



The catalytic influence of alumina nanoparticles on epoxy curing

J. Baller*, M. Thomassey, M. Ziehmer, R. Sanctuary

Laboratory for the Physics of Advanced Materials, University of Luxembourg, 162a avenue de la Faiencerie, L-1511 Luxembourg, Luxembourg

ARTICLE INFO

Article history:

Received 9 October 2010

Received in revised form 10 January 2011

Accepted 20 January 2011

Available online 26 January 2011

Keywords:

Nanocomposites

Thermosets

Curing

Catalysis

Hydroxyl

Epoxy

ABSTRACT

The curing process of diepoxide–triamine systems filled with water and untreated alumina nanoparticles has been investigated. The influence of both types of fillers on the curing process is very similar. This is reflected by a similar shape of the heat flow (HF) and specific heat capacity curves during curing. A catalytic effect of hydroxyl groups in the water and on the nanoparticles surfaces is made responsible for the observed curing behaviour. It turns out that the strength of the catalytic effect depends on the type of filler. The described influence of alumina nanoparticles on thermoset curing is looked upon as being representative for nanocomposites consisting of epoxy thermosets and metal oxide nanoparticles without surface treatment.

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1. Introduction

Composites consisting of epoxies as matrix material and alumina particles as fillers have been in the focus of many investigations (see e.g. [1–7]). A lot of these studies are directed towards application due to the technological importance of these systems [4–7]. The alumina particles are often functionalized at the surface [6,8], e.g. with silane–coupling agents [9,10] which leads to chemical interactions of the nanoparticles with the matrix material. The effect of untreated alumina nanoparticles on the curing process of the epoxy matrix is less frequently studied [11,12] despite the fact that these systems show interesting mechanical properties [7].

Even without alumina nanoparticles, the growth of macromolecules in two-component reactive systems is a very complex issue since chemical as well as physical processes are involved [13–15]. To start polymerization and/or crosslinking, the two components are usually intimately mixed. At this stage, chemical reactions as well as physical processes – flow or diffusion of reacting groups – start to take place. In principle, segregation of educts due to bad miscibility might occur in such systems [16]. The present study is however restricted to diepoxide–triamine systems. For these systems the assumption of a uniform distribution of reacting groups throughout the volume (without phase separation) is justified as long as the mixing process is effective (see the review article by Dušek [13]). As a consequence, reactions start everywhere in the samples directly after mixing the reactants. The curing

process is often studied under isothermal conditions [12,17,18]. In the first stages of isothermal curing, chemical reactions dominate the temporal evolution of the curing process [15,19–22]. At room temperature, two types of reactions can be found for diepoxide–triamine systems: epoxy groups reacting with primary or secondary amine groups [15,23]. Each of these reactions can be catalysed by –OH groups which are by-products of these reactions [15,20]. The catalysed version of these reactions has significantly higher reaction rates than the un-catalysed form [20]; it is dominating the curing process. Beside the hydroxyl groups, tertiary amines are also known to catalyse epoxy/amine reactions. Catalysis by –OH groups is mainly made responsible for the autocatalytic appearance of the epoxy/amine curing process [20]. In the later stages of isothermal curing, diffusion processes dominate the temporal evolution of network formation because the reactants mobility is significantly reduced by growing network fragments [12,17,18].

How is the crosslinking changed when nanoparticles are added to the epoxy matrix? It has to be expected that the situation becomes even more complex as all kind of interactions, physical as well as chemical, can take place at the nanoparticles surfaces. Untreated alumina nanoparticles have already been used as model systems for hydrophilic filler particles [12,24]. Calorimetric investigations depicted that these kinds of fillers have an accelerating effect on isothermal diepoxide–triamine curing at least at the beginning of the reaction [12]. This experimental finding was confirmed by rheological measurements [12]: the increase of zero shear viscosity caused by the epoxy network growth during isothermal curing is faster in the systems with alumina nanoparticles than in the pure epoxy systems. It is known that water also has an accelerating effect on the curing process of epoxy/amine systems [15].

* Corresponding author. Tel.: +352 466644 6755; fax: +352 466644 6329.
E-mail address: joerg.baller@uni.lu (J. Baller).

