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Thermal stability of high temperature epoxy adhesives by thermogravimetric and adhesive strength measurements

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ABSTRACT

The thermal degradation of two high temperature epoxy adhesives has been measured in terms of weight loss and adhesion loss and the lifetime predictions are compared for the two independent measurements of thermal degradation. Weight loss measurements were performed at high temperature under accelerated thermal aging conditions. Adhesion loss measurements were performed at lower temperatures closer to typical continuous operating temperatures. An Arrhenius relationship is validated for the thermal degradation of the epoxy adhesives, and the extent of degradation in terms of weight loss and adhesion loss is modelled with an autocatalytic rate expression. The degradation kinetic parameters and models are compared between the two thermal degradation measurements and are found to give similar predictions for the lifetime of the adhesives. In addition, the relationship between network degradation and loss of adhesive strength is discussed.

1. Introduction

High temperature adhesives able to operate continuously at high service temperatures are an important class of adhesives and have use in electronics, automotive, and aerospace. It is crucial in these high temperature applications to have an accurate prediction of the adhesive life in order to predict failure in applications that tend to push adhesives to their thermal limit.

Measurement of adhesive life has heavily relied on thermogravimetric analysis (TGA) to determine material degradation kinetics under accelerated thermal aging.[1–4] Thermal degradation studies performed through TGA measurement relate the rate of mass loss to the rate of bond scission. Degradation of the thermoset network occurs through the scission of chemical bonds. In TGA experiments, the rate of mass loss is measured and is assumed to be proportional to the rate of bond scission. As chemical bonds are broken, volatile species are released leading to a loss of mass. For the small sample size employed in TGA experiments, the mass loss of volatiles is assumed to be much faster than bond scission and therefore rate limited by the scission of chemical bonds.

A criticism of TGA measured degradation is that it measures degradation at temperatures far above the anticipated operating environment of the adhesive and relies on large temperature extrapolations to lower service temperatures under the assumption of a consistent degradation mechanism [5,6]. In addition, TGA measures degradation in terms of weight loss. In many applications, loss of adhesive strength is the more important variable leading to ambiguity in how TGA weight loss measurements relate to loss of adhesive strength at the anticipated service temperature.

Epoxy thermosets are the largest class of adhesive materials used in industry today. They are relatively easy to process, have excellent adhesion to substrates, and can be formulated for many diverse applications. Epoxy thermosets however are limited to lower temperature applications. The continuous service temperature is generally in the range of sub-ambient to 120 °C. Some formulations have extended the continuous upper operating temperature up to 200 °C [7]. Other classes of adhesives are able to operate at higher temperatures but lack the advantages of epoxy adhesives such as high adhesive strength, easy processing, and good wetting properties [8]. As the thermal requirements of many specialized applications in electronics, automotive, and aerospace continue to demand more thermal stability from adhesive technology, it is important to validate the TGA high temperature measurement of material degradation at temperatures closer to the adhesive operating temperature and better understand the relationship between weight loss measured degradation and thermal degradation induced loss of adhesive strength.

In this work, the validity of TGA degradation has been tested by a second independent measurement of the adhesive thermal stability, loss of adhesive strength. The extent of degradation of two epoxy adhesives known for their thermal stability was measured in

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terms of loss of adhesive strength and compared to high temperature accelerated TGA weight loss measurements. The loss of adhesive strength is measured by napkin ring torsional adhesion measurements. Epoxy bonded napkin ring cells were thermally aged over long time at temperatures closer to the probable service temperature. The napkin ring measurements are directly compared to TGA weight loss measurements. Many processes can result in the loss of adhesion: temperature, moisture, stress. In these experiments aged at elevated temperature in a relatively dry environment and under no load, the driving force for loss of adhesion is limited to network degradation. We are interested in characterization of the loss of adhesion at temperatures closer to potential continuous operating temperatures of high temperature resistant adhesives in order to compare the thermal sensitivity of adhesion loss and weight loss degradation measurements and test an Arrhenius relation of epoxy thermal degradation over a wider temperature range through two independent measurements of thermal degradation. The comparison allows information to be gained about the relationship between loss of adhesion and degradation of the polymer network. In theory, the loss of adhesion is governed by bond scission of the polymer network in a manner similar to TGA weight loss measurements and will have a similar sensitivity to temperature.

2. Experimental

2.1. Materials

The epoxy systems used in this work are EPON828/4,4′-Methylenebis[2-methylcyclohexylamine] and EPON828-1031/4,4′-aminophenylsulfone. The amine curative is added to the epoxy resin in a 1:1 equivalent of glycidyl to amine. In the second epoxy system, the EPON828 and EPON1031 are a 50–50 wt% mixture of the two resins. EPON828 and EPON1031 were purchased from E. V. Roberts. 4,4′-aminophenylsulfone (DDS) was purchased from Sigma–Aldrich. 4,4′-Methylenebis[2-methylcyclohexylamine] was purchased from Air Products under the trade name Ancamine2049. Samples were cured with predetermined thermal cure schedules that resulted in complete cure. Complete cure was validated by DSC and DMA up-down-up thermal sweep.

2.2. DSC

The extent of cure of the epoxy system and the glass transition temperature were measured by differential scanning calorimetry (DSC). DSC measurements were performed on a TA Instruments DSC Q2000. Samples of approximately 5 mg were loaded in sealed hermetic aluminium pans. Heat flow was measured during thermal ramp experiments with a ramp rate of 10 °C/min for up-down-up thermal sweeps. In Fig. 1, the heat flow of EPON828/Ancamine2049 and EPON828-1031/DDS are shown for two heating ramps from an up-down-up temperature sweep. For EPON828/Ancamine2049, the second heat flow profile is essentially the same as the first showing negligible residual cure. The step transition at a temperature of 165 °C is the glass transition temperature, T_g, which is also relatively unchanged from the first to the second heating ramps. For EPON828-1031/DDS, the step transition in the first heating ramp at a temperature of 250 °C is the glass transition temperature of the DDS cured system. There is a small exotherm after the glass transition indicating a small amount of residual cure. The second heating ramp is similar to the first except the step transition at 250 °C has become nearly indistinguishable. This is likely due to the high crosslink density of the material and the high density of aromatic structures which create an extremely rigid structure and make it difficult to detect the glass to rubber transition. The residual cure exotherm at high temperature is also no longer present in the second heating curve.

