Review Article

Fibres and films from polyolefin blends

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Among the various polymeric materials being developed, using the polymer blending concept, to obtain new materials with specific applications, polymer blends of various polyolefins have recently received increased attention. The present paper, which is an extension of our previous paper on fibres from polymer blends [Indian J Fibre Text Res, 16 (1991) 65], describes the rheological and crystallization behaviours of polyolefin blends and the role of interfacial agents in these blends with specific examples such as polyethylene-polyethylene, polyethylene-polypropylene, polypropylene-polypropylene, polyethylene or polypropylene with (ethylene-propylene) copolymers and ethylene-propylene diene terpolymers.

Keywords: Block copolymers, Compatibility, Co-crystallization, Interfacial agents, Polyolefin blends

1 Introduction

Within the rapidly growing literature on polymer blends, crystalline polyolefins occupy only a very small part. The reason for this lies in the molecular incompatibility of the polymeric constituents which causes these blends to separate into individual phases. However, blends of olefins are now used commercially because of their high impact strength, low temperature toughness and improved processability. Presently, the polyolefins constitute one of the largest classes of macromolecules that are commercially produced each year because of the low production costs and wide range of properties. More recently, blends of various polyolefins have received increased attention in order to obtain new materials with specific applications. Materials ranging from brittle plastics to elastomers can be obtained by the proper selection of blend constituents and its composition. In addition to developing new materials, some consideration has also been directed to recycling plastics where polyolefins constitute major sources of such a potential waste problem. Polyolefin blends which have been investigated extensively include binary and ternary blends prepared from various types of polyethylene (PE), polypropylene (PP), ethylene-propylene copolymer (EPR), and ethylene-propylene diene terpolymer (EPDM). This review on polyolefin blends, complementary to several recent reports and monographs1-10, lays emphasis on control of phase morphology, crystallization behaviour and mechanical properties.

2 Control of Phase Morphology

Although many polymer pairs have been identified, most combinations are immiscible. In many instances, phase-separated blends are preferred for achieving useful results. Tailoring blends to achieve desired properties requires, among other things, control over the spatial arrangement or morphology of phases, and some degree of stability once formed. Both these parameters are strongly dependent on rheological behaviour and crystallization phenomena. The most important way of improving or manipulating the morphological behaviour of polymer blends, through the modification of interphase with the help of compatibilizers, is also discussed along with the rheological and crystallization behaviours in polymer blends.

2.1 Rheological Aspect

The key factor for control of phase morphology is the skilful manipulation of polymer blend rheology during processing11-13. The ratio of the component rheological characteristics determines the results of dispersive mixing, i.e. the fineness of the dispersion of the minor component14. The elastic properties of the components determine, in turn, the formation of droplet-in-matrix or layer-in-matrix texture upon completing the lamellar melt mixing stage of the blending process15. Reliable knowledge of the rheological characteristics over a wide range of shear rate or shear stress is of paramount importance in predicting or modelling the blending process. The complementary physical characteristics required for these applications are molecular weight and its distribution, chain branching, macromolecular structure, uniformity of components16-19, surface tension of molten polymers12, and a knowledge of the interphase layer behaviour18.
In preparing polyblend fibres or films, one would expect the major component to form the matrix and the minor one to form the inclusions. This arrangement is indeed the one usually observed in fibres spun from intimate blends. However, phase reversal sometimes occurs if the two polymers differ in melt viscosity\(^8,20-22\). It is generally agreed that when the viscosity and elasticity of the minor component are greater than that of the major component, the minor component will be dispersed coarsely, and the extent of deformation would be less (Fig. 1a, b). A relatively rigid element, such as a latex particle, would not deform at all. In general, to produce fibrils with larger length/diameter ratios by this route, it is important that interfacial tensions be small and the relative viscosity or elasticity of the dispersed phase be smaller as compared to that of the matrix\(^23\) (Fig. 1c). It is also important to realize that fibrillar elements of fluid are unstable\(^24\) and may tend to break up into small droplets if the dispersed phase is of low viscosity and larger interfacial tension. The phase structure usually found in this type of blends is the matrix-fibril type when one component is in minor quantity. The driving force for this arrangement is the reduction in energy dissipation that occurs in the flowing polymers when the lower viscosity fluid moves to the higher shear rate regions. A classical example of how the polymer viscosity can control which component forms the matrix and which the fibrils has been given by Tsuji\(^25\). According to Danesi\(^26\), the dispersion level in PP/elastomer blends can effectively be controlled by varying the temperature and mechanical shear during the extrusion process. For instance, when the mixture is held at the lowest practical temperature above the melting point of PP, a better dispersion can normally be achieved. In a shear environment, elastomers show only a moderate viscosity decrease as the temperature increases. Polypropylene, on the other hand, characteristically undergoes a rapid decrease in viscosity. In this temperature range (165-180°C), the viscosities of the two components are very similar and the mechanical shear can be effectively transferred to the mixture to enforce a good dispersion of the phases. However, in addition to the finer dispersion level, it is also essential to control fluid flow in polymer blend processing to preserve the dispersion level obtained in the mixing step. After mixing, the polymer fluid must be delivered by laminar flow under relatively small stresses to extrusion die for the stability of state of dispersion achieved in the mixing step. During this transport, opportunities exist for deleterious changes in the state of dispersion, such as coalescence of small dispersed particles into larger ones, deformation of dispersed domains and split up of deformed domains into smaller ones; here, coalescence is a competing process. At die entrance, a rapid acceleration begins, which produces an elongational and shear flow that deforms dispersed particles into fibrils. The extent of the particle elongation depends on the relative rheological characteristics of the two phases, type and magnitude of fluid motion, interfacial tension and die geometry.

