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On the curing reaction of an epoxy resin based on mesogenic naphthalene derivative

Summary — The curing reaction of diglycidyl ether of 2,7-dihydroxynaphthalene (2,7-DGEDHN), epoxy mesogenic monomer, in the presence of the curing agents, namely, 4,4′-methylene-bis(3-chloro-2,6-diethylaniline) (MCDEA), 2,7-diaminofluorene (DAF) or 2-aminobiphenyl (2-ABP), was studied using differential scanning calorimetry (DSC), optical microscopy under crossed polarizers and wide angle X-ray scattering (WAXS) techniques. The curing reaction of 2,7-DGEDHN/MCDEA mixture led to a product without liquid crystalline properties. The product obtained by the curing reaction of 2,7-DGEDHN/DAF mixture is characterized by a texture of smectic-like structure of Schlieren type. The curing reaction of 2,7-DGEDHN/2-ABP mixture led to an isotrope non-crosslinked product.

Key words: epoxy resins, liquid crystalline polymers, curing, differential scanning calorimetry, wide angle X-ray scattering, optical microscopy under crossed polarizers.

REAKCJA UTWARDZANIA ŻYWICY EPOKSYDOWEJ NA PODSTAWIE MEZOGENICZNEJ POCHODNEJ NAFTALENU

Streszczenie — Badano reakcję utwardzania eteru diglycydylowego 2,7-dihydroksynaftalenu (2,7-DGEDHN), mezogenicznego monomeru epoksydowego, w obecności jednego ze środków sieciujących: 4,4′-metyleno-bis(3-chloro-2,6-dietyloaniliny) [MCDEA, wzór (I)], 2,7-diaminofluorenu [DAF, wzór (II)] lub 2-aminobifenylu [2-ABP, wzór (III)]. Przebieg reakcji monitorowano za pomocą różnicowej kalorymetrii skaningowej (DSC) (rys. 1, 2 i 5) oraz techniki szerokokątowego rozpraszania promieni rentgenowskich (WAXS) (rys. 4). Teksturę utwardzonej żywicy obserwowano używając mikroskopu optycznego ze skrzyżowanymi polaryzatorami (rys. 3). Stwierdzono, że reakcja utwardzania w układzie 2,7-DGEDHN/MCDEA prowadzi do produktu nie mającego właściwości ciekłokrystalicznych, a w układzie 2,7-DGEDHN/DAF do produktu o strukturze podobnej do smektycznej, typu Schlieren′a. Natomiast zastosowanie 2-ABP jako środka utwardzającego daje nieusieciowany, liniowy produkt.

Słowa kluczowe: żywice epoksydowe, polimery ciekłokrystaliczne, utwardzanie, różnicowa kalorymetria skaningowa, szerokokątne rozpraszanie promieni rentgenowskich, mikroskopia optyczna ze skrzyżowanymi polaryzatorami.

Epoxy resins are the most important thermosetting polymers, widely used as structural adhesives and matrices for fibre compositions [1]. Linear epoxy resins are converted into a three dimensional crosslinked thermoset network during cure process [2, 3]. Epoxy resins, after crosslinking, show good thermal, electrical and mechanical properties, but they are brittle and show poor resistance to crack propagation [4—7]. Toughness and other properties of epoxy resins can be significantly improved by their modification, using fillers and flexibilizing agents, polymers, additives, reactive liquid rubbers, curing agents, reactive diluents, and so on [8—10].

Because the industry, with special reference to the aeronautic one, is looking for new materials with high technological characteristics, researchers focus on the obtaining epoxy resins with properties differing from those shown by conventional ones. In the last few years attention has been paid to liquid crystalline (LC) networks for their good mechanical, thermal and rheological properties. So, LC epoxy polymers were the subjects of increased research interest and technological applications [11].

One way to synthesize the LC epoxy resin is the curing reaction of some functionalized mesogenic rigid molecules with a suitable curing agent. The most known mesogens are the compounds with aromatic rings [12—17].

