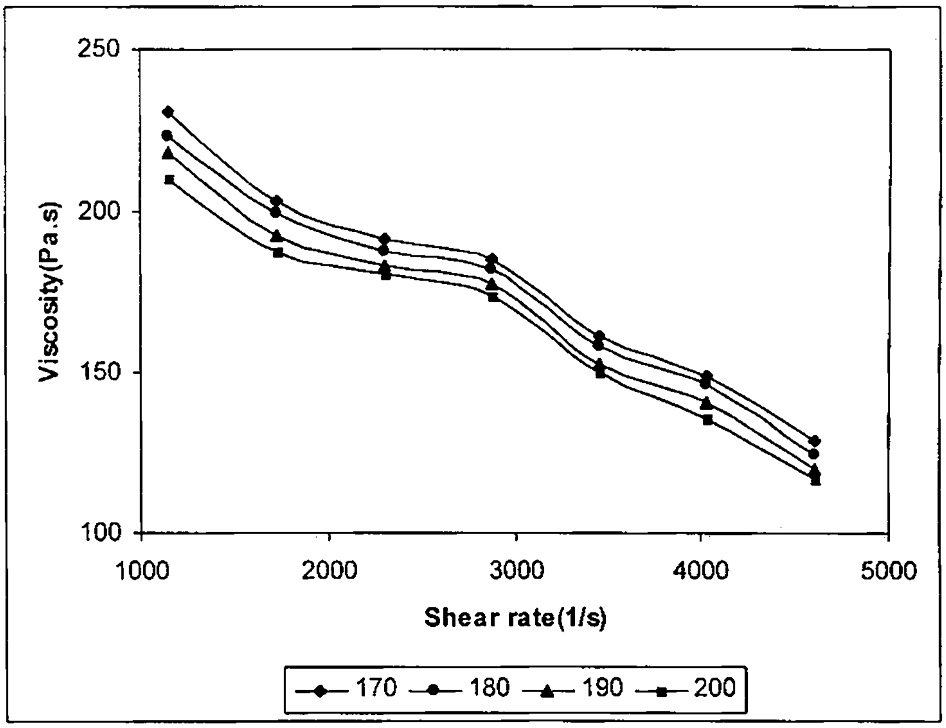

Fig 3.20 Variation of viscosity with shear rate at different temperatures for modified LLDPE

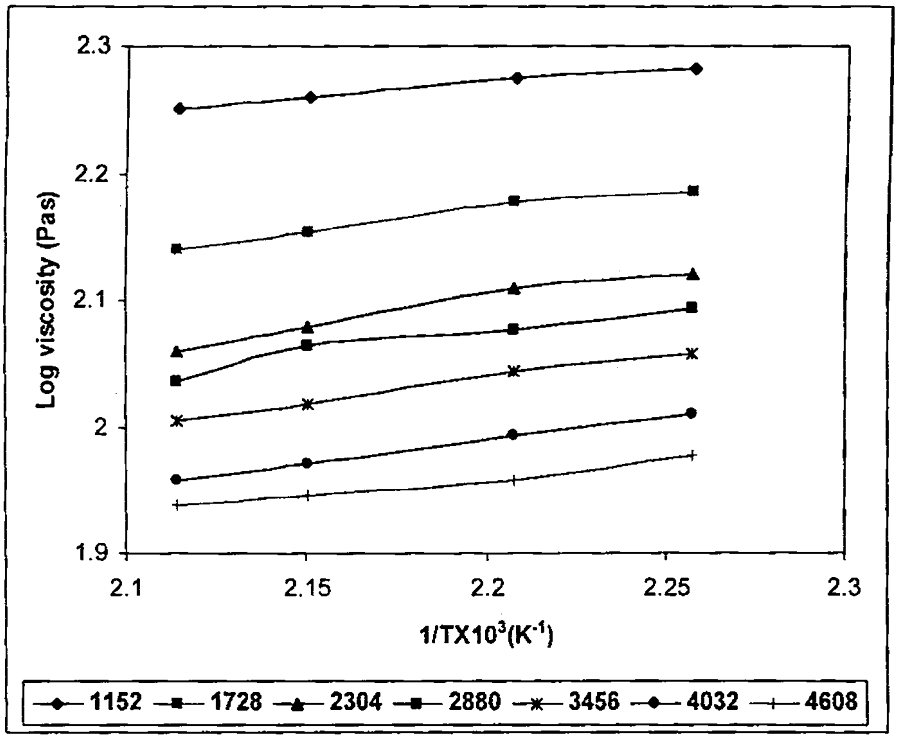

Fig 3.21 Temperature dependence of viscosity of LDPE

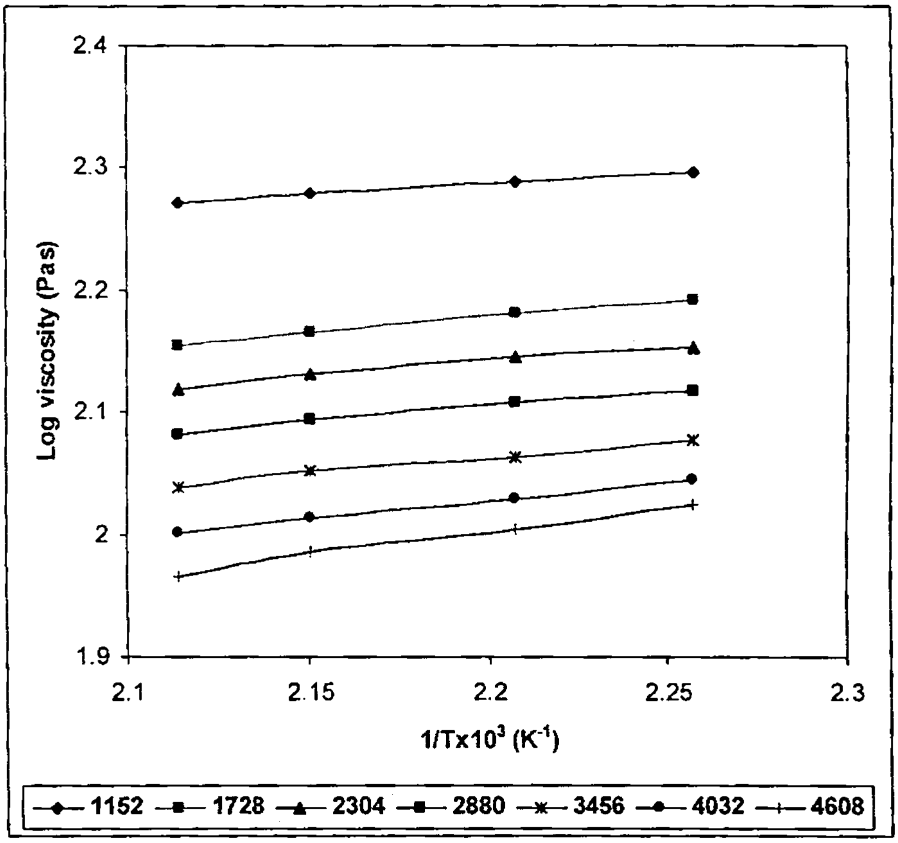

Fig 3.22 Temperature dependence of viscosity of blend

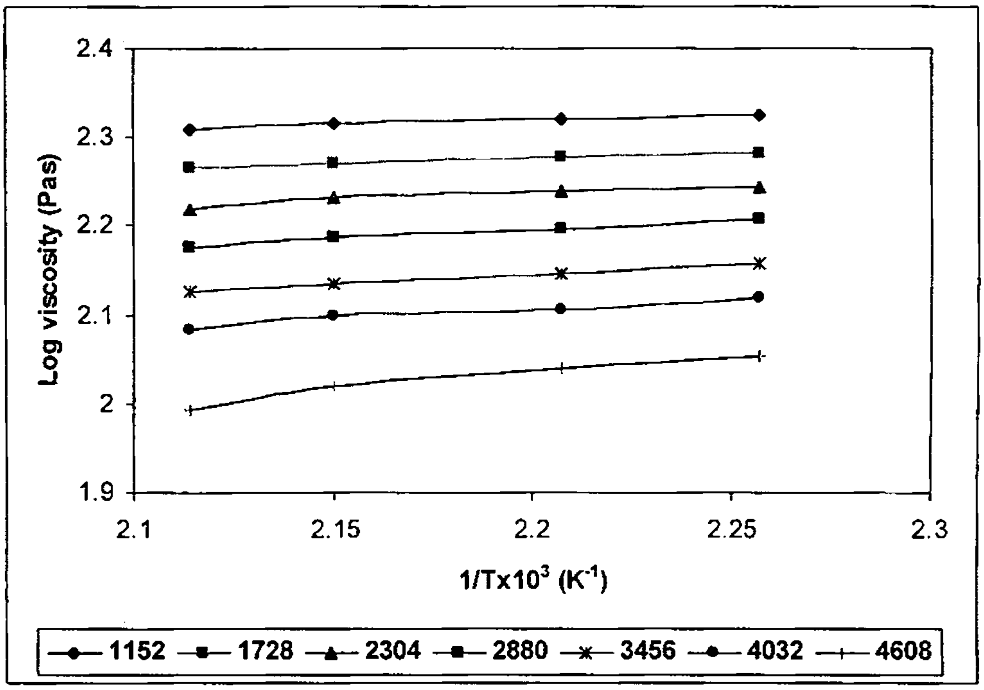

Fig 3.23 Temperature dependence of viscosity of LLDPE

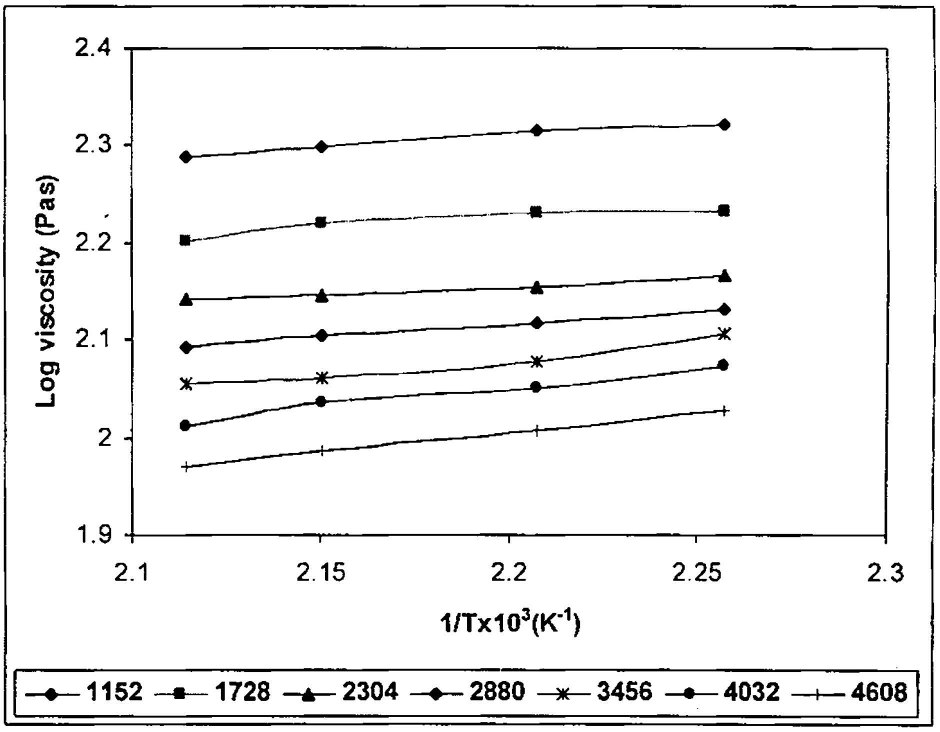

Fig 3.24 Temperature dependence of viscosity of modified LDPE

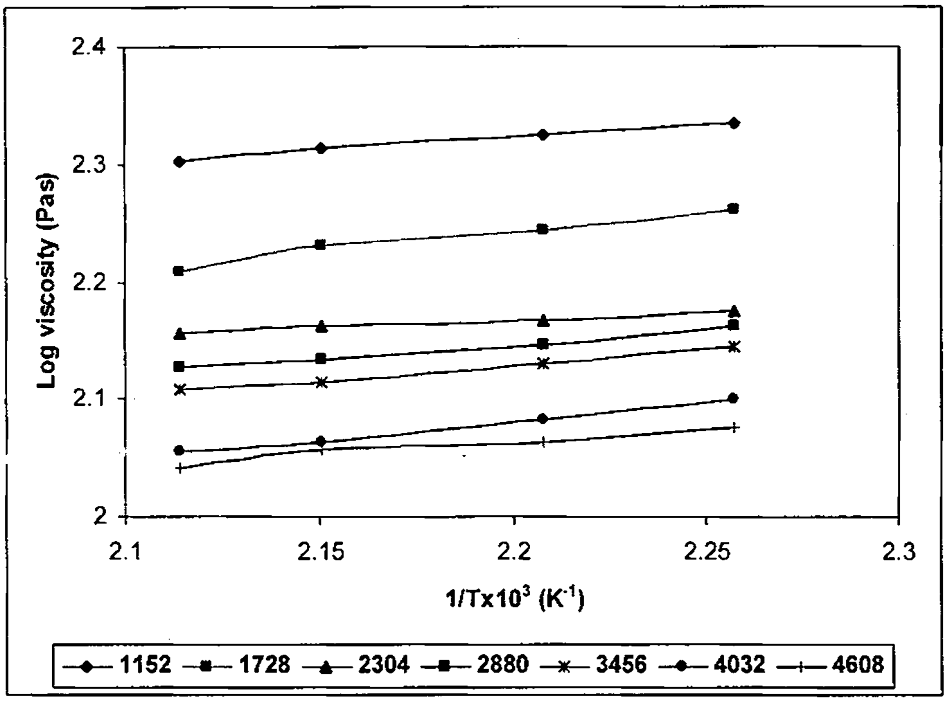

Fig 3.25 Temperature dependence of viscosity of modified blend

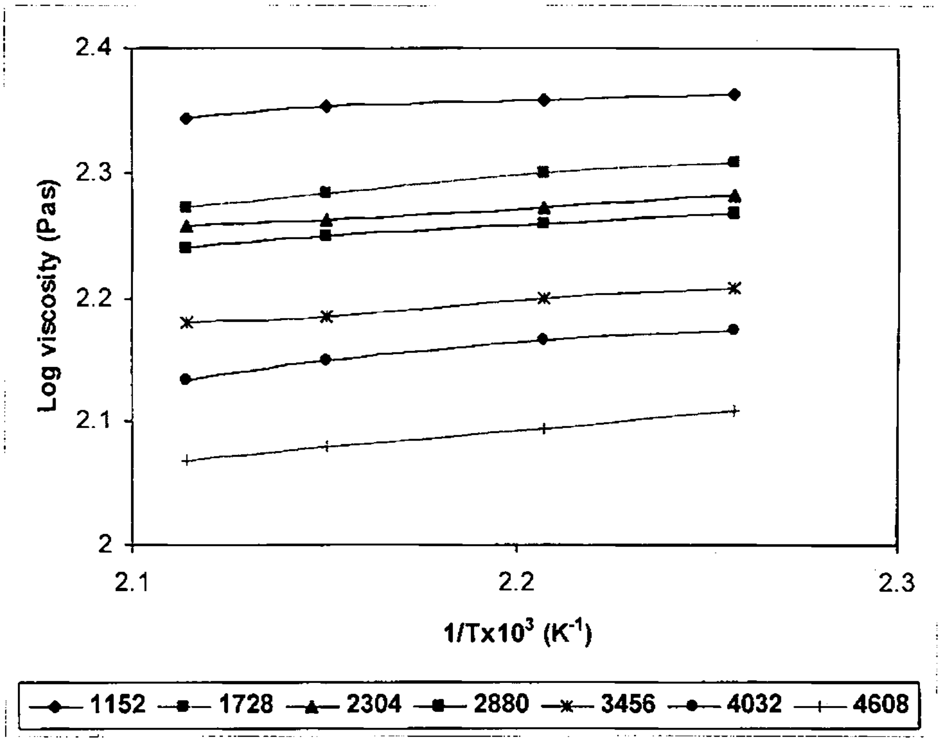

Fig 3.26 Temperature dependence of viscosity of modified LLDPE

The activation energy values are shown in table3.3. The crosslinked polymers show marginally higher activation energy as expected. The difference in activation energy with crosslinking gradually increases with LLDPE content. This is likely to be due to the higher crosslink density in LLDPE than in LDPE.

Table.3.3 Variaton of activation energy of the polymers at different shear rates.

Shear rate (1/s)	Activation energy (kJ/mol)					
	LDPE	LDPE+ 1%DCP	BLEND	BLEND+ 1%DCP	LLDPE	LLDPE+ 1%DCP
1152	0.899	1.109	0.929	1.015	1.042	1.264
1728	0.924	1.451	1.054	1.214	1.186	1.456
2304	1.340	1.573	1.281	1.683	1.486	1.723
2880	1.601	1.788	2.154	2.328	2.269	2.645
3456	1.819	2.076	2.565	2.802	2.599	2.952
4032	2.234	2.617	2.977	3.067	3.128	3.318
4608	3.352	3.780	3.357	3.861	3.468	3.921

The thermogravimetric curves of unmodified and modified LDPE are shown in fig3.27. DCP modification introduces improvement in thermal stability as expected. The coagent (TAC) modified LDPE gives better thermal stability. The thermogravimetric curves of unmodified and modified LLDPE and LDPE/LLDPE blend are shown in fig3.28.DCP modified LLDPE and LDPE/LLDPE blend shows better thermal stability than DCP modified LDPE.

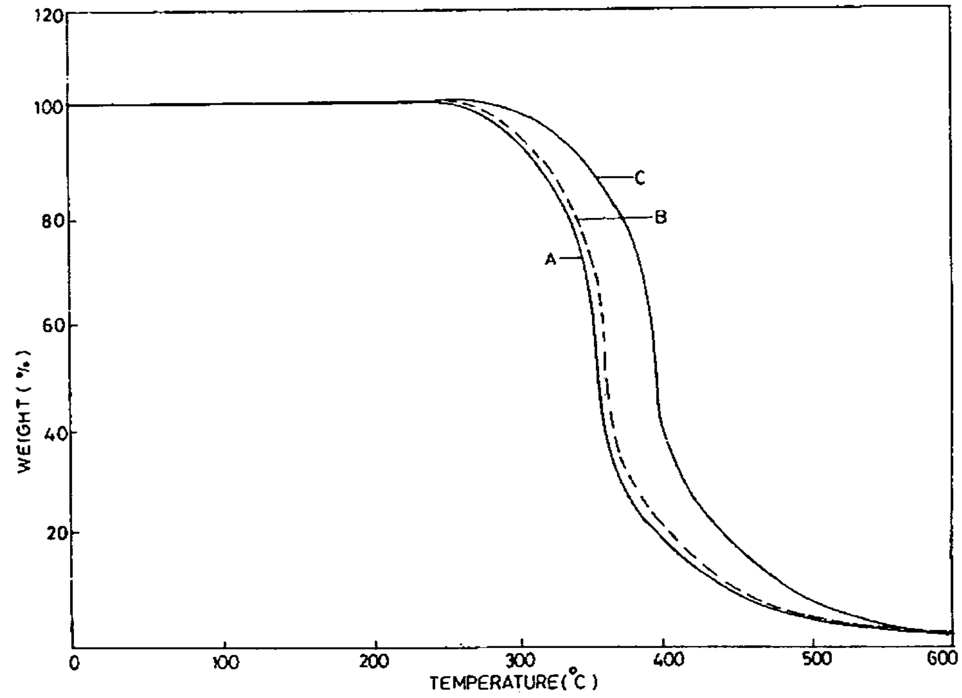

Fig. 3.27 TGA CURVES OF (A) LDPE, (B) LDPE +1% DCP, (C) LDPE + 1%DCP + 0.5%TAC

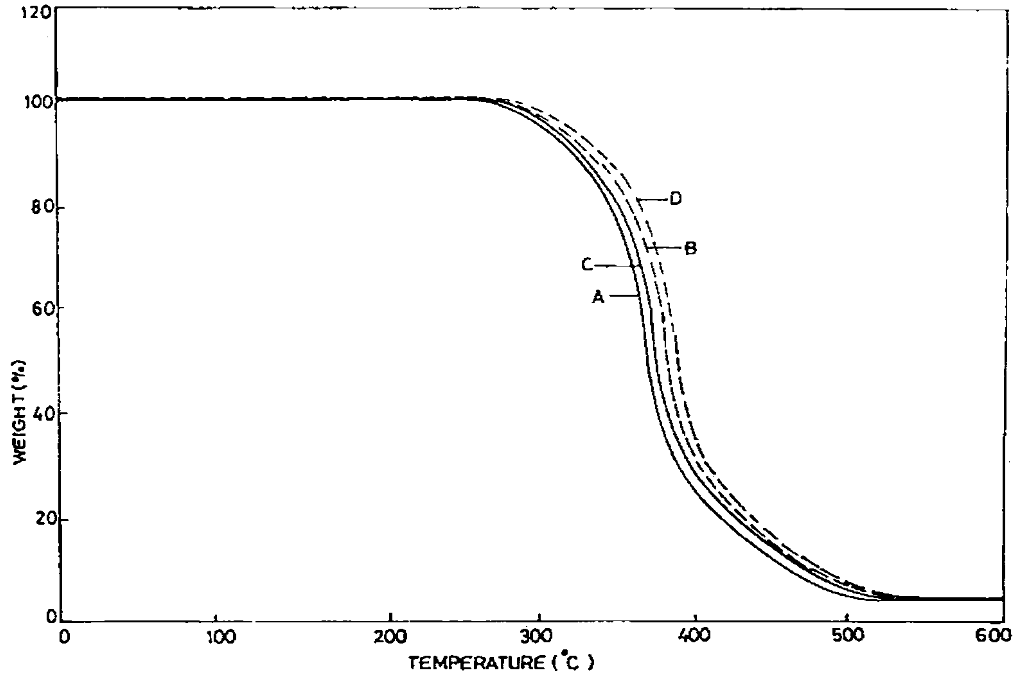

Fig 3.28 TGA CURVES OF (A) BLEND, (B) BLEND +1% DCP, (C) LLDPE (D) LLDPE + 1% DCP

Decomposition temperatures are given in table3.4. The LLDPE phase shows a higher improvement in decomposition temperature than that of LDPE, probably because of the higher crosslink density.

Table3.4. The temperature of derivative weight % peak

Material	Peak temp (°C)
LDPE	373.8
LDPE + 1% DCP	378.1
LDPE + 1% DCP + .5% TAC	400
BLEND	380.3
BLEND + 1% DCP	391.0
LLDPE	383.5
LLDPE + 1% DCP	394.8

The densities of unmodified and modified LDPE, LLDPE and their blend are shown in table3.5.The densities of the modified polymers are found to get marginally reduced upon modification. This behaviour can be attributed to reduction in crystallinity, because of network formation [8].

Table3.5 Variation of density with modification

Material	Density (g/cc)
LDPE	0.973
LDPE+1%DCP	0.961
LDPE+1%DCP+.5%TAC	0.951
BLEND	0.957
BLEND+1%DCP	0.948
LLDPE	0.947
LLDPE+1%DCP	0.931

3.4. CONCLUSIONS

The study shows that a single screw extruder can be used for reactive extrusion of polyethylenes. The optimum reaction conditions viz temperature, shear rate and residence time can be determined on a torque rheometer and then these conditions can be used in actual extrusion.

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CHAPTER 4

SILANE GRAFTING OF POLYETHYLENES

SILANE GRAFTING OF POLYETHYLENES

4.1. INTRODUCTION

Grafting in an extruder reactor involves reaction of a molten polymer with a monomer or mixture of monomers capable of forming grafts to the polymer backbone. Free radical initiators and less commonly air or ionizing radiation have been used to initiate the reaction. Extruder reactors for performing graft reactions may include intensive mixing sections and screw segments designed to expose the maximum surface area of polymer substrate to grafting agent.[1-6]

Grafting of vinylsilanes to polyolefine substrates in the presence of peroxide is the most common example of a graft reaction performed in extruder reactors. The sole purpose of the peroxide is to initiate the grafting reaction. Polyolefines grafted with vinyl silanes are readily crosslinked by moisture and the materials have a large commercial market as wire coating and pipe insulation.[7-15]

The crosslinking of polyethylene molecules by main bonds into three-dimensional networks leads to significant improvements of the material properties, which greatly enlarge the application fields of these low cost polyolefines. Compared with the untreated material, crosslinked polyethylene especially shows enhanced impact strength, better thermal performance and higher chemical resistance. Further, considerable improvements can be found in the resistance to wear, creep and ageing[16-24]. Also, crosslinked products can incorporate high amounts of fillers without a remarkable deterioration of the material properties.

Dialkyl or diaralkyl peroxides are the most commonly used radical donors for the organosilane grafting. The sole purpose of the peroxide is to initiate the grafting reaction. They degrade, due to the instability of their O-O bond, to free radicals, when exposed to higher temperatures. The service temperature of crosslinked polyethylene can be extended to significantly higher temperatures than those of thermoplastic polyethylene. For example, an important application of peroxide crosslinked polyethylene is in hot water piping installations where the combination of high temperatures and pressures has caused failure of thermoplastic polyethylene and polypropylene[25-36].

In addition to the disadvantage of high cost special equipment necessary for the production of peroxide crosslinked piping, and coatings in the wire and cable industry, other production methods (eg. Injection moulding and blow moulding) are still unavailable or uneconomical. A more versatile technology developed by Dow corning, for manufacturing crosslinked polyethylene products using conventional thermoplastic processing techniques is recently becoming important.[37-43] Polyethylene reacted with an organosilane in a compounding extruder gives silane grafted polymer containing Si-OR groups.

Currently, different techniques are in use for the production of crosslinked polyethylene whereby the thermally initiated peroxide method, the crosslinking via γ or β radiation and the silane method are by far the most important.[44-50] The silane method, differs from the other crosslinking techniques when considering the processing procedure. Compounding of such a mixture in the melt at a high temperature causes decomposition of the peroxide and grafting of alkoxy silyl groups to the polyolefine chains. In a first step, during the processing of the polymer, H atoms are abstracted from the macromolecules by free radicals, which are generated from thermally degradable organic peroxides. Silane can link upto these activated sites whereby the radical character is transferred to the linking element. The actual crosslinking takes place subsequently to the grafting step. The functional end groups saponize to silanoles in a hydrolysis reaction with water molecules. The generated OH groups then condense with adjacent Si-O-H groups to main Si-O-Si bonds. The polymer is thus crosslinked.[7]

The use of extruders as continuous reactors for processes such as polymerization, polymer modification or compatibilization of polymer blends involves technologies that are gaining increasing popularity and compete with conventional operations with respect to efficiency and economics. In this chapter the optimum conditions for silane grafting viz: temperature, shear rate, silane and DCP concentrations were determined on a torque rheometer in the case of low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and their blend and then actual extrusion of these polymers was performed using these conditions in a laboratory extruder. Silane grafting of low density polyethylene (LDPE) in the presence of peroxide was performed with and without addition of water.

4.2. EXPERIMENTAL

Reactive Extrusion

Comparison of single step and double step silane grafting

Conditions for reactive extrusion were first determined on a Brabender plasticorder mixer model PL3S equipped with roller type rotors, having a capacity of 40g. Changes in torque obtained are a measure of the changes in the melt viscosity of the polymer. Different mixing conditions were generated by varying the temperature and rpm. The dosage of silane was varied from 1-5% of the total weight of the polymer. Dicumyl peroxide (DCP) at concentrations of 2-6% of the silane was added along with the polymer. Reactive extrusion was done on a laboratory general purpose plastic extruder attached to a Brabender plasticorder model PL2000 with an L/D ratio of 25, a compression ratio of 2 and fitted with a ribbon die. The temperatures of the barrel and that of the die and the rpm of the screw were fixed as per the results obtained from the mixer.

Reactive extrusion was performed both in a single step and double step process. In the single step process, silane, DCP and the polymer were added to the hopper of the extruder and extrusion was performed in one stage. In the double step process, the extruded material collected from the ribbon die was cut in to small pieces and again fed into the hopper of the extruder.

4.3. RESULTS AND DISCUSSION

On addition of LDPE, DCP and silane to the Brabender mixer, the torque rises due to melting/crosslinking/grafting, reaches a maximum value and then stabilises at a lower value. The grafting/crosslinking may be estimated either from the maximum torque or the stabilised torque. Fig 4.1 shows the variation of stabilised torque with silane content at 190°C and 60rpm in the torque rheometer keeping the level of DCP content at 4% of the silane level. An initial increase in torque is observed on silane grafting/crosslinking as expected. Polyethylene reacted with the oraganosilane in the compounding extruder gives silane grafted polymer containing Si-OR groups. Water molecules cause hydrolysis of Si-OR groups and formation of Si-O-Si crosslinks by condensation[6]. The highest value of stabilised torque is obtained for 3% silane, which shows that under the conditions maintained, the maximum extent of grafting/crosslinking occurred at this concentration of silane; hence 3% silane was chosen for further trials. The optimum percentage of silane content was also verified from the variation of tensile strength of the samples. The variation of tensile strength with percentage silane after processing at 190°C at 60rpm is shown in Fig 4.2. Maximum tensile strength is obtained for 3% silane.

