

Enhanced oil resistance and mechanical properties of nitrile butadiene rubber/lignin composites modified by epoxy resin

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ABSTRACT: This is probably the first report on developing nitrile butadiene rubber (NBR) composites with enhanced performances via lignin bridged epoxy resin in the rubber matrix. NBR/lignin masterbatch has been prepared through latex-compounding method, and then epoxy resin (F51) was added in the NBR/lignin compounds by the melt compounding method. Lignin-epoxy resin networks were synthesized *in situ* during the curing process of rubber compounds through epoxide–hydroxyl reactions. Compared with lignin filler, lignin-F51 networks showed an improved oil resistance ability and led to increased mechanical properties, crosslinking density, and thermal stability of the rubber composites. This method provides a new insight into the fabrication of novel interpenetrating polymer networks in rubber composites and enlarges the potential applications of lignin in high performance rubber composites. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42922.

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INTRODUCTION

Nitrile butadiene rubber (NBR) is noncrystalline with a low gum tensile strength. Therefore, reinforcing fillers are often required in this matrix to improve the modulus, hardness, and to reduce the material costs. Among several fillers, carbon black (CB) is one of the most commonly used reinforcing fillers in rubber for its excellent reinforcement in combination with low costs. As the source of CB is petroleum, and the preparation and processing of CB are hazardous.¹ Therefore, it is important to seek for environmentally-friendly reinforcing fillers that are inexpensive, readily available, light in weight, and renewable.

Lignin is the second most abundant² and fascinating biomaterials next to cellulose, and it is an aromatic polymer that makes up 15–30% of the cell walls of terrestrial plants.³ Nowadays, lignin is widely available as a major byproduct in the pulp and paper industry as well as the emerging bioethanol industry,^{4,5} and its potential is not fully exploited. The impressive properties of lignin, such as its high abundance, low density, and its environmentally friendly, antioxidant, antimicrobial, and biodegradable nature, along with its CO₂ neutrality and reinforcing capability,⁶ makes it an ideal reinforcing fillers for the rubber. Various academic articles regarding preparations of rubber/lignin compounds have been published.^{4,7–14} Usually, there are two ways to improve the performance of rubber/lignin composites, one is to chemically modify the surface of lignin, such as

using cyclohexylamine,⁸ hexamethylenetetramine,¹¹ benzoyl peroxide¹⁵ or using the coupling agent, such as polybutadiene-g-poly(pentafluorostyrene),¹⁶ to improve the adherence between the matrix and lignin. Another method is to hybrid lignin with other filler, such as carbon black,⁷ montmorillonite,^{10,13} and layered double hydroxides,¹⁷ to improve the mechanical or dynamic mechanical performance of rubber/lignin composites.

NBR is a nitrile butadiene rubber copolymer, which has a good compatibility with the epoxy resin. There are numerous scientific articles relating to preparations of acrylonitrile butadiene rubber¹⁸ (or its derivatives, such as amine-terminated,¹⁹ carboxyl-terminated,²⁰ hydroxyl-terminated,²¹ and epoxy-terminated²² acrylonitrile butadiene copolymer) as toughener for epoxy resin. However, few studies have focused on using epoxy resin to reinforce NBR.

Since the abundance of hydroxyl in lignin makes it possess potential ability for the formation of covalent bond with the epoxy resin through epoxide–hydroxyl reactions, and we can imagine that the epoxy can be crosslinked by lignin in the absence of an external crosslinking agent (i.e. imidazole or amine), thus a new strategy is proposed to reinforce the rubber by lignin-epoxy resin networks.²³ As is well known, NBR has high polarity and is one of the most important industrial raw materials, oil resistance is supposed to be one of the most important properties. There are few study related the oil

resistance of NBR/lignin composite¹⁵ and the mechanical property of rubber/lignin composite after oil swelling are rarely reported. The present work intends to verify the effectiveness of the lignin-F51 networks on the oil resistance and mechanical performance towards NBR. In the present article, we prepare the NBR/lignin compound by latex compounding method to achieve the fine dispersion of lignin in NBR matrix, and the liquid epoxy is mixed with NBR/lignin along with rubber additives (sulfur etc.) by the two-roll rubber mill. Both epoxy resin networks cured by lignin and rubber networks cured by sulfur are synthesized during the curing process of rubber compounds. And the full-interpenetrating polymer networks in the rubber compounds have been prepared. To the best of our knowledge, this is the first time to use lignin-epoxy networks formed by lignin and epoxy resin to improve the oil resistance and mechanical properties of the polar rubber, and the experimental results indicate that the lignin-F51 networks could effectively improve the oil resistance, thermal stability, and mechanical properties towards polar NBR.

EXPERIMENTAL

Materials

NBR latex, containing 26% acrylonitrile monomer, was purchased from Sinopec Qilu Branch Company (China). Lignin (industrial sulfate lignin), with an average molecular weight of 4235 g/mol and polydispersity index of 2.4, was provided by Guangzhou Linge Polymer Material Co. (China). Epoxy resin (the type of epoxy resin is novolac epoxy resin, its structure is shown in related reference,²⁴ the tradename is F51, which is a transparent, yellowish, and sticky liquid with low molecular weight, the epoxy value is 0.51~0.54, it is industry grade and its density is 1.22 g/cm³) was provided from Nanya Plastics Corporation in China. Hydraulic oil (IRM 903) was obtained from Calumet Lubricants Company. All the rubber ingredients such as zinc oxide (ZnO), stearic acid (SA), *N*-tertbutyl-2-benzothiazole sulfonamide (CBS), dioctyl phthalate (DOP), 2,2'-dibenzothiazole disulfide (DM), tetramethylthiuram disulfide (TMTD), and sulfur (S) were industrial grade and used as received. Other ingredients were bought from local sources.

