รายงานวิจัยฉบับสมบูรณ์

โครงการ พฤติกรรมวัฏภาคและสมบัติของคอมโพสิทระหว่างสไตรีนิกพอลิเมอร์ที่มีการเสริมแรงด้วยเส้นใยขนาดเล็กของพอลิเอทิลีน เทอเรพทาเลต ที่ผ่านการใช้งาน

Phase Behavior and Characteristics of Styrenic Polymers Self-Reinforced with Postconsumer Poly(Ethylene Terephthalate) Microfibrils

โดย

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สัญญาเลขที่ MRG 5080415

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สนับสนุนโดย
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ACKNOWLEDGEMENTS

The author wishes to express his profound gratitude and sincere appreciation to the New Research Grant (MRG5080415), Office of Commission on Higher education and Thailand Research Fund for the opportunity and financial given in undertaking this study. Also his great thankfulness is expressed to Center of Excellence for Innovation in Chemistry for partial financial support. His deep appreciation is expressed to Associate Professor Dr. Taweechai Amornsakchai, a research mentor, for his kind supervision, valuable guidance and helpful discussion throughout this research. His sincere gratefulness is expressed to Professor Dr. Sauvarop Bualek-Limcharoen for giving the Rodrun LC3000 liquid crystalline polymer. Lastly, his appreciation is also appreciate to his undergraduate student, Miss Panpirada Limpisawasdi for the research encouragement.

Sunan Saikrasun

บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาศักยภาพของพอลิเอธิลีน เทอเรพทาเลตที่ผ่านการกระบวนการนำกลับมาใช้ใหม่ (rPET) เพื่อใช้เป็นวัสดุช่วยในการหล่อลื่น เพิ่มเสถียรภาพทางความร้อนและเสริมความแข็งแรงให้กับพอลิเมอร์เชิงประกอบที่มีการเสริมแรงแบบอิน-ซิทู ด้วยเส้นใยขนาดเล็ก โดยเปรียบเทียบกับพอลิเมอร์ผลึกเหลว (LCP) วัฏภาคกระจายที่ใช้ในงานวิจัยนี้ก็คือ LCP กับ rPET โดยนำมาผสมกับสไตรินิกพอลิเมอร์สองชนิดคือ พอลิสไตรีน (PS) และสไตรีน-เอทิลีน บิวทิลีน-สไตรีน (SEBS) ทำการศึกษาวิทยากระแส สัณฐานวิทยา ความเสถียรต่อความร้อน และสมบัติเชิงกลของพอลิเมอร์ผสมที่มีสัดส่วนขององค์ประกอบแตกต่างกัน พอลิเมอร์ผสมทุกระบบแสดงพฤติกรรมแบบ shear thinning ในขณะที่ rPET มีพฤติกรรมแบบ Newtonian การผสม LCP และ rPET ลงในพอลิเมอร์เมทริซ์ช่วยปรับปรุงการผสมได้ดีขึ้นโดยการช่วยทำให้ความหนืดของระบบลดลง จากผลของสัณฐานวิทยา พบว่า มีเส้นใยของ LCP เกิดขึ้นในเส้นอัดรีด อย่างไรก็ตามแม้ว่าอัตราส่วนความหนืดของระบบที่มี rPET ผสมอยู่มีค่าต่ำมากแต่ก็ยังพบอนุภาคของ rPET ที่มีลักษณะเป็นเม็ดกลมเกิดขึ้นในเส้นอัดรีด การเติม rPET หรือ LCP ลงในสไตรินิกพอลิเมอร์ช่วยทำให้ความต้านทานความร้อนดีขึ้นมากในอากาศ แต่ไม่ได้ช่วยเพิ่มความต้านทานความร้อนในไนโตรเจน ระบบของ LCP/PS สามารถนำไปขึ้นรูปเป็นเส้นใยได้ที่อัตราส่วนการดึงตั้งแต่ 3 ถึง 8 ซึ่งสามารถทำการดึงได้ง่ายกว่าระบบ rPET/PS ส่วนระบบพอลิเมอร์เชิงประกอบ rPET/SEBS และ LCP/SEBS ซึ่งเป็นอิลาสโตเมอร์สามารถเตรียมและขึ้นรูปได้เป็นเส้นใยเดี่ยว และการเกิดเป็นเส้นใยของวัฏภาคกระจายดีขึ้น เมื่อเพิ่มอัตราส่วนการดึง จากผลที่ได้แสดงให้เห็นถึงศักยภาพของ rPET ในการเป็นสารช่วยผสม ตัวเสริมแรงและช่วยเพิ่มเสถียรภาพทางความร้อนแทนที่ LCP ได้

Abstract

In this work, the potential use of recycled poly(ethylene terepthalate) (rPET) as a well-defined lubricant, enhancing thermal stability and reinforcing material for the *in situ* microfibrillar reinforced composite (iMFC) was investigated in comparison with that of liquid crystalline polymer (LCP). iMFCs based on two dispersed phases, LCP and rPET melt blended with styrenic polymers; polystyrene (PS), styrene-(ethylene butylene)-styrene (SEBS) were prepared using extrusion process. The rheological behavior, morphology, thermal stability and mechanical properties of all blends systems containing various dispersed phase contents were investigated. All blends and LCP exhibited shear thinning behavior, whereas Newtonian fluid behavior was observed for rPET. The incorporation of both LCP and rPET into both matrices significantly improved the processability by bringing down the melt viscosity of the blend system. Some fibrillation of LCP dispersed phase was clearly observed in as-extruded strand. Although the viscosity ratio of rPET-containing blend system is very low, rPET domains mostly appeared as droplets in as-extruded strand. The addition of LCP or rPET into the styrenic polymers improved the thermal resistance significantly in air but not in nitrogen. The LCP/PS system could be drawn as fiber at the draw ratios of 3-8. The drawing ability for fiber preparation was found to be easier in LCP/PS system when compared with that of the rPET-containing blends. The LCP/SEBS and rPET/SEBS elastomer systems were prepared in the form of monofilament. The better fibrillation of dispersed phase with increasing draw ratios was observed for all systems. The obtained results demonstrated the high potential of using rPET in replacing the more expensive LCP as processing aid, reinforcing material and also to thermal resistance of styrenic polymers was improved.

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CONTENTS (continued)

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) have been one of the most advanced materieals used in electronic devices and fiber composites due to its excellent mechanical properties, improved processability, good thermal, chemical and dimensional stabilities. There has been an increasing application of TLCPs, either alone, or as reinforcements or matrices for advanced composites. Upon melting, TLCPs give rise to highly organized liquid phase (mesophase) that tend spontaneously to pack parallel to one another to form highly oriented domains. Under elongational processing conditions, these oriented domains can develop a fibrillar morphology with a high degree of orientation leading to enhanced mechanical properties. These properties enable TLCPs to be used as a reinforcing filler which is not present as a solid phase during processing of the composite, but instead forms when the material is cooled to a solid state. These blends have been called "*in situ* composite" because of their self shaping during processing [1]. *In situ* composites have attracted a great deal of interest because they can solve some problems that arise during the processing of conventional fiber-reinforced composites [2-4]. However, TLCPs are often too expensive for general engineering applications and not readily available in developing industrial countries. On the other hand, there are considerable supplies of engineering plastics in the form of post consumer scraps, which are a low cost source of raw material for forming polymer blends [5]. An alternative way is to find a substitute for TLCPs in fiber-reinforced composite application as a new type of processing route.

In particular, polyethylene terephthalate (PET) is extensively used for the production of fibers, films, and bottles for water and other beverages (especially carbonate drinks) as well as containers for other edible products because of its combination of unique physical, mechanical and permeant properties, as well as processability. As an engineering plastic, it offers, among others, excellent high-temperature properties, clarity, color ability, creep and solvent resistance [6, 7]. In this regard, it is particularly fortunate because it is easily separable from other waste and allows a relatively economical recovery when properly assisted by the education of citizens and regulation. Contrarily, the recovered material after cleaning is not considered suitable for the production of bottles for beverages or water and a new route must be developed for its transformation into usable products in addition to a rather limited and specialized fiber production. A possible upgrading and recycling approach consist of the blending of PET with different polyolefins with the objective of obtaining a composite material with an increased value with respect to the starting polymers. For example, the blends of rPET with common thermoplastics such as polypropylene [5, 8-10] and polyethylene [11-14] based on the concept of *in situ* microfibrillar-reinforced composites (iMFCs)[15] have received much attention during the last decade. Most of the previous works suggested that the presence of PET in a polyolefinic material could enhance mechanical properties of the composites. Moreover, polystyrene (PS) *in situ* reinforced with virgin PET through compatibilized blending has also been investigated by few research groups [16-17] and resulted in better interfacial adhesion and enhanced mechanical properties of final products. However, to the author's knowledge, very limited information is available with regard to the rPET/PS and rPET/Thermoplastic elastomer (TPE) blends and a direct comparison of phase behavior and properties between LCP- and rPET-containing blend system has not been investigated.

In this study, the uncompatibilized blends were prepared and investigated in order to clearly elucidate and compare the effect of dispersed phases on rheological behavior, morphology and thermal decomposition properties of both composite systems. The main goal of this study is to explore the potential of rPET to use as low-cost and easy providing reinforcing material for microfibrillar-reinforced composites, compared with LCP.

SCOPE OF THE RESEARCH

In this work, styrene-(ethylene-butylene)-styrene (SEBS) or polystyrene (PS) melt blend with LCP (Rodrun LC3000) (60 mol% p-hydroxy benzoic acid (HBA)/40 mol% poly(ethylene terephthalate) (PET) and recycled poly(ethylene teraphthalate) (rPET) as reinforcing agents. Styrene-ethylene-butylene-styrene grafted maleic anhydride (SEBS-g-MA) and polypropylene grafted maleic anhydride (PP-g-MA) will be used as compatibilizers. All blends at various compositions will be prepared using a single-screw extruder. The extrudates will be melt spun using mini-extruder and then drawn to enhance molecular orientation. The rheological behavior, morphology, thermal and mechanical properties of extrudates and fiber of LCP and rPET-containing blends will be investigated and compared. The melt rheological properties were studied using plate-and-plate rheometer. The morphology of the fracture surface of the extruded strand and fibers were observed by using SEM. The nonisothermal and isothermal TGA in nitrogen and in air will be performed using TA instruments. Tensile properties of the monofilaments and fibers will be measured using Instron mechanical tester. The dynamic mechanical properties will be characterized using dynamic mechanical analyzer.

OBJECTIVES

1. To explore the potential use of rPET as low-cost and readily available reinforcing material for microfibrillar-reinforced composites, compared with the more expensive LCP.

2. To investigate the effects of rPET or LCP contents on melt rheology, morphology thermal properties and mechanical properties of styrenic thermoplastic and thermoplastic elastomer blends in comparison with LCP.

3. To prepare and develop the composite fibers based on styrenic polymer and rPET.

In this research, the two types of styrenic polymers, PS and SEBS, were used as the polymer matrices. Therefore, the details of experiment, results and discussion and conclusion were divided into two parts.

Part I: Comparative study on phase and properties between rPET/PS and LCP/PS *in situ* microfibrillar-reinforced composites

Materials

The polymer dispersed phases used in this work were Rodrun LC3000, a TLCP, supplied by Unitika Co. (Tokyo, Japan) and rPET collected from postconsumer soft drink bottles. 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 this LCP was not obtainable, since no solvent was found to dissolve Rodrun LC3000. The rPET bottles were cleaned and cut into small pieces with dimension of about 3 mm × 3 mm. The melting temperature of rPET is found to be 252-255°C (examined by using DSC). The matrix phase used in this study was polystyrene (PS) (STYRON^{TM} 685D), purchased from Dow Chemical Pacific LTD. The specific gravity and melt flow rate of PS were 1.04 (ASTM D792) and 1.6 g/10min (ASTM D1238), respectively. All materials were dried in a vacuum oven at 70°C for at least 12 h before used. In this paper, Rodrun LC3000 liquid crystalline polymer was represented by LCP.

Blend preparation

The blends of LCP/PS and rPET/PS 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 80 rpm. The temperature profiles for preparation of LCP/PS and rPET/PS were 190-220-220-225°C and 190-250-255-

260°C, respectively. The temperature profiles shown here represent 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, pelletized and subsequently dried in a vacuum oven. The sample codes of the extruded strand blends are designated as PS-*x*LCP or PS-*x*rPET where *x* depicts the content of LCP or rPET in wt%.

Rheological measurements

Measurements of rheological properties in the molten state for all 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 pellets and compression-molded at 200°C into a sheet about 1.5 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^{-1}. The measuring temperatures for LCP/PS and rPET/PS systems were 225 and 260°C, respectively. The gap between the two plates was set at 0.9 mm.

Morphological characterization

The fracture surfaces of both types of extruded strand blends 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.

Measurement of thermal decomposition behavior

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 and DSC data were simultaneously 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).

Measurement of tensile properties

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 of 1 kN. The stress is engineering stress which was calculated from the original cross section area of the sample. The average value of five measurements was determined.

RESULTS AND DISCUSSION

Rheology

In this study, the different temperature profiles were used for preparation of LCP/PS and rPET/PS blends due to different melting temperature of LCP and rPET dispersed phases. Therefore, rheological measurements in the molten state of LCP/PS and rPET/PS blends were carried out at 225°C and 260°C, respectively. Figure 1 shows the frequency (ω) dependence of complex viscosity (η^*) for neat polymers and their blends. For LCP/PS blend system, the flow curves of all neat and blend samples exhibit shear thinning behavior; the viscosity decreases with increasing shear rate (or shear frequency) due to the shear-induced chain orientation, leading to a reduction in the chain entanglement density. It is seen that a decrease in η^* becomes more pronounced as the percentage of LCP in PS is increased. This indicates that the addition of LCP into PS matrix is melt processable. Similarly for rPET/PS blend system, the incorporation of rPET in PS significantly reduces of the viscosity of the blends, especially at high frequency. However, the viscosity-reduction dependence of rPET contents is not observed in low frequency region. This may be due to that the flexible chains of rPET which could not maintain the chain alignment during long-range relaxation. It is interesting to note that only rPET exhibits Newtonian fluid behavior over the frequency range examined. Although a high amount of rPET was added into the matrix, the Newtonian flow region is not observed in any of the rPET-containing blends.

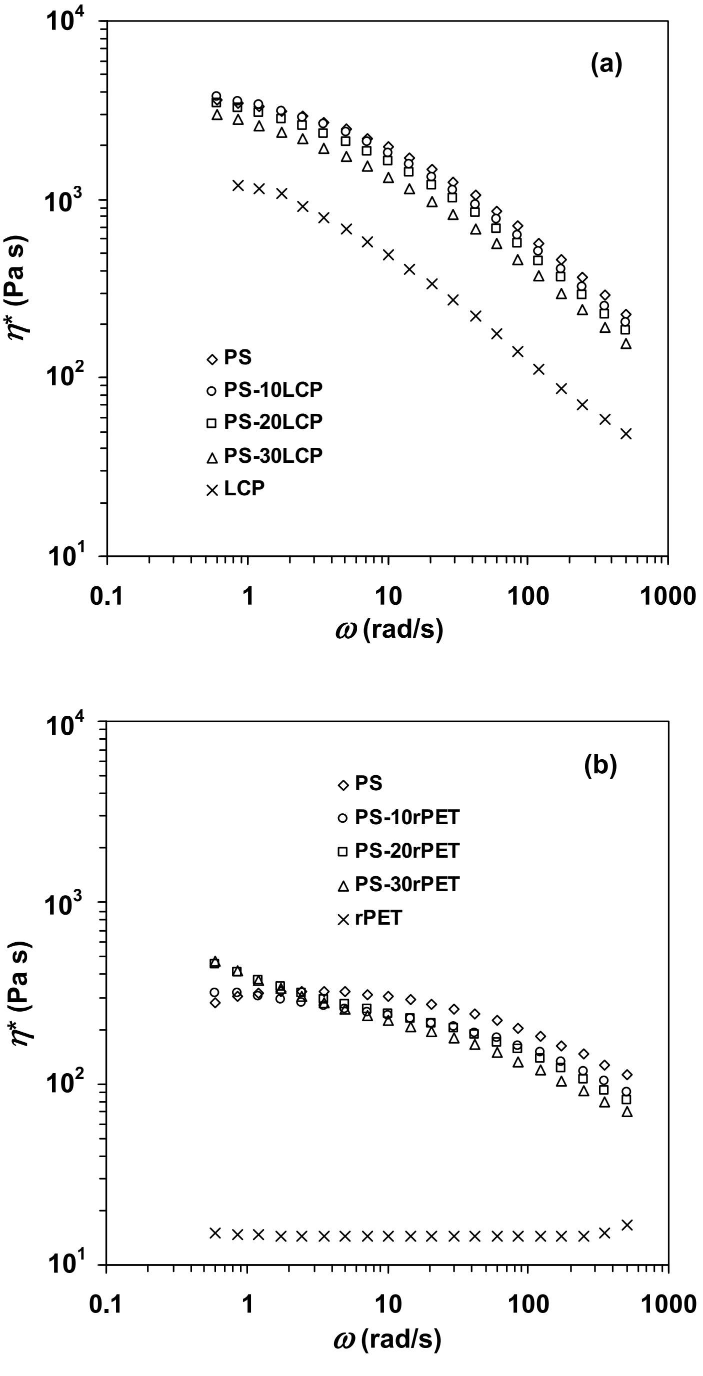

Figure 1 η^* vs. ω for (a) LCP/PS and (b) rPET/PS blends containing various dispersed phase contents, measured at 225°C and 260°C, respectively.

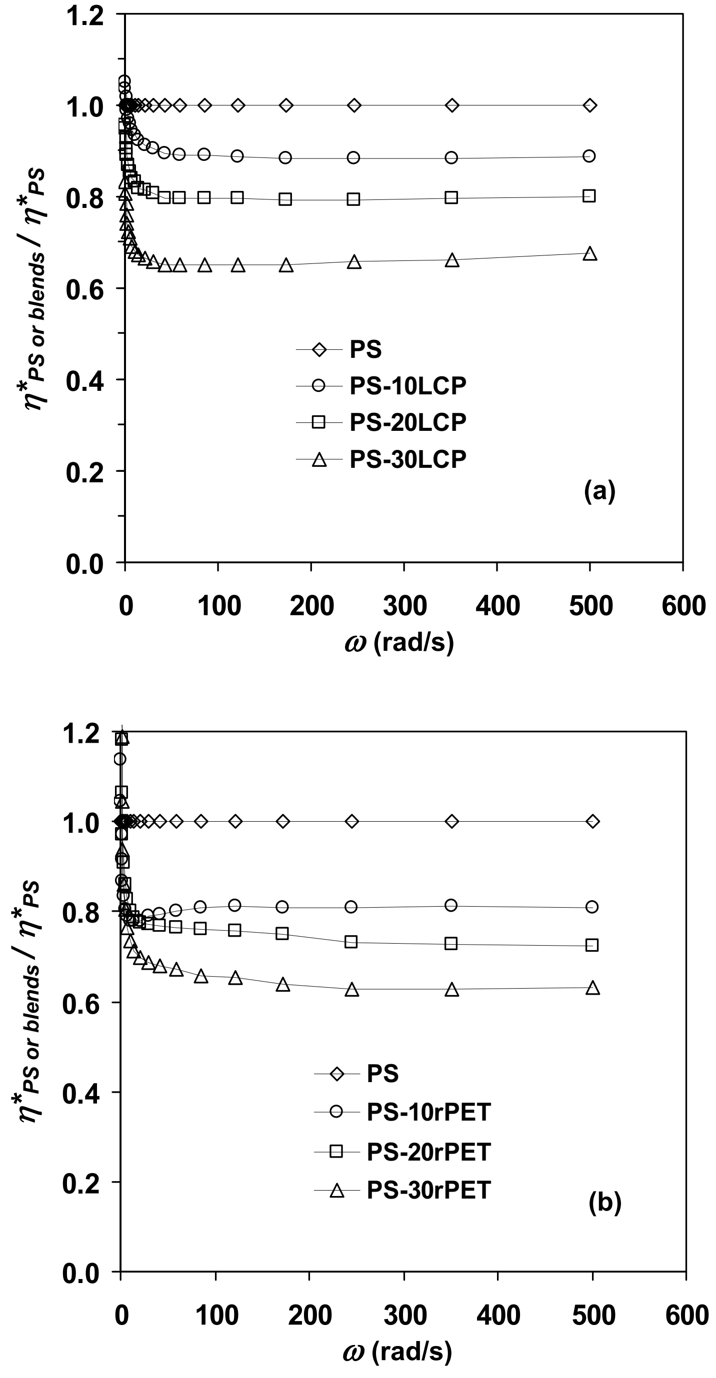

Figure 2 Relative η^* vs. ω for (a) LCP/PS and (b) rPET/PS blends containing various dispersed phase contents, measured at 225°C and 260°C, respectively.

In order to evaluate the potential of rPET as the processing lubricant component compared with that of LCP, the relative viscosity defined as the ratio of viscosity of PS or blends to that of the matrix phase was examined and presented in Figure 2. For LCP/PS system, the decrease in the relative viscosity strongly depends on LCP loadings as seen from Figure 2 (a). The obtained results show that further addition of LCP into PS significantly improves the melt processability. Similarly for rPET/PS system (Fig. 2 (b)), even when a small amount of rPET was added into PS, the relative viscosity of the rPET-containing blends is much lower than that of the neat PS. For example, the relative viscosity decreases about 20% lower than that of the neat PS with 10 wt% rPET loading. It is interesting to note that the reduction of relative viscosity of 10 wt% rPET-containing blend is higher than that of the corresponding composition of LCP-containing blend system. The obtained results suggest that the efficiency of rPET as the processing aid by bringing down the melt viscosity of the blend system is as good as that containing LCP.

The elastic and viscous characteristics of both blend systems can be considered from the plots of storage modulus (G') and loss modulus (G''), respectively, as a function of ω. The plots of G' and G'' as a function of ω for LCP/PS and rPET/PS are shown in Figure 3. The values of G' and G'' at low frequency generally provide information about long-range (beyond entanglement distance) relaxation, while the values at high frequency provide information about short range (motion with entanglement) relaxation [18]. As seen from Figure 3, G' and G'' increase with increasing ω, indicating a dependence of viscoelastic properties on the time scale of molecular motion. For LCP-containing blend systems, the neat PS matrix seems to shows the highest value of G' and G'' and these values progressively decrease as the content of LCP increases. This phenomenon can be explained that the

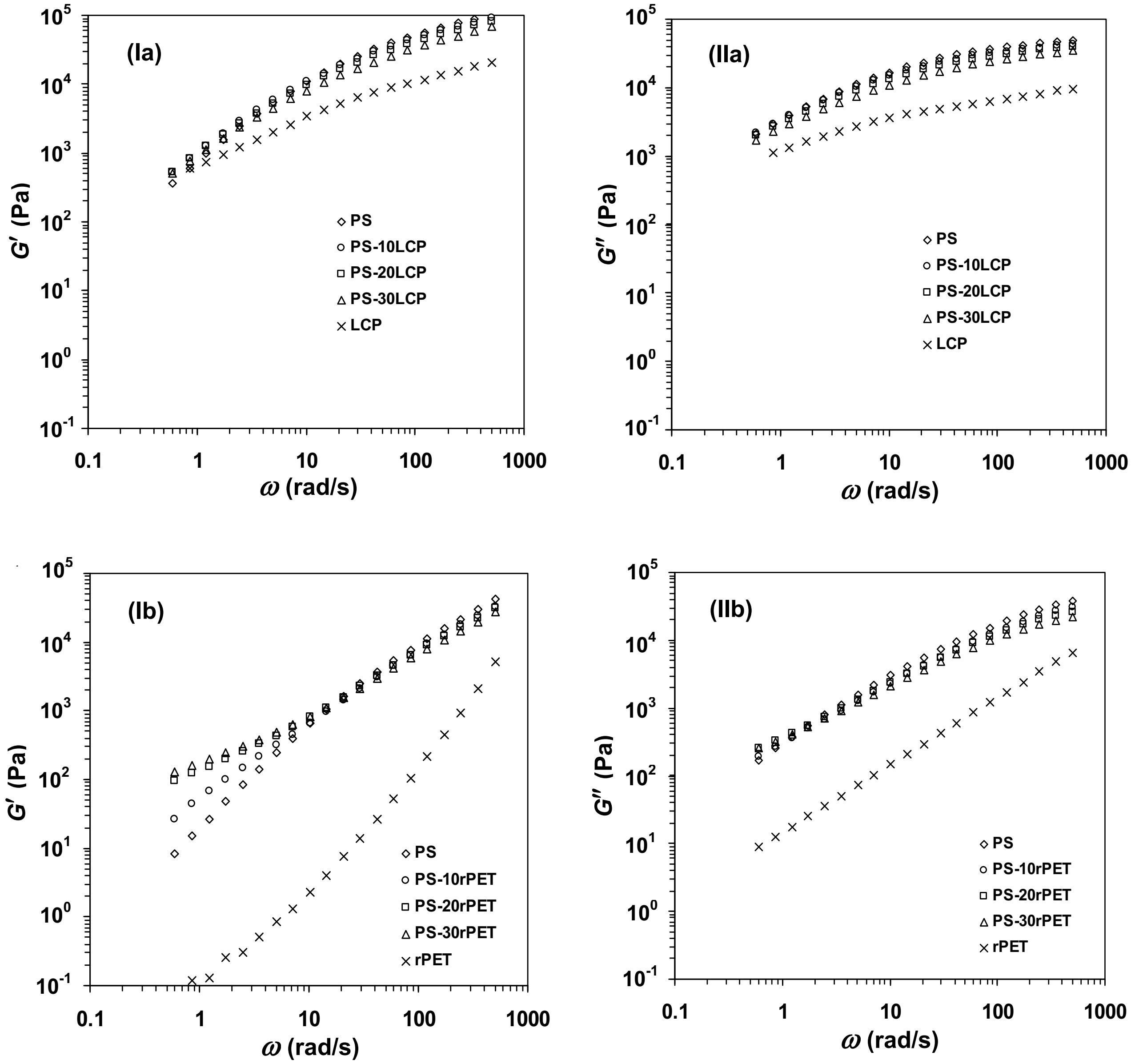

Figure 3 *G′* (column I) and *G″* (column II) vs. *ω* for (a) LCP/PS and (b) rPET/PS blends containing various contents of dispersed phase. The measurements of *G′* and *G″* for LCP/PS and rPET/PS blends were carried out at 225°C and 260°C, respectively.

