Composites: Part B 43 (2012) 616–620

Contents lists available at SciVerse ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

Combinatory model of curing process in epoxy composite

A. Kondyurin [a,*], L.A. Komar [b], A.L. Svistkov [b]

[a] *School of Physics, University of Sydney, Sydney, Australia*
[b] *Institute of Continuous Media Mechanics, Russian Academy of Science, Perm, Russia*

ARTICLE INFO

Article history:
Received 6 January 2011
Received in revised form 6 September 2011
Accepted 1 November 2011
Available online 10 November 2011

Keywords:
A. Resins
B. Rheological properties
E. Cure
Raman and FTIR Spectroscopy

ABSTRACT

A combinatory model of curing process in a mixture of multifunctional active components was developed. The model was tested with an analysis of curing kinetics in epoxy resin based on Bisphenol A with amine hardener. The experimental kinetics data obtained with FTIR and Raman spectroscopy, chromatography and viscosimetry methods were applied. The theoretical results show good agreement with experiment. The model can predict a concentration of middle products during curing reaction. The model is developed for calculation of the curing kinetics in free space environment.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Composite materials based on epoxy resins and fibre fillers are widely used as materials for durable constructions, including specific applications such as space satellites and space supporting constructions [1–3]. One of the main requirements for the processing of such materials is a controlled curing reaction, that provides high mechanical strength of the composite material with minimal residual and temperature stresses as well as high adhesion in matrix/filler interface.

As a rule, the processing of the composite materials with highest mechanical characteristics includes multistage heating and cooling with controlled temperature increase and decrease. In the cases of constructions of strategic importance (military, aerocraft and space applications), the completeness of curing, internal stresses and defects are investigated with a number of experimental methods. This process is used for the creation of ready-to-use constructions. However, in some cases the control of the process is impossible. One of the such processing is the curing of composite materials in free space environment.

The curing of composite materials in free space environment can be used for building a large-size space station, Moon bases, space orbital plants, space hotels, large size telescopes, reflectors, shields, which can not be transported in ready-to-use state from Earth to space due to their large mass, size or shape [4–6]. The curing process is critical for the repairing technology of space constructions in orbit, for example, such as Shuttle and International Space Stations.

In space the usual curing process of the composite matrix, that requires step-by-step temperature increase and atmospheric pressure, is impossible. The conditions of free space include high vacuum (up to 10^{-5} Pa near wall of space ship), wide temperature fluctuations from -100 to $+100$ °C, high flux of charged particles with high energy including atomic oxygen of 5 eV energy, ion flux of some GeV energy from Sun and stars, electron flux of some GeV energy, X-rays, γ-rays, UV and vacuum-UV light, infrared irradiation. These factors cause evaporation of low-molecular weight fractions, including chemically active molecules, as well as the occurrence appearance of active free radicals, local thermal spikes, and temperature gradient in lateral and normal directions of the material. The intensity of these factors depends on the regime of flight, the orbit parameters , the reflectance/irradiation coefficients of the material surface, Earth season and space weather. All these conditions and their variations have significant influence on the polymerisation regime, and a considerable study of the polymerisation processes in variable space conditions has to be done to predict exploitation characteristics of the materials.

However, an experimental investigation of the polymerisation process in free space environment is difficult and expensive. On the other hand, an adequate laboratory simulation of free space environment acceptable for the polymerisation process investigation is impossible. In such case, a theoretical investigation of the polymerisation process and key-experiments to investigate the separate factors of space environment is the only realistic way.

In this paper we investigate the polymerisation process in epoxy resin with amine hardener. This curing system is used for

---

* Corresponding author.
E-mail address: kond@mailcity.com (A. Kondyurin).

