A perspective on the inherent oxidation sensitivity of epoxy materials

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ABSTRACT

There has long been awareness that epoxy materials are not inert to high temperature-induced degradation and therefore have performance limits. 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 do not yet exist. Two different epoxy material types were chosen: a DGEBA based resin (Epon 828) was cured with either a cycloaliphatic amine (Ancamine 2049) or a polyether amine (Jeffamine D230) for comparison. Due to generally low O_2 permeability in epoxies any oxidation will be limited to the surface; hence experiments were conducted for thin films under non-diffusion limited conditions to obtain unbiased rate data. We have succeeded to show for the first time that oxidation behavior of epoxies at moderate temperatures can be approached experimentally. This study offers an overview on the intrinsic oxidation sensitivity of two cured epoxy thermo-set materials between 25 and 140 °C. Excellent Arrhenius behavior was observed with activation energies in the 70–80 kJ/mol range. These epoxy materials are surprisingly reactive and show higher oxidation rates than anticipated, even at moderate temperatures. In any applications where epoxy materials are used at elevated temperatures under non-inert conditions, oxidation will result in material chemistry changes and this will affect their performance with regard to adhesion or properties in composites.

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1. Introduction

It is well known that epoxies and related composites will degrade when exposed to temperatures above 150 °C, yet past studies have mostly relied on empirical evidence such as discoloration, stress embrittlement originating at the surface coupled with further ingress into the material or modulus changes in a degraded layer [1–4]. Similar trends have been shown for other thermo-set materials [5,6] with a comprehensive overview for durability issues of composites provided by Pochiraju et al. [7]. Composites at high temperatures degrade in a diffusion controlled manner. Once a specific oxidation state at the surface is reached a 'degrading layer' then propagates into the material [8]. This involves two processes, initially regular equilibrium diffusion limited oxidation (DLO) followed by a secondary mechanism where the growing degrading zone depends on cracks creating new surfaces and diffusivity changes throughout the degraded material.

Oxidative chemistry is certainly associated with thermal or radiation exposure [9–11] also at lower temperatures; yet mechanistic details are challenging to establish if, for example, DLO conditions interfere with bulk property changes. In many studies it has been shown that oxidation is a key concern and is clearly associated with failure [12–17], yet the exact oxidation rates for predictive DLO behavior have not been demonstrated. The chemical mechanism of epoxy oxidative degradation is convoluted. Kinetic models have been proposed [18], but the exact degradation chemistry remains the subject of ongoing work [9–11]. IR studies provide some evidence that in thermal degradation of polyamidoamine cured epoxies the methylene carbon next to the nitrogen linkage (i.e. amine addition to the epoxy group) is oxidation sensitive to form amides [9]. Oxidative degradation under radiation exposure involves classical free radical chemistry with carbonyl formation and hydroperoxide involvement [10]. An epoxy cured with polypropylene ether amine with more abundant tertiary carbons was regarded as being more oxidation sensitive (based on IR) then the polyamidoamine system [11]. The methylene linkage between two aromatic rings commonly encountered in epoxy has also

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been considered as being sensitive to oxidation and scission [17,19]. Oxidation of epoxies is associated with limited chain scission [11] and effects on Tg, with oxidation in some cases believed to generate a new secondary phase with increased Tg [17]. Epoxy oxidation has also been shown to increase the elastic indentation modulus and affects the DMA signature in a complex manner [20], is also seen to be associated with shrinkage [16] and leads to more brittle fracture sensitivity [21]. Oxidized surfaces generally result in crack initiation [7,21]. There is some evidence that antioxidants in epoxies may not prevent oxidation, but it is unclear how surface oxidative versus bulk inert conditions were considered [22].

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 [23–25]. At the same time, neither thermal nor photo-oxidative degradation phenomena are well understood, as far as intrinsic thermally driven oxidation behavior 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.

Over the last 20 years we have successfully applied oxidation rate (i.e. oxygen consumption or ox-uptake) measurements to a range of polymers [26–28]. For many polymers an oxidation process is the underlying long-term degradation process that results in a change in the chemical make-up of the material. This in turn is coupled with changes in molecular weight and in the macroscopic properties of modulus, elasticity or other mechanical performance parameters [29]. If one is to understand and predict polymer performance then knowledge of intrinsic oxidation sensitivity in the temperature range where the materials will be used is imperative. Oxidation rates can often be measured over a large temperature range, allowing rate behaviors to be established and conversion or oxidation levels to be predicted with time. Such studies have also shown that oxidation of polymers does not always follow linear Arrhenius behavior as curvature in the Arrhenius plots of rates has often been observed [30]. This has implications for lifetime prediction models.

It is clear that polymer performance, wherever oxygen is present, is fundamentally dependent on the oxidation behavior of the material. Thermally driven oxidation is an integral part of polymer degradation, even if in some cases the oxidation sensitivity can be amplified by additional exposure conditions, such as UV or other radiation sources. In general, thermo-oxidative degradation of polymers and performance predictions are complicated by polymer physics, namely oxygen diffusion processes, since oxidation of a polymer often will not proceed in a homogenous manner. Further, the biggest problem in accelerated aging, which is meant to help us predict polymer performance, is the heterogeneity of the oxidation process [31,32]. This has resulted in misinterpretation of aging data and often overly optimistic qualification properties. When oxidation rates are very high, i.e. during exposure of polymers to high temperature or intense irradiation, oxidation will proceed only in a thin surface layer and the bulk of the material remains non-oxidized. This is in contrast with more mundane environments where polymers will oxidize more homogeneously and bulk properties will change in greater depth with time. It is clear that based on DLO a complete disconnection between the slow oxidative aging of a material and accelerated aging studies can exist. This dilemma is often difficult to resolve, particularly when oxidation rates are not known. Therefore, knowing oxidation rates is an integral part of better predictive capabilities [30].

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 mixing ratios were 1:0.317 (Epon 828 to Ancamine 2049) and 1:0.608 (Epon 828 to Jeffamine D230), respectively. The Ancamine 2049 system cure was facilitated by the addition of 0.25% 1-methyl imidazole as a catalyst. Both systems were initially cured at RT for 1 to 3 days and then further post-cured for 1 h at 125 °C to yield a higher glass transition temperature and cure conversion. This cure process minimized thermo-oxidative damage during cure and also allowed casting of thin epoxy films on a release polymer (PVF) placed on a flat solid laboratory bench top surface. 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 100 μm 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 O_2 diffusivity we verified that non-diffusion limited oxidation behavior for the chosen films 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 [26,33–35]. The technique has been established as a routine analysis with the instrumental response being calibrated using standard gas mixtures under specific range setting. Total oxygen loss in a sample and the resulting rates can also be compared against other materials with known oxidation rates [33]. Known amounts of samples (∼0.1 g at the highest and 1 g at the lowest temperature) were sealed at room temperature in ampoules of ∼21 cc volume and filled with air from a gas cylinder to provide consistent composition. In order to maintain air conditions of equal partial pressure at the elevated temperatures the samples were quickly vented when hot; hence aging was always conducted at 630 mm-Hg air pressure (ambient conditions in Albuquerque with $pO_2 = \sim130$ mm-Hg) independent of temperature. The containers were then aged for periods of times which led to an oxygen consumption of between ∼0.03% of the oxygen available in the closed ampoule (0.001 cc STP O_2 absolute) at a high sensitivity setting, i.e. the lowest rate for short oxidation times, and ∼11% of available oxygen (0.5 cc STP O_2 absolute) for high oxidation rates and/or