SCIENTIFIC BULLETIN OF THE TECHNICAL UNIVERSITY OF LODZ
No. 1010 Physics, Vol. 28 2007

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# CURING PROCESS AND THE CURING PRODUCT OF A NEMATIC EPOXY RESIN CONTAINING ESTER GROUPS

*Curing process and the product of curing of one liquid crystalline epoxy monomer with a standard amine were examined. The reactions were monitored by DSC measurement and dielectric spectroscopy. Progress of curing of the examined mixture at different temperatures was shown. Influence of curing conditions on the final product was discussed and compared with other similar systems. DSC thermograms of the curing product were also analysed.*

**Keywords:** Liquid crystalline polymer network, dielectric properties, curing process.

## 1. INTRODUCTION

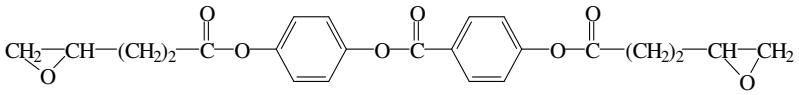
Technical development requires constant search for new materials, having special properties. Liquid crystalline polymer networks (LCPN) constitute one group of such new materials. Properties of polymer networks of that kind are heavily influenced by both permanent linkage between chains and external conditions of the curing reaction. The possibility of modifying molecular orientation during the reaction (by means of e.g. external magnetic field, or selection of sample substrate) can result in anisotropy of some physical properties of the product [1,2]. Liquid crystalline polymer networks are obtained in well-known curing reactions, using typical liquid crystalline monomers.

Typical curing agents used in reactions involving epoxy monomers are aromatic amines [3]. Due to liquid crystalline properties of epoxy monomers the progress of the curing reaction is more complex than in the case of traditional epoxy materials [4]. Dielectric spectroscopy is very well suited to monitoring the curing process of such systems. This method enables precise observation of changes in ionic mobility or conductivity in the course of the reaction and has been successfully applied to traditional epoxy-amine systems [5]. Application of this technique to liquid crystalline epoxy monomers in earlier works gave interesting results [6]. In this paper dielectric spectroscopy is used to trace changes in ionic mobility in the course of isothermal curing of a liquid crystalline epoxy monomer with a standard amine. Due to high ionic conductivity at the curing temperatures, dielectric response in thelow frequency range is analysed in terms of the electric modulus M (defined as $M^* = 1/\varepsilon^*$, where $\varepsilon^*$ is the complex permittivity). This is an alternative approach to the analysis of dielectric relaxation data in ionic materials. In the modulus representation, the observed frequency of the peak in the imaginary part of the modulus - M" - is directly proportional to ionic conductivity. The temperatures of phase transitions and type of mesophase of the studied material were reported elsewhere [7,4]. In our earlier studies of similar systems using other amines the curing process required high temperatures, at which the material would often lose its mesomorphic properties. Using a different amine as curing agent for the investigated material one can expect to improve the conditions of the reaction (temperature and duration of curing). The obtained results are compared with earlier studies.

## 2. MATERIALS

The material studied in this work (identified hereafter by the acronym MU1) is an epoxy monomer containing ester groups in the mesogen. Its molecular structure is shown in the figure below (Fig. 1) along with the amine (DAT) used for curing. The monomer was synthesized earlier and its structure and purity were carefully studied and reported elsewhere [7,4]. Temperatures of phase transitions of the monomer are shown in Tab. 1. The mixtures for curing were prepared from stoichiometric amounts of the monomer and the amine at room temperature. The mixtures were isothermally cured at the temperatures of 120$^o$C and 140$^o$C.

