Modelling Dispersive Mixing of the Ingredients of Rubber Compounds

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The objectives of this work are to carry out the theoretical description of the mixing process accompanied by dispersing the polymer blends and to submit the fractal model of the dispersive mixing process which can be useful for engineering calculation of the apparatuses for mixing the ingredients of rubber blends. Rubber mixing process is extremely complex in its mechanism. In fact, there are two basic processes combined - mixing and dispersing with a simultaneous increase in the specific surface area of the interface between the blend components. The paper offers for discussion the theory of dispersive mixing process which is based on the model of generated Brownian diffusion over the fractal medium. The results of mathematical modeling and natural experiments have been presented.

1. Introduction

The process of mixing the filler ingredients with rubber compounds is a critical stage in technology of rubber production (Amash et al., 2001). The intensity of rubber mixing process largely determines the basic quality indicators of finished rubber (Barkanui et al., 2011).

Rubber mixing process is extremely complex in its mechanism (ten Brinke et al., 2003). In fact, there are two basic processes combined, namely: mixing and dispersing with a simultaneous increase in the specific surface of the contact between the blend components (Rodgers, 2004). Physical mechanisms of rubber mixing processes and rubber production can be described with the help of the regularities of rheology of viscous flow and deformation of polymers (ter Brinke et al., 2003). The mixing process occurs in conditions of non-stationary field of deformation speed and temperature (Nakajima, 1994). It is accompanied by transformations in the internal structure of the polymers and by changes in their physical and chemical properties (Nazir and ratnan, 1989).

Two groups of problems linked to the investigation of the mixing process can be assigned (Blackley, 1983). The first problem is in studying the characteristics of the components to be mixed, i.e., in determining the quality of the mixture, and the second problem is the description of the process of changing the quality over time (Chukwu, 2011).

There are a lot of approaches to the classification of mechanisms of mixing of the disperse materials (Cazerta et al., 2013). For example, the mixing processes can be classified by temporary phases of the mixing device. In the early stages of the process the convective mixing dominates, what manifests in the intensive displacement of whole groups and layers of components into the working volume (White and Kim, 2008).

The diffusion transfer, however, at this stage is not intensive, as the specific interface between the components is small. Segregation (separation) of the mixture at this time is also negligible due to the immobility of the particles inside the movable layers. The mixing process mainly determines the character of the movement of components in a mixer (Erman et al., 2013).

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The rates of convective mixing and diffusion transfer become comparable only after the initial distribution of the components into the working volume (Youwai and Bergado, 2003). Diffusive mixing becomes prevalent when the interfacial surface between the phases reaches a certain value. In the case of mixtures consisting of dispersed solids with different physical-mechanical properties, as it occurs generally in practice, movement trends of different components are different (Sui et al., 2007). The rates of
accumulation of particles of the same type at different areas in the working volume of a mixer are also not identical (Wu et al., 2004). So, the segregation begins to affect the course of mixing (Zondervan et al., 2013).

Therefore, to create a general mathematical model of the process, including a full system of differential equations and boundary conditions, and, especially, to solve such a system, are not possible to date (Dieza et al., 2013).

So the studies related to the development of simplified mathematical models that would clarify the physical basis and can reflect the most important observable and measurable characteristics of the process are of particular relevance. The objectives of this work are to carry out the theoretical description of the mixing process accompanied by dispersing the polymer blends and to submit the fractal model of the dispersive mixing process which can be useful for engineering calculation of the apparatuses for mixing the ingredients of rubber blends.

2. Fractal model of mixing

The simplest description can be based on a model of dispersive mixing on the approximation of first-order reaction (Rodgers, 2004). Such an approach is acceptable, however, only at the initial stages of mixing and cannot estimate the kinetic characteristics of the process (Kaewsakul et al., 2011).

In this paper we propose an approach to modeling the process of dispersing mixing based on the concepts of generalized Brownian motion of the particles mix ingredients (Feder, 1986) and fractal manifolds (Mandelbrot and Van Ness, 1968). The random walk of particles of ingredients can be described as follows.

At each time interval $\tau$ with a typical duration determined by the energy consumption for mixing, the probability of a particle drift $s$ is defined using a Gaussian, i.e. the normal probability law of the distribution (Feder, 1986)

$$p(s,\tau) = \frac{1}{\sqrt{4\pi D \tau}} \exp\left(-\frac{s^2}{4D \tau}\right)$$  \hspace{1cm} (1)

Here $D$ is the characteristic diffusion coefficient which obeys the Einstein formula:

$$D = \frac{1}{2\tau} \left[M(s^2)\right]$$  \hspace{1cm} (2)

where $M(s^2)$ is the variance of the random variable.

Then the probability of distribution of dispersing mixing is given by:

$$P(\Delta x) = \frac{1}{\sqrt{4\pi D(t-t_0)}} \exp\left(-\frac{(\Delta x)^2}{4D(t-t_0)}\right)$$  \hspace{1cm} (3)

In dimensionless form the corresponding movement reads

$$\Delta X = \frac{\Delta x}{\sqrt{2D(t-t_0)}}$$  \hspace{1cm} (4)

The essence of the concept of generalized Brownian motion over fractal manifolds, which are the structures with very complex geometry, is that the relation (4) is replaced by the following (Mandelbrot and Wallis, 1969).

$$\Delta X = \frac{\Delta x}{\sqrt{2D \tau (\Delta t/\tau)^H}}$$  \hspace{1cm} (5)

where $H$ is the composite index which is not equal to 0.5 in the general case.

