

Phase Behavior and Properties of In Situ-Reinforcing Elastomer Composites Based on Thermoplastic Elastomers and Thermotropic Liquid Crystalline Copolyester

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ABSTRACT: In situ reinforcing composites based on two elastomer matrices very different in melt viscosity, styrene-(ethylene butylene)-styrene triblock copolymer (Kraton G1650) and styrene-(ethylene propylene) diblock copolymer (Kraton G1701), and a thermotropic liquid crystalline polymer (TLCP), Rodrun LC3000, were prepared using a twin-screw extruder. The rheological behavior, morphology, mechanical and thermal properties of the blends containing various LC3000 contents were investigated. G1650 was found to have much higher shear viscosity than G1701. All neat components and their blends exhibited shear thinning behavior. Melt viscosity of the blends gradually decreased with increasing LC3000 contents. Despite a large difference in melt viscosity of the two matrices, the results showed that the fibrillar morphology was obtained for both as-extruded

strands of LC3000/G1650 and LC3000/G1701 with up to 30 wt % LC3000. At 40 wt % LC3000 or more, the lamellar structure was observed for both types of blends because of the coalescence of liquid TLCP threads that occurred during extrusion. The addition of LC3000 into both elastomer matrices enhanced the tensile modulus considerably whereas the extensibility remarkably decreased. The results obtained from thermogravimetric analysis suggested that an addition of LC3000 into both elastomer matrices improved the thermal resistance significantly in air, but not in nitrogen. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1610–1619, 2006

Key words: polymer in situ composite; liquid crystalline polymer; rheological behavior; mechanical property; thermal degradation; thermoplastic elastomer

INTRODUCTION

The mechanical properties of thermoplastic elastomers (TPEs) can be improved by addition of fibrous fillers.^{1–5} However, an incorporation of solid fibers into the polymer matrix normally encounters numerous problems during processing and fabrication. The presence of the solid fibers in the molten polymer matrix increases the viscosity of the system and causes abrasion on the surface of the processing equipment. Furthermore, some fibers are broken down into fragments due to the high shear stress during mixing, resulting in a significant reduction in the properties of the composite materials. A new possible way to circumvent these problems is an in situ generation of short fibers in an immiscible blend of a thermotropic liquid crystalline polymer (TLCP) with the elastomer.^{6–16} TLCPs are known to possess superior physical properties, such as high strength, good thermal properties and low melt viscosity. Under appropriate

processing conditions and fabrication method, the dispersed TLCP droplets can be elongated by an elongational flow field and frozen in the matrix after rapid cooling. This type of blend is called in situ composite.¹⁷ However, the main problem to be investigated for this type of blend is to find the optimum processing condition to obtain a fibrillar morphology of the TLCP phase. The morphology and the resultant properties of the blends are highly dependent on the processing conditions and the composition of the blend components. Moreover, it has been reported that the viscosity ratio and the strain rate are also the important parameters governing the fibrillation of TLCP in the blend.^{18–20} Generally, the fibrillation of TLCP is enhanced as the viscosity ratio of TLCP to polymer matrix becomes mostly less than unity^{21–23} and it has also been reported that the elongational flow causes more extensive fibrillation than the shear flow.^{24–26}

So far, a very exhaustive study was done with TLCP-thermoplastics blends, but very limited information is available with regard to the TLCP-elastomer blends. Lorenzo et al.⁶ studied the viscoelastic behavior of a TLCP blended with styrene-butadiene rubber (SBR) and reported that the complex viscosity of the blend exhibited minima at 10% TLCP. Verhoogt et al.^{7,8} investigated the blends of TLCP (Vectra A900) and the styrene-(ethylene butylene)-styrene (SEBS,

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Kraton G1650) and suggested that the polymers were immiscible. A shift in glass transition temperature (T_g) was observed and was attributed to the adsorption of the elastomeric phase on the TLCP domains. They also observed a fibrillar morphology in the blends with less than 30 vol % TLCP and found that the addition of TLCP resulted in a substantial increase in both modulus of elasticity and tensile strength. Machiels et al.⁹ studied the fiber formation, stability, and properties of TPE (Arnitel EM630)/Vectra A900 blends and reported that the mechanical properties increased with increase in draw ratio of the extrudate as a result of an increase in the fiber aspect ratio and molecular orientation in the TLCP phase. Seo and coworkers^{13,14} investigated ethylene-propylene-diene monomer rubber (EPDM)/Vectra B950 blends and suggested the effect of elongational deformation on the fibrillation of TLCP. Chakraborty et al.¹⁵ studied the self-reinforcing characteristics of Vectra A950 in EPDM. They reported that interconnecting fibrillation was possible under the shear field processing of the blend and the incorporation of TLCP enhanced the thermal stability of the blend. In addition, the properties of ethylene-propylene-rubber (EPR) in situ reinforced with TLCP have been reported by Sahoo and Das.¹⁶

Recently, we have investigated the blends of SEBS (Kraton G1652) in situ reinforced with TLCP (Rodrun LC3000). The rheological behavior, mechanical properties, and morphology of the blends have been reported.^{10–12} From our previous work, the addition of Rodrun LC3000 into Kraton G1652 significantly enhanced the mechanical properties and improved processability of the blend. However, despite the viscosity ratio of the LC3000/G1652 system was as low as 0.1, most of the dispersed TLCP domains in as-extruded strands were found to appear as droplets.^{10,11} In this study, the in situ composites based on two elastomer matrices possessing very different melt viscosity and Rodrun LC3000 were further investigated. The aim of this work is to obtain fibrillar morphology in as-extruded strands blends. To obtain such morphology, we have chosen to increase the matrix viscosity further from G1652 studied previously. Alternative was also sought by changing the elastomer structure away from G1652 while keeping the viscosity at the same level. This would allow us to study the influence of different elastomer matrices of very different melt viscosity and structure on rheological behavior, morphology, and properties of the blends containing Rodrun LC3000 and compare the results with previously studied LC3000/G1652 blend system.¹⁰