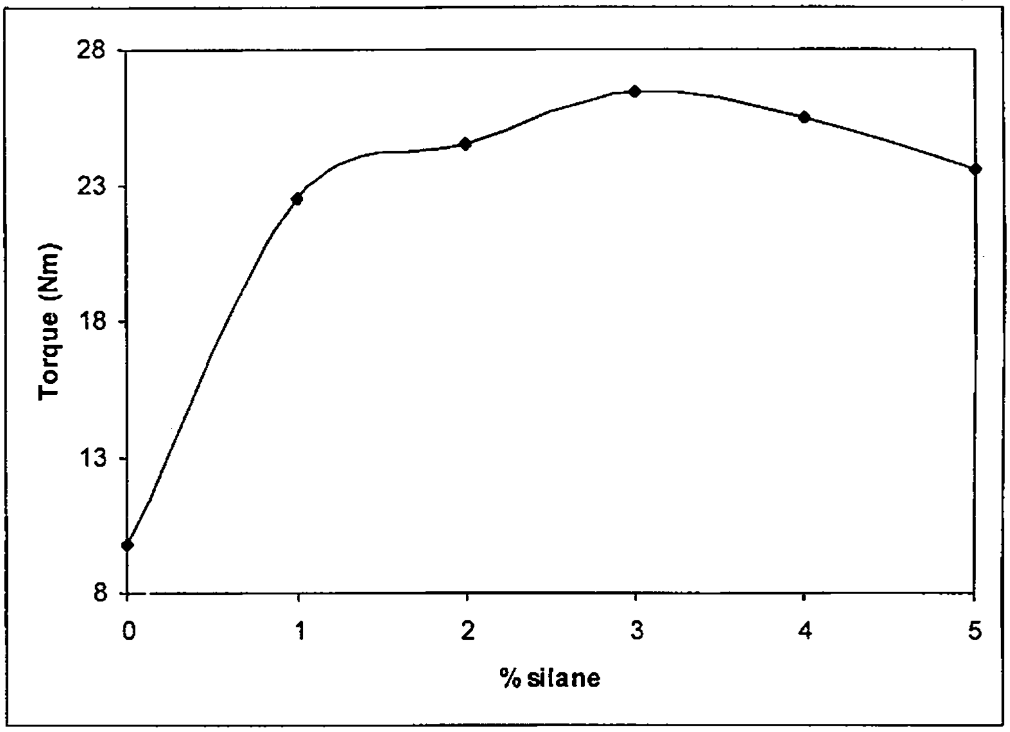

Fig 4.1 Variation of stabilised torque with silane content at 190° C

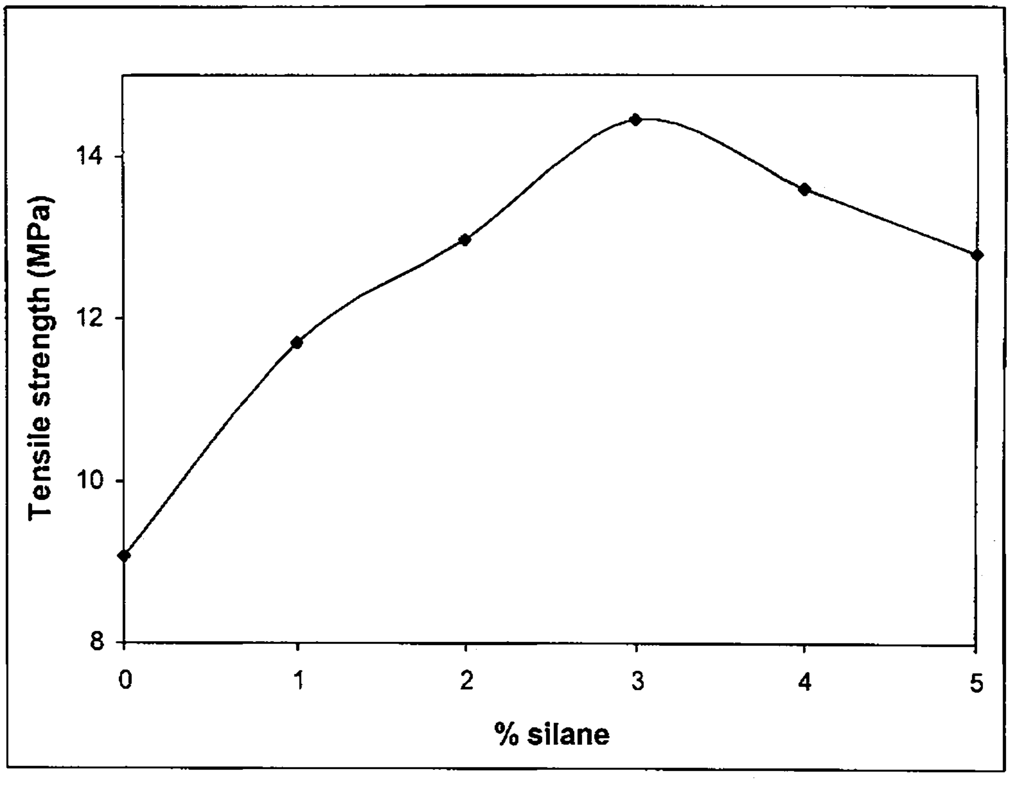

Fig 4.2 Variation of tensile strength with silane content at 190°C

The variation of stabilised torque with DCP content at 190°C and 60rpm keeping silane concentration constant at 3phr is shown in Fig 4.3. Maximum torque is obtained for 4% DCP (percent of silane level) and hence 4% DCP was chosen as the optimum concentration. The optimum percentage DCP content was also determined taking the tensile strength as the critical property. Fig 4.4 shows the variation of tensile strength with percent DCP after processing at 190°C and 60rpm. Maximum tensile strength is obtained for 4%DCP. Fig 4. 5 shows the variation of stabilised torque with rpm at 190°C for modified and unmodified LDPE. In the case of silane grafted polymer maximum torque is obtained at 60rpm. This shows that the shear rate at this rpm is optimum for silane grafting.

Fig 4. 6 shows the variation of stabilised torque with temperature at 60rpm for pure LDPE and LDPE containing 3%silane and 4%DCP with and without addition of water. In presence of water, torque increases indicating a higher crosslinking. The torque rises when the temperature of the mixer increases from 130°C to 190°C indicating progressive improvement in grafting/crosslinking after which the torque decreases. This result suggests that there is an optimum radical concentration to promote grafting efficiency, beyond which the graft content levels off and termination reactions become prominent.

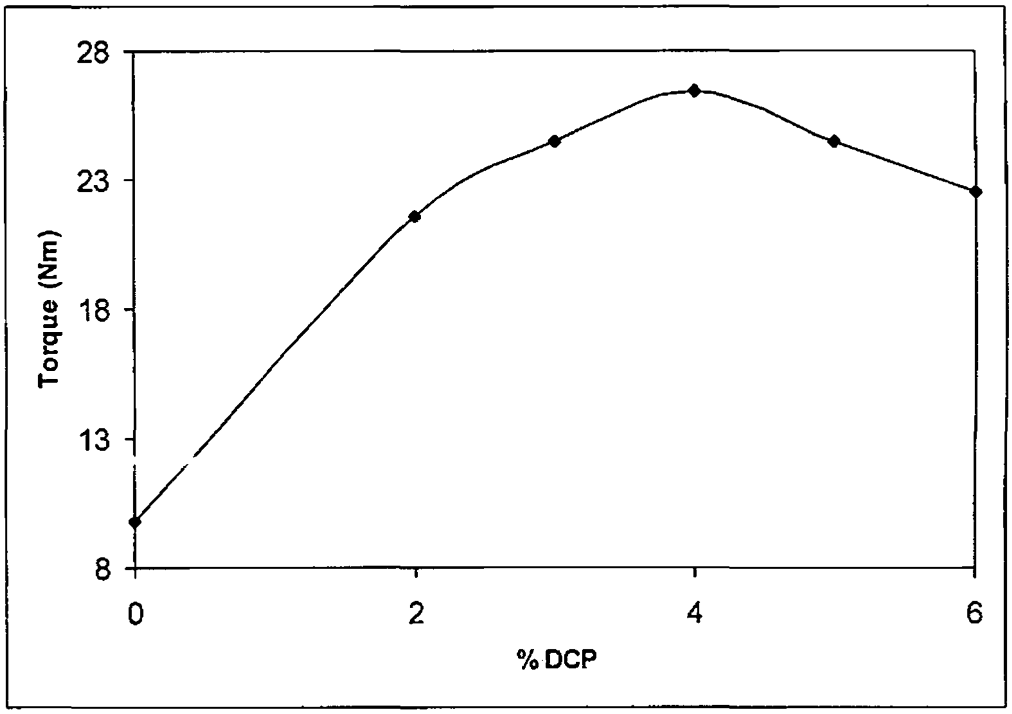

Fig 4.3 Variation of stabilised torque with DCP content at 190° C

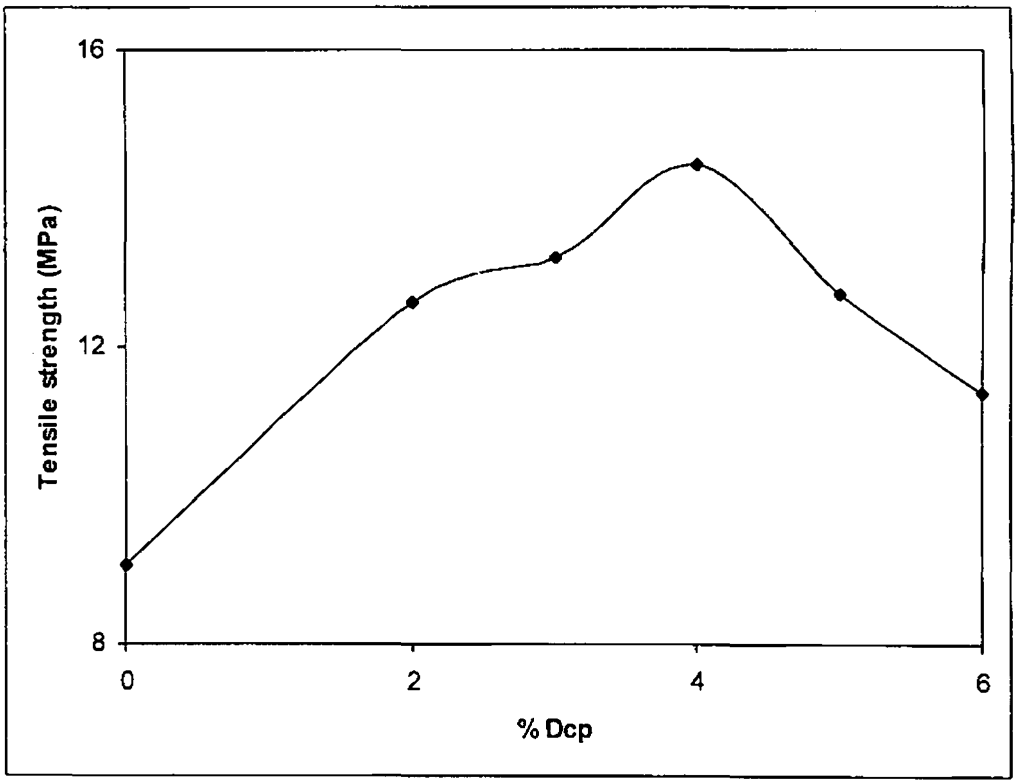

Fig 4.4 Variation of tensile strength with DCP content at 190° C

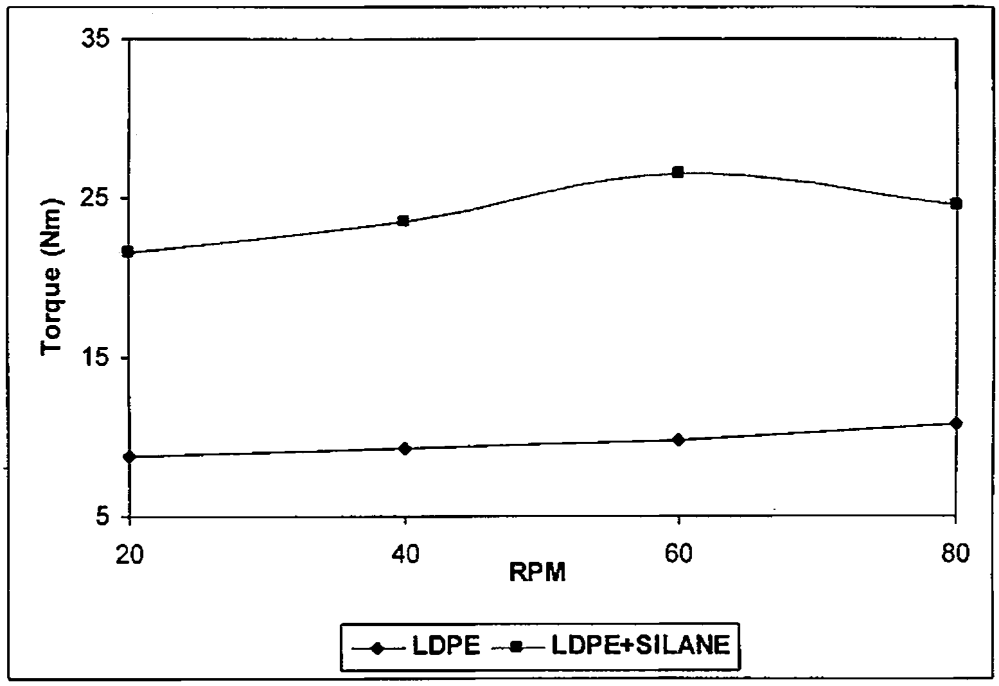

Fig 4.5 stabilised torque vs rpm at 190° C

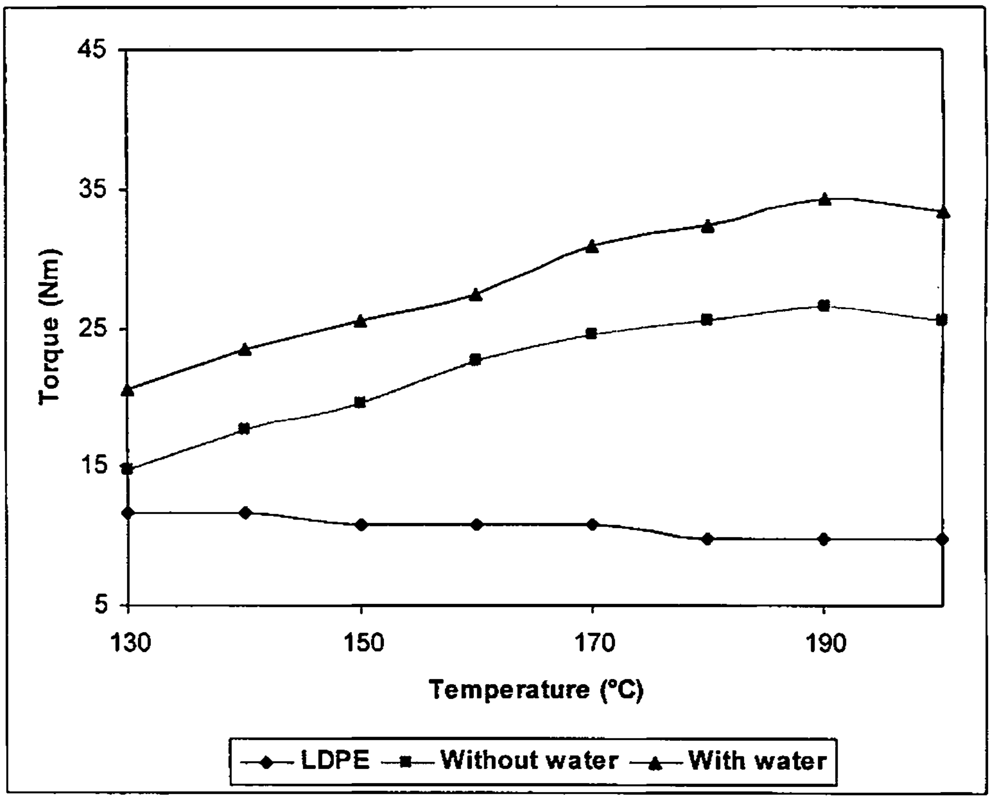

Fig 4.6 Stabilised torque vs temperature

Fig 4.7 shows the effect of residence time for the onset of grafting/crosslinking at different temperatures, at 60 rpm, measured as the time for attaining the maximum torque. It may be observed that the time for the onset of grafting/crosslinking decreases with increase in temperature as expected. The time for the onset of crosslinking at 190°C is about 1minute.

The optimum conditions obtained from the torque rheometer have been adopted for reactive extrusion. Silane grafting of polyethylene was carried out in the laboratory extruder by using the optimum temperature (190°C) and optimum concentrations of silane (3%) and DCP (4% of silane) as per the results obtained from the torque rheometer. Further, the average residence time for the extrudate was found to be about 1min. at190°C, at 60rpm. Hence 190°C and 60rpm were tried as the optimum extruder parameters for the grafting/crosslinking. To verify whether these conditions are the optimum, reactive extrusion was conducted at other temperatures and rpms also. Fig 4.8 shows the variation of tensile strength with temperature in the case of single step and double step processing. There is an increase in tensile strength on silane grafting and the maximum value is obtained at 190°C for the single stage as expected. Tensile strengths from double step processing are higher than the single step values at lower temperatures, and increases with increasing temperature, but less than the single stage rate of increase. They coincide at 180°C.

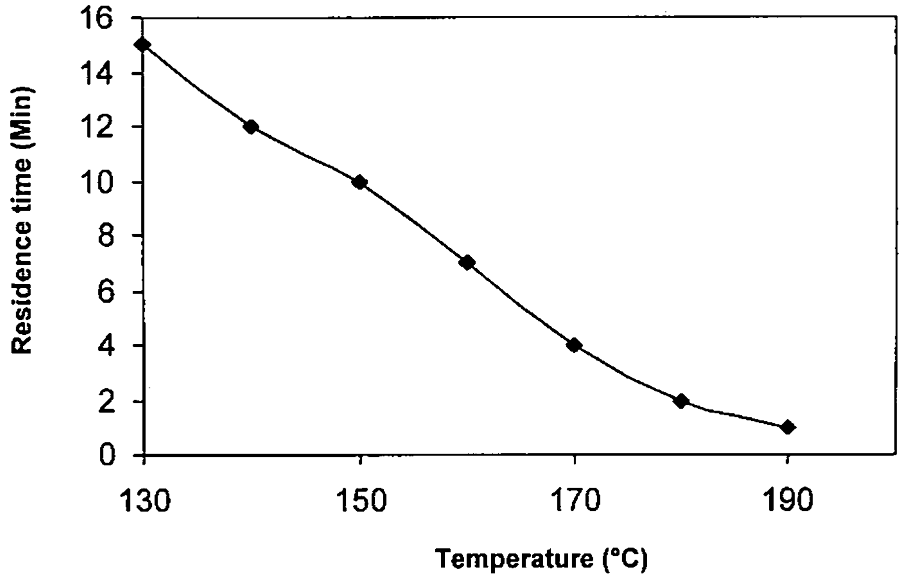

Fig 4.7 Variation of time for the onset of grafting/ crosslinking at different temperatures at 60 rpm

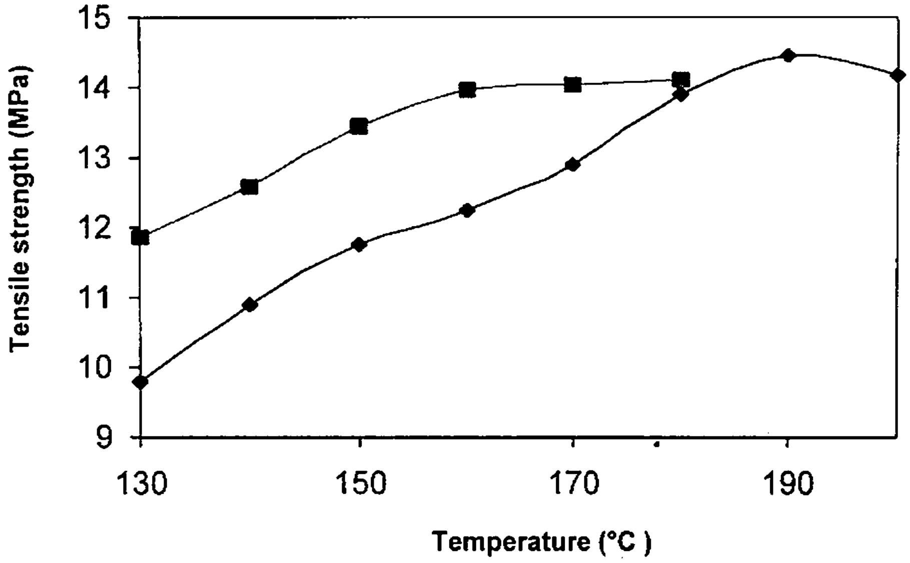

Fig 4.8 Tensile strength vs temperature

Fig 4.9 shows the variation of tensile strength with rpm for single stage and double stage processing. The tensile strength increases with rpm and a maximum value of tensile strength is obtained at 60rpm, further confirming that the shear rate/residence time at this rpm is the optimum.

Fig 4.10 shows the gel content variation with temperature for single step and double step processing. Maximum gel content is obtained at 190°C confirming the earlier observations for the other characteristics. The gel content values for double step are less than for single step. Fig 4.11 shows the variation of viscosity of unmodified and modified LDPE at different shear rates at 170°C. An increase in viscosity is obtained on silane grafting since the melt viscosity is sensitive to peroxide initiated C-C branching reactions and silane grafting. Again, this can be explained by a reduction of the chain mobility due to silane grafting and by peroxide initiated branching effects. Product obtained from single stage grafting shows higher viscosity than the one obtained from double stage process. It may be concluded that under the conditions employed, single stage grafting is sufficient. Fig 4.12 shows the thermogravimetric curves of unmodified LDPE and silane grafted LDPE. Silane grafting shows improvement in thermal stability.

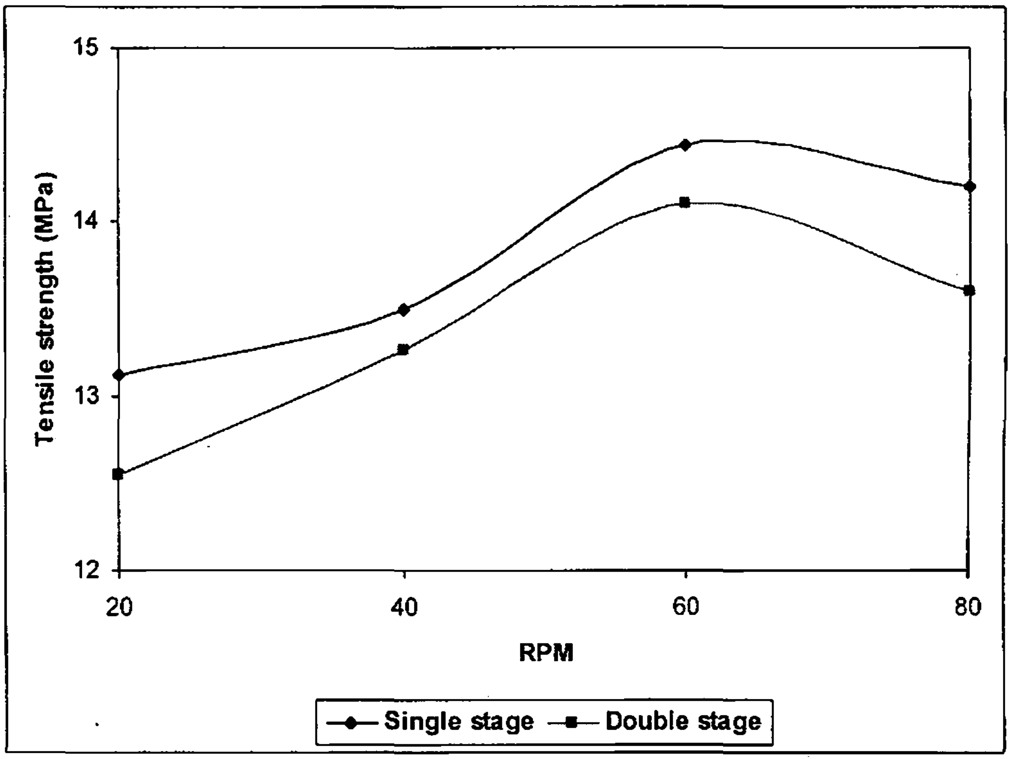

Fig 4.9 Tensile strength vs rpm

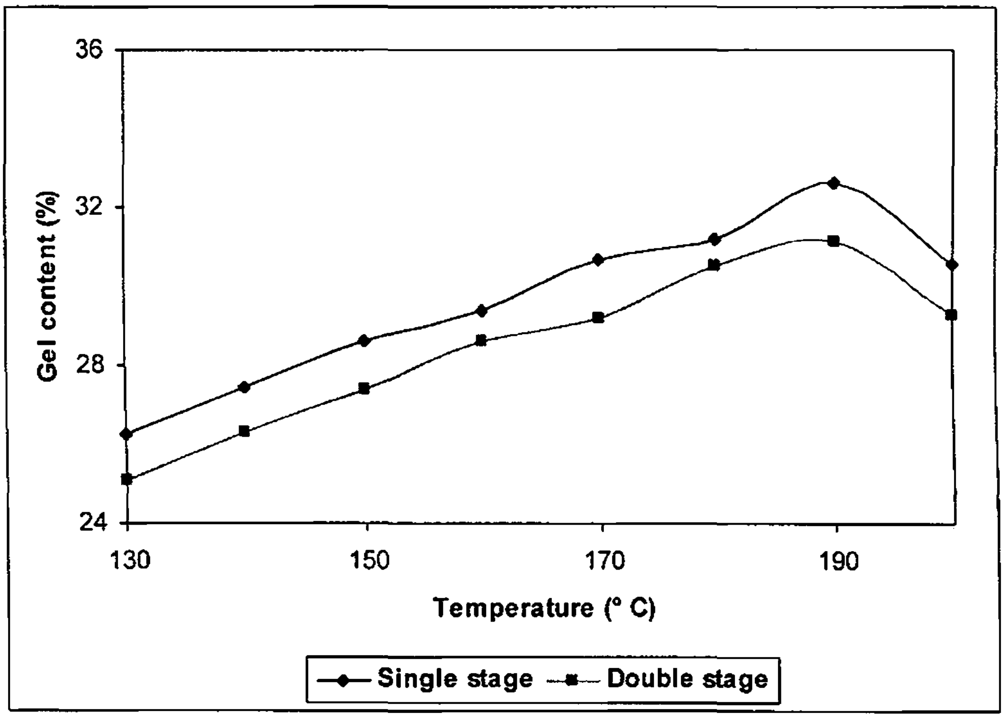

Fig 4.10 Gel content vs temperature

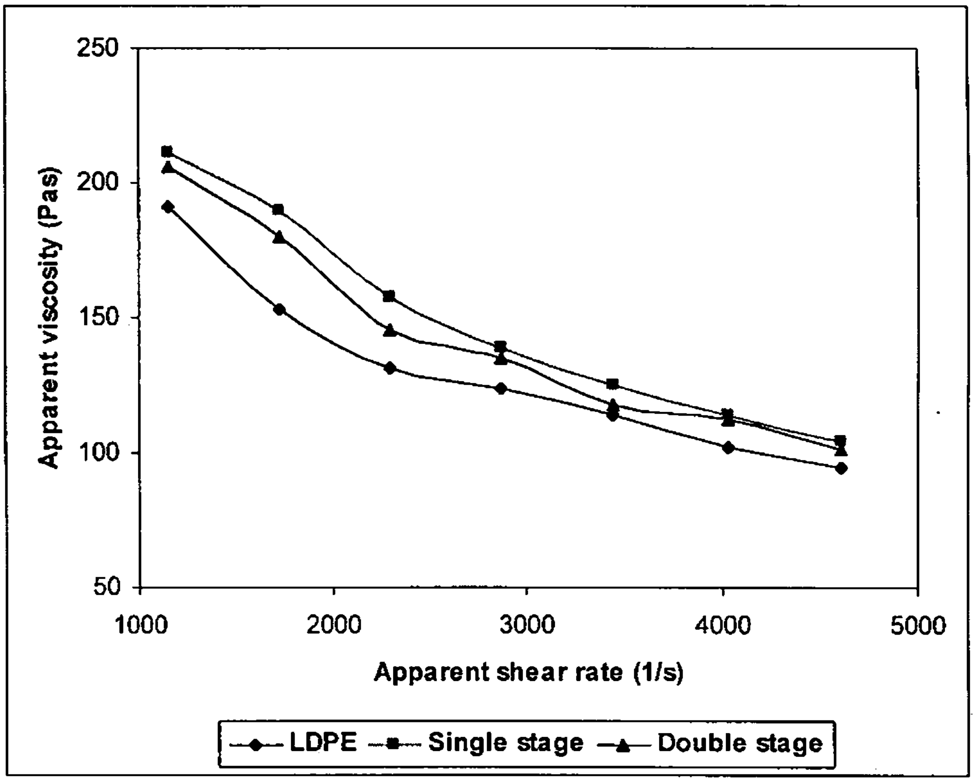

Fig 4.11 Flow curves of unmodified and modified LDPE

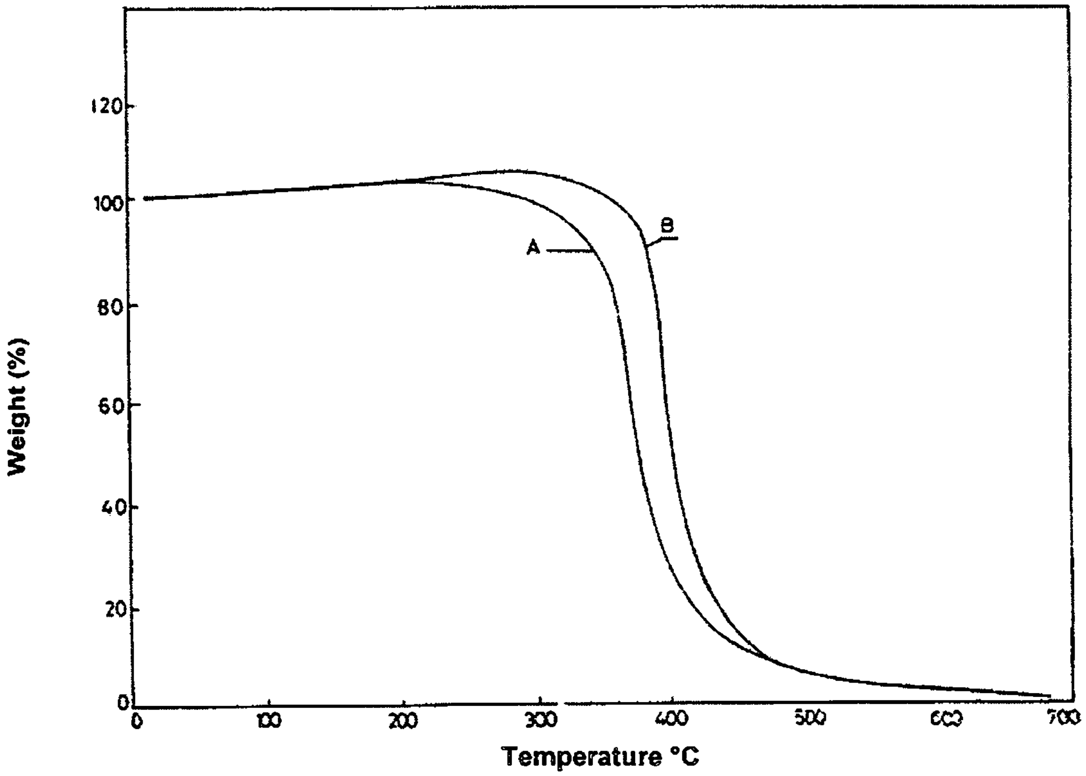

Fig 4.12 TGA curves of (A)LDPE, (B) LDPE + SILANE

From the foregoing studies on silane grafting of LDPE under the conditions employed, it was found that single step grafting is sufficient since the double step process does not show much improvement in properties. Further, silane grafting was done on LLDPE and LDPE/LLDPE blend and the optimum conditions for silane grafting were determined.

