

# Interfacial Modification of High Density Polyethylene/Glass Fiber Reinforced and Non Reinforced Polyamide 66 Blends

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**ABSTRACT:** High density polyethylene (HDPE) and polyamide (PA66) are well known to be incompatible. An ionomer (Surlyn) was added as a compatibilizer to HDPE and glass fiber reinforced (HDPE/GFRPA66) and non-reinforced (HDPE/PA66) blends. Two compositions were considered: 25/75 wt % and 75/25 wt %, with an emphasis on the former formulation. The influence of the compatibilizer on the rheology, thermal properties, and the morphology, as well as mechanical properties of the blends, was investigated using melt flow index measurements, DSC, scanning electron microscopy (SEM), and impact strength. The ionomer was found to be more effective as a compatibilizer with HDPE as a minor phase compared to the case when HDPE becomes the major phase. The results indicated that the interfacial properties of the blends were improved, with a maximum appearing at a critical concentration of the ionomer (7.5 vol %). At this level of compatibilization, SEM analysis revealed better interfacial adhesion and a finer dis-

persion. MFI results revealed a probable reaction between the amine groups of PA66 and the acid functions of the ionomer. The mechanical properties support the above results and showed that the addition of 25 wt % HDPE did not affect the properties of PA66 much and the presence of glass fiber did not hinder the effect of the compatibilizer. Only 20% decrease in notched Izod impact strength of the blends is observed at 7.5 vol % ionomer content, suggesting that the addition of 25 wt % of HDPE to PA66 is not detrimental at this level of compatibilization. The emulsification curve was established and revealed that, in terms of impact properties, the finer the particle size, the higher the impact strength corresponding to 7.5 vol % ionomer content. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1748–1760, 2005

**Key words:** emulsification curve; HDPE; interfacial modification; ionomer; PA66; reinforced polymer blends

## INTRODUCTION

Polymer blending and/or alloying has been proved to be an economically viable and versatile way for tailoring new specific materials.<sup>1,2</sup> There are 4500 patents produced annually devoted to polymer blends and alloys, with an annual growth of 9–11% against 2–4% for neat resins.<sup>3</sup>

Due to thermodynamic immiscibility that is generally the rule among the high molecular weight polymer pairs as well as mechanical incompatibility, polymer blends are generally multiphase systems characterized by high interfacial tension and weak phase adhesion, leading to well defined morphologies with coarsely phase separated structures and inferior ultimate mechanical properties.<sup>4</sup>

Methods to reduce interfacial tension and to improve phase adhesion between two immiscible components have been the subject of intensive research

activity. One approach is the use of interfacial agents known as “compatibilizers” that are able to mediate an attractive interaction between the phases and bridge the phases as do surfactants in oil-oil emulsions.<sup>5</sup> Block and graft copolymers have been the customary non reactive compatibilizers, as well as reactive compatibilizers used to compatibilize blends.<sup>6</sup>

The reactive compatibilizer has specific functional groups that can generate *in situ* formation of block or graft copolymers at the interface during the blend preparation through the reaction of functional groups incorporated onto the blend components. This is a one step process as opposed to the conventional two step process, in which a compatibilizer is synthesized first and then added to a blend.<sup>7</sup>

Copolymers that are formed *in situ* during reactive extrusion may reduce the interfacial tension and increase the adhesion between the phases, allowing a finer dispersion and more stable morphology to be created. The morphology and blend properties also depend on parameters such as composition, viscosity ratio, and processing conditions during mixing.<sup>8</sup>

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Polyolefins (PO) and polyamides (PA) are two important classes of polymers. Due to low cost, light weight, low coefficient of friction, high barrier properties to moisture, good optical properties, and ease of processing, high density polyethylene (HDPE) is an ideal material for film and container application. However, its high permeability to solvents and vapors, such as hydrocarbons, limits its potential. Polyamide, on the other hand, is an engineering thermoplastic. It finds its applications in electrical, mechanical, and automotive parts due to its very high strength, wear and heat resistance, ease of fabrication and processing, and excellent barrier properties to oils. Unfortunately, PA is relatively high priced, has poor impact strength, and poor dimension stability, as well as poor barrier properties to moisture, which limit its applicability.<sup>9</sup>

Blends of commodity (polyolefins) and engineering (polyamides) polymers combining properties of both components would be of considerable interest. For example, by blending HDPE and PA, one might be able to combine the thermal and mechanical properties of PA with the insensitivity to moisture that characterizes HDPE to obtain materials with low cost, low moisture absorption, and improved processability, as well as good impact resistance and flexural modulus.<sup>10</sup> However, PA/PO blends are immiscible in the total range of composition. This is mainly due to differences in viscoelastic properties, structure, and morphology between these materials.<sup>11</sup>

PA/PO blends have been reported regularly since 1960, particularly in the patent literature.<sup>12</sup> In rare cases, the two polymers are prepared without the addition of a third component, by different blending methods. More often, the ethylene component is modified chemically or prepared in the form of a copolymer. In other cases, a third component, homopolymer, or copolymer is added to the mixture to act as a compatibilizing agent.<sup>13</sup> Functionalized polyolefin compatibilizers are popular third components that are added to aid both adhesion and mixing in the PA/PO systems. These have been developed by grafting reactive groups, such as maleic-anhydride (MAH)<sup>14,15</sup> and acrylic acid,<sup>16,17</sup> onto the polyolefin backbone through reactive processing.

Most compatibilizing agents used for PA/PO blends were polyethylene-co-methacrylic acid (EMA) copolymer "ionomers," usually containing between 4 and 15 mol % of methacrylic acid units, and usually in the sodium (Na) or zinc (Zn) salt form. These have been shown to be particularly successful and are generally believed to interact with both polyolefin and polyamide, although the nature of these interactions is unknown. MacKnight et al.<sup>18</sup> suggested an amidation reaction between the amine (NH<sub>2</sub>) terminal groups of PA and the acid groups (COOH) of the copolymer, in addition to possible hydrogen bonding between the

two phases, at least when the copolymer is in the acid form.

Binary PA/PO blends have been studied by several groups.<sup>19,20</sup> So far, however, only few articles have dealt with their compatibilization, especially when reinforced with glass fibers. Ide and Hasegawa<sup>21</sup> reported that the use of maleic-anhydride grafted polypropylene (PP-g-MAH) as a compatibilizer improves the physical properties; while Willis and Favis<sup>22</sup> report that a much finer dispersion of the minor phase in the matrix can be achieved by using ionomers as compatibilizers. The influence of interfacial modification through the use of an ionomer in PA/PO blends has been considered extensively.<sup>23,24</sup> However, very few studies<sup>15,17</sup> have considered the reinforced blends of such systems. Our present work is a mere contribution to fill in this gap.

The objective of the present work is to investigate the possibility of improving the compatibility of glass fiber reinforced and unfilled blends of HDPE/PA66 (25/75 and 75/25 wt %) prepared by reactive extrusion using a Surlyn ionomer as a compatibilizer. This has been done in terms of rheological, mechanical, thermal, and morphological properties.

## EXPERIMENTAL

### Materials

High density polyethylene "HDPE" (HD9089 from DSM, The Netherlands) and nylon-66 (TechnylA216 and Technyl A216 V30-from Rhone Poulenc Company, France) are the base resins employed in this study. Technyl A216V30 (GFRPA66) is the same grade as Technyl A216 (PA66) but is 30% glass fiber reinforced and red colored. Because HDPE will be mixed with nylon at high temperature (275°C), it is stabilized with 0.2% heat stabilizer (Irganox1010 from Ciba Geigy Company) to prevent thermal oxidation. The compatibilizer is Surlyn 9020 ionomer from Du Pont de Nemours and Co. Inc., a terpolymer of Mw = 25,000 g/mol consisting of 80% of ethylene and 20% mixture of methacrylic acid partially zinc neutralized (approximately 70%), and isobutyl acrylate.<sup>22</sup>

### Compounding

The first operation consists of mixing HDPE, 0.2% antioxidant, and the ionomer (2.5, 5, 7.5, and 10 vol % based on HDPE) in a Betol single screw extruder (L/D: 24/1) at 80 RPM and a die temperature of 180°C. Then the blends of HDPE/PAV6,6 and HDPE/GFRPA6,6 (25/75 wt %) were prepared in a Haake-Buchler internal mixer. The mixer chamber was always filled to set 50 cm<sup>3</sup> constant volume. Blending conditions were maintained at 275°C and 100 rpm for 8 min (3 min for feeding and 5 min for mixing). Prior

to a typical mixing operation, the sample mixture was dried overnight at 85°C to minimize hydrolytic degradation of nylons during processing.<sup>20</sup>

### Testing

Melt flow index (MFI) of neat components and the blends was measured according to ASTM D-1238-73 on a CEAST melt flow indexer model 6452/005 at 275°C under a load of 1000g.