Sample Preparation

The NBR/lignin (100/50) compound was obtained via latex compounding. Typically, the lignin solution (the dry weight ratio of lignin to NBR is 50 : 100) was added dropwise to the NBR latex with vigorous stirring, and then 5 wt % diluted acid solution was added to co-coagulate the mixture. The obtained slurry was filtered, water washed, and then dried in oven. It should be noted that the phr value would be used in this article and the phr refer to parts per hundreds of rubber. Various amounts of F51 and other additives including the vulcanizing ingredients (5 phr ZnO, 5 phr DOP, 2 phr SA, 1.5 phr CBS, 0.5 phr DM, 0.3 phr TMTD, and 1.5 phr S) were mixed into the NBR/50lignin compound in a two-roll mill. The well-mixed compounds were press-cured into 1 mm thick sheets at 160°C. The sample name NBR/50lignin/ χ F51 denotes a compound with 50 phr lignin and χ parts F51 (relative to 100 parts NBR).

In addition, to verify the crosslinking reaction between F51 and lignin, *N*-NBR/50lignin/F51 compounds were prepared with the

same procedure of NBR/50lignin/F51 except that no rubber additives (sulfur etc.) were added. The prefix 'N' means that no rubber additives were added in the sample.

Characterizations

Tensile stress-strain and tear properties were measured according to ASTM D412 and ASTM D624 specifications, on a U-CAN UT-2060 instrument (U-CAN DYNATEX, Taipei, Taiwan) with crosshead speed of 500 mm/min.

Thermal gravimetric analysis (TGA) was carried out in a TA Q5000 (TA Corporation, New Castle) thermogravimetric analyzer over a temperature range from 30°C to 700°C at a heating rate of 10°C/min, nitrogen was used as purging gas.

The curing characteristics of the *N*-NBR/50lignin/F51 composites were determined at 160°C by U-CAN UR-2030 vulcameter (U-CAN DYNATEX, Taipei, Taiwan).

Strain sweep of uncured composites or cured composites was carried out in a Rubber Process Analyzer (RPA2000, Alpha technologies Co.) at 60°C and 60 cpm.

Scanning electron micrographs (SEM) of the composites were conducted by a Nova NanoSEM 430 instrument (FEI, the Netherlands). The *N*-NBR/50lignin/F51 samples were firstly fractured at liquid N₂ temperature, then they were etched by butanone and the etched surfaces were obtained. The tensile fracture surfaces were directly obtained from the tensile tests. After that, all the surfaces were sputter coated with gold before examining under the SEM. The voltage of the electron beam used for SEM observation was 10 kV.

Crosslinking Density Measurement. The apparent crosslinking density of the rubber composites are determined by Equilibrium Swelling Technique according to the reference.²⁵ The crosslinking density can also be determined by magnetic resonance crosslinking density spectrometer (XLDS-15, IIC Innovative Imaging Corporation, Germany) with a magnetic field intensity of 15 MHz at 90°C. Data analysis was performed with the IIC Analysis Software package, using a non-linear Marquardt-Levenberg algorithm.

Swelling and Oil Resistance Measurement. Swelling ratio test was performed by immersing the rubber specimens in motor oil at 100°C for 3 days, and the changes of the volume and mass after the oil immersion were detected according to the China National Standard, GB/T 1690-2010.²⁶ The change of the tensile properties of specimens after oil immersion were also used to determine the oil resistance according to GB/T 1690-2010. The dumbbell-shaped test specimens were immersed in oil at 100°C for 72 h. Thereafter, we removed the specimens from the oil, eliminated the excess oil on the specimen surfaces, and tested the mechanical properties. And the change of mechanical property after oil immersion was obtained.

RESULTS AND DISCUSSION

interaction between Lignin and F51 in the NBR Matrix

The authors believe that the OH groups (or COOH groups) of lignin could react with the epoxy groups of F51 by the ring-opening reaction.^{23,27} Since F51 and lignin are both the multi-functional polymers, F51 and lignin would link into an

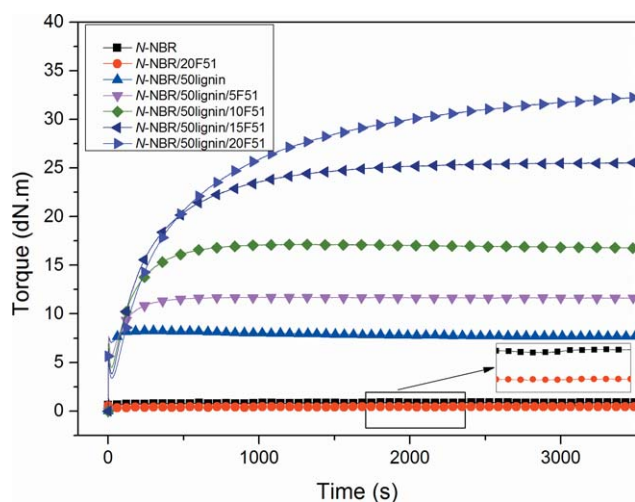


Figure 1. Curing curves of the *N*-NBR/F51 and *N*-NBR/50lignin/F51. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

insoluble, rigid, 3-D structure networks. *N*-NBR/50lignin/F51 compounds are subjected to torque analysis by the vulcameter. As noted before, the prefix 'N' means that no rubber additives (sulfur etc.) were added in the samples, thus the disturbance of