Silane grafting of LDPE, LLDPE and their blend

On addition of polymer, DCP and silane to the Brabender mixer, the torque rises due to melting/crosslinking/grafting, reaches a maximum value and then stabilises at a lower value. The grafting/crosslinking may be estimated either from the maximum torque or the stabilised torque. Fig 4.13 shows the variation of stabilised torque with silane content in the case of silane grafted LDPE, LLDPE and LDPE/LLDPE blend, at 190°C and 60rpm in the torque rheometer keeping the level of DCP content at 4% of the silane level. An initial increase in torque is observed on silane grafting/crosslinking as expected. Polyethylenes reacted with the oraganosilane in the compounding extruder gives silane grafted polymer containing Si-OR groups. Water molecules cause hydrolysis of Si-OR groups and the generated OH groups then condense with adjacent Si-OH groups to main Si-O-Si bonds. The polymer is thus crosslinked. The highest value of stabilised torque is obtained for 3% silane, which shows that under the conditions maintained, the maximum extent of grafting/crosslinking occurred at this concentration of silane; hence 3% silane was chosen for further trials.

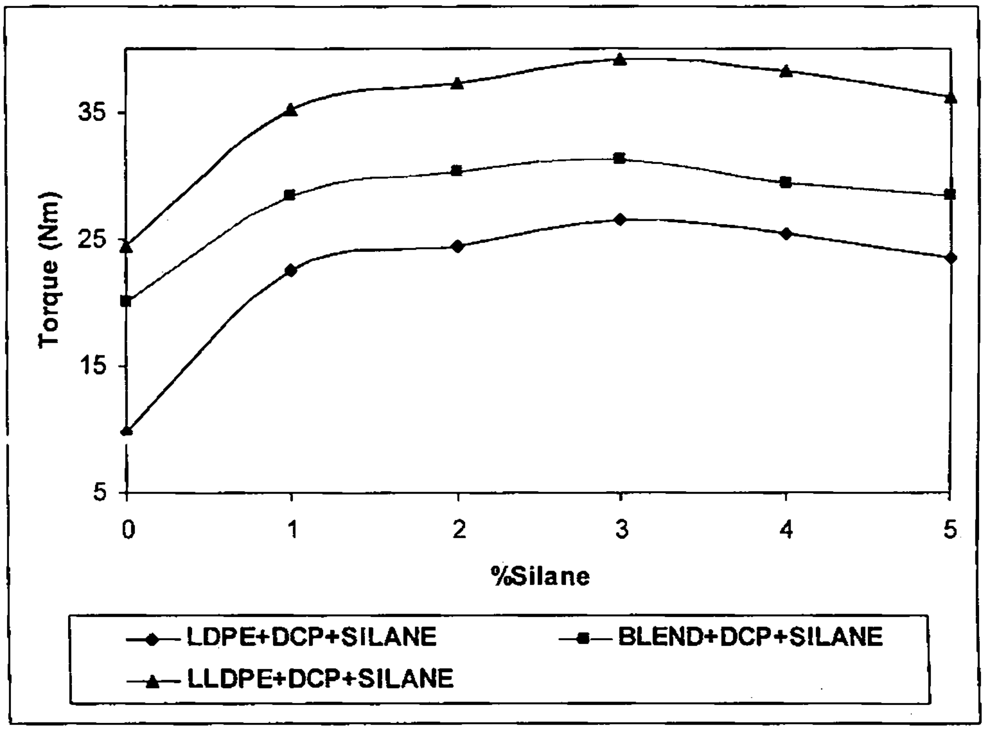

Fig 4.13 Variation of stabilised torque with silane content at 190 ° C

The optimum percentage of silane content was also verified from the variation of tensile strength of the samples. The variation of tensile strength for LDPE, LLDPE and their blend, with percentage silane after processing at 190°C at 60rpm is shown in fig 4.14. Maximum tensile strength is obtained for 3% silane.

The variation of stabilised torque for LDPE, LLDPE and their blend, with DCP content at 190°C and 60rpm keeping silane concentration constant at 3phr is shown in fig 4.15. Maximum torque is obtained for 4% DCP (percent of silane level) in all the cases and hence 4% DCP was chosen as the optimum concentration. The optimum percentage DCP content was also determined taking the tensile strength as the critical property.

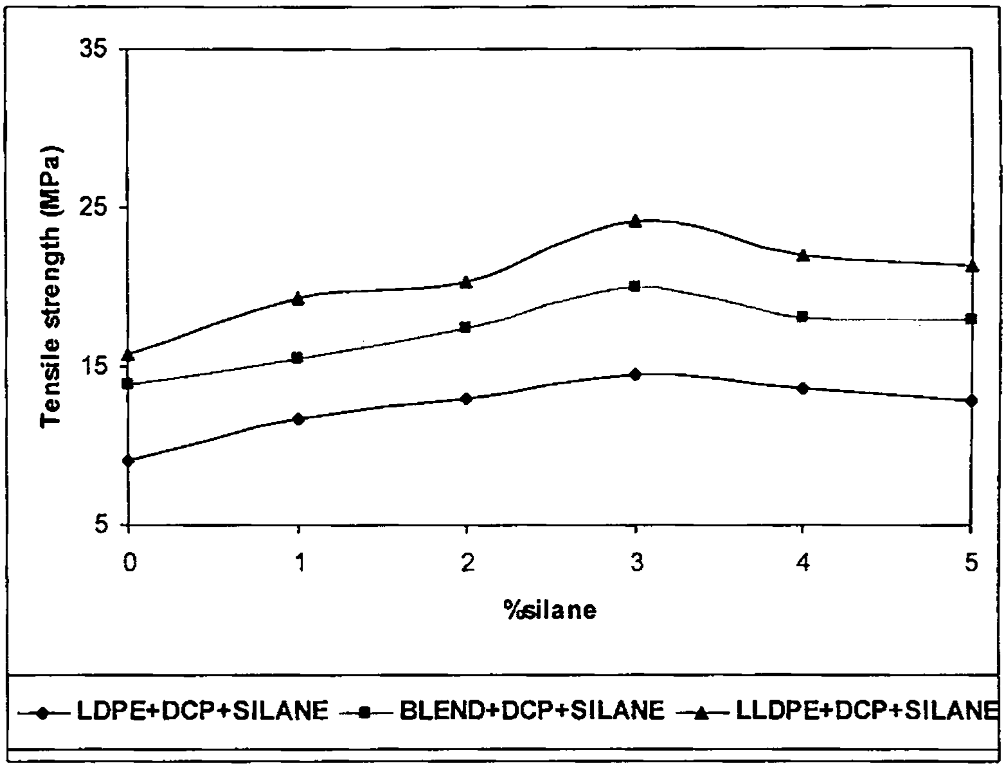

Fig 4.14 Variation of tensile strength with DCP content at 190° C

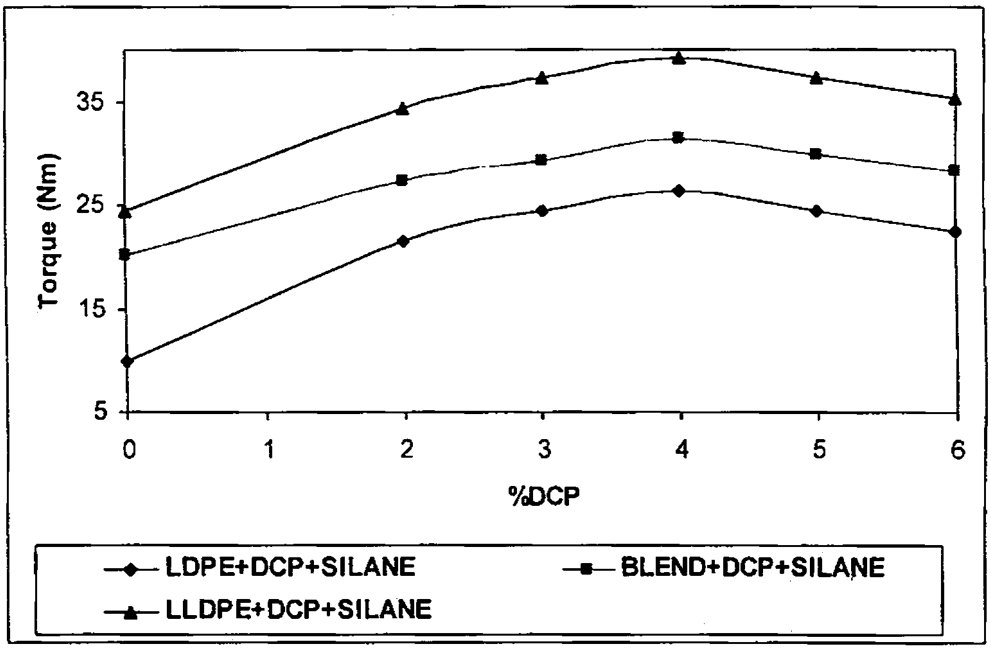

Fig 4.15 Variation of stabilised torque with DCP content at 190° C

Fig 4.16 shows the variation of tensile strength for LDPE, LLDPE and their blend with percent DCP after processing at 190°C and 60rpm. Maximum tensile strength is obtained for 4%DCP in all the cases. The increase in tensile strength is more pronounced in the case of LLDPE. Fig 4.17 shows the variation of stabilised torque with rpm at 190°C for modified (3% silane and 4%DCP) LDPE, LLDPE and their blend. In all the cases maximum torque is obtained at 60rpm. This shows that the shear rate at this rpm is optimum for silane grafting.

Fig 4.18 shows the variation of torque with temperature at 60rpm for unmodified and modified LDPE, LLDPE and their blend containing 3%silane and 4%DCP. For pure polymers, the torque is almost parellel to the x-axis as expected. In the case of silane grafted polymers the torque rises when the temperature of the mixer increases from 130°C to 190°C indicating progressive improvement in grafting/crosslinking after which the torque decreases. This result suggests that there is an optimum radical concentration to promote grafting efficiency, beyond which the graft content levels off and the termination reactions become prominent.

The optimum conditions obtained from the torque rheometer have been adopted for reactive extrusion. Silane grafting of polyethylenes was carried out in the laboratory extruder by using the optimum temperature (190°C) and optimum concentrations of silane (3%) and DCP (4% of silane) as per the results obtained from the torque rheometer. Hence 190°C and 60rpm were tried as the optimum extruder parameters for the grafting/crosslinking. To verify whether these conditions are the optimum, reactive extrusion was conducted at other temperatures and rpms also.

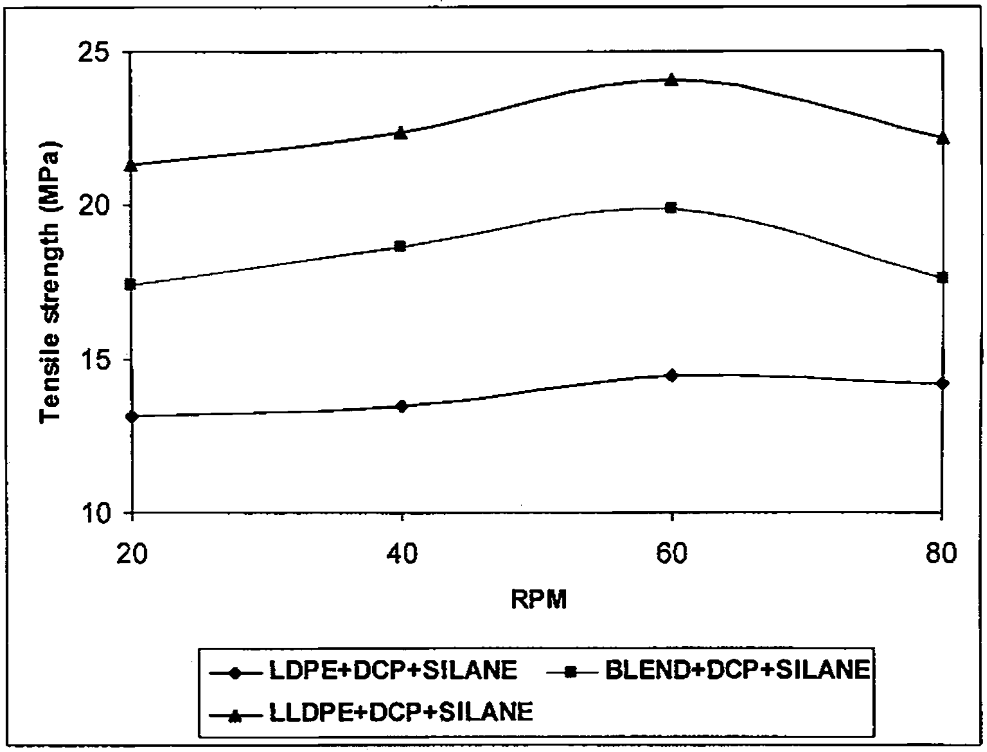

Fig 4.16 Variation of tensile strength with DCP content at 190° C

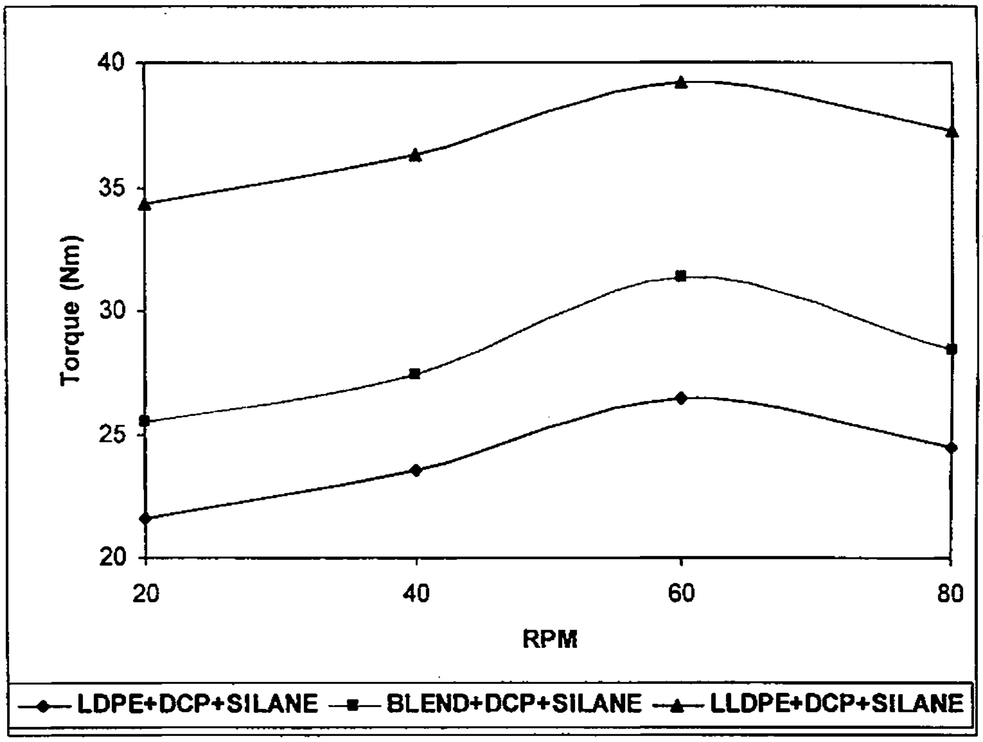

Fig 4.17 Variation of stabilised torque with rpm at 190° C

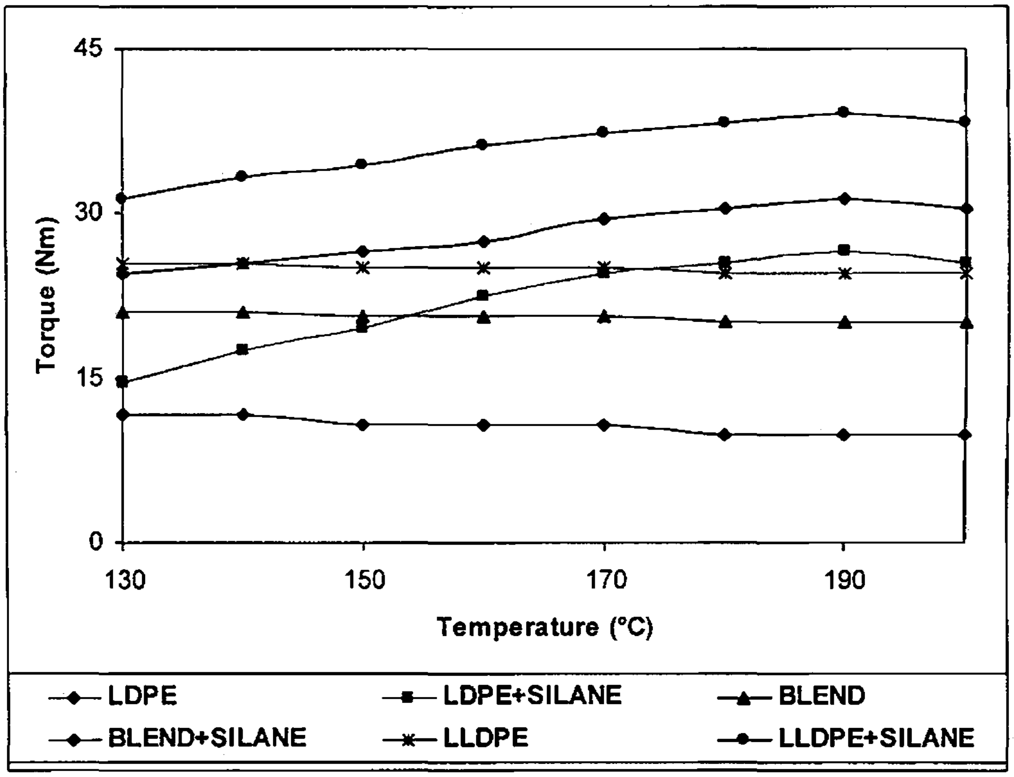

Fig 4.18 Variation of torque with temperature at 60 rpm

Fig 4.19 shows the variation of tensile strength with temperature at 60 rpm in the case of unmodified and silane grafted LDPE, LLDPE and their blend containing 3% silane and 4% DCP. There is an increase in tensile strength on silane grafting and the maximum value is obtained at 190°C, in all the cases, as expected. Fig 4.20 shows the variation of tensile strength with rpm, at 190°C for silane grafted LDPE, LLDPE and their blend. The tensile strength increases with rpm and a maximum value of tensile strength is obtained at 60rpm,in all the cases, further confirming that the shear rate/residence time at this rpm is the optimum.

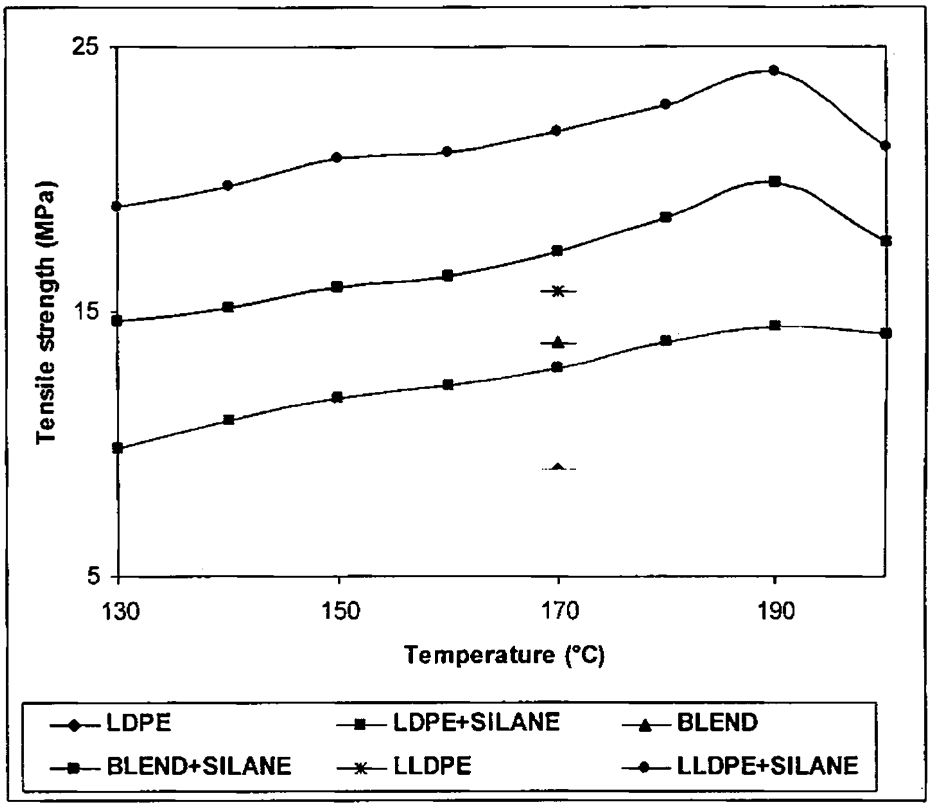

Fig 4.19 Tensile strength vs temperature at 60 rpm

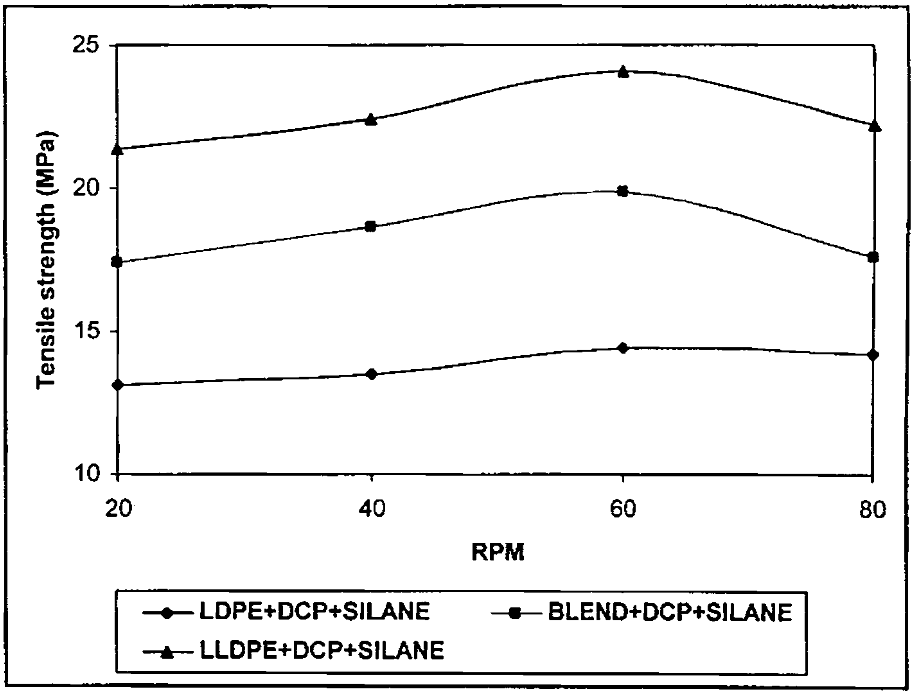

Fig 4.20 Tensile strength vs rpm at 190° C

Fig 4.21 shows the variation of elongation at break (EB) with temperature, in the case of unmodified and silane grafted LDPE, LLDPE and their blend. It is found that the EB values decreased on silane grafting and crosslinking as expected.

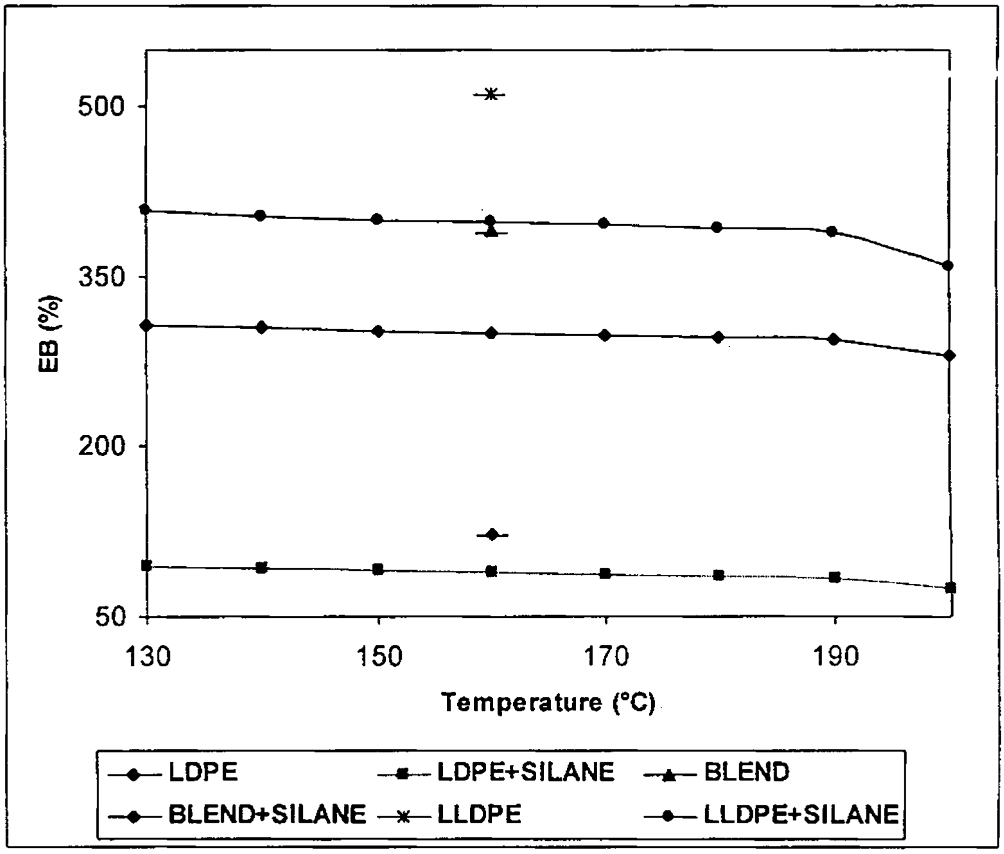

Fig 4.21Variation of EB with temperature

Fig 4.22 shows the variation of EB with percent silane in the case of silane grafted LDPE, LLDPE and their blend at 190° C. On silane grafting, EB values are found to be decreased. Fig 4.23 shows the variation of EB with DCP content in the case of silane grafted LDPE, LLDPE and their blend at 190° C. As the percent of DCP increases, EB values are found to be decreased.

