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Impact Modification of Isotactic Polypropylene with Ethylene-Propylene Diene Monomer Rubber

The present work was done to improve the impact property of isotactic polypropylene (PP), especially at low temperatures, by incorporating ethylene propylene diene monomers (EPDM). This was done by ensuring compatibility between the two polymers with phase modifiers polyethylene grafted with maleic anhydride (PE-g-MA) and initiator dicumyl peroxide (DCP). In addition, attempts were also made to understand the fundamentals of impact toughening as well as fracture toughness, and to correlate the results with that of morphological evidences obtained from scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods. Varying the ratios of all blend composition, mechanical properties were studied. It was observed that as the rubber fraction increased, the impact property as well as fracture toughness increased. All these tests also showed promising results when PE-g-MA was added, leading to more improvement in all the mechanical properties including increase in crystallite size. It had shown plasticization effect on the compositions, which could be further confirmed by differential scanning calorimetry (DSC) compared to the uncompatibilized ones. But when DCP was added, it behaved like an initiator which directly reacted with the PP matrix, decreasing the molecular weight of the blend with decreasing size of the crystallites.

1 Introduction

For a long period of time, researchers have been studying on blending of several polymers together so as to generate optimized properties out of them and also to make them economically viable (Utracki, 1989). Polypropylene (PP)/ethylene-propylene diene monomer rubber (EPDM) blend is one of such industrially important blends, since it has received commercial success in terms of applications in various industrial fields; mainly owing to the fact that the composition dependent properties of the blends can meet the diverse requirement of industrial applications. PP has good balance of mechanical and thermal properties and is a widely used commodity thermoplastic (Brydson, 1999). It has high isotacticity, narrow molecular weight distribution, high heat distortion temperature, low price and adequate stiffness. However, it has low notched toughness, which restricts its application as an engineering plastic. There-

fore, in order to improve the low temperature impact strength of PP, EPDM or ethylene-propylene rubber (EPR) are usually being added in blends with PP (Van der Wal et al., 1998; Van der Wal and Gaymans, 1999a; Jiang et al., 2000; Wei et al., 2004). EPDM, on the other hand, possess good weatherability and chemical resistance, however it suffers from insufficient tensile strength. Therefore, in order to obtain optimized properties out of these two polymers, they were blended together. Researchers have studied the mechanism by which deformation takes place in case of such blends. Van der Wal and Gaymans (1999) had mentioned the effect of test temperature on the fracture behavior of the blends. Focus had also been given on the fact that the fracture behavior depends on the blend morphology and test speed. The role of EPDM rubber is to relieve the volume strain by cavitations and then act as a stress concentrator. PP shows a clear brittle-to-ductile transition with increase in temperature for notched impact test. This brittle-to-ductile temperature is of enormous importance to polymer scientists because this crucial parameter determines the applicability of the blend in industries. Jiang et al. (2000) studied the brittle-to-tough transition temperature (BDT) of PP/EPDM blends in terms of inter-particle distance (ID), temperature and strain rate. Van der Wal et al. (1994) studied the effect of the matrix crystallinity and matrix molecular weight on the brittle to ductile transition of PP/EPDM blends. The matrix crystallinity of blends with different isotacticity was studied. ID has been considered to be an important morphological parameter (Van der Wal et al., 1986). Wu reported that if ID is lesser than ID_c (critical value), then the blend is considered to be tough but otherwise it is brittle (Wu, 1985).

Despite the structural similarity, however, EPDM itself is not compatible with PP. The EPDM phase exists as separate particles in the PP matrix due to stratification segregation, and phase inversion. The incompatibility of the blends is majorly due to the poor interface adhesion. The interface instabilities lead to poor and undesirable mechanical properties. To improve the compatibility of the PP/EPDM blends, various compatibilizers have been prepared by molecular design, and incorporated into the blends. In addition, a very convenient way of preparing compatibilizer has been suggested – the so-called reactive processing methods. Various vinyl monomers can be grafted or block-co-polymerized onto the mother polymer such as PP, polyethylene (PE), EPR and EPDM. Many attempts have been made to enhance the interfacial adhesion between different components of a blend by interfacial agents which influence the phase morphology of immiscible polymer blends

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by compatibilizing effect (Zhang et al., 2006). *In situ* grafting (reactive blending) of maleic anhydride (MA) into the blend of PP/EPDM improves the mechanical properties and morphology of the blend by improving the interfacial adhesion between PP and EPDM. This has also been achieved by using a compatibilizer, i. e. block copolymers. The compatibilizer acts as emulsifier which causes a finer dispersion of phases and improves physico-mechanical properties and morphology of the blends. In the past, researchers have worked on compatibilization of PP/EPDM blends using different techniques (Zhou and Dai, 2002). In the present effort, approach has been taken to consolidate the effects of compatibilization, as well as, the effects of processing. Furthermore, focus has been given on understanding the mechanism of rubber toughening of plastic using different characterization tools and relating the findings to blend morphology.

Low temperature impact property of isotactic PP (i-PP) is of significant interest to the automotive industry. The focus of this present study is to render improvement upon this particular property by adopting the approach of blending of PP with EPDM. Compatibility between the two polymers was ensured by utilization of phase modifiers and grafts, i. e. PE grafted with MA (PE-g-MA) and initiator dicumyl peroxide (DCP). Although this study deals with a very well-studied system PP/EPDM blends; however, there are certain aspects which demand attention. Accordingly, this work focuses on the effects rendered by the type of compatibilizer on the thermal, mechanical and morphological properties of the blend. In addition, investigation on the role of disperse (rubber) phase as well as the compatibilizer on the fracture behavior of the abovementioned blend has also been carried out. Moreover, focus has also been given on developing expertize in fracture mechanics through "single-edge-notch (SEN)" fracture studies, followed by microscopic observation disclosing the proper mechanism of toughening which involves crazing, cavitation and yielding of the blend. The impact toughening of polymer blends were also studied through changes in phase morphology with varying particle size.

