Continuous Mixing Process

Properties of E-SBR/Silica/Silane based Rubber Filler Composite

The performance of a tire tread compound depends on how well the additives and fillers are distributed in the rubber matrix and it is based on the manner the mixing is performed. Rubber compounds are traditionally mixed in internal mixers for almost a century. The conventional way of rubber mixing is carried out in a batch process. Especially in the manufacturing of tires, batch mixing is used with optimum productivity by increasing the rotor speed as well as the filling degree. Various studies were carried out on rubber mixing in internal mixers [1–2]. Due to batchwise production in an internal mixer, batch to batch variations occur. These batch to batch variations directly affect the final properties of the product [3]. The discontinuous mixing takes place in multi-stage compounding processes. This process is energy and time consuming. The batch to batch variations as well as multi-stage compounding processes can be overcome by means of using a one step continuous mixing process. Here, the multistage process can be reduced to a one-stage process with reduced mixing energy and mixing time. Several continuous mixing aggregates such as twin screw extruders, ring extruders, planetary mill extruders, etc. can be used in a continuous rubber mixing process [4–5].

The continuous mixing aggregates require however the availability of free flowing raw materials or other adequate feeding forms. An essential contribution for continuous rubber compounding process has been the development of free flowing Rubber/Filler-Composites (RFC) [6–7]. RFC consists of rubber and filler, where the filler portion in the product also serves to reduce tackiness of the rubber and thus also ensure long term stability. Another advantage of these materials is that the filler is already incorporated and therefore has less need to be incorporated during the compounding process. Several RFC products are today available in a pilot scale quantity or in a developmental form to the rubber producer such as E-SBR/carbon black [8], NR/carbon black [9], E-SBR/silica/silane [10] and S-SBR/silica/silane [11]. With regard to continuous mixing of Rubber/Filler-Composites, many investigations have been carried out and published during the last few years [12–16].

Silica has been used as an important reinforcement agent in rubber compounds together with carbon black [17–19]. The mixing of a silica based rubber compound with help of a conventional discontinuous mixing process is regularly performed with a minimum of 3 mixing stages. These stages are necessary to complete the silanization reaction. The precipitated silica has a unique characteristic of having hydroxyl groups on its surface [20]. Because of strong intermolecular hydrogen bonds between hydroxyl groups, silica can aggregate tightly [19, 21]. This aggregation can cause poor dispersion of silica in a rubber compound. Inorganic silica and organic rubber are highly incompatible materials which makes the mixing difficult. The silica surface can be chemically modified by means of silica to achieve compatibilization of the silica to the rubber where the silane is bonded to the surface of the silica. This chemical bonding process between silica and silane is called silanization reaction [22–25]. Hence, to complete this silanization reaction, the mixing time and energy is very high. Alternatively, the free flowing RFC based on E-SBR/silica/silane or S-SBR/silica/silane, where the silanization reaction is already completed, could be used. These compounds reduces substantially the mixing energy and time. For our experimental work, E-SBR/silica/silane based RFC compound is used. This paper deals with the continuous mixing of E-SBR/silica/silane based RFC compounds in a co-rotating twin screw extruder. The study

Authors

J. W. G. Mani, S. Luther, R. H. Schuster, Hannover, U. Görl, Frankfurt

Corresponding author: J. W. G. Mani

Deutsches Institut für Kautschuktechnologie e.V.

Eupener Str. 33, 30519 Hannover

Tel. 05 11/42 01-47

Fax: 05 11/8 38 68 26

Email: Joseph.Gnanamani@DIKautschuk.de
Discover more interesting articles and news on the subject!

www.kgk-rubberpoint.de

Entdecken Sie weitere interessante Artikel und News zum Thema!
is focussed on the influence of process parameters such as screw configuration, screw speed and throughput on material properties. The increase in throughput and screw speed under constant filling degree has been studied for the first time in E-SBR/silica/silane based RFC compound.

Materials

RFC based on E-SBR/Silica/Silane

The rubber filler composite (RFC) based on E-SBR, silica and silane is supplied by Degussa AG, Germany (Table 1). The material is granulated and the size of the granules is approximately 0.5–3 mm. Other additives such as activators, antioxidants and cross-linking chemicals are also in free flowing form. They are fed continuously into the mixing aggregates. The final compound formulation together with RFC is shown in Table 2.

