Isothermal Decomposition Behavior and Dynamic Mechanical Properties of *In Situ*-Reinforcing Elastomer Composites Based on Thermoplastic Elastomers and Thermotropic Liquid Crystalline Polymer

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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 isothermal decomposition behavior and dynamic mechanical properties of the extruded strands were investigated by means of thermogravimetry (TG) and dynamic mechanical analysis (DMA), respectively. No significant change in the shape of TG curves for the neat matrices and their LC3000-containing blends was observed under isothermal heating in nitrogen. In air, G1650 and G1701 showed a single weight-loss stage and rapid decomposition whereas their blends with 30 wt % LC3000 showed different profiles of weight loss depending on isothermal temperatures. The calculated kinetic parameters indicated that the thermal stability of the polymers is much higher in nitrogen than in air and suggested an enhancement of thermal resistance of the elastomer matrices by addition of TLCP. DMA results showed a great enhancement in dynamic moduli for the blend with 10 wt % LC3000 when compared with the neat matrix. The tan δ peaks corresponding to the elastic and hard phases in both matrices mostly shifted to the lower temperature with LC3000 loading. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 917–927, 2007

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

INTRODUCTION

Thermoplastic elastomers (TPEs) are materials that have the processing characteristics of thermoplastics as well as the elastic performance of conventional thermoset rubbers.[1] The ease of processing extends their applications. An improvement in the mechanical properties of TPEs can be obtained by the addition of organic or inorganic fibrous fillers.[2–5] However, the incorporation of these solid fibers into the polymer matrix has caused some technical difficulties, such as an increase in viscosity of the blend system, a machine wear problem, poor mold filling, and increased power consumption. A possible new way to circumvent these problems is the *in situ* generation of short fibers in an immiscible blend of thermotropic liquid crystalline polymer (TLCP) with a TPE.[6–12] TLCPs are known to possess superior physical properties, such as great strength, good thermal properties, and low melt viscosity. Under the appropriate conditions for melt blending of a TLCP and thermoplastic or TPE, the dispersed TLCP droplets can be deformed into fibrils and frozen in the matrix after rapid cooling.[13–16] This type of immiscible blend, resulting in a so-called *in situ* composite,[17] has been reported to exhibit excellent mechanical properties because of the self-reinforcing effect of TLCP fibrils. Two major advantages gained by the addition of small amount of TLCP to a polymer matrix are improved processability and enhancement of mechanical properties.

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, Kraton G1650) and suggested that the polymers were immiscible. They found that 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 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 coworkers[18,19] 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.[20] 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.[21]

For the last few years, 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 blends. 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] Recently, the *in situ* composites based on two elastomer matrices (G1650 and G 1701) possessing very different melt viscosity and TLCP (Rodrun LC3000) were investigated.[22] 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 blends with addition of LC3000 up to 30 wt %. On the basis of the previous results, it may be summarized that by increasing viscosity of the matrix, fibrillar morphology can be obtained in as-extruded strands. By keeping the same viscosity, it is also clear that fibrillar morphology can be obtained by changing the structure of the matrix and hence interfacial tension of the blend. Moreover, we also found that the addition of LC3000 into both TPE matrices improved the tensile modulus considerably and was found to significantly retard thermal decomposition in air but not in nitrogen under dynamic heating. However, it is additionally necessary to examine the thermal decomposition behavior under isothermal heating and dynamic mechanical properties to fully elucidate the properties of both

blend systems. In this work, we further investigated the isothermal decomposition behavior and dynamic mechanical properties of the LC3000/G1650 and LC3000/G1701 *in situ* composites by performing isothermal thermogravimetric (TG) analysis and dynamic mechanical analysis (DMA), respectively. To characterize the relative importance of pyrolytic and thermo-oxidative processes, the isothermal TG measurements were investigated in nitrogen and in air.

EXPERIMENTAL

Materials

The polymer dispersed phase used in this work was Rodrun LC3000, a TLCP, supplied by Unitika Co. (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 matrix phases used in this study were Kraton G1650 and Kraton G1701. Kraton G1650 is an SEBS triblock copolymer with a styrene/rubber wt % ratio of 29/71 and Kraton G1701 is a styrene–(ethylene propylene) (SEP) diblock copolymer with 37 wt % polystyrene. The specific gravities of G1650 and G1701 are 0.91 and 0.92, respectively. Both polymer matrices were provided by Shell Chemical Co. (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.

Blending

The blending equipment and processing conditions for preparation of LC3000/G1650 and LC3000/G1701 blends at various compositions were the same as described in the previous paper.[22] 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 %.

Isothermal TG measurements

The TG analyses were carried out using TA Instruments, SDT Q600 (Luken's drive, New Castle, DE). The pellet of the sample (8–10 mg) was loaded in alumina crucible. The isothermal tests were measured at 340, 360, 380, and 400°C for 100 min. Before isothermal heating, the sample was heated at a rate of 20°C/min from ambient temperature to the selected temperature of isothermal degradation. As soon as the system reached the selected temperature, the variations of sample weights with times were registered. The isothermal tests were 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).

Kinetic analysis

Taking into account the complex nature of polymer degradation, the reaction is generally described by the extent of reaction or degree of conversion (α):

$$\alpha = \frac{x_0 - x_t}{x_0 - x_f} \tag{1}$$

where x_0, x_t, and x_f denote initial, actual, and final values of measurable reaction parameters such as mass, concentration, enthalpy, etc. In this particular study, the sample mass was measured. The rate of a solid-state degradation reaction ($d\alpha/dt$) can be generally described by[23–25]

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \tag{2}$$

In eq. (2), $k(T)$ represents the reaction rate constant and $f(\alpha)$ is a conversion function. By substitution of the Arrhenius equation, $k(T) = A\ e^{-E_a/RT}$, eq. (2) becomes

$$\frac{d\alpha}{dt} = f(\alpha) A e^{-E_a/RT} \tag{3}$$

where A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant, and T is the absolute temperature. By integration of eq. (3), an integral type of kinetic function is obtained:

$$g(\alpha) = A e^{-E_a/RT} t \tag{4}$$

where t is a degradation time. Depending on the assumed reaction mechanism, many expressions for $g(\alpha)$ were derived.[25–28] Kinetic parameters can be obtained from isothermal kinetic data by applying these rate laws with traditional model-fitting methods or with isoconversional (model-free) methods. By taking the natural logarithm of eq. (4), the isoconversional equation is derived:

$$\ln t = \ln g(\alpha) - \ln A + \frac{E_a}{RT} \tag{5}$$

Equation (5) is called standard isoconversional method.[29] By plotting ln t against $1/T$ according to eq. (5), the activation energy can be determined at any given α values from the slope of a regression straight line.

