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Determination of glass transition temperature for polymers by methods of thermoactivation spectroscopy

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Determination of glass transition temperature for polymers by methods of thermoactivation spectroscopy

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Abstract. For rapid determination of glass transition temperature for polymers, we propose a method of thermally stimulated luminescence. The experiments were carried for epoxy polymers dyed and undyed with organic dyes. It is shown that glass transition temperature depends on curing temperature and concentration of the dye. The comparison with the thermogravimetric analysis showed coincidence of the results obtained.

1. Introduction

The glass transition temperature of polymers is an important characteristic defining their practical application in a particular area [1–4].

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A large number of methods have been currently developed to determine the glass transition temperature for polymers:

- Differential Thermal Analysis (DTA). In this method, when glass transition temperature is attained, the slope of the specific volume of the sample temperature changes [5, 6];
- Single Differential Thermal Analysis (Single DTA), which combines both, DTA and thermogravimetric method [7]
- Differential Scanning Calorimetry (DSC). This method measures the heat flow to/or from a small sample, when the sample is subjected to a programmed temperature variation [2, 5, 8];
-Thermogravimetric Analysis (TGA). This method measures the change in mass of the sample in a linear temperature change [5, 6, 8, 9];
- Evolved Gas Analysis (EGA). EGA is a family of methods to analyze the nature and amount of volatile gaseous product evolving from the sample which is subjected to programmed temperature variation. The most important methods are mass spectrometry and infrared spectroscopy. EGA is often used in combination with TGA. [10];
- Thermomechanical Analysis (TMA). TMA measures deformation (typically one-dimensional deformation) of the sample as a function of temperature. Different varieties of the method use the mode of constant, increasing or modulated power. [11];

Dynamic Mechanical Analysis (DMA). In this method, the sample is subjected to sinusoidal mechanical impact. The amplitude, phase shift, and other characteristics are the functions of temperature [12–14];

- and others.

Most of the methods described above demand for the realization of complex and expensive equipment.

In this paper for the rapid determination of the glass transition temperature polymers, we propose a method of thermoactivation spectroscopy.

2. Methods of thermoactivation spectroscopy (TAS)

The physical nature underlying TAS methods is implies that when the temperature of the sample changes under a certain law, the transition from the nonequilibrium state to a new state approaching the thermal equilibrium is thermally stimulated. This transition may be foolowed by thermally-stimulated luminescence, TSL) [15]), by emission electron (thermally-stimulated emission of electrons, TSE [16]), by the change in conductivity (thermally-stimulated conductivity [17]), etc. The analysis of the temperature dependence for the changing physical property of an object allows exploration of the parameters of electrically or optically active defects, mechanisms of relaxation processes occurring in the substance.

3. Results and discussion

The experimental scheme in the TSL method is simple: the polymer was irradiated with the ultraviolet deuterium lamp 400 W (any other source of ultraviolet radiation can be used) for 5–10 minutes at T = 80 K through the quartz window and a combination of light filters that produce the emission band lamp with 300 nm. The temperature of the sample (1 mm thick and 10 mm in diameter) was measured by the copper-constantan thermocouple one junction of which was mounted on the sample surface, and the other one was placed in a Dewar vessel with melting ice. The sample was heated at a constant rate of 0.15 K/s through a copper chip carrier via an electric heater. The integral emission of the sample was detected by a photomultiplier tube and then the signal entered the input of the DC amplifier and the display.

Figure 1 shows the integral curve of the thermally-stimulated luminescence for epoxy polymers obtained under various curing temperatures: 100 ° C (1), 140 ° C (2), 200 ° C (3).

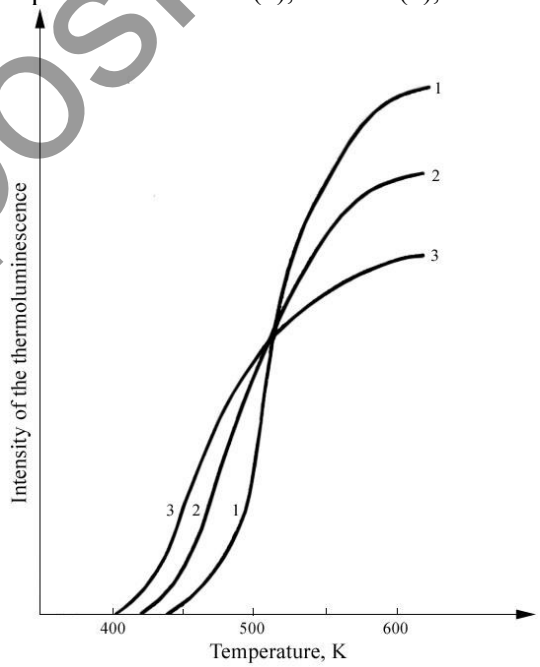

Figure 1. Thermally-stimulated luminescence of the undyed polymer produced under different curing temperatures

The corresponding curves in Arrhenius coordinates ($\ln I \sim 10^3/T$) intersect the horizontal axis at points with temperatures T_{C1}, T_{C2}, T_{C3}. Table 1 shows these values along with the results of the thermogravimetric analysis.

Fig. 2 shows the integral curve of the thermally-stimulated luminescence of the epoxy polymer dyed in yellow with rhodamine of different concentration.

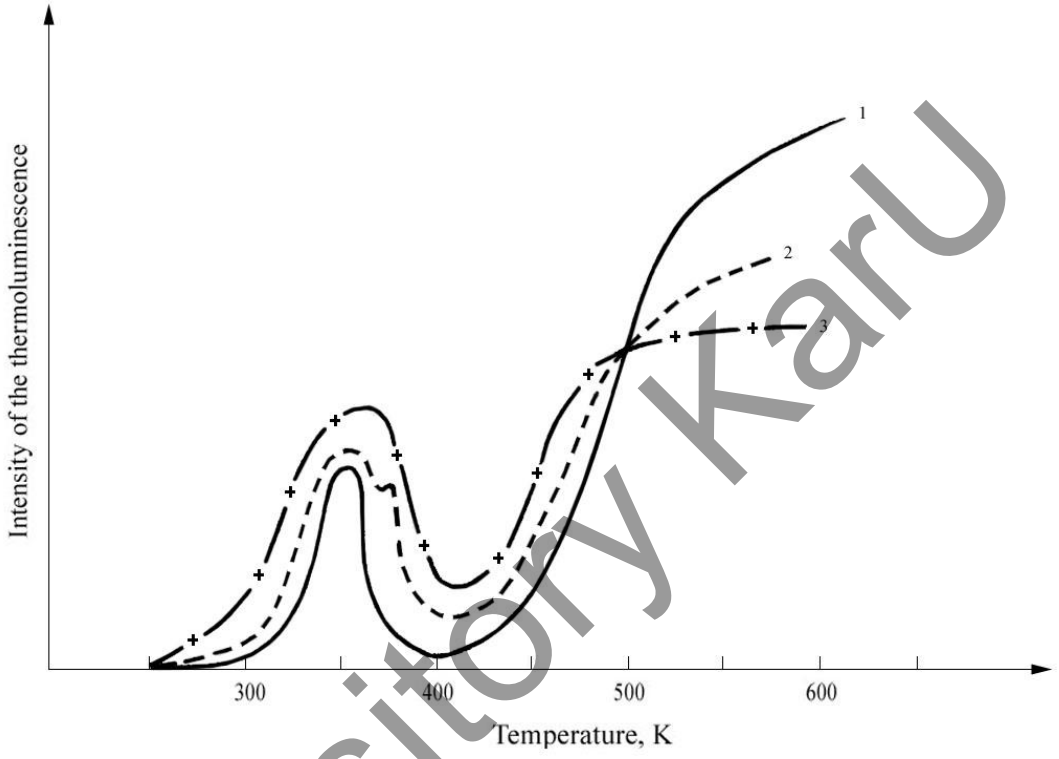

Figure 2 Thermally-stimulated luminescence of the dyed epoxy polymer

Table 1. Glass transition temperature for epoxy polymer

Sample	Method	T_{C1} (K)	T_{C2} (K)	T_{C3} (K)
Undyed epoxy polymer	TSL	471.6	446.4	423.7
	TGA	479	450	426
Epoxy polymer dyed with rhodamine 6Y	TSL	400	383	379
	TGA	406	392	384

The data provided in the Table 1 show:

1) the values of the glass transition temperature T_c obtained by the method of thermally stimulated luminescence are in good agreement with the thermogravimetric measurements, which allows its application to determine T_c along with conventional methods;

2) the glass transition temperature T_c of the polymer produced under different curing conditions varies considerably (in this case, almost by 50 K), which allows the use of the method of thermally stimulated luminescence as a rapid method when developing the polymer production technology;

3) the glass transition temperature T_c of the polymer decreases when its base is doped with dye molecules (up to 70 K in this case), and as the concentration of the latter grows, it continues to decrease.

4. Conclusion

With no regard to the issues related to the mechanism of excitation of thermally stimulated luminescence in undyed and dyed epoxy polymers after exposure to UV radiation, it should be noted that the method of thermally stimulated luminescence in its sensitivity is significantly superior to optical absorption techniques, electron paramagnetic resonance and other spectroscopic methods. It is sufficiently simple, reliable and does not require expensive equipment.

In our opinion, further investigation of the method with other types of polymers will provide engineers with a simple method to control the production technology of polymer materials with desired properties.

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