

Compatibilization by Main-Chain Thermotropic Liquid Crystalline Ionomer of Blends of PBT/PP

AILING ZHANG,¹ BAOYAN ZHANG,¹ ZHILIU FENG²

¹ Department of Chemistry, Northeastern University, Shenyang 110006, People's Republic of China

² Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Received 17 July 2001; accepted 17 October 2001

ABSTRACT: The miscibility and mechanical properties of the blends of polybutylene terephthalate (PBT) and polypropylene (PP) with a liquid crystalline ionomer (LCI) containing a sulfonate group on the terminal unit as a compatibilizer were assessed. SEM and optical microscopy (POM) were used to examine the morphology of blends of PBT/PP compatibilized by LCI. DSC and TGA were used to discuss the thermal properties of PBT/PP blends with LCI and without LCI. The experimental results revealed that the LCI component affect, to a great extent, the miscibility and crystallization process and mechanical property of PBT/PP blends. The fact is that increasing LCI did improve miscibility of PBT/PP blends and the addition of 1% LCI to the PBT/PP blends increased the ultimate tensile strength and the ultimate elongation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1110–1117, 2002

Key words: miscibility; morphology; polypropylene; blends; liquid crystalline polymer

INTRODUCTION

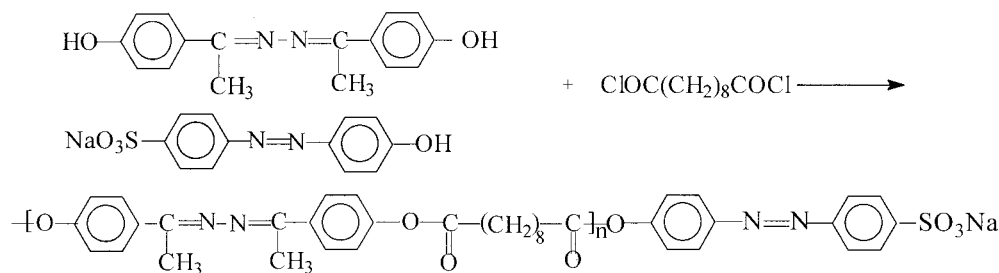
For the past 2 decades, blends of liquid crystalline polymers (LCPs) with other polymers have been a popular research topic, and now the literature on the subject is quite extensive. A number of reviews summarize the published article on this subject.^{1,2} In general, blends of LCPs with other thermoplastic polymers have weak interfacial adhesion between the dispersal microfiber LCP phase and the thermoplastic matrix phase. Intensive work has been focused on improving the properties of LCPs and their adhesion with other polymers by introducing compatibilizers into the blends to promote interchain interaction. In the

latest series of articles, ionomer has been studied to determine the compatible effect on ternary blends; for example, Weiss^{3,4} reported that slightly sulfonated polystyrene ionomers (Zn-SPSs) are effective compatibilizers for blends of a wholly aromatic liquid crystalline polyester (LCP) with nylon 66 (PA66) and polycarbonate (PC); Zn-SPS is miscible with PC, PA66, and LCP; and the origins of miscibility are different for the three binary blends. Zn-SPS is miscible with LCP/PA66, because of strong intermolecular attractive interactions between the sulfonate and amide groups, while the ionomer is miscible with PC and the LCP as a result of intramolecular repulsive interactions along the ionomer molecules. M. Joshi⁵ using the ethylene methacrylic acid copolymer partially neutralized by Na ions (ionomer, Surlyn 8660) as a compatibilizer improves the adhesion of PBT and PE. Thermotropic liquid crystal ionomer as a novel compatibilizer has attracted more and more attention during recent

Correspondence to: B. Zhang (baoyanzhang@hotmail.com).

Contract grant sponsors: National Natural Scientific Fundamental Committee of China and the Natural Scientific Fundamental Committee of Liaoning Province.

Journal of Applied Polymer Science, Vol. 85, 1110–1117 (2002)
© 2002 Wiley Periodicals, Inc.



Scheme 1

years owing to their special excellent mechanical rheological processing and adhesive properties in blends. In the previous articles, we reported the synthesis of main-chain and side-chain thermotropic Liquid crystal ionomers containing sulfonate and carboxylic groups.^{6,7} In this article, we seek to evaluate the compatibilization of PBT/PP blending main-chain liquid crystalline ionomer (LCI) as the compatibilizer. Because PBT is polar and PP is nonpolar, blends of PBT/PP are incompatible. LCIs have not only the advantage of liquid crystalline polymers but also the advantage of ionomers, so they can improve properties of the blends as a compatibilizer. The effect of ionic aggregation of LCI in the blends of PBT/PP on the miscibility property, thermal transition, morphology, and mechanical properties are discussed in this article.

