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Dynamically Vulcanized Biobased Polylactide/Natural Rubber Blend Material with Continuous Cross-Linked Rubber Phase

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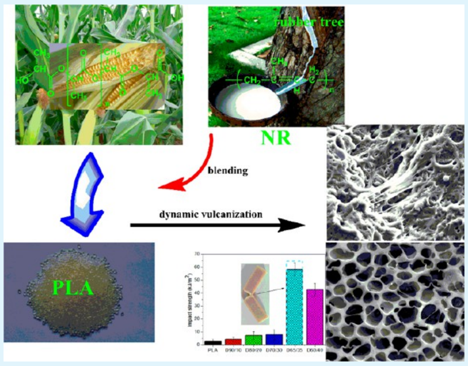
ABSTRACT: We prepared a biobased material, dynamically vulcanized polylactide (PLA)/natural rubber (NR) blend in which the cross-linked NR phase owned a continuous network-like dispersion. This finding breaks the traditional concept of a sea-island morphology formed after dynamic vulcanization of the blends. The scan electron microscopy and dissolution/swell experiments provided the direct proof of the continuous cross-linked NR phase. This new biobased PLA/NR blend material with the novel structure is reported for the first time in the field of dynamic vulcanization and shows promise for development for various functional applications.



KEYWORDS: *dynamic vulcanization, PLA/NR, morphology, interfacial adhesion*

INTRODUCTION

Recently, biobased materials have attracted much attention because of environmental issues. Polylactide (PLA), a polycondensation material of lactic acid, is one interesting biomaterial being able to break down by hydrolytic scission to its monomeric form, lactic acid, which can be eliminated from the body by incorporation into the tricarboxylic acid cycle.[1] Because of its excellent biocompatibility, biodegradability, and mechanical strength, PLA has found plenty of applications in a broad range of medical procedures, including drug delivery systems and tissue engineering, among others.[2,3] Until now, various biodegradable or nonbiodegradable polymers, such as poly(butylene adipate-co-terephthalate),[4] polyhydroxyalkanoate copolymers,[5] poly(ether)urethane elastomer,[6] poly(butylene succinate-co-adipate),[7] thermoplastic polyolefin elastomer,[8] acrylonitrile-butadienestyrene copolymer,[9] poly(ethylene-glycidyl methacrylate),[10] and glycidyl methacrylate-grafted poly-(ethylene-octene),[11] have been used in blend with PLA, acting as toughening components.

Natural rubber (NR), known as a "green" and renewable material from rubber tree, is a suitable candidate to be used as an impact modifier for PLA based on the concept of biobased materials.[12] Recently, M.A. Lopez-Manchadoa, et al.[13] reported the blends of PLA with NR to improve the brittleness of PLA. However, a lack of compatibility between the two polymers was observed. It is well-known that the final properties of immiscible polymer blends are strongly influenced by the interface of the dispersed phase and, hence, compatibilisers are often required in order to improve the properties. Later, Lopez-Manchadoa[14,15] incorporated the organoclays into PLA/NR blends, which were preferentially located at the interface acting as compatibilisers between both polymer phases, further improving the properties of PLA/NR blends. Y. Ruksakulpiwat[16] also reported using glycidyl methacrylate-grafted natural rubber (NR-g-GMA) as a compatibilizer for PLA/NR blend. However, almost all of the reported PLA/NR systems were uncross-linked blends thus have a limitation in achieving fine phase structure and better interfacial compatibility, and to the best of our knowledge, no study on dynamic vulcanization for PLA/NR blend system is reported until now. It is well-known that dynamic vulcanization can achieve fine morphologies and better interfacial interaction (the possible grafts at interphase—if peroxides are used as cross-link agent), thus, a peroxide-induced dynamic vulcanization may provide new route for improving the interfacial compatibility and properties of PLA/NR blend.

In this paper, by using a cross-linking agent, dicumyl peroxide (DCP), and a dynamic vulcanizing technique, a significantly toughened biobased PLA/NR blend material was produced. The dynamic vulcanization refers to a process of selectively vulcanizing rubber phase during melt-mixing with a thermoplastic polymer, leading to a two-phase material in which the cross-linked rubber phase is usually in particulate forms dispersed in the plastic matrix. This classical sea-island morphology has been widely observed in various dynamically vulcanized rubber/plastic systems, e.g., polypropylene/ethylene-propylene-diene monomer,[17] poly(vinylidene fluoride)/silicone rubber,[18] polypropylene/natural rubber,[19] and so on.

