

Development of Dispersion in Rubber-Particle Compounds in Internal and Continuous Mixers

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ABSTRACT: Experiments of mixing silica, carbon black, and CaCO₃ into various elastomers (EPDM, NBR, and SBR) were carried out in this paper. We have investigated the breakup of filler agglomerates in the mixing process and compared the mixing results between the internal mixer and the NEX-T continuous mixer. We have evaluated the impact of the elastomer type, filler type, filler loading, and mixing

time on the breakup of filler agglomerates. When the filler agglomerates break up, the agglomerate size was reduced to a steady state size. The steady state size primarily depends on the type and primary particle size of the filler. A model was developed for the rate of agglomerate breakup. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3940–3943, 2006

INTRODUCTION

There have been few basic investigations of compounding small particles into rubber in different types of mixing equipment.^{1–6} These have largely involved carbon black but also include naturally occurring calcite, clay and talc as well as synthetically prepared silica and zinc oxide. These particles are commercially available in various particulate sizes.

There have also been few comparisons of the relative mixing characteristics of different particles in polymer systems. Various researchers^{7–13} have studied the breakup of carbon black agglomerate in rubber matrices. Rwei et al.^{9–12} have described studies on the breakup of agglomerates of carbon black in silicone oil. They measured the breakup of roughly spherical agglomerates of carbon black as a function of time and applied shear stress.

The purpose of this study is to investigate the breakup of filler agglomerates in the mixing process and compare the mixing results between the internal mixer and the NEX-T continuous mixer. We have evaluated the influence of elastomer type, filler type, filler loading, and mixing time on the breakup of filler agglomerates.

EXPERIMENTAL

Materials

The elastomers used in this research included poly(ethylene-*co*-propylene-*co*-diene) (EPDM, Uniroyal,

Royalene IM 7200), poly(butadiene-*co*-styrene) (SBR, Goodyear, Plioflex 1502), and poly(butadiene-*co*-acrylonitrile) (NBR, Goodyear, Chemigum P612). The EPDM used had a 76% ethylene content, the SBR had a 23.5% styrene content, and the NBR had a 33% acrylonitrile content.

Seven different kinds of particles were used; these included four types of silica (PPG, Hi-Sil 190, Hi-Sil 255, Ciptane 255, and Silane 732), two types of carbon black (Cabot, N110, and N762), and one type of calcium carbonate (Specialty Minerals, Multiflex MM).

The particle concentrations were set at 10 or 20 vol %.

Mixing

Internal mixer

The internal mixer used in this research is a PL-2000 Computerized Plasti-corder made by C.W. Brabender Instruments. A material fill factor of 0.6 was used for all experimental trials. The mixing chamber temperature was set to 100°C and the mixing time for different compounds varied between 60 and 900 s.

The rotors used were a pair of adjustable four flighted rotors that were operated synchronally at the same speed of 30 rpm in a counter-rotating mode. These rotors were originally designed and used by Cho et al.⁵

Continuous mixer

The continuous mixer used was a product of Kobelco Stewart Bolling, Model NEX-T 60. This type of continuous mixer has been discussed by various authors.^{14–18} The machine consisted of two sections: a top mixing chamber and bottom single screw ex-

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truder. A top mixing chamber had an L/D ratio of 7 and housed two counter rotating rotors with a diameter of 60 mm. The rotors had screw sections near the feed port followed by forward and backward pumping rotor sections. Both rotors were driven by a 50 HP motor and operated at the same speed. There was a discharge gate (orifice) at the end of the mixing chamber. The gate was of 60 mm length and 63 mm width.

The feed rate was set as 10 kg/h. Prior to each trial, the rubber pellets and the filler were tumble mixed. The mixture was then fed into the hopper of machine at a constant feed rate.

Scanning electron microscope (SEM) and characterization

A Hitachi S-2150 Scanning Electron Microscope (SEM) was used to characterize the filler agglomerate size. The average filler agglomerate sizes were calculated by an Image Analyzer. The average agglomerate size was generally represented in terms of higher order average of individual agglomerate size to avoid the problem of subjectivity in dealing with very small particles. Specifically, we used the "mass" average size as

$$d = \frac{\sum N_i d_i^3}{\sum N_i d_i^2} \quad (1)$$

where d is the mass average size of agglomerates. The d_i is the individual agglomerate size and N_i is the amount of agglomerates with a size of d_i .

Residence time distribution

Residence time distributions for the Kobelco continuous mixer were measured using aluminum flakes. This indicates the length of time during which the material stays in the continuous mixer.^{16,17}

RESULTS

Mixing in internal mixer

Compounds produced by the internal mixer were observed using a scanning electron microscope (SEM). By image analysis of these SEM photomicrographs, the mass average agglomerate size was obtained from eq. (1). Typical plots of agglomerate size " d " as a function of mixing time are plotted in Figure 1 for 10 vol % filler loaded EPDM compounds. For 20 vol % filler loaded NBR and SBR elastomer compounds, the tendency and behavior of the results are very similar.

