



Dynamically vulcanized polylactide/nitrile butadiene rubber blends with continuous cross-linked rubber phase

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Received: 4 August 2018 / Accepted: 3 December 2018 / Published online: 7 December 2018
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Abstract

Thermoplastic vulcanizates (TPVs) based on polylactide (PLA)/nitrile butadiene rubber (NBR) blends were prepared by dynamic vulcanization and the PLA matrix was plasticized by dioctyl phthalate (DOP). The surface morphologies of the etched PLA/DOP/NBR TPVs were studied by field emission scanning electron microscope, and the element contents in the TPV surface were characterized by energy dispersive X-Ray spectroscopy; moreover, the dissolution/swell behaviors, infrared spectra and rheological behavior of the prepared PLA/DOP/NBR TPV were also characterized. Experimental results indicated that the cross-linked NBR in the PLA/DOP/NBR TPVs owned a continuous network-like structure due to the much difference in the viscosity between the NBR rubber and the PLA resin. This unique finding breaks the traditional concept of a sea-island morphology which was formed after dynamic vulcanization of the thermoplastic resin/rubber blends. PLA grafted onto NBR under the action of DCP vulcanizing agent, leading to the improving interface compatibility. It should be noted that this PLA/DOP/NBR TPV with the novel microstructure has never been reported.

Keywords Dynamic vulcanization · Polylactide · Nitrile butadiene rubber · Co-continuous · Morphology

Introduction

Thermoplastic elastomers (TPEs) are a class of polymers having the properties of both conventional vulcanized rubbers and thermoplastics [1] which can be processed at an elevated temperature. Thermoplastic vulcanizates (TPVs), as a special class of TPEs, are prepared via a dynamic vulcanization technology [2, 3]. Dynamic vulcanization was firstly described by Gessler [4] in 1962 and then developed by Fisher [5], Coran [6] and Abdou-Sabet [7]. Traditionally, the rubber phase is vulcanized and finely dispersed in a continuous resin matrix under the shear force during the dynamic vulcanization [8, 9], and the resulting materials exhibit the excellent mechanical properties and can be recycled repeatedly under melting conditions. This technology led to the commercialization of a

large number of new TPE products in the mid- to late-1980s [10, 11]. Because of their unique characteristics, TPVs played a very important role in the applications of automotives, building constructions, wires and cables, and so on [12]. However, a novel co-continuous microstructure in the dynamically vulcanized polylactide (PLA)/natural rubber (NR) blends was firstly discovered by Chen [13]; moreover, Yuan [14] found a similar microstructure in the dynamically vulcanized PLA/epoxidized natural rubber (ENR) blends.

With the increasing awareness of environmental protection, biodegradable materials have attracted more and more attention [15]. PLA, which is formed by the polycondensation of lactic acid, is a bio-based and biodegradable polymeric material [16, 17]. It can be broken down by hydrolytic to its monomeric form, lactic acid [13, 18]. PLA has lots of applications in medical fields, including surgical suture, drug controlled release system and gene therapy vector due to its excellent biocompatibility, biodegradability and mechanical strength. At present, various of materials such as NR [13], ethylene-co-vinyl copolymer (EVA) [19] and ENR [14], have been combined with PLA. Nitrile butadiene rubber (NBR) is a copolymer of butadiene and acrylonitrile which has excellent properties including oil resistance, heat resistance and

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adhesion. It has become an essential elastic material in the automotive, aerospace, petroleum, photocopying and other industries.

In this paper, we prepared a series of PLA/DOP/NBR TPVs which were cross-linked by using dicumyl peroxide (DCP). Surprisingly, a co-continuous phase structure was observed in the dynamically vulcanized PLA/DOP/NBR blends.