The epoxy compounds with naphthalene mesogen, in the presence of aromatic amines used as the curing agents, produce high heat-resistant LC networks [18, 19]. Naphthalene mesogen is thermally stable and stabilizers LC phase of the synthesized network.

In our previous work [20] we studied the synthesis and the characterization of some LC epoxy thermosets obtained by the curing reaction of diglycidyl ether of

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2,7-dihydroxynaphthalene (2,7-DGEDHN) epoxy mesogenic resin with sulphanylamide (SAA), diaminopyridine (DAP) or diaminodiphenylsulphone (DDS), used as the curing agents. As results of the curing reaction, 2,7-DGEDHN/SAA mixture led to a texture of nematic-like structure, the mixture 2,7-DGEDHN/DAP showed a smectic-like structure while 2,7-DGEDHN/DDS mixture formed a network without LC properties.

This paper reports new data regarding the curing reaction of 2,7-DGEDHN in the presence of aromatic amines, used as the new curing agents, namely, 4,4′-methylene-bis(3-chloro-2,6-diethylaniline), 2,7-diaminofluorene or 2-aminobiphenyl.

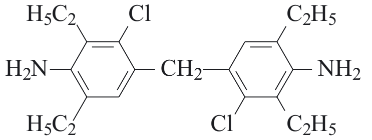
EXPERIMENTAL

Materials

2,7-DGEDHN used as monomer was synthesized starting from 2,7-dihydroxynaphthalene (2,7-DHN), epichlorohydrin (EPI) and NaOH [16].

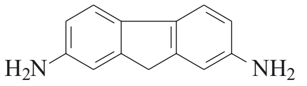
As the curing agents three amines from Aldrich Chemical Co. were applied (without further purification):

— 4,4′-methylene-bis(3-chloro-2,6-diethylaniline) [MCDEA, formula (I)],



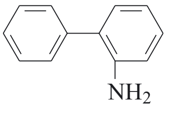
(I)

— 2,7-diaminofluorene [DAF, formula (II)],



(II)

— 2-aminobiphenyl [2-ABP, formula (III)].



(III)

Methods of testing

The epoxy equivalent (*EE*) of the synthesized monomer was evaluated in a pyridine-HCl solution, as previously reported [21].

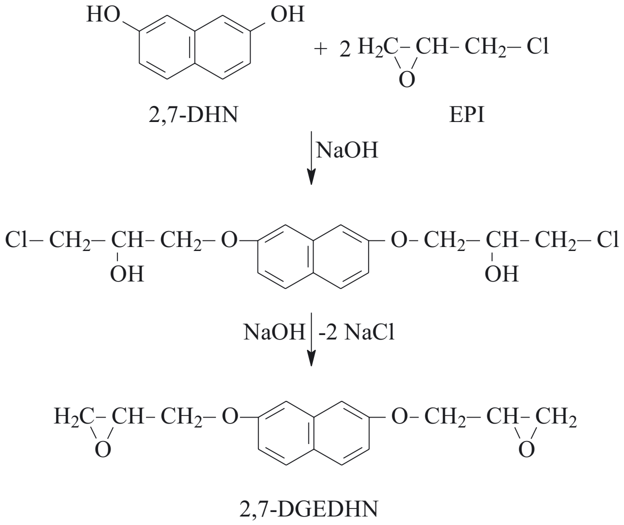
The curing reaction of 2,7-DGEDHN was monitored by differential scanning calorimetry (DSC), optical microscopy under crossed polarizers, and wide angle X-ray scattering (WAXS).

The DSC studies were carried out using Perkin-Elmer DSC-7 calorimeter. The texture of the obtained LC epoxy resin was observed by means of an optical microscope Reichert Yung under crossed polarizers, equipped with hot stage Linkam THMS 600. The WAXS analyses were carried out using a Philips Electronics PW 1830 generator provided with a Copper autocathode tube having a nickel filter. The generator was operated at 45 kV and 30 mA.

