Effects of Different Drying Methods on the Microstructure and Thermal Oxidative Aging Resistance of Natural Rubber

Chen Mei,[1] Wang Yong-Zhou,[1] Lu Guang,[1] Wang Xiao-Ping[2]

[1]*Ministry of Agriculture Key Laboratory of Tropical Crops Processing, Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001, Guangdong, People's Republic of China*
[2]*Department of Polymer Materials Science and Engineering/Institute of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, Guangdong, People's Republic of China*

Received 27 April 2010; accepted 6 February 2011
DOI 10.1002/app.34300
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this work, the wet natural rubber granules were dried by hot air and by microwave at 115°C, respectively; the morphological structures of dried natural rubber granules were studied by using a scanning electronic microscope, whereas the thermal oxidative properties of dried natural rubber granules were investigated by comparison of variation in properties before and after aging, and the changes in the thermal oxidative decompose temperatures. The results showed that it needed 13.47 min for microwave drying and 210.00 min for hot air drying to reduce the moisture content of wet natural rubber to the required value. The granules of natural rubber dried by microwave were of rough surfaces and the cutting traces produced during the processing of wet natural rubber remained on the natural rubber surface; whereas, the natural rubber granules dried by hot air were of smooth surfaces, and the cutting traces produced during the processing of wet granules disappeared. The thermal oxidative resistance of vulcanized natural rubber dried by microwave improved significantly. The initial plasticity (P_0), plasticity retention index, and thermo-oxidative decomposition temperature of natural rubber dried by microwave were higher than those of natural rubber dried by hot air. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: natural rubber; drying; microwave; hot air; SEM; property

INTRODUCTION

At present, wet natural rubber granules are usually dried by hot air produced by the burning of diesel oil or heavy oil for about 4 h at 115°C. However, this conventional dry system is adverse to the properties of natural rubber. In hot air drying, the thermal energy is conducted inward from the surface to interior of the natural rubber, whereas the moisture in the wet natural rubber is diffused outward from the interior of natural rubber to the surface, and heat conduction and water diffusion are at an opposite direction. However, natural rubber is a kind of poor thermal conductive material and slow in heat conduction, which may causes the first dried surface layer to form a thick and hard skin, resulting in a long-time drying and the incomplete drying or the stickiness of natural rubber, thus an unstable quality of this material. Therefore, more attentions have been paid to this problem.[1]

Microwave drying is one of the most interesting methods for drying materials. Microwaves are electromagnetic waves within frequency bands of 300 MHz to 300 GHz. The common frequency for commercial microwave systems is 2.45 GHz with a wavelength about 122.4 mm. Compared with hot air drying methods, microwave drying systems have several advantages, including reduced drying time, high production and energy efficiencies, drying uniformity, and improved product quality,[2,3] and so on.

Unlike in hot air drying, in the microwave drying of natural rubber, the polarity orientation of water in natural rubber changes with the variation of external electromagnetic field, the 2.45-GHz high-frequency microwave can make the water molecules to collide with each other, and the energy resulted from this collision is instantaneously transformed into thermal energy to heat the whole of the natural rubber, and the temperature increasing of natural rubber and evaporation of water occur simultaneously in the whole material. Because of the cooling down by water evaporation, the temperature on natural rubber surface is slightly lower than that in the internal layers, and the thermal energy produced in the

Correspondence to: C. Mei (chgdzjcm@yahoo.com.cn).
Contract grant sponsor: National Science Foundation of China; contract grant number: 50663003.

interior causes the suddenly increasing of water vapor pressure to form a pressure grads, and the heat conduction and moisture diffusion is at the same direction, which will greatly improve the migration of water during drying. This is of course much better than the conventional hot air drying. Also, because of the existence of pressure grads, the dried layer are first formed in the interior of the natural rubber, then gradually expand outward, which will prevent the formation of a hard and thick skin layer like in hot air drying; therefore, continuous outward migration of water from the interior of natural rubber can be fulfilled. So, the use of microwave can dry the wet natural rubber rapidly and improve the quality of natural rubber.

