

Morphology and mechanical properties of PVC/straw-fiber coated with liquid nitrile-butadiene rubber composites

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ABSTRACT: This study exhibited an approach of high-value utilization of straw fiber (SF) in polymer composites. The rigid poly(vinyl chloride) [PVC]/SF and PVC/SF coated with liquid nitrile-butadiene rubber (PVC/LNBR-SF) composites were both fabricated by melt mixing. The chemical structure and crystal structure of LNBR-SF were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). The mechanical properties and micro-structure of PVC/SF and PVC/LNBR-SF composites were also studied. FTIR and XRD results showed that the chemical structure and crystal structure of SF did not change after modifying with LNBR. The mechanical properties analysis showed that the PVC/LNBR-SF composites exhibited better tensile strength, elongation at break and notched impact strength than those of PVC/SF composites owing to the compatibilization and toughening effect of LNBR. Scanning electron microscope results indicated that the LNBR improved the dispersion of SF in PVC matrix to some extent. The interface adhesion between SF and PVC matrix with adding LNBR was also enhanced. These results suggested that PVC/LNBR-SF composites exhibited promising potential for practical application in substitute for wood. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44119.

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INTRODUCTION

Wood-plastic composites (WPCs) are defined as a kind of composites made by wood or fiber-based material and plastic. Since they were been made, WPCs have drawn more and more attention owing to environmentally friendly and recyclability.^{1–4} They have been widely used in many areas due to their excellent performance given by both wood and plastic. Generally, the most popular thermoplastics among WPCs are polyethylene (PE),^{5–7} polypropylene (PP),^{8–10} and poly(vinyl chloride) (PVC).^{11–14} The woody filler in WPCs usually consists of ground wood waste or wood fiber.

Despite numerous advantages, WPCs also have certain drawbacks such as poor interaction between wood and polymer matrix and high sensitivities of moisture and heat. Most researchers have focused on these weak points to improve their properties. Chemical modification of filled wood flour can markedly improve the interfacial bond between wood flour and polymeric matrix.^{15–18} Dichromate in oxalic acid was used as an oxidant to enhance bonding between cellulose fibers and polymer.¹⁵ Beshay and Hoa has developed a new method to generate free radicals on the cellulosic fibers, which increased the tensile

strength of PVC and polystyrene with these fibers.¹⁶ Wolkenhauser *et al.* used plasma treatment to enhance the adhesion properties of adhesives and paints on WPCs.¹⁷

The other method that has been used to solve this problem is to use various coupling agents to provide a lower surface energy between the woody materials and the polymer matrix. Coupling agents play an important role in the improvement of interfacial adhesive strength in WPCs. Coupling agents in general can improve the compatibility between hydrophilic-like wood and hydrophobic-like thermoplastics.^{19–21} Therefore, choosing the suitable coupling agents is one of the key factors in preparing WPCs with excellent properties. Kim *et al.* synthesized a novel coupling agent for improving the interfacial adhesion between PVC and bamboo flour in PVC/bamboo flour composites.¹⁹ Hong *et al.* examined the effects of impact modifier types and addition levels on the mechanical properties of rigid WC/wood-fiber composites.²⁰ Shah *et al.* investigated novel coupling agents that were composed of chitin and chitosan on PVC-based WPCs.²¹ However, the above methods have some universally problems such as the complex treatment and long modification period. Therefore, it is really important to search for a simple and effective method to modify the wood flour.

