RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Lewis acid type deep eutectic solvents as catalysts for epoxy resin crosslinking

Honorata Mąka, Tadeusz Spychaj*, Jakub Adamus

West Pomeranian University of Technology in Szczecin, Polymer Institute, ul. Pulaskiego 10,
70-322 Szczecin, Poland, tel. +48914494684, fax. +489144944247
e-mail: Tadeusz.Spychaj@zut.edu.pl

Abstract

The curing process of epoxy resin with deep eutectic solvents (DES), composed of choline chloride and $ZnCl_2$ or $SnCl_2$, as cationic catalysts has been investigated using rheometry, DSC and FTIR techniques. The differences between two DES types in the catalytic activity towards epoxy resin were discussed based on the pot life at room temperature evaluation, as well as onset temperatures and temperatures at maximum of DSC exotherms, as a function of DES/epoxy resin weight ratio. Moreover, the curing mechanism was proposed. Thermomechanical properties (glass transition temperature, tan δ), crosslink density, thermal resistance as well as the flammability of cured epoxy materials were determined.

Introduction

Epoxy resins are applied in various industrial fields in the form of coatings, adhesives, cast systems or composites reinforced with fibers or powder type (nano)fillers [1,2]. Besides the conventional epoxy curing agents, such as polyamines and organic acids anhydrides also catalytic crosslinkers initiating epoxy polymerization according to anionic (e.g. tertiary amines) or cationic (e.g. BF_3 adducts) mechanism are used. The latter are applied in lower and nonstoichiometric ratios to epoxy resin, typically from several to 15 wt. parts per 100 wt. parts of the resin (phr) [1].

In the past decade, room temperature molecular ionic liquids (ILs) – very often of imidazolium type, but also phosphonium – were applied for epoxy resin curing allowing to formulate the epoxy compositions with tailored pot life and valuable properties after curing [3-7].

Besides molecular ILs, a growing technological interest to apply deep eutectic solvents (DESs) in various areas is observed [8-10]. DESs constitute a class of polar substances obtained by a simple mixing and heating (usually up to 100°C) of two or more compounds exhibiting deep melting points depression compared to the melting points of particular components. Such eutectic solvents are usually liquids at ambient conditions, cheap, more environmentally safe and often biodegradable. A hydrogen donor type compound and hydrogen acceptor are necessary to compose DES. A classic example of a such system is mixture of choline chloride (ChCl) with urea (1:2 molar ratio) exhibiting m_p=12°C, whereas m_p values of the components are: 305 and 133-135°C, respectively

[11]. Even a higher m_p depression, (i.e. ca. 260°C) was observed for $ChCl/ZnCl_2$ (1:2 molar ratio) DES (m_p=23-25°C; m_p $ZnCl_2$ is 283°C) [12].

DESs are used for polymer dissolution or as media for modification, especially for biorenewable materials such as celulose [13], starch [14] or chitin [15].

The first paper on DES application for epoxy resin curing was reported in 2012 [16], where ChCl mixtures with imidazole (IM) [16] and subsequently with urea (U) or guanidine derivatives [17] were applied as curing catalysts. The kinetics of the epoxy resin curing with ChCl/U and ChCl/U+aliphatic polyamine has been recently investigated [18]. The most characteristic features of the relevant epoxy/DES systems are the following: (i) pot life at room temperature between 7 days and above half a year, dependent on DES type and DES/epoxy ratio, (ii) glass transition temperature: 127-156°C, (iii) tan δ values 0.45-0.90 indicating increased viscous response in comparison to the epoxy materials cured with conventional molecular ILs. Curing process of epoxy resin with the above mentioned DESs based on choline chloride and amine derivatives is polyaddition and/or anionic polymerization reaction [16-18]. The present work describes different types of epoxy curing agents, i.e. DESs containing Lewis acid metal chloride ($SnCl_2$ or $ZnCl_2$) component capable initiating polymerization according to the cationic mechanism. Such DES type can additionaly play a role of flame retardant for epoxy resin materials.

For cationic polymerization of epoxy resin, besides the salts with BF_4^- anion, also other Lewis acids with fluoride anions as: PF_6^-, AsF_6^- are active. These salts decompose under the influence of elevated temperature or UV radiation and initiate epoxy polymerization [1]. Between the Lewis acids also transition metal chlorides are known as cationic catalysts. The majority of Lewis acids in a form of metal halides is difficult to handle and unstable in the presence of water (e.g. $SnCl_4$, $AlCl_3$, and BF_3) which hamper their use at a larger scale [19]. In that context $ZnCl_2$ and $SnCl_2$ are especially interesting because they are free of drawbacks exhibited by above mentioned halides of other metals. These two chlorides are efficient catalysts in the Friedel-Crafts acylation or Fischer indole synthesis [20]. The tin (II) catalysts are widely used in industrial scale in a ring-opening polymerization of L-lactide as well as polyester synthesis or the transesterification reactions [19,21-23]. The catalytic activity of transition metal chlorides depends on their Lewis acidity. It was found that their catalytic efficiency for esterification reaction was enhanced with stronger Lewis acidity [23]. The trials to combine the electronegativity of some metal chlorides ($AlCl_3$ > $FeCl_3$ > $ZnCl_2$ > $SnCl_2$ [24]) with the catalytic efficiency for bisphenol-A synthesis revealed that the salts with intermediate Lewis acidity (i.e. Zn^{2+} and Sn^{2+}) provided the highest catalytic activity [25]. The catalytic effect of ligand type in zinc and tin (II) compounds is important considering its influence on the solubility in the reaction medium [22,23]. It was described that $ZnCl_2$ could act as a catalyst for glycidyl phenyl ether cationic polymerization. However, only a trace amount of low molecular weight oligomer was formed after heating at 150-180°C/12 h [26]. In the literature there are some reports on DES containing $ZnCl_2$ or $SnCl_2$ exhibiting an enhanced catalytic activity in comparison to the neat metal salts, i.e. in the reactions of oleic acid esterification [23] or epoxy compounds aminolysis [27].

According to the authors best knowledge no reports on epoxy resin crosslinking with $ZnCl_2$ or $SnCl_2$ alone as well as with DES containing these salts are accessible. In this work was described the application of DES with $ZnCl_2$ or $SnCl_2$ for epoxy resin curing. The pot life, curing characteristics, thermomechanical, thermal properties and the flammability of the cured epoxy materials were investigated. A comparison of curing characteristics and the thermomechanical properties of epoxy materials cured in the presence of Lewis acid based DES with those earlier reported based on amine derivatives was also presented.

