LILIANA ROSU, CONSTANTIN CIOBANU, DAN ROSU[*)], CONSTANTIN N. CASCAVAL

"Petru Poni" Institute of Macromolecular Chemistry
41A Alley Gr. Ghica Voda, Iasi-70487, Romania

Preparation and characterization of silver sulfathiazole-epoxy resin networks

Summary — A new synthetic material was prepared starting from silver sulfathiazole compound and Ropoxid 501 epoxy resin based on bisphenol A. The synthesized product was crosslinked with ethylenediamine, in the presence of poly(diethylene adipate lactate)diol (PDEAL), as a biodegradable external plasticizer. The composite materials (networks) were analyzed by infrared spectroscopy, differential scanning calorimetry and thermogravimetry. The values of density, volume shrinkage, water absorption and fungicidal action of the synthesized networks were also evaluated. The presence of the silver in the epoxy networks led to important modifications of the resin properties towards the fungicidal action.

Key word: epoxy resin, silver sulfathiazole, crosslinking, plasticization, thermal stability, fungicidal action.

OTRZYMYWANIE I CHARAKTERYSTYKA USIECIOWANYCH UKŁADÓW NA PODSTAWIE ŻYWICY EPOKSYDOWEJ I SOLI SREBROWEJ SULFATIAZOLU

Streszczenie — Opisano syntezę nowych, różniących się składem usieciowanych etylenodiaminą układów opartych na otrzymywanej z bisfenolu A żywicy epoksydowej i soli srebrowej sulfatiazolu z udziałem poli(adypiniano-mleczanu dietylowego) (PDEAL) użytego w charakterze biodegradowalnego plastyfikatora zewnętrznego (tabela 1). Produkty te charakteryzowano metodami IR (rys. 1 i 2), DSC (tabela 4, rys. 3) oraz termograwimetrii (rys. 4). Ponadto określano gęstość, skurcz objętościowy (tabela 2) i absorpcję wody (tabela 3) uzyskanych usieciowanych układów. Wyniki analizy IR prowadzą do wniosku, że srebrowa pochodna sulfatiazolu zostaje wbudowana w sieć żywicy epoksydowej. Ustalono, że obecność PDEAL zmniejsza skurcz objętościowy i gęstość usieciowanych produktów oraz obniża ich temperaturę zeszklenia. Obecność srebra nadaje natomiast produktom aktywność grzybobójczą, pogarszając jednocześnie ich termostabilność.

Słowa kluczowe: żywica epoksydowa, sól sodowa sulfatiazolu, sieciowanie, plastyfikacja, termostabilność, działanie grzybobójcze.

In recent years, the need of new materials with improved properties has oriented the research towards the polymeric composites. Among the different polymers used as matrixes in the compounding of composites, epoxy resins find wide applications thanks to their easy processability, high rigidity, chemical resistance and excellent thermal and mechanical properties [1]. As a result, advanced materials have been prepared starting from epoxy resins [2—7].

Composites based on polymers as matrixes and metals are considered as the future materials (nanocomposites), having peculiar properties [8, 9]. New polymeric materials, including polymers and oligodynamic silver ions (*i.e.*, ions show toxic effect upon the living cells-algae, molds fungus *etc.*) were obtained and used for fabrication of drugs and medical devices, such as catheters and implants [10, 11]. Some composites were manufactured as antimicrobial agents by including silver sulfadiazine in nylon cloth [12].

The polymeric composites with epoxy matrix and silver are materials which combine the properties of the epoxy resins with antibacterial, fungicidal and cicatrization effect of silver. New conductive adhesives based on epoxy resins and silver particles have been prepared to replace partially the traditional electric materials used for manufacturing of the electronic devices, such as emitting diodes and integrated circuits [13, 14].

The aim of this study consists in synthesis and characterization of a new polymeric material (network) prepared from an epoxy resin based on bisphenol A and silver sulfathiazole. The last shows strong antibacterial activity similar to that of silver nitrate [15]. The influence of poly(diethylene adipate lactate)diol (PDEAL) [16], used as external biodegradable plasticizer on the properties of the synthesized network was also investigated.

