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Barrier properties of hydrogenated acrylonitrile-butadiene rubber composites containing modified layered aluminosilicates

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The resistance to permeation by the selected solvents of flat membranes made of cured hydrogenated acrylonitrile-butadiene rubber (HNBR) materials without any fillers and containing 5 phr of layered aluminosilicate nanofiller (bentonite), modified with various types of ammonium salts or N330 type carbon black, was investigated. The barrier properties were assessed on the basis of the breakthrough time of a liquid with low (cyclohexane) or average (butyl acetate) thermodynamic affinity to HNBR, determined according to EN 6529:2001, through a cured elastomer sample.

The addition of bentonite, irrespectively of the method of modification of its particles, was found to increase the cured HNBR breakthrough time by 20 – 35 % in the case of slowly permeating non-polar cyclohexane, and by 50 – 130 % in the case of polar butyl acetate permeating more rapidly, in comparison with the barrier material containing no filler. The layered aluminosilicate nanofillers increased the breakthrough time of the material sample for both the tested solvents. In particular, the breakthrough time for polar butyl acetate was even longer than for conventional carbon black. Additionally, the increase of the breakthrough time was observed to depend on the modifier of bentonite particle surface.

Keywords: *solvents permeation, barrier material, elastomer, nanofillers, layered aluminosilicate*

1. Introduction

During the recent years, considerable attention has been paid to the research assessing the effect of nanometric fillers on the properties of polymer nanocomposites, including mechanical strength, resistance to fire and chemicals, as well as barrier properties [1–4]. Such features are also very desirable in the case of polymer materials used in production of clothing and gloves protecting against harmful chemical substances. The results of studies completed to date concerned primarily the assessment of the effect of nanofillers on permeation velocity of gaseous chemicals through elastomer nanocomposites. Stephen [5] observed that the permeation of gases through elastic membranes, containing nanometric layered aluminosilicates is much slower than in the case of material samples containing conventional silica. Nitrogen and oxygen permeation velocity through membranes made of natural rubber (NR) filled with nanometric layered aluminosilicate amounted to $4.5 \cdot 10^{-10}$ and $13 \cdot 10^{-10}$ mol/m·s·Pa for nitrogen and oxygen, respectively, and was twofold reduced for both gases in comparison with NR vulcanizate containing conventional silica as a filler. In the case of carboxylic styrene-butadiene rubber (XSBR), the difference in oxygen permeability between material samples containing bentonite or silica, amounting to $0.3 \cdot 10^{-10}$ and $1.25 \cdot 10^{-10}$ mol/m·s·Pa, was fourfold higher.

Takahashi [6] observed that the addition of vermiculite as a nanofiller up to 30% by weight to butyl rubber (IIR) leads to over 20-fold reduction of the permeability of helium, hydrogen, oxygen,

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nitrogen, methane and carbon dioxide through vulcanizates of this rubber, as well as to reduction of the values of diffusion coefficient by two orders of magnitude for these gases in comparison with IIR samples containing no filler. The aforementioned studies demonstrated the favorable effect of nanofillers on reduction of permeation velocity of gases through elastomer materials; however, because of the differences in sizes and shapes of gas and liquid molecules, they cannot be directly extrapolated to permeation of liquids. In our previous studies [7, 8], we observed very differentiated effects of commercially available Nanofil 15 nanofiller on permeation of non-polar cyclohexane and polar butyl acetate through vulcanizates of non-polar butyl rubber, depending on the type of liquid chemical and on the filler content.

Occupational hazards involve frequent exposures of the workers to the effect of liquid chemicals; therefore, the study aimed at the investigation of the effect of nanofillers (layered aluminosilicates – modified bentonites) on permeation of the selected liquid chemicals (solvents) through membranes composed of polar specialty elastomer, namely hydrogenated acrylonitrile-butadiene rubber (HNBR). The barrier properties of protective items were studied and analyzed on the basis of the determined breakthrough time t_p, defined according to EN ISO 6529 as: "the time interval between the initial moment of the test, i.e. contact of the liquid chemical with the material, and the moment when it reaches a particular permeation velocity" [9]. The organic solvents, often used at industrial worksites, characterized by known and proven skin absorption, were selected for the study [10, 11].