Continuous mixing in twin screw extruder

The continuous mixing of RFC compound is performed using a twin screw extruder equipped with co-rotating screws. The technical details of the twin screw extruder used are given in Table 4. Figure 1 shows a schematic representation of the continuous mixing process for the production of RFC based rubber compound. The barrels in twin screw extruder are cooled with a water flow rate of 3900 l/h. The extruder die is kept open and the experiments are carried out at room temperature. There are open cylinders along the barrel used for dosing materials as well as for venting purposes. Gravimetric single screw loss-in-weight feeders are used for feeding RFC and double screw loss-in-weight feeders are used for feeding activators, antioxidants and cross-linking chemicals.

In a co-rotating twin screw extruder, various types of screw elements are available for varying and optimising the screw configuration. The final properties of the rubber compound are basically determined and influenced by the chosen screw configuration. The compound passes through regions of high shear stress, for example in kneading blocks and through conveying element regions with low shear stress. In our study, the screw is designed with mixing zones consisting of turbine elements, forward conveying elements and backward conveying kneading blocks. The screw configuration consists of high shear stress regions where each screw is equipped with six reverse kneading block elements, as shown in Figure 1. The turbine elements are used where the oil is dosed. For all the experiments in twin screw extruder, the same screw configuration is used.

Sample preparation and measurements

All materials produced by twin screw extruder and internal mixer are shortly treated over a two roll mill with a large gap (5 mm) at 70 °C, in order to get sheets. The vulcanization of the compounds are performed at 165 °C according to DIN 53529 in a compression moulding machine for yielding sheets of 2 mm thickness. The Mooney viscosity (DIN 53523) is detected to evaluate the processing behaviour of the unvulcanized compounds. The visco-elastic behaviour of the rubber mixes is measured with the Rubber Process Analyser 2000 (Alpha technologies). Strain sweeps are carried out at 0.5 Hz at a constant temperature of 60 °C. Other tests such as tensile strength and elongation (DIN 53504), hardness (DIN 53505) and abrasion (DIN 53516) are also determined.

Results and discussion

Properties of reference compound

The material properties of two reference compounds produced in internal mixer are shown in Table 6. First reference compound consists of 13 minutes mixing time with three stage mixing and a second reference compound of 4 minutes mixing time with one stage mixing are shown. The compound properties shows an increase in Mooney viscosity and storage modulus at low strain (G’xø) with decrease in mixing stage and mixing time. This shows that there is an direct influence of mixing stage and mixing time on compound properties. The vulcanized properties show also a variation with respect to mixing stage and mixing time. The vulcanize properties such as tensile strength, elongation and hardness are high-
er and abrasion is lower with decrease in mixing stage and mixing time. As the experiments in twin screw extruder is a one step mixing process, the properties of the compound mixed for 4 minutes are taken as a reference for comparison of the continuous mixing in twin screw extruder.

**Continuous mixing of E-SBR/Silica/Silane based RFC in twin screw extruder**

The manufacture of silica based rubber compounds in the internal mixer involves a highly technical effort. As inorganic silica and organic rubber are highly incompatible materials, they have to be bonded chemically together by means of bifunctional organosilane [23]. Several mixing stages are necessary to complete the so-called silanization reaction between silica and silane. This takes place during the mixing operation in the internal mixer where large amounts of ethanol are released [25]. This results in mixing time of upto 12–15 minutes with a necessary dump temperature of 150–165 °C. Alternatively, when RFC filled with silica is used, the silanization reaction has already been completed. This leads to marked reduction in mixing time and mixing stages. As these materials are free flowing, it allows for the use of these materials in continuous processing. In continuous processing, optimum process parameters in twin screw extruder are necessary to achieve required material properties. The influence of process parameters on outlet temperature, specific energy input and material properties are of major significance in practise. Filling degree in the twin screw extruder also plays a significant role to control the degree of dispersion of filler and a low mixing temperature in order to prevent scorching of the rubber compound. In case of silica based compounds, the dispersion is of paramount importance in micro-level range because a number of rubber compound’s physical properties like, for example, its tensile strength and tear strength are determined by the degree of filler dispersion.

In order to develop and optimize a one step continuous mixing process including crosslinking chemicals on the co-rotating twin screw extruder, the effects of these important criteria on the process are examined. The effect of the two parameters throughput and screw speed under constant filling degree has been studied for the first time in E-SBR/silica/silane based RFC compound. Figure 1 shows a schematic representation of the continuous mixing process for the production of RFC based rubber compound.

