

Mechanical Properties of Silicon Carbon Black Filled Natural Rubber Elastomer

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Abstract A pyrolyzed ash containing about 50% carbon, named silicon carbon black(SiCB), was prepared by the anoxic pyrolysis of rice husk. Fourier transform infrared spectroscopy(FTIR), thermogravimetric analysis(TGA), Brunauer-Emmett-Teller(BET), transmission electron microscopy(TEM) and universal material testing machine were used to analyze the stress-strain relationship, Mullins effect and static viscoelastic properties of SiCB-filled vulcanized natural rubber(NR), and SiCB was compared with a commercially available semi-reinforcing furnace(SRF) carbon black. The results show that the vulcanized natural rubber filled with SiCB had similar reinforcing properties to those of that filled with traditional SRF, but obvious differences between them exist in stress-strain properties and stress softening resistance. We tried to discuss the related phenomena with the aid of the modified two-layer theory. And it is successfully predicted and verified that SiCB has good compression resistance and obvious stress relaxation advantages in compression stress relaxation.

Keywords Silicon carbon black; Natural rubber; Stress-strain relationship; Stress relaxation

1 Introduction

Carbon black and carbon white are traditional elastomer reinforcing agents and they can interact with elastomer to form particles with double-layer structure. These particles are embedded in vulcanized rubber mesh with complicated 3D network^[1], forming a composite system. The composite elastic system has moderate rigidity and good viscoelasticity for industrial application.

Nowadays, with the further implementation of environmental protection and the requirements of sustainable development, more and more attention has been paid to finding and utilizing renewable resources instead of traditional reinforcement complexes. Rice husk ash(RHA) is the product of rice husk combustion. Because the rice husk contains 80% lignocellulose and 20% silicon dioxide, and they are regularly distributed in the rice husk, the pyrolyzed rice husk ash(PRHA) must contain both biomass carbon and silicon dioxide. Studies^[2–4] have shown that the stable chemical bonds exist between biomass carbon and silicon dioxide. Regularly, PRHA has fine particle size(<50 μm), irregular shape and high porosity, which makes it possible for PRHA to be used to form an appropriate filling elastic system in polymers^[5,6]. For example, Haxo *et al.*^[7] used rice husk ash prepared under special conditions as a reinforcing filler to form elastomers in styrene butadiene rubber(SBR), ethylene-propylene-diene monomer(EPDM) and natural rubber(NR). It is pointed out in Haxo and Metha's work that the filler itself has no adversely

effect on the vulcanization and crosslinking process or the aging behavior of rubber-based elastomers. On the other hand, Oui *et al.*^[8] studied the effects of filler loading between RHA and commercial fillers in natural rubber system. And they found that the mechanical properties(tensile strength, modulus, hardness, and wear resistance) of RHA are different from those of carbon black and/or carbon white. However, most of the RHA samples used in those studies, with low carbon content, low yield and unstable properties, were obtained under oxygen-enriched combustion.

According to the structural characteristics of the periodic arrangement of nano-silica and natural polymers in rice husk, we designed and prepared silicon/carbon biphasic materials, named silicon carbon black(SiCB) with a mass ratio of 43:57, uniform particle distribution and a diameter of 10—35 μm *via* selective pyrolysis and directional comminution technique. Earlier studies have found that SiCB as filler needs no surface treatment to increase the compatibility with rubber because of its high carbon content, and SiCB has reached a certain level in the reinforcement of natural rubber. At the same time, we have found that the change of the network structure of composite elastomer of SiCB and natural rubber under dynamic strain can directly reflect the elastomer performance, and make a possible prediction of the elastomer under stress change. Mullins effect^[9,10] is the most convincing phenomenon to characterize the change of filler network structure under dynamic strain. On the other hand, stress relaxation is one of the viscoelastic properties of rubber materials, which mainly reflects the

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movement of molecules in elastomeric materials^[11].