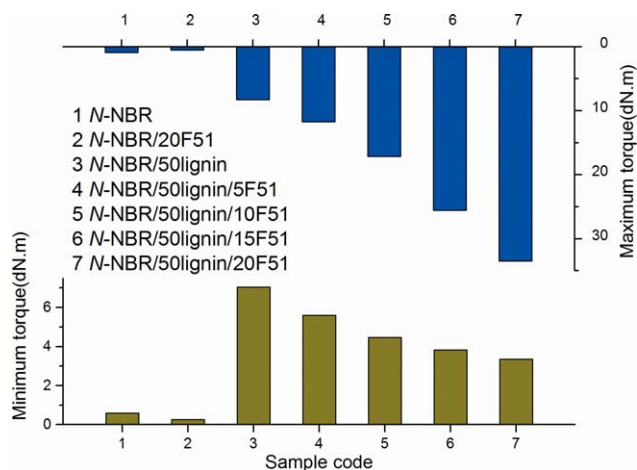


Figure 2. Minimum and maximum torque of the *N*-NBR/F51 and *N*-NBR/50lignin/F51. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the rubber chain crosslink reaction in the torque study is eliminated, therefore, an increase in the torque can be a measure of crosslink reaction between lignin and F51.

As shown in Figures 1 and 2, the maximum torque (MH) of *N*-NBR/20F51 is lower than that of *N*-NBR, which means that F51

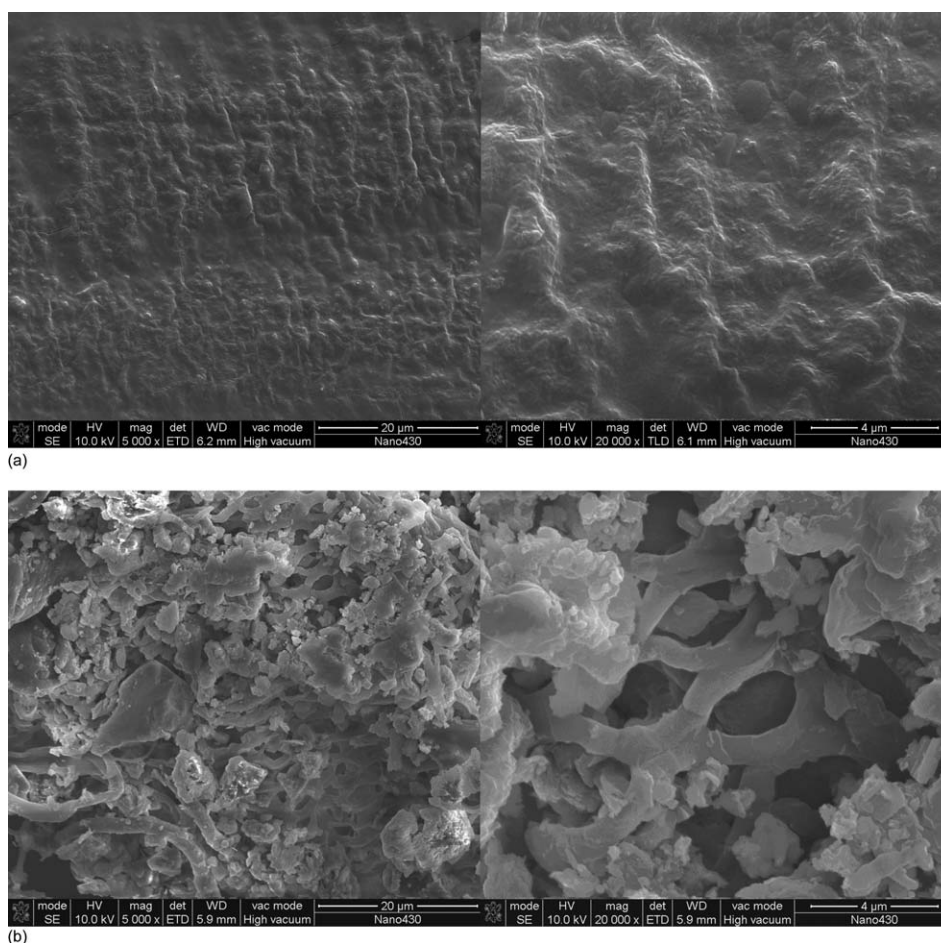


Figure 3. SEM photos of the samples etched by 2-butanone (a) *N*-NBR/50lignin and (b) *N*-NBR/50lignin/15F51.

