Possible Lead Free Nanocomposite Dielectrics for High Energy Storage Applications

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Abstract: There is an increasing demand to improve the energy density of dielectric capacitors for satisfying the next generation material systems. One effective approach is to embed high dielectric constant inclusions such as lead zirconia titanate in polymer matrix. However, with the increasing concerns on environmental safety and biocompatibility, the need to expel lead (Pb) from modern electronics has been receiving more attention. Using high aspect ratio dielectric inclusions such as nanowires could lead to further enhancement of energy density. Therefore, the present brief review work focuses on the feasibility of development of a lead-free nanowire reinforced polymer matrix capacitor for energy storage application. It is expected that Lead-free sodium Niobate nanowires ($NaNbO_3$) and Boron nitride will be a future candidate to be synthesized using simple hydrothermal method, followed by mixing them with polyvinylidene fluoride (PVDF)/ divinyl tetramethyl disiloxanebis (benzocyclobutene) matrix using a solution-casting method for Nanocomposites fabrication. The energy density of $NaNbO_3$ and BN based composites are also be compared with that of lead-containing ($PbTiO_3$/PVDF) Nano composites to show the feasibility of replacing lead-containing materials from high-energy density dielectric capacitors. Further, this paper explores the feasibility of these materials for space applications because of high energy storage capacity, more flexibility and high operating temperatures. This paper is very much useful researchers who would like to work on polymer nanocomposites for high energy storage applications.

Keywords: Dielectrics, Polymers, Nanowires, Nanocomposites, Energy storage devices.

1. Introduction

The development of high energy density storage systems with reduced size is highly demanded in many applications, e.g., consumer electronics, space-based and land-based pulsed power applications, commercial defibrillators, etc. [1]. The electrostatic energy density that can be stored in a material is directly proportional to its dielectric permittivity at the local field and the square of the operational electric field. This necessitates that modern materials for high energy density should not only posses high dielectric permittivity, but also provide high operational electric fields with low dissipation factors. The apparent absence of one single-phase material exhibiting such a combination of properties emphasizes the need to integrate two or more materials with complimentary properties, thus, in turn, creating a composite with performance far better than that of its constituents. Ferroelectric oxides have high dielectric permittivity, but suffer from low dielectric strengths. Polymers, on the other hand, have high breakdown field tolerances, but are limited to low dielectric constants. A diphasic composite consisting of these two could provide a material with high dielectric constant [2] and high breakdown field, affording high storage density for a

given thickness. The properties of such composites can be tailored through material selection and composition, as well as through percolation and connectivity of phases present within [3-4]. Recent efforts to obtain high energy density materials have primarily focused on randomly dispersed nano- or micron-sized ceramic particulates in a polymer matrix.

The dielectric properties of nanocomposites have been found to be better in comparison to microcomposites and neat polymers. Various proposed models with some experimental evidence have attributed this property enhancement to the interfacial effects related to filler-polymer interactions in nanocomposites. In this regard, this paper has focused on finding the ways to enhance the energy storage capacity of polymer nanocomposites by concentrating on interfacial interactions between polymer and filler particle surfaces within an applied field. The main objectives of this research paper are:

1) To modify the surface of nano-sized particles ceramic particles with bifunctional organophosphate coupling agents so as to achieve a covalent interface when used within an epoxy polymer matrix composites.

2) To study the influence of covalent interface on electrical properties, especially dielectric breakdown strength of polymer nanocomposite dielectrics compared to physically adsorbed interface based nanodielectrics and neat polymer.

3) To study the influence of electronic nature of surface functionalized filler particles on dielectric properties of their composites in epoxy. The electron donating and electron accepting functional groups were used as surface modifying reagents, attached via an organophosphate ligand on to the surface of filler particles.

4) To enhance the energy density of polymer nanocomposites by compromising the decrease in dielectric breakdown strength with increase in permittivity at higher filler particle volume concentration [5].

