Research Paper

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Effect of Temperature on Dielectric Properties of P(VDF-TrFE) Copolymer Films

Engineering

KEYWORDS : P(VDF-TrFE) copolymer, piezoelectric, dielectric properties, temperature dependence

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ABSTRACT

Piezoelectric materials have been major area of focus for development of sensors and actuators for almost a century. Apart from the single-phase materials like polymers, copolymers have also been studied extensively in terms of achieving combination of material properties, tailoring of parameters and ease of fabrication. One such copolymer is Poly(vinylidene fluoride)/trifluoroethylene [P(VDF-TrFE)], which exhibits attractive properties to make it useful as transducers in various applications. Being dielectric material, the investigation of dielectric properties of P(VDF-TrFE) is essential. In the present investigation, copolymer films were prepared by hot press method and their dielectric properties have been investigated. Since P(VDF-TrFE) film has good thermal stability, the effect of temperature on dielectric properties of P(VDF-TrFE) copolymer has also been studied. Present work evaluates the dielectric properties such as relative permittivity, capacitance, dielectric loss and intrinsic conductivity, etc. of these films as function of frequency at various temperatures.

INTRODUCTION

Piezoelectric polymers have been known to exist for more than four decades. In recent years, they have grown as a class of "smart materials". The most widely known piezoelectric polymer is Polyvinylidene fluoride (PVDF). Due to its favorable chemical and mechanical properties, good flexibility, biocompatibility, low acoustic and mechanical impedance, being lightweight, and having low cost, PVDF has been widely used for many engineering applications.

Despite having such attractive properties, the process of manufacturing PVDF films involves many steps and complicated process of mechanical stretching for achieving piezoelectric beta phase [1]. Previously work has been done on manufacturing of PVDF films and its blends in non-polar alpha phase by different procedures like solvent casting [2], extrusion, hot pressing [3, 4] and spin coating [5], etc. These films then need to be thermo-mechanically stretched to achieve beta phase, which is critical and cumbersome process. However, the process of stretching can be avoided by using P(VDF-TrFE) copolymer, which can be directly obtained in piezoelectric beta phase [2].

Copolymer of vinylidene fluoride with trifluoroethylene [P(VDF-TrFE)], is one of the most promising PVDF ferroelectric copolymers. P(VDF-TrFE) is synthesized using two homopolymers viz. PVDF and PTrFE. It has tremendous applications in electronic industry, such as soft transducers, infrared imaging, and compact capacitors and holds a promising future in the field of non-volatile memory [6]. It also finds many applications in electro-mechanical devices, to perform energy conversion between the electric and mechanical forms such as artificial muscles, smart skins for drag reduction, actuators for active noise and vibration controls, and micro-fluidic systems for drug delivery and micro-reactors [7]. One of the most unique applications of P(VDF-TrFE) is their utilization as active piezoelectric elements in self-powered, nanosecond time-resolved, dynamic stress gauges for the study of shock-wave compression phenomena [8-10]. Earlier, researchers like V. Sencadas et al. have studied the phase transition and piezoelectric properties of P(VDF-TrFE) [11]. Further, Li et al [12] reported that P(VDF-TrFE) is useful for sensors, actuators, and high-density memories.

In the present study, P(VDF-TrFE) films were prepared by hot press method and their dielectric properties were studied as function of frequency at various temperatures. Their piezoelectric properties were also verified.

EXPERIMENT DETAILS

DEVELOPMENT OF P(VDF-TRFE) FILMS BY HOT PRESS

METHOD

A known weight of P(VDF-TrFE) copolymer granules were used to prepare 200 μm thick films using hot press technique.