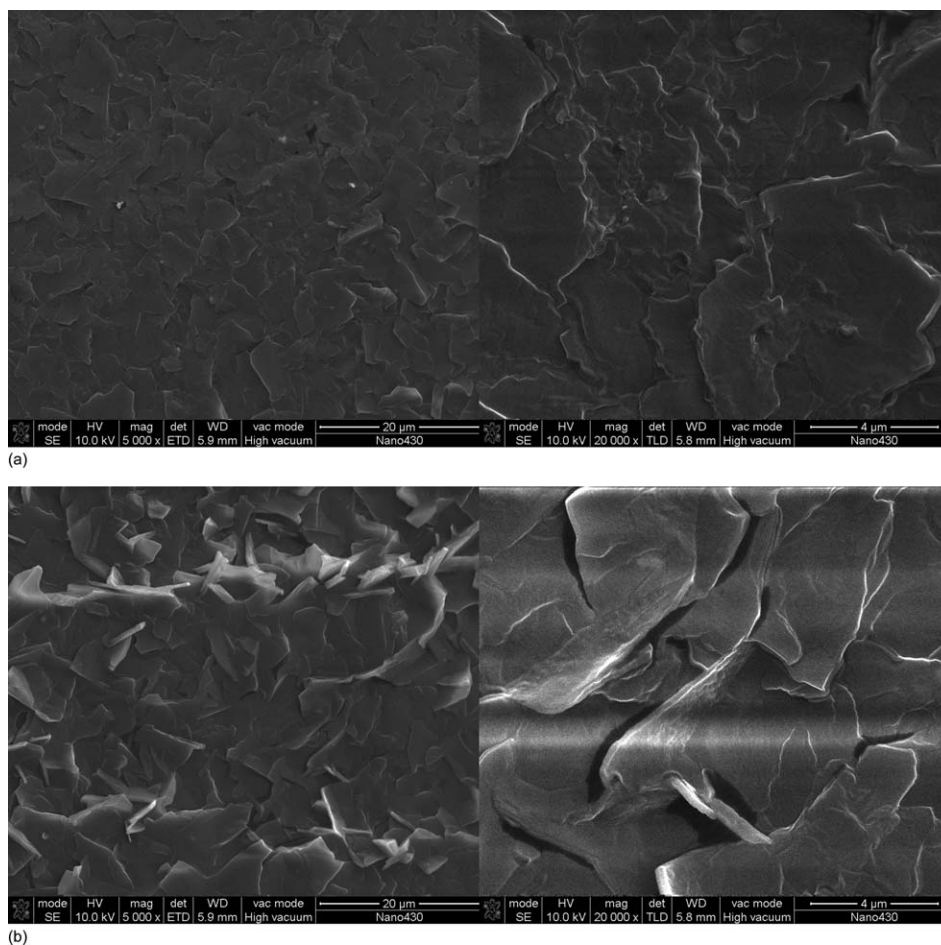


Figure 4. SEM images of the tensile fracture surfaces. (a) NBR/50lignin, (b) NBR/50lignin/5F51, (c) NBR/50lignin/10F51, and (d) NBR/50lignin/20F51.

are not cured and remains liquid, indicating that there are no crosslink reaction between NBR and F51. The MH of *N*-NBR/50lignin is much higher than that of *N*-NBR, and this is because that there will be a rubber-filler interaction as well as usual volume fraction effects after addition of lignin filler.²⁸

The MH of *N*-NBR/50lignin/F51 shows a growth with the increase of F51. We can image that an increasing number of epoxy groups react with the surface hydroxyl groups of lignin and consequently more covalent bonds are formed, thus a stronger lignin-F51 networks are formed with the increase of F51. It is evident that the crosslinked networks are formed as the F51 could crosslink with lignin rather than NBR.

MORPHOLOGY STUDY

To observe the lignin-F51 networks in the matrix. The *N*-NBR/50lignin/F51 compounds are fractured at liquid N₂ temperature and then etched by 2-butanone for 20 days to remove the free NBR matrix (2-butanone is a good solvent for the uncured NBR, and the NBR phase are not crosslinked since no sulfur was added in the 'N' series samples), and the etched surfaces are observed by SEM. As shown in Figure 3, no networks can be observed in the sample of *N*-NBR/50lignin, and it is difficult to observe the lignin in Figure 3(a) *N*-NBR/50lignin. We can image that lignin is wrapped and cemented by NBR, and lignin

particles could fall off when the NBR was dissolved, thus a relatively smooth surface is remained. However, as shown in Figure 3(b), the network is obvious and disperses uniformly in the sample of NBR/50lignin/15F51. Since there would be crosslinking reaction between lignin and F51 after the introduction of F51, thus the general morphology of insoluble rigid lignin-F51 networks are roughly outlined in Figure 3(b) when the free and uncrosslinked NBR was dissolved in the 2-butanone. Therefore, the SEM demonstrates existence of lignin-F51 networks in the matrix.

SEM images of the tensile fractured surfaces of NBR/50lignin and NBR/50lignin/F51 composites are shown in Figure 4. As shown in Figure 4(a), it is clear that the surface of the NBR/50lignin composite is smooth, indicating that when external stress is applied into the composites, it is not efficient enough to transfer the load from the matrix to the lignin particles. It should be noted that the sample of NBR/50lignin/F51 exhibits much more rugged fracture surfaces than those of NBR/50lignin, and we can image that these protuberances are the lignin-F51 networks, which are wrapped with NBR molecules. All of these observations indicate the good compatibility and strong adhesion between lignin-F51 networks and NBR matrix in the NBR/50lignin/F51 composites. We can infer that the lignin-F51 networks can bear much external forces when an exerted stress