It was found that interface layers in the nanocomposites might be more conductive than the polymer matrix, which mitigated the space charge accumulation and field concentration by fast charge dissipation. Zhang and coworkers demonstrated large enhancement in the electric energy density and electric displacement level in the nanocomposites of P(VDF-TrFE-CFE) terpolymer/ZrO_2 nanoparticles [6]. Through the interface effect, the presence of 1.6 vol% of ZrO_2 nanoparticles raised the maximum electric displacement D from 0.085 C/m^2 under 400 MV/m in the neat terpolymer to more than 0.11 C/m^2 under 300 MV/m in the nanocomposites. The dielectric nanocomposites composed of P(VDF-TrFECTFE) [7] and surface-functionalized TiO2 nanoparticles with comparable dielectric permitivities and homogeneous nanoparticle dispersions were prepared [8]. It was found that the presence of the nanoscale filler favors the formation of smaller crystalline domains and a higher degree of crystallinity

in the polymer. In drastic contrast to their weak-field dielectric behavior, substantial enhancements in electric displacement and energy density at high electric fields have been demonstrated in the nanocomposites.

Miniaturization and the current need for high-power density, high voltage capacitors and power-storage devices has stimulated a new field of research interest in polymer nanocomposites as composite dielectrics (C) [9-15]. By incorporating high permittivity inorganic nanoparticles into a polymer matrix with low dielectric loss and high breakdown strength, one may be able to develop new composite materials that have improved dielectric properties, dielectric strength, permittivity and dielectric losses, and retain unique attributes of polymers.

The most distinctive feature of polymer nanocomposites in comparison with conventional microcomposites is the participation of interfacial surface area between the nanoparticles and the polymer matrix. The smaller the size of the embedded nanoparticles, the larger the surface area to volume ratio, which leads to larger interfacial regions [16-17]. For filler nanoparticles with modest loadings, the surface area associated with the internal interfaces becomes dominant in nanocomposites compared to microcomposites [18]. The properties of these interface areas may differ substantially from those of both the base polymer matrix and the nanoparticle material [18-19]. From literature, polymer nanocomposites with metal oxide nanoparticle fillers exhibited enhanced electrical breakdown strength and voltage endurance compared to their unfilled or micrometer sized particle filled counterparts.

While the use of nanowire could lead to higher energy density capacitor, most of the high dielectric constant inclusions used has lead- (Pb-) containing materials, such as PZT and PLZT, which make the resulting nanocomposites toxic and not compatible with biological applications. Expelling lead from commercial applications and materials such as solders, glass, and gasoline has been receiving extensive attention because of the concerns regarding its toxicity. Therefore, our present work focuses on the development of a lead-free nanowire reinforced polymer capacitor with comparable dielectric properties to lead-containing capacitors.

The dielectric constant and breakdown strength of nanocomposites with volume fractions ranging from 5 % to 30 % were experimentally tested to determine the energy densities of both nanocomposites. Testing results have shown that the NNO/PVDF composites have higher dielectric constants, lower dielectric loss, and comparable energy density. Therefore, this may demonstrate the feasibility of developing lead-free high-energy polymer capacitors to ultimately replace lead-containing ones. Further, BN nanosheets are thus envisaged to be one of the best fillers in composites owing to the highly insulating and thermoconductive properties. The fabricated PMMA/ BN composite plastics are, thus, envisaged to be valuable for diverse functional applications in many fields, especially for

the new-generation thermoconductive insulating long-lifetime packaging materials [21].

2. Role of Interface

Incorporation of nanoparticles into polymer matrix for developing nanocomposites, which has produced interesting results in last few years, has led researchers to investigate mechanisms for the improved dielectric properties. Researchers have emphasized the critical role of the interfacial region and present hypotheses for multiscale phenomena operating in polymer nanocomposites dielectrics [18-19]. Fig. 1 shows the physical description of the interfacial region in polymer nanocomposites [18]. In thermoplastics, the interfacial polymer can exhibit changes in crystallinity, group mobility, chain conformation, molecular weight, and chain entanglement density. There is an additional complication of changes in cross link density, in thermosets, due to small molecule migration to or from the interface.

