Microwave Dielectric Properties of Rubber Compounds Undergoing Vulcanisation

Part 2. Influence of Carbon Black

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Microwave dielectric measurements were shown to be a promising method for the characterization and monitoring of the crosslinking process in thermosets and elastomers [1–4]. The advantage of microwave methods is the possibility to study the carbon black filled compounds with high ohmic conductivity [1]. In part 1 of this publication [5] we have compared microwave dielectric properties of natural rubber with and without carbon black filler. In part 2 we consider the influence of the type and the concentration of carbon black on dielectric and mechanical parameters of the rubber compounds in detail. Carbon black (powder) is a good electronic conductor, the conductivity of which varies in four orders [6] depending on the size, shape and surface properties of the particles, i.e. on the “activity” of carbon black. We used two types of carbon black as a filler: non-active Corax N 762 and active Corax N 330. For a better understanding our microwave dielectric data are compared with additional torsion pendulum measurements.

Experiment: methods, materials

Seven kinds of materials based on natural rubber were prepared (see Table 1): sample K – natural rubber, sample U – compound of natural rubber and vulcanisation system, samples C1, C2, C3 – compounds of natural rubber, vulcanisation system and non-active carbon black, samples A3, A5 – compounds of natural rubber, vulcanisation system and active carbon black. The compounds of natural rubber with the vulcanisation system and carbon black are prepared by a milling process at about 70 °C [7]. The milled sheets had a thickness of about 2 mm. They were stored at –20 °C. For the mechanical measurements the pure rubber K was additionally milled to decrease the thickness, but for microwave measurements the K samples were cut directly from the unmilled bulk.

All the experiments, both microwave and mechanical measurements, were carried out in the same way as described in part 1 [5]. I.e., the same methods were used (microwave impedance method for the section of a rectangular waveguide with an incorporated sample at about 20 GHz [8, 9] and torsion pendulum type ATM3, Myrenne, Germany), the same sample processing, the same temperature regimes of measurements. All temperature dependences of dielectric permittivity ε’ and loss ε” were measured in the following way: 1) first heating from room temperature to 150 °C (i.e. above vulcanisation temperature); 2) cooling from 150 °C to room temperature; 3) second heating from room temperature to 150 °C. So, the behaviour of unvulcanised (first heating) and vulcanised materials (cooling and second heating) can be compared.

Dielectric parameters: microwave method – vulcanisation – elastomers – monitoring

The application of microwave measurements to the characterisation of rubber compounds vulcanisation is considered. The behaviour of mechanical and microwave (20 GHz) dielectric parameters during vulcanisation was investigated for rubber compounds with different concentrations of active and non-active carbon black. An increase of concentration or activity of carbon black results in the increase of both dielectric permittivity ε’(T) and loss ε”(T) and in the increase of torsion modulus as well. The start of the vulcanisation reaction is indicated by an increase of dielectric permittivity and torsion modulus in all investigated unvulcanised compounds with carbon black. While for compounds with non-active carbon black the vulcanisation can be better indicated by the ε’(T) anomaly, for compounds with active carbon black it is more clearly seen by the change of ε”(T) behaviour.

Mikrowellen dielektrische Eigenschaften von Gummi-mischungen während der Vulkanisation

Teil 2. Einfluss von Ruß

Dielektrische Parameter – Mikrowellenmessungen – Vulkanisation – Elastomere – Überwachen


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Table 1: Compound description

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>Vulcanisation System</th>
<th>Carbon Black Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>Natural rubber</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>C1</td>
<td>Natural rubber</td>
<td>None</td>
<td>Active</td>
</tr>
<tr>
<td>C2</td>
<td>Natural rubber</td>
<td>None</td>
<td>Non-active</td>
</tr>
<tr>
<td>C3</td>
<td>Natural rubber</td>
<td>None</td>
<td>Non-active</td>
</tr>
<tr>
<td>A3</td>
<td>Natural rubber</td>
<td>None</td>
<td>Active</td>
</tr>
<tr>
<td>A5</td>
<td>Natural rubber</td>
<td>None</td>
<td>Non-active</td>
</tr>
</tbody>
</table>

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dences of mechanical parameters were measured during heating from \(-150 ^\circ C\) (below the glass transition temperature \(T_g\) at about \(-60 ^\circ C\)) to 160 \(^\circ C\), and then during cooling from 160 \(^\circ C\) to room temperature.

