

<연구논문>

Coupling Agent를 이용한 Polyamide 6와 Polyester Elastomer의 반응동반 블렌드

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Melt viscosity and Morphology of Reactive Blends

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요 약

DGEBA(diglycidyl ether of bisphenol A) 및 PBO(2-1,4 phenylene bis(2-oxazoline))를 coupling agent(CA)로, polyamide 6(PA 6)와 polyester elastomer(PEL)의 용융블렌드를 동방향 이축압출기에서 제조하였다. coupling agent, 특히 DGEBA의 첨가와 더불어 PA 6/PEL 블렌드는 물론 PA 6의 낮치 충격강도가 증가하였으며, 블렌드의 최대 충격강인화는 0.6% DGEBA 즉, 입자크기가 최소인 조성에서 나타났다. 미처리 저주파수 영역에서 블렌드의 용융점도는 기초수지 이상으로 증가하였다. 블렌드 뿐만 아니라 기초수지의 용융점도는 CA의 첨가와 더불어 증가하였으며, 그 효과는 DGEBA, PA 6 및 PA 6-rich 조성에서 더욱 뚜렷하였다.

Abstract—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), viz. diglycidyl ether of bisphenol A (DGEBA) and 1,4-phenylene bis(2-oxazoline) (PBO). Notched impact strength of PA 6 as well as PA 6/PEL blends increased with the addition of coupling agent, especially with DGEBA and the maximum impact toughening of the blend was obtained with 0.6%(by mol) DGEBA, where a minimum domain size was observed from SEM. Melt viscosities of the untreated blends were higher than those of base resins at low frequencies. Viscosities of base resins as well as 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.

Keywords:

1. Introduction

The development of new polymer materials by 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]. Several hundreds of polymers which 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 by reacting the pre-functionalized polymeric components.

Polyamide 6 (PA 6) has notch sensitivity. The notched impact strength of PA 6 can be improved by blending it with an elastomer of certain level of compatibility[16-21]. The utility of polyamide can be greatly enhanced through functionalization reactions.

As a continuation of our earlier works on reactive blends[22-27], melt blends of PA 6 and polyester elastomer (PEL) were prepared with two types of coupling agents viz. 1,4-phenylene bis(2-oxazoline) (PBO) and diglycidyl ether of bisphenol A (DGEBA). The terminal amide group of PA 6 and 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 have been

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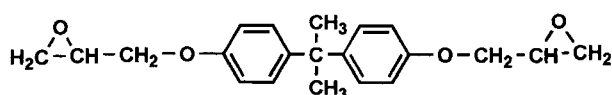
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studied in terms of rheology, morphology and impact properties of the blends.

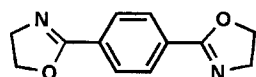
2. Experimental

2.1. Materials and Compounding

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



diglycidyl ether of bisphenol A (DGEBA)



1,4-phenylene bis(2-oxazoline) (PBO)

Blends with the formulations given in Table 1 were prepared by melt mixing in a counter-rotating twin screw extruder (Berstorff), operating at 300 rpm and 240~250°C. The extrudates were quenched in cold water and

Table 1. Formulations of simple and compatibilized PA6/PEL blends

run #	PA 6	PEL	Coupling agent
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	DGEBA 0.6
DG-PEL 15	85	15	DGEBA 0.6
DG-PEL 30	70	30	DGEBA 0.6
DG-PEL 50	50	50	DGEBA 0.6
DG-PEL 100	0	100	DGEBA 0.6
PBO-PEL 0	100	0	PBO 0.6
PBO-PEL 15	85	15	PBO 0.6
PBO-PEL 30	70	30	PBO 0.6
PBO-PEL 50	50	50	PBO 0.6
PBO-PEL 100	0	100	PBO 0.6
DGEBA 0.3	70	30	DGEBA 0.3
DGEBA 0.6	70	30	DGEBA 0.6
DGEBA 1.0	70	30	DGEBA 1.0
PBO 0.3	70	30	PBO 0.3
PBO 0.6	70	30	PBO 0.6
PBO 1.0	70	30	PBO 1.0

pelletized. Specimens for Izod impact test were injection molded with the same temperature profile as extrusion. Prior to testing, the materials were dried under vacuum overnight at 80°C to avoid plasticizing and hydrolyzing effects of humidity. The impact strength was measured by notched Izod impact tester.