Experimental

Materials

The epoxy resin applied was the bisphenol A-based low molecular weight Epidian 6 (E6, Organika Sarzyna, Poland), epoxy equivalent 185 g/equiv. (viscosity ca. 15 Pas at 23°C). The components used for DES preparation and their physical properties were characterized in Table 1. Choline chloride (ChCl, 99%), zinc chloride ($ZnCl_2$, 98%) and tin (II) chloride ($SnCl_2$, 98%) were supplied by Sigma-Aldrich and used as delivered.

The eutectic mixtures were prepared by mixing solid components of ChCl/inorganic salt with the molar ratio 1:2 at ambient temperature and then heating them at 100°C for 2-10 h to obtain liquid products.

The epoxy compositions for storage time determination and curing tests were obtained by mixing epoxy resin with ChCl/$ZnCl_2$ or ChCl/$SnCl_2$ using various weight ratios of DES/epoxy resin: 4.5, 6, 8, 10 and 13 wt. parts/100 wt. parts E6 (phr).

Methods of characterization

The FTIR measurements were performed using a Nexus instrument with Golden Gate (ATR mode, Thermo Nicolet Corp.) equipped with Omnic software. For each sample 32 scans were taken from 4000-400 cm^{-1}. The accuracy of the wavenumber measurements is ±2 wavenumbers if a spectrum is measured at 4 cm^{-1} resolution [28].

The pot life of epoxy/DES compositions was determined on a basis of rheometric measurements at 23-25°C using ARES rheometer (Rheometric Scientific), the plate-plate system with ϕ=40 mm, and a gap of 1 mm. The curing process of epoxy compositions was investigated using differential scanning calorimeter DSC Q-100 (TA Instruments, USA), and ARES rheometer at a heating rate of 5°C/min, in the temperature range of 30-300°C. The precision of DSC measurements as related to characteristic temperatures determination (onset T_o and at exoterm maximum T_{max}) is in the range

1-2°C [29]. The reproducibility of rheometric T_o data is on a similar level..

The glass transition temperatures (T_g), tan δ and crosslink density of the crosslinked materials were determined by dynamic mechanical thermal analysis (DMTA Q – 800, TA Instruments) with dual cantilever, at heating rate of 3°C/min from 30 to 250°C, frequency 1 Hz. The precision of T_g determination is evaluated as ±1°C. The samples for DMTA measurements were prepared by curing the epoxy compositions at temperature regime: at 140°C for 2h, and subsequently at 160°C for 2h in Teflon molds.

Thermogravimetric analysis (TGA) was performed using TGA Q500 (TA Instruments), under air atmosphere, heating rate 10°C/min, temperature range 40-900°C.

The limiting oxygen index (LOI) of epoxy materials was measured using oxygen concentration meter (GOX 100, Greisinger Electronic GmbH) at room temperature, in accordance with PN-EN ISO 4589-2. The thin strips (10x1x0.4 cm) of each material were clamped vertically and ignited at the top.

Result and discussion

Pot life at ambient conditions

Latent curing activity at room temperature and a short gel time after heating of the epoxy systems are beneficial features from technological viewpoint. The viscosity changes of epoxy compositions prepared with various weight ratios of components containing ChCl/$ZnCl_2$ or ChCl/$SnCl_2$ after storage under ambient conditions were shown in Table 2. It was evident that the systems with ChCl/$SnCl_2$ exhibited shorter storage times than those with ChCl/$ZnCl_2$. The pot lives of epoxy compositions obtained with the latter DES exceeded 13 weeks regardless of DES/epoxy resin ratio. The systems with ChCl/$SnCl_2$ were more reactive and showed lower values of that parameter, i.e. about 2 weeks for composition containing up to 13 phr DES and ca. 4 weeks for those with 10 phr DES. On the other side both types of the epoxy systems investigated exhibited higher latency than earlier described systems cured with ChCl/imidazole or ChCl/guanidine derivatives but lower than that with ChCl/urea (Table 3). One can state that the pot life value for epoxy compositions based on ChCl/metal halide catalysts could be acceptable from technological viewpoint.

Curing at higher temperatures

Epoxy resin curing process was followed using rheometry, DSC and FTIR techniques. The rheometric curves of investigated epoxy systems in various DES/epoxy resin ratio: 4.5, 6, 8, 10 and 13 phr were presented in Fig 1. The onset temperature (T_o), i.e. the beginning of viscosity jump indicating gelation, for E6_ChCl/$ZnCl_2$ system was similar (177°C) over a wide range of DES content (6-13 phr). A higher T_o value (185°C) was observed only for epoxy composition with the lowest DES amount. The mentioned viscosity increase reached about 5 decades, from ca. 33 up to

$6 \cdot 10^4$ or $3 \cdot 10^5$ Pa·s (Fig.1). However, an upper viscosity level noted for material cured with E6_ChCl/ZnCl$_2$_4.5 was about 1 decade lower than for residual samples of that series. Other set of the rheometric curves was registered for E6_ChCl/SnCl$_2$ system, i.e. a distinct shift of T$_o$ with DES content increase in the epoxy compositions (195 → 185 → 182 → 173 →165°C, Fig 1, for DES 4.5 → 6 → 8 → 10 →13 phr, respectively). Moreover, the range of viscosity increase using E6_ChCl/SnCl$_2$ was wider than in case of DES based on ZnCl$_2$ (0.7 up to 10^6 Pa·s, i.e. more than 6 decades).

