Study on Preparation and Performance of Biomass carbon/Natural Rubber Composite

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Abstract

Natural rubber (NR)/biocarbon composites were prepared by mechanical blending. Thermogravimetric (TG) analysis method, dynamic thermomechanical research method, infrared test and other research methods were used to study the change process of each component and its composite materials. The results showed that biomass carbon materials have a certain reinforcing effect in rubber. At the same time, it is necessary to pay attention to adjusting the process conditions and the ratio of raw materials when using the mechanical blending method to prepare composite materials. This study determined that the component content of the NR composite prepared by the mechanical blending method has good maneuverability, which can provide a reference for the research on the high-value transformation and utilization of biomass resources.

Keywords

Mechanical blending method; natural rubber; biomass carbon; composite materials.

1. Introduction

Biomass waste is a widespread resource in nature. In recent years, researchers have used biomass materials to reinforce rubber and have achieved good results. However, few people have proposed using biomass carbonized inorganics to replace carbon black (CB) as a supplement. Strong rubber. Biomass resource-reinforced rubbers are mostly cellulose extracted from biomass resources to reinforce rubber. Based on the above-mentioned factors, the use of biomass carbon (BC) as a reinforcing agent in this study can greatly broaden the application range of waste biomass resources. , Improve economic efficiency, can also replace CB produced by petroleum cracking, this research will greatly promote the sustainable development strategy of energy. This paper studies bio-carbon/natural rubber composite materials, in which bio-carbon is the reinforcing phase and natural rubber is the matrix phase. By testing the physical properties of composite materials after vulcanization and molding, this research is of great significance for making full use of waste biomass resources.

2. Experiment

2.1. Main raw materials

Natural rubber latex (NRL), the mass fraction of solids is 0.6, Hainan Rubber Group; Biological carbon water dispersion, the mass fraction is 0.4, self-made. Vulcanization system, commercially available.

2.2.   Main equipment and instruments

JTC-572 open type rubber mixing machine, manufactured by Zhanjiang Machinery Plant in Guangdong Province; XLB-D 350×350×2 flat vulcanizing press, Shanghai Rubber Machinery Factory; XL-50A tensile testing machine, Guangzhou Guangcai Testing Instrument Co., Ltd.; LX-A Shore Rubber Hardness Tester, Jiangdu Mingzhu Testing Machinery Factory; XUT-Thickness Gauge, Yingkou Material Testing Machine Co., Ltd.; Mettle AB265-S Electronic Balance, Shanghai Yousheng Weighing Apparatus Co., Ltd. DY-800Y multifunctional sample preparation crusher, product of Henan Xinyuan Coal Quality Analysis Instrument Co., Ltd.; QM-QX4 type ball mill, product of Nanjing Nanda Instrument Co., Ltd.; SK-168 open mill, product of Shanghai Shuangyi Rubber Machinery Co., Ltd. ; QLB-400X400X2 flat vulcanizing machine, product of Qingdao Yadong Rubber Machinery Co., Ltd.; MM4130C type rotorless vulcanizer; TS2005b type tensile testing machine, product of Uken Technology Co., Ltd.

2.3.   Sample preparation

The preparation process of bio-carbon/natural rubber composite material is divided into 3 steps: (1) Preparation of bio-carbon: crush the macadamia husk to 0.8mm (2) put in a tube furnace and pour nitrogen into it, keep it at 400 ℃ for 3 hours (3) Molding and processing of biomass carbon/natural rubber composite materials. Add biomass carbon to deionized water in a certain proportion; add natural rubber latex (solid content 0.62) into the solution, and finally add acetic acid for demulsification, coagulation and leaching, and dry for use. The rubber compound is mixed on an open mill. First masticate the NR with MCC dispersed on an open mill for 12 times, then add zinc oxide, stearic acid and accelerator, cut 3 knives on the left and right sides, add sulfur and then cut 3 knives on the left and right sides, and then cut the slices 6 times. The rubber compound is vulcanized on a plate vulcanizer under the vulcanization condition of 145 ℃×t_{90}.

2.4.   Test analysis

(1) Physical performance test. The Shore A hardness and tensile properties of composite materials are tested in accordance with the corresponding national standards.

(2) XRD analysis. The XRD spectrum of the composite material was tested with an XRD instrument, using a Cu/Kα emission source, a voltage of 40 kV, a current of 40 mA, a scanning speed of 5 ℃·min-1, and a test range of 5°-45°.

(3) SEM analysis. The morphology of the tensile section of the composite material was observed by SEM, and the tensile section was sprayed with gold.

