Study on the Reactants Molar Ratio Influence on the Properties of Standard Epoxy Resin / Glycols-Modified Epoxy Resin Compounds

MAGDALENA ADRIANA LADANIUC[1]*, GHEORGHE HUBCA[2], RALUCA GABOR[1], CRISTIAN ANDI- NICOLAE[1], TEODOR SANDU[1]

[1]National Research and Development Institute for Chemistry and Petrochemistry- ICECHIM, 202 Splaiul Independentei, 060021, Bucharest, Romania

[2] Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Gh Polizu Str., 011061, Bucharest, Romania

The paper deals with the synthesis of compounds based on standard epoxy resin/ modified epoxy resin with different molar ratios of glycols and with the characterization of cured products to investigate the influence of the addition of various amounts of modified resin on the compound flexibility as compared to standard epoxy resin. Modification of epoxy resins with glycols results in a wide range of specific properties superior to neat epoxy resin. These properties are highlighted by characterizing the products obtained using various types of glycols and different standard resin/ modified resin weight ratios by physical- mechanical analyses and Dynamic Mechanical Analyses (DMA).

Keywords: glycol-modified epoxy resins, glass transition, dynamical properties and mechanical properties.

Aromatic epoxy resins of diglycidylether of bisphenol-A (DGEBA) represent an important class of thermoset compounds involved in a wide range of applications due to their enhanced mechanical, thermal and viscoelastic features [1, 5].

However, because of the three-dimensional network fragility (weak resistance to crack propagation and shock) as compared to other thermosetting materials, their use is limited [6-9].

One of the possibilities of increasing the flexibility of standard epoxy resins consists of chemical modification by insertion of polyglycol chains in their structure. Chains containing polyglycol ether groups (-C-O-C-) are expected to increase flexibility [10-14].

The paper presents results of the study on the effect of the weight and chain length glycol content on the mechanical and thermo-mechanical properties cured made epoxy compounds.

Experimental part

Materials

The following materials were used in the synthesis of standard epoxy resin / glycols-modified epoxy:

- astandard epoxy resin (Ropoxid 501, POLICOLOR SA) with the molecular weight (M) of 379.5g/mol and the epoxy value (IE index) of 0.527 Eq /100g);

- ethylene glycol (EG), diethylene glycol (DEG), tetraethylene glycol (TTEG), provided by Merck, were used as received;

- a crosslinking agent used in the curing reaction, namely 4,4' diaminodiphenylmethane (DADM, ACROS ORGANICS) 97 % purity, with .the following features: (M = 198, p.t.= 89-91°C, p.f. = 221°C);

- a catalyst for synthesis of epoxy resin modified (LiCl) available from Merck, was used as 50% solution in distilled water;

- a modified epoxy resin by laboratory synthesis (molar ratio: 2/1) with:

EG (IE = 0.289Eq/ 100); M = 821g/ mol; DEG (IE = 0.267 Eq/ 100); M = 865g/ mol; TTEG (IE = 0.250Eq/ 100g); M = 953g/ mol.

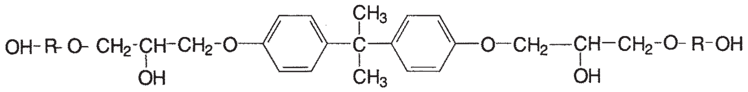
-a modified epoxy resin by laboratory synthesis (molar ratio: 1/2) with:

EG (I_{OH}=222.84mg KOH/100g); M= 503.5 g/mol; DEG (I_{OH}=198.68 mg KOH/100g); M= 591.5g/mol; TTEG (I_{OH}= 146.18 mg KOH/100g); M= 767.5g/mol.

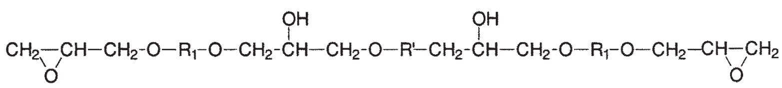
Modified epoxy resins were obtained by a process of chemical transformation of standard epoxy resins by insertion of low molecular weight glycols (using a molar ratio of 1/2 and of 2/1, respectively) in order to improve the low stress cracking properties.

