EFFECT OF THE MODIFIED SOLID PRODUCT FROM WASTE TYRES PYROLYSIS ON THE PROPERTIES OF STYRENE-BUTADIENE RUBBER BASED COMPOSITES

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ABSTRACT

Being resistant to moisture, oxygen, ozone, solar radiation, microbiological degradation, etc., waste car tyres and their deposition present a great environmental problem. Pyrolysis is an environment-friendly process for their recycling. This paper presents data referring to the study of the effect of the solid product from waste tyres pyrolysis on the properties of styrene-butadiene rubber (SBR) based composites. It is found that the further modification of the pyrolysis carbon black decreases two times the ash content and six times the zinc oxide concentration in the ash but the curing characteristics of the investigated SBR based compounds remain unaffected. The values of the modulus 100, the tensile strength and Shore A hardness of vulcanizates containing modified pyrolysis carbon black increase, while the elongation at break and the residual elongation decrease slightly. The effects observed are related to the decreased ash content of the pyrolysis carbon black following the modification as well as to the increased silicon oxide concentration in the remaining ash.

Keywords: rubber, waste tyre, carbon black, pyrolysis.

INTRODUCTION

Being resistant to moisture, oxygen, ozone, solar radiation, microbiological degradation, etc., waste car tyres and their deposition present a great environmental problem. On the other hand, that waste is flammable and its uncontrolled combustion endangers further the environment.

The different methods for waste tyres reuse involve:
- Recovery of the used tyres;
- Mechanical grinding/shredding (obtaining of rubber powder);
- Obtaining a rubber reclaim;
- Devulcanization;
- Pyrolysis, etc.

Pyrolysis is the process of thermal destruction of organic materials. It proceeds in absence of oxygen at temperatures in the range from 500°C to 800°C. The waste tyres subjected to pyrolysis (directly or having undergone some preliminary treatment) are heated gradually starting from an ambient temperature to 700°C-800°C at constant purging by nitrogen, carbon dioxide and/or water vapour [1]. There is a renewed interest to pyrolysis as a method for recycling and reuse of waste tyres because it is an environmentally friendly process yielding useful products. The latter include pyrolysis oil (40 - 60
%, solid carbon residue (30 – 40 %), steel and gaseous products [2]. Each of those products can find various industrial applications. For instance, the pyrolysis oil, which is a complex mixture of organic components, can be used as a plasticizer in rubber industry, as diesel oil [2 - 5] or as a carbon black source [6]. The application of the pyrolysis products in the former two cases is hampered by the high carbohydrates concentrations [7 - 10]. The gaseous products contain H₂, H₂S, CO, CO₂, CH₄, C₂H₄, C₃H₆, etc. They can be used as the energy source required for the pyrolysis proceeding [2]. The solid product of waste tyres pyrolysis (called also pyrolysis carbon black) includes carbon black (80 - 90 %) and inorganic substances (10 - 20 %) which are always present in the rubber compounds used to manufacture car tyres. The briquetted product can be burnt in industrial furnaces. Though being very calorific, containing ca 20-25% of ash, it is not lucrative. It is hypothesized that the pyrolysis carbon black can entirely or partially replace the conventional carbon black in rubber industry following a subsequent mechanical or chemical treatment. That product may be quite effective in manufacturing less demanding rubber items such as floorings for various usages, isolation stall mats, hit resistant coatings, etc.

The present paper aims at presenting the investigations on the effect of the modified solid product from waste tyres pyrolysis on the properties of composites based on styrene-butadiene rubber (SBR).

**EXPERIMENTAL**

**Materials**

The investigations were performed on 1500 type styrene-butadiene rubber (Ravaflex SBR 1500) supplied by Ravago Group. It is a copolymer of styrene (23,5%) and butadiene and is easily processed. The solid pyrolysis product was obtained in accordance with the procedure described in [1].