Therefore, the stress-strain description, Mullins effect and stress relaxation of SiCB filled rubber, a silicon/carbon biphasic material, were explored in this paper. We will try to understand its structural particularity, describe the impact of structural particularity on viscoelastic properties, and then predict the performance of the composite elastomers.

2 Experimental

2.1 Reagents and Instruments

Ribbed smoked sheet 1(RSS1) was purchased from Shanghai Duokang Industrial Co., Ltd.(Shanghai, China); fast extruding furnace(FEF) carbon black, and semi-reinforcing furnace(SRF) carbon black were purchased from Jiangxi Black Cat Carbon Black Co., Ltd.(Nanchang, China); SiCB was made by Jilin Kaiyu Biomass Development and Utilization Co., Ltd.(Changchun, China); zinc oxide and stearic acid with analytical purity were purchased from Sinopharm Group Chemical Reagent Co., Ltd.(Beijing, China); accelerators, antioxidants and sulphur were all chemically pure.

CMT-20 universal testing machine was from Jinan Lian-gong Testing Technology Co., Ltd.(Jinan, China); DTG-60H Thermogravimetric Analyzer and FTIR-8400S Fourier Transform Infrared Spectrometer were made by Shimadzu Corporation; ASAP-2420 Fully Automatic Surface Physical Adsorption Instrument was from Micromeritics Corporation(USA); field emission transmission electron microscope(TEM) was made by FEI Corporation.

2.2 Experimental Process

2.2.1 Preparation of SiCB by Gasification Pyrolysis

After an appropriate amount of rice husk was filled in the down draft gasifier, and then ignited, the proper air intake was maintained, with a thickness of 30—40 cm of the combustion layer kept, and the furnace temperature was controlled at 600—700 °C. Intermittently rice husk was added to maintain continuous pyrolysis in the furnace while the ash was discharged by vibration. The ash was naturally cooled to about 200 °C and sent to the separation and secondary crushing section to collect the powder of SiCB below 35 μm.

2.2.2 Preparation of Vulcanized Test Sample

Mixed rubber: the speed of mixer was 30 r/min, the temperature of mixing chamber was 120 °C, and the pressure of mixer top cover was set at 0.6 MPa. According to the standard tread formula of natural rubber, the final rubber was obtained

by two-step mixing. Vulcanized rubber: the sulfuration temperature was 140 °C, the vulcanization pressure was 20 MPa. The standard test sample was made by molding.

2.2.3 Filler Characterization

The filler was tested by thermogravimetric analysis and the test conditions were as follows: the temperature was from room temperature to 800 °C, and the heating rate was 10 °C/min, nitrogen atmosphere and air atmosphere were used, respectively. The specific surface area of the filler was determined by the automatic physical adsorption apparatus. The structure of the filler was determined by the absorption value of dibutyl phthalate, and the average value was taken from the measurements of three times. Fourier transform infrared spectroscopy(FTIR) was used to measure the filler and the wave-number from 400 cm⁻¹ to 4000 cm⁻¹. After the filler was dispersed, the sample was observed by means of field transmission electron microscopy at 200 kV.

2.2.4 Vulcanization Performance Test

Cyclic tensile stress and strain tests were carried out on a CMT-20 universal testing machine at a tensile strain rate of 0.075 s⁻¹. The strip vulcanization samples were stretched repeatedly according to the test standard, and the stress changes during the whole process were recorded. Constant strain compressive stress relaxation was made at a standard laboratory temperature, the specimen with the known height was compressed with CMT-20 universal testing machine to the specified strain in 90 min, and the stress change per 0.1 s was recorded. Cyclic compressive stress and strain were made at a standard laboratory temperature, and the specimen with a known height was reciprocally compressed with the CMT-20 universal testing machine at a compressive strain rate of 0.4 min⁻¹ to the specified strain 4 times, and the stress changes were recorded in the whole process.

