

Rectorite Powder Modified by Butadiene-Styrene-Vinyl Pyridine Rubber: Structure and Its Dispersion in Styrene-Butadiene Rubber

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ABSTRACT: Rectorite (REC) powders modified by butadiene-styrene-vinyl pyridine rubber (VPR) were prepared by spray drying, designated as REC-VPRs. X-ray diffraction (XRD), Scanning electron microscope (SEM), and transmission electron microscopy (TEM) analyses showed that in the REC-VPRs, VPR did not intercalate into the intergallery of layers. However, compared with REC, the layers of REC-VPRs had more wrinkles and piled loosely. To strengthen the interfacial interaction between VPR and REC, a REC-VPR was treated by volatilized hydrochloric acid, resulting in the formation of ion bonds between REC and VPR, according to Fourier transform infrared spectra measurements. XRD analyses revealed that the intercalated structure emerged in acid treated REC-VPR filled styrene-butadiene rubber (SBR). However, the better dispersion was observed for the SBR composite filled with REC-VPR without acid treatment, indicating that a proper interfacial interaction between REC and VPR is the key to improve the dispersion of REC layers in SBR. Acid treatment did not improve the tensile and tear strengths of the SBR composite filled with REC-VPR. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

KEYWORDS: rectorite; butadiene-styrene-vinyl pyridine rubber; structure; dispersions; interfaces

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INTRODUCTION

Layered silicate/polymer nanocomposites have attracted great interest since the emergence of layered silicate/polyamide nanocomposites in early 1990s,^{1,2} due to the improved mechanical properties, thermal stability, gas barrier ability, and fire retardance.^{3–6} In addition, layered silicates have been widely used in rubber matrices as a kind of filler. Up to date, most of the layered silicate/rubber nanocomposites are prepared by latex compounding or melt compounding methods.^{7–10} More recently, a butadiene-styrene-vinyl pyridine rubber (VPR)/montmorillonite (MMT) nanocomposite with an exfoliated structure was prepared by latex compounding method.¹¹ Similar to MMT, rectorite (REC) can also be completely exfoliated into individual layers in dilute aqueous solution by vigorous stirring.¹² However, the latex compounding method is viable only when REC amount is not higher than 20 parts per hundred rubber (phr). If the REC amount is of a higher amount, it is difficult to co-coagulate the rubber latex and the REC aqueous suspension. In contrast to co-coagulating approach, spray-dry-

ing method can dry liquid droplets quickly via hot gas or air, which has been widely used to produce biopolymer microsphere materials for drug delivery.^{13,14} This technique was also applied to prepare organoclay/poly(methyl-methacrylate) (PMMA),¹⁵ MMT/Polystyrene (PS), and MMT/styrene-butadiene rubber (SBR) nanocomposites.¹⁶

In this study, we intend to apply spray-drying method to prepare RECs modified with VPR (designated as REC-VPRs). It also should be stressed that VPR is used as a modifier, and the amount of VPR is less than that of REC. This feature makes the present study far different from the work reported in literature; for example in the work from Lu, et al.,^{15,16} PMMA, PS, or SBR acted as a matrix, and their amount was much higher than that of clay. We also hope to highlight that such modified REC powders can be directly melt-blended into the rubber matrix to prepare nanocomposites. Furthermore, to strengthen the interfacial interaction between REC and VPR, the REC-VPR powder was treated with volatilized hydrochloric acid (HCl) to form ion bonds between REC and VPR by introducing hydrogen ions.

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Herein, the treated REC-VPR was named as REC-HVPR. Finally, the dispersion of REC-VPR and REC-HVPR in SBR matrix and the mechanical properties of the corresponding SBR composites were compared.

EXPERIMENTAL

Materials

ESBR1502 was supplied by Jilin Chemical Industry (China). VPR Latex (VP-106, solid content 40.8%; the weight ratio of butadiene : styrene : vinyl pyridine is 70 : 15 : 15; average single latex particle size 150 nm; zeta potential -12.8 mV) was produced by the Goodyear South Africa (South Africa). Calcium-REC with cation exchange capacity of 44.9 meq/100 g was kindly provided by Hubei Celebrities Rectorite Technology (China). Other chemicals were commercially available.

