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Gloves against mineral oils and mechanical hazards: composites of carboxylated acrylonitrile–butadiene rubber latex

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Resistance to permeation of noxious chemical substances should be accompanied by resistance to mechanical factors because the glove material may be torn, cut or punctured in the workplace. This study reports on glove materials, protecting against mineral oils and mechanical hazards, made of carboxylated acrylonitrile–butadiene rubber (XNBR) latex. The obtained materials were characterized by a very high resistance of the produced materials to oil permeation (breakthrough time > 480 min). The mechanical properties, and especially tear resistance, of the studied materials were improved after the addition of modified bentonite (nanofiller) to the XNBR latex mixture. The nanocomposite meets the requirements in terms of parameters characterizing tear, abrasion, cut and puncture resistance. Therefore, the developed material may be used for the production of multifunctional protective gloves.

Keywords: gloves; oils; permeation; XNBR latex; bentonite; nanocomposite

1. Introduction

Direct contact of human skin with harmful chemicals, which include, among others, mineral oils, without adequate protection poses a risk to the health of workers in the engineering industry. At the same time, for many workstations in these sectors, due to the activities performed by employees, there is also the risk of tearing, rupturing or puncturing protective material related to the weakening of the mechanical strength in contact with chemicals.

Barrier and mechanical properties are the basic parameters characterizing the potential applicability of materials for the production of gloves protecting hands against harmful chemical substances. Resistance to the permeation of noxious chemical substances should be accompanied by resistance to mechanical factors because gloves may be torn, cut or punctured in the workplace. Furthermore, materials may be also weakened due to swelling caused by chemical substances. The requirements imposed on glove materials are specified in relevant standards pertaining to personal protective equipment (PPE), including Standard No. EN 374-1:2003 [1] on permeation resistance to selected substances. The requirements concerning resistance to mechanical factors are listed in Standard No. EN 388:2003 [2]; they include abrasion, cut, puncture and tear resistance. The parameters mentioned are classified according to performance levels, which denote the protection class of materials, and are determined by experimental methods. Protective glove materials should be at least protection class 1 (performance level 1) in terms of resistance to permeation by a selected chemical substance and at least protection class 1 for all of the stated parameters characterizing the mechanical properties of the material. The classification of materials according to performance levels given in Standard No. EN 388:2003 [2] is presented in Table 1.

Materials used in PPE must meet strict requirements, so research efforts in this area are focused on improving their properties while also ensuring comfort when using the products. Thus, new materials are still being sought for gloves protecting against mineral oils and mechanical factors. Hazards linked to mineral oils are faced in the chemical, petrochemical, machine, metal and automotive industries because these oils are used as lubricants, anti-corrosives, cooling and hardening substances, anti-adhesives in the ceramic and construction industries, softeners in the production of rubber and polymer materials, fuels, greasing agents in the textile industry, as well as constituents of cosmetics and pharmaceuticals.[3–5].

This study is devoted to materials protecting against mineral oils and made of carboxylated acrylonitrile–butadiene rubber (XNBR) latex, combining very good oil resistance with considerable mechanical strength, which is highly desirable in multifunctional protective products.

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Table 1. Performance levels for glove materials protecting against chemical substances and mechanical hazards.[2] in the scope of abrasion, tear and puncture resistance there are four performance level. In the scope of cut resistance there is five performance level. In the scope of permeation resistance there is six performance level.

Parameter	Performance level					
	1	2	3	4	5	6
Permeation resistance to chemical substance (breakthrough time) (min)	10	30	60	120	240	480
Abrasion resistance (cycles)	100	500	2000	8000	–	–
Cut resistance (index I_n)	1.2	2.5	5.0	10.0	20.0	–
Tear resistance (N)	10	25	50	75	–	–
Puncture resistance (N)	20	60	100	150	–	–

While in the literature there are some examples of crosslinking XNBR with metal oxides, rubber latexes are typically crosslinked with sulfur.[6,7] European Patent EP 0486183 [8] describes the technology of manufacturing gloves from XNBR, in which a conventional crosslinking system, containing sulfur, an accelerator and zinc oxide, was applied. The latex gloves made from that rubber are characterized, depending on the XNBR type, by a tensile strength at break of $TS_b = 40$–45 MPa and an elongation at break of $E_b = 490$–580%. However, the parameters required for multifunctional gloves were not analyzed. A method of making oil-resistant gloves from XNBR is also given in European Patent EP 1128776.[9] In this case, preliminary crosslinking of latex with methacrylic acid, sulfur and a polyvalent metal oxide as crosslinking agents was applied at 40 °C for 48–96 h. An alternative method of crosslinking XNBR involves aluminum lactate (1 per hundred parts [phr]).[10] Crosslinking may be conducted at ambient temperature, but a very long process time (up to 2 weeks) is a major disadvantage of this method. The obtained films were characterized by a tensile strength at break of $TS_b = 12.7$–29.8 MPa at an elongation of $E_b = 446$–562%. Chemical resistance was studied using an indicator combining the chemical and mechanical strength of the vulcanizate. Samples were supported by clamping with a desired tensile force applied, and immersed in acetone. However, this indicator may not be correlated with resistance to permeation expressed by the breakthrough time. Interesting results were reported from a study of XNBR blends with chlorosulfonated polyethylene (CSM) crosslinked by means of zinc oxide.[11] It was found that such blends, characterized by improved flame resistance (higher oxygen index), contain both covalent crosslinks and interelastomer ionic bridges, with magnesium ions playing the role of a XNBR/CSM compatibilizer.