The experiments are carried out at different throughputs and screw speeds as shown in Table 5 with a constant filling degree of 21.5 %. The crosslinking agents are mixed continuously along with other ingredients in a one step mixing process. Figure 2 (a) shows the specific energy input during continuous mixing process. It shows that with increasing throughput and screw speed, the specific energy input decreases. Figure 2 (b) shows residence time and outlet temperature as a function of throughput. With increase in throughput and screw speed, the residence time decreases and the outlet temperature increases. The residence time reduces from 64 seconds at 35 kg/h to 44 seconds at 50 kg/h. The outlet temperature increases from 117 °C at 35 kg/h to 143 °C at 50 kg/h. This shows that the heat dissipation is enormous at such low residence times which can be directly seen by an almost linear increase in outlet temperature.

### Material properties of reference compound from internal mixer

<table>
<thead>
<tr>
<th>Properties</th>
<th>Internal mixer (RFC)</th>
<th>Internal mixer (RFC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing stages</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Mixing time [min]</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>Spec energy [KWh/kg]</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>ML 1+4 (100 °C) [MU]</td>
<td>47.6</td>
<td>67.6</td>
</tr>
<tr>
<td>G’ ′′′′ [KPa]</td>
<td>532.7</td>
<td>863.7</td>
</tr>
<tr>
<td>Scorch time [min]</td>
<td>5.1</td>
<td>4</td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>19.2</td>
<td>20.5</td>
</tr>
<tr>
<td>Elongation [%]</td>
<td>508.6</td>
<td>549.4</td>
</tr>
<tr>
<td>Hardness Shore A</td>
<td>56</td>
<td>62</td>
</tr>
<tr>
<td>DIN abrasion [mm^3]</td>
<td>105.6</td>
<td>90</td>
</tr>
</tbody>
</table>

(a) Specific energy input as a function of throughput, (b) Residence time and outlet temperature as a function of throughput
But, further increase in throughput and screw speed is limited due to the possibility of pre-scorch at higher outlet temperatures.

The Mooney viscosity and scorch time are shown as a function of throughput in Figure 3(a). The Mooney viscosity stays almost constant throughout the entire feeding rate. The addition of DPG along with RFC in zone 1 additionally helps in effective incorporation of filler in the rubber matrix. The scorch time found to slightly increase with feed rate. This shows that pre-scorch in rubber compound has not taken place in the obtained outlet temperatures.

The storage modulus at low amplitude is used to study the filler-filler interaction which is regularly used to evaluate the micodispersion. As shown in Figure 3(b), with increase in throughput, the values show an almost constant storage modulus at low amplitude. The screw configuration with reverse kneading blocks leads to sufficient shearing rate and duration time therefore creates a high level of uniformity of filler dispersion seen by the filler-filler interaction $(G''_{\text{tan}})$. Even at higher outlet temperatures, the dispersion efficiency is found to be consistent due to the effectiveness of the screw configuration. Hence, with this screw configuration it is possible to achieve closely the compound properties attained with the internal mixer (Table 6).

The tensile strength and elongation as a function of throughput are shown in Figure 4(a) and the hardness and abrasion as a function of throughput are shown in Figure 4(b). Although there are slight differences in values, the vulcanize properties remain almost constant across the entire feed range. Hence, a significant throughput range of up to 50 kg/h is achieved with almost constant material properties where the crosslinking agents remain almost constant across the entire feeding speed and throughput. The basis of this continuous mixing process is an optimum screw configuration containing mixing elements at required locations. A significant throughput range of up to 50 kg/h is achieved with almost constant material properties where the crosslinking agents are also mixed continuously in a one step mixing process. The specific energy input decreases at higher throughputs and screw speeds. This is economically advantageous compared to discontinuous mixing. The properties of the compounds and vulcanized materials obtained such as tensile strength and abrasion correspond to the properties of the reference compound from the internal mixer.

From this study, the potential to be realised with continuous mixing is already evident on the bases of this trials, especially for silica based tire compounds. The less mixing energy and mixing time are an obvious advantage in comparison to discontinuous mixing. Thanks to the fact that the silanization process has been completed and silica is completely incorporated in the rubber matrix. This leads to simplification of rubber compounding process and allows continuous production in twin screw extruder.

Acknowledgement
The authors thank the Degussa AG for the financial support and the Rubber/Filler Composites.

References