WELD LINE BEHAVIOUR OF POLYMER BLENDS WITH SPECIAL REFERENCE TO PP/HDPE, PP/PS AND HDPE/LDPE BLENDS

Thesis submitted to the

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LAKSHMIKUTTY AMMA B.

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KOCHI-682022

NOVEMBER, 2005

CERTIFICATE

This is to certify that this thesis entitled **'Weld line behaviour of polymer blends with special reference to PP/HDPE, PP/PS and HDPE/LDPE blends'** is a report of the original work carried out by Smt. Lakshmikutty Amma B. 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.

DR. K.E. GEORGE
Professor
Department of Polymer Science and
Rubber Technology
Cochin University of Science and Technology

Kochi - 22
23rd November, 2005

DECLARATION

I hereby declare that the thesis entitled **'Weld line behaviour of polymer blends with special reference to PP/HDPE, PP/PS and HDPE/LDPE blends'** is the original work carried out by me under the supervision of **Dr. K. E. George**, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682022, and no part of the work reported in this thesis has been presented for any other degree from any other institution.

Lakshmikutty

LAKSHMIKUTTY AMMA B.

Kochi - 22
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PREFACE

Injection moulding is one of the most widely used polymer processing techniques in the industry due to its high production rate and product quality, short cycle times and the versatility of the moulds that can be used. Moulding of bulky parts requires multigated moulds and the final product is formed by the rejoining of separate streams forming weld lines. The weakness created by the formation of a weld line gets aggravated when polymer blends are used. The present study is aimed at determining the extent of weld line weakness in the blends of the most widely used thermoplastic materials polypropylene, high density polyethylene, low density polyethylene and polystyrene.

Chapter 1: A review of the relevant literature and the scope and objectives of the work are presented in chapter 1.

Chapter 2: The details of the materials used and experimental methods employed in this study are described. The preparation of blends using Thermo Haake Rheocord, preparation of samples by injection moulding, evaluation of mechanical properties using UTM and DMA, evaluation of flow properties using capillary rheometer and morphology by SEM are described.

Chapter 3: The weld line behaviour of semicrystalline homopolymers PP, HDPE and their blends are described in this chapter. The effect of addition of EPDM and DCP as modifiers on the weld line strength, the effect of processing temperature, blending conditions and blend composition are reported. The effects of flow behaviour of the constituents and blends on the weld line strength are also presented. Comparison of SEM of the fracture surface with and without weld lines for modified and unmodified samples is also given.

Chapter 4: The weld line behaviour of polyethylenes is described in this chapter. The effect of melt temperature and addition of DCP on the weld line strength of blends formed by two different grades of LDPE, the weld line behaviour of blends of HDPE and LDPE are described. The effect of addition of filler and the effect of ageing and weathering on the weld line strength are also included. The effect of flow behaviour of the blends on the weld line strength and their correlation is also reported.

Chapter 5: The weld line behaviour of blends formed by an amorphous plastic PS and a semicrystalline plastic PP is presented in this chapter. The effect of adding HIPS as a modifier for PP/PS blends for improving the weld line strength is presented. The effect of processing temperature on the weld line strength is also described. The response of the weld line under dynamic stressing and the fracture behaviour of the samples with and without weld line using SEM are also presented in this chapter.

Chapter 6: The summary and conclusions of the investigations are presented in the last chapter.

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Chapter 1

Introduction

Polymers are the most rapidly growing materials in terms of use and innovations in processing technology. One of the main reasons for the widespread use of polymers over other engineering materials like ceramics and metals is their easy processability. Materials, design and processing are the three main barriers for getting a suitable product and they are interlinked as shown in figure 1.1.

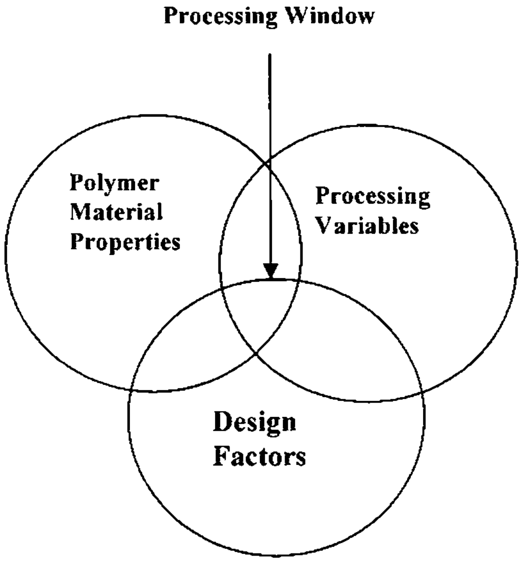


Figure 1.1 *Factors determining product quality of plastics*

For example, design of a product may be limited by the material and processing technique and thus all the three variables are interrelated.

Injection moulding and extrusion are the most important plastics processing techniques. Weld lines are observed in injection moulding and extrusion when separated streams of melt are rejoined [1]. The result is quite often a visible mark of reduced mechanical strength. Depending on the final shape of the product it becomes necessary that the plasticated raw material is separated in individual streams of melt and rejoined. A typical example is the injection moulding of large parts like car bumpers where multigated mould cavities are necessary in order to avoid freezing of the polymer before the cavity is completely filled. In this case, the finished product will invariably contain weld lines which are formed when the polymer flow fronts from the different gates meet during the filling process. In the case of injection moulding of parts with moulded in holes and other inserts also weld lines are unavoidable. Extrusion of hollow profiles involving spider fins will lead to more than one weld line. Weld lines or knit lines are portions of inferior mechanical and optical properties and are a practical problem for many products. With increasing demand for high quality plastic items the importance of weld lines is more and more recognized. The problem is more acute in the case of processing of plastics blends since the immiscibility of the components further deteriorates the weld line strength. This study has been undertaken to determine the intensity of weld line weakness in blends of standard plastics and to explore methods to mitigate such weakness.

1.1 Plastics

Plastics occupy a major place and pivotal position among engineering materials today, though its use started as a cheap substitute for traditional materials after World War II. Modern age is rightly named as plastics age as plastics are replacing traditional materials like wood, metals and ceramics in almost all walks of life. In performance characteristics, application prospects and diversity they offer versatility not found in other types of materials. Plastics industry is now a multibillion dollar industry globally and the product range vary from construction materials to light emitting diodes. Plastics are part of a larger group called polymers and constitute a family of materials, not a single material, with each member of it having its own distinct and special advantages. For most practical purposes, a polymer may be defined as a large molecule built up by repetition of small, simple chemical units called monomers. The name polymer originated from the Greek word polymeros meaning many parts. There are different types of plastics. Plastics can be made hard, elastic rubbery, tough, crystalline, opaque, strong, stiff, and outdoor weather resistant, insulating or electrically conductive, biodegradable or practically any property that is desired, depending on the choice of the starting materials and the method of moulding [2]. Plastics fall into two main classes: thermoplastics and thermosets.

Thermoplastic materials consist of long molecules either linear or branched held together by weak van der Waal's forces. Thus they can be repeatedly softened and hardened by heating and cooling. During heating the forces weaken and it becomes soft and flexible and eventually flows as a viscous melt. When the material is cooled it solidifies again via vitrification or crystallization to give the desired shape. Thermoplastics can be reshaped any time by heating and cooling. Usually thermoplastics resins are available as pellets or can be formed, and then cooled, so that they harden into the final desired shape. No chemical changes generally take place during forming.

In thermosetting resins, reactive portions of molecules form cross-links between the long molecules during polymerization. The linear polymer chains are thus bonded together to form a three dimensional network. Therefore once polymerized or hardened, the material cannot be softened by heating without degrading some linkages. Thermosets are usually available as liquid monomer-polymer mixtures or a partially polymerized moulding compound. In this uncured condition, they can be formed to the finished shape with or without pressure and polymerized with chemicals or heat. In addition to the covalent bonds which join the atoms together, thermosets have covalent bonds which link the polymer chains one to another. These links are called crosslinks.

1.1.1 Amorphous, Crystalline and Semicrystalline Plastics

Polymers are large molecules with strong intermolecular forces and entangled chains. When cooled from molten state, different polymers exhibit different tendencies to crystallize at different rates depending on their chemical nature, structural regularity or molecular symmetry. Bulky pendant groups or short chain branches of different lengths hinder molecular packing and inhibit crystallization. Some polymers are amorphous and have very poor tendency to get oriented to ordered and oriented structures on cooling. In a crystalline polymer there are several crystalline and amorphous zones. Crystalline zones are made of intermolecular/intramolecular alignment or orderly arrangement of molecules or chain segments. Polymers showing a high degree crystallinity are termed crystalline polymers. The bulk properties are explained using interlamellar amorphous model in which stacks of lamella are interspaced with and connected by amorphous regions. Highly crystalline polymers are rigid, high melting, and less affected by solvent penetration. Crystallinity makes a polymer strong, but also lowers their impact resistance. Amorphous polymers are softer, have lower melting points, and are penetrated more by solvents than are their crystalline counterparts.

At low temperatures molecular motion in an amorphous region is restricted to molecular vibrations, but the chains cannot rotate or move in space. This form is the glassy state of the amorphous region. The glassy state can be thought of as being a supercooled liquid where the molecular motions have been frozen in. The glassy state is hard, rigid, and brittle like a crystalline solid, but retains the molecular disorder of a liquid. When the material is heated the polymer will reach a temperature at which segments (20 - 50 atoms long) of the entangled chains can move. At this temperature, called the glass transition temperature, the amorphous region becomes rubbery. When an amorphous polymer is in its rubbery state it is soft and flexible.

Semi-crystalline polymers have both crystalline and amorphous regions. Semi-crystallinity is a desirable property for most plastics because they combine the strength of crystalline polymers with the flexibility of amorphous polymers. Semi-crystalline polymers can be tough with an ability to bend without breaking; isolated lamellar single crystals are obtained by crystallization from dilute solution. When crystals are formed from the melt, chain entanglements are extremely important. In this case the solid is more irregular with polymer chains meandering in and out of ordered crystalline portions. The crystalline portion is in the lamellae; the amorphous portion is outside the lamellae. Polymers such as this are said to be semi-crystalline. The crystals are small and connected to the amorphous regions by polymer chains so there may be no sharp well-defined boundaries between the two types of regions. For some polymers, such as polyvinyl alcohol, there is a fairly distinct separation between the crystalline and amorphous regions, though. In other cases, the structure basically is crystalline with uniformly-distributed flaws and imperfections.

1.2 Commodity Plastics

The majority of synthetic polymers used nowadays are thermoplastics. Among this large category, the commodity plastics polyethylene (PE), polystyrene (PS), polypropylene (PP), and polyvinyl chloride (PVC) share 80% of the market volume. The largest group of commodity thermoplastics is polyolefins.

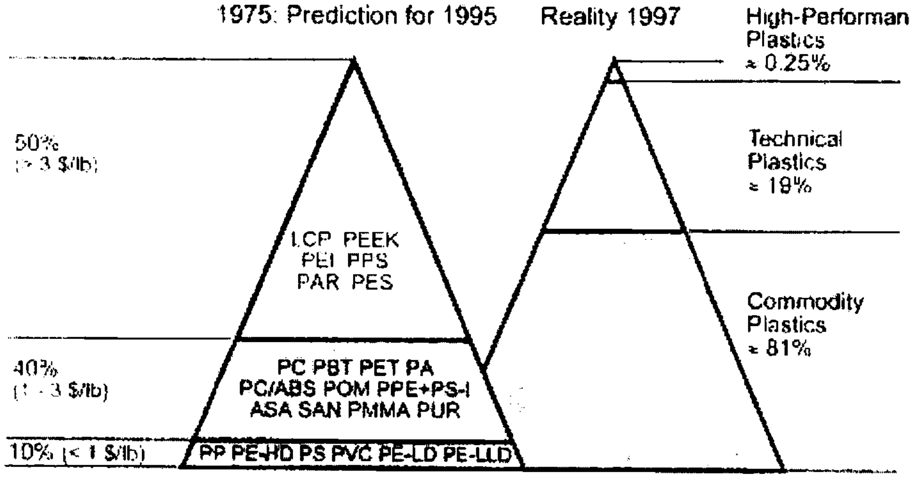


Figure 1.2 Commodity *Plastics – Market prediction and reality*

[G.W. Ehrenstein, Polymeric Materials, Hanser, Munich, 2001]

Though the predictions in 1975 were that engineering and high performance plastics are to rule the market, leaving only a 10% share for commodity plastics, the present day statistics shows that commodity plastics occupy a key position with more than 80% market share. The main reason is that processing techniques used for commodity plastics permit a fully automated, easy and reproducible manufacturing of a diversity of products in mass fabrication technology characterized by either continuous processing as in films, profiles, fibers or by short cycle times as in injection or blow moulding. The quest for new materials with special properties is met to a great extent by blending of thermoplastics with other plastics or elastomers and the melt processing technology of thermoplastics can be applied to such blends. Thus polymer blending is a very attractive option compared to development of new polymer materials.

1.2.1 Polyethylenes

Polyethylenes are the highest volume plastic in the world. Its high toughness, ductility, excellent chemical resistance, low water vapor permeability, and very low water absorption, combined with the ease with which it can be processed, make polyethylene of all different density grades an alternative choice for a variety of goods. Polyethylene is limited by its relatively low modulus, yield stress and melting point. Polyethylene is used to make containers, bottles, film and pipes among other things. It is an incredibly versatile polymer with large variety due to copolymerization potential, a wide density range, a molecular weight that ranges from very low to very high and the ability to vary molecular weight distribution (MWD).

Its repeat structure is ($-CH_2\ CH_2-$). Polyethylene homopolymer are made up exclusively of carbon and hydrogen atoms and just as the properties of diamond and graphite (which are also materials made up of entirely of carbon and hydrogen atoms) vary tremendously; different grades of polyethylene have markedly different thermal and mechanical properties. While polyethylene is generally a whitish translucent polymer, it is available in grades of density that range from 0.91 to 0.97 g/cm^3. The density of a particular grade is governed by the morphology of the backbone- long linear chains with very few side branches can assume a much more dimensionally compact, regular, crystalline structure. Commercially available grades are

- Low density polyethylene (LDPE)
- Linear low density polyethylene (LLDPE)

- High density polyethylene (HDPE)
- Ultra high molecular weight polyethylene (UHMWPE)

Generally, yield strength and melt temperature increase with density, while elongation decreases with increased density.

Low density polyethylene is formed by a free radical polymerization mechanism when high temperature and high pressure polymerization is used. Because of these extreme reaction conditions many branches are formed, which are quite long and hence close packing of the chains are prevented. The crystallinity is low of the order of 40% and the structure is highly amorphous. This material is one of the most widely used plastic accounting for more than 20%of the plastic consumption. Its major application is in packaging films and its outstanding dielectric properties permit its wide acceptance as an insulator. Domestic wares, tubing, squeeze bottles, cold water tanks etc are also made from this.

High-density polyethylene is one of the highest volume commodity plastics produced in the world. The most common method of processing high-density polyethylene is blow moulding, where resin is turned into bottles (especially for milk and juice), house wares, toys, pails, drums and automotive gas tanks. It is also commonly injection molded into house wares, toys, food containers, garbage pails, milk crates and cases. HDPE films are commonly found as bags in supermarkets and departmental stores and as garbage bags.

When low temperatures and pressures are used during polymerization process, branching is less prominent and a linear polymer with a few short branches is obtained. Commercially two polymerization methods are most commonly practiced: one involves Phillips Catalyst (chromium oxide) and the other involves Ziegler Natta Catalyst systems (supported heterogenous catalysts such as titanium halides, titanium esters and aluminium alkyds on a chemically inert support such as polyethylene or polypropylene). Molecular weight is governed by primarily through temperature control with elevated temperature resulting in reduced molecular weights. The catalyst support and chemistry also play an important factor in controlling molecular weight and molecular weight distribution.

1.2.2 Polypropylene

Polypropylene is an extremely versatile plastic and is the lightest homopolymer known. PP is produced from propylene polymerization using Ziegler-Natta catalyst. The presence of methyl group leads to products of different tacticity, ranging from completely isotactic and syndiotactic structures to atactic molecules. The isotactic type is comparatively more rigid, stiff and stronger than HDPE. Its melting point is nearly 50^0C higher than the melting point of HDPE. Having a much higher concentration of tertiary carbon atoms in its chain, PP is much more prone to oxidation or ageing than HDPE and LDPE. The high melting point of PP allows the moulded articles to be steam sterilized. PP is brittle close to 0^0C and hence inferior to HDPE for low temperature applications. Its low density combined with stiffness, strength, fatigue and chemical resistance makes it attractive for moulding crates, machine parts, car components, chairs, tool handles, cabinets, etc. Its excellent fatigue resistance is used for moulding integral hinges as in accelerator pedals. Ropes, carpet backing and packaging films are also produced from this.

1.2.3 Polystyrenes

1.2.3.1 General Purpose Polystyrene

Polystyrene is a highly popular commodity plastic along with PE, PP and PVC. Its popularity is due to its transparency, low density, relatively high modulus, excellent electrical properties, low cost and ease of processing. The outside housing of the computer, model cars and airplanes, foam packaging and insulation, plastic drinking cups, toys, and the housings of things like hairdryers, and kitchen appliances are all made of polystyrene. Polystyrene is a vinyl polymer. Structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom. Polystyrene is produced by free radical vinyl polymerization, from the monomer styrene. The steric hindrance caused by the presence of bulky benzene side groups results in brittle mechanical properties, with ultimate elongations only around 2 to 3 percent depending upon molecular weight and additive levels. Most commercially available polystyrene grades are atactic and in combination with the large benzene groups, results in an amorphous polymer. The amorphous morphology provides not only transparency but the lack of crystalline regions also means that there is no clearly defined temperature at which the plastic melts. Polystyrene is a glassy solid until its T_G of ~100°C is reached, whereupon further heating softens the plastic gradually from a glass to a liquid. Also the lack of a heat of crystallization means that high heating and cooling rates can be achieved. These reduce cycle time and thus increase the process economy. Upon cooling, polystyrene does not crystallize. This gives polystyrene low shrinkage values (0.004 to 0.005mm/min) and high dimensional stability during moulding and foaming operations. Commercial polystyrene is segmented into easy flow, medium flow and high heat resistance grades.

1.2.3.2 High Impact Polystyrene

The styrene family is well suited for applications where rigid, dimensionally stable molded parts are required. Polystyrene is a transparent, brittle, high modulus material with a multitude of applications, primarily in packaging, disposable cups, and medical ware. When the mechanical properties of polystyrene homopolymer are modified to produce a tougher, more ductile blend as in the case of rubber modified high impact grades of polystyrene(HIPS), a far durable molded items including radio, television and stereo cabinets as well as compact disc jewel cases etc. Polybutadiene and polystyrene homopolymers don't mix. HIPS is a graft polymer. So the polybutadiene branches try as best they can to phase separate, and form little globs. But these little globs are always going to be tied to the polystyrene phase. So they have an effect on that polystyrene. They act to absorb energy when the polymer gets hit with something. They give the polymer a resilience that normal polystyrene doesn't have. This makes it stronger, not as brittle, and capable of taking harder impacts without breaking than regular polystyrene.

1.3. Plastics Blends

The last decade has seen intense activity to tailor new plastic materials in the form of blends or alloys using melt processing equipment. This approach is more advantageous than production of materials in the polymerization reactors. The annual growth rate of blends is about 10% whereas the growth rate for plastics alone is 3%.Polymer blends are mixtures of homopolymers or copolymers of different molecular structure. Immiscible polymer blends possess a minor phase that may undergo severe deformation and acquire an anisometric configuration during melt processing. This results in a structure characterized by a distribution of shape factor ratios, concentration and orientation throughout the thickness of the moulded part. For immiscible polymer blends addition of a compatibilizer is found to reduce the interfacial tension and the size of the dispersed phase so that better mechanical properties are achieved [3-9].

The imperatives that encourage one to go for blending are (a) To maintain a more favorable cost-performance ratio, and (b) to achieve reinforcement of a desired property. An expensive polymer whose property spectrum is much higher than is needed for a specific application is blended with an inexpensive polymer with a property spectrum of a level that makes the blend suitable for the application at an attractive cost performance ratio. Also the demerits from a poor property of a polymer may be effectively overcome by blending it with another which has a higher property value. Thus available polymers can be selected appropriately and blended to get the desired properties without having to develop new polymers and thus investment in new plants can be done away with.

The ultimate behaviour of blends depend on (1) The extent of phase separation (2) Nature of phases provided by the matrix material (3) Character of the dispersed phase (4) Interaction between the component polymers.

The physical properties of blends can be altered to satisfy a wide range of applications. A desirable performance can be achieved by proper selection of blend ingredients, followed by control of morphology by appropriate methods of compatibilization, compounding and processing. Blending is known to improve the impact strength, mechanical properties, chemical and solvent resistance to enhance processibility, abrasion resistance flame retardancy etc. Improvement in processability is becoming the most important criteria as the emphasis is shifting to high performance, difficult to process specialty resins. The processing temperature, *Tp* can be above the thermal degradation temperature and blending can reduce the processing temperature by about 60 ^{0}C.

Once the blend components are selected, the properties can be controlled by morphology (which depends on the molecular parameters of the components) and composition, as well as by the compounding and processing methods. In the case of amorphous blends, the morphology is defined by the size and shape of the two phases, their distribution and orientation. This type of morphology is referred to as macro morphology. In blends of semicrystalline polymers, blends affect the crystallinity. This is referred to as micro morphology.

Macro and micro morphology depends as the thermodynamic and rheological properties of the ingradients and the methods of compatibilization as well as on the deformation and thermal histories. The macro morphology of polymer blends describes the form and size of the macromolecular phases formed during compounding or blending. A great majority of polymer blends are immiscible due to the negligibly small entropy of mixing.

The miscibility of two polymers is determined by the free energy of mixing which includes both entropic and enthalpic terms [3].

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$= \Delta E_{mix} + P\Delta V_{mix} - T\Delta S_{mix}$$

Flory-Huggins theory is the classical theory for calculating the free energy of mixing. Originally derived for small molecule systems, it assumed that each molecule occupied one site on a lattice. The theory was expanded to model polymer systems by assuming that the polymer consisted of a series of connected segments each of which occupied one lattice site. Assuming that the segments are randomly distributed, the free energy of mixing per mole of lattice sites for a mixture of polymer A and polymer B is:

$$\frac{\Delta G_{mix}}{RT} = \left(\frac{\phi_A}{N_A}\right)\ln\phi_A + \left(\frac{\phi_B}{N_B}\right)\ln\phi_B + \chi_{FH}\phi_A\phi_B$$

where R is the gas constant, Φ the volume fraction and χ the Flory-Huggins interaction parameter. The first two terms on the right hand side of the equation represent the combinatorial contribution to the entropy of mixing, which is derived by calculating all the different ways that chains can randomly pack on a lattice. In the original theory, the entropy of mixing was assumed to be purely combinatorial, but it has been known for many years now that non-combinatorial contributions are also important in polymer systems. These are variously known as free volume effects, equation of state effects, and packing effects. Once the Flory-Huggins χ parameter (which, in classical Flory - Huggins theory, includes only the enthalpic contribution to the free energy of mixing) is known, the entire phase behavior of the system can be calculated.

For most polymer blends, the Flory - Huggins binary thermodynamic interaction parameter is large $\chi > 0$, engendering low degree of molecular entanglement in the interfacial region. As a result the interfacial adhesion as both molten and solid state is poor. For uncompatiblized blends the solid state properties (ultimate elongation) versus composition show a strong negative deviation from additivity rule. Preparation of commercially viable blends must involve compatibilization, by means of compatibilizer addition or reaction blending. Thermodynamics should allow for prediction of miscibility of polymers. The necessary condition for phase separations is

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2{}^2}\right)_{T,P} = 0$$

where G_m is the Gibb's free energy of mixing. For miscibility $\Delta G_m < 0$ at the same time the configurational entropy of mixing is $\Delta S_m \geq 0$. The only way to achieve homogeneous blend is to secure specific mer 1 mer 2 interactions. These interactions can be ionic or dipolar in nature. Polymer miscibility decreases with T and increases with P.

For miscible blends the property of the blend is given by

$$P = P_1 \Phi_1 + P_2 \Phi_2 + I \Phi_1 \Phi_2$$

Where P is the property of interest, Φ is the concentration and I is the interaction parameter which can be positive, negative or zero based on which the blend property can be synergistic, antisynergistic or additive [9].

For immiscible systems

$$\frac{P}{P_1}=\frac{1+AB\phi_2}{1-B\varphi\phi_2}$$

A depends on the shape and orientation of the dispersed particles and upon the nature of the interface. It can vary from zero to infinity. B depends on the value of the properties of the components and is defined by

$$B=\frac{\frac{P_2}{P_1}-1}{\frac{P_2}{P_1}+A}$$

P_1 – property of the continuous or matrix phase, P_2 – property of the dispersed phase. φ - reduced concentration term which is function of the maximum packing fraction ϕ_m.

Since it is impossible to pack particles so that there is no void space between them, particles appears to occupy a volume which is greater than their true volume. The maximum packing fraction is defined as

ϕ_m =True volume of particles/Apparent volume of particles or

ϕ_m = Bulk density/ True density of the particles

φ is defined as

$$\varphi=1+\left[\frac{1-\phi_m}{\phi_m{}^2}\right]\phi_2$$

when $\phi_m = 1$ $\varphi = 1$ at all concentrations

When these are two continuous phase like interpenetrating network mats and felts filled with air etc. the properties are predicated by

$$P^n = P_1^n\ \phi_1 + P_2^n\ \phi_2 \quad (n \text{ between -1 and 1})$$

when $n = 0$ the equation can be written as

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

Plastics will continue to be one of the world's fastest growing industries, ranked as one of the few billion dollar industries. Its three major processing methods are injection moulding, extrusion and blow moulding. Approximately 32% by weight of all plastics go through injection moulding machines, 36% through extruders and 10% blow moulding machines (extruder and injection moulding types).

1.4 Plastics Processing

Plastics are the most versatile of all known materials today and have therefore established themselves in an enviable position from where they are not even possible to be displaced. Ease of processing is one of the most important properties of plastics which helped in retaining the prime position of thermoplastic. The most important processing methods for conversion of plastics to end products are

1. injection moulding
2. extrusion
3. compression moulding
4. blow moulding
5. thermoforming.

1.4.1 Injection moulding

The injection molding process is one of the most important polymer processes by which polymer resins are converted into useful finished products [10-17]. A wide variety of complex geometry articles varying from very small parts such as precision gear wheels to relatively large parts such as exterior and interior automotive parts like bumpers can be produced. Injection moulding is so versatile that parts as small as a fraction of a gram and as large as 150 kg are successfully produced in large tonnage automatic machines. Production is at high frequency with virtually no wear of the processing machinery. High production rate, short cycle times and small percentage of scrap are further attractions. During this process, molten plastic is forced (injected) into a mould and cooled until the melt solidifies. When the part is cooled sufficiently, the mould is opened, the part is ejected from the mould and the mould is closed again to repeat the cycle.

The original injection moulding machines were based on the pressure die casting technique for metals. The first machine is reported to have been patented in the United Sates in 1872, specifically for use with the celluloid. This was an important invention but probably before its time because in the following years very few developments in injection moulding processes were reported until the 1920s.

The next major development in injection moulding, i.e. the introduction of hydraulically operated machines, did not occur until the late 1930s when a wide range of thermoplastics started to become available.

In principle injection moulding is a simple process. The thermoplastic material, in the form of granules or powder, is taken from a feed hopper and plasticized in a single screw extruder, and the molten polymer accumulates at the tip of the reservoir. This melt is pushed forward by the screw whose displacement is controlled by the hydraulic pressure. The melt flows through the nozzle, which connects the extruder to the mould, passes through the sprue, along the runner, through the gate and into the mould cavity. The sprue is designed to offer as little resistance to flow as possible while minimizing the amount of wasted polymer. The runner is designed to carry melt to the mould cavity. The gate represents the entrance to the mould and its location is of utmost importance to the appearance of the part. The gate is to be made as small as possible for cosmetic reasons as well as for facilitating the separation of the part from the rest of the material solidified in the runner. The melt enters the cold cavity where it begins to solidify as it touches the cold wall. As semicrystalline polymers solidify, they shrink as a result of increase in density. Pressure is maintained during the cooling process to ensure that the melt continues to flow into the mould. Once solidification is complete the mould plate opens and the part is ejected. Although the screw is being pulled back, it rotates plasticating more polymer. Mould filling involves high deformation and high cooling rates. A considerable amount of orientation and structure or morphology can be developed in an injection moulded part. There is a distribution of shrinkage with a local maximum and the shrinkage distribution depends on the flow velocity and there is variation in the flow and transverse direction.

The shrinkage distribution and hence the orientation is described by the fountain flow model proposed by Tadmor [12] as given in Figures 1.3, 1.4 and 1.5. As the melt leaves the gate, the flow front occupies various positions in the mould at different times. The flow at the front is stagnation flow and the flow well behind the front is shear flow. A fluid element near the centerline will decelerate as it approaches the front and become compressed along the x direction and stretched along the y direction. The element is stretched further at the front and laid up on the wall where it rapidly solidifies in a highly oriented state. The fountain flow associated with the advancing front is extremely important to the properties of materials made by injection moulding. In the case of blends, extensional flow at the front leads to a morphology in which the minor component exists as fibrils.

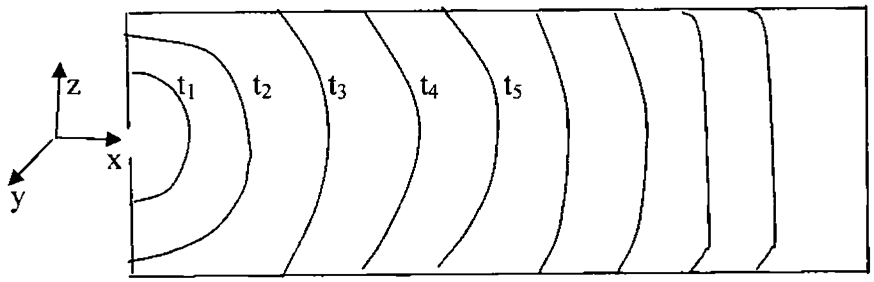
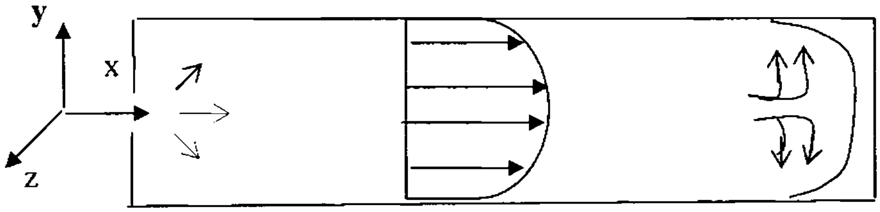


Figure 1.3 *Flow Patterns in an end gated mould-top view of Flow front as a function of time at t =* t_1, t_2, t_3, t_4, t_5



Fully developed region

Front region
Fountain effect

Figure 1.4 *Side view of velocity profile*

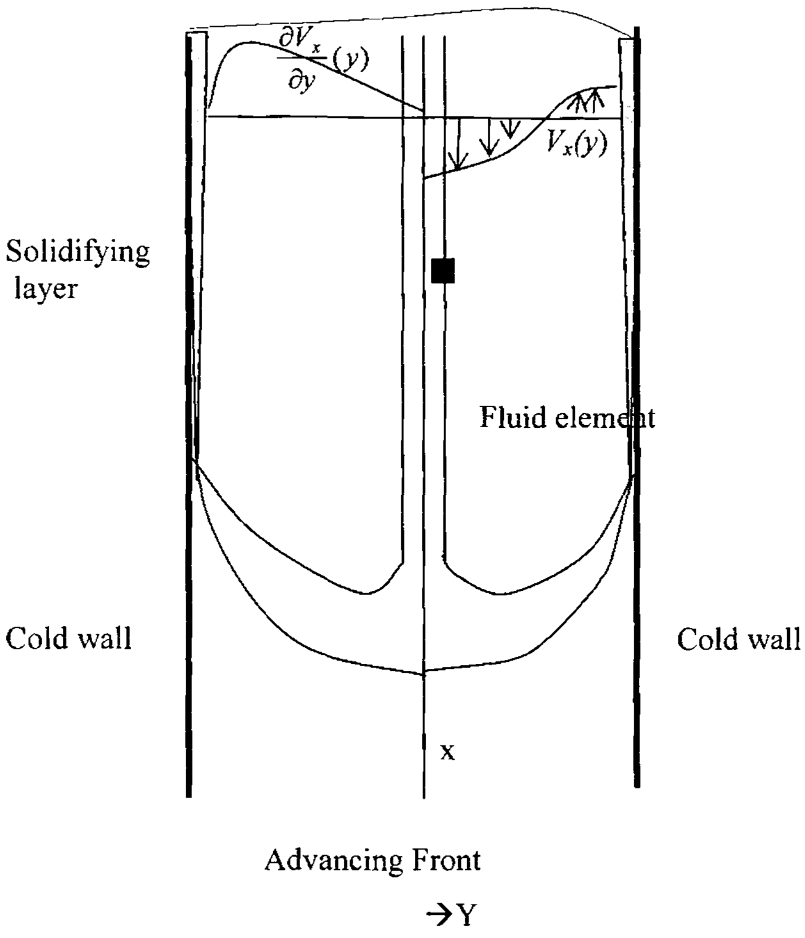


Figure 1.5 *Flow patterns in the advancing front for flow between two parallel plates*

Pressure is maintained during the cooling process to ensure that the melt continues to flow into the mould. Once solidification is complete the mould opens and ejects the part. The major advantages of the process include its versatility in moulding a wide range of products, the ease with which automation can be introduced, the possibility of high production rates and the manufacture of articles with close tolerances. The basic injection moulding concept can also be adapted for use with thermosetting materials. Once the cavity is filled additional material is forced into the cavity to compensate for an increasing polymer density arising from crystallization and compressibility of the melt.

1.4.1.1 Quality of moulding

The moulded item may contain a range of defects which include weld lines, sink marks, internal voids, and flash lines and locked – in strains.

1.4.1.2 Orientation and Anisotropy

When a polymer melt is forced along channels and into mould cavities there is a tendency for the molecular chains to become aligned. This is referred to as orientation and causes anisotropy in the component. In general therefore orientation effects are undesirable although they can seldom be avoided.

1.4.1.3 Shrinkage

Shrinkage is the main problem in precision moulding. It is defined as the difference between the dimensions of the cold mould and the dimensions of the cooled moulding. The result of this is that in addition to the shrinkage effects, if the plastic is crystalline then there will be shrinkage due to the closer packing of the molecules in the crystalline state. Hence the shrinkage of these materials is high, typically 1-4% as compared with 0.3 – 0.7% for amorphous materials.