[*)] Corresponding author: e-mail: drosu@icmpp.ro

EXPERIMENTAL

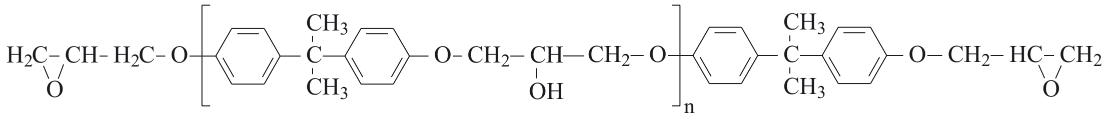
Materials

— Epoxy resin is a commercial resin based on bisphenol A [Formula (I)], which was manufactured by Policolor SA Bucharest-Romania under trade name Ropoxid 501. The resin has an epoxy equivalent 0.525 equiv/100 g and a number-average molecular weight ($\overline{M}_n$) equal 380.

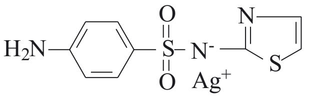
— Silver sulfathiazole [Formula (II)] was synthesized in water, starting from sulfathiazole and silver nitrate, at temp. 60 °C, as was described elsewhere [17].

Table 1. Parts of compounds used for syntheses of the systems investigated

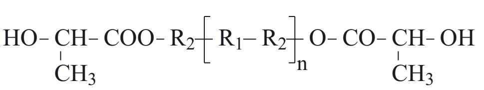
Sample	Ropoxid 501, %	Silver sulfathiazole, %	Plasticizer %	Ethylenediamine, %
Etalon	89.3	—	—	10.7
1	88.5	0.9	0	10.6
2	80.5	0.9	8.9	9.7
3	72.3	0.9	18.1	8.7
4	64.1	0.9	27.3	7.7
5	55.4	0.9	37.0	6.7



(I)



(II)



$$HO-\underset{CH_3}{CH}-COO-R_2\left[R_1-R_2\right]_n O-CO-\underset{CH_3}{CH}-OH$$

(III)

where: $R_1 = -OOC-(CH_2)_4-COO-$

$R_2 = -(CH_2)_2-O-(CH_2)_2-$

n = 1,14

— Ethylenediamine — curing agent, was chemically pure reagent (Aldrich) and was used without further purification.

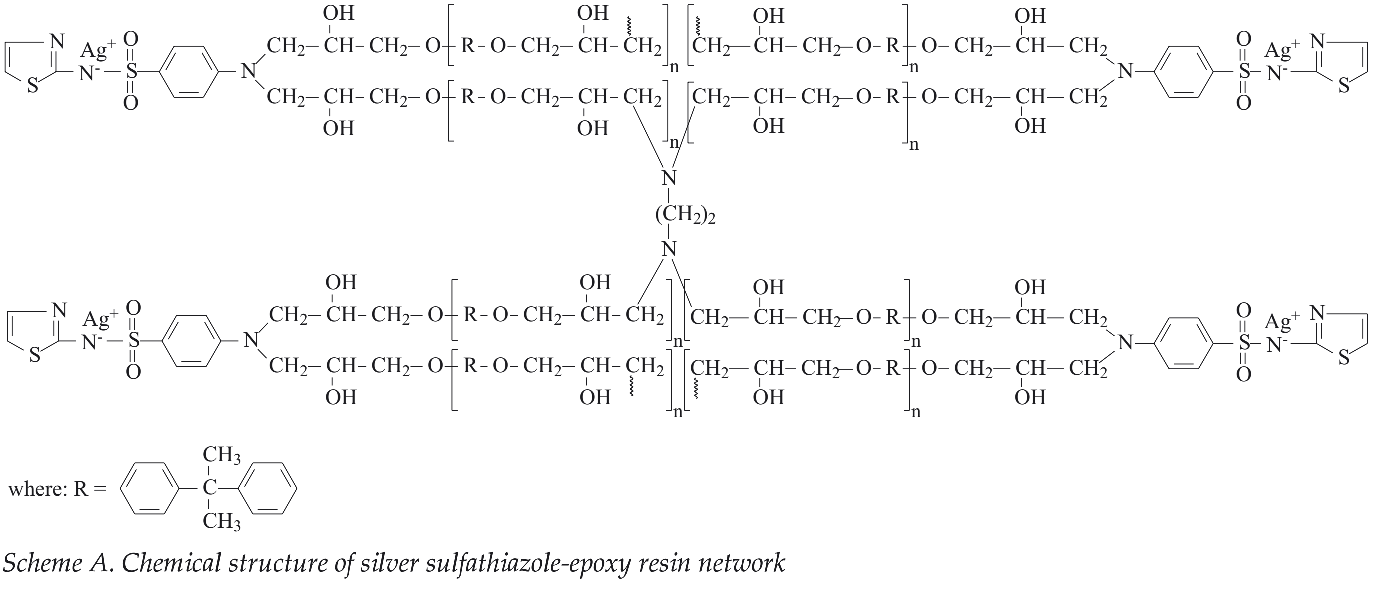
— PDEAL [Formula (III)] was synthesized starting from adipic acid, lactic acid and diethylene glycol as previously reported [18]. A direct condensation was carried out at 180 °C, for 6 h, under reduced pressure.