Table I. The Compositions of Rigid PVC/SF and PVC/LNBR_x-SF_y Composites

Sample	PVC (phr)	SF (phr)	LNBR _x -SF _y (phr)	Processing aids (ACR-201) (phr)	Heat stabilizer (phr)	Lubricant (phr)	Antioxidant 1010 (phr)
neat PVC	100	—	—	5	4	1	0.5
PVC/SF ₁	100	1		5	4	1	0.5
PVC/SF ₃	100	3		5	4	1	0.5
PVC/SF ₅	100	5		5	4	1	0.5
PVC/SF ₁₀	100	10		5	4	1	0.5
PVC/SF ₂₀	100	20		5	4	1	0.5
PVC/(LNBR ₉₀ -SF ₁₀) ₁	100		1	5	4	1	0.5
PVC/(LNBR ₉₀ -SF ₁₀) ₃	100		3	5	4	1	0.5
PVC/(LNBR ₉₀ -SF ₁₀) ₅	100		5	5	4	1	0.5
PVC/(LNBR ₉₀ -SF ₁₀) ₁₀	100		10	5	4	1	0.5
PVC/(LNBR ₉₀ -SF ₁₀) ₂₀	100		20	5	4	1	0.5
PVC/(LNBR ₈₀ -SF ₂₀) ₁	100		1	5	4	1	0.5
PVC/(LNBR ₈₀ -SF ₂₀) ₃	100		3	5	4	1	0.5
PVC/(LNBR ₈₀ -SF ₂₀) ₅	100		5	5	4	1	0.5
PVC/(LNBR ₈₀ -SF ₂₀) ₁₀	100		10	5	4	1	0.5
PVC/(LNBR ₈₀ -SF ₂₀) ₂₀	100		20	5	4	1	0.5
PVC/(LNBR ₇₀ -SF ₃₀) ₁	100		1	5	4	1	0.5
PVC/(LNBR ₇₀ -SF ₃₀) ₃	100		3	5	4	1	0.5
PVC/(LNBR ₇₀ -SF ₃₀) ₅	100		5	5	4	1	0.5
PVC/(LNBR ₇₀ -SF ₃₀) ₁₀	100		10	5	4	1	0.5
PVC/(LNBR ₇₀ -SF ₃₀) ₂₀	100		20	5	4	1	0.5
PVC/(LNBR ₆₀ -SF ₄₀) ₁	100		1	5	4	1	0.5
PVC/(LNBR ₆₀ -SF ₄₀) ₃	100		3	5	4	1	0.5
PVC/(LNBR ₆₀ -SF ₄₀) ₅	100		5	5	4	1	0.5
PVC/(LNBR ₆₀ -SF ₄₀) ₁₀	100		10	5	4	1	0.5
PVC/(LNBR ₆₀ -SF ₄₀) ₂₀	100		20	5	4	1	0.5

The goal of this study was to find a high-value way to utilize straw fiber (SF) in PVC composites. First, the SF was modified with different mass ratios of liquid nitrile-butadiene rubber (LNBR) through the high-speed mixer. Then, the rigid PVC/ SF and PVC/ SF coated with LNBR (PVC/LNBR-SF) composites with varying contents of SF and LNBR-SF were fabricated through melt mixing. The morphology and mechanical properties of the resulting composites were subsequently investigated.

EXPERIMENTAL

Materials

The PVC resin (SG5, *K* value = 66) was purchased from Guizhou Jinhong Chemical Company. The SF with average diameter and length of 100 μm and hundreds of microns respectively was prepared in laboratory using rice straw as main raw material. The industrial grade processing aid acrylic ester (ACR-201) was supplied by Laiwu Chemical Company, Shandong, China. The other industrial grade additives, such as lead complex thermal stabilizer, internal lubricant (stearic acid) and external lubricant (polyethylene wax) were provided by Haolong Chemical Company, Tianjin, China. The industrial grade LNBR with 28% acrylonitrile (AN) content was supplied by Shanghai

Succeed International Trading Co., Ltd with carboxyl terminated butadiene nitrile rubber as its main component.

Fabrication

First, the SF and LNBR were mixed with weight ratio of 90/10, 80/20, 70/30 and 60/40 in a high-speed mixer at 28,000 rpm for 120 s. The size of the SF coated with liquid nitrile-butadiene rubber (LNBR-SF) did not change after high speed mixing and further processing. The average diameter and length of the LNBR-SF were about 100 μm and hundreds of microns, respectively. Second, varying percentage of mixed LNBR-SF, PVC and other additives were dry-blended in the high-speed mixer for 120 s. Then, the melt mixing process was run in the torque rheometer at a constant temperature of 175 °C for 5 min. The rotor speed was 50 rpm and the weight charge was set at 75 g. To compare with the PVC/LNBR-SF composites, PVC/SF composites were also prepared in the torque rheometer at the same condition. The SF was also treated with the same method of LNBR-SF in the high-speed mixer before adding into PVC matrix. The compositions of the five kinds of composites were showed in Table I.

