Polymer Nanocomposite Containing High Permittivity Nanoparticles for Energy Storage Application

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Abstract
Polymeric dielectric materials used for energy storage application should have essentially high dielectric constant, high energy storage density, low dielectric loss and retaining dielectric strength. The dielectric properties can be improved by adding suitable high permittivity nanoparticles into base polymeric material. The enhancement of dielectric properties of polymer nanocomposite mainly depends upon the inherent quality of nanoparticles and base polymer matrix. In this analysis of work Polyetherimide (PEI) and multi walled carbon nanotubes (MWCNT) are used as the base polymer and nanofiller respectively. PEI/MWCNT nanocomposite samples were prepared and experiments were conducted to measurement of dielectric properties with respect to various filler loadings. Simulation of electric field distribution in unfilled and nanocomposite are studied using Finite Element Method (FEM) and correlated with the experimental results. The significant improvement in dielectric properties of PEI nanocomposites is observed with lower concentration fillers and achieved the noteworthy improvement in dielectric properties.

Keywords: Nanocomposites, Nanofiller, Dielectric Properties, Energy storage

I. INTRODUCTION
Polymers are the primary choice of materials for energy storage capacitors application due to low cost, low dielectric loss, and light weight. Polymer dielectric materials for
energy storage applications must have high dielectric constant to achieve high capacitance density. In order to increase the dielectric constant of polymeric materials, composite materials provide a unique solution. Recently, most of the work has been focused on development of polymer dielectric, which meets the requirement for embedded capacitor application. In this regard, conductive polymer nanocomposite have been identified and developed for capacitor as energy storage applications [1-3]. Introduction of nanoparticles into polymer matrices to form dielectric polymer nanocomposites represent one of the most exciting and promising avenues for energy storage capacitors used in battery management system in micro grid and which are non-toxic materials that are free from the pollution [4]. Compare with the micro-sized filler, nanoparticles have larger interfacial area per unit volume, when the particles are well dispersed into the polymer material. The Capacitance of polymer nanocomposite has increased and mainly depends upon the inherent permittivity of nanoparticles, nanofiller loading and interfacial behaviour between polymer and nanoparticle.

Appropriate selection of nanofillers based upon the shape, size and nature influence the enhancement of dielectric properties of the polymer nanocomposites. There are two types of nanofillers are there to synthesize the polymer nanocomposites, that is non-conducting and conducting fillers [5]. Most recently, polyimide nanocomposite films have been prepared by incorporating the functionalized multi-walled carbon nanotubes (MWCNTs) The resulting polyimide/MWCNT films are of high quality, optically transparent and homogenous [6,7]. As per Suibin Luo., et al. it can be seen that the enhancement of the dielectric properties of polymer based composites with hybrid fillers and surface modified polymer matrix [8]. Similar work done by Enis Tuncer, electrical properties of Polyetherimide films were tested and results obtained in the favour of energy storage application [9].

Polyetherimide is an amorphous and transparent thermoplastic type. It has temperature resistance, impact strength, creep resistance and rigidity, very high tensile strength, good flame resistance and low smoke emission. It is resistant to acids, hydrocarbon solvents and alcohols. It has good hydrolytic stability. The dielectric constant of polyetherimide is in the range of 3.1-3.2. It has excellent dimensional stability, outstanding strength and modulus at elevated temperatures, good UV and hydrolysis resistance etc. Polyetherimide used in various engineering applications like electrical/electronics, automotive, medical, industrial to manufacture different types of objects [10].

Carbon Nanotubes divided into single walled and multi-walled Nanotubes. Multi-wall Carbon Nanotubes are first discovered in 1991 by Iijima. Carbon Nanotubes are rolls of multiple graphene sheets with outside diameter of 10~20nm. Later Single-wall Carbon Nanotubes are discovered with diameter 1~3nm [11]. It is difficult to identify the deterministic value of permittivity for various kinds of MWCNT, because it completely depends on the accurate determination of number of graphene sheets
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wrapped, radius, length, surface oxidation and molecular defects [12]. Carbon Nanotubes are having properties like, high electrical conductivity, high tensile strength, highly flexible—can be bent without damage, very elastic ~18% elongation to failure, high thermal conductivity, low thermal expansion coefficient. While comparing to other capacitors, Carbon Nanotubes super capacitors have high capacitance, high conductivity, and high dielectric constant [13]. In the present work polyetherimide (PEI) used as a polymer matrix and Multi-wall Carbon Nanotubes (MWCNT) used as nanofiller with various wt% loading and the dielectric properties of PEI-MWCNT nanocomposite are studied. For composite containing 1.5 wt% loading of MWCNT (30nm), a dielectric constant of 8.5 and low dielectric loss 0.09 (at 100 KHz) can be achieved.

