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Influence of complexing treatment and epoxy resin coating on the properties of aramid fiber reinforced natural rubber

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ABSTRACT: In this work, natural rubber/aramid fiber (NR/AF) composites were prepared with master batch method. AF was modified by using epoxy resin (EP) and accelerator 2-ethyl-4-methylimidazole (2E4MZ) through surface coating on the basis of the complexing treatment with CaCl₂ solution. Hydroxyl-terminated liquid isoprene rubber (LIR) was regarded as a compatibilizer between EP and NR. It is found that the crystallinity on AF surface is decreased by complexing reaction with CaCl₂ solution. Swelling and mechanical properties of the vulcanized composites, such as swelling degree, tensile and tear strength, tensile modulus at 300% elongation, are measured, and the tensile fracture morphology and dynamic mechanical analysis of the composites are investigated. The results show that the mechanical properties of composites with modified fibers are improved obviously and interfacial adhesion between matrix and the fiber is enhanced, especially for the AF coated with EP and imidazole. The best comprehensive mechanical properties of the composites are obtained with using CaCl₂-EP/2E4MZ system when the ratio of m(EP)/m(AF) is 3%. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42122.

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INTRODUCTION

Natural rubber (NR) is well known to exhibit various significant properties due to its ability to crystallize under stretching.¹ Carbon black (CB) has been widely used as the main reinforcing filler in NR, but in some special occasions, it is still difficult to meet the application requirement for CB/NR vulcanizates. For example, premature failure of tires is often caused by the cut of the sharp stones. Therefore, it is essential for vulcanized NR materials to provide a more effective way for reinforcement. With the development of the spurt technology in fiber, fiber-reinforced polymer materials are becoming the powerful means to improve the strength and stiffness of polymers. It is generally known that short fiber-reinforced thermoplastics have been widely applied in the modern industrial technology;^{2–5} however, the studies of short fiber-reinforced rubber material under the condition of large deformation haven't gone far enough.

Aramid fiber (AF) is more frequently used as a reinforcing material in tires and other mechanical rubber goods, such as hoses, belts, etc.⁶ AF is a kind of high-performance organic fiber which exhibits higher tenacity, higher modulus, excellent heat resistance, and cutting resistance comparing to other fibers used

in rubber composites. The studies of AF applied to rubber have been widely reported.^{7–9} However, the AF has the disadvantages, surface smooth, high crystallinity, less chemical activity, which is easy to lead to gaps and defects in composite interface and hard to produce effective interface bonding with polymer matrix.¹⁰ These drawbacks have limited its direct application in many fields. Investigation on modification method for AF is still a hot issue in recent years. In general, the surface modification methods for AF are various, including surface coating, surface grafting, plasma processing, and gamma ray radiation method.^{11,12} But most of them can be hardly used in practical production. So it is crucial to develop a new method of surface treatment for AF to improve the properties of AF/NR composites.

Many studies have showed that amide groups had certain ability of coordination complexation with metal ions, such as Ca^{+2} , Li^{+1} , etc.,^{13–16} which greatly reduces the hydrogen bonding interaction and the crystallinity of polymer. Based on this, the technology that treated AF with $CaCl_2$ solution was applied to surface treatment of AF in this article in order to change its surface features. However, it is well known that it is difficult for short AF to disperse well in rubber matrix in the preparation of

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NR/AF composites. In recent years, the application of liquid rubber in rubber composites, especially for NR modification, has been investigated profoundly, such as liquid isoprene rubber (LIR).^{17,18} As far as we know, there are several reasons for application of LIR: first, low viscosity is advantageous to the filler dispersion and distribution in the process of mixing lubrication effect; second, it has good compatibility with rubber, which can achieve homogeneous mixture in the macro and micro; third, it can occur curing reaction with rubber in the process of vulcanization. Master batch method is an effective way to improve the dispersibility of fillers and additives used in rubber.^{19,20} However, few studies in the literature pay attention to the preparation of master batch in the terms of short fiber reinforced rubber composites. Although the ratio of length to diameter of fiber in rubber matrix will be further reduced with master batch method during the manufacturing process, it is very beneficial for short fibers dispersing in the NR. Hence, complexing treatment for AF surface, master batch method and hydroxylterminated liquid rubber is used to solve the problems on interfacial adhesion and short fiber dispersion in this article.