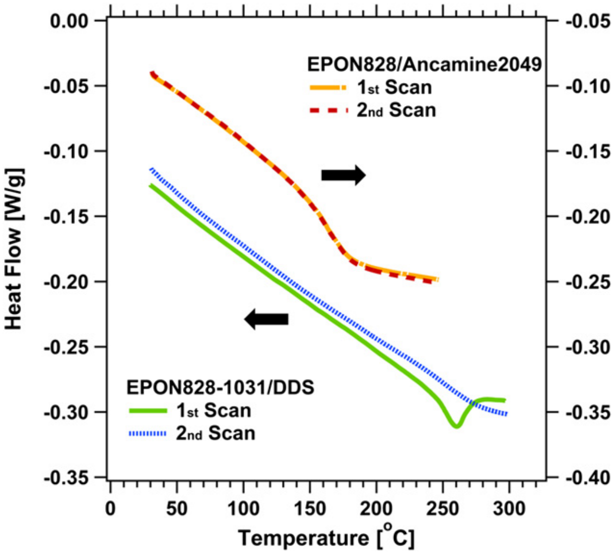

Fig. 1. Differential scanning calorimetry measurement of the specific heat flow versus temperature of EPON828/Ancamine2049 and EPON828-1031/DDS.

2.3. DMA

Dynamic mechanical measurements were performed using single cantilever beam geometry on a TA Instruments DMA Q800. The low strain in-phase and out-of-phase deformation response was measured when applying an oscillatory controlled force, and the resulting moduli were calculated. The temperature was ramped at 3 °C/min over a temperature range spanning the glass to rubber transition. Fig. 2 shows the storage and loss moduli and tanδ for EPON828/Ancamine2049 and EPON828-1031/DDS for two successive heating ramps. The moduli measurements of the EPON828/Ancamine2049 system are unchanged from the first and second heating ramp verifying complete cure which agrees with the DSC assessment. The loss modulus peak occurs at a temperature of 160 °C which is a measure of T_g. The peak in tanδ is considered a second measurement of T_g and occurs at a slightly higher temperature than the peak in the loss modulus. The moduli measurements of EPON828-1031/DDS show a small shift in the loss modulus peak to higher temperature, 240 °C–245 °C, meaning T_g has increased from the first to the second heating ramp. The increase in T_g is explained by a small residual cure that is completed upon heating to high temperature. The small exotherm at high temperature in the 1st DSC scan of EPON828-1031/DDS supports a small residual cure completed at high temperature.

2.4. TGA

Thermogravimetric measurements were performed with a TA Instruments TGA Q5000. Samples of approximately 5–10 mg were isothermally aged at temperatures of 325, 350, and 375 °C. The TGA is equipped with infrared heating which allows ballistic heating capability and rapid achievement of the desired isothermal temperature which helps resolve short time weight loss measurements.

2.5. Napkin ring adhesive aging

Adhesive strength was measured using napkin ring geometry. Napkin ring tooling was machined from 304 stainless steel. The

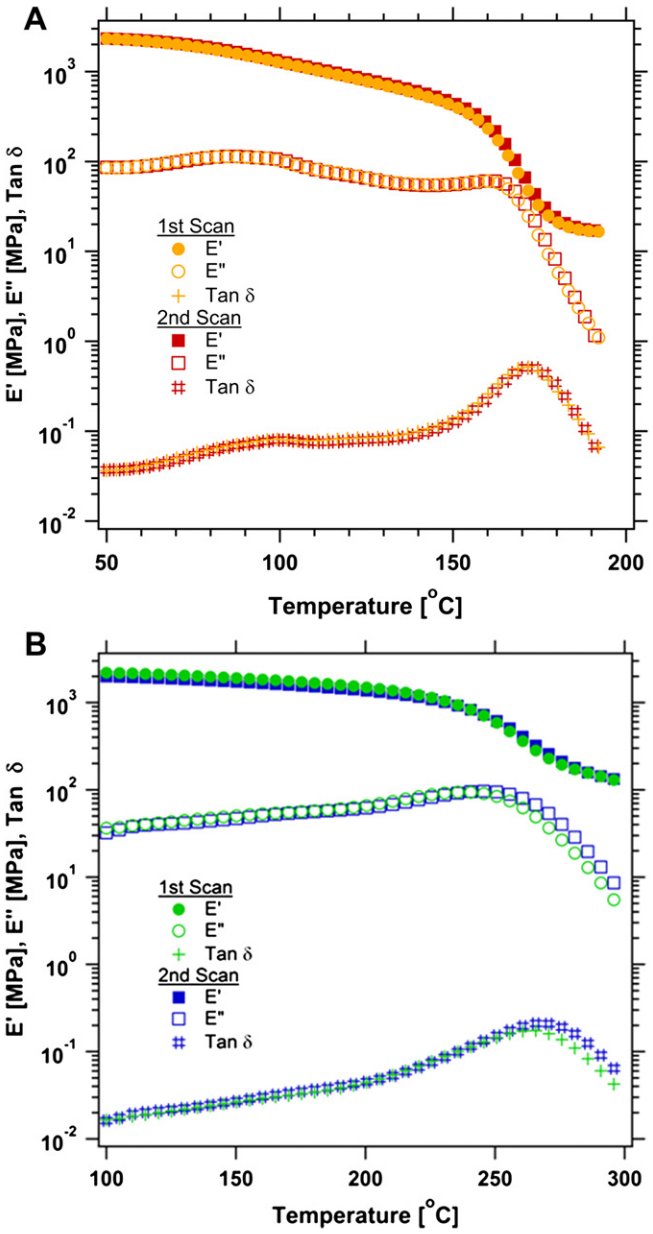

Fig. 2. Dynamic mechanical analysis measurement of the storage and loss moduli and tanδ versus temperature of A) EPON828/Ancamine2049 and B) EPON828-1031/DDS.

tooling consists of two 1 inch cylindrical fixtures. The two napkin ring fixtures are bonded through the epoxy system between a 0.1 inch wide annulus on the top fixture and a smooth surface on the opposing bottom fixture. A dowel insert holds the top and bottom cylindrical fixtures in alignment. The adhesive strength of the epoxy was measured with an Instron torsional load frame at room temperature. The bonded napkin ring cells were torqued to failure at an angular rate of 5 deg/min. The shear adhesive strength, τ_a, is calculated from the max torque, $T_{\max}$, at failure through the relation

$$\tau_a = \frac{\text{Force}}{\text{Area}} = \frac{3T_{\max}}{2\pi\left(R_o^3 - R_i^3\right)} \quad (1)$$

where R_o and R_i are the outer and inner annulus radius[9].