1359-8368/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compositesb.2011.11.019

creation of the composite materials applicable in aerospace technologies, including rockets, satellites, antennas, reflectors and other space constructions. The kinetics of the curing process was investigated experimentally and presented in a number of publications [7–24]. The reaction of epoxy resin with amine hardener proceeds on auto-catalyst/auto-inhibition mechanism. The rate of reaction depends on conditions of curing, composition of mixture and additives, microphase separation and crystallisation. The reaction kinetics of epoxy resin based on Bisphenol A with amine hardener follows equation [25]:

$$\frac{\partial\beta}{\partial t} = K(1-\beta)(1+C_0\beta)(1-\xi\beta), \tag{1}$$

where β is a conversion of the epoxy groups, K is a kinetics rate, C_0 is an auto-catalyst constant, ξ is an auto-inhibition constant. This equation was supported by direct experimental measurements of reaction groups by epoxy group titration method [26,27], radioactive markers method [28], chromatography [29,30], infrared and Raman spectroscopy [31], and by indirect methods of curing kinetics such as viscosity measurement [32], Dynamical Mechanical Analysis (DMA) and hardness measurement [33,34], calorimetry [35], refractometry [36] and dielectric spectroscopy [37]. Following the results of the experimental methods, a number of theoretical models of epoxy resin curing were developed. Some of the models take into account different side reactions, influence of microphase separation, thermal effects, mechano-destructive phenomena, residual and thermal stresses appearance, influence of passive and active additives and reinforcement agents [38–40,28,41–44]. However, the reactionable mixture is considered as continuous media in all these models and the molecular structure in all these models is ignored. It means, that the models cannot include an evaporation of components, appearance of new active components and change of curing constants and, therefore, these models cannot be used for the analysis of curing processes in space environment.

The calculation of polymerisation in space needs a molecular model of curing, where the molecular structure of separate components and its activity can be separately introduced and analysed. Some of acceptable molecular models were developed for specific curing conditions. For example, the curing model for epoxy resin on the solid substrate was developed by quantum mechanics methods [45] and by semi-empirical function methods [46]. However, these models are limited by the number of calculated molecules and cannot be used for complex multicomponent mixtures. A suitable model o curing reaction based on a molecular behaviour is required.

Considering all the above conditions, a curing model of the epoxy resin was developed that contains amine hardener based on combinatory method of separate molecules. This model is similar to the model of bound blocks [47] and atomic model [48,49]. But our model gives a possibility to remove and to add the active components during the curing process that can be used to simulate specific factors caused by free space environment such as evaporation, temperature fluctuations and radiation damage.

2. Theory

Let consider the epoxy resin molecule with two epoxy groups in curing reaction with triethylenetetraamine (TETA) with 6 active amine groups. This mixture is well known in literature [50]. We assume, that there are 3 different kinds of epoxy resin molecules and 7 different kinds of TETA molecules in the course of curing reaction. The number of reacted molecule groups – the number of bonds with neighbouring molecules – predetermines the kind of used molecule. For example, TETA molecule of "0" kind is a molecule without any bond to epoxy molecule. TETA molecule of 1st kind has one bond to epoxy resin molecule. The molecules of 2, 3, 4, 5 and 6 kinds have 2, 3, 4, 5 and 6 bonds to epoxy resin molecules accordingly. The same logic is applied for kinds of epoxy resin molecules. "0" kind of epoxy resin molecule is non-bonded molecule, "1" kind molecule has 1 bond and "2" kind molecule has two bonds with amine molecule. Following these terms, the curing reaction is transformation of one kind of molecule to another. A combination of different transformations between kinds of molecules gives a number of equations. The concentration of corresponding (i and j) kinds of amide (n_i^{am}) and epoxy resin (n_j^{ep}) molecules could be described by following equations for amine molecules:

$$\frac{dn_6^{am}}{dt} = \sum_{j=0}^{1} f(n_5^{am}, n_j^{ep}),$$

$$\frac{dn_i^{am}}{dt} = \sum_{j=0}^{1} [f(n_{i-1}^{am}, n_j^{ep}) - f(n_i^{am}, n_j^{ep})], \quad i = 1,2,3,4,5 \tag{2}$$