3 Results and Discussion

In order to clearly reflect the characteristics of SiCB, commercial fillers(FEF and SRF) were selected as the comparison for the test and characterization. The static mechanical results of all reinforcement samples are shown in Table 1. As can be seen from Table 1, the static mechanical properties of the natural rubber(NR) with SiCB as reinforcement filler are almost the same as those of that with semi-reinforced SRF as filler and weaker than those of that with reinforcement FEF as filler. All the following tests in this article will be discussed with reference data of SRF.

Table 1 General mechanical characterizations of different reinforcing fillers

Filler	Tensile strength/MPa	Elongation(%)	100% Strain-stress//MPa	300% Strain-stress/MPa	Right-angled tearing strength/(kN·m ⁻¹)
SiCB	14.64	1339.38	1.59	3.16	39.96
FEF	19.93	794.58	2.42	7.03	51.88
SRF	15.11	1044.90	1.46	3.72	43.76

3.1 Thermogravimetric Analysis

The curves of filler burning in nitrogen and air are shown in Fig.1 and Fig.2, respectively. When the temperature rises to

800 °C in nitrogen atmosphere, the mass loss of SRF or SiCB is separately 5% or 7%; in air atmosphere, the mass loss of SRF begins at 550 °C apparently, and completely decomposition occurs at 780 °C. The curves of SiCB have two distinct stages. The first stage of mass loss occurs below 100 °C, and a small

amount of this loss comes from the adsorbed free water in the sample, and the rest is caused by volatile molecules, accounting for about 7% of the total mass. The second stage of mass loss occurs at around 450 °C, and the mass loss rate is almost 50%. This process is mainly the oxidation and decomposition of the carbon component of SiCB, leaving only about 40% of the total mass of silica.

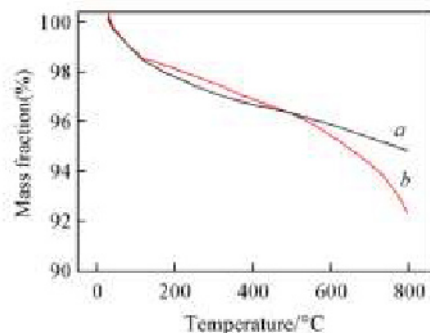


Fig.1 TG curves of SRF(a) and SiCB(b) in N₂ atmosphere

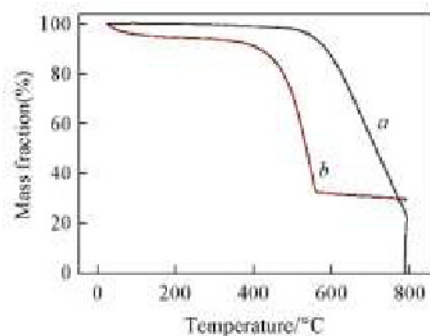


Fig.2 TG curves of SRF(a) and SiCB(b) in air

3.2 Structure and BET Analysis

The structure of filler is one of the important factors affecting the reinforcing effect of polymer. The oil absorption value reflects the compactness of filler structure. The closer the structure is, the higher the structural compactness is, and the greater the oil absorption value is. Generally speaking, high structured fillers show that the larger the void volume of matrix molecules, the stronger the binding capacity of filler molecules and matrix molecules, and the better the reinforcement performance^[12]. The Dibutyl Phthalate oil absorption values (DBP) and specific surface areas of the two fillers are shown in Table 2. The oil absorption value of SRF is about twice that of SiCB, indicating that SRF should contain more developed branched chains and there may be no aggregated branch chain structure in SiCB. However, the specific surface area of SiCB reaches 239.42 m²/g, which might be attributed to the pore structure of SiCB inherited from rice husk carbonization.