EXPERIMENTAL

The polymer dispersed phase used in this work was Rodrun LC3000, a TLCP, supplied by Unitika (Tokyo, Japan). Rodrun LC3000 is a copolyester of 60 mol %

p-hydroxy benzoic acid (HBA) and 40 mol % poly(ethylene terephthalate) (PET) with a melting point of 220°C and a density of 1.41 g/cm³. The matrix phases used in this study were Kraton G1650 and Kraton G1701. Kraton G1650 is an SEBS triblock copolymer with a styrene/rubber weight percent ratio of 29/71 and Kraton G1701 is a styrene-(ethylene propylene) diblock copolymer with 37 wt % polystyrene. Both polymer matrices were provided by Shell Chemical (Houston, TX). All materials were dried in a vacuum oven at 70°C for at least 12 h before used. In this article, Rodrun LC3000, Kraton G1650, and Kraton G1701 were represented by LC3000, G1650, and G1701, respectively.

The blends of LC3000/G1650 and LC3000/G1701 at various compositions were prepared with a corotating, intermeshing, twin-screw extruder (TSE 16-TC, Prism, Staffordshire, UK) with a screw diameter of 16 mm, length-to-diameter ratio (L/D) of 25, a die diameter of 2 mm, and a screw speed of 60 rpm. The temperature profile was 190–220–220–225–225°C, representing the temperatures at the hopper zone, three barrel zones, and heating zone in the die head, respectively. The extruded strand was immediately quenched in a water bath and was subsequently dried in a vacuum oven. The blending equipment and processing conditions for preparation of LC3000/G1650 and LC3000/G1701 blends in this study were the same as those of LC3000/G1652 as described in the previous article.¹⁰ The sample codes of the extruded strand blends are designated as G1650-X or G1701-X where X depicts the content of LC3000 in wt %.

The complex viscosity (η^*) measurements of the neat components and the blends were carried out with a plate-and-plate rheometer (Rotovisco RT 20, Haake, Karlsruhe, Germany). The extruded strands were cut into small pieces and compression-molded at 200°C into a sheet about 1 mm thick. The sheet was then punched into a disk 20 mm in diameter. The η^* values and storage modulus (G') of all specimens were measured in the oscillatory shear mode within the angular frequency (ω) range from 0.6 to 200 rad/s. The measuring temperature and the gap between the two plates were set at 225°C and 0.9 mm, respectively.

The fracture surfaces of LC3000/G1650 and LC3000/G1701 extruded strands were observed under the scanning electron microscope (SEM) (Jeol; JSM-6460LV, Tokyo, Japan) operated with an accelerating voltage of 15 kV. Prior to examination, the extruded strands were dipped in liquid nitrogen for 30 min and fractured. The specimens were sputter-coated with gold for enhanced surface conductivity.

To inspect clearly the actual size of TLCP fibers in the extruded strands, the matrices were dissolved away with toluene. The geometry of TLCP fibrils was directly observed with a polarizing optical microscope (OM; Zeiss, model Axiolab, Carl Zeiss Jena GmbH,

Jena, Germany) attached to a digital camera (Sony DSC-S85, Japan).

The uniaxial stress-strain measurement of the extruded strand was performed on an Instron mechanical tester (model 5569, Instron, Canton, MA) at room temperature, set at a grip length of 25 mm, cross-head speed of 50 mm/min and a full scale load cell of 1 kN. The stress is engineering stress which was calculated from the original cross section area of the sample. The averaged value of five measurements was determined.

The thermogravimetric analysis (TGA) was carried out using TA instruments, SDT Q600 (Luken's drive, New Castle, DE). The pellet cut from the extruded strand of 8–10 mg was loaded in alumina crucible. The sample was nonisothermally heated from ambient temperature to 1000°C at a heating rate of 10°C/min. The TGA was performed in nitrogen and in air with the flow rate of 100 mL/min. The TG data were recorded online in TA instrument's Q series explorer software. The analyses of the TG data were done using TA Instrument's Universal Analysis 2000 software (version 3.3B).

RESULTS AND DISCUSSION

Rheological behavior in the molten state

It is generally known that the morphology of immiscible blend is governed by the viscosity ratio of the dispersed phase to the continuous phase. For simple shear flow, fibrillar morphology is predicted to occur if the viscosity ratio is lower than unity.²⁷ However, in the system we have studied, i.e., LC3000/G1652 where the viscosity ratio was as low as 0.1, we still could not obtain fibrillar morphology in as-extruded strand.^{10,11} In this study, we further investigated two blend systems based on matrices with very different viscosity. We will present first the change in complex viscosity, η^* , of each system as a function of ω at 225°C. The results for LC3000/G1650 and LC3000/G1701 blends containing up to 50 wt % LC3000 are presented in Figure 1(a,b), respectively. All flow curves exhibit shear thinning behavior; the viscosity decreases with increase in shear rate (or shear frequency). This is due to the shear-induced chain orientation, leading to a reduction in the chain entanglement and, hence, a drop in the viscosity. Even with the low shear rate limit examined here, Newtonian behavior is not observed and this precludes the determination of the zero-shear viscosity for each sample. The shapes of these flow-curves are similar to those of the LC3000/G1652 blends.¹⁰ The η^* values of both LC3000/G1650 and LC3000/G1701 systems clearly decrease with increasing LC3000 content, indicating that the addition of LC3000 into the elastomer matrices is melt processible. As seen from the flow curves, the η^* of the neat G1650 is much higher than that of

