

Novel ternary blends of natural rubber/linear low-density polyethylene/thermoplastic starch: influence of epoxide level of epoxidized natural rubber on blend properties

Skulrat Pichaiyut¹  · Suwaluk Wisunthorn¹ · Chattrapa Thongpet¹ · Charoen Nakason¹

Received: 17 February 2016 / Accepted: 2 July 2016 / Published online: 11 July 2016
© Iran Polymer and Petrochemical Institute 2016

Abstract Novel degradable materials based on ternary blends of natural rubber (NR)/linear low-density polyethylene (LLDPE)/thermoplastic starch (TPS) were prepared via simple blending technique using three different types of natural rubber (i.e., unmodified natural rubber (RSS#3) and ENR with 25 and 50 mol% epoxide). The evolution of co-continuous phase morphology was first clarified for 50/50: NR/LLDPE blend. Then, 10 wt% of TPS was added to form 50/40/10: NR/LLDPE/TPS ternary blend, where TPS was the particulate dispersed phase in the NR/LLDPE matrix. The smallest TPS particles were observed in the ENR-50/LLDPE blend. This might be attributed to the chemical interactions of polar functional groups in ENR and TPS that enhanced their interfacial adhesion. We found that ternary blend of ENR-50/LLDPE/TPS exhibited higher 100 % modulus, tensile strength, hardness, storage modulus, complex viscosity and thermal properties compared with those of ENR-25/LLDPE/TPS and RSS#3/LLDPE/TPS ternary blends. Furthermore, lower melting temperature (T_m) and heat of crystallization of LLDPE (ΔH) were observed in ternary blend of ENR-50/LLDPE/TPS compared to the other ternary blends. Also, neat TPS exhibited the fastest biodegradation by weight loss during burial in soil for 2 or 6 months, while the ternary blends of NR/LLDPE/TPS exhibited higher weight loss compared to the neat NR and LLDPE. The lower weight loss of the ternary blends with ENR was likely due to the stronger chemical interfacial interactions. This proved that the blend

with ENR had lower biodegradability than the blend with unmodified NR.

Keywords Thermoplastic elastomer · Biodegradation · Ternary blends · Natural rubber · Thermoplastic starch · Epoxidized natural rubber

Introduction

Thermoplastic elastomers (TPEs) are polymeric materials that combine elastomer and thermoplastic characteristics. They are probably the fastest growing sector in the polymer market. An important class of TPEs is prepared by blending rubber and thermoplastics under proper control of blend morphology. This type of TPEs has received considerable attention in the recent years due to their relatively low manufacturing costs with plastic processing equipment, and their properties that match various applications [1]. Typically, synthetic rubbers have been used as the elastomeric component in TPEs. However, also natural rubber can be used to prepare thermoplastic elastomer materials known as thermoplastic natural rubbers (TPNRs) [2–4]. The main benefits of TPNRs are their green, environmentally friendly character and their renewable raw materials. Natural rubber does not rely on petrochemicals; it has intrinsically good mechanical properties, good elasticity, low build-up of heat from flexing and cyclic deformation, high resistance to tearing, good dynamic performance and low level of damping [5].

The use of natural rubbers (NR) in TPE blends with optimal choices of the thermoplastics may lead to TPNRs with superior properties. Apart from unmodified NR, modified NRs or NR derivatives have been used to prepare TPNRs. Generally, the modified NR has been developed to

✉ Skulrat Pichaiyut
skulrat.p@psu.ac.th

¹ Department of Rubber Technology, Faculty of Science and Industrial Technology, Prince of Songkla University, Surat Thani Campus, Surat Thani 84000, Thailand

overcome the drawbacks of NR, which include poor heat and solvent resistance, and polarity and adhesion properties. The two most frequently used modified NRs are epoxidized natural rubber (ENR) and maleated natural rubber (MNR). The ENR has been widely used to prepare TPNR materials by blending with poly(vinyl chloride) (PVC) [6, 7], high-density polyethylene (HDPE) [8, 9], polypropylene (PP) [10, 11], polyamide-12 (PA-12) [12], ethylene–vinyl acetate (EVA) [13], poly(methyl methacrylate) [14], thermoplastic polyurethane (TPU) [15, 16], and copolyester (COPE) [17]. On the other hand, the MNR has also been used to prepare TPNRs by blending with high-density polyethylene [18], polypropylene [19, 20], COPE [21] and copolyamide (COPA) [22]. Other types of modified NR that have been used in TPNRs include natural rubber-g-poly(methyl methacrylate) [23] and NR-g-poly(dimethyl(methacryloyloxymethyl) phosphonate) [24].

Recently, environmentally friendly and degradable materials based on blending thermoplastics and natural polymers have received increasing attention [25]. One of the most frequently used raw materials in degradable formulations is starch or starch-based materials. Starch is also a natural and renewable product from a great variety of crops. Its thermoplastic derivative (TPS) is generally prepared by plasticization of native starch at high temperature under shear [26]. The main advantages of TPS are biodegradability and renewable character. Also, TPS can be blended with other polymers to tailor the properties, and this has been tried with various thermoplastics, such as poly(lactic acid) (PLA) [27], poly(ϵ -caprolactone) (PCL) [28], low-density polyethylene (LDPE) [29, 30] and EVA [31].

Thermoplastic derivative of starch (TPS) has also been blended with natural rubber in recent years [32–34]. It was found that adding TPS into the blends typically gave inferior mechanical properties, in particular, tensile strength and elongation-at-break, due to the incompatibility of hydrophilic starch and hydrophobic rubber, which leads to the poor dispersion of starch [35]. Therefore, blend compatibilizers have been applied. For example, polyethylene-grafted maleic anhydride (PE-g-MA) was used as a compatibilizer in HDPE/NR/TPS ternary blends [36]. It was found that mechanical properties improved and the dispersed TPS particles were smaller in the presence of compatibilizer. Also, a chemically modified NR, namely oxidized natural rubber (ONR), was used in a blend with TPS [37]. It was found that plasticity improved due to the good interfacial compatibility of ONR and TPS, and this enhanced water resistance and decreased brittleness.

This work is motivated to development of degradable material; we aim to prepare novel degradable TPE by ternary blends with rubber/LLDPE/TPS by a simple blend technique (i.e., without curatives) with fixed proportions of rubber/LLDPE/TPS blends of 50/40/10 wt%. Three different types

of natural rubber (i.e., ribbed smoked sheets (RSS#3) and epoxidized natural rubber (ENR) with 25 and 50 mol% epoxide) were used in ternary blends. Modified NR in the form of ENR should improve compatibility and related properties of the blends due to the polarity of ENR and TPS phases. Dynamic, thermal, morphological, and biodegradability properties of the ternary blends were investigated, as well.

Experimental

Materials

Two types of natural rubber; ribbed smoked sheets (RSS#3) and ENR were exploited in this work. The RSS#3 was purchased from a local factory operated by Na Born Farmer Cooperation (Nakorn Si Thammarat, Thailand). ENRs with 25 and 50 mol% epoxide (i.e., ENR-25 and ENR-50) were prepared in laboratory by reacting natural rubber high ammonia (HA) concentrated latex with performic acid. The HA concentrated NR latex with ~60 wt% dry rubber content (DRC) was manufactured by Inter Rubber Latex Co., Ltd (Surat Thani, Thailand). The in situ performic epoxidation was performed by first reacting formic acid with hydrogen peroxide (manufactured by Riedel-de Haen, Seelze, Germany) to generate performic acid. The HA concentrated NR latex was then reacted with the performic acid using preparation and characterization procedures, as described elsewhere [38]. Injection molding grade LLDPE, L2020 FA with density 0.92 g/cm³ and melt flow index (MFI) of 20.0 g/10 min, was used as the thermoplastic blend component. It was manufactured by Thai Polyethylene, Co., Ltd. (Rayong, Thailand). Cassava starch was used to prepare the TPS. This food grade material was manufactured by Kriangkrai Co., Ltd. (Nakorn Prathom, Thailand). Glycerol with density of 1.26 g/cm³ was used as a plasticizer to prepare the TPS; it was manufactured by Univar Co., Ltd. (Seattle, USA).

Preparation of thermoplastic starch

Cassava starch was first dried at 60 °C for 24 h to eliminate the moisture. It was then mixed with 30 wt% of glycerol using a kitchen blender with a stirring speed of 1000 rpm for 10 min. Then, the cassava starch–glycerol mix was conditioned in a desiccator at room temperature for 24 h. It was then further mixed in an internal mixer with a 500-cm³ mixing chamber (Charoen-Tat Co., Ltd., Bangkok, Thailand) at 140 °C and 60 rpm. Mixing was continued until the material was homogeneous which generally took about 6 min. The material was then removed from the mixing chamber and cooled down to room temperature. Mechanical properties, thermal properties, and biodegradability properties of the TPS were then investigated.

