Effect of layered silicate on the barrier properties of cured butyl rubber

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Abstract. The aim of the study was to investigate the effect of layered silicate nanofiller (bentonite: Nanofil 15, Poro Additive) on the barrier properties of non-polar butyl rubber (the IIR, BK 1675 N brand) conventionally cured with sulphur in respect of selected organic solvents. The barrier properties were assessed on the basis of determination of standardized breakthrough time for cured IIR exposed to the selected solvents with different thermodynamic affinities to IIR, i.e. polar butyl acetate and non-polar cyclohexane.

In the case of the non-polar solvent – cyclohexane – no effect of the content of the layered silicate (5 - 20 phr) on improvement of barrier properties of the tested IIR vulcanizates was observed. In contrast, a favorable effect of the silicate nanofiller was observed in the case of the polar solvent – butyl acetate, for which the breakthrough time tested for filler-containing vulcanizate (10 - 20 phr) reached 160 - 200 min, whereas the breakthrough time obtained for unfilled vulcanize was 129 min only.

The testing of barrier properties of IIR vulcanizates containing various fillers (layered silicate Nanofil 15 and active silica Ultrasil VN3) added in the amount of 20 phr, indicate the favorable effect of layered silicate only in tests with the polar solvent used (an increase in breakthrough time from 129 to 164 min). Contrary, the presence of conventional silica leads to decrease of breakthrough time (to 118 min). In the case of the non-polar solvent, no effect of the filler type on barrier properties of the tested vulcanizates was observed.

1 Introduction

Permeation of toxic chemicals present in the working environment through the skin is a safety hazard for the workers exposed to such chemicals. The problem is especially important in the case of volatile solvents commonly used in the chemical industry. Under such conditions, it is necessary to use a personal protective equipment, including the primarily protective clothing. Such products are subject to specific requirements concerning the resistance to permeation by chemicals and durability. The most important protection parameter is the breakthrough time of the material tested against specific substances. Breakthrough time is defined according to EN ISO 6529 as: „the time interval between the starting point of the test, i.e. contact of the liquid chemical with one side of the material, and reaching a certain standardized velocity of permeation through the tested material”. A longer breakthrough time evidences a higher resistance of the material to exposure to the test substance and a
valuable clue for the selection of material for workers exposed to specific chemicals present as
hazardous factors at the workplace.

Garments protecting against chemicals are made primarily of coated materials. The most frequently
used systems include: polyamide or polyester fabrics coated with polyvinyl chloride (PVC) or
materials made of butyl, chloroprene or fluorine rubber. Fillers are one of the components
incorporated into compounds used for production of barrier materials. They are added to obtain
appropriate processing properties of the compound, and specific application properties of the cured
rubber. Recently, considerable interest has been focused on layered nanofillers [1], including
montmorillonite, hectorite, bentonite and saponite [2 - 4].

As it follows from a few literature reports, layered silicates – a new generation of nanofillers may
favorably influence on the barrier properties of cured butyl rubber [5 - 6].

The aim of the study was to investigate the effect of a filler type and content on permeation of
solvents commonly encountered at a workplace through cured butyl rubber vulcanisates (IIR) filled
with layered silicate (bentonite, Nanofil 15) and active silica (Ultrasil VN3).

2 Methodology

2.1 Materials

The tested materials were the butyl rubber (BK 1675 N from Russia; cured with sulphur – 1.5 phr in
the presence of activators, ultra- and semiultraaccelerators), containing 0 - 20 phr of a the filler -
Nanofil 15 (bentonite, manufactured by PORO Additive Sp. z o.o.) hereinafter marked with symbols
B5 – B8 and samples containing 20 phr of the active silica - Ultrasil VN3 (Degussa) as a conventional
filler, hereinafter marked with symbol B11. Cured unfilled IIR, hereinafter marked with symbol B3,
was the reference sample.

2.2 Preparation of samples

Rubber mixtures were prepared in a conventional way, using a laboratory two rolls mill. The
vulcanization time was selected on the basis of vulcametric determinations (22 ÷ 25 min,
depending on the filler type), performed according to ISO 3417. The vulcanization temperature was
160°C. Vulcanizate samples of 0.35 mm thickness were prepared by compression moulding.

2.3 Chemical substances

The barrier properties of IIR vulcanizates were assessed by determination of the breakthrough times
under exposure to the selected organic substances:

- n-butyl acetate, a polar solvent, with average thermodynamic affinity to IIR (significantly
  higher solubility parameter – 17.4 MPa\(^{0.5}\) than that of IIR – 15.7 MPa\(^{0.5}\));
- cyclohexane, a non-polar solvent, with high thermodynamic affinity to IIR (the solubility
  parameter similar to that of IIR, equal to 16.4 MPa\(^{0.5}\)).

2.4 Apparatus

The following equipment was used in the study:

- gas chromatograph, FID flame ionisation detector, capillary chromatographic column (Rtx-5,
  length 7 m, internal diameter 0.32 mm) for cyclohexane analysis,
- gas chromatograph, FID flame ionisation detector, packed chromatographic column (without
  packing, internal diameter 3 mm) for n-butyl acetate analysis,
- injecting valves (gaseous sample of 1 ml volume),
- two-chamber permeation cell for testing the material resistance to permeation by liquid
  chemicals in the mode of single permanent contact and multiple intermittent contact (Fig. 1),
- thermostates,
- thickness gauge with 10 mm plate diameter and 4.9 Pa pressure.