2.2. Measurements

The rheological properties of the blends were measured using a Rheometrics Dynamic Analyzer (RDA) with parallel plate fixture at 240°C. For the morphology measurements 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 of 85/15 and 70/30 (PA6/PEL) blends or PA6 of 50/50 blend was respectively etched in o-chlorophenol or chloroform for 30 min at 60°C.

3. Results and Discussion

3.1. Mechanical Properties

Fig. 1 shows notched Izod impact strength of untreated and coupling agent(0.6% DGEBA and PBO) treated PA 6/PEL blends. Impact strength of the untreated blends increases with increasing PEL content up to 30% due to the elastomeric nature of PEL, and further increases 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

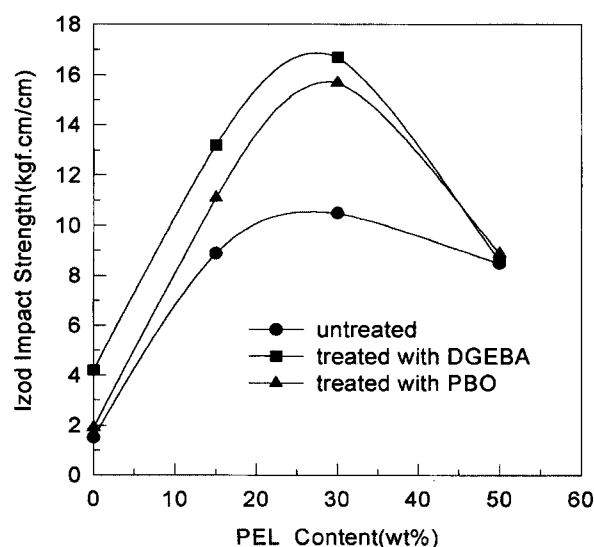


Fig. 1. Notched Izod impact strength of untreated and coupling agent (0.6mol%) treated PA6/PEL blends vs. PEL content.

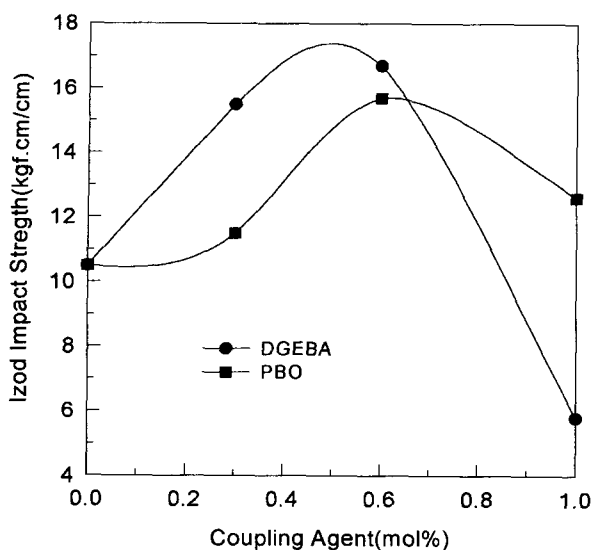


Fig. 2. Notched Izod impact strength of PA6/PEL (70/30) blend vs. coupling agent content.

with PBO. Maximum toughening is obtained with 0.6% CA, especially with DGEBA(Fig. 2). Further addition of CA lowers the impact strength due probably to the plasticizing effect of the unreacted CA.