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 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°C to 150°C with a heating rate of 5°C/min in a flow of nitrogen.

RESULTS AND DISCUSSION

Isothermal decomposition behavior

In this study, the isothermal decomposition behavior of the neat matrices (G1650 and G1701) and their blends containing 30 wt % LC3000 (G1650-30 and G1701-30) in nitrogen and in air was examined. Figure 1 shows the isothermal TG curves of G1650 and G1650-30 in nitrogen and in air at 340, 360, 380, and 400°C. The shapes of isothermal TG curves for both samples strongly depend on degradation temperature, atmosphere, and blend composition. In nitrogen atmosphere, G1650 exhibits a slow and steady decomposition at 340°C and the decomposition becomes relatively more rapid with increasing temperature, as seen in Figure 1(Ia). In air, the single-step weight loss and dramatical decomposition of G1650 were observed during the first 20 min of isothermal heating at all isothermal temperatures. A remarkable reduction in isothermal stability for G1650 in air can be ascribed to the additional thermo-oxidative reaction during degradation process. In the case of LC3000-containing blend (G1650-30), the isothermal TG curves in nitrogen [Fig. 1(Ib)] reveal a slow and steady decomposition at 340°C similar to the neat G1650 matrix. The decomposition of G1650-30 in nitrogen becomes more relatively rapid under isothermal heating at temperature higher than 340°C. This change relates well with the nonisothermal decomposition of G1650-30, previously reported[22]; G1650-30 starts to thermally degrade in nitrogen above 340°C. More interestingly, the isothermal TG curves of G1650-30 in air exhibit a much slower degradation rate at the isothermal temperature of 340°C and 360°C as compared with neat G1650. The blend becomes rapidly degraded with heating at higher temperatures of 380°C and above similar to neat G1650. This indicates that the thermal stability of the blends contributed from the incorporation of TLCP is not pronounced at very high temperature. This means that the addition of LC3000 into the elastomer matrices render the retardation of the thermo-oxidative reaction under the isothermal heating in air only up to 360°C. The similar
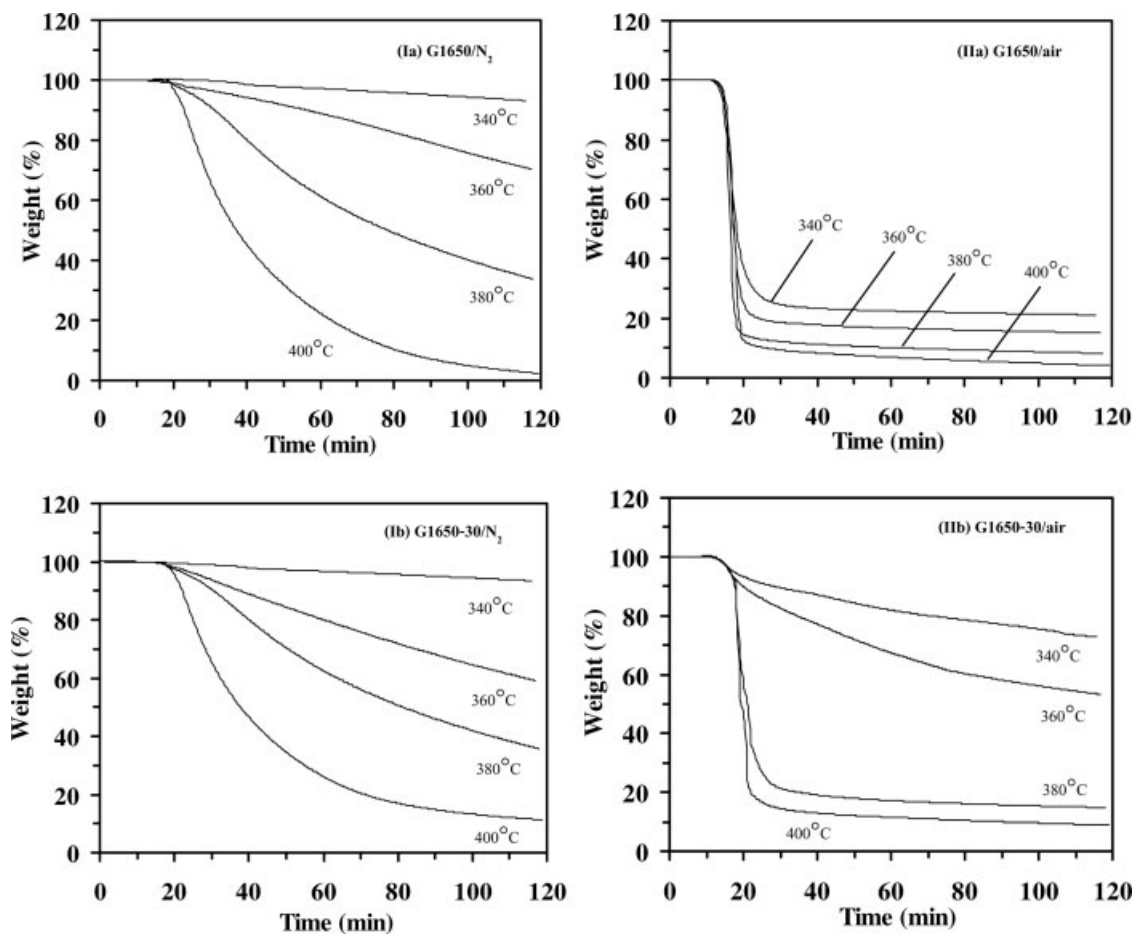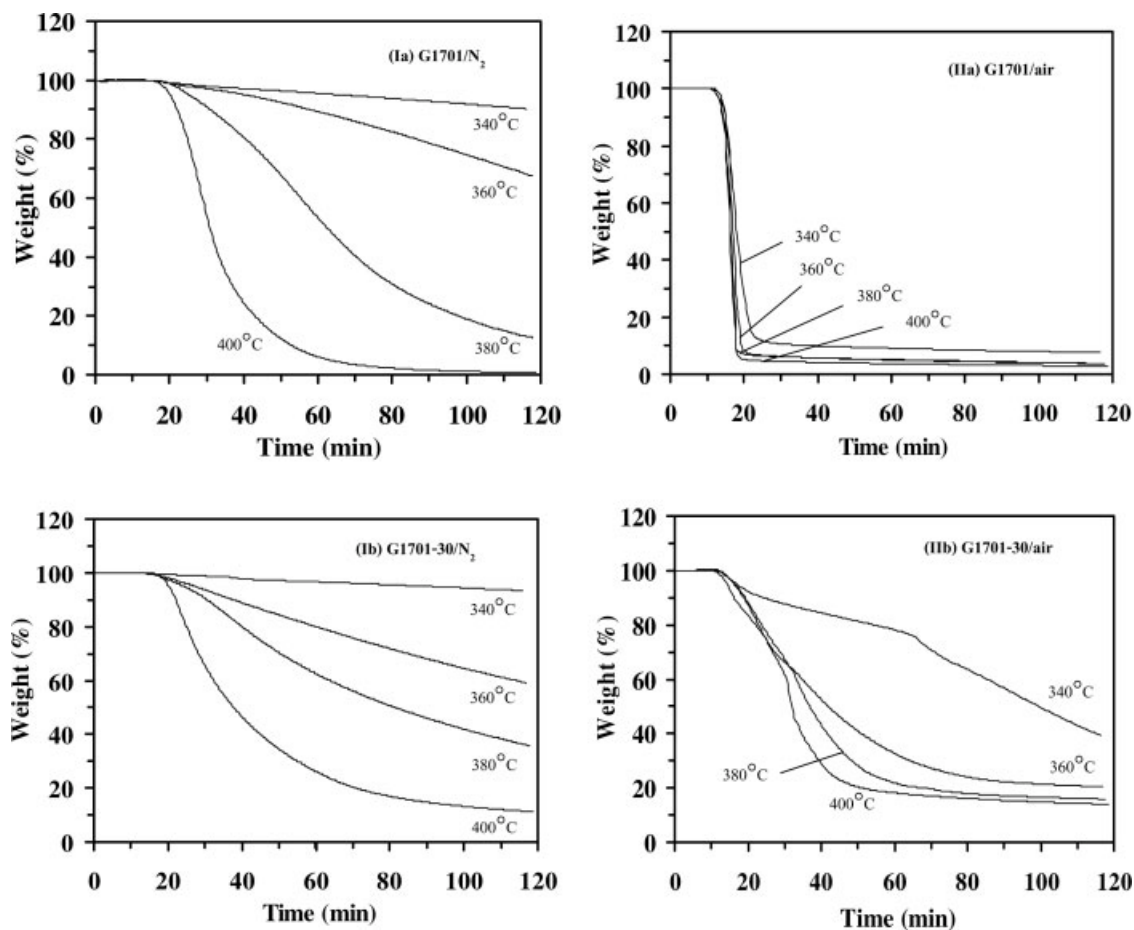
Figure 1 Isothermal TG curves of G1650 (row a) and G1650-30 (row b) performed in nitrogen (column I) and in air (column II).

