



Test method

Comparison of the effectiveness of epoxy cure accelerators using a fluorescent molecular probe



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ABSTRACT

A simple optical method for quantitative comparison of the effectiveness of epoxy cure accelerators, used for speeding up the crosslinking process of epoxy resins with cyclic anhydrides, is described. Fluorescent molecular probes and a miniature fiber optic spectrometer have been applied for measurement of the cure kinetics of a model epoxy resin/anhydride composition in the presence of various cure accelerators. A quantitative index of accelerator performance has been determined for several of the most common accelerators.

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1. Introduction

Epoxy resins constitute a broad class of polymeric materials with a wide range of applications. Their use for coatings, adhesives, laminates, composite materials, electrical insulators and electronic encapsulation materials is the most common. The epoxy resins are usually viscous liquids, which are converted into solid polymeric products either by ionic polymerization using appropriate catalysts or, more often, by polyaddition reaction with various reagents called crosslinkers or hardeners. Various organic compounds, such as multifunctional aliphatic or aromatic amines, oligomeric dithiols, dicarboxylic or multicarboxylic acids and carboxylic acid anhydrides are used as the hardeners for epoxy systems. However, for electrical and electronic applications the epoxies are usually crosslinked with cyclic anhydrides. Phthalic, hexahydrophthalic, methyltetrahydrophthalic, methyl nadic, pyromellitic and benzophenonetetracarboxylic acid anhydrides are used most often. The epoxy resin/anhydride mixtures exhibit low viscosity, long pot life, relatively low reaction heat in

comparison to other chemically crosslinked systems, and also low shrinkage when cured at elevated temperatures. Due to their low exothermicity, the epoxy/anhydride systems are readily adaptable for bulk applications [1].

Anhydride-cured epoxy polymers exhibit much better electrical properties than the systems crosslinked with other types of hardener [2]. Unfortunately, the epoxy resin/anhydride systems require heating at relatively high temperatures for the curing process to take place, which constitutes a problem in most electronic applications. To speed up the curing process or to lower the curing temperature, it is necessary to add a cure accelerator or catalyst to the epoxy formulations. To-date, a number of epoxy cure accelerators have been developed and applied to various epoxy resin/anhydride systems. However, most research has focused on mechanisms of epoxy cure [3–5], and the mechanisms of acceleration of the crosslinking process by particular accelerators [6–8], while the practical aspects, such as quantitative evaluation of the effectiveness of different accelerators or catalysts in particular systems, have usually been neglected. The variety of epoxy resins, variety of hardeners and ever increasing demand for a designer range of properties of the epoxy end-use products make it necessary to match the accelerator performance to particular epoxy compositions, or to optimize accelerating systems, so that a maximal cure rate at lowest possible

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temperature is achieved. For that, a simple effective method for quantitative comparison of the effectiveness of different accelerators in epoxy formulations, not requiring the use of expensive instrumentation, would be handy for industrial applications. In this paper, such a method is proposed and tested based on several example cure accelerators.

