

# Effect of the Compatibilizer on the Morphology and Properties of Dynamically Cured PP/POE/Epoxy Blends

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**ABSTRACT:** Dynamic vulcanization was successfully applied to epoxy resin reinforced polypropylene (PP)/ethylene-octene copolymer (POE) blends, and the effects of different compatibilizers on the morphology and properties of dynamically cured PP/POE/epoxy blends were studied. The results show that dynamically cured PP/POE/epoxy blends compatibilized with maleic anhydride-grafted polypropylene (MAH-g-PP) have a three-phase structure consisting of POE and epoxy particles dispersed in the PP continuous phase, and these blends had improved tensile strength and flexural modulus. While using maleic anhydride-grafted POE (MAH-g-POE) as a compatibilizer, the structure of the core-shell complex

phase and the PP continuous phase showed that epoxy particles could be embedded in MAH-g-POE in the blends, and gave rise to an increase in impact strength, while retaining a certain strength and modulus. DSC analysis showed that the epoxy particles in the blends compatibilized with MAH-g-PP were more efficient nucleating agents for PP than they were in the blends compatibilized with MAH-g-POE. WAXD analysis shows that compatibilization do not disturb the crystalline structure of PP in the blends. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2423–2429, 2012

**Key words:** compatibilizer; epoxy resin; PP; POE

## INTRODUCTION

Polypropylene (PP) has an important place among the synthetic polymers because of its growing commercial applications. However, its application as a structural material is somewhat limited because of its relatively low impact resistance. The impact toughness of PP can be improved dramatically by the addition of elastomers, such as ethylene propylene rubber (EPR), ethylene-propylene diene elastomer (EPDM), ethylene-octene copolymer (POE), and styrene-ethylene butylene-styrene triblock copolymer (SEBS).<sup>1,2</sup>

The incorporation of elastomers into PP leads to a drastic reduction in the modulus and strength. Therefore, issues concerning the simultaneous reinforcing and toughening of PP have attracted considerable attention.<sup>3,4</sup> The incorporation of inorganic fillers or short glass fibers into PP/elastomer blends provides an attractive means of maintaining the stiffness-to-toughness balance.<sup>5,6</sup>

Dynamic vulcanization is an effective method of preparing thermoplastic vulcanizate materials.<sup>7–9</sup> It consists of vulcanizing an elastomer during its melt-mixing with a molten plastic. This technology has

led to a significant number of new thermoplastic elastomer products, commercialized during the mid- to late-1980s.<sup>10</sup> However, there are few articles concerning the dynamic vulcanization of thermoplastic resin/thermosetting resin blends.

Our laboratory has used dynamic vulcanization to prepare a new type of PP/epoxy blend.<sup>11,12</sup> The blends were prepared in the mixing chamber of a Haake rheometer RC90 by dynamically curing an epoxy resin in the molten PP. Because the epoxy resin and PP were immiscible, maleic anhydride-grafted polypropylene (MAH-g-PP) was used as a compatibilizer. Dynamic cure of the epoxy resin led to an improvement in the modulus and stiffness of the PP/epoxy blends, and the addition of MAH-g-PP resulted in increased impact strength and tensile strength.

In this work, the morphology, toughness, and stiffness of blends made by the dynamic cure of an epoxy resin in PP/POE, were investigated, using maleic anhydride-grafted POE (MAH-g-POE) and MAH-g-PP as compatibilizers.

## EXPERIMENTAL

### Materials

PP, grade F401, was produced by Yangzi Petrochemical, China, with a melt flow index (MFI) of 1.9 dg/min (230°C, 2.16 kg). Diglycidyl ether of bisphenol-A resin (DGEBA,  $M_w$ : 4500 g/mol) was supplied by

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Shanghai Resin, China. The curing agent, 2-ethylene-4-methane-imidazole (EMI-2,4) was produced by Shanghai Chemical Agent Company (China). MAH-g-PP and MAH-g-POE with MAH content of 1% were prepared by Shanghai Sunny New Technology Development, China.

### Sample preparation

Before blending, MAH-g-PP, MAH-g-POE and epoxy resin were dried at 80°C under vacuum for about 8 h. Unless otherwise specified, dynamically cured blends were prepared in the mixing chamber of a Haake Rheometer RC90 at 190°C and 50 rpm. MAH-g-PP or MAH-g-POE and PP were first mixed for 2 min, and then the epoxy resin was added. Two minutes later, the curing agent was added with the mixing continuing. The total mixing process lasted about 10 min. The composition was removed from the mixer and compression-moulded in a press at 195°C for 10 min, then cold pressed to give samples for testing.