2. Experimental

2.1. Materials

Hydrogenated acrylonitrile-butadiene rubber (HNBR) Therban A 3407 (34% by weight of bound acrylonitrile, hydrogenation level >99% mol.) manufactured by Bayer AG/Lanxess AG, was used in the study. The rubber was cured with dicumyl peroxide (DCP, Luperox DCP®, Aldrich), used in the amount of 10 mmol DCP/100 g rubber. A small amount, i.e. 5.0 phr, of layered aluminosilicate nanofiller – bentonite was modified with dimethyldistearylammonium chloride (Nanofil 15; produced by Süd-Chemie PORO Additive), alkyl dimethyl benzyl (C_{12-18}) ammonium chloride (Nanobent ZR1, ZGM "Zębiec" S.A.) dimethyldidecylammonium chloride (Nanobent ZR2, ZGM "Zębiec" S.A.) or N330 type conventional carbon black (Degussa Poland SA). The selected properties of the layered aluminosilicate nanofillers have been listed in Table 1. The rubber mixtures were prepared using a conventional method with a laboratory rolling mill and cured for 60 min at 433 K, i.e. under the conditions ensuring decomposition of > 99% of peroxide, determined on the basis of vulcametric studies according to ISO 3417 [12]. Nanocomposite membranes of 0.35 ± 0.03 mm thickness were obtained by pressing and by molding under pressure.

By the use of the method of wide angle X ray scatter (WAXS), it was observed that during mixing and dispersion of nanofillers in the elestomer matrix, as well as during the subsequent curing, the distance between laminas of the nanofiller in powder form, equaling 2.80, 1.91 and 2.10 nm, increased by 1.04, 1.21 and 0.84 nm in the composites containing Nanofil 15, Nanobent ZR1 or Nanobent ZR2, respectively, which indicates intercalation and partial exfoliation of the nanofillers by HNBR chains. It was confirmed by scanning electron microscope (SEM) analysis of fractures of the investigated nanocomposites, which indicates that nanofiller particles with distinct laminar structure are distributed evenly in the elastomer matrix and characterized by good adhesion to rubber. Both single nanofiller laminas and their agglomerates of 30 – 50 μm size were found to occur in the studied nanocomposites. It is illustrated in Fig. 1, which presents an example of a SEM image of a brittle fracture of cured HNBR, containing Nanofil 15 in the amount of 5 phr/100 phr HNBR.
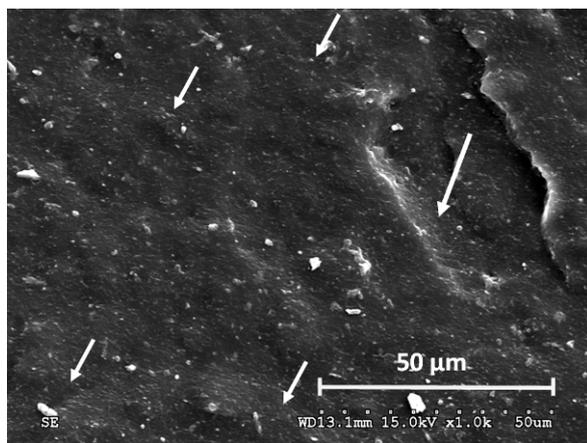
Fig. 1. The SEM image of a brittle fracture of HNBR nanocomposite (5 phr Nanofil 15) at 1000 x magnification (short white arrows indicate bright lines representing nanofiller distribution, a long white arrow indicates a nanofiller agglomerate).

The selected properties of the obtained nanocomposites are listed in Tables 1 – 2. In view of HNBR susceptibility to crystallization or elongation, no significant effect of the studied nanofillers on the increase of tensile strength TS_b of the nanocomposites was observed. As it follows from the evaluation of equilibrium swelling of the cured HNBR composites in methylethylketone (Q_v^{MEK} = 3.31; 3.66; 3.99; 3.84 and 3.94 ml/ml rubber phase for the sample with no filler, with carbon black or nanofillers Nanofil 15, Nanobent ZR1 or Nanobent ZR2), respectively although the added nanofillers reduce the effectiveness of DCP curing activity to some extent, the investigated materials are characterized by very similar values of cross-linking density, and therefore its influence on the determined breakthrough time can be omitted in the further analyses, (see also [13]).