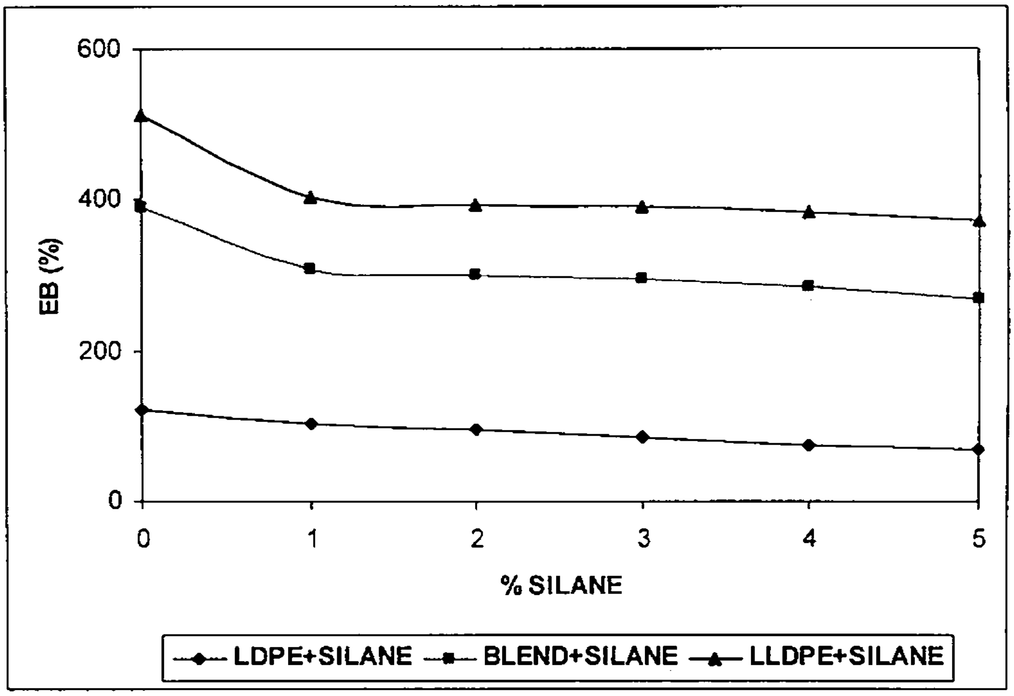

Fig 4.22 Variation of EB with silane content at 190° C

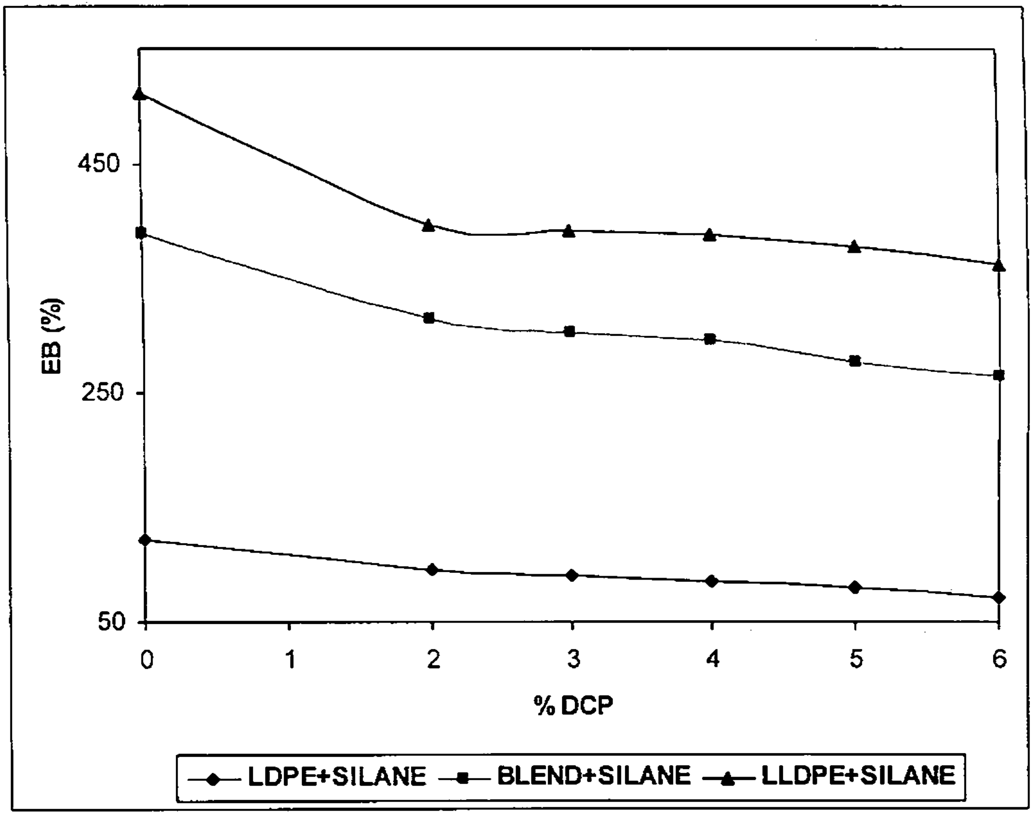

Fig 4.23 Variation of EB with DCP content at 190° C

The silane grafting on the polymer chains was confirmed by FTIR spectra. The FTIR spectra of unmodified LDPE, LLDPE, silane grafted LDPE, LDPE/LLDPE blend and LLDPE are shown in figures 4.24-28.The IR spectra of silane grafted polymers show additional absorption band at 1081 cm^{-1} which is characteristic of the Si-O-Si bonds. Fig 4.29 shows the IR spectrum of silane grafted LDPE with addition of water. The bands are much pronounced in this spectrum. The absorption band at 2020 cm^{-1} is characteristic of Si-C bond.

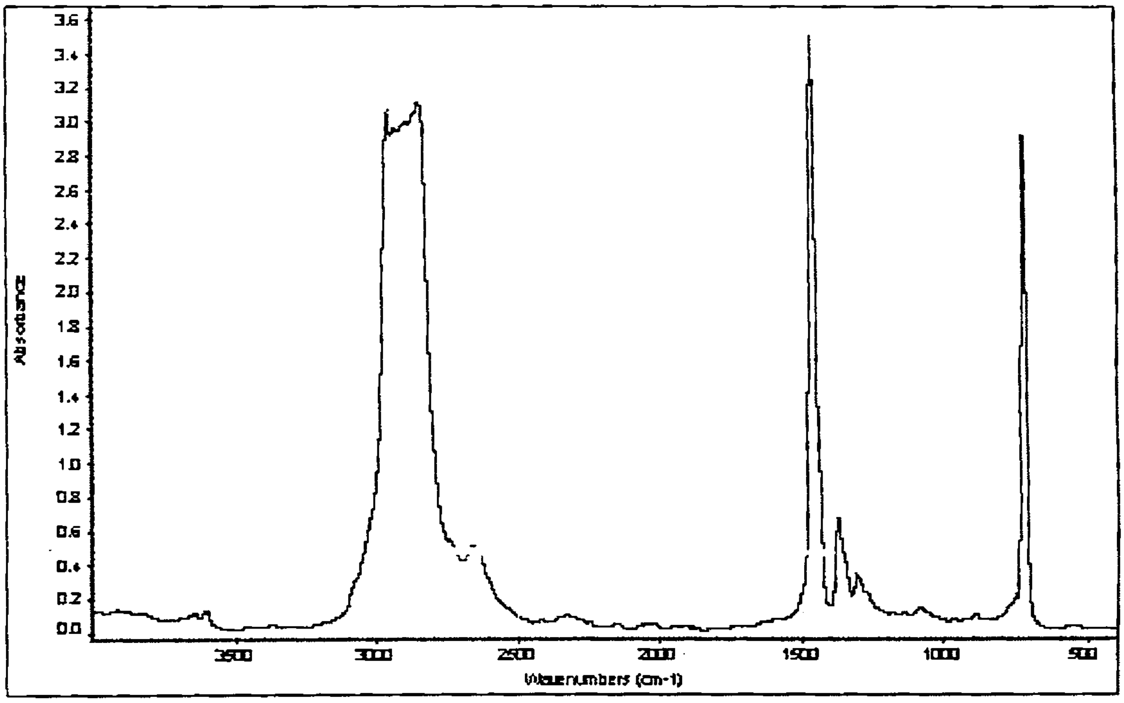

Fig 4.24 FTIR spectrum of LDPE

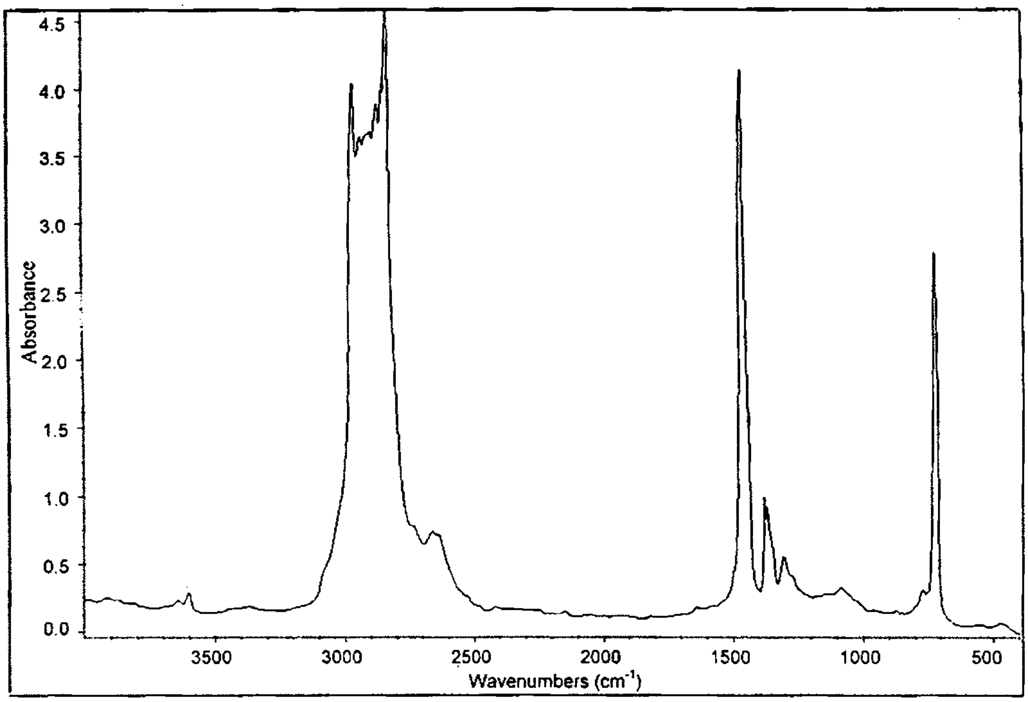

Fig 4.25 FTIR spectrum of LLDPE

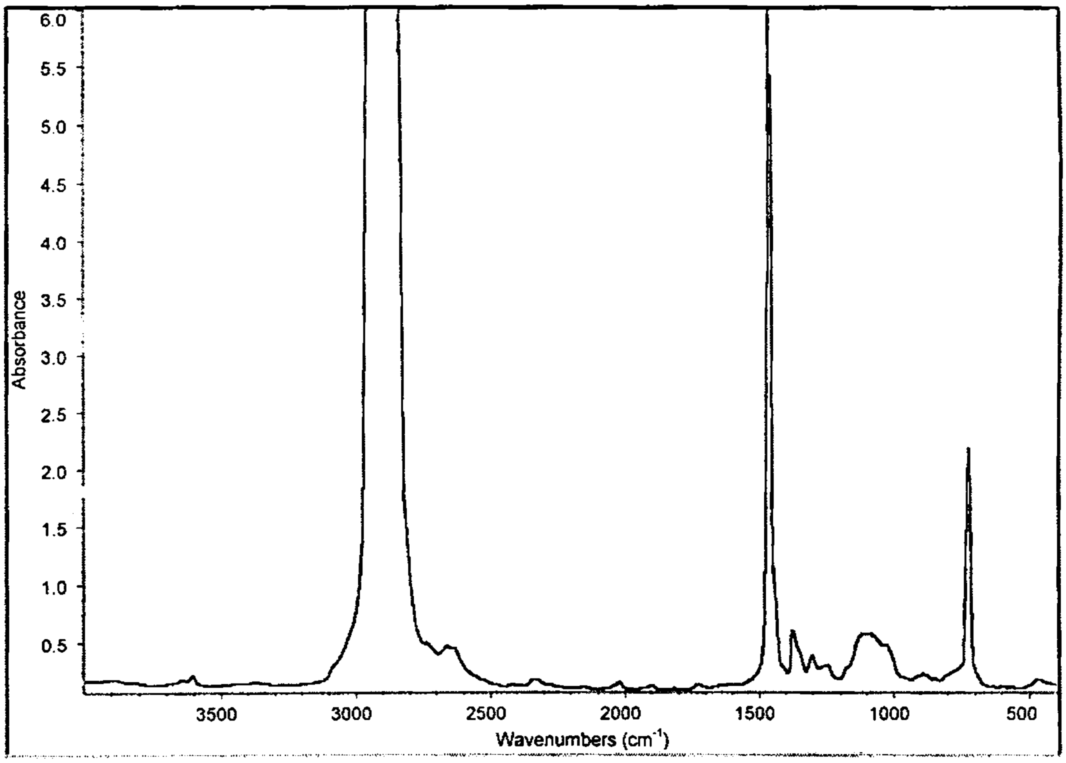

Fig 4.26 FTIR spectrum of silane grafted LDPE

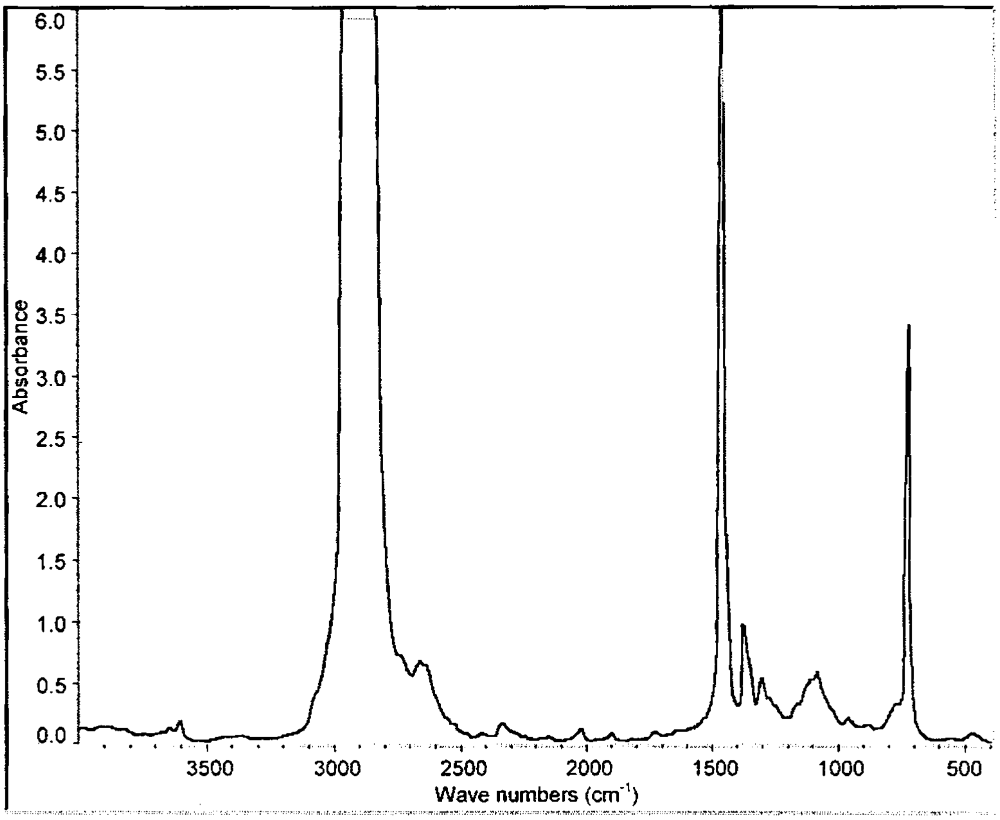

Fig 4.27 FTIR spectrum of silane grafted blend

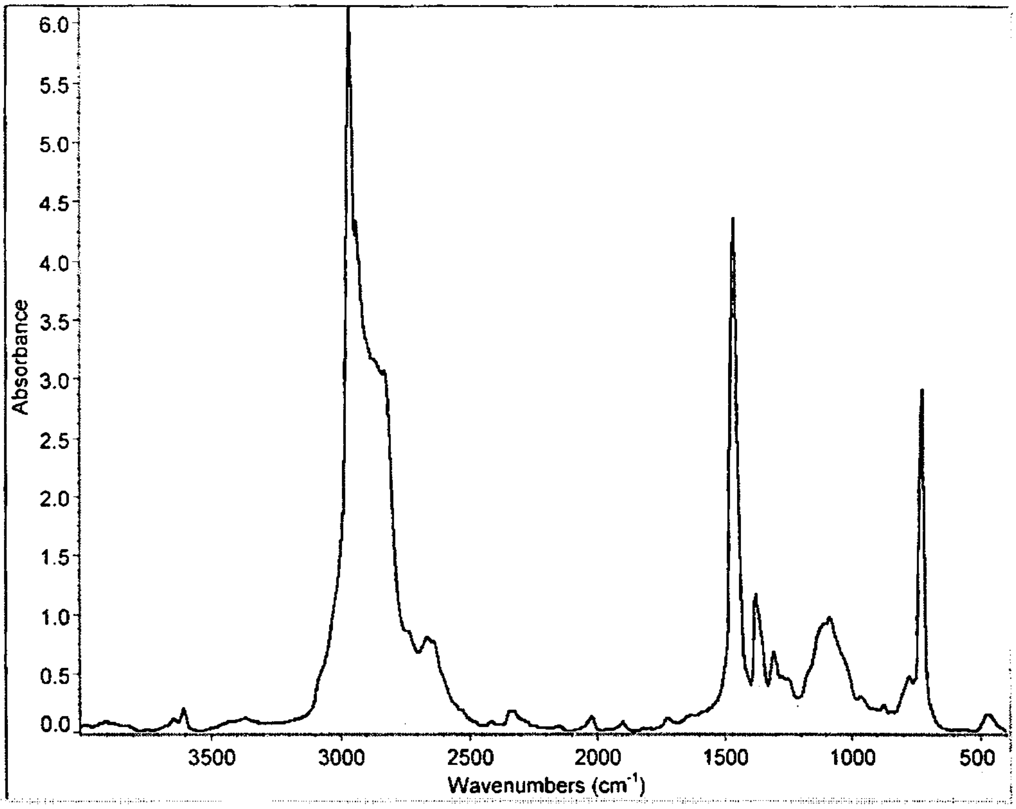

Fig 4.28 FTIR spectrum of silane grafted LLDPE

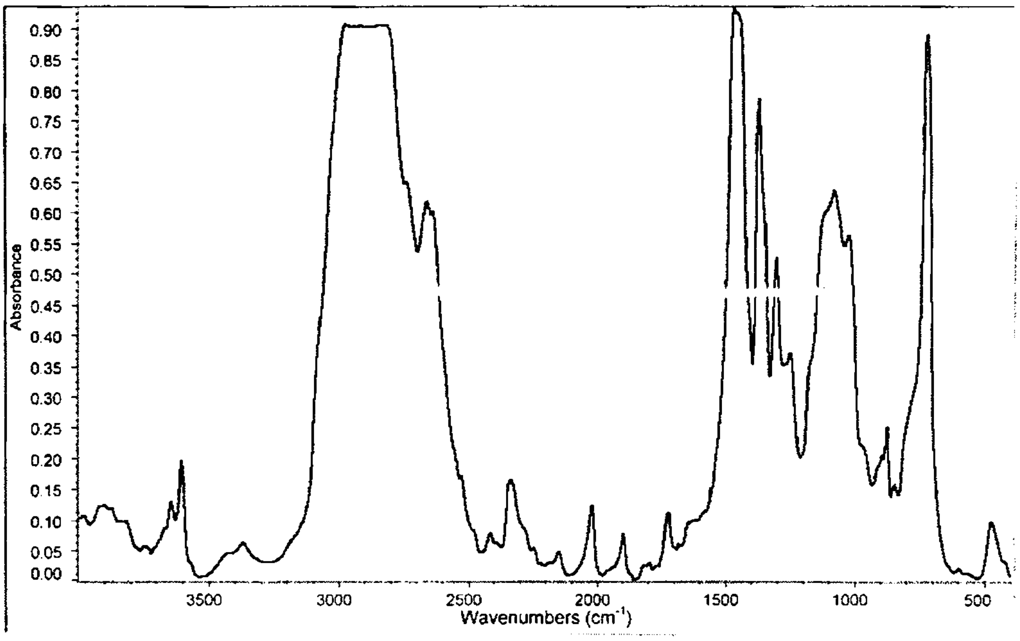

Fig 4.29 FTIR spectrum of silane grafted LDPE with addition of water

Fig 4.30 shows the variation of viscosity at different shear rates, at 170°C, in the case of LDPE, silane grafted LDPE, LLDPE and silane grafted LLDPE. An increase in viscosity is obtained on silane grafting as expected. The increase in viscosity is due to the introduction of Si-O-Si links between the chains. However, the increase in viscosity is only marginal and hence may not affect the processability. Fig 4.31 shows the variation of viscosity at different shear rates, at 170° C, in the case of blend, and silane grafted blend. Here also silane grafting shows increase in viscosity.

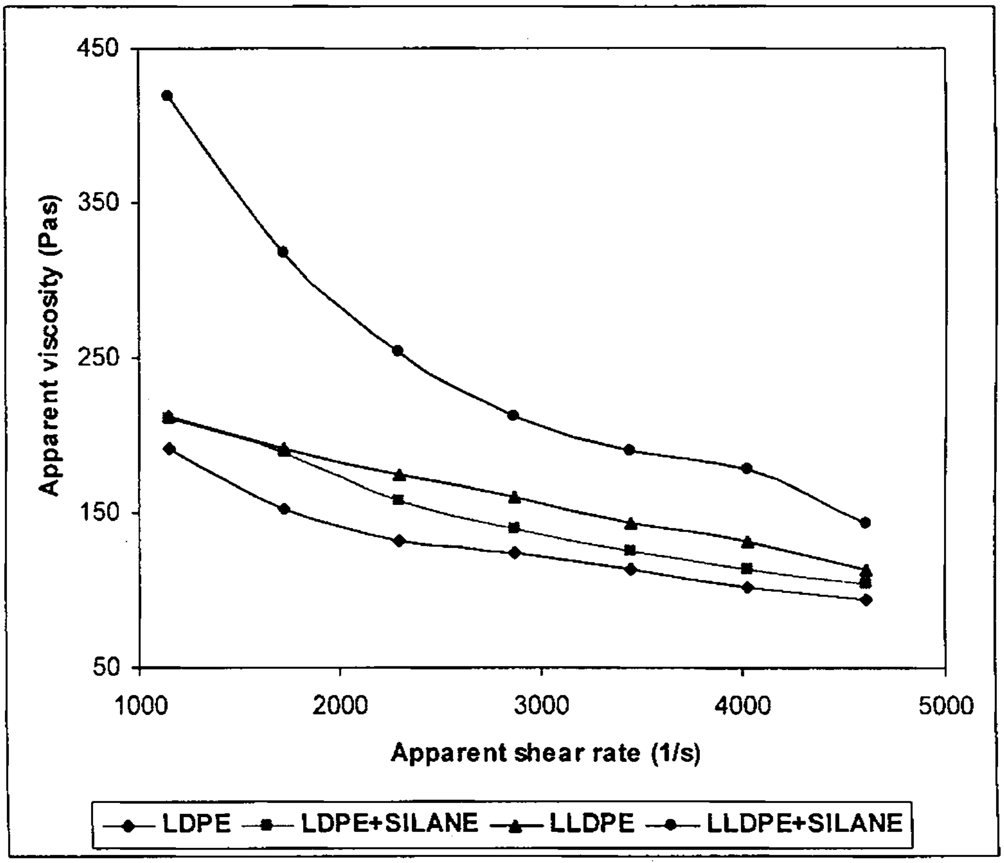

Fig 4.30 Flow curves of unmodified and modified LDPE and LLDPE

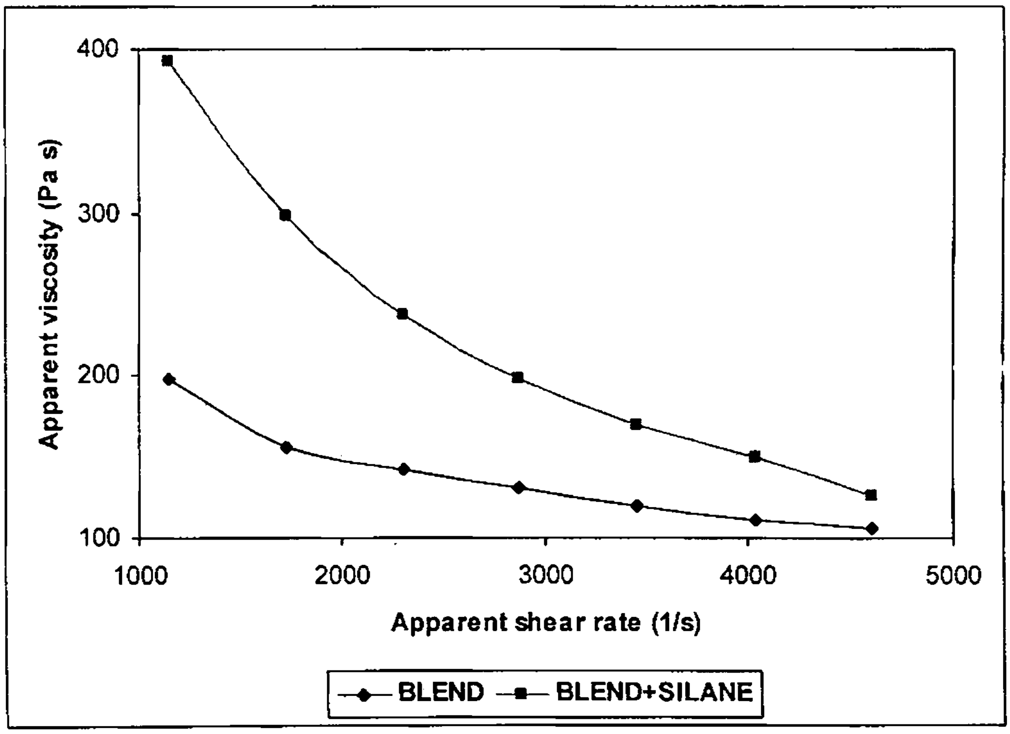

Fig 4.31 Flow curves of unmodified and modified blend

Figs 4.32-34 show the extrudate swell ratio vs shear rate of unmodified and silane grafted LDPE, LLDPE and their blend. It can be seen from the figures that the extrudate swell ratio (De/D) increases with the shear rate. This is expected because the recoverable elastic energy built up in the melt while flowing in the capillary increases as shear rate is increased. The figures also reveal that the extrudate swell ratio increases on silane grafting in all the cases. The increase in swell ratio may be due to crosslinking of the polymer and subsequent reduction in crystallinity.