The interfacial region has a direct impact on the dielectric properties of the composites. Therefore it is important to study the interfacial region. A multi-core model was proposed, which tries to capture the charge behavior and structure of the interfacial region. The metal oxide nanoparticle has a surface charge, which creates a Stern layer at the 2D interface, which is screened by a charged layer in the polymer. The next layer is a diffuse double layer of charge with around 10 nm of radial depth in a resistive medium (polymer). Since the diffusion double layer is a region of mobile

charge, both the dispersion of nanoparticles and the resulting dielectric properties in the polymer nanocomposites have significant influence.
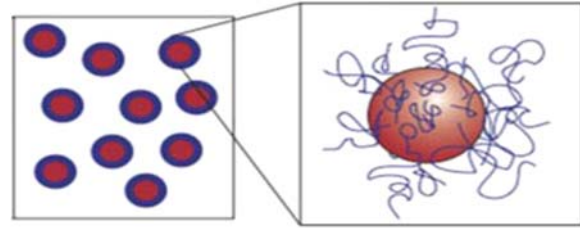

Fig. 1. Physical depiction of the interface re Based on the interfacial structure, hypotheses to explain the impact of interfacial region on the dielectric properties are summarized as following: [18].

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The interfacial region becomes more dominant, as the size of the filler is reduced. The density and perhaps the depth of trap sites are altered due to the change in local structure which affects the carrier mobility and energy. The carriers are accelerated over shorter distances and have reduced energy if they are trapped more often and same is the case for carriers that are scattered. As a result, the dielectric life time of the polymer is increased (Fig. 2).
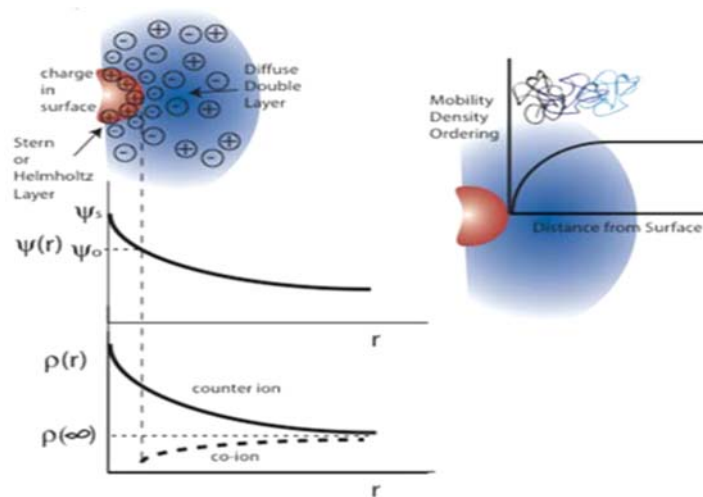

Fig. 2. Physical depiction of the interface region in polymer nanocomposites [19].

The voltage required for charge injection is increased as the homocharge resulting from carrier trapping mitigates the electric field at the electrodes. Thus the voltage required for the short term breakdown is also increased. The breakdown strength becomes the function of the rate of measurement (A.C., D.C., or impulse) as the charge takes time to build up. As the nanocomposites have larger

interfacial area, it increases the probability for scattering. Scattering may become the primary mechanism for the increase in the breakdown strength of nanocomposites during impulse test conditions, since significant shielding homocharge cannot be accumulated in such a short time. Because interfacial area is so large, while some of the above mechanisms may operate in micron sized filler filled polymer

composites, they are then overshadowed by the large defects the micron scale fillers introduce and the field enhancements they create. Microcomposites exhibit Maxwell-Wagner interfacial polarization, which is generally finite in nanocomposites and depends on filler concentration and filler material [18-19]. Electroluminescence, photoluminescence, thermally stimulated currents, X-ray secondary emission spectroscopy and electron paramagnetic resonance provided experimental evidence to suggest the working of the hypothesis [18, 20].

