Effect of Mineral Fillers Surface Treatment on Gas Permeability of Filled Vulcanized Rubber Compounds

BETIK M.\textsuperscript{a,*}, MALAC J.\textsuperscript{b}, FRYZELKA V.\textsuperscript{a}.
\textsuperscript{a}Department of Polymer Engineering, Tomas Bata University in Zlin, Faculty of Technology, nám. T.G. Masaryka 275, 762 72, Zlin, 
\textsuperscript{b}Centre of Polymer Systems, Tomas Bata University in Zlin, Faculty of Technology, nám. T.G. Masaryka 5555, 760 01, Zlin
CZECH REPUBLIC
betik@centrum.cz http://www.ft.utb.cz

Abstract: The study deals with the influence of mineral fillers surface modification on properties of some filled elastomer systems. The mineral fillers (calcined kaolin and precipitated silica) were tested in styrene-butadiene rubber compounds. For surface treatment of both fillers two types of organic acids were used as modification agents (stearic and benzoic acid). In this work the influence of fillers surface modification on vulcanization characteristics, gas permeability and physical-mechanical properties of SBR rubber compounds was measured and evaluated. Obtained results indicate improvement in some properties by used mineral filler surface modification, which could be result of better filler surface/polymer matrix interaction.

Key-Words: Gas permeability, surface modification, calcined kaolin, silica.

1 Introduction

The most important components of rubber compounds are rubber (natural, synthetic or their combinations) and filler. Fillers include carbon blacks and different types of mineral fillers (e.g. kaolin, silica, calcium carbonate, talc). Fillers influence not only properties of rubber compounds but also properties of vulcanizates [1],[2]. Fillers very markedly decrease elasticity and so influence process ability of rubber compounds; they decrease permeability for gases and contribute to better physical-mechanical properties of vulcanizates as tensile strength, elongation at break, hardness, abrasion resistance and others [2]. Organo-clay minerals are being used as a filling material to different polymer systems as are epoxy resin, polyurethane, styrene-butadiene rubber, natural rubber, nitrile rubber and ethylene-propylene polymers. Result is modification of properties for both rubber compounds and vulcanizates [3].

The improvement of vulcanizate properties by adding fillers is called reinforcement. The presence of reinforcing fillers in a vulcanizate give always rise to multiphase systems which are characterized by very complicated morphology. The extent of reinforcement depends mainly on the structure of fillers, a surface activity and also on a size of filler particles [3]. Properties of filled rubber depend on physical interaction between filler and rubber matrix which can determine a degree of adhesion on the boundary of phases. Generally, the degree of adhesion depends on surface energy and on activity of functional groups on the filler surface [1-5]. Chemical and physical properties of rubber and filler, just as quantity of each element in a compound, can influence interaction between components [6]. The interaction filler-rubber depends also on chemical composition of rubber segments and on constitution and configuration of rubber molecule [7].

The reinforcing effect is influenced by many characteristics of fillers. It is primarily specific surface area in m\textsuperscript{2}/g, interaction filler-elastomer, a shape of particles and distribution of particle sizes. The chemical composition of mineral filler surface plays also very important role [1],[2],[8]. The filler surface and rubber molecules can be connected with different types of bonds which sometimes can be result of chemical reactions among a surface of mineral filler with components of a compound.

Mineral fillers surface modification improves dispersion of filler in an elastomer and regulates its interaction with a polymer matrix. White fillers have many active parts in their structures. They are mainly silanol groups Si-OH, Bronsted-Lowry acids, and replaceable cations among layers of fillers [2],[6],[8]. The properties of mineral fillers can be improved by surface treatment using e.g.
bonding agents which increase a number of active places on surface of filler particles and co-vulcanize with rubber matrix.

The surface of majority of white fillers is polar unlike the majority of elastomers which are non-polar. Polar silicium fillers with a high content of silanol groups Si-OH are often modified by chemical hydrophobilisation by organosilanes [11],[9-13]. They are mainly organosilanes with two reactive chemical groups in one molecule. The group of trialkoxysilyl is able to create stable siloxane bonds with mineral surfaces and by this it modifies the filler. The second group of silane usually reacts with used polymer [11].

The vulcanizates with mineral fillers modified with reactive organosilanes have unique properties which can be sometimes better than for vulcanizates filled by carbon black. The result could be improvement of properties as high modulus, low hysteresis, higher resistance to abrasion, low viscosity and higher resistance to oxidation [11],[14-17]. However, organosilanes are expensive compounds and silanization is a complicated process. Therefore, looking for modification agents capable of replacing at least partly effect of organosilanes is important.

2 Experimental

2.1 Materials and surface treatment

In this study styrene-butadiene rubber (Kralex SBR 1500, Synthos) was used as rubber matrix. As mineral fillers were used precipitated silica (Perkasil KS 408, Grace Davison) and calcined kaolin (Filemon P05 – calcined at temperature 750 °C, Refracer).

