# *In situ* dispersion and compatibilization of lignin/epoxidized natural rubber composites: reactivity, morphology and property

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ABSTRACT: Lignin, a naturally occurring polymer, was viewed as a potential substitute of carbon black for reinforcing rubber materials. However, it shows no reinforcing effect if directly mixed with rubber. In this study, lignin was *in situ* dispersed at submicrometer size and highly compatible with epoxidized natural rubber (ENR) by using a high-temperature dynamic heat treatment (HTDHT). Rheology analysis indicated that the ring opening reaction between lignin and ENR occurred at 160°C or above, which was further confirmed by infrared spectroscopy. Due to the consumption of acidic groups of lignin by ENR, the retardant vulcanization effect of lignin was weakened. Morphology observation and dynamic mechanical analysis demonstrated the perfect lignin dispersion and the strong interactions between lignin and ENR. The mechanical properties of the lignin/ENR composites were significantly improved by using HTDHT. Compared to the directly mixed rubber composites, the tensile strength and tear strength of the heat treated rubber composites filled with 40 phr lignin were increased by 114% and 23%, respectively. Especially, the 300% modulus of the heat treated rubber composite was increased by ca. 400%. X-ray diffraction results indicated that the reinforcement of the composites originated from the presence of lignin rather than the strain-induced crystallization of ENR. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42044.

## INTRODUCTION

Lignin, a primary constituent (15–35 wt %) of all higher plants, is considered to be the most abundant renewable aromatic biopolymer in nature. It mainly consists of phenyl propane units interconnected by various C—C or C—O—C bonds.[1] Currently, about 50 million tons of lignin per year is separated from lignocellulosic materials in pulp and paper industry. Most of them are used as fuel to recover energy. Only a small proportion is utilized for value added products.[2] In the near future, a larger amount of lignin, about 225 million tons, will be produced from the emerging bioethanol industry.[3] In this context, the exploitation of the value-added applications based on lignin is becoming significantly important.

The incorporation of lignin into polymeric materials has been substantiated to be an effective and promising way to fully realize its potential. Recently, the applications of lignin in polymeric materials have been well reviewed by some researchers.[4,5] One of the most important applications is the use of lignin in rubber based materials. As the first study on the lignin based rubber composites is reported about 70 years ago,[6] lignin has been viewed as a potential candidate for the replacement of the conventional rubber filler carbon black, due to its natural abundance, low density and cost competiveness. Until now, extensive researches have been focused on improving the reinforcing effect of lignin on rubber based materials.[7–9] Actually, previous studies have illustrated that lignin can reach the reinforcing level of carbon black or silica by the coprecipitation of rubber latex and alkaline solutions of lignin.[10] However, the coprecipitation method must employ acid as flocculant, which results in the irreversible aggregation of lignin particles and thus deteriorate the performance of rubber.[11] Furthermore, the flocculation and filtration of lignin/rubber coprecipitates are extremely slow.[12] This also seriously limits the development of lignin based rubber composites. Hence, direct mixing of lignin and rubber is highly pursued because of its industrial availability. Unfortunately, lignin shows little or no reinforcing effect if directly mixed with rubber.[13] It is believed to be the following two factors in causing this phenomenon: large particle size of lignin and the lack of strong interfacial interactions between lignin and rubber matrix.

To improve the reinforcing efficiency of lignin, some researchers adopted surface chemical modifications[14,15] or hybrid fillers[16–19] to address the issue of the dispersion and compatibility of lignin

in rubber matrix. For example, Frigerio et al. reported that lignin treated with hexamethylenetetramine possessed a higher reinforcing ability than unmodified one.[15] Bahl et al. also demonstrated that lignin modified with cyclohexylamine showed a better compatibility with nonpolar styrene butadiene rubber. This led the rubber composites to the increase in tensile strength, modulus and rupture elongation.[14] However, the surface modifications just provided the external surface of lignin agglomerates a better affinity toward rubber matrix. The interfacial adhesion between those surface modified lignins and rubber is not strong enough to promote the dispersion of lignin at a smaller size under conventional compounding conditions. So the reinforcing effect of lignin on rubber composites by surface chemical modifications is very finite. Lignin combined with montmorillonite,[17,18,20] layered double hydroxides[16] and carbon black[19] as hybrid fillers in rubber composites has shown more advantages in the preparation of lignin/rubber composites with higher tensile strength, thermal stability and low rolling resistance. This is because lignin as a component of hybrid fillers can suppress the formation of filler network and in return other fillers also facilitate the dispersion of lignin in rubber matrix. Nevertheless, the interfacial interactions between lignin and rubber matrix is still poor in the hybrid fillers/rubber composites. In addition, the preparation of these lignin based hybrid fillers is time consuming and involves the use of water or organic solvents, which are unfavorable for industrial production. So far, simple and effective approaches to prepare lignin/rubber composites with good dispersion quality and interfacial interactions are still missing.

Epoxidized natural rubber (ENR) is one modified natural rubber with a random distribution of epoxy groups along with the polymer backbone.[21] These epoxy groups in ENR are readily reacted with nucleophilic reagents,[22–25] which impart ENR the miscibility with other polymer[26] or active fillers[27] by reactive compatibilization. In our previous study, self-crosslinked and self-reinforced lignin/ENR composites were prepared via the ring opening reaction between the hydroxyl groups of lignin and epoxy groups of ENR.[28] In the self-crosslinked lignin/ENR system, lignin acted as not only reinforcing filler, but also crosslinker to vulcanize ENR. Most importantly, lignin was well dispersed and exhibited a great compatibility with ENR by a high-temperature dynamic heat treatment (HTDHT) procedure, also referred to as reactive compounding. Thus, it is possible to maximize the reinforcing efficiency of lignin by this *in situ* dispersion and compatibilization strategy when a conventional sulfur-vulcanized system is applied. To prepare the lignin/ENR composites with optimum performance, the reactivity between lignin and ENR must be sufficiently considered. Hence, in present work, we have made an attempt to investigate the effect of the reactive compounding on the mechanical properties, dynamic mechanical properties, vulcanization behavior and morphology of the lignin/ENR composites vulcanized by sulfur.