1.4.1.5 Injection pressure

Injection pressure has an important influence on shrinkage. By using high pressures it is possible to compensate for the dimensional changes which occur in the material due to crystallization and thermal contraction, thus reducing the shrinkage.

1.4.1.6 Hold – on time

The time during which the screw remains forward also has an important effect on shrinkage. The maximum beneficial hold- on time for a particular component may be determined gradually increasing the hold- on time until the weight of the moulding reaches a maximum.

1.4.1.7 Gate size

Increasing the gate size will reduce the shrinkage because it increases the time taken for the gate to freeze of. This in turn increases the time during which the injection pressure is available to compensate for shrinkage.

1.4.1.8 Mould temperature

Higher mould temperatures will increase the time taken for the gate to freeze off. This is one method therefore of overcoming mould filling problems due to small gates.

1.4.1.9 Part thickness

Thick sections in a moulding reduce the cooling rate and promote crystallization. Shrinkage will therefore increase as the part thickness increases.

1.4.1.10 Melt temperature

In general the effect of melt temperature on shrinkage is relatively small. Attempts to remedy shrinkage problems by adjusting melt temperature are generally unproductive and not recommended.

1.4.1.11 Warpage

Warpage occurs as a result of unequal moulded in stresses and strains in the component. It can be caused by poor part design, poor mould design or incorrect moulding conditions.

1.4.1.12 Annealing

If a moulded article has an unacceptable level of moulded – in strain due to shrinkage and orientation, annealing may be necessary. The purpose of annealing is to accelerate the relaxation of the material, thereby reducing the level of internal stresses and stabilizing the part dimensions.

1.5 Weld lines

In the case of injection moulding of large parts, multigated mould cavities are necessary in order to avoid freezing of the polymer before the cavity is completely filled. In this case, the finished product will invariably contain weld lines which will form when the polymer flow fronts from the different gates meet during the filling process [18- 38]. Weld lines are also present when the mould cavity contains inserts around which the flow front is divided and then recombined at the opposite side of the insert.

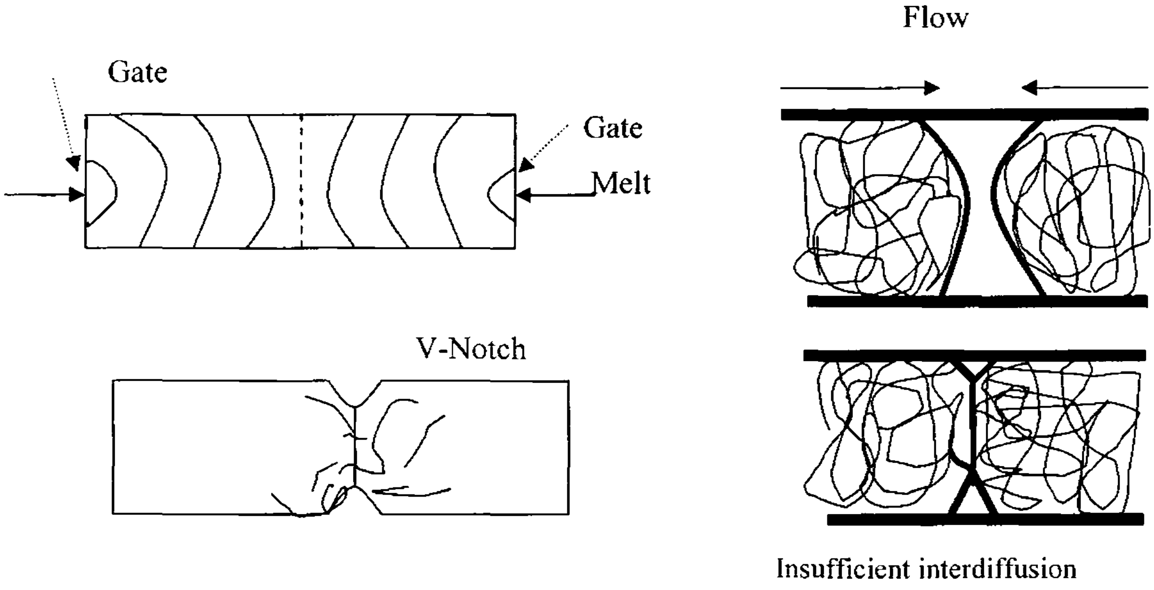


Figure 1.6 *Causes of formation of weld line*

Gate position can have an important bearing on whether or not welds will occur. For example for an injection moulded cup will have a weld line as the flow separates at the gate to flow in opposite directions around the circumference. If the cup was gated at the centre of the base then the melt would spread out uniformly and no weld would occur. If welds are unavoidable then their strength can be improved by ensuring sufficient temperature and pressure at the interface to facilitate welding. Venting at a known weld location will also ensure that there are no trapped air pockets which would cause voids.

Simulation of injection moulding process can be done to predict cavity layout, fill rate gate location, weld line position, cooling time, molecular orientation, warpage and shrinkage. Computer programs are available for specific applications. The presence of weld lines is accounted in the simulation by appropriate use of boundary conditions.

The basic equations of continuity, momentum and energy for flow of molten polymer into a thin rectangular cavity can be written to model the injection moulding system [11].The velocity field is considered to consist of two components, v_x and v_y that depend primarily on z but not on x or y ($\partial v_x/\partial x \langle\langle \partial v_x/\partial z$).

The Equation of motion becomes

$$0=\frac{\partial}{\partial z}\left(\eta\frac{\partial v_x}{\partial z}\right)-\frac{\partial p}{\partial x}$$

$$0=\frac{\partial}{\partial z}\left(\eta\frac{\partial v_y}{\partial z}\right)-\frac{\partial p}{\partial y}$$

where η is the viscosity which is in the form $\eta=\eta(\gamma,T)$

where $\gamma=\sqrt{\left((\frac{\partial v_x}{\partial z})^2+(\frac{\partial v_y}{\partial z})^2\right)}$

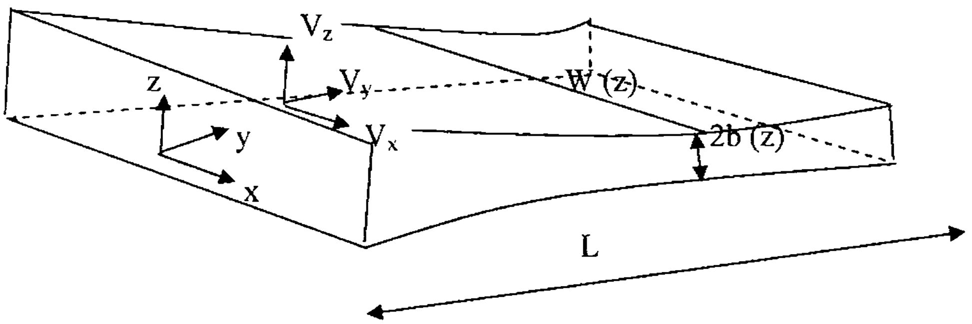


Figure 1.7 *basic flow elements for flow equations-The planar element*

The continuity equation is of the form

$$0 = \frac{\partial}{\partial x}(bv_x) + \frac{\partial}{\partial y}(bv_y)$$

where b is the half thickness. The equation of energy is

$$\rho C_p\left(\frac{\partial T}{\partial t} + v_x\frac{\partial T}{\partial x} + v_y\frac{\partial T}{\partial y}\right) = k\frac{\partial^2 T}{\partial z^2} + \eta\gamma^2$$

These equations can be solved by the boundary conditions:

$$\text{At } z = b\text{: } v_x = v_y = 0; \quad T = T_w$$

$$\text{At } z=0\text{: } \frac{\partial v_x}{\partial z} = \frac{\partial v_y}{\partial z} = 0 = \frac{\partial T}{\partial z}$$

The solution of equation of motion is as follows.

$$\eta\left(\frac{\partial v_x}{\partial z}\right) = \left(\frac{\partial P}{\partial x}\right)z$$

$$\eta\left(\frac{\partial v_y}{\partial z}\right) = \left(\frac{\partial P}{\partial y}\right)z$$

These equations can be modified as

$$\frac{\partial}{\partial x}\left(S\frac{\partial p}{\partial x}\right)+\frac{\partial}{\partial y}\left(S\frac{\partial p}{\partial y}\right)=0 \quad \text{where } S=\int_{0}^{b}\frac{z^{2}dz}{\eta}$$

The boundary conditions become

Along the advancing front: $p = 0$

At the entry to the mould: $p = p_e(x, y, t)$

At the mould wall: $\partial P/\partial n = 0$

In the case when a **weld line** is present, the **boundary conditions** are that the pressure and normal velocity be continuous, that is

$$P^{+} = P^{-}$$

and

$(S\,\partial P/\partial n)^{+} = -(S\,\partial P/\partial n)^{-}$ where + and – signs denote the values on either side of the weld line. The viscosity is expressed in terms of a power law model.

Once the cavity is filled additional material is forced into the cavity to compensate for an increasing polymer density arising from crystallization and compressibility of the melt.

It is well known that the weld lines are a potential source of weakness and are characterized by poor mechanical and optical properties. The weakness of the product is attributed to several reasons.

(1) The advantages of flow orientations are lost because of the molecular orientation at the weld, which is perpendicular to the weld. There is deformation of polymer after the collision of the two melt fronts and the orientation of the molecules will be along the weld line rather than across it.

(2) There is stress concentration at the weld line caused by a V notch formed at the surface when the two melt fronts meet.

(3) Insufficient interdiffusion between the two melt fronts, reducing the number of molecular entanglements.

The effect of processing parameters on the morphology and mechanical properties of particular polymers has been an active area of interest [25-31]. The problem is complex since the materials range from amorphous to highly crystalline and includes homopolymers, copolymers and blends. The morphology and mechanical properties of weld lines are very much affected by the way in which they are processed. The processing parameters of importance in injection moulding which would affect weld line strength are the following.

(i)The Melt temperature

The ability of a material to heal the weld region is determined by the ability of the molecules to reestablish the level of molecular entanglements that are characteristic of the bulk material. The chain segments gain increased ability to flow with an increase in temperature. The diffusion coefficient increases with increase in temperature and the distance of diffusion of the molecules increases giving better molecular entanglements. For strength equal to that of the bulk better interpenetration at the higher temperature is desirable.

(ii) The Temperature of the Mould

The temperature of the melt should remain high enough for sufficient time for the segments of the chain to become entangled. This is made possible by having a high mould temperature so that the melt will not cool too rapidly. This can greatly affect the morphology at the weld region.

(iii) Injection Pressure

High pressure of injection is reported to affect the weld quality, but its importance is not significant as that of temperature.

(iv) Speed of Filling Mould Cavity

The melt begins to cool as soon as it enters the mould cavity. It becomes more difficult to heal at the molecular level as the temperature falls. The filling of the mould cavity as rapidly as possible will minimize the cooling at the weld front.

Though the presence of weld lines was recognized from the beginning, the fabricators were interested only in the elimination of the surface markings associated with it.

A number of rules of thumb were developed to minimize the undesirable effects of weld lines without any systematic investigation. Some of the recommended remedies were:

1. Gate the mould so as to minimize the flow around an insert.
2. Provide venting at the weld line
3. Increase part thickness at the weld line
4. Increase cylinder temperature, screw back pressure and screw speed
5. Increase injection pressure and speed
6. Open gate to reduce restriction of flow

There were limited amount of information about the strength of weld lines of different materials provided by manufacturers like the strength at the weld line is 90 % of the bulk etc. Boundy et al [36] recognized the vital importance of weld lines and they denoted the name 'hot weld line' for weld lines formed by inserts and 'cold weld lines' for directly impinging flow fronts. They reported that for polystyrene for cold weld lines the strength is 50% and for hot weld lines it is 75%. The impact strength of PVC and ABS was reported by Hubbauer [37] and the effect of injection pressure was also investigated. Morphology and mechanical properties of ABS type materials were reported by Hagerman [25]. He attributed the weld line weakness to lack of mechanical mixing and diffusion at the interface. A volcano flow pattern which produced a flow orientation perpendicular to the direction of flow was reported and he noticed a v notch at the interface. He concluded that the weld process placed a stress concentrator, the entrapped air groove, at a point which had an orientational and structural flaw. Hobbs [18] investigated the effect of melt temperature and mould temperature on the strength and morphology of PP.

So many parameters are found to influence the weld line strength. In the case of homopolymers both amorphous and semicrystalline, the mechanical properties of welded regions are found to be sensitive to processing conditions. Malaguarnera and Manisali [19, 20] have studied the effect of melt temperature, mould temperature, injection speed and injection pressure on the tensile properties of commercial grades of polystyrene (PS), high impact polystyrene (HIPS) and polypropylene (PP). They found the most important processing parameters are melt temperature and mould temperature. A number of studies have focused on the effect of processing parameters like melt temperature, holding pressure, holding time, injection velocity and mould temperature on the weld line strength. Depending on the material each of the above parameters are found to influence the weld line strength to various degrees.

The melt temperature is the most important parameter influencing the weld line strength. In general it is reported that high melt temperature, high holding pressure and high mould temperature increases the weld line strength. The processing parameters beneficial to the molecular diffusion across the weld line increase the weld line strength. Other techniques such as tooling modifications [39] mould line feed injection moulding process [40] and shear controlled orientation in injection moulding for improvement of weld line strength [41] were also investigated. Besides processing parameters the weld line strength depends on the properties of materials. For unfilled polymers, the lowest weld line strength was obtained for brittle amorphous polymers and rod like polymers like polystyrene (PS), polymethyl methacrylate (PMMA), Acrylonitrile-butadiene styrene (ABS), Acetal etc. Higher values are obtained for ductile amorphous or crystalline polymers such as polypropylene (PP), polyethylene (PE), polyethylene terepthalate (PET), polyvinylchloride (PVC) and polycarbonate (PC). Using PMMA having different molecular weight, Mennig [30] found that the weld line strength decreases with increasing molecular weight. This finding is in line with that of the model developed by Kim and Suh [29].

V notch formation in amorphous polymers is attributed to a viscosity increase in the outermost layer of the moulding. For semi crystalline polymers, the situation is more complicated. The degree of crystallinity, the size and distribution of crystallites in the weld line region do also have important effects on the weld line strength. The effect of processing parameters like mold temperature, melt temperature, cooling rate and injection pressure is however found to be similar to that observed for amorphous plastics. The more pronounced shrinkage of the semi crystalline polymers as compared to amorphous ones is found to have an important effect on the V notch formation. The pressure of inhomogenities is also found to affect weld line strength through nucleation of crystallites.

The surface defects associated with weld lines have two origins, an incompletely filled cavity and differential shrinkage during solidification and cooling.

1.6 Weld lines in the Injection Moulding of Plastics Blends

In the case of processing of plastics blends, even when weld lines are not present the specific features of heterophase systems such as morphology, size of dispersed phase, and interphase interactions are to be considered along with the effect of processing parameters considered for homopolymers. Morphology and dispersed phase size are highly influenced by processing conditions. Min and White [42] found that the variation of blending temperature [180 to 240 ^{0}C] during extrusion, for polyethylene with different molecular weight has a slight influence on the morphology of PE/PS blends. The increase of shear rates induced a fine morphology. Han and coworkers [43] have studied the injection moulding of HDPE/PS blends and PS/PP blends. After optimizing the moulding conditions for the studied systems, they investigated the influence of the mode of preparation on the state of dispersion of the minor phase in the blend. They concluded that the state of dispersion of the components has a great effect on the mechanical properties of two phase systems. Paul and coworkers [8] studied the mechanical properties of injection moulded and compression moulded PE/PS/copolymer blends. As copolymer is added the ductility is improved but yield stress and modulus are found to decrease. There is a difference in properties of the samples moulded by compression and injection which are due to the crystallinity and orientation induced during moulding.

In the case of multiphase systems the presence of weld lines has an even larger impact on the properties of blends arising to the incompatibility of most polymers. [44-58]. In addition the morphology obtained near the weld line also has a great effect on the final properties of the blends [52-55]. However very few publications only are available in literature reporting the effect of weld lines on the mechanical properties of the polymer blends. Mekhelief et al suggested a model to predict the weld line behavior of immiscible blends and verified it experimentally for HDPE/PC [50]. The degree of bonding near the interface was predicted by a diffusion model based on Flory-Huggins theory. Effect of adding an in situ compatibilzer for PA/EPR blends is discussed by Jin Kon Kim [51]. Use of an in situ compatibilizer altered the flow induced morphology and the morphology of the dispersed domain. The injection moulded blend exhibited traditional skin core morphology which was strongly affected by the amount of the compatibilizer EPR-M. The orientation and deformation of the dispersed phase was reduced at the weld line with increasing amount of EPR-M. Fellahi and Fisa [52, 53] investigated the morphology and mechanical properties of PA6/HDPE blends with a compatibilizer. Their study revealed a skin/core effect, a diminution of the thickness of the skin and weld line region with interfacial modification and reduction in size of the minor phase. Use of compatibilizers is found to increase the weld line strength for PS/PE systems [56]. There was an optimum copolymer concentration where the strength of the weld lines was maximum. The copolymer was found to induce important changes in the morphology of the blend. The interdiffusion of the polymer fronts in the weld region was also improved by the presence of the copolymer. A modified model prediction and experimental verification for PS/PMMA blends is reported by Shaoyun Guo et al [49]. This model based on Flory-Huggins theory takes into account the diffusion thickness which is a function of injection pressure and contact time.

1.7 Models Available for Amorphous Polymers and their Blends

Kim and Suh [29] have developed a model for the prediction of weld line strength as a function of temperature and cooling time for glassy and amorphous polymers. Assuming that diffusion at the weld line is only due to pure diffusion of the molecules across the interface; the strength of the weld line is given in terms of degree of bonding defined as the ratio of bonded area to the total area at time t as

Degree of bonding

$$\frac{\sigma_w}{\sigma_b} = \frac{A_0 - A_N}{A_0}$$

where σ_w and σ_b are the tensile strength of the injection moulded part with and without weld line respectively, A_0 is the initial cross sectional area, A_N is the non bonded area and A_0 -A_N is the bonded area at the specific contact time.

The rate of diffusion at the interface is given by Fick's law.

From Fick's Law

$$\frac{dA}{dt} = C\frac{D\Delta G}{kT}$$

where C is the limit of the equation when T tends towards T_g. D is the diffusion coefficient and k is the Boltzmann constant. ΔG is the free energy difference between intermediate adhesion step and complete adhesion and it represents the potential of adhesion by diffusion. ΔG can also be expressed in terms of the sum of the surface energy of the unbonded area and the configurational entropy of mixing ΔS_m as,

$$\Delta G = -2\gamma A - T\Delta S_m$$

where γ is the surface tension and

$$\Delta S_m = -kA\partial x\partial n_0 \ln\frac{1}{2}$$

Combining these equations the degree of bonding can be obtained as a function of temperature and time as

$$\frac{\sigma_w}{\sigma} = 1 - \exp\left[\frac{-CD}{kT}\left(2\gamma - kT\partial x\partial n_0 \ln\frac{1}{2}\right)t\right]$$

The self diffusion coefficient D as a function of the viscoelastic parameters of the material is given by [29, 49, 50, 59-61]

$$D = \frac{(\rho RT)^2 R_g{}^2 M_c(T)}{135 G_N{}^0 M_W{}^3 \eta_0(T)}$$

where G_N^0 is the plateau modulus which can be computed as $\rho RT/M_e$ where M_e is the entanglement molecular weight ($M_e=M_c/2$), ρ is the density, R is the gas constant, T is the absolute temperature. η_0 is the zero shear viscosity at temperature T and critical molecular weight M_c, R_g^2 is the radius of gyration which is the mean square end to end distance , M_W is the molecular weight and $M_c(T)$ the critical molecular weight of entanglement at temperature T. Rg^2/M_w is essentially constant for any bulk polymer. All these viscoelastic parameters are available from standard references.

The self diffusion coefficient can also be calculated as

$$D\eta = (A\rho kT/36)R^2/M$$

The mouldability of a polymer depends on the rheological and thermal properties. For a given mould and fixed moulding conditions of melt temperature T, injection pressure P, and mould temperature T_m, the ease of flow into the mould is determined by the limiting distance of diffusion$\langle l^2 \rangle$, which is also called the quadratic distance of diffusion. The value of $\langle l^2 \rangle$ depends on the temperature dependence of viscosity and its thermal diffusivity. $\langle l^2 \rangle$ can be large if either the viscosity is low or thermal diffusivity is low. If $\langle l^2 \rangle$ is large because of low values of thermal diffusivity, then cycle times have to be excessively large to permit solidification. The distance of diffusion depends on the diffusion coefficient D which is related to molecular weight (M_W) as $D \infty M_W^{-2}$ .This is in accordance with reptation theory for entangled polymer systems. According to this theory, each polymer chain is confined to a tube surrounding its own contour, whose walls are made up by neighbouring chains. The diffusion of the polymer chain is assumed to proceed primarily by reptation, which is similar to the motion of snakes as they move through a fixed set of obstacles. This diffusion path is the one that offers the least resistance, since the tube walls impede the lateral motions of the polymer chain.

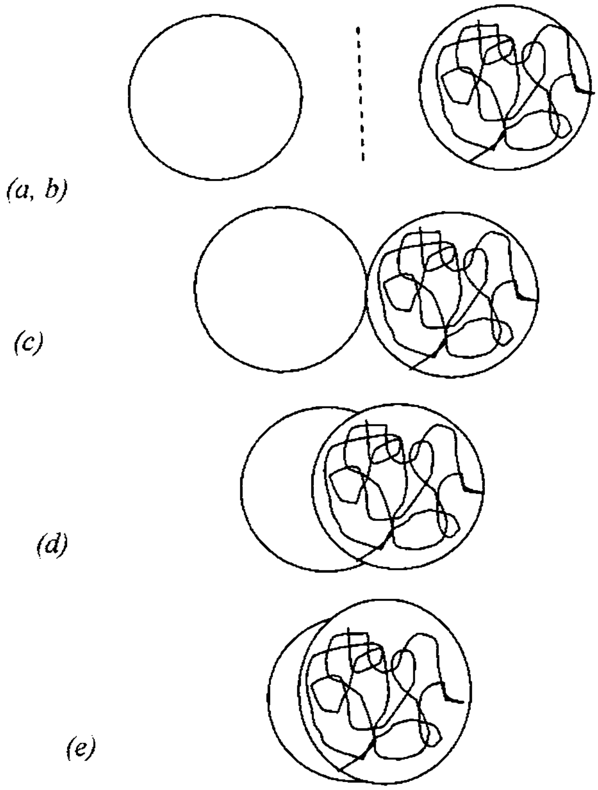


Figure 1.8 *Interdiffusion of random coil chains at a polymer-polymer interface(--) (a, b) surface rearrangement and approach (c) wetting, (d) diffusion, (e) virgin state*

The center of mass of the polymer chain will move a distance approximately equal to R_g in the longest relaxation time and from this the molecular weight dependence of D is determined. D is also directly proportional to the temperature.

$$\langle l^2 \rangle = 2Dt$$

where t is the time of diffusion. Hence the quadratic distance of diffusion is related to the molecular weight, temperature and time of diffusion.

When two substances are brought into contact they exert attractive forces on each other and adhesion takes place when the forces are sufficient for the substances to resist separation. Adhesion is primarily a surface phenomenon. Cohesion is a bulk phenomenon and the attractive forces are acting among like molecules. Cohesive forces are responsible for close packing of molecules in solids and liquids. In weld lines an adhesive bond is formed initially and because of chain diffusion the interface gradually disappears and the bond becomes cohesive in nature. So for strong weld lines the distance of diffusion should be greater than the entanglement radius. Interdiffusion can occur as long as the temperature is high enough to permit a significant degree of segmental mobility.

At a polymer interface, the chains have been physically separated at time t = 0 such that the diffusion to a distance x equal to the R_g will be necessary to reestablish the interpenetrated structure of the virgin state of the melt as shown in figure 1.8 [59-63]. The time to achieve this state of interpenetration can be designated as the weld time t_w. One dimensional Fickian diffusion gives $\langle l^2 \rangle$ $=2Dt$

For polymer welding $\langle l^2 \rangle = R_g^2$ at t= t_w and hence $t_w \propto R_g^2/2D$

$t_w \propto M_w^2$ and for highly entangled molecules $D \propto M_w^{-2}$ so that the weld time t_w is estimated as $t_w \propto M_w^3$

Thus small difference in molecular weight will result in large differences in time to achieve optimal weld conditions. Diffusivity D depends on the temperature which is position and time dependent in injection moulding. The temperature distribution can be obtained by the solution of the heat equation. The heat equation for this case assuming effect of heat of crystallization is negligible and there is no resistance to heat transfer at the interface of the melt and the mould is [11, 64]

$$\frac{dT}{dt} = \alpha \frac{\partial^2 T}{\partial z^2}$$

where α is the thermal diffusivity.

$\alpha = \frac{k}{\rho C_p}$, k is the thermal conductivity, ρ is the density and C_p is the specific heat, T is the temperature and z is the thickness of the sample. The weld line strength of the blend will be the same as that without weld lines when intermolecular forces are attractive, which is when the quadratic distance of diffusion $\langle l^2 \rangle$ is greater than the radius of gyration R_g^2. When there is perfect thermal contact between the cooling medium and the melt, then the solution of the equation can be obtained using the following boundary conditions.

At $z = b$, T = mould temperature where b = half thickness of the slab

$$\text{At } z = 0 \qquad \frac{\partial T}{\partial z} = 0$$

Initial condition

$$\text{At } t = 0 \qquad T(z,0) = \text{melt temperature}$$

The distance of diffusion can be obtained as

$$\langle l^2 \rangle = 2 \int_0^{t_{diff}} D(t)dt$$

For immiscible blends of amorphous and semicrystalline polymers the models available are [49, 50]

$$\frac{\sigma_w}{\sigma} = 1 - \Phi_1{}^2 \exp\left[\frac{-C_1 D_1}{kT}\left(2\gamma_1 - kT\partial x_1 \partial n_{01} \ln\frac{1}{2}\right)t\right] -$$

$$\Phi_2{}^2 \exp\left[\frac{-C_2 D_2}{kT}\left(2\gamma_2 - kT\partial x_2 \partial n_{02} \ln\frac{1}{2}\right)t\right] - (1 - \phi_1{}^2 - \phi_2{}^2)$$

$$\exp\left[- C_{12} D_{12} / kT[(\gamma_1 + \gamma_2) + [RT\partial_{12}(\frac{\rho_1}{M_1}\phi_1{}' \ln \phi_1{}' + \frac{\rho_2}{M_2}\phi_2{}' \ln \phi_2{}' + \chi_{AB})]]t \right]$$

where

$$\partial x_1 = (2D_1 t)^{1/2}$$

where suffix 1 and 2 represent the phases and $\phi_1{}'$ & $\phi_2{}'$ represent the volume fractions that contributed to the diffusion. Relationships are available for the prediction of parameters in the above equation.

Another simple model for blends is

$$\sigma = \sigma_1 \phi_1{}^2 + \sigma_2 \phi_2{}^2$$

1.8 Scope and Objectives of the Proposed Study

With increasing demand for high quality plastic items having special properties and the widespread use of plastics blends, the importance of weld lines in the injection moulding of plastics blends is more and more recognized. The main objective of the work has been to study the weld line behaviour of blends of commercially important semi crystalline plastics such as PP and HDPE, HDPE and LDPE and semi crystalline and amorphous polymers like PP and PS. Though there is a wide spectrum of studies on the weld line behaviour of pure polymers there is very limited study on the weld line behaviour of such blends. The use of modifiers for improving the weld line strength is still mostly an unexplored area. It is proposed to study the effect of processing parameters and modifiers for improving the weld line strength of the blends. Test samples with and without weld lines are proposed to be injection moulded at identical conditions for comparison.

Polypropylene blends constitute one of the most rapidly growing segments of the plastics industry. PP/HDPE blends are immiscible and hence have very poor mechanical properties at all compositions. The properties are still lower when weld lines are present. Ethylene-propylene-diene monomer (EPDM) which is a compatibilizer for this blend may also act as a weld line modifier. It is proposed to try EPDM as a weld line modifier for these blends. The effects of processing parameters are also proposed to be investigated. The effect of crosslinking agents for weld line modification is another area proposed for investigation.

The blends of polypropylene and polystyrene are considered to be prototype materials for studying blend behaviour of a semicrystalline plastic with that of an amorphous plastic and hence this blend is proposed to be selected for studying weld line behaviour of such blends. Use of Dynamic Mechanical Analysis (DMA) is proposed to be studied for assessing the behaviour of the blends at the use temperature.

The weld line behaviour of the blends of different grades of the same plastics is proposed to be investigated using two grades of LDPE. The weld line behaviour of blends of HDPE and LDPE is also proposed to be investigated. The flow behaviour of the plastics has a most important bearing on its weld line behaviour. Hence it is proposed to study the rheology of all the blends to relate the flow behaviour to the weld line strength. The morphology at the weld line is another significant factor influencing the weld line strength, Hence the morphology at the blend is proposed to be investigated using Scanning Electron Microscope (SEM).The strength of the weld line depends on the molecular entanglement which in turn depends on the diffusion coefficient. An attempt at correlating the weld line strength in terms of the diffusion coefficient is also aimed at.

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Chapter 2

Materials and methods

The materials used and methods adopted in the present investigation are given in this chapter.

2.1 Materials used

1. Polypropylene homopolymer (PP)

REPOL H200MA, with a melt flow index of 20g/10min, was supplied by Reliance Industries Limited, Mumbai, India.

2. Low density polyethylene (PE1)

LDPE Grade Indothene16 MA 400 was supplied by Indian petrochemicals limited (IPCL), Baroda, India, with density 0.918 g/cm^3 and MFI 30 g/10 min.

3. Low density polyethylene (PE2)

LDPE Grade Indothene 24 FS 040 was supplied by Indian petrochemicals limited (IPCL), Baroda, India, with density 0.922 g/cm^3 and MFI 4 g/10 min

4. High density polyethylene (HDPE)

HDPE Grade Indothene HD 50 MA 180 was supplied by Indian petrochemicals limited (IPCL), Baroda, India, with density 0.950 g/cm^3 and MFI 20 g/10 min

5. Polystyrene (PS)

PS grade LGG104 was supplied by LG Plastics with MFI 18g /10 min.

6. High impact polystyrene (HIPS)

HIPS grade LGH 302 was supplied by LG plastics with MFI 18 g /10 min.

7. **Precipitated Calcium carbonate** commercial grade as filler
8. **Dicumyl peroxide (DCP)** commercial grade which is 40% active
9. **EPDM grade 301 T** supplied by Herdelia Unimers
10. **Accinox TQ** (Polymerised1, 2, dihydro 2,2,4 trimethyl quinoline) supplied by ICI India Ltd., West Bengal as antioxidant

2.2 Melt Mixing in Thermo Haake Torque Rheometer

A Thermo Haake Torque rheometer (Rheocord 600) was used for melt mixing and blending (Figure 2.1). Torque rheometers are multipurpose instruments that are well suited for formulating multicomponent polymer systems, and studying flow behaviour, thermal sensitivity, shear sensitivity and batch compounding. The mixing chamber had a volumetric capacity of 69 cm^3 and was fitted with roller type rotors for blending. In the chamber the rotors rotate in opposite directions in order to effect a shearing action on the material mostly by shearing the material against the walls of the mixing chamber. The rotors have chevrons which perform additional mixing function by churning the material and moving it back and forth through the mixing chamber. The granules in the desired proportion were fed to the chamber through a vertical chute with a ram. There is a small clearance between the rotors which rotate at different speeds at the chamber wall. In these clearances dispersive mixing takes place. The shape and motion of the rotors ensure that all particles undergo high intensive shearing flow in the clearances. The mixer consists of three sections and each section is heated and controlled by its own heater and temperature controller. It is designed to maintain very accurate and uniform temperature profiles throughout the mixer. Since mechanical dissipation heat is developed in the small gap between rotors and chamber, the heat conducts to the center bowl and raises the set temperature. In this case, the heater at the center bowl is automatically shut off and circulation of cooling air is activated. For blending at higher temperature a separate antioxidant was added. The temperature for blending, time of blending and rpm were optimized for each blending.

A mixing time of 5 minutes at a counter rotating rotor speed of 40 rpm was found to be adequate. The temperature selected depended on the material. In all cases the torque stabilized to a constant value in the selected mixing conditions. The rpm and temperature are automatically controlled at the set values and the torque and energy required for blending are recorded as a function of time.

2.3 Fabrication of Moulds

Moulds were fabricated with single gating for samples without weld lines and with double gating for samples with weld lines as in Figure 2.3. Tensile test samples of size conforming to ASTM-D-638 with and without weld lines were moulded using the moulds which were fabricated

2.4 Preparation of Test Specimens

The hot mix from the mixing chamber was immediately passed through a laboratory size two-roll mill and the resulting sheets were cut to small pieces. The test specimens [1] were prepared using a semi-automatic plunger type injection-moulding machine. The melt temperature was set to be automatically controlled in the injection moulding machine.

