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Electrical properties of polyvinylidene fluoride/cellulose acetate blend modified by cenosphere

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In the present research work we successfully modified the polyvinylidene fluoride (PVDF) and cellulose acetate (CA) blend by cenosphere (CS). We have disclosed the significant effect of cenosphenere on electrical properties of modified polymer blends. The real dielectric constant ($\mathcal{E}_r$) decreases and dissipation factor (tan (δ)) increases as a function of cenosphere (wt %). The impedance analysis demonstrates the decrease in bulk resistance as a function of temperature. The inorganic nature of cenosphere increases the AC and DC conductivity and may be covalent ionic contribution of cenosphere. This investigation is highly useful for the structural applications and glass micro balloons fabrication.

Keywords: PVDF, CA, CS, Dielectric constant, Dissipation factor, AC, DC Conductivity, Impedance

1 Introduction

PVDF is a semicrystalline engineering thermoplastic which has excellent thermal, chemical and oxidation resistance. In PVDF amorphous phase of the polymer provides the flexibility in membranes and the crystalline phase enable the better thermal stability. These properties of PVDF exposed to demonstrate very attractive material for microfiltration[1], ultrafiltration[2] and membrane distillation[3]. The major disadvantages of PVDF ore is extensive shrinkage of wet film during processing and severe hydrophobicity of the membrane. PVDF is widely used in membrane manufacturing process due to high chemical resistance, oxidative treatment and film-forming properties. It is easily fabricated through phase inversion methods and readily dissolved in organic solvents. It is extensively used for water treatment applications. It improves the anti-fouling properties towards proteins[4], hydrocarbons and other organic contaminants[5]. We motivated to select the cellulose acetate (CA) for blending the PVDF due to various applications, economic, easy for processing, moderate chlorine resistance[6], good biocompatibility[7] and hydrophilicity[8]. In the past three decades, CA membrane is used in the broad spectrum of applications such as bioengineering[9], pharmaceutical[10] and food industries[11]. CA has attracted a great deal of attention for electrospun nanofiber membranes[12]. Due to low toxicity and high compatibility CA membranes are suitable for cell culture[13], drug delivery[14], tissue engineering[15], removal of toxins from solutions[16], bio-processing[17] and medical filtration[18].

Cenosphere (CS) is the most abundant minerals such as quartz and alumina derived from various thermal power plants. Cenosphere consists of tiny particles having the wide range of dimension (0.005 mm to 0.035 mm). Recently CS particles (size 0.117 mm) demonstrated the high compressive strength (7.38 MPa). CS particles offer a very high electrical resistivity (2.26×10^8 Ω). It was used as an electrical and thermal insulating material. CS is thermally stable at high temperature gradient (1000 °C) with the negligible mass loss. It is made up of hollow spheres having thickness around (10 %) of the spherical diameter. It has unique properties such as stable, non-toxic, light weight and good insulation which has been used for the fabrication of light weight composite[19]. It is widely used in electromagnetic wave absorption, high light reflected devices and catalysts. Metal coating cenosphere is widely used in number of methods such as electrodeless plating[20], magnetron sputtering deposition[21], physical vapor deposition[22] and sol-gel methods. The main characteristics of cenosphere are hollow spheres with

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*Corresponding author (E-mail: varadgm@gmail.com) spherical morphology, particle size ranging from sub-micron to millimetres in size, ultra-low density, low thermal conductivity, high particle strength, resistant to acids and low water absorption. Cenosphere is widely used in other products such as sports equipment, insulations, automobile bodies, marine craft bodies, paints, fire and heat protection devices.

Cenosphere is free flowing powder which is composed of hard shelled, hollow and minute spheres. A small quantity of pulverised fuel ash (PFA) produced from the combustion of coal in power station is formed as cenosphere. It is made up of silica, iron and alumina. It has a size range varying from 1 to 500 microns and has a colour range from white to dark grey. The other name for cenosphere is referred as microspheres, hollow spheres, hollow ceramic microspheres and micro balloons or glass beads. Hence we motivated to investigate the electrical properties of polymer blends as function of CS loading.

