

Measurement of Thermophysical Properties of Polyester Cured with Styrene in the Range 300–450 K

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SYNOPSIS

A pulse method for the simultaneous determination of thermal diffusivity, a , specific heat capacity, C_p , and thermal conductivity, λ , are measured for a series of curing of polyester and styrene in the presence of 10, 20, and 30% carbon black in the temperature range 300–450 K. The results show a dependence of the above-mentioned properties on temperature and composition. The mechanism of heat transfer through the specimens is also discussed.

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1. INTRODUCTION

A flash method basic technique is used for determining thermal properties (thermal conductivity, capacity, and diffusivity).^{1–3} The aim of this work was the measurement of these properties of polyester cured with styrene in the presence of 10, 20, and 30% carbon black and to study the thermal properties of the polyester resin cured with styrene and also of the composite formed from carbon black as a conductor and polyester cured with styrene monomer as a semiconductor.

The polyester chain is very stable and the resistance to deterioration by heat is very good. Styrene monomer is widely used as the curing agent for industrial applications of unsaturated polyester, and its use changes the physical properties of the polyester.

By studying the structure and heat conduction mechanism parameters at a range of temperature of these compositions will help to present a clear view of the structure and heat conduction mechanism of these materials.^{4,5}

Theory of Method Used

The theory of the pulse method for measuring the thermal diffusivity, a , was detailed in Refs. 6 and 7, where a is given by

$$a = 0.139 \frac{l^2}{t_{0.5}}$$

where $t_{0.5}$ is the time required for the lower surface of the sample to reach half-maximum of the temperature rise and l is the sample thickness. The specific heat capacity, C_p , is measured by the relation

$$C_p = \frac{q}{M \cdot Tm}$$

where q is the power dissipated through the sample; M , the mass of the sample; and Tm is the maximum temperature rise.

The heat losses by radiation from the boundaries were taken into consideration. The thermal conductivity coefficient was calculated from the relation

$$\lambda = \rho C_p a$$

where ρ is the density of the sample.

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2. EXPERIMENTAL

Figure 1 shows the block diagram of the experimental setup, where the sample is heated by a furnace to achieve a mean temperature and the optical flux is provided by a powerful incandescent lamp (2000 W) focused on the upper surface of the sample. The radiation pulse from the flash lamp was chosen to be negligible in comparison with the characteristic rise time of the sample.

Because of the short duration of the radiant heat flux, heat losses are carefully adjusted and the mean temperature of the sample is compensated in order to detect only the temperature rise due the pulse on the lower surface of the sample. The thermal inertia of the system is taken into consideration.

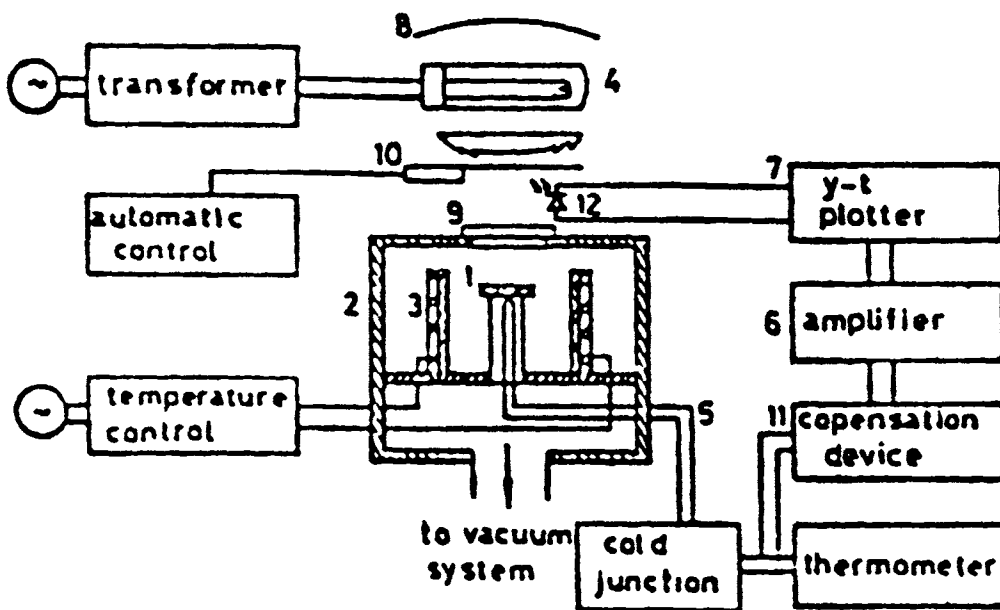
Figure 2 shows the typical shape at the $y-t$ recorder for the temperature rise at the lower surface of the sample, where the duration time of the pulse

