Electrical and Electrochemical studies of Polyurethane diol/Polycaprolactone- Iron Oxide nanocomposites

A Suhasini¹, K P Vinod Kumar², A Maria Sheela¹ and N SheenKumar³

¹Assistant Professor, Department of Chemistry, St.Xavier’s Catholic College of Engineering, Nagercoil, Tamilnadu, India
² Assistant Professor, Department of Chemistry, University College of Engineering, Nagercoil, Tamilnadu, India
³ Assistant Professor, Department of Physics, St.Xavier’s Catholic College of Engineering, Nagercoil, Tamilnadu, India

Corresponding email: suhasiniaugustin@gmail.com

Abstract: Electrically conducting composite materials consisting of different weight percentage of iron oxide nanoparticles dispersed in Polyurethane diol/Polycaprolactone were prepared. As a function of temperature between 30-70°C and frequency in the range of 1 kHz to 1000 kHz the dielectric constant and conductivity of polymer nanocomposites were studied. The dielectric constant value increased with increase in temperature and decreased with increase in frequency. Conductivity was found to be in the order of $10^{-6}$ to $10^{-5}$ S/cm and increased with increase in temperature. Cyclic voltammetry investigations revealed that the material has the potential to perform as an alternative catalyst for fuel cell applications.

1. Introduction

Polyurethanes (PU) are multipurpose materials because they can be easily shaped and established excellent workability. Therefore, they are broadly used in various fields of applications like construction, electrical, automotive industry, electronics, footwear production and biomedical applications like heart valves, dialysis membranes [1], artificial joint, artificial blood vessel, fracture fixation, controlled release devices etc., [2,3]. Polyurethane diol (PUD) is the family of polyurethane and are used as a transformer for auto coatings, suspensions in wood, water-soluble resins and appliances [4]. Polycaprolactone (PCL) is one among the manmade biodegradable polymers used to make compostable polymeric electronic devices and in medical field as artificial bone, artificial skin, knee dislocation and containers for continuous drug delivery [5, 6]. Polymer blending is an important process to synthesize new materials, which have better properties than a single polymer. Polyurethane/polycaprolactone blends are used in orthopaedic binding or molding, prosthetic socket cone production, radiotherapy patient immobilization and plastic reconstructive surgery [7, 8]. Polymer blending can combine organic and inorganic components to get different materials with desirable properties [9,10]. Polymer blends revealed greater conductivity and additional mechanical strength when compared to that of pure polymers [11-13]. The iron oxide nanoparticles have superior catalytic activity, super paramagnetic behaviour and large surface area, so they can be used in solar energy transformation, diagnostic changing, magnetic liquids, during delivery, biological separation, magnetic storage media, electrode materials, [14,27], electronics, purification processes and catalysis. The present work explains the effect of electrical and electrochemical properties of polymeric nanocomposites prepared with Fe₂O₃ nanoparticle incorporated in PUD/PCL blend. The nanocomposites prepared were investigated for mechanical, thermal, dynamic mechanical thermal analysis, magnetic, X-ray diffraction, HR-SEM and TEM and already reported [15].

2. Materials and methods

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2.1 Materials

Polycaprolactone, average molecular weight ~ 45,000 was used after dehydration under vacuum at 60 °C for 4hrs. Polyurethane diol (PUD), average molecular weight ~320 was used after removal of water at 100 °C for 12 hours in a vacuum air oven. 4, 4’-diaminodiphenylmethane (DDM) and a catalyst Dibutyltindilaurate (DBTDL), Iron oxide nanoparticles were purchased from Sigma Aldrich and hexamethylene diisocyanate (HDI) from Fluka were used as received with no extra purification.

2.2 Methods

The nanocomposites prepared were fabricated in the form of pellet and enclosed by graphite to get a good conducting surface layer. The pellet size was measured by means of a travelling microscope. The dielectric constant and conductivity measurements were analyzed by means of an LCR meter (Agilent 4284 A). The CV measurements were approved by electrochemical workstation 604D, CHI Instruments, USA electrochemical analyzer.