The thermal behavior of the reactive extrusion blends and the pure components was characterized using a Perkin-Elmer DSC 7 Differential Scanning Calorimeter coupled to a data acquisition station. The investigation was carried out on dried samples (~ 5 mg) at a heating and cooling rate of 10°C/min under nitrogen purge to avoid oxidative degradation, and calibration was accomplished with pure indium ( $T_m = 156.60^\circ\text{C}$ ,  $\Delta H_f = 28.5 \text{ J/g}$ ). To maintain uniform thermal history between samples, all specimens were exposed to the following thermal history: Initially, the temperature of the sample was raised from 30 to 300°C and held at this temperature for 5 min to erase the thermal history experienced during compounding. Then the sample was cooled down to 30°C. Finally, the sample was heated up again from 30 to 300°C. The crystallization and the second melting thermograms from the second scan and third scan were, respectively, recorded, and the results were analyzed in terms of: melting ( $T_m$ ) and crystallization ( $T_c$ ) temperatures, cited as the temperatures at the maxima and minima at the peak of the heating and cooling thermograms, respectively.

For morphological characterization, Scanning Electron Microscopy (SEM) photomicrographs were taken on the fractured surface of specimens from tensile measurements at 5 mm/min cross-head-speed, and the fracture surface was made conductive through the deposition of a layer of gold/palladium alloy in a vacuum chamber using a Polaron SEM coater. Investigation was done using a Hitachi S-570 SEM operating at 10–15 kV. Representative micrographs were taken in the magnification of the order of 3000 for all samples; and in the absence of an image particle analyzer, an average diameter of 100 particles for each sample were hand determined and converted to the corresponding magnification. Using a computer program, data were interpreted using a number average diameter,  $D_N$ , and volume average diameter ( $D_v$ ) defined by<sup>15</sup>:

$$D_N = \frac{\sum n_i d_i}{\sum n_i}$$

$$D_v = \frac{\sum n_i d_i^4}{\sum n_i d_i^3}$$

Notched and unnotched Izod impact strength were determined at room temperature (23°C) according to the procedure described in ASTM D-256 method A. Injection molded specimens had dimensions of 63.5 × 12.7 × 3.17 mm and a notch of type A (i.e., angle = 45°, radius = 2.5 mm). The tests were performed using a Zwick apparatus equipped with a 2.7 Joule pendulum. Prior to testing, samples were dried overnight at 85°C and allowed to equilibrate at 25°C and 50% humidity for at least 48 h.<sup>15</sup>

The impact strength was determined as follows:

$$IS = \frac{\theta}{(W - I)t}$$

where IS is impact strength (J/m<sup>2</sup>), W is width of specimen (m), l is notch depth (m), t is thickness of specimen (m), and  $\theta$  is impact energy (J).

Each data point represents the average value of at least ten determinations carried out on the different components.

## RESULTS AND DISCUSSION

### Rheological properties

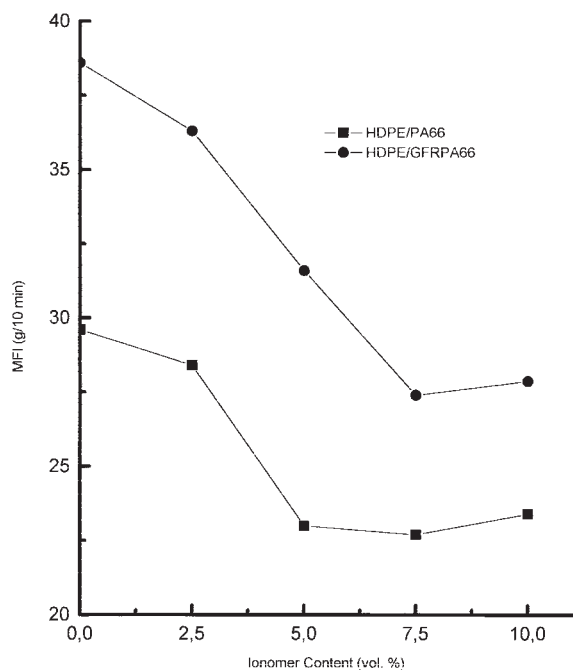
Rheological measurements have been used successfully to obtain qualitative information about chemical reactivity and the extent of reactions in the blends.<sup>25</sup> Chemical reaction between the components of a blend will be reflected in the viscosity. An increase in viscosity in the presence of a compatibilizer may thus indicate that there are strong interactions at the interface.<sup>26</sup>

In the absence of a viscometer, the measurement of Melt Flow Index (MFI) is taken as a mean to evaluate the rheological properties of the studied blends. The MFI results of both unfilled and reinforced (25/75 wt %) blends as a function of ionomer content are depicted in Figure 1.

The MFI is a measure of the fluidity of the molten polymers and, according to the drastic reduction of the viscosity, a maximum is observed for the uncompatibilized blends. Initially, the addition of 25 wt % HDPE to polyamides caused an increase of 16.2% and 39.4% in MFI for unfilled and reinforced blends, respectively. The uncompatibilized blends show higher MFI (lower viscosity) than that of the neat HDPE and polyamides, indicating that the two homopolymers were immiscible with each other in the blend system. This drastic increase in MFI (reduction in viscosity) has been correlated with the presence of slippage between the two immiscible phases as a result of lower interactions and poor adhesion.<sup>27</sup>

### HDPE/PA66 (25/75 wt %) blends

Figure 1 clearly shows that the presence of the ionomer in both blends is able to cause a significant drop



**Figure 1** Effect of ionomer content on MFI of HDPE/polyamides (25/75 wt %).

in MFI values. The observed MFI decreases with an increasing amount of compatibilizer, and the minimum decrease occurs at 7.5 vol % ionomer content. This result can only be attributed to the efficient compatibilizing effect of the ionomer that developed some interactions between HDPE and the polyamides at the interface through the probable amidation reaction of the terminal amine groups of the polyamide and the acid functions of the ionomer, in addition to physical interaction, mainly hydrogen bonding, as was reported by Mac Knight et al.<sup>18</sup> This goes along with the literature that the formation and stabilization of the dispersed phase in immiscible compatibilized blends is the result of a balance of rheological and interfacial forces.<sup>28</sup>

The molecular weight increase (expressed as an MFI decrease in this study) through the grafting reaction between the probable amidation reaction of the terminal amine groups of the polyamide and the acid functions of the ionomer is believed to be the major contribution to the viscosity increase of the blends.<sup>29</sup> The *in situ* formed PA-g-PE copolymer tends to concentrate at the interface and, therefore, raises the interfacial friction under shear stress and causes flow difficulties. The increase of interfacial friction of the compatibilized blends compared to that of the uncompatibilized ones is another reason for the observed higher viscosity (lower MFI in the present study). This increase in viscosities was also observed with an ionomer compatibilizer by Willis et al.<sup>22</sup> and Serpe et al.<sup>30</sup> in binary blends of ethylene-maleic an-

hydride copolymer and polyamide. A similar result was also reported by Marco et al.<sup>31</sup>

Blends containing glass fibers exhibited higher MFI compared to the unreinforced ones (Fig. 1). The presence of glass fibers may have favored a slippage effect while oriented in the flow direction.

The effect of the ionomer on the MFI is similar to that on the unfilled blends. A critical ionomer content appears at 7.5 vol % in both blends, beyond which no further decrease in MFI is observed. This is attributed to a saturation of the interface that corresponds to maximum interaction, as was reported by Rahma et al.<sup>17</sup> and some other authors.<sup>22,23</sup> The fact that the same trend has been observed for both blends suggests that the presence of glass fiber did not hinder the effect of the ionomer.

