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Crystallization Behavior of PLA in PLA/NR Compared with Dynamic Vulcanized PLA/NR

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Abstract

PLA has been an interesting biopolymer widely used in various applications. It has been widely known that crystallization of PLA is rather slow. After melt processing, crystallinity of PLA could be lost. The study of PLA added with fibers, particles or even nano-particles has been studied extensively. Nonetheless, the suffering in some mechanical characteristic such as toughness has been encountered. Our research was aimed to enhance toughness of PLA by melt blending NR, and dynamic vulcanized NR into PLA using an internal mixer. PLA:NR and PLA:NR vulcanizate with the ratio of 90:10, 80:20, 70:30, 60:40 and 50:50 were studied. Crystallization behavior and thermal stability of the blend were investigated using DSC and TGA respectively. It was found that, for the former systems, at low content of NR, i.e. 10-30 %, rubber particles were found to be presented as spherical disperse phase in PLA. Meanwhile at higher content, such as 40-50 % NR, polymers were found as co-continuous. Having NR in PLA did not affect T_g of the plastic but could induced cold crystallization and subsequently the crystallinity of the plastic. This resulted in the change of melting temperatures of PLA. Surprisingly, at the temperature higher than T_m of PLA, exothermic behavior upon heating was found, at the content at 10-30 % of NR. This is the cross polymerization between NR and PLA molecule and cause the rapidest degradation temperature of polymer blend to be increased. In the case of PLA:NR vulcanizate, dispersed NR particles were also present in PLA continuous phase. But the particles were found larger at the higher content of NR. The effect of NR particle onto the crystallization of PLA was found to be similar to the previous case. However, the cross polymerization between two polymers was not found in DSC thermograms. This also resulted in the two distinct degradation steps in the blends and less stability of PLA upon TGA than the previous system.

Introduction

As environment pollution effected by plastic waste has been a crucial issue for the scientist all over the world. Using disposable plastic packaging is one of the many ways to solve the problem. Among the many types of disposable plastic, polylactic acid (PLA) has been intensively paid attention as a biodegradable polymer which can be degraded by both environment and micro-organism.(1) Polylactic acid has been able to be produced for many kinds such as disposable cutlery, cups, plates, straws, stirrers, lids, certain packaging applications, plates and containers for foods.(2) Some drawbacks, such as its high brittleness and poor crystallization behavior(3,4) have still been found. In order to overcome these limitations, copolymerization, blending and filling techniques has been ~~a~~ widely used. Blending other polymer with PLA has been one of the interesting methods. Several synthetic polymers, such as low density poly(ethylene), poly(propylene glycol) and poly(ethylene glycol), polymeric plasticizers, or biodegradable polymers such as polycaprolactone, poly(butylene succinate), poly(butylenes adipate)-co-terephtalate, and poly(ethylene succinate) have been used.(3-6) Most of these blends are incompatible thus compatibilizers are required in order to obtain the desired properties. In addition, most of these polymers are not biocompatible which limits its application.

As it has been known that Thailand has a vast area that plant a great number of natural rubber (NR) or hevea brasiliensis.(7,8) NR is a natural elastomeric materials that could be able to improve toughness of brittle polymer. It was reported by N. Bitinis, R. Verdejo, P. Cassagnau, M.A. Lopez-Manchado(9) that addition of NR into PLA with the content of 10 %, PLA was shown ductility and its crystallization has been increased.

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In term of rubber vulcanizate which is generally struggle with the re-processability. Thermoplastic vulcanizates (TPV) then have become a very useful class of thermoplastic elastomers. These materials have the processing characteristics of a thermoplastic and the functional performance of a conventional thermoset rubber which is prepared by blending NR with PLA. The rubber phase is vulcanized during the mixing process at high temperature, and the process is known as dynamic vulcanization (DV).(10)

The aim of this research was to study crystallization behavior of PLA blended with NR at various contents. Crystallization and mechanical properties of both PLA/NR blends and PLA/NR thermoplastic vulcanizates (TPV) will be investigated.

Materials and Experimental Procedures

Materials

Polylactic acid with the grade of 2003D was supplied by Global Connection Thailand. NR sheet was supplied by Charoenthut, Thailand. All the rubber additives were kindly supported by Innovation group Thailand.

