

Reinforcing Effect of Compatibilizers Containing Oxazoline Groups in Liquid Crystalline Polymer/ Polypropylene Blending Material

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ABSTRACT

The effects of compounds containing oxazoline groups and the presence of maleic anhydride-grafted polypropylene (PP-g-MAH) on the spectral, morphological, and tensile properties of polypropylene (PP)/liquid crystalline polymer (LCP) blends were investigated. A wholly aromatic LCP having a low melting point which was copolyester, namely AL-7000 have been used, because thermal decomposition of PP and compatibilizer must be prevented. Compression molding was selected as the molding method because it allows molding with a small amount of sample. The binary blends of PP and LCP showed a degradation of tensile properties compared to pure PP. However, the addition of 2,2'-bis(2-oxazoline) and PP-g-MAH as compatibilizers dramatically improved the dispersion of LCP in the PP matrix, resulting in improved tensile properties. In particular, the tensile elongation at break was significantly increased, and cohesive failure (breakage within the matrix rather than at the PP/LCP interface) was observed in scanning electron microscopy images.

KEYWORDS: *Polymer blends, Compatibilization, Liquid crystalline polymer, Polypropylene, Interfacial strength.*

INTRODUCTION

Liquid crystalline polymers (LCPs) exhibit high strength and modulus in the flow direction due to their self-reinforcing effect. In addition, it has

high thermal properties and excellent flow ability, so it is mainly used for micro connectors. It is also expected to be effective as a filler material, and blends with various other resins

such as polypropylene (PP), polyamide^[1], poly(trimethylene terephthalate)^[2], and cyclic olefin copolymer^[3] are being investigated. In particular, blends of PP with LCP have been focused on understanding the morphology, rheology, thermal and mechanical properties.^[4,5] Other aspects have been evaluated from a wide range of perspectives, such as higher order structure^[6,7] and gas barrier properties.^[8] There are two major issues that have been identified in the research of PP/LCP blends to date: the melting point of LCP is too high compared to PP, and the compatibility is low.

LCP can be broadly divided into wholly aromatic LCP and semi-aromatic LCP. In general, the former type of LCP has a higher melting point and mechanical strength.^[9] Since LCPs are often used in applications that require heat resistance, most LCPs on the market today are wholly aromatic LCPs with melting points of 280°C or higher. In a report by Kozłowski and La Mantia, it was confirmed that when a wholly aromatic LCP (Vectra A950) with a melting point of about 280°C was used as a blend material for PP, the strength decreased due to thermal degradation of PP.^[10] In contrast, when semi-aromatic LCP (SBHN) with a melting point of 205°C was used, the thermal degradation of PP was suppressed, but the strength of PP was not improved. One of the reasons is thought to be that the strength of SBHN is inferior to that of A950. In order to solve the above problem, it is necessary to use LCP with mechanical strength like A950 (wholly aromatic LCP) and melting point like SBHN (semi-aromatic LCP).

LCPs typically shows poor dispersion in binary blends with PP, such that it is difficult to

significantly improve the mechanical properties of the PP. Therefore, studies have been conducted to improve the compatibility between PP and LCP by using various compatibilizers as the third component^[11,12], changing the type of PP^[13], and employing side-chain liquid crystal ionomers instead of LCP.^[14] Compatibilizers assessed to date include PP with grafted maleic anhydride moieties (PP-g-MAH), copolymers of ethylene and acrylic acid, copolymers of dodecanol, dimer acids and terol, and graft copolymers of PP with semi-aromatic LCPs (PP-g-LCP). Blends containing PP-g-MAH have improved tensile strength and elastic modulus, although there are exceptions, and blends using copolymers of ethylene and acrylic acid or of dodecanol, dimer acid and terol have been found to have increased tensile modulus with decreased elongation at break.^[15,16] The addition of PP-g-LCP compounds has produced improved elastic modulus and crystallization temperature values.^[7,17] In all cases, no cohesive failure of LCP was observed, suggesting insufficient improvement in the interfacial strength between PP and LCP. It has been reported that the mechanical strength can be improved by using a polymer containing oxazoline groups together with PP-g-MAH as compatibilizers for PP/carbon fiber (CF) blends. In such blends, the oxazoline moieties react with the carbonyl groups on the CF to improve the interfacial strength in the PP/CF. LCP has a carboxy or hydroxy group at the end of the molecular chain. Therefore, it may be possible to increase the interfacial strength of PP/LCP blends by using a compound incorporating oxazoline groups as a compatibilizer.