#### HDPE/PA66 (75/25 wt %) blends

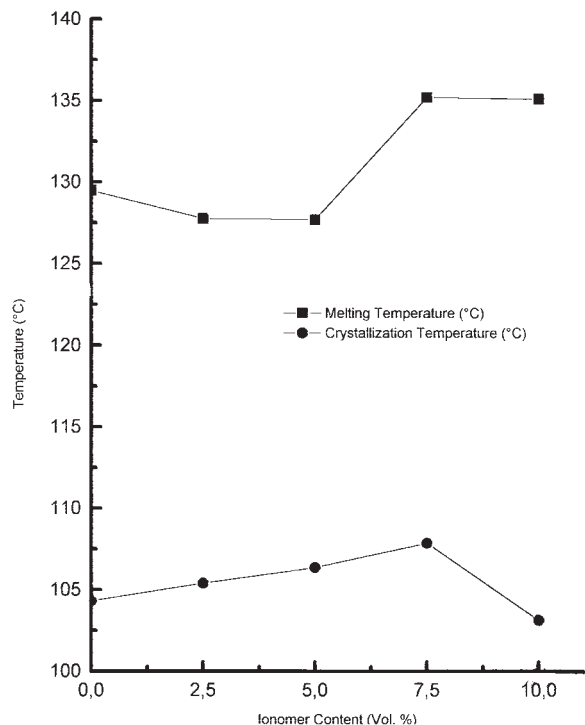
In the situation where the HDPE is the matrix, that is, in blends of HDPE/PA66 (75/25 wt %) the addition of 25 wt % PA66 to HDPE increases the MFI of the blends (Table I). This increase was 29 and 16% for unfilled and reinforced blends, respectively. This indicates poor adhesion between the blend components, which witnesses their immiscibility. When 10 vol % ionomer was added to these blends, a marginal effect on their MFI was observed. In this case, the increase in MFI was only 27 and 14% for unfilled and reinforced blends, respectively. This clearly indicates that the ionomer is not as efficient as in the case where the matrix was PA66. This is probably due to the lower interfacial area available for higher reaction yield, leading to the conclusion that the extent of compatibilization depends on the stoichiometry between the amine groups of polyamides and the acid groups of the ionomer, as reported by Chang et al.<sup>29</sup>

#### Thermal properties

Both HDPE and polyamides are semi crystalline polymers. Their melting and crystallization peaks are still

**TABLE I**  
Melt Flow Index Results for the Starting Materials and the 75/25 vol % HDPE/PA66 Blends

Materials	Melt Flow Index (MFI) (g/10 min)
HDPE	18.60 ± 0.41
Ionomer	2.33 ± 0.70
PA66	24.80 ± 0.63
GFRPA66	15.20 ± 0.56
0% Compatibilizer HDPE/PA66	26.20 ± 0.42
10% Compatibilizer HDPE/PA66	25.61 ± 0.51
0% Compatibilizer HDPE/GFRPA66	22.20 ± 0.77
10% Compatibilizer HDPE/GFRPA66	21.78 ± 0.71



**Figure 2** Melting and crystallization temperatures of HDPE in HDPE/PA66 (25/75 wt %) blends as a function of ionomer content.

visible at their approximately corresponding positions in the uncompatibilized blends, indicating the absence of cocrystallization and, hence, their complete immiscibility.<sup>32</sup>

The melting temperatures ( $T_m$ ) of HDPE, Surlyn, PA66, and GFRPA66 are, respectively, 135.23°C, 94.57°C, 263.98°C, and 264.48°C; and their crystallization temperatures ( $T_c$ ) are 107.87°C, 57.29°C, 230.50°C, and 230.86°C.

#### HDPE/PA66 (25/75 wt %) blends

Thermal properties of the unfilled and reinforced blends are illustrated in Figures 2 through 5.

For both unfilled and reinforced blends, the addition of ionomer shifted modestly the melting ( $T_m$ ) and crystallization ( $T_c$ ) temperatures of HDPE to a relatively higher temperature, and nylons to lower temperatures. Such melting point increase and depression, respectively, is attributed to better interaction and favorable free energy of mixing between blend components.<sup>32</sup>

The increase of  $T_m$  of HDPE suggests either kinetic hindrance of nucleation of the HDPE dispersed phase in the PA66 matrix that might arise from branching with *in situ* formed copolymer PA66-g-HDPE, or the enhanced phase adhesion by reduced interfacial tension for a given content of the compatibilizer. This increase could also be morphological in origin, caused

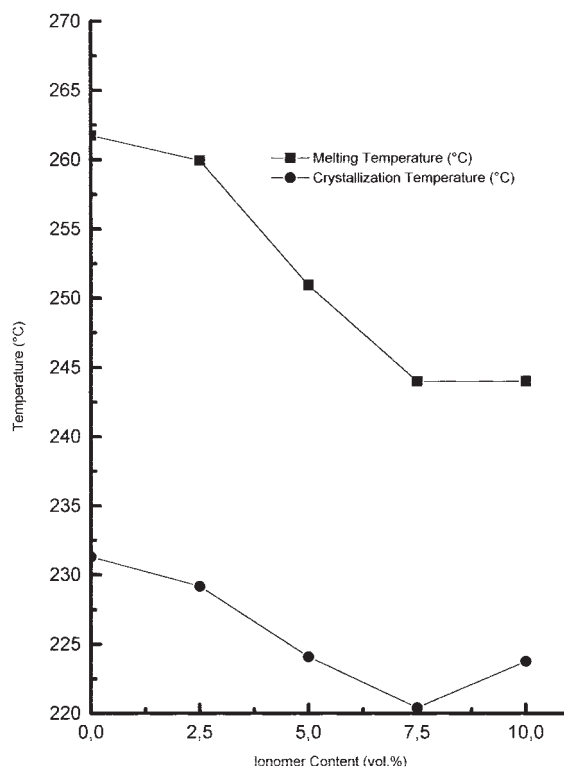
by a corresponding decrease in the lamellar thickness of the crystals having the most probable value in the distribution of lamellar thickness.<sup>26</sup>

The decrease in melt and crystallization temperatures of PA66 is attributed to the chemical reaction between the amine groups of PA66 and the acid functions of the ionomer that has reduced chain mobility for crystallization.

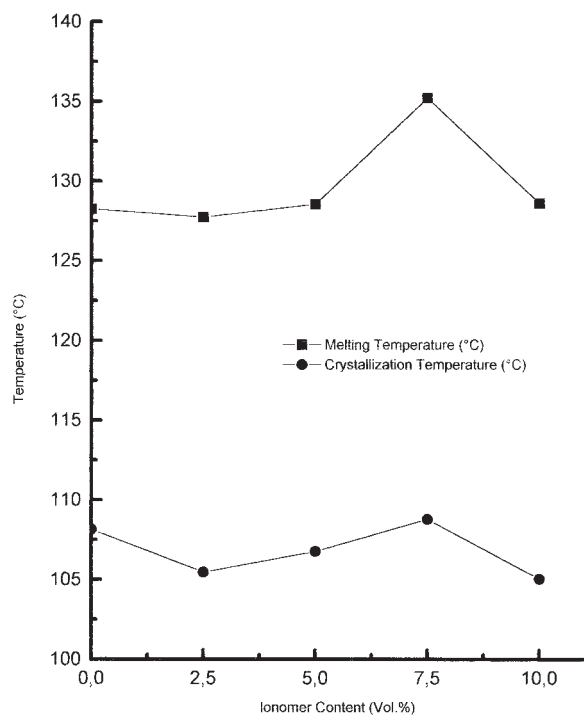
The depression in melt temperatures is more pronounced for PA66 than for HDPE. This clearly demonstrates that the ionomer has better interaction with nylons through the amidation reaction than with HDPE where only dipole-dipole interactions are present. The results of the present study go along with the results of Chalifoux et al.<sup>9</sup> in their study of PE/ionomer and PA6/ionomer.

The plots in Figures 2–5 show the effect of the ionomer on  $T_m$  and  $T_c$  of HDPE and PA66 in the blends. It is clearly observed that these temperatures increase and decrease, respectively, as the ionomer content increases up to 7.5 vol %, beyond which these temperatures stabilize. This confirms the existence of a critical concentration, as was reported in the MFI results.

Beyond this concentration, the compatibilizer locates at the interface<sup>22</sup> (flocculation phenomena); and because of the absence of further interactions, the



**Figure 3** Melting and crystallization temperatures of PA66 in HDPE/PA66 (25/75 wt %) blends as a function of ionomer content.