## EXPERIMENTAL

### Materials

ENR, containing 25 mol % epoxy groups, was purchased from the Tropical Crops Research Center of Zhanjiang (China).

Lignin (industrial sulfate lignin), with an average molecular weight of 3801 and polydispersity index of 2.15, was purchased from Tralin Paper Co., Ltd. (Shandong, China). All the rubber ingredients such as zinc oxide (ZnO), stearic acid (SA), N-tert-butyl-2-benzothiazole sulfonamide (CBS), 2, 2′-dibenzothiazoledisulfde (DM) and sulfur (S) were industrial grade and used as received.

### Sample Preparation

Before use, lignin was purified as previously described.[11] Purified lignin (0, 10, 20, 30, or 40 phr) was mixed with 100 phr ENR on an open two-roll mill, where phr represents parts per hundred rubber. Subsequently, the rubber compounds underwent a HTDHT procedure, that is, sealing in a Haake Polylab mixer with a rotate speed of 60 rpm at a certain temperature for 30 min. After that, the resulting rubber mixtures were compounded with rubber ingredients (5 phr ZnO, 2 phr SA, 1.5 phr CBS, 0.5 phr DM, and 1.5 phr S) on the open two-roll mill and then subjected to compression at $143 \pm 1°C$ for optimum vulcanization time, which was determined by the U-CAN UR-2030 vulcameter. In addition, the lignin directly filled ENR composites with the same lignin content were also prepared, that is, using the same compounding procedure as above described except the HTDHT.

### Characterization

HTDHT procedure was performed on a Haake torque rheometer (HAAKE400P, Germany). The corresponding torque curves were recorded. The reaction between lignin and ENR was identified by attenuated total internal reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) on Bruker Vertex 70 FTIR spectrometer at a spectral resolution of 2 $cm^{-1}$ and 32 scans from 600 to 4000 $cm^{-1}$. The morphology of lignin and lignin/ENR rubber composites was observed by field emission scanning electronic microscopy (FESEM) on a Nova NanoSEM 430 instrument (FEI, Netherlands) at an acceleration voltage of 10 kV. The fracture surfaces of rubber samples for FESEM were obtained by the splitting of bulk samples, which was quenched in liquid nitrogen. Before the observation, all samples were plated with a thin layer of gold. The vulcanization behaviors of the rubber compounds were measured at 143°C on U-CAN UR-2030 vulcameter. After the vulcanization of rubber composites in a standard mold, the tensile and tear tests of the vulcanizates were performed according to ISO 37–2005 and ISO 34–2004, respectively. The crosslinking density measurements of the rubber composites were carried out on a magnetism resonance crosslinking density spectrometer (IIC Innovative Imaging Corporation, Germany) with a magnetic field intensity of 15 MHz at 60°C. Dynamic mechanical analysis (DMA) spectra of the rubber composites were obtained by using a DMA 242D dynamic mechanical analyzer (NETZSCH Company, Germany). The specimens were measured in tensile mode at a constant frequency of 1 Hz, a strain of 0.5%, and a temperature range from −100 to 80°C at a heating rate of 3°C/min. XRD experiments were conducted at ambient temperature on a Rigaku Dmax/III diffractometer (Rigaku Corporation, Tokyo, Japan) using a Cu Kα radiation. The generator was operated at 40 kV and 30 mA. The samples under stretch state in a homemade mould were scanned from 5° to 30°, with a step length of 0.04°.
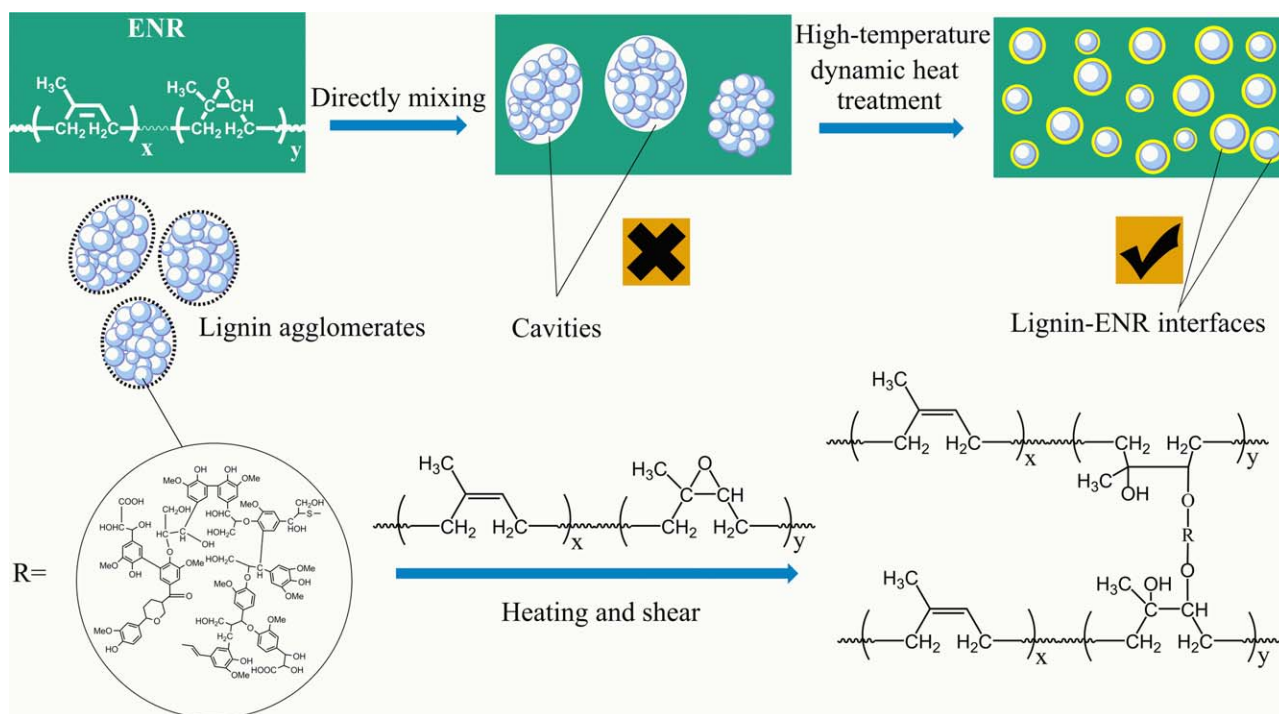
**Figure 1.** Schematic illustration for the preparation of lignin/ENR composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## RESULTS AND DISCUSSIONS