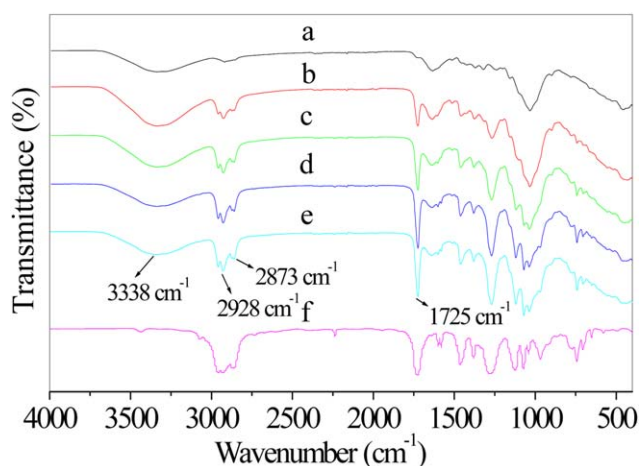


Figure 1. FTIR spectra of (a) straw fiber, (b) LNBR₉₀-SF₁₀, (c) LNBR₈₀-SF₂₀, (d) LNBR₇₀-SF₃₀, (e) LNBR₆₀-SF₄₀, and (f) LNBR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Testing and Characterization

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a Thermo Nicolet Nexus spectrometer (Thermo Nicolet, America) between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 2 cm^{-1} at room temperature.

D/Max-RB X-ray diffraction meter (Rigaku, Japan) with Cu-K α radiation ($\lambda = 0.154 \text{ nm}$) was used to carry out wide angle X-ray diffraction (XRD) test of composites. A scanning rate of 0.2°/min and diffraction angle from 5 to 75° was taken. Bragg's equation, $\lambda = 2d \sin\theta$ was used to calculate the crystallographic spacing.

Tensile strength tests were performed according to GB1040-2002 standard. The tensile tests were conducted at a crosshead speed of 10 mm/min. Notched impact strength tests were performed according to GB1043-2002 standard at room temperature. The notch radius of the samples we used in this study was $0.25 \pm 0.05 \text{ mm}$.

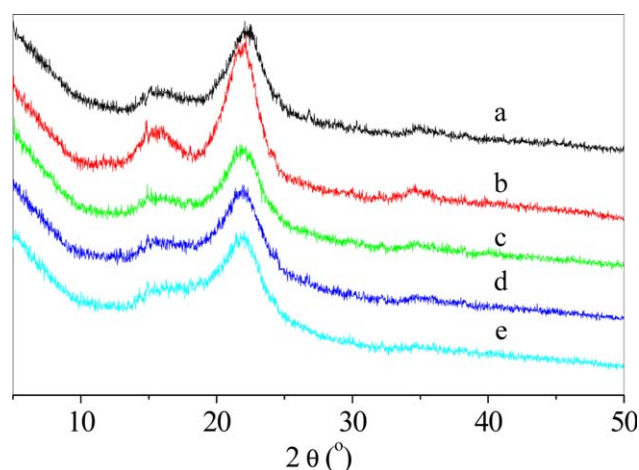


Figure 2. XRD patterns of (a) straw fiber, (b) LNBR₉₀-SF₁₀, (c) LNBR₈₀-SF₂₀, (d) LNBR₇₀-SF₃₀, and (e) LNBR₆₀-SF₄₀. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The morphology of the PVC/SF and PVC/LNBR₇₀-SF₃₀ sample's fractured surface obtained in notched impact test was studied by scanning electron microscope (SEM). All the fractured surfaces were coated with gold-palladium film. The center of the fractured surface for each sample was examined on Quanta FEG scanning electron microscope (FEI, Netherlands).

