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Ionomer compatibilised PA6/EVA blends: mechanical properties and morphological characterisation

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Abstract

The compatibilisation of PA6/EVA blends with the addition of an ionomer on the mechanical properties and morphology were studied as a function of ionomer concentration with the primary aim of enhancing the impact strength of PA6 by EVA. The level of EVA was kept at 20%, which formed the dispersed phase, and the ionomer content was varied from 0 to 1.6 wt%. It was found that notched Izod impact strength of PA6/EVA/ionomer blends increased with the incorporation of ionomer to about three times of the value for uncompatibilised PA6/EVA blends. Further, it was observed that on incorporation of the ionomer the tensile strength also increased significantly. Analysis of the tensile data using predictive theories indicated an enhanced interaction of the dispersed phase and the matrix. SEM studies of cryogenically fractured surfaces indicated a decrease in dispersed phase domain size with the addition of the ionomer, while the impact fractured surfaces of PA6/EVA blends indicated extensive deformation with the formation of rumples indicating increased interfacial adhesion as compared to PA6/EVA blends. An attempt has been made to evaluate the compatibilising efficiency of ionomer in PA6/EVA blends.

Keywords: Polyamide6/ethylene vinyl acetate blends; Ionomer; Compatibilisation

1. Introduction

The development of new multiphase polymeric materials with desired mechanical properties often involves the strategy of blending. A majority of polymer blends are thermodynamically immiscible in nature due to the low entropy of mixing [1]. The unfavourable entropy of mixing leads to a coarse and unstable phase morphology in binary blends with high interfacial tension and low interfacial adhesion [2]. Thus, the mechanical properties of immiscible polymer blends are inherently inferior in nature. The problem of interfacial properties can be attenuated by introducing a block or graft copolymer, which in turn stabilises the phase morphology [3–5]. Blends of polyamide6 (PA6) and ethylene vinyl acetate (EVA) are immiscible in nature [6]. The incompatible nature of the PA6/EVA blends has been characterised by large domain size, wider domain size distribution and sharp interface with increasing EVA level, which manifests in nominal increase in impact strength [6]. It has been further reported that PA6/EVA blends were compatibilised by using EVA-*g*-MA utilising the reactive route [7]. Ethylene acrylic acid has been employed as a cooperative compatibiliser for PA6/EVA blends and the effect of compatibilisation has been evaluated in terms of mechanical, morphological and rheological properties [8]. Several ionomers have also been found to be effective as a compatibiliser in PA6/PE and PA6/PP blend system as reported in the literature [9,10]. The compatibilising activity has been demonstrated by suitable modification of the morphology, which leads to the superior mechanical properties. The impact strength of PA6/rubber blends depends on rubber concentration, rubber particle size and particle size distribution, and adhesion between the two phases [11]. It was also shown that PA6 could be toughened with a dispersed rubber having a particle size of 0.1–2 μm [12]. The effect of concentration and the particle size of rubber on the brittle–tough transition temperature of PA6/ethylene propylene diene methylene (EPDM) blends has been investigated [13]. The brittle–tough transition temperature shifted to lower value when the rubber content increased or the rubber particle size decreased.

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In the present paper, the effects of the addition of an ionomer on the mechanical and morphological properties of PA6/EVA blends are reported. Mechanical properties such as impact strength and tensile properties are studied as a function of ionomer concentrations. Morphology of the blends has been studied by scanning electron microscopy (SEM). An attempt has been made to evaluate the compatibilising efficiency of ionomer in PA6/EVA blends.

2. Experimental

2.1. Materials

Polyamide6 (PA6) was obtained from Gujarat State Fertilizer Corporation, Vadodara, India (GUJLON M28RC, relative viscosity 2.8). Ethylene vinyl acetate (EVA) with vinyl acetate content of 18 wt% and melt flow index of 2 g/10 min (EVA 1802) from National Organic Chemical Industries Ltd, Mumbai, India, was used as the blending polymer. The ionomer (Surlyn 1601) was obtained from DuPont South Asia Ltd, New Delhi, India. This is a copolymer of ethylene and methacrylic acid neutralised by sodium salt. The polymers were dried in a vacuum oven at 80 °C for over 24 h to ensure removal of moisture.