**Figure 4** Melting and crystallization temperatures of HDPE in HDPE/GFRPA66 (25/75 wt %) blends as a function of ionomer content.

PA66 and HDPE  $T_m$  and  $T_c$  level up. Furthermore, the  $T_m$  data imply that the reactions occurs mainly between the free amine end groups of PA66 and the Surlyn ionomer,<sup>18</sup> and in addition to probable reaction of the amide linkages of nylons because it was noticed that  $T_m$  of nylons in the blends are lower than those of the homopolymers, which could be attributed to a reduction of the lamella thickness of nylons.

## Morphological properties

### Morphological features

In general, the morphology of polymer blends depends on shear history in the mixing device, viscosity ratio, composition, and the interfacial tension between the matrix and the minor phase.<sup>32</sup> In particular, the interfacial tension between two polymers is very important for phase morphology, and the added compatibilizer plays a major role in lowering the interfacial tension and thereby forming a finer morphology.<sup>33,34</sup>

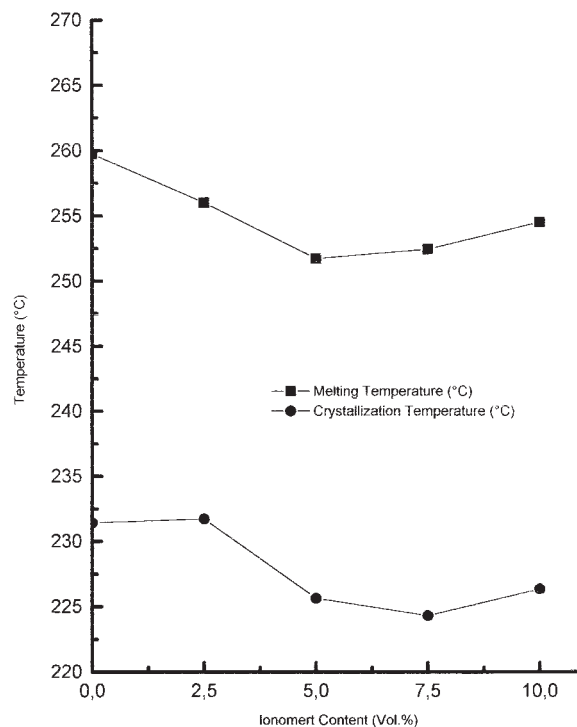
The overall morphology of binary and ternary blends was investigated using tensile fractured surfaces of only HDPE/PA66 (25/75 wt %) blends using scanning electron microscopy (SEM).

In Figures 6 and 7, the morphology of the uncompatibilized blends is displayed. Also shown in the same figures for comparison are the morphologies for the binary blends with different ionomer content. For

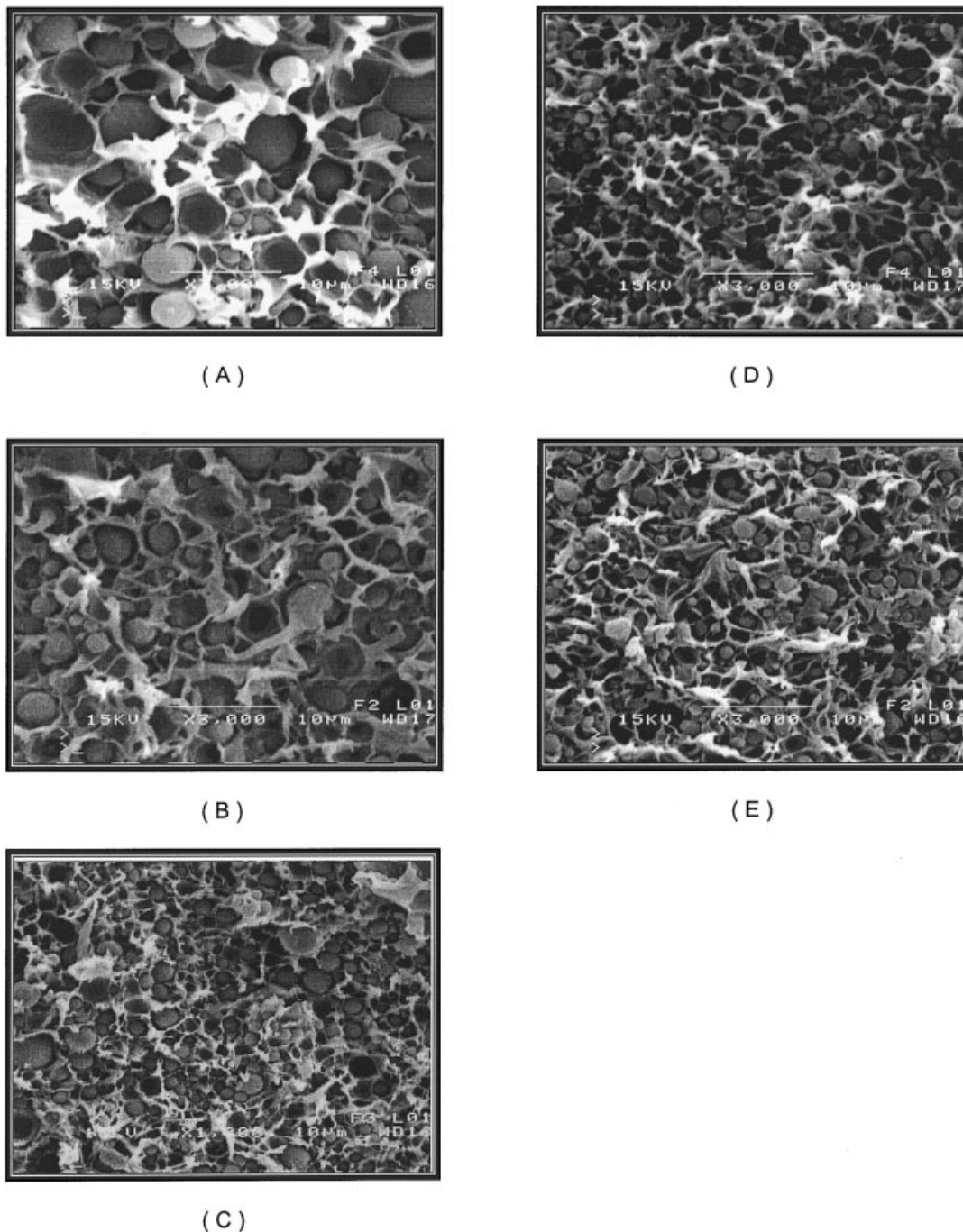
both unfilled and reinforced blends, the observed morphology is apparently a particle-in-matrix structure, where the major phase forms the matrix and the minor phase has been segregated into spherical domains.<sup>5,35</sup> The average HDPE phase size diameter of the uncompatibilized blends was about 3.5  $\mu\text{m}$  and 4  $\mu\text{m}$  for unfilled and reinforced blends, respectively.

SEM micrographs of the uncompatibilized blends [Figs. 6(a) and 7(a)] show a coarse morphology. The droplets formed by the minor phase are spherical in shape, and their size varies in a wide interval (1–10  $\mu\text{m}$ ), reflecting high polydispersity. Even more important, HDPE dispersed particles are practically unaffected by the fracture process. For both blends, a distinct phase separation is clearly observed and no morphological evidence of good interfacial adhesion between the phases can be seen. It is interesting to note that the polyolefin domains have almost completely smooth surfaces with no adhered polyamide,<sup>5,36,37</sup> and during the fracture process many domains have been pulled-out away from their previous positions, which remain as big craters with smooth surfaces. This result reflects the poor adhesion between the phases and suggests that the high surface tension of PA66 relative to HDPE should be the major cause of the delamination at the interface between the phases.<sup>10</sup>

The lack of adhesion and the coarse morphology confirm that PA66 and HDPE are highly incompatible



**Figure 5** Melting and crystallization temperatures of GFRP66 in HDPE/PA66 (25/75 wt %) blends as a function of ionomer content.