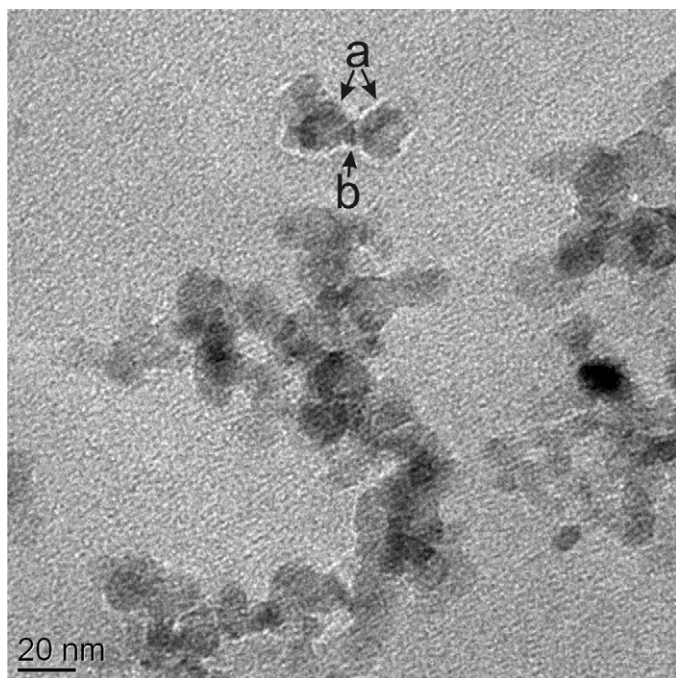


Fig. 1. TEM micrograph of a chemical aggregate of alumina nanoparticles inside cured epoxy resin ($x=0.07$); (a) primary particles and (b) sinter neck. Sample cut with microtome; TEM device: JEOL JEM 2011.

As already discussed above, the $-OH$ groups of the water have a catalytic effect on the chemical reaction. Thus, this study investigates isothermal curing of a diepoxide–triamine system under the influence of different amounts of water and compares the results to the results of the study of diepoxide–triamine systems filled with alumina nanoparticles.

2. Experimental

All resin nanocomposites have been obtained from a master batch of diglycidyl ether of bisphenol A (DGEBA) filled with 28.9 wt% of alumina nanoparticles. The DGEBA used is D.E.R. 331 obtained from Dow Plastics, Germany. The epoxy equivalent weight (EEW) of the pure system ($x=0$) was determined by wet analysis (DIN EN ISO 3001 [25]) to 190 g/mol. This value lies inside the range of 182–192 g/mol given by the producer. The alumina nanoparticles are AEROXIDE Alu C produced by Evonik Industries, Germany. According to the producer, the average diameter of the primary particles produced by noble gas condensation is about 13 nm.

During the production process, primary particles (circular structures in Fig. 1) sinter to irregularly shaped, chemically bonded aggregates (Fig. 1). This leads to nanoparticles with linear dimensions between 13 and 200 nm (Figs. 1 and 2). Since the nanoparticles are not surface treated and have hydrophilic character, physical (van der Waals) forces lead to the formation of agglomerates with sizes far beyond the nanoscale.

Both alumina nanoparticles (with agglomerates) and DGEBA resin were tempered at 400 K for 8 h and then mixed together. This guarantees that the epoxy resin is free of crystals and that some of the volatile contaminations of the nanoparticles surfaces are removed. To break the physically bonded agglomerates, the master batch was mechanically dispersed under vacuum at 369 K using a combined dissolver/bead mill (Torus Mill from VMA–Getzmann, Germany). This dispersion process leads to a relatively homogeneous distribution of the alumina aggregates (see Fig. 2). 28.9 wt% of alumina particles is the maximum amount which can be incorporated by using this type of dissolver/bead mill.

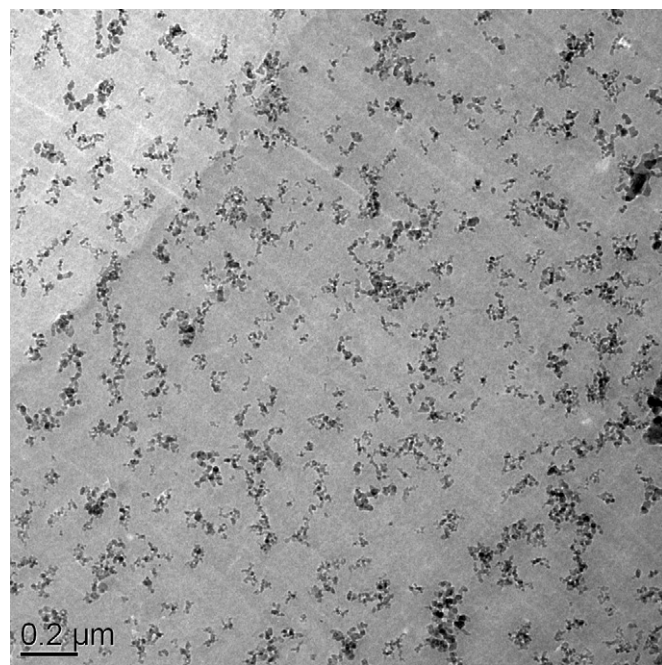


Fig. 2. TEM micrograph of cured alumina nanocomposites after mechanical dispersion ($x=0.07$); sample cut with microtome, TEM device: JEOL JEM 2011.