LCP dispersed phase in the polymer matrix plays an important role in promoting the chain mobility leading to decrease in chain rigidity. At the same composition for LCP-containing blends, G' values of the neat polymers the blends are higher than the corresponding G'' values in the whole frequency range. This indicates that the elastic characteristics for these samples are dominant factor. Oppositely for rPET/PS blends at low frequency ($\omega < 10$ rad/s), even the G' of rPET is much lower than that of PS matrix, further addition of rPET does not lower the G' of the blends. However, at high shear frequency, the G' dependence of rPET contents displays a similar trend to that of LCP-containing blend system. The viscous characteristics (G'') for rPET/PS blend systems, especially at high frequency region, is found to decrease with increasing dispersed phase contents. In addition, the dependence of shear frequency on the elastic and viscous characteristics of rPET is more pronounced than that of LCP.

It is generally known that the morphology of immiscible blend is governed by the viscosity ratio of the dispersed phase to the matrix phase. For simple shear flow, fibrillar morphology is predicted to occur if the viscosity ratio is lower than unity [19-21]. In general, the lower the viscosity ratio, the higher the possibility of forming fibrillar morphology would be. 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 of the dispersed phase. The viscosity ratios as a function of frequency for LCP/PS and rPET/PS blend systems at 225°C and 260°C, respectively, was evaluated and presented in Figure 4. It is seen that the viscosity ratios of both blend systems are much lower than unity over the entire frequency region being investigated. The viscosity ratio of LCP/PS system decreases sharply first from 0.35 to 0.22 within the frequency range of 0-50 rad/s and then gradually increases as the frequency increases.

In the case of rPET/PS system, the viscosity ratio gradually increases from 0.05 to 0.15 as the frequency increases from 0-500 rad/s. It is seen that the viscosity ratio of rPET/PS system is much lower than that of the LCP/PS system when compared at the same measuring frequency. The difference in viscosity ratio arising from the large different viscosity of between the matrix and dispersed phases for both types of the blends is expected to affect the fibrillation of LCP and rPET. Based on the results of viscosity ratios obtained from the present study, it may be expected that both LCP and rPET would form the fibrillation morphology and the better fibrillation should be observed in rPET-containing blends. The relation between morphological observation and the viscosity ratio for both blend systems will be discussed in the next section.

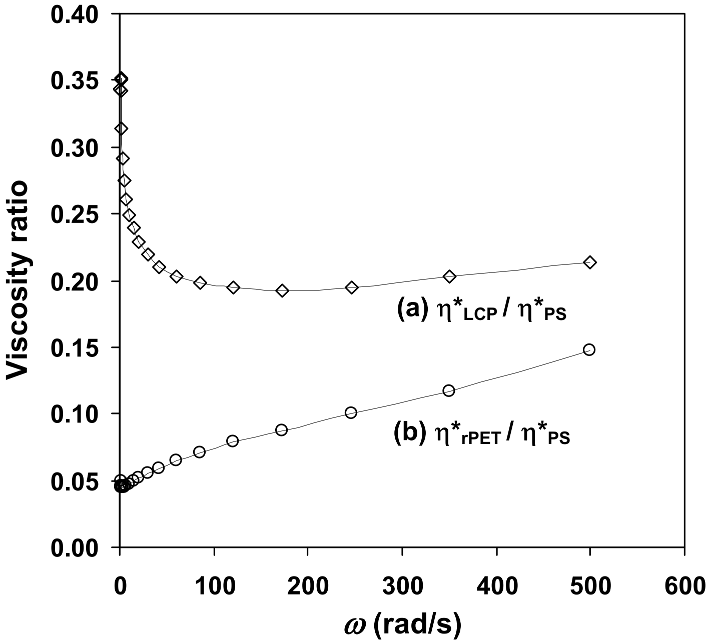

Figure 4 Viscosity ratios vs. *ω* for (a) LCP/PS and (b) rPET/PS blending systems, measured at 225°C and 260°C, respectively.

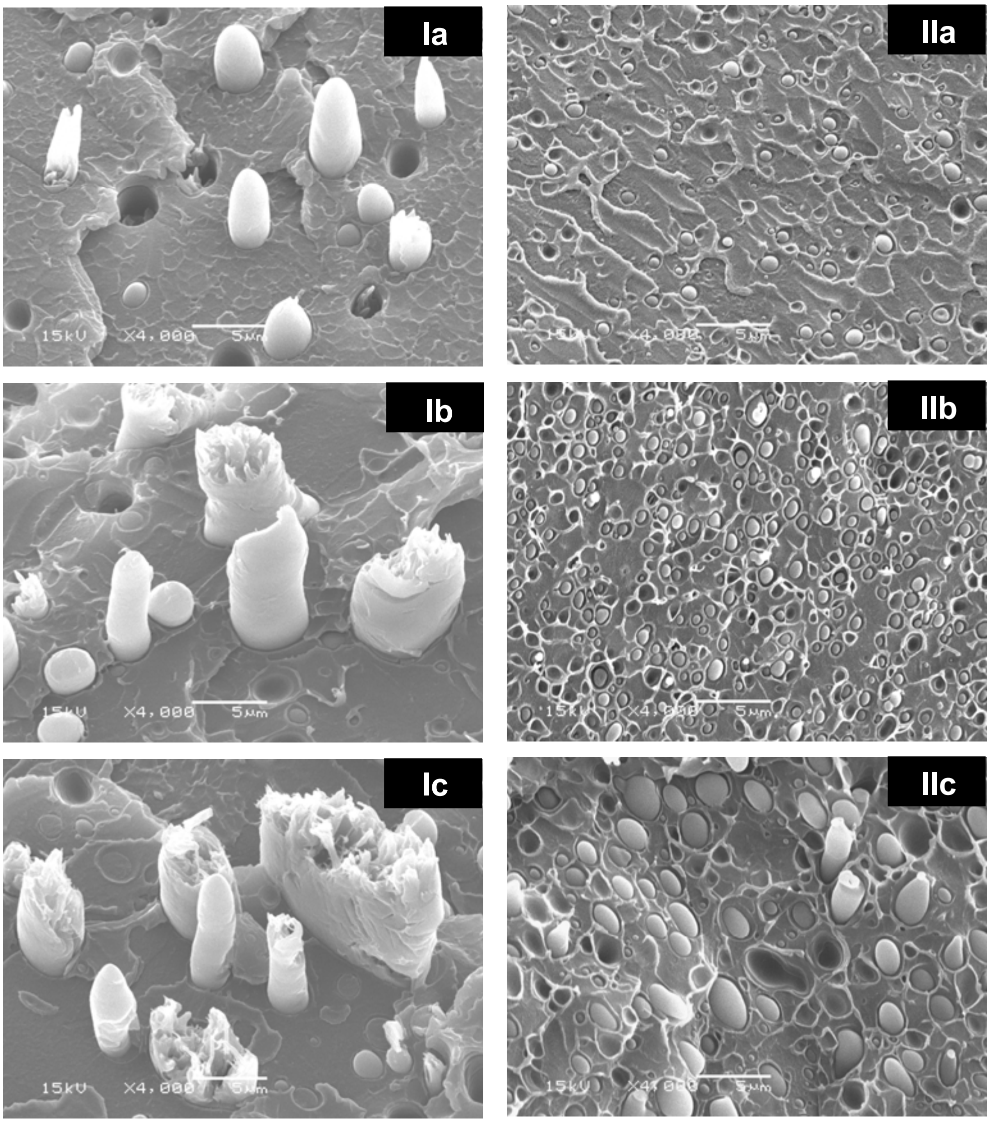

Figure 5 SEM micrographs of the fracture surface for LCP/PS (column I) and rPET/PS (column II) blends containing (a) 10, (b) 20 and (c) 30 wt% dispersed phase.

Morphology

It is well known that the final properties of the *in situ* microfibrillar-reinforced composites depend on its phase morphology which is affected by several important factors such as rheological behavior, composition, interfacial tension, processing condition and fabrication techniques. In the present study, the morphology of the fracture surface was studied by means of scanning electron microscopy (SEM). Figure 5 shows the SEM micrographs of the fracture surface for the LCP/PS and rPET/PS extruded strands containing various LCP and rPET contents. In LCP-containing blend with 10 wt% LCP (Fig.5Ia), droplets and elongated LCP domains are mostly observed. The increase in diameter of elongated LCP domains is observed in the blend with 20 wt% LCP (Fig. 5-Ib). With addition of LCP up to 30 wt%, the coalescence of liquid LCP threads tends to occur in the blends containing high amount of LCP during extrusion [22-24].

In the case of rPET/PS system, most of rPET domains in 10 wt% rPET-containing blend appear as small droplets with the diameter of about 0.5-1 μm and the diameter of rPET domains increases with rPET loading. It is noticed that few elongated rPET domains are observed in the blends with 30 wt% rPET. Interestingly, the domain size of rPET in the blends is much smaller than that of LCP when compared at the same composition. According to the results of viscosity ratio shown earlier, it may be expected that, from the viscosity ratios of both blend systems which is much lower than unity, these blend systems will have fibrillar morphology. However, the morphological results from the present study clearly show that fibrillar morphology in as-extruded strand is obtained only with LCP/PS system. This would suggest that perhaps there are differences in the interfacial tension between LCP/PS and rPET/PS systems. Generally, the deformation of dispersed-phase droplets into fibrillation structures or coalescence of dispersed-phase domains 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 by [25]

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

where η_m is the viscosity of the matrix; $\dot{\gamma}$, the shear rate; *b*, the initial diameter of dispersed droplets; and σ the interfacial tension between the matrix and dispersed phase. 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 [25]. The influence of the capillary number on the stability of the dispersed phases especially for LCP morphology has been studied by a number of researchers [26, 27]. The results of their studies indicate the influence of both viscous and interfacial forces on the final morphology, confirming the importance of Capillary number. In the case of rPET/PS system, even the viscosity ratio is lower than 0.15, the fibrillation of the rPET domains is not observed in as-extruded strand. According to eq. (1), one may propose that the interfacial tension of this blend is relatively high. In addition, the dispersed phase-pullout feature which reveals poor interaction at the interface is observed for both blend systems because these blend systems are immiscible. This is an important requirement for the production of *in situ* microfibrillar-reinforced composites.

Thermal decomposition behavior

Normally, polymers must encounter elevated temperatures at almost every stage in manufacturing, compounding, and processing stages, in service, and during repairing step. Therefore, an 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 LCP and rPET on thermal decomposition of LCP/PS and rPET/PS blends. The dynamic TG curves of the two blend systems are presented in Figure 6. The TG measurements were carried out in nitrogen and in air at a heating rate of 10°C/min. The TG results of LCP/PS blends (Fig. 6IA) obtained in nitrogen will be considered first. The nonisothermal TG profile of PS reveals only a single weight-loss step at the temperature range around 380-450°C which corresponds to the chain scission followed by depolymerization and the formation of the main evolved products, styrene monomer, dimer and trimer [28, 29]. In the case of LCP, the first major degradation mainly occurs at PET block, whereas the second minor degradation process could be attributed to the degradation of HBA block [30, 31]. Although the blend system may be complicated due to the presence of many copolymer components, a single degradation step similar to the neat PS matrix is observed for the blends containing 10-30 wt% LCP. Although the thermal stability of LCP is much higher than that of the neat PS, the thermal resistance of the blends in nitrogen is not significantly affected by LCP loading. This result is similar to those of the *in situ* elastomer composite when styrenic or polyolefinic based thermoplastic elastomer (TPE) was used as the base polymers, as reported by the authors [24, 32]. Under dynamic heating in air (Fig.6IB), a single decomposition process of PS that occurs between 250 and 400°C of PS is observed. The fact that PS degrades at a lower temperature in air than it does in nitrogen is a properly found in many polymers. This appears to occur as a result of switching the limiting step from random scission to decomposition of the hydroperoxide radical, which occur with a lower activation

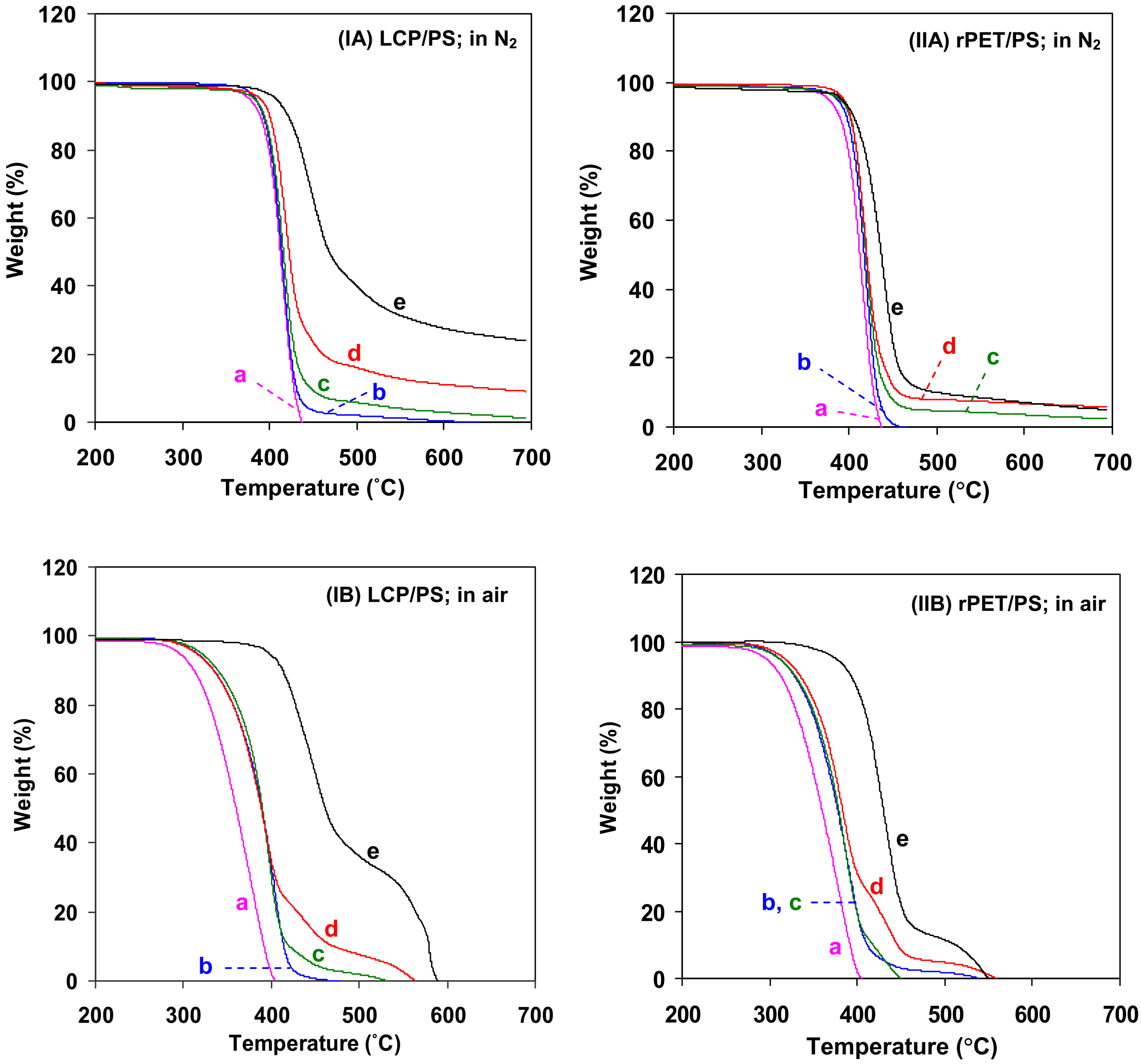

Figure 6 Dynamic TG curves of LCP/PS (column I) and rPET/PS (column II) blends containing (a) 0, (b) 10, (c) 20, (d) 30 and (e) 100 wt% LCP or rPET at a heating rate of 10°C/min in nitrogen (row A) and in air (row B).

Table 1 Nonisothermal decomposition characteristics of LCP/PS and rPET/PS blends in nitrogen and in air.

	LCP/PS blending system						rPET/PS blending system					
LCP or rPET content (wt%)	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	$(d\alpha/dt)_{max1}$ (%/min)	$(d\alpha/dt)_{max2}$ (%/min)	Char yield at 600°C (wt%)	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	$(d\alpha/dt)_{max1}$ (%/min)	$(d\alpha/dt)_{max2}$ (%/min)	Char yield at 600°C (wt%)
In nitrogen												
0	396	415	-	29.2	-	0.00	396	415	-	29.2	-	0.00
10	398	417	-	29.8	-	0.03	403	410	-	31.3	-	0.00
20	400	417	-	27.1	-	0.25	404	421	-	30.0	-	0.30
30	403	420	-	23.2	-	1.05	403	419	-	27.6	-	0.57
100	419	448	-	10.5	-	27.6	414	441	-	20.8	-	7.13
In air												
0	324	378	546	12.9	0.67	0.00	324	378	546	12.9	0.67	0.00
10	376	401	532	24.1	0.64	0.00	343	392	544	14.1	0.76	0.00
20	366	397	554	19.4	1.50	0.00	349	391	538	15.9	1.26	0.00
30	351	395	567	14.1	2.38	0.00	347	382	551	13.5	1.34	0.00
100	410	449	573	9.58	19.8	0.00	399	433	553	16.3	5.16	0.00

energy [29]. Interestingly, the incorporation of LCP into PS effectively enhances the thermal stability in air more than in nitrogen. This result agrees well with that of the styrenic based TPE *in situ* reinforced with LCP investigated by the authors.[24] However, the results of thermal stability of LCP/PS blends presented here are different from those of LCP/polyolefinic based TPE system which a slight improvement in thermal resistance is observed with LCP loadings. These results suggest that although the thermal stability of LCP is much higher than those of the polymer matrices, an improvement in thermal stability of the final *in situ* composite is not only contributed from thermally stable LCP but also the inherent characteristics of the polymer matrix.

In the case of rPET/PS blending system in nitrogen (Fig. 6IIA), the single weight-loss are observed for all neat polymers and the blends at 360-460°C. Several studies have been conducted on the thermal degradation products of PET [33-35], which suggests that the thermal degradation of PET is initiated by chain scission of ester-linkage, yielding carboxyl and vinyl ester groups. In air (Fig. 6IIB), at least two weight-loss steps are observed for all blends and PET indicating that the degradation process is more complex in air than in nitrogen. To clearly compare the dispersed phase-content dependence of thermal stability for the two types of blends in more quantitative way, the thermal decomposition parameters in nitrogen and in air are compared and summarized in Table 1. 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. It is seen that T_{onset} and $T_{\max}$ of all polymers are higher in nitrogen than in air. In fact, 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. $T_{\max1}$ of both systems seems to mostly increase with addition of the dispersed phases indicating the efficiency of thermally stabilized dispersed phase. At the same composition in nitrogen, $T_{\max1}$ of LCP-containing blends is comparable to that of the corresponding rPET-containing blends. It is noticed that at the same composition, $(d\alpha/dt)_{\max}$ of all polymers are wholly higher in nitrogen than in air . By comparing between the two types of the blends in nitrogen, $(d\alpha/dt)_{\max}$ of rPET-containing blend is higher than that of the corresponding LCP-containing blend. Contrarily in air, $d\alpha/dt)_{\max}$ of rPET-containing blend is lower than that of the corresponding LCP-containing blend. Note that, in air, $(d\alpha/dt)_{\max2}$ of the LCP and rPET dispersed phases are much higher than that of the matrix phase.

For LCP/PS blend system, no char residues at 600°C were left for the neat PS whereas the amount of char residues increases with increasing LCP contents. The increase in char residues mainly arises from the increase in HBA block (by increasing amount of LCP content) which will decrease the number of hydrogen atoms and retard the formation of volatile degraded products [36]. However, the amount of char residues is mostly found to be higher in LCP/PS than in rPET/PS blends when compared at the same composition. Note that, for both blend systems in air, no char residues of the neat polymers and the blends were left within the experimental temperature being studied.

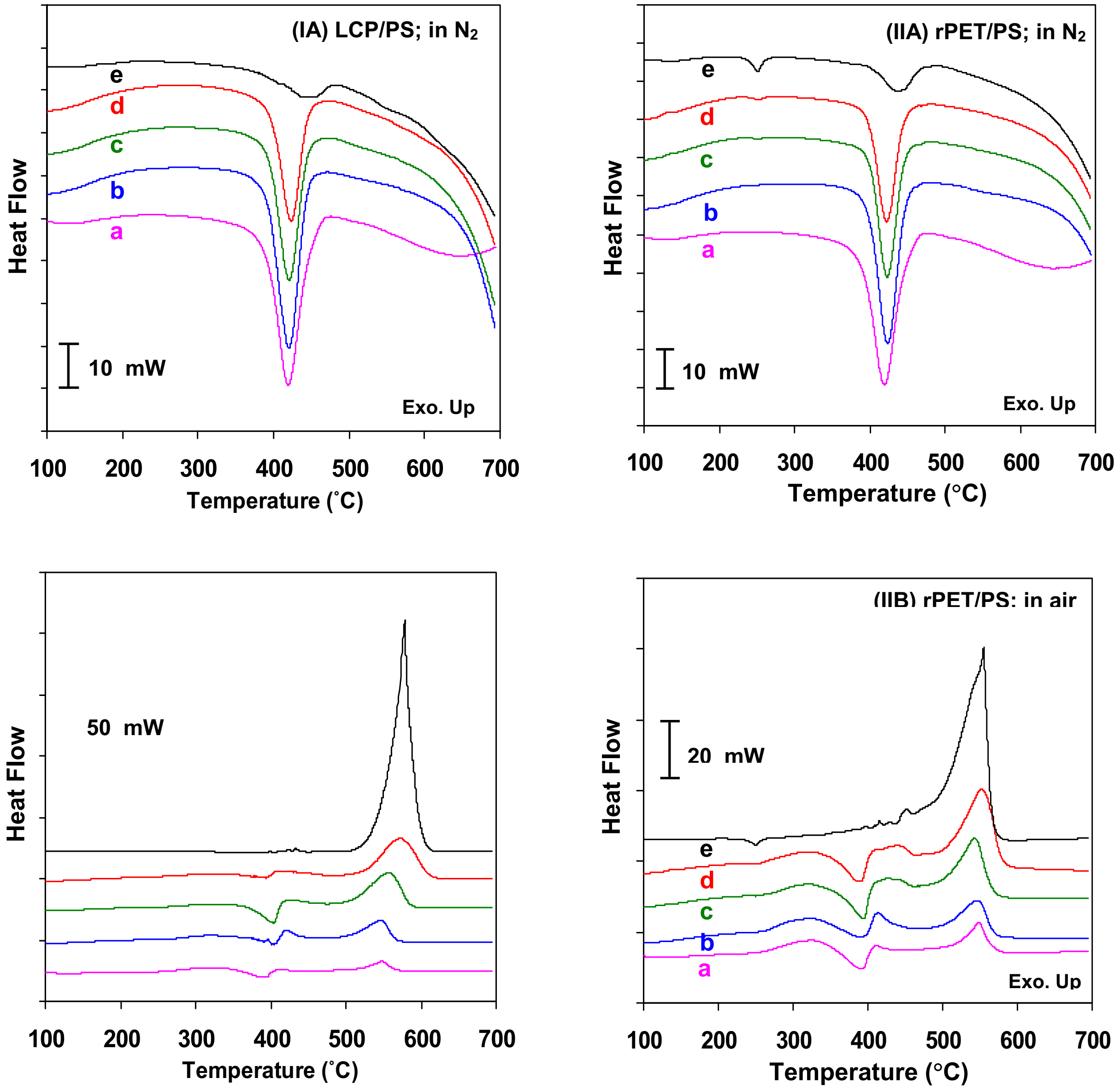

Figure 7 Simultaneous DSC curves of LCP/PS (column I) and rPET/PS (column II) blends containing (a) 0, (b) 10, (c) 20, (d) 30 and (e) 100 wt% LCP or rPET at a heating rate of 10°C/min in nitrogen (row A) and in air (row B).

Table 2 Simultaneous DSC data of LCP/PS and rPET/PS blends under thermal degradation in nitrogen and in air.

LCP or rPET	LCP/PS blending system				rPET/PS blending system			
content (wt%)	T_m (°C)	ΔH_m (kJ/g)	T_{d1}/T_{d2} (°C)	$\Delta H_{d1}/\Delta H_{d2}$ (kJ/g)	T_m (°C)	ΔH_m (kJ/g)	T_{d1}/T_{d2} (°C)	$\Delta H_{d1}/\Delta H_{d2}$ (kJ/g)
In nitrogen								
0	-	-	420/-	1.05/-	-	-	420/-	1.00/-
10	-	-	420/-	0.69/-	-	-	424/-	0.57/-
20	-	-	420/-	0.55/-	-	-	423/-	0.67/-
30	-	-	423/-	0.42/-	252	0.06	423/-	0.74/-
100	-	-	436/-	0.12/-	251	0.04	437/-	0.20/-
In air								
0	-	-	390/548	0.35/0.40	-	-	390/548	0.35/0.40
10	-	-	405/547	0.54/0.81	-	-	391/546	0.40/0.57
20	-	-	403/557	0.60/1.41	-	-	393/543	0.54/0.91
30	-	-	394/573	0.22/2.48	-	-	398/552	0.42/1.15
100	-	-	-/579	-/0.67	251	0.04	-/555	-/3.18

Simultaneous DSC data of thermal decomposition

Simultaneous DSC traces and DSC data for thermal decomposition of PS, LCP, rPET and the blends are shown in Figure 7 and Table 2, respectively. T_m and ΔH_m represent the melting temperature and melting enthalpy, respectively, whereas T_d and ΔH_d represent the peak temperature and the enthalpy associated with thermal degradation process. Subscripts 1 and 2 correspond to the first and the second peaks, respectively. It is seen that the DSC profiles of the samples are different in nitrogen and in air, arising from the different degradation mechanisms. The DSC curves of PS and LCP in nitrogen (Fig. 7(IA)) show a degradation endotherm which is a characteristic of typical depolymerized mechanisms. The DSC traces of PS and LCP in nitrogen have a well-defined endothermic peak centered at 420 and 436°C, respectively which is near the region of maximum weight loss in the TGA data. In the case of rPET blend system in nitrogen (Fig. 7-IIA), the endothermic peak associated with the fusion of the crystalline fraction is observed at about 251°C. In addition, the largest endothermic peak of rPET is observed at about 437°C corresponding to the thermal degradation process of rPET. Although the degradation temperatures of rPET and LCP dispersed phases are higher than that of the neat PS, the incorporation of dispersed phases into PS does not significantly influence the degradation temperature (T_d) of the blend in nitrogen. As seen from Table 2, the enthalpy of thermal decomposition (ΔH_d) of rPET, LCP and their blends are lower than that of the neat PS matrix in nitrogen. Under heating in air, PS exhibits an endotherm at 390°C and a small exothermic peak is also observed at 548°C. It is seen that, in air, T_d and ΔH_d of the blends mostly increased with LCP or rPET loadings. This may contribute from the relatively higher T_d and ΔH_d values of both dispersed phase when compared with that of the neat PS matrix.