2.3 Synthesis of PUD/PCL-Fe$_2$O$_3$ nanocomposites

40g of polyurethane diol was taken in a warmed mixer and heated at around 90°C and then 10 g of polycaprolactone was added. The mixture was heated at 120°C and agitated at a rotor speed of 415 rpm for 30 minutes constantly. Polycaprolactone pellet was completely miscible with the melted polyurethane diiol. To this homogeneous mixture, 0.5g of Fe$_2$O$_3$ nanomaterial was added slowly and agitated at 415 rpm for 45 minutes. One hour of sonication allowed the nanoparticles to dissolve regularly throughout the blend. Heating was stopped and then 12 ml hexamethylene diisocyanate and 4g dianimodiphenylmethane were added and agitated. The whole content was relocated to the mold and dehydrated overnight at room temperature in a vacuum air oven and at 100 °C for 1hour.

2.4 Electrode preparation for electrochemical characterization

Electrochemical workstation 604D, CHI Instruments, USA electrochemical analyser with a three-electrode cell assembly consisting of a saturated calomel electrode as reference electrode, Pt wire served as supporting electrode and PUD/PCL-Fe$_2$O$_3$ nanocomposite slurry coated copper foil as working electrode with 1M KOH as the electrolytic solution were used for cyclic voltammetry measurements. 0.1mm thickness copper foil electrode was prepared with a dimension of 1 cm$^2$. 0.1g of the nanocomposite was dissolved in DMF and a colloidal solution was prepared by sonication for 15 min. Then the slurry was spread on the exterior of a copper foil and dried at room temperature to get a film on the surface of the copper foil.

3. Results and discussion

3.1 Temperature dependence dielectric constant

The relative permittivity variation of the polymer nanocomposites as a function of temperature over frequency of 1kHz,10kHz,100kHz and 1000kHz are depicted in figure 1(A-D). The dielectric performance with temperature variation is different for different temperature. It is clear that from the graphs, the dielectric constants are low at low temperature and when the temperature is raised, the value rises correspondingly. At room temperature, the effect of grain boundaries is dominant, which is reflected in the low magnitude of dielectric properties. Nevertheless, as the temperature is increased, the sizes of grains become more, which results in the increase of dielectric properties [16]. Furthermore, the relative permittivity ($\varepsilon_r$) of the pure blend was very low, when compared to various Fe$_2$O$_3$ nanoparticles loaded PUD/PCL blend. This is attributed to the fact that the dielectric properties of polymeric material are determined by the charge dispersal along with the statistical thermal motion of their polar groups [17]. In the case of polar polymers, the dielectric
constant begins to drop at a certain temperature invariably for all frequencies, which is also observed in the nanocomposites prepared [18]. This can be attributed to the phase changes that occur around 50°C for different composites prepared at all frequency ranges. These variations in dielectric values can be attributed to the changes in orientation polarization caused by temperature change [19].

Figure 1. (A-D) relative permittivity and temperature dependence curves for the frequencies 1KHz, 10KHz, 100KHz, 1000KHz for nano iron oxide composites (a)Pure blend (b) 0.5 wt% nano iron oxide composite (c) 1.0 wt% nano iron oxide composite (d) 1.5 wt% nano iron oxide composite (e) 2.0 wt% nano iron oxide composite (f) 2.5 wt% nano iron oxide composite.

3.2 Frequency dependence dielectric constant

The dielectric constant variation with frequencies at 30°C and 70°C for dissimilar concentration of Fe₂O₃ nanoparticles are given in the figure 2 (A& B). It is observed from the figure, as the frequency increases the dielectric constant decreases. This change is due to the charge carriers
located at the boundaries of the nanoparticles and polymer matrix forming space charges. Along the applied field, these space charges will orient themselves, while the electric field is applied. When the frequency of the applied field increases, polarization decreases and hence the dielectric constant decrease [17]. The dielectric constant value for pure blend at 30°C has extremely low value, but the addition of nano iron oxide filled blend shows approximately 10 times higher values. The low value for blend may be owing to the space charge division at sample –electrode border, whereas high values may be connected to the orientation polarization effects due to relaxing dipoles. The tiny increase at high temperature may be due to faster ion migration at high temperature above \( T_m = 50°C \) due to the polymer matrix phase change [20].

3.3 Conductivity

The conductivity variation for different frequency ranges of pure PUD/PCL blend and with different weight percentage of \( \text{Fe}_2\text{O}_3 \) nanoparticles loaded nanocomposites over the temperature of 30-70°C are displayed in figure 3. Pure polyurethane electrical conductivity is between \( 10^{-12} \) to \( 10^{-8} \) S/m [21]. The reported conductivity value for polycaprolactone is \( 1.86x10^{-11} \) Scm\(^{-1}\) at room temperature [22]. But the electrical conductivity of iron oxide at room temperature is found to be in the order of \( 10^{-2} \) S/cm [23]. It can be seen; the conductivity of blend was found to be \( 4.215 \times 10^{-6} \) to \( 6.38 \times 10^{-6} \) S/cm. For \( \text{Fe}_2\text{O}_3 \) nanoparticles loaded composites, the conductivity values increased from \( 3.13 \times 10^{-5} \) to \( 4.69 \times 10^{-5} \) S/cm for different frequency ranges selected with temperature. Since the conducting polymer nanocomposites electrical conductivity variations depend on the conductivity of the conducting polymer matrix and the filler particles [24,25]. Since the temperature increases, the charge carriers are thermally introduced and the free volume increase, which in turn results more empty places for the motion of ions, and hence increases the conductivity [17].
Figure 3. (A-C) Conductivity of frequencies 1 KHz, 10 KHz, 100 KHz for nano iron oxide composites. (a) Blend (b) 0.5 wt% Nano iron oxide composite (c) 1.0 wt% nano iron oxide composite (d) 1.5 wt% nano iron oxide composite (e) 2.0 wt% nano iron oxide composite (f) 2.5 wt% nano iron oxide composite.

3.4 Cyclic voltammetry analysis

Cyclic voltammetry for Polyurethane diol/Polycaprolactone polymer blend and Fe$_2$O$_3$ nanoparticle filled nanocomposites were studied in the potential applied between -0.8V to 1.2V verified at 50mVS$^{-1}$ scan rates with 1 M KOH, and are presented in figure 4. The anodic peaks and cathodic peaks were observed for PUD/PCL-Fe$_2$O$_3$ nanocomposites. The cathodic potential value for pure blend is 0.117V. But for nanocomposites of higher Fe$_2$O$_3$ nanoparticles concentrations viz., 0.5, 1.0, 1.5, 2.0 and 2.5 wt %, reduction potential values are less positive at -0.378V, -0.379, -0.381V, -0.385, and -0.390 respectively. The anodic oxidation peak value for 1.0, 1.5, 2.0 and 2.5 wt % loaded composites, the values are -0.666V, -0.669V, -0.678V, and -0.679V. From the peak values, the current of the nanocomposites increased from the lower concentration to higher concentration by the loading of iron oxide nanoparticles added. This improved electrochemical behaviour can be attributed to the electrical conductivity of the Fe$_2$O$_3$ nanocomposites on the electrode surface [26]. The electrochemical response revealed the ability of the material to perform as a potential alternative promoter and base for catalyst in fuel cells.
4. Conclusion

The temperature dependence analysis showed that at low temperature, the dielectric constant was low and at higher temperature dielectric constant was increased. As the temperature was increased, the size of grains becomes more that results in the rise of dielectric constant value. Frequency dependence dielectric constant graphs showed that when the frequency was increased, the dielectric constant value decreased. The space charges orient themselves along the applied field, while the electric field was applied. When the applied field frequency increases, polarization and also dielectric constant values decreases. The conductivity value for nanocomposites increased than the pure blend for different frequency ranges selected for different temperature. This can be attributed to the fact that the conducting polymer nanocomposites electrical conductivity changes depend on the conductivity of the filler particles into conducting polymer matrix. Cyclic voltammetry studies shown that the electrochemical response of the material to perform as a potential alternate catalyst. This novel polymer nanocomposites prepared can be utilized for various field of electronics and fuel cells.

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