2 Experimental

2.1 Materials

i-PP can be obtained in various forms but the form used for this study was natural, unfilled grade obtained from Reliance Industries Ltd. (Mumbai, India) under the trade name of REPOL. The grade used (H200MA) was recommended by suppliers for injection molding process. The melt flow index (MFI) of the grade is 20 g per 10 min at 230 °C per 2.16 kg. EPDM rubber, that was used for this study, was under the trade name of Nordel IP 4770 R and was obtained from Dow Chemicals, Midland, USA, with Mooney viscosity (ML 1+4, at 125 °C) of 70. The density of the material is 0.87 gm cm^{-3} with ethylene content of 70 %, diene content of 5 % and propylene content of 25 %. PE-g-MA, used for this study, was under the trade name Amplify GR 216 (Plastomer) obtained from Dow Chemicals with MA graft level of 0.5 – 1.0 wt%. DCP used for this study was under the trade name Perkadox (95 %) from Akzonobel, Amsterdam, The Netherlands.

2.2 Sample Preparation

PP/EPDM, PE-g-MA and DCP were mixed separately in a twin screw extruder (ZSK-25/1) in different ratios as dictated by DOE. In the present study, all the batches were prepared at 300 rpm, along with a throughput of 15 kg h^{-1}. After compounding, the strands were pelletized and dried at 60 °C for 4 h. The injection molding of the specimen was done using a L & T injection molding machine, having a capacity of 85 T (model: LTM Demag, Mumbai, India). The sample specimens were kept for 48 h under ASTM condition. The detailed sample code of the different compositions has been presented in Table 1.

2.3 Characterization Techniques

2.3.1 Scanning Electron Microscopy (SEM)

The blend morphology was observed by employing a scanning electron microscope (Model: JEOL SEM). The SEM specimens were prepared by taking a small portion of the sample and blocking it using a scalpel. Sample was kept at cryo temperature of –60 °C, and stained stubs were then prepared for SEM analysis. The instrument was maintained at bright field and transmitted mode.

2.3.2 Impact Testing

The Izod impact tests were carried out on ceast-resil impactor at varying temperatures of –30 °C, 0 °C and 23 °C, following ISO-180 method. The specimen dimension was kept at 80 × 10 × 4 mm. 4 J and 1 J hammers were used for this purpose.

2.3.3 X-Ray Diffraction (XRD)

XRD was carried out for the raw material and the compounded samples. The XRD for all the compositions were carried out

Sample codes	Composition details
P20Rn	"P" stands for PP (MFI = 20 g/10 mins), "R" stands for rubber content and n (concentration of rubber in the blend, wt%) = 5, 30, 50 wt% of EPDM rubber
P20RnG5	"P" stands for PP (MFI = 20 g/10 mins), "R" stands for rubber content and n (concentration of rubber in the blend, wt%) = 5, 30, 50 wt% of EPDM rubber and G5 stands for 5 wt% of PE-g-MA
P20RnD0.15	"P" stands for PP (MFI = 20 g/10 mins), "R" stands for rubber content and n (concentration of rubber in the blend, wt%) = 5, 30, 50 wt% of EPDM rubber and D0.15 stands for 0.15 wt% of DCP

Table 1. Abbreviation Used for Different Compositions

using Philips X'pert PRO PANalytical (Almelo, The Netherlands) to determine average crystallite size (assuming spherulitic growth). At first an experimental run was carried on pure PP, in order to get the reference peak. The 2θ angle was varied between $10°$ to $50°$.

The crystallite size (L_{hkl} in nm) perpendicular to the (hkl) diffraction plane was obtained by using the Scherrer equation (Alexander, 1969):

$$L_{hkl} = \frac{k\lambda}{\beta \cos\theta}, \tag{1}$$

where, β is the measured FWHM of the experimental peak (in degrees), K is the Scherrer factor (which is ~ 0.9 if the Gaussian equation is employed), λ is the X-ray wavelength (the value is 1.5405 Å) and 2θ is the Bragg angle.

2.3.4 SEN Test

The fracture behavior was studied by a tensile test on the notched bars referred to as a SEN tensile test. The injection molded bar (ISO 180/1, $74 \times 10 \times 4$ mm), having a single-edge 458V-shaped notch (with depth of 2 mm and tip radius of 0.25 mm), was milled in the specimens; and then the notch was further propagated by a razor blade and was tested by a tensile machine (Instron, Norwood, USA) at a speed of 50 mm min^{-1} with a grip distance of 50 mm. The test (five measurements) was carried out on a Z020 tensile machine (Zwick Roell Group, Ulm, Germany), equipped with Zwick software. ISO standard tested specimens were tested by the tensile machine and the plastically deformed length was being measured by an optical microscope.

From the load-elongation (F-l) response of the SEN test specimens, the fracture toughness was determined by the following relation:

$$K_{CT} = (F_{max}/BW) * a^{0.5} * f\left(\frac{a}{W}\right), \tag{2}$$

where, F_{max} is the maximum force in the F-l graph; B is the thickness of the specimen; W is the width of the specimen; a is the total notch length (produced by saw and razor blade); and f (a/W) is the geometry correction factor. The correction factor is given by:

$$F\left(\frac{a}{W}\right) = 29.6 - 185.5\left(\frac{a}{W}\right) + 655.7\left(\frac{a}{W}\right)^2 - 1017\left(\frac{a}{W}\right)^3$$
$$+ 638.9\left(\frac{a}{W}\right). \tag{3}$$

2.3.5 Differential Scanning Calorimetry (DSC)

Thermal characterization was done using Modulated Differential Scanning Calorimetry (MDSC). Q1000 machine, manufactured by TA instrument (USA), was heated at a rate of $10°C$ min^{-1} in an inert atmosphere (nitrogen atmosphere) from $-100°C$ to $250°C$ (heating cycle). This was followed by cooling to $-100°C$ at the same ramp (cooling cycle). The samples were further heated to $250°C$ (heating cycle). Aluminum pans were used to carry the samples.

