

Permeability of Nitrogen Gas through Chemically Modified and Vulcanized Polybutadiene[†]

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ABSTRACT: Permeability of N₂ gas through partly dichlorocyclopropanated and vulcanized polybutadienes was studied. *cis*-1,4-Polybutadiene was modified with dichlorocarbene which was generated by the reaction of CHCl₃ with aqueous NaOH solution in the presence of a phase transfer catalyst. A series of modified polymers containing dichlorocyclopropane rings in the main chain were produced and pressed into plane membranes in the presence of vulcanizing agent. Permeability of N₂ gas through these cured membranes with reacted double bonds decreased in a logarithmic fashion in proportion to the amount of dichlorocyclopropane rings partly introduced in the polybutadiene. Increase in a glass transition temperature of the dichlorocarbene-modified polymers corresponded to a decrease in permeability. The low permeability of the modified polymers are attributed to low internal mobility of the polymer chains and to an increase in the density of the modified polymers.

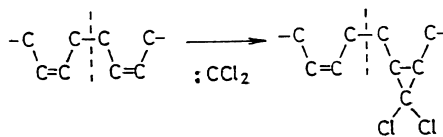
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Glass Transition Temperature /

The epoxidation of a natural rubber has been investigated using a natural rubber latex, and the epoxidized rubber exhibits resistance to swelling with hydrocarbon oils and retains high strength typical of *cis*-1,4-polyisoprene.^{1,2}

We previously studied the epoxidation of polybutadiene by an organic peracid, and determined the sequence distribution of monomer units in the partly epoxidized polydiene by the proton-decoupled ¹³C NMR spectra.³⁻⁵ The sequence distribution of monomer units in the modified polymers agreed with that calculated on the basis of random distribution of unreacted and epoxidized units. This suggests that the sites of the epoxy groups are not affected by the same kind of groups previously formed.^{4,5}

Komoroski and his coworkers reported the

¹³C NMR spectra, glass transition temperatures, and phase morphology of a number of dichlorocarbene adducts of polybutadiene.^{6,7} For *cis*-1,4-polybutadiene, the formation of an adduct is illustrated as



It has been described that dichlorocyclopropane rings are randomly incorporated into polymers over the entire range of the ring content.

Concerning the formation of three-carbon rings, the addition of dichlorocarbene to an unsaturated double bond is the same as epoxidation. From this point, it is expected that

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chemically modified polybutadiene with dichlorocarbene has very similar chemical and physical properties to the epoxidized natural rubber of high durability. Furthermore, it is interesting to investigate the specific nature of the partly dichlorocyclopropanated polybutadiene from the viewpoint of its industrial application in the production of tires with no tubes.

We report in this article the permeability of N_2 gas for modified polybutadiene with dichlorocyclopropane rings.

EXPERIMENTAL

Preparation of Dichlorocyclopropanated Polybutadiene

cis-1,4-Polybutadiene used in this study was UBEPOL BR #150 consisting of *ca.* 98% *cis*-1,4-structure, and $[\eta]$ was 2.2 dl g^{-1} . Reagents were used without purification after purchase.

To a solution of 108.2 g polymer in 340 cm^3 of CHCl_3 , which contained 1.0 g tetrabutylammonium bromide, was added dropwise a 50% aqueous NaOH solution with vigorous stirring over several hours to form dichlorocarbene *in situ*. The temperature was thermostated in a water bath at 45°C . The chloroform solution was washed with deionized water until neutral. The modified polymer was precipitated by pouring the chloroform solution into a large volume of methanol and dried at room temperature under vacuum.

Polymer Analysis

The percent of reacted double bonds (%-RDB) was determined by elemental analysis of chlorine.⁶

Glass transition temperature (T_g) was measured using a DUPONT 910 Differential Scanning Calorimeter. A 10 mg sample was heated at 10°C per minute over the temperature range of -120 to 70°C .

Densities of a modified polymers were measured by the replacement method in methanol, using a pressed cube of the sample polymer.