Melt Blending of PLA/NR

PLA was oven dried at 30°C for at least 3 hours before melt blending with NR in an Internal Mixer (Chareonthut, Thailand) with the rotating speed of 50 rpm, at the temperature of melting at 170°C. The mixing time after plasticization was completed was carried on for 15 minutes in order to completely disperse NR into PLA continuous phase. The blending composition was varied at the content of NR at 10, 20, 30, 40 and 50 %. The blended materials were the compression in compression moulding machine at 170°C at the pressure of 90 bar and then dumbbell specimens were prepared by laser cutter.

Preparation of PLA/NR Thermoplastic Vulcanizate

In this part, NR was first compounded with sulfur curing system (zinc oxide 3 phr, stearic acid 1phr, N-t-butylbenzothiazole-2-sulfenamide (TBBS) 0.8 phr and sulfur 1 phr) on a two roll mill. The scorch time was previously determined and was found to be more than 2 minutes. PLA was then melted mixing with NR compound in the internal mixer under the same condition as section 2.2. The TPV slabs were also prepared in the same manner as explained in section 2.2.

Morphological study of PLA/NR and PLA/NR TPV

Phase morphology of PLA/NR and PLA/NR TPV were investigated using a scanning electron microscopy (SEM), CAM SCAN, UK. All the samples were prepared by cryogenic fractured after immersion in liquid nitrogen and the fractured specimens were sputter coated with gold in order to prevent electrical discharge during observation under electron beam.

Thermal Properties

The crystallization process was examined in a differential scanning calorimetry using DSC7 Perkin Elmer, USA. The following procedure was adopted: samples of about 10 mg were firstly heated from 50°C to 250°C (to 200 in TPV) at a scan rate of 3°C min^{-1} to erase the thermal history, then they were rapidly cooled to 50°C, and, finally a second heating scan from 50°C to 250°C (to 200 in TPV) at 3°C min^{-1} was carried out. The experiments were performed in a nitrogen atmosphere.

The thermal stability of the blends was revealed using thermal gravimetric analyzer (TGA Perkin Elmer, USA). The following procedure was adopted: samples of about 10 mg were heated from 50°C to 600°C at a scan rate of 5°C min^{-1}. The experiments were performed in a nitrogen atmosphere.

Result and Discussion

PLA/NR BLEND

Morphology of PLA/NR Blends

Morphology of PLA/NR blends were shown in Figure 1. NR phase was found to be dispersed in PLA matrix as spherical particles, especially for the content of NR at 10 – 30 %. The increase in NR contents led to larger size of NR particles. The co-continuous phase of both polymers was also found at high rubber contents. It seems to be appeared that PLA phase was covered with rubber phase, as could be seen in Figure 1(f) where PLA/NR was 50/50 and investigated at x1000. This occurred by the fact that rubber phase that was frozen during cryogenic treatment. After kept to room temperature, rubber phase could be able to flow and then cover PLA phase and could be found as the interfacial layer covering PLA co-continuous phase. It is interesting to notice the heating scan of PLA/NR blends as can be seen in Figure 2 and will be discussed in detail in the following section.

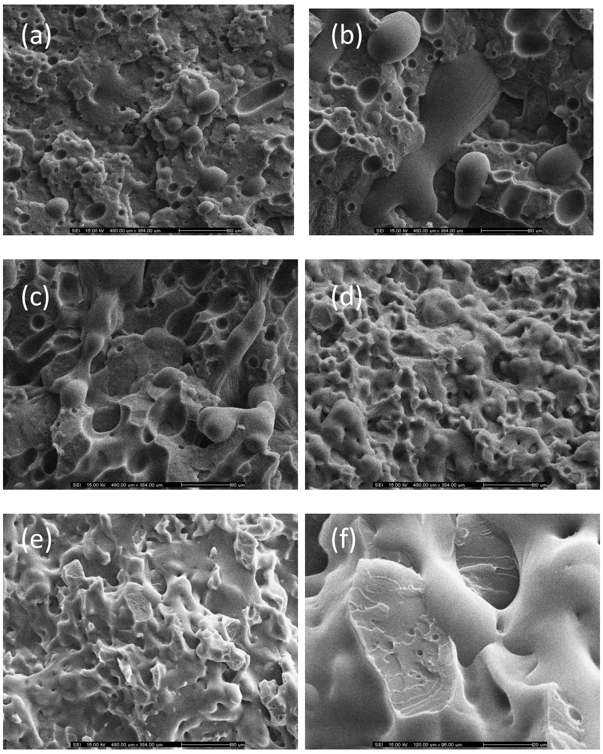

Figure 1. Cryogenic fractured surface of PLA/NR melted blend at various NR contents, with (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 % at the magnification of 250X and (f) of 50 %NR at magnification of 1000X.

