

## Abstract

The present work is a study of the electrical and electro-mechanical properties of PVDF/BaTiO<sub>3</sub> ferroelectric composites. The polymer used is polyvinylidene fluoride (PVDF), while the ferroelectric material used is barium titanate (BT) in the powder form. PVDF/BaTiO<sub>3</sub> composite films were prepared by mixing PVDF powder with BT powder in certain concentrations and then stirring at room temperature for several minutes using a droplet of acetone, the mixture was fused at 473 K for few minutes to get a solid paste. The mixture paste was sandwiched between two thin aluminium foils and pressed in a hot press for two minutes at a temperature of  $483 \pm 2\text{K}$  to obtain a film of polymer / ferroelectric composites. The films are then quenched in cold water and aluminium foils were then removed. The samples were coated with silver conductive paint on the opposite major faces with an area of about  $0.2\text{ cm}^2$  to perform electrical and dielectric measurements.

The properties of these composites were studied by measuring the dielectric properties  $\epsilon'$ ,  $\epsilon''$ , the real part ( $M'$ ) and imaginary part ( $M''$ ) of the electric modulus, Ac conductivity ( $\sigma_{ac}$ ), Dc electrical conductivity ( $\sigma_{dc}$ ), thermally stimulated polarization current (TSPC), thermally stimulated depolarization current (TSDC), x-ray analysis and differential scanning

calorimetry (DSC). The effects of annealing and drawing on some of these measurements were also investigated.

The temperature dependence of the real part  $\epsilon'(T)$  exhibits a shoulder in the temperature range (240 – 350 K) while  $\epsilon''(T)$  shows a sharp peak in the same temperature range, which is shifted to a higher temperature with increasing frequency. These features, which are strongly frequency dependent, are similar to those observed in many polar polymers and are attributed to the micro Brownian dipolar motion of the main chain in the amorphous region of the polymer ( $\beta$ - relaxation process). The other peak appeared at a high temperature above 420 K characterized the  $\alpha$ -relaxation process which associated with the crystalline part of the polymer. The  $\epsilon'(T)$  exhibits a sharp minimum at 440 K corresponding to the dynamic melting temperature  $T_m$  of the polymer. The increase in  $\epsilon'(T)$  at lower frequency is ascribed to inhomogeneous conduction due to interfacial polarization.  $\epsilon'(T)$  increases with increasing the BT content in the sample while  $\epsilon''(T)$  is only slightly affected by composition.

The behaviour of  $\epsilon'(f)$  is dependent on the temperature of measurements and is independent of composition. There is no relaxation peaks associated with  $\epsilon''(f)$  but it decreases with frequency at higher temperatures. On the other hand  $\epsilon'(T)$  peaks are affected by the thermal treatment (annealing) of the samples

especially at lower frequencies where they are shifted to higher temperatures for slowly cooled samples. The dielectric permittivity  $\epsilon'(T)$  increases while  $\epsilon''(T)$  decreases for drawn PVDF up to 30% of the original length compared to an undrawn sample.

The electric modulus representation is used to overcome the problem of interfacial polarization, which appears in heterogeneous systems at lower frequencies, i.e.  $M''(f)$  shows a peak unlike  $\epsilon''(f)$ . The temperature dependence of the ac conductivity ( $\sigma_{ac}$ ) is strongly frequency as well as temperature dependent. The maximum loss peaks ( $\beta$ - and  $\alpha$ -relaxations) appeared for all studied compositions.  $\sigma_{ac}(T)$  behaves like  $\sigma_{dc}(T)$  at high temperatures and lower frequencies, showing a positive temperature coefficient (PTC), but at higher frequencies it behaves differently, showing a negative temperature coefficient (NTC).  $\sigma_{ac}(T)$  increases slightly by increasing BT-content in the sample. It is noticed that  $\log \sigma_{ac}$  linearly rises with frequency at low temperatures while it is frequency independent at high temperatures.  $\sigma_{ac}(f)$  is found to be sensitive to annealing in the temperature range of crystalline melting only.

The temperature dependence of  $\sigma_{dc}$  shows a positive temperature coefficient and decreases slightly at high values of the applied voltage. The effect of a drawing ratio of 40 % gives a slight decrease of  $\sigma_{dc}(T)$ . The

calculated activation energy for this system indicates that the conduction mechanism may be ionic in nature.

Thermally stimulated polarization current (TSPC) shows a broad peak in the temperature range of 335 K. The fluctuations in the peak height and position are attributed to space charges in addition the production of displacement currents from electric dipoles. The behaviour of TSPC is affected by drawing due to the orientation of molecular chains which enhance crystallinity and eliminate some of the space charges that reduce the fluctuation in TSPC spectra. On the other hand, thermally stimulated depolarization current (TSDC) shows a maximum value in the same temperature range of TSPC (335 K). The peak height increases by increasing BT-content, and decreases by increasing the poling temperature, while it is independent of temperature at very high applied poling voltage (4 kV).

X- ray diffraction analysis is used to show the structure variation that occurred in the samples. It is found that the structure for pure PVDF and low BT content belong to orthorhombic  $\alpha$ -phase, but adding more BT changes the structure to orthorhombic  $\beta$ -Phase. The high BT content sample (30 % by wt., BT) has a tetragonal structure similar pure BaTiO<sub>3</sub> (for  $T < 393$  K). The unit cell parameters may suggest that slowly cooled samples are in the  $\beta$ -phase because

the strong reflection from (200) is present and the reflections from (110) and (020) for  $\alpha$ -phases are not observed.

Differential scanning calorimetry (DSC) shows that the melting temperature of the samples during the heating process is around 445 K, which is in agreement with dielectric data. The glass transition temperature obtained from DSC-scan for the sample containing 20% by wt., BT is 238 K which is attributed to the glass-transition temperature of PVDF. However the DSC-thermogram for the annealed sample shows a more defined peak where its position appeared at a higher temperature compared to the other samples.

Finally, the electromechanical coupling coefficient ( $K^2$ ) for the studied samples was determined at different temperatures from the dielectric data.