$$\frac{dn_0^{am}}{dt} = -\sum_{j=0}^{1} f(n_0^{am}, n_j^{ep}),$$

where

$$f(n_i^{am}, n_j^{ep}) = K_{ij}\ n_i^{am}\ n_j^{ep} \tag{3}$$

K_{ij} is the rate constant of reaction for i and j kinds of amine and epoxy resin molecules, t is the time of reaction. The same functions are used for the following equation for epoxy resin molecules:

$$\frac{dn_2^{ep}}{dt} = \sum_{i=0}^{5} f(n_i^{am}, n_1^{ep})$$

$$\frac{dn_1^{ep}}{dt} = \sum_{i=0}^{5} [f(n_i^{am}, n_0^{ep}) - f(n_i^{am}, n_1^{ep})] \tag{4}$$

$$\frac{dn_0^{ep}}{dt} = -\sum_{i=0}^{5} f(n_i^{am}, n_0^{ep}).$$

Function $f(n_i^{am},\ n_j^{ep})$as decay rate of active groups in mixture depends on concentration of reactionable molecules and their activity. The solution for the Eqs. (2) and (4) needs the K_{ij} function in (3) to be determined. The K_{ij} function is calculated with a combinatorial analysis of different kind of reacting molecules and assumption that the rate of individual reaction depends on activity of the reacting molecules. It is assumed, that the higher number of bonds decreases the activity of molecules due to steric difficulties and decreases the mobility of the molecules due to the molecular mass of the whole molecular fragment. This assumption is supported by the theory of activated complex, which is formed as intermediate unstable product. According to this theory, the formation of the complex needs adjustment of the molecules to each other, what needs sufficient mobility of the molecules and opening position of the reacting groups. In this case, each new bond between molecules decreases its mobility and steric freedom to adjust the right position and conformation for activated complex. Therefore, the probability of activated complex formation decreases with the increase of i and j indices. Moreover, the amine hardener has two kinds of amine group: end and middle. Following these assumptions, the function K_{ij} is presented as $K_{00} = 4k_a$; $K_{10} = 2k_a$; $K_{01} = 2k_a$; $K_{11} = k_a$; $K_{20} = 8k_b$; $K_{30} = 6k_b$; $K_{40} = 4k_b$; $K_{50} = 2k_b$; $K_{21} = 4k_b$; $K_{31} = 3k_b$; $K_{41} = 2k_b$; $K_{51} = k_b$, where k_a and k_b are different chemical rate constants for end and middle amine groups. Such model was applied to the real epoxy resin composition.

3. Experiment

The epoxy resin based on Bisphenol A (average molecular mass 374, viscosity 1 Pa·sec at 250C, Aldrich) was used in the experiments, as well as the Triethylenetetramine (Aldrich) hardening agent. The ratio of resin and hardening agent was 10:1 in weight parts. The glass fabric of satin weave was impregnated by liquid epoxy resin with hardener.

FTIR spectra of epoxy resin composition were recorded with the usage of Nicolet Magna 650 and Bruker IFS 66 spectrometers. The uncured composition was placed between Teflon foils and pressed between KBr windows. The absorbance of 915 cm^{-1} line following the Bouger-Lambert law was used for the analysis of epoxy group concentration.

Micro-Raman spectra ($\lambda = 532.14$ nm) were obtained in the backscattering mode using a diffraction double monochromator spectrometer HR800, Jobin Yvon, LabRam System 010. The spectral resolution was 4 cm^{-1} and the number of scans and integration time were varied to ensure the sufficient signal-to-noise ratio. An optical microscope (Olympus BX40) with a 100 × objective was used to focus the laser beam and collect the scattered light. LabRam™ software was used to analyse the spectra. The intensity of 1134 cm^{-1}, 1160 cm^{-1} and 1430 cm^{-1} lines of structure deformation vibrations of epoxy ring and bending vibration of methylene group in epoxy ring were used for the calculation of epoxy group concentration. The kinetics measurement was done with time of the curing reaction at stable position of the sample and optical elements of spectrometer. Therefore, the intensity of lines depends only on the chemical transformations in the composition.