2 Role of Cenosphere in PVDF/CA

Cenosphere is obtained from two Greek words such as kenos (empty) and sphaira (sphere). It has a light weight which comprised of silica and alumina and has the specific gravity of 0.4-0.8 g/cm^3. Cenosphere is collected from ash lagoon of TSTPS, Kanhia Odisha state in India. It also collected from ash dyke in gunny bags. The reason for choosing cenosphere is that it exhibits a high compression, low specific gravity, good thermal and acoustical insulation properties, inertness to acids and alkalis. It is widely used in various industries. When cenosphere is added with PVDF and CA, it exhibits low dielectric constant (ε_r), high loss and used as an automobile bodies and heat protection devices.

3 Experimental

3.1 Materials

Polyvinylidene fluoride (PVDF) powder has a molecular weight (MW) of 5,34,105 g/mol was procured from Pragati Plastics Pvt Ltd, New Delhi, India. Cellulose acetate (CA) in powder form CAS No: 9004-3-0 supplied by C. Jivanlal and Company, Navi Mumbai, India. N-N-dimethyl formamide (DMF) Batch No: 378787 having the molecular weight of 73.10 g/mol of AR grade was purchased from Sisco Research Laboratories, PVT, Ltd; Mumbai, India and was used as a solvent to dissolve the polymer PVDF, cellulose acetate and cenosphere.

3.2 Modification of PVDF/CA polymer blends as function of CS loading

PVDF/CA/CS polymer blends were prepared by solution blending in the ratio of 5, 10, 15 and 20 CS (wt %) loading. Initially 7 g of PVDF and 2 g of CA was dissolved in 150 ml of dimethyl formamide (DMF) (at 60°C stirred at 410 rpm for 2 h). Then the 2 g of cenosphere is sonicated in 25 ml of DMF (for 10 min) stirred at room temperature for 1 h.

The co-solution of PVDF/CA/CS (90/5/5, 80/10/10, 70/15/15 and 60/20/20) were mixed and stirred (at 410 rpm at 50 °C for 3 h). The homogeneous solution was poured in the petri dish and kept in the oven for 8 h at 40 °C to obtain the polymer blends. Finally the film was peeled from the petri dish and used for further characterization. The detailed protocol to obtain the polymer blends was shown in Fig. 1.

3.3 Characterization techniques

The electrical characterization of PVDF/CA/CS blends was performed by using N4L, PSM 1735 impedance analyser. It was silver pasted on both sides were placed in a fixture. The ALAB BTC 9100 is temperature controller. We operated the sample across the broadband frequency range (10 Hz-2 kHz) with the temperature range (30 °C-150 °C).

4 Results and Discussion

4.1 Dielectric constant of PVDF/CA/CS

Dielectric material exhibits various physical properties and used to achieve the realizable applications. It is widely used in capacitors and memory devices. Based on these applications we are

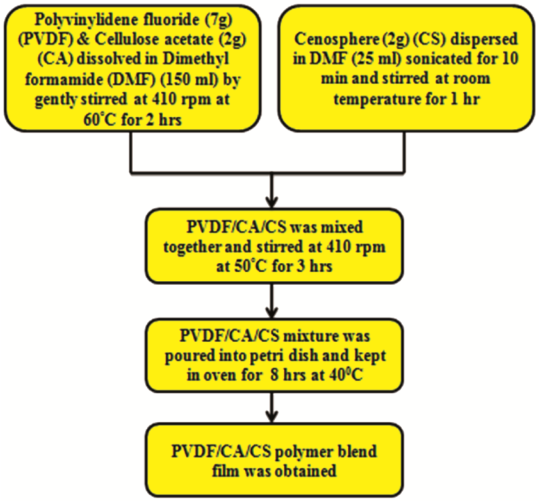

Fig. 1 — Basic protocol to obtain the PVDF/CA/CS polymer blend film.

motivated to test the dielectric properties of PVDF/CA/CS polymer blends across the broad band frequency at (10 Hz-2 KHz) and a temperature range of (30 °C-150 °C). Figure 2 shows the plots of ε_r of (a) virgin PVDF/CA, (b-e) 90/5/5, 80/10/10, 70/15/15 and 60/20/20 loading (wt %) of PVDF/CA/CS. From Fig. 2, we observed at lower frequency that the ε_r is decreased with increase in the frequency and exhibits the frequency independent behaviour at high frequency region (2 KHz). This is due to the ions which are unable to oppose the effect of electric field and tightly attached to the polymer chain[23]. At 2 KHz the charge carriers will no longer be able to rotate sufficiently so the oscillations lag behind the electric field which resulted in decrease in ε_r. At 10 Hz frequency the permanent dipoles align themselves along the electric field and fully contribute to the total polarization of the dielectric. This makes the ε_r which becomes negligible at lower frequency region. Hence ε_r decreases with increase in the frequency. The decrease in ε_r can also be explained from interfacial polarization.