2.3.6 High Shear Viscosity (HSV)

HSV was done in order to compare the melt viscosity change between the compatibilized and the uncompatibilized blends. The melt viscosities of the blends were measured with an automated capillary rheometer (Rheograph-6000) from Göttfert, Rockhill, USA, having a die diameter of 9.53 mm. Viscosity was measured at a temperature of $230°C$ with varying shear rate from 100 S^{-1} to 10,000 S^{-1}.

3 Results and Discussion

In this work, the impact strength of PP at low temperature has been improved through incorporation of EPDM rubber, and then subsequently the compatibilizer PE-g-MA has been used to improve the low temperature impact property of PP evidently. PE-g-MA compatibilized PP/EPDM blends have shown significant increase in impact strength and toughness even at a very low temperature.

3.1 Analysis of Impact Strength of the Compatibilized and the Uncompatibilized Blends

Figure 1 shows the variation of impact strength with EPDM content for both the compatibilized and the uncompatibilized PP/EPDM blends at different temperatures. It was observed from Fig. 1A that PP/EPDM blends exhibited increase in impact strength with increase in rubber content at room temperature. Moreover, for all the compositions, the blends have shown increase in impact strength with increase in EPDM content. Usually, semi-crystalline polymers, like PP, exhibit high crack initiation energy but low crack propagation energy under impact. When there is a sharp crack or notch present in the polymer, it fails in a catastrophic manner without absorbing much energy. Upon addition of rubber the symmetry of the PP matrix get distorted, which helps in initiating matrix plastic deformation, leading to dissipation of large amount of energy before fracture. PP/EPDM blends compatibilized with 5 wt% of PE-g-MA had shown much higher impact strength value than that of uncompatibilized blends at all ratios of PP and EPDM. Pure PP had shown impact strength value of 3.29 kJ m^{-2}, which drastically got increased to 50 kJ m^{-2} upon addition of 30 wt% of EPDM content for PP/EPDM blends. It was found that for uncompatibilized blends, owing to weak interfacial interaction between PP and EPDM phase, the internal cavitation of the dispersed rubber gets inhibited to some extent. The failure in internal cavitation restricts the plastic deformation of PP matrix, leading to brittle fracture, as compared to PE-g-MA compatibilized blends. Upon addition of the compatibilizer the two phases get increasingly stabilized, leading to improved interfacial adhesion; and thus helps in improving the impact strength of the blend. Qin et al. (2009) had studied the effect of compatibilizer SMA on the impact strength of PA6/ABS blends. It was observed that the impact strength of PA6/ABS blend increases with SMA content up to a certain concentration (due to melt interfacial interaction) but afterwards deteriorates the impact property of the blends. Zhang et al. (2006) had studied the effect of the compatibilizer PP-g-AA on the impact strength

of PP/EPDM blends. It was observed that PP/EPDM blends, having epoxidized EPDM, form covalent bond with the acid group of PP-g-AA that facilitate the improvement of impact strength of PP/EPDM blends as compared to PP/PP-g-AA/EPDM blends. It was also observed that the value of impact strength of PP/EPDM blends depends on temperature, and it was further observed that the value of impact strength decreases with temperature. In fact, it was known that the mechanical hysteresis represents the energy dissipated during the loading and unloading cycle under stress (Lu et al., 1996). At higher temperature, due to high plasticity of the material, it un-

dergoes extensive plastic deformation which increases the hysteresis of the material with low yield stress. Consequently, this increases the value of impact strength of the blends with increase in temperature. It was also observed from Fig. 1 that the impact strength of PP/EPDM blends with DCP had shown lower values as compared to P20Rn and P20RnG5 compositions. The presence of DCP leads to peroxide reaction with PP which involves either hydrogen abstraction from PP chains (Suwanda et al., 1988), after the homolytic cleavage of DCP into two reactive radical to form functional graft, or PP may undergo β-scission producing terminal double bond or terminal free radical (Xanthos, 1992). These two processes may also proceed simultaneously. There remain possibilities that EPDM phase may also undergo crosslinking. Bouhelal et al. (2007) had studied the effect of peroxide in presence of sulphur and accelerator on the toughening mechanism of PP, and it was observed that the impact strength of PP matrix showed remarkable improvement. It can be explained further that owing to the presence of sulfur and accelerator, the blends have underwent effective crosslinking that led to improvement of impact strength. But, in this work, P20RnD0.15 blends had shown decreased impact strength as compared to other compositions even with increase in rubber content. So, in this work, it might be the β-scission of PP matrix that led to deterioration of the impact property of P20RnD0.15 blends.

In order to examine the brittle to tough transition temperature (BDT) for the blend components, the impact strength vs. temperature was investigated. BDT is defined as a temperature which designates the onset of plastic deformation. BDT depends on several factors like rubber content, dispersed EPDM phase size, interfacial interaction between EPDM phase and PP matrix, and also the shear modulus of the rubber phase. Here, only the effect of three above-mentioned factors on BDT had been studied. Figure 2 shows the variation of impact strength of different compositions of PP/EPDM blends with or without compatibilizer. BDT was mainly obtained from midpoint of the S-curve of impact strength vs. temperature plot. It was observed from Fig. 2A that a sudden change in the value of impact strength had occurred at two temperatures for P20R30, which designated two BDT. Similar result was also observed by Borggreve et al. (1987) for PA6/EPDM blends, where a second brittle-ductile transition occured due to the incorporation of EPDM rubber in PA6 matrix. The second transition was mainly because of the dispersion of EPDM in PA6 - matrix, and was discontinuous represented by sudden increase in impact strength value within a small range of temperature. In this work, the energy transaction took place from 5 kJ m^{-2} to 16 kJ m^{-2} around BDT for P20R30 blends. Whereas, PE-g-MA compatibilized PP/EPDM blends P20R30G5 had shown only one BDT transition, which exhibited a change in energy from 8 kJm^{-2} to 16 kJm^{-2} at a low temperature range of −10 °C to −30 °C. BDT depends on the interparticle distance and the particle size of the dispersed phase. So in order to study about the BDT of PP/EPDM blends, it is important to focus on the mean diameter and ID of the EPDM phase.