Figure 1: P(VDF-TrFE) copolymer film by hot press method

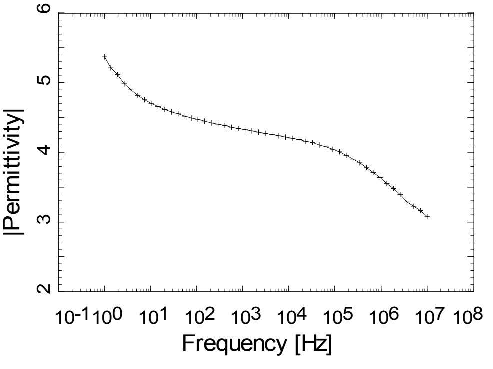
In this technique, the granules of P(VDF-TrFE) copolymer are placed in between two Teflon sheets. These sheets were then subjected to uniaxial stress of 300-400 kPa for 3-4 min at melting temperature to obtain P(VDF-TrFE) film, which were in β-phase. Conditions are optimized to obtain uniform β-phase P(VDF-TrFE) copolymer films, as shown in the Figure 1.

RESULT AND DISCUSSION

DIELECTRIC PROPERTIES OF P(VDF-TrFE) COPOLYMER FILMS AT ROOM TEMPERATURE

Figures 2(a) and 2(b) show the relative dielectric permittivity and dielectric loss of P(VDF-TrFE) film as a function of frequency at room temperature.

Figure 2: (a) Relative permittivity of P(VDF-TrFE) film



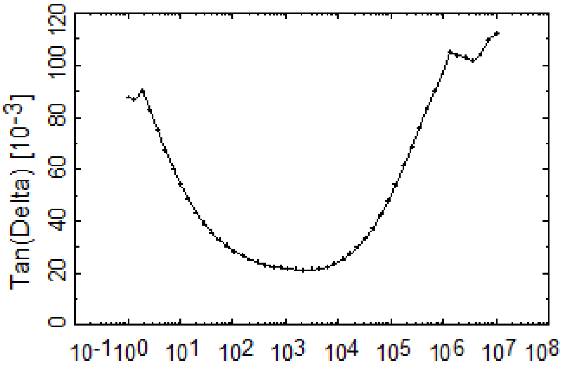


Figure 2: (b) Tan delta of P(VDF-TrFE) film

The dielectric permittivity of P(VDF-TrFE) film was higher at lower frequency and was found to decrease as the frequency increases. The dielectric loss (Tan delta), however, was considerably lower in frequency range 100 Hz-100 kHz, while having much higher losses at lower and higher frequencies. It was found that P(VDF-TrFE) films exhibit lesser dielectric loss than pure PVDF (0.02 as compared to 0.03 for PVDF at 1 kHz). It indicates the modification by adding TrFE into PVDF polymer is an effective approach for the increasing the dielectric constant but reduction of the dielectric loss at low fields.

Figure 3: (a) Real part capacitance of P(VDF-TrFE) film

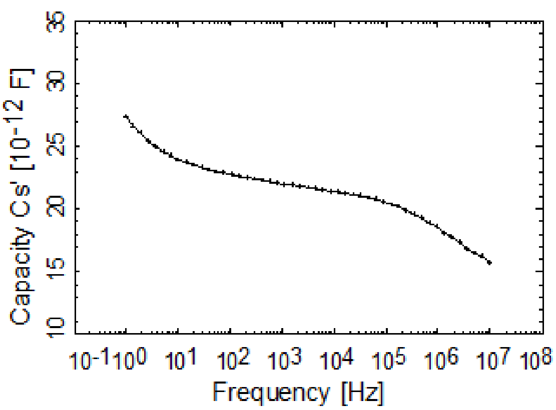
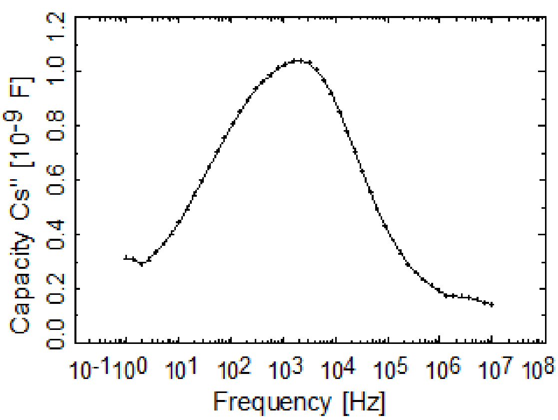