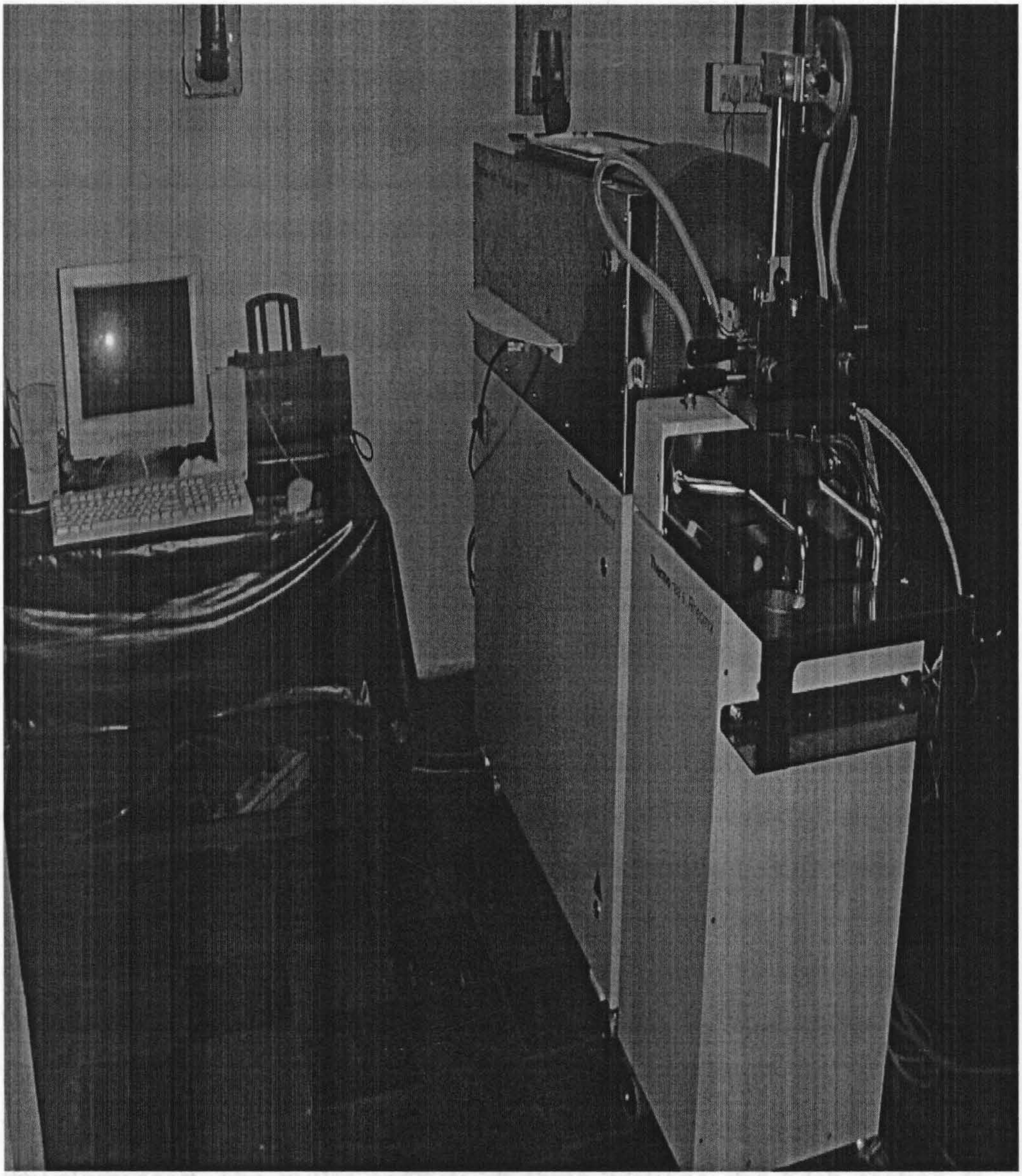
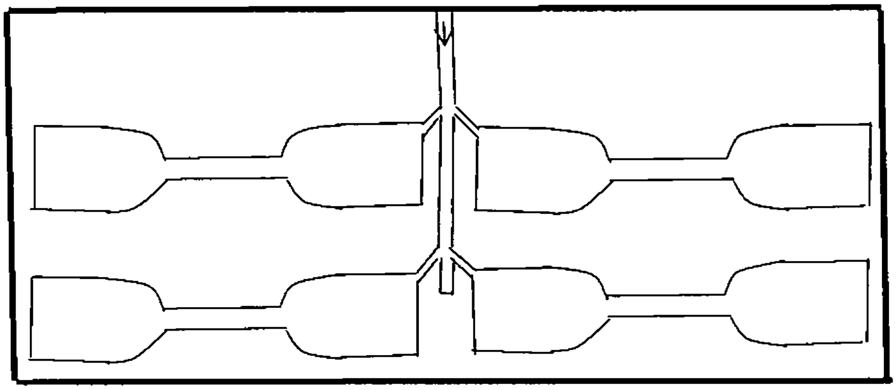
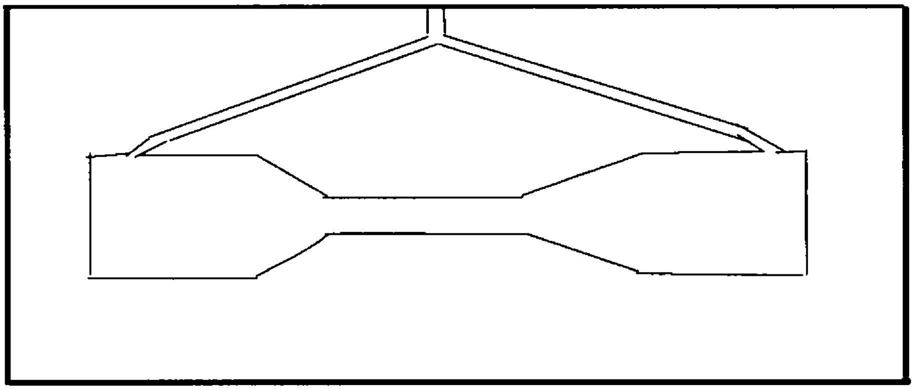


Figure 2.1 *Thermo Haake Rheocord*



Mould without weld line



Mould with weld line

Figure 2.2 *Mould with and without weld line*

Mouldings were made at identical conditions for samples with and without weld lines and the properties are taken as the average property of six test samples. The mould was preheated to 50°C and the feed materials were preheated for moisture removal. The temperatures were set according to the melt temperature of the material and the injection pressure and holding time were adjusted to get the best properties.

2.5 Mechanical properties

2. 5.1 Tensile Properties

The tensile properties of the samples were determined using dumb-bell shaped specimens with a Universal Testing Machine (Shimadzu AG1) at a crosshead speed of 50 mm/min according to ASTM-D-638. The length between the jaws at the start of each test was fixed to 40 mm and at least six concordant measurements are taken to represent each data point.

2.5.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis involves the determination of dynamic mechanical properties of polymers and their assemblies. As a result of this the relationships between the dynamic properties and structural parameters like crystallinity, molecular orientation, crosslinking, plasticization, etc. and external variables like temperature, pressure, time, frequency, type of deformation can be explained. In order to determine the dynamic mechanical properties such as dynamic modulus E', the loss modulus E'' and the damping or internal friction tan $\delta = E''/E'$, the response of the material to periodic forces is measured. Generally the dynamic measurements are conducted over a frequency range at constant temperature or over a temperature range at constant frequency. The commonly used frequency range for DMA of polymeric materials is from 10^{-2} to 10^{6} Hz.

When a sinusoidal excitation is given to the applied force, then the resulting deformation also varies sinusoidally with time. For linear viscoelastic materials the strain will alternate sinusoidally , but will be out of phase with the stress. This phase lag results due to the time necessary for molecular rearrangements and is associated with relaxation phenomena. The stress σ and strain ε can be expressed as given by the equations below.

$$\sigma = \sigma_0 \sin(\omega t + \delta):$$

$$\varepsilon = \varepsilon_0 \sin \omega t$$

where ω is the angular frequency and δ is the phase angle.

The stress can be considered to consist of two components, one in phase with the strain which is $\sigma_0 \cos \delta$ and the other part $\sigma_0 \sin \delta$,90° out of phase with the strain. Dividing by the strain the modulus can be obtained as an in-phase component which is real and an out of phase component which is imaginary.

$$\frac{\sigma}{\varepsilon} = E' + iE'' \quad \text{where } E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \text{ and } E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta$$

The real part of the modulus is called the storage modulus as it is related to the storage of energy as potential energy and its release in the periodic deformation and the imaginary part is called loss modulus as it is associated with the dissipation of energy as heat when materials are deformed. The loss tangent tan δ is called internal friction or damping and is the ratio of energy dissipated per cycle to the maximum potential energy stored during a cycle. Hence DMA results give data concerning deformation of materials due to vibrational forces [2].

The storage modulus and tan δ were measured using fixed dynamic analysis techniques. A dynamic mechanical analyser (Q 800, TA Instruments) was made use of for this purpose. Rectangular specimens of

35 mm length, 4 mm breadth and 2 mm thickness were used. DMA tests were conducted at a constant frequency of 1 Hz. A temperature ramp was run from 30°C to 150°C at 3°C/min to get an overview of the thermo mechanical behaviour of the samples with and without weld lines at the use temperatures.

2. 6 Melt rheology

2. 6.1 Melt flow measurements

The melt rheological measurements were carried out using Shimadzu (model AG1) capillary rheometer (50 kN) at different plunger speeds from 1-500 mm/min. The capillary used was made of tungsten carbide with a length to diameter (L/D) ratio of 40 at an angle of entry 90°. The sample for testing was loaded inside the barrel of the extrusion assembly and forced down the capillary using a plunger. After giving a residence time of 5 min the melt was extruded through the capillary at 6 predetermined plunger speeds. The initial position of the plunger was kept constant in all experiments and shear viscosities at different shear rates were obtained from a single charge of the material. The measurements were carried out at three different temperatures viz. 180 and 220 and 250 °C.

Shear stress was calculated as

$$\tau_w = \frac{PR}{2l}$$

where τ_w is the shear stress of the wall Pa, P is the pressure drop Pa, l is the length of the capillary and R is the radius of the capillary. Shear rate at the wall was calculated using the equation

$$\gamma_w = \frac{32Q}{\pi d_c^{\,3}}$$

where γ_w is the shear rate s^{-1}, Q is the volumetric flow rate $mm^3\ s^{-1}$, d_c is the diameter of the capillary in mm.

Apparent viscosity η (Pa s) was calculated using the equation

$$\eta = \frac{\tau_w}{\gamma_w}$$

A straight line relationship on a log-log plot indicates the variables are related by the power law equation $\tau_w = k\gamma_w{}^n$ where k is the consistency index and n is the power law index as given by the power law model of Oswald de Waele. The power law index represents the degree of non Newtonian behaviour and the consistency index denotes the viscosity [3-8].

2. 6. 2 Rheological measurements using Haake Rheocord

The rheological measurements were also made on Haake torque rheometer since it represents real processing equipment. The rheological interpretation of the measurements was based on the analysis of Blyler and Daane [6]. Goodrich and Porter [7] considered the torque rheometer measuring head as two adjacent rotational viscometers with irregular concentric cylinders. They succeeded in converting torque rheometer data into fundamental rheological units for materials that exhibit Newtonian viscosity. Blyler and Daane extended this work to materials with non-Newtonian and derived the equation,

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

where M is the torque, K and n are parameters of the famous power law equation,

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

The parameter K depends on temperature and often has an Arrhenius type dependence ascribed to it such that,

$$K = K_0 \exp(\Delta E / RT)$$

ΔE is the flow activation energy. R is the gas constant and K_0 is a coefficient S is the rpm and $C(n)$ a characteristic constant.

Hence the Rheocord torque and rotor speed can be separately related to some average shear stress and rate of shear, respectively of the polymer melt for Newtonian and non- Newtonian materials as follows.

(1) The slope of the log M Vs log S plot at constant temperature obtained for a polymer melt with the Haake is identical to the slope of the logτ-log γ curve at constant temperature obtained from capillary rheometer. Consequently the power law index can be obtained from Haake data also.

(2)The Haake can be calibrated by using melts of known K and n to determine $C(n)$ and can be used to characterize a polymer.

(3) The energy required to plasticise a polymer for a period of time at a given temperature can be calculated from the area under the torque-time curve at a preset temperature for the specified period of time. The energy W is obtained from the formula at a given temperature and shear rate as

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

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

2. 6. 3 Die swell measurements

The rheological behaviour of the polymers exhibit a dual nature, ie, they combine features of elastic solids and viscous liquids and are hence 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 the flow direction also generates normal stresses within the melt. These normal stresses are the cause of unusually high inlet and outlet pressure losses and of swelling effects at changes in cross sections of flow passages. The extrudate swell ratio is a direct meaure of melt elasticity and die swell has effect on the weld line strength. The extrudates were carefully collected as they emerged from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured after 24h of extrusion. The die swell ratio B was calculated using the relation,

$$B=\frac{D_p}{d_c}$$

where D_p is the extrudate diameter and d_c is capillary diameter

2.7. Calculation of diffusion coefficient and theoretical value of weld line coefficient (Details given in Appendix)

The strength of the weld line is given in terms of the degree of bonding defined as the ratio of the bonded area to the total initial area. This is expressed by the following equation [9-16].

$$\sigma_w=\sigma_b\left(\frac{A_0-A_N}{A_0}\right)$$

where σ_w and σ_b are the tensile strength of the injection moulded part with and without weld line respectively, A_0 is the initial cross sectional area, A_N is the non bonded area and A_0 -A_N is the bonded area at the specific contact time.

The diffusion coefficients are found out as a function of temperature for PP, HDPE and PS. The heat equation is solved and the temperature distribution is obtained. The values of quadratic diffusion distance is calculated using the following equation,

$$\langle l^2\rangle=2\int_0^{t_{diff}}D(t)dt$$

and is compared with the radius of gyration to examine the nature of the weld. The dimensionless distance z/b represents the ratio of the bonded area to the total area and hence the value of z/b where the radius of gyration is less than the distance of diffusion gives the WLC.

The properties of PP, PS and PE are obtained from charts and from the polynomials for properties as a function of temperature T [9, 15, 19-22]. Computations are done for the case of melt temperature 200°C, 220°C, 240°C, 260°C and mould temperature 50°C.

2.8 Morphological studies- Scanning Electron Microscopy

Scanning electron microscope (JOEL JSM 840A) was used to investigate the morphology of the fractured surfaces [23]. In this technique, an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in a cathode ray tube and photographed using black and white film. The SEM observations reported in the present study were made on the fracture surfaces of the tensile specimens. Thin specimens were prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in an E-101 ion- sputtering unit for gold coating of the sample to make it conducting. The gold-coated sample was used for SEM analyses.

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Chapter 3

Weld line behaviour of polypropylene/high density polyethylene (PP/ HDPE) blends

3.1 Introduction

Due to the ease of processibility and low cost polyethylenes constitute the largest group of commodity thermoplastics .Polyethylene (PE) covers 45% of all plastics and one of the reasons for its popularity is the development of blending technology for property modification. Polypropylene (PP) is a versatile polymer that continues to grow rapidly because of its excellent performance and improvements in production economics. The blends of PE with PP have attracted much commercial interest. One of the reasons for adding PE to PP is to improve the low temperature impact behaviour of PP. PP/PE blends find application in automobiles, appliances, house wares, furniture, sporting goods, toys, packaging, chemical processing equipments and industrial components, most of which are injection moulded large parts where weld lines are unavoidable [1]. The choice of optimum processing parameters and the amount of modifiers required to get maximum properties when weld lines are present in blends is of great importance.

PP/PE blends are immiscible. From a mechanical point of view PP/HDPE blends have generally been considered as very unsatisfactory materials [2]. They show very poor ultimate mechanical properties in comparison with those of the components. The ultimate mechanical properties of the blend can be improved by adding a third component having intermediate molecular characteristics between the two polymer species which acts as a compatibilizing agent in their amorphous regions. Depending on the type and molecular parameters of the components and the degree of immiscibility successful compatibilizing agents tried are random copolymers ethylene propylene rubber (EPR) or ethylene propylene diene monomer (EPDM) [3, 4]. Compatibilization of PP/PE blends can be done by addition of copolymer EPR or EPDM, by reactive blending or by post blending treatment using chemical cross linking, electron beam or by irradiation. Reactive compatibilization is done by adding peroxide. The reaction leads to degradation of PP and branching or cross linking of PE. Tight control of the process is required for optimization. Both reactive compatibilization and irradiation lower the blend crystallinity. The micromorphology is controlled by composition, presence of nucleating agents, type of compatibilizer and thermal or radiation treatment [5]. Blends of isotactic polypropylene with high density polyethylene with ethylene propylene diene monomer (EPDM) is of particular commercial importance and they constitute a large and important segment of the plastic market. Rubber toughened PP/HDPE blends are important because of the need for thermoplastic materials with the characteristics of vulcanized rubber. The morphology of ternary blends of PP/HDPE/EPDM blends is reported in [5, 6] where it is shown that in systems with HDPE as the matrix PP lamella entered the EDPM dispersed phase and when HDPE was the dispersed phase, PE lamella entered the PP matrix. The presence of PE did not affect the crystal form of PP. Blending of PP with PE engenders two competing effects. The presence of two immiscible polymers creates a two phase structure that may be detrimental to blend performance at large strains. Also increase of mixing time or intensity not only improves the degree of dispersion but also increases thermal and mechanical degradation. Because of immiscibility in PP/PE blends at large strains, poor ultimate mechanical properties result. Ethylene – propylene copolymer are shown to adhere better to each polymer component than the components adhere to each other [7].

Polymer- polymer adhesion plays a significant role in determining the ductility related properties of immiscible blends [8]. Better adhesion between ductile and brittle components improves ductility. The extent of segmental diffusion across the interface between components is given by the interface thickness *a* which is related to Flory-Huggins interaction parameter χ_{AB}.

$$a = c/(\chi_{AB})^m$$

where *c* and *m* are slightly different constants. This equation suggests that the strength of the adhesive bond increases as χ_{AB} approaches zero. Thus an interfacially active block or graft copolymer strengthens the interfacial zone.

PE and PP are both tough and ductile homopolymers with similar chemical structure. They form brittle immiscible mixtures when melt blended and injection moulded. Immiscible blends show very poor ductility when injection moulded, producing a weld line at right angles to the load bearing direction. Some improvement in ductility can be made across the weld line by adding a compatibilizer but the improvement is small [9].

The characteristics of the material at the weld line are substantially different from the bulk material as the molecular chains at the melt front are stretched parallel to the weld line and the orientation of the molecules change. Several studies have attributed the causes of weld line weakness of homopolymers to different reasons. Hobbs [10] has studied the weld line behaviour of PP and has reported that isotactic polypropylene morphology is different at the weld lines and he established that this is due to fountain flow. Mielewski [11] has established that the presence of hindered phenolic antioxidant additive in PP systems introduce weld line weakness. Malguarnera [12, 13] reported increasing tensile strength for higher melt temperatures for PP and has attributed this to better molecular entanglement at higher melt temperatures. Various studies have focused on the effect of processing conditions on the strength of the weld line for homopolymers. In the case of immiscible polymer blends the weld lines are found to be much weaker than homo polymers. Paul et al [9] has reported that for PP/PE systems the ductility of the samples containing weld lines can be improved by addition of EPDM. A review of the knit line behavior of polypropylene and polypropylene blends is given by Mennig [5]. Fellahi and Fisa [14-15] investigated the morphology and mechanical properties of PA6/HDPE blends with a compatibilizer. In comparison to studies on homopolymers literature is less abundant in studies on weld line strength of blends. Weld lines in injection moulded polymer blends is not a well documented subject. Stability of the morphology while processing is of prime concern. It is believed that addition of an interfacial modifier leads to a better stabilization of the morphology and this is investigated by Fellahi et al by detailed morphological studies of weld line samples of PA6/HDPE. Use of compatibilizers is found to increase the weld line strength for PS/PE systems [16].Models have been suggested to predict the weld line behavior of pure polymers and immiscible blends of semicrystalline and amorphous polymers [17-19].

Injection moulding is characterized by complex and nonisothermal flow into a closed and cooled cavity. This process generally results in an anisotropic skin core structure. The filling of mould cavity occurs through fountain flow. During moulding the polymer in contact with the cooled mould wall freezes immediately to form the skin where the shear will be maximum. Dispersed deformable particles will be elongated in the direction of flow. The hot core will be less deformed and has sufficient time to relax. The result of this complex process is the skin-core structure. Poor weld line strength is reported for PP/EPDM blends and HDPE/PA-6 blends due to skin core morphology.

The weld line behaviour of HDPE and PP, their blends and effect of processing parameters, use of compatibilizers EPDM and modifiers in improving weld line behaviour of these blends are proposed to be investigated in this chapter.

3.2 Experimental

3.2.1 Materials

HDPE grade 50 MA 180 made by Indian petrochemicals limited (IPCL) with MFI 18 g/10 min.

PP Repol H 200 MA made by Reliance Petrochemicals with MFI 20 g/10 min.

EPDM grade 301 T supplied by Herdelia Unimers,

Antioxidant TMQ, Dicumyl peroxide (DCP) 40% active

3.2.2 Mixing and moulding

Thermo Haake Rheocord 600 having a mixing chamber of volume 69 cm^3 with roller type rotors was used for blending. The hot mix from the mixing chamber was immediately passed through a two roll mill and cut into small pieces. The test specimens with and without weld lines were molded in a semi automatic plunger type injection molding machine.

3.3 Results and Discussion

3.3.1 Effect of melt temperature on weld line strength of PP and HDPE

The weld line coefficient (WLC) is defined as the ratio of a property for the sample with weld line to that without weld line when both the samples are prepared under identical conditions [20]. The processing temperature has influence on the yield stress and elongation at break as is seen from figures.3.1 and 3.2. In the case of HDPE, WLC increases with increase of processing temperature from 190°C to 250°C. The strength of the weld line depends on the melt temperature, mould temperature and contact time available for the melt fronts to diffuse together. Since the melt temperature and contact time for moulding is constant for all the mouldings, the factors which influence the weld line strength are the flow velocity inside the mould which in turn is inversely proportional to the viscosity, the rate of cooling while in contact with the mould and the diffusion coefficient. The viscosity decreases with increase of temperature and the diffusion coefficient increases with temperature, weld line strength will increase with temperature till degradation temperature. The rate of cooling is dependent on the properties of the melt especially thermal diffusivity. Since PP and HDPE are semicrystalline the rate of crystallization and the amorphous regions in the solidified samples also affect the weld line strength. But WLC decreases with further increase in temperature probably due to the onset of degradation reactions. For PP the WLC for yield stress and elongation at break starts its downward trend steeply from 240°C. This may be expected since PP is more prone to degradation due to the presence of tertiary hydrogen. The average values for mechanical properties are as given in table 3.1. The elongation at break is high for HDPE and very low for PP. PP breaks without necking and the weld line samples of PP are very brittle.

Table 3.1 *Properties of pure polymers*

Material	*T*°C	No weld line			Weld line		
		Yield stress, MPa,	Elongation at break,%	Modulus MPa	Yield stress, MPa	Elongation at break%	Modulus MPa
HDPE	240	31.64	465.8	10.8	28.4	404.7	10.48
PP	240	40.11	11.83	12	33	7.83	8.34

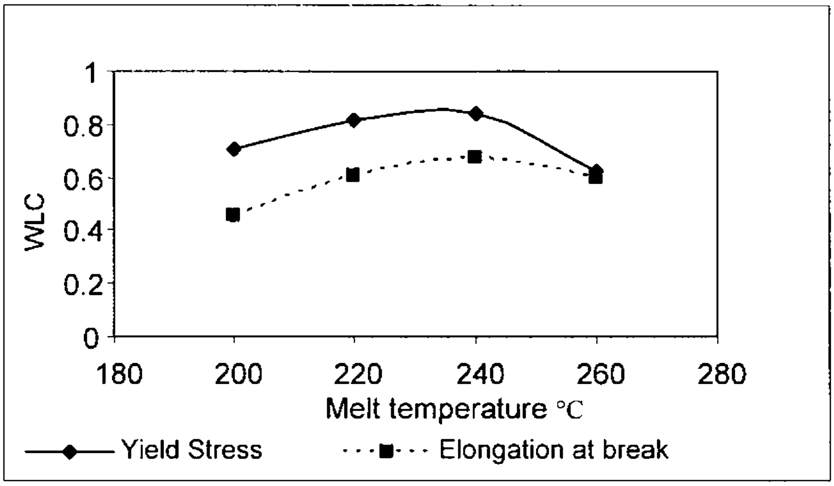

Figure 3.1 *Variation of WLC with processing temperature for PP*

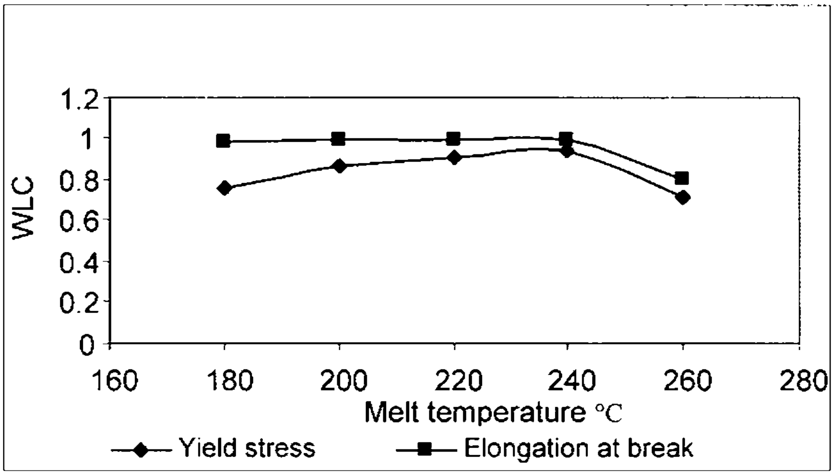

Fig 3.2 *Variation of WLC with processing temperature for HDPE*

3.3.2 Theoretical prediction of WLC of the pure polymers

Theoretical values can be predicted as explained in the previous chapter. The diffusion coefficients for PP and HDPE calculated are as in figure 3.3 and 3.4.The values of diffusion coefficients are high for HDPE and low for PP.

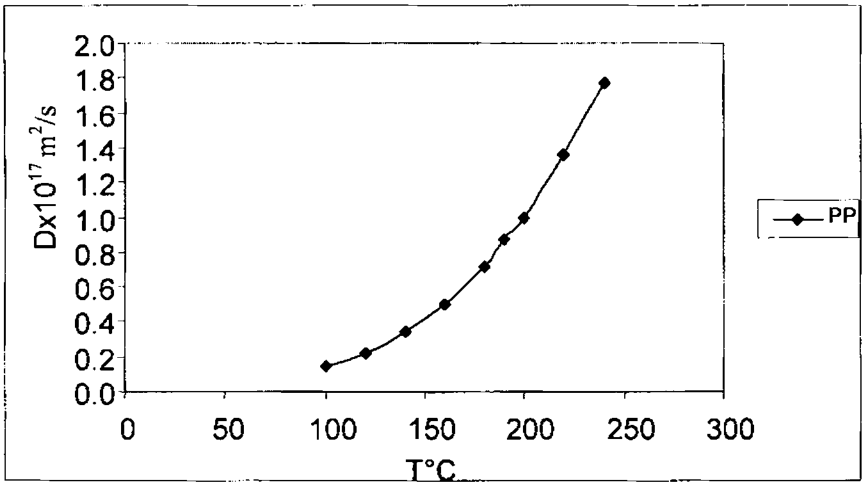

Figure 3.3 *Diffusion coefficient as a function of temperature for PP*

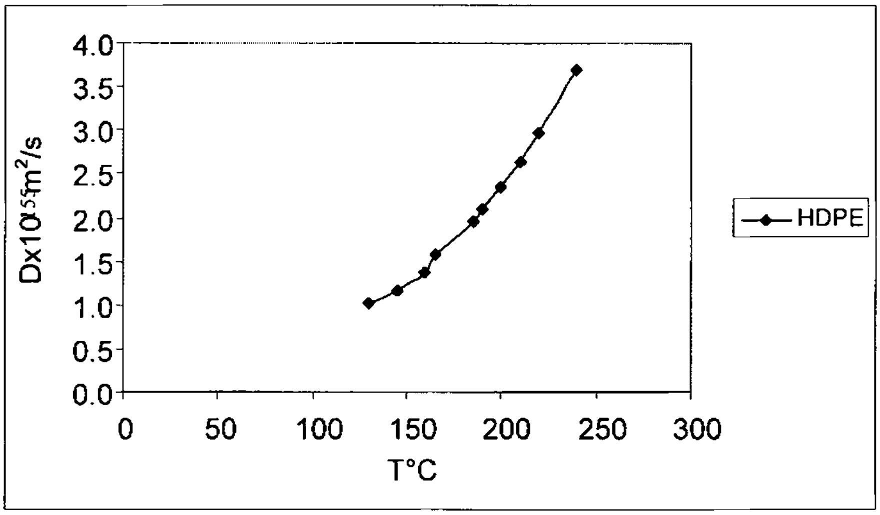

Figure 3.4 *Diffusion coefficient as a function of temperature for HDPE*

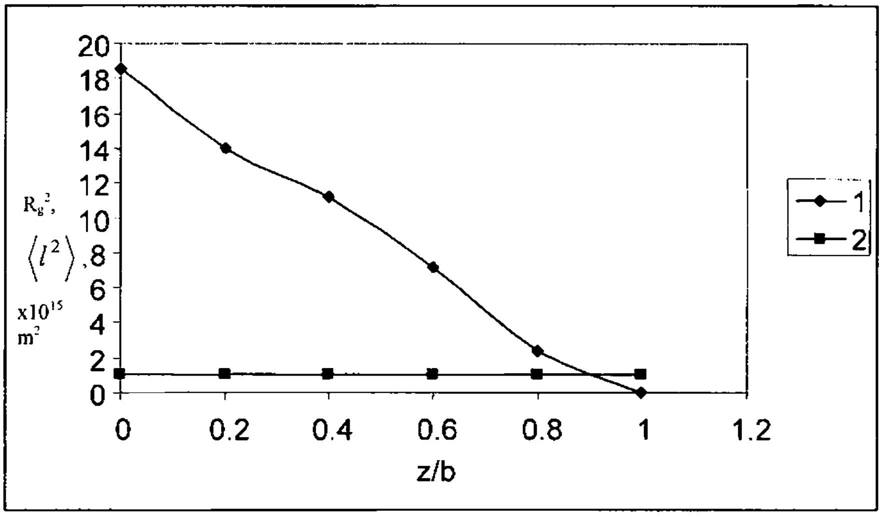

Figure 3.5 *Distance of diffusion as a function of dimensionless thickness of the sample for HDPE at 240°C* **1-**$\langle l^2 \rangle$ **2-** R_g^2

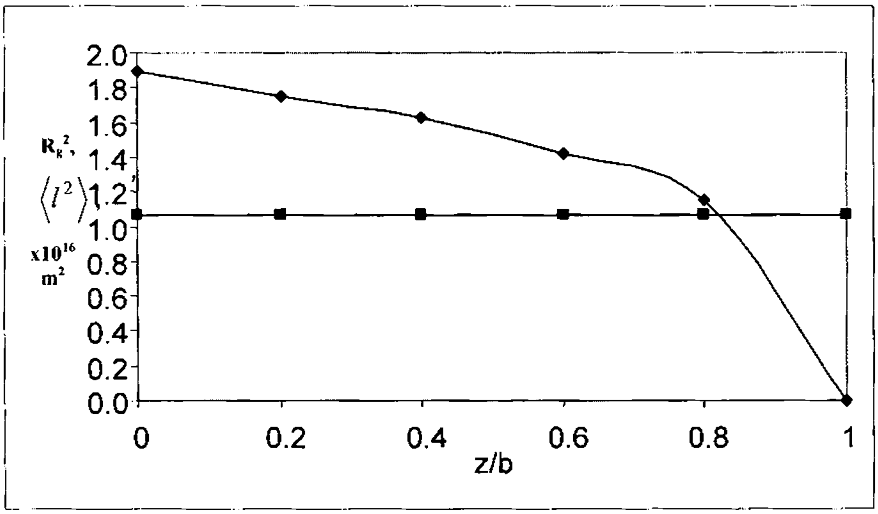

Figure 3.6 *Distance of diffusion as a function of dimensionless thickness of the sample for PP* ◆ $\langle l^2 \rangle$ ■ R_g^2

The distance of diffusion is computed for PP and HDPE. For this, at each location the time of diffusion is found out from the chart of $\frac{T-T_0}{T_w-T_0}$ vs z/b given in [21]. (The chart is reproduced in appendix). For each position for the time of diffusion, the temperature can be found out. Using this time, temperature and calculated values of diffusivities, the distance of diffusion is found out graphically from the relationship, given by equation for each location.

$$\langle l^2 \rangle = 2\int_0^{t_{diff}} D(t)dt$$

These calculations are repeated for other temperatures and the location at which the distance of diffusion is greater than R_g^2 is found out.

Computations are done for the case of melt temperature 200°C, 220°C, 240°C, 260°C and mould temperature 50°C the temperature distribution in the moulding of half thickness 1 mm . The properties of PP and PE are obtained from chart and from the polynomials for properties as a function of temperature T [21-26].

Table 3.2 *Properties of PP and HDPE*

T 200°C	k w/mK	ρ kg/m3	C_p J/kgK
PP	0.142	867	2800
HDPE	0.255	782	2650

From chart 5.10 [21] the time to reach 130°C for a melt of 200°C is as follows for HDPE

$$\frac{T-T_0}{T_w-T_0}=0.467 \quad T\text{=130°C},\ T_0\text{=200°C},\ T_w\text{=50°C}$$

Dimensionless distance z/b	0	0.2	0.4	0.6	0.8	1.0
Dimensionless time at/b^2	0.38	0.35	0.30	0.18	0.045	1.0
Time t, s	3.1	2.85	2.44	1.47	0.37	0

For PP at melt temperature of 240°C

$$\frac{T-T_0}{T_w-T_0}=0.74$$

Dimensionless distance z/b	0	0.2	0.4	0.6	0.8	1.0
Dimensionless time at/b^2	0.7	0.6	0.58	0.5	0.19	1.0
Time t, s	12	10.3	9.8	8.6	3.3	0

The following available data are used [21-26].

Polypropylene

G_N^0 =4.9x10^6 dynes/cm^2

M_e=4800 g/mol

R_g^2/M_w =1.07x10^{-17}cm^{2}mol/g

The activation energy E_D for diffusive transport in the melt state can be computed from thermal-physical properties of polymers by the equation

$\frac{E_D}{R} = C_D \frac{T_m'^2}{T_m' - T_g}$ where T_m' is the thermodynamic equilibrium melting temperature which is different from the true melting temperature .For PP it is 447K and T_g for PP is 267 K. C_D=5.0. $\eta_{0(Mc)}$ can be computed from WLF equation given in Graessley [23, 24] and from the relation

$$\eta_{0,cr} = \eta_0 (\frac{M_c}{M_w})^{3.4}$$

HDPE

$(R_g^2/M_W)^{1/2}$ =0.46(°A-mole$^{1/2}$/g$^{1/2}$)

R_g^2/M_W=1.0x10^{-16}cm^2/g/gmole

M_c = 3800 g/g mole

$$(G_N{}^0 = \frac{\rho RT}{M_e}) \quad G_N^0 = 2\text{x}10^7 \text{ dyne/cm}^2$$

$\eta_{0,cr}$=0.32 poise

$$\eta_{0,cr} = \eta_0 (\frac{M_c}{M_w})^{3.4}$$

Activation energy for self diffusion of HDPE 23 kJ/mol.

The theoretical values and experimental values of weld line coefficient are plotted in Figures 3.7 and 3.8 which are in fairly good agreement.