The viscosity of the epoxy resin composition was measured with ARES viscosimeter. The uncured mixture was placed between two metal discs of 25 mm diameter with the 2.474 mm gap between them. The upper disc was periodically turned on 0.02 rad with 1 Hz frequency by sinusoidal function. The bottom disc was connected with the sensor for load detection. The measurements were done in thermostatic cell at constant temperature (±0.1 °C) in nitrogen flow. The viscosity was measured with the time of curing reaction before the composition becomes hard and was peeled off the discs at turning.

Liquid chromatography was used for the concentration analysis of residual part of unreacted epoxy resin in the mixture. The mixture of epoxy resin with different amount of amine hardener was prepared, kept 72 h at room temperature, dissolved in chloroform and inserted into the chromatography column. UV detector was used for passing components.

The original codes in MATLAB (MathWorks, USA) numerical computing environment was used for the calculations.

4. Results

The kinetics Eqs. (2) and (4) were solved for the case of equimolar initial concentrations of epoxy resin and hardener active groups: $n_0^{ep}(t_0) = 75\%$ and $n_0^{am}(t_0) = 25\%$. The theoretical value for integral epoxy group concentration is calculated as $(2 \cdot n_0^{ep}(t) + n_1^{ep}(t))/(2 \cdot n_0^{ep}(t_0))$ and compared with the intensity of epoxy group vibrations in FTIR and Raman spectra. The deviation of experimental curves of epoxy resin concentration by FTIR and Raman spectra data and theoretical integral epoxy group concentration were used for the fitting of k_a and k_b parameters. The experimental and theoretical data for integral value of epoxy group concentration normalised on the initial concentration of epoxy groups are shown on Fig. 1. Coefficients in the equation show how many epoxy groups are belonging to kind of epoxy resin molecule.

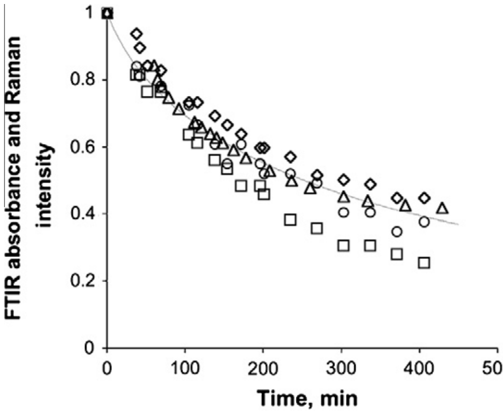

Fig. 1. Kinetics of epoxy group in theory (line) and by intensity of FTIR spectra (triangles – line at 915 cm^{-1}) and Raman spectra (cubic – 1134 cm^{-1}, rhombus – 1160 cm^{-1} and circle – 1430 cm^{-1} lines).

