Reactive Blends of Polyamide 6 with Polyester Elastomer Using Coupling Agents

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ABSTRACT: *In situ* compatibilized melt blends of polyamide 6 (PA-6) with polyester elastomer (PEL) were prepared in a corotating twin-screw extruder using two types of coupling agent (CA): diglycidyl ether of bisphenol A (DGEBA) and 1,4-phenylene bis(2-oxazoline) (PBO). The notched impact strength of PA-6 and PA-6/PEL blends increased with the addition of coupling agent, especially DGEBA, and the maximum impact toughening of the blend was obtained with 0.6 mol % DGEBA, the composition of minimum domain size observed from SEM. Viscosities of the untreated blends increased over those of the base resins at low frequencies. Viscosities of both the base resins and the blends increased with the addition of CA, and the effect was much more pronounced with DGEBA, especially for PA-6 and PA-6–rich blends. The crystallization temperature (T_c) of PEL increased over 10°C, whereas the T_c of PA-6 decreased by 2–3°C in the blends. With the addition of coupling agents, the crystallization melting temperature (T_m) and T_c of PA-6 decreased by up to 5°C with DGEBA, implying that the crystallization of PA-6 is disturbed by the *in situ* formed PA-6–CA–PEL or PA-6–CA–PA-6 type copolymer. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3966–3973, 2004

Key words: melt blends; polyester elastomer; polyamide 6; coupling agent; crystallization

INTRODUCTION

The study of polymer blends and alloys is a subject of considerable interest. The development of new materials by polymer blending has become an increasingly important industrial activity because it is an economically viable and versatile way of modifying some basic properties of existing polymers.[1–4] Much research has been focused on the preparation of miscible polymer blends (i.e., those in which a single phase on a molecular scale is afforded). Several hundreds of polymers that are miscible, either in all proportions or over limited composition ranges, have been discovered.[5–9] However, it is not difficult to achieve a polymer blend consisting of two or more phases with an interfacial energy sufficiently low enough to give a good combination of physical and mechanical properties. In other cases, the polymer components must be "compatibilized" by the addition of appropriate block or graft copolymers that act as interfacial agents.[10–15] It is also possible to form *in situ* block or graft copolymer needed, by reacting the prefunctionalized polymeric components. Sometimes, even if properly compatibilized, a polymer blend needs a further component, usually an impact modifier, to display good mechanical properties. Polyamide 6 (PA-6) has a notch sensitivity relative to impact properties. The notched impact strength of PA-6 can be improved by blending it with an elastomer of a certain level of compatibility.[16–21] The utility of polyamide can be greatly enhanced through functionalization reactions carried out on the polymer melt.

In this investigation, melt blends of PA-6 and polyester elastomer (PEL) were prepared in the presence of coupling agents, 1,4-phenylene bis(2-oxazoline) (PBO) and diglycidyl ether of bisphenol A (DGEBA). The terminal amide group of PA-6 and the acid group of PEL are expected to react with the oxazoline group of PBO and epoxy group of DGEBA. Compatibilizing effects of the *in situ* formed copolymers for the PA-6/PEL blends were studied in terms of rheology, morphology, thermal, and impact properties of the blends.

EXPERIMENTAL

Materials and compounding

Materials used in this study were commercial grades of PA-6 (PA1011, Hyosung) and PEL (KN3355; Kolon Industry, Kumi, Korea). These resins were dried in a hot-air circulating oven at 80°C for 48 h before use. DGEBA and PBO were used as coupling agents. Epoxy groups containing DGEBA and PBO with oxazoline groups were supplied by Kookdo and TCI, respectively, and their chemical structures are given below.

