

## X-Ray Diffraction and Differential Scanning Calorimetry of BaTiO<sub>3</sub>/Polyvinyl Chloride Nanocomposites

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### Abstract

Aiming to improve the inferior properties of polyvinyl chloride polymer, (BaTiO<sub>3</sub>)<sub>x</sub>(PVC)<sub>100-x</sub> composite samples were prepared and investigated. The structural changes of the composite (BaTiO<sub>3</sub>)<sub>x</sub>(PVC)<sub>100-x</sub> were studied as a function of BT content using FTIR, XRD and DSC measurements. Attention is paid to the tetragonality changes during composition changes.

It was found that the hindrance to the PVC crystallization becomes less and less serious with the increase of BT ratio in the composite. This behavior could be attributed to the interaction between Ba<sup>+2</sup> ions and Chlorine in the polymer. The FTIR spectra indicate a clear interaction between PVC and BaTiO<sub>3</sub> particles as is concluded from XRD results.

The Scherrer formula was used to estimate the grain size for the included BT in the (BT)<sub>x</sub>(PVC)<sub>100-x</sub> composite samples. The composite samples show abnormally small tetragonality for its BT content less than unity ( $c/a < 1$ ). It seems that in (BaTiO<sub>3</sub>)<sub>x</sub>(PVC)<sub>100-x</sub> composite samples, the stress that stabilized the tetragonal phase of the core regions of BT decreased, leading to lower tetragonality ( $c/a$  ratio). It seems that  $T_g$  of the composite samples increases with the increase of its BT content. Also DSC results reveal the increase of crystallization with the increase of BT content in the composite.

**Keywords:** Barium Titanate/polyvinyl chloride, XRD, DSC, tetragonality.

### 1. Introduction

The Superior mechanical and physical properties of PVC make it one of the most widely used plastic materials in the world. The commercial PVC polymer is estimated to be of 7–20% crystallinity [1,2]. Normally, PVC molecules consist of about 1000 vinyl chloride monomer units, joined in predominantly head-to-tail fashion. Other arrangements could also be found and are considered to be defects. This depends on the polymer preparation technique [3-7].

Nevertheless, due to its inherent drawbacks, such as small thermal stability and brittleness, PVC and its composites are exposed to some constraints in some applications [8,9] and work is still in progress aiming to improve its inferior properties. One big topic of investigation is the effect of additives like plasticizers, heat stabilizers, lubricants, fillers and other polymers on its properties [10]. In the same line, electroactive ceramics are added to the polymer, and the composite properties are studied [11]. These composites combine the advantages of both ceramics

and polymers, for industrial applications. It has good comprehensive properties and potential applications including its uses in embedded circuits [12–14]. BaTiO<sub>3</sub> is widely used as the ceramic material in the polymer–ceramic composites due to its superior physical properties such its high dielectric constant, non-toxicity and low cost [15–17]. BaTiO<sub>3</sub> particles larger than 0.5 μm usually show a tetragonal-to-cubic phase transition at a Curie temperature and its tetragonality is known to be particle size dependent [18]. BT shows piezoelectric characteristics in the tetragonal phase, below its Curie point. The best dielectric properties for BT are obtained with tetragonal phase [19]. One of its industrial applications is the multilayer ceramic capacitors (MLCCs). The powder BT used in MLCCs industry must have a tetragonality value higher than 1.008 [20]. Tetragonality, the lattice distortion ( $=c/a$ ), or the degree of ferroelectricity, is defined as the relative ratio of lattice parameter of c-axis to a-axis as

measured by X-ray diffraction (XRD). Generally, most polymers are classified as typical insulators. The conductivity of polymer composites predominantly depends on the content, properties of the used filler and their distribution within the polymer material, in addition to the interaction between the filler surface and the polymeric matrix [21]. For BT/PVC composites, the dielectric properties were found to be a combination of those of pure PVC polymer and BaTiO<sub>3</sub> ceramics [20]. Also, the dielectric losses are larger for high BaTiO<sub>3</sub> content composites [21]. In this work, the structural changes of the composite BT/PVC were studied as a function of BT content using FTIR, XRD and DSC measurements. Moreover, despite the technical importance of BT tetragonality changes, little is known in literature about the changes of BT tetragonality with the change of Bt content in the polymer composite. So attention is paid to the tetragonality changes during composite composition changes.