RESULTS AND DISCUSSION

FTIR Analysis of SF and LNBR_x-SF_y

Figure 1 shows the FTIR spectra of SF, LNBR and LNBR_x-SF_y. As can be seen from Figure 1(b–d), there are no new absorption bands can be found in the FTIR spectra of LNBR_x-SF_y which are no different from the FTIR spectra of SF and LNBR. For example, as shown in Figure 1(e), the absorption band of 3338 cm^{-1} is attributed to -OH stretching vibration of SF. The absorption band of 2928 cm^{-1} , 2873 cm^{-1} , and 1725 cm^{-1} are attributed to -CH₂, -CH₃, and C=O stretching vibration of LNBR, respectively. The results indicated that the modification of SF surface coated with LNBR is a physical interaction.

XRD Analysis of SF and LNBR_x-SF_y

To further evaluate the crystal structure of SF coated with LNBR modification, the XRD patterns of SF and LNBR_x-SF_y are shown in Figure 2. It can be seen that the XRD patterns of LNBR_x-SF_y are basically similar with that of original SF. It means that the crystal structure of SF did not change after modifying with LNBR. Thus, it is reasonable to infer that the interaction of SF and LNBR is just a physical interaction during the high speed mixing modification.

Mechanical Properties of PVC/SF And PVC/LNBR_x-SF_y Composites

Figure 3 displays the effect of variations in the SF and LNBR_x-SF_y content on tensile strength for the PVC/SF and PVC/LNBR_x-SF_y composites. It can be seen that the tensile strength of PVC/LNBR₉₀-SF₁₀ and PVC/LNBR₈₀-SF₂₀ composites is basically flat with that of neat PVC resin when the LNBR_x-SF_y content is 1 phr. The tensile strength of PVC/LNBR₇₀-SF₃₀

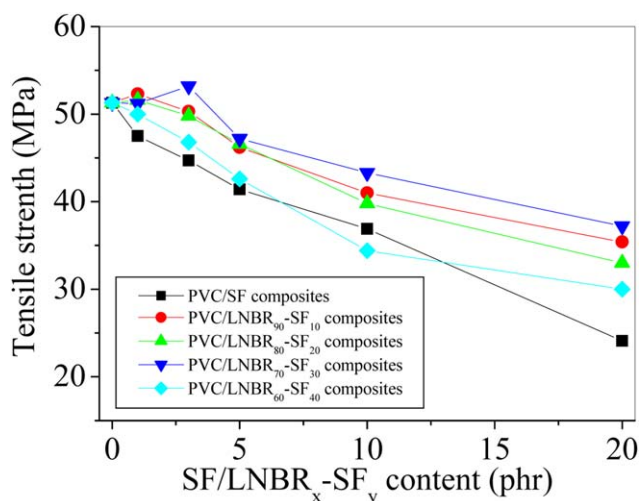


Figure 3. Tensile strength of PVC/SF and PVC/LNBR_x-SF_y composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

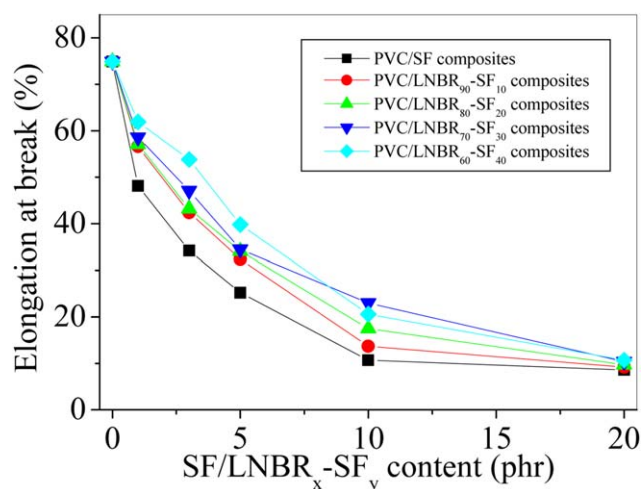


Figure 4. Elongation at break of PVC/SF and PVC/LNBR_x-SF_y composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composites shows a small increase compared with that of neat PVC resin when the LNBR₇₀-SF₃₀ content is less than 3 phr. It is noted that the tensile strength of PVC/LNBR₇₀-SF₃₀ composites achieves the maximum value when the LNBR₇₀-SF₃₀ content is 3 phr. In addition, the tensile strength of PVC/SF and PVC/LNBR_x-SF_y composites decreases as the content of SF and LNBR_x-SF_y increases. However, the tensile strength of PVC/LNBR_x-SF_y composites is higher than that of PVC/SF composites at the same LNBR_x-SF_y and SF content.