3. Surface Modification of Nanoparticles

As the properties of polymer nanocomposites are often influenced by the interfacial region, control of interface becomes very important. Failure to control the interface results in aggregation or agglomeration of nanoparticles in polymer matrix, which leads undesirable properties due to poor film quality and inhomogeneities [12]. Thus, proper dispersion of nanoparticles in polymer nanocomposites plays an important role in polymer nanocomposites. Without proper dispersion and distribution of filler particles in polymer, the high surface area of nano-sized particles is compromised and the aggregates can act as defects, which limits properties [22].

The most common method to achieve proper dispersion is to modify the surface of nanoparticles. The first aspect of modifying the surface of nanoparticles is to attain stabilization of particles against agglomeration to accomplish homogeneous nanocomposites. The second aspect is to render the guest material (nanoparticle filler) compatible with host material (polymer). The third interest in nanoparticles modification is to enable their self-organization [23]. Surface modification of nanoparticles can be obtained by using suitable surfactants that yield an adsorptive interface or by grafting organic groups on the surface of metal oxide nanoparticles, e.g., using phosphates, phosphonates or silanes as coupling agents or dispersants which yields stable and complex organic oxide interface [24-25].

4. Role of Volume Fraction

Previous studies have shown that as the volume fraction of the high permittivity component, nano particle fillers, is increased, the effective permittivity of the nanocomposites also increases [26-28]. However, increasing the volume fraction of the nanoparticles typically decreases the apparent dielectric breakdown strength of the nanocomposite due to the enhancement of the local electric field in the host material [29] and nanocomposites with large volume fractions of nanoparticles typically exhibit porosity that is detrimental to their dielectric performance. Therefore, the role of volume fraction of

high permittivity nanoparticles on the dielectric properties (permittivity, loss and breakdown strength) is important and should be rationally chosen in order to maximize the stored electrical energy density.

Many mixing models like parallel model, series model, Lichteneckers rule exist which are able to predict electrical properties based on the dc conductivity/resistivity and work best for dilute composites at low volume fractions [30]. Another popular method of predicting the properties of composites is percolation theory, which is based on the assumption that the properties will change when the second phase is totally connected, i.e., percolated, from one side of the composite to the other [31]. The volume fraction at which percolation occurs is called the "percolation threshold." Percolation threshold depends on many factors, including the connectivity of the phases, the size of each phase, the shape of each phase and the wetting behavior of the phases. Percolation models allow for a large, orders of magnitude, change of properties over a very small concentration range [32].

As a mixing system, composites filled with inorganic fillers are ideal objects from the point of view of percolation theory. When the concentration of fillers is low, the composites will behave more like the insulating matrix. Once the volume fraction of fillers nears the percolation threshold, for example, 16 % or 19 % considering impurities, the electrical properties of the composites can be obviously changed by the channels formed in which charge carriers connect inorganic fillers [33]. The percolation threshold for a 2-dimentional system is accurately predicted as 50 % by effective medium theory and the predicted percolation threshold for 3-dimentional system is at 33 % by effective medium theory [33-34].

5. Dielectric Breakdown

The dielectric material will suddenly begin to conduct current if the voltage across it becomes too high. This phenomenon is called „dielectric breakdown" [35] and the maximum voltage that can be applied without breaking is called „dielectric breakdown strength". In solid dielectrics, electrical breakdown usually results in permanent damage.

The breakdown in a dielectric material is controlled by several mechanisms shown in [36-37]. Under a variety of field stresses, the breakdown suffered by dielectric materials presents a very strong time dependent relationship and can be divided into five or more kinds by breakdown speed. Electrical, thermal and electromechanical breakdown mechanisms are known as the short-term breakdown or degradation mechanisms [38] mechanisms and the others are long term Fig. 3. Schematic depicting times and electric fields at which various electrical breakdown in polymers and composite dielectrics is limited by high field carrier injection and charge trapping electrode-dielectric interface [37].

