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THERMOPHYSICAL CHARACTERISTICS OF POLYMER COATINGS

L. A. Sukhareva, V. A. Voronkov, and P. I. Zubov

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The correlation between internal stresses and thermal properties of coatings based on polyester resins is established. It is shown that the thermophysical characteristics and the internal stresses change in opposite directions both in the process of formation and as a function of coating thickness.

In previous papers it was established that the internal stresses that develop in polymer films coated onto a rigid backing exert a considerable influence on the mechanical and adhesion properties of the films and, in a number of cases, determine their durability [1]. We postulated that the internal stresses should also affect other physicochemical properties of the coatings, in particular, their thermophysical properties. The work described is an experimental verification of this hypothesis.

The thermal characteristics of the polymer films were determined by the method of nonstationary heat flux with instantaneous heat source [2, 3]. It is a feature of this method that it makes possible a determination of all the thermophysical characteristics of a polymer film from one experiment.

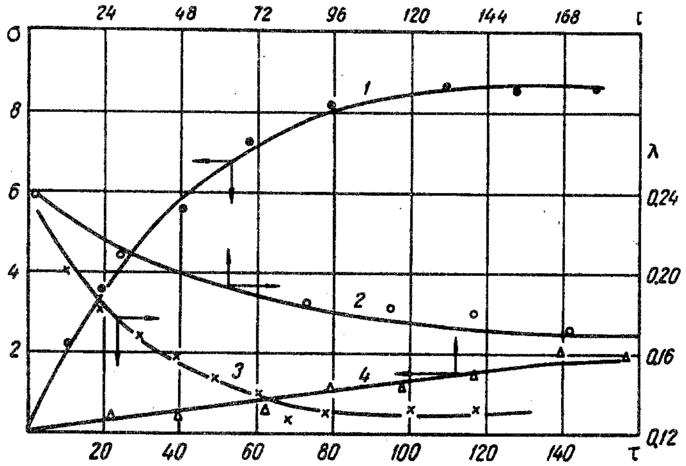

Fig. 1. Kinetics of change in heat conductivity ($\lambda \cdot 1.163^{-1}$, W/m · deg) and buildup of internal stresses ($\sigma \cdot 0.1^{-1}$, milli-Newton/m^2) during formation of polyester coatings 350 μ thick at 20–2, 4 and at 80° C–3, 1.

The feasibility of using this method for studying the thermophysical characteristics of polymer coatings is governed by the fact that the duration of the heat pulse is two seconds. The prolonged action of heat in the presence of a temperature gradient causes redistribution of the solvent and additional curing of the sample during the experiment. The test samples were films and coatings based on PN-1 polyester resin from 200 to 1500 μ thick. The method of preparation of the samples was as follows. Free films measuring 50 × 50 mm were prepared on fluoroplastic. Coatings were formed on a copper substrate. The samples were cured at temperatures of 20° and 80° C. As a standard, we took a filled rubber with thermophysical characteristics close to those of the resin films.

The test samples were placed between reference calorimeters with known thermal conductivity and diffusivity. The heater was placed in the lower part of the standard 3.0–3.5 mm away from the test material.

The thermal coefficients of the standard were determined by the same method. The pulse was supplied by a flat electrical heater made of permalloy 0.2 mm thick. Temperature measurements were made with a chromel-copel thermocouple with thermoelectrodes 0.2 mm in diameter mounted in the upper plate of the standard close to the boundary with the coating. The thermocouple was connected to a mirror galvanometer and calibrated. The heat pulse was created by connecting the heater with the power supply across a stepdown transformer and an electronic timer controlled by a magnetic starter [3]. Current was passed for 2.5–3 sec.

The quantity of heat released on passage of the electric current through the heater was determined by means of the timer, electric clock, voltmeter, ammeter, and wattmeter. The power of the heat pulse was 9.12 W. The distance from the heater to the hot junction of the thermocouple varied from 3.5–4.5 mm depending on the thickness of the sample. When this distance was increased to over 5 mm, the heating time increased sharply.

Table 1

Thermophysical Characteristics Measured by Different Methods

Sample	t, °C	ρ, kg/m^3	λ/1.163, W/m·deg	a/277.78 × × 10^{-2}, m^2/sec	Source
Distilled water	20 20	— —	0.489 0.515	4.92 5.10	[5]
Quartz sand (dry)	20 20	1500 1500	0.264 0.265	2.58 —	[7]
Rubber	20 0	1200 1200	0.160 0.140	3.43 3.50	[8]
Plastic based on PN-1 resin	20 20	1300 1300	0.158 0.150	3.85 3.85	[4]

The thermophysical coefficients were calculated from formulas obtained on the basis of a solution of the problem with an instantaneous heat source for an unsymmetrical system of solids with different thermophysical coefficients in thermal contact [3].

