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EFFECTS OF RADIATION ON THERMAL CONDUCTIVITY OF SOME POLYMER RESINS

B. A. Briskman and S. I. Rozman

UDC 678.742:046

A study was made concerning the effect of radiation on the thermal conductivity of grade VK-9 adhesive (consisting of epoxy and polyamide resins) and of a "Kriosil" compound based on silicone resin.

A study was made to determine the effect of radiation on the thermal conductivity λ of the grade VK-9 polymer adhesive and the "Kriosil" compound. The former is a compound of grade ÉD-20 epoxy resin (60 wt.%) and grade PO-300 polyamide resin (40 wt.%). The initial density of this polymer is 1.04 g/cm^3 at 20°C. The "Kriosil" compound consists of grade DFMK$_r$ silicone resin (45 wt.%), grade L-20 low-molecular-weight polyamine (25 wt.%), boron nitride, and Aerosil. The density of this material is 1.20 g/cm^3.

Method of Irradiation and Thermal Conductivity Measurement. Test specimens of these materials were produced in the form of disks 15 mm in diameter and 1.5-2.5-mm thick. They were irradiated in air with γ quanta in doses up to 0.01 and 1 MGy from a ^{60}Co source (dose power 3 Gy/sec) as well as with mixed γ-neutron flux in doses to 1, 3, 10, and 20 MGy from a nuclear reactor (dose power 11 Gy/sec). The irradiation temperature was 30°C for the ^{60}Co source and 50°C for the reactor channel.

In order to check for the possibility of radiation effects depending on the kind of radiation, irradiation in the reactor to 1 and 3 MGy was effected in core channels where fast neutrons m amounted to 50-60% of the dose absorbed by polyethylene, Irradiation to doses of 10 and 20 MGy was effected in reflector channels with m $\sim$ 5%.

The thermal conductivity was measured with model IT-λ-400 instruments operating in the mode of monotonic heating at a rate of approximately 6°C/min, at temperatures from −100 to +180°C for the VK-9 adhesive and from −110 to +220°C for the Kriosil. The systematic error of measurements was 4-6%; the reproducibility of results was within 3%.

Grade VK-9 Adhesive. The thermal conductivity of grade VK-9 adhesive, based on the results of this study, is shown in Fig. 1 as a function of the temperature and in Fig. 2 as a

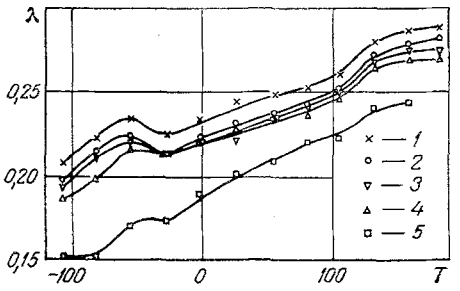

Fig. 1

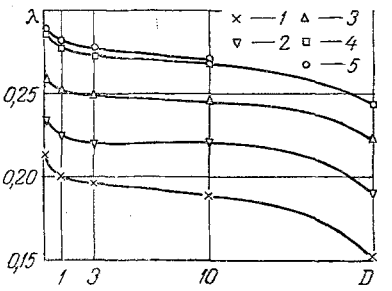

Fig. 2

Fig. 1. Temperature dependence of the thermal conductivity of grade VK-9 adhesive: λ (W/m·K), T (°C), with irradiation dose as parameter: 1) 0; 2) 1; 3) 3; 4) 10; 5) 20 MGy.

Fig. 2. Dependence of the thermal conductivity of grade VK-9 adhesive on the absorbed radiation dose, λ (W/m·K), D (MGy), with test temperature as parameter: 1) −100; 2) 0; 3) 100; 4) 150; 5) 180°C.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 42, No. 3, pp. 448-453, March, 1982. Original article submitted September 30, 1980.

0022-0841/82/4203-0327$07.50

function of the absorbed radiation dose. As the temperature increases from −100 to +180°C, the thermal conductivity λ increases by 40-45%. It decreases as the absorbed radiation dose increases to 20 MGy, with the magnitude of the decrement of λ increasing with lower temperatures from 14% at 150°C to 28% at −100°C. At temperatures above 158°C the thermal conductivity of the specimen with a 20 MGy irradiation dose was not measured, because of softening of the material.