Experimental

Materials

PLA, injection grade, was provided by Nature Works USA with a melt flow index (MFI) of 20 g 10 min⁻¹ (190 °C, 2.16 kg). NBR rubber (3305 type, with acrylonitrile content of 35 wt% and ML₁₊₄ (100 °C) = 45) was commercially manufactured by Lanzhou Petrochemical Co., Ltd., China. DOP plasticizer was produced by Tianjin Guangcheng Chemical Industry Co., Ltd., China. Zinc oxide (ZnO) was used as an activator and obtained from NewLe Qinshi Zinc Co., Ltd., China. Stearic acid was used as an activator and obtained from Wanyou Co., Ltd., China. Dicumyl peroxide (DCP), used as a vulcanizing agent, was obtained from Gaoqiao Petrochemical Co., Ltd., China. Antioxidant D and Poly (1,2-dihydro-2,2,4-trimethyl-quinoline) (Antioxidant RD) was used as an antioxidant and obtained from Shengao Chemical Co., Ltd., Caoxian, China. Tetramethyl thiuram monosulfide (TS) and N-cyclohexyl-2-benzothiazole sulfenamide (CZ) were used as accelerators and manufactured by Northeast Auxiliary Chemical Industry Co., Hebei, China. Sulphur was used as a vulcanizing agent and obtained from NewLe Qinshi Zinc Co., Ltd., Xinle, China.

Preparation of dynamically vulcanized PLA/DOP/NBR blends

PLA, NBR, DOP and the industry raw materials as shown above were used for the preparation of the blends. The formula of NBR rubber system using DCP as cross-linking agent was shown by weight (phr) as below: 100 phr NBR, 2 phr DCP, 5 phr ZnO, 1 phr stearic acid, 1 phr Antioxidant D. The S-containing accelerating system recipe consisted of the following ingredients: 100 phr NBR, 1 phr S, 1.2 phr TS, 1.5 phr CZ, 5 phr ZnO, 1 phr stearic acid, 1 phr Antioxidant RD; and the S-containing accelerating system was only used in the specimen listed in Table 2.

The dynamically vulcanized PLA/DOP/NBR blends were produced via a two-step mixing process (S(S)K-160, Shanghai Qun Yi Rubber Machinery Co., Ltd.). Firstly, the pre-blends containing NBR rubber and other additives were prepared in a two-roll mill at room temperature.

Then the pre-blends were removed from the two-roll mill after 3 min. Secondly, the TPVs were prepared by melt-mixing the NBR pre-blends with various amounts of PLA which was dried for 2 h in a vacuum oven at 80 °C and DOP plasticizer using a Brabender PLE 331 plasticorder (Brabender GmbH, Germany). The mixer temperature was kept at 165 °C. The PLA/NBR blending ratio varied from 20/80 to 60/40, and the DOP dosage was always 5 wt.% of PLA. The requisite quantities of PLA resin and DOP were charged into the mixer and allowed to melt and mix. The NBR pre-blend was added after 3 min, and the mixing was continued for another 8 min. Finally, the compound was removed from the mixer and then passed through the cold two-roll mill in the molten state to obtain sheets which were about 2 mm thick. The sheets were pre-heated at 165 °C for 10 min in a plate vulcanizing machine (50 T, Shanghai Qun Yi Rubber Machinery Co., Ltd.), and then compression-molded under a pressure of 15 MPa at 165 °C for 6 min, followed by cold compression in another molding machine (25 T, Shanghai Qun Yi Rubber Machinery Co., Ltd.) for 8 min. Test specimens were die-cut from the compression-molded sheet and used for testing after 24 h. And NBR static vulcanizate was prepared in a compression-molded machine under the preparation condition of 165 °C for 8 min.

Characterization

Mechanical experiments

The dumbbell-shaped specimens for the measurement of tensile properties were prepared according to ASTM D412. Moreover, the unnotched 90° angle test piece was used to test the tearing strength according to ASTM D624. Both tensile and tearing tests were performed on a universal testing