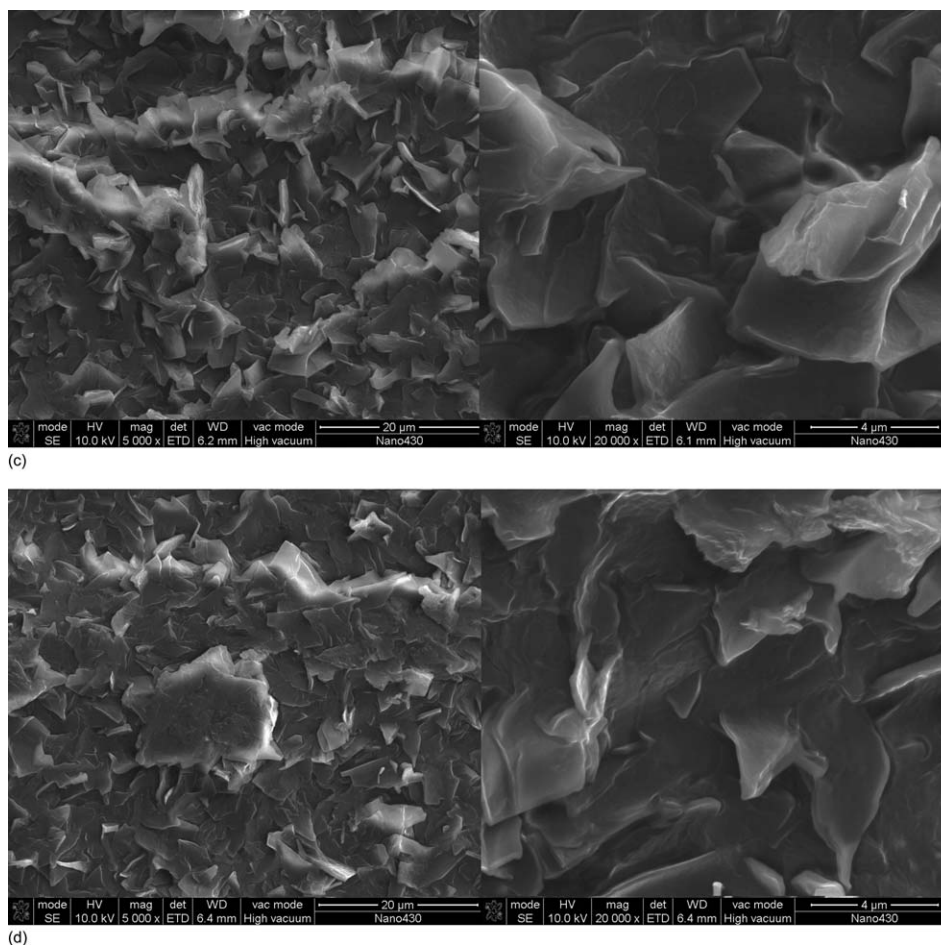


Figure 4. Continued.

is applied to the matrix, and this is in accordance with the mechanic performances below.

Dependence of Shear Modulus (G') for Rubber Compounds on Strain

To further validate the existence of rigid lignin-epoxy networks in the NBR matrix, rubber process analyzer (RPA) is used to analyze the shear modulus (G') of rubber composites before and after curing. As shown in Figure 5(a), the modulus of the uncured compounds decreases with the increase of F51 through

all the strain. Since the uncured epoxy resin is the viscous liquid, it acts as plasticizers and lubricants. It indicates that adding F51 could weaken the filler network interaction and reduce the Payne effect, and then improve the processability. However, as shown in Figure 5(b), the G' of the vulcanizates increases with the increase of F51 through all the strain, and the authors ascribe this phenomenon to the covalent bonding interaction between lignin and epoxy resin after cure process. Once the rigid lignin-epoxy resin networks are formed, the constitutive mobility of NBR segments would significantly be restricted due

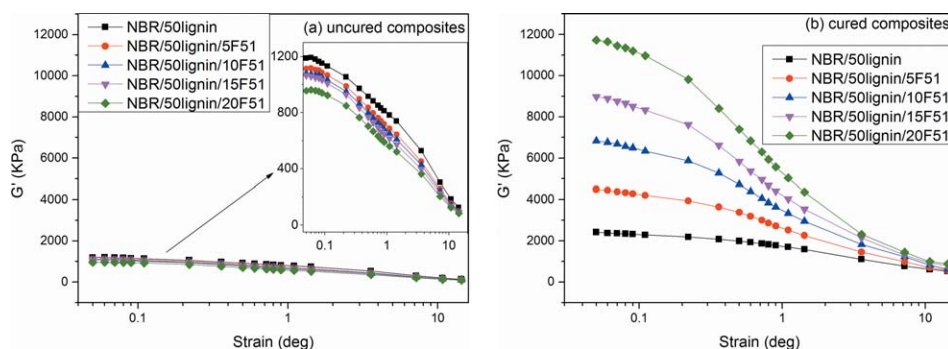


Figure 5. Strain dependence of G' : (a) uncured composites and (b) cured composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

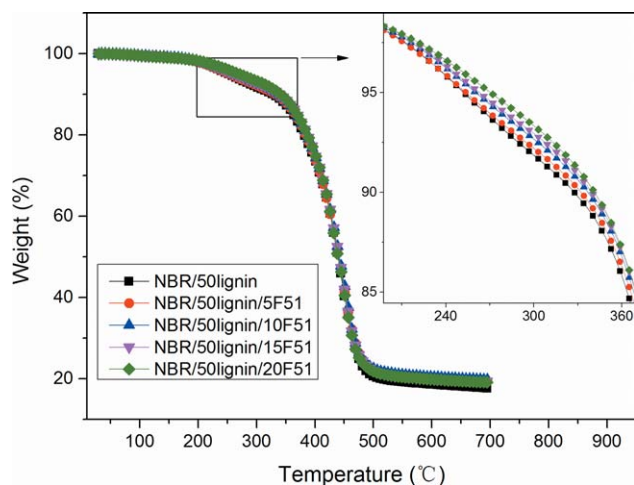


Figure 6. TGA curves of NBR/50lignin/F51. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the entanglement between lignin-epoxy resin networks and rubber chains. There will be more rubber trapped or caged in the lignin-F51 network with the increase of F51, and the trapped rubber would be at least partially 'dead', behaving like filler. As a consequence, the shear modulus of NBR/50lignin/F51 composites are considerably increased. When the strain reaches a high amplitude, there will be deformation-induced changes in the microstructure and the trapped rubber will be 'free', and the G' of all compounds drop to almost the same low value. The RPA results indicate that the formation of the lignin-F51 networks happens in the vulcanization process instead of mixing process, and the lignin-F51 networks have a significant reinforcement towards NBR.