EXPERIMENTAL

Materials

PBT was obtained from PBT Engineering Plastic Plant of YIZHENG Chemical Fiber Group Corp.

(China). Its intrinsic viscosity was 0.75 ± 0.02 dL/g and MFI 90–120 g/10 min. PP (F401, 97%) supplied by Liaoning Huajin Chemical Group Corp. (China) and its MFI was 1.7–3.1 g/10 min. The thermotropic liquid crystalline ionomer (LCI) containing sulfonate groups on the terminal unit of the chain was synthesized by an interfacial condensation reaction from 4,4'-dihydroxy- α,α' -dimethyl benzalazine (DDBA) and the monofunctional dye 4-hydro-phenylazobenzene sulfonic acid, and a sebacoyl dichlorides (Scheme 1) according to the procedures reported by Zhang,⁶ and Zhi.⁸ The LCI was semicrystalline and melted at 167°C to form nematic phase that was stable over a wide temperature range of ca. 67°C. Its nematic range is 167–230°C.

Sample Preparation

All blends (B₀–B₁₀)'s compositions were shown in Table I. The blending was performed in an XSS-30 Torque Rheogoniometer made in China with a mixing chamber of 60 cm², and operated at 240°C and 32 rpm for 10 min. Before blending, all materials were dried in a vacuum oven for 12 h at 100°C.

Table I DSC Date of Components and Blends with LCI

Sample Composition PBT/PP/LCI (wt %)	T_m (°C)		ΔH_f (J/g)		T_c (°C)		$T_{5wt\%loss}$ (°C)
	PP	PBT	PP	PBT	PP	PBT	
PBT 100/0/0		214.1, 223.6		48.4		191.4	371.8
PP 0/100/0	163.0		99.0		114.0		392.7
B ₀ 50/50/0	163.2	215.2, 224.0	45.8	11.6	121.9	193.7	379.8
B ₁ 49.5/49.5/1.0	163.5	213.9, 223.3	49.3	14.4	121.9	191.7	373.7
B ₂ 49.0/49.0/2.0	164.1	214.7, 224.1	48.5	14.1	122.9	192.4	372.1
B ₄ 48.0/48.0/4.0	164.0	212.4, 224.7	50.6	14.5	122.7	190.2	369.8
B ₆ 47.0/47.0/6.0	163.0	210.9, 221.8	48.9	17.8	122.3	189.7	366.9
B ₈ 46.0/46.0/8.0	163.6	210.6, 221.6	50.5	15.9	123.0	188.1	366.7
B ₁₀ 45.0/45.0/10.0	163.5	208.8, 221.0	46.7	18.9	122.6	187.9	363.8

Characterization

The crystallization behaviors and miscibility of the blends were measured with a TA Instrument Corp. USA in a DSC 2910 system, operating at nitrogen flow. Specimens were first heated to 250°C in 20°C/min heating rate, maintaining the temperature for 3 min to eliminate heating history, then cooled to 20°C at 10°C/min cooling rate; the second heating rate was the same as the first. The glass transition temperature (T_g) was defined at the midpoint of the change in the special heat. The miscibility of a blend was inferred from the observation of a single T_g ; multiple T_g s indicated phase separation. Thermal stability of the samples were determined with a TA Corporation TGA-2950 thermogravimetric analyzer using a nitrogen atmosphere and a 20°C/min heating rate from 0 to 600°C.

Polarizing optical microscopic examination was performed by using a Zeiss-Jena microscope equipped with a Metler FP2 heating stage.

The structures of blends were determined with a Nicolet 510-PF1 using Fourier Transform Infrared spectroscopy, using all samples on a KBr sheet.

Mechanical property measurements were made with a model 1000N Tensile Tester (made in China). The mechanical property was measured by a GB 1040-79.

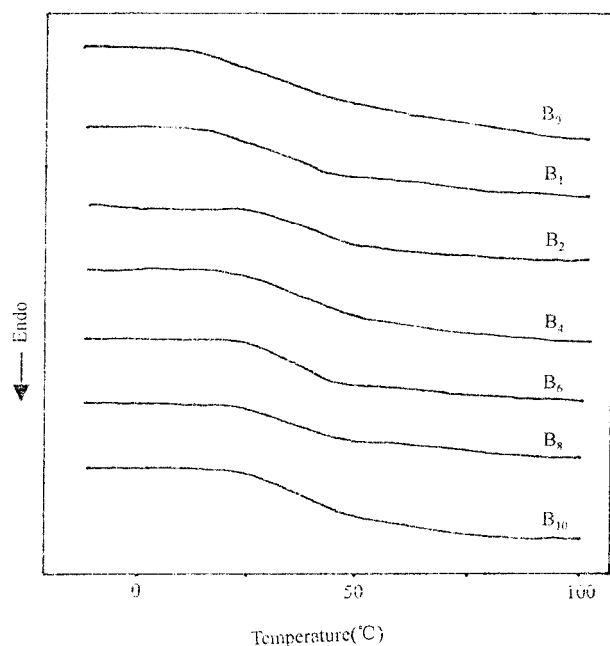


Figure 1 T_g s of PBT /PP and PBT/PP/LCI blends determined by DSC first scans.