3.2. Rheological Properties

Fig. 3 shows η^* (magnitude of complex viscosity) vs. ω (oscillating frequency) of PA 6/PEL blends as a function of PEL content. Viscosity functions of the blends show greater frequency dependence as compared with the base resins. Particularly, viscosities of the blends increase over the base resins at low frequency range. With the addition of DGEBA (Fig. 4), viscosities of the base resins and the

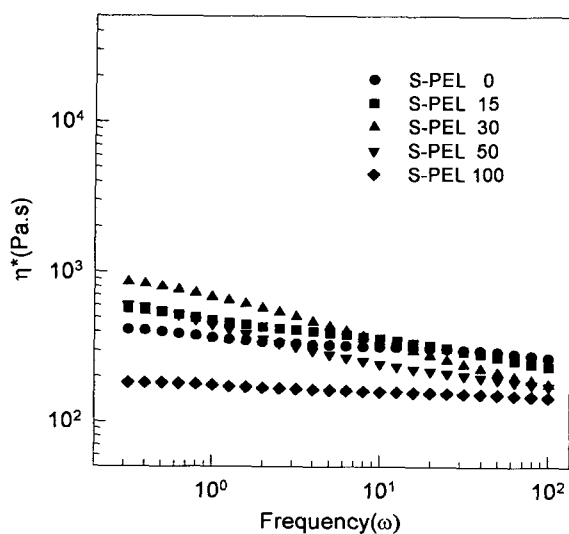


Fig. 3. η^* vs. ω for PA6/PEL blends at 240°C.

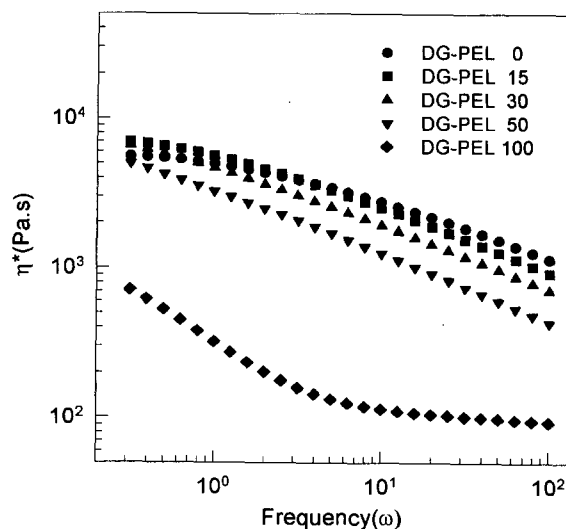


Fig. 4. η^* vs. ω of DGEBA (0.6 mole%) treated PA6/PEL blends at 240°C.

blends increased over approximately one order of magnitude except PEL. This is a direct indication of chemical reactions between the coupling agents and polymers. Notably DG-PEL 100 shows viscosity yield at low frequency. Since, with the addition of DGEBA, viscosity increase is much more pronounced with PA 6 than with PEL(15 times vs. 4 times), the reactivity of terminal (-NH₂) groups of PA 6 with the epoxy groups of DGEBA seems much higher than the (-OH) groups of PEL with DGEBA. On the other hand, viscosities of base resins and the blends slightly increase with the addition of PBO(Fig. 5). Fig. 6 shows the effect of DGEBA content

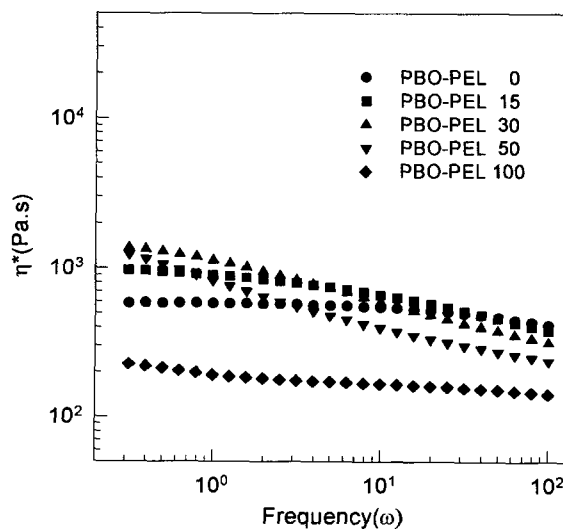


Fig. 5. η^* vs. ω of PBO (0.6 mole%) treated PA6/PEL blends at 240°C.

