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Characterization of thermally reworkable thermosets: materials for environmentally friendly processing and reuse

Jir-Shyr Chen[a], Christopher K. Ober[a,*], Mark D. Poliks[b]

[a]Department of Materials Science and Engineering, Cornell University, Bard Hall, Ithaca, NY 14850, USA
[b]IBM Microelectronics, Endicott, NY 13760, USA

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Abstract

In recent years, several research groups have created reworkable thermoset systems. A prominent use of such materials is in microelectronics packaging areas to enable the repair or reprocessing of electronic components. A wider implication of such an application is that it may facilitate the future recycling or reuse of older computer systems. Recent studies indicate millions of computers are discarded each year due to obsolescence or other factors. The research presented here involves studies of thermosets incorporating a cycloaliphatic epoxy monomer that contains a tertiary ester linkage. When part of a fully crosslinked network, the reworkable epoxy unit will disconnect the network under predetermined thermal conditions. We studied the chemical and thermo-mechanical breakdown mechanisms of the monomer and resulting polymer networks as a function of their rework conditions. Via analytical chemistry techniques, the materials were found to degrade in a controlled fashion consistent with prior polyester degradation studies. Monitoring the change in glass transition temperature of the materials under rework conditions yielded both kinetic and mechanistic data of the degradation process, as well as providing insight into the materials' mechanical strength. © 2001 Published by Elsevier Science Ltd.

Keywords: Reworkable thermosets; Polymer network degradation; Ester degradation

1. Introduction

Epoxy resins have been in use for decades and are widely employed as adhesives, coatings, underfills, and encapsulants. As a sign of their technological importance, the microelectronics industry has used these resins as the basis of a number of packaging materials in the production of electronic devices [1]. Many applications make use of an epoxy adhesive to enhance the mechanical and thermal resilience of components in a circuit board. Epoxy resins are used because the uncured epoxy resins flow easily into complex shapes, but once fully cured the highly crosslinked three-dimensional networks have superior adhesive and thermomechanical properties. The resulting networks permanently affix the components; and while the intractability of these materials is desirable from a reliability aspect, it is undesirable from a reworkability or recyclability point of view.

The network structure of a typical epoxy resin means that neither solvent nor heat can be used to easily remove these materials. For a material to be successfully reworkable, it must have initial properties similar to or exceeding those of conventional materials, but must also be removable under controlled conditions. For example, if just one processor among several in a processed electronic device was to be defective, the entire circuit board must be discarded due to the inability to remove and replace the errant processor. In this and other circumstances, an adhesive that could be circumstantially removed would be ideal. It is estimated that 95% of a computer system's parts can be reused or recycled [2]. Based on a recent study released by the National Safety Council, approximately 20.6 million personal computers became obsolete in 1998. With faster microprocessors being introduced at an increasing rate, the number of computers discarded per year could increase dramatically. The availability of a reworkable material, that is, one that undergoes controlled network breakdown, expands the potential routes to repairing, replacing, or removing assembled structures and devices. Implementing reworkable materials early could ease recycling issues that may develop later.

To address these issues, several research groups have created reworkable materials with most incorporating cleavable linkages into their monomers [3–15]. Tesoro et al. [8,10,11] utilized disulfide-containing crosslinking agents. The disulfide links could be cleaved via chemical

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* Corresponding author. Tel.: +1-607-255-8417; fax: +1-607-255-6575.
E-mail address: cober@ccmr.cornell.edu (C.K. Ober).

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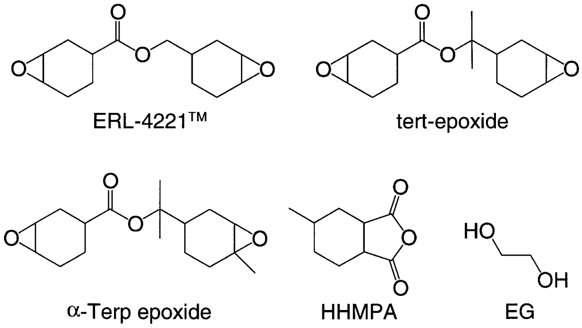


Fig. 1. Chemical structures of the compounds used.

reduction, thereby breaking down the formed network. Buchwalter et al. [3–5] created epoxy monomers incorporating chemically cleavable acetal and ketal links into their monomers. The resulting thermoset networks could be degraded by applying acid-containing solvent mixtures. A third class of reworkable material relies on heat to degrade the networks. This has the advantage that it should be easier to localize the rework process, thereby allowing for more precise control over what will be reworked and what will not. Yang et al. [15] synthesized a series of epoxy monomers containing thermally labile secondary and tertiary ester groups. This design leads to thermoset networks that fall apart in a controlled manner at temperatures ranging from 200 up to 300°C. Wang et al. [13,14] also created a series of thermally reworkable epoxy thermosets by introducing carbamate groups into their epoxies, resulting in networks that undergo thermal cleavage in the 200–300°C range. However, the changes that occur to the epoxy network during the rework process is presently poorly understood.

