

Barrierity of Hydrogenated Butadiene-Acrylonitrile Rubber and Butyl Rubber After Exposure to Organic Solvents

Sylwia Krzemińska

Department of Personal Protective Equipment, Central Institute for Labour Protection – National Research Institute (CIOP-PIB), Łódź, Poland

Władysław M. Rzym ski

Institute of Polymer and Dye Technology, Technical University of Łódź, Łódź, Poland

Resistance of antichemical clothing primarily depends on the type of material it is made from, in particular on the type of polymer used for coating the fabric carrier. This paper reports on systematic investigations on the influence of the cross-linking density of an elastomer and the composition of a cross-linked elastomer on its resistance to permeation of selected organic solvents. Tests of barrier material samples made from nonpolar butyl rubber (IIR) and polar hydrogenated butadiene-acrylonitrile rubber (HNBR) showed that (a) in rubber–solvent systems with medium thermodynamic affinity, cross-linking density influenced resistance to permeation and (b) the polarity of the system had a significant influence on barrierity.

permeation of solvents barrier material elastomers exposure to organic solvents

1. INTRODUCTION

Permeation of toxic chemicals through the skin in the working environment is a hazard faced by workers exposed to such chemicals. This problem is especially important in the case of volatile solvents commonly used in industry, where it is necessary to use personal protective equipment, especially protective clothing. Such products are subject to specific requirements concerning the durability and resistance to permeation by chemicals. The most important protection parameter is the breakthrough time of the material tested against specific substances. Standard No. EN ISO 6529:2001 defines breakthrough time as the time between the beginning of the test, i.e., contact of the liquid chemical with one side of the material, and the point when a certain

standardized velocity of chemical substance permeation through the tested material [1]. Longer breakthrough time indicates higher resistance of the material to exposure to the test substance and provides valuable help in selecting material, mostly elastomers, for workers exposed to specific hazardous chemicals in the workplace.

Some studies have focused on optimal conditions for cross-linking of elastomers, on various cross-linking substances leading to formation of particular bonds between macromolecules, as well as on the effect of the type of cross-links on the parameters of the network [2]. However, there are few studies on the effect of the chemical and physical structure of polymer and elastomer macromolecules on permeability by chemical substances, especially organic solvents.

This paper has been prepared on the basis of the results of a research task carried out within the scope of the first stage of the National Programme “Improvement of safety and working conditions” partly supported in 2008–2010—within the scope of state services and statutory activity—by the Ministry of Labour and Social Policy. The Central Institute for Labour Protection – National Research Institute is the Programme’s main co-ordinator.

Correspondence and requests for offprints should be sent to Sylwia Krzemińska, CIOP-PIB, ul. Wierzbowa 48, 90-133 Łódź, Poland. E-mail: <sykrz@ciop.lodz.pl>.

The aim of this study was to investigate how the degree of cross-linking of an elastomer affects the permeation of solvents through (a) elastomer membranes made of hydrogenated acrylonitrile-butadiene rubber (HNBR) cured to various extent with dicumyl peroxide and (b) membranes made of butyl rubber (IIR) cured to various extent with sulphur.

2. METHODOLOGY

2.1. Materials

The study was carried out on HNBR (Therban A 3407; LANXESS, Germany; bound acrylonitrile 34 wt %, hydrogenation grade >99%), cross-linked with dicumyl peroxide (Luperox[®] DCP; Sigma-Aldrich, USA) and on IIR (BK 1675 N; Togliattikauchuk, Russia), cross-linked with sulphur.

Cured HNBR vulcanizates were obtained using various amounts of dicumyl peroxide: 50, 75, 100, 125 or 150 mmol/kg of rubber; they will be referred to, respectively, as H1, H2, H3, H4 and H5. Cured IIR samples were manufactured using various contents of sulphur: 0.5; 1.0; 1.5 and 2.0 phr (parts per hundred of rubber); they will be referred to, respectively, as B1, B2, B3 and B4.

Rubber compounds were prepared conventionally on a laboratory two-roll mill (Bridge, UK) and cured to optimum state (HNBR: 60 min, IIR: 22–25 min at 160 °C) determined in vulcetric experiments, according to Standard No. ISO 3417:2008 [3]. Cured rubber sheets were prepared by molding under pressure.