TGA Analysis Results

The thermal decomposition expressed in terms of weight loss as a function of the temperature for the NBR/50lignin/F51 with different F51 loading is represented in Figure 6 and Table I. Table I shows the thermal degradation characteristics of the composites. The thermal degradation behavior of all composites with one main mass loss step is similar. We can image that lignin-epoxy networks are completely covered by the NBR molecules and the compatibility between them is very good. It can also be seen from Table I that F51 has practically no effect on the 50% weight loss temperature of all the samples. However, a

Table I. Thermal Degradation Characteristics of the Rubber Composites^a

| Samples | T _{5%} (°C) | T _{10%} (°C) | T _{50%} (°C) | Residue (%) |
|--------------------|-------------------------|--------------------------|--------------------------|----------------|
| NBR/50lignin | 251.1 | 327.2 | 439.1 | 17.6 |
| NBR/50lignin/5F51 | 252.4 | 331.0 | 440.4 | 19.3 |
| NBR/50lignin/10F51 | 257.9 | 335.8 | 442.0 | 19.7 |
| NBR/50lignin/15F51 | 262.2 | 339.2 | 441.2 | 19.3 |
| NBR/50lignin/20F51 | 267.8 | 340.0 | 439.5 | 19.1 |

^aT_{5%}- temperature corresponds to the 5% weight loss. T_{10%}- temperature corresponds to the 10% weight loss. T_{50%}- temperature corresponds to the 50% weight loss.

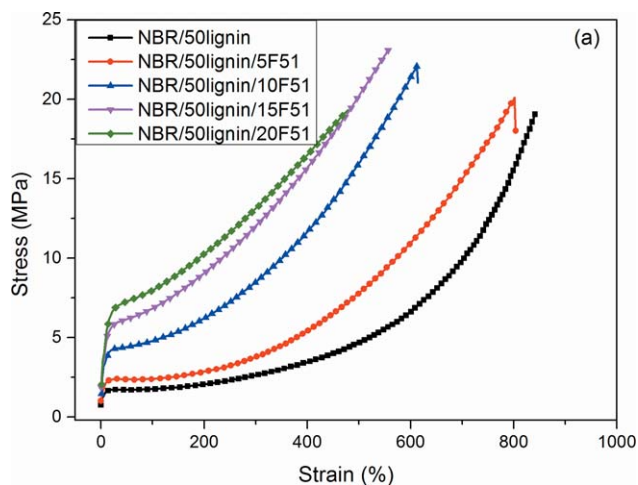


Figure 7. Typical tensile stress-strain curves for NBR/50lignin/F51. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

notable shift of 5% and 10% weight loss to higher temperature can be observed with the increasing loading of F51. For instance, the T_{5%} and T_{10%} of NBR/50lignin/20F51 is 267.8°C and 340.0°C, which are about 16°C and 13°C higher than those of NBR/50lignin. Indicating the lignin-F51 networks can improve initial thermal stability of the rubber composites. On the one hand, the presence of well-dispersed lignin-F51 networks can hinder the permeability of volatile decomposed products out of the composites in comparison with the NBR/50lignin. That is to say, the byproducts and heat of decomposition will be difficult to penetrate into the composites in this case, and the lignin-F51 networks delay in mass transport and remarkably increase thermal stability of the composites. On the other hand, the thermal stability of the crosslinked novolac epoxy resin is pretty good,²⁹ that is to say, the incorporation of heat-resistant novolac epoxy resin can effectively enhance the thermal stability of the rubber composites.

MECHANICAL PROPERTIES

Considering the polar nature of lignin and epoxy resin, the polar lignin-epoxy resin networks should have an excellent compatibility and reinforcing ability towards NBR. As shown in Figure 7 and Table II, the mechanical properties of the NBR/50lignin/F51 are compared with those of the NBR/50lignin. Surprisingly, a steady increase in the tear strength is observed for NBR/50lignin/F51 composites. The homo-dispersion of lignin-F51 networks can be in favor of avoiding the stress concentration of the cracks and dissipating energy during the tearing process. Simultaneously, the rigid lignin-F51 networks with high modulus can also prevent the expansion of the crack, leading to a very efficient load transfer from the matrix to lignin-F51 networks. As to the tensile behavior, the composites behave like rigid plastics after the addition of F51, exhibiting definite yielding. Such yielding behavior is more apparent with higher F51 content, this further demonstrates the existence of rigid lignin-F51 networks. The tensile strength and modulus at 100% and 300% of NBR/50lignin/F51 increased dramatically with the

