Self-Reinforcing Elastomer Composites Based on Polyolefinic Thermoplastic Elastomer and Thermotropic Liquid Crystalline Polymer

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ABSTRACT: *In situ* reinforcing elastomer composites based on Santoprene thermoplastic elastomer, a polymerized polyolefin compound of ethylene–propylene–diene monomer/polypropylene, and a thermotropic liquid crystalline polymer (TLCP), Rodrun LC3000, were prepared using a single-screw extruder. The rheological behavior, morphology, mechanical, and thermal properties of the blends containing various LC3000 contents were investigated. All neat components and their blends exhibited shear thinning behavior. With increasing TLCP content, processability became easier because of the decrease in melt viscosity of the blends. Despite the viscosity ratio of dispersed phase to the matrix phase for the blend system is lower than 0.14, most of TLCP domains in the blends containing 5–10 wt % LC3000 appeared as droplets. At 20 wt % LC3000 or more, the domain size of TLCP became larger because of the coalescence of liquid TLCP threads that occurred during extrusion. The addition of LC3000 into the elastomer matrix enhanced the initial tensile modulus considerably whereas the extensibility of the blends remarkably decreased with addition of high TLCP level (>.20 wt %). The incorporation of LC3000 into Santoprene slightly improved the thermal resistance both in nitrogen and in air. Dynamic mechanical analysis results clearly showed an enhancement in dynamic moduli for the blends with 20–30 wt % LC3000. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2375–2384, 2008

Key words: polymer *in situ* composite; liquid crystalline polymer; rheology; thermal property; mechanical property; thermoplastic elastomer

INTRODUCTION

Thermoplastic elastomers (TPEs) are materials that combine elastomeric properties with many of the attributes of thermoplastics. They can be made by copolymerizing two or more monomers, using either block or graft polymerization techniques or by blending two or more polymers with a proprietary treatment. Santoprene is an example of the latter and is the first brand vulcanizate thermoplastic elastomer resin developed by Monsanto in 1981. All grades of Santoprene are polymerized polyolefin compounds of ethylene–propylene–diene monomer (EPDM) and polypropylene (PP) and they require no postcuring or annealing to attain their full range of performance and properties. This material is a useful engineering polymer that combines the performance characteristics of vulcanized rubber with the processing ease of thermoplastics.[1–3] Santoprene is widely used in applications such as hose connectors, plugs, windshild spacers, vibration isolators, flexible cords, submersible cables, filter, and pump seals, etc. However, the acceptability of Santoprene for a specific application depend ultimately on its performance requirements and hence, the properties such as stiffness, thermal stability, processabilty, chemical resistance, and heat distortion temperature must be carried out before it is used.

The mechanical properties of TPEs can be improved by addition of fibrous fillers.[4–8] 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 because of 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.[9–22] TLCPs are known to possess superior physical prop-

erties, such as high strength, good thermal properties, and low melt viscosity. Under appropriate processing conditions, optimum TLCP content, 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.[23] 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.[24–27] Generally, the fibrillation of TLCP is enhanced as the viscosity ratio of TLCP to polymer matrix becomes mostly less than unity[28,29] and it has also been reported that the elongational flow causes more extensive fibrillation than the shear flow.[30–32]

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.[9] 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.[10,11] investigated the blends of TLCP (Vectra A900) and the styrene-(ethylene-butylene)-styrene (SEBS, 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.[12] studied the fiber formation, stability, and properties of TPE (Arnitel EM630)/Vectra A900 blends and reported that the mechanical properties increased with increasing 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 et al.[16,17] investigated EPDM monomer rubber /Vectra B950 blends and suggested the effect of elongational deformation on the fibrillation of TLCP. Chakraborty et al.[18] 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.[19]

Recently, we have investigated the *in situ* reinforcing elastomer composites based on TLCP (Rodrun LC3000) and two elastomer matrices; SEBS (Kraton G1650, Kraton G1652) and styrene-(ethylene propylene) (SEP) diblock copolymer (Kraton G1701). The rheological behavior, morphology, dynamic mechanical, mechanical, and thermal properties of the blends have been reported.[13–15,20–22] From our previous works, the addition of Rodrun LC3000 into each elastomer matrix significantly enhanced the mechanical properties and improved processability of the blends. We also suggested that the 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.[20] To the authors knowledge, most of the published works, including ours, focused on simple system where the polymer matrix is a neat homopolymer or copolymer, for example, SEBS,[10,11,13–15,20–22] EPDM,[16–18] and PP.[33–37] Complex system which contains plasticizer or oil such as Santoprene, which is used in our present study, is much less studied. In this type of complex system, the interfacial tension can play a very significant role. In the present study, the *in situ* composites based on Santoprene polyolefinic TPE and Rodrun LC3000 were investigated. Rheology, morphology, mechanical, and thermal properties of LC3000/Santoprene *in situ* composites prepared by melt extrusion were characterized.