The research reported here involves study of an epoxy monomer that is suitable for curing as a thermally reworkable thermoset or composite matrix. The specific monomer studied is a cycloaliphatic epoxy derived from the esterification of cyclohexenoic acid with α-terpineol with subsequent epoxidation. Consequently, the epoxy monomer has been dubbed the α-Terp epoxy monomer. The tertiary ester linkage in the monomer enables thermal reworkability. Therefore when part of a fully crosslinked network, the reworkable epoxy monomer permits the formed network to break apart under predetermined thermal conditions. Based on prior studies of polyester degradation [16], it is expected that the tertiary ester linkage will cleave at modestly high temperatures. The focus of the current study is to understand the breakdown mechanism of the α-Terp monomer and the changing polymer network constructed from it. The knowledge gained will enable creation of improved reworkable materials, as well as aid in the formulation and processing of existing materials.

The concept of a reworkable thermoset is still quite new; thus there are few established methods available to characterize its more important property — the ability to breakdown under controlled conditions. In our work, experiments based on chemical and thermal analysis techniques were used to elucidate the reworkable nature of the materials. By using gel permeation chromatography (GPC), Fourier-transform infrared (FT-IR) spectroscopy, and ^{13}C nuclear magnetic resonance analyses, the chemical breakdown mechanism of the monomer and network system was deduced. Also, it was found that the most useful technique for directly evaluating a reworkable thermoset's network formation and breakdown is by following its glass transition temperature. Fracture toughness tests were also conducted to demonstrate the reworkable thermoset's ability to breakdown in a controlled manner.

2. Experimental

2.1. Materials

The chemical structures of most of the compounds used in this study are detailed in Fig. 1. The original synthesis of the α-Terp epoxy monomer and the *tert*-epoxy monomer has been published elsewhere [15]. The α-Terp epoxy monomer used in this study was donated by Loctite Corporation and was used as received. Hexahydro-4-methylphthalic anhydride (HHMPA), ethylene glycol (EG), and *N*,*N*-dimethylbenzylamine (BDMA) were used as received from Aldrich. ERL-4221™, a cycloaliphatic diepoxide monomer originally made by Union Carbide, was used as a reference material for some of the experiments because of its structural similarities to the α-Terp monomer, its non-reworkability, and because it has been implemented as a first-generation packaging material. Samples of the ERL-4221™ were donated by IBM Corporation and used as received. To clarify terminologies used below, *resin* describes the NEAT epoxy monomer, and *system* describes a mixture of the monomer and all cross-linking agents involved — including hardener, initiator, catalyst, and any other added components.

2.2. Curing conditions

The epoxy monomers were crosslinked using HHMPA as a curing agent, EG as an initiator, and BDMA as a catalyst. The order in which samples were mixed is as follows: the curing agent was added to the monomer, followed by the addition of the initiator, and lastly the addition of the catalyst. The catalyst was added last to minimize the advancement of the uncured samples at room temperature. A molar ratio of epoxide groups to HHMPA of 1.00:0.87 was used for all systems. The amount of initiator and catalyst used was 1.5% by weight of each compound. The mixed samples were subsequently degassed for a few minutes under vacuum at room temperature to remove any trapped air bubbles. Samples that were not used immediately were stored at −40°C for later use. To crosslink the samples, the mixtures were first poured into either an aluminum mold or a silicone–rubber mold, then pre-cured in an oven at 110°C for 1 h, followed by a final cure at 140°C for 6 h. The samples were then allowed to cool to room temperature at a rate of approximately 1–2°C/min.

2.3. Thermal degradation/rework conditions

The terminology 'rework condition' used in this paper refers to the amount of thermal treatment a fully crosslinked epoxy sample received. The primary variables were the isothermal time and temperature to which the system was exposed. A large concern when treating samples isothermally is the rate at which the samples reach the desired temperatures and the control and uniformity of the temperatures surrounding the samples. To overcome this, a home-built oven was used. Using this oven for temperatures up to 250°C, the samples reached the desired isothermal temperatures within 30 s of inserting the samples. Also, once the isothermal temperature was reached, the temperature fluctuation was approximately ±0.7°C. All thermal treatments were conducted under an air atmosphere.

2.4. Characterization

GPC was conducted using a Waters 150-C ALC/GPC using tetrahydrofuran (THF) as the solvent. The columns used in the GPC were Styragel™ HR 0.5, 1, 2, and 4 sized columns. The samples were prepared by creating solutions of the desired compound at a concentration of 100 mg per 25 ml of THF. Polystyrene was used as a calibration standard, however due to the small size of the compounds analyzed, the data obtained was used qualitatively, only.

FT-IR analyses were done on a Perkin Elmer 1720-X Infrared Fourier Transform Spectrometer and a Mattson 2020 Galaxy Series FT-IR spectrometer. Samples containing just the α-Terp monomer were created by solvent casting onto potassium bromide salt crystals using methyl ethyl ketone as the solvent. Samples involving the cured α-Terp network were prepared by curing the α-Terp system between two pieces of double-polished silicon wafer [15]. Double-polished silicon wafers are transparent to infrared radiation, thus the samples could be easily mounted onto a hot stage to allow for FT-IR measurements at high temperatures. ^{13}C NMR analyses were done on a Bruker AM-360 and a Varian VXR-400S. All NMR samples were prepared by dissolution in deuterated chloroform with a TMS reference. For samples that did not dissolve in deuterated chloroform, the samples were allowed to swell in the solvent for two days prior to testing.

