

THERMAL CONDUCTIVITY AND KINETICS OF POLYMERIZATION OF AN ACRYLATE POLYMER COATING

A. P. Drin', V. V. Efanova, and
N. I. Shut

UDC 536.2:541.64

The formation of the thermal conductivity and other thermophysical characteristics of a polymerized protective coating on metal is investigated experimentally. Distinctive features of the experimental data are due to metastable structures in the polymer coating.

Thermal conductivity is an index of the heat transport and degree of structurization of the composite material in a polymer coating. The thermal conductivity of the polymer coating, having very low values, creates the potential for the destructive effect of high temperatures and especially a heat shock [1]. High values of thermal conductivity indicate a dense and perfect structure of a homogeneous material, sparse imperfections, a multichannel mechanism of conduction, etc.

Information on the thermal conductivity of a polymer coating is taken into account in developing the optimum composition and structure of the coating as well as during its use under prolonged exposure to elevated temperatures and aggressive media. As a rule, in this case the problem of enhancing heat transfer in the environment-coating-metal system by decreasing the coating thickness and increasing its thermal conductivity arises.

Incidentally, the possibility of expanding the informativeness of thermophysical measurements both by increasing the number of thermophysical characteristics (TPC), i.e., thermal conductivity, specific heat, etc., and by obtaining supplementary data on the investigated system in the form of kinetic characteristics, i.e., "lifetime," the maximum of the polymerization effect, hardening time, etc., arises.

It is pertinent to note that the improvement of the thermal conductivity of dielectric materials is a complex problem. High thermal conductivity and low electrical conductivity are, as a rule, mutually exclusive properties of materials [2] and only heat-conducting dielectrics with strong interatomic bonds, used as dispersed fillers of polymer compositions, are apparently capable of increasing the thermal conductivity with no substantial increase in the electrical conductivity of the composite material. In connection with these aspects of thermal conductivity problems of experimentally estimating of TPC of polymer coatings of different compositions and developing a procedure for thermophysical testing of polymer coatings in the technological process of their formation arise.

The thermophysical properties of polymer composite materials in thin coatings differ from the corresponding properties in bulk specimens owing to the limited dimensions in one direction and the action surface forces from the side of the coated material. Therefore it would be more correct to perform the experimental study of thermophysical properties of the material in the coating state, which is not a simple experimental problem. It is evident that a sensor of thermophysical properties should have dimensions commensurable with the coating thickness. This condition is satisfied by the absolute nonstationary heated-wire method (ANHWM).

The application of the ANHWM in this case can be realized by two ways. The first way is to use the sensor as a direct substrate. This very interesting and little studied way could give useful information on properties of the boundary layer which is largely responsible for the reliability of very thin coatings. However, the theory of the ANHWM is cumbersome and not totally clear for these conditions (small Fo numbers). In addition, application of

M. P. Dragomanov Kiev State Pedagogical Institute. Institute of New Physical and Applied Problems of the Academy of Sciences of Ukraine, Kiev. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 66, No. 2, pp. 184-191, February, 1994. Original article submitted May 18, 1992.