Lignin is highly branched polyphenolic biopolymer. When it is recovered from solutions, lignin macromolecules entangle together and form micrometer sized secondary particles.[29] Once formed, lignin agglomerates cannot be disaggregated into primary particles and dispersed in rubber matrix using a regular compounding process, attributed to the strong intermolecular and intramolecular hydrogen bonding[30] and $\pi$-$\pi$ interactions[31] in lignin molecules as well as the internal molecule entanglement. However, as a thermoplastic material, lignin can be soften and readily crushed into smaller particles under heating and shear force. In addition, by using ENR as rubber matrix, the hydroxyl groups of lignin can react with the epoxy groups of ENR, which will further facilitate the dispersion of lignin and improve the compatibility of lignin and rubber. According to this proposal, we prepared the lignin/ENR composites with perfect lignin dispersion and interfacial compatibility by using the method described in Figure 1, and discussed the effect of the preparation process on the properties of the lignin/ENR composites.

### Reactivity of Lignin and ENR

The torque curves obtained from Haake torque rheometer reflected the dependence of the viscosity of rubber compounds on temperature and time, which could indirectly identify the reaction between lignin and ENR. As shown in Figure 2(a), the torque values of the rubber compounds consistently reduced with increasing heat treat temperature at the initial stage of mixing (before 10 min). This should be due to the decreased viscosity of the systems caused by heating. In addition, the balance torques of those rubber compounds were found to remain stable at 80°C, slightly decrease at 100–140°C and increase at 160°C and 180°C. The difference in the balance torque at the final stage of mixing was attributed to the competition of the ENR decomposition caused by thermal oxidation[32] and the crosslinking of ENR and lignin caused by the ring opening reaction between them. The former leaded to the decrease in the viscosity of the rubber compounds while the latter increased the viscosity. At low temperature ($<100$°C), there were no chain scission of ENR macromolecules and no reaction in the rubber compounds, thereby the torque was constant. As temperature increased to 100–140°C, the oxidation decomposition of ENR got more serious[32] and governed the decrease of the balance torque, while the crosslinking reaction between lignin and ENR was too weak to offset the decomposition of ENR. Beyond 140°C, the balance torque of the rubber compounds rose, which sufficiently verified the occurrence of the reaction between lignin and ENR. It was evident that the increment of the balance torque was more intensive at 180°C than that at 160°C, indicating the higher reaction degree with increasing heat treat temperature. Hence, lignin/ENR composites should be prepared at 180°C to obtain good dispersion quality and compatibility within a shorter time.

Figure 2(b) shows the effect of lignin content on the torque of rubber compounds. It could be seen that the torque of pristine ENR continuously decreased with increasing time, whereas the torque of the lignin filled ENR compounds linearly increased. This further verified the ring opening reaction in lignin/ENR systems. Moreover, the torque increment of these lignin/ENR compounds seemed to be more prominent as increasing lignin
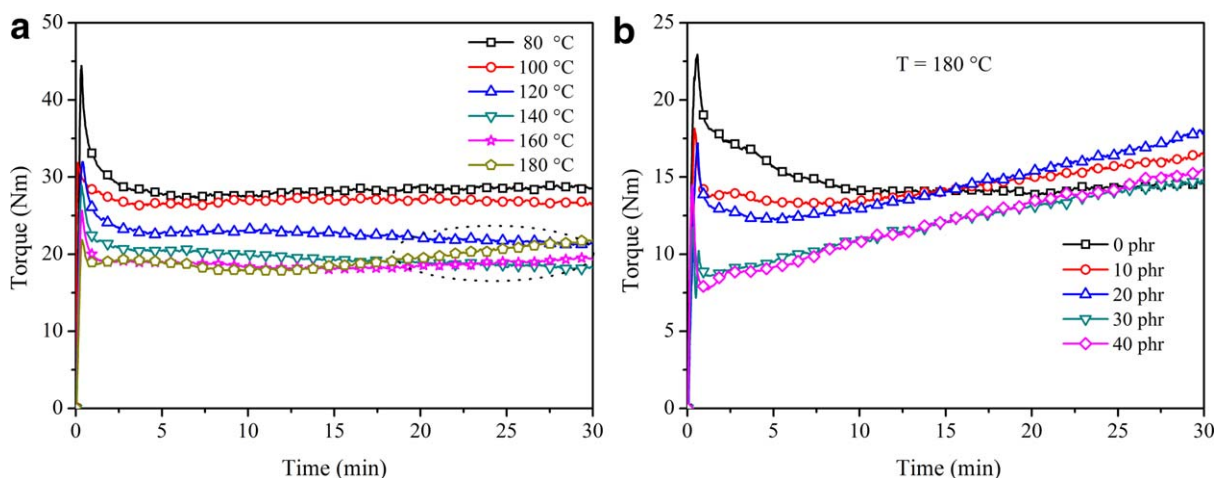
**Figure 2.** The Haake torque curves of rubber/ENR compounds (a) at different heat treatment temperature with10 phr lignin and (b) with different lignin content at 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

content. This could be due to the fact that increasing lignin content increased the collision probability between ENR and lignin, thereby resulting in a higher reaction degree within the same time.