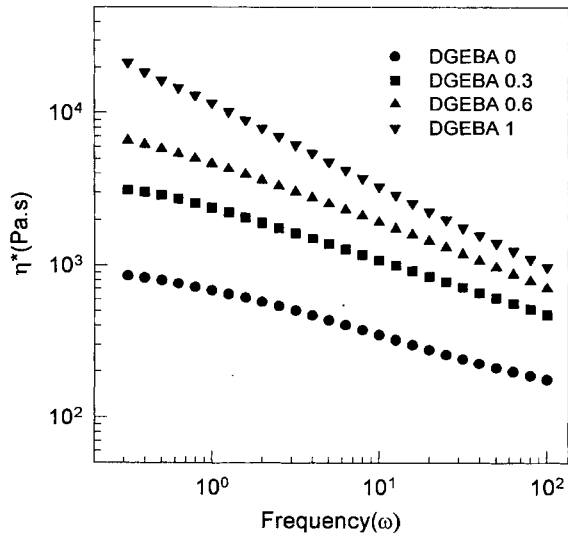


Fig. 6. Effect of DGEBA content on η^* of PA6/PEL (70/30) blend at 240°C.

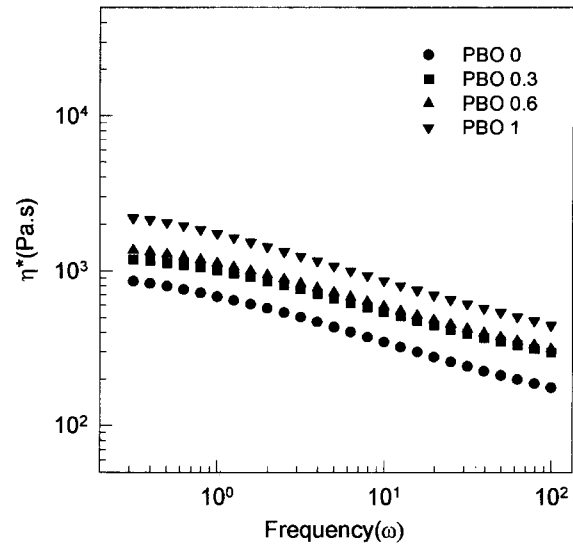


Fig. 7. Effect of PBO content on η^* of PA6/PEL (70/30) blend at 240°C.

on η^* of PA 6/PEL (70/30) blend. Viscosity increases remarkably with increasing DGEBA content. With 1% DGEBA, the viscosity at low frequency increases over 20 times and the viscosity function is nearly a straight line in log-log plot, like the one for crosslinked materials. On the other hand, PBO exerts much smaller effect as compared with DGEBA (Fig. 7). With 1% PBO, viscosity is approximately doubled at low frequency.

3.3. Morphology

Fig. 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 dispersed domain in 50/50 blends. In immiscible blends, it has often been observed that the dual phase continuity or phase inversion occurs at composition given by [28];

$$\frac{\eta_1}{\eta_2} \sim \frac{\varphi_1}{\varphi_2} \tag{1}$$

where η is the viscosity and φ is the volume fraction, and subscript 1 and 2 are the blend components. Assuming the shear rate at the compounding condition in the twin screw extruder corresponds to about 10^2 1/s, melt viscosity of PA 6 is about 1.5 times greater than that of PEL. The above rheology rule is agreed with the morphology, i.e., PEL has been dispersed and etched in 85/15 and 70/30 blends, whereas PA 6 in 50/50 blend is in part due to its large volume fraction as compared with the PEL in 85/15 and 70/30 blends, but it is mainly due to its greater viscosity over the continuous phase (Fig. 4). With greater dispersed phase viscosity over the continuous phase, the breakup of the dispersed phase becomes difficult. This can be easily

