INFLUENCE OF THE MEASURING CONDITIONS ON THE RHEOLOGICAL PROPERTIES OVER THE “BOUNDED” RUBBER CONCENTRATION IN RUBBER COMPOUNDS

D. Zheleva, I. Ginev

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: darinajeleva@abv.bg

ABSTRACT

The purpose of present work is to investigate the influence of measuring conditions on the rheological properties of filled rubber compounds in presence of different amounts of stearic acid over the “bounded” rubber concentration. The measurements were performed at different revolutions per minute of Brabender Plasticorder rotors in the mixing camera, respectively 0, 3, 10, 20 and 30 min⁻¹. After the measurements the concentration of “bounded” rubber was determined.

The obtained dependencies (concentration of “bounded” rubber at different rotor revolutions) are quite complex and is affected both by the amount of stearic acid and the revolutions of rotors in the mixing camera during the torque measurements. This diverse change of the concentrations of “bounded” rubber in the compounds after the measurement explains smaller variations in torque maximum compared with the effective viscosity. These results are due to the fact that in the camera a further intensive homogenization of the compound ingredients is carried out as well as further dispersion of carbon black in it. Such processes cannot be observed in capillary viscometer.

Keywords: rubber compounds, rheological properties, “bounded” rubber, torque.

INTRODUCTION

Rubber compounds are a multicomponent system. Besides the rubber, they contain different ingredients. The stearic acid is an important ingredient with multifunctional effect in the rubber compounds. It plays very important role in the system rubber-carbon black; and improves the processing of filled rubber compounds. It acts as a dispersing agent for the carbon black, an irreplaceable activator (together with ZnO) during the sulphur vulcanization [1].

In our previous investigations [2] was proved that by measuring the rheological properties can be determined the dispersing effect of the stearic acid with respect to carbon black in different types of rubbers and to determine the concentration of maximum dispersion effect of stearic acid.

The rheological properties of the filled rubber compounds with different amounts of stearic acid were measured by both types of rheometers: capillary viscometer under constant pressure and Brabender Plasticorder PLE 561 [2,3]. The dispersing effect of the stearic acid in SBR (styrene-butadiene rubber) and NBR (acrylonitrile-butadiene rubber) based compounds filled with N-550 carbon black was investigated. It was found that at the dependence of the effective viscosity \( \eta_e \), respectively torque \( M_b \) on the concentration of the stearic acid have been observed maximum at different concentrations of stearic acid for each of rubbers. This is an indication for the optimal carbon black dispersion. The maxima of \( M_b \) of the same compounds measured by Plasticorder in dependence of the stearic acid concentration are relatively smaller (10÷20%) compared to those effective viscosity \( \eta_e \) values measured by capillary
viscometer (30÷120%) [2,3].

In order to explain this difference at the experiments with both types rheometers was suggested that during the measurements by Plasticorder this may be due to the decreasing the “bounded” rubber concentration.

The aim of present study is to investigate the influence of the measuring conditions on the rheological properties of filled rubber compounds with different amount of the stearic acid over the “bounded” rubber concentration by Plasticorder Brabender.

EXPERIMENTAL

Objects of investigation

Styrene-butadiene rubber (SBR) – synthetic rubber with generally destination. SBR is a copolymer on the butadiene and styrene (23,5%); molecular weight ~200000 and density 0,93 g/cm³. The rubber used has a commercial name Bulex 1500.

Acrylonitrile-butadiene rubber (NBR) – synthetic rubber with special destination. NBR is a copolymer on the butadiene and acrylonitrile. It is with polar nature and with two important properties: elasticity at low temperature and very good resistance to the oil, petrol, and chemicals. The rubber used has a commercial name SKN-40, with 40% of acrylonitrile amount.

Carbon black (N550) – used as a filler in rubber compounds, with a particles diameter 31-60 nm; specific surface BET 36-52 m²/g; pH of water dispersion 9.3; DBP-adsorption 96-110 ml/100g.

