

Compatibilization of Side-Chain, Thermotropic, Liquid-Crystalline Ionomers to Blends of Polyamide-1010 and Polypropylene

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ABSTRACT: A novel side-chain, liquid-crystalline ionomer (SLCI) with a poly(methyl hydrosiloxane) main chain and side chains containing sulfonic acid groups was used in blends of polyamide-1010 (PA1010) and polypropylene (PP) as a compatibilizer. The morphological structure, thermal behavior, and liquid-crystalline properties of the blends were investigated by Fourier transform infrared, differential scanning calorimetry, thermogravimetric analysis, and scanning electron microscopy. The morphological structure of the interface of the blends containing SLCI was improved with respect to the blend without SLCI. The compatibilization effect of greater than 8 wt % SLCI for the two phases, PA1010 and PP, was better than the effects of other SLCI contents in the blends. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2749–2754, 2002; DOI 10.1002/app.10179

Key words: liquid-crystalline ionomers; polyamides; poly(propylene) (PP); blend compatibilization

INTRODUCTION

The compatibilization of polar polymers with non-polar polymers usually is not very easy. Therefore, intensive work has been focused on improving the compatibilization of their blends. One approach for improving this property is to introduce a compatibilizer into the blend to promote inter-chain interactions. Recently, many different kinds of compatibilizers have been reported by

researchers such as Eisenberg and Smith¹ and Weiss et al., who obtained miscible blends with ionic polymers² such as sulfonate and carboxylate ionomers. Blends of liquid-crystalline polymers (LCPs) with other thermoplastic polymers have been popular research topics over the past decades, and there is an extensive literature on the subject.^{3–5} However, the properties of LCP/polymer blends are far behind expectations, mainly because of the poor interfacial adhesion between the dispersed microfibrillar LCP phases and the thermoplastic matrix phases. Liquid-crystalline ionomers (LCIs) are being used as novel compatibilizers mainly because of their excellent mechanical rheological processes and adhesive properties in blends.⁴ In our previous articles, we reported the syntheses of main-chain and side-chain, thermotropic LCIs containing sulfonate and carboxy-

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Table I Compositions and DSC and TGA Thermogram Data of the Blends

Sample	Composition (wt %)			T_m (°C)		ΔH_f (J g ⁻¹)		T_d (5 wt % Loss)
	PA1010	PP	SLCI	PA1010 phase	PP phase	PA1010 phase	PP phase	
B ₀	50.0	50.0	0	206.5	169.8	19.6	40.7	423
B ₁	49.5	49.5	1.0	206.0	169.5	15.4	47.0	427
B ₂	49.0	49.0	2.0	205.2	169.0	19.6	49.7	432
B ₄	48.0	48.0	4.0	205.1	168.7	17.5	45.9	426
B ₈	46.0	46.0	8.0	203.3	167.6	21.8	44.6	431
B ₁₂	44.0	44.0	12.0	203.5	168.4	18.7	43.5	432
B ₁₆	42.0	42.0	16.0	203.3	167.1	22.8	41.0	424
PA1010	100.0	—	—	201.4	—	48.9	—	401
PP	—	100.0	—	—	163.5	—	81.3	385

Preparation of the Blends of PA1010 and PP

PA1010, PP, and SLCI were dried at 100°C *in vacuo* for at least 12 h and then were mixed in a single-screw extruder (L/D 12 model Baoye SJ-12, Shenyang City, Liaoning Province, China) at 225°C and a speed of 25 rpm. Compositions of all the blends are listed in Table I.

Measurements

Thermal phase transitions were measured with a TA Instruments Corp. DSC 2910 system (DSC, Perkin-Elmer, Foster City, CA). A 20°C/min heating rate and a 10°C/min cooling rate were used under a nitrogen atmosphere. The thermal stabilities of the polymers were determined with a PerkinElmer TGA-7 thermogravimetric analyzer (TGA, Perkin-Elmer) with a nitrogen atmosphere and a 20°C/min heating rate. The blend morphology was characterized with a Philips Corp. model 505 (SEM, Philips, Holland). Extruded fiber samples were frozen-fractured in liquid nitrogen, and the fracture surfaces were observed with scanning electron microscopy (SEM). The structures of the blends were determined with a Nicolet 510-PFT IR spectroscope (FTIR, Nicolet, Madison, WI), with all samples on KBr sheets.

