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TSDC STUDY ON PURE PVF AND PVF/PVDF ISOMORPHIC POLYBLENDS

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Abstract:-Thermally stimulated depolarization currents (TSDC) have been measured in short-circuit configuration as the function of temperature, field and composition on pure PVF and polyblends containing different wt% of poly (vinly fluoride) (PVF) and poly (vinlylidene fluoride) (PVDF). DSC thermo gram was used to characterize the Tg of pure PVF and PVF/PVDF polyblend (i.e. 50:50). To evaluate the polar C-F group in pure PVF and PVF/PVDF polyblends FTIR spectrum was used. Such measurements have clearly indicated that polarization in pure PVF and PVF: PVDF polyblends arise due to dipolar orientation and trapping of injected space charge carriers. The polarization phenomenon is modified on blending PVDF in PVF. The electrets made of PVF: PVDF polyblends store considerable amount of charge for a sufficiently long period of time.

Keywords:PVF, PVDF, Isomorphic Polyblend and TSDC

INTRODUCTION

The development of new polymeric materials through blending is experiencing a period of tremendous growth. The ability to tailor properties through a combination of materials to meet a unique set of specification is a key force driving this growth. There is no doubt that the main reason for blending, alloying etc. is economical; a material can be generated at a lower cost with properties meeting desired specifications. Although, full set of desired properties are hard to achieve, but can definitely be explored by selecting the components in such a way that the principal advantages of the first polymer will compensate for deficiencies of the second, and vice-versa.

A careful screening of the literature available gives an idea about the extent to which work has been done in case of the two polymers polyvinyl fluoride (PVF) and polyvinyldene fluoride (PVDF), when they are taken together mostly as in isomorphic situation [1-3]. Isomorphism is believed to be possible when the polymer chains (blend) or monomer units (co-polymer) are similar in conformation and size in the crystalline state. PVF and PVDF, which are vinyl fluoro polymers, have good weather resistance and are used for outdoor applications. PVDF is reported to be piezoelectric and also apparently ferroelectric in nature. Since PVDF is moldable, hence transducers are readily fabricated. The manner of blending the two polymers affects the resultant properties, like impact strength, hardness, toughness tensile strength and electrical breakdown strength etc.1.   Most of the interesting physical properties of polymers are attributed to molecular motions, which are very complex. These motions are evident from relaxation measurements such as mechanical relaxation and dielectric relaxation. One favorable method of assessing the dielectric properties of polymers is to carry out thermally stimulated depolarization current (TSDC) measurements. After a thermal conditioning phase, the sample is subjected to a chosen regime of electric field and temperature ranges. The result is assessed by finally heating the sample, usually at a linear rate, and observing the resulting peaks of current thermo grams. Originally this technique was used to measure charge detrapping in low-molecular-weight-organic and inorganic compounds. Since the technique is straight forward, it has been extensively used for studying the fundamental mechanisms of charge storage and transport in non metallic solids. Hence, the present status of experimental and theoretical development of TSDC is such that there is an enormous number of an experimental paper and a large number of theoretical models formulated to clarify the experimental data obtained on various charge storage and transport mechanisms and the interpretation of the observed TSDC peak structures.

The shape of TSDC thermo gram depends on the phenomenon causing the storage of charge and the area under the thermo gram is proportional to the total charge stored in the electrets. However, apart from charge estimation TSDC thermo grams can also be used for obtaining information about the distribution function for relaxation times and activation energies,

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and also dielectric constants at ultra low frequencies. The shape of TSDC curves is sensitive towards internal parameters like activation energy, trap depth and relaxation times and the experimental parameters like heating rate, forming and storage temperature forming time and field [4,5]. Valuable information regarding these internal parameters can, however, be obtained by a set of TSDC experiments with suitable experimental conditions. Thus, the advances made in TSDC techniques have offered immense possibilities for studying various relaxation processes in pure and blended polymeric dielectrics [6]. The technique is particularly suited for investigating the fine structure of polymers: semi crystalline polymers, copolymers and blends, polymer complexes and resins. TSDC also appears to be uniquely suited for determining the influence of additives, dopants, plasticizers, and water content. The present paper reports the results of careful investigation of thermally stimulated depolarization currents in pure PVF and PVF: PVDF polyblends with the view to understand the nature of charge storage and transport in these polymers