2.2. Chemical substances

The barrier properties were assessed on the basis of the determined cured HNBR breakthrough times for two solvents (pure or analytic grade, POCH SA Poland):

1. cyclohexane – a non-polar, volatile solvent (boiling point 80.8 °C), with a low thermodynamic affinity to rubber, estimated on the basis of solubility parameter δ, equaling δ = 16.4 MPa$^{0.5}$ at δ_{HNBR} = 19.3 MPa^{0,5};
2. butyl acetate – a polar, less volatile solvent (boiling point 127 °C), with an average thermodynamic affinity to HNBR (δ = 17,4 MPa$^{0.5}$) [14–17].

2.3. Apparatus

The apparatus used for testing the resistance of HNBR vulcanizates to permeation by solvents and for the assessment of breakthrough times included:

1. gas chromatograph Trace GC, Flame Ionisation Detector (FID), capillary chromatographic column (Rtx-5, length 7 m, internal diameter 0.32 mm) for cyclohexane analysis;
2. gas chromatograph Unicam Ati 610, Flame Ionisation Detector (FID), packed chromatographic column (without packing, internal diameter 3 mm) for butyl acetate analysis;
3. injecting valves and thermostats;
4. two-chamber permeation cell for testing the material resistance to permeation by liquid chemicals made from stainless steel (Fig. 2); compare [8, 9, 13].

2.4. Testing method

The material samples (diameter: 40 mm, thickness: 0.35±0.03 mm) were placed in the permeation cell (Fig. 2). The testing cells along with the samples and chemical substances in glass flasks were thermostated for 30 min at the same temperature as during the tests, i.e. 23±3 °C. After that time, the upper chamber of the cell was filled with 10 ml of the solvent. An airflow with flow intensity of 85 cm^3/min was transferred through the lower chamber to collect the permeated solvent molecules and to transport them to the chromatographic analysis. The air-solvent vapour mixture was directed to an injection valve coupled with the chromatograph. The test was continued for 6 h.

By the use of the calibration curves and the chromatograms obtained, the concentration

Table 1. Selected properties of the used bentonite/silicate.

Property/Filler type		Nanobent ZR1	Nanobent ZR2	Nanofil® 15[1]
Form		Powder		Powder
Colour		Cream		Cream
Bulk density, g/cm^3		< 0.6	< 0.6	0,48
Density, g/cm^3		2.01-2.03	2.01-2.03	No data
Sieve analysis		Sieve residue, wt.%		No data
Sieve	100 μm	0	0	No data
	63 μm	≤ 40	≤ 35	No data
	45 μm	≤ 40	≤ 40	No data
	20 μm	≤ 20	≤ 25	No data
Moisture content, %		≤ 2.0	≤ 2.0	< 3
Interlayer distance, Å		19.1	21.0	28.0
pH of water dispersion		6.5-7,0	6.5-7,0	No data
Weight loss at 550 °C, wt.%		25-30	25-30	No data
Weight loss at 220 – 400 °C, wt.%		22	29	No data
Decomposition temperature, °C		220	210	>250
Sorption of xylene, vol.%		>5	>20	No data

[1] Medium particle size 25 μm; moisture content < 3%; after Data Sheet of Süd-Chemie AG

Table 2. Selected properties of investigated nanocomposites prepared of cured, hydrogenated acrylonitrile-butadiene rubber (HNBR).

Sample Filler content 0 or 5 phr	Equilibrium swelling in methylethyl-ketone Q_v, [ml/ml HNBR]	Tensile strength TS_b^1 [MPa]	Elongation at break E_b^1 [%]	Tensile stress at 100, 200 and 300% elongation[1] S_{e100}, S_{e200}, S_{e300} [MPa]		
				S_{e100}	S_{e200}	S_{e300}
H0 – no filler	3.31	21.3±2.1	580±107	1.32±0.00	1.63±0.10	1.85±0.10
H1 - Nanofil® 15	3.99	21.9±2.5	665±87	1.91±0.10	2.56±0.10	3.24±0.20
H2 - Nanobent ZR1	3.84	19.9±2.1	573±130	1.44±0.10	1.73±0.10	2.12±0.20
H3 – Nanobent ZR2	3.94	2)	2)	2)	2)	2)
H4 - carbon black N330	3.60	28.3±0.6	612±52	1.43±0.10	1.65±0.10	2.14±0.30