**Modification of the solid pyrolysis product**

The solid pyrolysis product was placed in a round bottom flask and hydrochloric acid (5 %) was added at a ratio of 1:4. The mixture was boiled under a reflux condenser for 20 min. Then the product was washed with distilled water over a buchner funnel till obtaining a clear filtrate, which gave no white residue in presence of silver nitrate. A strong odour of hydrogen sulphide was evolved during the modification indicating that the sulphur and sulphur-containing compounds were removed from the carbon black. The modification of the solid pyrolysis product was performed to reduce its ash content being one of its drawbacks. The solid pyrolysis product will be further referred to as pyrolysis carbon black.

**Rubber compounds**

Four SBR based compounds containing virgin and modified pyrolysis carbon black were prepared. Their formulations are presented in Table 1. Aiming an objective comparison, the added amount of pyrolysis carbon black was estimated on the ground of the carbon (active substance) content, i.e. the compensated ash content which was determined in advance. Thus 60 g and 83.3 g of virgin pyrolysis carbon black in compounds denoted by SBR 1 and SBR 2 correspond to 50 g and 70 g conventional carbon black, respectively. While 54.7 g and 76.6 g of modified pyrolysis carbon black in compounds denoted by SBR 3 and SBR 4 correspond to 50 g and 70 g conventional carbon black, correspondingly.

**Preparation and vulcanization of the rubber compounds**

The rubber compounds were prepared using an open two-roll laboratory mill (L/D 320x160 and friction of 1.27) according to a specific recipe and blending regime. The speed of the slow roll was 25 rpm.

The rubber was plasticized on the rolls for several minutes prior to adding the ingredients.

The mill had to be cooled at each blending cycle to avoid compounds sticking onto the rolls. The blend was cut diagonally when the ingredients were absorbed in the rubber matrix and the strap prepared was transferred to the opposite side of the steam-roller. Then the compound was homogenized by making a roll and driving it through a narrow shank. The compounds obtained in the form of a sheet were kept for 24 prior to the vulcanization proceeding.

The specimens were vulcanized on an electrically heated hydraulic press at 10,0 MPa and 160°C according to the optimums of each rubber compound that were determined using an moving die rheometer (MDR 2000).

**Experimental Methods**

**Characterization of the virgin and modified pyrolysis carbon black**
**Determination of the losses on heating performed according to ISO 15651/2-91**

1. The weighing glass vessel and its lid were dried separately in a drying oven for 30 min at 105 ± 2°C and subsequently transferred to a dessicator to cool to an ambient temperature. Then they were weighed with an inaccuracy < 0.1 mg.

2. About 2 g of pyrolysis carbon black were weighed in a glass vessel with an inaccuracy < 0.1 mg.

3. The uncovered weighing glass vessel containing the sample and its lid were dried in a drying oven for 1 h at 105 ± 2°C.

4. The weighing glass vessel was covered with the lid and transferred to the dessicator. Its lid was removed again and it was cooled to an ambient temperature. Then the lid was put on and the vessel was weighed with an inaccuracy < 0.1 mg.

The weight loss on heating was calculated in % according to the formula:

\[
\left(\frac{m_1 - m_2}{m_1 - m_0}\right) \times 100, \% \tag{1}
\]

where \(m_0\) is the weight of the weighing vessel (g), \(m_1\) is the total weight of the weighing vessel with the lid and the sample prior to the heating (g), while \(m_2\) is the total weight of the weighing vessel with the lid and the sample after the heating (g).

**Determination of the ash content according to ISO 15651/3-91**

1. The crucible and its lid were put into a muffle furnace set at 550 ± 25°C for 1 h, then transferred to a dessicator and cooled to an ambient temperature. It was weighed with an inaccuracy < 0.1 mg.

2. A pyrolysis carbon black sample of a mass > 2 g was dried in a drying oven for 1 h at 105 ± 2°C.

3. About 2 g of the pyrolysis carbon black sample were put into the preheated crucible and weighed with an inaccuracy < 0.1 mg.