Table 2 Oil absorption factor and BET of SRF and SiCB

Filler	DBP/(cm ³ ·100 g ⁻¹)	BET/(m ² ·g ⁻¹)
SRF	131.69	41.71
SiCB	67.02	239.42

3.3 TEM Analysis

Fig.3(A) and (B) show the TEM images of SRF and SiCB,

respectively. From Fig.3, we can see that the SRF aggregates are grape-like chains and the primary carbon black aggregates are about 50 nm in size, while the SiCB is massive, and there is no obvious chain structure. The aggregates of SiCB are about 300 nm in size, composed of spheres of about 20 nm in size. The morphology may correspond to the oil absorption value. SRF has more chain branch structure, so it is high structured and its oil absorption value is larger; the surface roughness of SiCB is related to its carbonization process and the morphology of SiO₂. These two factors lead to the easy formation of pores and cracks on the particle, which provides larger BET data to SiCB.

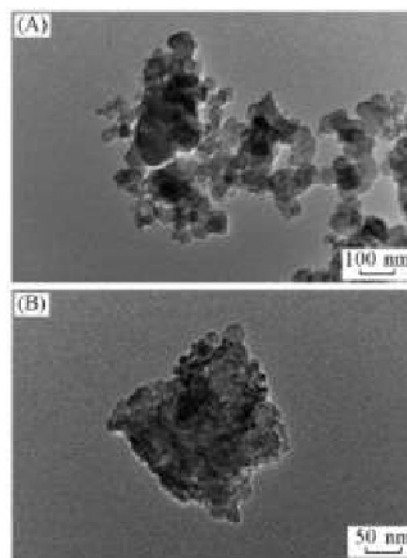


Fig.3 TEM images of SRF(A) and SiCB(B)

3.4 FTIR Analysis

The FTIR spectra of SiCB and SRF are shown in Fig.4. Owing to the presence of large amounts of silica in SiCB, obvious differences in the spectrum can be observed. There are asymmetric stretching vibration peaks of Si—O—Si of SiCB from 1000 cm⁻¹ to 1300 cm⁻¹, and the swing, symmetric stretching and asymmetric stretching vibration peaks of Si—O—Si bonds at 450, 800 and 1080 cm⁻¹, respectively. While in the FTIR spectrum of SRF, the peak at 3680 cm⁻¹ is attributed to the hydrogen-bonding interaction between water and phenolic hydroxyl group. The stretching vibration peak at 1737 cm⁻¹ is C=O group corresponding to carboxyl and phenolic ester on the surface of carbon black. The peak at 1620 cm⁻¹ corresponds

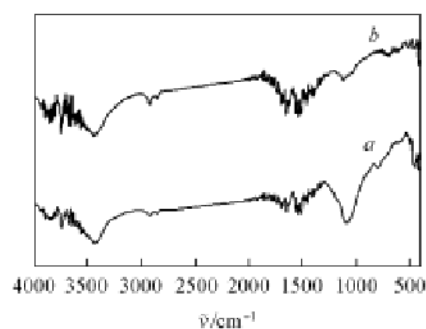


Fig.4 FTIR spectra of SRF(a) and SiCB(b)

to the stretching vibration of C=C aromatic ring. These characteristic peaks fully indicate that a considerable number of active groups exist on the surface of SRF, while absorption peaks at 3200 and 1705 cm^{-1} in SiCB spectrum may indicate carboxyl groups on SiCB surface.

3.5 Effect of SRF or SiCB on Mullins Effect of Vulcanization in NR System

Mullins effect refers to the stress required to reach a certain strain for the first time, which is always greater than that required for subsequent loading when carbon black filled rubber is stretched. This effect is also called stress softening phenomenon^[13,14]. As shown in Fig.5, filler SiCB, like SRF, causes stress softening during cyclic tensile loading and unloading. But the stress softening of SRF is more obvious than that of SiCB. Fig.5 shows that the maximum stress of SRF or SiCB at 50 parts per hundreds of rubber(phr) is decreased by 4.599% or 3.303%, respectively, after the fourth cyclic loading and unloading at 350% strain.

