1. Introduction

The copolymer Styrene butadiene rubber (SBR), a general-purpose synthetic elastomer widely used in the rubber industry, is nonpolar and noncrystalline with a low gum tensile strength. Therefore, a reinforcing filler is often required in this matrix to improve the physical mechanical properties of SBR composites and reduce the material cost [1, 2]. Lignin, one of the most abundant biopolymers on earth, is a polyphenolic macromolecule which is comprised of 9-carbon phenol propane units (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) linked together by different types of bonds. Large amounts of lignin have been generated by the papermaking industry and emerging cellulosic ethanol production [3]. Lignin is mainly used as a low-grade fuel and its potential is not fully exploited. It is economically and environmentally desirable to convert lignin into valuable reinforcing additives for rubbers. Various academic papers regarding preparations of rubber/lignin compounds have been published [4–8]. Most recently, Xiao et al. [1] prepared styrene-butadiene rubber/lignin-layered double hydroxide composites by melt mixing. Jiang et al. [9] fabricated natural rubber/nano-lignin composites. Jiang et al. [10] also fabricated cationic lignin/montmorillonite nanosheets and used it to reinforce SBR. Frigerio et al. [11] prepared lignin modified by hexamethylenetetramine as a filler for styrene butadiene rubber. Liao et al. [12] and Cao et al. [13] fabricated a lignin-montmorillonite complex as a novel rubber filler and used it in acrylonitrile butadiene rubber composites. Bahl and Jana [14] modified lignosulfonate by cyclohexylamine and used it as a filler into SBR.
[15] also exploited non-covalent interactions between lignin and carbon black to lower the viscoelastic dissipation in rubber compounds. Numerous scientific articles relating to preparations of lignin as curing agent in epoxy resin have been published [16, 17]. Self-crosslinkable lignin/epoxidized natural rubber composites were prepared by the ring-opening reaction between lignin and epoxidized natural rubber in our research group [18]. Epoxy resins also have been synthesized by an in-situ vulcanization to reinforce SBR [19]. Meanwhile, various interpenetrating polymer networks in the rubber compounds have been prepared [20–23]. However, to the best of our knowledge, there is no report about lignin-novolac epoxy resin networks reinforced SBR. Novolac epoxy resin (F51) was incorporated into SBR/lignin compounds to form lignin-F51 networks composites by in-situ reaction between epoxy groups of F51 and OH groups (or COOH groups) of lignin at the vulcanization condition of the rubber, therefore it could be pointed out that the lignin acts not only as a reinforcing agent but also as a crosslinking agent of F51. Thanks to the whole strong lignin-F51 networks constructed in the rubber matrix, the stress is partially transferred by lignin-F51 networks themselves, thus the reinforcement will not be so much dependent on the interfacial properties, polarity discrepancy and dispersion of the filler, which were traditionally considered as crucial factors of reinforcement for the polymer [24]. This novel reinforcing strategy irrespective of the great polarity discrepancy between polar lignin and non-polar SBR is highly desirable. The formation and characteristics of lignin-F51 networks were investigated. The mechanical performances and vulcanization behaviors were studied as well as the thermal stability.

2. Materials and methods

2.1. Materials

Industrial sulfate lignin (the average molecular weight is 4235 and the polydispersity index is 2.4) was kindly provided by Guangzhou Linge Polymer Material Co., Ltd. (China). SBR latex with trade name of SBR 132 (the solid contents of the latex was 65 wt%) was obtained from Dongguan Benke Latex Co., Ltd. (China), which is a random copolymer consisting of 25 wt% styrene monomer. Novolac epoxy resin (tradename F51, which is a low molecular weight liquid) was purchased from Nanya Plastics Corporation (the epoxy value is 0.51) in China. The structures of the materials are given in Figure 1. The reagents used in rubber formula such as zinc oxide (ZnO), Stearic acid (SA), Sulfur (S), Accelerator N-

![Figure 1. Structures of raw materials](image-url)
cyclohexyl-2-benzothiazole sulfonamide (CZ) and Accelerator 2,2’-dibenzothiazole disulfide (DM) were provided by Rubber Institute of Guangzhou in China.