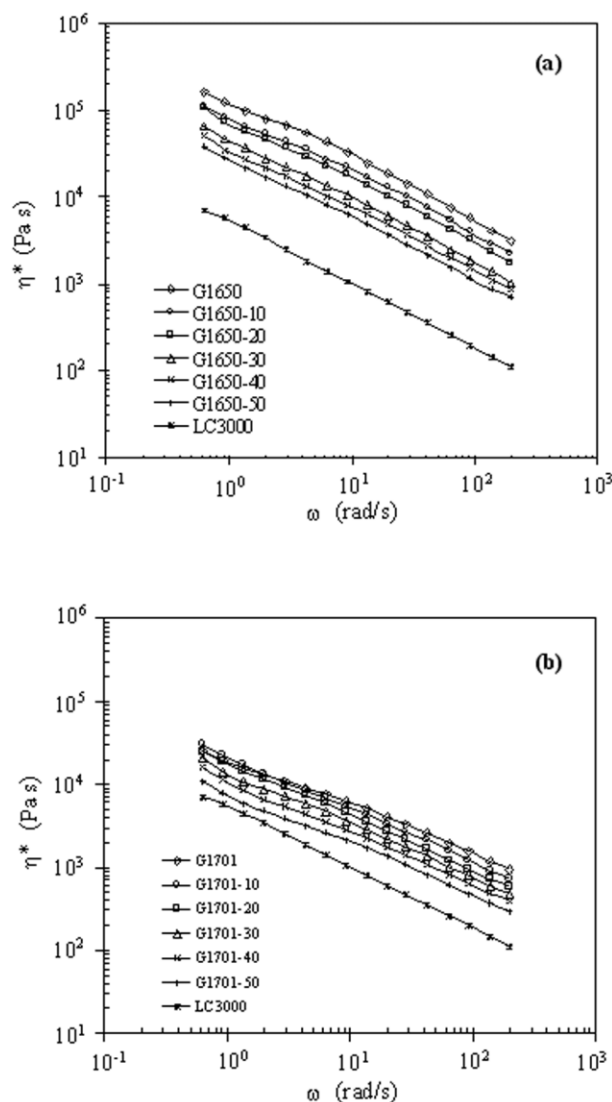


Figure 1 η^* vs. ω at 225°C for (a) LC3000/G1650 and (b) LC3000/G1701 blends containing various LC3000 contents.

the G1701 within the experimental frequency. Therefore, the η^* values of LC3000/G1650 blends are also higher than those of LC3000/G1701 blends when compared at the same composition. Note that, the η^* values of G1701 diblock copolymer are found to be comparable to G1652 triblock copolymer¹⁰ reported previously.

The elastic characteristic of the polymer systems can be considered from a plot of their storage modulus, G' , as a function of ω . In general, the value of G' at low frequency provides information about long-range (beyond entanglement distance) relaxation, while the value at high frequency provides information about short range (motion with entanglement) relaxation.²⁸ The plots for LC3000/G1650 and LC3000/G1701 blends are shown in Figure 2(a,b), respectively. For both type of blends, G' increases with increasing ω indicating dependent of G' on the time scale of mo-

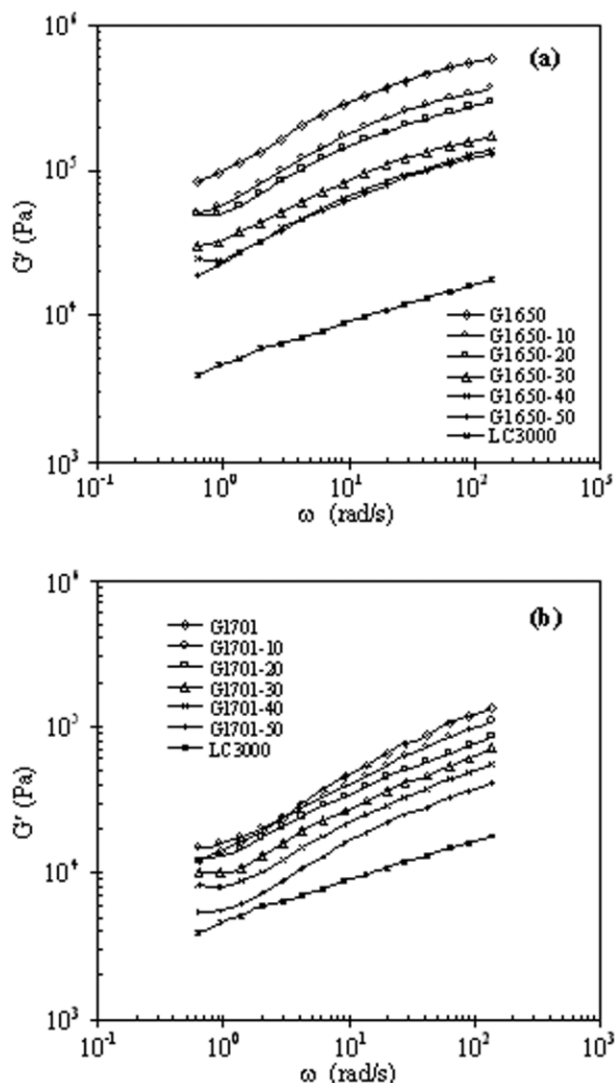


Figure 2 Storage modulus (G') vs. ω at 225°C for (a) LC3000/G1650 and (b) LC3000/G1701 blends containing various LC3000 contents.

lecular motion. Among the samples examined, the neat matrix displays the highest value of G' , while LC3000 displays the lowest G' . The low value of G'' (for LC3000 is due to its rigid molecular structure, yielding a high molecular orientation and less chain entanglement. With further addition of LC3000, the G' values of the blends mostly decrease as a result of the contribution from the TLCP. It is seen that the G' of G1650 is higher than that of G1701 within the experimental frequency range. The obtained results indicate that all viscous and elastic characteristics of G1650 are higher than those of G1701. As the contribution from G1650 matrix, the G' values of LC3000/G1650 blends with 10–50 wt % LC3000 are also greater than those of LC3000/G1701 compared at the same composition. (Do we need to say all this? Does it help anything? Perhaps we only need to say that G' of G1650 is much

higher than G1701 and as a result its blend will have higher G' .)

