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Influence of cure schedule and stoichiometry on the dynamic mechanical behaviour of tetrafunctional epoxy resins cured with anhydrides

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Epoxy networks based on *N,N,N′,N′*-tetraglycidyl-4,4′-diamino diphenylmethane (TGDDM) prepolymer were prepared with *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA) curing agent at anhydride/epoxy group ratios varying from 0.3 to 1.0. For post-cured mixtures, dynamic mechanical tests show that the glass transition temperature reaches the maximum value at stoichiometric ratios between 0.8 and 0.9. This behaviour has been related to the crosslink density of the formed networks, and also to etherification reactions occurring during cure which lower the amount of anhydride needed in order to complete the curing process. The study of cure cycle variations on the viscoelastic properties showed that for epoxy/anhydride mixtures high post-cure temperatures could be needed to reduce the amount of unreacted epoxy groups after curing. Fourier transform infra-red spectroscopy has been used to analyse the residual epoxy groups and also to study the influence of the different cure reactions on the physical properties of these networks.

(Keywords: epoxy; anhydride; dynamic mechanical behaviour)

INTRODUCTION

Although epoxy resins can be cured with different families of hardeners, most studies performed to date have been devoted to different aspects related to epoxy resins cured with aminic curing agents[1–8]. Nevertheless, despite the fact that anhydride-like hardeners become serious outsiders when choosing a curing agent, not so many papers have been devoted to epoxy/anhydride mixtures[9]. In fact, anhydride-like curing agents are preferred for electrical and electronic applications or when chemical safety has to be taken into account[9,10]. In cured epoxies, the three-dimensional molecular network structure formed—which is a function of the prepolymers and curing agents, and of the stoichiometric ratio used[1–3] and also of the advance of crosslinking[11,12]—determines the glass transition temperature and other physical properties of these materials[13–17]. Indeed, when highly heat-resistant materials are needed, tetrafunctional epoxides are preferred to bifunctional epoxide prepolymers[18].

On the other hand, although the main suppliers of anhydride hardeners suggest to use around 80–90 wt% of the anhydride/epoxy stoichiometric ratio in order to obtain better properties, there are few studies investigating the reasons for using this amount[9,10,19]. In addition, nowadays the influence of post-curing on the glass transition temperature and other physical properties of epoxy mixtures cured with aminic curing agents is well known[3,11,18,20,21].

In the present study, the dynamic mechanical behaviour of a commercial epoxy system based on *N,N,N′,N′*-tetraglycidyl-4,4′-diamino diphenylmethane (TGDDM) cured with tetrahydrophthalic anhydride (THPA) and containing different anhydride/epoxy stoichiometric ratios has been investigated. The variations obtained in the elastic modulus in the rubber region above the glass transition have been used to analyse the crosslink density of the networks. The influence of the cure schedule used on the dynamic mechanical behaviour has also been shown. The study of the variation of epoxy group conversion for mixtures cured with different cure schedules using Fourier transform infra-red spectroscopy (*FT*i.r.), along with analysis of the rubber modulus changes, allow us to correlate the reported physical behaviour to the internal structure of the crosslinked mixtures.

EXPERIMENTAL

A commercial epoxy prepolymer, MY-9512 supplied by Ciba-Geigy, consisting largely of *N,N,N′,N′*-tetraglycidyl-4,4′-diamino diphenylmethane (TGDDM), was cured with *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA), Fluka quality. They were used without further purification. The chemical structures are shown in *Scheme 1*.

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