

The Effect of Molecular Weight of Glycols on the Properties of Epoxy Resins

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The article presents and discusses experimental data regarding synthesis and characterization of epoxy resins modified with glycols of different molecular weight, synthesized in a 2: 1 molar ratio resin / glycol. The synthesis of epoxy resins modified with glycols was examined by using the spectrophotometer (FT-IR methods) against analytical (chemical) methods, by determining the content of the epoxy groups in time. Furthermore, in order to determine the influence of the glycol nature on the characteristics of the resulted resins, they were cured by using an aromatic polyamine hardener such as 4,4'-diaminodiphenylmethane (DDM), and the resulted epoxy resins were characterized by using both conventional mechanical analyses and the dynamic mechanical analyses (DMA). From the DMA determinations we noticed that resin flexibility increases in the same time with the polyetheric chain length.

Keywords: epoxy resin, glycol, glass transition, dynamical properties, mechanical properties

Epoxy resins of diglycidylether of bisphenol A (DGEBA) were considered to be one of the most important categories of thermosetting material due to their remarkable properties: adhesion and high chemical resistance [1]. Due to these characteristics, epoxy resins have multiple uses, in different domains, such as varnishes and paints, adhesives, casting and encapsulation resins, laminated materials, and stabilizers [2, 3].

The standard epoxy resins have the disadvantage of an extreme stiffness, which makes them easily breakable. For this reason, epoxy resins have limited use in surface coatings.

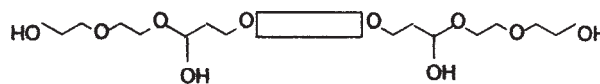
A series of methods were proposed in order to increase the flexibility of three-dimensional epoxy systems, including flexible hardeners, flexible epoxy resin, plasticizers or flexibilizers materials [4]. Another way of increasing the flexibility of the ordinary epoxy resin is to introduce flexible chains in their molecular structure e.g. the flexible chains of polyglycol chains [5]. Starting from these considerations, epoxy resins modified with glycols of different molecular weight were synthesized in a 2: 1 molar ratio epoxy resin: glycol.

The purpose of this paper is to study the influence of the glycol molecular weight on the speed of their reaction with the DGEBA as well as the influence of the polyether chain length on the final characteristics of crosslinking resins. We also aimed at observing the influence of the glycol molecular weight on the reaction speed and how this speed influences the mechanical characteristics of crosslinking resins. Depending on the ratio resin / glycol, two types of compounds can result:

-products with terminal hydroxyl groups (structure 1) when using glycol in excess:



-products with terminal epoxy groups (structure 2) when using resin in excess.



Further on, the synthesis of an epoxy resin was chosen starting from the DGEBA which becomes flexible by adding different glycols (molar ratio resin / glycol 2:1) and to be cross linked with a DDM amine hardener.

Experimental part

Materials, equipment and methods

Ethylenglycol (EG), diethylenglycol (DEG), tetraethyleneglycol (TTEG) were provided by Merck and used as received.

Epoxy resins ROPOXID 501 was received from Policolor. The resin characteristics were: dynamic viscosity 14600mPa.s (25°C); Epoxy Index (IE) = 0.529 equivalents (eq). Epoxy/100g, M = 379 g/mol.

The catalyst for the chemical modification of the epoxy resin was LiCl from Merck, used as a 50% solution in distilled water. An amount of 50 ppm catalyst solution was used for the ROPOXID 501 resin.

The crosslinking agent for the modified epoxy resin was the 4,4'-diaminodiphenylmethane (DDM), purchased from ACROS ORGANICS, with the following characteristics: M = 198 g/mol, m.p. = 89°C-91°C; b.p. = 398°C.

The FT-IR spectrophotometer measurements were performed by using a JASCO FT / IR 6300 spectrophotometer equipped with an ATR Specac Golden Gate (sapphire/diamond) accessory (30 scans, resolution 4 cm⁻¹).