After mechanical dispersion, the master batch was diluted with DGEBA to get resin nanocomposites with four different concentrations x of alumina nanoparticles ($x = m_{Al_2O_3} / (m_{DER331} + m_{Al_2O_3})$): $x=0, 0.07, 0.12, 0.16$. Due to the fact that a higher concentration of nanoparticles yields an increased viscosity of the nanocomposites [12,24], this study is restricted to a maximum concentration of 16 wt% for the sake of easy sample handling.

For the samples containing water, DGEBA was mixed with three different concentrations x of purified water ($x=0.0025, 0.005, 0.01$) by using an advanced laboratory mixer (SpeedMixer from Hauschild, Germany). To ensure that the water content remained constant throughout the time needed for preparation and measurement, the sample weight was checked several times.

All samples were cured with diethylene triamine (DETA, purity >97%) obtained from Sigma/Aldrich, France. A ratio $s = m_{DETA} / m_{DER331} = 0.142 \pm 0.001$ was applied [24]. For each sample, the point in time $t_{cure} = 0$ represents the moment when the hardener (DETA) was injected into the samples at a temperature of 298.2 K; all components (samples, laboratory tools) used for sample preparation have also been put to 298.2 K by using a temperature-controlled chamber. Injection of hardener was followed by stirring the samples by hand for 5 min. Then, the samples were transferred to the calorimeters.

Isothermal measurements were performed at 298.15 K using temperature modulated differential scanning calorimetry (TMDSC) on a DSC823e (Mettler Toledo, Switzerland). A modulation period of 120 s along with a modulation amplitude of 0.5 K was used for all TMDSC measurements. Before sample preparation, the temperature of the calorimeters was stabilized at 298.15 K allowing the measurements to be started about 6–8 min after injecting the hardener into the resins. After a curing time of 10 h, the slope of the heat flow curves is almost zero (see Fig. 4). This allowed us to shift the heat flow curves vertically to zero to correct for different base lines.

For the determination of the overall reaction enthalpy, temperature scans with classical differential scanning calorimetry (DSC) have been performed on a DSC821e (Mettler Toledo, Switzerland). The calorimeter was set to the start temperature of 210 K before sample preparation. This ensured that the curing reaction was

immediately stopped after inserting the samples into the calorimeter. Subsequently, a temperature scan with a heating rate of 3 K/min was performed up to a temperature of 450 K. Comparable to the TMDSC measurements, the DSC scans were also started about 6–8 min after injecting the hardener into the resins.

In order to estimate the amount of reaction heat which occurred before inserting the samples into the calorimeter and starting the DSC and TMDSC measurements, we linearly extrapolated the isothermal measurements (Fig. 4) to $t_{\text{cure}} = 0$. It turned out that less than 1.3% of the total reaction heat during isothermal curing was released before the measurements have been started.

Calibration of temperature and heat flow was done for both calorimeters by using samples of water, indium, naphthalene and benzoic acid. Specific heat capacities were calibrated using an aluminum standard. The calorimetric measurements have been carried out with a sampling rate of one data point per second. In most of the following figures, symbols are only used for the sake of clarity; data points lie much closer and are represented by solid lines unless stated otherwise. Sample masses for DSC and TMDSC measurements were typically about 20 mg.

3. Results and discussion

3.1. Total reaction enthalpy

The total reaction enthalpy is the maximum heat of reaction which is produced during curing if the chemical reactions are not hindered by limited diffusion due to chemical vitrification. For the alumina nanocomposites under study these enthalpies have been determined by classical DSC scans from 210 to 450 K [12]. It has been shown that the total reaction enthalpy is reduced with increasing nanoparticle content. As an attempt to explain this experimental fact, the limitation of the reactants' mobility in the interphases around the nanoparticles was discussed [12]. Another reason for the reduction of the reaction enthalpy could be a diminishment of the number of functional groups by the presence of the nanoparticles or by the dispersion process. This should be reflected by an increase of the EEW. In a previous work [18], we used measurements of the EEW by the hydrogen bromide method [25,26] to investigate the influence of surface-treated silica nanoparticles on the reactivity of a similar epoxy resin. It could be shown that the EEW is not changed by the presence of silica particles. Application of the same method to the alumina nanocomposites failed due to the hydrophilic character of the alumina particles. Thus the question whether alumina takes influence on the EEW and is thus responsible for the reduced reaction enthalpy remained open [12]. For the present work, a different kind of wet analysis [25], the pyridinium chloride method [26,27] has been used; results are shown in Fig. 3.

