In situ compatibility of polystyrene and liquid crystalline polymer blends

Yei-Po Chiou, Dor-Yaw Chang and Feng-Chih Chang*
Institute of Applied Chemistry, National Chiao-Tung University, Hsin-Chu, Taiwan, Republic of China
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The styrene–glycidyl methacrylate (SG) copolymer can be used to compatibilize the immiscible and incompatible blends between polystyrene (PS) and liquid crystalline polymer (LCP) copolyester. The epoxy functional groups present in the SG copolymer can react with the carboxylic and/or the hydroxyl terminal groups of the LCP at interface to form the SG-g-LCP copolymer during melt processing. This in situ-formed graft copolymer tends to reside along the interface to reduce the interfacial tension in the melt state and to increase the interphase adhesion in the solid state. However, the compatibilized PS/LCP blends reduce the number of LCP fibrils formed and have a tendency to form droplet LCP domains. The overall mechanical properties, stiffness and toughness of the blends improved after compatibilization, but the extent of the improvement is not very significant. It appears that the gain from the adhesion enhancement is more than offset by the loss due to the reduction in LCP fibril formation. The ethyl triphenylphosphonium bromide catalyst can further improve the compatibility of the blends by increasing the rate of the graft reaction.

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INTRODUCTION

Liquid crystalline polymers (LCP) are known to form in situ reinforcing fibrils when blended with a thermoplastic under appropriate processing conditions. This is due to the inherent nature of thermotropic LCPs to form elongated rod-like structures in the nematic phase during processing. Two major advantages gained by the addition of a small amount of LCP to a thermoplastic are processability improvement and enhancement of mechanical properties, especially for modulus and tensile strength in the machine direction. Polymer blends of LCPs with isotropic thermoplastic polymers have attracted considerable attention since the early 1980s, and have been the subject of recent reviews. Compatibilization of an immiscible and incompatible thermoplastic blend usually results in a finer and more stable morphology, better processability, and improved mechanical properties. Methods, classifications, and strategies of compatibilization of thermoplastic polymer blends have been reviewed recently. Other than certain blend pairs with structural similarity, most thermoplastic/LCP blends are considered to be immiscible and incompatible, with the expected poor interphase adhesion. This is the reason why the mechanical properties achieved from most LCP fibril-reinforcing composites are less than the theoretically calculated values.

In order to enhance compatibility between thermoplastic/LCP blends, a few attempts have been reported by modifying the LCP structure. Heitz et al. were able to improve the miscibility between LCPs with polystyrene (PS) by using an LCP containing PS side-chains. Eisenbach et al. succeeded in achieving compatible blends in rigid-rod polymers with poly(styrene-co-4-vinylbenzoic acid) and poly(styrene-4-styrene sulfonic acid) via ion–ion interaction. These two examples are not considered to be compatibilized blends according to the conventional definition of compatibilization: they belong to the binary blend system with improved compatibility throughout modification of the blend component structure.

The concept of using a third component (a compatibilizer), reactive or non-reactive, in compatibilizing the binary thermoplastic/thermoplastic systems is well established but has rarely been extended to thermoplastic/LCP systems. The transesterification reaction can improve the miscibility between the LCP and isotropic polyesters. The ester interchanged products of polycarbonate (PC) and LCPs have been used to compatibilize PC/LCP blends. Using most interchanged products as the compatibilizer usually results in a reduction of toughness and crystallinity, which was described in detail in our recent review. Compatibilized polypropylene (PP)/LCP blends are the one particular thermoplastic/LCP system that has received great interest lately. PP/LCP blends compatibilized with PP functionalized by maleic anhydride and acrylic acid resulted in an increase in stiffness (tensile strength and modulus) but a decrease in toughness (tensile elongation and impact strength). In contrast, the PP/LCP blends compatibilized with epoxy-containing copolymers and an ethylene-based reactive terpolymer resulted in an increase in toughness...
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Table 1 Processing conditions

(a) Extrusion

<table>
<thead>
<tr>
<th>Stage</th>
<th>1</th>
<th>2</th>
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<th>5</th>
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<th>7</th>
<th>8</th>
<th>9</th>
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<tbody>
<tr>
<td>Temperature (°C):</td>
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<td>255</td>
<td>275</td>
<td>290</td>
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<td>290</td>
<td>290</td>
<td>290</td>
<td>290</td>
<td>265</td>
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</tbody>
</table>

Motor rate: 210 rpm
Feeder rate: 200 g min⁻¹

(b) Injection moulding

<table>
<thead>
<tr>
<th>Zone:</th>
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<th>2</th>
<th>3</th>
<th>4</th>
</tr>
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<tbody>
<tr>
<td>Temperature (°C):</td>
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<td>290</td>
<td>290</td>
<td>280</td>
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</table>