## 2. Experimental

### 2.1 Sample preparation

Barium Titanate (BT) and polyvinyl chloride (PVC) used in this work were obtained from Fluka Chemika Co. and Polymer Laboratories (Essex, UK) respectively. Tetrahydrofurane (THF) was supplied by Aldrich, Germany. All chemicals were of analytical grade and were used as received without further purification.

To prepare PVC/ BaTiO<sub>3</sub> nanocomposite films, the BT nanoparticles were added in different weight % (0, 0.5, 1, 2, 5, and 20) to PVC according to

$$x(\text{wt.}\%) = \frac{w_f}{(w_f + w_p)}$$

Where  $w_f$  and  $w_p$  represent the weights of BT and PVC respectively.

PVC powder was dissolved in THF at room temperature using Ultrasonic stirrer (Omni –Ruptor 250) until a clear solution is obtained (~0.5hr). BT solutions with the required concentrations were prepared by dissolving different amounts of BT in THF for 10 min using the Ultrasonic stirrer.

Each BT concentration was mixed together with its proper PVC solution by continuous Ultrasonic stirring for 20 min to get a homogeneous mixture of PVC/BT composite. Finally, the solution was casted on to a petri dish and kept to dry at room temperature for 24 hr. until a homogeneous film was obtained. The thicknesses of the samples are almost equal to 0.17mm.

### 2.2 Measurements

The (BaTiO<sub>3</sub>)<sub>x</sub>(PVC)<sub>100-x</sub> composite samples were characterized using XRD analysis and Electron Microscopy. XRD of composite samples was performed using a PANalytical's X'Pert PRO. The measurements were performed at room temperature in the range of  $2\theta = 10^\circ - 50^\circ$ . Scanning electron microscopy (SEM; Inspect S, FEI, Holland) images were taken for the composite films. AFM was carried out by Shimadzu Wet-SPM (Scanning Probe microscope), Japan, DSC measurements for all samples were achieved at 10 °C/min heating rate between 40°C and 180°C using a Pyris 1 DSC outbalance (From Perkin Elmer).

## 3. Results and Discussions

### 3.1 Microscopy

Fig.1 shows SEM image of (BT)<sub>1</sub>(PVC)<sub>99</sub> composite sample as a representative one. Particles are almost spherical and dispersed with some aggregates. Some of the BaTiO<sub>3</sub> particles seem to be embedded in the polymer matrix and start coalescing due to the surface adsorption property of PVC. We observe that some fine grains of BaTiO<sub>3</sub> when coated with PVC tend to coalesce and form some agglomerates. So, the atomic force microscopy image was used for pure BaTiO<sub>3</sub> (Fig.2) to get the particle size. It shows that all powders have nearly spherical shape with mean radius equal to 24nm.

### 3.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) studies provide full information about crystal structure, crystal orientation, crystallite size and the existed material phases through the presence of sharp diffraction rings or peaks. Also, the amorphous materials are characterized by broad "halos".

The X-ray diffraction patterns of pure PVC, and its composite samples are shown in Figs. 3(a–g), respectively. It is evident from Fig.3 (a) that PVC exhibits an amorphous phase. The XRD spectrum of BT (Fig. 3g) shows 4 peaks in the 10°–50° range. These peaks appear in the XRD patterns of all composite samples. We observe that there is no change in the position of the BT reflection peaks, that is, all the four BT characteristic XRD peaks appear in the composite samples in the same position of pure BT whatever the BT content. The peaks appear at  $2\theta$  values of 22.218, 31.548, 38.898, and 45.338. This behavior (the absence of any shift in the reflection peaks of BT) could suggest that there is no change in the morphology of BT, although it was coated by PVC particles. With respect to the nanocomposite films, the intensities of the BT diffraction peaks were increased with BT content. This is because the BT particles dispersed in the PVC might have an important effect on the crystallization of the PVC polymer [22]. That is

to say the crystallinity of the nanocomposite films was increased with the increase of BT content. This behavior could be ascribed to the interaction between Ba<sup>2+</sup> ions and Chlorine in the polymer as the following. PVC (polyvinyl chloride) is not an ionomer; the highly depolarized C- Cl bond is capable of forming a weak acid-based complexation with barium and thus retards the order of crystalline PVC.

