

Chapter 19

THE CALCULATION OF TEMPERATURE STRESSES IN POLYMERS

B. M. Yazyyev

The Strength of Materials Chair, RSBU 162,
Sotzialisticheskaya Street Rostov-on-Don

To study the kinetics of temperature stresses in polymers, to analyse the influence of various factors on the flow of the examined processes, and to model the relaxation behaviour in polymers, a nonlinear constitutive differential equation is used in the paper. This equation was proposed by G.I. Gurevich [1], who called it “the nonlinear generalized Maxwell equation” out of respect for J. Maxwell’s ideas [2] that served as a partial basis for deducing the equation. Total deformation is regarded as the sum of elastic, viscoelastic and temperature deformations:

$$\varepsilon = \varepsilon_e + \varepsilon^* + \varepsilon_T \quad (1)$$

Hooke’s law holds true for elastic deformations ε_e , temperature deformations ε_T are calculated using the formula

$$\varepsilon_T = \int_0^T \alpha(T) dT \quad (2)$$

while in a three-dimensional case the correlation of stresses, time and viscoelastic strains is described by the generalized Maxwell equation:

$$\frac{\partial (\varepsilon_{ik}^*)_s}{\partial t} = \left[\frac{3}{2} (\sigma_{ik} - p \delta_{ik}) - E_{\infty s} \cdot (\varepsilon_{ik}^*)_s \right] \cdot \frac{1}{\eta_s^*} \quad i, k = x, y, z; \quad \delta_{ik} = \begin{cases} 0 & \text{npu } i = k \\ 1 & \text{npu } i \neq k \end{cases} \quad (3)$$

Here: the index s ($s=1,2,3,\dots$) indicates the viscoelastic strain spectrum constituent that corresponds to a certain relaxation time; p is the average stress; $E_{\infty s}$ stands for highly elastic strain modules; η_s^* is the relaxation viscosity defined by the formula:

$$\eta_s^* = \eta_{0s}^* \cdot \exp \left\{ - \frac{1}{m_s^*} \left[\gamma_s^* p + \left| \frac{3}{2} (\sigma_{rr} - p) - E_{\infty s} \cdot (\varepsilon_{rr}^*)_s \right| \right] \right\}. \quad (4)$$

In this equation η_{0s}^* is the initial relaxation viscosity factor, proportional to the relaxation time, i. e. viscosity in absence of stresses; m_s^* is the speed module reflecting the influence of the strain rate on the speed of relaxation processes; γ_s^* is the volume factor that accounts for the influence of uniform expansion or compression on relaxation speed. The indices rr denote main strains and stresses.

Relations (3) and (4) are true for relaxing medium that has an elastic constant carcass, able to restore its unstrained state. For plastically (finitely) deformable medium in (3) and (4) $E_{\infty s} = 0$ is to be introduced.

All the parameters included in (3) and (4) are rather complex temperature functions, and it has been impossible so far to determine these dependencies theoretically. The dependencies under question as well as the parameters themselves are obtained from macroexperiments on isothermal uniaxial tension, compression or shift in various modes at various temperatures.

Relying on the analysis of the experimental data, a number of works [3,4 et al.] prove that for the description of long-standing relaxation processes in polymers under quasi-static tests two constituents of viscoelastic strain are to be taken into consideration in (3) and (4) — a fast ‘older’ ε_1^* constituent and a slow ‘younger’ ε_2^* component. As a rule, for the description of relatively short-term quasi-static processes merely one - the ‘older’ - constituent is sufficient; its relaxation time is significantly shorter than for ε_2^* .