The viscosity ratio will now be examined as it is one of the criteria which have been used to determine the possibility of fibril formation. The viscosity ratios of the two blend systems at 225°C were evaluated and presented in Figure 3. For LC3000/G1650 blend, the viscosity ratio slightly drops from 0.05 to 0.03 at the low frequency range and then stays roughly constant as the frequency increases. The viscosity ratio of the LC3000/G1701 blend system decreases sharply first from 0.29 to 0.15 within the frequency range of 0–20 rad/s and then gradually decreases as the frequency increases. A profile of the viscosity ratio for the LC3000/G1701 blend system is similar to that of the LC3000/G1652 blend system.¹⁰ The difference in viscosity ratio arising from the different matrix viscosity is expected to affect the fibrillation of LC3000 dispersed phase. Based on our previous results on G1652, it may be expected that LC3000/G1701 may not form fibrillar morphology while LC3000/1650 may. We will consider this again in the morphology section.

Morphology

It is well known that the final properties of the in situ composites depend on its phase morphologies which is affected by several important factors such as rheological behavior, composition, interfacial tension, and processing condition. In the present study, the evolution of the morphology as a function blend composition of the blends was studied by means of scanning electron microscopy (SEM) and polarizing optical microscopy (OM). Figure 4 shows the SEM micrographs of the fracture surfaces at 2000× magnification (col-

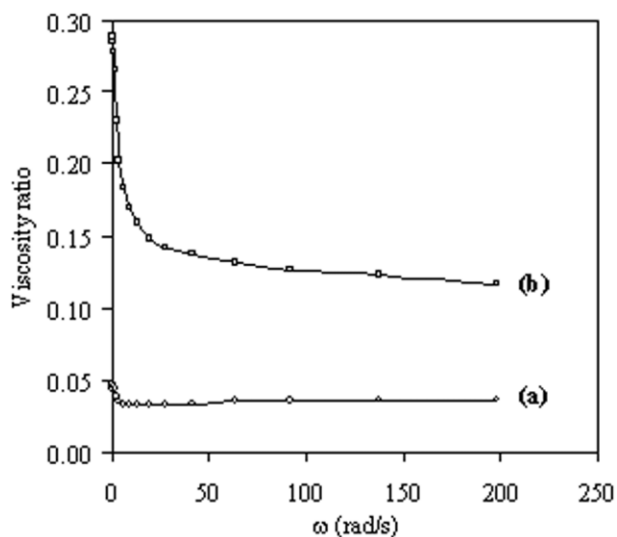


Figure 3 Viscosity ratios vs. ω at 225°C; (a) $\eta_{LC3000}^*/\eta_{G1650}^*$ and (b) $\eta_{LC3000}^*/\eta_{G1701}^*$.

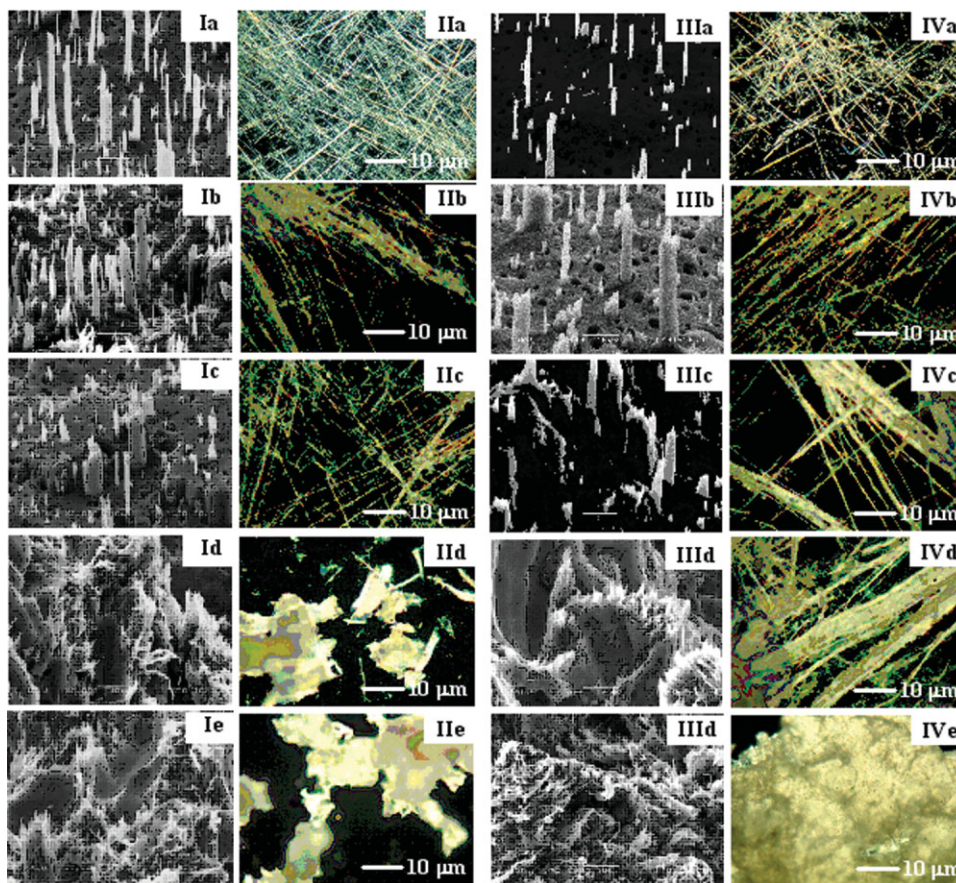


Figure 4 SEM micrographs (columns I and III) of fracture surfaces and OM micrographs (columns II and IV) of LC3000 domains extracted from the extruded strands for LC3000/G1650 (columns I and II) and LC3000/G1701 (columns III and IV) blends containing (a) 10, (b) 20, (c) 30, (d) 40, and (e) 50 wt % LC3000. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