In this study, PP/LCP blends were prepared using AL-7000, a wholly aromatic LCP having a low melting point, and compounds containing oxazoline groups and PP-g-MAH were used as compatibilizers. The spectral, morphological, and mechanical properties of blended materials molded using compression molding, which allows molding with small sample volumes, were investigated.

EXPERIMENTAL

Materials

The matrix thermoplastic used in this study was a PP homopolymer (J105G, having a melt mass-flow rate of 9.0 g/10 min) supplied by Prime Polymer (Tokyo, Japan). AL-7000 (Ueno Fine Chemicals Industry, Tokyo, Japan) was employed as the LCP, the chemical structure of which is shown in Figure 1(a). AL-7000 is a wholly aromatic copolyester composed of 6-hydroxy-2-naphthoic acid, p-hydroxybenzoic acid, a diol component (X in the figure) and a dicarboxylic acid component (Y). This polymer has a melting point of approximately 178°C and its mechanical properties are summarized in Table 1 together with those for A-5000 (another wholly aromatic LCP produced by Ueno Fine Chemicals Industry) and LC-5000 (a semi-aromatic LCP produced by Unitika, Osaka, Japan) for comparison.

Attempts were made to improve the adhesion between the PP and LCP by adding several different compatibilizers, as presented in Figure 1(b). Compatibilizer A was a commercially available material consisting of PP with grafted maleic anhydride moieties (UMEX1001) supplied

by Sanyo Chemical Industries (Kyoto, Japan). Compatibilizer B was a synthetic vinyl oxazoline-vinylpyrrolidone copolymer, and compatibilizer C was a commercially available compound 2,2'-bis (2-oxazoline) supplied by Tokyo Chemical Industries (Tokyo, Japan).

It should be noted that compatibilizer B is a laboratory synthesized product and the molding method is limited due to the small amount of only a few grams.

Preparation of Blends

In each trial, quantities of the LCP, a compatibilizer and PP were first manually mixed. The compositions of the different PP/LCP/compatibilizer blends are presented in Table 2(a) and the mol of reactive functional groups in 1 g of composite is shown in Table 2(b). However, it should be noted that the amount of terminal carboxylic acid of AL-7000 is calculated using the weight average molecular weight of common LCP. Note that the LCP was dried in an oven at 130°C for 4 h before use. Following this, 2 g quantities of each of these blends were subsequently kneaded for 10 min in a LABO PLASTOMILL μ (TOYOSEIKI) mixing chamber at 200°C with a rotation rate of 60 rpm.

Processing

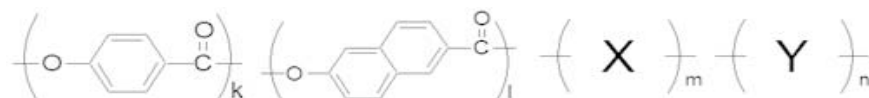
Compression molding was selected as the molding method because it allows molding with a small amount of sample. A sample of 0.2 g of each blend was taken and compressed at 200°C and 5 MPa for 5 min, then quenched while compressed at 20°C and 5 MPa for 3 min to prepare a dumbbell-shaped tensile test piece. These test pieces were similar to those required by the JIS K6251-7 standard, with a neck width of 2 mm and a thickness of 0.5 mm.

TABLE 1. Mechanical properties of various LCPs.