If in (4) the exponent is formally substituted by ‘one’, we get a linear (or linearized) equation of connection that for one member of the spectrum can be recast in the following form:

$$\frac{\partial \varepsilon_{ik}^*}{\partial t} = \left[\frac{3}{2} (\sigma_{ik} - p \delta_{ik}) - E_{\infty} \cdot \varepsilon_{ik}^* \right] \cdot \frac{1}{\eta_0^*} \quad (5)$$

As it has been noted, for elastic materials (for example, certain metals) $E_{\infty} = 0$ is to be introduced in (5). Then, in a one-dimensional case, the well-known linear Maxwell equation is achieved:

$$\frac{\partial \varepsilon}{\partial t} = \frac{\sigma}{\eta_0}$$

On the grounds of the above-mentioned equation of connection (3) we subsequently provide the solution of the problem that concerns the determining of temperature stresses in a polymer rod at temperature changes according to the linear law:

$$T(t) = T_0 + kt .$$

While solving the problem, the following assumptions are made: the temperature field in the rod is homogenous; the ends of the rod are rigidly fixed while in the rod the uniaxial stress state is observed ($\sigma_x \neq 0$); the plane section hypothesis holds true; volume strains (or the average stress) exhibit an insignificant influence on the relaxation process speed; two members of the relaxation times spectrum are taken into consideration.

As a result of these assumptions for the problem under question, equation (3) in consideration of (4) takes on form:

$$\frac{\partial \varepsilon_{x,s}^*}{\partial t} = \frac{\sigma_x - E_{\infty,s} \cdot \varepsilon_{x,s}^*}{\eta_{0,s}^*} \exp \left| \frac{\sigma_x - E_{\infty,s} \cdot \varepsilon_{x,s}^*}{m_s^*} \right| \quad (6)$$

For the total deformation increment in accordance with (1) there is:

$$d\varepsilon_x = \frac{d\sigma_x}{E} + \sum_{s=1}^2 d\varepsilon_{x,s}^* + \int_0^T \alpha(T) \cdot dT \quad (7)$$

The equilibrium equation and the Cauchy formula look like:

$$\frac{\partial \sigma_x}{\partial x} = 0 ; \varepsilon_x = \frac{\partial u}{\partial x} \quad (8)$$

Thus, for the unknown σ_x , ε_x , $\varepsilon_{x,s}^*$, u a complete system of equations has been derived. The system describes the history of the rod stress and strain conditions.

Assuming that before heating (cooling) the rod was in the equilibrium (limp) state, the following initial conditions can be written as:

$$t = 0 ; T = T_0 ; \sigma_x = 0 ; \varepsilon_{x,s}^* = 0 \quad (s = 1,2) . \quad (9)$$

The conditions at the rod edges will look like:

$$x = 0, l ; u = 0 \quad (10)$$

$\varepsilon_x = 0$ is derived from the second equation (8), or in the differential form:

$$d\varepsilon_x = 0 \quad (11)$$

System (6) - (8) under the initial conditions or under condition (11) is solved using the numerical method of 'layer' integration enunciated in [5] and applied in many subsequent works [6 et al.]. The calculation is performed at each time 'layer', if the time increment Δt is constant. If Δt is a variable, then $t_i = t_{i-1} + \Delta t_i$ ($i = 0, 1, 2, \dots$). For i -layer at $\Delta t = const$ a system of algebraic equations is obtained:

$$\left. \begin{aligned} \Delta T &= k \cdot \Delta t \\ \Delta \sigma_i &= -E_i (\Delta \varepsilon_i^* + \alpha_i \cdot \Delta T) \\ \Delta \varepsilon_i^* &= \sum_{s=1}^2 \Delta \varepsilon_{s,i}^* = \sum_{s=1}^2 \left(\frac{d\varepsilon_s^*}{dt} \right)_{i-1} \cdot \Delta t \\ \sigma_i &= \sigma_{i-1} + \Delta \sigma_i; \quad \varepsilon_i^* = \varepsilon_{i-1}^* + \Delta \varepsilon_i^* \\ \left(\frac{d\varepsilon_s^*}{dt} \right)_i &= \frac{\sigma_i - E_{\infty s,i} \cdot \varepsilon_{s,i}^*}{\eta_{0s,i}^*} \exp \left| \frac{\sigma_i - E_{\infty s,i} \cdot \varepsilon_{s,i}^*}{m_{s,i}^*} \right| \end{aligned} \right\} \quad (12)$$

These equations are to be supplemented with the initial conditions:

$$i = 0; \quad t_0 = 0; \quad T = T_0; \quad \sigma_0 = 0; \quad \varepsilon_{s,0}^* = 0 \quad (13)$$