[1] determined according to PN-ISO 37:1998
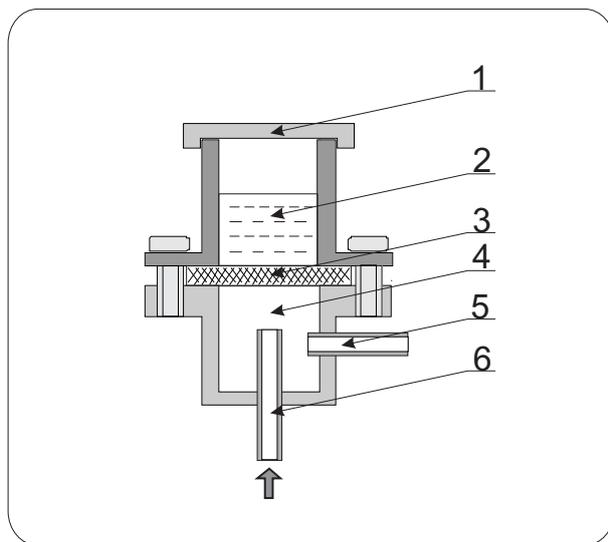
[2] not determined

Fig. 2. A scheme of the test cell for investigation of the resistance of polymer materials to permeation by liquid chemicals
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.
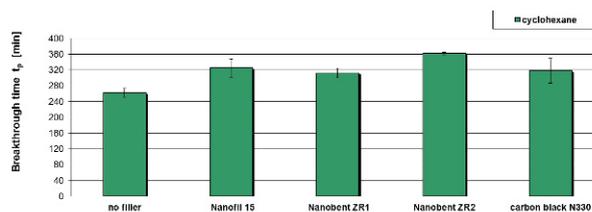

Fig. 3. Cyclohexane breakthrough time for cross-linked HNBR without a filler, or containing 5 phr of nanofiller: Nanofil 15, Nanobent ZR1, Nanobent ZR2, or 5 phr of conventional carbon black N 330.
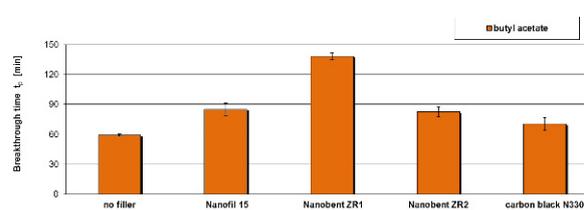

Fig. 4. Butyl acetate breakthrough time for cross-linked HNBR without a filler, or containing 5 phr of nanofiller: Nanofil 15, Nanobent ZR1, Nanobent ZR2, or 5 phr of conventional carbon black 330.

at which the threshold velocity of compound permeation through the material reached a given value of $P = 1$ $\mu g/cm^2 min$, the breakthrough time according to EN ISO 6529 standard was determined or read directly from chromatograms. The deviation of the tested sample thickness from the reference thickness (0.35 mm) was taken into account. As a result of the experiment, the breakthrough time t_p – an arithmetic average of three assessments, each from a different sample - was determined.

3. Results and discussion

The aim of the study was to determine the effect of three selected layered aluminosilicate nanofillers on permeation of organic solvents, i.e. butyl acetate and cyclohexane with different thermodynamic affinities to rubber through cured hydrogenated acrylonitrile-butadiene rubber (HNBR) nanocomposites. The determined values of breakthrough time were analysed from the point of view of statistical significance of the results in

order to find out whether the breakthrough time of material samples for the solvents used depended on the type of nanofiller added. Statistical calculations were carried out using the analysis of variance ANOVA and Excel software at the adopted level of significance P = 0.05. The results are presented in Figs. 3 and 4.