The reactivity between lignin and ENR during HTDHT process was evaluated by ATR-FTIR. Meanwhile, to identify whether the reaction existed in conventional mixing process, the ATR-FTIR spectra of the directly mixed rubber composites with different
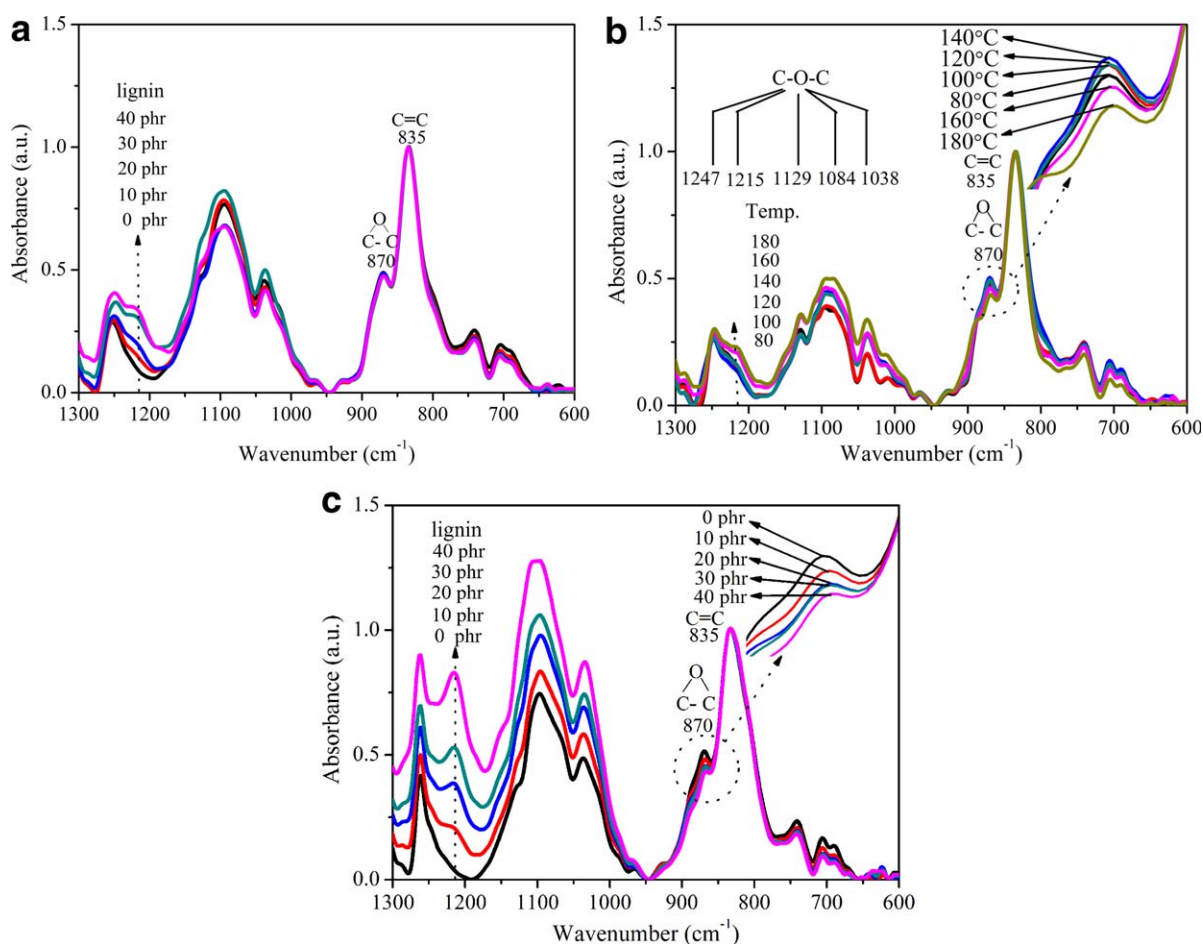


**Figure 3.** The ATR-FTIR spectra (1300–600 cm$^{-1}$ region) of lignin/ENR compounds (a) prepared by directly mixing, (b) with 10 phr lignin and prepared at different heat treatment temperature and (c) prepared by HTDHT at 180°C. Note: the spectra were normalized at 835 cm$^{-1}$ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lignin content were also taken. All ATR-FTIR spectra were normalized to the 835 cm$^{-1}$ band, the C=C vibrations of isoprene units in ENR,[33] to analysis the ring opening extent of epoxy groups in ENR.

Figure 3(a) shows the ATR-FTIR spectra of the directly mixed rubber composites. It was apparent that the characteristic bands of lignin at 1215 cm$^{-1}$ (aromatic ether)[34] consistently increased, which were proportional to the lignin content. However, the intensity of the band at 870 cm$^{-1}$, assigned to the epoxy groups of ENR, was unchanged. This demonstrated that lignin could not react with the epoxy groups of ENR during conventional mixing process. In the case of the heat treated rubber compounds, the dependence of the ring opening reaction on heat treatment temperature is shown in Figure 3(b). It could be seen that the band related to epoxy groups in the rubber compounds prepared at 100°C, 120°C, and 140°C was more intensive than that of the rubber compound prepared at 80°C. This was because the ratio of the double bonds to the epoxy groups in ENR was constant, but the double bonds in ENR were oxidized into carboxyl form at those higher temperatures, which resulted in the relative increase in the absorption intensity of the epoxy groups after the normalization of the C=C band. We supposed that lignin could not react with ENR. Thus, the absorption intensity of the epoxy groups would be continually increased at higher heat treatment temperatures when the C=C band of ENR was normalized. However, the absorption of epoxy groups in those rubber compounds prepared at 160°C and 180°C was less than that of the rubber compound prepared at 80°C. It was a solid evidence of the occurrence of ring opening reaction during HTDHT process, which was well consistent with the results obtained from Figure 2(a).The effect of lignin content on the ring opening reaction of ENR during HTDHT process was also

investigated by ATIR-FITR. As shown in Figure 3(c), the absorption of epoxy groups significantly decreased with increasing lignin content. This was indicative of the increase in the ring opening degree of ENR in those rubber compounds prepared by HTDHT, which was also consistent with the torque increment shown in Figure 2(b). Furthermore, as compared to that of directly mixed rubber compounds, the characteristic bands of the aromatic and aliphatic ether[34] (1247 cm$^{-1}$, 1215 cm$^{-1}$, 1129 cm$^{-1}$, 1084 cm$^{-1}$, and 1038 cm$^{-1}$) in the lignin/rubber compounds prepared by HTDHT were more intensive than that of directly mixed rubber compounds at the same lignin loadings. This mainly originated from the newly formed C—O—C bonds between lignin and ENR and the relatively less C=C content of ENR because of its oxidization in the heat treated rubber compounds. From the above, it could be confirmed that lignin reacted with ENR at 160°C or above via ring opening reaction during HTDHT process, which improved the compatibility between lignin and ENR.