3.   Results and discussion

3.1.   Physical properties

The effect of the amount of biochar on the physical properties of biochar/natural rubber (NR) composites is shown in Table 1. It can be seen from Table 1 that compared with the NR compound without biochar, the hardness, tensile stress and tensile strength of the biochar/NR composite are increased, especially when the amount of biochar is 2 and 3 parts. , The tensile strength of the bio-carbon/NR composite material exceeds 24 MPa, and the tensile strength of the bio-carbon/NR composite material is greater when the amount of biomass carbon is 3 parts, which is 10. 2% higher than that of the pure NR compound, It shows that biochar can effectively increase the tensile strength of NR.

Table 1 The influence of the amount of biochar on the physical properties of composite materials

project	Biological carbon consumption / serving				
	0	1	2	3	4
Shore A hardness	41	41	42	42	41
300% fixed elongation stress/MPa	1.89	2.07	2.17	2.42	2.35
500% fixed elongation stress/MPa	3.83	7.06	7.06	9.77	8.45
Tensile Strength/MPa	22.09	22.26	22.22	24.34	22.94
Elongation at break/%	735	658	649	656	649

3.2. XRD analysis

The XRD spectrum of the BC/NR composite before and after stretching is shown in Figure 1. It can be seen from Figure 2 that the characteristic peaks (002) and (100) of biochar are more obvious. Natural rubber composite materials also show weaker characteristic peaks, because the content of bio-carbon in composite materials accounts for a minority. There is no obvious difference between the natural rubber composite material and the BC crystal peak shape and crystallinity, indicating that the presence of natural rubber does not affect the degree of graphitization of BC.
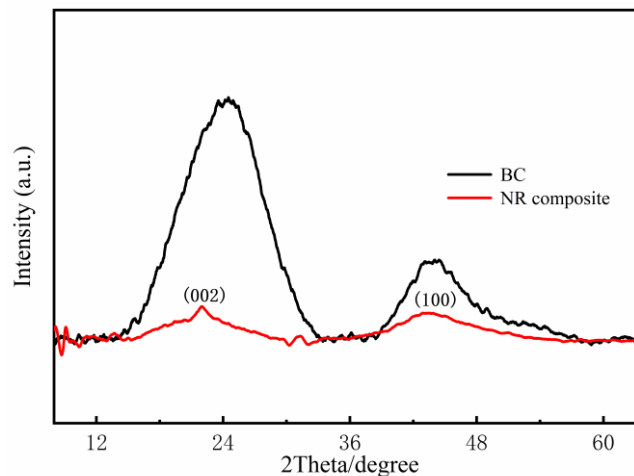