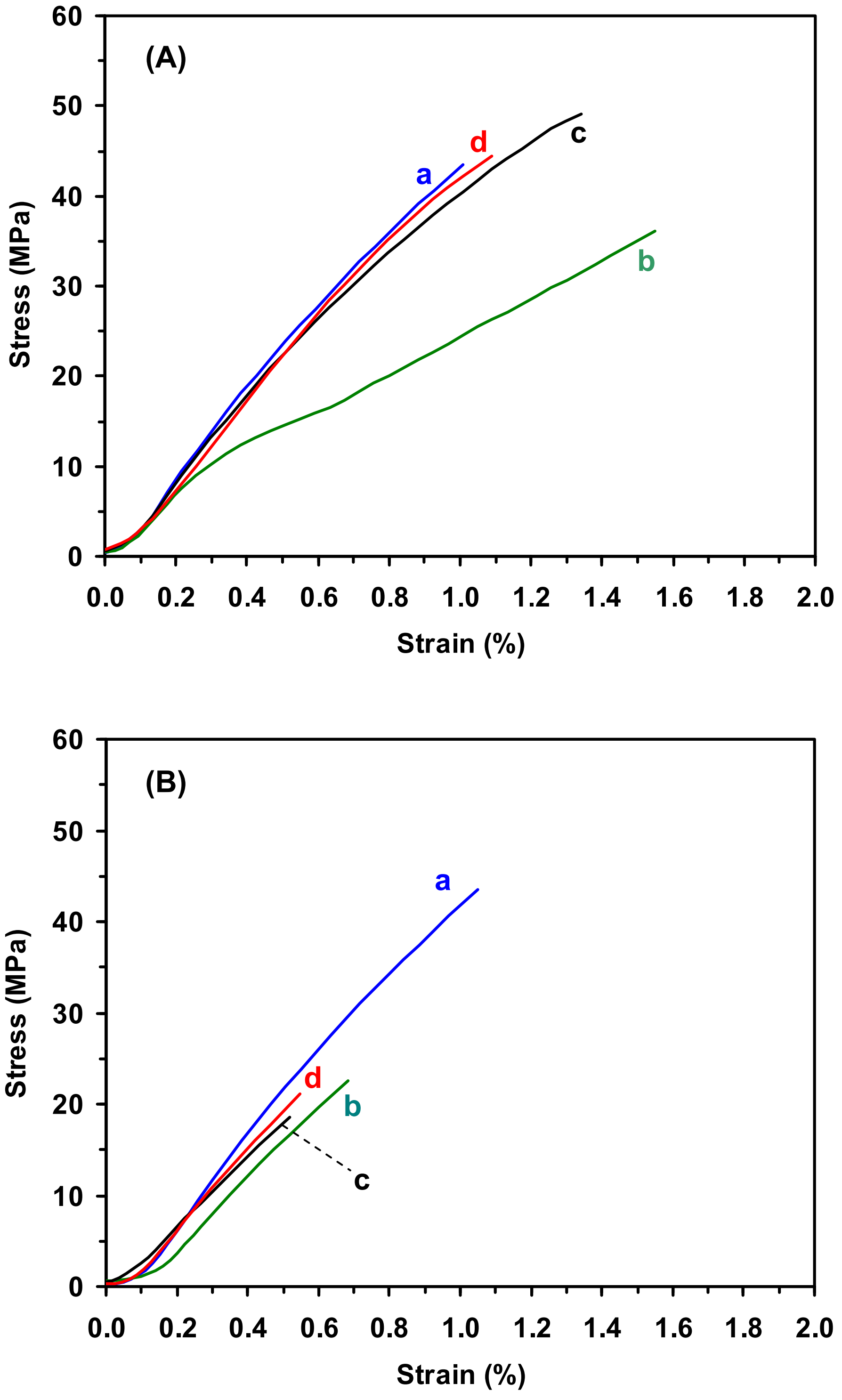

Figure 8 Stress-strain curves at 25°C for LCP/PS (A) and rPET/PS (B) blends containing (a) 0, (b) 10, (c) 20 and (d) 30 wt% LCP or rPET.

Tensile properties

Figure 8 displays the stress-strain curves of the blend extruded strands for the LCP/PS and rPET/PS systems and stress at 0.5% strain, tensile strength and elongation at break of all samples are shown in Table 3. The blend extruded strands contain 0-30 wt% LCP or rPET. The stress reported here is the nominal (engineering) stress, that is, the force divided by the cross-section area of the initial undeformed state. We will first consider the LCP/PS blend system. Under uniaxial stretching, the neat PS behaves like hard and brittle materials. It is interesting to note that, at the strain > 0.2%, the stress of the blend containing 10% LCP is clearly lower than that of the neat PS. At higher LCP concentration, the stress of the extruded strands and the neat PS are comparable. The tensile strength (maximum stress) of the neat PS and the blends lie between about 47-50 MPa and the blends with 20 wt% LCP shows the highest value of tensile strength compared among all samples examined. In addition, the elongation at break (maximum strain) of the blend containing 10 wt% LCP is somewhat higher than that of the neat PS matrix.

In the case of rPET/PS blend system, the stress at 0.5% strain and tensile strength of all rPET-containing blends are comparable and much lower than that of the neat PS. At high strain (>0.3%), the stress of the blend containing 10 wt% rPET is lower than that of the neat PS. The tensile strength of rPET-containing blends in the range of about 15-20 MPa are observed which are about half lower than that of the neat PS. Note that, at the same composition, the tensile strength and elongation break of the rPET-containing blend are lower than that of the corresponding LCP-containing blends.

Generally, the mechanical properties of the *in situ* composite are expected to be improved by optimum addition and/or enhancing the ability of fibrillation of dispersed phase. The low stress observed in the blend with low LCP content (10 wt% LCP) is evident from the droplet and ellipsoidal morphology of LCP domains as observed from SEM. With increasing LCP content, the good fibrillation of LCP dispersed phase are observed and results in an enhancement of tensile properties. However, some coalescence of LCP domains occur with addition of LCP content up to 30 wt% or higher, resulting in the reduction of extensibility [22-24]. For rPET-containing blend system, as evident from the droplet morphology of rPET dispersed phase, the tensile properties of all blends are mostly lower than those of the neat matrix. This indicates the mechanical properties dependence of dispersed-phase morphology, which in turn depends on the dispersed-phase content. On the basis of the results obtained from the present study, the mechanical of PS *in situ* reinforced with LCP or rPET are expected to be improved to approach those of the conventional composite by enhancing the fibrillation of the dispersed phases 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 some properties.

Table 3 Tensile properties at 25°C of LCP/PS and rPET/PS extruded strands containing various LCP and rPET contents.

Sample Code	Stress at 0.5% strain (MPa)	Tensile strength (MPa)	Elongation at break (%)
PS	23.8 ± 5.2	45.1 ± 6.7	0.93 ± 0.12
PS-10LCP	14.6 ± 3.8	38.4 ± 3.7	1.6 ± 0.32
PS-20LCP	22.5 ± 4.2	49.6 ± 7.2	1.3 ± 0.55
PS-30LCP	22.6 ± 3.6	46.6 ± 2.4	1.1 ± 0.20
PS-10rPET	16.4 ± 3.7	20.1 ± 4.2	0.65 ± 0.04
PS-20rPET	17.6 ± 3.1	18.5 ± 5.1	0.53 ± 0.10
PS-30rPET	18.5 ± 5.3	15.5 ± 6.3	0.58 ± 0.20

CONCLUSION

In this work, LCP/PS and rPET/PS *in situ* microfibillar-reinforced composites were prepared using extrusion process. The influence of LCP and rPET dispersed phases on rheology, morphology and thermal stability of the elastomer composites was investigated. The incorporation of rPET into PS significantly reduces the melt viscosity of the blend system similar to that of LCP. The fibrillar morphology of dispersed phase can only be obtained in as-extruded strand of LCP/PS blend system. For rPET/PS system, rPET domains appear as small droplets even the viscosity ratio of this blend system is relatively lower than that of LCP/PS system. The incorporation of LCP or rPET into PS matrix is found to retard the thermal degradation significantly in air. The obtained results suggest the high potential of rPET as the processing aid by bringing down the melt viscosity of the blend system and the thermally stable reinforcing-material similar to LCP. At the same composition, the LCP-containing blends showed better tensile properties when compared with the corresponding rPET-containing blends. The results of tensile properties indicate the mechanical properties dependence of dispersed-phase morphology, which in turn depend on the amount of the dispersed phase.

Suggestion for further works

1. The preparation and characterization of LCP/PS and rPET/PS will be further studied.
2. The rPET containing- composite fiber possessing the best properties will be selected for sheet preparation using woven method and characterized.

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Part II: Effect of LCP and rPET as Reinforcing Materials on Rheology, Morphology and Thermal Properties of *In Situ* Microfibrillar-Reinforced Elastomer Composites

Background

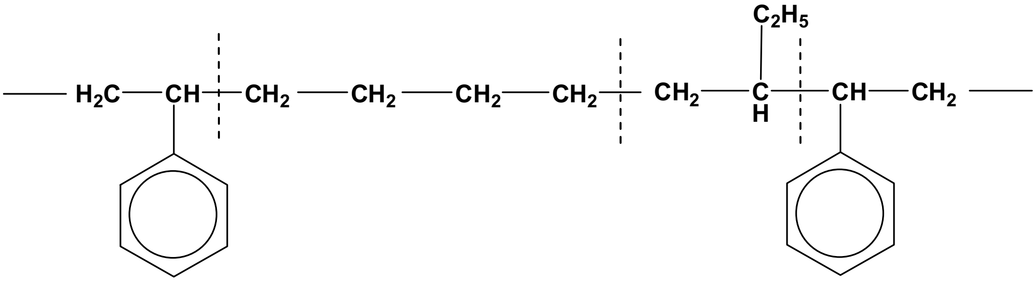
Blending two or more polymers is a versatile way of developing new materials with a desirable combination properties. Among such blending system, immiscible blends of thermotropic liquid crystalline polymers (TLCPs) with thermoplastics or thermoplastic elastomers (TPEs) have received much attention over the past two decades.[1-3] TLCPs are known to possess superior physical properties, such as high strength, good thermal properties, and low melt viscosity. Under appropriate shear or elongational flow field, dispersed TLCP droplets can be elongated and frozen in the matrix after cooling. This type of blend is called *in situ* composite.[4] Two major advantages gained by the additon of small amount of TLCP into a polymer matrix are improved processability and enhancement of mechanical properties. However, the main problem to be investigated for these types of the blends is to find the optimum processing condition, composition of the blend component, viscosity ratio (disperesed phase to matrix phase), processing condition and fabrication techniques in order to obtained a fibrillar morphology of the dispersed phase. Despite of the numerous advantages of TLCP as a minor blend component which can improve the melt processability and enhance mechanical properties, TLCPs are often too expensive for general engineering applications and not readily available in developing industrial countries. On the other hand, there are considerable supplies of engineering plastics in the form of post consumer scraps, which are a low cost source of raw material for forming polymer blends.[5] An alternative way is to find a substitute for TLCPs in fiber-reinforced composite application as a new type of processing route.

Poly(ethylene terephthalate) (PET) is one of the most important polymers for industrial production due to rapid growth in its used. It is regarded as an excellent material for many applications and is widely used for making liquid containers (bottles). It has excellent tensile and impact strength, chemical resistance, clarity, processability, color ability and reasonable thermal stability. Nowadays, soft drink bottles are preferentially made with PET. However, there are increasing pressures from the public for recycling of these PET bottles in order to reduce the demand on land-fill space. The common forms of plastic recycling include incineration with the recovery of thermal energy, transforming the PET waste back to the feed stock and thermo-mechanical recycling including the formation of PET blends and alloys.[6] Numerous studies have been carried out in order to investigate the possibilities of recycling PET (mainly bottles) for the production of injection-moldable, extrudable, and thermoformable PET resins that could be used to make structural parts of vehicles, automatives, textiles, food containers, bottles etc.[7-9] At present, the developed industrial countries are drawing up legislation and special program to promote bottle recycling. There is a continuing need for the availabilty of efficient, cost-effective recovery and recycling systems that can convert scrap bottles into useful products. Most of rPET goes into low-end products such as fiberfill for pillows, outwear, polyester foams and strapping.[10]

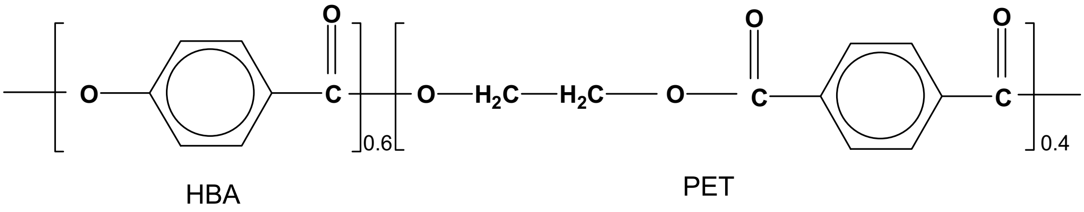
So far, the use of rPET as the blend component is one of the most important recycling of PET. Especially, the blends of rPET with common thermoplastics such as polypropylene[5,11-13] and polyethylene[14-17] based on the concept of *in situ* microfibrillar-reinforced composites (iMFCs)[18] have received much attention during the last decade. However, to the author’s knowledge, very limited information is available with regard to the rPET-thermoplastic elastomer (TPE) blends and a direct comparison of phase behavior and properties between TPE/LCP and TPE/rPET blend system has not been investigated. In this study, styrene-(ethylene butylene)-styrene (SEBS) triblock copolymer, a TPE, was melt blended with LCP and rPET using extrusion process. Rheological behavior in the molten state, morphology and thermal properties of SEBS/LCP and SEBS/rPET blend systems were investigated and compared. The main goal of this study is to explore the potential of rPET to use as low-cost and easy providing reinforcing material for microfibrillar-reinforced elastomer composites. The obtained results for SEBS/rPET system were compared with those of SEBS/LCP blend system.

Materials

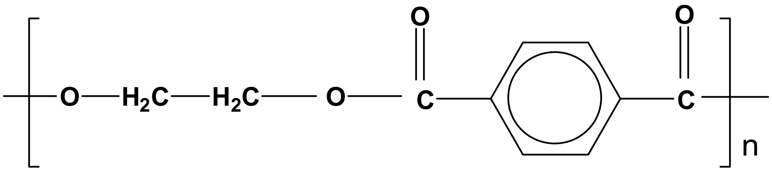
The polymer dispersed phases used in this work were Rodrun LC3000, a TLCP, supplied by Unitika Co. (Tokyo, Japan) and rPET collected from postconsumer soft drink bottles. Rodrun LC3000 is a copolyester of 60 mol% *p*-hydroxy benzoic acid (HBA) and 40 mol% poly(ethylene terephthalate) (PET) with a melting point of 220°C and a density of 1.41 g/cm^3. The rPET bottles were cleaned and cut into small pieces with dimension of about 3 mm × 3 mm. The melting temperature of rPET is found to be 252-255°C (examined by using DSC). The matrix phase used in this study was SEBS triblock copolymer (Kraton G1650) consisting a styrene/rubber weight percent ratio of 29/71. The SEBS polymer matrix was perchased from Toyota Tsusho (Thailand) Co.,Ltd. The chemical structures of all the polymers employed in the present study are shown in Scheme I. All materials were dried in a vacuum oven at 70°C for at least 12 h before use. In this paper, Rodrun LC3000 liquid crystalline polymer was represented by LCP.



(a) SEBS



(b) LCP (Rodrun LC3000)



(c) PET

Scheme I Chemical structures of (a) SEBS, (b) LCP (Rodrun LC3000) and (c) PET.

Blend preparation

The SEBS/LCP and SEBS/rPET blends 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 100 rpm. The temperature profiles for preparation of SEBS/LCP and SEBS/rPET were 190-220-220-225°C and 190-250-255-260°C, respectively. The temperature profiles shown here represent 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 subsequently dried in a vacuum oven. The sample codes of the extruded strand blends are designated as SEBS-*x*LCP or SEBS-*x*rPET where *x* depicts the content of LCP or rPET in wt%.

Rheological measurements

Measurements of rheological properties in the molten state for all 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 pellets and compression-molded at 200°C into a sheet about 1.5 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^{-1}. The measuring temperatures for the SEBS/LCP and SEBS/rPET systems were 225 and 260°C, respectively. The gap between the two plates was set at 0.9 mm.

Morphological characterization

The fracture surfaces of both types of extruded strand blends 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.

Measurement of thermal decomposition behavior

The thermogavimetric analysis (TGA) was carried out using TA instruments, SDT Q600 (Luken's drive, New Castle, DE). The pellets, 8-10 mg cut from the extruded strands were loaded in alumina crucible. The samples were 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 and DSC data were simultaneously 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

In this study, different temperature profiles were used for preparation of the two types of blends due to different melting temperature of the dispersed phases. Rheological measurements in the molten state of SEBS/LCP and SEBS/rPET blends were carried out at 225°C and 260°C, respectively. Figure 1 shows the frequency (ω) dependence of complex viscosity (η^*) for all analyzed samples. All neat and blend samples, except rPET, exhibit shear thinning behavior; the viscosity decreases with increasing shear rate (or shear frequency) due to the shear-induced chain orientation, leading to a reduction in the chain entanglement density. We will now consider the SEBS-LCP system first (Figure 1(a)). SEBS displays the highest viscosity while LCP displays the lowest viscosity. SEBS-LCP blends show viscosity in between these ranges and the viscosity decreases with increasing LCP content. This indicates that the addition of a small amount of LCP into SEBS matrix improves melt processability significantly. For SEBS-rPET system, similar trend is seen. However, despite rPET has much lower viscosity than LCP, addition of rPET into SEBS does not decrease the viscosity to the same extent that LCP does.

The relative viscosity, defined as the ratio of the viscosity of SEBS or the blends to that of the matrix phase, was calculated and presented in Figure 2, in order to evaluate the potential of rPET as the processing lubricant component compared with that of LCP. For the SEBS/LCP system, the decrease in the relative viscosity strongly depends on LCP contents as seen from Figure 2 (a). The reduction of the relative viscosity for the SEBS/LCP system enhances with LCP loading, indicating that higher the LCP content the higher the improvement in the melt processability.

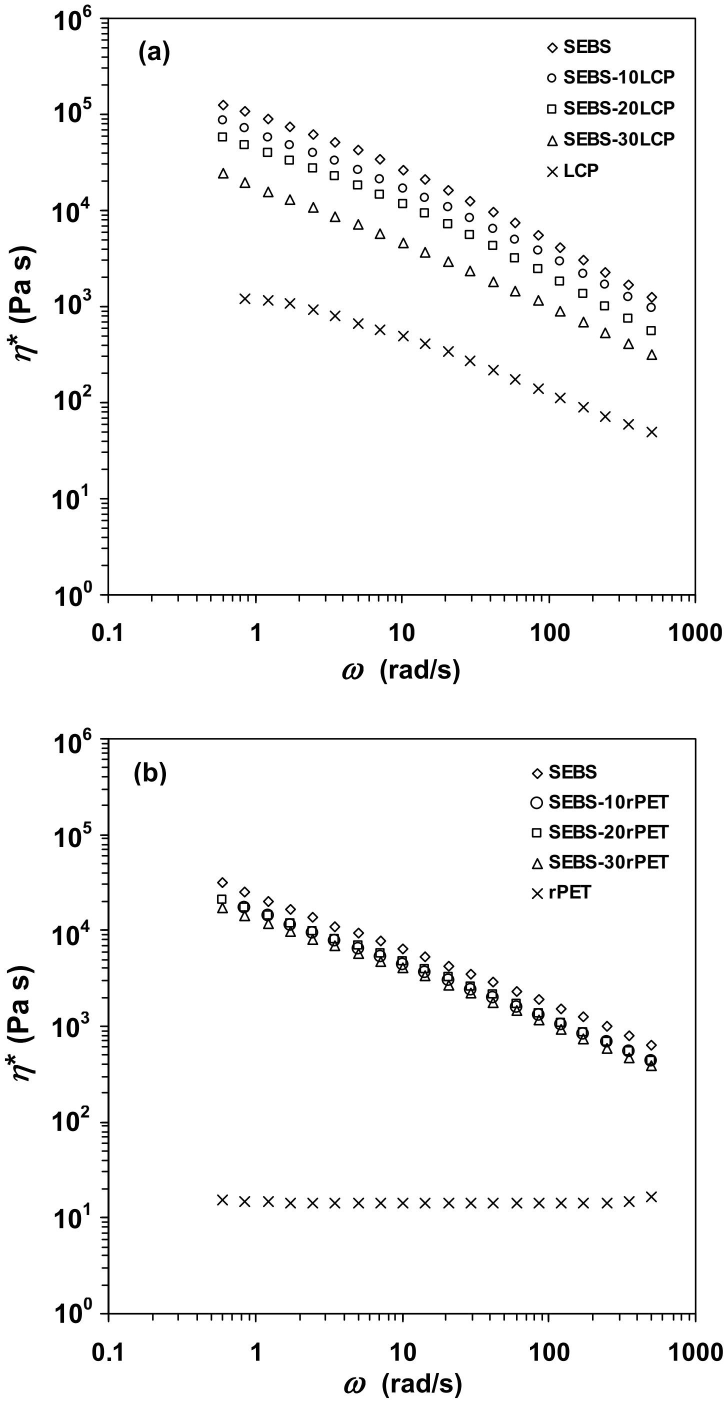


Figure 1 η^* vs. ω for (a) SEBS/LCP and (b) SEBS/rPET blends containing various dispersed phase contents, measured at 225°C and 260°C, respectively.

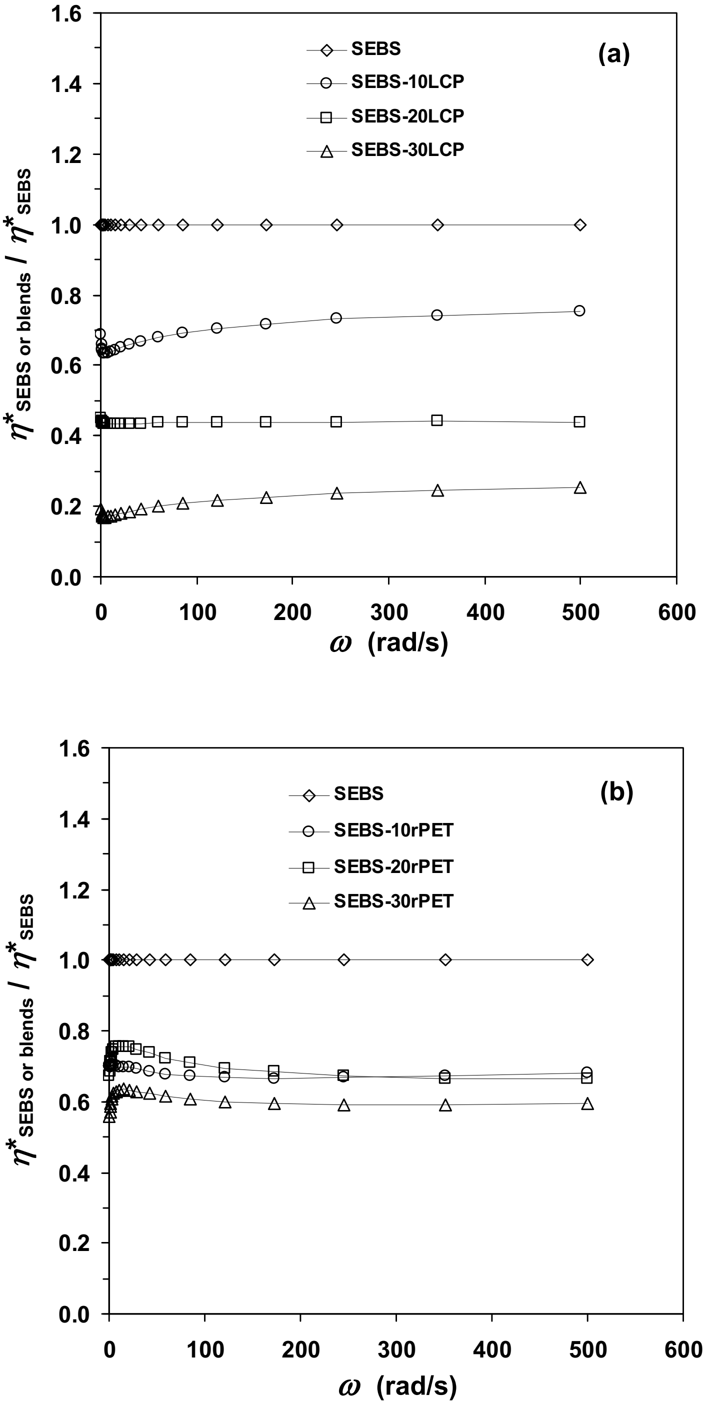


Figure 2 Relative η^* vs. ω for (a) SEBS/LCP and (b) SEBS/rPET blends containing various dispersed phase contents, measured at 225°C and 260°C, respectively.

Similarly for SEBS/rPET system (Fig. 2 (b)), the relative viscosity of the rPET-containing blends is also lower than that of the neat SEBS. It is interesting to note that the reduction of relative viscosity for both types of the blends with 10 wt% dispersed phase is comparable (the relative viscosity reduces by ~20-25% than that of the neat SEBS). With further addition of rPET up to 20-30 wt%, the efficiency of rPET as the processing aid for the blend system is not as good as that containing the same amount of LCP. However, the incorporation of small amount of rPET into SEBS significantly reduces the melt viscosity of the blend system.

Since both SEBS-LCP and SEBS-rPET are immiscible, the reduction in viscosity of the blend systems would be similar to the action of external lubricant. LCP is known to have good melt lubricity and addition of LCP could reduce the viscosity of the system by reducing friction at the interface of the polymer and the surface of the equipment or between the interface of polymer streams. The fact that the low viscosity of rPET does not translate to the low viscosity of the blend would suggest that the lubrication capability of rPET itself is not as good as LCP. However, at about 10% content, rPET could reduce the viscosity of SEBS in the same extent as LCP.

The elastic and viscous characteristics of the blend system can be considered from the plots of the storage modulus (G') and the loss modulus (G''), respectively, as a function of ω, Figure 3. The values of G' and G'' at low frequency generally provide information about long-range (beyond entanglement distance) relaxation, while the values at high frequency provide information about short range (motion with entanglement) relaxation.[19] As seen from Figures 3Ia and Ib, G' increases with increasing ω indicating a dependence of G' on the time scale of molecular motion.