RESULTS AND DISCUSSION

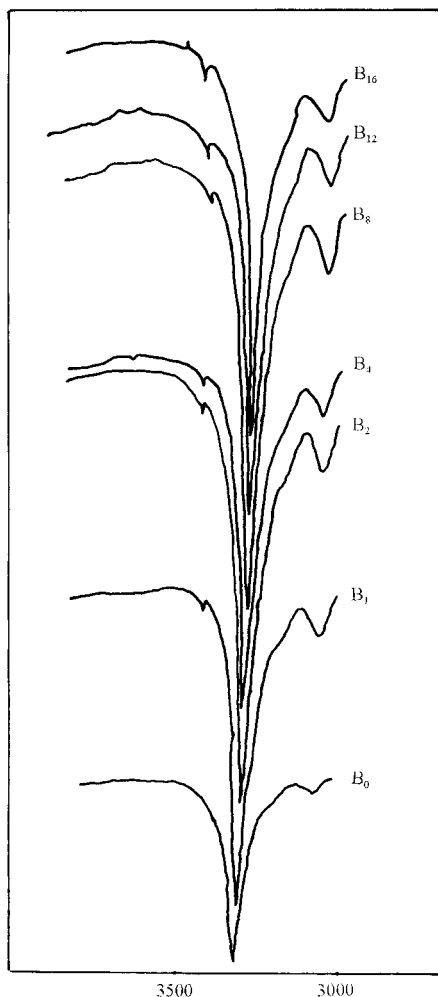
IR Spectra Analysis

Some special IR spectra of PA1010, SLCI, and their blends are listed and shown in Table II and Figure 1, respectively. For sulfonic acid, two series of peaks of the IR spectra at 1164–1169 and 1190–1197 cm⁻¹ can be observed, and both of these peak bands of SLCI-modified blends (samples B₁–B₁₆) shift to lower wave numbers with respect to the SLCI itself. These results are due to the hydrogen-bond interaction between —CO—NH of PA1010 and —SO₃H of SLCI, and the wave numbers decrease with an increasing amount of the SLCI in B₁–B₁₆. Also, a new peak at 3086 cm⁻¹ appears, and the strength of B₁–B₁₆ increases with an increase in the sulfonate content; this indicates that a new band, N—H⁺, formed. This is similar to the results obtained by Weiss et al.²

The peak positions of the N—H band vibrations in the IR spectra of the B₀–B₁₆ blends (from 3308.1 to 3305.1 cm⁻¹) are different from the 3300.0 cm⁻¹ peak position of PA1010, all of the N—H band peaks shift toward a lower frequency, and the strength of the peaks from B₁–B₁₆ in-

Table II Some IR Absorption Bands of Blends B₀–B₁₆

Group	Wave Number (cm ⁻¹)									
	SLCI	PA1010	PP	B ₀	B ₁	B ₂	B ₄	B ₈	B ₁₂	B ₁₆
—SO ₃ H	1197.9	—	—	—	1190.9	1190.7	1190.8	1190.7	1190.9	1190.3
	1169.1	—	—	—	1166.8	1166.4	1166.6	1166.0	1165.9	1164.3
N—H	—	3300.0	—	3308.1	3306.8	3306.7	3305.5	3304.9	3304.1	3303.5



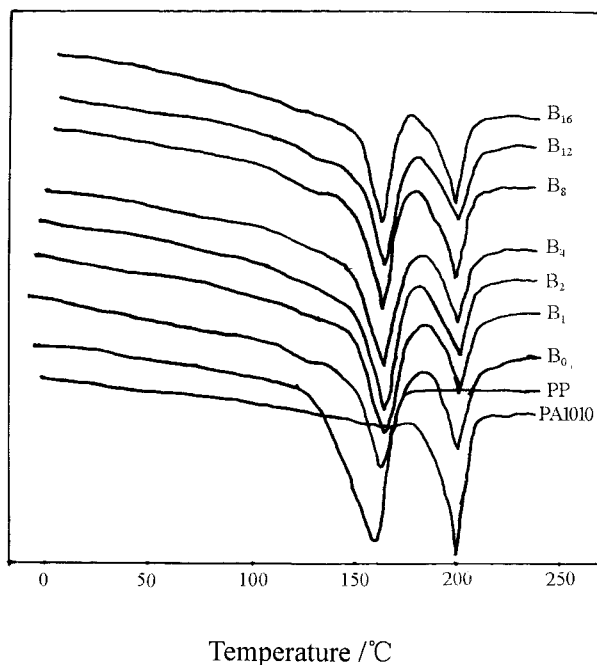
Wavenumber/cm⁻¹

Figure 1 IR spectra of B₀–B₁₆.