Table 1 Mixing schedule to prepare 50/40/10 natural rubber/LLDPE/TPS ternary blends

Mixing step	Mixing time (min)
Warm LLDPE/TPS without rotation	0
Mix LLDPE/TPS at a rotor speed of 60 rpm	6
Adding natural rubber ^a	8
Dump	16

^a RSS#3 or ENRs

Preparation of NR/LLDPE/TPS ternary blends

Linear low-density polyethylene (LLDPE), NR and TPS were first dried in a hot air oven at 40 °C for 24 h. Ternary NR/LLDPE/TPS blends with the fixed proportions 50/40/10 wt% were then prepared. In this work, three different types of rubber were used: unmodified NR (RSS#3), ENR-25 and ENR-50. The mixing schedule used to prepare the ternary blends is shown in Table 1. The LLDPE and TPS were first incorporated and conditioned in the mixing chamber without rotation for about 6 min to preheat these materials. The LLDPE and TPS were then mixed at 160 °C and 60 rpm rotor speed for another 2 min before adding the natural rubber. Blending was then continued for another 8 min. The blend product was then sheeted out on a two-roll mill and fabricated to 2-mm-thick sheets by compression molding (Charoen-Tat Co., Ltd., Bangkok, Thailand) at 160 °C under 1500 psi pressure for 3 min. The sheets were then cooled down by water circulation under the same pressure for 20 min. Dumbbell-shaped test specimens were prepared by die cutting for further testing and characterization.

Morphological characterization

Morphological characterization was performed using a scanning electron microscope (SEM) (FEI Quanta 400, FEI Company, Hillsboro, USA). The specimens were first cryo-fractured in liquid nitrogen to create the fresh surfaces and to prevent phase deformations during the fracturing. The TPS phase in the blends was then preferentially removed by extraction with 37 % hydrochloric acid (HCl) at 25 ± 2 °C for 72 h. Also, the rubber phase was removed from some blends by extraction with toluene at 60 ± 2 °C for 72 h.

Mechanical properties

Tensile properties were tested at room temperature at the fixed 500 mm/min extension speed according to ASTM D412, using Hounsfield Tensometer model H 10KS (Hounsfield Test Equipment Co., Ltd., Surrey, England). It is noted that the dumbbell-shaped specimens were prepared from compression-molded sheets. The stress–strain curves

were captured; also, 100 % modulus, tensile strength and elongation-at-break were estimated based on the curves. The Young's modulus was also determined from a slope of the stress–strain curve in a linear elastic region. In this study, 10 % elongation was used to calculate Young's modulus. The tension set at 100 % elongation was determined at room temperature according to ASTM D412. The samples were kept under fixed 100 % elongation for time intervals of 10 min. Dimensions of the samples were then determined compared to their initial values. Indentation hardness of the samples was tested using an indentation durometer Shore A, according to ASTM D2240.

Thermal properties

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are two thermal characterization techniques exploited to analyze the thermal properties of the neat parent polymers and the natural rubber/LLDPE/TPS ternary blends. The TGA was performed using a PerkinElmer STA600 (New Shelton, USA). A sample of ~5–20 g weight was first placed in the platinum pan under nitrogen atmosphere. The test was then performed under a 10 °C/min heating rate over the temperature range 25–600 °C.

The DSC was performed using a PerkinElmer DSC-7 (New Shelton, USA). A sample of ~3–10 g weight was first heated at 10 °C/min rate from 25 to 180 °C, and was then left at this temperature for 2 min to eliminate its thermal history. The sample was subsequently cooled down to –100 °C at 10 °C/min rate. A second heating was performed from –100 to 180 °C at 10 °C/min rate, during which the data were captured.

Dynamic properties

Dynamic properties of the NR/LLDPE/TPS ternary blends were characterized using a rubber process analyzer (RPA 2000, Cuyahoga Falls, USA). Frequency sweeps from 0.02 to 25 Hz were performed at 160 °C and 3 % strain amplitude. The storage modulus (G') and complex viscosity (η^*) of the blends were quantified as functions of oscillation frequency.

Biodegradation test

Biodegradation tests were performed using rectangular 30 × 30 × 1 mm specimens. The test specimens were buried in the soil for 2 and 6 months [39]. Weight losses after the burials were calculated as follows [40]:

$$\text{Weight loss (\%)} = \left[\frac{(W_2 - W_1)}{W_1} \right] \times 100, \quad (1)$$

where W_1 is the initial mass of specimen (g) and W_2 is the mass of specimen after soil burial (g).

Results and discussion

Morphological properties

Before adding TPS into the rubber/LLDPE blend, we needed to assess phase separation and phase continuity in the NR/LLDPE and ENR/LLDPE blends. The types of rubber used to prepare binary blends with LLDPE were unmodified NR (RSS#3) and modified NRs (i.e., ENR-25 and ENR-50).

Figure 1 shows SEM micrographs of the various natural rubber/LLDPE blends at the fixed 50/50 blend ratio after toluene extraction. It can be seen that the phase morphology was co-continuous in all these 50/50 natural rubber/LLDPE blends. Also, it is seen that the RSS#3/LLDPE blend had the finest grain morphology due to the mutual affinity of the blended pair because of hydrophobicity of both polymers.

In the ENR-25/LLDPE, coarser grain morphology was observed due to the hydrophilic ENR-25 that has polar epoxirane rings. In Fig. 1, it is clear that the largest grain morphology was observed in the ENR-50/LLDPE. This was attributed to the ENR-50 having the highest content of polar functional groups and the highest hydrophilicity which made it incompatible with the hydrophobic LLDPE.

Figure 2 shows SEM micrographs of the toluene-extracted 50/40/10 NR/LLDPE/TPS ternary blend with 10 wt% TPS. It can be seen that the NR and LLDPE were still co-continuous with TPS dispersed as spherical particles. Furthermore, smaller TPS particles were observed with polar natural rubbers (i.e., ENR-25 and ENR-50) than with the unmodified NR as shown in the SEM micrographs of Fig. 3. The TPS phase was preferentially removed by extraction with 37 % HCl at 25 ± 2 °C for 72 h; hence, the sample surface had cavities observed by SEM imaging. In Fig. 3, it is clear that the unmodified NR, RSS#3/LLDPE/TPS ternary blends (Fig. 3a) had the largest TPS particles. This might be attributed to poor compatibility of hydrophilic TPS with hydrophobic RSS#3 and LLDPE phases. Therefore, the TPS tended to form agglomerates or larger domains instead of dispersing well in the major phases.

The TPS phase in the ternary blends with ENR-25 (Fig. 3b) and ENR-50 (Fig. 3c) had smaller particles, and the ENR-50/LLDPE/TPS ternary blend had very fine grained dispersion of TPS. This may be due to strong chemical interactions of the polar functional groups in TPS and ENR that enhanced blend compatibility, with possible chemical reactions shown in Scheme 1. The polar functional groups in starch molecules may form covalent

