

Polymer Blends of Polyamide-6 (PA6) and Poly(phenylene ether) (PPE) Compatibilized by a Multifunctional Epoxy Coupler

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ABSTRACT: A tetrafunctional epoxy monomer, *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM), has demonstrated to be a highly efficient reactive compatibilizer in compatibilizing the immiscible and incompatible polymer blends of polyamide-6 (PA6) and poly(2,6-dimethyl-1,4-phenylene ether) (PPE). This epoxy coupler can react with both PA6 and PPE to form various PA6-*co*-TGDDM-*co*-PPE mixed copolymers. These interfacially formed PA6-*co*-TGDDM-*co*-PPE copolymers tend to anchor along the interface to reduce the interfacial tension and result in finer phase domains and enhanced interfacial adhesion. A simple one-step melt blending has demonstrated to be more efficient in producing a better compatibilized PA6/PPE blend than a two-step sequential blending. The mechanical property improvement of the compatibilized blend over the uncompatibilized counterpart is very drastic, by considering the addition of a very small amount, a few fractions of 1%, of this epoxy coupling agent. © 1998 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 36: 1805–1819, 1998

Keywords: polymer blend; PA6; PPE; epoxy; reactive compatibilizer; coupling agent

INTRODUCTION

The inherent properties of polyamide-6 (PA) and poly(phenylene ether) (PPE) suggest that a combination of PA6 and PPE should produce materials with balanced properties, provided that the advantages from one component are able to compensate for the deficiencies of the other. Polymer blends of PA and PPE have attracted great interest from both industries and academia. The simple melt blending of PA6 and PPE generally shows deterioration in impact performance and tensile properties. Such a reduction in properties is frequently a reflection of poor interfacial adhesion between dispersed and continuous matrix that leads to rapid initiation and growth of a crack. The most common approach to achieve a better

compatibilization of an incompatible blend is by the addition of a third component, usually a non-reactive block or graft copolymer, leading to modification of the polymer interfacial properties and, hence, the performance of the blends.^{1,2}

More commonly, compatibility of polymer blends can be improved by a reactive compatibilizer. A conventional reactive compatibilizer of the type C-X (where X is a reactively functional group) may compatibilize a binary A/B blend, provided that the C segment is structurally similar to or miscible with the A component, while X is capable of reacting with the B component.^{3,4} The copolymer C-X-B may be formed *in situ* at the interface, which tends to remain at the interface to act as an emulsifier of the A/B blend.¹

A general review of total 15 articles and patents on the area of PA/PPE blends^{5–19} had been made in our previous report.²⁰ Additionally, Brown²¹ reported that the reaction of an aryloxytriazine-functionalized PPE with an amine-terminated PA results in PA–PPE copolymer formation as the *in*

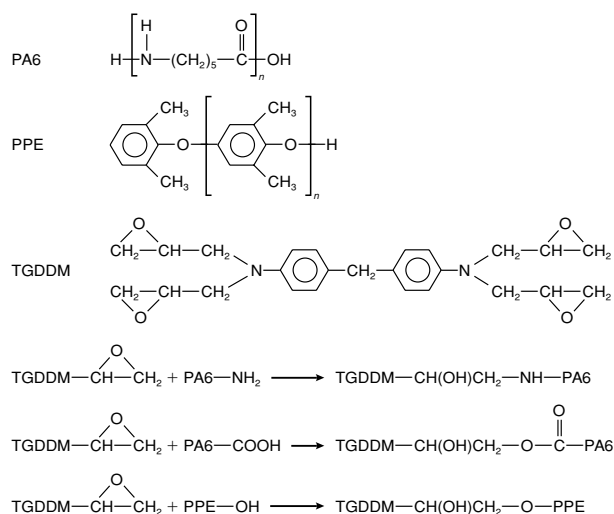
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situ reactive compatibilizer of the PA/PPE blend. Miyata et al.²² reported that a heterarm star-shaped block copolymer with a cyclotriphosphazene core is able to act as the compatibilizer of immiscible PA6/PPE blends. Ting et al.²³ demonstrated by calorimetry that the poly(styrene-*co*-vinylphenyl hexafluorodimethyl carbinal) (PHFA) is compatible with PPE. Jo et al.²⁴ reported that the styrene-acrylic acid random copolymer (SAA) having acrylic acid content higher than 36 mol is an effective interfacial agent for the PA6/PPE blend. Bhatia et al.²⁵ demonstrated that the compatibilized PA/PPE blends show a decrease in surface PA enrichment with increasing of the *in situ*-formed copolymer content. In our previous work, both styrene-glycidyl methacrylate²⁶ and styrene-maleic anhydride²⁰ had demonstrated to be highly effective in compatibilizing PA6/PPE blends.

A coupling agent or coupler is a multifunctional molecule (monomer, oligomer, or polymer) that is capable of reacting with a polymer to give chain extension, branching, or even to build melt viscosity by crosslinking (if the functionality is greater than 2). The coupling approach in polymers has been briefly reviewed by Brown,²⁷ Liu,²⁸ and Xanthos.³ A similar approach applied on the multiphase polymer blends as a coupling-type reactive compatibilizer has been explored recently.^{29–35} Rudin et al.²⁹ reported that a direct grafting of polystyrene onto polyethylene can be carried out in a twin-screw extruder with an organic peroxide (dicumyl peroxide, DP) and a coupling coagent (triallyl isocyanurate, TAIC). The extruded blends exhibited enhancement in impact properties at an optimum level of peroxide and coupling coagent. Pernice et al.³⁰ claimed that the impact modified PA/PPE blend containing 0.5 to 3.0 wt % of an organic diisocyanate such as 4,4'-(diphenyl methane) diisocyanate or 2,4-toluene diisocyanate has a good balance of mechanical, thermal, and processing properties. The synthesized difunctional unsaturated-isocyanate compounds used as sizing agents on carbon fibers can substantially improve the fiber/acrylic-matrix bonding and its mechanical properties.³¹ Several blend systems such as PET/LCP,^{32,33} PBT/PA66,³⁴ PET/PPE,³⁵ and PA6/PPE³⁶ were effectively compatibilized by various multifunctional epoxy resins as coupling-type reactive compatibilizers.

A multifunctional epoxy monomer, under suitable condition, is expected to react with terminal —NH₂ and —COOH groups of PA and phenolic—



Scheme I. The chemical structures and reactions of PA6, PPE, and TGDDM components.

OH of PPE simultaneously to form various PA6-*co*-Epoxy-*co*-PPE copolymers at the interface. The chemical structures of PA6, PPE, and TGDDM and the related reactions involved are shown in Scheme I. These *in situ*-formed mixed copolymers produced at the interface containing segments of PA6 and PPE are expected to remain at the interface to function as an effective compatibilizer of the PA6/PPE blend. In a series of studies on the compatibilization of PA6/PPE blends, this article will report results of using TGDDM epoxy monomer as a coupling agent to compatibilize PA6/PPE blends. We intend to report their specific miscibility and correlation with their resultant morphological, thermal, and mechanical properties.

