

Preparation and Thermal Stability of Brominated Natural Rubber from Latex

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ABSTRACT: The effects of pH value of reaction system, reaction time, reaction temperature, bromine concentration, and amount of potassium persulfate on the bromination reaction in the preparation of brominated natural rubber (BNR) from natural rubber latex were discussed. It has been found from the thermal analysis, that is, the thermal degradation of BNR in nitrogen is a two-step reaction, and 16% carbonide with a stable structure

remained at 470–650°C. The thermo-oxidative degradation of BNR in air is also a two-step reaction, and the percentage of degraded BNR reaches to nearly 100% at 600°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 25–29, 2010

Key words: bromination; rubber; natural rubber latex; stabilization; thermogravimetric analysis

INTRODUCTION

Natural rubber (NR) can be modified with chlorine and bromine to prepare chlorinated NR (CNR) and brominated NR (BNR). Chlorinated NR, which is prepared by the chlorinated modification of NR from solution or latex, has properties, such as excellent film-forming ability, adhesiveness, weatherability, abrasive resistance, corrosion resistance, flame retardancy, good insulation ability, and thermal stability.¹ As a consequence, CNR has been widely used in the production of the raw materials for paints, coatings, adhesives, and inks, and has become one of the most important industrial derivatives of NR. Up to the present, a great amount of research work has been done about the preparation, structure, properties, and reaction mechanism of CNR.^{2–9}

BNR can be prepared by the brominated modification of NR from solution and the solubility and structure of BNR product were investigated.¹⁰ In the

solution process, the BNR was prepared by dissolving the NR in the solvent, such as tetrachloromethane, and then brominating. The solution process has an advantage of easily controlling the reaction, with fast bromination and getting BNR with required bromine content in a short time. But the drawback is the high equipment investment and cost. Besides, it should treat and recover a great amount of toxic solvent, and the easy leakage of the solvent during the production causes environmental hazards and is harmful to the health of workers. Therefore, the solution process will be replaced by other processes sooner or later.

This article reports a new way for preparing BNR directly from NR latex. NR latex is a natural polymer of isoprene (most often *cis*-1,4-polyisoprene) with a molecular weight of 100,000–1,000,000 g mol⁻¹. Typically, a small percent (up to 5% of dry mass) of other materials, such as proteins, fatty acids, resins, and inorganic materials (salts) are found in NR. Although a great amount of research work has been done about the preparation, structure, and properties of brominated polymers, such as brominated styrene–butadiene rubber,¹¹ brominated styrene,¹² and brominated butyl rubber,^{13–15} and so forth, there are still no reports of brominated modification of NR from latex. In general, easy coagulation will occur as brominating agent added to NR latex and thus the bromination can not be carried on satisfactorily. In this article, BNR is prepared successfully from latex under the action of the stabilizer. The effects of pH value of reaction system,

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reaction time, reaction temperature, bromine concentration, and amount of potassium persulfate on the bromination reaction are discussed. The thermal stability of the products is studied by use of the thermogravimetry analysis (TGA).

EXPERIMENTAL

Materials

The high ammonia nature rubber latex (60 wt % of solid NR) was purchased from Xihua Farm in Danzhou City of Hainan Province, PR China. Absolute ethanol, bromine and sodium hydroxide were purchased from Chemical Reagent Company of Guangzhou. Concentrated nitric acid was purchased from Anpu Chemical Company of Lianjiang City, Guangdong Province. Hydrogen peroxide and formaldehyde were purchased from Xilong Chemical Company of Shantou City, Guangdong Province. These chemicals were reagents of analytical purity and used without any further purification.

Preparation of brominating agent and stabilized NR latex

Fifty milliliters of absolute ethanol and 50 mL distilled water were introduced into a glass vessel, then 20 mL liquid bromine was added and stirred to prepare the solution of brominating agent.

Hundred grams of NR latex was diluted with 100 g distilled water, then 6 g nonionic surfactant was added. Formaldehyde was added to neutralize the ammonia until pH value of the latex reached to 7, then 2 mol/L of nitric acid solution was added to adjust the pH value to 1. The acidic stabilized NR latex was thus prepared.

Preparation of BNR from latex

Ten grams of stabilized NR latex, 20 mL distilled water, 4 g nonionic surfactant, and 2 mL 30% hydrogen peroxide were introduced into a glass reactor equipped with a magnetic stirrer, keep the temperature constant with a water bath; then a certain amount of brominating agent was added to initiate the bromination reaction. The mixture was allowed to react for a predetermined time with stir. To stop the bromination reaction, 20% sodium hydroxide solution was added to adjust pH value to 7 and then 50 mL 95% ethanol was added to the solution. The precipitated BNR products were filtrated, then washed with distilled water. Put the products into a thermostatic oven at a temperature of $50 \pm 1^\circ\text{C}$ for drying 3 h to get the white-powdered BNR products.

