Study of antioxidant migration into surface layer of diene elastomers

The migration of antioxidants into the surface layer of elastomers has been investigated. The main aim of the investigation was to evaluate of the migration of common antioxidants used for rubber. Derivatives of phenol, such as 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) (BKF), and amines such as N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) were used as antioxidants in styrene-butadiene (SBR) and isoprene (IR) elastomers. Migration of antioxidants has been evaluated from the changes of BKF or IPPD content in the surface layer after different time of elastomers storage. Concentration of antioxidants has been determined by Fourier Transformer Infrared Spectroscopy with attenuated total reflection (FT-IR ATR) and gas chromatography (GC) methods. It was found that the concentration of antioxidants in the surface layer has gradient profile and depends on the time of storage of elastomers.

Key words: elastomers, IR, SBR, antioxidants, IPPD, BKF, migration, surface layer

Badania migracji przeciwutleniaczy do warstwy wierzchniej elastomerów dienowych

Zbadano migrację przeciwutleniaczy do warstwy wierzchniej wyrobu gumowego. Skoncentrowano się na badaniach migracji przeciwutleniaczy pochodzących z technologii gumin – pochodnych fenolowych (2,2'-metyleno-bis-(4-metylo-6-tert-butofenol) (BKF)) i aminowych (N-isopropyl-N'-fenylo-p-fenylenediamina) (IPPD) w kompozycjach elastomerowych kauczuku izoprenowego (IR) i butadienowo-styrenowego (SBR). Migrację oce­niano na podstawie zmian stężenia przeciwutleniaczy w warstwie wierzchniej elastomeru po różnych okresach przechowywania próbek od momentu ich vul­canizacji. Zmiany stężenia przeciwutleniaczy w warstwie wierzchniej elastome­ru zbadano wykorzystując spektrofotometrię FT-IR pracującą w układzie całko­witego wewnętrznego odbicia – ATR oraz analizę chromatograficzną GC eks­traktów z warstwy wierzchniej elastomerów. Stwierdzono gradientowy i zmie­niający się w czasie rozkład stężeń przeciwutleniaczy w warstwie wierzchniej badanych elastomerów.

Słowa kluczowe: elastomery, IR, SBR, przeciwutleniacze, IPPD, BKF, migra­cja, warstwa wierzchnia

1. Introduction

Based on rubber technology practice it is known that the formation of thin layers of any components on the surface of rubber vulcanizates (blooming) exerts an ef­fect on adhesive properties of vulcanizates, its resis­tance to aging, thermal stability and finally their ap­pearance. Chemical composition, structure and mor­phology of the surface layer have significant influence on the conditions of processing of rubber and of­ten times decides on the quality of vulcanizates.

A slight migration of antiozonants and antioxidants substances on the one hand has a positive effect due to the increases of resistance to thermal oxidation and ozone aging [1, 2] but on the other hand the migration of high quantity of these substances leads to the forma­tion of distinct bloom that may disqualify products in terms of their application and processing.

Some chemical substances added to rubber comp­ound well these substances which are formed during the vulcanization process can undergo the migration into the surface layer. Blooming onto rubber surface is the result of the migration of low molecular weight chemical substances from the bulk of rubber vulcani­zates.
Table 1. The parameters of solubility of the antioxidants and rubbers studied
Tabela 1. Parametry rozpuszczalności badanych przeciwutleniaczy i kauzuków

<table>
<thead>
<tr>
<th>Antioxidants rubber</th>
<th>Parameters of solubility $\delta$, $10^{-3}$ J m$^{-1.5}$/mol $^{0.5}$ according to Hoftyzer – Van Krevelen method [5]</th>
<th>Literature [6,7]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) (BKF)</td>
<td>18.0 2.0 10.5 20.9 -</td>
<td></td>
</tr>
<tr>
<td>N-isopropylN'-phenyl-p-phenylenediamine (IPPD)</td>
<td>18.0 1.5 5.3 18.9 -</td>
<td></td>
</tr>
<tr>
<td>cis-1,4-polyisoprene (IR)</td>
<td>14.6 0 0 14.6 16.3-18.4</td>
<td></td>
</tr>
<tr>
<td>Styrene-butadiene rubber (SBR) 23.5% of bounded styrene</td>
<td>17.5 0.7 0 17.5 17.5</td>
<td></td>
</tr>
</tbody>
</table>

Tendency towards the migration onto the surface shows up for the crystalline substances of limited solubility in elastomers which concentration in rubber exceeds their solubility limit as well as for the amorphous substances that do not dissolve in rubber and form physical mixtures.

According to literature data [3, 4] the mechanism of blooming of crystalline substances onto the surface of rubber vulcanizate is related to the reproduction of a crystalline phase after cooling.