RESULTS AND DISCUSSION

The chemical reactions used for synthesis of 2,7-DGEDHN compound is presented in Scheme A.

The *EE* value determined for the synthesized monomer was 0.68 mol/100 g resin (0.735 theoretic).



Scheme A

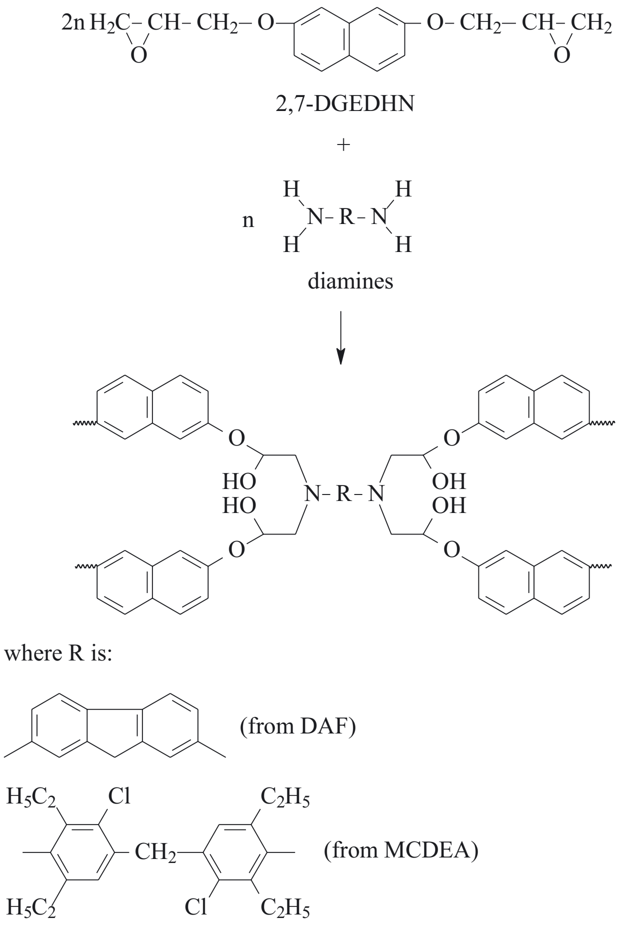
As it was previously reported [22], 2,7-DGEDHN melted at 64 °C and behaved as an isotropic liquid. The curing reaction of the rigid monomer with both tetrafunctional aromatic amines and difunctional aromatic amine was monitored by observation of phase transformation of the isotropic monomer. The amines used as the curing agents were in an isotropic state.

The reactions between 2,7-DGEDHN and MCDEA or DAF amines are shown in Scheme B, while 2-ABP in Scheme C.

Curing reactions of 2,7-DGEDHN/MCDEA mixture

The curing reaction of 2,7-DGEDHN/MCDEA mixture was studied using DSC in dynamic conditions for a heating rate of 10 °C/min, and the temperature interval between -20 and 260 °C. Corresponding to this reaction DSC trace is shown in Fig. 1.

As can be noticed, the fusion of the studied mixture takes place in the temperature interval between 27 and 96 °C. This interval is characterized by the presence of some multiple peaks, which are determined by the successive fusion of the epoxide and the amine. The enthalpy of the mixture fusion is around 30.9 kJ/g. The crosslinked reaction of 2,7-DGEDHN/MCDEA mixture