Epoxy resin (EP) has been proved to be a versatile and effective resin with outstanding chemical and corrosion resistance as well as prominent mechanical and thermal properties once cured.^{21–23} The epoxy group in EP molecule has high reaction activity with various polar groups, especially accelerated by catalyst. In order to improve the interfacial adhesion, a kind of bisphenol A epoxy resin with highly active epoxy group on both ends of the molecular structure and the catalyst is used in surface coating, which has chemical affinity with hydroxyl groups of hydroxyl-terminated liquid rubber and amide or amino of AF after complexing treatment.

In the present work, the applications of CaCl₂-EP and CaCl₂-EP/2-ethyl-4-methylimidazole (2E4MZ) systems to the AF surface modification were discussed. To be specific, AF was modified with epoxy resin and curing agent 2E4MZ through surface coating on the basis of the treatment with CaCl₂ solution. First, master batch was prepared by incorporating NR, LIR and modified AF, and then the NR and master batch were mixed and cured. The tensile stress, tear strength, tensile modulus at 300% elongation, swelling properties, dynamic mechanical analysis, fractured surfaces of NR/AF composites have been investigated and discussed further.

EXPERIMENTAL

Materials

Nature rubber, ribbed smoked sheet 1(RSS1), was supplied by Xishuangbanna Kang Guanlei Rubber Factory, China. Hydroxylterminated liquid isoprene rubber (LIR-565), weight average molecular weight (M_w) of 50,000, the viscosity of 500 Pa s, was obtained from Puyang Linshi Chemical New Material Co. Ltd., China. Aramid fiber (AF-1000, 1500D) was produced by South Alkex Company, Korea. Epoxy rein (E51) that epoxy value is 0.51 with epoxy groups on both ends was obtained from Shanghai Resin Factory Co. Ltd., China. Besides, 2-ethyl-4methylimidazole (2E4MZ) was provided by Shikoku Chemical Corporation, Japan. Calcium chloride (CaCl₂) and xylene was provided by Shikoku Chemical Corporation, Chengdu Linjiang Table I. Formulations of the Vulcanized Rubber

Components (part per 100 rubber)	Phr
NR	98
LIR	2
Sulfr	1.71
ZnO	5
Stearic acid	4
2-Mercaptobenzothiazole (M)	2.21
2,2'-Dibenzothiazyl disulfide (DM)	1.96
Diphenylguanidine (D)	0.5
Tetramethylthiuram disulfide (TMTD)	0.32
Styrenated phenol (SP-C)	1.5
Aramid fiber	4

Chemical Factory and Tianjinzhiyuan Chemical Reagent Co. Ltd., China, respectively. It is essential to keep m(2E4MZ)/m(EP) is 5% during the experiment.

Surface Treatment of AF

AF was chopped to a length of approximately 20 mm, put in a beaker and left to dry after using acetone ultrasonic cleaning 2 h, then the fiber was soaked in a concentration of 20% $CaCl_2$ solution for 1 h at 90°C and dried. The treated fiber was uniform mixed with EP or EP/2E4MZ/acetone solution [m(EP) is variable, m(2E4MZ)/m(EP) is 5%] in a beaker at room temperature, left to dry in an oven at 90°C for 3 h, all the EP was present on AF surface. The content of EP was calculated as weight percentage based on AF.

Preparation of Master Batch

NR and LIR were compounded in a kneading machine (NJH, Shandong Laizhou Xinggeer Chemical Plastic Machinery Co. Ltd., China) for 6 min at 60°C to obtain the compounded blends. And then 90 g blends was picked up to torque rheometer (XSS-300, Shanghai Kechuang Rubber and Plastic Machinery Equipment Co. Ltd., China) at 150°C for 4 min under the ratio of 80 r/min. After that, 12 g the modified AF were added into the torque rheometer and mixed for 6 min.

Preparation of Vulcanized Composites

The rubber materials including the above master batch were masticated according to the recipe listed in Table I with a two-roll-mill operation (XK-160-A, Fujian Yongchun Light Industrial Machinery Factory, China). The specification of the mill is as follows: Φ 160 \times 320, the ratio of 1 : 1.22. Firstly, rubber was mixed with stearic acid and ZnO. Then, master batch and other ingredients were mixed into the system. Vulcanization characteristics were measured with a rheometer (M2000FAN, Taiwan High Speed Rail Technology Co. Ltd., China), and cure time tc₉₀ was determined. A square preform cut from the uncured sheet was vulcanized at 145°C with a press vulcanizer (XLB, 25t, Jiangdu Pearl Experiment Machine Factory, China) according to the standard of tc₉₀.