Many authors observe that all properties of the final products may be affected not only by the kind of rubber, but also by the degree and type of crosslinking.[12,13] Therefore, the present work was aimed at determining the influence of crosslinking type and degree of XNBR on its permeation resistance to mineral oils and on the mechanical parameters of the materials made of its latex, as characterized by puncture, cut, abrasion and tear resistance. Latex was conventionally crosslinked with sulfur and unconventionally with magnesium oxide, at different concentrations, in order to determine the relationship between the type and amount of the crosslinking agent and the properties of the crosslinked composites, and also those containing a layered aluminosilicate nanofiller.

The materials were produced by dipping with preliminary chemical coagulation. Considering the relationship between the structure of rubber macroparticles and the degree of its crosslinking, it was expected that the application of different crosslinking agents would lead to materials with different crosslinking degrees, some of which may meet all of the requirements concerning barrier and mechanical properties of the materials obtained.

Taking into account the rapid development of nanotechnology and the increasing use of nano-additives in the production of polymeric materials, the undertaken research aimed at developing materials with the addition of modified bentonite as a representative of layered silicates. The purpose was primarily to improve the mechanical properties of the material, such as resistance to tearing, abrasion, puncture and cutting.

2. Experimental

2.1. Materials

XNBR latex (trade name XVT-LA; solid content: 45%, viscosity: 45 mPa·s, surface tension: 33 mN/m) was obtained from Synthomer (Germany).

The crosslinking agents were ground sulfur (article No. 527795704; content: 99.85%, bulk density: 400–500 kg/m^3) from Chempur (Poland) and magnesium oxide (trade name Pur Mag 140; content: 98.5%, average particle size: 3.2 μm, bulk density: 500 kg/m^3) from SMA Mineral Magnesia AS (Norway).

The nanofiller was bentonite, a layered aluminosilicate (trade name Nanobent ZR1; bentonite modified with quaternary ammonium salt ($R_1R_2R_3R_4N^+Cl^-$), where R_1 = benzyl substituent; R_2, R_3 = methyl substituents; $R_4 = C_8$–C_{12} aliphatic substituent), obtained from ZGM Zębiec S.A. (Poland; manufactured by ZGM Zębiec S.A. according to the technology developed as part of target

grant No. 03933/C ZR7-6/2007 by a team at the Rzeszow University of Technology, Poland). Bentonite modification was conducted in an 8% aqueous suspension of Specjal-enriched bentonite following the procedures described in Polish Patents 178900 and 178866.[14,15].

The activator was zinc oxide (article No. 112664700; density: 5.61 g/cm^3 at 20 °C, bulk density: 300–500 kg/m^3) purchased from Chempur.

The dispersants were sodium salt of formaldehyde and naphthalenesulfonic acid condensation product (trade name Tamol NN 9401; water solubility: 400 g/dm^3) and 2,2′-methylenebis[6-(1-methylcyclohexyl)]-p-cresol (water solubility: < 0.01 g/dm^3) purchased from Enkev Poland (produced by BASF, Germany).

The accelerator was zinc diethyldithiocarbamate (trade name LUVOMAXX ZDEC; density: 1.480 g/cm^3 at 20 °C, bulk density: 330–370 kg/m^3, practically insoluble in water) produced by Lehmann&Voss&Co. (Germany).

The stabilizer was polyglycol ether (trade name Emulvin WA; readily soluble in water, viscosity: 984 mPa·s, density: 1.1 g/cm^3 at 20 °C), produced by Lanxess (Germany) and purchased from HSH (Poland).

All of the chemical reagents were of analytical grade.

2.2. Preparations of samples

The latex formulations used for the production of flat film samples contained (phr of XNBR) from 1.5 to 8.0 phr of a crosslinking agent (ground sulfur or magnesium oxide), 0.6 or 0.7 phr of 2,2′-methylenebis[6-(1-methylcyclohexyl)]-p-cresol, 0.32 or 0.5 phr of sodium salt of condensate of formaldehyde with naphthalenesulfonic acid, 0.5 phr of polyglycol ether, 7.5 phr of modified bentonite and 8.0 phr of zinc oxide and/or 1.1 phr of zinc diethyldithiocarbamate (zinc oxide and zinc diethyldithiocarbamate were used in XNBR crosslinked with sulfur). The composition of the formulations is presented in Table 2.