Preparation of REC-VPR

First, calcium-REC was dispersed in de-ionized water with vigorous stirring and an aqueous suspension of REC (solid content 1.6 wt %, zeta potential -33.6 mV) was obtained. Then, a given amount of VPR latex was added into the aqueous suspension and the mixture was stirred for a given period of time to obtain the homogeneous REC/VPR slurry with solid content 2.5% and pH 7.0. Three kinds of REC-VPR powder with varied REC/VPR mass ratios (5/1, 5/3, and 5/5) were prepared, referred to as REC-VPR-1, REC-VPR-3, and REC-VPR-5, respectively. All the samples were spray dried under the same conditions: the inlet and outlet air temperatures are 220 and 100°C, respectively; the feeding rate is 400 mLh⁻¹.

Preparation of REC-HVPR

REC-VPR-5 was spread over a sheet of filter paper on a beaker containing concentrated HCl solution for 12 and 24 h. The two kinds of powder with acid treatment are designated as REC-HVPR-12 and REC-HVPR-24, respectively.

Preparation of REC/SBR Composites

To compare the dispersion of REC-VPR and REC-HVPR in the rubber matrix, 20 phr REC-VPR-5 and REC-HVPR-12 were mixed into 100 phr SBR in an open two-roll mill for 5 min at room temperature. The two blends were named as REC-VPR-5/SBR and REC-HVPR-12/SBR, respectively. Then other ingredients in the basic formulae (Table I) were mixed into the compounds at room temperature. Finally, the obtained compounds were vulcanized at 150°C for the optimum time determined by a disc rheometer 750 (made by Beijing Huan Feng Mechanical Factory) in a standard mold under 15 MPa pressure to produce the REC/SBR composites. The SBR composite without reinforcing filler was prepared as the reference.

Characterization

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectra (FTIR) were obtained from an accumulation of 32 scans at a resolution of 4 cm⁻¹ by the attenuated total reflection mode with a TENSOR27 FTIR spectrometer (Bruker Optic GmbH, Germany) at ambient temperature. The pill-like samples of REC-VPRs and REC-HVPRs were shaped by maintaining the powder in a tablet compression machine under 20 MPa for 15 min at room temperature. The sheet-like samples of VPR in different states were also prepared in the same way above.

Table I. Basic Formulae of REC/SBR Composites

Sample	SBR	REC-VPR-5/SBR	REC-HVPR-12/SBR
SBR	100	90	90
REC-VPR-5	0	20	0
REC-HVPR-12	0	0	20
Zinc oxide	5	5	5
Stearic acid	2	2	2
Antioxidant 4010NA ^a	1	1	1
Accelerator DM ^b	0.5	0.5	0.5
Accelerator D ^c	0.5	0.5	0.5
Accelerator TT ^d	0.2	0.2	0.2
Sulfur	2	2	2

^aAntioxidant 4010NA: *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine., ^bAccelerator DM: dibenzothiazole disulfide., ^cAccelerator D: diphenylguanidine., ^dAccelerator TT: tetramethylthiuram disulfide.

X-Ray Diffraction Analysis. X-ray diffraction (XRD) analyses were carried out on a 2500 VB2 + PC diffractometer (Rigaku, Japan) with CuK α radiation (40 kV; 50 mA) at a scan rate of 1° min⁻¹ from 1° to 10°.

Scanning Electron Microscopy. Scanning electron microscope (SEM) micrographs of REC and REC-VPRs were taken using an S-4700 SEM (Hitachi, Japan).

Transmission Electron Microscopy. The samples of REC and REC-VPRs used for transmission electron microscopy (TEM) observation were prepared as follows: the ethanol suspension of the powder prepared by ultrasonic oscillation was dripped on the carbon-coated copper grids, followed by solvent evaporation in air at room temperature. The samples of REC/SBR compounds were prepared via ultrathin sections using a cryo-ultramicrotome. TEM micrographs were taken with an H-800 TEM (Hitachi, Japan) at an acceleration voltage of 200 kV.

Mechanics Performance Test. The mechanical properties were measured according to ASTM D412 using a CMT 4104 electrical tensile tester (SANS, Shenzhen, China), at a speed of 500 mm min⁻¹. Dumb-bell shape specimens and right-angle shape specimens were prepared for tensile and tearing tests, respectively. XY-1 rubber hardness apparatus (fourth Chemical Industry Machine Factory, Shanghai, China) was used to measure the hardness (Shore A) according to ASTM D2240-75.

