Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Polymer 46 (2005) 2016–2019

polymer

www.elsevier.com/locate/polymer

Polymer Communication

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

Masaaki Kojima[a], Shinzo Kohjiya[a], Yuko Ikeda[b,*]

[a]*Kyoto University, Institute for Chemical Research, Uji, Kyoto 611-0011, Japan*
[b]*Kyoto Institute of Technology, Faculty of Engineering and Design, Matsugasaki, Sakyo, Kyoto 606-8585, Japan*

Received 21 September 2004; received in revised form 13 December 2004; accepted 20 December 2004
Available online 26 January 2005

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

---

* Corresponding author. Tel.: +81 75 724 7558; fax: +81 75 724 7580.
E-mail address: yuko@ipc.kit.ac.jp (Y. Ikeda).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.12.053

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

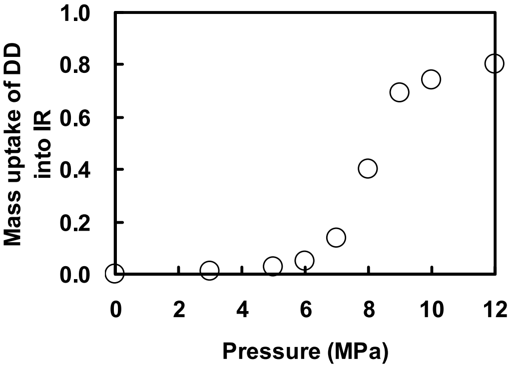

Fig. 1. Effect of pressure on the mass uptake of DD into the IR matrix at 313 K for 10 h soaking in CO_2.

supercritical state of CO_2 was found to significantly affect the selective impregnation of DD into the crosslinked IR. The solubility of DD in CO_2 seems to be a little under the ambient pressure, but it may become larger with the increase of CO_2 pressure, because the solubilizability of CO_2 is generally reported to increase with the increase in pressure [12,13]. Therefore, it is speculated that once DD was dissolved in CO_2, the transference of DD into the IR matrix must have been fast, which might result in the increase of mass uptake of DD in the IR network. This point will be appeared in near future.

The effect of soaking time on the mass uptake of DD into the IR matrix at 313 K under 10 MPa is shown in Fig. 2. The mass uptake of DD increased with the increase of soaking time, and the equilibrium of the mass uptake was reached after ca. 22 h where it remained constant at ca. 0.91. Apparently, DD was efficiently transferred and impregnated into the IR matrix, and most of DD was present in the crosslinked IR than in $scCO_2$ at equilibrium. The diffusion coefficient of DD in the crosslinked IR under $scCO_2$ was estimated to be 3.2×10^{-11} m^2/s using Eq. (2). Generally, it is reported that the diffusivity of solutes in the polymers strongly depends on the molecular diameter of the solutes and those of small gases in the plasticized polymers are higher by two or three orders than those of the low molar mass molecules such as plasticizers [15]. Additionally, the diffusion coefficient of CO_2 in the crosslinked IR was 1.1×10^{-9} m^2/s at 323 K under 10 MPa. Therefore, the obtained result on the diffusion coefficient of DD in the IR matrix under $scCO_2$ seems to be reasonable. It was also reported that the diffusion coefficient of dye (Disperse Red 324) in poly(ethylene terephthalate) in $scCO_2$ at 373 K under 15 MPa was 2.4×10^{-15} m^2/s and the diffusion coefficient increased with the increase of both pressure and temperature [11]. Although the experimental conditions were different between the study on the dye and ours, the diffusivity of a low molar mass molecule into the rubbery polymer is suggested to be faster than that into the glassy polymer.

The distribution of DD in the crosslinked IR is also important factor to increase the efficiency of decrosslinking reaction for the IR network. Thus, a distribution coefficient (K_c) of DD for IR matrix in $scCO_2$ was compared with that in toluene which was the most conventional swelling solvent for crosslinked rubbers. In order to calculate K_c, the degree of swelling of the crosslinked IR in both solvents was measured in advance. It is noted that the degree of swelling of IR vulcanizate in $scCO_2$ was 1.15, whereas that in toluene was 7.10. As shown in Fig. 3, the images of the crosslinked IR before and after the swelling in $scCO_2$ were not much different. Appreciable swelling of the rubber vulcanizate in good solvents was not observed in $scCO_2$. Taking the degree of swelling of the crosslinked IR in each solvent, the K_c values were calculated to be 1150 and 0.28 for $scCO_2$ and for toluene, respectively. Surprisingly, the former was about 4000 times larger than the latter, although the degree of swelling of IR vulcanizate in $scCO_2$ was very low. Toluene is one of the best swelling solvents for the crosslinked IR as shown in the result of swelling measurement, and also a good solvent for DD. Therefore, the high impregnation of DD into the IR matrix was expected to take place in toluene, but the result was the opposite.