2.2 Crystallization Behaviour

It is well known that crystallization of a blend component can differ remarkably from that of the corresponding homopolymers. As in polymers, in general, the course of crystallization in blends is governed by equilibrium thermodynamics and kinetic boundary conditions, such as mutual dispersion of the components, super molecular structure, structure of the interface, etc. These boundary conditions change remarkably with blending, thus causing a lot of technically important and interesting effects. Depending on the blend components under consideration, a large number of physical and physico-chemical phenomena may originate of which some may have non-equilibrium thermodynamic basis. For melt-compatible polymer blends, among other effects, a variation of the crystallization process due to altered nucleation and growth conditions has been reported\(^1,6,27,28\). The usual mixing-induced melting point depression has been observed too\(^1,6,27,28\). For polymer blends with extended interfacial regions, these phenomena were also reported to apply to the bulk of the phase boundaries\(^29,30\). The investigation of incompatible polymer blends revealed the induction of specific crystal modifications\(^31\), rejection, engulfing and deformation of the dispersed compo-

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**Fig. 1**—Different types of dispersion of a polymer (dark regions) in the matrix of an immiscible polymer. The spherical droplets (a) are progressively extended into platelets (b) or fibrils (c) by deformation.

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nent by the growing spherulites of the matrix material\textsuperscript{27}, and the nucleation at interface\textsuperscript{27,32}. In general, studies on melt-extruded blends have suggested that the crystallization of one of the polymers is affected by the presence of other polymer. Even if the polymers are thermodynamically miscible, crystallization results in phase segregation unless the polymers can form isomorphic blends. It is also recognized that the differential rate of polymer crystallization during extrusion affects the processing behaviour of the polymer blends\textsuperscript{33,34}.

The reported investigations concerning polymer crystallization in blends may be categorized in three main groups, viz. partially miscible, immiscible and miscible blends, as shown schematically in Fig. 2. In first case, partial molecular miscibility of components is possible. In such a case the blend may consist of two phases, each containing two molecularly mixed components in different volume ratios\textsuperscript{35}. Crystallization of components in such a system will be influenced by the composition of individual phase and will involve demixing in the microscopic scale. Both the dispersion and the partial molecular miscibility of components in the blend can involve altering of the crystallization kinetics and resultant morphology of polymers constituting the blend. The usual result being reduction in the rate and amount of crystallinity\textsuperscript{35-37}, slight melting point depression due to imperfect crystal formation\textsuperscript{38}, and appearance of a single melting peak or a third melting peak in addition to the two homopolymer peaks as a result of co-crystallization formation. In immiscible blends, due to lack of interaction between two components, there will be only two melting peaks of homopolymers as no co-crystallization will take place. Here, the melting temperatures of the component polymers are important from the point of view of defining the mode of nucleation. Depending on the melting point difference, a component polymer may crystallize in presence of molten phase of the other component or in the presence of solidified particles. Thus, in case of blends with large differences in the melting points of component polymers, the crystallization of high melting polymer takes place in presence of the molten phase of other component. The presence of second molten phase may affect the crystallization process through the effect of it's viscosity on the mobility of the crystallizing polymer chains. On the other hand, the low melting polymer crystallizes in presence of the solidified particles of the other component, which may act as nucleating agents. Thus, the crystallization of the low melting polymer would take place in a heterogeneous nucleation mode and at higher viscosity of the system as a result of solidified particles of other component\textsuperscript{39}.

![Fig. 2—Morphologies of a blend of polymer A (solid lines) and polymer B (dashed lines) [(a) miscible, (b) immiscible, and (c) partially miscible] ](https://example.com/figure2.png)

The other important aspect of crystallization behaviour in polymer blends is the rate of cooling. Grebowicz and Pakula\textsuperscript{40} studied the crystallization behaviour of PP/HDPE blends at varying crystallization rates and showed that the sequence of crystallization of PP and PE depends on the cooling rate. At very slow cooling rate, PP crystallized at higher
temperatures while at high cooling rate, the opposite sequence was observed. For the cooling rate of 2°C/min, only a very small shift in the crystallization temperature of PP against PE was observed while for 50°C/min cooling rate the shift was considerable. They also observed slight difference in the crystallization temperatures of blended and pure samples and related it to the early crystallization of PP phase in blended samples due to the availability of PE heterogeneous nuclei. However, some authors also reported that these blends segregate into two discrete phases with a negligible influence of the PE phase on the crystallization behaviour of PP. In a similar study on crystallization behaviour of PP/LDPE and PP/HDPE blends, Plesek and Malac observed two distinct crystallization peaks for PP/LDPE blends at slow as well as very high cooling rates. On the other hand, for PP/HDPE blend, the same conclusion hold true only for the lowest cooling rate. For higher cooling rates, only one crystallization peak was observed.