Characterization and Measurements

Swelling Test. Vulcanizate that the weight was known were put in methylbenzene solvent at 50°C for swelling to balance, then



measured the sample weight after swelling, and the swelling degree of vulcanized rubber (Q) was estimated based on the following equation:

$$Q = (W_1/\rho_1 + W_2/\rho_2)/(W_2/\rho_2)$$

where W_1 is the solvent weight in sample after swelling, W_2 is the weight of rubber composite in sample after swelling, ρ_1 is the density of solvent, ρ_2 is the density of rubber composite before swelling.

Scanning Electron Microscopy (SEM). The morphologies of fractured surfaces of the composites were observed with a SEM (KYKY-2800B, Beijing KYKY Technology Co. Ltd., China) under the condition of 25 KV, and all samples were coated with gold prior to SEM examination.

X-ray Diffraction (XRD). XRD analyses were performed using a diffractometer with the type of X Pert PRO from Panalytical, Netherlands. Test conditions are following: Cu-K α radiation, tube voltage with 40 kV, tube current with 40 mA, K = 0.15432 nm, scan range from 10° to 40°, scan rate with 2°/min.

Fourier Transform-Infrared (FT-IR). Functional groups were detected with Infrared spectrum test with Fourier infrared spectrophotometer (NEXUS 670) from Thermo Company in the United States. The master batch was dissolved in xylene at 110° C and extracted for 10 h, then, part of the fibers were removed from the residuals carefully and cleaned with xylene. The fiber samples mixed with potassium bromide (KBr) were compressed into plates for FT-IR spectra analysis. The samples were analyzed in the spectral range of 4000–400 cm⁻¹ at room temperature.

Mechanical Properties. Mechanical properties of the composites were evaluated on a universal material tester with WdW-10c, which has a large deformation accessory that can record the strain of rubber precisely, from Shanghai Hualong Test Instrument Company, China. Tensile properties were measured according to ISO 37-2005, and tear strength was calculated according to ISO 34-1-2010 (right angle). All the values were calculated as averages from five samples.

Dynamic Mechanical Analysis (DMA). Dynamic mechanical thermal characteristics of the composites were tested with a dynamic mechanical properties testing machine (Q800, TA) in a double cantilever beam deformation mode, and temperature range of -100 to $+40^{\circ}$ C. All samples were carried out at a frequency of 5 Hz at a heating rate of 3°C/min. The strain amplitude used in the DMA test was 8 μ m.

RESULTS AND DISCUSSION

Surface Modification of AF with CaCl₂ Solution

In this work, 20 wt % $CaCl_2$ solution was used to treat AF at 90°C. Only the processing time was changed to obtain modified AF with different degree of complexation. The SEM morphologies of AF with $CaCl_2$ in different treating time are displayed in Figure 1. The surface morphology of AF is affected by the addition of $CaCl_2$ solution. It can be seen from Figure 1(a) that the surface of AF without any treatment is very smooth, even without any defects. However, fiber surface becomes rough and



(a)





Figure 1. SEM morphologies of AF with $CaCl_2$ in different treating time. (a) 0 min; (b) 60 min; (c) 180 min.

appears a "thread" appearance after treated with $CaCl_2$ solution for 60 min, as shown in Figure 1(b). It is clearly observed from Figure 1(c) that fiber surface has been destroyed partially and forms fibrillation with a shape of filament or flake when the



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Figure 2. The XRD patterns of AF with different treatment conditions: (a) untreated; (b) 20 wt % CaCl₂ solution at 90°C, 1 h; (c) 20 wt % CaCl₂ solution at 90°C, 3 h.

processing time is prolonged to 180 min. Therefore, it is conclude that $CaCl_2$ solution can obviously change the surface structure of AF.

Amide groups have certain ability of coordination complexation with metal ions via the lone pair electrons of nitrogen atom from amide groups entering into empty orbital of metal ion, and the hydrogen bond of AF is destoryed,¹⁵ which leads to a decrease of the degree of crystallinity of AF. Figure 2 illustrates the XRD patterns of AF with different treatment condition. It is found from Figure 2 that four characteristic diffraction peaks appear at $2\theta = 14.2^{\circ}$, 17.1° , 20.0° , and 22.4° , indicating that the crystal type of AF do not change after surface treatment with CaCl₂. Peak area for every curve of XRD is determined in Table II by using the curve fitting and normalization method. Table II shows peaks area are getting smaller for diffraction peaks area in the same position from curve a to curve c, which indicates that the formation of the complex between CaCl₂ and amide of AF makes the crystal structure of AF surface to be imperfect.