trend of decomposition behavior under isothermal heating in nitrogen and in air at 340, 360, 380, and 400°C was observed for G1701 and G1701-30 as can be seen from Figure 2.

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.[22] Allen et al.[30] studied the thermal oxidation of SEBS and reported that the oxidation and chain scission were found to dominate at the boundary of the polystyrene-olefin phases. This was found to give rise to the formation of acetophenone ends groups on the styrene units and carboxylic acids on the olefin chain ends. Concurrent and further reaction give rise to the formation of anhydrides and peresters/acids in the longer term together with vinyl and α, β-unsaturated carbonyl products, predominantly carboxylic acids. The olefin phase was found to exhibit severe oxidation and crosslinking associated with the initial formation of unstable primary hydroperoxide species. The presence of a hindered phenolic antioxidant and phosphate were also higher synergistic in inhibiting oxidation and phase separation at the boundaries by destroying the acetophenone end groups and preventing excimer disaggregation. In this study, the degra-

dation of G1650 and G1701 in air may involve the chain degradation, scission, and oxidation which occur primarily at the boundary of styrene-olefin phase, giving rise to the formation of acetone end groups on the styrene units and carboxylic acids on the olefin chain ends as suggested by Allen et al.[30] For the LC3000-containing blends, the degradation mechanism additionally involves the degradation process of LC3000. The degradation mechanism of LC3000 might be similar to that of X7G polymer (a TLCP consisting of 60% HBA/40% PET produced by Eastman Kodak) reported by Sato et al.[31] They reported that the main evolved gas species corresponding to the thermal degradation and combustion process of X7G under inert and quasi-air atmospheres were CO, CO_2, phenol, and aliphatic compounds such as ethylene and acetaldehyde. They also suggested that phenol is released from HBA moiety and the formation of ethylene and acetaldehyde can be attributed to the moiety of PET. Therefore, the degradation mechanism of LC3000 mainly involves the removal of ester, ethylene groups, and hydrogen atom in the polymer chains. From the information of degradation mechanism for the components of the blend systems, we can say that the degradation mechanism of the LC3000-containing

Figure 2 Isothermal TG curves of G1701 (row a) and G1701-30 (row b) performed in nitrogen (column I) and in air (column II).

blends is very complex; there are more than one reaction for the thermal decomposition in nitrogen and in air.

