Polymer Bulletin 48, 75-82 (2002)

Polymer Bulletin

Influence of hydrothermal ageing and thermal treatments on the viscoelastic behavior of DGEBA-MCDEA epoxy resin

Didier Colombini [1 #], J. J. Martinez-Vega (✉)[2], Gérard Merle [1]

[1]Laboratoire Matériaux Polymères et Composites, UMR-CNRS 5041, Université de Savoie, 73376 Le Bourget du Lac Cedex, France
[2]Laboratoire de Génie Electrique de Toulouse, Université Paul Sabatier, UMR-CNRS 5003, 31062 Toulouse Cedex, France
[#]present address : Department of Polymer Science and Engineering, Centre for Chemistry and Chemical Engineering, Lund Institute of Technology, Lund University, Box 124 - 22100 Lund, Sweden

Received: 27 September 2000/Revised version: 12 February 2002/ Accepted: 12 February 2002

Summary

The influence of both hydrothermal and physical ageing on the viscoelastic behaviour of an epoxy resin (DGEBA-MCDEA) was investigated. The samples were first immersed in distilled water and then tested on dynamic mechanical analyser all along thermal treatments. Three relaxations of epoxy networks were observed on mechanical spectra: the main relaxation (α) at higher temperatures, the secondary relaxation (β) at lower temperatures, and the intermediate ω-relaxation. As a result of the plasticization effect of water on DGEBA-MCDEA network, all viscoelastic characteristics (width, magnitude, and temperature location) of both β- and ω-relaxations were shown to be enhanced. It was also observed that bimodal β-relaxation appears unconcerned about the structural recovery following physical ageing. On the opposite, it was concluded that each step of the thermal ageing treatment induce several changes in the viscoelastic characteristics of the ω-relaxation.

1. Introduction

Epoxy resin-based composites are often used for structural applications where their long-term properties are of primary importance. Consequently, a great deal of effort has been devoted to evaluate and characterise their performance under various deleterious conditions. Thus, it is well recognised that:

Epoxy resins can suffer substantial losses in their properties, particularly mechanical, following the pick-up of water (1-9). As a matter of fact, when such material is exposed to a hydrothermal environment, the glass transition temperature (T_g) usually decreases. This modification in T_g reflects both the degree of resin plasticization and water/resin interactions occurring in the material. However, as a consequence of the complexity of epoxy systems, discussions about the interactions between water and epoxy systems at a molecular level remains rather limited and sometimes contradictory.

Amorphous solid systems, such as epoxy resins, are not in thermodynamic equilibrium at temperatures below their glass transition. As a result of differences in preparation and/or in thermal histories of samples, time-dependent variations are usually detailed concerning mechanical and physical properties of epoxy networks. More commonly reported as “physical ageing”, this phenomenon leads (10-11) in particular, to the increase of the density of such materials, to the loss of their ductility, and also to the decreases of both mechanical damping and stress-relaxation rates.

In the present work, the influence of both water and volume recovery (resulting from “physical ageing” process) on the viscoelastic behaviour of an epoxy resin has been investigated.

2. Experimental

2.1. Material

An epoxy prepolymer, the diglycidyl ether of Bisphenol A (DGEBA from Dow Chemical DER 332, M_n = 348.5g/mol) with a low dispersity index (n = 0.03) was used. The 4,4’ methylene bis[3-chloro-2,6-diethylaniline] (MCDEA from Lonza, M_n = 380g/mol) was used as hardener (stoichiometric ratio amino-hydrogen-to-epoxy equal to 1). The cure schedule was 7h at 135ºC followed by post-curing at 185ºC for 2h. The synthesis of the epoxy network, i.e. the reaction kinetics and further characterisation, was detailed previously (12).

2.2. Samples characterization

Differential Scanning Calorimetry (DSC) thermograms were recorded using a DSC 7 Perkin Elmer device with a heating rate of 10ºC/min under a nitrogen atmosphere.

For the dynamic mechanical properties, the analyser Rheometric Scientific DMTA MK III was used, under nitrogen atmosphere, operating in a double cantilever mode under isochronal conditions at frequencies of 0.3, 1, 3, and 10Hz, to measure the temperature dependence of the viscoelastic properties E^* (storage, E', and loss, E'', moduli) from –130ºC to 250ºC with a heating rate of 1ºC/min. The samples were approximately 27 mm long, 6 mm wide, and 1 mm thick.