Effect of AF Surface Coated with EP on the Interfacial Adhesion of the Composites

The AF samples with different treatment were from extraction of the master batch, to be specific, AF was treated with $CaCl_2$ solution complex modification, AF was coated with 3% EP based on treating AF with $CaCl_2$ solution, and AF was coated with 3% EP/2E4MZ based on treating AF with $CaCl_2$ solution.

Table II. Peak Area for XRD

Peak	Area (curve a)	Area (curve b)	Area (curve c)
1	0.11968	0.10898	0.09972
2	0.40591	0.38011	0.34304
3	1.69464	1.58486	1.58000
4	1.70891	1.70142	1.69034



Figure 3. FT-IR spectra of: (a) AF that only was treated with $CaCl_2$; (b) the extracted residue in which AF was treated with $CaCl_2$ solution at 90°C for 1 h; (c) the extracted residue in which AF was coated with EP/acetone solution base on being treated with $CaCl_2$; (d) the extracted residue in which AF was coated with EP/2E4MZ/acetone solution base on being treated with $CaCl_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The FT-IR spectra of the fiber residues collected by different treatment are shown in Figure 3. For comparison, the FT-IR spectra of the AF which was only treated with CaCl₂ solution (the fiber was not mixed with rubber) is also listed in Figure 3. For the extracted residue of AF modified through surface coating with EP/2E4MZ after complexing treatment with CaCl₂ solution, the curve d appears much higher absorption peak at 2851 cm^{-1} , 2928 cm^{-1} , and 2962 cm^{-1} , which corresponds to the C-H symmetric stretching vibration of -CH2-, C-H asymmetric stretching vibration of -CH2-, and C-H asymmetric stretching vibration of -CH3, respectively. For curves b and c, it is also observed that the three absorption peaks appear, however, the peaks are weaker than these of curve d. At the same time, it is found from Figure 3 that these absorption peaks do not appear in the curve a. This indicates that the absorption peaks at 2851 cm⁻¹, 2928 cm⁻¹, and 2962 cm⁻¹ derived from rubber. In other words, all the different treated AF surfaces still are adhered by a certain amount of rubber after the extraction of master batch, and the amount of residue rubber on the surface of AF with EP/2E4MZ coating obviously increase. Therefore, the interfacial adhesion between rubber and AF is improved by comprehensive modification for AF surface with CaCl₂ solution complex processing and EP/2E4MZ coating.

Figure 4 shows the FT-IR spectra in the range of 2100-1000 cm⁻¹ of about four samples of fiber residues after extracted. For comparison, the FT-IR spectra of cured resin of E51/2E4MZ is listed in Figure 4(a). It is seen from Figure 4(d) that the residue of AF modified with CaCl₂ and E51/2E4MZ show the absorption peaks at 1128 cm⁻¹, 1180 cm⁻¹, and 1375 cm⁻¹, corresponding to C—O stretching vibrations in different chemical environments. The peaks at 1128 cm⁻¹ and 1180 cm⁻¹ also appear for the cured resin of E51/2E4MZ, as shown in Figure 4(a), corresponding to stretching vibrations of C—O of epoxy resin, which indicates that epoxy resin is





Figure 4. FT-IR spectra of (a) cured resin of E51/2E4MZ; (b) the extracted residue in which AF was treated with CaCl₂ solution; (c) the extracted residue in which AF was coated with EP/acetone solution base on being treated with CaCl₂; (d) the extracted residue in which AF was coated with EP/2E4MZ/acetone solution base on being treated with CaCl₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

remained on AF surface after extracted. Moreover, a peak appears at 1375 cm⁻¹, corresponding to N—O stretching vibration. The above results provide evidence for the reaction of epoxy resin with amide or terminated amine groups of AF catalyzed by the imidazole.

Under the accelerating effect of imidazole, epoxy resin can react with hydroxyl-terminated liquid rubber and polar groups present in AF surface which releases from the crystal structure by complexing treatment.²⁴ The accelerated effect of tertiary amine of 2E4MZ on the reaction can be described as shown in Scheme 1. The reactivity of epoxy resin is enhanced after the ring is opened.