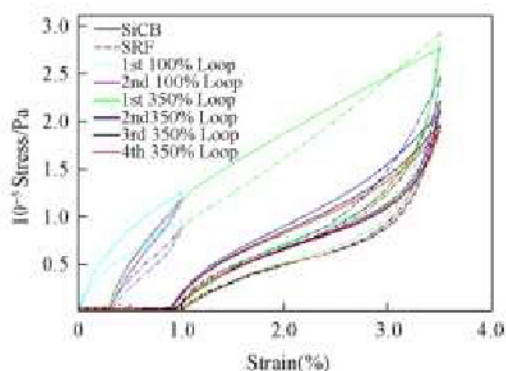


Fig.5 Mullins effect observed on SRF or SiCB filled NR submitted to cyclic uniaxial tension

It should be pointed out that in the low strain range (Strain<3), the stress of SiCB is greater than that of SRF under the corresponding strain in both loading and unloading regions. However, in the high strain region, the inversion occurs, and the position of the inversion point in the loading region moves to the high strain region with the increase of the number of cycles.

Fig.6 lists the stress-strain curves of vulcanized NR systems with different fillers at different phr under uniaxial tension. It can be seen from the Fig.6 that with the increasing of the phr, the constant tensile stress reaches a certain strain for the first time, in the low strain region($\lambda < 1.0$) and the high strain region($\lambda < 3.0$). It shows an increasing trend, and the increase of it caused by SRF is greater, especially in the high strain region. At the same time, the area of hysteresis ring of rubber cyclic tension loading or unloading curve is also increasing, which is generally defined as the energy consumption of material^[15]. The energy consumption is calculated according to the following formula:

$$U_{\text{hyst}} = \frac{1}{h_0} \int_{\text{loading}}^* \sigma d\delta - \int_{\text{unloading}}^* \sigma d\delta$$

where, U_{hyst} is the energy consumption; h_0 is the length of the sample; σ is the tensile stress; δ is the tensile strain.

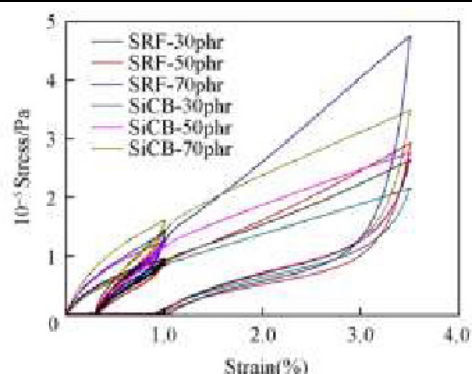


Fig.6 Stress-strain curves of vulcanized NR systems with SRF or SiCB at the different filler loading(phr)

The energy consumption values of vulcanized rubber filled with SRF fillers at 30, 50 and 70 phr during cyclic stretching are 104.532, 143.481 and 249.073 kJ/m^3 , then 72.431, 120.804 and 175.375 kJ/m^3 for SiCB fillers. From the relationship between energy consumption and filler phr, the two fillers have the same law as the first strain stress, that is, with the increase of filler phr, the internal friction energy is also increasing. In the filled rubber, the interaction between rubber and filler will hinder the movement of molecular chain. In addition, the destruction and reconstruction of the network of filler aggregates will lead to the increase of energy consumption with the increase of filler content. This is mainly because that with the increase of filler phr, the crosslinking density increases, and the filler plays a good role in fixing the rubber grid, there are more filler-filler and filler-rubber bonds in the sample^[16,17].

However, with the increase of the number of tensile unloading cycles, the SiCB curves show different results. As shown in Fig.7, the maximum stress inversely decreases with the increase of the amount of SiCB, which is completely different from that shown by SRF.

