Study on Preparation of Chlorinated Natural Rubber from Latex and Its Thermal Stability

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ABSTRACT: The effects of pH value of reaction system, reaction time, and reaction temperature on the chlorination reaction in the preparation of chlorinated natural rubber (CNR) from natural rubber latex were discussed. It has been found from the thermal analysis that the thermal degradation of CNR in nitrogen is a one-step reaction, and 30% carbonide with a stable structure remained at 360 to 700°C; whereas the thermo-oxidative degradation of CNR in air is a multistep reaction, and the thermal degradation ratio reaches to 100% at 560°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2863–2867, 1999

Key words: chlorination; chlorinated natural rubber; stability; natural rubber latex

INTRODUCTION

The chlorinated natural rubber (CNR), which is acid-proof, alkali-proof, wear-resistant, ageing-resistant, and corrosion-resistant in sea water, has an important use in industry.[1,2] CNR is mainly used as raw material for paint, especially ship paint, container paint, and mark paint for airports and roads. It also used as the raw material for adhesive and for acid-proof and alkali-proof products.

In the traditional solution process, the CNR was prepared by dissolving the natural rubber (NR) in the solvent, such as tetrachloromethane, and then chlorinating. The solution process has an advantage of easily controlling the reaction, with fast chlorination and getting CNR with required chlorine 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. Some countries have recently prohibited from producing CNR through the solution process.[3] The solution process will be replaced by other processes sooner or later.

For a long time, some research workers have tried to prepare CNR directly from NR latex. As early as the 1930s, the preparation of CNR from latex had been reported.[4] Then, other workers have tried many ways, such as highly diluting the NR latex, mixing with diatomite, drying to powder, adding base, vulcanizing, or adding stabilizer, as well as adding sodium hypochlorite and chloric acid; but they all failed in obtaining the satisfactory results.[5] CNR with a chlorine content of 60% was prepared by G. J. Van Amerrongen in 1952 through adding stabilizer, then adding concentrated chloric acid or sulfuric acid to make the latex in a positive state and then passing the chlorine gas into the latex to carry out the chlorination reaction.[5] But the product did not have a good solubility. Recently, the workers of the Rubber Research Institute of Sri Lanka have launched research on preparing CNR from latex for years and have already prepared a stable CNR with good solubility.[3] It is said that the Japanese

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workers have succeeded in preparing CNR with latex process.[6]

This article reports a new way for preparing CNR from latex, and the stability of the products is studied by use of the thermal gravity (TG).

EXPERIMENTAL

The experimental procedure is as follows: Add distilled water in a three-neck, round-bottomed flask; keep the temperature constant with a water bath; adjust the pH value with concentrated chloric acid; pass the chlorine gas into the distilled water to saturation; and add the stabilized NR latex. Pass the chlorine gas into the flask continuously. The CNR with the preliminary chlorination will be produced. Pass the chlorine gas into the flask continuously to the predetermined time and stop the reaction.

Neutralize the product to make the pH value of the reaction system 7 with the dilute sodium hydroxide solution. Then filtrate the product, wash with distilled water, and filtrate 3 times. Put the product into a thermostatic oven at a temperature of 50°C ± 1°C for drying 3 h to get the powdered CNR.

The chlorine content was determined according to the method introduced by Volhard.[7]

The thermal analysis was carried out by use of a Perkin–Elmer Thermal Gravity Analyzer in the air. The temperature rose from room temperature to 700°C at the heating rate of 10°C/min.