Figure 5 shows the SEM micrographs of the tensile fracture surfaces of AF reinforced NR under the different conditions of surface treatment. Comparing with AF only treated with $CaCl_2$ solution [Figure 5(a)] and AF coated with EP based on treated with $CaCl_2$ complex [Figure 5(b)], it is seen that AF is cohered with more rubber after AF is coated with EP/2E4MZ based on $CaCl_2$ complex [Figure 5(c)]. This is consistent with the results of FT-IR analysis. The enhanced bonding between modified AF and matrix is described as scheme 2.

The SEM micrographs of AF reinforced NR in the absence of LIR in different conditions have been shown in Figure 6. From Figure 6(a), fiber dispersion is not uniform and there is no obvious adhesive rubber on aramid fiber. What's more, Figure 6(b) shows that fiber dispersion has been improved in the presence of epoxy, but there is no obvious adhesive rubber on aramid fiber also. Comparing Figures 4 with 5, it indicates that the



Scheme 1. The accelerated effect of tertiary amine of 2E4MZ.



25 KV 300 X 100 um KYKY-2800B SEM SN:2822





Figure 5. The morphology of fracture surface of composites: (a) AF was treated with CaCl₂ solution; (b) AF was coated with EP/acetone solution base on AF complex with CaCl₂ solution; (c) AF was modified through surface coating EP/2E4MZ/acetone solution on the basis of the complexing treatment with CaCl₂ solution.



enhanced bonding is attributed to the combined effect of EP/ 2E4MZ and LIR.

Influence of EP Content on Swelling Property of NR/AF Composites

Swelling properties of polymer-matrix composites can reflect the situation of interfacial bonding,^{25,26} so the effect of EP or EP/2E4MZ content on the swelling property of the NR/AF composites has been tested, and the results are listed in Table III. AF is treated with 20 wt % CaCl₂ solution at 90°C for 60 min, and the AF content is 4 phr (constant) in the composites. It can be seen from Table III that the value of swelling degree (Q) decreases with the increasing of EP content. And the minimum value of Q is obtained when EP content is 3%, which is attributed to the increase of the interaction between AF and rubber molecular chain to enhance swelling resistance. Moreover, the value of Q slightly increases when EP/2E4MZ is more than 3%, so it is concluded that 3% may be the optimal EP/2E4MZ content for AF surface treatment.

Mechanical Properties

The mechanical properties of vulcanized NR and NR/LIR (NR:LIR = 98 : 2, weight ratio) without AF are listed in Table IV. It can be seen from Table IV that the difference of mechanical properties between the two materials is not obvious, so the mechanical properties of NR cannot be improved by the addition of LIR alone.

The influence of EP or EP/2E4MZ content on mechanical properties of AF/NR composites are listed in Table V. Comparing to the results in Table IV, tear strength and tensile modulus at 300% elongation increase significantly in Table V, which indicates the effect of low content AF in rubber is very obvious. However, the tensile strength decreases slightly when 4 phr AF is added into the composites due to the dilution effect of fiber reinforced rubber.²⁷ The values of the tensile strength, tear strength, and tensile modulus at 300% elongation on the direction of MD increase at the beginning and then show a slightly decline with increasing the content of EP (or EP/2E4MZ), and



b b

(a)

Figure 6. The morphology of fracture surface of composites: (a) AF treated with $CaCl_2$ and without LIR in the composite; (b) AF treated with $CaCl_2$ and 5 wt % EP/2E4MZ and without LIR in the composite

the effect of surface treatment with CaCl₂-EP/2E4MZ on mechanical properties of the composites is more remarkable than that of surface treatment with CaCl₂-EP. It can be found from Table V that the best comprehensive mechanical properties of the composites are obtained when the content of EP is 3%, which is in agreement with the results obtained from the swelling test (listed in Table III). After two steps surface treatment for AF, interface bonding performance between AF and rubber matrix is enhanced so as to improve mechanical properties of the composites. When EP content is more than 3 wt %, the redundant content of EP in the matrix has a plasticizing effect,

Table III. Influence of EP Content on Swelling Property of NR/AF Composites

		1%		3%		5%		7%	
EP Content	0%	1#	2#	1#	2#	1#	2#	1#	2#
Q	3.95	3.90	3.89	3.84	3.67	3.81	3.72	3.76	3.70

1#: AF coated with EP reinforced NR composites [m(EP) variable], 2#: AF coated with EP/2E4MZ reinforced NR composites [m(2E4MZ)/ m(EP) is 5%].