**Experimental results**

**Microwave dielectric properties**

**First heating**

In Fig. 1 dielectric permittivity for all samples, including pure natural rubber, natural rubber with vulcanisation system and with various carbon black fillers, is presented. The ordinate is spanned to show the curves for different absolute values in an optimal manner. In Fig. 2 the data for dielectric loss are summarised. The value of microwave dielectric permittivity of the pure natural rubber (\(\varepsilon' = 2.4\)) is the lowest one and corresponds to literature data [6, 10, 11]. Comparison of U and K shows that the vulcanisation chemicals do not change MW dielectric permittivity of the pure natural rubber essentially. However the carbon black filling results in a remarkable increase of both dielectric permittivity and losses. For both types of carbon black there is a distinct influence of concentration. The higher the amount of carbon black the higher the dielectric permittivity and the dielectric loss at room temperature. The carbon black activity shows also an influence – with the same concentration but higher activity of carbon black the values of dielectric permittivity and loss are increased.

With temperature increase the dielectric permittivity of all materials, except natural rubber, decreases remarkably. The value of the decrease in the temperature interval from 20 \(^\circ C\) to 120 \(^\circ C\) is nearly the same for all compounds (\(\Delta \varepsilon \approx 0.4\)). Dielectric loss mainly increases with temperature increase. The higher concentration, the higher activity of carbon black – the higher is the rate of increase (slope of the \(\varepsilon''(T)\) dependences).

At about 120 \(^\circ C\), where the vulcanisation reaction starts [10, 12, 13], anomalies of both dielectric permittivity and loss are observed for all materials except pure natural rubber: a change of slope of both \(\varepsilon'(T)\) and \(\varepsilon''(T)\) dependences. For the compounds with non-active carbon black the most noticeable feature during first heating is the change of slope of \(\varepsilon'(T)\) at 120 \(^\circ C\). Obviously the vulcanisation effects an increase of permittivity. A similar effect is seen for compounds with active carbon black, but the vulcanisation is accompanied by a more clear change of slope of \(\varepsilon''(T)\). The increase of dielectric permittivity due to the vulcanisation depends on carbon black concentration and activity but is small for all compounds, in the range of \(\Delta \varepsilon \leq 0.05\). The change of slope of \(\varepsilon''(T)\) at about 120 \(^\circ C\) depends on the carbon black activity: an increase for the compounds with non-active carbon black and a decrease

### Table 1. Composition of the samples

<table>
<thead>
<tr>
<th>Content (in phr)</th>
<th>K</th>
<th>U</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>A3</th>
<th>A5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Vulcanisation</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>system</td>
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<td></td>
<td></td>
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<tr>
<td>Vulkanox 4010 NA</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc oxide</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Vulkacit DM</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Sulfur</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Carbon black</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Corax N 762</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Corax N 330</td>
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<td></td>
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</tr>
</tbody>
</table>

**Fig. 1. Temperature dependences of microwave (20 GHz) dielectric permittivity of the unvulcanised materials at first heating: K – natural rubber; U – natural rubber with vulcanisation system; C1, C2, C3 – natural rubber with vulcanisation system and non-active carbon black; A3, A5 – natural rubber with vulcanisation system and active carbon black.**
for the compounds with active carbon black are observed.

**Cooling and second heating**

To show the results for all materials with carbon black filler more in detail the dielectric parameters of unvulcanised compounds during first heating (labelled by addend _1), of vulcanised compounds during cooling (labelled by _2) and second heating (labelled by _3) are given in Fig. 3 to 6. Details of C1 were already published in part 1 [5].

The difference in temperature dependences of dielectric parameters between first and second heating is essential for all compounds with carbon black. As expected, the temperature dependences of \( \varepsilon'(T) \) and \( \varepsilon''(T) \) become more linear and there is no remarkable difference between the cooling and the second heating. A decrease of the dielectric permittivity with temperature increase is still observed. The anomalies at 120 °C have disappeared or at least become less pronouncing.