Depending on the resin / glycol ratio, three epoxy matrixes can be obtained by synthesis:

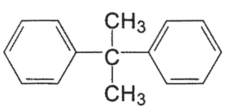
- product with terminal hydroxyl groups (structure 1) when using glycol in excess:



- product with terminal epoxy groups (structure 2) when using an excess of standard epoxy resin:

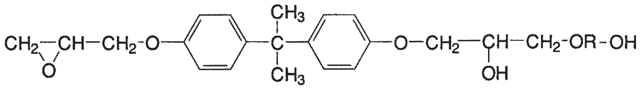


R': $-(CH_2-CH_2-O)_n$; R1:



* email: magdaladaniuc@yahoo.com;; Tel: 0727774587.

- product with epoxy groups mixed with product with hydroxyl groups (structure 3).



Epoxy resins modified with EG, DEG and TTEG, at the molar ratio resin/ glycol = 2/1 and 1/2, were synthesized using an epoxy resin-glycol mixture in the presence of lithium chloride as catalyst at temperatures in range 150-170°C.

Using these materials, compounds with the standard epoxy resin/ modified epoxy resin weight ratio of 50/50 were obtained.

The characteristics of the obtained compounds, determined by chemical analysis, are given in table 1.

Sample characterization

To study the influence of flexible chains incorporated into the three-dimensional structure of the epoxy resin on the thermal and mechanical properties of the resulting compositions, the compounds thus obtained were tested by DMA at 1 Hz frequency.

DMA tests were conducted on a TA Instruments Q800 device using oscillation amplitude of 20 μm. Each sample was heated with 3°C/min, from 25 to 200°C.

Thermal stability of the modified epoxy compositions has been investigated by Thermal Gravimetric Analysis (TGA). TGA curves were recorded on a Q5000IR (TA Instruments) under air atmosphere at a flow rate of 40mL/min.

Each sample was heated from 120 to 700°C with 3°C/min. TGA was used for a comparative analysis of the thermal degradation process occurrence for modified and for standard epoxy resin, respectively. Furthermore, reproducibility of chemical modification was also checked.

Results and discussions

To highlight the ability of controlling the properties by modifying epoxy resins with glycols data obtained both by physical- mechanical analysis and DMA were centralized for different glycols at the same standard resin/ modified resin weight ratio. The investigation of cured compounds physico-mechanical properties (figs. 1-3) reveals a wide range of applications as a result of standard resins modification with glycols. For this reason, various types of glycols were used at a molar ratio of 1/2 and 2/1, respectively.

From these figures, one may notice that compounds density is not significantly influenced by the chain length of the glycol involved in the modification process and by the composition of the mixture, the values being very close to the standard epoxy resin.

The investigated mechanical properties, such as flexural strength at break, strength, Shore A hardness, elongation at break and impact strength are strongly affected by both the nature of the used glycol in the modification process and by the weight ratio of the involved components in the compound obtaining.

Thus, there is a significant decrease in tensile strength, flexural and a significant increase hardness and elongation

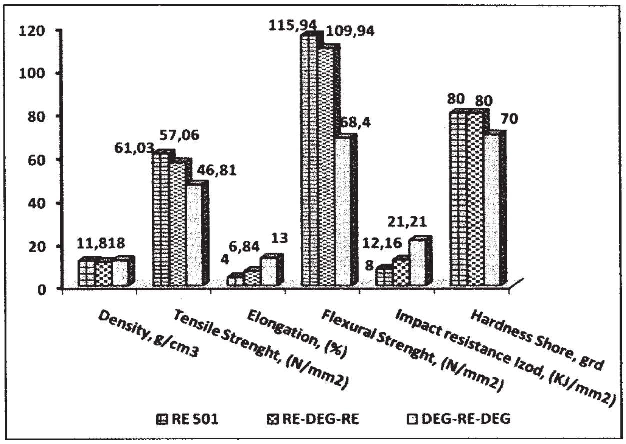


Fig.1 Influence of the type of network on physico- mechanical properties of cured standard RE / EG-modified epoxy resin compounds, depending on the molar ratio of reactants