Table II. Mechanical Properties of the Composites (The Standard Error is Presented in Brackets)

| Samples | Tensile strength (MPa) | 100% Modulus (MPa) | 300% Modulus (MPa) | Elongation (%) | Hardness (shore A) | Tear strength (kN/m) |
|--------------------|------------------------|--------------------|--------------------|----------------|--------------------|----------------------|
| NBR/50lignin | 19.8 (1.1) | 1.8 (0.2) | 2.7 (0.2) | 835 (47) | 58 | 39.8 (2.6) |
| NBR/50lignin/5F51 | 19.9 (0.9) | 2.4 (0.1) | 4 (0.3) | 791 (32) | 73 | 46.3 (3.1) |
| NBR/50lignin/10F51 | 22.3 (1.5) | 4.9 (0.3) | 8.4 (0.2) | 628 (37) | 79 | 58.1 (2.9) |
| NBR/50lignin/15F51 | 22.9 (1.4) | 6.9 (0.2) | 12.4 (0.5) | 551 (42) | 83 | 72.4 (4) |
| NBR/50lignin/20F51 | 20.8 (2.1) | 8.2 (0.4) | 13.3 (0.4) | 460 (36) | 87 | 84.5 (4.7) |

increase of F51 content. It is definitely deduced that the main reason for the reinforcement in this case is the formation of rigid lignin-F51 networks into NBR matrix. With the increase of F51 content, more epoxy groups react with the surface hydroxyl groups of lignin and consequently more covalent bonds are formed, leading to the increase of mechanical performance, and the reinforcement is also possible associated with excellent compatibility between soft NBR chains networks and rigid lignin-F51 networks.

The Crosslinking Density, Interaction between Rubber and Filler

The apparent cross-link density refer to the volume fraction of rubber (V_r) in the swollen vulcanizates, many researchers^{25,30} use the V_r to indicate the crosslink density because V_r has a direct relationship with the crosslink density. In particular, the higher the value of V_r , the higher the reinforcing ability of the filler.³¹ Thus we can infer that the reinforcing ability of lignin-F51 networks is promoted when the lignin-F51 networks become stronger with the increase of F51 in the composites.

To further determine the rubber-filler interaction in rubber composites. The Park and Lorenz equation³² are used given as follows:

$$\frac{Q_f}{Q_g} = ae^{-z} + b$$

where z is the ratio by weight of the filler to the rubber hydrocarbon in the vulcanizates; and a and b are the constants. Q is the amount of solvent absorbed by 1 g of rubber and subscripts f and g refer to filled and gum vulcanizates. (Swelling was done for 72 h at room temperature in toluene.)

Table III. Crosslinking Density of Rubber Composites^a

| Samples | Swelling | | XLDS | | | |
|--------------------|----------|-----------|--|-------------|-----------|------------------------|
| | V_r | Q_f/Q_g | Crosslinking density (10^{-5} mol/cm ³) | Mc (Kg/mol) | A(Mc) (%) | A(T ₂) (%) |
| NBR/50lignin | 0.26 | 0.97 | 10.15 | 10.94 | 52.33 | 46.27 |
| NBR/50lignin/5F51 | 0.29 | 0.86 | 10.72 | 10.35 | 56.56 | 39.48 |
| NBR/50lignin/10F51 | 0.32 | 0.73 | 10.79 | 10.29 | 58.61 | 38.69 |
| NBR/50lignin/15F51 | 0.36 | 0.63 | 11.24 | 9.88 | 61.06 | 37.53 |
| NBR/50lignin/20F51 | 0.38 | 0.58 | 11.76 | 9.44 | 63.28 | 35.86 |

^a V_r : the apparent cross-link density refer to the volume fraction of rubber in the swollen vulcanizates; Q_f/Q_g is the ratio of solvent absorbed by filled and gum vulcanizates. Mc: the average molecular weight between two crosslinking point; A(Mc): the motion of inter crosslink chain; A(T₂): the motion of dangling chain ends and free chain.

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times \alpha}$$

where α is the mass fraction of the rubber in the composites. As show in Table III. The value of Q_f/Q_g is decreasing with increase of F51, and this is attributed to the formation of lignin-F51 networks which can hinder the rubber matrix from swelling. Besides, to some extent the formation of lignin-F51 networks makes the rubber composite compact, which means that there were less empty spaces or voids in the matrix, and the diffusion of solvent molecules would be hindered, thus less solvent get absorbed and the Q_f/Q_g values would decrease. Since the lower Q_f/Q_g values mean a higher extent of the interaction between the filler and the rubber matrix.³³ We can conclude that interaction between the lignin-F51 networks and the rubber matrix become stronger when the lignin-F5 networks become stronger.

The NMR method is relatively new method to detect the crosslink density of rubber composites, and nuclear magnetic resonance (NMR) technique can provide more comprehensive information about rubber work structure, which also has a short test time, less errors, and good repeatability results. The network structure characterization of vulcanizate with Magnetic Resonance Crosslink Density Measurements has been successfully tested and described in full detail by Kuhn *et al.*³⁴⁻³⁶ The calculation of Mc (average molecular weight between crosslinks) is also described in the references.^{37,38} Mc decreases with the increase of the XLD (crosslink density measured through NMR technique).³⁹ The measurement of crosslink density by NMR is based upon the analysis of the shape and time constant of the magnetization decay of the hydrocarbon protons as obtained by spin-echo measurement,⁴⁰ and the

Table IV. Oil Resistance of Rubber Composites

| Samples | Change of the properties after immersion of oil (100%) | | | | | |
|--------------------|--|--------------------|------------------|--------------|--------------|---------------------|
| | Volume swelling ratio | Massswelling ratio | Tensile strength | 100% Modulus | 300% Modulus | Elongation at break |
| NBR/50lignin | +18.2 | +14.4 | -51.2 | -14.7 | -0.4 | -34.8 |
| NBR/50lignin/5F51 | +16.8 | +13.6 | -42.4 | -8.8 | -1 | -30.6 |
| NBR/50lignin/10F51 | +14.6 | +12.8 | -38.2 | -3 | +6.3 | -29.9 |
| NBR/50lignin/15F51 | +12.2 | +11 | -26.1 | +2.5 | +8.4 | -24.1 |
| NBR/50lignin/20F51 | +10.9 | +9.2 | -19.2 | +1.2 | +8.6 | -19.5 |

parameters of NMR results reflected the comprehensive and integrated information of NBR/50lignin/F51 composites. As shown in Table III, the increasing of the cross density is caused by the cross-link reaction between F51 and lignin, the formation of lignin-F51 networks can bring on more crosslinking points. As mentioned above, the interaction between the rubber networks and lignin-F51 networks would be enhanced when the lignin-F51 become stronger with the increase of F51, and this would restrain the mobility of the molecule chain, thus the $A(T_2)$, which represents the percentage of high-mobile fractions, is reduced, while $A(M_c)$, which represents percentage of crosslinking fractions, is raised up.