Zinc oxyde (ZnO) – particles size 0,8÷2,0 μm; moisture content < 0,2%.

Stearic acid ($C_{17}H_{35}COOH$) – used technical stearic acid with melt point $T_m$=50÷58 °C; relative density 0, 960; acidity index ~200; iodine index ~30.

Basic formulations and compounding of rubber blends

The basic formulations of rubber compounds are presented in Table 1. The compounding of rubber compositions, filled with carbon black with varying the stearic acid concentration, is performed by open laboratory mixing rolls with dimensions: L/D 320x360, revolutions of the slower roll 25 min⁻¹ and friction 1,27.

Methods for investigation

**Brabender Plasticorder PLE 561**

The rubber compounds are measured by Brabender, model PLE 561 with mixing camera 60 cm³. Revolutions of 3, 10, 20 and 30 min⁻¹ are chosen and applied on the rotors in the camera. The torque $M_b$ values are reported, and as well as one corresponding temperature of the compound indicated on a precise voltmeter, which connected with a thermoelectric couple in the mixing camera. The mixing camera is not temperate because during the measurements as a result of the high viscosity of the compounds, heat is generated and the temperature increases to constant value. At the same time the torque $M_b$ decreases with increasing temperature of the compounds. The measurements are carried out according to modified methodic [4].

**Determination of “bounded” rubber concentration in uncured compounds**

Accurately weighted 0,8 (± 0,1) g sample of the

<table>
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<th>Compounds code</th>
<th>$S_0$</th>
<th>$S_1$</th>
<th>$S_{1,5}$</th>
<th>$S_2$</th>
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<tbody>
<tr>
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<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black N550</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
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<td>1,0</td>
<td>1,5</td>
<td>2,0</td>
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</table>

<table>
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<tr>
<th>Compounds code</th>
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<th>$N_{1,5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber – NBR (SKN-40)</td>
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<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black N550</td>
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<td>50</td>
<td>50</td>
<td>50</td>
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<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0</td>
<td>0,5</td>
<td>1,0</td>
<td>1,5</td>
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</table>
given rubber compounds are poured with 50 cm³ chloroform in a closed Erlenmeyer bulb. The weight of obtained dry residue corresponds to the amount of the soluble rubber. The amount of the “bounded” rubber is evaluated by these experimental data as well as from the data concerning the rubber quantity in the compounds according to the recipe and it is presented in percentage.

RESULTS AND DISCUSSION

Investigation the rheological properties of the rubber compounds by Plasticorder

Rubber compounds based on SBR (Bulex 1500)

The rubber compositions based SBR (Bulex1500) were compounding on the mixing rolls with varying the stearic acid amount (0; 1,0; 1,5 and 2,0 phr) and were investigated by Brabender methodic [4]. Fig.1 shows the dependence of the torque $M_b$ on the temperature of the material in the mixing camera at chosen rotors revolutions: 3, 10, 20 and 30 min\(^{-1}\). As it can be seen $M_b$ decreases with increasing the temperature for each rotors revolution. Through graphical interpolation of the experimental curves at 30 min\(^{-1}\) and 130 ºC, values of $M_b$ were obtained for all compounds, respectively:

for S-0 → $M_b$ = 68; S-1 → $M_b$ = 77; S-1,5 → $M_b$ = 79; S-2 → $M_b$ = 74.

Thus, the values obtained show a maximal $M_b$ of the compound S-1,5, i.e. containing 1,5 phr stearic acid. The value of $M_b$ in the maximum have a deviation of 16%, which coincides with results obtained in [2,3], where the measurements were carried out at 20, 30 and 40 min\(^{-1}\).

Rubber compounds based on NBR (SKN-40)

The dependencies of the torque $M_b$ of these compounds on the temperature also tend to decrease the $M_b$ with increasing the temperature (Fig.2).