Table 2 presents the variation of the value of T_g of the PP phase for different compositions of both the compatibilized and the uncompatibilized PP/EPDM blends. It is evident from the table that the value of T_g decreases with the addition of rubber, signifying the increase in chain flexibility of the PP phase
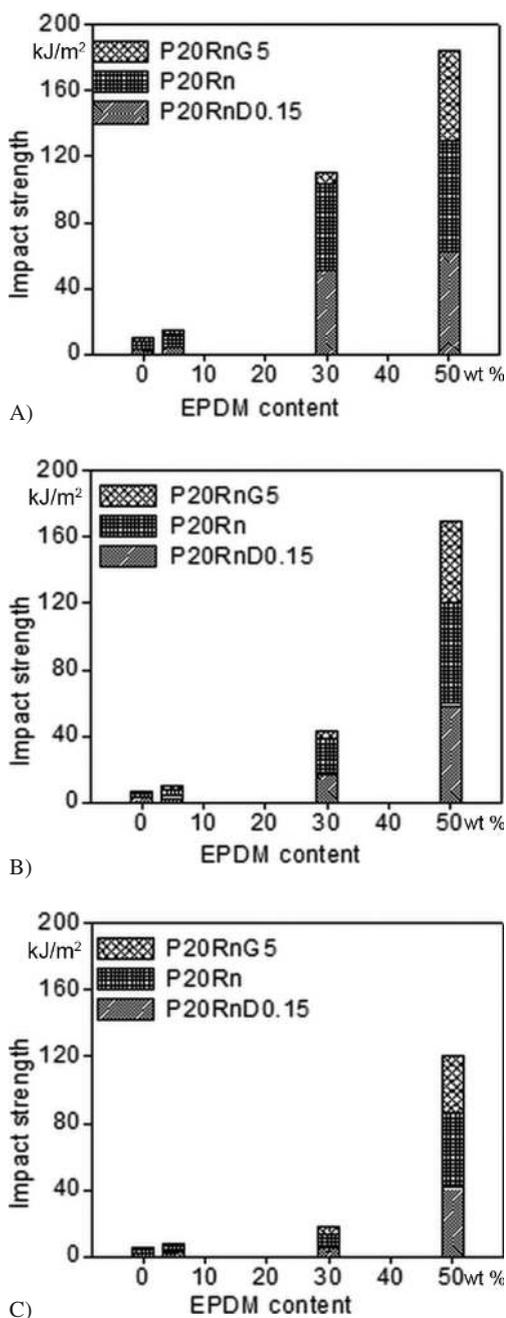

Fig. 1. Variation of impact strength with EPDM content at (A) 23 °C, (B) 0 °C and (C) −30 °C

upon addition of the EPDM phase. The value of T_g of the PP phase has been observed to decrease significantly with incorporation of PE-g-MA, which may be attributed to the more effective segmental motion of the PP phase due to the plasticization effect of PE-g-MA. Owing to the low molecular weight, PE-g-MA acts as a spacer. This eventually increases space for the polymer chain molecules to rotate efficiently, leading to a decrease in the T_g value. On the other hand it was observed that the value of T_g of the PP phase somewhat increases upon the addition of DCP, owing to the chain scission of the PP phase.
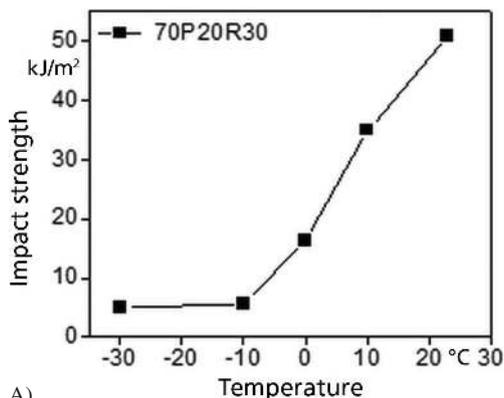

A)
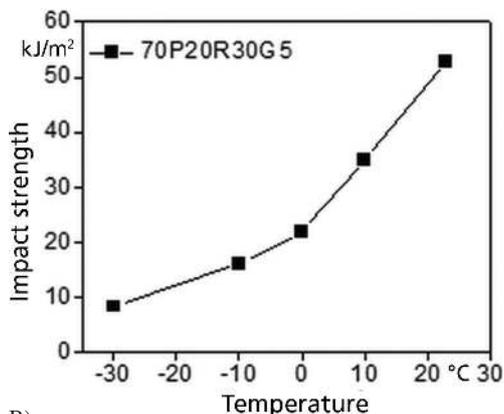
B)

Fig. 2. Impact strength vs. temperature for compositions having (A) 30 wt% EPDM and (B) 30 wt% EPDM and 5 wt% PE-g-MA

Samples	T_g $^\circ$C
P20R5	−14.2
P20R5G5	−16.6
P20R5D0.15	−13.5
P20R30	−16.4
P20R30G5	−17.4
P20R30D0.15	−13.8
P20R50	−17.6
P20R50G5	−19.1
P20R50D0.15	−17.3