The DSC thermograms of the investigated epoxy systems were given in Fig. 2. The characteristic parameters i.e. onset temperature, T$_o$, temperature at exotherm maximum T$_{max}$, and the reaction enthalpy ΔH were collected in Table 4. The T$_o$ values for epoxy resin cured with ChCl/ZnCl$_2$ were over a relatively narrow temperature range 154-160°C, whereas the range for epoxy systems with ChCl/SnCl$_2$ was substantially wider (162 → 135°C) and decreased with DES/epoxy resin weight ratio increase. The differences of relevant T$_o$ values measured by rheometry (higher values) and DSC (lower values) resulted from various nature of the applied techniques, i.e. a kinetic character of rheological flow and static equilibrium phenomenon of heat flow. A comparison of T$_{max}$ values for epoxy compositions with ZnCl$_2$/ChCl or SnCl$_2$/ChCl (with lower and higher DES content) with relevant values for earlier investigated DES cured epoxy systems [16,17] revealed distinct differences (Table 3). The values of that parameter for the former compositions are higher (above 170 or 180°C in dependence on DES/epoxy resin weight ratio) than those cured with DES based on imidazole (below 120°C) or guanidine derivatives (137-154°C), however comparable to the systems cured with urea/ChCl. Moreover, the DSC thermograms for E6_ChCl/ZnCl$_2$ showed bimodal exothermic maxima in the temperature ranges 185 → 201°C and 246 → 286°C. On the contrary, for compositions with ChCl/SnCl$_2$ unimodal DSC thermograms were registered. It seems that more intensive exothermic peaks (at lower temperature range) for E6_ChCl/ZnCl$_2$ can be attributed to the epoxy resin polymerization catalyzed by the Lewis acid. A minor peak at higher temperature region could be associated with another mechanism of epoxy crosslinking, e.g. homopolymerization initiated by ChCl or its thermal decomposition products [2,30]. In that way the residual reactive groups of epoxy resin are consumed. This DSC observation are in accordance with storage time and rheometric data of both investigated epoxy systems. Generally, the values of exothermic enthalpy effect during curing of epoxy resin with ChCl/ZnCl$_2$ were slightly higher than with ChCl/SnCl$_2$. Considering the thermal effects of E6_ChCl/ZnCl$_2$ reaction: the major exotherms constituted ca. 90% of total exotherms observed (Fig. 2 and Table 4).

The FTIR was used for epoxy curing reactions evaluation. This technique is often applied for such purposes including the systems cured with ionic liquids [3-5]. In Figure 3 the spectra of E6_ChCl/SnCl$_2$ (10 phr) composition performed directly after components mixing and after various time/or schedule of curing, i.e. 15 min/140° C, 30 min/140°C, 60 min/140° C, 2h/140°C and 2h/140°C + 2h/160°C were collected. The most significant changes of FTIR spectra registered before and after thermal treatment of composition could be observed at: 831 cm^{-1} (stretching C-O-C of oxirane ring), 918 cm^{-1} (epoxy group absorption), 1026 cm^{-1} (stretching C-O-C of ethers) and 3150-3600 cm^{-1} (hydroxyl group stretching). The changes of two bands seem to be worth commenting: (i) gradual disappearance of epoxy ring at 918 cm^{-1} with epoxy curing reaction time, and (ii) decreasing intensity of a broad band characteristic for the OH groups at 3150-3600 cm^{-1} with epoxy resin polymerization. There was only a slight trace of the former absorbance band after 60 min/140°C (or longer reaction time). This fact confirms the catalytic activity of ChCl/SnCl$_2$ in epoxy polymerization. Moreover, a decrease of OH absorption band with reaction time (and temperature) showed that the OH groups introduced into reacting composition with epoxy resin (in rather low amount because of low molecular weight of E6 resin) as well as with ChCl could implicate the mechanism of epoxy resin polymerization.

Mechanism of epoxy resin curing

The Lewis acids are species with electrons deficiency that can activate the substrates rich in electrons. They are often used as catalysts in various organic chemistry reactions. It is generally accepted that the catalytic activity of Lewis acids in the form of metal chlorides is associated with electron acceptability in the strength of acidity, i.e. AlCl$_3$ > FeCl$_3$ > ZnCl$_2$ > SnCl$_2$ [24]. In accordance with the above order ZnCl$_2$ is more active than SnCl$_2$ in (poly)esterification or trans-esterification reactions [22] or bisphenol-A synthesis from substrates (i.e. acetone and phenol) [25].

However, some reports announced that the catalytic activity of these Lewis acids can be reversed. Such a situation was found when rearrangements of alcohols [20] or alcoholysis of vegetable oils [23] were performed. Similarly, the results on the cationic polymerization of epoxy resin showed a higher catalytic activity of SnCl$_2$-based DES than ChCl/ZnCl$_2$.

The proposed polymerization mechanism of epoxy resin with DES containing SnCl$_2$ and ZnCl$_2$ was presented in Fig. 4. The basis of cationic polymerization of epoxy compounds were described by Kubisa and Penczek [31]. As can be seen the competition between activated chain end mechanism and activated monomer mechanism was reported. In activated monomer mechanism OH bearing species (i.e. OH groups of epoxy resin and ChCl molecules) are engaged in growth of the epoxy network. It should be mentioned that DES based on ChCl and 1,1-tris(hydroxymethyl)propane (i.e. nonactive to epoxy group component) caused the resin gelation above 220°C [30]. This fact supports proposed mechanism of catalytic activity of applied metal halides as the Lewis acid components of DES with ChCl at substantially lower temperature range.

Moreover, it should be mentioned that applying DES with ZnCl$_2$ or SnCl$_2$ for epoxy resin curing allowed to: (i) perform polymerization in homogenous environment (DESs are fully miscible/soluble with epoxy resin), (ii) intensify Lewis acid catalytic activity, similarly to other reaction systems (e.g. oleic acid oligomerization [23] or solvent-free room temperature aminolysis of epoxides with aromatic amines [26] using ChCl/MeCl$_2$ or guanidine/MeCl$_2$ DESs, respectively, where Me is Sn or Zn).

Properties of cured epoxy materials

The thermomechanical parameters of epoxy materials cured with DESs at various weight ratios, i.e. glass transition temperature, (T_g) and tan δ values were compiled in Table 5. One could see that in a case of E6_ChCl/ZnCl$_2$ system T_g increased with growing DES content. However, for lower DES content (4.5 and 6 phr) no efficient crosslinking was found indicated by nonmeasurable or very low T_g value (77°C). The highest T_g was observed for material cured with the highest dosage of ZnCl$_2$ -based catalyst (i.e. 127°C and 13 phr, respectively).

Significantly higher T_g values were registered for materials cured with ChCl/SnCl$_2$ (132-154°C), and maximum T_g was registered for epoxy material cured with 6-10 phr DES; the values of this parameter were comparable to the highest ones reported for other ChCl-based DESs applied for epoxy resin curing containing imidazole (157°C) [16] and urea (158°C) [17]. Glass transition temperatures for E6_ChCl/SnCl$_2$ (4.5 and 10 phr) materials are higher than relevant temperatures for GTC/ChCl or TBG/ChCl cured system, comparable to samples with U/ChCl and lower than crosslinked with IM-based DES catalyst (Table 3).