Also by graphical interpolation of the experimental curves at 30 min\(^{-1}\) and 130 ºC, values of $M_b$ were obtained for all compounds, respectively:

for N-0 → $M_b$ = 93; N-0,5 → $M_b$ = 99; N-1 → $M_b$ = 96; N-1,5 → $M_b$ = 87.

The comparison of the obtained values of $M_b$ depending on the stearic acid concentration in the compounds shows maximum at 0,5 phr stearic acid with maximal deviation of about ~7%. This result coincides with the data obtained in [2,3], where the measurements were carried out at 20, 30 and 40 min\(^{-1}\).

Investigation the influence of the measuring conditions by Plasticorder over the “bounded” rubber concentration in the studied compounds

For the “reinforcement” on the rubbers with fillers, the interaction between these solid substances plays an important role. This means that the reinforcing effect of the fillers is due to the surface forces and to the limit resolution between both phases. The bonds spectrum
extends from the Van der-Vaals to chemical bonds [5-7].

During the mixing process of the rubber with fillers, especially carbon black, “bounded” rubber is formed, i.e. fraction, which cannot be extracted with organic solvents [8].

The “bounded” rubber is a parameter that can be easily measured, but the factors affecting the experimental data are very sophisticated [9]. In some investigations [10], the decreasing of the “bounded” rubber amount per unit surface area CTAB (m²/g) was observed. According to the interpretation of these authors, the smaller amount of “bounded” rubber per unit surface of carbon black, which have greater area, could be due to the changes in rubber molecular weight. Another reason could be the multisegmental adsorption, which leads to reduced effectiveness of fillers surface to form a “bounded” rubber. At multisegmental adsorption two or more active sites of the filler could be occupied by the same molecule without increasing the “bounded” rubber amount. The multisegmental adsorption can occur between neighboring particles of filler or their aggregates. This phenomenon is explained by multisegmental adsorption between the aggregates [10].

Determination the amount of “bounded” rubber in the compounds based on SBR

Fig. 3 shows the dependence of the amount of “bounded” rubber on the rotors revolutions in the mixing camera. This concentration was determined after the measurements by Plasticorder at different revolutions of the rotors (3, 10, 20 and 30 min⁻¹). The concentrations of “bounded” rubber were plotted on the graph at zero revolutions of the rotors before measuring them by Plasticorder.

As it can be seen, the amount of “bounded” rubber at 3 min⁻¹ is almost the same for all compounds studied. Increasing the revolutions of rotors to 3 min⁻¹, “bounded” rubber content in the compound increased by ~26 %, at 10 min⁻¹ is about ~40% for the compound S-2 and almost does not change for the compound S-1.5. The amount of “bounded” rubber decreases at higher rotors revolutions with the exception of S-1.5, and to this compound it increased. At the highest rotors revolutions it decreases to one of the compounds, while for the others it remains the same, but for the S-1 increases slightly.

These dependencies are quite sophisticated and are influenced both by the amount of the stearic acid, and by the revolutions of rotors during the measurements of the torque $M_b$. These diverse changes in the amount of “bounded” rubber in the compounds after measurement explains smaller deviations obtained at the maximums of torque $M_b$ compared with the capillary viscometer (Fig. 4) [2,3].

These results confirm the assumption which we have made in our previous investigation [2,3] that in the camera of the Plasticorder is carried out further intensive homogenization of the compounds ingredients and further dispersion of carbon black in it. Such processes cannot be observed at capillary viscometer.

Determination of the amount of “bounded” rubber in the compounds based on NBR

Fig. 5 shows the dependence of the “bounded” rubber...
Fig. 5. Dependence of “bounded” rubber content on rotors revolutions for the compounds based on NBR with different amount of stearic acid.

It was found that for filled compounds based on NBR at different amounts of stearic acid the concentration of “bounded” rubber increases with increasing the rotors revolutions in like compounds of SBR, but also depends differently on the amount of stearic acid for each revolution of the rotors.

REFERENCES