The adhesive strength of long time thermally aged epoxy was measured at several temperatures where the adhesive proved to fail on the order of days to several months. For EPON828/Ancamine2049, bonded napkin rings were aged isothermally at temperatures of 195, 205, 215, 225 °C. For EPON828-1031/DDS system, bonded napkin rings were aged isothermally at

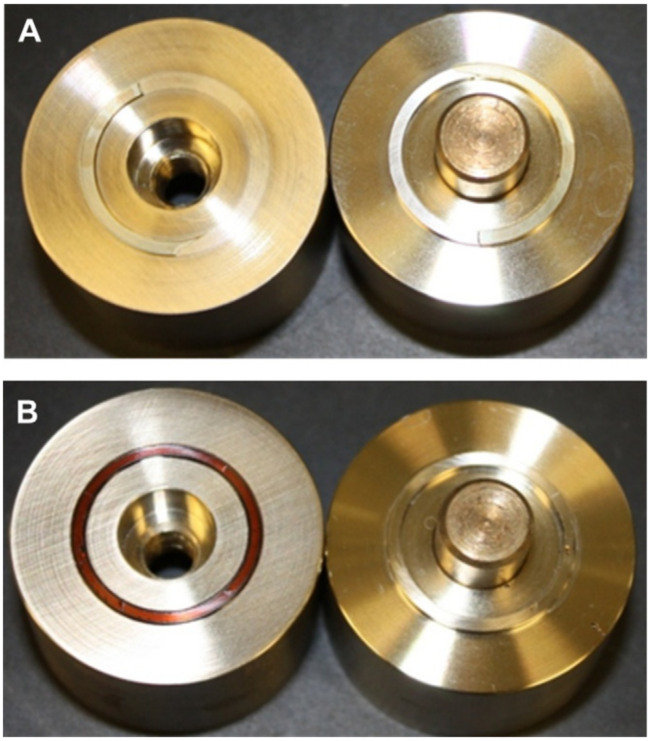

Fig. 3. EPON828/Ancamine2049 napkin rings after torque to failure of A) an unaged bond and B) an aged bond at 195 °C at 12 weeks.

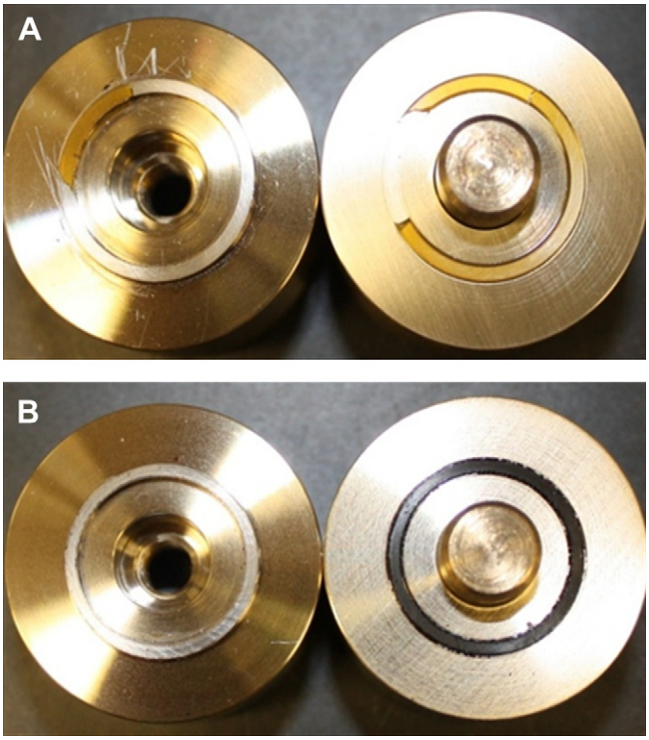

Fig. 4. EPON828-1031/DDS napkin rings after torque to failure of A) an unaged bond and B) a bond aged at 220 °C at 16 weeks.

temperatures of 220, 230, 240, 250 °C. Commercial high temperature epoxy adhesives are marketed as being able to offer short term continuous operation at temperatures in the range of 175–205 °C and withstand limited exposure up to 250 °C. [7] The relative humidity was 5% referenced to 25 °C. Three samples were removed from an air-convection oven every 2–3 days for the highest temperature experiment to every two weeks for the lowest temperature experiment. Figs. 3 and 4 show pictures of an initial napkin ring cell and final aged napkin ring cell for the lowest aging temperature after torque to failure of EPON828/Ancamine2049 and EPON828-1031/DDS, respectively. The discoloration is believed to be the result of oxidative degradation that initiates at the air–epoxy interface at short times and propagates into the samples at long time.