Figure 3 shows a noticeable splitting of the XRD peaks of BT in the (BT)<sub>x</sub> (PVC)<sub>100-x</sub> composite samples at 2θ = 45°. These peaks, corresponding to (200) diffraction plane, are used to distinguish a cubic structure from a tetragonal structure [23]. At this angle, each of these peaks seems not to be single. Theoretically, 100% tetragonal BT has two separate peaks between 2θ = 44° and 47°. Complete cubic barium titanate shows only one peak. A mixture of tetragonal and cubic BT will show all intermediate forms between one and two peaks. In addition to the ratio c/a; tetragonality can also be expressed by comparing the relative height of the (002) and (200) peaks [24].

Nanosized BT powder with a high tetragonality is essential in the manufacturing of MLCCs. Tetragonality diminishes with a decrease in particle size and disappears below a critical particle size. Many researchers studied the BT critical particle size at which the tetragonality disappears. All results show differences in this critical particle size [25–27]. We used the following Scherrer formula to estimate the grain size for the used BT (from the XRD pattern of Fig. 3 [28]):

$$d_{XRD} = k\lambda / \beta \cos\theta \quad (1)$$

where λ is the X-ray wavelength, β the full width at half maximum (FWHM) of the diffraction line, and θ the diffraction angle with the constant k = 1. The average particle size values obtained are ~50 nm. Also, the atomic force microscope was used to confirm the mean radius of BT particle; it gave 24nm.

Figure 4 shows the XRD patterns of (BT)<sub>x</sub> (PVC)<sub>100-x</sub> composite samples for 2θ = 44–46°. The figure shows two reflection peaks: (002) and (200). The peaks are enlarged to compare the BT tetragonality. Curves of Fig. 4 were fitted to two Gaussian curves that correspond to BT (200) and (002) peaks using [Microcal (TM) origin, ver.7/Microcal Software, Northampton, USA] program. The measured BT tetragonalities (c/a) were found to decrease with the addition of the polymer. The composite samples show abnormally small tetragonality less than unity (c/a < 1) which shown in table 1.

It seems that in (BaTiO<sub>3</sub>)<sub>x</sub>(PVC)<sub>100-x</sub> composite samples the stress that stabilized the tetragonal phase of the core regions of BT decreased, leading to lower tetragonality (c/a ratio).

**Table 1: The tetragonality change with BT content in (BT)<sub>x</sub> (PVC)<sub>100-x</sub> composite samples**

BT ratio	100	20	5	2	1
C/a	1.004505	0.993342	0.996887	0.998667	0.996887

The observed trend for the results of (BT)<sub>x</sub> (PVC)<sub>100-x</sub> composite samples does not agree with our earlier published work [29]; where the BT tetragonality in (BaTiO<sub>3</sub>)<sub>x</sub> (PVDF)<sub>100-x</sub> composite samples were found to increase with the increase in BT content up to 30%, where it shows a saturation value. The (BT)<sub>x</sub> (PVC)<sub>100-x</sub> tetragonality results are completely different; it gets small values less than unity. This puts major limitations for the industrial applications of this composite materials.