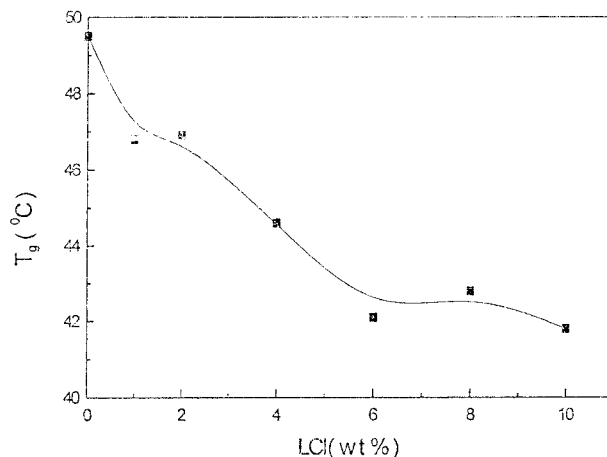


Figure 2 T_g curve of PBT/PP and PBT/PP/LCI blends determined by DSC first scans.

The blend morphology was characterized with a modal 505 from Philips Corporation (SEM). The samples were freeze fractured in liquid nitrogen, and the fracture surface was observed with a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

DSC

Figure 1 shows the DSC heating thermograms for PBT/PP and PBT/PP/LCI blends. For the semicrystalline PBT/PP blend, only a T_g is seen at 49.5°C, which is identical to that of the PBT component (ca. 48.4°C),⁹ and the T_g corresponding to the PP component is not observed. Figure 1 demonstrates the effect of the LCI content on the T_g of the PBT component of the blends. The T_g of the PBT/PP blend, whose composition is 50% PBT and 50% PP, estimated calculated according to the Fox equation is ca. 15°C in our study, assuming that neither phase contain any LCI and the two phases are miscible. When the LCI was added from 1 to 10%, the T_g for the PBT phase of the PBT/PP blends decreased ca. 5°C from 46.8 to 41.8°C. The smallest T_g of the blends measured by DSC was about 27.8°C, which is higher than that predicted by the Fox equation. This may represent the LCI as a compatibilizer, making PBT/PP partial miscible. The degree of compatibility of PBT and PP is demonstrated by the shift in the T_g of the PBT-rich phase, which is summarized in Figure 2, when the LCI is added to the blends. This result is consistent with a separation

study of ionomer/polymer blends, which concluded that mixing was due to strong intermolecular interactions with the ionomer.^{10,11} It appears that miscibility of LCI with PBT/PP is due to specific intermolecular interaction. The miscible effect of the LCI demonstrated by the T_g of the blends decreased when LCI was increased in the blends. LCI, which was to be micelle, is in the interface of the PBT/PP where the intermolecular force is formed by the polar part, ionic groups of LCI, and carboxylate groups of PBT. Meanwhile, the intermolecular force connected the nonpolar part ($-\text{CH}_2-$) of LCI, and ($-\text{CH}_2-$) of PBT and nonpolar ($-\text{CH}(\text{CH}_3)-$) of polypropylene, so that a new area was formed and the T_g was decreased when LCI was increased.

The thermal transitions measured by DSC are summarized in Table I and the second heating scans are shown in Figure 3. From Table I we can see that the melting temperatures (T_m) of the PP component do not change much in all the blends, and the melting temperatures (T_m) of the PBT show double, which both tend to a slight decrease with increasing the LCI content to the blends. These results suggest that the crystalline size is slightly decreased for the PBT component in the blends, whereas that of the PP component remains unchanged. This is because some of the PP probably come into the PBT-rich phase with LCI as the compatibilizer.

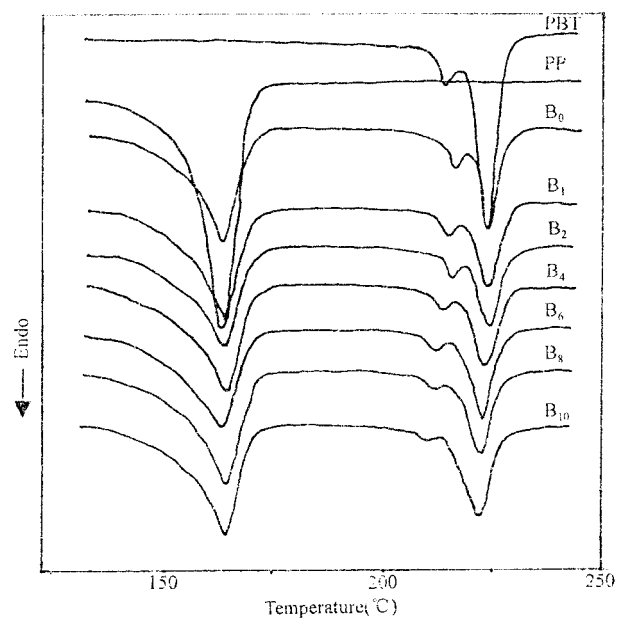


Figure 3 DSC thermograms at second heating of the blends B_0 – B_{10} .