3. Results

3.1. TGA

The normalized extent of weight loss as a function of time is shown in Fig. 5A for EPON828/Acamine2049 and in Fig. 6A for EPON828-1031/DDS. The extent of weight loss, p_w, is defined as

$$p_w = (w_i - w)/\left(w_i - w_f\right) \tag{2}$$

where w is the weight of the sample, w_i is the initial weight, and w_f is the final weight. The extent of weight loss is routinely used as a measure of the extent of degradation. As network bonds are

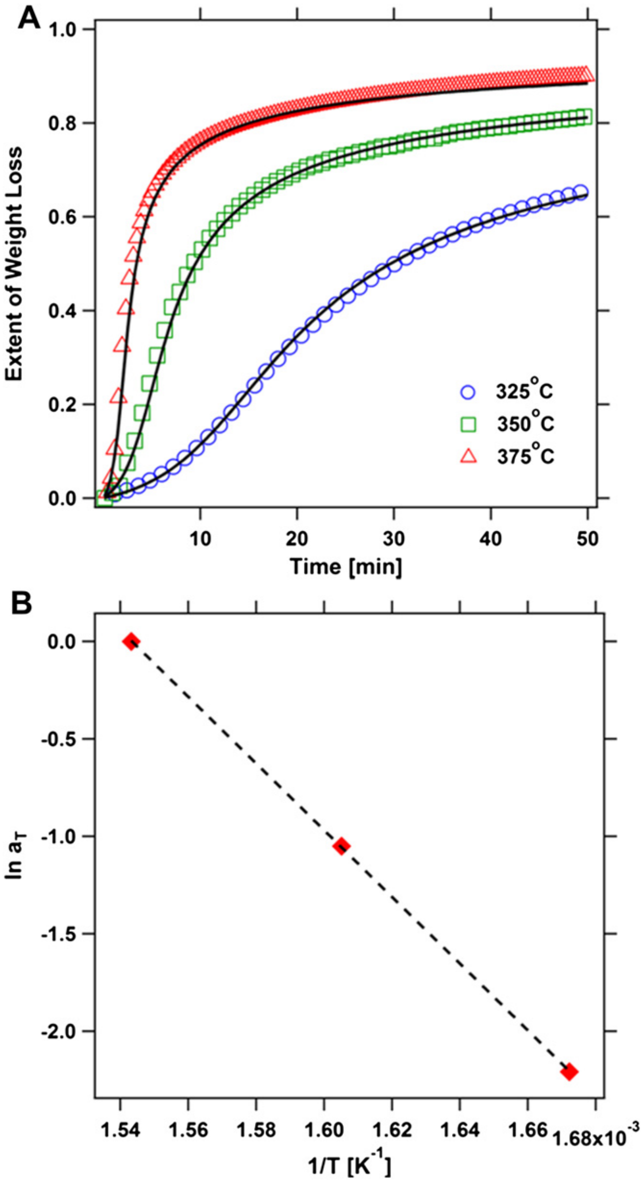

Fig. 5. (A) The extent of degradation as measured by TGA weight loss measurements versus time of EPON828/Ancamine2049 at isothermal temperatures of 325, 350, and 375 °C. Solid lines are non-linear least squares fits by the autocatalytic degradation rate model (Eq. (4)). (B) Arrhenius plot of the temperature shift factors (T_{ref} = 375 °C) versus the inverse temperature from time–temperature superposition of the TGA measured extent of degradation of EPON828/Ancamine2049.

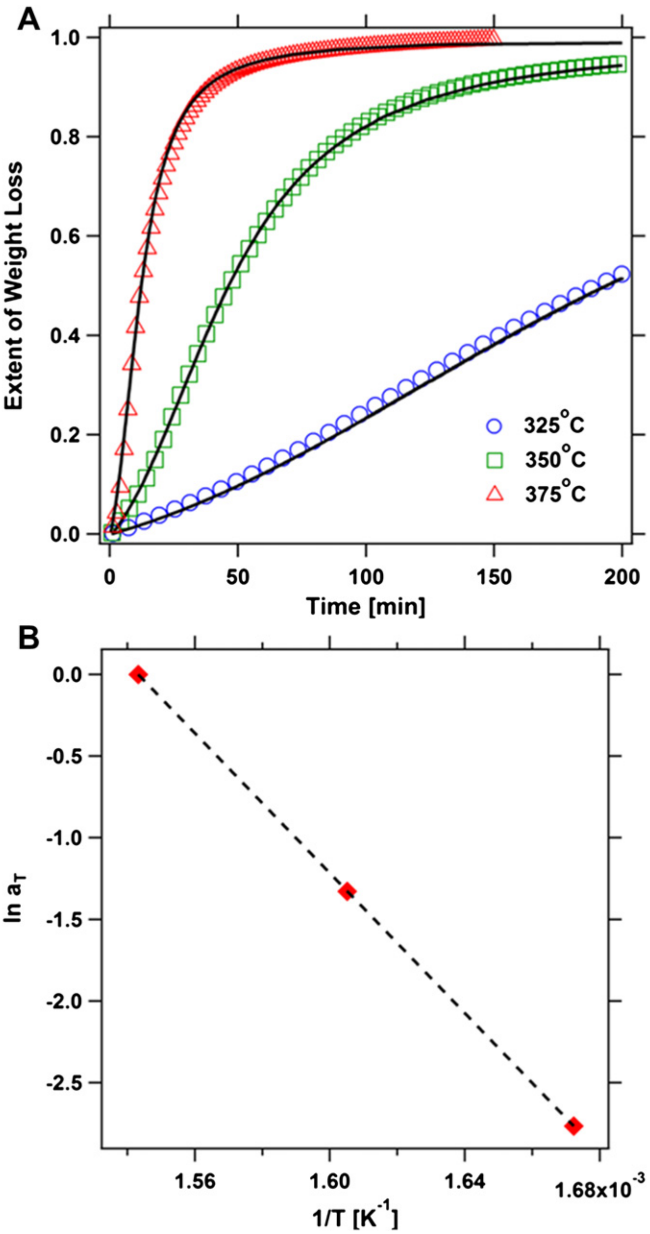

Fig. 6. (A) The extent of degradation as measured by TGA weight loss measurements versus time of EPON828-1031/DDS at isothermal temperatures of 325, 350, and 375 °C. Solid lines are non-linear least squares fits by the autocatalytic degradation rate model (Eq. (4)). (B) Arrhenius plot of the temperature shift factors (T_{ref} = 375 °C) versus the inverse temperature from time–temperature superposition of the TGA measured extent of degradation of EPON828-1031/DDS.

broken, volatile degradation species are released from the material leading to loss of weight. Notice that this definition of the extent of degradation does not imply 100% weight loss at an extent of degradation of unity. A portion of the thermal degradation products are non-volatile. The extent of reaction references the final weight of the sample which is asymptotically approached at long time.