Several analyses and applications of the microwave heating process in foodstuff, medicines, ceramic, nanomaterials, rubber, and other polymers processing, and so on, can be found in the literature.[4,5]

Earlier works have shown that study on the structures and properties of natural rubber and natural rubber composite materials by investigating the morphological structures or microstructure of these materials would produce a better effect.[6,7]

In this work, the wet natural rubber granules were dried by 115°C hot air from an electrothermal oven and by microwave (frequency, 2450 MHz; with the surface temperature of natural rubber controlled at 115°C), respectively; the variations in the morphological structures and the physical properties of dried natural rubber were studied.

EXPERIMENTAL

Materials

The fresh natural rubber latex was supplied by the Guangdong Natural Rubber Industrial Group, Guangdong, China; the micro-organism coagulant was supplied by the Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences.

Preparation of the samples

The preparation of natural rubber samples dried by hot air and microwave is as follows: the fresh natural rubber latex was first coagulated using a self-developed micro-organism coagulation process to obtain natural rubber coagulum. The coagulum was then sheeted, cut and granulated to obtain wet natural rubber granules, which were of irregular sizes and forms, and partly adhering together. The wet natural rubber granules were finally dried for 210.00 min by 115°C hot air from an electrothermal oven and dried for 13.47 min by microwave with the surface temperature of wet natural rubber samples was controlled at 115°C, respectively, in order to reduce the moisture contents of both wet natural rubber samples to a value below 0.8%, the maximum moisture content required by the Chinese national standard GB/T 8081-2008. And, the masses of wet natural rubber sample during drying was automatically recorded by a dry analyzer, every 4 s to calculate the moisture content and water loss rate of samples at every drying moment.

The vulcanized natural rubber samples from the above-mentioned natural rubber granules dried by hot air and microwave was prepared according to Chinese national standard GB/T 6038-2006.

Characterization and testing

The moisture content of natural rubber was determined by a dynamic weighing microwave drying instrument[8] and an electric oven—electronic balance Master sequencer for microwave and hot air drying processes, respectively, and the mass of natural rubber can be weighed in real time, with an accuracy of 0.1 mg.

The moisture content of natural rubber at every drying moment was calculated by the following equation:

$$\text{Moisture content} = (Mt - Ms)/M \times 100\% \quad (1)$$

where ***Mt*** is the mass of wet natural rubber at each moment during the drying process, ***Ms*** is the mass of dried natural rubber, and ***M*** is the mass of wet natural rubber before drying, respectively.

The morphological microstructure of the fractured surface and surface of dried natural rubber samples dried by microwave and hot air were observed with a HITACHI-3000N scanning electronic microscope (SEM) (HITACHI Company, Tokyo/Japan). The fractured surface was obtained by splitting of the quenched natural rubber sample in liquid nitrogen. A sputter was used to precoat a layer of conductive gold onto the surface and fractured surface of natural rubber before SEM observation.

The plasticity index (P_0) was measured using a REF.P.1.MK-11 Wallace plastometer (WALLACE Company, London/UK) according to Chinese national standard GB/T3510-2006.

The plasticity retention index (PRI) was measured using a REF.P.1.MK-11 Wallace plastometer (WALLACE Company, London/UK) and a REF010 Wallace aging oven (WALLACE Company, London/UK) according to Chinese national standard GB/T3517-2002.

The tensile properties of vulcanized natural rubber were measured using an Instron IX 3365 machine (INSTRON Company, Gardena/California), according to Chinese national standard GB/T528-2009, with a crosshead speed of 500 mm/min.

The vulcanization of the natural rubber samples and the testing of physical properties before and after thermal oxidative aging were carried out in an aging oven, the aging conditions are 100°C × 24 h. The variation rates of properties for natural rubber samples before and after aging were calculated by the following equation.

$$\text{Variation rate} = (P_2 - P_1)/P_1 \times 100\% \qquad (2)$$

where P_1 and P_2 are the values of properties tested before and after aging, respectively.

A Perkin Elmer TG-7 thermogravimetric analyzer (Perkin Elmer Company, Waltham/Massachusetts) was used for the thermal oxidative decomposition measurements. The measurement of the films (about 10 mg) was carried out from 100 to 600°C and a heating rate of 10°C/min under an atmosphere of air with a flowing rate of 50 mL/min. And, T_0 was the onset temperatures of decomposition, T_p was the temperatures of the maximum weight-loss rate, T_f was the end temperature of degradation, respectively.