The DMA measurements (dynamic mechanical analysis) were performed by using Q800 TA-Instruments. On specimens of about 60mm x3.5mm x4 mm, a temperature ramp method in air being used, at a heating

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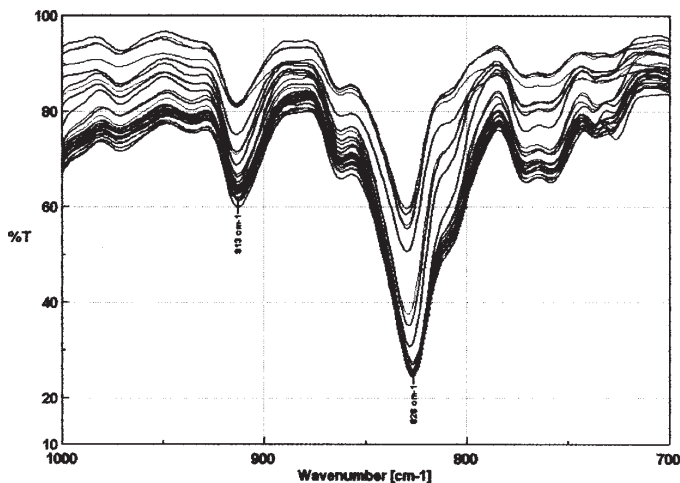


Fig.1. IR spectrum of epoxy resins modified with ethylenglycol 50 ppm LiCl 50%; 150°C; [DGEBA]/ [EG] = 2:1

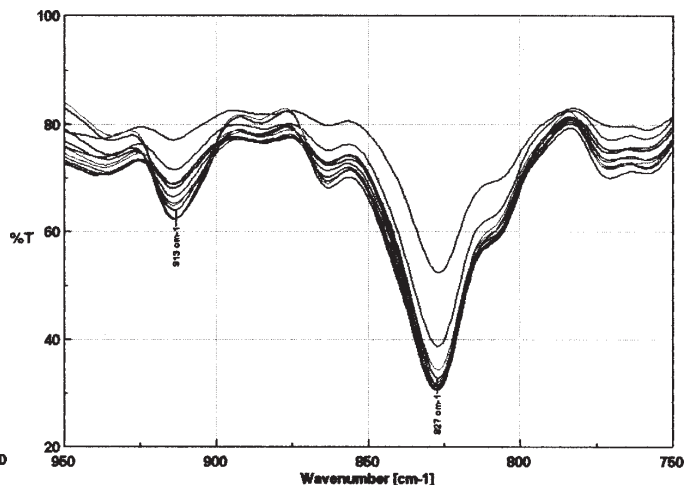


Fig.3. IR spectrum of epoxy resins modified with tetraethylenglycol 50 ppm LiCl 50%; 150°C; [DGEBA]/ [TTEG] = 2:1

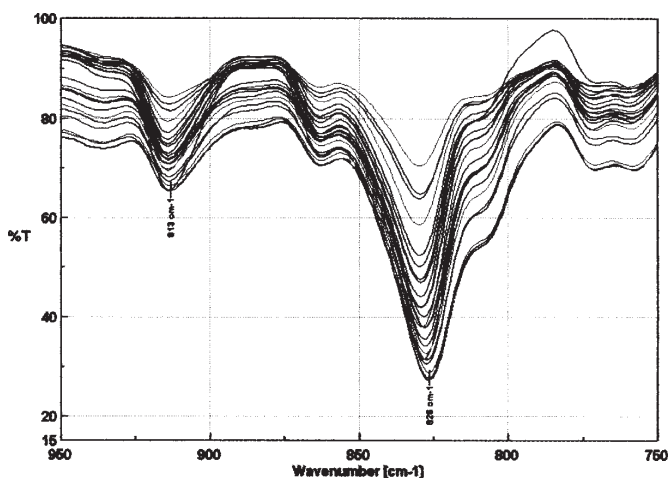


Fig.2. IR spectrum of epoxy resins modified with diethylenglycol 50 ppm LiCl 50%; 150°C; [DGEBA]/ [DEG] = 2:1