EXPERIMENTAL

Materials

The polyamide-6 (PA6) used in this study is the general purpose grade, NOVAMIDE 1010C2, supplied by the Mitsubishi Kasei Co. Ltd. of Japan. Unmodified poly(2,6-dimethyl-1,4-phenylene ether) (PPE) powder was obtained from the GE Plastics Co. that has an intrinsic viscosity of 0.4 dL/g measured in chloroform at 25°C. The coupling type reactive compatibilizer, a tetra-functional epoxy monomer, *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM), was obtained from Ciba-Geigy of Switzerland.

Table I. Processing Condition

A. Extrusion Condition												
Composition			Barrel Temperature (°C)									
PA6	PPE	Stage:	1	2	3	4	5	6	7	8	9	Die
30	70		210	270	280	290	290	285	285	285	285	285
Screw speed: 260 rpm. Feeding rate: 125 g/min.												
B. Injection Condition												
Composition			Barrel Temperature (°C)				Mold Temp. (°C)					
PA6	PPE	Stage:	1	2	3	Nozzle						
30	70		290	300	310	310	120					

Melt Blending

All blends were prepared by a corotating 30 mm twin-screw extruder (L/D = 36, Sino-Alloy Machinery Inc. of Taiwan) with a decompression zone. The rotating speed of screw was set at 260 rpm. The barrel temperatures were set from 210 to 290°C. The extruded pellets were dried in an oven at 100°C for at least 8 h and injection molded into standard ASTM $\frac{1}{8}$ inch testing specimens using an Arburg 3 oz injection-molding machine from Germany. The detailed processing conditions for extrusion and injection molding are listed in Table I.

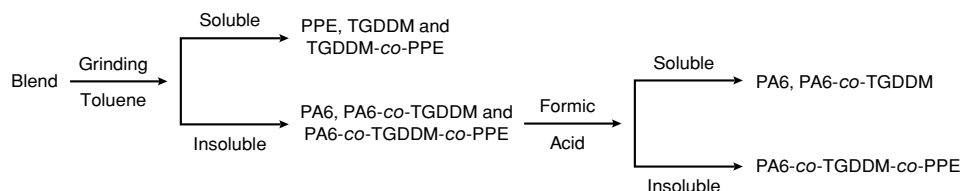
Solvent Extractions

Several solvent extraction techniques^{5,37–39} have been reported to give successful separation of the blended components of immiscible polymer blends. In order to isolate and identify the *in situ*-formed PA6-*co*-TGDDM-*co*-PPE copolymers produced during melt blending, complicated solvent extractions have been carried out. Powder (2 g) of the compatibilized blend was immersed and agitated in 50 mL toluene for 24 h. The resultant suspended mixture was separated by centrifugation at 13000 rpm for 50 min. The clear upper solution containing PPE, TGDDM, and TGDDM-*co*-PPE was collected by a pipette. The bottom undissolved solid was reextracted by the same procedures for at least five times to assure complete removal of PPE, TGDDM, and TGDDM-*co*-PPE from the compatibilized blend. After repeated extractions by the toluene, the solid resi-

due was dried in an oven to remove the toluene solvent. The residue was then extracted with excess of formic acid at ambient condition for 12 h to remove the unreacted PA6 and PA6-*co*-TGDDM from the residue. The suspended mixture was poured into a separatory funnel and settled for 24 h. The clear bottom phase containing PA6 and PA6-*co*-TGDDM was removed. The white and undissolved top layer was collected into a beaker for next formic acid extraction. Similar formic acid extraction was repeated for at least five times. The upper white and undissolved layer containing mostly the PA6-*co*-TGDDM-*co*-PPE copolymers was rinsed with water and dried in an oven. To ensure that all the remaining PPE, TGDDM, and TGDDM-*co*-PPE have been removed, this dried residue was extracted again by toluene and chloroform in sequence. This solvent extraction procedures have been described previously,³⁷ as shown in Scheme II.

Fourier Transform Infrared Spectroscopy (FTIR)

To characterize the components from extractions by toluene and formic acid, Fourier transform infrared spectroscopic (FTIR) analyses were carried out using a Nicolet 500 Infrared Spectrophotometer. Additionally, to prove the reaction of TGDDM with PPE has indeed occurred, FTIR spectra of PPE/TGDDM = 100/1 mixtures by dry mixed and melt blending were compared. The solvent cast film from the dry-mixed mixture of PPE/TGDDM = 100/1 was prepared from the chloroform solution. The cast film of the melt-blended PPE/



Scheme II. Solvent extraction procedures.

TGDDM = 100/1 mixture was first melted mixed in a Brabender Plasti-Coder mixer at 290°C prior to the solvent film casting.

Rheological Properties

To verify the reaction of PPE (and PA6) with TGDDM based on viscosity increase, torques vs. time measurements were carried out in a Brabender Plastic-Corder mixer with the capacity of 30 mL. The rotational speed was set at 30 rpm and the temperature was controlled at 290°C. Capillary rheological measurements were carried out at 290°C using a Kayeness Galaxy Capillary Rheometer with a die orifice radius of 0.04 inch and a die length of 0.8 inch. Melt flow rates (MFRs) of matrices and blends were measured at 290°C using a 5-kg load.

Thermal Properties

Thermal properties of blends were studied using a differential scanning calorimetry (DSC). Heating and cooling rates were controlled at 10°C/min, and measurements were made between 40 and 300°C on a DSC-7 Analyzer from the Perkin-Elmer Co. The percent of the PA6 crystallinity in the blend was determined by the following equation:

$$X_c(\%) = (\Delta H_{PA6} / \Delta H_{PA6}^0)(100/X)$$

X_c is the percent crystallinity of PA6 component in the blend. ΔH_{PA6} is the measured heat of fusion of the PA6 component of the blend provided that no heat of crystallization is released during heating scan. ΔH_{PA6}^0 is the theoretical heat of fusion of the 100% crystallinity of the pure PA6. X is the mass fraction of the PA6 component in the blend. The heat of fusion of PA6 at 100% crystalline state (ΔH_{PA6}^0) is 190.6 J/g.³⁸

Scanning Electron Microscopies (SEM)

The morphologies of the injection-molded specimens were examined using a Hitachi S-570 scan-

ning electron microscopy (SEM) from Japan at an accelerating voltage of 20 kV. The cryogenically fractured surfaces of the molded specimens were coated with thin film of gold to prevent charging prior to the SEM examination.

Mechanical Properties

Tensile tests were conducted at ambient conditions using an Instron Universal Testing Machine Model 4201 according to the ASTM D638. The crosshead speed was controlled at 5 mm/min. Unnotched Izod impact strengths were measured at ambient conditions according to the ASTM-D256 method. All injection-molded specimens were conditioned in the laboratory atmosphere for a minimum of 7 days before testing.

RESULTS AND DISCUSSION

Rheological Properties

The addition of TGDDM results in viscosity increase of PA6/PPE blends as indicated by the recorded extruder input current (Table II). The increase of the measured extruder current due to the expected molecular weight increment by chain extension and coupling reactions of TGDDM with PA6 and PPE (Scheme I). The compatibilized blends indeed increased slightly for the resultant melt viscosity but did not encounter any noticeable viscosity-induced processing problem. In fact, the compatibilized blend actually improved extrusion processibility by reducing or eliminating problems of melt fracture and die swelling of the uncompatibilized blend.