4.2 Dielectric loss tangent of PVDF/CA/CS

Dissipation factor is defined as the ratio of dielectric permittivity to the dielectric loss, i.e., capacitive energy to the resistive energy. It is widely used in charge storing applications. Based on these applications we are motivated to plot the dielectric loss tangent (tan (δ)) of PVDF/CA/CS polymer blends across the frequency range of (10 Hz - 2 KHz) with respect to temperature (30 °C – 150 °C) and is shown in Fig. 3 (a - e). We observed that tan (δ) is decreased with increase in the frequency. This is due to inducting the cenosphere in PVDF/CA polymer blends. This also may be due to conduction loss[24]. Further tan (δ) is occurred due to vacancy and shows the highest value in the lowest frequency region (1 Hz) and remains independent towards the higher frequency region (2 KHz). We also observed that tan (δ) is increased by increasing the temperature and shows the α-relaxation process[25]. This is due to the hopping frequency of the charge carriers which is associated with the polymer blends.

4.3 Impedance analysis of PVDF/CA/CS blends

Impedance spectroscopy is an important analysis used to study the rates of chemical reaction, corrosion, defects and microstructures. It is widely used in fuel cells, electro chemical process and study the membrane behaviour in living cells. Figure 4 represents the complex impedance plots of PVDF/CA/CS polymer blends. We observed that data shows the semicircle at the temperature range of (60 °C, 120 °C and 150 °C) in Fig. 4 (a-e). The semicircle behaviour confirms the Debye relaxation process and larger diameter exhibits the charge transfer resistance and becomes small at the lower