Figure 3: (b) Imaginary part capacitance of P(VDF-TrFE) film



In dielectric measurements, capacitance of material is a complex term containing both real and imaginary parts. Figures 3(a) and 3(b) represent the frequency dependence of real and imaginary part of capacitance of the P(VDF-TrFE) copolymer film. It was found that at lower frequency, the real part of capacitance was high and as frequency increases it starts decreasing. On the other hand, the imaginary part capacitance is maximum for frequency between 1-10 kHz and decreases for both the other sides of frequency spectra. This implies higher difference in phase of current and voltage in this frequency range.

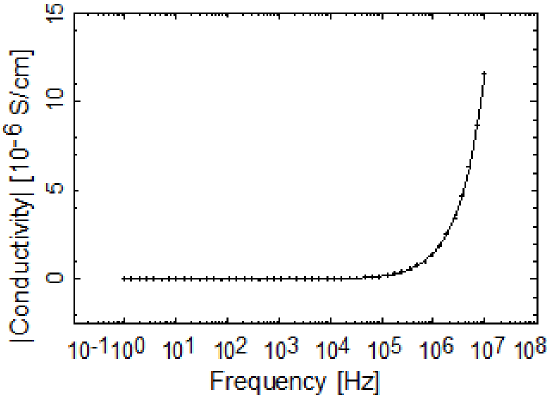


Figure 4: (a) Conductivity of P(VDF-TrFE) film

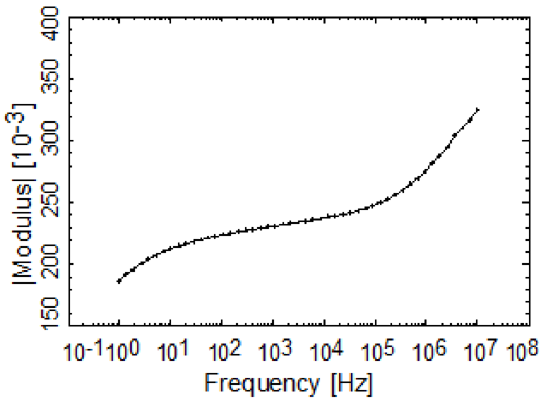


Figure 4: (b) Modulus of P(VDF-TrFE) film

Figure 4(a) show the frequency dependence of electrical conductivity for the P(VDF-TrFE) copolymer, As expected, being a dielectric material, the conductivity is very low. But it was seen that the introduction of TrFE to PVDF signifies slight increase in the electrical conductivity of the copolymer (2.1 nS/cm as compared to 8.8 nS/cm for PVDF). Since the dielectric losses at frequencies larger than kHz mainly originate from the electrical conduction and dipolar polarization, this result indicates that the decrease of dielectric loss in the copolymer should be mainly attributed to the highly restricted polymer chain motion by addition of TrFE. Figure 4(b) represent the frequency dependence of dielectric modulus of P(VDF-TrFE) copolymer film. It was found that the modulus increases steadily with increasing frequency. A sharp increase was observed at very high frequency ~10^6 Hz.

EFFECT OF TEMPERATURE ON DIELECTRIC PROPERTIES

The temperature dependence on the dielectric behavior of P(VDF-TrFE) copolymer films was also investigated and the results collected at various temperatures ranging from 40-75°C, are illustrated in Figure 5(a) and 5(b).

