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Shelf stability of reactive adhesive formulations: A case study for dicyandiamide-cured epoxy systems

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ABSTRACT

Positron annihilation lifetime spectroscopy was used to study the curing behavior of epoxy resins of DGEBA with a hardener of dicyandiamide, from the initial viscous state of the formulation to the cured polymer. Isothermal measurements were done in the range from 50 to 80 °C. Gelation resulted in an increase of the intensity of ortho-positronium (*o*-Ps) and a sharp decrease in the lifetime. Change of *o*-Ps lifetime was used as a measure for the degree of curing. Applying the Johnson–Mehl–Avrami–Kolmogorov approach, these changes could be characterized and growth exponent '*n*' and reaction constant '*k*' were determined. Hence, we are able to project the shelf life of this one-component epoxy at room temperature by extrapolation.

1. Introduction

Epoxy resin based networks are known for their excellent adhesion, chemical and heat resistance, suitable mechanical properties and good electrical insulating properties. The chemistry of epoxies and the range of modifications that are commercially available, allow cured polymers to be produced with a very broad range of properties. Different variations offering high thermal insulation or thermal conductivity combined with high electrical resistance for electronics applications, are on offer these days. The extensive applications for epoxy-based materials include coatings, adhesives and composite matrix materials in aerospace, automobile and electronic industry [1]. Successful performance of epoxy-based systems depends on proper selection and formulation of components. The components that have the most significant influence on the curing behavior and the network structure are the epoxy resins and the curing agents. There are numerous choices of epoxy resins and curing agents, presenting a wide variety of structure and functionality. Most common epoxy resins, such as Diglycidyl ether of bisphenol-A (DGEBA), are produced from a reaction between epichlorohydrin and bisphenol-A. Epoxy resins are converted into solid, infusible, and insoluble three-dimensional thermosetting networks for their uses, by curing with cross-linkers. Optimum performance properties are obtained by cross-linking the right epoxy resins with the proper cross-linkers, often called hardeners or curing agents [1,2].

Dicyandiamide (DICY) is one of the first curing agents to be used with epoxy resins. The latent nature of this solid is due to its insolubility in epoxy resins at room temperature. Cure of epoxies with DICY occurs only while heating to temperatures of at least 150 °C. DICY may react with epoxy resin upon heating and stops reacting temporarily when the heat is removed. The resulting partially cured or "B-staged" state is ideal for prepreg applications. [Epoxy Adhesive Formulations, edited by Edward M. Petrie, pp. 106–107, McGraw Hill, 2006]. Typically, DICY is used at levels of 5–7 parts per 100 parts of liquid epoxy resins and 3–4 parts per 100 parts of solid epoxy resins by weight [2]. For industrial applications a single batch formulation is relevant. DICY can be mixed with epoxy resins to provide a one-package formulation with good storage stability of up to six months at ambient temperatures. To achieve low temperature hardening an accelerator may be added to speed up the reaction. As on the other hand mixing the components directly before usage is not practical in industrial surrounding and for large scale applications, a considerable shelf life of such pre-mixed one-component formulations is required. Packages like hobbocks are transported and stored at room temperature and, when connected to a pumping system, may be heated up to temperatures around 60 °C for several days in order to improve the flowability.

The epoxy curing process is an important factor affecting the cured epoxy performance. To obtain optimum network structure and performance, it is imperative to understand the curing process and its kinetics to design the proper cure schedule. A good number of reviews on this topic are already available in the literature [3,4]. However, from the industrial point of view it is still of utmost relevance, to establish reliable means of experimentally predicting the shelf life of new formulations of

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one-component epoxies, which is usually guessed from accelerated tests at elevated temperatures relying on selected reference measurements. In order to achieve predictability it is important to understand the complete curing mechanism of epoxies, so that the reaction kinetics can be further elaborated in the light of available standard models and further extrapolated to shelf life at storage temperatures.