2.2. Preparation of SBR/50lignin compounds
Lignin was dissolved in deionized water at a mass concentration of 10% and the pH was adjusted to 12.5. The lignin solution (the dry weight ratio of lignin to SBR is 1:2) was dropped slowly into the SBR latex with vigorous stirring, and then 5 wt% sulfuric acid solution was added to co-coagulate the mixture. The mixture was filtered, water washed and then dried in oven at 70°C until a constant weight was obtained, the compounds were named SBR/50lignin.

2.3. Preparation of SBR/50lignin/F51 compounds and SBR/F51 compounds
F51 was added in the SBR/50lignin (or SBR) compounds by using a two-roll mill, followed by adding zinc oxide, stearic acid, accelerator CZ, accelerator DM and sulfur according to the recipe listed in Table 1. The compounds were compression molded and vulcanized at 160°C for optimum vulcanization time ($T_{90}$), which was determined by the U-CAN UR-2030 vulcameter. The preparation of SBR/50lignin/F51 compounds is schematically depicted in Figure 2. The compounds were named SBR/50lignin/xF51 or SBR/xF51 compounds, where x refers to the phr of F51 in the compounds (phr refers to parts per hundred of rubber).

2.4. Preparation of Model Compounds
In order to explore the possible interactions between lignin and F51, two model compounds were designed. Model Compounds A: 100 g lignin and 20 g F51 were mixed in the high-speed multi mill (the speed was 30,000 rpm) for 5 minutes, then put it in the oven for a curing process at the 160°C for 30 minutes. Fourier-transform infrared (FTIR) spectroscopy was used to characterize the possible reactions between lignin and F51 before and after curing. For comparison, neat lignin and neat F51 were also studied by FTIR.

Model Compounds B: $N$-SBR/50lignin/F51 compounds were prepared with the same procedure of SBR/50lignin/F51 except that no rubber additives (sulfur etc.) were added. For comparison, $N$-SBR and $N$-SBR/20F51 were also prepared. Note that $N$ means that no rubber additives were added in this paper.

Table 1. Formulation of the mixtures and purposes

<table>
<thead>
<tr>
<th>Samples</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR, SBR/5F51, SBR/10F51, SBR/15F51, SBR/20F51.</td>
<td>To determine the influence of F51 on curing behavior of SBR vulcanizates.</td>
</tr>
<tr>
<td>SBR/50lignin, SBR/50lignin/5F51, SBR/50lignin/10F51, SBR/50lignin/15F51, SBR/50lignin/20F51.</td>
<td>To determine the influence of F51 on SBR/50lignin vulcanizates.</td>
</tr>
</tbody>
</table>

*rubber ingredients: ZnO 5, Stearic acid 2, S 1.6, Accelerator CZ 1.5, Accelerator DM 0.5.

Figure 2. The preparation of SBR/50lignin/F51
2.5. Characterizations

Fourier transform infrared spectra (FTIR) were recorded in transmission mode on a Bruker Vertex 70 infrared spectrum analyzer (BRUKER OPTICS, Germany) with KBr pellets within the wave number range from 4000 to 400 cm\(^{-1}\). The scanning was performed 32 times with a resolution of 4 cm\(^{-1}\).

Mechanical properties measurements. The tensile and tear tests of the vulcanizates were performed according to ASTM D412 and ASTM D624 specifications, respectively. U-CAN UT-2060 (U-CAN Dynatex Inc., Taiwan) instrument was used with the strain rate of 500 mm/min.

The curing characteristics of the compounds were determined at 160°C by U-CAN UR-2030 vulcameter (U-CAN Dynatex Inc., Taiwan).

Dynamic mechanical analysis was conducted on a Netzsch 242C DMA equipment (Netzsch, Germany). The tensile mode was selected. The measurements were carried out at a frequency of 2 Hz, a heating rate of 5°C/min over a temperature range of –90 to 200°C.

Measurements of crosslink density was carried out on Magnetism Resonance crosslinking density spectrometer (XLDS-15, IIC Innovative Imaging Corporation, Germany) according to the IIC test and analysis software package with a magnetic field intensity of 15 MHz at 85°C. Rubber sample with a length of 10 mm and a diameter of approximately 6 mm was placed into a glass tube for the test.

Thermal gravimetric analysis was carried out in a TA Q20 (TA Corporation, New Castle, America) thermogravimetric analyzer over a temperature range from 30 to 700°C at a heating rate of 10°C/min. Nitrogen was used as purging gas.