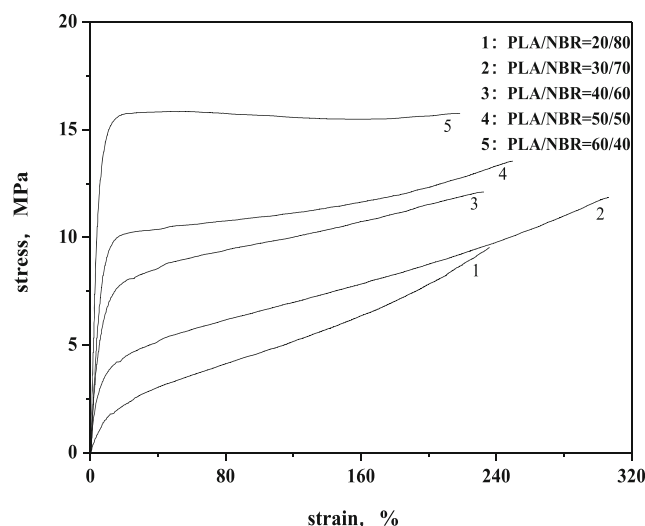


Fig. 1 Stress-strain curves of dynamically vulcanized PLA/NBR blends

Table 1 Mechanical properties of dynamically vulcanized PLA/NBR blends

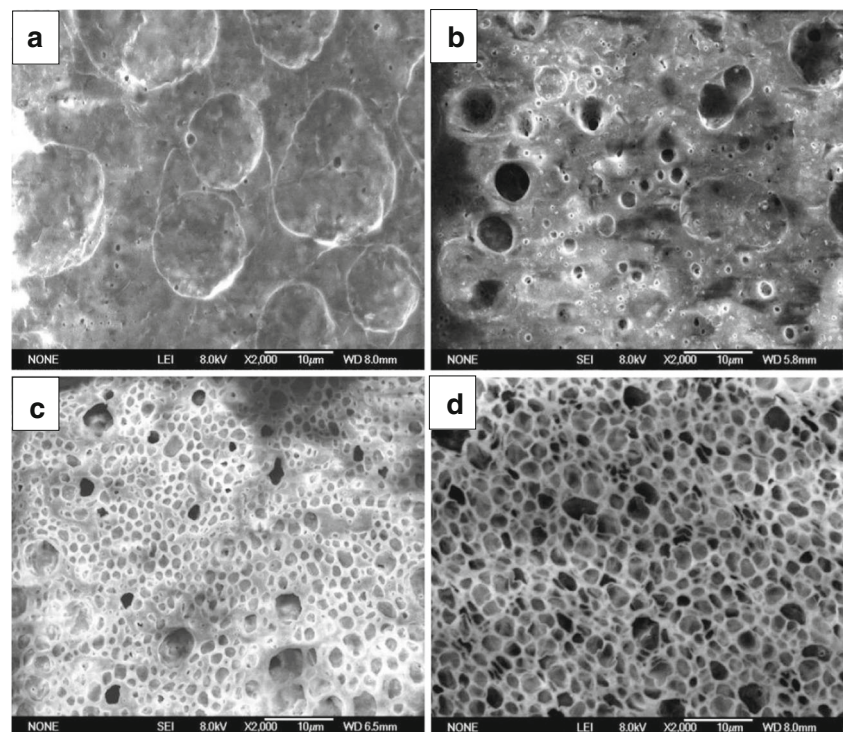
Mechanical properties PLA/NBR	Tensile strength/ MPa	Elongation at break/%	Tensile set at break/%	Tearing strength/ KN/m	Shore A hardness
20/80	10.6	243.6	2.5	53.8	81
30/70	11.9	309.0	5.0	65.3	87
40/60	12.1	238.4	15.0	75.9	89
50/50	13.6	252.6	30.0	107.3	90
60/40	15.9	224.2	42.5	118.1	91

machine (TCS-2000, Gottech Testing Machines Inc., Taiwan, China) at a crosshead speed of 500 mm/min. The shore A hardness was determined using a handheld Shore A Durometer according to ASTM D2240. The average value of all the tests were calculated for five test specimens at 23 °C.

Microscopy analysis

Morphological study was carried out by FE-SEM (FE-SEM, 6700F, Japan Electron Co., Ltd., Tokyo, Japan). The elements analysis was tested by Energy dispersive X-ray spectroscopy (EDX, Oxford Co., Ltd., UK). The PLA phase in the surface of specimens was extracted by immersing the blends into dichloromethane at 25 °C for 10 min. Then the specimens were dried in a vacuum oven at 40 °C for 24 h. The etched surfaces of the specimens were sputtered with thin layers of platinum and imaged using the FE-SEM.

