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Perspective and Developments in Composite Films Combining Lead-Free Ferroelectric Ceramic and PVDF for Energy Storage Capacitors

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Abstract

To enhance the advancement of excellent energy storage capacity in lead-free dielectric capacitors, we conducted an extensive review of recent research articles focusing on the utilization of energy storage in various lead-free dielectric materials, including ceramics and polymer-based composites. Devices that can store and release electrical energy when needed are called energy storage capacitors. They are used in many different industries, including power electronics, electric cars, and renewable energy. However, conventional dielectric materials for capacitors have low energy density and high leakage current, which limit their performance and reliability. New materials that have a high energy density, little loss, and good stability must thus be developed. Using polyvinylidene fluoride (PVDF) using ferroelectric ceramic free of lead to make composite films is one approach that seems promising. Ferroelectric ceramics free of lead exhibit strong polarization and permittivity, while PVDF has high breakdown strength and flexibility. The composite films can achieve synergistic effects of both components and enhance the energy storage properties. This review article outlines the latest developments and difficulties in the synthesis, characterization, and creation of composite films for PVDF-based energy storage capacitors and lead-free ferroelectric ceramics. It also discusses the potential applications and prospects of these materials [1][2][3][4].

Keywords: *Polyvinylidene Fluoride (PVDF), lead zirconate titanate (PZT), and high energy storage density*

1. Introduction

Ferroelectric ceramics and ferroelectric polymer composites are rapidly growing in popularity for a variety of applications. Composites are often used in sensors such as accelerometers, pressure sensors, hydrophones, and pyroelectrics. The ceramic phase distributed in a polymer matrix makes up the majority of the basic ceramic-polymer composite [5]. Due to their desirable electrical properties, lead-based materials like leaded glass and leaded ceramics were often used as dielectrics. However, there has been a shift towards lead-free substitutes as a result of environmental concerns and laws prohibiting the use of lead. Lead-free dielectrics can be made from substances like barium titanate (BaTiO3), strontium titanate (SrTiO3), or other ceramic materials. The Lead-free ferroelectric ceramics (1x) Bi0.5Na0.5TiO3 -xBaTiO3 is prepared by various methods such as solid-state combustion method, sol-gel method, etc., for the (1-x) Bi0.5Na0.5TiO3 -xBaTiO3 composition, where x = 0.06. The ceramics show high ferroelectric properties at the morphotropic phase boundary (MPB) after adding BaTiO3 to Na0.5Bi0.5TiO3. The ceramics with x = 0.06 have optimal ferroelectric and dielectric capabilities. PVDF can be used with high dielectric constant ferroelectric ceramic materials devoid of lead to increase the breakdown strength of composite materials and dielectric constant, which will increase their energy storage density. In a recent review paper, Wang et al discussed the recent advances in lead-free ferroelectric ceramic composite films and PVDF for high-energy-density capacitors in a review paper published recently. They have looked at the essential components of ferroelectric ceramics devoid of lead and composites based on poly (vinylidene fluoride) for capacitors with high energy densities. Numerous studies have been conducted to examine the effects of filler shape, core-shell structure, layered arrangement, and interface qualities on the dielectric properties, energy density, and breakdown strength of composites that incorporate filled-type and layer-type fillers. Moreover, an outline of the current issues of polymer and lead-free ferroelectric ceramic composite films (vinylidene fluoride) has been provided [6][7][8][9]. Lead-free Hanani et al. examined the features of the Ceramics' structural, dielectric, and ferroelectric characteristics Ba0.85Ca0.15Zr0.10Ti0.90O3 in a different recent study. The investigation's findings demonstrated that grain size improved the dielectric and ferroelectric qualities of BCZT ceramics as well as an increase in ceramic density. The work also showed that BCZT powders with strong ferroelectric and dielectric characteristics could be synthesized at 160°C is a low temperature—roughly 840°C lower than sol-gel methods and 1200°C lower than solid-state reactions. In general, Lead-free ferroelectric ceramics' dielectric constant is often influenced by the material's composition, grain size, and technique of synthesis. Lead-free ferroelectric ceramics can have their dielectric constant increased by mixing them with other materials, such as PVDF [9][10][11].