The ash content was calculated according to the formula:

\[
\left(\frac{m_2 - m_0}{m_1 - m_0}\right) \times 100, \% \tag{2}
\]

where \(m_0\) was the weight of the crucible with its lid (g), \(m_1\) was the weight of the crucible with its lid and the sample loaded (g), while \(m_2\) was the weight of the crucible with its lid and the ash obtained (g).

**Determination of dibutyl phthalate absorption (oil absorption number) according to ISO 9665-76**

The tested pyrolysis carbon black (0.5 g weighed with an inaccuracy < 0.001 g) was placed in a porcelain mortar and several drops of dibutyl phthalate (DBP) were added using a microburette. The mixture was ground carefully with the pestle till the disappearance of DBP oil stains on the mortar or on the plate surface. In fact the introduction of DBP continued till all carbon black could be gathered on the pestle. The absorption of DBP (X) in ml/100 g, was calculated according to the formula:

\[
X = \left(\frac{V}{G}\right) \times 100 \tag{3}
\]

where \(V\) was the quantity of absorbed DBP (ml), while \(G\) was the weight of the pyrolysis carbon black sample (g).

**Determination of the iodine number by the titration method according to ISO 15651/1-91**

The pyrolysis carbon black sample, already preliminary dried, was weighed and stirred intensively with a certain amount of iodine solution of a predetermined concentration. Then the solid was separated by centrifugation, while the residual solution was titrated with a solution of sodium thiosulfate of a certain concentration.

The iodine number \(I_{AN}\) per 1 mg iodine, i.e. the iodine adsorbed by 1 g of pyrolysis carbon black (with an inaccuracy < 0.1 mg/g) was calculated by the formula:

\[
I_{AN} = \left(\frac{V_1 - V_2}{5}\right) \times \frac{C_i}{4n} = \frac{158.6 \left(\frac{V_4 - V_3}{C_i}\right)}{m} \tag{4}
\]

where \(V_1\) was the volume of sodium thiosulfate solution used to titrate the iodine solution in the blank sample (ml), \(V_2\) was the volume of sodium thiosulfate solution used to titrate the iodine solution in the sample (ml), \(C_i\) was the concentration of sodium thiosulfate solution (mol/dm³), while \(m\) was the weight of pyrolysis carbon black sample (g).

**Determination of the specific surface area according to Klyachko-Gurvich method**

The solid body specific surface area was determined...
by Klyachko-Gurviech method. The method is based on the dependence of macromolecular surface on the volume of the gas needed for its formation in m³. The dependence is linear in accordance with the BET theory. The latter shows that a linear section of the adsorption isotherm starts to outline with the formation of a monomacromolecular layer on the adsorbent surface.

The determination of the specific surface area by this method involves measuring the decrease of the adsorbate pressure (that of the gaseous nitrogen) due to its adsorption on the surface of a given specimen at a constant temperature (in this case –196°C referring to the liquid nitrogen temperature) in a system of a fixed volume.

Fig. 1 presents the equipment used.

The specific surface area was determined in accordance with:

\[ S_0 = \frac{\Delta P}{\Delta P_0} \]

(5)

where \( \Delta P \) was the decrease of the adsorbate pressure due to the adsorption of the sample and the ‘dead’ volume of the apparatus at –196°C, \( \Delta P_0 \) was the decrease of the adsorbate pressure due to the ‘dead’ volume of the apparatus. It is worth adding that

\[ \Delta P_0 = f(m,d) \]

(6)

where \( m \) was the sample mass, while \( d \) was the sample density. The specific surface area was defined by:

\[ S = \frac{S_0}{m}, \text{ m}^2/\text{g} \]

(7)

Characterization of the ash content of the virgin and modified carbon black by a full silicate analysis (an weight analysis, AAS, ICP-OES)

Average samples of virgin and modified carbon black were prepared by grinding to obtain particles of a size < 100 µm.