The measured EEW is slightly higher than the calculated values ($\text{EEW}_{\text{calc}}(x) = (\text{EEW}_{\text{meas}}(x=0))/(1-x)$, see [18]). This means that the number of epoxy groups is lower due to the presence of the alumina nanoparticles and/or due to the preparation/dispersion process. Taking the total specific reaction enthalpy ΔH determined by classical DSC scans from ref. [12], one can first calculate the heat of reaction per gram epoxy [18]:

$$\Delta H^{\text{epoxy}} = \frac{(s - xs + 1)\Delta H}{s(1-x) + 1-x} \quad (1)$$

and then use the newly measured epoxy equivalent weight to calculate the reaction heat per mol of epoxy groups:

$$\Delta H^{\text{epoxy group}} = \Delta H^{\text{epoxy}}(1+s)\text{EEW} \quad (2)$$

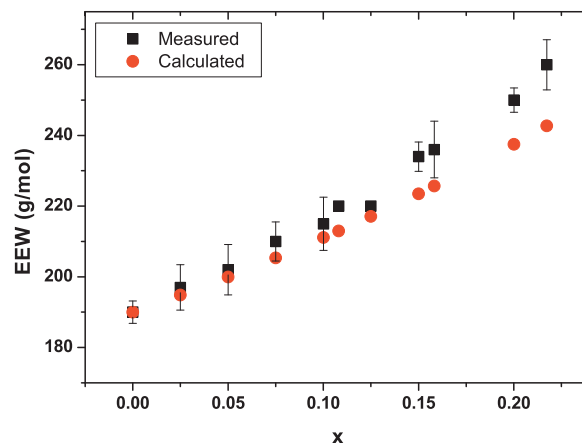


Fig. 3. Epoxy equivalent weight of the resin nanocomposites as a function of alumina particle concentration x .

The factor $(1+s)$ corrects for the amount of DETA in the epoxy part. Table 1 shows the results as a function of nanoparticle concentration.

The reaction enthalpy per mol of epoxy groups is close to a value of 110–118 kJ/mol found for a variety of epoxy/amine systems (see [15] and citations therein) and does not change by the incorporation of alumina nanoparticles. This means that the reduction of the specific reaction enthalpy which remained an open question in ref. [12] is solely caused by an increased EEW of the resins and thus neither by an influence of the alumina nanoparticles on the curing reaction nor by a reduction of the molecular mobility of the reactants by the filler particles.

The EEWs of epoxy resins with small amounts of purified water were also measured by the pyridinium chloride method. They did not show any difference to the values of pure epoxy resins.

3.2. Isothermal curing

In the following the influence of both water and alumina nanoparticles onto isothermal curing shall be examined by TMDSC. The heat flow signal recorded during these measurements is directly proportional to the reaction rate of the curing process. In order to compare the results for the different type of fillers, heat flow curves are displayed per mol epoxy groups by using the EEW values as described in Section 3.1. Fig. 4 shows the temporal evolution of the heat flow during isothermal curing for both fillers.

Several common features can be found in all of the curves, irrespective of the type of filler:

- (i) The higher the filler concentration, the higher the initial and the maximum reaction rate.
- (ii) The maximum in reaction rate occurs earlier with increasing filler concentration.
- (iii) The inflection point occurs earlier with increasing filler concentration.

Table 1

Reaction enthalpy per mol of epoxy groups for different mass concentrations x of alumina nanoparticles.

x	$\Delta H^{\text{epoxy group}}$ (kJ/mol)
0	123 ± 7
0.07	122 ± 7
0.12	123 ± 7
0.16	119 ± 8

