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Effect of Peroxide and Organoclay on Thermal and Mechanical Properties of PLA in PLA/NBR melted blend

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Abstract

Acrylonitrile butadiene rubber, NBR, was added to poly(lactic acid), PLA, in order to improve the brittleness of PLA. NBR with the content of CN 34 % was melt blended into PLA. This work was carried out in three parts. NBR with the content of 5, 10, 15, 20, 15, 20, 25 and 30 % by weight was melt blended in an internal mixer. The second part, PLA, with the same contents as the first part, was melt blended with NBR compound (using dicumyl peroxide, DCP as vulcanizing agent) was dynamic vulcanized by melt blending with PLA in an internal mixer. Organic modified montmorillonite (OMMT), Cloisite 30B®, was added into NBR together with DCP. Cloisite 30B filled NBR compound was dynamic vulcanized with PLA by melt blending in the internal mixer. In the third part, the composition of NBR added in the blend was at 20, 25 and 30 % by weight. The results showed phase separation between PLA and NBR. Tensile strength and tensile modulus were found decreased with the content of NBR whereas elongation at break was increased with NBR content, up to 10 % NBR, then the elongation was decreased. Thermal stability of PLA was enhanced by the addition of NBR. For dynamic vulcanized NBR in PLA, the two phases was shown more compatible. Tensile elongation of PLA/dynamic vulcanized NBR blend was improved about 700-1100% compared to neat PLA. It was found that at 20 % of NBR tensile elongation was increased about 1120%. Tensile strength and modulus of thermoplastic vulcanizate of PLA/NBR (PLA/NBR TPV) were found decreased 37% and 65 % respectively, compared to neat PLA. The PLA/NBR TPV showed drawback in crystallization meanwhile thermal stability was very much improved. In order to improve mechanical properties of PLA/NBR TPV, OMMT was added. The results showed that modulus and tensile strength were enhanced whereas elongation at break was suffered due to the distribution of OMMT. It was shown in the form of aggregate rather than intercalated and exfoliated.

Keywords: PLA/NBR blend, DCP and Cloisite 30B, Thermal properties, mechanical properties

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1. Introduction

Poly (lactic acid) (PLA) is biodegradable and biocompatible thermoplastic. PLA is produced by renewable resource derived to aliphatic polyester with high strength and stiffness [1]. PLA is produced on large scale and used for various applications such as packaging for medicine, agriculture and textile. Unfortunately, the brittleness of PLA is major drawback to restrict its applications. In order to overcome these limitations, improvement the toughness of PLA by copolymerization, plasticization, blending or by the production of filled composites [2-4] has been of interest.

Blending PLA with other polymers provides the most practical to toughening PLA. Elastomer has commonly been considered because elastomer particle behave as stress absorber enhancing fracture energy absorption of brittle polymer [5-6]. Thongpin and coworker [7] blended PLA with NR and ENR with compositions from 0-30% by weight. The partially compatibilization between PLA and ENR was responsible for coarse surface, i.e. very fine particles of ENR dispersion was shown. Incorporation of NR would enhance the crystallization ability of PLA better than ENR. The ductility of PLA has been significantly improved by blending with NR [7].

Acrylonitrile-Butadiene Rubber (NBR) is an emulsion copolymer of acrylonitrile and butadiene. Polarity in NBR is introduced by copolymerization with the polar monomer i.e. acrylonitrile. NBR has higher polarity than NR and should be more compatible and suitable for toughening PLA. This research was aimed to prepare PLA blended with NBR containing 34% acrylonitrile content. The research focuses on the mechanical properties, thermal properties and morphology of PLA/NBR blend.

NBR was also compounded with dicumyl peroxide as a curing agent and was dynamic vulcanized in PLA matrix during melt blending. This will obtain thermoplastic vulcanizate of PLA/NBR and will be named as PLA/NBR TPV. The addition of organo clay is thought to be able to improve tensile properties. In this study cloisite 30B will be added into NBR compound before melted blending with PLA.

