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A perspective on the inherent oxidation sensitivity of epoxy materials

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Abstract

It is well-known that epoxy materials are not inert to high temperature-induced degradation and therefore have performance limits. This paper shows how thermal aging of epoxy materials can be approached experimentally and offers an overview on the intrinsic oxidation sensitivity of two epoxy thermo-set materials between 25 and 140°C. They are surprisingly reactive and show higher oxidation rates than anticipated, even at moderate temperatures.

Key words: Polymer materials performance, Epoxy thermo-sets, Oxidation behavior

1. Introduction

As organic polymers, epoxy thermo-sets and composite materials will degrade under thermo-oxidative conditions with loss of useful properties in adhesion or mechanical toughness, and this degradation may initiate at the surface. While high temperature empirical data on the depth of degradation profiles have been made available for some materials, precise data on the intrinsic oxidation sensitivity of epoxy materials does not exist. Past studies have mostly relied on empirical evidence such as discoloration, stress embrittlement originating at the surface or modulus changes in a degraded layer of the material [1-4]. Similar trends have been shown for other thermo-set materials [5, 6]. Further, oxidative chemistry will be associated with thermal or radiation exposure [7-9], yet details are challenging to establish if, for example, diffusion limited oxidation (DLO) conditions interfere with bulk property changes. For epoxy coatings it is also known that photo-oxidation under UV is a significant concern which allows coating degradation to be examined in a phenomenological manner [10-12]. At the same time, neither thermal nor photo-oxidative degradation phenomena are well understood, as far as intrinsic oxidation at lower temperatures is concerned. Therefore we are faced with ongoing challenges in regard to lifetime prediction and performance of epoxy materials. Detailed measurements of epoxy oxidation sensitivity, particularly at lower temperatures, have so far not been available. This is due to challenges in measuring accurate oxygen absorption and DLO complications when experiments are not properly conducted.

If one is to understand and predict polymer performance, then knowledge of oxidation sensitivity in the temperature range where the materials will be used is imperative. No matter how we approach polymer performance and our need to understand how polymers change their properties, we have to acknowledge that oxidation sensitivity is the root cause for a change in the chemical make-up of polymers; epoxies will not be an exception. This study attempts to gain a first perspective on the behavior of epoxies at moderate thermal exposure conditions. Exact oxidation rates for epoxies have never been reported. For an introductory examination of epoxy oxidation sensitivity in this study, we decided to select two curatives representative of the two major classes of non-aromatic amines, namely a basic aliphatic amine and a polyether amine. The use of Ancamine 2049, a cycloaliphatic amine, and Jeffamine D230, a polypropylene ether amine, should provide a good perspective on the generic properties of aliphatic amine-cured epoxy systems.

2. Experimental procedure

2.1. Materials

Two epoxy thermo-set materials were prepared by blending a diglycidylether bisphenol A resin (Epon 828) with a cycloaliphatic amine (Ancamine 2049; 2,2'-dimethyl-4,4'-methylenebiscyclohexylamine) and a polypropylene ether amine (Jeffamine D230) in stoichiometric quantities with regards to amine-hydrogen activity at room temperature. The Ancamine 2049 cured system was measured by multi-ramped DSC to have a max. Tg of 150-155°C, while the Epon 828/D230 system has a max Tg of ~95°C. For oxidation rate measurements, thin films of approximately 100μm were prepared to minimize diffusion limited oxidation effects, namely to achieve homogenous oxidation conditions throughout the material thickness during the experiment. From other experiments not reported here and knowledge of O2 diffusivity we verified that non-diffusion limited oxidation (DLO) was valid to at least 125°C with very subtle effects most likely beginning at 140°C.

2.2. Oxygen consumption (uptake) measurements

The consumption of oxygen (i.e. oxidation rate measurement) during thermal aging was determined using a commercial Oxzilla instrument with the experimental approach having been described previously [13-15]. The technique has been established as a routine analysis with the instrumental response calibrated using standard gas mixtures and a pre-determined range setting. As an important requirement, the sample must be sufficiently thin to avoid diffusion-limited oxidation conditions, so that a homogenous oxidation reaction occurs throughout the sample, and the measured rate can be adequately expressed as per total mass of the sample.