The addition of 5 phr of Nanofil 15, Nanobent ZR1, Nano-bent ZR2 nanofillers, or a conventional filler – N 330 carbon black to HNBR, caused a significant increase of cured rubber breakthrough time for both solvents, confirmed by the statistical analysis of the results. The breakthrough time of relatively slowly permeating, non-polar cyclohexane, in the case of composite containing Nanobent ZR2, increased from 262 min (samples containing no filler) to 360 min, i.e. by over 35%, for the material containing that nanofiller, (see Fig. 3). A significant increase of cyclohexane breakthrough time by ca. 20% was also observed for the material samples containing other fillers (Nanofil 15, Nanobent ZR1 or carbon black).

A similar effect of the studied fillers was also observed in the case of material permeation by polar butyl acetate of higher thermodynamic affinity to rubber than cyclohexane. The breakthrough time of butyl acetate for non-filled, cured HNBR is 59 min and – as expected – is much shorter than the breakthrough time of non-polar cyclohexane. The breakthrough time of polar butyl acetate in the case of composites containing carbon black, Nanofil 15 or Nanobent ZR2 increased by 10-15 min, i.e. by ca. 20%, without a significal impact of the filler type. However, the addition of Nanobent ZR1 caused an increase of breakthrough time to 138 min, i.e. by over 130% in comparison with non-filled, cured HNBR, Fig. 4.

The differences in the influence of the type of the studied fillers on HNBR breakthrough time for composites of different thermodynamic affinities to rubber are likely to be associated both with different susceptibility of these liquids to sorption on energetically differentiated surfaces of filler particles having different chemical structures (carbon black and aluminosilicates) and with differentiated structures of ammonium chlorides used as modifiers of surface properties of the studied aluminosilicate nanofillers. An impact of presumably different degree of dispersion and aggregation of particles of the studied nanofillers on the barrier properties of HNBR composites cannot also be excluded.

It should be emphasized that in the earlier studies of HNBR nanocomposites containing only 2.5 phr of Nanofil 15 [18] it was observed that such small amount of that filler did not increase the breakthrough time; instead, it caused a deterioration of the properties of HNBR composite barrier against butyl acetate (Fig. 5). The addition of twofold larger amount, i.e. 5 phr of this nanofiller significantly increased the breakthrough time of the composite, both for the polar and nonpolar solvents (Figs. 5, 6). The results of the above evaluations allow us to draw a conclusion that from the point of view of barrier properties, as in the case of mechanical properties, there is a specific range of contents of a conventional filler or a nanofiller, for which a favourable effect of the
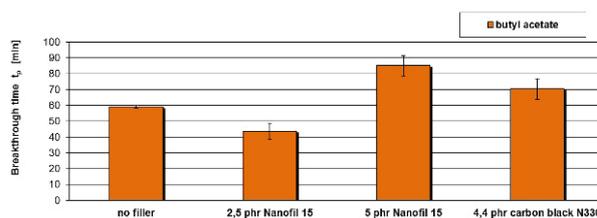

Fig. 5.   Butyl acetate breakthrough time for cross-linked HNBR without a filler, or containing a nanofiller Nanofil 15 in the amount of 2.5 or 5 phr.
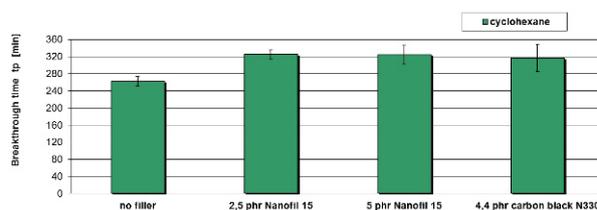

Fig. 6.   Cyclohexane breakthrough time for cross-linked HNBR without a filler, or containing a nanofiller Nanofil 15 in the amount of 2.5 or 5 phr.

filler on the barrier properties of resulting material is observed. It means that the amount and the type of the filler used to modify the produced composite must be analysed and adjusted from the point of view of a complex set of its properties, taking into consideration the specific factors the composite is exposed to and the conditions of its use.

The observed impact of the amount of Nanofil 15 nanofiller on the barrier properties of HNBR composites is qualitatively consistent with the results obtained by El-Tantawy [19]. He reported that the coefficient of naphtha diffusion through butyl rubber (IIR) composites decreases significantly with an increase in the content of titanium carbide used as a filler in this rubber.