Latex formulations were made by adding to XNBR latex previously prepared aqueous dispersions of the following:

(1) a crosslinking system (sulfur, accelerator, antioxidant, dispersant or magnesium oxide, antioxidant, dispersant), and
(2) zinc oxide (activator) and stabilizer, in the order already given.

Dispersions were prepared using a 1-L ball mill containing 280 balls made of acid-resistant stainless steel with a diameter of 12 mm (Biomix, Poland). Depending on the type of dispersion, the mill was run at 30–50 rpm over a period of 16–72 h. The dispersions were added to XNBR latex placed in a container made of a polymer material. During the addition of the dispersions, they were mixed with the latex using a BMX-15R mechanical mixer (Biomix). The mixer was run at 20–30 rpm for 12–18 min.

Flat film samples were made by one-time dipping of the mold in the latex mixture, using a solution of calcium nitrate (35 wt%) or calcium chloride (20 wt%) in methanol as a coagulation bath. The molds were either metal cylinders (manufactured to order; Secura, Poland) or ceramic plates made of sintered aluminum oxide, type 799 (Institute of Refractory Materials, Poland) (Figure 1). The molds were dipped in the coagulation bath, and then dried at 30–50 °C in a SUP-3 laboratory dryer (Zalmet, Poland). The molds were subsequently immersed in the latex mixture, and then dried at 55–60 °C. Next, they were crosslinked at 100–115 °C for 180 min. Following this, the samples were removed from the molds and washed with tap water. Finally, the samples were dried in a laboratory dryer at 65 °C for 3 h. The samples produced in this way were 0.52–0.58-mm thick.

2.3. Chemicals

The resistance of the studied materials to chemical substances was tested using IRM 903 mineral oil, which is a mixture of specially processed petroleum fractions. It is a reference mineral oil representative of oils with a low content of additives. This mineral oil was chosen according

Table 2. Formulation of carboxylated acrylonitrile–butadiene rubber (XNBR) latex composites used for sample preparation.

Component	Sample (per hundred parts)			
	S 1.5	MgO 2.0	MgO 4.0	MgO 8.0
XNBR latex (solid content 45%)	222.2	222.2	222.2	222.2
Ground sulfur	1.5	–	–	–
Magnesium oxide	–	2.0	4.0	8.0
Zinc oxide	8.0	–	–	–
Zinc diethyldithiocarbamate	1.1	–	–	–
2,2′-Methylenebis[6-(1- methylcyclohexyl)]-p-cresol	0.6	0.7	0.7	0.7
Sodium salt of condensation product of formaldehyde and naphthalenesulfonic acid	0.5	0.3	0.3	0.3
Polyglycol ether	0.5	0.5	0.5	0.5

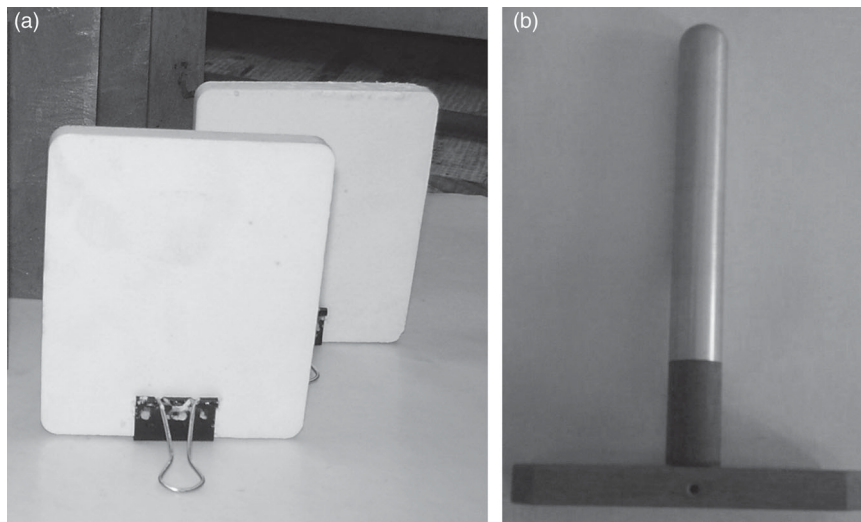Note: MgO = magnesium oxide; S = sulfur; – = not used.

Figure 1. Photographs of molds used for the production of samples: (a) ceramic; (b) metal.

to the testing methodology for materials designed for protective clothing and gloves.

2.4. Test methods

2.4.1. Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) was used to assess the degree of nanofiller dispersion in modified bentonite ZR1 and in the samples to determine whether the materials containing bentonite may be treated as nanocomposites. Measurements were conducted using Dron 234 (Dron, Russia) and Nanostar (Bruker, Germany) X-ray diffractometers with Cu-K$_\alpha$ radiation. The samples were strips 35 and 40 mm long.

2.4.2. Testing barrier properties

The testing of barrier properties, i.e., the determination of the resistance of the studied materials to permeation by the selected mineral oil, was conducted pursuant to Standard No. EN 374-1:2003.[1] Thus, the protection parameter characterizing the resistance of a given material to permeation by the selected chemical substance was determined. According to the standard, this parameter is the breakthrough time, or the time elapsed from the moment the material makes contact with a given chemical substance to the moment the permeation rate of the substance has reached 1 μg/cm^2·min.

