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The Effect of Rubber on Morphology, Thermal Properties and Mechanical properties of PLA/NR and PLA/ENR blends

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Abstract

The biodegradable thermoplastic poly(lactic acid) (PLA) that has restricted its application due to its high brittleness and poor crystallization behavior. Toughness properties of PLA can be developed by blending with natural rubber (NR) and epoxidized natural rubber (ENR). Blending PLA with NR and ENR were prepared at various compositions from 0-30% by weight. Morphology, crystallization behavior, thermal stability and mechanical properties of blends were investigated. The rubber phase of NR was dispersed in the continuous PLA matrix with small droplet. Increasing of NR content, the large droplet size of rubber will be resulted. However, the partially compatible between PLA and ENR was responsible for coarse surface, i.e. very fine particles of ENR dispersion. Incorporation of NR would enhance the crystallization ability of PLA better than ENR but thermal stability was decreased with both rubbers. The ductility of PLA has been significantly improved by blending with NR. The amount of NR at 10 % weight seems to give optimum property. At high content of NR, it seems to suffer tensile properties. In the case of the addition of ENR, it reduced crystallization ability, thermal resistance and tensile properties of the blend.

1. INTRODUCTION

Recently, biodegradable polymers derived from renewable resource have much interested that can be an alternative to petroleum based polymers as well as a solution to waste disposal problems. Hence, the

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development of materials is an important issue in order to decrease the environmental impact from the plastic production and waste.

Poly(lactic acid) (PLA) is a biodegradable and biocompatible thermoplastics, and can be produced by renewable resource. Poly(lactic acid) is now produced on a large scale and used for various application in difference domain : packaging, medicine, agriculture, and textile. However, high stiffness, brittleness, slow crystallization and permeability to gases of this polymer do not allow replacing commodity polymers in large scale applications [1-4]. In order to overcome these limitations, the copolymerization of lactides with other monomers have been a widely used approach [5-6], but without any success for commercial application. Blending of PLA with other polymer is more practical and less expensive. Hence, blending with other polyester, such as polycarprolactone, poly(butylene succinate), poly(butylene adipate)-co-terephthalate and poly(ethylene succinate), could achieve a more ductile multiphase material, by taking in to account the effect of composition on phase distribution. However, most of these blends are incompatible and compatibilizers are required in order to attain the desired properties [1, 3, 5, 7].

On the other hand, rubber has been used as a second phase polymer to toughen brittle thermoplastics. The rubber particles behave as stress concentrators enhancing the fracture energy absorption of brittle polymers and ultimately results in a material with improved toughness. Natural rubber (NR) and epoxidized natural rubber (ENR) are renewable resource that exhibits a unique combination of toughness, flexibility, biocompatibility and biodegradability with its low cost makes it was an alternative to improve the toughness of PLA [2, 8-9].

This work aims to compare the mechanical properties, thermal properties and morphology of thermoplastic elastomer that prepared from Poly(lactic acid) (PLA)/Natural Rubber, Poly(lactic acid) (PLA)/Epoxidized Natural Rubber (ENR) prepared by dynamic vulcanization.

2. EXPERIMENTAL

2.1. Materials

PLA (3051D injection molding grade) produced by NatureWorks Co. Ltd., USA was dried at 70°C for 24 hours, in a hot air oven before used. Natural rubber used in this work was STR5L obtained from Srijareon Rubber Co. Ltd., Thailand. ENR was purchased from Muang Mai Guthrie Public Co. Ltd., Thailand (Mooney viscosity: ML(1+4)100°C = 70.9 and %epoxidation = 24.24).

2.2. Sample preparation

The PLA melt blending with NR or ENR were carried out in an internal mixer, (MX 105-D40L50, Chareon TUT Co., Ltd., Thailand) at 170 °C with the rotor speed of 50 rpm. The ratios of the PLA/Rubber were as follows: 100/0, 90/10, 80/20 and 70/30 % by weight. The mixing was proceeded by firstly plasticized PLA in the internal mixer for 2 minutes and subsequently added quantified rubber to the chamber. The mixing was then carried on for further 13 minutes. The obtained blended plastic was then compressed, at 170 °C and with the pressure of 1500 psi, in a compression molding machine (PR1D-W300L350, Chareon TUT Co., Ltd, Thailand) to obtain 2 mm thick plastic sheet for dumbbell shape sample preparation.

