

Preparation and Properties of NBR Composites Filled with a Novel Black Liquor–Montmorillonite Complex

Zhonglin Cao,¹ Zedong Liao,¹ Xi Wang,¹ Shengpei Su,¹ Jianxiang Feng,² Jin Zhu²

¹Key Laboratory of Sustainable Resources Processing and Advanced Materials of Hunan Province, Hunan Normal University, Changsha, People's Republic of China

²Polymers and Composites Division, Ningbo Institute of Material Technology & Engineering Chinese Academy of Science, Ningbo, People's Republic of China

Correspondence to: S. Su (E-mail: sushengpei@gmail.com)

ABSTRACT: A novel rubber filler, black liquor–montmorillonite complex (BL–MMT) was prepared by dehydration of a mixture of MMT and BL and used in the preparation of acrylonitrile butadiene rubber (NBR) composites by mechanical mixing method. The BL–MMT/rubber composites were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and differential scanning calorimeter (DSC). Experimental results of XRD and TEM indicated that MMT was well-dispersed in the rubber because of the presence of lignin. DSC, thermo-oxidative aging measurements and TGA results demonstrated that the thermal properties of NBR were improved due to the addition of BL–MMT. The tensile properties including tensile strength, elongation at break, and modulus were also tested. All experimental results indicated that this BL–MMT complex could be an effective reinforcing agent in rubber for cost-saving and environment benefits. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: montmorillonite; black liquor; NBR composites; thermal properties

Received 22 March 2012; accepted 29 April 2012; published online

DOI: 10.1002/app.37984

INTRODUCTION

Black liquor (BL) containing NaOH and lignin is the main pollution source of pulp and paper industry. Alkali recovery is one of the most important methods for the treatment of the BL where lignin was used as a fuel source¹; however, for the last decades researches indicated that lignin is a valuable renewable nature polymer with properties such as processing ability, stabilizing effect, reinforcing effect, and biodegradability.^{2,3} It can be converted to valuable products, such as reinforcing additives for rubbers and carbon fiber. Now people realize that a novel method should be developed to replace the alkali recovery method to save this renewable nature polymer resource and reduce the disposing of carbon dioxide.

It is well known that lignin is a three-dimensional natural amorphous polymer composed of phenyl propane units with carbonyl, phenolic hydroxyl, alcohol hydroxyl, and methoxyl groups.⁴ The incorporation of lignin into rubber has attracted much attention due to many advantages of rubber/lignin composites such as low hardness, large elongation, and good flexibility. Haxs and Mills⁵ have reported the possibility of lignin-re-

inforced rubber vulcanizates by co-precipitating lignin with rubber latex. Kumaran and De^{6,7} proposed the incorporation of lignin into styrene-butadiene rubber (SBR) and natural rubber (NR) to replace carbon black. Jiang⁸ has investigated the possibility of using lignin separated from the BL of soda pulping as a reinforcing agent in rubber. However, as a reinforcing filler, lignin is still not compared to carbon black due to the poor thermal properties.⁹ In addition, lignin used in these above reports is purified from BL. Most purified processes will produce sufficient washing effluent with high chemical oxygen demand (COD) and biological oxygen demand (BOD) which are required to be treated before discharge. For instance, Liao et al.¹⁰ prepared the filler CLM by co-precipitating of BL and montmorillonite (MMT). The CLM coprecipitates were purified and incorporated into the rubber. The CLM/rubber composites present good properties. But the time-consuming and expensive treatment process hindered the application of lignin in rubber industry.

MMT, a smectite clay, possesses a 2-to-1 layered structure with a single octahedral aluminum layer located between two layers

© 2012 Wiley Periodicals, Inc.

of silicon tetrahedral.¹¹ It is well acknowledged that MMT is easy to adsorb polymers such as lignin on the side or surface.^{12,13} The incorporation of MMT to polymers could enhance properties of composites such as mechanical, thermal stability, and aging properties due to the special clay platelets structure and morphology in matrices.^{14–16} However, in most of cases, MMT has to be organically modified to obtain well-dispersion in the composites which is considered as the most important factor for obtaining full enhancements.¹⁴

In this article, a novel rubber filler, BL–MMT complex (BL–MMT) will be prepared by dehydration of a mixture of MMT and BL rather than purifying the coprecipitates. One of the objectives for this study is to prepare a series of BL–MMT with different clay contents to achieve the full treatment of BL in the pulp industry with no waste water discharge; The other objectives is to test the application of this BL–MMT as filler in the preparation of acrylonitrile butadiene rubber (NBR) composites and realize well-dispersion of clay in NBR composites in the presence of lignin.