RESULTS AND DISCUSSION

The drying characteristic curves of natural rubber dried by hot air and microwave

Figure 1 shows the drying curves of natural rubber by hot air and microwave, respectively. It was found that the moisture contents of wet natural rubber samples were all 25.4%, and the surface temperature of wet natural rubber sample was controlled at 115°C. To reduce the moisture contents of the dried natural rubber samples to a value below the maximum required value (0.8%), it needed 210.00 min by hot air, but only 13.47 min by microwave, which is 16 times less than that needed by hot air, and the final moisture content for these two natural rubber samples were 0.782 and 0.796%, respectively. This is because that unlike in hot air drying, in the microwave drying of natural rubber, the temperature increasing of natural rubber and evaporation of water occurs simultaneously in the whole material. Because of the cooling down by water evaporation, the temperature on natural rubber surface is slightly lower than that in the internal layers, and the thermal energy produced in the interior causes the suddenly increasing of water vapor pressure to form a pressure grads, and the heat conduction and moisture diffusion is at the same direction, which will greatly improve the migration of water during drying. This is of course much better than the conventional hot air drying.

The microstructures of natural rubber samples dried by different methods

The surface microstructures of natural rubber samples dried by hot air and microwave are shown in Figure 2(a–d), respectively. It can be seen from Figure 2(a,b) that, the natural rubber granules dried by hot air are of a smooth surface resulted from melting by the high drying temperature and long drying time, and it seems that the granule surfaces and the small rubber threads linking the granules were enveloped by a layer of thin film [Fig. 2(a)]; the cutting traces produced during the processing of wet natural rubber disappeared [Fig. 2(b)]; Whereas Figure 2(c,d) show that, the natural rubber granules were of a rough surface and the cutting traces produced during the processing of wet natural rubber remained on the surface, and the surface micropores of natural rubber granules resulted from the outward movement of interior water to the surface of natural rubber granules can also be observed.

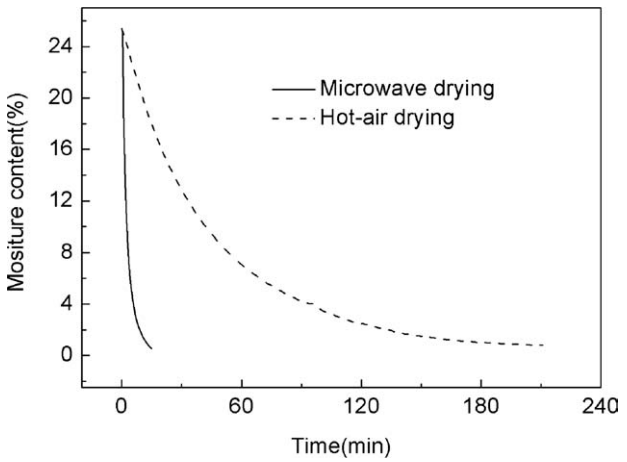

Figure 1 Drying curve of natural rubber by different drying methods.

The unvulcanized natural rubber tends to be sticky when it is heated for a comparative long time at high temperature. In this experiment, hot air drying sample was dried for 210 min at 115°C, in which the surface of wet natural rubber was first dried when it was heated, resulting a hard and thick skin-like dried layer to block the capillaries of natural rubber, because natural rubber is a poor heat conductor and slow in heat transferring, which can cause difficulty for the interior water to migrate to the natural rubber surface. Therefore, the natural rubber was of a smooth surface resulting from melting by over drying. However, during the drying of wet natural rubber by microwave, energy can penetrate into the interior of sample, the energy absorbed by the natural rubber was instantaneously transformed into heat to increase the temperature of the whole sample including the natural rubber and water in the center, and the water vapor was driven out of the sample by a suddenly increased pressure of water. Therefore, a dried layer was first formed in the center of the material, then gradually expand outward[9,10]; therefore, many micropores formed as a