2.3. Morphology of the sample

The morphology of cryogenic fractured of compressed samples and fractured surface of stretched samples were examined using Hitachi S-3400N Japan Scanning electron microscopy (SEM) and 10 kV. All the samples were suputtered coated with gold before examination.

2.4 .Thermal Analysis

Differential Scanning Calorimetry (DSC) measurements were performed by using a Perkin Elmer Shelton CT06484 USA. For all samples, on the first heating scan, the samples were scanned from 50°C to 250°C with the heating rate of 3 °C /min. The second scanning step was cooling with the cooling rate of 3°C/min from 250 °C to 50°C. Finally, the third heating scan was carried on at the same temperature range and rate of heating.

Thermogravimetric analysis (TGA) measurements were performed under nitrogen atmosphere by using a Themogravimetric Analyzer, Perkin Elmer (TGA 7), USA. All samples were heated from 50 to 650°C with the heating rate of 10°C/min.

2.5. Mechanical properties

Tensile tests for all samples were performed according to ASTM D 638 type I on an Instron machine Model 5969, Instron Engineering corporation USA, at 25°C, and with the cross-head speed of 5 mm/min. Dumbbell shaped specimen were prepared from the sheet obtained by compression-moulding with the pressure of 1200 psi. At least five specimens of each sample were tested to determine the mean value of the results.

3. RESULTS AND DICUSSIONS.

3.1. Morphology of blends

The SEM micrographs of fractured surfaces of PLA/NR and PLA/ENR blends are shown in Fig. 1. As can be seen all the PLA/NR blends shows phase separated morphology where the rubber particles dispersedly occurred as small droplets in PLA matrix. The phase morphology apparently showed weak interfacial adhesion evident by the empty spherical grooves on the surface.
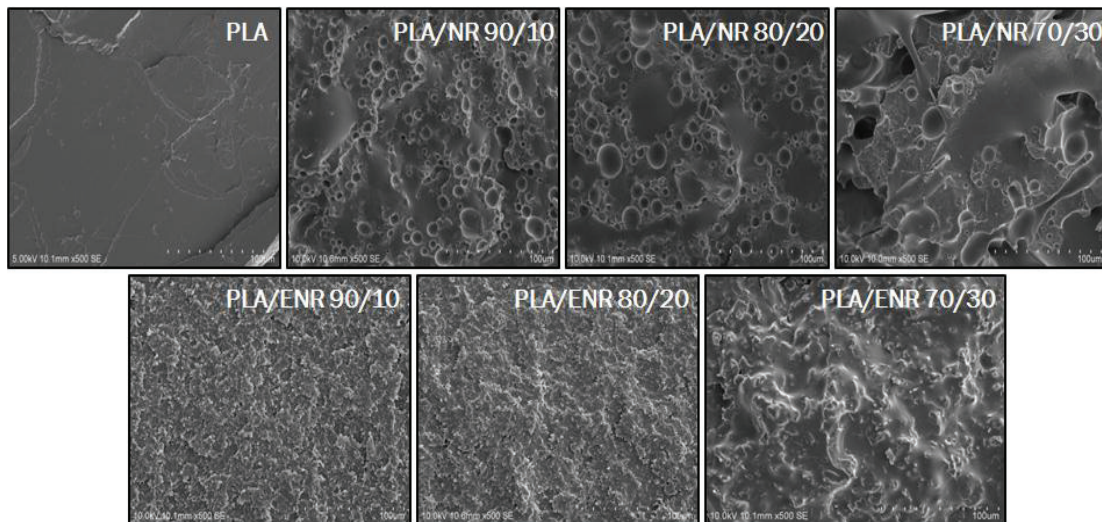

Fig. 1. SEM micrographs of PLA/NR and PLA/ENR blended at various rubber contents stated in the micrograph

With the increasing of NR content, the large droplet size of rubber was resulted. This generally occurred in an immiscible binary polymer blend, where the size of dispersed phase increase with increase amount of the minor phase in the blend [2, 10]. This is due to the coalescence phenomena. Therefore, at high content of dispersed phase rubber, the development of a phase inversion would be obtained. Considering the result of PLA/NR system, from this research, at the blend ratio of 90/10, the particle size of droplets is approximately at 5-10 μm. For higher rubber contents, i.e. 80/20 and 70/30, the dispersed rubber particles were also shown as the similar shape and size together with phase inversion.

