

FEATURES OF THERMOPHYSICAL PROPERTIES OF MODIFIED EPOXY COMPOSITES AT LOW TEMPERATURES.

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ABSTRACT

The thermal conductivity, thermal diffusivity and specific heat of epoxy composite materials were investigated from 5 to 400 K. Experimental results of thermal expansion measurements in the temperature range 77 – 380 K are also presented. The introduction of an anthraquinone and a rubber into an epoxy resin enhanced its thermal conductivity and the thermal diffusivity in the “plateau” region. The spectrum of relaxation transitions is obtained by two independent methods: calorimetric and dilatometric.

1. INTRODUCTION

An essential failure of epoxies is their high fragility at low temperatures. So modified or composite materials based on epoxies are made which have a higher cryogenic stability. Often various rubbers are introduced into epoxy resins to improve the stability to thermal cycling. Some quinones are introduced into epoxies to improve the radiation stability of the material. Such composites may be heterophase or single-phase materials.

Due to the complex structure of these kinds of polymers they are characterized by a number of separate relaxations. The majority of works devoted to the investigation of relaxation processes in polymers by calorimetric methods starts at 77 K [1-3]. Moreover, usually separate thermophysical properties such as thermal conductivity, specific heat and thermal expansion are studied.

The aim of the present investigation is the experimental determination of the thermal conductivity, thermal diffusivity and specific heat of epoxy composite materials simultaneously in the temperature range 5-400 K, and thermal expansion in the temperature range 77-373 K. Relaxation spectrometry based on independent calorimetric and dilatometric methods has also been performed.

2. EXPERIMENTAL DETAILS

Investigations have been performed on the epoxy dian resin, on epoxysilica organic resin, on the epoxy-rubber composite material and on the epoxy resin modified by anthraquinone.

Measurements were carried out by a quasistationary method, which allowed us to determine the thermal conductivity, thermal diffusivity and specific heat simultaneously on the same samples in the temperature range 5-400 K [4]. First, the sample was cooled to 4.2 K and then heated under adiabatic conditions at a heating rate of 2 K/min. The temperatures and the temperature gradient within the thickness of the sample were determined by Cu+0.01%Fe:chromel thermocouples. The maximum relative error was 7%. The thermal expansion was measured by an automatic quartz indicator vertical dilatometer (Japan). The heating rate of samples was 2 K/min.

3. RESULTS & DISCUSSION

The experimental results for the thermal conductivity of the samples with and without anthraquinone are presented in *Figures 1*. The temperature dependences of the thermal conductivity show the typical plateau of glassy materials between 4 and 15 K. But the plateau for the modified epoxy resin is longer (5 – 18 K) than that of pure epoxy resin (5 -14 K).

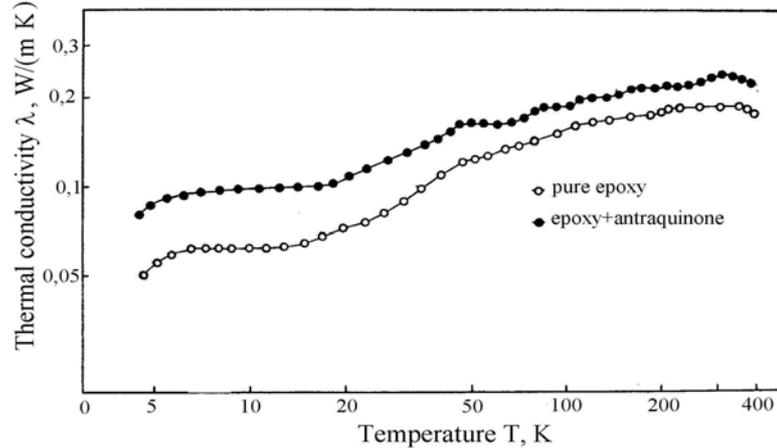


Figure 1. Temperature dependences of the thermal conductivity for the pure and anthraquinone-modified epoxy resin.

The most important fact is that thermal conductivity values for the anthraquinone-modified epoxy resin are approximately 60% greater than those of pure epoxy resin in the plateau region, and approximately 40% greater in the room temperature region.

Other studies [5,6] have shown that thermal conductivity below 20 K is smaller for more highly cross-linked samples. Therefore anthraquinone inclusions diminish the cross-link density of the epoxy resin. Moreover, the rise in the quantity of double bonds increases the elastic characteristics and so leads to an increase in thermal conductivity. Plasticizers and rubber induced in epoxy resins have a similar influence on thermal conductivity. Temperature dependences of thermal conductivity for epoxy silica organic resin and rubber-modified epoxy resin are presented in *Figure 2*.