The average diameter and length of the SF after mechanical treatment were about 100 μm and hundreds of microns, respectively. The micron-sized SF can decrease the tensile strength of PVC/SF composites as the poor dispersion in PVC matrix and weak interaction with PVC matrix. There are two main reasons for the variation trend of the PVC/LNBR_x-SF_y composites' tensile strength with the LNBR_x-SF_y content increases. One is that the LNBR is compatible with PVC resin. It can improve the dispersion of SF in PVC matrix to some extent. The interface adhesion between SF and PVC matrix with adding LNBR is also enhanced. However, the average diameter and length of the LNBR_x-SF_y after mechanical treatment are still in micron-size. Based on the above analysis, only a small amount of micron-sized SF coated with LNBR modification can exhibit reinforcement for the PVC matrix. When the LNBR_x-SF_y content continues to increase, there are a large amount of aggregates formed in PVC matrix. The aggregates are easy to form cracks during tensile process, which leads to the deterioration of tensile strength. The other is that LNBR is not only the compatibilizer of PVC and SF, but also the toughening modifier of PVC resin. The high LNBR content also leads to the decrease of the tensile strength of the PVC/LNBR_x-SF_y composites. The tensile strength of PVC/LNBR₆₀-SF₄₀ composites exhibits continuous decrease when the LNBR₆₀-SF₄₀ content increases owing to the toughening effect of LNBR for PVC resin.

The elongation at break of PVC/SF and PVC/LNBR_x-SF_y composites with varying SF and LNBR_x-SF_y content is shown in

Figure 4. It can be seen that the elongation at break of PVC/SF and PVC/LNBR_x-SF_y composites decreases when the SF and LNBR_x-SF_y content increases. It is noted that the decline of elongation at break of PVC/LNBR_x-SF_y composites is much lower than that of PVC/SF composites at the same LNBR_x-SF_y and SF content. Through the above analysis, it can be inferred that SF and LNBR_x-SF_y does not exhibit the reinforcement for the elongation at break of PVC/SF and PVC/LNBR_x-SF_y composites. It may be due to the micron size of SF and LNBR_x-SF_y. However, the dual role of LNBR in the PVC/LNBR_x-SF_y composites slows down the deterioration of the elongation at break of PVC/LNBR_x-SF_y composites. The LNBR_x-SF_y which coated with more LNBR has better effect on slowing down the deterioration of the elongation at break.

Figure 5 illustrates the notched impact strength of the PVC/SF and PVC/LNBR_x-SF_y composites with varying SF and LNBR_x-SF_y content. As shown, the notched impact strength of PVC/SF and PVC/LNBR_x-SF_y composites first increases and then decreases with increasing SF and LNBR_x-SF_y content. It indicates that a small amount of SF and LNBR_x-SF_y can improve the toughness of the PVC matrix. In addition, the notched impact strength of the PVC/LNBR_x-SF_y composites is higher than that of PVC/SF composites with equivalent content of SF and LNBR_x-SF_y. When the optimum LNBR_x-SF_y content value achieves 1 phr, the notched impact strength of the PVC/LNBR₉₀-SF₁₀, PVC/LNBR₈₀-SF₂₀, PVC/LNBR₇₀-SF₃₀, and PVC/LNBR₆₀-SF₄₀ composites reach 6.12 kJ/m², 5.44 kJ/m², 5.04 kJ/m², and 4.88 kJ/m², respectively. It increases 64.5%, 46.2%, 35.5%, and 31.2% compared with that of neat PVC resin, respectively.

