

Radio Thermoluminescence in Composites PENP + X Vol. % Ln_2Se_3

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Abstract. The interest in studying the electrophysical properties of polymers and composites based on the latter is caused by the expansion of their fields of application. They are practically indispensable in electronic engineering, construction, insulation, medicine, etc. Due to the unique physical and mechanical properties, the specific structure of polymer composite materials (PCM), their electret state is characterized by a number of features. With an in-depth study, new effects can be expected to have a significant impact on the performance of polymer composites. In this regard, in recent years, the number of publications has increased, where the process of charge accumulation and transfer in polymers and composites based on them is studied. We report experimentally defined activation energies of charges and radio-thermoluminescence spectra of PENP + x vol.% In_2Se_3 composite materials. It has been determined that these materials have tunable luminescent properties. It is precisely the factors listed in the aforementioned direction that characterize the relevance of the research.

Keywords: Composite, Radioluminescence, Filler, Spectrum.

1 Introduction

The radio thermoluminescence (RTL) method is based on the observation at low temperatures of thermoluminescence of the studied substances irradiated by fast electrons or gamma rays. This glow is associated with the recombination of ions stabilized in the substance during its low-temperature (usually at 77K) irradiation. A characteristic feature of RTL is that the intensity of the glow increases sharply (passes through maxima) in those temperature ranges in which the movement of segments of molecules or molecules as a whole begins. The curve of illumination of the studied substance - the presence of maxima on it, the shape of maxima - allows us to assess the position of structural transitions, their nature, and the degree of crystallinity of the sample. By examining TL at different defrosting rates, the activation energy of structural transitions and the glass transition process of the polymer are determined. This feature of RTL makes it possible to apply this method to study structural transitions in substances and various solid composite materials [1]. RTL has become especially widespread in the study of molecular relaxation processes. Considering that the defrosting of the mobility of fragments consisting of a different number of atomic groups leads to a sharp change in the temperature dependence of the luminescence intensity, radio thermoluminescence can be considered as one of the methods of relaxation spectrometry. At the same time, various maximum parameters based on the temperature dependence of the intensity of RTL allow us to obtain information about the features of the mechanism of molecular mobility under specific conditions [2].

In the study of composite materials, special attention is paid to the study of RTL spectra in them [3, 4].

2 Literature Review

Polymers are substances containing a large number of structural units joined by the same type of linkage. These substances often form a chain-like structure. It has been approximately 60 years since researchers first began exposing polymeric materials to ionizing radiations, and today, a substantial

commercial industry is in place based on the processing of polymers with radiation. Polymers are of low atomic number and low density and thus lightweight materials. Polymers possess high durability, and they are tough. Also, they are cost-effective, need low maintenance, and stable over a wide temperature range [5]. Based on processing under changing temperature, polymers are categorized as thermosets and thermoplastics, also thermoplastics including elastomers can be divided into semi crystalline and amorphous polymers. Both the thermoset and thermoplastic polymers have some pros and cons, but thermoplastics are preferred for radiation shielding applications due to their superior properties as shown in Table 1. Also, thermoplastic polymers are highly recyclable and possess remolding abilities and eco-friendly manufacturing is possible using them [6]. Polymers proved their effectiveness in wide range of applications including CO₂ capture [7], safe gene delivery [8], dye removal [9], water and wastewater treatment [10], metal ions removal from wastewater [11], [12], [13] and drug delivery [14].

3 Method

The RTL method consists of three stages: irradiation of the test sample at a low temperature, subsequent gradual heating of the irradiated sample and simultaneous registration of the glow [15]. The samples were irradiated at a temperature of 77 K in the dark with a source of: γ rays. The dose rate does not play a significant role. It is only important that the total dose lies in the range from 0.01 to 1 Mrad. Irradiated samples for RTL analysis are stored for a long time before heating in the dark at 77 K. Both irradiation and subsequent storage of samples are carried out in a vacuum. To obtain a brighter flash of light, the samples were pumped out for 1 - 3 hours at 300K and 0.133Pa before freezing.

4 Results and Discussion

Most of polymer materials and some of polymer based composite materials emit light waves in the visible region of the spectrum if irradiated at low-temperatures (usually $T=77$ K) with a subsequent heating to the ambient temperatures. This phenomenon is known as radio-thermo-luminescence. The RTL usually consists of three consecutive steps: an irradiation of the sample at low temperatures, its subsequent smooth heating, and simultaneous recording of the luminescence signal.

The first step, namely the irradiation happens during very short time, typically in the range of 0.1 ns. During this process, electrons and holes are trapped by the trapping centers formed in the irradiated sample. The latter consist of various structural defects generated in the polymer matrix, and various atoms and molecules of additives. The release of charges from the traps can be accomplished either thermally or optically. Depending on the rate of charge activation, thermo, photo and other types of luminescence are distinguished. Usually, one or more maxima can be observed in the temperature dependence of RTL intensities, indicating the presence of one or more types of traps in the irradiated sample. For inorganic substances, these maxima are generally not related to their molecular weight.