In Figure 1, the symbols represent the experimental data. It is found that the agglomerate size decreases rapidly with mixing time to reach a steady state size d^* . Once d^* is achieved, further mixing does not de-

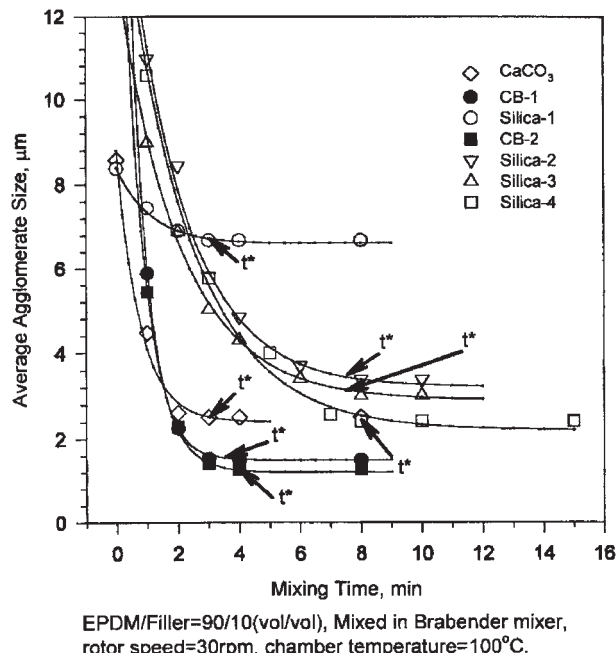


Figure 1 Agglomerate Size versus Mixing Time for Mixing EPDM with Fillers in Internal Mixer (10% Filler loading).

crease agglomerate size. We call the mixing time to reach d^* as the "critical mixing time" t^* . It is observed that t^* is different for different filler loaded compounds. For 10 vol % filler loaded EPDM compounds, the mixing time t^* was ordered as

Silica-4 > Silica-3 ≈ Silica-2 >

CB-1 ≈ CB-2 > Silica-1 ≈ CaCO₃

From Figure 1, the steady state agglomerate size d^* , for the fillers, was ordered as

Silica-1 > Silica-2 > Silica-3 > CaCO₃

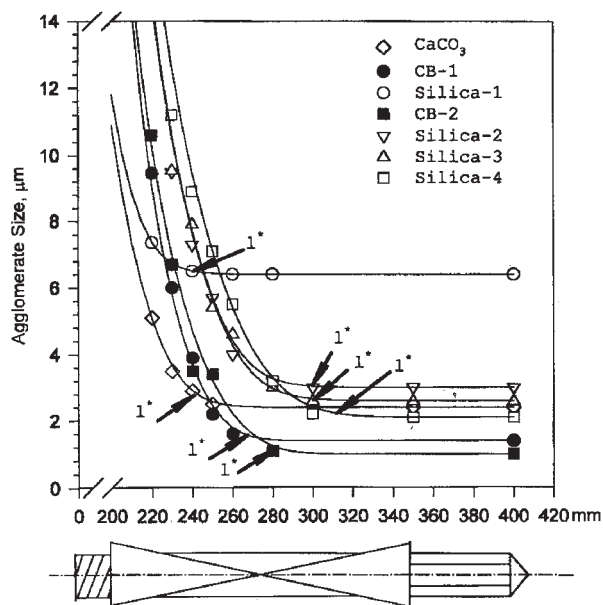
Silica-4 > CB-1 > CB-2

The behavior of NBR and SBR compounds is similar to that of the EPDM compounds

Mixing in continuous mixer

When the mixing in the continuous mixer reaches a steady state, the machine was shut down and the machine's chamber was opened. It was noted that the compound fully filled the whole rotor section, but the machine was starved in the region near the hopper.

The agglomerate sizes determined as a function of position along the mixer rotor are plotted in Figure 2 for 10 vol % filler loaded EPDM compounds. It is seen that the agglomerate size at first decreases as a func-



Processing Parameters:
Rotor speed=60 rpm, barrel temperature=140°C, gate
temperature=140°C, gate position = 100% open.

Figure 2 Agglomerate Size versus Rotor Position for Mixing EPDM with Fillers in NEX-T Continuous Mixer (10% Filler content).

tion of position but then reaches a constant value, which is then maintained.

DISCUSSION

Comparison of batch and continuous mixer

The mixing results in the internal mixer (Fig. 1) and the continuous mixer (Fig. 2) indicate that when a certain mixing time or a rotor position is reached, the agglomerate size remains constant. After this critical point, lengthening the mixing time has no effect on the decrease of the agglomerate size.

We found that the values of d^* for the filler in the internal mixer and in the continuous mixer are similar and indeed almost equal.