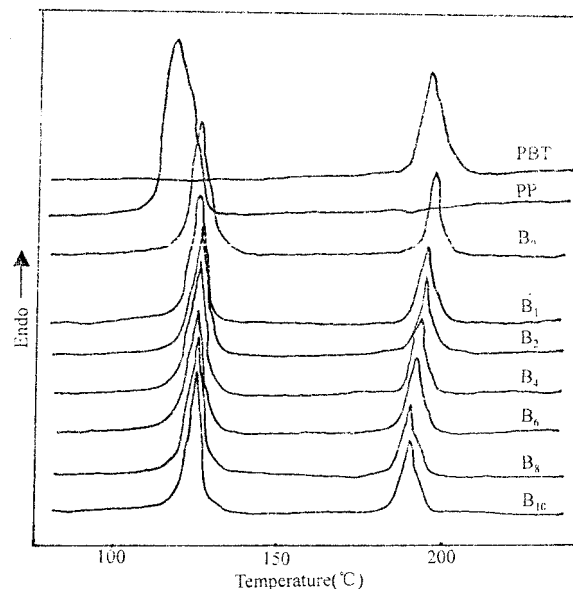


Figure 4 DSC cooling scanning curves of the blends B_0 – B_{10} .

Figure 4 shows the DSC cooling thermograms for PBT/PP and PBT/PP/LCI blends, and dates are listed in Table I. The crystallization temperature (T_c) is determined as the maximum of the crystallization peak that tends to shift to a lower temperature region with increasing the LCI in the blends. It is interesting to note that the T_c of the PP component of all the blends nearly has no change, while blends from B_0 to B_{10} start to crystallize at a somewhat lower T_c than pure PBT. It is generally known that the degree of supercooling, ΔT , can be used to characterize the crystallization behavior of polymer melts. It is defined by the difference between the peak melting temperature and onset crystallization. An increase in ΔT generally indicates that the crystallization rate of polymer is retarded. ΔT values of the specimens investigated are summarized in Figure 5, which shows that the ΔT of the PBT component of the blends tends to increase with increasing the LCI in the blends, and ΔT of PP in the blends is first increased then decreased with increasing the LCI composition. From Figure 5 it is evident that the crystallization rate of the PBT phase is depressed in the PBT/PP blends due to the introduction of LCI, and the crystallization rate of PP phase is depressed then increased. When the samples containing LCI of less than 6 wt % as the compatibilizer, the effect of depression is largest. Such a behavior has been observed in other polymer blends when the miscibility between their blend

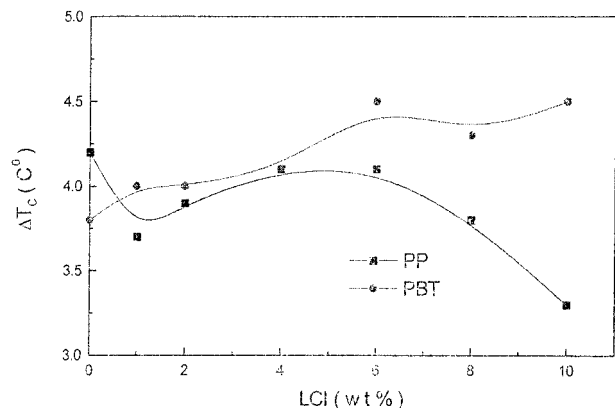


Figure 5 Crystallization rate ΔT_c of blends dependent on the LCI content.

components is improved.¹² Several workers^{13,14} have used ΔT values to describe the crystallization behavior of polymer blends.