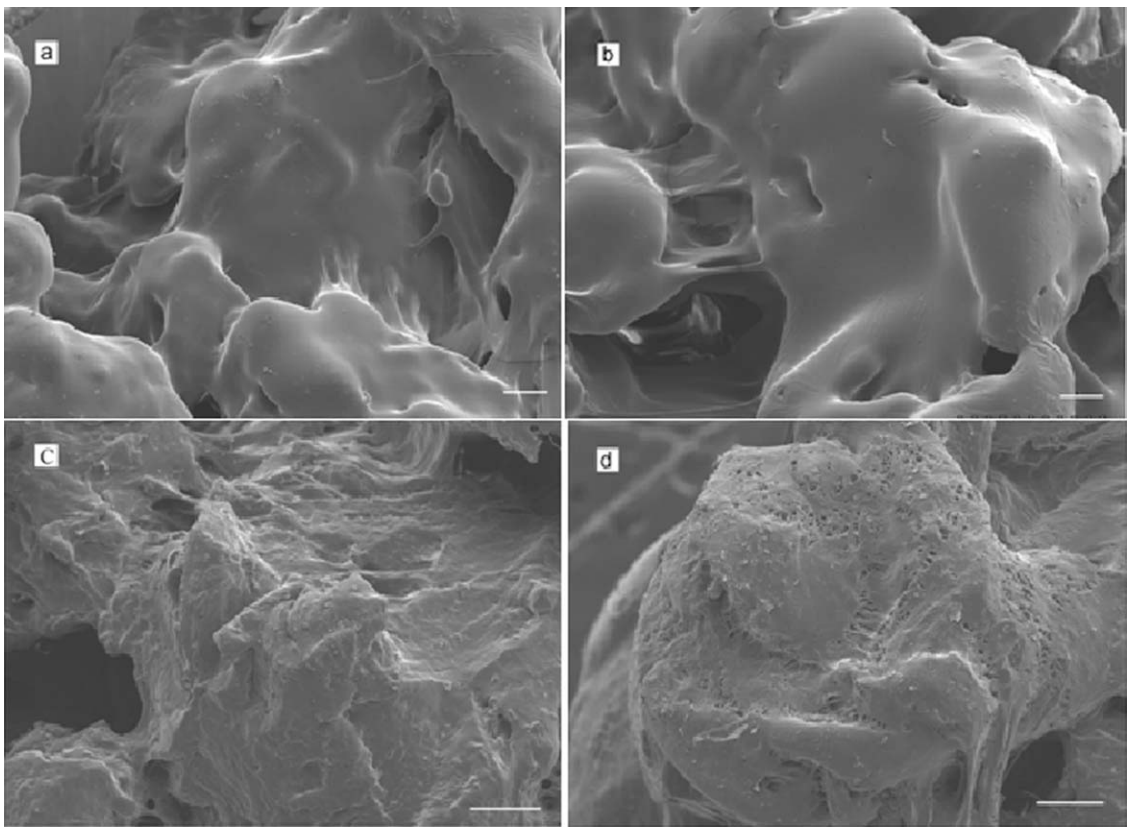

Figure 2 SEM micrographs of the surface of natural rubber samples obtained by different drying methods (Bar = 30μm).

result of the migration of water vapor, as found on the natural rubber surface, which was not damaged during drying.

The microstructures of fractured surface of natural rubber samples dried by microwave and hot air are shown in Figure 3(a,b), respectively. It can be seen from these figures that, there were many big air pores on the sponge-like surface of natural rubber granules dried by microwave, and the interface between the air pores and the natural rubber was very distinct for these big air pores, which were not adhered with each other; whereas, the air pores on natural rubber granules dried by hot air were very small and adhered with each other, and the interface between the air pore and natural rubber was very fuzzy. The reason for this was the same as that for Figure 2(a–d). And, it can also be seen from Figure 3(b) that, some parts of the natural rubber granules dried by microwave were