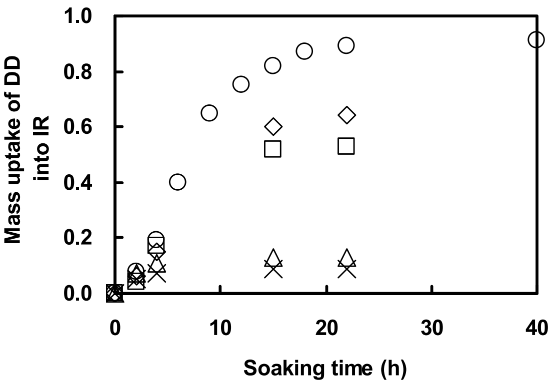

Fig. 2. Effect of soaking time on the mass uptake of DD into the IR matrix at 313 K under 10 MPa in $scCO_2$. ○, Diphenyl disulfide; △, tetradecane; □, docosane; ×, xylene; ◇, phenyl ether.

On the other hand, the solubilizability of $scCO_2$ was not so high for DD. DD is considered to be transported from the CO_2 phase to the IR matrix. Thus, the major function of $scCO_2$ is concluded not to dissolve DD but to accelerate DD permeation into the rubbery matrix. It should be pointed out that this phenomenon was detected for only DD in this moment. As illustrated in Fig. 2, other low molar mass molecules such as tetradecane, docosane, xylene and phenyl ether show less mass uptakes at 313 K under 10 MPa in sc CO_2 than DD. The modest solubility of DD in $scCO_2$ and high affinity of DD for IR are considered to result in the high mass uptake of DD in the IR network. These results mean that $scCO_2$ is the most efficient solvent for the impregnation of decrosslinking reagent 'DD' into the poly(isoprene) segment for chemical recycling of IR and NR products.

Furthermore, the dispersion of DD in the IR matrix was found to be homogenous, that was appeared by an infrared spectroscopy measurement for the cross section of spherical sample. The absorbance ratio between the peaks of out of plane deformation vibration for aromatic CH of DD at 740 cm^{-1} and out of plane deformation vibration for olefinic CH of poly(isoprene) at 837 cm^{-1} was used for the quantitative analysis of the concentration of DD in the IR matrix. As shown in Fig. 4, the ratios remain almost constant at all points from the surface of the spherical crosslinked IR for both samples which were soaked in $scCO_2$ for 24 h and 96 h. The effect of soaking time on the amount of DD impregnated into the IR matrix was clearly observed for the spherical shaped samples. However, DD was able to be transferred into the IR matrix homogeneously during the impregnation process in this study, not depending on the soaking time. This can be attributed to the unique properties of $scCO_2$. DD may be easily diffused into the

