

Influence of aluminosilsesquioxane on epoxy resin curing process (*Rapid Communication*)

Danuta Matykiewicz^{1,*}, Beata Dudziec², Tomasz Sterzyński¹

DOI: dx.doi.org/10.14314/polimery.2014.855

Abstract: The curing process of epoxy resin Epidian 6 with bis(heptaisooctylaluminosilsesquioxane) (AIPOSS) was investigated. Curing kinetics of the composition was studied with differential scanning calorimetry (DSC) at different heating rates. Activation energy (E_a) was calculated based on Kissinger method. Fourier transform infrared (FT-IR) spectroscopy was used to monitor the development of curing process and chemical changes in the epoxy matrix. The research results indicated that AIPOSS may be used as a curing agent for epoxy resins.

Keywords: epoxy resin, aluminosilsesquioxanes, curing kinetics, epoxy resin curing.

Wpływ aluminosilseskwioksanu na proces utwardzania żywicy epoksydowej

Streszczenie: Zbadano proces utwardzania żywicy epoksydowej Epidian 6 za pomocą bis(heptaizooktyloglinosilseskwioksanu) (AIPOSS). Kinetykę procesu sieciowania oceniano na podstawie wyników pomiarów metodą różnicowej kalorymetrii skaningowej (DSC) z zastosowaniem różnych szybkości ogrzewania. Wartości energii aktywacji (E_a) procesu sieciowania żywic różniących się zawartością AIPOSS wyznaczono metodą Kissingera. Postęp procesu sieciowania oraz zachodzące zmiany chemiczne w matrycy epoksydowej badano za pomocą spektroskopii w podczerwieni z transformatą Fouriera (FT-IR). Wyniki badań potwierdziły, że AIPOSS może być stosowany jako środek utwardzający do żywic epoksydowych.

Słowa kluczowe: żywica epoksydowa, aluminosilseskwioksany, kinetyka sieciowania, utwardzanie żywic epoksydowych.

The modification of commercial polymeric materials for different applications have recently been gaining ground among scientists as the main focus of scientific research [1–3]. Epoxy resins are an important group of thermosetting materials frequently used as a matrix for composites in the aviation, automotive and construction industry [4, 5]. The main advantages of epoxy composites are: good mechanical and thermal properties as well as high chemical resistance. In order to obtain specific properties different hardeners, accelerating agents and reinforcing fibers have been introduced into epoxy matrix [6, 7].

The polyhedral oligomeric silsesquioxanes (POSS) are inorganic-organic modifiers, made of cube-octameric frameworks with silica-like core and surrounded by eight organic functional groups [8, 9]. The wide range of

functionalization possibilities for these modifiers led to the increase of their application in polymer processing [10, 11]. They may be added to epoxy compositions as modifiers, reinforcement, processing aids and flame retardants [12, 13]. Metal functionalized silsesquioxanes can be applied as flame retardants, cure promoters, catalysts, initiators of the ring-opening and the living polymerizations [14–19]. In our previous works the methods of curing epoxy resin with aluminosilsesquioxanes and thermomechanical properties of the modified epoxy casts were presented [20–23].

The aim of this paper was to study the influence of bis(heptaisooctylaluminosilsesquioxane), applied as a curing agent, on the epoxy resin curing process. Curing kinetics of the composition was studied using differential scanning calorimetry (DSC) at different heating rates. Activation energy was calculated based on Kissinger method. Fourier transform infrared (FT-IR) spectroscopy was used to monitor chemical changes in epoxy matrix after the curing process.