Comparison of real time and residence time

In the internal mixer, the agglomerate size decreases with increase in mixing time and reaches the steady state size d^* . The mixing time for breaking the agglomerates to d^* is different for different type of fillers. For the continuous mixer, all the materials were mixed at the same processing condition. The average material residence time was 165 s, which means the average mixing time for each compound in the continuous mixer is equal to 165 s. If this time is compared with the critical mixing time in the internal mixer, it is

found that it takes longer time for a filler agglomerate to break down to d^* in the internal mixer than in the continuous mixer. Indeed the internal mixer mixing times to reach d^* are 240–540 s when compared with a fraction of 165 s found for the continuous mixer.

These phenomena can be accounted for as follows: (1) The internal mixer processes compounding in a batch mode; (2) The internal mixer's chamber is filled by material to a fill factor ϕ , which is necessarily smaller than 1. In this research, ϕ was set as 0.6 for all the compounds. Because the mixing chamber is not fully filled by the compound, there is always an empty space in the machine. At any time, only part of the material is sheared by the rotor and the barrel wall. The other material is allowed to escape from the shearing action. If we consider this in view of mixing time, the real mixing time is smaller than the residence time of material in the machine. On the contrary, our results and the studies of Galle and White¹⁶ show that rotor sections in the NEX-T continuous mixer chamber are fully filled. In this fully filled mixing section, no material can escape from the shearing action.

Kinetic model

To model this we suggest that the agglomerate breakup rate is proportional to the hydrodynamic forces acting on the agglomerates. According to Stokes' law¹⁹ for Newtonian fluids, this force is proportional to the agglomerate diameter. So the agglomerate breakup rate can be estimated to be proportional to the agglomerate size. On the other hand, we consider that re-agglomeration occurs between the contact of two agglomerates and is greater for smaller particles. We take the re-agglomeration rate to be proportional to the total surface area of the agglomerates. This leads to

$$d(d)/dt = -kd + k'(1/d^2) \quad (2)$$

when t approaches infinity, the agglomerate size will reach a steady state size of d^* . From eq. (2), this is

$$d^* = (k'/k)^{1/3} \quad (3)$$

Substituting eq. (3) into eq. (2), and integrating gives

$$d(t) = [(d_0)^3 - (d^*)^3 \exp(-3kt) + (d^*)^3]^{1/3} \quad (4)$$

Where d_0 is the filler agglomerate size at the beginning of mixing, and k is the agglomerate breakup rate constant, and k' is the agglomerate re-agglomeration rate constant. k and k' are the functions of stress, filler concentration, type of particle, particle size, or BET surface area of the particle.

The mixing time for the material at a specific rotor position in the continuous mixer should be approxi-

TABLE I
Kinetic Constants (k) [eq. (2)] of Mixers
used in this Study

Materials	Continuous mixer	Internal mixer
Silica-1	2.784	0.9301
Silica-2	2.414	0.5815
Silica-3	2.381	0.5609
Silica-4	2.101	0.4802
CB-1	3.250	1.056
CB-2	2.850	0.9858
CaCO ₃	2.905	1.058

mately proportional to the distance from the beginning of the rotor to this rotor position. The mixing time at any position should be the product of the fractional fill length and the residence time. For our conditions, the residence time was 165 s.

$$t = (L/200) \times 165 = 0.825L \quad (5)$$

The total fill length was 200 mm. Thus substituting eq. (5) into eq. (4), the decrease of agglomerate size as a function of rotor position can be written as

$$d(L) = \{[(d_0)^3 - (d^*)^3] \exp(-0.04125kL) + (d^*)\}^{1/3} \quad (6)$$

Here d_0 is the filler agglomerate size at the beginning of mixing, k is the agglomerate breakup rate constant, d^* is the agglomerate size at steady state. Here k and d^* are functions of stress, filler concentration, type of particle, BET surface area of a particle, etc.

The experimental results are compared with calculated agglomerate sizes in Figure 2. Each symbol in Figure 2 represents experimental data, while the curved lines are calculated from the beginning of the rotor from where the material has fused and the mixing starts.

The agglomerate breakup rate constant k in the continuous mixer and internal mixer has been compared. Values of k in these two mixers, when 10% filler is mixed into EPDM, were listed in Table I. In Table I,

k_{con} and k_{int} represent the value of k in the continuous mixer and the internal mixer, respectively.

It is found that k_{con} in the continuous mixer is significantly larger than k_{int} in the internal mixer and the ratio of k_{con} to k_{int} is about three. This is also true for the 20% filler loading mixing and for other elastomer matrices.

The reason for this as indicated earlier that the mixing in the pressurized fully filled region is more efficient. The stress fields must be more consistently intense. Therefore, the agglomerate breakup rate constant k in the continuous mixer is larger than that in an internal mixer.

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