Torque measurements have been used successfully to obtain qualitative information concerning the chemical reactivity and the extent of reactions in a compatibilized blend.⁴⁰ Plots of torque versus mixing time at 290°C for PA6, TGDDM, and PA6/TGDDM = 100/1 mixtures are given in Figure 1. The measured torques for PA6 and TGDDM are very low and remain almost constant at this tem-

Table II. Extruder Current and Melt Flow Rate of the PA6/PPE Blends

Composition	Extruder Current (Amp)	Melt Flow Rate (g/10 min)
PA6/PPE = 30/70	18.1–20.2	17.7
PA6/PPE/TGDDM = 30/70/0.1	19.6–20.8	17.9
PA6/PPE/TGDDM = 30/70/0.3	23.1–24.5	8.9
PA6/PPE/TGDDM = 30/70/0.5	27.7–30.0	3.0

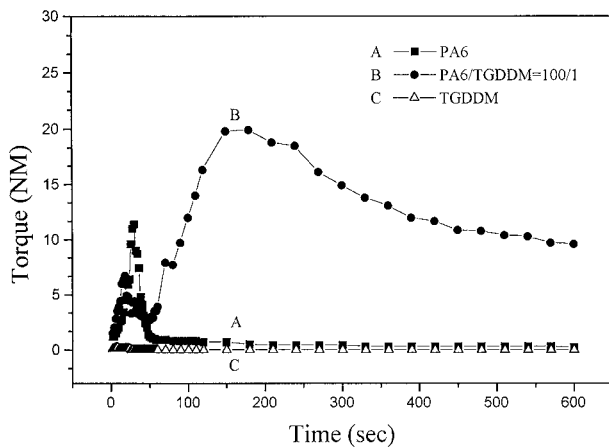
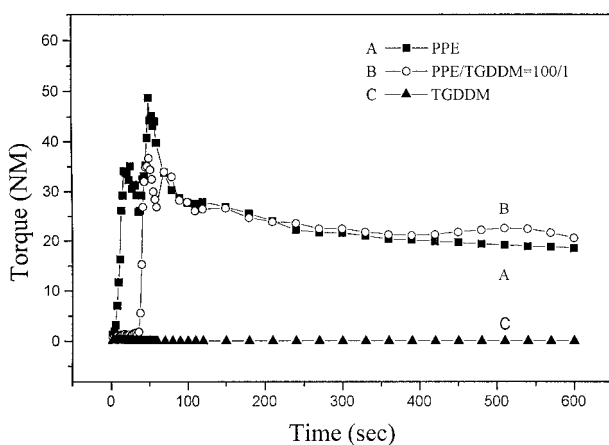
Screw speed: 260 rpm.
Feeding rate: 115 g/min.

perature. That means the ring opening or cross-linking reaction by this epoxy monomer does not occur at this temperature. The torque value of the PA6/TGDDM = 100/1 mixture is significantly higher than that of PA6 and TGDDM due to the molecular weight increase from the expected chain extension reactions between PA6 terminal groups ($-\text{NH}_2$ and $-\text{COOH}$) and the TGDDM epoxides. However, when the mixing time is greater than 150 s, the torque decreases gradually probably due to the thermal degradation. Figure 2 illustrates the torque vs. time curves for PPE, TGDDM, and PPE/TGDDM = 100/1 mixture. The torque value of neat PPE is high but decreases gradually after 120 s. The mixture of PPE/TGDDM has slightly higher torque value than the neat PPE, which indicates the possible reaction between phenolic-OH end group of PPE and the TGDDM but at a slower rate and a less extent. Because every PPE molecule possesses only one terminal $-\text{OH}$, we would not expect excessive chain extension reaction relative to that of PA6, and less viscosity increase observed is also expected. If no reaction occurs between PPE and the

low molecular weight TGDDM, we should expect a viscosity drop from the PPE/TGDDM blend.

Melt flow rates of uncompatibilized and compatibilized blends are summarized in Table II. Without the presence of this epoxy compatibilizer, the PA6/PPE blend results in higher MFR, as would be expected. The presence of 0.1 phr TGDDM compatibilizer does not affect the blend MFR significantly. The addition of 0.3 phr or higher results in substantial reduction of the MFR as shown in Table II.

The shear viscosity vs. shear rate plots of uncompatibilized and compatibilized PA6/PPE blends at 290°C are shown in Figure 3. The uncompatibilized blend has the lowest viscosity, as would be expected. Again, the addition of 0.1 phr of TGDDM compatibilizer does not cause any viscosity increase, which is consistent with the previous MFR data. The compatibilized blends containing more than 0.3 phr compatibilizer result in substantial viscosity rise, especially pronounced at lower shear rates. The molecular weight increase through chain extension and coupling reaction is believed to be the major

**Figure 1.** Plots of torque vs. time for the PA6, TGDDM, and PA6/TGDDM blend.**Figure 2.** Plots of torque vs. time for the PPE, TGDDM, and PPE/TGDDM blend.

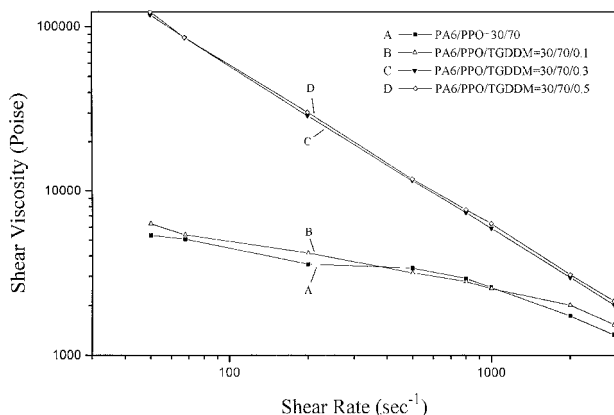


Figure 3. Plots of shear viscosity vs. shear rate of the uncompatibilized and compatibilized PA6/PPE = 30/70 blends.

contributor to the observed viscosity increase of these compatibilized blends.

Fourier Transform Infrared Spectroscopy (FTIR)

The IR peak at 907 cm^{-1} is a characteristic response of the epoxy group that has been used to monitor qualitatively the reaction between TGDDM and PPE terminal group. Figure 4 shows FT-IR spectra of neat PPE, PA6, and TGDDM, respectively. The PPE shows two characteristic bands of the ether at 1023 and 1190 cm^{-1} , corresponding to the C—O stretch as shown in Figure 4(A). The ring stretching of the PPE gives a band at 1609 cm^{-1} . Figure 4(B) shows the characteristic absorption bands of the pure PA6 at 1640 and 1546 cm^{-1} , corresponding to the carbonyl stretching ($\nu_{\text{C=O}}$) and N—H bending ($\nu_{\text{N-H}}$), respectively. Figure 4(C) shows that the epoxy group of TGDDM gives the characteristic absorption band at 907 cm^{-1} . The ring stretching of TGDDM occurs at the absorption band of 1613 cm^{-1} . Figure 5 compares the IR spectra of the PPE/TGDDM = 100/1 mixtures by dry mixing [Fig. 5(A)] and melt blending [Fig. 5(B)]. No reaction is expected from this dry-blended mixture. The weak epoxy characteristic peak (907 cm^{-1}) disappeared after melt blending [Fig. 5(B)]. This result indicates that the reaction between TGDDM and PPE terminal phenolic—OH group may occur. On the other hand, reaction between epoxy and amine has been well recognized.⁴¹ Epoxy groups can react with the $-\text{NH}_2$ and $-\text{COOH}$ terminal groups of PA6 and result in the formation of vari-

ous PA6-*co*-TGDDM and PA6-*co*-TGDDM-*co*-PA6 products.