EXPERIMENTAL PART

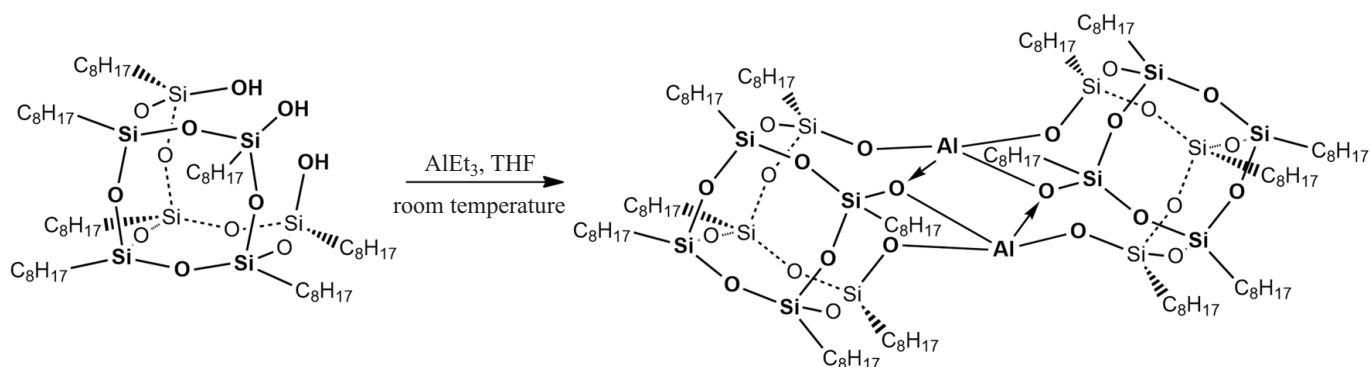
Materials

The following materials were used in the investigation:

¹ Poznan University of Technology, Institute of Materials Technology, Polymer Processing Division, Piotrowo 3, 61-138 Poznań, Poland.

² Adam Mickiewicz University, Faculty of Chemistry, Department of Organometallic Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland.

* Author for correspondence; e-mail: danuta.chmielewska@put.poznan.pl



Scheme A

– epoxy resin Epidian 6 (EP6) based on bisphenol A (BPA, epoxy number $EN = 0,510–0,540$, viscosity $\eta = 10–15 \text{ Pa} \cdot \text{s}$, density $d = 1.16 \text{ g/cm}^3$), produced by Chemical Works Organika-Sarzyna (Poland);

– curing agent which was bis(heptaisooctylaluminosilsesquioxane) (AlPOSS, $\text{C}_{112}\text{H}_{238}\text{Al}_2\text{O}_{24}\text{Si}_{14}$, synthesized in Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Poland).

The structure and synthesis route of AlPOSS is shown in Scheme A. AlPOSS was prepared according to the procedure analogical to that described by Jones *et al.* [17].

The synthesis was carried out under argon using standard Schlenk-line and vacuum techniques. The chemicals required for reactions were obtained from Sigma-Aldrich. All solvents and liquid reagents were dried and distilled under argon prior to use.

The NMR characterization of AlPOSS was as follows:

– ^1H NMR (400 MHz, CDCl_3 , 300 K) δ (ppm) = 0.3 (s, 6H SiCH₃), 0.54–0.59, 0.74–0.78, 0.95, 1.05, 1.19, 1.30–1.34, 1.85i (m, i-Oc);

– ^{13}C NMR (100.6 MHz, CDCl_3) δ (ppm) = 22.68, 23.69, 24.96, 25.05–25.60, 29.68, 30.31, 31.17, 38.13, 54.50;

– ^{29}Si NMR (79.5 MHz, CDCl_3) δ (ppm) = -67.26, -68.23, -68.62, -70.85.

To prepare a reference epoxy sample, another curing agent, Z1 (triethylenetetramine), also produced by Organika-Sarzyna, was used.

Samples preparation

AlPOSS was dissolved in tetrahydrofuran at the mass ratio 1:1 in order to achieve high dispersion in the epoxy matrix. The epoxy resin with the appropriate amount of AlPOSS mass was mixed with the use of a high speed mechanical stirrer to produce homogeneous dispersion which was devolatilized for 15 min. The samples of resin with 5, 10 and 15 wt % of AlPOSS were designated with symbols EP6_5AlPOSS, EP6_10AlPOSS and EP6_15AlPOSS, respectively. The reference sample was prepared from epoxy resin Epidian 6 (EP6) cured with commercial Z1 curing agent (13 parts of Z1 per 100 parts of EP6 by weight), in the same way.

Methods of testing

The DSC measurements were performed using Phoenix DSC 204 F1 Netzsch, in standard conditions. Hence, samples of about 10 mg closed in aluminum crucible were heated from 20 to 350 °C under nitrogen atmosphere with heating rates of 5, 10, 20 or 40 °C/min. The DSC measurements were carried out immediately once the mixing procedure of the components was completed. As a result, DSC curves of the curing process were registered.

Curing kinetics and the activation energy were determined using the Kissinger method [24–26] according to the equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \text{const.} - \frac{E_a}{RT_p} \quad (1)$$

where: β – the heating rate, T_p – the temperature corresponding to the peak on the DSC curve obtained for a given value β , R – the gas constant, E_a – the activation energy.

The values of E_a were determined as values of slope coefficient of a straight line described by eq. (1).

The FT-IR analysis was conducted for the samples post-cured at 180 °C with Fourier transform spectrometer Vertex 70, at the ambient temperature (23 °C). The samples were mixed with KBr powder and pressed into pellets. In all cases a total of 64 scans at 1 cm^{-1} resolution were used to record the spectra.