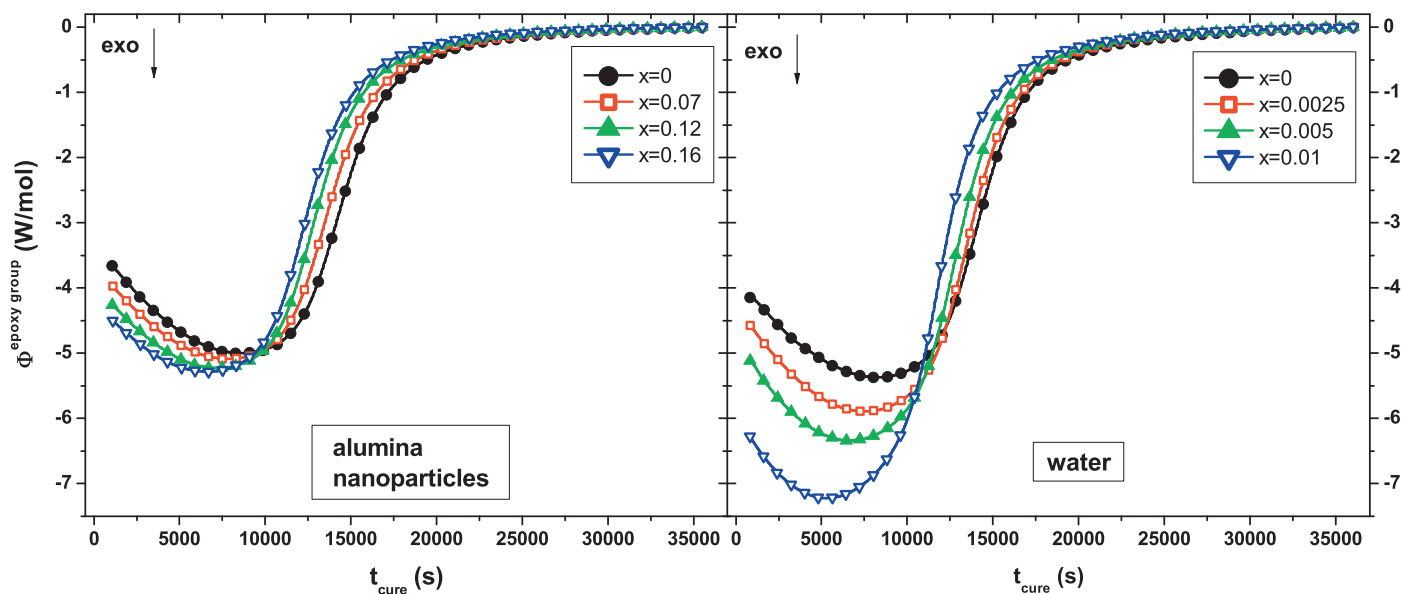


Fig. 4. Heat flow per mol of epoxy groups during isothermal cure at 298.15 K for different filler concentrations x .

All of the features can be attributed to a catalytic effect of the fillers. It is not astonishing that the strength of a catalytic effect is different for different fillers. This is illustrated in Fig. 5a which shows the dependence of the maximum heat flow on the concentration of the fillers. As expected, the slope is different for alumina and water fillers.

To better compare the heat flow curves shown in Fig. 4, they are scaled vertically by the factors shown in Fig. 5a. The result is shown in Fig. 6. All curves are similar. To verify if they have exactly the same shape, the inflection points $t_{IP}(x)$ have been determined (Fig. 5b). The point in time of the inflection point linearly shifts with filler concentration x .

The heat flow curves are shifted horizontally by the difference $\Delta t(x) = t_{IP}(x) - t_{IP}(0)$. The result is shown in Fig. 7. All curves do coincide, irrespective of the type of filler; a “master curve” could be created.

Beside the measurement of the heat flow curves related to the heat released by the chemical reaction, the TMDSC technique

allows for simultaneously determining the complex specific heat capacity [28,29]. Taking the $\Delta t(x)$ values determined from the heat flow curves, one can tentatively shift the curves of the modulus of the complex specific heat capacity shown in Fig. 8 by the same values $\Delta t(x)$.

The result is shown in Fig. 9. All c_p curves coincide. This is interesting because the c_p curves are deduced from dynamic measurements by applying linear response theory whereas the $\Delta t(x)$ values have been calculated from static DSC measurements. Moreover this result signifies that the point in time of the chemical glass transition $t_g(x)$ is shifted by the corresponding value of $\Delta t(x)$ determined by the inflection points of the heat flow curves. This reflects the mutual interference of dynamic/static physical properties of the growing network and the chemical reaction.

The fact that “master curves” of the specific heat capacity and the heat flow can be constructed for both water and alumina fillers suggests that the influence of both fillers on curing is very similar. Possible reactions between epoxy (resin, hardener or network