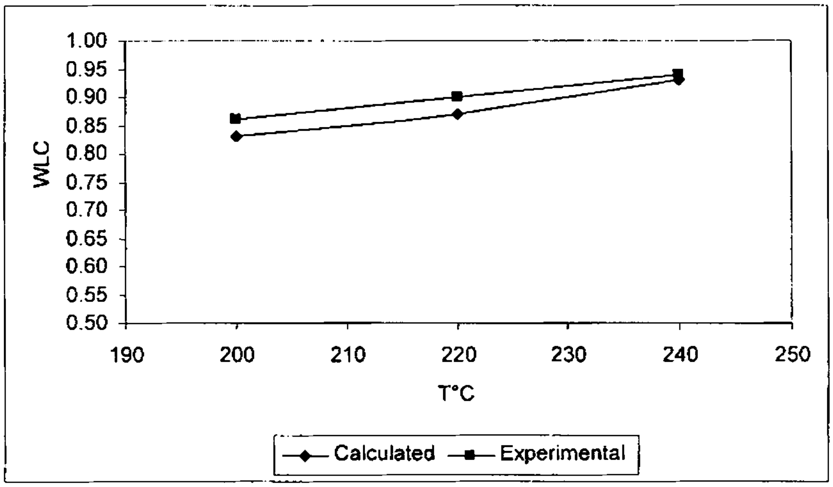

Figure 3.7 *Theoretical and experimental values of weld line coefficient(WLC) for HDPE*

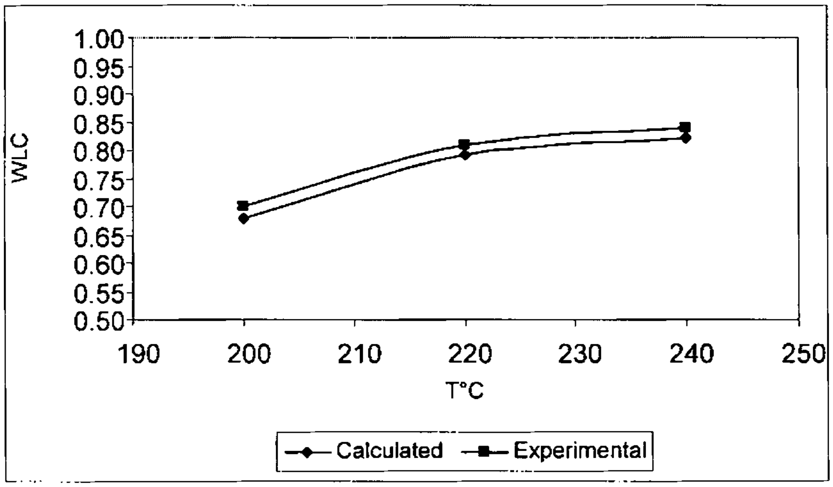

Figure 3.8 *Theoretical and experimental values of weld line coefficient(WLC) for PP*

3.3.3 Weld line strength for PP/PE blends

The mechanical properties for PP/PE blends are poor and this is more pronounced when weld lines are present as can be seen from Figure 3.9.The samples with weld lines could be moulded only at around 240 °C and at higher temperature the samples got degraded.

PP and HDPE are thermodynamically incompatible. For blends of A and B, there are three interfaces namely A/A, B/B, A/B. The area fractions of contact are F_{AA}, F_{BB}, F_{AB} such that $F_{AA}+F_{BB}+F_{AB}=1$

$F_{AA}=1-(F_{BB}+F_{AB})=1-\Phi_B$ where Φ_B is the volume fraction of B

$F_{BB}=\Phi_B^2$ approximately and $F_{AB}=\Phi_B-\Phi_B^2$. The contribution of Φ_B^2 term is negligible and can be neglected

For strength development at the polymer interface of semicrystalline polymer blends the important parameters are the interdiffusion thickness of the interface and crystallization. Both PP and PE are having a spherulite structure and voids and defects are induced by density changes due to crystallization occurring in the melt. With difference in melting points and crystallization rates one polymer will crystallize while the other is in liquid state. This will cause interspherulite influxes and local crystallizations. The interface strength depends on the thermal history and whether the PP is crystallized against PE or PE crystallized against PP.

3.3.4 Effect of addition of EPDM

EPDM at concentration levels of 2 to 10 weight %of total weight of polymers was tried as a weld line modifier. It is seen that the yield stress and elongation at break are improved both for samples with and without weld lines. The improvement in yield stress for the entire range of composition with the addition of 6% by weight of EPDM is shown in Figure 3.9.The improvement in yield stress with the addition of EPDM is a clear indication of improvement in weld line strength since even after addition of a soft component the yield stress increases for the blend while this causes a proportional decrease in the pure samples. The improvement in weld line strength can be attributed to the change in morphology of binary system by addition of EPDM. In the ternary system having one matrix phase and two dispersed phases the tendency of the minor phases encapsulating each other is characterized by the spreading coefficient [31]. If the spreading coefficients of the minor phases are negative, the phases will tend to remain separately. If the EPDM phase is encapsulated by the PE phase a finer dispersion will result. Because of the adhesion of phases the brittle nature of the weld line is changed to ductile nature and also there is marked difference in flow properties as the rheological studies revealed. It was established by D'Orazio et al and more recently by B. D. Favis et al [31] that the ternary blend of PP/PE/EPDM will have a minimum of surface energy and the EPDM phase will encapsulate the PE phase when PP is the matrix phase.

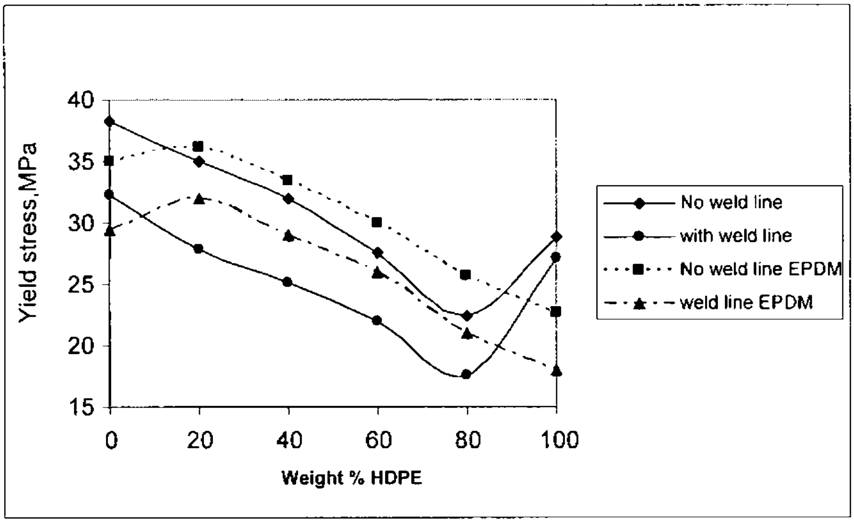

Figure 3.9 *Yield stress with and without 6 weight % EPDM.*

3.3.5 Optimum content of EPDM

The optimum weight % of EPDM for a 50/50 PP/PE blend with weld line and without weld line samples are different as seen from Figure3.10. The maximum strength is obtained at about 6 weight percent in the case of samples with weld lines whereas for samples without weld lines the maximum yield stress is obtained at a lower value of about 4 %. So it may be seen that for samples with weld lines a higher weight percent of EPDM is to be used for getting maximum strength. The elongation at break is increasing for samples with and without weld line as the EPDM content is increased as can be seen from Figure 3.11, but the increase is marginal for weld line samples.

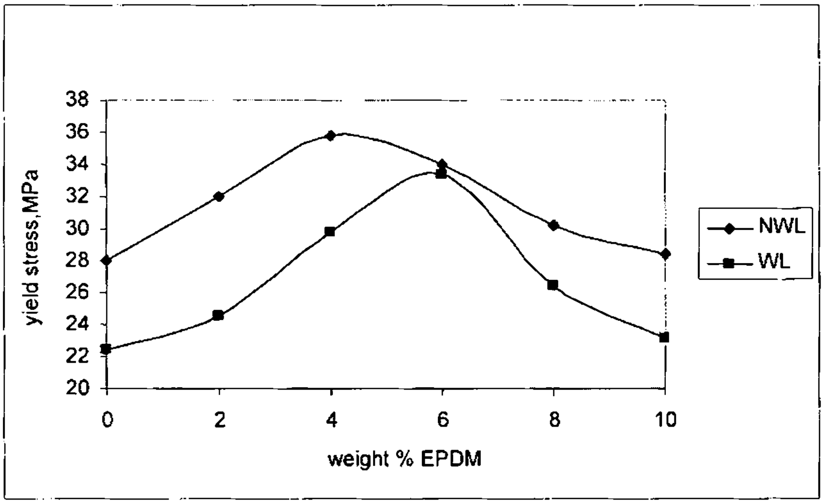

Figure 3.10 *Optimum EPDM content for samples with and without weld line for 50/50 PP/HDPE blends*

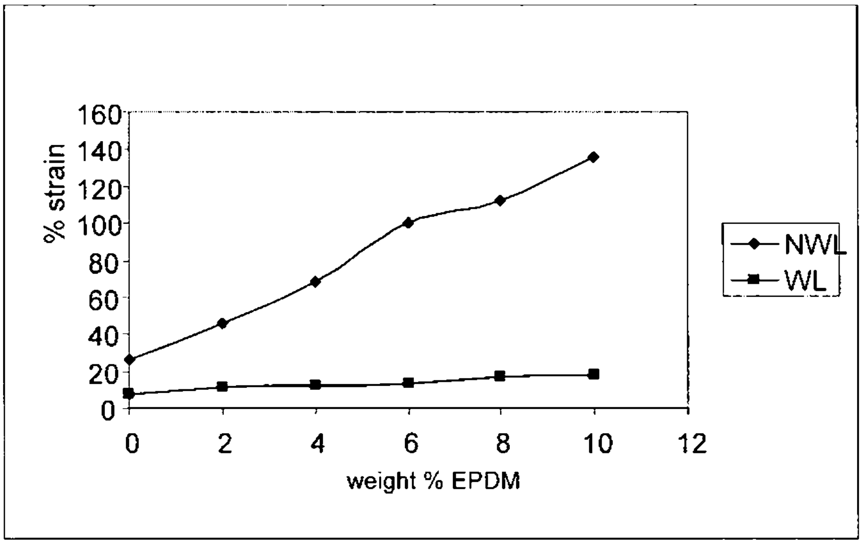

Figure 3.11 *Elongation at break for 50/50 PP/HDPE blend for varying EPDM content*

3.3.6 Effect of temperature of the melt

The melt temperature has no significant effect on 50/50 blend of PP/HDPE for samples without weld line, up to 240°C, after which there is a reduction in strength which may be due to degradation as in the case of pure samples (Figure 3.12). But in the case of the blends with weld line a clear optimum processing temperature is observed at about 240°C. A further evidence for weld line modification by EPDM was that the blends could be moulded at lower temperatures in the presence of EPDM. Annealing for 2hours at 100°C in air for short durations is found to modify the weld line as is seen from Figure 3.13, but ageing for 48 hours at 70°C in air reduces the strength of both the weld line and no weld line samples.

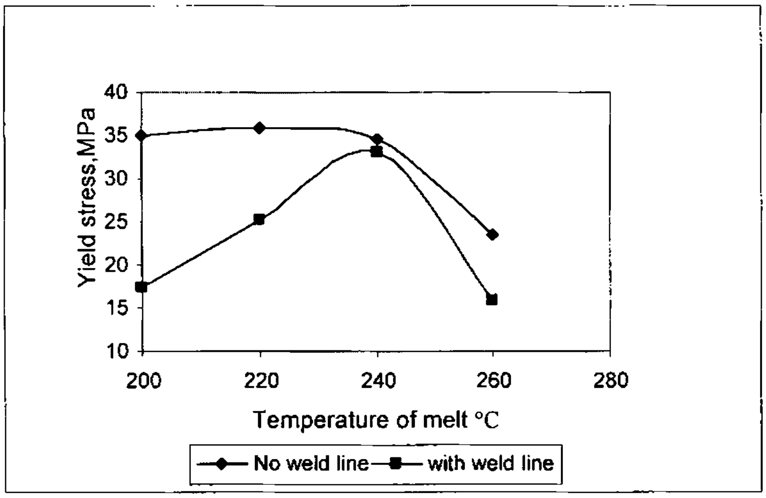

Figure 3.12 *Effect of temperature of melt on the weld line strength of 50/50 PP/HDPE containing 6 weight % EPDM*

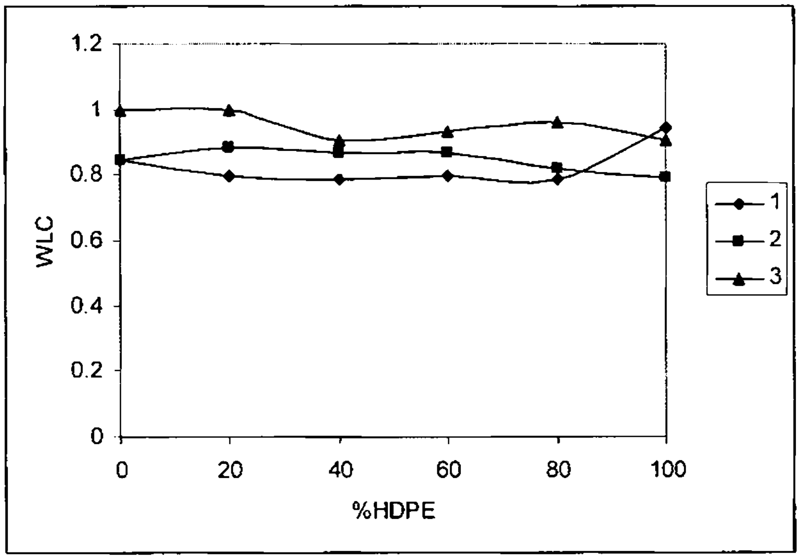

Figure 3.13 *Effect of annealing on WLC of PP/HDPE/EPDM*
1-*PP/HDPE,* **2**-*PP/HDPE/EPDM* **3**-*PP/HDPE/EPDM Annealed*

3.3.7 Rheology

Physical and chemical interactions across phase boundaries are known to control the overall performance of immiscible polymer blends. Strong interactions result in good adhesion and efficient stress transfer from continuous to dispersed phase. Although interfacial adhesion controls primarily the mechanical properties such as strength and toughness, rheological and processing characteristics are also affected. Most of the polymers do not mix during processing and as a result a sharp interface may occur between the two phases. Blends of this type are often preferred since they combine some of the important characteristics of both constituents. The overall performance is related to the size and morphology of the dispersed phase and its stability to coalescence. It is now well established that in addition to composition, rheological properties and type and extent of interactions between the blend components play a prominent role in determining the weld line strength. Thus viscosity and elasticity of the blend components at processing conditions affect the size and shape of the dispersed phase. Type and extent of specific interactions between constituents are known to control the size of the dispersed phase and adhesion. Compatible blends have low interfacial tension and strong adhesion between phases and such blends give good mechanical properties and in turn good weld line strength. Suitable additives reduce the interfacial tension. They act on the interface as emulsifiers. Crosslinking agents do not necessarily act at the interface though they are compatibilizers. Thus the flow characteristics of the blends are very important when considering weld line behaviour.

The effect of EPDM on the flow behaviour and viscosity of PP/HDPE 50% blends is shown in Figures 3.14 and 3.15 respectively. There is a decrease in viscosity of the blends on addition of EPDM in the range of 4 to 6% and there is an optimum of EPDM content of 6% for improved flow behaviour.

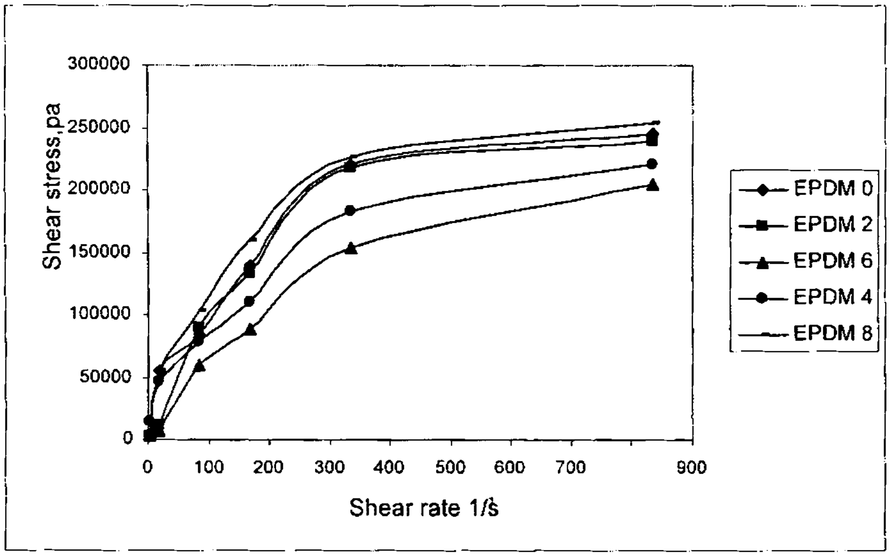

Figure3.14 Shear *stress vs shear rate for 50/50 PP/HDPE blends with different EPDM contents*

The same behaviour is observed for other blend compositions also as indicated in Figures 3.16 and 3.17. Figure 3.18 shows a comparison of the viscosity of the different blends with the optimum EPDM content.

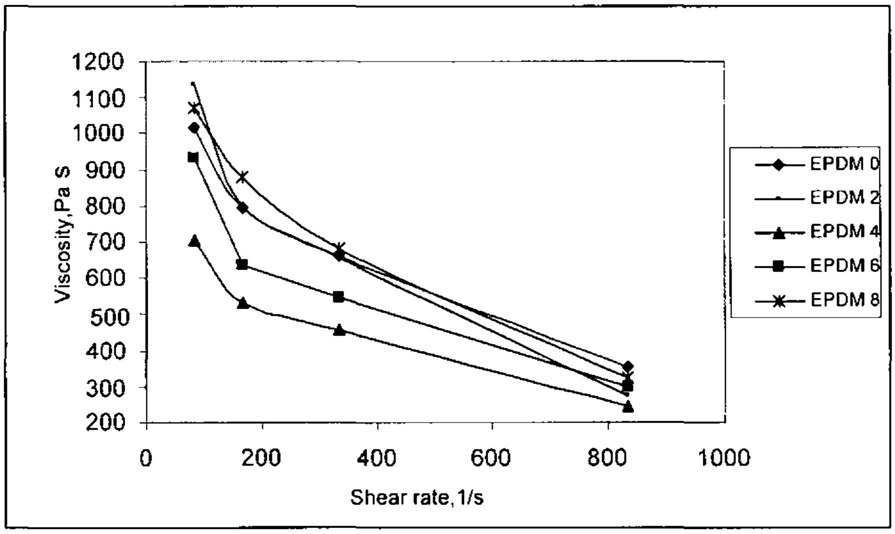

Figure 3.15 *Flow curves for 50/50 blends of PP/HDPE with different EPDM contents*

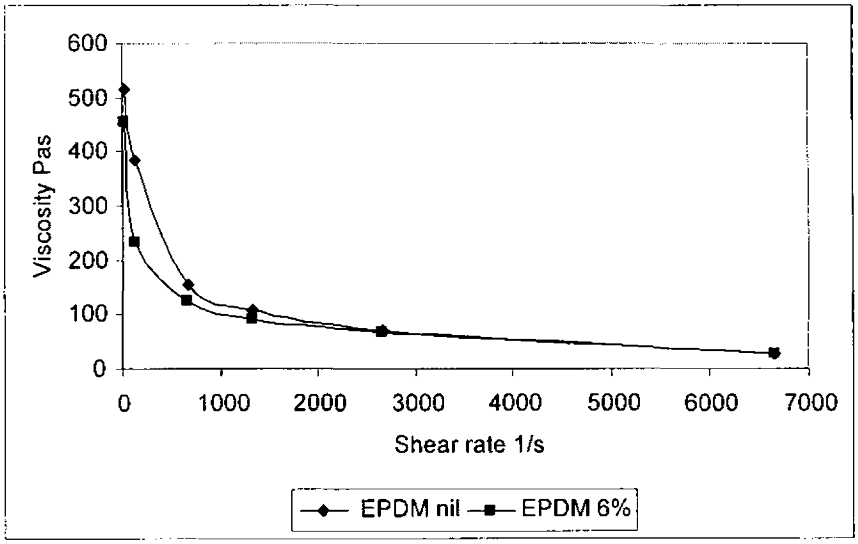

Figure 3.16 *Effect of addition of EPDM on viscosity for PP/HDPE 80/20 blend*

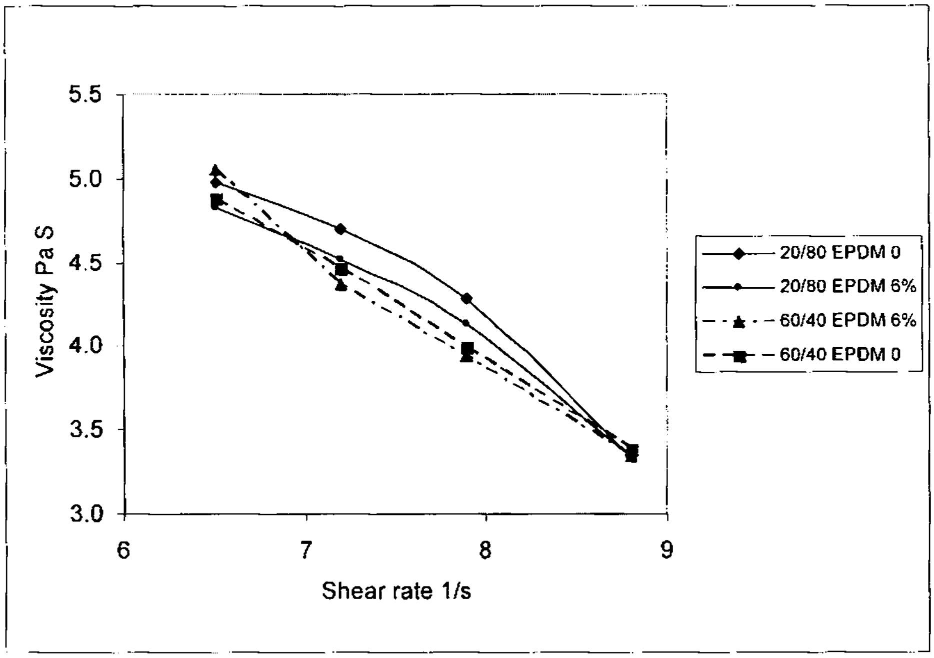

Figure 3.17 *Effect of EPDM on viscosity*

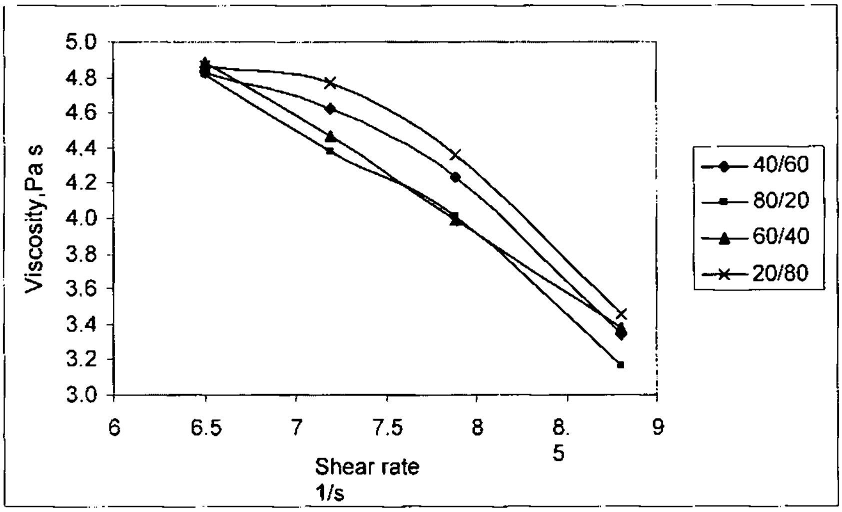

Figure 3.18 *Viscosity with optimum content (6%) of EPDM for PP/HDPE blends*

The reciprocal of the viscosity represents the material mobility and the high mobility (low viscosity) adds to the weld line strength [28]. The viscosity is least when EPDM is 6% and hence the weld line strength is maximum for this blend. At high shear rates the flow behaviour is nearly the same for blends with and without EPDM and hence it can be concluded that the processing by injection moulding is aided by the presence of EPDM.

3.3.8 Effect of parameters of blending

The influence of variables like temperature of blending, rpm and time of mixing on the weld line strength were studied and the results show that about 185°C, 40 rpm and 5 minutes mixing time are the optimum in this case. The mode of preparation influences the state of dispersion of the components of the blend and influences the mechanical properties as is evident from the Figures 3.19 to 3.21. The results shown are for 50/50 HDPE and PP blend. The moulding was done at 240°C in all cases.

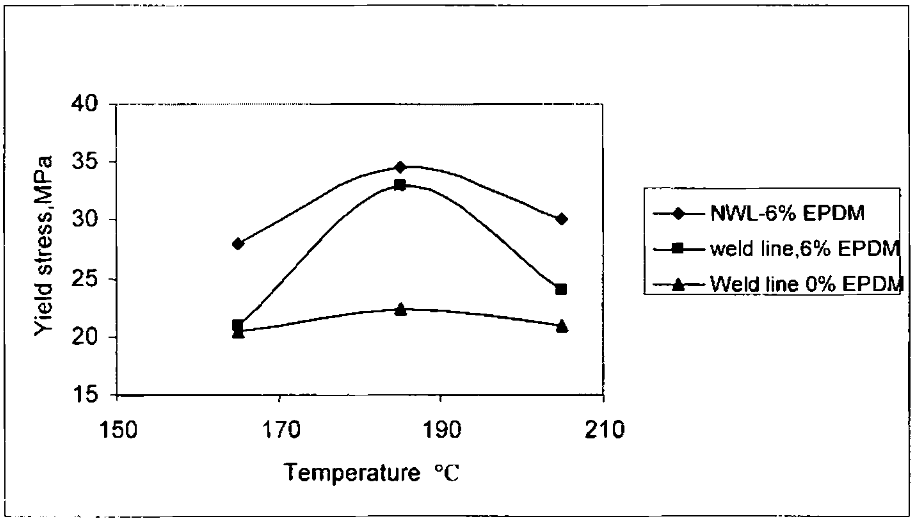

Figure 3.19 *Effect of blending temperature for samples with and without weld line*

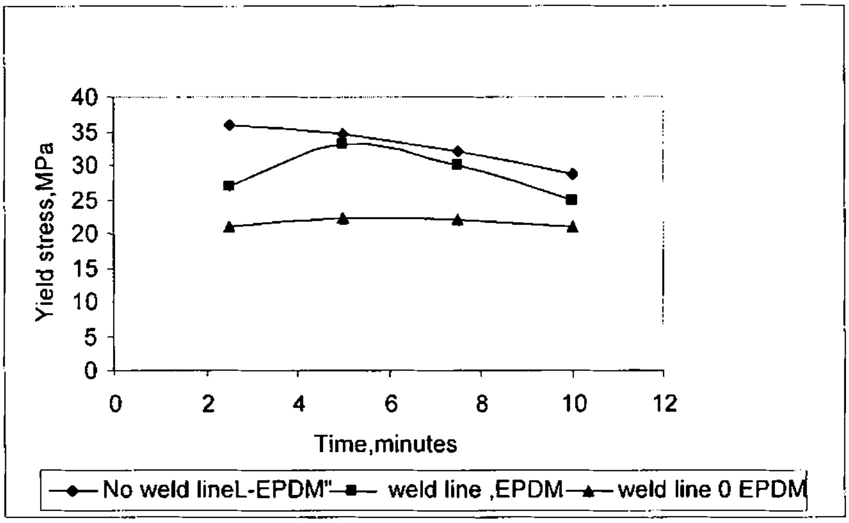

Figure 3.20 *Effect of blending time*

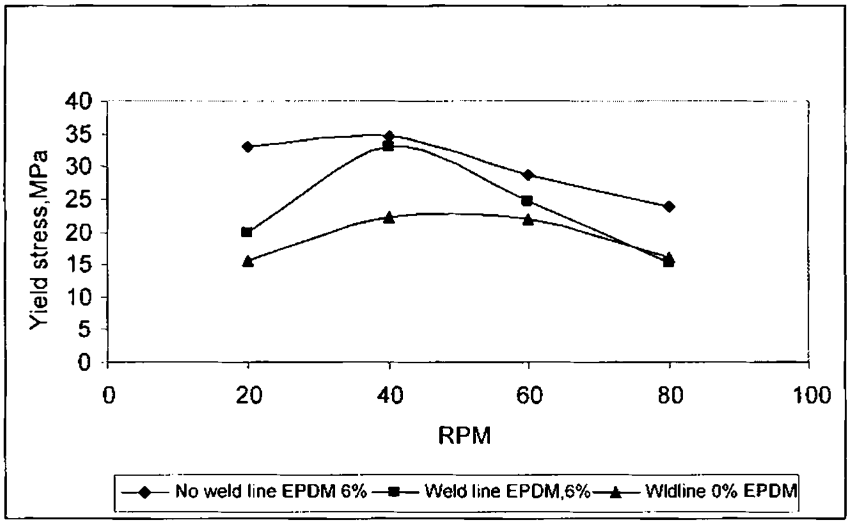

Figure 3.21 *Effect of shear rate on blending*

3.3.9 Die Swell

The extrudate swell $B = D/d$ where D and d are the extrudate and die diameter. The die swell is temperature sensitive and is dependent on the strain rate. At the capillary entrance the drops become deformed and the retractions of these fibers cause large extrudate swell. At high strains both phases will be strained and smaller B values are obtained. The swelling is mainly due to strain recovery of fibrillated drops. The die swell behaviour of PP/HDPE blends at two temperatures and shear rates with and without EPDM is shown in Figure 3.22. As expected the die swell increases with increase in shear rate but decreases for increase in temperature.

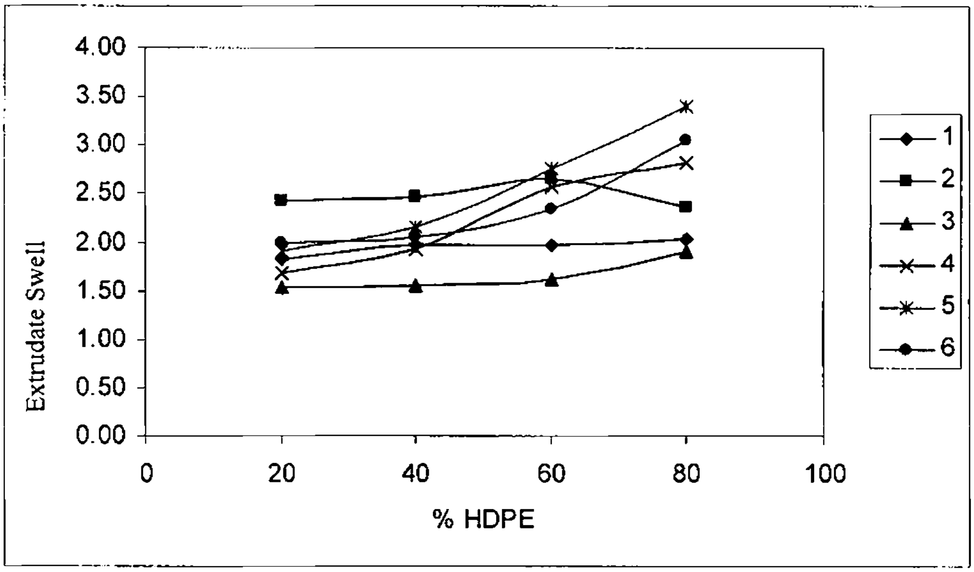

Figure.3.22 *Extrudate swell for blends with and without EPDM (6%)*

1-PP/HDPE/EPDM 250°C (high shear)
2-PP/HDPE/EPDM 180°C (high shear)
3-PP/HDPE/EPDM 250°C (low shear)
4-PP/HDPE/EPDM 180°C (low shear)
5-PP/HDPE 250°C (High shear)
6-PP/HDPE 180°C (high shear)

The viscoelastic effects are important in injection moulding when stresses in the melt may relax slowly relative to the heat transfer rate and residual stresses are frozen into the part. Die swell is a function of wall shear stress and the relaxation time of the fluid. As temperature is increased it is seen that the die swell decreases especially for high HDPE content. This is probably due to increased interlayer slip caused by lowering of viscosity. The weld line strength increased as temperature is increased. This shows that the weld line strength is directly related to the die swell. Addition of EPDM reduced the die swell. This is due to the lowering of viscosity by addition of EPDM at the optimum level for weld line strength.

Die swell can be related theoretically by using Tanner equation [21].

$$\frac{D_p}{D_o} = 0.1 + \left[1.0 + 0.5 (\frac{N_1}{2\tau_w})^2 \right]^{\frac{1}{6}}$$

where D_p is the extrudate diameter and D_0 is the die diameter, N_l is the primary normal stress difference. For high shear rates used in injection moulding N_l is predicted using non linear viscoelastic models which are readily available or computed from viscosity data. N_l is directly proportional to the viscosity and relaxation time. In general the die swell for blends follows a parabolic relation

$$B = B_l w_l + B_2 w_2 + B_{l2} w_l w_2$$

3.3.10 Morphology at the weld line

Studies on morphology at the weld line for PP/HDPE/EPDM blends are few in literature. Fellahi and Fisa [15] investigated the weldline morphology for PA6/HDPE blends with a compatibilizer. Brahmi et al [16] studied the system HDPE/PS with a compatibilizer. Jarus et al investigated PVC/HDPE system and

J.K.Kim et al studied Nylon/AN/EPR system [29]. The conclusions from these studies are the following.

1. The blend with compatibilizer exhibited reduced thickness of the skin layer, decreased width of the weld line region and more isotropic weld line morphology compared with a specimen without compatibilizer.
2. Tensile strength of the blend increased with addition of compatibilizer
3. The tensile strength increased with decreased weld line width.
4. There was brittle fracture when the dispersed domain in the blend elongated towards the thickness direction of the specimens.
5. Addition of compatibilizer reduced the dispersed domain sizes and hence improved the weld line strength.

Scanning Electron Micrographs of the fracture surface of 50/50 PP/HDPE blend with 6%EPDM taken on a JOEL JSM 840 operated at an acceleration voltage between 10 and 15 kV are shown in Figures 3.23 to 3.28.