EXPERIMENTAL

Material used

For preparation of pure and polyblend samples, commercially available polymers; poly (vinyl fluoride) (PVF) (BDH UK), molecular weight 126,000 and poly (vinylidene fluoride) (PVDF) (Aldrich, USA) molecular weight 140,000 in powder forms were used as received.

Thin film Preparation

The solution cast technique has been used to prepare pure and polyblend specimens of PVF and PVDF. The two polymers were dissolved in their common solvent dimethyl formamide (DMF), at a temperature of 60^0C with constant stirring. A known quantity of the homogenous solution obtained was poured on a glass plate floating over mercury pool inside a microprocessor-controlled oven. The solvent was allowed to evaporate at 60^0C over a period of 6 hours. Thus the specimens obtained were in the form of thin films of thickness of ±25 micron (approx).

CHARACTERIZATION

FT-IR

The Fourier Transform Infrared Spectrum (FT-IR) of pure PVF, PVDF and their poly blend specimens were obtained with FTIR-LX 18-5255 instrument, Perkin Elmer, Singapore.

DSC

Modulated Differential Scanning Calorimetery (DSC) (TA Instrument model 2910), Perkin Elmer, Singapore was used to characterize the glass transition temperature (T_g), in the temperature range from -800 to 40^0 C. Liquid nitrogen was used to undergo the temperature up to -80^0C at the rate of 10^0C/min.

TSDC Measurement

For TSDC measurements the samples were vacuum aluminized over a central circular area of 5 cm diameter. Such metallized samples were then polarized to saturation with various fields of 80 and 100 kV/cm at polarizing temperature of 40, 60, 80 and 100^0C. The field was applied for 45 min. after which the sample was cooled to room temperature in a period of another 45 min., the total time of polarization was adjusted to 1 and ½ hr. in each case. The samples so polarized were then depolarized by reheating at a linear rate of about 4°C per min. and the depolarization current was recorded using Keitheley Electrometer model 61^0C.

RESULT AND DISCUSSION

The polarization in a thermally charged specimen may arise due to various mechanisms, the important amongst which are orientational or dipolar polarization, translational or space charge polarization and interfacial polarization. The charge originated in TSDC due to dipolar orientation or trapping of space charges in defect or dislocation sites is known to give rise to a uniform polarization, which is heterocharge. On the other hand, space charge build up by migration of ions over microscopic distance gives a non uniform heterocharge, whereas trapped injected space charge results in a no uniform homo- or hetero-charge depending upon the work function of the metal electrode.

The decay of heterocharge during TSDC gives a current in a direction opposite to that of the charging current or negative current while decay of homo charge results in a current in the same direction as the charging current called positive

current. The classical theory of Gubkin [7] Perlman [8] and others for the decay of charge in a charged dielectric assumes the superposition of homo charge and hetro charge. Homo charge is produced by the discharge in air gap between the poling electrode and the surface of the sample and is the space charge consisting of ions and electrons. Its relaxation time is assumed to be the product of the resistance R and capacitance C of the sample as shown in the eqn. (1),

$$\sigma_{homo} \quad \sigma 0 \exp(-t/RC) \quad \sigma_o \text{ -------------- } (RC \gg 1) \qquad \text{----------eqn. (1)}$$

Since the electrical insulation of polymers is very good, we may assume the relaxation time RC is much larger than the time of observation. Then the homo charge is approximated to be its initial value σ_0 as shown in eqn. (1)

The decay constant of heterocharge is given by

$$\sigma_{homo} \quad \sigma_{f0} \exp(-\alpha t) \qquad \text{----------eqn. (2)}$$

At low temperature the decay of heterocharge appears to be mainly caused by the disorientation of dipoles. The initial value of hetro charge is denoted by σ f0 in eqn. (2). At t = 0 when the poling process is finished, the initial value of charge s 0 is given by $\sigma_0 = \sigma_0 + \sigma_{f0}$ and the sign of charge correspond to the effective charge.