### Measurements of mechanical properties

The tensile properties were measured using an Instron 4465 Tester (USA) at a crosshead speed of 20 mm/min according to ASTM D638. Notched Izod impact strengths were tested using a Ray-Ran Universal Pendulum Impact Tester (UK) at an impacting pendulum speed of 3.5 m/s, according to ASTM D256. Flexural properties were measured using the Instron 4465 Tester and a three-point-loading rig, at a speed of 1.7 mm/min, according to ASTM D790. In each of the tests, at least five samples were tested, and the average results were reported.

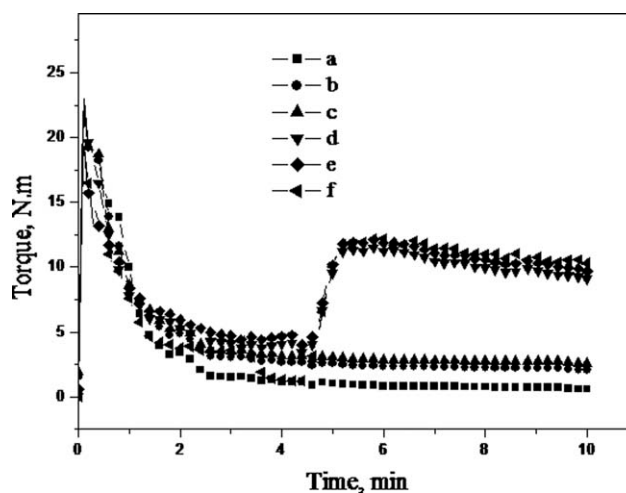
### Scanning electron microscopy

A scanning electron microscope (SEM, HITACHI-S-2150) was used to examine the morphology of the samples. All the samples were fractured in liquid nitrogen. The samples were etched using *n*-heptane for 10 min, and then covered with a thin gold layer for further observation.

### DSC analysis

The crystallization behavior of PP and the curing behavior of the epoxy resin in the blends were analyzed using a Perkin-Elmer DSC (Paris 1) (USA) in a nitrogen atmosphere.

Samples of about 4 mg were taken from the moulded plaques. Nonisothermal crystallization was performed as follows: a sample was first heated to 200°C at 50°C/min and then maintained at this temperature for 5 min in order to eliminate any



**Figure 1** Plot of torque versus time for PP/POE/epoxy blends at 190°C (a) PP/POE/epoxy = 75/25/10; (b) PP/MAH-g-PP/POE/epoxy = 65/10/25/10; (c) PP/POE/MAH-g-POE/epoxy = 75/15/10/10; (d) PP/POE/epoxy/EMI-2,4 = 75/25/10/0.4; (e) PP/POE/MAH-g-POE/epoxy/EMI-2,4 = 75/15/10/10/0.4; (f) PP/MAH-g-PP/POE/epoxy/EMI-2,4 = 65/10/25/10/0.4.

previous thermal history. The sample was subsequently cooled down to 40°C at a cooling rate of 10°C/min and then heated to 200°C at 10°C/min for data collection. The curing of the epoxy resin in the blends was performed as follows: the sample was heated from 40 to 200°C at 10°C/min.

### WAXD analysis

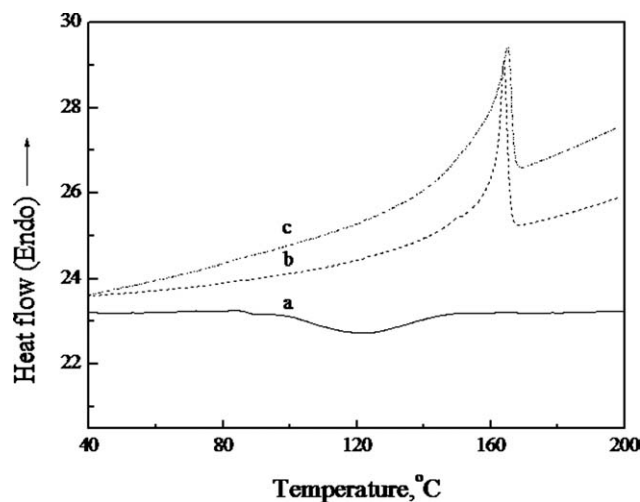
The X-ray diffraction experiments were performed using a Rigaku Dmax-rC diffractometer (Japan) with Cu target and a rotating anode generator operated at 40 kV and 100 mA. The scanning rate was 2°/min from 5° to 35°. The samples for WAXD measurement were prepared by compression-moulding at 200°C and 5 MPa.