A sample of the examined material was fixed between the two chambers of a permeation cell. The external surface of the material contacted with mineral oil, while the internal surface made contact with a solid absorbent medium, i.e., GF/A and GF/C Whatman glass microfiber filters. Subsequently, 10 ml of mineral oil was poured into the upper chamber of the permeation cell and timing was started. Interval measurements were conducted,

which means that at certain points in time (10, 30, 60, 120, 240 and 480 min after the start) the filters were taken for analysis. These intervals corresponded to the protection levels given in Standard No. EN 374-1:2003 for gloves because of the non-volatile nature of the oil, which requires the use of a solid absorbent medium for absorbing the oil particles permeating through the material. The filters were subjected to ultrasound-assisted extraction with cyclohexane.[16] The filters were immersed in a container with a solvent and placed in an ultrasonic bath. Quantitative analysis was made using gas chromatography with a flame-ionization detector (FID). A Trace GC gas chromatograph (Unicam 610, UK) equipped with a FID and a capillary chromatographic column (Rtx-5; length 30 m, internal diameter 0.25 mm, Restek, USA) were used. Oil determination was conducted in accordance with Standard No. EN ISO 9377-2:2000.[17] The test lasted 480 min.

2.4.3. Measuring of crosslinking degree

The degree of crosslinking was determined by means of equilibrium volume swelling experiments and calculating the Mooney–Rivlin elasticity constants. Equilibrium volume swelling was determined by measuring the weight and volume gain of a sample under the influence of a solvent (2-butanone). The procedure was analogous to that used in our previous work.[18].

The Mooney–Rivlin elasticity constants were determined using the standard technique, according to the protocol applied in previous studies.[19,20].

2.4.4. Testing mechanical properties

The mechanical properties of the materials, i.e., tear, puncture, abrasion and cut resistance, were determined in accordance with Standard No. EN 388:2003.[2].

Puncture and tear resistance parameters were measured using a 4465 universal tester (Instron Ltd, UK). The results are expressed as mean of four samples. The tester head movement rate was 100 ± 10 mm/s.

Abrasion resistance was measured using a Nu-Martindale tester (James H. Heal Ltd, UK). Four samples were tested. The pressure exerted on the samples during abrasion was 9 ± 0.2 kPa.

Cut resistance was tested using a Couptest machine (Sodemat, France). This parameter was calculated based on results for 10 samples of the same kind. The cutting angle was 30–35°.

Prior to the tests, the samples were conditioned in air at 21 ± 3 °C and a relative humidity of $50 \pm 5\%$.

2.5. Statistical analysis

The test results were subjected to statistical analysis. The analysis of results was performed with Statistica version 10, separately for each parameter. Conformity observed distributions with the theoretical normal distribution were analyzed using the Shapiro–Wilk test and the homogeneity of variance for tested materials was analyzed using Levene's test. The results were analyzed with analysis of variance (ANOVA) and post-hoc Tukey's test; $p = 0.05$ was adopted to determine the significance of differences between results for the different material variants.

3. Results and discussion

3.1. Modification of bentonite

Modification effectiveness was evaluated by comparing differential scanning calorimetry (DSC) results for unmodified bentonite (BS) and for bentonite modified with the ammonium salt (Nanobent ZR1). Measurements were made using a Mettler Toledo DSC 822^e apparatus (Mettler Toledo, Switzerland) with the following parameters: measurement time: 45 min; temperature range: 0–450 °C; heating rate: 10 °C/min.

The DSC curve (Figure 2) for BS exhibits one sharp peak in the temperature range of 70–140 °C, with a maximum at 120 °C, which is connected to the removal of absorbed humidity and crystallization water. A similar effect, but in the temperature range of 40–100 °C and of lesser intensity, is also present for bentonite modified with a quaternary ammonium salt (Nanobent ZR1). Additionally, the Nanobent ZR1 curve exhibits two marked endothermic peaks attributable to the decomposition of the modifier in the temperature ranges of 220–280 °C and 410–430 °C.

Examination of the distribution of aluminosilicate nanoplatelets in modified bentonite (Nanobent ZR1) using WAXS showed that the distance between them increased significantly, from 12.6 Å in unmodified BS bentonite to about 29.6 Å in modified bentonite (Figure 3). Greater
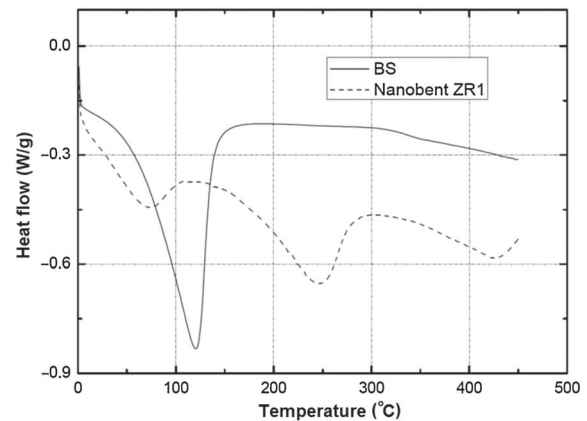

