New aromatic diamine-based deep eutectic solvents designed for epoxy resin curing

(*Rapid Communication*)

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Abstract: New deep eutectic solvents (DESs) based on choline chloride (ChCl) and aromatic amines: *m*-phenylenediamine (MPDA) and 2,4-diaminotoluene (DAT) were prepared for the first time and applied for bisphenol A-based low molecular epoxy resin curing. Some physicochemical features of both DESs were presented and discussed on a basis of literature data. Curing process of epoxy compositions with stoichiometric and substoichiometric amounts of amine hydrogens was characterized *via* differential scanning calorimetry (DSC). The resulting cured materials possess acceptable thermomechanical properties. Advantages of DES based on ChCl and MPDA allowed to determine possible application areas of this epoxy resin curing agents.

Keywords: deep eutectic solvent, aromatic diamine, epoxy resin curing.

Nowe ciecze głęboko eutektyczne na podstawie amin aromatycznych do sieciowania żywicy epoksydowej

Streszczenie: Nowe ciecze głęboko eutektyczne (DESs – ang. *deep eutectic solvents*) z chlorku choliny (ChCl) i aromatycznych amin: *m*-fenylenodiaminy (MPDA) i 2,4-diaminotoluenu (DAT) otrzymano po raz pierwszy i zastosowano do sieciowania małocząsteczkowej żywicy epoksydowej na podstawie bisfenolu A. Przedstawiono wybrane właściwości fizykochemiczne DESs oraz przedyskutowano je w odniesieniu do danych literaturowych. Proces sieciowania kompozycji epoksydowych ze stechiometrycznym oraz substechiometrycznym udziałem aminy scharakteryzowano metodą różnicowej kalorymetrii skaningowej (DSC). Przedstawiono także wyniki analizy termomechanicznej utwardzonych materiałów epoksydowych. Zalety DES otrzymanej z ChCl i MPDA pozwoliły na określenie możliwości zastosowania tego środka sieciującego do utwardzania żywic epoksydowych.

Słowa kluczowe: ciecz głęboko eutektyczna, diamina aromatyczna, sieciowanie żywicy epoksydowej.

Aromatic amines are often applied as epoxy resin curing agents. Popular aromatic diamines such as *m*-phenylenediamine (MPDA) and methane-4,4′-dianiline (MDA) are solids at room temperature and require elevated temperatures for homogenization with the resin and effective curing. These curatives are widely used in filament winding and prepreg applications, offering the materials with high heat and chemical resistance [1, 2]. Considering their solid state, the mentioned amines are difficult to handle in mixing operations with the resin as they have to be heated to liquefaction. In the result, the pot life of relevant epoxy compositions is substantially shortened. Instead, liquid eutectic mixtures of aromatic amines, *e.g.*, MPDA + MDA, are applied allowing to control the curing rate and gel characteristics or to modify epoxy material properties [3]. Such eutectic mixtures of aromatic diamines designated for epoxy resin curing are commercially available (*e.g.*, Ancamine 1482 composed of 45 wt % MPDA, < 36 wt % MDA and < 20 wt % polymeric MDA) [2].

In recent years a new class of epoxy resin curing agents belonging to the group of deep eutectic solvents (DESs) has been described [4, 5]. Deep eutectic solvents are usually liquids at room temperature (or more generally below 100 °C) formed simply by mixing and heating two components: hydrogen bond acceptor (often choline chloride, ChCl) and hydrogen bond donor (*e.g.*, compounds with hydroxyl, carboxyl, amide or amine groups) [6, 7]. DESs

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based on ChCl and the hydrogen bond donors such as: imidazole, guanidine thiocyanate, 1-(*o*-tolyl)biguanide, or urea were used for epoxy curing [4, 5]. The mentioned DESs were applied in substoichiometric amounts to epoxy resin. Dependent on the type of DES and its content – the epoxy compositions exhibited a wide range of pot lives (from 2 days up to above 6 months), whereas glass transition temperature values, T_g, for cured samples were most often below 150 °C [4, 5]. Although DESs based on ChCl and amine group bearing compounds are known from literature (*e.g.*, with hydrogen bond donors such as ethanolamines or aminoacids) [8, 9], up to date no examples of DESs based on ChCl and solid aromatic amines have been described.