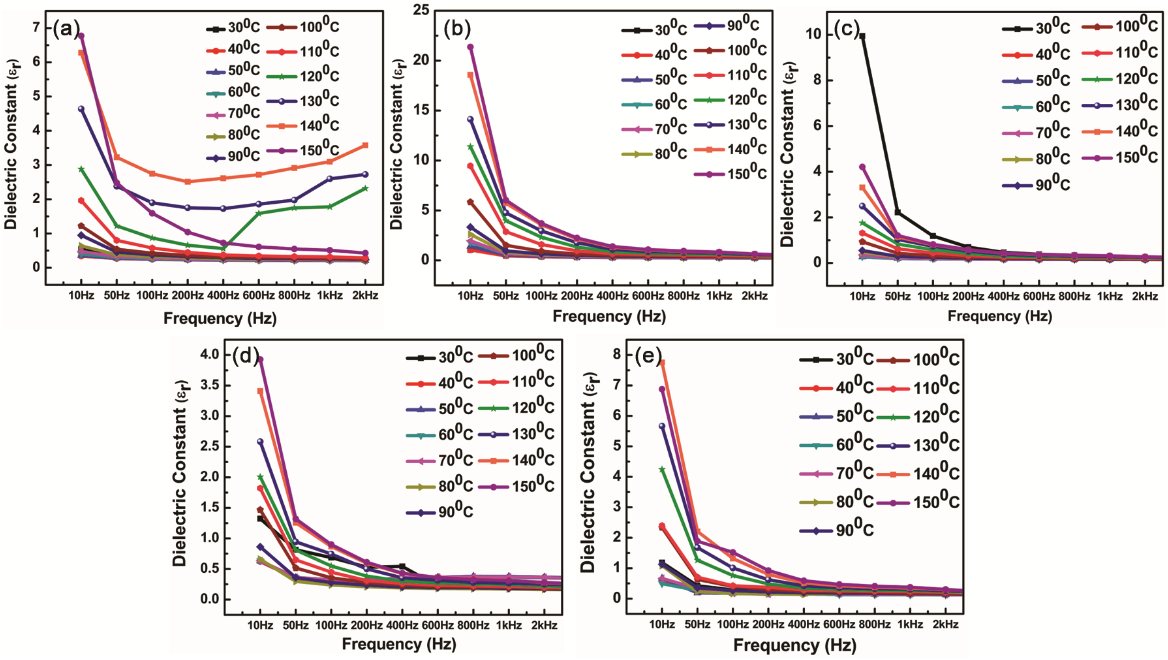

Fig. 2 — Dielectric constant of (a) virgin PVDF/CA, (b) 90/5/5, (c) 80/10/10, (d) 70/15/15 and (e) 60/20/20 PVDF/CA/CS polymer blends as a function of frequency at various temperatures.

frequency region. It may also due to the parallel combination of grain resistance (R_g) and grain capacitance (C_g).

We also observed that semicircle trend which is decreased with increase in temperature and grain resistance also decreased[26]. We observed that the shape of semicircle appears to be electrode spikes in Fig. 4 (b - e) at the temperature range of (30 °C, 60 °C and 90 °C). This may result in increased electrolyte leading upwards and ionic conductivities which confirms the non-Debye relaxation process[27]. This may also be due to increase in concentration of cenosphere and function of temperature. Effect of increased temperature demonstrated the grain resistance decreases and shifts towards the lower impedance value.

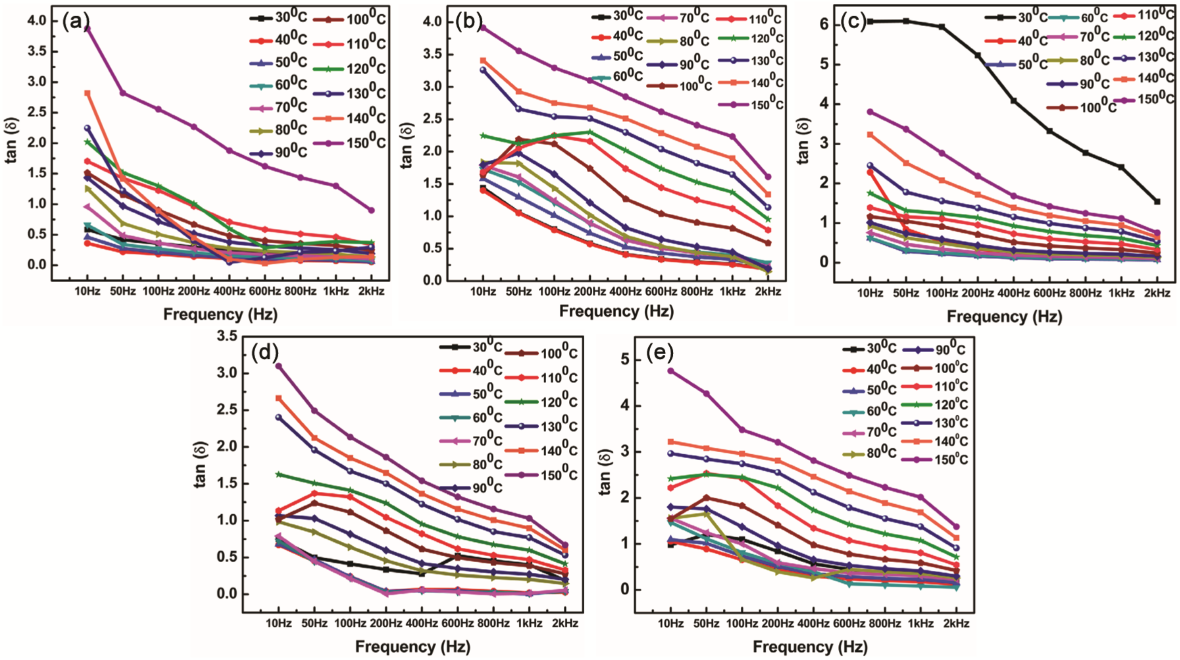

Fig. 3 — Dissipation factor of (a) virgin PVDF/CA, (b) 90/5/5, (c) 80/10/10, (d) 70/15/15 and (e) 60/20/20 PVDF/CA/CS composites as a function of frequency at various temperatures.