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/cm^3. The molecular weight for the TLCP was not obtainable, since no solvent was found to dissolve Rodrun LC3000. The polyolefinic TPE used in the present work was Santoprene 691-73W175, purchased from Advanced Elastomer Systems. The specific gravity and the brittle point of this material are 0.98 and < −60°C, respectively. The elastomer contains 18 wt % PP.[7] Santoprene was supplied as fully-flowing pellets and ready to be used as received without further compounding. All materials were dried in a vacuum oven at 70°C for at least 12 h before used. In this article, Rodrun LC3000 was represented by LC3000.

The blends of LC3000/Santoprene at various compositions were prepared with a single screw extruder (Haake Rheomex, Thermo Electron (Karlsruhe) GmbH, Karlsruhe, Germany), with a screw diameter of 16 mm, length-to-diameter (L/D) ratio of 25, a die diameter of 2 mm, and a screw speed of 20 rpm. The temperature profile was 190–220–220–225°C, representing the temperatures at hopper

zone, two 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 sample codes of the extruded strand blends are designated as San-X, where X depicts the content of LC3000 in wt %.

Measurements of rheological properties in the molten state for the neat components and the blends were carried out with a plate-and-plate rheometer (Physica Anton Paar, MCR5000, Physica Messtechnik GmbH, Stuttgart, 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 25 mm in diameter. The complex viscosity (η^*), storage modulus (G', and loss modulus (G'') of all specimens were measured in the oscillatory shear mode with the strain amplitude of 5% within the angular frequency (ω) range from 0.6 to 500 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/Santoprene 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 immersed in liquid nitrogen for 30 min and fractured. The specimens were sputter-coated with gold for enhanced surface conductivity.

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 thermogavimetric 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 instruments Q series explorer software. The analyses of the TG data were done using TA Instruments Universal Analysis 2000 software (version 3.3B).

Dynamic mechanical analysis (DMA) was performed on Mettler Toledo DMA/SDT861[e] (Mettler-Toledo, OH) to obtain the dynamic mechanical storage modulus (E') and the loss tangent (tan $\delta = E''/E'$), where E'' is the dynamic mechanical loss modulus of the extruded strands. The glass transition temperature (T_g) can be obtained from the peaks of the

tan δ curves. The tension mode was applied at an oscillating frequency of 10 Hz. The maximum force and maximum amplitude were set at 0.3 N and 50 μm, respectively. The measurements were carried out from −100 to 150°C with a heating rate of 5°C/min in a flow of nitrogen.

## RESULTS AND DISCUSSION

Rheological behavior in the molten state

The complex viscosity (η^*) of the neat components and the blends at various compositions, measured at 225°C are presented in Figure 1. All flow curves exhibit shear thinning behavior; the viscosity decreases with increasing shear rate (or shear frequency) because of the shear-induced chain orientation, leading to a reduction in the chain entanglement density. Even with the lowest shear rate limit examined here, Newtonian behavior is not observed and this precludes the determination of the zero-shear viscosity for each sample. The η^* values of the blends clearly decrease with increasing LC3000 content, indicating that the addition of LC3000 into the elastomer matrix is melt processable.

The elastic and viscous characteristics of the blend system can be considered from the plots of storage modulus (G') and loss modulus (G''), respectively, as a function of angular frequency (ω). The plots of G' and G'' as a function of ω is shown in Figure 2. The values of G' and G'' at low frequency generally provide information about long-range (beyond entanglement distance) relaxation, whereas the values at high frequency provide information about short range (motion with entanglement) relaxation.[38] As seen from Figure 2(a), G' increases with increasing ω
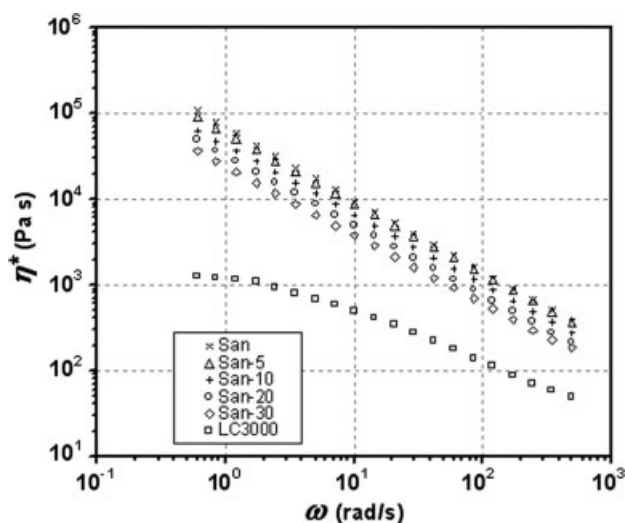
Figure 1 η^* versus ω at 225°C for LC3000/Santoprene blends containing various LC3000 contents.
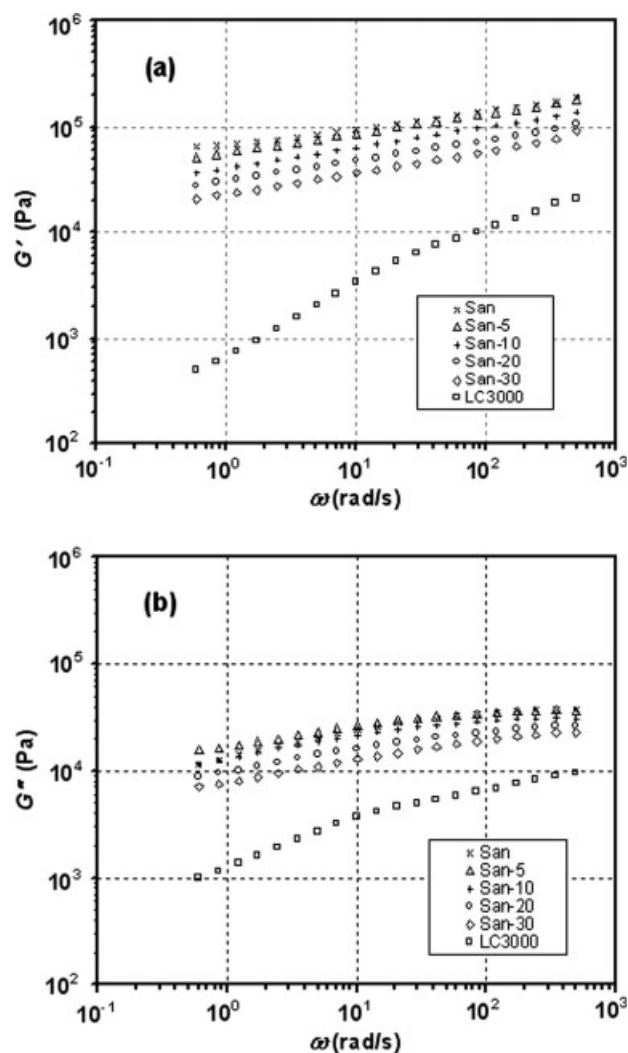
Figure 2 Storage modulus, G' (a), and loss modulus, G'' (b) versus ω at 225°C for LC3000/Santoprene blends containing various LC3000 contents.