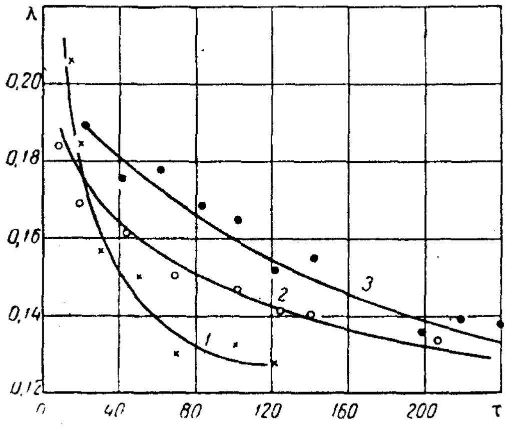

Fig. 2. Kinetics of change in thermal conductivity ($\lambda \cdot 1.163^{-1}$, W/m · deg) during formation of polyester films of different thickness at 80° C: 1) 4000 microns; 2) 1200; 3) 1600.

The accuracy of the device for thin samples was estimated using distilled water, quartz sand, and rubber as standard materials with thermophysical parameters closest to plastics based on polyester resins, and films of PN-1 resin [4]. Comparative data determined by the instantaneous heat source method on samples less than 1 mm thick, by the steady-state method [5], and by the dynamic heating method [4, 6] are given in Table 1. It is seen that for all the materials tested the heat transfer coefficients and thermal conductivities determined by the instantaneous heat source method on thin samples conform with the literature data to within 5%.

It should be noted that for samples consisting of polymer plates more than 5 mm thick the thermophysical characteristics are unstable, changing even after 200 hr of curing at 80° C. This phenomenon was apparently connected with nonuniform polymerization over the thickness and surface of the plates [9] and the complex stress state of the samples [10].

Figure 1 shows kinetic data on the variation of heat conductivity and internal stresses in the process of formation of coatings at different temperatures. It is seen that the heat conductivity and buildup in internal stresses* have opposite trends and depend on the conditions of formation of the coating. Thus, for coatings cured at 80° C the heat conductivity, like the internal stresses, attains a (minimum) limiting value after 1.5 hr, and at 20° C after 160 hr. The final value of the heat conductivity, like the internal stresses, also depends on the conditions of formation of the coating.

A considerable influence on the rate of the thermophysical characteristics of coatings and free films during the formation process is exerted by their thickness.

Table 2

Change in Thermophysical Characteristics During Formation of Films

Curing time, min	$a \cdot 10^{-4}$, m^2/hr	c/4186.8 J/kg · deg
20	2.85	0.58
30	2.80	0.50
40	2.60	0.49
60	2.20	0.48
80	2.00	0.47
100	2.00	0.47
120	2.00	0.47

Here we give values of the thicknesses for completely cured polyester resin films and coatings. Shrinkage of films

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* Internal stresses were determined by an optical method using an automatic recording device [11].

during formation was 8–10%, and was taken into consideration in obtaining kinetic data on the change in the thermal coefficients during the formation process.

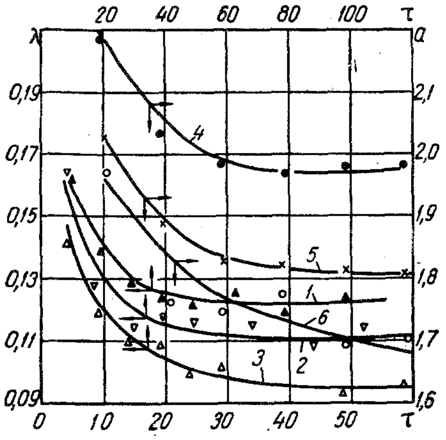

Fig. 3. Kinetics of change in thermal conductivity ($\lambda \cdot 1.163^{-}$, W/m · deg) and thermal diffusivity ($a \cdot 2.7778^{-1}$, m^2/sec) of polyester coatings of different thickness formed at 80°C: 1, 4) 60 μ; 2, 5) 200; 3, 6) 350.

Figure 2 shows data on the change of heat conductivity of free films of different thickness (from 400 to 1600 μ) cured at 80° C. It is seen that, with increase in the thickness of the film, the time to attain the limiting value of the heat conductivity increases sharply, but the final value does not change.

Table 2 gives data on the change of other thermophysical characteristics (thermal diffusivity and heat capacity) for polyester resin films cured at 80° C.