Rubber process analysis (RPA) was carried out in a RPA2000 (Alpha technologies Co, USA). Strain sweeps of uncured composites: During the strain sweeps, the temperature and frequency were kept at 60°C and 60 cpm, respectively. The range of the strain sweeps was 0–200%. Storage modulus (\(G'\)) was measured as a function of strain. Strain sweeps of cured composites: the temperature was raised to 160°C to cure the compound for \(T_{90}\). Then, the temperature was reduced to 60°C again. During the strain sweeps, the temperature and frequency were kept at 60°C and 60 cpm. The range of the strain sweeps was 0–140% for the vulcanizates.

Scanning electron micrographs (SEM) of the composites were taken by a Nova Nano SEM 430 instrument (FEI, Netherlands), the voltage of the electron beam used for SEM observation was 10 kV. Preparation of the tensile fracture surface: the tensile fracture surfaces of SBR/50 lignin and SBR/50 lignin/20F51 were obtained by the tensile tests. Preparation of the etched surfaces of \(N\)-SBR/50 lignin/F51: \(N\)-SBR/50 lignin/F51 compounds were fractured at liquid N\(_2\) temperature and then etched by toluene for 10 days to remove the free SBR matrix (the SBR phase are not crosslinked since no sulfur was added), then the etched surfaces were obtained. Note that all the samples were plated with a thin layer of gold before any observations.

3. Results and discussion

3.1. Reactions between lignin and F51

In the present study, it is believed that the OH groups (or COOH groups) of lignin could react with the epoxy groups of F51 by the ring-opening reaction, the reaction between OH and epoxy groups is schematically illustrated in Figure 3.

In order to eliminate the disturbance of SBR molecules in the FTIR investigation, the FTIR of F51/lignin = 5:1 (uncured and cured), F51 and lignin were performed and the results are presented in Figure 4. In the spectrum of lignin, the broad strong band between 3700 and 3200 cm\(^{-1}\) belongs to the hydroxyl stretching vibrations of lignin hydroxyls or absorbed water, and the peaks at about 2935 and 1460 cm\(^{-1}\) are attributed to CH stretching of methyl (CH\(_2\)) or methylene groups (CH\(_3\)). The absorption at about 1700 cm\(^{-1}\) are attributed to C=O stretching.

![Figure 3](image_url). Schematic of the reaction between the epoxy groups of F51 and OH groups of lignin
of lignin, and the absorption at 1510, 1424 and 1600 cm\(^{-1}\) is assigned to the aromatic skeletal vibration. Compared to lignin, in the case of uncured F51/lignin, there are some new absorption peaks appeared, and the peaks at 910 cm\(^{-1}\) are assigned to the stretching vibration of the C–O of the epoxy, which belong to characteristic absorptions of F51. This band almost disappeared after curing, indicating that F51 could react with lignin via the ring-opening reaction under the curing process of 160°C. Curing analysis of Model Compounds B were carried out to characterize the possible interactions between lignin and F51. As shown in Figure 5, the maximum torque (\(M_H\)) of N-SBR/20F51 is lower than that of N-SBR, this is because that F51 remains a low molecular weight liquid which acts as a plasticizer and lubricant in the SBR/20F51. Indicating there are no crosslinking reaction between F51 and SBR. The \(M_H\) of N-SBR/50lignin is higher than that of N-SBR, this is because that there will be the rubber-filler interaction as well as usual volume fraction effects after addition of lignin, and this tends to impose extra resistance to flow of the SBR composites as a higher restriction to motion of the SBR molecules [25]. The \(M_H\) of N-SBR/50lignin/F51 compounds increases significantly with the increasing loading of F51. As an increase in torque is proportional to the crosslinking density [18]. It is evident that the crosslinked networks are formed due to the crosslinking reactions between lignin and F51. In order to further substantiate the formation and existence of lignin-F51 networks in the composites, the etched surfaces of N-SBR/50lignin/F51 are observed by SEM. As shown in Figure 6, no networks are observed in the sample of N-SBR/50lignin. However, preliminary networks embedded in the matrix are observed which disperse uniformly in the sample of N-SBR/50lignin/5F51, and the network pores are approximately 200–500 nanometers. In the sample of SBR/50lignin/10F51, the morphologies of the networks resemble glass fibers, the networks become more obvious and the network pores become smaller. In the sample of SBR/50lignin/15F51, irregular spherical particles are formed and interconnected. In the sample of SBR/50lignin/15F51, the morphologies of the networks resemble glass fibers, the networks become more obvious and the network pores become smaller. In the sample of SBR/50lignin/15F51, irregular spherical particles are formed and interconnected. It should be noted that the lignin-F51 networks are not exactly the identical with the networks observed in Figure 6, this is because if a rubber and a filler are mixed, they interact in such a way that even a good solvent can only partially dissolve the rubber which originally is completely soluble in the solvent. The insoluble rubber is often referred to as the bound rubber [26]. We can infer that the networks observed in Figure 6 is complex of lignin-F51 networks and bound rubber held together by lignin-F51 networks. Since the networks observed in Figure 6 is closely related with lignin-F51 networks, we can say that the general morphology of F51-lignin networks is roughly outlined in the SEM when the free SBR was dissolved by toluene. So we demonstrate the existence of lignin-F51 network.