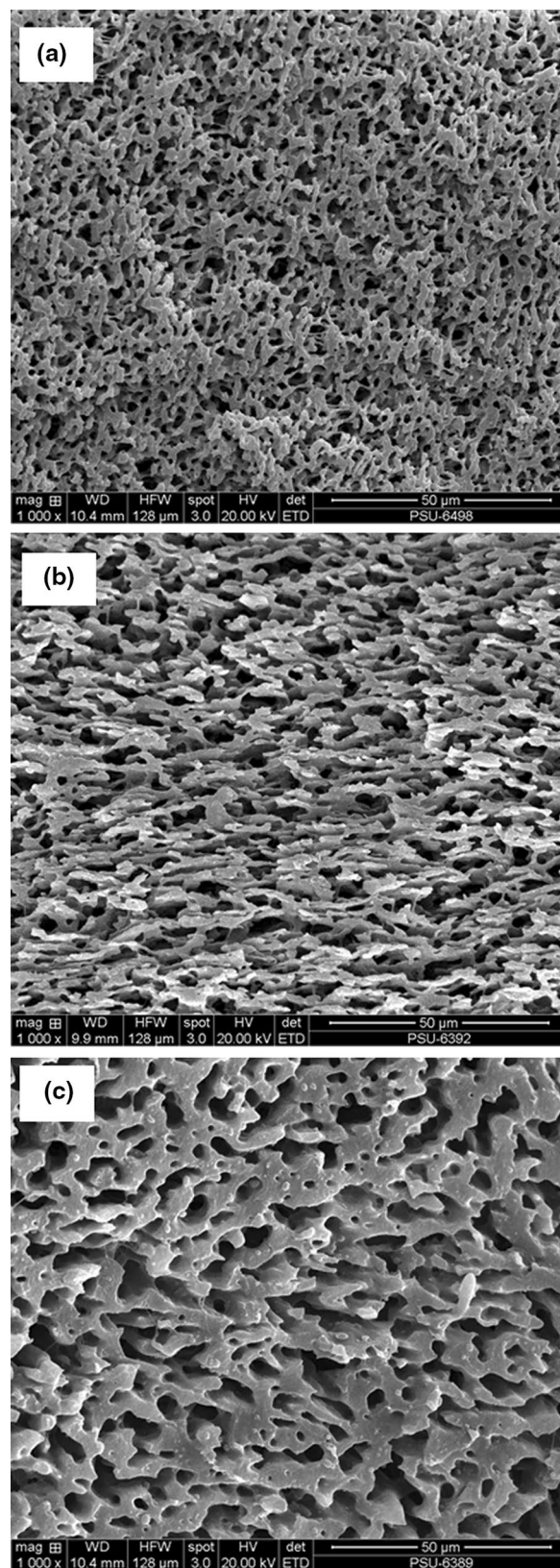


Fig. 1 SEM micrographs of natural rubber/LLDPE blends at the fixed 50/50 blend ratio after toluene extraction: **a** RSS#3/LLDPE/TPS, **b** ENR-25/LLDPE/TPS, and **c** ENR-50/LLDPE/TPS

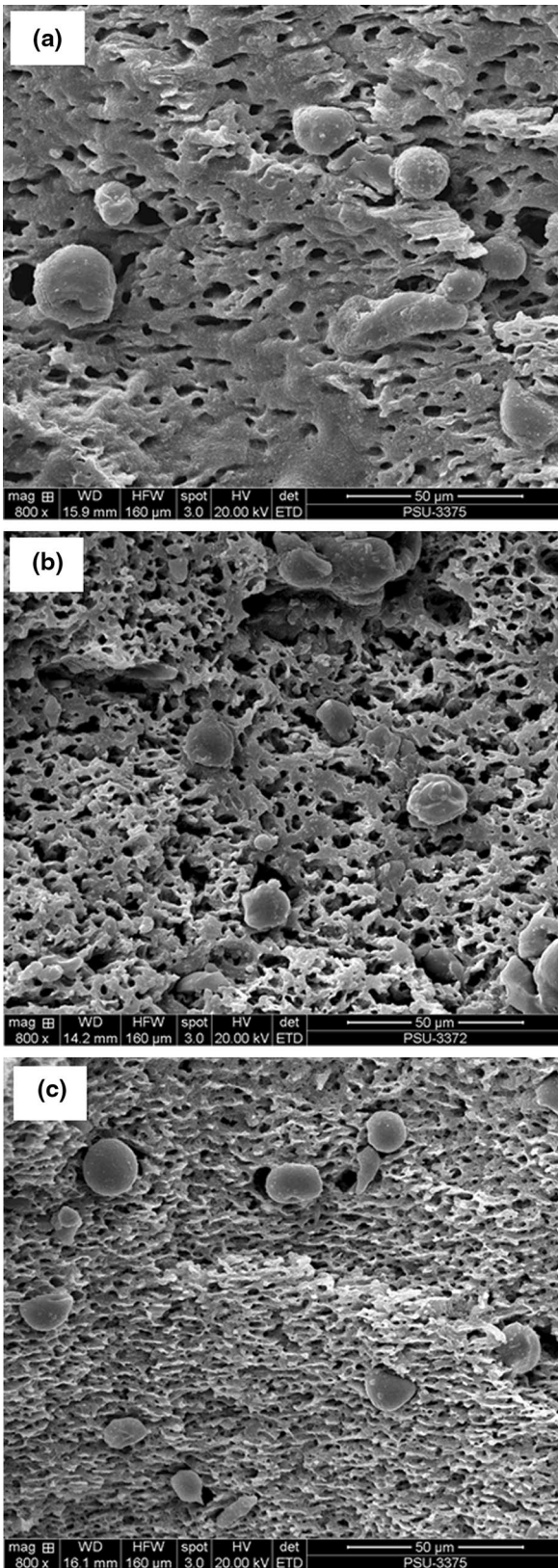


Fig. 2 SEM micrographs of 50/40/10 natural rubber/LLDPE/TPS ternary blends after toluene extraction: **a** RSS#3/LLDPE/TPS, **b** ENR-25/LLDPE/TPS, and **c** ENR-50/LLDPE/TPS

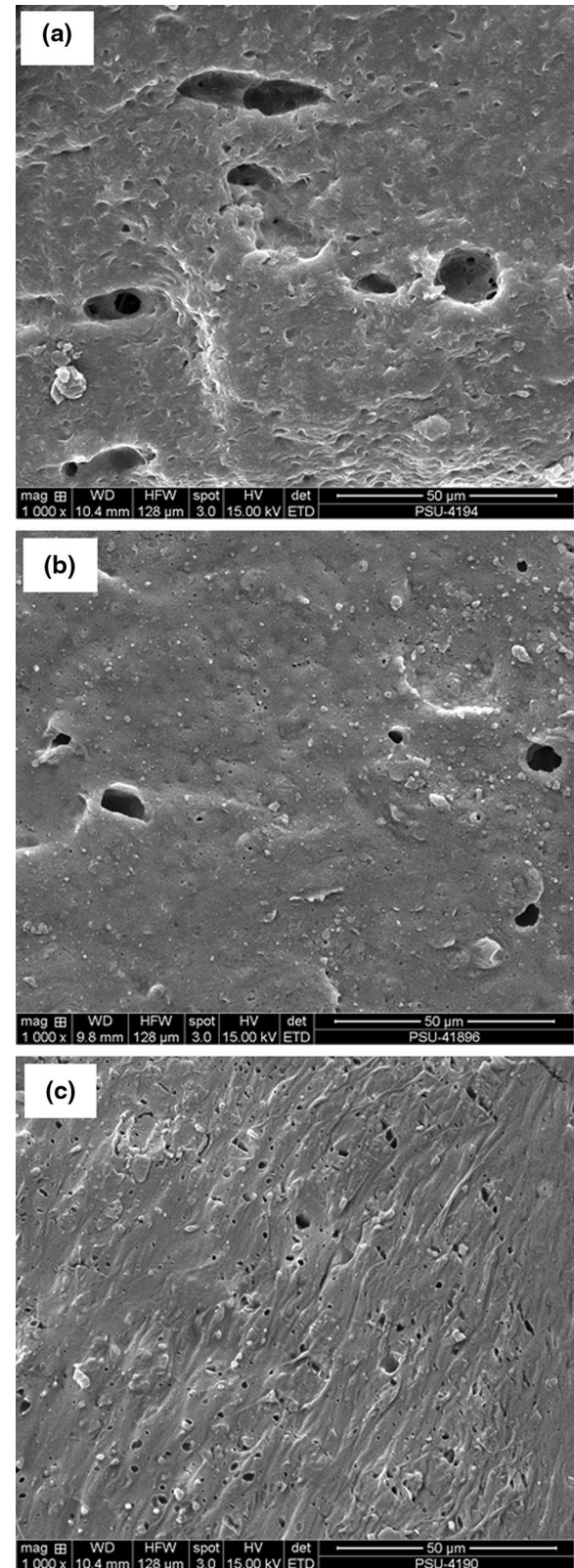
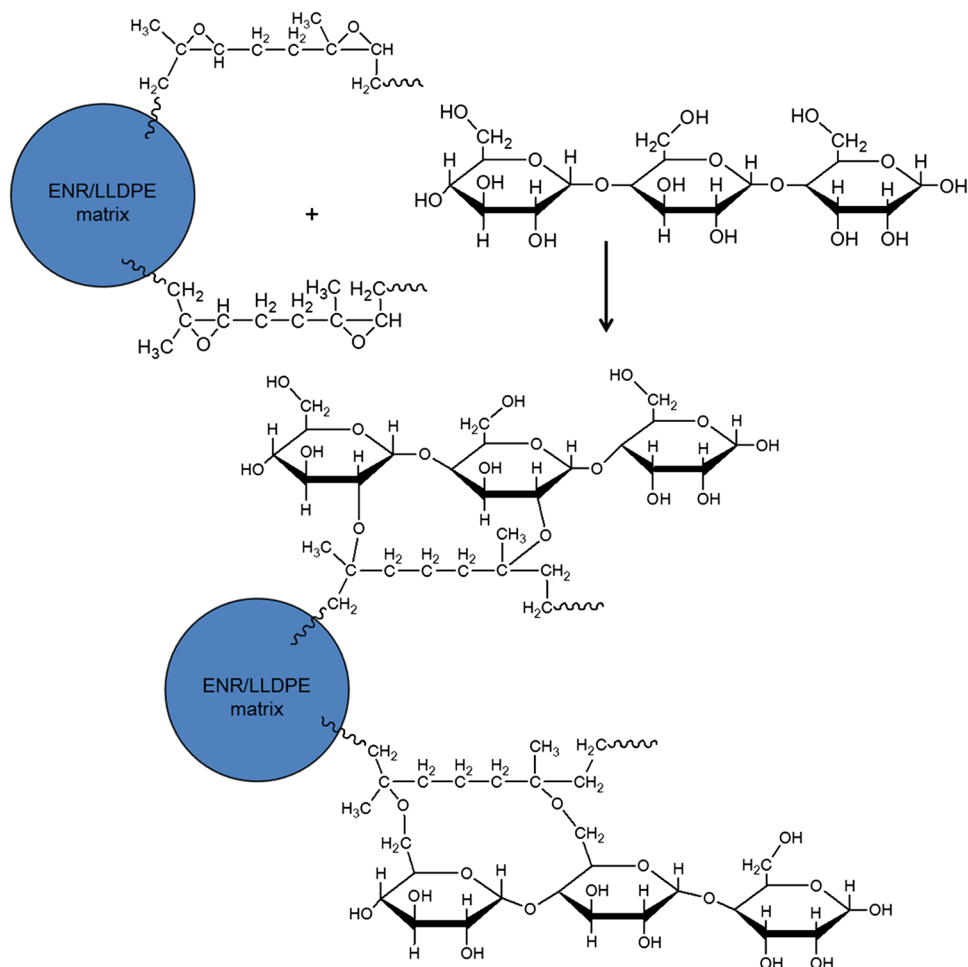