RESULTS AND DISCUSSION

Effect of the pH Value of Reaction System on Chlorination

When NR latex was chlorinated with chlorine gas, the chlorine gas would cause a series of reactions in water phase as follows:

$$Cl_2 + H_2O \xrightarrow{k_1} H^+ + Cl^- + HClO$$

$$k_1 = 4.8 \times 10^{-4}$$

$$HClO \xrightarrow{k_2} H^+ + ClO^-$$

$$k_2 = 1.1 \times 10^{-8}$$

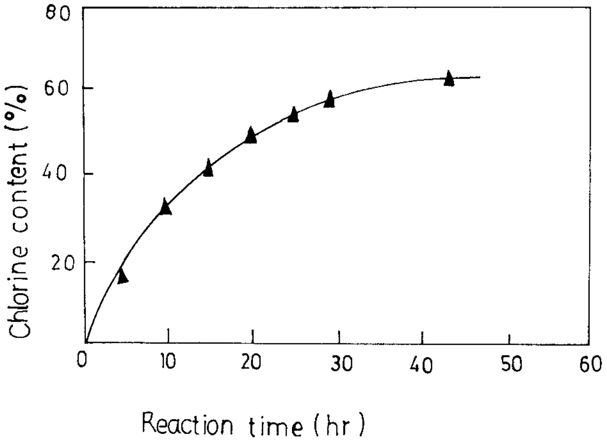

Figure 1 The effect of reaction time on chlorination reaction.

The above reactions at a neutral or basic condition would form a great amount of hypochloric acid or hypochlorite, which is harmful to the chlorination of NR. The thermal stability and solubility of the hypochlorite product are poorer than those of the chlorinated product.[8] According to the rule of the common-ion effect, the above disproportionation reaction can be prohibited effectively by adding chloric acid. Therefore, the strong 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 stability and solubility of the product are good.

Effect of Reaction Time on Chlorination

The effect of reaction time on chlorination of NR latex is shown in Figure 1. It can be seen from Figure 1 that the chlorination rate of the NR in latex is fast at the beginning and slows down gradually when chlorine content of the rubber reaches to about 30%. But when the chlorine content reaches to about 60%, it is difficult to rise the chlorination rate; and even if the reaction time prolongs to 45 h, it has no apparent effect on the chlorine content. Compared with the solution process, preparation of CNR from latex requires a longer reaction time in order to obtain a product with high chlorine content. The difference is obviously caused by the reason that the NR molecules are in different states during the chlorination. The NR molecules are in a spreading state and can move freely during the solution process,

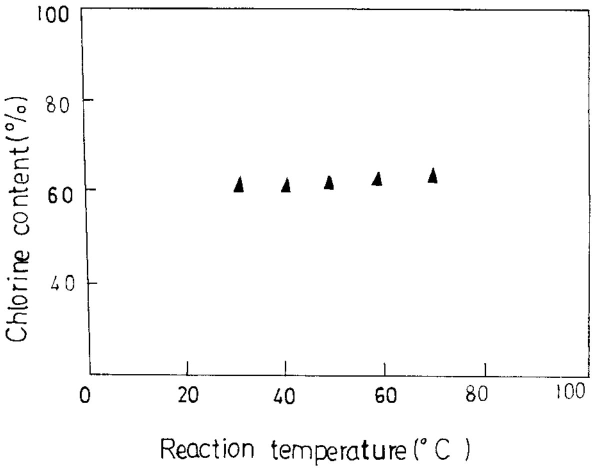

Figure 2 The effect of reaction temperature on chlorination reaction.

so the chlorine molecules can easily contact with every part of NR molecules. But in latex, the NR molecular chains are confined to the internal scope of NR particles in a coiling state, and the chlorine molecules needs to go through the outer layer of the NR particles so as to contact with the NR molecules and react with them. When the degree of chlorination becomes higher and higher, the volume of CNR in the particles will be larger and larger, the available space in the particles gets smaller and smaller, and the molecular motion tends slower and slower, so the reaction rate decreases in the late stage of chlorination.

Effect of Reaction Temperature on Chlorination

The effect of reaction temperature on the chlorination is shown in Figure 2. It can be seen from the test result that the reaction temperature has no obvious effect on chlorination. On the contrary, CNR will dehydrochlorinate slowly at a high temperature for a long time and forms nonsoluble compounds, which affect the quality of the product. In addition, the high temperature will make the solubility of chlorine gas in water become lower. Thus, the chlorination of NR latex should be carried on at lower temperature such as 30–50°C.