Figure 1: XRD analysis of composite materials

3.3. SEM analysis

The SEM picture of the tensile section morphology of the BC/NR composite is shown in Figure 2.It can be seen from Figure 2 that the size of the BC precipitated in the BC/NR composite material is quite different, the diameter of the large particles is about 900 nm, these particles are poorly combined with the NR matrix, and they are easy to peel off from the NR matrix; With a diameter of 0.5 to 1 μm, these particles have a good combination with the NR matrix and play a major role in reinforcement. It can also be seen from Figure 2(c) and (d) that some BC fibrous particles with aspect ratio are precipitated in the NR matrix, and these particles may be beneficial to improve the modulus of the BC/NR composite.
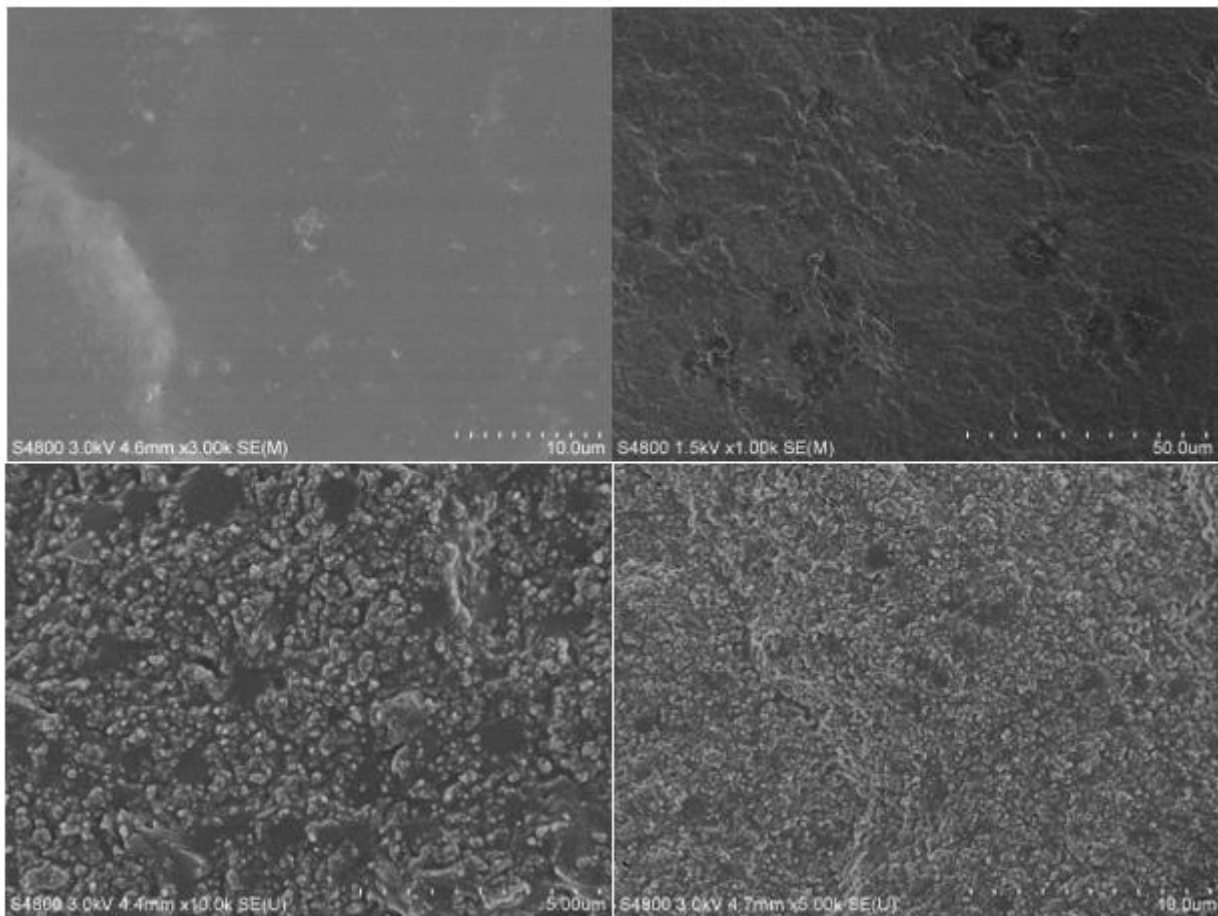
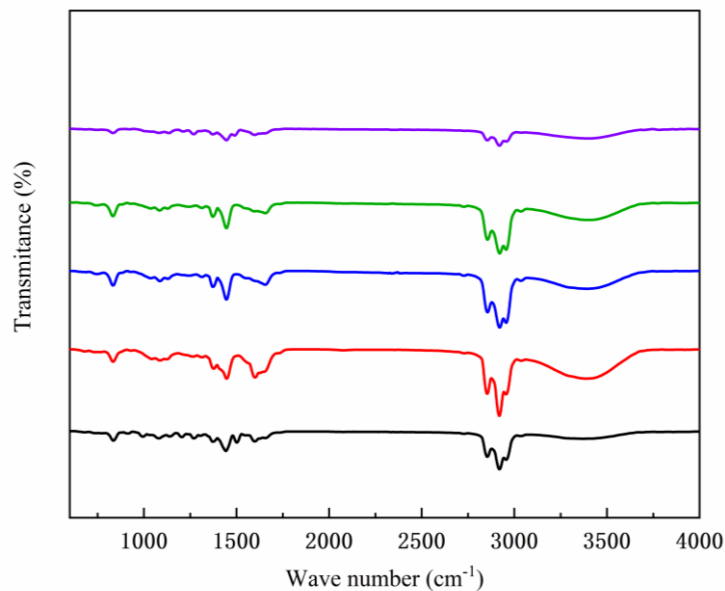Figure 2: SEM analysis of different filling amounts

Figure 3: Fourier curve of composite material

3.4.   FTIR analysis of composite materials

The FTIR spectra of pure rubber and composite materials are shown in Figure 3. It can be seen from Figure 3 that, compared with pure rubber, the composite material has a $-CH_2-$ stretching vibration absorption peak at 2899 cm^{-1} and a peak at 1467 cm-1. $-CH_2-$ bending vibration absorption peak is enhanced, the absorption peak at 814 cm-1 corresponds to the absorption

peaks of antisymmetric stretching vibration, symmetric stretching vibration and bending vibration of CO-Si, and the absorption peaks at 1200^{-1} and 670 cm^{-1} respectively Corresponding to the absorption peaks of stretching vibration and bending vibration of Si-CH2, the absorption peaks at 1100, 1000 and 630 cm^{-1} correspond to the absorption peaks of Si-O.