Tan δ can be used to characterize the modulus of a material. It is a measure of the energy dissipation of material and is defined as a ratio of loss to the storage moduli (tan δ=E'/E'', where E'' is storage modulus and E' – loss modulus). A value of δ should range between 0° (purely elastic behavior) and 90° (purely viscous behavior). The values of tan δ for epoxy materials cured with ChCl/ZnCl$_2$ were in a range 0.51-0.54 (with exception of not completely crosslinked E6_ChCl/ZnCl$_2$ 6 phr system). On the other hand, the samples cured with ChCl/SnCl$_2$ exhibited a lower range of that parameter 0.32-0.49 (with exception of E6_ChCl/SnCl$_2$ 13 phr). Considering tan δ definition lower value~~s~~ of the parameter for latter materials imply a higher crosslinking efficiency than for epoxy materials cured with ChCl/ZnCl$_2$. Epoxy materials cured with SnCl$_2$/ChCl exhibited as a rule distinctly lower tan δ values than other DES crosslinked samples earlier investigated (Table 3), i.e. are more elastic than viscous at elevated temperatures.

The crosslinking density was evaluated on a basis of equation: $\nu_e = E_r/3RT_r$ (where: ν_e – crosslinking density, E_r – "rubbery" modulus, i.e. storage modulus at $T_r = T_g+30$, R – universal gas constant) [30,32]. The results in Table 5 showed that crosslinking density of epoxy materials cured with ChCl/ZnCl$_2$ were substantially lower (1168-1540 mol/m^3) than these catalysed with ChCl/SnCl$_2$ (up to 4590 mol/m^3 for E6_ChCl/SnCl$_2$ 6 phr). The highest ν_e values were found for 6 and 8 phr DES in epoxy materials; whereas a relatively deep decrease (to 2024 mol/m^3) was observed for material cured with the highest DES content. These data correlate with T_g and tan δ values for the relevant epoxy materials (Table 5).

The epoxy materials cured in the presence of ChCl/$SnCl_2$ exhibited higher temperatures for 5 and 10 % mass losses (determined by thermogravimetric measurements): 319-337°C and 321-343°C for middle range of DES/epoxy resin ratios: 6-10 phr than in case of E6_ChCl/$ZnCl_2$ samples (Table 5). These values were, however, lower than observed for epoxy materials cured with other ChCl-based DES, i.e.: ChCl/imidazole [16] or ChCl/guanidine derivative and ChCl/urea [17].

Using $ZnCl_2$ as a flame retardant for finishing of textiles from rayon [33] or wood [34], and as additive for intumescent flame-retardant polypropylene [35] was reported. Tin halides, including $SnCl_2$, were effective flame retardants when incorporated at levels 10-15 wt.% into polyamide 6 fibers [36]. Some examples of $SnCl_2$ flame-retarding features in the interaction with other compounds were presented by Lomakin et al [37].

The limiting oxygen index (LOI) results were presented in Table 5. All investigated epoxy materials exhibited LOI values above 23% O_2. A typical level of LOI for conventional epoxy crosslinked with polyamine (e.g. triethylenetetramine) is ca. 21 [38]. The LOI values of samples cured with ChCl/$ZnCl_2$ were in a range 23-25, whereas those with ChCl/$SnCl_2$ exhibited substantially higher level 27.9-33.0. Generally, the materials with LOI index lower than 22 are considered as flammable, with LOI 22-25 are self-extinguishing, and if the parameter exceeds 26 are defined as flame retarding [39]. Thus, E6_ChCl/$SnCl_2$ materials exhibited evidently flame-retarding features. This finding is novelty and no reports on $SnCl_2$ application for epoxy resin flame retardation is accessible.

Considering above one can see extraordinary features of ChCl/$SnCl_2$ deep eutectic solvent as simultaneous curing catalyst and the flame retardant of epoxy resin.

Conclusions

The epoxy compositions cured with tin (II) or zinc chloride-based deep eutectic solvents with choline chloride (2:1 molar ratio) exhibited some latency at room temperature: above 2 weeks in a case of the former and above 13 weeks for the latter one (and dependent on DES/epoxy resin weight ratio). The onset temperature of epoxy systems with ChCl/$ZnCl_2$ determined rheometrically was similar (ca. 177°C) whereas its distinct shift with increasing DES content was observed for ChCl/$SnCl_2$ catalyst (195 → 165°C). The temperatures at maximum of exothermic peaks were 40-50°C higher for epoxy compositions cured in the presence $ZnCl_2$-based DES (201 → 185°C) than for materials with ChCl/$SnCl_2$ (162 → 135°C). DES containing $ZnCl_2$ and $SnCl_2$ allowed to perform epoxy resin polymerization in the homogeneous environment. DES based on $SnCl_2$ was more efficient epoxy polymerization catalyst than $ZnCl_2$-based one. For ChCl/$SnCl_2$ catalyst higher crosslinking densities of epoxy materials were found (up to 4590 mol/m^3), i.e. about 3-times higher than using ChCl/$ZnCl_2$ (up to 1540 mol/m^3). As a consequence also higher glass transition temperature (152-154°C for E6_ChCl/$SnCl_2$ 6 and 8 phr) and lower tan δ values (0.32-0.36 for E6_ChCl/$SnCl_2$ 4.5-10 phr) were observed. Moreover, the introduction of ChCl/$SnCl_2$ into epoxy resin resulted in a substantial increase of limiting oxygen index parameter (up to 33 for E6_ChCl/$SnCl_2$ 10 phr). Such a material can be considered as a flame retardant. Thus, DES based on ChCl and $SnCl_2$ could be simultaneously an efficient polymerization catalyst of epoxy resin and antiflaming agent.

Literature

[1] P. Czub, Z. Bończa–Tomaszewski, P. Penczek, J. Pielichowski, *Chemistry and technology of epoxy resins*, 2002, WNT, Warsaw.

[2] J. P. Pascault, R. J. J. Williams, *Epoxy polymers,* 2010*,* Wiley-VCH, Weinheim.

[3] K. Kowalczyk, T. Spychaj, Ionic liquids as convenient latent hardeners of epoxy resin, *Polimery* (Warsaw), 2003, **48**, 833–835.

[4] A. M. Rahmathullah, B. Jeyarajasingam, B. Merritt, M. Van Landingham, S. H. McKnight, G. R Palmese, Room temperature ionic liquids as thermally latent initiators for polymerization of epoxy resins. *Macromolecules,* 2009*,* **42**, 3219–3221.