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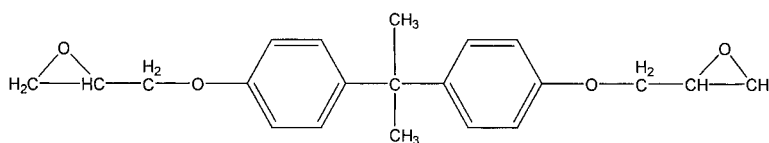
diglycidyl ether of Bisphenol A (DGEBA)
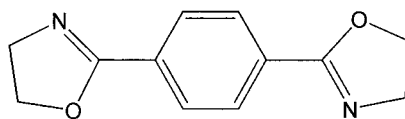
1,4-phenylene bis(2-oxazoline) (PBO)

Blends with the formulations given in Table I were prepared by melt mixing in a corotating twin-screw extruder (Berstorff), operating at 300 rpm and 240–250°C. The extrudates were quenched in cold water after which they were pelletized. Specimens for the Izod impact test were injection molded with the same temperature profile as that for extrusion. Before testing, the materials were dried under vacuum overnight at 80°C to avoid the plasticizing and hydrolyzing effects of humidity. The impact strength was measured by notched Izod impact tester.

Measurements

The rheological properties of the blends were measured using a Rheometrics dynamic analyzer (RDA;

Rheometrics, Amherst, MA) with parallel-plate fixture at 240°C. Thermal analysis was performed using a Perkin–Elmer differential scanning calorimeter (DSC 7; Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 20°C/min. For the morphological structure of the blends, injection-molded specimens were cryogenically fractured in liquid nitrogen and the surfaces were sputtered with gold in vacuum before viewing under scanning electron microscope (SEM). PEL (85/15) and PA-6/PEL (70/30) blends or PA-6 (50/50) blend, respectively, were etched in o-chlorophenol or chloroform for 30 min at 60°C.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the notched Izod impact strength of untreated and coupling agent (0.6 mol % DGEBA and PBO)–treated PA-6/PEL blends. The impact strength of the untreated blend increased with increasing PEL

TABLE I
Formulations of Simple and Compatibilized PA 6/PEL Blends

| Run number	PA 6	PEL	Coupling agent (mol %)
S-PEL 0	100	0	0
S-PEL 15	85	15	0
S-PEL 30	70	30	0
S-PEL 50	50	50	0
S-PEL 100	0	100	0
DG-PEL 0	100	0	DGEBA0.6
DG-PEL 15	85	15	DGEBA0.6
DG-PEL 30	70	30	DGEBA0.6
DG-PEL 50	50	50	DGEBA0.6
DG-PEL 100	0	100	DGEBA0.6
PBO-PEL 0	100	0	PBO .6
PBO-PEL 15	85	15	PBO .6
PBO-PEL 30	70	30	PBO .6
PBO-PEL 50	50	50	PBO .6
PBO-PEL 100	0	100	PBO .6
DGEBA 0.3	70	30	DGEBA0.3
DGEBA 0.6	70	30	DGEBA0.6
DGEBA 1.0	70	30	DGEBA1.0
PBO .3	70	30	PBO .3
PBO .6	70	30	PBO .6
PBO 1.0	70	30	PBO 1.0
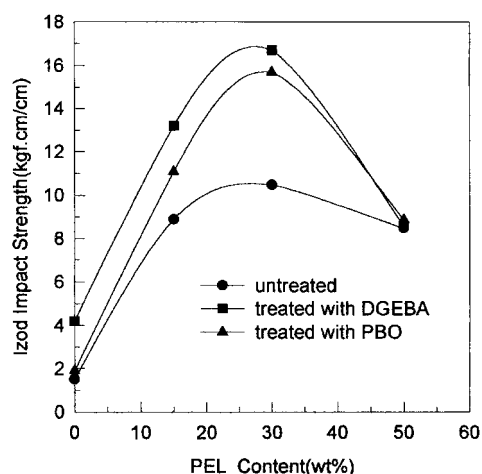
Figure 1 Plot of notched Izod impact strength of untreated and coupling agent (0.6 mol %)–treated PA-6/PEL versus PEL content (wt %).
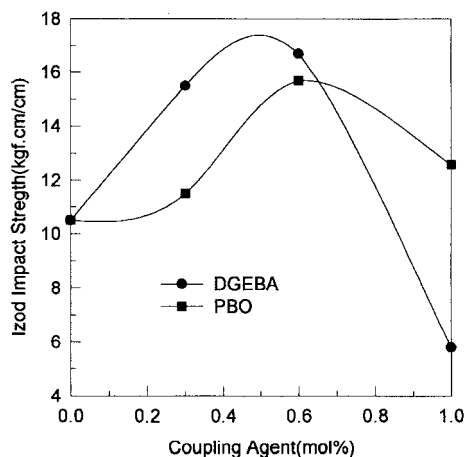
Figure 2 Plot of notched Izod impact strength of PA-6/PEL (70/30) blend versus coupling agent content.

