

에폭시 수지로 상용화된 Nylon 6와 비스페놀-A PC 블렌드의 열적거동

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Thermal Behavior of Nylon 6 and Bisphenol-A Polycarbonate Blends Compatibilized with an Epoxy Resin

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Abstract: Diglycidyl ether of bisphenol-A (DGEBA) was selected as a compatibilizer in Nylon 6 and bisphenol-A polycarbonate (PC) blends. SEM revealed a much finer morphology in the presence of DGEBA. The thermal properties, such as glass transition, melting point, crystallization temperature and rate, of the blends were examined using DSC. Overall, the introduction of DGEBA caused a strong dependence of these thermal properties on the composition due to compatibilization.

Keywords: Nylon 6, polycarbonate, DGEBA.

Introduction

Through continuing developments polymer blends have become a source of new and tailor-made materials. The increased knowledge of the relationships among molecular structures, processing conditions, and final properties has remarkably progressed, as a result, it is often possible to obtain desired chemical composition and phase structures. Within this framework, a relatively recent field of investigation involves the blending of different polymers leading to new materials with synergistic properties.

Nylon 6 and bisphenol-A polycarbonate (PC) are important engineering plastics, each providing outstanding properties in various applications. However, they present some negative aspects that are in some way symmetrical. Nylon 6 is strongly resistant to organic solvents while PC is not; PC is insensitive to moisture while Nylon 6 greatly suffers from its considerable hygroscopicity. Nylon 6 is brittle at low temperatures while PC is somewhat tougher. Taking this into account, it is natural

to consider whether they may complement each other in a blend, overcoming the disadvantages while maintaining the advantages of neat polymers.

Compared with the huge number of patent literatures, the scientific works on the subject of Nylon 6/PC blends are relatively scarce. In their series works, Gattiglia *et al.*^{1–3} showed that Nylon 6 and PC are substantially immiscible. Blends show always two glass transition temperatures and their morphologies are characterized by two well-defined homophases of Nylon 6 and PC. As a result, the mechanical properties are poor and the elastic modulus and the strength at break much inferior to those of the neat constituents. Nevertheless, for blends containing very low PC percentage (5 wt%), chemical reaction between two polymers is probable, if suitable mixing conditions are applied. It was suggested that at high temperatures and long mixing times, Nylon 6 and PC chemically react forming Nylon 6/PC copolymers that act as a compatibilizer. The decrease in T_g of PC as well as slower crystallization kinetics of Nylon 6 would indicate the presence of some interactions between the two polymers. Similar results have been obtained by several works.^{4–9}

Polymers containing ether groups show some miscibility

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with Nylon 6.¹⁰ For example, Costa *et al.*^{11–13} proposed that when the poly(propylene oxide) (PPO) interacts with the Nylon 6, the compatibility of the Nylon 6–PPO blends is improved due to hydrogen bonding between C=O and C–OH groups of PC and PPO, respectively.

The alloy of Nylon 6 and PC is an old story, which is well known and commercialized. However, although the generation of Nylon 6/PC block copolymer was observed,^{1,2} the effect of compatibilization and plasticization were marginal and fine dispersion of the two components was not achieved. In addition, the requirement for long mixing time and high mixing temperatures were not good for practical processing. As a result, the compatibilization of this system is worth to further exploration. In this work, an epoxy resin, diglycidyl ether of bisphenol–A (DGEBA) is selected as a compatibilizer between Nylon 6 and PC. The terminal epoxy group on DGEBA may react with the terminal amino groups on Nylon 6, the bisphenol–A on DGEBA may produce strong interaction with the same moieties on the PC and thus improving the compatibility of the systems. As the first part of this work, the morphology and thermal behavior are investigated through DSC and SEM micrographs.

Experimental

Materials. The polymers used as starting materials were commercial grade products: bisphenol–A polycarbonate (Makrolon 2605, $M_w=35000$) and Nylon 6 (Durethan B30S, $M_w=40000$) were from Bayer Ltd. Diglycidyl ether of bisphenol–A (DGEBA, trade name E51, $M_n=1700$) was from WUXI resin manufacturer, China. Chloroform and formic acid were commercial reagents from Beijing HONGXING chemical Corp. All polymers and reagents were used as received without further purification.