2. Materials and Methods

2.1 Materials

PLA, grade 3052D, was commercially supplied by NatureWorks LLC. NBR, grade 6240 with 34 % acrylonitrile, was supplied by LG Chem, trading by Chareontut Thailand. Cloisite 30B was purchased from Southern clay, USA.

2.2 NBR compounding

NBR was compounded on a two roll mill with 1 phr of dicumyl peroxide (DCP). The scorch time of compound was found 3 seconds. NBR compound filled with 3 phr of Cloisite 30B was also prepared on a two roll mill. Its scorch time was found shorter, about 2 seconds. However, the cure rate of rubber compound was rather slow.

2.3 Blend preparation

PLA was oven dried at 50°C over night before mixing with required weight of NBR in an internal mixer, Charoentut Thailand, at 170 °C and 70 rpm. The content of NBR was varied from 5, 10, 15, 20, 25 and 30 % by weight. The PLA/NBR TPV with the NBR 20-35% were selected to be filled with Cloisite 30B. The mixing was carried on for 15 minutes before discharging from the chamber. The pre-weighted PLA/NBR blend was then compressed in a compression molding machine at 170 °C by preheated the compound for 3 minutes before the compression load of 1000 psi was applied. PLA/NBR was then left under pressure for 3 minutes before taking the mold out from heating and left to cool under pressure. PLA/NBR slab were then cut into dumbbell shape to investigate tensile properties of the blends according to ASTM D638. Tension test was performed with the cross-head speed at 50 mm/min.

2.4 Thermal characterization of PLA/NBR

Some part of PLA/NBR which was discharged from the chamber of the internal mixer was investigated for crystallization behavior using DSC 7 Perkin Elmer and thermal stability using TGA 7 Perkin Elmer.

2.5 Morphology

Cryogenic fractured surface of polymer blends and tensile fractured surface from dumbbell specimens were investigated using SEM, TM3030 TABLETOP MICROSCOPE, Hitachi.

3. Results and Discussions

3.1 Morphology of the blend

Fig. 1 showed the morphology of PLA/NBR melt blend and PLA/NBR thermoplastic vulcanizate at various NBR contents. It could be seen that the PLA/NBR TPV showed better phase compatibility than that in PLA/NBR blends system. This could be due to crosslinking induced by free radical derived from DCP, occurring in both PLA and NBR [8]. It can also be seen in the figure that there was no gap between the interfaces in every composition. The crosslinking reaction at the interface between PLA and NBR was thought to occur. It was noticeable from FTIR spectrum shown in Fig. 2 that C=O stretching band of PLA/NBR TPV was shifted from 1730 cm^{-1} to 1741 cm^{-1} . This indicated that the molecular interaction between PLA molecule was released by the cross polymerization of PLA and NBR at the interfaces. Fig. 3 shows the morphology of PLA/NBR TPV with Cloisite 30B. The agglomeration of Cloisite 30B was found. As DCP could scorch NBR very fast, scorch time was found 3 second, hence the Cloisite 30B was not able to be dispersed. It was shown as agglomerated large particles in PLA matrix.