2.2. Blending and preparation of test specimens

The granules were dry-mixed in appropriate ratios and binary and ternary blends of PA6, EVA and ionomer were prepared in a corotating, intermeshing twin screw extruder (ZSK25, $L/D = 46$) with a screw speed of 150 rpm and 230 °C. The details of the blending compositions are given in Table 1. In case of ternary compositions of PA6, EVA and ionomer a two-step mixing sequence was adopted for melt mixing. In the first step, ionomer was melt blended with EVA at 230 °C and subsequently in the second step PA6 was melt mixed with the blend of EVA/ionomer. The extruded strands were quenched immediately after extrusion in a water bath kept at room temperature. The extrudates were then chopped into granules and finally dried at 80 °C for over 24 h before moulding. Test specimens for determining the mechanical properties were prepared by injection moulding at 230 °C and at a screw speed of 80 rpm (Windsor SP-1).

2.3. Characterisation studies

2.3.1. Mechanical properties

Notched izod impact strength was measured on CEAST impact tester (Model Resil 25) following ASTM D-256 test procedures. Impact strength measurements were made at five different temperatures (−25, 0, 23, 40 and 80 °C). The test results reported are the average values of at least five specimens tested in each case and the deviation of the data around the mean value was less than 5%. Tensile properties namely tensile strength, tensile modulus and elongation at break were determined on an Instron Universal Tester (Model 4301) according to ASTM D-638; type 1 procedure at an extension rate of 50 mm/min.

2.3.2. Morphology

Morphological studies were conducted by SEM analysis using a Cambridge Stereoscan Microscope (Model S4-10). For morphological analysis, cryogenically fractured tensile specimens etched by *o*-xylene to remove EVA and impact fractured (at 23 °C) specimens were used. For each blend, different micrographs with a total amount of around 200 particles were made. These micrographs were analysed using an image analyser. Number average diameter (D_n), weight average diameter (D_w) and volume average diameter (D_v) of the domains were determined according to the following relationships:

$$D_n = \sum N_i D_i / \sum N_i \quad (1)$$

$$D_w = \sum N_i D_i^2 / \sum N_i D_i \quad (2)$$

$$D_v = \sum N_i D_i^3 / \sum N_i D_i^2 \quad (3)$$

The interfacial area (A_{3D}) per unit volume of dispersed phase (V_{3D}) was calculated from the total perimeter of the particles (P_{2D}) divided by the total area of the particles (A_{2D}) as obtained from the micrographs:

$$A_i(\mu m^2/\mu m^3) = P_{2D}/A_{2D} = A_{3D}/V_{3D} \quad (4)$$

Table 1
Mechanical properties of PA6/EVA/ionomer blends

Sample code	Composition of PA6/EVA/ionomer (wt%)	Stress at peak (MPa)	Stress at break (MPa)	Strain at break (%)	Tensile modulus (MPa)
N20	80/20/0	39	38	264	820
N20S2	80/19.6/0.4	43	42	350	862
N20S4	80/19.2/0.8	42	40	365	848
N20S6	80/18.8/1.2	42	42	382	830
N20S8	80/18.4/1.6	41	40	325	825

3. Results and discussion

3.1. Impact properties

The addition of EVA copolymer to PA6 increases the notched impact strength of PA6 to a limited extent due to immiscibility/incompatibility of the two polymers [6]. On addition of 20 wt% EVA, the notched impact strength of the PA6/EVA blends increased by a factor of two as compared to pure PA6 at 23 °C. However, impact strength of the blends still remains in the brittle regime [6]. In this study, the variation of notched impact strength of PA6/EVA/ionomer blends as a function of ionomer level as well as at different temperatures has been determined and presented in Figs. 1 and 2. It was found that at 23 °C, the notched impact strength of ionomer modified PA6/EVA blends increased at all levels of the ionomer. The notched impact strength of PA6/EVA/ionomer blends registered about 3.1 fold higher values at 0.4 wt% ionomer level, 3.4 fold higher values at 0.8 wt% ionomer level, 3.3 fold higher values at 1.2 and 1.6 wt% ionomer levels as compared to 80/20 PA6/EVA blend. The increase in impact strength is believed to be due to the emulsifying effect of the ionomer in the PA6/EVA blend system, where ionomer acts as a compatibiliser. The emulsifying effect of the ionomer in PA6/PE and PA6/PP blend systems has been reported in the literature, where it has been shown that the addition of small amounts of ionomer in PA6/PE and PA6/PP system resulted in enhanced interfacial adhesion between the two phases [9]. Thus, in the presence of an ionomer the interfacial adhesion between the phases increases and in turn produces better stress transfer. It is also observed (Fig. 2) that on incorporation of an ionomer, the brittle to tough transition temperature (T_{bt}) of the blend system shifts to 23 °C. Thus, in effect, it can be inferred that the ionomer is acting as a suitable compatibiliser that enhances the impact strength of PA6/EVA blend.