umns I and III) and OM micrographs of extracted LC3000 fibers (columns II and IV) for LC3000/G1650 blends (columns I and II) and LC3000/G1701 blends (columns III and IV). Both types of the blends contain 10–50 wt % LC3000. By looking at the SEM and OM micrographs, highly elongated fibrils of LC3000 with the diameters of about 1–4 μm are observed for the G1650–10 (Ia and IIa). The elongated LC3000 fibrils are also achieved for the G1701–10 as seen in IIIa and IV. It can be seen that the TLCP fibrils in G1701–10 are less elongated than those in G1650–10. This may be because of the higher viscosity ratios of the LC3000/G1701 systems.

The deformation of the TLCP droplets into fibrillation structures or the coalescence of the TLCP domains generally depends on the ratio between the viscous forces (that tend to elongate the droplets) and the interfacial forces (that tend to keep the drop spherical). This ratio is frequently described by the Capillary number (Ca) which is defined by¹³

$$Ca = \frac{\eta_m \dot{\gamma}}{(\sigma/b)} \quad (1)$$

where, η_m is the viscosity of the matrix; $\dot{\gamma}$, the shear rate; b , the initial diameter of TLCP droplets; and σ is the interfacial tension between the matrix and the TLCP dispersed phases. In the simple shear flow of Newtonian fluids, a dispersed droplets will be elongated if $Ca > 0.5$, indicating that the ratio of shear stress ($\eta_m \dot{\gamma}$) should be larger than a half of the interfacial energy (σ/b).¹³ Until now, most studies of in situ composite preparation focused on the supply of high shear stress to the dispersed phase for the enhancement of droplet deformation. However, the easiest way to provide high shear stress is to increase the viscosity of the matrix. The influence of the Capillary number on the stability of the TLCP morphology has been studied by a number of researchers.^{29–31} The results of their studies indicate the influence of both viscous and interfacial forces on the final morphology, confirming the importance of the Capillary number.

If we consider the viscosity results shown earlier and that reported previously,¹⁰ it may be expected that only LC3000/G1650 will have fibrillar morphology but not the LC3000/G1701 system. However, the morphology results from the present study clearly

show that the fibrillar morphology is obtained with LC3000/G1701 system. This would suggest that perhaps there are differences in the interfacial tension between LC3000/G1652 and LC3000/G1701 systems. According to eq. (1), it may be proposed that the interfacial tension of LC3000/G1701 is lower than that of LC3000/G1652 and leads to higher Capillary number. Based on results shown earlier, it may be summarized that by increasing viscosity of the matrix, fibrillar morphology can be obtained in as-extruded strands. It is also clear that by keeping the same viscosity, fibrillar morphology can be obtained by changing the structure of the matrix and hence interfacial tension of the blend. The fibrillation of LC3000 obtained for as-extruded strand in both systems is as good as that of the monofilament of G1652-10 or G1652-20 blends which were prepared by two-step process.¹¹ In term of processing, the single-step process reduces the risk of contamination and thermomechanical degradation of the material and the subsequent loss of properties. Therefore, the additional benefit for investigation of LC3000/G1650 and LC3000/G1701 blends in this study is not only the reduction of energy consumption because of the reduction of fabrication steps but also the reduction of serious problems arising from the thermomechanical degradation during repeated processing. The good fibrillation of TLCP was also observed for G1650 in situ reinforced with 10–20 vol % Vectra A900 reported by Verhoogt et al.⁷

With addition of 20–30 wt % LC3000, the fibrillation of LC3000 in both matrices is still achieved and the diameters of LC3000 fibrils increase to 5–8 μm . As seen from Figures 4IIIc and 4IVc, some lamellar structure appears in G1701-30 blend presumably because of the coalescence of liquid TLCP threads that occurred during extrusion.^{7,10} At 40 and 50 wt % LC3000, only lamellae were observed for both types of blends. These results are similar to those of LC3000/G1652 blends previously reported by our group¹⁰ and the Vectra A900/G1650 blends with a TLCP content greater than 20 vol % reported by Verhoogt et al.⁷

Tensile properties

The stress-strain curves of the blends containing 0–50 wt % LC3000 for LC3000/G1650 and LC3000/G1701 blends are shown in Figure 5(A,B), respectively. The averaged values of modulus at 100% strain (M_{100}), ultimate tensile stress (TS) and elongation at break (EB) of the neat matrices and the blends were listed in Table I. As seen from Figure 5(A), the neat G1650 exhibits the lowest stresses in the strain region <400% and shows a strain-hardening behavior similar to a typical elastomer. At low strain, an increase in LC3000 content mostly leads to an enhancement in the strength of the blends. For instance, the respective moduli at 100% strain of G1701-10 and G1701-20 are