2.3 Interphase Modification

It is well known that the mixing of two polymers generally leads to heterogeneous system, since the compatibility between them is rather a rare event. The formation of two-phase heterogeneous systems is not necessarily an unfavourable event, as many useful characteristics of single phase may be preserved in the blend while other properties may be averaged according to the blend composition. Proper control of overall blend morphology and good adhesion between the phases are, in any case, required in order to achieve good end-use properties. This can be achieved by a physical or chemical action that results in the stabilization of polymer blend morphology and is generally referred to as compatibilization process. The compatibilization methods can be divided into three categories loosely labeled as mechanical, chemical and physical. The aim of mechanical compatibilization is development of non-equilibrium morphology which in one respect is relatively stable and reproducible, yet in another respect leads to enhancement of properties. Chemical compatibilization involves chemical reaction as an essential factor for (i) formation of interpenetrating network structure, (ii) reversible or permanent crosslinking/vulcanization, (iii) exchange reaction creating in situ the compatibilizing copolymer, and (iv) reactive processing. The last category of compatibilization method is physical compatibilization. To this category belong (i) modification of polymeric structure to enhance miscibility (e.g. by introduction of ionic or hydrogen bonding groups), (ii) control of crystallization as a mean to lock-in developed morphology, and (iii) addition of compatibilizing agents. The addition of compatibilizers is by far the most popular method of alloying. The most frequently used compatibilizers are block, graft copolymers, interacting copolymers and co-solvents. The theory of compatibilization by addition of diblock copolymers has been developed by Hong and Noolandi. The A-B block copolymer was assumed to selectively dissolve block A in polymer A, and block B in polymer B, binding the two phases A and B via chemical bonds of copolymers as shown in Fig. 3. It is well established that such bonding is strongly dependent on the presence of the blend of appropriate block or graft copolymers having chain segments chemically identical to that of homopolymer blend components, type of blending process and on the processing parameters employed. The influence of these copolymers, generally referred to as “interfacial agents”, has been related to their tendency to be preferentially located at the interface between phases, and to the compatibility of their individual chain segments to penetrate into the phase to which they are chemically identical or similar. Also important are the interactions between the polymers at their interfaces. The interfaces between the phases of polymer blends are sometimes called interphases since some localized intermolecular mixing or interdiffusion can occur in polymer blends which approach thermodynamic compatibility. In other words, small domains of a mixed phase can exist between the “pure” phases. This molecular interdiffusion can increase the wetting of one polymer by the other, increases the adhesion between the phases, or reduces the effective interfacial tension. Increased adhesion or interdiffusion between the phases would be expected to have improved ultimate properties of the blends. The decreased interfacial tension would be expected to give more extensive subdivision of particles during melt mixing. The smaller particles generally give rise to improved
blend properties, as shown by Coran and Patel\textsuperscript{46}, and depend upon the interfacial tension\textsuperscript{47}. However, the desired effect may still result if one of the arms (segments) of the block or graft is miscible with or adhere to one of the phases.

The activity of these compatibilizers is effective in very large range of block copolymer and homopolymer molecular weights. For block copolymer to locate at blend interface, it should have the propensity to segregate into two phases. This tendency in block copolymers depends on the interactions between the two segments and their molecular weights. In particular, the segments should be long enough to have sufficient cohesive forces to anchor them firmly into the domains they penetrate, but not more than optimum required for efficient utilization\textsuperscript{44}.

It has been found that block copolymers are usually better interfacial agents than graft copolymers because in the latter, multiple branches restrict the penetration into similar homopolymer phases. For the same reason, di-blocks are more effective than tri-blocks. Block or graft copolymers have to segregate into two phases in order to localize at the blend interface. This specific behaviour of block and graft copolymer as well as their immiscibility only in one of the homopolymer phases depends on the interactions between two segments and their molecular weights. The amount of compatibilizer required depends on many factors of which conformation and molecular weight are the most important ones. Is is possible to estimate this amount for a given molecular weight $M$ of the compatibilizer to saturate all the interface in a blend. In this calculation one takes into consideration the interfacial area per unit volume of the blend in correlation with the volume fraction $\phi_A$ of polymer A which is dispersed in the form of spherical particles of radius $R$ in a matrix of polymer B. When each of the compatibilizer molecule occupies an area $P$ at the interface, then the ratio of the mass $m$ of block copolymer required per unit volume of the blend equals $3\phi_AM/\text{PRN}_A$, where $N_A$ is the Avogadro's number. When the value of $P$ is assumed to be $50$ (Å)$^2$, one can calculate for $\phi_A = 0.2$ and $R = 1$ µm that one needs about 20% of the block copolymer by weight with $M = 10^5$ to fill up the interface. When the molecular weight of the compatibilizer is reduced to $10^4$, then this amount drops to 2%. These arguments show the advantage of lower molecular weight compatibilizers but it should be mentioned that higher molecular weight compatibilizers are needed in order to penetrate deep enough into phases and to be anchored firmly\textsuperscript{44,46}.

Other molecular parameters of AB copolymers, important for their emulsifying efficiency, are the molecular architecture, molecular weight of individual segments and the chemical composition. The most important are the mixture of copolymer composition and the ratios of molecular weights of A and B segments of the copolymer to those of A and B homopolymers respectively\textsuperscript{44}.

The morphology of blends of polymer A with polymer B and copolymer of AB type has been studied by many researchers\textsuperscript{41-51}. According to them, the size of domains in homopolymer blends were reduced by addition of a suitable block copolymer. This provides direct evidence that block copolymers restrain the phase segregation of the homopolymers in their macroscopic domains and, therefore, facilitate mixing of the two immiscible homopolymers. There seems to be universal agreement that stabilization of above type only occurs when the molecular weights of the homopolymers are less than or comparable to the molecular weights of corresponding segments in the block copolymer\textsuperscript{48-51}. When the homopolymer molecular weight is higher than that of the corresponding block segment, the homopolymer forms a separate phase and is poorly solubilized into the domains of the block copolymers.