The bromine content of BNR products was determined according to the method introduced by Vollhard.^{10,16}

Thermal analysis

The thermal analysis was carried out with a Perkin-Elmer Thermal Gravimetric Analyzer. The mass of the sample was about 8.00 mg. The carrier gas was either air or nitrogen with a flow rate of 50 mL/min. The temperature rose from room temperature to 650°C at the heating rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Influence of reaction conditions on bromination of NR latex

pH value of reaction system

When NR latex was chlorinated with chlorine gas, chloric acid was added during preparation so that the chlorination would take place in an acidic condition. The test shows that when the pH value of reaction system is less than 1, the chlorination can be carried on successfully, and the thermal stability and solubility of the product are good.²

The effect of pH value on the bromination of NR latex was investigated, the results show that bromine content of BNR products keeps constant with different pHs, such as 1, 2, 3, 4, and 5. However, strong acidic condition can improve the mechanical stability of NR latex. When pH value of reaction system is equal to or less than 1, the bromination can be carried on over 4 h without the occurrence of coagulation. The experiment shows that compared with sulfuric acid and hydrochloric acid, nitric acid has an obvious effect on the mechanical stability of NR latex. Therefore, nitric acid was added during preparation so that the bromination would take place in an acidic condition.

Reaction time

The effect of reaction time on bromination of NR latex is shown in Figure 1. It can be seen from Figure 1 that the bromination rate of the NR in latex is very fast. For example, bromine content of the rubber reaches to 48% when reaction time is only 10 min. But after that it is difficult to rise the bromination rate; and even if the reaction time prolongs to 8 h, it has no apparent effect on the bromine content.

The byproduct of hydrogen bromide (HBr) was observed releasing from the latex almost simultaneously after the brominating agent was added. The HBr was detected by its strong acidic property in water and the reagent of silver nitrate. Combined with the result of Figure 1, it can be concluded that

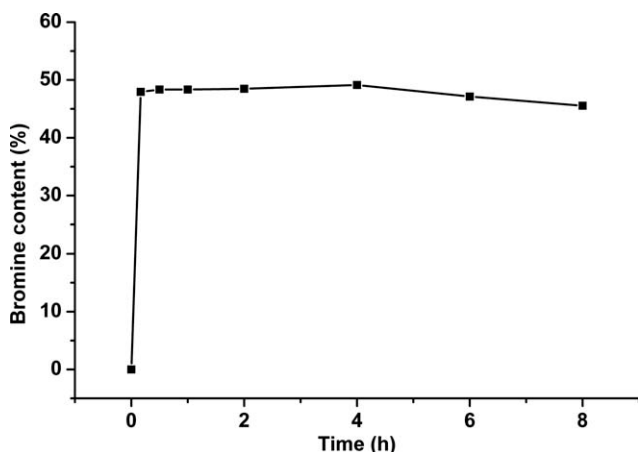


Figure 1 The effect of reaction time on bromination reaction.

there is no induction period in the bromination reaction. During the latex process, though the NR molecular chains are confined to the internal scope of particles in a coiling state,² the bromine molecules in the reaction system can still easily move to the NR particles and contact with every part of NR molecules. Therefore, the bromine added can react with NR molecules in a short time.

Reaction temperature

The effect of reaction temperature on the bromination is shown in Figure 2. It can be seen from the test result that the bromine content of BNR slightly decreases with reaction temperature. The high temperature will make the volatilization of bromine become easier, and BNR may dehydrobrominate slowly at a high temperature for a long time; which make the bromine content of BNR product slightly decrease. Thus, the bromination of NR solution

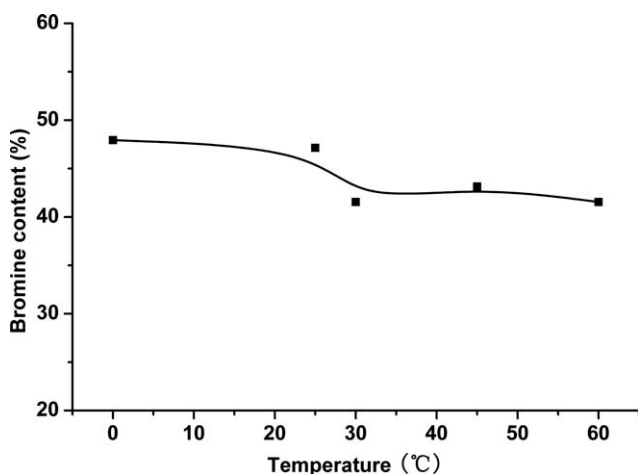


Figure 2 The effect of reaction temperature on bromination reaction.