The extent of weight loss degradation is modelled by fitting to a kinetics rate expression. A kinetics rate expression takes the form

$$\frac{\mathrm{d}p}{\mathrm{d}t} = k(T)f(p) \tag{3}$$

where $k(T)$ is a temperature sensitive Arrhenius rate constant and $f(p)$ is an extent of reaction dependent function that depends on the reaction mechanism. The autocatalytic reaction mechanism has been successfully applied in the past to model cure and degradation processes of epoxy systems.[10] In the autocatalytic model, $f(p)$ is of the form $(a+p^m)(1-p)^n$. Exponents m and n are order parameters that model the degradation mechanism, and the constant a accounts for an initial degradation rate at $t = 0$ that may be nonzero. The overall rate expression applied to the extent of weight loss is written as

$$\frac{\mathrm{d}p_w}{\mathrm{d}t} = k_0 e^{-E_a/RT}\left(a+p_w^m\right)\left(1-p_w\right)^n \tag{4}$$

k_0 is the pre-exponential factor, E_a is the degradation activation energy, R is the gas constant, and T is temperature.

Of particular interest is the degradation activation energy of the Arrhenius expression which is a measure of thermal sensitivity and the dependent parameter for predicting material lifetimes at other temperatures. According to an integrated linearization of the autocatalytic rate equation, ln$t$ is linear with $1/T$ at constant level of degradation, [3]

$$\ln t = \ln\left[\int_0^{p_w} \frac{\mathrm{d}p'_w}{\left(a+p'^{m}_{w}\right)\left(1-p'_w\right)^n}\Big/ k_0\right] + \frac{E_a}{RT} \tag{5}$$

A time–temperature superposition of the extent of weight loss was constructed by plotting the extent of weight loss versus $a_T t$ where a_T is a temperature shift factor used to superimpose the data at a constant level of degradation. The data for EPON828/Ancamine2049 and EPON828-1031/DDS was found to superimpose which implies a consistent degradation mechanism at the three

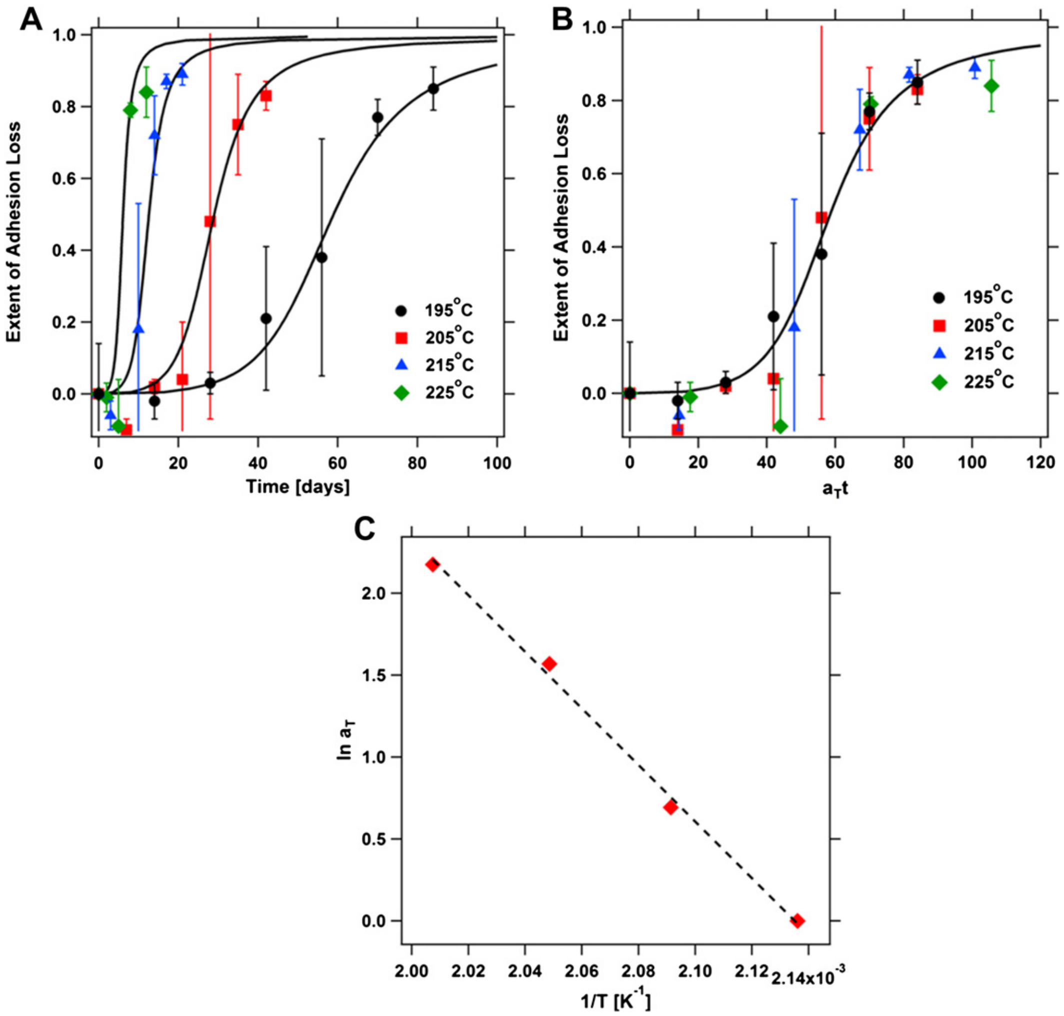

Fig. 7. (A) The extent of adhesion loss degradation of EPON828/Ancamine2049 bonded napkin rings isothermally aged at temperatures of 195, 205, 215, and 225 °C. Solid lines are non-linear least squares fits by the autocatalytic degradation rate model (Eq. (6)). (B) Time–temperature superposition at a reference temperature of 195 °C of the extent of adhesion loss of aged EPON828/Ancamine2049. Solid line is the autocatalytic model prediction at 195 °C. (C) Arrhenius plot of the temperature shift factors ($T_{\mathrm{ref}} = 195$ °C) versus the inverse temperature from time–temperature superposition of the extent of adhesion loss of EPON828/Ancamine2049.

isothermal aging temperatures. According to Eq. (5), the temperature shift factor should be linear with $1/T$ with a slope of E_a/R. An Arrhenius relation of the extent of weight loss as a function of time with temperature was validated by the construction of an Arrhenius plot of $\ln a_T$ versus $1/T$ [Figs. 5B and 6B]. The slope of the linear best fit gives activation energies of 142 ± 4 kJ/mol and 180 ± 4 kcal/mol for EPON828/Ancamine2049 and EPON828-1031/DDS, respectively. Utilizing these activation energies, the extent of degradation at the three aging temperatures is well fit by the autocatalytic model [Eq. (4)] using a non-linear least squares regression analysis.