Effect of the Amount of Catalyst on Chlorination

The clorination of NR in latex is a free radical substitution reaction, and the free radical initiators can accelerate the chlorination. We selected the potassium persulfate as the catalyst; its suitable amount used is 1% (see Fig. 3). Too much the usage will result in coagulation of NR latex.

Solubility of CNR

When the chlorine content surpasses 60%, the solubility of product in toluene is good. Whereas the solubility of the product with low chorine content is very poor, even when only swelling happens. This is a common problem that is faced in the preparation of CNR from latex. We think the reason may be that the intermolecular and intramolecular crosslinking have also occurred in the NR molecules during the chlorination replacement and addition and cyclization. But this conclusion needs the further confirmation. With the prolonging of the chlorination time and the rising of chlorine content of CNR, the solubility of CNR in the toluene becomes higher and higher. When the chlorine content reaches to 60%, the product can be dissolved in toluene quickly and completely. The viscosity of the 20% CNR toluene solution is 10 centipoises only. These results show that the scission has actually occurred to the NR molecular chain during the chlorination.

Thermal Stability of CNR

It is known the thermal stability of chlorinated polymers has an important effect on their preparation, storage, processing, and applying properties. So the thermogravimetric (TG) analysis and derivative thermogravimetry (DTG) methods

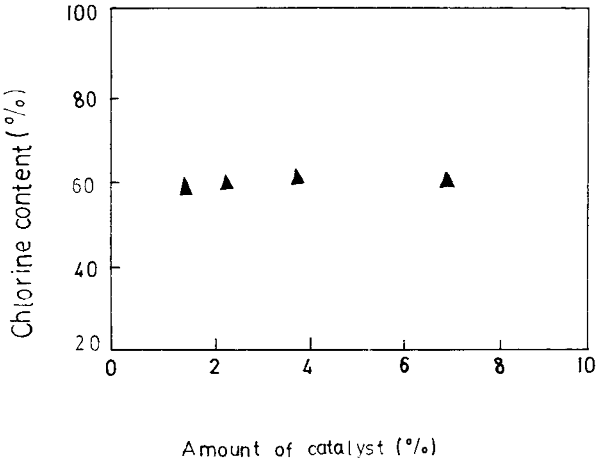

Figure 3 The effect of the amount of catalyst on chlorination reaction.