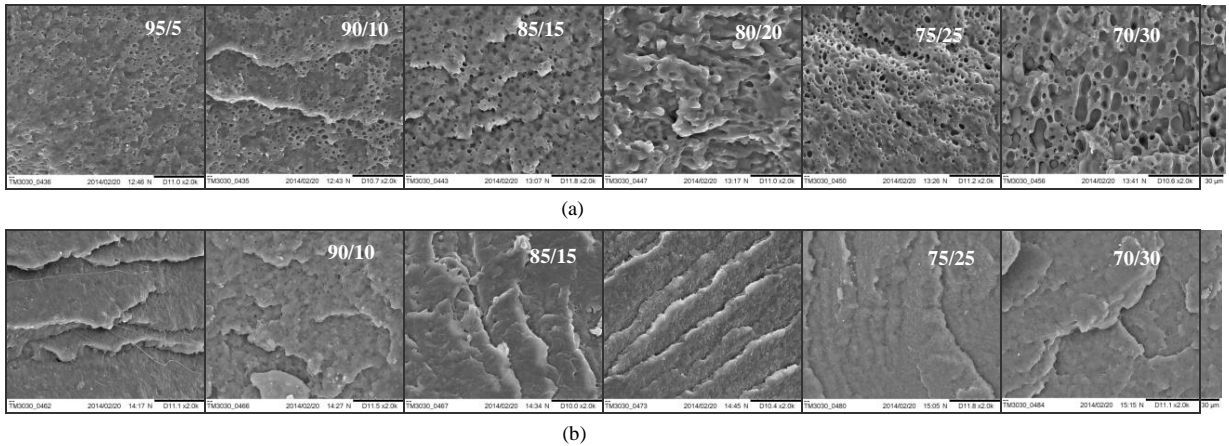


Fig. 1 SEM micrograph of cryogenic fractured (a) PLA/NBR and (b) PLA/NBR TPV.

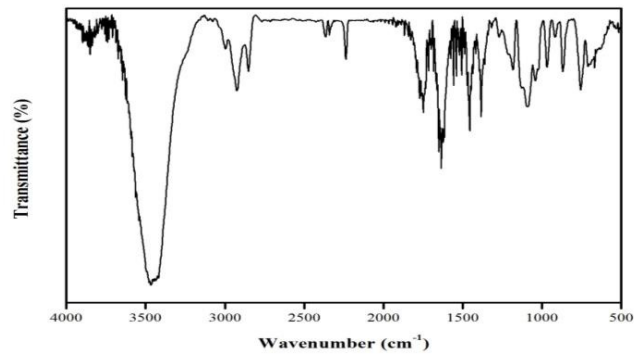


Fig. 2 FTIR spectrum of PLA/NBR TPV

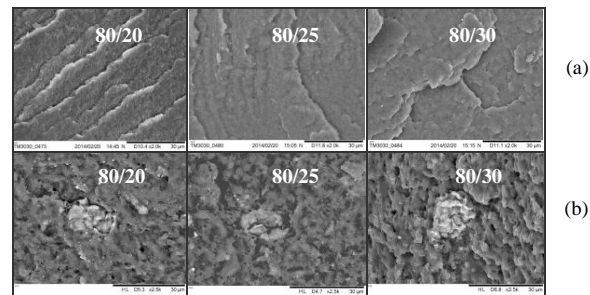


Fig. 3 SEM micrograph of (a) PLA/NBR TPV and (b) PLA/NBR TPV with Cloisite 30B

3.2 Thermal Properties of PLA/NBR blend

- *Crystallinity of PLA*

The presence of NBR did not significantly reduce T_g of PLA as shown in Table 1. Cold crystallization of PLA in PLA/NBR blends was not changed significantly, except for high NBR contents such as 25-30 %. This was caused by the phase separation between these two polymers. However, at high contents of NBR, crystallization of PLA was seemed to be obstructed by NBR particles. This was confirmed by characteristic of non-spherulitic morphology of PLA crystallization observed by optical microscope (the results did not show here). Nonetheless, the presence of NBR did not affect both T_m and the degree of crystallinity of PLA.

In the case of PLA/NBR TPV, as shown in Table 1 (with highlight), T_g of PLA was also unchanged. With the increased of NBR compound content, T_{cc} of PLA was found to be decreased. In fact, PLA could also be able to crosslink via free radical reaction. The crosslink reaction of PLA, however, would be able to occur at the interface between NBR and PLA. This is similar phenomenon to bound rubber where PLA was bound with rubber particles. The mobility of PLA chain was limited in local area. When PLA was second heated, local PLA molecules started to cold crystalline. This led to lower T_{cc} of PLA. However, the degree of cold crystallization is lower than that in non-crosslinked blend system. Two T_m s of PLA was also found to be unchanged. This indicated crystal structure of PLA should be unchanged. The crystallinity of PLA in PLA/NBR TPV was found decreased with the contents of NBR compound. This indicated the obstruction of crystallization of PLA by the presence of dynamic cured NBR particles and act as boundary for PLA, as explained earlier.