II. Experimental Details

A. Materials Used

Polyetherimide pellets (Ultem AUT 100) was purchased from SABIC, (Ultem AUT 100, SABIC ltd., C\textsubscript{37}H\textsubscript{24}O\textsubscript{6}N\textsubscript{2}, Density: 1.27 g/cm\textsuperscript{3}, Mol.wt: 592 g/mol, Tg: 216 °C). The nano filler used was Multi Wall Carbon Nano Tube (Number of walls: 3–15, Carbon purity: min. 98%) which was prepared by chemical vapor deposition (CVD) method and procured from Nanoshell, USA.

B. Choice of Nanofiller and Weight Percentage Loading

It is important to determine the interparticle distance as a function of sizes and shapes to understand the behaviour of effect of filler concentration and the interface on the dielectric properties. Interparticle distance is calculated between nanoparticles for various filler loadings. The inter particle distance calculated using the equation given by Tanaka et al. and is given as

\[
D = \left( \frac{\pi}{6} \rho_m \frac{100}{\rho_n \text{wt}\%} \left[ 1 - \frac{\text{wt}\%}{100} \left( 1 - \frac{\rho_m}{\rho_n} \right) \right] \right)^{\frac{1}{3}} d
\]

(1)

Where \( \rho_m \) and \( \rho_n \) are the specific gravity of the polymer matrix and nanofiller respectively (\( \rho_m = 1.27 \text{ g/cm}^3 \), \( \rho_n = 2.1 \text{ g/cm}^3 \)) and \( d \) is the thickness of the nanofiller in nm [14]. The interparticle distance for PEI/MWCNT nanocomposites are as shown in Figure 1. It can be seen that, the interparticle distance decrease when increase of wt\% loading of nanoparticle into the base polymer matrix.
At 2 wt% loading interparticle distance is approximately equal to thickness of the nanofiller. Further addition of nanoparticles leads to the agglomeration in polymer matrix which degrades the properties. From the interparticle distance calculation up to 2 wt% loading of nanoparticles are considered in PEI/MWCNT nanocomposite.

C. **Sample Preparation of PEI/MWCNT Nanocomposite**

The ULTEM PEI polymer pellets were smashed into powder form through solvent precipitation process and dry it, mix it with MWCNT’s in high speed mixer. Improvement in wetting between the nanofiller MWCNT and Polymer matrix PEI is expected from this process. Technique like dissolving both polymer matrix and filler in organic solvent is wet mixing where this substance leads to volatile organic compound (VOC) emissions, trapping of solvent in the nanocomposites and reduction of MWCNT aspect ratio. By using injection molding type method according to ASTM D 638 standards, PEI/MWCNT nanocomposite was prepared [15].

III. **Results And Discussions**

Dielectric properties of prepared PEI nanocomposite are measured using precision LCR 3532 at room temperature and at constant applied voltage 1.3V. The permittivity and tan delta measurements are performed using 7600 Precision LCR Meter for in accordance with ASTM D 150, IPC-TM-650 and IEC-60250 in the frequency range of \((2 \times 10^2 - 2 \times 10^5)\)Hz.

A. **Dielectric Constant of PEI nanocomposite**

Effective permittivity is a quantity that measuring the ability of a substance to store
electrical energy in an electric field. The effective permittivity in nanocomposite mainly depends upon the dielectric polarization at interface. Since nanocomposite has a large volume of interfacial polarizations, the effective permittivity in nanocomposite is determined with respect to frequency of applied electric field. The effective permittivity of PEI nanocomposites increases with the permittivity of the filler and with the filler concentration.

a) Frequency dependence

The influence of nanoparticles type on the relative permittivity of PEI nanocomposites for various frequencies is shown in Figure 2. Reduction in dielectric permittivity has been observed with increase in frequency for unfilled and PEI/MWCNT nanocomposites. The reduction in permittivity with frequency is because of the problem in reorienting the dipolar groups. The dielectric permittivity of PEI/MWCNT nanocomposite with various filler loading decreases between the frequency ranges (3 * 10⁵ − 10 * 10⁵) Hz [16].

