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Role of supercritical carbon dioxide for selective impregnation of decrosslinking reagent into isoprene rubber vulcanizate

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Abstract

The behavior of supercritical CO_2 ($scCO_2$)/low molar mass molecule/crosslinked rubber ternary system was investigated in relation to the impregnation of reagent into the isoprene rubber (IR) vulcanizates, which was the first step of new decrosslinking reaction. The diffusion coefficient of decrosslinking reagent, diphenyl disulfide (DD), into the IR network in $scCO_2$ was 3.2×10^{-11} m^2/s. The distribution coefficient (K_c) of DD between the solvent and IR matrix was also determined for $scCO_2$ and toluene. The K_c for $scCO_2$ was higher about four orders of magnitude than that for toluene. DD was uniformly dispersed in the crosslinked IR matrix under 10 MPa at 313 K in $scCO_2$. These phenomena are advantages of use of $scCO_2$ for the effective decrosslinking reaction of IR vulcanizate.

Keywords: Supercritical carbon dioxide; Impregnation; Isoprene rubber

1. Introduction

Rubber industry is confronting the problem how to handle the used rubber products [1–4]. Devulcanization process is the most favorable method for the handling. Generally, the used rubbers are swollen in organic solvents for decrosslinking reaction in order to introduce some decrosslinking reagents into the rubber networks. After the decrosslinking reaction, however, the swelling solvents have to be removed from the rubbers for obtaining high quality of recycled rubbers. Both high efficiencies for the decrosslinking reaction and the purification of recycled rubbers are necessary in the processing. Therefore, the choice of solvent becomes very important for the chemical recycling of rubber products. Up to now, an impregnation of low molar mass molecule into a polymeric matrix by using an intermediation of supercritical fluids (SCF) has been focused on, and extensively reviewed [5–11]. The density and solvent strength of SCF are continuously tunable as functions of temperature and pressure up to liquidlike values [12,13]. These results provide us an ability to control the degree of swelling of rubber products and the distribution of low molar mass penetrant between the swollen rubber phase and the fluid phase. The low viscosity and zero surface tension of SCF were reported to bring about the faster mass transfer of penetrants into the swollen polymers comparing with conventional solvents in some instances [5,6]. Among several SCFs, supercritical CO_2 ($scCO_2$) is expected to be the most advantageous intermedium for decrosslinking reaction of rubber networks, because it is chemically inactive, nontoxic, nonflammable and inexpensive. Additionally, a removal of CO_2 is very easy, because CO_2 is gaseous at an ambient atmosphere. In fact, from these advantages, $scCO_2$ has been utilized in the pharmaceutical production [8] and supercritical fluids dying [9–11], so on.

Using $scCO_2$, we have studied a new decrosslinking process for isoprene rubber (IR) [2] and natural rubber (NR) vulcanizates [3,4], where sulfur-cured IR and NR vulcanizates were efficiently decrosslinked with a selective scission at crosslinking sites in the networks. Diphenyl disulfide (DD) was found to be the most effective decrosslinking reagent for the process. However, the factors for these useful decrosslinking reactions have not been appeared yet. In this

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study, the behavior of $scCO_2$/low molar mass molecule/crosslinked rubber ternary system is fundamentally investigated in relation to the impregnation of decrosslinking reagent into the IR vulcanizate in $scCO_2$.