**MU1**



**DAT**

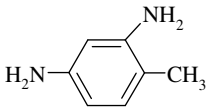


Fig. 1. Chemical structure of the studied compounds

Table 1

Temperatures of phase transitions detected in the investigated material. N – nematic, L – isotropic liquid

| Temperatures of phase transitions [°C] | |
|---|---|
| Solid → 78 (N) → 116 (L) | Heating |
| Solid ← 59 (N) ← 115 (L) | Cooling |

## 3. RESULTS AND DISCUSSION

The process of curing the epoxy nematic liquid crystal MU1 with the amine DAT was analysed with the use of DSC and dielectric spectroscopy. DSC measurements revealed the temperatures at which cross-linking takes place. A dynamic DSC curve for the investigated system, recorded during heating at a constant rate of 10 deg/min, is shown in Fig. 2. The first endothermic peak corresponds to melting of the amine and the monomer. The exothermic peak accompanying the curing reaction becomes visible above 125°C, but holding the mixture for some time at a temperature above 100°C is also sufficient to initiate slow progress of the reaction. Obviously, curing time is longer in lower temperatures, as the reaction runs slower. Curing at lower temperatures (below 125°C) can also result in the reaction stopping before reaching full conversion. For these reasons samples cured at lower temperatures require post-curing treatment at a higher temperature. This is a normal practice for epoxy materials.

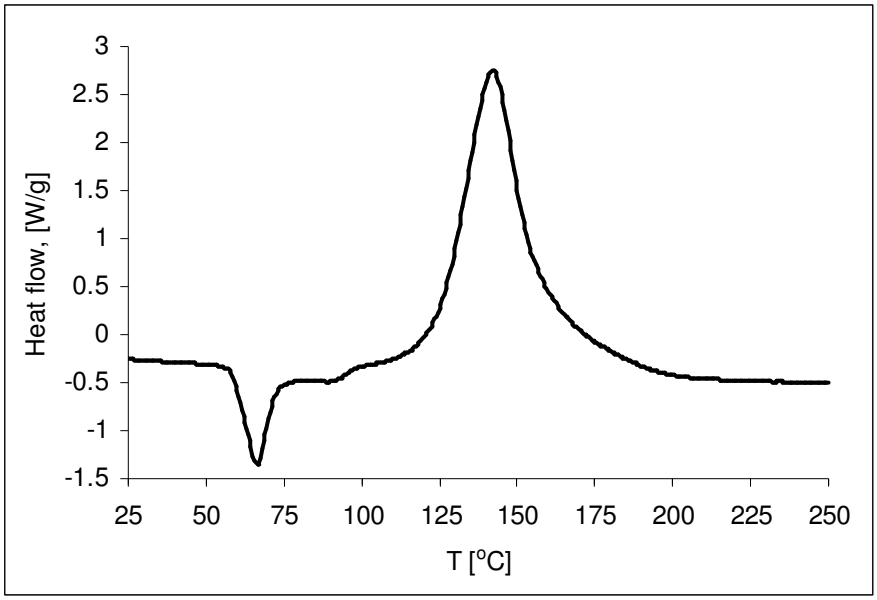



Fig. 2. Dynamic DSC thermogram for curing of the mixture MU1/DAT

Precise image of the reaction progress can be obtained by measuring changes in the dielectric response of the reacting system over time. In the present work dielectric measurements were applied to study changes in ionic conductivity during the reaction, by expressing experimental data in terms of the electric modulus M. This approach turned out to be fruitful, since the changes occurring in the cured system are well reflected in the plots of the electric modulus vs. frequency recorded at different times during the reaction, enabling observation of reaction dynamics in detail. The measurements were performed in the course of curing carried out at two different temperatures - 120°C and 140°C. The dynamics of the process at 120°C (Fig. 3) is quite different than that observed at 140°C (Fig. 4). At the lower temperature conductivity is constantly changing for the first 80 minutes, then the process slows down. It can be seen that after 80 minutes the process is going on very slowly as the curves recorded at later times are very similar to each other. It means that the process is practically frozen, though the reaction is not fully completed yet. This conclusion can be drawn from comparison of the described results with the progress of curing carried out at the temperature of 140°C (Fig. 4).

