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Effect of elastomer on polypropylene/nylon-12 blends

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Various compositions of polypropylene (PP)/nylon-12 blends with elastomer were prepared. Morphologies and mechanical properties of the blends were studied. In particular, the effect of ethylene–propylene (EP) elastomer and maleic anhydride-grafted ethylene–propylene elastomer (Ma–g–EP) on the PP/nylon-12 blends were investigated. The results showed that PP/nylon-12 blends have inferior mechanical properties because of their poor compatibility and dispersion. The EP elastomer has a limited effect on the blends since the mechanical properties of PP/nylon-12 blends were controlled by their interface. The Ma–g–EP elastomer improved the mechanical properties of PP/nylon-12 blends through improvement of the interface between PP and nylon-12, and compatibility between the elastomer and nylon-12. Differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were used to characterize microstructures. The dispersion of components and the compatibility between PP and nylon-12 were significantly improved with addition of the Ma–g–EP elastomer.

1. Introduction

Polypropylene (PP) blends with polyamides (nylons) are attractive engineering polymer blends for commercial applications especially after maleic anhydride-grafted polymers were used as compatibilizers [1–7]. For different commercial purposes, PP/nylon blends can be divided into two groups. One is high PP content blends, in which the PP content is higher than 70 wt%. In these blends nylon acts as an organic reinforcement to increase tensile properties, such as yield strength. The other is high nylon content blends, in which the nylon content is higher than 70 wt%. In the high nylon content blends, PP is used to decrease cost and increase water resistance.

PP/nylon blends are immiscible and incompatible blends because their interfacial adhesion is weak, which results in poor dispersion of components and inferior mechanical properties. In this particular blend, PP is a hydrophobic nonpolar polymer, while nylon-12 is a hydrophilic polar polymer. Due to this dual characteristic, proper blending of them requires not only optimization of the composition and processing conditions but also suitable compatibilizers to improve their interface. Maleic anhydride grafted polypropylene (Ma–g–PP) has been widely used as compatibilizer. The compatibilization is considered to occur through chemical linkage of the anhydride on the compatibilizer chain and the nylon end group, forming amide and imide linkages [8]. Previous work has confirmed the formation of the graft copolymer through reaction of the anhydride with the nylon end group using solvent extraction [8, 9]. Similarly, maleated copolymer (PP–Ma–g–PEO) [7] and acrylic acid-functionalized PP [10] can also be used as a compatibilizer for PP/nylon blends.

Recently, compatibilized PP/nylon-12 blends using maleic anhydride grafted PP have been reported [6, 7]. Varlet *et al.* [6], using X-ray diffraction techniques characterized an orientation of the crystalline phase which occurs in the samples as a result of the injection-moulding process. Tang *et al.* [7] studied the compatibilization of the blends. Blends of PP with nylon-12 have some specific characteristics, such as nylon-12 has similar melting temperature as PP and lower moisture absorption than nylon-6 and nylon-6,6.

In this work, the effects of elastomers on the morphologies and mechanical properties on PP/nylon-12 blends were studied. In particular, the relationship between microstructure and toughness was investigated. In previous work, there are numerous reports about EP elastomers which have been successfully used to improve toughness for both PP and nylons. The mechanisms of EP elastomer toughened PP and nylons have also been well investigated and it is believed they are similar in that excessive stress overlap created by the EP particles induces numerous crazes and shear yielding in the matrix thus toughening the materials [12, 13]. Due to the morphologies of phase separation, the mechanical properties of PP/nylon blends are controlled by their compatibility. A study of the effect of an elastomer on PP/nylon blends has scientific and commercial interest. In this paper, the relationship between morphologies and mechanical properties of various PP/nylon-12 blends and the effect of an elastomer on the blends will be described. In

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TABLE I Main characteristics of polymer materials

Materials	Trade name	Source	T_m	T_c	Modification
PP	LYM-120	ICI	162.73	112.59	
Nylon-12		BASF (Australia)	177.07	152.05	
EP	PE-805	Exxon			
Ma–g–EP	Exxlon-808	Exxon			1.14 wt% maleic

particular, the effect of maleic anhydride grafted ethylene–propylene elastomers (Ma–g–EP) on the PP/nylon-12 blends will be discussed.