The characteristic feature of RTL in organic substances stems from the fact that the RTL maxima are observed at temperatures where various kinetic and structural transitions and relaxations occur in the polymer. Such transitions are basically caused by the delocalization of charges at different segments of macromolecules or by molecular movements of the polymer in crystalline and noncrystalline regions. The intensity of RTL increases with the enhancement of the mobility of different segments of macromolecules. Overall, the character of temperature dependences of RTL curves depends on the peculiarities of the polymer structure and its thermomechanical properties. In crystalline polymers the maxima on the $I = f(T)$ curve is observed in the areas of kinetic and phase transformations, whereas in non-crystalline samples - in the areas of kinetic transformations (transitions).

In total, RTL provides an information on thermoluminescence in polymers, as well as on the type of traps and charge trapping properties. Thus, the RTL method can be used to calculate the values of structural transition temperatures (glass transition temperatures, melting temperatures, etc.) in the temperature range 77-300 K. The shapes of the observed maxima allow us to study the nature of structural transitions. It is also possible to determine the activation energy of the molecular motion process, since as the heating rate increases, the maxima located in the region of relaxation transitions

shift toward higher temperatures. With this method it is possible to determine the degree of homogeneity of two-component mixtures of high molecular weight compounds and the compatibility of the components with each other. This method allows the analysis of multicomponent polymers containing low molecular weight fillers. To visualize the above, the RTL spectrum in composites of a new composition obtained by adding a compound to a low-density polymer was investigated.

The study of the spectrum of RTL in composites HDPE + x vol.% In_2Se_3 is presented in Figure 1.

As can be seen from the figure, for pure polyethylene, the RTL curve shows three maxima at temperatures 131 K, 165 K and 241 K and two minima at temperatures 144 K and 197 K (curve 1). For the composite of PENP + 3 vol.% In_2Se_3 , the RTL curve showed pronounced three maxima at temperatures 126 K, 150 K and 250 K, respectively, and two minima at temperatures 134 K and 174 K (curve 2). With the increase in filler volume content up to 5 vol.% In_2Se_3 , maximums were observed at temperatures 118 K, 144 K and 215 K on the RTL curve and minimums at temperatures 120 K and 168 K (curve 3). In the RTL curve of the PENP + 7 vol.% In_2Se_3 composite, the intensities of the maxima decrease slightly and were observed at temperatures of 121 K, 146 K and 198 K, while the minima were observed at temperatures of 127 K and 165 K (curve 4). The maxima on the RTL curve of the PENP + 10 vol.% In_2Se_3 composite were observed at temperatures of 110 K, 132 K and 203 K, while the minima

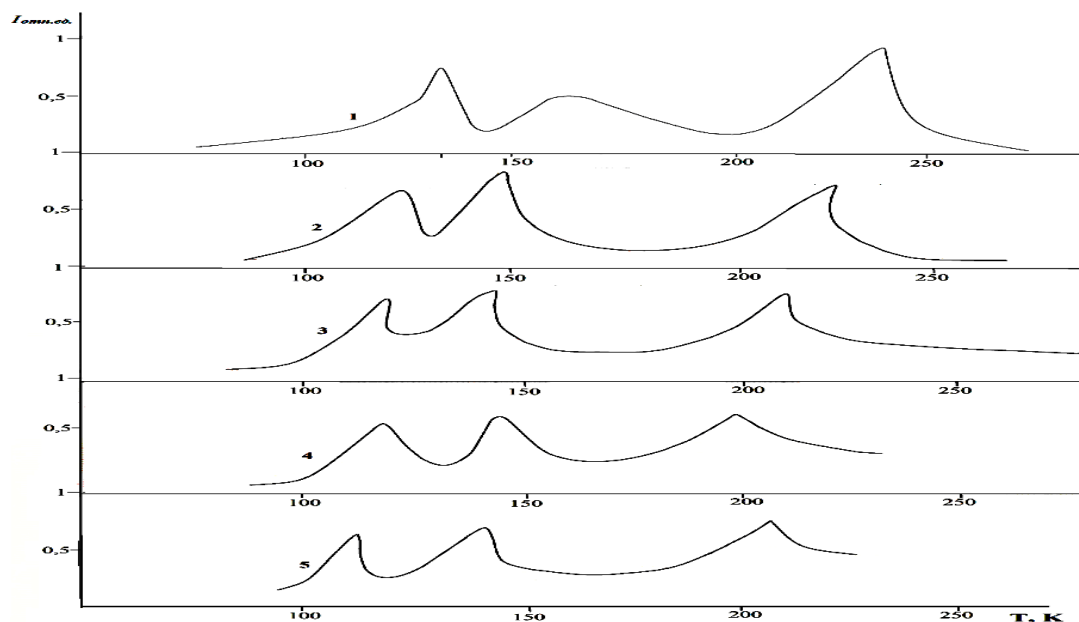


Fig.1. RTL spectrum of PENP+x vol.% In_2Se_3 composites, where 1- x = 0; 2- x = 3; 3- x = 5; 4- x = 7; 5- x = 10

were observed at temperatures of 115 K and 160 K (curve 5). Thus, the addition of additives to PENP leads to retardation of the β relaxation process at the RTL characteristic of the polymer-additive system. Relaxation transitions of composites in the temperature regions of 110-150K (γ -transitions) determine the temperature interval of the additive mobility unfreezing, and the position of the maximum within the transition is determined by the type of additive and its concentration.

The above results show that the usually recorded PTL curve of the polymer depends on impurities and additives and thus cannot serve as an individual characteristic of either the polymer or the impurity or additive separately, but refers to the system as a whole. The observed shift in the positions of β and γ transitions which depends on the content and type of filler, hence, can serve as a measure of interactions between the components of the nanocomposite [15].

The analysis of the PTL spectra of PENP+x vol.% In_2Se_3 composites shows that all the studied composites are characterized by two low-temperature and one high-temperature maxima. We assume

that the introduction of In_2Se_3 additives into the polymer matrix leads to the retardation of the β -relaxation process. It is easy to notice that all characteristic "polymer" maxima can be interpreted as the composite behaves like a solid quantum system with special temperature points (STP) or coincides with STP values being multiple of 12.5 K. The assumption about the existence of a system of STP with relaxation processes in polymers contradicts the established theoretical frameworks about the role of relaxation phenomena in the properties of these materials. It is usually considered that the parameters of molecular mobility of polymers are deduced from averaging the parameters which characterize heterogeneous relaxation associated by the distribution of activation energies or relaxation times according to continuous distribution spectra. Therefore, with increasing temperature the relaxation times should change monotonically. The presence of discreteness in relaxation phenomena, i.e. the existence of STP, quantization of the relaxation activation energy could be assumed only for the crystalline phase or for objects with very small volumes [16].

It should be mentioned that, the existence of STP has already been confirmed in practice. However, the temperature interval observed in current study may vary due to unknown processes occurring in the system. For example, first and second order reaction equations can be used to describe the kinematics of the temperature dependence of the studied parameters of any physicochemical process. If we take into account the non-uniform distribution of ions in the irradiated polymer, then radiation recombination will correspond to the mono-molecular reaction equation rather than to the bi-molecular equation (as it would be in the case of uniform ion distribution). If the ions are uniformly distributed in the irradiated polymer, the changing rate of charge concentrations will be a single-valued bonding equation during recombination. The rate is then determined according to the bi-molecular kinetic theory,

$$dN/dt = -gN^2 \quad (1)$$

Here N is the number of the charges, and g is the unfolding velocity of molecular mobility in a one mole of substance, defined as,

$$g = g_o \exp\left[\frac{-U_{akt}}{RT}\right] \quad (2)$$

g_o is the limiting velocity at very high temperatures $T \rightarrow \infty$, U_{akt} is the activation energy of charges necessary to leave the traps, R is the universal gas constant, and T is the temperature.

According to the experimental results, the $J - \text{RTL}$ intensity was proportional to dN/dt , passing through a maximum at the temperature corresponding to the maximum of this ratio. If a polymer sample with an initial temperature of T_o , is heated at a constant rate ω , its temperature at time t is equal to

$$T = T_o + \omega t \quad (3)$$

If we use equations (1)-(3), the following differential equation will be obtained:

$$\frac{dN}{dt} = -\frac{g_o}{\omega} N^2 \exp\left(-\frac{U_{akt}}{RT}\right) dT \quad (4)$$

The integral of (4) leads to the following conclusion

$$\frac{1}{N} - \frac{1}{N_o} = -\frac{g_o}{\omega} \exp\left(-\frac{U_{akt}}{RT}\right) \quad (5)$$

According to the condition of maximum intensity of RTL

$$\frac{dI}{dT} \approx -\frac{d^2N}{dT^2} = 0 \quad (6)$$

Then from (5) and (6), the maximum temperature value of T_m , corresponding to the illuminance maximum can be calculated as,

$$\frac{\omega}{N_o} = 2g_o RT_m^2 \exp\left(-\frac{U_{akt}}{RT_m}\right) - g_o \int_{T_o}^{T_m} \exp\left(-\frac{U_{akt}}{RT}\right) dT \quad (7)$$

From eq. (7) it is evident that T_m depends on the ratio of the heating rate to the initial concentration. Experimental data confirm the increase of T_m as ω increases, but for other polymer-based samples, unfortunately, a clear dependence of T_m on ω was not yet established.