Fig. 2 FE-SEM images of the dynamically vulcanized PLA/NBR TPV with 50/50 weight ratio after being etched in dichloromethane for: (a) 1 min, (b) 3 min, (c) 7 min and (d) 10 min



Rheological analysis

Rheological behaviors of the blends were analyzed using Rosand Precision Rheometer (Bohlin Co., Ltd., Britain) under Double-bore experiment mode at 165 °C. The L/D ratios of the capillaries were 16/1 and 0, respectively. All the rheological data was subjected to Bagley and Rabinowitch calibration and the results were processed by the software afforded by Bohlin Instrument.

FT-IR spectrum

The absorption spectrums were recorded using a Nicolet FT-IR-Magna-750 with a wave number from 600 cm^{-1} to 4000 cm^{-1} . For the dynamically vulcanized PLA/NBR TPV, the TPV specimen was first extracted with dichloromethane at room temperature for 72 h to selectively remove the free PLA thoroughly, then the residue cross-linked NBR was tested using the attenuated total reflectance (ATR) model.

Table 2 Mechanical properties of dynamically vulcanized PLA/NBR (50/50) TPVs with different vulcanization systems

Mechanical Properties Vulcanization system	Tensile strength/MPa	Elongation at break/%	Tensile set at break/%	Tearing strength/ (kN·m ⁻¹)	Shore A hardness
Sulfur	5.73	134.8	20.5	74.9	94
DCP	13.55	252.6	30.0	110.1	90

Result and discussion

Mechanical properties of the dynamically vulcanized PLA/NBR blends

Figure 1 shows the stress-strain behaviors of the dynamically vulcanized PLA/NBR blends with different weight ratios. The stress-strain traces show drastic difference with increasing PLA dosage. Initially, an obvious increase in tensile stress and modulus could be observed. Upon further deformation, the slope of curves decreased with the stress increasing almost linearly until fracture occurred. All the stress-strain curves showed the representative elastomeric character of being soft and tough. Tensile strength, elongation at break, tensile set at break, tearing strength and shore A hardness of the dynamically vulcanized PLA/NBR blends were shown in Table 1. As can be seen in Table 1, increasing the PLA loading in the blends led to the increasing tensile strength, tearing strength and hardness, whereas the elongation at break and tensile set at break were decreased. It should note that the comprehensive properties of the PLA/NBR TPV with 50/50 weight ratio were better (Fig. 2).

Table 2 shows the influence of vulcanization system on the mechanical properties of PLA/NBR TPV with 50/50 weight ratio. As can be seen from Table 2, tensile strength, tearing strength and elongation at break of the specimen cross-linked by DCP is larger than that of specimen vulcanized by sulfur, indicating that the existence of DCP enhanced the interface between PLA and NBR significantly.

Morphology and microstructure of PLA/NBR TPVs

From the FE-SEM images, we can observe the NBR phase showing a continuous structure directly. The PLA phase on the surfaces of the TPVs was etched by dichloromethane.

Fig. 3 Dichloromethane extracted the PLA/NBR TPVs with 40/60 and 60/40 weight ratio. (a) PLA/NBR TPV with 40/60 weight ratio, (b) PLA/NBR TPV with 60/40 weight ratio