## Morphology Study

The dispersion of lignin in the rubber composites was investigated by FESEM. Figure 4 shows the effect of heat treat temperature on the dispersion of lignin. As shown in Figure 4, at the heat treatment temperature of 80°C, the profile of lignin could be clearly identified, suggesting poor interfacial interactions between lignin and ENR matrix. These lignin particles were founded to be irregular and owned diameters ranging from several hundred nanometers to several micrometers. When the heat treatment temperature increased, large lignin agglomerates gradually disaggregated into smaller particles. Moreover, lots of lignin particles were embedded into ENR matrix and wrapped by ENR, showing a faint interface. However, some micrometer sized lignin particles were still preserved in those rubber
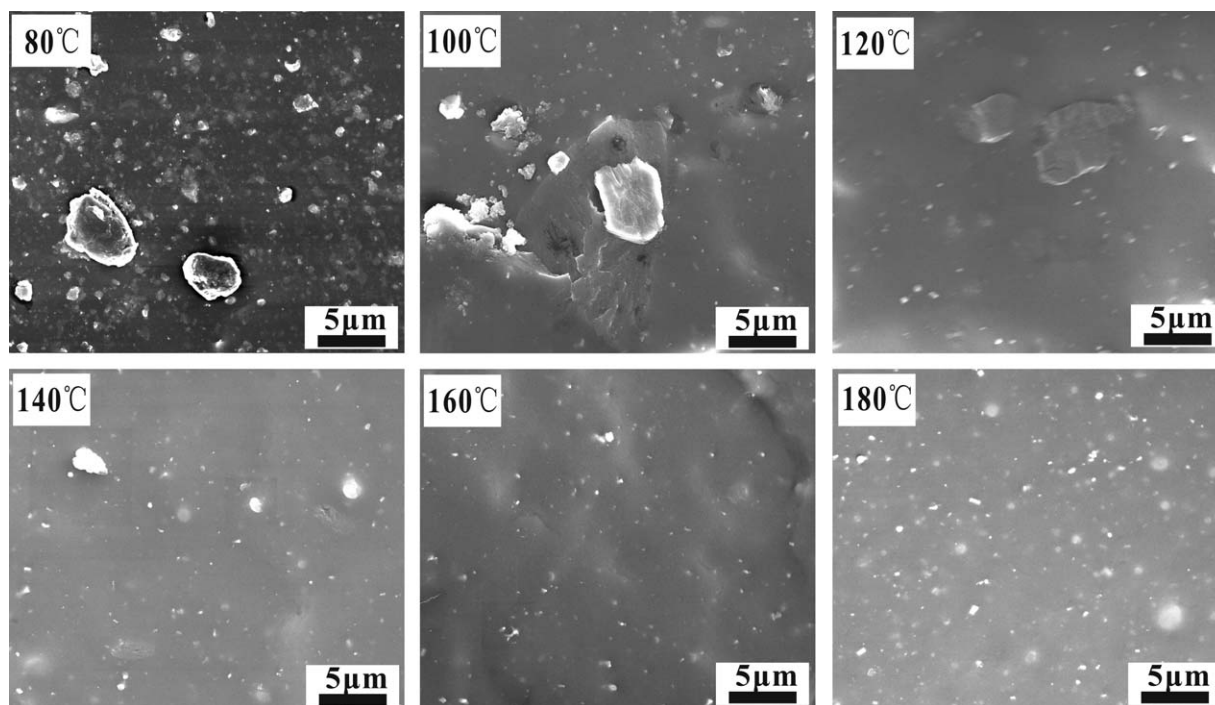


**Figure 4.** FESEM photos of the lignin/ENR composites prepared at different heat treatment temperatures.
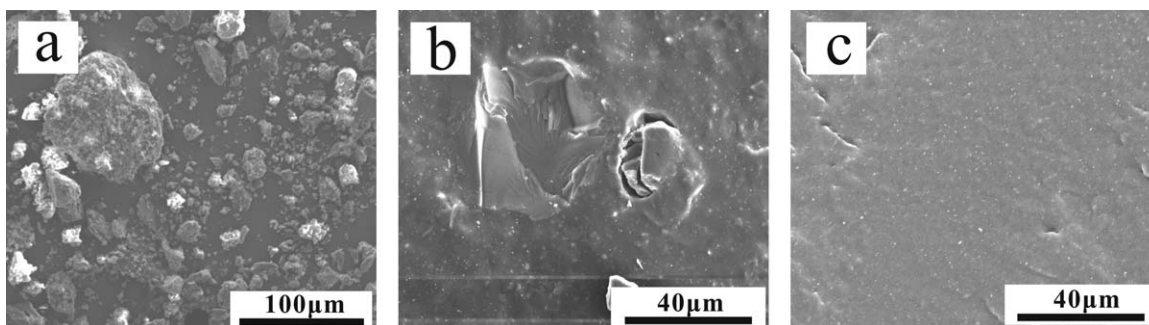
**Figure 5.** FESEM photos of (a) lignin powder, (b) the directly mixed and (c) heat treated lignin/ENR composite with 40 phr lignin.

composites, due to the insufficient plasticization of lignin and the lack of strong chemical reaction. At the heat treatment temperatures of 160°C and 180°C, most of lignin was reduced to submicrometer size and well dispersed throughout ENR matrix. The interfacial phase between lignin and ENR was very blurry, indicating an excellent compatibility between them. It should be mentioned that the bright dots in all FESEM photos indicated the rubber ingredients such as zinc oxide and stearic acid.[35] All the results from Figure 4 sufficiently demonstrated that lignin was *in situ* dispersed during HTDHT process and highly compatible with ENR matrix via ring opening reaction.