EXPERIMENTAL

Materials

NBR (N41, acrylonitrile content 29 wt %) was purchased from PetroChina Lanzhou Petrochemical, which was used as an elastomer in experiments. Calcium MMT (Ca–MMT, CEC90 meq/100g) was provided by Zhejiang Fenghong Montmorillonite Chemicals Co. (Hangzhou, China). BL was provided by Hongjiang Wanyuan Chemicals Co. (Huaihua, China) in which the content of lignin, alkali are about 25%, 10%, respectively. Zinc oxide (ZnO, AR) was purchased from Tianjin Hengxing Chemical Reagent Co. (Tianjin, China). Stearic acid (stA, AR) was purchased from Shanghai Pushan Chemical Co. (Shanghai, China). Sulfur (S, AR) was purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). N-cyclohexylbenzothiazole-2-sulfenamide (CZ) was of commercial grade. All those materials were used without further purification.

Preparation of BL–MMT Complexes

In general, a suspension of 100 g pristine Ca–MMT and 1000 mL distilled water was stirred for 24 h at room temperature, and then mixed with BL at different mass ratios of MMT to lignin (0 : 1, 1 : 3, 1 : 1, 3 : 1, and 1 : 0), where the amount of BL added is calculated by the lignin content in BL. Subsequently, the pH of this mixture was adjusted to 6–7 with 1.8 mol/L H₂SO₄ solution. Then, this mixture was ball-milled at a speed of 150 r/min for 3 h. The BL–MMT complexes were obtained by rotary evaporating at 60°C under 15 mm Hg until the content of water in the BL–MMT complexes is about 50%. The obtained complexes were labeled BL, 3 : 1-BL–MMT, 1 : 1-BL–MMT, 1 : 3-BL–MMT and MMT, respectively.

Preparation of BL–MMT/NBR and MMT/NBR Composites

The BL–MMT/NBR composites were prepared on an open two-roll mill by mechanical mixing and their formulations were listed in Table I. First, rubber was mixed with BL–MMT complex at 100°C on the open two-roll mill to evaporate the water in the mixture until constant weight. After the mixture and the rollers were cooled to room temperature, the other additives

Table I. The Formulations of NBR Composites

Compositions	phr ^a
NBR	100
S	2.5
ZnO	5.0
stA	2.0
CZ	1.0
Filler	30

^aParts per hundred rubbers.

were added individually in the order presented in the formulations, and then the mixture was placed in 23 ± 2°C for 24 h according to GB/T 2941-2006. Finally, the compounds were compression-molded at 135°C under 10 MPa for the optimum cure times (*T*₉₀) which were determined with a moving Die Rheometer to yield vulcanizates. The preparation of MMT/NBR was similar to BL–MMT/NBR, but did not add BL. The content of MMT is 30 phr. and labeled MMT/NBR.

Characterization

The rheometric curves and cure parameters were determined using a Tianyuan TY 6002 non-rotor rheometer (Jiangdu, China). The tests were carried out at 135°C, arc ±1°. X-ray diffraction (XRD) patterns were collected from 3 to 10° using a step size of 0.02° on a Bruker-D8 instrument (Karlsruhe, Germany) using monochromatic CuK α radiation. Transmission electron microscopy (TEM) images of the composites were obtained at 100 kV with a Tecnai F20 instrument (FEI, U.S.A.). The ultra-thin sections of the samples were prepared by ultramicrotomy (Leica Ultracut UCT) at –100°C with a thickness of about 100 nm. The sections were transferred from the knife edge to 600 hexagonal mesh Cu grids. Differential scanning calorimeter (DSC) was performed on a Netzsch 200F3 instrument (Bavaria, Germany) from –70 to 130°C under a flowing nitrogen atmosphere at a scan rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on a Netzsch STA409PC instrument (Bavaria, Germany) under a flowing air atmosphere at a scan rate of 10°C/min from 30 to 1000°C. Temperatures are reproducible to ±1°C, the error bars on the fraction of nonvolatile material is ±1%. Thermal oxidative aging of the samples was carried out in an air-circulating oven for 3 days at 100°C according to GB/T 3512-2001. Tensile testing of the NBR samples were carried out using a Kexin WDW3020 electronic universal testing machine (Changchun, China) according to the standard GB/T 528-1998 at a strain rate of 500 mm per minute at 25 ± 2°C. The Shore A hardness of the samples was measured by using a Huayin LX-A Durometer (Laizhou, China) according to GB/T 6031-1998.