3. Results and discussion

As shown in Fig. 1 oxidation rates were measured on a cumulative basis for extended exposure times. This allows for trends in rates to be examined as the material oxidizes. Most polymers oxidize with reasonably steady rates [13, 14, 16-21], whereas some polymers tend to show some decreasing rate with time [22-24]. Between 25 and 110°C steady rates are observed, at 125 and 140°C a delayed decrease in rate with time is noticeable. This is consistent with a significant oxidation level when these rates are integrated even over short time frames. High oxidation levels can result in reduced sensitivity to further oxidation; hence they represent a self-limiting behavior when significant conversion has occurred. For example, many elastomers show significant changes in their mechanical properties when the polymer has experienced about 2 to 3% oxidation [13, 16, 17, 20, 21]. After integration of rates, a cumulative oxidation level trend is obtained, as shown in Fig. 2. Since the rates are steady at nearly all temperatures, linear oxidation increases with time result. It is also apparent that at 125 and 140°C the %-oxidation begins to level off towards a 10 to 20% level. This is consistent with the drop in associated rate and shows the material may have depleted readily oxidizable sites, i.e. the most sensitive chemical structures where oxidative attack can most easily occur.

The oxidation rate data can be easily time-temperature superposed to obtain the relative rate differences or acceleration factors of the oxidation process with temperature [17, 21, 25, 26]. This superposition is shown in Fig. 3, which results in reasonably linear behavior. The shift factors that were used to multiply the individual time data to obtain a superposition on a single time-axis are shown in the legend and are the direct reactivity ratios of oxidation sensitivity. For example, for the first epoxy 110°C has a shift factor of 523, and 50°C a shift factor of 8.11, respectively. This means that the ratio in oxidation reactivity between these two temperatures is approximately 65. The epoxy oxidizes about 65 times faster at 110°C than at 50°C. Any other reactivity comparison can be derived as needed. The shift factors obtained as part of the time-temperature superposition analysis contain the underlying temperature dependence of the oxidation process. Therefore they can be used as relative rate information and plotted in an Arrhenius analysis. This is shown in Fig. 4, where the reactivities have been normalized to represent a shift factor of 1 for the slowest condition, here the rate of the 828/D230 system at 25°C. Excellent Arrhenius behavior is observed with an activation energy of ~75 kJ/mol for the 828/D230, and ~71 kJ/mol for the 828/A2049 system. In comparison with other polymers these activation energies are at the lower end of what has been observed [25]. Of interest is the strong linearity here over a wide temperature range showing that the chemical reaction and associated reaction pathway are very consistent over the temperature range examined. This is not always the case as significant curvature in Arrhenius plots for the oxidation rates of other polymers has been observed [25].

Despite that the 828/D230 epoxy system has a Tg of ~95°C, we note that there is no apparent irregularity in the oxidation rate behavior with temperature. The Arrhenius plot shows excellent linear behavior for both systems. Of course, since the Tg is 150-155°C for the 828/A2049 system, oxidation rates were all measured below Tg. Since the rates were measured on films sufficiently thin to avoid oxygen diffusion effects, we conclude that the oxidation represents an intrinsic chemical property that does not depend on the physics of any molecular rigidity reflective of Tg. It suggests that the chemical oxidation of these epoxy materials can proceed in localized domains where the interaction between oxygen sensitive sites and dissolved oxygen in the polymer matrix is by no means restricted in mobility, both in terms of physical supply of oxygen and the resulting oxidation chemistry. We conclude that oxygen is sufficiently small to diffuse into the material and results in oxidative attack on the epoxy even well below Tg. This interpretation of sufficient oxygen mobility and oxidative attack irrespective of Tg is consistent with a nano-heterogeneous phase description of epoxies. This implies some local variance in rigidity due to alternating aromatic (common epoxy resin) and aliphatic chain segments (common curative) [12] as well as small molecule diffusion in such crosslinked systems [27-29]. Of course to expand this discussion, we can consider molecular phase separation, whereby the epoxy may be macroscopically rigid (i.e. having a high Tg), yet there exist sufficient local molecular mobility variations between the more rigid DGEBA segments and the aliphatic amine segments for oxidation to proceed. In fact, it is quite possible that the majority of the oxidation could occur in the amine section of the cured epoxy network.