To further prove that PA6-*co*-TGDDM-*co*-PPE mixed copolymers are indeed produced during a typical melt blending, complicated extractions on this compatibilized blend were carried out to isolate and identify these copolymers as described in Scheme II. For the uncompatibilized PA6/PPE = 30/70 blend, no reaction is expected and no PPE-containing copolymer was found in the final formic acid extracted insoluble residue. A similar result was previously reported by Chambell et al.⁵ The *in situ* reactions among PA6, TGDDM, and PPE during melt mixing may form various PA6-*co*-TGDDM-*co*-PPE copolymers that are insoluble in toluene and in formic acid. This reactively compatibilized PA6/PPE/TGDDM = 30/70/0.5 blend may contain the following possible species: PA6, PA6-*co*-TGDDM, TGDDM, TGDDM-*co*-PPE, PPE, and PA6-*co*-TGDDM-*co*-PPE. Copolymers of PA6-*co*-TGDDM-*co*-PPE are the only components expected to be insoluble on both solvents. The insoluble residue after repeated extractions by toluene and formic acid can be assumed to be those mixed copolymers but requires further identification. The FTIR spectrum of this insoluble residue, assumed to be these PA6-*co*-TGDDM-*co*-PPE copolymers, is shown in Figure 6. Comparing Figure 6 with the spectra of Figure 4(A)–(C), this undissolved residue gives the characteristic bands of the PA6 segment, the carbonyl stretching at 1638 cm^{-1} , and the N—H bending at 1543 cm^{-1} , respectively. Figure 6 also possesses the PPE characteristic C—O stretching of the phenylene ether at 1023 and 1192 cm^{-1} . The ring stretching of the PPE segment at 1610 cm^{-1} is overlapping with the carbonyl absorption band of the PA6 segment at 1638 cm^{-1} . The characteristic epoxy band of the pure TGDDM cannot be detected from the spectrum of this undissolved solid residue, probably due to small quantity or being completely consumed in reactions. Based on the above information, the formation of the desirable PA6-*co*-TGDDM-*co*-PPE copolymers during melt blending has been positively identified. The weight fraction of the undissolved residue was approximately 3.5% of this compatibilized blend. The rest of the added TGDDM was either unreacted or consumed in reacting with one blend component to form TGDDM-*co*-PA6 and TGDDM-*co*-PPE.

Thermal Properties

The compatibility of a polymer blend can be probed by its thermal and crystallization behav-

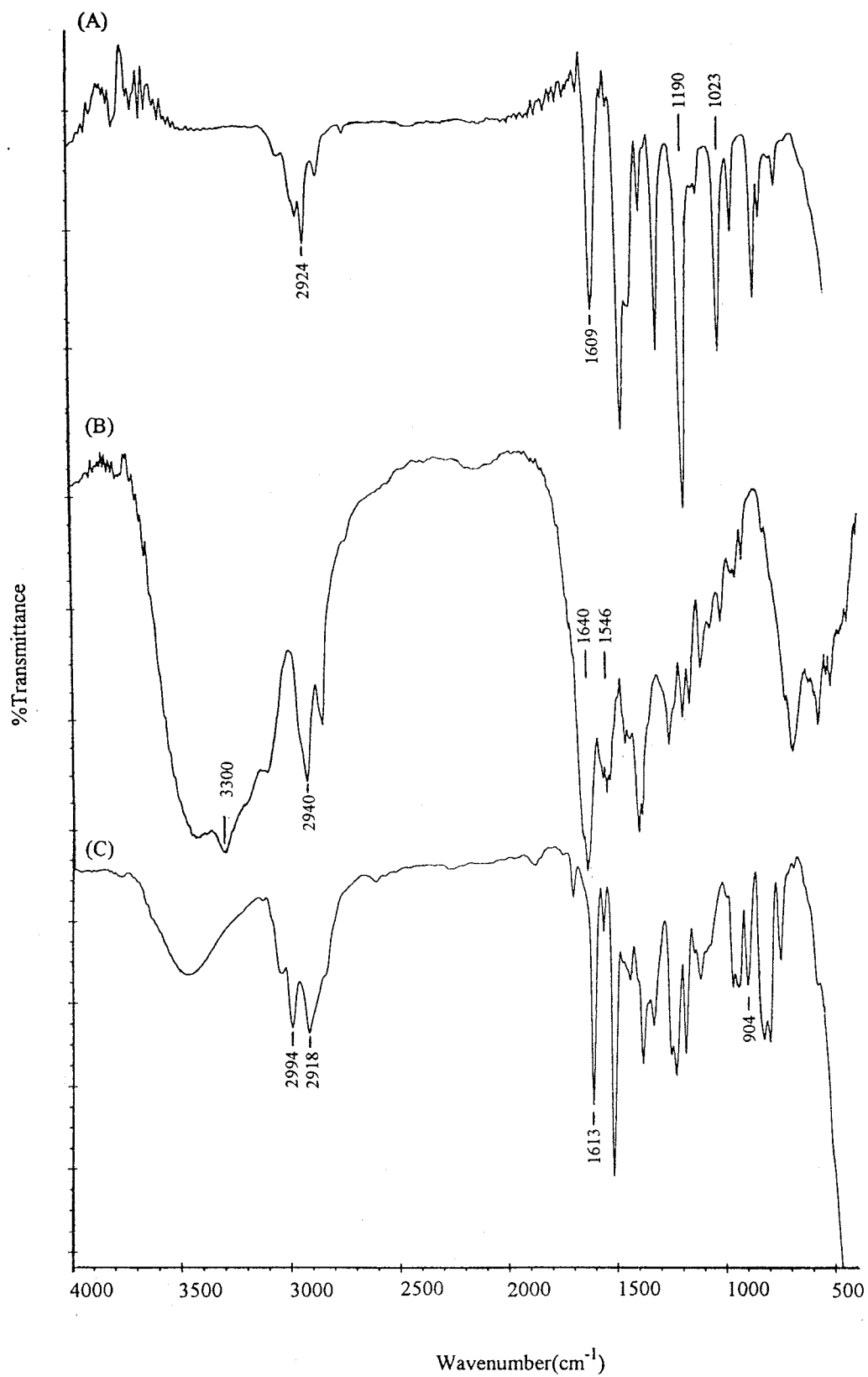


Figure 4. Infrared spectra of neat components, (A) PPE, (B) PA6, (C) TGDDM.