Figure 2. Differential scanning calorimetry curve for unmodified Specjal bentonite (BS) and modified bentonite (Nanobent ZR1).
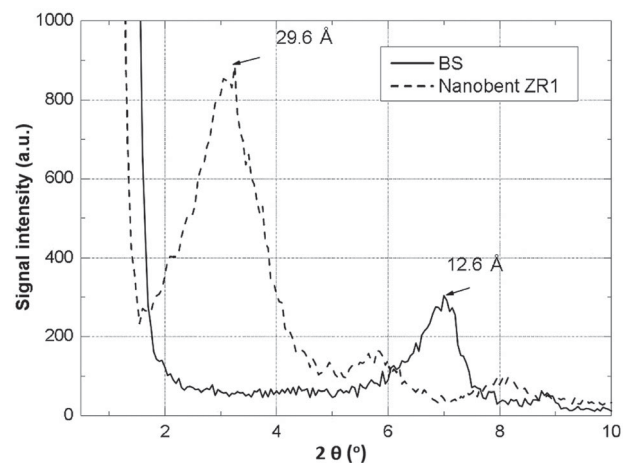

Figure 3. Wide-angle X-ray scattering curve for unmodified bentonite (BS) and modified bentonite (Nanobent ZR1). Note: a.u. = arbitrary unit.

dispersion of bentonite nanoplatelets makes the intercalation of polymer chains between the nanofiller layers possible, which helps in generating an intercalated or exfoliated nanocomposite structure.

3.2. The influence of the type and amount of the crosslinking agent on the barrier and mechanical properties of the materials

Table 3 presents the results of testing mineral oil permeation resistance and the measured mechanical properties (puncture, tear, abrasion and cut resistance) for XNBR crosslinked with sulfur or magnesium oxide without bentonite.

It was found that the application of 1.5 phr of sulfur or 2.0 phr of magnesium oxide for XNBR crosslinking did not affect the mineral oil breakthrough time for the different types of crosslinked rubber (Table 3), with both materials characterized by a very long breakthrough time (> 480 min). This confirms the expected highest level of

Table 3. Properties of materials made of carboxylated acrylonitrile–butadiene rubber (XNBR) latex crosslinked with sulfur or magnesium oxide.

Sample	Property	Test result	Performance level
S 1.5[a]	Oil permeation resistance (min)	> 480	6
	Abrasion resistance (cycles)	2000	3
	Tear resistance (N)	2.7 ± 0.4	0
	Puncture resistance (N)	63.0 ± 3.5	1
	Cut resistance (index I_n)	1.4 ± 0.1	1
MgO 2.0[b]	Oil permeation resistance (min)	> 480	6
	Abrasion resistance (cycles)	2000	3
	Tear resistance (N)	6.3 ± 1.1	0
	Puncture resistance (N)	47.7 ± 3.8	1
	Cut resistance (index I_n)	1.3 ± 0.0	1
MgO 4.0	Oil permeation resistance (min)	> 480	6
	Abrasion resistance (cycles)	2000	3
	Tear resistance (N)	7.5 ± 0.6	0
	Puncture resistance (N)	42.3 ± 4.7	1
	Cut resistance (index I_n)	1.9 ± 0.2	1
MgO 8.0	Oil permeation resistance (min)	> 480	6
	Abrasion resistance (cycles)	2000	3
	Tear resistance (N)	9.8 ± 2.1	0
	Puncture resistance (N)	52.0 ± 2.0	1
	Cut resistance (index I_n)	1.3 ± 0.0	1

Note: MgO = magnesium oxide; S = sulfur. [a]Elasticity constants under standard conditions: $2C_1 = 5.07$ kG/cm^2, $2C_2 = 10.41$ kG/cm^2; equilibrium swelling in 2-butanone: $Q_v = 3.23$ ml/ml. [b]Elasticity constants under standard conditions: $2C_1 = 1.23$ kG/cm^2, $2C_2 = 5.75$ kG/cm^2; equilibrium swelling in 2-butanone: $Q_v = 17.15$ ml/ml.

resistance of crosslinked XNBR to oil permeation, which corresponds to the highest performance level for materials used in products protecting against oils, as defined in Standard EN 374-1:2003.[1] Similarly, higher concentrations of magnesium oxide (4.0 or 8.0 phr) did not alter the mineral oil breakthrough time (Table 3).

XNBR crosslinked with sulfur exhibits a higher network density (according to the elasticity constants and measurements of swelling degree in butanone), but inferior mechanical properties, and in particular tear resistance, as compared with XNBR crosslinked with magnesium oxide (Table 3).