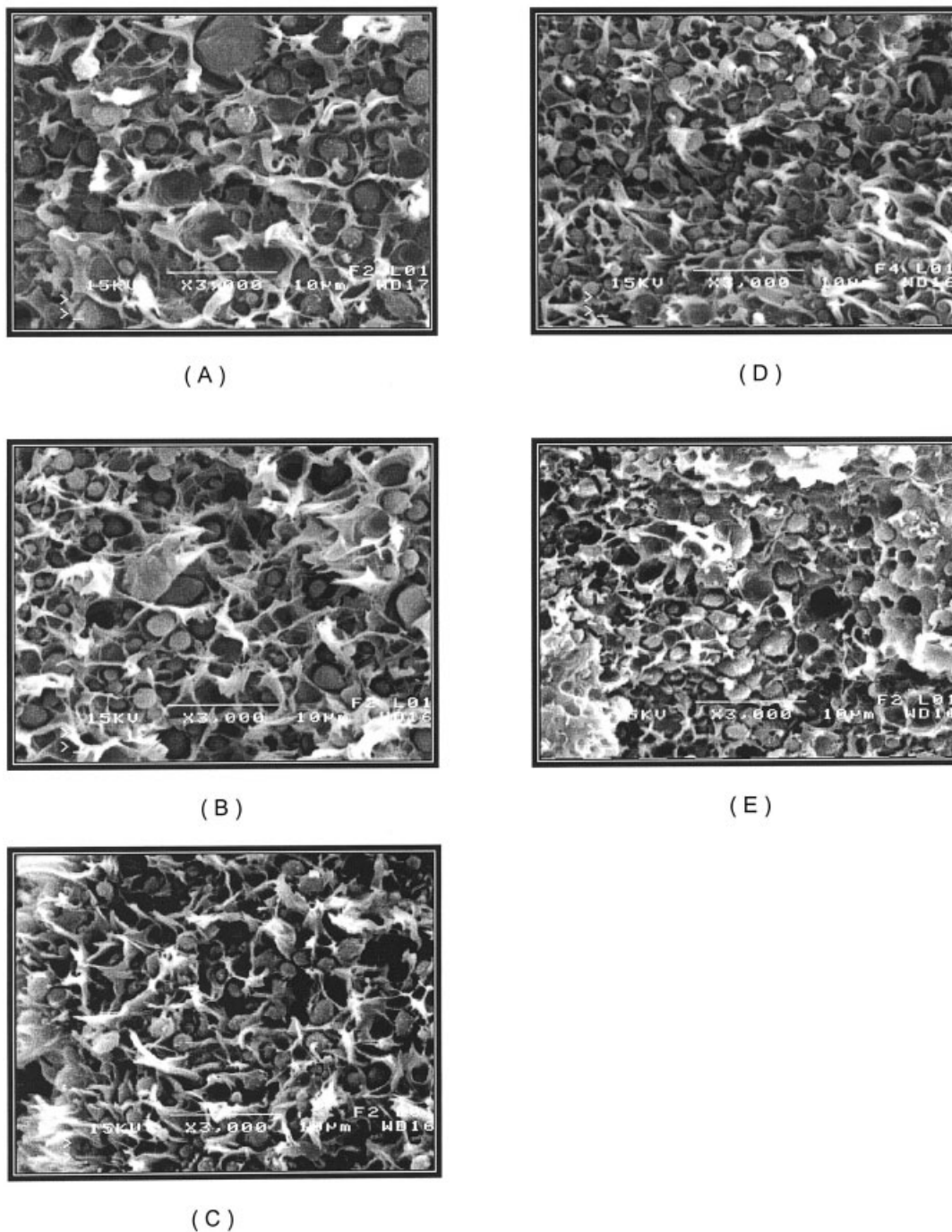
**Figure 6** SEM micrographs of tensile fractured specimens of HDPE/PA66 (25/75 wt %) at 5 mm/min straining rate at different ionomer contents: (A) 0, (B) 2.5, (C) 5, (D) 7.5, and (E) 10 vol %.

and seem to be the primary factors resulting in the weak and brittle behavior of the blends as obtained in the Izod impact results and MFI measurements. This is also consistent with the results from thermal measurements.

Figures 6(b–e) and 7(b–e) depict the SEM micrographs of unfilled and reinforced blends, respectively. The presence of the Surlyn 9020 ionomer made the morphology undergo a considerable change in the

dimensions of the dispersed phase and interfacial adhesion, a result of much reduced incompatibility of PA66/HDPE systems.<sup>22,26,38</sup>

Addition of the ionomer produced a dispersion of fairly uniform HDPE particles with low polydispersity and a smaller particle size (1–2.5  $\mu\text{m}$ ). This suggests the inhibition of coalescence attributed to the positive surfactant effect of the compatibilizer. Worthy of note is that the presence of fibers does not seem to alter the



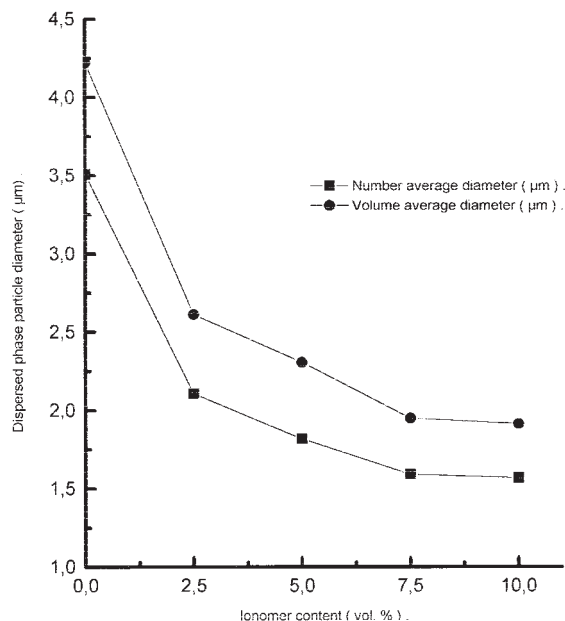
**Figure 7** SEM micrographs of tensile fractured specimens of HDPE/GRFPA66 (25/75 wt %) at 5 mm/min straining rate at different ionomer contents: (A) 0, (B) 2.5, (C) 5, (D) 7.5, and (E) 10 vol %.

morphology of the blends nor their behavior towards compatibilization.

The effect of ionomer content on the particle phase size of unfilled and reinforced blends is illustrated in Figures 8 and 9, respectively. The plot clearly demonstrates that HDPE particle size initially decreased with an increasing amount of compatibilizer. This is well known from emulsion studies, that dispersed particle phase size diminishes when a surfactant is added to

the mixture. This effect is due to the ability of the surfactant to reduce the interfacial tension between the dispersed phase and the matrix.<sup>22</sup> The particle size then reached a constant value of about 1.6  $\mu\text{m}$  for unfilled blends and 2.2  $\mu\text{m}$  for reinforced ones at the 7.5 vol % ionomer concentration that represents a twofold decrease for both blends. When increasing further the compatibilizer content, no effect on phase dimension was observed and the values level-up. This





**Figure 8** Effect of ionomer content on dispersed phase particle diameter in HDPE/P A66 (25/75 wt %) blends.

suggests a saturation of the interface at this ionomer concentration beyond which no emulsifying effect of the compatibilizer is observed. This is consistent with classical oil/water emulsion studies where the dispersed phase size stabilizes as the interface becomes saturated with the emulsifier.<sup>15,39</sup> Such trends have also been observed for other interfacially modified polymer blend systems.<sup>17,23,33</sup>

The observed trend is very similar to the previous melt flow index measurements in terms of the presence of a critical value and the emulsifying effect of the compatibilizer. Hence, the better compatibilized blend has higher viscosity and smaller domain size.