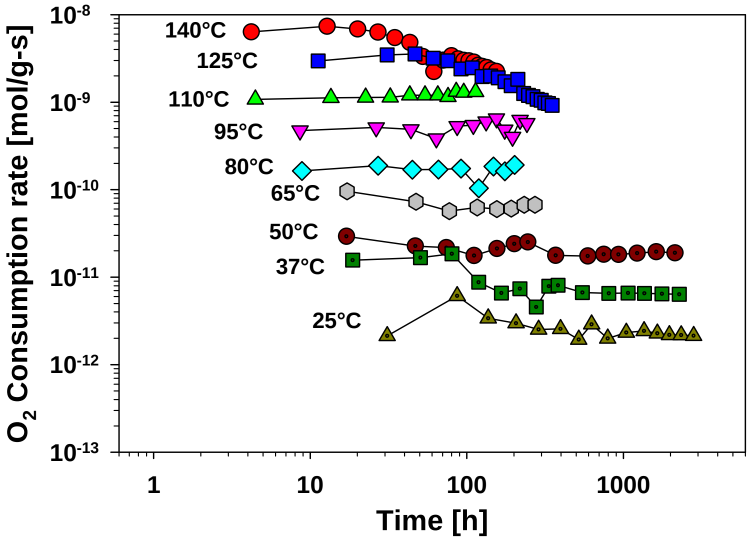

Fig. 1: Consecutive oxidation rates of the Epon828/Ancamine2049 epoxy system.

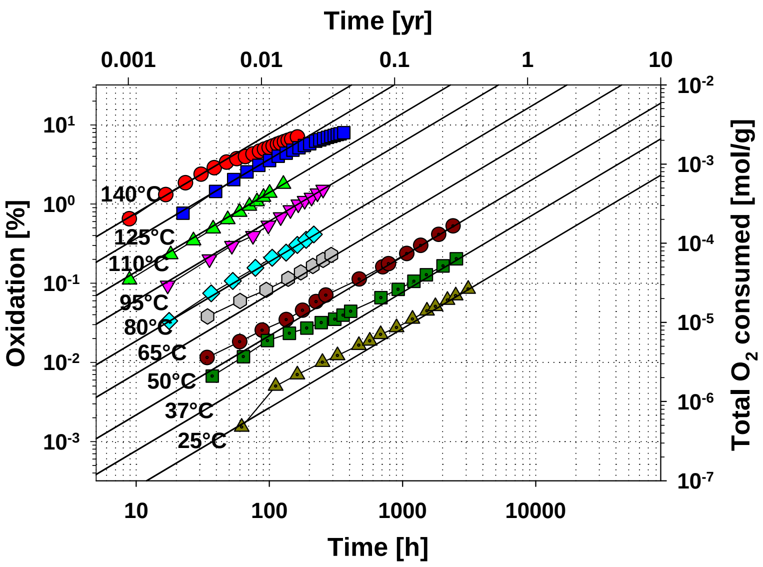

Fig. 2 Cumulative oxidation and projections for the Epon828/Ancamine2049 epoxy system.