In order to check whether or not certain mixtures composed of aromatic diamines and ChCl form DESs and how they act towards epoxy resin, two systems containing MPDA and 2,4-diaminotoluene (DAT) were applied. Some physicochemical characterization of these DESs, viscosity changes of epoxy resin/DES systems during storage as well as curing features registered by DSC and thermomechanical measurements *via* DMTA are presented and discussed.

EXPERIMENTAL PART

Materials

Epoxy resin: bisphenol A-based low molecular weight Epidian 6 (E6), epoxy equivalent 185, viscosity 18 Pa · s at 23 °C (Organika-Sarzyna, Poland).

Components for deep eutectic solvents (DESs) preparations, *i.e.*, *m*-phenylenediamine (MPDA, ≥ 99 %, T_m = 64–66 °C), 2,4-diaminotoluene (DAT, ≥ 98 %, T_m = 97–99 °C) and choline chloride (ChCl, ≥ 98 %, T_m = 302 °C) (all from Sigma Aldrich).

Preparation of DESs and epoxy resin composition

DESs have been prepared by mixing the components in a molar ratio amine : ChCl 2 : 1 at ambient temperature and then heated up to 80 °C for 1 h, to obtain liquid products. Visual description of both DESs is given in Table 1.

Eutectic mixtures were combined with E6 at room temperature at weight ratios corresponding to 100, 90 or 80 % of amino protons relative to epoxy group content by adjusting the amount of DES. For comparison, epoxy compositions with aromatic diamines alone, *i.e.*, MPDA or DAT, at stoichiometric amounts, were also prepared (by heating the amine with resin to *ca.* 80 °C, and then cooling to room temperature). All epoxy compositions tested are listed in Table 2.

Epoxy systems were cast into aluminum cuvettes and cured by heating at 80 °C for 2 h and then at 120 °C for another 2 h.

Methods of testing

The storage time for epoxy resin/crosslinker systems at ambient temperature was determined directly after the preparation of compositions and 24 h of storage at 22–24 °C by measuring changes in their viscosity using

Table 1. Characterization of DES based on ChCl and aromatic diamines

DES acronym (molar ratio)	View	Remarks
ChCl/MPDA (1 : 2)	Light colored transparent liquid, gradually darkening on air	After preparation viscosity slightly increased but DES is still liquid. Glass transition temp. -57 °C (DSC).
ChCl/DAT (1 : 2)	Black colored, liquid with very low viscosity	Few hours after preparation crystallization occurred. Melting point 49 °C (DSC).

Table 2. Description of investigated epoxy compositions and viscosity changes during storage at room temperature

Sample acronym	Weight ratio DES/resin g/100 g	Stoichiometric ratio of amine hydrogens/epoxy groups %	Viscosity, Pa · s		
			0 h	24 h	48 h
E6/MPDA 100	14.0	100	19.5 ± 0.3	> 10 000	Solid
E6/ChCl/MPDA 100	23.0	100	20.0 ± 0.1	764.8 ± 1.9	Solid
E6/ChCl/MPDA 90	20.7	90	23.2 ± 0.1	370.0 ± 1.2	Solid
E6/ChCl/MPDA 80	18.4	80	23.0 ± 0.2	274.7 ± 0.6	Solid
E6/DAT 100	16.0	100	29.2 ± 0.9	383.0 ± 1.2	Solid
E6/ChCl/DAT 100	25.0	100	19.3 ± 0.3	Solid	Solid
E6/ChCl/DAT 90	22.5	90	29.5 ± 1.3	Solid	Solid
E6/ChCl/DAT 80	20.0	80	34.0 ± 1.3	6126.0 ± 12.2	Solid

Solid – after gelation sample solidified.

ARES stress rheometer (Rheometric Scientific), a plate-plate Φ 40 mm, a gap of 1 mm, 1 Hz.