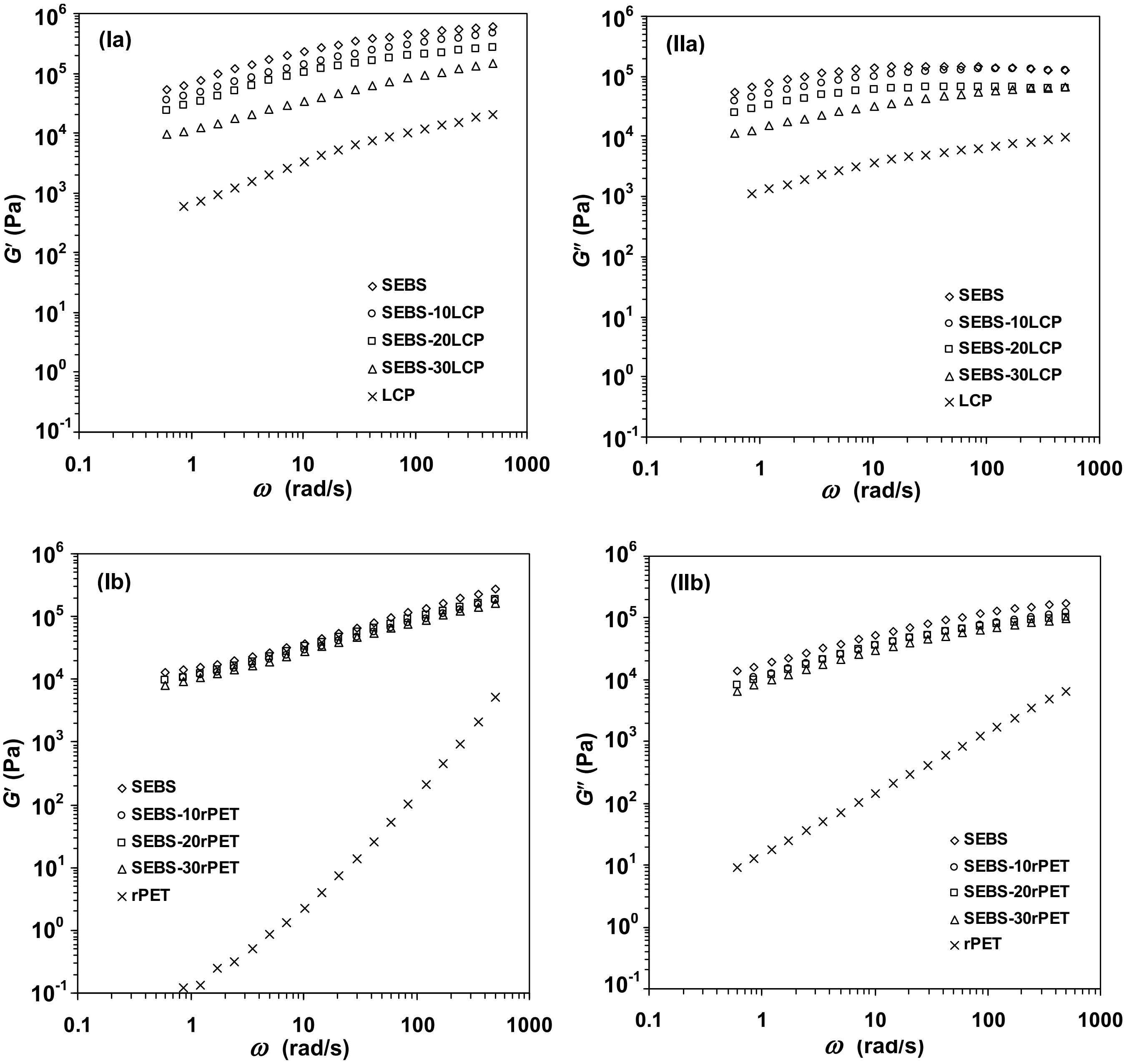


Figure 3 G' (column I) and G'' (column II) vs. ω for (a) SEBS/LCP and (b) SEBS/rPET blends containing various contents of dispersed phase. The measurements of G' and G'' for SEBS/LCP and SEBS/rPET blends were carried out at 225°C and 260°C, respectively.

For both the blend systems, the neat SEBS matrix shows the highest value of *G′* whereas *G′* of LCP and rPET display the lowest values among the corresponding blend samples. The decrease in *G′* is observed for the SEBS/LCP and SEBS/rPET blend systems with increase in the concentration of the LCP or rPET as a result of the contribution of the dispersed phases. This means that LCP and rPET in the polymer matrix play a role in promoting the chain mobility leading to a decrease in chain rigidity. However, although the *G′* of rPET is much lower than that of SEBS, a slight reduction of *G′* is observed for the blends containing 10-30 wt%rPET. For the LCP-containing blend system, the reduction in *G′* is clearly observed, indicating that the change in elastic properties of SEBS matrix by blending with LCP is more pronounced than that by blending with rPET. This should arise from the fact that the LCP molecules contain rigid parts which could slide pass each other easily and results in good lubricity. On the other hand, the chains of rPET are more flexible and would take random coil configuration. Chain entanglements are likely to occur and this will be less effective in lubricating the system. Interestingly, the elastic characteristics of rPET (Fig. 3Ib) are strongly affected by the applied frequency as seen from the dramatical increase in *G′* with increasing frequency because the elastic energy stored in the molecules is greater when the deformation from a random coil configuration takes place within shorter times.[20] As a consequence, the *G′* of rPET is close to those of SEBS and the blends at high frequency.

The viscous characteristics (*G″*) for both blend systems is found to decrease with increasing dispersed phase contents as seen from Figures 3IIa and IIb for SEBS/LCP and SEBS/rPET blends, respectively. At the same composition for both types of the blends, *G′* values of the neat SEBS, LCP and all blends are higher than the corresponding *G″* values in the whole frequency range. This indicates that the elastic characteristics for these samples are dominant factor. In turn, it clearly appears that for rPET analyzed, the *G″*dominates with respect to the *G′*, especially in the low frequency range. This arises from the fact that, by comparing with LCP, the molecular weight of rPET is relatively low and it has narrow molecular weight distribution, enabling the chain motion with low level of molecular entanglement. Unfortunately, the molecular weights of both the dispersed phases could not be numerically compared because so far the molecular weight of LCP is not obtainable, since no solvent is found to dissolve this polymer. The dominant viscous characteristic of rPET observed in this study is in well accordance with those of the vergin PET and bottle grade PET reported by Daver et al.[20] and Incarnato et al.[21]

It is generally known that the morphology of immiscible blend is governed by the viscosity ratio of the dispersed phase to the matrix phase. For simple shear flow, fibrillar morphology is predicted to occur if the viscosity ratio is lower than unity.[22-24] In general, the lower the viscosity ratio, the higher the possibility of forming fibrillar morphology would be. 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 as a function of frequency for the SEBS/LCP at 225°C and SEBS/rPET blend systems at 260°C were evaluated and presented in Figure 4. It is seen that the viscosity ratios of both the blend systems are lower than 0.05 over the entire frequency region investigated. The viscosity ratio of the SEBS/LCP system increases sharply first from 0.01 to 0.02 within the frequency range of 0-30 rad/s and then increases gradually as the frequency increases further. The increase of viscosity ratio with increasing frequency arises from the faster drop of the viscosity of SEBS than that of LCP in the high frequency range. Similarly, the viscosity ratio for the SEBS/rPET system progressively increases with increasing frequency. However, the

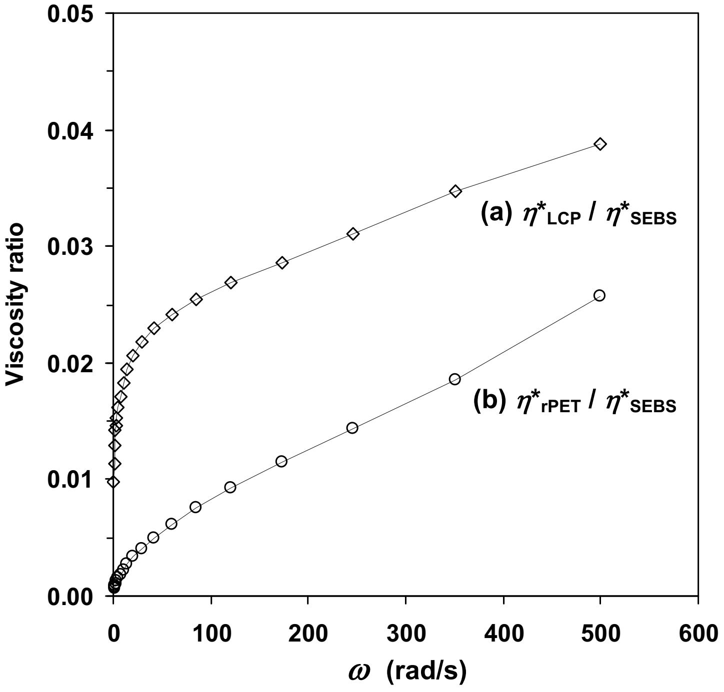


Figure 4 Viscosity ratios vs. ω for (a) SEBS/LCP and (b) SEBS/rPET blending systems, measured at 225°C and 260°C, respectively.

viscosity ratio of the SEBS/rPET system is much lower than that of the SEBS/LCP system at all measuring frequencies. The difference in viscosity ratio arising from the different dispersed phase viscosity is expected to affect the fibrillation of the LCP and the rPET. Based on the obtained results of viscosity ratios, it may be expected that both LCP and rPET can form the fibrillation morphology and the better fibrillation should be observed in the rPET-containing blends.

Morphology

It is well known that the final properties of the *in situ* microfibrillar-reinforced composites depend on its phase morphology which is affected by several important factors such as rheological behavior, composition, interfacial tension, processing condition and fabrication techniques. In the present study, the morphology of the fracture surface was studied by means of scanning electron microscopy (SEM). Figure 5 shows the SEM micrographs of the fracture surfaces for the SEBS/LCP and SEBS/rPET extruded strands containing various LCP and rPET contents. In the LCP-containing blend with 10 wt% LCP (Fig.5Ia), most of the LCP domains appeared as droplets, and few elongated LCP domains are observed. The fibrillation of LCP domains is clearly observed in the blend with 20 wt% LCP (Fig. 5-Ib). However, with the addition of LCP up to 30 wt%, some lamellar structure is observed because of the coalescence of the liquid LCP threads that occur during extrusion. The lamellar structure is also observed in other LCP-containing blend systems with incorporation of high LCP concentration.[25-27]

In the case of the SEBS/rPET system, most of the rPET domains in SEBS-10rPET appear as small droplets with diameter of about 0.5-1 μm and the diameter of the rPET domains slightly increases with rPET loading. Some elongated rPET domains are also observed in the SEBS/rPET blends. In addition, limited coalescence of rPET domains are observed in the SEBS-30rPET extruded strands. Interestingly, the domain size of the rPET is much smaller than that of the LCP. According to the results of viscosity ratio shown earlier, figure 4, it may be expected, from the low viscosity ratios for the SEBS/LCP and the SEBS/rPET systems, that these blend systems will have fibrillar morphology. However, the morphological results from the present study clearly show that good fibrillar morphology is obtained only with the SEBS/LCP system. The fact that rPET break down into small droplets may be due to the high viscosity of the system (Figure 1) and limited coalescence. Furthermore, the difference in morphology of the SEBS/LCP and the SEBS/rPET systems could be explained as follows. Generally, deformation of the dispersed-phase droplets into fibrillation structures or coalescence of the dispersed-phase domains 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 by[28]

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

where η_m is the viscosity of the matrix, $\dot{\gamma}$ the shear rate, *b* the initial diameter of dispersed droplets and σ the interfacial tension between the matrix and dispersed phase. In the simple shear flow of Newtonian fluids, a dispersed droplet will be elongated if $Ca > 0.5$, indicating that the ratio of shear stress and the interfacial energy should be larger than half.[28] The influence of the capillary number on the stability of the dispersed phases especially for LCP morphology has been studied by a number of researchers.[29,30] The results of their study indicate the influence of both viscous and interfacial forces on the final morphology, confirming the importance of Capillary number. In the case of SEBS/rPET system, even if the viscosity ratio is lower than 0.03, the fibrillation of the rPET domains is not clearly observed in as-extruded strand. According to eq. (1), there can be two possibilities that cause the Capillary number to be low. They are small initial diameter of the dispersed phase and the high interfacial tension. The former is apparent from Figure 5. rPET droplets are so small and coalesence of droplets does not occur even at high rPET content. The fibrilation of rPET therefore does not occur. However, thermotropic LCPs are essentially rigid-rod long chain molecules with some irregularity or flexibility incorporated into the polymer chain to lower the melting point below the decomposition temperature. The

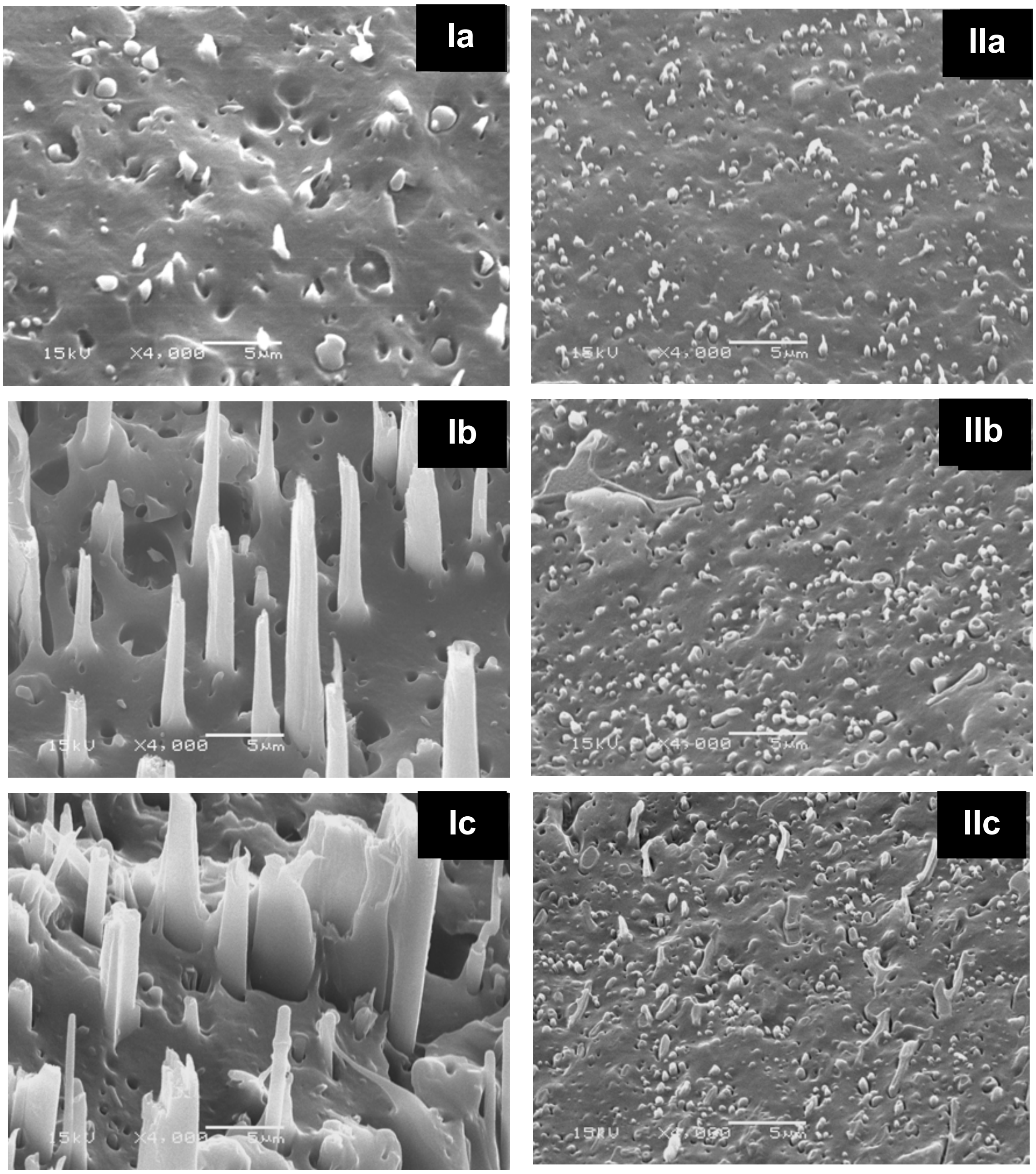


Figure 5 SEM micrographs of the fracture surface for SEBS/LCP (column I) and SEBS/rPET (column II) blends containing (a) 10, (b) 20 and (c) 30 wt% dispersed phase.

rigid-rod molecular structure allows these materials to exhibit molecular order in a liquid mesophase resulting in a tendency toward easy orientation in the flow direction. In contrast, the random coil structure and relatively flexible structure of rPET tend to appear in the molten state. Thus, the fibrillation tendency of rPET is not as good as that of highly-orientated nature LCP.

Thermal decomposition behavior

Normally, polymers must encounter elevated temperatures at almost every stage in manufacturing, compounding, and processing stages, in service, and during repairing step. Therefore, an 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 the LCP and the rPET on thermal decomposition of the SEBS/LCP and the SEBS/rPET blends. The nonisothermal TG curves of the two blending systems are presented in Figure 6. The TG measurements were carried out in nitrogen and in air at a heating rate of 10°C/min.

TG results of the SEBS/LCP blends (Fig. 6IA) obtained in nitrogen will be considered first. The nonisothermal TG profile of SEBS reveals only a single weight-loss step at the temperature range around 400-480°C. The single weight-loss step of SEBS in nitrogen revealed in this study, which corresponds mainly to the chain scission at the boundary of the polystyrene-olefin phase, is similar to that of SEBS under nonisothermal heating in argon flow reported by Zucolotto et al.[31] Although the blend system may be complicated due to the presence of many copolymer components, a single degradation step similar to the neat SEBS matrix is observed for the blends containg 10-30 wt% LCP. The onset of decomposition in nitrogen seems

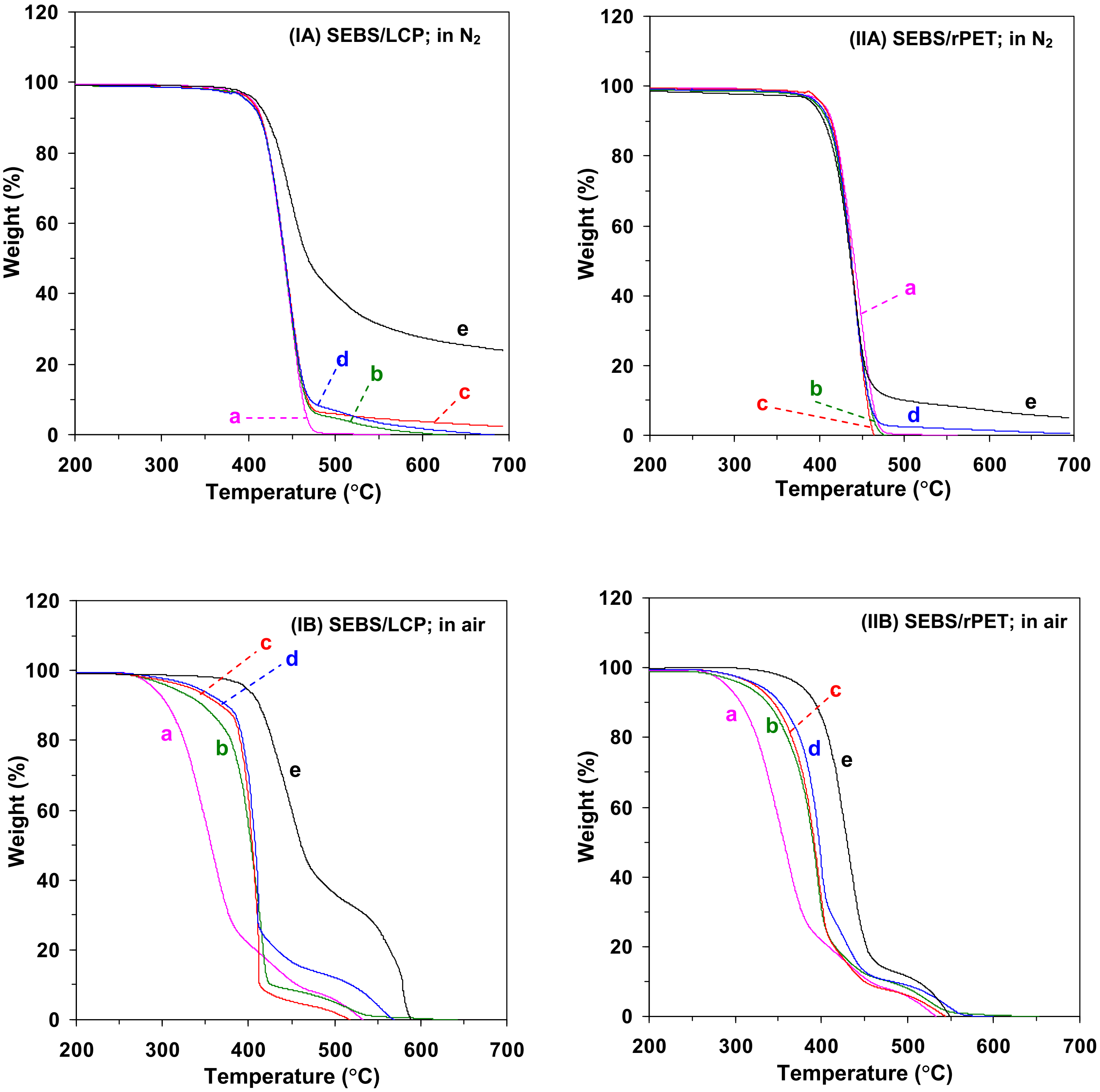


Figure 6 Dynamic TG curves of SEBS/LCP (column I) and SEBS/rPET (column II) blends containing (a) 0, (b) 10, (c) 20, (d) 30 and (e) 100 wt% LCP or rPET at a heating rate of 10C/min in nitrogen (row A) and in air (row B).

not to be affected by the LCP loading. In the LCP-containing blends, the degradation mechanism additionally involves the removal of ester, ethylene groups, and hydrogen atoms in the polymer chains of LCP.[32] That is, there are more than one reaction for the decompositon. In the case of LCP, the first thermal degradation mainly occurs at the PET block, whereas the second degradation process could be attributed to the degradation of the HBA block.[32,33] It is seen that no char residues were left for the neat SEBS whereas the amount of char residues increases with increasing the LCP contents. The increase in char residues arises from the increase in the HBA block (by increasing amount of LCP content) which will decrease the number of hydrogen atoms and retard the formation of volatile degraded products.[34] Moreover, the formation of char residues is probably due to the branch formation and crosslinking of the product obtained mostly from the HBA unit during the thermal degradation under nitrogen.

Under dynamic heating in air (Fig.6IB), the thermal degradation of the SEBS, the LCP and their blends occur in two steps. The neat SEBS exhibits the first weight-loss step at 250-380°C, whereas the first major weight-loss of the LCP occurs around 400-500°C. For the thermal degradation of SEBS 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.[35] Concurrent and further reaction give rise to the formation of anhydrides and perester/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 hindered phenolic antioxidant and phosphate were also higher synergistic in inhibiting oxidation and separation at the boundaries by destroying the acetophenone end groups and preventing excimer disaggreation. Note that, in air, no char residues of the neat polymers and the blends were left within the experimental temperature.

In the case of SEBS/rPET blend system in nitrogen (Fig. 6IIA), the single-step weight-losses are observed for the neat polymers and the blends at 380-460°C. Several studies have been conducted on the thermal degradation products of PET,[36-39] which indicate that the thermal degradtion of PET is initiated by chain scission of ester-linkage, yielding carboxyl and vinyl ester groups. In air (Fig. 6IIB), at least two weight-loss steps are observed for all samples indicating that the degradation process is more complex in air than in nitrogen.

To compare the dispersed phase-content dependence of thermal stability for the two types of blends in more quantitative way, the thermal decompositon data in nitrogen and in air are compared and summarized in Table 1. T_{onset} represents the onset degradation temperature. $T_{\max}$ represents the temperature at the maximum weight-loss rate, $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$. 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} between the SEBS/LCP and SEBS/rPET blends are observed when compared at the same blend composition. $T_{\max 1}$ of the LCP-containing blends are slightly higher than that of the corresponding rPET-containing blends. It is noticed that at the same composition, $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$ of the SEBS/LCP blend systems are lower than those of the SEBS/rPET blend systems. This indicates that incorporation of the LCP into SEBS results in somewhat higher thermal resistance when compared with the rPET-containing blends at the same composition.

Table 1 Nonisothermal decomposition characteristics of SEBS/LCP and SEBS/rPET blends in nitrogen and in air.

	SEBS/LCP blending system						SEBS/rPET blending system					
LCP or rPET content (wt%)	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	$(d\alpha/dt)_{max1}$ (%/min)	$(d\alpha/dt)_{max2}$ (%/min)	Char yield at 600C (wt%)	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	$(d\alpha/dt)_{max1}$ (%/min)	$(d\alpha/dt)_{max2}$ (%/min)	Char yield at 600°C (wt%)
In nitrogen												
0	417	448	-	20.4	-	0.00	417	448	-	20.4	-	0.00
10	417	445	-	20.0	-	0.38	416	440	-	25.6	-	0.00
20	418	451	-	23.2	-	0.05	419	439	-	30.1	-	0.00
30	417	437	-	20.5	-	0.15	419	443	-	24.0	-	0.14
100	419	448	-	10.5	-	27.6	414	441	-	20.8	-	7.13
In air												
0	310	354	528	11.0	1.99	0.00	310	354	528	11.0	1.99	0.00
10	385	410	518	33.4	1.18	0.02	366	391	523	19.7	1.65	0.03
20	402	405	527	52.8	1.63	0.00	367	387	538	19.9	1.62	0.00
30	401	408	552	48.8	2.57	0.00	377	400	549	33.3	1.79	0.00
100	410	449	573	9.58	19.8	0.00	399	433	553	16.3	5.16	0.00

In air, it is interesting to note that T_{onset} and T_{max1} of the two types of blends are much higher than those of the matrix but are lower than those of the corresponding dispersed phase. This means that incorporation of the LCP and rPET into the SEBS matrix effectively enhance the thermal stability in air but not in nitrogen. It is found that T_{onset} and T_{max1} of the blends with 10-30 wt% LCP are shifted by about 75-90°C and 50-55°C, respectively, higher than those of the neat matrix, whereas the respective T_{onset} and T_{max1} of the blends with 10-30 wt% rPET are shifted about 56-67°C and 34-46°C higher than those of the neat SEBS. It is seen that $(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max1}}$ of the LCP- and rPET-containing blends are higher than that of the neat matrix and they decrease with increasing dispersed phase content, indicating the rapid weight-loss process with more complex degradation mechanism. Normally, the thermal stability of polymer in air is somewhat lower than that in nirogen. However, the situation that polymer has been exposed in air is more common than in nitrogen during real processing and application. Note that $(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max2}}$ of the LCP and rPET dispersed phases are much higher than that of the matrix phase whereas T_{max2} seem to mostly increase with the addition of LCP and rPET dispersed phases.