### 3-3 The Fourier Transform Infrared Spectroscopy

From FTIR spectra (Fig.5) it is shown that BaTiO<sub>3</sub> is reacting with PVC, resulting in the bonding of Ba<sup>2+</sup> ions to the chlorine atoms forming BaCl<sub>2</sub>. This compound (BaCl<sub>2</sub>) gives vibrations at 690 and 1674 cm<sup>-1</sup>. The bonding of Ti<sup>4+</sup> ions to both CH<sub>2</sub> and O<sub>2</sub> forms CH<sub>2</sub>/Ti-O scissoring/ vibrations appear at 1428 cm<sup>-1</sup>[30], and the formation of new carbonyl group (C=O) appears at 1721, 1722 cm<sup>-1</sup> [31]. The existence of O-H stretching peak at 2968 cm<sup>-1</sup> with the (C=O) is an indication of the existence of carboxylic group. The increasing of peak intensities at 610-637 cm<sup>-1</sup> (which is attributed C-Cl bonds) is an indication of increasing crystallinity of the polymer reactants. The intensity of these peaks is a measure of the degree of crystallinity of PVC. In general the intensity is clearly increased. This may be due to the fact that the addition of the BaTiO<sub>3</sub> nanoparticles to PVC increases the degree of crystallinity of PVC. These observations indicate a clear interaction between PVC and BaTiO<sub>3</sub> nanoparticles as is concluded from XRD results.

### 3.3 DSC Measurements

Fig. 6 shows that, the obtained glass-transition temperatures (T<sub>g</sub>) is around 80°C which agrees with the previously published data. The T<sub>g</sub> of the nanocomposite films was found to be increase with the increase of BT ratio, this may be attributed to the aggregation of BT nanoparticles in the free volume between the chains of PVC matrix.

Generally, the mobility of chain segments in polymers is reflected in its T<sub>g</sub> [32,33] i.e a lower mobility resulted from a higher T<sub>g</sub>. This could be ascribed to the interaction between the PVC chain segments and the BT [32-34].

Also, the observed exothermic peak at about 130°C which increase in height with increases in the BT content can be attributed to the enhancement of crystallinity for the nanocomposite films than that of pure PVC. This result is agreed with the XRD data.

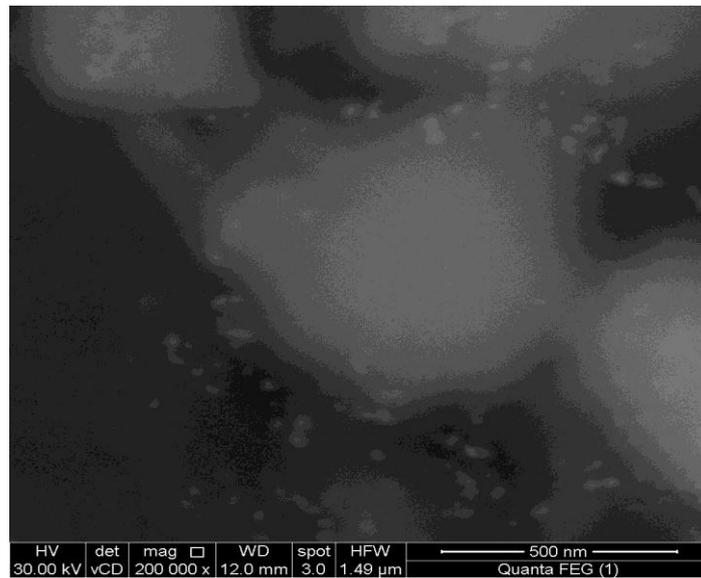


Figure 1: SEM image of (BT)<sub>1</sub>(PVC)<sub>99</sub> composite sample.

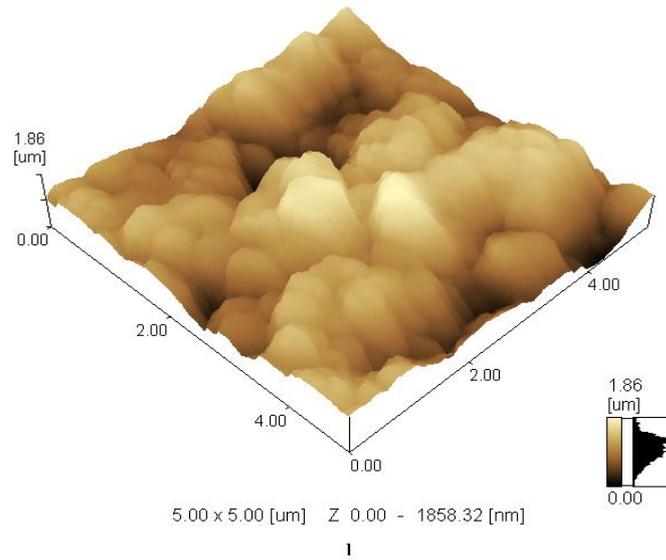


Figure 2: AFM 3D image of Barium Titanate

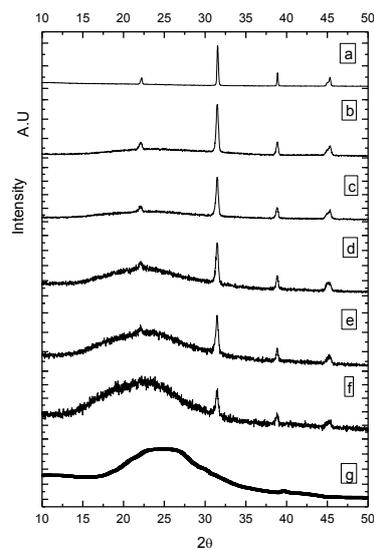


Figure3. X-ray diffractograms of (BT)<sub>x</sub>(PVC)<sub>100-x</sub> composite samples: (a) x=100 (b) x=5, (c) x=2, (d) x=1, (e) x=0.7, (f) x=0.5 and (g) x=0.

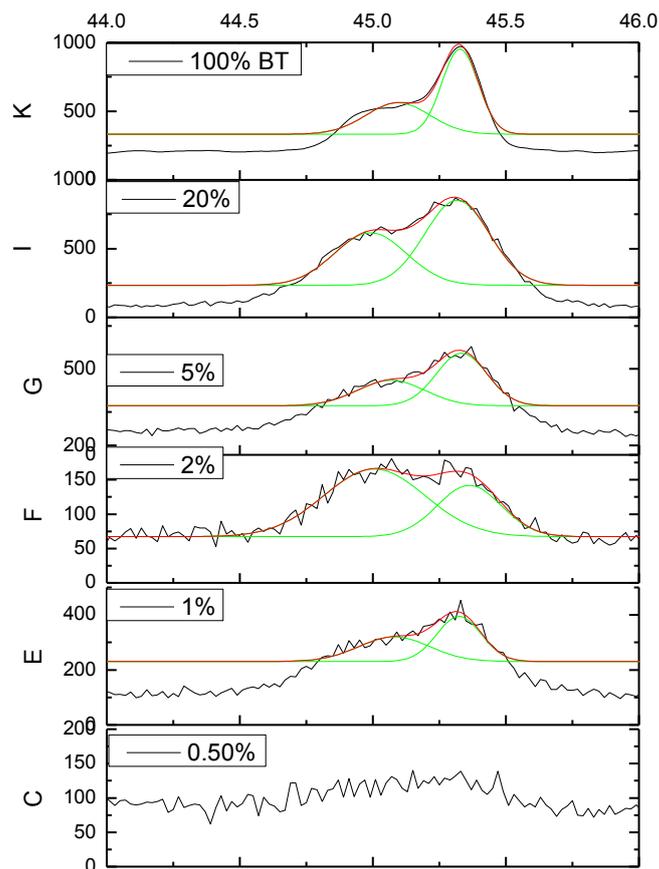


Figure 4: X-ray diffractograms of  $(BT)_x(PVC)_{100-x}$  composite samples for  $2\theta 44^\circ-46^\circ$  Original curve, — Gauss fit for original curve, — Gauss fit for peak1; — Gauss fit for peak2.