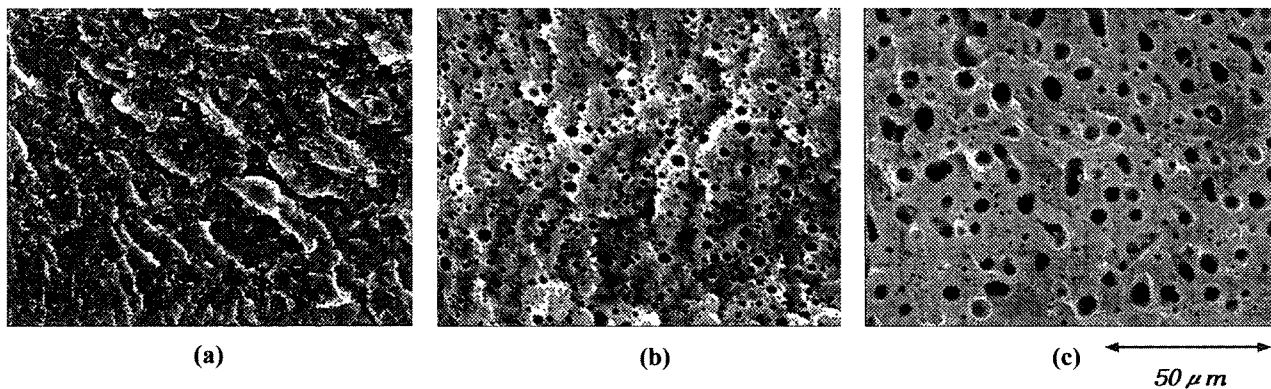


Fig. 8. SEM micrographs of untreated PA6/PEL blends; (a) S-PEL 15, (b) S-PEL 30 (c) S-PEL 50.

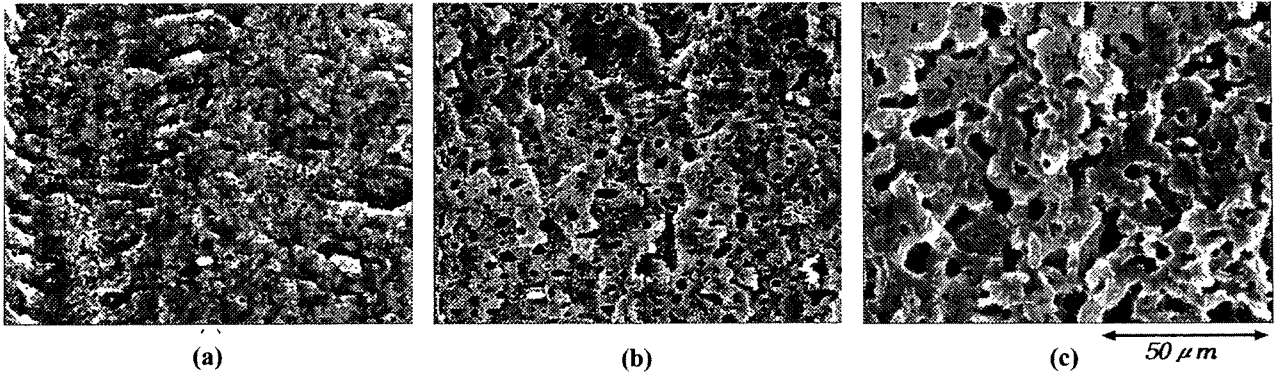


Fig. 9. SEM micrographs of DGEBA (0.6 mole%) treated PA6/PEL blends; (a) DG-PEL 15, (b) DG-PEL 30, (c) DG-PEL 50.