3.2. Tensile properties

Tensile stress–strain curves are shown in Fig. 3. Various tensile properties such as stress at peak, stress at break, tensile modulus and elongation at break determined from these curves are presented in Table 1. It is observed from Fig. 3 that all the blend compositions of PA6/EVA/ionomer show prominent yield point with higher yield stress accompanied by much higher elongation at break as compared to 80/20 PA6/EVA blend composition. The elongation at break increased from 264 to 350% on addition of 0.4% ionomer in PA6/EVA blend system. This suggests that during the tensile experiment the deformation process is facilitated by the ionomer.

It can be seen from Table 1 that the yield strength of PA6/EVA/ionomer system increased at all compositions, showing about 1.2 fold higher at 0.4% ionomer level, and being about equal at 0.8, 1.2 and 1.6 wt% as compared to 80/20 PA6/EVA blend system. The increase in tensile strength may be due to higher interfacial adhesion in the presence of ionomer, thus producing better stress transfer from one phase to other.

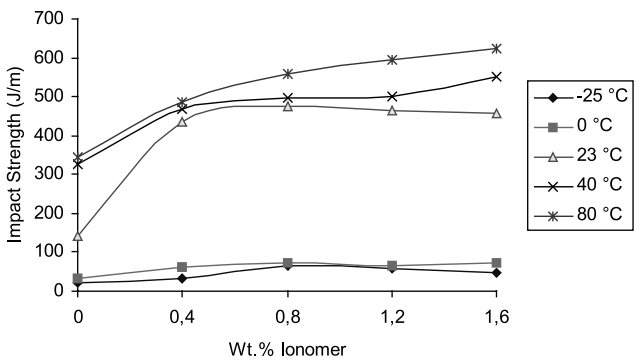

Fig. 1. Plot of notched impact strength versus wt% ionomer at different temperature.

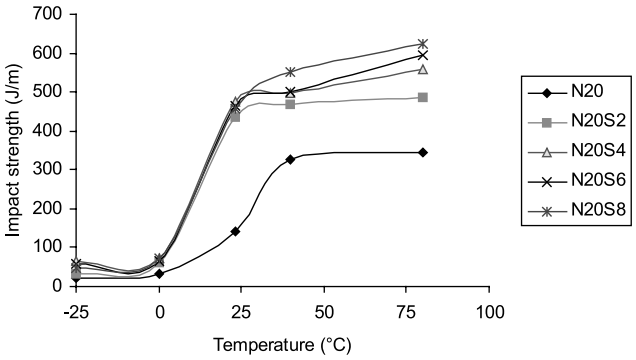

Fig. 2. Plot of notched impact strength versus temperature at different ionomer concentration.