The enthalpy (ΔH_f at T_m) of the PBT and PP phases were $11.6 \text{ J} \cdot \text{g}^{-1}$ and $45.8 \text{ J} \cdot \text{g}^{-1}$ of the PBT/PP blend; both of them decreased more than half ΔH_f compared with ΔH_f of pure PBT ($48.4 \text{ J} \cdot \text{g}^{-1}$) and PP ($99.0 \text{ J} \cdot \text{g}^{-1}$) (see Table I). It indicated that the crystallization of the two phases in the blends was not perfect compared with pure PBT and PP; the ΔH_f of the PBT phase increased and ΔH_f of the PP phase increased then decreased with generally increasing LCI in the blends. It is possible that the compatibilization of LCI to the PBT was a bit better than PP; the reason for this is that there is an intermolecular force between LCI and PBT. But the LCI is a good compatibilizer for polar polymer (PBT) and nonpolar polymer (PP), as it contains ionic groups and nonpolar chains. The fractional crystalline degree of each component in the blends was calculated by measuring the areas under the melting peaks. After graphical separation of the peaks, the ΔH_m values were calculated for each component and normalized for fractional content. Figure 6 displays the total degree of crystallinity (X_c), vs. different LCI composition of the PBT/PP blends. X_c is calculated as the sum of crystalline degree of the pure component in the blends by the following equation.

$$X_c = (\Delta H_{\text{PBT}}/\Delta H_{\text{PBT}}^*) \times W_{\text{PBT}} + (\Delta H_{\text{PP}}/\Delta H_{\text{PP}}^*) \times (1 - W_{\text{PBT}})$$

where ΔH_{PBT} and ΔH_{PP} are the melting heats of PBT and PP, respectively, according to the DSC,

and W_{PBT} is the weight fraction of PBT. In the calculation, the ΔH_{PBT}^* and ΔH_{PP}^* , which are PBT and PP with 100% crystallinity at equilibrium melting temperature, are $144.5 \text{ J} \cdot \text{g}^{-1}$ and $209.0 \text{ J} \cdot \text{g}^{-1}$ according to the literature,^{9,15} respectively.

Figure 6 shows variation of the crystalline degree of blends with the LCI content. It can be seen that X_c increases significantly with increasing the LCI content. This observation is in good accordance with the crystallinity behavior of other LCP/thermoplastic blends. Although the introduction of the LCI retards the crystallization rate of PBT and PP due to some intermolecular interactions between the LCI and PBT in the PP phases, the oriented LCI dispersed phase can act as the sites for nucleation of spherulites and enhance the degree of crystallinity of PBT and PP. It is worth noting that the degree of crystallinity of the blends with LCI content 1 wt % (B_1) increase more rapidly than that containing LCI content >4%. This is due to the miscibility between the PBT and PP in the blends, with lower LCI content better than that with higher LCI content. Thus, the LCI acts as a more effective nucleating agent and miscibility agent for the blends with lower LCI content.

FTIR

Evidence for specific interaction between the ester groups of PBT and sulfonate groups of LCI was obtained from FTIR. Figure 7 shows the FTIR spectral region for the carbonyl group of the PBT in the B_0 and B_1 , B_6 , B_{10} specimens. The addition of LCI had influence on the position of

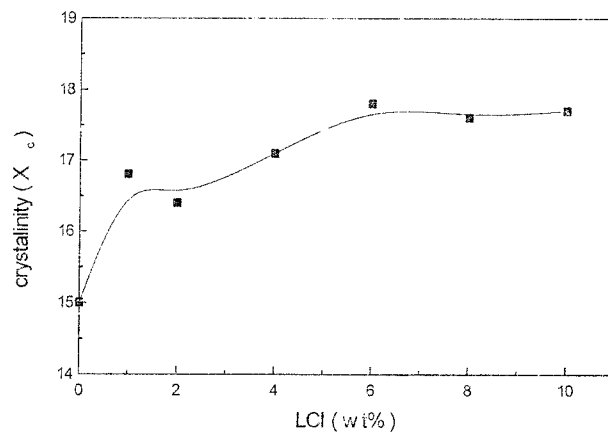


Figure 6 Degree of crystallinity curve of PBT/PP and PBT/PP/LCI blends determined by DSC second scans.

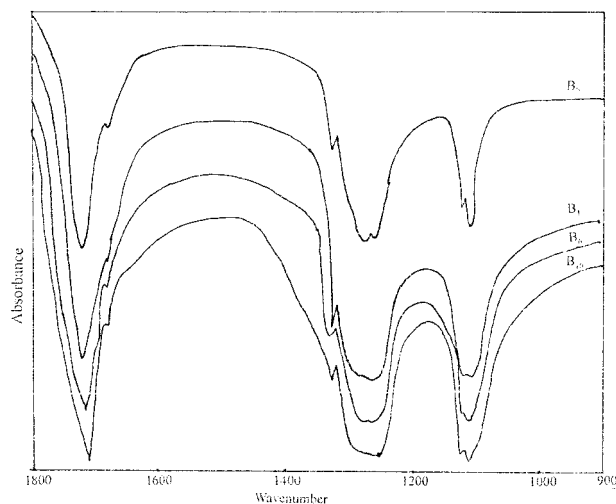


Figure 7 FTIR spectrum of the blends B₀; B₁; B₆; B₁₀.

the C=O stretching vibration peak at 1716 cm^{-1} , which shift to lower wave numbers of 1713 , 1711 , and 1707 cm^{-1} , respectively.