Those materials were tested for cross-linking density with the equilibrium swelling method. Testing was based on determining the weight increase of a sample material induced by a particular solvent. For calculations, Flory-Huggins parameters available in the literature were used.

2.2. Chemical Substances

Barrier properties of cured rubber were assessed by determining breakthrough times for two organic solvents: (a) n-butyl acetate, a polar solvent (solubility parameter $\delta = 17.4 \text{ MPa}^{0.5}$) with medium thermodynamic affinity to HNBR

($\delta_{\text{HNBR}} = 19.3 \text{ MPa}^{0.5}$) and medium affinity to IIR ($\delta_{\text{IIR}} = 15.7 \text{ MPa}^{0.5}$); and (b) cyclohexane, a nonpolar solvent ($\delta = 16.4 \text{ MPa}^{0.5}$) with low thermodynamic affinity to HNBR ($\delta_{\text{HNBR}} = 19.3 \text{ MPa}^{0.5}$) and high affinity to IIR ($\delta_{\text{IIR}} = 15.7 \text{ MPa}^{0.5}$).

The main criteria for selecting these substances were common use at work sites and the thermodynamic properties defined by the solubility parameter δ of the chemicals and the cured rubbers that were used. The chemicals (from POCH, Poland) were analytically pure.

2.3. Apparatus

The following equipment was used in the study:

- a gas chromatograph Trace GC (Thermo Finnigan, UK), a flame ionization detector (FID), a capillary chromatographic column (Rtx-5, length: 7 m, internal diameter: 0.32 mm; Restek, USA) for cyclohexane analysis;
- a gas chromatograph Unicam Ati 610 (Unicam, Italy), FID, a packed chromatographic column (without packing, internal diameter: 3 mm; Supelco, USA) for n-butyl acetate analysis;
- injecting valves and thermostats;
- a custom-made two-chamber stainless-steel permeation cell for testing the resistance of the material to permeation by liquid chemicals (Jazpol, Poland) (Figure 1);

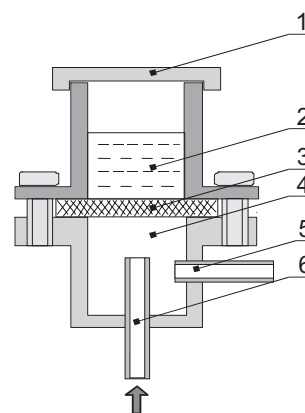


Figure 1. A test cell for investigating resistance of polymer materials to permeation by liquids under conditions of single permanent contact. Notes. 1—lid; 2—chamber with the test chemical; 3—tested material sample; 4—chamber with the collection medium; 5—collection medium outlet; 6—collection medium inlet.

The parameters of the chromatographic analysis were adjusted to make this an isothermal analysis:

- for cyclohexane analysis
 - column, dispenser and detector temperature: 40, 110 and 180 °C, respectively;
 - hydrogen and air flow: 35 and 350 ml/min, respectively;
 - nitrogen pressure: 20 kPa;
 - detector sensitivity range: 1;
- for n-butyl acetate analysis
 - column, dispenser and detector temperature: 200, 200 and 250 °C, respectively;
 - hydrogen and air pressure: 15 and 10 psi, respectively;
 - nitrogen flow: 73 ml/min;
 - voltage measured with a detector: 100 mV;
 - detector sensitivity range: high.

2.4. Test Method

To test their permeation, cut-out rubber samples (diameter: 40 mm, thickness: 0.32–0.38 mm) were placed in permeation cells [4, 5, 6] (Figure 1). They were placed so that one side faced the chamber filled with the liquid chemical. The upper chamber of the cell was filled with a precise amount of the solvent (10 ml). An airflow of 85 cm³/min was directed through the lower chamber; it collected the permeated solvent molecules and transported them for the chromatographic analysis. The testing cells along with samples and chemical substances in glass

flasks were thermostated for 30 min in the same temperature as during the tests, i.e., 23 ± 3 °C.

After the end of thermostating, software was turned on to record the duration of the tests and the concentration of the permeating chemicals as peaks on the chromatograms. Every minute (for the chromatograph with a packed column) or every 2 min (for the chromatograph with the capillary column), the injection valve automatically transferred precisely 100 µl of the air from under the tested sample into the injector of the chromatograph. Whether the vapour samples were collected every 1 or 2 min depended on the technical possibilities of the apparatus. The experiment took 6 h [7, 8]. Figure 2 is an outline of the experiment.