Oil Resistance Analysis Results

As is well known, oil resistance property is supposed to be primary concern of the NBR composites. The vulcanized compos-

ite does not dissolve in the oil but only swells due to the effect of cross-linking. The results of the swelling study are shown in Table IV.

The swelling ratio is decreasing with the increase of F51. The tensile strength of all compounds decreases and the magnitude of reduction in tensile strength is smaller with the loading of F51. The Change of the properties after immersion of oil as an indicator for oil resistance reveal that NBR/50lignin/20F51 yields the highest relative tensile strength and thus the greatest oil resistance. It should be noted that the 300% modulus of the composites increase after the oil immersion, this scenario can be attributed to the formation of extra crosslinks during the oil immersion test.⁴¹ It is obvious that NBR/50lignin/F51 composites have a better anti-swelling property compared with

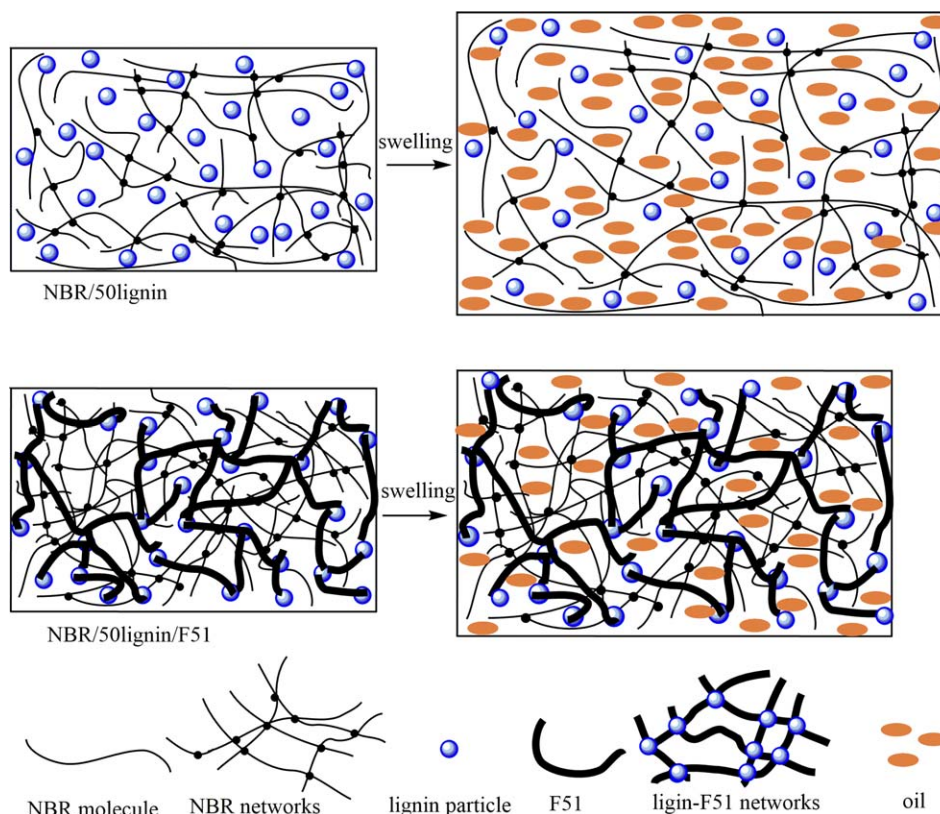


Figure 8. Schematic of NBR/50lignin and NBR/50lignin/F51 before and after oil immersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

NBR/50lignin, and the anti-swelling property of NBR/50lignin/F51 composites increase with the loading of F51. As we know, there are two main factors responsible for the result of oil resistance in filled blends, crosslink density, and phase morphology.⁴² On the one hand, it is logical that the vulcanizates has been converted to less penetrable materials by the oil if it has a higher crosslink density. That is to say, as shown in Figure 8.

The samples with a stronger well-dispersed lignin-F51 network has the more compact complex structure while the penetrating power of the solvent remains constant. And the oil-resistance results are consistent with the results of the crosslinking density. On the other hand, the formation of lignin-F51 networks also makes the penetrant inevitably travel along a tortuous path and decreases the relative permeability in the composites, which improve the oil resistance property.

CONCLUSIONS

A typical lignin-F51 interpenetrating polymer network structure was formed in the polar NBR matrix during the curing process rather than mixing process. Torque study, SEM, and RPA analysis demonstrate the existence of lignin-F51 networks. It was found that NBR/lignin/F51 composites exhibit higher tensile strength, tensile modulus (M100 M300), thermal stability, and oil-resistance than NBR/lignin composites. It is obvious that the formation of rigid lignin-F51 networks were responsible for the observed reinforcement and morphological characteristics of the hybrids. Further work will focus on the studies of the degree of epoxy conversion and cross-linking kinetics of the interpenetrating polymer network (IPN).

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