## RESULTS AND DISCUSSION

### Compatibilization and dynamic cure

Torque measurements can be used to give qualitative information about the chemical reactivity and extent of reaction in reactively compatibilized blends.

Figure 1 shows the relationship between the torque and time for PP/POE/epoxy blends at 190°C. The addition of 10 wt % MAH-g-PP or MAH-g-POE to the PP/POE/epoxy blends obviously increased the torque at equilibrium. As MAH-g-PP and MAH-g-POE both contain active maleic anhydride (MAH) groups, the functional groups can react with the hydroxyl or epoxy groups of the epoxy resin in the blends, and the reactions lead to an increase in the viscosities of the blends through the addition of



**Figure 2** DSC curves of (a) epoxy/EMI-2,4 (100/4); (b) PP/POE/MAH-g-POE/epoxy/EMI-2,4 = 75/15/10/10/0.4; (c) PP/MAH-g-PP/POE/epoxy/EMI-2,4 = 65/10/25/10/0.4.

MAH-g-PP or MAH-g-POE. Shieh et al.<sup>13</sup> reported using MAH-g-PP and a multifunctional epoxy resin as dual reactive compatibilizers for PP/poly(butylene terephthalate) (PBT) blends.

As shown in Figure 1, the addition of the curing agent (EMI-2,4) at the mixing time of 4 min led to an obvious rise in the torque of the PP/POE/epoxy blends. This shows that the epoxy resin had been cured by EMI-2,4 during its mixing with molten PP and POE. The curing behavior of the epoxy resin in the blends can be analyzed from the DSC curves. Figure 2 shows the DSC heating scans of epoxy/EMI-2,4 and dynamically cured PP/POE/epoxy (75/25/10) blends. There was an obvious exothermic enthalpy reaction resulting from the curing of the epoxy/EMI-2,4 blend, and the curing temperatures ranged from 80 to 150 °C. No exothermic enthalpy associated with the curing reaction could be seen in the dynamically cured PP/POE/epoxy (75/25/10) blend, only the enthalpy of fusion of the PP. This shows that the epoxy resin was fully cured.

### SEM analysis

Figure 3 shows the effect of the different compatibilizers on the morphology of dynamically cured PP/POE/epoxy blends. To distinguish the phase structure of each component in the blends, the POE in the samples was etched using *n*-heptane. For the PP/POE (75/25) blend [Fig. 3(a)], the holes with diameters of 3–8  $\mu\text{m}$  show that the POE was dispersed in the PP matrix. In the case of the PP/POE/MAH-g-POE (75/15/10) [Fig. 3(b)] and PP/MAH-g-PP/POE (65/10/25) [Fig. 3(c)] blends, their morphology was similar to that of PP/POE (75/25).

Figure 3(d) shows the etched SEM micrograph of the dynamically cured PP/POE/epoxy (75/25/10)