Table 2. Values of T_g for Different Composition of PP/EPDM Blends

Figure 3A shows the variation of mean diameter of the dispersed phase of the blend with the rubber content of different composition of both compatibilized and uncompatibilized blends. From the figure, it was observed that the mean diameter of the PP/EPDM blends increased with increase in EPDM content. In case of PE-g-MA compatibilized PP/EPDM blends, the mean diameter was observed to decrease as compared to the uncompatibilized ones. But the mean diameter of DCP compatibilized PP/EPDM blends had shown higher value of mean diameter than PE-g-MA compatibilized and uncompatibilized PP/EPDM blends. Figure 3b shows the variation of ID with the EPDM content. It was observed from the figure, that for both compatibilized as well as for uncompatibilized PP/EPDM blends the ID value decreases with the rubber content. With increase in rubber content, the distance between the rubber agglomerates decreased with increase in agglomerates size. For the compatibilized blends as the rubber particle size gets decreased, it helped in yielding of the matrix, which increased the fracture energy. Similar observation was also studied by van der Wal et al. (1999b). This decrease was found to be more prominent in case of P20RnD0.15 blends followed by P20Rn blends as compared to P20RnG5 blends. Jiang et al. (2000) had observed that for PP/EPDM blends, the value of ID decreased with EPDM content but the mean diameter showed no significant change with EPDM content. ID depends on the in-
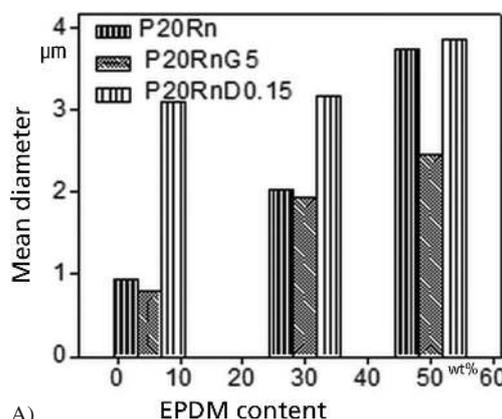
A)
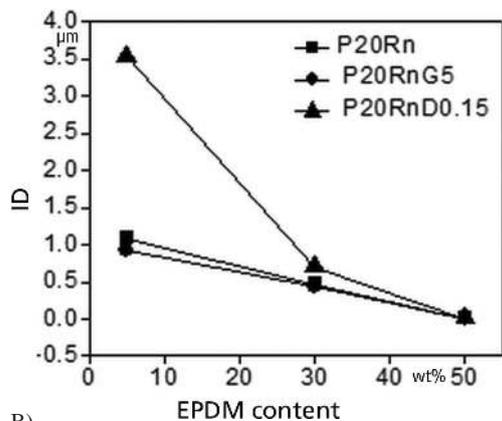
B)

Fig. 3. Variation of (A) mean diameter of the particle and (B) inter-particle distance (ID) of the particle with the different compositions of the blends

teraction of the matrix and that of the dispersed phase. PP/EPDM blends had shown a value of 0.15 μm of IDc whereas PA6/EPDM blends exhibited a value of 0.3 μm (Jiang et al., 1999).

In order to assess the morphology of PP/EPDM blends that were developed with addition of EPDM, SEM was done. The SEM images provided a detailed description of the dispersion of rubber in PP matrix. Figure 4 shows the SEM micrographs of the different compositions of PP/EPDM blends with or without compatibilizer PE-g-MA and DCP. The uncompatibilized PP/EPDM blends had shown droplet-matrix morphology and these blends were considered to possess broad, non-uniform and unstable morphology. It was observed from the Fig. 4A, D, G that the size of the dispersed domain increased with an increase in the wt% of EPDM rubber. All the uncompatibilized PP/EPDM blends had shown two phase morphology. The instability of the uncompatibilized PP/EPDM blends increased more with increasing rubber content. This observation was mainly attributed to a higher degree of coalescence in the blend with increase in EPDM levels, owing to lack of compatibility of PP and EPDM. There might be a number of factors, like van der waals forces between the dispersed phase, mechanical forces acting on the dispersed phase, capillary forces and even difference in density of the two phases, which dominates the coalescence process of the dispersed phase in PP matrix. Figure 4 (b, e and h) depicts the SEM micrographs of PP/EPDM blends compatibilized with PE-g-MA, P20RnG5. It was observed from the SEM micrographs that with addition of the compatibilizer PE-g-MA to PP/EPDM blends, the particle size of the dispersed phase got decreased. The compatibilized blends showed narrower distribution of dispersed particle size as compared to the uncompatibilized PP/EPDM blends. This

indicated that in presence of compatibilizer, the coalescence process was slow due to the in situ formation of graft-copolymer at the interface. Because of this reaction, an emulsifying effect was induced in the system by the compatibilizer, which led to finer dispersion. In case of the compatibilized blends P20Rn, a diffused interphase was found to be formed between PP and EPDM phase by the compatibilizer that facilitate the stress transfer, resulting in cavitation of rubber phase; and thus increase the plastic deformation of the matrix. PE-g-MA acts as a chemical compatibilizer that form covalent bonds between the two phases. The MA group of PE-g-MA reacts with the double bond present in the norborene group of EPDM phase and the PE group of PE-g-MA interacts with PP phase owing to non-polar interaction. Thus the compatibilized blends with higher rubber content had showed significant signs of plastic deformation in izod-impact test even at low temperature, but the uncompatibilized PP/EPDM blends did not show any such signature at low level of rubber content. It was further observed from the SEM micrographs that the particle size of the dispersed phase increase with addition of even 0.15 wt% of DCP. It was known that the PP matrix underwent β-scission, which led to the formation of low molecular weight and reduced melt viscosity of PP matrix. This increase in the difference between the melt viscosities of PP and EPDM phases increased the interaction between the EPDM droplets in the melt. Whereas, the results obtained by Babu et al. (2010) contradicts the above result. According to that work, the particle size was observe to decrease with addition or even increase in DCP content above 2 wt% and below 4 wt% of DCP, but afterwards again showed a decreasing trend. The contradicting result can be explained on the basis of the amount of DCP content of the blends. In this work, an attempt had been taken to avoid the crosslinking of

A)