3 Selected Examples of Polyolefin Blends

3.1 Polyethylene-Polyethylene Blends

Various types of polyethylene are distinguished in terms of their density as high density (HDPE), low density (LDPE) and linear low density (LLDPE) polyethylenes. These polyethylenes differ from one another, mainly in the molecular structure, molecular weight distribution and chemical composition distribution as well as in the bulk structure including the spherulitic structure, lamellar size and crystalline/amorphous interphase structure\textsuperscript{52,53}. The different densities result from a variation in the crystalline packing ability of polyethylenes due to a difference in the degree and length of branching. For example, the density of LLDPE decreases with the $\alpha$-olefin comonomer content at an extent depending on the olefin chain length. Moreover, the shape and size of the spherulites are strongly dependent on the length and frequency of branching\textsuperscript{53}. The spheru-
lites in LLDPE are smaller and less regular than those in HDPE. However, they are markedly larger than those in LDPE of similar density and melt flow index (MFI).

Several investigations have been performed to elucidate the mechanical properties, morphology and compatibility of various types of polyethylene blend. These studies have examined binary and ternary blends prepared from low, linear low and high density polyethylenes which show that the miscibility between two polyethylenes is not apparent. In principle, accounting for their behaviour in the molten state, these blends should be considered as miscible. However, on cooling from the molten state, molecular fractionation occurs. When crystalline polymers undergo crystallization, fractionation has been known to occur which depends on various parameters such as crystallization rate and molecular weight and its distribution. However, several studies involving different experimental techniques have shown that during isothermal crystallization, excepting in very low molecular weight species, co-crystallization also occurs among the different species and almost universally during rapid crystallization. Binary blends of LLDPE and HDPE and the ternary blends of low-, medium- and high-density polyethylenes showed two endotherms in differential scanning calorimetry (DSC) studies. The lower peak is attributed to melting of co-crystals of low- and medium-density polyethylenes, whereas the higher endotherm is associated with melting of HDPE crystals. On the other hand, predominant co-crystallization was observed by Kyu et al. and Gupta et al. for blends prepared from LLDPE and HDPE, both at slow and rapid crystallization. No segregation was observed at the higher order structural levels of crystalline lamellae or spherulite. The blend manifested intermediate mechanical and optical relaxation in the α- and β-regions. Kyu et al. explained the phenomena by considering that the crystallization of HDPE in the first stage of the process becomes the driving force for the crystallization of those segments within the branched chains that are long enough to deposit in the growing substrate. This means that although short segments between branches are rejected, they are bound to crystallize segments and complete segregation is, therefore, not possible. This is not the case for the blends of HDPE/LLDPE where clear segregation takes place for weight fractions of linear polymers of 50 and 25%. Blends of high polydispersity HDPE/LLDPE were shown to be incompatible by Norton and Keller, while co-crystallization of the two PE samples was reported by Donatelli and Datta and Birley. Clampitt also investigated the melt-compounded blends of LDPE of MFI-2 with 10 grades of HDPE of MFI 0.2-0.9 by differential thermal analysis (DTA). The majority of blends exhibited three well defined melting peaks corresponding to LDPE, mixed crystals of LDPE/HDPE and HDPE crystals. It was observed that at low HDPE content (less than 30%), blends of some grades of HDPE exhibited only two peaks, corresponding to the melting of LDPE and co-crystals. Thus, the blends of HDPE grades with LDPE could be divided into two groups: one exhibiting three well defined melting peaks and the other exhibiting two well defined melting peaks. Clampitt also studied the blends of HDPE with five grades of LDPE based on different MFI and degree of branching. These blends also exhibited three melting peaks. It was observed that the co-crystals peak height was sensitive to both the degree of branching and the MFI of LDPE. It was found that a low MFI and a low degree of branching of LDPE favoured the formation of large co-crystals. No co-crystals peak was observed for blends of LDPE containing the highest degree of branching (30 methyl groups per 1000 carbon atoms) due to the decreased ability of LDPE chains to get packed in the crystallites. Also, the co-crystal melting peak height decreased with increasing MFI of LDPE.

Similar three melting peaks have also been reported for LLDPE/LLDPE blends and HDPE/LDPE blends. Studies on blend of LLDPE/LDPE of identical density for 1:1 composition show three shallow melting peaks around 124, 117 and 108°C while that of the composite film of identical composition show only two relatively sharp melting peaks at 126 and 109°C corresponding to the melting temperatures of the pure components. Hence, the additional broad melting peak between the main peaks of pure components, observed for the blended sample, indicates some level of co-crystallization. Upon cooling from melt, these blended films exhibited two crystallization exotherms at 111 and 96°C, corresponding to pure polymer of LLDPE and LDPE respectively, where the lower temperature exotherm was found to be broad. This difference stems from the changing crystallization environment. LLDPE crystallizes out first from a molten blend, the composition of which changes during the crystallization process, while LDPE mainly crystallizes from a blend in the presence of already crystallized LLDPE. Moreover, some of the LDPE gets co-crystallized with LLDPE chains, mainly with those containing more densely distributed branches. The latter may be responsible for broad lower temperature exotherm observed for blends. In another study, it has been shown that both binary low/high...
and ternary low/medium/high density polyethylene blends exhibit two melting peaks. For the binary systems, the peaks were associated with the separate melting of the low- and high-density crystalline regions. However, for the ternary systems, the low-temperature peak was assigned to the melting of co-crystals of the low- and medium-density polyethylene.