Figure 4 Plot of η^* versus ω of DGEBA (0.6 mol %)–treated PA-6/PEL blends at 240°C.

content up to 30% because of the elastomeric nature of PEL. The impact strength further increased with the addition of CA. This implies that PA-6–CA–PEL type copolymers are formed *in situ* and act as an effective compatibilizer to modify the interfaces. It is seen that the toughening effect is more pronounced with DGEBA than with PBO. Maximum toughening was obtained with 0.6 mol % CA, especially with DGEBA (Fig. 2). Further additions of CA, especially DGEBA, significantly lowered the impact strength, mainly because of the coarsening of the phase structure (discussed below in the section on morphology).

Rheological properties

Figure 3 shows η^* (complex viscosity) versus ω (oscillating frequency) of PA-6/PEL blends as a function of PEL content. Viscosity functions of the blends show greater frequency dependency compared with that of the base resins. In particular, viscosities of the blends
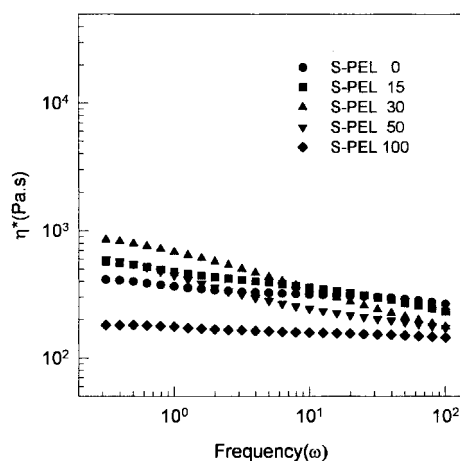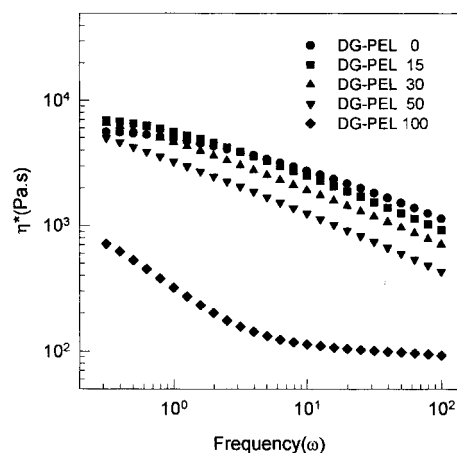
increase over the base resins at low frequency range. With the addition of DGEBA (Fig. 4), viscosities of base resins and the blends increased over approximately one order of magnitude. This is a direct indication of chemical reactions between the coupling agents and base resins. Notably DG–PEL 100 shows viscosity yield at low frequency. With the addition of DGEBA, because the increase in viscosity is much more pronounced with PA-6 than with PEL (15 versus 4 times), the reactivity of terminal –NH$_2$ groups of PA-6 with the epoxy groups of DGEBA seems much higher than that of the –OH groups of PEL with DGEBA. This implies that DGEBA primary contributes to the chain extension of PA-6. On the other hand, viscosities of base resins and the blends slightly increased with the addition of PBO (Fig. 5).