Polar polymers show two main relaxations designated as α- and β- relaxations. The α- relaxation arises due to the main chain segmental motion and occurs around and above Tg. The β- relaxation occurs in the glassy state of the polymer and is due to the hindered rotation of polar side groups around carbon-carbon link of the main chain. If there are polar groups in the polymers, side chain capable of orientation in an electric field independent of one another and having different relaxation times, two separate - relaxations are observed. Each relaxation process gives rise to a peak at its characteristic temperature during TSDC.

The depolarizing current recorded in the present investigation was found to flow in the same direction as that of the charging current or positive current and thus always corresponded to homo charge. Hence, processes responsible for homo charge formation are dominant in the present case. This homo charge may arise due to trapped injected space charge.

The initial value of current is always high indicating that there exists a relaxation at temperature lower than the room temperature, and which could not be observed in the present investigation. In pure PVF film it could be due to molecular motions in the amorphous region of the polymers, while in the PVF: PVDF polyblends, it could be due to molecular motions in the crystalline regions or the amorphous regions.

From the various thermo grams (Figs. 1-4) it is evident that no clear current peaks are observable; nevertheless, the behaviour of TSDC thermo grams can be understood in the light of reported relaxations in PVF and PVDF. PVF is an amorphous polymer with polar C-F groups symmetrically arranged cleared by FTIR spectrum (Fig. 5) and its glass transition temperature is -12^{0}C as shown by DSC thermo gram (Fig. 6). Molecular relaxations occurring in pure PVF film have not been properly reported, it however exhibits piezoelectricity and pyroelectricity of approximately one third of that observed in polarized PVDF [9, 10].

α- relaxation was investigated and attributed to amorphous regions as well as crystalline regions [11-12]. Later on convincing evidence of a crystalline transition was reported [13]. The β– relaxations in PVDF have been attributed to micro-Brownian motion of amorphous segments [14, 15]. It is related to glass transition and occurs around (-40^{0}C). Another β'- relaxation has also been reported to occur at 50C. This occurs in amorphous region and has been attributed to chain fold motion. The τ-relaxation has been observed at around –70C and is associated with chain relaxation in amorphous regions [16].

From the various curves exhibiting effect of polarizing field on the TSDC thermo grams, it is clear that in case of pure PVF the discharge current increase in magnitude with increase in the polarizing field and the polarizing temperature. Increase in temperature increases the flexibility of polymeric chains, and mobility of intrinsic space charges and injected charges. The charges are trapped in various available sites in the bulk of the polymer. The number of such charges increases with increase in the magnitude of applied step field resulting in increase in the polarization of the polymer. It has been observed that for high polarizing temperatures, the discharge current decreases with increase in the applied field but for moderate field it again shows an increase in magnitude. For very high fields and moderate temperatures it again exhibits a decrease. This can be explained in terms of localization of space charges in shallow and deep traps. At low temperature, the charges are trapped in shallow traps. Under the conditions of high temperatures, the space charges have high mobility and consequently the charge carriers are shifted to deeper traps. The detrapping of carriers from such traps requires high activation energy making their release difficult. As a result the discharge current decreases. As the step field increases the number of intrinsic and injected space charges increases again filling shallow traps as well as the deeper traps, the current thus shows increase in magnitude. At very high temperatures when the carrier mobility is quite high and under the strong directing action of the applied field of large magnitude it appears that the charges with increased mobility are shifted and trapped in deeper traps resulting in the decrease of discharge current. Under the condition of very high temperature together with very high field, the number of charge carriers generated/injected increases enormously occupying various shallow as well deep traps. The detrapping of a large number of such charge carriers during discharge cycle gives a current increased considerably in magnitude as observed in case of 80 kV/cm and 100 kV/cm field in the present investigation.