The curing mechanism of DGEBA/DICY and similar systems is rather complex, involving several simultaneous reactions. There are a number of different mechanisms proposed in the literature [5–7]. Epoxy curing process can be monitored by a number of experimental techniques such as analysis of the disappearance and/or formation of functional groups by infrared (IR), near IR [8], or nuclear magnetic resonance (NMR) spectroscopy. The thermal properties of the system reflect the degree of cure, and thermal analyses such as differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA) and thermogravimetric analysis (TGA) are used extensively in studies of epoxy resins [9]. Correlation between the glass transition temperature (T_g) and degree of cure has been well established for many systems. Chemorheology, which utilizes rheological measurement in combination with DSC has been applied to study epoxy cure [10]. Since curing involves epoxy ring opening and the generation of polar groups, which have a high dipole moment, dielectric measurements have been applied to monitor cures. [11–18]. Dielectric methods encompass both macroscopic and microscopic features: the dipoles being oriented during dielectric measurements are on a microscopic scale, whereas the degree and rate of orientation may depend on macroscopic properties such as viscosity and density [19,20]. Precisely, indirect estimation of cure conversion as a function of time is done with a combination of several experimental techniques and the available theoretical models.

In metal physics, the Avrami equation, (also known as Johnson–Mehl–Avrami–Kolmogorov equation due to the many authors, who significantly contributed to this equation), is a widely accepted model to study phase transformations, e.g. crystallization or austenite-to-martensite transformations [21]. According to the *Avrami* equation, for solid-state transformations displaying the kinetic behavior, the fraction of transformation X is a function of time t [22];

$$X_t = 1 - \exp[-kt^n] \tag{1}$$

which is often written in its logarithmic form as follows:

$$\ln[-\ln(1 - X_t)] = \ln k + n \ln t \tag{2}$$

Here, 'n' is termed as the Avrami exponent, which is characteristic for the type of transformation (diffusion or reaction controlled, quenched in nuclei or random nucleation, shape of the particles of the new phase). A detailed overview is given e.g. in Refs. [21,22]. The constant 'k' is named the reaction constant, which is in turn temperature dependent, often via a simple Arrhenius law. In such cases, by performing several isothermal experiments at different temperatures, one can extract the activation energy E_a of the rate-determining step by plotting the reaction constant 'k' on a logarithmic scale *against* the reciprocal temperature. Thence, under the assumption, that the type of reaction and the rate-determining step do not change with temperature (i.e. the exponent 'n' stays constant for different temperatures), the Avrami equation can be used to extrapolate the transformation behavior to other temperatures at least in the early stages of transformation, i.e. for transformed fractions $X_t \leq 0.5$. (for larger fractions the boundary conditions underlying the Avrami equation are not fulfilled). The basic idea of the present paper is to apply this model to the curing of the epoxide system, i.e. we attribute the nucleation period of crystallization to the initial period of reaction and the diffusional part to the proceeding of the reaction until saturation is reached. This is in contrast to usual reaction kinetic models, which are of first or second order and do not include any incubation time.

Isothermal and non-isothermal curing behaviors of epoxy resins have already been studied in the light of the Avrami equation in past [23–27] but only for high curing temperatures and to the best of our knowledge neither growth exponent nor reaction constant have been interpreted nor extrapolation to room temperature has been done. However, this is of major importance for predicting storage stability of industrial one-component formulations at room temperature.

It is generally accepted that a key property for all amorphous polymers is the available microscopic free volume, which can be detected by several atomic probes and described by molecular dynamic simulations. Positron annihilation lifetime spectroscopy (PALS) is a widely accepted experimental tool to characterize the free volume in amorphous polymers [28–33] and has been used for epoxy resins [34] and epoxy-based polymers as well [35–37]. PALS uses the positronium (Ps), a neutrally charged particle with the mass of two electrons, and the size of a hydrogen atom, as a probe to measure the size of sub-nanometric holes in amorphous solids or liquids [38,39]. Ps is formed in molecular matter and (Anderson) localized at local free volumes (denoted as holes). The long-lived ortho state of Ps (o-Ps) is very sensitive to the hole size. Its lifetime decreases from 142 ns in infinitely large holes (self-annihilation in a vacuum) to the low ns range in subnanometer-size holes and mirrors the hole size at the moment of annihilation. The decrease in lifetime occurs since o-Ps may annihilate with an electron other than its bound partner, and with opposite spin, during a collision with a molecule in the hole wall (pick-off annihilation) [38,39]. Assuming the shape of the holes (e.g. spherical or cylindrical), the hole size can be calculated from the o-Ps lifetime τ_3, using a quantum-mechanical Tao-Eldrup model [40–42] from the following equation

$$\lambda_{po} = 1/\tau_{po} = 2ns^{-1}\left[1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi}\sin\left(\frac{2\pi r_h}{r_h + \delta r}\right)\right] \tag{3}$$

where δr=1.66 Å [41,42] describes the penetration of the Ps wave function into the hole walls. The mean hole volume is usually calculated from $v_h(\tau_3)$=$(4/3)\pi r_h^3(\tau_3)$. Where necessary, the distribution of the hole size and suitable weighting have to be taken into account.