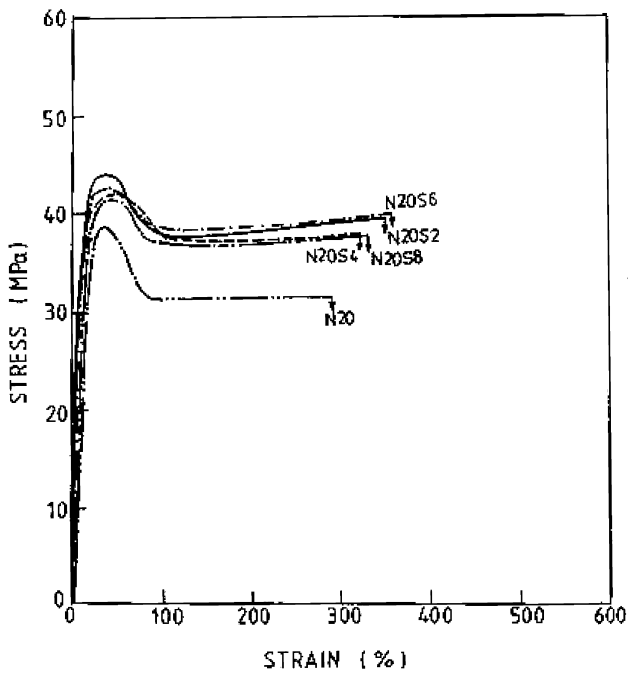

Fig. 3. Stress–strain curves of PA6/EVA/ionomer blends.

Table 2
Values of stress concentration parameters (S, S' and K_b) in PA6/EVA/ionomer blends

Sample[a]	S	S'	K_b
N20	1.01	1.25	0.60
N20S2	1.13	1.39	0.34
N20S4	1.09	1.34	0.44
N20S6	1.10	1.36	0.42
N20S8	1.07	1.33	0.47
Mean	1.08	1.33	0.45

[a] Volume fraction of either EVA or EVA plus ionomer in each sample = 0.233.

3.3. Theoretical analysis of tensile strength (stress at peak)

Predictive models were used to analyse the tensile strength data of polymer blends in order to assess the level of interfacial interaction. Kunori and Geil [14] have used such models to analyse blends of polycarbonate and high density polyethylene as well as the blends of polycarbonate and polystyrene. Other reported studies also used similar models in polymer blends and composites [15–17]. Three models used to analyse the tensile strength results obtained in this study are as follows:

Model 1
Neilsen's first power law model [18]

$$\frac{\sigma_b}{\sigma_p} = (1 - \phi_1)S \tag{5}$$

Model 2
Neilsen's two-third power law model [18]

$$\frac{\sigma_b}{\sigma_p} = (1 - \phi_1^{2/3})S' \tag{6}$$

Model 3
Nicolais and Narkis model [19]

$$\frac{\sigma_b}{\sigma_p} = (1 - K_b\phi_1^{2/3}) \tag{7}$$

where σ_b and σ_p represent the tensile strength of the blend and the PA6, respectively, ϕ_1 is the volume fraction of EVA in the blends, S and S' are the Neilsen's parameter in the first and two-third power law models, respectively. These parameters account for the weakness in the structure brought about by the discontinuity in stress transfer and generation of stress concentration at the interfaces in case of composites and blends. The maximum value of S and S' is unity for no stress concentration effect. K_b in equation 7 is an adhesion parameter; the maximum value of K_b being 1.21 for spherical inclusion of the minor phase having no adhesion [19]. The three models described above have been employed to analyse the tensile strength results in order to evaluate interfacial adhesion, if any, by comparing the experimental values with those predicted by the models. The values of S, S' and K_b are listed in Table 2 giving a comparison between the experimental data and theoretical models. The minor phase of all these compositions were kept at 20% by weight. It is assumed during the analysis that the density of EVA and ionomer are almost the same so that the volume fraction of EVA together with ionomer remains the same as that of pure EVA in the ternary compositions. The analysis was made in comparison with the uncompatibilised 80/20 compositions of PA6/EVA. It was found from the analysis that the experimental values for ionomer compatibilised blends are higher than those predicted from the above models taking into account the values of $S = 1.00$ and 1.08, respectively. The relative tensile strength of all the compositions predicted from model 1 with $S = 1.00$ is found to be 0.76, while the value is found to be 0.82 with $S = 1.08$. The experimental relative tensile strength values of ionomer compatibilised blends are found to be higher as compared to the values predicted from model 1. This shows that all the ionomer compatibilised compositions can take excessive stress since the interfacial adhesion is improved as compared to uncompatibilised blend. Similarly, the experimental relative tensile strength values are found to be higher as compared to the values predicted from model 2 taking into account $S' = 1.00$ and 1.33. This is again in favour of higher interfacial adhesion in ionomer compatibilised blends. Thus, by comparing the values of Neilsen's parameters (S and S') of the two power laws, it is found that the extent of deviation of S value from 1.00 is less than that of S' value. This shows that the first power law establishes its better suitability than the fractional power law model. The analysis also shows an average value of K_b to be 0.45 that is much less than 1.21. Thus, the relative tensile strength values of the ionomer compatibilised blends are higher than the uncompatibilised blend, again representing high level of adhesion.