![Figure 2: Dielectric constant of PEI/MWCNT nanocomposites at different weight percentages as a function of frequency](image)

b) Comparison between Calculated and Measured Value of Effective Permittivity Value of PEI/MWCNT Nanocomposites

The effective permittivity of PEI/MWCNT nanocomposites can be calculated using Maxwell-Garnett model is given as

\[
\varepsilon_{\text{eff}} = \varepsilon_m \left[ 1 + \frac{3V_f(\varepsilon_f - \varepsilon_m)}{V_m(\varepsilon_f - \varepsilon_m) + 3\varepsilon_m} \right]
\]  

(2)

In the equation (2) \(V_m\) and \(V_f\) are the volume fractions of the polymer and the filler.
$\varepsilon_m$ and $\varepsilon_f$ are the permittivity of polymer and the filler.$\varepsilon_{ef}$ is the effective permittivity of the polymer nanocomposites [17]. Figure 3 explains the comparison between experimental values at 1MHz and theoretical values as a function of different weight percentages. Theoretical calculation of effective permittivity based on Maxwell-Garnett model approximately matches with the experimental values. The increase trend of effective permittivity is observed with increased wt% loading of nanofiller.

![Figure 3: Comparison between the experimental values at 1MHz and theoretical values of effective permittivity.](image)

**B. Dielectric Loss or Dissipation Factor**

Tan $\delta$ mainly depends on the filler concentrations and filler permittivity. In polymer nanocomposites the interfacial dipoles form big cluster due to polarization. This orientation of dipoles reverses in each cycle when alternating field applied. But as the frequency increases the dielectric loss may increases because this reversal of field is quick and dipole orientation will lags the field. So, the dielectric loss increases, as increase in frequency because of the less time to orient dipoles among themselves. Figure 4 describes the dielectric loss (tan $\delta$) values of PEI/MWCNT nanocomposites for different weight percentages as a function of frequency. As shown in Figure 4 dielectric loss increased as the increase in frequency in the case of 1%, 1.5% as compared to unfilled PEI. However the value of tan $\delta$ in unfilled PEI, 1and 1.5 wt% MWCNT nanocomposites has the range as per standard specification [18].
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Figure 4: Dielectric loss values variation as a function of frequency

C. Capacitance

Capacitance is the ability of a material to store electric charge at given voltage. Capacitance value calculated by using the equation

\[ C = \frac{\varepsilon_r \varepsilon_0 A}{d} \]  

(3)

From equation (3), \( \varepsilon_r \) is a permittivity of polymer nanocomposites and \( \varepsilon_0 \) is permittivity of free space (8.854 \( \times \) 10\(^{-12} \)). A is the area of sample (cm\(^2\)), and d is the thickness (mm) of the sample [3]. Figure 5 describes the capacitance values at 1MHz as a function of filler loading. It can be seen that the capacitance value is observed high at 1.5% of MWCNT filler loading due to high value of permittivity. The decreased trend of capacitance value is observed after 1.5wt% loading of MWCNT filler. According to the SEM image at 2wt% loading the nanofillers were agglomerated and influence the change in the dielectric properties. Hence the 1.5% filler loading may be suitable for capacitor applications in further studies.

Figure 5: Capacitance values as a function of weight percentage of PEI/MWCNT nanocomposites
D. Dielectric strength studies of PEI/MWCNT nanocomposites

The ac dielectric strength of PEI/MWCNT nanocomposite is mainly influenced by the type, size and inherent permittivity of nanoparticles.

a) Experimental Setup

By using high voltage test kit breakdown studies are conducted on unfilled PEI and PEI/MWCNT nanocomposites as per standard [ASTM-D149-97a, 2004]. The electrodes used for the experiment are 25 mm in diameters with an edge radius of 3.2 mm. Author used 6 samples for breakdown voltage test as per the standard. All the tests are carried out at room temperature. The samples are placed between the parallel plate electrodes and the kit is filled with transformer oil (free from particle and moisture) to avoid flashover. The kit is connected to ac (50Hz) supply and then the voltage is slowly applied at a speed of 1000V/s to the samples step by step until puncture or breakdown is occurred. The dielectric strength of unfilled and filled PEI is calculated as \( E = \frac{V}{d} \), where V is the measured value of breakdown voltage (V) and d is the thickness of the sample in milli meters. Figure 6 describes the breakdown strength of the polymer nanocomposite as a function of filler loading. Due to introduction of conductive nature high permittivity nanofiller into polyetherimide there is reduction in dielectric strength has been observed.