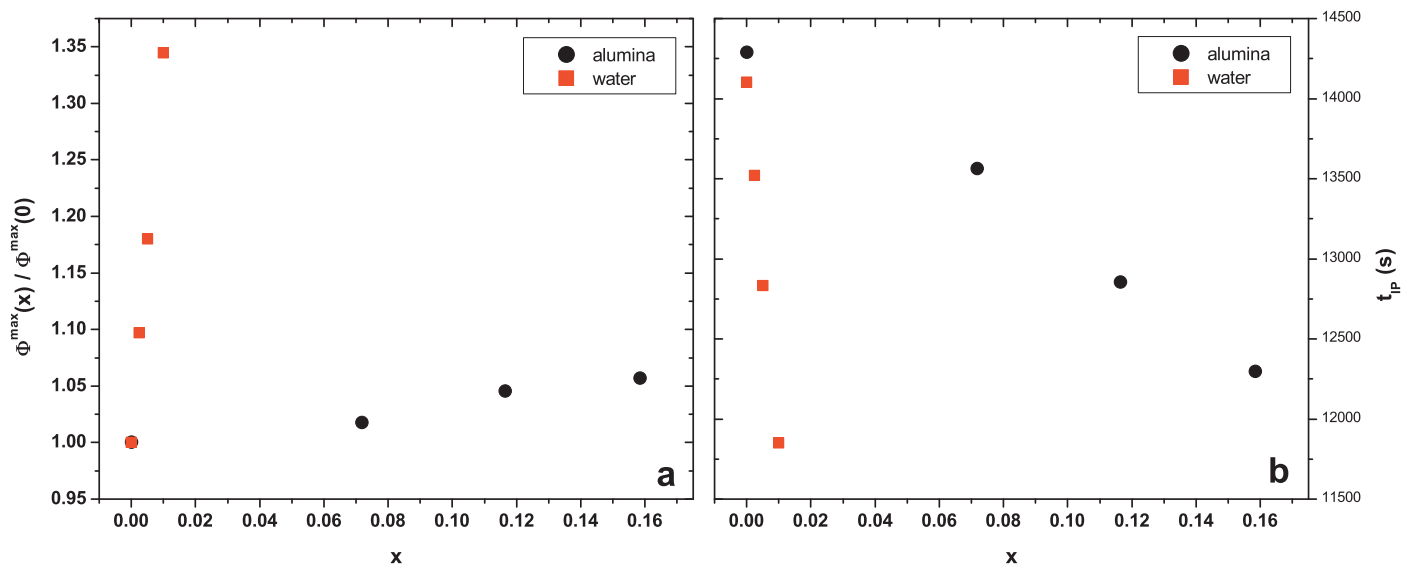


Fig. 5. Isothermal cure at 298.15 K: dependence on the filler concentrations of (a) maximum heat flow per mol of epoxy groups $\Phi^{max}(x)$ normalized with $\Phi^{max}(x=0)$. (b) Point in time t_{IP} of the inflection points of the heat flow curves.

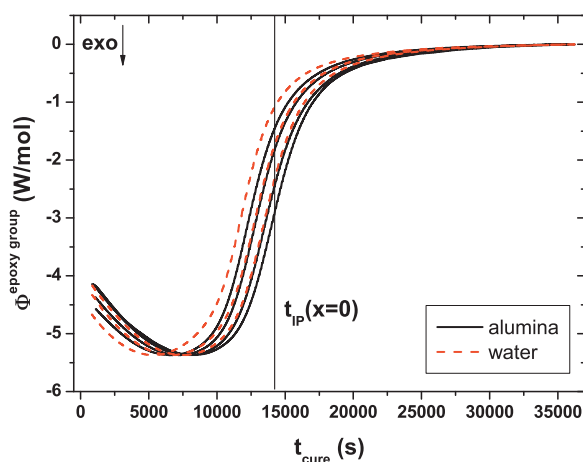


Fig. 6. Heat flow curves of Fig. 4 scaled vertically by the factors shown in Fig. 5a. $t_{IP}(0)$: inflection point of the heat flow curve for $x=0$.

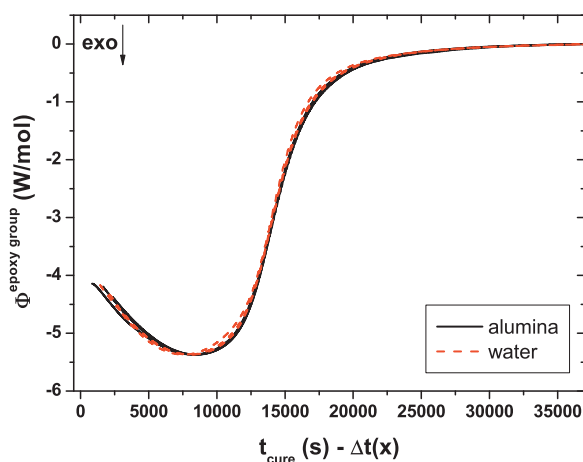


Fig. 7. Heat flow "master curve" during isothermal curing for all concentrations and both types of fillers.

fragments) and alumina or water fillers cannot be accompanied by considerable reaction enthalpies since the kinetics of the reactions seem to be unaffected by the fillers and due to the fact that it is possible to construct master curves for heat flow and specific heat capacity. Water is known to catalyse the epoxy/amine curing reaction [15]. We therefore conclude that the –OH groups

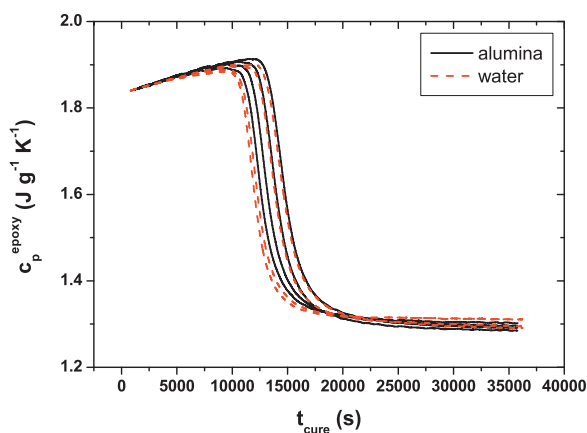


Fig. 8. Modulus of the complex specific heat capacity per gram epoxy of the nanocomposites during isothermal curing at 298.15 K with different weight percent x of fillers (alumina measurements taken from [12]).