Table 3
Morphological parameters of cryogenically fractured etched surfaces of PA6/EVA/ionomer blends

Sample code	D_n (μm)	D_w (μm)	D_v (μm)	A_i (μm^2/μm^3)
N20	1.80	2.70	3.81	0.38
N20S2	1.18	1.58	2.02	0.59
N20S4	0.74	0.99	1.20	0.94
N20S6	1.04	1.54	2.12	0.64
N20S8	1.30	1.69	2.13	0.53

3.4. Phase morphology

This section deals with the morphological studies carried out using SEM for the PA6/EVA/ionomer blends in which the level of ionomer was varied from 0 to 1.6 wt% keeping the ratio of PA6 to EVA plus ionomer at 80/20 (Table 3).

The uncompatibilised (80/20) PA6/EVA blend composition was analysed as a control sample. In this context, it is to be mentioned that ionomer was introduced in the PA6/EVA blend system keeping in mind that the ethylene phase of the ionomer would be miscible with the ethylene phase of EVA and the carbonyl group of the ionomer would have some interaction with the amine group of PA6 thus improving interfacial adhesion. The SEM micrographs of the cryogenically fractured etched surfaces of all the blends are presented in Fig. 4. It is observed that these sets of blend can be characterised by particle-dispersed type of morphology in which the minor component is dispersed in the form of spherical domains. The morphological parameters in terms of D_n, D_w, D_v and A_i for the domains are presented in Table 3. The domain size distributions of EVA for all the compositions are presented in Fig. 5. It is evident from Table 3 that the number average domain size of EVA decreases steadily from 1.80 to 0.74 μm with increasing level of ionomer up to 0.8 wt%. With further increase in the level of ionomer the number average domain size of EVA increases but is still lower than that of uncompatibilised 80/20 PA6/EVA blend. It is also evident from Fig. 5 that the EVA domain size distribution is narrower in all the ternary compositions of PA6/EVA/ionomer as compared to PA6/EVA blend. Fig. 5 depicts a significant decrease in the width of the size distribution for the PA6/EVA/ionomer blends; the largest size of the EVA domain varied from 6.1 to 2.2 μm as the ionomer content in the blend varied from 0 to 0.8 wt%. Blends with 0.8 wt% ionomer concentrations show the narrowest size distribution. The reduction of average domain size and the development of narrower domain size distribution may be due to slower rate of