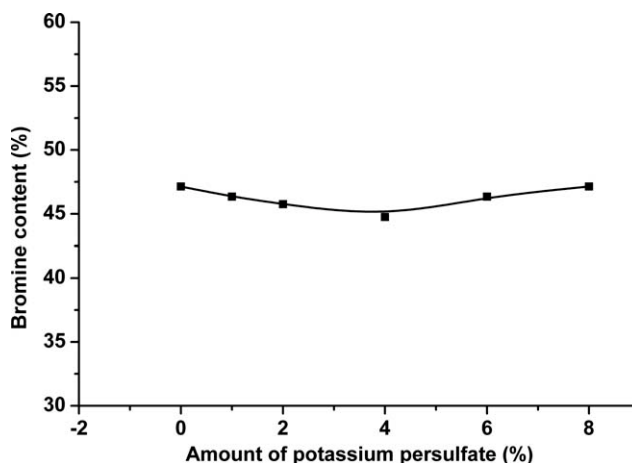


Figure 3 The effect of amount of potassium persulfate on bromination reaction.

should be carried out at lower temperature such as 10–30°C.

Amount of potassium persulfate

Just like NR chlorination,² the bromination of NR in latex may be a free radical substitution reaction. Because the free radical initiators usually accelerate the bromination, so we selected the potassium persulfate as the catalyst. It can be seen from Figure 3 that amount of potassium persulfate has no obvious effect on the bromine content of BNR. Bromine content of the rubber reaches to 47% when amount of potassium persulfate is zero; it means that the bromination can be carried on successfully without the presence of potassium persulfate.

Bromine concentration

The effect of bromine concentration on the bromination is shown in Figure 4. It can be seen from Figure

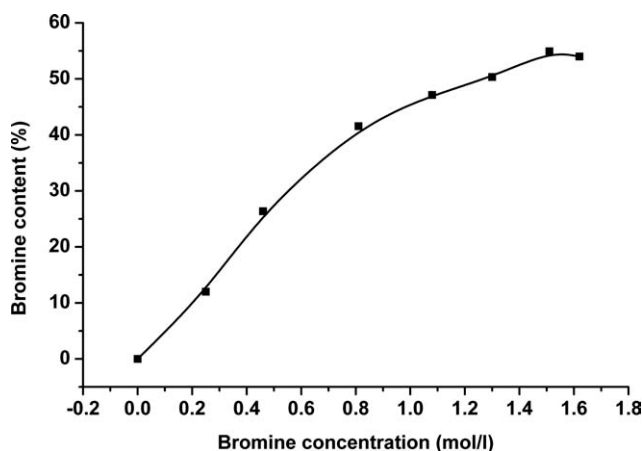


Figure 4 The effect of bromine concentration on bromination reaction.

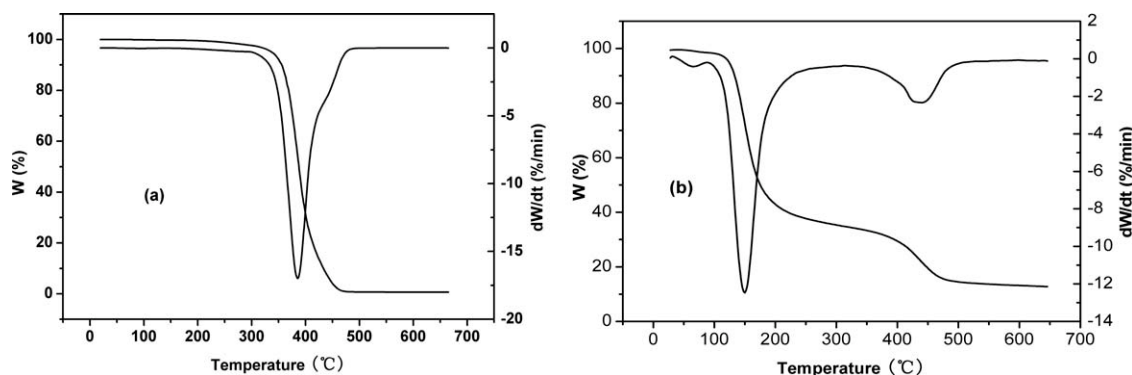


Figure 5 TG and DTG curves of thermal degradation for (a) NR and (b) BNR in nitrogen.

