

Determination of the Trapping Parameters of TL Glow Curves of Polyacrylamide (PAAM)-Polyvinylalcohol (PVA) Polyblends By Employing Computer Simulation

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Abstract. *The thermoluminescence (TL) glow curves of UV irradiated PAAM-PVA polyblend have been studied. The experimental glow curves show the presence of two peaks with glow peak temperatures at 373K and 479K. The values of activation energy and frequency factors are determined by employing computer simulation. Most of the TL glow curves obey non first order kinetics. The results obtained by using TL experimental technique are correlated with the differential scanning calorimetry (DSC) results. The increase in crystalline component with increase in PVA component in the blend has been confirmed by noting the formation of spherulites around an indenter mark on the blend, employing Optical microscopy.*

Keywords: *Thermoluminescence, trapping parameters, frequency factors, order of kinetics, polyacrylamide, polyvinyl alcohol, differential scanning calorimetry (DSC), optical microscopy.*

INTRODUCTION

Experimental investigations were carried out in polymer blends have gained significant importance, in view of their commercial acceptance, studies on several polymer blends have been reported [1], although the formation of a single phase, homogeneous, compatible blends is thermodynamically unfavorable. Several experimental techniques have been employed to study the polymer blends such as dielectric relaxation [2-3], nuclear magnetic resonance [4-5] and electron spin resonance [6]etc. Thermally stimulated discharge current (TSDC) studies in polyacrylamide(PAAM), studies on electrical conduction phenomena and TSDC studies in polyvinylalcohol(PVA) in the low temperature range viz. below room temperature have been reported earlier[7-11]. Generally in semicrystalline polymers, there will be two α -relaxation processes, one associated with bulk amorphous regions (T_g), which is broader and the other relatively sharper and occur at still higher temperature due to the crystalline

melting of polymer. The secondary relaxations (β and γ) arise in polymers due to the motion of side chains or rotation of pendent groups on thermal stimulation.

The present article is devoted to study the thermoluminescence phenomena in polymer blends of Polyacrylamide (PAAM) and semicrystalline Polyvinyl alcohol (PVA) for single composition, to demonstrate the effect of the crystalline melting and bulk amorphous glass transition in the polymers during the TL process.

EXPERIMENTAL

Polyacrylamide (PAAM) in the form of powder (mol.wt = 5×10^6) and Polyvinyl alcohol (PVA) supplied by BDH, England are employed to prepare the blends. Both PAAM and PVA are water soluble resins. Then polymer blends of PAAM-PVA with different compositions are obtained by evaporation of a solution of these polymers on to glass slides, to yield good quality, optically transparent and mechanically stable polymer blend films.

The TL experiment has been done in a light tight box; by keeping the UV irradiated thin film in front of a UV sensible photomultiplier RCA- 931A. Photomultiplier output current is measured employing the electrometer amplifier, constant heating rate of 5^0 per minute has been maintained during TL experiment.

The glow curves were analyzed with a curve fitting computer program for thermally activated process using a PC. The program uses a linear least square minimization procedure to determine the peak temperature, peak intensity, activation energy and kinetic order. Two different models used in the computer program. In the first model, the glow curve is approximated with the first-order TL kinetics by using the expression

$$I_{TL} = n_0 \cdot s \cdot \exp\left\{-\frac{s}{kT}\right\} \cdot \exp\left\{\left(-s/\beta\right) \int_{T_0}^T \exp\{-E/kT^s\} dT\right\}$$

Where,

$$\int_{T_0}^T \exp\{-E/kT^s\}dT^s = T \exp(-x)[x + 3.0396]/[x^2 + 5.0364x + 4.1916]$$

and $x = E / kT$,

S - frequency factor (sec^{-1})

In the second model, the glow curve is approximated with the second-order TL kinetics by using the expression

$$I_{TL} = n_0^2 \cdot s' \cdot \exp\left\{-\frac{S}{kT}\right\} \cdot [1 + (n_0 s' / \beta)] \int_{T_0}^T \exp\left\{-\frac{E}{kT^s}\right\} dT^s$$

Where, n_0 - the number of trapped electrons (m^{-3}) at $T = 0$;

S' - the frequency factor ($\text{cm}^3 \text{sec}^{-1}$),

E - the activation energy (eV),

T - the absolute temperature (K),

k - Boltzmann's constant (eV K^{-1}),

β - heating rate ($^{\circ}\text{C min}^{-1}$).

RESULTS AND DISCUSSION

Prior to the analysis of TSL glow curves, thermal bleaching technique has been adopted to isolate the glow curves resulted for the PAAm-PVA (1:1) polymer blend. Same heating rate has been maintained during thermal bleaching. Analysis of TSL glow curves of thermally bleached glow curves for PAAm-PVA (1:1) blend has been carried out to evaluate the trap parameters such as activation energies and frequency factors for the TSL emission and to know the kinetics of the mechanism of luminescence. Analysis of TSL glow peaks for PAAm-PVA (1:1) blend as shown in figure 1 has been carried out employing three different methods viz. (i) Initial rise method (ii) Chen's method and (iii) Numerical curve fitting methods for different kinetic processes of luminescence.

(i). Initial rise method

This method was originally proposed by Garlick and Gibson [12] for the analysis of TSL glow curves is approximate. Initial rise method is suitable only for the glow peaks which are well isolated and are well resolved without any overlap of other glow peaks. During the initial rise of the TSL glow peaks for PAAm-PVA (1:1) blend, well below the glow peak maximum (T_{max}) at 373K and 479K, the intensities

of the TSL emission at various temperatures are noted. The values of activation energy in eV for TSL glow curves of PAAm-PVA (1:1) blend are tabulated.

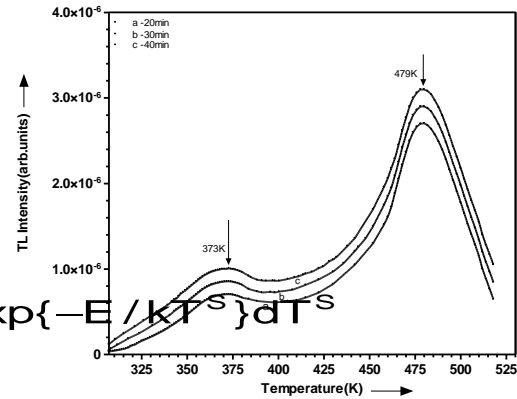


FIGURE 1 Thermally stimulated luminescence (TSL) spectra of PAAm-PVA(1:1) blend

(ii). Chen's method

The analysis of TSL glow curves employing Chen's method [13-14] has been made by determining the form factor (δ/ω) and for various kinetic processes. The total half-width (ω), the low temperature half-width (τ) and the high temperature half-width (δ) of the TSL glow peaks for PAAm-PVA (1:1) blend are noted and the form factor (δ/ω) is evaluated. The activation energies for different kinetic processes are evaluated from the expression given below. Activation energies E_{ω} , E_{τ} , E_{δ} are evaluated from the expression for TSL glow curves of the polymer blend and are tabulated.

$$E_a = C_a k T_m^2 / a - b_a (2 k T_m)$$

(iii). Numerical curve fitting method

Randall and Wilkins [15] have proposed an expression for the luminescent intensity as a function of temperature by following first order kinetics neglecting retrapping probability and Garlick and Gibson [12] have derived an expression for luminescent intensity, by considering the probabilities of retrapping and recombination to be equal, following Second-order kinetics.

For various iterations of the values of activation energy (E) for the TSL glow peak temperature of PAAm-PVA (1:1) blend at 373K, the value of E for which the mean square deviation (MSD) is minimum and is considered to be the best fit.

Theoretical glow curves are generated for various values of E for the glow peak temperature of PAAm-PVA (1:1) blend at 373K, using the first and second order kinetic equations. Computer simulated glow curves of PAAm-PVA (1:1) blend at 373K for various iterations of the values of activation energy (E) employing second order kinetics is as shown in figure 2. The experimental and theoretical curves are normalized to the same peak intensity; the theoretical curve obtained is plotted on isolated experimental TSL glow curve of PAAm-PVA (1:1) blend. The best fit corresponds to the least deviation between the two curves by using second order kinetics is as shown in figure 2.

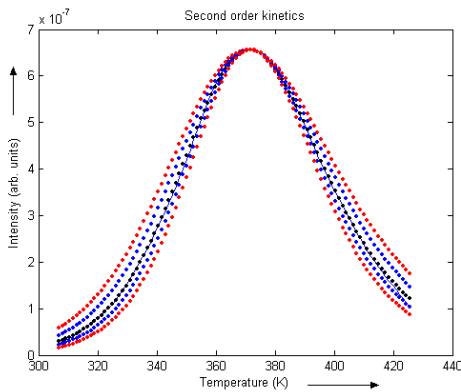


FIGURE 2. Computer simulated glow curves of PAAm-PVA (1:1) blend at 373K for various iterations of the values of activation energy(E) in eV employing second order kinetics, solid line is experimental curve, dotted lines are theoretical curves

For various iterations of the values of E for the TSL glow peak temperature of PAAm-PVA (1:1) blend at 479K, the value of E for which the mean square deviation is minimum and is considered to be the best fit.