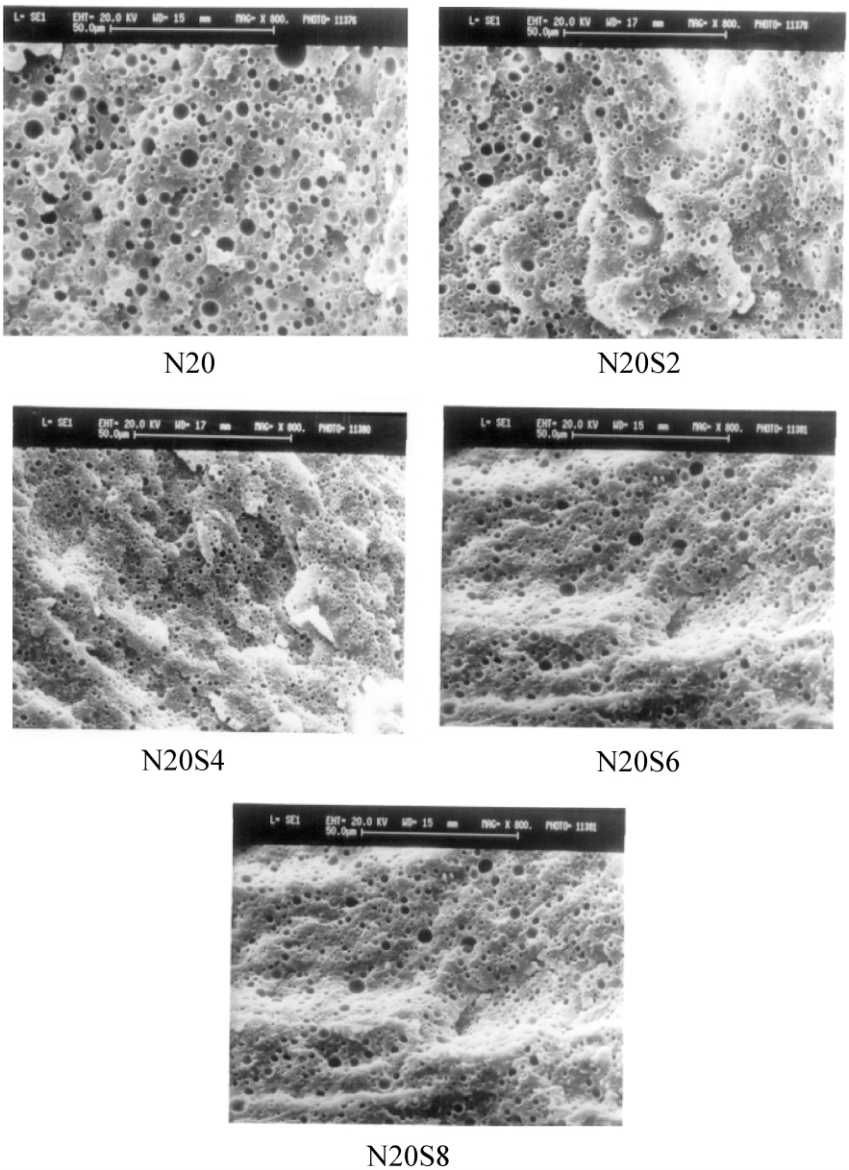

Fig. 4. Scanning electron micrographs of cryogenically fractured etched surfaces of PA6/EVA/ionomer blends: (a) N20, (b) N20S2, (c) N20S4, (d) N20S6, (e) N20S8.