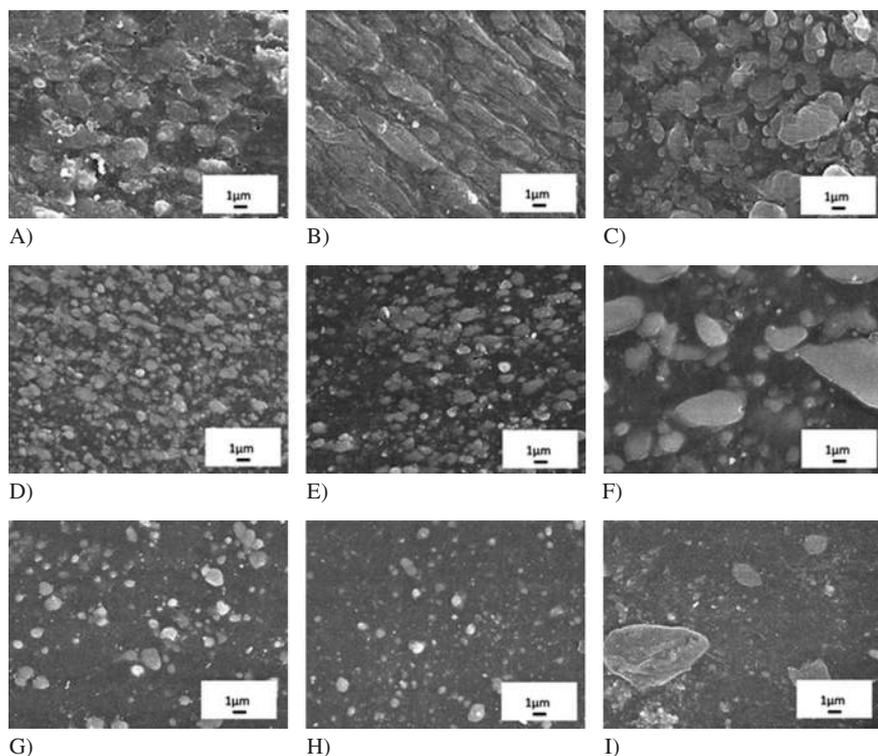B)

C)

D)

E)

F)

G)

H)

I)

Fig. 4. SEM micrographs of (A) P20R50, (B) P20R50G5, (C) P20R50D0.15, (D) P20R30, (E) P20R30G5, (F) P20R30D0.15, (G) P20R5, (H) P20R5G5 and (I) P20R5D0.15

the EPDM rubber (with <2 wt% of DCP). Figure 5 had shown that the melt viscosity of the uncompatibilized PP/EPDM blends and those compatibilized with PE-g-MA had nearly similar melt viscosity values. It can be also observed that addition of 0.15 wt% of DCP to PP/EPDM blends had led to reduction in melt viscosity. The reduction of melt viscosity of the blends occurred due to chain scission of PP matrix and this reduction in melt viscosity of P20RnD0.15 blends compared to P20Rn and P20RnG5 get increased with decrease in the rubber content.

In Fig. 6A and B, a comparison had been done to study the effect of wt% of rubber content on the %crystallinity of both the compatibilized and the uncompatibilized PP/EPDM blends. It should be noted that the degree of crystallinity values for all the blend compositions has been presented normalized to that of the pure PP. The data obtained from both XRD and DSC had shown similar trend. The %crystallinity of PP/EPDM blends was found to get decreased with increase in rubber content for both the compatibilized and the uncompatibilized ones. It was further observed that with addition of the compatibilizer (PE-g-MA) to PP/EPDM blends, more pronounced decline in %crystallinity of PP/EPDM blends took place. Further, it is also clear from the figure that the %crystallinity values obtained for both the compatibilized and the uncompatibilized PP/EPDM blends from XRD had shown higher values as compared to DSC. It is evident that the WAXS method provides accurate true crystallinity values for semi-crystalline polymers, such as isotactic PP, related to material state (equilibrium or non-equilibrium). DSC as a method for crystallinity determination is reliable for providing accurate crystallinity values for materials in the equilibrium state but fails for materials in non-equilibrium state, such as i-PP, by plastically deformed process or generally in systems in which relaxation processes are activated by temperature elevation. The decrease in %crystallinity value was mainly attributed by the increase in the crystallite size (confirmed from XRD data) of PP due to addition of the rubber particle. This effect showed much more promising result in case of the compatibilized blend. From Fig. 6C, it was observed that the crystallite size of both the compatibilized and the uncompatibilized PP/EPDM blends get decreased with the rubber content.

It was observed that the compatibilizer not only affects the size and shape of the dispersed phase (regarded as macro-morphology) but also affects the matrix crystalline form (micromorphology). It was also observed to affect the total crystallinity of the blends. The result could be explained by solidification effect. When rubber was added initially, the crystallite size decreased owing to nucleation effect of the EPDM rubber and with increase in the rubber content. The prolonged crystallization of i-PP matrix took place, which led to easier chain transfer in the EPDM melt during the crystallization process; and

A)

B)

C)

Fig. 6. Comparison of %crystallinity obtained from (A) DSC, (B) XRD and (C) crystallite size (obtained from XRD) vs. EPDM content for the PP/EPDM blend with 5 wt% PE-g-MA and 0.15 wt% of DCP
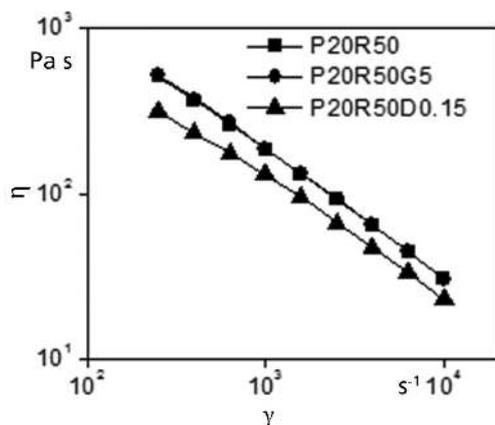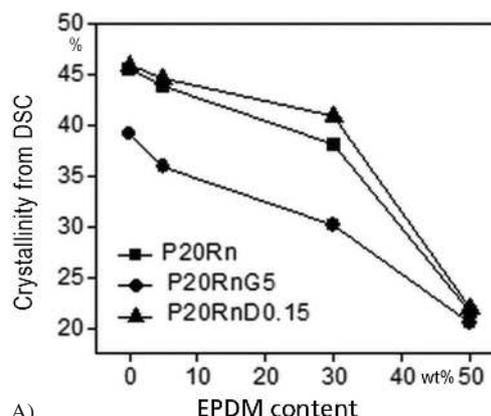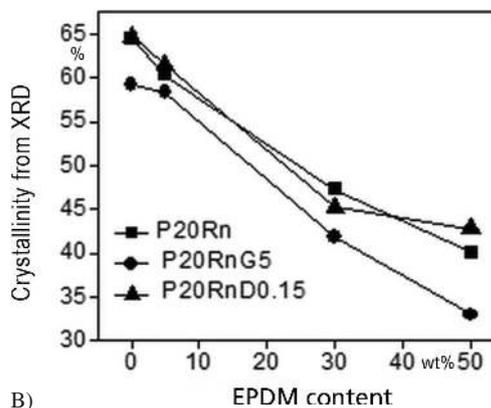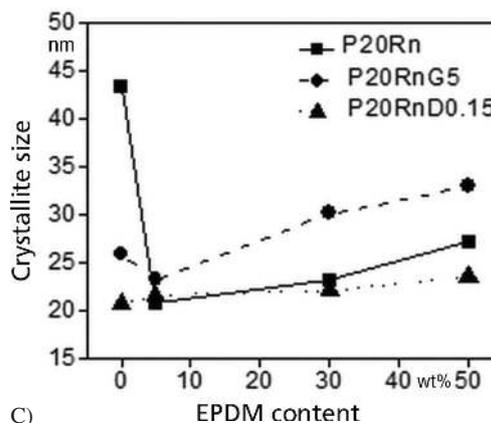