In the case of PLA/NBR TPV with Cloisite 30B, T_g of PLA was found unchanged meanwhile T_{cc} of PLA was found very much lower than that of unfilled PLA/NBR TPV. Cloisite 30B that was filled in NBR compound shortened scorch time of the rubber compound. This produced large rubber particles and also produced localized rubber bound PLA. Hence PLA will locally crystalline and crystalline faster.

The first melting temperature of PLA in PLA/NBR TPV filled with Cloisite 30B was disappeared. This indicated the crystallization mechanism of PLA was changed due to the NBR vulcanizate and the presence of Cloisite 30B.

At NBR contents of 25-30 % TPV filled Cloisite 30B, PLA showed 15 % increased in crystallinity. This could be due to the dispersed Cloisite 30B that can act as nucleating agent.

Table 1 DSC first heating scan of PLA in PLA/NBR blends, PLA/NBR TPV (highlight) and PLA/NBR TPV with Cloisite 30B (italic).

Formulae	PLA/NBR blend				PLA/NBR TPV				<i>Cloisite 30B/PLA/NBR TPV</i>			
	T_g (°C)	T_{cc} (°C)	T_m (°C)	χ_c (%)	T_g (°C)	T_{cc} (°C)	T_m (°C)	χ_c (%)	T_g (°C)	T_{cc} (°C)	T_m (°C)	χ_c (%)
100/0	59.46	99.82	148.50,159.03	25.88	59.46	99.82	148.50,159.03	25.88				
95/5	57.87	101.44	150.58,160.06	26.26	59.56	-	149.58,158.95	24.50				
90/10	58.03	98.83	148.42,159.05	25.45	58.57	97.68	148.52,158.90	23.89				
85/15	58.93	100.94	149.57,159.05	25.17	59.53	101.40	149.55,159.01	21.33				
80/20	57.96	99.83	149.57,159.00	26.00	57.89	99.83	147.97,158.90	21.92	60.07	94.56	-,159.94	25.68
75/25	58.38	103.00	150.02,159.05	26.24	58.53	97.70	148.44,158.42	20.00	58.99	94.61	-,159.03	30.21
70/30	60.00	103.01	150.54,160.02	25.58	58.97	97.68	148.42,158.91	20.49	59.77	94.62	-,158.93	27.08

- *Thermal Stabilization*

Thermal stabilization of the blends was investigated using TGA. The results exhibits in Table 2 and it shows that thermal stability of PLA/NBR TPV was enhanced. The addition of Cloisite 30B could improve thermal stability of PLA/NBR TPV.

In the case of PLA/NBR, onset degradation temperature, T_{onset} of the blend was decreased at the low contents of NBR, i.e. 5-10 % contents. Rapidest degradation temperature, T_{rpd} , of the blend, was increased with the presence of NBR. This is due to the high thermal degradation of NBR. It was found that PLA/NBR TPV could enhance the thermal stability of the system. The presence of crosslinking and also the cross polymerization of PLA at the interface were responsible for enhancement of T_{onset} and T_{rpd} of the blends. With the presence of Cloisite 30B as filler, thermal stabilization was also improved. This is due to thermal absorption of Cloisite 30B.

Table 2 TGA results, T_{onset} and T_{rpd} of PLA/NBR, PLA/NBR TPV and PLA/NBR TPV filled with Cloisite 30B

PLA/NBR	T_{onset}	T_{rpd}	T_{onset}	T_{rpd}	T_{onset}	T_{rpd}
100/0	293.46	306.21	293.46	306.21	293.46	306.21
95/5	284.74	326.40	296.81	340.15		
90/10	288.65	329.80	297.76	333.17		
85/15	303.18	335.89	294.41	326.32		
80/20	296.64	331.04	311.36	338.81	316.17	337.47
75/25	292.02	320.28	304.68	333.96	318.44	339.12
70/30	303.73	320.35	308.95	329.50	309.26	330.23

3.3 Mechanical Properties

Fig. 4 (a) shows stress-strain curves of PLA/NBR blends. Addition of NBR at 5-10 % contents improved ductility of PLA. Whitening had occurred during tension which indicated yielding in the blend with 5-10 % NBR contents. However, necking, referred permanent deformation, was not observed. At NBR content of 15-30 % in PLA, the stress-strain curves shows soft and weak behavior. This was caused by the phase separation and large particles of NBR in the blends. Fig. 4 (b) concluded tensile strength and tensile elongation of PLA/NBR blends. It was shown that tensile strength was steadily decreased with the content of NBR. SEM micrographs in Fig. 7, at the content of NBR compound of 10-30 %, fractured surface shows plastic deformation.