creases with an increase in the SLCI content of the blends. These results indicate that light interactions between C—H of PP and —CO— of PA1010 formed and made the N—H peak position of the PA1010 phase of blend B₀ shift to a higher wave number in comparison with the N—H peak position (3300.0 cm⁻¹) of pure PA1010. However, when SLCI was introduced to the blends of PP and PA1010, the peak positions of B₁–B₁₆ all moved to a lower frequency in comparison with the peak position of B₀, which proves that the compatibilization effect of SLCI for PA1010 and PP in the B₁–B₁₆ blends did occur and that the greater the content of SLCI in the blends was, the stronger the compatibilization was, and the peak moved closer toward N—H (3300.0 cm⁻¹) of PA1010.

Thermal Analysis

The thermal transitions of the blends were determined with differential scanning calorimetry (DSC); the second heating scans are shown in Figure 2, and the transition temperatures are summarized in Table I. The glass-transition temperatures did not show up clearly enough, so that the compatibilization of the blends was studied by the T_m and melting enthalpy (ΔH_f) values. The T_m values of the two phases PA1010 and PP in sample B₀ (without SLCI content) increased about 5 and 6°C, respectively, with respect to pure PA1010 ($T_m = 201.4^\circ\text{C}$) and PP ($T_m = 163.5^\circ\text{C}$). It could be concluded that PA1010 and PP did not compatibilize in B₀; they were heterogeneous nuclear reagents for each other. The compatibilizing effect of SLCI was demonstrated by the T_m values of the blends (B₁–B₁₆) decreasing slightly with an increasing amount of SLCI in the blends, which means that compatibilization increased with an increasing amount of SLCI in B₁–B₁₆. This phenomenon is the same as that reported by Nish and Wang,⁷ that the T_m value of the phase of a crystal polymer decreases in a compatible system of polymer blends. First, SLCI was micellar at the interface of PA1010 and PP, where there were hydrogen bonds and intermolecular forces formed by polar parts of —SO₃H of SLCI and



Temperature /°C

Figure 2 DSC heating thermographs of B₀–B₁₆, PP, and PA1010.

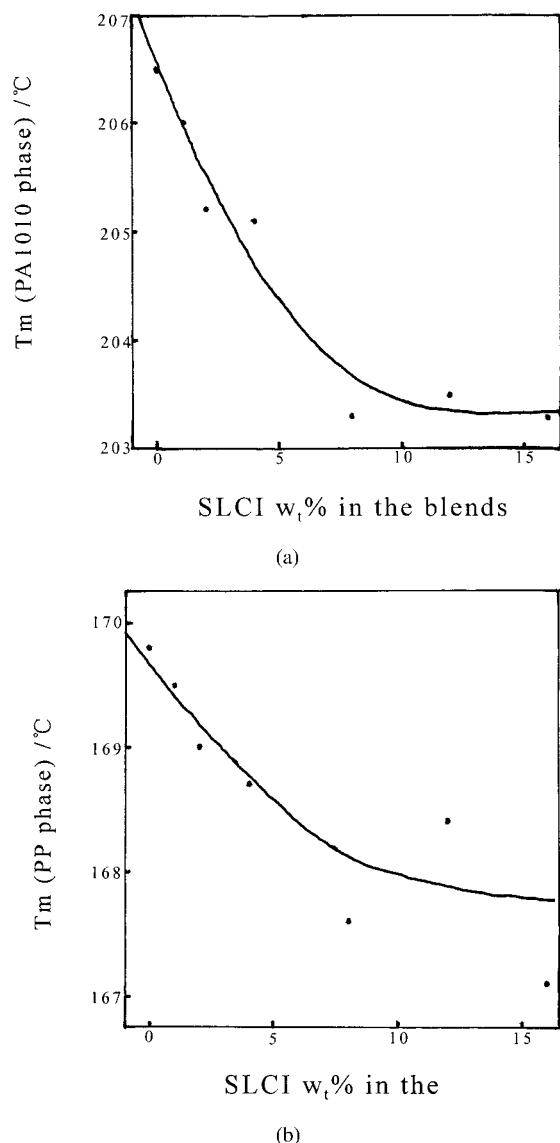


Figure 3 Relationship of T_m of (a) the PA1010 phase and (b) the PP phase and the SLCI content of the blends.