Fig. 3 SEM micrographs of 50/40/10 natural rubber/LLDPE/TPS ternary blends with three types of natural rubber after HCl extraction: **a** RSS#3/LLDPE/TPS, **b** ENR-25/LLDPE/TPS, and **c** ENR-50/LLDPE/TPS

Scheme 1 Chemical reaction routes between TPS and ENR/LLDPE matrix in a ternary blend



bonds with opened rings of epoxidized natural rubber. This caused strong bonding of the matrix and the TPS particles; afterward, that strong shear or elongational stresses were required to break the TPS phase to smaller particles. This is why the ternary blends of ENR-50 exhibited the finest grain morphology of TPS particles.

In Fig. 2, it is also seen that the co-continuous structure of ENR-50/LLDPE/TPS ternary blends was finer than those with ENR-25 or RSS#3. This is attributed to stronger chemical interactions of TPS, ENR-50 and LLDPE phases, which enhanced the blend compatibility. Similar results have been observed with the addition of TPS in NR/HDFPE matrix [36]. It is clear that fine grained co-continuous phase morphology prevailed in the ternary blends with ENR. This was opposite to the binary blends shown in Fig. 1, where RSS#3/LLDPE had the finest and ENR-50/LLDPE had the coarsest morphological structure. It is therefore clear that TPS strongly influenced the evolution of phase morphology. That is, the TPS might behave as a blend compatibilizer promoting the miscibility of the ENR and LLDPE phases that have different polarities. This is indeed why the ENR-50/LLDPE/TPS ternary blends showed the finest and

the RSS#3/LLDPE/TPS ternary blends presented the coarsest grain morphologies, while the ENR-25/LLDPE/TPS ternary blends had an intermediate morphology. It is concluded that the TPS by interacting with the polar functional groups in the rubber matrix plays a very important role in controlling the morphological characteristics and properties, in particular, the grain morphology of the blends.

Mechanical properties

Figure 4 shows stress–strain curves of neat LLDPE, neat TPS, and the ternary blends 50/40/10 ratios of RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS. It can be seen that the neat LLDPE showed the characteristic deformation behavior of a semi-crystalline thermoplastic, with yield stresses at extension beyond 80 %. On the other hand, the neat TPS exhibited softer and poorer mechanical properties in terms of tensile strength, elongation-at-break and moduli. In Fig. 4, it is also seen that ternary blends of natural rubber/LLDPE/TPS had typical stress–strain curves of thermoplastic elastomers. That is, high elongation-at-break, moderate Young's modulus (i.e.,

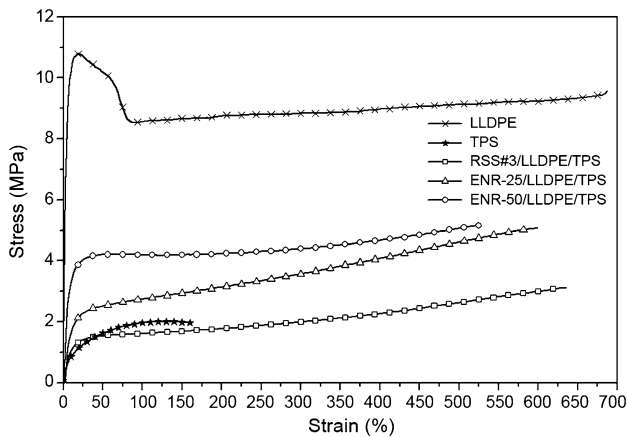


Fig. 4 Stress–strain curves of neat LLDPE, neat TPS, and 50/40/10 ternary blends of RSS#3/LLDPE/TPE, ENR-25/LLDPE/TPE and ENR-50/LLDPE/TPS

the initial slope of the curve) and lower mechanical strength than those of the neat LLDPE. Furthermore, the yield point of the semi-crystalline thermoplastic disappeared.

Therefore, the blend of natural rubber and LLDPE with TPS had reduced stress responses and, hence, degraded mechanical properties (i.e., Young's modulus, 100 % modulus, tensile strength and elongation-at-break) compared with the original properties of the neat LLDPE, as summarized in Table 2. It is seen that ternary blends with the ENRs had superior stiffness and mechanical strength in terms of Young's modulus, 100 % modulus and tensile strength over those with unmodified NR (RSS#3).

Furthermore, increasing the epoxide level in ENR molecules from 25 to 50 mol% enhanced the moduli and tensile strength but reduced the elongation-at-break value. This might be attributed to the strong chemical interactions of polar functional groups in TPS and ENR, which eventually caused the fine grained morphology of the ENR-50/LLDPE/TPS blend. Also, the strong interfacial adhesion led to small TPS particles dispersed in the ENR/LLDPE

matrix (Fig. 2). Nevertheless, in Table 2, it is clear that the ternary blends of ENR showed less elongation-at-break values than the blend with unmodified NR (RSS#3). This might be also due to the chemical interactions of polar functional groups in TPS with oxirane groups in ENR molecules, which enhances the strength properties but limits the extensibility of the blends. In Table 2, it is also seen that the highest indentation hardness (Shore A) was observed for the ternary blends with ENR-50, followed by the ternary blends with ENR-25 and RSS#3 in this order. This might be a combined effect of the intrinsic hardness of the parent polymers and the chemical interactions of polar functional groups in ENR and TPS.

In Table 2, it is also seen that the ternary blends had lower tension set than the neat LLDPE. This indicated the improved rubber elasticity or tendency to recover the original shape after a prolonged deformation. In addition, low tension set or high rubber elasticity was also observed for the ternary blends with ENRs. That is, the blend with ENR-50 exhibited the lowest tension set followed by the blends with ENR-25 and RSS#3. Therefore, the chemical interactions of polar functional groups in TPS and ENR not only provided strength but also enhanced the elastic properties. It is noted that the tension set of neat TPS could not be determined due to rupturing before 100 % extension.

Dynamic properties

Figure 5 shows the storage or elastic modulus (G') as a function of frequency for the neat polymers and the 50/40/10 ratio ternary blends RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS. The storage modulus is a measure of the stored energy, representing the elastic characteristics of deformation. It can be seen that for all samples, the storage modulus increased with the oscillation frequency. This may be due to the shorter time available for molecular relaxations.