XNBR crosslinked with sulfur is characterized by much higher density of the network than that crosslinked with magnesium oxide. As a lower network density is conducive to greater deformability of polymer chains in the rubber matrix, and by the same token to greater material extendibility during tearing, the force necessary to tear XNBR crosslinked with magnesium oxide is greater. The higher levels of tear resistance of XNBR crosslinked with magnesium oxide may also be linked to the presence of ionic crosslinks, as they make it possible to produce materials with better mechanical properties as compared with materials with sulfur crosslinks.[6].

Xu and Que Hee [21] studied oil permeation through barrier materials, and stressed that while permeation testing is much more expensive and time-consuming than swelling tests, it is more suitable for analyzing oil resistance. This has also been confirmed by our own studies, which did not find any direct quantitative correlation between the thermodynamic similarity of elastomer–solvent systems characterized by solubility (cohesive) parameters and the barrier properties of elastomeric materials.[22] Predictions about the barrier properties of elastomer–solvent systems on the sole basis of the thermodynamic similarity between the elastomer and the solvent may be only treated as qualitative indicators. Likewise, in some cases, if the elements of a butyl rubber–solvent system exhibit a different polarity, the solvent breakthrough time for crosslinked rubber (a non-equilibrium process) may vary considerably despite a similar difference in the solubility parameters (equilibrium parameters) of rubber–solvent systems.

The effect of the type and amount of the crosslinking agent was found to be much greater for mechanical properties. The use of sulfur or magnesium oxide for crosslinking XNBR latex led to differences in two of the four investigated mechanical parameters (Figures 4–6). Significant differences were observed in tests for puncture and tear resistance ($p = 0.0002$–0.0005). The application of magnesium oxide led to considerably reduced puncture resistance of the materials (by about 30%). In contrast, the tear resistance of XNBR crosslinked with this compound was more than twice as high.

Despite the use of different XNBR crosslinking methods (with conventional sulfur or unconventional magnesium oxide), the materials did not meet even the lowest (first) level of protection in terms of tear resistance (10 N).
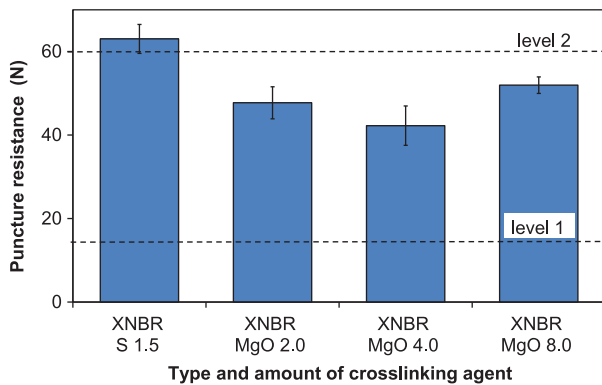
Figure 4. Effect of the type of crosslinking agent (sulfur or magnesium oxide) and its amount (in the case of magnesium oxide) on the puncture resistance of crosslinked carboxylated acrylonitrile–butadiene rubber (XNBR).
Note: Error bars denote standard deviation. MgO = magnesium oxide; S = sulfur.
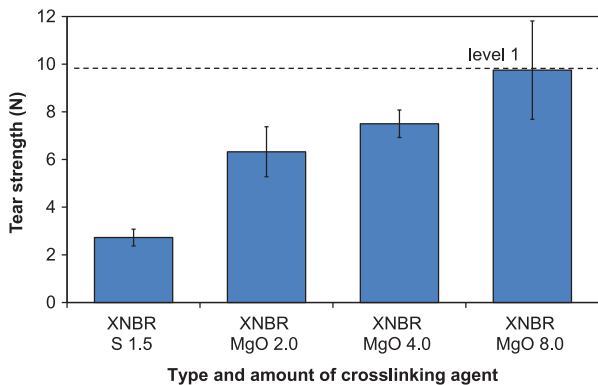

Figure 5. Effect of the type of crosslinking agent (sulfur or magnesium oxide) and its amount (in the case of magnesium oxide) on the tear resistance of crosslinked carboxylated acrylonitrile–butadiene rubber (XNBR).
Note: Error bars denote standard deviation. MgO = magnesium oxide; S = sulfur.
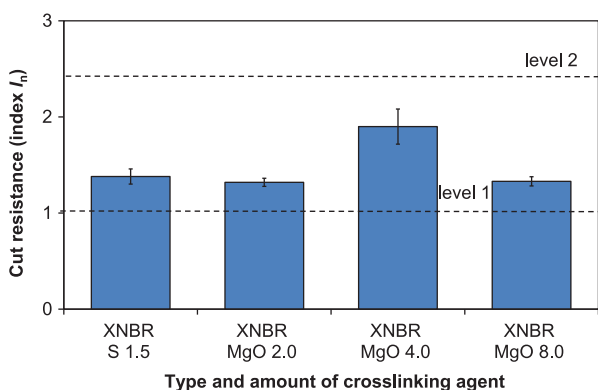

Figure 6. Effect of the type of crosslinking agent (sulfur or magnesium oxide) and its amount (in the case of magnesium oxide) on the cut resistance of crosslinked carboxylated acrylonitrile–butadiene rubber (XNBR).
Note: Error bars denote standard deviation. MgO = magnesium oxide; S = sulfur.