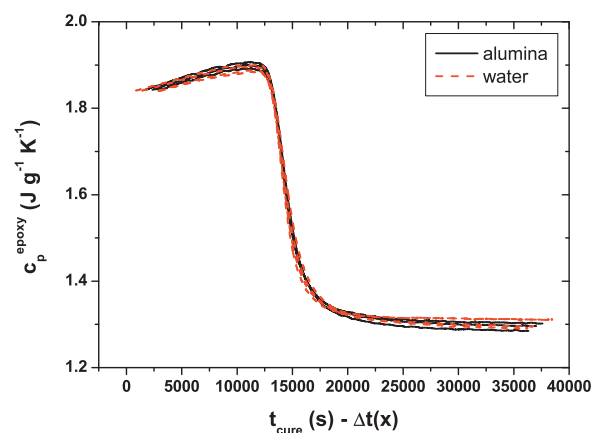


Fig. 9. "Master curve" of the modulus of the complex specific heat capacity per gram epoxy during isothermal curing at 298.15 K with different type and weight percents of fillers.

on the nanoparticles surfaces have the same effect as the –OH groups in the water. It is only the strength of the catalytic effect that depends on the type of filler. Since there is no mechanistic model [23,30,31] yet available for epoxy curing in the presence of water or alumina nanoparticles, the identification of an experimental parameter such as the maximum heat flow (see Fig. 5a) as measure for the strength of the catalytic effect is not possible at the moment. This will be subject of further studies. Prior examinations of the relaxation dynamics of uncured epoxy/alumina nanocomposites [24] gave hints for a physical interaction between alumina nanoparticles and epoxy oligomers. It was shown that the mobility of the epoxy oligomers is slowed down by the presence of the alumina nanoparticles. It was expected that these interactions should also influence the curing process, but it turns out that the catalytic effect is dominating curing.

4. Conclusions

Network formation of epoxy thermosets filled with different amounts of water and alumina nanoparticles has been investigated. A very similar behaviour of the temporal evolution of heat flow and specific heat capacity during isothermal curing of DGEBA/DETA composites was found; master curves for these thermal properties could be created for both types of fillers. The occurrence of the master curves is attributed to a similar influence of water and alumina nanoparticles on the curing process. The –OH groups in the water and at the surface of the alumina nanoparticles act as catalysts. It is believed that the same behaviour can be found for many other types of hydrophilic nanoparticles and that the nanocomposites examined in the present work can be looked upon as model systems for epoxy thermosets with untreated metal oxide nanoparticles. Further studies will use mechanistic modeling to describe the epoxy/amine reaction in the presence of hydrophilic nanoparticles and water.

Acknowledgment

This work was kindly supported by the National Research Fund, Luxembourg.

References

- [1] B.N. Dudkin, G.G. Zainullin, P.V. Krivoschapkin, E.F. Krivoschapkina, M.A. Ryazanov, Influence of nanoparticles and nanofibers of aluminum oxide on the properties of epoxy composites, *Glass Physics and Chemistry* 34 (2008) 187–191.