Furthermore, in Fig. 5a, at a given oscillating frequency, all the rubber samples (i.e., RSS#3, ENR-25 and ENR-50)

Table 2 Mechanical properties of neat polymers and 50/40/10 natural rubber/LLDPE/TPS blends

Sample code	Young's modulus (MPa)	100 % modulus (MPa)	Tensile strength (MPa)	Elongation-at-break (%)	Hardness (Shore A)	Tension set (%)
Neat LLDPE	64.99 ± 2.54	5.33 ± 0.29	10.62 ± 0.28	673 ± 8.08	90.0 ± 0.50	44.5 ± 0.40
Neat TPS	7.67 ± 1.38	1.97 ± 0.24	1.96 ± 0.24	162 ± 19.60	67.0 ± 0.29	^a
RSS#3/LLDPE/TPS	11.54 ± 1.87	1.61 ± 0.30	3.11 ± 0.31	635 ± 16.16	79.5 ± 0.29	39.5 ± 0.30
ENR-25/LLDPE/TPS	17.83 ± 2.04	2.74 ± 0.25	5.07 ± 0.20	599 ± 17.50	80.0 ± 0.76	39.0 ± 0.30
ENR-50/LLDPE/TPS	34.97 ± 1.98	4.24 ± 0.37	5.13 ± 0.13	528 ± 14.73	82.5 ± 0.29	28.5 ± 0.40

^a Rupture of the sample

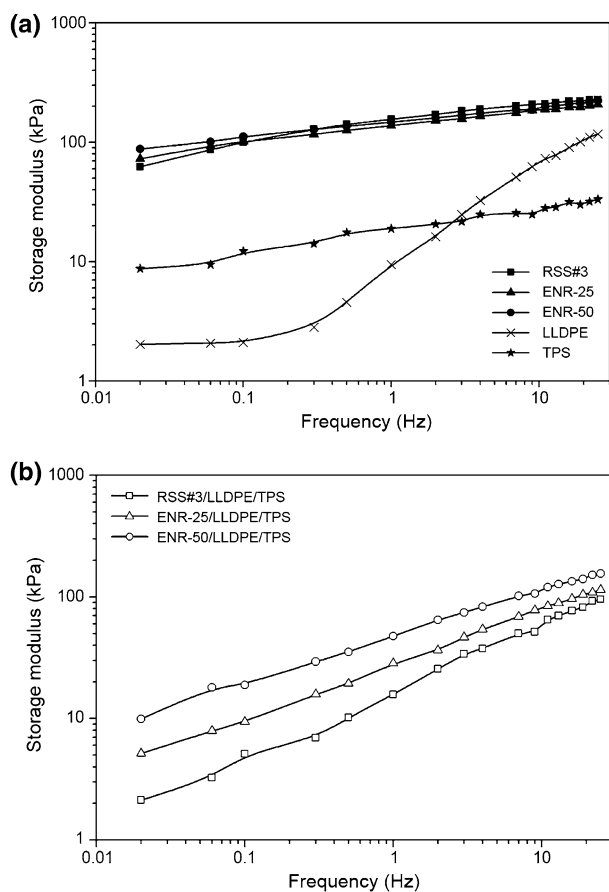


Fig. 5 Storage modulus as a function of frequency for: **a** neat LLDPE, neat TPS, neat RSS#3, neat ENR-25 and ENR-50, and **b** 50/40/10 ternary blends of RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS at 160 °C

have higher storage moduli than the LLDPE and TPS blend components. This indicates the ability of elastic rubber to store energy. In Fig. 5b, the ternary blend with ENR-50 exhibited the highest G' value. This is attributed to the strong interfacial interactions of polar functional groups in TPS and epoxide groups in ENR that caused fine co-continuous structure with small TPS particles dispersed in the matrix (Fig. 2). It is also clear that the G' of natural rubber/LLDPE/TPS blend followed the trend observed in the mechanical properties in terms of Young's modulus, 100 % modulus and tensile strength (Table 2).

Figure 6 shows the complex viscosity as a function of frequency for the neat polymers and the 50/40/10 ternary blends RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS. It can be seen that the complex viscosity decreased with the oscillating frequency, which reflects shear-thinning behavior. It is clear that the neat natural rubbers (i.e., RSS#3, ENR-25 and ENR-50) showed higher viscosity curves than the neat TPS and LLDPE. Furthermore, the neat LLDPE exhibited less shear thinning than the TPS or the rubbers, as it had lower gradient

of the viscosity curve, which caused crossover at 0.85 Hz frequency.

In Fig. 6b, various types of complex viscosity (η) curves are observed for the ternary blends. That is, higher η curves were observed for the ternary blends with ENRs. This was again due to the chemical interactions of polar functional groups in TPS and ENR (Scheme 1) and, possibly, also due to high chain entanglement of the polymer molecules. These caused high flow resistance of the polymer blends. On the other hand, in the RSS#3/LLDPE/TPS ternary blend, poorer interfacial adhesion is caused by lack of chemical interactions between the phases. Therefore, the interlayer of interface might slip, and this would reduce flow resistance and complex viscosity.

TGA

Thermal stabilities of neat polymers and ternary blends were investigated by TGA under nitrogen atmosphere. Figure 7 shows TGA and DTG thermograms for the neat

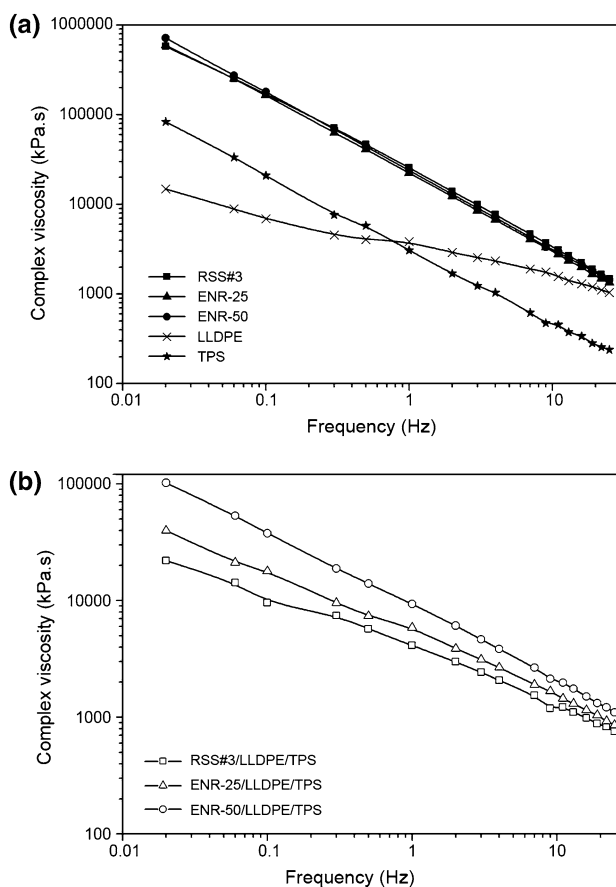


Fig. 6 Complex viscosity as a function of frequency for: **a** neat LLDPE, neat TPS, neat RSS#3, neat ENR-25 and ENR-50, and **b** 50/40/10 ternary blends of RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS at 160 °C

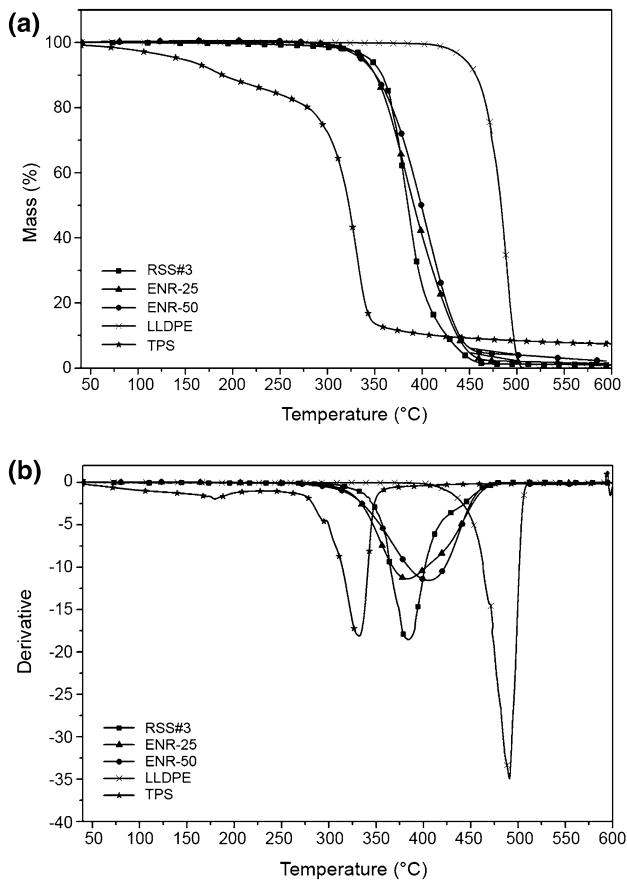


Fig. 7 a TGA and b DTG thermograms of neat rubbers

polymers (i.e., LLDPE, TPS, RSS#3, ENR-25 and ENR-50). Also, the temperatures at which 10 and 50 % mass loss (T_{10} and T_{50} , respectively) and degradation temperature (T_d) of neat polymers and their blends are summarized in Table 3. It is seen that neat LLDPE, RSS#3, ENR-25 and ENR-50 exhibited a single degradation step with a single peak in the DTG curves, with degradation temperatures (T_d) approximately at 480.2, 375.9, 378.6 and 405.6 °C, respectively. However, the neat TPS had two degradation steps with a major weight loss, and a major DTG peak

approximately at 316.5 °C, which matches the degradation of cassava starch [35]. The smaller degradation peak at about 130 °C indicates the loss of water, volatile compounds and glycerol in TPS [36, 41].