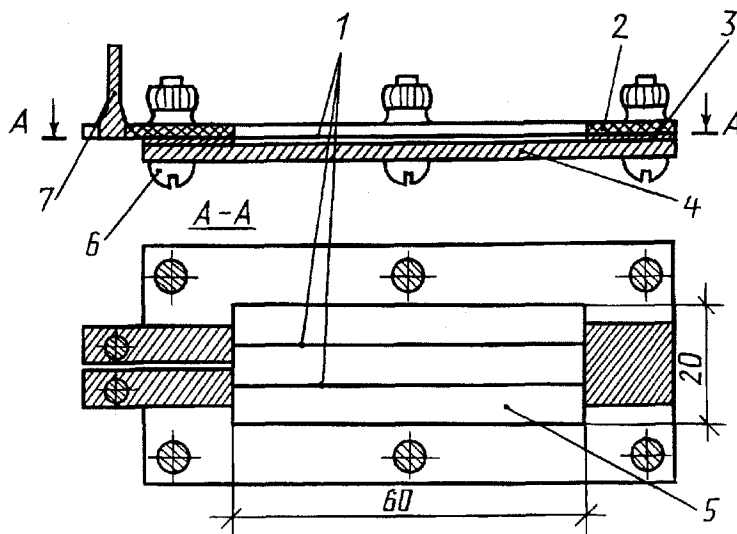


Fig. 1. Cell with a primary transducer of TPC for thermoprobe investigations of polymer coatings: 1) segments of a stretched microwire, 2) supporting frame of foiled glass-cloth-base laminate; 3) changeable sealing gasket-index of the microwire height; 4) substrate of the polymer coating (St 3 steel); 5) working volume of a filling specimen of a coating; 6) clamping screw with a nut.

uniform polymer coatings on superthin wires is a complex technological problem. The wire material does not always replace the material of an investigated substrate with a complex surface. More acceptable is the second way [3], involving the introduction of a fine sensor into the polymer coating and simulation of the required measurement conditions by varying the radius of probing the material a temperature field and selecting the correct measuring "window" of the signal-response.

Application of the ANHWM to measuring the TPC of polymer coatings is hampered by the following problems: 1) placement of the linear source inside the coating material; 2) brief and minimum effect on a rheologically complex polymer system and identification of the measuring signal-response against the background of the internal heat releases; 3) correct selection of the measuring time "window" of the probing thermal field, not distorted by the boundary conditions.

The first problem is solved by the developed design of the primary transducer of the TPC (Fig. 1). Two (or more) segments of nickel microwire 1 with diameter $50 \mu\text{m}$ and total length 120 mm, which are arranged in parallel and are connected in series, are slightly stretched inside the supporting frame 2 made of foiled glass-cloth-base laminate. The height of the microwire above the surface of the substrate 4 is set by the thickness of the sealing dielectric gasket 3. The three-layer stack (the substrate, the gasket, and the frame), tightened by screws 6, forms the flat airtight cell 5 with the dimensions $60 \times 20 \times 2$ mm, in which a polymer coating specimen with a microwire in the center is formed by filling a liquid composition.

To exclude the influence of external temperature effects, the measuring cell in a foam-plastic shell is placed in an ultrathermostat chamber. The specimen temperature is controlled with accuracy ± 0.01 K from the readings of decades of the comparison arm of a balanced bridge circuit. The measuring part of the experimental setup does not differ fundamentally from that described in [4, 5].

The second problem is solved by relatively rapid measurements as compared to the kinetics of heat releases in the reacting system. The minimal thermal effect on the object causes no noticeable violations of the natural course of the polymerization process.

The heating time for the microwire is 3.5 sec. The power of the wire source is 0.72 W. The total increase in the average temperature of the polymer system in the cell volume ($2.4 \times 10^{-6} \text{ m}^3$) in one act of thermoprobng did not exceed $\Delta T = P \tau / c \rho V = 0.35$ K. The minimum time between two consecutive measurements is 4-5 min.

For lengthy polymerization processes one may consider that measuring TPC by the given procedure are measured under isothermal conditions.

To solve the third problem, the working time interval for recording thermograms of heating the wire for calculating the TPC is selected within the limits $\tau_{\min} < \Delta\tau < \tau_{\max}$. The value of τ_{\min} is determined by: a sufficient depth of penetration of the nonstationary temperature field, at which it is possible to ignore thermal nonuniformities associated with the presence of the microwire; a thermal contact between the wire and the medium of finite dimensions; the heat capacity of the wire transducer; rapid operation of the recording equipment. The value of τ_{\max} is determined by: the necessary depth of penetration of the cylindrical temperature field, i.e., the half-thickness of the investigated coating; the permissible error from the nonuniformity of the temperature field caused by the thermal effect of the polymerization reaction.