Until now PALS experiments have been focused mainly on cured epoxy resin systems, with a few throwing light on curing behaviors but from a completely different perspective [43,44]. One of us has investigated the in-situ curing behavior on thin films of DGEBA/DETA (diethylenetriamine) with PALS [35,45]. For the present investigation curing is relevant, as the cured fraction is measured as a function of time and temperature.

In order to apply PALS parameters in combination with the JMAK equation to the curing kinetics, several boundary conditions need to be fulfilled. Firstly, it is possible to correlate the PALS parameters (i.e. o-Ps lifetime and intensity) and the transformed (cured) fraction X_t. There is a good correlation between the shrinkage of epoxy during curing, with the changes in macroscopic volume measured by PVT (pressure–volume–temperature measurements, see for e.g. paper Dlubek) and the microscopic free volume measured by PALS [37]. Secondly, in order to make a reliable extrapolation from the experimentally covered temperature range it is necessary that the reaction pathway does not change with temperature. If the growth exponent 'n' is found to be independent of temperature, this indicates that the reaction mechanism remains the same in the observed temperature interval. Both conditions are fulfilled here, as will be discussed later.

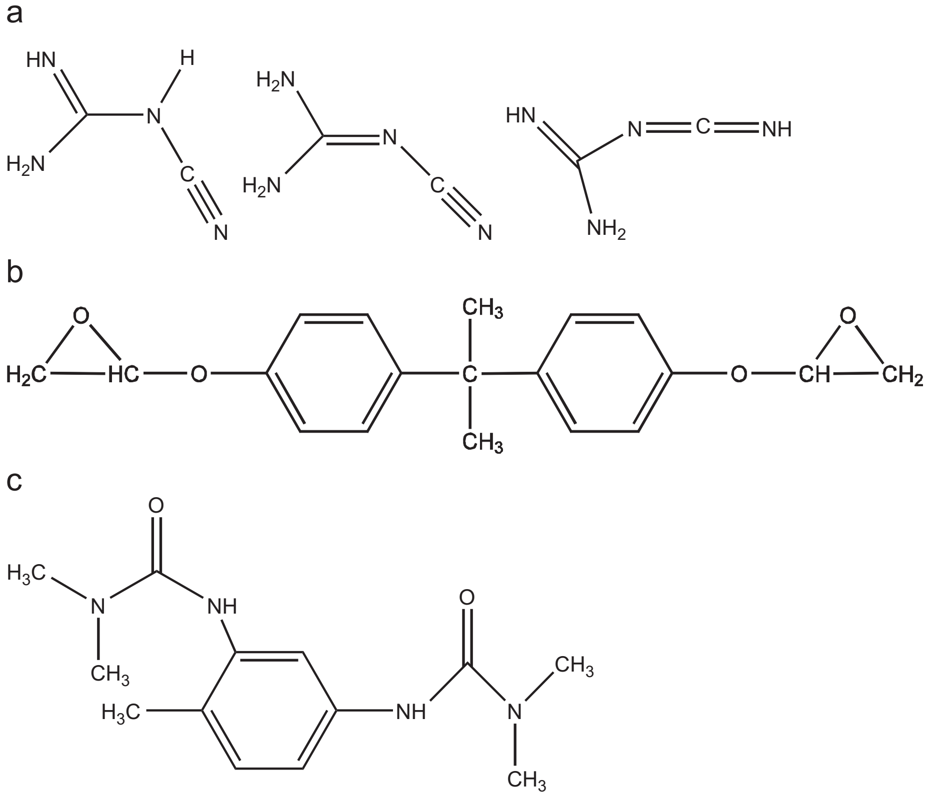

Fig. 1. Chemical structures of (a) DICY—Dicyandiamide, showing distinct tautomers, (b) DGEBA—Diglycidyl ether of bisphenol-A, (with a degree of polymerization i.e. n=0) and (c) Dyhard UR500.

The aim of the present investigation is to study the low temperature isothermal curing behavior of Dicyandiamide based epoxy resin system by means of PALS. The average *o*-Ps lifetime τ_3 proved to be a good approximation of transformed volume fraction. The reaction mechanism is similar at mediate and low temperature. Furthermore, the calculated Avrami parameters will be determined and used for prediction of low temperature storage stability.