3.2. Curing analysis of SBR/50lignin/F51 compounds and SBR/F51 compounds
As shown in Figure 7 and Table 2, the \(T_{90}\) of SBR/F51 compounds is increased significantly with the increasing loading of F51, indicating that F51 delays the vulcanization, which is ascribed to the consumption of rubber additives by epoxy group of
Figure 6. SEM images of the samples etched by toluene (a) N-SBR/50lignin, (b) N-SBR/50lignin/5F51, (c) N-SBR/50lignin/10F51, (d) N-SBR/50lignin/15F51
The $T_{90}$ of SBR and SBR/50lignin is 11.18 and 39.54 min respectively, indicating that incorporation of lignin in rubber matrix delays the vulcanization of rubber matrix, which is ascribed to the adsorption between lignin and vulcanization additives [14]. Compared to SBR/50lignin, the scorch time of SBR/50lignin/F51 are reduced, which is attributed to the reaction between lignin and F51. However, with the increasing loading of F51, $T_{90}$ of SBR/50lignin/F51 is initially decreased. When the F51 content is higher than 5 phr, $T_{90}$ starts to rise. There are three factors regulating the values of $T_{90}$ of SBR/50lignin/F51 compounds. Firstly, the interactions between F51 and lignin actually act as efficient crosslinks in the vulcanizates, resulting in accelerated vulcanization [28]. Secondly, F51 reacts with lignin which would adsorb vulcanization additives, and this two effects tend to promote the vulcanization. Thirdly, F51 consumed rubber additives as mentioned above. This effect tends to delay the vulcanization. When the F51 content is relatively low (5 phr), the first and second effects play the leading role, resulting in accelerated curing behavior. When the F51 content is high enough (exceeding 5 phr), the consumption of the rubber additives by F51 plays the leading role, resulting in delayed curing behavior. The $M_H$ of the SBR/50lignin/F51 is increased with F51 loading, suggesting more F51, more crosslinks between lignin and F51. While the $M_L$ (the minimum torque) of the SBR/50lignin/F51 is decreased with F51 loading, and this is related to the fact that the F51 acts as a lubrication agent and plasticizer in the rubber compound. As it is known, a relatively low $M_L$ suggested superior flow ability [29]. Therefore it could be concluded that the inclusion of F51 leads to a better processability.

### 3.3. RPA analysis results

RPA was used to analyze the dynamic viscoelastic properties of SBR/50lignin/F51 composites before and after curing. As shown in Figure 8, it is found that the modulus decreases dramatically with the increase of strain amplitude for all compounds, and this was because filler networks will be destroyed when the strain reaches a high amplitude, and the Storage modulus ($G'$) of all compounds drops to almost the same low-value. This can be explained by the Payne effect [30]. As shown in Figure 8a, the initial modulus of SBR/50lignin uncured compound is higher than that of those uncured compounds adding F51. Moreover, with the increase of F51, the initial modulus of the compounds decreases, and this was because the F51 molecules act as plasticizers and lubricants. This is similar to the article of He et al. [31] that filler network interaction in SBR/rectorite was reduced by adding glycerin or aromatic oil. It indicates that adding F51 could weaken the filler network interaction and reduce the Payne effect, and then enhances the processability of the compounds.