RESULTS AND DISCUSSIONS

Curing Characteristics of the Composites

The cure parameters are important to the manufacture processing and the final properties of rubber. In this study, the influence of the type of complex on cure characteristics of NBR was investigated. The scorch time (*T*₁₀) and the optimum cure time (*T*₉₀) of each composite were recorded and listed in Table II.

Table II. The Cure Parameters of NBR Composites

Materials	T_{10}/min	T_{90}/min	$\text{CRI}/\text{min}^{-1}$
NBR	39.84	47.97	12.3
BL/NBR	2.89	4.77	53.19
3:1-BL-MMT/NBR	3.26	5.19	51.95
1:1-BL-MMT/NBR	3.80	5.76	51.15
1:3-BL-MMT/NBR	5.03	8.65	27.62
MMT/NBR	62.21	87.15	4.01

T_{10} , a measure of the scorch safety of the rubber compound, is the time required for the torque value to reach 10% of maximum torque. T_{90} , a measure of cure time of the rubber compound, is the time required for the torque value to reach 90% of maximum torque. The cure rate index (CRI) is calculated using the following equation: $\text{CRI} = 100/(T_{90} - T_{10})$. A high value of CRI indicates a fast cure rate. Experimental data showed that the MMT/NBR exhibit a longer scorch time, longer cure time and smaller CRI compared with NBR. This could be contributed to the adsorption of the vulcanization agent by MMT, which made the formation of active intermediate and crosslinking net delayed.^{17,18} Compared with pure NBR and MMT/NBR, the BL-MMT/NBR and BL/NBR showed shorter T_{10} and T_{90} and larger CRI. Moreover, T_{10} and T_{90} decrease as the ratio of lignin to MMT increased. Improved CRI of BL-MMT/NBR composites suggested an increasing cure rate, which would benefit the improvement of production efficiency.

Morphology Study

X-Ray Diffraction Measurements. XRD is used to measure the change in the d -spacing of the clay which occurred at the preparation process of composites. The XRD patterns obtained from MMT, BL-MMT/NBR, and MMT/NBR composites are shown in Figure 1. One can see a peak at 2θ of 6.89° corresponding to d -spacing of 1.28 nm in the XRD pattern of MMT (Trace a) used in this experiment, and a peak at 2θ of 6.16° corresponding to d -spacing of 1.43 nm in pristine MMT/NBR composites (Trace b). This difference in d -spacing is due to the insertion of water into the silicate layers after stirring with distilled water and the mechanical mixing could not evaporate the water drastically. Noticeably, the intensity of the peak near $2\theta = 6.16^\circ$ of 1 : 3-BL-MMT/NBR (traces c) reduced significantly compared with that of MMT/NBR (Traces b), which may attribute to the decrease of MMT or the change of crystalline form because of the addition of BL. The absence of peaks for 1 : 1-BL-MMT/NBR (Trace d) and 3 : 1-BL-MMT/NBR (trace e) may indicate that the exfoliation and randomly dispersion of MMT in NBR matrix have occurred due to the addition of BL. But, the absence of peaks is also possibly caused by the geometry effects in the samples or lack of sensitivity of apparatus and TEM must be used to identify the morphology.

Transmission Electron Microscopy. The morphologies of BL-MMT/NBR and MMT/NBR composites were examined by TEM. The TEM images at low and high magnification are shown in Figures 2 and 3, respectively. From the low magnification images in Figure 2, it can be seen that there is better dispersion of the clay in the BL-MMT/NBR composites compared

with MMT/NBR composites. As the ratio of lignin to MMT in the BL-MMT complexes increased, the dispersion became better. From the high magnification images in Figure 3, it also can be seen that the dispersion became better, but the exfoliation had not been observed. These could be attributed to that lignin could partially dissolve in the rubber matrix¹⁹ and had a better compatibility with rubber than MMT, and meanwhile lignin could be absorbed by MMT through the interactions between its phenolic hydroxyl groups and the positive charges on the edge of clay layers.¹² One can conclude that lignin played a key role in improving the dispersion of MMT in NBR.

Thermal Properties

The Glass Transition Temperature of the Composites. Figure 4 showed DSC patterns obtained from NBR and BL-MMT/NBR composites. One can see that there are only one glass transition temperature from the traces obtained from lignin and pure NBR vulcanizates, but two glass transition temperatures in the BL-MMT/NBR and MMT/NBR composites.