indicating a dependence of G' on the time scale of molecular motion. Among the sample examined, the neat Santoprene matrix displays the highest value of G', whereas LC3000 displays the lowest G'. The low value of G' for LC3000 is due to its semirigid molecular structure, yielding a high molecular orientation and less chain entanglement. With further addition of LC3000, the G' values of the blends progressively decrease as a result of the greater contribution from the TLCP. As seen from Figure 2(b), the similar trend of the viscous characteristics (G'') for the blends with LC3000 loading was observed. In addition, G' values of all compositions are higher than their respective G'' values throughout the frequency range being studied, indicating that the elastic characteristic is a dominant factor for these blend systems.

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.[28,29,39] 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 ratio of the LC3000/Santoprene system as a function of frequency at 225°C was evaluated and presented in Figure 3. The viscosity ratios are in the range of 0.01–0.13 over the entire frequency region being investigated. It is found that the viscosity ratio increases sharply first from 0.01 to 0.08 within the frequency range of 0–50 rad/s and then gradually increases as the frequency increased. The increase of viscosity ratio with increasing frequency arises from the faster drop of the viscosity of Santoprene than that of TLCP in the high frequency range. Since the degree of entanglement for flexible molecule in Santoprene is normally higher than that for the semirigid TLCP molecules, the reduction in the degree of entanglement in the matrix phase at high shear rate is therefore more pronounced.

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 of the blend composition for LC3000/Santoprene extruded strands was studied by means of scanning electron microscopy (SEM). Figure 4 shows the SEM micrographs at a core region of the fracture surfaces for the blend extruded strands containing 5–30 wt % LC3000. At low percentage, TLCP distribute into
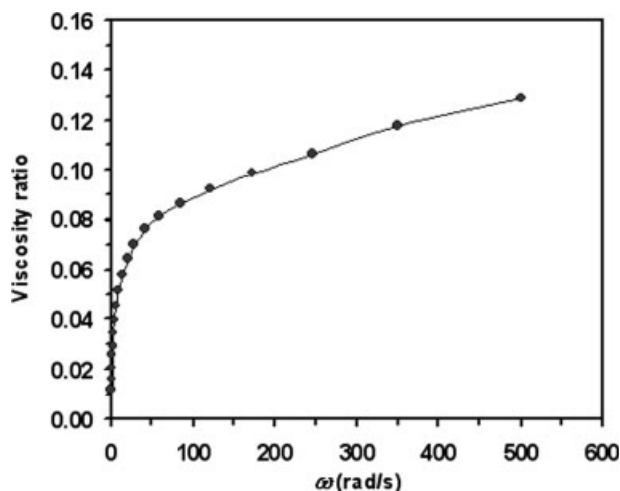
Figure 3 Viscosity ratio ($\eta^*_{LC3000}/\eta^*_{Santoprene}$) versus ω at 225°C.
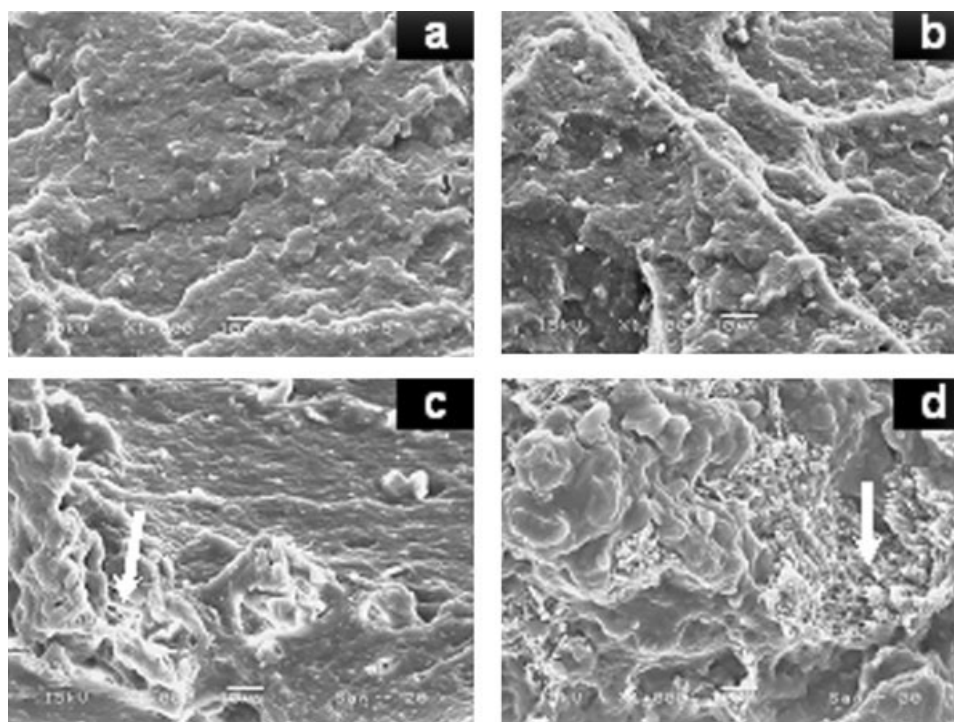
Figure 4 SEM micrographs of the fracture surface for LC3000/Santoprene extruded strands contaning (a) 5, (b) 10, (c) 20, and (d) 30 wt % LC3000.