Simultaneous DSC data of thermal decomposition

The DSC traces of degradation for the SEBS, LCP, rPET and the blends in nitrogen and in air are shown in Figures 7. The DSC curve of SEBS in nitrogen (Fig. 7(IA)) shows a minimum degradation endotherms at ≈ 450°C whereas that of the LCP exhibits a broad degradation endotherm with a peak minimum at 430°C. It is noticed that the peak minimum of the SEBS is little affected by the incorporation of LCP.

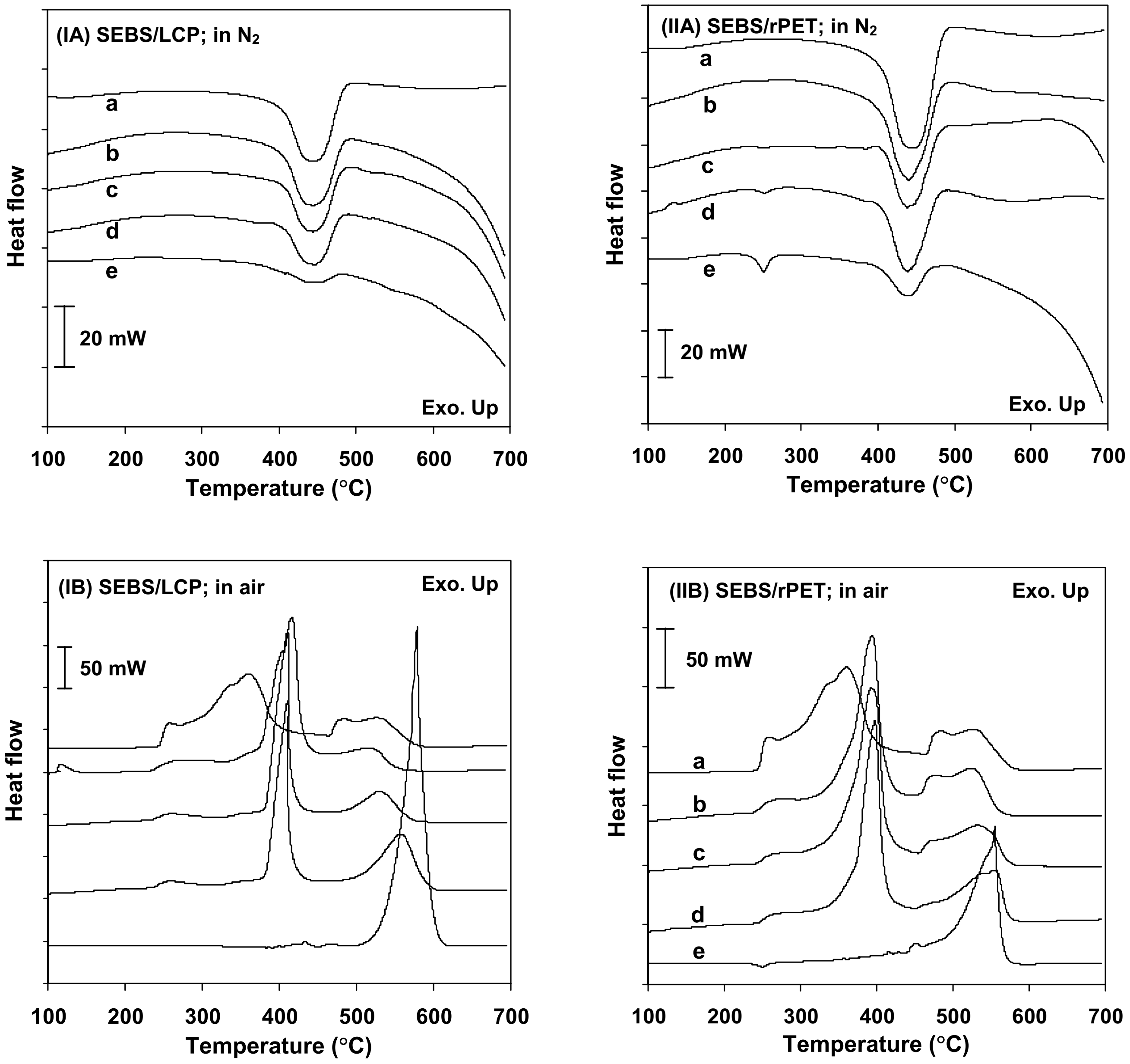


Figure 7 Simultaneous DSC curves of SEBS/LCP (column I) and SEBS/rPET (column II) blends containing (a) 0, (b) 10, (c) 20, (d) 30 and (e)100 wt% LCP or rPET at a heating rate of 10C/min in nitrogen (row A) and in air (row B).

Table 2 Simultaneous DSC data of SEBS/LCP and SEBS/rPET blends under thermal degradation in nitrogen and in air.

LCP or rPET	SEBS/LCP blending system				SEBS/rPET blending system			
content (wt%)	T_m (°C)	ΔH_m (kJ/g)	T_d (°C)[a]	ΔH_d (kJ/g)	T_m (°C)	ΔH_m (kJ/g)	T_d (°C)[a]	ΔH_d (kJ/g)
In nitrogen								
0	-	-	449	1.08	-	-	449	1.08
10	-	-	445	0.83	-	-	441	0.85
20	-	-	444	0.73	-	-	439	0.63
30	-	-	446	0.71	253	6.15	439	0.56
100	-	-	436	0.12	251	0.04	437	0.20
In air								
0	-	-	360	0.80	-	-	360	0.80
10	-	-	416	6.75	-	-	394	4.05
20	-	-	411	5.68	-	-	393	4.28
30	-	-	411	2.54	-	-	397	3.32
100	-	-	579	6.79	251	0.04	555	3.18

[a] Under heating in air, T_d reported here associates with the first major exothermic peak.

In the case of SEBS/rPET (Fig. 7-IIA), the exothermic peak, known as “cold crystallization”, is not clearly observed, whereas the endothermic peak associated with the fusion of the crystalline fraction is observed at about 275°C. In addition, the largest endothermic peak of rPET is observed at about 460°C corresponding to the degradation process of rPET. However, although the degradation temperature of rPET is higher than that of the neat SEBS, the incorporation of rPET into SEBS does not seem to influence the degradation temperature of the blend in nitrogen.

Under heating in air, the exothermic degradation process is observed for all the samples due to the fact that the concurrent and further degradation mechanisms in air tend to involve the formation reaction. SEBS shows a very broad degradation endotherm that stretches from 250°C to 560°C. It is interesting to note that an extremely sharp exotherm is noticed at 400°C with addition of the LCP. At high concentration of LCP (20-30 wt% LCP), the second minor exotherm corresponding to the degradation process of LCP is observed. Interestingly, although LCP starts to degrade in the first step at the temperature range of 400-500°C, the exotherm associated with this region is not observed. The simultaneous data of both blend systems are also quantitatively presented in Table 2. T_m and ΔH_m represent the melting temperature and heat flow of melting process, respectively, whereas T_d and ΔH_d represent the peak temperature and heat flow, respectively, associated with the thermal degradation process. In nitrogen, incorporation of the LCP or rPET into SEBS seems to affect little the T_d of the blends. In air, T_d of the blends are much higher than those of the polymer matrix. It is seen that ΔH_d of the blends decreased mostly with LCP or rPET loading due to the dilution effect of the polymer matrix. Moreover, at the same concentration of the dispersed phase, the extent of heat flow is much higher in air than in nitrogen. This indicates that there are not only typically thermal degradation reaction but also thermooxidative reaction which additionally occurs in air.

CONCLUSION

In this work, SEBS *in situ* reinforced with two types of reinforcing materials, LCP and rPET, were prepared. The influence of LCP and rPET dispersed phases on rheology, morphology and thermal stability of the elastomer composites was investigated. It was found that the incorporation of small amount of LCP and rPET (10wt%) into SEBS significantly reduces the melt viscosity of the blend system. At higher concentration, only LCP that continues to lower the viscosity of the blend system further while much less effect was observed for rPET. The large reduction in viscosity in LCP containing system is due to its inherent lubricating property. SEBS/LCP displays fibrillar morphology at 20 and 30 wt% LCP while SEBS/rPET does not. The incorporation of LCP or rPET into the elastomer matrix was found to retard the thermal degradation significantly in air but not in nitrogen. These demonstrate the high potential of using rPET in replacing the more expensive LCP as processing aids and also to improve thermal resistance of SEBS.

Suggestion for further work

1. Preparation of LCP- and rPET-containing blends in the form of monofilament will be carried out.
2. The morphology, thermal, mechanical and dynamic mechanical properties of the monofilament will be characterized.

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APPENDIX

Outputs of the research

1. **Saikrasun S.*,** Limpisawasdi P., Amornsakchai T. Effect of LCP and rPET as Reinforcing Materials on Rheology, Morphology and Thermal Properties of *In Situ* Microfibrillar-Reinforced Elastomer Composites. *Journal of Applied Polymer Science*, **2009**; 12: 1897-1908. (impact factor = 1.306 /JCR 2007)

2. **Saikrasun S***, Limpisawasdi P, Amornsakchai T. Comparative study on phase and thermal properties between rPET/PS and LCP/PS *in situ* microfibrillar-reinforced composites. *Journal of Polymer Research*, **2009** doi: 10.1007/s10965-008-9247-6. (impact factor = 0.616/JCR2007)

Effect of LCP and rPET as Reinforcing Materials on Rheology, Morphology, and Thermal Properties of *in situ* Microfibrillar-Reinforced Elastomer Composites

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Received 6 February 2008; accepted 11 November 2008
DOI 10.1002/app.29715

ABSTRACT: Microfibrillar-reinforced elastomer composites based on two dispersed phases, liquid crystalline polymer (LCP) and recycled poly(ethylene terephthalate)(rPET), and styrene-(ethylene butylene)-styrene (SEBS) were prepared using extrusion process. The rheological behavior, morphology, and thermal stability of SEBS/LCP and SEBS/rPET blends containing various dispersed phase contents were investigated. All blends and LCP exhibited shear thinning behavior, whereas Newtonian fluid behavior was observed for rPET. The incorporation of both LCP and rPET into SEBS significantly improved the processability by bringing down the melt viscosity of the blend system. The fibrillation of LCP dispersed phase was clearly observed in as-extruded strand with addition of LCP up to 20–30 wt %. Although the viscosity ratio of SEBS/rPET system is very low (0.03), rPET domains mostly appeared as droplets in as-extruded strand. The results obtained from thermogravimetric analysis suggested that an addition of LCP and rPET into the elastomer matrix improved the thermal resistance significantly in air but not in nitrogen. The simultaneous DSC profiles revealed that the thermal degradation of all polymers examined were endothermic and exothermic in nitrogen and in air, respectively. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1897–1908, 2009

Key words: elastomer; composites; liquid crystalline polymer (LCP); thermal degradation; recycled PET (rPET); thermal stability

INTRODUCTION

Blending two or more polymers is a versatile way of developing new materials with a desirable combination of properties. Among such blending systems, immiscible blends of thermotropic liquid crystalline polymers (TLCPs) with thermoplastics or thermoplastic elastomers (TPEs) have received much attention over the past 2 decades.[1–3] TLCPs are known to possess superior physical properties, such as high strength, good thermal properties, and low melt viscosity. Under appropriate shear or elongational flow field, dispersed TLCP droplets can be elongated and frozen in the matrix after cooling. This type of blend is called *in situ* composite.[4] Two major advantages gained by the addition of small amount of TLCP into a polymer matrix are improved processability and enhancement of mechanical properties. However, the main problem to be investigated for these types of the blends is to find the optimum processing conditions, composition of the blend component, viscosity ratio (dispersed phase to matrix phase), and fabrication techniques to obtain a fibrillar morphology of the dispersed phase. Despite the numerous advantages of TLCP as a minor blend component, which can improve the melt processability and enhance mechanical properties, TLCPs are often too expensive for general engineering applications. On the other hand, there are considerable supplies of engineering plastics in the form of post consumer scraps, which are a low cost source of raw material for forming polymer blends.[5] An alternative way is to find a substitute for TLCPs in fiber-reinforced composite application as a new type of processing route.

Poly(ethylene terephthalate) (PET) is one of the most important polymers for industrial production because of rapid growth in its uses. It is regarded as an excellent material for many applications and is widely used for making containers (bottles) for liquids. It has excellent tensile and impact strength,

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Contract grant sponsor: Office of Commission on Higher Education and Thailand Research Fund; contract grant number: MRG5080415.

Journal of Applied Polymer Science, Vol. 112, 1897–1908 (2009)

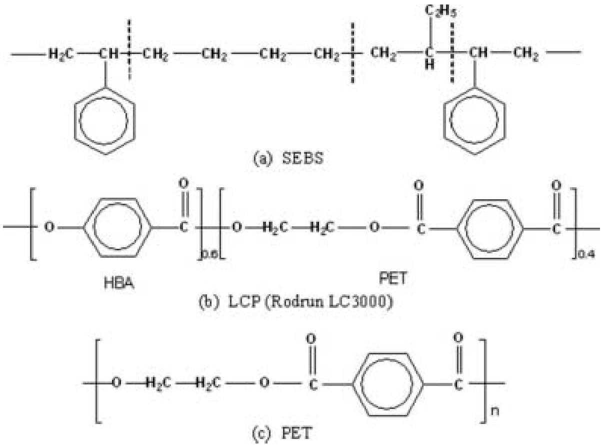
chemical resistance, clarity, processability, color ability, and reasonable thermal stability. Nowadays, soft drink bottles are preferentially made with PET. However, there are increasing pressures from the public for recycling of these PET bottles to reduce the demand on land-fill space. The common forms of plastic recycling include incineration with the recovery of thermal energy, transforming the PET waste back to the feed stock and thermomechanical recycling including the formation of PET blends and alloys.[6] Numerous studies have been carried out to investigate the possibilities of recycling PET (mainly bottles) for the production of injection-moldable, extrudable, and thermoformable PET resins that could be used to make structural parts of vehicles, automatives, textiles, food containers, bottles, etc.[7–9] At present, the developed industrial countries are drawing up legislation and special program to promote bottle recycling. There is a continuing need for the availability of efficient, cost-effective recovery and recycling systems that can convert scrap bottles into useful products. Most of recycled PET (rPET) goes into low-end products such as fiberfill for pillows, outwear, polyester foams, and strapping.[10]

So far one of the most important use of rPET is as a blend component. Especially, the blends of rPET with common thermoplastics such as polypropylene[5,11–13] and polyethylene[14–17] based on the concept of *in situ* microfibrillar-reinforced composites (iMFCs)[18] have received much attention during the last decade. However, to the authors' knowledge, very limited information is available with regard to the rPET-TPE blends and a direct comparison of phase behavior and properties between TPE/LCP and TPE/rPET blend system has not been investigated. In this study, styrene-(ethylene butylene)-styrene (SEBS) triblock copolymer, a TPE, was melt blended with LCP and rPET using extrusion process. Rheological behavior in the molten state, morphology and thermal properties of SEBS/LCP, and SEBS/rPET blend systems were investigated and compared. The main goal of this study is to explore the potential of rPET as low-cost and easily available reinforcing material for microfibrillar-reinforced elastomer composites. The results for the SEBS/rPET system were compared with those of the SEBS/LCP blend system.

EXPERIMENTAL

Materials

The polymer dispersed phases used in this work were Rodrun LC3000, a TLCP, supplied by Unitika Co. (Tokyo, Japan) and rPET collected from post consumer soft drink bottles. Rodrun LC3000 is a copolyester of 60 mol % *p*-hydroxy benzoic acid (HBA) and 40 mol % PET with a melting point of 220°C and a density of 1.41 g/cm^3. The rPET bottles were cleaned and cut into small pieces with dimension of about 3 mm × 3 mm. The melting temperature of rPET is found to be 252–255°C (examined by using DSC). The matrix phase used in this study was SEBS triblock copolymer (Kraton G1650) consisting a styrene/rubber weight percent ratio of 29/71. The SEBS polymer matrix was purchased from Toyota Tsusho (Thailand) Co. The chemical structures of all the polymers used in the present study are shown in Scheme 1. All materials were dried in a vacuum oven at 70°C for at least 12 h before use. In this article, Rodrun LC3000 liquid crystalline polymer was represented by LCP.



Scheme 1 Chemical structures of (a) SEBS, (b) LCP (Rodrun LC3000), and (c) PET.

Blend preparation

The SEBS/LCP and SEBS/rPET blends 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 100 rpm. The temperature profiles for preparation of SEBS/LCP and SEBS/rPET were 190-220-220-225°C and 190-250-255-260°C, respectively. The temperature profiles shown here represent 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 subsequently dried in a vacuum oven. The sample codes of the extruded strand blends are designated as SEBS-*x*LCP or SEBS-*x*rPET where *x* depicts the content of LCP or rPET in wt %.

Rheological measurements

Measurements of rheological properties in the molten state for all 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 pellets and compression-molded at 200°C into a sheet about 1.5 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^{-1}. The measuring temperatures for the SEBS/LCP and SEBS/rPET systems were 225 and 260°C, respectively. The gap between the two plates was set at 0.9 mm.

Morphological characterization

The fracture surfaces of both types of extruded strand blends were observed under the scanning electron microscope (SEM) (Jeol; JSM-6460LV, Tokyo, Japan) operated with an accelerating voltage of 15 kV. Before 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.

Measurement of thermal decomposition behavior

The thermogravimetric analysis (TGA) was carried out using TA instruments, SDT Q600 (Luken's drive, New Castle, DE). The pellets, 8–10 mg, cut from the extruded strands were loaded in alumina crucible. The samples were non-isothermally 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 and DSC data were simultaneously 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

In this study, different temperature profiles were used for preparation of the two types of blends because of different melting temperature of the dispersed phases. Rheological measurements in the molten state of SEBS/LCP and SEBS/rPET blends were carried out at 225°C and 260°C, respectively. Figure 1 shows the frequency (ω) dependence of complex viscosity (η^*) for all analyzed samples. All neat and blend samples, except rPET, 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. We will now consider the SEBS-LCP system first [Fig. 1(a)]. SEBS displays the highest viscosity whereas LCP displays the lowest viscosity. SEBS-LCP blends show viscosity in between these ranges and the viscosity decreases with increasing LCP content. This indicates that the addition of a small amount of LCP into SEBS matrix improves melt processability significantly. For SEBS-rPET system, similar trend is seen. However, despite rPET has much lower viscosity than LCP, addition of rPET into SEBS does not decrease the viscosity to the same extent that LCP does.

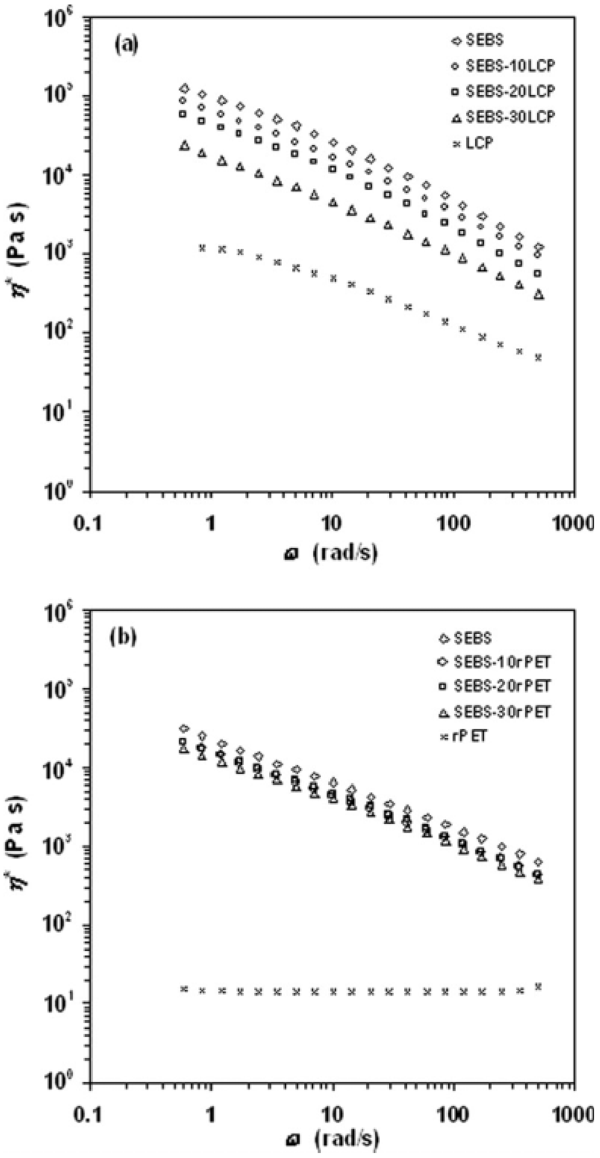


Figure 1 η^* versus ω for (a) SEBS/LCP and (b) SEBS/rPET blends containing various dispersed phase contents, measured at 225°C and 260°C, respectively.

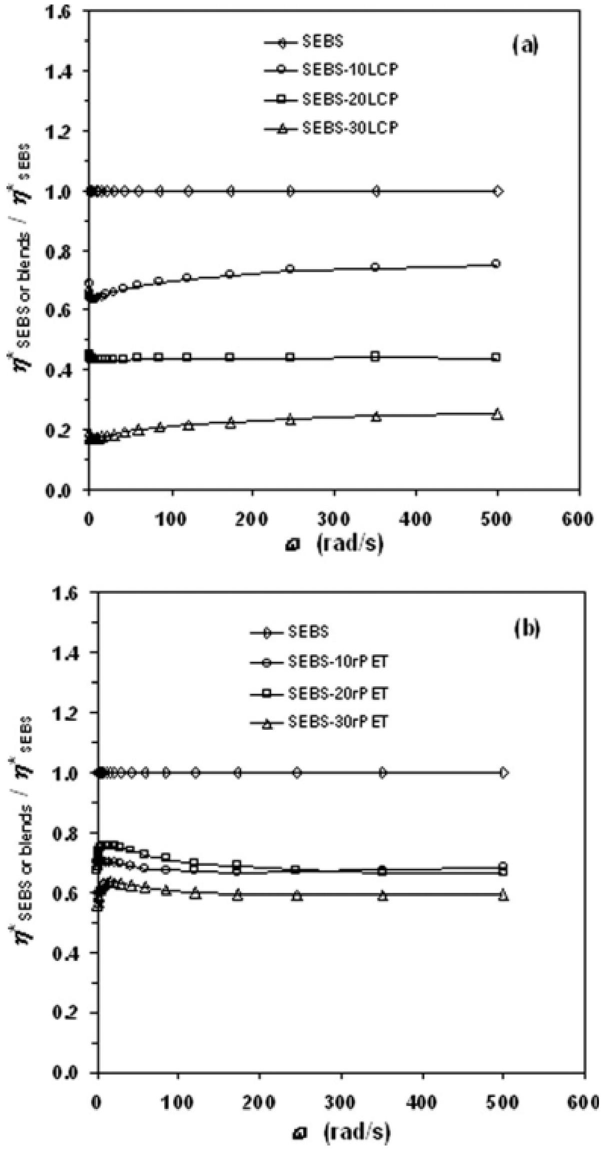


Figure 2 Relative η* versus ω for (a) SEBS/LCP and (b) SEBS/rPET blends containing various dispersed phase contents, measured at 225°C and 260°C, respectively.

The relative viscosity, defined as the ratio of the viscosity of SEBS or the blends to that of the matrix phase, was calculated and presented in Figure 2, to evaluate the potential of rPET as the processing lubricant component compared with that of LCP. For the SEBS/LCP system, the decrease in the relative viscosity strongly depends on LCP contents as seen from Figure 2(a). The reduction of the relative viscosity for the SEBS/LCP system enhances with LCP loading, indicating that higher the LCP content the higher the improvement in the melt processability. Similarly for SEBS/rPET system [Fig. 2(b)], the relative viscosity of the rPET-containing blends is also lower than that of the neat SEBS. It is interesting to note that the reduction of relative viscosity for both types of the blends with 10 wt % dispersed phase is comparable (the relative viscosity reduces by 20–25% than that of the neat SEBS). With further addition of rPET up to 20–30 wt %, the efficiency of rPET as the processing aid for the blend system is not as good as that containing the same amount of LCP. However, the incorporation of small amount of rPET into SEBS significantly reduces the melt viscosity of the blend system.

Because both SEBS-LCP and SEBS-rPET are immiscible, the reduction in viscosity of the blend systems would be similar to the action of external lubricant. LCP is known to have good melt lubricity and addition of LCP could reduce the viscosity of the system by reducing friction at the interface of the polymer and the surface of the equipment or between the interface of polymer streams. The fact that the low viscosity of rPET does not translate to the low viscosity of the blend would suggest that the lubrication capability of rPET itself is not as good as LCP. However, at about 10% content, rPET could reduce the viscosity of SEBS in the same extent as LCP.