Table I. Compound recipes for vulcanization

Composition in vulcanization ^a	Run numbers	
	1—6	7
Polymer	100	100
TT ^b	0.1	1
DM ^c	—	2
Sulfur	1.2	—
DPG ^d	1	—
ZnO	2	1
Antioxidant D ^e	1	1
Stearic acid	1	1

^a Weight ratio of each component.

^b Tetramethylthiuram disulfide.

^c Dibenzothiazyl disulfide.

^d Diphenyl guanidine.

^e Phenyl- β -naphthylamine.

Vulcanization

Vulcanization of the dichlorocyclopropanated polymers was carried out by use of common additives shown in Table I. To avoid a remarkable decrease of permeability by the combined sulfurs, the amount of sulfur contained in the vulcanized polymers was kept comparably low.

All samples were mixed on a roll mill and crosslinked in the form of plane membranes by hot-pressing at 150°C and 100 kg cm^{-2} pressure to moderate rubbery modulus as measured by a JSR culastometer. The thickness of the membranes was *ca.* 0.2 mm.

Measurement of Permeability of N_2 Gas

The permeability of N_2 gas was measured by the vacuum gas permeation technique using a Yanagimoto Gas Permeation Apparatus (Model GTR-30) in the temperature range from 293 to 333 K. The apparatus was enclosed in an oven maintained at a certain temperature. The apparatus consisted of a gas cell divided into two chambers by the membrane being tested. One of the chambers was charged with N_2 gas at a certain pressure. The amount of N_2 gas transmitted to the other chamber was determined by gas-chromatography.

Permeability coefficient P was calculated at a steady state using eq 1:

$$P = \frac{q \cdot l}{(p_1 - p_2) \cdot a \cdot t} \quad (1)$$

where q is flux, p_1 and p_2 are pressures on a high-pressure and low-pressure sides, respectively, l is film thickness, a is film area and t is time. The thickness of a membrane was measured with a conventional thickness gauge. The general theory of gas transport in polymer and the detailed methods of measurement and calculation of permeability were published elsewhere.⁹⁻¹¹

RESULTS AND DISCUSSION

A part of the results of the %RDB, indicating percent of dichlorocarbene addition to unsaturated double bonds, glass transition temperatures (T_g) and density of the dichlorocyclopropanated polymers, is listed in Table II. Figure 1 shows plots of the %RDB and T_g in Table II. T_g increased in proportion to the amount of dichlorocyclopropane rings in the polymers. This can be explained well by the fact that the glass transition temperature is related to the mobility of polymer chains. The polymers listed in Table II were used for measurement of permeability after vulcanization under the conditions in Table I.

In general, solubility and diffusivity of a gas in a membrane are closely related to the chemical structure and physical characteristics of molecules constituting the membrane.⁹ On the other hand, as factors controlling both chemical and physical properties, a plasticizer¹² and a filler¹³ affect also solubility and diffusivity. Therefore, to eliminate these factors, the membranes in our study were prepared without using a plasticizer and a filler such as reinforcing carbon black.

Permeation of a gas through rubbery material is more complex than diffusion, since the former involves both dissolution and evaporation processes. A permeability coefficient of a

Table II. Analysis of dichlorocyclopropanated polybutadiene

Sample	% RDB ^a	T_g^b °C	Density ^c
1	0	-104	0.907
2	10	- 88	
3	23	- 72	
4	30	- 59	1.125
5	39	- 40	
6	48	- 33	1.215
7	70	1	

^a % reacted double bond, calculated from chlorine content by the Schoniger oxygen flask method.

^b Measured using a differential scanning calorimeter.

^c Measured by a replacement method, g/cm⁻³.