Blends Preparation. Nylon 6/PC blends with and without DGEBA were prepared by melt blending using a twin-screw extruder. The die temperature was 250 °C. The extrudate 1 mm in diameter was cut to pellets about 3 mm long, which was employed in the subsequent measurements. The content of DGEBA was exclusively 1 wt part per one hundred wt parts of Nylon 6 plus PC. The homopolymers, Nylon 6 and PC, were carefully dried in vacuum at 110 °C overnight. The weight ratio of Nylon 6 to PC ranged from 80/20 to 20/80 wt/wt. All samples were stored in desiccator under P_2O_5 before examination.

Characterization and Measurements. The melting point (T_m), crystallization (T_c), and glass transition (T_g) temperatures were measured with a Perkin–Elmer DSC 2 differential scanning calorimeter. Specimens, about 5 mg by weight,

underwent the following thermal cycle: heating at 10 °C/min from 40 to 270 °C, holding for 3 min at 270 °C, cooling at 10 °C/min to room temperature to perform the non-isothermal crystallization. T_m and T_c were determined as peak temperatures; T_g was recorded in heating run as the temperature corresponding to the midpoint of the specific heat change. The morphology of the blends was observed after selective dissolution by either formic acid or chloroform using scanning electron microscopy (SEM, S-250, UK, Cambridge). Wide-angle x-ray diffraction patterns (WAXD) were obtained from a diffractometer Rigaku D/max-2400 at room temperature using copper filtered Cu K_α radiation (40 KV, 200 mA). Impact properties of the blends were tested with an impact tester (XJC-50, CHENGDE, China) according to ASTM D256. For all the above measurements, the samples were dried at 110 °C overnight before examination.

Results and Discussion

Glass Transition Temperature. The heating DSC traces were presented in Figure 1. The figure on each trace denoted the

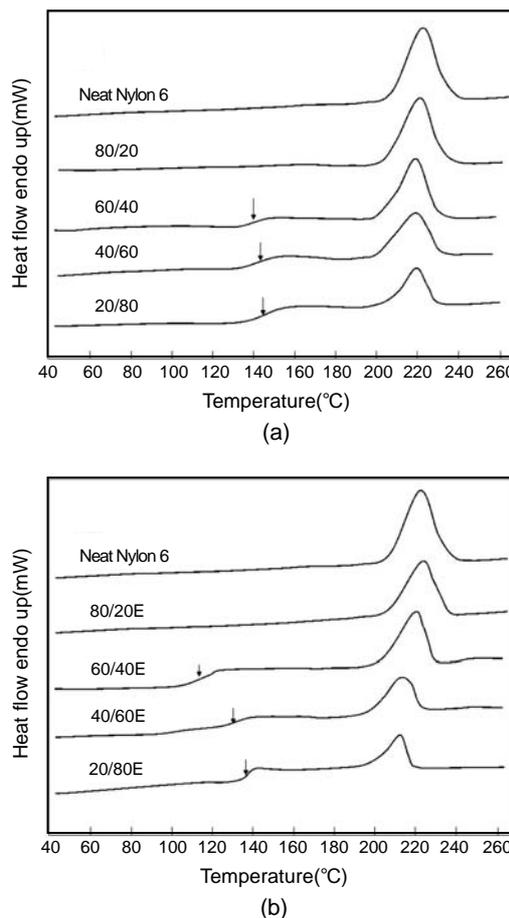
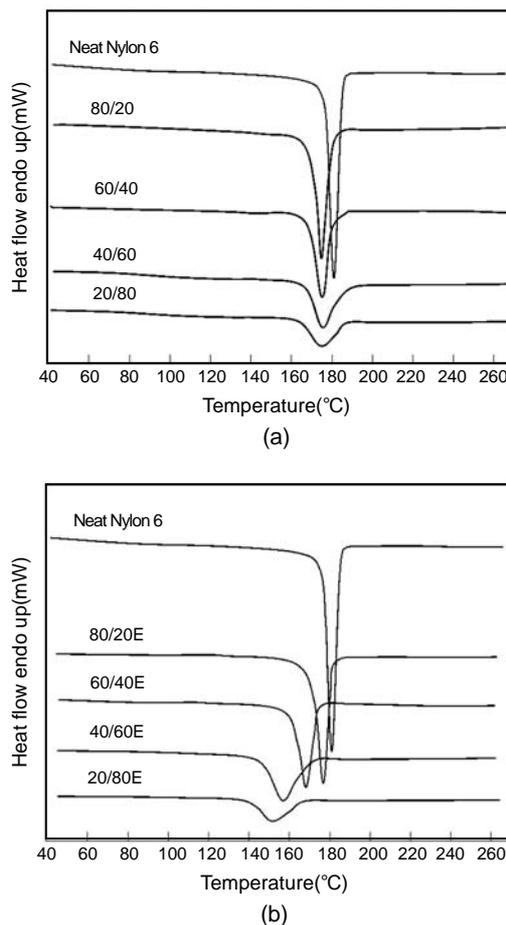