Viscosity of ChCl/MPDA was determined at 25 °C using Brookfield Model DV-III Programmable Rheoviscometer with small sample adapter CP-44Y, volume: 0.5 cm^3, spindle CP-51. Repeatability of viscosity measurements was 0.2 %. The curing process of the epoxy compositions was followed using DSC Q-100 (TA Instruments) at the heating rate 5 °C/min in temperature range of 30–300 °C in nitrogen atmosphere. The T_g (from the peak of tan δ curve), and storage modulus E' values of the cured epoxy materials were measured using DMTA Q-800 (TA Instruments) with dual cantilever, at the heating rate 3 °C/min from 30 to 250 °C and frequency 1 Hz. Estimated repeatability of specific temperatures determination by DSC measurements was 1–2 °C, whereas ΔH 2–3 %. Uncertainty of DMTA results, *i.e.*, repeatability of T_g, tan δ and determination was 1 %.

RESULTS AND DISCUSSION

DESs characteristics

From Table 1, it follows that ChCl/MPDA is a liquid with T_g = -57 °C. At room temperature it is stable for long time (at least 6 months). Viscosity of that DES is 4060 mPa · s at 25 °C (measured 24 h after preparation). The fresh light and clear liquid gradually starts to darken in contact with air. On the other hand, ChCl/DAT after preparation is a black colored and very low viscous liquid showing tendency to crystallization after few hours of store. The melting point of ChCl/DAT is 49 °C. Taking above into account it may be concluded that the depression of T_g or melting point (ΔT_m), related to the lower melting point component of DES (*i.e.*, aromatic diamine), is *ca.* 121 °C for ChCl/MPDA and only 49 °C for DES based on DAT. For the former, ΔT_m value is rather high, comparable to that for conventional DES based on ChCl and urea (*ca.* 122 °C) [6].

As the physicochemical data for DESs based on ChCl and aromatic amines are not known, an influence of the amine structure on the physical properties of ChCl/MPDA and ChCl/DAT can be interpreted on the basis of available results for DESs consisting of ChCl mixtures with other aromatic hydrogen bond donors, such as phenols, namely unsubstituted phenol and *p*-cresol. Freezing points of DESs based on ChCl with phenol (-30 °C) and ChCl with *p*-cresol (-8 °C) were reported in a patent specification [7]. Moreover, Zhu *et al.* [10] have recently found that the structure of phenols closely determines the ability of hydrogen bond formation between phenol OH groups and Cl anion of ChCl, thus influencing the physicochemical properties of DES. High viscosity of DES based on phenol (unsubstituted) is mainly attributed to the presence of a massive hydrogen bond network between each component resulting in reduced mobility of free species within the DES. By analogy: strong hydrogen bond formation seems to cause a substantial depression of melting point and high viscosity of ChCl/MPDA system. Methyl group present in the aromatic ring results apparently in a weaker hydrogen bond interaction between ChCl and DAT as well as lower both ΔT_m and viscosity of the DES than in the case of ChCl/MPDA.

Pot life at ambient temperature

The viscosity of epoxy compositions with DESs increased relatively fast during storage at room temperature (Table 2). This behavior is similar to that reported for other epoxy/DES systems. The gelation time for E6/ChCl/imidazole system was reported to be in the range between 24 and 48 h (even though DES ratio to epoxy resin and curing mechanism were different [4]). From Table 2 it is also evident that viscosities of epoxy compositions with ChCl/MPDA measured directly after preparation are not significantly different from those for the reference sample cured with MPDA alone (20.0–23.2 Pa · s for E6/ChCl/MPDA samples and 19.5 Pa · s for E6/MPDA). On the contrary, after 24 h of storage the viscosities of epoxy compositions with ChCl/MPDA are clearly lower than that of the reference system (*ca.* 275–765 Pa · s *versus* ≥ 10 000 Pa · s). The gelation points are shifted to longer times in comparison to E6/MPDA system. It is estimated that pot lives of epoxy compositions with ChCl/MPDA are about 50 % longer than for the reference system. Rather different changes of viscosity are observed for E6/ChCl/DAT system. A decrease is observed from 29.2 to 19.3 Pa · s for E6/ChCl/DAT 100 when compared with E6/DAT system. The viscosity increased again to 29.5 and 34.0 Pa · s for the systems with substoichiometric amounts of ChCl/DAT. It is noteworthy that practically all epoxy compositions with ChCl/DAT exhibited very high level of viscosity (or gel) after 24 h of storage time.