LCP/description		Tensile strength (MPa)	Tensile modulus (GPa)	Tensile elongation at break (%)	Melt temperature (°C)
AL-7000	Wholly aromatic with low melting point	114	18.7	1.8	178
A-5000	Wholly aromatic	164	11.4	5.1	278
LC-5000	Semi-aromatic	89	7.7	3.9	286

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a)



b)

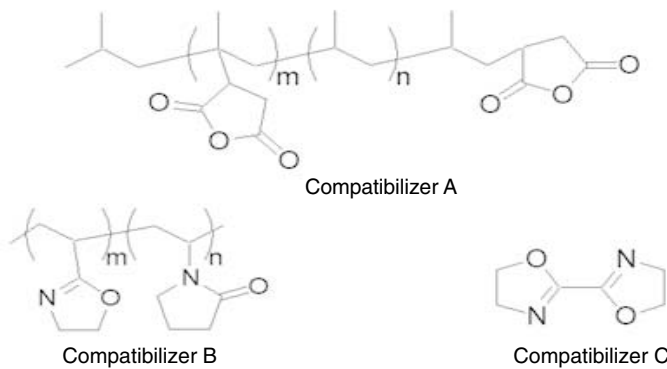


Figure 1. Chemical structures of (a) AL-7000, (b) Compatibilizers A to C.

TABLE 2(a). Compositions of PP/LCP blends containing compatibilizers.

Blend	Weight percentage of each component				
	Homo-PP	LCP (AL-7000)	Compatibilizer		
			(A)	(B)	(C)
I	100	0	0	0	0
II	90	10	0	0	0
III	89.1	9.9	1	0	0
IV	88.2	9.8	1	1	0
V	88.2	9.8	1	0	1

TABLE 2(b). Mol of reactive functional groups in 1 g of composite.

Blends	Mol of reactive functional groups in 1 g of composite ($\times 10^{-6}$)			
	LCP AL-7000	Compatibilizer		
		(A)	(B)	(C)
Functional groups	Carboxylic acid	Maleic anhydride	Oxazoline	Oxazoline
I	3.4	0	0	0
II	3.4	0	0	0
III	3.4	4.7	0	0
IV	3.4	4.7	106	0
V	3.4	4.7	0	150

Measurements

Fourier transform infrared spectroscopy (FTIR) of the blends in solid state was obtained by the diffuse reflection method performed on a FT/IR-4600 (JASCO) spectrophotometer. The blend samples were cryofractured in liquid nitrogen and the resulting fractured surfaces were coated with platinum before observations by microscope operated at 3.0 kV and under high vacuum. The mechanical analysis was carried out by testing dumbbell shaped specimens in a MCT-2150 instrument (A & D) at room temperature. A gauge length of 15 mm and a cross-head speed of 10 mm/min were used.

RESULTS AND DISCUSSION

FTIR spectra

The FTIR spectrum of the blend is shown in Figure 2. The absorption peaks at 1730 cm^{-1} and 1595 cm^{-1} were observed for blend II with AL-7000 added to PP. LCP has a structure containing an ester group and a benzene ring, and these peaks correspond to the C=O band

of the ester and the C=C bond of the benzene ring, respectively. No significant change in the peaks was observed with the addition of compatibilizer A (blend III). This may be due to the small amount of PP-g-MAH added. Further addition of a compatibilizer containing oxazoline groups (blends IV and V) resulted in the appearance of a new absorption band at 1650 cm^{-1} . This peak corresponds to the C=O of the amide bond, respectively, indicating the formation of the amide bond. Previous studies have suggested that the oxazoline group reacts with the carboxylic acid group by a mechanism similar to that shown in Figure 3.^[18] It shows that the carboxylic acid present at the end of LCP reacted with the oxazoline group of the compatibilizer to form an amide bond. The increase in the peak intensity around 1730 cm^{-1} corresponding to the C=O band of the ester is also attributed to the reaction shown in Figure 3. These results indicate that the

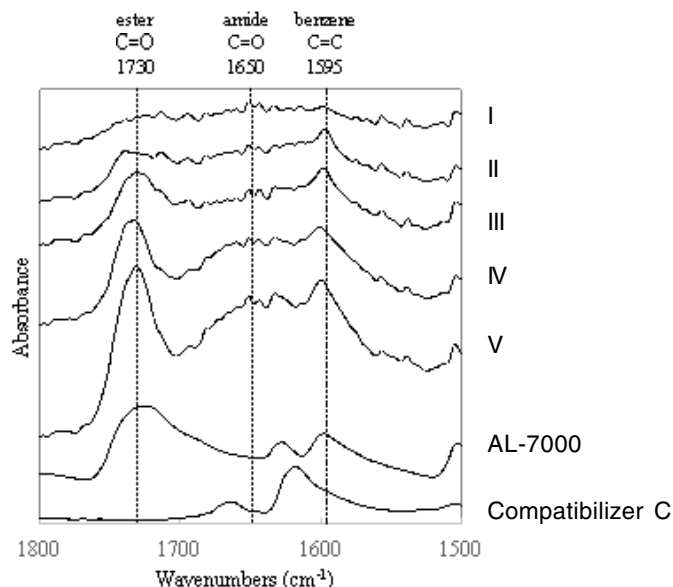


Figure 2. FTIR spectra of PP/LCP blends.