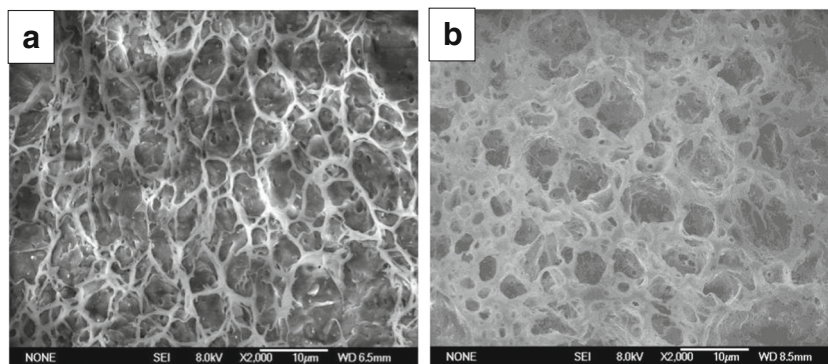


Figure 2a-d shows the surfaces of the PLA/NBR TPV at 50/50 weight ratio etched by dichloromethane for 1, 3, 7, and 10 min, respectively. As can be seen from the Fig. 2, the NBR phase shows a continuous network structure which breaks the concept of the traditional sea-island structure during the dynamic vulcanization. From Fig. 2a-d, we can observe the network structure becomes more and more obviously as increasing the etching time. We also observed the PLA/NBR TPVs with 40/60 and 60/40 weight ratio to ensure that the appearance of co-continuous structure in the PLA/NBR TPV with 50/50 was not accidental (Fig. 3). As can be seen from Fig. 3, the NBR phase in the PLA/NBR TPVs with 40/60 and 60/40 weight ratio also showed the continuous microstructure.

Dissolution/swell studies of NBR static vulcanizate, neat PLA and PLA/NBR TPV

Figure 4 is the digital photographs of the swelling experiment. It can be clearly seen that the pure PLA was completely dissolved in dichloromethane at room temperature. The surface of pure PLA began to dissolve and generate a lot of bubbles when it was immersed in the dichloromethane. After 10 min, the part of PLA immersed in dichloromethane was dissolved completely. It shows that the NBR vulcanizate was only slightly swollen but not dissolved even after immersed in dichloromethane for 10 min due to the cross-linking structure. As for the PLA/NBR TPV with 50/50 weight ratio, it only swelled and the structure did not collapse even after 10 min. This corresponds to the FE-SEM results (Fig. 2a, b, c and d) which confirms that the cross-linked NBR phase in the PLA/NBR TPV with 50/50 weight ratio is a continuous microstructure.

We represented the cross-link density of NBR phase by measuring the volume fraction of NBR swollen in the