Fig. 5. Variation of viscosity of different compositions of PP/EPDM blends with 50 wt% of EPDM rubber

this outweighed the nucleation effect. It is now important to discuss about the observation when DCP was added to PP matrix. It was observed that in case of P20RnD0.15 blends, the crystallite size of PP increased and the %crystallinity of PP decreased with the rubber content. In presence of DCP, the PP matrix underwent chain scission leading to the formation of low molecular weight short chains, branches or even micro crosslinks, which diminished the crystallization sites for nucleation; thus restricting the growth of the crystallization process (Cao and Lü, 2011). Hence the crystallite size of P20RnD0.15 blends had shown lower values as compared to the P20Rn and P20RnG5 blends.

3.2 Evaluation and Characterization of the Fracture Toughness

In this work, the fracture toughness of PP/EPDM blends with and without compatibilizer had been studied through SEN test. Fracture toughness (K_C) is defined as the resistance offered by the specimen to resist the crack propagation. In general, fracture toughness depends on the thickness of the specimen. The stress state adjacent to the crack preformed changes according to the thickness of the specimen, but after a critical fracture toughness value (K_{IC}) its value become independent of the thickness of the specimen. K_{IC} is considered as the highest value of stress intensity that exist at the tip of crack, so that, whenever the stress increased from a critical value, the crack undergoes plastic deformation before the ultimate fracture. In case of PP, crazes are the dominating factors that play an important role in fracture mechanism. These crazes are formed in the weak points near the intercrystalline region. Several researchers have studied that the amorphous region present near the intercrystalline region is mainly responsible for the crack initiation, crack growth and even failure (Dasari et al., 2003). The addition of rubber particles in PP matrix as tougher may act as a stress concentrator either to initiate or to terminate the crazes (Yokoyama and Ricco, 1998). Under stress, the rubber phase undergoes extensive and massive cavitation, leading to shear yielding of the PP matrix. Through cavitation, the rubber phase relieves the triaxial stress developed on the tip of the crack formed.

At low temperature, in the brittle region, mainly the crazing mechanism dominates; whereas at room temperature, in the ductile region, the fracture toughness takes place through shear yielding. At the intermediate region of temperature, both the mechanism takes place simultaneously. Researchers have studied the fracture mechanism of polymers using several models (Anderson, 1995; Hodgkinson and Williams, 1981; Frassine, 1997). It has been realized that at low temperature and high strain rate, the fracture mechanics is dominated by linear elastic fracture mechanics (LEFM); whereas at higher temperature range, the fracture mechanics is governed by non-linear elastic fracture mechanics (NLEFM) using CTOD or j-integral (Cocco, 2007). However, in the brittle-ductile transition range neither LEFM nor NLEFM explain the fracture mechanism of polymer blends. In this study, an attempt has been made to study the fracture toughness of PP/EPDM blends at low temperature. Hence, in this context, LEFM is used in this work to study the fracture mechanism of PP/EPDM blends. Figure 7

had shown the variation of fracture toughness of both the compatibilized and the uncompatibilized PP/EPDM blends at –30 °C. Single notched pure PP has shown a brittle fracture initiating at the notch at low temperature with low fracture toughness, which confirms predominantly unstable crack growth. Similar observation has also been reported earlier (Grellmann, 2001). It was observed from the figure that with increase in the EPDM content, the fracture toughness got improved. Moreover, it was observed that blends with rubber have shown stable crack growth without fracture of the test specimen. The trend observed from Fig. 7 can be explained by the fact that with increase in rubber content agglomeration takes place, which led to the increase of rubber particle size, and thus, decreases the distance between the two particles; therefore, more energy was required to propagate the crack. It may be postulated that the fracture toughness increases with decrease in interparticle distance between the dispersed phases. The increase in rubber content helps in more efficient cavitation and shear deformation of dispersed phase, leading to higher dissipation energy.