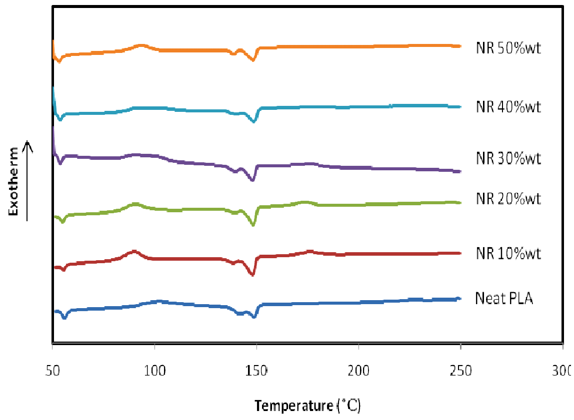

Figure 2. DSC First heating scan thermogam of PLA/NR blend at various content of NR

Crystallization of PLA/NR Blend

First heating scan of PLA/NR blend at various NR contents is shown in Figure 2 and thermal properties of PLA/NR are shown in Table 1. Glass transition temperature of PLA was found to slightly decrease with the present of NR. As it was mentioned in the previous section (3.1) that at high contents of NR in PLA, i.e. 30-50 %, PLA and NR turned to be co-continuous phase and NR was found as interfacial covering on the PLA surface which could increase flexibility and hence decreased T_g of PLA in the blends. In fact during melt blending of PLA and NR, rubber molecules were sheared and dispersed in PLA continuous phase. After cooling to room temperature PLA molecules was frozen and also crystallization was so slow that amorphous phase was dominate. On the first heating, the relaxation of PLA was therefore appeared very clearly. The crystallization of amorphous domain, shown by the large exothermic peaks, was simultaneously crystalline above T_g.

Table 1. Thermal properties and crystallinity of PLA/NR on the first heating scan.

PLA/NR	T_g (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	%X_c
100/0	55.93	101.77	141.91	151.18	27.20
90/10	55.34	89.68	138.49	150.19	29.39
80/20	54.99	90.17	139.24	148.11	29.97
70/30	54.11	91.42	139.40	147.62	38.54
60/40	53.74	91.72	139.68	148.35	36.24
50/50	53.18	93.07	138.58	148.10	31.14

Consider two melting peaks of the blends in Figure 2 it was found 2 T_ms which is the characteristic of this particular grade. Interestingly, with the present of NR, both T_{m1} and T_{m2} were shifted to lower temperature. This is due to the crystalline occurring during cold crystallization was heterogeneous nucleation mechanism with NR as nucleating agent.(9) In this case the crystalline could be formed faster hence higher in crystallinity. From the heating thermogram, shown in Figure 3, at NR contents of 10, 20 and 30%, exothermic peak at about 170°C were appeared. This clearly showed the reaction between these two polymers.

For the second heating scan, in Figure 4, without NR, T_g of PLA should occur at the temperature lower than 50°C due to amorphous domain after first heat treatment. Broaden exothermic cold crystallization peak of PLA was found to occur at higher temperature than the first scan. This was because the flexibility of polymer chains both by the present of rubber and disappearing of heat history by the first scan.