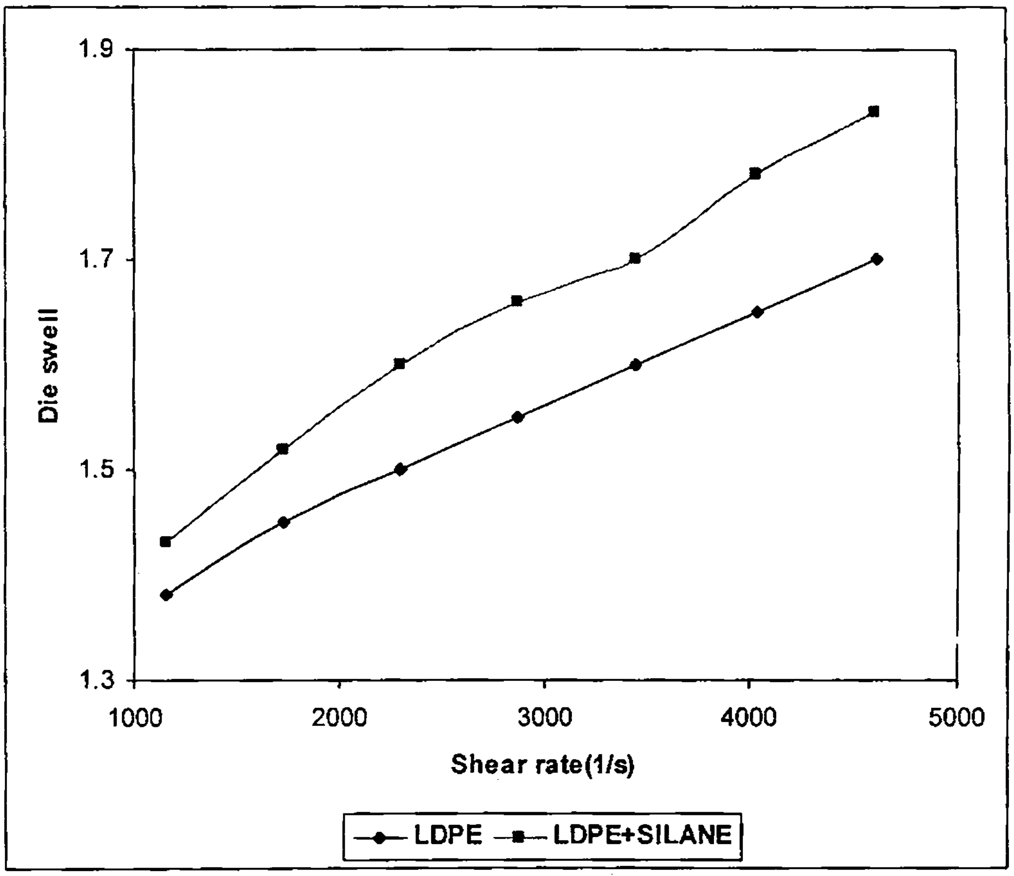

Fig 4.32 Extrudate swell ratio vs shear rate

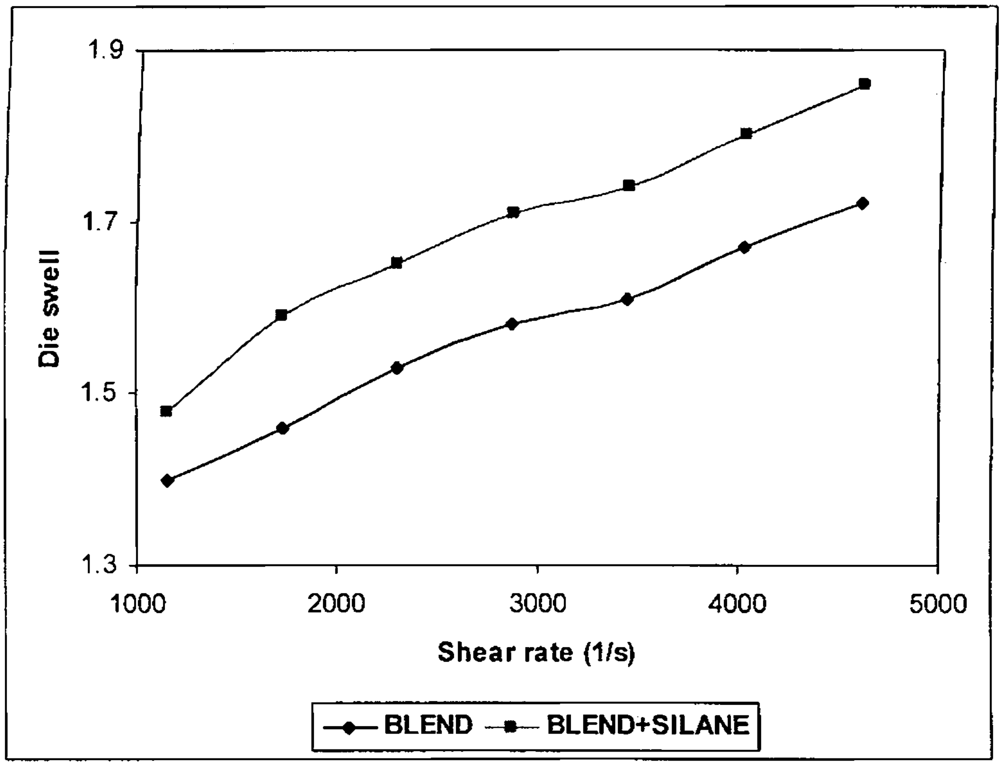

Fig 4.33 Extrudate swell ratio vs shear rate

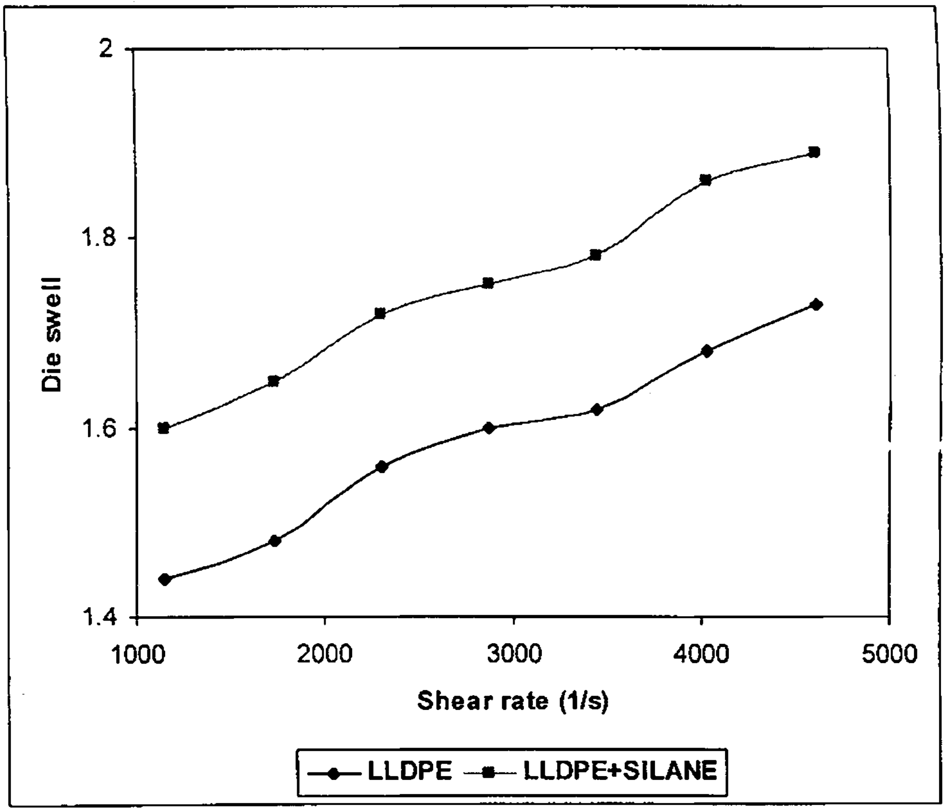

Fig 4.34 Extrudate swell ratio vs shear rate

Fig 4.35-37 show the variation of viscosity with shear rate at different temperatures for silane grafted LDPE, LLDPE and their blend. The viscosity decreases with increase in temperature as expected.

The variation of log viscosity with reciprocal of absolute temperature at various shear rates of the unmodified and silane grafted LDPE, LLDPE and their blend are shown in figures 4.38-40.The slope of these lines is proportional to the activation energy for viscous flow.

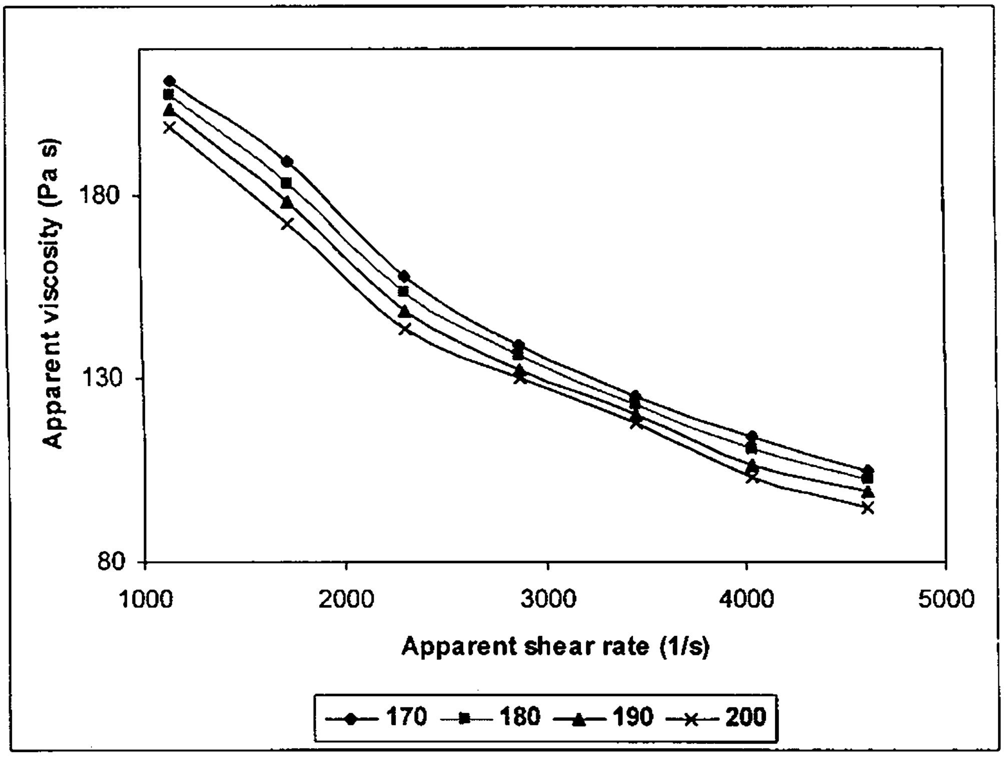

Fig 4.35 Variation of viscosity with shear rate at different temperatures for silane grafted LDPE

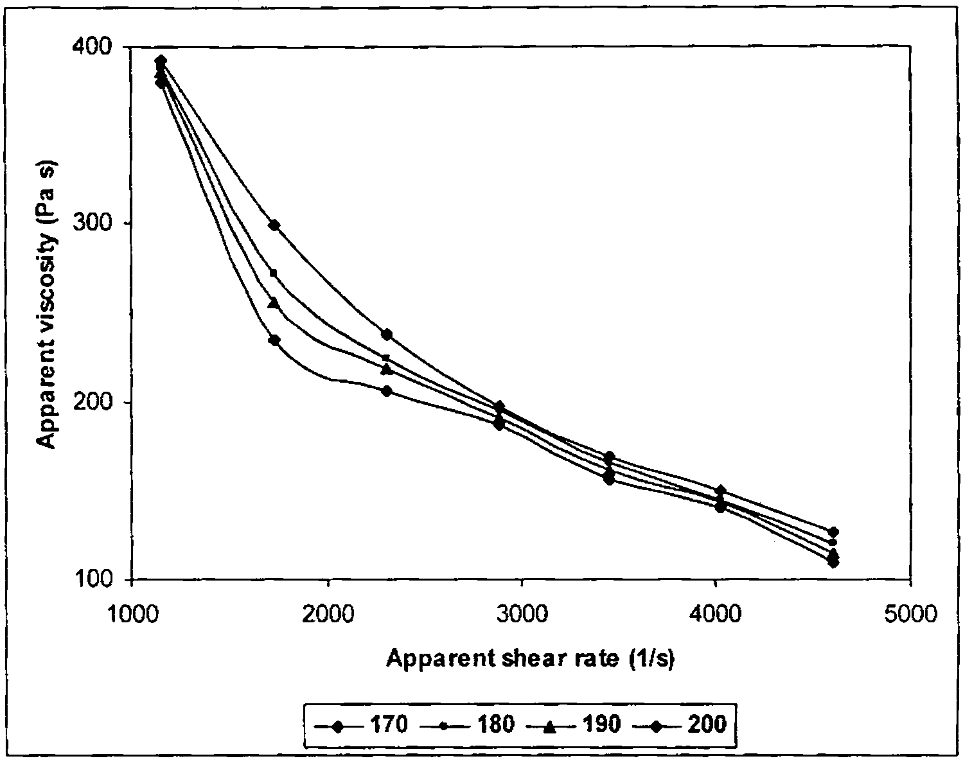

Fig 4.36 Variation of viscosity with shear rate at different temperatures for silane grafted blend

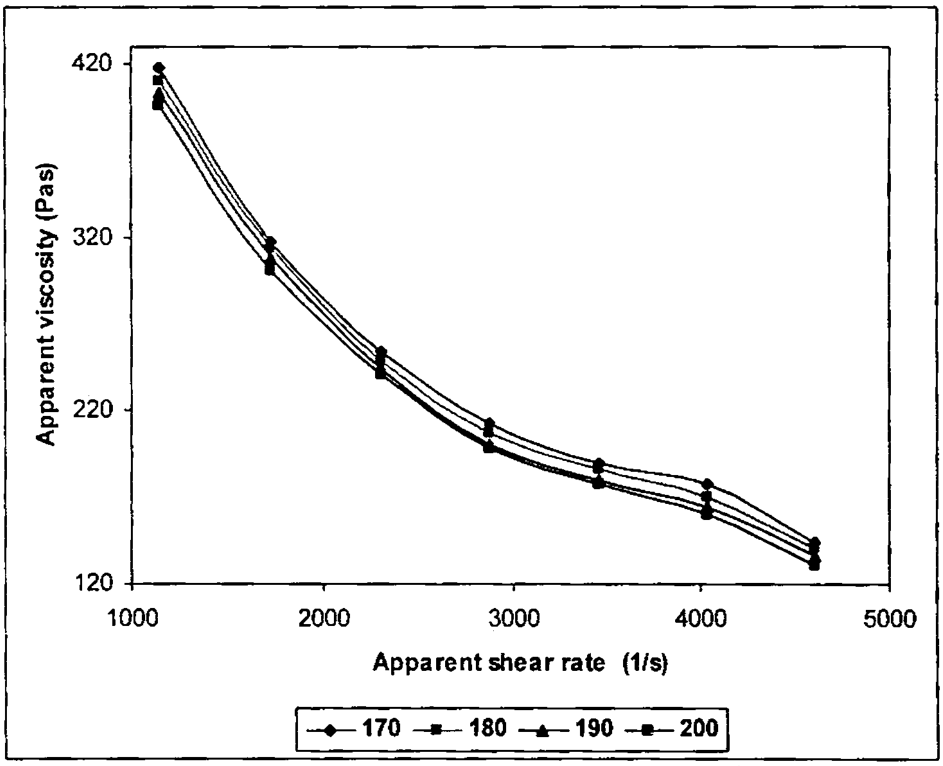

Fig 4.37 Variation of viscosity with shear rate at different temperatures for silane grafted LLDPE

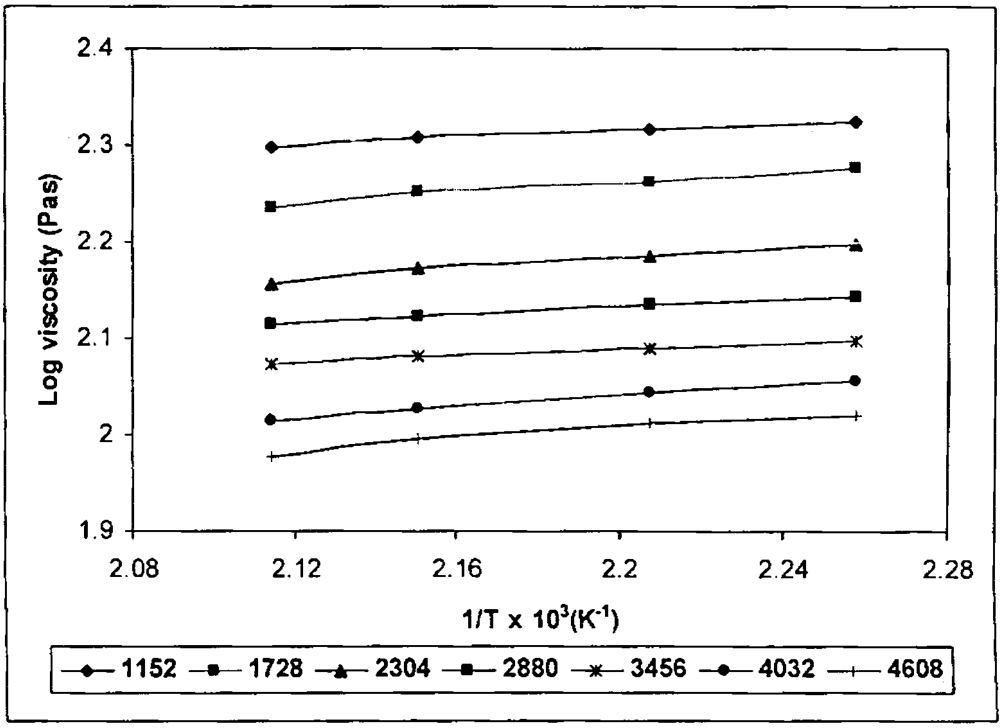

Fig 4.38Temperature dependence of viscosity of silane grafted LDPE

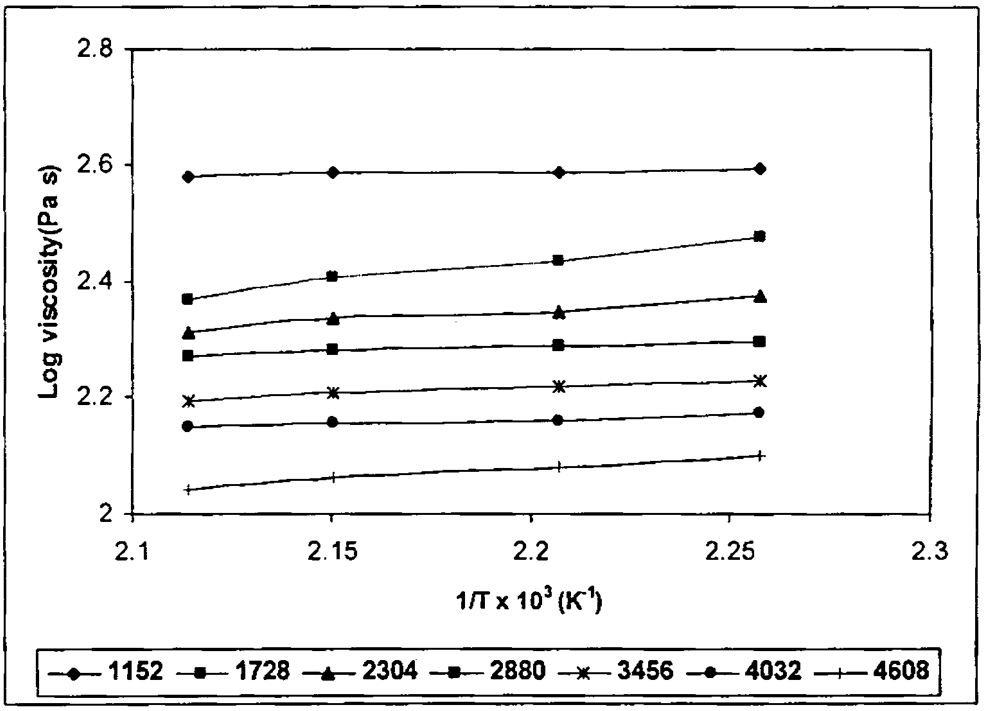

Fig 4.39 Temperature dependence of viscosity of silane grafted blend

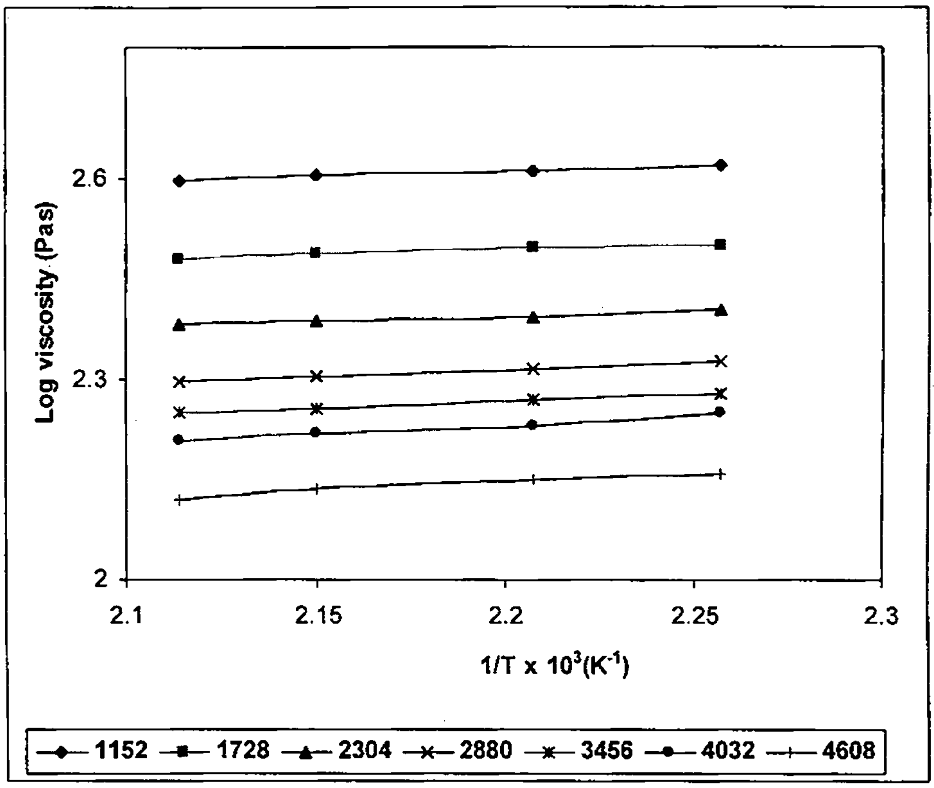

Fig 4.40 Temperature dependence of viscosity of silane grafted LLDPE

The activation energy values are shown in table 4.1. The silane grafted polymers show marginally higher activation energy as expected. The difference in activation energy with crosslinking gradually increases with LLDPE content. This is likely to be due to the higher crosslink density in LLDPE than in LDPE.

Table.4.1 Variaton of activation energy of the polymers at different shear rates.

Shear rate (1/s)	Activation energy (kJ/mol)					
	LDPE	LDPE+ SILANE	BLEND	BLEND+ SILANE	LLDPE	LLDPE + SILANE
1152	0.89	1.22	0.92	1.24	1.04	1.47
1728	0.92	1.50	1.05	1.39	1.18	1.68
2304	1.34	1.72	1.28	1.80	1.48	1.90
2880	1.60	1.92	2.15	2.56	2.26	2.88
3456	1.81	2.75	2.56	3.27	2.59	3.10
4032	2.23	3.28	2.97	3.38	3.12	3.85
4608	3.35	3.91	3.35	5.79	3.46	3.99

The thermogravimetric curves of unmodified and silane grafted LDPE and LLDPE are shown in fig 4.41. Silane grafting shows improvement in thermal stability as expected.

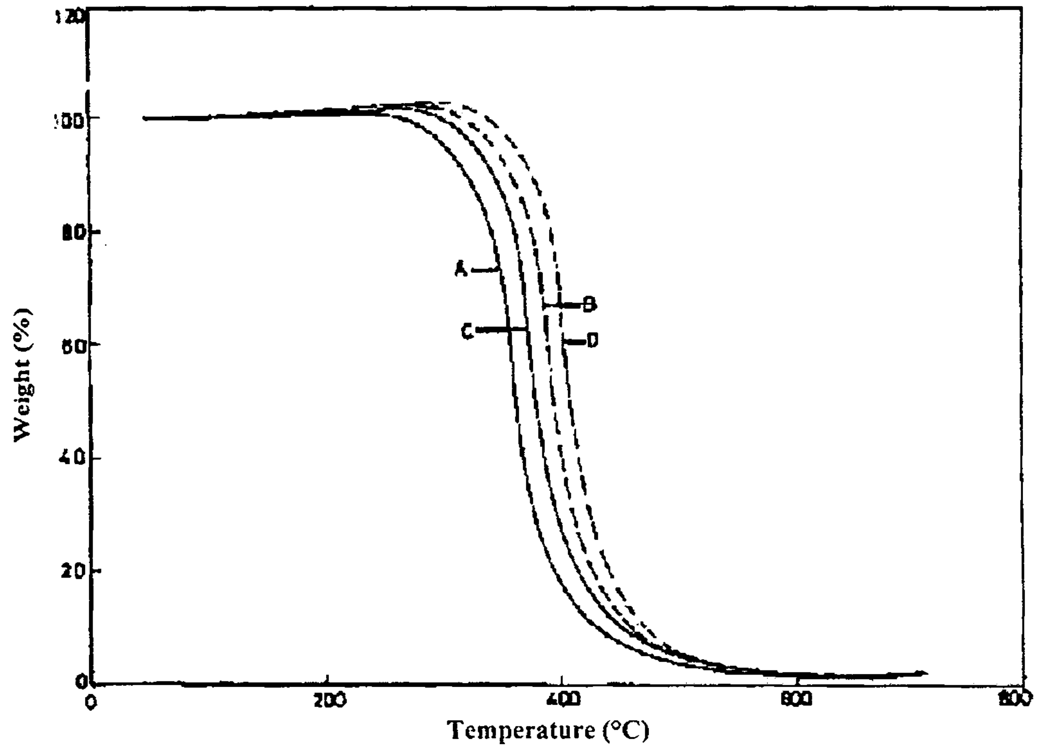

FIG 4.41 TGACURVES OF (A) LDPE, (B) LDPE + DCP + SILANE, (C) LLDPE, (D) LLDPE + DCP + SILANE

The thermogravimetric curves of unmodified and silane grafted LDPE/LLDPE blend are shown in fig4.42. Silane grafted LLDPE and LDPE/LLDPE blend shows better thermal stability than silane grafted LDPE.

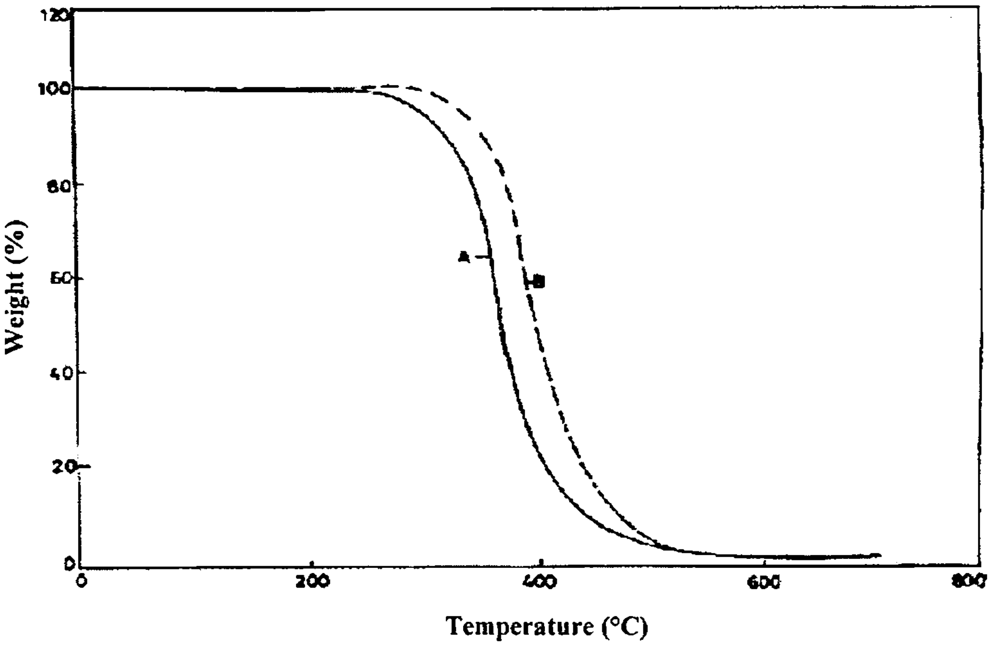

FIG 4.42 TGA CURVES OF (A) BLEND, (B) BLEND+DCP+SILANE

Decomposition temperatures are given in table 4.2. The LLDPE phase shows a higher improvement in decomposition temperature than that of LDPE, probably because of the higher crosslink density.

Table4.2 The temperature of derivative weight % peak

Material	Peak temp (°C)
LDPE	373.8
LDPE + DCP +SILANE	386.1
BLEND	380.3
BLEND + DCP +SILANE	392.7
LLDPE	383.5
LLDPE + DCP + SILANE	397.3

The gel content of silane grafted LDPE is compared with that of LLDPE and 50/50 LDPE/LLDPE blend in table 4.3. LLDPE has a higher crosslink density than LDPE. Gel content, which relates to the three dimensional network structure, increases with LLDPE content, indicating that the LLDPE phase forms a relatively denser network structure.

Table 4.3 Gel content values at 190° C

Material	Gel Content (%)
LDPE + DCP +SILANE	32.6
BLEND + DCP + SILANE	38.2
LLDPE + DCP + SILANE	40.6

The densities of unmodified and modified LDPE, LLDPE and their blend are shown in table 4.4.The densities of the modified polymers are found to get marginally reduced upon modification. This behaviour can be attributed to reduction in crystallinity, because of network formation.

Table 4.4 Variation of density with modification

Material	Density (g/cc)
LDPE	0.973
LDPE+DCP + SILANE	0.959
BLEND	0.957
BLEND+DCP +SILANE	0.939
LLDPE	0.947
LLDPE + DCP + SILANE	0.923

4.4. CONCLUSIONS

The study shows that a low level of silane grafting can be introduced to polyethylenes during their extrusion on a single screw extruder and that optimum parameters of reactive extrusion can be obtained from torque rheometer studies. The low level of grafting/crosslinking does not seem to affect the processing of the material, but improves its mechanical behaviour and thermal stability.