3.2. Adhesive strength

Long time thermally aged napkin ring adhesion experiments were performed to assess degradation in terms of loss of adhesive strength. The extent of adhesion loss is shown in Figs. 7A and 8A for EPON828/Ancamine2049 and EPON828-1031/DDS, respectively. The extent of adhesion loss, p_a, is defined as $(\tau_{a,i}-\tau_a)/\tau_{a,i}$ where τ_a is the shear adhesion strength of the thermally aged napkin ring bond and $\tau_{a,i}$ is the initial shear adhesion strength of an unaged napkin ring bond. The error bars define the standard error determined from the shear adhesion strength of three napkin ring samples. The standard error tends to be larger for samples in the fall off zone of the adhesion strength. One explanation for the large error limits is temperature gradients in the aging oven which has a ±2 °C temperature specification. The temperature step size for the adhesion aging experiments is 10 °C making the potential temperature variation in the oven to be 20% of the temperature step size. Samples were randomly taken from different locations in the aging oven to minimize error from oven temperature gradients.

A time–temperature superposition of the extent of adhesion loss for the two epoxy systems at the four aging temperatures is constructed in a manner similar to the extent of weight loss measurements [Figs. 7B and 8B]. Of interest is whether the loss of adhesion can be well described by an Arrhenius relation. An Arrhenius plot of the temperature shift factors, a_T, versus $1/T$ gives a straight line validating the Arrhenius relation between loss of adhesion and temperature [Figs. 7C and 8C]. The slope of the linear best fit gives activation energies of 144 ± 7 kJ/mol and 184 ± 5 kcal/mol for EPON828/Ancamine2049 and EPON828-1031/DDS, respectively. Utilizing the derived activation energy, the extent of adhesive degradation was well fit by the autocatalytic model [Eq. (6)] using a non-linear least squares regression analysis.

$$\frac{\mathrm{d}p_a}{\mathrm{d}t} = k_0 e^{-E_a/RT}\left(a + p_A^m\right)(1 - p_a)^n \tag{6}$$

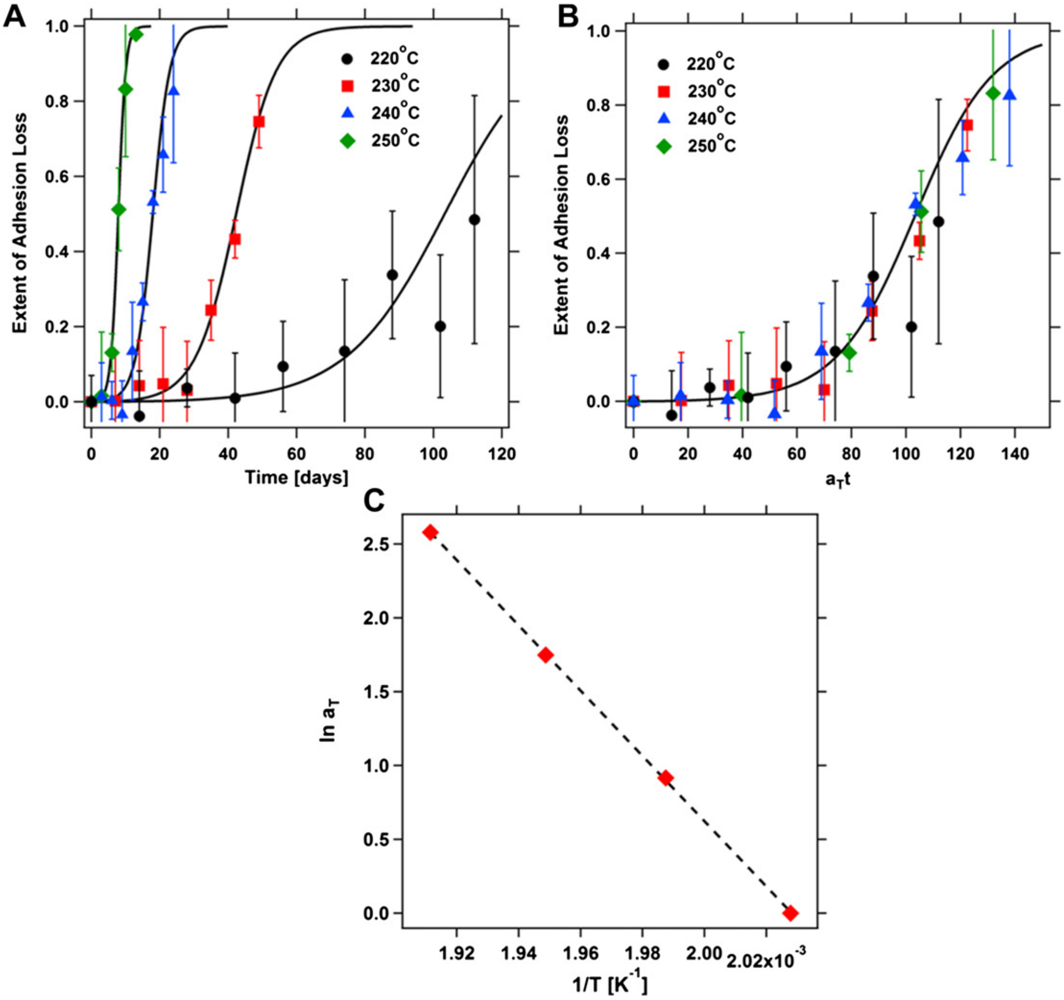

Fig. 8. (A) The extent of adhesion loss degradation of EPON828-1031/DDS bonded napkin rings isothermally aged at temperatures of 220, 230, 240, and 250 °C. Solid lines are non-linear least squares fits by the autocatalytic degradation rate model (Eq. (6)). (B) Time–temperature superposition at a reference temperature of 220 °C of the extent of adhesion loss of aged EPON828-1031/DDS. solid line is the autocatalytic model prediction at 220 °C. (C) Arrhenius plot of the temperature shift factors ($T_{\mathrm{ref}} = 220$ °C) versus the inverse temperature from time–temperature superposition of the extent of adhesion loss of EPON828-1031/DDS.