While an increase in the content of magnesium oxide from 2.0 to 8.0 phr led to a higher force necessary to tear the samples, it was still below 10 N.

Irrespective of the amount of magnesium oxide used as a crosslinking agent, the materials were found to exhibit the same level of abrasion resistance (2000 cycles) and similar puncture resistance (in the range of 42–52 N; Figure 4).

As it can be seen, the use of sulfur or magnesium oxide for crosslinking XNBR did not give products that would meet all of the mechanical requirements, especially in terms of tear resistance, even at the first performance level. Therefore, it was decided to apply modified bentonite, because previous own research showed that the use of 5–10 phr of the nanofiller Nanobent ZR1 led to increased tensile strength of crosslinked butyl rubber (IIR), from 2.81 MPa for the vulcanizate without the nanofiller to 18.2 or 20.4 MPa for vulcanizates containing 5.0 or 7.5 phr or the nanofiller, respectively.[23] Consequently, in the present study, Nanobent ZR1 bentonite was added to XNBR latex mixtures as a reinforcing nanofiller. Table 4 presents the composition of the mixtures containing modified bentonite.

3.3. Examination of the structure of nanomaterials

WAXS diffractograms for the samples of the studied materials revealed that the peak present in the WAXS curve for Nanobent ZR1 aluminosilicate was absent from the curves obtained for the composites (Figure 7). This means that the composites are characterized by an exfoliated structure, i.e., a structure with full dispersion of bentonite nanoplatelets in the elastomeric matrix. Based on the maxima in WAXS diffractograms, the size of bentonite nanoplatelets before and after the production of the composite material containing this nanofiller was calculated using the Scherrer formula.[24].

The results show that QAS (quaternary ammonium salts) modification led to a slight decrease in measured nanoplatelet size, from 235 Å for BS to 225 Å for Nanobent ZR1 (Table 5). In the case of vulcanizates containing 7.5 phr of bentonite, it was impossible to determine the nanoplatelet size due to the absence of a maximum on the WAXS curve, which is characteristic of nanocomposites with an exfoliated structure.[25,26] Such a structure may have a significant effect on the properties of the nanocomposites produced, as suggested by Aina and Azura,[27] who reported that the type of nanofiller added to XNBR latex (silicate, mica, soot or calcium carbonate) and its amount (10–20 phr) influence the morphology and mechanical properties of the produced composites. However, at such nanofiller concentrations, it was difficult to achieve a suitable level of nanofiller dispersion in the latex and in the XNBR matrix.

3.4. The influence of the nanofiller on the barrier and mechanical properties of nanocomposites

The addition of 7.5 phr of Nanobent ZR1 to XNBR latex

Table 4. Formulation of carboxylated acrylonitrile–butadiene rubber (XNBR) latex composites with Nanobent ZR1.

Component	Sample (per hundred parts)		
	S 1.5 ZR1	MgO 1.5 ZR1	MgO 2.0 ZR1
XNBR latex	222.2	222.2	222.2
Ground sulfur	1.5	–	–
Magnesium oxide	–	1.5	1.5
Zinc oxide	8.0	–	–
Zinc diethyldithiocarbamate	1.1	–	–
2,2′-Methylenebis[6-(1- methylcyclohexyl)]-p-cresol	0.6	0.7	0.7
Sodium salt of condensation product of formaldehyde and naphthalenesulfonic acid	0.5	0.32	0.32
Polyglycol ether	0.5	0.5	0.5
Nanobent ZR1	7.5	7.5	7.5

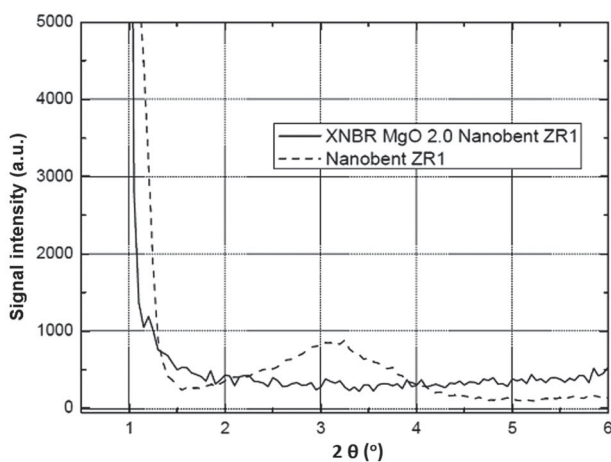Note: MgO = magnesium oxide; S = sulfur; – = not used.

Figure 7. Wide-angle X-ray scattering curves for modified bentonite powder (Nanobent ZR1) and for a carboxylated acrylonitrile–butadiene rubber (XNBR) film crosslinked with 2 phr of magnesium oxide in the presence 7.5 phr of modified bentonite.
Note: a.u. = arbitrary unit; phr = per hundred parts; MgO = magnesium oxide; S = sulfur

Table 5. Measured nanoplatelet sizes and distances between nanoplatelets in the studied bentonites and bentonite-containing carboxylated acrylonitrile–butadiene rubber (XNBR) composites.