Blends of LDPE/LLDPE have gained such importance that they have been commercialized. LLDPE is added to LDPE owing to its superior mechanical properties, e.g. higher tensile strength, elongation at break, and impact strength. In addition to this, it allows a higher degree of down-gauging of LDPE films. On the other hand, addition of small amount of LDPE to LLDPE modifies its extensional viscosity and improves bubble stability, optical clarity and the productivity of tubular blown films. Hadjandreou et al. studied the blends prepared from LDPE with HDPE or LLDPE and showed that improved solid-state mechanical properties can be achieved from blended films of 20% HDPE or LLDPE with LDPE, particularly the creep behaviour for short-term load applications. Similar results were also obtained by Yilmazer for blends of LLDPE/LDPE. The mechanical properties for blended films followed additivity rule except in the range of 20-40% LLDPE content, for which the tensile properties were higher, implying compatibility in this range. However, the tear strength of blended films improved only in the transverse direction and it decreased in the machine direction.

As far as the ultra high molecular weight polyethylene (UHMWPE) blends with conventional polyethylenes are concerned, there are a limited number of publications available in the literature. A study of this kind is due to Dumoulin et al. who investigated the properties of UHMWPE blends at up to 6% UHMWPE content less than 6%. The primary reason for this is associated with the ultra high melt viscosity of the material, which restricts the polymer processability by the conventional techniques. Kuy and Vadhar, in their study on UHMWPE with LDPE, LLDPE and HDPE, showed that co-crystallization takes place in the UHMWPE/LLDPE and UHMWPE/HDPE blends. However, separate crystals are formed in UHMWPE/LDPE. They attributed the formation of separate crystals in latter case to long chain branching of LDPE. More or less similar results were also obtained by Vadhar and Kuy on UHMWPE/LLDPE blends. The appearance of dual peaks at lower UHMWPE contents and observation of a single endotherm at higher UHMWPE fractions indicate that co-crystallization takes place between UHMWPE/LLDPE blends at higher UHMWPE fractions. This phenomenon is attributed to better mixing of two components at higher UHMWPE fractions. At lower UHMWPE content, the lower shear stress between the components results in inhomogeneous mixing of two components. This kind of phenomenon is commonly observed in the blends where the viscosity of major component is significantly lower than that of the minor component. On the other hand, Bhateja and Andrews showed that the melting point did not vary significantly with composition, indicating no change in the perfection of crystallites. Further, the degree of crystallinity in the blend was lower as compared to that in homopolymer, because of the suppressed mobility and crystallizability of LDPE in the presence of highly viscous melt of UHMWPE.

Termonia et al. investigated the mechanical properties of highly oriented polyethylene blend fibres prepared from binary mixtures of UHMWPE and HDPE of $3 \times 10^6$ and $59 \times 10^3$ molecular weights respectively. The gel-spun fibres prepared from these binary mixtures, covering the entire composition range, showed systematic linear increase in tensile strength and initial modulus with increasing high molecular weight fraction. However, elongation at break was found to be dominated by the high molecular weight component over a large composition range; it decreased only at high concentrations of shorter chains.

3.2 Polypropylene-Polypropylene Blends

There are very few reports on studies of blends prepared from different molecular weights of PP. Blends of different fractions of PP showed lower impact resistance; however, the processing of such blends was superior to that of the PP of comparable intrinsic viscosity. Blends of PP resins were found to have better spinning performance for fine denier fibres than those prepared from individual resins. Depura et al. studied the crystallization behaviour of PP and high molecular weight PP (HMPP) blend system of various compositions. In case of 3% HMPP addition to PP, increased crystallization rate, compared to that for PP, was observed as a result of enhanced nucleation and growth rate. However, at higher HMPP compositions, the growth rate decreased. The breaking strength and initial modulus of 6% HMPP blend fibres were 0.75 GPa and 7.34 GPa respectively as compared to 0.65 GPa and 5.2 GPa for PP fibres. The improvement in mechanical properties is attributed to the increased amorphous orientation ($f_{am}$) and inter-crystalline tie molecules. On heat-setting, the rate of decrease of $f_{am}$ with heat-setting temperature was found to be less for 6% HMPP blended fibres as compared to that for PP fi-
bres. Similar observations were also made by Geleji et al. for fibres prepared from homologue mixtures of polypropylene. The study showed improvement in tensile strength and modulus with increasing high molecular weight component.

3.3 Polyethylene-Polypropylene Blends

Processability and improvement in impact properties of PP are often the reason for preparation of PE/PP blends. The morphology and properties of PE/PP blends have been studied extensively. In particular, studies on these blends showed some interesting aspects from the theoretical and practical point of view. Deanin and Sansone and Greco et al. found synergistic improvement in mechanical properties for some blend compositions. The reason for this synergism has been qualitatively ascribed to interfacial effects and partial miscibility of PE and PP chains in the molten state. Lack of co-crystallization, owing to the differences in the molecular structure of PE and PP, supported by the presence of individual melting temperature of the polymers in their blends indicate incompatibility of the system in the solid state. In liquid state, some interactions between chains can not be excluded owing to the small differences in polarity and free volume.