Scheme B

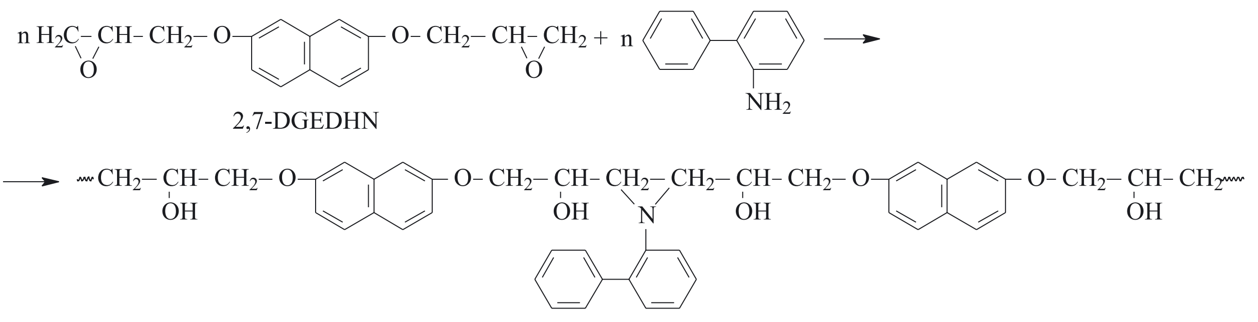
takes place in a large interval of temp. 158—259 °C. In this interval the reactivity of the amine used as the curing agent is much diminished by the inductive effects of electron donors due to the chlorine atoms. For the crosslinking process there is a peak centered at temp. T_{peak} = 231 °C, with the enthalpy of reaction ΔH =121.4 kJ/g.

The curing reaction of 2,7-DGEDHN/MCDEA mixture was also observed by optical microscopy under crossed polarizers. This technique showed that the epoxide melts starting from temp. 30 °C, while an amine, as a solid powder dispersed in the melted epoxide, is melted temp. around 90 °C. 2,7-DGEDHN/MCDEA mixture is in isotropic liquid state at temperature 95 °C. At high temperature the studied mixture remains in the isotropic state. The conclusion is that the curing reaction of 2,7-DGEDHN/MCDEA mixture leads to a network not showing LC properties.

Curing reaction of 2,7-DGEDHN/DAF mixture

The DSC thermogram obtained for the curing reaction of 2,7-DGEDHN/DAF mixture, at a heating rate of 10 °C/min, is shown in Fig. 2.

This thermogram starts with the melt of the epoxide between 36 and 59 °C, with a peak centered at 54 °C, and ΔH = 5.5 kJ/g. The fusion of amine takes place at temp. of 72 °C, with ΔH = 8.5 kJ/g. The curing reaction of 2,7-DGEDHN/DAF mixture takes place in a large inter-



Scheme C

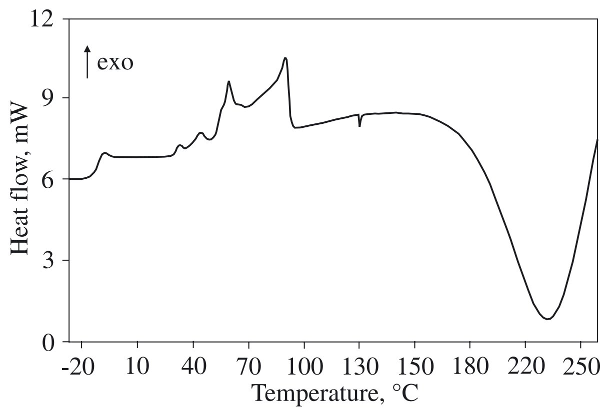


Fig. 1. DSC thermogram of 2,7-DGEDHN/MCDEA mixture heated with rate 10 °C/min

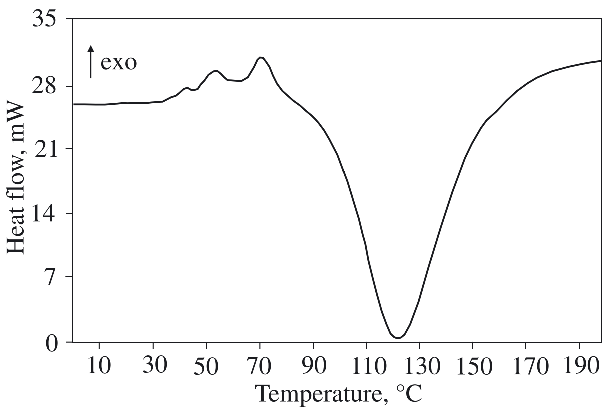


Fig. 2. DSC thermogram of 2,7-DGEDHN/DAF mixture heated with rate 10 °C/min

val of temperature, between 81 and 171 °C, with T_{peak} = 122 °C and ΔH = 372.1 kJ/g.