Figure 6 shows the effects of DGEBA content on η^* of PA-6/PEL (70/30) blends. Viscosity increased substantially with increasing DGEBA content. With 1 mol % DGEBA, the viscosity at low frequency increased
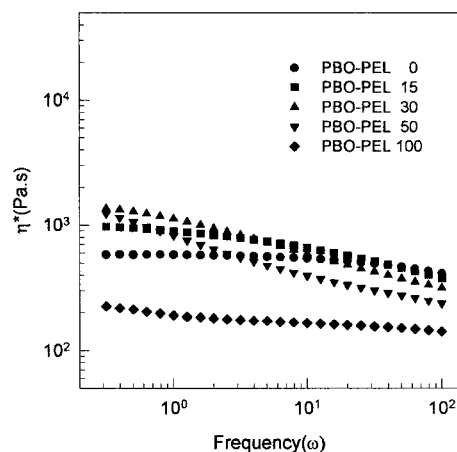

Figure 3 Plot of η^* versus ω of PA-6/PEL blends at 240°C.

Figure 5 Plot of η^* versus ω of PBO (0.6 mol %)–treated PA-6/PEL blends at 240°C.
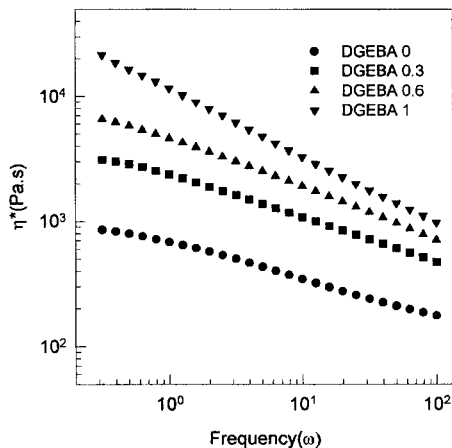
Figure 6 Effect of DGEBA content on η^* of PA-6/PEL (70/30) blend at 240°C.

over 20 times and the viscosity function was nearly a straight line in the log–log plot, like that for crosslinked materials. On the other hand, PBO exerted a much smaller effect compared with that of DGEBA (Fig. 7). With 1 mol % PBO, viscosity approximately doubled at low frequency.

Morphology

Figure 8 shows the SEM micrographs of untreated PA-6/PEL blends. In 85/15 and 70/30 blends, PEL is dispersed and its size increases with its content. On the other hand, PA-6 forms a dispersed domain in 50/50 blends. In immiscible blends, it has often been observed that the dual-phase continuity or phase inversion occurs at a composition given by[22]

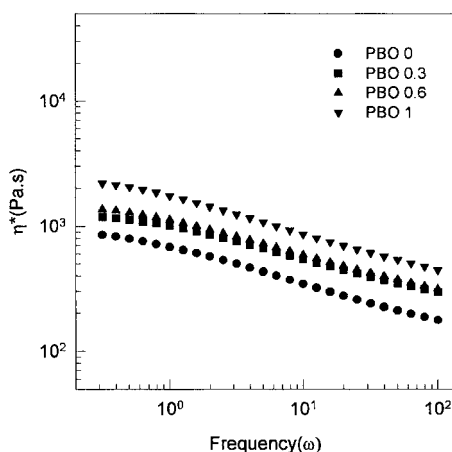$$\frac{\eta_1}{\eta_2} \sim \frac{\phi_1}{\phi_2} \tag{1}$$

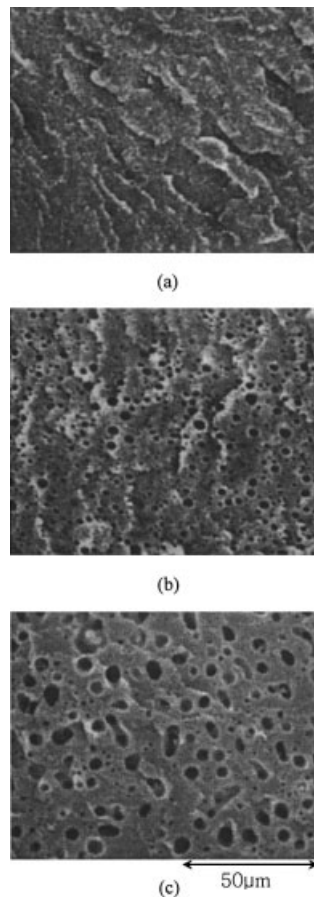**Figure 7** Effect of PBO content on η^* of PA-6/PEL (70/30) blend at 240°C.