[5] H. Mąka, T. Spychaj, R. Pilawka, Epoxy resin/ionic liquid systems. Influence of imidazolium cation size and anion type on reactivity and thermomechanical properties. *Ind. Eng. Chem. Res.* 2012, **51**, 5197-206.

[6] A. A. Silva, S. Livi, D. B. Netto, B. G. Soares, J. Duchet, J. F. Gerard, New epoxy systems based on ionic liquid, *Polymer*, 2013, **54**, 2123.

[7] H. Mąka, T. Spychaj, R. Pilawka, Epoxy resin/phosphonium ionic liquid/carbon nanofiller systems: chemorheology and properties, *Express Polym. Lett.,* 2014, **8**, 723-732.

[8] E. L. Smith, A. P. Abbott, K. S. Ryder, Deep eutectic solvents (DESs) and their applications, *Chem. Rev.,* 2014, **114**, 11060-11082.

[9] Y. Dai, J. van Spronsen, G. J. Witkamp, R. Verpoorte, Y. H. Choi, Natural deep eutectic solvents as new potential media for green technology, *Analytica Chim. Acta,* 2013, 766, 61-68.

[10] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, Deep eutectic solvents: syntheses properties and applications, *Chem. Soc. Rev.,* 2012, **41**, 7108-7146.

[11] A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed, V. Tambyrajah, Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains, *Chem. Commun.*, 2001, 2010-2011.

[12] A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, Ionic liquids based upon metal halide/substituted quaternary ammonium salt mixtures, *Inorg. Chem.,* 2004, 43, 447-3452.

[13] S. Xia, G. A. Baker, H. Li, S. Ravula, H. Zhao, Aqueous ionic liquids and deep eutectic solvents for cellulosic biomass pretreatment and saccharification, *RSC Adv.*, 2014, **4**, 10586-10596.

[14] M. Zdanowicz, T. Spychaj, Ionic liquids as starch plasticizers or solvents, *Polimery* (*Warsaw*), 2011, **56**, 861-864.

[15] M. Sharma, Ch. Mukesh, D. Mondal, K. Prasad, Dissolution of α-chitin in deep eutectic solvents, *RSC Adv.*, 2013, **3**, 18149-18155.

[16] H. Mąka, T. Spychaj, Epoxy resin crosslinked with conventional and deep eutectic ionic

liquids, *Polimery* (*Warsaw*), 2012, **57**, 34-40.

[17] H. Mąka, T. Spychaj, W. Sikorski, Deep eutectic ionic liquids as epoxy resin curing agents, *Int. J. Polymer Anal. Charact.,* 2014, **19**, 682-692.

[18] F. Lionetto, A. Timo, M. Frigione, Curing kinetics of epoxy-deep eutectic solvent mixtures, *Thermochim. Acta*, 2015, **612**, 70-78.

[19] A. B. Ferreira, A. L. Cardoso, M. J. da Silva, Tin-catalyzed esterification and transesterification reactions. A review, *ISRN Renewable Energy*, 2012, ID142857, 13 pp.

[20] P. C. Doolan, P. H. Gore, R. Hollingworth, D. N. Waters, J. Al-Ka'bi, J. A. Farooqi, Kinetic studies of Lewis acidity. Part 2. Catalysis by tin(IV) chloride, by some organotin(IV) chlorides, and by tin(II) chloride of the anionotropic rearrangement of 1-phenylprop-2-en-1-ol in tetramethylene sulphone solution, *J. Chem. Soc. Perkin Trans.* II, 1986, paper 5/137, 501-506.

[21] F. R. Abreu, D. G. Lima, E. H. Hamú, S. Einloft, J. C. Rubim, P. A. Z. Suarez, New metal catalysts for soybean oil transesterification, *J. Am. Oil Chem. Soc.*, 2003, **80**, 601-604.

[22] A. Casas, M. J. Ramos, J. F. Rodríguez, A. Pérez, Tin compounds as Lewis acid catalysts for esterification and transesterification of acid vegetable oils, *Fuel Proces. Technol*., 2013, **106**, 321-325.

[23] N. F. Adnan, N. A. M. Nordin, N. Hamzah, M. A. Yarmo, Lewis acid ionic liquids: as new addition catalysts for oleic acid to monoestolide synthesis, *J. Sci. Technol*., 2010, **2**, 25-33.

[24] Y. Feng, F. Zhang, Ionic electronegativity, *J. Dallan Inst. Light Ind.,* 1998, **17,** 70-76.

[25] B. H. Wang, J. S. Dong, S. Chen, L. L. Wang, J. Zhu, ZnCl2 - modified ion exchange resin as an efficient catalyst for the bisphenol-A production, *Chin. Chem. Lett*. 2014, 25, 1423-1427.

[26] M. Kim, F. Sanda, T. Endo, Polymerization of glycidyl phenyl ether with phosphonic acids esters as nowel thermally latent initiators, *Macromolecules,* 1999, **32**, 8291-8295.

[27] J. G. Cao, H. M. Cao, Y. J. Lin, D. P. Liang, H. F. Duan, S. Y. Han, X. Z Zhao, Lewis acid guanidinium ionic liquids: novel efficient and recyclable catalysts for aminolysis of epoxides, *Chem. Res. Chinese Univ.,* 2011, **27**, 780-783.

[28] B.C. Smith, Fundamentals of Fourier Transform Infrared Spectroscopy, sec. ed., CRC Press, 2011, Bocca Raton

[29] M. Schmid, Precision of DSC measurements: results of interlaboratory tests, www.eurostar-science.org/MAP1/Schmid.pdf, July 21, 2015

[30] H. Mąka, T. Spychaj, K. Kowalczyk, Imidazolium and deep eutectic ionic liquids as epoxy resin crosslinkers and graphite nanoplatelets dispersants, *J. Appl. Polym. Sci.*, 2014, **131**, 40401

[31] P. Kubisa, P. Penczek, Cationic activated monomer polymerization of heterocyclic monomers, *Progr. Polym. Sci.*, 1999, **24**,1409-1437.

[32] J. D. LeMay, R. N. Kelley, Structure and ultimate properties of epoxy resins. Epoxy Resins and

Composites III, *Adv. Polym. Sci.,* 1986, **78**, 115-148

[33] G. Rosace, V. Migani, E. Guido, C. Colleoni, chapt. 9, Flame retardant finishing for textiles, in Flame retardants, P. M. Visakh, Y. Arao (eds.), Springer Int. Publ. Heidelberg 2012.