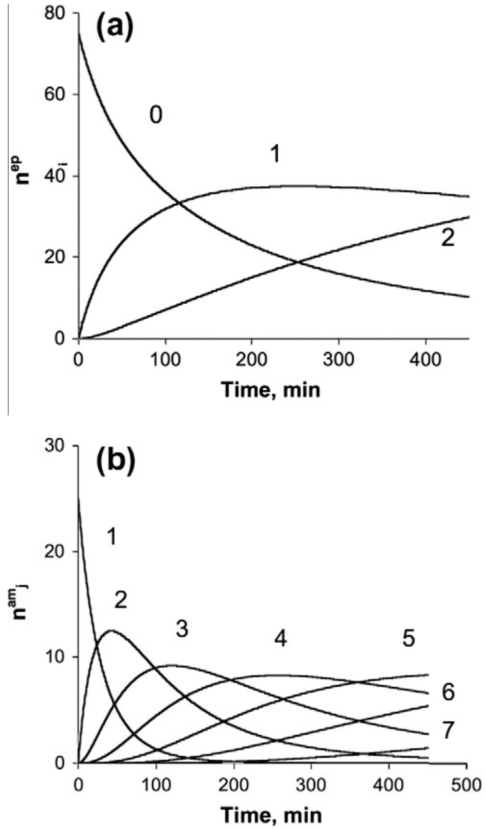

Fig. 2. Modelled concentration of epoxy molecules (a) with different number of bonds (from 0 to 2) to amine molecules; and the modelled concentration of amine molecules (b) with different number of bonds (from 0 to 6) to epoxy molecules with time of curing reaction. The initial concentration of TETA hardener corresponds to stoichiometric ratio.

Following (2)–(4) equations, the concentration of different kinds of the epoxy resin molecules and TETA molecules with different number of bonds are presented on Fig. 2. The concentrations are normalised on the initial concentrations of the groups. As shown, the TETA and epoxy resin molecules with higher number of bonds appear at the time of reaction. With time, the rate of the reaction decreases which corresponds to the formation of polymer network, the increase of viscosity, decrease of molecular mobility and appearance of solid polymer. The epoxy and amine groups do not disappear entirely. It corresponds to the experimental data of epoxy resin curing and the phenomenological models of epoxy resin curing.

The theoretical results show, that free amine molecules disappear completely. The composition with stopped reaction does not contain the initial amine molecules without bonds. At least one bond is presented for each molecule. Most of amine molecules have 3, 4 and 5 bonds with epoxy resin molecules. However, some amount of non-bonded epoxy resin molecules remains in the composition.

The Eqs. (2)–(4) were used for calculation of kinetics with non-stoichiometric ratio of components, when 5%, 10%, 20% and 30% of TETA of equimolar ratio were present in the initial mixture. In this case, the calculation showed, that all the amine groups take part in the reaction and the final mixture has all hardener molecules with 6 bonds (Fig. 3). Some amount of epoxy resin molecules remains non-bonded (Fig. 4). This fact provides the possibility to measure the non-bonded epoxy resin molecules.

The amount of non-bonded epoxy resin molecules was measured by liquid chromatography. The mixture of epoxy resin and TETA hardener were prepared with mentioned above concentrations and after complete reaction were dissolved in chloroform and measured. The mixtures of 5–20% TETA were dissoluble in chloroform. The mixture of 30% TETA gives the insoluble gel in chloroform. The gel-fraction was filtered and soluble part of the composition was measured. The chromatography curves for initial epoxy resin and residual soluble part of epoxy resin after reaction are similar. It does not show any additional peaks interpreted as partially bonded epoxy resin molecules or non-bonded amine molecules. It means, that the products of the curing reaction could not come through the chromatography column. The area under the chromatography peaks shows the amount of non-bonded epoxy resin molecules. The calculated amount of non-bonded epoxy resin molecules is in agreement with experimental data (Fig. 5).

The calculated concentrations of epoxy resin and amine hardener molecules were used for viscosity calculation of the mixture during the reaction. The viscosity increases from initial viscosity of mixture η_m up to infinite value corresponding to phase transition from liquid state to solid state of the composition. The viscosity increase is caused by the appearance of bonded molecules due to the curing reaction. As the model shows, the mixture during the reaction contains a number of monomer epoxy resin and hardener molecules and a number of bonded molecules with different number of jointed monomers. It means, that the composition is not homogeneous. The bonded molecules are considered as jointed to conglomerate. The molecular mass of conglomerate of bonded molecules is higher than monomers and the mobility of these conglomerates is lower. Therefore, the composition can be considered as a mixture of two phases with different molecular mobility: liquid phase that consists of monomer mixture, and solid phase that consists of conglomerates of bounded molecules. In this case, the viscosity of heterogeneous mixture can be described by the Chong function [51]:

$$\eta_c = \eta_m\left(1 + \frac{1.25\varphi}{1 - \varphi/\varphi_{\max}}\right)^2, \tag{7}$$