2.3. Hydrothermal and thermal ageing treatments

To investigate successively the influence of both water and physical ageing on the viscoelastic behaviour of DGEBA-MCDEA network, samples were first immersed in distilled water and then tested on dynamic mechanical analyser. Then, thermal ageing was performed.

Hydrothermal ageing :

During 3 months, samples were placed into distilled water, at ambient temperature. They were weighed periodically using a digital balance (0.1 mg resolution) to determine weight change and, thus, water uptake. It was observed that samples reached maximum water gain (0.8wt.%) after 3 months in water.

Thermal ageing treatment:

The different temperatures concerning the thermal ageing treatment were defined from differential scanning calorimetry experiments. The DSC trace displays the glass transition temperature T_g of DGEBA-MCDEA network at 175°C (onset). No exothermal peak (during the first heating) and no increase of T_g (during a second heating) were observed. As a consequence, the epoxy system can be considered as fully reacted, i.e. 175°C is the maximum T_g and the following treatment can not induce any chemical changes. The temperatures that were considered for further thermal treatments, are the following:

195ºC (T_g+20ºC) as the temperature for which the samples are refreshed.

155ºC (T_g-20ºC) as a temperature which leads to structural recovery (physical ageing).

As a consequence, in this paper, the samples were denoted as:

"as received" for samples without any hydrothermal or thermal treatment after curing. Nevertheless, the samples have been left at least 18 months, in classical laboratory conditions, before our first experiments.

"wet" for "as received" samples immersed 3 months in water at ambient temperature.

"refreshed" for "wet" samples treated 30 min at T_g+20ºC in the furnace of the DMTA, under nitrogen atmosphere, and then cooled down to –130ºC at about 15ºC/min.

"aged" for "refreshed" samples treated, under nitrogen atmosphere, for 45h at T_g-20ºC and then cooled down to –130ºC with a cooling rate of 1ºC /min.

Figure 1 shows the DSC traces of "as received" DGEBA-MCDEA sample as well as these ones obtained after both "refreshing" and "ageing" thermal treatments. DSC scans for "as received" and "aged" samples show an endothermal peak near the onset of the transition from the glassy state to the rubbery state. The occurrence of such a peak is well known (10) for reflecting that "physical ageing" is a thermoreversible phenomenon. Such results also confirm the availability of chosen thermal ageing treatment.

3. Results and Discussion

3.1 Viscoelastic behaviour of DGEBA-MCDEA network

The experimental dynamic mechanical values of the storage modulus (E') and the loss factor (tan δ) at 1Hz for the "as received" DGEBA-MCDEA sample are given in Figure 2.

Three typical relaxation modes of epoxy networks can be shown:

the α-relaxation mode – associated with the glass transition – appears at higher temperatures (maximum of tan δ values at about 186°C at 1Hz).

the β-relaxation mode – associated (13-16) with motions of small units of the macromolecular chains (hydroxyether groups and diphenylpropane units) is detected around –70°C at 1Hz. It is often reported (13,16) that motions of diphenylpropane units are located at lower temperatures than motions of hydroxyether groups.

the slight relaxational process, evidenced between the main (α) and the secondary (β)relaxations of DGEBA-MCDEA network, can be related to the **ω-relaxation** of epoxy materials. Numerous papers (1-3, 6, 13-18) concerning epoxy-resin based composites reveal such an intermediate relaxation. In the past, Pogany (17) and Arridge and Speak (18) attributed it to motions of less-crosslinked zones in the