From the spectrum and thermo gram of FTIR and DSC (Fig. 7 and 8) it is evident that the depolarization current behaviour is modified considerably on blending PVDF with PVF (i.e. 50:50 wt %). The discharge current in case of PVF: PVDF:: 90:10 and 70:30 samples is less than that in pure PVF (Fig. 9, 10).

However, magnitude of discharge current in 70:30 blend is larger than that in 90:10 blend. Further, the decrease in current magnitude with increase in field is observed now at lower temperature instead of moderate temperature as in case of pure PVF. This can be understood in terms of modification in trap structure of the polymer system such that initially a net decrease in the number of sites available for trapping of charge carriers results in decrease in discharge current. It may also happen that even under condition of lower temperatures the space charges have mobility sufficient enough that they are shifted to deeper traps, and are localized there resulting in decrease in the depolarization current. The local energy levels are, therefore, affected by modification in their molecular environment resulting in band structures shaped by potential barriers with every atom or group of atoms having its own modified energy level. This randomization will cause corresponding randomization of trap depths. Several kinds of traps exist in polymers. Structural defects such as carbonyl groups or double bonds yield shallow or intermediate trapping levels in polymers, while foreign molecules and structural modification i.e. branching and crystallinity are responsible for deeper traps. As the wt% content of PVDF is increased to 30% i.e. in case of 70:30:: PVF:PVDF blend, the trapping sites are increased again such that the discharge current is greater than that of 90:10 blend but less than pure PVF specimens. The discharge current is therefore, expected to increase as observed in the present case. The 70:30 blend samples are characterized by a hump located in between 45-55C, which become clearer for samples charged at higher temperatures. These blends retain considerable amount of charge up to sufficiently high temperatures indicating again that charges are localized in deeper traps from where their release requires high activation energy. The hump appearing at 45-55°C may be attributed to relaxation associated with chain fold motions in the amorphous region of PVDF. This is further confirmed by the fact that it is more clearly developed in case of 50:50 blends (Fig. 11, 12).

Decrease in depolarization current in case of blends and modification of trap structure on blending can also be understood in terms of number of shallow and deep traps. It appears that traps in case of pure PVF are mainly shallow traps in which the space charges are trapped and localized. Blending of PVDF with PVF result in increase in the number of deeper traps. Localization of charge carriers in deeper traps leads to a decrease in the depolarization current. This is because detrapping of charge carriers from such traps requires higher activation energy. The depolarization current has, however, been found to be greater in case of 70:30 blend Fig. 9-12. As the wt% content of PVDF increases, number of shallow traps also increases. More space charge is trapped in these blends during charging resulting in a higher depolarization current. Low magnitude of depolarization current can further be explained in terms of contribution of dipolar orientation to polarization. Crystallization of polar phase of PVDF (- phase) is reported to take place in presence of PVF [17] in PVF: PVDF blends. Further, structural changes in PVDF from known polar form II to an intermediate polar form II have also been reported to be induced by an applied high electric field (~2 X 10^8 Vm^{-1}). At fields higher than this further transition from intermediate polar form II to the polar form I.

The contribution of net dipole orientation to total polarization is expected to be modified with increase in the PVDF content. Dipole orientation, however, results in heterocharge, which gives in current in a direction opposite to that of the homo charge current, or a negative discharge current. The net charge is superposition of hetro charge and homo charge. However, the large homo current in view of excessive trapping is expected to overcome the hetro charge current so that the sign of the current corresponds to that of the homo charge.