Network preparation

Ropoxid 501 epoxy resin was heated at 60 °C and stirred in a 3-neck round bottom flask, under nitrogen atmosphere. Silver sulfathiazole was introduced progressively into the flask under stirring and the mixture was heated at 60 °C for 3 h, until the mixture became homogeneous. That time PDEAL polymer was introduced into the reaction vessel and stirring was continued for 2 h. The obtained epoxy resin/silver sulfathiazole/PDEAL product was then mixed with appropriate quantities of ethylenediamine (see Table 1). Some networks were obtained with structures as in Scheme A.

Methods of testing

$\overline{M}_n$ values characterizing both the Ropoxid 501 epoxy resin and the product obtained in reaction between the



Scheme A. Chemical structure of silver sulfathiazole-epoxy resin network epoxy resin and silver sulfathiazole were determined by gel permeation chromatography (GPC PL-END 950 apparatus) by means PL gel 5 μm MIXED-D columns and *N,N*-dimethylformamide (DMF) as a solvent.

— The IR spectra of the samples were recorded using a M80 Specord spectrophotometer, with KBr pellets and a nominal resolution of 4 cm^{-1}.

— Glass transition temperature (T_g) values of the networks were obtained by means of a Mettler DSC 12 E instrument, in dynamic conditions (10 °C min^{-1} heating rate). The midpoint temperature of the specific heat transition during the second heat course was taken as the value of T_g.

— The network density (ρ) was measured at temp. 25 °C, using a picnometer. The weight of each sample (around 1 g) was measured both in air (*a*) and in water (*b*), and ρ was calculated by means of formula (1) [19]:

$$\rho = \frac{a}{a-b}\rho_0 \qquad (1)$$

where: ρ_0 *means water density at temp. 25 °C.*

The volume shrinkage of the networks was calculated by means of formula (2):

$$\text{Shrinkage (\%)} = \frac{\frac{1}{\rho_{\text{uncured}}} - \frac{1}{\rho_{\text{cured}}}}{\frac{1}{\rho_{\text{uncured}}}} \cdot 100 \qquad (2)$$

— The equilibrium water absorption was measured by submersing small blocks (3 × 3 × 2 mm) of each sample in water, at temp. *ca.* 22 °C [19]. The samples were daily weighed and the equilibrium absorption was reached after 2 months.

— The thermooxidative stability of the studied samples was analyzed by thermogravimetry (TG) technique. The thermograms were recorded using a MOM Budapest (Hungary) derivatograph, in temperature range from 25 °C up to 600 °C, with heating rate of 10 °C min^{-1}, in an air atmosphere.

RESULT AND DISCUSSION

Some of the synthesized products were investigated by IR spectroscopy, with the main goal to ensure that the reaction between silver sulfathiazole and epoxy resin took place.

The IR spectra, both of the silver sulfathiazole and the silver sulfathiazole/epoxy resin reaction product, were recorded in the range between 4000 and 3000 cm^{-1}, and are shown in Fig. 1, while Fig. 2 presents the IR spectrum of the epoxy resin together with IR spectrum of silver sulfathiazole/epoxy resin product, this time using the range between 1000—750 cm^{-1}.

The assignment of the peaks in the silver sulfathiazole spectrum was carried out by means of literature data [20]. Infrared absorbances at 3404 and at 3340 cm^{-1}, assigned to asymmetric and to symmetric vibrations of $-NH_2$ in silver sulfathiazole and in silver sulfathiazole/epoxy resin reaction product, were used to quantify the conversion of $-NH_2$ groups. These absorbances, which characterize the sulfathiazole compound (curve A in Fig. 1) significantly decreased when the silver sulfathiazole reacted with epoxy resin (curve B in Fig. 1). After 3 h of reaction the conversion of $-NH_2$ groups was 46 %. The absorbance at 912 cm^{-1}, specific to the epoxy group in the Ropoxid 501 spectrum (curve A in Fig. 2), diminished in IR spectrum of silver sulfathiazole-epoxy resin product (curve B in Fig. 2).