The case $H = 0.5$ corresponds to an independent increments and describes the usual Brownian motion. The proposed approach, in contrast to the case of simple Brownian motion, allows considering the prehistory of the mixing process with the help of varying the index. Hence it is possible to describe correctly the most important features in temporal changes of a disperse polymer blend, namely, the
change in its statistical characteristics during the mixing process. And the characteristic time acquires the sense of the relaxation time.

Then the process of particle drift on mean statistical approximation obeys

$$\Delta x \sim s |t - t_0|^H$$

(6)

Hence the estimate of the standard deviation reads

$$\sigma(\Delta t) \sim (\Delta t)^H$$

(7)

Let us introduce the dimensionless time coordinate $\eta = t/\tau$ and write the law of generalized Brownian motion in the following form (Mandelbrot and Van Ness, 1968)

$$\Delta X_H = \frac{1}{\Gamma(H + \frac{1}{2})} \int_0^n K(\eta - \eta_i) dX(\eta_i)$$

(8)

Here $\Gamma(x)$ is the gamma-function.

According to this definition a value of random function at the moment depends on all preceding moments in contradistinction to the usual normal random process with zeroth average and unitary dispersion (Mandelbrot and Wallis, 1969). The kernel of the nonlocal relation (8), can be defined as follows:

$$K(\eta - \eta_i) = (\eta - \eta_i)^{H-\frac{1}{2}}$$

(9)

Discrete analog of this law for approximate calculations and computer experiment can be obtained by the methods of (Feder, 1986)

$$X(t) - X(t-1) = \frac{1}{\Gamma(H + \frac{1}{2})} \sum_{i=n(t-\tau)}^{n(t)} K\left(\frac{m-1}{n}\right) n^{-\frac{1}{2}} \rho_i$$

(10)

where $\rho_i$ - a set of normally distributed random variables.

This mixing law is nonlocal in the sense of that when the parameter $H > 0.5$, the mixing intensity at any given time $\eta$ depends on the pre-history of the process, i.e. depends on the kinetic characteristics at all preceding moments $\eta_i \leq \eta$.

For $H = 0.5$ the correlation between past and future deviations is absent. And the phenomena of persistence or non-persistence can be observed for $H \neq 0.5$. The persistence which is typical for $H > 0.5$ means that the main tendency in system deviations will be maintained.

So, the main hypothesis accepted in this work is that diffusion process under dispersing mixing can be described with the help of mathematical technique of generalized Brownian diffusion.

Important feature of the dispersive mixing is the principal dependence of the effective diffusion coefficient (mixing coefficient) on current time. According to the model, this feature has been modelled with the help of the coefficient of anomalous fractal diffusion

$$Def = D(\Delta t)^{2H-1}$$

(11)

Figure 1 shows some typical graphs of evolution of the effective diffusion coefficient in time. Some experimental data, which are commented in the next part of our article, are also presented in Figure 1.
Figure 1: The effective diffusion coefficient as a function of time for persistence systems

Figure 2: The typical drifts of particles while mixing (1: simple mixing; 2: dispersing mixing)

Since the model predicts an increase in the effective diffusion coefficient in time, respectively, the range of variations of the particles coordinates increases in time too (Figure 2).

3. Experimental study and model identification

Experimental studies of the process of dispersing mixing were carried out in a batch mixer of a roller type. The bath mixer of the type RS-250-40 of Russian made with overall sizes 8,500 × 1,300 × 6,000 was used. Two rubber compounds were investigated, namely, undertread and protector mixtures. The mixing processes for blends prepared on the base of two types of rubbers were investigated. The first one is the synthetic methyl-styrene rubber with the methyl-styrene content of 30 % (rubber 1), and the second is the synthetic divinyl rubber (rubber 2).
Figure 3: Model Identification and determination of the parameter $H$

The time analysis of the dispersion content of mixed composition was carried out on the basis of known techniques (Rodgers, 2004). Determination of the effective diffusion coefficient was performed by using a tracer dye.

The experimental curves which depict the dependences of effective diffusion coefficients on current time are shown in Figure 2. The experiments demonstrate the real growth of the effective diffusion coefficient in time. So it can be concluded that this change is well described with the help of the generalized fractal diffusion model.

Figure 3 is a graph showing the effective diffusion coefficient after the complete cycle of the rubber mixing as a function of control parameter $H$.

As a result of experiments it can be concluded that the process of mixing the ingredients with rubber 1 agrees well with the fractal-diffusion model at the control parameter $H \approx 0.71$, and for mixing with rubber 2 - at $H \approx 0.73$. This difference is explained due to the higher viscosity of rubber 2. At the same time the rubber 1 is a brittle material. It means the more viscosity the more the parameter $H$. So, the parameter $H$ gives adequate description of the system persistency.

4. Conclusions

The regularities of the process of dispersive mixing of the filler ingredients with raw rubber are principally different from the regularities of the process of simple mixing which is not accompanied by dispersing of the particles in the blend. The main results and scientific novelty of the work are the following. The stochastic model of dispersive mixing of polymer blends has been carried out. The expressions for calculating the evolution of the effective diffusion coefficient in time during dispersive mixing of the ingredients of rubber compounds are obtained on the basis of the concept of generalized diffusion over fractal media. The mixing processes for blends prepared on the base of two types of rubbers have been experimentally investigated. The first one is the synthetic methyl-styrene rubber with the methyl-styrene content of 30% (rubber 1), and the second is synthetic divinyl rubber (rubber 2). The results of experiments confirm that the complex process of dispersive mixing can be described with the help of the model of generalized Brownian diffusion over the fractal medium. The composite index $H$ plays a role of the control parameter in this mathematical technique, and this parameter gives good description of the system persistency. The following values of the index $H$ were obtained: for high viscosity system (rubber 1) $H \approx 0.73$, and for the brittle system (rubber 2) $H \approx 0.71$. 
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