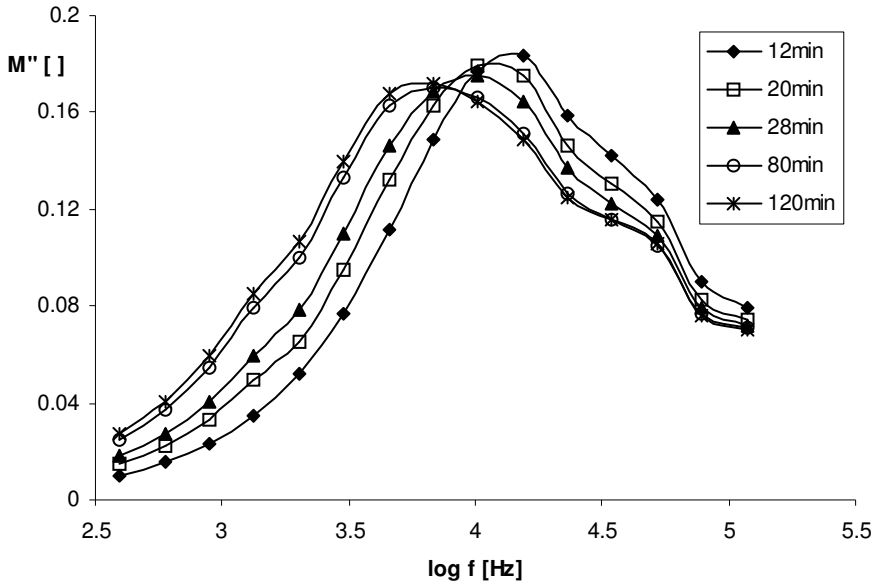



Fig. 3. Progress of isothermal curing of the MU1/DAT system at 120°C. The plots show the imaginary component of the electric modulus M" vs. frequency in various phases of the reaction

At the higher temperature the changes are larger (initially, the maximum of the electric modulus is beyond the scope of the plot, as a result of high conductivity at this temperature). In effect of the progressing reaction, conductivity changes significantly and after 40 minutes the peak can be seen within the frequency range covered by the measurements. With time, the changes are slower and after 120 minutes the conductivity practically becomes constant. Comparing the reaction dynamics at 120°C and 140°C we can conclude that achieveable degree of conversion depends on the curing temperature and therefore post-curing treatment at an elevated temperature may be required for the mixture to react fully, especially when the initial curing temperature was moderate. Precise analysis of the curing process is very important because a system cured at a lower temperature and annealed later may have different properties than the same mixture cured at a higher temperature, due to liquid crystallinity range of the monomer. At a lower temperature it is easier to achieve desired orientation of the monomer molecules during the reaction. The obtained results complement earlier studies of similar systems, where observations of the curing process were carried out through viewing

changes in dipolar mobility [7]. In both cases dielectric measurements enable tracing the dynamics of the curing process, which may slightly vary for particular systems. The studies on the curing process of the same monomer with other amines in earlier works required somewhat higher temperatures to initiate the reaction [4,7]. However, it must be noted that optimal selection of the curing conditions (temperature, reaction time and other) of mesomorphic epoxy materials in order to obtain desired physical properties is generally a complex issue.

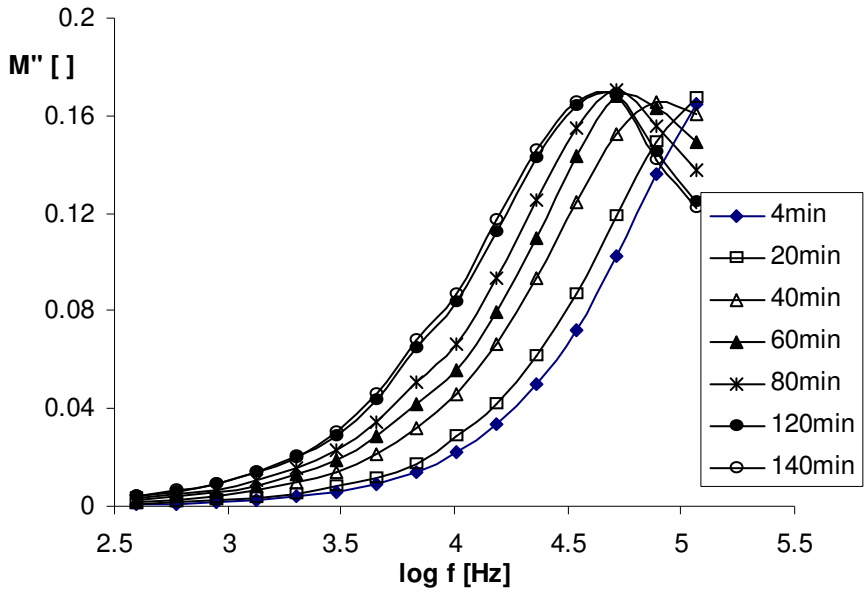



Fig. 4. Progress of isothermal curing of the MU1/DAT system at 140°C. The plots show the imaginary component of the electric modulus M" vs. frequency in various phases of the reaction