2. Methodologies

2.1 Fabrication of BNBT

Sol-gel technique is used to create BNBT nanofibers and particles. Barium, bismuth, sodium, and tetrabutyl titanium were basic ingredients to create NBT-0.06BT as the precursor solution, which was then used to create the BNBT particles. Throughout the manufacture, a volume ratio of 1:1 between 2-methoxyethanol and acetic acid were employed as the solvents. Tetrabutyl titanium was initially dissolved in acetylacetone to inhibit hydrolysis in the air. A five percent excess of bismuth acetate was then added to make up for any bismuth that was lost during the high-temperature annealing process. The completed mixture was swirled for 24 hours at room temperature. Following the high-temperature evaporation of the organic solvent, then an electrospinning process was also used to create BNBT nanofibers [14][15][16].

2.2 Preparation of PVDF

2.2.1 Solution casting method

One popular technique for creating PVDF and related copolymer-based films is solution casting. Common organic solvents like DMF, N, methyl ethyl ketone (MEK), acetone, dimethyl sulfoxide (DMSO), N-dimethylacetamide (DMAc), and 1,3-dioxolane are viable options for dissolving PVDF and its related copolymers in diluted PVDF pellets (DXL). The disintegration often takes place at room temperature. There are times when a temperature significantly higher than 70°C is needed. But spontaneous dissolution is challenging [17,18,19] Therefore, a popular technique for enhancing dissolution is ultrasonication. The duration of the ultrasonication process varies from case to case and ranges from a few minutes to 3 hours. Since ultrasonication can heat the combined solution, the PVDF powder can be easily dissolved. Another way to enhance dissolution is to stir. The PVDF-TrFE/MEK solution is made by stirring it for 45 minutes at 70°C, then heating it to 140°C and boiling it for 20 minutes to make it viscous [20,21]. In contrast to ultrasonication, stirring typically takes more than 30 minutes. PVDF/CoFe2O4 composites were made using the solution casting method. Using magnetic stirring overnight will help to thoroughly dissolve PVDF in DMF [22,23,24].

2.2.2 Hot press method

Hot pressing is another method used to make films of PVDF and its copolymers [7,28]. Despite the benefits of solution casting, like low cost and ease of preparation, there are occasions when evaporation is incomplete and the environment can have a significant impact. PVDF films are made in a hot press either by entire evaporation or by not dissolving in the organic solvent. High-temperature pressing and high-pressure cooling are common components of a hot press. Temperature, pressure, and operating time are the three primary factors in the hot press. Most hot press operations require a temperature of at least 150°C, and occasionally even 200°C [26, 27]. Depending on the experimental circumstances, the hot press's pressures differ from one another. According to the reports that have been published, the lowest pressure is above 5 MPa, and the highest is 30 MPa. Typically, this process only takes a few minutes, commonly as little as 5 minutes. In addition to working on PVDF or its copolymers, hot pressure can be employed to shape, prepared samples into the necessary sizes [28][29][30][31].

2.2.3 Electro-spinning method

PVDF films, especially ultrathin films, are frequently made using the electrospinning technique. The electrospinning procedure involves two steps: injecting and preparing the precursor solution. Solution casting process preparation is comparable to precursor solution preparation. The β-phase is formed when the PVDF molecular chains uniaxially elongate along the fiber axis due to the strain in the injection that is given to the combined solution [32]. The other benefit is electro spun PVDF films can demonstrate piezoelectricity without poling because the poloring can be achieved using the electrospinning process's whipping and polymer jet elongation. Electrospun nanofibrous materials are heated to produce PVDF films with α, β, or γ phase dominance. Moreover, precise regulation of heating before, during, or after the electrospinning procedure enables the fabrication of cross-linked membranes with optimal mechanical characteristics. The process is affected by various factors including solution parameters, voltage, needle diameter, humidity, temperature, tip-to-collect distance, flow rate, collector rotation speed, and the incorporation of additional nanofillers. There are findings indicating that the β-phase growth is less affected by the annealing temperature. The β-phase fraction is also influenced by the molecular weight [30][31].

2.3 PVDF Incorporated with BNBT to form a composite

The BNBT particles and nanofiber were dispersed to create PVDF-BNBT (particle) and PVDF-BNBT (nanofiber) composite nanofibers (30 weight percent of the PVDF powder weight) throughout the spinning solution made of PVDF before electrospinning. After that, the electrospinning procedure was conducted exactly like it was for pure PVDF [14][17]. Generally, to evaluate the properties of composite films various characterization techniques are employed. Some of the techniques are: -

[1]. **FTIR:** One of the most often used methods for examining is FTIR (Fourier transform infrared spectroscopy). The importance of FTIR microscopy is the micro-destructive study of tiny samples and the advent of mapping and imaging technology has made it possible to gather several FTIR spectra on a surface and produce a distribution map of recognized substances [26]. Figure 1 displays the results of calculating the relative beta phase using FTIR spectra [17].