where η_c is the viscosity of the composition, η_m is the initial viscosity of the composition before the curing reaction, $\phi_{\max}$ is the maximal partial volume of solid fraction. The partial volume of solid fraction ϕ is calculated from the amount of bounded molecules as:

$$\varphi = \frac{V_{ep}(n_1^{ep} + n_2^{ep}) + V_{am}(n_1^{am} + n_3^{am} + n_4^{am} + n_5^{am} + n_6^{am})}{V_{ep}(n_0^{ep} + n_1^{ep} + n_2^{ep}) + V_{am}(n_0^{am} + n_1^{am} + n_2^{am} + n_3^{am} + n_4^{am} + n_5^{am} + n_6^{am})} \tag{8}$$

where V_{ep} and V_{am} the volume of one monomer of epoxy resin and TETA.

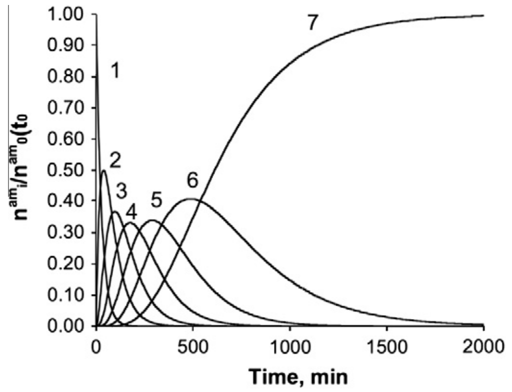

Fig. 3. Modelled concentration of amine molecules with different number of bonds to epoxy molecules at the time of curing reaction. The initial concentration of TETA hardener is 5% of stoichiometric ratio.

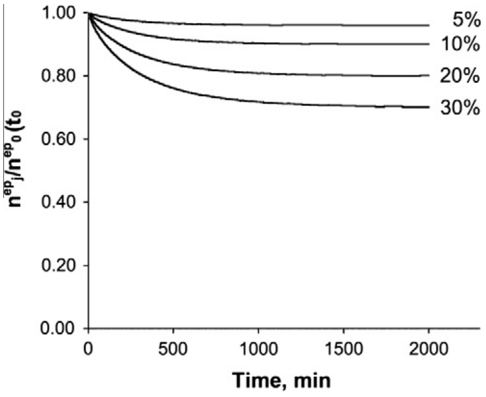

Fig. 4. Modelled kinetics of unbounded epoxy resin molecules at various concentration of TETA hardener: 5%, 10%, 20% and 30% of stoichiometric ratio.

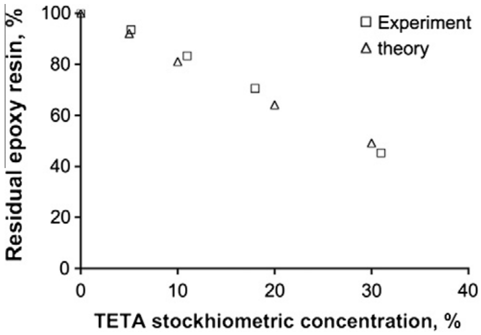

Fig. 5. Calculated (triangle) and experimental (cubic) data of residual unbounded epoxy resin concentration in dependence on stoichiometric ratio of TETA hardener.

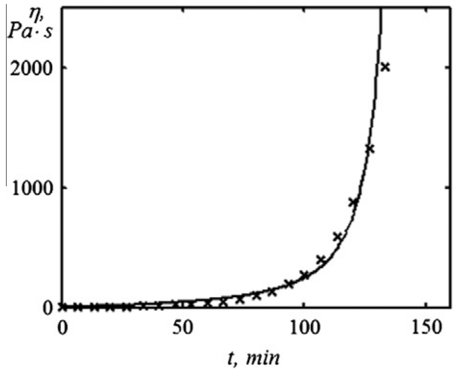

Fig. 6. Viscosity of the epoxy resin composition with time of curing reaction: triangles show experimental points, curve corresponds to the model data.