Figure 1. Heating DSC traces of Nylon 6/PC blends.

Table 1. T_g Values of PC for Blends from DSC Measurements

Nylon 6/PC (w/w)	T_g value (°C)	ΔC_p (J/g. °C)	$\Delta C_p /$ (J/g PC. °C)
60/40	140	0.116	0.291
40/60	144	0.178	0.297
20/80	145	0.235	0.294
0/100	149	0.303	0.303
60/40E	116.2	0.138	0.344
40/60E	129.5	0.217	0.362
20/80E	138.7	0.313	0.391

weight ratio of Nylon 6 to PC, with the letter “E” denoting the presence of DGEBA. Because of the relatively high degree of crystallinity of Nylon 6, the changes in T_g value of Nylon 6 was not sensitive to DSC measurements, even not sensitive to DTMA measurements.¹ Accordingly, such values were considered constant in Nylon 6/PC blends, only the T_g value of PC was measured in this work, which was listed in Table 1. Also for the sensitivity, DSC cannot detect clearly T_g of PC when its concentration was 20% by weight. Nevertheless, the general features correspond satisfactorily. As reported that except for very low PC contents (below 5 wt%), Nylon 6 and PC are generally immiscible.¹⁴ In this case, the T_g value of PC should not be affected by the presence of another phase. Indeed, when the compatibilizer DGEBA was absent, the T_g of PC phase diminishes only slightly on increasing Nylon 6 content. The change in specific heat can also be considered constant. This behavior suggested that Nylon 6 was only slightly soluble in PC, the solubility was too small to justify the observed T_g reduction. However, in presence of DGEBA, both the T_g value and change in specific heat decreased steadily and continuously with increasing Nylon 6 content. Compared between the T_g s of the same composition, the one with DGEBA was considerably lower than that without DGEBA, indicating the strengthened interaction between Nylon 6 and PC induced by the compatibilizer. The T_g value of Nylon 6 was reported around 50 °C, such interaction would definitely reduce the T_g of PC to a lower level. This statement was based on a consideration that PC interacts with non-crystalline phase of Nylon 6 only. If PC segments interacted with also the crystalline phase, its T_g value would have been increased instead of decreased. However, taking account of the chemical nature of the two components and the compatibilizer, the connection of Nylon 6 chains and DGEBA could only occur at the ends of the chains, which possess different structure compared with the repeating units, and could never be embedded in the bulk crystal. For this reason, the interaction between PC and crystalline phase of Nylon 6 could be neglected.

**Figure 2.** Cooling DSC traces of Nylon 6/PC melts.**Table 2.** The Nonisothermal Behavior of Nylon 6 in Nylon 6/PC Blends

Nylon 6/PC (w/w)	T_c (°C)	Width of half height (°C)	ΔH (J/g Nylon 6)
100/0	181.9	4.4	62.0
80/20	178.2	4.9	68.9
60/40	178.1	7.2	69.8
40/60	177.7	10.9	68.3
20/80	176.2	12.5	67.5
80/20E	176.8	5.5	59.4
60/40E	164.6	8.4	62.3
40/60E	156.8	11.6	60.4
20/80E	151.6	13.2	58.1