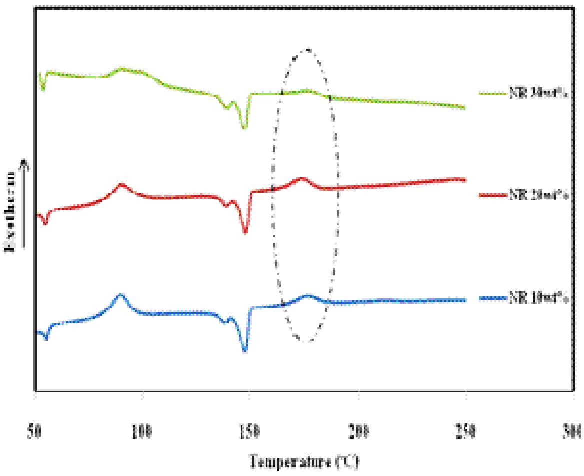

Figure 3. DSC First heating scan thermogam of PLA/ NR blend at the content of NR at 10-30%.

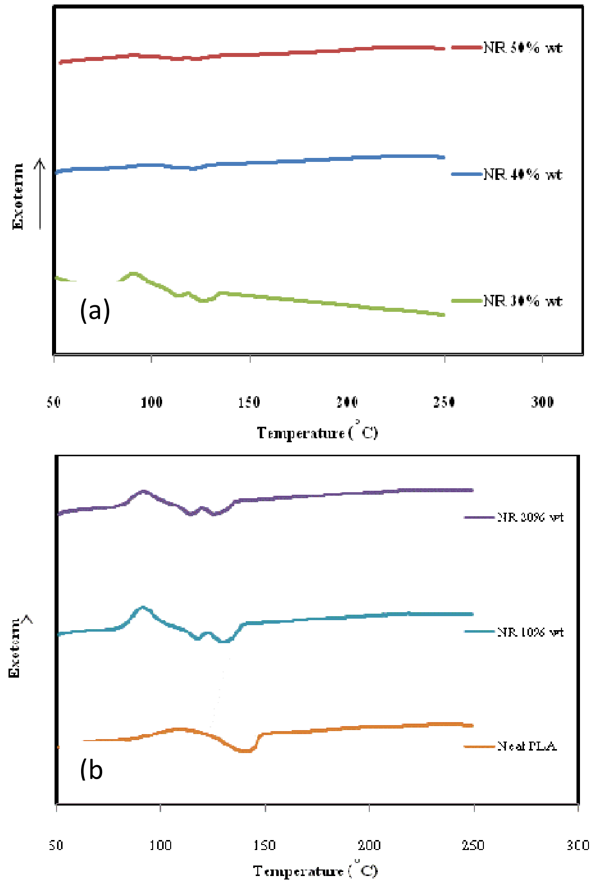

Figure 4. DSC Second heating scan thermogram of PLA/NR at (a) 30-50% and (b) 0-30%

It is noticeable that PLA with the present of NR, at the content of 10-30% NR, both exothermic peak and endothermic peaks could still be clearly observed. Meanwhile at the NR content of 40-50% endothermic peak of melting started before the completion of exothermic cold crystallization. This could be because the decrease in amorphous domain from the first heating.

Both melting temperatures of PLA were shifted to lower temperature compared to the first heating scan. Crystallinity of PLA was also increased with the NR content compared with neat PLA. The degradation of PLA upon thermal treatment is responsible for the shift of T_{m1} and T_{m2} including the crystallinity of PLA.

As it was mentioned earlier (on the first heating scan of PLA/NR blend) that PLA and NR appeared to have exothermic reaction after melting. The covering of NR at the inter-phase of the blends observed from SEM micrographs also confirmed the interaction between NR and PLA. The blends were also found to be partly suspended and non-dissolved in chloroform, as shown in Figure 6. FITR spectrum of the residue is shown in Figure 7 and the appearance of both polymers characteristic occurred. This phenomenon could be resulting in the sluggish of molecular motion during cold crystallization hence lowering in T_{m1} and T_{m2} and crystallinity.

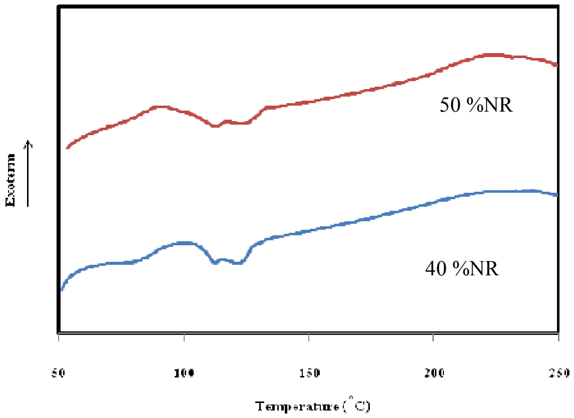

Figure 5. Second heating scan of PLA/NR at the high percentage of NR in the blend.