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CHAPTER 5

MALEIC ANHYDRIDE GRAFTING OF POLYETHYLENES

MALEIC ANHYDRIDE GRAFTING OF POLYETHYLENES

5.1. INTRODUCTION

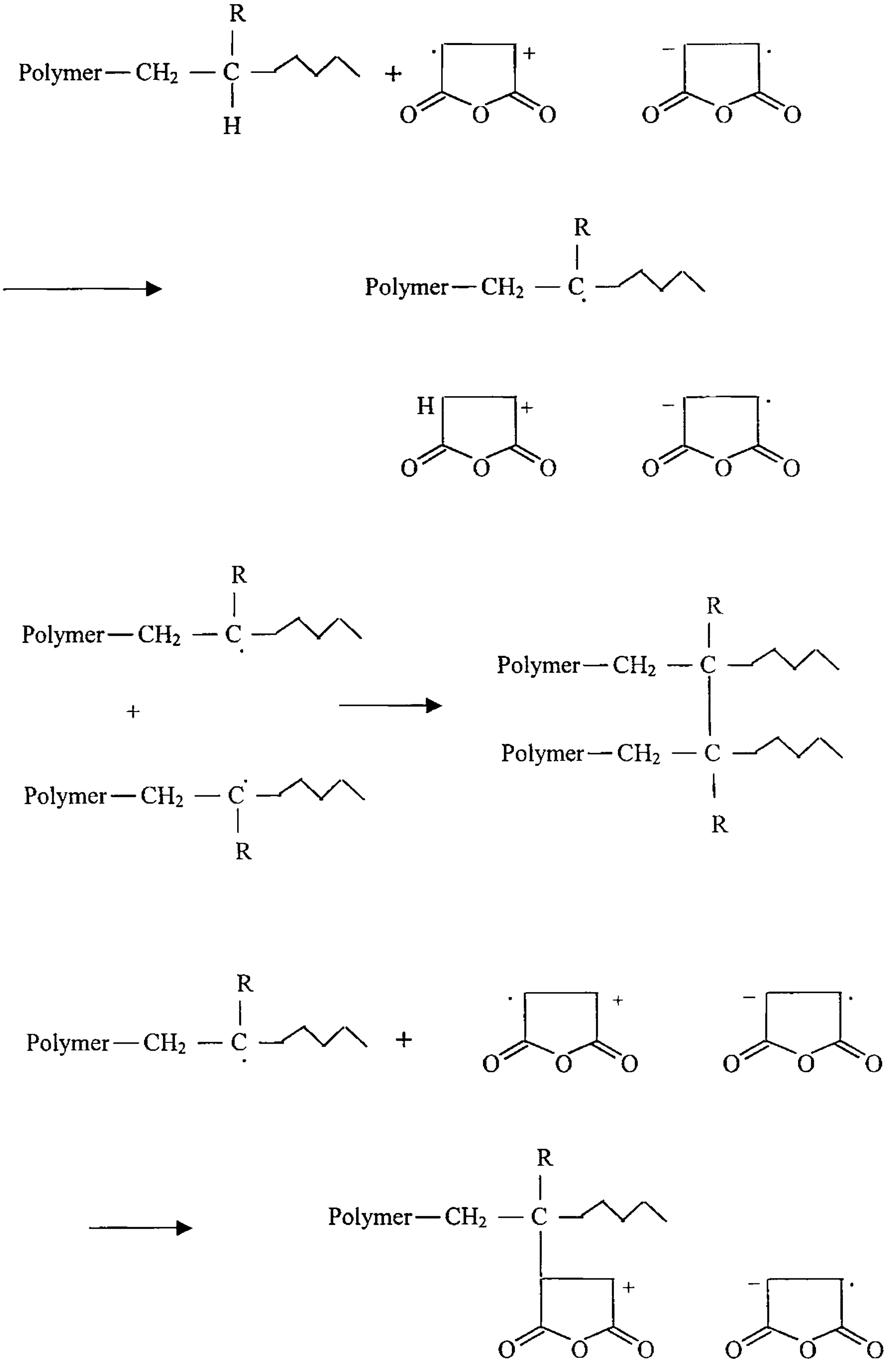
Grafting in an extruder reactor involves reaction of a molten polymer with a monomer or mixture of monomers capable of forming grafts to the polymer backbone.[1-5] Polyolefines have been modified with maleic anhydride (MA) for improving various properties such as compatibility. The modification is usually carried out in the melt and in the presence of free radical initiators like peroxides.[6-10] Under such conditions the maleic groups are introduced to polymer macromolecules. Grafting is usually accompanied by the formation of crosslinks and hence improves the mechanical properties of the polyolefines and their blends.[11-15]

The crosslinking of polyethylene molecules by main bonds into three dimensional networks leads to significant improvements of the material properties, which greatly enlarge the application fields of these low cost polymers. Compared with the untreated material, crosslinked polyethylene shows enhanced impact strength, better thermal performance and higher chemical resistance. Further, considerable improvements can be found in the resistance to wear, creep and ageing.[16-20] Also, crosslinked products can incorporate large amounts of fillers without remarkable deterioration of the material properties.

The use of polymer blends to achieve property and price advantages has been a rapidly expanding field of research. Developing a blend with satisfactory overall physicomechanical behaviour will depend on the ability to control interfacial tension to generate a small phase size and strong interfacial adhesion to transmit applied force effectively between the component phases.[21-35] The process of reactive processing permits the preparation of functionalized polymers, including copolymers containing carboxyl groups which can not be made directly by the polymerisation process and opens up significant possibilities for the creation of new speciality and engineering plastics.[36-50]

The reaction of a molten saturated polymer with maleic anhydride in the presence of a radical catalyst, under the appropriate conditions, yields a polymer containing appended individual succinic anhydride and maleic anhydride units, but accompanied by side reactions, including crosslinking and / or degradation. It has been proposed by Gaylord and Mehta that the additional crosslinking of the ethylene copolymer which occurs during reaction with MA, is due to the generation of additional radical sites on the polymer as a result of hydrogen abstraction by the excited MA. These additional sites can couple and / or add excited MA.

The proposed mechanism is shown in the following scheme.



Suggested mechanism for MA grafting of polyethylene

The extruder is an ideal reactor for polymer modification in that it serves as a pressure vessel equipped for intensive mixing, shear, control of temperature, control of residence time, venting of by-product and unreacted monomer as well as the transport of molten polymer through the various sections of the extruder, each serving as a mini-reactor and removal therefrom. Further, reactive extrusion is economically attractive since the extrusion and grafting are done in a single stage. However care should be taken to optimise the reaction conditions since reaction has to be completed along with the shaping. In this study the optimum parameters for maleic anhydride modification of low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and their blend have been determined on a torque rheometer and these parameters have been utilised in actual reactive extrusion.

5.2. EXPERIMENTAL

Reactive Extrusion

Conditions for reactive extrusion were first determined on a Brabender torque rheometer model PL 3S equipped with roller type rotors, having a capacity of 40g. Different mixing conditions were generated by varying the temperature and rpm. The dosage of maleic anhydride (MA) was varied from 1-5% of the total weight of the polymer while that of dicumyl peroxide (DCP) at concentrations of 2-6% of the maleic anhydride content. Reactive extrusion was done on a laboratory general purpose plastic extruder attached to a Brabender plasticorder model PL 2000 with an L/D ratio of 25 and a compression ratio of 2 and fitted with a ribbon die. The temperatures of the barrel and that of the die and the rpm of the screw were fixed as per the results obtained from the mixer.

5.3. RESULTS AND DISCUSSION

When the Polyethylenes are introduced in to the mixer the torque rises and stabilises at a value due to melting and homogenisation. The variation of stabilised torque with maleic anhydride content, of LDPE, LLDPE and their blend, at 160^{0}C and 60 rpm in the torque rheometer mixer keeping the level of DCP content at 5% of the maleic anhydride, is shown in fig5.1. An increase in torque is observed with maleic anhydride content, probably due to the increase in the extent of maleic anhydride grafting/ crosslinking as expected. Highest value of stabilised torque is obtained for 5% maleic anhydride content showing that maximum amount of grafting/crosslinking occurs at this level of maleic anhydride and hence 5% maleic anhydride was chosen as the optimum[11]. However, the efficiency of grafting reaction is dependent upon the structure, abstraction power, temperature and radical lifetime of the initiator employed. Hence the optimum percentage of maleic anhydride was also verified from the variation of tensile strength of the samples. Fig5.2. shows the variation of tensile strength of MA grafted LDPE, LLDPE and their blend, with percentage MA added at 160^{0}C at 60 rpm. Maximum tensile strength is obtained for 5% MA, confirming that maximum grafting/crosslinking occurs at this MA content.

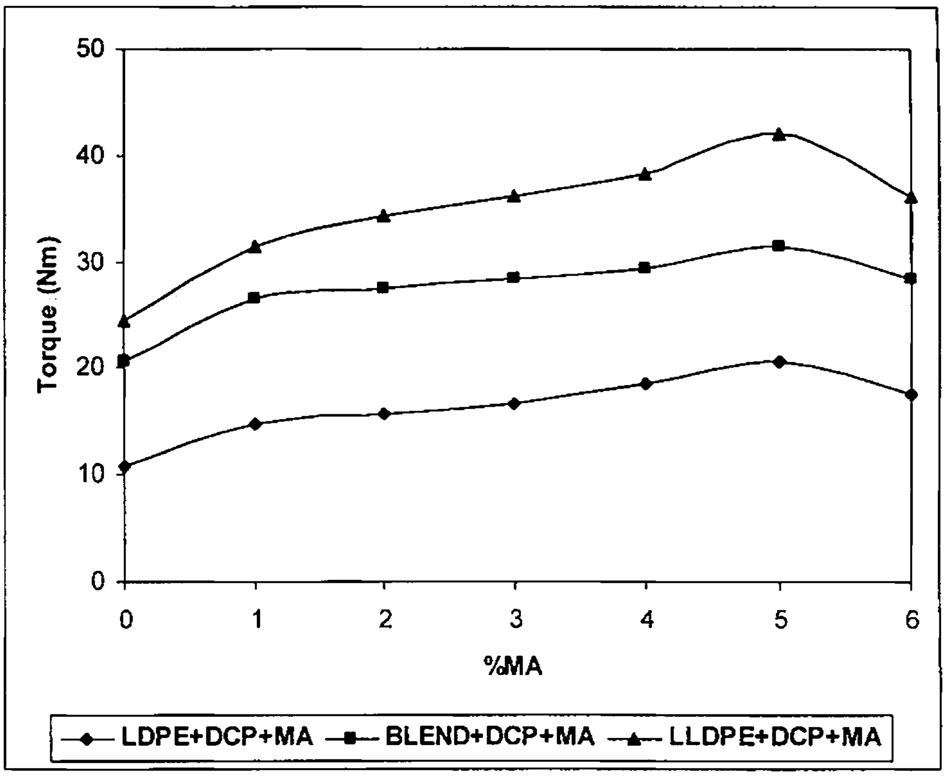


Fig 5.1 Variation of stabilised torque with MA content at 160°C

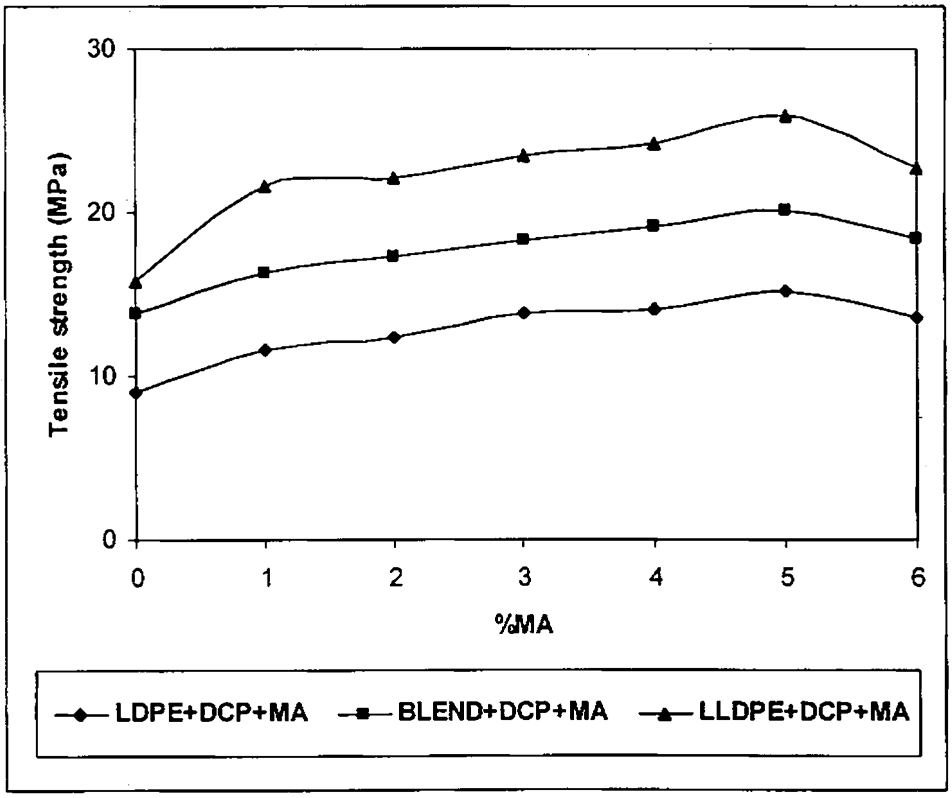
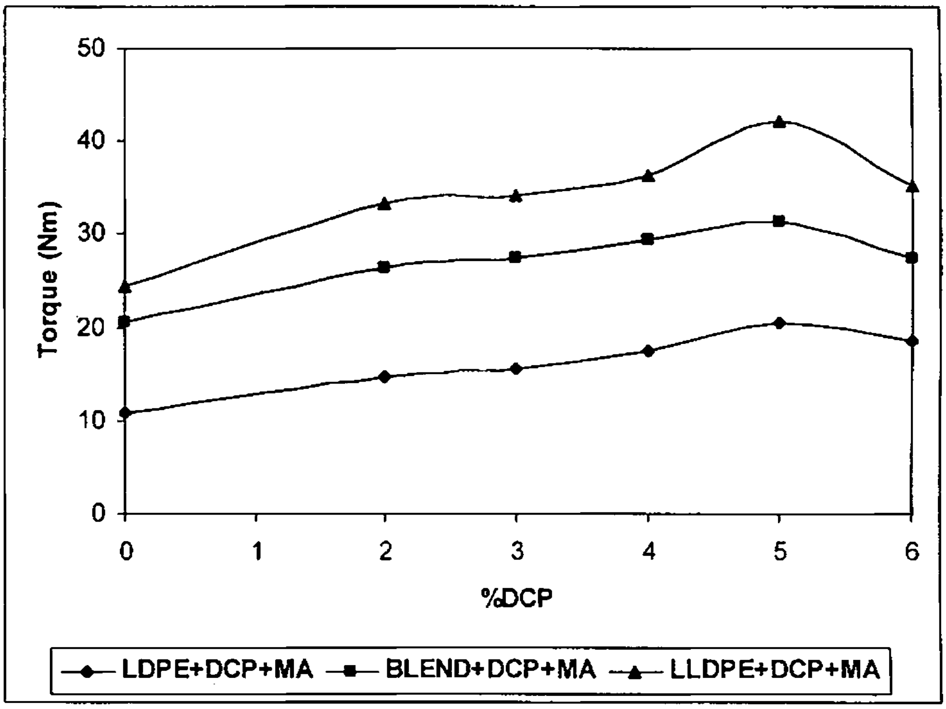


Fig 5.2 Variation of tensile strength with MA content at 160° C

Fig 5.3. shows the variation of stabilised torque with DCP content of MA grafted LDPE, LLDPE and their blend at 160^0C and 60 rpm keeping maleic anhydride concentration constant at 5phr. The stabilised torque increases with DCP content, reaches a maximum and then decreases indicating there is an optimum DCP concentration. Maximum torque is obtained for 5% DCP (percent of MA) and hence 5% DCP was chosen as the optimum concentration. This result also suggests that there is an optimum radical concentration which depends on the [peroxide]/ [monomer] ratio to promote grafting efficiency, beyond which the graft content levels off and termination reactions become prominent.[11] The optimum DCP content was also verified from the variation of tensile strength of the samples. Fig5.4. Shows the variation of tensile strength of MA grafted LDPE, LLDPE and their blend, with DCP content at 160^0C and 60rpm. Maximum tensile strength is obtained for 5% DCP (percent of MA). Fig5.5 shows the variation of stabilised torque with rpm at 160^0C for maleic anhydride grafted LDPE, LLDPE and their 50/50 blend. In the case of maleic anhydride grafted polymers, maximum torque is obtained at 60rpm. This shows that the shear rate at this rpm is optimum for maleic anhydride grafting.

Generally, temperature is a critical factor of any chemical reaction, and this is especially true in the case of grafting reaction in the extruder. Furthermore, the grafting efficiency will depend upon the number of free radicals produced and its mobility and stability. Also, diffusion plays an important role as the reactions are carried out in the extruder. Fig5.6 shows the variation of torque with temperature at 60rpm for LDPE, LLDPE and their blend with and without DCP& MA.



5.3 Variation of stabilised torque with DCP content at 160°C

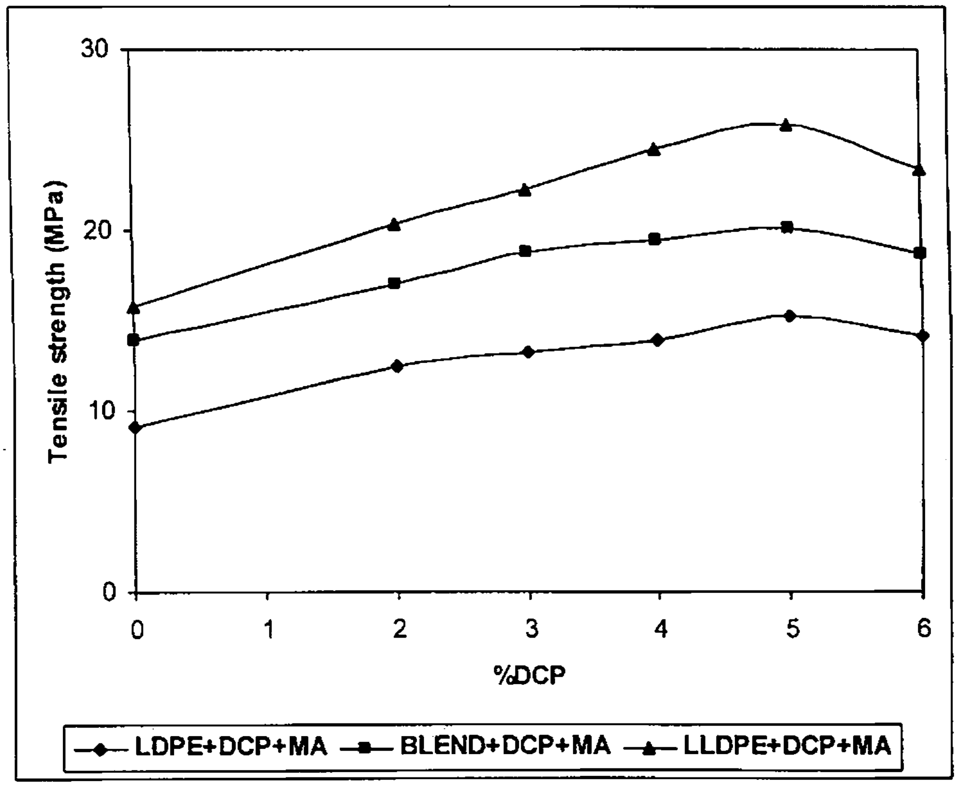


Fig 5.4 Variation of tensile strength with DCP content at 160°C

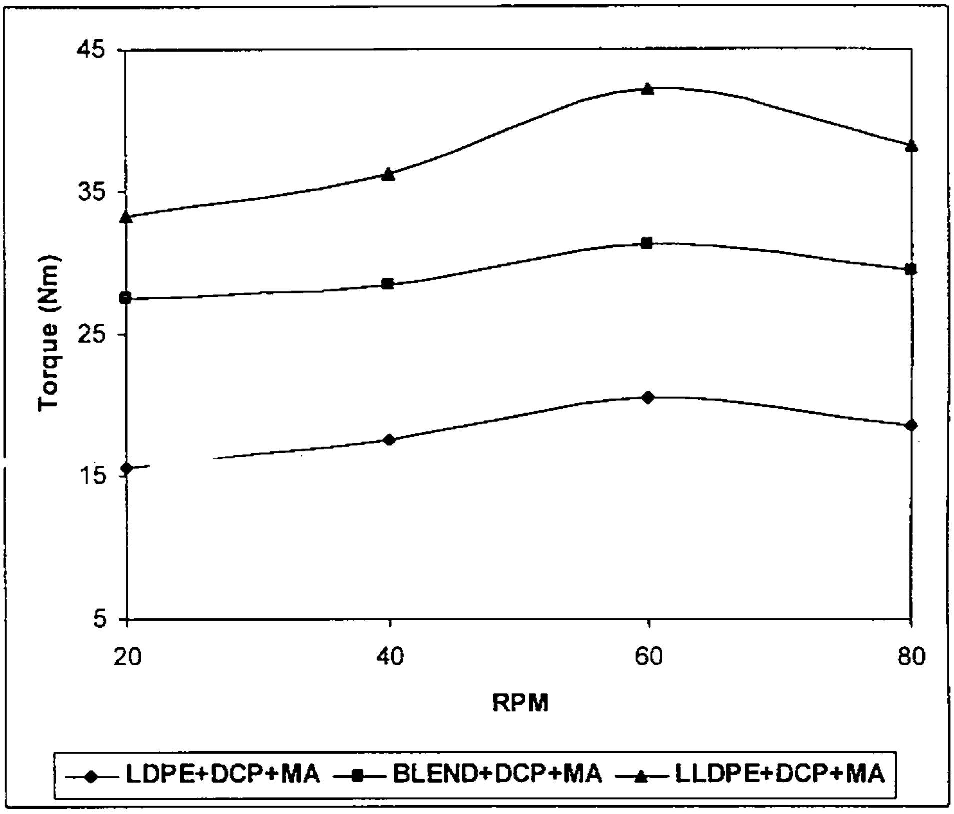


Fig 5.5 Stabilised torque vs rpm

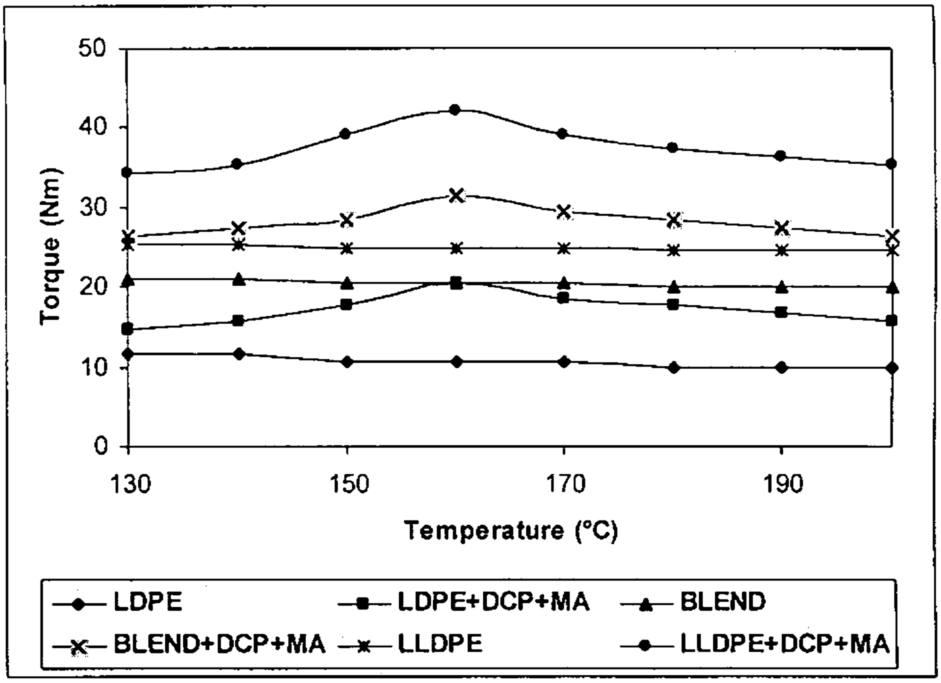


Fig 5.6 stabilised torque vs temperature

The torque rises when the temperature of the mixer increases from 130^0C to 160^0C indicating progressive improvement in grafting/ crosslinking after which the torque decreases. This is probably because an increase in temperature causes a faster and complete decomposition of the initiator and hence produces more radicals and hence results in a higher graft content. 160^0C registers the highest torque for all the combinations. This is probably due to better grafting/crosslinking efficiency at this temperature at the conditions employed.

The optimum conditions obtained from the torque rheometer have been adopted for reactive extrusion. Maleic anhydride grafting of polyethylenes was carried out in a laboratory extruder by using the optimum temperature (160^0C), rpm (60) and optimum concentrations of maleic anhydride (5%) and DCP (5% of MA). To verify whether these conditions are the optimum, reactive extrusion was conducted at other temperatures and rpms also. Fig5.7 shows the variation of tensile strength with temperature of extrusion for unmodified and modified LDPE, LLDPE and their 50/50 blend at 60rpm. Maximum tensile strength is obtained at 160^0 C as in the case of the mixer showing that the results obtained from the mixer can be employed in actual extrusion. Fig5.8. shows the variation of tensile strength with rpm in the case of modified LDPE, LLDPE and their 50/50 blend at 160^0C. A maximum value of tensile strength is obtained at 60rpm in all the cases. This shows that the shear rate/ residence time under these conditions give the best choice for maleic anhydride grafting.

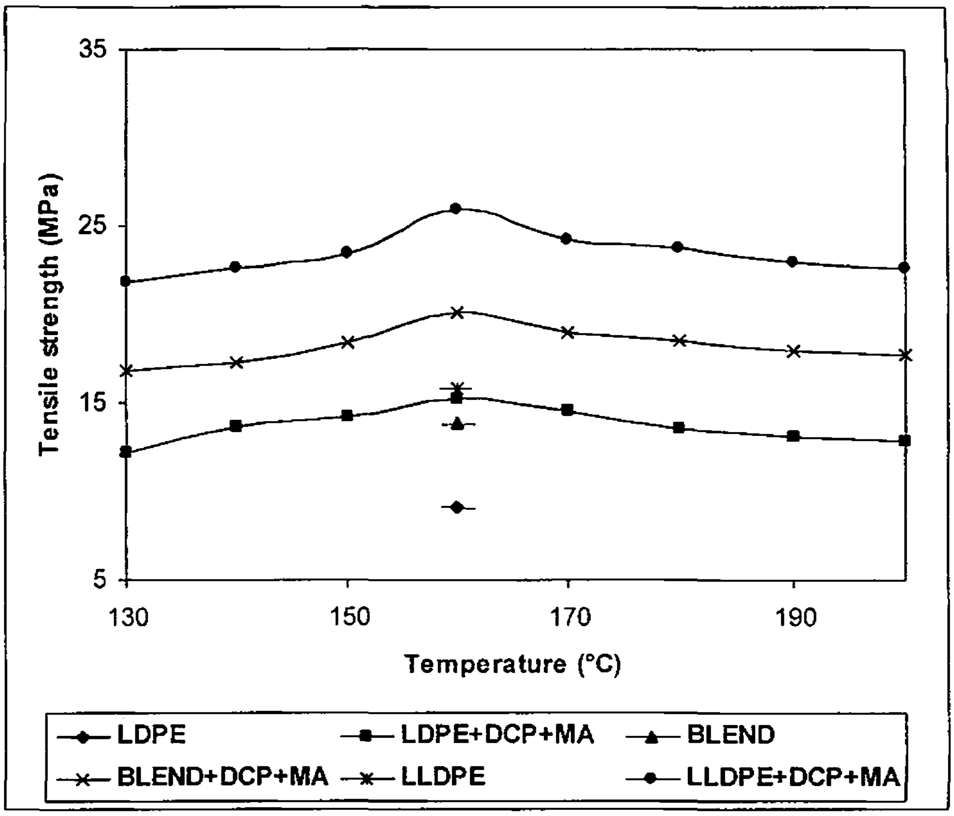


Fig 5.7 Tensile strength vs temperature

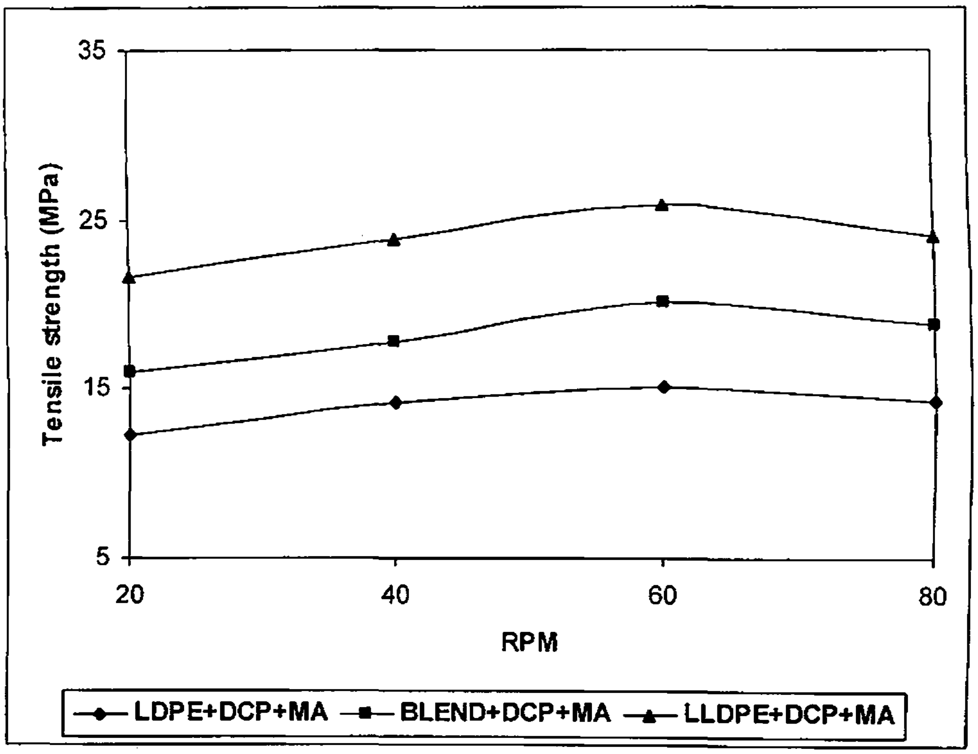


Fig 5.8 Tensile strength vs rpm

Fig5.9 shows the variation of elongation at break (EB) with temperature, in the case of unmodified and MA grafted LDPE, LLDPE and their blend. It is found that the EB values decreased on MA grafting as expected.Fig5.10 shows the variation of EB with MA content in the case of MA grafted LDPE, LLDPE and their blend at 160° C. EB values are decreased due to MA grafting.