RESULTS AND DISCUSSION

XRD Analysis of REC-VPRs with Varied VPR Amounts

The XRD patterns of REC-VPRs with varied VPR amounts are presented in Figure 1. The peak around 4° corresponding to a layer spacing of about 2.2 nm appears in the spectra, which is the diffraction peak of (001) lattice plane of REC.¹⁷ From Figure 1, compared with REC, the peak intensities of REC-VPRs decrease. It is worth to notice that the full-width-at-half-maximum of diffraction peaks of REC-VPR increases with enhancing the VPR amount, indicating the reduction of the well-arranged layers in REC-VPRs. During the process of spray drying, as soon as the liquid flowed out of the nozzle, it was disintegrated into

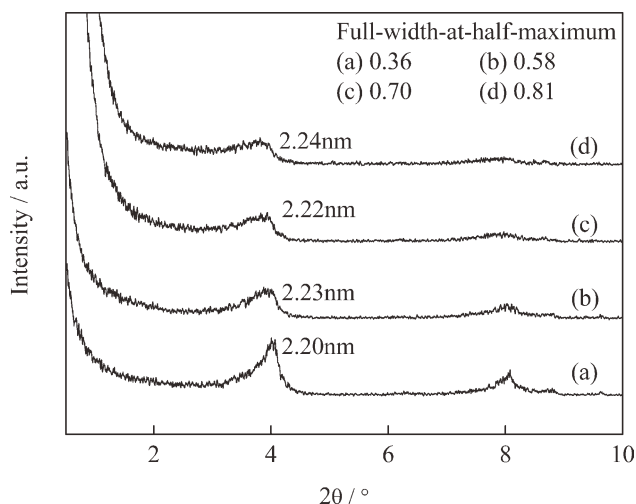


Figure 1. XRD patterns of REC-VPRs: (a) REC; (b) REC-VPR-1; (c) REC-VPR-3; (d) REC-VPR-5.

many tiny spray droplets by the strong frictional force caused by the large velocity difference between the liquid and the inlet air. Therefore, the specific surface area of the liquid drops was drastically increased and the drying process was completed instantly. Both the increased VPR amount and the rapid volatilization of

water made it difficult for most of the individual layers in aqueous suspension to rearrange into ordered structure in such a short time. Thus, the full-width-at-half-maximum of diffraction peaks increased with enhancing the VPR amount.

Morphology of REC-VPRs with Varied VPR Amounts

To acquire more information about the morphology of REC-VPRs, SEM micrographs of REC-VPRs are obtained and presented in Figure 2. As shown in Figure 2, the granulate size of REC/VPRs is 4–7 μm , smaller than that of pristine REC,¹⁸ demonstrating that the agglomeration of REC layers were blocked by the instantly spray-drying process. The reason is as follows: the surfaces of REC layers and VPR latex particles are both negatively charged, and the highly dispersion of REC layers in the blend suspension could be held by the static electrical repulsion; further the dispersion structure was fixed in the dried REC-VPR powder by the rapid spray-drying process. With increasing the amount of VPR latex, the REC layers were better isolated by VPR latex particles and presented a wrinkled flower-like morphology in REC-VPR particles, due to the surface shrinkage of thinner REC layers.

To further observe the layers of REC-VPRs, TEM pictures are also taken and demonstrated in Figure 3. Compared with the pure REC, more wrinkles are observed in the layers of REC-VPRs, in agreement with the SEM observation as shown in Figure 2, and the layers in REC-VPRs are more transparent,