Heating losses were determined by weighing the samples placed in platinum crucibles. Analytical scales were used. The crucibles were heated in a muffle furnace at 1000°C for 1 h. The losses on heating were determined by the balance of the samples weight before and after the heating.

Silicon dioxide amount was determined by the weighing method. The samples were placed in platinum crucibles and decomposed by melting in presence of potassium-sodium carbonate. The melt still hot was dissolved in dilute hydrochloric acid. The sediment was filtered off from the solution and subsequently washed with dilute hydrochloric acid and water. The sediment and the filters were put in a platinum crucible preheated to a constant weight in a muffle furnace at 1000°C for 1 h. The residues were in fact pure SiO₂. They were weighed and the percentage amount of the component was calculated taking into account that of the reference sample. The solution left after melt removal was transferred to a measuring cylinder to be used in determining the metals content by ICP-OES spectrometric analysis.

The samples were additionally dissolved in a mixture of acids (HF, HClO₄, HNO₃) aiming the determination of the alkali metals content. They were placed in platinum pans and heated slowly in a sand bath. The dry residue was dissolved in dilute hydrochloric acid and the solution obtained was transferred to a measuring cylinder. The amount of Mg, Ca, Cu, Fe, Zn, Al, Pb, Ti was determined by ICP-OES method using a Prodigy high dispersion ICP-OES spectrometer (Teledyne Leeman Labs) of dual view configurations (radial/axial) and 0.007 nm resolution. The amount of Na and K was estimated by AAS using a Perkin Elmer 5000 atomic absorption spectrophotometer working in an emission regime (acetylene/air flame, K wavelength of 766.5 nm).

Table 1. Formulations of SBR compounds filled with virgin (non-modified) and modified pyrolysis carbon black (phr).

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>SBR 1</th>
<th>SBR 2</th>
<th>SBR 3</th>
<th>SBR 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Styrene-butadiene rubber SBR 1500</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2. Zinc oxide</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3. Stearic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4. Non-modified pyrolysis carbon black</td>
<td>60.0</td>
<td>83.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5. Modified pyrolysis carbon black</td>
<td>-</td>
<td>-</td>
<td>54.7</td>
<td>76.6</td>
</tr>
<tr>
<td>6. N-Tert-Butyl-2-Benzothiazole Sulfenamide (TBBS)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>7. Sulphur</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
</tr>
</tbody>
</table>
nm, Na wavelength of 589.0 nm).

The spectral results referring to the components concentrations were recalculated as oxides.

**Determination of the vulcanization characteristics**

The vulcanization characteristics of the rubber compounds were determined on an MDR 2000 moving die rheometer (Alpha Technologies) according to ISO 3417:2010.

A sample of the rubber compound was placed in a hermetic chamber at pressure lower than that initially determined. It was kept constant at high temperatures. The piston rod penetrated the sample and oscillated at small rotation amplitude (the oscillation angle was 0.5°). That caused shear deformation of the sample. The torque moment required for the disk oscillation depended on the deformation resistance (shear modulus) of the rubber. The torque moment was recorded graphically as a function of time.

**Determination of the mechanical properties of the vulcanizates obtained**

**Shore A Hardness**

Shore A hardness of the samples was determined 24 h after the vulcanization on a Mitutoyo portable hardness testing machine according to ISO 7619:2012. The hardness was determined by the penetration of a tester into the material under conditions previously set.

**Determination of the stress-strain properties**

Double sided belts were cut from the rubber samples on a plate punching machine 24 h after the vulcanization. The belts were measured by a micrometer with precision of 0.01 mm. The determination of modulus 100 and modulus 300, the tensile strength, the elongation at break of the vulcanizates studied were determined on a dynamometer at a 500 mm/min speed of the wedge action jaws according to ISO 37:2008.