From the comparison on the morphology of dry lignin powder, directly mixed and heat treated rubber composites shown in Figure 5, we could further elucidate the advantage of HTDHT process on the preparation of lignin/ENR composites with perfect lignin dispersion. It could be clearly seen that purified lignin in dry state was irregular agglomerates with polydisperse size ranging from several micrometers to several hundred micrometers [Figure 5(a)]. Generally, filler size is a prerequisite for preparing high performance rubber composites. Such large lignin particles were believed to have no reinforcing capacity for any rubber materials. As observed from Figure 5(b), lignin still retained its shape and size in rubber matrix when directly mixed with ENR, indicating that lignin could not be dispersed into rubber matrix during directly mixing process. Furthermore, the cavity around the lignin agglomerates in the directly mixed rubber composites was clearly observed, showing poor interfacial adhesion and immiscibility between lignin and ENR. As a consequence, when external stress was applied in the rubber composites, lignin agglomerates could not bear the external stress, which deteriorated the performance of rubber composites. However, lignin was adequately dispersed at submicrometer size in the heat treated rubber composites and highly compatible with ENR matrix [Figure 5(c)]. There were strong interfacial interactions between lignin and ENR in heat treated rubber composites, which could sufficiently transfer external stress from ENR matrix to lignin particles. In addition, the smaller lignin particles could bear a higher stress, which was the origination of the reinforcing effect of lignin on rubber materials. So, it could be predicted that the rubber composites prepared by HTDHT procedure possessed a better performance compared to the directly mixed rubber composites.

## Vulcanization Behavior and Crosslinking Density

As we know, lignin has plenty of acidic functional groups involving carboxyl and phenolic groups, which can interact with basic rubber ingredients. Therefore, in the previously reported lignin based rubber composites, lignin presented a retardant effect on the vulcanization of rubber.[7,9,11] In this study, the effect of the mixing methods on the vulcanization behavior of lignin/ENR compounds was investigated and summarized in Figure 6. The vulcanization characteristics of the rubber composites were expressed in terms of the vulcanization time, scorch time (Tc10) and optimum curing time (Tc90), as well as the minimum and maximum torque (ML and MH, respectively). From the vulcanization parameters in Figure 6(a), in both the directly mixed and heat treated rubber compounds, Tc10 and Tc90 continuously increased with increasing lignin content. This, again, indicated the retardant effect of lignin on the vulcanization of rubber compounds. However, the retardant vulcanization effect of lignin in the heat treated rubber composites was weaker than that found in the directly mixed rubber compounds, that is, the Tc10 and Tc90 for the heat treated rubber composites were much lower than those for the directly mixed rubber compounds. This could be ascribed to the fact that a part of the acidic groups of lignin were consumed by the epoxy groups of ENR during HTDHT process, and the lignin particles were wrapped by ENR preventing the combination of lignin and rubber ingredients.

In rubber composites, ML and MH are dependent on the filler dispersion, filler-rubber network and rubber–rubber network. With the incorporation of lignin in rubber compounds, the actual amount of the rubber ingredients, which participate in the formation of the rubber–rubber network, was reduced because of the consumption of the rubber ingredients by lignin. Consequently, the ML and MH in both the directly mixed and heat treated rubber compounds were reduced as increasing lignin content [Figure 6(b)]. However, due to the crosslinking reaction between lignin and ENR during HTDHT process, the filler–rubber network in the heat treated rubber compounds was enhanced. Moreover, the better filler dispersion in the heat treated rubber compounds gave rise to an increase in the filler–filler network. Besides, the reduced combination of lignin and rubber ingredients, due to the envelopment of lignin by ENR, also contributed to the rubber–rubber network in the heat treated rubber compounds. All the improvement of the three
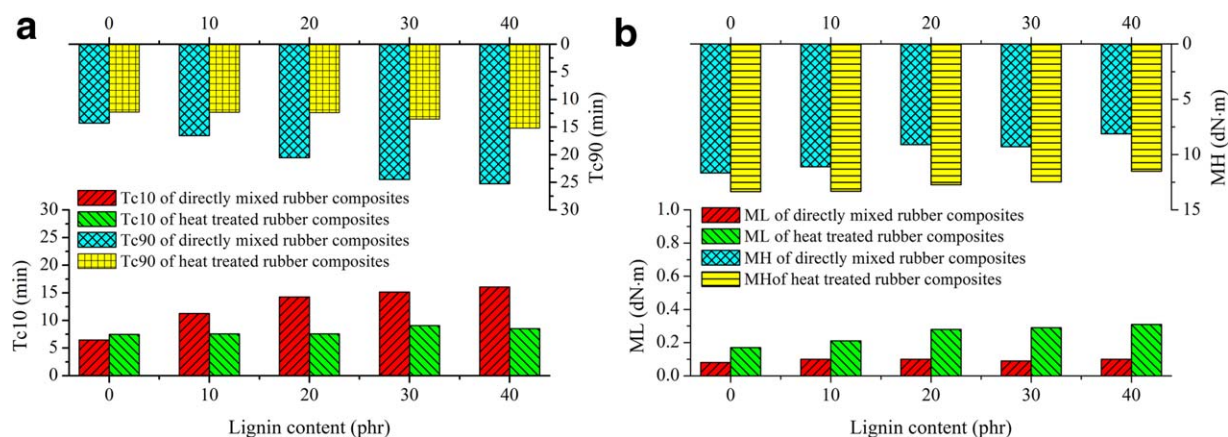
**Figure 6.** (a) Tc10 and Tc90, (b) ML and MH of the directly mixed and heat treated lignin/ENR compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

networks in the heat treated rubber compounds could partially offset the substantial decrease of the rubber–rubber network caused by lignin. Hence, the ML and MH for the heat treated rubber compounds were much bigger than that of the directly mixed rubber compounds at same lignin content.

The crosslinking density of the rubber compounds was presented in Table I, which could further identify the difference in the vulcanization network of the lignin/ENR composites. As illustrated in Table I, in both the directly mixed and heat treated lignin/ENR vulcanizates, the crosslinking density ($Vc$) was consistently decreased with increasing lignin content, indicating the destructive effect of lignin on the network structure of lignin/ENR composites. Remarkably, the heat treated rubber composites showed a higher $Vc$ than that of the directly mixed rubber composites, demonstrating a more compact crosslinking network in the heat treated rubber composites. This result was well consistent with the analysis for vulcanization behavior of the rubber composites. On the basis of the vulcanization behavior and crosslinking density of rubber composites, it could be confirmed that the HTDHT process could weaken the retardant vulcanization effect of lignin and improve the network structure of the lignin based rubber composites.