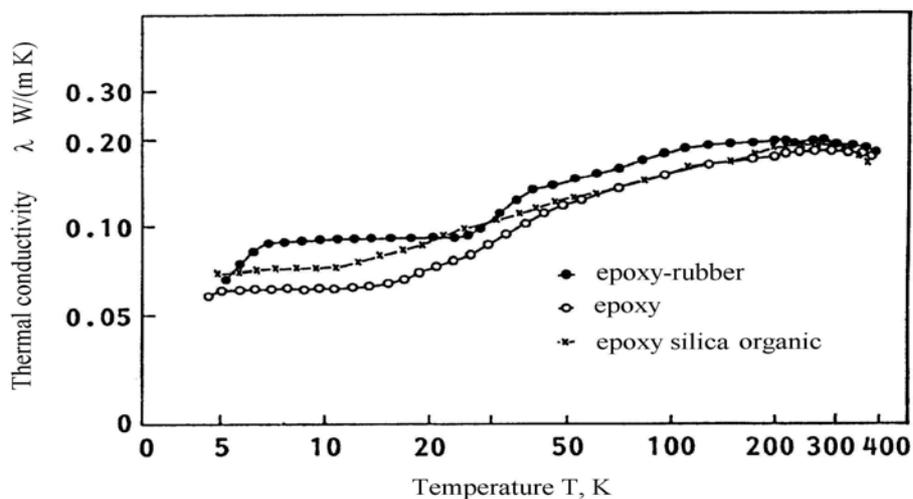


Figure 2. Temperature dependences of the thermal conductivity for the pure and modified epoxy resin.

This brings attention to the fact that the thermal conductivity for the epoxy silica

organic resin has a shortest plateau (4 –12 K), and the epoxy-rubber plateau extends to $T=25$ K. It is evident that the extended plateau is the result of the presence of rubber and plasticizer in the composite. The modifying of epoxy resins by rubber and the introduction of plasticizers diminishes the cross-link density and leads to an increase in the thermal conductivity.

There is an interval between 200 and 300 K where the thermal conductivity of the epoxy silica organic resin is constant and equals $0.195 \text{ W/(m}\cdot\text{K)}$; it then decreases with increase in temperature. The thermal conductivity for all samples exhibits a maximum, above which the transition to the viscoelastic state and an increasing free volume starts. The rise in molecular mobility with the introduction of plasticizers and rubber in epoxy resin lowers the glass transition temperature.

Figure 3 presents the temperature dependences of the specific heat for the epoxy resin and the epoxy-rubber composite, and the temperature dependence of the thermal expansion for the epoxy-rubber composite.

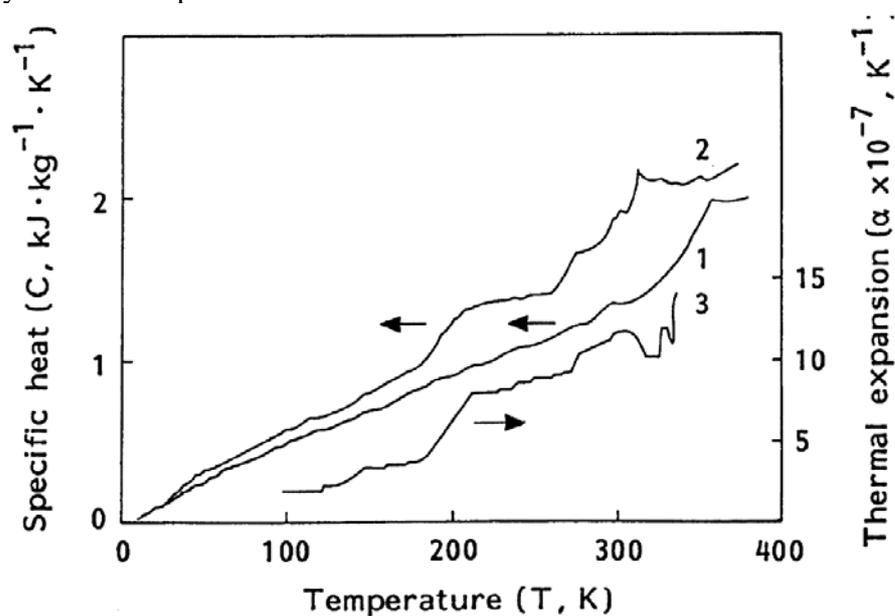


Figure 3. Temperature dependences of the specific heat and thermal expansion for the pure (1) and rubber modified (2,3) epoxy resin.

Figure 4 shows $C(T)$ and $\alpha(T)$ for the epoxysilica organic resin. The specific heat for the epoxy-rubber composite is larger than that for the epoxy resin, since the presence of the olein acid and the rubber has a plasticizing, loosening effect on the composite structure (the density is reduced from 1.18 to 1.04 g/cm^3). This, in turn, leads to an increase in the specific heat.