RESULTS AND DISCUSSION

The representative DSC curves of the epoxy compositions cured with AlPOSS are presented in Fig. 1. The presence of exothermic peak on DSC curves confirms that the curing reaction takes place. The values of T_p for all compositions corresponding to various β are collected in Table 1. These results show that an increase in AlPOSS content causes a decrease in T_p . The curing conditions are dependent on the types of pendant groups in POSS and miscibility between the epoxy matrix and silsesquioxane. The values of T_p for epoxy compositions cured with aluminosilsesquioxane with isooctyl substituents (AlPOSS)

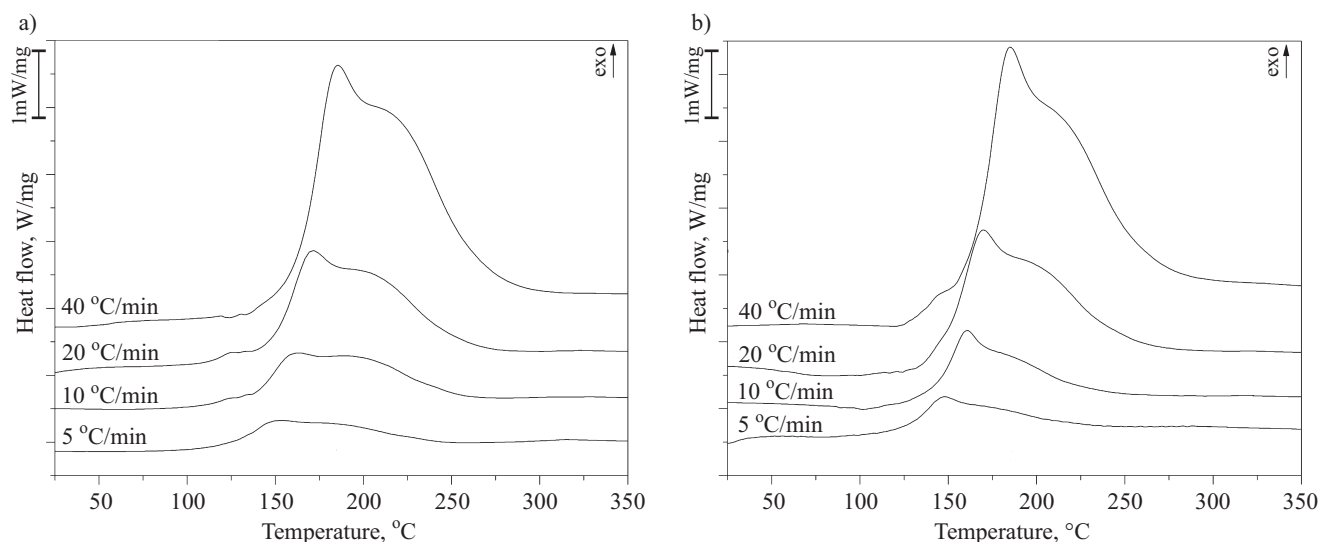


Fig. 1. DSC curing curves of epoxy resins: a) EP6_10AlPOSS, b) EP6_15AlPOSS

were higher than the one for epoxy compositions cured with aluminosilsesquioxane with phenyl substituents investigated previously [21, 22]. Moreover, epoxy resin with AlPOSS was not reactive in the ambient temperature compared to epoxy resin with bis(heptaphenylaluminosilsesquioxane) [21, 22]. Therefore, epoxy resin with bis(heptaisooctylaluminosilsesquioxane) can be stored at the room temperature.

Table 1. Values of temperature corresponding to exothermic peaks of DSC curves (T_p) and activation energy (E_a) calculated based on Kissinger method

Symbol of sample	Heating rate, °C/min				E_a kJ/mol
	5	10	20	40	
	T_p , °C				
EP6	89	101	114	128	56.6
EP6_5AlPOSS	206	221	234	250	90.9
EP6_10AlPOSS	153	160	171	186	94.7
EP6_15AlPOSS	151	159	170	185	83.4