Crystallization Kinetics. The crystallization kinetics was studied in nonisothermal conditions, and the DSC traces were presented in Figure 2. Nylon 6 is able to crystallize whatever the blend composition. Three parameters were measured and presented in Table 2, that is, crystallization temperature, width of half height of the exothermic peak, and the heat of crystallization which representing the degree of crystallinity. One may notice that the nonisothermal crystallization temperatures possessed a dependence on PC concentration,

whether the compatibilizer was used or not. When DGEBA was absent, the crystallization temperature seemed independent of the PC concentration, although a slight decrease could be identified. In contrast, the compatibilizer caused a serious reduction in crystallization temperature with increasing PC content: about 30 °C of reduction when the PC content increased from 20 to 80 wt%. A parallel effect was the crystallization rate, characterized by the width of half height of the exothermic peak. The larger the width, the slower the crystallization rate. It was equal to say that the crystallization rate became slower as the content of PC increased. In the case with compatibilizer, the slowing down of crystallization rate was more obvious. Several authors^{15,16} have shown that the crystallization rate was reduced when partial miscibility between the two polymers in the melt occurs. This explanation was suitable for our case when the compatibilizer was present. However, when the compatibilizer was absent, there was hardly partial compatibility. For incompatible blends, others¹⁷ suggested that the crystallization rate reduction was due to the increase of blend melt viscosity. However, global viscosity of the system had hardly influence on the local diffusion processes, especially where Nylon 6 formed a continuous phase. As a result, as indicated by the data in Table 2, the influence was just marginal.

It is interesting to note that the crystallization heat, which reflected the degree of crystallinity, of Nylon 6 in the incompatible blends was somewhat higher than that in neat Nylon 6, whereas those in compatibilized blends were comparable with or a little lower than that of neat Nylon 6. Such phenomenon was related to the morphology of the blends, for this reason we are to provide the explanation in the sub-section of morphology.

Melting Behavior. Table 3 collected temperature and enthalpy of melting recorded for as-mixed samples (shown in Figure 1). The data referred only to the Nylon 6 phase, since PC did not crystallize from the melt. The data of incompatible blends showed negligible dependence of T_m on PC content. It

Table 3. The Melting Behavior of Nylon 6 in Nylon 6/PC Blends

Nylon 6/PC (w/w)	T_m	ΔH_m (J/g blend)	ΔH_m (J/g Nylon 6)
100/0	222.8		56.7
80/20	221.4	44.8	55.9
60/40	220.1	37.6	62.7
40/60	219.6	24.1	60.3
20/80	220.6	12.3	61.6
80/20E	222.8	37.8	47.3
60/40E	220.1	33.3	55.5
40/60E	216.6	21.3	53.3
20/80E	211.8	10.8	54.2

was easy to explain because the melting point was only controlled by morphological effects (lamella thickness, defects, spherulitic morphology) in the present case. The immiscibility of the two components minimized the interaction between different segments, resulting in the independent crystallizing behavior of Nylon 6 phase. However, a weak effect of the PC content could be identified in the data of compatibilized blends. This is a necessary result of the strengthened interaction between PC and DGEBA segments attached to the ends of Nylon 6 chains, which depressed the movement of Nylon 6 segments resulting in less-perfection of the crystallization. The resulted thinner lamella and defects may reduce slightly the melting point. Wide angle x-ray diffraction (WAXD) data demonstrated such slight effects.

Nylon 6 exhibits basically two crystalline modifications, namely the α -phase and the γ -phase, both phases exhibit a monoclinic structure.¹⁸ Crystallizing Nylon 6 from the molten state generally leads to the formation of the α -phase. In this work, all the samples gave rise to similar WAXD spectra and some typical ones were presented in Figure 3. One may notice that two peaks located around 19~20° and 23° (2θ) were

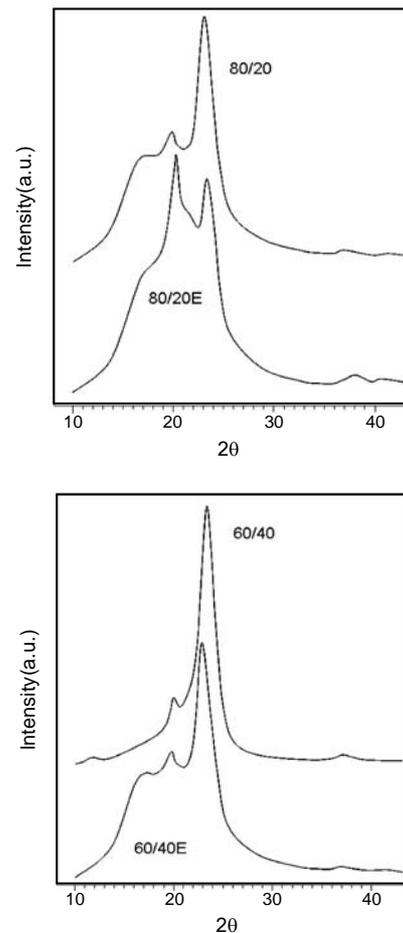


Figure 3. Typical diffraction profiles of Nylon 6/PC blends.