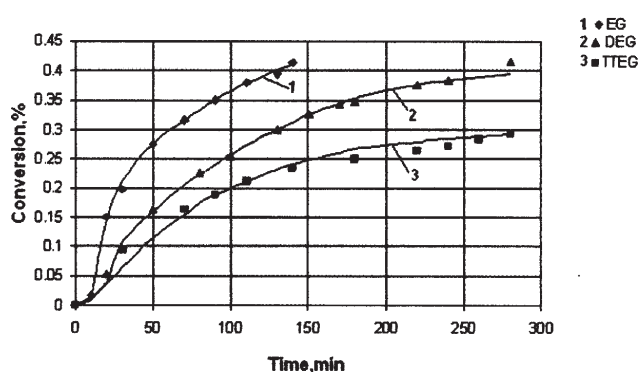


Fig.4. Variation of the epoxy index in time depending by the type of glycol in analytical method

speed of 3°C/min within the temperature range of 25-220°C, at a frequency of 1Hz and an oscillation amplitude of 20 μm.

The tensile properties (tensile strength, elongation at break) of the sample were measured on a universal testing machine in static regime, class I, 4kN, $v=5\text{mm/min}$.

The bending mechanical measurements were performed on a machine for static testing/trial TINIUS OLSEN, 0-10kN, class I, $v=2\text{mm/min}$, and impact Charpy machine CEAST, 4kJ, was used for determining the resistance to shock.

A 2:1 molar ratio of low molecular weight epoxy resin (Ropoxid 501) and glycols (EG, DEG, TTEG) were introduced under stirring, in a steel reactor equipped with heating jacket, agitator, coupled with a thermostat.

A 50 ppm.50% aqueous solution was used as catalyst at a temperature of 150°C LiCl, which was maintained constant throughout the reaction.

To determine the degree of conversion reactions of epoxy resin and glycol, the samples were characterized by determining the epoxy equivalent, both by chemical analysis and by spectrophotometer measurements (FT-IR). To avoid secondary reactions depending on the nature of the glycol used, the reaction was stopped at an index value of epoxy resin 0.289 g eq/100.

For physical and mechanical characterization, epoxy resins modified with glycols were cross linked with a DDM-type amine hardener, in a 2:1 molar ratio resin / hardener.

The resin-hardener mixture was poured into a Teflon mold, the specimen parts being crosslinked in the following in two steps (7h/60°C and 7h/120°C).

Results and discussions

The determination of the degree of conversion of the polyaddition reaction of epoxy resins in reaction with glycol was performed by the quantitative determination of epoxy group during synthesis, as well as by the spectrophotometric method, aiming at the decrease of the (A_{913}/A_{828}) ratio [6-8].

Taking into account the conclusions of the kinetic study on the DEG-modified epoxy resin performed both by using the classic procedure and in a microwave field, the reaction was monitored by the conversion variation, measured with the FT-IR spectrophotometer, the results being comparable to those obtained by the analytical method.

By using the two methods, the reaction could be stopped at the desired conversion degree without getting into the domain of secondary polyaddition reactions.

Figures 1, 2 and 3 show the evolution of the absorption band of epoxy group at 913 cm^{-1} decreasing in time.

By analyzing the values of the modified epoxy resin conversion, given in the charts obtained by the analytical and the FT-IR method, we can notice increased response times along with the increase of the glycol chain length (fig.4, 5).

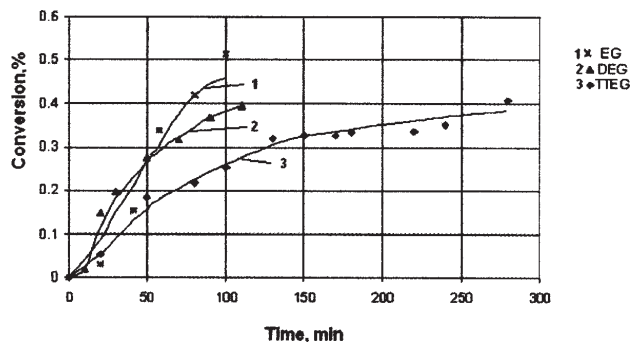


Fig. 5. Variation of the epoxy index in time depending on the type of glycol from FT-IR method