Thermal analyses were conducted using a TA Instruments DSC 910. All samples were placed in hermetically sealed aluminum DSC pans and heated at a rate of 20°C/min under nitrogen. To determine the glass transition temperature (T_g) from the DSC data, the computer-calculated transition-point temperature was averaged with the temperature at which the maximum in the first-order derivative with respect to temperature was detected.

Fracture toughness tests were done utilizing a double-torsion sample configuration. The overall sample dimensions were 2.3 cm × 2.3 cm × 0.4 cm. The crosshead speed of the MTS material testing system was 0.064 cm/min and the width of the pusher tip was 0.25 cm. The distance between the parallel supports was 1.8 cm. All experiments were conducted at room temperature.

3. Results and discussions

3.1. Monomer decomposition

The thermal degradation process of polyesters is well documented in the literature [16]. However, the α-Terp epoxy monomer is unique in that it is designed to cleave through its tertiary ester bond when exposed to high temperatures, thus the primary purpose of studying the thermal degradation mechanism involved in cured α-Terp systems is to confirm the mechanism as well as establish a generic procedure for studying reworkable thermosets.

To prepare samples for each of the analyses, individual samples of the α-Terp monomer were thermally treated at 230°C for various lengths of time. The isothermal times ranged from 0 to 30 min, with 0 min being the untreated, as-received material. The spectroscopic data for GPC, ^{13}C NMR, and FT-IR analyses are shown in Figs. 2–4, respectively. In each figure, only the isothermal data sets taken at 0-, 8-, 10-, 12-, and 14-min are shown to highlight the pertinent findings.

The as-received monomer and all thermally reworked monomer samples were completely soluble in THF. The GPC trace of the non-reworked α-Terp resin showed it to have a single peak at 130 g/mol. Comparing relative intensities of the peaks in Fig. 2, it is readily evident that under the thermal conditions applied, the α-Terp monomer cleaved into smaller fragments with maximum peak intensities at 100 g/mol. As the isothermal time was slowly increased, the intensity of the unreacted monomer peak decreased relative to the decomposed fraction's peak. The additional peaks seen at the larger molecular weights were most likely due to side-reactions, such as self-polymerization

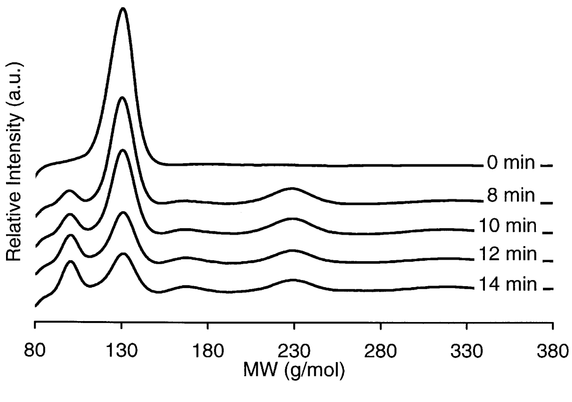


Fig. 2. GPC traces of the α-Terp monomer heat-treated at 230°C for 0, 8, 10, 12, and 14 min.

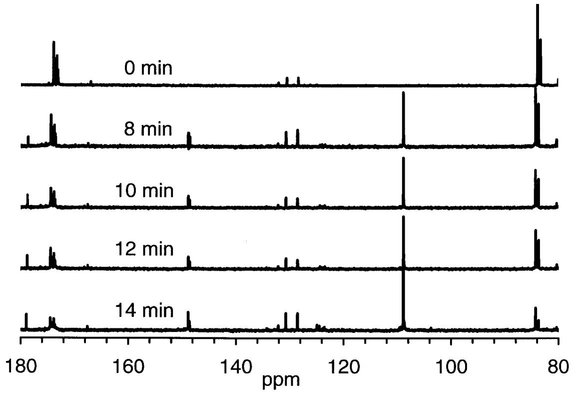


Fig. 3. ^{13}C NMR spectra of the α-Terp monomer heat-treated at 230°C for 0, 8, 10, 12, and 14 min.

at the elevated temperatures. It must be re-emphasized that the small hydrodynamic volume of materials tested permit only comparative analysis.

The original monomer and all thermally reworked monomer samples were also completely soluble in deuterated chloroform, thus facilitating the NMR analyses. Based on the GPC results, cleavage of the α-Terp monomer was expected at the rework conditions used. Therefore, assuming the degradation mechanism was consistent with ester degradation, the key peaks to examine in ^{13}C NMR would be those associated with, or near, the tertiary ester. In the 0-min trace in Fig. 3, the primary peaks of interest corresponded to the tertiary carbon atom adjacent to the ester linkage (84 ppm) and the carbonyl group (174 ppm). As the sample was thermally treated, both peaks were seen to decrease in relative intensity, thereby indicating that there was a chemical change occurring near those carbon atoms. Also, several new peaks appeared, in particular those located at 109, 149, and 179 ppm. The peaks at 109 and 149 ppm correspond to alkene moieties, and the peak at 179 ppm corresponds to an acid anhydride moiety. Whereas the relative intensities of the peaks at 84 and 174 ppm decreased with increasing isothermal treatment, the relative intensities of the peaks at 109, 149, and 179 ppm increased with increasing isothermal time. Based on this observation, it was evident that the tertiary ester linkage was cleaving to form other components, namely alkenes and anhydrides. Although there were impurities in the system as evidenced by peaks centered around 130 ppm, their presence did not over complicate the interpretation of the results.