The first T_g (T_{g1}), which is assigned to NBR matrices, has no change with the incorporation of pristine MMT (curves h), however, The T_{g1} of BL/NBR and BL-MMT/NBR (Curves b, c, d, and e) decreases by 1.3°C compared with NBR. It can be attributed to the plasticizing effect of the low-molecular weight organic materials from BL.¹⁹

We can draw a conclusion from the traces a, b, c that lignin is partly compatibility with NBR matrices. The second T_g (T_{g2}) of BL-MMT/NBR composites can be assigned to lignin. The T_g of lignin first shifts to the higher temperature with increasing of the content of MMT, then reaches the maximum when the ratio of lignin to MMT is 1 : 3, and finally decreases with increasing of the content of MMT. The increasing of T_g of lignin could be contributed to the adsorption of MMT^{12,13} and reduced the mobility of lignin. The total specific surface area of MMT particles was increased owing to the increasing content of MMT in the BL-MMT complex as the ratio of lignin and MMT decreased, which leads to the increased T_g of lignin. While the

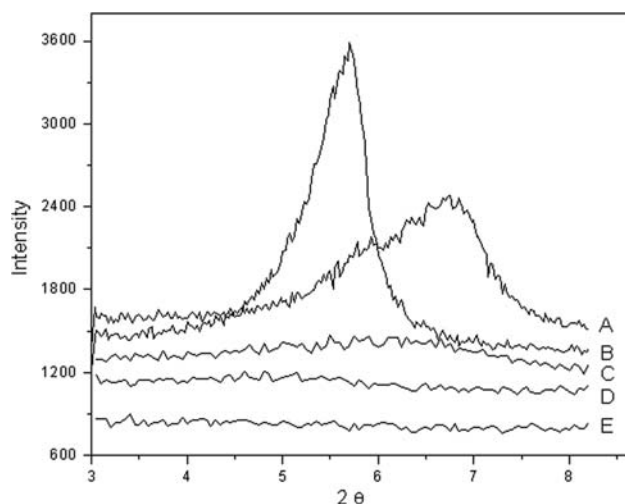


Figure 1. Patterns obtained from: (A) MMT; (B) MMT/NBR; (C) 1:3-BL-MMT/NBR; (D) 1:1-BL-MMT/NBR; and (E) 3:1-BL-MMT/NBR.