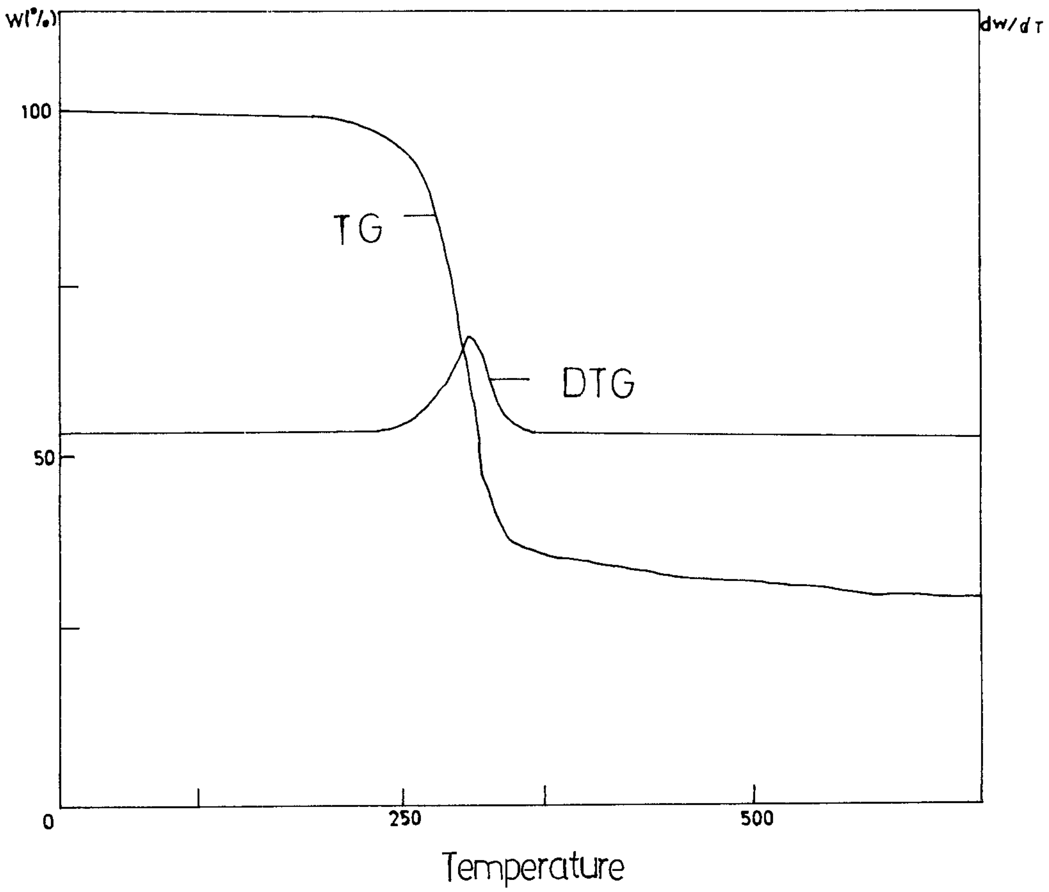

Figure 4 The TG and DTG curves of the thermal degradation of CNR in nitrogen.

were adopted to study the stability of CNR prepared. The TG and DTG curves of degradation of CNR in nitrogen are shown in Figure 4. Only at 291°C does a peak appear on the DTG curve, which indicates that the thermal degradation of CNR is a one-step reaction. The beginning temperature of thermal degradation of CNR calculated from TG curve by use of bitangant method is 283°C. It can be seen from TG curve that the thermal degradation of CNR tends to stabilize at 350°C, where the thermal degradation ratio is about 70%, or 30% carbonide remained. The weight loss of the carbonide from 350 to 700°C is only 3%, which indicates that the carbonide is stable.

The TG and DTG curves of thermo-oxidative degradation of CNR in air are shown in Figure 5. Two peaks appear on DTG curve at 294.5 and 487.5°C, respectively, which indicates that the thermo-oxidative degradation of CNR is a multistep reaction. The first peak may be caused by the dehydrochlorination of CNR molecular chains, and the second one may be caused by the oxidative scission of the CNR molecules. The beginning temperature of thermo-oxidative degradation of CNR calculated from the TG curve by use of bitangant method is 266°C. The thermo-oxidative degradation ratio of CNR reaches to 99.9% at 560°C; that is to say, the reaction goes thoroughly, which is different from that of thermal degradation of CNR.

The effect of reaction circumstances on degradation of CNR 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 beginning temperature of the two degradations is only 3°C. The main factor that affected the degradation is temperature. At the late stage, the oxygen accelerates the decomposing of degradation product, so there no carbonide remained, and the thermo-oxidative degradation ratio reaches nearly 100%. It can be concluded that the mechanisms of the two reactions are different.