Table I shows the isothermal decomposition data of the neat matrices and their blends in nitrogen and in air. t_{max} represents the time at maximum weight-loss rate, $(d\alpha/dt)_{max}$. The t_{max} of the neat matrices and their blends are mostly comparable both in nitrogen and in air whereas most of $(d\alpha/dt)_{max}$ values for all samples are much higher in air than in nitrogen indicating the rapid weight-loss process with more complex degradation mechanism in air. The amount of char yield for the neat elastomers and their blends decreases progressively with raising isothermal temperatures and is mostly lower in air than in nitrogen.

Isothermal decomposition kinetics

According to the standard isoconversional method, the plot of ln t versus $1/T$ was investigated to evaluate the E_a value at a particular weight loss. Five straight lines corresponding to particular weight losses ranging from 0.5 to 7 wt % of G1650 and G1650-30 are illustrated in Figure 3. A similar trend of straight lines

as shown in Figure 3 was also observed for G1701 and G1701-30 although the plots were not shown here. The respective E_a and ln A values evaluated from the slopes and intercepts of the straight lines for all samples are listed in Table II. For both in nitrogen and in air, the kinetic parameters (E_a and ln A) of all samples progressively increase with increasing weight loss, indicating that the degradation mechanism varies with the weight loss. For both in nitrogen and in air, G1650 shows higher E_a value than G1701. The incorporation of LC3000 renders an improvement in thermal stability considerably as seen from an increase in E_a value of the blends when compared with that of the neat matrix. As reported in the previous article,[32] the respective average E_a and ln A values for Rodrun LC3000 were found to be 110 kJ/mol, 17.1 min^{-1} in nitrogen and 103 kJ/mol, 15.9 min^{-1} in air which are higher than those of the neat matrices and the blends (G1650-30 and G1701-30) presented in this study. This means that the addition of TLCP into both matrices resulted not only in an improvement of processability and mechanical properties[22] but also in significant enhancement of thermal stability. At the same weight loss, E_a, and ln A of all samples are much higher in

TABLE I
Thermal and Thermo-Oxidative Data for the First Weight-Loss Step of G1650, G1701, G1650-30, and G1701-30 Obtained from Isothermal TG Measurements

Temperature (°C)	G1650			G1701			G1650-30			G1701-30		
	t_{max1} (min)	$(d\alpha/dt)_{max1}$ (wt %/min)	Char yield[a] (%)	t_{max1} (min)	$(d\alpha/dt)_{max1}$ (wt %/min)	Char yield[a] (%)	t_{max1} (min)	$(d\alpha/dt)_{max1}$ (wt %/min)	Char yield[a] (%)	t_{max1} (min)	$(d\alpha/dt)_{max1}$ (wt %/min)	Char yield[a] (%)
In nitrogen												
340	–	–	94.4	–	–	91.9	–	–	94.4	–	–	94.0
360	–	–	75.8	–	–	74.7	–	–	64.5	–	–	81.2
380	39	1.20	40.2	56	1.51	18.9	38	1.09	41.9	40	0.96	30.7
400	25	3.66	4.95	28	5.35	1.11	24	3.59	13.2	32	3.62	16.7
In air												
340	16	15.0	21.4	17	14.5	7.96	16	1.29	75.5	16	1.31	49.5
360	17	20.7	15.5	17	26.8	4.03	16	1.90	56.1	16	2.71	21.4
380	17	30.4	8.73	17	29.8	4.12	18	18.5	15.4	22	2.24	16.6
400	18	27.6	4.91	17	30.1	3.06	18	32.3	9.61	24	2.60	14.8

[a] Char yield is determined after heating for 100 min.

nitrogen than in air. This indicates that the thermal stability of the neat G1650 and G1701 samples and their LC3000-containing blends is less stable in air than in nitrogen. Normally, the thermal stability of polymer in air is somewhat lower than in nitrogen. An improvement in thermal stability in air with the addition of LC3000 may be regarded as very significant as the situation that the polymer is exposing to air is more common than to nitrogen both during real processing and applications.

To evaluate the order (n) of isothermal degradation, the isoconversional procedure introduced by Friedman[33] was employed. This method is based on taking the natural logarithm of eq. (3) giving

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + \ln f(\alpha) - \frac{E_a}{RT} \quad (6)$$

Term $f(\alpha)$ represents the mathematical expression of the kinetic model. Generally, $f(\alpha)$ is complicated and valid only for limited range of experimental condition. If it is assumed that the degradation reaction is the "simple nth order reaction," $f(\alpha) = (1 - \alpha)^n$, eq. (6) can be expressed as

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln(1 - \alpha) - \frac{E_a}{RT} \quad (7)$$

By plotting $\ln(d\alpha/dt)$ against $\ln(1 - \alpha)$ at a constant temperature, the isothermal order can be calculated from the slope of the linear relation. For instance, the plots of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ for G1650, G1701, G1650-30, and G1701-30 at 400°C in nitrogen are presented in Figure 4. The straight lines with relatively steeper slope were observed for the same sample in air but the plots are not shown here. The isothermal decomposition orders of all samples are summarized in Table III. It is observed that the n values of all samples examined are higher in air than in nitrogen, suggesting that the degradation mechanism is more complex in air than in nitrogen. The incorporation of TLCP into both matrices yields an increase in thermal decomposition order because there are many monomer components in the blend system, and hence, the degradation mechanism becomes more complex.