It is clearly observed in Figures 6(b–e) and 7(b–e) that the appearance of the fracture surfaces proves the adhesion between phases. Indeed, HDPE are tightly bound and seem to be much anchored in the polyamide matrix. Another evidence of better interfacial adhesion is the slight number of craters with rough surfaces, in addition to signs of fraying and fibrils unraveling on HDPE particles caused by the fracture. It is interesting to note that the extent of protrusion may also be taken as another measurement of compatibilization, in addition to the size and distribution of these holes.<sup>40</sup>

These results are in agreement with the theoretical predictions showing that the addition of a compatibilizer reduces the interfacial tension, which leads to finer dispersion and more stable structure.<sup>41,42</sup>

Conclusively, better dispersion and improved interfacial adhesion should be attributed to the compatibilizing effect of *in situ* formed PA66-g-HDPE through the amidation reaction and hydrogen bonding, as was

discussed in the MFI results and as was reported elsewhere.<sup>18</sup>

#### Emulsification curve

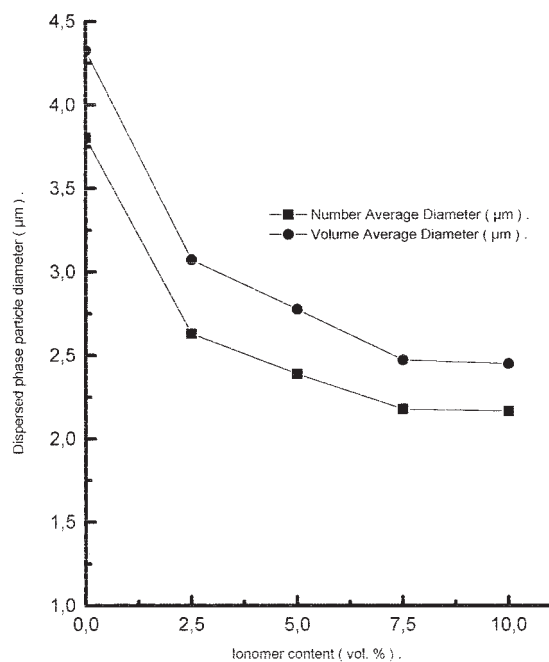
The emulsification effect of the ionomer has been studied by determining the reduction in the dimension of the dispersed phase as a function of the quantity of ionomer added to the blends. In the absence of an image analyzer, the evaluation of phase size of the blends was hand performed. An average of 100 measurements of the diameters were made for each sample.

The number average  $D_N$  and the volume average  $D_V$  diameters were measured for the blends using several SEM micrographs for each concentration of the compatibilizer using the following equations:<sup>15,43</sup>

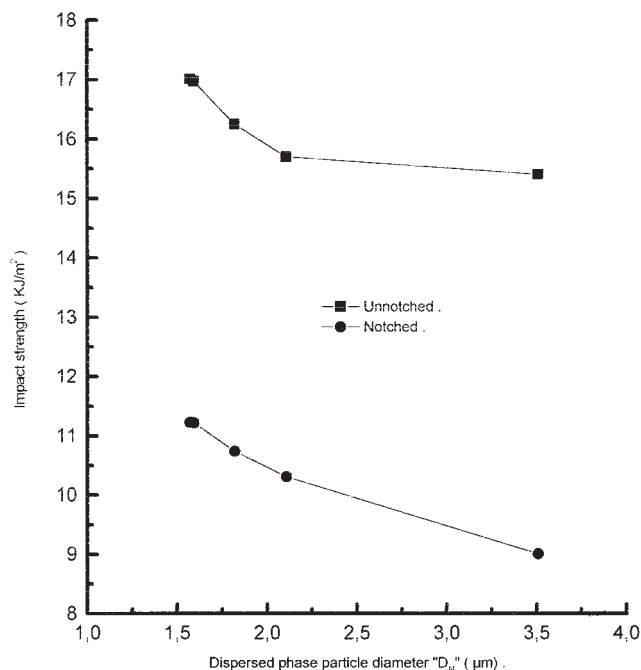
$$D_N = \frac{\sum n_i d_i}{\sum n_i}$$

$$D_V = \frac{\sum n_i d_i^4}{\sum n_i d_i^3}$$

Figures 8 and 9 illustrate the emulsification curve of unfilled and reinforced blends of HDPE/PA66 (25/75 wt %). They show the dependence of  $D_N$  and  $D_V$  upon the ionomer content for the blends. It appears that approximately 7.5 vol % ionomer based on the minor phase size is sufficient to produce minimum reduction of the dispersed phase size. No further decrease in



**Figure 9** Effect of ionomer content on dispersed phase particle diameter in HDPE/GFRPA66 (25/75 wt %) blends.



**Figure 10** Impact strength as a function of dispersed phase size diameter in HDPE/PA66 (25/75 wt %) blends.

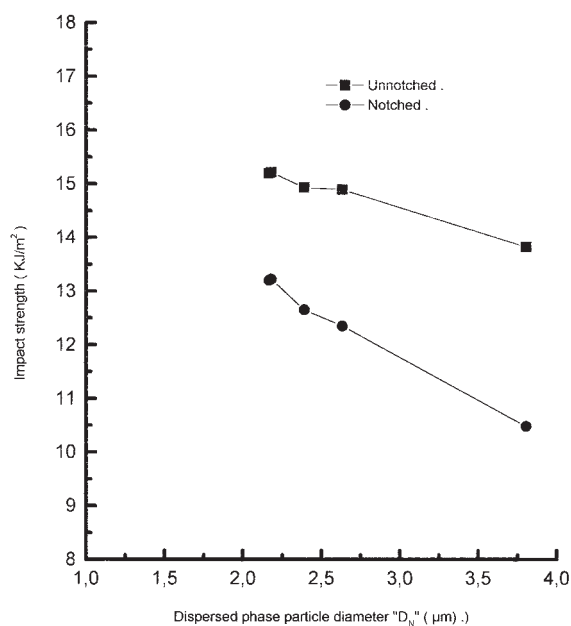
phase size is achieved by adding more ionomer, as seen from the plateau region of the plot shown in Figures 8 and 9. The existence of such a plateau region has been reported by Lee et al.<sup>44</sup> and was attributed to the saturation of the interface with the compatibilizer, corresponding hence to the maximum interactions. Willis et al.<sup>38</sup> observed the same behavior for blends of PA6/PP and PA6/PE compatibilized by Surlyn 9020. Lee et al.<sup>44</sup> reported a similar trend for ionomer compatibilized PA6/PS blends. These observations clearly indicate that the reduction of the mobility of the interface facilitates the breakdown of the dispersed phase to a smaller size and stabilizes the dispersed phase towards subsequent coalescence.<sup>22</sup>

The average size of the dispersed domain of uncompatibilized blends was  $3.5 \mu\text{m}$  and  $3.8 \mu\text{m}$  for unfilled and reinforced blends, respectively, and the distribution of domain sizes was broad. However; a narrower distribution in particle phase size was attained for both blends after addition of 7.5 vol % ionomer. The phase size was  $1.6 \mu\text{m}$  and  $2.2 \mu\text{m}$  for unfilled and reinforced blends, respectively. That represents nearly a twofold decrease for both blends. This can be explained by the fact that the size of the dispersed phase is proportional to the interfacial tension as well as a coalescence reduction.<sup>45</sup> Many researchers<sup>46,47</sup> have reported that the interfacial tension in reactive blends decreases as observed upon addition of a block copolymer to homopolymer blends.

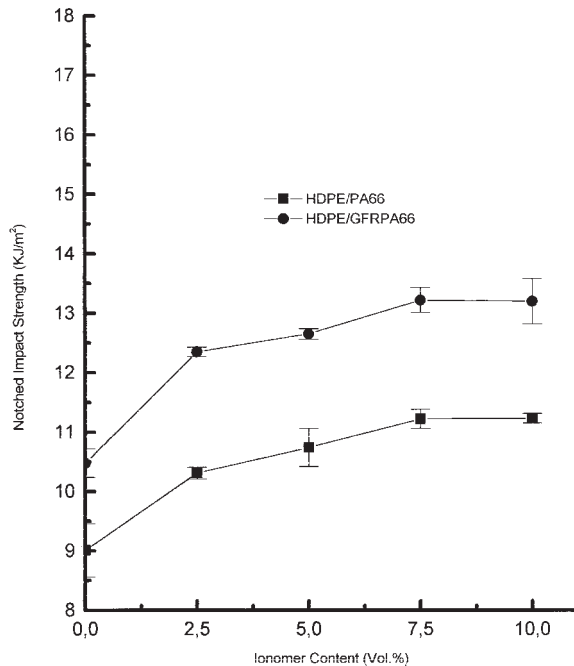
However, the breadth of the domain size distribution cannot be explained by the reduction of interfacial

tension, especially in the uncompatibilized system. It means that coalescence effects may be a more important factor in determining the final blend morphology in the melt blending, as already reported by many researchers.<sup>22</sup> In the case of the uncompatibilized system, very small domains may result from the break up process in the high shear regions, while increased coalescence due to more domain interaction will result in very large domains.<sup>44</sup> However, in the case of the reactive compatibilizer system, that is, the blends with ionomer in this study, the coalescence process is prevented because the *in situ* formed graft copolymer at the interface may form an interphase that must be overcome for coalescence to occur.<sup>48</sup> As a result, with increasing ionomer content in the blends, the breadth of the domain size distribution becomes narrower.