[34] S. L. Levan, Chemistry of fire retardancy, *The Chemistry of Solid Wood*, 1984, 531-574.

[35] L. Ye, Y. Zhang, S. Wang, G. Gao, J. Liu, Y. Zhou, H. Liu, Synergistic effects and mechanism of $ZnCl_2$ on intumescent flame-retardant polypropylene, *J. Therm. Anal. Calorim.,* 2014, **115,** 1065-1071.

[36] S. J. Blunden, P. A. Cusack, The industrial uses of tin chemicals, The Royal Society of Chemistry, London 1985, 202

[37] S. M. Lomakin, G. E. Zaikov, Modern polymer flame retardancy, Brill Academic Publ., Zeist 2003.

[38] P. Murias, Epoxy resin with heteroatoms, PhD Thesis, Rzeszow Technological University, Rzeszow 2013, Poland

[39] M. Y. Shen, C. F. Kuan, H. C. Kuan, C. H. Chen, J. H. Wang, M. C. Yip, C. L. Chiang, Preparation, characterization, thermal, and flame-retardant properties of green silicon-containing epoxy/functionalized graphene nanosheets composites, *J. Nanomater.* 2013, ID 747963, 10 pp.

Table 1. Characteristics of components and DES prepared

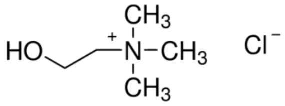	$ZnCl_2$		$SnCl_2$
choline chloride (ChCl) m_p=302-305°C M=139.6	zinc chloride m_p=293°C M=136.3		tin (II) chloride m_p=246°C M=189.6
DES	T_m, °C	ΔT_m, °C	Description
$ChCl/ZnCl_2$ 1:2 mol	23-25 [11]	~269	Transparent colourless liquid
$ChCl/SnCl_2$ 1:2 mol	37 [12]	~209	Transparent yellowish liquid

Table 2. Viscosity change during epoxy composition storage at ambient temperature

Composition acronym	**Viscosity, Pa·s** (days)										
	1	8	14	22	28	39	49	56	64	83	90
E6_2$ZnCl_2$/ChCl 4.5	22.0 ± 0.1	30.6 ±0.3	35.6 ±0.3	33.5 ±0.3	36.4 ±0.4	34.2 ±0.1	35.3 ±0.2	47.1 ±0.3	56.4 ±0.4	54.1 ±0.3	59.5 ±0.2
E6_2$ZnCl_2$/ChCl 6	29.5 ±0.1	39.6 ±0.3	37.1 ±0.1	48.2 ±0.3	48.7 ±0.3	46.2 ±0.3	44.3 ±0.2	59.8 ±0.2	65.8 ±0.4	72.9 ±0.6	74.1 ±0.4
E6_2$ZnCl_2$/ChCl 8	51.2 ±0.4	54.5 ±0.2	53.4 ±0.2	74.0 ±0.5	73.1 ±0.1	71.7 ±0.6	70.1 ±0.2	81.6 ±0.1	92.8 ±0.2	119.5 ±0.6	122.3 ±0.3
E6_2$ZnCl_2$/ChCl 10	77.2 ±0.5	71.2 ±0.6	77.1 ±0.2	92.7 ±0.5	105.6 ±0.5	97.5 ±0.7	91.4 ±0.9	105.3 ±0.2	130.1 ±0.7	163.0 ±0.6	172.1 ±0.3
E6_2$ZnCl_2$/ChCl 13	109.4±0.2	114.3 ±0.5	120.4 ±0.3	149.3 ±0.5	156.3 ±0.1	137.5 ±0.2	125.3 ±0.8	141.5 ±0.4	170.7 ±0.8	219.0 ±0.5	224.7 ±0.3
E6_2$SnCl_2$/ChCl 4.5	40.2 ±0.1	84.0 ±0.5	116.5 ±0.2	126.7 ±0.4	185.0 ±0.5	210.2 ±0.4	278.4 ±0.5	434.2 ±0.5	500.7 ±0.7	590.3 ±0.4	1554.6 ±0.5
E6_2$SnCl_2$/ChCl 6	56.6 ±0.1	145.0 ±0.5	224.2 ±0.3	340.0 ±0.5	462.7 ±0.4	550.6 ±0.3	766.7 ±0.5	1199.4 ±0.9	1600.0 ±0.8	gel	
E6_2$SnCl_2$/ChCl 8	91.3 ±0.4	251.5 ±0.8	463.7 ±0.8	865.1 ±0.5	1220.7 ±0.5	1458.5 ±0.7	1657.0 ±0.7	gel	-	-	
E6_2$SnCl_2$/ChCl 10	100.2±0.4	309.6 ±0.5	657.5 ±0.6	1315.4±0.7	1624.5 ±0.7	gel	-	-	-	-	
E6_2$SnCl_2$/ChCl 13	204.0±0.8	1402.0 ±0.9	1678.8 ±0.5	gel	-	-	-	-	-	-	

Table 3. Comparison of some characteristic parameters of epoxy compositions and crosslinked epoxy materials cured with various DESs

Epoxy material acronym	**Epoxy composition before curing**		**Cured epoxy material**			**Ref.**
	rheometry	**DSC**	**DMTA**		**TG**	
	pot life days	T_{max} °C	T_g °C	tan δ	$T_{10\%}$ °C	
E6_7IM/3ChCl 3	7	117	157	0.38	409	[16]
E6_7IM/3ChCl 9	2	111	156	0.45	367	[16]
E6_2GTC/ChCl 4.5	30	139	64	1.80	352	[17]
E6_2GTC/ChCl 9	8	137	127	0.95	332	[17]
E6_2TBG/ChCl 4.5	30	154	85	1.58	367	[17]
E6_2TBG/ChCl 9	8	150	136	0.91	356	[17]
E6_2U/ChCl 4.5	>150	181	114	0.81	370	[17]
E6_2U/ChCl 9	>150	173	143	0.80	347	[17]
E6_2ZnCl$_2$/ChCl 4.5	>90	201	-	-	-	this work
E6_2ZnCl$_2$/ChCl 10	>90	188	111	0.51	303	this work
E6_2SnCl$_2$/ChCl 4.5	90	180	132	0.32	337	this work
E6_2SnCl$_2$/ChCl 10	28	173	146	0.36	321	this work

GTC- guanidine thiocyanate, TBG-1-(o-tolyl)biguanide

Table 4. Characteristic parameters determined during rheometric and DSC measurements of epoxy compositions