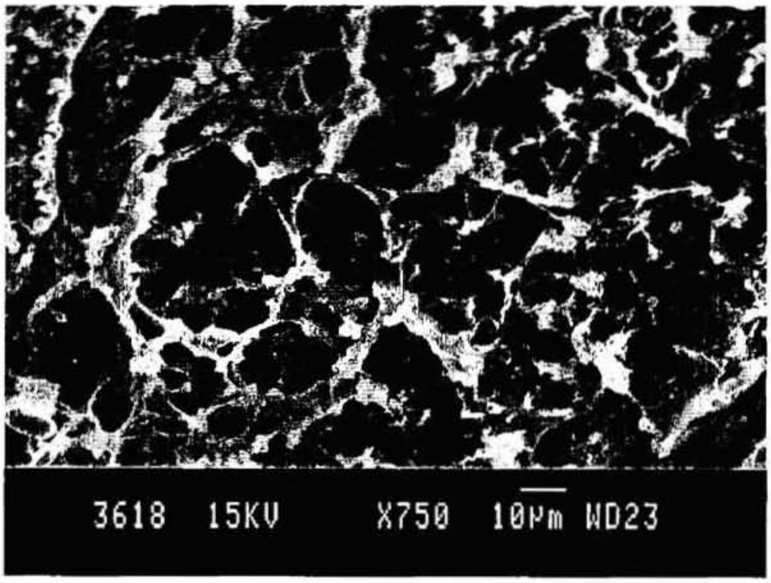

Figure 3.23 *PP/PE Fracture surface without weld line*

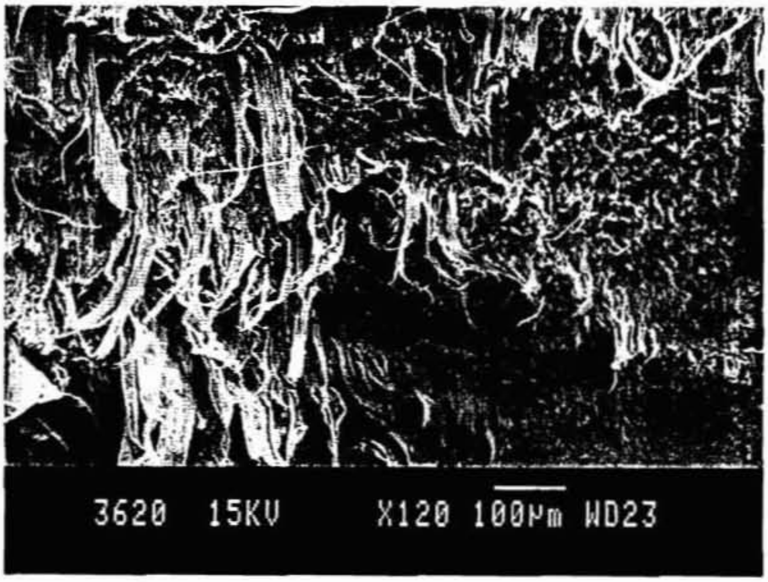

Figure 3.24 *PP/PE/EPDM Fracture surface without weld line*

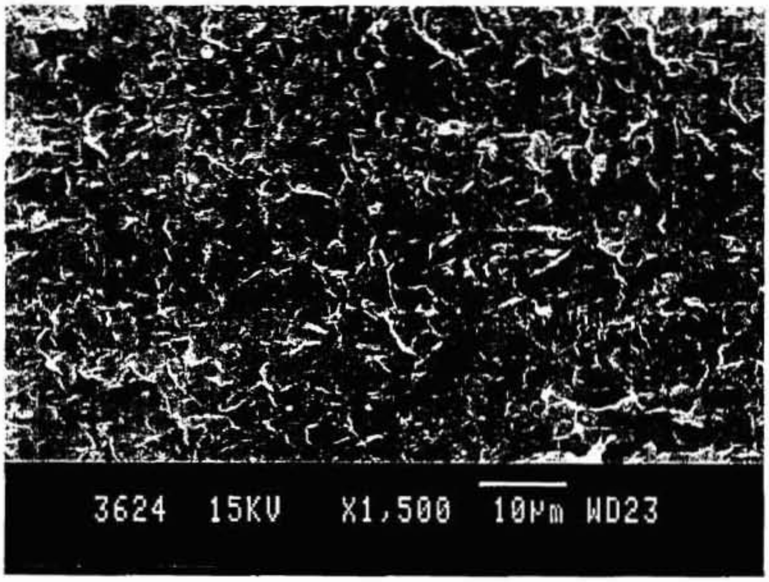

Figure 3.25 *PP/PE/DCP Fracture surface with weld line*

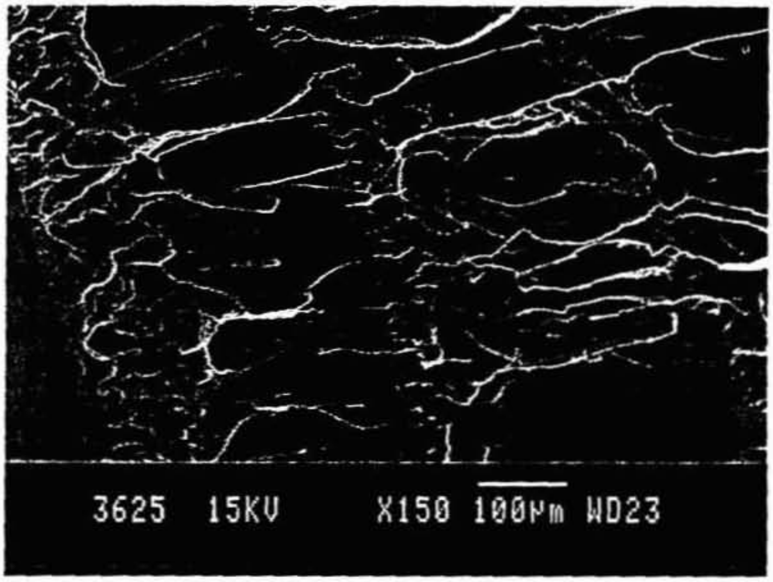

Figure 3.26 *PP/PE Fracture surface with weld line*

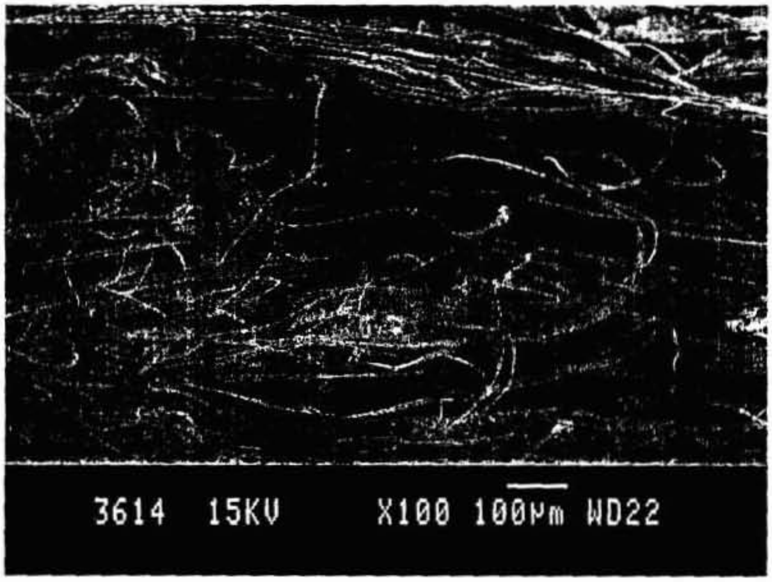

Figure 3.27 *PP/PE/EPDM Fracture surface with weld line*

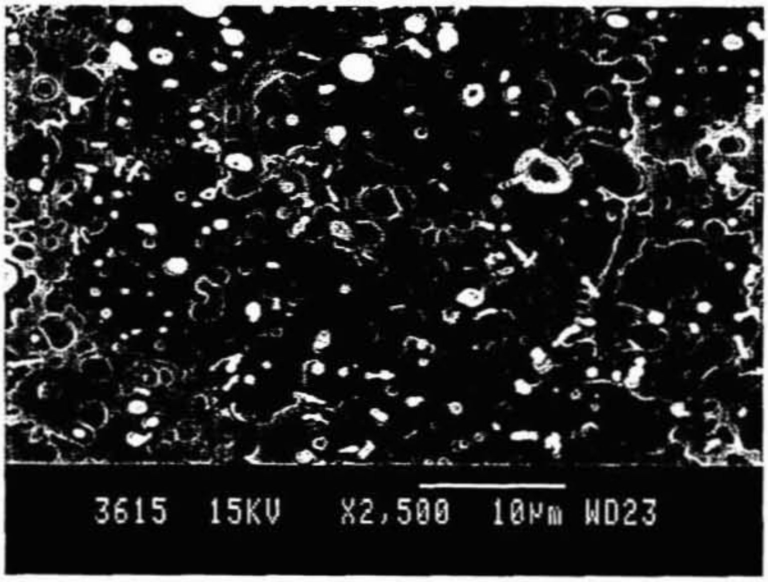

Figure 3.28 *PP/PE/EPDM Fracture surface at the weld line magnified*

The micrographs give evidence for ductile fracture when EPDM is present. SEM micrographs of the ternary mixture show extensive presence of fibrils indicating a ductile fracture mechanism. The presence of EPDM in the weld lines is found to transform the brittle fracture to ductile nature and since there is improved adhesion the weld line strength and elongation at break are higher than that of samples without EPDM. It is well established that EPDM acts as an interfacial agent favouring adhesion between PP and PE and reducing the dimensions of the domains of the dispersed phase. Crack formation and quick propagation is reduced. The presence of fibrils can be observed in the SEM micrographs for both weld line and no weld line samples. Evidence of modified fracture mechanism and overall surface morphology is obtained from the SEM. The presence of fibrils indicates that shear yielding mechanism is active.

The sub-skin layer covers almost the entire thickness thus reducing the effect of the formation of skin core morphology as is seen from the SEM images.

Near the cavity wall the molten polymers are immediately solidified, thus the skin layer is formed, implying that the dispersed domains near the walls are not elongated by the shear stress. The largest elongation of dispersed domain occurs at the sub-skin where the shear stress is the largest, just below the skin layer. At the center, which is called the core the shear stress is minimum, and the dispersed domain structures are not changed with the flow. There is no evidence of formation of V-Notch in samples with and without EPDM.

3.4 Conclusions

The study shows that the weld line strength of the blends of PP/HDPE can be improved in several ways. The blending temperature, shear and time of blending can be properly selected to improve weld line strength. The actual moulding temperature also significantly affects the weld line strength as it influences the diffusion time profoundly. However, when using a higher moulding temperature care is to be taken to prevent degradation of the polymers. A notable finding of the study is that compatibilizers can improve the weld line strength. The concentration of the modifier required for maximum improvement in weld line strength is higher than that required for optimum compatibilization.

3.5 Effect of DCP

Polyolefins are sometimes modified with organic peroxides to alter their processability and mechanical properties [30]. 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. 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 site to form a C-C cross link.

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, extrusion or injection moulding. By cross linking the thermoplastic material is converted into a thermoset material thus improving its properties and broadening of the scope of applications. The controlled degradation of PP is done by peroxide crosslinking. Under processing conditions of high temperature and shear polyolefins may undergo chain scission reactions leading to a decrease in molecular weight [23]. The most important use of controlled degradation is the visbreaking reaction, a process based on β scission reaction occurring in PP that results in a decrease of average molecular weight and a narrowing of the molecular weight distribution. The flow behaviour of the parent polymer is considerably improved and the shear viscosity approaches a Newtonian character. These characteristics are advantageous for injection moulding as they can be processed at lower temperatures and more output can be obtained with few processing problems on modern high speed equipments.

Dicumyl peroxide was tried as a weld line strength modifier for PP/HDPE blends. The addition of DCP reduces the strength of both samples with and without weld line at high concentrations of PP, and the strength increases at high concentrations of HDPE as is seen from Figure 3.29.

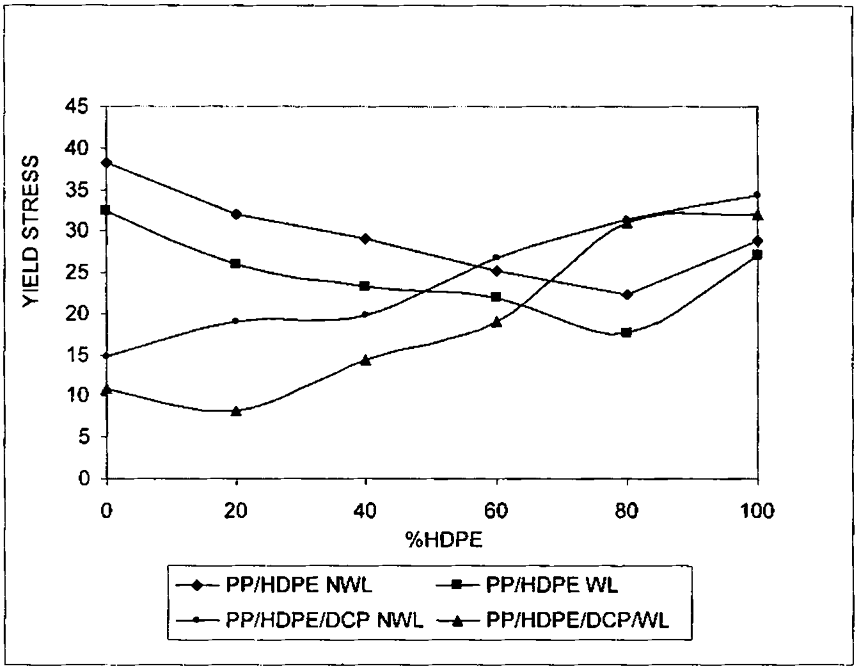

Figure 3.29 *Effect of DCP (1phr) on the weld line strength of PP/HDPE blends*

At high concentration of PP there is degradation of PP and at high concentrations of HDPE there is crosslinking. These can be seen from the torque curve obtained during mixing (Figure 3.30). The rheological data obtained from capillary rheometer represented in Figure 3.31 also confirms this. As the HDPE is increased the viscosity is high whereas for high percentages of PP a degraded material with low viscosity is obtained. Since at high shear rates the viscosities are not very high for HDPE rich blends, processing by injection moulding will not pose any difficulty. The SEM micrograph at the weld line with and without DCP indicates the change in morphology with the addition of DCP.

Table 3.2 *Effect of DCP on PP&HDPE*

	Yield stress, MPa			Strain,%				
		NWL	WL	NWL		WL		
DCP (phr)	1.5	1	1.5	1	1.5	1	1.5	1
HDPE	38.3	34.3	33	32	167.9	240.5	20.5	65
PP	-	14.71	-	10.85	-	2.8	-	1

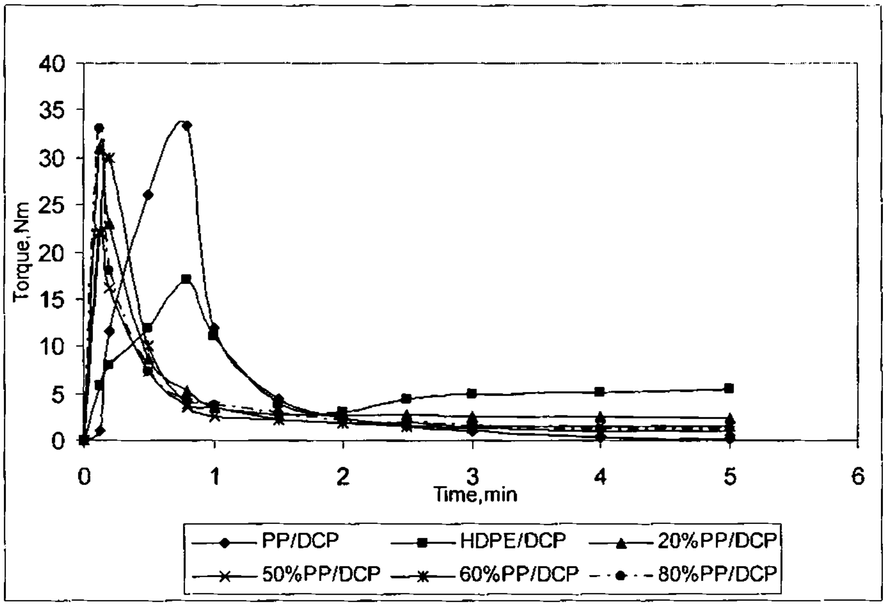

Figure 3.30 *Effect of DCP(1 phr) on Torque for PP, HDPE and PP/HDPE blends*

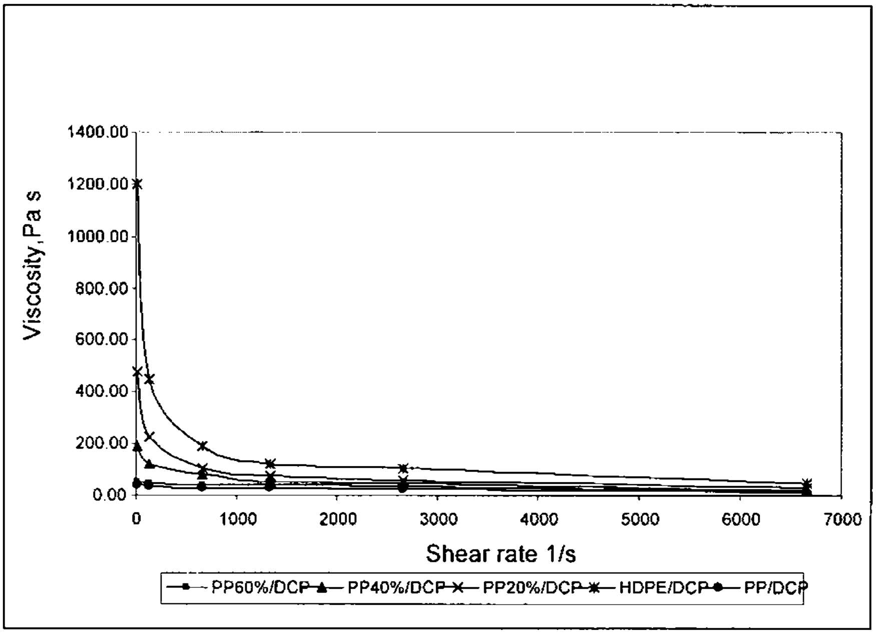

Figure 3.31 *Effect of DCP (1 phr) on viscosity of PP, HDPE and PP/HDPE blends*

3.6 Conclusions

The study shows that peroxide modification of PP/HDPE blends can be advantageously used to improve the weld line strength of these blends especially in HDPE rich blends. Dicumyl peroxide at concentration levels of 1 phr improves the weld line strength at HDPE concentrations above 60 percent by weight for PP/HDPE blends. The improvement results from a small degree of crosslinking which stabilizes the weld line even though the melt viscosity is marginally higher due to this effect.

3.7 References

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Chapter 4

Weld line behaviour of polyethylene blends

4.1 Introduction

Polyethylenes since their discovery in 1933 have seen a continuous rise in consumption to more than 40% of all the plastics market. This growth rate can be attributed to the continuous modification and developments of this polymer. Low density polyethylene (LDPE) which is produced by the radical polymerization of ethylene under high pressure conditions is branched with crystallanity in the range of 40% is having a melting point of 110 -130°C and density of around 0.91-0.92 g/cc. High density polyethylene (HDPE) made using coordination catalysts or supported metal oxide catalysts are produced at much lower pressure and temperature. They are linear having much fewer branches and have upto 90% crystallanity with density 0.94-0.965 g/cc and melting points in the range of 140-150°C. Their properties like inertness to chemicals, resistance to break up, moisture resistance, insulating properties etc, combined with their low cost and easy processabilty by a wide variety of techniques put them to a large spectrum of applications like films, cable insulation, pipes, toys, acid resistant containers, household articles etc. It is estimated that more than 50% of the polyethylenes enter the market as blends for improved properties and a significant fraction of it is formulated for improving the processability without affecting the PE performance. Blends of different grades of polyethylene fall in this category.

Since the homologous polymer blends are known to be miscible, the mixtures of different grades of LDPE and LDPE with HDPE are miscible [1, 2].

Available information on the miscibility of PE blends indicates that in the absence of strong thermodynamic interactions both the dissolution and phase separation are diffusion controlled. Though homogeneous melt can be generated by solution blending, melt blending will result in a phase separated material [3, 4]. There is direct evidence of true miscibility of homologous polymer blends, while even a small change in polymerization method, polymer composition or structure may lead to apparent immiscibility [5, 6]. Since for high molecular weight industrial PE the conformational entropy of mixing is negligibly small and there are no specific interactions between two polyethylenes of different structure, in these systems the miscibility is controlled by small departure from zero of the free energy of mixing.

HDPE/LDPE blends were studied by Dobrescu et al [2] and they concluded that they are immiscible with a strong positive deviation from log additivity rule. Kammer et al [7] also reported that HDPE/LDPE blends indicated PDB. White et al [8] have reported that HDPE/LDPE blends they investigated showed NDB. Reported results indicate that HDPE/LDPE blends are immiscible, although the immiscibility may be marginal, disappearing at higher temperatures for low molecular weights and their behaviour can be diverse.

The objective of the present chapter is to investigate the weld line behaviour of two grades of low density polyethylenes PE1 and PE2, their blends and blends of PE1 with high density polyethylene (HDPE) and to study the effect of crosslinking agent and filler on the weld line strength. It is also proposed to investigate the effect of ageing and weathering on the weld line strength of these polymers and blends.

4.2. Experimental

4.2.1 Materials used

LDPE grade 16 MA 400 made by Indian petrochemicals limited (IPCL) with MFI 30 g/10 min (PE1)

LDPE grade 24 FS 040 made by Indian petrochemicals limited (IPCL) with MFI 4 g/10 min (PE2)

HDPE grade 50 MA 180 made by Indian petrochemicals limited (IPCL) with MFI 18 g/10 min

Dicumyl peroxide (commercial grade 40% active), Calcium carbonate (commercial grade)

4.2.2 Mixing and moulding

Thermo Haake Rheocord 600 having a mixing chamber of volume 69 cm^3 with roller type rotors was used for blending. The parameters for melt mixing viz. melt temperature, rpm and time of mixing were fixed after optimizing to get the best properties and also without allowing for mechanical or thermal degradation. The temperature, rpm, time of mixing, torque and energy are automatically recorded. In the case of addition of DCP, the blend was blended properly and DCP was added such that the time of mixing given was not sufficient for crosslinking. This was fixed after studying the torque vs time curve for each blend. The hot mix from the mixing chamber was immediately passed through a two roll mill and cut into small pieces. The test specimens with and without weld lines were moulded in a semi automatic plunger type injection moulding machine for various melt temperatures.

4.2.3 Mechanical Testing

Tensile properties were evaluated on a 10 kN universal testing machine (Shimadzu) make at a crosshead speed of 50 mm/minute as per ASTM D 638

4.2.4 Rheology

The rheological measurements were carried out using a capillary rheometer attached to 50 kN universal testing machine (Shimadzu) using a die of L/D ratio 40. The details of the set up are given in section 2.6.1.

4.2.5 Ageing and weathering studies

Ageing studies were done on a laboratory hot air oven by keeping the samples for 48 hours at 70°C.Weathering studies were done as per ASTM D1435 for a period of three months in the hot season which provided harsh conditions for polymer degradation.

4.3 Results and Discussion

4.3.1 Effect of temperature of melt

The weld line co-efficient (WLC) is defined as the ratio of tensile strength for the sample with weld line to that with out weld line when both the samples are prepared under identical conditions. The operating conditions have influence on the WLC as is seen from the data for PE2 and HDPE (Figures 4.1 and 4.2). It is seen that as the temperature increases the WLC increase for a range of temperature from 170°C to 270°C. However above this temperature range the WLC falls probably due to the degradative effect surpassing the better flow rate for the higher temperature. In the case of PE1 as it has a high MFI of 30 g/10min, it is easily injection mouldable and effect of variation of melt temperature could not be studied as it degrades in a very low range of temperature.

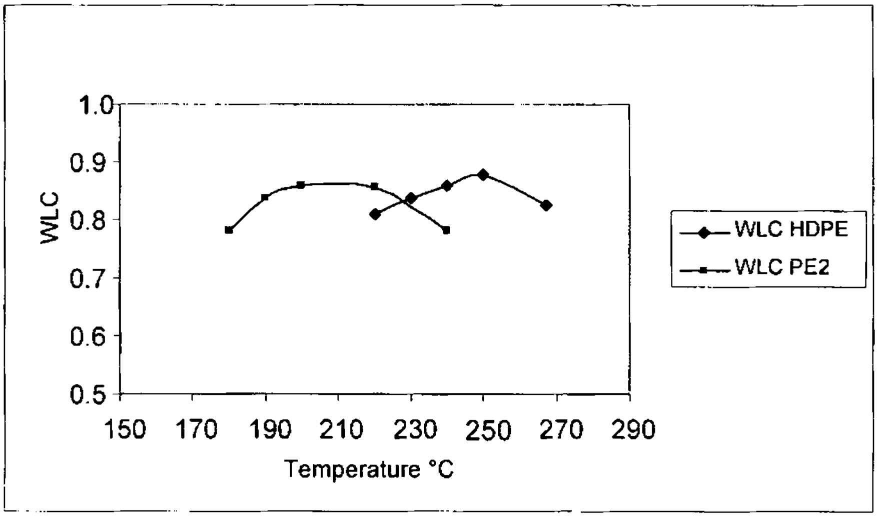

Figure 4.1 *Variation of weldline coefficient with variation in melt Temperature for pure PE2&HDPE*

The weld line coefficient will be high when there is good entanglement between molecules. The molecular entanglements will be high if the melt contact time is sufficient for achieving distance of diffusion greater than R_g the radius of gyration .According to reptation theory the distance of diffusion $\langle l^2 \rangle$ is given by

$$\langle l^2 \rangle = 2Dt$$

where D is the coefficient of diffusion and t is the time of diffusion.

For polymer welding $\langle l^2 \rangle = R_g^2$ at $t = t_w$ and hence $t_w \propto R_g^2/D$. From [9-16] for highly entangled molecules $D \propto M^2$

Thus small difference in molecular weight will result in large difference in time to achieve optimal weld conditions. So for LDPE of two different molecular weights the weld line coefficients will be proportional to the ratio of the molecular weights and in turn the ratio of the melt flow indexes.

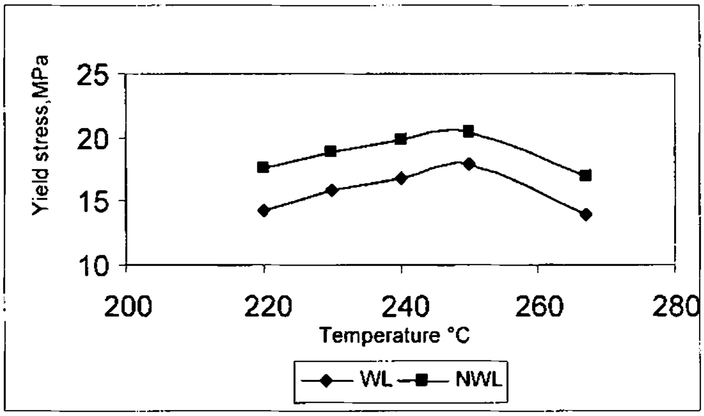

Figure 4.2 *Tensile strength with and without weld line for HDPE for different melt temperatures.*

4.3.2. Weld line strength of PE1/PE2 blends

Table 4.1 *Yield stress of pure polymers*

Material	Yield stress, MPa	Yield stress, MPa	Ratio
	Weld line	No Weld line	Weld line coefficient
PE1	8.34	8.88	0.94
PE2	9.98	11.75	0.85
HDPE	15.85	18.92	0.84

PE2 with melt flow index 4 is having a lower value for WLC as compared to PE1 with melt flow index 30. This is because the flow properties are better for higher

MFI as the molecular weight is lower and this combined with the dependence of molecular entanglement on diffusion coefficient and molecular weight.

As the MFI is higher for PE1 the viscosity is lower and the melt streams will bond together better as the mould cools, whereas for PE2 which has a lower MFI and hence higher molecular weight, is more viscous and the flow velocity will be lower. This will result in poor entanglement of molecules at the weld before cooling and hence the strength at the weld line is poor. When blends of these are prepared and the viscosity is found out as a function of the percentage of PE1, it is seen that as the percentage of PE1 is increased there is a gradual decrease in viscosity and hence a proportional decrease in molecular weight. So for blends of the same type of material of two grades the WLC is dependent on the flow characteristics or mobility of the molecules which is the inverse of the viscosity. For the blends of PE1/PE2 as they are of the same type and hence compatible as the composition changes the viscosity is changing and WLC is a direct function of viscosity. From Figure 4.3 and 4.4 it can be seen that the WLC and viscosity are inversely related.

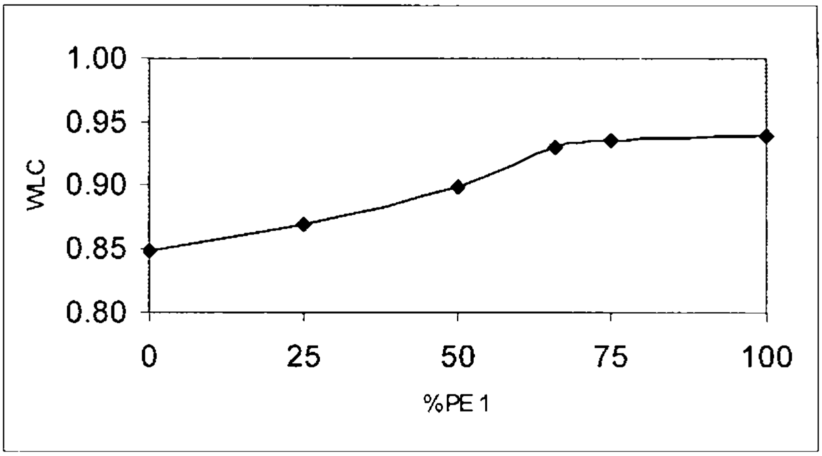

Figure 4.3 *Variation of WLC (yield stress)with composition PE1/PE2 blends*

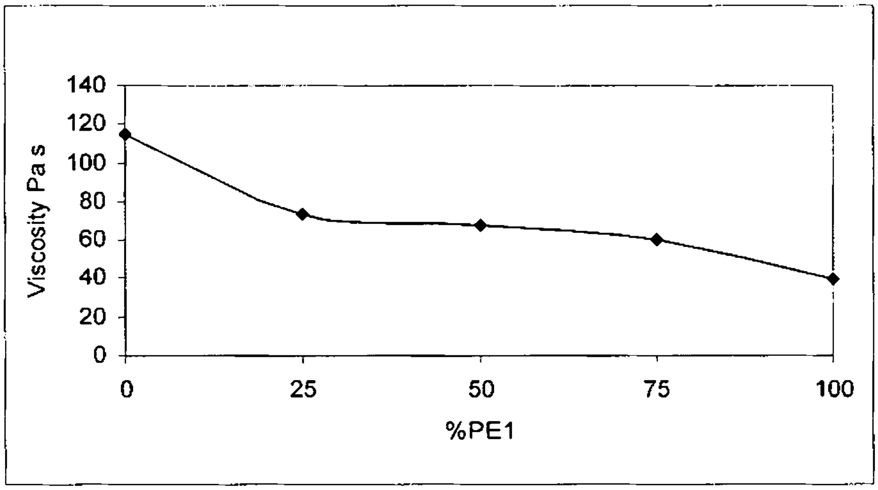

Figure 4.4 *Variation of viscosity of PE1/PE2 blends with composition at a constant shear rate of 1333.3 s^{-1})*

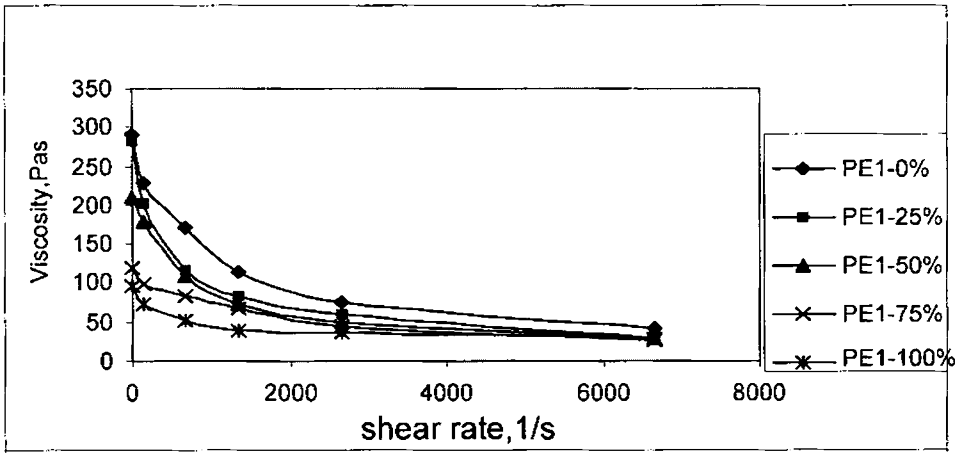

Figure 4. 5 *Flow curves of PE1/PE2 blends*

The viscosity of the blends at different shear rates is given in Figure 4.5. It can be seen that at high shear rates that are representative of injection moulding the viscosity of the blends are nearly the same.

Both the materials and their blends are having similar flow behaviour as can be seen from the torque versus rpm plots for the individual polymers and their blends given in Figure 4.6. The viscosities of the blends are between those of the pure polymers and they obey the logarithmic additive rule.

$$\log \eta_m = w_1 \log \eta_1 + w_2 \log \eta_2$$

Log torque vs log rpm are almost linear and parallel for the blend indicating that the power law index are the same for the blends and pure polymers.