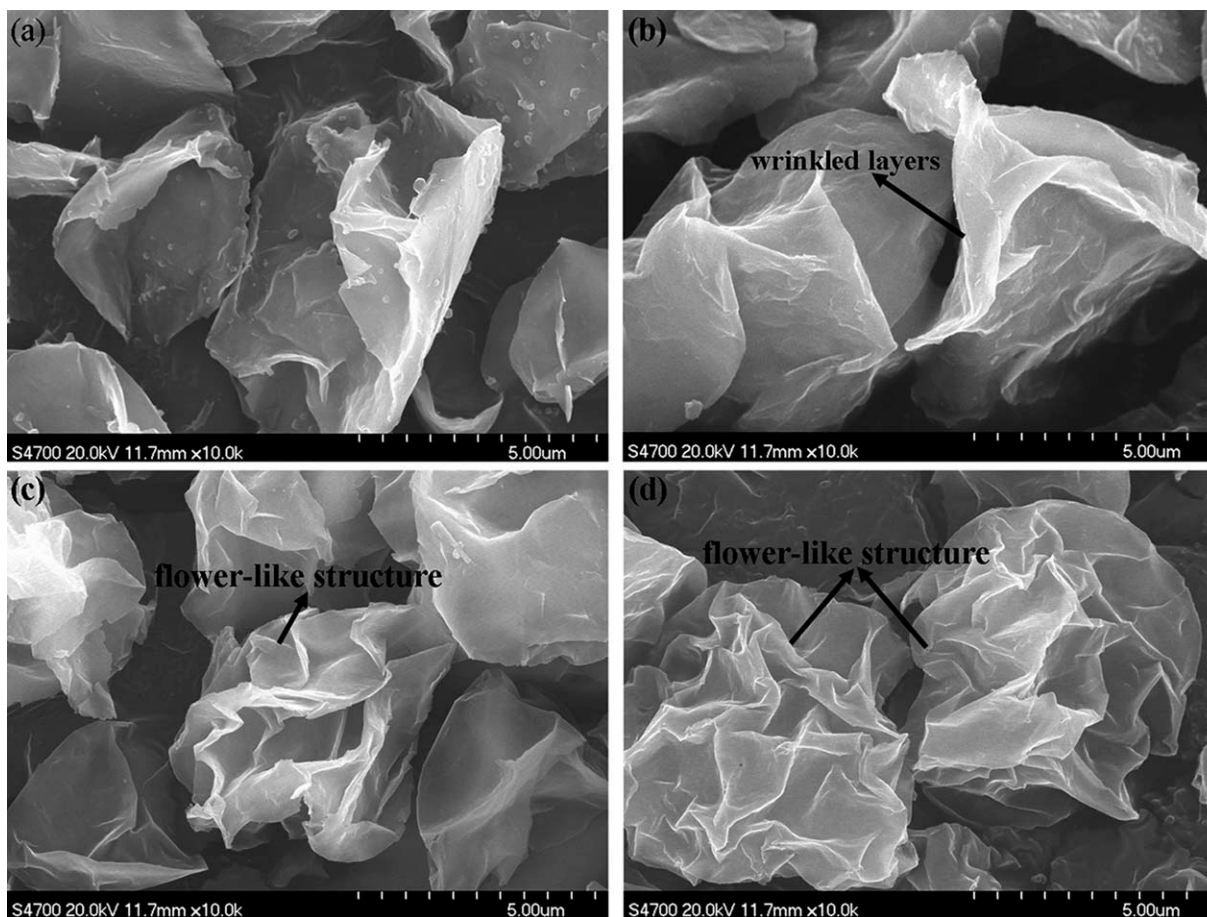


Figure 2. SEM images of REC-VPRs: (a) REC; (b) REC-VPR-1; (c) REC-VPR-3; (d) REC-VPR-5.