Breakthrough time was determined directly from chromatograms with the calibration curves, the obtained chromatograms and the concentration at which the threshold velocity of compound permeation through the material reached the given value of $P = 1 \mu\text{g}/\text{cm}^2 \text{ min}$, according to Standard No. EN ISO 6529:2001 [1]. Deviation of the thickness of the tested sample from the reference thickness of 0.35 mm was taken into consideration.

As a result of the experiment, the breakthrough time, which was an arithmetic average of determinations from three different samples, was calculated.

3. RESULTS

Figures 2–5 illustrate the determined breakthrough times of HNBR and IIR of different crosslink density by selected solvents.

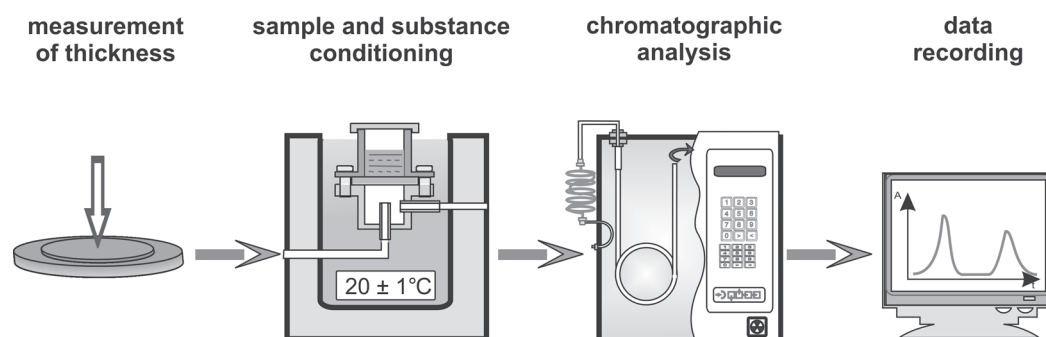


Figure 2. Testing permeation of a solvent through barrier materials.

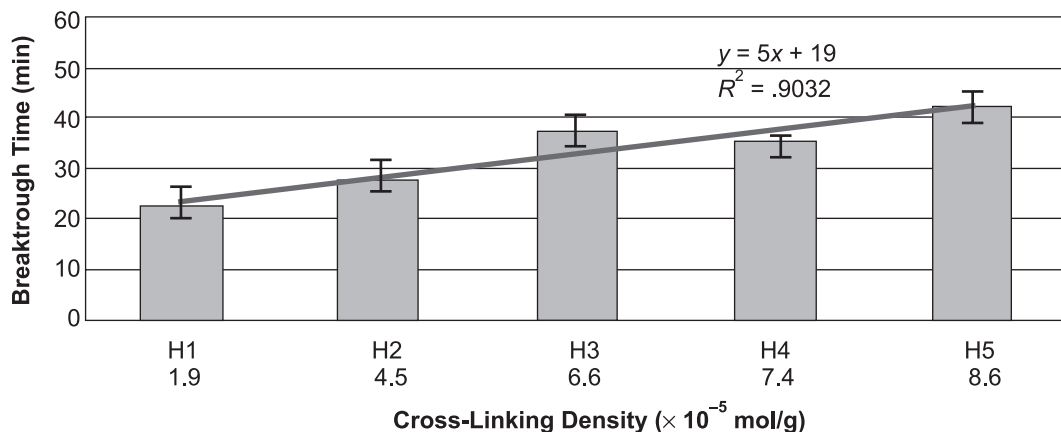


Figure 3. Breakthrough time of n-butyl acetate through hydrogenated acrylonitrile-butadiene rubber cured with dicumyl peroxide.