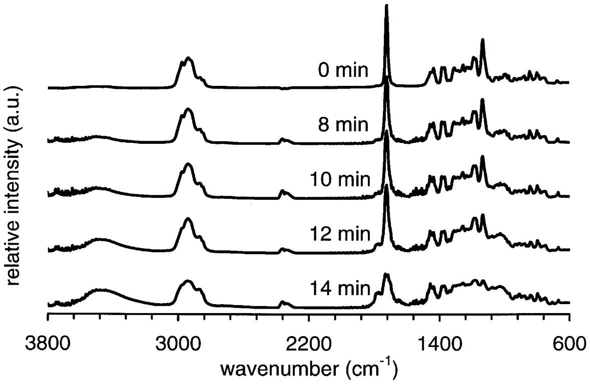
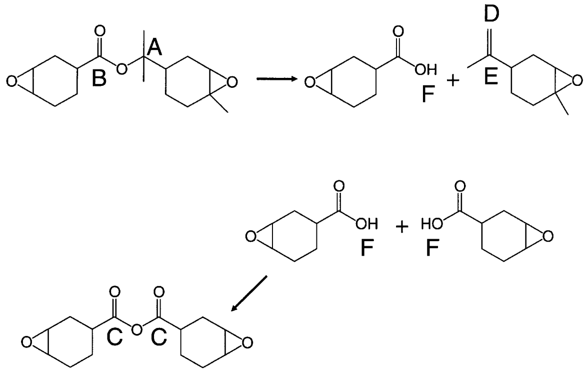


Fig. 4. FT-IR spectra of the α-Terp monomer heat-treated at 230°C for 0, 8, 10, 12, and 14 min.



Scheme 1.

FT-IR analyses yielded similar findings to that of ^{13}C NMR. As seen in Fig. 4, the absorbance of the carbonyl peak (1724 cm^{-1}) in the FT-IR trace decreased in intensity as the α-Terp monomer was thermally treated. At the same time, the formation of an acid anhydride shoulder (1770 cm^{-1}) and a broad hydroxyl peak (3450 cm^{-1}) developed. The appearance of a weak peak around 908 cm^{-1} could be indicative of alkene formation. During the thermal treatment, peaks also evolved at 1018, 1130, and 2350 cm^{-1}. The peak at 2350 cm^{-1} was most likely due to absorption from carbon dioxide in air; however, assignments to the peaks at 1018 and 1130 cm^{-1} cannot be determined at this time.

The NMR and FT-IR data again suggest that the α-Terp monomer does degrade in a manner entirely consistent with that known for tertiary esters. A general decomposition mechanism of the α-Terp monomer (as it is reworked) is shown in Scheme 1, and a corresponding summary of the spectroscopic data is listed in Table 1. When isothermally treated at high temperatures (e.g. 230°C), the α-Terp monomer first cleaves at its tertiary ester linkage to rearrange and form alkene and carboxylic acid moieties. At the elevated temperatures, some of the carboxylic acid groups further react to form acid anhydrides.

Table 1
Location of the key peaks in the FT-IR and ^{13}C NMR analyses

Atom letter	^{13}C (ppm)	FT-IR (cm^{-1})
A	84	–
B	174	1724
C	179	1770–1790, 1870
D	109	908
E	149	908
F	–	3450

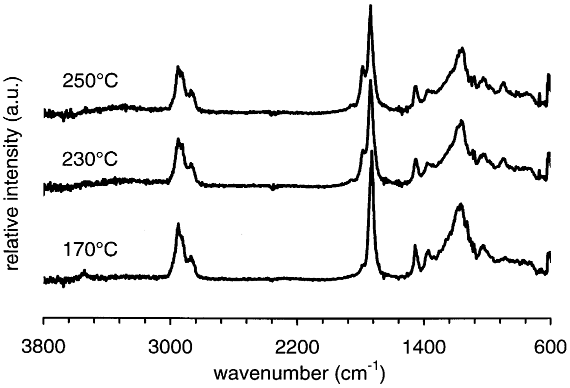


Fig. 5. FT-IR spectra of the α-Terp network heat-treated from 30 to 250°C at 5°C/min.

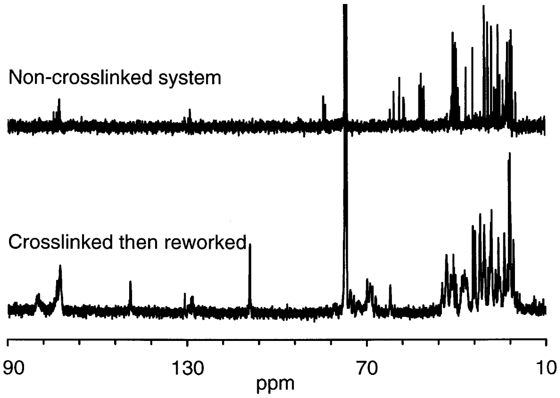


Fig. 6. ^{13}C NMR spectra of a non-crosslinked α-Terp system and a crosslinked then reworked α-Terp system.

3.2. Network decomposition: chemistry

Section 3.1 showed that the α-Terp monomer cleaved as expected; however, the more important issue is whether the network formed from the monomer will also break down to permit rework. A set of experiments similar to those used for probing the monomer breakdown was used to examine the network decomposition mechanisms. As with the α-Terp monomer, the α-Terp network was expected to break down in a manner consistent with tertiary ester degradation.