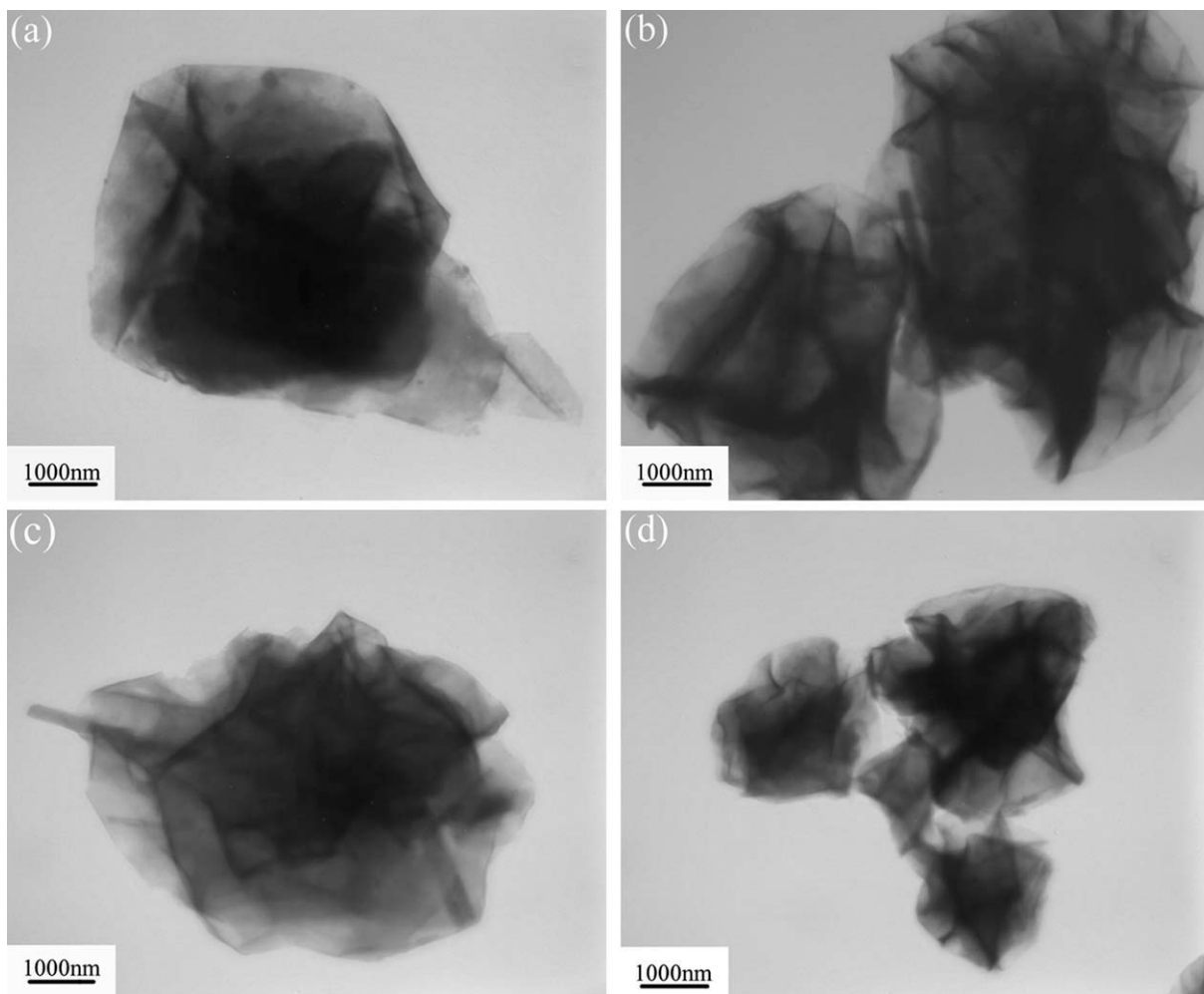


Figure 3. TEM micrographs of REC-VPRs: (a) REC; (b) REC-VPR-1; (c) REC-VPR-3; (d) REC-VPR-5.

indicating that they are thinner and piled more loosely. It is expected that the loosely-piled layers in REC-VPRs can be dispersed in the rubber matrix easily. This will be discussed later.

Effects of Acid Treatment on the Interfacial Interaction Between REC and VPR

Since a strong ionic interfacial interaction can be generated by acidified pyridine and electronegative silicate,¹¹ REC-VPR-5 was

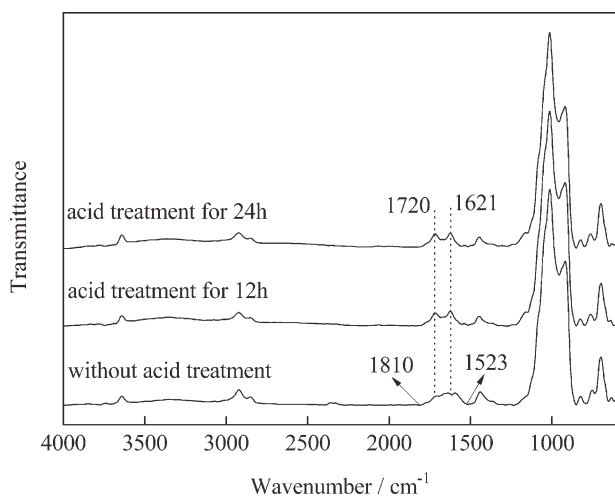


Figure 4. FTIR spectra of REC-VPR-5 before and after acid treatment.

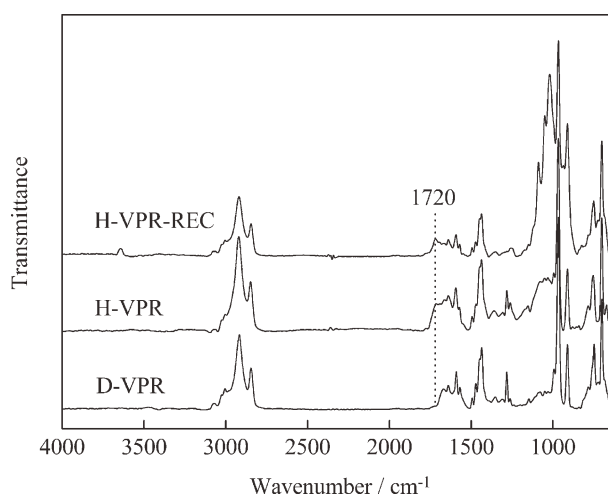


Figure 5. FTIR spectra of VPR in different states.