CONCLUSION

Thermally stimulated depolarization currents measured in short circuit configuration have indicated that polarization in pure PVF originates from homo space charges in the amorphous regions. Space charges are localized in various traps in case of pure PVF these are mainly shallow traps. Blending PVDF with PVF; modifies considerably the trap structure of PVF. Structural modification increases the number of deeper traps in the blend such that polyblend samples retain considerable amount of charge up to considerably higher temperatures i.e. for longer periods of time. Orientation of molecular dipoles is also found to contribute to a certain extent to the total polarization in the blend samples. Thus polyblends of PVF/PVDF may be used as storage device at high temperature in microelectronics.

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LEGEND TO FIGURES

Figure 1. Temperature dependence of discharge current of pure PVF, 100:00 at 80 kV for different polarizing temperature.

Figure 2. Temperature dependence of discharge current of PVF: PVDF: : 90:10 at 80 kV for different polarizing temperature.

Figure 3. Temperature dependence of discharge current of PVF: PVDF:: 70:30 at 80 kV for different polarizing temperature.

Figure 4. Temperature dependence of discharge current of PVF: PVDF::50:50 at 80 kV for different polarizing temperature.

Figure 5. FT-IR spectrum of pure PVF.

Figure 6. DSC thermogram of Pure PVF.

Figure 7. FT-IR spectrum of PVF/PVDF i.e. 50:50.

Figure 8. DSC thermogram of PVF/PVDF i.e. 50:50.

Figure 9. Discharging current with different composition of PVF and PVDF at 80 kV and 40 Tp for 60 °C and 80 °C.

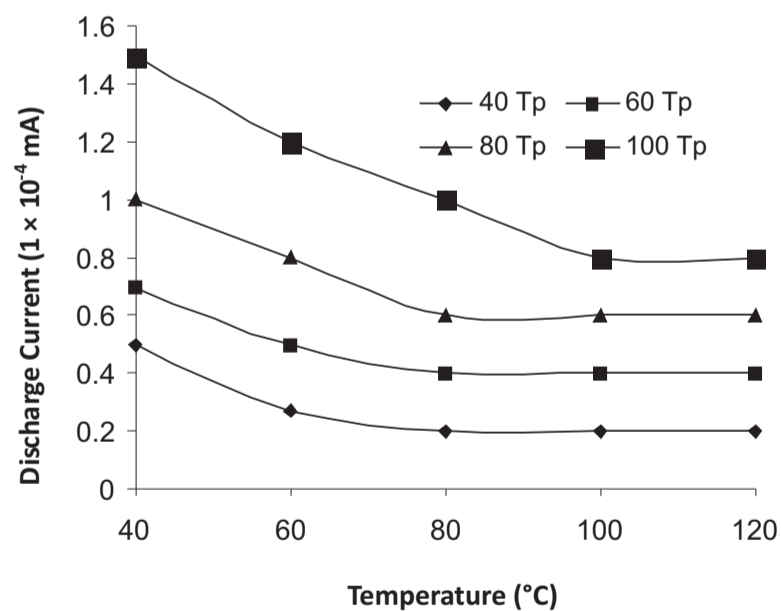Figure 10. Discharging current with different composition of PVF and PVDF at 80 kV and 60 Tp for 60°C and 80 °C.
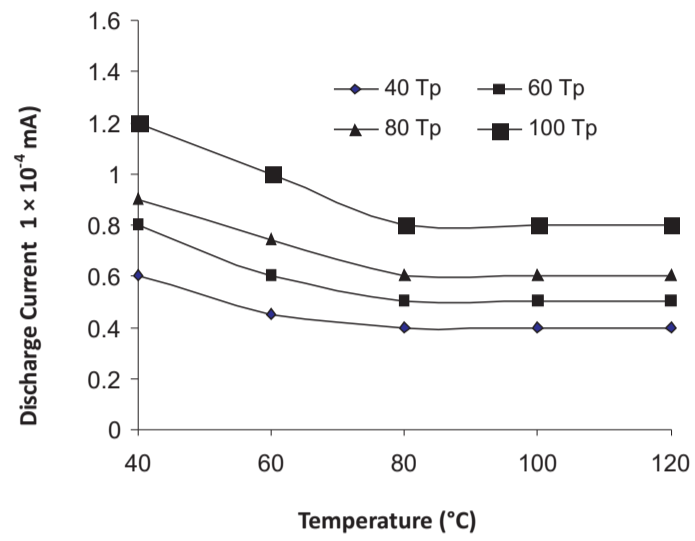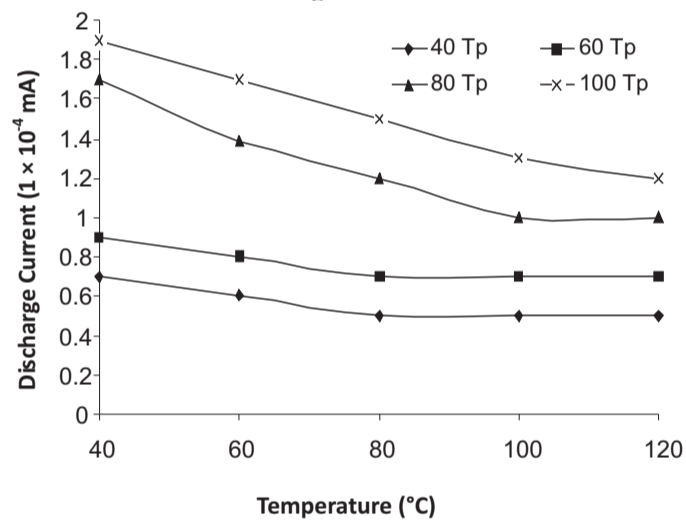
Figure 11. Discharging current with different composition of PVF and PVDF at 80 kV and 80 Tp for 60 °C and 80 °C.