2. Experimental

Dicyandiamide (DICY, Dyhard DF 50 EP within an epoxy-based paste used as curing agent, and blocked Urone accelerator (Dyhard UR 500) were supplied by Degussa Evonik GmbH and AlzChem, Diglycidyl ether of bisphenol-A (DGEBA, Araldite GY 250, with epoxy equivalent weight EEW=187 g/mol) was obtained from Huntsman. For this particular epoxy-hardener pair the mass ratio is approximately seven parts of DICY hardener, in equivalent weight, per hundred parts of resin, i.e., 7 phr. The applied formulation is similar to the one of published technical systems [46]. Basic chemical structures of DGEBA, DICY and Dyhard UR500 are shown in Fig. 1.

Positron annihilation lifetime experiments were performed with a fast–fast coincidence setup under high vacuum conditions as described in a previous work in more detail [31]. The time resolution was 285 ps (FWHM, ^{22}Na source) and the analyzer channel width was 25.3 ps. The resin, hardener and accelerator were thoroughly mixed at room temperature and after approximately 1 h of preparation two identical samples of precursor were sandwiched around a 1 MBq positron source: ^{22}NaCl, deposited between two 7-μm-thick Kapton foils. To prevent sticking of the source to the samples, each sample was held in an aluminum container of 1 mm width and $8 \times 8\ \text{mm}^2$ area with a window made of foils of 25-μm-thick Kapton. There were several isothermal scans at 50, 60, 70 and 80 °C (accuracy of ± 1 K), for different sets of samples. For each sample the first spectrum was always measured at room temperature (RT) followed by an isothermal run at temperatures as indicated for several hours. Each measurement lasted 2 h leading to a lifetime spectrum with a high number of annihilation events ($\sim 5 \times 10^6$).

3. Results and discussion

3.1. Analysis of lifetime spectra

Five million counts per spectrum were necessary to analyze the spectrum with the routine LT9.0 in its distribution mode in order to take into account the distribution of free volume size. The final resolution function used in the spectrum analysis was determined as a sum of two Gaussian curves. The lifetime spectra were deconvoluted into three components: τ_1=0.15–0.25 ps, τ_2=0.45–0.60 ns and τ_3=1.9–2.6 ns. Here, τ_1 is the shortest lifetime component, which is attributed to the annihilation of *para*-positronium (*p*-Ps). The intermediate lifetime component τ_2 is attributed to annihilation of *free*-positrons (e^+) and the component τ_3 is attributed to the ortho-positronium (*o*-Ps). This is the relevant quantity for the free volume and for the curing investigated here. A typical set of data is given in Fig. 2.

The plateau of the *o*-Ps lifetime τ_3 observed in the early stages of the lower temperature investigations shows that the mixture is still in its precursor state. The following sharp decrease in *o*-Ps lifetime indicates that the curing sets in. Finally, the cured state is achieved, which is indicated by reaching the saturation limit. One should note that in the course of the process τ_3 is decreasing,

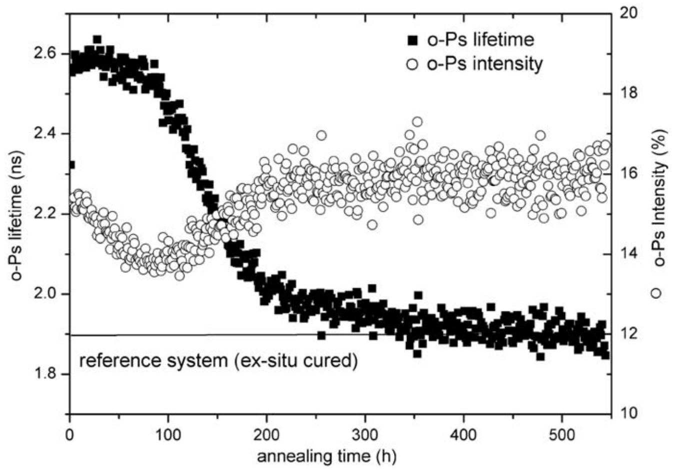

Fig. 2. *o*-Ps lifetime, dispersion and intensity as function of curing time at 50 °C. Also shown reference values (ex-situ cured @ 150 °C).