For PLA/NBR TPV, stress-strain curves are presented in Fig. 5 (a). Tensile strength and tensile elongation of the TPV are concluded in Fig. 5 (b). Tensile elongation of PLA/NBR TPV at NBR content of 10-20 % was higher than PLA about 500-1000 %. The small dispersed NBR particles and crosslinking between PLA and NBR was responsible for the toughening and ability to elongate. Yielding was also clearly occurred for TPV, shown by SEM micrographs in Fig. 7. This was caused by the crosslinking of NBR and cross polymerization between NBR and PLA at the interface.

At NBR content of 25-30 %, tensile elongation was decreased but still higher than that of neat PLA. At high content of NBR, the rubber tended to aggregate and was present as larger particles than at 5-20% NBR contents (see also Fig. 1). The crosslinking of NBR, and cross-polymerization NBR with PLA at the interface was still occurred. This led to higher elongation at break, of high NBR in the TPV.

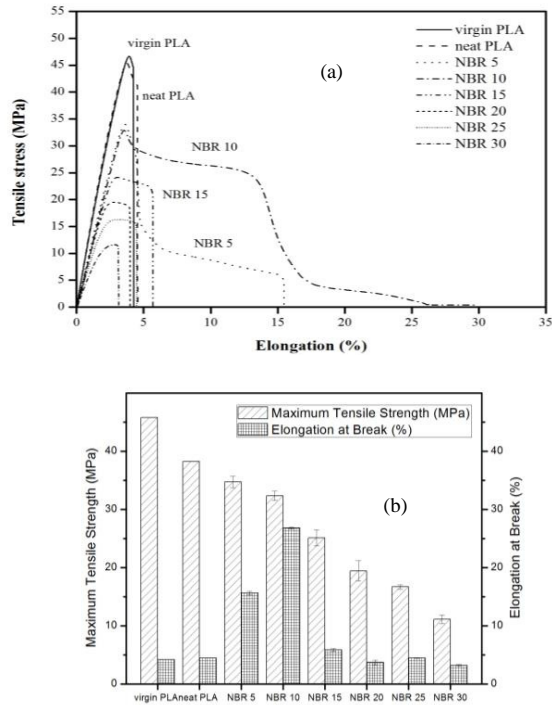


Fig. 4 (a) Stress-strain curves (b) tensile strength and tensile elongation of PLA/NBR blends.

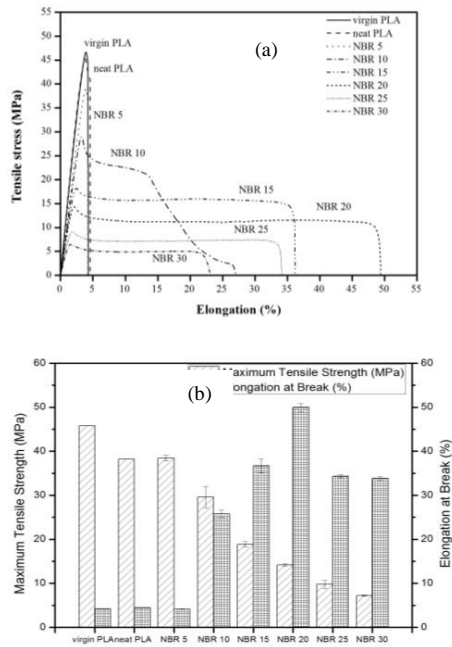


Fig. 5 (a) Stress-strain curves and (b) tensile strength and tensile elongation of PLA/NBR TPV.