2. Experimental procedure

2.1. Materials and specimen preparation

All the materials used in this study are commercially available. Table I lists the main characteristics of the polymers. The DSC melting and crystallization temperatures were measured at 10 °C min^{-1} heating and cooling rates. Both maleic anhydride modified EP elastomer and nylon-12 were dried at 70 °C for 16 h before compounding. EP-805 and Exxlon-808 are similar base polymers. All the materials were used from the same batch with clear identification.

Various components were mixed then extruded with a Haake twin screw extruder (diameter 42 cm, diameter:length = 1:7) operated at 200 °C with 60 rpm. The test specimens were moulded using a Johns-600 injection moulding machine with mould temperature of 40 °C.

2.2. Testing of mechanical properties

2.2.1. Testing of tensile properties

The specimens were injection-moulded according to ASTM method D638 (width of narrow section = 10 mm, thickness = 2 mm, gauge length = 85 mm). Tensile tests were performed in accordance with this method on a Lloyd 200 apparatus using a crosshead speed of 50 mm min^{-1}. The tests were carried out at 20 ± 2 °C. All data were recorded and processed through a computer with Lloyd Instruments software (Ver. 2.01).

2.2.2. Testing of impact strength

The specimens were injection-moulded as a 2 mm thick round plate with a 58 mm diameter. High-rate fracture tests were performed using a computer controlled impact tester (ITR-200), which enabled a force versus time curve to be recorded during the test. The data could then be processed in order to obtain other parameters, such as the fracture energy, the displacement and the velocity, as a function of time. Fig. 1 shows a schematic representation of force versus time for a typical ductile specimen. Typical brittle specimens only show part of the curve before peak point. Each parameter in the figure was calculated by a computer with ITR-200C software. All test bars were left at room temperature for 48 h before the mechanical testing was performed.

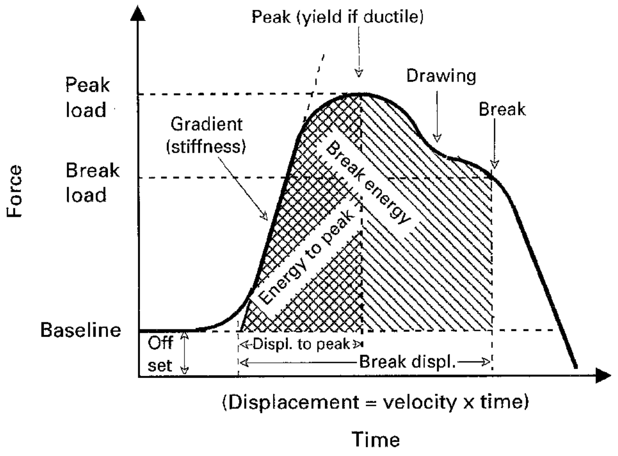

Figure 1 Schematic representation of a typical force versus time curve for a ductile sample.

2.3. Morphological characteristics

Morphologies of PP/nylon-12 blends were examined under a Nikon polarizing microscope (Labophot-2) equipped with a Mettler hot-stage (FP-90). The experimental procedure consisted of the preparation of 20 μm thick films of the blends using a microtome. Each film was heated from room temperature to 200 °C and held at that temperature for 2 min to destroy residual nucleus and then cooled at a rate of 10 °C min^{-1}. Visible observations were made using a magnification of 200×.

Undeformed fracture surfaces were obtained through breaking specimens perpendicularly to the injection-moulding direction after immersion of the specimens in liquid nitrogen for 20 min. The fracture surfaces were examined using a Jeol JSM-840A SEM after coating with gold-palladium alloy. In order to avoid distortion of the surface the coating was applied for 10 s, then paused for 10 s, then the coating was repeated to a total of 100 s.

A Perkin-Elmer DSC7 apparatus was used to study the thermal behaviour and microstructure. Measurements were made on approximately the same sample mass which was cut from impact specimen bars with about 30 μm thickness. Melting temperature, T_m, and crystallization temperature, T_c, were obtained by heating and cooling samples at 10 °C min^{-1}.