Attention is drawn to the non-monotonous character of the dependences $C(T)$ and $\alpha(T)$ of the composite; anomalous changes in the specific heat and thermal expansion are observed in the temperature range 185-250 K. This is connected with the glass transition of rubber. The glass transition of the material as a whole occurs at a rather low temperature, $T=312 \text{ K}$, as a consequence of more mobile groups in the plasticized composite. Temperature transitions observed from $\alpha(T)$ and $C(T)$ coincide with an accuracy of $\pm 2 \text{ K}$. At the glass transition interval a sharp rise in α occurs, followed by a decrease due to incomplete polymerization and additional cross-linking. Experiments with the completely hardened resin show that the decrease in $\alpha(T)$ is reduced and finally disappears with additional thermal processing. Structural studies of epoxy resin with high rubber content show the existence of two phases in the material, and thus the material has two glass transition regions.

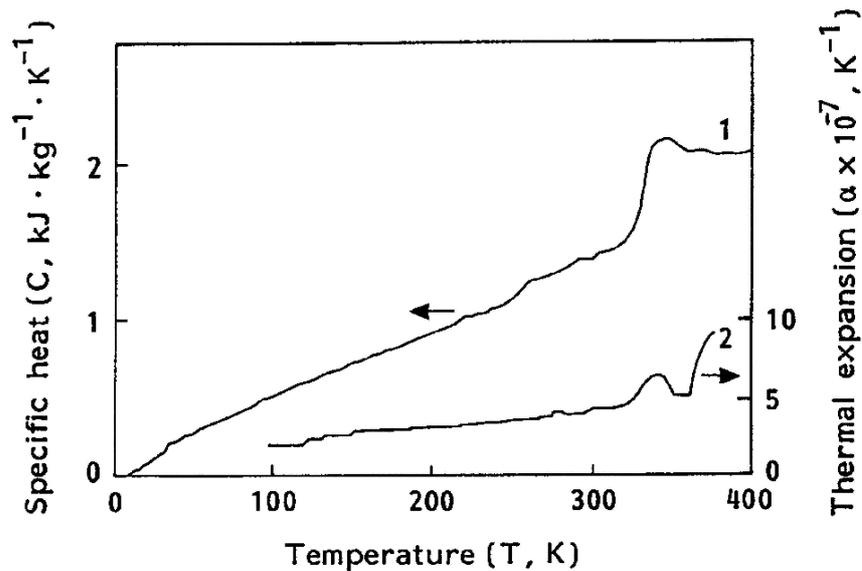


Figure 4. Temperature dependences of the specific heat and thermal expansion for the epoxy silica organic resin.

As well as these two α -transitions, a large number of small-scale temperature transitions (β - and γ -transitions) are observed, which correspond to unfreezing of kinetic units of polymer macromolecules. The number and temperatures of these transitions in the epoxy resin above 77 K correspond approximately to the results obtained for the epoxy resin ED-6 [3]. In references 1 and 3, the authors suggest that the mobility of the smallest kinetic units (structural elements) of the epoxy polymer, $-\text{CH}_2-$, is unfrozen at 117 K. Another author [8] assumes that for polymers with phenyl rings in the main chain, their motion is responsible for the relaxation transition at 100 K. The low temperature transitions in polymers with side methyl groups are connected with reorientation by quantum-mechanical tunneling of methyl groups over the potential barrier, which restricts their rotation around the C_3 symmetry axis [9,10]. At elevated temperatures tunneling and classical processes may overlap.

Figure 5 shows how the specific heat for the materials tested changes at cryogenic temperatures. Since the absolute values of specific heat are very close they are displaced comparatively with respect to each other. Steps, characterizing relaxation transitions, are observed in the temperature dependences $C(T)$. Unlike the epoxy resin, the epoxy-rubber composite has transitions displaced in the lower temperature region, which may be an effect of the plasticizer. The plasticizer moves polymer macromolecules back, disorientates them and shields groups, which are capable of reaction. Cohesive interaction of the chains is weakened. Potential barriers to every kind of movement are reduced and the relaxation spectrum may change. Since the interchain interaction exercises an essential influence on the specific heat in the temperature range below 50 K, the transition temperatures can shift to the lower temperature region for the modified epoxy materials in comparison with the pure epoxy. Two transitions observed in the epoxy resin at 45 and 52 K are superimposed in the epoxy-rubber composite and create a wide region of transition in the temperature interval, where interchain interaction ceases to influence the specific heat and intrachain interaction takes over from interchain interaction. In addition, the slope of $C(T)$ changes sharply.