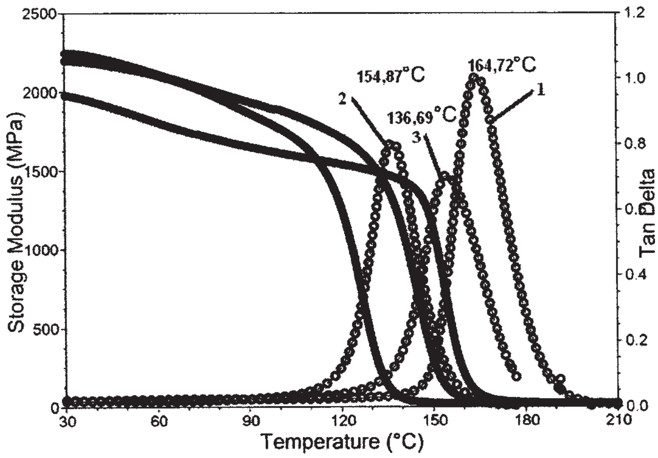


Fig.2 The dependence of storage modulus and tanδ on temperature cured compounds made epoxy resin standard / EG- modified epoxy resin on the molar ratio of reactants: **1**-RE 501; **2** - Standard combination RE / EG -modified RE to molar ratio (2/1); **3**-Standard combination RE/ EG -modified RE to molar ratio(1/ 2)

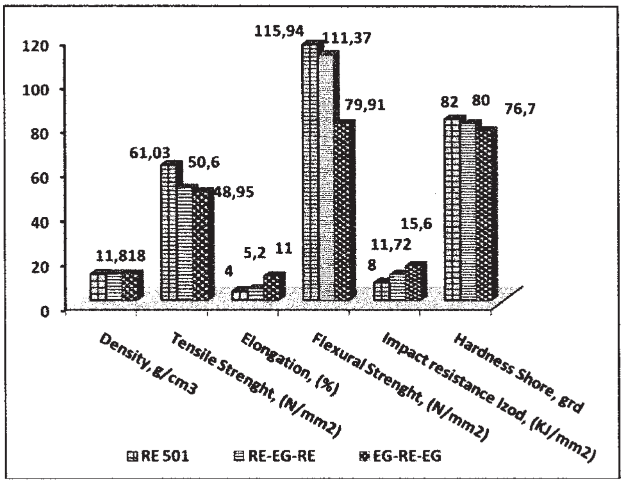


Fig.3 The influence of the type of network on the physico-chemical properties of standard RE / DEG-modified epoxy resin compounds, depending on the molar ratio of reactants

Table 1
STANDARD RE/ GLYCOL-MODIFIED RE COMPOUNDS

Glycols for modification	Epoxy value (Eq/100g) for molar ratio of 2/1	Epoxy value (Eq/100g) for molar ratio of 1/2
EG	0.4210	0.2180
DEG	0.4235	0.3116
TTEG	0.4220	0.3112