3. Results and discussion

3.1. Morphologies

Anisotropy of phase morphology and gradients in the morphology throughout the 4 mm thick specimen were observed. The morphologies reported here were for specimens taken from the centre of cross-sections

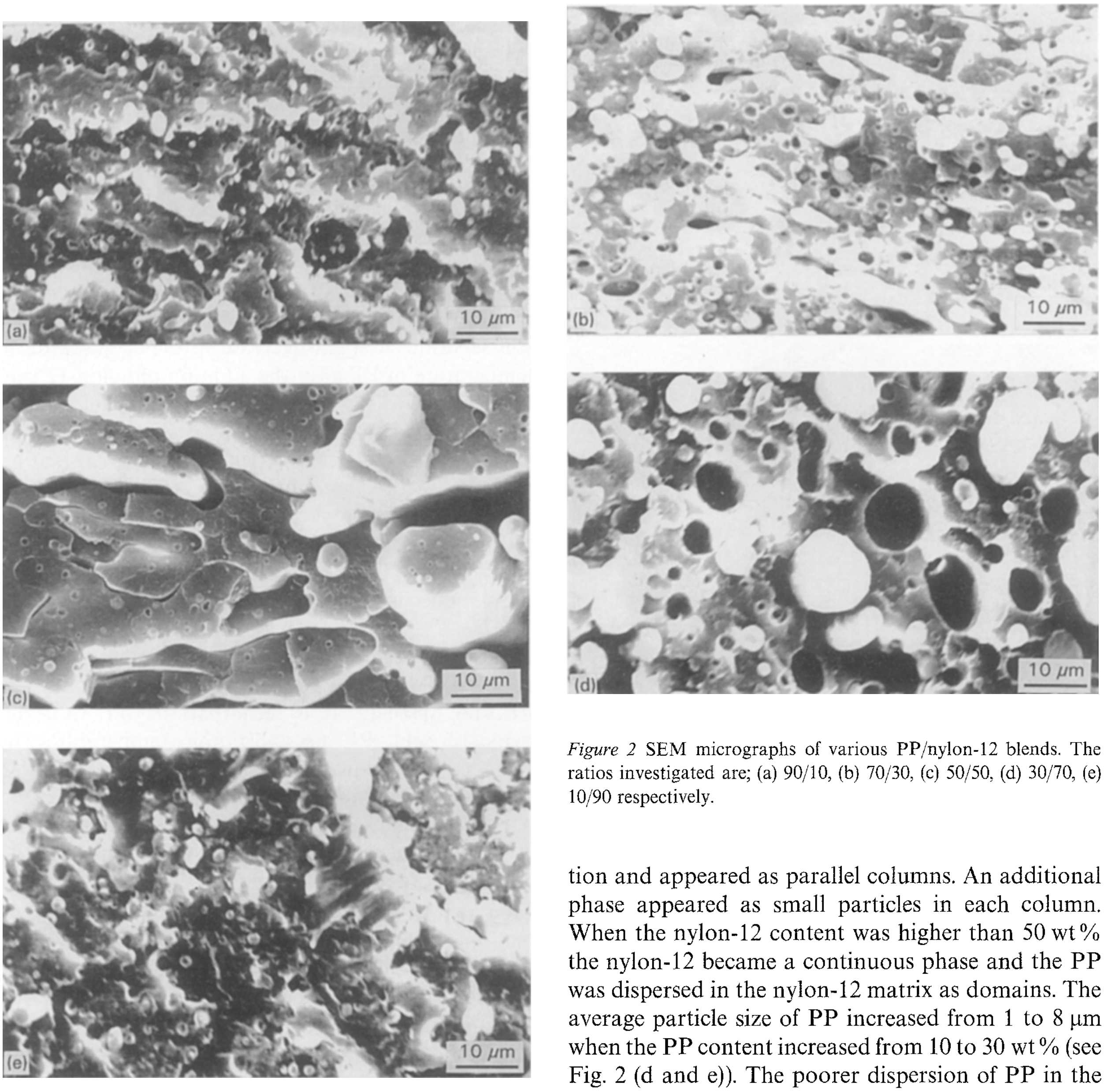

Figure 2 SEM micrographs of various PP/nylon-12 blends. The ratios investigated are; (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, (e) 10/90 respectively.

perpendicular to the mould-filling direction. Polypropylene and polyamide-12 can be distinguished using polarized optical microscopy. Continuous phase and dispersed phase polymer were confirmed by polarized optical microscopy.