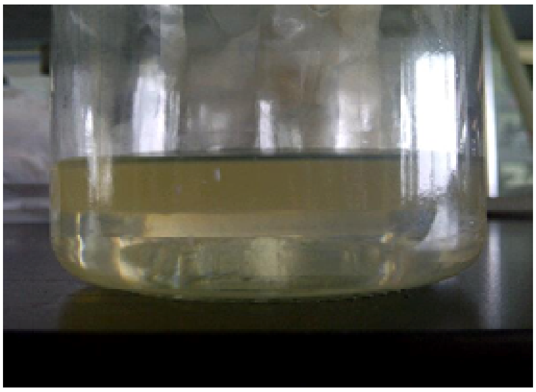

Figure 6. Camera picture show non-dissolved PLA/NR blend

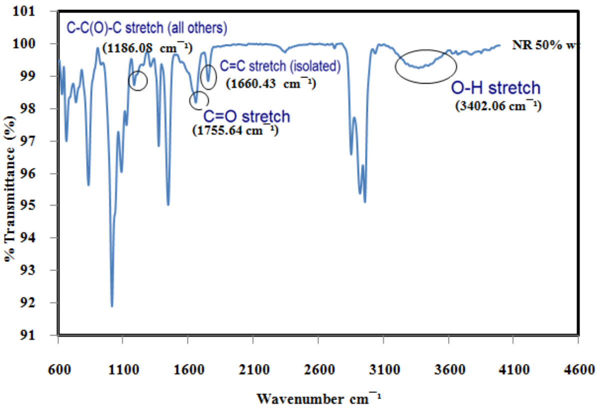

Figure 7. FTIR spectrum of PLA/NR blend residue dissolved in chloroform.

Thermal Stability of PLA/NR Blend

The result from thermo gravimetric analysis (TGA) of PLA/NR was shown in Figure 5 where onset temperature and rapidest degradation temperature, obtained from the inflection point of the TGA thermograms, were shown in Table 2. The characteristic of the weight loss versus temperature showed only one step degradation. Onset and inflection temperatures illustrated in Table 2 indicated that having NR dispersed in PLA could thermally stabilized PLA. The reaction of PLA and NR found in previous section could be attributed to the stabilization.

Table 2. Thermal properties and crystallinity of PLA/NR on second heating scan

PLA/NR	Melting (°C)		%Xc
	T_{m1}	T_{m2}	
100/0	142.12	-	20.90
90/10	118.03	130.08	28.29
80/20	114.74	125.99	26.52
70/30	118.77	131.12	30.20
60/40	114.00	121.34	7.15
50/50	112.50	124.09	8.55

Table 3. Thermo gravimetric temperature of PLA/NR

PLA/NR	Onset (°C)	Inflection point (°C)
100/0	293.87	305.74
90/10	315.48	336.00
80/20	317.81	339.87
70/30	312.68	334.67
60/40	316.71	339.15
50/50	320.02	341.37
0/100	319.56	345.89

PLA/NR Dynamic Vulcanized (TPV)

Morphology of PLA/NR TPV

SEM micrographs of PLA/NR TPV, Figure 9, shows quite similar to PLA/NR blends but NR phase in TPV seems to exhibit smaller spherical shape and better dispersion. It was also noticeable that the interaction between the polymers has occurred as can be seen on the rough surface of NR vulcanized particles. The flow of rubber could also be noticed in Figure 9 (c)-(d).