Fig 5.11 shows the variation of EB with DCP content in the case of MA grafted LDPE, LLDPE and their blend at 160° C. EB values are decreased with DCP content. The maleic anhydride grafting on the polymer chains was confirmed by FTIR spectra. The FTIR spectra of MA grafted polymers are shown in figures 5.12-14.The IR spectra of maleic anhydride grafted polymers show the absorption at 1783 cm^{-1} which is characteristic of the succinic anhydride groups.

Fig 5.15 shows the variation of viscosity at different shear rates. at 170°C, in the case of LDPE, LLDPE, MA grafted LDPE and LLDPE. An increase in viscosity is obtained on MA grafting as expected. The increase in viscosity is due to the introduction of crosslinks between the chains. However, the increase in viscosity is only marginal and hence may not affect the processability. Fig5.16 shows the variation of viscosity at different shear rates, at 170° C, in the case of blend and MA grafted blend. Here also MA grafting shows increase in viscosity.

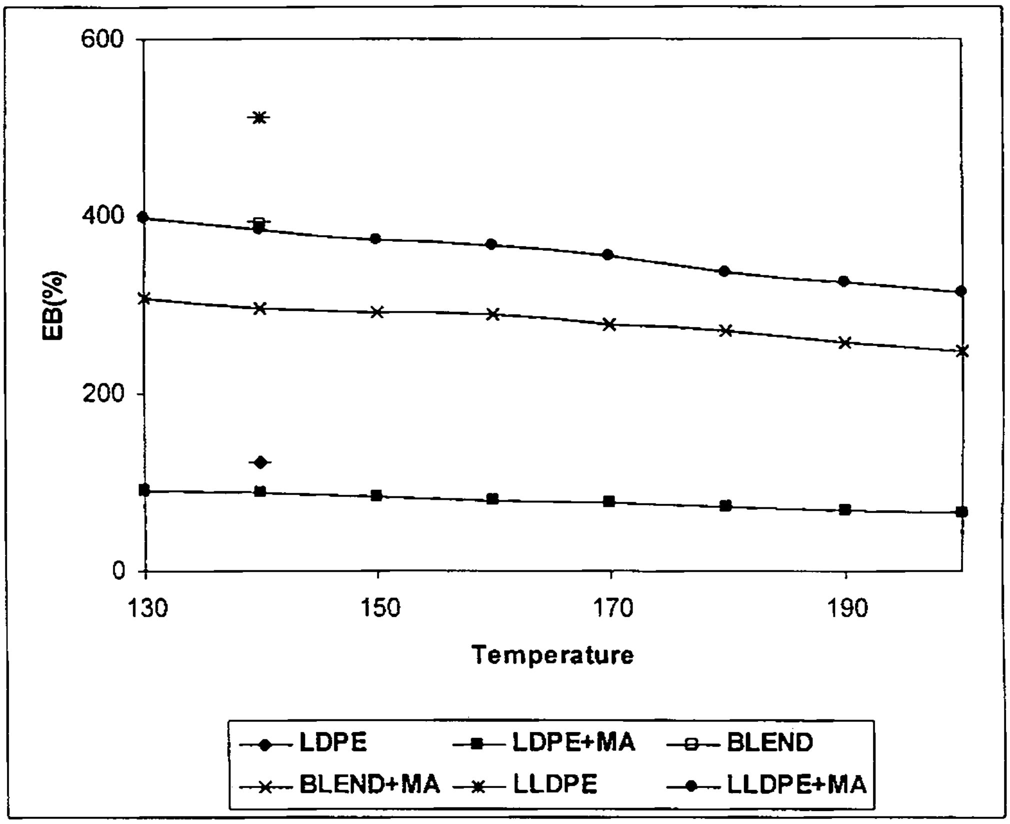


Fig 5.9 Variation of EB with temperature

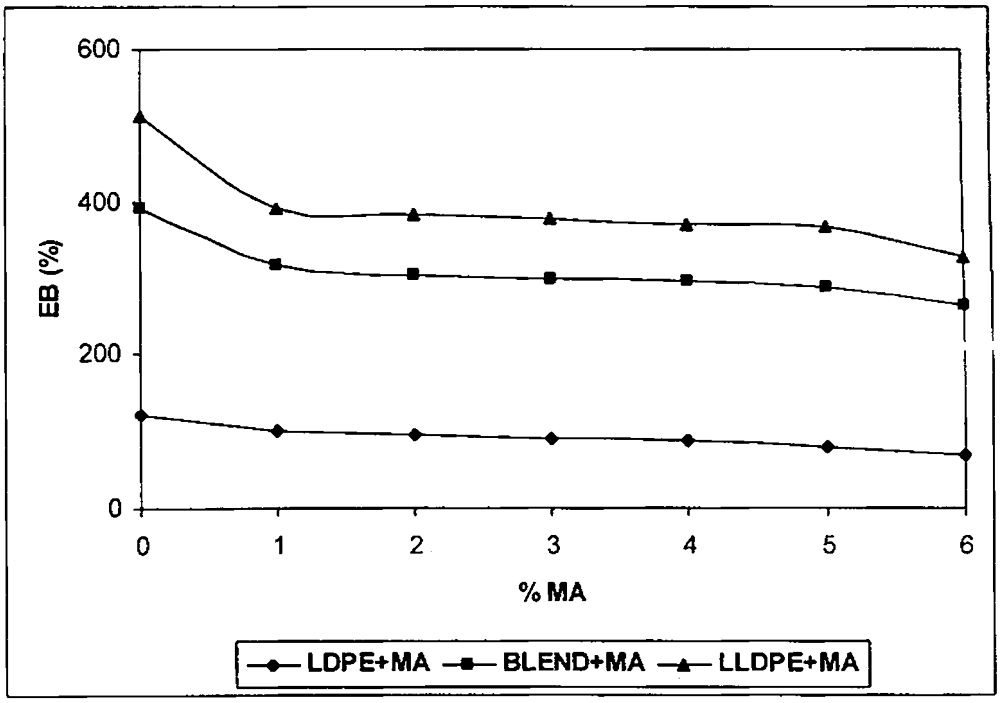


Fig 5.10 Variation of EB with MA content at 160° C

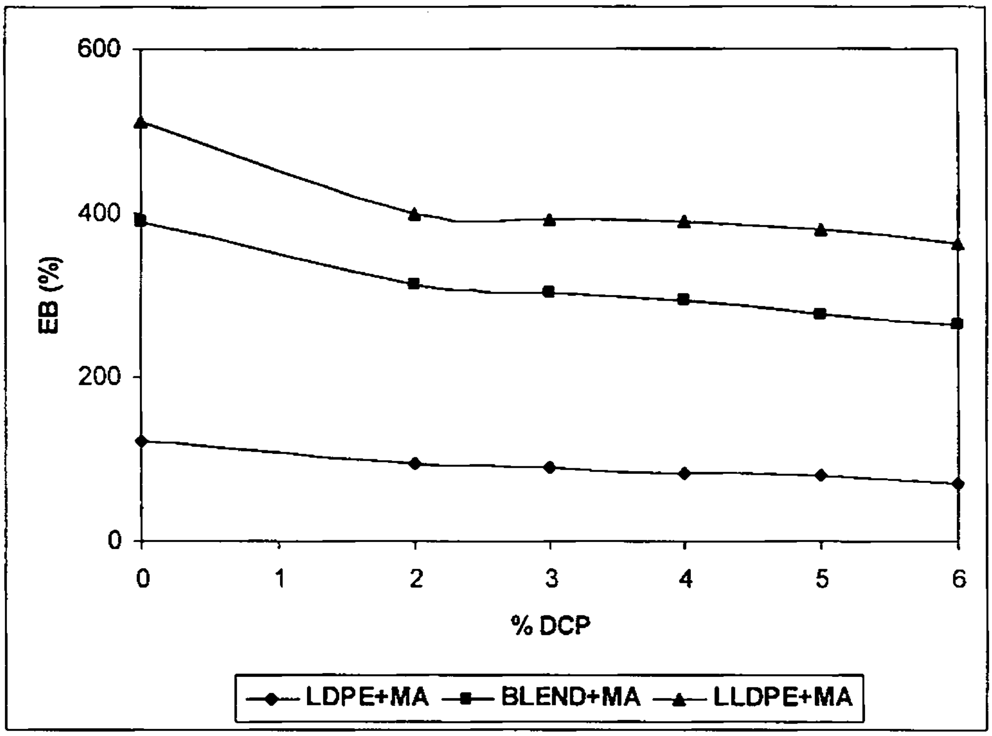


Fig 5.11 Variation of EB with DCP content at 160°C

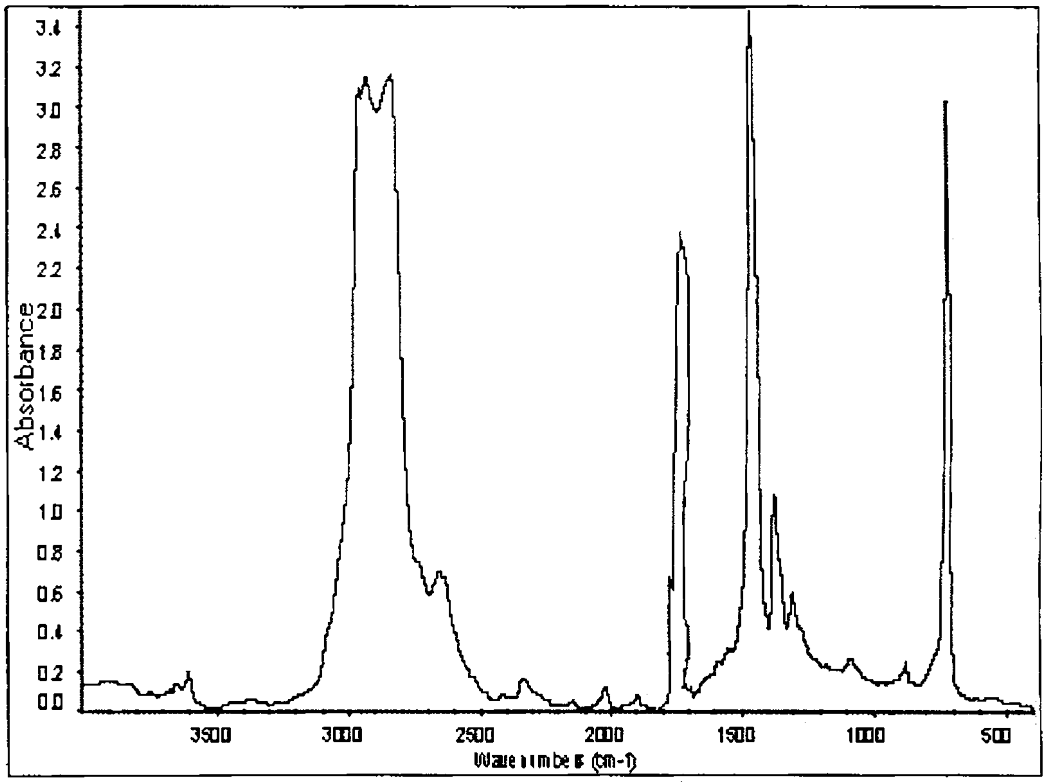


Fig 5.12 FTIR spectrum of MA grafted LDPE

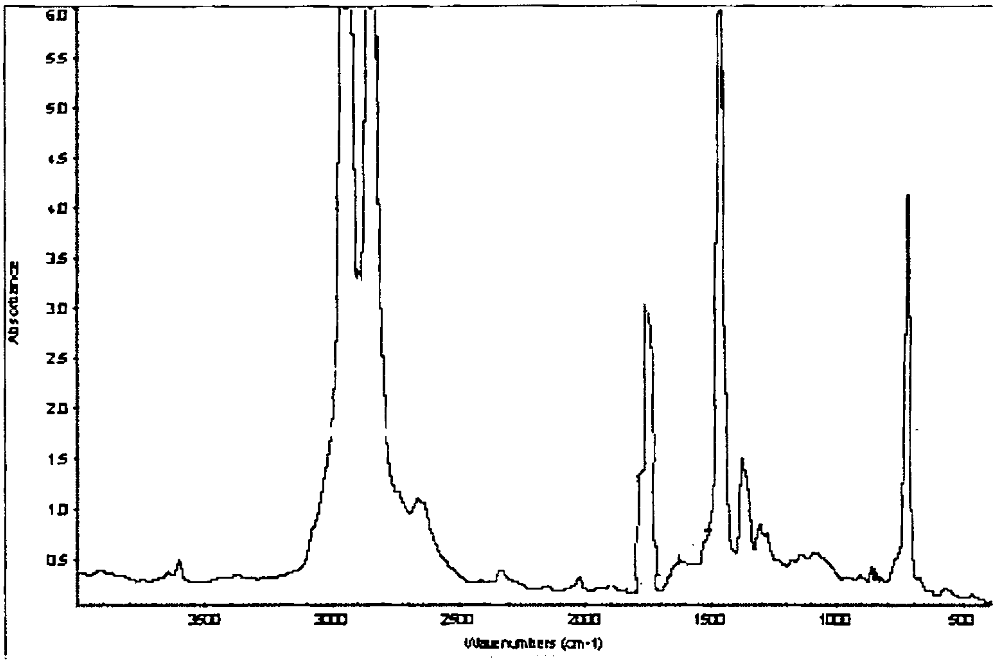


Fig 5.13 FTIR spectrum of MA grafted blend

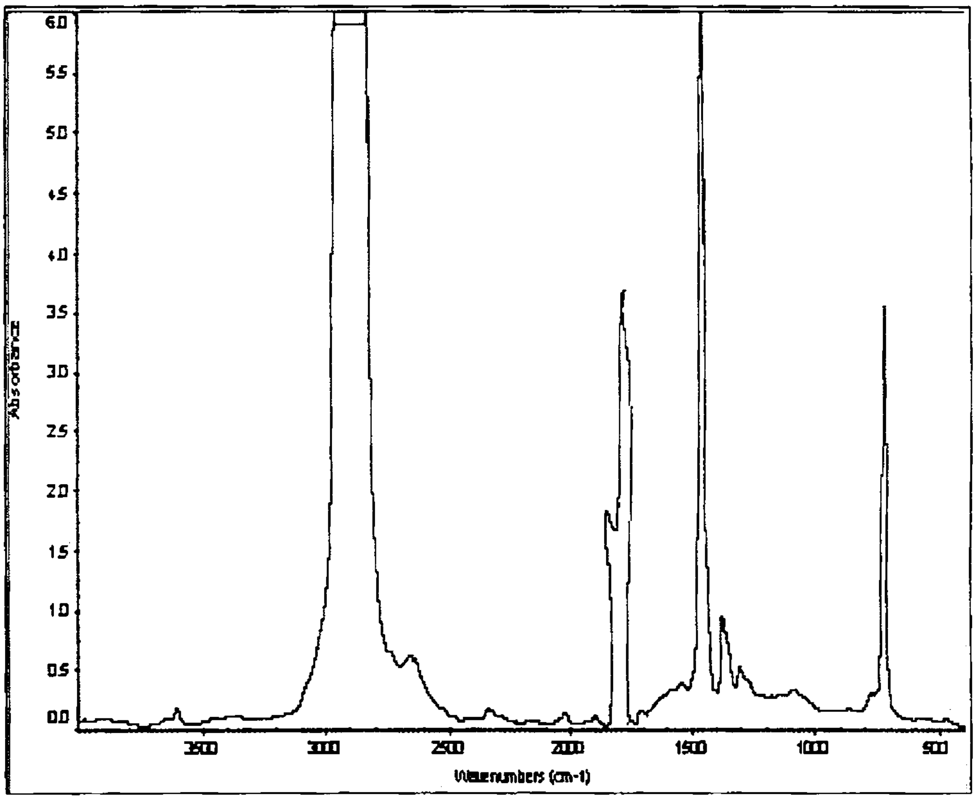


Fig 5.14 FTIR spectrum of MA grafted LLDPE

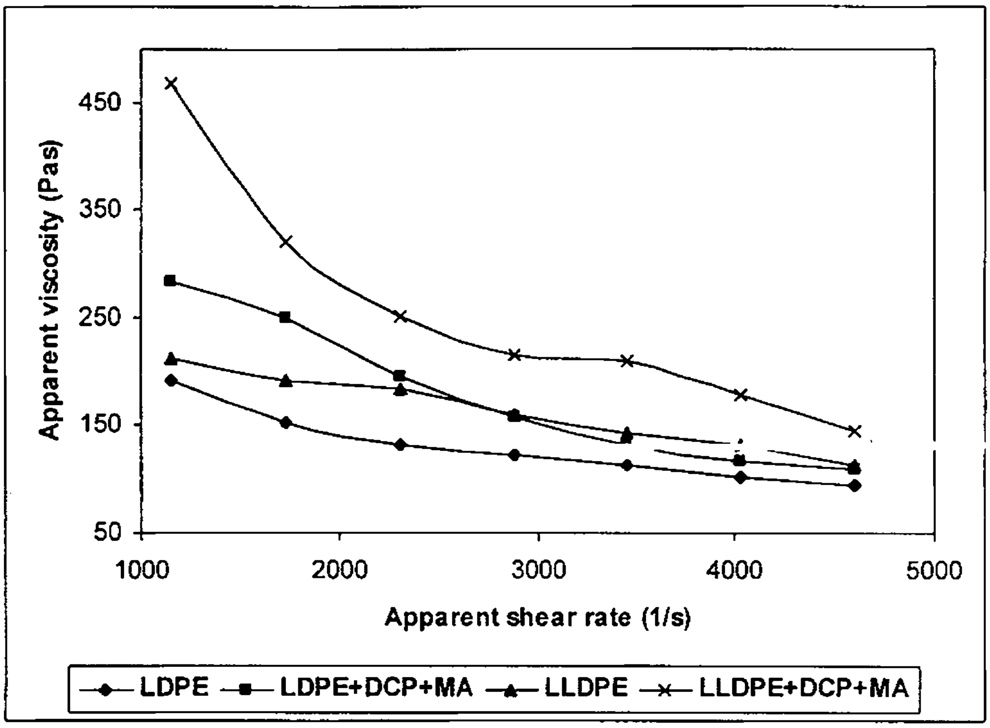


Fig 5.15 Flow curves of unmodified and modified LDPE and LLDPE

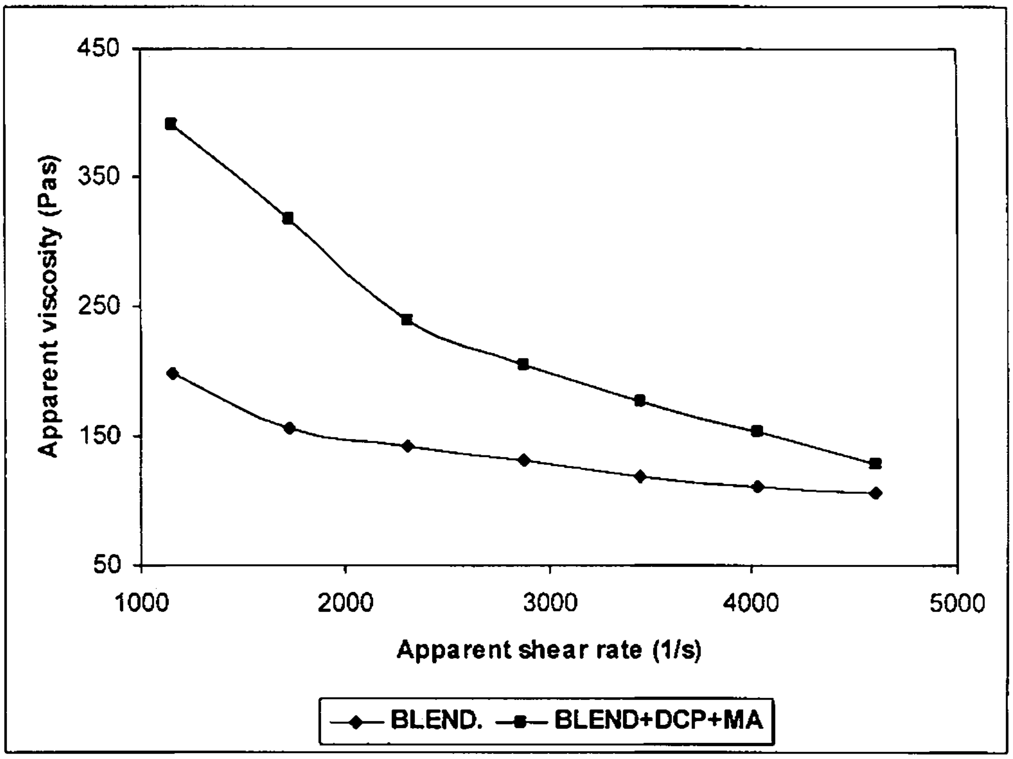


Fig 5.16 Flow curves of unmodified and modified blend

Fig 5.17 shows the variation of gel content with mixing temperature for LLDPE. Maximum gel content is obtained at 160^{0}C confirming that maximum grafting/ crosslinking occurs at this temperature. The increase in graft content is due to the increase in radical formation through the decomposition of initiator. The higher the radical concentration, the higher will be the chain transfer to the polymer backbone and hence higher the grafting. The gel content of LDPE is compared with that of LLDPE and 50/50 LDPE/LLDPE blend in table5.1. LLDPE has a higher crosslink density than LDPE. Gel content, which relates to the three dimensional network structure, increases with LLDPE content, indicating that the LLDPE phase forms a relatively denser network structure.

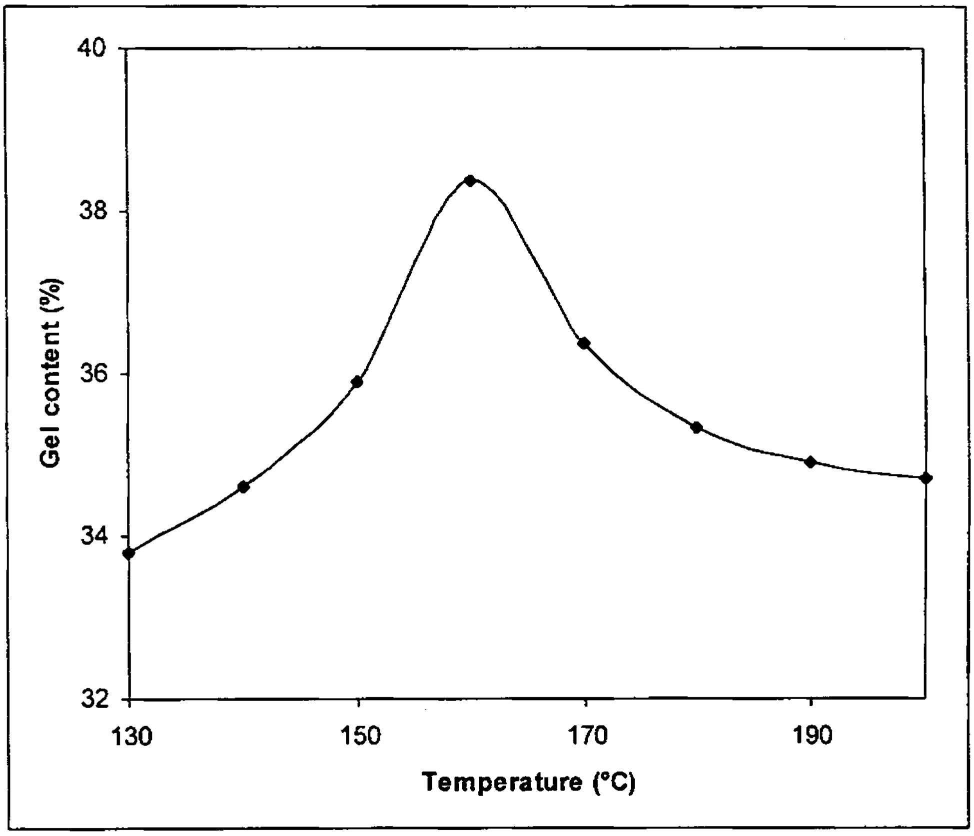


Fig 5.17 Variation of gel content with temperature of MA grafted LLDPE

Table 5.1 Gel content values at 160° C

Material	Gel Content(%)
LDPE + DCP + MA	36.3
BLEND + DCP + MA	40.1
LLDPE + DCP + MA	42.2

Figs5.18-20 show the extrudate swell ratio vs shear rate of unmodified and MA grafted LDPE,LLDPE and their blend. It can be seen from the figures that the extrudate swell ratio (De/D) increases with the shear rate. This is expected because the recoverable elastic energy built up in the melt while flowing in the capillary increases as shear rate is increased. The figures also reveal that the extrudate swell ratio increases on MA grafting. The increase in swell ratio may be due to marginal reduction in crystallinity resulting from crosslinking.

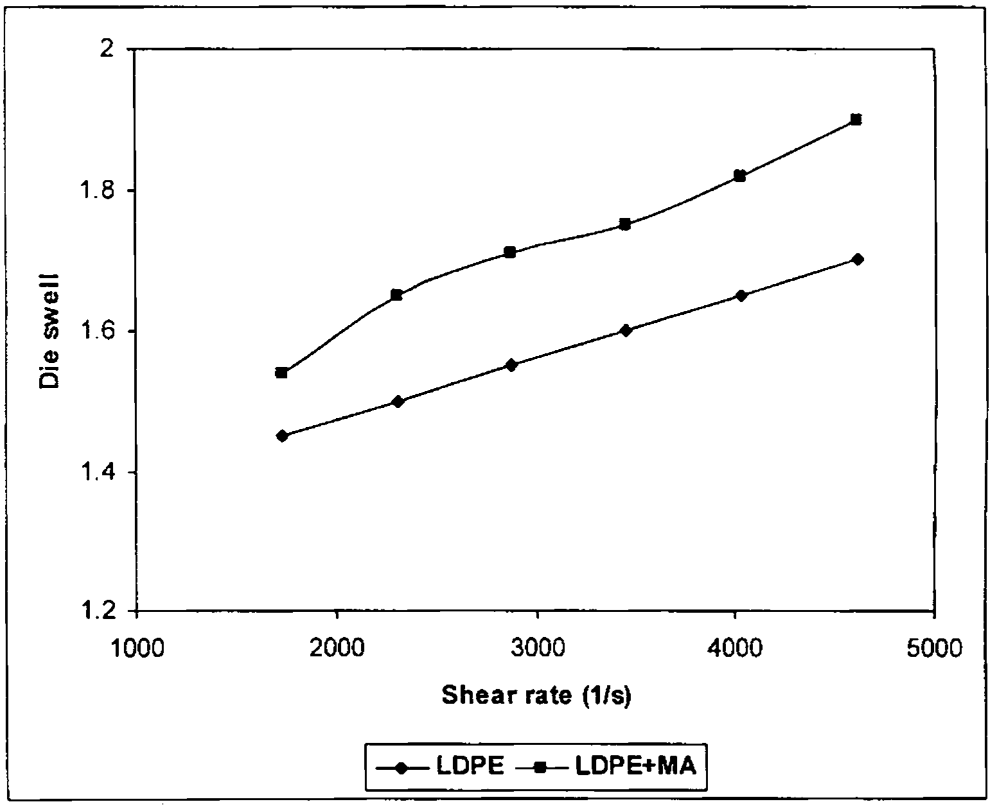


Fig 5.18 Extrudate swell ratio vs shear rate of unmodified and modified LDPE

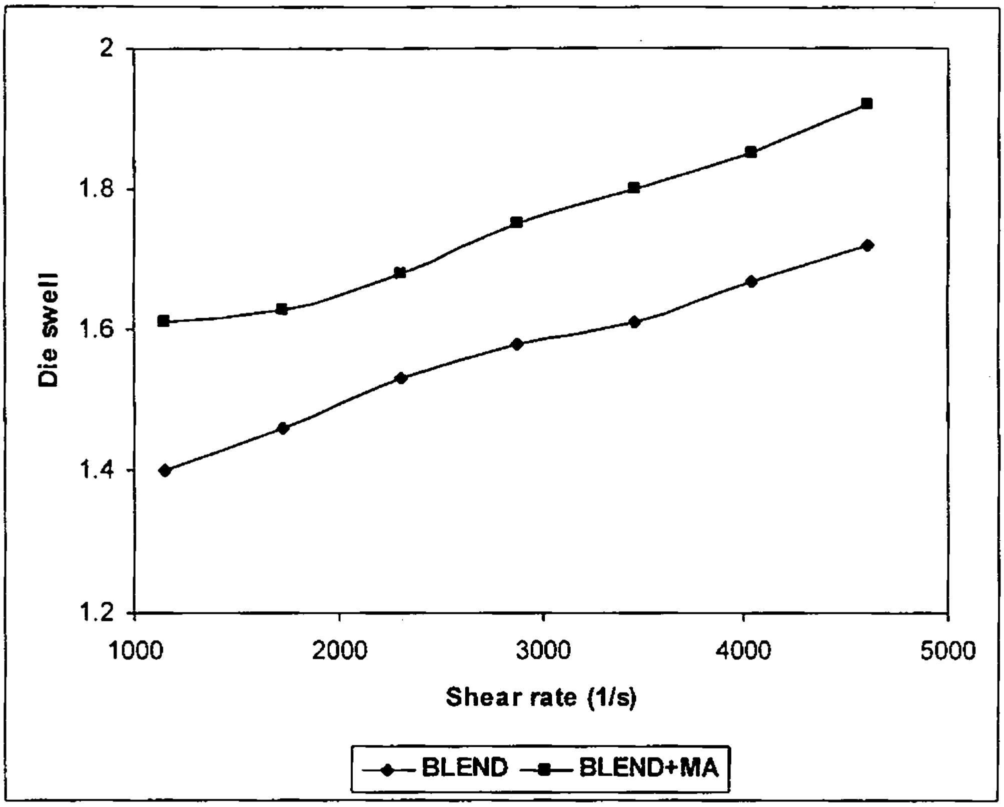


Fig 5.19 Extrudate swell ratio vs shear rate of unmodified and modified blend

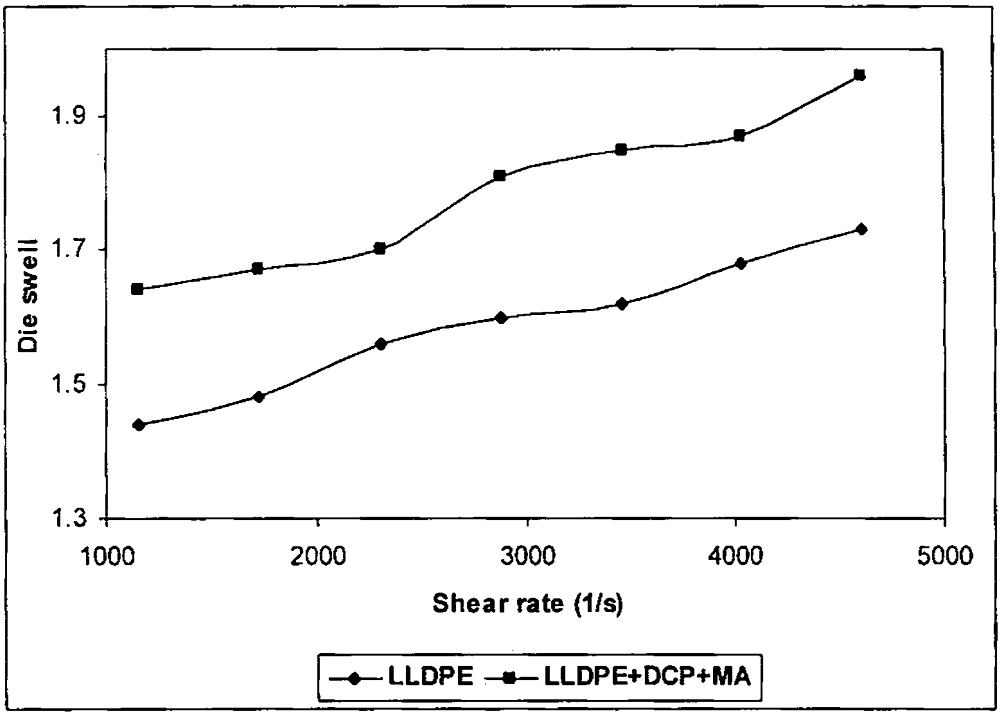


Fig 5.20 Extrudate swell ratio vs shear rate of unmodified and modified LLDPE

Figs 5.21-23 show the variation of viscosity with shear rate at different temperatures of the MA grafted LDPE, LLDPE and their blend. The viscosity decreases with increase in temperature as expected.