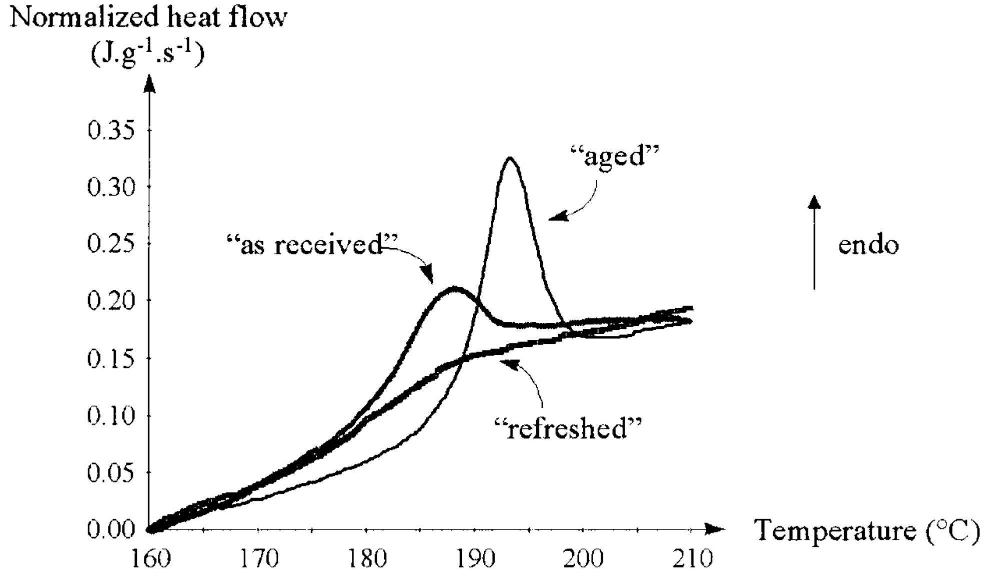

Figure 1 Differential scanning calorimetry traces of "as received", "refreshed" and "aged" DGEBA-MCDEA samples.

network, but now epoxy-amine networks are well known to be homogeneous. Ochi and co-workers (16) associated ω with motions of the *p*-phenylene groups. Other authors (1, 3, 6) consider this additional relaxation as a probe of the structural or molecular arrangements within the network resulting from the moisture sorption. Thus, ω-relaxation seems to be also sensitive to moisture sorption: the magnitude of its corresponding peak on the viscoelastic spectra could increase in the presence of water. In spite of all these results, the ω-relaxation assessment in terms of molecular mobility remains uncertain in literature. Dynamic mechanical thermal analyses were performed in a frequency range from 0.3 to 10Hz. As well known, the temperature positions of relaxations are shifted to higher temperatures when frequency increases. Considering an Arrhenius dependence of the relaxational process, apparent activation energies of the α- and β-relaxations were estimated at (550±50) kJ/mol and at (70±2) kJ/mol, respectively. These values are close to other ones, corresponding to various epoxy networks and reported earlier (4, 13, 15, 19). However, such an approach can not be done to estimate the apparent activation energy of the ω-relaxation, because the temperature position of the maximum of tan δ, corresponding to this relaxational process, can not be accurately determined.

3.2 Consequences of hydrothermal and thermal ageing treatments

3.2.1. Experimental results

The influence of the overall ageing treatment on the β- and ω-relaxation processes can be evidenced. Figure 3 gives the dynamic mechanical spectra of loss factor tan δ obtained at 1Hz, for both "as received" and "wet" DGEBA-MCDEA samples. It can be observed that after the hydrothermal ageing:

the magnitude of both β- and ω-relaxations significantly increase.

the width of the tan δ peak corresponding to the ω-relaxation is higher.

the splitting of the tan δ peak corresponding to the β-relaxation is amplified in presence of water. As a consequence, the relaxational process can be considered as the addition of two contributions: one at lower temperatures (near -80°C), the other at higher temperatures (at about -40°C).