Figure 12. Discharging current with different composition of PVF and PVDF at 80 kV and 100 Tp for 60°C and 80 °C.
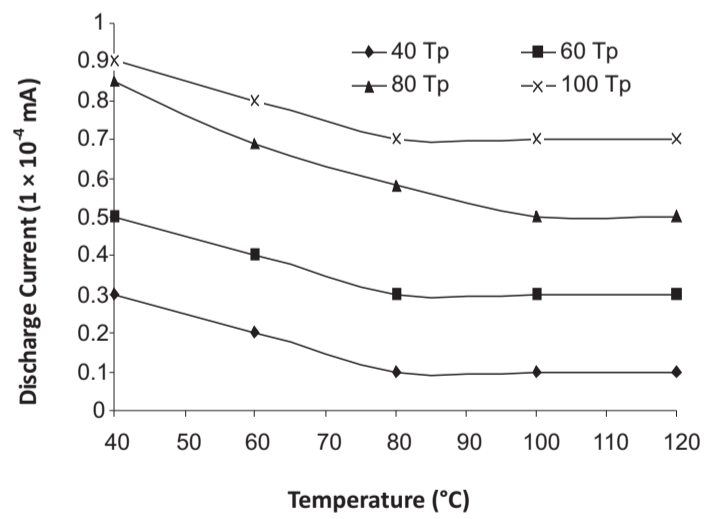