Figure 5: (a) Dielectric permittivity of P(VDF-TrFE) film for

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different temperatures

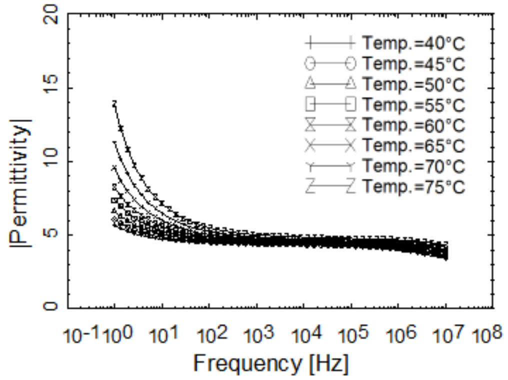
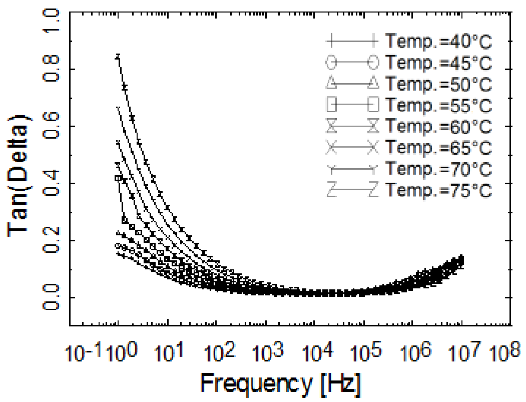


Figure 5: (b) Tan delta of P(VDF-TrFE) film for different temperatures



The study showed that over a relatively broad frequency range (from 100 Hz to 100 kHz), the relative dielectric permittivity and tan delta of the P(VDF-TrFE) copolymer films was quite stable with respect to temperature, except at lower frequencies. Moreover, as temperature increases marginal increase in permittivity and tan delta was found For example, relative dielectric permittivity of 4.9 and tan delta of 0.039 was observed at 1 kHz and a temperature of 75°C, compared to 4.3 and 0.021 resp. for room temperature for P(VDF-TrFE) copolymer film.

Figures 6(a) and 6(b) represent the frequency dependence of real and imaginary part of capacitance of the P(VDF-TrFE) copolymer film at several selected temperature.

Figure 6: (a) Real part capacitance of P(VDF-TrFE) film for different temperatures

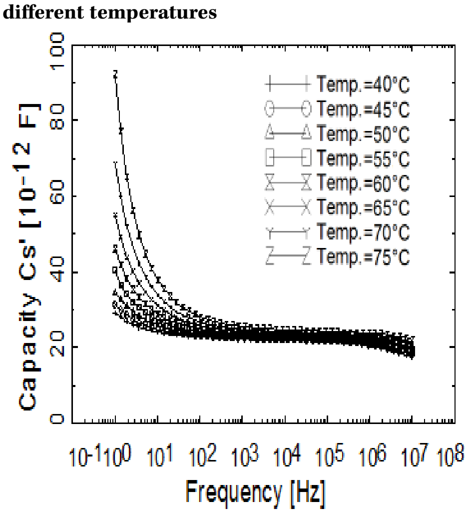
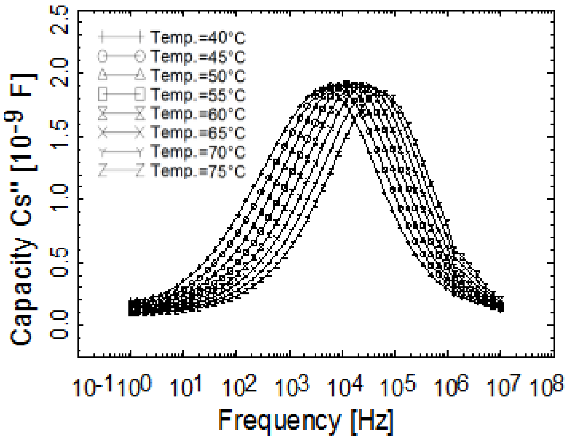


Figure 6: (b) Imaginary part capacitance of P(VDF-TrFE) film for different temperatures



It was found that at lower frequency, the real part of capacitance was high and as frequency increases it starts decreasing for all temperatures. However, a slight increase was observed with increase in temperature. On the other hand, the imaginary part of capacitance is maximum near 10 kHz and is quite low on both other side of frequency spectrum. A shift in maxima was observed for imaginary capacitance with increase in temperature, indicating different phase behavior of current and voltage at different temperatures. Real part capacitance was found to be 27.9 pF at 100 Hz for 75°C and 22.7 pF for room temperature.