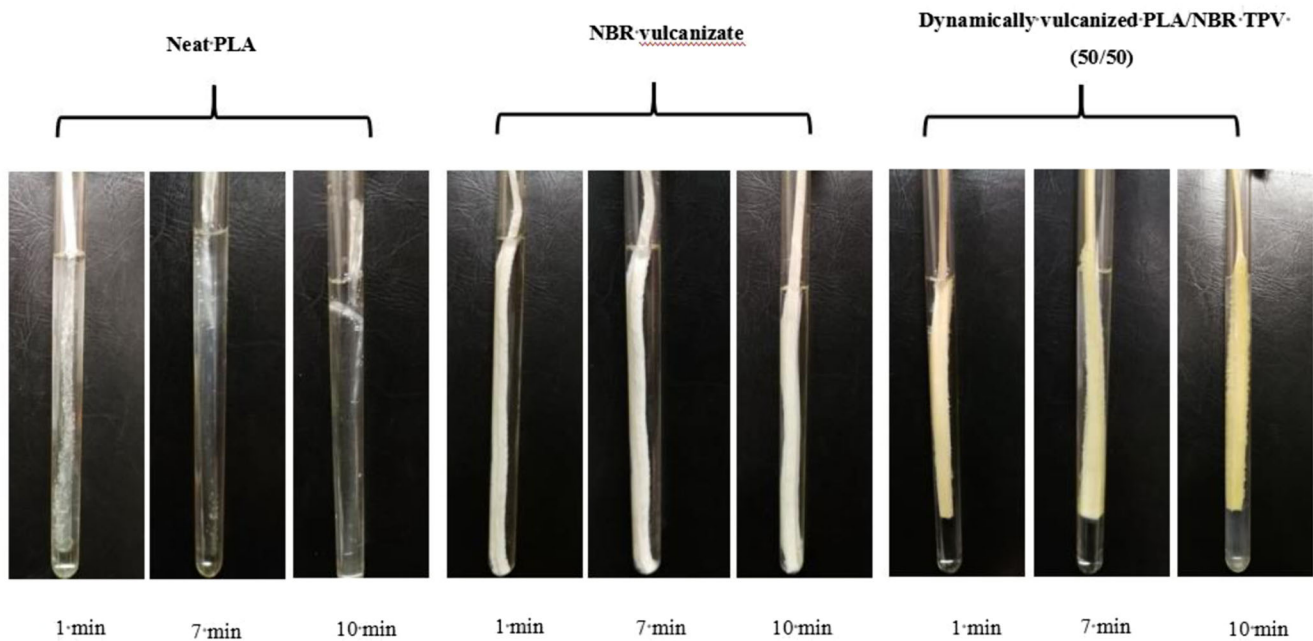


Fig. 4 Digital photographs of swelling experiments for a neat PLA, neat NBR vulcanizate and PLA/NBR (50/50) TPV

specimen in order to prove that the NBR phase has been cross-linked. Firstly, PLA/NBR TPVs were weighted and then immersed in toluene at 25 °C; after 120 h, the TPVs had reached the swelling equilibrium. Secondly, the swelled specimens were dried in an oven at 40 °C for 24 h to remove the solvent, and the remainders should be the NBR phase parts which were cross-linked and only swollen in toluene. Lastly, the remainders were weighted again in the same analytical balance. The cross-link density was represented by the volume fraction of rubber swollen in the specimen. The calculation method is shown as below [13]:

$$V_r = 1/[1 + (m_2/m_1 - 1) \times (\rho_r/\alpha\rho_s)] \quad (1)$$

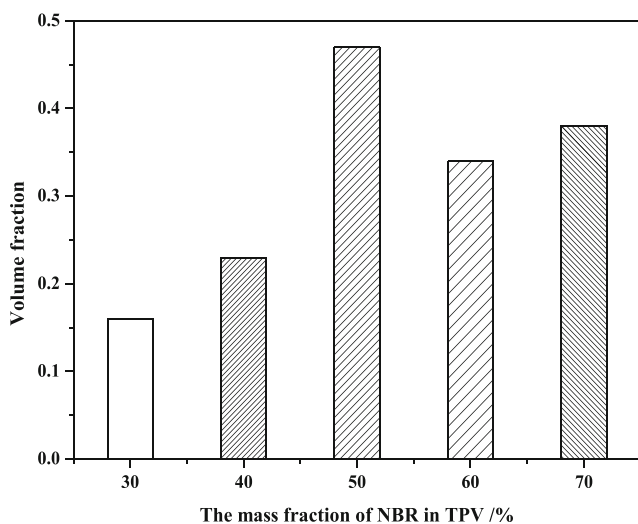


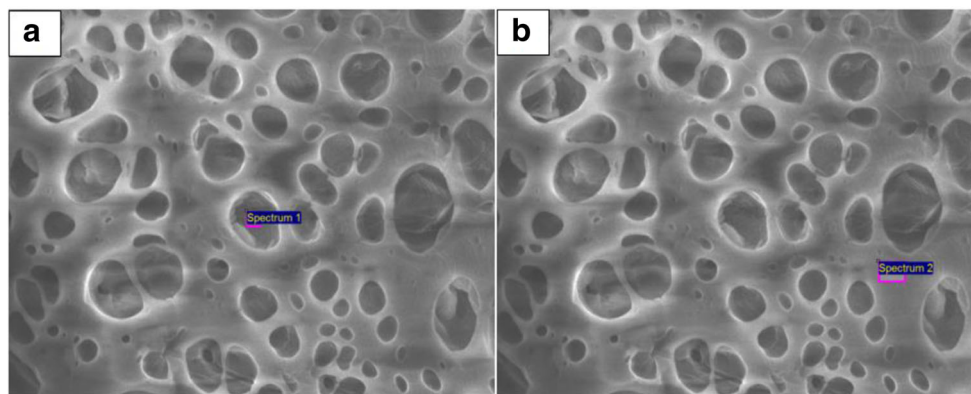
Fig. 5 Volume fraction of the cross-linked NBR phase of the PLA/NBR TPVs with different NBR contents of 30%, 40%, 50%, 60% and 70%

Where m_1 is the weight of the specimen before swollen and the m_2 is the weight of the specimen after swollen; ρ_r , the NBR density and the ρ_s , toluene density which is 0.865 g/cm³; the mass fraction of NBR in the specimen is represented with α . Figure 5 shows the volume fraction of cross-linked NBR phase in PLA/NBR TPVs with different NBR content. As can be seen from the Fig. 5, there was a certain volume fraction of cross-linked NBR phase in every specimen and the volume fraction reached the maximum value when the PLA/NBR TPV with 50/50 weight ratio.