Dynamic mechanical properties

DMA is a very useful method for investigation of mechanical properties, relaxation process, and the associated molecular motions and internal changes in polymeric materials as a function of temperature. In this work, we performed DMA measurements from −100°C to 150°C to investigate the strength and stability of polymer materials at high temperatures. Figure 5 presents plot of E' versus temperature for neat G1650 and blends containing up to 50 wt % LC3000. The E'
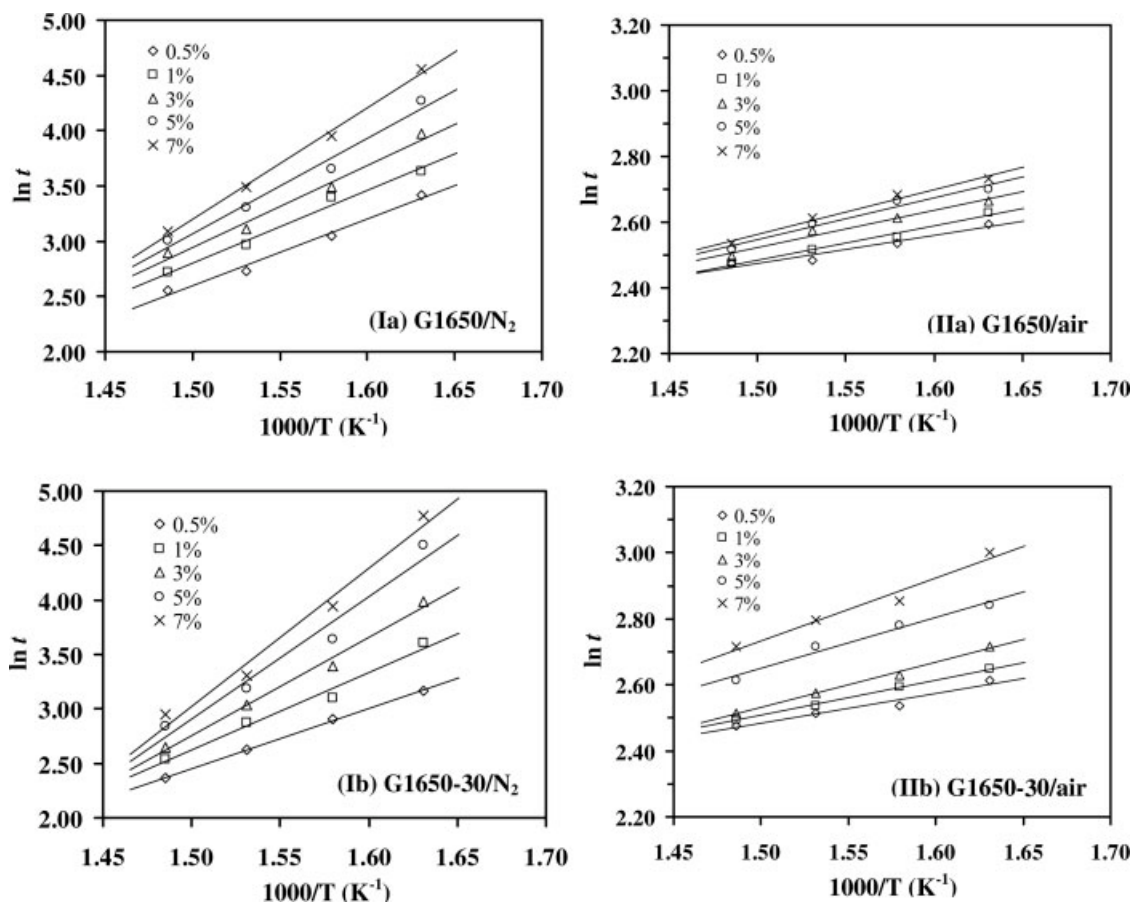
Figure 3 Application of isoconversional method to the thermal degradation of G1650 (row a) and G1650-30 (row b) in nitrogen (column I) and in air (column II).

values for all specimens at 25°C and 120°C are shown in Table IV. An examination of Figure 5 shows that the magnitude of E' decreased with increasing temperature and that all specimens exhibited three state regions: glassy, rubbery, and melting states. The first transition point was due to the relaxation of the soft elastomeric ethylene butylene (EB) block in G1650, which was around −30°C, and the second transition

TABLE II
Kinetic Parameters for Isothermal Degradation of G1650, G1701, G1650-30, and G1701-30 in Nitrogen and in Air Calculated by Using Standard Isoconversional Method

Weight loss (%)	$E_a{}^a(R^b)/\ln A^a$			
	G1650	G1701	G1650-30	G1701-30
In nitrogen				
0.5	50.2 (0.9849)/6.47	44.3 (0.9916)/5.47	45.9 (0.9981)/5.83	41.5 (0.9614)/5.04
1	54.6 (0.9845)/7.05	49.1 (0.9892)/6.28	59.2 (0.9802)/8.06	53.0 (0.9770)/6.88
3	62.0 (0.9813)/8.23	57.8 (0.9919)/7.57	74.8 (0.9901)/10.8	61.3 (0.9951)/8.23
5	71.5 (0.9782)/9.84	70.0 (0.9816)/9.58	93.7 (0.9651)/14.0	81.3 (0.9617)/11.7
7	84.1 (0.9951)/12.0	82.4 (0.9903)/11.7	10.5 (0.9770)/16.0	95.2 (0.9486)/14.0
Average	*64.5/8.72*	*60.7/8.12*	*75.8/10.9*	*66.5/9.17*
In air				
0.5	7.08 (0.9374)/−1.20	6.57 (0.9514)/−1.23	7.45 (0.9481)/−1.14	5.43 (0.9094)/−1.43
1	8.72 (0.9809)/−0.91	7.31 (0.9749)/−1.15	8.86 (0.9973)/−0.99	7.49 (0.9371)/−1.09
3	9.37 (0.9720)/−0.83	8.91 (0.9197)/−0.90	11.3 (0.9932)/−0.49	10.6 (0.9496)/−0.57
5	10.7 (0.9645)/−0.62	9.61 (0.8909)/−0.80	12.8 (0.9727)/−0.33	12.5 (0.9793)/−0.29
7	11.3 (0.9860)/−0.61	11.1 (0.9108)/−0.55	15.8 (0.9688)/−0.11	14.7 (0.9719)/−0.10
Average	*9.43/−0.82*	*8.71/−0.93*	*11.24/−0.57*	*10.1/−0.70*