Screw rate: 200 rpm
Mould temperature: 70°C
Back pressure: 55 psi (3.8 bar)
Cycle time: 30 s

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BACKGROUND

The concepts of compatibilizing an immiscible and incompatible thermoplastic polymer blend are well established. An effectively compatibilized blend can usually result in reduced interfacial tension, finer phase domains, higher interfacial adhesion, higher heat distortion temperature, better phase stability against coalescence, and improved mechanical properties than the corresponding uncompatibilized blend. To any isotropic thermoplastic blend pair, all the above-listed changes by compatibilization are desirable from the viewpoint of improving material quality. However, it is not that straightforward when applying the same compatibilization concept to thermoplastic/LCP blends. The creation of LCP fibrils in the thermoplastic/LCP blends is essential for reinforcement of the matrix, and leads to stronger mechanical properties. Due to the intrinsic nature of the thermotropic LCP polymers, several variables can affect the ability to form the desirable fibrillar LCP structure, including extensional flow, LCP content, viscosity ratio, draw ratio, temperature, shear rate and cooling rate. Some of above variables may be mutually correlated. Dispersed phase morphology and interfacial adhesion are the two most decisive changes by compatibilization that can affect directly the resultant mechanical properties. The improvement in interfacial adhesion of an effectively compatibilized thermoplastic/thermoplastic blend has been generally accepted, and this should also be extended to the thermoplastic/LCP blends. From the limited available literature, the compatibilized thermoplastic/LCP blends indeed resulted in finer LCP phase domains as would be expected. Other than the expected finer LCP domain size, some articles reported that the number and length of the LCP fibrils were decreased or even converted into droplet domains\textsuperscript{16,17}. In the Noryl/LCP blends, the LCP fibrils became finer with a higher aspect ratio after compatibilizing\textsuperscript{18}. In addition to the adhesion improvement, the finer LCP fibrils in the compatibilized Noryl/LCP blends resulted in substantial improvements in essentially all properties including stiffness, toughness and heat distortion temperature. Processing conditions are also very critical to control the final morphology of the blends, compatibilized or uncompatibilized, and

Figure 1  IR spectra of SG5, the LCP, and the powder-blended and melt-blended PS/LCP blends

Figure 2  Torque versus time curves for the LCP, SG5, and the LCP/SG5 and LCP/SG5/Cat blends
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MELT FLOW RATE FOR PS/LCP

Figure 3 Effect of SG5 and catalyst on MFRs of various PS/LCP blends

should also be taken into consideration. In general, the compatibilized thermoplastic/LCP blends have a tendency to reduce the number and length of LCP fibrils or even form droplet domains depending on the blend system and the processing conditions.

A reactive compatibilizer in a binary A/B blend is a selected reactive C-X copolymer which has C segments structurally identical or miscible with component A, and X can have a covalent reaction with component B to form C-X-B graft or block copolymers during melt processing. Before the reaction takes place, the C-X copolymer is usually miscible or nearly miscible with component A, and the extent of miscibility depends upon the X content in the C-X copolymer. Therefore, the reaction is expected to occur only at the interface, and the in situ-formed C-X-B copolymer tends to remain along the interface to reduce the interfacial tension of the A/B blend. The C-X copolymer itself is not considered as a compatibilizer for the A/B blend; only the in situ-formed C-X-B copolymer can function as a compatibilizer. Such a reactive compatibilization approach is not universally applicable to all polymers. Reactive compatibilization is applicable only to those polymers containing certain functional groups (as chain ends or within the main chain) that can be reacted with the reactive compatibilizer. In general, a blend constituent possessing chain-end functional groups is particularly suitable for such in situ reactive compatibilization. Typical examples are -COOH (and/or -OH) of polyesters, phenolic -OH of PPO, and -NH2 of polyamides. The X in the C-X reactive compatibilizer can also be as chain ends or evenly distributed within the main chain to produce a block copolymer (former) or a graft copolymer (latter). Excessive grafting is expected to produce a highly branched comb-like graft copolymer or even a cross-linked network, which is considered to be less effective as a phase compatibilizer. Usually, a lightly grafted copolymer, one or only a few grafts per main chain, is more effective than a heavily grafted one28,29. It is essential to control the graft reaction by optimizing the reactive group content, blending sequence, catalyst and processing conditions to achieve the best performance of the resultant blend30.