Figure 7: (a) Conductivity of P(VDF-TrFE) film for different temperatures

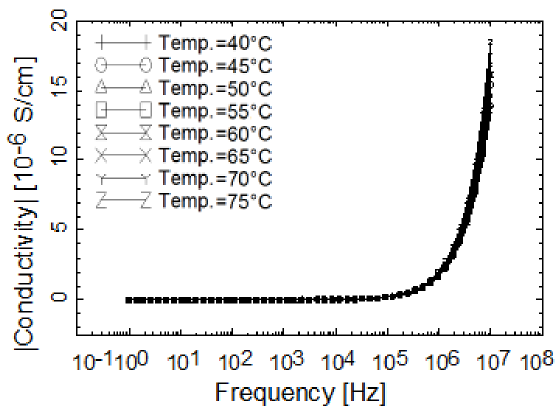
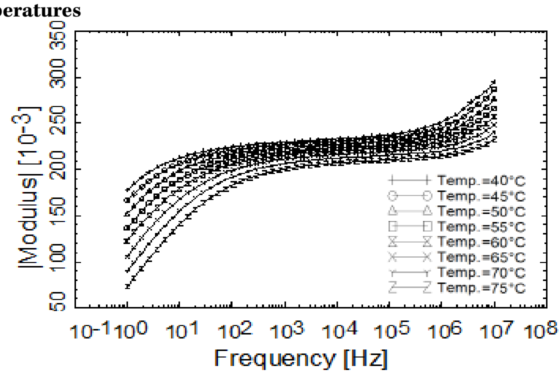


Figure 7: (b) Modulus of P(VDF-TrFE) film for different temperatures



Figures 7(a) and 7(b) show the frequency dependence of electrical conductivity and dielectric modulus for the P(VDF-TrFE) copolymer. At all the temperatures (40-75°C), the electrical conductivity of the copolymer remains same and very low, indicating no change in insulator behavior On the other hand, the modulus reduces with increase in temperature. The maximum value of electrical conductivity and dielectric modulus were obtained at a very high frequency of 10^7 Hz and their values were found to be 0.18 μS/cm and 0.23 respectively for temperature 75ºC.

POLING METHOD AND PIEZOELECTRIC PROPERTIES OF P(VDF-TRFE) COPOLYMER FILMS

Poling is an important step to achieve and enhance the piezoelectric properties in all piezoelectric materials. P(VDF-TrFE) copolymer films were electroded with silver paste and poled using thermal and corona poling method by application of high DC electric field of the order of 80 kV/mm at an elevated temperature. This aligns the dipoles in the crystalline regions in the field direction. Subsequent cooling to room temperature under the applied field stabilized the polar alignment resulting in permanent polarization. The piezoelectric charge coefficients were measured using piezometer PM300. The average value of piezoelectric charge coefficient d^{33} obtained was 12 pC/N and the maximum value obtained was 38 pC/N, after optimization of poling process and parameters.

CONCLUSIONS

The P(VDF-TrFE) copolymer films are prepared using hot press method. These films were tested for dielectric, and piezoelectric properties in the frequency range 1 to 10^7 Hz. The dielectric parameters of P(VDF-TrFE) films were evaluated by the measurement of dielectric constant, capacitance, dielectric loss and intrinsic conductivity, etc. at various temperatures ranging from 40-75ºC. The maximum relative dielectric permittivity value of 4.99 (at 1 kHz) was obtained at 75ºC. The dielectric loss was found to be minimum at ~22 kHz for all temperature, with least value of 0.02 at room temperature. The conductivity was found to be very low even at high temperatures and increased at high frequency only, indicating dielectric breakdown at higher frequencies. The average piezoelectric charge coefficient obtained was 12 pC/N and the maximum value obtained was 38 pC/N.

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