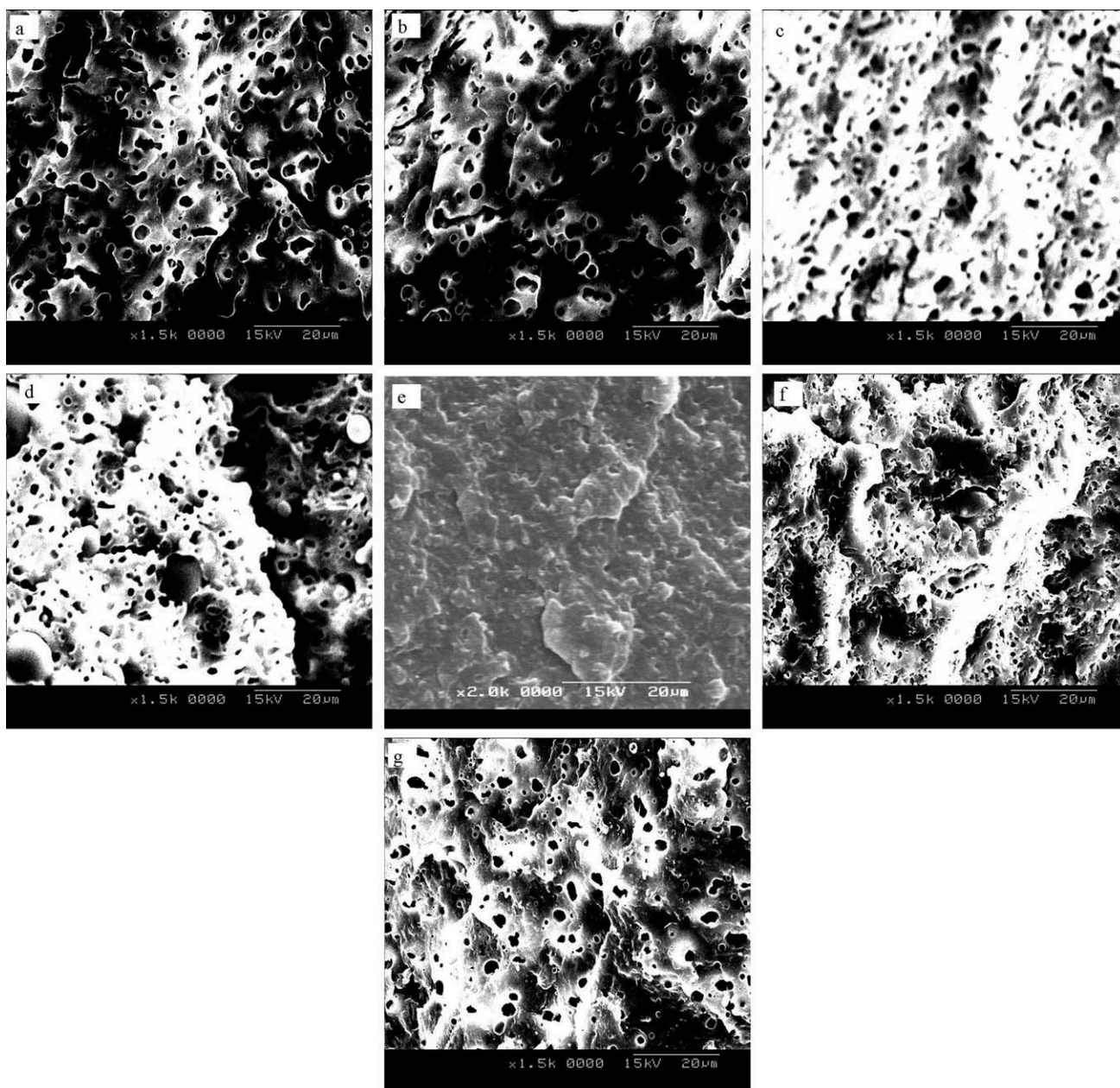
blend [Fig. 3(d)]. Holes represent POE, and epoxy particles with diameters of about 4–12  $\mu\text{m}$  existed in the PP matrix. This shows that there was a three-phase structure in the dynamically cured PP/POE/epoxy blends, probably a POE dispersed phase, and an epoxy dispersed phase and a PP continuous phase. The size of epoxy particles in dynamically cured PP/POE/MAH-g-POE/epoxy (75/15/10/10) blend [Fig. 3(e)] is obviously smaller than that in dynamically cured PP/POE/epoxy (75/25/10) blend [Fig. 3(d)], the MAH groups of MAH-g-POE could be react with the epoxy resin, it shows that MAH-g-POE improves the compatibility between the PP and epoxy resin. The epoxy particles may be embedded in MAH-g-POE, and form the structure of core-shell complex phase and PP continuous phase in the blend. A number of smaller holes representing a core-shell complex phase with POE and epoxy particles were observed in the etched dynamic cured PP/POE/MAH-g-POE/epoxy (75/15/10/10) blend [Fig. 3(f)]. The number of holes was greater in this blend than in the analogous PP/POE/epoxy (75/25/10) blend. Similar structures of three-component polymer/elastomer/fillers have been reported by other authors.<sup>14,15</sup> When MAH-g-POE and POE were etched by *n*-heptane, a lot of epoxy particles were detached along with the MAH-g-POE and POE. The dynamically cured PP/MAH-g-PP/POE/epoxy (65/10/25/10) blend [Fig. 3(g)] has a structure with the holes from POE and there were a number of epoxy particles with diameters of about 0.3–0.8  $\mu\text{m}$  in the PP matrix. The number of holes left by the epoxy particles was more than that had been seen in the case of the dynamically cured PP/POE/MAH-g-POE/epoxy (75/15/10/10) blend. This shows that MAH-g-PP can improve the compatibility between PP and epoxy resin. There was also a three-phase structure of PP/MAH-g-PP/POE/epoxy blends, consisting of a POE dispersed phase, an epoxy dispersed phase and a PP continuous phase.