The value of the \( \varepsilon' \) decrease during the second heating from 20 °C to 120 °C depends on the concentration and activity of carbon black. The decrease is higher than during the first heating for the compounds with active carbon black (A3, A5); it is nearly the same as during the first heating for the compounds with a high concentration of non-active carbon black (C2, C3); it is two times lower than during the first heating for the compound with a low concentration of non-active carbon black (C1).

The level of dielectric loss \( \varepsilon'' \) of all vulcanised compounds with carbon black increased remarkable comparatively to the unvulcanised ones, especially in the case of compounds with active carbon black. The character of the temperature dependence of dielectric loss does not change for the compounds with non-active carbon black (C1, C2, C3): increase with increasing temperature, as during the first heating. For the compounds with active carbon black (A3, A5) the change is well observed: dielectric loss becomes less temperature dependent,
slightly decreases with temperature increase, opposite to the first heating.

**Mechanical properties: torsion modulus**

The torsion modulus results for all compounds with carbon black filler are combined in Fig. 7. Unvulcanised and vulcanised compounds show a glass-rubber transition at about –60°C. The missing of few measuring points is caused by a too high damping of the material at the region of a glass-rubber transition. Carbon black concentration or activity has no measurable influence on the glass transition temperature. In the rubber region all materials show a small reduction in modulus near 0°C and for some samples also near 50°C. At about 100°C a slight increase and at about 120°C a sharp increase by a factor of 5 to 10 of the modulus is registered. Obviously this is the result of the vulcanisation reaction. At about 140°C vulcanisation process is finalised and the value of torsion modulus saturates or even decreases with further temperature increase. The effect of vulcanisation is seen during the cooling experiment. The modulus is now on a higher level and less temperature dependent. The higher the concentration or the activity of carbon black, the higher is the modulus of unvulcanised as well as of vulcanised compounds. But the value of torsion modulus increase due to vulcanisation does not depend remarkably on the carbon black concentration or activity; it is nearly equal for all studied compounds with carbon black filler.

Generally, the change of mechanical properties of carbon black filled rubber compounds during vulcanisation coincides with the change of microwave dielectric properties. Variation of the activity and concentration of carbon black results in similar effect on both mechanical and microwave parameters.

**Discussion and conclusions**

For the explanation of the observed dielectric and mechanical behaviour the processes in both components of rubber compounds (rubber matrix and filler) should be taken into account. Consequently, the following phenomena can contribute to the temperature dependences of microwave and mechanical parameters in the region from 20°C to
150 °C: vulcanisation (120 °C–150 °C); melting of polymer crystals (at about 35 °C [10, 12–14]); relaxation of the internal stresses, created during mechanical processing of elastomers production; temperature dependence of the conductivity of carbon black; temperature expansion.

Microwave dielectric and mechanical properties are influenced by concentration and activity of carbon black filler. As expected, the increase of concentration of carbon black leads to an increase of dielectric permittivity and loss of unvulcanised compounds at room temperature. Permittivity can be increased by a conducting filler via the action of isolating interlayers. Dielectric loss is a direct function of ohmic conductivity:

\[
\varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega} + \varepsilon_D,
\]

where: \(\sigma\) – ohmic conductivity, \(\varepsilon_0\) – dielectric constant of vacuum, \(\omega\) – angular frequency, \(\varepsilon_D\) – dielectric loss caused by polarisation processes.

Since the activity is a function of surface area and of mesostructure of the carbon black particles [6, 15, 16], it influences the ohmic conductivity of carbon black powders and of the carbon black filled compounds as well [16]. Our experimental estimation of a microwave surface resistance \(R_s\) of carbon black powders shows that active Corax N 330 has 5 times lower \(R_s\) than non-active Corax N 762 at 20 GHz. It corresponds to the difference in high-frequency conductivity of about 25 times. That is why an increase of activity of carbon black can effect the microwave parameters of rubber compounds in the same way as an increase of the concentration: the increase of both permittivity and loss are observed. Our results correlate with the recent study of the ohmic conductivity of rubber compounds with various carbon black fillers [16].