Electromechanical breakdown is controlled by mechanical properties of dielectric material under high electrical stress and structural parameters. Generally large changes in dielectric breakdown strength at temperatures approaching glass transition temperature are attributed to be related to electromechanical

breakdown mechanism (Fig. 3). Where gas is present inside any voids in the dielectric material, gas gets ionized leading to breakdown or discharge within the void under high electric fields leading to the phenomenon known as partial discharge breakdown.
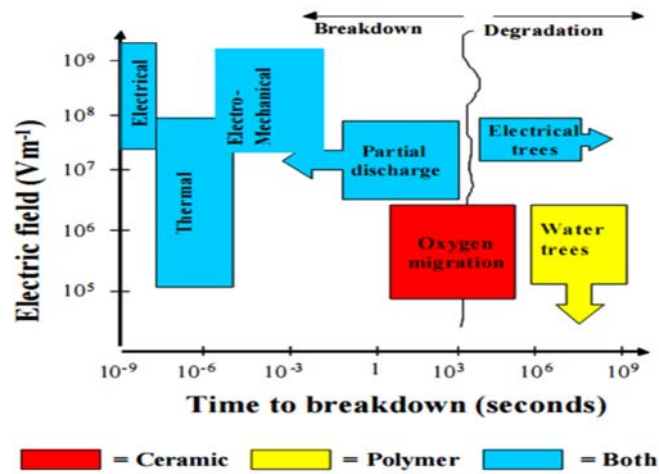

Fig. 3. Schematic depicting times and electric fields at which various electrical breakdown in polymers and composite dielectrics is limited by high field carrier injection and charge trapping electrode-dielectric interface [37].

The discharge damages the structure of the materials and voids or cracks becomes larger, which can be considered as degradation, which erodes the dielectric resulting in breakdown. Discharge may also take place in surface of the dielectric if the surface is contaminated by dirt, water or any other impurities.

Various factors influence the dielectric breakdown event, which include temperature; defects and inhomogenity of material; thickness, area and volume of the material; duration of time for which the dielectric is subjected to electric field; surface conditions and the method of placing the electrodes; area of the electrodes; composition of the electrodes; moisture (humidity) and other contaminations; aging and mechanical stress.

6. Feasiblity NaNbO₃-PVDF Based Nanocomposite

It was found that interface layers in the nanocomposites might be more conductive than the polymer matrix, which mitigated the space charge accumulation and field concentration by fast charge dissipation. Zhang and coworkers demonstrated large enhancement in the electric energy density and electric displacement level in the nanocomposites of (PVDF-TrFE-CFE) terpolymer/ZrO_2 nanoparticles. Through the interface effect, the presence of 1.6 vol % of ZrO_2 nanoparticles raised the maximum electric displacement D from 0.085 C/m^2 under 400 MV/m in the neat terpolymer to more than 0.11 C/m^2 under 300 MV/m in the nanocomposites. The dielectric nanocomposites composed of P(VDF-TrFECTFE) and surface-functionalized TiO_2

nanoparticles with comparable dielectric permittivities [38-40] and homogeneous nanoparticle dispersions were prepared. It was found that the presence of the nanoscale filler favors the formation of smaller crystalline domains and a higher degree of crystallinity in the polymer. In drastic contrast to their weak-field dielectric behavior, substantial enhancements in electric displacement and energy density at high electric fields have been demonstrated in the nanocomposites. However, with the increasing concerns on environmental safety and biocompatibility, the need to expel lead (Pb) from modern electronics has been receiving more attention. Using high aspect ratio dielectric inclusions such as nanowires could lead to further enhancement of energy density. Therefore, the present review focuses on the development of a lead-free nanowire reinforced polymer matrix capacitor for energy storage application. Lead-free sodium niobate nanowires ($NaNbO_3$) were synthesized using hydrothermal method, followed by mixing them with polyvinylidene fluoride (PVDF) matrix using a solution-casting method for nanocomposites fabrication. Capacitance and breakdown strength of the samples were measured to determine the energy density. The energy density of $NaNbO_3$/PVDF composites was also compared with that of lead-containing ($PbTiO_3$/PVDF) nanocomposites and previously developed $Pb(Zr0.2Ti0.8)O_3$/PVDF composites to show the feasibility of replacing lead-containing materials. The energy density of $NaNbO_3$/PVDF capacitor is comparable to those of lead-containing ones, indicating the possibility of expelling lead from high-energy density dielectric capacitors.

