EPOXIDATION AND DEGRADATION OF NATURAL RUBBER

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1. Introduction

Effective recycling of waste tires is important for environmental protection and resource utilization. Natural rubber (NR) is one of major components of tires. In order to achieve effective recycling of waste tires, it is necessary to investigate the utilization of its main rubber components. Epoxidation is a long-standing technique to improve the properties of rubbers. Hydrogen peroxide is one of effective stable catalysts with a broad scope for olefin epoxidations and alcohol oxidations because of its character of cheap, clean and give water as the sole byproduct. Catalysts based on tungsten in situ activation of H_2O_2 for the epoxidation of olefins are particularly attractive since tungsten is a readily available and inexpensive transition metal, with good catalytic stability and recycling efficiency without any specially designed organic ligands.

In this paper, by combining sodium tungstate with the generally adopted acetic acid / hydrogen peroxide epoxidation system, natural rubber can be effectively oxidized to prepare telechelic epoxidized liquid natural rubber (TELNR).

2. Experimental

The epoxidation and degradation reactions were carried out in air in a 250mL three necked round-bottomed flask equipped with a magnetic stirrer and a thermometer. Typically, 4.08 g (60 mmol C=C) of natural rubbers were dissolved in toluene, then added 45 mol% acetic acid; 0.85 mol% $Na_2WO_4 \cdot 2H_2O$ was dissolved in 10 ml H_2O_2 (30%) solution and added dropwise to the polymer solution at 60℃ with stirring continuously. After reaction, the product were precipitated with ethanol, and then washed with distilled water; The products were marinated in the 1% Na_2CO_3 solution for about 24 hour and then washed with distilled water; The products were then dried in a vacuum oven at 50°C until constant weight has been reached.The chemical structure of the products was characterized by FT-IR, ^{1}H-NMR and GPC.

3. Results and Discussion

By comparing the infrared spectrum of NR and DENR, it can be clearly seen that the characteristic signals of epoxide ring at 1241.4 (symmetric stretching of epoxide ring) and 874.6 cm^{-1} (asymmetric stretching of epoxide ring) appeared while the carbon-carbon double bound at 3034.4 (stretching of carbon-carbon double bound) and 837.0 cm^{-1} (bending of carbon-carbon double bound) decreased after reaction. On the other hand, according to the ^{1}H-NMR spectrum for NR and TELNR, two signals at 1.2 and 2.7 ppm assigned to methyl and methine protons of the epoxy group, respectively, appeared in the spectrum of TELNR. These results strongly prove the NR has been successfully epoxidized.

As for the epoxidazation efficiency, it can be seen that the traditional peracetic acid only owns low epoxidation efficiency for NR (Tab.1). The degree of epoxidation was no more than 1.0% at 60 ℃ after 6 h, and it only reached to 5.6% after reacting for as long as 24 h. Interestingly, by combing acetic acid with Na_2WO_4, the epoxidation efficiency was sharply increased (6 h: 9.2%, 24 h: 37.2%), proving the $Na_2WO_4/CH_3COOH/H_2O_2$ system possesses high-efficiency for epoxidation of NR.

Tab. 1 Effects of sodium tungstate on the epoxidation and degradation of natural rubber.

Na_2WO_4 (% molar ratio)	t (h)	Epoxidation (%)	$\overline{M_w}$ ($\times 10^5$)[a)]	$\overline{M_n}$ ($\times 10^5$)[a)]	PDI
-	-	-	5.77	4.15	1.39
0	6	1.0	5.53	4.28	1.29
0	24	5.6	4.30	2.30	1.87
0.85	6	9.2	3.93	2.23	1.76
0.85	24	37.2	0.93	0.19	4.93

a) Caculated from GPC.

The weight and number-average molecular weight ($\overline{M_w}$ and $\overline{M_n}$) and polydispersity index (PDI) of the NR before and after reaction calculated according to the GPC curves were also listed in Tab. 1.The decrease of the molecular weight has been observed for the $Na_2WO_4/CH_3COOH/H_2O_2$ system, after reacting for 24 h, the $\overline{M_w}$ of TELNR was significantly decreased from 5.77×10^5 Da to 0.93×10^5 Da.

4. Conclusions

By combining sodium tungstate with the geneally adopted acetic acid / hydrogen peroxide epoxidation system, natural rubber can be effectively oxidized to prepare telechelic epoxidized liquid natural rubber (TELNR). In this reaction system, natural rubbers were reacted at 60 ℃ for 24 h, a TELNR with an epoxidation degree of 37.2% and weight average molecular weight of 0.93×10^5 has been obtained.

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