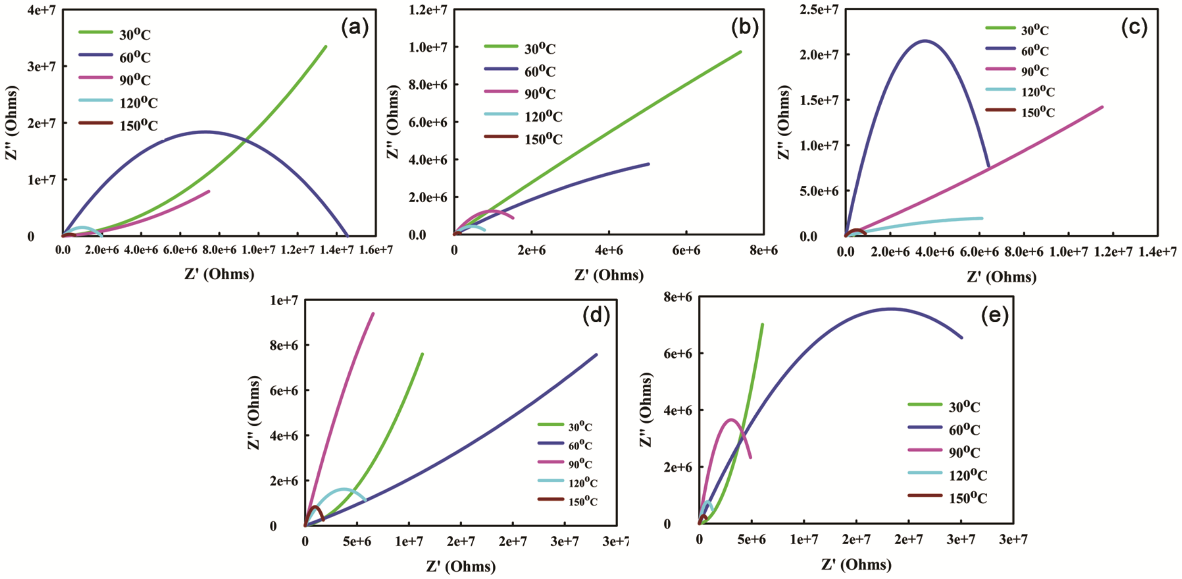

Fig. 4 — Complex impedance plots (Z' vs Z'') of (a) virgin PVDF/CA, (b) 90/5/5, (c) 80/10/10, (d) 70/15/15 and (e) 60/20/20 PVDF/CA/CS composites.