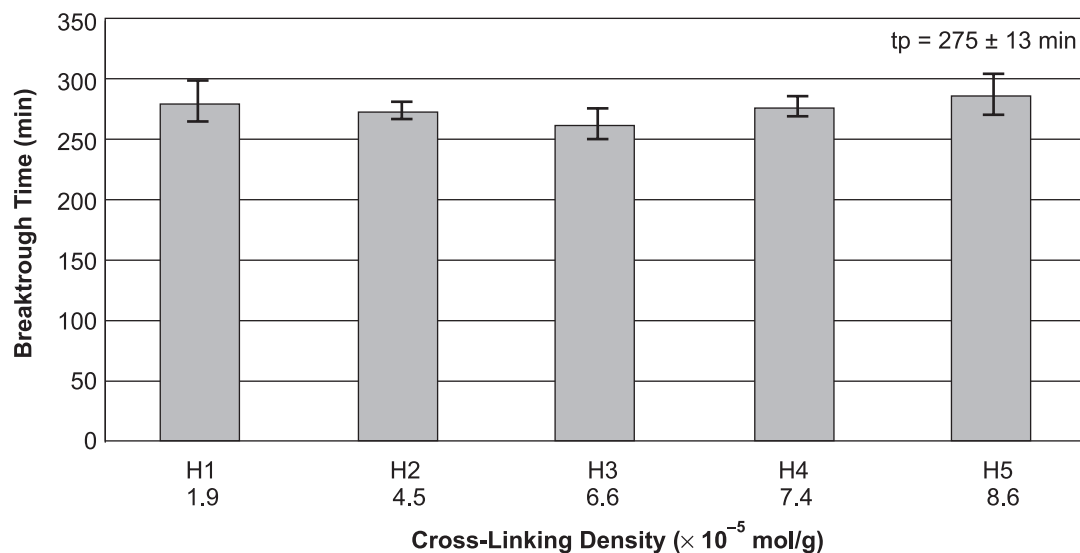


Figure 4. Breakthrough time of cyclohexane through hydrogenated acrylonitrile-butadiene rubber cured with dicumyl peroxide.

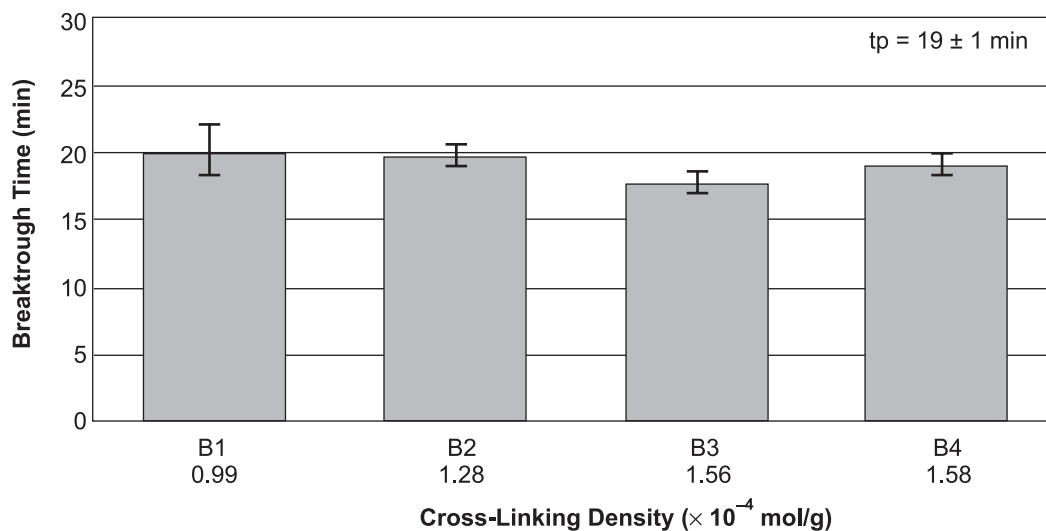


Figure 5. Breakthrough time of cyclohexane through butyl rubber cured with sulphur.