F4

F2 F3

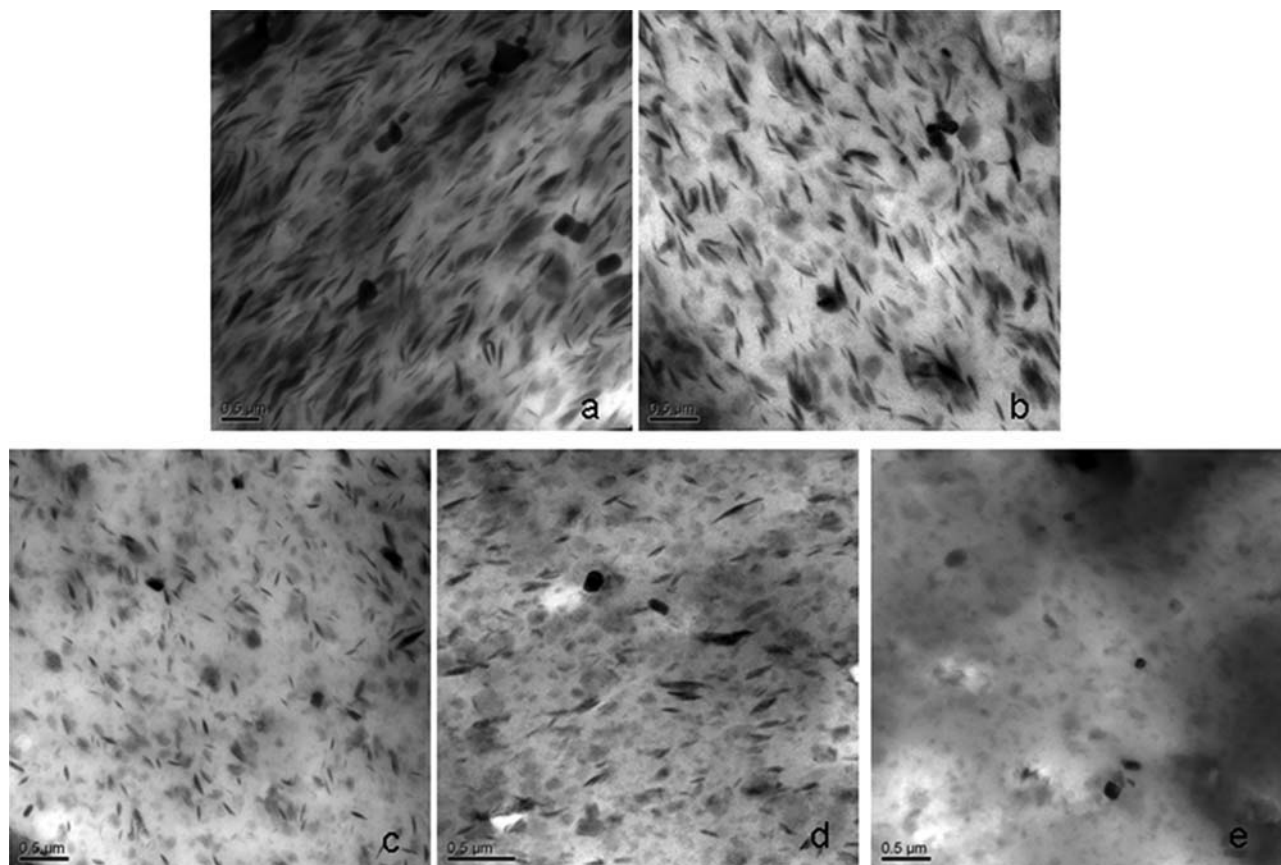


Figure 2. The low magnification TEM images of NBR composites: (a) MMT/NBR; (b) 1:3-BL-MMT/NBR; (c) 1:1-BL-MMT/NBR; (d) 3:1-BL-MMT/NBR; (e) BL/NBR.