The results of the FT-IR analyses of the α-Terp network breakdown are shown in Fig. 5. The samples were isothermally treated under slightly different conditions than that of the α-Terp monomer decomposition study, because not all of the reworked network samples were soluble in organic solvents to allow for solvent casting. The FT-IR samples were prepared by first fully curing the α-Terp system between two pieces of double-polished silicon wafer and then allowed to cool to room temperature. The samples were then heated from room temperature to 250°C at a rate of 5°C/min. The data in Fig. 5 shows FT-IR traces at selected temperatures to highlight the relevant information. At 170°C, the α-Terp network showed slight signs of degradation, with the formation of absorbance shoulders at 1790 and 1870 cm^{-1}, a peak at 3550, and at 908 cm^{-1}. These peaks correspond to an anhydride group, a hydroxyl group, and an alkene group, respectively. As the temperature was increased, the absorbance signals at 1790, 1870, and 908 cm^{-1} became more pronounced, whereas the signal at 3550 cm^{-1} seemed to have disappeared. This would indicate that at the lower degradation temperatures, the conversion of carboxylic acid groups to anhydride groups is slow enough to allow for the detection of both moieties. However, at higher temperatures, the formation of any carboxylic acid groups is quickly followed by a reaction to form anhydrides. The alkene groups that were evolved did not seem to react to any appreciable extent at these temperatures as witnessed in the FT-IR traces.

The partially reworked α-Terp network did not completely dissolve in deuterated chloroform, but the fully reworked α-Terp network did. So for the ease of experimental analysis, only the uncured α-Terp system and the fully reworked α-Terp network were tested using ^{13}C NMR. The resulting spectra are shown in Fig. 6. The trends noticed originally in the α-Terp monomer ^{13}C NMR decomposition study were also evident in the analysis of the α-Terp network, namely the evolution of peaks at 109, 149, and 179 ppm corresponding to alkene and anhydride moieties. Also, the peak corresponding to the tertiary carbon atom adjacent to the tertiary ester linkage at 84 ppm completely disappeared. Therefore chemically, the α-Terp system behaves and reworks as expected. When incorporated into a fully crosslinked network, the α-Terp epoxies' tertiary ester linkages cleave into alkene and carboxylic acid moieties, thereby breaking apart the network.

3.3. Network decomposition: kinetics

Characterization techniques abound for the study of conventional epoxy materials. There are experiments available for examining virtually every aspect of an epoxy thermoset, describing the materials before and after they are crosslinked, how they crosslink, and to what extent the material has crosslinked. However, with the new breed of reworkable thermosets, there is no simple test for determining how well a material reworks. Prior work carried out by several groups [13,15] has made use of thermal gravimetric analysis (TGA) to gain insight into a material's reworkability, and it has been shown to be effective as a first-pass tool for evaluating different reworkable thermosets.

Generally, a material that is more thermally stable (i.e. requires a higher rework temperature) will tend to begin degrading at a higher temperature in the TGA than a material that is less stable. The TGA has been shown to be effective for determining important values such as the activation energy associated with a material's degradation. However, the experimental basis of TGA is that it derives its data by measuring the weight loss of a material at high temperatures. Thus, the network needs to be degraded to such an extent that it becomes volatilized, or loses weight, in the TGA. Any reworkable thermoset whose network is partially disconnected but has not yet become volatilized will appear to have the same network properties as a non-reworked material at the temperatures tested in a TGA.

In essence, to study the reworkability of a thermoset is to study the extent to which the thermally cleavable links break apart. This, in turn, should be analogous to measuring the decrease in the material's effective crosslink density. As the thermally labile groups in the reworkable network cleave, the effective distance between crosslinks increases. Therefore, the tools used to evaluate the crosslink density of a material should also be a good metric for evaluating its reworkability.

Typical approaches employed to determine a thermoset's crosslink density include the use of swelling experiments and dynamic mechanical analyses (DMA), while the latter is a more common method. As described in the theory of rubber elasticity [17,18], an effective crosslink density may be directly calculated from knowledge of a system's modulus in its rubbery region (i.e. $T \gg T_g$). The inherent downside of such a technique is the need for large quantities of material per sample and the potential errors associated with experimental measuring techniques (e.g. small errors in sample dimension measurements yield large errors in the measured modulus value). Also, not all materials are amenable to being tested in a DMA. It has been reported that some reworkable materials begin to decompose at temperatures just above their glass transition temperature, thereby rendering the system too compliant for testing at the temperatures needed for measuring the rubbery plateau modulus [15].

Swelling techniques are used less frequently for determining crosslink densities of thermosets because of the highly crosslinked nature of the material. Generally, swelling methods have proven effective when measuring elastomeric materials [18,19]. Limited success has been reported with epoxy materials; however, it has been shown to yield quantitative results [20,21].