—CO—NH— of PA1010. Meanwhile, the intermolecular forces connected the nonpolar parts of —Si—O— and —CH₂— of SLCI, —CH₂— of PA1010, and —CH(CH₃)— of PP, so that a new area formed in the interface between PP and PA1010. The enhanced coherence between two phases made the crystalline degree of the PA1010 and PP phases decrease. The dilution effect of SLCI in B₁–B₁₆ could be another reason for the decrease in the crystal degree of blends containing SLCI. However, the T_m values of the blends evidently did not decrease, the weight ratios of PA1010 and PP are higher than those of SLCI in

the blends, and the influence of SLCI on the thermal properties of the blends is not very strong. Figure 3(a,b) shows the relationship of the T_m value of the PA1010 phase and the T_m value of the PP phase with the SLCI weight percentage in the blends; T_m decreased almost linearly with an increase in SLCI until SLCI reached 8%, and then T_m remained almost constant with the increase in SLCI beyond 8%; it is possible that the saturation of SLCI in the blends occurred at that value in the blend.

The enthalpies (ΔH_f at T_m) of the PA1010 and PP phases were 19.6 and 40.7 J g⁻¹, respectively, for sample B₀, both less than half of the ΔH_f values of pure PA1010 (48.9 J g⁻¹) and PP (81.3 J g⁻¹), as shown in Table I. This indicates that the crystallization of the two phases in the blends was not perfect. The change in ΔH_f of the PA1010 phase was not regular as its T_m , but ΔH_f of the PP phase decreased with an increase in SLCI in the B₁–B₁₆ blends. The decrease in ΔH_f of PP was due to the increase in the compatibilization of SLCI in B₁–B₁₆, which indicates that the degree of crystallization of PP decreased with increasing adhesion of SLCI in B₁–B₁₆.

Thermogravimetric analysis (TGA) thermogram data of the blends obtained under a nitrogen atmosphere and the 5 wt % loss temperatures are tabulated in Table I. The temperatures of 5 wt % loss of B₁–B₁₆ were 20–30°C higher than that of pure PA1010 (401°C at 5 wt % loss). This might have been due to the physical interactions existing between PA1010 and PP in the blends.

SEM Analysis

Shown in Figure 4 are SEM micrographs of the blends B₀, B₄, B₈, and B₁₂. The micrograph of blend B₀ without SLCI shows that the PP particles were spherical and that the interfacial phase between the PA1010 and PP phases was very clear. The size of the dispersed PP phase was rather big, and some of the particles in sample B₀ without SLCI were up to $\phi = 25 \mu\text{m}$. Such morphology is characteristic of typically incompatible alloy structures with poor adhesion between two phases, in this case PA1010 and PP. However, the micrographs of the blends containing SLCI exhibit compatibilized structures, and the compatibility of the phases PA1010 and PP increased with increasing SLCI. The blend containing 4 wt % SLCI (B₄) exhibited even better dispersion of PP, and the size of the spherical particles decreased significantly to $\phi = 7 \mu\text{m}$ in the blend.