small domain with the diameters of about 0.5–3 μm. Distinguishing TLCP domain from the Santoprene matrix can be difficult but possible. As the amount of TLCP was increased up to 20–30 wt %, a poor dispersion and the coalescence of TLCP domains was observed. The regions with fibrillar fracture help distinguishing TLCP domain from the Santoprene matrix (see arrow). It was found that for the blends possessing the same composition, no significant difference in morphology of TLCP domains at core and edge regions is observed (SEM micrographs of the edge region are not shown here). The slightly deformed TLCP domains at core region was observed for Vectra B950/EPDM extruded strand reported by Soe et al.[17] They also found that the TLCP domains in the strand, prepared using a twin-screw extruder equipped with 3 mm-diameter straight die and the screw speed of 10 rpm, appeared as large particle in the core region. Furthermore, more elongated Vectra B950 domains were observed at the edge region which has encountered mostly shear flow. Chakraborty et al.[18] also found that the fiber phase formation of Vectra B950 in EPDM was observed even in a shear field. 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 break the fibril and keep the droplets spherical). This ratio is frequently described by the Capillary number (Ca) which is defined by[16]

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

where, η_m is the viscosity of the matrix, $\dot{\gamma}$ is the shear rate, b is 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).[16] In the case of the present study, even the viscosity ratio of the blend system is lower than 0.14, the fibrillation of TLCP domains is not observed. According to eq. (1), one may propose that the interfacial tension of this blend system is rather high. In addition to these material properties, the processing equipments, processing conditions, and fabrication techniques are also important factors governing the droplet deformation of TLCP dispersed phase.

Tensile properties

Figure 5 displays the stress–strain curves of the blend extruded strands containing 0–30 wt % LC3000. The stress is the nominal (engineering) stress, that is, the force divided by the cross-section
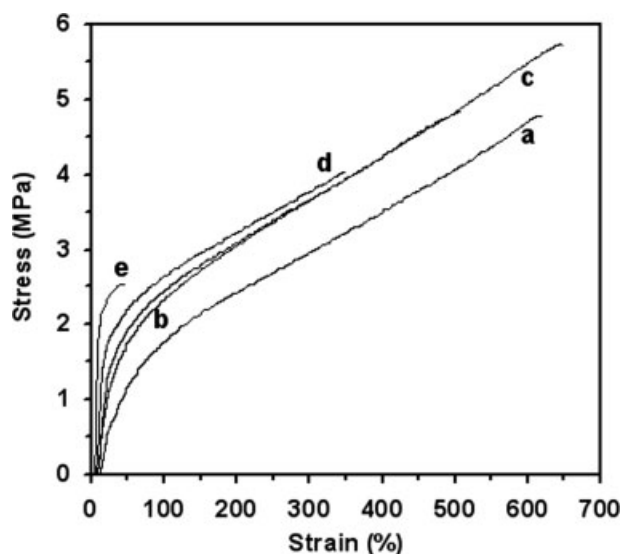
Figure 5 Stress–strain curves at 25°C for LC3000/Santoprene extruded strands containing (a) 0, (b) 5, (c) 10, (d) 20, and (e) 30 wt % LC3000.