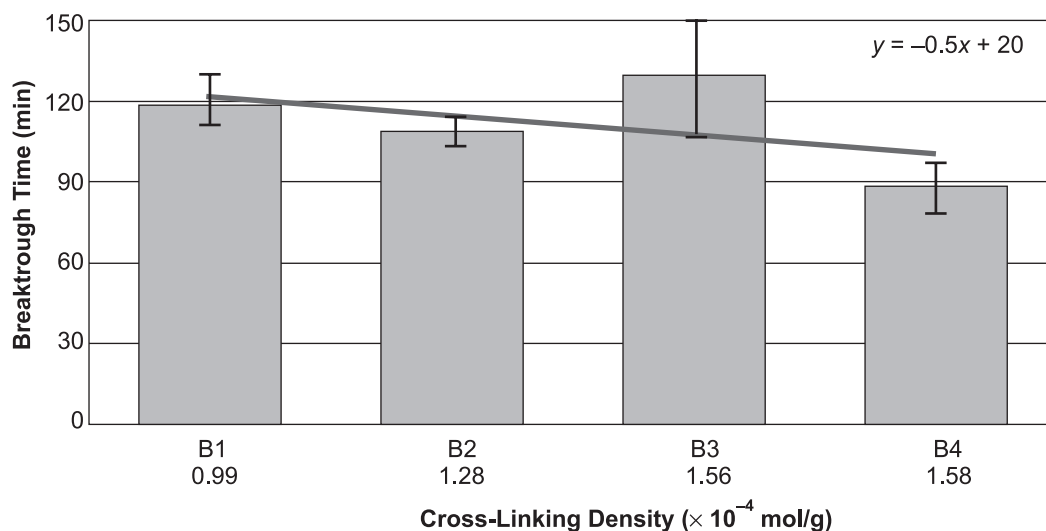


Figure 6. Breakthrough time of n-butyl acetate through butyl rubber cured with sulphur.

The analysis showed that barrier properties of cured HNBR and IIR against chemical substances, characterized by the determined breakthrough times, depended on the properties of the test solvent. Those determined breakthrough times were analysed to test the statistical significance of the differences found in relation to cross-linking density of the tested samples of cured HNBR and IIR. Analysis of variance (ANOVA) in Excel was used, with the significance level of $p = .05$.

The analysis of the results showed that for permeation of cyclohexane through HNBR and IIR, there was no statistically significant difference between individual variants; in all cases $p > .05$. In contrast, when n-butyl acetate permeation was tested, there was no significant statistical difference in breakthrough time between the following material variants of HNBR: H1 and H2, H1 and H3, H1 and H4, H1 and H5 and also of IIR: B1 and B4. The p values ranged from .010 to .103.

In the case of HNBR, the permeation tests with a nonpolar solvent (cyclohexane), characterized by low thermodynamic affinity to an elastomer, showed no effect of cross-linking density on barrier properties of the material (Figure 2). Breakthrough times ranged from 278 min for the sample with the lowest network density (H1, $1.85 \cdot 10^{-5}$ mol/g) to 285 min for the sample with the highest one (H5, $8.57 \cdot 10^{-5}$ mol/g).

In contrast, in the case of the polar n-butyl acetate, characterized by medium thermodynamic affinity to HNBR, an increase in network density in the vulcanizate led to a remarkable increase in breakthrough time (Figure 3). The breakthrough time determined for the sample with the lowest cross-linking density (H1) was 21 min, whereas for that with the highest one (H5) breakthrough time was twice as long, ~42 min. This means that the increase in the degree of curing of HNBR results in improving barrier properties against a polar solvent. The correlation of the obtained breakthrough times and HNBR cross-linking density was close to linear (linear correlation coefficient $R = .903$).

Tests on cross-linked IIR samples indicate that in the case of a nonpolar solvent (cyclohexane, high thermodynamic affinity to IIR), the curing degree had no effect on barrier properties. Breakthrough times ranged from 20 min for the sample with the lowest (B1, $0.99 \cdot 10^{-4}$ mol/g) to 19 min for the sample with the highest network density (B4, $1.58 \cdot 10^{-4}$ mol/g), comparable to cyclohexane permeation tests through polar HNBR.

However, in the case of the polar solvent (butyl acetate with medium thermodynamic affinity to IIR), cross-linking density influenced breakthrough time. This time for the sample with the lowest cross-linking density (B1) was 118 min, whereas for cured IIR with the highest

one (B4) reached 88 min. In contrast to HNBR, the barrier properties of sulphur-cured IIR became gradually unfavourable with increased curing degree.

The comparison of results obtained for the permeation of polar and nonpolar solvents (n-butyl acetate, cyklohexane) through nonpolar IIR and through polar HNBR demonstrates that in the case of an elastomer–solvent system with medium or good thermodynamic affinity polar breakthrough times are rather short (20–40 min). On the other hand, breakthrough times determined for systems of poor thermodynamic affinity, e.g., differing in polarity, are significantly longer (100–280 min). Thus, the difference in the polarity of the system component has an important effect on barrier properties and it is more predictable (and thus safer) to use materials made of rubber differing in polarity from that of the solvent.