It is generally known that morphological features would affect the mechanical properties of the blends.<sup>49,50</sup> Figures 10 and 11 illustrate the effect of the dispersed phase particle diameter ( $D_N$ ) on both notched and unnotched Izod impact strength for HDPE/PA66 and HDPE/GFRPA66 blends, respectively. As can be seen, the decrease in particle size corresponds to an increase of impact strength. Uncompatibilized blends have coarse morphology  $3.5 \mu\text{m}$  and  $3.8 \mu\text{m}$  and lower unnotched impact strength  $15.4 \text{ KJ/m}^2$  and  $13.82 \text{ KJ/m}^2$ , respectively, for unfilled and reinforced blends. As can be seen from the plots (Figs. 10 and 11), the decrease in particle size with increasing ionomer content resulted in an increase in impact strength. A brittle to tough transition is observed at 7.5 vol % ionomer, for which the unnotched impact strength and phase size of unfilled and reinforced



**Figure 11** Impact strength as a function of dispersed phase size diameter in HDPE/GFRPA66 (25/75 wt %) blends.



**Figure 12** Notched Izod impact strength of HDPE/PA66 (25/75 wt %) and HDPE/GFRPA66 (25/75 wt %) blends as a function of ionomer content.

systems are successively 16.97 KJ/m<sup>2</sup> and 15.01 KJ/m<sup>2</sup>, 1.6  $\mu$ m and 2.2  $\mu$ m. The same brittle to tough transition was reported by Fellahi et al.<sup>15,17</sup>

One can conclude that the morphology features are related with the increase in the Izod impact strength when the ionomer is added. In addition, the fact that the same trend and the same critical ionomer concentration of 7.5 vol % was observed for both blends clearly suggests that glass fibers did not hinder the effect of the compatibilizer.

### Impact properties

The notched and unnotched Izod impact strength (IS) values of the homopolymers and the studied blends were determined at room temperature on predried samples. In unnotched samples, the measured energy to break represents the total energy necessary for crack initiation and propagation. For notched samples, it only represents the resistance to crack propagation.

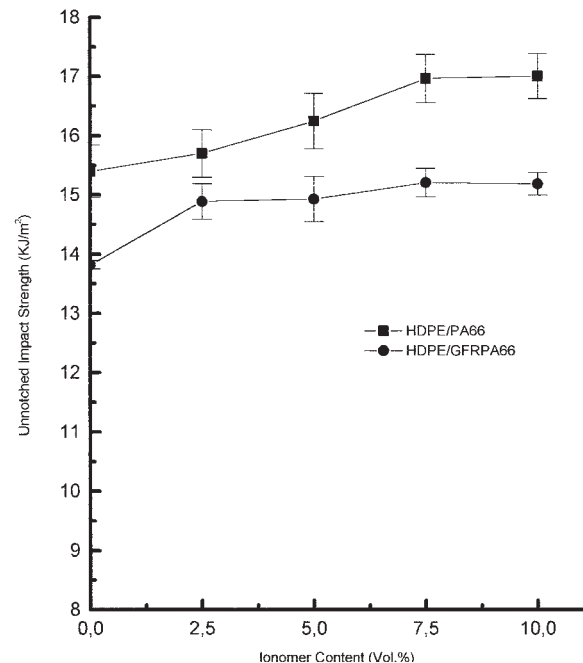
Unnotched samples of both HDPE and PA66 did not break; however, when notched, they have an impact strength (IS) of 14.23 KJ/m<sup>2</sup> and 13.80 KJ/m<sup>2</sup>, respectively. This means that they resist better to crack initiation but modestly to crack propagation. The 30% GFRPA66 has higher (18%) notched impact strength of 16.95 KJ/m<sup>2</sup> as compared to neat PA66, but even unnotched it breaks at 44.72 KJ/m<sup>2</sup>. Hence, the presence of glass fiber in PA66 makes it less notch sensitive but induces brittleness to the material. This highlights

the better contribution of the glass fibers in the fracture mechanism in the notched materials.

### HDPE/PA66 (25/75 wt %) blends

Figures 12 and 13 illustrate the effect of the ionomer on notched and unnotched impact strength (IS) of both unfilled and reinforced nylon rich blends, respectively. The results show that the notched IS of glass fiber reinforced blends is higher than those of unfilled ones. This is attributed to the orientation of the glass fibers in the flow direction transverse to the impact one, evidencing thus their contribution in enhancing the toughness of the materials. In contrast, the unnotched IS results of unfilled blends are higher than those of glass fiber reinforced blends. This is because the former tend to break, showing a tough fracture, whereas the second break, showing a brittle fracture.

It is worthy of note that addition of only 2.5 vol % ionomer caused a change in IS values of both blends. The IS of the blends increased rapidly, then moderately, as the ionomer content increased. Better improvement was detected at 7.5 vol % ionomer, beyond which further addition of compatibilizer is useless. At this concentration the interface is probably saturated, corresponding to the maximum chemical and physical interactions. As opposed to the uncompatibilized blends, the decrease in IS of both blends at the critical concentration of 7.5 vol % was only 19% for unfilled blends and 22% for reinforced ones as compared to



**Figure 13** Unnotched Izod impact strength of HDPE/PA66 (25/75 wt %) and HDPE/GFRPA66 (25/75 wt %) blends as a function of ionomer content.

PA66 and GFRPA66. This clearly indicates that the Surlyn 9020 ionomer does function quite well as a compatibilizer for toughening HDPE/PA66 blends provided that its content is at least 7.5 vol % based on the dispersed phase. This enhancement in IS properties is attributed to better adhesion between the phases and the finer dispersion of HDPE particles, as was observed through the morphological study of the blends. These are attributed to the chemical compatibilization of PA66 and HDPE through the amidation reaction (between free terminal amine groups of nylons and the acid groups of the ionomer) and the efficient emulsifying effect imparted by the ionomer. Such a reaction has been reported by Macknight et al.<sup>18</sup> in the case of PA/ionomer and HDPE/ionomer/PA blends. Rahma et al.<sup>17</sup> reported that 5–7.5 wt % PP-g-AA appeared to be the optimum content to realize a threefold increase in IS of PP/GFRPA6 (30/70 wt %) blends.

It is to be mentioned that the IS values of neat nylons were not reached due probably to a low extent of reaction because the ionomer is 70% zinc neutralized and the desired particle size and distribution were not yet attained at 7.5 vol % ionomer for better toughness.

The IS of the blends are somewhat comparable to the constituent polymers, proving that addition of HDPE to both nylons was not very detrimental at the compatibilizing level of 7.5 vol % ionomer.

Addition of 10 vol % ionomer did not much affect the IS of the blends and the values seem to level up. These results parallel those of MFI and thermal properties in that the interface is already saturated at 7.5 vol % ionomer, corresponding to maximum interactions.

In addition, it is clearly observed that the compatibilizer reduced the notch sensitivity of the blends. The notch sensitivity, calculated as the ratio  $IS_{\text{Notched}}/IS_{\text{Unnotched}}$ , was 42 and 24% for unfilled and reinforced uncompatibilized blends, respectively; and at 7.5 vol % ionomer, the respective values were 34 and 12%. This is mainly due to the soft nature of the compatibilizer.<sup>20</sup>

#### HDPE/PA66 (75/25 wt %) blends

In the case of HDPE rich blends, the addition of nylons to HDPE caused a detrimental decrease of its notched IS and induced some brittleness, since the unnotched specimens did break (Table II). The decrease of impact strength for the uncompatibilized blends was 61 and 53% for unfilled and reinforced blends, respectively. These results demonstrate the incompatibility of these blends.