Composition acronym	**Rheometry**	**DSC**					
	T_o, (°C)	T_{o1}, (°C)	T_{max1}, (°C)	ΔH_1, (J/g)	T_{o2}, (°C)	T_{max2}, (°C)	ΔH_2, (J/g)
E6_2ZnCl$_2$/ChCl 4.5	185	155	201	298	271	286	11
E6_2ZnCl$_2$/ChCl 6	177	157	193	349	264	282	24
E6_2ZnCl$_2$/ChCl 8	177	160	191	355	258	274	32
E6_2ZnCl$_2$/ChCl 10	177	154	188	354	252	271	37
E6_2ZnCl$_2$/ChCl 13	177	157	185	322	246	262	44
E6_2SnCl$_2$/ChCl 4.5	195	162	180	241			
E6_2SnCl$_2$/ChCl 6	185	156	177	262			
E6_2SnCl$_2$/ChCl 8	182	151	175	290			
E6_2SnCl$_2$/ChCl 10	173	147	173	330			
E6_2SnCl$_2$/ChCl 13	165	135	164	307			

Table 5. Results of DMTA, TGA and LOI measurements of epoxy materials cured with DES based on ChCl and zinc or tin (II) chlorides

Epoxy material acronym	**DMTA**			**TGA**		**LOI**
	T_g, °C	tan δ	Crosslink density, mol/m^3	$T_{5\%}$, °C	$T_{10\%}$, °C	vol. % O_2
E6_2ZnCl$_2$/ChCl 6	77	0.70	1410	312	322	25.2
E6_2ZnCl$_2$/ChCl 8	102	0.52	1540	303	310	
E6_2ZnCl$_2$/ChCl 10	111	0.51	1168	296	303	23.0
E6_2ZnCl$_2$/ChCl 13	127	0.54	1296	289	294	23.1
E6_2SnCl$_2$/ChCl 4.5	132	0.32	3247	333	337	27.9
E6_2SnCl$_2$/ChCl 6	154	0.36	4590	337	343	
E6_2SnCl$_2$/ChCl 8	152	0.36	4200	325	328	31.2
E6_2SnCl$_2$/ChCl 10	146	0.36	2971	319	321	33.0
E6_2SnCl$_2$/ChCl 13	133	0.49	2024	307	310	30.8

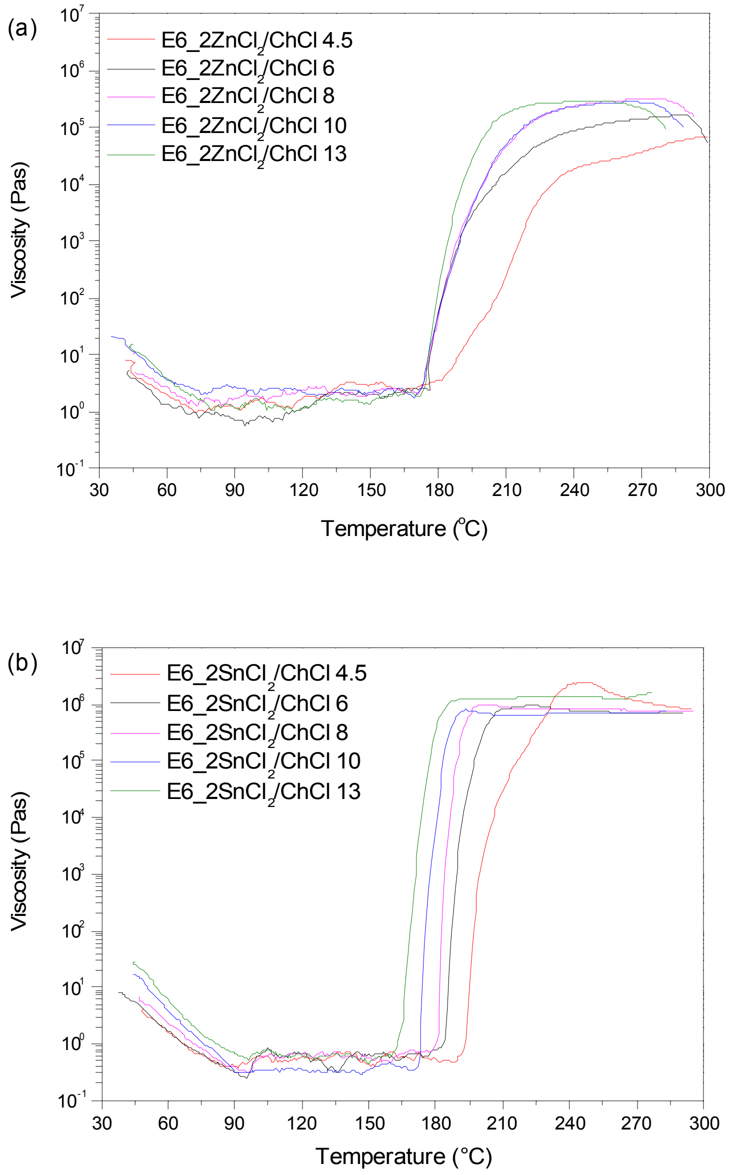

Fig. 1. Rheometric curves of epoxy compositions cured with various ratios of DES: a – systems with ChCl/ZnCl$_2$, b – systems with ChCl/SnCl$_2$