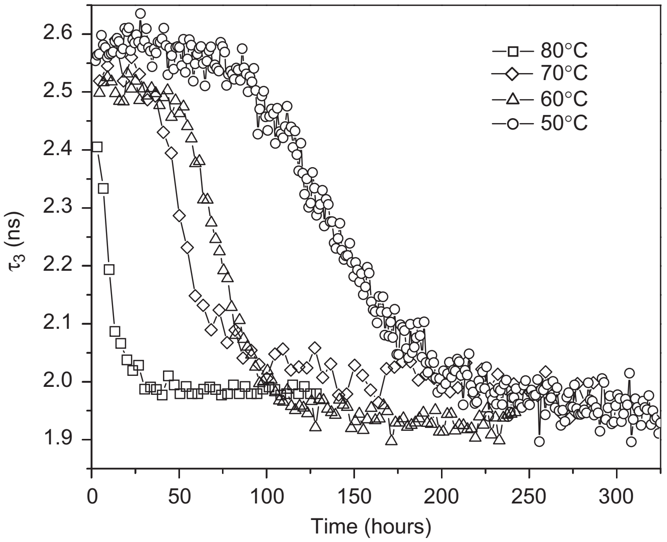

Fig. 3. *o*-Ps lifetime as a function of curing time for Epoxy/DICY precursors at 50, 60, 70 and 80 °C, respectively. Lines between data points only to guide the eye.

Table 1
List of the calculated Avrami parameters and curing times for a complete series of measurements.

T (°C)	τ_0 (ns)	τ_∞ (ns)	$t_{1/2}$ (h)	*n*	k
50	2,59	1,90	140,29	3,60	1,18E-08
60	2,53	1,91	73,33	3,63	1,12E-07
70	2,56	1,96	51,70	3,61	3,84E-07
80	2,41	1,98	6,07	3,67	1,89E-06

reflecting a decrease in hole size, as expected for shrinkage during curing [37]. The slight reduction in the intensity during curing may be an indication that there are reactive groups inhibiting Ps formation. The half-life of the curing process is also indicated.

Fig. 3 shows the *o*-Ps lifetime τ_3 as a function of time for different annealing temperatures of 50, 60, 70 and 80 °C as indicated. From this, it can be observed that curing time of one-component epoxy resin systems is temperature dependent i.e. the lower the temperature, the longer is the time required for similar stage of curing. The curing times as measured by PALS for the complete temperature range are summed up in Table 1. From this table it is also obvious that the higher the curing temperature, the higher the initial τ_0 as expected due to thermal expansion. We also remark that the final τ_∞ is similar for all samples and in the same range as for an externally high temperature cured sample.

3.2. Curing kinetics and Avrami equation

As discussed in the introduction, the *o*-Ps lifetime τ_3 is a measure for the degree *X* of transformation, i.e. the degree of curing. Hence, we derive from the PALS data

$$X = \frac{\tau - \tau_0}{\tau_\infty - \tau_0} \tag{4}$$

where τ_0 is the *o*-Ps lifetime of the uncured sample and τ_∞ the *o*-Ps lifetime of the fully cured sample (see Table 1). As also discussed in the introduction, the Avrami approach is limited to a finite fraction of transformed material, which reflects the boundary condition of undisturbed growth of the cross-linked phase being generated. In order to use the appropriate range for fitting in our data for the determination of the Avrami parameter we re-plotted these data according to Eq. (2) as shown in Fig. 4.

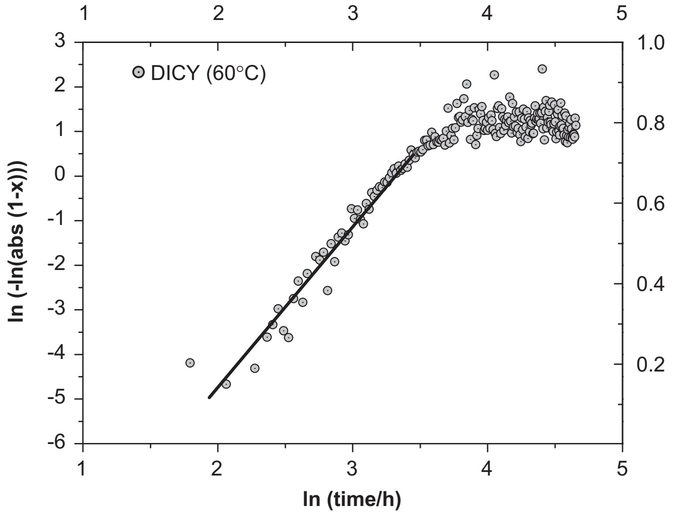

Fig. 4. Typical plot of $\ln[-\ln(1-X_t)]$ as a function of $\ln t$, according to Eq. (2). The straight line where '*n*' is the slope and '$\ln k$' is the intercept is obtained. For clarity reason only the plot of the curing temperature 60 °C is shown.