REFERENCES

- [1] Gurevich, G.I. 1974 Media Deformability and Seismic Wave Transmission. Moscow, Nauka. p. 483.
- [2] Maxwell, J.Cl. 1927 *The Sci. papers of J.Cl. Maxwell*. Paris, Hermann. p. 616.
- [3] Rabinovich, A.L. 1970 The Introduction into the mechanics of Reinforced Polymers. Moscow, Nauka. p. 482.
- [4] Goldman, A.Y. *The Investigation of Deformation Mechanisms in Certain Rigid Network Polymers Bounding at Shifts*. Ph.D. Thesis, Moscow, 1966. p. 250.
- [5] Andreyev, V.I. On the Rigidity of Polymer Rods at Creep. In: *The Mechanics of Polymers*, 1968, V.1, pp. 15-22.
- [6] Turusov, R.A. *Mechanical Phenomena in Polymers and Composites* (in Formation Processes). Doctoral Thesis, Moscow, 1983. p. 363.

Chapter 20

COMPOSITES ON THE BASIS OF POLYHYDROXIETHERS AND GRAPHITES

*D. A. Beeva, A. K. Mikitaev, G. E. Zaikov, R. Z. Oshroeva,
V. K. Koumykov and A. A. Beev**

¹Kabardin-Balkar State Academy of Agriculture, 360004, Nalchik,
Tarchokov Street, 1a, Russia

²Kabardin-Balkar State University, Chernyshevskogo Street, 173, Russia

ABSTRACT

By settle polycondensation the polymeric compositions were created, in which high crystalline graphite of the scaly form, using as filler was entered into polymer during synthesis of polyhydroxiethers.

The results of experiment showed, that in the presence of synthetic graphite the viscosity of polymer increases; this proves our earlier assumption, that selective adsorption leads to the increase of the local concentration of monomers on the surface of fillers and to the increase of polycondensation reaction speed.

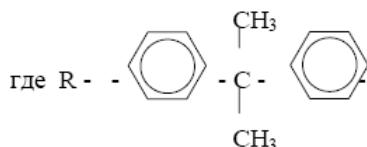
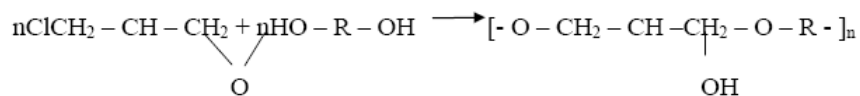
Keywords: Polyhydroxiethers, compounds, polycondensation, graphite, heterophase conditions.

Polyhydroxiethers (PHE), representing high-molecular epoxy compounds, are perspective polymers because of a complex of valuable properties, first of all adhesion to various surfaces. They find their application as a basis of varnishes, glues, film-forming substances, constructional materials in electronic and electrical engineering industries, in automobile and ship constructing and in the number of other branches of industry.

*Correspondence to: 360030, KBR, Nalchik, st. Tarchokov, 1a, Kabardin-Balkar State Academy of Agriculture, faculty of chemistry, Beev A.A. mailto: beevaues@front.ru

However, the further expansion of areas of their application attributes to the creation of new, more perfect compounds with required operational characteristics such, as electric and heat conductivity at high indicators of physic mechanical and antifriction properties.

It was earlier informed [1] about the developed one-phase method of synthesis of PHE by settle polycondensation at heterophase conditions. The scheme of proceeding reaction at use of besphenol and epychlorhydrine as initial substances can be presented as follows:



Polycondensation at the presence of solid inorganic compositions, on the one hand, carrying out a role of catalysts, and with another being fillers for formed polymers have both theoretical, and practical value and is connected to practical problems of production of polymeric composite materials.

Use of graphite is one of perspective directions of creation of composites on the basis of PHE. Absence of laws of formation of PHE-graphite boundary layers and regulation of adhesive interaction in system PHE - graphite, due to modifying of filler surface, defines a topicality of the present paper.

At present time methods of polymeric composite materials production, in which the filler is entered in polymer during synthesis, are widespread. Thus the filler influences not only on the kinetics of polymerizations or polycondensation, but also substantially defines the structure of polymer, and consequently, on the properties of a composite material.

By settle polycondensation the polymeric compositions were created, in which high crystalline graphite of the scaly form, using as filler was entered into polymer during synthesis of PHE.