PLA/NBR TPV at the NBR content of 25-30% were selected to study the effect of Cloisite 30B. The content of Cloisite 30B was fixed at 3 phr. The stress-strain curves of Cloisite 30B/PLA/NBR also exhibited ductile behavior.

However, the tensile elongation was suffered with the presence of Cloisite 30B. As evidence in Fig. 3, Cloisite 30B seemed to agglomerate and hence tensile elongation was inferior compare to PLA/NBR TPV. It was found that tensile modulus, not show here, was found to be improved about 23 %. As mentioned earlier that NBR compound is scorchy when Cloisite 30B was added. This caused Cloisite 30B to be rather difficult to disperse. It is evident in Fig. 7 (c) that the fractured surface was found more brittle than Fig. 7 (b) and Cloisite 30B agglomerated covered with cured NBR. It could be noticed by the white circle indicated in the figure.

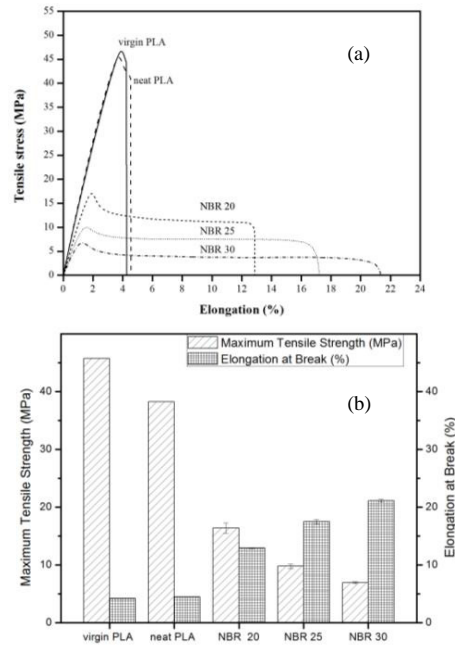


Fig 6 (a) Stress-strain curves and (b) tensile strength and tensile elongation of PLA/NBR TPV filled with Cloisite 30B.

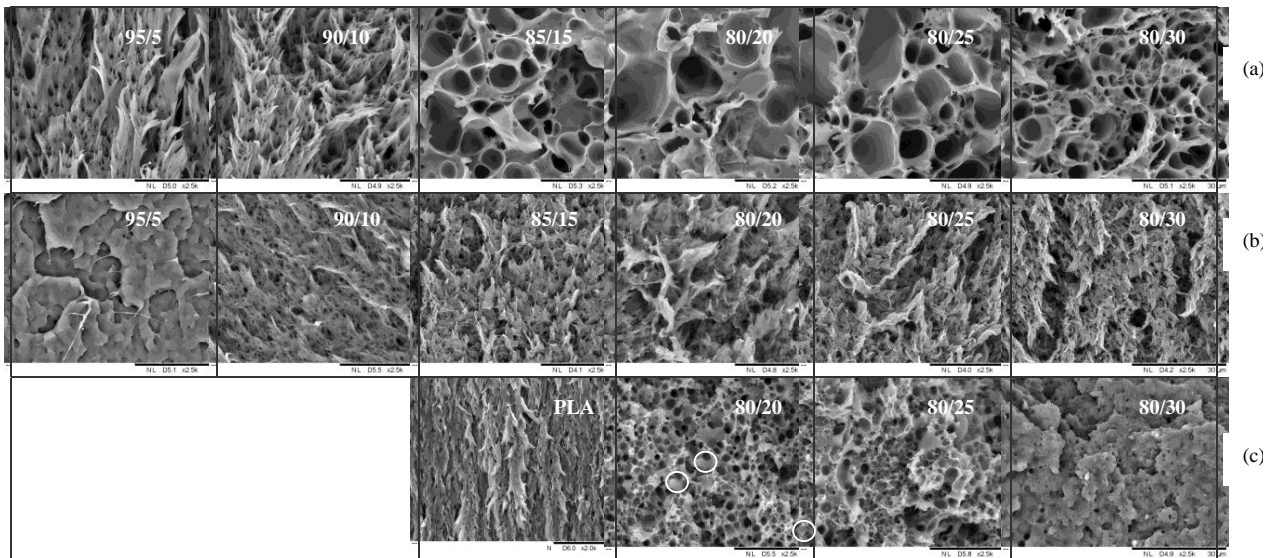


Fig.7 SEM micrographs of tensile fracture surface of (a) PLA/NBR blends, (b) PLA/NBR TPV and (c) PLA/NBR TPV filled with Cloisite 30B