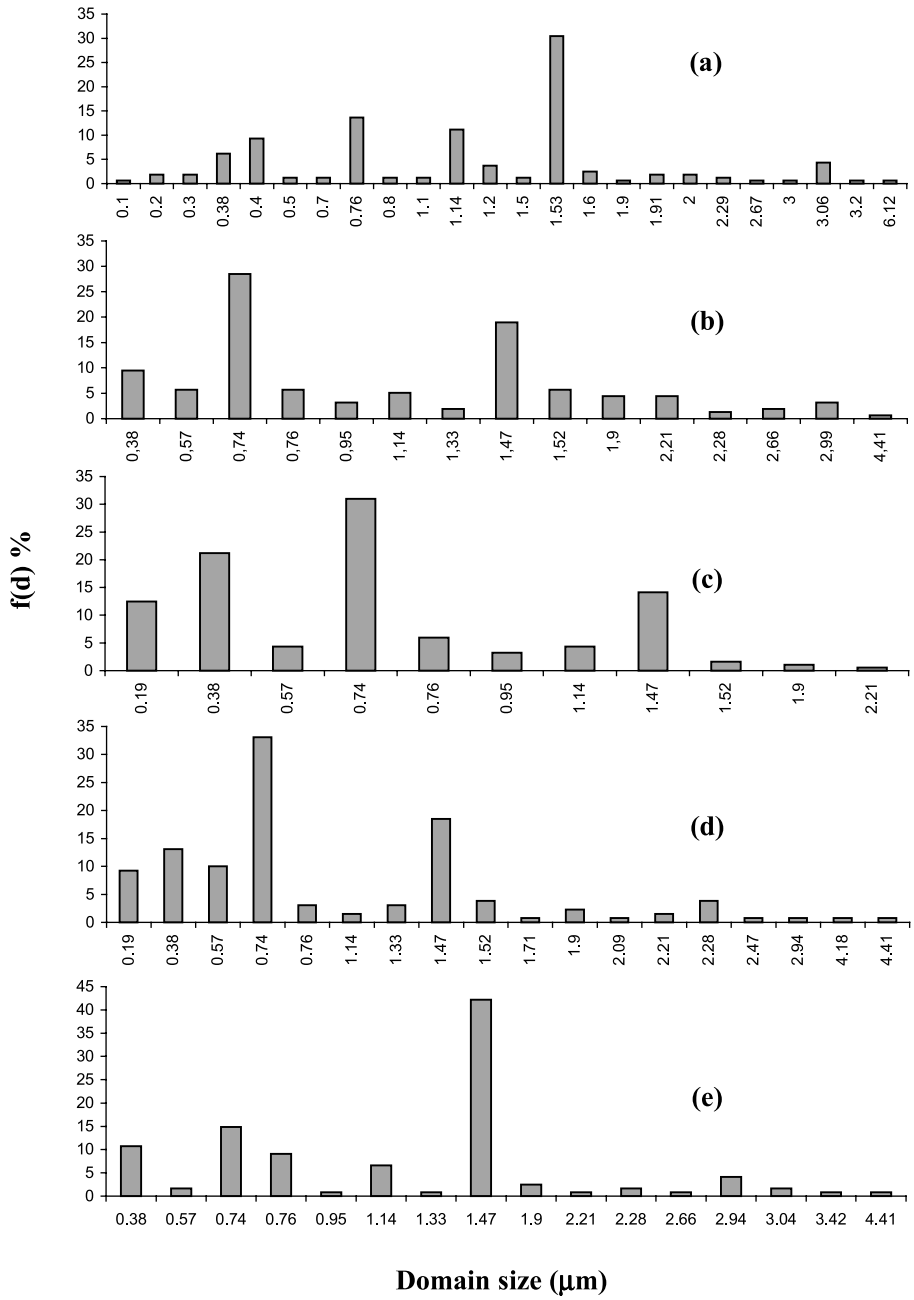

Fig. 5. Domain size distribution of PA6/EVA/ionomer blends: (a) N20, (b) N20S2, (c) N20S4, (d) N20S6, (e) N20S8.

coalescence in the presence of ionomer. In other words, ionomer is expected to act as an emulsifier in PA6/EVA/ionomer blends. Similar kind of observation has also been reported in PE/PA6 and PP/PA6 blends compatibilised with ionomer [8,9]. It is also reported that the values of A_i has been utilised as a measure of interfacial thickness in the multiphase polymer systems [20]. In the ternary blends of PA6/EVA/ionomer, the value of A_i has been found to increase as compared to that of uncompatibilised 80/20 PA6/EVA blend (Table 3). This suggests a diffuse interphase in the presence of the ionomer. In brief, the PA6/EVA/ionomer blends are characterised by smaller EVA domains, narrower domain size distribution with higher interfacial thickness. In contrast uncompatibilised blends show large EVA domains, wider domain size distribution and sharp interface in PA6/EVA blends. Thus, the observed morphological parameters strongly suggest that ionomer is an effective compatibiliser for PA6/EVA blend system.

3.5. Fracture surface morphology

The SEM micrographs of the notched impact fractured surfaces of all the blends are presented in Fig. 6. It is reported that pure PA6 exhibits ductile fracture while PA6/EVA blends show debonding of hemispherical bumps

