

Preparation and Characterization of Lignin-Layered Double Hydroxide/Styrene-Butadiene Rubber Composites

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ABSTRACT: Lignin-layered double hydroxide (lignin-LDH) complex was synthesized by *in situ* method, and then styrene-butadiene rubber (SBR)/lignin-LDH composites were prepared by the melt compounding method. X-ray diffraction analysis showed that crystal lignin-LDH was successfully obtained and transmission electron microscopy analysis showed well dispersion of lignin-LDH in SBR matrix. The tensile strength, elongation at break, 300% modulus and hardness of lignin-LDH/SBR were significantly improved compared to LDH/SBR composites. Thermogravimetric analysis indicated that the thermal degradation temperature of the lignin-LDH/SBR at 10% weight loss (T_{10}) decreased whereas 50% weight loss (T_{50}) was much higher than that of pristine LDH/SBR due to barrier property of the well dispersed Lignin-LDH in SBR matrix. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1308–1312, 2013

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INTRODUCTION

Carbon black used to be the most important reinforcing agent in the rubber materials industry. But its polluting nature, the monotonous black color of the filled rubber material, and its dependence on petroleum caused researchers to develop other satisfying reinforcing agents instead. Clay has been tested as a rubber filler for many years.¹ Generally, clays need to be organically modified to have good compatibility with different rubber matrix.² One of research works has proved organoclay as an effective reinforcing agent for natural rubber; only 10 phr of the organoclay are enough to obtain a similar mechanical behavior as 40 phr of carbon black.³

Styrene-butadiene rubber (SBR), a general-purpose synthetic elastomer widely used in the rubber industry, is noncrystalline and nonpolar with a low gum tensile strength (~2 MPa).⁴ Therefore, the reinforcing filler is often required in this matrix. Recently, quite a number of publications exist in the field of SBR/clay composites.^{5–13}

During the past decade, compared to layered silicates, the use of another type of clay, layered double hydroxide (LDH), in the rubber matrix has been rather less extensively studied. The critical reason is that it is difficult to obtain a well dispersion of LDH in rubber due to organic–inorganic incompatibility and

strong attractive forces between the two hydroxides layers of LDHs.² Organically modified LDH could be achieved by intercalating charge balancing organic anions with different functionalities, such as carboxylate, sulfonate, phosphonate, and others. However, this process dramatically increases the price of the final material limiting its application at industrial level.

Lignin is one of the most important bioresources that are nontoxic and extremely versatile in performance. Production of lignin as a by-product of pulping process in the world is over 30 million tons per year.¹⁴ The most significant and urgent problem is the profitable utilization of the vast quantities of lignin.¹⁵ As the second most abundant natural polymer in the world, lignin has drawn much attention from many scientists for several centuries.¹⁶ It has the potential of becoming a major source of polymer-based products including building board adhesive binders, coatings, adhesives, foam insulation, etc. Recently, researches indicate that lignin could be used as dispersion agent for fillers including montmorillonite and carbon nanotube in polymer matrix.^{17–19}

In this work, lignin will be used to improve the dispersion of LDH in rubber matrix, and lignin-LDH/SBR composites will be prepared by a melt compounding method. It is expected that the presence of lignin could strongly promote the dispersion of

Table I. Compound Formulations for Lignin-LDH/SBR Composites

Materials	[phr] ^a
SBR	100
Lignin	3, 9, 15
LDH	30
Zinc oxide	5
Stearic acid	2
CZ	1.5
Sulfur	2.5

^aParts per hundred rubber.

LDH leading to a significant enhancement of the mechanical and thermal properties of LDH/SBR composites.

EXPERIMENTAL

Materials

Styrene-butadiene rubber [SBR1502 with Mooney viscosity of 44–56 ML (1 + 4) at 100°C] was purchased from China Petrochemical Corporation (Lanzhou, China). Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were purchased from Taiyuan Xinjida Chemicals. NaOH was purchased from Tianjin Damao Chemicals. Alkaline Lignin was kindly provided by Hongjiang Wanyuan Chemicals. Other rubber ingredients including *N*-cyclohexylbenzothiazole-2-sulfenamide (CZ), zinc oxide, stearic acid, and sulfur were of analytical grade.