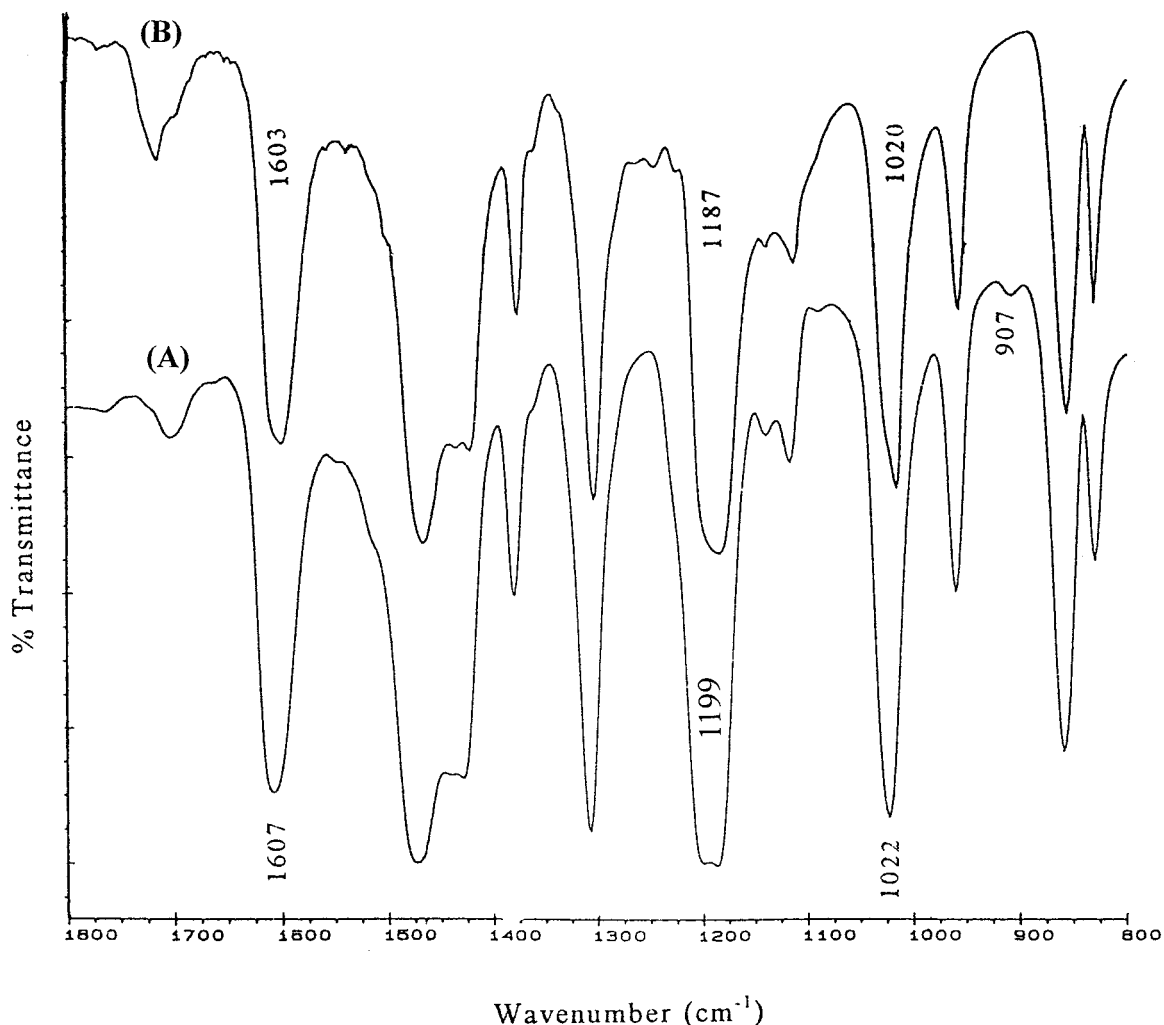


Figure 5. Infrared spectra of the mixtures. (A) Dry-blended PPE/TGDDM = 100/1 mixture, and (B) melt-blended PPE/TGDDM = 100/1 mixture.

iors based on DSC measurements. The DSC heating scans of all the materials tested are summarized in Table III and Figures 7 to 8. Figure 7 demonstrates that the PPE is amorphous with glass transition temperature (T_g) at 218°C (curve B, Fig. 7). PA6 is a semicrystalline polymer with melting temperature at 222°C (curve A, Fig. 7). However, the glass transition of the PPE component in these uncompatibilized and compatibilized PA6/PPE blends cannot be detected because the larger melting peak of the PA6 is overlapped with the glass transition of the PPE. Melt temperatures of PA6 component in the blends, uncompatibilized and compatibilized, are lower than the neat PA6 (Table III and Fig. 7). The crystallinity of the PA6 component in the blend decreases with increasing of the TGDDM content (Table III).

That means the crystallinity of the PA6 in the compatibilized PA6/PPE blends are lower than that in the uncompatibilized blend. Figure 8 shows the DSC cooling scans of PA6 and all the PA6/PPE = 30/70 blends. Crystallization temperature (T_c) of the PA6 component in these uncompatibilized and compatibilized blends are substantially higher than that of the neat PA6 (Fig. 8 and Table III). Peak widths of these blends are substantially smaller than the neat PA6. The presence of PPE in these uncompatibilized and compatibilized blends may act as nucleating agent⁴² to increase crystallization rate of the PA6 component. However, the presence of these *in situ*-formed PA6-co-TGDDM-co-PPE copolymers tends to hinder the PA6 crystallization and results in lower PA6 crystallinity in these compati-