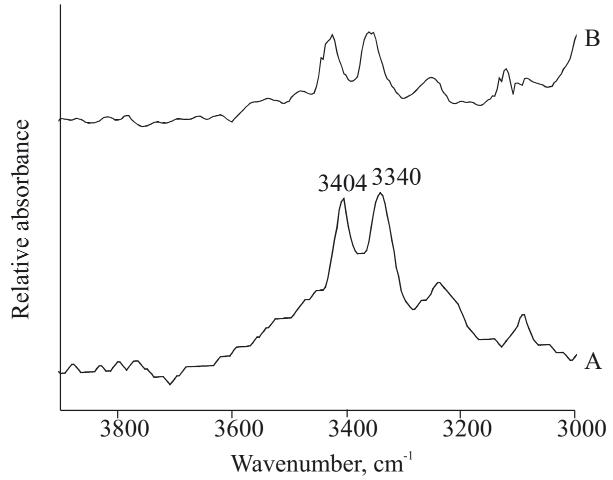


Fig. 1. IR spectra of silver sulfathiazole (A) and silver sulfathiazole/epoxy resin reaction product (B) recorded in the range 4000—3000 cm^{-1}

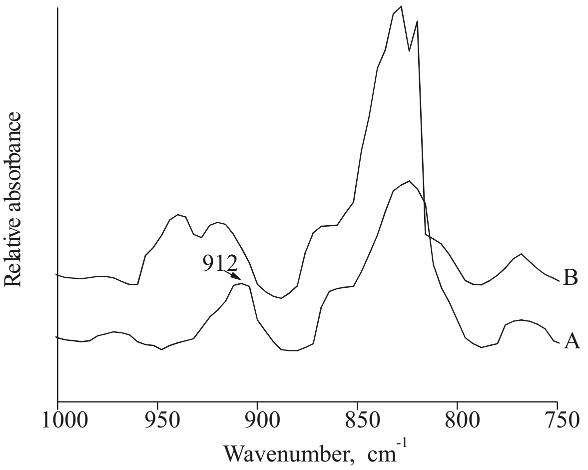


Fig. 2. IR spectra of Ropoxid 501 (A) and silver sulfathiazole/epoxy resin reaction product (B) recorded in the range 1000—750 cm^{-1}

$\overline{M}_n$ values of neat epoxy resin and of silver sulfathiazole/epoxy resin were appropriately, 380 and 930. The last value is very closed to the theoretical value of $\overline{M}_n$ (971). The increase in $\overline{M}_n$ value from 380 up to 930 is associated with the decrease in the epoxy equivalent from 0.525 equiv/100 g (Ropoxid 501 resin) to 0.215 equiv/100 g (epoxy resin/silver sulfathiazole reaction product). The results obtained by GPC and the epoxy equivalent measurements complete the IR data and support the conclusion that a reaction took place between oxirane group of the epoxy resin and amino group from silver sulfathiazole compound. The unreacted epoxy groups of Ropoxid 501 resin in the presence of ethylenediamine react with amine groups what leads to silver sulfathiazole-epoxy networks (see Scheme A).

Some properties of the synthesized networks, such as the density and the volume shrinkage, are influenced by both the silver sulfathiazole and PDEAL concentration (Table 2).

It can be noted that a density of the cured sample increases in comparison with the density of the uncured one. Simultaneously, both the density and the volume shrinkage values of the analyzed samples significantly diminished with increase in PDEAL content.

Table 2. Values of density (ρ) and volume shrinkage of silver sulfathiazole/epoxy resin composites

Sample*)	ρ, g/cm^3		Volume shrinkage, %
	uncured**)	cured	
Etalon	1.069	1.204	11.2
1	1.159	1.278	9.8
2	1.153	1.255	8.3
3	1.151	1.228	6.3
4	1.142	1.170	2.4
5	1.140	1.158	1.6

*) For samples symbols see Table 1.
**) The composites as in Table 1, without ethylenediamine.

Table 3. Water absorption of the cured etalon and silver sulfathiazole/epoxy resin

Sample*)	Water absorption, %
Etalon	2.60
1	4.72
2	4.75
3	4.94
4	5.08
5	5.21

*) For samples symbols see Table 1.