Detailed analyses of the PP blends, including those with LDPE, have been carried out by many workers. The morphological studies clearly show that these blends are heterogeneous two-phase systems, the components of which crystallize separately. The occlusions of the dispersed polyethylene phase do not influence significantly the formation and growth of PP spherulites, but the nucleation density is decreased. Martuscelli et al. reported that isothermal radial growth rate of PP spherulites in the molten state remained unchanged by the addition of LDPE when measured at temperatures well above the melting point of LDPE. Still the overall crystallization rate was found to decrease in isothermal studies by DSC. This implies that nucleation of PP is affected adversely by the presence of LDPE in melt. Teh showed that the addition of LDPE enhanced the nucleation of small PP spherulite (α-form). The crystallinity of LDPE and PP in the blends, as measured by DSC and WAXS (wide angle X-ray scattering) was found to be unaffected and followed the rule of additivity of mixture. However, Dumoulin et al. reported increase in crystallinity for LLDPE/PP blends containing up to 10 wt % LLDPE. In contrast to LLDPE/PP and HDPE/PP blends, which are compatible polymers and may be mixed partially in the amorphous region over a wide range of blend ratios, most other combinations do not harmonize. A certain degree of compatibility has been found in the selected combinations of LDPE/PP, even though the thermodynamic compatibility of these two polymers is insufficient to produce homogeneous melts in every ratio of the two components; their structural similarity guarantees good adherence between both polymers, although phase separation occurs on micro-scale during crystallization. Film tapes made from blends of LDPE with PP in certain mixing ratios show remarkably good end-use properties. Deanin and Sansone also reported a significant improvement in maximum tensile strength and work of rupture of 20:80 LDPE/PP blend. According to a patent of ICI Ltd, film tapes can be manufactured from a blend of 20:80 LDPE/PP having tensile strength of about 6.5 cN/dtex (7.2 gpd) with improved fibrillation resistance. Undoubtedly, LDPE in blends with PP allows a more effective reduction of the fibrillation tendency than HDPE, especially when applied in the proper ratio and in good correspondence with the melt index of the blending polymer.

Lovingir and Williams studied the morphology of HDPE/PP blends for the entire composition range. They found that structures having up to 50% PP consisted primarily of interpenetrating networks of the two polymers, while the blends having 50% PP or more were typified by PE domains dispersed in a PP matrix. Addition of HDPE to PP resulted in reduction of average spherulite size of PP for all the blend compositions, indicating increase in PP nucleation density due to blending. Bartczak et al. reported that blends of HDPE/PP show PP spherulites with a grain like structure constituted by HDPE inclusions even after the complete crystallization process. For the crystallization temperatures up to 127°C, disappearance of heterogeneous nuclei from PP matrix was observed due to their migration toward HDPE phase. However, an overall increase in heterogeneous nuclei was observed due to the presence of interface of HDPE crystals growing at these temperatures and acting as nucleating agent for PP. For crystallization temperatures above 127°C, it was observed that presence of HDPE phase in molten state adversely affects the homogeneous nucleation of PP and thus decreases the nucleation density and increases the resultant spherulite size of PP.

Martuscelli et al. extensively studied the isothermal crystallization kinetics of HDPE/PP blends and showed that the crystallization of HDPE is greatly delayed by the addition of small amount of PP up to 10 wt %. The half crystallization time τ/2 for these blends increases to around three and four times larger than that of HDPE and PP respectively.
The retardation of crystallization rate, despite the presence of solidified PP for heterogeneous nucleation of HDPE, has been attributed to the increase in melt viscosity of HDPE phase due to presence of solidified PP. In another study on crystallization kinetics of HDPE/PP blends in non-isothermal mode, Grebowski and Pakula found that components in blends, for all compositions, crystallize at higher temperatures compared to homopolymers, and the sequence of crystallization of PP and HDPE depends on the cooling rate. At very slow cooling rate, PP crystallizes earlier while at higher cooling rate the opposite sequence is observed.

Some authors have also reported the tensile properties of PE/PP blends. The earliest of such works are those of Slonimskii et al. and Plochocki who found a monotonic increase in tensile strength with PP content. On the other hand, Noel and Carley obtained a maximum in ultimate strength and initial modulus at 90% PP, whereas Deanin and Sano found similar results at 80% PP. Recently, Gallagher et al. have studied 1:1 HDPE/PP blends and homopolymers in highly oriented state. They observed a clear phase separation of two blend components with nearly similar structure, morphology and crystalline c-axis orientation. The same study also indicates that mechanical response of blend samples to the external macroscopic stress can be well described by a simple parallel model in which the two blend components, although mechanically linked, act more or less independently.

### 3.4 Blends of Polyethylene or Polypropylene with (Ethylene-Propylene) Copolymer

Blends based on PP and ethylene-propylene copolymers, such as EPR, are gaining increasing industrial importance beyond the traditional applications of high-impact polymers. Moreover, the recent development of ethylene-propylene thermoplastic copolymers has greatly increased the potential applications of such blends. Polypropylene and EPR are generally incompatible and their mixtures are thus heterogeneous. Phenomena such as segregation, stratification and phase inversion are, therefore, to be expected as in other multiphase polymer systems. The phase structure is complex and varies with PP content and processing conditions. With more than 50% PP, i.e. in the plastic materials, the PP forms a continuous phase. Below 50% PP, either PP or the copolymer may be continuous. However, phase segregation is also reported in some cases even at 8% PE content of the PP-PE copolymer. The correct choice of the grade of PP and copolymer is important in order to obtain the required phase structure and the mechanical properties of fibres and films.