PP/nylon-12 binary blends showed poor interfacial adhesion and dispersion of the components. Morphologies of PP/nylon-12 blends depended on their composition. When the nylon-12 content was lower than 30 wt%, PP was a continuous phase and nylon-12 appeared as domains in the PP matrix (see Fig. 2 (a and b). The average particle size of nylon-12 increased from 1 to 4 μm when the content of nylon-12 increased from 10 to 30 wt%. Some large particles, 10 μm, can be observed in the PP/nylon-12 70/30 blend (see Fig. 2b). Poor interfacial adhesion was evident from the large voids left on the fracture surface when particles separated from the matrix and also from the smooth surfaces of the exposed nylon-12 particles. A phase transformation occurred when the nylon-12 content was increased to 50 wt% (see Fig. 2c). In the PP/nylon-12 50/50 blend, both PP and nylon-12 were highly elongated in the injection direction and appeared as parallel columns. An additional phase appeared as small particles in each column. When the nylon-12 content was higher than 50 wt% the nylon-12 became a continuous phase and the PP was dispersed in the nylon-12 matrix as domains. The average particle size of PP increased from 1 to 8 μm when the PP content increased from 10 to 30 wt% (see Fig. 2 (d and e)). The poorer dispersion of PP in the nylon-12 compared to the nylon-12 dispersion in PP can probably be explained by the higher viscosity of PP in melting state. The large particle size, combined with no evidence of adhesion between PP and nylon-12, confirmed that the two components were incompatible.

Fig. 3 shows the morphology after the addition of 20 wt% of elastomer in the PP/nylon 50/50 blend. It is seen that EP elastomer did not affect the morphology of the blend significantly. Both PP and nylon-12 still appeared as parallel columns in the injection direction. Large voids are left on the fracture surface where the columns separate from each other and also smooth surfaces of the exposed columns are observed. The only difference in the morphology from the PP/nylon 50/50 binary blend (see Fig. 2c) is that particles (about 2 μm in size) appeared in both PP and the nylon-12 matrix, which are believed to be EP elastomer. Although PP and EP are compatible, the poor interfaces between nylon-12/EP and nylon-12/PP were not expected to change the compatibility of the PP/nylon-12 blends significantly.

Fig. 3b shows the morphology after the addition of the maleic anhydride grafted ethylene–propylene elastomers (Ma–g–EP) to the PP/nylon 50/50 blend. It can be seen that the morphology changed significantly

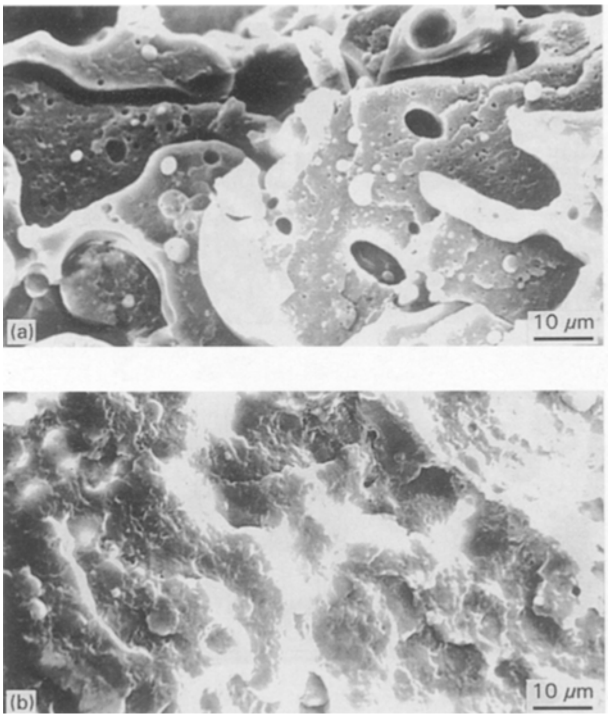

Figure 3 SEM micrographs of addition of (a) EP and (b) Ma–g–EP to PP/nylon-12 50/50 blend.

due to the Ma–g–EP acting as a compatibilizer. In the compatibilized blends, the two separated phases disappeared. Ma–g–EP appeared between PP and nylon-12. Although Ma–g–EP and nylon-12 are immiscible their compatibility has been improved through the formation of a Ma–g–EP/nylon copolymer by the reaction of anhydride groups with the terminal amine groups of nylon-12 during melt mixing.