The situation is different for coatings, formation of which is accompanied by a buildup of internal stresses. In this case, with growth in coating thickness, not only the time to attain the limiting value of the thermal coefficients, but also their absolute value changes.

Figure 3 gives data on changes in the heat conductivity and thermal diffusivity of polyester coatings of different thickness formed at 80° C on a copper substrate. It is seen that increasing the thickness increases the time to attain the limiting values of the coefficients and sharply decreases their absolute value. Analogous conclusions apply to the other thermophysical characteristics, in particular, the heat capacity.

It should be noted that the data on the kinetics of change in thermophysical characteristics during formation of coatings correlate with the kinetics of the buildup of internal stresses during curing of polyester coatings of different thickness [11].

The magnitude of the thermophysical characteristics of polyester coatings, conditions of formation, but also on the film thickness.

Figure 4 gives the dependence of the thermophysical characteristics and internal stresses on the thickness of the coatings and free films. It is seen that the thermophysical characteristics of free films do not depend on thickness. Other laws apply to supported coatings. As may be seen from Fig. 4, with increase in thickness a nonmonotonic change in thermophysical characteristics is observed. Initially, with increase in thickness, they decrease linearly, but then after the beginning of spontaneous peeling of the film, they begin to increase. Upon complete peeling, the thermophysical characteristics of the coatings and free films become the same.

From the data presented, it follows that the change in thermophysical characteristics with thickness is opposite to that of the internal stresses.

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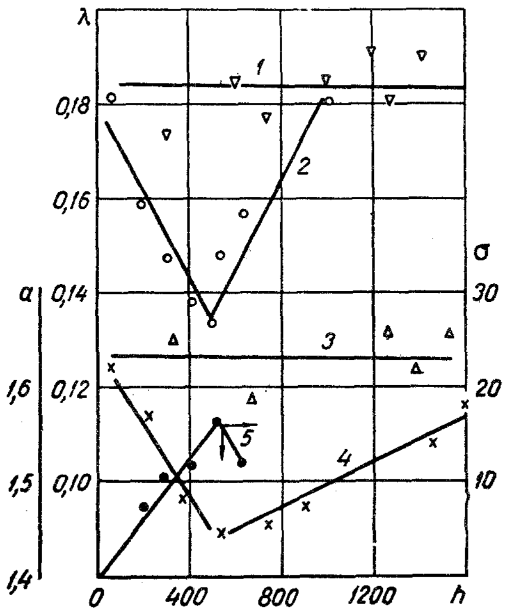

Fig. 4. Thermophysical characteristics and internal stresses as a function of thickness for polyester coatings (2, 4, 5) and free films (1, 3).

We assume that the influence of thickness on the thermophysical properties of polymer coatings is connected with an orientation effect, determined by the magnitude of the internal stresses that develop in the coatings during their formation. A significant reduction in the thermophysical characteristics of polymer materials stretched in a direction perpendicular to the direction of heat flow was observed by other investigators [12, 13].

REFERENCES

1. P. I. Zubov, L. A. Sukhareva, and Yu. P. Smirnova, DAN SSSR, 150, no. 2, 1963.
2. A. V. Lykov, Theory of Heat Transfer [in Russian], GITTL, 1952.
3. M. V. Kulakov, collection: Heat and Mass Transfer [in Russian], 1, 1962.
4. V. S. Bil and N. D. Avtokratova, Teplofizika Vysokikh temperatur, no. 2, 1964.
5. M. A. Mikheev, Fundamentals of Heat Transfer [in Russian], Gosenergoizdat, 1949.
6. N. S. Platunov, Izv. VUZ. Priborostroenie, no. 4, 1961.

7. O. Krisher, Scientific Basis of Drying Technology [Russian translation], IL, 1961.
8. M. M. Goland, Design and Testing of Thermal Insulation [in Russian], Gostekhizdat, 1961.
9. A. T. Lomakin, A. T. Sanzharovskii, and P. I. Zubov, Lakokrasochnye materialy i ikh primenenie, 5, 1964.
10. R. De Waard, R. Stock, and T. J. Alfrey, ASTM Bulletin, 55, 53, 1952.
11. P. I. Zubov and L. A. Lepilkina, Vestnik AN SSSR, 3, 39, 1962.
12. Yu. A. Kirichenko, B. N. Oleinik, and T. Z. Chadovich, IFKh, no. 5, 1964.
13. K. Eiermann, Kunststoffe, 51, 512, 1961.

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Institute of Physical Chemistry, AS USSR, Moscow