Consider PLA/ENR blend, the morphology of these blends was difference from the previous system. As can be seen, the better compatibility between PLA and ENR than the former system. The partially compatible between PLA and ENR was responsible for coarse surface, i.e. very fine particles of ENR dispersion. It was explained elsewhere [9] that there was chemical interaction probably occurred between oxirane ring on ENR with hydroxyl group in PLA which can be attributed to their compatibility.

3.2. Crystallization behavior of PLA in the blends

In this particular case, samples from melt mixing were used for investigation. The results are shown in Fig. 2. On the first heating scan, the cold-crystallistion exothermic peak was observed in both PLA/NR and PLA/ENR blends. These results suggest that the incorporation of NR and ENR would enhance the crystallization PLA. In general, crystallization behaviour of a crystallisable matrix in immiscible blends can be affected by two major phenomena which are the migration of impurities during melt-mixing and the nucleating activity at the interface between these two polymers. The small molecules, which migrated from the rubbers could act as nuclei for PLA [2, 12-13]. Increasing the rubber content can lead more migration of small molecules and the nuclei density in crystallisable phase increased. It is also observed that increasing rubber content could result in the formation of larger droplets and cause a lower interfacial contact area. The crystallinity was therefore decreased.
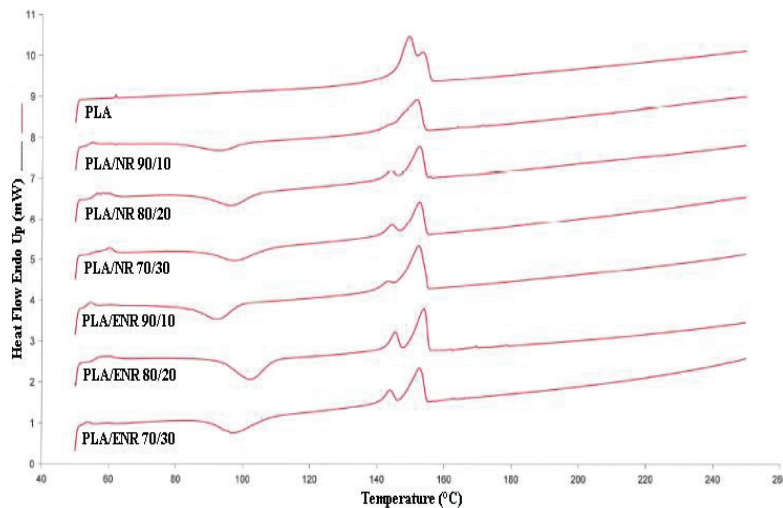

Fig. 2. DSC Thermograms of PLA blended with various contents of NR/ENR obtained from first heating scan compared with pristine PLA

The crystallinity of PLA in PLA/NR and PLA/ENR blends are shown in Table 1. It was found that the crystallinity was decreased with the content of rubber whereas the crystallinity of PLA in PLA/ENR

blends is higher than that in PLA/NR blends. Having considered PLA/ENR system, crystallinity of PLA was found much higher than that of PLA/NR. This is very much due to the better compatibility between PLA and ENR than the latter system, as elucidate by SEM.

Table 1. Thermal properties of PLA obtained from DSC 1st heating scan of PLA and PLA blends NR and PLA/ENR blends

	$T_{g,PLA}$ (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_f (J/g)	X_c (%)
PLA	61.2	-	-	149.45	34.92	37.31
PLA/NR 90/10	53.63	93.09	-	151.81	25.25	29.98
PLA/NR 80/20	54.59	96.51	143.95	152.56	16.89	22.56
PLA/NR 70/30	54.16	98.04	144.25	152.64	14.55	22.21
PLA/ENR 90/10	52.94	92.34	-	152.32	30.84	36.61
PLA/ENR 80/20	55.24	102.32	145.39	153.97	20.41	27.26
PLA/ENR 70/30	52.35	97.53	143.85	152.57	18.19	27.77