area in the initial undeformed state. The neat Santoprene and the blend samples containing 5–20 wt % LC3000 behave like rubbery materials and they exhibit high extensibility; the elongation at break (maximum strain) is higher than 350%. It is noticed that the elongation at break of the blend with 30 wt % LC3000 dramatically drops from about 350 to 50%. The sudden drop in the extensible characteristic of the specimen with high concentration of TLCP may be due to the loss of connectivity in the elastomer phase, and so the blend becomes like plastic materials. This was evident from the coalescence of TLCP domains, clearly observed from SEM for the 30 wt % LC3000-containing blend. That is, the possibility of TLCP coalescing during processing increases as the TLCP content increases. In addition, the incorporation of small amount of LC3000 into the elastomer matrix leads to an enhancement in the tensile stress of the blend. In previous work,[7] we have investigated the conventional composites based on Kevlar aramid fibers (poly(p-phenylene terephthalamide)) and Santoprene (the same grade as used in this study). The composites were prepared using internal mixer and compression molded as a sheet and then characterized the tensile properties. The previous results showed that the stress ratio (the stress of the composite to that of the neat Santoprene) at 50% strain of the 3 wt % untreated Kevlar/Santoprene composite in machine direction was found to be 1.9 whereas the stress ratio at 50% strain of the *in situ* composite nearly containing amount of the dispersed phase (5 wt % LC3000) investigated in this study is found to be 1.6. Somewhat lower value in the stress ratio for the *in situ* composite may be because of the droplet morphology of the dispersed TLCP phase as

seen from SEM. On the basis of the results obtained from the present study, the mechanical properties of Santoprene *in situ* reinforced with LC3000 are expected to be improved to approach those of the conventional composite by enhancing the fibrillation of TLCP with high aspect ratio. One of the possible ways to improve the mechanical properties is that the blends should be fabricated at high extension. Alternatively, the finished products obtained from the first-step extrusion should be repeatedly extruded in the second step using higher elongational or shear force. However, in term of processing, the processing step should be reduced as possible to avoid the risk of contamination and thermomechanical degradation of the material and the subsequent loss of properties.

It is interesting to note that all samples exhibit a definite inflection in the stress–strain curves, indicating the occurrence of yielding. The yield stress and yield strain for the blends with various LC3000 contents are shown in Figure 6. With an increasing LC3000 content, the yield stress and yield strain gradually increase and decrease, respectively. In the same meaning, the yielding in the blends with higher amount of LC3000 shows the higher stress and takes place at the smaller strain than that with lower LC3000 content. The yielding characteristic dependence of TLCP contents was also observed for the LC3000-containing SEBS blends reported by the authors.[13,15,20] Moreover, the incorporation of LC3000 into Santoprene elastomer matrix significantly improves an initial modulus of the blends as seen from Figure 7. For instance, the initial moduli for 20 and 30 wt % LC3000-containing blends are by about 5- and 10-fold, respectively, when compared with that of the neat matrix.
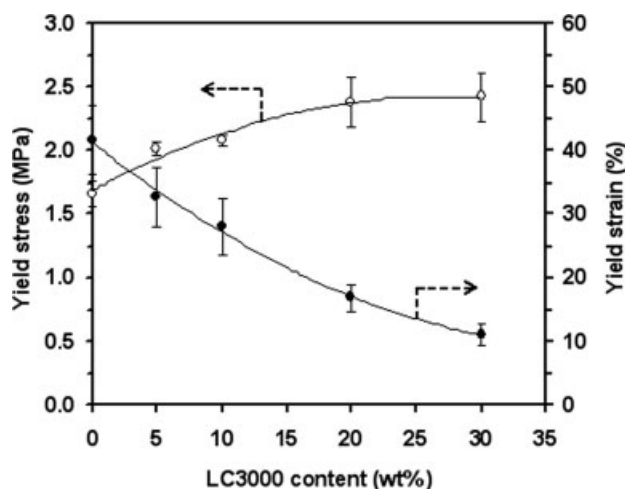
Figure 6 Yield stress and yield strain at 25°C of LC3000/Santoprene extruded strands containing various LC3000 contents.
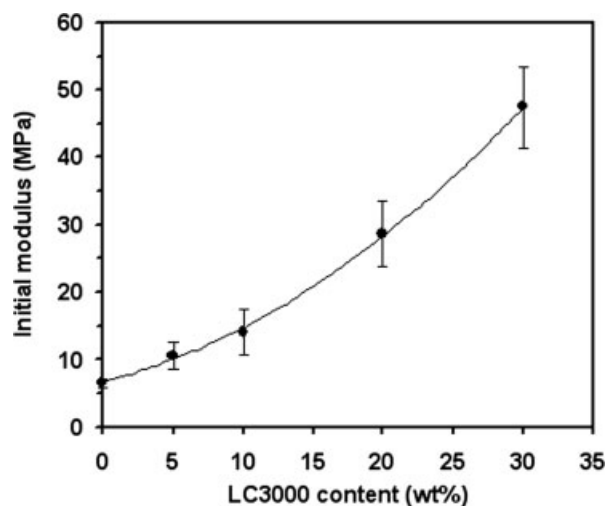
Figure 7 Initial modulus at 25°C of LC3000/Santoprene extruded strands containing various LC3000 contents.