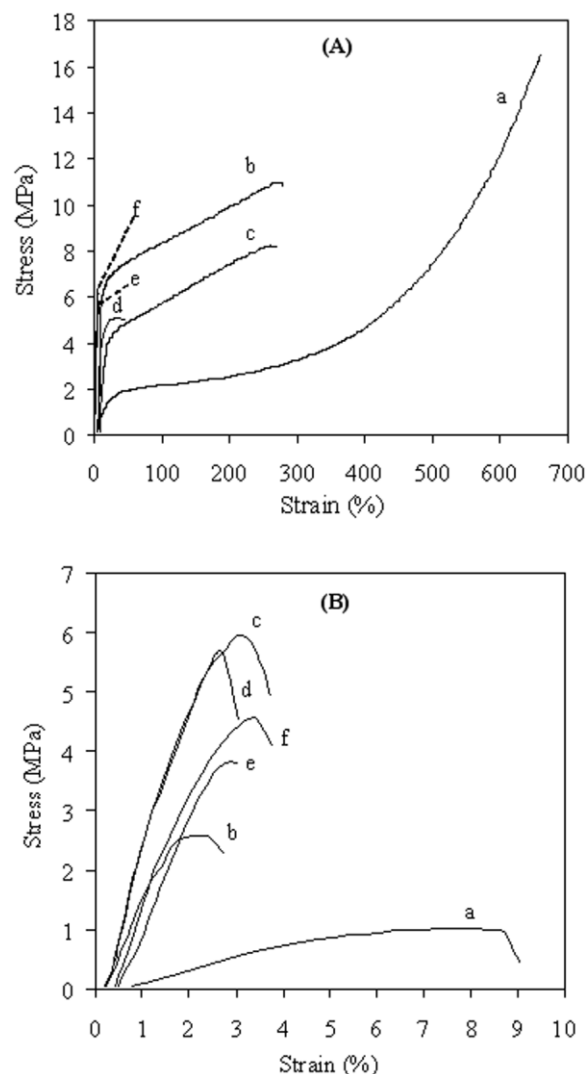


Figure 5 Stress-strain curves at 25°C for (A) LC3000/G1650 and (B) LC3000/G1701 extruded strands containing (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 wt % LC3000.

about four times and three times that of the neat G1701 as shown in Table I. Note that, the stresses at all strains of G1650-20 [Fig. 5(A-c)] are lower than those of G1650-10 [Fig. 5(A-b)]. As evident from the morphology, the lower stresses of the G1650-20 may be because of the lower fibrillation of LC3000 as the concentration increases. The addition of LC3000 into G1650 significantly reduces the extensibility of the blends. For instance, elongation at break dramatically drop from about 660–270% with addition of 10–20 wt % LC3000 whereas the elongation at break decreases down to about 5% with addition of 40 wt % LC3000 or more. The sudden reduction in the extensibility of the samples with addition of LC3000 is due to the loss of connectivity in the elastomer phase and also because of the increase in interfacial area, where the interaction is weak. The stress-strain curves of 40–50 wt % LC3000-containing blends [Figs. 5(A-e,f)] show a de-

TABLE I
Tensile Properties at 25°C of LC3000/G1650 and LC3000/G1701 Blends: Modulus at 100% Strain (M100), Ultimate Tensile Stress (TS), and Elongation at Break (EB)

LC3000 content (wt %)	LC3000/G1650			LC3000/G1701		
	M100 (MPa)	TS (MPa)	EB (%)	M100 (MPa)	TS (MPa)	EB (%)
0	2.2 ± 0.4	16 ± 2.6	660 ± 140	–	1.1 ± 0.2	9.2 ± 0.8
10	8.1 ± 0.5	11 ± 1.5	270 ± 88	–	2.7 ± 0.6	2.8 ± 0.6
20	5.6 ± 0.3	7.8 ± 0.63	265 ± 34	–	5.9 ± 0.5	3.3 ± 0.5
30	–	5.1 ± 0.07	47 ± 29	–	5.6 ± 0.8	2.9 ± 0.3
40	–	5.6 ± 0.51	8.0 ± 3.1	–	3.8 ± 0.4	3.1 ± 0.3
50	–	6.1 ± 0.49	4.6 ± 1.3	–	4.4 ± 0.7	3.6 ± 0.4

flection in slope which is like plastic materials. This may be related to the lamellar structure in the blends because the possibility of TLCP liquid threads coalescing during processing increases as the LC3000 concentration increases. The influence of the lamellar morphology on a marked reduction of the extensibility was similarly observed for the LC3000/G1652 blend system.¹⁰ In that case, with addition of 10–20 wt % LC3000 into G1652, the extruded strands samples still exhibit a high extensibility similar to that of the neat G1652; the elongation at break of the blends with 10–20 wt % LC3000 is higher than 600%. The maintenance of high extensibility in the LC3000/G1652 blends may be partly due to the morphology of the dispersed phase; most TLCP domains in G1652–10 and G1652–20 appear as droplets. Thus, the possibility of the connectivity in the elastomer phase is higher (less interfacial area) (if particles are smaller, we would have larger interfacial area) than that of the TLCP domains generated as long fibrils. In addition, the neat G1650 and their blends with 10–20 wt % LC3000 exhibit a yield-like feature at the strain of about 20%. This behavior agrees well with the results of structural studies on oriented SEBS triblock copolymers reported by Lee et al.³² and Daniel et al.³³ These authors explained that the styrene block becomes deformed as the cylindrical domains are oriented parallel to the flow direction when the polymer is extruded through a narrow capillary die. As a consequence of this deformation, the material is relatively stiff and exhibits a yield point. Do we have similar structure?

As seen from Table I and Figure 5(B) for LC3000/G1701 blends, very low strain was observed for all specimens after subjecting to the tensile force; the elongation at break is lower than 10 and 5% for the neat G1701 and the blends, respectively. The ultimate stress of the specimen progressively increases as the content of 10–20 wt % LC3000 was added into the matrix. For instance, the ultimate stress of G1701–20 is about six times that of the neat G1701. With further addition of LC3000 (>20 wt % LC3000), the drop of the ultimate stress is observed because of the generation of lamellar structure in the blends, evident from the observing morphology. The poor extensibility of

the LC3000/G1701 is largely due to the low extensibility of the neat G1701 matrix. This is due to fact that G1701 is a diblock copolymer and also partly due to a larger amount of hard domains (37% of styrene-hard phase) in the polymer chains. Note that, the ultimate tensile stress and elongation at break for LC3000/G1701 blends with 10–20 wt % LC3000 are lower and are much lower, respectively, than those of LC3000/G1650 blends, when compared at the same composition.