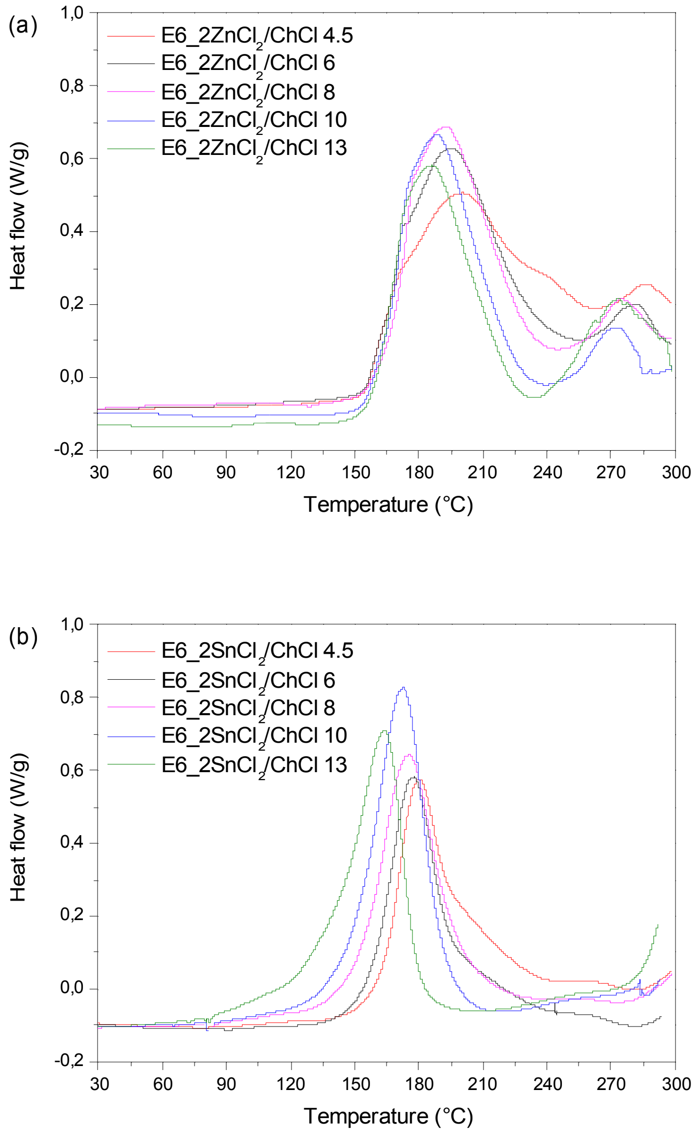

Fig. 2. DSC thermograms of epoxy compositions cured with various DES/epoxy resin weight ratios: a – system with ChCl/ZnCl$_2$, b – system with ChCl/SnCl$_2$

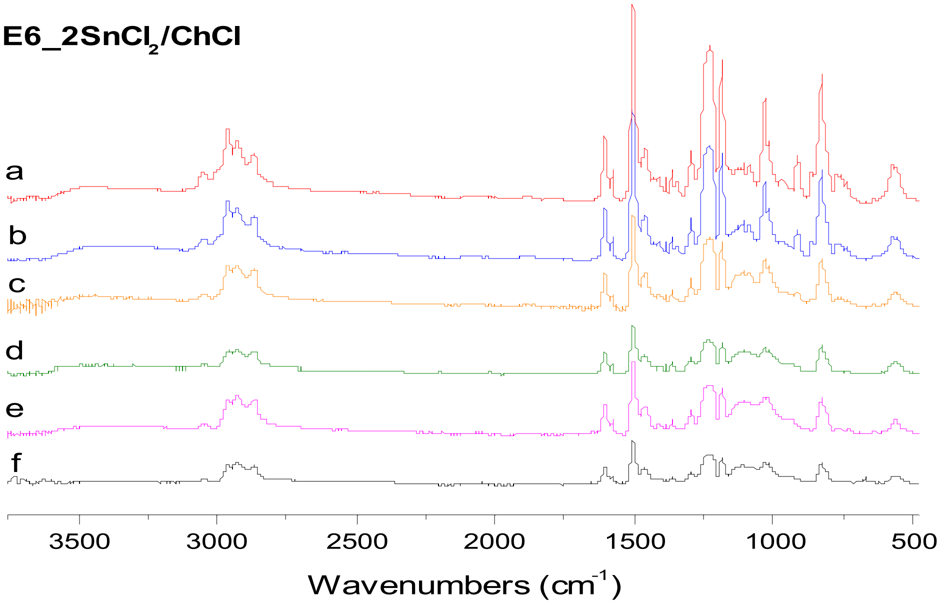

Fig. 3. FTIR spectra of E6_ChCl/SnCl$_2$ (10 phr) a) directly after mixing, and after heating for: b) 15min/140°C, c) 30min/140°C, d) 60min/140°C, e) 2h/140°C, and f) 2h/140°C+2h/160°C

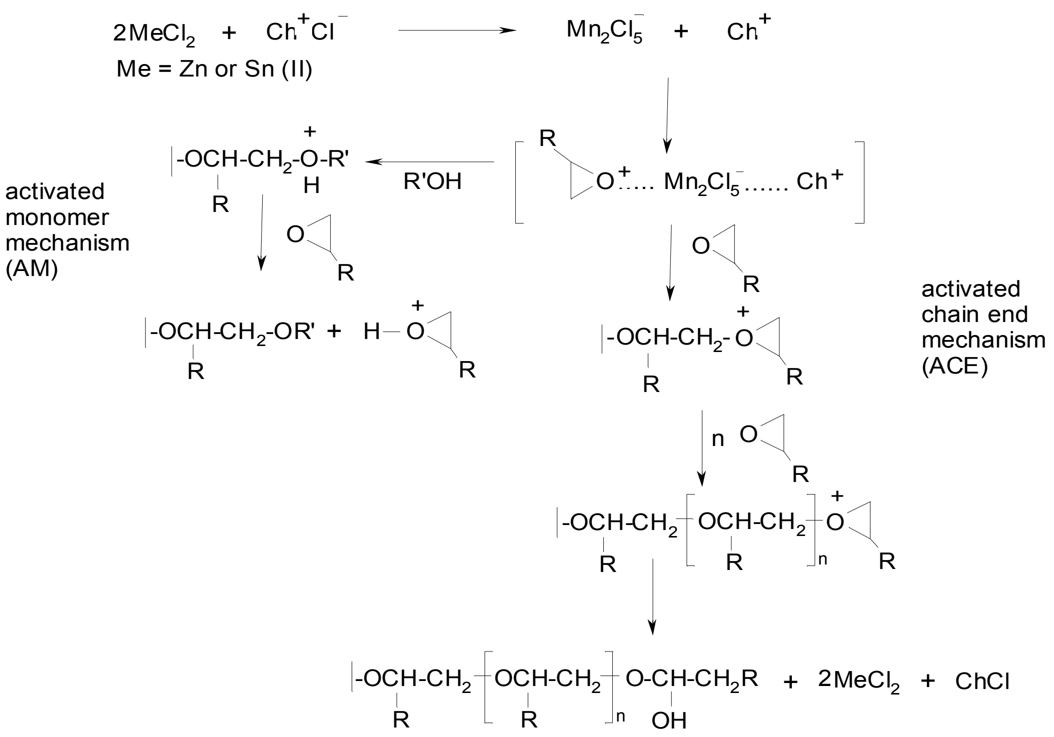

Fig. 4. Proposed mechanisms of epoxy cationic polymerization initiated with $ZnCl_2$ or $SnCl_2$ – based DES