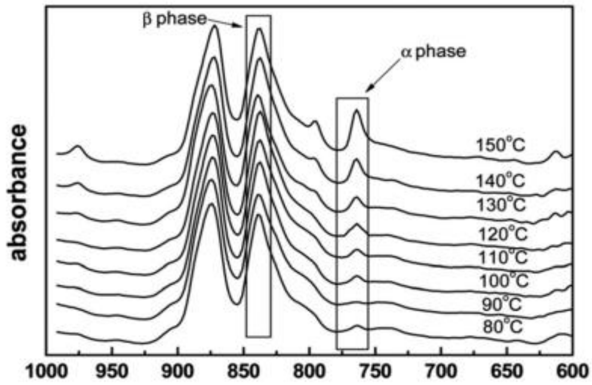

Figure 1 Relative beta phase computation using FTIR spectra [17]

[2]. **SEM:** A multifunctional, cutting-edge tool called SEM is frequently used to study material surfaces. A scanning electron microscope (SEM), which offers information on a material's topography, morphology, composition, chemistry, grain orientation, crystallographic features, etc., exposes the sample to a high-energy electron beam. Topography describes an object's surface characteristics, including its texture, smoothness, and roughness, whereas morphology describes an object's size and form.[20]

[3]. **TEM:** The shape, crystalline structure, and elemental information of membrane materials have all been extensively studied using transmission electron microscopy (TEM). The two main TEM modes are

bright-field mode and dark-field mode. The use of TEM may also reveal the crystal structure and elemental makeup of specimens.

[4]. **X-ray diffractometer (XRD):** The only laboratory method that accurately and non-destructively gathers data about the chemical composition, crystal structure, crystal size, lattice strain, preferred orientation, and layer thickness is X-ray diffraction (XRD). Therefore, XRD is used by materials scientists to examine a variety of materials, including powders, solids, thin films, and nanomaterials. The distinct phases that are present in the initial stage and calcined powders, as well as the sintered specimens, are identified using an X-ray diffractometer (XRD). Over an angle range of 2θ from 20 to 80°, the diffraction patterns were captured. Using Scherrer's formula, tc = Kλ/ßcosθ, the crystallite sizes (tc) of several samples were estimated [21]. XRD of PVDF and BNT-BT are shown in Figures 2 & 3.

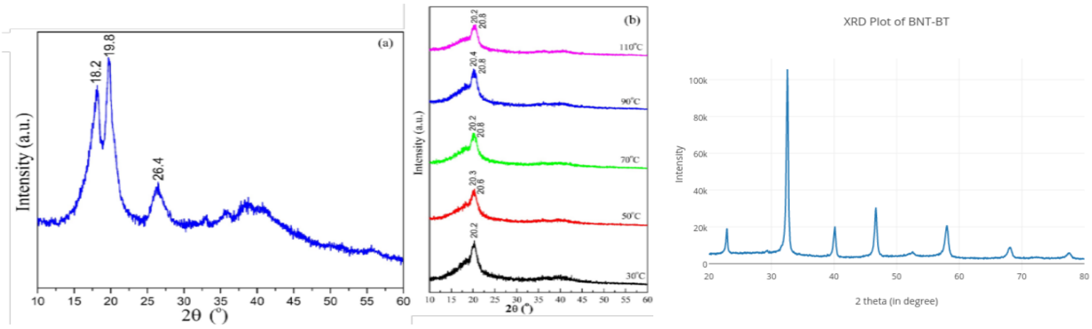

Figure 2 XRD of PVDF and BNT-BT

3. Results and Discussions

Lead's harmful consequences are Weakness, pain in the belly, and aches in the muscles and joints, and other symptoms are significant signs of lead poisoning. Given its negative impact on neurological and cerebral development, lead poisoning has long been regarded as an environmental health risk. The respiratory tract is the main pathway of lead absorption in adults, in which between 30 and 70 percent of lead that is absorbed (mostly as oxides and salts, an inorganic form) enters the respiratory system. Blood led levels vary from 1.45 to 2.4 mol L-1 for a comparatively well-controlled occupational exposure. Table 1 below shows the symptoms and signs of lead poisoning.