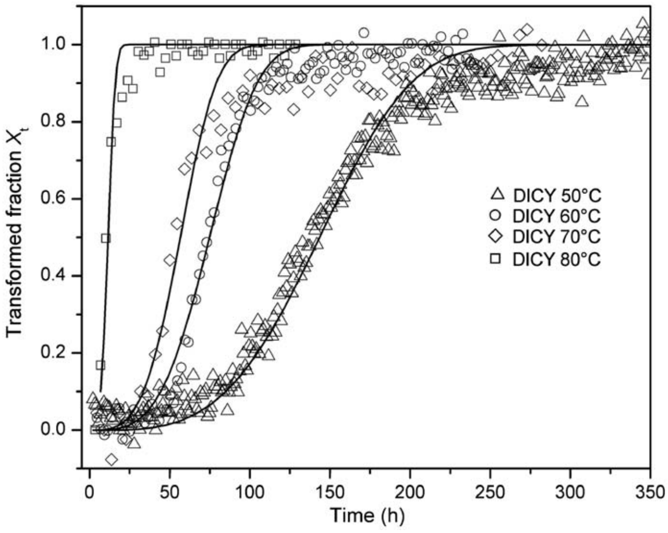

Fig. 5. Fit of JMAK kinetics with $n=3.6$ and appropriate reaction constants to the normalized PALS data. Note the small deviation at higher fractions which is interpreted to be due to deviations in growth behavior for nuclei/grains in contact.

We fitted a straight line through the linear range as indicated in Fig. 4. Evaluating the line parameters gives us the values of Avrami exponent 'n'. With $X_{t\,\max}$ being the range which yields a constant value of slope, the value obtained is n=3.6. The maximum for a reasonable fitting range of X_t=0.6 corresponds to the fact that for more volume transformed, the more nuclei come into contact competing for molecular species to be introduced into the growing polymer grains and the boundary condition of the Avrami equation (undisturbed growth) is not fulfilled any more.

In order to take into account the whole set of data, even in the early stages of reaction, we fitted the normalized PALS data vs. time of storage (see Fig. 5) again with Eq. (1), with a starting value of n=3.6. The fits are in good agreement but only for transformed fraction $X<0.7$. In particular for the high temperatures we included values for t=0 estimated from room temperature measurements in order to get reasonable starting values for τ_0. For all data measured so far the corresponding parameters are summarized in Table 1.

Obviously, it is found that the growth exponent is always the same within the error margin, indicating that the rate-determining step of the curing reaction does not change with temperature, a condition necessary for extrapolation of curing times to lower temperatures. If we assume that we can compare crystallization of an amorphous material with a chemical reaction here (cross-linking of an epoxy from the monomers) we can use the interpretation from the original derivation. A growth exponent of n=4 has been derived in the original papers under the boundary conditions of random nucleation and diffusional growth, whereas n=3 was derived from quenched in nuclei and diffusional growth [21]. This is in good accordance with the expectations of curing behavior in the present system. We may expect random nucleation of cross-linking centers via stimulated nucleation, triggered by action of the accelerator to occur simultaneously. Correspondingly, urone accelerators have been reported to act as initiators of polymerization reactions [5]. However, there is not only one molecular mechanism describing the reaction of the urone used in this work. After thermal activation, the comparatively reactive Dyhard® UR 500 accelerator may react in at least three ways. First of all, as an accelerator for the polyaddition reaction between DGEBA and DICY. Secondly, as a catalyst for the epoxy homopolymerisation reaction and finally, as a curative which is consumed during the polyreaction. The formulation used for the present investigations had not been optimised with respect to a consumption of all the DICY in the reactive mixture within the curing schedule applied.

Assuming thermally activated behavior, the reaction constant k can reasonably be plotted on a logarithmic scale versus the reciprocal temperature in order to verify an Arrhenius-type activation behavior (c.f. Fig. 6). The slope directly yields an activation energy of approximately 160 kJ/mol. This corresponds to the energy of the rate-limiting step of the reaction. This value is distinctly larger than the values usually given for reaction of various epoxides. (for data overview see e.g. S. Vyazovkin, N. Sbirrazzuoli, Macromol. Chem. Phys. 200 (1999) 2294). However, on the one hand these authors discuss in their paper that the calculated activation energies are model dependent; on the other hand, we do not only take into account the mere chemical reaction, but also the change in the mobility of molecular species due to increased cross-linking and transport effects in the system during curing.