As surface treatment for silica and kaolin were used three organic acids: stearic, and benzoic. The concentration of these acids was 10 wt. % per filler. Surface modification of calcined kaolin and precipitated silica was carried out in the following way: First, the modification agent was added to the filler and the system was mixed in mixer (KRUPS F417 Power Mix) for 15 minutes. The obtained mixture was then heated in Al-foil covered container for 2 hours at 150 °C. After cooling the surface modified filler was mixed into a rubber compound.

2.2 Preparation of rubber compounds

Rubber compounds were prepared on a laboratory two roll mill (roll size 150x400 mm) according to the compound formula in Table 1. The prepared rubber compounds were labelled as shown in Table 2.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration [phr]</th>
<th>Time of addition [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1500</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Filler</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>Stearin</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>MBTS</td>
<td>1.2</td>
<td>17</td>
</tr>
<tr>
<td>MBT</td>
<td>0.7</td>
<td>18</td>
</tr>
<tr>
<td>DPG</td>
<td>0.5</td>
<td>19</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>Total</td>
<td>140.4</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 2: Labels of prepared compounds

<table>
<thead>
<tr>
<th>K</th>
<th>compound with unmodified kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-SA</td>
<td>compound with kaolin + stearic acid</td>
</tr>
<tr>
<td>K-BBA</td>
<td>compound with kaolin + benzoic acid</td>
</tr>
<tr>
<td>S</td>
<td>compound with unmodified silica</td>
</tr>
<tr>
<td>S-SA</td>
<td>compound with silica + stearic acid</td>
</tr>
<tr>
<td>S-BBA</td>
<td>compound with silica + benzoic acid</td>
</tr>
</tbody>
</table>

2.3 Measuring of vulcanization characteristics

Vulcanization characteristics of rubber compounds were obtained by Rubber Process Analyser 2000. These characteristics were measured in accordance with standard ČSN ISO 3417. For all rubber compounds were determined ts2-scorch time, t90-technical cure time (optimum cure), ML-minimum torque, and MH-maximum torque.

2.4 Measuring of gas permeability

The gas permeability of polymers is usually measured for gases such as nitrogen, oxygen, air, hydrogen, helium, and carbon dioxide. The principle of test lies in measuring of time dependence of gas pressure in low-pressure part of apparatus into which the gas diffuse from high-pressure part through tested polymer membrane. Generally, the process of gas passing through elastomer material consists from 3 parts: absorption of gas into material (solubility, S), transmission of gas through material (diffusion, D), and desorption of gas on the side with lower pressure. The gas permeability coefficient Pe is equal to product of these coefficients:

\[ Pe = S \cdot D \] (1).

For calculation of gas permeability coefficient Pe (mol/m.s.Pa) at most gases and stream is used formula:

\[ Pe = \frac{dp}{dt} \cdot \frac{V}{R \cdot T} \cdot \frac{L}{A \cdot P_i} \] (2),
where \( \frac{dp}{dt} \) is the downstream volume steady-state pressure change (Pa/s), \( V \) is the downstream volume (m\(^3\)), \( T \) is experimental absolute temperature (K), \( R \) is the gas constant (J/mol.K), \( L \) is the film thickness (m), \( A \) is the film area (m\(^2\)) and \( P_i \) is the upstream absolute pressure (Pa) [8],[14],[15],[16].

The gas permeability in this work was measured for nitrogen in accordance with standard ČSN 64 0115. The values of gas permeability coefficient were obtained at temperatures 35 °C, 50 °C and 65 °C on apparatus using a method of constant volume. The specimens for measuring of gas permeability had diameter of 90 mm and were cut from films pressed in a laboratory hydraulic press at 150 °C for an optimum cure time t90 + 5min. The effective area of membrane was 30.533 cm\(^2\). The thickness of membrane was obtained from arithmetic average of 5 values. The downstream volume was 19.515 cm\(^3\) and differential pressure was 3 bars.

2.4 Measuring of tensile properties

Tensile properties of the specimens were measured by standard ČSN ISO 37 (62 1436) on the T2000 Tensile tester (Alpha Technologies) at crosshead speed of 500 mm/min. The specimens for tensile tests (length 115 mm, width 6 mm and thickness 2 mm) were cut from plates prepared in a laboratory hydraulic press at 150 °C for an optimum cure time t90 plus 5 minutes.

3 Results and Discussion

3.1 Vulcanization characteristics

The effect of our two modifying agents (stearic acid, benzoic acid) used to surface treatment of two mineral fillers on the vulcanization characteristics of our rubber compounds is apparent from Figures 1-4. As can be seen from Fig.1 and 2, surface modification of kaolin and silica by used acids increases scorch time ts2 and optimum cure time t90 of rubber compounds. Indeed, the deceleration of sulphur vulcanization process by acids is well-known effect.