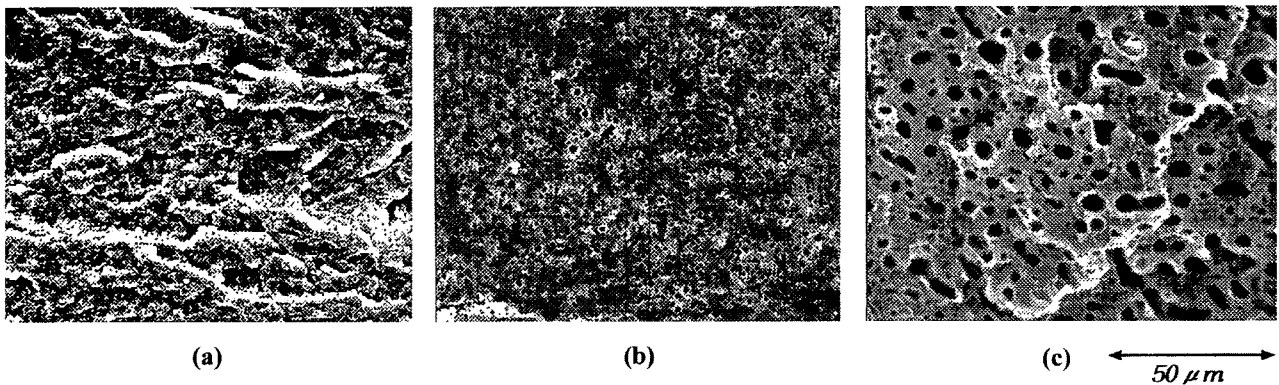


Fig. 10. SEM micrographs of PBO (0.6 mole%) treated PA6/PEL blends; (a) PBO-PEL 15, (b) PBO-PEL 30, (c) PBO-PEL 50.

understood by assuming stress continuity at the interfaces [29]:

$$\dot{\gamma}_d = \frac{\eta_c}{\eta_d} \dot{\gamma}_c \quad (2)$$

where $\dot{\gamma}$ is the rate of shear, and subscripts c and d designate continuous and dispersed phases.

Fig. 9 shows the SEM micrographs of 0.6% DGEBA treated PA 6/PEL blends. When compared with the untreated blends, the dispersed domain slightly increased in size when PEL is dispersed and significantly increased

when PA 6 is dispersed. The increased domain size should mainly be due to the decreased and increased viscosity ratio of the dispersed phase to the continuous phase, since the finest breakup is often observed with viscosity ratio of unity[29]. Melt viscosity of PA 6 is increased over approximately 15 times upon treating with DGEBA while that of PEL about 4 times. So, when PEL is dispersed viscosity ratio decreases below the untreated one and when PA 6 is dispersed viscosity ratio increases above the untreated one, resulting in difficult breakup in both cases.

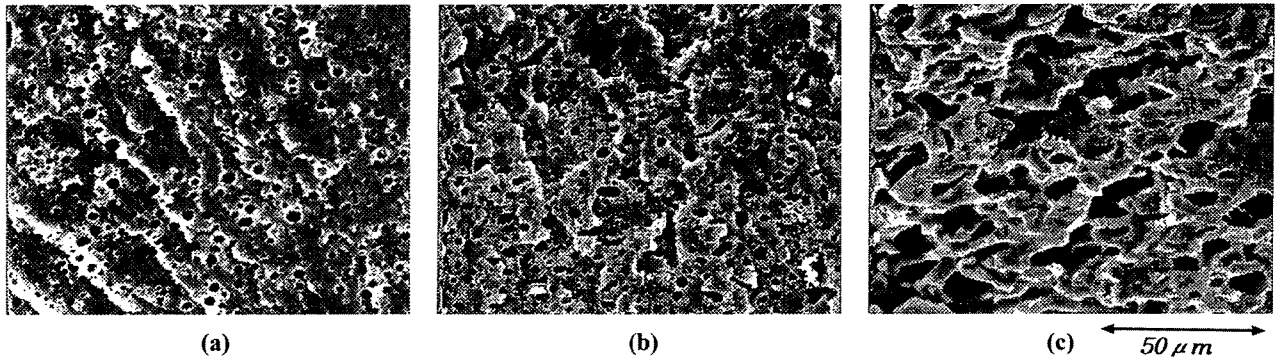


Fig. 11. SEM micrographs of DGEBA treated PA6/PEL(70/30) blends; (a) DGEBA 0.3, (b) DGEBA 0.6, (c) DGEBA 1.0 mole%.