As shown in Figure 8b, in vulcanized compounds, the values of $G'$ of all compounds drops to almost the same low-value. This can be explained by the Payne effect [30]. As shown in Figure 8a, the initial modulus of SBR/50lignin uncured compound is higher than that of those uncured compounds adding F51. Moreover, with the increase of F51, the initial modulus of the compounds decreases, and this was because the F51 molecules act as plasticizers and lubricants. This is similar to the article of He et al. [31] that filler network interaction in SBR/rectorite was reduced by adding glycerin or aromatic oil. It indicates that adding F51 could weaken the filler network interaction and reduce the Payne effect, and then enhances the processability of the compounds.

### Table 2. Curing parameters of the rubber compounds (160°C)

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{S2}$ [min]</th>
<th>$T_{90}$ [min]</th>
<th>$M_L$ [dN.m]</th>
<th>$M_H$ [dN.m]</th>
<th>$M_L$ [dN.m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>1.50</td>
<td>11.18</td>
<td>0.9</td>
<td>9.03</td>
<td>8.13</td>
</tr>
<tr>
<td>SBR/5F51</td>
<td>3.26</td>
<td>46.28</td>
<td>0.85</td>
<td>7.81</td>
<td>6.96</td>
</tr>
<tr>
<td>SBR/10F51</td>
<td>7.03</td>
<td>51.12</td>
<td>0.84</td>
<td>7.53</td>
<td>6.69</td>
</tr>
<tr>
<td>SBR/15F51</td>
<td>10.32</td>
<td>66.06</td>
<td>0.76</td>
<td>7.44</td>
<td>6.68</td>
</tr>
<tr>
<td>SBR/20F51</td>
<td>12.52</td>
<td>78.30</td>
<td>0.70</td>
<td>6.93</td>
<td>6.20</td>
</tr>
<tr>
<td>SBR/50lignin</td>
<td>3.00</td>
<td>39.54</td>
<td>8.15</td>
<td>25.57</td>
<td>17.42</td>
</tr>
<tr>
<td>SBR/50lignin/5F51</td>
<td>0.44</td>
<td>22.42</td>
<td>7.92</td>
<td>27.02</td>
<td>19.10</td>
</tr>
<tr>
<td>SBR/50lignin/10F51</td>
<td>0.48</td>
<td>36.37</td>
<td>7.48</td>
<td>29.84</td>
<td>22.36</td>
</tr>
<tr>
<td>SBR/50lignin/15F51</td>
<td>0.45</td>
<td>48.58</td>
<td>7.24</td>
<td>33.30</td>
<td>26.06</td>
</tr>
<tr>
<td>SBR/50lignin/20F51</td>
<td>0.43</td>
<td>52.37</td>
<td>6.49</td>
<td>34.64</td>
<td>28.15</td>
</tr>
</tbody>
</table>

$M_L$: the minimum torque; $M_H$: the maximum torque; $\Delta M$: the difference between maximum torque and minimum torque; $T_{S2}$: scorch time; $T_{90}$: optimum cure time.
further promote restriction on the mobility of rubber chains, indicating that the formation of the lignin-F51 networks have a significant reinforcement.

3.4. DMA analysis results
The dynamic mechanical properties of the SBR/50lignin/F51 composites were characterized by DMA. As shown in Figure 9a, there is an increase in storage modulus ($E'$) after incorporation of F51, which can be attributed to the formation of strong lignin-F51 networks and the networks have a significant restriction on SBR matrix. $E'$ is widely accepted as directly proportional to the degree of elasticity, which correlates well with crosslink density [30], and this is in accordance with our findings below.

As shown in Figure 9b. DMA studies reveal that the SBR/lignin/F51 composites exhibit two glass transition temperature: one occurring at low temperature ($T_{g1}$) is associated to SBR and the second at high temperature ($T_{g2}$) corresponds to the lignin-F51 networks. The $T_{g1}$ of SBR is shifted from $-56.63$ to $-55.15^\circ C$ with increasing loading of F51 from 0 to 20 phr. Furthermore, it can be observed that the tan peak values and half-peak width of $T_{g1}$ are decreased with the increase of F51 content, suggesting continuously decrease in rubber chain mobility [24, 32], and this is due to the strong interaction between the rigid lignin-F51 network and SBR matrix. There is an evident $T_{g2}$ after incorporation of F51 at a level above 5 phr, and the tan peak of $T_{g2}$ become increasingly obvious with the increasing loading of F51. It is logical to conclude that the $T_{g2}$ is the glass transition temperature of lignin-F51 [33, 34]. The emergence of $T_{g2}$ further substantiate the existence of the F51-lignin networks.