With respect to the chemical reactions occurring during storage at room temperature as compared to curing at temperatures of up to 180 °C, it may be expected that according to the latency of the hardener DICY at room temperature its influence on the network forming reaction will increase with increasing temperatures [5]. Details of the respective reaction chemistry will be published separately [47]. Finally we extrapolated for the present system the shelf lifetime to T=20 °C and got an upper limit of 850 h (T=30 °C, t=500 h) which we could compare to nearly three months (2000 h) of storage of a sample at the same temperature. Hence, the model seems to be useful to give at least lower limits of storage stability.

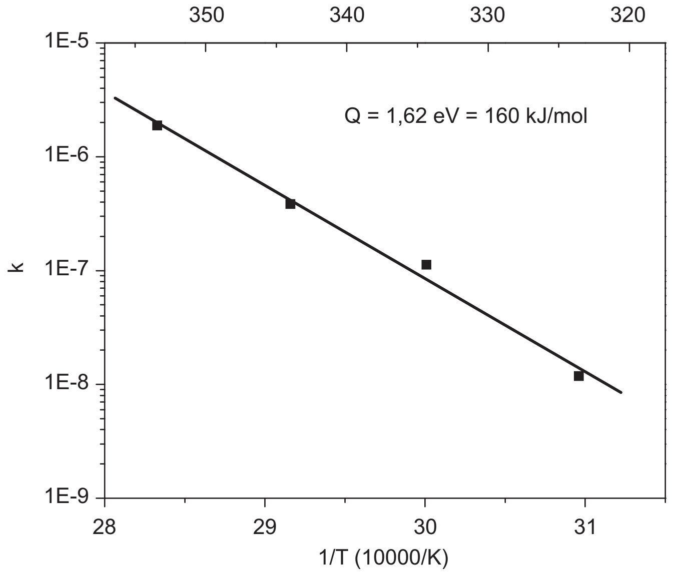

Fig. 6. Arrhenius plot of the reaction constant k vs reciprocal temperature demonstrating temperature independent activation energy. One should note that k has no reasonable units due to the fractional growth exponent. The plot may be applied for extrapolation of shelf life at a storage temperature of 20 °C.

4. Conclusion

For the first time, positron annihilation lifetime spectroscopy has been applied to in-situ observation of curing of a typical epoxide with high accuracy and time resolution. Based on transformed fractions of reactive species calculated from characteristic reference values for o-Ps lifetime τ_3 within the reactive system, shrinkage and a decreased molecular mobility within the forming network are monitored, following the chemical reactions limiting the storage stability of the formulations. Applying the Johnson–Mehl–Avrami–Kolmogorov equation to the curing data, appropriate kinetic parameters could be derived. Such proceeding allows to extrapolate the shelf life of one-component epoxy systems at room temperature.

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References

[1] May A, Clayton A. Epoxy resins: chemistry and technology, Second ed. New York: Marcel Dekker Inc; 1987 p. 794.