The approach used in this study was to follow the change in the reworkable thermoset's glass transition temperature (T_g) as a function of its rework conditions, i.e. isothermal time and temperature conditions. It is known that there is a relationship between a thermoset's glass transition temperature and its crosslink density. For example, it is possible to monitor curing of a thermoset by assessing its T_g [22]. As the crosslinks are forming, the T_g will increase due to the decreased mobility of the network. Several equations have been developed that relate the molecular weight between crosslinks, M_c, to the glass transition temperature of a thermoset [18]. Although most equations are empirically based, some are derived from theoretical considerations [23]. In all cases, the T_g varies inversely with M_c and linearly with the crosslink density. Based on these concepts, we have devised a simple method for studying network breakdown in reworkable thermosets. As the reworkable systems are isothermally treated at elevated temperatures, the effective crosslink density decreases as the tertiary ester linkages cleave, leading to a decrease in the system's glass transition temperature. Accordingly, this experimental method will be referred to as the T_g-shift characterization technique in subsequent sections of this paper.

The primary advantage of using either DMA or swelling methods is that they offer the ability to obtain quantitative crosslink density values. Also, it is yet to be resolved whether or not the glass transition temperature of a thermoset can be used as a quantitative measure of the crosslink density. However, the T_g-shift technique does have its advantages. Because one may easily use a DSC to determine the glass transition temperature of samples, very little material is needed to determine the systems' rework characteristics. Also, in contrast to using a TGA where only the non-volatilized components are measured, the DSC tends to reveal information regarding the overall network behavior of the material. Additionally, errors associated with sample preparation may be greatly reduced, thereby avoiding potential errors as with the DMA.

Our reworkable materials are based on a thermally activated breakdown. Therefore, it would stand to reason that the cleavage of the tertiary ester linkages would proceed via a simple kinetic model, i.e. $\mathrm{d}C/\mathrm{d}t = -kC$, where C is the concentration of non-cleaved tertiary ester linkages, and k is a rate constant related to the degradation reaction(s). Integration yields $C(t)/C_0 = \mathrm{e}^{-kt}$, where C_0 is the initial concentration of tertiary ester linkages. As a first approximation, we assume the increase in molecular weight between crosslinks varies linearly with increasing cleavage of tertiary ester linkages. Also, we assume the glass transition temperature does indeed vary linearly with the crosslink density. Subsequently, the glass transition temperature should also vary in a manner analogous to the cleavage of tertiary ester linkages, i.e.

$$T_g = A\mathrm{e}^{-kt} + B \tag{1}$$

where A is a pre-exponential factor and B is introduced because the glass transition temperature should always be a finite number greater than zero. This means that as our material systems are reworked, the glass transition temperature should vary with isothermal treatment time in a manner as described by Eq. (1).

Fig. 7 shows the T_g-shift data of samples that were prepared by exposing a fully cured α-Terp system to a series of isothermal heating times and temperatures. The symbols represent experimental data points (T_g) obtained from DSC measurements, and the solid lines represent mathematical fits for each of the isothermal temperatures used. The mathematical fits are of the form

$$T_g = C\mathrm{e}^{-k_1 t} + D\mathrm{e}^{-k_2 t} + E \tag{2}$$

where C and D are pre-exponential factors, t is the time in minutes, k_1 and k_2 are the respective rate constants, and E is analogous to B in Eq. (1). The excellent correlation between

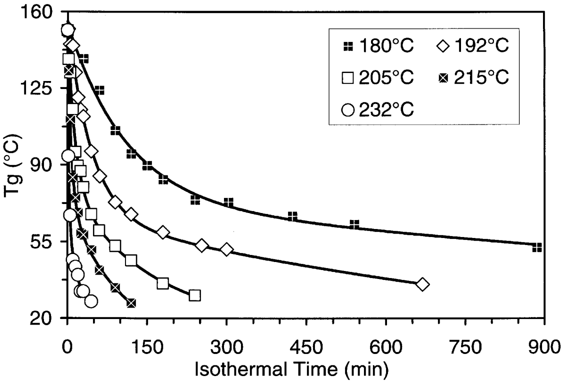


Fig. 7. T_g-shift results of a cured α-Terp network heat-treated under various isothermal conditions.

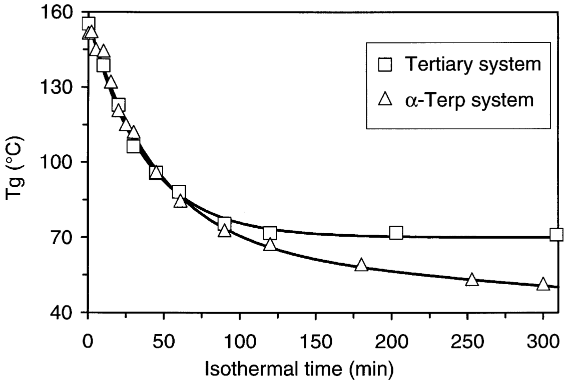
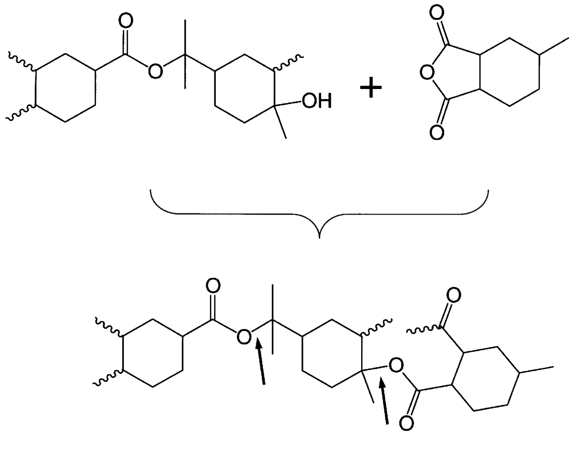