Etalon sample absorb around 2.6 % of water at saturation, while the other cured samples show higher affinity for water (see Table 3). The water absorption increases gradually up to 5.21 %, being a function of PDEAL content.

Both the etalon and the network samples were analyzed and by DSC technique. Figure 3 shows the DSC thermograms recorded for the studied samples, while Table 4 lists T_g values obtained using the curves shown in Fig. 3.

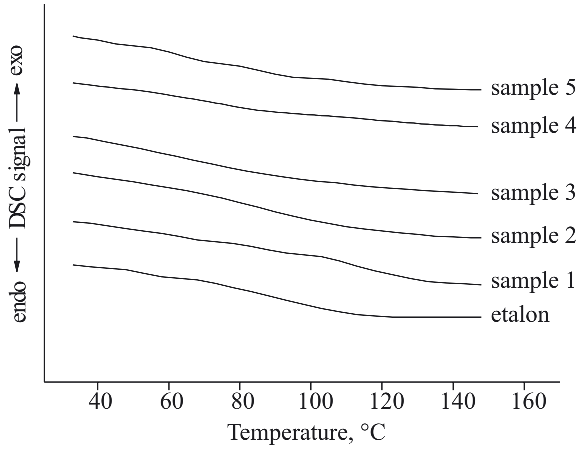


Fig. 3. DSC thermograms of the synthesized products (for symbols see Table 1)

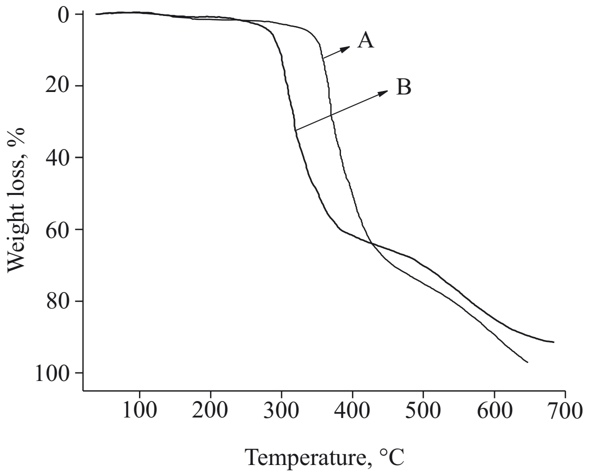


Fig. 4. TG curves of cured etalon (A) and sample 1 (B) (for symbols see Table 1)

The T_g increase by 18 °C for the network 1 (without plasticizer) in comparison with uncured sample is an indication of the network enlargement. This behavior can be due to the mobility decrease in the chain segments in the network caused by the presence of silver sulfathiazole. Table 4 shows that the presence of PDEAL has an important contribution to the decrease in T_g value of the synthesized networks because it probably acts as an external plasticizer. It is well known that the external plasticizers decrease T_g values of the polymers because they reduce the interactions between the polymer chains [21].

Table 4. T_g values of silver sulfathiazole/epoxy resin networks

Sample*)	T_g, °C
Etalon	94
1	112
2	84
3	63
4	62
5	58

*) For samples symbols see Table 1.

The effect of silver sulfathiazole on the thermal stability of the silver sulfathiazole/epoxy resin networks has been studied by TG technique. Due to the silver action as an active participant upon oxidation, the thermal stability of the networks is much lower than that shown by the etalon sample (Fig. 4). Some data obtained using the curves in Fig. 4 such as initial decomposition temperature (T_i), temperature corresponding to 10 % weight loss (T_{10}), temperature corresponding to 50 % weight loss (T_{50}) and temperature corresponding to maximum rate of decomposition (T_M), are listed in Table 5.

Table 5. Some characteristics of the thermal decomposition of the silver sulfathiazole/epoxy resin network and of etalon samples

Sample[*)]	T_i, °C	T_{10}, °C	T_{50}, °C	T_M, °C
Etalon	147	355	399	417
1	127	297	351	331

[*)] For samples symbols see Table 1.

The curves in Fig. 4 and the data summarized in Table 5 show that the synthesized network (sample 1) has much lower thermal stability in comparison with the uncured sample. The presence of the plasticizer in the networks (samples 2 up to 5) leads to a higher decrease in thermal stability in comparison with the sample 1.