TGA

A TGA thermogram of the blends measured using a nitrogen atmosphere and the temperatures at which 5 wt % loss was tabulated is shown in Table I. The temperature of thermal degradation 5 wt % of blends decrease with increasing LCI, but the decrease is less than 8°C comparing with pure PBT (371.8°C at 5 wt % loss). In this case, the cause is due to the specific intermolecular interactions occurring between PBT and PP in all the blends with LCI.

POM Analysis

Figure 8(a)–(d) shows the hot-stage polarized optical micrographs of compression-molded PBT/PP/LCI blends. It is evident from these micrographs that the B₀ sample [Fig. 8(a)] exhibits a very clear interfacial phase-separated phase. The boundary of PP and PBT blend is rather clear, and the morphology is typical of an incompatible alloy structure with poor adhesion between the

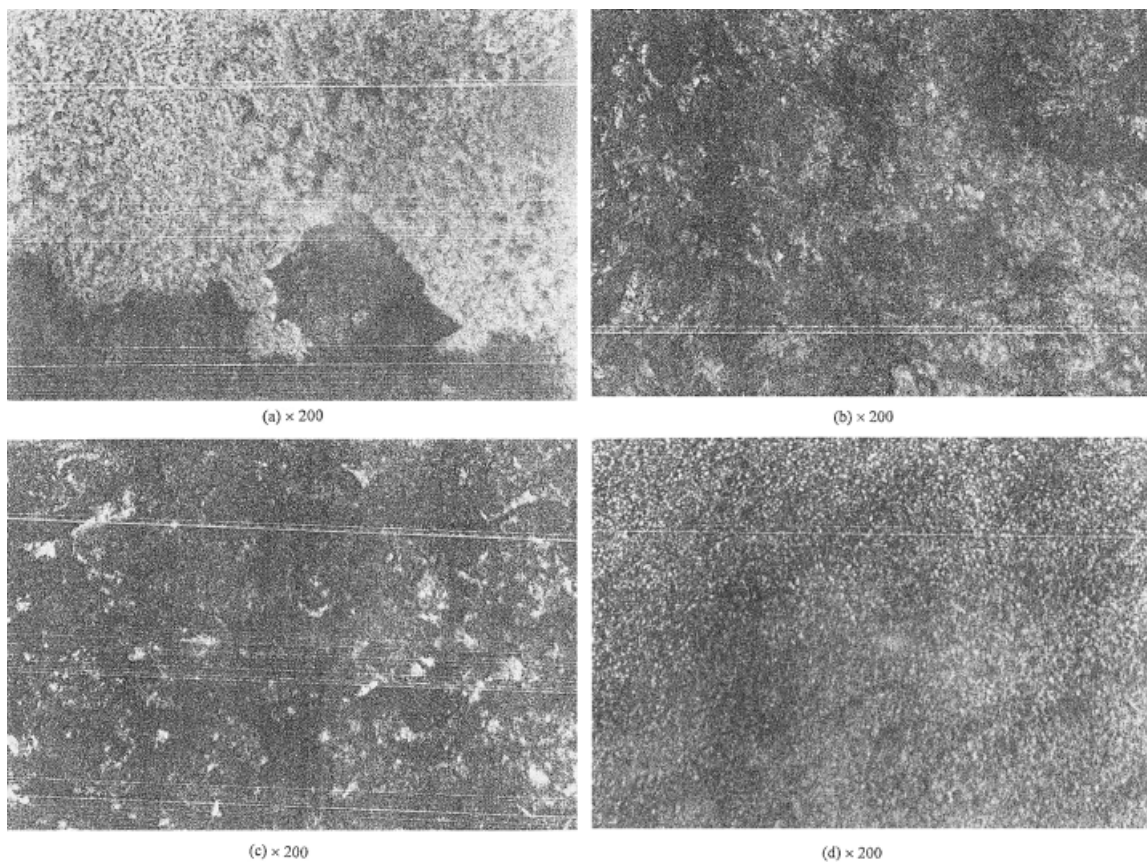


Figure 8 Polarized micrographs taken at room temperature for (a) B₀; (b) B₁; (c) B₆; (d) B₁₀.