**Determination of the residual elongation**

The residual elongation in the treated part of the samples was measured at least 1 min after the break. The two parts of the broken belt were reconnected and the length of the treated part was measured. The residual elongation was calculated by the formula:

\[
\varepsilon_r = \left( \frac{l_2 - l_0}{l_0} \right) \times 100
\]

where \(\varepsilon_r\) was the residual elongation (%), \(l_0\) was the initial belt length (before tensioning), while \(l_2\) was the elongation observed 1 min after the release.

**Determination of accelerated heat ageing resistance**

The accelerated heat ageing resistance was determined according to ISO 188:2009 for 72 h at 100°C in a thermochamber ventilated by forced air convection. The aging coefficients were calculated by the formula:

\[
K = \left[ \frac{B - A}{A} \right] \times 100
\]

where \(B\) was the parameter value prior to aging, while \(A\) was the parameter value found after the aging. It is worth adding that the negative value of the aging coefficient (%) is indicative of aggravated mechanical properties.

**RESULTS AND DISCUSSION**

**Characterization of virgin and modified pyrolysis carbon black**

The results from the investigation of the properties of virgin and modified pyrolysis carbon black are summarized in Table 2.

The comparison of the properties of pyrolysis carbon black prior to and after the modification reveal that:
- The losses on heating of pyrolysis carbon black

<table>
<thead>
<tr>
<th>Properties</th>
<th>Virgin pyrolysis carbon black</th>
<th>Modified pyrolysis carbon black</th>
</tr>
</thead>
<tbody>
<tr>
<td>Losses on heating, %</td>
<td>1.45</td>
<td>1.78</td>
</tr>
<tr>
<td>Ash content, %</td>
<td>16.2</td>
<td>8.6</td>
</tr>
<tr>
<td>Dibutyl phthalate absorption (oil number), ml/100 g</td>
<td>120</td>
<td>127</td>
</tr>
<tr>
<td>Iodine adsorption (iodine number), mg/g</td>
<td>182</td>
<td>171</td>
</tr>
<tr>
<td>Specific surface area, m²/g</td>
<td>137.95</td>
<td>120.85</td>
</tr>
</tbody>
</table>

Table 2. Properties of the pyrolysis carbon black investigated.
change slightly upon modification mainly because of moisture and other volatile substances presence. The losses on heating are less than 1.8%.

- The ash content obtained after the modification is almost two times lower - 16.2% prior to and 8.6% after modification, correspondingly. Taking into consideration the main purpose of the treatment, it can be concluded that the goal is achieved.

- The modification does not affect the structure of pyrolysis carbon black because the oil number values of virgin and modified pyrolysis carbon black are close. The same is valid for the specific surface area and the iodine number, i.e. the modification results predominantly in decrease of the ash content of pyrolysis carbon black. The latter was subjected to additional analyses expecting further decrease of its content. The results from the weight analysis, AAS and ICP-OES are summarized in Table 3. The latter shows that ZnO content in pyrolysis carbon black is almost six times lower after its treatment with hydrochloric acid, which in turn verifies the conclusion that the main purpose of the modification was achieved. The content of SiO₂ is the highest in the ash of modified pyrolysis carbon black as it does not react with hydrochloric acid. In fact SiO₂ is present as the material subjected to pyrolysis included “green tyres” as well. It is known that they use silicon dioxide but not carbon black as filler. Another reagent, such as hydrofluoric acid, is required to remove SiO₂ but in fact its removal is not a must in case of pyrolysis carbon black as it is active filler. An option would be to introduce some silane coupling agent to the rubber mixture like it is usually done when filling with fresh silicon dioxide is carried out. Silane bifunctional nature improves the elastomer-filler interaction. On the other hand, the significantly decreased zinc oxide amount in the ash can be considered a significant success. The decrease of zinc oxide concentration in rubber compounds is a challenge worldwide because of zinc ions ecotoxicity. The greatest concentration decrease results from the modification in case of Na₂O, K₂O, Fe₂O₃, MgO and CaO. There are no changes in the concentration of TiO₂ and PbO.