Figure 8 SEM micrographs of untreated PA-6/PEL blends: (a) S–PEL 15; (b) S–PEL 30; (c) S–PEL 50.

where η is the viscosity, ϕ is the volume fraction, and subscripts 1 and 2 are the blend components. Assuming that the shear rate at the compounding condition in the twin-screw extruder corresponds to about 10^2 s^{-1}, the melt viscosity of PA-6 is about 1.5 times greater than that of PEL. The above rheology rule is in agreement with the morphology; that is, PEL was dispersed and etched in 85/15 and 70/30 blends, whereas PA-6 was dispersed and etched in the 50/50 blend. The larger PA-6 domain in the 50/50 blend is attributed in part to its large volume fraction compared with that of PEL in 85/15 and 70/30 blends, although it is mainly attributed to the greater viscosity of the dispersed PA-6 phase over that of the continuous PEL phase (Fig. 4). With greater dispersed phase viscosity over the continuous phase, breakup of the dispersed phase becomes difficult. This can be easily understood by assuming stress continuity at the interfaces,[23] according to the following expression:

$$\dot{\gamma}_d = \frac{\eta_c}{\eta_d}\dot{\gamma}_c \tag{2}$$

where $\dot{\gamma}$ is the rate of shear, and subscripts c and d designate continuous and dispersed phases, respectively.
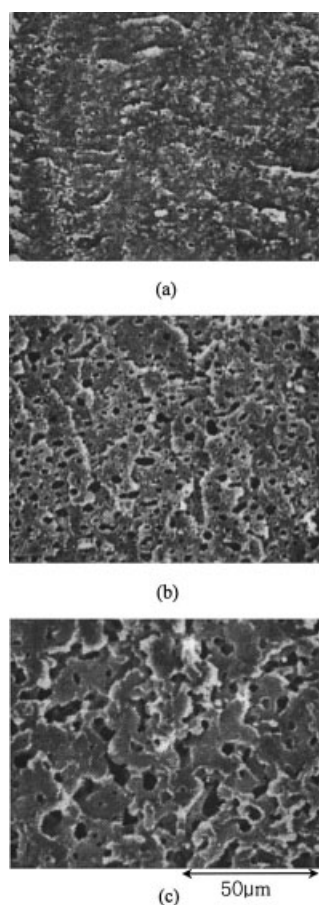
Figure 9 SEM micrographs of DGEBA (0.6 mol %)–treated PA-6/PEL blends: (a) DG–PEL 15; (b) DG–PEL 30; (c) DG–PEL 50.

Figure 9 shows SEM micrographs of 0.6 mol % DGEBA-treated PA-6/PEL blends. Compared with the untreated blends, these blends are dispersed when PA-6 is dispersed. The increased domain size should mainly be attributable to the decreased and increased viscosity ratio of the dispersed phase to the continuous phase, given that the most thorough breakup is often observed with a viscosity ratio of unity.[23] The melt viscosity of PA-6 is increased $\cong$15 times after treating with DGEBA, whereas that of PEL is increased about 4 times. Thus, when PEL is dispersed, the viscosity ratio decreases below that of the untreated one (much greater than unity), resulting in a difficult breakup in both cases.