Figure 8. Storage modulus ($G'$)-strain sweeps: (a) the uncured and (b) cured SBR/50lignin/F51 composites

Figure 9. Storage modulus $E'$ (a) and tan $\delta$ (b) of SBR/50lignin/F51
3.5. TGA analysis results

Figure 10 illustrates the TG and DTG curves of SBR/50lignin/F51 with different F51 loading respectively. Table 3 shows the thermal degradation characteristics of the composites. The thermal degradation behavior of all SBR/50lignin/F51 composites with one main mass loss step are similar. A notable shift of 5, 10% weight loss to higher temperature can be observed with the loading of F51. For instance, the $T_{5\%}$ and $T_{10\%}$ of SBR/50lignin/20F51 is 274.7 and 336.0°C, which are about 25 and 10°C higher than those of SBR/50lignin, and this is attributed to the introduction of novolac epoxy resin with high concentrations of aromatic rings which can improve thermal stability [35] and lignin-F51 networks hindering the diffusion of small molecules generated during the thermal decomposition. Besides, to some extent the improvement of the crosslinking density can promote the thermal stability. However, the peak degradation temperature ($T_{\text{max}}$) of SBR/50lignin/F51 is slightly lower than the $T_{\text{max}}$ of SBR/50lignin, which is attributed to the possibility of the epoxy resins decomposition at higher temperature.

![Figure 10. TGA curves (a) and DTG curves (b) of SBR/50lignin/F51](image)

Table 3. Thermal degradation characteristics of the rubber compounds

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{5%}$ [°C]</th>
<th>$T_{10%}$ [°C]</th>
<th>$T_{\text{max}}$ [°C]</th>
<th>Residue at 700°C [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR/50lignin</td>
<td>249.4</td>
<td>325.4</td>
<td>456.9</td>
<td>14.2</td>
</tr>
<tr>
<td>SBR/50lignin/5F51</td>
<td>253.6</td>
<td>328.1</td>
<td>456.1</td>
<td>14.2</td>
</tr>
<tr>
<td>SBR/50lignin/10F51</td>
<td>265.6</td>
<td>334.1</td>
<td>455.9</td>
<td>14.8</td>
</tr>
<tr>
<td>SBR/50lignin/15F51</td>
<td>268.6</td>
<td>334.3</td>
<td>453.2</td>
<td>14.2</td>
</tr>
<tr>
<td>SBR/50lignin/20F51</td>
<td>274.7</td>
<td>336.0</td>
<td>453.4</td>
<td>14.9</td>
</tr>
</tbody>
</table>

$T_{5\%}$ – 5% weight loss temperature. $T_{10\%}$ – 10% weight loss temperature. $T_{\text{max}}$ – the peak degradation temperature.

3.6. Crosslink density analysis

Recently, many researchers use Magnetic Resonance Crosslink Density Measurements to the determinate the crosslink densities in rubber materials [36–39], and not only this method simple to use and time-saving but also this method can provide several more parameters characterizing the molecular dynamics of the network. Such as the average molecular weight of chains between two adjacent crosslinks ($M_c$), the motion of dangling chain ends and free chain ($A(T_2)$), and the percentage of inter crosslink chain $A(M_c)$ etc. $A(T_2)$ represents the percentage of high-mobile fractions while $A(M_c)$ represents percentage of crosslinking fractions [40]. A less Crosslink Density value usually corresponds to a bigger $M_c$ value [38, 41] and a less $A(T_2)$ value usually corresponds to a bigger $A(M_c)$ value [38].