The energy dispersive X-ray spectroscopy of PLA/NBR TPV

Figure 6 shows the EDX testing areas in the etched surface of PLA/NBR TPV with 50/50 weight ratio. In order to confirm that the residual network structure in the etched surface was a cross-linked NBR network, the surface was analyzed by EDX. In our research, the activator ZnO particles were mixed in the NBR pre-blend, and we can identify the NBR phase by testing Zn element content in the different regions of the etched surface. The test results of the regions in Fig. 5 are showed in Table 3. As can be seen from Table 3, the Zn element content of the grid region in Fig. 5b is 5.77%, which is much higher than the Zn element content (0.85%) in the etched region in Fig. 5a, indicating that the network structure is NBR phase. In our research, the ZnO particles were mixed into the NBR pre-blend; however, Zn element can be still detected in PLA area. On the one hand, some ZnO particles maybe move from NBR to PLA during the dynamic

Fig. 6 EDX testing areas in FE-SEM photos of etched PLA/NBR (50/50) TPV



vulcanization; on the other hand, EDX usually has a certain detection depth and can detect the Zn element in the rubber phase which is below the resin phase.

FT-IR spectrum of PLA/NBR TPV

Figure 7 shows the FT-IR absorption spectra of individual polymers and dichloromethane-extracted PLA/NBR TPV in the range of $600 \sim 4000 \text{ cm}^{-1}$. The absorption peak at 2900 cm^{-1} is the stretching vibration of methylene groups ($-\text{CH}_2$ stretching) and the absorption peak at 2250 cm^{-1} belongs to the nitrile groups ($\text{C}\equiv\text{N}$) in NBR. The stretching vibration of carbonyl groups ($\text{C}=\text{O}$ stretching) in the PLA attributes to the absorption peak at 1750 cm^{-1} . For the etched PLA/NBR TPV with 50/50 weight ratio which was immersed into dichloromethane for 72 h, the spectrum was closely identical to that of pure NBR. It is noteworthy that an absorption peak at 1758 cm^{-1} was visible in dichloromethane-extracted PLA/NBR TPV, indicating that the graft reaction had occurred at PLA and NBR interface due to the existence of DCP.

Rheological properties of PLA and raw NBR

At present, there is no clear explanation for the formation mechanism of the co-continuous phase structure. During the dynamic vulcanization, the rubber phase is generally broken

Table 3 Energy dispersive X-ray spectrometer (EDX) composition content of the selected areas in the etched PLA/NBR (50/50) TPV surface

Elements content (wt.%)	Zn	C	O	N
a	0.85	73.02	17.17	8.96
b	5.77	69.01	25.02	0.20

up to form the dispersed phase. Wu [20] proposed a correlation for the extruded polymer blends:

$$\dot{\gamma} \eta_m \alpha / d = 4k^{\pm 0.84} \quad (2)$$

Where $\dot{\gamma}$, d , α , η_m and η_d is shear rate, particle diameter, interfacial tension, matrix viscosity and dispersed-drop viscosity, respectively; moreover, $k = \eta_d / \eta_m$. The exponent of k is negative for $k < 1$ and positive for $k > 1$. The size of the dispersed droplets is proportional to the interfacial tension and the ± 0.84 power of viscosity ratio. When the interfacial tension is relatively lower and the viscosity ratio is closer to unity, the dispersed drops are smaller. Moreover, when the contact time required for droplet coalescence is shorter, the reduction in matrix viscosity is beneficial to the coalescence of the dispersed phase droplets [21], leading to the formation of co-continuous microstructure.