The only expected reactions in this study are the reactions between epoxy groups in SG5 and -COOH and -OH of the LCP end-groups, which are well established4-6,16-18,28,30-34 as shown in equations (1) and (2).

\[
\text{SG-O-CH}_2-\text{CH-CH}_2+\text{LCP-COOH} \\
\rightarrow \text{SG-O-CH}_2-\text{CH-CH}_2-\text{OCONH-LCP} (1)
\]

\[
\text{SG-O-CH}_2-\text{CH-CH}_2+\text{LCP-OH} \\
\rightarrow \text{SG-O-CH}_2-\text{CH-CH}_2-\text{OH-LCP} (2)
\]
The reaction mechanisms for ethyl triphenylphosphonium bromide catalysing the reactions between epoxy and carboxylic acid or hydroxyl groups were described in our previous paper\textsuperscript{18}. Ethyl triphenylphosphonium bromide first dissociates into triphenylphosphine and ethyl bromide by maintaining the equilibrium. Nucleophilic attack by triphenylphosphine then opens the epoxy ring and abstracts a reactive hydrogen from the carboxyl or hydroxyl group to yield the carboxylate or the hydroxylate anion. The carboxylate or the hydroxylate anion reacts with the electrophilic carbon attached to the positive phosphorus atom to regenerate the catalyst to complete the cycle of catalytic reaction.

Fourier transform infrared spectroscopy

Figure 1 gives the i.r. spectra of SG5, LCP and the powder-blend, and melt-blended LCP/SG5 = 90/10 mixtures. The epoxy characteristic peak at 913.2 cm\(^{-1}\) of the powder-blended mixture disappears after melt blending and, this can be attributed to the reactions between the epoxy group of the SG5 with the carboxylic acid and hydroxyl end-groups of the LCP. Since the reduction of the epoxy peak observed does not account for all the epoxy groups consumed in the reaction, epoxy hydrolysis or other unknown reactions may also be involved\textsuperscript{28}.

Torque versus time

Figure 2 gives the torque versus time curves for the LCP, SG5, LCP/SG5 = 50/50, and LCP/SG6/Cat = 50/50/0.02 blends. Both the LCP and SG5 show signs of a gradual decrease in torque with time. In contrast, the torques of the mixtures of LCP/SG5 and LCP/SG5/Cat increase continuously after about 175 s. The presence of 200 ppm of catalyst in the mixture increases the rate of torque rise. This observed torque increase can be attributed to the molar mass increase from the expected graft reactions between the LCP and SG5.

Melt flow rates

Figure 3 summarizes all melt flow rates (MFRs) measured in this study. The trend clearly shows the decrease in MFR (molar mass increase) after
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compatibilization from all compositions. By maintaining constant 5 phr (parts per hundred parts of resin) SG5 compatibilizer, the extent of the MFR reduction is greater for the blends containing lower amounts of the PS component. Since the SG5 concentration present in the PS phase is higher for the blends with a smaller PS content while the graft reaction can take place only at the interface, more graft reaction can therefore be expected to form a greater number of grafted copolymers and more grafts per chain of the graft copolymer during melt processing.

Capillary rheometry

Both the LCP and PS exhibit non-Newtonian flow behaviour within the shear rates investigated (50–3000 s⁻¹). The viscosity of PS is greater than that of the LCP at 280°C, but the order is reversed at 290°C. That means the viscosity of PS is more temperature-dependent with a lower activation energy for viscous flow than that for the LCP. The temperature range between 280 and 290°C is very critical in terms of the change in viscosity ratio and therefore the resultant phase morphology. Figure 4 compares the viscosity versus shear rate plots at 280°C for the uncompatibilized and compatibilized PS/LCP = 50/50 blends. The observed trend is similar to the MFR data, the better compatibilized blend resulting in higher viscosity.

Morphologies

Only a few selected morphologies emphasizing the morphological changes due to compatibilization are presented here. Figure 5 shows the fracture surface scanning electron micrographs at the core region of the uncompatibilized and compatibilized PS/LCP = 75/25 and PS/LCP = 25/75 blends viewed from the plane perpendicular to the processing flow direction. Figure 5A shows the morphology of the uncompatibilized PS/LCP = 75/25 blend where the dispersed LCP phase is present as coarse lamellar domains.
After compatibilization, the LCP domain size has been significantly reduced, as shown in Figures 5B and 5C. A similar phenomenon has also been observed in other series of blends if the PS is the major component of the blend. Figures 5D–5F show the morphologies of the uncompatibilized and compatibilized PS/LCP = 25/75 blends where the LCP is the major component. Again, the better compatibilized blend results in finer phase domain as would be expected. In those LCP-dominant blends, high toughness of the LCP matrix causes an extensive LCP tearing on the fracture surfaces. Figure 6 shows the morphologies near the skin region of the same specimens as shown in Figure 5, viewed from the plane parallel to the injection flow direction. Figure 6A shows the formation of LCP fibres near skin region of this uncompatibilized PS/LCP = 75/25 blend. Essentially all the LCP fibres disappeared, and were converted into LCP droplets after compatibilization as shown in Figure 6B and 6C. Therefore, the expected advantages of the fibre-reinforcement in this PS/LCP system decreases or disappears after compatibilization. Figures 6D–6F show the fibrillar LCP structure from both uncompatibilized and the compatibilized PS/LCP = 25/75 blends when PS is the minor component of the blend. The PS phase is also present as elongated domains within the LCP fibres in those blends in which the LCP is a matrix. The LCP has higher melting point, and would solidify and then quickly cool down to the Ts of PS. Therefore, the elongated PS phase may not have the time to relax and retract to form the droplet domains.