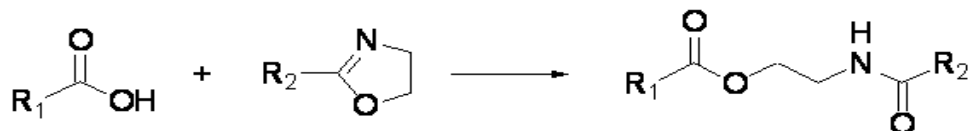


Figure 3. Reaction of carboxylic acids with oxazoline.

oxazoline group-containing compounds and PP-g-MAH are likely to function as compatibilizers to improve the interfacial strength of PP/LCP.

Morphology

SEM images of specimens of blends I to V are provided in Figure 4. In these images, the minor LCP phase is seen to have been in the form of nearly spherical droplets distributed throughout the PP matrix, with or without compatibilizer. It is known that the morphology of the LCP phase can be either droplet-like or fibrous, depending on the shear force applied during molding. The LCP droplets observed in the present research are attributed to the low-pressure compression molding process that was employed. Because the mechanical properties of such blends differ depending on the morphology of the LCP phase, only the mechanical properties of those specimens in which the LCP was dispersed in the form of droplets are compared in the subsequent mechanical properties section.

In the binary blends consisting only of PP and LCP, the LCP droplets were not uniform and ranged in size from 2 to 100 μm . The addition of PP-g-MAH reduced the diameter of the LCP droplets to the range of about 2 to 80 μm , and the addition of compounds containing oxazoline groups further reduced the droplet size. In particular, blend V had the smallest LCP diameter (1–20 μm) among the blends in this

study, and was the only one in which aggregation breakdown occurred within the LCP phase. Megagnini et al. previously reported that blending PP with a semi-aromatic LCP [copolymers of sebacic acid (S), 4,4'-dihydroxy-biphenyl (B) and 4-hydroxybenzoic acid (H); SBH] gave LCP droplets from about 20 to 70 μm in size.^[19] The addition of 5% PP-g-SBH copolymer to PP/SBH blends resulted in SBH droplets with average sizes in the range of about 5–10 μm , but no reports on aggregation breakdown of the SBH phase have been made. This indicates that the inclusion of PP-g-SBH improved the dispersibility of the SBH phase in the blend, but did not improve the PP/SBH interfacial strength. The reason for the cohesive failure in blend V is thought to be that the oxazoline group reacted with both carboxylic acid groups at the end of the LCP molecule to form an amide bond, which increased the adhesive strength at the PP-LCP interface, as shown by the FT-IR results.

Mechanical Properties

As noted above, the mechanical properties of the blends differed greatly depending on the manner in which the LCP was dispersed. Therefore, this section assesses only those blends in which the LCP phase was dispersed as droplets. Representative stress-strain curves of the blends are shown in Figure 5, and the graphs of tensile strength, modulus, and elongation are shown in Figure 6. Figure 5