4. Conclusions

- NBR was melt blend into PLA and could improve ductility of PLA at the NBR content of 5-10 % by weight. At higher NBR contents, the blends turned to be soft and weak due to the phase separation between PLA and NBR.

- Dynamic vulcanization of NBR, cures with DCP, during melt blending could improve the compatibility, between PLA and NBR, by the crosslinking between these two polymers. The phase separation was not found clearly in TPV case. SEM micrograph of tensile fractured surface showed evidence of yielding. Yielding without necking also occurred under tension. The addition of Cloisite 30B led to brittleness of thermoplastic vulcanizate of PLA/NBR. The presence of Cloisite 30B led to shorten of scorch time of NBR hence dispersion and curing was competitive. Cloisite 30B was then could not be dispersed.

- T_g of PLA was found slightly decreased with the presence of NBR. Cold crystallization of PLA was found affected by the rubber bound PLA. It was decreased about 3 °C. Having Cloisite 30B in PLA/NBR TPV, T_{cc} was even lowered. This was caused by the crosslinking of NBR and bound PLA. Crystallinity of PLA in PLA/NBR TPV filled with Cloisite 30B was slightly enhanced by the nucleating effect of clay.

- Thermal stability of PLA/NBR was increased indicated by T_{onset} and T_{tpd} . Dynamic vulcanized NBR can improve both parameters. The thermal stability of PLA/NBR TPV could be enhanced by Cloisite 30B.

- It was found that tensile strength and tensile elongation were improved by dynamic vulcanization of NBR phase. The cross polymerization between PLA and NBR at the interface was also responsible for the properties.

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References

- [1] Paul M.A., Alexandre M., Degee P., Henrist C., Rulmont A., and Dubois P., New nanocomposite materials based on plasticized poly(L-lactide) and organo-modified montmorillonites: thermal and morphological study, *Polymer*, 2003, 44, p.443-450.
- [2] Lemmouchi Y., Murariu M., Santos A.M.D., Amass A.J., Schacht E. and Dubois P., Plasticization of poly (lactide) with blends of tributyl citrate and low molecular weight poly(D,L-lactide)-b-poly-(ethylene glycol) copolymers, *Eur. Polym. J.* 2009, 45, p.2839-2848.
- [3] Anderson K.S. and Hillmyer M.A., The influence of block copolymer microstructure on the toughness of compatibilized polylactide/polyethylene blends, *Polymer*, 2000, 445, p.8809-8823.
- [4] Jiang L., Zhang J., and Wolcott M.P., Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: reinforcing effects and toughening mechanisms, *Polymer*, 2007, 48, p.7632-7644.
- [5] Han J.J., and Huang H.X., Preparation and characterization of biodegradable polylactide/thermoplastic polyurethane elastomer blends, *J. Appl. Polym. Sci.*, 2011, 120, p.3217-3223.
- [6] Imre B., Bedo D., Domjan A., Schon P., Vancso G.J., and Puaszky B., Structure, properties and interfacial interactions in poly (lactic acid)/polyurethane blends prepared by reactive processing, *Eur. Polym. J.* 2013, 49, p.3104-3113.
- [7] Pongtanayut K., Thongpin C. and O. Santawitee, The effect of rubber on morphology, thermal properties and mechanical properties of PLA/NR and PLA/ENR blends, *Energy Procedia*, 2013, 34, p.888 – 897.
- [8] Coltelli M.B., Bronco S. and Chinea C., The effect of free radical reaction on structure and properties of poly(lactic acid) (PLA) based blends, *Polymer Degradation and Stability*, 2010, 95, p. 332-341.