Table 4. Diffraction Angles and d -Spacings of the Nylon 6/PA Blends

Nylon 6/PC (w/w)	$\alpha(200)$		$\alpha(002,202)$	
	2θ ($^\circ$)	d (nm)	2θ ($^\circ$)	d (nm)
20/80	20.060	0.442	23.621	0.376
20/80E	19.884	0.446	23.500	0.378
40/60	20.100	0.441	23.661	0.376
40/60E	19.861	0.447	23.442	0.379
60/40	20.137	0.441	23.500	0.378
60/40E	20.019	0.443	23.240	0.382
80/20	20.462	0.434	23.920	0.372
80/20E	19.484	0.455	23.441	0.379

distinguishable, which could be indexed as 200 and 002/202 reflections by setting the lattice constant a as the hydrogen bond direction and c as the chain axis, respectively. The calculated d_{200} and $d_{002/202}$ spacings (between the respective crystallographic planes) were listed in Table 4. Because the perfect α -phase of Nylon 6 exhibits d -spacings 0.37 and 0.44 nm,¹⁹ one may judge the perfection of crystallization in each sample from the deviation of the d -spacings from the ideal values. It was clear that all the d -spacing values for the compatibilized blends were slightly more deviated from the ideal values, indicating the less perfect crystalline and thus lower melting points.

As in the case of crystallization kinetics, the dependence of the ΔH_m , the melting heat, on composition was difficult to be simply sorted out, the data just stated that the compatibilization caused a lower degree of crystallinity. The reason would be similar to that for the melting point: the stronger interaction between different components resulted in less perfection of crystallization. However, for the phenomenon that the blending did not reduce, or even enhance the degree of crystallinity, a detailed explanation would be given after the examination of the morphology.

Morphology. Figure 4 showed the morphology of the samples after selective dissolution, by either chloroform or formic acid. The insoluble continuous phase remained and thus the phase information could be confirmed by scanning electron microscopy. Without DGEBA the compatibilizer, the blends gave rise to either sea-island or bi-continuous morphology. The PC phase kept continuous in all concentration range studied, whereas Nylon 6 phase transformed from dispersed to continuous phase with increasing content. Figure 4(c1) indicated that the composition of Nylon 6/PC=40/60 (wt/wt) could be considered as the crossover for Nylon 6 component from dispersed to continuous phase. The PC constituted the continuous matrix even at concentrations lower than 20%; only at very low concentration could it be efficiently reduced to small particles. This could probably be explained as the crystallization tendency of Nylon 6: during the