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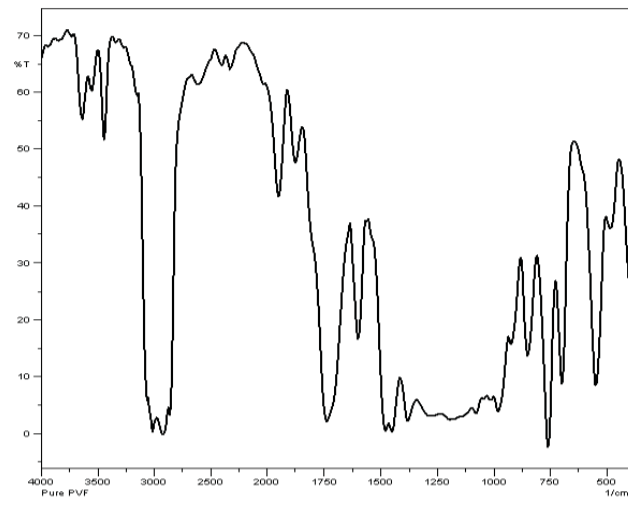
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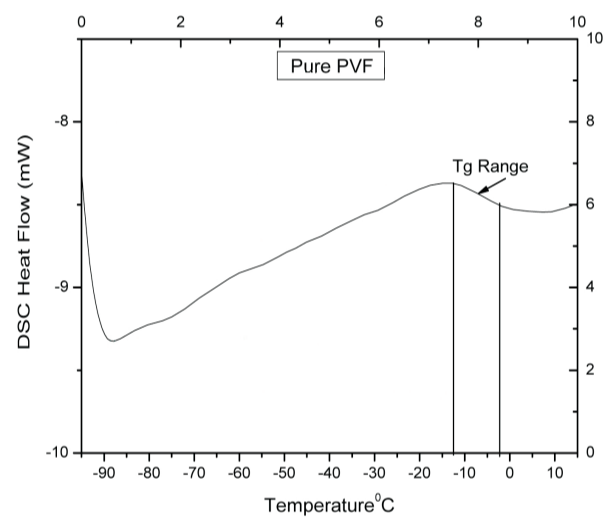
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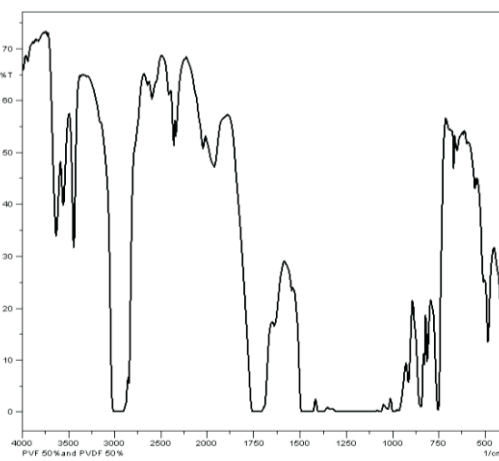
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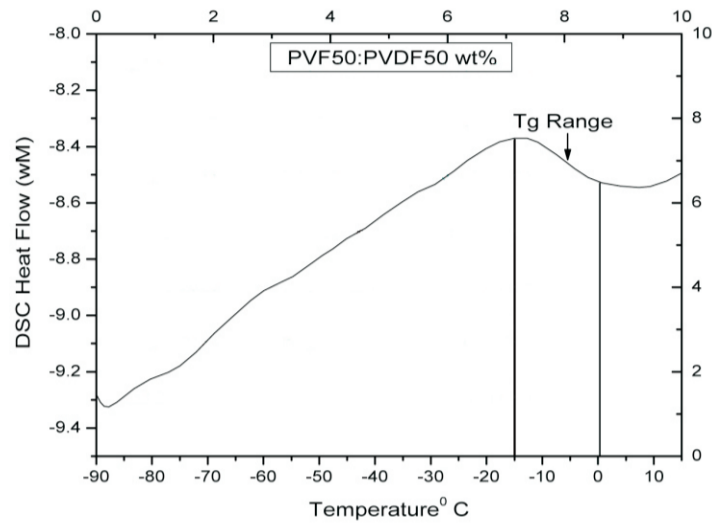