### Mechanical properties

Most chemically different polymers are immiscible, and blending them leads to materials with weak interfacial adhesion and poor mechanical performance. The conversion of the immiscible blend to a useful polymeric product with the desired properties requires manipulation of the interface. One of the classical routes to ensure adhesion between phases is the use of a third component, known as a compatibilizer, which is compatible or miscible with both phases.<sup>14</sup> As in this case the epoxy resin is immiscible with POE and PP, MAH-g-POE and MAH-g-PP were used as compatibilizers.

Figure 4 shows the effect of different compatibilizers on the mechanical properties of the dynamically



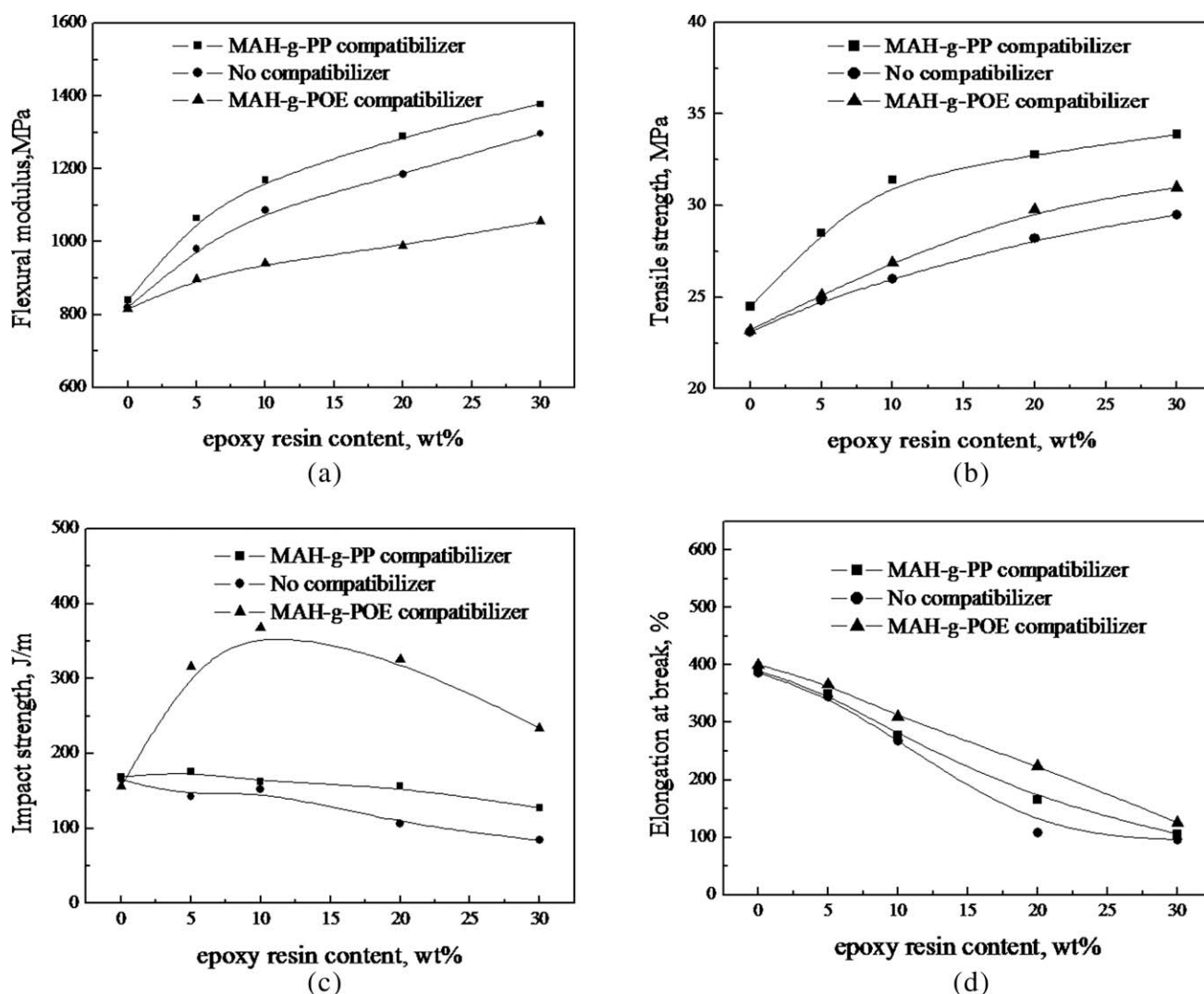


**Figure 3** SEM photographs of the etched blends (a–d, f–g) and nonetched blend (e) (a) PP/POE = 75/25, (b) PP/POE/MAH-g-POE = 75/15/10, (c) PP/MAH-g-PP/POE = 65/10/25 (d) PP/POE/epoxy/EMI-2,4 = 75/25/10/0.4, (e, f) PP/POE/MAH-g-POE/epoxy/EMI-2,4 = 75/15/10/10/0.4, (g) PP/MAH-g-PP/POE/epoxy/EMI-2,4 = 65/10/25/10/0.4.

cured PP/POE/epoxy blends. With the same proportion of epoxy resin, the tensile strength and flexural modulus of the dynamically cured PP/POE/epoxy blends compatibilized with MAH-g-PP were higher than those of the non compatibilized blends and the blends compatibilized with MAH-g-POE, but the impact strength was obviously lower; the noncompatibilized blends had