

Processing characteristics and thermal stabilities of gel and sol of epoxidized natural rubber

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Abstract

The processing performances and aging behaviours of gel and sol separated from epoxidized natural rubber (ENR) using organic solvents were studied by using rubber processing analyzer (RPA), thermogravimetric analysis (TGA) and difference FT-IR method. As the gel with intermolecular ether structure is formed by the ring-opening reactions of a part of epoxy groups during the preparation and storage of ENR, the molar percentage of epoxy groups of gel is lower than that of sol. The gel shows higher elastic moduli to temperature and frequency responses, lower $\tan \delta$ to frequency and strain response and higher elastic torque to strain response as comparing to those of sol. Therefore, the formation of gel will reduce processing performance of ENR. When the aging behaviours of gel and sol were analyzed by different methods, the aging reactions and their degrees were different because of the differences of aging conditions. Compared to gel, the sol is easy to be crosslinked, leading to a higher $\Delta \tan \delta$ from the RPA analysis and it is also easy to be oxidized into small molecules, leading to lower onset temperature and apparent activation energy when being analyzed by TGA. However, the variations of functional groups of gel are more obvious than those of sol when analyzed by difference FT-IR method. As the mechanical properties of ENR will be varied with the variations of molecular structures, the formations of gel during preparation and storage of ENR will reduce the oxidative aging resistance of ENR.

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1. Introduction

The epoxidized natural rubber (ENR) is a derivative from the chemical modification of natural rubber (NR). With a part of carbon–carbon double bonds on the NR molecular chains being converted

into the polar epoxy groups (to obtain ENR), the free volumes of chain phases are decreased and the density and polarity of the derivative are increased, which provides the ENR with excellent air impermeability, oil and organic solvent proofness and wet road grip performance and so on [1,2]. During the preparation of ENR, the epoxidation reactions are always accompanied with the further ring-opening reactions of epoxy groups. Acidity and temperature appear to be the main

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factors resulting in the formations of the ring-opening products. At high acid strength and/or high temperature, the major products obtained from the epoxidation of NR latex are even those derived from the ring-opening reactions of epoxy groups [2–4]. The nature of the ring-opening products depends on the initial degree of epoxidation. At low modification levels, the majority of epoxy groups are isolated, due to the randomness of the epoxidation reaction, and the major ring-opening products are those expected from simple olefin chemistry, e.g., hydroxyl-acetates, diols and intermolecular ethers [1]. Many researchers believed that it is the formation of intermolecular ether that leads to the formation of gel. With the modification level increasing, the number of adjacent epoxy groups increase consequently. And through the intramolecular attacking of a hydroxyl group on an adjacent epoxide unit, the 5- or 6-membered cyclic ether might be formed gradually [2]. At the same time, the mass-fraction of intermolecular ether increases as well. For example, the intermolecular ether content of about 75% can be resulted from ENR with an epoxy group molar percentage of 50%.

Some authors presumed that, under carefully controlled conditions, the ring-opening reactions could be avoided to give a clean modified NR with any desired level of epoxidation [1,2]. However, the mild reaction conditions will extend the preparation time, which is not helpful to the scaled production of ENR. In practice, no matter how to control the preparation conditions of ENR, the ring-opening products are still formed. So the reaction products obtained actually are complex mixtures that might be neither useful nor reproducible if the ring-opening products are in a high content [2,5]. Therefore, the properties and applications of ENR will be affected by the presences of ring-opening products. It is commonly accepted that a high content of gel is helpful to the film formation of ENR latex. Whereas it is not beneficial to the milling of ENR when being used as dried rubber, because extra energy will be consumed to break the crosslinking structures. As to the effects of ring-opening products on the aging behaviour of ENR, some research workers suggested that during the aging process, the crosslinking ether bonds, which are sensible to heat and O₂, might act as reaction centers leading to the thermal degradation of ENR [3,4]. But up till now, no researches of the effects of intermolecular ether on the processing performance of ENR have been presented in any reports.

The objective of the present investigation is to separate the gel and sol of ENR obtained by the epoxidation of NR latex with in situ formed performic acid, and to study the thermal aging and processing behaviours of gel and sol with the help of the rubber processing analyzer (RPA), thermogravimetric analysis (TGA) and infrared spectrometry.

2. Experimental

2.1. Material and reagents

The high ammonia natural rubber latex concentrate with a dry rubber content of 60% was produced in Hainan Province, PR China. Both the formic acid (Fluka) and hydrogen peroxide (Shanghai Chemical Reagents, China) were analytically pure reagents and were standardized before use. The toluene, alcohol, pentone-2 and acetone (Shanghai Chemical Reagents, China) were chemically pure reagents.

2.2. Preparation of epoxidized natural rubber

The natural rubber latex concentrate (1.00 mol calculated as isoprene segment) was stabilized with a nonionic surfactant and diluted with a predetermined amount of distilled water. Formic acid (0.25 mol) and H₂O₂ (0.75 mol) solutions were added slowly to the latex under stirring. The reaction was carried out for 24 h at 50 °C to obtain ENR latex. The temperature of the reaction system was then reduced to room temperature using a cool water bath, and then a proper amount of aqueous ammonia was added to adjust the pH up to 9. The ENR latex could now be ready for further analysis. The molar percentage of epoxy groups, determined with FT-IR method, was 48.4 mol%.

A certain amount of ENR latex was poured into a clean culture dish and coagulated with alcohol. The serum of upper stratum was removed, and the coagulum was washed with alcohol and acetone for three times. The coagulum was dried to mass constant under reduced pressure at 50 °C after the volatilization of solvent.

The dried ENR (5 g) was swollen in toluene (100 ml) at room temperature for three days, and then filtered with a stainless-steel screen (120 ± 10 μm). After the volatilization of solvent from the filter solution, the residual rubber was dried in vacuum to obtain the sol. The unsolved rubber remained on the screen was further swollen in pentone-2 for three days at room temperature and then

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