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Evolution of transient states and properties of an epoxy–silica hybrid cured at ambient temperature

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ABSTRACT

An epoxy–silica hybrid was produced from a mixture of an amine-silane functionalized bisphenol-A resin and a siloxane precursor derived from tetraethoxysilane with small amounts of glycidoxypropyltrimethoxysilane coupling agent. The low temperature curing characteristics and final properties of the hybrid system were compared to those of two epoxy controls. Examinations were carried out by differential scanning calorimetry, dynamic mechanical analysis, electron microscopy, thermogravimetric analysis, UV–Vis spectroscopy, SAXS and densitometry. The modulus, strength and ductility were measured in 3-point bending mode at 23 and 50 °C.

The siloxane hybridization of the original epoxy resin was found to increase the glass transition temperature (Tg) of cold cured systems by more than 10 °C and to produce large improvements in mechanical properties. The study has also provided new insights for the events taking place during gelation, vitrification and curing to the equilibrium state.

1. Introduction

Several types of organic–inorganic hybrids (O–I) have been reported in the literature in recent years [1–4]. Epoxy O–I hybrids have evolved from the early pioneering work for the production of unsintered glass coatings by the sol–gel method, which have relied on the incorporation of small amounts of functionalized organic trialkoxysilanes in the silica network as a means of enhancing the film formation characteristics and increasing the ductility of the cured products [5–10]. Extensive studies have been reported on these systems to monitor the reactions and to illustrate the morphology of the final products [11–13]. The main emphasis of these studies has frequently been placed on the effect of environmental conditions and type of catalysts on the chemical structure determined by ^{29}Si NMR and on the nanostructure examined by small angle light scattering methods.

Only a limited amount of information is available on the bulk mechanical properties and there is a lack of knowledge on how these can be related to the nature of the basic components and preparation method. The awareness of the potential and the interest in these materials is growing both in academic research and in the industrial sector. Spirkova et al. [14] have shown that the mechanical properties of epoxy-silica hybrids can be fine-tuned by changing the epoxy/amine ratio and the chemical nature of the amine hardener, making it possible to produce materials with mechanical behaviour ranging from glassy to rubbery at room temperature. Ochi et al. [15] have measured the flexural strength of cured epoxy silica hybrids and have found improvements over the neat resin at high temperatures.

A few reports have been found on the evaluation of epoxy hybrids for use as adhesives. Ochi et al. [16] have exploited the swelling characteristics of the trialkoxysilane coupling agent, γ-glycidoxypropyltrimethoxysilane (GOTMS), for silicone elastomers for the bonding of 'cured' sheets, while May et al. [17] have obtained an increase in

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lap-shear strength of aluminum alloy and mild steel sheets by the *in situ* generation of silica particles and the incorporation of preformed nanoparticles of γ-Al_2O_3 or carbon nanotubes epoxy–silica adhesive system.

The main interest in epoxy–silica hybrids capable of being cured at ambient temperatures lies in the possibility of overcoming the main limitations of conventional cold-cured epoxy resins, which require long curing times, while the Tg of the final products can only achieve values about 10–20 °C higher than the temperature used for curing [18,19]. Moreover, the Tg of 'cold cured' epoxides can decrease to even lower values through the absorption of water via their strong association with OH and NH groups [20,21]. Very recently, it has been shown that cold cured epoxy–silica hybrids, based on silane functionalized epoxy resins, can exhibit a higher Tg than the cured original resin/hardener mixture. The composition could also be adjusted to produce a further increase in Tg through controlled water absorption to hydrolyze the residual alkoxysilane groups, thereby accelerating also the condensation reactions within the siloxane domains [22].

The present work seeks to provide a better understanding of the relative contribution of the components of epoxy–silica hybrids at various stages during curing at ambient temperature, aiming also to achieve enhancements in mechanical properties and higher Tg values through a scheduled control of the preparation and curing conditions. An important feature of the procedure used is the total omission of added water to the siloxane precursor mixture, relying entirely on the absorption of moisture from the atmosphere during mixing operations, processing and open air curing as a means of inducing sufficient hydrolysis to start the condensation reactions according to Scheme 1.

The latter approach has previously been used by Amerio et al. [23] in the preparation of epoxy–silica hybrids cured with a cationic initiator through photoactivation reactions at room temperature, while Ochi et al. [16] have used only 1% water in the formulation for the hydrolysis of the alkoxysilane component.

A combination of low temperature curing conditions and a deficient quantity of water is expected to provide a route for the delaying of condensation reactions between the alkoxysilane components, which allows the epoxy network to be formed first, so as to prevent the growth and large scale segregation of siloxane domains. In this way a continuation of condensation reactions will take place within the confines imposed by the surrounding epoxy network. These will take place at the later stages of curing and during ageing via the absorption of moisture from the environment.

2. Experimental

2.1. Materials and synthesis

The system examined is essentially a two-part formulation. One part consists of a mixture containing a silane-functionalized epoxy resin mixture and an alkoxysilane component based on a fixed combination of tetraethoxysilane (TEOS) and γ-glycidoxypropyltrimethoxysilane (GOTMS). The other part is a cycloaliphatic amine hardener for the epoxy resin. Each formulation was based on a liquid bis-phenol epoxy (DGEBA) with an epoxy equivalent value of 184–190 g, commercially known as Epikote 828 (obtained from Resolution Performance Products). The DGEBA was partially functionalized with bis-(γ-propyltrimethoxysilane) amine (NPTEOS) obtained from Aldrich (purity >90%), using a reaction procedure described elsewhere [24], which takes place according to Scheme 2. This procedure has previously been found to enhance considerably the formation of co-continuous phases by balancing the rate of reactions for the evolution of the epoxy network to the condensation reactions between the alkoxysilane species present on the system.

A model system of the resin for the effect of the tertiary amine groups introduced in the alkoxysilane functionalization was also produced with the same procedure, using an analytical grade of dibutyl amine (supplied by Aldrich). This control system was deemed to be necessary as a means of separating the effect of the tertiary amine groups on the cross-linking of the epoxy resin from that provided by the condensation reactions via the alkoxysilane groups.

TEOS and GOTMS, supplied by Aldrich (purity >97%), were added to the silane-functionalised epoxy resin at molar ratio of 1:0.12 in amounts that would produce a nominal siloxane content in the region of 20 wt% (equivalent to about 13 wt% derived SiO_2). This molar ratio has previously been found to provide the fastest gelation, both in the isolated system and in combination with the host polyimide

Hydrolysis reactions

(a) $$Si(OEt)_4 + n\,H_2O \rightarrow (HO)_nSi(OEt)_{4-n} + n\,EtOH$$

(b) $$\text{Organic*units}[\text{-}Si(OMe)_3]_x + m\,H_2O \rightarrow \text{Organic*units-}[(HO)_m Si(OMe)_{3-m}]_x + m\,MeOH$$

Condensation reactions

i) $$\equiv SiOEt + HOSiO\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + HOEt \quad (\textit{silica})$$

ii) $$\text{Organic*units}[\text{-}Si(OMe)_3]_x + y\,HOSiO\equiv \rightarrow \text{Organic*units}[\text{-}Si(OMe)_{(3-y)}]_x\text{-}O\text{-}Si\equiv + y\,MeOH$$

iii) Statistical co-reactions from steps i) and ii) → (*siloxane*)

*Chain in the silane functionalized epoxy resin and organic segments of silane coupling agent

Scheme 1. Reactions leading to the formation of the siloxane domains.

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