the lowest impact strength. With increasing epoxy resin content, the tensile strength and flexural modulus of all the dynamically cured PP/POE/epoxy blends increased gradually, but the elongation at break decreased dramatically. In the case of the dynamically cured PP/POE/epoxy blends

compatibilized with MAH-g-POE, the impact strength increased with increasing epoxy resin content (0–10 wt %) and reached a maximum of 370 J/m at an epoxy resin content of 10 wt %.

When the epoxy resin content was over 10 wt %, the impact strength decreased. But for the dynamically cured PP/POE/epoxy blends compatibilized with MAH-g-PP and also in the case of non compatibilized blends, the impact strength decreased slightly with increasing epoxy resin content. The results show that the dynamically cured PP/POE/epoxy blends compatibilized with MAH-g-POE or MAH-g-PP had better mechanical properties than



**Figure 4** Effect of different compatibilisers on the mechanical properties of dynamically cured PP/POE/epoxy blends Formulation: (PP+MAH-g-PP 10) 75, (POE+MAH-g-POE 10) 25, epoxy variable, EMI-2,4 (4 parts per 100 parts epoxy).

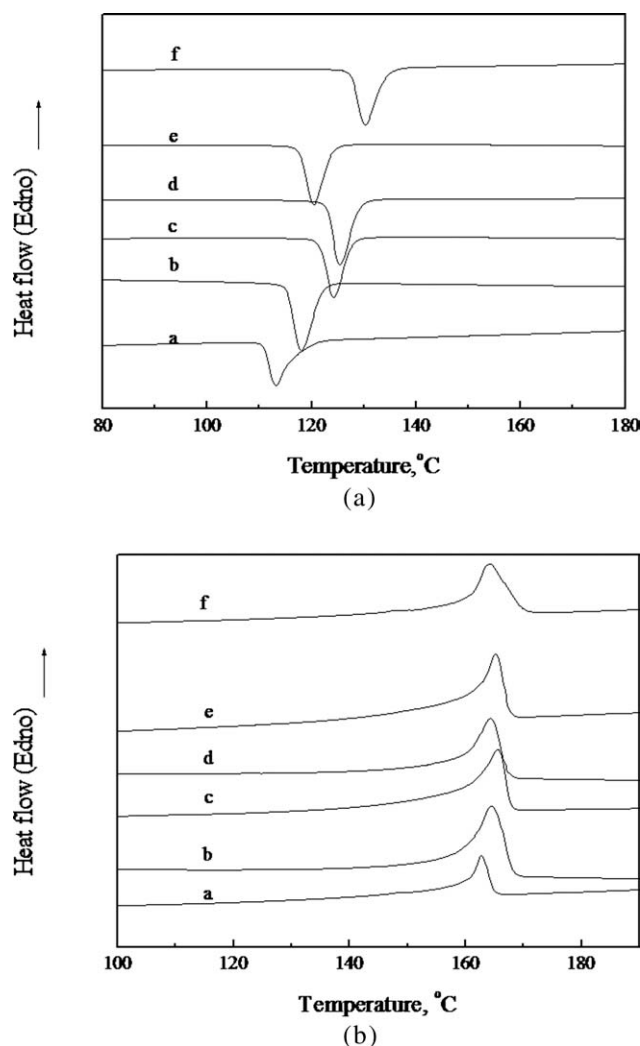
the noncompatibilized analogues, but the effect of different compatibilizers on the mechanical properties was different. Blends compatibilized with MAH-g-PP had higher tensile strength and flexural modulus values, but blends compatibilized with MAH-g-POE had higher impact strength.