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 the blends containing various LC3000 contents at a heating rate of 10°C/min in nitrogen and in air are presented in Figure 8. In nitrogen [Fig. 8(A)], the nonisothermal TG profiles of the neat Santoprene and the blends reveal two major steps of weight loss at the temperature ranges of 200–400°C and 400–500°C, respectively. The first stage degradation for Santoprene can be attributed to the thermal degradation of plasticizers and oils usually added to the TPE formulations.[40] The second weight loss step of Santoprene mainly involves the thermal degradation of PP and EPDM components in Santoprene. The degradation processes of PP and EPDM occur via a random chain-scission mechanism and followed by radical transfer process for the PP component.[41–45] In the case of LC3000, the first major degradation occurs in the temperature range of 350–480°C, whereas above 450°C, the second minor stage of degradation is observed. The first stage of thermal degradation of LC3000 mainly occurs at PET block whereas the second degradation could be attributed to the degradation of HBA block.[46,47] In the case of the blends with 5–30 wt % LC3000, although the blend system may be complicated due to the presence of many copolymer components, two degradation steps of weight loss similar to the neat matrix is

observed. The degradation mechanisms of the blends may additionally involve the removal of ester, ethylene groups, and hydrogen atoms in polymer chains of LC3000.[46] Interestingly, the presence of LC3000 in the elastomer matrix slightly affect the thermal stability of the blends in the temperature range of 320–430°C. At this region, no significant change for the TG profiles in nitrogen among the neat Santoprene, the blends with 5 (the TG curve is not shown here due to the overlapping) and 10 wt % LC3000, whereas the thermal stability of the blends was somewhat enhanced with addition of LC3000 up to 20–30 wt %.

Under dynamic heating in air [Fig. 8(B)], two major weight-loss processes at 200–380°C and 380–440°C for the first and second degradation steps, respectively, are observed. In addition, the third weight-loss pro-
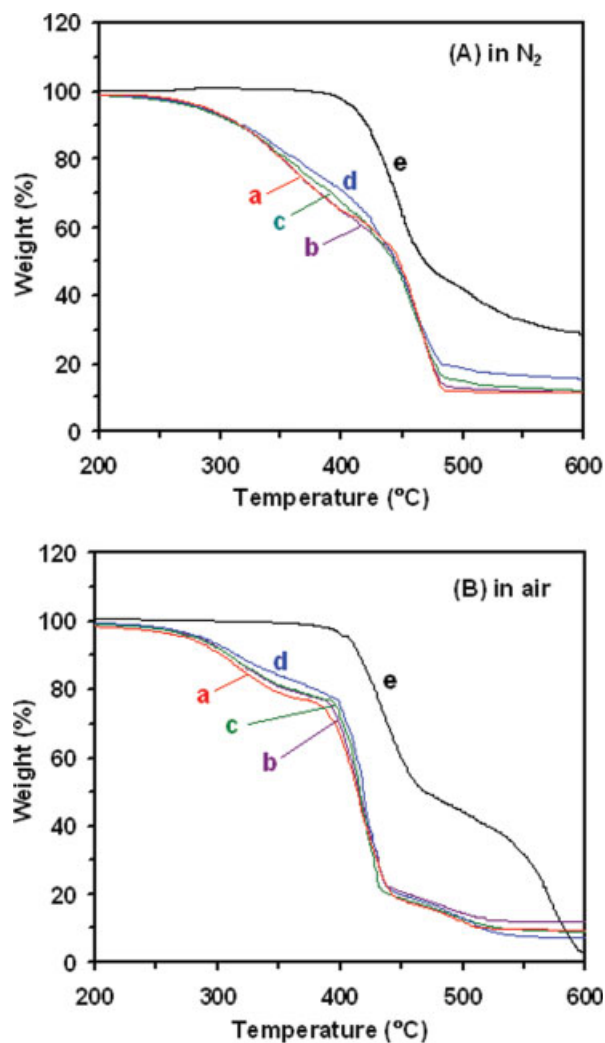
Figure 8 Nonisothermal TG curves in nitrogen (A) and in air (B) of LC3000/Santoprene blends containing (a) 0, (b) 10, (c) 20, (d) 30, and (e) 100 wt % LC3000. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cess seems to appear above 380°C. However, in this article, the study is focused only on the first and second major weight loss step when compared with the obtained results investigated in nitrogen atmosphere. In the temperature range of 250–420°C, the thermal stability of the blends is higher than that of the neat matrix indicating the enhancement of thermal resistance of the blend in air similar to the thermal decomposition behavior in nitrogen for the blends with high level of LC3000 loading. In the case of LC3000/SEBS blend systems previously reported by the authors,[20,22] the addition of LC3000 into SEBS improved the thermal resistance significantly in air, but not in nitrogen. For the present study, the improvement of thermal stability is similarly observed, significantly in air with adding small amount of LC3000 (5–10 wt %).