Thomas et al. (2014) had studied that the toughening effect of PP/EPDM blends was due to the presence of rubber. This toughening effect was found to depend on the particle size of the dispersed phase which varied between 4 to 8 µm and even lower than that. When the particle size of the dispersed phase was around 1 to 3 µm, toughening phenomenon was dominated by the formation of shear banding; whereas, in case of particle much lower than this, cavitation and shear yielding took place. Figure 3 shows that for P20Rn blend the particle diameter is between 1 to 3 µm, which confirmed that the fracture mechanism was dictated by shear banding; whereas, the P20RnD0.15 blends had exhibited much higher values of particle diameter. It was observed visually that the samples of the P20Rn blends exhibited plastic deformation before fracture, whereas the P20RnD0.15 blends had shown brittle fracture under tensile stress. However, for the PE-g-MA compatibilized PP/EPDM blends the particle diameter got reduced below 1 µm at a low rubber content (i.e. 5 wt%), which suggests that the fracture mechanism was dominated by cavitation or shear yielding; whereas, at higher concentration of rubber P20RnG5 blends exhibited particle diameter around 1 to 3 µm, which indicated
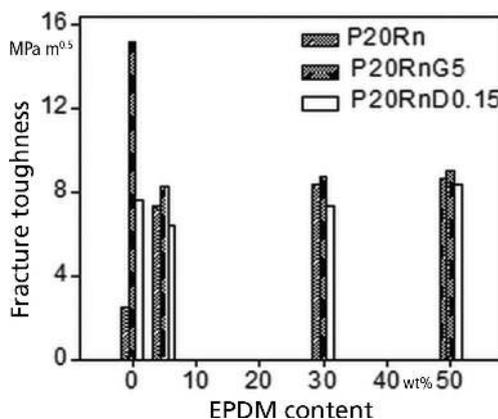

Fig. 7. Variation of fracture toughness with EPDM content for both the compatibilized and the uncompatibilized blends

shear banding. Moreover, the P20RnG5 blend compositions had exhibited high extent of plastic deformation without fracture, resulting only in elongation of the samples. It was also observed that the PE-g-MA compatibilized PP/EPDM blends had shown much higher fracture toughness as compared to the P20Rn and P20RnD0.15 blends. The reason behind the high ductility of these compatibilized PP/EPDM blends envisages from their finer and smaller dispersed phase of rubber in PP matrix. The smaller particle size of the compatibilized blends mainly attributed from the high interfacial interaction between the two phases and control of phase morphology by the compatibilizer. These compatibilizers help in incorporating different deforming modes in the PP/EPDM blends, and thus, facilitate higher degree of toughening. Similar observations were also obtained from Wong and Mai (1999) in case of PP/PA6 blends compatibilized with a tri-block copolymer (SEBS) with different MA content. Basically, these graft copolymer compatibilizer are placed between the two phases, reducing the interfacial tension, and thus, improving the adhesion between the two phases. This argument has been supported by many other previous reports (Anastasiadis et al., 1989; Li et al., 2007; Wang and Xie, 2006). In case of the compatibilized blends the rubber domain size gets decreased as the compatibilizer were spaced at the interphase between the two components. This increases the number of rubber domain, thus increasing the fracture toughness compared to the uncompatibilized blends.

In this study the PE-g-MA might have acted as a chemical compatibilizer, interacting similarly as that of compatibilizers like PP-g-MA. Owing to their chemical and structural similarities, it can be expected that the PE-g-MA should react similar to PP-g-MA. Hence, it can be suggested that the anhydride part of the PE-g-MA reacted with the diene part of EPDM (following Diels-Alder reaction); while the PE part got physically mixed with the non-polar PP phase owing to the existing hydrophobic interaction. Moreover, it can also be suggested that due to the low molecular weight of the compatibilizer (PE-g-MA), it may act as a plasticizer which facilitate the segmental motion of the polymeric chain; thus improving the impact properties of the blends at low temperature. This can be further explained by the observed decrease in the value of the T_g upon addition of PE-g-MA to PP/EPDM blends owing to their plasticization effect (Table 2). However, in case of P20RnD0.15 blends, the value of fracture toughness of the blends got reduced with addition of DCP as compared to the P20RnG5 and P20Rn blends. This may be attributed to the fact that owing to the presence of DCP, PP chains underwent scission; a phenomenon further supported by the observed increase in %crystallinity and decrease in crystallite size. The increase in crystalline fraction with addition of DCP to PP/EPDM blends is mainly attributed to decrease in energy required to undergo deformation. This consequently decreased the fracture toughness of the P20RnD0.15 blends.

4 Conclusions

In this work, an attempt had been taken to improve the impact properties of i-PP, especially at low temperature, using EPDM. It was observed that the impact property of PP had improved significantly using EPDM rubber at higher rubber content.

Here a comparative study was done to investigate the effect of the compatibilizers, PE-g-MA and DCP, on the impact modification of PP. In this work, a study was done to correlate the mechanical properties with the morphologies of the PP/EPDM, PP/PE-g-MA/EPDM and PP/DCP/EPDM blends. It was observed that with increase in rubber content, a significant increase in the impact strength and elongation at break had taken place, which helped in increasing the toughness of the blend. With the addition of grafted copolymer, PE-g-MA, to the PP/EPDM blends, the adhesion between the two phases was found to get improved. The grafted copolymer was expected to reduce the interfacial tension and stabilized the particle size by improving the interfacial adhesion, and hence, leading to reduced rate of coalesce. The reduction in interfacial tension was also associated with the broadening of the interfacial region through the penetration of copolymer chain segments into the corresponding adjacent phases. Whereas, DCP acts as a nucleating agent, it undergoes β-scission with PP leading to reduction of molecular chain length, contributing to smaller crystallite size, and thereby increasing the crystallinity of the blends. The extent of increase in melt viscosity values of the compatibilized blends compared to the uncompatibilized ones was attributed to the extent of reaction taking place between the phases. Furthermore, the reduction in domain size was also considered as an attribution to the occurrence of reaction between the components, thereby, resulting in reduction of the interfacial tension and increase in the interfacial adhesion. Hence, it is evident that the smaller particle size and the increased phase adhesion results in improved physical properties. In this study, a comparison between the crystallinity values obtained by DSC and WAXS techniques showed a large discrepancy, which was attributed to the previous thermo-mechanical history of the materials and the intrinsic characteristics of the test method. Apart from these, a proper correlation had been done between the inter-particle distance values of each blend with that of fracture toughness. It was concluded that with increase in the rubber content the rubber domain increases owing to agglomeration, which simultaneously decreases the inter-particle distance, and thus, contributes towards the increase in the value of fracture toughness.

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