A DSC study supported the improvement of compatibility through the addition of the Ma–g–EP elastomer to the PP/nylon-12 blends. Fig. 4 shows the DSC curves of PP and nylon-12 crystallization. It can be seen that there are two separate crystallization peaks for PP and nylon-12 in all of the blends, which confirms that the PP/nylon-12 blends were immiscible. The addition of different components affects the crystallization temperature of the PP and nylon-12 but the crystallization peaks of PP and nylon-12 are still separate. A slight decrease in the crystallization temperature of PP after the addition of nylon-12 can be explained by the migration of nuclei during mixing [14, 15]. The interfacial free energy of such potential nucleus in nonpolar PP is clearly higher than that in polar nylon-12. The interfacial energy difference between the nucleus and the melt on the components of the blends derived as the potential nucleus crossed the interface to nylon-12. A detailed study of crystallization kinetics will be discussed in a separate paper.

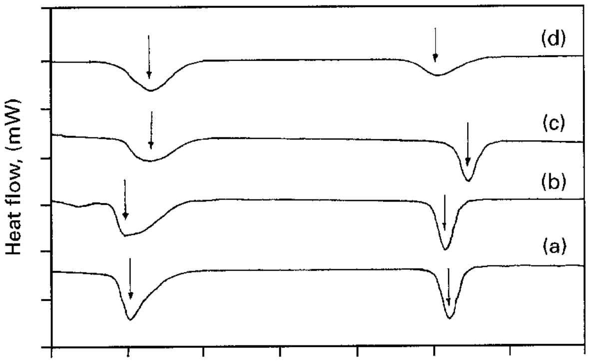

Figure 4 Effect of additional components on the crystallization of PP and nylon-12. The plots are for (a) PP/nylon-12 50/50, (b) (PP/nylon) with EP, (c) (PP/nylon) with $CaCO_3$ and (d) (PP/nylon) with Ma–g–EP.

TABLE II Effects of additional components on the crystallization of PP and nylon-12

Materials	$T_{\text{nylon-12}}$	T_{PP}	ΔT
PP/nylon-12 50/50	152.10	110.37	41.73
(PP/nylon-12 50/50) 80/20 EP	151.64	110.02	41.62
(PP/nylon-12 50/50) 80/20 EX	150.71	113.29	37.42
(PP/nylon-12 50/50) 90/10 $CaCO_3$	154.89	113.74	41.66

$\Delta T = T_{\text{nylon-12}} - T_{\text{PP}}$ was used to evaluate the miscibility of the blends. Table II gives the effect of the addition of extra components on the crystallization of PP and nylon-12. It is seen that the ΔT value of nylon-12 and PP crystallization temperatures is 41.73 °C. The addition of EP slightly decreased the crystallization temperature of both nylon-12 and PP, but did not affect the ΔT value. The slight change in crystallization can be explained by a reduction of nuclei. In order to prove this hypothesis 10 wt% of $CaCO_3$ was added to PP/nylon-12 blends as a nucleating agent. It was found that $CaCO_3$ only changed the crystallization temperatures but not ΔT, which is a similar behaviour to that observed on the addition of EP. When Ma–g–EP was added to PP/nylon blends the situation was different in that the crystallization temperature of nylon-12 decreased whilst that of the PP increased resulting in a decrease in ΔT to 37.42 °C. The compatibility of PP and nylon-12 was clearly improved, which was confirmed with SEM observations.

3.2. Mechanical properties of various composites of PP/Nylon-12 blends

Fig. 5 shows the mechanical properties of various composites of PP/nylon-12 blends. It is seen that the yield stress of nylon-12 is higher than that of PP. The yield stress of PP/nylon-12 blends is between PP and nylon-12. When the PP content is higher than 50% the yields stress of the blends did not change significantly. For high PP contents, the PP was a continuous phase (see Fig. 2 (a and b)). Small particles of nylon-12 were expected to increase the tensile properties of PP because nylon-12 can act as a reinforcement. However poor interfacial adhesion between PP and nylon-12 resulted in nylon-12 particles behaving as voids and thereby reducing the effective cross-section. Physical adhesion must have provided some degree of stress transfer to the nylon-12 particles. The rest of the results showed that the yield stress of PP did not