The recombination of ions by the first order reaction results in the intensity,

$$I \approx -\frac{dN}{dt} = gN \quad (8)$$

which might explain the deviations between theory and experiment. The proportionality coefficient g in eq. (8) is determined from eq. (2). From eq. (8) and eq. (2), the maximum temperature of RTL intensity can be determined as,

$$\frac{U_{akt}}{RT_m^2} \frac{\omega}{g_0} = \exp\left(-\frac{U_{akt}}{RT_m}\right) \quad (9)$$

and is independent of N_o . From eq. (9), it follows that T_m^{-1} and $\ln \omega$ are directly related to each other. This conclusion agrees well with the obtained experimental results.

The RTL method allows us to determine the activation energy when the light curves have maxima defined by molecular motion. The energy U_{akt} can be determined from the shape of the emission maximum by the following approximate relation.

$$U_{akt} = Ak \frac{T_m \cdot T'}{T_m - T'} = A'' k \frac{T_m \cdot T'}{\Delta T'} \quad (10)$$

Here A - is a constant depending on temperature, k - is Boltzmann's constant, T_m - the temperature corresponding to the illumination maximum, T' - the left-side lower temperature corresponding to the half of the maximal thermoluminescence intensity. The activation energy can also be determined by the following relation,

$$U_{akt} = Ak \frac{T_m^2}{T'' - T_m} = A'' k \frac{T_m^2}{\Delta T''} \quad (11)$$

Here T'' is the right-side temperature at which the illumination intensity is equal to the half of the intensity of the maximum. In both methods (10) and (11), the value of the half of the width of the thermo-luminescence curve is used to determine U_{akt} . The most accurate estimate of the dependence of U_{akt} on the shape of the light curve can be calculated at different heating rates and initial velocities. When using the method of different heating rates, U_{akt} can be calculated using the formula:

$$\frac{\omega U_{akt}}{kT_m^2} = \nu_o \exp\left(-\frac{U_{akt}}{kT_m}\right) \quad (12)$$

Here ω - is the heating rate, ν_o - frequency coefficient. At this time, the activation energy can be determined from the maximum of its dependence $\ln(T_m^2 / \omega) = f(T_m^{-1})$. When determining U_{akt} by the method of initial velocities,

$$I(T) = \nu_o n^p \exp\left(-\frac{U_{akt}}{kT}\right) \quad (13)$$

the initial part of the graph magnification determined by the intensity dependence is used. Where n - is the concentration of charges in a unit volume of substance, p - is the probability that the charges emit quanta in each recombination act. The activation energy for the low-temperature part of the maximum is determined by formulas (10),

and for the high-temperature part by formulas (11).

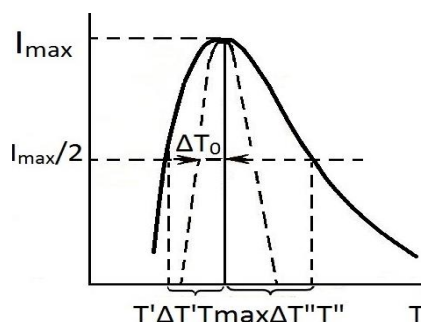


Fig. 2. Schematic representation of the RTL intensity used to determine the effective activation energy

The values of activation energies determined from the states of the 1st, 2nd and 3rd maxima of the experimentally obtained curves for PENP+ x vol.% In_2Se_3 composites by this method are given in the table below.

Table 1. Activation energy of composites PENP+x vol.% In_2Se_3

Composites PENP+x vol.% In_2Se_3	Activation energy of composites					
	I maximum		II maximum		III maximum	
	by Equation 10	by Equation 11	by Equation 10	by Equation 11	by Equation 10	by Equation 11
x=0	14.08	12.51	36	14.2	19.4	11.3
x=3	15.46	27.6	14.93	21.8	18.6	33.4
x=5	22.5	53.3	21.01	9.84	32.2	102.2
x=7	10.5	29.3	9.62	42.05	33.4	92.45
x=10	10.48	17.4	11.3	8.5	19.95	25.2

5 Conclusion

It was revealed that the recorded RTL curves of the compositions depend on impurities and additives and cannot serve as a characteristic of the polymer, impurities or additives separately, but refers to the systems as a whole. Shift of positions of β and γ transitions depending on the content and filler type can serve as a measure of interactions between composites. As a result of studying the RTL spectra, the intensity of the two maxima increases with increasing volume content. Filler and nanoparticles, while the region of spectral sensitivity does not depend on the filler content.

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