![Dielectric Strength vs Filler Loading](image)

**Figure 6:** Dielectric strength of PEI/MWCNT nanocomposite as a function of filler loading

b) Energy Density

Energy density is mainly depends on the dielectric constant and breakdown strength of the material. Here electric energy density of PEI/MWCNT nanocomposite is calculated by using equation
$E = \frac{1}{2} k E_b^2$ \hspace{1cm} (4)

Where in equation (4), \(E\) is the electric energy density, \(k\) is the permittivity and \(E_b\) is the breakdown strength of the polymer nanocomposite [3]. In general polymers have high breakdown strength and low dielectric constant. Hence the introduction of conductive nature of nanofiller into polymer influences the increase value of dielectric constant and enhances the energy density of polymer nanocomposite. Figure 7 describes the calculated energy density value of the PEI/MWCNT composite. As shown, the energy density is high at 1, 1.5 wt% loading of MWCNT than the unfilled. At 0.5wt% loading the capacitance and energy density were observed lower than the unfilled, this may be reason of non-uniform dispersion of nanofillers into the polymer material.

![Figure 7: Energy density values as a function of filler loading of PEI/MWCNT composite](image)

E. Simulation Studies on Electric Field Distribution in Polyetherimide and Carbon Nano Tube Nanocomposite

Studies of electric field distribution on polymer nanocomposites can open up new avenues for the choice of nanofillers with diverse permittivity and its concentration. When the nanofiller added to base polymer matrix alter the electric field stress at the interface. Using Finite Element Method (FEM), the effective properties of composite can be calculated [19].

a) Simulation of Electric Field Distribution in Unfilled PEI

In this simulation Polyetherimide (PEI) (with permittivity value 3.5) is used as polymer matrix of the sample model. The dimension of model used in the simulation is 248nm side length of a square. The dielectric strength of the polyetherimide is varies between
28 to 35 kV/mm. Figure 8 describes the simulated electric field distribution across the 2D model when subjected to 60V. One of the boundaries was set to port as the input voltage, while opposite boundary was maintained at ground. All other boundaries set to periodic continuity condition. This makes the geometry analogous to a parallel-plate capacitor with a voltage applied across its plates.

From the Figure 8 it is observed that, the electric field distribution is uniform because of no interface or any interruptions and it gradually decreased at the lower plate.

b) Simulated Results of Electric Field Distribution in Polymer Nanocomposite at 1.5 wt% loading of MWCNT

In this simulation, PEI is taken as a polymer matrix with 1.5 wt% of MWCNT (permittivity is ~300) nanofiller in the sample. The sample dimension is 248nm length of the side of the square. From the BDV experiment the dielectric strength of this sample obtained was (40 - 41 kV/mm). Small dimension (nm) of unit cell taken into account for simulation and based on dielectric strength the voltage is calculated to this dimension as 60V. MWCNT nanofiller placed according to interpartic le distance calculation in the section. Figure 9 depicts the distribution of electric field in PEI with 1.5 wt% MWCNT nanocomposite.

The electric field distribution in polymer nanocomposites is mainly influenced by permittivity of the matrix and the nanofiller. From the Figure 9, high electric stress is observed at the interface of polymer and the filler. Low value of electric stress is observed in the nanoparticle due to high inherent permittivity.
**Figure 9:** Simulation result of electric field distribution in PEI with 1.5 wt% MWCNT nanocomposites

In simulation when the nanocomposite model sample subjected to external voltage the electric field inside the nanofiller influenced by permittivity. Figure 10 and Figure 11 shows the graph of field distribution inside the nanocomposite. From the Figure 10 it is observed that in unfilled sample the electric field distribution is uniform throughout the sample. But in Figure 11 when 1.5 wt% of MWCNT added to PEI, electric field distribution is not uniform, because of permittivity difference between the polymer matrix and filler.

**Figure 10:** Electric Field distribution in unfilled PEI
In the Figure 11 at some points the electric field became very less because of high permittivity of nanofiller present in the polymer. At the interface the stress is very high than the other places in the sample [20].

IV. Conclusion

The polymer nanocomposites are prepared by injection molding method. The material characterization of polymer nanocomposite was studied using SEM morphology techniques. The main contribution of this work is the identification of suitable filler for the improvement of various dielectric properties. From the theoretical, simulation and experimental analysis, it is concluded that the effective permittivity of the nanocomposite depends upon the inherent permittivity of fillers. Tan delta values can be kept within the limit of dielectric by having lower filler concentration. Breakdown strength on the nanocomposite decreases and hence it can be inferred that the higher permittivity of the polymer nanocomposite can be obtained by adding high permittivity nanoparticles at the expense of lower breakdown strength, suitable polymer nanoparticle combination for energy storage application is identified. For an energy storage application the permittivity, capacitance and energy density properties are important. And those values are appropriate at 1.5wt% loading of PEI/MWCNT nanocomposite and considered as the option for energy storage application.

References