In an attempt to increase the adhesion between the blends, 10 vol % ionomer compatibilizer was added. As a result, a marginal improvement in impact

**TABLE II**  
Notched and Unnotched Impact Strength of HDPE, PA66, GFRPA66, and the 75/25 vol % Blends

Materials	Unnotched Izod impact strength (IS) (KJ/m <sup>2</sup> )	Notched Izod impact strength (IS) (KJ/m <sup>2</sup> )
HDPE	NB*	14.23 ± 0.97
PA66	NB*	13.80 ± 0.63
GFRPA66	44.72 ± 0.87	16.95 ± 0.93
0% Compatibilizer HDPE/PA66	10.01 ± 0.22	5.56 ± 0.23
10% Compatibilizer HDPE/PA66	11.47 ± 0.51	6.12 ± 0.77
0% Compatibilizer HDPE/GFRPA66	12.73 ± 0.26	6.66 ± 0.13
10% Compatibilizer HDPE/GFRPA66	15.08 ± 0.51	7.18 ± 0.30

\* NB: no break.

strength for both blends was observed. The decrease in notched IS was 57 and 50% for unfilled and reinforced blends, respectively. These results show clearly that the ionomer was not as efficient as in the case where the continuous phase was polyamide. The same observations were reported previously,<sup>18,22</sup> and the lower efficiency was attributed to the lower affinity of the ionomer to polyamide, and hence its difficulty to migrate totally to the interface to strengthen it. In addition, the interface in this case would be less strong due to the difference in the coefficient of expansion between PA66 and HDPE. On cooling, the nylon will freeze first because of its higher melting point ( $T_m = 264^\circ\text{C}$ ) compared to that of HDPE ( $T_m = 135^\circ\text{C}$ ), creating thus some voids at the interface that could be another factor for the lower efficiency of the ionomer.

In the light of these results, one may presume that appropriate compatibility at the interface of the blends was necessary for initiating a particular type of fracture mechanism and for improving impact resistance. The results also prove that adhesion with the matrix, by the use of reactive compatibilizer, is not an essential condition for fracture toughness improvements. The nature of the compatibilizer and the size of the dispersed phase are also relevant parameters. Finally, one may conclude that a good compatibilizer in a binary blend does not generally warrant the improvement of its mechanical toughness.

## CONCLUSIONS

HDPE and PA66 form a two-phase blend with poor adhesion. The addition of an ionomer improved the adhesion between the components and consequently enhanced the mechanical properties. For HDPE/PA66 and HDPE/GFRPA66 (25/75 wt %), 7.5 vol % ionomer was found to be a critical concentration beyond which no further emulsifying effect is observed. The ionomer

caused a decrease of the MFI, suggesting that it affected the specific interactions between the polymers through the amidation reaction between the amine groups of PA and the acid groups of the ionomer, and possible hydrogen bonding. SEM analysis revealed a fine dispersion and better adhesion and proved the compatibilizing effect of the ionomer.

The mechanical properties supported the above results and showed that the addition of 25 wt % HDPE did not much affect the properties of PA66 and the presence of glass fiber did not hinder the effect of the compatibilizer. Only 20% decrease in notched Izod impact strength of the blends is observed at 7.5 vol % ionomer content, suggesting that the addition of 25 wt % of HDPE to PA66 is not detrimental at the level of compatibilization. The emulsification curve was established and revealed that, in terms of impact properties, the finer the particle size the higher the impact strength corresponding to 7.5 vol % ionomer content.

## References

- Misra, A.; Swaney, G.; Kumar, R. A. *J Appl Polym Sci* 1993, 50, 1179.
- Rosch, J. *Polym Eng Sci* 1995, 35, 1917.
- Utracki, L. A. *Polymer Alloys and Blends, Thermodynamics and Rheology*; Hanser: Munich, 1989.
- Vocke, C.; Atila, U.; Seppala, J. *J Appl Polym Sci* 1999, 72, 1443.
- Kim, D.; Park, J. H.; Kim, J.; Ahn, J.; Kim, H.; Lee, D. S. *Polymer* 1996, 20, 611.
- Tan, N. C. B.; Tai, S. K.; Briber, R.M. *Polymer* 1996, 37, 3509.
- Kim, J. K.; Lee, H. *Polymer* 1996, 37, 305.
- Brydson, J. A. *Plastics Materials*; Butterworth Scientific: London, 1982.
- Favis, B. D.; Chalifoux, J. P. *Polym Eng Sci* 1987, 27, 1591.
- Fairley, G.; Prud'homme, R. E. *Polym Eng Sci* 1987, 27, 1495.
- Kamal, M. R.; Jinnah, I. A.; Utracki, L. A. *Polym Eng Sci* 1984, 24, 1337.
- Favis, B. D.; Lavalée, C.; Derdouri, A. *J Mater Sci* 1992, 27, 4211.
- Hudec, I.; Sain, M. M.; Sunova, V. *J Appl Polym Sci* 1993, 49, 425.
- Lu, M.; Keskula, H.; Paul, D. R. *Polym Eng Sci* 1994, 34, 33.
- Abacha, N.; Fellahi, S. *Macromol Symp* 2002, 178, 131.
- Dagli, S. S.; Kamdar, K. M.; Xanthos, M. *SPE ANTEC Preprints* 1993, 18.
- Rahma, F.; Fellahi, S. *Polym Int* 2000, 49, 519.
- Macknight, W. J.; Lenz, R. W.; Musto, P. V.; Somani, R. J. *Polym Eng Sci* 1985, 25, 1124.
- Liang, Z.; Williams, H. L. *J Appl Polym Sci* 1992, 44, 699.
- Fellahi, S.; Favis, B. D.; Fisa, B. *J Mater Sci* 1995, 30, 5522.
- Ide, F.; Hasegawa, H. *J Appl Polym Sci* 1974, 18, 963.
- Willis, J. M.; Favis, B. D. *Polym Eng Sci* 1988, 28, 1416.
- Willis, J. M.; Favis, B. D.; Lavalée, C. J. *J Mater Sci* 1992, 27, 1749.
- Fellahi, S.; Fisa, B.; Favis, B. D. *SPE ANTEC Preprints* 1994, 637.
- Oshinski, A. J.; Keskula, H.; Paul, D. R. *Polymer* 1992, 33, 268.
- Holsti-Miettinen, R. M.; Seppala, J. V. *Polym Eng Sci* 1994, 34, 395.
- Zhang, X. M.; Hin, J. H. *Polym Eng Sci* 1997, 37, 197.
- Padwa, A. R. *Polyblends-91, 11th NRCC/IMI Symposium, Montreal, 1991*; p 18.
- Maa, C. T.; Chang, F. C. *J Appl Polym Sci* 1993, 49, 913.
- Serpe, G.; Jarin, J.; Dawans, F. *Polym Eng Sci* 1990, 30, 523.
- Marco, C.; Ellis, G.; Gomez, M. A.; Fatou, J. G.; Arribas, J. M.; Campoy, I.; Fontecha, A. *J Appl Polym Sci* 1997, 65, 2665.
- Favis, B. D. *Can J Chem Eng* 1991, 69, 619.
- Yang, M.; Li, Z.; Feng, J. *Polym Eng Sci* 1998, 36, 879.
- Lee, J. D.; Yang, S. *Polym Eng Sci* 1995, 35, 1821.
- Majumdar, M.; Keskula, H.; Paul, D. R. *J Appl Polym Sci* 1994, 54, 339.
- Armat, R.; Moet, A. *Polymer* 1993, 34, 977.
- Ning, P.; Ko, T. M. *Polym Eng Sci* 1997, 37, 1226.
- Willis, J. M.; Favis, B. D. *Polym Eng Sci* 1990, 30, 1073.
- Willis, J. M.; Caldas, V.; Favis, B. D. *J Mater Sci* 1991, 26, 4742.
- Wu, C. J.; Kuo, J. F.; Chen, C. Y. *Polym Eng Sci* 1993, 33, 1329.
- Jafari, S. H.; Gupta, A. K. *J Appl Polym Sci* 1999, 71, 1153.
- De Roover, B.; Devaux, J.; Legras, R. *J Mater Sci* 1997, 15, 1313.
- Lomellini, P.; Matas, M.; Favis, B. D. *Polymer* 1996, 37, 5689.
- Lee, B.; Park, J.; Song, H. *Adv Polym Tech* 1994, 13, 75.
- Wu, S. *Polym Eng Sci* 1987, 27, 335.
- Dagli, S. S.; Xanthos, M.; Biesenberger, J. A. *Polym Eng Sci* 1994, 3, 1720.
- Majumdar, B.; Keskula, H.; Paul, D. R. *Polymer* 1994, 35, 3164.
- Sundaraj, U.; Macosko, C. W. *Macromolecules* 1995, 28, 2647.
- Mekhilef, N.; Kadi, A. A.; Ajji, A. *Polym Eng Sci* 1992, 32, 894.
- Fellahi, S.; Favis, B. D.; Fisa, B. *Polymer* 1996, 37, 13.