Fig. 8. T_g-shift results of a cured α-Terp network and a cured *tert*-epoxy system heat-treated isothermally at 193°C.

the experimental data and the superposition of two exponential decay functions is strong evidence that there are two unique decomposition events occurring. If the network degradation was based on a single thermal event, that is only the cleavage of the tertiary ester group contained within the α-Terp resin, one would expect a single exponential decay function similar to Eq. (1). However, a closer inspection of the crosslinking mechanism reveals a second bond cleavage site. As seen in Scheme 2 (depiction of the formation of additional tertiary ester linkages due to the curing chemistry), two distinct types of tertiary ester linkages exist in the α-Terp network due to the crosslinking chemistry of this particular system. The reaction of the acid anhydride hardener with the α-Terp monomer created an additional tertiary ester bond near the methyl-substituted epoxy group such that for each α-Terp monomer reacted, two tertiary ester linkages are introduced into the final cured network [15]. For clarification purposes, items associated with the tertiary ester group inherent to the monomer will be known as primary items, whereas items related to the tertiary ester group introduced via the crosslinking reaction will be known as secondary items.

In order to elucidate the effects of the second tertiary ester linkage, a specifically synthesized version of the α-Terp monomer lacking a methyl-substituted epoxy group was examined using T_g-shift experiments. The new monomer is simply dubbed the tertiary or *tert*-epoxide monomer. As seen in Fig. 1, the *tert*-epoxide monomer does not have the additional methyl group adjacent to the epoxide function, therefore when this monomer is crosslinked with HHMPA, it should not form additional tertiary ester linkages. The results of the T_g-shift experiment are shown in Fig. 8. In contrast to the mathematical fit for the α-Terp system, the fit for the *tert*-epoxy system is a single, first-order exponential decay function, i.e. $k_2 = 0$. This is as expected for a system with a single decomposition site per monomer. Thus, it is apparent that the additional tertiary ester linkage does directly affect the rework characteristics of the α-Terp system and that these effects are reflected in the T_g-shift behavior.



Scheme 2.

As already noted in Fig. 7, the reworkable material's T_g decreased as the material was exposed to high temperatures. As the isothermal temperature was increased, the T_g dropped more rapidly with time, a behavior consistent with a thermally activated process. Because the decomposition rate constant(s) should be a function of temperature, it can be expressed in an Arrhenius form and then re-arranged to

$$\ln k = \ln F - \frac{E_a}{RT} \tag{3}$$

where E_a is the activation energy associated with the ester bond cleavage, R is the universal gas constant, and F is the frequency factor. A plot of ln k vs $1/T$ was generated for both k_1 and k_2 of the α-Terp system, and for k_1 of the *tert*-epoxy system. As seen in Fig. 9, with the α-Terp system, the calculations yield activation energies of 148 and 222 kJ/mol for processes 1 and 2. The *tert*-epoxy system has a decomposition activation energy of 146 kJ/mol. The frequency factors for the α-Terp system were determined to be 1×10^{15} and 6×10^{21} min^{-1} for the primary and secondary degradation processes, and the frequency factor for the *tert*-epoxy system was 1×10^{15} min^{-1}.

The calculated activation energies of decomposition of

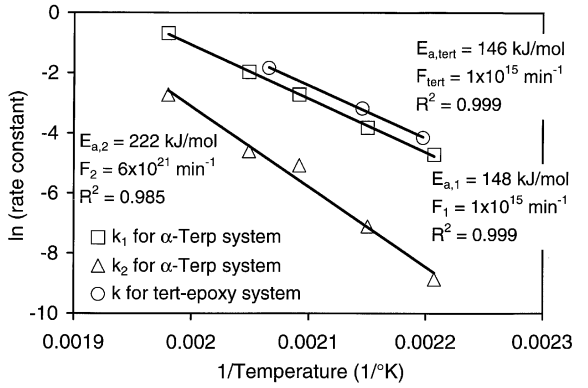


Fig. 9. Activation energy calculations using the mathematical fits of the T_g-shift data.

the primary tertiary ester linkages are in good agreement with values obtained via isothermal TGA methods. The similarity between the *tert*-epoxy's decomposition activation energy to that of the α-Terp system's primary decomposition activation energy tends to validate the technique used and the results. The similarity of the two systems' frequency factors lends further merit. However, the calculated activation energy of the second degradation process and its associated frequency factor are both considerably higher than that of the primary degradation process. At face value, the higher activation energy would imply the second tertiary ester group is considerably more stable than the primary tertiary ester group. Also, the frequency factor difference between the primary and secondary degradation mechanisms may be interpreted to mean that under the same isothermal conditions, the second cleaving site degrades at a faster rate than the primary site. However, this explanation is unlikely because the cleaving sites are all tertiary ester bonds, which means any differences found in the activation energy or frequency factor should be minor. The two degradation processes as revealed by the T_g-shift experiments most likely represent (1) the cleavage of tertiary ester bonds, and (2) the effects of having two possible cleavage sites per monomer instead of one. Recall that both the primary and secondary cleaving sites are part of a single monomer unit, so the two cleaving sites are not independent of one another with respect to the overall crosslink density. If one of the cleavable sites is degraded, the effects of the remaining tertiary ester bond would be less apparent with regard to degrading the network further because the local crosslink density would have already been reduced. So, the activation energy associated with k_1 (148 kJ/mol) describes the general cleavage of tertiary ester linkages, whereas the activation energy associated with k_2 (222 kJ/mol) describes the degradation of the network above and beyond what would be expected from a single cleavable site. Because k_2 describes the added effects, it makes sense that its frequency factor, F_2, is much greater than than F_1. A value of F_2 smaller than F_1 would imply the effects of the additional tertiary ester group are masked by the primary decomposition mechanism, which is not the case. Also, it is reasonable for $E_{a,2}$ to be greater than $E_{a,1}$ because additional energy is needed to cleave the additional tertiary ester groups.