The network structure characterization of vulcanize with Magnetic Resonance Crosslink Density Measurements is described in detail in the references [42–44]. The results of crosslinking density are shown in Table 4, it is shown that the crosslink density of SBR vulcanize is higher than that of SBR/50lignin, this is because that there are abundant acidic OH in lignin since acidic agents have an adverse effect on the vulcanization of the rubber [36]. The $A(T_2)$ of SBR vulcanize is higher than that of SBR/50lignin. This is because that the addition of lignin could impose extra restriction to the mobility of the SBR and reduce the proportion of activity units. Compared to SBR/50lignin, the crosslink density of SBR/50lignin/F51 shows an increasing trend with the increase of F51, owing to the crosslink reaction between F51 and lignin. As the
integrity of crosslink network was improved, $A(M_c)$ increased and $A(T_2)$ decreased [38]. This result shows that the formation of lignin-F51 networks can bring on more crosslinking points, fewer activity units, and lower activity ability. The crosslink density results of SBR/50lignin/F51 is consistent with the maximum torque of curing test, Shore A hardness and tensile modulus.

### 3.7. Mechanical properties

As shown in Figure 11 and Table 5. It can be observed that the tensile strength of SBR and SBR/10F51 are very poor, indicating that F51 alone shows almost no reinforcing effect. It could be seen that the tear strength, 300% modulus and Shore A hardness of the SBR/50lignin/F51 composites increase with the increase of F51, for instance, the tear strength and 300% modulus are increased from 49.4 kN/m, 3.6 MPa of SBR/50lignin to 62.2 kN/m and 10.0 MPa, respectively, when 20 phr F51 is added. This is because the stress will transfer from SBR molecular chains to the lignin-F51 networks effectively before a catastrophic breakage happens, which demonstrates the good reinforcement by the rigid lignin-F51 network. However, the elongation at break of SBR/50lignin/F51 decreases with the increase of F51 content. This is because the lignin-F51 networks decrease the deformation resistance of rubber chains. Additionally, the strong interactions between the rigid lignin-F51 networks and SBR matrix can prevent the recovery of the rubber molecular chains after deformation, resulting in the increased permanent set.

As shown in Figure 12, the tensile fracture surface of SBR/50lignin and SBR/50lignin/20F51 are observed by SEM. It should be noted that the sample of SBR/50lignin/20F51 exhibits much more rugged fracture surfaces than those of SBR/50lignin, indicating that the lignin-F51 networks can bear more external force when an exerted stress is applied to the matrix. This investigation has demonstrated that lignin-F51 networks could be an effective route for the enhancement of SBR.

### 4. Conclusions

A novel reinforcing strategy for SBR via the lignin-F51 networks in the SBR matrix is proposed. The F51 can form covalent bonds with lignin via the ring-opening reaction between F51 and lignin, which is substantiated by the results of FTIR. The existence

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### Table 4. Crosslink density of SBR/50lignin/F51 compounds

<table>
<thead>
<tr>
<th>Properties</th>
<th>Samples(SBR/lignin/F51)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100/0/0</td>
</tr>
<tr>
<td>XLD [10⁻¹⁵ mol/cm³]</td>
<td>9.33</td>
</tr>
<tr>
<td>$M_c$ [K g/mol]</td>
<td>10.18</td>
</tr>
<tr>
<td>$A(M_c)$ [%]</td>
<td>53.06</td>
</tr>
<tr>
<td>$A(T_2)$ [%]</td>
<td>46.33</td>
</tr>
</tbody>
</table>

$XLD$: crosslinking density; $M_c$: the average molecular weight between two crosslinking point; $A(M_c)$: the motion of inter crosslink chain; $A(T_2)$: the motion of dangling chain ends and free chain.

---

### Table 5. Mechanical properties of rubber compounds

<table>
<thead>
<tr>
<th>Properties</th>
<th>Samples(SBR/lignin/F51)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100/0/0</td>
</tr>
<tr>
<td>Modulus at 300% [MPa]</td>
<td>1.9</td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>2.2</td>
</tr>
<tr>
<td>Elongation at break [%]</td>
<td>339.7</td>
</tr>
<tr>
<td>Permanent set [%]</td>
<td>8.0</td>
</tr>
<tr>
<td>Tear strength [kN/m]</td>
<td>10.9</td>
</tr>
<tr>
<td>Hardness [Shore A]</td>
<td>40.0</td>
</tr>
</tbody>
</table>
of F51-lignin networks is demonstrated by the results of SEM and its glass transition temperature is observed by DMA. The lignin-F51 networks show good reinforcement towards the SBR compounds and improved initial thermal stability of the rubber composites. This novel reinforcing strategy is suitable for other rubbers, such as natural rubber and nitrile butadiene rubber, theoretically.

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References