Figure 10 shows the SEM micrographs of PBO-treated PA-6/PEL blends. Regardless of blend composition, finer dispersions are obtained compared with those of DGEBA-treated blends. This is probably attributable to the compatibilizing effect of copolymers formed *in situ*, given that the viscosities of PEL and PA-6, and thus their ratio, are scarcely changed with PBO treatment.

Figures 11 and 12 show SEM micrographs of PA-6/PEL (70/30) blends with varying amounts of CA. With

DGEBA, the domain size is similar with 0.3 and 0.6 mol % DGEBA, and it increases significantly with 1 mol % DGEBA, probably as a result of the high viscosity ratio. The domain size of PBO-treated blends is much smaller compared with that of the DGEBA-treated blend, and it more or less decreases with increasing PBO content. The decrease of domain size with PBO content implies the formation of copolymers, and the compatibilizing effect seems to operate when the viscosity ratio is not significantly changed.

Thermal properties

Figure 13 shows the DSC thermograms of untreated PA-6/PEL blends. The crystallization temperature (T_c) of PEL increases over 10°C, whereas T_c and T_m (crystallization melting temperature) of PA-6 decrease 2–3°C as the content of the other component increases. It seems that PA-6 provides PEL with nucleating sites because PEL crystallizes in the presence of crystallized PA-6, and PEL induces a dilution effect in PA-6. With the addition of DGEBA (Fig. 14), T_m and T_c of PA-6 decrease by about 5°C. T_c of PEL also decreased by
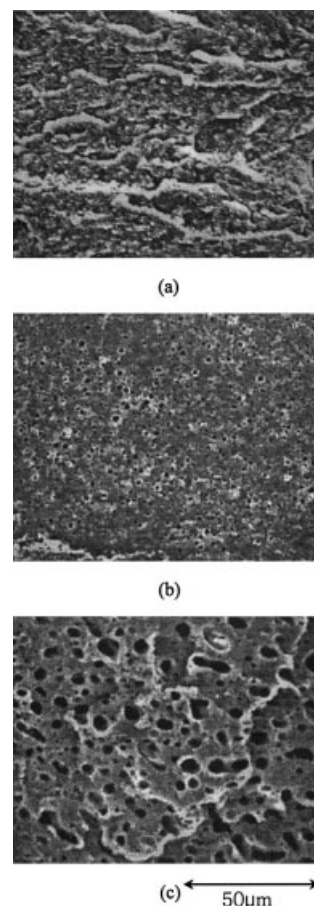

Figure 10 SEM micrographs of PBO (0.6 mol %)–treated PA-6/PEL blends: (a) PEO–PEL 15; (b) PEO–PEL 30; (c) PEO–PEL 50.
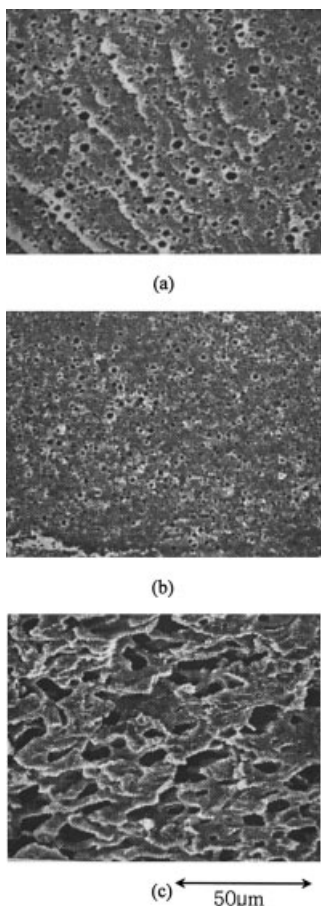
Figure 11 SEM micrographs of DGEBA-treated PA-6/PEL (70/30) blends (in mol %): (a) DGEAB 0.3; (b) DGEBA 0.6; (c) DGEBA 1.0.
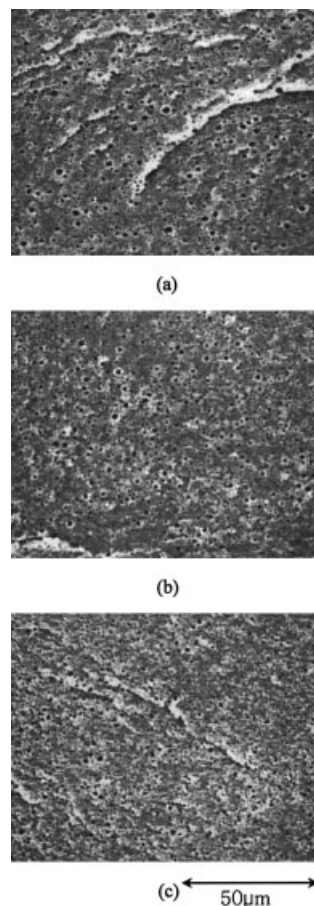