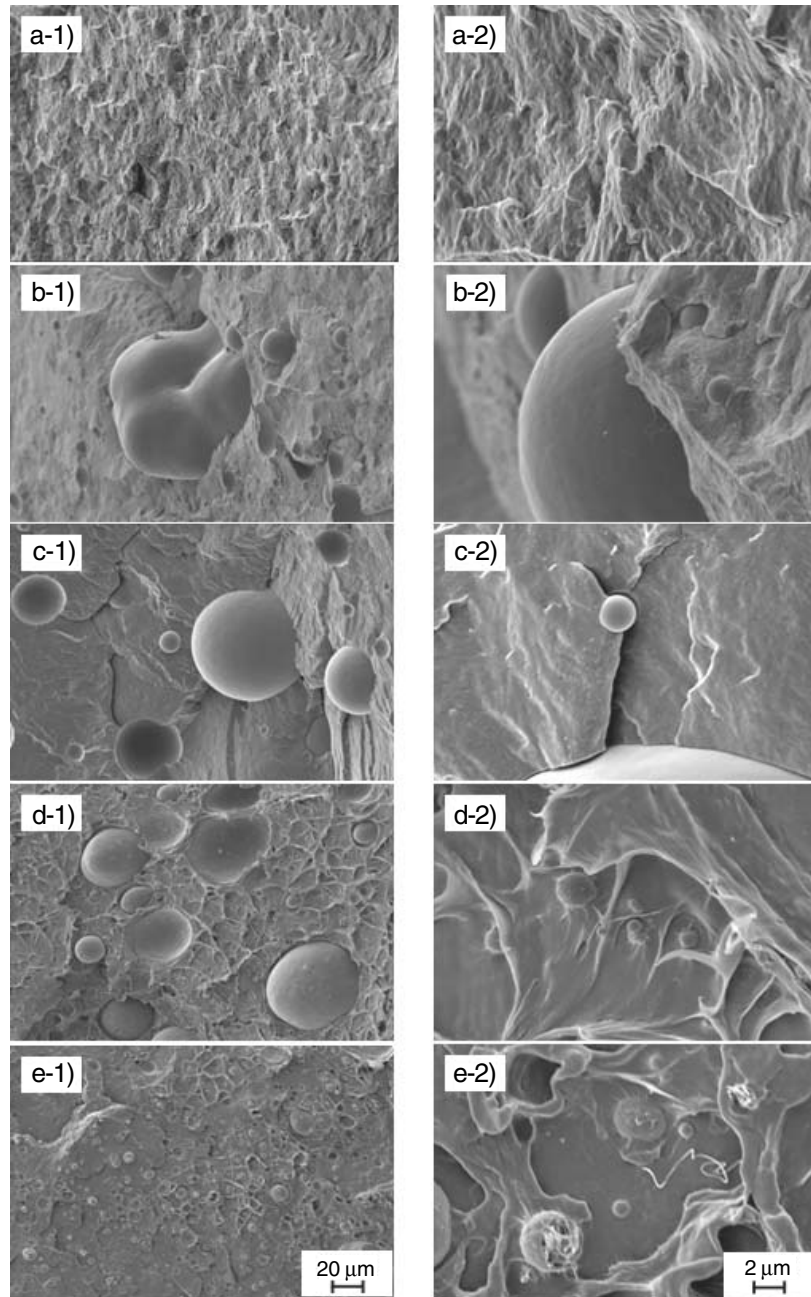


Figure 4. SEM images of fractured surfaces of blends (a) I, (b) II, (c) III, (d) IV, and (e) V. (1) Magnification 500x, (2) Magnification 5000x.

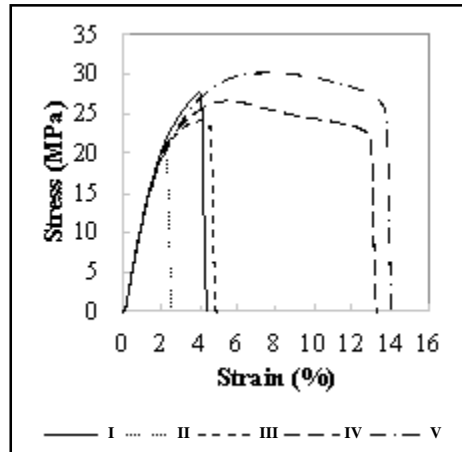


Figure 5. Stress-strain curves obtained for various blends.