The curing reaction of 2,7-DGEDHN/DAF mixture was studied also by optical microscopy under crossed polaryzers. A complete fusion of the mixture at temperature higher than 80 °C was observed, followed by appearance of well define, birefringent zones, which correspond to a texture of high density of Schlieren type (Fig. 3).

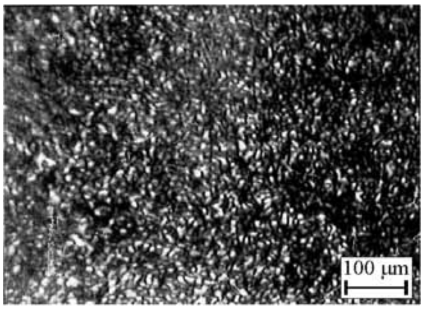


Fig. 3. The Schlieren texture, under crossed polaryzers, of crosslinked product of 2,7-DGEDHN/DAF mixture

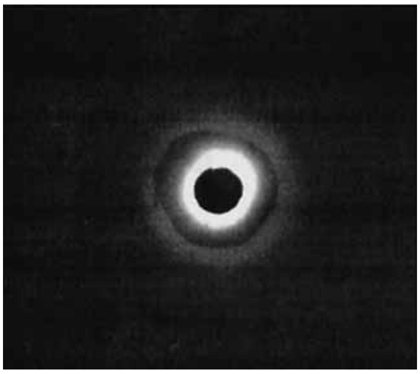


Fig. 4. WAXS pattern of 2,7-DGEDHN/DAF mixture

The WAXS pattern of the crosslinked 2,7-DGEDHN/DAF product is shown in Fig. 4. The pattern contains a sharp inner ring and a number of outer rings with a *d*-spacing of 4.5 Å. This distance is characteristic to a smectic texture of C type.

Curing reaction of 2,7-DGEDHN/2-ABP mixture

The DSC thermogram of 2,7-DGEDHN/2-ABP mixture obtained in dynamic conditions is shown in Fig. 5.

The two studied monomers melt in a large interval of temperature between 21 and 79 °C, with the enthalpy ΔH = 31.2 kJ/g. The reaction between 2,7-DGEDHN and 2-ABP amine takes place with a slow rate, starts at temp. of 128 °C, and the process is finished at around 250 °C. For this process ΔH = 216.3 kJ/g.

The study carried out by optical microscopy under crossed polaryzers showed that the melted mixture is in isotrope state. The same behaviour was observed using WAXS technique.

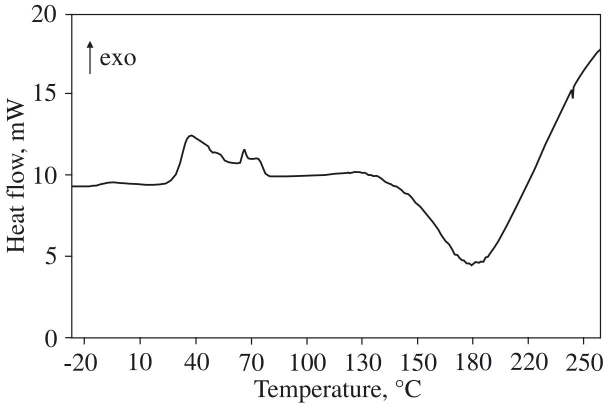


Fig. 5. DSC thermogram of 2,7-DGEDHN/2-ABP mixture heated with rate 10 °C/min

As in the case of 2,7-DGEDHN/MCDEA mixture, 2-ABP amine shows an unfavorable influence on the appearance of the mesophase, when it is used as the curing agent for 2,7-DGEDHN epoxy monomer. The side position of the biphenyl versus the reactive amine groups diminished both the rigidity of the main chain and its linearity. In conclusion, 2-ABP amine is not a suitable agent for the curing of 2,7-DGEDHN compound. The linear compound originates as a result of the reaction between the functional groups of the two monomers.