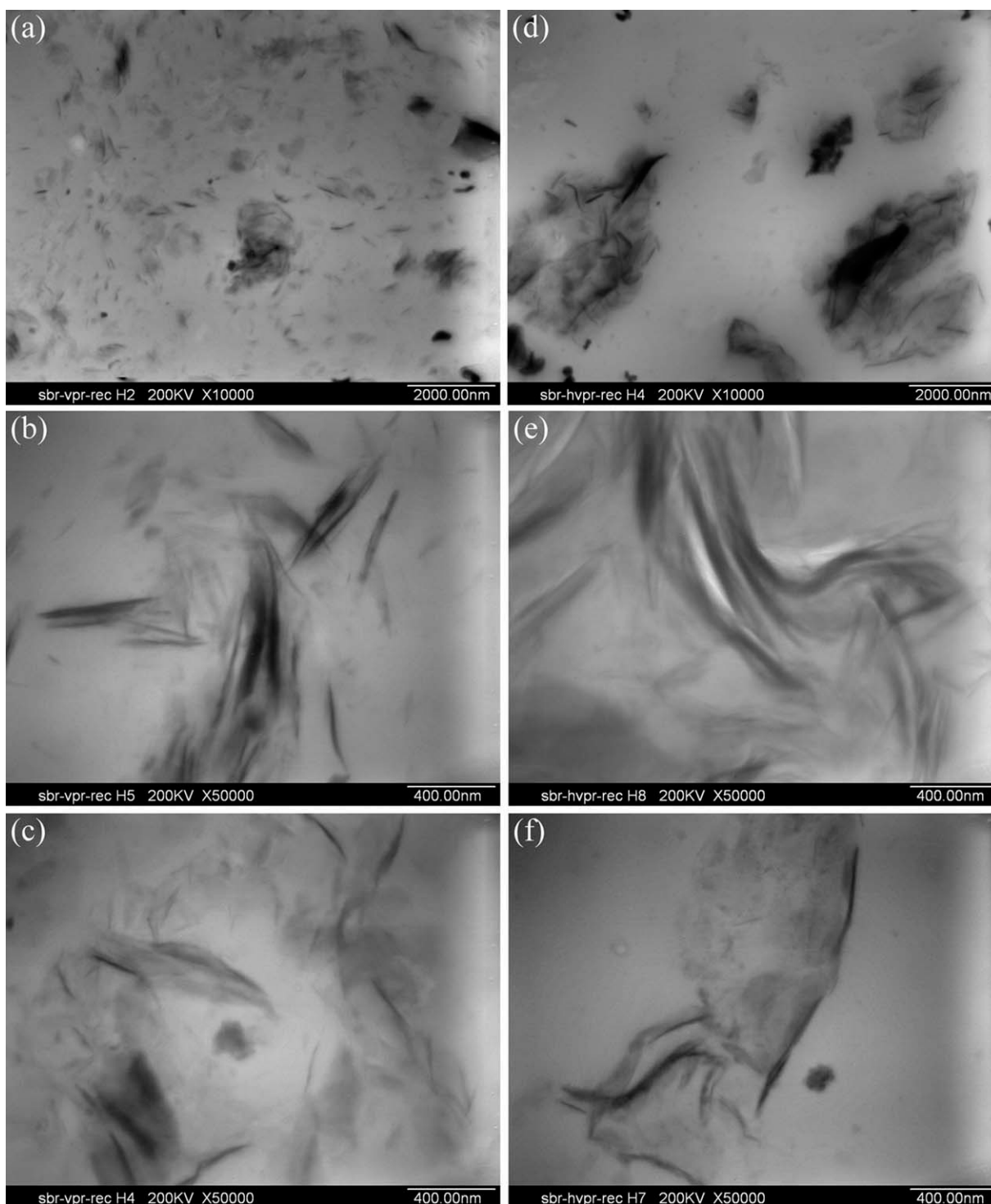


Figure 6. TEM micrographs of the two modified REC filled SBR compounds at varied magnifications: (a), (b), and (c) REC-VPR-5/SBR; (d), (e), and (f) REC-HVPR-12/SBR.

treated with volatilized HCl to strengthen the interaction between the REC layers and VPR by introducing hydrogen ions at the nitrogen atom of pyridine in VPR. To confirm this assumption, we conducted FTIR analysis of REC-VPR-5 before and after acid treatment.