Epoxy resin curing analyzed by DSC

DSC thermograms of epoxy compositions with both aromatic amines alone and with DESs, registered during heating runs are presented in Fig. 1, whereas characteristic temperatures are collected in Table 3.

Onset temperature (T_p) for compositions cured with MPDA and ChCl/MPDA differed slightly showing 3–4 °C higher values than the systems cured with DES used at various weight ratios. In similar manner, the temperatures at maximum of exotherms (T_{max}) for E6/MPDA (131 °C) and the set of E6/ChCl/MPDA compositions (129–133 °C) are changed. Higher differences of respective T_p and T_{max} values were found for the second series of epoxy compositions based on DAT. Thus for E6/DAT and E6/ChCl/DAT 100 samples T_p changed from 97 to 92 °C and T_{max} from 136 to 128 °C. More distinct increases of both characteristic temperatures are observed for epoxy materials cured with the DES used at decreasing

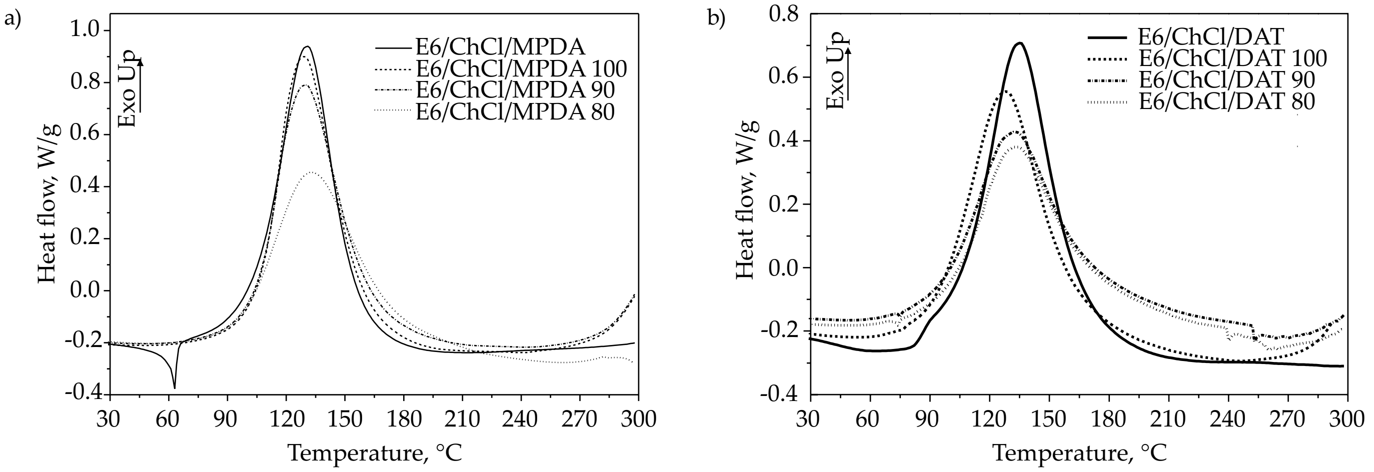

Fig. 1. DSC thermograms of epoxy resin compositions with DESs based on ChCl and: a) *m*-phenylenediamine, b) 2,4-diaminotoluene

Table 3. Results of DSC and DMTA measurements for epoxy materials cured with DESs based on ChCl and aromatic diamines