On the λ = f(T) curves there appears a peak at −54°C, its magnitude gradually decreasing with increasing irradiation dose and disappearing completely at D = 20 MGy. With the relative magnitude of this peak characterized by the ratio $\Delta = \lambda_{-54}/\lambda_{-27}$ of λ at the temperatures −54 and −27°C, respectively, as a function of the absorbed radiation dose, the dependence of this ratio on that dose is approximately linear:

D, MGy	0	1	3	10	20
Δ	1.040	1.048	1,030	1,015	0,975

It is to be noted here that the maximum at −54°C (or the minimum at −27°C) is expressible in a more sharply defined form, inasmuch as the values of λ given here are mean-integral ones over the $T_1 - T_2$ temperature interval at specimen end surfaces

$$\bar{\lambda} = \frac{\int_{T_1}^{T_2} \lambda(t)\, dt}{T_1 - T_2}, \qquad (1)$$

where the difference $T_1 - T_2$ reaches 50°C.

The radiation effects on the thermal conductivity of grade VK-9 adhesive were found not to depend on the kind of radiation. This can be deduced from the fact that the variance between λ values for specimens irradiated with gamma quanta from the ^{60}Co source and for specimens exposed to the mixture of γ-neutron radiation from the reactor in doses up to 1 MGy does not exceed 5%, which is within the limits of measurement error including the spread of λ values from one specimen to another.

It is now universally recognized that changes in the thermophysical properties of polymers due to radiation are determined by radiative macroeffects: 1) in partially crystalline polymers radiation-induced change in the degree of crystalline, viz., amorphization or much more rarely an increase of crystallinity, play the major role; 2) in amorphous polymers the predominance of radiative crosslinkage of polymer chains or radiative breakdown in the case of a sufficiently high radiative-chemical yield of these processes [1-6] plays the major role. Owing to the large difference between the thermal conductivity of the crystalline phase (λ_c) and that of the amorphous phase (λ_a) (viz. $\lambda_c > \lambda_a$, because the mean free path for phonons is longer in crystals than in amorphous material), a decrease of crystallinity x results in a lower thermal conductivity λ of the polymer. Crosslinkage results in a denser packing of molecular chains or, which is equivalent, a larger number of thermal bridges. As a consequence, the effective mean free path for phonons becomes longer and thus λ increases. Breakdown of the polymer has the opposite effect on its thermal conductivity λ.

With data on the change in crystallinity as a result of irradiation available, it is possible to interpret the trend of λ in each component of a two-phase system [7]. Most applicable to our case has been found the Maxwell—Euken relation

$$\lambda = \frac{2\lambda_a + \lambda_c + 2\gamma(\lambda_c - \lambda_a)}{2\lambda_a + \lambda_c - \gamma(\lambda_c - \lambda_a)}\,\lambda_a, \qquad (2)$$

where γ is the volume fraction of crystallinity.

The grade VK-9 compound constitutes a two-component three-phase system of amorphous epoxy resin and partially crystalline polyamide resin. Data on the thermal conductivity of polyamide resin grades PW-6, PW-6,6, PW-6,10 (trade names "Ultramid" B3M, A3, S3 respectively) are given in [8]. In that reference are also given data on λ_c and λ_a as functions of the temperature. The ratio λ_c/λ_a varies from 2.0 at − 100°C to 1.68 at +50°C.

In order to establish which mechanism determines the lowering of the thermal conductivity of the compound, amorphization of polyamide resin or breakdown of either one or both resins,

TABLE 1. Change in Thermal Conductivity of Grade VK-9 Compound: Calculations and Experiment

T, °C	λ_a/λ	ε_λ	$1-\lambda/\lambda_0$, D=10 MGy	$1-\lambda/\lambda_0$, D=20 MGy
—100	0,69	0,124	0,105	0,281
— 50	0,74	0,104	0,077	0,265
0	0,76	0,096	0,064	0,188
+ 50	0,76	0,096	0,060	0,165
+100	0,74	0,104	0,050	0,132