4 that bromine content of BNR rises quickly when bromine concentration in the latex reaches to 0.81 mol/L and slows down gradually when it reaches to about 1.51 mol/L; after that it is difficult to rise the bromine content of BNR.

Compared with reaction time, reaction temperature, and amount of potassium persulfate, bromine concentration has an apparent effect on the bromine content of BNR. Therefore, different bromine content of BNR products can be obtained by using different bromine concentration in the latex. The highest bromine content of BNR product is 55% when bromine concentration reaches to 1.51 mol/L.

Solubility of BNR

When the bromine content surpasses 47%, the solubility of product in toluene is good, whereas the solubility of the product with low bromine content is very poor, even when only swelling happens. With the prolonging of the bromination time and the rising of bromine content of BNR, the solubility of BNR in the toluene becomes higher and higher. When the bromine content reaches to 55%, the product can be dissolved in toluene quickly and completely. The viscosity of the 20% BNR toluene solution is 4 centipoises only. These results show that

the scission has actually occurred to the NR molecular chain during the bromination.

Thermal stability of BNR

It is known the thermal stability of brominated polymers has an important effect on their preparation, storage, processing, and applying properties. So, TGA and derivative thermogravimetry (DTG) methods were adopted to study the stability of BNR prepared. The TG and DTG curves of degradation of NR and BNR (bromine content is 55%) in nitrogen are shown in Figure 5. Two peaks appear on DTG curve of NR at 390°C and 450°C, which indicates that the thermal degradation of NR is a two-step reaction. The peak appears on the DTG curve of NR is caused by the degradation of NR molecules. It can be seen from TG curve that the thermal degradation of NR tends to stabilize at 470°C, where the percentage of degraded NR is about 99%, or 1% carbon residue remained.

Two peaks appear on DTG curve of BNR at 152 and 439°C, respectively, which indicates that the thermal degradation of BNR is also a two-step reaction. The first peak appears on the DTG curve of BNR may be caused by the dehydrobromination of BNR molecular chains. The initial temperature of

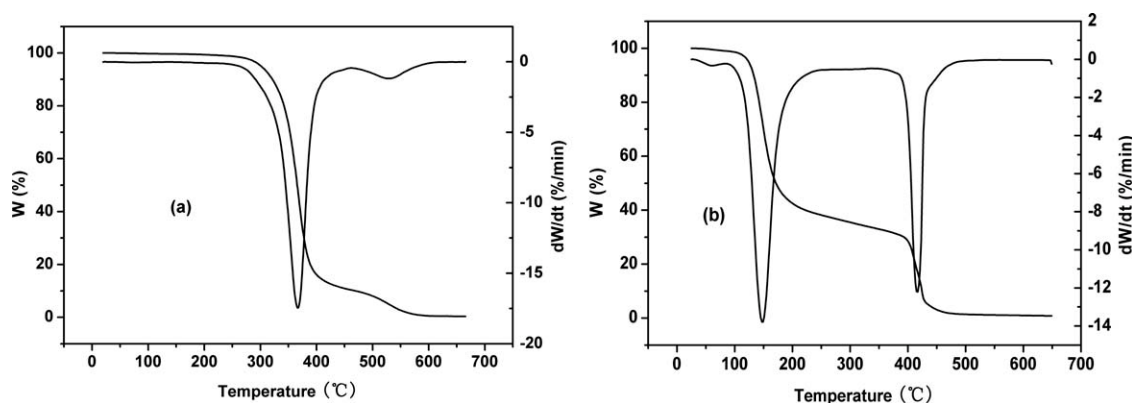


Figure 6 TG and DTG curves of thermal-oxidative degradation for (a) NR and (b) BNR in air.

first-step decomposition of BNR calculated from TG curve by use of bitangent method¹⁷ is 129°C, and that of second-step is 399°C. It can be seen from TG curve that weight of BNR decreases quickly from 100 to 450°C, but tends to stabilize at 470°C as the weight loss of BNR from 470 to 650°C is only 3%, which also indicates that the carbon residue is stable. The percentage of degraded BNR at 470°C is about 84%, or 16% carbon residue remained.

The TG and DTG curves of thermal-oxidative degradation of NR and BNR in air are shown in Figure 6. Two peaks appear on DTG curve of NR at 360 or 520°C and BNR at 150 or 418°C, respectively, which indicates that the thermal-oxidative degradation of both NR and BNR is a two-step reaction. The first peak appears on the DTG curve of NR is probably caused by the degradation of NR molecules, and the second one by the oxidative scission of the remaining NR molecules. The first peak appears on the DTG curve of BNR is probably caused by the dehydrobromination of BNR molecular chains, and the second one by the oxidative scission of the BNR molecules. The initial temperature of first-step decomposition of BNR is 129°C and that of second-step 400°C. The percentage of degraded BNR reaches to 99.1% at 600°C; that is to say, the reaction goes almost thoroughly, which is different from that of thermal degradation of BNR.