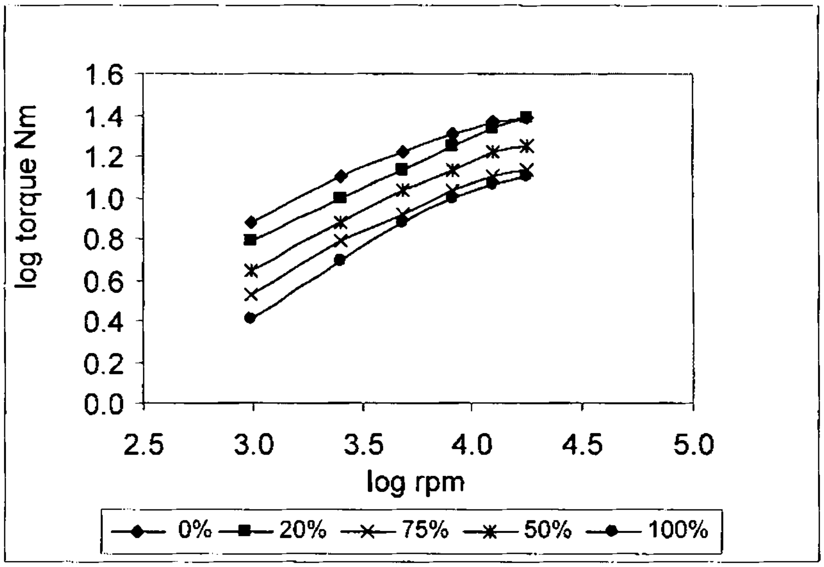

Figure 4.6 *Flow curves for the blends of PE1 and PE2 for different weight % of PE1 from Haake Torque Rheometer*

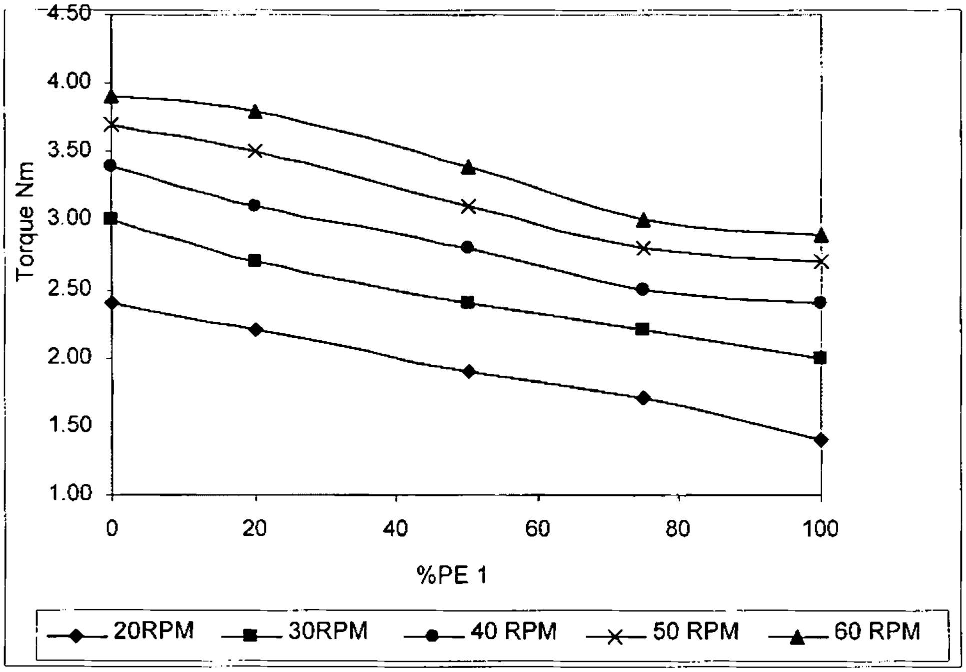

Figure 4. 7 *Variation of Torque with composition of PE1/PE2 blends at various rpm*

4.3.3 Weld line behaviour of HDPE/PE1 blends

With blends of HDPE and PE1 it is seen that the weld line co-efficient (WLC) is increasing as the percentage of PE1 is increased as in Figure 4.8 The WLC is increasing because as HDPE is blended with LDPE of a lower molecular weight there is improved flow and the time of welding will be sufficient to get a better weld than pure HDPE. But the absolute values of the yield stress are lower than that of HDPE.

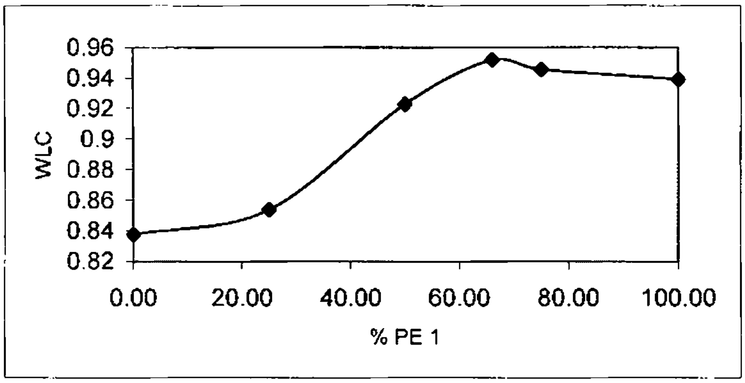

Figure 4.8 *Variation of WLC with composition forHDPE/PE1 blends*

4.3.4 Effect of crosslinking

Dicumyl peroxide (DCP) is known to be a crosslinking agent for polyethylene and is extensively used in improving the processability and mechanical properties of finished goods. The effect of crosslinking to reduce the effect of weld lines is investigated. From torque studies in the Rheomix it was seen that crosslink occurs in the range of 190°C for various percentages of DCP ranging from 0.2 to 2 phr. It can be seen from the sample graph of PE2 (Figure 4.9), very low concentrations of DCP has no significant effect on the torque and for higher concentrations the torque is high and the time for cross linking is short. The samples with the weld lines are difficult to mould for higher concentrations of DCP. So the DCP content of 1.5 phr is the optimum. DCP was mixed with the pure polyethylene and their blends. The tensile strength of the samples increased with the introduction of DCP. It is seen that the weld line coefficient has increased to nearly 1.0 when DCP was used. The tensile strength of the weld line samples increased by about 25%for the samples of the blends as seen from Figure 4.11

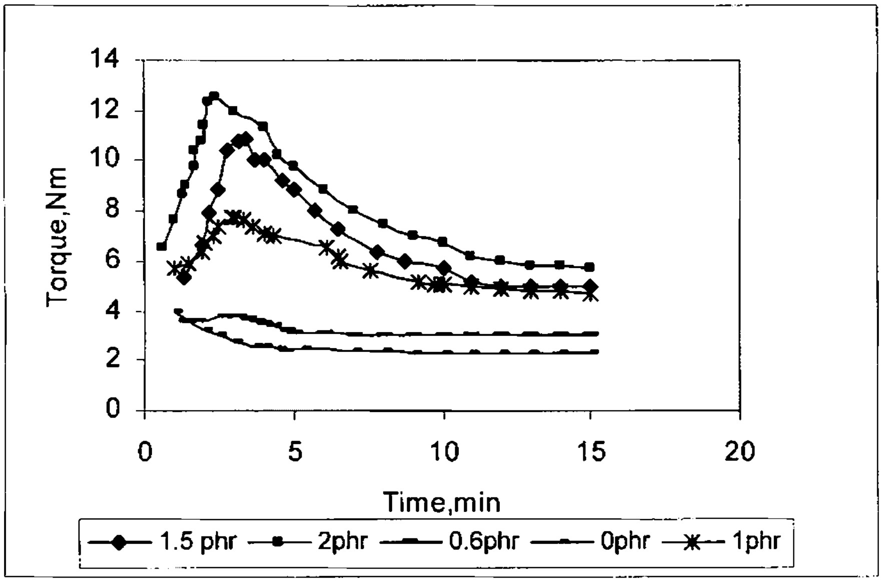

Figure 4.9 *Effect of DCP content on PE2*

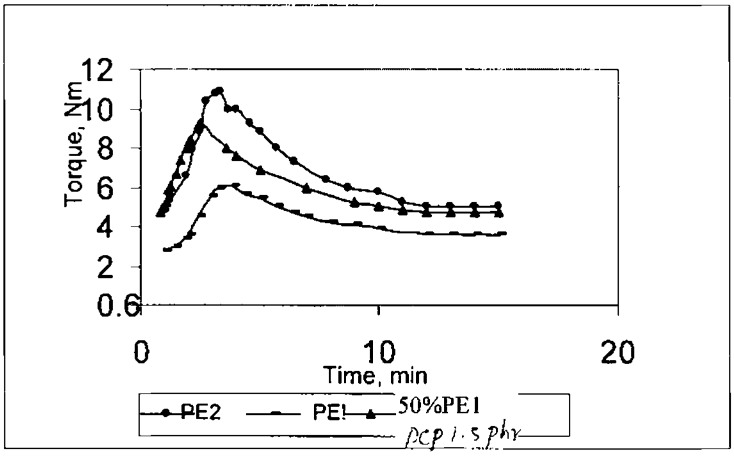

Figure 4.10 *Effect of DCP content on Torque of PE1,PE2 and their blends at a fixed shear rate(40 rpm)*

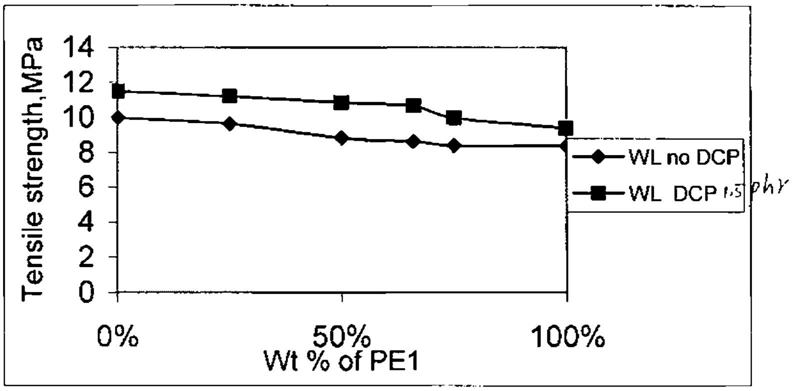

Figure 4.11 *Effect of DCP content on the tensile strength of PE1/PE2 blends*

The viscosity of the pure polymers and the blends increases due to the addition of DCP as is seen from the Figure 4.12 to 4.14. Even though flow behaviour is most important for weld line strength, here the effect of cross linking is predominant.

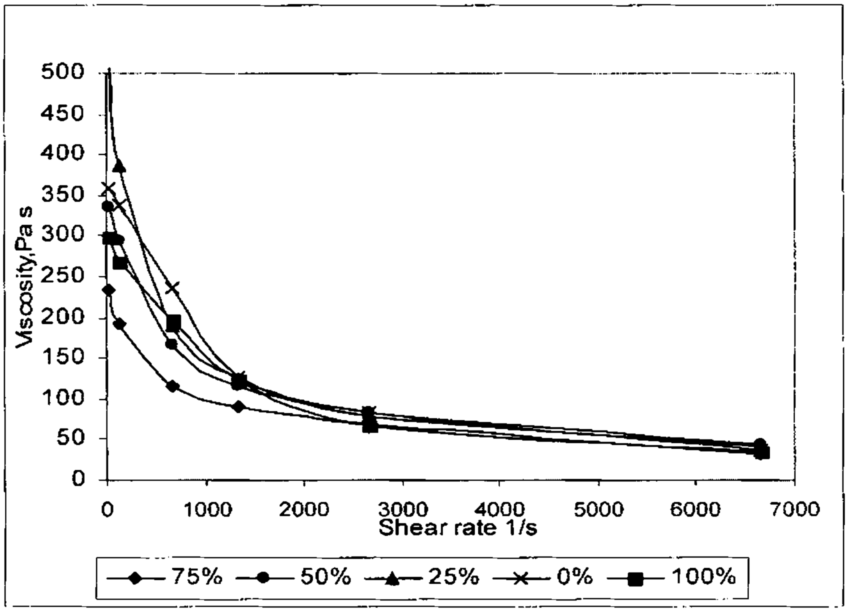

Figure 4.12 *Variation of viscosity ofPE1/PE2 blends with DCP content of 1.5 phr for vaying weight % of PE1*

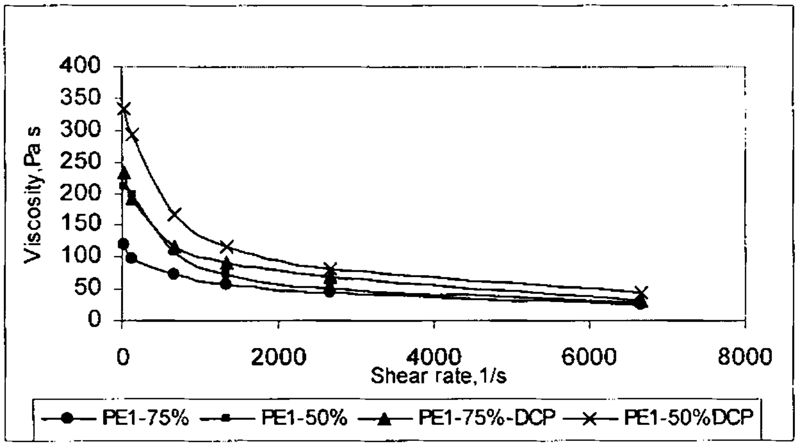

Figure 4.13 *Effect of DCP (1.5 phr) content on viscosity of PE1/PE2 blends*

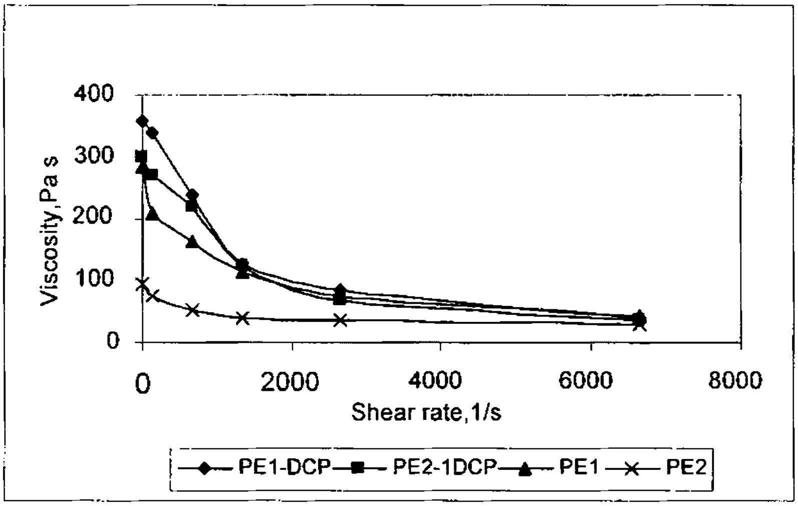

Figure 4.14 *Effect of DCP content (1.5 phr) on viscosity of PE1&PE2*

4.3.5 Effect of addition of filler on PE1

The weakness of weld lines in filled and reinforced polymers is attributed to the aspect ratio of the dispersed phase [18, 19]. A serious reduction in strength is reported for polymers reinforced with glass fibers of high aspect ratio. The higher the aspect ratio, the weaker the weld line. However for spherical additives lead to negligible difference for strength of weld line and no weld line. $CaCO_3$ filler is having nearly isometric particles.

The effect of $CaCO_3$ filler was investigated by adding $CaCO_3$ up to 10% by weight. It was observed that the WLC is increasing for the filler content up to 8%.The yield stress for both weld line and no weld line samples are both lower than the samples without filler, but there is no significant difference in yield stress for both WL and NWL samples.

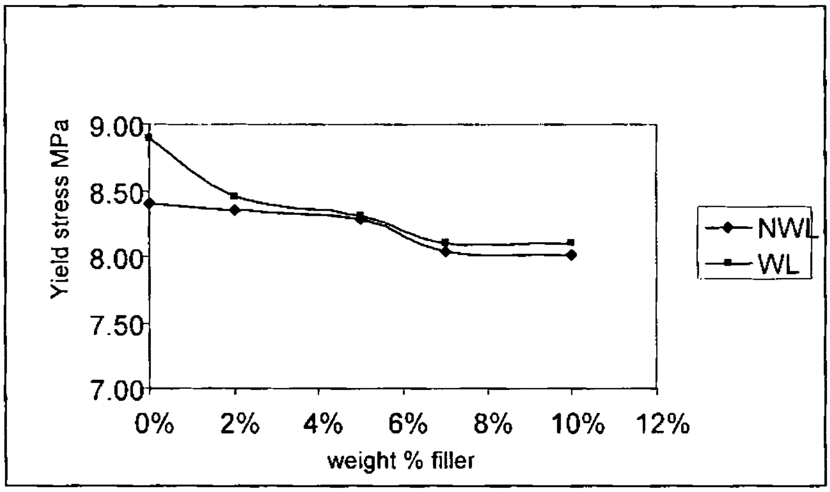

Figure 4.15 *Effect of filler content on the yield strength of PE1*

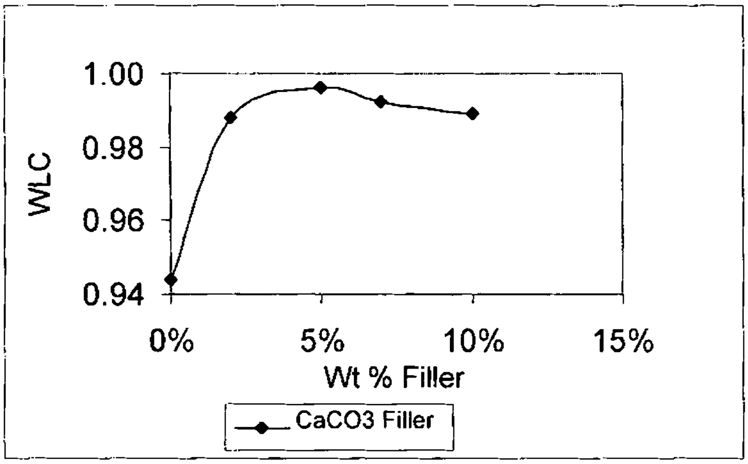

Figure 4.16 *Effect of filler content on the WLC of PE1*

4.3.6 Effect of addition of filler on blends of PE1/PE2 and PE1/HDPE

In a number of engineering applications the thermoplastic material of choice are multiphase systems containing blends having fillers. The weld line behaviour of such systems needs to be investigated [20, 21]. It was observed that the weld line coefficient is found to be slightly increasing for the case of $CaCO_3$ filler up to 8% for both blends of PE1/PE2 and PE1/ HDPE as given for the blends containing 5% filler as seen in Figures 4.17 and 4.18.The strength of the weld line sample is nearly equal to that without weld line as seen from Figure 4.15. The samples are brittle and the breakage occurred at the weld lines. The presence of filler affects the compatibility of the blends as pointed out by Jarus et al [22] that to eliminate the elongated and oriented domains parallel to the weld line that cause poor strength, increase in the viscosity of the dispersed phase can be a key factor.

Selective addition of filler does not significantly affect the strength of the weld line samples in the case of the blends studied. Figure 4.19 - 4.21 shows the SEM photographs of the fracture surface of the weld line samples with and without filler and with DCP.

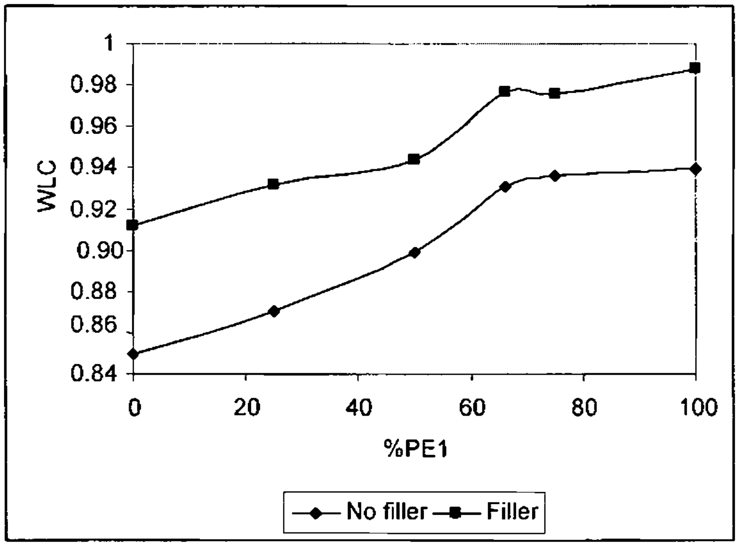

Figure 4.17 *Effect of filler (5% $CaCO_3$) on blends of PE1andPE2*

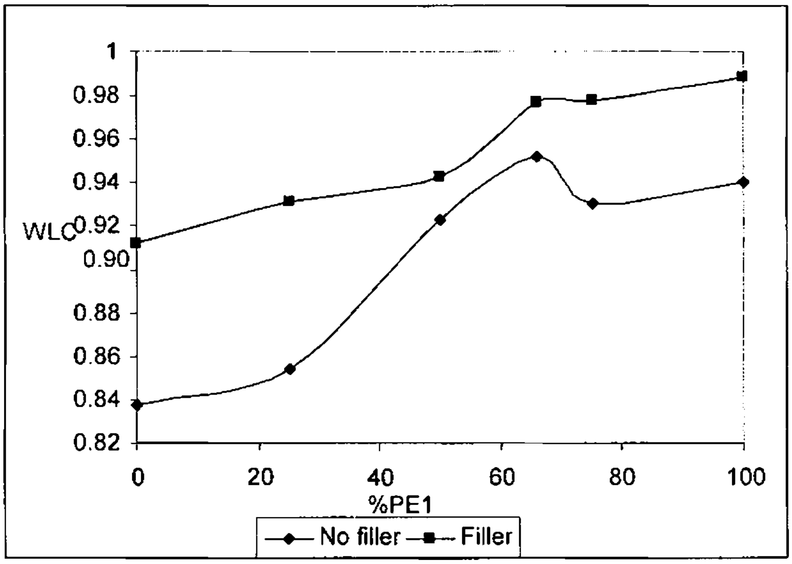

Figure 4.18 *Effect of filler (5% $CaCO_3$) on blends of HDPE andPE1*

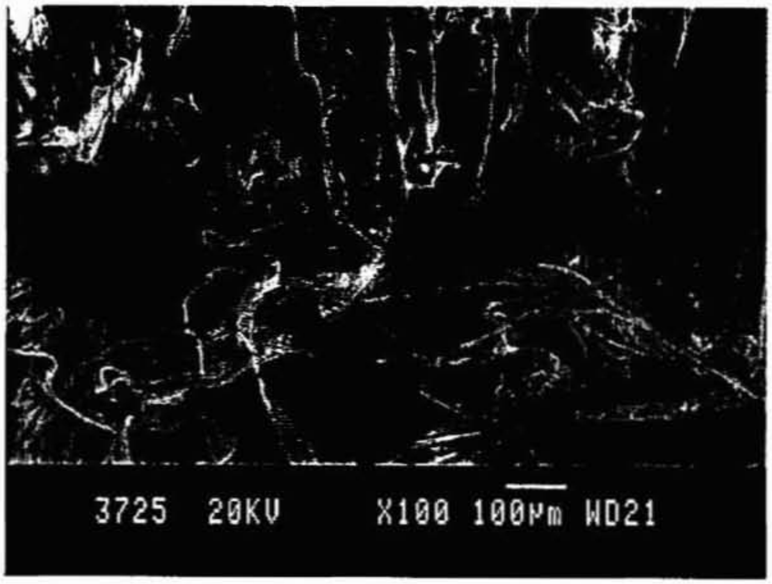

Figure 4.19 *PE1/PE2 blend fracture surface with weld line(No DCP)*

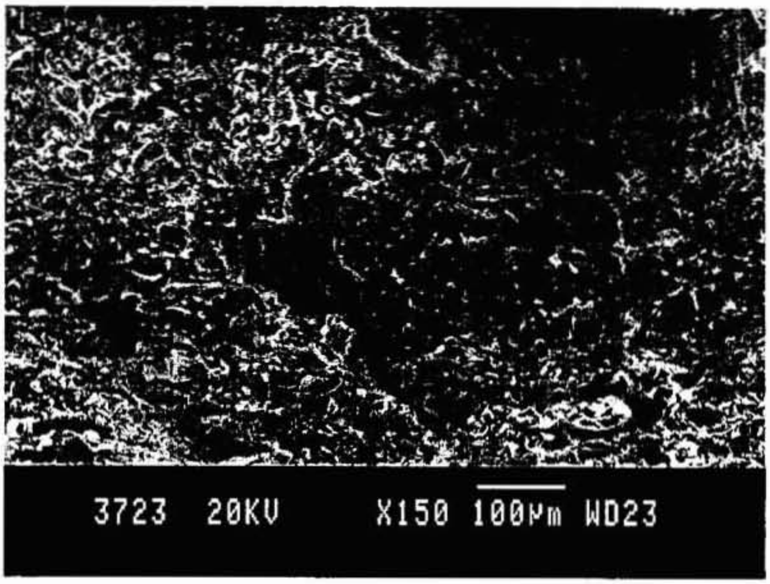

Figure 4.20 *PE1/PE2 blend fracture surface with weld line(with DCP)*

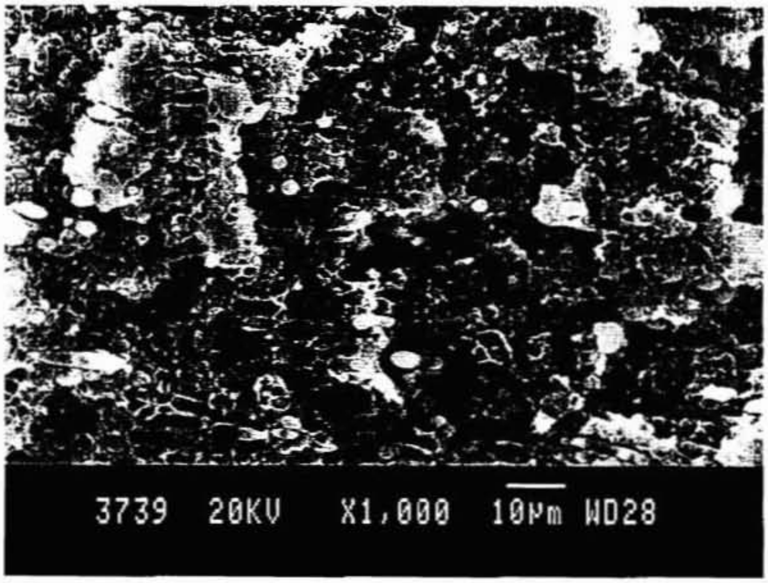

Figure 4.21 *PE1/PE2 blend fracture surface with weld line (with filler)*

4.3.7 Effect of ageing and weathering

Results of laboratory ageing and weathering by outdoor exposure are shown in Figures 4.22 to 4.26. In the case of PE1 containing calcium carbonate filler, ageing reduces the WLC yield stress after 2% filler (Figure 4.22). This shows that the weld line of filled samples is stable in ageing for low concentrations of filler. In the case of elongation at break, Figure 4.23 shows that the WLC is lower than that of samples that are not aged indicating that the presence of filler makes the weld line samples more brittle with ageing. In the case blends of PE1 with HDPE, Figures 4.24 and 4.25 shows that weathering decreases the WLC of elongation and WLC yield stress in comparison to the raw samples.

The effect of ageing and weathering for blends of PE1/PE2 with calcium carbonate filler (8% by weight) is shown in Figure 4.26. There is an increase in WLC for aged and weathered samples with filler.

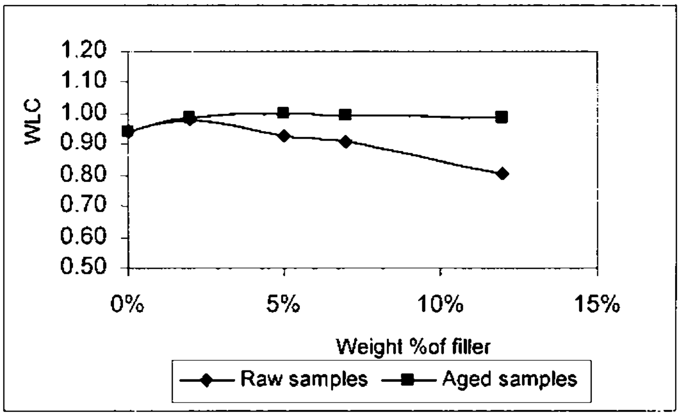

Figure 4.22 *Effect of ageing on WLC (yield stress) of PE1 (70°C, 48 hours in air)*

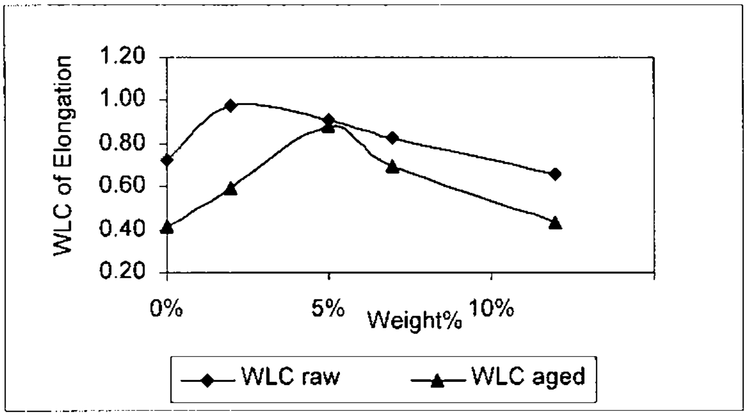

Figure 4.23 *Effect of ageing on the WLC (Elongation at break) of PE1 (70°C, 48 hours in air)*

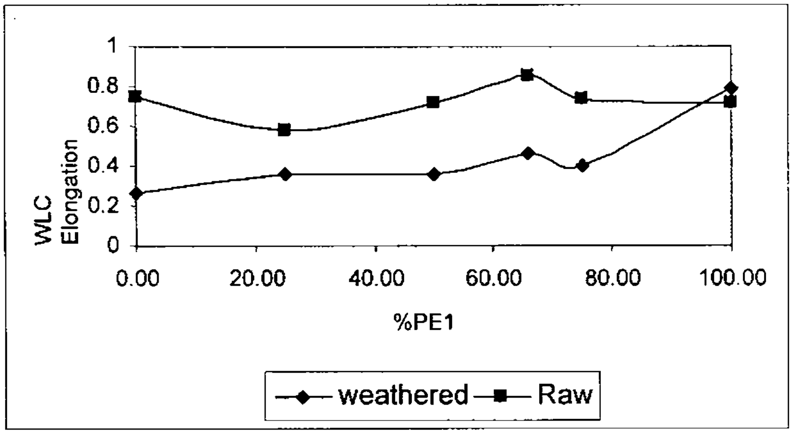

Figure 4.24 *Effect of weathering on WLC (Elongation at break) of HDPE/PE1blends*

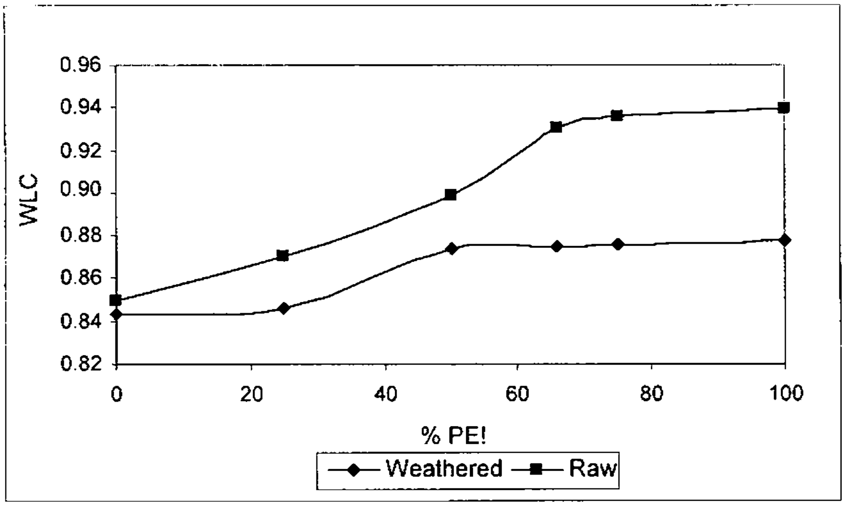

Figure 4.25 *Effect of weathering on WLC (yield stress) of HDPE/PE1 blends*

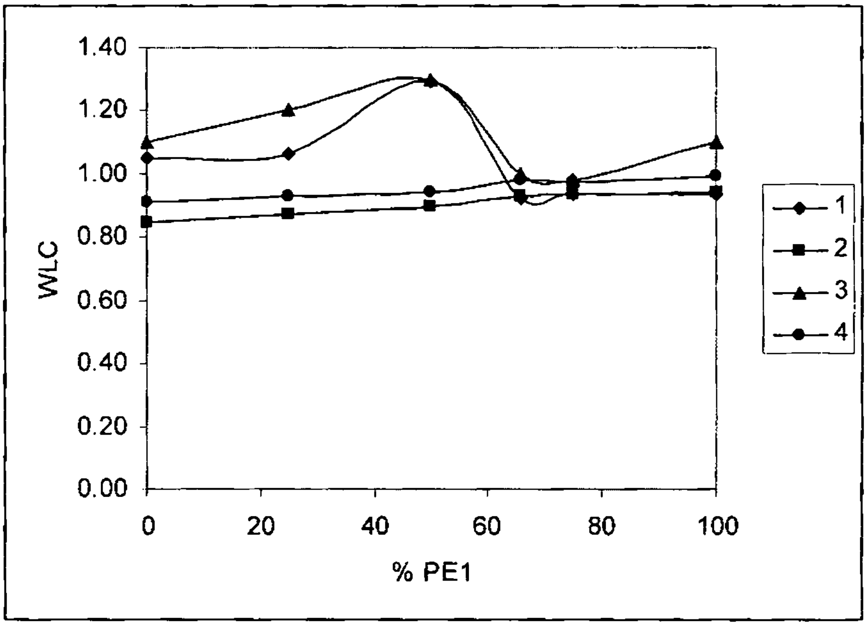

Figure 4.26 *Effect of ageing and weathering of blends of PE1/PE2 on WLC yield stress*

1–Weathered sample with filler 2-Raw sample with filler

3 - Aged sample with filler 4- Raw sample without filler

4.4 Conclusions

The study shows that two grades of same polymer can give significantly different weld line behaviour and different blend compositions can be used to optimize weld line behaviour. In the case of these blends the presence of filler can make the weld line more stable against ageing and weathering. Peroxide modification can be used to improve the strength of the weld line in the blends because both components of the blends behave in the same fashion unlike that of PP/HDPE blend.

4.5 References

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Chapter 5

Weld line behaviour of polypropylene/ polystyrene blends

5.1 Introduction

While there are a good number of papers on the weld line behaviour of PP and PS, there are hardly any material available on the weld line behaviour of their blends. PP blends constitute one of the most rapidly growing segments of the plastics industry. The practical use of two component PP/PS blends is based on flow segregation causing migration of the PP phase to the surface, thus allowing for higher temperature applications and grease resistance [2, 3]. Studies of PP/PS blends indicated strong interlayer slip. Rheological behaviour reported NDB at all compositions and extrudate structure at the fractured surface showed the less viscous component primarly concentrated on the outside. Incompatible polymer blends have very poor ductility and toughness compared to the pure components, which often precludes practical use of these materials. The ultimate mechanical properties of these blends are reported to be poor owing to weak adhesion between PP and PS phases. PP/HIPS blends are reported to show good mechanical properties and large strain at break. Thus modification of micro and macro morphology of the system is necessary. PP being a semicrystalline polymer with high degree of crystallinity and PS being an amorphous polymer, the weld line behaviour of their blends is worth investigating, HIPS is proposed to be tried as a weld line modifier for this system. Weld line behaviour of PP/PS, PP/HIPS, and PP/PS/HIPS are proposed to be investigated in the present study.