To-date, DSC and IR methods have been usually used for study of the epoxy/anhydride systems [9–12]. These methods provide information about cure kinetics of epoxy systems that can be used for comparison of the effectiveness of various epoxy cure accelerators. However, the DSC and IR methods require sophisticated and expensive instrumentation, suitable for large research laboratories, the cost of which is prohibitive for small or medium size companies. Recently, Fluorescence Probe Technology (FPT) has gained considerable interest as a tool for monitoring polymerization processes [13–15], because of its high sensitivity, precision and nondestructive character, while availability of inexpensive miniature fiber optic spectrometers and LEDs emitting in the UV range have made this technique particularly attractive for both industrial and laboratory applications [16–18]. The FPT relies on measurement of changes of fluorescence characteristics of an appropriate fluorescent compound, called a “probe”, with change of physico-chemical properties of the system studied, such as the change of the system polarity or its rigidity in the probe surroundings, called “microviscosity”. The probe is usually added to the system at a concentration of 0.1% by weight, or less [19]. In crosslinking systems, such as the epoxy/hardener compositions, the system polarity changes when reactive functional groups in the monomers react with each other to form a polymer, while the system microviscosity increases when the liquid composition is cured into a solid polymeric product. These changes affect the probe response, which can be measured precisely with a spectrometer. When a changing system containing a fluorescent probe is illuminated with light of the wavelength absorbed by the probe, the probe molecules are excited to their higher energy electronic level. The absorption of a photon is extremely fast (i.e., it occurs in less than 10^{-15} s). Hence, the excited state formed immediately after the absorption act has the same conformation as that before absorption, which usually does not correspond to lowest vibrational and rotational energy level of the electronic excited state. Within the lifetime of the excited states, which usually is of the order of nanoseconds, the excited probe molecules interact with their surroundings which causes their stabilization, and they undergo relaxation to energetically more favored conformations of the excited state. These relaxation processes change the energy gap between the ground and the excited state. Consequently, the characteristics of fluorescence emitted from the excited states depend on the degree of solvation of the excited molecules by their environment and the degree the molecules have been able to relax before the moment of emission, which depend on polarity and microviscosity of the probe surroundings. Consequently, when a reacting system changes, the fluorescent probe responds to these changes by changing its fluorescence characteristics.

Fluorescent molecular probes have been used widely in various biochemical applications [20,21], as well as for monitoring changes occurring in polymeric systems [22]. Their applicability for cure monitoring of epoxy/anhydride systems at elevated temperature have already been demonstrated by several authors [23–25]. However, to-date no attempts have been made to derive from the fluorescence data any concentration-independent parameter that would depend only on the accelerator type (and possibly temperature), and that would characterize quantitatively the accelerator performance in epoxy/anhydride systems. Hence, in this paper we report an application of the FPT method for quantitative determination of relative effectiveness of cure accelerators.

2. Experimental section

2.1. Materials

Epidian 5 (EP5, Organika-Sarzyna) with epoxy value $5,1 \text{ mol kg}^{-1}$ and hexahydrophthalic anhydride (HHPA, Sigma-Aldrich) were selected as a model epoxy resin and an anhydride hardener for this study, while 7-diethylamino-4-methylcoumarin (Coumarin 1, Sigma-Aldrich) was applied as the fluorescent probe. The following compounds were tested as accelerators of the crosslinking process of epoxy resins with the organic anhydride: 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30), triethanolamine (TEA), N,N-dimethylaniline (DMA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), glycerin (Glyc) and tin(II) 2-ethylhexanoate (TIN-2ETH). All of these accelerators were purchased from Sigma Aldrich and were used as received. Their structure is shown in Fig. 1.

Epidian 5 is a classic epoxy resin based on bisphenol A. It is composed of over 80% of bisphenol A diglycidyl ether and minor amounts of higher molecular weight condensation products of bisphenol A with epichlorohydrin. Hence, it is a good model resin to study the performance of curing accelerators. Hexahydrophthalic anhydride is the most often used anhydride hardener for epoxy resins, because of its low melting point and good miscibility in liquid state with the resins, much better than that of phthalic or pyromellitic anhydrides.

The accelerators selected for this study (Fig. 1) are just examples of different types of accelerators reported in literature. DMP-30 is the classic cure accelerator used in industry for epoxy/anhydride systems. DMA is a representative of aromatic amines. Although DMA has not been applied yet as an epoxy cure accelerator, recently its catalytic effect on epoxy/anhydride systems has been documented [26]. DBU is a cycloaliphatic amine used as an effective cure accelerator of the epoxy compositions used for electronic encapsulation materials. Triethanolamine (TEA) was selected because it was suggested that alcohols could co-catalyze the epoxy/anhydride cure in the presence of tertiary amines [27,28]. In TEA, both the alcohol and the amine functionality are within the same molecule. On the other hand, the presence of free hydroxyl groups in an epoxy/anhydride composition is believed to be essential for cure initiation. Therefore, glycerin was selected as the source of both primary and secondary hydroxyl groups to

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