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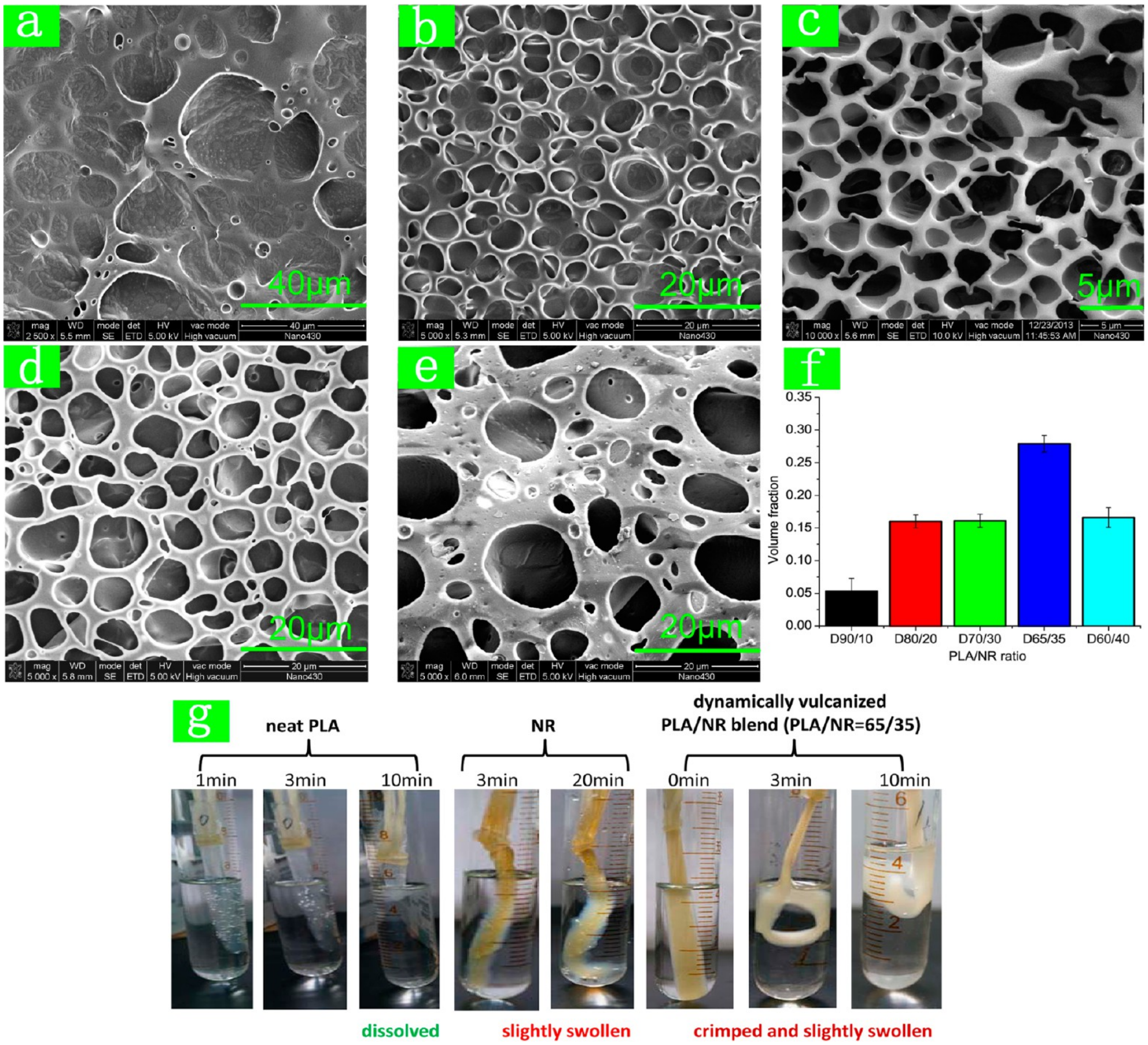

Figure 1. SEM images of the dynamically vulcanized D65/35 (PLA/NR = 65/35) blend samples after being etched in dichloromethane for: (a) 1 min, (b) 3 min and (c) 6 min; (d) dichloromethane-extracted D70/30; (e) dichloromethane-extracted D60/40; (f) Volume fraction of the cross-linked NR phase of the PLA/NR blends with different NR contents of 10% (D90/10), 20% (D80/20), 30% (D70/30), 35% (D65/35) and 40% (D60/40); (g) Digital photographs of swelling experiments for a neat PLA, neat NR and PLA/NR (65/35) blend.