5.2. Experimental

5.2.1 Materials used

PP Repol H 200 MA made by Reliance Petrochemicals with MFI 20 g/10 min. PS grade LGG104 supplied by LG Plastics. HIPS grade LGH 302 made by LG plastics with MFI 18 g/10 min.

5.2.2 Mixing and moulding

Thermo Haake Rheocord 600 having a mixing chamber of volume 69 cm^3 with roller type rotors was used for blending. The hot mix from the mixing chamber was immediately passed through a two roll mill and cut into small pieces. The test specimens were moulded in a semi automatic plunger type injection moulding machine.

5.2.3 Mechanical Testing

Tensile properties were evaluated on a 50 kN universal testing machine Shimadzu make at a crosshead speed of 50 mm/minute as per ASTM D 638

The storage modulus and tan δ were measured using fixed dynamic analysis techniques. A dynamic mechanical analyser (Q 800, TA Instruments) was made use of for this purpose. Rectangular specimens of 35 mm length, 4 mm breadth and 2 mm thickness were used. DMA tests were conducted at a constant frequency of 1 Hz. A temperature ramp was run from 30°C to 150°C at 3°C/min to get an overview of the thermo mechanical behaviour of the samples with and without weld lines at the use temperatures.

5.3 Results and Discussion

5.3.1 Effect of melt temperature on weld line strength of homo polymers

The variation of tensile yield stress with weld line (WL) and without weld line (NWL) for pure PP, PS and HIPS are given in Figures 5.1 to5.3. In the case of PS the yield stress for NWL is found to decrease while for WL the strength is increasing. PS being an amorphous polymer the weld line coefficient (WLC) which is the ratio of the property with weld line to that without weld line is in the range of 0.5. For PP the weld line strength increases with temperature up to 240°C and then decrease due to the onset of degradation. For HIPS the WLC is nearly one. HIPS being a graft copolymer with rubber the greater mobility help in getting high WLC. As seen in Figure 5.3 for HIPS the yield stress is nearly the same for the weld line and no weld line samples.

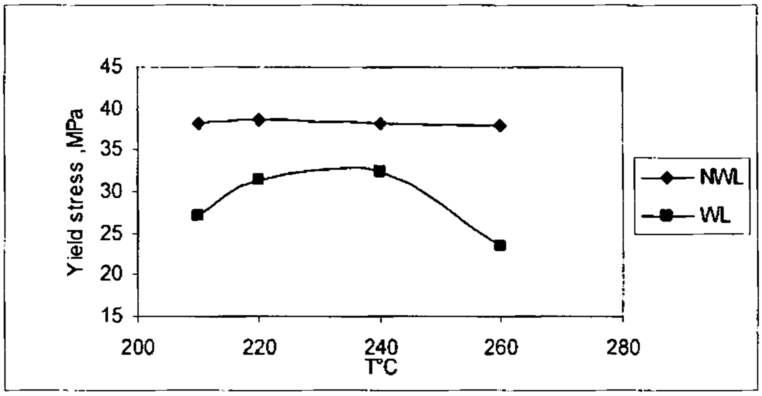

Figure 5.1 *Effect of moulding temperature on yield stress for PP*

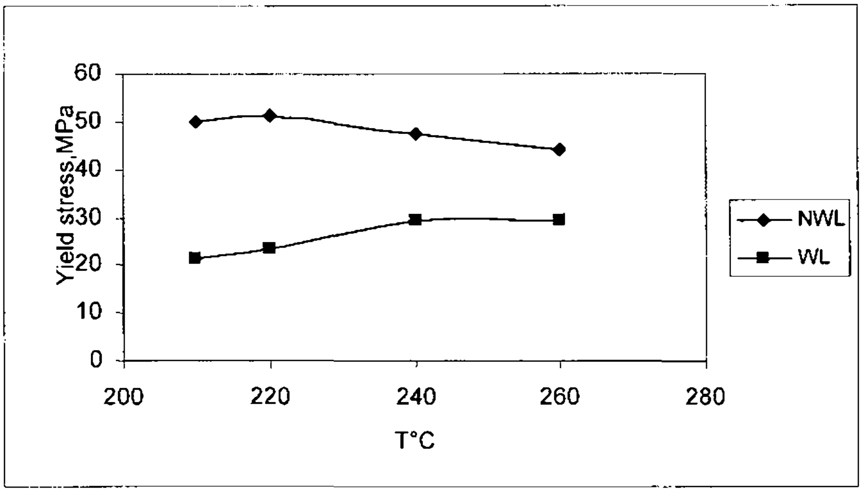

Figure 5. 2 *Yield stress of PS as a function of temperature*

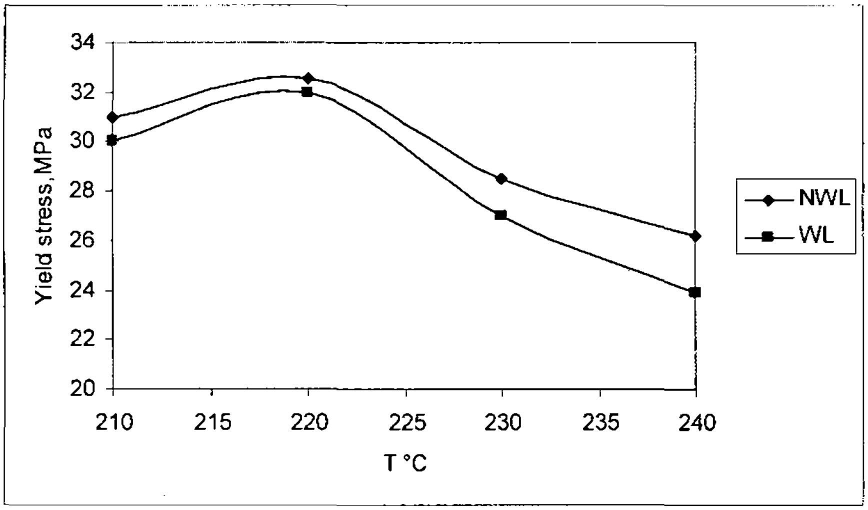

Figure 5.3 *Effect of moulding temperature on yield stress for HIPS*

5.3.2 Theoretical values of WLC

Theoretical values of WLC can be computed as explained in chapter 2. The values of self diffusion coefficient for PS are computed and are as in Figure 5.4. The following properties are used [4-14].

Polystyrene (PS)

$$G_N^0 = 2\text{x}10^6 \text{ dyne/cm}^2$$

$$R_g^2/M_W = 4.68\text{x}10^{-17} \text{cm}^2\text{/g/mol}$$

Activation energy for self diffusion of PS is 90 kJ/mol. The values of self diffusivity as function of MW is available for PS and PE.

The WLF equation

$$\log(\frac{\eta}{\eta_{T_g}}) = \frac{-C_1(T-T_g)}{C_2+(T-T_g)}$$

with C_1=14.5 and C_2=50.4, η_{Tg} =1x10^{13} poise and $\eta_{0,cr} = \eta_0(\frac{M_c}{M_w})^{3.4}$,together with Arrhenius relation is used for finding the zero shear viscosity at the critical molecular weight and temperature T. The distance of diffusion is computed and is plotted versus the dimensionless thickness.

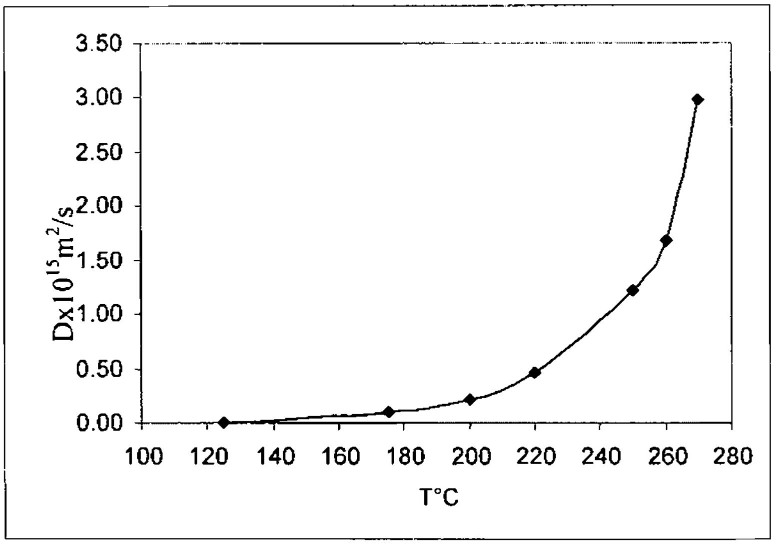

Figure 5. 4 *Self Diffusion coefficient for PS*

Figure 5.5 shows the graph for 260°C. Similar computations are done for other temperatures and the theoretical values of weld line coefficient are found out. Since weld line coefficient is the ratio of bonded area to total area, for a rectangular slab it is the same as z/b.

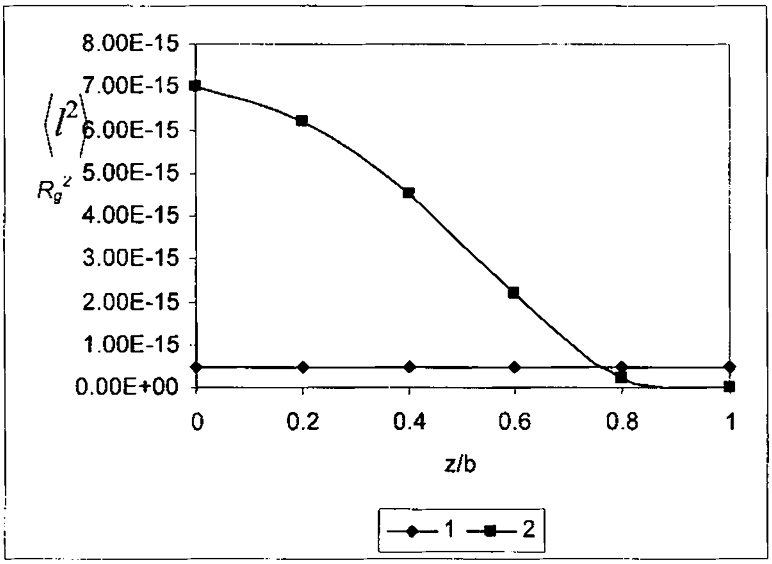

Figure 5.5 *Diffusion length of PS at various positions from the mid-plane of the slab at 260°C 1- R_g^2, 2- $\langle l^2 \rangle$*

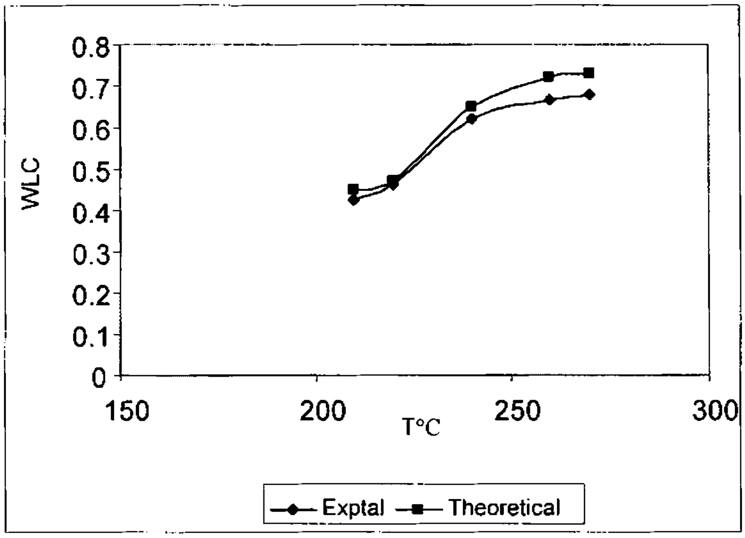

Figure 5.6 *WLC of PS - comparison of experimental and theoretical values*

5.3.3 Weld line strength for PP/HIPS and PP/PS blends

The mechanical properties of the blends of PP/PS are poor as seen from Figures 5.7 - 5.9. Similar results are shown by PP/HIPS blends. For PP/HIPS, the samples without weld lines show good mechanical properties, but the samples with weld lines have poor mechanical properties as is seen from Figures 5.10 and 5.11. The variation of mechanical properties with and without weld line is not significant at low concentrations of HIPS.

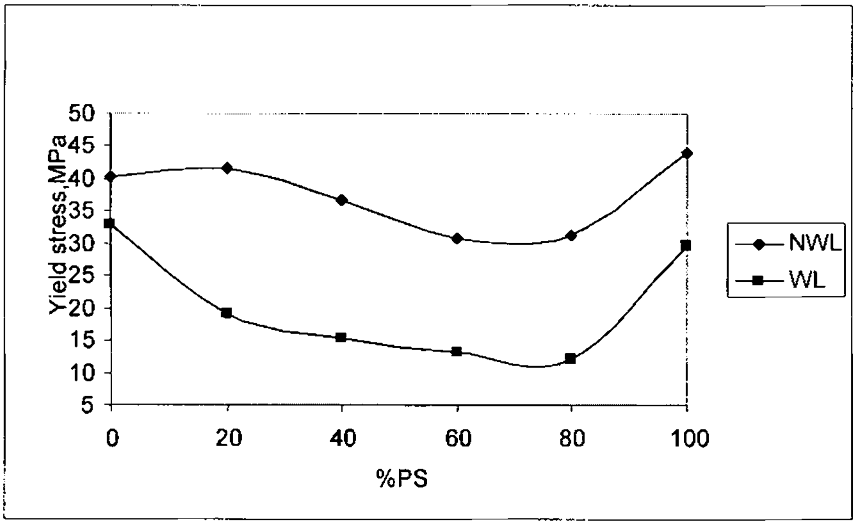

Figure 5.7 *Yield stress vs composition for PP/PS blends*

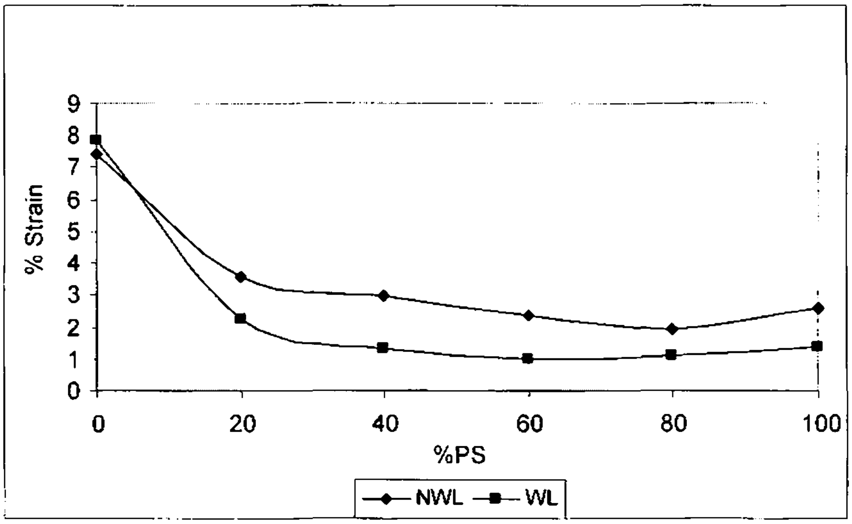

Figure 5.8 *Percentage strain vs composition for PP/PS blends*

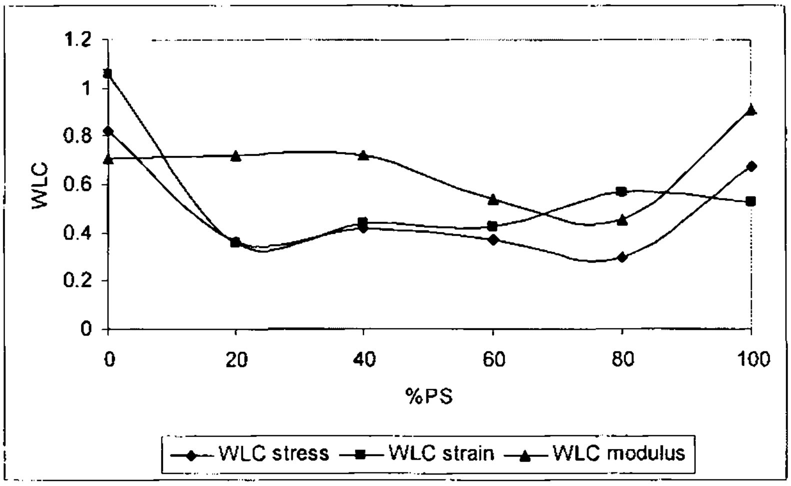

Figure 5.9 *WLC of the PP/PS blends as a function of composition*

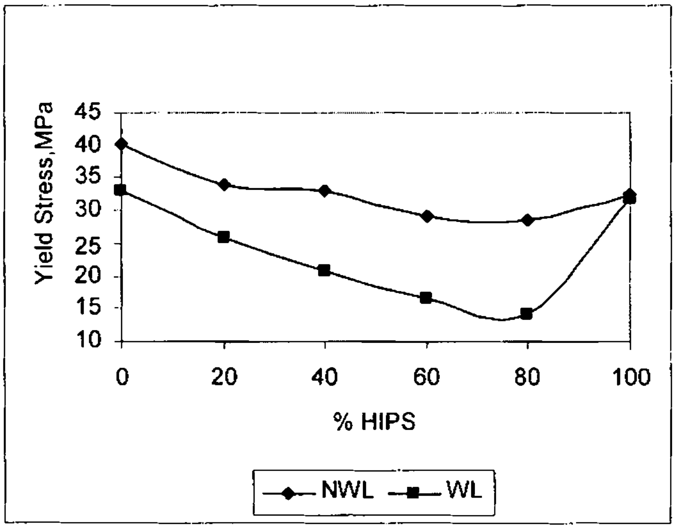

Figure 5.10 *Variation of yield stress with composition of PP/HIPS*

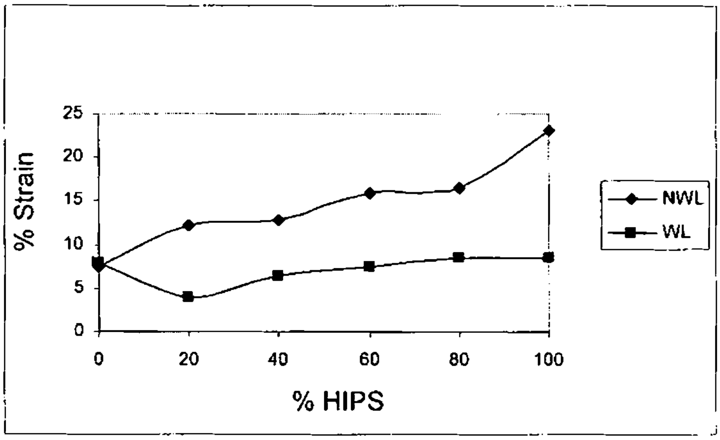

Figure 5.11 *Variation of elongation at break with composition of PP/HIPS blends*

5.3.4 Effect of adding HIPS as a compatibilizer in PP/PS 80/20 blends

From the above results it is seen that weld line weakness is acute in the case of PP/PS blends at all compositions. Modification of micro and macro morphology of the system by trying HIPS as a compatibilizer is investigated for improvement of the weld line strength. As can be seen from Figures 5.12 and 5.13 there is reduction in yield stress but improvement in elongation for the weld line samples as HIPS content is increased. Low concentrations of HIPS with PP and PS blends (80/20) are seen to improve the strength and elongation. Addition of HIPS is seen to modify the weld line strength as is seen from Figure 5.12. The yield stress of the weld line samples are doubled by addition of 4 to 6 % HIPS.

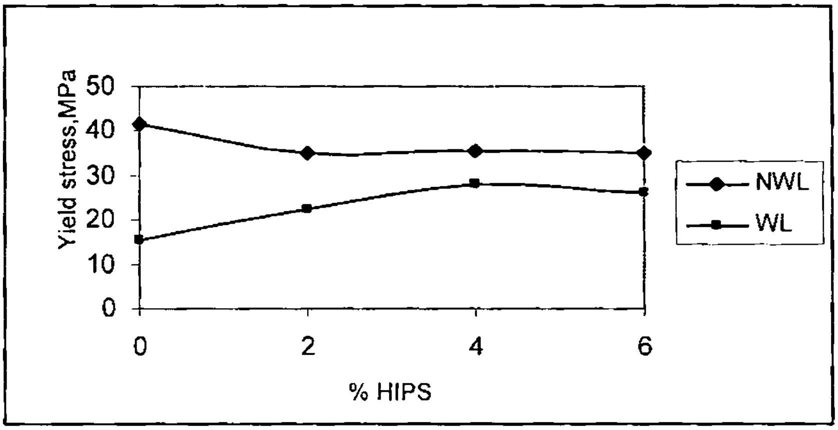

Figure 5.12 *Effect of HIPS concentration on yield stress of 80/20 PP/PS blends*

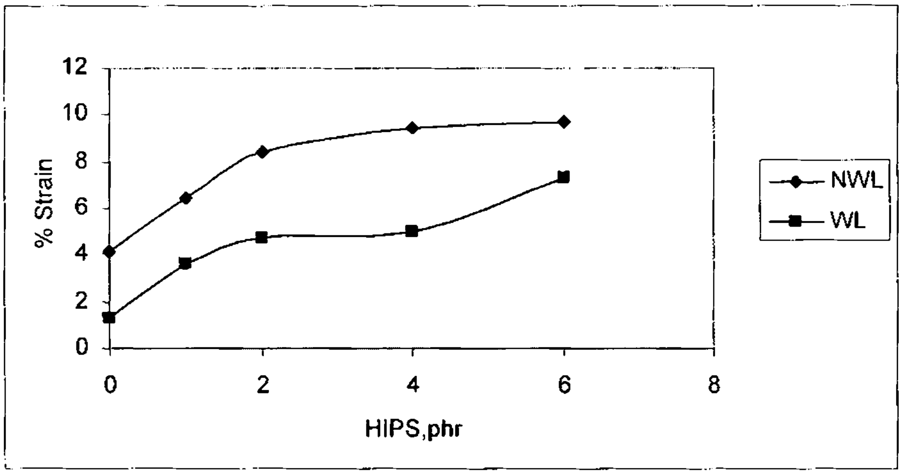

Figure 5.13 *Effect of HIPS concentration on Elongation of 80/20 PP/PS blends*

The improvement is obviously due to the change in morphology as indicated by the SEM micrographs. The brittle nature of PP/PS blend is altered to one of ductile nature as shown in SEM.

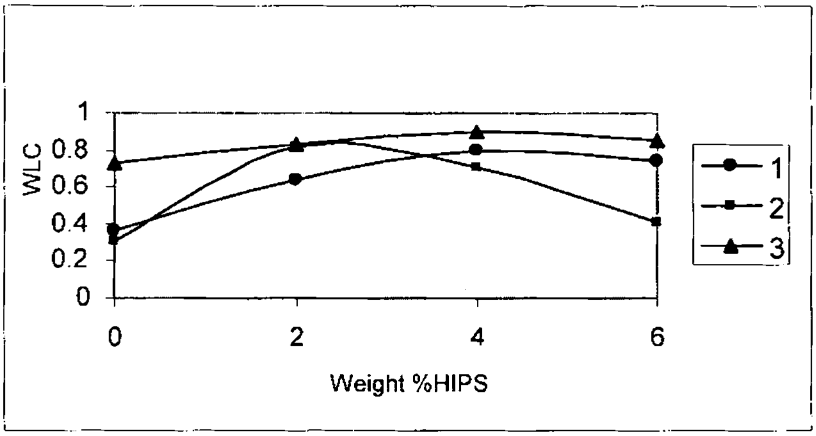

Figure 5.14 *Effect of HIPS concentration on WLC of 80/20 PP/PS blends*

1-Yield stress, 2-Elongation at break, 3-Modulus

5.3.5 Melt rheology

The mixing torque with time as obtained from Thermo Haake Rheocord is shown in Figure 5.15. The rotor speed, time of mixing and temperature of mixing is optimized to get maximum value for yield stress without the material getting thermally or mechanically degraded by using high speed and temperature. It was found that 190°C, 40 rpm and mixing time of 5 minutes was the ideal conditions. Use of HIPS as 4% weight or higher results in higher viscosity at low shear rates which is synonymous with interfacial interactions.

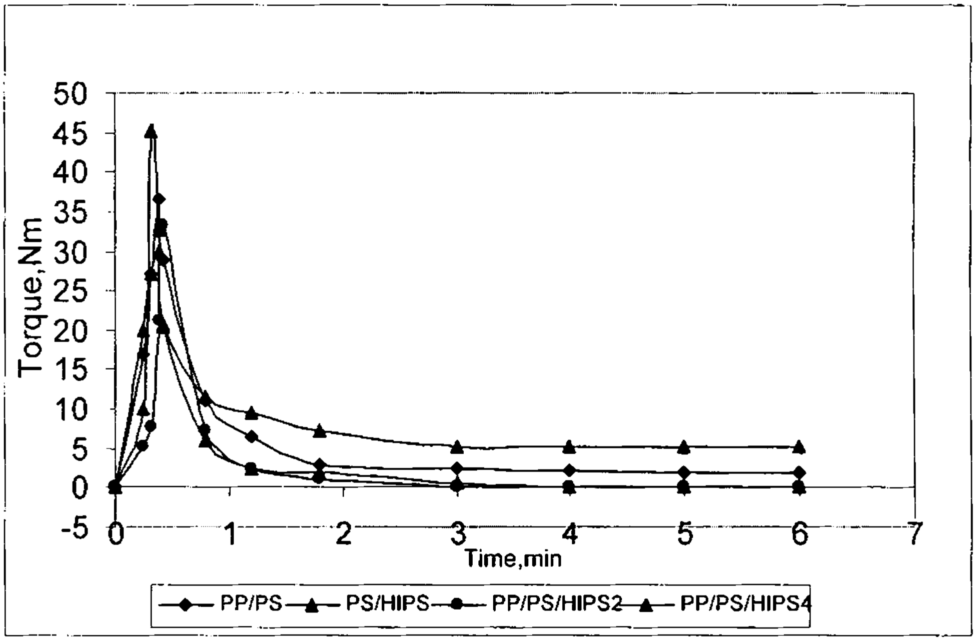

Figure 5.15 *Effect of HIPS on mixing torque as a function of time for PP/PS blends*

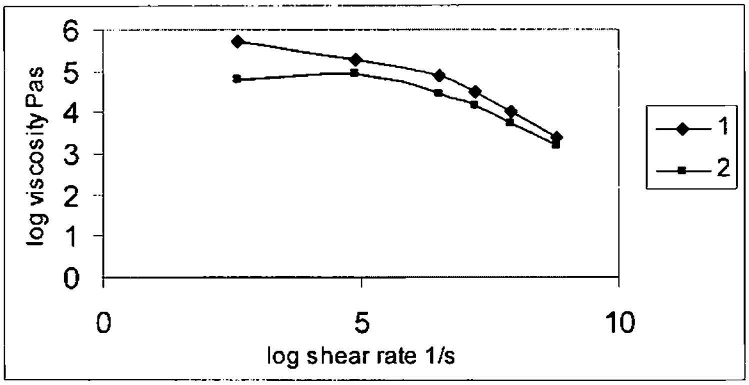

Figure 5.16 *Viscosity vs shear rate at 220°C* (1) *and 250°C* (2) *of HIPS*

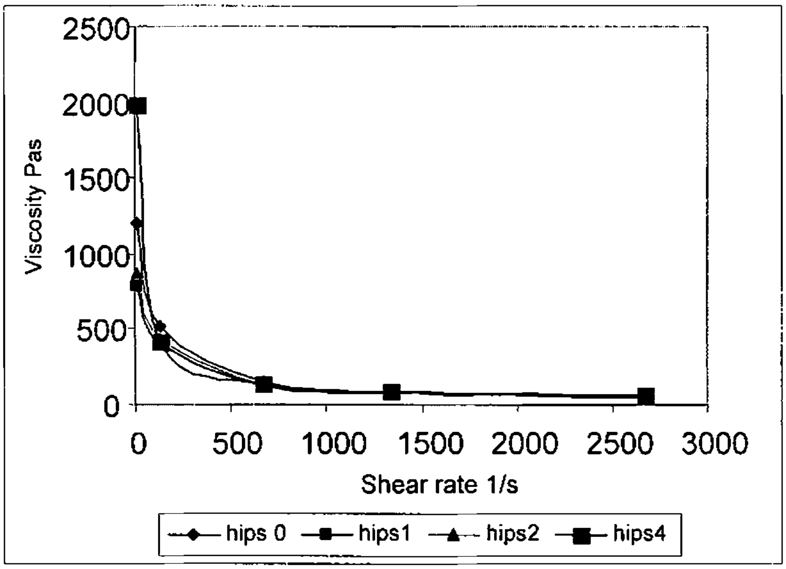

Figure 5.17 *Viscosity vs shear rate at 220°C for PP/PS/HIPS blends*

The same results are obtained from capillary rheometer studies. Addition of HIPS at low weight percentages does not have any marked change in viscosity whereas at higher weight percentages the viscosity is high for low shear rates. These shows that HIPS at higher percentages acts as a compatibilizer

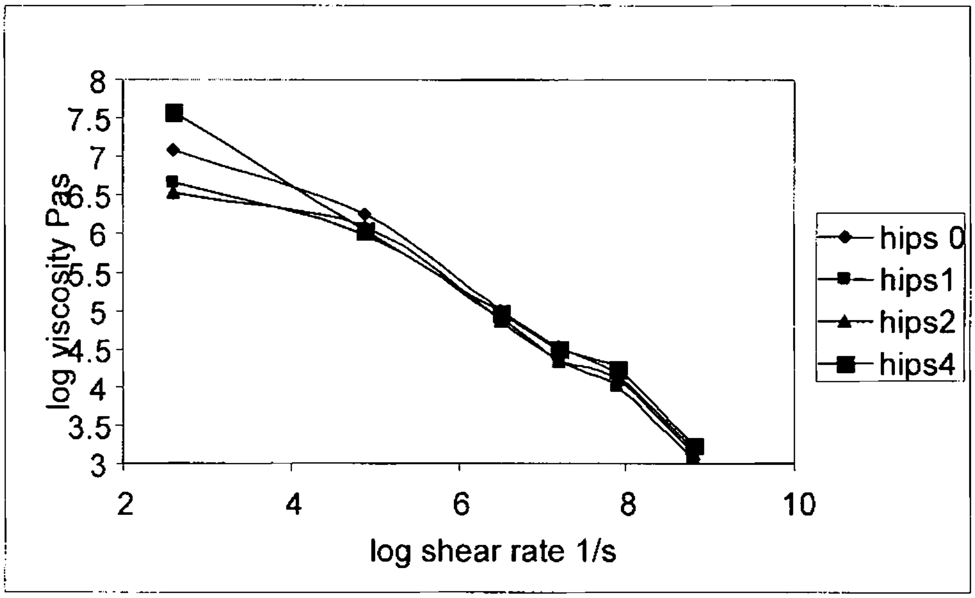

Figure 5.18 *Viscosity vs shear rate at 220°C for PP/PS/ HIPS*

From Figure 5.18 it can be seen that addition of HIPS by 4phr weight increase the viscosity at low shear rates and has no significant effect at high shear rates. So addition of HIPS does not pose any processing difficulty as injection moulding takes place at high shear rates. Figure 5.19 shows the effect of temperature on viscosity when HIPS is added. The flow activation energy is drastically reduced at high shear rates.

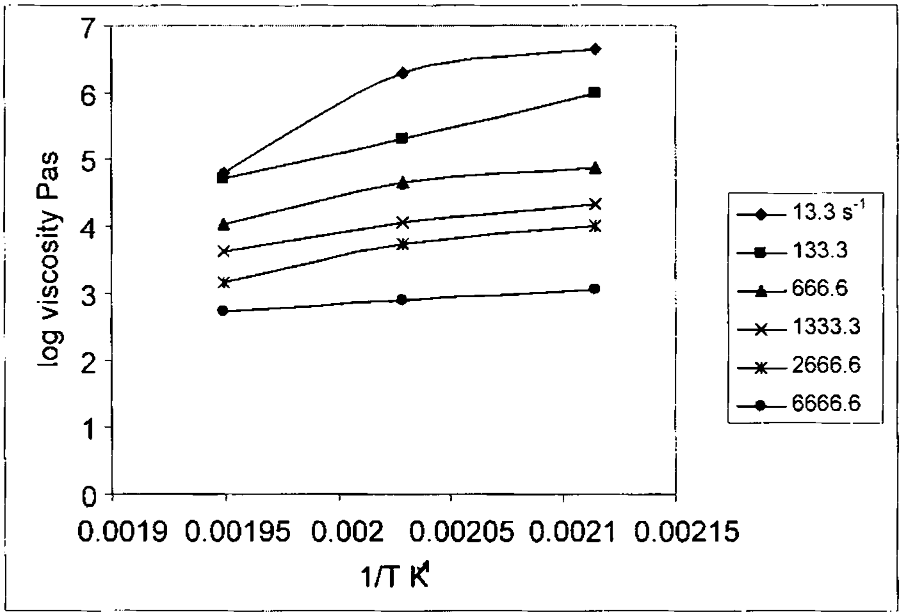

Figure 5.19 *Log viscosity vs 1/T at different shear rates for PP/PS/HIPS blends*

5.3.6 DMA studies

Heterogeneous mixtures will have a wide spread in T_g while homogeneous solutions will show a single sharp transition. The damping curve of the dynamic properties of the heterogeneous system reflects the broadening of the transition region due to the increase in heterogeneity. If the molecular interaction between the components of the mixture is high, effects of interchain heterogeneity is small and hence there will be a sharp peak. In the case of homogeneous mixtures only the position of the dispersion only shifts leaving the shape of the dispersion intact as the composition changes. If for composition change the damping peaks are broader in the transition region, it can be concluded that microheterogenity due to different segmental environment exists [15].