The penetration depth r of the front of a cylindrical temperature wave emanating from a linear source localized inside a polymer coating can be calculated using the Blackwell equation

$$\Delta T(r, \tau) = -\frac{1}{4\pi} \text{Ei} \left(-\frac{1}{4 \text{Fo}} \right),$$

which for large Fo takes the form

$$\Delta T(r, \tau) = \frac{q_L}{4\pi\lambda} \ln \frac{4a\tau}{Cr^2},$$

where ΔT is the excess temperature at an arbitrary point at a distance r from the wire heater axis. On the temperature wave front $\Delta T = 0$ and

$$r = \frac{2}{\sqrt{C}} \sqrt{a\tau} \approx 1.50 \sqrt{a\tau},$$

where $C = e^\gamma$ ($\gamma = 0.5772$ is the Euler constant).

To obtain the kinetics of formation of the TPC of polyacrylate coatings 2×10^{-3} m thick, one can measure the excess temperature of the wire without fear of distortion of the field by the interface in the time interval up to

$$\tau_{\max} = \frac{r^2}{2.25a} = 5.5 \text{ sec},$$

taking into account that a for polyacrylates lies within $(4-8) \times 10^{-8}$ m²/sec.

The lower time boundary is, as a rule, limited by the lag of the recording instrument. In our variant it is the time in which the carriage of the recorder runs the entire scale, i.e., $\tau_{\min} = 1$ sec.

With due regard for other factors the experimental time "window" was 1.5-3.5 sec in practice. The depth of probing the polymer coating by the temperature field does not exceed $(4-9) \times 10^{-4}$ m, depending on the specimen thermal diffusivity.

The objects of the investigation were basalt-filled and nonfilled acrylate polymer compositions used as polymerization bonding bases for production of paintwork materials, glues, impregnating compounds, fittings, machine parts, and other purposes. The sphere of their applications is steadily expanding, including the field of protective polymer coatings.

The coating specimens were produced under laboratory conditions by batching, mixing, filling in, and subsequent polymerization of liquid components according to the following formula:

- Acrylate base 19 mass parts
- ATZh product 10 mass parts
- Paste of benzoyl peroxide in dimethylphthalate 6 mass parts
- Basalt plate filler 13 mass parts