Nanofiller or material	Distance between bentonite nanoplatelets (d_{001}) (Å)	Bentonite nanoplatelet size (Å)
Unmodified BS bentonite	12.6	235
Modified Nanobent ZR1 bentonite (powder)	29.6	225
S 1.5 ZR1	∞	–[a]
MgO 2.0 ZR1	∞	–[a]

Note: MgO = magnesium oxide; S = sulfur.
[a]Nanoplatelet size could not be calculated because no maximum was present on the wide-angle X-ray scattering curve, which is characteristic of nanocomposites with exfoliated structure.

mixtures crosslinked with sulfur or magnesium oxide did not have any effect on barrier properties. The breakthrough time measured for XNBR crosslinked conventionally with sulfur or unconventionally with magnesium oxide was very long and, as in the case of materials without the nanofiller, amounted to over 480 min, which means that the nanocomposites exhibit very good permeation resistance against mineral oil (Table 6).

In accordance with expectations, the use of an aluminosilicate nanofiller led to improved tear resistance, which now met the minimum performance level. The XNBR nanocomposite crosslinked with 2.0 phr of magnesium oxide and containing 7.5 phr of modified bentonite fulfilled the requirements concerning all four parameters characterizing tear, abrasion, cut and puncture resistance. It should be emphasized that while the material exhibited only the lowest performance level in terms of tear resistance, this

parameter is thought to be one of the most drastic requirements imposed on polymer films, especially those not containing a textile carrier.

The nanofiller was not found to have any effect on the cut or abrasion resistance of the studied XNBR nanocomposites. These parameters remained constant irrespective of the type of crosslinking (2000 abrasion cycles, cut index $I_n = 1.3$) (Table 6). On the other hand, the puncture resistance somewhat decreased in materials containing bentonite, but they still met the minimum performance level.

The improved tear resistance of the nanocomposite with Nanobent may be due to the fact that XNBR crosslinked with magnesium oxide contains both highly labile ionic crosslinks and a certain number of covalent crosslinks with anhydrous structure.[27] In turn, the use of sulfur (1.5 phr) leads to the formation of less labile monosulfide and disulfide crosslinks, and vulcanizates containing them have been found to have inferior mechanical properties.[28] Nevertheless, a major advantage of

Table 6. Test results for materials made of carboxylated acrylonitrile–butadiene rubber (XNBR) latex with and without 7.5 phr of Nanobent ZR1, crosslinked with sulfur (1.5 phr) or magnesium oxide (2.0 phr).

	Property				
Sample	Breakthrough time (min)	Abrasion resistance (cycles)	Tear resistance (N)	Puncture resistance (N)	Cut resistance (index I_n)
S 1.5	> 480	2000	2.7 ± 0.4	63.0 ± 3.5	1.4 ± 0.1
S 1.5 ZR1	> 480	2000	6.8 ± 0.5	55.0 ± 6.3	1.3 ± 0.0
MgO 2.0	> 480	2000	6.3 ± 1.1	47.7 ± 3.8	1.3 ± 0.0
MgO 2.0 ZR1	> 480	2000	10.9 ± 0.9	31.9 ± 2.7	1.3 ± 0.0

Note: MgO = magnesium oxide; phr = per hundred parts; S = sulfur.

sulfur-based crosslinking is the easier processing of the latex mixture, free of difficulties linked to the excessive tendency of XNBR latex to coagulate during the preparation of mixtures.

The developed method of producing XNBR materials, meeting both the barrier criteria and exhibiting all of the mechanical properties required of protective glove materials, is the subject of Polish Patent 219209.[29].

4. Conclusions

The use of sulfur or magnesium oxide for crosslinking XNBR in latex mixtures did not cause the resulting films to exhibit different levels of mineral oil permeation resistance as determined by the oil breakthrough time. Both materials containing sulfide crosslinks and those containing ionic crosslinks were characterized by a very long oil breakthrough time (> 480 min). This attests to the very high resistance of the produced materials to oil permeation. The amount of the applied crosslinking agent (magnesium oxide) did not have a significant influence on the tear, abrasion, cut or puncture resistance of the materials made of XNBR latex. Similarly, the type of crosslinking agent, and consequently the type of the crosslinks formed (sulfide or ionic), did not have a substantial effect on the properties of the materials produced without a nanofiller. The mechanical properties, and especially tear resistance, of the studied materials were improved only after the addition of the nanofiller Nanobent ZR1 (7.5 phr) to a XNBR latex mixture crosslinked with 2.0 phr of magnesium oxide. The nanocomposite produced in this way met the requirements both in terms of barrier properties and all four parameters characterizing tear, abrasion, cut and puncture resistance. Therefore, the developed material may be used for the production of multifunctional protective gloves.

Acknowledgements

Disclosure statement

Funding

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