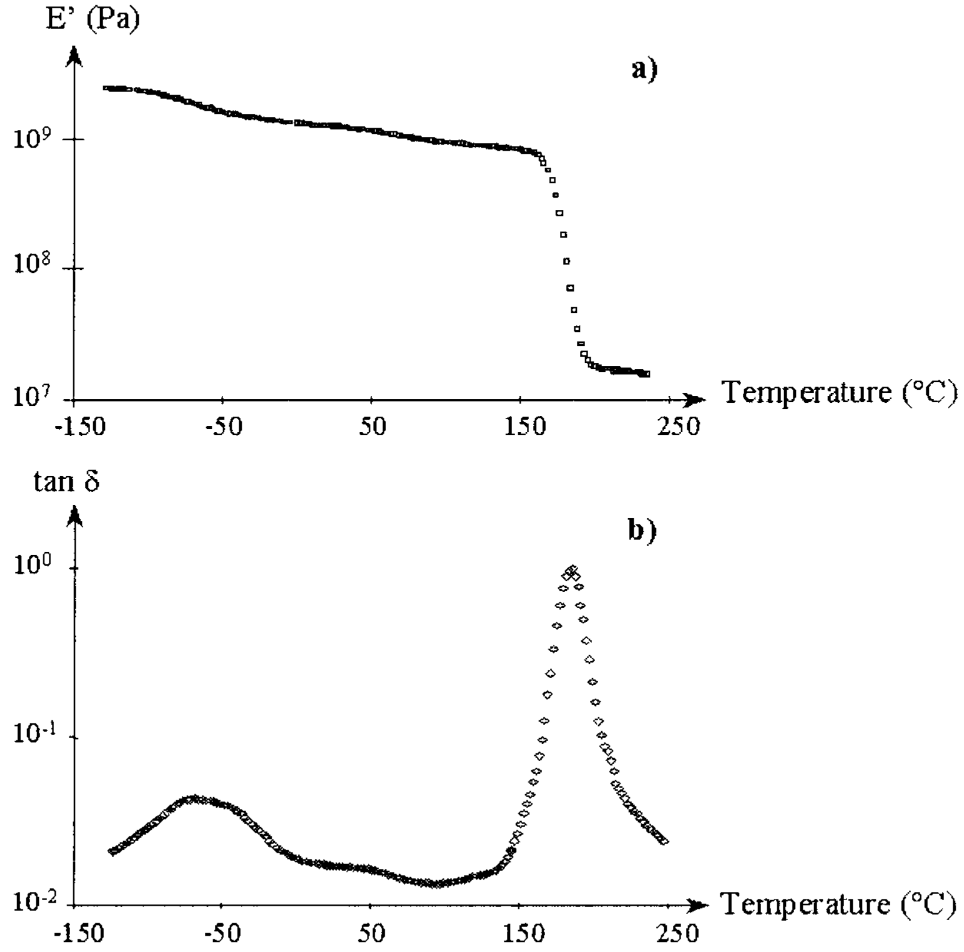

Figure 2 Viscoelastic characteristics *versus* temperature at 1Hz for "as received" DGEBA-MCDEA samples. **a)** Storage modulus, E' **b)** Loss factor, tan δ

The experimental viscoelastic spectra at 1Hz – recorded step by step all along the ageing treatment described previously (denoted "as received", "wet", "refreshed", and "aged") – are given in Figure 4. It can be seen that:

as soon as the "refreshing" treatment is achieved, i.e. for "refreshed" and "aged" samples, both magnitude and temperature location of the β-relaxation mode become close to that of "as received" DGEBA-MCDEA sample. As a result, the β-relaxation seems to be more affected by water sorption than by physical ageing.

both magnitude and temperature location of the ω-relaxation are influenced by each step of the ageing treatment. Thus, although the main modifications are observed for the "refreshed" DGEBA-MCDEA sample, the ω-relaxation appears to be affected simultaneously by both water and volume recovery phenomenon.

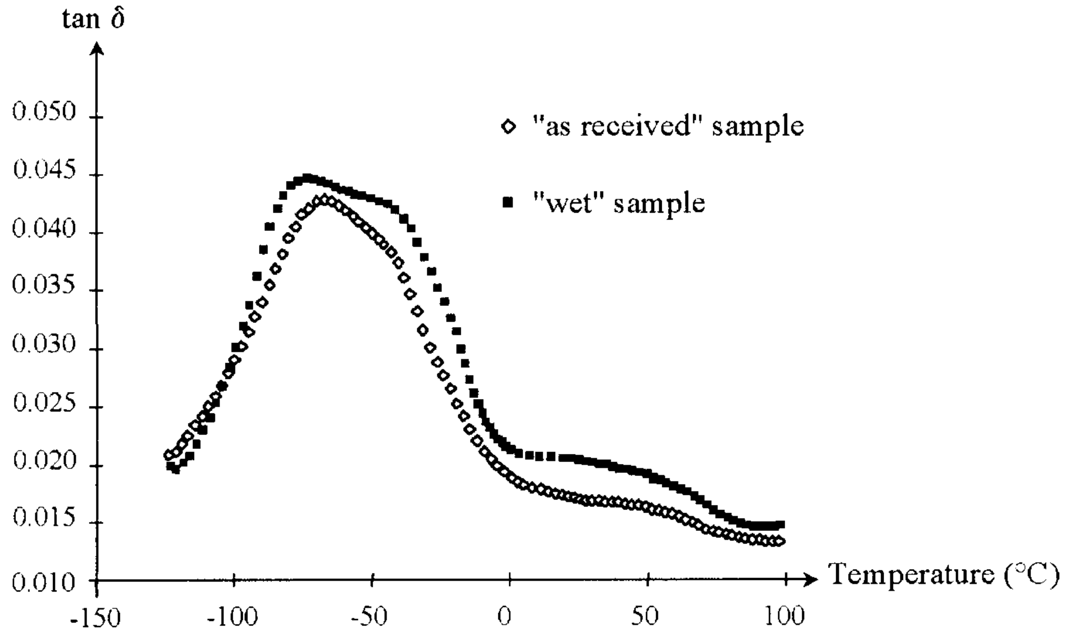

Figure 3 Viscoelastic characteristics *versus* temperature at 1Hz for "as received" (◇), and "wet"(■) DGEBA-MCDEA samples.