The results are somewhat consistent with those published elsewhere. Generally, an increase in rubber cross-linking density contributes to reduced permeability of gases [9]. There is a considerably smaller number of studies on permeation of liquid chemicals, and the problem seems much more complex. Thus, no unequivocal conclusions have been presented. George, Varughese and Thomas's study on selected systems consisting of cured polypropylene/acrylonitrile-butadiene rubber blends (50/50 wt/wt) and toluene as a liquid substance indicated that increased cross-linking density leads to decreased permeation of toluene [10].

4. CONCLUSIONS

On the basis of the results concerning the effect of cross-linking density, a selected parameter characterizing the structure of cured elastomer materials (nonpolar IIR and polar HNBR), on their permeation and chemical barrier properties against organic solvents, the following conclusions can be made:

- for rubber–solvent systems with high or low thermodynamic affinity, cross-linking

density of the tested materials does not affect breakthrough time;

- for rubber–solvent systems with medium thermodynamic affinity, cross-linking density influences breakthrough time, irrespective of the polarity of the rubber.
- the polarity of the system has an important effect on barrier properties and it is more predictable (safer) to use materials made of rubber differing in polarity from that of the solvent used.

This study provides recommendations for the development of barrier materials made of cured elastomers. In the cases of very significant and very slight differences in solubility parameters for the rubber–solvent system, where the cross-linking density is not a critical parameter affecting breakthrough time, the degree of curing of the rubber used should be determined by functional properties and economic factors. On the other hand, for systems with a medium difference of solubility parameters of rubber and solvent, and a confirmed effect of network density on barrier properties, the extent of cross-linking should be established in preliminary tests.

REFERENCES

1. European Committee for Standardization (CEN). Protective clothing—protection against liquid chemicals—test method: resistance of materials to permeation by liquids (Standard No. EN ISO 6529:2001). Brussels, Belgium: CEN; 2001.
2. Smejda-Krzewicka A, Rzymski WM, Tarniowy A. Novel elastomers containing carboxyl groups. In: Parasiewicz W, Rzymski WM, editors. *Elastomery i przemysł gumowy*. Piastów, Poland: Instytut Przemysłu Gumowego/Łódź, Poland: Politechnika Łódzka; 2006. p. 29–47. In Polish.
3. International Organization for Standardization (ISO). Rubber—measurement of vulcanization characteristics with the oscillating disc curemeter (Standard No. ISO 3417:2008). Geneva, Switzerland: ISO; 2008.

4. Krzemińska S. Determination of organic solvents mixtures permeating through butyl rubber membranes by means of gas chromatography. *Polish Journal of Applied Chemistry*. 2007;51(1–2):49–53.
5. Krzemińska S, Rzymiski WM. Effect of layered silicate on barrier properties of cured butyl rubber. *J Phys: Conf Ser*. 2009;146(1). Retrieved January 17, 2011, from: <http://iopscience.iop.org/1742-6596/146/1/012007>
6. Krzemińska S, Rzymiski WM. Effect of condition treatments of organic solvents on barrier properties of cured butyl rubber. *Polimery*. 2008;53(4):60–6. In Polish.
7. Krzemińska S, Rzymiski WM. Study on barrier properties of elastomers. In: XII Research Workshop: Processing of Polymer Materials. Toruń, Poland: Instytut Przetwórstwa Tworzyw Sztucznych “Metalchem”; 2007. p. 121–5. In Polish.
8. Krzemińska S, Rzymiski WM. Barrier properties of butyl rubber vulcanizates exposed to organic solvents. *Elastomery*. 2007;11(5):3–9. In Polish.
9. George SC, Ninan KN, Thomas S. Permeation of nitrogen and oxygen gases through styrene-butadiene rubber, natural rubber and styrene-butadiene rubber/natural rubber blend membranes. *European Polymer Journal*. 2001;37(1):183–91.
10. George S, Varughese KT, Thomas S. Molecular transport of aromatic solvents in isotactic polypropylene/acrylonitrile-co-butadiene rubber blends. *Polymer*. 2000; 41(2):579–94.