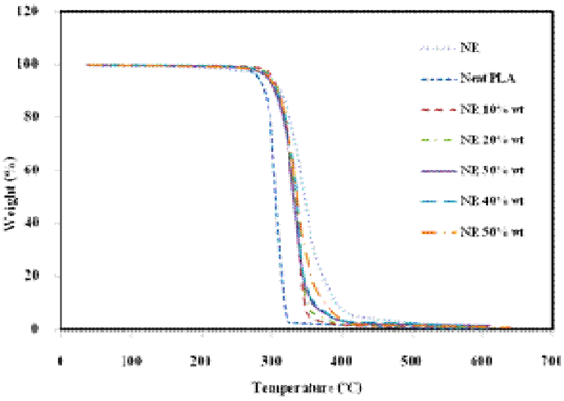

Figure 8. TGA thermogram of PLA, PLA/NR and NR

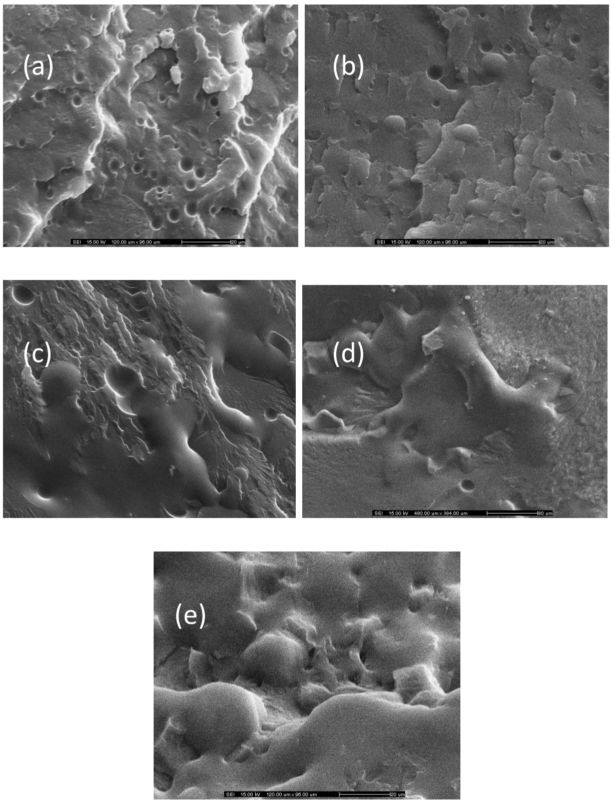

Figure 9. SEM micrographs of PLA/NR TPV with weight of NR at (a) 10, (b), 20 (c), 30 (d) 40 and (e) 50 %

Crystallization of PLA/NR TPV

It was found from DSC thermogram, in Figure 10, of the TPV that glass transition temperature, T_g, of PLA was found to shift to lower temperature. This due to the interaction of PLA and NR led to flexibility of PLA chain. The degradation of PLA occurred by the de-esterification of PLA with stearic acid from curing additive also responsible for the shift of T_g.

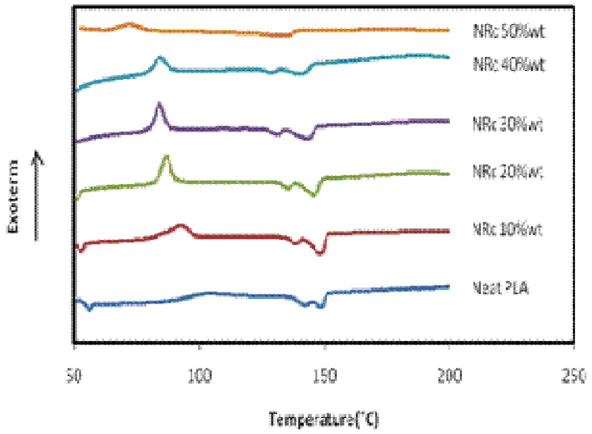

Figure 10. DSC thermogram of PLA/NR TPV at various contents of NR compound

With the same reasons, the exothermic cold crystallization peak of PLA, after glass transition temperature, were also shown to shift to lower temperature according to the content of NR compound added. The endothermic melt crystalline were also affected by the NR compound added.

Table 4 concluded the thermal properties of PLA in the TPV obtained from DSC thermograms. The degraded PLA during melt mixing and dynamic vulcanization are responsible for low T_g of PLA and low T_{cc}. The exothermic cold crystallization and endothermic melting peaks of PLA were either found at lower temperature compare to the other systems. The interaction between the two polymers also was clearly shown on the rubber particles explained by SEM micrographs. This resulted in higher crystallinity of the particular system. On the second heating scan (the result was not shown), some amorphous domain was already disappeared. Thus exothermic cold crystallization was not detectable, in some PLA/NR ratio. The degradation of PLA during heating is thought to be occurred indicated by the lower crystallinity compared to the first heating scan.