- [2] M. Akatsuka, Y. Takezawa, S. Amagi, Influences of inorganic fillers on curing reactions of epoxy resins initiated with a boron trifluoride amine complex, *Polymer* 42 (2001) 3003–3007.
- [3] S. Zhao, L.S. Schadler, R. Duncan, H. Hillborg, T. Auletta, Mechanisms leading to improved mechanical performance in nanoscale alumina filled epoxy, *Composites Science and Technology* 68 (2008) 2965–2975.
- [4] C.H. Chen, J.Y. Jian, F.S. Yen, Preparation and characterization of epoxy/gamma-aluminum oxide nanocomposites, *Composites Part A: Applied Science and Manufacturing* 40 (2009) 463–468.
- [5] Y.A. Gorbatkina, V.G. Ivanova-Mumzhieva, T.M. Ul'yanova, Adhesiveness of an epoxy oligomer filled with aluminum oxide powders, *Polymer Science Series C* 49 (2007) 131–134.
- [6] Z.H. Guo, T. Pereira, O. Choi, Y. Wang, H.T. Hahn, Surface functionalized alumina nanoparticle filled polymeric nanocomposites with enhanced mechanical properties, *Journal of Materials Chemistry* 16 (2006) 2800–2808.
- [7] B. Wetzel, F. Hauptert, M.Q. Zhang, Epoxy nanocomposites with high mechanical and tribological performance, *Composites Science and Technology* 63 (2003) 2055–2067.
- [8] Q.L. Ji, M.Q. Zhang, M.Z. Rong, B. Wetzel, K. Friedrich, Tribological properties of surface modified nano-alumina/epoxy composites, *Journal of Materials Science* 39 (2004) 6487–6493.
- [9] D.J. Kim, P.H. Kang, Y.C. Nho, Characterization of mechanical properties of gamma Al_2O_3 dispersed epoxy resin cured by gamma-ray radiation, *Journal of Applied Polymer Science* 91 (2004) 1898–1903.
- [10] E. Vassileva, K. Friedrich, Epoxy/alumina nanoparticle composites I. Dynamic mechanical behavior, *Journal of Applied Polymer Science* 89 (2003) 3774–3785.
- [11] A. Omrani, L.C. Simon, A.A. Rostami, The effects of alumina nanoparticle on the properties of an epoxy resin system, *Materials Chemistry and Physics* 114 (2009) 145–150.
- [12] R. Sanctuary, J. Baller, B. Zielinski, N. Becker, J.K. Kruger, M. Philipp, U. Muller, M. Ziehmer, Influence of Al_2O_3 nanoparticles on the isothermal cure of an epoxy resin, *Journal of Physics: Condensed Matter* 21 (2009) 035118.
- [13] K. Dušek, Network formation in curing of epoxy resins, *Advances in Polymer Science* 78 (1986) 1–59.
- [14] B.G. Min, Z.H. Stachurski, J.H. Hodgkin, Cure kinetics of elementary reactions of a DGEBA/DDS epoxy resin: 1. Glass transition temperature versus conversion, *Polymer* 34 (1993) 4908–4912.
- [15] B.A. Rozenberg, Kinetics, thermodynamics and mechanism of reactions of epoxy oligomers with amines, *Advances in Polymer Science* 75 (1986) 113–165.
- [16] K. Dusek, J. Plestil, F. Lednicky, S. Lunak, Are cured epoxy-resins inhomogeneous, *Polymer* 19 (1978) 393–397.
- [17] G. Van Assche, A. Van Hemelrijck, H. Rahier, B. Van Mele, Modulated differential scanning calorimetry: isothermal cure and vitrification of thermosetting systems, *Thermochimica Acta* 268 (1995) 121–142.
- [18] J. Baller, N. Becker, M. Ziehmer, M. Thomassey, B. Zielinski, U. Müller, R. Sanctuary, Interactions between silica nanoparticles and an epoxy resin before and during network formation, *Polymer* 50 (2009) 3211–3219.
- [19] I.T. Smith, The mechanism of the crosslinking of epoxide resins by amines, *Polymer* 2 (1961) 95.
- [20] J. Mijovic, J. Wijaya, Reaction-kinetics of epoxy/amine model systems – the effect of electrophilicity of amine molecule, *Macromolecules* 27 (1994) 7589–7600.
- [21] S. Paz-Abuin, A. Lopez-Quintela, M.P. Pellin, M. Varela, P. Prendes, Autoacceleration and inhibition: free volume epoxy-amine kinetics, *Journal of Polymer Science Part A: Polymer Chemistry* 36 (1998) 1001–1016.
- [22] B.G. Min, Z.H. Stachurski, J.H. Hodgkin, Cure kinetics of elementary reactions of a DGEBA/DDS epoxy-resin. 1. Glass-transition temperature versus conversion, *Polymer* 34 (1993) 4908–4912.
- [23] V.L. Zvetkov, Mechanistic modeling of the epoxy-amine reaction – model derivations, *Thermochimica Acta* 435 (2005) 71–84.
- [24] R. Sanctuary, J. Baller, J.K. Krüger, D. Schaefer, R. Bactavatchalou, B. Wetzel, W. Possart, P. Alnot, Complex specific heat capacity of two nanocomposite systems, *Thermochimica Acta* 445 (2006) 111–115.
- [25] H. Lee, K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
- [26] J.L. Jungnickel, E.D. Peters, A. Polgar, F.T. Weiss, Determination of the alpha-epoxy group, in: *Organic Analysis*, Interscience, New York, 1953, pp. 127–154.
- [27] B. Dobinson, W. Hofmann, B.P. Stark, *The Determination of Epoxide Groups*, Pergamon Press, Oxford, 1969.
- [28] M. Reading, D. Elliott, V.L. Hill, A new approach to the calorimetric investigation of physical and chemical-transitions, *Journal of Thermal Analysis* 40 (1993) 949–955.
- [29] J.E.K. Schawe, About the changes of heat capacity, glass transition temperature and relaxation time during the polymerization reaction of thermosetting systems, *Thermochimica Acta* 391 (2002) 279–295.
- [30] C.C. Riccardi, F. Fraga, J. Dupuy, R.J.J. Williams, Cure kinetics of diglycidylether of bisphenol A-ethylenediamine revisited using a mechanistic model, *Journal of Applied Polymer Science* 82 (2001) 2319–2325.
- [31] M. Blanco, M.A. Corcuera, C.C. Riccardi, I. Mondragon, Mechanistic kinetic model of an epoxy resin cured with a mixture of amines of different functionalities, *Polymer* 46 (2005) 7989–8000.