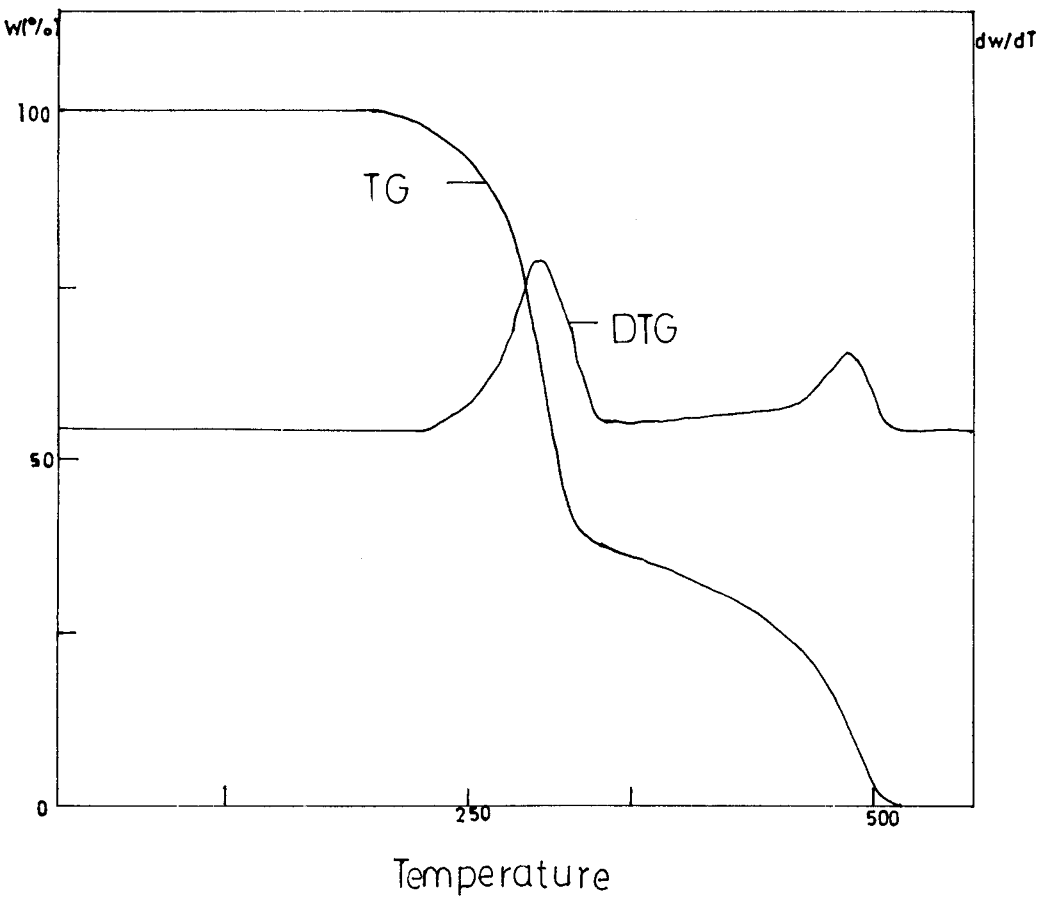

Figure 5 The TG and DTG curves of the thermal-oxidative degradation of CNR in air.

CONCLUSION

The stable dispersion can be prepared by preliminary chlorination of latex particles under the action of the stabilizer. With further chlorination, the CNR with chlorine content of 60% can be prepared. This method overcomes the defect of easy coagulation and the side reaction of NR latex during chlorination. It is a new way to prepare the CNR from latex.

The chlorination of NR latex is carried out under the acidic condition, where the pH value is equal to or less than 1. The rate of chlorination is fast at early stage, then slows down gradually. The effect of temperature on the chlorination is not obvious.

The quality of the CNR prepared by this method is in conformity with the specification of the relevant Chinese standards. The CNR is suitable for producing ship paint.

The beginning temperatures of thermal and thermo-oxidative degradation of CNR are 283 and 266°C, respectively. The thermal degradation of CNR is a one-step reaction, and 30% carbonide still remains at 350 to 700°C. The thermo-oxidative degradation of CNR is a multistep reaction, dehydrochlorination occurs at the early stage, and the scission of main molecular chains occurs at late stage. The degradation ratio reaches 100% at 560°C.

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