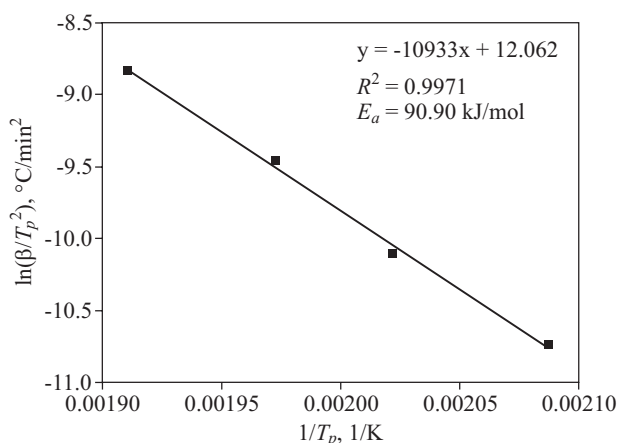


Fig. 2. Plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ of investigated EP6_5AlPOSS epoxy composition

The representative plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ of the investigated EP6_5AlPOSS composition is presented in Fig. 2. Based on Kissinger method, E_a values were calculated from the slope of the lines showed in Fig. 2 and the obtained results are collected in Table 1. E_a values for epoxy resin compositions cured with AlPOSS were higher than for the resin cured with amine. It is worth noticing that E_a decreased significantly for the sample containing 15 wt % of AlPOSS. Moreover the values of T_p decreased with the increase of AlPOSS content. Therefore, it can be concluded that the curing process of epoxy system with AlPOSS can be effectively initiated by addition of 15 wt % of this modifier.

AlPOSS, which is considered as polymeric Lewis acids, is first prepared and described by Feher *et al.* [27–29]. These modifiers can be applied as catalysts and promoters of curing reactions. The spectra of all the com-

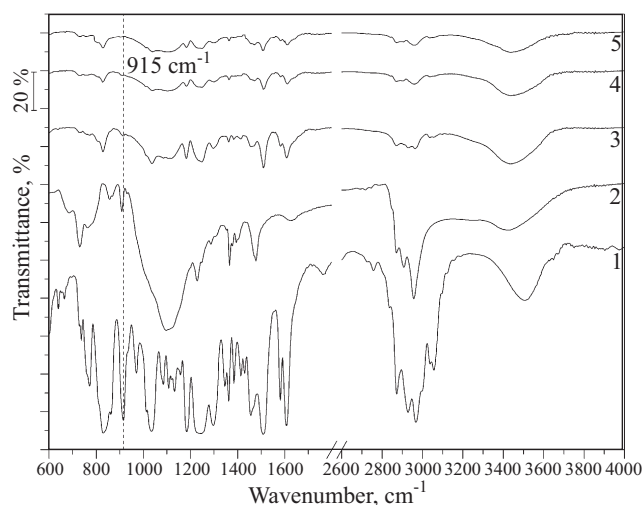


Fig. 3. Comparison of IR spectra for: 1 – uncured epoxy resin, 2 – AlPOSS, 3 – EP6_5AlPOSS, 4 – EP6_10AlPOSS, 5 – EP6_15AlPOSS

pounds and casts are presented in Fig. 3. For AIPOSS a characteristic peak at 1100 cm^{-1} attributed to the Si-O-Si bond was noted [12]. The peak at 915 cm^{-1} , corresponding to the C-O deformation of the oxirane group, was used to follow the development of the epoxy group. The disappearance of this peak in all samples cured with AIPOSS proved the occurrence of curing reaction and network formation.

CONCLUSIONS

The kinetics of the curing process of epoxy resin (Epidian 6) with bis(heptaisooctylaluminosilsesquioxane) (AIPOSS) was investigated by DSC method at different heating rates. On the basis of the Kissinger method activation energy of curing was determined. The results proved that the activation energy for curing process activated with AIPOSS was higher than for the process activated with amine. This phenomenon may stem from the silsesquioxane cube-octameric structures. The occurrence of the curing process of epoxy resin with AIPOSS was confirmed by FT-IR analysis. The results of the research indicated that bis(heptaisooctylaluminosilsesquioxane) may be used as a curing agent for epoxy resins, as long as the curing reaction takes place at high temperature.

This work was supported by the European Regional Development Fund under the Innovative Economy Operational Programme for 2007–2013 (Project No. UDA-POIG.01.03.01-30-173/09).