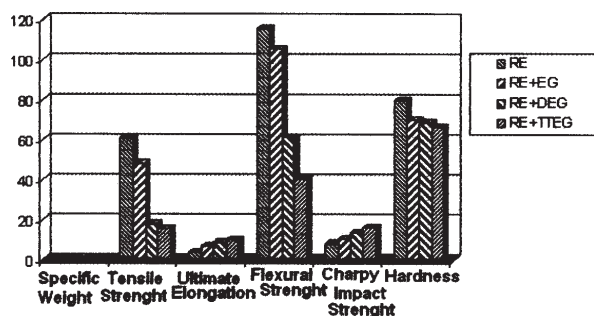


Fig. 6. Variation of mechanical properties depending on the type of glycol -7h/ 60°C, 7h/ 120°C

It is noticeable that the reaction with EG takes place much faster, reaching a conversion of 0.4%-0.45% after about 140 min., while with DEG, the 0.4% conversion is reached after 270 min, and a conversion of only 0.3% for TTEG. This is due to the increasing viscosity of systems, with effect on the diffusion of reactant species, which hinders the way in which the chemical reactions takes place. For higher weight glycols, an extension of the reaction time does not lead to a significant improvement of the conversion.

The mechanical behavior [9] of the epoxy resins modified with glycols crosslinked with DDM and undergoing a thermal treatment of 7h/60°C, and 120°C was studied as well. The figure 6 shows the mechanical properties of the modified products comparatively, depending on the nature of glycol reported to the standard resin (Ropoxid 501).

By analyzing the mechanical characteristics corresponding to the range of plastic deformation and fracture, determined on the TTEG epoxy resin specimens bars modified with glycol, it was noticed that, for the same TTEG-modified epoxy resin, the resistance to traction decreased about four times, whereas the flexural strength decreased about three times. Moreover, ultimate elongation as well as resistance to shock doubled.

In conclusion, an increase of material flexibility can be noticed as the length of the polyglycol chain grows.

The influence of the polyglycol chain length on the physical and mechanical properties was studied through DMA thermo-mechanical analyses [10-12]. The most common use of DMA is the determination of T_g , usually the top peak temperature T_g , where appears a maximum in the curve of loss modulus or the loss factor. In the T_g region, physical properties change drastically and the material evolves from a hard glassy to a soft rubber state.

The samples showed decreasing values of the glass-transition temperature with the increase of the chain length. Thus, it can be observed from the DMA analyses of the modified resin specimens, that the T_g temperature

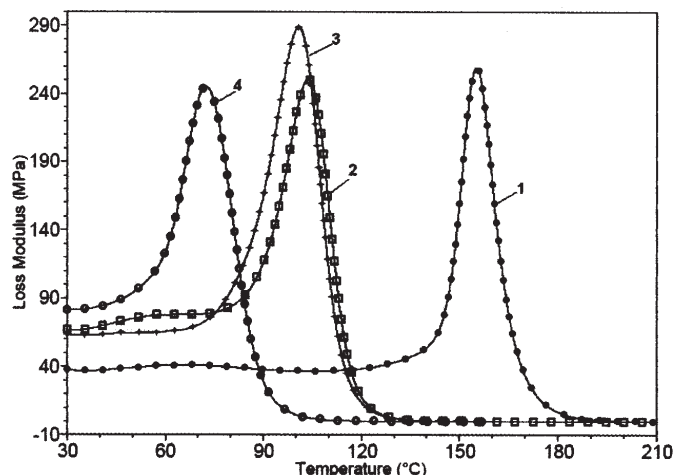


Fig. 7. Dependence of loss modulus on temperature at 1Hz frequency for the systems: 1-standard epoxy resin; 2- EG-modified epoxy resin; 3- DEG-modified epoxy resin; 4- TTEG-modified epoxy resin