In the presence of disperse particles with complicated surfaces, an adsorption of monomers on a surface of fillers takes place. As a result the local concentration of monomers at a surface of fillers increases.

It is known, that graphite has selective adsorption ability. Organic substances are adsorbed on a surface of graphite the more strongly, than more they contain aromatic rings. Therefore in presence of high crystalline graphite the selective adsorption of dioxydifenilpropan takes place.

At adsorption of besphenol on a surface of graphite the conjugation of π -electron clouds of aromatic rings of 4,4' dioxydifenilpropan and graphite is possible. As a result of such interaction the nuclearphility of phenol hydroxyl group reduces and as consequence the reactionary ability of phenol hydroxyl groups also reduces.

On figure 1 the dependence of the reduced viscosity of PHE from the maintenance of graphite is illustrated. At the presence of graphite monotonous decrease in viscosity of formed polymer (a curve 1 on fig. 2) is observed.

With the purpose of check of the assumption about selective adsorption ability of crystal graphite, the synthesis of PHE in the presence of isotropic synthetic graphite of mark MPG-8 was processed. The results of experiment have shown, that at the presence of synthetic graphite there is an increase in viscosity of formed polymer (fig.1, curve 3). It confirms the assumption made earlier that as a result of selective adsorption the local concentration of monomers at the surface of feelers increases, that leads to the increase of speed of polycondensation reaction.

At oxidation of graphite, on its surface various, chemically active, oxygen containing groups, which irreversibly chemisorbs besphenol A, are formed. This is a result of chemical interaction of hydroxyl groups of besphenol A with surface groups of graphite and as consequence the decrease in the viscosity of polyhydroxiether synthesized at the presence of graphite (figure 1, curves 2 and 4).

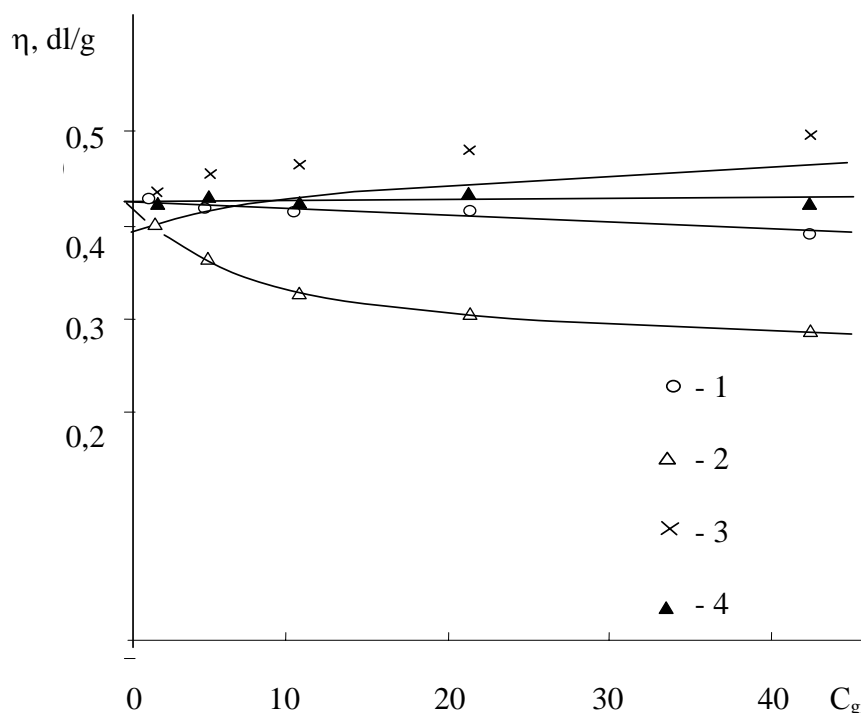


Fig. 1. Influence of graphite on the reduced viscosity of the obtained polymer at the presence of graphite. 1 - non processed GL graphite, 2 - processed GL graphite, 3 – non processed MPG graphite, 4 – processed MPG graphite

The indirect proof of influence of graphite processing on a polymeric matrix is the fact that at dissolution of a polymeric matrix of composites in chloroform there is a subsidence of particles of graphite in the samples made by mechanical mixture. For samples with the processed graphite, made by synthesis of polymer, steady enough suspension is formed.

