A study of the stages of mixing of a model mixture of rubber and carbon black on a Brabender plastograph

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Selected from International Polymer Science and Technology, 42, No. 11, 2015, reference KR 15/04/32; transl. serial no. 17607

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Mixing of the elastomer with filler is generally the most prolonged and energy-intensive part of the process of manufacturing rubber mixes. The intensity of the mixing process and its characteristics depend on a large number of factors, chief among which are the nature and the rheological properties of the elastomer, the degree of dispersion and the physicochemical nature of the surface of the filler, the content (dosage) of filler in the mixture, and the temperature and deformation parameters of the process.

Irrespective of the type of filler, the process of mixing consists of three successive stages: the incorporation of the filler into the elastomer; the uniform distribution of the filler within the mixture; the dispersion of agglomerates of the filler in the elastomer.

For the production of rubber mixes of stable and high quality, all these successive stages are necessary in the process of mixing.

There are many methods that directly characterise the quality of dispersion of carbon black (CB) [1, 2], but, to characterise the stages of mixing of rubber with carbon black, the mixing process has to be interrupted, which complicates determination and introduces error into the experiment. Determination of the mixing stages directly during the process is possible by recording the following parameters: the rotor shaft torque, the temperature, and the torque spread or electrical conductivity of the rubber mix; according to literature data, it is possible to determine the black incorporation time (BIT), i.e. the time at which the process of carbon black dispersion ends [3–7, 12].

It is also worth noting that attempts have been made on more than one occasion in the literature to describe the kinetics of mixing of rubber with carbon black by means of a first-order reaction equation [6, 8, 9, 10], but the equations proposed have not been widely used and have characterised only the interaction of rubber with carbon black.

The aim of this investigation was to study the stages of mixing of a model mixture of rubber and carbon black on a Brabender plastograph.

In accordance with the aim of the investigation, the following tasks were set:

1. The development of a model formulation and parameters of the mixing process to obtain characteristic points on the curves of change in torque and temperature of the mixture in the process of its manufacture on a Brabender plastograph.

2. A qualitative analysis of model mixtures at characteristic points of the diagram.

Under laboratory conditions, a rubber mix formulation based on 100 parts emulsion-polymerised styrene butadiene rubber of grade SKS-30ARKM-15 and 65 parts N234 carbon black was selected.

The preparation of rubber mixes was carried out in the mixing attachment to a Brabender plastograph under the following conditions: utilisation factor 0.80; initial chamber wall temperature 80°C; rotor speed in mixing cycle 60 min⁻¹; total duration of mixing cycle under pressure 8 min.

After discharge, the rubber mix was subjected to mill sheeting in four passes with a roll gap of 4 mm.

The following properties of the rubber mixes were determined:

- Their processing characteristics during mixing were determined using a Brabender plastograph: the rotor shaft torque; the torque spread; the temperature of the
rubber mix. To lower the level of random noise (error) making it difficult to find the regular component, the indices were subjected to mathematical processing by calculating the exponentially weighted moving average.

- The structure-dispersed parameters $X$ and $Y$ were determined using a Disperester-3000 instrument in accordance with ISO 11345 and ASTM D2663-14. To a ten-rating scale, parameter $X$ characterises the quality of mixing by comparison with the reference, while parameter $Y$ characterises the presence of filler particles of over 23 µm.

- The viscoelastic properties and dynamic indices were determined on an RPA-2000 instrument.

- The amount of combined rubber was determined in accordance with the industry procedure for determining ‘rubber–carbon black’ gel in unvulcanised carbon-black-filled mixes.

The dependences obtained of torque, mix temperature, and torque spread on mixing time are presented in Figure 1. On each of the presented dependences, the characteristic points at which significant changes in rubber mix properties occur are noted. Thus, the characteristic time points for torque are 46 and 176 s, the characteristic time points for temperature are 50, 92, 188, and 256 s, and the characteristic time points for torque spread are 52, 128, and 246 s.

It must be pointed out that, in the time interval from 0 to 50 s, the carbon black is not entirely incorporated into the rubber and is present in the mixer chamber in free form.