It is widely known that PLA is a very slow crystallizing material. It is even slower than that of PET. Therefore, after cooling at 3 °C/min, the crystallization could not be able to perform except for the case of having such good nucleating agent that the crystallization could be induced, as seen in Fig. 3. In the case of PLA with NR dispersed phase system, cold crystallization of PLA, in the blends were shifted to higher temperature, as seen in Table 2. This indicates the crystallization kinetic of PLA was effected by the presence of NR. Considering the melting temperatures of PLA, there are two distinctly sharp peaks present in the thermograms. This could be by the different crystalline structure of PLA, i.e. beta and alpha forms of crystalline PLA, whereas there are only α and α' for the virgin PLA [13-14].
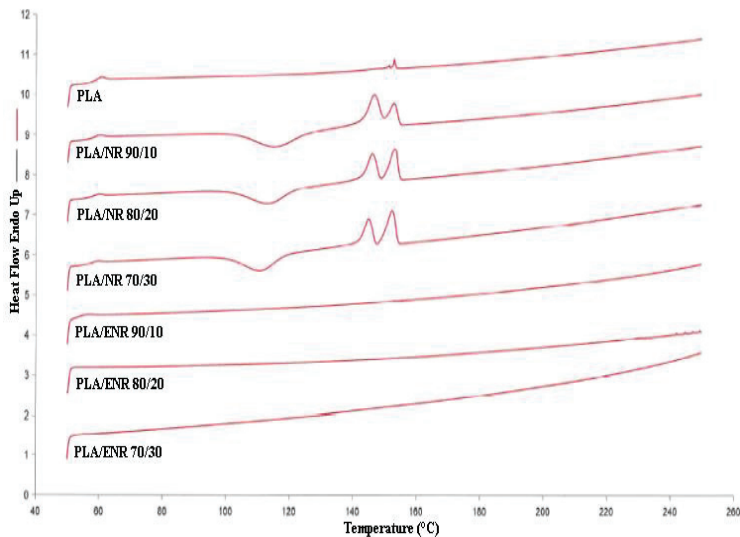

Fig. 3. DSC Thermograms of PLA blended with various contents of NR/ENR obtained from second heating scan compared with pristine PLA

In the case of PLA/ENR blends, at the second heating scan, there was no cold crystallization and melting found on the traces. This is because the compatibility between this two polymer, i.e. PLA and

ENR as shown by SEM micrographs. Therefore, the nucleation of PLA in this particular system was then hindered. Hence crystallization was impossible.

Table 2. Thermal properties of PLA obtained from DSC 2nd heating scan of PLA and PLA blends NR and PLA/ENR blends

	$T_{g,PLA}$ (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_f (J/g)	X_c (%)
PLA	58.25	-	151.32	152.94	0.65	0.69
PLA/NR 90/10	57.91	115.06	146.74	152.97	16.03	19.03
PLA/NR 80/20	57.21	113.3	146.02	153.12	20.70	27.64
PLA/NR 70/30	56.83	111.08	144.9	152.32	19.07	29.11
PLA/ENR 90/10	-	-	-	-	-	-
PLA/ENR 80/20	-	-	-	-	-	-
PLA/ENR 70/30	-	-	-	-	-	-

3.3. Thermal stability of blends

Fig. 4 and Fig. 5 show the TGA and DTG thermograms of PLA, NR, ENR and the blends. The thermal degradation characteristic values obtained from the investigation were concluded in Table 3.
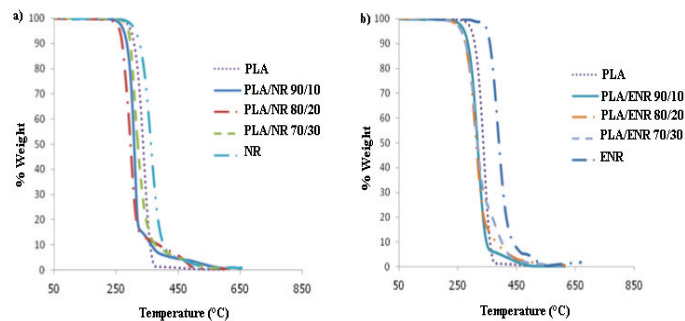