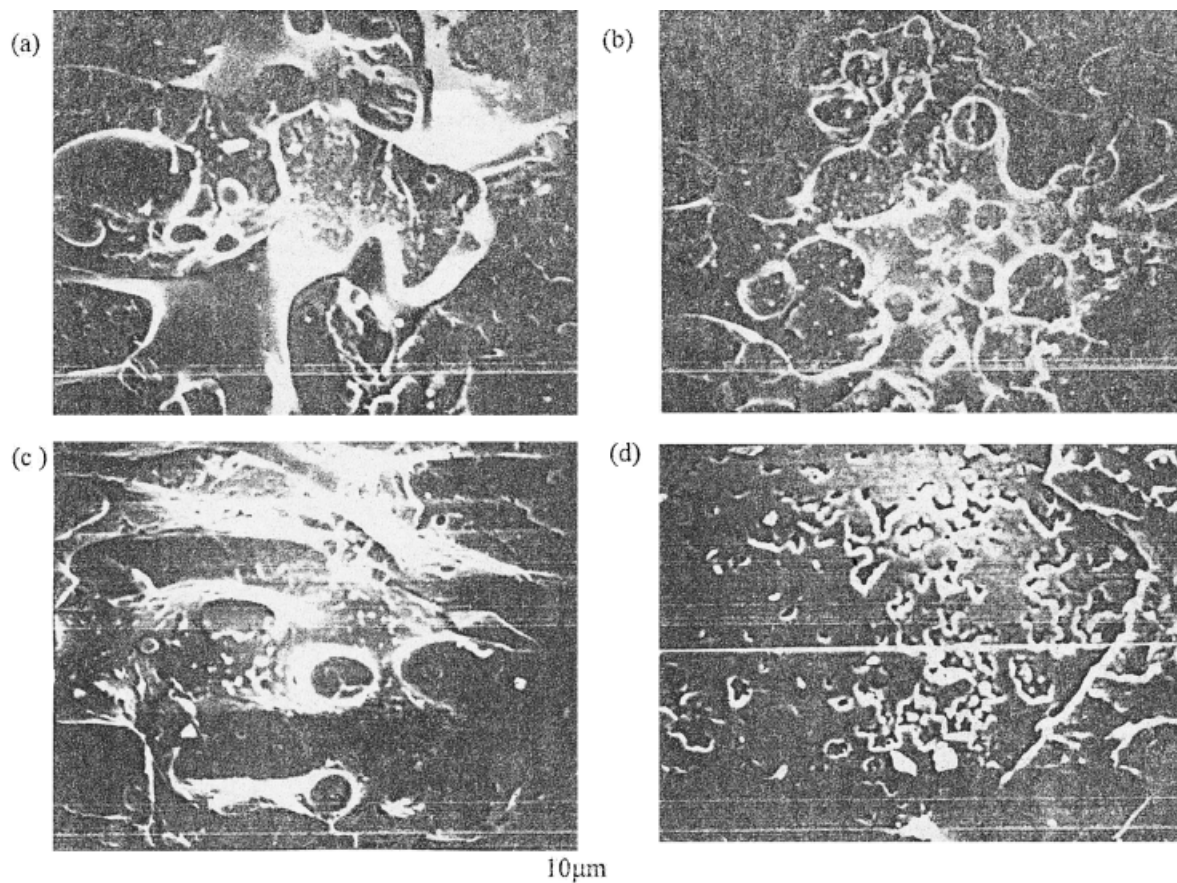


Figure 9 SEM micrographs of the B_0 , B_1 , B_6 , B_{10} .

two phases of PBT and PP. In contrast, the photomicrograph of the B_1 sample [Fig. 8(b)] exhibits a miscible structure, and the compatibility of the two phases of PBT and PP increases. The photomicrograph of the B_6 [Fig. 8(c)] and B_{10} [Fig. 8(d)] exhibit an even better dispersion of PP, and the microscope separation of PBT/PP decreases. In B_{10} , two distinct regions of PBT and PP become much more, and the region of the PP domain becomes smaller. It is interesting to note this interfacial compatibility of the PBT/PP blends increases with increasing the LCI content, and the phenomenon is consistent with the result of T_g .

SEM Analysis

Figure 9 gives some SEM micrographs of the blends (B_0 – B_{10}), respectively. It is found that the morphologies of the investigated blends is clearly dependent on the LCI content in the blends. The blend B_0 [Fig. 9(a)] shows a large size of the dispersed phase and the smooth surface. The ternary blend B_1 [Fig. 9(b)] with a low-content LCI

shows a narrow distribution of particle size where the average particle diameter is 8–10 μm , and that seems to have liquid crystalline microfibrils and liquid crystalline fiber of B_1 significantly more than that of B_6 in the blends. The phase size of sample B_1 decreased and liquid crystalline microfibrils formed are evident that the presence of LCI improved adhesion of the two phases of PBT and PP where a new penetrating network structure with small spherical particles are formed [Fig. 9(b)]. For the blend B_6 [Fig. 9(c)] with a higher amount of LCI than blend B_1 , the average particle diameter increases to about 12 μm . The reason is the same as the above IR Spectra Analysis, Thermal Analysis, and POM. More interesting, it is found that the morphology of sample B_{10} [Fig. 9(d)] is phase separated. It is possible that the blends are supersaturated by the LCI, as LCI is more than 6 wt % and the excess LCI forms a repulsive effect and does not play compatibilization. The result will effect the mechanical property.