Chemical reactivity of substances, in particular their compliance to oxidation which occur, for example, as the result of the reaction of ozone with p-phenylenediamine (PPD) influences the mechanism of migration. As the result of reaction the surface gradient of PPD concentration is formed. The gradient of concentration is responsible for the initiation of migration process of PPD towards the surface of rubber vulcanizates and formation of fit, ozone protective layer of PPD oxidation products on the surface.

In the present work, the migration of low molecular weight components of rubber compounds towards the surface layer of rubber products has been attempted to study.

The main topic of the study is the evaluation of the migration of technological antioxidants – 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) (BKF), and N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) commonly used in diene elastomers – styrene-butadiene (SBR) and isoprene (IR) rubber.

The analysis of solubility parameters of rubbers (8) shows (Table 1) that SBR has higher polarity than IR. In the case of SBR the value of polar component of the solubility parameter $\delta_p$ is 0.7, whereas in the case of IR it is zero. The BKF and IPPD antioxidants are characterized by higher values of solubility parameters in comparison to the rubbers tested and the value of polar and hydrogen components of the solubility parameters are different. Different values of solubility parameters and their components allow to foresee limited solubility of BKF and IPPD antioxidants in IR and SBR. With respect to that the segregation of antioxidants onto the surface of rubber ought to be different, being depend on the chemical structure and polarity of elastomers and the reactivity of antioxidants.

In the literature [8-11] there are a lot of information about the investigations on the migration and surface segregation of chemical substances, used as the components of elastomers materials, by using Fourier Transform Infrared Spectroscopy with attenuated total reflection (FT-IR ATR).

In our work the migration of antioxidants into surface layer of diene elastomers has been studied by means FT-IR ATR and GC methods which was used additionally to analyze of extracts from their surface layer.

2. Experimental

2.1. Materials

The subjects of investigation have been antioxidants belonging to phenol derivatives group – 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) (BKF) and to amines derivatives – N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD). They have been added to rubber compounds containing isoprene rubber (IR) or styrene-butadiene rubber (SBR). The compounds have contained 2.5 phr of BKF or IPPD and crosslinking system which consisted of zinc oxide, stearic acid, accelerator of vulcanization – CBS (N-cyclohexylbenzolilosulphenamide) and sulphur. The compounds have been vulcanized at 160 °C.

2.2. Methods

- Extraction of the plates of vulcanizates (140 × 140 × 2 mm) was performed with acetone during 5 min at room temperature after 7, 30, 60 and 90 days of vulcanization
- Gas chromatography (GC), thin-layer chromatography (LTC) and Fourier Transform Infrared Spectroscopy FTIR – were applied for the determination of antioxidants in acetone extracts
- Fourier Transform Infrared Spectroscopy with attenuated total reflection attachment (FT-IR ATR)
equipped with the crystals of different refractivity indices: Ge - n=4.0 and ZnSe - n=2.4, was applied to study the composition of the surface layer at the depth of 0.99 ± 0.45 μm in the case of Ge crystal and 2.50 ± 1.39 μm in the case of ZnSe one respectively as calculated according to Harrick’s equation [12] for spectral region 1520 - 836 cm⁻¹.

The contribution index of antioxidants was defined as the relation of absorbance of some bands characteristic for chemical groups which are in antioxidants and in products of their reaction with oxygen or ozone to the sum of corresponding absorbance bands characteristic for rubber and antioxidants present in the sample.

The following formula makes it possible to calculate the contribution index (X) of BKF and IPPD antioxidants:

\[
X_{\text{BKF}} = \frac{A_{\text{BKF}}}{A_R + A_{\text{BKF}} + A_{R+\text{BKF}}},
\]

\[
X_{\text{IPPD}} = \frac{A_{\text{IPPD}}}{A_R + A_{\text{IPPD}} + A_{R+\text{IPPD}}},
\]

where:
- \(X_{\text{BKF}}\) – contribution index of BKF
- \(X_{\text{IPPD}}\) – contribution index of IPPD
- \(A_{\text{BKF}}\) – absorbance of BKF band (1235 cm⁻¹)
- \(A_{\text{IPPD}}\) – absorbance of IPPD band (1517 cm⁻¹)
- \(A_R\) – absorbance of rubber band (836 cm⁻¹ for IR and 966 cm⁻¹ for SBR)
- \(A_{R+\text{BKF}}\), \(A_{R+\text{IPPD}}\) – absorbance bands characteristic for chemical groups both of rubber and antioxidant (1380 cm⁻¹ for IR + BKF and IR + IPPD, 1447 cm⁻¹ for SBR + BKF and 1310-1295 cm⁻¹ for SBR + IPPD)

3. Results and discussion

3.1. The solvent extraction / Gas chromatography method

It was recognized that the analysis of solvent extracts obtained from the surface of vulcanizates ought to give some information about the changes of antioxidant quantity in their surface layer.