All of the above injection-moulded specimen morphologies were based on an identical processing condition with processing temperature range between 280–290°C (Table 1). As shown earlier, the viscosity ratio change is highly temperature-dependent in this particular temperature range. A slight change in processing temperature is expected to alter the resultant morphology substantially. It was reported that a viscosity ratio (\( \frac{\eta_{LCP}}{\eta_{thermoplastic}} \)) of between 0.5 and 1.0 can result in the most spontaneous LCP fibre formation.35

**Mechanical properties**

Table 2 summarizes all the mechanical properties of the uncompatibilized and compatibilized blends investigated in this study. The compatibilized blends have slightly higher tensile strength relative to the uncompatibilized blends from all compositions. The addition of 200 ppm of catalyst further increases the resultant tensile strength. The compatibilized blends also result in a higher tensile modulus, similar to the increase in tensile strength. The observed mechanical property improvements after compatibilization are more substantial for the blends in which the LCP is the major component than for those in which PS is the matrix. The MFR reduction after compatibilization for those LCP-dominant blends is also more pronounced than the PS-dominant blends. As we mentioned earlier, a higher SG5 concentration in the PS phase for those LCP-dominant blends provides more chance of forming a greater number of grafted copolymers and more grafts per chain of the graft copolymer during melt processes.

That means those LCP-dominant blends are relatively better compatibilized. Both tensile strength and modulus are considered to comprise the material stiffness, while the tensile elongation and impact strength comprise the material toughness. Most previously reported compatibilized thermoplastic/LCP blends usually resulted in either an improvement in stiffness (but lower toughness) or an increase in toughness (but lower stiffness). Similar to the results from the Noryl/LCP blends,18 this study shows both stiffness and toughness improvements simultaneously after compatibilization. However, after closely comparing the results, the extent of the mechanical property improvements from this PS/LCP system is not as substantial as for the previously mentioned Noryl/LCP system18. This difference can be explained by the LCP morphology changes after compatibilization.
from these two systems. In the Noryl/LCP system, the LCP fibrils were mostly retained and even became finer with a higher aspect ratio after compatibilization. In the PS/LCP system, compatibilization caused the number of the LCP fibrils to be reduced and also had the tendency to form droplet morphology. Interfacial adhesion improvement is expected from both systems. Therefore, in the PS/LCP system, the gain from the interfacial adhesion after compatibilization is able to offset the loss due to the reduction in the number of LCP fibrils. The main difference between these two systems arises from the chemistry of the reactions involved. In the Noryl/LCP blend system, the SG compatibilizer can react with both the LCP and PPO with comparable reactivity. That means a mixed graft SG-g-LCP-g-PPO copolymer can also be produced. This mixed graft copolymer with its long PPO branch chain deeply penetrating into the Noryl phase is able to anchor along the interface more strongly to act as a better compatibilizer than the SG-g-LCP copolymer. In the PS/LCP system, the SG compatibilized can only react with the LCP to form the SG-LCP copolymer, which is probably less effective as a compatibilizer.

CONCLUSIONS

The SG copolymer can be used as a reactive compatibilizer for blends between PS and the LCP. The epoxy functional groups in the SG copolymer can react with -COOH and/or -OH terminal groups of the LCP to form the SG-LCP copolymer during melt processing. The in situ formed graft copolymer tends to reside along the interface to reduce the interfacial tension, and this increases the adhesion of the blends. The presence of a small amount (200 ppm) of ethyl triphenylphosphonium bromide catalyst further promotes the graft reaction. Compatibilization causes a reduction in the number of LCP fibrils formed, and has the tendency to form the droplet morphology. The compatibilized PS/LCP blends have higher product stiffness and toughness than the corresponding uncompatibilized blends. It appears that the advantages of adhesion improvement more than offset the loss due to a reduction in the number of LCP fibrils in the compatibilized blend.

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