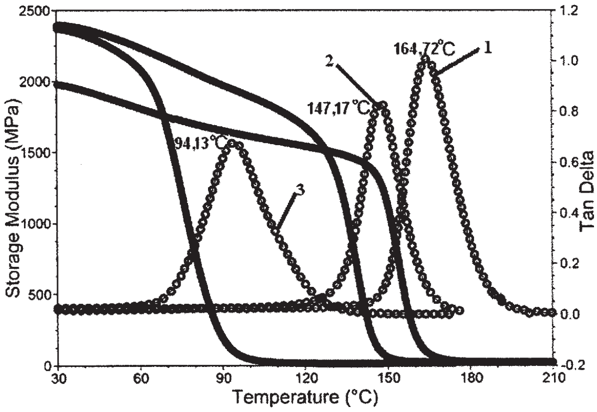


Fig.4 The dependence of storage modulus and tanδ on temperature for cured standard epoxy resin/ DEG-modified epoxy resin compounds depending on the molar ratio of reactants:**1**- RE 501; **2**– Standard combination RE / DEG-modified RE with to molar ratio: (2/1); **3**- Standard combination RE / DEG- modified RE to molar ratio (1/2)

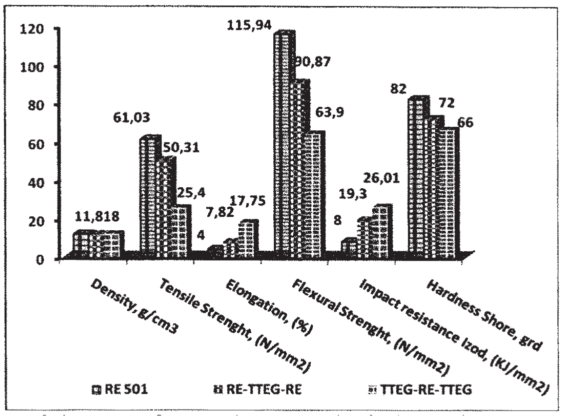


Fig.5**.** The influence of the type of network on the physico-chemical properties of compounds standard RE / TTEG-modified epoxy resin, depending on the molar ratio of reactants

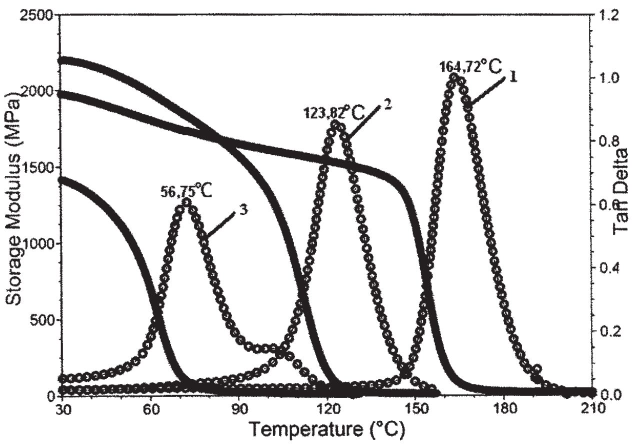


Fig.6 The dependence of storage modulus and tanδ on temperature for cured made epoxy resin standard/ TTEG-modified epoxy resin compounds according to the molar ratio of reactants **1**- RE 501; **2**– Standard combination RE/ TTEG-modified RE with at a molar ratio of (2/1); **3**- Standard combination RE / TTEG-modified RE with at a molar ratio of (1/2).

at break and impact resistance according to the nature glycol, which is eloquent proof, reinforced made compounds to enhance flexibility.

Standard resin/ glycols-modified resin weight ratio of 1/2 influences, also, the flexibility of cured compounds.

In figures 4-6, DMA curves are presented for standard resin and for various modified resin with (EG, DEG, TTEG)

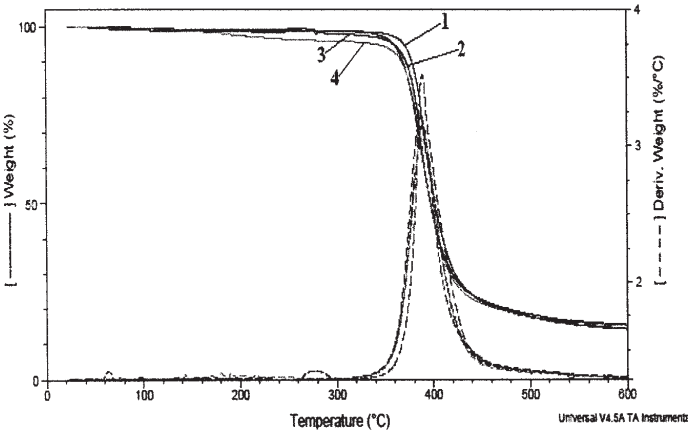


Fig.7. TGA curves corresponding by 2/1 molar ratio standard RE / modified RE **:**
1– RE 501; **2** -50 Standard RE/50 EG-modified RE; **3**-50 RE/50 DEG-modified RE;
4- 50 Standard RE/50 TTEG-modified RE.