Surprisingly, a continuous cross-linked NR phase was observed in the dynamically vulcanized PLA/NR blend system in our experiment, which has never been reported before. The realized continuous cross-linked NR phase and the excellent interfacial adhesion between the two phases greatly enhanced the toughness and other mechanical properties of the blend material. We report this novel structure for the first time in the field of dynamic vulcanization, and it may open up a specific end-use applications.

■ RESULTS AND DISCUSSION

The SEM images give a direct investigation of the continuous NR structure. We used dichloromethane to etch the PLA layer on the surfaces of the blends at room temperature. Figure 1a−c shows the surface SEM images of samples of D65/35 (PLA/NR = 65/35) which were etched by dichloromethane for 1, 3, and 6 min, respectively. It is clearly seen that the remaining NR phase on the surface layer shows a continuous honeycomb-like network structure, which breaks the traditional concept of a sea-island morphology formed after dynamic vulcanization of the blends. It is noted that the network of NR phase seems collapsed and deformed in Figure 1c. This is because of the softness which caused the NR network collapsing without the support of PLA phase. This specific continuous honeycomb-like network structure of NR phase is also found in D70/30 (Figure 1d) and D60/40 (Figure 1e). The digital photographs of swelling experiments are shown in Figure 1g. It is clearly seen that the neat PLA was easily dissolved in dichloromethane at room temperature. When the PLA sample was immersed in dichloromethane, the PLA at surface layer began to be dissolved, accompany with lots of bubbles. After immersed for 10 min, the immersed part of the neat PLA was dissolved completely. However, dichloromethane is a poor solvent for NR. It shows that the NR sample was only slightly swollen rather than dissolved after immersed in dichloromethane for 20 min. As for the D65/35 blend system, the immersed sample was crimped after 3 min because the softness nature of NR phase without the support of PLA phase, and the crimped sample was only slightly swollen even after 10 min. This is in consistent with the SEM result (Figure 1a−c) and verifies that

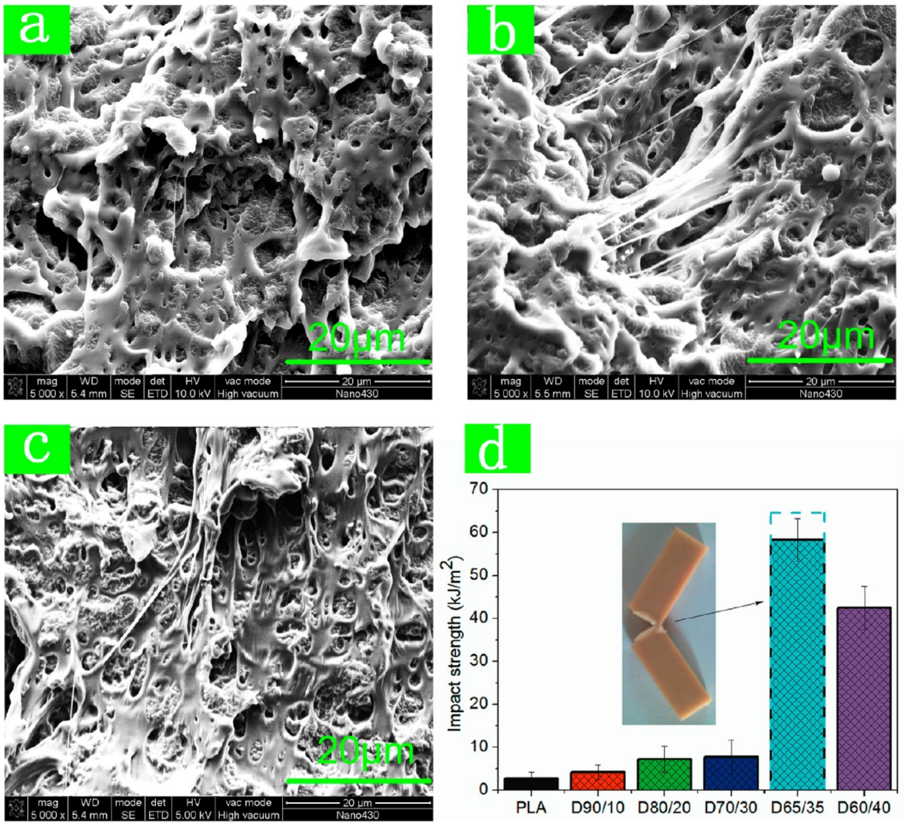

Figure 2. SEM images of the dynamically vulcanized D65/35 samples with (a) a cryo-fracture surface, (b) a fractured surface without complete cryogenically frozen, and (c) an impact fractured surface; and (d) the Notched Izod impact strength of a neat PLA and dynamically vulcanized PLA/NR blends with different NR contents.