4. Discussion

Activation energies from the Arrhenius plots and the pre-exponential factors and degradation order parameters from fitting data to the autocatalytic degradation rate model are shown in Table 1. The activation energy of EPON828/Ancamine2049 is higher than most other cycloaliphatic diamine cured epoxy resins and comparable to aromatic diamine cured epoxy resins [11–13]. This result supports the claim by the suppliers of Ancamine2049 as to the similar performance to other aromatic diamine curatives. The activation energy of EPON828-1031/DDS system is on the high end of epoxy high temperature adhesives [11–13].

A comparison of the activation energies between TGA and adhesion aging experiments finds the parameters to be similar for both epoxy systems. The similarity of the activation energies is impressive since both experiments quantify degradation through different means of measurement. The similarity of the two parameters implies that adhesion and mass loss are controlled by the same intrinsic degradation process at the studied temperatures. The reaction order of the degradation rate equation modelled by the exponents of the autocatalytic rate model is an expression of the measured property's dependence on degradation and is not expected to be similar. The pre-exponential factor captures the rate of the degradation reaction leading to bond scission for reactants with sufficient thermal energy to traverse the degradation transition state. Yet, in these experiments where degradation is measured through a secondary means of measurement, the pre-exponential factors are not expected to be similar. Therefore, it is surprising that the pre-exponential factors from modelling the two degradation measurements for the EPON828/Ancamine2049 system are similar. In contrast, the pre-exponential factor from the adhesive degradation model is more than an order of magnitude greater than in the TGA degradation model for the EPON828-1031/DDS system. It is difficult to reason why the pre-exponential factor is similar for one system and significantly larger for the other. Network degradation will affect loss of adhesion by breaking bonds at the adhesion surface which will reduce the cohesive strength of the epoxy and lower the adhesion strength, but the direct relationship of adhesion loss and mass loss on chemical degradation of the thermoset network is unclear. The differences in the pre-exponential could be attributed to the sensitivity of fitting the degradation data to the autocatalytic model which is more sensitive to changes in activation energy than pre-exponential. The similarity of the activation energies shows that the loss of adhesion at the lower aging temperatures is dependent on network degradation as is mass loss.

A comparison of the two models shows that even though the epoxy systems are experiencing network degradation as evidenced by mass loss, the epoxy systems still maintain considerable adhesive strength at short time. A plot of the two degradation model equations derived from TGA and adhesive strength measurements are shown in Figs. 9 and 10 at a reference temperature of 200 °C. The extent of adhesion loss of the epoxy systems is predicted to be less than 0.01 up to an extent of degradation of 0.06 of the polymer network from weight loss. The EPON828-1031/DDS system is much more thermally stable than EPON828/Ancamine2049 evidenced by a larger degradation activation energy which causes the loss of adhesion to occur over a much longer period of time at a similar reference temperature. An extent of adhesion loss degradation of 0.01 occurs over a period of 0.77 yrs for EPON828-1031/DDS compared to the 0.037 yrs for the EPON828/Ancamine2049. The results show the EPON828-1031/DDS system to have significantly greater thermal stability over the EPON828/Ancamine2049 system.

Table 1
Degradation modeling parameters.

Epoxy system	Measurement	E_a [kJ/mol]	k_0 [min^{-1}]	a	m	n
EPON828/	TGA	142 ± 4	7.8×10^{11}	0.017	1.1	3.6
Ancamine2049	Napkin Ring	144 ± 7	8.4×10^{11}	0.0015	1.15	1.6
EPON828-1031/	TGA	180 ± 4	5.8×10^{13}	0.13	0.9	1.6
DDS	Napkin Ring	184 ± 5	1.35×10^{15}	0.001	1.02	1.0

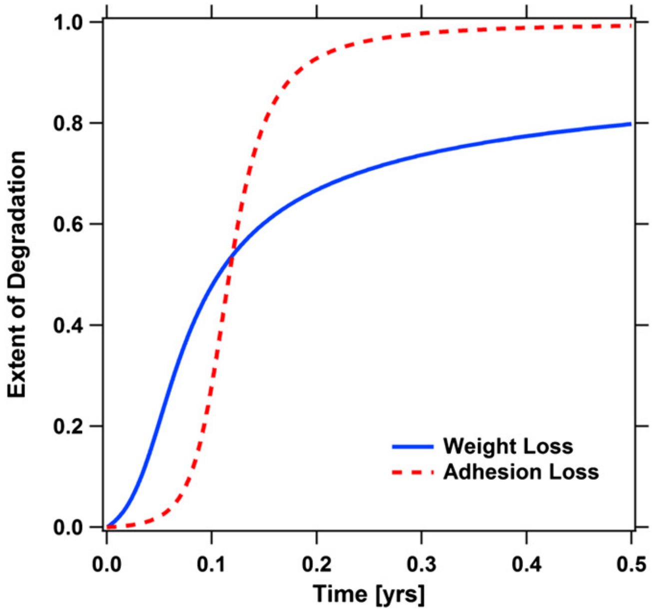

Fig. 9. Predictions of the autocatalytic degradation model as determined from TGA weight loss measurements and napkin ring adhesive strength measurements for EPON828/Ancamine2049 at an isothermal temperature of 200 °C.