Preparation of Lignin-LDH Complex

A certain amount of lignin (varying from 4 to 20 g) was dissolved in 200 mL 20 wt % NaOH solution. A mixed metal nitrate solution containing 0.5 mol L⁻¹ Mg(NO₃)₂ and 0.25 mol L⁻¹ Al(NO₃)₃ was dropped into the lignin solution until the pH value was close to 7. The resultant slurry was aged at 65°C for 24 h. Finally, the precipitate was filtered, washed with distilled water, and dried under vacuum until the weight of the lignin-LDH complex equaled to two times of the weight of dried lignin-LDH complex powder to make the complex contain 50% water. The lignin-LDH complexes were named 30LDH-3Lignin, 30LDH-9Lignin, 30LDH-15Lignin, according to the lignin content. For example, 30LDH-3Lignin refers to lignin-LDH complex whose ratio of LDH to Lignin is 10 to 1. Pristine LDH refers to LDH contains no lignin.

Preparation of Lignin-LDH/SBR Composites

The lignin-LDH/SBR composites were prepared following a two-step melt compounding method. In the first step, the hydrated lignin-LDH complexes were added into SBR and mixed at 100°C until the weight of master batch reached constant as to make sure all nonbonded water were evaporated in the processing. In the second step, all the curatives were added to the lignin-LDH-SBR mixture at room temperature in 20 min. Finally, the compounded composites were kept for maturation for 24 h and then vulcanized in a compression molding press at 160°C temperature under a pressure of 10 MPa. The vulcanization time for each compound was determined from the rheometric analysis of the uncured samples. The compound formulations for each set of the composites are given in Table I.

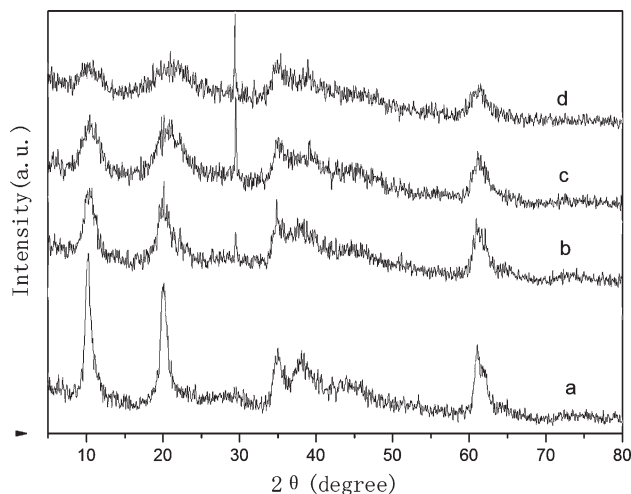


Figure 1. XRD spectra of pristine LDH and Lignin-LDH complex (a) pristine LDH, (b) 30LDH-3Lignin, (c) 30LDH-9Lignin, (d) 30LDH-15Lignin.

The lignin content was varied from 3 to 15 phr whereas the LDH content was kept constant.

Characterization

The cure characteristics were recorded on a moving Die Rheometer (Tianyuan, China). X-ray diffraction (XRD) patterns were collected from 5° to 80° using a step size of 0.1° on a Bruker-D8 instrument (Karlsruhe, Germany) using monochromatic Cu K α radiation. Transmission electron microscopy (TEM) was performed on a Tecnai F20 instrument (FEI, U.S.A.) under an accelerating voltage of 200 kV and bright field illumination. The ultra-thin sections of the samples were prepared by ultramicrotomy (Leica Ultracut UCT) at -100°C with a