The effects of EPR and other types of copolymer on the crystallization behaviour of PP were investigated by Karger-Kocsis et al. The blends containing up to 40% EPR by weight were studied by using the techniques such as DSC, WAXS and SAXS (small-angle x-ray scattering). The WAXS diffractograms showed a significant change in structure of PP. The intensity of peak at 2θ = 16°, which corresponds to (300) reflection of the hexagonal phase, decreased markedly with increasing concentration of EPR. It is also reported that the proportion of the monoclinic and hexagonal phase altered in EPR blend samples as a result of large change in nucleation process. However, no significant difference was observed in long period, as determined from SAXS studies. It was also observed that the incorporation of EPR in PP matrix leads to significant changes in the crystallization behaviour and morphology of PP.

The degree of supercooling of PP decreased from 60° to 42°C with increasing EPR content, indicating enhanced nucleation. This observation was also supported by a decrease in the spherulitic size of PP. Similar results were also reported by Martuscelli et al. for some isothermally crystallized PP/EPR blends. It was found that during crystallization the pre-existing copolymer particles are occluded, mainly in the intra-spherulitic regions, and such a process is found to produce large structural modifications in the spherulitic structure. Moreover, it was observed that the presence of copolymer drastically influences the process of primary and secondary nucleation which is a function of physical and chemical properties of copolymer. The decrease in the viscosity of elastomer and the increase in both the elastomer content in blends and the ethylene content in the elastomer have been found to reduce the spherulitic size in the blend samples. Recently, D’Orazio et al. have also reported similar results for isothermally crystallized PP/EPR blends, as discussed earlier. They observed that for a given crystallization temperature, the thickness of the crystalline lamellae (Lc) of PP crystallized from its blends decreases, whereas the thickness of the amorphous interlamellar layer (Lm) increases with EPR content and crystallization temperature. They related this phenomenon to the hindering of PP crystal growth by low molecular weight EPR molecules which can diffuse easily in PP amorphous phase and form domains, more or less interconnected with the amorphous PP phase.

In a detailed study on liquid and solid state thermodynamic compatibility of PP/EPR system carried out with the help of small-angle neutron scattering (SANS) it was observed that phase separa-
ation occurred even when the ethylene content of EPR was as low as 8%. Furthermore, the separated phase domains grew rapidly at melting temperatures. On the other hand, the blends of atactic PP with isotactic PP showed miscibility upon melting. The gross phase separation, however, was observed in both the cases during solidification or crystallization process. Wang and Huang also investigated the crystallization behaviour of EPR, PP-EPR block copolymers and PP/EPR blends with the help of DSC, WAXS and other techniques. The thermal analysis exhibited single endothermic melting peak and single exothermic crystallization peak for EPR copolymers corresponding to the ethylene sequence of the EPR copolymer. However, PP-EPR and PP-EPR-PP copolymers and their corresponding mechanical blends showed two melting endotherms, one at 154-162°C and the other at 119-121°C, attributed to the crystallites of PP and PE sequences in the EPR block respectively. Similar results were found for the crystallization temperatures. Wang and Huang also observed significant lowering in melting temperature as well as delayed crystallization for PP and PE phases of copolymers as compared to that of blends and related it to the \( \gamma \)-modification of PP, lowering of PP crystal sizes in (110) direction, imperfect crystalline structure, and reduced chain mobility due to hindrance caused by covalently bonded PP-EPR blocks in the mechanical blends.

Onogi et al. reported that although the quenched samples of virgin PP crystallized in the hexagonal structure (\( \beta \)-form), the PP in the melt-blended PP/EPR blends crystallized in a monoclinic structure under the similar conditions of quenching. These results suggest that the addition of an elastomer results in a significant decrease in the proportion of hexagonal (\( \beta \)-form) PP crystallites. These results are in agreement with the findings of Karger-Kocsis et al., who have also reported a decrease in the hexagonal crystal form of PP when blended with elastomers. In addition, Karger-Kocsis et al. also observed a significant reduction in the degree of supercooling of PP, indicating enhanced nucleation. The study also showed increase in deformation ratio with increase in PP content of blends. The blends having PP content more than 60% showed necking phenomena and larger increase in dichoric crystallite orientation function \( f_{P} \) for PP crystallites, while the blends containing less than 40% PP showed almost no increase in \( f_{P} \). They related these observations to the large increase in viscous flow of EPR molecules at room temperature. In a similar study on deformation behaviour of PP/EPR blends, Kammer et al. showed that increase in EPR content and drawing temperature above 155°C can produce bimodal texture of PP crystals. They also observed that under the similar crystallization and drawing conditions, the index of anisotropy, \( \lambda_{4} \) (crystallite C-axis orientation to the fibre axis), decreases with increasing EPR content, and related it to the disturbances caused by EPR molecules during the orientation process. On the other hand, Coppola et al. showed that ductility for PP/EPR blends markedly increases up to 20% EPR content and is a strong function of drawing and crystallization temperatures of precursor films. The results also show that presence of EPR molecules decreases significantly the overall crystallinity and spherulite size and acts as a lubricating agent, decreasing the internal friction during morphological transformation from spherulitic to fibrillar structure. The improved mechanical properties for PP and PP/EPR blends were observed for higher drawing temperatures. However, at all the drawing temperatures, PP/EPR blends showed lower modulus values than PP.