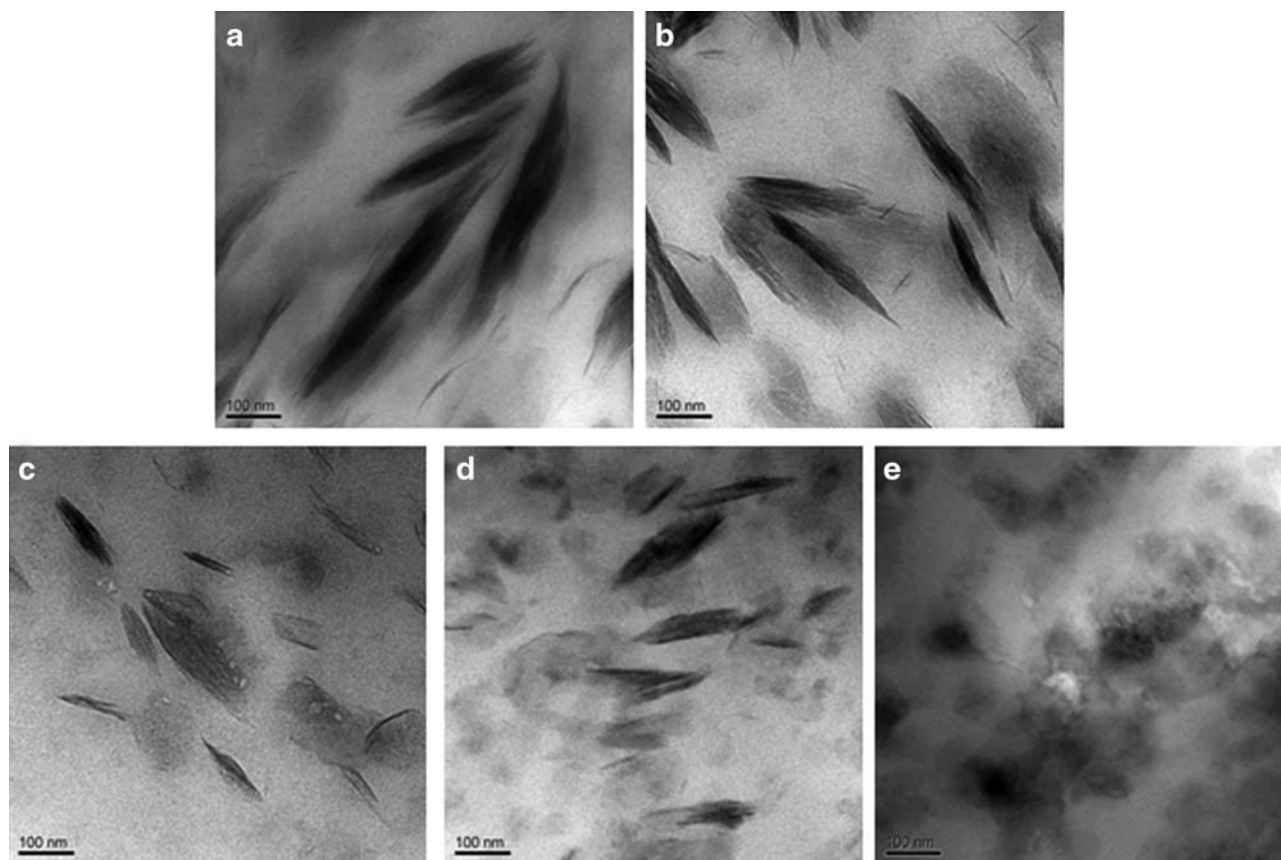


Figure 3. The high magnification TEM images of NBR composites: (a) MMT/NBR; (b) 1:3-BL-MMT/NBR; (c) 1:1-BL-MMT/NBR; (d) 3:1-BL-MMT/NBR; (e) BL/NBR.

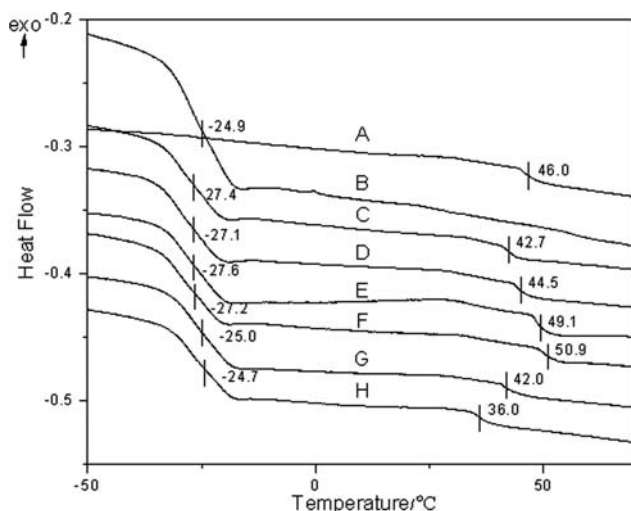


Figure 4. DSC traces obtained from: (A) Lignin; (B) NBR; (C) BL/NBR; (D) 3:1-BL-MMT/NBR; (E) 1:1-BLMMT/NBR; (F) 1:3-BL-MMT/NBR; (G) 1:6-BL-MMT/NBR; and (H) MMT/NBR.

ratio of lignin and MMT was below 1 : 3, the total specific surface area of MMT particles was decreased owing to the aggregation of MMT particles significantly, which leads to the decreased T_g of lignin.

Tsagaropoulos et al. reported that the inorganic/polymer composites exhibit two T_g s.²⁰ The first T_g of MMT/NBR around -25°C was related to the usual polymer glass transition, while the other, occurring at a higher temperature around 60°C , was assigned to the glass transition of regions containing polymer chains of reduced mobility which can contribute to adsorption of MMT.

Thermal Stability of the Composites. The thermal stability of the pure NBR and composites was assessed by TGA. The TGA traces obtained from pure NBR, BL precipitate (BL) and composites are shown in Figure 5. The data analysis has been

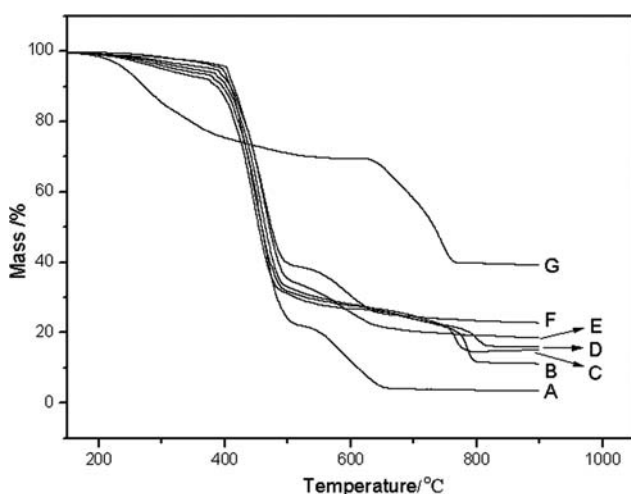


Figure 5. TGA traces obtained from: (A) NBR; (B) BL/NBR; (C) 3:1-BL-MMT/NBR; (D) 1:1-BL-MMT/NBR; (E) 1:3-BLMMT/NBR; (F) MMT/NBR and (G) BL.