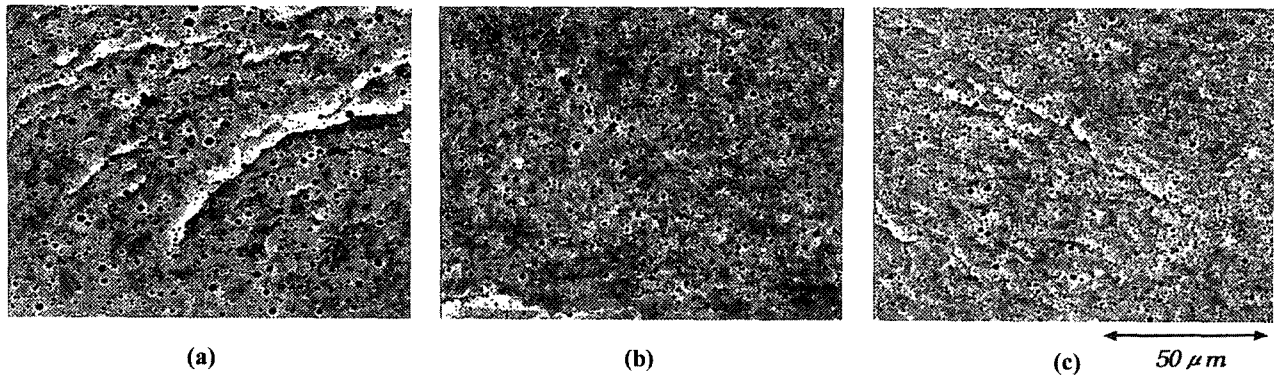


Fig. 12. SEM micrographs of PBO treated PA6/PEL(70/30) blends; (a) PBO 0.3, (b) PBO 0.6, (c) PBO 1.0 mole%.

Fig. 10 is the SEM micrographs of PBO treated PA 6/PEL blends. Regardless of blend composition, finer dispersions are obtained as compared with the DGEBA treated blends. This is probably due to the compatibilizing effect of copolymers formed in-situ since the viscosities of PEL and PA 6, and hence their ratio is not much changed with PBO treatment.

Fig. 11 shows SEM micrographs PA 6/PEL (70/30) blends with different amount of DGEBA. The domain size is minimum with 0.6% DGEBA, consistent with the maximum impact toughening (Fig. 1). The domain size increases with less (0.3%) and more (1%) addition of DGEBA, due respectively to the insufficient coupling reactions and too high viscosity ratio.

Fig. 12 shows SEM micrographs of PA6/PEL(70/30) blends as a function of PBO content. It is seen that the domain size is much smaller as compared with DGEBA treated blends. In addition, reduction in domain size with increasing PBO content is pronounced.

4. 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 1,4-phenylene bis(2-oxazoline). The coupling reactions are not only between PA 6 and PEL, but also between PA 6 and PA 6, and PEL and PEL, based on the viscosity increase of the blends and the base resins. Viscosity increase was much more pronounced with DGEBA than with PBO, and for PA 6 and PA 6-rich blends, indicative of much higher reactivity of epoxy groups with terminal amide groups of PA 6.

The dispersed domains increased in size with DGEBA

due to the significantly increased and decreased viscosity ratio of dispersed phase to the continuous phase. On the other hand, 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 not much changed upon coupling treatment.

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