[a] The units of E_a and $\ln A$ are kJ/mol^{-1} and min^{-1}, respectively.
[b] R means the correlation coefficient for the linear fit analysis.
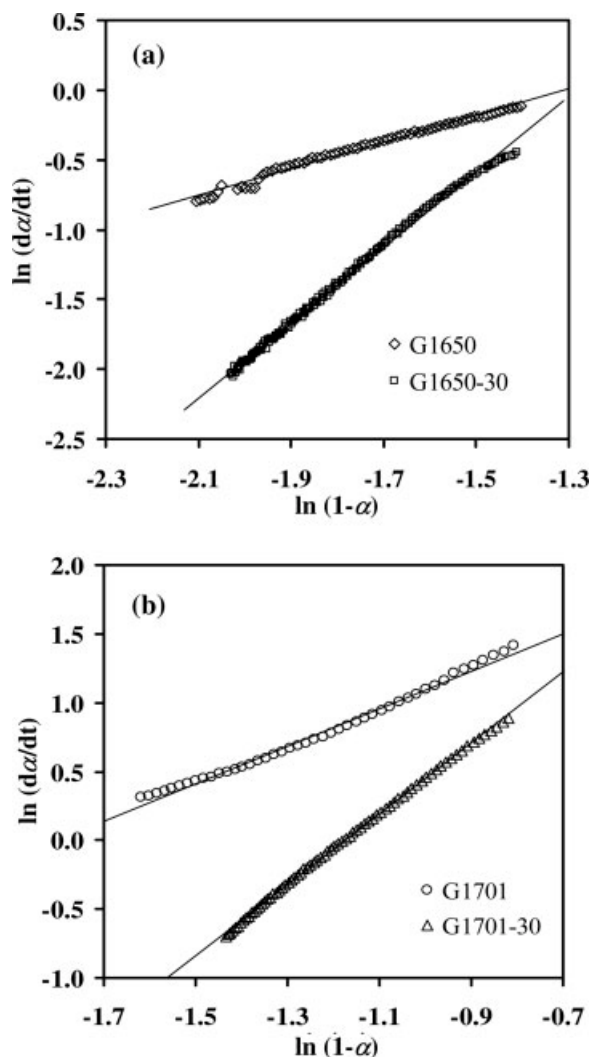
Figure 4 Plots of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ for the neat G1650, G1701, and their blends under isothermal degradation at 400°C in nitrogen.

at about 113°C corresponded to the glass-transition temperature (T_g) of the styrene (S) block. Although the transition has been reported to occur at −105°C for SEBS G1652 due to the cooperative movement of the methylene groups of the EB segments,[34] the change of E' curves for G1650 is not clearly observed. In rubbery state (from −30°C to 70°C), E' increased with addition of LC3000 because of the reinforcement

TABLE III
Isothermal Orders of G1650, G1701, G1650-30, and G1701-30 in Nitrogen and in Air

	n (R^a)			
	G1650	G1701	G1650-30	G1701-30
In nitrogen	0.95 (0.9858)	1.4 (0.9912)	2.7 (0.9971)	2.6 (0.9992)
In air	1.8 (0.8913)	2.3 (0.8692)	4.4 (0.8389)	3.8 (0.8645)

[a] R means the correlation coefficient for the linear fit analysis.

of TLCP domains. Interestingly, the blends with 10 and 20 wt % LC3000 showed a big jump in the value of E' in all states. In the rubbery state, for example, it increased by a factor of about 6. This result agree well with the tensile modulus at low strain and the best TLCP fibrillation with the longest fibers in comparison with the other blend compositions, as reported in the previous paper.[22] The increase in the E' value with the addition of LC3000 clearly indicates an improvement in stiffness over that of neat matrix for the whole temperature range. The improvement of thermomechanical stability with addition of LC3000 is in accordance with the results obtained with TGA. In rubbery region, G1650-30 shows the lowest E' value compared with other compositions. This may partly arise from the fact that the lamellar morphology occurred in as-extruded strand,[22] and hence, lowering the mechanical properties. However, the lamellar structure was observed for G1650-40 and G1650-50 but their E' values are comparable and higher, respectively, than those of G1650-10 and G1650-20. The obtained results indicate that, at high level of TLCP contents (> 30 wt % LC3000), the dilution-effect dependence of mechanical properties is more pronounced than that of the fibrillation one. Verhoogt et al.[7] investigated the dynamic mechanical properties of a Vectra A900/G1650 blend prepared as extruded strand and found that the increase of E' in the blend containing 10 vol % Vectra A900 at 25°C was about 117% compared with that of the neat matrix. In this study, for G1650-10 (7 vol % LC3000), E' was found to be 453% higher than that of the matrix. The greater improvement of E' in our blend system may be because of the higher degree of fibrillation with high fiber aspect ratio (the morphology of both LC3000/G1650 and LC3000/G1701 systems was shown in Ref. 22). For the LC3000/G1652
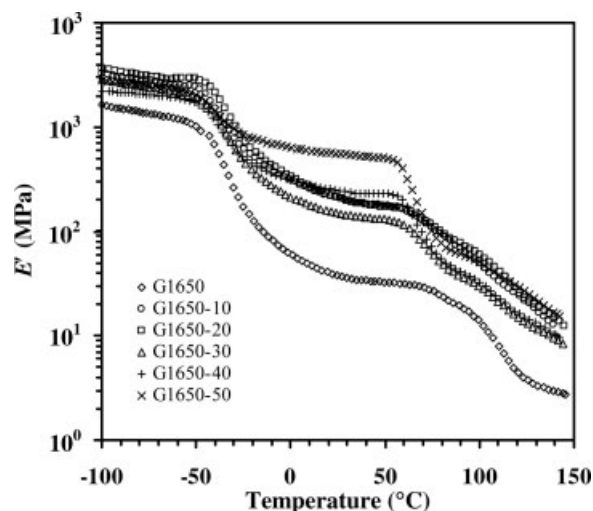
Figure 5 Dynamic storage modulus (E') as a function of temperature for G1650-X extruded strands, where X depicts the content of LC3000 in wt %.