Ceramics are the other common material broadly used in dielectric capacitors [41]. Compared with polymers, ceramics such as $BaTiO_3$, $Pb(Zr_xTi1-x)O_3$ (PZT), and lanthanum doped PZT (PLZT) have significantly higher relative dielectric constants. However, the breakdown strength of ceramics is typically two orders of magnitude lower than dielectric polymers [42]. Moreover, due to its fragility and brittleness, it is difficult to manufacture ceramic capacitors with desired capacity for energy storage applications [43].

Therefore, a good deal of research effort has been devoted to combine the high dielectric constant of ceramics and high breakdown strength of polymers through the composite approach. To date, many research groups increased the energy density of dielectric capacitors using a nano composite approach, including barium titanate ($BaTiO_3$) nano particles reinforced polycarbonate (PC) [44] and poly(vinylidene fluoride- co-hexafluoropropylene) (PVDF-HFP) [45], modified BaTiO3 nanoparticle with PVDF [46-47], tanium dioxide (TiO_2) nanoparticles with PVDF terpolymer [48], calcium copper titanate (CCT) reinforced polyimide [49], ,silver nanoparticle/poly (vinyl pyrrolidone) core-shell structure for high dielectric constant and low loss epoxy matrix composite [50] and PZT or PLZT powders reinforced PVDF [51-52].

Recently, Andrews, *et al.* developed a micromechanics model to show that using higher aspect ratio nanowires instead of nanoparticle inclusions could lead to significant increase in the dielectric constant of the nanocomposites [53]. Further, Tang, *et al.* [54] experimentally demonstrated that the use of nanowires instead of nanoparticles could significantly increase the dielectric energy density of the nanocomposites.

7. Preparation of NNO/PVDF Nanocomposites

The fabrication process of the NNO/PVDF nanocomposites utilized a two-step procedure; NNO nanowires were first synthesized using hydrothermal technique, r followed by dispersing nanowires in PVDF and dimethylformamide (DMF) solution to form nanocomposites by solution casting method. Samples with volume fractions ranging from 5 % to 30 % were prepared to study the nanowire volume fraction influence on energy density.

6.1. NaNbO3 Nanowires Synthesis

Sodium niobite nanowires were synthesized following a hydrothermal method developed by Jung, *et al.* [20]. In a typical process, a 12 M NaOH solution was prepared by dissolving 33.6 g of NaOH (Acros Organics, 98 %) into 70 mL of deionized water (DI).

Subsequently, 3.5 g of Nb_2O_5 (Aldrich, 99.99 %) were added into the NaOH solution. After stirring for a period of 30 minutes at room temperature, the mixture was transferred into a 160 mL Teflon lined stainless steel autoclave with a fill factor of 80 %. The autoclave was placed inside an electrical oven to undergo hydrothermal reaction at 180 °C for 4 h. After cooling down to room temperature, white precipitate was filtered, washed with DI water for several times, and dried at 80 °C for 12 h. Finally, NNO powders were annealed at 550 °C for 4 h in order to obtain crystallized NNO nanowires [55].

PVDF and DMF (99.8 %) were mixed at a 1:10 weight ratio and heated up at 80 °C for 30 minutes to fully dissolve the PVDF. Nanocomposites were prepared by dispersing NNO or PTO nanowires into PVDF/DMF solution by manual stirring and horn sonication until a homogeneous mixture was obtained. Subsequently, solution was casted onto a PTFE film and dried at 80°C for 6 h [55]. In order to achieve a consistent thickness over the entire film, nanocomposites were hot pressed at 160 °C for 15 minutes under a constant pressure of 1 ton. Finally, top and bottom surfaces of nanocomposites were coated with silver paint as electrodes for electrical testing. The fabrication process of the nanocomposites is schematically shown in Fig. 4 [55].
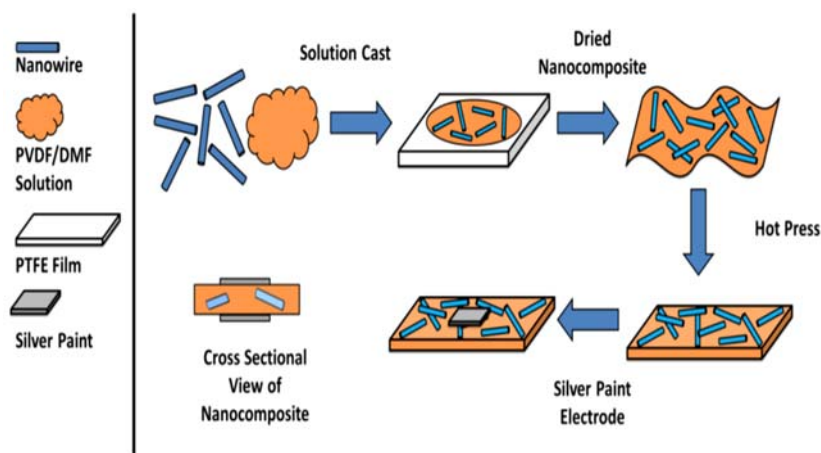