is detected by a photodiode and appears as a small ramp. The $t_{0.5}$ is measured from the starting time of the photodiode response to the time the lower surface attained one-half of its maximum temperature rise. The accuracies attained are 3% for thermal diffusivity, 2% for heat capacity, and 5.5% for thermal conductivity.

3. PREPARATION OF SAMPLES

(a) Styrene Monomer

Styrene monomer was a product of BDH. The ratio of styrene monomer to polyester resin was 30 : 100 (weight/weight). The main function of the monomer is to act as a solvent for the unsaturated polyester that is a highly viscous liquid and to copolymerize with the unsaturation in the polyester chain, thus yielding a cured thermoset product with the gel time of 180 min.



The block diagram of the experimental setup.

- | | |
|--------------------|--------------------------|
| (1) Tested Sample | (7) Y - t Plotter |
| (2) Vacuum Chamber | (8) Reflector |
| (3) Furnace | (9) Quartz Window |
| (4) Flash Lamp | (10) Shutter |
| (5) Thermocouple | (11) Compensation Device |
| (6) Amplifier | (12) Photodiode |

Figure 1 Block diagram of the experimental setup.

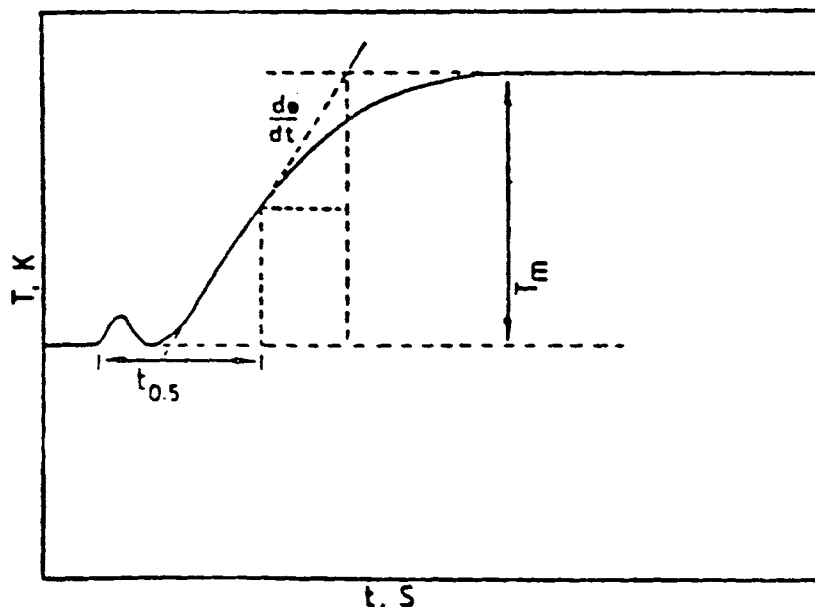


Figure 2 Typical oscillogram for the temperature rise at the lower surface of the sample.

(b) Black Carbon

Black carbon was of the HAF type (high-abrasion furnace) with a particle size of 28 nm. The specific surface area was 65–70 m²/g with oil adsorption of 130 cm³/100 g. The percentage of carbon black in the polyester composite was 10, 20, and 30%. The compatibility of higher percent was not good.