The FTIR spectra of REC-VPR-5 before and after acid treatment are presented in Figure 4. After acid treatment, the broad peak in the region of $1523\text{--}1810\text{ cm}^{-1}$ is split into two peaks at 1720 and 1621 cm^{-1} . The band at about 1621 cm^{-1} presented in the salts of pyridine was reported in literature,^{19,20} involving nuclear

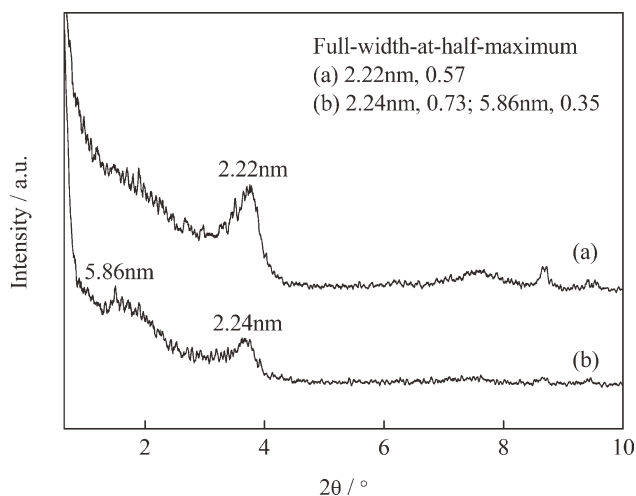


Figure 7. XRD patterns of two modified REC filled SBR compounds: (a) REC-VPR-5/SBR; (b) REC-HVPR-12/SBR.

vibrations of the pyridinium ring.²⁰ So, it is proposed that the peak at 1621 cm^{-1} is attributed to the protonation of pyridine ring.

To further clarify the origin of the peak at 1720 cm^{-1} , we further prepared three samples: the D-VPR sample was prepared by directly drying the VPR latex in an infrared oven; the H-VPR was prepared by coagulating the VPR latex using HCl solution; the H-VPR-REC was also prepared by co-coagulating the VPR latex and REC aqueous suspension (VPR/REC mass ratio 100/20) with HCl solution. There is no H^+ in D-VPR, while H^+ exists in the H-VPR and H-VPR-REC. The FTIR spectra of the three samples are shown in Figure 5. It is observed that the peak at 1720 cm^{-1} emerges in both H-VPR and H-VPR-REC, consistent with 1720 cm^{-1} peak in REC-VPR after acid treatment in Figure 4. This confirms the formation of ion bonds between REC and VPR after acid treatment. Therefore, acid treatment can improve the interfacial interaction between REC and VPR.

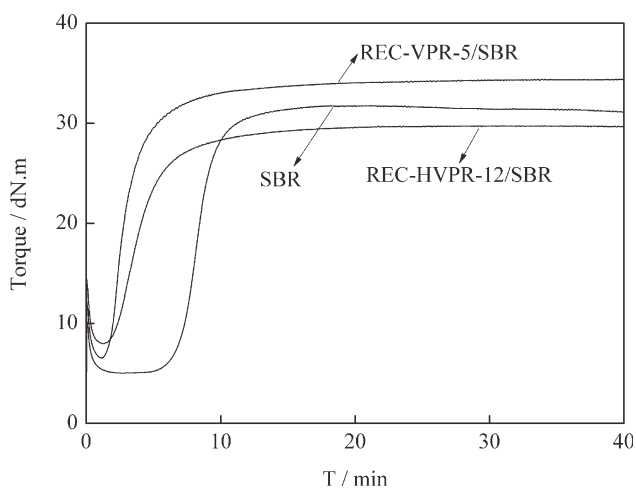


Figure 8. Vulcanization curves of REC/SBR composites.

Comparison of the Dispersion States of REC-VPR and REC-HVPR in SBR Matrix

The TEM micrographs of the two modified REC/SBR compounds are shown in Figure 6, in which the dark lines are cross-sections of REC layers. In Figure 6(a), REC layers in REC-VPR were broken into finer ones by shearing force and were uniformly dispersed in SBR matrix during the melt-blending process. However, in Figure 6(d), the dispersion of REC layers was not uniform, indicating that acid treatment deterred the dispersion of REC-HVPR powder, which seems to be unexpected. It can be explained that after acid treatment, strong ionic interactions formed between VPR and REC layers, and thus the REC layers tightly wrapped by VPR could withstand shearing force during the mixing process, which prevented the dispersion of REC layers in SBR. As also can be observed in the micrographs at high magnification from Figure 6(b, c, e, f), REC layers in REC-VPR were more prone to be delaminated into finer ones and be uniformly dispersed in SBR matrix by shearing force.