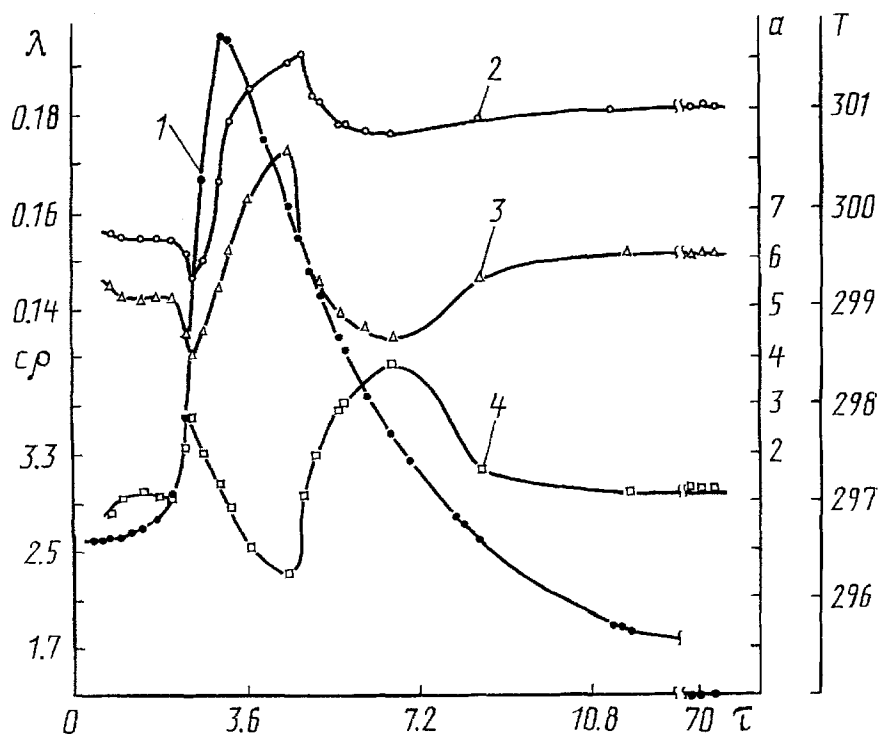


Fig. 2. Temperature (1) and TPC: thermal conductivity (2), thermal diffusivity (3) and volumetric specific heat at constant pressure (4) of an unfilled acrylate composition of a coating vs. polymerization time. T , K; λ , $W/(m \cdot K)$; c_p , $MJ/(m^3 \cdot K)$; a , $10^{-8} m^2/sec$; τ , $10^3 sec$.

In the experiments the acrylate base was a liquid mixture of reactive monomers and other starting reagents, capable of polymerization by opening of multiple bonds. The base of the composition is balanced according to general and special requirements for polymer coatings: wetting power, adhesion to the covered surface and cohesive strength, shrinkage, and heat resistance.

Polyacrylate coatings were produced by radical polymerization in the presence of a peroxide initiator in paste form. Benzoyl peroxide, easily decomposing into free radicals and noted for high efficiency of initiation of monomer molecules, served as the chemical initiator of polymerization.

The ATZh modifier – the product of interaction of allyl alcohol with toluilin-diisocyanate – was used as an active plasticizer, fixed in the network of the forming polymer.

A fused basalt powder with a silver tint, which was added to it by colorless transparent particles of plate form, was used as a filler. The plate particle dimensions were characterized by a high ratio of the average diameter $d = (0.25-0.5) \times 10^{-3} m$ to the thickness, which attained 150. The choice of the filler was dictated by strong reinforcement of the polymer coating caused by overlapping of plates in the flow plane of filling.

Figure 2 gives results of measuring the TPC of an unfilled acrylate polymer coating in its polymerization on a steel substrate according to the data of the ANHWM.

As the figure shows, variations of the polymerized coating temperature have a distinct extremum character, indicating the exothermicity of the polymerization reaction. The fixed temperature maximum is shifted in time to the right, i.e., there are practically no heat releases in the reaction mixture of the coating for 35 min. The shape of the maximum is asymmetric: the left ascending branch is much sharper than the right descending branch. The maximum rate of heat releases is observed 45 min after initiation of the reaction. The temperature maximum comes at 55 min, the superheating attaining 5.2 K at room temperature.

The thermal conductivity of the acrylate coating as a whole increases in polymerization from 0.155 $W/(m \cdot K)$, characteristic of a mixture of liquid components, to 0.182 $W/(m \cdot K)$ for a solid composition. The thermal conductivity jump is 17%.

TABLE 1. Thermophysical and Kinetic Characteristics of Coatings Hardened at Room Temperature

Composition	λ , W/(m·K)	$a \cdot 10^8$, m ² /sec	c_p , MJ/(m ³ ·K)	$\tau_{\text{life}} \cdot 10^{-3}$, sec	$\tau_{\text{max}} \cdot 10^{-3}$, sec	$\tau_s \cdot 10^{-3}$, sec
Unfilled	0.155	6.1	2.98	2.10	3.20	10.80
Basalt-filled	0.182	10.2	1.98	2.10	3.05	6.60

In the initial (under 35 min) and final (at ~3 h) periods the thermal conductivity of the composition is constant in time. The most intensive increase in the thermal conductivity and, hence, acceleration of the polymerization process are observed in the region of the exothermal maximum of the coating temperature (42–78 min).

In the time regions corresponding to the increase and decrease in the coating temperature, on the kinetic curve of variation of the thermal conductivity wavelike bends are observed, which indicate the metastability of the formed structure of the polymer composition and the corresponding character of the heat transfer in it [6].

Variations in the thermal diffusivity a of the polymerized coating qualitatively mirror the distinctive features of the behavior of the thermal conductivity, i.e., are similar to the variations of λ . Variations of the volumetric specific heat c_p are opposite to the variations of λ and a .