3.2 Gas permeability

The effect of stearic and benzoic acid used as surface modification of kaolin and silica on the gas permeability coefficients of our rubber compounds is evident from Table 3 and can be seen in Figures 5-10.
Table 3: Gas permeability coefficients of vulcanizates with kaolin and silica

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Values of Pe $\times 10^{-15}$ [mol/m.s.Pa] at temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 °C</td>
</tr>
<tr>
<td>K</td>
<td>2.072</td>
</tr>
<tr>
<td>K-BA</td>
<td>1.621</td>
</tr>
<tr>
<td>K-SA</td>
<td>1.493</td>
</tr>
<tr>
<td>S</td>
<td>2.128</td>
</tr>
<tr>
<td>S-BA</td>
<td>1.976</td>
</tr>
<tr>
<td>S-SA</td>
<td>1.667</td>
</tr>
</tbody>
</table>

Gas permeability coefficient (Pe) at temperatures 35 °C, 50 °C, and 65 °C for rubber compounds with organic acid modified kaolin in Fig.5-7 is in all cases lower than that for unmodified kaolin. Behaviour of Pe for organic acid modified silica in Fig.8-10 is more complicated. The obtained decrease of gas permeability coefficient (Pe) for compounds with fillers modified by acids could be result of increase in polymer/filler interaction strength caused by presence of organic acids (which could be temperature dependent).
3.3 Tensile properties

Following figures show tensile properties of kaolin and silica filled vulcanizates, characterized by tensile strength, elongation at break, modulus M100, and modulus M300.

Modulus M100 and M300 of rubber vulcanizates with kaolin in Fig.11 is not much influenced by modification of filler surface by acids. Modest increase in M300 is apparent only for kaolin modified by benzoic acid.

Modulus M100 and M300 of rubber vulcanizates with silica surface modified by acids in Fig.12 is in all cases higher than that for unmodified silica. The highest increase was obtained for modification with benzoic acid.

As M100 and M300 are related to filler-rubber interaction and dispersion of filler in elastomer matrix, presence of acids on the filler surface can probably influence these properties and higher reinforcement effect in some cases is the result.

Tensile strength of rubber vulcanizates with kaolin and silica surface modified by acids in Fig.13-14 is only slightly different from strengths with unmodified fillers. Modest increase in tensile strength was obtained for kaolin modified by benzoic acid in Fig.13.

Higher elongation at break of rubber vulcanizates with kaolin in Fig.15 was obtained for modification by benzoic acid. For vulcanizates with silica in Fig.16 is higher elongation apparent for stearic acid modification. On the other hand, elongation at break with silica modified with benzoic acid is lower than that for unmodified silica.
As was already shown for modulus M100 and M300, presence of acids on the filler surface can probably influence the filler-rubber interaction and dispersion of filler in elastomer matrix. The same could be valid also for tensile strength and elongation of rubber samples.

4 Conclusions

This study deals with the influence of calcined kaolin and precipitated silica surface modification with stearic and benzoic acid on vulcanization characteristics, gas permeability and tensile properties of styrene-butadiene rubber compounds.

As we expected, higher concentration of acids in the compounds (present on the surface of fillers) prolonged scorch time ts2 and optimum cure time t90. Minimum torque ML for rubber compounds with organic acid modified silica was in all cases lower than that for unmodified silica, probably as a result of lubricating effect of used organic acids.

Gas permeability coefficient (Pe) for vulcanized rubber with organic acid modified kaolin was in all cases lower than that for rubber with unmodified kaolin. The decrease of gas permeability coefficient (Pe) by acids modification of fillers is probably consequence of increase in polymer/filler interaction (which could be temperature dependent).

Modest increase in modulus for vulcanized rubber with kaolin was apparent only for M300 and modification by benzoic acid. Modulus M100 and M300 of vulcanized rubber with silica modified by acids was in all cases higher than that for unmodified silica. The highest increase was here observed for modification with benzoic acid. This increase in modulus could be consequence of higher filler-rubber interaction and better dispersion of filler in presence of acid.

Moderate increase in tensile strength and higher elongation at break of vulcanized rubber with kaolin were obtained after kaolin modification by benzoic acid. Vulcanizates with silica have higher elongation at break after stearic acid filler surface modification.

As was already mentioned, the effect of filler surface modification by acids on properties of vulcanized rubber could be result of different filler-rubber interaction and dispersion of filler in elastomer matrix. Presence of acids on the fillers surface could influence also strength of filler-filler interaction. Important role in properties of vulcanized rubbers with acids surface modified fillers could play strength of bond among carboxyl groups of organic acids and silanol groups on surfaces of tested silicate fillers.

Acknowledgements

We gratefully acknowledge partial support of this work by the internal grant IGA/23/FT/11/D incurred at the Tomas Bata University in Zlín, which has been financed in support of specific university research.

This article was created with support of Operational Programme Research and Development for Innovations co-funded by European Regional Development Fund (ERDF) and national budget of Czech Republic within the framework of the Centre of Polymer Systems project (reg. number: CZ.1.05/2.1.00/03.0111).

References: