Effect of surface modification of BiFeO₃ on the dielectric, ferroelectric, magneto-dielectric properties of polyvinylacetate/BiFeO₃ nanocomposites

O. P. Bajpai¹, J. B. Kamdi¹, M. Selvakumar¹, S. Ram², D. Khastgir¹, S. Chattopadhyay^{1*}

¹Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

²Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

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Abstract. Bismuth ferrite (BiFeO₃) is considered as one of the most promising materials in the field of multiferroics. In this work, a simple green route as well as synthetic routes has been used for the preparation of pure phase BiFeO₃. An extract of *Calotropis Gigantea* flower was used as a reaction medium in green route. In each case so formed BiFeO₃ particles are of comparable quality. These particles are in the range of 50–60 nm and exhibit mixed morphology (viz., spherical and cubic) as confirmed by TEM analysis. These pure phase BiFeO₃ nanoparticles were first time surface modified effectively by mean of two silylating agent's viz., tetraethyl orthosilicate (TEOS) and (3-Aminopropyl)triethoxysilane (APTES). Modified and unmodified BiFeO₃ nanoparticles were efficiently introduced into polyvinylacetate (PVAc) matrix. It has been shown that nanocomposite prepared by modified BiFeO₃ comprise superior dispersion characteristics, improved ferroelectric properties and favorable magneto-dielectric properties along with excellent wettability in compare to nanocomposite prepared by unmodified BiFeO₃. These preliminary results demonstrate possible applications of this type of nanocomposites particularly in the field of multiferroic coating and adhesives.

Keywords: polymer composites, multiferroics, magnetic properties, polyvinylacetate, *Calotropis Gigantea*

1. Introduction

Bismuth ferrite (BiFeO₃) is one of the most promising materials owing to its favorable room temperature multiferroic characteristics [1–8]. In recent time, structure and properties of bismuth ferrite have been intensively studied because it comprises both ferromagnetic as well as ferroelectric characteristics simultaneously. As a result, an electric field can induce change in magnetization and an external magnetic field can induce electric polarization. This phenomenon is known as the magneto-electric effect [9]. However, current leakage problem of BiFeO₃ constricts its practical applications [10–12]. To resolve current leakage problem as reported in literature, one must come up with a potential route

for the preparation of impurity free BiFeO₃. To date, synthesis of pure phase BiFeO₃ is still a challenging task. So far, bismuth ferrite particles were prepared mostly by the solid state and solution chemistry methods (i.e., precipitation/co-precipitation, sol-gel, hydrothermal and sonochemical) [13–19]. However, it resulted in the formation of coarser particles. Therefore, we tried to synthesize pure phase bismuth ferrite via controlled sol-gel process through a green route by using flower extract of *Calotropis Gigantea* in dilute concentration of acid at low temperature. We choosed plant extract process because synthesis mediated by plant extracts is eco-friendly, economical and can provide nanoparticles with minimum toxicity. *Calotropis Gigantea* is a shrub com-

*Corresponding author, e-mail: santanuchat71@yahoo.com

mon in the eastern and southern parts of India, Ceylon and Eastern Asia. The milky juice obtained from *Calotropis Gigantea* is used for medicinal and insecticidal purposes [20]. The roots and leaves of *Calotropis Gigantea* are also used traditionally for treatment of abdominal tumors, boils, syphilis, leprosy, insect-bites and elephantiasis [21]. Extract of *Calotropis Gigantea* leaves also has significant antioxidant property. As reported in literature, there are numerous bio-organic compounds present in the plant systems such as flavonoids, terpenoids, proteins, reducing sugars and alkaloids [22, 23]. These bio-organic compounds are supposed to be involved either as reducing agents or as stabilizing agent in the formation of nanoparticles. It is assumed that formation of nanoparticles occurs through the ionic or electrostatic interactions between the metal complexes and the functional groups on the biomass surfaces. But due to the bio-diversity of the plant biomasses, the exact mechanism by which bio-constituents of plants have contributed to the synthesis process is so far not completely understood.

Moreover, though BiFeO_3 have many favorable properties, but still it is difficult to use directly. Being ceramic, as such BiFeO_3 is brittle in nature, very less shock resistive and has poor moldability [24]. To make it even more advantageous these disabilities ought to be rectified. The best way to do so is by making the composite of BiFeO_3 with a suitable polymer, since most of the polymers have better shock resistance, easy processability and being cheaper too. Also by judicious selection of polymer with some specific attributes, potential applications including in the field of adhesives and coatings of new composite material can be envisaged [25–27]. Large array piezoelectric devices and miscellaneous electromagnetic devices need joints or coatings. For these, coating materials are supposed to have electromagnetic properties as well as the ability to spread and wet the surface. Though, today we have a large gamut of polymers of diverse applications but considering above mentioned facts, we have chosen polyvinyl acetate (PVAc) for this work. PVAc is a type of thermoplastic with hydrophobic nature and comprises the characteristics of coating and adhesive [28–30]. As a result, ultimate product of BiFeO_3 /PVAc composite can be used in the field of magneto-electric coating or adhesives. Magneto-electric adhesives can be used to adjoin piezoelectric, magnetic or multiferroic components [31]. This com-

pound may also be used for under water applications with adjustable buoyancy. Major concern about the polyvinyl acetate is the sensitivity of ester groups to base hydrolysis. With time PVAc also slowly converts into polyvinyl alcohol and acetic acid. Hence, necessary precaution should be taken accordingly. Thus owing to broad efficacy of BiFeO_3 , properties of bismuth ferrite polymer nanocomposites must be explored, but interestingly very limited number of literature on the related area is available so far [32–35]. Therefore, motivated from above mentioned issues we prepared BiFeO_3 nanoparticles via sol-gel process through a green route by using flower extract of *Calotropis Gigantea* as well as by using other complexing agent (citric acid) and dispersant (polyethylene glycol) at lower temperature. Till now synthesis of gold and silver nanoparticles have been reported by using this type of extract, but there is no paper available on BiFeO_3 synthesis [36–38]. To achieve required properties of composites proper dispersion of BiFeO_3 into polymer matrix is desirable. Hence, prepared BiFeO_3 nanoparticles were first time surface modified by means of two different silanes viz., tetraethyl orthosilicate and (3-Aminopropyl)triethoxysilane [39]. Subsequently, modified and unmodified BiFeO_3 nanoparticles were introduced into polyvinyl acetate matrix to make this novel class of nanocomposite.

2. Experimental

2.1. Materials

For preparation of BiFeO_3 raw materials such as bismuth nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$, iron nitrate nonahydrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, anhydrous citric acid, polyethylene glycol (MW- 600 Da) and nitric acid (69% GR) were obtained from Merck Specialties Chemicals Ltd, Mumbai, India (Analytical grade, 99% purity). Silane based surface modifier e.g., tetraethyl orthosilicate (TEOS) and (3-Aminopropyl)triethoxysilane (APTES) were purchased from Sigma Aldrich, USA. Complexing agent from bio-resources e.g., leaves and flowers of *Calotropis Gigantea* were collected from Agriculture & Food Department, IIT Kharagpur, India. Polyvinyl acetate (PVAc) of molecular weight ($4.2 \cdot 10^5$ Da) was purchased from Pidilite Industries Ltd, Mumbai, India. It has $(92 \pm 2)\%$ polyvinyl acetate content and $(5 \pm 1)\%$ polyvinyl alcohol. All these materials were used as such without any further purification.

2.2. Preparation of extract of *Calotropis Gigantea* flower

The leaves and flowers were initially separated from the main plant's body and rinsed with distilled water. After proper washing with distilled water, they were cut into small pieces. Then 5 g petals were weighed and mixed with 20 mL distilled water. Subsequently, this mixture is subjected to 1.5 h of heating at 85°C and cooled up to room temperature. Afterward, petals were separated through filtration process and extract obtained is concentrated and used later as a complexing agent for the preparation of bismuth ferrite nanoparticles.

2.3. Preparation of BiFeO₃ nanoparticles

To prepare BiFeO₃ nanoparticles by extract route, 0.04 M [Bi(NO₃)₃·5H₂O] and 50 mL concentrated flower extract were mixed together, and solution was ultrasonicated about 30 minute followed by microwave treatment about three minute (at 900 Watt) to make it dry. Subsequently, solution of 50 mL concentrated flower extract and 0.04 M [Fe(NO₃)₃·9H₂O] were added into it followed by six minutes of microwave treatment (at 900 Watt). This resulted in blackish fluffy powder which is further annealed at 600°C.

To prepare BiFeO₃ nanoparticles by synthetic route, bismuth nitrate pentahydrate [Bi(NO₃)₃·5H₂O] and iron nitrate nonahydrate [Fe(NO₃)₃·9H₂O] were taken in equimolar proportion, and dissolved in distilled water to make a solution of 0.2 M followed by five minutes of stirring. While stirring, 20 mL dilute HNO₃ (20%) solution was added to the mixture. Thereafter 12 g of citric acid was added to the solution followed by the addition of 2 g of PEG as dispersant (addition of PEG can be optional). Resultant yellowish solution was heated with continuous stirring of about 1 h. Subsequently, concentrated solution mixture was kept into oven at 150°C for 5 h to get powdered material. In addition to this, powdered material was annealed at 600°C.

Following above processes, four different types of samples of BiFeO₃ were prepared [e.g., prepared by using a complexing agent (a) citric acid, (b) citric acid with PEG, (c) none (without complexing agent), and (d) an extract of a *Calotropis Gigantea* flower]. Subsequently, crystal structure as well as surface functionality was analyzed by X-ray diffraction and FTIR techniques.

2.4. Surface modification of BiFeO₃ nanoparticles

Prepared BiFeO₃ nanoparticles were surface modified by means of two different silylating agent's viz., tetraethyl orthosilicate (TEOS) and (3-Aminopropyl)triethoxysilane (APTES). In the process of surface modification a mixture of 100 mg BiFeO₃, 80 mL ethanol and 50 mL water was taken in a round bottom flask and ultrasonication for 1 h. Thereafter, 20 mL 30% ammonia solution was added followed by 6 h of mechanical stirring. While stirring silylating agent's (e.g., TEOS or APTES) were added dropwise (0.1 mL in 10 mL of water) at room temperature. After 6 h of stirring silica coated nanoparticles were separated and washed 4–5 times by using ethanol and distilled water. Subsequently, prepared nanoparticles were dried in vacuum oven and used for the preparation of nanocomposite with PVAc.

2.5. Preparation of PVAc/BiFeO₃ nanocomposite

PVAc/BiFeO₃ nanocomposite films were prepared via simple solution casting technique. In the process 4 g of PVAc was dissolved in the 20 mL of distilled water followed by 30 minutes of ultrasonication. Subsequently, 80 mg of BiFeO₃ nanoparticles were separately mixed, and resultant solution was ultrasonicated for 30 minutes. Then both solutions were mixed together under mechanical stirring and further ultrasonicated for 4 h. Thereafter blend solution were cast in teflon petri dish and dried at room temperature (about 10 days) to get smooth films. Following above process four different samples [viz., PVAc reinforced with 2.0 wt% of (a) pristine BiFeO₃, (b) TEOS modified BiFeO₃, (c) APTES modified BiFeO₃ and (d) neat PVAc] were prepared and characterized.

2.6. Characterization techniques

Structural phase analysis was carried out by X-ray powder diffraction using Philips PW-1710 X-ray diffractometer with CuK_α radiation ($\lambda = 1.54 \text{ \AA}$) at accelerating voltage of 40 kV and at a beam current of 20 mA. Fourier transform infrared spectroscopy (FTIR) studies were performed on a Perkin Elmer FTIR spectrophotometer by using KBr pellets. Morphology analysis was performed on an Analytical TEM (FEI-TECHNAI G2 20S-TWIN, USA) at operating voltage 200 kV. Field Emission Scanning

Electron Microscopy (FESEM) and dot mapping was carried out with an (Model SUPRA 40 Field Emission Scanning Electron Microscope) acceleration voltage 10.0 kV. Thermo gravimetric analysis (TGA) was carried out in a TGA Q50 (TA instrument, USA) from ambient temperature to 600°C at a programmed heating rate of 20°C/min in nitrogen atmosphere. The contact angle measurement was performed by using dynamic contact angle analyzer (Model: FTA 200-First Ten Angstroms, Virginia, USA). The dielectric properties were measured using precision LCR meter (Model. Quad Tech 7600) coupled with a home-made cell that has parallel plate circular electrodes (up to MHz). M-H loop measurements were carried out up to the field strength 2.5 T using SQUID VSM DC magnetometer, Quantum Design, USA. Ferroelectric behavior was examined at room temperature using an automatic P-E loop tracer manufactured by Marine India Elect. Pvt. Ltd. Magneto-dielectric measurement were carried out up to the field strength 1.93 T with applied current ranging from 0.05 to 3 A.

3. Results and discussion

3.1. Characterization of BiFeO₃

3.1.1. X-ray diffraction analysis

Figure 1 illustrates XRD patterns of the annealed BiFeO₃ synthesized by using different complexing agents. It is apparent that well crystalline BiFeO₃ formed in both cases (e.g., citric acid and green route). In both cases so formed BiFeO₃ particles are of comparable quality. All peaks specify the forma-

Figure 1. XRD patterns of BiFeO₃ prepared by using a complexing agent (curve a) citric acid, (curve b) citric acid with PEG (dispersant), (curve c) none (without complexing agent), and (curve d) an extract of a *Calotropis Gigantea* flower, with photographs of the samples before annealing in the right

tion of rhombohedral structure of BiFeO₃ with lattice parameters $a = b = 5.57 \text{ \AA}$, $c = 13.86 \text{ \AA}$ and space group $R3c$ (161). These are well consistent with reported data (JCPDS No.86-1518). Sample prepared without complexing agent and with PEG also confirms the formation of BiFeO₃ but with slight indication of phase impurity (viz., Bi₂Fe₄O₉ and Bi₂₅FeO₄₀) [40]. Interestingly, it is also observed that all four samples display different colors before annealing (side view, Figure 1).

3.1.2. FTIR analysis

Figure 2 illustrates FTIR spectra showing the effect of complexing agents on precursors used to synthesize BiFeO₃. Absorptive band at around 400–600 cm⁻¹ in all samples indicate formation of FeO₆ octahedra of the perovskite structure. These peaks are due to the Fe–O stretching and bending vibration which confirms formation of metal-oxygen bond. In Figure 2 curve d absorption bands at around 1040–1150, 1350–1480 and 1350–1480 cm⁻¹ are the characteristics of C–O stretching, C–H bending and C=O stretching respectively. Existence of carbonyl group indicates that some amounts of bio-organic compounds are still present in the sample prepared by extract process. Therefore extract process needs some additional steps to remove excess amount of bio-organic compounds. Bands at around 810–820 cm⁻¹ are due to the presence of traces of trapped NO₃⁻ ion in the sample. Thus, FTIR study confirms

Figure 2. FTIR spectra showing the effect of a complexing agent on a precursor used to obtain BiFeO₃ (curve a) citric acid, (curve b) citric acid with PEG (dispersant), (curve c) none (without complexing agent), and (curve d) an extract of a *Calotropis Gigantea* flower

the formation of perovskite structure of prepared BiFeO_3 .

3.2. Characterization of surface modified BiFeO_3

3.2.1. FTIR analysis

Figure 3 illustrates FTIR spectra showing effect of surface modification on BiFeO_3 . Absorption bands at 1075 and 1070 cm^{-1} are present in the modified samples, which are assigned to the asymmetric stretching vibrations of the Si–O–Si bond. These bands confirm surface modification of prepared BiFeO_3 . However, absorption bands at 400–600, 2920, 2860 and 3310 cm^{-1} are the characteristics of Fe–O stretching, symmetric and asymmetric stretching of (–CH₂–) and –NH₂ stretching respectively. Bands at around 810–820 and 2340 cm^{-1} are

Figure 3. FTIR spectra of (curve a) pristine BiFeO_3 , (curve b) TEOS modified BiFeO_3 , and (curve c) APTES modified BiFeO_3

Figure 4. TEM images of (a, b) pristine BiFeO_3 , (c) TEOS modified BiFeO_3 , and (d) APTES modified BiFeO_3

due to the traces of trapped NO_3^- ion and CO_2 present in the sample.

3.2.2. Morphology by analytical TEM

Figure 4 displays TEM photomicrographs of BiFeO_3 before and after surface modification. It is clearly evident that before modification particles are very much agglomerated (Figure 4a, 4b), and these particles have mixed morphology (viz., spherical and cubic). However, nanoparticles modified by TEOS and APTES are comparatively well separated (Figure 4c, 4d). Approximate size range (50–60 nm) of the prepared BiFeO_3 has been obtained by image analysis of TEM photomicrographs.

3.3. Characterization of PVAc/ BiFeO_3 nanocomposite

3.3.1. FESEM analysis

Figure 5 illustrates FESEM images of BiFeO_3 /PVAc nanocomposites with 'Bi' dot mappings. It is distinctly observed that nanocomposite made by using unmodified BiFeO_3 exhibits very rough surface with lot of cracks and pores (Figure 5a). On the other hand, surface roughness is reasonably reduced in the case of nanocomposites made by modified BiFeO_3 with a lesser amount of cracks and pores (Figure 5b and 5c). Observed improvements in the

surface roughness of nanocomposites are due to the superior dispersion of modified BiFeO_3 in the PVAc matrix. This is further supported by the corresponding dot mapping images (Figure 5d–5f). Dot mapping micrographs clearly demonstrate enhanced dispersion of the nanoparticles in the case of nanocomposites made by modified BiFeO_3 . Among all, nanocomposite prepared using TEOS modified BiFeO_3 exhibits best quality of dispersion.

3.3.2. Thermal analysis

Figure 6 illustrates TGA and DTA thermograms of neat PVAc and its BiFeO_3 based nanocomposites. It is apparent from TGA and DTA thermograms that decomposition of nanocomposites took place in two major steps (Figure 6). In first step majority of mass loss took place around 340°C . It could be due to the elimination of side groups (viz., acetate group), solvent and decomposition of chelated complex formed by citric acid. In second step, further smaller mass loss took place between 410 to 490°C . This might be due to the breakdown of the polymer backbone at higher temperatures. Perhaps due to the filler and impurities, a non volatile residue of approximately of 10 weight% is formed at the end. From the thermogram, it is clearly evident that thermal stability of the nanocomposites prepared by using modified

Figure 5. FESEM images of reinforced PVAc with 2.0 wt% of (a) pristine BiFeO_3 , (b) TEOS modified BiFeO_3 , and (c) APTES modified BiFeO_3 , with (d–f) Bi dot mappings

Figure 6. TGA and DTA thermograms of reinforced PVAc with 2.0 wt% of (curve a) pristine BiFeO₃, (curve b) TEOS modified BiFeO₃, (curve c) APTES modified BiFeO₃ and (curve d) neat PVAc, with magnified graph in the inset

BiFeO₃ is fairly enhanced as compared to nanocomposite prepared by using unmodified BiFeO₃ (Figure 6 inset). It is due the surface modification of the BiFeO₃ particles with silanes that improves its thermal stability. However, as compared to neat PVAc, the thermal stability of all nanocomposites moderately decreased. This decrease in thermal stability of the nanocomposites is attributed to the loss of crystallinity of the polymer chains due to BiFeO₃ loading, which accelerates thermal degradation of polymers by allowing easier diffusion of degradation products.

3.3.3. Dielectric analysis

Figure 7 illustrates the variation of permittivity and $\tan \delta$ of neat PVAc and its BiFeO₃ based nanocom-

posites with frequency at room temperature. Lowest permittivity is found for the neat PVAc and measured permittivity at lower frequency is always greater than those at higher frequency. In the lower frequency range (e.g., 10–10³ Hz) permittivity of the nanocomposites made by using TEOS modified BiFeO₃ is found similar to unmodified one, but somewhat lower permittivity is observed for nanocomposites made by using APTES modified BiFeO₃. However, in the higher frequency range (e.g., 10⁴–10⁶ Hz) permittivity is found higher for the nanocomposites made by using modified BiFeO₃ than those of unmodified one (Figure 7 inset).

In each case, as the frequency increases dielectric permittivity decrease significantly up to 10⁴ Hz and beyond which the changes in the values are marginal. Actually at low frequency the dielectric permittivity depends upon various types of polarizations i.e., interfacial, ionic/dipolar, electronic, atomic polarization. However, at high frequency only electronic and atomic polarizations are responsible for constituting the permittivity. Consequently, there is a sharp decline in permittivity at low frequency, as at higher frequency interfacial and dipolar relaxation could not contribute significantly. But increase in the permittivity at higher frequency for the modified BiFeO₃ filled nanocomposites clearly indicates that silane coating enhances electronic or atomic polarizations. It may be due to the possible electronic interaction between silane coating agents and BiFeO₃ which ultimately lead to increase in the permittivity. This is what we also got in the magneto-dielectric measurement. Moreover, drastic

Figure 7. Variation of dielectric permittivity (a) and $\tan \delta$ (b) of reinforced PVAc with 2.0 wt% of (curve a) pristine BiFeO₃, (curve b) TEOS modified BiFeO₃, (curve c) APTES modified BiFeO₃ and (curve d) neat PVAc, with magnified permittivity graph in the inset

increase in the permittivity for the BiFeO₃ filled nanocomposites are mainly due to the effect of high permittivity of filler (BiFeO₃) compared to the polymer matrix. The permittivity value of phase pure BiFeO₃ is more than 100 at kHz (e.g., even higher for less than kHz frequency) [41]. More or less similar behavior is observed in the $\tan \delta$ versus frequency plot of nanocomposites i.e., incessant decline of $\tan \delta$ in all cases. It is found highest for nanocomposites made by using unmodified BiFeO₃ and lowest for neat PVAc. This shows that nanocomposites prepared by using modified BiFeO₃ exhibits decrease of $\tan \delta$ significantly as compared to that of unmodified one.

3.3.4. Ferroelectric measurement

Ferroelectric hysteresis loops of BiFeO₃/PVAc nanocomposites at room temperature are shown in (Figure 8). It is evident that nanocomposites prepared by using modified BiFeO₃ show more remnant polarization and coercivity than those of unmodified one. Nanocomposite made by using TEOS modified BiFeO₃ exhibit superior ferroelectric properties with remnant polarization ($2Pr \approx 6.08 \mu\text{C}/\text{cm}^2$) and the coercive field ($2Ec \approx 21.89 \text{ kV}/\text{cm}$). Whereas unmodified one shows remnant polarization ($2Pr$) $\approx 4.98 \mu\text{C}/\text{cm}^2$. This is because coating of modifying agent on the surface of BiFeO₃ nanoparticles contributes additional polarizability, consequently improves ferroelectric properties. Observed values are good agreement for ferroelectric applications of BiFeO₃/PVAc nanocomposites material with low current leakage contribution.

Figure 8. Comparison of P - E loops of reinforced PVAc with 2.0 wt% of (curve a) pristine BiFeO₃, (curve b) TEOS modified BiFeO₃, and (curve c) APTES modified BiFeO₃

Figure 9. Magnetic hysteresis loops of reinforced PVAc with 2.0 wt% of (curve a) pristine BiFeO₃, (curve b) TEOS modified BiFeO₃, and (curve c) APTES modified BiFeO₃

3.3.5. Magnetic property measurement

Magnetic properties of the BiFeO₃/PVAc nanocomposites have been studied using SQUID VSM at room temperature (Figure 9). Measured M - H curves are indicative of super paramagnetic nature. However, nanocomposites made by using modified BiFeO₃ displays less magnetization than those of unmodified one and it is found lowest in case of nanocomposite prepared by using APTES modified BiFeO₃. This could be due to the drop of amount of BiFeO₃ per gram owing to coated outer surface and as a result magnetization (emu/g) decreased.

3.3.6. Magneto-dielectric analysis

Magneto-dielectric measurement characterizes degree of the coupling between magnetic and electric polarizations. Here change in dielectric constant with applied magnetic field is characterized by magneto-dielectric coupling or magneto-capacitive factor [$\approx (\epsilon_H - \epsilon_0)/\epsilon_0 \cdot 100\%$].

The magnetocapacitive effect is relative to the term P^2M^2 (P – polarization, M – magnetization) in the Ginzburg–Landau free energy [9, 33]. In the multi-ferroic polymer nanocomposites, coupling of electric and magnetic phenomena happens through elastic interaction. Hence, magneto-electric effect in the composites is extrinsic in nature and depends on the composite microstructure and coupling interaction across the magnetic and ferroelectric interfaces.