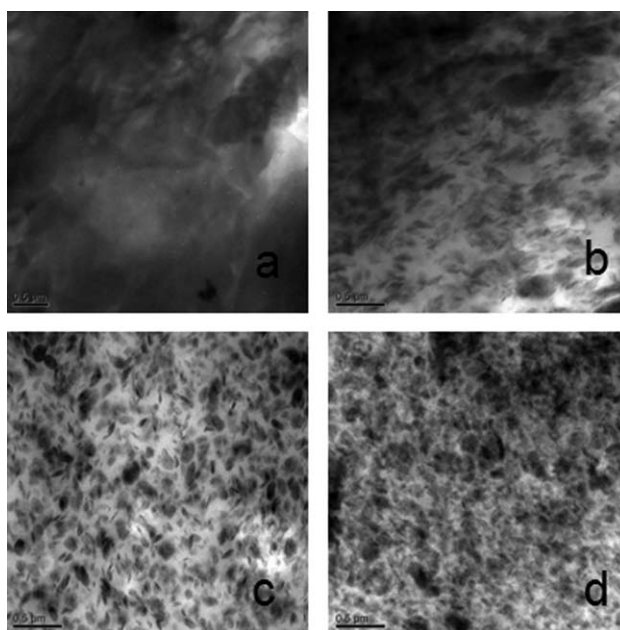


Figure 2. TEM micrographs of LDH/SBR and lignin-LDH/SBR composites (low magnification): a—30LDH/SBR; b—30LDH-3Lignin/SBR; c—30LDH-9Lignin/SBR; d—30LDH-15Lignin/SBR.

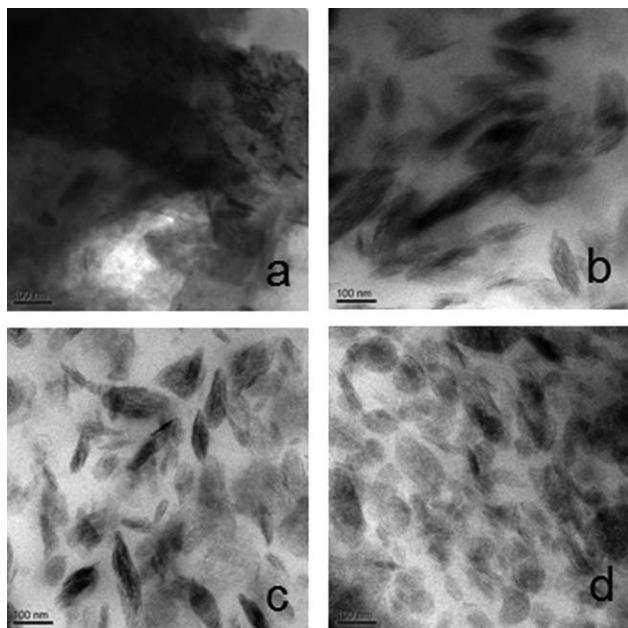


Figure 3. TEM micrographs of LDH/SBR and Lignin-LDH/SBR composites (high magnification): **a**—30LDH/SBR; **b**—30LDH-3Lignin/SBR; **c**—30LDH-9Lignin/SBR; **d**—30LDH-15Lignin/SBR.

thickness of about 100 nm. Differential scanning calorimeter (DSC) analysis was performed on Netzsch 200F3 instrument (Netzsch, Germany) from -70 to 0°C under a flowing nitrogen atmosphere at a ramp rate of $10^{\circ}\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was conducted from 30 to 800°C at a scan rate of $20^{\circ}\text{C min}^{-1}$ on a Netzsch STA409PC instrument (Netzsch, Germany) under nitrogen atmosphere with a flow speed of 20 mL min^{-1} .

RESULTS AND DISCUSSION

X-ray Diffraction Characterization

The WAXD patterns of the LDH materials are shown in Figure 1. It is apparent that both LDH and lignin-LDH complexes are with layered structure. However, in comparison to pristine LDH, the XRD traces of lignin-LDH complexes are broad and the intensity decreases as the increase of lignin concentration. This indicates that LDH particles in lignin-LDH have a more disordered structure.²⁰

Morphological Structure of LDH/SBR Composites

The TEM images of composites of SBR and LDH (SBR/LDH = 100/30) at different loadings of lignin are shown in Figures 2 and 3.