Table	IV.	Mechanical	Properties	of tl	he '	Vulcanized	NR	and	NR/	LIR
Comp	osit	es								

Measurements	NR	NR/LIR
Tensile strength (MPa)	25.9	26.5
Tear strength (kN/m)	36.6	37.4
Tensile modulus at 300% elongation	1.9	2.0
Elongation at break (%)	2310	2219

which makes the tear strength and tensile modulus at 300% elongation decrease. It is found that the values of tensile strength and tensile modulus at 300% elongation increase in direction of MD compared to the direction of TD. The improvement is mainly due to the advantage of fiber orientation.

Dynamic Mechanical Analysis (DMA)

Ashida *et al.*²⁸ proposes that the relationship of interfacial adhesion with the peak value of tan δ of composite $(\tan \delta_{\max})_c$ and the peak value of tan δ of matrix $(\tan \delta_{\max})_m$ can be expressed as follow:

$$(\tan \delta_{\max})_c = (\tan \delta_{\max})_m - \alpha \phi_f$$

where ϕ_f is the volume fraction of the fiber, and α is called interfacial adhesion parameter. The bigger α is, the better the interfacial adhesion is. Because the peak value of tan δ of matrix $(\tan \delta_{\max})_m$ is constant, so the lower $(\tan \delta_{\max})_c$ corresponds to the better interfacial adhesion.

The samples of AF reinforced vulcanized NR were prepared in which the AF was complexing treated with CaCl₂ solution and coated with different content of EP/2E4MZ. The effect of the EP/2E4MZ content on the loss factor is shown in Figure 7. The value of $(\tan \delta_{max})c$ decreases with increasing the content of EP/2E4MZ, which indicates interfacial adhesion between AF and NR is enhanced due to the increase of EP/2E4MZ content.



Figure 7. Effect of EP/2E4MZ content on the loss factor.

The peak of loss factor $(\tan \delta_{\max})c$ is reduced, which is attributed to AF greatly limits the movement of rubber molecular chain when the interfacial adhesion between rubber and AF is improved.

CONCLUSIONS

Surface treatments of AF were carried out with CaCl₂ solution complexing and EP or EP/2E4MZ coating. NR, modified AF, and hydroxyl-terminated liquid isoprene rubber (LIR) were mixed to prepare master batch. AF reinforced vulcanized NR composites were prepared with master batch method. The main conclusions are following:

1. The complexation reactions between CaCl₂ solution and amide on AF surface result in the decrease of crystallinity on AF surface. The chemical interactions of EP with the complexed AF and hydroxyl-terminated liquid rubber take place

Table V. Influence of EP Content on Mechanical Properties of NR/AF Composites

		1%		3%		5%		7%	
m(EP)/m(AF)	0%	1#	2#	1#	2#	1#	2#	1#	2#
Tensile strength (MPa)									
MD	23.8	23.9	24.1	25.7	26.0	23.2	24.1	22.6	24.4
TD	22.2	22.7	24.3	23.9	24.5	22.4	23.0	21.5	23.6
Tear strength (KN/m)									
MD	58.6	61.6	64.7	64.8	67.4	63.3	66.4	64.4	65.3
TD	50.6	50.1	53.7	52.2	54.3	50.2	52.6	53.4	51.4
Tensile modulus at 300% elongation (MPa)									
MD	4.3	4.5	4.8	4.9	5.1	4.7	4.8	4.6	4.6
TD	2.6	2.7	2.8	2.9	3.1	2.6	2.8	2.7	2.7
Elongation at break (%)									
MD	1744	1684	1704	1710	1659	1756	1793	1654	1715
TD	1890	1868	1874	1807	1812	1889	1889	1852	1868

 $1^{#}$: AF/EP/NR composites [m(EP) variable]; $2^{#}$: AF/EP/2E4MZ/NR composites [m(2E4MZ)/ m(EP) is 5%], MD: sample with fiber parallel to the tensile force direction; TD: sample with fiber perpendicular to the tensile force direction.



under the catalyst of imidazole, which improves the interface bonding between short aramid fiber and rubber matrix.

2. The interface bonding between NR and processed AF is significantly improved by CaCl₂-EP/2E4MZ system compared with unprocessed AF. The results show that NR/AR composite has the best comprehensive performances when the content of m(EP)/m(AF) is 3% (including accelerator 2E4MZ), and the tensile strength, tear strength and tensile modulus at 300% elongation of AF/NR composites increase by 9.2%, 15.0%, and 18.4%, respectively (the direction of MD), compared with the composites with uncoated AF.

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