Attention is drawn to the insignificant overall increase in a in polymerization of the acrylate coating (13%) and to the practically constant value of the volumetric specific heat c_p , which is due to the relatively equal increase in λ and a .

Analysis of the sequence of structurization in exothermal reactions of cold self-hardening of protective polymer coatings as compared to kinetic effects in the TPC curves permits identification of the following five periods:

The first period (0–35 min) is an induction one or a "lifetime" period of the composition, which is characterized by relatively stable TPC and a constant temperature. The duration of this period determines the gelation time [7], and the final moment determines the gelation point (gel-point).

The second period (35–41 min) is a relatively short interval, characterized by a sharp and insignificant decrease of λ and a and the same increase of c_p . Variations of the TPC in this period indicate the disordering of the formed structure of the liquid mixture components and increased molecular mobility of its elements: the old structure "cracks," increasing its thermal resistance, and "is destroyed," increasing its heat capacity and decreasing the thermal diffusivity in the overall process of breaking of weak bonds. Formation of a friable "supercooled" metaphase-1 occurs. The increased temperature in this period is a result of an increasingly predominant exoeffect of the polymerization reaction; the "destruction" endotherm does not appear here.

The third period (41–79 min) is the main one, with a sharp initial increase and final significant increase, tending to saturation, of λ and a and the same decrease of c_p . This period corresponds to an interval of elevated temperatures with a maximum, the branch of increasing temperature corresponding to a drastic change in the TPC and the branch of decreasing temperature corresponding to a slower rate of change of the TPC.

The third period is followed by a sudden decrease of λ and a and increase of c_p (inversion of properties), which indicates the process of formation of a considerable number of unstable random bonds of a dense "superheated" metaphase-2 in the third period and their destruction in the subsequent fourth period. The third period of polymerization is a period of rapid growth and cross-linking of polymeric chains of the acrylate coating and their conversion into a three-dimensional molecular network, which penetrates the entire volume of the reaction mixture. In this period the process of polymerization usually develops with self-acceleration due to the gel-effect and abruptly ceases as a result of the breakoff of growing chains or a drastic decrease in their mobility. The initial friable metaphase-1 disappears.

The increase of λ and the corresponding variation of other TPC in the third period are apparently related to a change in the heat conduction. The "relay-race" mechanism of transmission of translational, rotational, and vibrational thermal motion of liquid molecules in the reaction mixture of the coating gives way to a phonon mechanism of transmission of the growing three-dimensional network of molecular bonds.

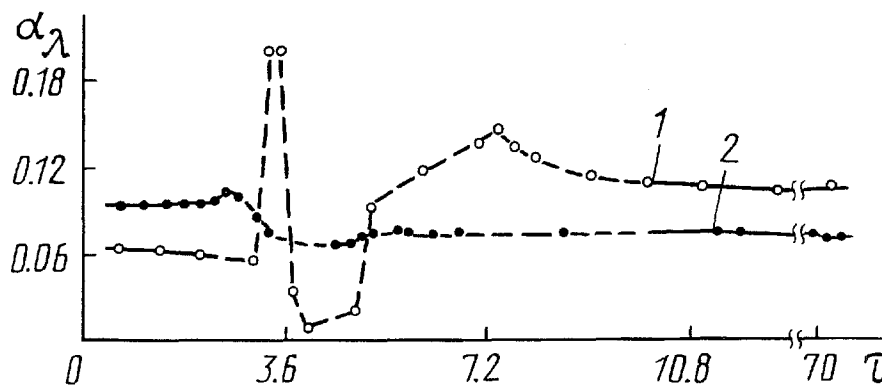


Fig. 3. Relative index of change in the thermal conductivity in filling of an acrylate polymer coating vs. its polymerization time: 1) experimental data; 2) calculation by the additivity rule. α_λ , rel. units.

The fourth period (79-110 min) is the breaking of the system of random bonds of the metaphase-2 with decreasing temperature. A regular structural process, corresponding to the process of crystal melting, occurs: λ and α decrease and c_p increases.