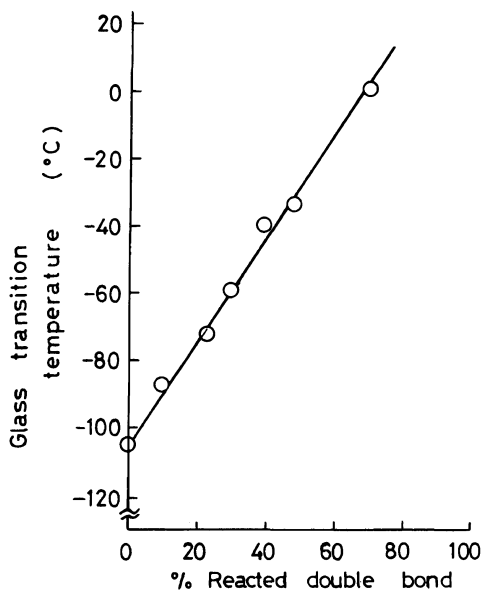


Figure 1. Glass transition temperatures of the partly dichlorocyclopropanated *cis*-1,4 polybutadiene as a function of the reacted double bond.

gas, however, is experimentally easier to obtain than a diffusion coefficient.

From among many different kinds of gases, N₂ gas was selected in our study as the most typical and normal gas for the measurement of permeability. According to our preliminary examination, differences in the vulcanization conditions scarcely affected the permeability

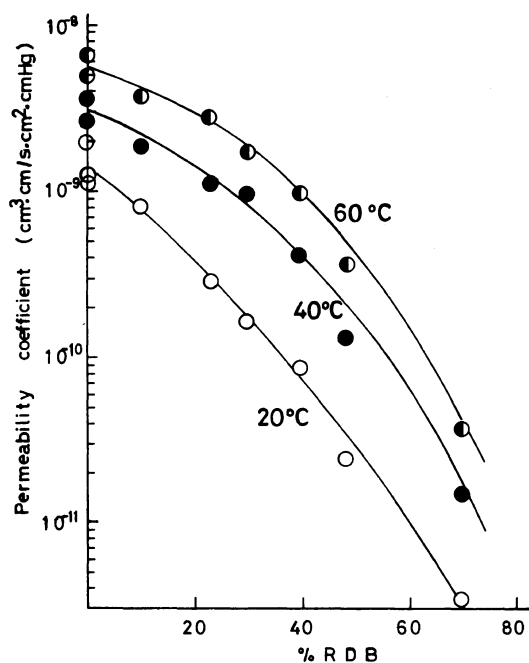


Figure 2. Semilogarithmic plots of permeability coefficients of the vulcanized polymers for N_2 gas vs. % reacted double bond before vulcanization.

coefficient as long as the same modified polymers are used. Therefore, it can be quite certain that permeability of the partly modified polymers is dependent their nature.

Figure 2 shows the dependence of the permeability coefficient for N_2 gas at three different temperatures, 20, 40, and 60°C. The permeability of N_2 gas through the partly dichlorocyclopropanated and vulcanized polybutadiene membranes increased with an increase in temperature. This experimental result indicates that these membranes have no disagreeable pinholes and they are uniform.

It was reported that vulcanization of a rubber involving both the formation of crosslinks and the introduction of combined-sulfur groups, leads to decrease of the permeability of N_2 gas.^{14,15} It was considered that the combined sulfurs,¹⁴ like other polar groups, increase the cohesive energy of the elastomer molecules, and that cohesive energy and crosslinks formed¹⁵ could reduce the mobility of the polymer

molecules.

It is concluded that the decrease of N_2 gas permeability with increase in %RDB for the vulcanized polymers is attributed principally to the increase in T_g and density of the dichlorocyclopropanated polymers solely in consideration of diffusivity.

The diffusivity of a rubber is linearly correlated with its density and thermal expansion, that is, a rubber with higher density has lower diffusivity.⁹ In fact, the density of the modified polymers before vulcanization increased with increase in the amount of dichlorocyclopropanated units in the polymers. On the other hand, the solubility of N_2 gas may decrease in the modified polymers which have fewer unsaturated bonds, and to some extent this may be responsible for lowering permeability. For a further detailed study of permeability of the dichlorocyclopropanated and vulcanized polybutadiene, it is necessary to do work on the measurement of the diffusion constant.

Consequently, the permeation of N_2 gas through partly dichlorocyclopropanated and vulcanized polybutadiene can be primarily controlled by the content of dichlorocyclopropane rings.

We also think that these new materials with much lower permeability to gas than the original polybutadiene have high possibility for commercial use in the production of tires with no tubes.

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