Theoretical glow curves are generated for various values of E for the TSL glow peak temperature of PAAm-PVA (1:1) blend at 479K, using the first and second order kinetic equations. Computer simulated glow curves of PAAm-PVA (1:1) blend at 479K for various iterations of activation energy (E) employing second order kinetics is as shown in figure3. The experimental and theoretical curves are normalized to the same peak intensity; the theoretical curve obtained is plotted on the isolated experimental TSL glow curve of PAAm-PVA (1:1) blend. The best fit corresponds to the least mean square deviation between the two curves by using second order kinetics is as shown in figure 3. The second order curve fitting is considered to be the best fit to the isolated experimental TSL glow curve.

Thermally bleached two isolated TSL glow curves and total experimental TSL glow curve are plotted as shown in figure 4.

Figure 5 shows the DSC (Differential Scanning Calorimetry) thermogram recorded for the PAAm-PVA (1:1) polymer blend. The endothermic peak at 318 K is attributed to the γ -relaxation. The broader endothermic peak is associated with the secondary β -relaxation of the blend partners within the blend and is broader covering the temperature range 353-440 K. The two endothermic peaks at 498K and 558K, one is associated with glass transition of PAAm-PVA blend, which is broader, the other relatively sharper which is associated with the crystalline melting of PAAm-PVA blend and is attributed to the α -relaxation processes.

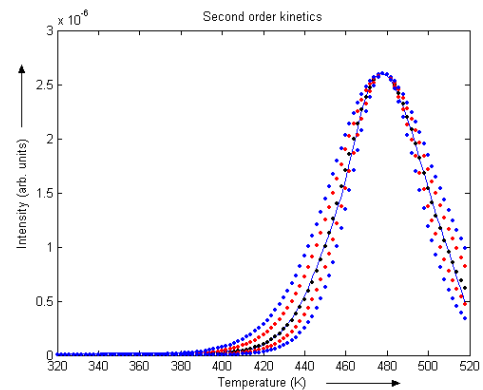


FIGURE 3. Computer simulated glow curves of PAAm-PVA (1:1) blend at 479K for various iterations of the values of activation energy(E) in eV employing second order kinetics, solid line is experimental curve, dotted lines are theoretical curves

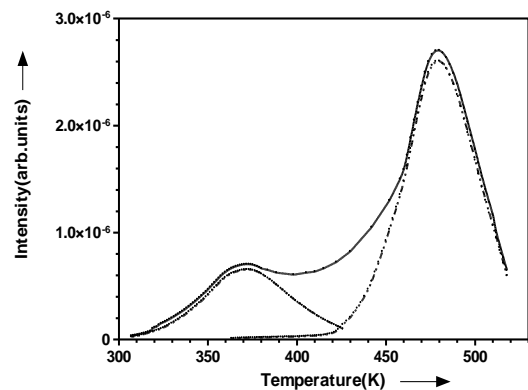


FIGURE 4. TSL glow curve for PAAm-PVA(1:1) polymer blend. Curve (1)- TSL spectrum of PAAm- PVA(1:1)blend, curve(2)-TSL curve after thermal bleaching and curve(3)- point by point subtraction of curve(2) from curve(1)

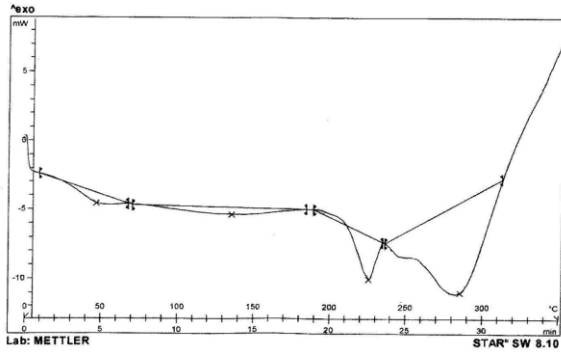


FIGURE 5. DSC thermogram of PAA-PVA(1:1) blend

The increase in crystalline component with increase in PVA component in the blend has been confirmed by noting the formation of spherulites around an indenter mark on the blend, employing Optical microscopy, as shown in figure 6.