Sample acronym	DSC			DMTA		Storage modulus
	T_p, °C	T_{max}, °C	ΔH, J/g	T_g, °C	tan δ	E', MPa
E6/MPDA 100	98	131	514	154	1.17	2545
E6/ChCl/MPDA 100	101	129	511	154	1.08	2501
E6/ChCl/MPDA 90	102	130	508	154	0.95	2290
E6/ChCl/MPDA 80	101	133	455	150	1.05	2473
E6/DAT 100	97	136	529	163	0.68	1751
E6/ChCl/DAT 100	92	128	486	144	0.86	1935
E6/ChCl/DAT 90	97	133	392	149	1.09	2101
E6/ChCl/DAT 80	101	134	371	135	0.85	2625

weight ratios (T_p 92 → 101 °C and T_{max} 128 → 134 °C). Relatively large differences of reaction heats determined by DSC were registered for both series of epoxy compositions (Table 3). In the case of curing agents containing MPDA, similar ΔH values were found for E6/MPDA and E6/ChCl/MPDA compositions with two higher DES contents (*i.e.*, 100 and 90 % of the amine stoichiometry). These values are in the range 99.6–98.8 % of the ΔH value for the reference system, respectively. Third composition E6/ChCl/MPDA 80 exhibited somewhat lower ΔH (455 J/g), corresponding to 88.5 % of the reference system value. For the second set of epoxy compositions, a high value of ΔH (529 J/g) was measured only for the reference system with DAT alone. For epoxy compositions containing DES, the value of reaction heat decreased to 92 % for E6/ChCl/DAT 100, or to 74 and 70 % for epoxy systems with lower DES contents. The DSC results suggest that DES based on ChCl and MPDA seems to be more effective as a curing agent of epoxy resin than those based on ChCl and DAT.

Thermomechanical properties

The glass transition temperatures, tan δ, and storage moduli for the epoxy materials studied are presented in Table 3. Generally, inspection of T_g shows that the values of that parameter for E6/MPDA and E6/ChCl/MPDA are not affected when DES at stoichiometric amounts were applied (154 °C), but slightly decreased for the system with reduced DES content (150 °C for E6/ChCl/MPDA 80). These T_g values are evidently higher than those recorded for the epoxy materials cured with other DESs [5]. On the other hand, T_g for the set of epoxy materials cured with DAT and ChCl/DAT showed a descreasing trend from 163 °C for E6/DAT to 135–149 °C for the samples cured with lowering amounts of ChCl/DAT. This descending trend is clear even though the relevant data in Table 3 are rather scattered.

The second thermomechanical parameter, *i.e.*, tan δ represents the ratio of viscous to elastic response of viscoelastic material (tan $\delta = E''/E'$, where E' is the storage, and E'' the loss modulus). It can be seen that: (i) the value of tan δ for epoxy material cured with MPDA alone is the highest and it slightly decreases when lowering ChCl/MPDA amounts are applied (1.17 → 0.95–1.08), (ii) somewhat smaller values of that parameter were measured for E6/DAT and E6/ChCl/DAT samples (0.68 → 0.85–1.09). The observed pattern of tan δ changes shows that the epoxy materials cured with MPDA and ChCl/MPDA exhibit more important contribution of viscous portion of energy dissipated as heat (represented by E'' not shown in Table 3), considering also relatively high elastic portion of the stored energy exemplified by *E'*, than the second set of the tested samples based on DAT. As it was mentioned earlier, somewhat higher (and narrowly placed) values of storage moduli *E'* were registered for epoxy materials based on MPDA curatives, than for DAT based systems, with slightly decreasing tendency when lower DES contents were used. An opposite feature was observed for epoxy materials with DAT and DAT-based DES, *i.e.*, here *E'* increased with similar sequence of ChCl/DAT changes.

CONCLUSIONS

Deep eutectic solvents based on aromatic amines were prepared for the first time and tested as epoxy resin curing agents. One of the developed DESs based on ChCl and MPDA (at molar ratio 1 : 2) is a viscous liquid at room temperature (but with viscosity *ca.* 4-times lower than that of epoxy resin) and can be easily cold-homogenized with the liquid resin. Consequently, less viscous compositions with pot life extended by about 50 % can be formulated when the DES is applied using stoichiometric or substoichiometric MPDA content (*i.e.*, ≥ 80 % amine stoichiometry). The resulting cured materials possess acceptable thermomechanical properties and can be designated especially for filament wound pipes, pressure vessels, and prepreg production.

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