The results obtained in the studies of barrier properties of cured HNBR containing various fillers are also qualitatively consistent with the "tortuous path model" postulated in the literature [1]. The model presumes the necessity for the permeating substance to cover a longer distance due to tortuous course of free spaces in composites containing layered aluminosilicates with elongated, plate-like particle shape [1].

Laminar structure of the nanofillers used in the study was confirmed by high-resolution scanning microscopy (SEM), indicating such structure type in particles of the tested nanofillers and predominant orientation of their distribution in one direction in the analysed composites (Fig. 1).

4.   Conclusions

The application of layered aluminosilicate nanofillers such as Nanofil 15, Nanobent ZR1 or Nanobent ZR2, as well as N330 type conventional carbon black, in the amount of 5 phr/100 phr rubber, leads to a significant increase in the breakthrough time of polar hydrogenated acrylonitrile-butadiene rubber both by polar butyl acetate, a solvent characterized by average thermodynamic affinity, and non-polar cyclohexane, a liquid with low thermodynamic affinity to HNBR, and therefore to a significant improvement of the barrier properties of the investigated composites.

The most significant, over 100%, increase of butyl acetate breakthrough time was obtained using Nanobent ZR1, i.e. bentonite modified with alkyl dimethyl benzyl (C_{12-18}) ammonium chloride, and in the case of cyclohexane – using Nanobent ZR2, i.e. bentonite modified with dimethyldidecylammonium chloride. The test results indicate a significant impact of the method of aluminosilicate modification on the efficacy of its effect as a modifier of barrier properties of HNBR composites.

Acknowledgement

References

[1] PINNAVAIA T. J. and BEALL G. W., Polymer Clay Nanocomposites, Wiley, Chichester, 1997.
[2] GOŁĘBIEWSKI J., *Przem. Chem.*, 83/1 (2004), 15.
[3] ZABORSKI M. and KUNERT A., Properties of elastomer containing fillers, W. Parasiewicz and W.M. Rzymski (Eds.), Works of Institute of Rubber Industry STOMIL and Technical University of Łódź, (2006), 229
[4] MAI Y.W. and YU Z.Z., Polymer Nanocomposites, Woodhead Publishing Ltd., Cambridge, 2006.
[5] STEPHEN R., RANANGANATHAIAH C., VARGHESE S., JOSEPH K., THOMAS S., *Polymer*, 47 (2006), 858.
[6] TAKAHASHI S., GOLBERG H. A., FEENEY C. A., KARIM D. P., FAREL M., O'LEARY K., PAUL D. R., *Polymer*, 47 (2006), 3083.
[7] KRZEMIŃSKA S., RZYMSKI W.M., *Elastomery*, 211 (2007), 3.
[8] KRZEMIŃSKA S., RZYMSKI W.M., *Intern. J. Phys. Conf. Series*, 146 (2009), 012007.
[9] Standard No. EN ISO 6529:2001, CEN 2001.
[10] KOSTRZEWSKI P. and GROMIEC J. P., Works of the Institute of Labour Medicine, Łódź, (2000).
[11] VERMEULEN R., KROMHOUT H., BRUYNZEEL D. P., de BOER E. M., BRUNEKREEF B., *Epidemiology*, 11 (2001), 350.
[12] Standard No. ISO 3417:2008, ISO 2008.
[13] KRZEMIŃSKA S. and RZYMSKI W. M., *Int. J. Occup. Saf. Ergon.*, 17 (2011), 41.
[14] RZYMSKI W. M., JENTZSCH J., SROGOSZ A., *Plaste Kautsch.*, 41 (1994), 19.
[15] BARTON A. F. M., *Chem. Rev.*, 75 (1975), 751.
[16] SHEEHAN C. J. and BISIO A. L., *Rubber Chem. Technol.*, 39 (1996), 149.
[17] BARTON A. F. M., Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press Inc. Boca Raton, Florida, 1983.
[18] KRZEMIŃSKA S., RZYMSKI W.M., European Conference on Protective Clothing (ECPC) and NOKEBETEF 9, Holland, Papendal (2009), 50.
[19] EL-TANTAWY F., *Polym. Degrad. Stabil.*, 73 (2001), 289.