### Dynamic Mechanical Properties

Figure 7 is the temperature dependence of the storage modulus ($E'$) and loss tangent (tan $\delta$) of the heat treated lignin/ENR composites. The storage modulus can be regarded as the elastic modulus of the rubber composites and loss tangent is related to the energy dissipation as heat. As illustrated in Figure 7, the $E'$ of the rubber composites increased with increasing lignin content in the entire observed temperature range. The increase in $E'$ indicated a higher stiffness of materials, which should be

attributed to the addition of rigid lignin particles and the enhanced filler–rubber interactions. This also reflected the reinforcing nature of lignin on rubber materials. Additionally, the tan $\delta$ peaks of the rubber composites shifted to higher temperatures and the glass transition temperature ($T_g$) taken at the maximum value of the tan $\delta$ continually increased from $-50.5°C$ to $-27.0°C$ with increasing lignin content. This was attributed to the fact that the ENR molecules were covalently bonded to lignin particles during the HTDHT process, which extremely restricted the mobility of chain segments of ENR. Besides, the tan $\delta$ peak height significantly decreased from 1.76 to 1.34 with increasing lignin content. These results sufficiently demonstrated that there were the strong interfacial interactions between lignin and ENR. Such big increase in the $T_g$, 23.5°C, was unusual. As previously reported, in nanoparticles filled polymer composites, the increase in $T_g$ of the nanocomposites was generally less than 10°C.[36] Therefore, such an increment of $T_g$ in this lignin/ENR system implied the uniform dispersion of lignin and the change in the network structure of the lignin/ENR composites.

### Mechanical Properties

The mechanical properties of the lignin/ENR composites prepared by directly mixing or HTDHT, such as tensile strength, elongation at break, tear strength, hardness and tensile modulus at 100% and 300% strain as well as reinforcing index, were investigated and the results are shown in Figure 8. As shown in Figure 8(a), the tensile strength, tear strength, elongation at break of the directly mixed rubber composites substantially decreased with increasing lignin content. With the inclusion of 40 phr lignin, the tensile strength, tear strength and elongation at break for the directly mixed rubber composites were decreased by 58%, 32%, and 21%, respectively, as compared to

**Table I.** The Crosslinking Density ($Vc$, $\times 10^{-5}$ mol cm$^{-3}$) of the Directly Mixed and Heat Treated Lignin/ENR Composites

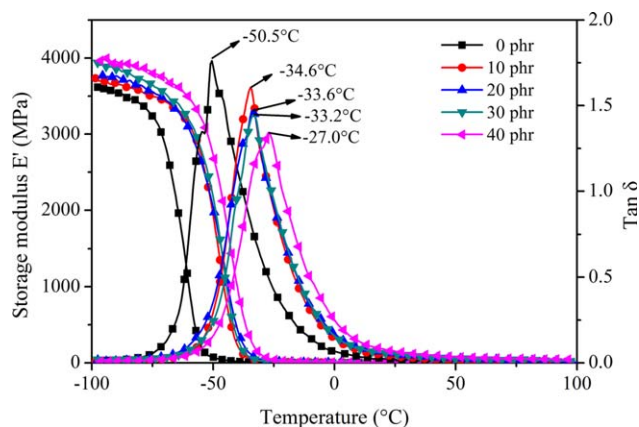| Lignin content (phr) | 0 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| Directly mixed rubber composites | 13.38 | 11.16 | 9.79 | 9.64 | 9.56 |
| Heat treated rubber composites | 13.42 | 12.82 | 12.99 | 11.56 | 11.46 |

**Figure 7.** The temperature dependence of the storage modulus (E′) and loss tangent (tan δ) of the heat treated lignin/ENR composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pristine ENR. This sufficiently indicated that lignin showed no reinforcing effect on ENR even deteriorates the performance of the rubber composites by using a conventional mixing method. However, the heat treated rubber composites showed higher tensile strength and tear strength than those of the directly mixed rubber composites at same lignin content. Especially, the tensile strength and tear strength of the heat treated rubber composites filled with 40 phr lignin were increased by 114% and 23%, respectively, as compared to the directly mixed rubber composite. Regarding elongation at break, both in the directly mixed and heat treated rubber composites, a decreased trend was observed with increasing lignin content. Even, the heated treated rubber composites showed a lower rupture elongation than that of the directly mixed rubber composites at the same lignin content. The difference in the decrease of rupture elongation for the two rubber composites was dependent the lignin dispersion status and the lignin–rubber interactions. In the directly mixed rubber composites, lots of lignin agglomerates existed in rubber matrix and the poor interfacial interactions failed to transfer external stress, which leaded the rubber composites to rupture at small deformations. However, the decrease of rupture elongation in the heat treated rubber composites was due to the covalent bonding of lignin and ENR during HTDHT process, which vastly restricted the mobility of ENR chains and resulted in the formation of more rigid network structure. Hence, the heat treated rubber composites were easily extended at smaller deformations. In addition, the hardness variation for the directly mixed and heat treated rubber composites showed an opposite trend. Generally, the addition of rigid particles in rubber materials should improve the hardness of the materials. However, a decreased hardness for the directly mixed rubber composites was observed. This was because lignin interacted with rubber ingredients, resulting in the decrease of rubber–rubber network. However, the hardness of the heat treated rubber composites was substantially increased with increasing lignin content. This was ascribed to the bigger effective volume of lignin and the stronger lignin–rubber interactions with increasing lignin content.

Some researchers considered that the reinforcing efficiency of filler on rubber materials can be measured by reinforcing index (RI), which is the ratio of the modulus at 100% strain to the modulus at 300% strain.[37,38] A high value of RI corresponds to high reinforcing effect and strong rubber–filler interaction. As observed from Figure 8(b), the 100% and 300% modulus of the directly mixed and heat treated rubber composites were increased with increasing lignin content. The increase in 100% and 300% modulus for the heat treated rubber composites were more prominent than that of the directly mixed rubber composites. Especially, the 300% modulus for the heat treated rubber composite with loading of 40 phr lignin was increased by ca. 400%, from 2.04 MPa to 10.59 MPa. The variation of RI followed the same trend as that of tensile modulus. The RI for the heat treated rubber composites was higher than that of the directly mixed rubber composites, indicating stronger lignin–rubber interactions. Overall, the maximum reinforcing efficiency of lignin could be achieved using HTDHT process.