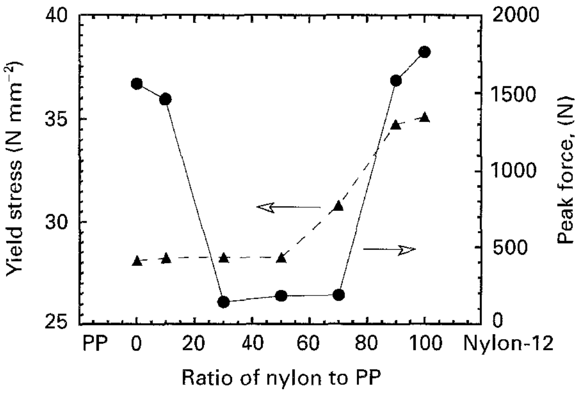

Figure 5 Mechanical properties of PP/nylon-12 blends in various component ratios.

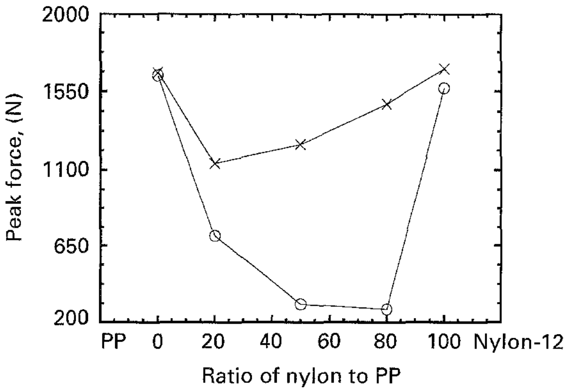

Figure 7 Effect of (○) EP and (×) Ma–g–EP elastomer on peak force of PP/nylon-12 blends.

change significantly. When the nylon-12 content was high the tensile strength of the blends decreased through the addition of low modulus and incompatible PP, especially when the PP particles were very large (see Fig. 2d).

The peak force in Fig. 1 was used to represent the toughness of the materials. The peak force of nylon-12 was higher than that of PP. The toughness of the blends was lower than the average value of the blends. This was especially noticeable in the range of high content of additional components where the peak force was much lower than any of the pure materials. The results can be explained by the poor dispersion of components and weak interfacial adhesion between PP and nylon-12. A morphology study has shown that when the nylon-12 content increased from 10 to 30 wt% the particle size of nylon-12 in PP increased from 1 to 4 μm (see Fig. 2 (a and b)). Similarly, when the PP content increased from 10 to 30 wt% the particle size of PP in nylon-12 increased from 1 to 8 μm (see Fig. 2 (d and e)).

3.3. Effect of elastomer on mechanical properties

Fig. 6 shows the effect of the elastomer on the tensile properties. As was expected the addition of the elastomer decreased the yield stress and modulus of all the PP/nylon-12 blends. The shape of the curves are similar and the tensile properties of the blends are between those of PP and nylon-12. It was noticed that the yield stress of the PP/nylon-12/Ma–g–EP blends in the range of high nylon-12 content was improved which indicated that compatibility between PP and nylon-12 was improved.

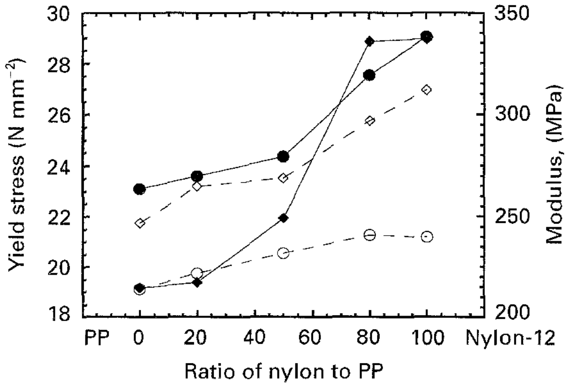

Figure 6 Effect of EP and Ma–g–EP elastomer on the tensile properties of PP/nylon-12 blends. The yield data is represented by; (●) for EP and (◆) for Ma–g–EP whilst the modulus data is represented by; (○) for EP and (◇) for Ma–g–EP.