Pressing at temperature 180°C of graphite, obtained after fivefold extraction of polyhydroxiether, has given the following result: all pressed samples of the raw graphite were

scattered at extraction from the form, while oxidized, at least were not scattered at extraction from the form. It may testify the presence of polyhydroxiether chemisorption on the surface of the processed graphite.

Thus, the crystallinity of graphite influences on the reactionary ability of besphenol A, and the big role is played the presence on a surface of feller, capable to interact with monomers, changing functionality of the last.

Thus, as a result of the lead researches the new method of obtaining of graphite feeling polyhydroxiethers with high parameters of adhesion to various surfaces, electrical conductivity, physic-mechanical and antifriction properties is offered.

The opportunity of improvement of physic mechanical properties of graphite feeling compositions due to reduction of aggregation of particles of feeler and improvements of adhesive interaction PHE and graphite as a result of graphite surface processing is shown.

REFERENCES

- [1] Beeva, D.A., Beev, A.A., Mikitaev, A.K. *Synthesis of polyhydroxiethers on the base of besphenol // Modern scientific technologies*. –Moscow. -RAS-publisher. -2004. –P.80-81.

Chapter 21

HEAT-CONDUCTING COMPOSITIONS ON THE BASE OF EPOXY POLYMERS

A. A. Beev^{1}, A. K. Mikitaev, R. Z. Oshroeva²,
D. A. Beeva² and V. K. Koumykov¹*

¹Kabardin-Balkar State Academy of Agriculture, 360004, Nalchik,
Tarchokov Street, 1a, Russia

²Kabardin-Balkar State University, Chernyshevskogo Street, 173, Russia

ABSTRACT

Heat conducting epoxy compositions on the base of phenol-formaldehyde new lacquer oligomers with low content of ion impurities and hydrolyzed chlorine are produced.

Keywords: Epoxy oligomer, electric insulation material, viscosity, heat conductivity.

Heat conducting epoxy compositions on the base of phenol-formaldehyde new lacquer oligomers with low content of ion impurities and hydrolyzed chlorine are developed.

Epoxy new lacquers were consolidating by corresponding new lacquer oligomers, mixing in relation 2:1 in presence of 1% 2-metilimidazol as consolidating catalyst. By yield of gel fraction the optimal step-by-step regime of consolidation was matched.

The results of experiment showed (fig.1 and 2, tab. 1), that the heat conductivity of epoxy new lacquer compositions may increase from 0,2 to 0,99 Wt/m.K. In this case the highest heat conductivity has the compositions filled by boron nitride. During the supplement to the system of aerosil in quantity of 2% the heat conductivity coefficients decrease; this fact may be explained by dilatation of structure and by formation of pores.

*Correspondence to: 360030, KBR, Nalchik, st. Tarchokov, 1a, Kabardin-Balkar State Academy of Agriculture, faculty of chemistry, Beev A.A. E-mail: beevaues@front.ru

Table 1. Heat conductivity of epoxy new lacquer filled compositions

BN, weight %	B ₄ C ₃ , weight %	λ , Wt/m·K
5	25	0,49
10	20	0,58
15	15	0,60
20	10	0,67
25	5	0,99