TABLE IV
Dynamic Mechanical Properties of the Extruded Strands for LC3000/G1650 and
LC3000/G1701 Composites Containing 0–50 wt % LC3000

Sample code	$T_{g(\text{EB or EP})}$ (°C)	$T_{g(\text{S})}$ (°C)	$T_{g(\text{PET})}$ (°C)	$E'_{25°C}$ (MPa)	$E'_{120°C}$ (MPa)
G1650	−30.1	113	–	37.8	4.41
G1650-10	−34.8	105	–	209	25.0
G1650-20	−29.0	119	–	209	26.4
G1650-30	−30.2	113	81.0	149	14.9
G1650-40	−33.3	108	78.3	247	16.7
G1650-50	−36.3	105	74.3	555	29.8
G1701	−36.6	130	–	40.5	6.01
G1701-10	−41.5	121	–	229	13.8
G1701-20	−38.9	122	–	220	18.9
G1701-30	−41.6	126	76.8	316	21.0
G1701-40	−40.8	119	72.9	432	23.3
G1701-50	−42.8	117	72.4	737	25.9

system previously investigated by our group,[10] the increase in E' at 25°C of G1652-10 is about 58% compared with that the neat G1652. The slight increase in E' for G1652-10 is mainly due to the appearance of droplet morphology of TLCP domains in as-extruded strand (the morphology of LC3000/G1652 blends was presented in Ref. 11). The attractive benefit of investigation of LC3000/G1650 blends is not only the great enhancement of mechanical properties but also the reduction of energy consumption because of the reduction of fabrication step. In terms of processing, a single-step process reduces the risk of contamination and thermomechanical degradation of material and the subsequent loss of properties.

The Halpin–Tsai equation[35] is often employed to predict the theoretical modulus of the fiber-reinforced composites. The assumption is made that a continuity of stress and strain exists along the interface during testing:

$$\frac{E_c}{E_m} = \frac{1 + ABX}{1 - BX} \quad (8)$$

where

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + A} \quad (9)$$

and E_c, E_m, and E_f represent the longitudinal moduli of the composite, the matrix, and the dispersed fiber, respectively, and X is the fiber volume fraction. The quantity A is equal to $2(l/d)$ where l/d is the length/diameter ratio (aspect ratio) of the fiber. The value E_c for G1650-10 ($X = 0.07$) is calculated as 450 MPa by substituting $E_f = 59$ GPa (taken from the literature[36] which was calculated by using an X-ray technique), $E_m = 37.8$ MPa (obtained from DMA data at 25°C; this value is approximately equivalent to Young's modulus), and an assumed l/d value of 80 (estimated from optical micrograph presented in the previous

article[22]), into eq. (8). This calculated value is about twice that of the measured E' value (209 MPa, at 25°C). The difference between the calculated and the measured E' value may be because of the broad distribution of the fiber aspect ratio in the real system. The contribution is also due to the very high value of tensile modulus of LC3000 employed in the calculation. However, the modulus of LC3000 in our system is expected to be much lower than 59 GPa but we are not able to measure it. From the results obtained from the calculation and measurement of E' of the composite, we can say that the conditions and techniques are an important key to approach the unique distribution of fiber aspect ratio, and hence, obtaining the close values of the calculated and measured mechanical properties.

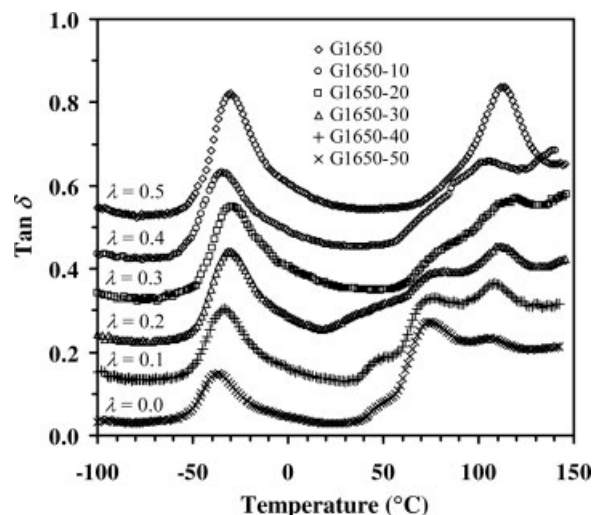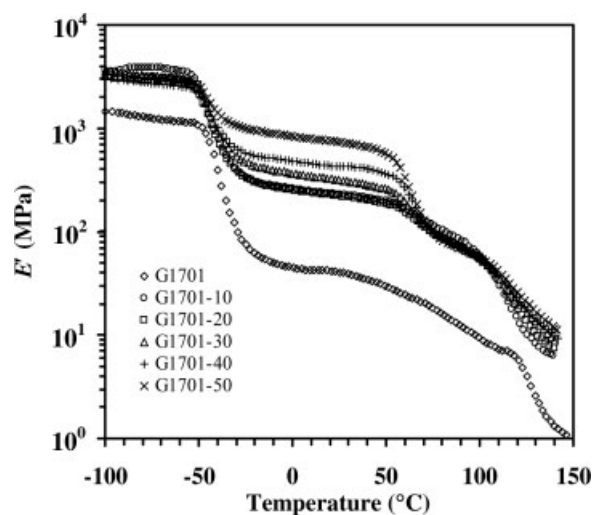Tan δ curves as a function of temperature for the extruded strands of the neat G1650 and LC3000/

Figure 6 Tan δ as a function of temperature for G1650-*X* extruded strands, where *X* depicts the content of LC3000 in wt % (λ = shift value).

Figure 7 Dynamic storage modulus (E') as a function of temperature for G1701-*X* extruded strands, where *X* depicts the content of LC3000 in wt %.