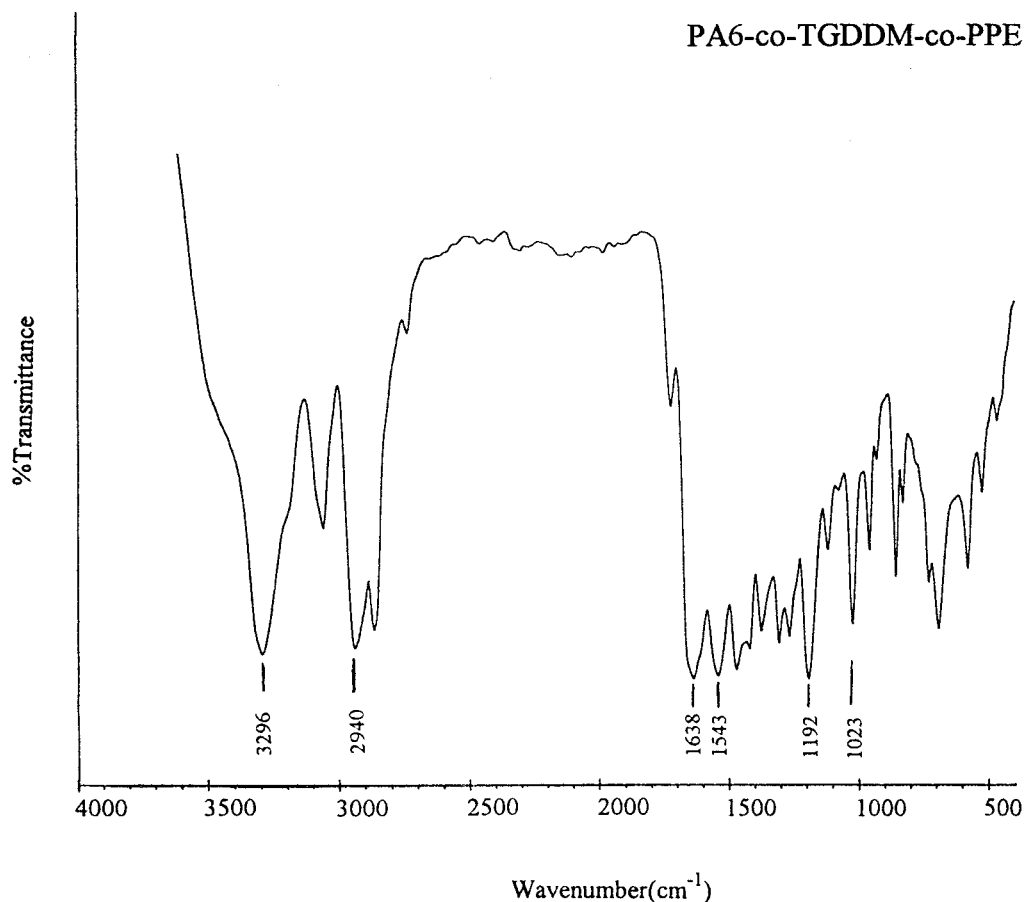


Figure 6. Infrared spectrum of the extracted residue.

bilized blends than the neat PA6 or the uncompatibilized blend.

SEM Morphologies

Melt blended immiscible polymer blends possess complicated morphologies depending on interfacial tension, viscosity ratio, blend constituents, volume fraction, and processing conditions. The most conve-

nient approach to differentiate the morphologies between compatibilized and uncompatibilized blends is by comparing their transmission electron microscopy (TEM) or SEM micrographs. An incompatible blend with higher interfacial tension usually results in coarser domains than the corresponding compatibilized blend. Finer phase domains imply better compatibilization of the blend that has been well recognized. SEM micrographs of those PA6/PPE

Table III. Thermal Properties of the PA6/PPE Blends

Composition	T_g (°C)	$T_{m,PA}$ (°C)	$T_{c,PA}$ (°C)	ΔH_{PA6} (J/g)	X_c (%)
PA6		222	182	95.0	49.8
PPE	218				
PA6/PPE = 30/70		219	196	26.1	45.7
PA6/PPE/TGDDM = 30/70/0.1		221	196	26.4	46.2
PA6/PPE/TGDDM = 30/70/0.3		220	194	25.5	44.8
PA6/PPE/TGDDM = 30/70/0.5		219	191	22.0	38.7

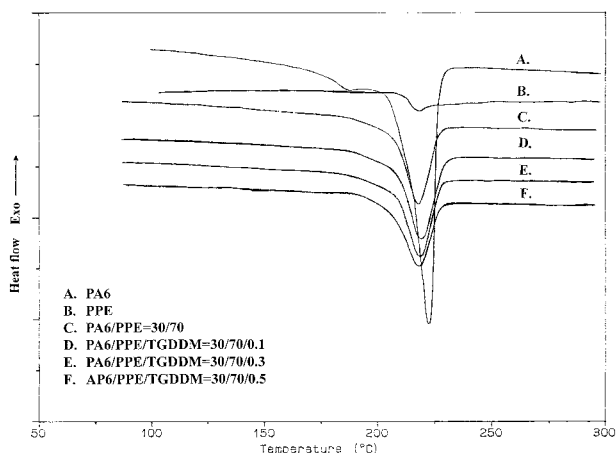


Figure 7. DSC heating scans of PA6, PPE, uncompatibilized and compatibilized PA6/PPE = 30/70 blends. (A) PA6, (B) PPE, (C) PA6/PPE = 30/70, (D) PA6/PPE/TGDDM = 30/70/0.1, (E) PA6/PPE/TGDDM = 30/70/0.3, (F) PA6/PPE/TGDDM = 30/70/0.5.

= 30/70 blends prepared by one-step melt blending, uncompatibilized and compatibilized, are given in Figure 9. This uncompatibilized PA6/PPE = 30/70 blend [Fig. 9(A)] gives a nearly co-continuous phase structure with PA6 particles inclusion within the PPE phase. PA6 is the minor component in this blend but tends to form co-continuously with PPE because the PA6 viscosity is significantly lower than PPE. Figure 9(B) shows the morphologies of the compatibilized PA6/PPE blend containing 0.1 phr TGDDM, where the domain size is fairly close to the uncompatibilized blend [Fig. 9(A)].

Table V lists the estimated equivalent numbers of all reactive groups involved in the PA6/PPE/TGDDM blends. Because the reactivity between epoxy and the amine terminal group of PA6 (PA6-NH₂) is substantially higher than the phenolic-OH of the PPE (PPE-OH) and the significantly higher equivalent numbers of -NH₂ than epoxide (35.3 vs. 9.5), the small amount of the added TGDDM (0.1 phr) is probably totally consumed in reacting with PA6-NH₂ and none or only insignificant amount of the desirable PA6-co-TGDDM-co-PPE copolymer is produced. The reactivities of epoxide with carboxyl terminal group of PA6 (PA6-COOH) and PPE-OH are believed to be comparable. Both compatibilized blends [Fig. 9(B) and (C)] also exhibit co-continuous structure, but the domain size of the blend containing 0.3 phr TGDDM is substantially smaller. The equivalent ratio of epoxide (from TGDDM) to PA6-NH₂ of this particular blend

containing 0.3 phr epoxy is 0.8 (Table V). That means the reaction between TGDDM with PPE-OH is highly possible to form the PA6-co-TGDDM-co-PA6 copolymer, although the reactivity difference is high. The introduction of 0.5 phr TGDDM to the PA6/PPE blend results in the most remarkable change in morphology [Fig. 9(D)]. The PPE phase exists as very fine particles distributed evenly within the PA6 phase. This blend has the epoxide equivalence exceeding the total PA6-NH₂ terminal groups (ratio = 1.35) and the formation of PA6-co-TGDDM-co-PA6 copolymers can be assured. It is interesting to note that PA6 is the minor component in this blend but tends to shift from a co-continuous into a continuous matrix by increasing the compatibilizer quantity. A similar trend in the morphological change has also been observed in our previous report.²⁰

The viscosity increase of the PA6 phase (chain extension) due to higher reactivity between PA6 and TGDDM can reduce the viscosity mismatch and may result in domain size reduction even without considering the formation of the mixed copolymer as a phase compatibilizer to reduce the interfacial tension. If the viscosity mismatch reduction is the only reason to cause the observed domain size reduction, we should expect an even smaller domain size by preblending PA6 with TGDDM then with PPE. To clarify this suspicion, a two-step sequential blending was carried out for direct comparison. SEM micrographs for those

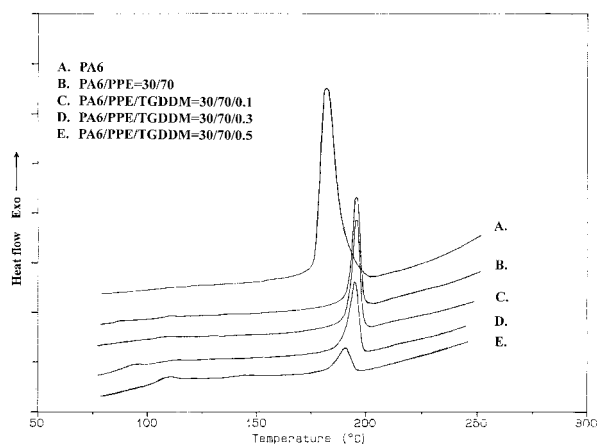


Figure 8. DSC cooling scans of PA6, uncompatibilized and compatibilized PA6/PPE = 30/70 blends. (A) PA6, (B) PA6/PPE = 30/70, (C) PA6/PPE/TGDDM = 30/70/0.1, (D) PA6/PPE/TGDDM = 30/70/0.3, (E) PA6/PPE/TGDDM = 30/70/0.5.