Chromatographic analysis parameters were adjusted as isothermic analysis:

- column temperature – 40°C,
- dispenser temperature - 110°C,
- detector temperature - 180°C.
2.5 Test method
The samples (diameter: 40 mm, thickness: 0.32 – 0.38 mm) were placed in the permeation cell for permeation test (Fig. 1). Then the permeation cell and the chemical sample were conditioned (30 min, 23±2 °C). After that time, 10 ml of the chemical substance was poured into the upper chamber and the test was started. The lower chamber was ventilated with pure air next passed to the bottom side of the test sample, which collected the solvent molecules diffused and desorbed at the bottom side of the membrane. The air was then directed to the automatic injecting valve in the gas chromatograph. The experiment was conducted for 6 h.

As a result of the experiments, chromatograms were obtained. Using the calibration curves, the concentration was determined at which the threshold velocity of compound permeation through the material reached the value of 1 µg/cm² min. According to the EN ISO 6529 standard, the time needed to reach this permeation velocity is referred to as the breakthrough time. Deviations of the tested sample thickness from the presumed reference thickness of 0.35 mm were taken into consideration.

1 – lid
2 – chamber with the test chemical substance
3 - tested material sample
4 - chamber with the collection medium
5 – collection medium outlet
6 – collection medium inlet

**Figure 1.** Design of a test cell for investigation of resistance of polymer materials to permeation by liquid chemicals.

### 3 Results
The results of breakthrough time determinations for the vulcanizate samples with different contents of the fillers – layered silicate or selected silica type - exposed to the selected solvents are presented in Figures 2-3.
Figure 2. Selected solvents breakthrough time for IIR vulcanizates with different Nanofil 15 content: B5 - 5 phr; B6 - 10 phr; B7 - 15 phr; B8 – 20 phr.

Figure 3. Selected solvents breakthrough time for cured IIR vulcanizates unfilled (B3) or filled with 20 phr of Nanofil 15 (B8) or filled with convention silica Ultrasil VN3 (B11)

The obtained breakthrough times were subjected to statistical analysis to determine the significance of the observed differences depending on the filler – layered silicate - content in the product or the filler type: layered silicate or active silica with the amount of 20 phr. Statistical conclusions were based on the variance analysis - ANOVA, performed using the Excel software, with adopted significance level P of 0.05.

In the case of a non-polar solvent (cyclohexane) with a considerable thermodynamic affinity to IIR, no effect of layered silicate content (5 - 20 phr) on improvement of barrier properties of the tested IIR
vulcanizates was observed (Fig. 2). The breakthrough time for the vulcanizate containing no filler was 18 min (B3), whereas for vulcanizates containing layered silicate it ranged from 12 to 19 min (B5 – B8).

In contrast, addition of a layered silicate filler to butyl rubber vulcanizates leads to a considerable improvement of barrier properties against a polar solvent (n-butyl acetate), characterized by a moderate thermodynamic affinity to IIR. In that case, the breakthrough time for vulcanizate containing no filler was 129 min, whereas for samples containing layered silicate (10, 15 and 20 phr) it was considerably longer. The longest breakthrough time was observed for the vulcanizate containing 15 phr of layered silicate (B7 – 200 min). An increase of nanofiller content up to 15 phr is associated with an extension of the breakthrough time and with an increase of resistance to permeation.

The tests of barrier properties of IIR vulcanizates containing various filler types (layered silicate - Nanofil 15 and active silica - Ultrasil VN3 in equal quantities of 20 phr) demonstrated no effect of filler type on the breakthrough time of the vulcanizates by the non-polar solvent. The breakthrough time obtained for the vulcanizate containing layered silicate was 19 min (B8) and did not differ from the breakthrough time obtained for the unfilled IIR one (B3 - 18 min), as well as from that containing silica filler (B11 - 22 min) (Fig. 3).

On the other hand, in the case of the tests with the polar solvent it was observed that the content of layered silicate has a more beneficial effect than that of conventional silica. In this case, the breakthrough time obtained for the vulcanizate containing layered silicate (B8 - 164 min) was significantly longer than that for the vulcanizate containing no filler (B3 - 129 min) and for the silica-filled vulcanizate (B11 - 118 min).

4 Conclusions
The results indicate that the quantity, as well as the type of the filler present in the cured butyl rubber effect the chemical barrier properties of elastomer materials.

It has been observed that in the case of a non-polar solvent with a considerable thermodynamic affinity (cyclohexane), the breakthrough time of IIR vulcanizates is short and does not exceed 22 min, whereas the vulcanizate breakthrough time for n-butyl acetate, the polar solvent with a moderate thermodynamic affinity to IIR, is much longer, ranging from 118 to 200 min.

As indicated by the test results, in the case of permeation of substances with solubility parameters similar to that of IIR and a short breakthrough time (cyclohexane), the addition of a filler into the material does not extend the breakthrough time.

In the case of permeation by polar solvent – n-butyl acetate, characterized by significantly higher solubility parameter in comparison with IIR, a significant improvement of barrier properties of the vulcanizates containing layered silicate was observed for the filler content higher than 5 phr. The breakthrough time for these vulcanizates was considerably extended. On the other hand, the incorporation of the silica into the IIR caused a decrease of the resistance to permeation and of the breakthrough time in comparison with the unfilled cured rubber.

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Acknowledgements

The authors wish to thank the PORO Additive Company for the supply of layered nanofillers.

The study was carried out within the scope of an activity of Central Institute for Labour Protection – National Research Institute in the years 2005-2007.