3.5. Thermogravimetric analysis of composite materials

It can be seen from Figure 4 that the thermal mass loss process of natural rubber composites is mainly divided into two stages. The temperature in the first stage is 100-200 ℃, and the mass loss rate is 7.58%. This may be the moisture and volatile components in the latex. Caused by volatilization; the second stage temperature is 200-500 ℃, and the mass loss rate is large, reaching 88.4%, which may be caused by the pyrolysis of NR and the loss of water-soluble matter and acetone extract; natural rubber latex flocculated by TG The mass fraction of the residue after the test is 0.0402, and the residue may be the ash content in NR. It can be seen from Figure 4 that there is only one major mass loss platform in the thermal decomposition process. The rubber basically does not decompose before 200 °C, and thermal decomposition begins after 200 °C. As the temperature rises, the thermal decomposition rate gradually increases to reach The decomposition is almost complete at 600 ℃, and the thermal cracking of the molecular chain occurs, accompanied by the oxidation of carbon.
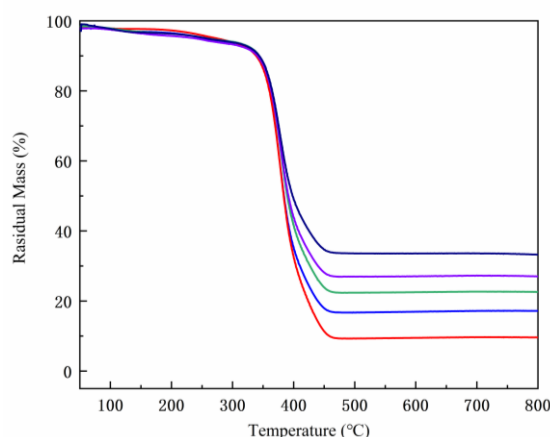

Figure 4: Degradation curve of composite material

3.6. Dynamic mechanical properties of natural rubber composites

Dynamic mechanical properties are the study of the changes in the storage modulus (G′) and loss factor (tanδ) of materials at different temperatures. The G′-temperature and tanδ-temperature curves of BC/NR composite materials are shown in Fig. 5. From Fig. 5(a), it can be seen that: from -75 to 20 ℃, the G′ of the four composite materials gradually decreases, and thereafter It tends to be flat; the initial G' of BC/NR composites is slightly lower than that of BC/NR composites, while the initial G' of BC/NR composites is slightly higher than that of NR composites, indicating that BC exhibits a certain reinforcing effect. Tanδ can characterize internal friction and is the ratio of loss modulus (E″) and E′. The larger the tanδ, the higher the heat generated by the internal friction of the material. The peak value of tanδ corresponds to the glass transition temperature (Tg). From Figure 5(b) It can be seen that the corresponding temperature of the tanδ peak of the four composite materials is around -42 ℃; the tanδ peak of the BC/NR composite material increases with the increase of the bio-carbon content. When the bio-carbon content is low, the composite material tanδ peak is obviously higher Small, this is due to the increased cross-linking density of the BC/NR composite material, which limits the movement of the rubber molecular chain, and the interaction between the filler and the rubber matrix is large, which reduces the friction and heat generation between the interface.
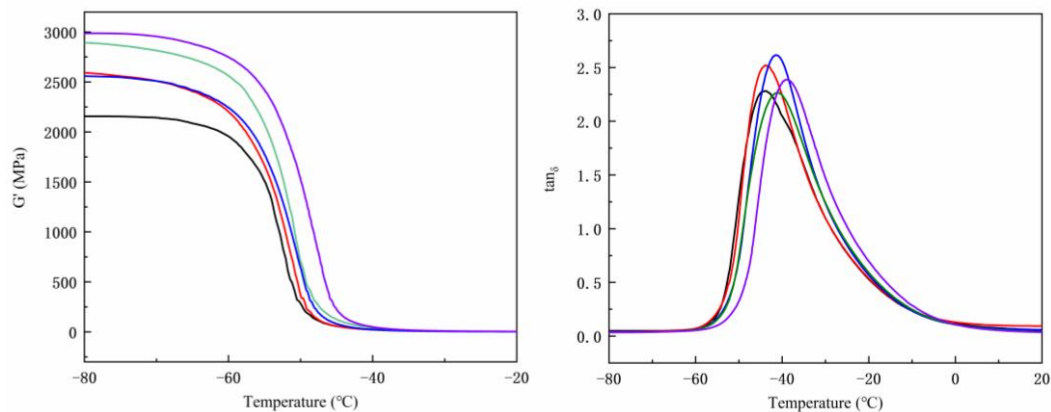
Figure 5: Analysis of dynamic mechanical properties of natural rubber composites

4. Conclusion

The NR/bio-carbon composite material was successfully prepared by the mechanical blending method.

Using TG and infrared analysis methods to study the quality change process of each component and its composite material under the program control temperature. According to the mass loss of a single component at a specific temperature, it is determined by a certain method based on its residual content. The actual content of each component in the composite material has a certain deviation from the theoretical content, which proves that the mechanical blending method will cause the quality loss of the composite material. When using the mechanical blending method to prepare the composite material, attention should be paid to adjusting the process conditions and raw materials. Matching ratio.

Determination of the composition content of the NR-based composite material prepared by the mechanical blending method through dynamic mechanical performance analysis, which can provide a reference for the study of composite materials prepared by the mechanical blending method.

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