The elastic and viscous characteristics of the blend system can be considered from the plots of the storage modulus (G') and the loss modulus (G''), respectively, as a function of ω (Figure 3). 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.[19] As seen from Figures 3(Ia) and (Ib), G' increases with increasing ω indicating a dependence of G' on the time scale of molecular motion. For both the blend systems, the neat SEBS matrix shows the highest value of G' whereas G' of LCP and rPET display the lowest values among the corresponding blend samples. The decrease in G' is observed for the SEBS/LCP and SEBS/rPET blend systems with increase in the concentration of the LCP or rPET as a result of the contribution of the dispersed phases. This means that LCP and rPET in the polymer matrix play a role in promoting the chain mobility leading to a decrease in chain rigidity. However, although the G' of rPET is much lower than that of SEBS, a slight reduction of G' is observed for the blends containing 10–30 wt % rPET. For the LCP-containing blend system, the reduction in G' is clearly observed, indicating that the change in elastic properties of SEBS matrix by blending with LCP is more pronounced than that by blending with rPET. This should arise from the fact that the LCP molecules contain rigid parts, which could slide pass each other easily and results in good lubricity. On the other hand, the chains of rPET are more flexible and would take

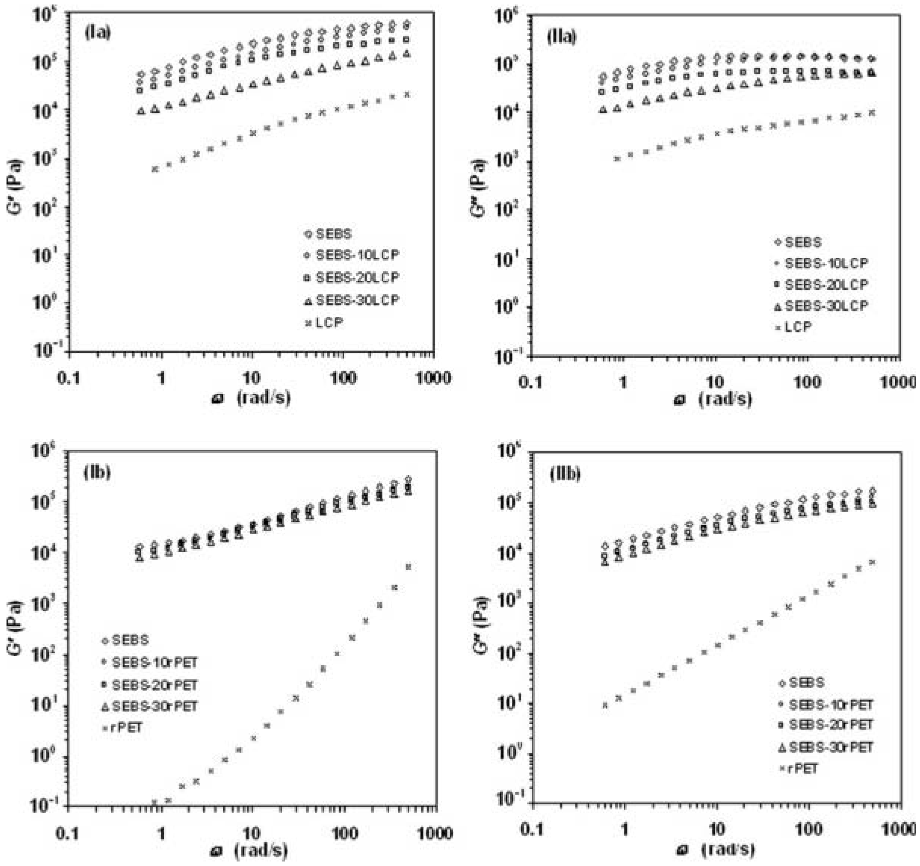


Figure 3 G' (column I) and G'' (column II) versus ω for (a) SEBS/LCP and (b) SEBS/rPET blends containing various contents of dispersed phase. The measurements of G' and G'' for SEBS/LCP and SEBS/rPET blends were carried out at 225°C and 260°C, respectively.

random coil configuration. Chain entanglements are likely to occur and this will be less effective in lubricating the system. Interestingly, the elastic characteristics of rPET [Fig. 3(Ib)] are strongly affected by the applied frequency as seen from the dramatical increase in G' with increasing frequency because the elastic energy stored in the molecules is greater when the deformation from a random coil configuration takes place within shorter times.[20] As a consequence, the G' of rPET is close to those of SEBS and the blends at high frequency.

The viscous characteristics (G'') for both blend systems is found to decrease with increasing dispersed phase contents as seen from Figures 3(IIa) and (IIb) for SEBS/LCP and SEBS/rPET blends, respectively. At the same composition for both types of the blends, G' values of the neat SEBS, LCP, and all blends are higher than the corresponding G'' values in the whole frequency range. This indicates that the elastic characteristics for these samples are dominant factor. In turn, it clearly appears that for rPET analyzed, the G''dominates with respect to the G', especially in the low frequency range. This arises from the fact that, by comparing with LCP, the molecular weight of rPET is relatively low and it has narrow molecular weight distribution, enabling the chain motion with low level of molecular entanglement. Unfortunately, the molecular weights of both the dispersed phases could not be numerically compared because so far the molecular weight of LCP is not obtainable, because no solvent is found to dissolve this polymer. The dominant viscous characteristic of rPET observed in this study is in well accordance with those of the vergin PET and bottle grade PET reported by Daver et al.[20] and Incarnato et al.[21]

It is generally known that the morphology of immiscible blend is governed by the viscosity ratio of the dispersed phase to the matrix phase. For simple shear flow, fibrillar morphology is predicted to occur if the viscosity ratio is lower than unity.[22–24] In general, the lower the viscosity ratio, the higher the possibility of forming fibrillar morphology would be. 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

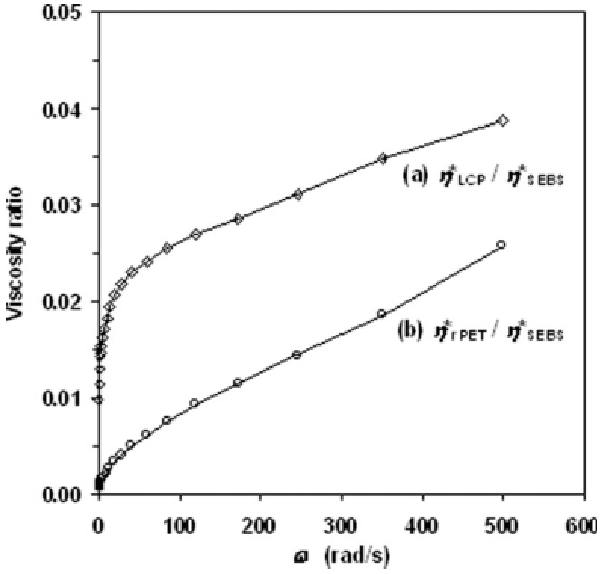


Figure 4 Viscosity ratios versus ω for (a) SEBS/LCP and (b) SEBS/rPET blending systems, measured at 225°C and 260°C, respectively.

as a function of frequency for the SEBS/LCP at 225°C and SEBS/rPET blend systems at 260°C were evaluated and presented in Figure 4. It is seen that the viscosity ratios of both the blend systems are lower than 0.05 over the entire frequency region investigated. The viscosity ratio of the SEBS/LCP system increases sharply first from 0.01 to 0.02 within the frequency range of 0–30 rad s and then increases gradually as the frequency increases further. The increase of viscosity ratio with increasing frequency arises from the faster drop of the viscosity of SEBS than that of LCP in the high frequency range. Similarly, the viscosity ratio for the SEBS/rPET system progressively increases with increasing frequency. However, the viscosity ratio of the SEBS/rPET system is much lower than that of the SEBS/LCP system at all measuring frequencies. The difference in viscosity ratio arising from the different dispersed phase viscosity is expected to affect the fibrillation of the LCP and the rPET. On the basis of the obtained results of viscosity ratios, it may be expected that both LCP and rPET can form the fibrillation morphology and the better fibrillation should be observed in the rPET-containing blends.

Morphology

It is well known that the final properties of the iMFCs depend on its phase morphology, which is affected by several important factors such as rheological behavior, composition, interfacial tension, processing condition, and fabrication techniques. In the present study, the morphology of the fracture surface was studied by means of SEM. Figure 5 shows the SEM micrographs of the fracture surfaces for the SEBS/LCP and SEBS/rPET extruded strands containing various LCP and rPET contents. In the LCP-containing blend with 10 wt % LCP [Fig. 5(Ia)], most of the LCP domains appeared as droplets, and few elongated LCP domains are observed. The fibrillation of LCP domains is clearly observed in the blend with 20 wt % LCP [Fig. 5(Ib)]. However, with the addition of LCP up to 30 wt %, some lamellar structure is observed because of the coalescence of the liquid LCP threads that occur during extrusion. The lamellar structure is also observed in other LCP-containing blend systems with incorporation of high LCP concentration.[25–27]

In the case of the SEBS/rPET system, most of the rPET domains in SEBS-10rPET appear as small droplets with diameter of about 0.5–1 μm and the diameter of the rPET domains slightly increases with rPET loading. Some elongated rPET domains are also observed in the SEBS/rPET blends. In addition, limited coalescence of rPET domains are observed in the SEBS-30rPET extruded strands. Interestingly, the domain size of the rPET is much smaller than that of the LCP. According to the results of viscosity ratio shown earlier, Figure 4, it may be expected, from the low viscosity ratios for the SEBS/LCP and the SEBS/rPET systems, that these blend systems will have fibrillar morphology. However, the morphological results from the present study clearly show that good fibrillar morphology is obtained only with the SEBS/LCP system. The fact that rPET break down into small droplets may be due to the high viscosity of the system (Fig. 1) and limited coalescence. Furthermore, the difference in morphology of the SEBS/LCP and the SEBS/rPET systems could be explained as follows. Generally, deformation of the dispersed-phase droplets into fibrillation structures or coalescence of the dispersed-phase domains 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 (C_a), which is defined by[28]

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

where η_m is the viscosity of the matrix, $\dot{\gamma}$ the shear rate, b the initial diameter of dispersed droplets, and σ the interfacial tension between the matrix and dispersed phase. In the simple shear flow of Newtonian fluids, a dispersed droplet will be elongated if $C_a > 0.5$, indicating that the ratio of shear stress and the interfacial energy should be larger than half.[28] The influence of the capillary number on the stability of the dispersed phases especially for LCP

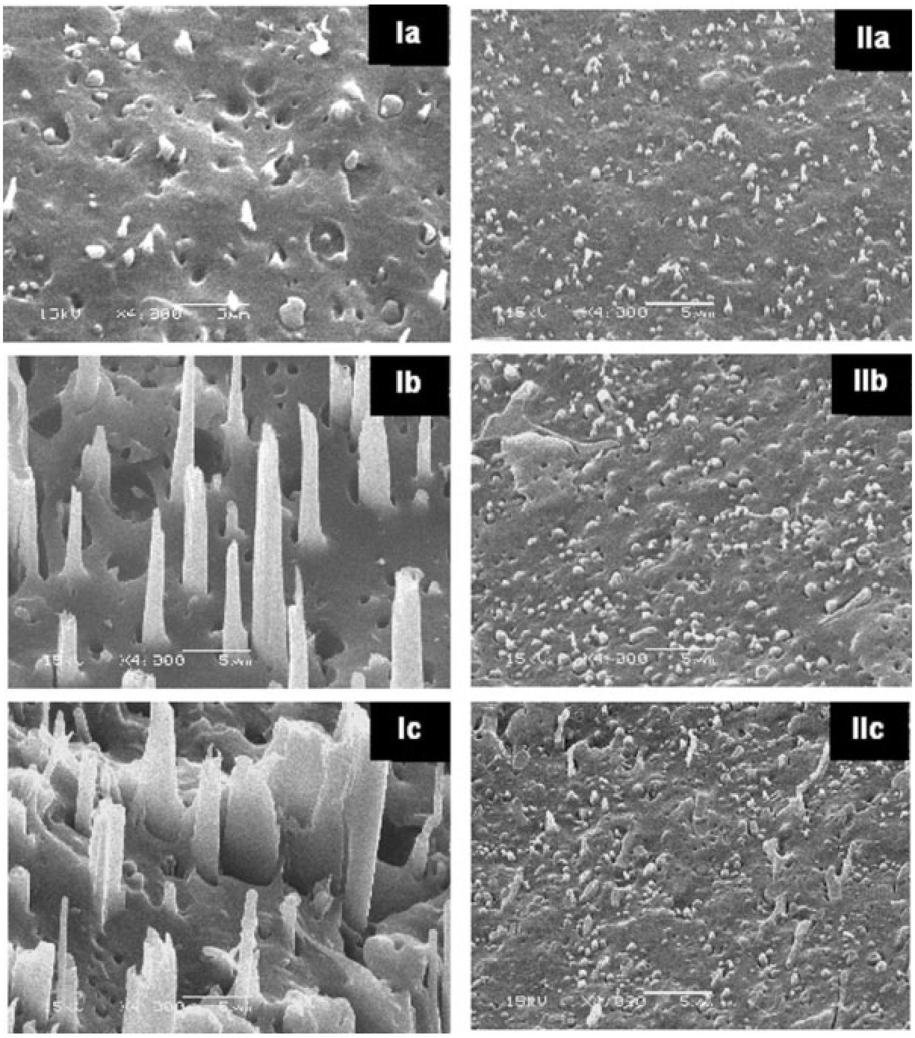


Figure 5 SEM micrographs of the fracture surface for SEBS/LCP (column I) and SEBS/rPET (column II) blends containing (a) 10, (b) 20, and (c) 30 wt % dispersed phase.

morphology has been studied by a number of researchers.[29,30] The results of their study indicate the influence of both viscous and interfacial forces on the final morphology, confirming the importance of Capillary number. In the case of SEBS/rPET system, even if the viscosity ratio is lower than 0.03, the fibrillation of the rPET domains is not clearly observed in as-extruded strand. According to eq. (1), there can be two possibilities that cause the Capillary number to be low. They are small initial diameter of the dispersed phase and the high interfacial tension. The former is apparent from Figure 5. rPET droplets are so small and coalesence of droplets does not occur even at high rPET content. The fibrilation of rPET therefore does not occur. However, thermotropic LCPs are essentially rigid-rod long chain molecules with some irregularity or flexibility incorporated into the polymer chain to lower the melting point below the decomposition temperature. The rigid-rod molecular structure allows these materials to exhibit molecular order in a liquid mesophase resulting in a tendency toward easy orientation in the flow direction. In contrast, the random coil structure and relatively flexible structure of rPET tend to appear in the molten state. Thus, the fibrillation tendency of rPET is not as good as that of highly-orientated nature LCP.

Thermal decomposition behavior

Normally, polymers must encounter elevated temperatures at almost every stage in manufacturing, compounding, and processing stages, in service, and during repairing step. Therefore, an 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

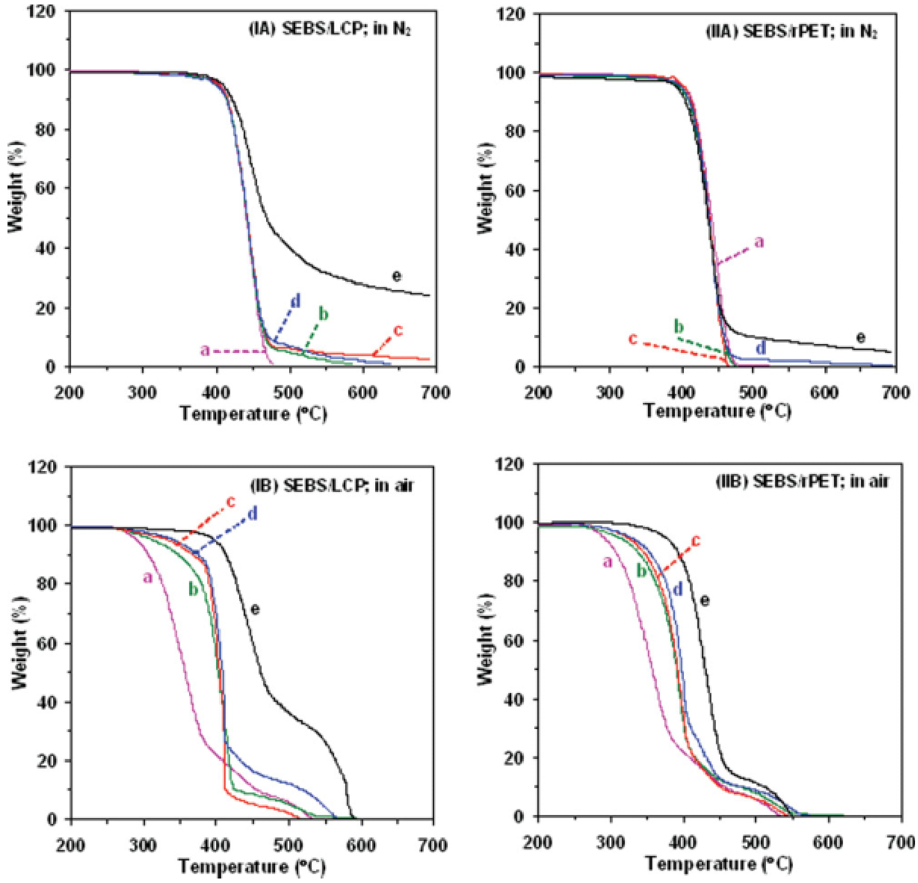


Figure 6 Dynamic TG curves of SEBS/LCP (column I) and SEBS/rPET (column II) blends containing (a) 0, (b) 10, (c) 20, (d) 30, and (e) 100 wt % LCP or rPET at a heating rate of 10°C/min in nitrogen (row A) and in air (row B). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

understanding of the effect of the LCP and the rPET on thermal decomposition of the SEBS/LCP and the SEBS/rPET blends. The non-isothermal TG curves of the two blending systems are presented in Figure 6. The TG measurements were carried out in nitrogen and in air at a heating rate of 10°C/min.

TG results of the SEBS/LCP blends [Fig. 6(IA)] obtained in nitrogen will be considered first. The non-isothermal TG profile of SEBS reveals only a single weight-loss step at the temperature range around 400–480°C. The single weight-loss step of SEBS in nitrogen revealed in this study, which corresponds mainly to the chain scission at the boundary of the polystyrene-olefin phase, is similar to that of SEBS under non-isothermal heating in argon flow reported by Zucolotto et al.[31] Although the blend system may be complicated due to the presence of many copolymer components, a single degradation step similar to the neat SEBS matrix is observed for the blends containing 10–30 wt % LCP. The onset of decomposition in nitrogen seems not to be affected by the LCP loading. In the LCP-containing blends, the degradation mechanism additionally involves the removal of ester, ethylene groups, and hydrogen atoms in the polymer chains of LCP.[32] That is, there are more than one reaction for the decompositon. In the case of LCP, the first thermal degradation mainly occurs at the PET block, whereas the second degradation process could be attributed to the degradation of the HBA block.[32,33] It is seen that no char residues were left for the neat SEBS whereas the amount of char residues increases with increasing the LCP contents. The increase in char residues arises from the increase in the HBA block (by increasing amount of LCP content), which will decrease the number of hydrogen atoms and retard the formation of volatile degraded products.[34] Moreover, the formation of char residues is probably due to the branch formation and crosslinking of the product obtained mostly from the HBA unit during the thermal degradation under nitrogen.

Under dynamic heating in air [Fig. 6(IB)], the thermal degradation of the SEBS, the LCP and their blends occur in two steps. The neat SEBS exhibits the first weight-loss step at 250–380°C, whereas the first major weight-loss of the LCP occurs around

400–500°C. For the thermal degradation of SEBS 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.[35] Concurrent and further reaction give rise to the formation of anhydrides and perester/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 hindered phenolic antioxidant and phosphate were also higher synergistic in inhibiting oxidation and separation at the boundaries by destroying the acetophenone end groups and preventing excimer disaggreation. Note that, in air, no char residues of the neat polymers and the blends were left within the experimental temperature.

In the case of SEBS/rPET blend system in nitrogen [Fig. 6(IIA)], the single-step weight-losses are observed for the neat polymers and the blends at 380–460°C. Several studies have been conducted on the thermal degradation products of PET,[36–39] which indicate that the thermal degradtion of PET is initiated by chain scission of ester-linkage, yielding carboxyl and vinyl ester groups. In air [Fig. 6(IIB)], at least two weight-loss steps are observed for all samples indicating that the degradation process is more complex in air than in nitrogen.

To compare the dispersed phase-content dependence of thermal stability for the two types of blends in more quantitative way, the thermal decompositon data 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} between the SEBS/LCP and SEBS/rPET blends are observed when compared at the same blend composition. $T_{\max1}$ of the LCP-containing blends are slightly higher than that of the corresponding rPET-containing blends. It is noticed that at the same composition, $(d\alpha/dt)_{\max}$ of the SEBS/LCP blend systems are lower than those of the SEBS/rPET blend systems. This indicates that incorporation of the LCP into SEBS results in somewhat higher thermal resistance when compared with the rPET-containing blends at the same composition.

In air, it is interesting to note that T_{onset} and $T_{\max1}$ of the two types of blends are much higher than those of the matrix but are lower than those of the corresponding dispersed phase. This means that incorporation of the LCP and rPET into the SEBS matrix effectively enhance the thermal stability in air

TABLE I
Nonisothermal Decomposition Characteristics of SEBS/LCP and SEBS/rPET Blends in Nitrogen and in Air

LCP or rPET content (wt %)	SEBS/LCP blending system						SEBS/rPET blending system					
	T_{onset} (°C)	$T_{\max1}$ (°C)	$T_{\max2}$ (°C)	$(d\alpha/dt)_{\max1}$ (%/min)	$(d\alpha/dt)_{\max2}$ (%/min)	Char yield at 600°C (wt %)	T_{onset} (°C)	$T_{\max1}$ (°C)	$T_{\max2}$ (°C)	$(d\alpha/dt)_{\max1}$ (%/min)	$(d\alpha/dt)_{\max2}$ (%/min)	Char yield at 600°C (wt%)
In nitrogen												
0	417	448	–	20.4	–	0.00	417	448	–	20.4	–	0.00
10	417	445	–	20.0	–	0.38	416	440	–	25.6	–	0.00
20	418	451	–	23.2	–	0.05	419	439	–	30.1	–	0.00
30	417	437	–	20.5	–	0.15	419	443	–	24.0	–	0.14
100	419	448	–	10.5	–	27.6	414	441	–	20.8	–	7.13
In air												
0	310	354	528	11.0	1.99	0.00	310	354	528	11.0	1.99	0.00
10	385	410	518	33.4	1.18	0.02	366	391	523	19.7	1.65	0.03
20	402	405	527	52.8	1.63	0.00	367	387	538	19.9	1.62	0.00
30	401	408	552	48.8	2.57	0.00	377	400	549	33.3	1.79	0.00
100	410	449	573	9.58	19.8	0.00	399	433	553	16.3	5.16	0.00

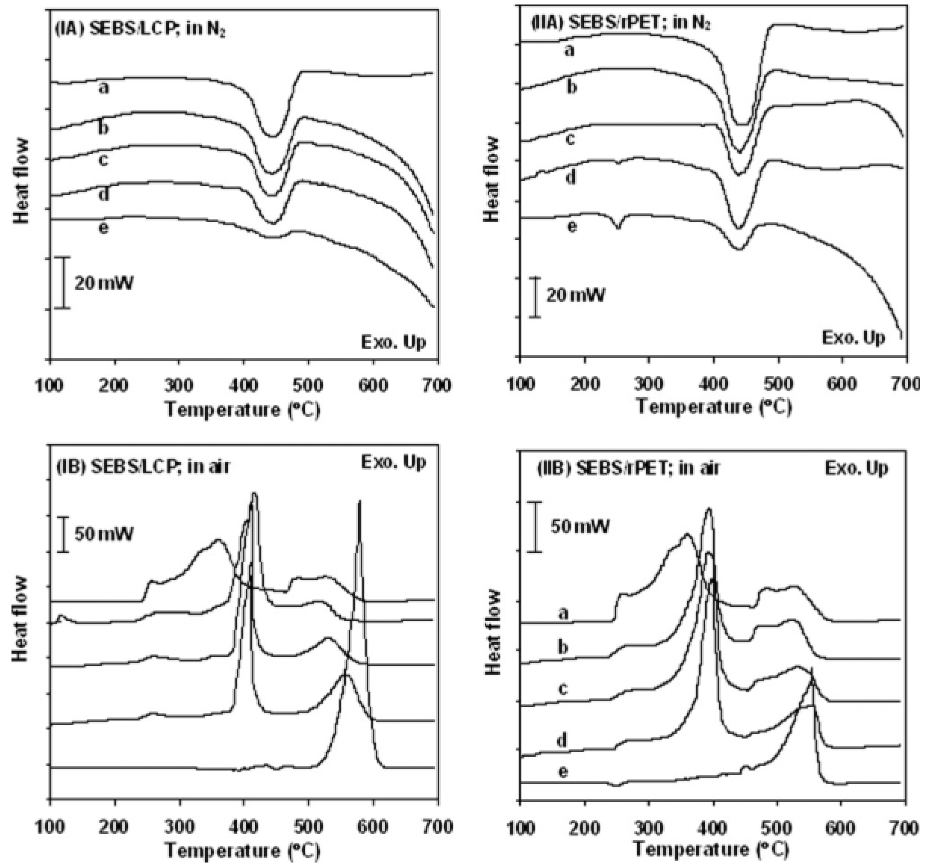


Figure 7 Simultaneous DSC curves of SEBS/LCP (column I) and SEBS/rPET (column II) blends containing (a) 0, (b) 10, (c) 20, (d) 30, and (e) 100 wt % LCP or rPET at a heating rate of 10°C/min in nitrogen (row A) and in air (row B).

but not in nitrogen. It is found that T_{onset} and T_{max1} of the blends with 10–30 wt % LCP are shifted by about 75–90°C and 50–55°C, respectively, higher than those of the neat matrix, whereas the respective T_{onset} and T_{max1} of the blends with 10–30 wt % rPET are shifted about 56–67°C and 34–46°C higher than those of the neat SEBS. It is seen that $(d\alpha/dt)_{max1}$ of the LCP- and rPET-containing blends are higher than that of the neat matrix and they decrease with increasing dispersed phase content, indicating the rapid weight-loss process with more complex degradation mechanism. Normally, the thermal stability of polymer in air is somewhat lower than that in nirogen. However, the situation that polymer has been exposed in air is more common than in nitrogen during real processing and application. Note that $(d\alpha/dt)_{max2}$ of the LCP and rPET dispersed phases are much higher than that of the matrix phase whereas T_{max2} seem to mostly increase with the addition of LCP and rPET dispersed phases.

Simultaneous DSC data of thermal decomposition

The DSC traces of degradation for the SEBS, LCP, rPET, and the blends in nitrogen and in air are shown in Figures 7. The DSC curve of SEBS in nitrogen [Fig. 7(IA)] shows a minimum degradation endotherms at (450°C whereas that of the LCP exhibits a broad degradation endotherm with a peak minimum at 430°C. It is noticed that the peak minimum of the SEBS is little affected by the incorporation of LCP. In the case of SEBS/rPET [Fig. 7(IIA)], the exothermic peak, known as “cold crystallization,” is not clearly observed, whereas the endothermic peak associated with the fusion of the crystalline fraction is observed at about 275°C. In addition, the largest endothermic peak of rPET is observed at about 460°C corresponding to the degradation process of rPET. However, although the degradation temperature of rPET is higher than that of the neat SEBS, the incorporation of rPET into SEBS does not seem to influence the degradation temperature of the blend in nitrogen.