[2] Encyclopedia of polymer science and technology. Vol. 9, Epoxy resins. Wiley; 2004.
[3] Ellis B. In: Ellis B, editor. Chemistry and technology of epoxy resins, First ed. Blackie Academic & Professional; 1993. p. 72–116.
[4] Pascault JP, Sautereau H, Verdu J, Williams RJJ. Thermosetting polymers. New York: Marcel Dekker, Inc.; 2001.
[5] Zahir SA. Advanced Org Coat Sci Technol Ser 1982;4:83.
[6] Gilbert M, Schneider N, MacKnight W. Macromolecules 1991;24:360.
[7] Poisson N, Maazouz A, Sautereau H, Taha M, Gambert X. J Appl Polym Sci 1998;69:2487.
[8] Billaud C, Vandeuren M, Legras R, Carlier V. Appl Spectr 2002;56:1413.
[9] Dusek K. In: Dusek K, editor. Epoxy resins and composites III, advances in polymer science 78. Berlin: Springer-Verlag; 1986. p. 1–59.
[10] Macosko CW, Miller DR. Macromolecules 1976;199:206.
[11] Andjelić S, Mijović J, Bellucci F. J Polym Sci: Part B: Polym Phys 1998;36:641–53.
[12] Bockenheimer C, Valeske B, Possart W. Int J Adhes Adhes 2002;22:349.
[13] Mijović J, Sy JW. J Non-Cryst Solids 2002;307:679.
[14] Mijović J. J Non-Cryst Solids 1998;235:587.
[15] Mijović J, Winnie Yee CF. Macromolecules 1994;27:7287.
[16] Mijović J, Andjelic S, Fitz, Zurawsky W, Mondragon I, Bellucci F, et al. J Polym Sci: Part B Polym Phys 1996;34:379.
[17] Neurohr H, Possart W. 7th European Adhesion Conference EURADH 2008, DECHEMA, Freiburg, Germany, p. 542.
[18] Venkateshan K, Johari GP. J Chem Phys 2006;125:156101.
[19] Senturia SD, Sheppard Jr NF. In: Dusek K, editor. Advances in polymer science 80. Berlin: Springer-Verlag; 1986. p. 1–47.
[20] Johari GP, Wasylyshyn DA. J Polym Sci, Polym Phys 2000;38:122.
[21] Christian JW. The theory of transformations in metals and alloys part I, equilibrium and general kinetic theory. Pergamon; 1975.
[22] Sperling LH. Introduction to physical polymer science. Wiley; 2005.
[23] Zhang XH, Min YQ, Zhao H, Wan HM, Qi GR. J Appl Polym Sci 2006;100:3483.
[24] Cao M, Xie P, Jin Z, Zhang Y, Zhang R, Chung TS, et al. J Appl Polym Sci 2002; 85:873.
[25] Lu MG, Shim MJ, Kim SW. J Therm Anal Calorimetry 1999;58:701.
[26] Chen DZ, He PS, Pan LJ. Polym Test 2003;22:689.
[27] Pollard M, Kardos JL. Polym Eng Sci 1987;27(11):829–36.
[28] Kilburn D, Dlubek G, Pionteck J, Alam MA. Polymer 2006;47:7774.
[29] Bamford D, Dlubek G, Dommet G, Horing S, Lupke T, Kilburn D, et al. Polymer 2006;47:3486.
[30] Dlubek G, Shaikh MQ, Krause-Rehberg R, Paluch MJ. Chem Phys 2007;126: 024906.
[31] Kruse J, Kanzow J, Rätzke K, Faupel F, Heuchel M, Frahn J, et al. Macromolecules 2005;38:9638.
[32] Kruse J, Rätzke K, Faupel F, Sterescu DM, Stamatialis DF, Wessling MJ. Phys Chem B 2007;111(50):13914.
[33] Lima de Miranda R, Kruse J, Rätzke K, Fritsch D, Abetz V, Budd PM, et al. PSS—Rapid Res Lett 2007;5:190.
[34] Dlubek G, Pionteck J, Shaikh MQ, Hassan EM, Krause-Rehberg R. Phys Rev E 2007;75:021802.
[35] Kanzow J, Faupel F, Egger W, Sperr P, Kögel G, Wehlack C, et al. In: Possart W, editor. Adhesion—current research and applications. Wiley-VCH; 2005. p. 465.
[36] Suzuki T, Hayashi T, Ito Y. Mat Res Innovat 2001;4:273.
[37] Somoza A, Salgueiro W, Goyanes S, Ramos J, Mondragon I. Rad Phys Chem 2007;76:118.
[38] Mogensen OE. Positron annihilation in chemistry. Berlin, Heidelberg: Springer; 1995.
[39] Jean YC, Mallon PE, Schrader DM, editors. Principles and application of positron and positronium chemistry. Singapore: World Scientific; 2003.
[40] Tao SJ. J Chem Phys 1972;56:5499.
[41] Eldrup M, Lightbody D, Sherwood JN. Chem Phys 1981;63:51.
[42] Nakanishi H, Wang SJ, Jean YC. In: Sharma SC, editor. Positron annihilation studies of fluids. Singapore: Wold Scientific; 1988. p. 292.
[43] Suzuki T, Oki Y, Numajri M, Miura T, Kondo K, Oshima N, et al. J Radioanal Nucl Chem 1996;210(2):555.
[44] Suzuki T, Hayashi T, Ito Y. Mat Res Innovat 2001;4:273.
[45] Kanzow J, Schulze-Horn P, Kirschmann M, Zaporojtchenko V, Dolgner K, Wehlack C, et al. Appl Surf Sci 2005;239:227.
[46] Dyhard booklet by Degussa Fine Chemicals, 2005.
[47] Shaikh MQ, Rätzke K, Faupel F, Gaukler JC, Possart W, to be published.