Estimation of kinetic parameters for curing of epoxy-anhydride compositions by DSC

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The kinetics of the curing process of epoxy resin (ED-22) in the presence of the anhydride hardeners (*iso*-methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, and dodecylsuccinic anhydride) and accelerators (2-methyl imidazole and *n*-butyltriphenylphosphonium bromide) has been investigated by DSC method in the dynamic mode. Processing of experimental DSC thermograms recorded at different heating rates was carried out within the frameworks of isoconvertional analysis in two versions, namely "model-free" method of Friedman and the Ozawa—Flynn—Wall method. The possibility to describe the kinetics of epoxy compositions curing in the frameworks of one-step autocatalytic reaction model has been demonstrated. Obtained kinetic parameters were used to predict the curing kinetics under isothermal conditions and for comparative analysis of the compositions.

Key words: epoxy-anhydride formulation, catalyst, curing kinetics, differential scanning calorimetry (DSC).

Polymer composite materials are widely used due to their outstanding strength-to-weight ratio. By manufacturing the products from polymer composite materials, it is necessary to take into account a number of technological factors, such as cure time, temperature, pressure, *etc*. Deviation from optimal conditions can lead to internal strains, incomplete curing of binders, increased porosity, *etc*. To minimize such defects, to obtain the final material with the best properties, and also to reduce the energy consumption, it is necessary to know the kinetic characteristics of the curing process of the binder. The DSC method is currently most convenient for studying epoxy compositions.[1—8] The curing process of epoxy compositions is usually complex, its mechanism and kinetic regularities can vary significantly depending on both the chemical structure of the components of the system and the external conditions. The effective activation energy for curing under isothermal conditions can vary due to the transition from kinetic to diffusion control. Such systems are difficult to parameterize. At present, the DSC method is widely used to obtain the kinetic parameters of the curing process. The curing of the compositions is most often carried out in a dynamic mode.[1—13]

There are two approaches to study the kinetics of curing, the first one, based on exact knowledge of mechanism and the second, the phenomenological one. The first approach is laborious and involves a detailed investigation of all steps of the curing process, which is not always possible. The phenomenological approach is semiempirical and it is mainly used for the purpose of compositions comparison. The process of curing of epoxy-anhydride compositions with the use of new accelerators, phosphonium salts, was studied earlier.[14] The synthesis method and characteristics are also presented in Ref. 14. It has been shown using the DSC method that the use of synthesized phosphonium salts allows curing at lower temperatures than in the case of widely used accelerator, 2-methylimidazole. A new scheme of the polymerization of epoxy-anhydride system catalyzed by phosphonium salts has been proposed by studying the mechanism of the curing reaction by mass spectrometry. This scheme differs from the mechanism known in the literature for curing of epoxy-anhydride compositions in the presence of imidazoles as catalysts. It has been established[15] that the lifetime of compositions with phosphonium salts is higher than in case of tertiary amines or imidazoles used as the catalysts. It was of interest to study the influence of the accelerator on the kinetics of the compositions curing. In this paper we present the results of determination of the effective kinetics parameters of the curing process for epoxy-anhydride binders in a dynamic mode using various methods of data processing. This information is useful for comparison of the activity of different compositions and for selection of curing modes for epoxy-anhydride systems using various catalysts.

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