Table II. The Cure Characteristics of LDH/SBR Composites at Different Lignin Loadings

	M_L (N m^{-1})	M_H (N m^{-1})	ΔM (N m^{-1})	t_{10} (min)	t_{90} (min)	CRI (min^{-1})
SBR	1.64	3.00	1.36	6.73	9.89	31.65
30LDH/SBR	2.29	4.23	1.94	2.76	4.43	59.88
30LDH-3Lignin/SBR	2.22	2.99	0.77	2.64	4.73	47.85
30LDH-9Lignin/SBR	2.38	4.01	1.63	2.68	7.19	22.17
30LDH-15Lignin/SBR	3.01	4.43	1.42	1.45	7.95	15.38

M_L —minimum torque; M_H —maximum torque; $\Delta M = M_H - M_L$; t_{10} —time required for the torque value to reach 10% of maximum torque; t_{90} —time required for the torque value to reach 90% of maximum torque; CRI—cure rate index, $\text{CRI} = 100/(t_{90} - t_{10})$

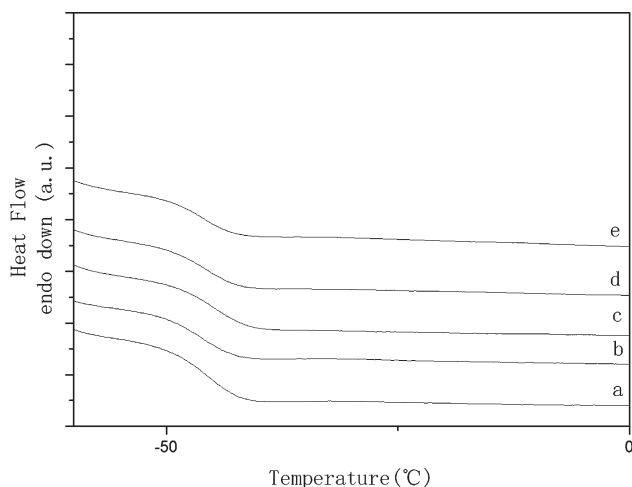


Figure 4. DSC curves obtained from SBR, LDH/SBR, and Lignin-LDH/SBR composites: **a**—SBR; **b**—30LDH/SBR; **c**—30LDH-3Lignin/SBR; **d**—30LDH-9Lignin/SBR; **e**—30LDH-15Lignin/SBR.

The darklines are the LDH layers and particles, whereas the bright area refers to SBR matrix. It is obvious that the dispersion of LDH particles is well improved in the presence of lignin. The size of LDH particle decreases as the increase of lignin loading. This evidence indicates that lignin does help the dispersion of LDH in SBR.

Cure Characteristics

The cure properties of the SBR composites are summarized in Table II. Compared to LDH/SBR composites, the minimum torque (M_L), maximum torque (M_H), and optimum cure time (t_{90}) of lignin-LDH/SBR composites increased as the increasing of lignin loading, however the scorch time (t_{10}) and cure rate index (CRI) have a decreasing trend. Lignin-LDH/SBR composites have less torque increment (ΔM) than that of LDH/SBR composites. These above evidences indicate that lignin is able to affect the curing behavior. This is probably due to the interaction of lignin with the vulcanization system as reported.²¹

The thermal transitions of SBR composites were studied by DSC and are displayed in Figure 4. Glass transition temperature (T_g) are summarized in Table III. It is clear that the T_g shows little or no change with the addition of lignin, which may be attributed to the lack of interactions between lignin-LDH and SBR.

Thermal Properties of LDH/SBR Composites

The thermal stability of the pure SBR, LDH/SBR and lignin-LDH/SBR vulcanizates at different lignin loadings was assessed

Table III. DSC Analyses of Lignin-LDH/SBR Composites

	T_g (°C)
SBR	-45.2
3OLDH/SBR	-45.7
3OLDH-3Lignin/SBR	-44.6
3OLDH-9Lignin/SBR	-45.5
3OLDH-15Lignin/SBR	-45.7

Table IV. TGA Data of Lignin-LDH/SBR Composites

	T_{10} (°C)	T_{50} (°C)	Residue at 760°C (wt %)
SBR	387	454	6.2
3OLDH/SBR	383	465	15.2
3OLDH-3Lignin/SBR	372	472	16.6
3OLDH-9Lignin/SBR	364	471	19.9
3OLDH-15Lignin/SBR	342	466	16.8

T_{10} (°C), temperature corresponds to the 10% weight loss.