On the torque–time curve, a second maximum is noted that is customarily assumed to be the time of incorporation of the filler and denoted as $\tau_{\text{BIT}}$ [10, 11]. This index is one of the main characteristics of the technological effectiveness of rubbers and fillers in the process of their mixing, and is also widely used in assessing the technological effectiveness of rubber mix formulations and the optimality of the mixing cycle and the temperature and deformation parameters of this process.

An analysis of data on the quality of dispersion (Figure 2) showed that, after 210 s, which corresponds to exit from the second maximum on the curve of change in torque (Figure 1), the rate of formation of the bound rubber decreases (there is a reduction in the slope of the curve), and after 300 s the amount of bound rubber becomes constant. Change in the parameter of dispersion $X$ with time decreases after 270 s, which is in fairly good agreement with the time of the start of reduction in temperature of the rubber mix. After mixing for 180 s, the dispersion quality index $Y$ does not undergo any significant changes, and consequently, after 180 s, particles of over 23 µm size are practically absent in the mix, which can be identified from changes on the time dependences of torque and temperature (see Figure 1).

It is known that the maximum storage modulus characterises the rigidity of the filler network in the rubber matrix, and also the magnitude of filler–filler interaction [8, 13] during mixing. Analysis of the results obtained showed (Figure 3) that the magnitude of the maximum storage modulus remains constant in the 50–120 s time interval (filler network of constant rigidity). However, after 270 s, the slope of the dependence decreases, which indicates a reduction in the dispersion rate, and consequently the rate of breakdown of the filler network decreases. The minimum value of the shear storage modulus is characterised by the sum of indices consisting of the storage modulus of the unfilled rubber mix and the hydrodynamic effect of the filler, and by strong rubber–filler bonds (rubber occluded in the structure of the filler, rubber in the pseudoglassy state on the surface of the filler) [13, 14]. From the presented graph...
it can be seen that the given magnitude finds a constant level after 240 s of mixing, i.e. by this time the amounts of occluded and bound rubber in the rubber mix are constant. The time data obtained are in agreement with the characteristic points noted on the graphs of the dependence of torque and torque fluctuation amplitude on mixing time. The work of strain that is spent on breaking the filler–filler bonds under conditions of shear strain remains constant after 240–270 s, which characterises the end of the process of dispersion of carbon black in the rubber matrix. Consequently, the time of the end of the carbon black dispersion process can be determined from the graphic dependences of torque spread and mix temperature on mixing time.

All the results obtained can be generalised by the graphic dependence of torque, temperature, and torque fluctuation amplitude on mixing time (Figure 4). On all the graphs it can clearly be seen that, at 50 s, there is no free carbon black in the chamber. However, the process of incorporation of rubber into the structure of the carbon black does not end but continues up to 120 s, and filling of the structural cavities of the carbon black by the rubber matrix occurs [15, 16]. Up to 180 s, the predominant dispersion is macrodispersion, the dispersion of particles of over 23 µm size; the end of the given process can be judged from the dependences of torque and temperature (maximum temperature growth rate). At the end of the macrodispersion process (up to 240 s), the process of microdispersion takes place; the end of the given stage of dispersion can be found from the start of reduction in temperature or from the torque spread finding a constant value. The subsequent process of simple mixing (homogenisation) proceeds up to 300 s, but there is no possibility of finding where this ends in the process of mixing on the Brabender plastograph.

Thus, a model rubber mix formulation has been developed, and the parameters of the process of mixing have been established to obtain the characteristic points on the curves of change in torque, torque spread, and mix temperature in the process of mix preparation on a Brabender plastograph; the relationship between the characteristic sections obtained on the curves of change in torque, torque spread, and mix temperature in the process of rubber mix preparation and the formation of its structure and properties has been established; the basic possibility of developing and controlling the mixing cycle according to the characteristic points of the diagrams has been shown.

ACKNOWLEDGEMENTS

This work was supported by the project ‘The development of modifiers and functional fillers for flame- and heat-protective polymer materials’, carried out by the university within the framework of a Ministry of Education and Science state assignment.

REFERENCES


Received 30.03.2015