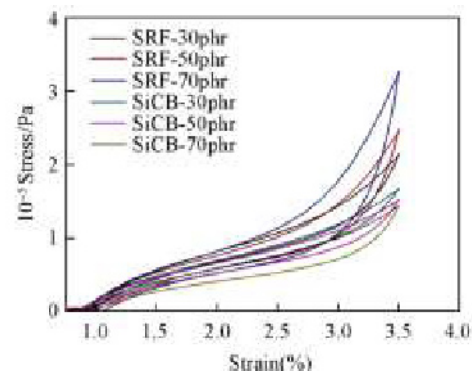


Fig.7 Stress-strain curves of vulcanized NR filled with SRF or SiCB at different filler loading submitted to the sixth cyclic uniaxial tension

3.6 Mechanism and Performance Prediction

According to the two-layer theory of Fukahori^[1], vulcanized rubber forms a double-layer wrapped structure with a total thickness of about 5—10 nm on the surface of filler particles, and these wrapped particles are embedded in the

cross-linking network of vulcanized rubber, as shown in Fig.8(A). The inner thin glass hard layer(GH layer) is attached to the surface of the particles, and its contribution to the viscoelasticity and reinforcement of the elastomer is less. The outer sticky hard layers(SH layer) can overlap and cohere with each other to form a complex and huge spatial network structure, which is the main body to provide corresponding strength for the filled elastomer under uniaxial tension.

When SiCB is filled in elastomers(Fig.9), on the one hand,

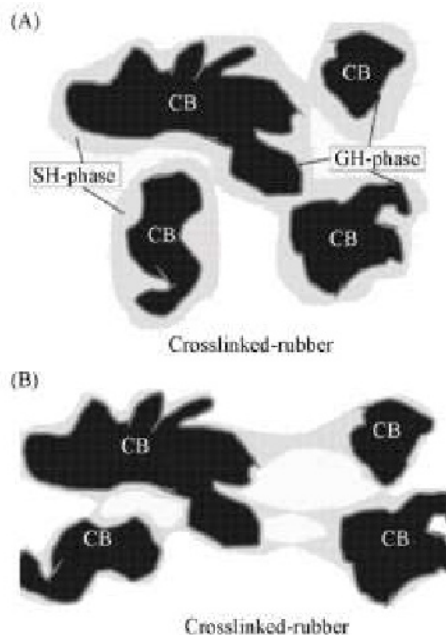


Fig.8 Modified double-layer interface model consisted of a GH layer and an SH layer(A) and a stretched SH layer(B) in cycle uniaxial tension when using CB as filler

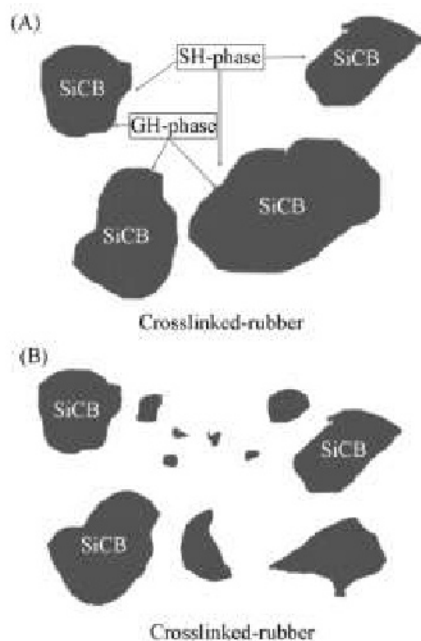


Fig.9 Modified double-layer interface model consisted of a GH layer and an SH layer(A) and a stretched SH layer(B) in cycle uniaxial tension when using SiCB as filler

the surface functional groups of SiCB are obviously different from those of conventional carbon black, such as SRF, which will have an obvious effect on the formation of GH layer. On the other hand, SiCB has a relatively small initial particle size, a large specific surface area and a relatively high degree of roughness of the surface, so the rubber with SiCB filler is easier to form cross-linked meshes to increase the overall crosslinking density of vulcanized system. The high strain of SiCB in low strain zone in Fig.5 is the direct evidence^[18].