Curing characteristics of the rubber compounds comprising virgin (non-modified) and modified pyrolysis carbon black

The vulcanization isotherms of the SBR based compounds containing various amounts of virgin (SBR 1 and SBR 2) and modified (SBR 3 and SBR 4) pyrolysis carbon black are shown in Fig. 2. It is seen that they have an identical curve pattern. A wide plateau of
vulcanization (equilibrium torque curves) is outlined, which in turn indicates that the compounds are suitable for thick-wall items manufacture. The compounds containing virgin and modified pyrolysis carbon black of an amount equal to 50 phr carbon black show overlapping isotherms, unlike those referring to amounts equal to 70 phr. The most important fact is that the usage of modified pyrolysis carbon black does not worsen the curing characteristics of the compounds, i.e. there is no reason to exclude the pyrolysis solid product as filler.

The curing characteristics (minimum torque - $M_L$, maximum torque - $M_H$, as well as the difference between them - $\Delta M$; the thermoplastic interval - $t_{S1}$; optimum curing time - $t_{90}$; curing rate – $V_c$) of the studied SBR based compounds obtained at 160°C are presented in Table 4. The latter shows that the values of the vulcanization pa-

Table 3. Ash content data as obtained from weight, AAS and ICP-OES analyses.

<table>
<thead>
<tr>
<th>Substances</th>
<th>Content, %</th>
<th>Virgin pyrolysis carbon black</th>
<th>Modified pyrolysis carbon black</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>38.80</td>
<td>87.32</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.77</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.31</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.50</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.41</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>5.65</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.53</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>46.10</td>
<td>7.22</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>0.19</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Losses on heating, 1000°C</td>
<td>4.69</td>
<td>2.83</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Curing characteristics of the studied SBR based compounds obtained at 160°C.

<table>
<thead>
<tr>
<th></th>
<th>$M_L$, dNm</th>
<th>$M_H$, dNm</th>
<th>$\Delta M$, dNm</th>
<th>$t_{S1}$, min</th>
<th>$t_{90}$, min</th>
<th>$V_c$, %/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1</td>
<td>4.54</td>
<td>31.48</td>
<td>26.94</td>
<td>1.44</td>
<td>10.28</td>
<td>12.8</td>
</tr>
<tr>
<td>SBR 2</td>
<td>8.06</td>
<td>41.52</td>
<td>33.46</td>
<td>1.02</td>
<td>10.50</td>
<td>10.8</td>
</tr>
<tr>
<td>SBR 3</td>
<td>4.56</td>
<td>32.00</td>
<td>27.44</td>
<td>1.44</td>
<td>10.57</td>
<td>11.8</td>
</tr>
<tr>
<td>SBR 4</td>
<td>9.13</td>
<td>47.38</td>
<td>38.25</td>
<td>1.05</td>
<td>10.54</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Table 5. Mechanical properties of the SBR based composites filled with virgin and modified pyrolysis carbon black.

<table>
<thead>
<tr>
<th></th>
<th>SBR 1</th>
<th>SBR 2</th>
<th>SBR 3</th>
<th>SBR 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus 100, MPa</td>
<td>3.2</td>
<td>5.2</td>
<td>3.6</td>
<td>6.3</td>
</tr>
<tr>
<td>Modulus 300, MPa</td>
<td>12.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tensile strength, σ, MPa</td>
<td>12.2</td>
<td>11.8</td>
<td>12.8</td>
<td>12.3</td>
</tr>
<tr>
<td>Elongation at break, $\varepsilon_{1}$, %</td>
<td>305</td>
<td>227</td>
<td>284</td>
<td>198</td>
</tr>
<tr>
<td>Residual elongation, $\varepsilon_{2}$, %</td>
<td>8</td>
<td>5</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Shore A Hardness, relative units</td>
<td>69</td>
<td>78</td>
<td>71</td>
<td>80</td>
</tr>
</tbody>
</table>
rameters increase at higher filler amounts, regardless of the presence or absence of modification, i.e. the pyrolysis carbon black has no effect on the vulcanization process.