There are two main reasons for the variation trend of the PVC/SF and PVC/LNBR_x-SF_y composites' notched impact strength with the SF and LNBR_x-SF_y content increases. On one hand, a small amount of SF can uniformly disperse in PVC matrix, and achieve good toughening for the PVC matrix. The toughening of SF is particularly obvious when the SF is coated with LNBR modification. Because LNBR is compatible with PVC resin, it

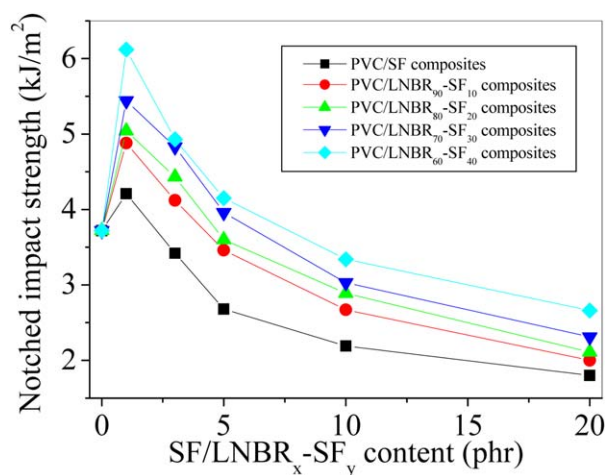


Figure 5. Notched impact strength of PVC/SF and PVC/LNBR_x-SF_y composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

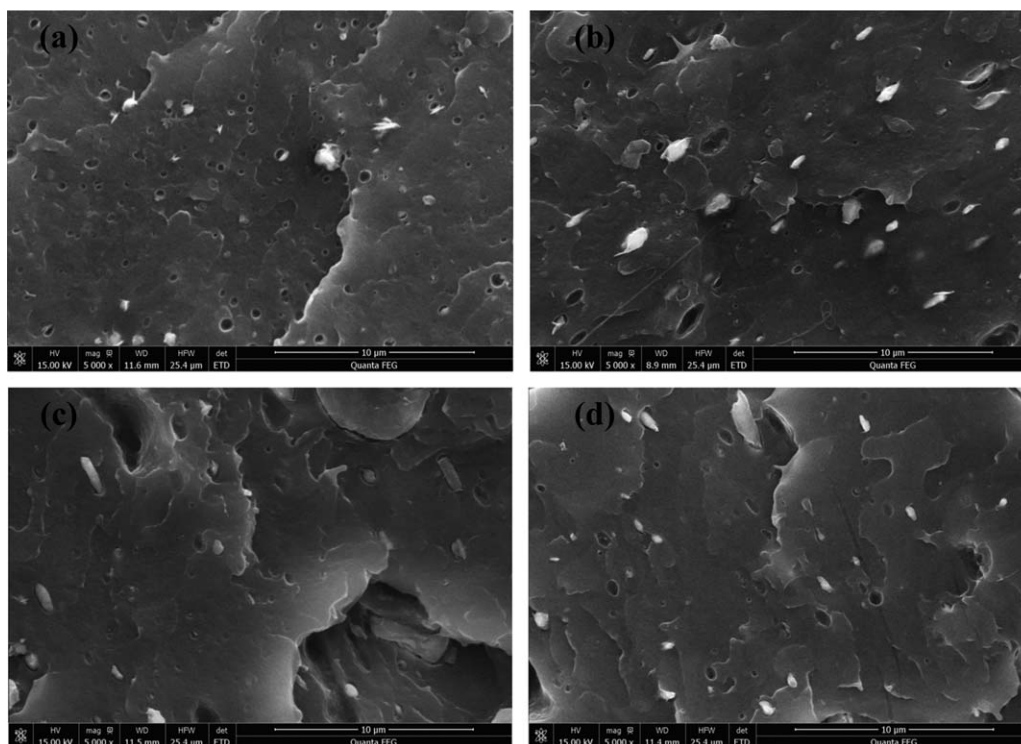


Figure 6. SEM images of (a) PVC/SF₅, (b) PVC/SF₁₀, (c) PVC/(LNBR₇₀-SF₃₀)₅, and (d) PVC/(LNBR₇₀-SF₃₀)₁₀ composites.