the cross-linked NR phase in the D65/35 blend is a continuous structure, not dispersed particles.

To further confirm that the NR component has been cross-linked, we measured the volume fraction of the NR swollen in the sample gel and used it to represent the cross-link density of the NR phase. To measure the cross-link-NR volume fraction, the weighed test pieces of PLA/NR blend samples were immersed in toluene at about 23 °C for a period of 120h to ensure that swelling equilibrium was reached. Then, the samples were blotted with tissue paper to remove the solvent, and the remainders should be the cross-linked NR parts which were not dissolved but swollen in toluene. The remainders were weighed again on an analytical balance. The volume fraction of rubber swollen in the sample gel was used to represent the cross-link density, determined by the following eq 1

$$V_r = \frac{1}{1 + \left(\frac{m_2}{m_1} - 1\right) \times \frac{\rho_r}{\alpha \rho_s}} \quad (1)$$

Where m_1 and m_2 are the mass of the sample before and after swollen; ρ_r and ρ_s are the NR and toluene density (ρ_s = 0.865 g/cm^3), respectively; α is the mass fraction of NR in the sample. Figure 1f shows the volume fractions of the cross-linked NR phases in the PLA/NR blends with different NR contents of 10% (D90/10), 20% (D80/20), 30% (D70/30), 35% (D65/35), and 40% (D60/40). It shows that each of the samples contains a certain volume fraction of cross-linked NR, which reached to the maximum value of 0.30 in the D65/35 sample with 35 wt % NR.

Figure 2a shows a SEM micrograph showing typical cocontinuous morphology feature of the cryo-fracture of the dynamically vulcanized D65/35 sample. It is clearly seen that the cocontinuous morphology shows two different phase domains: one showing relative smoother surfaces with network-like dispersion and the other showing rougher surfaces. Although it is hard to clearly distinguish the cross-linked NR phase from the PLA phase because the SEM only expresses 2D information, the well embedded one phase in the other is an evidence of good interfacial adhesion between the cross-linked NR phase and PLA phase. Fortunately, a specific fractured surface was obtained from a brittle fractured sample without complete cryogenically frozen, as shown in Figure 2b, which helps us better understanding the continuous cross-linked NR phase. From the SEM images in Figure 2b, it shows that the elongated polymeric zone is associated with the stretched NR phase. The good interfacial adhesion can be directly seen from the root segment of those elongated rubber domain—no debonding sign is observed. Deformation of rubber domain is due to extensive plastic deformation of the surround PLA in view of the heterogeneous stress field involved. The deformation process absorbs a large amount of energy, contributing to the high toughness of the blend system. It is worth noting that the elongated polymeric domain connects with the smooth phase. Therefore, the smooth phase is suggested to be the cross-linked NR phase, which forms a net-like structure embedded in the PLA phase (the one with rougher surfaces). Figure 2c shows a SEM image of an impact fractured surface of the D65/35 blend sample in the vicinity of the notch, which is similar to the cryo-fracture surface. The