The increase of concentration and activity of carbon black also results in the increase of torsion modulus in the rubber state. This effect is not lost by vulcanisation. Obviously carbon black stiffens the compound by building up its own network. Higher concentration or activity of carbon black enhances the network forming process.
For a detailed analysis of the influence of carbon black, temperature dependences of a normalised microwave dielectric permittivity during first heating are shown in Fig. 8. The permittivity decrease from 20°C to 120°C, probably caused by a reduction of the effective volume concentration of the molecular dipoles [1], is observed for all compounds. It is stopped at 120°C, where vulcanisation starts. $\varepsilon'(T)$ dependences are non-linear, a change of slope (from slow to fast decrease) takes place. The fast decrease starts earlier with higher concentration and with higher activity of carbon black but the final reduction of permittivity is nearly the same (~0.4) for all compounds with carbon black. The equal reduction of $\varepsilon'$ proves, that it is mainly defined by the change of dipole concentration in the rubber matrix. The non-linear character of $\varepsilon'(T)$ can be related to the relaxation of internal stresses, frozen by crystallisation (see part 1 [5] and [1]). Carbon black can effect the crystallisation/melting processes in rubber matrix (probably, it complicates the rubber crystallisation due to creation of its own network). We suppose: the higher the concentration or the higher the activity of carbon black, the more easily the internal stresses can relax, starting at lower temperature.

The temperature dependences of the mechanical and microwave parameters of all investigated unvulcanised compounds with carbon black during first heating indicate the start of the vulcanisation reaction at about 120°C. The increase of dielectric permittivity, corresponding to vulcanisation, can be explained by the increase of the concentration of the polar molecules and groups (see part 1 [5] and [10, 12, 13]). Both mechanical and microwave measurements during cooling show the behaviour of a vulcanised material: the anomalies at 120°C have disappeared. The value of permittivity increase due to vulcanisation depends slightly on the concentration and activity of carbon black (Fig. 8). It correlates with the nearly equal increase of torsion modulus for all compounds with carbon black (Fig. 7). So we can conclude that the change of dielectric and mechanical properties due to vulcanisation is mainly defined by the crosslinking of rubber matrix and only slightly modified by the processes in carbon black subsystem.

On the other hand, the influence of carbon black filler on the vulcanisation (and vice versa, of vulcanisation on the carbon black network) is clearly seen in microwave dielectric loss behaviour (Fig. 2 to 6). This can be expected, because generally dielectric loss is a more sensitive parameter than permittivity to the change in material's composition, structure or phase. For the first, the level of dielectric loss (which is mainly defined by carbon black properties and contents) of all vulcanised compounds increased remarkably comparatively to the unvulcanised ones. Then the change of slope of $\varepsilon''(T)$ dependence at 120°C due to vulcanisation is of opposite sign for the compounds with different type of carbon black: it increases for the compounds with non-active carbon black and decreases for the compounds with active carbon black. The difference in the behaviour of vulcanised compounds is even more noticeable. While the character of $\varepsilon''(T)$ dependences does not change after vulcanisation for the compounds with non-active carbon black, the change is well observed for the compounds with active carbon black: dielectric loss became less temperature dependent, $\varepsilon''$ slightly decreases with temperature increase, opposite to the unvulcanised compounds.

Such a high sensitivity of dielectric loss of the compounds with active carbon black to the vulcanisation process can be understood taking into account the improved ability of active carbon black to build its own network because of the high surface/volume coefficient and enhanced surface activity [6, 15]. Just this property defines the high conductivity [16] and consequently the high level and temperature dependence of dielectric loss of rubber compounds with active carbon black. On the other hand, the carbon black network is evidently very sen-
sitive to the changes in the rubber network, i.e. to the vulcanisation. After vulcanisation the dielectric loss remains on a high and nearly temperature independent level which points to a great influence of the vulcanisation network.

Summarising, microwave dielectric measurements are able to study and monitor vulcanisation reaction in carbon black filled rubber compounds. While for compounds with non-active carbon black the vulcanisation can be better indicated by the $\varepsilon''(T)$ anomaly, for compounds with active carbon black it is more clearly seen by the change of $\varepsilon''(T)$ behaviour.

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References


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VERANSTALTUNGEN

EVENTS

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Fachtagung:
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