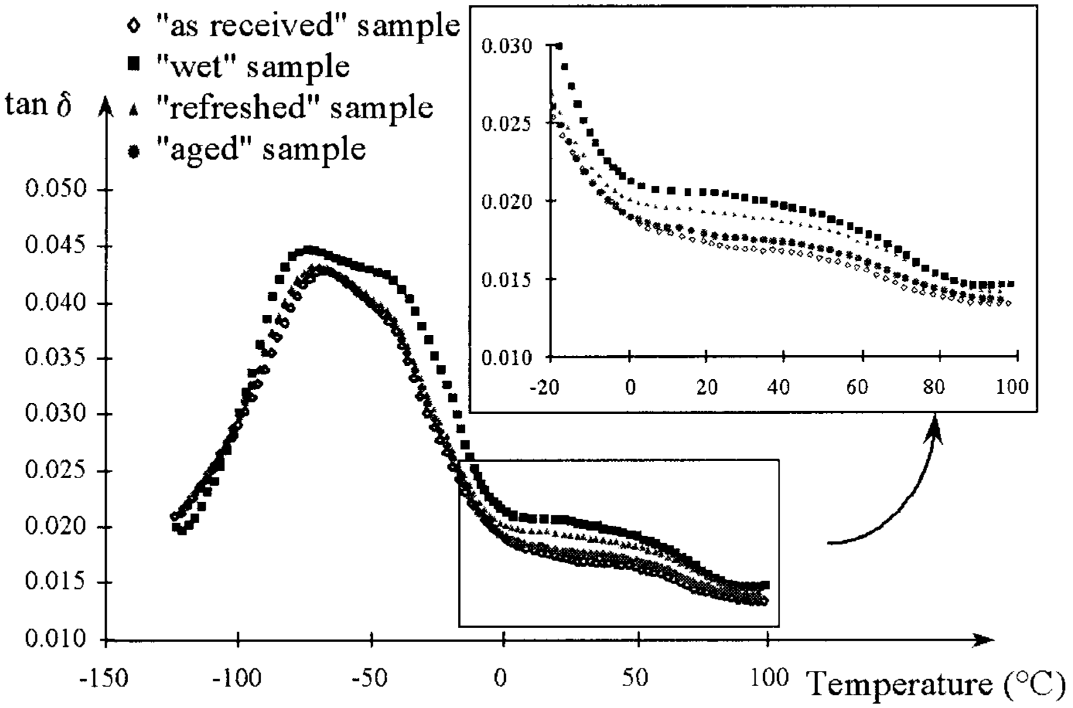

Figure 4 Viscoelastic characteristics at 1Hz *versus* temperature for various DGEBA-MCDEA samples during hydrothermal and thermal ageing treatments.

3.2.2. Influence of water sorbtion

Even though considerable research has focused on hygro- and hydrothermal effects, water diffusion mode and epoxy-water interactions remain not fully understood. Most of discussions are mainly done by using one of the two following approaches.

The first one (2-3) is based on the interaction concept that suggests water molecules couple strongly with certain hydrophilic functional groups of macromolecules. However, epoxy networks are known to exhibit complex chemical structures. As a consequence, different types of interactions must be established with sorbed water molecules and, according to our regard on this first approach, a range of different effects on physical properties are expected to be associated to each of them. Be that as it may, Maxwell and Pethrick (3) reported that such specific interactions could significantly reduce the molecular mobility at short distances in epoxy resins, which leads to an important decrease of the magnitude of both β- and ω-relaxations on the viscoelastic spectra.

The second approach (1, 6, 8) presumes that water diffuses into epoxy resins and resides in the free volume of the material. In this concept, bonding between water molecules and macromolecules are deemed insignificant, and water acts as a plasticizer. Mikols and co-workers (1) also proposed those structural or molecular rearrangements be sometimes envisaged to increase the amount of sorbed water. This leads to amplify the magnitude of β- and ω-relaxations on the dynamic mechanical spectra.