(c) Polyester

Unsaturated polyester was propylene glycol-maleate phthalate. The polyester has the following characteristics:

| | |
|--------------------------|-------------------------|
| Polymerizable | 100% |
| Viscosity at 25°C | 4 poises |
| Acid value | 30 |
| Density at 25°C | 1.125 g/cm ³ |
| Refractive index at 20°C | 1.54 |

(d) Initiator

1% solution of methyl ethyl ketone peroxide was used as initiator.

(e) Accelerators

Accelerators were added, in general, to accelerate the decomposition of the initiator to free radicals.

Cobalt naphthenate, 0.5%, was used at room temperature.

4. RESULTS AND DISCUSSION

(a) Specific Heat Capacity, C_p

Figure 3 shows the variation of the specific heat capacity, C_p , of polyester cured with styrene in the presence of 10, 20, and 30% carbon with different temperatures. It was found that the C_p of polyester cured with styrene slightly increased with an increase in temperature. As the carbon percentage increases, the specific heat increases. Our measurements were made in the temperature range of 300–450 K, which is above the Debye temperature (θ_p) of the investigated samples. It is more convenient to consider the C_p of polymers in relation to the C_p of dielectric crystals.

It is seen that C_p increases with temperature for all samples. This effect could be attributed to the anharmonicity of carbon atoms present.⁸ Also, C_p increases as carbon content increases. This is believed to be due to an increase in the density of the transverse vibrations that resulted from more holes in the structure due to carbon content. It was found that C_p slightly increases with an increase in temperature for all samples, indicating that there is no considerable change in the structure in the temperature range of measurements, because there are no peaks on the C_p T curves. The values as well as the

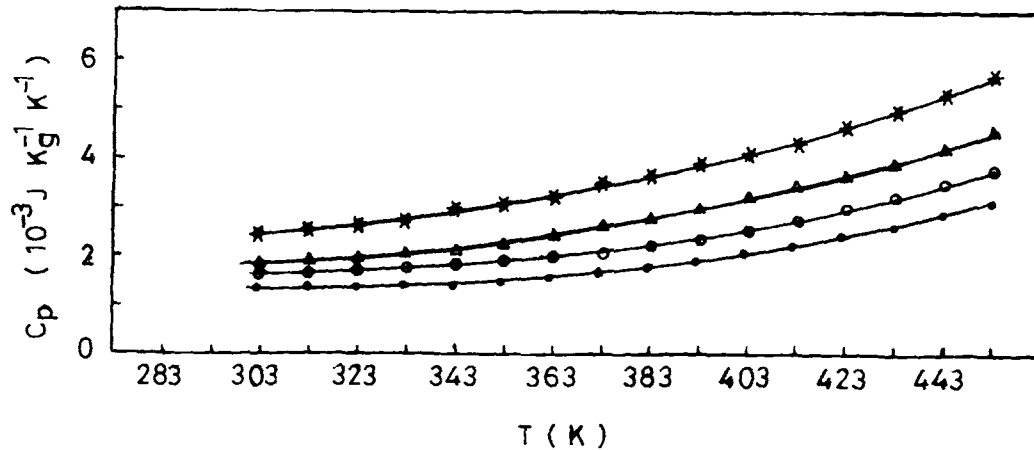


Figure 3 The specific heat capacity of (●) polyester cured with styrene, (○) in the presence of 10% carbon, (△) in the presence of 20% carbon, and (*) in presence of 30% carbon.

behavior of the C_p indicate that these materials are typical insulators.

(b) Thermal Conductivity, λ

Figure 4 shows the variation of thermal conductivity, λ , of the investigated samples with different temperatures. It is seen that λ increases with an increase in temperature for all samples. Also, the higher the carbon percentage, the higher value of λ . The difference between the values of λ for the four samples indicates the presence of another heat-conduction mechanism that can be explained as follows: The phonon part of thermal conductivity of dielectric solids is inversely proportional to an increase in temperature. In our measurements, the thermal conductivity coefficient increase with an increase in

temperature indicates that there are other mechanisms of heat transfer besides the phonon part. The thermal conductivity of carbon is very high and the interaction between the carbon center and the polyester network is strong. The carbon consists of an electron that moves through the lattice. The radiative part of thermal conductivity is negligible in the measured temperature range.

Therefore, we can conclude that the heat-conduction mechanism in polyester cured with styrene in the presence of 10, 20, and 30% carbon black is due to phonons and electrons.

(c) Thermal Diffusivity, a

The thermal diffusivity, a , of the investigated samples is shown in Figure 5. It slightly decreases with

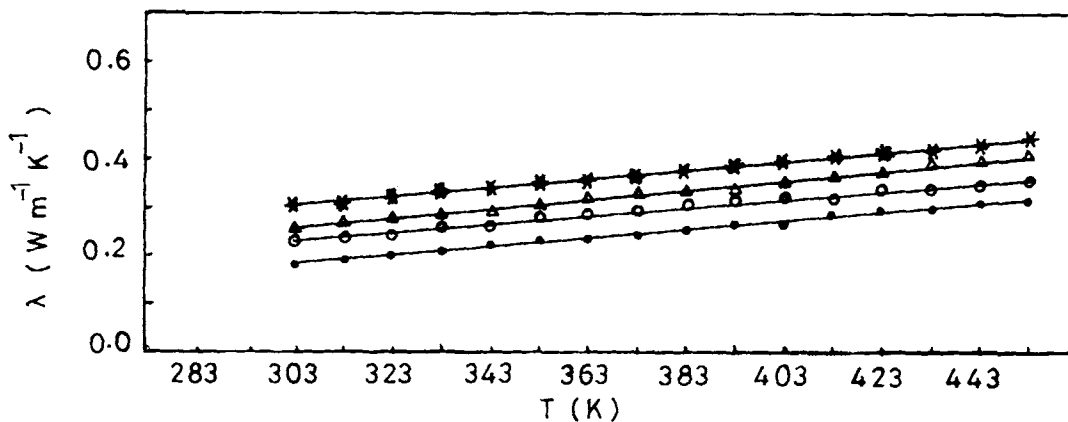


Figure 4 The thermal conductivity of (●) polyester cured with styrene, (○) in the presence of 10% carbon, (△) in the presence of 20% carbon, and (*) in the presence of 30% carbon.

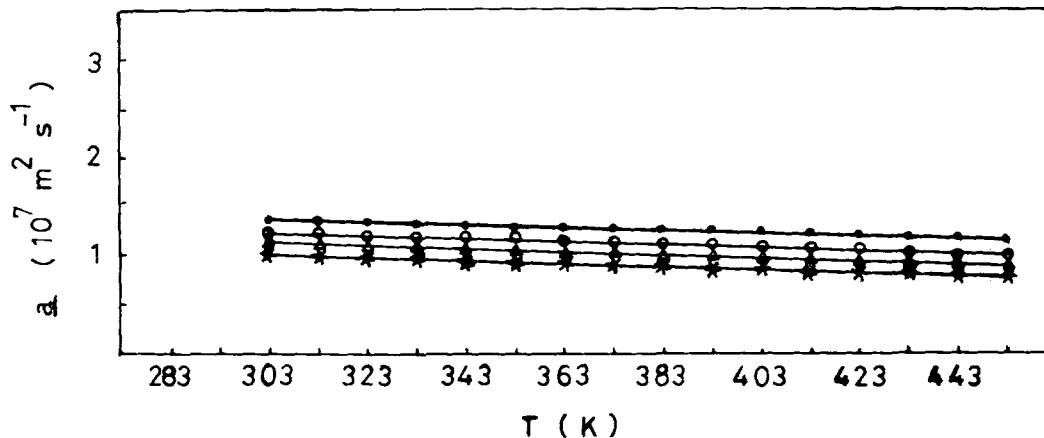


Figure 5 The thermal diffusivity of (●) polyester cured with styrene, (○) in the presence of 10% carbon, (△) in the presence of 20% carbon, and (*) in the presence of 30% carbon.

increasing temperature and is related to λ and C_p by the relation

$$a = \frac{\lambda}{\rho C_p}$$

where ρ is the density of the investigated sample. It might also be concluded that increasing the carbon percentage decreases the a of these samples.

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