Fig. 4. Preparation steps involved in nanocomposite [55].

The breakdown voltages were measured according to standard (Experimental setup utilized a 30 kV high voltage power supply and a digital oscilloscope, both connected to a 20 MHz function/arbitrary waveform generator In order to avoid arcing prior to breakdown, nanocomposites were held inside a 500 mL beaker filled with silicon oil. Breakdown voltage was recorded through a digital multimeter connected to the high voltage power supply.

The morphology of the synthesized NNO nanowires (NWs) is shows that NNO NWs have an average diameter of 400 nm with length up to 20 μm. As indicated from the SEM images, homogeneous dispersion of the nanowires throughout the entire sample is achieved and no voids are shown in the samples. As expected, SEM images displayed random orientation of nanowires inside the polymer matrix. After the characterization of dielectric constant and loss of the nanocomposites, breakdown strength testing is carried out to fully understand the energy density [55].

Recently, Penn state team [56] developed the boron nitride polymer composite it can handle high temperatures exceeding 480 °F under high voltage application. This material is easy to manufacture by first combining the nanosheets and the polymer. Then the polymer has to be cured using light or heat to generate crosslinks. As the nanosheets measure only around 2 nm in thickness and 400 nm in lateral size, they stay flexible. The combined material offers exceptional dielectric properties such as heat resistance, higher voltage capability and bendability. This composite polymer is made of divinyltetramethyldisiloxanebis (benzocyclobutene) surrounding boron nitride nano sheets. Boron nitride is structurally similar to graphene and forms sheets a single atom thick. The resulting material exhibits superior properties compared to anything already out there. In order to see how good this new dielectric really is, the team compared its properties to the best polymeric dielectrics on the market. They examined the dielectric constant at 10^4 Hz alternating current, a frequency common in power conditioning, and 300 °C. Under these conditions, they saw minor variations (less than 1.7 percent) compared to eight percent for the best existing system. They also looked at how the dielectric constant changed under direct current and found similar results [56].

8. Conclusions

In this paper we have made a thorough investigation of Pb free nanocomposites for high energy density applications. Expelling lead from commercial applications and materials such as solders, glass, and gasoline has been receiving extensive attention because of the concerns regarding its toxicity. Therefore, our present work focuses on the development of a lead-free nanowire reinforced polymer capacitor with comparable dielectric properties to lead-containing capacitors. We have also

emphasized the critical role of the interfacial region and present hypotheses for multiscale phenomena operating in polymer nanocomposites dielectrics. Further, increasing the volume fraction of the nanoparticles typically decreases the apparent dielectric breakdown strength of the nanocomposite due to the enhancement of the local electric field in the host material. The dielectric constant and breakdown strength of nanocomposites with volume fractions ranging from 5 % to 30 % were experimentally tested to determine the energy densities of both nanocomposites. Recent research suggests that the NNO/PVDF composites have higher dielectric constants, lower dielectric loss, and comparable energy density. Therefore, this may demonstrate the feasibility of developing lead-free high-energy polymer capacitors to ultimately replace lead-containing ones.

Acknowledgements

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