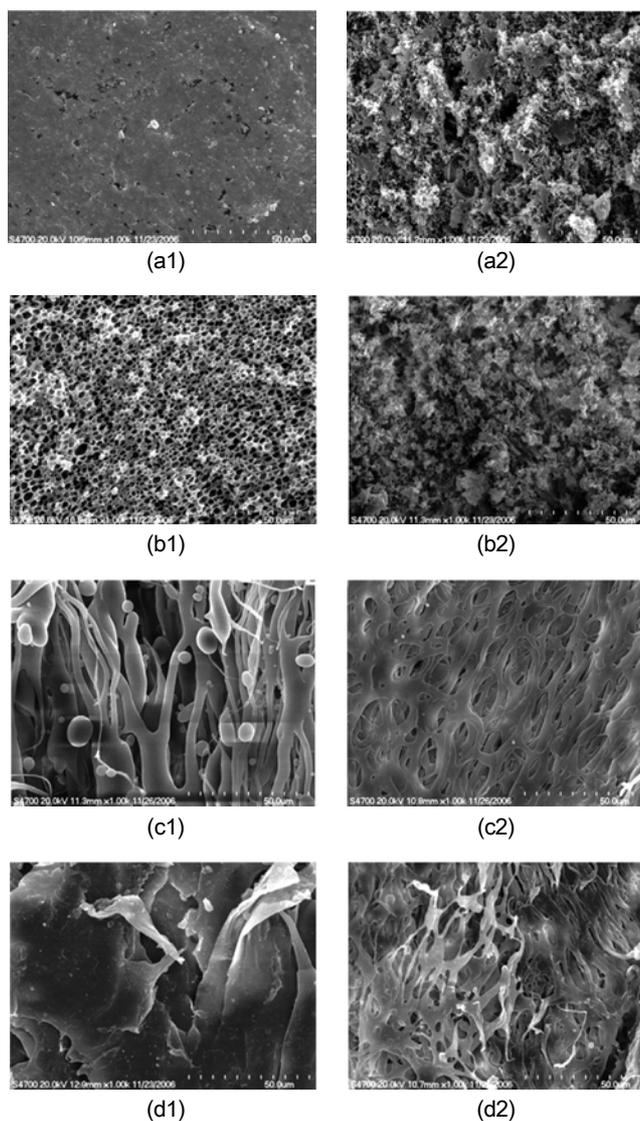


Figure 4. SEM micrographs of phase morphology of Nylon 6/PC blends. Nylon 6/PC wt ratio=(a) 20/80, (b) 40/60, (c) 60/40, (d) 80/20. 1: without DGEBA; 2: with DGEBA. a,b: after selective dissolution by formic acid, c,d: after selective dissolution by chloroform.

crystallization, the occupied volume of Nylon 6 became contracted and leaving free space for the PC species.

When DGEBA was introduced, the sea-island morphology could no longer be observed, bi-continuous phase was given for all composition ranges studied. It was clear that the morphology became much finer in presence of DGEBA, which corresponding to more uniform mixing. Micrographs on the right column provided the most powerful confirmation for the effectiveness of DGEBA as a compatibilizer between Nylon 6 and PC.

It was interesting to note the elongated domains visible in Figure 4(c1), which was a reflection of the processing history.

Table 5. Notched Izod Impact Strength of Nylon 6/PC Blends

Nylon 6/PC (w/w)	Impact strength (J/m)
80/20	29
60/40	35
40/60	44
20/80	56
80/20E	156
60/40E	294
40/60E	386
20/80E	518

As mentioned in the Experimental, the blends were prepared through a twin-screw extruded, where the materials were subjected a strong shear. Such a processing history, called mechanical modification, may impart the chains or lamina a state of orientation, even though it had no effect on the primary molecular characteristics, such as molecular weight and polydispersity.^{20,21} Exposure to annealing or solvent treatment enabled the orientation to recover to those of the original, unprocessed material. The mechanical modification was barely observable for linear polymers, however, with blended with PC, the orientation could be maintained even long exposure to annealing conditions. It was the orientation that made the degree of crystallinity of Nylon 6 in the blends was always higher than that in neat polymer (without a mixing process), especially in the case without DGEBA. When DGEBA was present, however, the Nylon 6 phase was subjected to finely dispersing, which was similar to a circumstance of strong annealing, for this reason the degree of crystallinity was lower.

Impact Strength. The notched Izod impact strength of the blends may well be served as an evidence of compatibilization, which was presented in Table 5. Because of the incompatibility, the plain blends were brittle, with the impact strengths lower than that of neat Nylon 6 (around 50 J/m) and much lower than that of neat PC (700 J/m).²² With the compatibilizer DGEBA introduced, the toughness was one order of magnitude increased.

Conclusions

The present results globally confirmed the effectiveness of diglycidyl ether of bisphenol-A (DGEBA) as a compatibilizer in the Nylon 6/PC system. Neat Nylon 6/PC system was substantially immiscible with coarse morphologies. After DGEBA was introduced, the morphology became much finer, the blends gave bi-continuous morphology in the composition range from Nylon 6/PC=80/20 to 20/80. Since DGEBA greatly strengthened the interaction between segments of Nylon 6 and PC, the T_g of PC decreased steadily with increasing

Nylon 6 content. The crystallization temperature lowered and the crystallization kinetics of Nylon 6 slowed down with increasing content of PC. During the preparation of the blend, Nylon 6 phase as orientated thus resulted in higher degree of crystallinity than neat Nylon 6. However, in present of the DGEBA, the orientation was effectively annealed and the resulted degree of crystallinity was lower. The effect of compatibilization of DGEBA was evidenced by the remarkably increase in impact strength of the blends.

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