The thermal decomposition data of the neat polymers and their blends in nitrogen and in air are compared and summarized in Table I. T_{onset} represents the onset degradation temperature. 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 thermal degradation, respectively. In nitrogen, no significant difference in T_{onset} and T_{max1} is observed for the neat Santoprene and the blends with 5–30 wt % LC3000, whereas T_{onset} and T_{max1} of LC3000 shows the highest values among all sample examined. It is noticed that $(d\alpha/dt)_{max}$ in nitrogen mostly decrease with increasing LC3000 content. This result indicates the improvement in thermal stability by addition of LC3000. In nitrogen, the thermal decomposition characteristics of the blends containing various LC3000 contents in the second step of weight loss show a similar trend as that in the first step. In addition, the char yield at 700°C in nitrogen seems to slightly increase as the content of LC3000 increases.

In air, no significant change of T_{onset} and T_{max1} for the neat matrix and the blends with 5–30 wt % LC3000 is observed, whereas T_{onset} and T_{max1} of LC3000 displays the highest values among all samples examined because of its good inherent thermal stability. The thermal decomposition characteristics of the LC3000/Santoprene system revealed in this study is different from that of LC3000/SEBS blend system recently reported by the authors.[20,22] For the LC3000/SEBS system, the initial degradation temperature and T_{max1} in air of the blends containing various LC3000 contents are much higher than those of the SEBS elastomer matrix. In the present study, although the high thermally stable LC3000 was incorporated into Santoprene at the same amount, only a slight improvement of thermal stability contributed from the TLCP dispersed phase is observed. This suggests that the enhancement of thermal stability for the polymer blend strongly depends on the inherent nature of the blend components, that is, the improved thermal stability of the final *in situ* composite is not only contributed from the TLCP dispersed phase but also the inherent characteristics of the matrix. Note that at the same composition, T_{onset}, T_{max}, and the char yield for Santoprene and its blends are higher in nitrogen than in air indicating that the thermal stability is better in nitrogen than in air. Normally, the thermal stability of polymer in air is somewhat lower than that in nitrogen. However, the situation that the polymer has been exposed in air is more common than in nitrogen during real processing and applications.
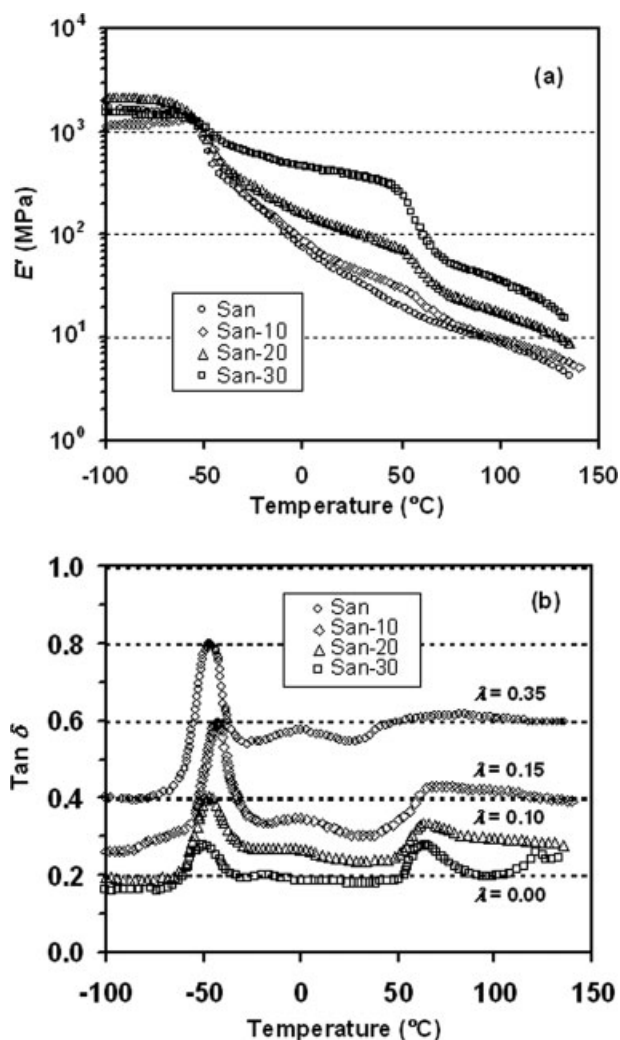
Dynamic mechanical properties

DMA is a very useful method widely used for investigation of mechanical properties, relaxation process and the associated molecular motions, and internal

TABLE I
Nonisothermal Decomposition Characteristics of LC3000/Santoprene Blends at Heating Rate of 10°C/min in Nitrogen and in Air

LC3000 content (wt %)	T_{onset} (°C)	1st degradation step		2nd degradation step		Char yield at 700°C (wt %)
		T_{max1} (°C)	$(d\alpha/dt)_{max1}$ (%/min)	T_{max2} (°C)	$(d\alpha/dt)_{max2}$ (%/min)	
In nitrogen						
0	285	358	3.38	467	13.5	10.5
5	284	355	3.33	466	12.5	9.74
10	290	355	3.30	467	12.3	10.4
20	284	359	2.83	466	10.4	10.6
30	284	359	2.48	464	9.69	14.0
100	407	451	10.2	513	2.53	26.9
In air						
0	265	321	2.97	411	14.5	8.48
5	267	325	3.20	403	13.4	8.79
10	266	321	2.86	406	16.7	11.1
20	268	321	2.55	410	25.5	8.16
30	263	315	2.10	414	24.3	6.34
100	413	453	8.98	589	7.75	0.91