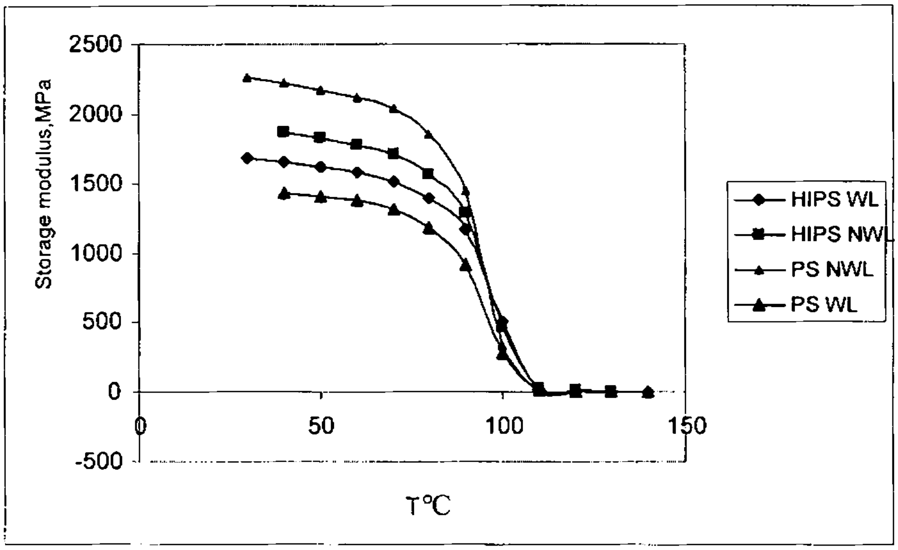

Figure 5.20 *Storage modulus vs Temperature for PS and HIPS*

Figure 5.20 shows the variation of storage modulus with temperature for PS and HIPS. In the case of pure PS there is a sharp reduction in storage modulus when a weld line is present. This shows that the dynamic load bearing capacity of PS is drastically reduced when weld lines are present. In the case of HIPS the storage modulus are not widely different showing that presence of the soft component can improve the weld line behaviour as seen in the case of EPDM for PP/HDPE blends. The same behaviour is seen in the case of tan δ behaviour also as seen in Figure 5.21. The addition of HIPS as a compatibilizer in PP/PS blends also improves the blend behaviour as is seen from Figure 5.22 and 5.23. The weld line behaviour is also significantly improved as shown by Figure 5.24 and 5.25.

The variation of storage modulus of 80/20 PP/PS blend containing different concentrations of HIPS with temperature is shown in Figure 5.26. The storage modulus decreases with increase in temperature as expected.

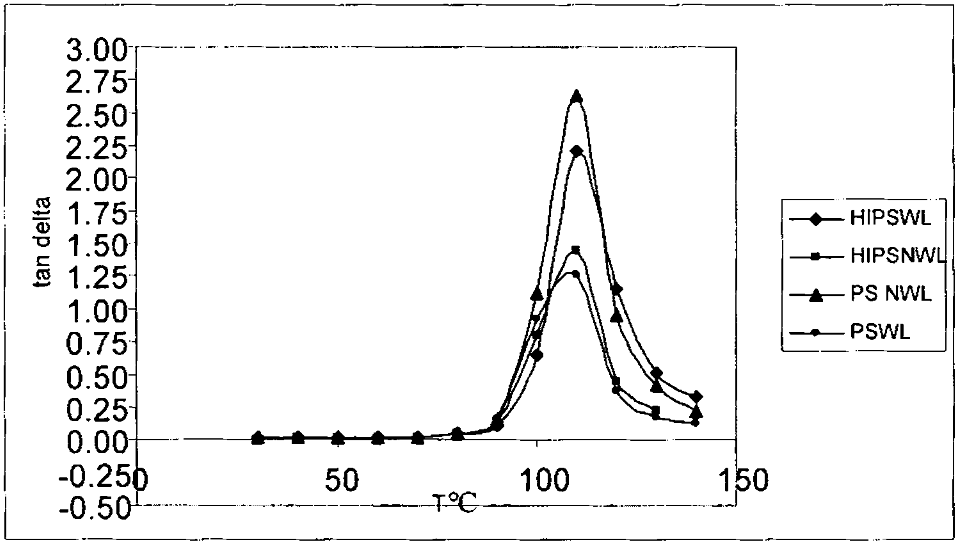

Figure 5.21 *Variation of tan delta with temperature for PS and HIPS*

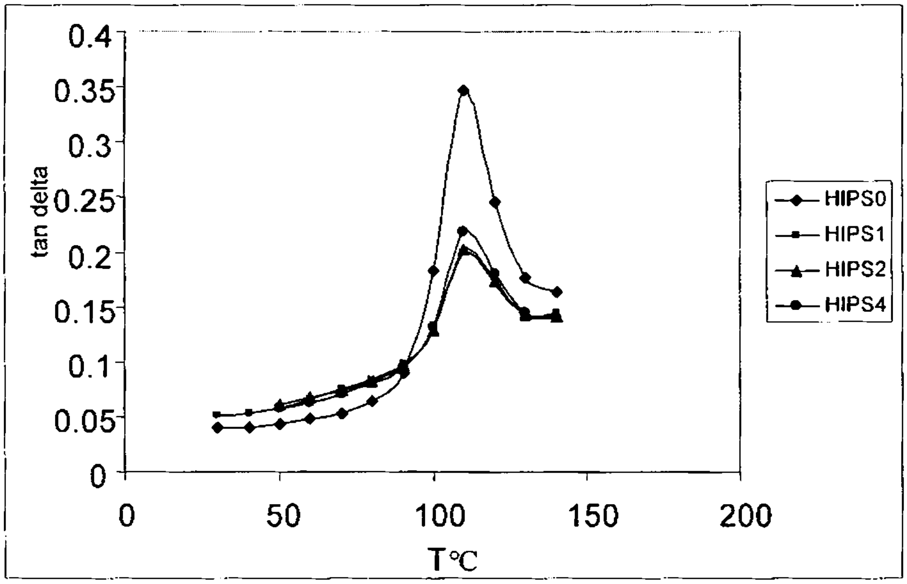

Figure 5.22 *variation of tan delta with temperature for PP /PS 80/20 blends for varying HIPS content*

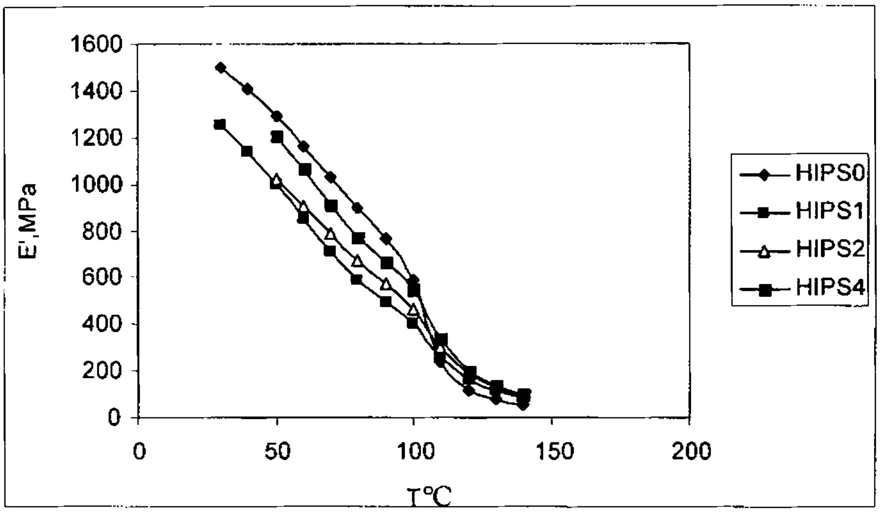

Figure 5.23 *Variation of storage modulus with temperature for PP /PS 80/20 blends for varying HIPS content*

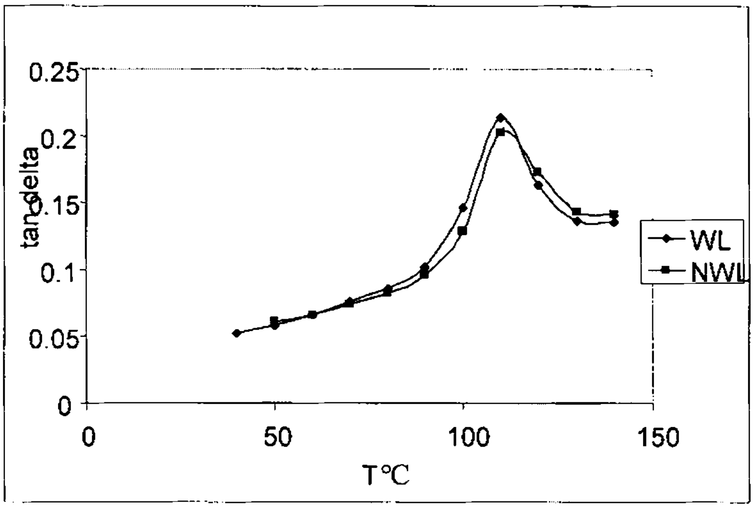

Figure 5.24 *Variation of tan delta with temperature for PP/PS/HIPS (80/20/4)*

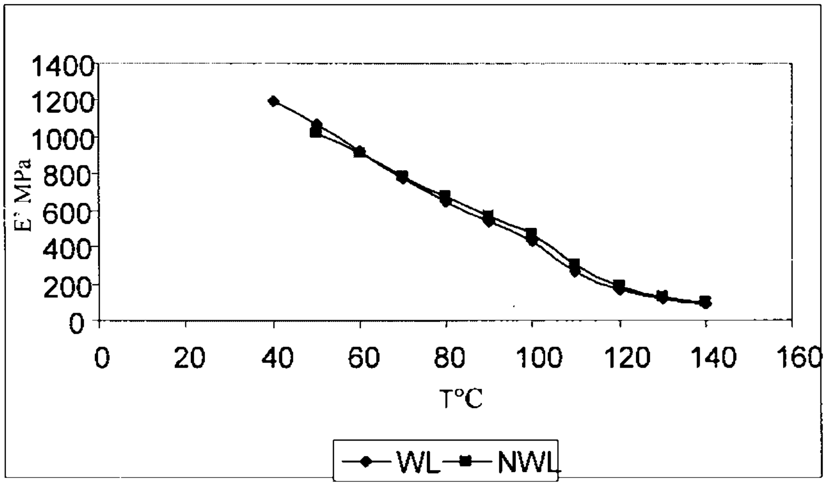

Figure 5.25 *Variation of storage modulus with temperature for PP/PS/HIPS (80/20/4)*

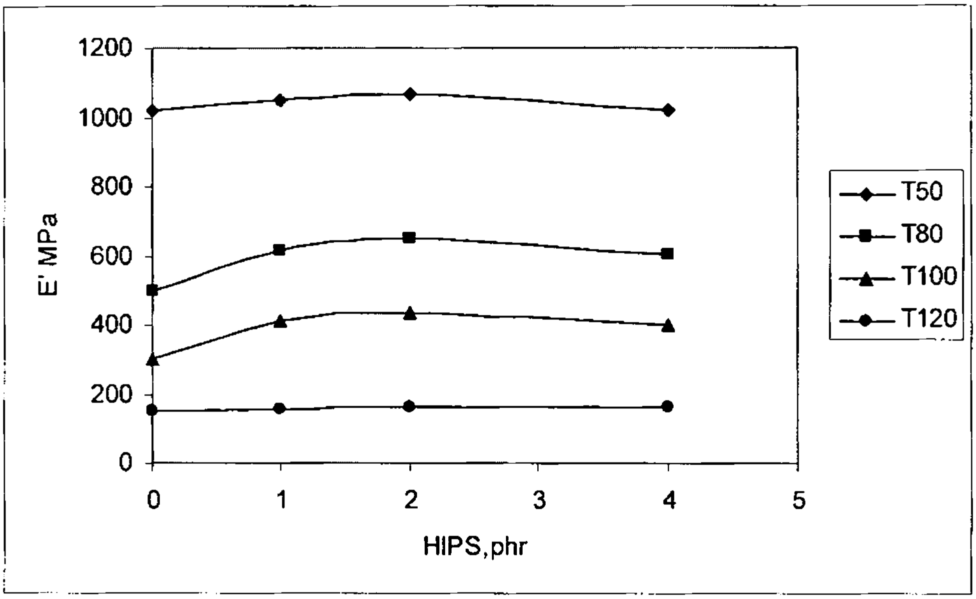

Figure 5.26 *Variation of storage modulus with HIPS content for PP/PS 80/20 blends at different temperatures*

5.3.7 Morphological studies

The Scanning micrographs of the fracture surface show that there is change in morphology for the addition of HIPS. The brittle fracture has shifted to ductile fracture as is seen from Figures 5.27 to 5.32. Weld line samples of PP/PS 80/20 are highly brittle as shown in Figure 5.29 whereas PP/PS/HIPS weld line samples shows ductility as is seen from Figure 5.31. Figures 5.30 and 5.31 show the fracture surface of PP/PS/HIPS blends without weld line. A magnified version of the fracture surface with weld line is given in Figure 5.28.

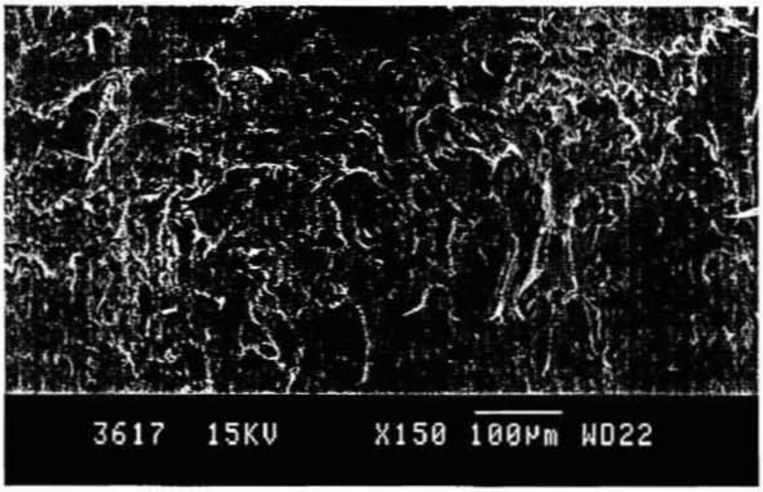

Figure 5.27 *SEM of fracture surface for PP/PS/HIPS without weld line*

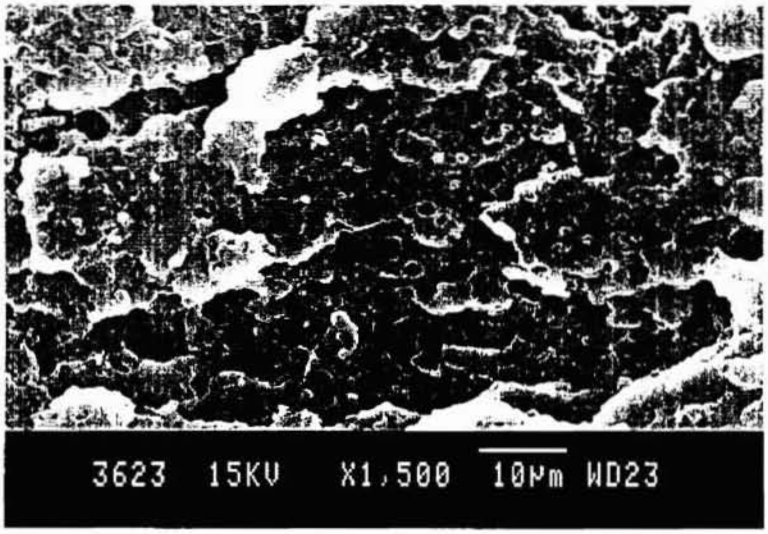

Figure 5.28 *SEM of fracture surface of PP/PS/HIPS with weld line*

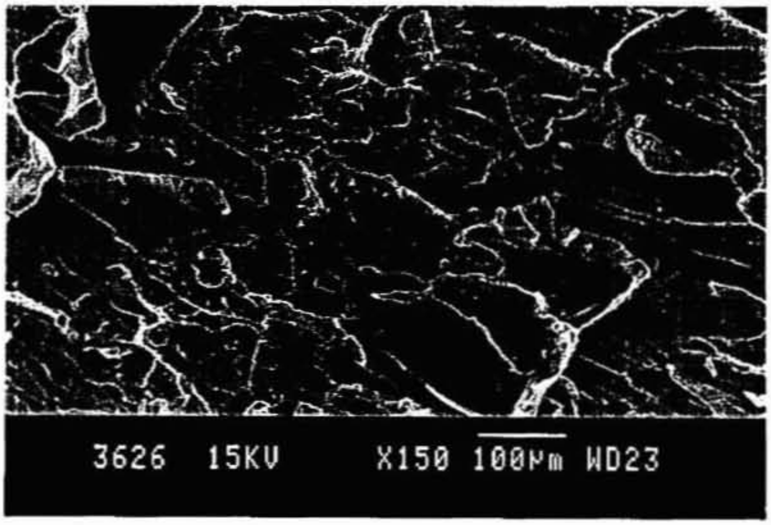

Figure 5.29 *SEM of fracture surface of PP/PS with weld line*

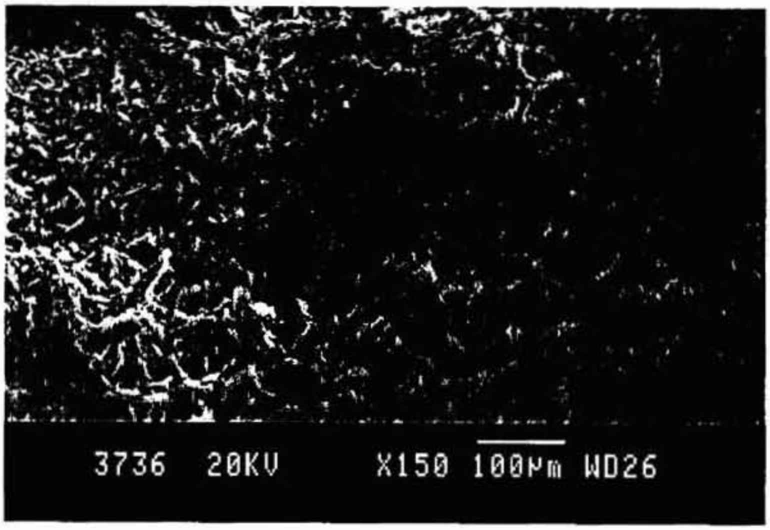

Figure 5.30 *SEM of fracture surface of PP/PS/HIPS without weld line*

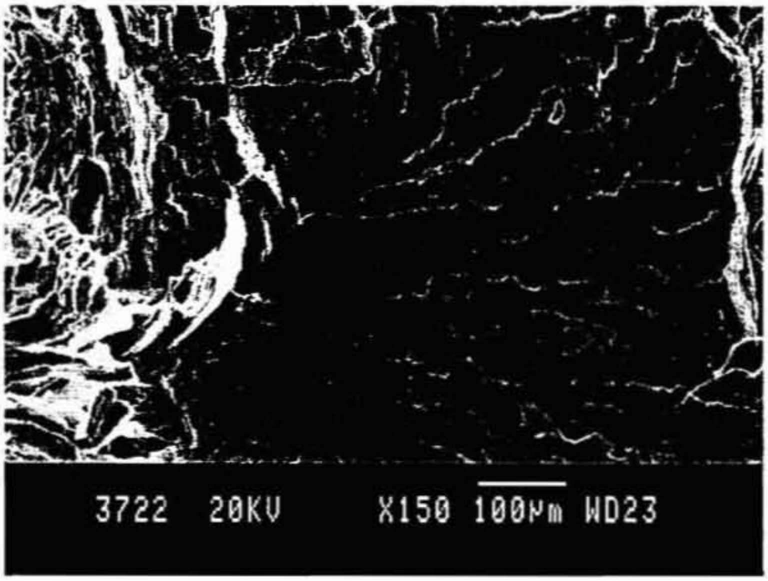

Figure 5.31 *SEM of fracture surface of PP/PS/HIPS with weld line*

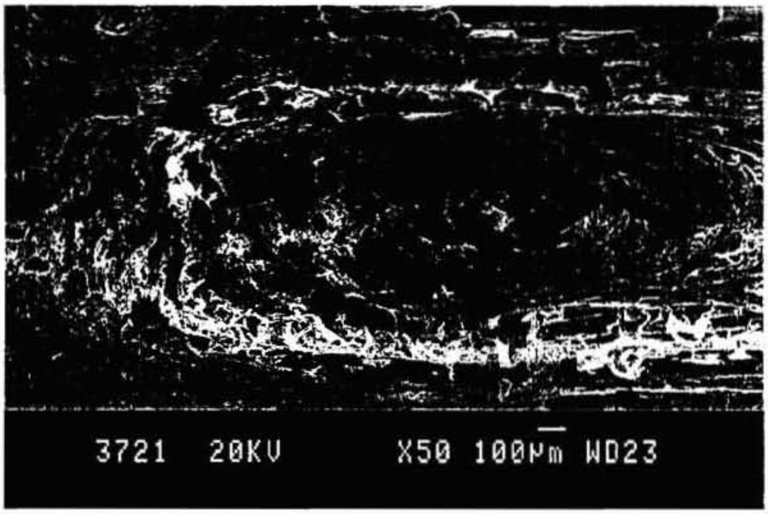

Figure 5.32 *SEM of fracture surface of PP/PS/HIPS with weld line*

5.4 Conclusions

The weld line behaviour of PP, PS, HIPS and their blends are investigated. In all the cases increase in melt temperature in injection moulding improves the strength of the weld line samples while the strength of the samples without weld line decreases. This shows that the weld line behaviour of both amorphous and crystalline polymers is dependent on the moulding temperature. In the case of PP/PS blends, while a small amount of HIPS reduces the mechanical strength it improves the strength of samples with weld lines. This shows that a soft component can strengthen the weld line of the blends, even though it affects the strength of the samples without weld line.

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Chapter 6

Summary and conclusions

This study was undertaken under the backdrop of the growing importance of the injection moulding of the blends of commodity plastics. The weld line behaviour of a few commercially important commodity plastics and their blends were investigated. To understand the weld line behaviour of blends the weld line behaviour of individual plastics was analysed first.

It was found that the melt temperature employed for injection moulding had a significant effect on the weld line behaviour of PP, HDPE, LDPE, PS and HIPS. Unlike in the case of the majority of polymers without weld lines the tensile yield stress improved significantly for samples with weld line as the melt temperature was enhanced in all the cases investigated. This shows that the weld line behaviour of the plastics supersedes the likely severity of degradation resulting from a higher processing temperature in all these cases.

The effect of melt temperature was most significant in the case of the lone amorphous member of the group, polystyrene. While the weld line coefficient under conventional melt temperature was below 0.5 for polystyrene an increase in melt temperature by 50°C improved the values of the weld line coefficient to 0.7. This is obviously due to the improved mobility in the case of a rigid molecule like polystyrene with increase in temperature. The moulding of polystyrene was easiest among the polymers explored as expected of PS, which has the best processing characteristics among the group. However, the low weld line coefficient was a serious handicap, which could be compensated to a large extent by increasing the temperature of the melt.

A major thrust of the investigation was to explore the effect of modifiers on the weld line behaviour of the blends and these modifiers were tried on the individual polymers also. The study showed that the compatibilizers for the blends could also act as weld line modifiers. However it was found that the concentration levels required for the optimum modification were different in the case of blends without weld line and with weld line. For the case of PP/HDPE blends EPDM which is a known compatibilizer for the system was also found to be an efficient weld line modifier and it was found that while a concentration of 4 weight percent gives the maximum strength for samples with out weld lines for a 50/50 blend a concentration of 6 weight percent is needed for getting maximum weld line strength.

It was also found that a material which does not have a significant compatibilizer action on a blend system also could be a modifier. For example in the case of PP/PS blends which have very poor weld line strength, use of HIPS as a modifier gave a significant improvement in the weld line strength. Use of HIPS reduced the yield stress and increased the elongation in the case of samples without weld lines. But the yield stress and elongation increased for the samples with weld lines.

One of the promising methods of inducing a proper weld line bond was by cocrosslinking of the polymer blends by a peroxide. In the case of most blends peroxide modification gave rise to an increase in viscosity, obviously due to a low level of crosslinks introduced, but resulted in a stronger bond. This shows that crosslink formation was still continuing during weld line formation. The improvement was most significant in the case of LDPE1/LDPE2 blends and HDPE/LDPE blends.

The modifiers that were tried on the blends were also tried on the individual plastics. It was found that addition of EPDM to pure PP and pure HDPE reduced the strength of the samples with and without weld line. The reduction in strength is more significant in the case of samples with weld lines. This behaviour may be due to the higher concentration of EPDM at the weld line site. However this effect is not pronounced in the case of the blends due to preferential encapsulation of EPDM by one of the components. Addition of HIPS to PP sample with weld line produced the same effect. This further shows that it is the blend formation which predominates in the case of these individual polymers with modifiers than weld line modification. Addition of peroxide as a modifier is beneficial even for individual polymers because of its different mode of action.

Another interesting result is the weld line behaviour of blends and individual plastics in the presence of fillers. The weld line coefficient of HDPE/LDPE blends and LDPE1/LDPE2 blends improves with filler content up to 8% by weight. Thus the presence of a choice filler can play the twin roles of cost reduction and weld line modification. Similar behaviour is observed in the case of individual polymers too. This result is probably due to the reorientation of molecules at the weld line site in the presence of the filler. Another attractive feature of the filled products with weld line is their better weather resistance.

The ageing /annealing behaviour of the blends and individual polymers shows that the annealing effect dominates the ageing effect during the initial period while the ageing/degradation dominates thereafter.

Annealing improves the weld line strength and hence if done under controlled conditions will be beneficial for products with weld lines.

In conclusion it may be said that weld lines which are unavoidable in injection moulding of plastics blends can be strengthened by choosing appropriate processing parameters and the weld line weakness can be mitigated by suitable choice of modifiers.

List of abbreviations

HDPE	High density polyethylene
LDPE	Low density polyethylene
PS	Polystyrene
PP	Polypropylene
DCP	Dicumyl peroxide
EPDM	Ethylene propylene diene monomer
HIPS	High Impact polystyrene
PVC	Poly vinyl chloride
PE	Polyethylene
WL	Weld line
NWL	No weld line
WLC	Weld line coefficient
NDB	Negative deviation blend
PDB	Positive deviation blend
ASTM	American society of testing materials
DMA	Dynamic Mechanical Analysis
SEM	Scanning Electron Microscope

List of symbols

b	Half thickness
D	Self diffusion coefficient
T	Absolute temperature
t	Time
G_m	Gibb's free energy of mixing
Φ	Concentration

η	Viscosity
v_x , v_y	Velocity field
ΔS_m	Entropy of mixing
γ	Surface tension
G_N^0	Plateau modulus
M_e	Entanglement molecular weight
ρ	Density
R	Gas constant
η_0	Zero shear viscosity at temperature T and critical molecular weight
M_W	Molecular weight
R_g^2	Radius of gyration which is the mean square end to end distance
$M_c(T)$	Critical molecular weight of entanglement at temperature T.
$\langle l^2 \rangle$	Quadratic distance of diffusion
α	Thermal diffusivity
k	Thermal conductivity
C_p	Specific heat
z	Thickness of the sample
ϕ_1'	Volume fractions that contributed to the diffusion
F_{AA}	Area fraction of contact of A/A
B	Extrudate swell
N_1	Primary normal stress difference
E'	Dynamic modulus
E''	Loss modulus
ω	Angular frequency
δ	Phase angle
τ_w	Shear stress
l	Length of the capillary
R	Radius of the capillary
γ_w	Shear rate
Q	Volumetric flow rate
d_c	Diameter of the capillary in mm
k	Consistency index
n	Power law index

M	Torque
D_p	Extrudate diameter
d_c	Capillary diameter
ΔE	Flow activation energy

List of publications

- Weld line behaviour of polyethylene and polyethylene blends. Lakshmikutty Amma.B and Dr. K.E. George. Presented in the International Conference on Advances in Polymer Technology APT CUSAT, Kerala, January 16-17, 2004.

- Weld line behaviour of injection moulded Polyethylene/polypropylene blends. Lakshmikutty AmmaB. and Dr. K.E. George. Presented in the 4th International Conference on Polymers for Advanced Technologies MACRO 2004, Thiruvananthapuram, Kerala, December 14-17, 2004.

- HIPS as weld line modifier for PP/PS blends; Lakshmikutty Amma B. and Dr. K.E. George. Presented in the International Conference on advances in polymer blends and composites ICBC 2005, MG University, Kerala March 21-23, 2005

- Studies on the effect of modifiers on the weld line strength of Polypropylene/ polyethylene blends (Communicated).
- Studies on the effect of modifiers and fillers on the weld line behaviour of Polyethylene blends (Communicated).
- Studies on the weld line behaviour of polypropylene/polystyrene blends (Communicated).
- Weld line behaviour of thermoplastics and their blends-A review (Communicated).

Appendix

Theory for weld line strength of homopolymers

The strength of the weld line is given in terms of the degree of bonding defined as the ratio of the bonded area to the total initial area. This is expressed by the following equation.

$$\sigma_w = \sigma_b \left(\frac{A_0 - A_N}{A_0} \right) \qquad (1)$$

where σ_w and σ_b are the tensile strength of the injection moulded part with and without weld line respectively, A_0 is the initial cross sectional area, A_N is the non bonded area and A_0 -A_N is the bonded area at the specific contact time.

The mouldability of a polymer depends on the rheological and thermal properties. For a given mould and fixed moulding conditions of melt temperature T, injection pressure P, and mould temperature T_m, the ease of flow into the mould is determined by the limiting distance of diffusion $\left\langle l^2 \right\rangle$, which is also called the quadratic distance of diffusion. The distance of diffusion depends on the diffusion coefficient D which is related to molecular weight M_W as $D \infty M_W^{-2}$ .This is in accordance with reptation theory for entangled polymer systems. According to this theory, each polymer chain is confined to a tube surrounding its own contour, whose walls are made up by neighboring chains. The diffusion of the polymer chain is assumed to proceed primarily by reptation, which is similar to the motion of snakes as they move through a fixed set of obstacles. This diffusion path is the one that offers the least resistance, since the tube walls impede the lateral motions of the polymer chain. The center of mass of the polymer chain will move a distance approximately equal to R_g in the longest relaxation time and from this the molecular weight dependence of D is determined. D is also directly proportional to the temperature.

$$\langle l^2 \rangle = 2Dt \qquad (2)$$

where t is the time of diffusion. Hence the quadratic distance of diffusion is related to the molecular weight, temperature and time of diffusion.

Diffusion coefficient D as a function of the viscoelastic parameters of the material is given by

$$D = \frac{(\rho RT)^2 R_g{}^2 M_c(T)}{135 G_N{}^0 M_W{}^3 \eta_0(T)} \qquad (3)$$

where G_N^0 is the plateau modulus which can be computed as $\rho RT/M_e$ where M_e is the entanglement molecular weight($M_e = M_c/2$), ρ is the density, R is the gas constant, T is the absolute temperature. η_0 is the zero shear viscosity at temperature T and critical molecular weight M_c, R_g^2 is the radius of gyration which is the mean square end to end distance , M_W is the molecular weight and $M_c(T)$ the critical molecular weight of entanglement at temperature T. Rg^2/M_w is essentially constant for any bulk polymer. All these viscoelastic parameters are available from standard references.

Diffusivity D depends on the temperature which is position and time dependent in injection moulding. The temperature is obtained by the solution of the heat equation. The heat equation for this case assuming effect of heat of crystallization is negligible and there is no resistance to heat transfer at the interface of the melt and the mould is

$$\frac{dT}{dt} = \alpha \frac{\partial^2 T}{\partial z^2} \qquad (4)$$

where α is the thermal diffusivity.

$\alpha = \dfrac{k}{\rho C_p}$, k is the thermal conductivity, ρ is the density and C_p is the specific heat, T is the temperature and z is the thickness of the sample. The weld line strength of the blend will be the same as that without weld lines when intermolecular forces are attractive, which is when the quadratic distance of diffusion $\langle l^2 \rangle$ is greater than the radius of gyration R_g^2.

The solution is of equation (4) is given as a function of dimensionless temperature and dimensionless thickness with Fourier Number at/b^2 as the dimensionless time which is a parameter when film resistance to heat transfer is negligible. For any set of melt temperature and mould temperature the temperature at any thickness is computed. Similarly the time required to reach the crystallization temperature at any thickness is computed. The chart used is attached. For the temperature range of interest D is calculated using equation (3). The time for diffusion t_{diff} for different melt temperatures is calculated. The distance of diffusion can be obtained as

$$\langle l^2 \rangle = 2 \int_0^{t_{diff}} D(t)dt \quad (5)$$

z/b represents the ratio of the bonded area to the total area as b is the half thickness of the sample and hence the value of z/b where the radius of gyration is less than the distance of diffusion gives the WLC. From time versus D values graphical integration is done to get $\langle l^2 \rangle$.

The Diffusivities for PP and HDPE are computed for the temperatures up to 130°C which is the crystallization temperature for PE and up to 98°C for PP for melt temperature 200°C, 220°C, 240°C, 260°C and mould temperature 50°C.

For 240°C, the sample calculation values obtained are given for HDPE for $z/b = 0$

t s	1	2	3.5
T°C	205	183	130
D x 10^{15} m^2/s	2.34	1.95	1.0

$\langle l^2 \rangle = 18.6\mathrm{x}10^{-15}$, $R_g^{\,2} = 1.42 \times 10^{-15} \mathrm{m}^2/\mathrm{s}$.

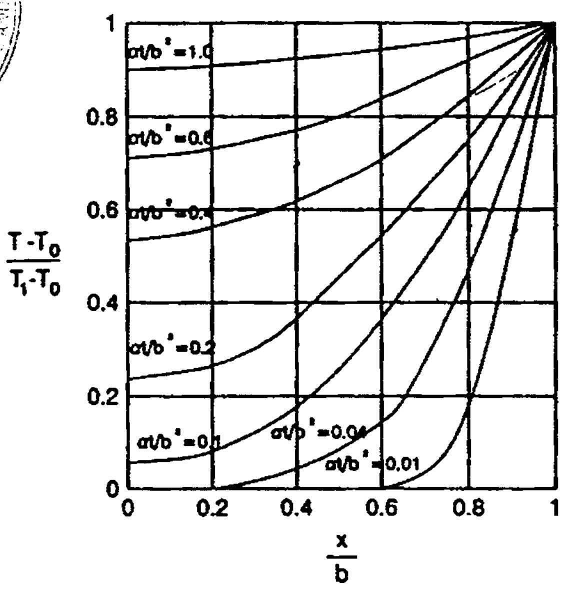

Figure 5.10 Dimensionless temperature versus dimensionless distance for a slab subjected to a step change in surface temperature (no thermal resistance). The parameter is the dimensionless time, t^*. T_0 is the initial temperature, and T_1 is the wall temperature.