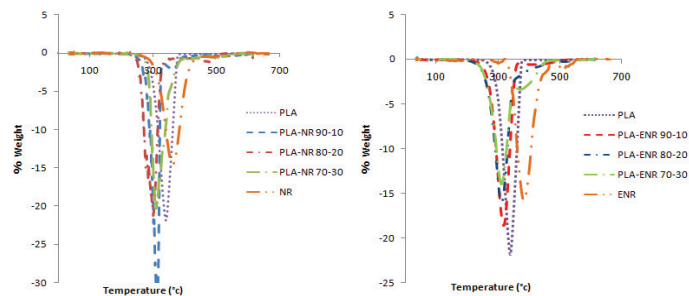Fig. 4. TGA thermogram of a) PLA/NR and b) PLA/ENR blends

Fig. 5. DTG thermogram of a) PLA/NR and b) PLA/ENR blends

Due to the degradation of PLA during mixing in the internal mixer [15, 16], the degradation onset temperature (T_{onset}), as well as rapidest degradation temperature (T_d), of PLA in the blends were shifted to low temperature, about 30°C lower that the virgin one.

Table 3. Thermal degradation of PLA, PLA/NR and PLA/ENR blends

	Onset Temperature (°C)	Degradation temperature (°C)
PLA	313.375	339.914
PLA/NR 90/10	283.682	303.486
PLA/NR 80/20	267.022	292.182
PLA/NR 70/30	289.391	313.966
PLA/ENR 90/10	289.788	318.786
PLA/ENR 80/20	281.058	311.012
PLA/ENR 70/30	280.062	310.441
NR	331.458	360.432
ENR	358.496	386.458

3.4. Mechanical properties of blends

- Modulus of blends

PLA is a rigid polymer with high modulus and breaks after yield without necking. Fig. 6 (a) shows the Young's modulus of PLA pristine and in the blends. The value tends to decrease with increasing NR and ENR content due to the flexibility of NR or ENR and the low crystallinity of PLA in the blends. In comparison, at the same content of rubber, NR did suffer modulus of PLA less than the ENR. This could be due to the compatibility simultaneously, low crystallinity and degradation induction by the ENR.

- Tensile strength

In term of tensile strength, it is normal that the tensile strength of the polymer was drop by the incorporation of soft materials. For this particular case, tensile strength of materials, shown in Fig. 6 (b). was also dropped with the content of the soft phase rubber. In most semicrystalline polymer, crystallinity contained in bulk should give rise to high tensile strength. The crystallinity of PLA in PLA/ENR blend was suppressed and this resulted in lower tensile strength than the previous system.

- Elongation at break

The elongation at break, under tension, of the blends in comparison with virgin PLA is shown in Fig. 6 (c). As mentioned earlier, PLA is a rigid and brittle polymer. It is therefore possesses low elongation. Addition of NR and ENR, the softness and flexibility of these polymers would increased the elongation of the blend. However, the ability to elongate is very much dependent upon dispersion and size distribution of rubber particle. As the particle size increased the discontinuity of the PLA matrix was intense, therefore elongation was suffered. However, the degraded of PLA in PLA/ENR system should be responsible for the shorter elongation at break of the blends.
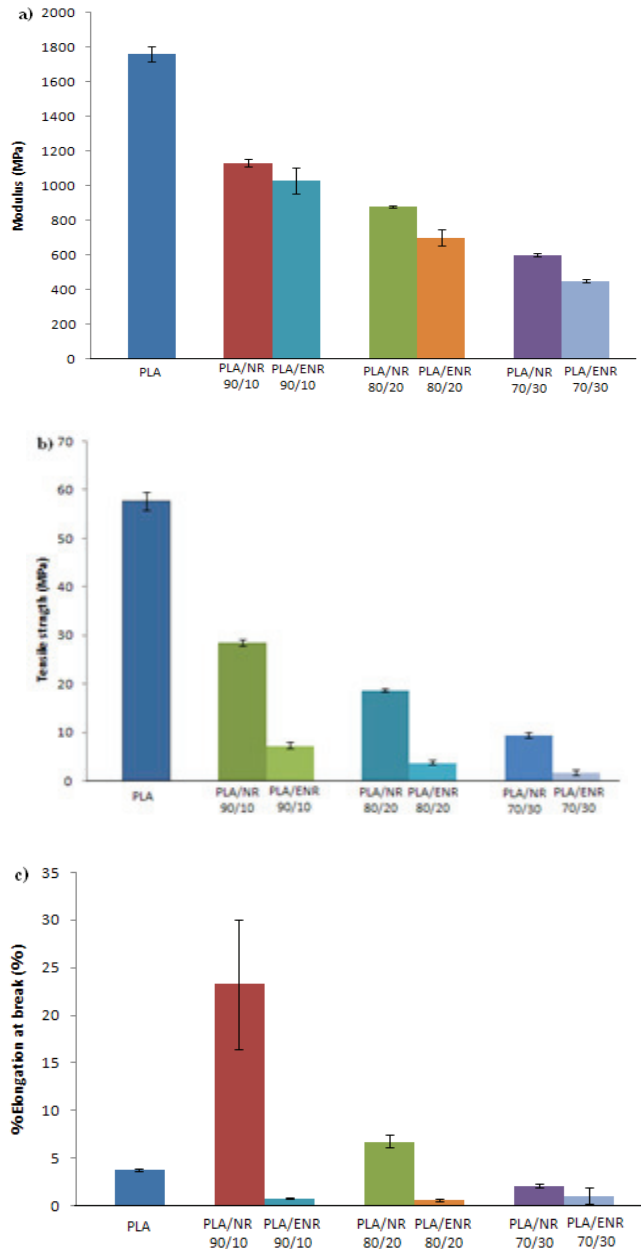
Fig. 6. Tensile properties of virgin PLA and PLA/rubber blends: (a) Young′s Modulus, (b) Tensile Strength and (c) Elongation at break