Table III. TGA Analysis of Pure NBR and NBR Composites

Materials	$T_{10\%}/^\circ\text{C}$	$T_{50\%}/^\circ\text{C}$	Char/%
NBR	408.6	458.6	3.7
BL	271.7	732.6	39.7
BL/NBR	386.6	453.8	11.5
3:1-BL-MMT/NBR	396.0	458.8	14.8
1:1-BL-MMT/NBR	402.3	464.2	16.2
1:3-BL-MMT/NBR	408.6	470.9	19.1
MMT/NBR	413.6	473.8	23.3

performed and results are shown in Table III. In general, TGA analysis information includes: the 10% weight loss temperature, $T_{10\%}$, the degradation initiation temperature; the 50% weight loss temperature, $T_{50\%}$, the degradation temperature; and the char content (residual weight percent at 900°C).

The $T_{10\%}$ and $T_{50\%}$ of the BL/NBR is lower compared with pure NBR due to the decomposition of lignin begins at 271.7°C . However, the $T_{10\%}$ and $T_{50\%}$ of the BL-MMT/NBR composites increased as the content of MMT increase in BL-MMT/NBR composites. When the ratio of lignin and MMT was 1 : 3, the $T_{10\%}$ could be comparable with NBR and $T_{50\%}$ was higher than NBR and BL/NBR. This could be attributed that the inclusion of inorganic components into organic materials could improve their thermal stability.²¹ The char of NBR composites increased as the ratio of lignin and MMT of fillers decrease.

Thermo-Oxidative Aging of the Composites. It is well known that the effect of thermo-oxidative aging on rubber properties is considered to be primarily important for the industrial applications in air at high temperature. In this study, the thermal oxidative aging properties of BL-MMT/NBR, MMT/NBR and NBR has been evaluated by the percent retention of tensile strength. The experimental data are shown in Figure 6.

It can be observed that the retention of tensile strengths of BL/NBR is significantly reduced compared with that of NBR, which

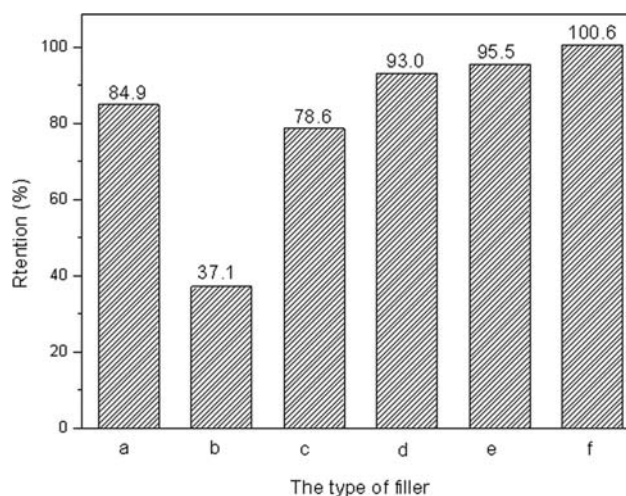


Figure 6. The therm-oxidative aging properties of NBR composites: (a) NBR; (b) BL/NBR; (c) 3:1-BL-MMT/NBR; (d) 1:1-BL-MMT/NBR; (e) 1:3-BL-MMT/NBR; and (f) MMT/NBR.

Table IV. The Mechanical Properties of NBR Composites

Materials	Tensile strength/MPa	Elongation at break/%	300% modulus/MPa	Hardness
NBR	4.6 ± 0.3	511 ± 13	1.9	54
BL/NBR	25.9 ± 1.4	809 ± 17	2.6	64
3:1-BL-MMT/NBR	26.6 ± 0.4	777 ± 19	2.9	65
1:1-BL-MMT/NBR	28.7 ± 0.5	813 ± 17	3.2	65
1:3-BL-MMT/NBR	24.2 ± 1.5	730 ± 18	5.4	66
MMT/NBR	18.6 ± 1.7	541 ± 52	9.4	67

indicate that some BL components can accelerate the thermo-oxidative aging of rubber. The retentions of tensile strength of NBR composites filled with the novel filler BL–MMT complexes were improved rapidly to 78.6%, 93.0%, and 95.5% respectively, which demonstrated that the novel filler BL–MMT complexes could improve the thermo-oxidative aging property of rubber. This improvement could be considered that the clay layers acted as barriers for the diffusion of oxygen from the outer surface into the interior of the rubber product^{22,23} and slowed down the aging process. The good aging property of MMT/NBR could be attributed to the barrier effect of MMT and no BL component in the composite.

Tensile Properties

The tensile properties of all the composites, including tensile strength, elongation at break, 300% modulus, and shore A hardness, have been evaluated and the experimental data are presented in Table IV.