The calculated curve and the experimental points are presented on Fig. 6. Only one parameter $\phi_{\max}$ was fitted to get the calculated curve close to the experimental points. Both the theoretical curve and the experimental data show the same character of viscosity during the curing reaction: the first period (from 0 to 100 min) corresponds to the slow viscosity increase; the second period (from 100 to 160 min) corresponds to the sharp increase up to the point of phase transition. Therefore, the theoretical calculations give a realistic model of viscosity behaviour during the curing reaction.

5. Conclusion

The combinatory model of the curing reaction in epoxy resin/amine hardener mixture was developed on simple consideration of chemical group combinations. The results of modelling are in good agreement with FTIR, Raman, chromatography and viscosimetry experimental data of curing reaction. The final results are in agreement with well-known models of the curing process, but the presented model gives a concentration of all possible products during the curing process. In particular, the model can be used to get the concentration of differently bonded molecules during reaction, what can be used for an analysis of the curing reaction under the specific conditions of free space environment.

Acknowledgement

The study was supported by Humboldt Foundation (A. Kondyurin).

References

[1] Gunyaev GM, Dushin MI, Ivonin YuN, Kvacheva LA, Mihailov VV, Nikoshin EF, et al. Mechanika Kompositsionnih materialov 1983;N2:211.
[2] Startsev OV, Rudnev VP, Ivonin YuN, Nikishin EF, Barbashev EA, Bogatov VA, et al. Visokomolekularnie soedineniya 1987;29(N12):2577.
[3] Startsev OV, Nikishin EF. Mechanika Kompositsionnih materialov 1993;29(N4):457.
[4] Kondyurin AV. Building the shells of large space station by the polymerisation of epoxy composites in open space. In Polym Sci Technol 1998;25(4):78–80.
[5] Kondyurin A, Kostarev K, Bagara M. Polymerization processes of epoxy plastic in simulated free space conditions. Acta Astronaut 2001;48(N2-3):109–13.
[6] Kondyurin A, Lauke B, Richter E. High Perform Polym 2004;16:163.
[7] Kochnova ZA, Zhavoronok ES, Chalih AE. Epoxy resins and hardeners: industrial products. Moscow: Peint-Media; 2006.
[8] Irzhak VI, Rosenberg BA, Enikolopyan NS. Network polymers. Nauka: Moscow; 1979.
[9] Chernin IZ, Smehov FM, Zherdev YuB. Epoxy polymers and compositions. Moscow: Khimiya; 1982.
[10] Mitzel E, Koenig J. Epoxy resins and composites, vol. 2. Berlin; 1986. p. 73.
[11] Arutunyan HA, Davtyan SP, Rosenberg BA, Enikolopyan NS. Visokomolekularnie soedineniya 1975;17(N2):289.
[12] Davtyan SP, Arutunyan HA, Shkadinskii KG, Rosenberg BA, Enikolopyan NS. Visokomolekularnie soedineniya. 1977;19(N12):2726.
[13] Pahomova LK, Salamatina OB, Artamenko SA, Berlin AA. Visokomolekularnie soedineniya 1978;7:554.
[14] Kush PP, Komarov BA, Rosenberg BA. Visokomolekularnie soedineniya 1979;21(N8):1697.