Thermal decomposition behavior

Normally, the polymer must encounter elevated temperatures at almost every stage in manufacturing, compounding and processing stages, in service, and during repairing step. Therefore, the understanding of thermal stability and thermal decomposition behavior of polymer is an essential information for development and extension of their applications. In the present study, TGA was performed to gain some understanding of the effect of LC3000 on the thermal decomposition of the blends. The nonisothermal TG curves of LC3000/G1650 and LC3000/G1701 blends containing various LC3000 contents are presented in Figure 6(A,B), respectively. The TGA was performed in nitrogen (column I of Fig. 6) and in air (column II of Fig. 6) at a heating rate of 10°C/min.

Results obtained in nitrogen will be considered first. The nonisothermal TG profiles of both G1650 and G1701 reveal only a single weight-loss step at the temperature range around 400–480°C. In the case of the blends with 10–40 wt % LC3000, although the blend system may be complicated due to the presence of many copolymer components, a single degradation step similar to the neat matrices is observed. The onset of decomposition seems not to be affected by the level of LC3000. However, the decomposition rate decreased and residue increased with increase in the level of LC3000. The thermal degradation of the neat G1650 and G1701 in nitrogen may be mainly ascribed to the chain scission at the boundary of the polystyrene-olefin phases. In the blends, the degradation mechanism additionally involves the removal of ester, eth-

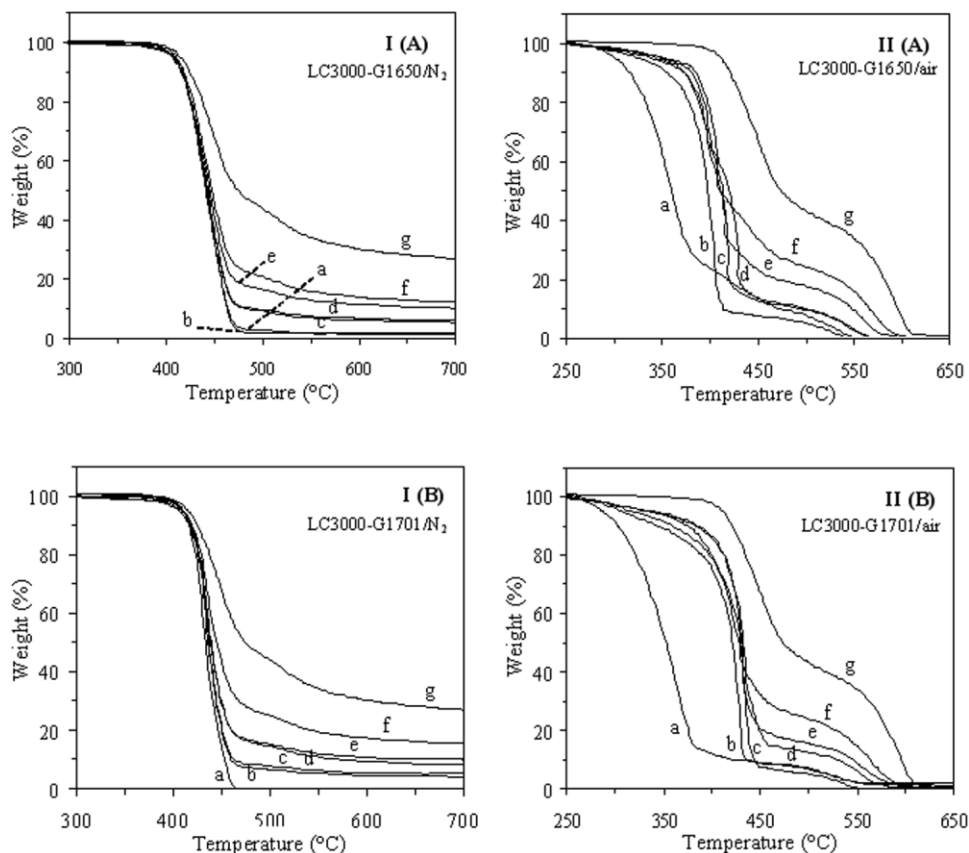


Figure 6 Nonisothermal TG curves in nitrogen (column I) and in air (column II) for (A) LC3000/G1650 and (B) LC3000/G1701 blends containing (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, and (g) 100 wt % LC3000.

ylene groups, and hydrogen atoms in polymer chains of LC3000.³⁴ (If we say this, it means that there are more than one reaction for the decomposition.) Above 480°C, the second minor step of thermal degradation is observed for 50 wt % LC3000-containing blends and LC3000. In the case of LC3000, the first thermal degradation mainly occurs at PET block, whereas the second degradation process could be attributed to the degradation of HBA block.^{34,35} No char residues were left for the neat G1701 whereas small residues were left for G1650 within the range of experimental temperature. For all blends, the amount of char residues increased with increasing LC3000 contents. Li et al.³⁶ investigated the thermal decomposition kinetics in nitrogen of synthesized poly(*p*-oxybenzoate (B)-*co*-ethylene terephthalate (E)), B/E polymer. They found that the char residues linearly increase with increasing B unit content, because an increase in the B unit content will decrease the number of hydrogen atoms and retard the formation of more volatile degraded products, thus resulting in an increase in char yield. They also suggest that the formation of the char residues is probably due to branch formation and crosslinking of the product obtained mostly from B unit during the thermal degradation under nitrogen. In this study, the amount of char residues after thermal degradation in

nitrogen was found to increase with increasing amount of HBA units (by increasing amount of LC3000 content), which may reduce the number of hydrogen atoms and retard the formation of more volatile degraded products as suggested by Li et al.³⁶