2. Experimental

IR (IR2200, JSR Co.) was mixed with 1 part per hundred rubber by weight (phr) of dicumyl peroxide (DCP, Nippon Yushi. Co.) on a 8-inch two-roll mill. The compound was cured at 443 K for 10 min to obtain a crosslinked IR. Since the sulfur-cured vulcanizate contains a lot of reagents for curing, the peroxide-cured vulcanizate was used in this study for the quantitative analysis of impregnated reagent into the rubber matrix. Crosslinking density of the IR vulcanizate was determined to be 8.4×10^{-5} mol/cm^3 by using the Flory–Rehner Eq. [14]. DD was a commercial grade origin (Nacalai Tesque, Inc.). Other reagents and solvents were commercial ones and used as received. Impregnation experiment was carried out at 313 K in a stainless steel cell (inner volume: 62 ml) equipped with a thermocouple and a pressure gauge. A glass vessel containing DD (0.100 g) was loaded into the cell. A sheet of the crosslinked IR (0.500 g, 15 mm × 15 mm × 2.3 mm) was suspended in the center of the cell. For an infrared spectroscopy measurement, a spherical crosslinked IR (1.52 g, 7.5 mm in radius) and 0.760 g of DD were used. Liquid CO_2 was charged into the cell through a high-pressure liquid pump at 313 K until a desired pressure was reached. (The critical point of CO_2 is 304.3 K under 7.38 MPa.) After a definite soaking time, CO_2 was discharged from the cell and the crosslinked IR was taken out. When CO_2 was removed completely, the sample was weighted, where the weight gain of the sample against its initial weight was regarded as an amount of DD impregnated into the sample. The impregnation experiment was also carried out in toluene with the same cell and sample. Sixty ml of toluene was poured into the cell at room temperature under ambient atmosphere, and the cell was heated up to 313 K. After keeping at that temperature for 72 h, the sample was taken out and dried completely. The impregnation experiments for tetradecane, docosane, xylene and phenyl ether as low molar mass molecules were also carried out in the same methods described above.

The mass uptake is defined as Eq. (1)

$$\text{Mass uptake} = m_t/M_0 \tag{1}$$

where m_t and M_0 stand for the mass of low molar mass molecule impregnated into the crosslinked IR at soaking time, t, and the mass of low molar mass molecule loaded in the cell, respectively. The diffusion coefficient of DD in the crosslinked IR under $scCO_2$ was estimated by the Fick's law described in Eq. (2)

$$\frac{\delta C}{\delta t} = D\frac{\delta^2 C}{\delta X^2} \tag{2}$$

where C is a concentration of solute, t is a time, X is a distance and D is a diffusion coefficient. The decrosslinking reagent, DD (solute) is considered to be distributed between crosslinked IR (rubber phase) and solvent phase at equilibrium in the impregnation experimental condition, and the distribution coefficient (K_c) of the solute is defined as following Eq. (3).

$$K_c = \frac{C_{\text{rubber}}}{C_{\text{solvent}}} \tag{3}$$

Where C_{rubber} and C_{solvent} are concentrations of the solute in the rubber phase and in the solvent phase at equilibrium, respectively.

After the impregnation experiments at 313 K under 10 MPa for 24 and 96 h, infrared spectroscopy measurements were performed on Fourier Transform infrared spectroscopy with microscopic displacement equipment (Shimadzu, IR Prestige AIM-8800) with a resolution of 2 cm^{-1}. The accumulation was 16 scans. The measurements were carried out for several points between the surface and the center of the cross-section of the spherical crosslinked IR.

A stainless steel cell (28 ml in volume) with two circular quartz windows (20 mm in diameter) at the both sides of the cell was used to measure the degree of swelling for the cylindrical shaped crosslinked IR in $scCO_2$ at 313 K under 10 MPa.

3. Results and discussion

The effect of CO_2 pressure on the mass uptake of DD into the IR matrix at 313 K is shown in Fig. 1. The mass uptake of DD was almost zero at 0.1 MPa, i.e. under the ambient pressure and gradually increased with the increase of CO_2 pressure up to ca. 6 MPa. At near critical pressure of CO_2 (7.38 MPa), the mass uptake of DD abruptly increased, and after the critical point it gradually increased again. The

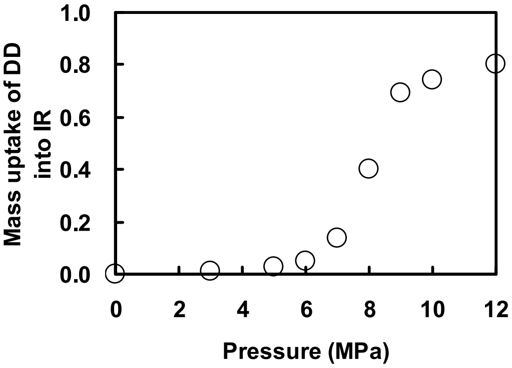

Fig. 1. Effect of pressure on the mass uptake of DD into the IR matrix at 313 K for 10 h soaking in CO_2.