Figure 9 Dynamic storage modulus (E′) (a) and tan δ (b) as a function of temperature for Santoprene/LC3000 extruded strands with various LC3000 contents. The blends are designated as San-X, where X depicts the content of LC3000 in wt % (λ = shift value).

changes of inpolymeric materials as a function of temperature. In this work, DMA was employed to investigate the strength and stability of Santoprene and LC3000-containing blends thereof. The dynamic storage modulus (E′) and loss tangent (tan δ) as a function of temperature for all samples are presented in Figure 9. The values of E′ for each sample at 25 and 120°C are listed in Table II. Beyond the glassy

state region (from −50 to 25°C), the neat Santoprene and San-10 have about the same value of E′ as seen from Figure 9(a). From this point up to 75°C, San-10 starts to decay off at the lower rate than Santoprene. This attributes to the reinforcing effect contributed from the TLCP domains. However, at higher temperaure, the E′ of both samples is comparable. By comparing the results with those of the simple elastomer-composite systems such as LC3000/G1650 and LC3000/G1701 recently reported by the authors,[21] it is noticed that the good fibrillation of TLCP domains incorporated in G1650 and G1701 matrices clearly results in the great improvement in E′ of the blend system (the increase of E′ at 25°C in the rubbery state was by fourfold with addition of 10 wt % LC3000 when compared with that of the neat matrix).[21] Moreover, the improvement of E′ with addition of LC3000 was observed over the whole temperature range being studied. In the case of the present study, the slight improvement of E′ at the definite range of temperature in for San-10 when compared with the neat matrix may mainly arise from the dispersion as droplet of TLCP phase. However, the enhancement of E′ is obviously observed with addition of LC3000 up to 20–30 wt %. The increase of E′ for San-20 at 25°C (rubbery state) and 120°C (melting state) is found to be 2- and 1-fold, respectively, whereas the respective increase of E′ for San-30 are about 10- and 3-fold. On the basis of the results, it is indicated that the dynamic mechanical properties of the polymer *in situ* composites can be enhanced by generation of TLCP fibrils or raising the TLCP concentration. However, in term of processing, the generation of fibrillation with addition of small amount of TLCP tends to be carried out first to improve the properties of the blend and reduce the cost arising from plenteous consumption of polymeric material.

Figure 9(b) shows tan δ curves versus temperature for Santoprene and the composites containing 10–30 wt % LC3000. The values of tan δ peaks corresponding to the transition of the polymer chains are also presented in Table II. The peaks at about −50°C are associated with the glass transitions of the EPDM part, and those at about 0°C with the PP part of Santoprene. It is seen that the EPDM peak shifts to the higher temperature with addition of 10 wt % LC3000. In contrary, with addition of LC3000 up to 20 and

TABLE II
Dynamic Mechanical Properties of Santoprene/LC3000 *In Situ* Composites

Sample code	$E'_{25°C}$ (MPa)	$E'_{120°C}$ (MPa)	$T_{g\ (EPDM)}$ (°C)	$T_{g\ (PP)}$ (°C)	$T_{g\ (PET)}$ (°C)
San	35.8	6.27	−46.2	0.659	–
San-10	46.4	7.23	−42.5	0.391	70.2
San-20	108	12.5	−47.0	–	63.5
San-30	379	23.3	−49.6	–	63.7

The composites are designated as San-X, where X depicts the content of LC3000 in wt %.

30 wt %, the T_g of EPDM, respectively, decrease when compared with that for the neat matrix. The tan δ peaks corresponding to T_g of PET in the TLCP component clearly appear with addition of LC3000 up to 20 wt % or more. However, the T_g of PET block seem to shift to the lower temperature with increasing LC3000 content similar to LC3000/G1650 and LC3000/G1701 blend systems.[21] This indicates that a part of chain segments in LC3000 may locate themselves among both soft and hard segments in the elastomer matrix, thereby resulting in the decreased chain entanglement. This is reflected in the decrease of T_g because of an increase in chain mobility in the elastomer matrix. In addition, the decrease in intensity of the tan δ peak of EPDM in Santoprene is clearly observed with increasing LC3000 loading.

CONCLUSIONS

In this work, *in situ*-reinforcing composites based on polyolefinic thermoplastic elastomer (Santoprene) and LC3000 were prepared. The influence of LC3000 contents on rheology, morphology, mechanical, and thermal properties of the blends was investigated. LC3000 acts a processing agent for the blends by bringing down the melt viscosity of the blend system and all neat and blend samples exhibited shear thinning behavior. Most of TLCP domains appeared as droplets with adding small amount of TLCP (5–10 wt %). At higher LC3000 concentration, high tendency of coalescence of the TLCP dispersed phase was observed. The incorporation of TLCP into Santoprene elastomer matrix significantly enhances the initial modulus of the blends. The thermal stability of all samples is better in nitrogen than in air. The reduction of thermal stability in air arises from the additional thermo-oxidative reaction during degradation. The further addition of LC3000 into Santoprene elastomer matrix is mostly found to slightly retard thermal decomposition, both in nitrogen and in air. The good enhancement in dynamic modulus was achieved in the extruded strand contaning 20–30 wt % LC3000.

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