Our results agree with the last approach. As a matter of fact, the plasticization effect of water on DGEBA-MCDEA network could significantly increase the molecular mobility of smaller units. As a result, the magnitude of β-relaxation is the highest on the viscoelastic spectrum of the “wet” DGEBA-MCDEA sample. Moreover, as suggested earlier (4), the above mentioned splitting of the tan δ peak corresponding to β-relaxation could also be considered as a probe of sorbed water. Lastly, as a consequence of the presence of sorbed moisture as well as the resulting increase in the molecular mobility at lower temperatures, all viscoelastic characteristics (*i.e.* width, magnitude and temperature location) of the ω-relaxation are shown to be enhanced.

3.2.3. Influence of physical agein

On the one hand, Figure 4 shows that β-relaxation mode seems to be unconcerned about thermal ageing treatment. First, the bimodal aspect of β-relaxation can therefore be interpreted as due to the sole effect of sorbed water. Then, this result also confirms that physical ageing affect slightly the molecular mobility at short distances in epoxy networks, as it is known for most of amorphous materials (10- 11).

On the other hand, an enlargement of the loss factor spectra in the temperature range where the ω-relaxation appears, is given in the right corner at the top of Figure 4. It can be shown that magnitude of the relaxation significantly decreases when acts physical ageing. Thus, the viscoelastic characteristics of the ω-relaxation are not only influenced by moisture sorption, but also by the volume recoveries following the thermal ageing treatment.

4. Conclusion

The influence of both hydrothermal and physical ageing on the viscoelastic behaviour of an epoxy resin was investigated in the present paper.

The viscoelastic properties of DGEBA-MCDEA network showed the three typical relaxations of epoxy networks: the main relaxation (α) at higher temperatures, the secondary relaxation (β) at lower temperatures, and the intermediate ω-relaxation with a very low magnitude.

It was shown that the β-relaxation mode, which appears bimodal, is mainly affected by water sorption and remains unconcerned about structural recovery following physical ageing. Furthermore, the effects of moisture sorption on the viscoelastic characteristics of such secondary relaxation mode seem to be reversible. As a matter of fact, the loss factor spectra of “refreshed” and “aged” samples were shown to be very close to that of “as received” sample, in the temperature range of the β-relaxation. On the opposite, the viscoelastic characteristics of the ω-relaxation are significantly influenced by each step of the hydrothermal and thermal ageing treatments. Moreover, the simultaneous influence of both water and structural recovery, seems only to be partially reversible on dynamic mechanical spectra.

References

1. Mikols W. J., Seferis J. C., Apicella A., Nicolais L. (1982) Polym. Comp. 3 : 118
2. Moy P., Karasz F. E. (1980) Polym. Eng. Sci. 20 : 315
3. Maxwell I. D., Pethrick R. A. (1983) J. Appl. Polym. Sci. 28 : 2363
4. Benzarti K. (1997) Phd Thesis, Univ. Claude Bernard Lyon (France)
5. Carfagna C., Apicella A., Nicolais L. (1982) J. Appl. Polym. Sci. 27 : 105
6. Wang J., Ploehn H. (1996) J. Appl. Polym. Sci. 59 : 345
7. Xiao G. Z., Shanahan M. E. R. (1998) J. Appl. Polym. Sci. 69 : 363
8. Gupta V. B., Drzal L. T. (1985) J. Appl. Polym. Sci. 30 : 4467
9. Zhou J., Lucas J. P. (1999) Polymer 40 : 5513
10. Struick L. C. E. (1978) Physical Ageing In Amorphous Polymers And Other Materials, Amsterdam, Elsevier
11. Kong E. S. W. (1986) Epoxy Resins And Composites Iv, Adv. Polym. Science 80 : 125, Springer-Verlag Berlin, Heidelberg
12. Girard-Reydet E., Sautereau H., Pascault J.P. (1999) Polymer 40 : 1677
13. Gerard J. F. (1988) Polym. Eng. Sci. 28 : 568
14. Schroeder J. A., Madsen P. A., Foistier R. T. (1987) Polymer 28 : 929
15. Colombini D., Martinez-Vega J. J., Merle G., Girard-Reydet E., Pascault J. P., Gerard J. F. (1999) Polymer 40 : 935
16. Ochi M., Yoshizumi M., Shimbo M. (1987) J. Polym. Sci. 25 : 1817
17. Pogany G. A. (1969) Brit. Polym. J. 1 : 177
18. Arridge R. G. C., Speak J. H. (1972) Polymer 13 : 450
19. Heux L., Halary J. L., Laupetre F., Monnerie L. (1997) Polymer 38 : 1767