G1650 blends are shown in Figure 6. Each tan δ curve was shifted in the vertical axis by addition with different shift values (λ) to avoid overlapping. The neat G1650 shows two peaks around −30°C and 113°C corresponding to the T_g's of EB block and S block, respectively. A broad peak at −30°C indicates a broad distribution of relaxation times due to the presence of amorphous EB segments.[37] The T_g values corresponding to the transition of EB block, S block in G1650, and PET block in TLCP component are included in Table IV. The T_g's of EB block and S block mostly shift to the lower temperature with increasing LC3000 contents. The T_g-values dependence of TLCP contents obtained from this study is different from those of the LC3000/G1652[10] and Vectra A900/G1650[7] blends. In both latter cases, the T_g's of EB block and S block increased with increasing LC3000 contents, suggesting a constraint of the SEBS component part that adhered onto TLCP fibers; this is because the aromatic S block in SEBS (G1650, G1652) was expected to be more compatible with TLCP. For the blends with 30 wt % LC3000 or more, a new peak appears at around 78°C corresponding to the T_g of PET block in TLCP component. It is clearly seen that with addition from 30 to 50 wt % LC3000, the T_g of PET block progressively decreases from 81°C to 74.3°C. In addition, the increasing LC3000 content significantly influences the relaxation processes of G1650 component; a reduced intensity of damping (tan δ) peaks is obviously observed.

Figures 7 and 8 show the E' and tan δ as a function of temperature, respectively, for the neat G1701 and LC3000-containing blends thereof. The E' values at 25°C and 120°C for all specimens are included in Table IV. As can be seen from Figure 7, G1701 exhibits three regions of behavior similar to G1650. The first

transition point around −37°C corresponds to the T_g of the ethylene propylene (EP) block in G1701 and the second transition at about 130°C corresponds to the T_g of S block. The E' of all states clearly increases with the addition of LC3000 because of the reinforcement of TLCP fibrils. By considering at the rubbery region, the E' values of G1701-10 and G1701-20 are comparable and these compositions show a large jump in the E' value when compared with the neat G1701. For instance, the E' values at 25°C increase up to ∼ 4.7- and 4.4-fold for G1701-10 and G1701-20, respectively, compared with those of the neat matrix. The great improvement of E' by incorporation of a small amount of LC3000 in as-extruded strand is attributed mainly to the reinforcement by TLCP fibrils with high fiber aspect ratio similar to the LC3000/G1650 system.

In the case of G1701-10, by substituting $E_m = 40.5$ MPa (from DMA data at 25°C), an assumed l/d value of 40 (estimated from optical micrograph[22]), and the same values of E_f and X as those of G1650-10, into eq. (6), the calculated E' value of G1701-10 is found to be 273 MPa which is slightly higher than that of the measured value (229 MPa).

As can be seen from tan δ curves in Figure 8 and DMA data in Table IV, the neat G1701 exhibits two peaks around −37°C and 130°C. The T_g's of EP and S blocks in G1701 are lower and higher, respectively, than those of EB and S block in G1650 and mostly shift to the lower temperature with addition of LC3000. The tan δ peaks corresponding to the T_g of PET in the TLCP component clearly appear with addition of LC3000 up to 30 wt % or more. At the same composition (from 30 to 50 wt % LC3000), the T_g's of PET block for the LC3000/G1701 system are lower than those for the LC3000/G1650 system. However, the T_g's of PET block progressively shift to the lower temperature
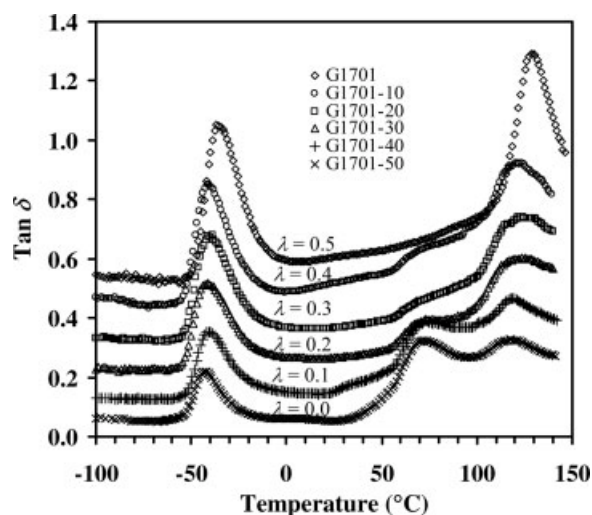
Figure 8 Tan δ as a function of temperature for G1701-*X* extruded strands, where *X* depicts the content of LC3000 in wt % (λ = shift value).

with increasing LC3000 content similar to the LC3000/G1650 system. This indicates that a part of chain segments in LC3000 may locate themselves among both soft and hard segments in the elastomer matrices, thereby resulting in the decreased chain entanglement. This is reflected in the decrease of T_g's because of an increase in chain mobility in the elastomer matrices. In addition, the decrease in intensity of the tan δ peak for EP and S blocks in G1701 component is observed with increasing LC3000 loading.

CONCLUSIONS

G1650, G1701, and their LC3000-containing blends exhibited different isothermal decomposition behavior depending on environmental atmospheres. In nitrogen, all neat matrices and the blends show a slow and steady decomposition at low temperature and the decomposition becomes relatively more rapid with increasing temperatures ($> 340°C$). The addition of LC3000 into both elastomer matrices influences the thermal stability significantly in air but not in nitrogen. In air, both neat matrices show dramatical increase in weight loss during the first 20 min of isothermal heating at all experimental temperatures because of the additional thermo-oxidative reaction during degradation process. G1650-30 and G1701-30 show a good retardation of thermo-oxidative reaction under isothermal heating at 340°C. Under undergoing isothermal heating in air at 360°C or more, more rapid degradation was observed for both blend systems indicating that the contribution from good thermally stable-LC3000 is not effectively pronounced at very high temperatures. Kinetic analysis of isothermal degradation reveals that all kinetics parameters (E, ln A, and n) are dependent on atmosphere and material composition. The isothermal stability of all samples examined is higher in nitrogen than in air. The incorporation of LC3000 into the elastomer matrices significantly improves the thermal stability through a complex degradation mechanism.

A great enhancement in dynamic moduli (E') was achieved in as-extruded strands containing small amount of LC3000 (10–20 wt %); the increase of E' at 25°C in the rubbery state was by four- to sixfold when compared with that of the neat matrices. The T_g's of the soft segments (EB or EP) and the hard polystyrene domains mostly shift to the lower temperature with increasing LC3000 contents, indicating the increase in mobility of the chain segments in the elastomer matrices due to of the penetration of chain segments in LC3000 component, and hence, resulting in a less entanglement of the polymer chains.

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