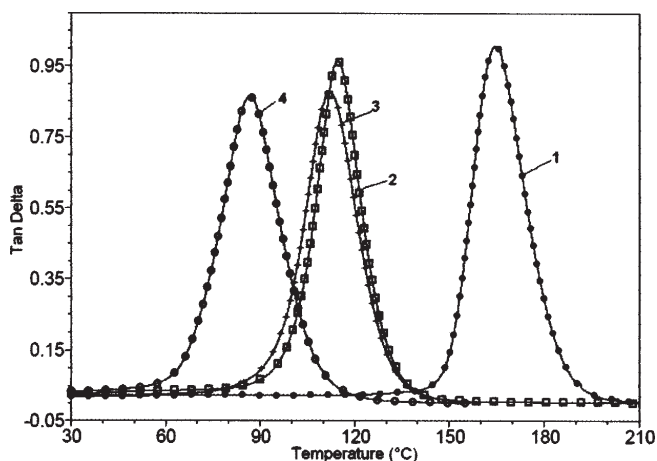


Fig. 8. Dependence of $\tan \delta$ parameter on temperature at 1Hz frequency for the systems: 1-standard epoxy resin; 2- EG-modified epoxy resin; 3- DEG-modified epoxy resin; 4- TTEG-modified epoxy resin.

decreases as the polyether chain is longer and, consequently the resin flexibility increases (fig.7-8).

In all the three cases of obtaining the modified resins, high peaks, due to the loss factor with values between 0.9 and 1.4 can be observed. The shifting towards low temperature values of the corresponding peak of $\tan \delta$ with the increase of the polyglycolic chain lengths proves the possibility of obtaining increasingly higher flexibility resins.

Accordingly, a T_g decrease (flexibility increase) with the length of the glycol chain which was used as a modifier of the standard resins it also noticeable.

The high values obtained for the $\tan \delta$ suggest the usefulness of such resins to be used in application concerning the reduction and control of structural vibrations.

Conclusions

To increase the flexibility of three-dimensional epoxy systems, standard epoxy resins need to be modified with different molecular weight polyglycol.

By analyzing the conversion values of the modified epoxy resins, an increased reaction time with the increase of the

glycolic chain length, was noticed while the maximum conversion reached is lower.

The epoxy resins modified with glycols and crosslinked with DDM are to be characterized from the physical and mechanical point of view in order to determine the flexibility degree introduced by the length of the polyglycol chain.

It can be observed that the modification of the epoxy resins with glycols allows the increase of their flexibility depending on the increase of the polyglycol chain length, the TTEG determining the highest reached flexibility.

The results obtained by DMA measurements point out the significant potential of modified resins to provide high values of damping capacity, an important characteristic from the standpoint of vibration control.

References

1. CLAYTON, A.M., Epoxy resins-chemistry and technology, 2nd Edition, Ed. Marcel Dekker, New York, 1988, p.368
2. GUERMAZI, N., ELLEUCH, K., AYEDI, H.F., Mater. Design, 30, 2009, p.2006

3. POSSART, G., PRESSER, M., PASSLACK, S., GEIB, P.L., KOPNARSKI, M., BRODYANSKI, A., STEINMANN, P., J. Adhesion and Adhesives, 29, 2009, p.478
4. MOTAWIE, A.M., SHERIF, M.H., BADR, M.M., AMER, A.A., SHEHAT, A.S., Australian J. Bas. Appl. Sci., 4(6), 2010, p.1376
5. LADANIUC, M.A., DUMITRACHE L., RADITOIU V., RADITOIU A., HUBCA G., U.P.B. Sci. Bull. - B, 73(1), 2011, p.49
6. GAREA, S.A., IOVU, H., Mol. Cryst. Liq. Cryst., 415, 2004, p.61
7. RADITOIU V., DUMITRACHE L., RADITOIU A., SERBAN S., WAGNER L., Mat. Plast., 47, no. 2, 2010, p.130
8. LI, W., WU, PEIYI, Macrom. Chem.and Physic., 205, 2004, p.1338
9. TSIAFIS, I., BOUZAKIS, K.-D., MICHAILIDIS, N., ASIMAKOPOULOS, A., LONTOS, A., J. Balkan Tribol. Assoc., 10(1), 2004, p.73
10. DAI, P., WANG, Y., HUANG, Z., J. Wuhan Univ. Techn.-Mater. Sci. Ed., 23(6), 2008, p.825
11. XIANG, W., HANXING, L., SHIXI, O., J. Wuhan Univ.Techn.-Mater. Sci. Ed. 23(3), 2008, p.411
12. LEE, C.H., PARK, J.J, Trans. on El. and Electr. Mat.11 (2), 2010, p.69

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