It must be very important to concentrate on the PLA/NR system with the content of 90/10 where the elongation at break is very much enhanced. In this particular composition, there was plastic deformation with whitening zone occurring during tensioning. It was clearly shown by the elongated deformed plastic on the fractured surface shown in Fig. 7. But the rest compositions seem to show no plastic deformation.
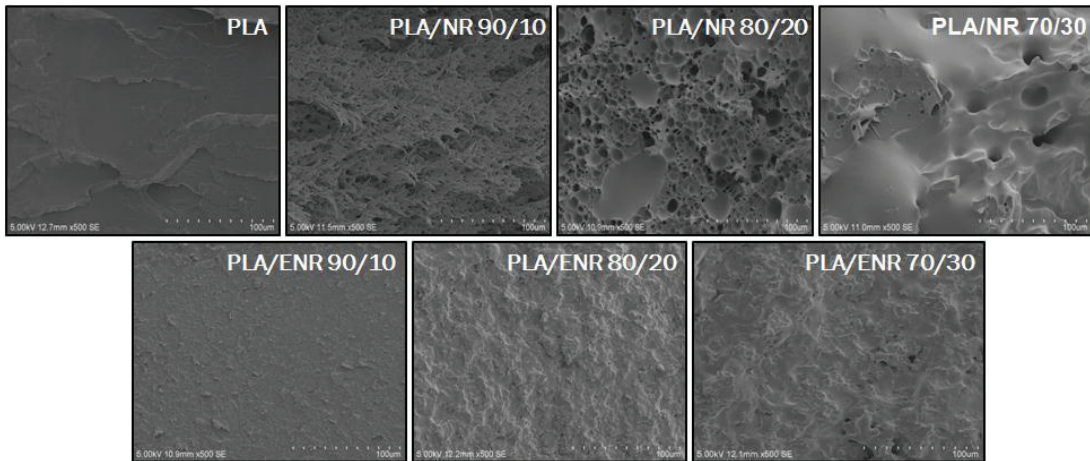
Fig. 7. SEM micrographs of tensile fractured surface of the blends with various rubber contents stated in the micrograph

4.   CONCLUSION

Toughness of PLA can be improved by blending with NR. Both NR content and particle size of NR affect to toughness properties. The optimal NR content that could improve the brittleness of PLA was found to be 10%. At this content the average particle size of NR provided smallest and well disperse in PLA matrix. However, blending PLA with ENR would reduce mechanical properties of blends. The crystallization ability of PLA in blends increased with the present of NR or ENR due to small molecules contained in rubber phase and surface of droplets could act as nucleating agent. Furthermore, the thermal stability of blends was found to be decreased with addition of NR and ENR. And PLA/ENR blends have more thermal stability than PLA/NR blends due to migrate of small molecules to surface of NR can lead to chain scission of PLA while mixing that can be decreased molecular weight of PLA with deceasing of Thermal stability.