3.5 Blends of Polyethylene or Polypropylene with Ethylene-based Elastomer

Blends of PP or PE with EPDM elastomers are the most studied of this group. The mechanical properties of these blends depend largely on the type of elastomer used for blending. Generally, a high molecular weight EPDM containing about 70-75% ethylene with long sequences of ethylene units in the copolymer chain is preferred. This leads to some ethylene crystallization in EPDM phase which seems to contribute to the physical cross-linking and hence greater elasticity of the blends with PP or PE phase. In contrast, a low molecular weight grade of matrix material such as PE or PP is preferred; this helps to keep the melt viscosity low and assist crystallization. Due to continuing crystallization process at temperatures below \( T_{c} \), polyolefin plastics/EPDM blends are generally heterogeneous. Thus, their properties will depend on the overall morphology of the blend, i.e. the shape and size distribution of PE and PP spherulites and of elastomer domains, adhesion at interface, nature and structure of the domains, and the kinetic factors such as the rates of crystallization and vitrification.

Starkweather extensively studied the structure and morphology of blends prepared from EPDM with LDPE and copolymers of ethylene-vinyl acetate. When LDPE was added to EPDM having an ethylene-propylene ratio of 4.5 and a low level of polyethylene type crystallinity, crystalline interactions were seen through changes in the size of the unit cell. As the EPDM was added to LDPE, the a-parameter of unit cell increased from 7.515 to
8.35 Å while the b- and c-parameters were almost constant. The unit cell dimensions for blends were close to those for methyl branched polyethylenes having the same overall concentration of methyl groups. The incorporation of this type of EPDM molecules in LDPE unit cell interferes with the development of spherulites and improves the transparency of films. On the other hand, the blends of HDPE with EPDM exhibited no significant effect on the spherulitic morphology of HDPE. Also, the unit cell parameters for HDPE remained unchanged. The results show that the interaction of EPDM is more pronounced with LDPE, resulting into miscible blend. It was also observed that the interaction between LDPE and EPDM increases with increasing ethylene content of EPDM. Thus, blending with EPDM significantly affected the crystallization of LDPE compared to HDPE. This effect was attributed to the interaction between LDPE and EPDM having similar cohesive energy densities in the amorphous phase. The dynamic mechanical studies also show a systematic shift in loss peak toward β-relaxation of polyethylene with increasing LDPE content, indicating miscibility in amorphous phase.

Similar blend systems based on EPDM were studied by Lindsay et al.\textsuperscript{127} and others\textsuperscript{128-130}. In fact, these authors reported that commercially important blends can be obtained with high ethylene EPDM and LDPE that have tensile strength higher than the tensile strength of either component polymers. Lindsay et al. also made DSC measurements that show significant decrease in the crystallization temperature of LDPE due to partial miscibility and molecular level interaction between LDPE and high-ethylene sequences of EPDM.

The situation is different when the performance of HDPE/EPDM blends is compared with PP/EPM (ethylene-propylene rubber) blends. Orazio et al.\textsuperscript{128} found that EPM copolymers act as the interfacial agent for PE/PP/EPM ternary blends, improving, for example, the adhesion between HDPE dispersed phase and PP matrix with reduction in domain size. These observations suggest that a certain amount of EPM molecules can be dissolved in the amorphous phase of HDPE and PP. On the other hand, the binary blends of PP/EPM showed a significant level of phase segregation compared to HDPE/EPM blend, indicating that the affinity of EPM molecules is likely to be higher with HDPE molecules than with PP.

Danesi and Porter\textsuperscript{129} studied the blends prepared from PP and EPDM with a view to establish relationship between morphology and physical properties and to examine the principles which govern the development of morphologies. The influence of blending conditions on dispersion states was also explored. They reported that in the melt-blended samples of PP with EPDM and EPM, the domain size of the dispersed phase varied with the blend composition, the difference in the melt viscosities of the component polymers and the annealing effects which take place during the residence period of the melt mixture inside the rheometer reservoir. However, these changes in phase morphology did not result in any significant change in the crystallinity of PP, as evidenced by a marginal change in the value of its heat of fusion, compared to virgin PP. The studies on crystallization behaviour of these blends also indicate that addition of EPDM to PP leads to a significant change in the crystallization behaviour, nucleation density, spherulitic growth rate and size, overall morphology and the thermal properties\textsuperscript{130}. In addition, they also observed a significant depression in equilibrium melting temperature, with respect to pure PP, for 20% EPDM addition and related it to the phenomenon of partial miscibility and molecular fractionation process. Jang\textsuperscript{131} studied the similar system for crystallization behaviour and resultant morphology. He reported that addition of EPDM phase results in an irregular spherulitic texture, smaller spherulites, loss in sharpness of spherulitic boundaries and decrease in degree of supercooling and melting temperature. However, no appreciable change in heats of fusion and crystallization other than a trivial volume effect was observed. The average spherulitic diameter of the sample containing 15% EPDM was about half of that of unmodified PP, indicating large increase in nucleation density for blends. Pukanszky et al.\textsuperscript{132} investigated the PP/EPDM blends in the entire compositional range and reported almost similar results as obtained by Martuscelli et al.\textsuperscript{130} and Jang\textsuperscript{131}. In addition, they also observed formation of hexagonal modification of PP crystal structure in 5-50 Vol % EPDM blend composition range under similar crystallization conditions as employed for PP. However, around 80 Vol % EPDM the crystallization process of PP changed significantly, reducing crystallization rate, crystallinity, crystal size and crystal perfection of PP.

The main advantages of film products made from PP/elastomer blends having 5-15 wt % elastomer are excellent flexibility, high resistance to abrasion and fibrillation\textsuperscript{92,99,100}. Unfortunately, it is difficult to mix these two polymers in the extruder. Moreover, the elastomers have a tendency to stick to extruder screw in the compression zone, affecting the
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