It can be seen that the tensile strength and elongation at break of BL/NBR are higher than those of NBR, which can be attributed to the reinforcing effects of lignin. It can also be seen that the reinforcing effects of all BL–MMT complexes on the tensile strength and elongation at break are superior to MMT. 1 : 1-BL–MMT/NBR composites showed the best tensile properties in all BL–MMT/NBR composites, where there were about 54% increase in tensile strength and 50% increase in elongation at break compared with MMT/NBR. The key factor for this improvement was due to good dispersion of MMT in BL–MMT/NBR, which is evidenced by the results of TEM. Three hundred percentage modulus and Shore A hardness were increased as the ratio of MMT and lignin increased which was contributed to the increasing of inorganic MMT in the composites.

Considering of the utilization efficiency of black liquid and comprehensive properties of BL–MMT/rubber composites, a conclusion could be obtained that the optimum ratio of lignin and MMT is 1 : 1.

CONCLUSION

In this article, the novel BL–MMT complexes have been prepared by dehydration of a mixture of BL and MMT without purifying process, and then used as a rubber reinforcing agent.

The process is a green technology, in which has achieved the full treatment of BL in the pulp industry with no waste water discharge and disposing of carbon dioxide. The good dispersion of clay in the BL–MMT/NBR was obtained due to the present of lignin. The mechanical properties, aging properties, and thermal stability of obtained BL–MMT/NBR composites were greatly improved due to the good dispersion of MMT. Evidences from experiments indicated that the treatment and application of BL in this article was a promising project in the industrial production due to cost-saving and environment benefits.

ACKNOWLEDGMENTS

The authors thank Hongjiang Wanyuan Chemical Company for black liquor and Zhejiang Fenghong Clay Chemical Company for clay products.

REFERENCES

- Pokhrel, D.; Viraraghavan, T. *Sci. Tot. Environ.* **2004**, 333, 37.
- Lora, J. H.; Glasser, W. G. *J. Polym. Environ.* **2002**, 10, 39.
- Kosikova, B.; Gregorova, A. *J. Appl. Polym. Sci.* **2005**, 97, 924.
- Gregorova, A.; Kosikova, B.; Moravcik, R. *Polym. Degrad. Stab.* **2006**, 91, 229.
- Mills, G. S.; Haxo, H. E., U. S. Patent 2,906,718, Sept. 29, **1959**.
- Kumaran, M. G.; De, S. K. *J. Appl. Polym. Sci.* **1978**, 22, 1885.
- Kumaran, M. G.; Mukhopadhyay, R.; De, S. K. *J. Polym. Sci. Polym. Lett. Ed.* **1979**, 17, 399.
- Jiang, T.; Huang, W.; Zhang, C. *Environ. Sci.* **1997**, 18, 81.
- Jiang, T., Lignin; Chemical Industry Press: Beijing, **2009**.
- Liao, Z. D.; Wang, X.; Su, S. P. *Polym. Adv. Technol.* 2011, DOI: 10.1002/pat.2011.
- Ho, D. L.; Briber, R. M.; Glinka, C. *J. Chem. Mater* **2001**, 13, 1923.
- Theng, B. K. G. *Clay. Clay. Miner.* **1982**, 30, 1.
- Zeng, R. *J. Cellulose Sci. Technol.* **2007**, 15, 75.
- Okada, A.; Usuki, A. *Mater. Sci. Eng.: C* **1995**, 3, 109.
- Gilman, J. *Appl. Clay. Sci.* **1999**, 15, 31.
- Su, S. P.; Jiang, D. D.; Wilkie, C. A. *Polym. Degrad. Stab.* **2004**, 83, 333.
- Zheng, H.; Zhang, Y.; Peng, Z. *Polym. Test.* **2004**, 23, 217.
- Chang, Y. W.; Yang, Y.; Ryu, S.; Nah, C. *Polym. Int.* **2002**, 51, 319.
- Kramarova, Z.; Alexy, P.; Chodak, I.; Spirk, E.; Hudec, I.; Kosikova, B.; Gregorova, A.; Suri, P.; Feranc, J.; Bugaj, P. *Polym. Adv. Technol.* **2007**, 18, 135.
- Tsagaropoulos, G.; Eisenberg, A. *Macromolecules* **1995**, 28, 6067.
- Wen, J.; Wilkes, G. L. *Chem. Mater.* **1996**, 8, 1667.
- Kader, M. A.; Kim, K.; Lee, Y. S.; Nah, C. *J. Mater. Sci.* **2006**, 41, 7341.
- Sanchez-Garcia, M. D.; Gimenez, E.; Lagaron, J. M. *J. Appl. Polym. Sci.* **2008**, 108, 2787.