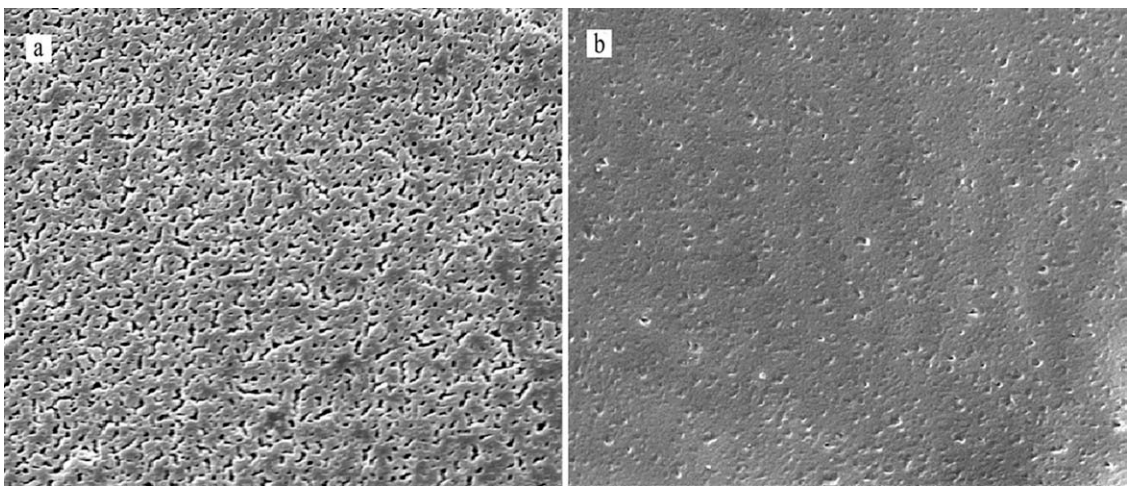

Figure 3 SEM micrographs of the fractured structure of natural rubber samples obtained by different drying methods (Bar = 1 μm).

TABLE I
Properties of Natural Rubber Samples Obtained by Different Drying Methods

Samples	Properties of natural rubber before aging		Variation of properties before and after aging		Natural rubber	
	Tensile strength (MPa)	Elongation at break (%)	Tensile strength (%)	Elongation at break (%)	P_0	PRI
Hot-air drying	23.37	855	−57	−87	32.2	79.8
Microwave drying	21.84	870	−37	−65	44.2	88.2

consisted of pores with no great difference in density and size [Fig. 3(a)]; however, the other parts were consisted of air pores obvious difference in size [Fig. 3(b)]. This might be attributed to the variation in different internal parts of wet natural rubber during natural rubber coagulation process.

The thermal oxidative aging resistance of natural rubber samples

It can be seen from Table I that the tensile strength of the vulcanized natural rubber dried by hot air was slightly higher than that of natural rubber dried by microwave; however, the thermal oxidative resistance of natural rubber vulcanized dried by microwave improved significantly, and the variation rates for tensile strength of −37% and elongation of break of −65% before and after aging for vulcanizate of natural rubber dried by microwave were apparently higher than those for vulcanizate of natural rubber dried by hot air, which were −57 and −87%, respectively; And the P_0 and PRI values of natural rubber sample dried by microwave were apparently higher than those of natural rubber sample dried by hot air. There is a certain relationship between P_0 and molecular weight of natural rubber, and also a relationship between PRI and thermal oxidative aging resistance properties of natural rubber, the higher the P_0, the higher the molecular weight of natural rubber; the higher the PRI, the better the thermal oxidative aging resistance of natural rubber.[11,12] This showed that the molecular weight and the thermal oxidative aging resistance of natural rubber sample dried by microwave was better than that of natural rubber sample dried by hot air.

This is because that natural rubber is an unsaturated olefin polymer, its molecular chains are easier to be damaged by heat and oxygen, comparing with saturated polymers.[13] The time for the drying of natural rubber sample by hot air at 115°C was 210.00 min; this long-time drying can cause the degradation of natural rubber molecular chains by oxidation. However, a much shorter time of 13.47 min for the microwave drying with a controlled natural rubber surface temperature of 115°C, would had only a small influence on the oxidative degradation of natural rubber molecular chains, which causes a higher number of terminating groups existing on natural rubber sample dried by hot air, and there would be more chances for these terminating group to contact with oxygen, resulting in a poorer aging resistance of natural rubber sample dried by hot air than those of natural rubber sample dried by microwave.

Figure 4 presents the thermogravimetric/derivative thermogravimetric (TG/DTG) curves of the natural rubber samples dried by hot air and microwave in an air atmosphere at a heating rate of 10°C/min. The primary thermal oxidative degradation temperatures of natural rubber samples dried by hot air and microwave were shown in Table II, which were obtained through analysis of Figure 4. Figure 4 shows that, the TG curve of the natural rubber sample dried by microwave moves to a higher temperature in comparison with that of the natural rubber sample dried by hot air, which can also be seen in Table II, that is, the T_0, T_p, T_f of microwave-dried natural rubber sample were higher than those of hot air-dried sample. This demonstrated that the thermal oxidative resistance of microwave-dried natural rubber sample was better than that of hot air-dried sample.