Furthermore, in Table 3, the neat LLDPE shows the highest T_{10} and T_{50} ; thus, it had the highest heat resistance. However, neat TPS had the poorest thermal properties in terms of T_{10} and T_{50} , while neat rubbers had intermediate values of T_{10} and T_{50} . Also, it can be seen that the residue content of TPS showed ~10 %. This might be due to water elimination via dehydration reactions of the starch during degradation of TPS, and the degraded starch forms a carbonaceous residue [42]. The carbonaceous residue from starch was oxidized in the air beyond 800 °C. However, in this work, the TGA was scanned only under nitrogen condition with heating rate of 10 °C/min over the temperature range of 25°C–600 °C. Under this condition, the carbonaceous residue from starch still remained.

Figure 8 shows the TGA and DTG thermograms of the 50/40/10 ternary blends RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS. The temperatures at 10 and 50 % weight losses (T_{10} and T_{50} , respectively) and degradation temperature (T_d) are summarized in Table 3. It is seen that all the ternary blends exhibited three major degradation steps at three degradation temperatures (T_d). The first significant step (T_{d1}) was observed in the temperature range 280–340°C. This indicates the degradation of cassava starch in the TPS. The second major step (T_{d2}) was found in the temperature range of 350–410 °C, which relates to the degradation of rubber. The last step (T_{d3}) in the temperature range 430–520 °C indicates the degradation of LLDPE. In addition, small degradation around 130 °C still occurred with all of the ternary blends. This indicates the loss of water, volatile compounds and glycerol in TPS.

In Table 3, it is also seen that the ternary blends with ENR had higher T_{10} and T_{50} than the blend with RSS#3. This might be due to the stronger chemical interactions with polar functional groups that enhanced interfacial adhesion. In Fig. 9b, it is also clearly seen that the T_{d1} (degradation temperature of TPS) and T_{d2} (degradation

Table 3 Temperatures for 10 and 50 % mass losses and the degradation temperature (T_d) for neat polymers and 50/40/10 natural rubber/LLDPE/TPS ternary blends

Sample code	T_{10} (°C)	T_{50} (°C)	T_d neat polymer (°C)	T_d of ternary blend (°C)		
				T_{d1}	T_{d2}	T_{d3}
Neat RSS#3	355.7	382.2	375.9	–	–	–
Neat ENR-25	348.5	385.5	376.6	–	–	–
Neat ENR-50	348.4	393.4	394.6	–	–	–
Neat LLDPE	454.9	483.1	489.2	–	–	–
Neat TPS	182.0	333.9	316.5	–	–	–
RSS#3/LLDPE/TPS	307.1	409.4	–	316.7	375.8	480.5
ENR-25/LLDPE/TPS	324.7	414.4	–	326.4	389.4	481.4
ENR-50/LLDPE/TPS	328.7	417.1	–	331.7	395.5	482.5

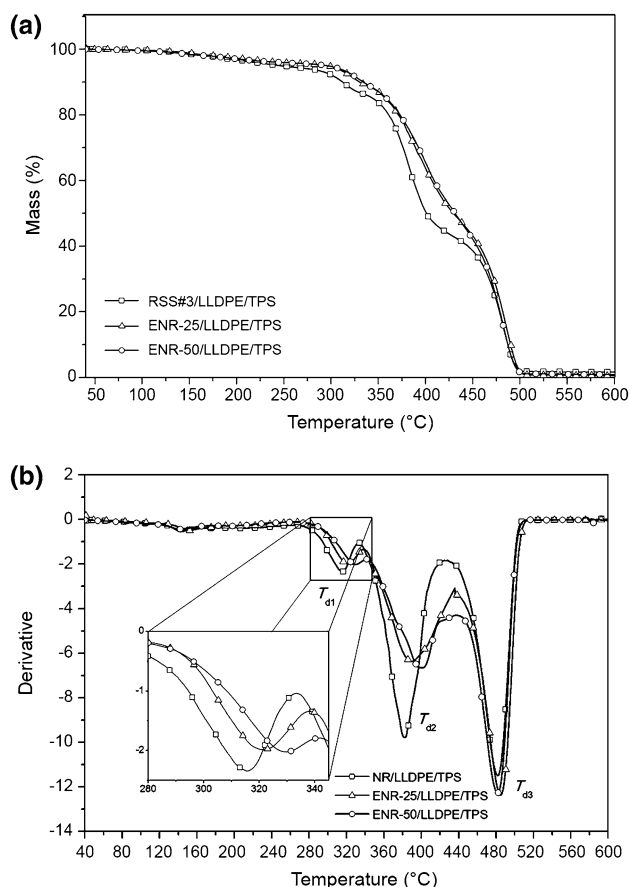


Fig. 8 **a** TGA and **b** DTG thermograms of 50/40/10 blends of RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS

temperature of rubber) for the ternary blend with ENR-50 are higher than those of the other ternary blends. This also confirms the chemical interactions of TPS and ENR-50 in the co-continuous phase structure of the ternary blend. Furthermore, it can be seen that the T_{d1} and T_{d2} of the ternary blends with ENR-25 and ENR-50 were higher than those of the neat TPS, neat ENR-25 and neat ENR-50 (Table 3). This again corroborates the chemical interactions of polar functional groups in TPS and oxirane groups in ENR, Querycreating strong interfacial links of the ENR/LLDPE matrix and the TPS particles. Therefore, the chemical interactions improved T_{d1} (degradation temperature of TPS) and T_{d2} (degradation temperature of rubber phase) of the ternary blends with ENRs. Also, the T_{d3} (i.e., degradation temperature of LLDPE) was still higher, but remained similar in all the ternary blends. Thus, the chemical interactions did not influence the T_d of LLDPE in the ternary blends. However, neat LLDPE had slightly higher T_d than the LLDPE phase in the ternary blends.

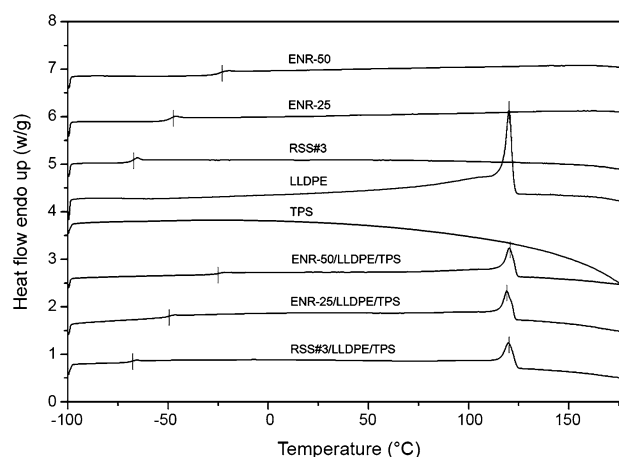


Fig. 9 DSC thermograms of neat rubbers, and 50/40/10 ternary blends

Table 4 Glass transition temperature (T_g), crystalline melting temperature (T_m), and heat of crystallization (ΔH) for neat polymers and natural rubber/LLDPE/TPS ternary blends

Sample code	T_g (°C)	T_m (°C)	ΔH (J/g)
Neat NR	-68.5	-	-
Neat ENR-25	-48.0	-	-
Neat ENR-50	-24.6	-	-
Neat LLDPE	-	120.2	129.1
Neat TPS	-49.1	-	-
NR/LLDPE/TPS	-67.3	120.4	35.7
ENR-25/LLDPE/TPS	-47.4	119.0	31.5
ENR-50/LLDPE/TPS	-22.8	119.4	31.3

DSC

Figure 9 shows DSC thermograms of neat polymers (i.e., LLDPE, TPS, RSS#3, ENR-25, and ENR-50) and of 50/40/10 ternary blends RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS. Table 4 summarizes the glass transition temperature (T_g), crystalline melting temperature (T_m) and heat of crystallization of LLDPE as a neat polymer and in the ternary blends. It is noted that T_g of the neat LLDPE could not be detected by DSC. On the other hand, T_g values for TPS, RSS#3, ENR-25 and ENR-50 were observed at -49.1, -68.5, -49.0 and -24.6 °C, respectively. In Fig. 9, it is also seen that ternary blends with the various rubber compartments show a single glass transition temperature, at -67.3, -47.4 and -22.8 °C in the ternary blends RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS, ENR-50/LLDPE/TPS, respectively. Possibly, the T_g values of TPS and rubber phases were overlapped; therefore, only one value was detected.