Table 1 Lead poisoning signs and symptoms

Mild	Moderate	Severe
Lethargy	Anemia	Convulsions
Abdominal discomfort	Abdominal cramps	Encephalopathy
Anorexia	Headache	Coma
Arthralgia	Gingival lead line	Renal failure
	Peripheral neuropathy(motor)	

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Dielectric properties: - Excellent characteristics of lead-free ceramics have been discovered, including high energy storage density, thermal stability, and favorable temperature, frequency, and electric field stability. They are utilized in many different applications, including energy storage capacitor applications, photonic applications, and ferroelectric random-access memory (FRAM). For example, research on a lead-free ceramic system denoted as BLNLT-BT (BaTiO3), revealed specific values for its composition: remnant polarisation (Pr), the measurements of the coercive field (Ec), dielectric constant (εr), dissipation factor (tan δ), piezo charge coefficient (d33), and 10.5 kV/cm, 5 µC/cm2, and 20 pC/N were made, respectively. Lead-free Ba0.85Ca0.15Zr0.10Ti0.90O3 (BCZT) ceramics showed better dielectric, ferroelectric, and piezoelectric properties than lead-based materials. Table 2 below provides an overview of the dielectric properties of various ferroelectric ceramic polymers.

Table 2 Distinct ferroelectric ceramic polymer dielectric characteristics

Ceramic	Matrix	P_r	ϵ_r	tan δ	References
PZ21	PVDF-TrFE	0.1	22	0.041	Dietze et al.2007
PZ21	PVDF-TrFE	0.2	29	0.034	
PZ21	PVDF-TrFE	0.3	34	0.036	
$BaTiO_3$	Epoxy	0.5	24		Sangyong lee et al.2007
$BaTiO_3$	Epoxy	0.6	45	0.035	Ramajo et al.2008; Das et al. 2008
PZ21	PVDF-TrFE	0.2	35	0.033	Matthias Dietze et al.2008
PZ21	PVDF-TrFE	0.3	45	0.032	
PZ21	PVDF-TrFE	0.4	65	0.026	
PZ21	PVDF-TrFE	0.5	72	0.023	
PZT	PVDF	0.7	140	0.3	Junlong Yao et al.2009
PZT	PVDF	0	8.86	0.018	Pailyn Thongsanitgrn et al.2010
PZT	PVDF	0.1	9.84	0.025	
PZT	PVDF	0.3	12.57	0.040	
PZT	PVDF	0.5	18.09	0.042	
PZT	PVDF	0.7	35.96	0.040	
PZT	PVDF	0.9	126.50	0.045	
PZT	PVDF	1.0	957.75	0.005	

Piezoelectric properties: - In this study, the voltage coefficient (g33) and piezoelectric strain coefficient (d33) for various ceramic and polymer composites were examined. The values of d33 and g33 along with the volume fraction are shown in Table 3. As the volume fraction rises, the d33 and g33 values always rise as well. This is because the polymer matrix now contains more ceramic than before. On the other hand, polymers such as PVDF-TrFE and PVC with PZT have nonlinear d33 and g33 values. This is due to the opposing polarizations of the polymer and ceramic phases.

Table 3 Values of d33 and g33

Polymer ceramic composite	ϵ_r	d_{33}(pCN^{-1})	g_{33} 10^{-3}(V-mN-1)	Reference
PZT-PVDF	93.09	17.87	21.68	Senthilkumar et al.2005
PZT/C/PVC	47.8	20	47.25	Liu Xiaofang et al.2005
PZT/PU	24	23.7	111.53	Malmonge et al.2008
	51	25		
	45	28		
PTCa/P(VDF-TrFE)	67	28	47.20	Malmonge et al.2008
PZT-PVC	8.61	4	52.47	Liu et al.2009
	25.06	6	27.04	
	39.30	15	43.10	
	73.11	22	33.98	
	97.78	31	35.80	

Conclusion

The research and developments in composite films combining lead-free ferroelectric ceramic and PVDF (Polyvinylidene fluoride) for energy storage capacitors have demonstrated promising perspectives for the future of energy storage technologies. Lead-free piezoelectric materials from the perovskite ferroelectric and bismuth layer-structured ferroelectric (BLSF) ceramics were looked into as the best possibilities for decreasing environmental damage. These materials have outstanding dielectric and piezoelectric capabilities. The perovskite-type ceramics made of bismuth sodium titanate appear to be appropriate for actuator and high-power applications. The possibility of enhancing their performance characteristics has served as an essential incentive for the development of lead-free materials with perovskite structure. Continued research and development efforts are needed to optimize the material properties, fabrication techniques, and device integration to realize the full potential of these composite films in practical energy storage applications. The pursuit of environmentally friendly and high-performance.

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