The underlying reinforcing mechanism of lignin on ENR could be disclosed by the XRD measurement of the rubber composites
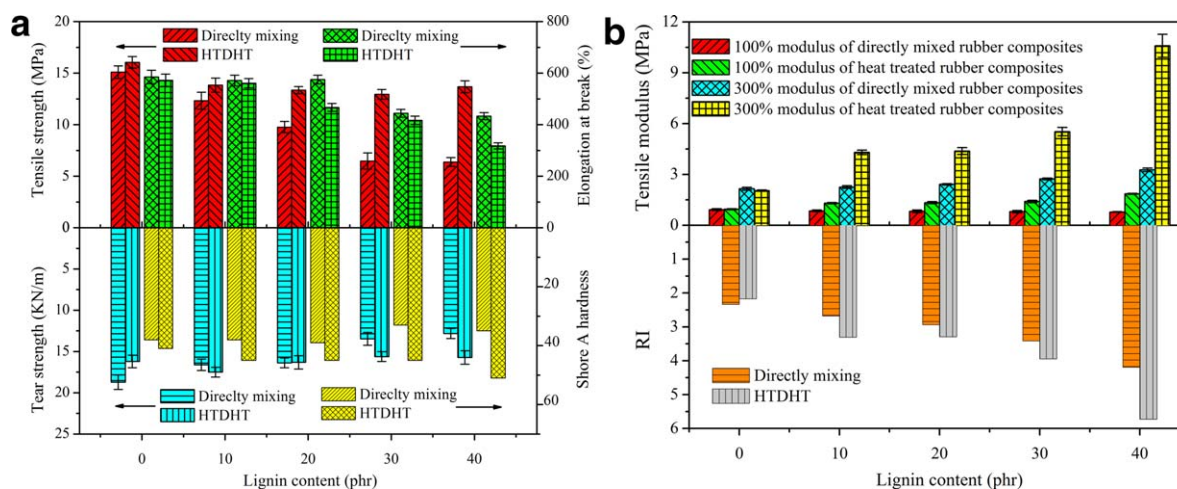


**Figure 8.** (a) Tensile strength, elongation at break, Tear strength and Shore A hardness; (b) Tensile modulus and reinforcing index (RI) of the lignin/ENR composites prepared by directly mixing or HTDHT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
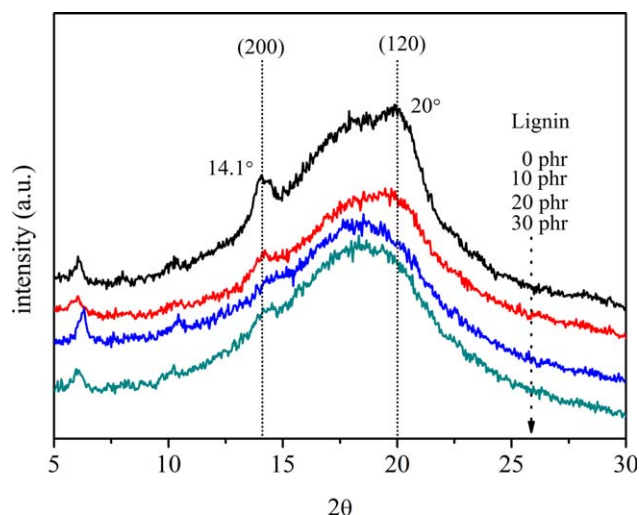
**Figure 9.** XRD curves of the lignin/ENR composites prepared by HTDHT under uniaxial extension at $\lambda = 3.5$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

under uniaxial tension, which showed the strain-induced crystallization of ENR. The crystallites of ENR could serve as additional crosslinks in the network, strain amplifiers, and to some extent as filler particles. Hence, the pristine ENR owned an excellent performance compared to other synthetic rubbers. Figure 9 shows the XRD curves of the heat treated rubber composites at extension ratio $\lambda = 3.5$. As illustrated in Figure 9, the pristine ENR exhibited two distinct reflections at $2\theta = 14.1°$ and $20°$, corresponding to the (200) and (120) plane reflections of crystallites formed by ENR macromolecules, respectively.[39] With increasing lignin content, the diffraction peaks of ENR crystallites gradually decreased until disappeared, indicating that lignin inhibited the strain-induced crystallization of ENR. The XRD curve of the rubber composite with 40 phr lignin was not shown, because the rupture elongation of the rubber composite was only 318%, less than 350%. The initial strain at which the strain-induced crystallization of ERN begins was considered to be $\lambda = 3.5$.[40,41] So there was no strain-induced crystallization in the rubber composites with 40 phr lignin. On the basis of the XRD measurements, we could deduce that the reinforcement of the rubber composites mainly originated from lignin rather than strain-induced crystallites of ENR.

## CONCLUSIONS

The lignin/ENR composites were prepared by HTDHT process. The rheological analysis of the rubber compounds indicated that lignin could react with the epoxy groups of ENR at 160 or above via ring opening reaction and the reaction extent increased with increasing lignin content. The ATR-FTIR measurements further confirmed the ring opening reaction between lignin and ENR. Morphology observation showed that lignin seriously aggregated and was immiscible with ENR matrix in the directly mixed rubber composites, whereas it could be well dispersed at submicrometer size and highly compatible with ENR matrix by using HTDHT. Due to the consumption of acidic groups of lignin by ENR during HTDHT process, the

retardant vulcanization effect of lignin was weakened. Thereby, the heat treated rubber composites possessed a higher crosslinking density compared to that of the directly mixed rubber composites. DMA results demonstrated that there were strong interactions between lignin and ENR matrix in the heat treated rubber composites. The mechanical properties of the heat treated rubber composites were significantly higher than that of the directly mixed rubber composites. XRD analysis disclosed that lignin inhibited the strain-induced crystallization of ENR. So the reinforcement of the heat treated lignin/ENR composites was dependent on lignin.

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