The fifth period (110–180 min and more up to the limiting stages of polymerization) is the final period; it is characterized by insignificant variations of the TPC in the form of saturation curves, which mirror the special features of the third, main period but on a smaller scale: there is a long process of eventual polymerization, increasing the fraction of the three-dimensional network, due to conversion of unreacted initial components.

The kinetics of formation of the TPC of the basalt-filled coating composition retains the general character of the change in temperature and TPC. The basalt plate filler noticeably increases the thermal diffusivity of the hardened protective coating, by 9% on average. The thermal diffusivity of the filled composition is 49% higher and the volumetric specific heat at constant pressure is 37% lower compared to the unfilled one.

The shape of the kinetic curves indicates the reduced kinetics of polymerization exoeffects upon introduction of the basalt filler. The thermophysical and kinetic characteristics of polymerization of the acrylate coatings are given in Table 1, from which it is seen that the basalt filler not only increases the transport properties of the composition but also reduces the time of the exothermal reaction of polymerization. The gelation time for the composition does not depend on filling.

Thus, when producing filled coatings with specified TPC, the TPC of the fillers and their influence on the kinetics of the polymerization reaction should be taken into account.

To estimate the efficiency of improvement of the thermal conductivity of a polymeric coating by filling, we calculated the relative index of change in the thermal conductivity:

$$\alpha_\lambda(\tau) = \frac{\lambda_f(\tau) - \lambda_0(\tau)}{\lambda_0(\tau)},$$

where $\lambda_f(\tau)$ and $\lambda_0(\tau)$ are the current values of the thermal conductivity of the basalt-filled and unfilled compositions.

Variations of α_λ in the polymerization process (Fig. 3) indicate moderately low and constant values of α_λ in the periods of existence of equilibrium structures (6 and 11% in the induction period and in the period of eventual polymerization respectively). In the periods of generation and destruction of nonequilibrium structures α_λ undergoes profound and manifold variations, maintaining a positive value.

The expected significant increase in the thermal conductivity of the polymer composite material of the coating is apparently not observed; 11.5 mass parts of the basalt filler yields the 6–11% increase in the thermal conductivity of the composition, which can be attributed mainly to the additive contribution of the thermal conductivity of the filler.

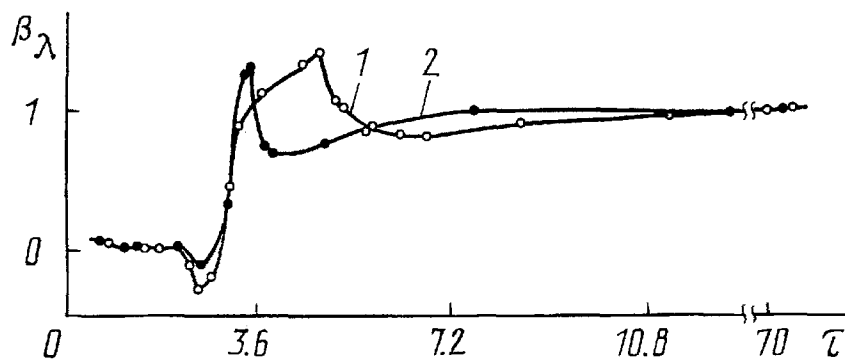


Fig. 4. "Heat-conducting" fractional conversions of the reaction of polymerization of the acrylate coating vs. polymerization time τ : 1) unfilled composition; 2) basalt-filled composition. β_λ , rel. units.

In the initial periods of polymerization, when the reactive mixture is still a liquid system, the index of increase of the thermal conductivity α_λ is lower than the one expected from the property of additivity. In the final period of polymerization, on the contrary, α_λ is higher than the expected one, which indicates the nonadditive character of the thermal conductivity, which is associated with a change in the thermal resistance of the filler boundary layer. The thermal resistance of the boundary layer apparently decreases with polymerization, under the action of the compacted polymerized matrix.