3.4. Network decomposition: fracture toughness

Although much insight is obtained by simply studying a material's glass transition temperature, an understanding of the T_g-shift behavior is not entirely adequate to describe the rework properties of a thermoset. In Fig. 10, the T_g-shift data of a reworkable material was compared to its fracture toughness. The maximum fracture toughness of the networks prior to rework was 1.75 MPa m$^{1/2}$, and then dropped to a minimum of 0.2 MPa m$^{1/2}$ after rework. Also, the T_g-shift curve correlates in an almost one-to-one manner to the fracture toughness data. It should be noted that the material used for the fracture toughness experiments was a mixture of a non-reworkable epoxy, the ERL-4221™ (35% of the total epoxy weight), and the α-Terp epoxy (65% of the total epoxy weight). The purpose of adding the non-reworkable component was to enhance the fracture toughness of the overall system so that the effects of the reworkable component could be more easily observed. Using the pure α-Terp system resulted in a great deal of scatter in the fracture toughness data. Additionally, because the α-Terp epoxy monomer and the ERL-4221™ have very similar molecular structures, the two were expected to mix easily and homogeneously. From DSC measurements, only one glass transition temperature could be detected, thereby indicating a homogeneous mixture.

The mechanical strength and fracture toughness of reworkable materials must decrease significantly during rework to enable removal of adhered components. While in many materials lower fracture toughness values correspond to higher glass transition temperatures, in our materials the opposite is true. In general, as a thermoset begins to cure, crosslinks are formed. At very low crosslink densities, the material is extremely brittle; however, as the system continues to cure, its crosslink density and strength

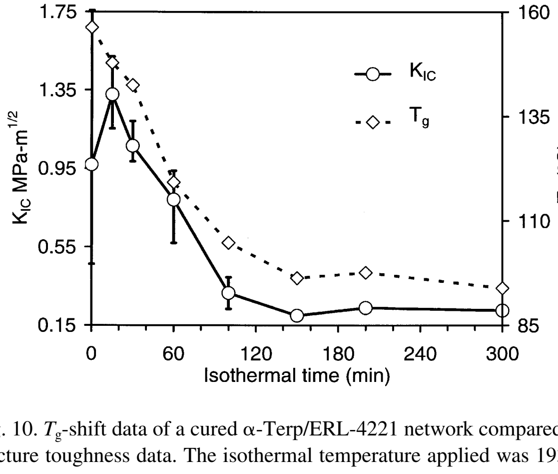


Fig. 10. T_g-shift data of a cured α-Terp/ERL-4221 network compared to its fracture toughness data. The isothermal temperature applied was 193°C.

increases. Reworking our materials is analogous to reversing the cure process where the crosslink density, strength, and T_g all decrease simultaneously. A more physical interpretation of the data is to view the decrease in fracture toughness as a result of defects being introduced into the network. Every time a tertiary ester bond is broken, a defect is created in the network at that site. As the system is reworked, more and more defects are created, thus leading to a decrease in the fracture toughness. Also, the glass transition temperature will decrease, because the reduction in crosslink density will increase the mobility of the polymer chains. Many thermal and mechanical properties are integrally related to the glass transition temperature of the material, thus a better understanding of the T_g-shift data may also provide insight into other important properties, as well.

Underlying all of the results and discussions is the fortuitous finding that these materials form rather ideal networks for studying rework. The experiments all tend towards the impression that the networks were homogeneously formed and degraded with few, if any, pockets of inhomogeneities. The T_g-shift data and the fracture toughness data both indicate a continuous degradation trend. Also, none of the DSC measurements showed signs of more than one glass transition temperature. If areas of the material had degraded at a significantly faster or slower rate, then one would expect to see more than one glass transition temperature per sample, as well as lower R^2 values for the linear fits as seen in Fig. 9.

4. Conclusions

The chemical degradation mechanisms of the α-Terp epoxy monomer and the α-Terp network were found to be consistent with tertiary ester degradation mechanisms. The thermally labile tertiary ester linkage cleaves at elevated temperatures, thereby breaking down the polymer network and forming carboxylic acid and alkene moieties. Some of the carboxylic acid groups react further to form anhydrides in the breakdown process. A novel method was developed to aid in characterizing the reworkable nature of the α-Terp epoxy systems. By following the change in the glass transition temperature as a function of rework conditions, activation energies, as well as kinetic information, were obtained with regards to the reworkability of the reworkable thermosets. This information also proved useful in explaining the effects of different monomer architectures on reworkability of a network and correlated extremely well with fracture toughness.

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