The different mechanical properties of the dynamically cured PP/POE/epoxy blends compatibilized with MAH-g-POE or MAH-g-PP can be attributed to their distinct morphology. When MAH-g-PP was used as compatibilizer, dynamically cured PP/POE/epoxy blends had epoxy resin particles finely dispersed in the PP matrix, and the cured epoxy particles acted as organic fillers to increase the stiffness of the blends. When MAH-g-POE was used as compatibilizer, the blends had epoxy particles containing embedded MAH-g-POE and POE which obviously improves its toughness, whereas a higher epoxy resin content (10 wt %) can be expected to

impair the toughness. Faulkner<sup>16,17</sup> studied the impact behavior of PP/mica/elastomer composites and tried to optimize stiffness and toughness, and thought that the embedded structure had better impact resistance.

#### DSC analysis

PP can crystallize rapidly, even under quenching conditions. Figure 5 shows the first cooling and second heating DSC scans of PP, PP/POE (75/25), PP/epoxy (75/25), dynamically cured PP/POE/epoxy (75/25/10), dynamic cured PP/POE/MAH-g-POE/epoxy (75/15/10/10), and dynamically cured PP/MAH-g-PP/POE/epoxy (65/10/25/10). Table I gives a summary of the crystallization and melting data from the DSC thermograms. The crystallinity of the PP component in the blends was calculated by using the following equation:



**Figure 5** DSC thermograms at first cooling and second heating of (a) PP; (b) PP/POE = 75/25; (c) PP/epoxy = 75/25; (d) PP/POE/epoxy/EMI-2,4 = 75/25/10/0.4; (e) PP/POE/MAH-g-POE/epoxy/EMI-2,4 = 75/15/10/10/0.4; (f) PP/MAH-g-PP/POE/epoxy/EMI-2,4 = 65/10/25/10/0.4.

$$X_c (\%) = (H/H_0) \times (100/x) \quad (1)$$

where  $X_c$  is the crystallinity of PP,  $H$  is the measured heat of crystallization of the blend,  $H_0$  (=170 J/g) is the heat of crystallization of 100% crystalline isotactic PP,<sup>18</sup> and  $x$  is the mass fraction of PP in the blend.

Only a single crystallization peak ( $T_p$ ) could be seen for PP, PP/POE, PP/epoxy and all the dynamically cured PP/POE/epoxy blends. All the crystallization peak temperatures of the blends were higher than the crystallization peak of PP (113.1°C). A shift of the crystallization peak to a higher temperature suggests that POE, MAH-g-POE, and epoxy resin in the blends can act as nucleating agents, accelerating the crystallization of PP.

The  $T_p$  of PP in PP/POE (75/25) was about 118.2°C, i.e. lower than that of the PP/epoxy (75/

25). The result shows that the epoxy resin was a more efficient nucleating agent than POE.

The  $T_p$  of PP in the dynamically cured PP/MAH-g-PP/POE/epoxy (65/10/25/10) was higher than that of PP in the PP/epoxy (75/25), dynamically cured PP/POE/epoxy (75/25/10) and dynamic cured PP/POE/MAH-g-POE/epoxy (75/15/10/10), showing that the smaller epoxy resin particles in the dynamically cured MAH-g-PP/POE/epoxy blends had resulted in an increase of the number of nucleating sites, increasing the crystallization peak temperature of PP. The  $T_p$  of dynamically cured PP/POE/MAH-g-POE/epoxy (75/15/10/10) was about 119.7°C, which is similar to that of PP/POE (75/25), but lower than that of the dynamically cured PP/POE/epoxy (75/25/10). Although, there were many smaller epoxy particles in the blends, the epoxy particles could have contained embedded MAH-g-POE and POE, decreasing the nucleating effect of the epoxy resin. Premphet and Horanont<sup>15</sup> also found that the nucleating effect of calcium carbonate on PP in PP/CaCO<sub>3</sub>/elastomers became worse when the CaCO<sub>3</sub> was embedded in the elastomer. In all cases, the crystallinity of PP in the blends was higher than that of pure PP (162.3°C), and the increase in the melting temperature of PP in the blends was directly related to the size of the PP crystals.<sup>19</sup>