Figure 12 SEM micrographs of PBO-treated PA-6/PEL (70/30) blends (in mol %): (a) PBO .3; (b) PBO .6; (c) PBO 1.0.

several degrees Celsius. This implies that PA-6–DGEBA–PEL-type copolymers are formed *in situ* and disturb the crystallization by bridging the two phases. Accordingly, the heat of fusion and heat of crystallization seem to decrease based on the area of the peaks. A similar effect is observed with PBO (Fig. 15); however, the effect is less pronounced compared with that of DGEBA. T_m, T_c, and the melting peak area of PA-6 in the blend (70/30) decreased with increasing CA content (Figs. 16 and 17), and the effect was not pronounced with DGEBA as it was with PBO. This again indicates that extensive couplings disturb the crystallization of the PA-6 phase.

CONCLUSIONS

Melt blends of polyamide 6 (PA-6) and polyester elastomer (PEL) were subject to *in situ* coupling reactions with the epoxy groups of diglycidyl ether of bisphenol A (DGEBA) and oxazoline groups of 1,2,4-phenylene bis(2-oxazoline). The coupling reactions were not only between PA-6 and PEL, but also between PA-6, PA-6/PEL, and PEL, based on the viscosity increase of the

blends and the base resins. The increase in viscosity was much more pronounced with DGEBA than with PBA, and for PA-6 and PA-6–rich blends, the increase
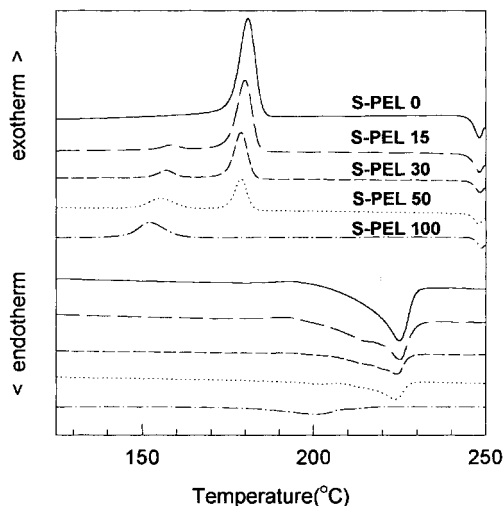

Figure 13 DSC thermograms of untreated PA-6/PEL blends.
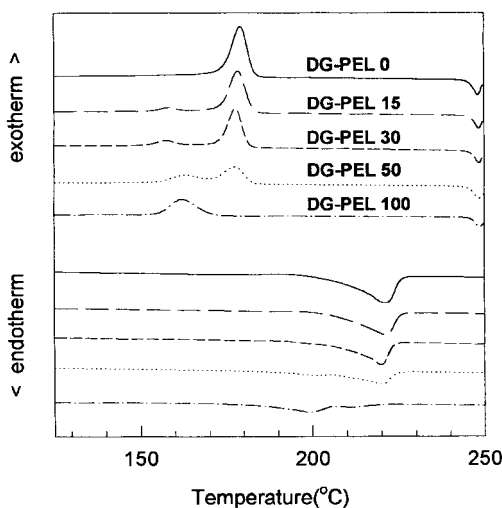
Figure 14 DSC thermograms of DGEBA (0.6 mol %)–treated PA-6/PEL blends.

was indicative of much higher reactivity of epoxy groups with terminal amide groups of PA-6.