Under dynamic heating in air (see column II of Fig. 6), the thermal degradation of all neat samples and blends occur in two steps. Both the neat G1650 and G1701 and their blends exhibit very similar decomposition behavior. The neat G1650 and G1701 polymers exhibit the first major degradation at 250–400°C, whereas the first major weight-loss of LC3000 occurs around 400–450°C. For degradation of G1650 and G1701 in air, the chain degradation, scission and oxidation occur primarily at the boundary of styrene-olefin phases, giving rise to the formation of acetone end groups on the styrene units and carboxylic acids on the olefin chain ends.³⁷ Note that, in air, very small char residues of the neat polymers and the blends were left within the experimental temperature being studied.

To compare the LC3000-content dependence of thermal stability for the two types of blends in more quantitative way, the thermal decomposition data in nitrogen and in air are compared and summarized in Table II. T_i represents the initial temperature of deg-

TABLE II
Nonisothermal Decomposition Characteristics of LC3000/G1650 and LC3000/G1701 Blends

LC3000 content (wt %)	LC3000/G1650					LC3000/G1701						
	T_i (°C)	T_{max1} (°C)	$(d\alpha/dt)_{max1}$ (%/min)	T_{max2} (°C)	$(d\alpha/dt)_{max2}$ (%/min)	Char yield at 700°C (wt %)	T_i (°C)	T_{max1} (°C)	$(d\alpha/dt)_{max1}$ (%/min)	T_{max2} (°C)	$(d\alpha/dt)_{max2}$ (%/min)	Char yield at 700°C (wt %)
In N ₂												
0	408	446	21.4	—	—	2.03	411	434	31.3	—	—	0.00
10	387	450	20.5	—	—	1.18	410	436	32.2	—	—	4.11
20	387	445	19.2	—	—	6.12	406	436	32.2	—	—	5.20
30	401	443	19.2	—	—	5.46	405	435	27.9	—	—	9.92
40	400	444	17.2	—	—	10.13	409	437	27.8	—	—	8.05
50	402	439	17.5	—	—	12.30	408	437	21.5	—	—	15.60
100	407	451	10.2	—	—	26.90	407	451	10.2	—	—	26.90
In air												
0	311	355	14.0	531	1.75	0.00	308	362	14.0	528	1.13	1.41
10	364	395	38.0	530	1.38	0.00	396	428	61.6	528	1.04	2.00
20	373	417	37.3	535	1.91	0.00	413	434	49.2	535	1.31	0.00
30	373	427	48.2	549	2.00	0.00	407	434	32.8	552	2.67	0.44
40	363	414	35.6	555	3.74	0.43	416	433	40.7	557	2.81	0.75
50	363	406	32.9	567	4.49	0.66	409	428	35.3	566	0.97	0.73
100	413	453	8.98	589	7.75	0.91	413	453	8.98	589	7.75	0.91

radiation. T_{max} represents the temperature at the maximum weight-loss rate, $(d\alpha/dt)_{max}$. The subscripts 1 and 2 represent the first stage and the second stage of the degradation, respectively. In nitrogen, no significant difference in T_i and T_{max1} is observed for both of the blends as the LC3000 contents increases, except that the T_{max1} of the neat LC3000 shows the highest values among all sample examined. It is noticed that, for both blend systems, the $(d\alpha/dt)_{max}$ in nitrogen mostly decrease with increasing LC3000 content. This result indicates the improvement in thermal stability by addition of LC3000.

For the decomposition of each blend system in air, T_i and T_{max1} of the blends are much higher than those of the matrix but are lower than those of LC3000. This means that the incorporation of LC3000 into both matrices effectively enhances the thermal stability in air more than in nitrogen. In air, the shift of the first degradation to higher temperature with addition of TLCP was similarly observed for the blends of EPDM rubber in situ reinforced with Vectra A950 (73% HBA and 27% hydroxynaphthoic acid) liquid crystalline polymer investigated by Chakraborty et al.¹⁵ They reported that the TLCP-containing blend was thermally more stable than the pure EPDM sample. Interestingly, $(d\alpha/dt)_{max1}$ of the blend are higher than that of the neat matrix and is found to be mostly decreased with increase in LC3000 content, indicating the rapid weight-loss process with more complex degradation mechanism. Moreover, the $(d\alpha/dt)_{max1}$ of both types of blends are mostly higher in air than in nitrogen when compared at the same composition. Normally, the thermal stability of polymer in air is somewhat lower than that in nitrogen. However, the situation that polymer has been exposed in air is more common than in nitrogen during real processing and application. Note that, T_{max2} and $(d\alpha/dt)_{max2}$ are mostly found to increase with addition of LC3000.

CONCLUSIONS

In this work, in situ-reinforcing composites based on elastomer matrices and LC3000 were prepared. The influence of different elastomer matrices possessing different melt viscosity and structure on rheology, morphology and properties of the blends containing various LC3000 contents was investigated. Melt viscosity of the blends gradually decreased with increasing LC3000 content and all exhibited shear thinning behavior. It was found that fibrillar morphology can be obtained in as-extruded strands if the matrix viscosity is high enough or else the interfacial tension of the blend must be low enough. However, the fibrillation was achieved in both blends only up to 30 wt % LC3000. At higher LC3000 concentration, a lamellar structure was formed due to the high tendency of coalescence of the dispersed phase. The addition of

LC3000 into both TPE matrices improved the tensile modulus considerably whereas the elongation at break remarkably dropped. The incorporation of LC3000 into the elastomer matrices was found to retard thermal decomposition significantly in air but not in nitrogen.

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