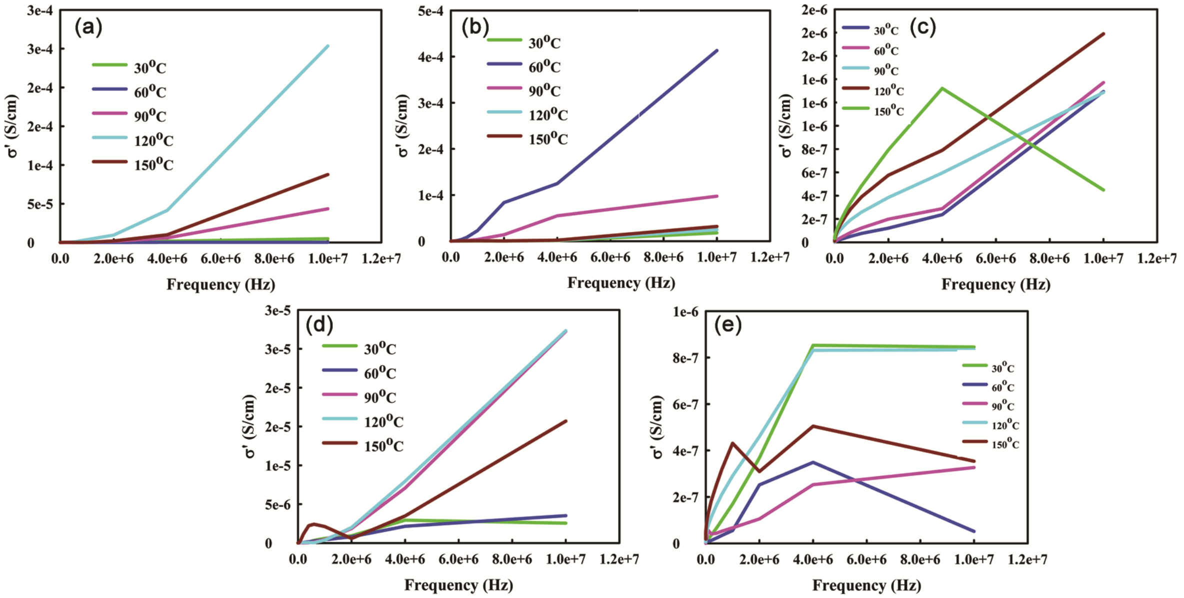

Fig. 5 — AC conductivity of (a) virgin PVDF/CA, (b) 90/5/5, (c) 80/10/10, (d) 70/15/15 and (e) 60/20/20 PVDF/CA/CS composites as a frequency at various temperatures.

4.4 AC conductivity of PVDF/CA/CS blends

Figure 5 shows the frequency dependent behaviour of AC conductivity of PVDF/CA/CS across broadband frequency range of (10 Hz – 1 MHz) at a temperature (30 °C - 150 °C). We observed that AC conductivity increased with increase in frequency with respect to temperature. From Fig. 5 (a, b & d) we observed that AC conductivity exhibits strong correlation with the frequency which is determined by the polarization effect.

The increase in the AC conductivity is mainly due to the flow of charges by variable hopping range (VHR) mechanism[28, 29]. We also observed that decrease in AC conductivity in Fig. 5 (c and e) at a temperature range of (60°C & 150°C) is due to the presence of cenosphere and makes the hopping charge carriers more difficult[30]. AC conductivity shows the linear trend in polymer blends which is due to the hopping of electrons between two pairs of localized states. We observed that AC conductivity is decreased as the temperature increases at lower value of frequency in Fig. 5 (e). This decrease in trend is due to the movement of electrons through charge carriers. We observed that there is a decrease in AC conductivity which is due to the liberation of water molecules and then sudden increase in the conductivity. The conductivity is increased at high frequency as the charge carrier mobility is high in maximum frequency. We observed that high conductivity at maximum temperature as the influence of polarization is high at 150 °C.

Table 1 — Activation energy

Sample Code	Sample details	Activation energy (kj/mol)
a	PVDF/CA	0.1614
b	PVDF/CA/CS (90/5/5)	0.1168
c	PVDF/CA/CS (80/10/10)	0.1481
d	PVDF/CA/CS(70/15/15)	0.1438
e	PVDF/CA/CS (60/20/20)	0.1362

4.5 DC conductivity of PVDF/CA/CS blends

DC conductivity with respect to temperature was investigated to explain the conduction mechanism in polymer blends. Figure 6 shows the logarithmic DC conductivity (log σ DC) versus (1000/T) of PVDF/CA/CS which was measured within the temperature range of (30 °C to 150 °C). We observed that DC conductivity increased with increase in temperature and exhibits the negative activation energy as a function of cenosphere composition. DC conductivity behaviour can be described by two mechanisms for electrical conduction in the blends[31].

The conductivity activation enthalpy (E_a) has been calculated using the Arrhenius equation:

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{KT}\right)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, K is the Boltzmann constant. The activation energy of PVDF/CA/CS is tabulated in Table 1. We observed that activation energy is decreased with increase in composition of cenosphere.

This is due to the large number of π-electrons in the polymer chain[32].

5 Conclusions

PVDF/CA/CS polymer blends were prepared by sonication route. Electrical properties were performed by impedance techniques. ε_r is increased and dissipation factor is decreased by loading (wt %) of cenosphere based on Maxwell-Wanger polarization model. Nyquist impedance plot confirms the non-Debye relaxation process and ionic conduction. The influence of cenosphere with PVDF/CA demonstrates the temperature dependent AC and DC conductivity and the ionic contribution of inorganic cenosphere. DC conductivity also confirms the decrease in activation energy by loading (wt %) of cenosphere. This investigation is feasible for various electronic and applications.

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