It is clear that among the neat rubbers, RSS#3 exhibited the lowest T_g value, followed by ENR-25 and ENR-50. Also, the T_g was similar for the TPS and ENR-25. In the ternary 50/40/10 rubber/LLDPE/TPS blends, T_g of the rubber phase increased only slightly relative to the neat rubber. Therefore, blends retained the good flexibility of the rubber chains in the co-continuous rubber and LLDPE matrix with the dispersed TPS.

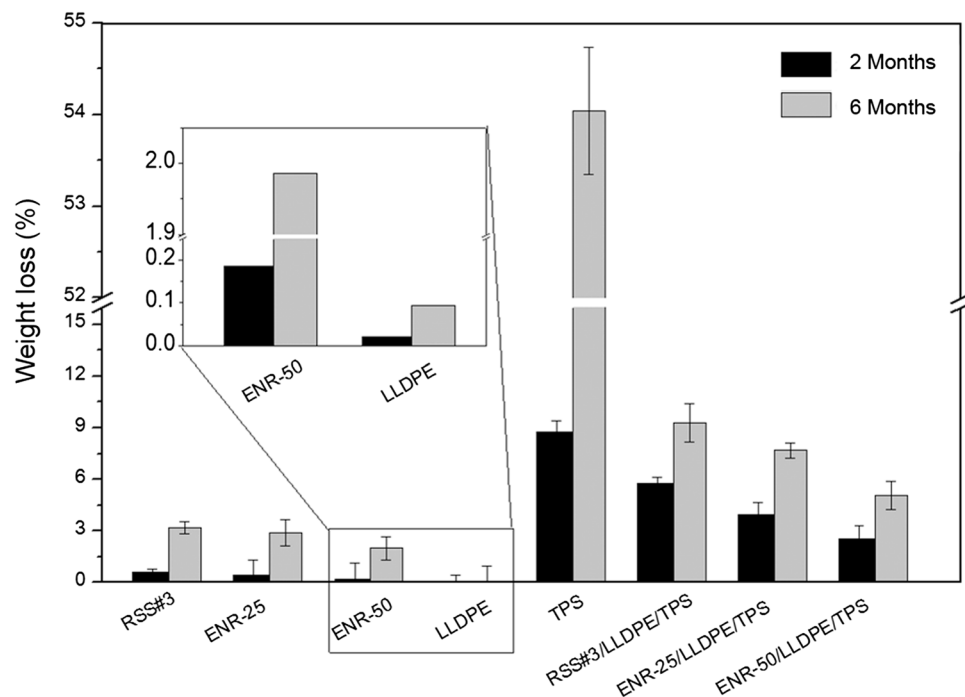
In Fig. 9 and Table 4, it is also clear that the crystalline melting temperatures (T_m) of LLDPE in various ternary blends showed only slight differences to the neat LLDPE. That is, the T_m of LLDPE in the RSS#3/LLDPE/TPS blend remained unchanged, while slightly lowered T_m of LLDPE was observed in ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS. However, it is clear that the heat of crystallization (ΔH) of LLDPE abruptly decreased in the ternary blends relative to the neat LLDPE. That is, the ΔH of neat LLDPE is about 129.1 J/g, while much lower $\Delta H < 40$ J/g of the LLDPE was observed in the ternary blends. Possibly, the regular chain region disappeared during blending at high temperature with high shear. Also, the chemical interactions of the phases might have created stronger networks that could interfere with the crystallization of LLDPE during cooling. Furthermore, the ternary blends with ENRs revealed slightly lower T_m and ΔH than the ternary blend with RSS#3. This may be attributed to stronger chemical interactions of the polar functional groups in TPS and ENR, forming strong networks and, hence, inhibiting the nucleation of crystalline LLDPE.

Biodegradation analysis

Biodegradation test was performed by determining weight loss after burial in soil for 2 and 6 months, for neat polymers and three ternary blends. Figure 10 shows the weight losses of neat rubbers (i.e., LLDPE, TPS, RSS#3, ENR-25, ENR-50), and the 50/40/10 ternary blends RSS#3/LLDPE/TPS, ENR-25/LLDPE/TPS and ENR-50/LLDPE/TPS. It can be seen that the neat TPS degraded faster than the other neat polymers or ternary blends. That is, the neat TPS lost 8.73 and 54.05 % of weight during burial for 2 and 6 months, respectively. This is due to the consumption of starch by microorganisms, and hydrophilic characteristics of starch that accelerated its biodegradation [40, 43]. Also, oxidative degradation, hydrolytic degradation and photo-degradation of blends occurred during burial in soil [43].

On the other hand, neat LLDPE lost very little of its weight (i.e., 0.02 and 0.09 wt% after burial for 2 and 6 months, respectively) followed by neat RSS#3, neat ENR-25 and neat ENR-50 in that order. This is due to the presence of high hydrocarbon contents with very low content of food ingredients that could be consumed by microorganisms. In Fig. 10, it is also seen that the ternary blend with unmodified NR (RSS#3) exhibited the highest weight losses (3.97 and 10.38 %), while the blends with ENR-25 or ENR-50 lost less weights. This may be due to the chemical interactions of TPS and ENR. Also, the low biodegradation rates of neat ENR-25 and ENR-50 may have

Fig. 10 Weight loss of neat rubbers, and 50/40/10 ternary blends after burial in soil for 2 and 6 months



contributed here. Thus, it can be concluded that the rubber/LLDPE/TPS ternary blends are intrinsically degradable because of the addition of TPS to the co-continuous phase of rubber/LLDPE blends.

Conclusion

Novel degradable materials based on natural rubber/LLDPE/TPS ternary blends were successfully prepared with three types of natural rubbers [i.e., unmodified natural rubber (RSS#3) and epoxidized natural rubber (ENR) with 25 (ENR-25) and 50 (ENR-50) mol % epoxide]. It was found that a 50/50 NR/LLDPE blend had co-continuous phase morphology, and RSS#3/LLDPE blend had the finest grained morphology due to similar polarities of the blend components, while the ENR/LLDPE blend showed coarser co-continuous phase structure. On adding TPS to the NR/LLDPE blends, the ENR-50/LLDPE blends showed the finest grained structure and the best dispersion of TPS particles in the matrix. This is attributed to the chemical interactions of polar functional groups in TPS and ENR. The chemical interactions also increased Young's and 100 % moduli, tensile strength, storage modulus and complex viscosity in the blends with ENR. Also, increasing the epoxide content in ENR molecules enhanced the thermal properties but lowered the melting temperature and the heat of LLDPE crystallization in the blend. Furthermore, neat TPS exhibited the fastest biodegradation by weight loss during burial in soil for 2 or 6 months, while neat LLDPE had the smallest weight losses. However, the ternary blends of natural rubber/LLDPE/TPS exhibited higher weight losses than the neat polymers. The ternary blends with ENR lost less weight than the blend with unmodified NR due to the chemical interactions of blend components.

Acknowledgements This research was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission, Prince of Songkla University, Contract No. SIT570565S. The author also would like to acknowledge Dr. Seppo Karilla who contributed to proof this manuscript.