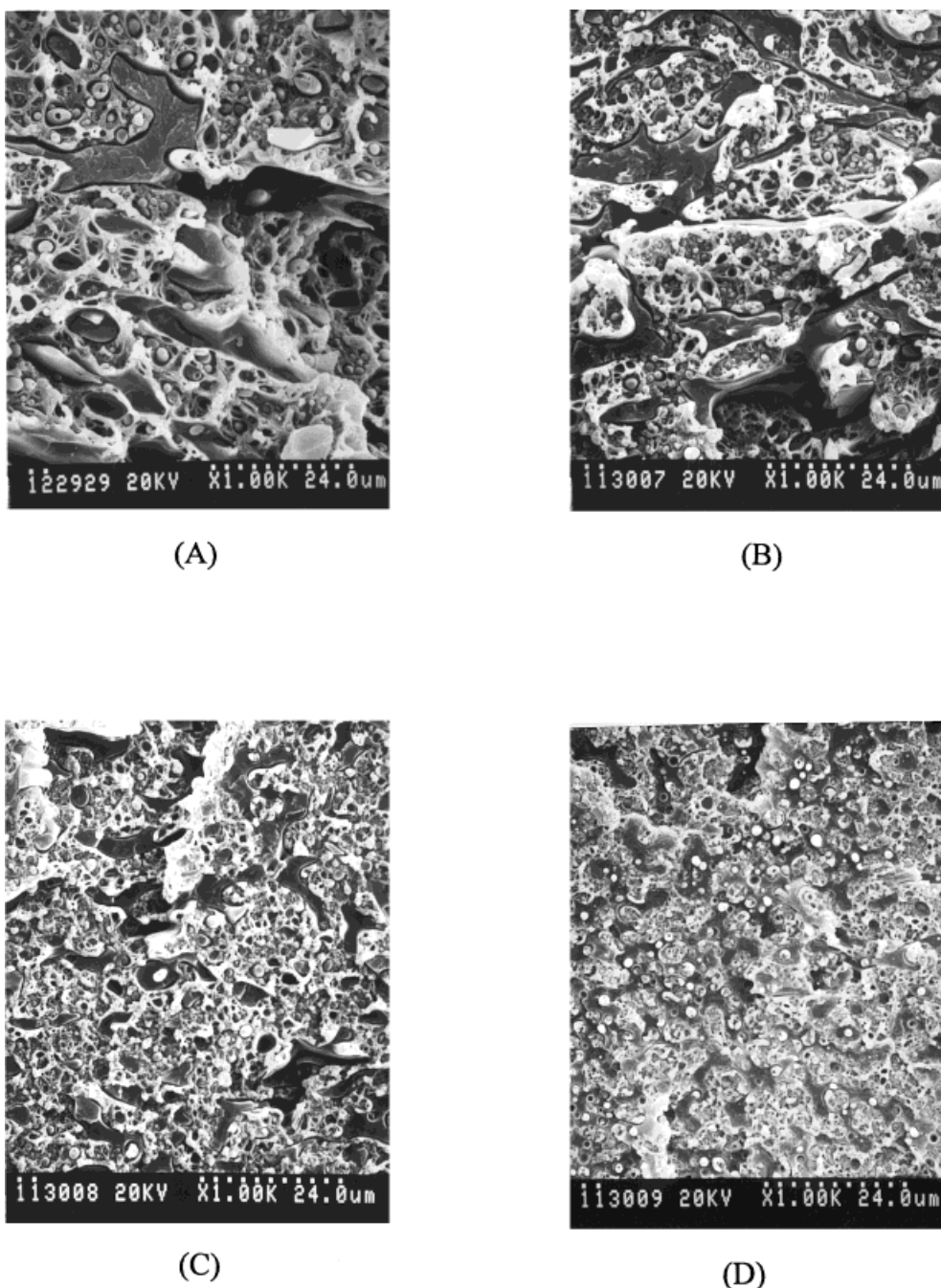
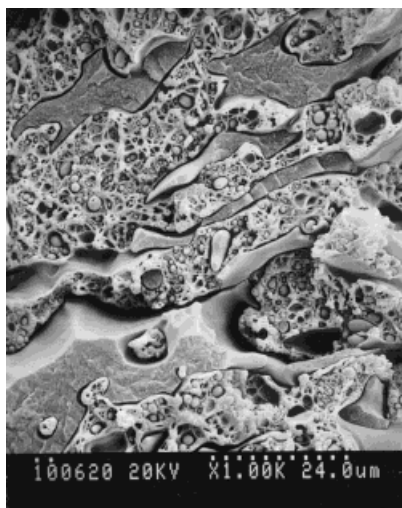


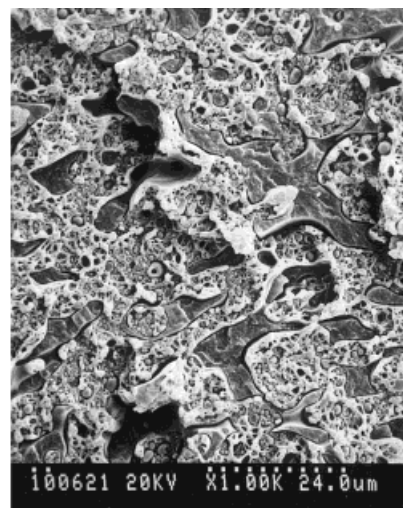
Figure 9. SEM micrographs of the uncompatibilized and compatibilized PA6/PPE = 30/70 by one-step blending, (A) PA6/PPE = 30/70, (B) PA6/PPE/TGDDM = 30/70/0.1, (C) PA6/PPE/TGDDM = 30/70/0.3, (D) PA6/PPE/TGDDM = 30/70/0.5.

blends by two-step sequential blending are given in Figure 10. Figure 10(A)–(C) show the morphologies from the two-step sequential blending, preblending PA6 with TGDDM then with PPE. Relative to those morphologies from the one-step blending [Fig. 9(B)–(D)], the blend containing