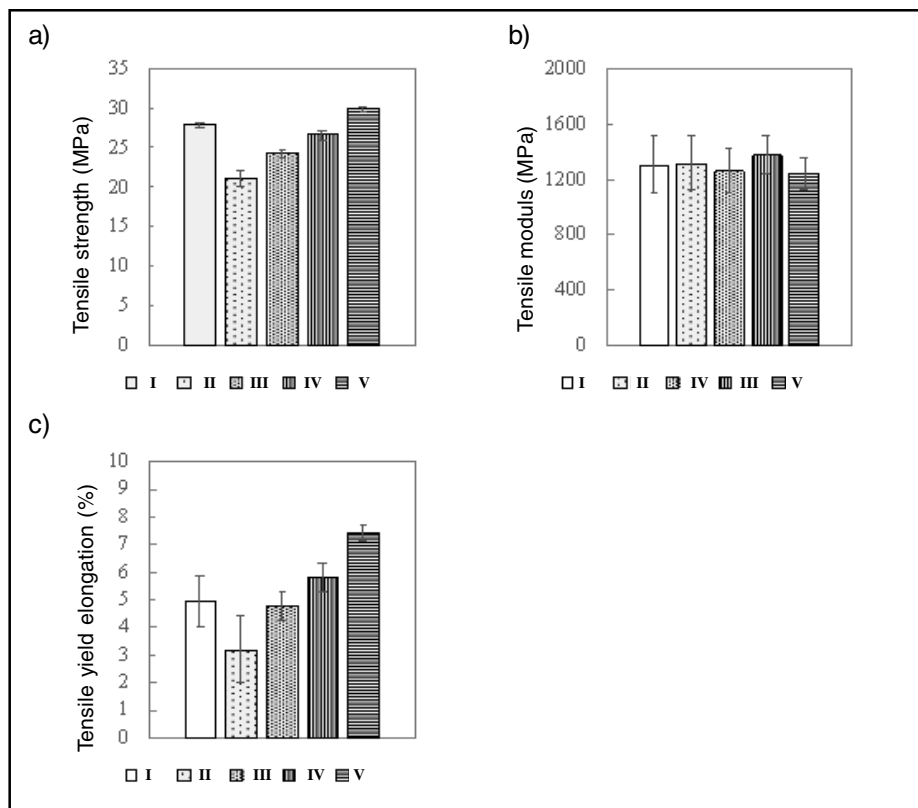


Figure 6. Plots summarizing (a) tensile strength, (b) tensile modulus, and (c) tensile yield elongation for various blends.

shows that brittle fracture occurred in the pure PP and PP/LCP binary blends, while ductile fracture occurred when a compatibilizer was added. Correspondingly, the tensile elongation at break was increased (blend III to V). It is possible that the compatibilizer functioned as a plasticizer, or that the chemical bond between the compatibilizer and the carboxylic acid group at the end of the LCP molecule became a cross-linking point, but it is not clear from this study.

Figure 6 shows that the binary blend of PP and LCP exhibited an improved tensile modulus relative to the pure PP, but a reduced tensile strength and tensile yield elongation. This result is consistent with data previously reported for kneaded PP/semi-aromatic LCP blends.^[10] The addition of compatibilizer A increased the tensile strength and tensile yield elongation but lowered the tensile modulus compared to the value for the PP/LCP binary blend. The incorporation of compatibilizer B or C increased the tensile strength and tensile yield elongation. Blend V, containing compatibilizers A and C, showed the largest increases in tensile strength and yield elongation, with higher values than those for the pure PP. This can be attributed to the increased adhesive strength at the PP-LCP interface due to the effect of the compatibilizer, which is also consistent with the cohesive failure of LCP confirmed by SEM observation. In addition, it is particularly noteworthy that the tensile yield elongation for blend V was nearly twice that for the pure PP. Various compatibilizers have been researched to date, but none have generated tensile yield elongation that significantly exceeded those of pure PP. These results indicate that the use of compatibilizer C and PP-g-MAH as

compatibilizers can improve the tensile properties (especially the tensile elongation) of PP/LCP blends.

CONCLUSIONS

The effects of the presence of oxazoline group-containing compounds and PP-g-MAH on the spectral, morphological and mechanical properties of PP/LCP blends were investigated. The addition of the oxazoline group-containing compound in combination with PP-g-MAH resulted in the formation of amide bonds, which improved the dispersibility of LCP. Furthermore, cohesive breakdown occurred within the LCP phase, and mechanical properties were improved. These results suggest that the oxazoline group reacted with the carboxylic acid group to enhance the interfacial strength of the PP/LCP blend. The molding method employed in this study dispersed the LCP in the form of droplets and so the mechanical strength of such blends could be further improved by applying shear to orient the LCP phase into a fibrous morphology during molding.

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Received: 01-06-2021

Accepted: 17-06-2021