Owing to the insufficient chain structure of SiCB on the aggregates, the number of residence adhesives on the surface of SiCB will be less. When the elastomer filled with SiCB is under uniaxial tension, especially in the case of large strain under external force, the GH layer may break and peel off from the surface of SiCB. At the same time, under the deformation of the SH layer and the cross-linked rubber network, the aggregates of SiCB may break up, and a large number of nano-silica particles will disperse. Many of these particles do not have or locally have a double-layer structure, which can provide limited help to the stress of the elastomer under large strain, resulting in the crack of elastomer under large strain stress. In this paper, the stress and internal friction data under high strain have been clearly reflected.

The differences between SiCB filled elastomer and SRF filled elastomer in strain stress and stress softening effect can be clearly discussed here. In the small strain range, the main stress of the elastic system is provided by the cross-linked NR molecular network, and SiCB filler is help to the cross-linking, so SiCB filled elastomer shows an obviously better stress than SRF filled one in this region. But when the strain reaches a relatively large range, SiCB is broken, GH layer is broken, and many such small particles scatter. Although the SH layer can provide some strength, the strength of the SH layer decreases significantly due to the breakage of the particles and GH layer. The strength from the vulcanization cross-linking network is still an important provider of stress, and this tensile stress produces a slight effect of stress softening^[9]. However, after repeated stress loading and unloading, many molecular chains in the crosslinking network will be blocked and fixed by the particles released by SiCB, and the stress intensity will be correspondingly reduced. With the stress softening effect of effective SH layer, the elastomers filled with SiCB will still show the characteristics of stress softening effect. Because the main stress intensity comes from the cross-linking network, the greater the SiCB filling is, the more the stress of the specimen decreases, which is reflected in Fig.7.

In order to verify the validity of the proposed theory, the compressive stress softening and compressive relaxation experiments of the samples were carried out. If our theory is correct, the relaxation of SiCB sample will decrease slightly due to the higher cross-linking density of SiCB and the immobilization of small released particles on the molecular chains. Moreover, because the compression can be equivalent to biaxial tension, the stress softening effect will also appear. However, the deformation caused by compression is relatively small, and SiCB may not show the same abnormal phenomenon in stress softening as in tensile process.

3.7 Effect of phr Dosage of SRF or SiCB on Compressive Stress and Strain of Vulcanized NR Systems

The compressive stress-strain curves of NR vulcanizates with 50 phr of SRF or SiCB fillers are shown in Fig.10. It can be seen that the phenomenon of stress softening during cyclic compression loading and unloading is not so obvious in tensile process, and it is obvious that the stress of SiCB vulcanizate is higher than that of SRF vulcanizate under the same strain. This means that under smaller strain, SiCB can provide greater stress and good compression resistance.

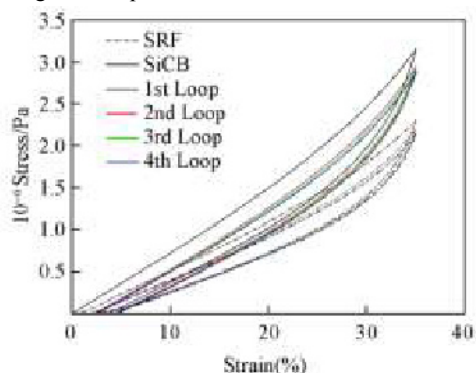


Fig.10 Stress-strain curves of 50 phr SRF or SiCB filled NR submitted to cyclic loading and unloading tests

At the same time, the maximum stress of 35% of 50 phr SRF or SiCB vulcanizates after 4th cyclic compression are 98.972% or 99.042%, respectively, of the third time, which indicates that the stress softening phenomenon of SiCB vulcanizate is weaker. Therefore, in the compression stress-strain experiment, SiCB shows better reinforcement performance.