can improve the dispersion of SF in PVC matrix, and enhance the interface adhesion between SF and PVC matrix to some extent. On the other hand, the LNBR is not only used as an interfacial compatibilizer for the SF and PVC matrix, but also a toughening modifier for the PVC matrix. The synergistic effect of SF and LNBR can significantly improve the notched impact strength of the PVC/LNBR_x-SF_y composites as the LNBR_x-SF_y content is less than 3 phr. When the LNBR_x-SF_y content continues to increase, the micron-sized LNBR_x-SF_y tends to form aggregates in the PVC matrix and decrease the toughness of the PVC/LNBR_x-SF_y composites. In addition, the higher LNBR content in the LNBR_x-SF_y is, the better notched impact strength of the LNBR_x-SF_y composites is with the same LNBR_x-SF_y content. Thus, the PVC/LNBR₆₀-SF₄₀ composite exhibits higher notched impact strength than those of PVC/LNBR₈₀-SF₂₀, PVC/LNBR₇₀-SF₃₀, and PVC/LNBR₉₀-SF₁₀ composites due to the higher LNBR content in LNBR_x-SF_y. Based on the above analysis, it is crucial that LNBR_x-SF_y improved toughness for the PVC matrix much better than SF.

Morphology of PVC/SF And PVC/LNBR₇₀-SF₃₀ Composites

Figure 6 (a–d) shows SEM micrographs of the fractured surfaces of PVC/SF and PVC/LNBR₇₀-SF₃₀ composites with varying SF and LNBR₇₀-SF₃₀ content. It is seen that the agglomerated SF can be observed in the fractured surfaces of the PVC/SF composites with adding 5 phr SF [Figure 6(a)] as the poor dispersion of the SF in the PVC matrix. Moreover, the amount of agglomerated SF rapidly increases with the SF content increases [Figure 6(b)]. Meantime, the interfacial adhesion between the SF and PVC matrix is weak. Numerous exposed SF and obvious holes can be observed in the fractured surfaces of PVC/SF

composites on account of the poor interfacial adhesion of SF and the PVC matrix.

LNBR is compatible with PVC resin. It can improve the dispersion of SF in PVC matrix, and enhance the interface adhesion between SF and PVC matrix to some extent. Thus, the LNBR₇₀-SF₃₀ shows better dispersion than SF in the PVC matrix. For example, a small amount of agglomerated LNBR₇₀-SF₃₀ is observed in the fractured surfaces of the PVC/LNBR₇₀-SF₃₀ composites with increasing LNBR₇₀-SF₃₀ content [Figure 6(c)]. In addition, the amount of exposed LNBR₇₀-SF₃₀ and holes significantly decrease.

CONCLUSIONS

In this work, to find a high-value approach of utilizing SF in PVC composites, the SF was modified with LNBR using high-speed mechanical mixing. Then the rigid PVC/SF and PVC/LNBR_x-SF_y composites were prepared via melt mixing. The chemical structure and crystal structure of LNBR-SF were characterized by FTIR and XRD, respectively. The mechanical properties and micro-structure of PVC/SF and PVC/LNBR-SF composites were also investigated. The results are as following:

1. FTIR and XRD results showed that the chemical structure and crystal structure of SF did not change after modifying with LNBR. It meant that the surface coated modification with LNBR on SF was a physical interaction.
2. The mechanical properties analysis indicated that the PVC/LNBR-SF composites exhibited better tensile strength, elongation at break, and notched impact strength than those of

PVC/SF composites owing to the compatibilization and toughening effect of LNBR.

- SEM results indicated that the LNBR improved the dispersion of SF in PVC matrix to some extent. The interface adhesion between SF and PVC matrix with adding LNBR was also enhanced. Integrated analysis implied that the PVC/LNBR₇₀-SF₃₀ composites exhibited the best mechanical properties. These results suggested that PVC/LNBR-SF composites exhibited promising potential for practical application in substitute for wood.

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