These experimental results are correlated with the results reported earlier for both the individual polymers [7] and semicrystalline polyvinyl alcohol[8]. The present article demonstrates the elegance of TSR technique to sense the crystalline component of a PAAm-PVA blend. These results are in close agreement with the results reported earlier for the same blend [16] for different compositions of the constituent homopolymers employing differential scanning calorimetry, in which the glass transition temperature (T_g) of the blend is found to increase with the increase in content of the semicrystalline PVA component.

TABLE 1. Trapping parameters of glow peaks of Polyacrylamide(PAAm) -Polyvinylalcohol(PVA) blend

Glow peak temp. (K)	Method	Activation Energy (eV)	Parameter
373	Initial rise method	0.5161	-
	Chen's method	$E_0= 0.6553$ $E_r= 0.6199$ $E_\delta= 0.6836$	Form factor $\delta/\omega = 0.516$ second order
	Curve fitting method	0.6570	Frequency factor ($\text{Cm}^3\text{Sec}^{-1}$) $1.8887\text{e}+008$
479	Initial rise method	1.1911	-
	Chen's method	$E_0= 1.3463$ $E_r= 1.3264$ $E_\delta= 1.3528$	Form factor $\delta/\omega = 0.509$ second order
	Curve fitting method	1.3330	Frequency factor ($\text{Cm}^3\text{Sec}^{-1}$) $3.3534\text{e}+013$

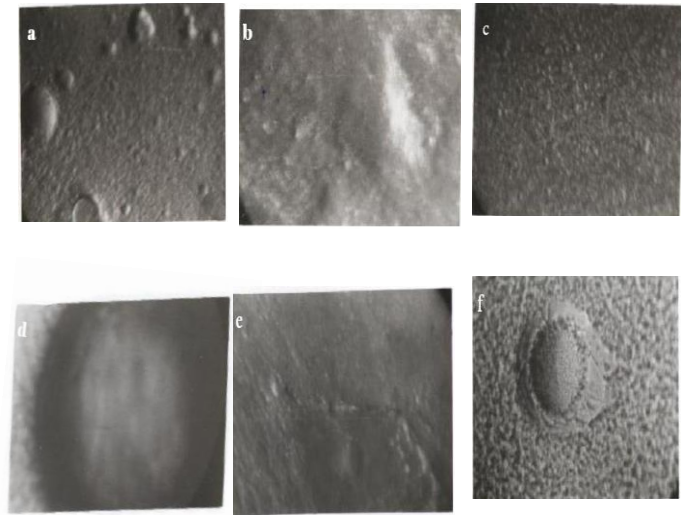


FIGURE 6. Optical micrographs for (a) PAA (b) PAA:PVA (1:1) (c) PVA (d) PAA:PVA (1:1)-crystalline region around indenter mark (e) PAA:PVA (1:2) (f) PAA:PVA (1:2) blends -region around indenter Mag.500X

CONCLUSIONS

Experimental investigations on thermally stimulated luminescence (TSL) in PAAm-PVA blends have been made and results are correlated with the results obtained from differential scanning calorimetry (DSC) and Optical microphotography, the following conclusions are made.

The presence of crystalline component viz. semicrystalline PVA component in the blend, resulted in a higher temperature TSL glow curve, which is relatively more sharp than that resulted due to the glass transition region. This result indicate that the detrapping of charge carriers due to large scale macromolecular motion near glass transition temperature, occur at a relatively lower temperature than the detrapping of charge carriers due to large scale macromolecular relaxations in the crystalline regions during thermal stimulation.

The above conclusion is further supported by the result that, an increase the crystalline component in the blend as resulted in a shift of the crystalline TSL peak to a higher temperature. Further, this shift in the crystalline TSL glow curve with increase in the crystalline component is also accompanied by a simultaneous disappearance of 430K glow peak near the glass transition. Thus, the TSL technique is more elegant in sensing the crystalline component in the blend.

Studies on the Differential scanning calorimetry (DSC) of the PAAm-PVA blend show four endothermic peaks at 318K, 353-440K, 498K and 558K, which are correlated to TSL glow peaks.

The increase in crystalline component with increase in PVA component in the blend has been confirmed by noting the formation of spherulites around an indenter mark on the blend.

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