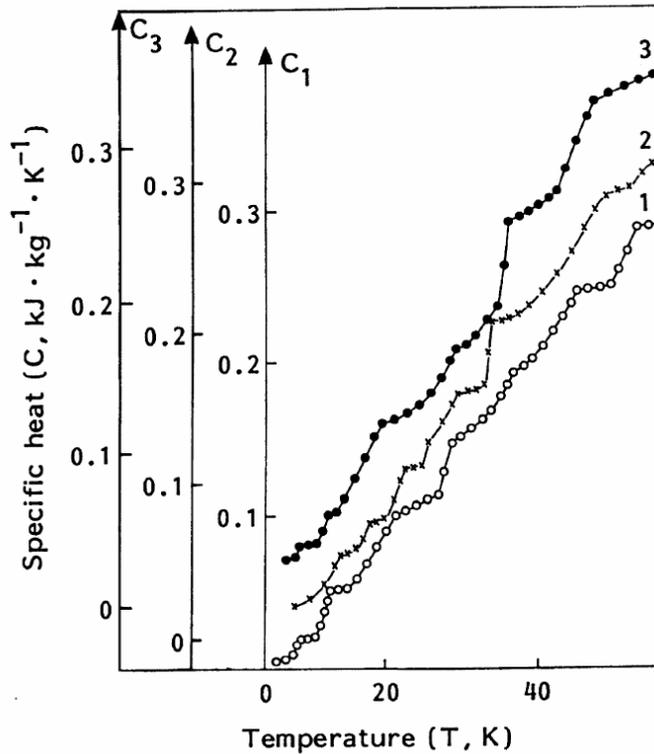


Figure 5. Temperature dependences of the specific heat for the epoxy (1), epoxy silica organic resin (2) and epoxy-rubber composite.

On this figure the specific heat for the epoxy silica organic resin is also presented. Its absolute values are close to those of epoxy resin, but the transition temperatures are different. Since there are more methyl groups in the epoxy silica organic resin than in the epoxy resin, and owing to a far greater potential barrier (because of the closer arrangement of methyl groups), the transition temperatures are displaced to a higher temperature region by roughly 6 K.

The temperature dependences of the thermal diffusivity at cryogenic temperatures are presented in *Figure 6*.

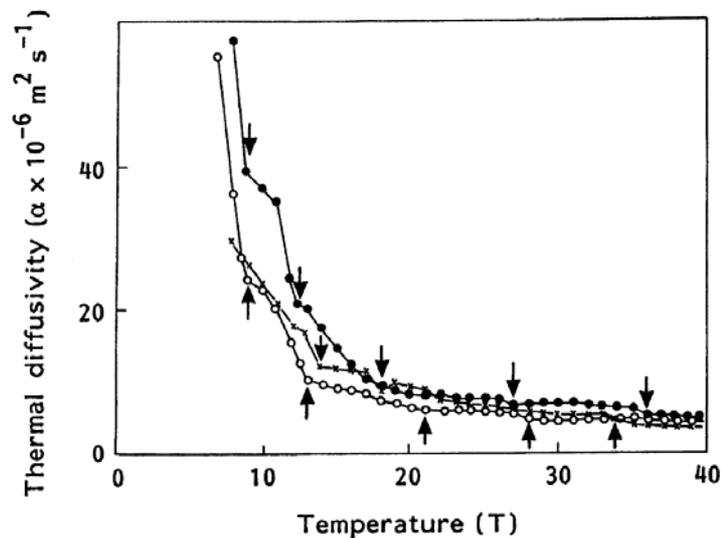


Figure 6. Temperature dependences of the thermal diffusivity for the epoxy (B), epoxy silica organic resin (x) and epoxy-rubber composite (X).

The values sharply decrease up to 20 K, resulting from a sharp reduction in the mean free path of phonons. Unlike other thermophysical properties, thermal diffusivity is directly connected to the mean free path ($a \propto l \propto T^1$) at cryogenic temperatures. Due to interactions with tunnel systems or the unfreezing of certain types of molecular motion a resonant increase of phonon dispersion occurs, which results in a sharp reduction of the mean free path, and therefore the thermal diffusivity. The characteristics are not monotonous but step-wise. Values for the thermal diffusivity of the anthraquinone epoxy resin are approximately 50-60% larger than the thermal diffusivity of the pure epoxy resin in that temperature region. Transition temperatures at $T = 9$ K and $T = 13$ K coincide for both materials, but the next two transitions at $T = 21$ K and $T = 28$ K are displaced in the higher temperature region about 3 K. The transition temperatures coincide with those from specific heat measurements.

Generally, the investigations have shown that there are relaxations in epoxy polymers not only above 77 K but also at cryogenic temperatures. Transition temperatures determined by two independent methods, calorimetric and dilatometric, coincide within ± 2 K accuracy. The quasi-stationary method of continuous heating of a sample under adiabatic conditions turned out to be very sensitive to the different kinds of processes taking place in the material at increased temperatures. Unfortunately identification of these transactions is rather difficult, because of the behavior of the thermophysical properties, and it is necessary to apply other test methods.

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