Additionally, the synthesized silver sulfathiazole/epoxy resin networks were tested regarding their behavior to the action of mold and fungi. The fungi species included *Aspergillum Niger*, *Aspergillum Furnigatus*, *Penicillium Glaucum* and *Trichoderma Viride*. The fungicidal properties, expressed by the ability of the samples to inhibit the appearance and the growth of mold zone, were examined after 21 days of fungi inoculation. It was observed that only sample 1, without plasticizer, shows a good inhibiting action against the fungi and mold. The increase in PDEAL content in the synthesized networks led to a decrease in the antifungal effect. The decrease in the resistance of PDEAL and silver sulfathiazole containing samples against the action of mold and fungi could be explained by PDEAL biodegradability. This effect leads to deterioration of the antifungal properties of the networks synthesized in presence of sulfathiazole and PDEAL in epoxy matrix.

CONCLUSIONS

A new synthetic material with macromolecular structure was prepared through the reaction between silver sulfathiazole and an epoxy resin. The progress of the reaction was analyzed using IR spectroscopy.

The reaction product was crosslinked with ethylenediamine, in the presence of PDEAL, used as a biodegradable external plasticizer.

The presence of silver in the epoxy network led to important modifications of some properties, namely increase in both the density and T_g of silver sulfathiazole/epoxy resin product, decrease in shrinkage volume, increase in water absorption and decrease in thermooxidative stability.

The silver sulfathiazole/epoxy resin network synthesized in an absence of plasticizer shows a good antifungal action.

REFERENCES

1. May C. A.: "Epoxy Resins. Chemistry and Technology", 2nd edition, Marcel Dekker, 1988.
2. Mazela W., Czub P., Pielichowski J.: *Polimery* 2004, **49**, 233.
3. Mititelu-Mija A., Cascaval C. N.: *Polimery* 2005, **50**, 839.
4. Shiota A., Ober C. K.: *Prog. Polym. Sci.* 1997, **22**, 975.
5. Cascaval C. N., Rosu D., Mititelu-Mija A., Rosu L.: *Polimery* 2006, **51**, 99.
6. Bednarz J., Pielichowski J., Niziol J.: *Polimery* 2006, **51**, 218.
7. Oleksy M., Heneczkowski M., Galina H.: *Polimery* 2006, **51**, 799.
8. Shin H. S., Yang H. J., Kim S. B., Lee M. S: *J. Colloid Interface Sci.* 2004, **274**, 89.
9. Pintér E., Patakfalvi R., Fülei T., Gingel Z., Dékány I., Visy C.: *J. Phys. Chem. B* 2005, **109**, 17 474.
10. *Pat. US* 6 716 895 B1 (2004).
11. *Pat. US* 6 905 711 B1 (2005).
12. Edwin A., Deitch E. A., Andrew A., Marino A. A., Malakanok V., Albright J. A.: *J. Trauma* 1987, **27**, 301.
13. Lo C. T., Chou K.-S., Chin W.-K.: *J. Adhes. Sci. Technol.* 2001, **15**, 783.
14. Rong M., Zhang M., Liu H., Zeng H.: *Polymer* 1999, **40**, 6169.
15. Stozkowska W., Wroczynska-Palka M.: *Med. Dosw. Microbiol.* 1999, **51**, 167.
16. Chelliny E., Sunamoto J., Migliaresi C., Ottenbreite R. M., Cohn D.: "Biomedical Polymers and Polymer Therapeutics", Kluwer Academic Publishers, New York 2002, p. 5.
17. Boregs A. D. I., Del Ponte G., Neto A. F., Carvalho I.: *Quin Nova* 2005, **28**, 727.
18. Ciobanu C., Stoica E., Cascaval C. N., Rosu D., Rosu L., State M., Emandi A., Nemes I., Petrescu F.: *J. Appl. Polym. Sci.* 2007, **103**, 659.
19. Li H.: "Synthesis, Characterization and Properties of Vinyl Ester Matrix Resins", PhD Thesis, Blacksburg, Virginia USA, 1998.
20. Lee S. B., Rockett T. J: *Polymer* 1992, **33**, 3691.
21. Braun D., Cherdron H., Rehahn M., Ritter H., Voit B.: "Polymer Synthesis: Theory and Practice Fundamentals, Methods, Experiments", 4th Ed., Springer, Berlin 2004, p. 359.

Received 5 V 2007.