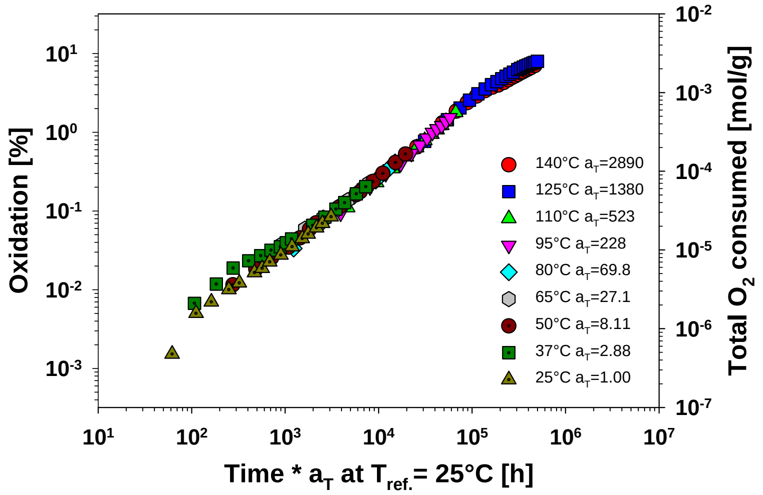

Fig.3 Time-temperature superposition of oxidation for the Epon828/Ancamine2049 epoxy system with the indicated shift factors.

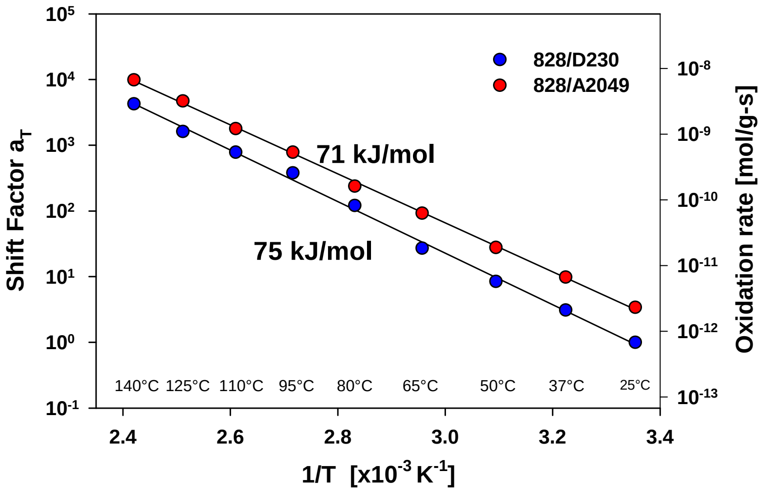

Fig. 4 Arrhenius plot of the superposition shift factors showing a relative oxidation rate comparison of the two epoxy systems and resulting activation energies. Average oxidation rates were obtained by a best fit linearization of oxidation level increases with respect to time at individual temperatures.

4. Conclusions

This study shows for the first time how epoxy materials are sensitive to oxidation as part of an intrinsic thermally-induced degradation process. We demonstrate that oxidation of epoxies can be measured and that oxidation proceeds at rates much faster than we would have anticipated. Interestingly, a cycloaliphatic and polyether amine-cured DGEBA (Epon 828) epoxy showed very similar behavior, suggesting a generic oxidation behavior of amine cured epoxy systems. Further, the intrinsic oxidation sensitivity is a chemical polymer property that was shown not to depend on Tg. Perfect Arrhenius behavior over the temperature range of 25 to 140°C was observed for the two epoxies examined. Activation energies were determined as 71 kJ/mol for the Epon 828/Ancamine 2049 system (Tg ~150-155°C), and 75 kJ/mol for the Epon 828/Jeffamine D230 system (Tg ~95°C), respectively.

We conclude that thermal exposure of epoxies will quickly affect surface properties as part of an oxidation process. This will have consequences for adhesive applications and coatings, yet the exact correlations between degradation chemistry and material physical properties are not known at this point. Thermal oxidation will also affect bulk properties, and composites protected with coatings, which are expected to have some oxygen permeability. Many coatings do not prevent oxygen permeation, unless they are sufficiently reactive on their own and DLO effects then prevent oxidation reactions in deeper layers as part of a protective reactive chemistry barrier.

The data presented here are the first thoroughly documented evidence for intrinsic epoxy oxidation sensitivity over a wide temperature range. This can provide guidance to polymer experts who deal with epoxies and need to consider potential material degradation. Since the rates reported here are significant and it is well known that oxygen diffusion in epoxies is low, we also imply that the oxidation process will be severely diffusion limited and hence proceed in a highly heterogeneous manner, even at moderate or low temperatures. Epoxy oxidation will be dominated by strong oxidation in exterior layers.

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