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RESEARCH ARTICLE

Thermally Stimulated Relaxations And Electrical Conductivity Studies Of Polyacrylamide- Polyacrylic Acid Blends.

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ABSTRACT

Thermally stimulated relaxations (TSR), employing thermally stimulated luminescence (TSL) and conductivity (TSC) as experimental techniques have been studied in Polyacrylamide-Polyacrylic acid (PAAm-PAA) blends; in the temperature range of 300-490 K. Measurements of electrical conductivity (σ) as a function of temperature; of the blends have been made. These studies are undertaken mainly (i) to establish the compatibility of the constituent polymers to form a homogeneous blend with a single phase or heterogeneous to form multiphase component system (ii) the compositional dependence of the polymer compatibility and (iii) to study the mechanism of electrical charge transport phenomena in relation to the macromolecular relaxation and transitions in polymer blends. The appearance of TSL/TSC glow curves is attributed to the detrapping of charge carriers facilitated by the primary and secondary relaxations; the transition temperatures, at which there are changes in slopes for $\log \sigma$ vs $1/T$ plots indicate the on-set of various relaxations of polymer blends. Experimental results obtained by TSL/TSC are correlated and analyzed to establish the compatibility of the constituent polymers in the blend, for various compositions.

Keywords: Thermally stimulated relaxations (TSR), Thermally stimulated luminescence (TSL), Thermally stimulated conductivity (TSC), Polyacrylamide (PAAm), Polyacrylic acid (PAA), electrical conductivity.

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INTRODUCTION

Polymers' blending is widely accepted in the industry for the production of polymeric materials with specific applications. The degree of compatibility [1, 2] plays the major role in the blending of polymers. However, the degree of compatibility is very much dependent over the interaction between the polymeric phases of the polyblend. The interactions between polyacrylamide (PAAm) and poly (acrylic acid) (PAA) have been studied in recent years using fluorescence spectroscopy and viscometry [3-7]. Interpolymer complexes resulting from these interactions possess unique properties which are different from those of the individual components [8]. Miscible polymer blends are receiving more importance in industrial applications [9, 10]. Experimental investigations on polymer blends are interesting and useful; since these materials with desired and optimized physical properties can be achieved; by suitably monitoring the composition of the blend partners. The existence of strong intermolecular forces and ability of the macromolecules to form interpenetrating networks, govern the polymer miscibility at molecular level, so as to form a single homogeneous, compatible blend. Although, a homogeneous polymer blend formation is thermodynamically unfavorable; a number of polymer blends with varying properties have been studied [11, 12]. Several experimental and spectroscopic techniques have been employed to study the compatibility of polymer blends; such as nuclear magnetic resonance (NMR) [13], dielectric depolarization relaxation [14] and spin labeled electron spin resonance (ESR) [15].

The most widely used method to evaluate compatibility is to determine the transition temperature. Compatible polymers are considered to be those which form single-phase blend with a single glass-transition temperature (T_g) dependent on the composition of the blend. Polymer blends which exhibit two or more glass transition temperature values (T_g) corresponding to the individual components are considered as incompatible. When phase domains are larger than several hundred angstroms, two distinct T_g values are observed, in a two-component incompatible blend.

The technique of thermally stimulated relaxation (TSR) [16, 17], however is considered to be relatively simple, economical and elegant method of studying molecular relaxations and transitions in polymer blends; and has been undertaken in the present investigations. Measurements of electrical conductivity (σ) as a function of temperature, in conjunction with the TSR studies to elucidate the mechanism of charge transport in relation to the macromolecular relaxations. The detrapping of the charge carriers facilitate the on-set of macromolecular relaxations in PAAm-PAA polymer blends.

EXPERIMENTAL

Polyacrylamide (PAAm) $[-CH_2-CH(CONH_2)-]_n$ and Polyacrylic acid (PAA) $[-CH_2-CH(COOH)-]_n$ in the form of powder have employed in the present investigations. Thin polymer films of PAAm-PAA blends have been obtained by evaporation of a solution of PAAm and PAA in methanol and water on to glass slides. UV-irradiation of these thin films has been carried out employing 300 W Xenon lamp.