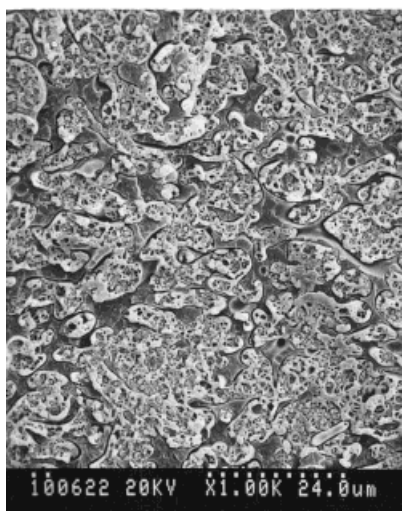
0.1 phr epoxy has about the same domain size. However, the domain sizes of those blends containing higher TGDDM (0.3 and 0.5 phr) are relatively larger than those from the one-step blending. That means reducing viscosity mismatch alone can not accomplish the observed domain



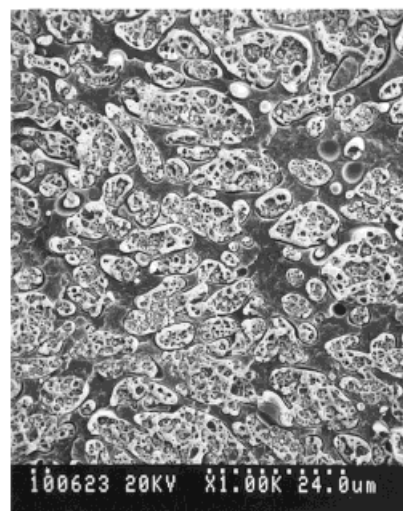
(A)



(B)



(C)



(D)

Figure 10. SEM micrographs of the compatibilized PA6/PPE blends by two-step sequential blending. (A) PA6/PPE/TGDDM = 30/70/0.1, preblending [PA6 + TGDDM] then PPE, (B) PA6/PPE/TGDDM = 30/70/0.3, preblending [PA6 + TGDDM] then PPE, (C) PA6/PPE/TGDDM = 30/70/0.5, preblending [PA6 + TGDDM] then PPE, (D) PA6/PPE/TGDDM = 30/70/0.5, preblending [PPE + TGDDM] then PA6.

size reduction by the one-step blending, and therefore, the *in situ*-formed PA6-co-TGDDM-co-PPE copolymers must play a more important role in reducing the interfacial tension and thus the

domain size. Reduced viscosity mismatch is undoubtedly the other contributor causing smaller domain. Figure 10(D) gives the SEM micrograph of the blend after two-step blending by preblend-

Table IV. Mechanical Properties of PA6/PPE Blends

Composition	Tensile Strength (MPa)	Tensile Elongation (%)	Unnotched Izod Impact (J/M)
PA6/PPE = 30/70	28.2	2.5	111
PA6/PPE/TGDDM = 30/70/0.1	37.5	2.8	171
PA6/PPE/TGDDM = 30/70/0.3	55.4	4.6	586
PA6/PPE/TGDDM = 30/70/0.5	61.2	5.9	2117
PA6/PPE/TGDDM = 30/70/0.1 ^a	38.9	2.9	150
PA6/PPE/TGDDM = 30/70/0.3 ^a	51.1	3.7	226
PA6/PPE/TGDDM = 30/70/0.5 ^a	50.2	3.8	186
PA6/PPE/TGDDM = 30/70/0.5 ^b	48.6	3.4	204

^a Preblending (PA6 + TGDDM) then with PPE.

^b Preblending (PPE + TGDDM) then with PA6.

ing PPE with TGDDM then with PA6. The domain size of this blend is also larger than that from the one-step blending [Fig. 9(D)]. This particular blend had experienced processing difficulty due to extremely higher viscosity, and some thermal degradation of PPE during first-step blending is expected. In this system, a simple one-step blending appears to be a better process to produce better compatibilized blends based on the above morphological observation and later mechanical properties.

Mechanical Properties

Mechanical properties of PA6/PPE blends including tensile properties and unnotched Izod impact strength are summarized in Table IV. When both blend components are notched sensitive, the unnotched impact strength is commonly used to differentiate toughness change through compatibilization. The improvement of the unnotched Izod impact strength of PA6/PPE blends by one-step

blending is so drastic by considering only less than 0.5 phr compatibilizer is employed. The increase of impact strength of the blend containing 0.5 phr TGDDM is about 20 times greater than the corresponding uncompatibilized counterpart. The impact strength of the corresponding blends by two-step blending (Table IV) is substantially lower. The improvements of the tensile strength and tensile elongation of PA6/PPE blends by one-step blending are also very drastic through compatibilization. Again, those blends by two-step blending show less improvement than those by one-step blending on tensile elongation and strength (Table IV). A compatibilized polyblend, in general, has finer phase domain size, greater interfacial contact area, and higher interfacial adhesion than those from the corresponding uncompatibilized blend. The addition of compatibilizer increases the compatibility between PA6 and PPE reflecting in the improvement of the mechanical properties of the blends. The *in situ*-formed PA6-*co*-TGDDM-*co*-PPE copolymers are believed to be responsible for such a highly effective

Table V. Estimated Numbers of Terminal Groups of PA6/PPE/TGDDM Blends

PA6/PPE/TGDDM	Functional Group Equivalence per 10 ⁶ g Sample			
	PA6-NH ₂	PA6-COOH	PPE-OH	TGDDM-Epoxy
30/70/0	35.3	17.6	35.0	0
30/70/0.1	35.3	17.6	35.0	9.5
30/70/0.3	35.3	17.6	35.0	28.5
30/70/0.5	35.3	17.6	35.0	47.5

^a PA6: MN = 17,000 g/mol, assumed equal —NH₂ and —COOH terminal groups.

^b PPE: MN = 20,000 g/mol, assumed one PPE-OH per mol of PPE.

^c TGDDM: MW = 442 g/mol, four epoxides per mol of TGDDM.

compatibilization for the PA6/PPE blends. It takes only about $\frac{1}{10}$ by weight of the compatibilizer used in this study relative to our previous reported system²⁰ to achieve the same high level of mechanical property improvement in compatibilizing the PA6/PPE blends.

CONCLUSIONS

Polyblends of PA6 and PPE are immiscible and incompatible with poor interfacial adhesion and large phase domains. A selected reactive coupling agent can be used to compatibilize certain incompatible blends provided both of the blend components possessing the necessary functional groups. This commercially available tetrafunctional epoxy monomer has demonstrated to be a highly efficient reactive compatibilizer for the incompatible PA6/PPE blends. This epoxy coupler is able to react with both PA6 and PPE simultaneously to form the desirable PA6-co-TGDDM-co-PPE copolymers at the interface. These mixed copolymers containing both PA6 and PPE segments tend to anchor along the interface to function as an effective compatibilizer by reducing interfacial tension and enhancing the interfacial adhesion. The domain size of the compatibilized PA6/PPE blends has been reduced drastically with the increase of the epoxy content. Simple one-step three-component blending has demonstrated to be a more efficient method than the two-step sequential blending in producing a better-compatibilized blend. Additionally, the improvement of the mechanical properties is also drastic after compatibilization. It takes only about $\frac{1}{10}$ by weight of this coupler type compatibilizer relative to the conventional type reactive compatibilizer (SMA) to achieve the same high level of mechanical property improvements of the compatibilized PA6/PPE blends.

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