The effect of reaction circumstances on degradation of BNR is different at the early and late stages of the degradation reaction. At the early stage, the oxygen has no obvious effect on the degradation. The difference of the first and second initial temperature of the two degradations is only 0 and 1°C. The main factor that affected the degradation is temperature. At the late stage, the oxygen accelerates the decomposing of degradation product, so there almost no carbon residue remained, and the percentage of degraded BNR reaches nearly 100%. It can be concluded that the mechanisms of the two reactions are different, which is similar with the thermal stability of CNR.²

CONCLUSIONS

BNR can be prepared by the brominated modification of NR latex under the action of stabilizer. This method overcomes the defect of easy coagulation and the side reaction of NR latex during bromination.

The bromination of NR latex is carried out under the acidic condition, where the pH value is equal to

or less than 1. The rate of bromination is fast at early stage, then slows down quickly. The bromine content of BNR slightly decreases with reaction temperature. Amount of potassium persulfate has no obvious effect on the bromine content of BNR. Bromine concentration has an apparent effect on the bromine content of BNR. The highest bromine content of BNR product is 55% when bromine concentration reaches to 1.51 mol/L.

The solubility of BNR in toluene prepared by this method is good. The decrease of thermal stability of BNR compared to NR is negative result for practical utilization of BNR. The initial temperatures of both thermal and thermo-oxidative degradation of BNR are 129°C. The thermal degradation of BNR in nitrogen is a two-step reaction, and 16% carbon residue still remains at 470 to 650°C. The thermo-oxidative degradation of BNR is also a two-step reaction, dehydrobromination occurs at the early stage, and the scission of main molecular chains occurs at late stage. The percentage of degraded BNR reaches to nearly 100% at 600°C.

References

1. Zhong, J. P.; Li, S. D.; Wei, Y. C.; Peng, Z.; Yu, H. P. *J Appl Polym Sci* 1999, 73, 2863.
2. Yang, D.; Li, S. D.; Fu, W. W.; Zhong, J. P.; Jia, D. M. *J Appl Polym Sci* 2003, 87, 199.
3. Li, S. D.; Cheung, M. K.; Zhong, J. P.; Yu, H. P. *J Appl Polym Sci* 2001, 82, 2590.
4. Chen, Y. S.; Yang, D.; He, L. Z.; Li, S. D.; Jia, D. M. *J Chem Stud Appl (China)* 2004, 16, 757.
5. Yang, D.; Zhong, J. P.; Li, S. D.; Jia, D. M. *Acta Polym Sin (China)* 2003, 4, 489.
6. Yang, D.; Jia, D. M.; Li, S. D.; Zhong, J. P.; He, L. Z. *J Chem Eng Chin Univ (China)* 2003, 17, 55.
7. Xu, Y. J.; Li, C. X.; Wang, Z. H. *J Beij Univ Chem Tech (China)* 2005, 32, 12.
8. He, L. Z.; Zhong, J. P.; Yang, L. *Chem Ind Eng (China)* 2005, 22, 83.
9. Yang, D.; Li, S. D.; Zhong, J. P.; Jia, D. M. *Rubber Ind (China)* 2003, 50, 656.
10. Ling, J.; Xue, X. X. *Advances in Modification of Natural Rubber*; Hainan Publishing House: Zhangjian, China, 2006; p 158.
11. Sepideh, K. *J Polym Engi Sci* 2007, 10, 86.
12. Atwell, R. W.; Hodgen, H. A. *US Pat.* 5,369,202, 1994.
13. Wu, Y. B.; Li, S. X.; Guo, W. L. *Synt Rubber Ind (China)* 2006, 29, 267.
14. Qian, H. D. *World Rubber Ind (China)* 2004, 31, 6.
15. Wang, B. Z. *World Rubb Ind (China)* 2006, 33, 36.
16. Fueman, N. H.; Scott, W. W. *Standard Methods of Chemical Analysis*; 5th ed.; Technical Press LTD: London, UK, 1986; p 2.
17. Cai, Y.; Li, S. D.; Li, C. P.; Li, P. W.; Wang, C.; Lv, M. Z.; Xu, K. *J Appl Polym Sci* 2007, 106, 743.