To estimate the influence of a filler on the kinetics of the polymerization reaction, we calculated the conventional "heat-conducting" fractional conversion of the reaction [8], also changing in the process of polymerization:

$$\beta_\lambda(\tau) = \frac{\lambda(\tau) - \lambda_0}{\lambda_e - \lambda_0}.$$

The characteristic curves for the two systems (filled and unfilled) are given in Fig. 4. It shows that the "heat-conducting" fractional conversion of the reaction of radical polymerization of the acrylate coating qualitatively mirrors the kinetics of the change in thermal conductivity, going beyond the threshold limits of its change ($0 < \beta_\lambda < 1$) in the periods when metastable phases exist. The average lifetime determined by the time of this passage is 12 min for the "supercooled" friable metaphase-1 and 30 min for the "superheated" dense metaphase-2.

Apparently, plate particles of dispersed fused basalt, playing the role of heterogeneous nuclei of elementary polymerization reactions (similarly to nucleation centers), contribute to the initiation of monomer molecules and drastically decrease the lifetime of metaphase-2 (by 4 times) and metaphase-1 (by 1.5 times).

Consequently, one would expect that thorough purification of the reaction mixture from foreign impurities and careful probing at a sufficiently low rate of the reaction of radical polymerization will contribute to a clearer manifestation of the observed effects of metastability. One can also assume that creating conditions that inhibit the observed metastability effects is one of the reserves for improving the quality of protective polymeric coatings.

NOTATION

λ , a , c , ρ , thermal conductivity, W/(m·K), thermal diffusivity, m²/sec, specific heat at constant pressure, J/(kg·K), density, kg/m³, of a polymeric coating; Fo, Fourier number; Ei, Euler function; r , spatial coordinate, m; τ , current time; q_L , power of a unit length of the wire source, W/m; $C = e^\gamma$, where $\gamma = 0.5772$ is the Euler constant; T , ΔT , absolute and excess temperatures, K; α_λ , relative index of change in the thermal conductivity of the polymer composition in filling; $\lambda_f(\tau)$ and $\lambda_0(\tau)$, current values of the thermal conductivity of the filled and unfilled compositions; $\beta_\lambda(\tau)$, "heat-conducting" fractional conversion of a reaction; λ_0 and λ_e , initial and equilibrium thermal conductivities of a polymer coating; τ_{life} , lifetime (gelation point), sec; τ_{max} , time of the maximum of the polymerization exoeffect, sec; τ_s , polymerization time, sec.

REFERENCES

1. A. P. Drin', A. V. Kasperskii, and O. S. Svechnikova, Abstracts of Papers of the Scientific-Technical Conference "Generalization of Experience and Development of Prospects for Applying Polymer Composite Materials in Constructions Intended for Shipbuilding and Related Branches" [in Russian], Leningrad (1990), pp. 112-114.
2. A. P. Drin', M. A. Sokolinskaya, and N. I. Shut, Sixth Republican Conference on High-Molecular Compounds: Abstracts of Papers [in Russian], Kiev (1988), pp. 75-76.
3. N. I. Shut, T. G. Sychkar, A. P. Drin', and V. P. Dushchenko, *Acta Polymerica*, **38**, No. 7, 446-449 (1987).
4. A. P. Drin' and N. I. Shut, *Inzh.-Fiz. Zh.*, **60**, No. 2, 284-291 (1991).
5. A. P. Drin', V. P. Dushchenko, T. G. Sychkar, and N. I. Shut, Processes of Heat and Material Transfer [in Russian], Kiev (1985), pp. 51-60.
6. A. P. Drin', A. V. Kasperskii, P. V. Berezhnoi, et al., Abstracts of Papers of the All-Union School-Seminar "News on Properties and Relaxation Phenomena for Processing and Development of Polymer Materials" [in Russian], Moscow (1991), p. 10.
7. L. A. Shits, "Gelation," in: *Encyclopedia of Polymers* [in Russian], Vol. 1, Moscow (1972), pp. 594-596.
8. Yu. S. Kargopolov, *Vysokomol. Soed.*, B, **33**, No. 6, 410-412 (1991).