Under heating in air, the exothermic degradation process is observed for all the samples due to the fact that the concurrent and further degradation mechanisms in air tend to involve the formation reaction. SEBS shows a very broad degradation endotherm that stretches from 250 to 560°C. It is

TABLE II
Simultaneous DSC Data of SEBS/LCP and SEBS/rPET Blends Under Thermal Degradation in Nitrogen and in Air

LCP or rPET content (wt %)	SEBS/LCP blending system				SEBS/rPET blending system			
	T_m (°C)	ΔH_m (kJ/g)	T_d (°C)[a]	ΔH_d (kJ/g)	T_m (°C)	ΔH_m (kJ/g)	T_d (°C)[a]	ΔH_d (kJ/g)
In nitrogen								
0	–	–	449	1.08	–	–	449	1.08
10	–	–	445	0.83	–	–	441	0.85
20	–	–	444	0.73	–	–	439	0.63
30	–	–	446	0.71	253	6.15	439	0.56
100	–	–	436	0.12	251	0.04	437	0.20
In air								
0	–	–	360	0.80	–	–	360	0.80
10	–	–	416	6.75	–	–	394	4.05
20	–	–	411	5.68	–	–	393	4.28
30	–	–	411	2.54	–	–	397	3.32
100	–	–	579	6.79	251	0.04	555	3.18

[a] Under heating in air, T_d reported here associates with the first major exothermic peak.

interesting to note that an extremely sharp exotherm is noticed at 400°C with addition of the LCP. At high concentration of LCP (20–30 wt % LCP), the second minor exotherm corresponding to the degradation process of LCP is observed. Interestingly, although LCP starts to degrade in the first step at the temperature range of 400–500°C, the exotherm associated with this region is not observed. The simultaneous data of both blend systems are also quantitatively presented in Table II. T_m and ΔH_m represent the melting temperature and heat flow of melting process, respectively, whereas T_d and ΔH_d represent the peak temperature and heat flow, respectively, associated with the thermal degradation process. In nitrogen, incorporation of the LCP or rPET into SEBS seems to affect little the T_d of the blends. In air, T_d of the blends are much higher than those of the polymer matrix. It is seen that ΔH_d of the blends decreased mostly with LCP or rPET loading because of the dilution effect of the polymer matrix. Moreover, at the same concentration of the dispersed phase, the extent of heat flow is much higher in air than in nitrogen. This indicates that there are not only typically thermal degradation reaction but also thermooxidative reaction, which additionally occurs in air.

CONCLUSIONS

In this work, SEBS *in situ* reinforced with two types of reinforcing materials, LCP and rPET, were prepared. The influence of LCP and rPET dispersed phases on rheology, morphology and thermal stability of the elastomer composites was investigated. It was found that the incorporation of small amount of LCP and rPET (10 wt %) into SEBS significantly reduces the melt viscosity of the blend system. At higher concentration, only LCP that continues to lower the viscosity of the blend system further whereas much less effect was observed for rPET. The large reduction in viscosity in LCP containing system is due to its inherent lubricating property. SEBS/LCP displays fibrillar morphology at 20 and 30 wt % LCP whereas SEBS/rPET does not. The incorporation of LCP or rPET into the elastomer matrix was found to retard the thermal degradation significantly in air but not in nitrogen. These demonstrate the high potential of using rPET in replacing the more expensive LCP as processing aids and also to improve thermal resistance of SEBS.

The authors acknowledge the financial support from the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education. Ministry of Education is also gratefully acknowledged. Finally, the authors thank Professor Sauvarop Bualek-Limcharoen for the gift of Rodrun LC3000 liquid crystalline polymer.

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J Polym Res (2009) 16:443–454
DOI 10.1007/s10965-008-9247-6

Comparative study on phase and properties between rPET/PS and LCP/PS in situ microfibrillar-reinforced composites

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Received: 26 February 2008 / Accepted: 22 October 2008 / Published online: 6 November 2008

Abstract Microfibrillar-reinforced composites based on two dispersed phases, liquid crystalline polymer (LCP) and recycled poly(ethylene terephthalate) (rPET), and polystyrene (PS) were prepared using extrusion process. The rheological behavior, morphology, and thermal stability of LCP/PS and rPET/PS blends containing various dispersed phase contents were investigated. All blends and LCP exhibited shear thinning behavior, whereas Newtonian fluid behavior was observed for rPET. The incorporation of both LCP and rPET into PS significantly improved the processability. The potential of rPET as a processing lubricant by bringing down the melt viscosity of the blend system was as good as LCP. The elongated LCP domains were clearly observed in as-extruded strand. Although the viscosity ratio of rPET/PS system was lower than that of LCP/PS system, most rPET domains appeared as small droplets. An addition of LCP and rPET into PS matrix improved the thermal resistance in air significantly. The obtained results suggested the high potential of rPET as a processing aid and thermally stable reinforcing-material similar to LCP. The mechanical properties of the LCP-containing blends were mostly higher than those of the corresponding rPET-containing blends when compared at the same blend composition.

Keywords Polymer in situ composite · Liquid crystalline polymer · Rheology · Thermal property · Recycled PET · Polystyrene

Introduction

Thermotropic liquid crystalline polymers (TLCPs) have been one of the most advanced materieals used in electronic devices and fiber composites due to its excellent mechanical properties, improved processability, good thermal, chemical and dimensional stabilities. There has been an increasing application of TLCPs, either alone, or as reinforcements or matrices for advanced composites. Upon melting, TLCPs give rise to highly organized liquid phase (mesophase) that tend spontaneously to pack parallel to one another to form highly oriented domains. Under elongational processing conditions, these oriented domains can develop a fibrillar morphology with a high degree of orientation leading to enhanced mechanical properties. These properties enable TLCPs to be used as a reinforcing filler which is not present as a solid phase during processing of the composite, but instead forms when the material is cooled to a solid state. These blends have been called “in situ composite” because of their self shaping during processing [1]. In situ composites have attracted a great deal of interest because they can solve some problems that arise during the processing of conventional fiber-reinforced composites [2–4]. However, TLCPs are often too expensive for general engineering applications and not readily available in developing industrial countries. On the other hand, there are considerable supplies of engineering plastics in the form of post consumer scraps, which are a low cost source of raw material for forming polymer blends [5]. An alternative way is to find a substitute for TLCPs in

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fiber-reinforced composite application as a new type of processing route.

In particular, polyethylene terephthalate (PET) is extensively used for the production of fibers, films, and bottles for water and other beverages (especially carbonate drinks) as well as containers for other edible products because of its combination of unique physical, mechanical and permeant properties, as well as processability. As an engineering plastic, it offers, among others, excellent high-temperature properties, clarity, color ability, creep and solvent resistance [6, 7]. In this regard, it is particularly fortunate because it is easily separable from other waste and allows a relatively economical recovery when properly assisted by the education of citizens and regulation. Contrarily, the recovered material after cleaning is not considered suitable for the production of bottles for beverages or water and a new route must be developed for its transformation into usable products in addition to a rather limited and specialized fiber production. A possible upgrading and recycling approach consist of the blending of PET with different polyolefins with the objective of obtaining a composite material with an increased value with respect to the starting polymers. For example, the blends of rPET with common thermoplastics such as polypropylene [5, 8–10] and polyethylene [11–14] based on the concept of in situ microfibrillar-reinforced composites (iMFCs) [15] have received much attention during the last decade. Most of the previous works suggested that the presence of PET in a polyolefinic material could enhance mechanical properties of the composites. Moreover, polystyrene (PS) in situ reinforced with virgin PET through compatibilized blending has also been investigated by few research groups [16, 17] and resulted in better interfacial adhesion and enhanced mechanical properties of final products. However, to the author's knowledge, very limited information is available with regard to the rPET/PS blends and a direct comparison of phase behavior and properties between LCP/PS and rPET/PS blend system has not been investigated.

In this study, the uncompatibilized blends were prepared and investigated in order to clearly elucidate and compare the effect of dispersed phases on rheological behavior, morphology and thermal decomposition properties of both composite systems. The main goal of this study is to explore the potential of rPET to use as low-cost and easy providing reinforcing material for microfibrillar-reinforced composites, compared with LCP.

Experimental

Materials

The polymer dispersed phases used in this work were Rodrun LC3000, a TLCP, supplied by Unitika Co. (Tokyo, Japan) and rPET collected from postconsumer soft drink bottles. 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 this LCP was not obtainable, since no solvent was found to dissolve Rodrun LC3000. The rPET bottles were cleaned and cut into small pieces with dimension of about 3×3 mm. The melting temperature of rPET is found to be 252–255 °C (examined by using DSC). The matrix phase used in this study was polystyrene (PS) (STYRON™ 685D), purchased from Dow Chemical Pacific LTD. The specific gravity and melt flow rate of PS were 1.04 (ASTM D792) and 1.6 g/10 min (ASTM D1238), respectively. All materials were dried in a vacuum oven at 70 °C for at least 12 h before used. In this paper, Rodrun LC3000 liquid crystalline polymer was represented by LCP.

Blend preparation

The blends of LCP/PS and rPET/PS 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 80 rpm. The temperature profiles for preparation of LCP/PS and rPET/PS were 190–220–220–225 °C and 190–250–255–260 °C, respectively. The temperature profiles shown here represent 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, pelletized and subsequently dried in a vacuum oven. The sample codes of the extruded strand blends are designated as PS-*x*LCP or PS-*x*rPET where *x* depicts the content of LCP or rPET in wt.%.

Rheological measurements

Measurements of rheological properties in the molten state for all 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 pellets and compression-molded at 200 °C into a sheet about 1.5 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^{-1}. The measuring temperatures for LCP/PS and rPET/PS systems were 225 and 260 °C, respectively. The gap between the two plates was set at 0.9 mm.

Morphological characterization

The fracture surfaces of both types of extruded strand blends 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.

Measurement of thermal decomposition behavior

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 1,000 °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 and DSC data were simultaneously 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).

Measurement of tensile properties

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 of 1 kN. The stress is engineering stress which was calculated from the original cross section area of the sample. The average value of five measurements was determined.

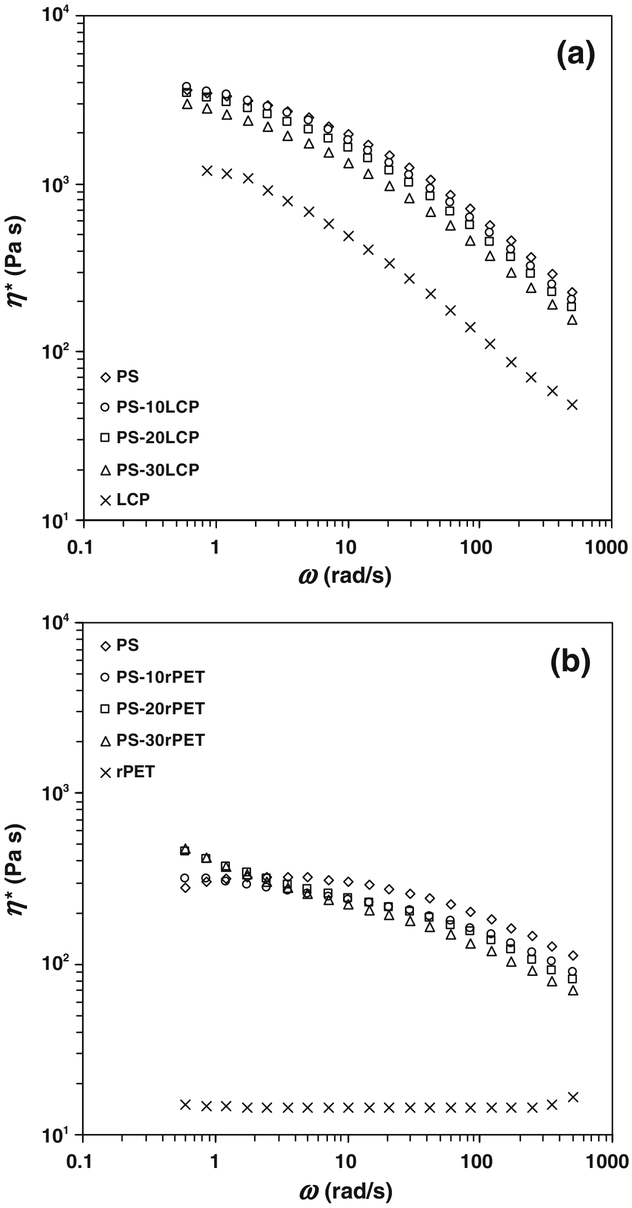

Fig. 1 η^* vs. ω for **a** LCP/PS and **b** rPET/PS blends containing various dispersed phase contents, measured at 225 and 260 °C, respectively

Results and discussion

Rheology

In this study, the different temperature profiles were used for preparation of LCP/PS and rPET/PS blends due to different melting temperature of LCP and rPET dispersed phases. Therefore, rheological measurements in the molten state of LCP/PS and rPET/PS blends were carried out at 225 and 260 °C, respectively. Figure 1 shows the frequency (ω) dependence of complex viscosity (η^*) for neat polymers and their blends. For LCP/PS blend system, the flow curves of all neat and blend samples exhibit shear thinning behavior; the viscosity decreases with increasing shear rate (or shear frequency) due to the shear-induced chain orientation, leading to a reduction in the chain entanglement density. It is seen that a decrease in η^* becomes more pronounced as the percentage of LCP in PS is increased. This indicates that the addition of LCP into PS matrix is melt processable. Similarly for rPET/PS blend system, the incorporation of rPET in PS significantly reduces of the viscosity of the blends, especially at high frequency. However, the viscosity-reduction dependence of rPET contents is not observed in low frequency region. This may be due to that the flexible chains of rPET which could not maintain the chain alignment during long-range relaxation. It is interesting to note that only rPET exhibits Newtonian fluid behavior over the frequency range examined. Although a high amount of rPET was added into the matrix, the Newtonian flow region is not observed in any of the rPET-containing blends.

In order to evaluate the potential of rPET as the processing lubricant component compared with that of LCP, the relative viscosity defined as the ratio of viscosity of PS or blends to that of the matrix phase was examined and presented in Fig. 2. For LCP/PS system, the decrease in the relative viscosity strongly depends on LCP loadings as seen from Fig. 2a. The obtained results show that further addition of LCP into PS significantly improves the melt processability. Similarly for rPET/PS system (Fig. 2b), even when a small amount of rPET was added into PS, the relative viscosity of the rPET-containing blends is much lower than that of the neat PS. For example, the relative viscosity decreases about 20% lower than that of the neat PS with 10 wt.% rPET loading. It is interesting to note that the reduction of relative viscosity of 10 wt.% rPET-containing blend is higher than that of the corresponding composition of LCP-containing blend system. The obtained results suggest that the efficiency of rPET as the processing aid by bringing down the melt viscosity of the blend system is as good as that containing LCP.

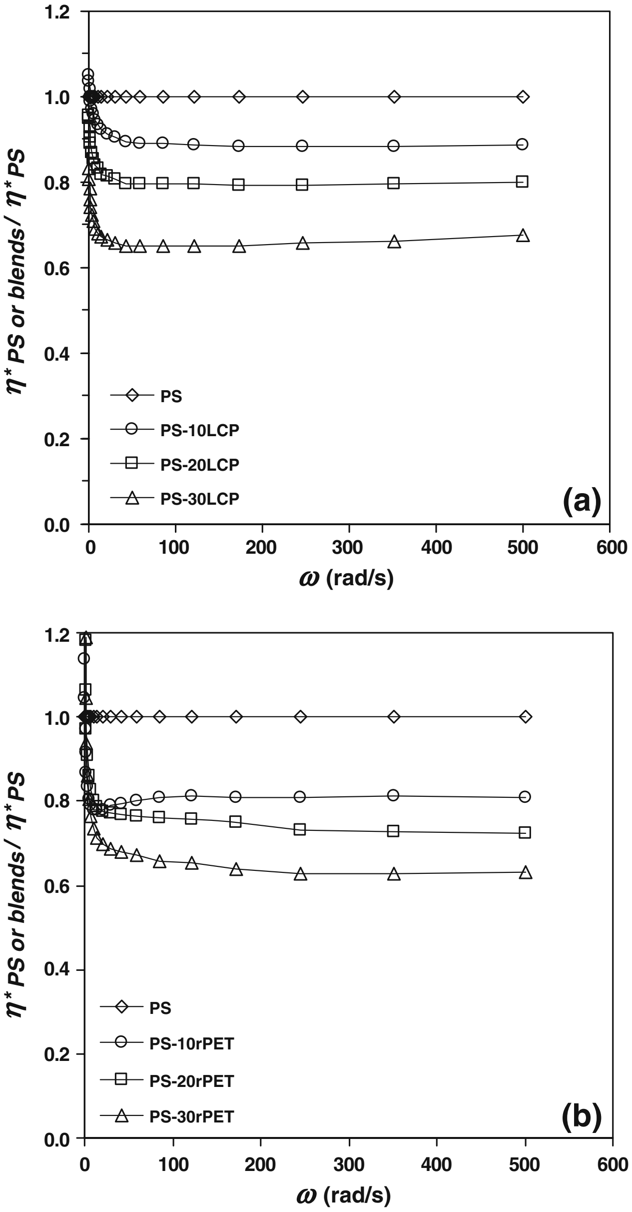

Fig. 2 Relative η* vs. ω for **a** LCP/PS and **b** rPET/PS blends containing various dispersed phase contents, measured at 225 and 260 °C, respectively

The elastic and viscous characteristics of both blend systems can be considered from the plots of storage modulus (G') and loss modulus (G''), respectively, as a function of ω. The plots of G' and G'' as a function of ω for LCP/PS and rPET/PS are shown in Fig. 3. The values of G' and G'' at low frequency generally provide information about long-range (beyond entanglement distance) relaxation, while the values at high frequency provide information about short range (motion with entanglement) relaxation [18]. As seen from Fig. 3, G' and G'' increase with increasing ω, indicating a dependence of viscoelastic properties on the time scale of molecular motion. For LCP-containing blend systems, the neat PS matrix seems to shows the highest value of G' and G'' and these values progressively decrease as the content of LCP increases. This phenomenon can be explained that the LCP dispersed phase in the polymer matrix plays an important role in promoting the chain mobility leading to decrease in chain rigidity. At the same composition for LCP-containing blends, G' values of the neat polymers the blends are higher than the corresponding G'' values in the whole frequency range. This indicates that the elastic characteristics for these samples are dominant factor. Oppositely for rPET/PS blends at low frequency (ω<10 rad/s), even the G' of rPET is much lower than that of PS matrix, further addition of rPET does not lower the G' of the blends. However, at high shear frequency, the G' dependence of rPET contents displays a similar trend to that of LCP-containing blend system. The viscous characteristics (G'') for rPET/PS blend systems, especially at high frequency region, is found to decrease with increasing dispersed phase contents. In addition, the dependence of shear frequency on the elastic and viscous characteristics of rPET is more pronounced than that of LCP.

It is generally known that the morphology of immiscible blend is governed by the viscosity ratio of the dispersed phase to the matrix phase. For simple shear flow, fibrillar morphology is predicted to occur if the viscosity ratio is lower than unity [19–21]. In general, the lower the viscosity ratio, the higher the possibility of forming fibrillar morphology would be. The viscosity ratio will now be examined as it is one of the criteria which have been used

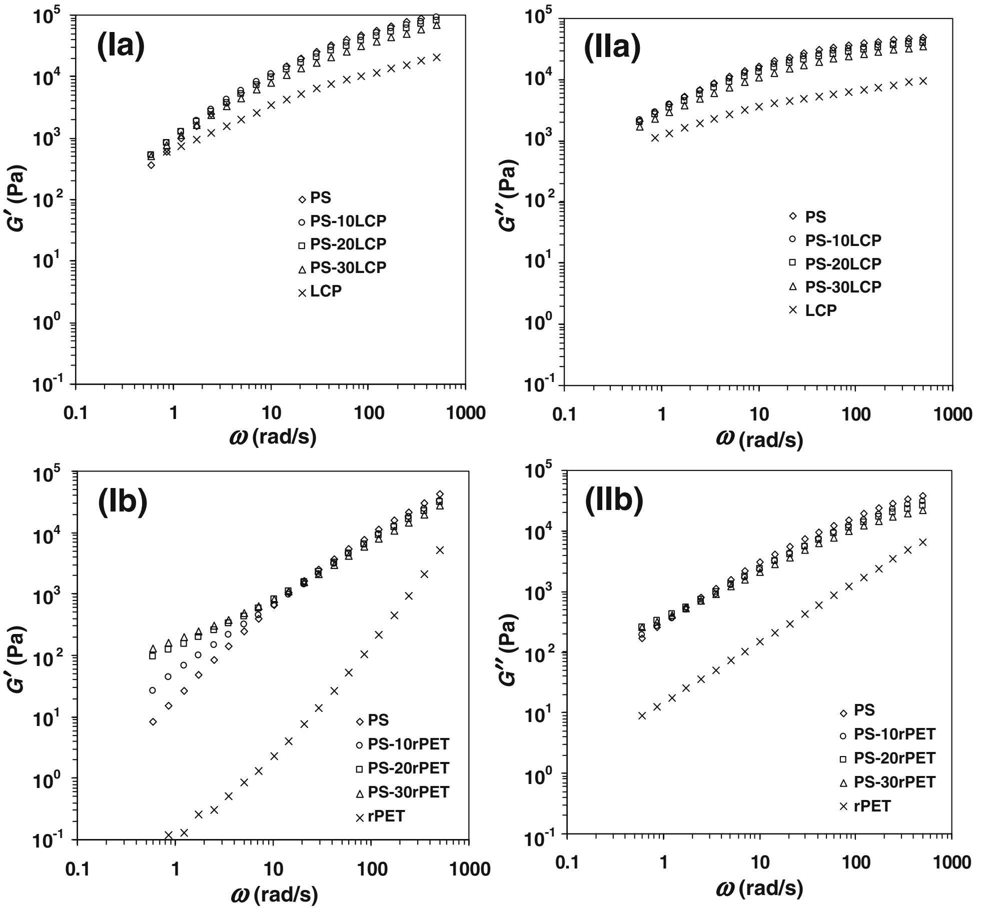

Fig. 3 *G′* (*column I*) and *G″* (*column II*) vs. *ω* for *a* LCP/PS and *b* rPET/PS blends containing various contents of dispersed phase. The measurements of *G′* and *G″* for LCP/PS and rPET/PS blends were carried out at 225 and 260 °C, respectively

to determine the possibility of fibril formation of the dispersed phase. The viscosity ratios as a function of frequency for LCP/PS and rPET/PS blend systems at 225 and 260 °C, respectively, was evaluated and presented in Fig. 4. It is seen that the viscosity ratios of both blend systems are much lower than unity over the entire frequency region being investigated. The viscosity ratio of LCP/PS system decreases sharply first from 0.35 to 0.22 within the frequency range of 0–50 rad/s and then gradually increases as the frequency increases. In the case of rPET/PS system, the viscosity ratio gradually increases from 0.05 to 0.15 as the frequency increases from 0–500 rad/s. It is seen that the viscosity ratio of rPET/PS system is much lower than that of the LCP/PS system when compared at the same measuring frequency. The difference in viscosity ratio arising from the large different viscosity of between the matrix and dispersed phases for both types of the blends is expected to affect the fibrillation of LCP and rPET. Based on the results of viscosity ratios obtained from the present study, it may be expected that both LCP and rPET would form the fibrillation morphology and the better fibrillation should be observed in rPET-containing blends. The relation between morphological observation and the viscosity ratio for both blend systems will be discussed in the next section.

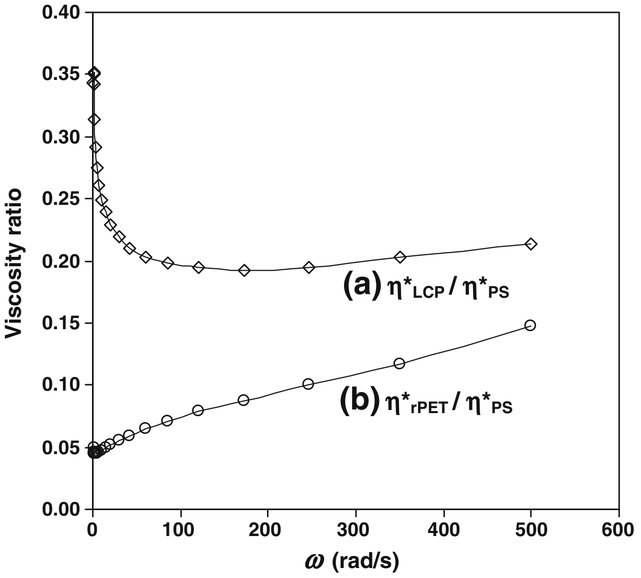

Fig. 4 Viscosity ratios vs. *ω* for *a* LCP/PS and *b* rPET/PS blending systems, measured at 225 and 260 °C, respectively

Morphology

It is well known that the final properties of the in situ microfibrillar-reinforced composites depend on its phase morphology which is affected by several important factors such as rheological behavior, composition, interfacial tension, processing condition and fabrication techniques. In the present study, the morphology of the fracture surface was studied by means of scanning electron microscopy (SEM). Figure 5 shows the SEM micrographs of the fracture surface for the LCP/PS and rPET/PS extruded strands containing various LCP and rPET contents. In LCP-containing blend with 10 wt.% LCP (Fig. 5Ia), droplets and elongated LCP domains are mostly observed. The increase in diameter of elongated LCP domains is observed in the blend with 20 wt.% LCP (Fig. 5Ib). With addition of LCP up to 30 wt.%, the coalescence of liquid LCP threads tends to occur in the blends containing high amount of LCP during extrusion [22–24].