Acknowledgements

References

[1] Gerard T, Budtova T, Morphology and molten-state rheology of polylactide and polyhydroxyalkanoate blends, *European Polymer journal* , **48** , 2012, 1110-1117.
[2] Bitinis N, Verdejo R, Cassagnanau, P., and Lopez-Manchado, M.A., Structure and properties of polylactide/natural rubber blends, *Materials Chemistry and Physics*, **129**, 2011, 823-831.
[3] Beatrice Coltelli M, Bronco, S., Chinea, C. The effect of free radical reactions on structure and properties of poly(lactic acid) (PLA) based blends, *Polymer Degradation and Stability*, **95**, 2010, 332-341.
[4] Huneault MA, Li H, Morphology and properties of compatibilized polylactide/thermoplastic starch blends, *Polymer*, **48**, 2007, 270-280.

[5]   Lin shan, Guo W, Chen C, Ma J, Wang B, Mechanical properties and morphology of biodegradable poly(lactic acid) /poly(butylene adipate-co-terephthalate) blends compatibilized by transesterification, *Materials and Design* , **36**, 2012, 604-608.

[6]   Garcia NL, Lamanna M, D'Accorso N, Aranguren M, Dufrense A, Goyanes S, Biodegradable materials from grafting of modified PLA onto starch nanocrystals, *Polymer Degradation and Stability*, 2012, 1-6.

[7]   Takayama T, Todo M, Tsuji, H, Effect of annealing on the mechanical properties of PLA/PCL and PLA/PCL/LTI polymer blends, *Journal of the mechanical behavior of biomedical materials*, **4**, 2011, 255-260.

[8]   Patcharaporn Somdee, Natural rubber toughened polylactic acid, [on-line serial], Retrieve September 10, 2012 from the World Wide Web: http://sutir.sut.ac.th:8080/sutir/bitstream/123456789/3352/2/Fulltext.pdf, 2009.

[9]   Ranumas Thipmanee, Rathanawan Magaraphan, Tarinee Nampitch, Mechanical properties and morphology of poly(lactic acid) (PLA) / epoxidized natural rubber (ENR)/organoclay nanocomposites, [on-line serial], Retrieve September 11, 2012 from the World Wide Web: http://kucon.lib.ku.ac.th/Fulltext/KC4706046.pdf.

[10] Sarazin P, Favis BD; Influence of temperature-induced coalescence effects on co-continuous morphology in poly(ε-caprolactone)/polystyrene blends, *Polymer*, **46**, 2005, 5966–5978.

[11] Somruetai Boonying, Crystalization behavior of poly(latic acid) composites, [on-line serial], Retrieve September 7, 2012 from the World Wide Web: http://sutir.aut.ac.th:8080/sutir/bitstream/123456789/3340/2/fulltext.pdf.

[12] Saeidolou S, Huneault MA, Li H, Park CB, Poly(lactic acid) Crystallization, *Progress in Polymer Science* , 2010, 17-23.

[13] Kullawadee Sungsanit, Rheologycal and mechanical behavior of poly(lactic acid)/poly(ethylene glycol), [on-line serial], Retrieve September 2, 2012 from the World Wide Web:http://researchbank.rmit.edu.au/view/rmit:12310.

[14] Signori F, Beatrice Cotelli, M, Bronco S, Thermal degradation of poly(lactic acid) (PLA) and poly(butylenes adipate-co-terephthalate) (PBAT) and their blends upon melt processing, *Polymer Degradation and Stability*, **94**, 2009, 74–82.

[15] Liu X, Khor S, Petinakis E, Yu, L, Simon G, Dean K, Baeman S, Effects of hydrophilic fillers on the thermal degradation of poly(lactic acid), *Thermochimica Acta*, **509**, 2010, 147–151.

[16] Zielin ska AJ, Noordermeer JWM, Talma AG, Duin MV, Di-azides cross-linked, iPP/EPDM-based thermoplastic vulcanizates, *European Polymer Journal*, **47**, 2011, 2311–2320.