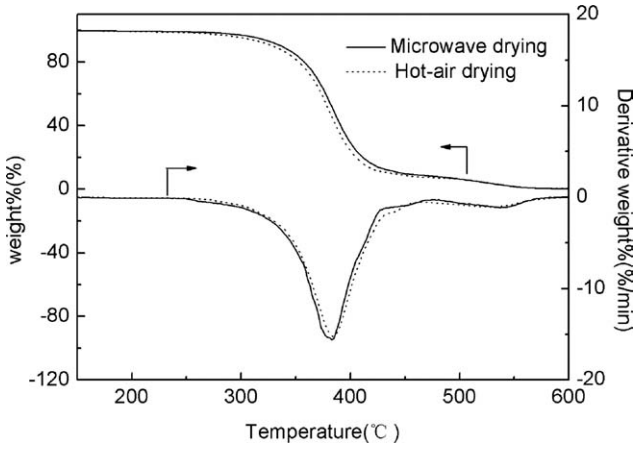

Figure 4 TG-DTG curve of natural rubber samples obtained by different drying methods in air.

TABLE II
Primary Degradation Temperatures of Natural Rubber Samples Obtained by Different Drying Methods in Air

Samples	T_0(°C)	T_p(°C)	T_f (°C)
A	343.402	380.110	404.438
B	345.882	383.559	410.362

CONCLUSIONS

1. The moisture content of natural rubber sample dried by microwave could be reduced to a value below the maximum required value by only in 13.47 min, whereas it took 210.00 min for hot air drying to reach the requirement.
2. The natural rubber granules dried by microwave were of rough surfaces and the cutting traces produced during the processing of wet natural rubber remained on the surface; whereas, the natural rubber granules dried by hot air are of smooth surfaces resulting from melting, and the cutting traces produced during the processing of wet natural rubber disappeared.
3. There were many big air pores on the fracture surface of natural rubber granules dried by microwave, and there was a clear interface between air pore and natural rubber, which was not adhered with each other; however, the air pores on the fractured surface of natural rubber granules dried by hot air were very small, and the interface between air vent and natural rubber was very fuzzy and seriously adhered with each other.
4. The aging resistance of vulcanized natural rubber dried by microwave was apparently better than that of vulcanized natural rubber dried by hot air from the electrothermal oven.
5. The values of P_0, PRI, T_0, T_p and T_f of natural rubber sample dried by microwave were higher than those of natural rubber dried by hot air. The natural rubber sample dried by microwave had a better thermal oxidative resistance compared with the natural rubber sample dried by hot air.

References

1. Bateman, L.; Sekhar, B. C. J Rub Research Institute of Malaya 1966, 19, 133.
2. Rattanadecho, P.; Suwannapum, N.; Watanasungsuit, A.; Duanduen, A. J Manuf Sci Eng 2007, 129, 157.
3. Sun, H. Y. Chin Traditional Pat Med 2004, 26, 667.
4. Martin, D.; Ighigeanu, D.; Mateescu, E.; Craciun, G.; Ighigeanu, A. Radiation Phys Chem 2002, 65, 63.
5. Inkpen, S. C.; Melcher, J. R. Polym Eng Sci 1985, 25, 289.
6. Ao, N. J. Chin J Appl Chem 1995, 12, 80.
7. Chen, M.; Ao, N. J.; Chen, Y. J Chin Electron Microsc Soc 2001, 20, 385.
8. Chen, M.; Deng, W. Y.; Li, H. M.; Liu, Q. G. China Patent ZL 20072019071349.
9. Chen, Z. G. Fundamentals and Application of Microwave Technology, China Beijing University of Posts and Telecommunications press: Beijing, 2002.
10. Wang, Z. L. The Application of Microwave Heating Technology, China Machine Press: Beijing, 2003.
11. Li, Z. J.; Li, P. S.; Ren, M. P. J China Rub Industry 1992, 39, 421.
12. Li, Z. J. Analysis and Testing of Natural Rubber, Chinese Agricultural University Press: Beijing, 2007.
13. Brazier. D. W. Rub Chem Technol 1980, 53, 437.