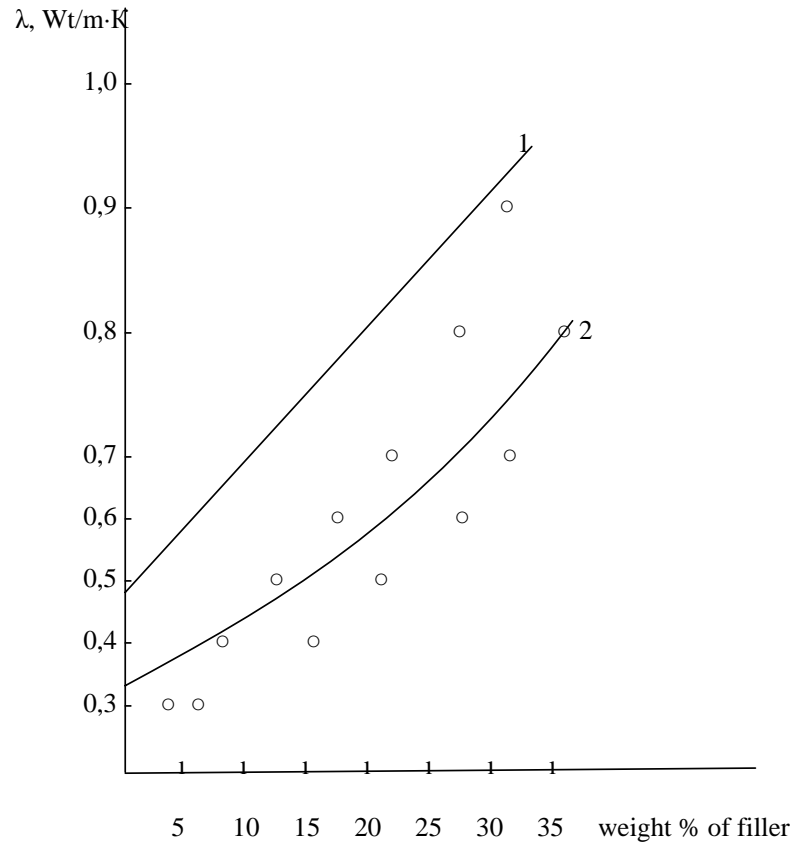


Fig. 1. The dependence of heat conductivity of compositions upon the content of boron nitride (1) and effect of aerosil additives (2)

The heat conductivity of epoxy compositions, filled by boron carbide, lower than those filled by boron nitride (tab. 1).

As it is shown on the figure 2, the compositions with filler particles with sizes from 20 to 150 micrometers more heat conductible than those with the sizes from 150 to 250 micrometers.

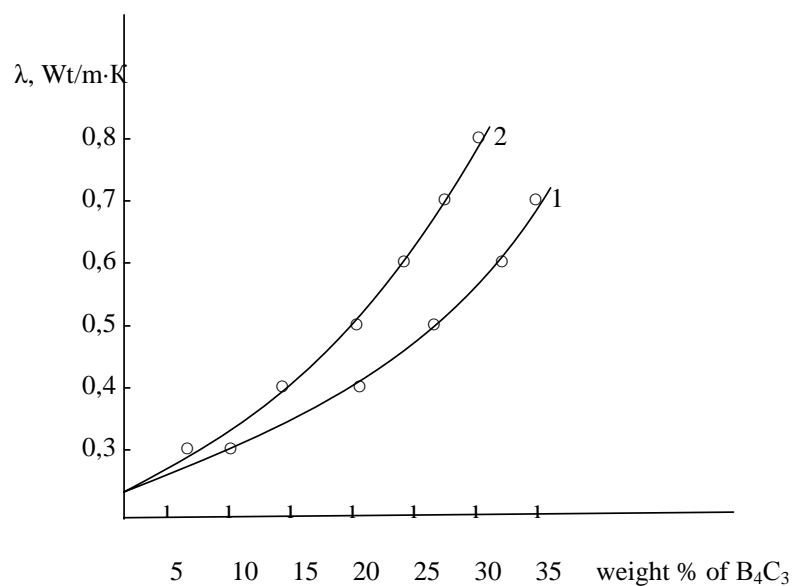


Fig. 2. The dependence of heat conductivity of epoxy new lacquer compositions upon the sizes of filler particles. 1 – (150-250) mcm; 2 – (20-150) mcm

Heat-resistance and dielectric properties of the compositions with highest heat conductivity were studied. The thermo gravimetric studies showed that samples without fillers decompose at $340\text{-}345^{\circ}\text{C}$ and samples with fillers – at $320\text{-}325^{\circ}\text{C}$.

During determination of dielectric constant ($\epsilon = 3,5\text{-}5,0$), tangent of angle of dielectric loss ($\text{tg}\delta = 0,02\text{-}0,03$), specific volume electrical resistance ($\rho = 10^{15} - 10^{17} \text{ Om}\cdot\text{cm}$) we came to the conclusion that nitride and carbide of boron do not deteriorate the electrical properties of compositions and they are useful for pressurization of semiconductor instruments of high reliability.

