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STUDY OF A POLYMER MIXTURE BY THE METHOD OF RADIOTHERMOLUMINESCENCE

At present it may be regarded as established that systems of mixed polymers should not be considered stable (1,2), since in practice, for any kinds of mixing, it is impossible to obtain an equilibrium degree of mixing (2,3). Therefore, during storage and use of such systems, diffusion processes take place in them, leading either to homogenization or to heterogenization and, consequently, to changes in their properties (1,2). Owing to the high viscosity of polymers, these processes proceed at a very low rate, which makes their observation difficult. The present article gives data on the evaluation of the homogeneity and stability of systems of mixed polymers by the method of radiothermoluminescence (4). This method, previously used for the study of individual polymers, can, as will be shown below, be applied to the study of the temperature region of glass transition in mixed systems. Because of its high accuracy, simplicity, and reliability, along with the rapidity of the determinations, this method apparently should find wide application.

As objects of study we chose mixtures of technical butadiene elastomers SKB and SKD, which were mixed on rolls in various proportions. These elastomers, having the same chemical nature, differ in the content of 1,2-type bonds ($\approx 60\%$ in SKB and $\approx 2.5\%$ in SKD). A mixture of SKD with polyethylene was also studied in less detail. After degassing, the samples were irradiated with fast electrons at 77° K (dose–1 Mrad) and then thawed at a rate of 10–12° per min. The glow curves of SKD and SKB were presented in (5). The glow curves of both initial elastomers are characterized by the presence of a well-resolved maximum, the position of which corresponds to the glass-transition temperature of the elastomer. The glow curve of a mixture of these elastomers (ratio 50%—50%), obtained with insufficient mixing, is shown in Fig. 1a. The curve has two maxima, the positions of which coincide with those given in (5), indicating the heterogeneity of the mixture. Similar curves were obtained over the entire range of component ratios. The positions of the maxima remained unchanged, independently of the composition of the mixture. Figure 1b shows the glow curve of an SKD–SKB mixture (ratio 50%—50%) obtained under optimal mixing conditions. In this case one maximum is observed, occupying an intermediate

Figure 1 and Figure 2: luminescence curves

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Figure 3 and Figure 4: glass-transition temperature and glow curve

Figure 2: Figure 3 and Figure 4: glass-transition temperature and glow curve

position relative to the maxima on the glow curves of each component. Glow curves for some rubber mixtures (at different SKD–SKB ratios) are given in Fig. 2, from which it follows that, under optimal mixing, one maximum is observed on all glow curves, the position of which depends on the composition of the mixture. Storage of mixtures prepared under optimal conditions does not lead to any visible changes in the system (the glow curves do not change when the mixtures are stored either under normal conditions or at elevated temperature), which indicates the attainment of "service compatibility."

concept introduced in work (1). Taking into account that obtaining a truly compatible system is unlikely (6), it may be assumed that the mixtures consist of microvolumes of each component with a diffuse phase-boundary surface, analogous to the mixtures observed in work (3). Figure 3 presents the dependence of the mixture T_g on

Fig. 1. Glow curves of a mixture of SKD with SKB, obtained under insufficient mixing (*a*) and optimal mixing conditions (*b*).

Fig. 2. Glow curves of the elastomers SKD (*1*), SKB (*5*), and their mixtures at SKB : SKD ratios of 30 : 70 (*2*), 50 : 50 (*3*), and 70 : 30 (*4*).

the composition of the components. The values of T_g were determined from the position of the maximum on the glow curve of the mixture of the given composition (4, 5). An analogous dependence of T_g on the mixture composition was obtained from thermomechanical measurements. From the results presented in Fig. 3 it follows that the sharpest decrease in the glass-transition temperature of the mixture is observed

Fig. 3. Dependence of the glass-transition temperature on the composition of a mixture of SKD with SKB.

Fig. 4. Glow curve of a mixture of SKD with powdered polyethylene.

upon the introduction of comparatively small amounts of SKD (up to 25%). A similar effect was observed by Kargin and co-workers in interchain plasticization of nitrocellulose (7).

Mixing SKD with powdered polyethylene at a temperature below the melting temperature of the latter leads to the formation of a system close to filled rubber mixtures. The glow curve of such a system has two clearly expressed maxima, the positions of which do not depend on the ratio of the components (Fig. 4).

Storage of the mixture for more than 4 months does not lead to a noticeable change in the glow curves.

The system obtained in this case is characterized by stability and, from this point of view, may be regarded as "operationally compatible." The presence of two maxima indicates that in this case the mixture is a two-phase system, where the polyethylene, in the form of dis-

the dispersed phase is distributed in the continuous phase of the elastomer. This conclusion is confirmed by microscopic study of a similar system ([2]).

Thus, this work has shown the possibility of applying the method of radiothermoluminescence to the study of polymer blends. Subsequently an attempt will be made to apply this method to a quantitative description of the processes occurring in mixed systems as a function of the conditions of their preparation and aging.

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