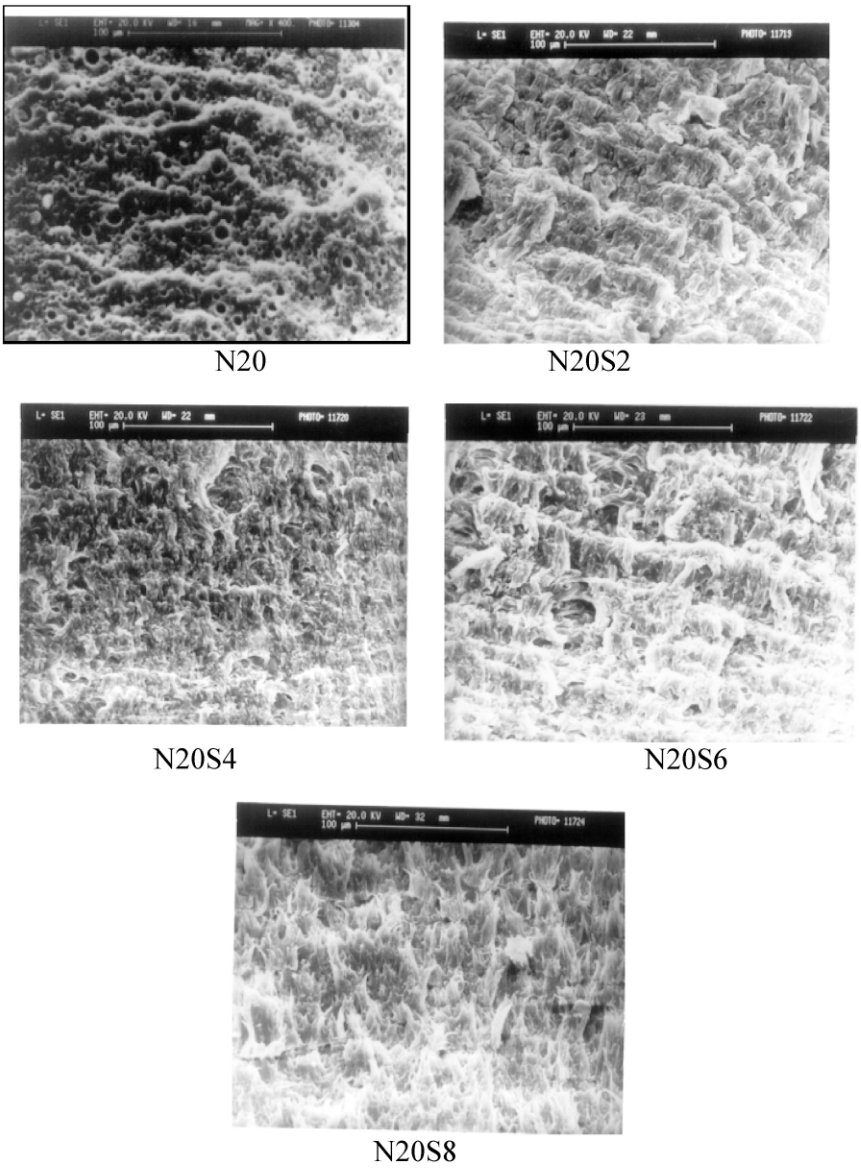

Fig. 6. Scanning electron micrographs of impact fractured PA6/EVA/ionomer blends: (a) N20, (b) N20S2, (c) N20S4, (d) N20S6, (e) N20S8.

indicating little adhesion between PA6 and EVA [6]. The uncompatibilised PA6/EVA blends are characterised by brittle fracture and there is no sign of plastic deformation or cavitation of EVA particles. On impact, only notch tip undergoes stress whitening. On the contrary, all the ternary compositions of PA6/EVA/ionomer blends exhibit extensive deformation leading to the formation of rumples. The entire fracture surface is stress whitened after impact testing. Tufts of drawn material were observed due to high rate of plastic deformation indicating high-energy dissipation mechanism during fracture. This may be due to better interfacial adhesion between PA6 and EVA in presence of ionomer. The fracture surface topology indicates that on addition of ionomer, the interfacial adhesion between PA6 and EVA improved significantly, which again manifests the compatibilising efficiency of ionomer as a compatibiliser in the PA6/EVA blends.

4. Conclusions

The addition of an ionomer to PA6/EVA blend system has been effectively used to modify the morphology and in turn enhance the impact strength. The major conclusions of the present study are as follows:

1. The notched impact strength of the PA6/EVA blends compatibilised by the addition of an ionomer is significantly higher as compared to that of uncompatibilised PA6/EVA blends.
2. The theoretical analysis of tensile properties suggests that there is an increase in the extent of interaction between PA6 and EVA in the presence of ionomer, which is also an indication of better interfacial adhesion between PA6 and EVA.
3. In the presence of ionomer, the rate of coalescence of the

dispersed phase is slower as evidenced by finer and stable dispersion of EVA domains in PA6 matrix.

4. The impact-fractured topology also indicates a process of high-energy dissipation in the presence of ionomer, which is indicative of better interfacial adhesion.

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