### Wide-angle X-ray diffraction analysis

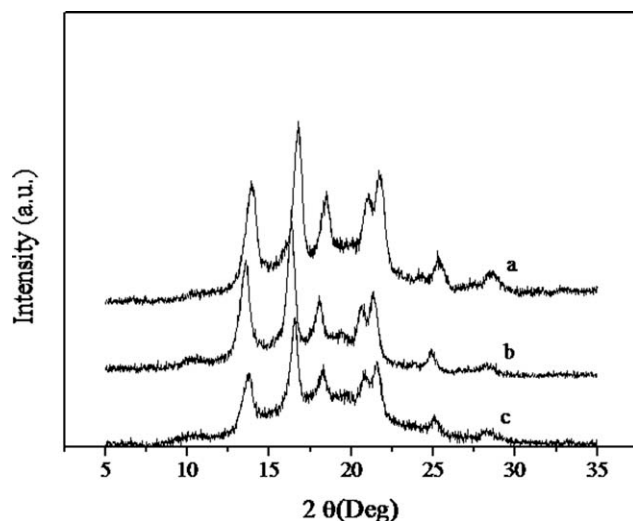
To investigate whether the crystalline structure formed by one component of the blend can be affected by the other component or the compatibilizer, X-ray diffraction studies were made on the corresponding PP and the blends. Figure 6 shows the WAXD patterns of PP, dynamically cured PP/MAH-g-PP/POE/epoxy (65/10/25/10), dynamically cured PP/MAH-g-POE/POE/epoxy (75/10/15/10). Several reflections in both the blends and PP are observed at  $2\theta = 13.9^\circ, 16.7^\circ, 18.3^\circ, 20.9^\circ, 21.8^\circ$ , which belong to the identical monoclinic  $\alpha$  form of the PP component. The

**TABLE I**  
DSC Analysis Results of PP and PP/Epoxy Blends

Composition	$T_m$ (°C)	$T_p$ (°C)	$X_c$ (wt %)
PP	162.3	113.1	56.1
PP/POE = 75/25	164.6	118.5	57.3
PP/epoxy = 75/25	165.3	124.3	56.5
PP/POE/epoxy/ EMI-2,4 = 75/25/10/0.4	165.6	125.6	58.0
PP/POE/MAH-g-POE/epoxy/ EMI-2,4 = 75/15/10/10/0.4	164.0	120.1	59.3
PP/MAH-g-PP/POE/epoxy/ EMI-2,4 = 65/10/25/10/0.4	164.1	129.8	60.9

$T_m$ , peak melting temperature;  $T_p$ , peak crystallization temperature,  $X_c$ , the crystallinity of PP.





**Figure 6** WAXD curves of (a) PP; (b) PP/POE/MAH-g-POE/epoxy/EMI-2,4 = 75/15/10/10/0.4; (c) PP/MAH-g-PP/POE/epoxy/EMI-2,4 = 65/10/25/10/0.4.

result shows that the dynamical cure of epoxy resin and compatibilization do not disturb the crystalline structure of PP in the blends.

### CONCLUSIONS

The effects of different compatibilizers on the morphology and properties of dynamically cured PP/POE/epoxy blends have been studied. Blends compatibilized by MAH-g-PP with a three-phase structure of POE and epoxy particles dispersed in the PP continuous phase were obtained, and they showed improved tensile strength and flexural modulus, although the impact strength varies slightly. When MAH-g-POE was used as compatibilizer, the blends possessed a structure consisting of a core-shell complex phase and a PP continuous phase, with epoxy

particles embedded in MAH-g-POE and POE in the blends. The core-shell structure gave rise to an increase in the impact strength, maintaining certain strength, and modulus. DSC analysis showed that the epoxy particles in the dynamically cured PP/MAH-g-PP/POE/epoxy blends were more efficient nucleating agents than those in the equivalent PP/POE/MAH-g-POE/epoxy blends, but the nucleating effect of epoxy particles embedded in the elastomer on PP in the blends became worse. WAXD analysis shows that the dynamical cure of epoxy resin and compatibilization do not disturb the crystalline structure of PP in the blends.

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