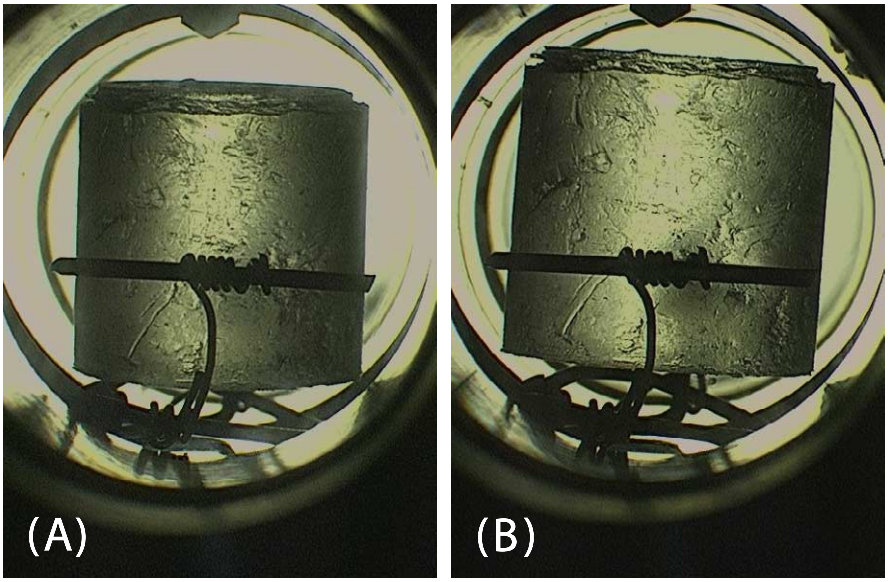

Fig. 3. Images of cylindrical crosslinked IR (A) before swelling and (B) in $scCO_2$ at equilibrium at 313 K under 10 MPa. The same bar was set inside for comparing.

rubber matrix with $scCO_2$ owing to the high diffusivity and zero surface tension of $scCO_2$.

In conclusion, the selective and homogeneous impregnation of decrosslinking reagent DD into the IR matrix was found to occur in $scCO_2$, which is ascribed to the effective decrosslinking reaction of rubber vulcanizates composed of isoprene segments. The high distribution coefficient and diffusion coefficient of DD to the IR matrix were observed in CO_2 under the condition of 10 MPa and 313 K, where CO_2 is supercritical state, which enhanced the characteristic impregnation of DD into the IR network. This result clearly suggests that the combination among $scCO_2$ and reactants is very important to take advantages of $scCO_2$ for new polymer processing with a high yield and quality.

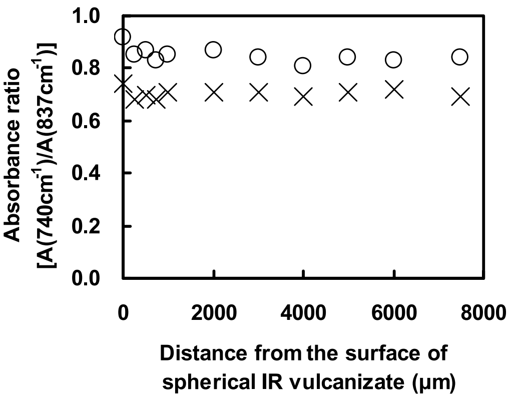

Fig. 4. Dispersion of DD from the surface of spherical IR vulcanizates. ×, Soaking for 24 h; ○, soaking for 96 h.

Acknowledgements

The authors are grateful to Messrs H. Mizoshima and K. Ogawa of Toyo Tire & Rubber Co., Ltd and to Mr Ohara of Kyoto Institute of Technology for the supporting of the experiments. Infrared measurement was kindly conducted in Shimadzu Co. This study was supported by Industrial Technology Research Grant Program in ID: 02B67006c from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

[1] Liu HS, Mead JL, Stacer RG. Rubber Chem Technol 2000;73:551.
[2] Kojima M, Ogawa K, Mizoshima H, Ikeda Y, Tosaka M, Kohjiya S. Rubber Chem Technol 2003;76:957.
[3] Kojima M, Tosaka M, Ikeda Y. Green Chem 2004;6:84.
[4] Kojima M, Tosaka M, Ikeda Y, Kohjiya S. J Appl Polym Sci 2005;95: 137.
[5] Shim JJ, Johnston KP. J AIChE 1989;35:1097.
[6] Berens AR, Huvard GS, Korsmeyer RW, Kunig FW. J Appl Polym Sci 1992;46:231.
[7] Watkins JJ, MaCarthy TJ. Macromolecules 1994;27:4845.
[8] Kazarian SG, Martirosyan GG. Int J Pharm 2002;232:81.
[9] Ngo TT, Liotta CL, Eckert CA, Kazarian SG. J Supercrit Fluids 2003; 27:215.
[10] Alessi P, Ireneo K, Angelo C, Alessia F, Mariarosa M. J Supercrit Fluids 2003;27:309.
[11] Sicardi S, Manna L, Banchero M. Ind Eng Chem Res 2000;39:4707.
[12] King JW, Friedrich JP. J Chromatogr 1990;517:449.
[13] Yang J, Griffiths PR. Anal Chem 1996;68:2353.
[14] Flory PJ, Rehner J. J Chem Phys 1943;11:521.
[15] Berens AR, Hopfenberg HB. J Membr Sci 1982;10:283.