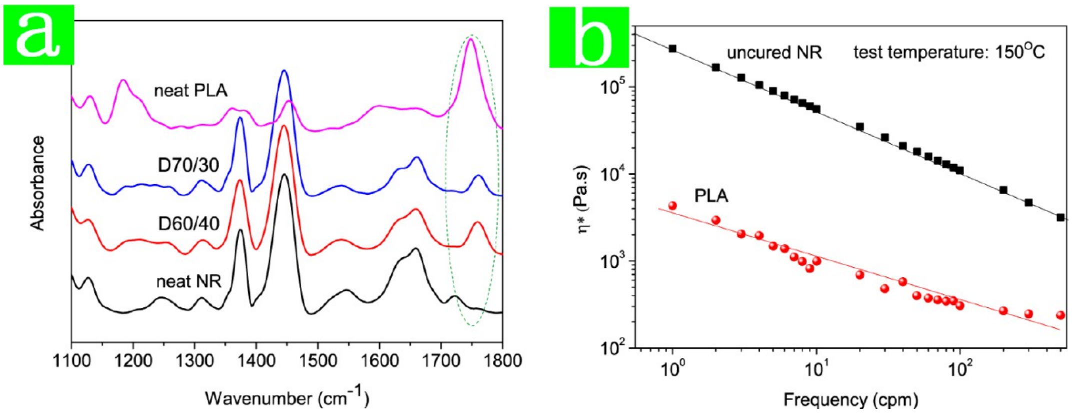

Figure 3. FTIR absorption spectra of individual polymers and dichloromethane-extracted PLA/NBR blends (a); Complex viscosities of PLA and NR vs frequency at the bending temperature (b).

morphology shows two different phase domains: one is the relative smoother rubber phase with perceptible deformation and the other is the PLA domain with rougher surfaces. No voids were observed on the impact fractured surface of D65/35, showing excellent adhesion between PLA/NR phases. Figure 2d shows the notched Izod impact strength of a neat-PLA sample and dynamically vulcanized PLA/NR blends with different NR contents. As shown in Figure 2d, the notched Izod impact strength of the neat PLA is only 2.75 kJ/m^2, reflecting a brittle characteristic of PLA. Surprisingly, a sharp brittle-ductile transition occurs at about 35 wt % of NR content (D65/35). Especially, D65/35 shows impact strength of 58.3 kJ/m^2, approximately being 21 times that of the neat PLA. When NR content is increased to about 40 wt % (D60/40), the impact strength is decreased to 42.5 kJ/m^2, but it is still 15 times higher than that of the neat PLA. A 35 wt % of NR content may be the value for achieving brittle−ductile transition in the present dynamically vulcanized PLA/NR blend system. Although D70/30 and D60/40 also formed the NR continuous network-like structure, their cross-link densities of the NR phase are lower than that of D65/35 (Figure 1f). Therefore, the cross-link extent of rubber phase may be one key factor for obtaining high toughness of the blend with this specific structure. It should be pointed out that during the impact measurements, all the samples of D65/35 were not completely fractured under the load condition, which is shown by the digital picture of the inset in Figure 2d. Considering the unfractured part which will absorb some more impact energy when it is fractured completely, the D65/35 sample should exhibit further higher impact strength as shown in Figure 2d by the dash rectangle. In this study, DCP was used as the cross-link agent, which possibly initiated the PLA grafting onto NR during melt-blending, resulting in an improved interfacial compatibilization. Figure 3a shows the absorption spectra of individual polymers and dichloromethane-extracted dynamically vulcanized blends in the range of 1100−1800 cm^{-1}. The absorption peak at 1750 cm^{-1} is attributed to the stretching vibration of carbonyl groups (C═O stretching) in the PLA. The spectrum of residues of the dichloromethane-extracted PLA/NBR blends is closely identical to that of the pure NR, indicating the complete removal of the free PLA component during dichloromethane extraction. Noticeably, an absorption peak at 1758 cm^{-1} is visible in the residues of all the dynamically vulcanized blends after thorough extraction with dichloromethane for 3 days, suggesting that PLA reacted with NR during melt-blending in the presence of DCP. This may be one of the reasons that good interfacial adhesion PLA-NR occurs.

However, the mechanism for the formation of the continuous cross-linked NR phase is still unclear at present. During processing, the components are melt-blended, and the minor phase is generally broken up to form the dispersed phase. A correlation was proposed by Wu[20] for extruded polymer blends, relating the average diameter of the dispersed phase (d) to the viscosity ratio (K) of the dispersed phase, the matrix viscosity (η_m), the shear rate ($\dot{\gamma}$) and the interfacial tension (α):

$$d = \frac{4\alpha K^{\pm 0.84}}{\dot{\gamma}\eta_m}$$

The exponent of K is negative for $K < 1$ and positive for $K > 1$. Thus, decreasing the matrix viscosity by increasing the temperature will result in an increase of the average droplet size of rubber domains in the blend. Moreover, a decrease of the viscosity of the matrix facilitates the coalescence of the droplets of the dispersed phase as the contact time required for drop coalescence is shorter.[21] In our study, the viscosity of PLA is much lower than the NR at the blending temperature (150 °C), as shown in Figure 3b. Presumably, there was an optimum melt strength ratio for the PLA and NR during melt-blending at which the blends achieved the cocontinuous phases in the blend system. This might be understood by the fact that if rubber melt strength is much higher than PLA, the rubber phase is difficult to be ruptured thus forming IPN (interpenetrating polymer network) structure. Therefore, even during dynamic vulcanization, the continuous NR phase can be maintained as continuous state, being cross-linked. Further details of the formation of continuous cross-linked NR phase are under investigation and will be reported in the future.