Fig.11 is the 4th cyclic compression curve of NR vulcanizates with different phr of SRF or SiCB. The constant strain compression stresses of both the fillers increase with the increase of phr. The areas of hysteresis loops of loading-unloading curves of rubber cyclic compression increase with the increase of phr^[19,20]. The energy consumption of vulcanized rubber filled with SRF fillers at 30, 50 and 70 phr during cyclic stretching are 126.539, 269.651 and 478.857 kJ/m³, then

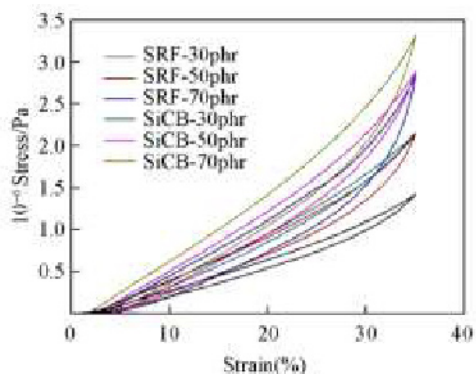


Fig.11 Stress-strain curves of vulcanized NR samples filled with SRF or SiCB at different filler loading submitted to the fourth cyclic uniaxial compression

115.714, 263.086 and 487.600 kJ/m³ for SiCB fillers during compression.

3.8 Effect of phr Dosage of SRF or SiCB on Compressive Stress Relaxation of Vulcanized NR Systems with SRF or SiCB

Stress relaxation is one of the most important mechanical properties of viscoelastic materials. Under certain strain conditions, after a long time, the stress that keeps its deformation will gradually decrease, and this phenomenon is called stress relaxation^[21,22].

Fig.12 shows the compressive stress relaxation curves of NR vulcanizates with SRF or SiCB fillers at different phr loading. It can be seen from Fig.12 that the two fillers show the same regularity in the change of compressive stress relaxation. The relaxation factor decays faster at the beginning^[23], and then gradually decreases and tends to a small slope, with a linear negative correlation. With the increase of filler phr, the relaxation factor of SRF filled sample decreases more^[24], while that of SiCB filled sample decreases less. From the compression relaxation test, we can see that the stress relaxation rate of SiCB is smaller and the elasticity is better. If SiCB is used as a filler of rubber products, its load bearing, shock absorption and sealing effect will be better than those of SRF.

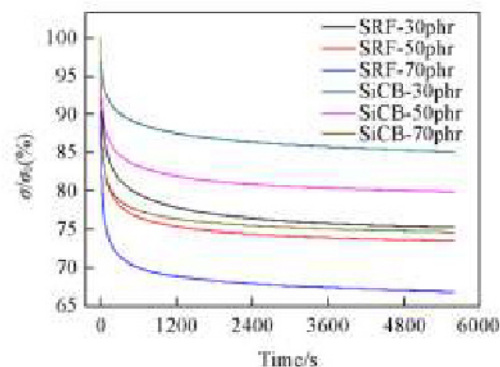


Fig.12 Compression stress relaxation curves of vulcanized NR samples filled with SRF or SiCB at different filler loading

4 Conclusions

From the above analysis, it can be seen that like SRF or SiCB, as a new filler, will produce stress softening and stress relaxation in natural rubber, and at the same filler phr, the vulcanizate with SiCB as filler exhibits better viscoelasticity than the corresponding vulcanizate with SRF as filler. Under uniaxial tension, the maximum stress of SRF or SiCB at 50 phr was decreased by 4.599% or 3.303%, respectively, after the sixth cyclic loading and unloading at 350% strain, and the relaxation factors of 70 phr SRF or SiCB at constant strain relaxation are 0.669 or 0.750, respectively. SiCB shows better resistance to stress softening and relaxation resistance than SRF. These characteristics and properties are directly related to the surface state or structure morphology of SiCB. We have explained the Mullins effect on the vulcanized natural rubber filled with SiCB very well with the modified double-layer

model theory, which can predict the good compression resistance and relaxation resistance. So long as we find a suitable method to modify SiCB so as to increase its surface activity and modify its structure, and also enhance its reinforcing property to rubber. It is expected to further expand its application scope, and make this kind of biochar with rice husk as raw material possess a better application prospect.

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