REFERENCES

- [1] Hardis R., Jessop J.L.P., Peters F.E., Kessler M.R.: *Composites, Part A* **2013**, 49, 100. <http://dx.doi.org/10.1016/j.compositesa.2013.01.021>
- [2] Czarnecka-Komorowska D., Mencil K.: *Przem. Chem.* **2014**, 93, 392.
- [3] Kelar K., Olejniczak J., Barczewski M.: *Przem. Chem.* **2013**, 92, 347.
- [4] Kushizaki Y., Yamada T., Igarashi M., Gamou M.: *J. Polym. Eng.* **2007**, 27, 313. <http://dx.doi.org/10.1515/POLYENG.2007.27.4.313>
- [5] Chmielewska D., Pacyna M., Sterzyński T.: *Przem. Chem.* **2014**, 93, 90.
- [6] Mąka H., Spychaj T., Kowalczyk K.: *J. Appl. Polym. Sci.* **2014**, 131, 5197. <http://dx.doi.org/10.1002/app.40401>
- [7] Włodarska M., Maj A., Mossety-Leszczak B., Bak G.W., Galina H., Okrasa L., Izdebski M.: *J. Polym. Res.* **2013**, 20, 227. <http://dx.doi.org/10.1007/s10965-013-0227-0>
- [8] Cho H., Liang K., Chatterjee S., Pittman Jr.C.U.: *J. Inorg. Organomet. Polym. Mater.* **2005**, 15, 541. <http://dx.doi.org/10.1007/s10904-006-9008-0>
- [9] Pielichowski K., Njuguna J., Janowski B., Pielichowski J.: *Adv. Polym. Sci.* **2006**, 201, 225. http://dx.doi.org/10.1007/12_077
- [10] Hao W., Hu J., Chen L., Zhang J., Xing L., Yang W.: *Polym. Test.* **2011**, 30, 355. <http://dx.doi.org/10.1016/j.polymertesting.2011.02.005>
- [11] Franchini E., Galy J., Gerard J.-F., Tabuani D., Medici A.: *Polym. Degrad. Stab.* **2009**, 94, 1728. <http://dx.doi.org/10.1016/j.polymdegradstab.2009.06.025>
- [12] Liu H., Zheng S., Nie K.: *Macromolecules* **2005**, 38, 5088. <http://dx.doi.org/10.1021/ma0504318>
- [13] Matejka L., Murias P., Pleštil J.: *Eur. Polym. J.* **2012**, 48, 260. <http://dx.doi.org/10.1016/j.eurpolymj.2011.11.009>
- [14] Murias P., Maciejewski H., Galina H.: *Eur. Polym. J.* **2012**, 48, 769. <http://dx.doi.org/10.1016/j.eurpolymj.2012.01.009>
- [15] Zhang Z., Liang G., Wang X.: *Polym. Bull.* **2007**, 58, 1013. <http://dx.doi.org/10.1007/s00289-007-0732-6>
- [16] Di Iulio C., Jones M.D., Mahon M.F., Apperley D.C.: *Inorg. Chem.* **2010**, 49, 10 232. <http://dx.doi.org/10.1021/ic101809r>
- [17] Jones M.D., Davidson M.G., Keir C.G., Wooles A.J.: *Dalton Trans.* **2008**, 3655. <http://dx.doi.org/10.1039/B805274C>
- [18] Fina A., Abbenhuis H.C.L., Tabuani D., Camino G.: *Polym. Degrad. Stab.* **2006**, 91, 2275. <http://dx.doi.org/10.1016/j.polymdegradstab.2006.04.014>
- [19] China Pat. 103387669 A (2013).
- [20] *Pol. Pat. Appl.* 407 052 (2014).
- [21] *Pol. Pat.* 217 788 (2014).
- [22] Chmielewska D., Barczewski M., Sterzyński T.: *Polimery* **2013**, 58, 270. <http://dx.doi.org/10.14314/polimery.2013.270>
- [23] Chmielewska D., Sterzyński T., Dudzic B.: *J. Appl. Polym. Sci.* **2014**, 131, 8444. <http://dx.doi.org/10.1002/app.40672>
- [24] Kissinger H.M.: *Anl. Chem.* **1957**, 29, 1702.
- [25] Hao W., Hu J., Chen L., Zhang J., Xing L., Yang W.: *Polym. Test.* **2011**, 30, 349. <http://dx.doi.org/10.1016/j.polymertesting.2011.02.005>
- [26] Herman Teo J.K., Teo K.C., Pan B., Xiao Y., Lu X.: *Polymer* **2007**, 48, 5671. <http://dx.doi.org/10.1016/j.polymer.2007.07.059>
- [27] Feher F.J., Budzichowski T.A., Weller K.J.: *J. Am. Chem. Soc.* **1989**, 111, 7288.
- [28] Abbenhuis H., van Herwijnen H., van Santen R.: *Chem. Commun.* **1996**, 1941.
- [29] Winkhofer N., Voigt A., Dorn H., Roesky H., Steiner A., Stalke D., Reller A.: *Angew. Chem. Int. Ed.* **1994**, 33, 1352.

Received 21 V 2014.