Electrical conductivity measurements of PAAm-PAA blend films were carried out employing a linear array of Four-point probe technique [18, 19]. The surface on which probes rest was mechanically lapped to ensure good electrical contact. The probes had an equal spacing of approximately 0.8 cm and the tips of the probe are coated with Zinc for good electrical contact. Different voltages (V) have been applied to the outer two probes and resulting current (I) between the inner two probes has been measured; by connecting electrometer amplifier in series with the inner two probes. The sample holder with four probes was kept in an oven, to vary the temperature of the specimen. The temperature of the sample could be monitored to an accuracy of $\pm 1^0$ C; using a digital temperature controller. The temperature controller may set to any desired temperature; the test sample was stabilized to this temperature, prior to the conductivity measurements. Electrical conductivity (σ) was evaluated using the expression $\sigma = I / 2\pi SV$, where I is the current in amperes, V is the voltage applied in volts and S is the probes spacing in cm.

The TSC of UV-irradiated PAAm- PAA films have been measured by keeping the film in between two electrodes; to which a suitable voltage (200-300 V) is applied. The resulting current is measured by connecting Keithley model 610C electrometer, in series with the metal electrodes. The polymer film is held between the electrodes, using a spring loading arrangement and the sample assembly was kept in an electrically powered oven to vary the temperature. Heating rate of 5^0 min^{-1} has been employed during thermal scan of the polymer film.



The TSL experiment has been done in a light-tight box; by keeping the UV-irradiated thin film in front of a UV sensitive photo multiplier RCA-931A. Photo-multiplier output current is measured employing the electrometer amplifier. Constant heating rate of $5^{\circ} \text{ min}^{-1}$ has been maintained during TSL experiment.

RESULTS AND DISCUSSION

The TSC spectra for PAAm-PAA (1:1) polymer blend are as shown in fig1; which show four glow curves with maximum at 322, 343, 445 and 467 K. The TSL spectra for PAAm-PAA (1:1) polymer blend is as shown in fig 2; which show two glow curves with maxima at 372 and 493 K. Curves A, B and C in both TSC and TSL spectra, show the glow curves recorded for UV-irradiated samples for 20, 30 and 40 minutes respectively. The intensities of these glow curves are found to increase with the dose of irradiation; the dose being controlled by the time of irradiation.

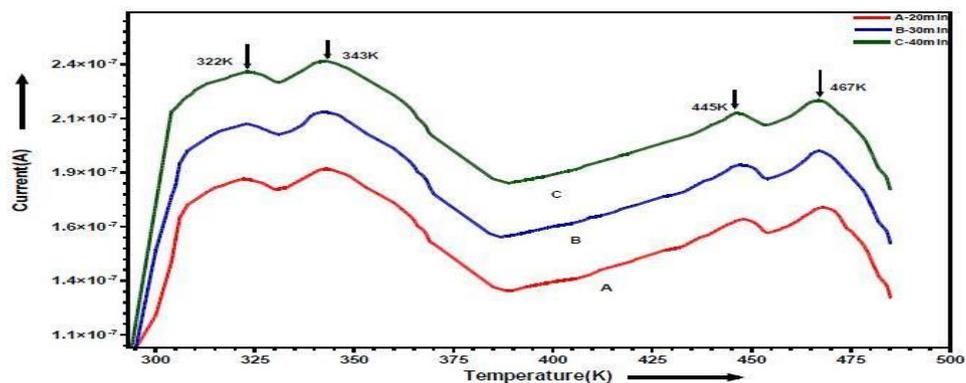


Figure 1: Thermally Stimulated Current (TSC) spectra of PAAm-PAA (1:1) blend

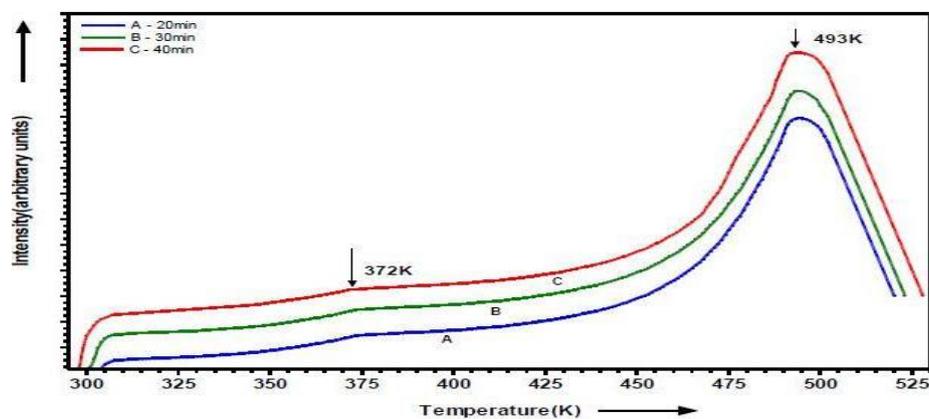


Figure 2: Thermally Stimulated Luminescence (TSL) spectra of PAAm-PAA (1:1) blend

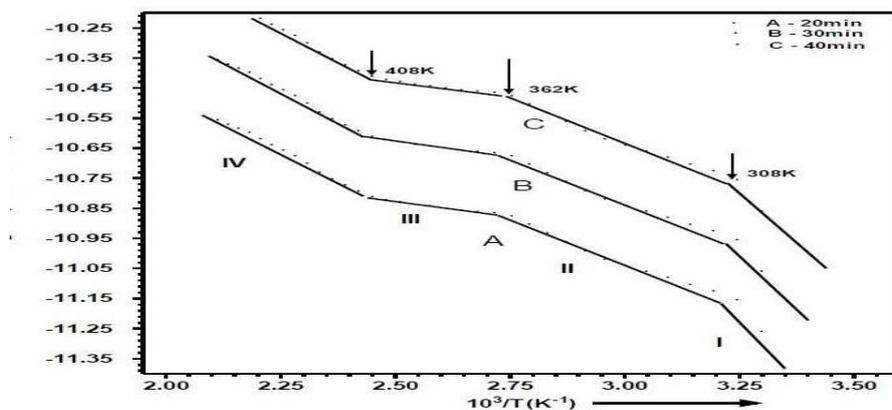


Figure 3: $\log \sigma$ Vs $1/T$ plots for PAAm-PAA (1:1) blend

Fig 3 shows the $\log \sigma$ vs $1/T$ plot for UV-irradiated PAAm-PAA (1:1) polymer blend; which show four distinct straight regions, marked I, II, III and IV. These lines show change in slopes at 308, 362 and 408 K.

The higher temperature TSC/TSL glow curves of the polymer blend (1:1) are associated with the primary glass-rubber transition (α -relaxation). The charge carriers generated and trapped on irradiation of the polymer blend; are considered to be released due to the on-set of large-scale macromolecular motion, involving the motion of the back bone chains of the polymer blend, near the glass transition temperature. The detrapping of charge carriers is facilitated by the on-set of macromolecular motion.

In respect of PAAm-PAA (1:2) polymer blend; the TSC spectra are as shown in fig 4. The glass transition temperature region is broader and the higher temperature peaks have shifted towards lower temperatures (438 and 460 K TSC peaks). The presence of two T_g glow curves in the glass transition region indicate that, for 1:2 composition, the blend, has two phases and polymer blend is incompatible.

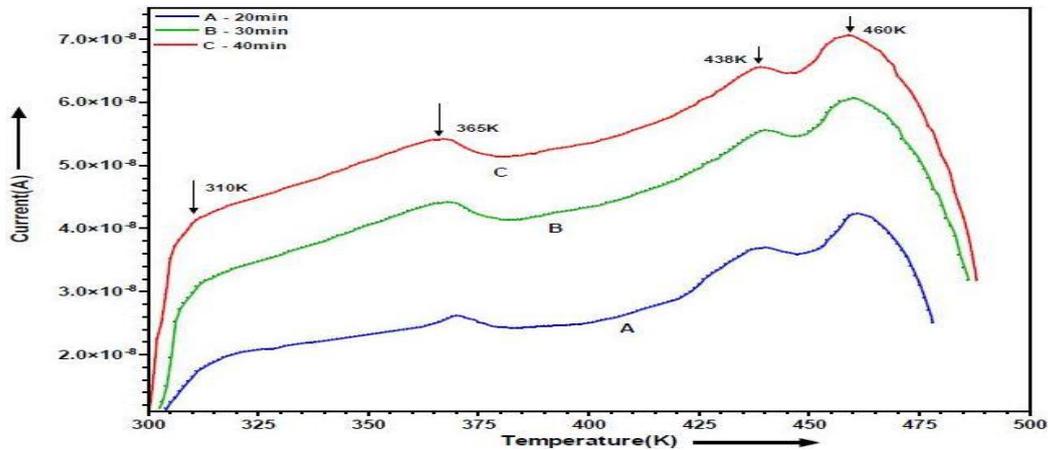


Figure 4: Thermally Stimulated Current (TSC) spectra of PAAm-PAA (1:2) blend

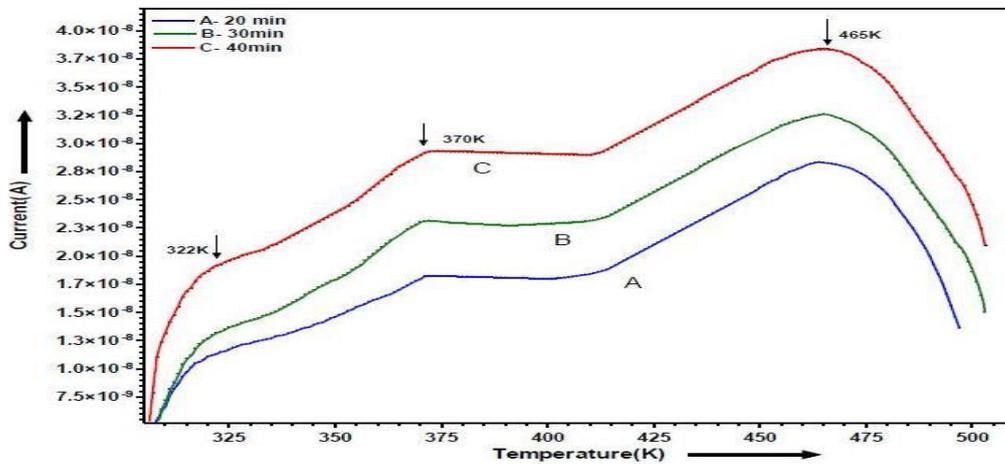


Figure 5: Thermally Stimulated Current (TSC) spectra of PAAm-PAA (2:1) blend.

The TSC spectra for PAAm-PAA (2:1) polymer blend is as shown in fig 5, which shows a broad glass transition region with a single glass transition maximum temperature (T_g) at 465 K; which indicate that the polymer blend is a homogeneous, single phase compatible polymer blend.

The lower temperature glow curves in both TSC and TSL are considered to be due to the emptying of the charge carriers, which are trapped at lower trap depths relative to the higher temperature, the detrapping is facilitated by the secondary (β -relaxation); which arise due to the side chain molecular motion or rotation of pendent groups.



The broader glass transition temperature region in TSC/TSL glow curves; the broadening is attributed to the presence of polydispersity of the constituent polymers of the blend i.e., presence of macromolecules of different molecular weight. The transition temperatures, at which there are changes in slopes, in the $\log \sigma$ vs $1/T$ plots; indicate the on-set of secondary and primary macromolecular relaxations in the polymer blend.

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