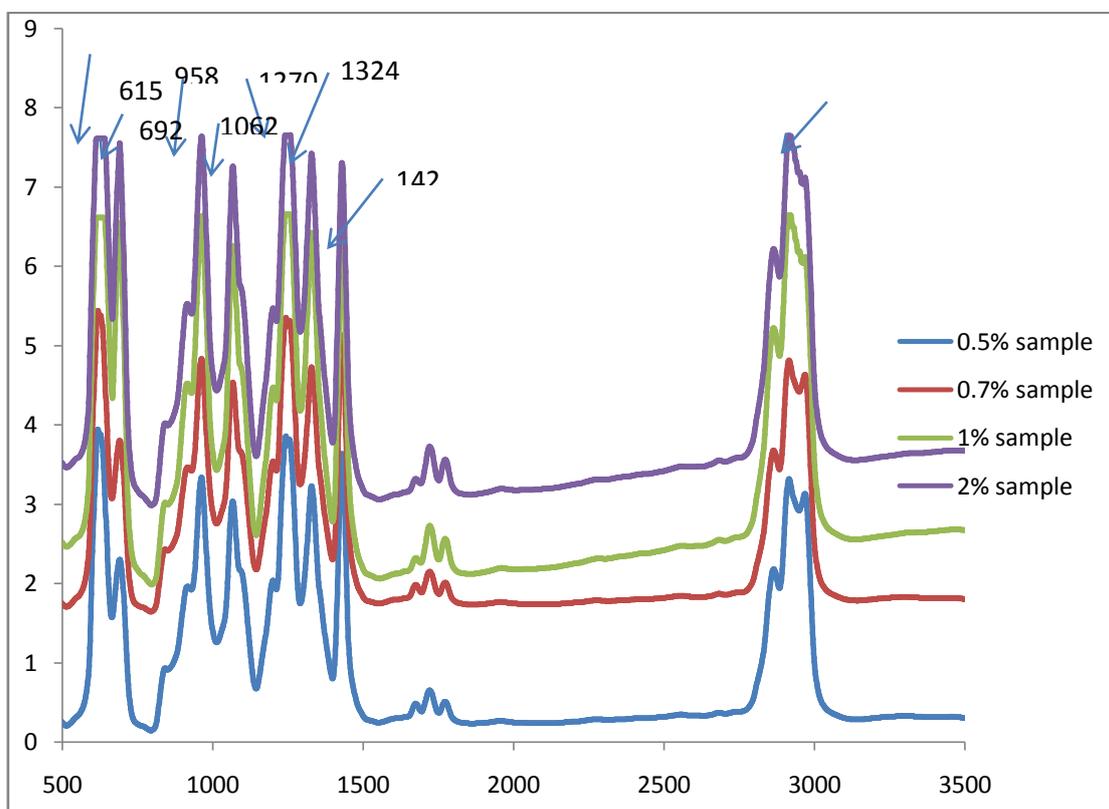


Figure 5: FTIR spectra of  $(BT)_x(PVC)_{100-x}$  composite samples

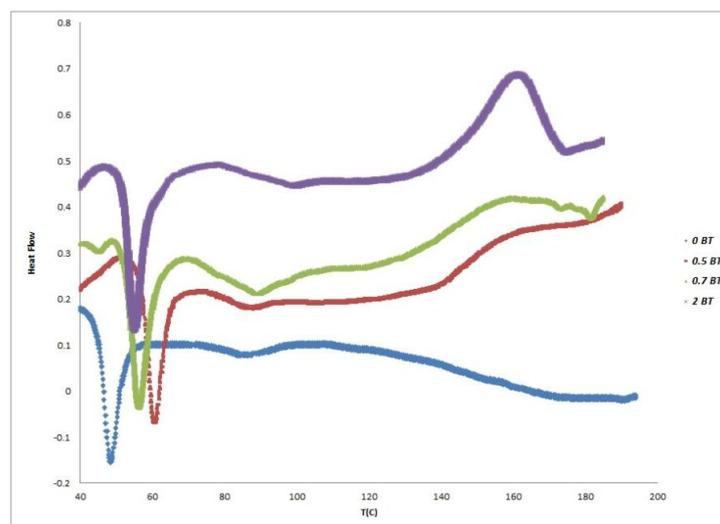


Figure 6: The DSC heating curves of  $(\text{BT})_x(\text{PVC})_{100-x}$  composite samples.

#### 4. Summary

The average particle size of BT nanoparticles is calculated by two different methods which are XRD and AFM, both measurements give average particle size about 50nm. Also, from XRD the tetragonality ratio ( $c/a$ ) decreases with the addition of BT content. Moreover, the degree of crystallinity increases with increases the BT content in the PVC matrix.

The FTIR shows that, a clear interaction between BT nanoparticles and PVC.  $T_g$  was found to increase with increasing of the BT content, and the increasing of the degree of crystallinity by the addition of BT nanoparticles.

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