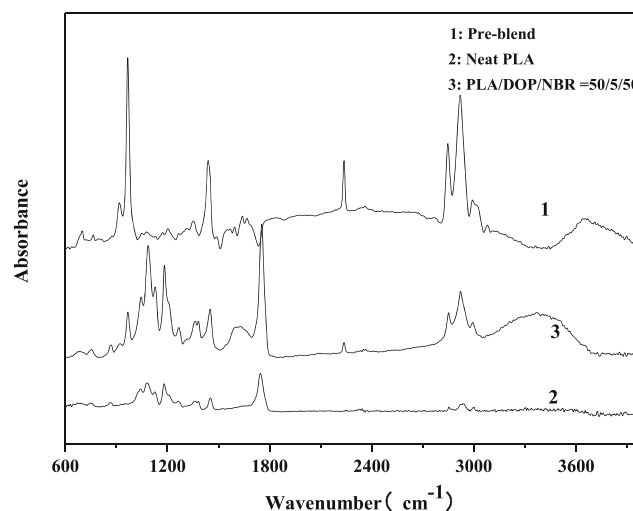


Fig. 7 FT-IR absorption spectra of individual polymers and dichloromethane-extracted PLA/NBR TPV

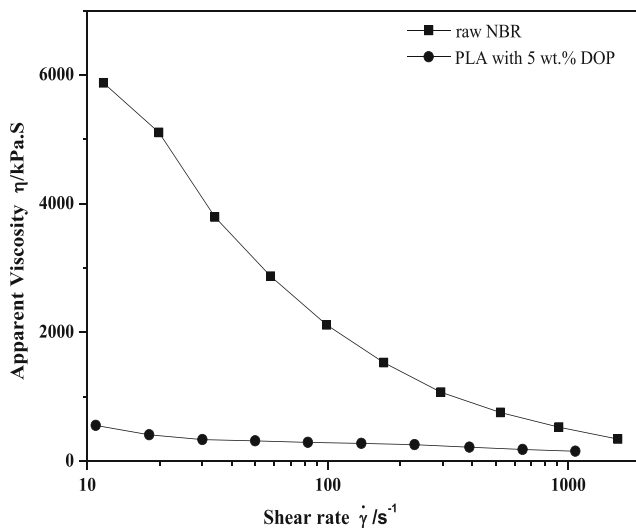


Fig. 8 Shear rheology curves of PLA incorporated with 5 wt.% DOP and raw NBR rubber

Figure 8 shows the shear rheology behavior of the PLA incorporated with 5 wt.% DOP and the raw NBR rubber at 165 °C. The pseudoplastic nature of these specimens can be indicated by the phenomenon that the apparent viscosity decreases significantly with increasing shear rate. As shown in Fig. 8, the apparent viscosity of PLA is much lower than that of the NBR. It was speculated that there was an optimum melt strength ratio for PLA and NBR during the dynamic vulcanization where the blends achieved the co-continuous phase in the blend. This can be understood by the following fact that when the melting strength of the rubber phase is much higher than that of the resin phase under molten condition, the rubber phase is difficult to be cracked during processing, resulting in the forming the interpenetrating network structure; moreover, the cross-linked NBR phase can maintain the continuous even during dynamic vulcanization. The details of the formation of continuous cross-linked NBR phase need the further confirmation.

Conclusions

TPVs based on PLA/NBR blends were prepared by dynamic vulcanization, where the cross-linked NBR phase had a continuous network-like structure. PLA grafted onto NBR under the action of DCP during the dynamic vulcanization, leading to the improved interface compatibility. The apparent viscosity difference between the PLA and the NBR was high, resulting in the formation of co-continuous phase structure. The PLA/NBR TPV with novel microstructure has never been reported and showed the promise for various functional applications.

Acknowledgments The work was supported by Shandong Provincial Natural Science Foundation, China (ZR2017MEM021;ZR2016EMM03) and Upgraded Project of Shandong Province for Guidance Ability of Graduate Tutors (SDYY17044).

Compliance with ethical standards

Statement This manuscript has not been published elsewhere and it has not been submitted simultaneously for publication elsewhere.

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