Fig. 7 shows the effect of the addition of 20 wt% of the elastomers on the toughness of the PP/nylon-12 blends. It is seen that the EP elastomer increased to some degree the peak force of the PP/nylon-12 blends, especially when the range of PP content was higher than 50 wt%. However the peak force was still much lower than that of the pure materials. This can be explained by the morphologies and the compatibility between EP/PP and EP/nylon-12. The morphology study has shown that the EP elastomer dispersed in both PP and nylon-12 as domains and that the PP and nylon-12 are not compatible. The efficiency of the EP elastomer as a toughening agent depended on whether PP was the continuous phase or the dispersed phase. When the PP content was high and it was the continuous phase, the EP elastomer increased the toughness of the blends through improving the toughness of the PP matrix. When nylon-12 was the continuous phase the efficiency of EP was not as high as in the PP case since the compatibility between PP-EP was higher than that between nylon-12-EP.

The toughness of the PP/nylon-12 blends have been improved significantly after the addition of Ma–g–EP to the blends. The peak force values of Mg–g–EP modified blends were much higher than those of EP modified blends in all the components (see Fig. 7). The morphology study has shown that the addition of Ma–g–EP to the PP/nylon-12 blends the two phases increased their dispersion (see Fig. 4). In the PP/nylon-12 blends, Ma–g–EP acted not only as a toughening agent but also as a compatibilizer.

Similarly the break energy in Fig. 1 can also be used to represent the toughness of the materials. Fig. 8 shows the effect of the elastomer on the break energy of PP/nylon-12 blends. It is seen that the break energy of the PP/nylon-12 blends modified by Ma–g–EP was much higher than that when modified by EP. The effect of EP and Ma–g–EP led to the

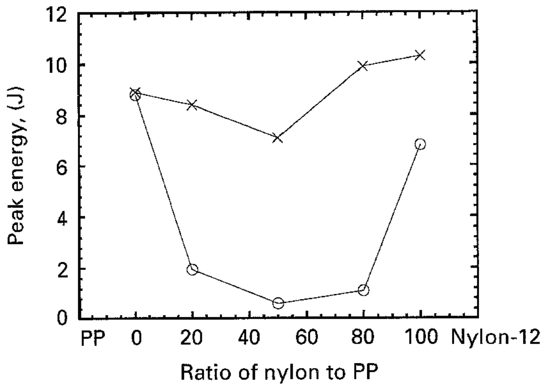

Figure 8 Effect of (○) EP and (×) Ma–g–EP elastomer on peak energy.

conclusion that the toughness of PP/nylon blends was mainly controlled by their compatibility.

4. Conclusion

Blends of PP/nylon-12 are immiscible and incompatible. The impact strength of the blends was lower than the average value for pure PP and nylon-12, especially in the range of high content of both PP and nylon-12 because one component appeared as larger particles in the matrix of the other component. This was particularly noticeable for PP in the nylon-12. The efficiency of the EP elastomer as a toughening agent depended on whether PP was the continuous phase or the dispersed phase. The EP rubber increased the degree of toughness of PP/nylon-12 blends in the range of nylon-12 content less than 50 wt%. This increase was mainly contributed by the EP toughened PP matrix. Maleic anhydride modified EP rubber increased toughness of the blends significantly through improvement of miscibility between PP and nylon-12 and the interface between PP and EP rubber.

The morphologies of PP/nylon-12 blends depended on their components. A phase transformation was observed in the PP/nylon-12 50/50 blends. PP/nylon-12 binary blends showed poor interfacial adhesion and dispersion. Poor interfacial adhesion was evident from the large voids left on the fracture surface where the particles had separated from the matrix and the smooth surfaces of the exposed particles. Upon addition of the EP elastomer to the PP/nylon-12 blends, the EP dispersed in the PP and nylon-12 matrix and did improve their compatibility. After addition of Ma–g–EP to the PP/nylon-12 blends the two phases became well dispersed. In the PP/nylon-12 blends, Ma–g–EP not only acted as a toughening agent but also as a compatibilizer. Separate melting peaks for PP and nylon-12 were observed in all the PP/nylon-12 blends, which confirmed PP/nylon-12 blends were immiscible. The addition of EP or $CaCO_3$ only affected the crystallization temperature through nucleation but not the miscibility of the PP/nylon-12 blend. Maleic anhydride modified EP decreased the ΔT between crystallization of nylon-12 and PP, which indicated the improvement of miscibility between PP and nylon-12.

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