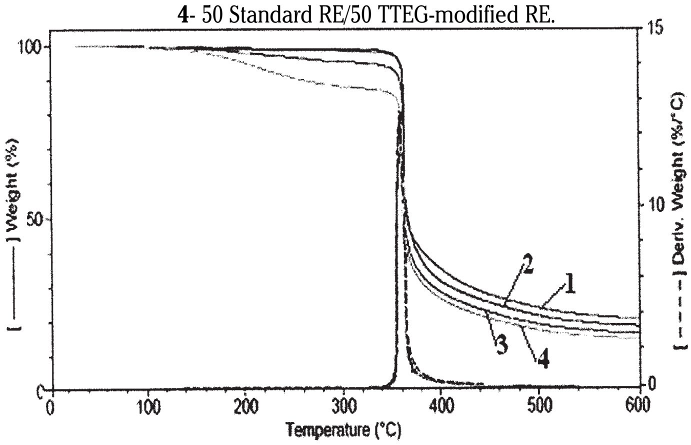


Fig.8. TGA curves corresponding by 1/2 molar ratio standard RE / modified RE**: 1**– RE 501; **2** -50 Standard RE/50 EG-modified RE: **3**-50 RE/50 DEG-modified RE; **4**-50 Standard RE/50 TTEG-modified RE

samples. Glass transition temperature (T_g) and storage modulus (E”) values were determined by DMA tests.

Comparing the T_g, tan δ, and E” values, one may notice T_g values are lower for modified resin as compared to standard resin, whereas E” and tanδ values are higher for modified resin. The increase in E” value is more significant when modifier chain is longer. The obtained products may be further used as damping materials.

The results obtained both by physical-mechanical and by thermo-mechanical analyses (DMA) reveal the influence of the glycol nature and of compounds composition on cured products flexibility. In terms of mechanical features a noteworthy improvement in flexibility occurred by increasing glycolic chain length, higher values being obtained for a standard resin/modified resins molar ratio of 1/2.

DMA curves were recorded for modified-resin compounds and compared to standard resin. The obtained glass transition temperature values are given in table 2.

This shows that flexibility epoxy systems it is even greater as glycol chains are longer, as well as the weight ratio of modified resin is higher.

Thus, the products can be used as cushioning materials with different degrees depending on their final use.

Comparing the T_g values, one may notice that the values corresponding to standard epoxy resin-based mixtures decrease with modifier chain length increase (table 2).

It was also investigated the thermal stability of compounds by TGA tests for all tested samples. Influence standard ratio RE/ RE modified is shown by TGA curves

Samples	Glass transition temperature, Tg(°C)	
	RE /modified resin to molar ratio 2/1	RE / modified resin to molar ratio 1/2
RE 501	164.72	164.72
50 RE /50 $RE_{modified}$ EG	154.87	136.69
50 RE /50 $RE_{modified}$ DEG	147.17	94.13
50 RE /50 $RE_{modified}$ TTEG	123.82	56.75

Table 2
DEPENDENCE OF T_g ON MOLAR RATIO EPOXY RESIN/ TYPE GLYCOL, USED AS CHAIN LENGTH MODIFIER

corresponding to the change made compounds molar ratio 2/1 and the 1/2 and are shown in figures 7 and 8.

TGA curves highlight that all obtained compounds are thermally stable up to a temperature of 300°C, stability is not affected either by the nature glycol compound or by composition.