The variation of log viscosity with reciprocal of absolute temperature at various shear rates of the MA grafted LDPE, LLDPE and their blend are shown in figures 5.24-26. The slope of these lines is proportional to the activation energy for viscous flow.

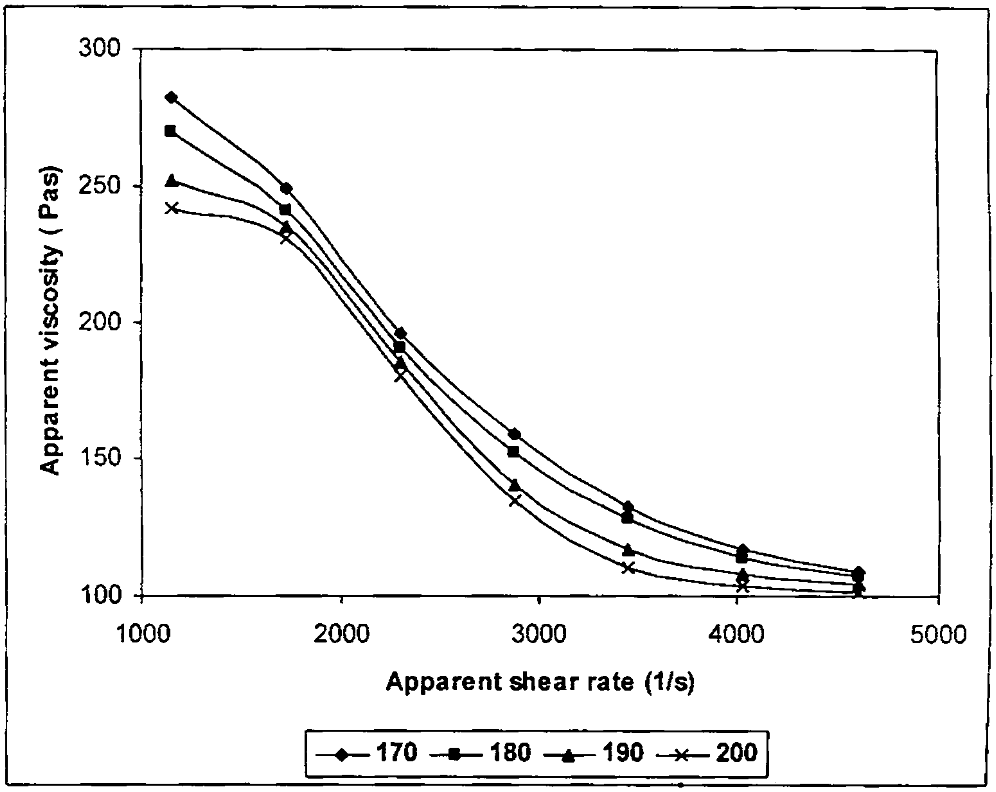


Fig 5.21 Variation of viscosity with shear rate at different temperatures of MA grafted LDPE

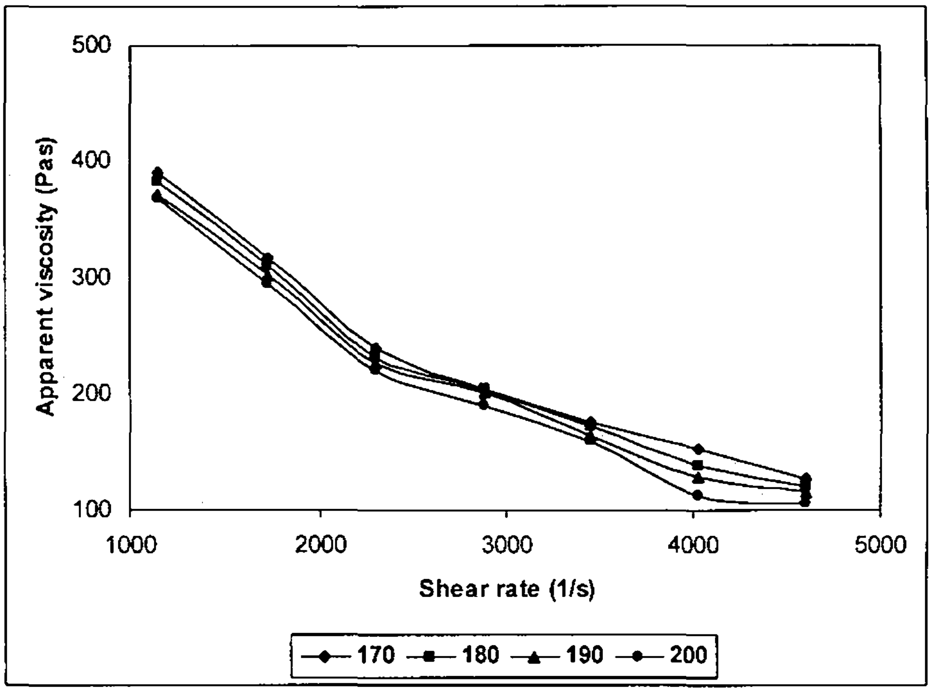


Fig 5.22 Variation of viscosity with shear rate at different temperatures of MA grafted blend

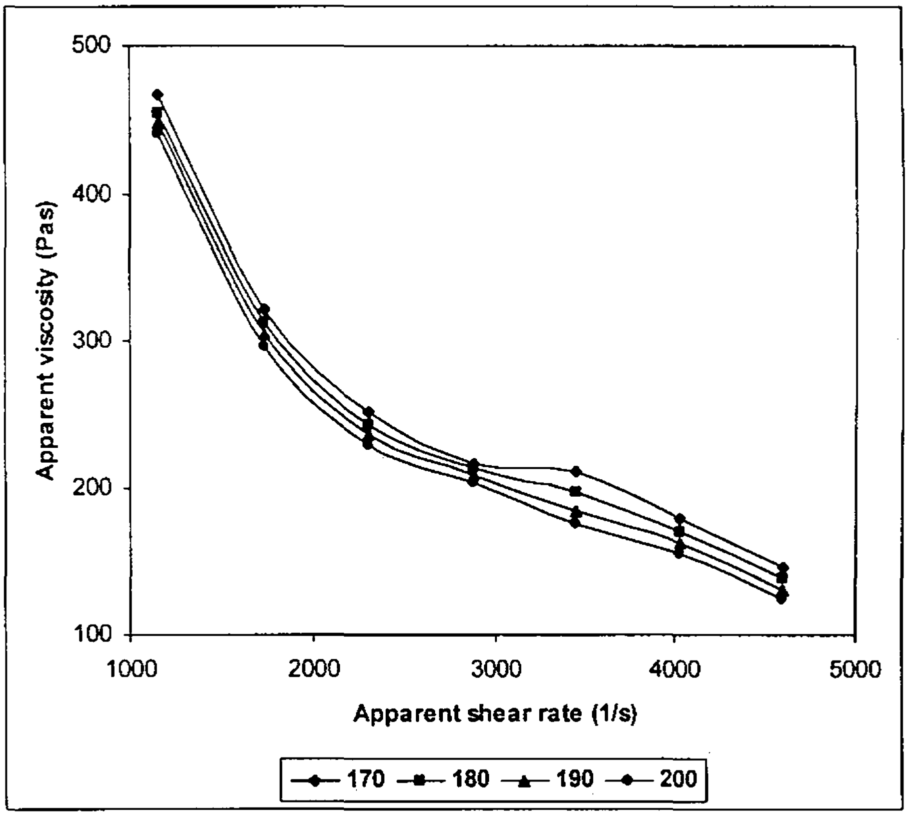


Fig 5.23 Variation of viscosity with shear rate at different temperatures of MA grafted LLDPE

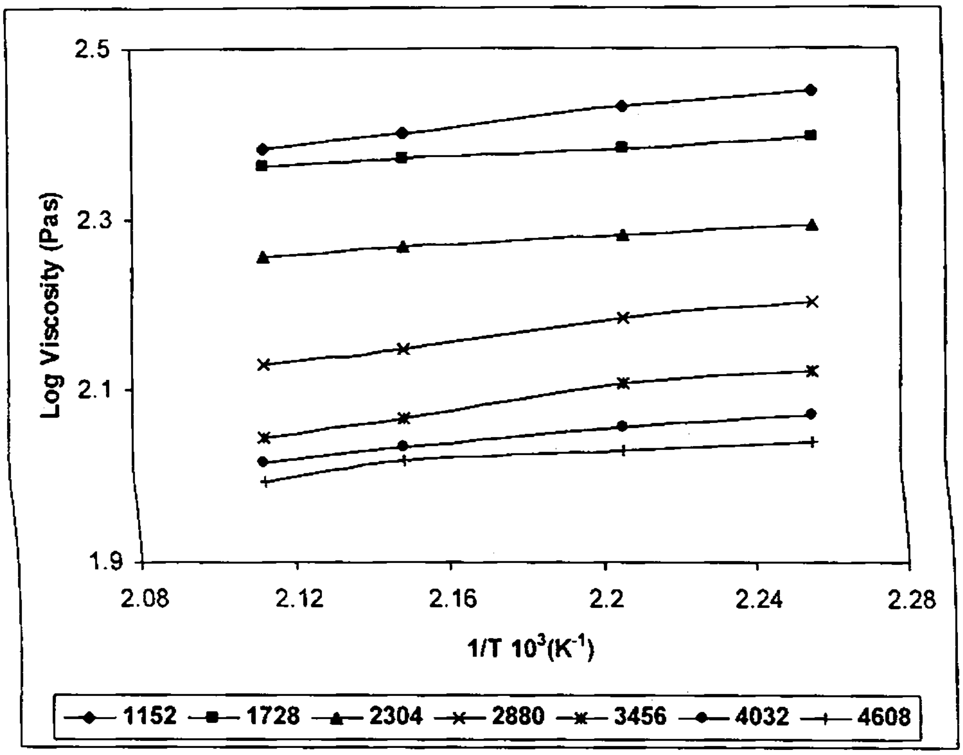


Fig 5.24 Temperature dependence of viscosity of MA grafted LDPE

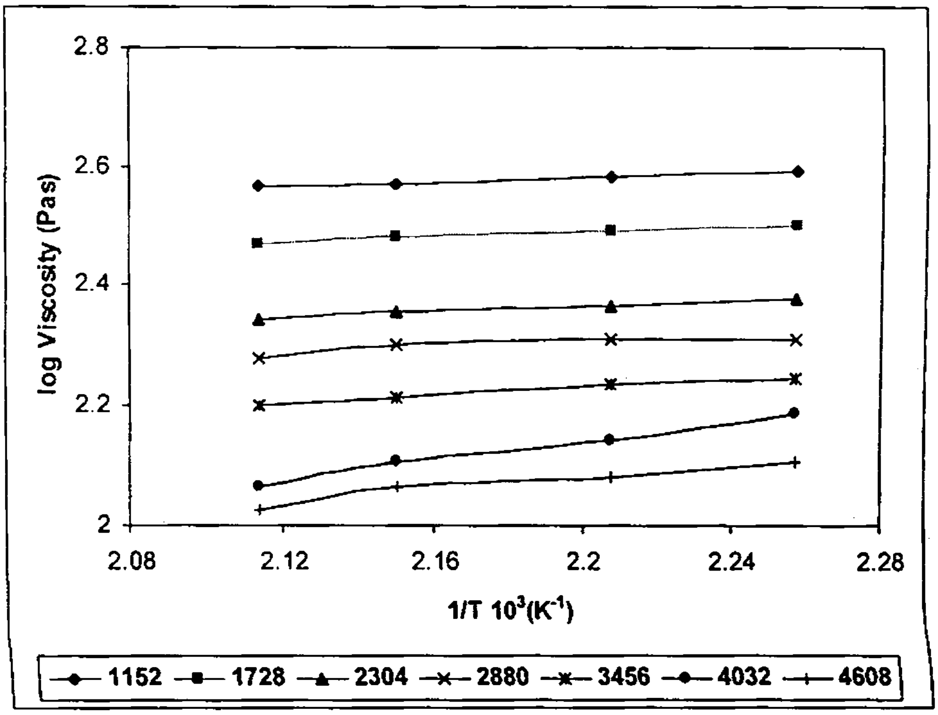


Fig 5.25 Temperature dependence of viscosity of MA grafted blend

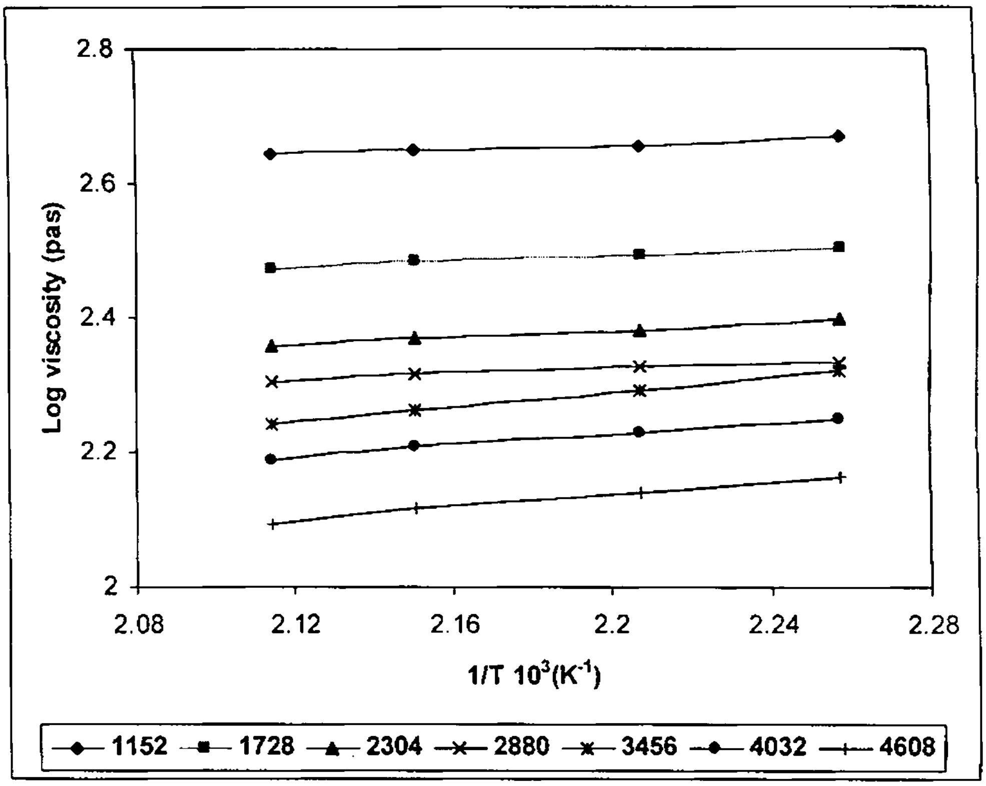


Fig 5.26 Temperature dependence of viscosity of MA grafted LLDPE

The activation energy values are shown in table5.2. The MA grafted polymers show marginally higher activation energy as expected. The difference in activation energy with grafting increases with LLDPE content. This is likely to be due to the higher crosslink density in LLDPE than in LDPE.

Table.5.2 Variaton of activation energy of the polymers at different shear rates:

Shear rate(1/s)	Activation energy (kJ/mol)					
	LDPE	LDPE+ DCP+MA	BLEND	BLEND+ DCP+MA	LLDPE	LLDPE +DCP+MA
1152	0.899	1.421	0.929	1.519	1.042	1.891
1728	0.924	1.603	1.054	1.716	1.186	2.042
2304	1.340	1.949	1.281	2.057	1.486	2.457
2880	1.601	2.305.	2.154	2.786	2.269	3.104
3456	1.819	3.593	2.565	3.649	2.599	3.959
4032	2.234	4.086	2.977	4.124	3.128	4.304
4608	3.352	4.599	3.357	5.632	3.468	6.819

The thermogravimetric curves of unmodified and MA grafted LDPE and LLDPE are shown in fig 5.27. MA grafting introduces improvement in thermal stability as expected. The thermogravimetric curves of unmodified and MA grafted LDPE/LLDPE blend are shown in fig5.28. MA grafted LLDPE shows better thermal stability than modified LDPE.

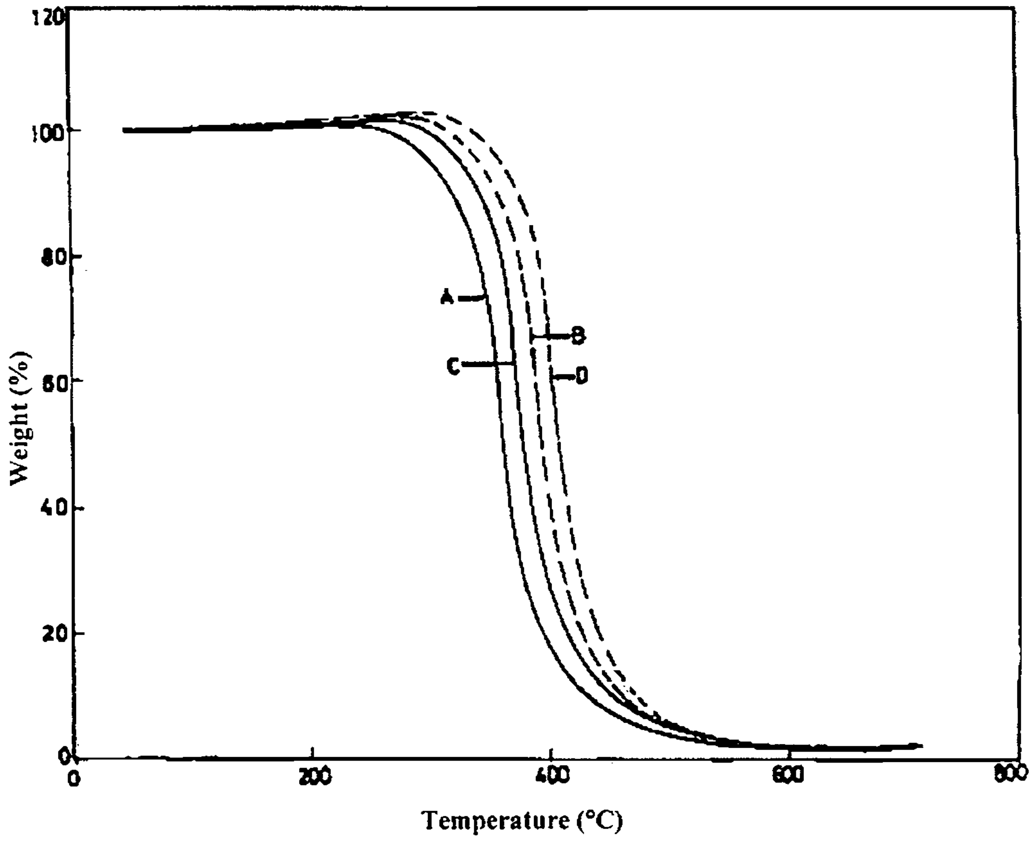


Fig 5.27. TGA Curves of (A) LDPE, (B) LDPE + DCP + MA, (C) LLDPE, (D) LLDPE + DCP + MA

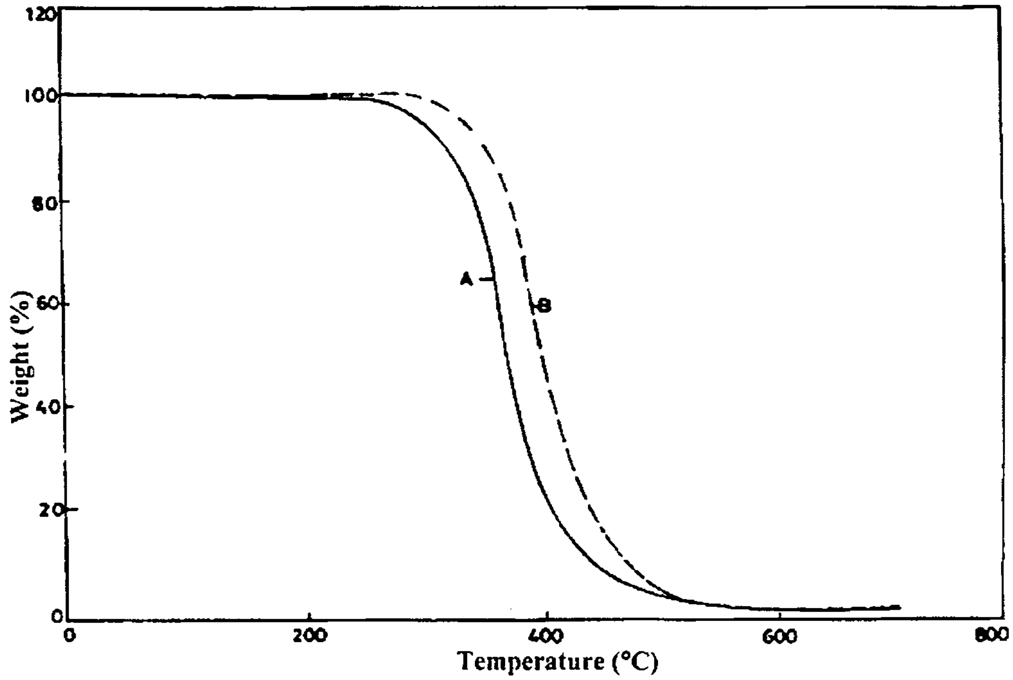


Fig 5.28. TGA Curves of (A) BLEND, (B) BLEND + DCP + MA

Decomposition temperatures are given in table 5.3. The LLDPE phase shows a higher improvement in decomposition temperature than that of LDPE, probably because of the higher crosslink density.

Table 5.3. The temperature of derivative weight % peak

Material	Peak temp(°C)
LDPE	373.8
LDPE + DCP + MA	388.3
BLEND	380.3
BLEND+ DCP + MA	396.1
LLDPE	383.5
LLDPE + DCP +MA	403.3

The densities of unmodified and modified LDPE, LLDPE and their blend are shown in table5.4.The densities of the MA grafted polymers are found to get marginally reduced upon modification. This behaviour can be attributed to reduction in crystallinity, because of network formation.

Table 5.4 Variation of density with modification

Material	Density (g/cc)
LDPE	0.973
LDPE+DCP+MA	0.949
BLEND	0.957
BLEND+DCP+MA	0.924
LLDPE	0.947
LLDPE+DCP+MA	0.912

5.4. CONCLUSIONS

The study shows that maleic anhydride can be grafted to polyethylenes through reactive extrusion, on a single screw extruder and that the optimum parameters of reactive extrusion can be obtained from torque rheometer studies. The low level of grafting/crosslinking introduced does not seem to affect the processing of the material, but marginally improves its mechanical behaviour and thermal stability.

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CHAPTER 6

SUMMARY AND CONCLUSIONS

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The main aim of the study was to optimise the reactive extrusion conditions in the conventional modification processes of polyethylenes in a single screw extruder.

The optimum conditions for peroxide crosslinking of low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and their blend were determined in a torque rheometer. The actual reactive extrusion was performed in a laboratory single screw extruder using the optimum parameters. The influence of the coagent, triallyl cyanurate (TAC), on the crosslinking of low density polyethylene in the presence of peroxide was also investigated. The peroxide crosslinking was found to improve the mechanical properties and the thermal stability of the polyethylenes. The efficiency of crosslinking was found to be improved by the addition of coagent such as TAC. The result of these studies are reported in chapter 3.

The optimum conditions for silane grafting viz temperature, shear rate, silane and DCP concentrations were determined on a torque rheometer in the case of LDPE, LLDPE and their blend. Silane grafting of LDPE in the presence of peroxide was performed with and without addition of water. Compounding of such mixtures in the melt at high temperatures caused decomposition of the peroxide and grafting of alkoxy silyl groups to the polyethylene chains. Water molecules caused hydrolysis of Si-OR groups and formation of Si-O-Si crosslinks was confirmed by FTIR spectra in chapter 4.

The optimum parameters for maleic anhydride modification of LDPE, LLDPE and their blend were determined. The grafting reaction was confirmed by FTIR spectroscopy. Modification of polyethylenes with maleic anhydride in the presence of dicumyl peroxide was found to be useful in improving mechanical properties. The improvement was found to be mainly due to the grafting of carboxyl group and formation of crosslinks between the chains. The crosslinking initiated improvements indicate extended property profiles and new application fields for polyethylenes.

On the whole the study shows that the optimum conditions for modifying polyethylenes can be determined on a torque rheometer and actual modification can be performed in a single screw extruder by employing the optimum parameters for improved mechanical/ thermal behaviour without seriously affecting their processing behaviour.

LIST OF PUBLICATIONS FROM THE WORK

1. Reactive processing of polyethylenes on a single screw extruder, Sheela Isac & K.E. George.

   Journal of Applied polymer Science (Accepted for Publication).

2. Optimisation of silane grafting on a single screw extruder, Sheela Isac & K.E. George.

   Plastics, Rubber and Composites. 30, (1), 34, (2001).

3. Grafting of maleic anhydride to polyethylenes on a single screw extruder, Sheela Isac & K.E. George.

   Polymer Plastics Technology & Engineering (Communicated).

4. Silane grafting of LDPE by reactive extrusion, Sheela Isac & K.E. George,

   Paper presented in 13th Kerala Science congress, Thrissur. 29-31 January 2001,

5. Modification of Polyethylenes by reactive extrusion, Sheela Isac & K.E. George,

   Paper presented in the national symposium on advances in polymer technology, Kochi, March 27-28, 1998.

6. Reactive processing of polyethylenes on a single screw extruder, Sheela Isac & K.E. George,

   Paper presented in the national seminar on current trends in macromolecular chemistry and technology, Ernakulam, August 23rd – 25th 2000.

7. Silane grafting of polyethylenes, by reactive extrusion , Sheela Isac & K.E. George,

   International Journal of Polymeric Materials (Communicated).