[15] Mutin II, Kush PP, Komarov BA, Arutunyan HA, Smirnov YuN, Davtyan SP, et al. Visokomolekularnie soedineniya 1980;22(N8):1828.
[16] Budnik YuM, Hozin VG, Babaevskii PG, Chalih AE, Voskresenskii VA. Visokomolekularnie soedineniya 1981;23(N2):354.
[17] Estrina GA, Davtyan SI, Rosenberg BA. Visokomolekularnie soedineniya 1981;23(N2):444.
[18] Astahov PA, Kulichihin SG, Golybenkova LI, Kozhina VA, Chibisova EI, Chernov YuP, et al. Visokomolekularnie soedineniya. 1984;11:864.
[19] Davadyan EA, Ivanova LL, Dubinina LA, Kush PP, Irzhak VI, Rosenberg BA. Mechanika Kompositsionnih materialov 1986;N6:1120.
[20] Davadyan EA, Ponomareva TI, Irzhak VI, Kozhina VA, Chernov YuP, Malkin AYa, et al. Mechanika Kompositsionnih materialov 1990;N5:771.
[21] Bolotina KS, Murashev BA, Tarasov VG. Mechanika Kompositsionnih materialov 1980;N4:749.
[22] Badalov DS, Belostotskii VV, Bolotina KS, Murashev BA, Sazhnev VA, Chudov VL. Mechanika Kompositsionnih materialov 1983;N3:550.
[23] Bolotina KS, Badalov DS, Chudov VL. Mechanika Kompositsionnih materialov 1983;N5:937.
[24] Ponomareva TI, Davadyan EA, Irzhak VI, Rosenberg BA. Mechanika Kompositsionnih materialov 1988;2:347.
[25] Malkin AYa, Begishev VP. Chemical processing of polymers. Moscow: Khimiya; 1991.
[26] GOST 12497-78. Plastmassi. Methods for epoxy group measurement.
[27] Poisson N, Lachenal G, Sautereau H. Vib Spectrosc 1996;12:237.
[28] Buist GJ, Hagger AJ, Howlin BJ, Jones JR, Parker MJ, Barton JM, et al. Comput Chem 1993;17(N.2):257.
[29] Steven Swier, Bruno Van Mele. Thermochim Acta 2004;411:149.
[30] Entlis SG. Soros Educ J 1996;N7:59.
[31] Fedoseev M, Gurina M, Sdobnov V, Kondyurin A. J Raman Spectrosc 1996;27:413.
[32] Chiou PL, Letton A. Polymer 1992;33(N.18):3925.
[33] Kondyurin A, Lauke B, Vogel R. Eur Polymer J 2006;42:2703.
[34] Laoubi S, Vergnaud JM. Thermochim Acta 1990;162:347.
[35] Blanco M, Corcuera MA, Riccardi CC, Mondragon I. Polymer 2005;46:7989.
[36] Ioffe B. Refractometrical methods in chemistry. Leningrad: Khimiya; 1974.
[37] Chernov IA, Deberdeev TR, Novikov GF, Garipov RM, Irzhak I. Plasticheskie massi 2003;N8.
[38] Cole KC. Macromolecules 1991;24:3093.
[39] Zhao L, Hu X. Polymer 2007;48:6125.
[40] Ramosa JA, Paganib N, Riccardib CC, Borrajob J, Goyanesc SN, Mondragon I. Polymer 2005;46:3323.
[41] Gumen R, Jones FR, Attwood D. Polymer 2001;42:5717.
[42] Blanco M, Corcuera MA, Riccardi CC, Mondragon I. Polymer 2005;46:7989.
[43] Larranaga M, Gabilondo N, Kortaberria G, Serrano E, Remiro P, Riccardi CC, et al. Polymer 2005;46:7082.
[44] Benard F, Campistron I, Laguerre A, Laval F. Polym Degrad Stab 2006;91:2110.
[45] Attwood D, Marshall PI. Composites 1996;27A:775.
[46] Wu C, Xu W. Polymer 2006;47:6004.
[47] Irzhak I. Uspehi khimii 1997;66(N3):598.
[48] Horie K, Hiura H, Sawada M, Mita I, Kambe H. J Polym Sci 1970;A8:1357.
[49] Zvetkov L. Thermochim Acta 2005;435:71.
[50] Mallick PK. Compos Eng Handbook. CRC Press; 1997.
[51] Chong JS, Christiansen EB, Baer AD. J Appl Polym Sci 1971;15:2007.