Over 300°C, quick start termooxidative sample degradation occurs, major weight loss being between 300-600°C.The maximum peaks of thermal degradation was determined from the first order derivative of the TGA curve and fit for all the samples in the temperature range of 400°C.

Conclusions

The study on the physical-mechanical and thermal properties of standard epoxy resin /glycols-modified resin compounds at 1/2 and 2/1 ratio, revealed that is possible to obtain compounds with controlled features.

The decrease in Tg values of the final compounds is correlated with the increase in the chain length of the glycol component as a result of changes in flexibility.

TGA results show that samples maintain their stability up to ~ 300 °C, which is not strongly dependent on the glycol nature and on the standard resin / modified resin weight ratio.

The obtained results highlight the multiple possibilities of amending epoxy resins flexibility, which significantly broadens the uses thereof for conventional composites, nanocomposites and coating materials.

Reference

1.J. P. PASCAULT and R. J. WILLIAMS, “Epoxy Polymers: New Materials and Innovations” Wiley-VCH Werlag GmbH& Co. KGaA, Weinheim, 2010, p 13-38.

2.EGGER, W.; SPERR, P., KÖGEL, G.; WETZEL, M.; GUDLADT, H., Applied Surface Science , 2008, vol.255, p.209-212

3.*** Chemistry and Technology, of Epoxy Resins, edited by B. ELLIS , Springer Science & Business Media , 2012, p.1-36.

4.RAMIREZ, C., Eur Polym. J, 2008, vol 10, p.3035-3045.

5E.M.PETRIE, “Epoxy Adhesive Formulations”, Adv. Funct. Mater. 2008, vol. 18, p.1898-1904.

6.E YILDIZ, TULAY Y, KUYULU ABD□LKADIR, “Toughening of Epoxy Resins by Amine Terminates Poly(arylene ether Ketone)s having Pendant Tertiary Butyl Groups”, Polymer Bulletin 2007, vol 58, p.503-511.

7.LIN ZHU, FAN-LONG JIN, SOO-JIN PARK, “Thermal Stability and Fracture Toughness of Epoxy Resins Modified with Epoxidized Castor and Al_2O_3 Nanoparticles”, Bull.Korean Chem.Soc. 2012, vol.33, p.2513-2516.

8.L Mary M. Caruso, Benjamin J. Blaiszik,Scott R. White, Nancy R. Sottos , “Full Recovery of Fracture Toughness Using a Nontoxic Solvent-Based Self-Healing System”., 2008, vol 18, p.1898–1904.

9.G.LEVITA, S.DE PETRIS, A.MARCHETTI, A. LAZETTI, “Crosslink density and fracture toughness of epoxy resins”, Journal of Materials Science, 1991, vol. 26, p.2348-2352.

10.BLANCO I, CICALA G, LO FARO C, MOTTA O, RECCA G “Thermomechanical and morphologicalproperties of epoxy resins modified with functionalized hyperbranched polyester. Polym Eng Sci, 2006, vol. 46, p.1502–1511.

11.M. PENOFF, P. OYANGUREN, W. SCHREINER AND P. MONTEMARTINI, “Chemical and Morphological Surface Modification of Epoxy Based Thermosets,” Materials Sciences and Applications, 2013, vol. 4, p. 1-9.

12.SCHERZER, N., J. Appl. Polym. Sci., 1994, vol.51, p.491.

13.WANG XIANG, LIU HANXING, OUYANG SHIXI,” Damping Properties of Flexible Epoxy Resin”, Journal of Wuhan University of Technology-Mater Sci. 2008, vol 23, p 411-414.

14.WANG XIANG, LIU HANXING, OUYANG SHIXI, “Effect of Thermal Crosslink Conditions on Dynamic Mechanical Behaviors of Flexible Epoxy”. Journal of Wuhan University of Technology-Mater. Sci, 2008.vol. 23, p.825-829.

Manuscript received: 9.06.2015