Figure 10 illustrates magneto-dielectric response of reinforced PVAc with 2.0 wt% of modified and unmodified BiFeO₃ at different frequencies. It is dis-

Figure 10. Magneto-dielectric response of a reinforced PVAc with 2.0 wt% (a) pristine BiFeO₃, (b) TEOS modified BiFeO₃, and (c) APTES modified BiFeO₃ at different frequencies

tinctly observed that dielectric permittivity increases as magnetic field increases in case of nanocomposite made by using modified BiFeO₃ (Figure 10b, 10c). Generally, surface modification leads to decrease in the piezoelectricity of the nanocomposites due to the reduction of piezoelectric response of the resultant nanoparticles. But in our case modified BiFeO₃ based nanocomposites displays improved magneto-dielectric response. It means surface elastic interaction produced by the modifying agents may lead to change in the spin structure/magnetic moment of the BiFeO₃ near the interface, and ultimately produces better interfacial contacts. The change in the spin structure of the BiFeO₃ indicates alteration in the bond angle of Fe–O–Fe bonds of FeO₆ octahedra. As a result redistribution of charges and orientation of dipoles within the polymer matrix eventually produces higher coupling. Highest coupling

about 1.08% is observed in case of nanocomposite made by using APTES modified BiFeO₃. However, in case of nanocomposite made by using unmodified BiFeO₃ not much change in the dielectric permittivity is observed with change in magnetic field, and shows insignificant coupling (less than 0.10%) (Figure 10a). It may be due to the weak interfacial contacts between the dispersed nanoparticles in the matrix which leads to failure of transferring elastic strain/stress from one component (piezoelectric) to other component (magnetostrictive). Notable point about this material is that it contains only 2 wt% BiFeO₃ but still shows favorable magneto-dielectric properties especially modified one. Hence, it can be used for magneto-electric applications after the comprehensive assessment of magneto-electrical properties.

3.3.7. Contact angle measurement

Wetting ability of the nanocomposites was determined by the contact angle measurement (Figure 11). Even though polyvinyl acetate is hydrophobic in nature, contact angle of neat polymer sample is found 59° (less than 90°). As per specification of purchased polyvinyl acetate (mentioned in material section) it contains 5% polyvinyl alcohol (PVA) which is hydrophilic material. Therefore, as water comes in contact with mixture of hydrophobic ($-\text{COOCH}_3$ group) and hydrophilic ($-\text{OH}$ group) material, hydrophilic material will move toward surface and hydrophobic material will move away. This makes shape like a ball in which $-\text{OH}$ repeat units are on the outer surface while $-\text{COOCH}_3$ are on the inner side of the ball (i.e., away from water) (Figure 11a). Consequently, while measuring contact angle as the water drops fall on surface of the

polymer, PVA will move towards the surface and being hydrophilic it gives less contact angle. This is the reason why neat polymer have contact angle less than 90° . On the other hand, in the case of nanocomposite made by unmodified BiFeO_3 contact angle is found more ($\sim 82^\circ$) than that of neat polymer (Figure 11b). This is because of the hydrophobic nature of bismuth ferrite. It is interesting to note that the water contact angle for the nanocomposites prepared from modified BiFeO_3 is found significantly low ($\sim 57^\circ$) compared (Figure 11c, 11d) to those of unmodified one (82°) that reflects its enhanced wettability in hydrophobic environment. These positive outcomes indicate possible applicability of $\text{BiFeO}_3/\text{PVAc}$ nanocomposites in the area of magnetic field controllable devices or in magneto-electric coatings and adhesives.

Figure 11. Contact angle images of (a) Neat PVAc, and reinforced PVAc with 2.0 wt% of (b) pristine BiFeO_3 , (c) TEOS modified BiFeO_3 , and (d) APTES modified BiFeO_3

4. Conclusions

First step toward synthesis of BiFeO₃ following a facile green route be accomplished effectively together with the synthetic route. In each case so formed BiFeO₃ particles are of comparable quality. Prepared BiFeO₃ nanoparticles were surface modified successfully by means of two different silanes (viz., TEOS and APTES). FESEM, TGA and contact angle analysis indicates nanocomposites made by using modified BiFeO₃ exhibit superior dispersion, enhanced thermal stability and suitable wetting ability in compare to unmodified one. Progressive growth in permittivity (especially in higher frequency range) and ferroelectric polarization is also observed in case of modified BiFeO₃ based nanocomposites. Magnetic property measurement confirms modification of nanoparticles reduces magnetization without any influence in its super paramagnetic nature. Magneto-dielectric measurements shows favorable coupling especially in case of nanocomposite made by using APTES modified BiFeO₃. Summing up all these valuable features, the possible applications of BiFeO₃/PVAc nanocomposite in the field of multiferroic coatings and adhesives can be envisaged. Still, comprehensive studies of magneto-electrical properties need to be investigated to stabilize practical device using such versatile nanocomposites.

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