The dispersed domains increased in size with DGEBA because of the significantly increased and decreased viscosity ratio of the dispersed phase to the continuous phase. On the other hand, the dispersed phase generally decreased in size with PBO, implying that the compatibilizing effect of *in situ* formed copolymers governs the morphology when the viscosity ratio is only slightly changed upon coupling agent treatment.

T_c and T_m values of PA-6 decreased, and the T_c of PEL increased in the blends. It seems that PA-6 acts as a nucleating agent for PEL, whereas PEL induces a dilution effect in PA-6. With the addition and increase of coupling agent, T_m, T_c, and their peak areas de-
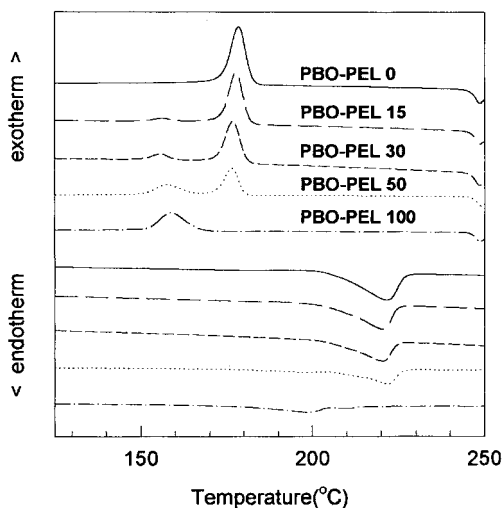

Figure 15 DSC thermograms of PBO (0.6 mol %)–treated PA-6/PEL (70/30) blend.
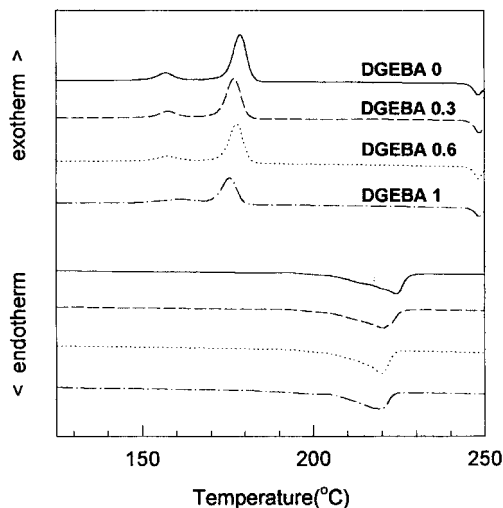

Figure 16 DSC thermograms of DGEBA (0.3–1.0 mol %)–treated PA-6/PEL (70/30) blend.
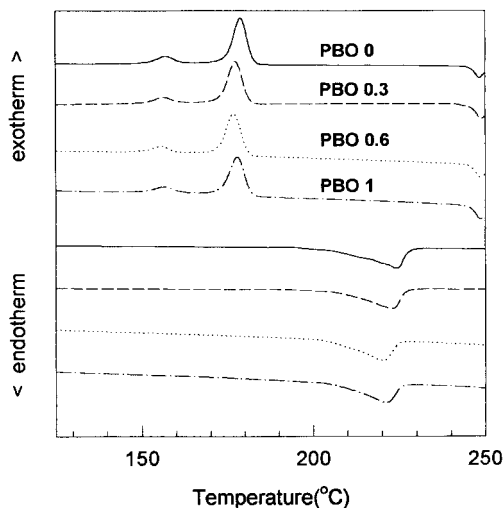

Figure 17 DSC thermograms of PBO (0.3–1.0 mol %)–treated PA-6/PEL (70/30) blend.

creased mainly because of the bridging effect of copolymers formed *in situ*.

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