**Mechanical properties of the SBR based composites filled with virgin and modified pyrolysis carbon black**

The mechanical properties of the SBR based vulcanizates are summarized in Table 5. It is seen that the values for the modulus $100 (M_{100})$ of all studied SBR based vulcanizates increase at higher filler amounts. The increase of $M_{100}$ values of vulcanizates containing less filler is smaller (11 %) in case of modification, while that of vulcanizates containing higher filler amounts is more pronounced (17,5 %).

Modulus 300 ($M_{300}$) is achieved only in case of a sample containing virgin pyrolysis carbon black of an amount equal to 50 phr carbon black.

The slight changes in the tensile strength values demonstrate that the modification of pyrolysis carbon black has a beneficial effect on that property.

The elongation at break decreases with the increase of pyrolysis carbon black amount. It is less than 10% for vulcanizates containing virgin and modified pyrolysis carbon black of an amount equal to 50 phr, while it is 13 %, when the amount considered is equal to 70 phr. Hence, the modification of the filler, despite of the slight tendency of decrease, has no significant effect on the values of that parameter.

The residual elongation decreases with the increase of pyrolysis carbon black amount, but does not change with the filler modification.

Shore A hardness values increase slightly with the filler amount increase for vulcanizates containing the same filler. Identical change is observed in case of filler modification.

The results presented show that the values of modulus 100, the tensile strength and Shore A hardness for vulcanizates containing modified pyrolysis carbon black increase slightly when compared to those referring to vulcanizates containing virgin pyrolysis carbon black. Meanwhile, the values of the elongation at break and the residual elongation are slightly lower. This is most probably due to the lower ash content in the modified pyrolysis carbon black and the fact that it consists predominantly of silicon oxide. It should be added that higher values of $M_{100}$ and $M_{300}$ of the tensile strength and hardness of the vulcanizates as well as the lower elongation values are characteristic of all compounds containing silicon oxide.

**Resistance to heat aging**

The heat aging coefficients of the SBR based vulcanizates are presented in Table 6. The heat aging resistance of the vulcanizates containing minimal amounts of virgin and modified pyrolysis carbon black (equal to 50 phr active substance) is improved in regard to the tensile strength and the elongation at break. The tendency remains unchanged with increase of pyrolysis carbon black amount.
The heat aging resistance coefficient with regard to Shore A hardness has positive values for all vulcanizates studied. The modification of pyrolysis carbon black affects the heat aging resistance of SBR based vulcanizates. The change in Shore A hardness values is smaller in case of modified pyrolysis carbon black. Hence those compounds are more aging resistant.

CONCLUSIONS

Pyrolysis carbon black obtained from waste tyres pyrolysis is successfully modified by a method designed to decrease the ash content and that of zinc oxide in particular. It is found that the modification introduced decreases two times the ash content and six times the zinc oxide concentration in the ash.

The studies on the curing characteristics, the mechanical properties and the heat aging resistance of SBR based vulcanizates containing virgin and modified pyrolysis carbon black demonstrate that:

- The curing characteristics are not affected by the modification of the pyrolysis carbon black.
- The values of modulus 100, the tensile strength and Shore A hardness for the vulcanizates containing modified pyrolysis carbon black increase, while the elongation at break and residual elongation decrease slightly. The effects observed are related to the decreased ash content in pyrolysis carbon black following the modification as well as to the increased silicon oxide concentration in the remaining ash.
- The modified pyrolysis carbon black has a beneficial effect on the heat aging resistance of the vulcanizates.

Additional decrease of the ash content in case of using pyrolysis carbon black can be achieved by a further modification with another reagent, e.g. hydrofluoric acid. This will result in silicon oxide elimination. Silane can be used instead of the secondary modification as it enhances the interaction between the rubber macromolecules and silicon dioxide. A reinforcement effect is expected. The latter will be the scope of further studies.

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