■ CONCLUSION

In summary, we demonstrated a super toughened biobased material of PLA/NR blends prepared via a dynamic vulcanizing technique, in which the cross-linked NR phase owned a continuous network-like dispersion. PLA grafting onto NR during melt-blending results in an improved interfacial compatibilization. This new biobased PLA/NR blend material with a novel structure is reported for the first time in the field of dynamic vulcanization and shows promise for development in various functional applications.

EXPERIMENTAL SECTION

PLA, of REVODE101 grade, MI (190 °C, 2.16 kg) = 5−8 g/10 min, average molecular weight (M_w) ≈ 150 000 g/mol, and ρ = 1.25 g/cm^3, was provided by Zhejiang Hisun Biomaterials Co., Ltd. NR, Standard Malaysian Rubber (SMR CV60) Mooney viscosity (ML(1 + 4)100 °C) = 60 ± 5, was kindly supplied by Guangzhou rubber industry research institute (China). Dicumyl peroxide (DCP) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and was purified by anhydrous alcohol recrystallization before use. Irganox 1010, antioxidant, of industrial grade, was obtained in the open market. The other chemicals were used as received.

PLA was dried for 6 h in a vacuum oven at 80 °C prior to use. NR was masticated before use. Then the dynamically vulcanized PLA/NR blends were prepared by melt blending in a system (Haake Rheocord 90) at 150 °C and at a rotor speed of 60 rpm.

PLA with quantitative Irganox 1010 was first shear-melted for 5−6 min and then the masticated NR was added. 5 min later, DCP was added and the mixing was continued for 5−7 min. Subsequently, the cured blends were removed from the cavity of an internal mixer and cooled down to room temperature. The block of the blends was chopped into small granules. The specimens for mechanical testing were prepared by injection molding machine (TTI-160F, Welltec Machinery & Equipment Co. Ltd., China). The temperature profile of the inject barrels was 165/170/170/175 °C from the first heating zone to nozzle, respectively. The injection pressure was set at 35 MPa.

For all cured blends, the weight ratio of DCP was maintained at a constant concentration relative to the amount of NR (1.5% weight of NR component). The concentration of Irganox 1010 in the blend was fixed at 0.2% weight of (PLA+NR).

CHARACTERIZATION

The Notched izod impact strength was used to evaluate the toughness of the samples. The notched specimens were tested with an impact test machine (ZWICK5331, German, Zwick/Roell) at room temperature, according to ISO 180−2000 standard. The average value was calculated from at least 5 test specimens.

The morphology of the samples was observed using a Nova NanoSEM 430 (FEI Company, USA). The cryo-fracture surface was obtained after the blend was immersed in liquid nitrogen and the impact fracture surface was obtained from the blend after impact strength test. In order to observe the cross-linked NR phase, the blends were subjected to dichloromethane wash (ambient temperature) to remove the PLA phase at the surface and then dried sufficiently. Before morphological observation, the surface of samples was sputter coated with gold to prevent electrostatic charging build-up during observation.

Melt rheological behaviors of the blends were analyzed by a rubber process analyzer (RPA 2000, Alpha Technologies, USA). All the specimens were directly loaded between the dies maintained at 150 °C and the tests were carried out in frequency sweep modes (frequencies ranging from 0.1 to 500 Hz at constant strain amplitude of 5%).

The absorption spectra were recorded using a Tensor 27 Spectrometer (Bruker, Germany) with a resolution of 4 cm^{-1} and 32 scans. For the dynamically vulcanized PLA/NR blends, the injection molded blend specimen was first extracted with dichloromethane at ambient temperature for 3 days to selectively remove free PLA thoroughly, then the residue cross-linked NR was compressed into disks for the FT-IR test using the attenuated total reflectance (ATR) model. All FT-IR samples were oven-dried under a vacuum to eliminate the effects of residual solvent and moisture prior to testing.

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Notes

The authors declare no competing financial interest.

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