TABLE 2. Calculated Changes in the Density of Grade VK-9 Compound

Polyamide	x	ρ_a, g/cm^3	ρ_c, g/cm^3	ρ, g/cm^3	ρ_a/ρ	ε_ρ, %
PW-6	0,36	1,10	1,23	1,147	0,959	1,64
PW-6,6	0,47	1,069	1,24	1,149	0,930	2,80
PW-6,10	0,46	1,041	1,151	1,094	0,952	1,92

we have made the following estimates. For grade PW-6,6 polyamide with an initial crystallinity $\mathbf{x} = 0.47$ we calculated, according to relation (2), the total thermal conductivity as well as the ratio λ_a/λ. The difference $1 - \lambda_a/\lambda$ represented then the maximum relative decrement of λ in the resin due to complete amorphization. Analogously

$$\varepsilon_\lambda = (1 - \lambda_a/\lambda)\,\mathbf{r},$$

with $\mathbf{r} = 0.4$ denoting the mass fraction of polyamide in the compound and ε_λ denoting the maximum relative decrement of λ in the compound due to complete amorphization of polyamide.

The results of these calculations are given in Table 1. Here in columns 4 and 5 appear the relative changes $1 - \lambda/\lambda_0$ due to respectively 10- and 20-MGy doses of radiation, λ_0 denoting the thermal conductivity of nonirradiated specimens.

According to the data in Table 1, the experimentally recorded change in λ of grade VK-9 compound due to irradiation with a 20-MGy dose is 1.3-2.3 times larger than a change which could be due to complete amorphization of polyamide. Not having available any data on the degree of crystallinity in irradiated polyamide, we used the data in [8] on the density of the amorphous phase (ρ_a) and of the crystalline phase (ρ_c) for three grades of the polymer for calculating its density ρ

$$\rho = \mathbf{x}\rho_c + (1 - \mathbf{x})\,\rho_a \qquad (3)$$

and the ratio ρ_a/ρ at 20°C. Just as in the case of thermal conductivity, we then determined the quantity

$$\varepsilon_\rho = (1 - \rho_a/\rho)\,\mathbf{r},$$

corresponding to the change in the density of the compound due to complete amorphization of the polyamide. The results are given in Table 2.

Accordingly, the density of grade VK-9 compound should have decreased by 1.5-3%. The density values obtained by measurement at 20°C do not correlate with the irradiation doses. Their spread does not exceed 1-1.5% up to the 20 MGy dose. Therefore, evidently, the amorphization process has not been completed even under that dose of 20 MGy.

One can only conclude that an appreciable part of the change in the thermal conductivity of grade VK-9 compound under irradiation is due to breakdown of this compound. The question as to whether both resins break down or only one of them does cannot be answered without additional data.

According to the data in Fig. 2 and Table 1, the thermal conductivity of grade VK-9 compound changes much more at low temperatures than at high ones (the change of λ is twice as large at — 100°C than at 150°C). One possible explanation could be based on the large dif-

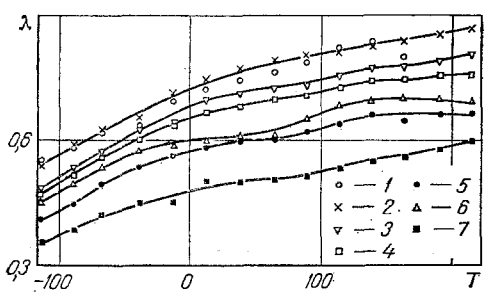

Fig. 3

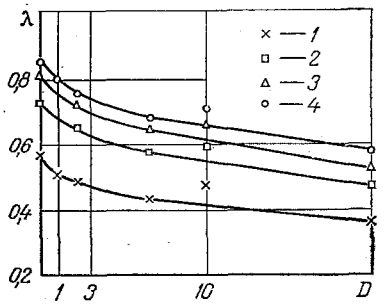

Fig. 4

Fig. 3. Temperature dependence of the thermal conductivity of Kriosil, with irradiation dose as parameter: 1) 0; 2) 0.01; 3) 1; 4) 2.2; 5) 6.6; 6) 10; 7) 20 MGy.

Fig. 4. Dependence of the thermal conductivity of Kriosil on the absorbed radiation dose, with test temperature as parameter: 1) 100; 2) 0; 3) 100; 200°C.

ference between λ_c and λ_a of polyamide and between the trends of their temperature dependence. While λ_c obeys the well-known relation $\lambda_c \sim 1/T$ derived by Euken for low-molecular-weight crystals, λ_a increases with rising temperature up to the glass transition point and then slowly decreases. Naturally, amorphization of polyamide should affect the thermal conductivity of the compound stronger at low temperature (where the difference $\lambda_c - \lambda_a$ is large), although on the basis of absolute values it is hard, according to the data in Table 1, to explain the temperature dependence of the radiation effect by amorphization of polyamide alone.