Figure 7 presents the XRD patterns of the two modified REC/SBR compounds. As can be seen in Figure 7, the interlayer spacing in REC-VPR-5/SBR is almost the same as that in the corresponding modified REC (Figure 1), demonstrating no intercalation of VPR or SBR macromolecules into the interlayer occurred during the mixing process. For REC-HVPR-12/SBR, besides the peak at 2.24 nm, there is a peak at around 5.86 nm, indicating that VPR intercalated into the intergallery of layers, due to the ionic bond formed in REC-HVPR as discussed above. In addition, it can be obviously seen that the peak at 2.24 nm in REC-HVPR-12/SBR is lower than that in REC-VPR-5/SBR, and the full-width-at-half-maximum increases to some extent, suggesting that there is a decrease in both unintercalated structure and well-arranged structure in REC-HVPR-12/SBR after acid treatment.

Therefore, combined TEM and XRD results indicate that REC-VPR-5 without acid treatment is easier to disperse in SBR than REC-HVPR-12, and the formed ionic interaction between REC and VPR in REC-HVPR-12 is unfavorable for improving the dispersion of REC layers in SBR.

Vulcanization Behaviors of REC/SBR Composites

The vulcanization behaviors of REC/SBR composites are presented in Figure 8 and Table II. It can be observed that addition of REC-VPR reduced the optimum cure time t_{90} , indicating that REC-VPR can accelerate the vulcanization process of SBR composites. Apart from the acceleration effect, the minimum torque (ML) was also increased by adding REC-VPR, indicating REC-VPR can increase the viscosity of SBR compounds as well.

Table II. Vulcanization Characteristics of REC/SBR Composites

	SBR	REC-VPR-5/SBR	REC-HVPR-12/SBR
T_{90} (min)	10.5	6.9	8.2
ML (dN m)	5.0	6.6	8.0
MH (dN m)	31.8	34.0	29.8
ΔM (dN m)	26.8	27.4	21.8

Table III. Mechanical Properties of REC/SBR Composites

Sample	SBR	REC-VPR-5/SBR	REC-HVPR-12/SBR
Shore A hardness (°)	51	59	59
Stress at 300% (MPa)	1.7	3.8	2.1
Tensile strength (MPa)	1.9	4.5	4.2
Elongation at break (%)	337	349	606
Tear strength (kN m ⁻¹)	14.4	25.2	26.7

Moreover, the viscosity was further enhanced for REC-HVPR-12/SBR, which could be originated from the improved interfacial interaction between REC layers and VPR by acid treatment. However, the difference between the maximum torque and ML (ΔM) of REC-HVPR-12/SBR were lower than those of other two composites, demonstrating that REC-HVPR-12 decreased the crosslink density of SBR composites,²¹ which may be attributed to the acidity of REC-HVPR-12 (the pH of REC-HVPR-12 slurry was 2.3).

Mechanical Properties of REC/SBR Composites

Table III shows the mechanical properties of REC/SBR composites. From Table III, compared with the unfilled SBR composites, the mechanical properties of REC-VPR-5/SBR and REC-HVPR-12/SBR were improved, indicating the reinforcement effect of REC layers on SBR composites. For REC-HVPR-12/SBR, the stress at 300% was lower and the elongation at break was longer than that of REC-VPR-5/SBR, resulted from the decreased crosslink density.²² However, the tensile and tear strengths of REC-HVPR-12/SBR and REC-VPR-5/SBR were almost at the same level.

CONCLUSION

We successfully prepared REC-VPRs by spray drying approach. Such REC-VPRs presented a flower-like structure and piled loosely. The interfacial interaction between REC layers and VPR can be further improved by acid treatment, and thus VPR can intercalate into the intergallery of layers in REC-HVPR-12/SBR during the mixing process. However, the dispersion of REC-HVPR in SBR matrix is less uniform than that of REC-VPR, indicating that the stronger interaction between REC layers and VPR deters the dispersion of REC. The tensile and tear strengths of REC-HVPR-12/SBR and REC-VPR-5/SBR are almost at the same level.

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