As degradation of the network progresses, the rate of adhesion loss becomes greater than the rate of weight loss as shown by the crossover of the extent of degradation of the two measured parameters. The comparison of the weight loss and adhesion loss degradation models suggests that a point is reached when

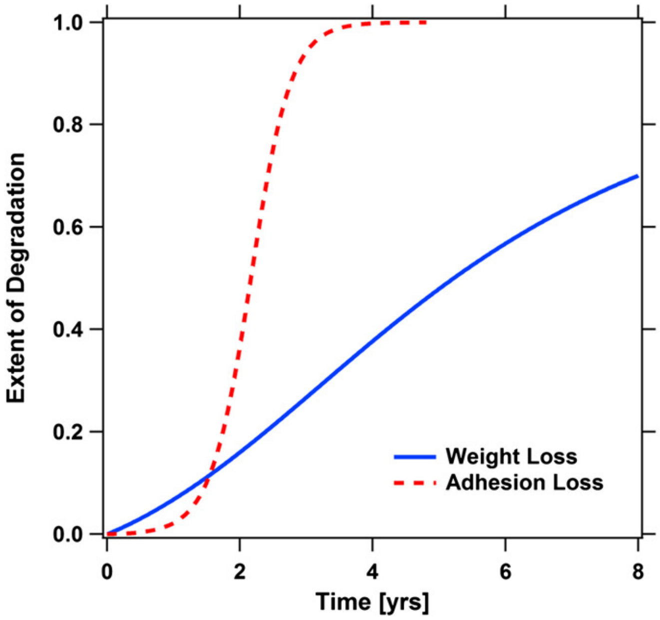

Fig. 10. Predictions of the autocatalytic degradation model as determined from TGA weight loss measurements and napkin ring adhesive strength measurements for EPON828-1031/DDS at an isothermal temperature of 200 °C.

degradation of the polymer network becomes severe leading to loss of adhesion. Further degradation of the polymer network results in rapid loss of adhesion. The adhesion loss approaches an extent of unity at much shorter time than the extent of weight loss. This trend is expected. The epoxy still undergoes more mass loss after adhesive failure due to continued scission of chemical bonds, yet the network has been degraded to an extent where it has minimal adhesive strength and readily fails under load.

The loss of adhesion is more severe for EPON828-1031/DDS than EPON828/Ancamine2049 when referenced to the rate of weight loss degradation. The maximum rate of adhesion loss occurs at an extent of adhesion loss degradation of 0.50 and 0.42 for EPON828-1031/DDS and EPON828/Ancamine2049, respectively. The extent of weight loss degradation is 0.18 at the maximum rate of adhesion loss for EPON828-1031/DDS compared to EPON828/Andcamine2049 where the extent of weight loss degradation is 0.48 at the maximum rate of adhesion loss. The assessment suggests that EPON828/Ancamine2049 maintains better adhesion to a greater extent of network degradation as evidenced by weight loss than EPON828-1031/DDS. However, the appearance of greater adhesion when referenced to weight loss for the EPON828/Acamine2049 system may be linked to greater volatility of the degradation species of the EPON828/Ancamine2049 system compared to the EPON828-1031/DDS system. As network bonds are broken, the EPON828/Ancamine2049 system may yield lower molecular weight species that volatilize more readily and give the appearance of greater adhesion strength to a higher extent of weight loss. In this regard, EPON828/Ancamine2049 may off gas more as it degrades than EPON828-1031/DDS.

5. Conclusions

In conclusion, the thermal degradation of two epoxy thermoset systems known to have good thermal stability was tested by two independent measurements of polymer degradation: TGA weight loss measurements and napkin ring adhesion loss measurements. The TGA weight loss measurements are directly compared to the loss of adhesive strength measurements. The similarity of the degradation activation energies determined from modelling the TGA measurements and the adhesive strength measurements shows that mass loss and adhesion loss are mutually dependent on chemical network degradation and proves an Arrhenius dependence of degradation on temperature over a wide temperature range. This study supports accelerated TGA measurement of epoxy thermoset degradation as a means of estimating thermal stability for these two epoxy systems and shows the relationship between polymer network degradation as measured by TGA to loss of adhesive strength.

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References

[1] Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature 1964;201:68–9.

[2] Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. Journal of Polymer Science Part B: Polymer Letters 1966;4:323–8.

[3] Nam J-D, Seferis JC. Generalized composite degradation kinetics for polymeric systems under isothermal and nonisothermal conditions. Journal of Polymer Science Part B: Polymer Physics 1992;30:455–63.

[4] Flynn JH. Degradation kinetics applied to lifetime predictions of polymers. Society of Plastics Engineers, Inc.; 1980. pp. 675–677.

[5] Flynn JH. Lifetime prediction for polymers from thermal analytical experiments - problems and how to deal with some of them. Thermochimica Acta 1988;134:115–20.

[6] Flynn JH. A critique of lifetime prediction of polymers by thermal analysis. Journal of Therml Analysis 1995;44:499–512.

[7] Petrie EM. Handbook of adhesives and sealents. New York: McGraw-Hill; 2007.

[8] Petrie EM. Epoxy adhesive formulations. New York: McGraw-Hill; 2006.

[9] Chai H. Deformation and failure of adhesive bonds under shear loading. Journal of Materials Science 1993;28:4944–56.

[10] Keenan MR. Autocatalytic cure kinetics from DSC measurements: zero initial cure rate. Journal of Applied Polymer Science 1987;33:1725–34.

[11] Rose N, Le Bras M, Bourbigot S, Delobel R. Thermal oxidative degradation of epoxy resins: evaluation of their heat resistance using invariant kinetic parameters. Polymer Degradation and Stability 1994;45:387–97.

[12] Barral L, Cano J, López J, López-Bueno I, Nogueira P, Abad MJ, et al. Decomposition behavior of epoxy-resin systems cured by diamines. European Polymer Journal 2000;36:1231–40.

[13] Patel RD, Patel RG, Patel VS. Kinetics of thermal degradation of cured epoxy resins based on triglycidyl-p-aminophenol. Thermochimica Acta 1988;128:149–56.