T_{50} (°C), temperature corresponds to the 50% weight loss.

by TGA and the data related to the thermal degradation corresponding to the 10% weight loss (T_{10}), 50% weight loss (T_{50}), are recorded in Table IV. The degradation of the SBR takes place in a single step between 400 and 500°C.²² TGA showed that T_{10} for LDH/SBR composite was lower than that for neat SBR. The LDH in LDH/SBR composites undergoes endothermic decomposition to liberate water. Such type of weight loss in the initial stage is extremely useful in promoting the charring process improving thereby the thermal stability of the rubber composites since an efficient charring process in a flame retardant polymer occurs at a temperature higher than its processing temperature but much lower than its decomposition temperature. The T_{10} of the lignin-LDH/SBR composites decreased with the increase of lignin loading due to the fact that lignin begins to degrade at about 190°C,²³ several degrees before the SBR degradation temperature. On the contrary, when 50% weight loss was selected as a point of comparison, the thermal degradation temperatures (T_{50}) for pure SBR and lignin-LDH/SBR nanocomposites containing 0, 3, 9, or 15 phr lignin were 454, 465, 472, 471, and 466°C, respectively. This indicated that the thermal degradation temperature of the lignin-LDH/SBR composites

was approximately 11–18°C higher than that of the pure SBR. This may be due to the presence of almost dispersed lignin-LDH in SBR matrix, which imparts barrier effect originated by anisotropic lignin-LDH platelets that interrupts the release of volatile degradation products from these rubber composites.²⁴ The observed improvements in thermal stability of lignin-LDH/SBR composites compared to neat SBR may also be associated with the total migration out-paths of small molecules as well as inner volatiles which ultimately reduces the permeability of nitrogen into the bulk of the SBR composites.²⁵ It is also observed that above 750°C only 6.2 wt % of residue is left for pure SBR, while the residue of lignin-LDH/SBR composites increased up to 19.9 and then decreased to 16.8 wt %.

Mechanical Properties

The mechanical properties of lignin-LDH/SBR composites are summarized in Table V. According to this, the low reinforcing effect of pristine LDH is obvious whereas the tensile strength of lignin-LDH/SBR composites increases rapidly from 4.0 to 10.9 MPa with the lignin content in the range 0–9 phr. This enhancement in the tensile strength value due to the addition of lignin-LDH may be ascribed to the improved dispersion of LDH particles in SBR matrix in the presence of lignin. The well-dispersed rigid lignin-LDH layers efficiently transfers stress from polymer and directly enhance the stiffness in the corresponding rubber composites. Interestingly, the elongation at break also increases with the lignin content. The enhanced modulus for these SBR composites correspond to the formation of some shear zones when the composites are under stress and strain conditions.²⁶ Such an improvement in mechanical properties can also be accounted on the basis of static adhesion strength as well as interfacial stiffness because of the efficient stress transfer at the interface originating elastic deformation from the large aspect ratio of the lignin-LDH filler.²⁷ These enhanced mechanical properties are mainly due to the better dispersion of LDH particles in SBR matrix in the presence of lignin which was also supported by the TEM studies discussed earlier.

CONCLUSION

Lignin-layered double hydroxide (lignin-LDH) complex was successfully synthesized by *in situ* LDH synthesis method and styrene-butadiene rubber (SBR)/LDH composites were prepared by the melt compounding method. X-ray diffraction showed that crystalline LDH was successfully obtained and transmission electron microscopy analysis showed well dispersion of lignin-

Table V. The Mechanical Properties of Lignin-LDH/SBR Composites

	Tensile strength/MPa	Elongation at break/%	300% Modulus/MPa	Shore "A" Hardness
SBR	2.0	353	1.7	46
3OLDH/SBR	4.0	528	1.8	48
3OLDH-3Lignin/SBR	7.2	606	2.3	50
3OLDH-9Lignin/SBR	10.0	697	2.5	51
3OLDH-15Lignin/SBR	10.9	759	2.4	53
15Lignin/SBR	4.5	500	2.2	48

LDH in SBR matrix. The tensile strength, elongation at break, 300% modulus, and hardness of lignin-LDH/SBR were significantly improved compared to LDH/SBR composites. Thermogravimetric analysis indicated that the thermal degradation temperature of the lignin-LDH/SBR at 10% weight loss (T_{10}) decreased whereas T_{50} was much higher than that of pristine LDH/SBR. These results indicated that this lignin-LDH complex will be a promising filler for rubber composites.

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