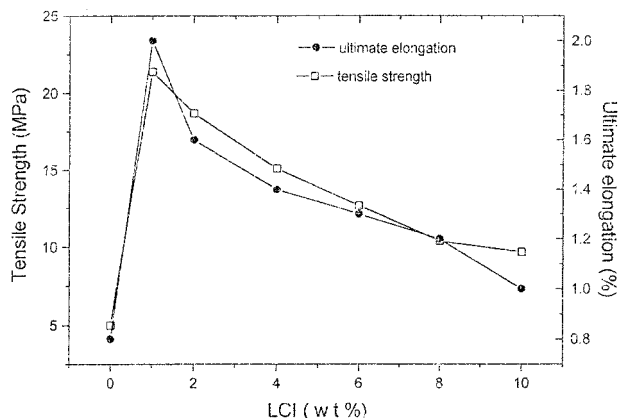


Figure 10 Tensile properties and ultimate elongation of the PBT/PP and PBT/PP/LCI blends.

Tensile Properties

Figure 10 shows the effect of the compatibilizer quantity on the tensile strength of the samples of B₀, B₁, B₂, B₄, B₆, B₈, and B₁₀. Comparing the tensile behavior of the compression-mould PBT, the addition of LCI to PBT/PP blends increased the tensile strength and ultimate elongation. It is interesting that the B₁ specimen exhibits a maximum tensile strength and ultimate elongation. The tensile strength of all blends decreasing with increasing LCI may be due to miscibility and a microfiber reinforce effect. Blend B₁ with 1 wt % LCI is not brittle in the PBT matrix because of the incorporation of some LCI into the PBT. When LCI composition increases only miscibility exists, and the microfiber effect makes the brittleness of the PBT disappear. It is evident that the blends are supersaturated by the added surplus LCI, as LCI is more than 6 wt % in the blends, and the excess LCI forms a repulsive effect. This indicates that the LCI is a compatibilizer for polar PBT and nonpolar PP. It is facilitated by a small amount of LCI being added to the blends. So the result is consistent with the results shown.

CONCLUSION

The compatibility and tensile property of the LCI in the blends of PBT and PP were studied. The

investigation indicates that blends of PBT/PP with a little LCI are partially miscible as a result of a strong specific intermolecular interaction between LCI and the ester groups. Accordingly, the miscibility of the blends increases with increasing the LCI. The lowest T_g was observed in the case of blends containing LCI at 10 wt %. The largest tensile strength of the blends with LCI is the B₀ sample containing 1% LCI, which is due to the fact that LCI has double properties of LCP and the ionomer that are miscible and microfiber reinforced.

The authors acknowledge financial support of National Natural Scientific Fundamental Committee of China, and the Natural Scientific Fundamental Committee of Liaoning Province.

REFERENCES

- Dutta, D.; Friuwala, H.; Kohl, A.; Weiss, R. A. *Polym Eng Sci* 1990, 30, 1005.
- Pawlikowski, G. T.; Dutta, D.; Weiss, R. A. *Annu Rev Mater Sci* 1991, 21, 159.
- Weiss, R. A.; Ghebremeskel, Y.; Charbonneau, L. *Polymer* 2000, 41, 3471.
- Dutta, D.; Weiss, R. A.; He, J. S. *Polymer* 1996, 37(3), 429.
- Joshi, M.; Mjsra, A.; Majtj, S. N. *J Appl Polym Sci* 1991, 43, 311.
- Zhang, B. Y.; Weiss, R. A. *J Polym Sci Part A Polym Chem* 1992, 30, 989.
- Zhang, B. Y.; Guo, S. M.; Shao, S. *J Appl Polym Sci* 1998, 68, 1555.
- Zhi, J. G.; Zhang, B. Y.; Wu, Y. Y.; Feng, Z. L. *J Appl Polym Sci*, to appear.
- Avramova, N. *Polymer* 1995, 36(4), 801.
- Weiss, R. A.; Beretta, C.; Sasongko, S.; Gerten, A. *J Appl Polym Sci* 1990, 41, 91.
- Lu, X.; Weiss, R. A. *Macromolecules* 1996, 29, 1216.
- Gopakumar, T. G.; Ponrathnam, S.; Lele, A.; Rajan, C. R.; Fradet, A. *Polymer* 1999, 40, 357.
- Martuscelli, E.; Pracella, M.; Yue, W. P. *Polymer* 1984, 25, 1097.
- Li, R. K. Y.; Tjong, S. C.; Xie, X. L. *J Polym Sci Part B Polym Phys* 2000, 38, 403.
- Chiu, Y. P.; Chiou, K. C.; Chang, F. C. *Polymer* 1996, 37, 4099.