It was assumed that during a very short time of solvent action on the surface of vulcanizate plates – 5 min at room temperature – only organic low molecular weight substances included inside the surface layer will be extracted but the substances included in the bulk of vulcanizate will not be extracted because of a very short time of extraction and low temperature.

The results from Fig. 1 show that the content of extracted substances is different depending on the polarity of rubber. The solvent extracts from the surface layer of SBR vulcanizates were higher then extracts from IR vulcanizates, irrespective of the kind of antioxidants – BKF or IPPD.

Analysis of the surface layer extracts from IR and SBR vulcanizates shows the presence of antioxidants...
added to rubber compounds, and other substances such as mercaptobenzothiazole and zinc stearate as well as trace quantities of p-phenylenediamine derivatives in the case of IR and p-phenol derivatives in the case of SBR composites (Table 2).

Probably very small amounts of derivatives of p-phenylenediamines and of p-phenol originate from antiaging substances used to protect raw rubbers, while mercaptobenzothiazole and zinc stearate formed as a result of chemical reaction of components of cross-linking system during vulcanization.

According to the literature data [3] the solubility of zinc stearate in rubber increases in the presence of amines due to the formation of zinc-amine complex. In a consequence of this it is in favour of migration and formation of the bloom of zinc stearate on the surface of vulcanizates. In this respect it is very difficult to look for a direct relationship between the migration of studied substances and the value derived from solvent extracts obtained after various time of samples storage after vulcanization.

In spite of this problem the evaluation of composition of the surface extracts, using GC method, given in Fig. 2, clearly shows that the migration of IPPD antioxidant was higher then one of BKF. However, it is difficult to establish the influence of storage time on the migration of antioxidants studied.

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**Fig. 2. Content of IPPD and BKF antioxidants in surface layers extracts from IR (A) and SBR (B) vulcanizates determined by GC method**

**Rys. 2. Zawartość przeciwutleniaczy IPPD i BKF oznaczona metodą GC w ekstrakach z warstw powierzchniowych wulkanizatów IR (A) i SBR (B)**

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**Fig. 3. Contribution index of IPPD (A) and BKF (B) antioxidants in the surface layer of IR vulcanizates determined by FT-IR ATR method**

**Rys. 3. Wskaźnik udziału przeciwutleniaczy IPPD (A) i BKF (B) w warstwie wierzchniej wulkanizatów IR (oznaczony metodą FT-IR ATR)**

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**Fig. 4. Contribution index of IPPD (A) and BKF (B) antioxidants in surface layer of SBR vulcanizates determined by FT-IR ATR method**

**Rys. 4. Wskaźnik udziału przeciwutleniaczy IPPD (A) i BKF (B) w warstwie wierzchniej wulkanizatów SBR (oznaczony metodą FT-IR ATR)**
3.2 Fourier Transformed Infrared Spectroscopy with attenuated total reflection (FT-IR ATR)

Values of contribution index for examined antioxidants present in the surface layer of vulcanizates, calculated from FT-IR ATR spectra using Ge and ZnSe crystals are presented in Fig. 3-4.

In the case of rubber containing BKF or IPPD antioxidants it was shown that the concentration gradient of the antioxidants in the surface layer of vulcanizates is present. Concentration of antioxidants in IR samples, evaluated on the base of contribution index was higher at surface layer of 0.99 ± 0.45 μm than at 2.50 ± 1.39 μm. The concentration changed with the time of storage. It may testify on the continuous diffusion of antioxidants towards the surface layer of vulcanizates.

The concentration of antioxidants in SBR samples was smaller at 0.99 ± 0.45 μm than at 2.50 ± 1.39 μm for the first period of storage – and higher afterwards.

On extension of the storage time of SBR samples up to 60 days the increase of antioxidants concentration at 0.99 ± 0.45 μm was found to be higher in comparison to 2.50 ± 1.39 μm depth due to their continuous migration towards the surface layer of vulcanizates.

4. Conclusion

- The results obtained pointed at on the surface gradient of antioxidants concentration present for examined vulcanizates. The gradient changes in time.
- Changes of the concentration of BKF and IPPD antioxidants in the surface layer of IR and SBR vulcanizates depend on storage time after vulcanization and may testify on the continuous migration of antioxidants from the bulk of vulcanizate material onto its surface, despite simultaneous consumption process due to reaction with oxygen or ozone.
- Concentration gradient of antioxidants in the surface layer depends on which process dominates – migration or oxidation.
- The kinetics of migration of the antioxidants studied depends on many factors such as the chemical structure of elastomer and antioxidant, the amount of antioxidant in compound, its chemical composition as well as on mutual interaction between the components. In respect to that it is difficult to establish the strict mechanism of migration of antioxidants in vulcanizates. It will be the subject of further studies.

References

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