In both studies cases, the investigated mixtures after post-cure heating up to 200°C were fully crosslinked. This is confirmed by DSC study of the products (Fig. 5) where no transitions related to melting of the monomer or the amine can be seen. On the thermograms of the obtained materials there is an inflection characteristic for the temperature of vitrification. However it seems doubtful for the investigated materials to have such a low $T_g$ as for traditional crosslinked epoxy resins this temperature is usually much higher. The inflection about the temperature of 50°C can be related e.g. to change in conformation of the aliphatic chains existing in the cured product. A similar shape of the DSC

curve was also observed in other cured liquid crystalline epoxy resins [4]. Similar inflection appeared regardless of the amine used as curing agent and for various monomers [4]. Further analysis of the physical properties of the cured products and how they are influenced by external conditions of curing is the subject of follow-on research.

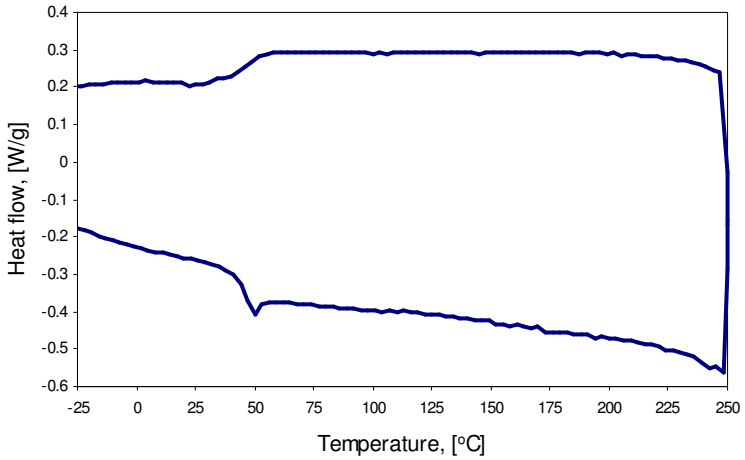



Fig. 5. DSC thermograms of the curing product of MU1/DAT mixture heated up to a high temperature (above 180°C)

## 4. CONCLUSIONS

1. Analysis of changes in ionic conductivity by means of dielectric spectroscopy in low frequency range proved to be very useful for monitoring of the progress of curing. This technique is a valuable complement to DSC, both methods together giving a more complete picture of the dynamics of curing.
2. Observations of changes in ionic conductivity performed with the use of dielectric spectroscopy for the MU1/DAT system demonstrated the need for post-curing treatment of the material which was cured at a temperature below 140°C.
3. Curing of the MU1/DAT mixture runs similarly to other systems, however the reaction can be initiated in this case at a temperature somewhat lower than in the case of the same monomer cured with other amines (DDM, PDA, DDE).

**Acknowledgments**

Part of this work was supported by EU project "DIELPOL" No MTKD-CT-2005-029670

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## PROCES SIECIOWANIA I PRODUKT REAKCJI NEMATYCZNEGO MATERIAŁU EPOKSYDOWEGO ZAWIERAJĄCEGO GRUPY ESTROWE

### Streszczenie

Badano proces sieciowania i produkt reakcji ciekłokrystalicznego materiału epoksydowego z typową aminą aromatyczną. Reakcje monitorowano za pomocą pomiarów DSC i spektroskopii dielektrycznej. Pokazano przebieg sieciowania badanej mieszaniny w różnych temperaturach. Przedyskutowano wpływ warunków sieciowania na produkt końcowy i dokonano porównania z innymi podobnymi układami. Przeanalizowano także termogramy DSC usieciowanego produktu.