CONCLUSIONS

The curing reaction of 2,7-DGEDHN in the presence of various amines showed that the process was complex and depended on the nature of the amine used as the curing agent.

The curing of 2,7-DGEDHN/MCDEA mixture takes place in a large interval of temperature, between 158 and 259 °C, with ΔH = 121.4 kJ/g, and leads to an isotropic material.

In the presence of DAF amine, the final product obtained by curing of 2,7-DGEDHN is characterized by a structure of high density of Schlieren type, which corresponds to a smectic texture of type C.

2-ABP amine, used as a curing agent for 2,7-DGEDHN epoxy monomer leads to a non-crosslinked product.

In DSC experiments of the investigated systems the second heating has not shown any residual release. This behaviour means that the studied reactions were completed [23].

REFERENCES

1. May C. A.: "Epoxy Resins. Chemistry and Technology", 2nd edition, Marcel Dekker, New York 1988.
2. Urbaniak M., Grudzinski K.: *Polimery* 2004, **49**, 89.
3. Kowalczyk K., Spychaj T.: *Polimery* 2003, **48**, 833.

4. Liaw D. J., Shen W. C.: *Polym. Eng. Sci.* 1994, **34**, 1297.
5. Stark E. B., Seferis J. C.: *Thermochim. Acta* 1984, **77**, 19.
6. Vaskil U. M., Martin G. C.: *J. Appl. Polym. Sci.* 1992, **46**, 2089.
7. Wright C. D., Muggee J. M.: "Structural Adhesives. Chemistry and Technology" (ed. Hartshorn S. R.), Marcel Dekker, New York 1986, p. 113.
8. Oprea S., Vlad S., Stanciu A., Macoveanu M.: *Eur. Polym. J.* 2000, **36**, 373.
9. Tanaka Y., May C. A.: "Epoxy Resins. Chemistry and Technology", Marcel Dekker, New York 1973.
10. Mustata B., Bicu I., Cascaval C. N.: *J. Polym. Eng.* 1997, **17**, 491.
11. Mazela W., Czub P., Pielichowski J.: *Polimery* 2004, **49**, 233.
12. Mossety-Leszczak B., Galina H., Wlodarska M.: *Polimery* 2003, **48**, 511.
13. Carfagna C., Amendola E., Giamberini M.: *Composite Struct.* 1994, **27**, 37.
14. Mormann W., Bröcher M.: *Macromol. Chem. Phys.* 1996, **197**, 1841.
15. Lu M. G., Shim M. Y., Kim S. W.: *Macromol. Chem. Phys.* 2001, **202**, 223.
16. Mormann W., Bröcher M.: *Polymer* 1998, **39**, 4905.
17. Barclay G., Ober C. K., Papathomas K., Wang D. W.: *J. Polym. Sci., Part A: Polym. Chem.* 1992, **30**, 1831.
18. Carfagna C., Amendola E., Giamberini M.: *Macromol. Chem. Phys.* 1994, **195**, 2307.
19. Lee J. Y., Jang J.: *J. Polym. Sci., Part A: Polym Chem.* 1999, **37**, 419.
20. Mititelu-Mija A., Cascaval C. N., Navard P.: *Design. Monom. Polym.* 2005, **8**, 487.
21. Cascaval C. N., Mustata F., Rosu D.: *Angew. Makromol. Chem.* 1993, **209**, 157.
22. Mititelu-Mija A.: Thesis, Ecole des Mines de Paris, UMR CNRS 7635, Sophia—Antipolis, France 2001.
23. Sbirrazzuoli N., Vyazovkin S., Mititelu-Mija A., Sladic C., Vincent L.: *Macromol. Chem. Phys.* 2003, **204**, 1815.

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