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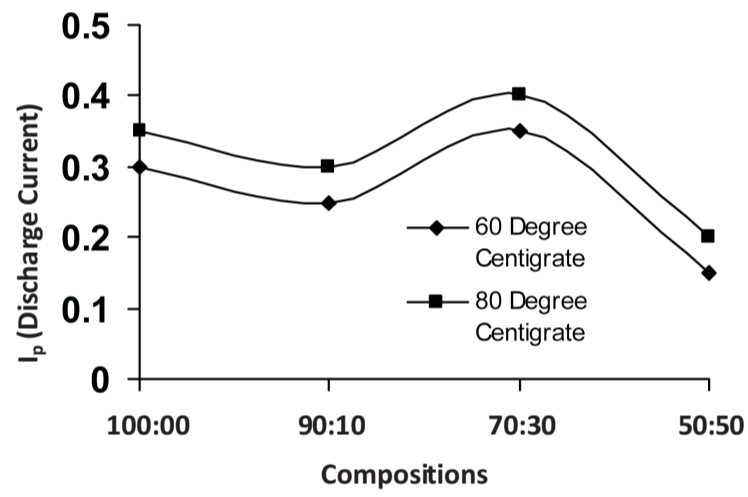
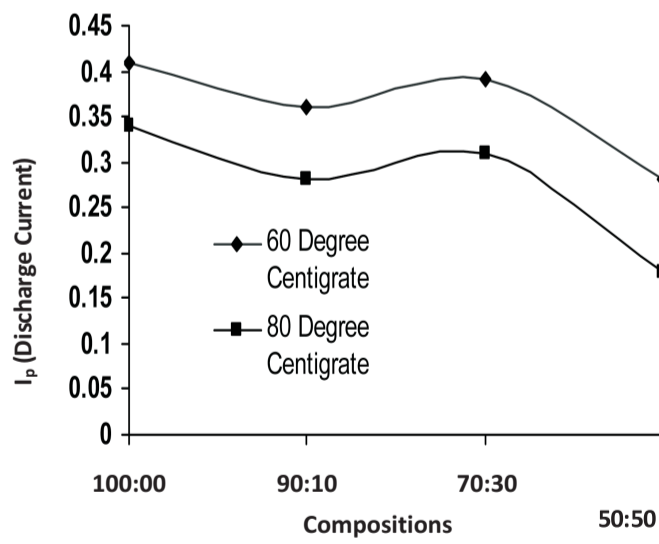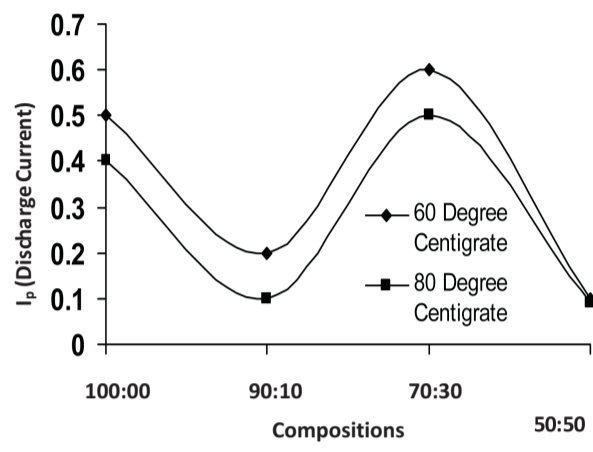**Figure 9**

Figure 10

Figure 11

Figure 12
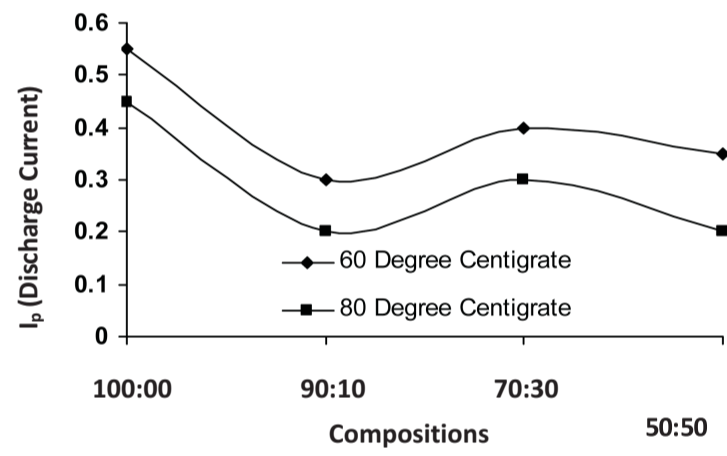
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