In the case of rPET/PS system, most of rPET domains in 10 wt.% rPET-containing blend appear as small droplets with the diameter of about 0.5–1 μm and the diameter of rPET domains increases with rPET loading. It is noticed that few elongated rPET domains are observed in the blends with 30 wt.% rPET. Interestingly, the domain size of rPET in the blends is much smaller than that of LCP when compared at the same composition. According to the results of viscosity ratio shown earlier, it may be expected that, from the viscosity ratios of both blend systems which is much lower than unity, these blend systems will have fibrillar morphology. However, the morphological results from the present study clearly show that fibrillar morphology in as-extruded strand is obtained only with LCP/PS system. This would suggest that perhaps there are differences in the interfacial tension between LCP/PS and rPET/PS systems. Generally, the deformation of dispersed-phase droplets into fibrillation structures or coalescence of

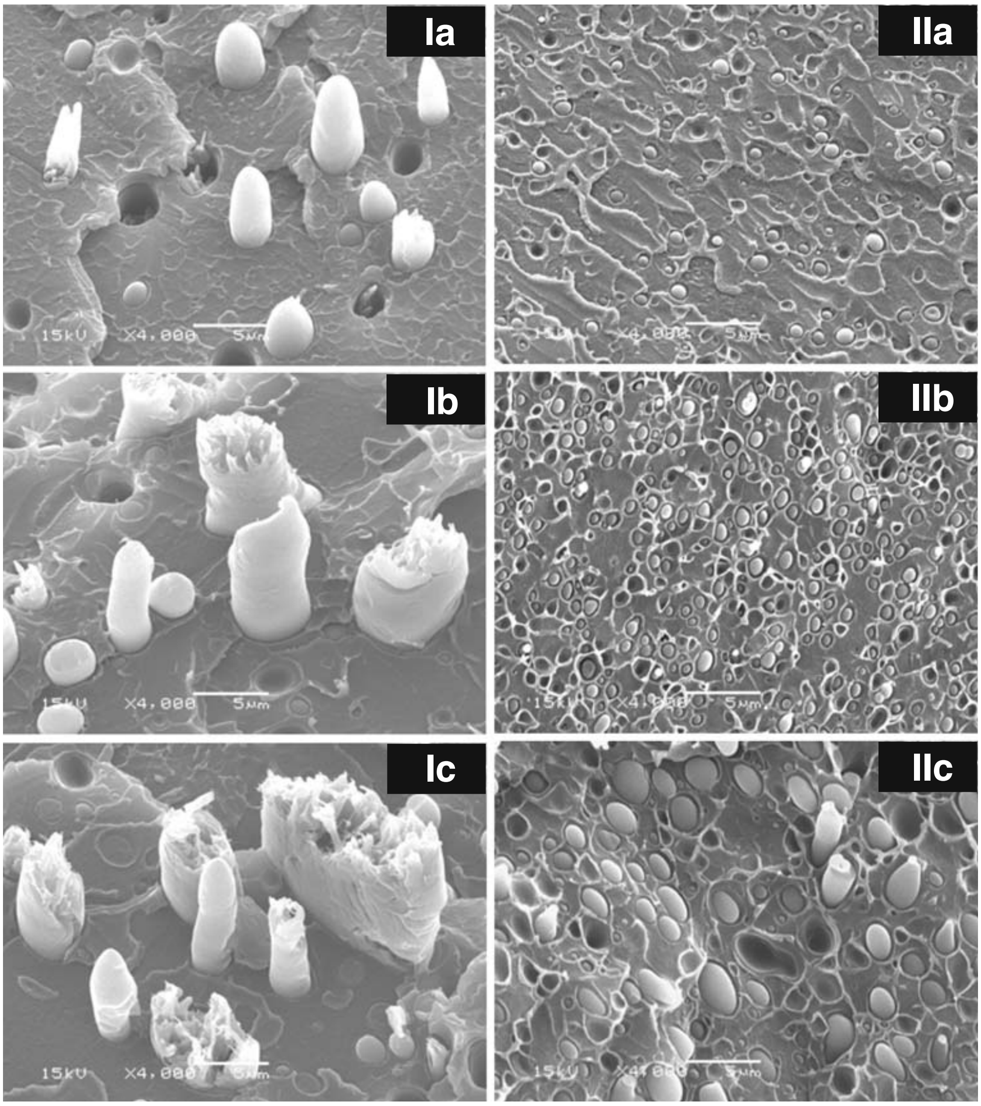

Fig. 5 SEM micrographs of the fracture surface for LCP/PS (*column I*) and rPET/PS (*column II*) blends containing *a* 10, *b* 20 and *c* 30 wt.% dispersed phase

dispersed-phase domains 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 by [25]

$$\mathrm{Ca} = \frac{\eta_{\mathrm{m}}\,\dot{\gamma}}{(\sigma/b)} \qquad (1)$$

where η_{m} is the viscosity of the matrix; $\dot{\gamma}$, the shear rate; b, the initial diameter of dispersed droplets; and σ the interfacial tension between the matrix and dispersed phase. In the simple shear flow of Newtonian fluids, a dispersed droplets will be elongated if $\mathrm{Ca}>0.5$, indicating that the ratio of shear stress $(\eta_{\mathrm{m}}\,\dot{\gamma})$ should be larger than a half of the interfacial energy [25]. The influence of the capillary number on the stability of the dispersed phases especially for LCP morphology has been studied by a number of researchers [26, 27]. The results of their studies indicate the influence of both viscous and interfacial forces on the final morphology, confirming the importance of Capillary number. In the case of rPET/PS system, even the viscosity ratio is lower than 0.15, the fibrillation of the rPET domains is not observed in as-extruded strand. According to Eq. 1, one may propose that the interfacial tension of this blend is relatively high. In addition, the dispersed phase-pullout feature which reveals poor interaction at the interface is observed for both blend systems because these blend systems are immiscible. This is an important requirement for the production of in situ microfibrillar-reinforced composites.

Thermal decomposition behavior

Normally, polymers must encounter elevated temperatures at almost every stage in manufacturing, compounding, and processing stages, in service, and during repairing step. Therefore, an 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 LCP and rPET on thermal decomposition of LCP/PS and rPET/PS blends. The dynamic TG curves of the two blend systems are presented in Fig. 6. The TG measurements were carried out in nitrogen and in air at a heating rate of 10°C/min. The TG results of LCP/PS blends (Fig. 6IA) obtained in nitrogen will be considered first. The nonisothermal TG profile of

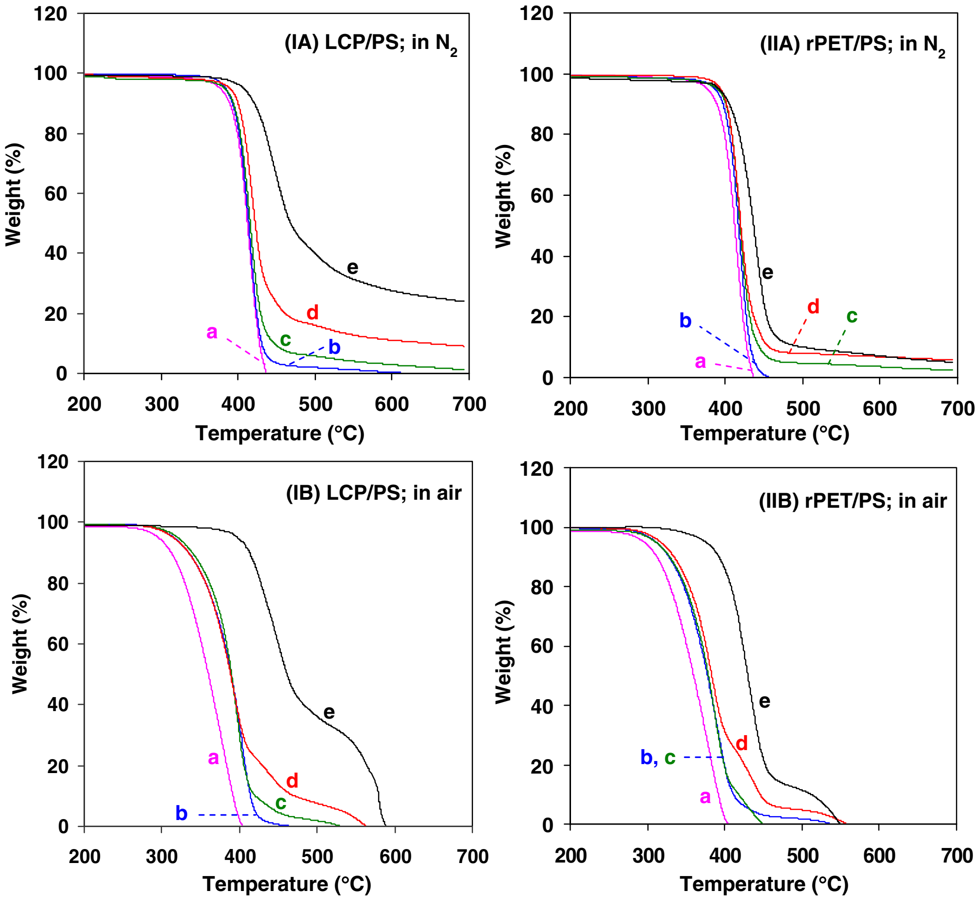

Fig. 6 Dynamic TG curves of LCP/PS (*column I*) and rPET/PS (*column II*) blends containing *a* 0, *b* 10, *c* 20, *d* 30 and *e* 100 wt.% LCP or rPET at a heating rate of 10°C/min in nitrogen (*row A*) and in air (*row B*)

PS reveals only a single weight-loss step at the temperature range around 380–450 °C which corresponds to the chain scission followed by depolymerization and the formation of the main evolved products, styrene monomer, dimer and trimer [28, 29]. In the case of LCP, the first major degradation mainly occurs at PET block, whereas the second minor degradation process could be attributed to the degradation of HBA block [30, 31]. Although the blend system may be complicated due to the presence of many copolymer components, a single degradation step similar to the neat PS matrix is observed for the blends containing 10–30 wt.% LCP. Although the thermal stability of LCP is much higher than that of the neat PS, the thermal resistance of the blends in nitrogen is not significantly affected by LCP loading. This result is similar to those of the in situ elastomer composite when styrenic or polyolefinic based thermoplastic elastomer (TPE) was used as the base polymers, as reported by the authors [24, 32]. Under dynamic heating in air (Fig. 6IB), a single decomposition process of PS that occurs between 250 and 400 °C of PS is observed. The fact that PS degrades at a lower temperature in air than it does in nitrogen is a properly found in many polymers. This appears to occur as a result of switching the limiting step from random scission to decomposition of the hydroperoxide radical, which occur with a lower activation energy [29]. Interestingly, the incorporation of LCP into PS effectively enhances the thermal stability in air more than in nitrogen. This result agrees well with that of the styrenic based TPE in situ reinforced with LCP investigated by the authors [24]. However, the results of thermal stability of LCP/PS blends presented here are different from those of LCP/polyolefinic based TPE system which a slight improvement in thermal resistance is observed with LCP loadings. These results suggest that although the thermal stability of LCP is much higher than those of the polymer matrices, an improvement in thermal stability of the final in situ composite is not only contributed from thermally stable LCP but also the inherent characteristics of the polymer matrix.

In the case of rPET/PS blending system in nitrogen (Fig. 6IIA), the single weight-loss are observed for all neat polymers and the blends at 360–460 °C. Several studies have been conducted on the thermal degradation products of PET [33–35], which suggests that the thermal degradation of PET is initiated by chain scission of ester-linkage, yielding carboxyl and vinyl ester groups. In air (Fig. 6IIB), at least two weight-loss steps are observed for all blends and PET indicating that the degradation process is more complex in air than in nitrogen. To clearly compare the dispersed phase-content dependence of thermal stability for the two types of blends in more quantitative way, the thermal decomposition parameters in nitrogen and in air are compared and summarized in Table 1. T_{onset} represents the onset degradation temperature. T_{max} represents the temperature at the maximum weight-loss rate, $(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max}}$. The subscripts 1 and 2 represent the first stage and the second stage of thermal degradation, respectively. It is seen that T_{onset} and T_{max} of all polymers are higher in nitrogen than in air. In fact, 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. T_{max1} of both systems seems to mostly increase with addition of the dispersed phases indicating the efficiency of thermally stabilized dispersed phase. At the same composition in nitrogen, T_{max1} of LCP-containing blends is comparable to that of the corresponding rPET-containing blends. It is noticed that at the same composi-

Table 1 Nonisothermal decomposition characteristics of LCP/PS and rPET/PS blends in nitrogen and in air

LCP or rPET content (wt.%)	LCP/PS blending system						rPET/PS blending system					
	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	$(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max1}}$ (%/min)	$(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max2}}$ (%/min)	Char yield at 600 °C (wt.%)	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	$(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max1}}$ (%/min)	$(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{max2}}$ (%/min)	Char yield at 600 °C (wt.%)
In nitrogen												
0	396	415	–	29.2	–	0.00	396	415	–	29.2	–	0.00
10	398	417	–	29.8	–	0.03	403	410	–	31.3	–	0.00
20	400	417	–	27.1	–	0.25	404	421	–	30.0	–	0.30
30	403	420	–	23.2	–	1.05	403	419	–	27.6	–	0.57
100	419	448	–	10.5	–	27.6	414	441	–	20.8	–	7.13
In air												
0	324	378	546	12.9	0.67	0.00	324	378	546	12.9	0.67	0.00
10	376	401	532	24.1	0.64	0.00	343	392	544	14.1	0.76	0.00
20	366	397	554	19.4	1.50	0.00	349	391	538	15.9	1.26	0.00
30	351	395	567	14.1	2.38	0.00	347	382	551	13.5	1.34	0.00
100	410	449	573	9.58	19.8	0.00	399	433	553	16.3	5.16	0.00

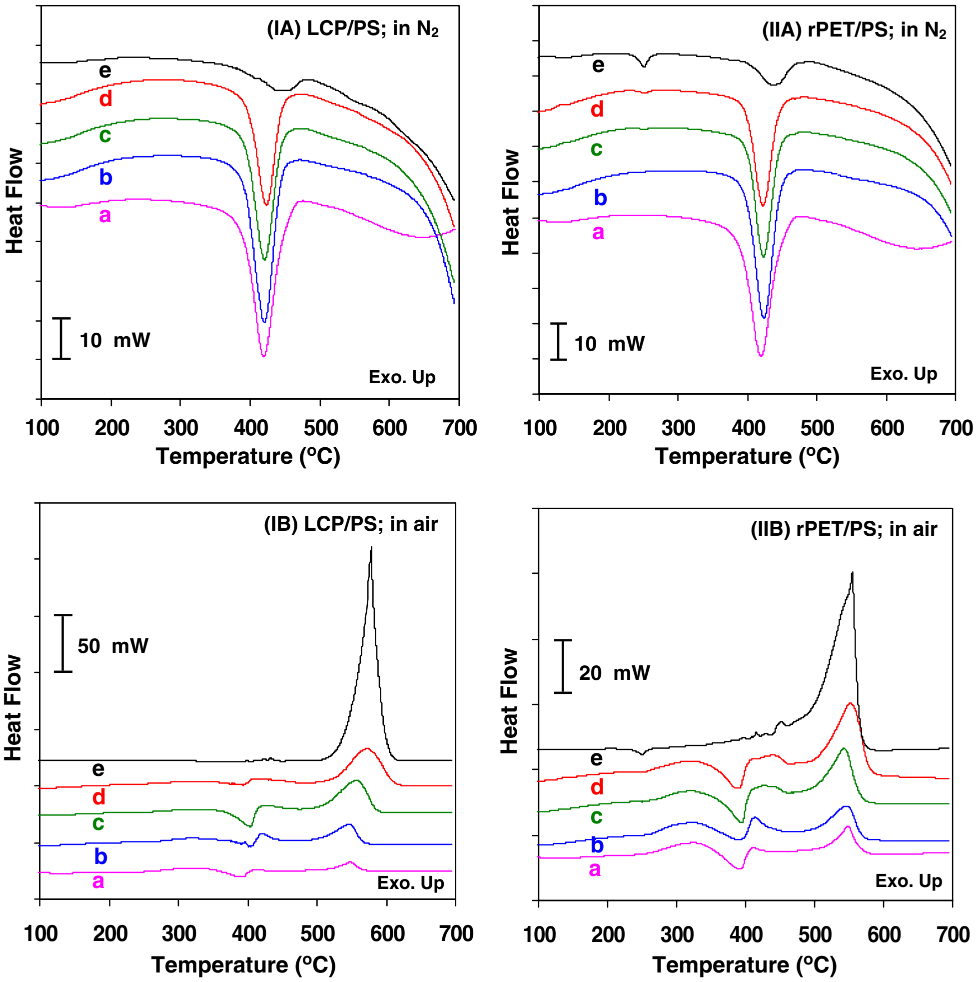

Fig. 7 Simultaneous DSC curves of LCP/PS (*column I*) and rPET/PS (*column II*) blends containing *a* 0, *b* 10, *c* 20, *d* 30 and *e* 100 wt.% LCP or rPET at a heating rate of 10°C/min in nitrogen (*row A*) and in air (*row B*)

tion, $(d\alpha/dt)_{max}$ of all polymers are wholly higher in nitrogen than in air. By comparing between the two types of the blends in nitrogen, $(d\alpha/dt)_{max}$ of rPET-containing blend is higher than that of the corresponding LCP-containing blend. Contrarily in air, $d\alpha/dt)_{max}$ of rPET-containing blend is lower than that of the corresponding LCP-containing blend. Note that, in air, $(d\alpha/dt)_{max2}$ of the LCP and rPET dispersed phases are much higher than that of the matrix phase.

For LCP/PS blend system, no char residues at 600 °C were left for the neat PS whereas the amount of char residues increases with increasing LCP contents. The increase in char residues mainly arises from the increase in HBA block (by increasing amount of LCP content) which will decrease the number of hydrogen atoms and retard the formation of volatile degraded products [36]. However, the amount of char residues is mostly found to be higher in LCP/PS than in rPET/PS blends when compared at the same composition. Note that, for both blend systems in air, no char residues of the neat polymers and the blends were left within the experimental temperature being studied.

Simultaneous DSC data of thermal decomposition

Simultaneous DSC traces and DSC data for thermal decomposition of PS, LCP, rPET and the blends are shown in Fig. 7 and Table 2, respectively. T_m and ΔH_m represent the melting temperature and melting enthalpy, respectively, whereas T_d and ΔH_d represent the peak temperature and the enthalpy associated with thermal degradation process. Subscripts 1 and 2 correspond to the first and the second peaks, respectively. It is seen that the DSC profiles of the samples are different in nitrogen and in air, arising from the different degradation mechanisms. The DSC curves of PS and LCP in nitrogen (Fig. 7IA) show a degradation endotherm which is a characteristic of typical depolymerized mechanisms. The DSC traces of PS and LCP in nitrogen have a well-defined endothermic peak centered at 420 and 436 °C, respectively which is near the region of maximum weight loss in the TGA data. In the case of rPET blend system in nitrogen (Fig. 7IIA), the endothermic peak associated with the fusion of the crystalline fraction is observed at about 251 °C. In addition, the largest endothermic peak of rPET is observed at about 437 °C

Table 2 Simultaneous DSC data of LCP/PS and rPET/PS blends under thermal degradation in nitrogen and in air

LCP or rPET content (wt.%)	LCP/PS blending system				rPET/PS blending system			
	T_m (°C)	ΔH_m (kJ/g)	T_{d1}/T_{d2} (°C)	$\Delta H_{d1}/\Delta H_{d2}$ (kJ/g)	T_m (°C)	ΔH_m (kJ/g)	T_{d1}/T_{d2} (°C)	$\Delta H_{d1}/\Delta H_{d2}$ (kJ/g)
In nitrogen								
0	–	–	420/–	1.05/–	–	–	420/–	1.00/–
10	–	–	420/–	0.69/–	–	–	424/–	0.57/–
20	–	–	420/–	0.55/–	–	–	423/–	0.67/–
30	–	–	423/–	0.42/–	252	0.06	423/–	0.74/–
100	–	–	436/–	0.12/–	251	0.04	437/–	0.20/–
In air								
0	–	–	390/548	0.35/0.40	–	–	390/548	0.35/0.40
10	–	–	405/547	0.54/0.81	–	–	391/546	0.40/0.57
20	–	–	403/557	0.60/1.41	–	–	393/543	0.54/0.91
30	–	–	394/573	0.22/2.48	–	–	398/552	0.42/1.15
100	–	–	–/579	–/0.67	251	0.04	–/555	–/3.18

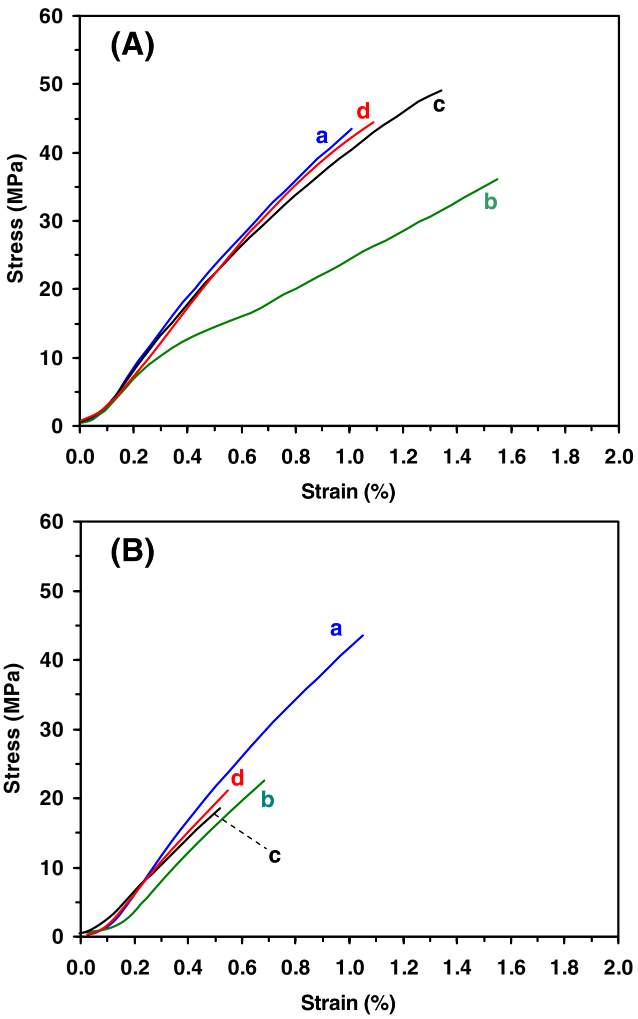

Fig. 8 Stress-strain curves at 25 °C for LCP/PS (**A**) and rPET/PS (**B**) blends containing *a* 0, *b* 10, *c* 20 and *d* 30 wt.% LCP or rPET

corresponding to the thermal degradation process of rPET. Although the degradation temperatures of rPET and LCP dispersed phases are higher than that of the neat PS, the incorporation of dispersed phases into PS does not significantly influence the degradation temperature (T_d) of the blend in nitrogen. As seen from Table 2, the enthalpy of thermal decomposition (ΔH_d) of rPET, LCP and their blends are lower than that of the neat PS matrix in nitrogen. Under heating in air, PS exhibits an endotherm at 390 °C and a small exothermic peak is also observed at 548 °C. It is seen that, in air, T_d and ΔH_d of the blends mostly increased with LCP or rPET loadings. This may contribute from the relatively higher T_d and ΔH_d values of both dispersed phase when compared with that of the neat PS matrix.

Tensile properties

Figure 8 displays the stress-strain curves of the blend extruded strands for the LCP/PS and rPET/PS systems and stress at 0.5% strain, tensile strength and elongation at break of all samples are shown in Table 3. The blend

Table 3 Tensile properties at 25°C of LCP/PS and rPET/PS extruded strands containing various LCP and rPET contents

Sample code	Stress at 0.5% strain (MPa)	Tensile strength (MPa)	Elongation at break (%)
PS	23.8±5.2	45.1±6.7	0.93±0.12
PS-10LCP	14.6±3.8	38.4±3.7	1.6±0.32
PS-20LCP	22.5±4.2	49.6±7.2	1.3±0.55
PS-30LCP	22.6±3.6	46.6±2.4	1.1±0.20
PS-10rPET	16.4±3.7	20.1±4.2	0.65±0.04
PS-20rPET	17.6±3.1	18.5±5.1	0.53±0.10
PS-30rPET	18.5±5.3	15.5±6.3	0.58±0.20

extruded strands contain 0–30 wt.% LCP or rPET. The stress reported here is the nominal (engineering) stress, that is, the force divided by the cross-section area of the initial undeformed state. We will first consider the LCP/PS blend system. Under uniaxial stretching, the neat PS behaves like hard and brittle materials. It is interesting to note that, at the strain >0.2%, the stress of the blend containing 10% LCP is clearly lower than that of the neat PS. At higher LCP concentration, the stress of the extruded strands and the neat PS are comparable. The tensile strength (maximum stress) of the neat PS and the blends lie between about 47–50 MPa and the blends with 20 wt.% LCP shows the highest value of tensile strength compared among all samples examined. In addition, the elongation at break (maximum strain) of the blend containing 10 wt.% LCP is somewhat higher than that of the neat PS matrix.

In the case of rPET/PS blend system, the stress at 0.5% strain and tensile strength of all rPET-containing blends are comparable and much lower than that of the neat PS. At high strain (>0.3%), the stress of the blend containing 10 wt.% rPET is lower than that of the neat PS. The tensile strength of rPET-containing blends in the range of about 15–20 MPa are observed which are about half lower than that of the neat PS. Note that, at the same composition, the tensile strength and elongation break of the rPET-containing blend are lower than that of the corresponding LCP-containing blends.

Generally, the mechanical properties of the in situ composite are expected to be improved by optimum addition and/or enhancing the ability of fibrillation of dispersed phase. The low stress observed in the blend with low LCP content (10 wt.% LCP) is evident from the droplet and ellipsoidal morphology of LCP domains as observed from SEM. With increasing LCP content, the good fibrillation of LCP dispersed phase are observed and results in an enhancement of tensile properties. However, some coalescence of LCP domains occur with addition of LCP content up to 30 wt.% or higher, resulting in the reduction of extensibility [22–24]. For rPET-containing blend system, as evident from the droplet morphology of rPET dispersed phase, the tensile properties of all blends are mostly lower than those of the neat matrix. This indicates the mechanical properties dependence of dispersed-phase morphology, which in turn depends on the dispersed-phase content. On the basis of the results obtained from the present study, the mechanical of PS in situ reinforced with LCP or rPET are expected to be improved to approach those of the conventional composite by enhancing the fibrillation of the dispersed phases 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 some properties.

Conclusion

In this work, LCP/PS and rPET/PS in situ microfibillar-reinforced composites were prepared using extrusion process. The influence of LCP and rPET dispersed phases on rheology, morphology and thermal stability of the elastomer composites was investigated. The incorporation of rPET into PS significantly reduces the melt viscosity of the blend system similar to that of LCP. The fibrillar morphology of dispersed phase can only be obtained in as-extruded strand of LCP/PS blend system. For rPET/PS system, rPET domains appear as small droplets even the viscosity ratio of this blend system is relatively lower than that of LCP/PS system. The incorporation of LCP or rPET into PS matrix is found to retard the thermal degradation significantly in air. The obtained results suggest the high potential of rPET as the processing aid by bringing down the melt viscosity of the blend system and the thermally stable reinforcing-material similar to LCP. At the same composition, the LCP-containing blends showed better tensile properties when compared with the corresponding rPET-containing blends. The results of tensile properties indicate the mechanical properties dependence of dispersed-phase morphology, which in turn depend on the amount of the dispersed phase.

Acknowledgements The authors gratefully acknowledge the financial support by the Office of Commission on Higher Education and Thailand Research Fund (contract grant number, MRG5080415). Financial support from Center of Excellence for Innovation in Chemistry is also gratefully acknowledged. Finally, the authors would like to thank Professor Sauvarop Bualek-Limcharoen for the gift of Rodrun LC3000 liquid crystalline polymer.

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