References

- Ibrahim A, Dahlan M (1998) Thermoplastic natural rubber blends. *Prog Polym Sci* 23:665–706
- Pechurai W, Sahakaro K, Nakason C (2009) Influence of phenolic curative on crosslink density and other related properties of dynamically cured NR/HDPE blends. *J Appl Polym Sci* 113:1232–1240
- Nakason C, Nuansomsri K, Kaesaman A, Kiatkamjornwong S (2006) Dynamic vulcanization of natural rubber/high-density polyethylene blends: effect of compatibilization, blend ratio and curing system. *Polym Test* 25:782–796
- Nakason C, Jamjinno S, Kaesaman A, Kiatkamjornwong S (2008) Thermoplastic elastomer based on high-density polyethylene/natural rubber blends: rheological, thermal, and morphological properties. *Polym Adv Technol* 12:85–98
- Dierkes W (2007) Raw material and compound in rubber industry, Chap 1. University of Twente, Enschede, pp 6–12
- Ishiaku US, Ismail H, Ishak ZAM (1999) The effect of mixing time on the rheological, mechanical and morphological properties of poly(vinyl chloride)-epoxidized natural rubber blends. *J Appl Polym Sci* 73:75–83
- Mousa A, Ishiaku US, Ishak ZAM (2000) Rheological properties of dynamically vulcanized poly(vinyl chloride)/epoxidized natural rubber thermoplastic elastomers: effect of processing variables. *Polym Test* 19:193–204
- Nakason C, Jarntong M, Kaesaman A, Kiatkamjornwong S (2008) Thermoplastic elastomers based on epoxidized natural rubber and high-density polyethylene blends: effect of blend compatibilizers on the mechanical and morphological properties. *J Appl Polym Sci* 109:2694–2702
- Nakason C, Jarntong M, Kaesaman A, Kiatkamjornwong S (2009) Influences of blend proportions and curing systems on dynamic, mechanical, and morphological properties of dynamically cured epoxidized natural rubber/high-density polyethylene blends. *Polym Eng Sci* 49:281–292
- Nakason C, Wannavilai P, Kaesaman A (2006) Thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends: effect of compatibilizers and reactive blending. *J Appl Polym Sci* 100:4729–4740
- Thitithammawong A, Nakason C, Sahakaro K, Noordermeer JWM (2007) NR/PP thermoplastic vulcanizates: selection of optimal peroxide type and concentration in relation to mixing conditions. *J Appl Polym Sci* 106:2204–2209
- Narathichat M, Kummerlöwe C, Vennemann N, Nakason C (2011) Thermoplastic natural rubber based on polyamide-12: influence of blending technique and type of rubber on temperature scanning stress relaxation and other related properties. *J Appl Polym Sci* 121:805–814
- Mohamad Z, Ismail H, They RC (2006) Characterization of epoxidized natural rubber/ethylene vinyl acetate (ENR-50/EVA) blend: effect of blend ratio. *J Appl Polym Sci* 99:1504–1515
- Nakason C, Tobprakhon A, Kaesaman A (2005) Thermoplastic vulcanizates based on poly(methyl methacrylate)/epoxidized natural rubber blends: mechanical, thermal, and morphological properties. *J Appl Polym Sci* 98:1251–1261
- Pichaiyut S, Nakason C, Kummerlöwe C, Vennemann N (2012) Thermoplastic elastomers-based natural rubber and thermoplastic polyurethane blends. *Iran Polym J* 21:65–79
- Kalkornsurapranee E, Nakason C, Kummerlöwe C, Vennemann N (2012) Development and preparation of high performance thermoplastic vulcanizates based on blends of natural rubber and thermoplastic polyurethanes. *J Appl Polym Sci* 128:2358–2767
- Sasdiyan K, Kaesaman A, Vennemann N, Nakason C (2014) Influence of blend ratio on properties of novel thermoplastic vulcanizates based on copolyester/epoxidized natural rubber blends. *Iran Polym J* 21:65–79
- Pichaiyut S, Nakason C, Kaesaman A, Kiatkamjornwong S (2008) Influences of blend compatibilizers on dynamic, mechanical, and morphological properties of dynamically cured maleated natural rubber and high-density polyethylene blends. *Polym Test* 27:566–580
- Nakason C, Saiwari S, Kaesaman A (2006) Thermoplastic vulcanizates based on maleate natural rubber/polypropylene blends: effect of blend ratios on rheological, mechanical, and morphological properties. *Polym Eng Sci* 46:594–600
- Nakason C, Saiwari S, Kaesaman A (2006) Rheological properties of maleated natural rubber/polypropylene blends with

- phenolic modified polypropylene and polypropylene-g-maleic anhydride compatibilizers. *Polym Test* 25:413–423
21. Lamlaeh S, Kaesaman A, Nakason C (2013) Thermoplastic natural rubber based on blending of maleated natural rubber and copolyester: effect of blend ratios on mechanical, thermal, dynamic and morphological properties. *Adv Mater Res* 626:66–70
 22. Sripornsawat B, Nakason C, Kaesaman A (2013) Effect of modified natural rubber on properties of thermoplastic natural rubber based on co-polyamide blends. *Adv Mater Res* 626:233–236
 23. Nakason C, Pechurai W, Sahakaro K, Kaesaman A (2005) Rheological, mechanical and morphological properties of thermoplastic vulcanizates based on NR-g-PMMA/PMMA blends. *Polym Adv Technol* 16:592–599
 24. Intharapat P, Derouet D, Nakason C (2010) Thermal and flame resistance properties of natural rubber-g-poly(dimethyl(methacryloyloxymethyl) phosphonate). *J Appl Polym Sci* 115:255–262
 25. Shi Q, Chen C, Gao L, Jiao L, Xu H, Guo W (2011) Physical and degradation properties of binary or ternary blends composed of poly(lactic acid), thermoplastic starch and GMA grafted POE. *Polym Degrad Stab* 96:175–182
 26. Kahar M, Wahab A, Ismail H, Othman N (2012) Effect of polyethyl-grafted maleic anhydride as a compatibilizer on the morphology and tensile properties of (thermal tapioca starch)/(high-density polyethylene)/(natural rubber) blends. *J Vinyl Addit Technol* 18:65–70
 27. Ayana B, Suin S, Khatua BB (2014) Highly exfoliated eco-friendly thermoplastic starch (TPS)/poly(lactic acid)(PLA)/clay nanocomposites using unmodified nanoclay. *Carbohydr Polym* 110:430–439
 28. Carmona VB, Correa AC, Manoel JM, Mattoso LHC (2015) Properties of a degradable of thermoplastic starch (TPS), poly(ϵ -caprolactone) (PCL) and poly(lactic acid) (PLA). *J Polym Environ* 23:83–89
 29. Tena-Salcido CS, Rodríguez-González FJ, Méndez-Hernández ML, Contreras-Esquivel JC (2008) Effect of morphology on the biodegradation of thermoplastic starch in LDPE/TPS blends. *Polym Bull* 60:677–688
 30. Sabetzadeh M, Bagheri B, Masoomi M (2015) Study on ternary low density polyethylene/linear low density polyethylene/thermoplastic starch blend films. *Carbohydr Polym* 119:126–133
 31. Róz AL, Ferreira AM, Yamaji FM, Carvalho AJF (2012) Compatible blends of thermoplastic starch and hydrolyzed ethylene-vinyl acetate copolymers. *Carbohydr Polym* 90:34–40
 32. Carvalho AJF, Job AE, Alves N, Curvelo AAS, Gandini A (2003) Thermoplastic starch/natural rubber blends. *Carbohydr Polym* 53:95–99
 33. Mondragón M, Hernández EM, Rivera-Armenta JL, Rodríguez-González FJ (2009) Injection molded thermoplastic starch/natural rubber/clay nanocomposites: morphology and mechanical properties. *Carbohydr Polym* 77:80–86
 34. Kahar AWM, Ismail H (2014) High-density polyethylene/natural rubber blends filled with thermoplastic tapioca starch: physical and isothermal crystallization kinetics study. *J Vinyl Addit Technol*. doi:10.1002/vnl.21422
 35. Kahar AWM, Ismail H, Othman N (2013) Properties of HVA-2 vulcanized high density polyethylene/natural rubber/thermoplastic tapioca starch blends. *J Appl Polym Sci* 128:2479–2488
 36. Kahar AWM, Ismail H, Othman N (2012) Effects of polyethylene-grafted maleic anhydride as a compatibilizer on the morphology and tensile properties of (thermoplastic tapioca starch)/(high-density polyethylene)/(natural rubber) blends. *J Vinyl Addit Technol* 18:65–70
 37. Trovatti E, Carvalho AJF, Gandini A (2015) A new approach to blending starch with natural rubber. *Polym Int* 18:605–610
 38. Nakason C, Wannavilai P, Kaesaman A (2006) Effect of vulcanization system on properties of thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends. *Polym Test* 25:34–41
 39. Agnantopoulou E, Tserki V, Marras S, Philippou J, Panayiotou C (2012) Development of degradable composites based on wood waste flour and thermoplastic starch. *J Appl Polym Sci* 126:E273–E281
 40. Bootklad M, Kaewtatip K (2007) Biodegradability, mechanical, and thermal properties of thermoplastic starch/cuttlebone composites. *Polym Compos* 36:1401–1406
 41. Yokeshachart C, Yoksan R (2011) Effect of amphiphilic molecules on characteristics and tensile properties of thermoplastic starch and its blends with poly(lactic acid). *Carbohydr Polym* 83:22–31
 42. Shanks R, Kong I (2012) Thermoplastic starch, thermoplastic elastomers. In: El-Sonbati A (ed) *InTech*. <http://www.intechopen.com/books/thermoplasticelastomers/thermoplastic-starch>. Accessed 16 May 2016
 43. Pang MM, Pun MY, Ishak ZAM (2013) Degradation studies during water absorption, aerobic biodegradation, and soil burial of biobased thermoplastic starch from agricultural waste/polypropylene blends. *J Appl Polym Sci* 129:3656–3664