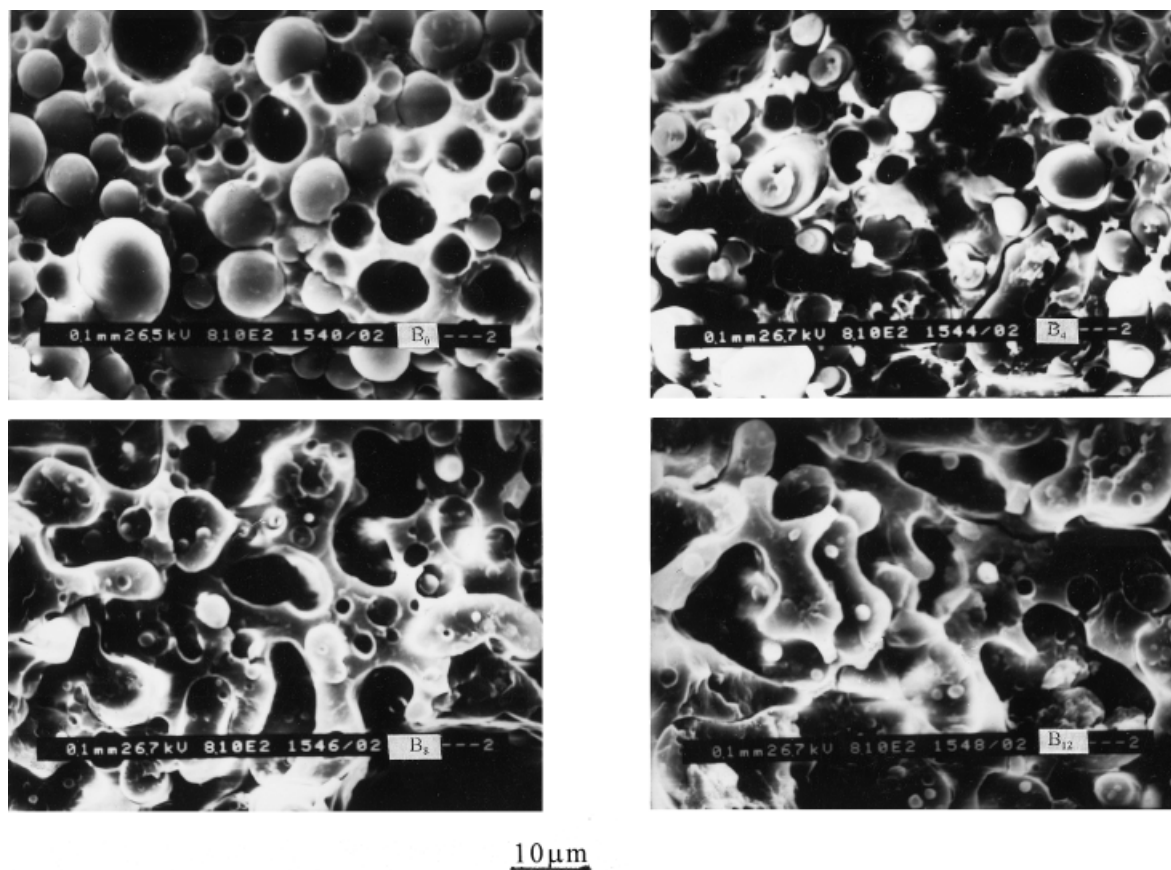


Figure 4 SEM micrographs of B₀, B₄, B₈, and B₁₂.

The size of the PP particles decreased with the increase in SLCI, the size of some PP particles with 8–12 wt % SLCI was only $\phi = 4 \mu\text{m}$, and the PA1010/PP interface was not very clear. The reason is the same as that given for IR spectral analysis and thermal analysis. The decrease in dispersion size and the increase in homogeneity were due to the interface energy decreasing and the interface adhesion increasing, respectively. The compatibility was almost stable with the increase in SLCI. If we compare the samples with 8 wt % SLCI (B₈) and 12 wt % SLCI (B₁₂), we see that the PP sizes in both of them were almost the same. It is possible that SLCI was supersaturated in the blends when the SLCI content was greater than 8% and the excess SLCI had no chance to assist with compatibilization.

CONCLUSIONS

The compatibilization effect of SLCI in blends of PA1010 and PP was studied and compared to the

effect for corresponding blends containing no SLCI. The investigations indicate that SLCI has a compatibilization effect on polar PA1010 and non-polar PP. The results of DSC, IR, and SEM also show that the compatibilization effect of SLCI is better when its content in blends is 8 wt % instead of other contents.

REFERENCES

1. Eisenberg, A.; Smith, P. *J Polym Sci Polym Lett Ed* 1983, 21, 223.
2. Dutta, D.; Weiss, R. A.; He, J. S. *Polymer* 1996, 37, 429.
3. Dutta, D.; Kohl, A.; Weiss, R. A. *Polym Eng Sci* 1990, 30, 1005.
4. Yuan, G. X.; Zhao, Y. *Polymer* 1995, 36, 2725.
5. Zhang, B. Y.; Weiss, R. A. *J Polym Sci Part A: Polym Chem* 1992, 30, 989.
6. Zhang, B. Y.; Guo, S. M.; Shao, B. *J Appl Polym Sci* 1998, 68, 1555.
7. Nish, T.; Wang, T. T. *Macromolecules* 1975, 8, 909.