The peak on the $\lambda = f(T)$ curves within the — 50°C temperature range is associated with glass transition of the polymer components. The gradual smoothing of the peak (attenuating phase transition of the second kind) has been observed before, viz., in the case of the specific heat of irradiated polystyrene [9]. A possible cause of this is formation of microinhomogeneities during the irradiation process, each of the new structures having its own glass transition point. The consequence of this is a phase transition "blurred" over a certain temperatrure range.

Kriosil. The presence of a large amount of boron nitride in this compound has made it possible to examine the dependence of the radiation effects on the thermal conductivity of this polymer on the linear radiation-energy loss, considering that dE/dx = 30-90 keV/μm for α-particles produced through capture of thermal neutrons by the ^{10}B boron isotope. For comparison, to gamma quanta from a ^{60}Co source corresponds dE/dx = 0.1 keV/μm. During intrareactor irradiation the dose due to thermal neutrons (in a core channel) is approximately equal to that due to γ-rays and fast neutrons. It must be taken into account that the error of dosage is in this case rather large (20-25%), inasmuch as the deformation of the thermal neutron flux inside specimens with a high ^{10}B content can be calculated only approximately.

The thermal conductivity of Kriosil, based on the results of this study, is shown in Fig. 3 as a function of the temperature and in Fig. 4 as a function of the absorbed radiation dose. As the temperature increases from —113 to 216°C, the thermal conductivity λ increases by 60-65%, and as the irradiation dose increases up to 20 MGy, it decrease by 37% at —100°C and by 32% at 200°C. Within the limits of λ measurement error and radiation dosage error, there was found to be no dependence on the kind of radiation.

There was also found to be hardly any change in the magnitude of the radiation effect with changing temperature, unlike in the case of grade VK-9 compound.

Characteristic of the amorphous polymers contained in Kriosil, silicone resin and polyamine, is their radiative breakdown. It is well known [10] that radiative breakdown in filled polymers occurs at a much faster rate than in unfilled silicone vulcanizers during irradiation, which could possibly be attributed to stress concentration in chains of the lattice close to the filler surface. Judging by the decrease of λ with increasing irradiation dose, in this case the crosslinkage processes cannot compete with the breakdown processes.

Such a mechanism of changing thermal conductivity has been confirmed by measurements of the density of Kriosil at 20°C. The density of this polymer decreases monotonically with in-

creasing irradiation dose, which is evidence in support of a breakdown process. The values of thermal conductivity λ at the 10 MGy dose are approximately 5-8% overestimated throughout the entire temperature range and correlate with the overestimated (by approximately 10%) initial density of specimens prior to irradiation with the same dose. Lack of data on the radiation stability of individual resins, components of Kriosil, makes it impossible to analyze the results obtained here in greater detail.

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EFFECT OF PARTICLE-SIZE COMPOSITION OF A NICKEL ALLOY POWDER ON ITS REFLECTIVITY

I. G. Vol'fovskii, É. F. Itsko, M. M. Seredenko, and V. P. Pilyavskii

UDC [677.61+661.874-492]:535.39-92+681.3

The effect of the duration of grinding and the most probable radius of the particles of a nickel alloy powder on its optical properties in the infrared region is investigated.

Considerable attention has been paid in recent years to the development of selective paints for use in solar energy converters [1-3]; such paints must have high absorptivity within the solar spectrum (0.2-3.0 μm) and high reflectivity in the infrared (IR) region (3-30 μm). These properties depend greatly on the particle-size composition of the pigments and fillers used. The effect of particle size of a nickel alloy power on its reflectivity in the IR region was investigated in [4]. The powder was subjected to wet grinding in a ball mill for 50, 100, 150, or 200 h and its particle-size composition was determined on a Hitachi (Japan) PSA-2 sedimentograph. Examples of differential particle-size distributions are shown in Fig. 1; the most probable particle radius r_m is determined from the position of the peak on the curve.

The spectral reflectivity of the investigated material was measured at six wavelengths (λ = 2.45, 4.0, 7.95, 10, 12, and 15 μm) by a special apparatus [5]. The integral reflectivity

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 42, No. 3, pp. 453-455, March, 1982. Original article submitted November 26, 1980.

0022-0841/82/4203-0331$07.50