Table 4. Thermal properties of PLA/NRc TPV at first heating.

Blend Ratio	T_g (˚C)	T_c (˚C)	T_{m1} (˚C)	T_{m2} (˚C)	Xc (%)
100/0	55.92	101.77	141.91	151.18	27.20
90/10	52.75	92.47	138.60	148.31	34.52
80/20	50.0	86.95	135.5	148.8	37.17
70/30	>50	84.04	131.15	143.19	37.92
60/40	>50	84.31	129.03	140.98	37.90
50/50	>50	72.5	118.17	133.45	34.25

3.6 Thermal Stability of TPV

TGA thermograms of PLA/NR TPV at various contents of NR compound are shown in Figure 11. PLA melt blended with 1 phr of stearic acid and NR vulcanized are also presented in Figure 11. The TGA trace of PLA/NR is found to exhibit 2 steps degradation which thought to be the degradation of PLA, on the first step, and NR dispersed vulcanized particles. This confirmed the phase separation of rubber and PLA. However, as stated by SEM micrographs, the interaction at the interface of the polymers still occurred hence NR still can be able to act as nucleating agent as resulted in higher crystallinity compared to neat PLA. The degradation temperature of PLA was found, in Table 5, to be decreased with the NR compound content. The increase in NR compound led to increase in stearic acid in the system. Therefore during dynamic vulcanization, PLA chain was degraded by de-esterifiy with the acid. Consequently the shorten chain PLA could therefore be easily degraded upon heating in thermo gravimetric analyzer. In term of NR vulcanized dispersed phase, The degradation temperature of the PLA/NR TPV were shifted to higher temperature. The reaction at the inter-phase between PLA and NR vulcanized particle was thought to be to be responsible for the shifting.

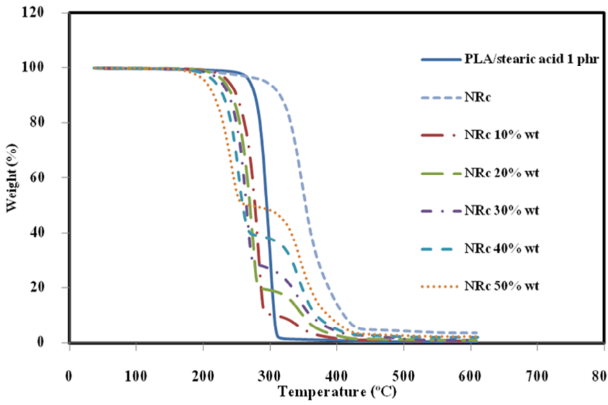

Figure 11. TGA thermograms of PLA/NR TPV at various contents of NR compound

Table 5. Degradation temperature of PLA/NRc TPV

Blend Ratio PLA/NRc	Inflection point 1 (˚C)	Inflection point 2 (˚C)
100/0	305.74	-
90/10	281.33	344.03
80/20	272,92	346.04
70/30	264.81	346.95
60/40	252.51	346.25
50/50	242.27	348.27
0/100	-	347.07

Conclusion

The addition of NR made PLA has higher percentage of crystallinity that made PLA changed from brittle polymer to ductile polymer. It was shown that at NR 10% by weight of PLA was found to show ductility with yield point. Thermal degradation of the blend with NR was found to show higher inflection point and onset point than neat PLA. This resulted from the reaction occurred at the interface of PLA/NR blends. Beside addition of NR compound led to high crystallinity of PLA. The degraded PLA during dynamic vulcanization explained the low cold crystallization temperature and low melting temperature of PLA. The interaction between rubber and PLA at the interface of the polymers can still be found and responsible for the nucleating agent behavior of NR in PLA/NR TPV. Degradation characteristic of TPV exhibited 2 steps. The first step was for PLA degradation and the second step was for vulcanized NR particles respectively. The degradation temperature of PLA was shifted to lower temperature due to the shorten chain during melt mixing with NR compound. Rubber phase found to be thermally degraded in TGA at higher temperature. The interaction at the interface should responsible for crystallinity and degradation.

Acknowledgements

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