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Electric field induced extrinsic strains in BaTiO₃-epoxy nanocomposite: a contact-less mechanical property tailoring smart material

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Abstract: Epoxy is an important class of thermosetting material which have been used in many fields such as aerospace, automobile and energy sectors. cured epoxy, however, exhibits poor resistance to crack initiation and growth, thus low toughness and brittleness at failure. To improve the mechanical properties, in numerous studies the epoxy matrix in polymer composites has been modified by various techniques such as the inclusion of a second phase (e.g. core-shell rubber, thermoplastics or nanofillers). Inclusion of these materials in epoxy improves toughness and the impact resistance properties, but very few studies have focused on offering an ‘active toughening’ mechanism, meaning an increase in toughness activated by a stimulation (mechanical, electrical, thermal etc.) in high-performance rigid structures. In this study, aerospace grade epoxy resin modified with tetragonal barium titanate (BaTiO₃) nanoparticles has been prepared, and its instantaneous toughening behaviour has been analysed under contact-less electromagnetic fields. For this reason, different wt.% of BaTiO₃ nanoparticles (1, 5, 10 wt%) have been functionalised with silane coupling agents and dispersed uniformly into epoxy Araldite LY1564, a diglycidyl ether of bisphenol A (DGEBA) associated with its curing agent Aradur 3487. Real-time strain measurement (Tensile measurements) of the modified epoxy along with in-situ Raman shift study have been carried out in situ under an electric field stimulation. The results demonstrate that the activation of dipole displacements in BaTiO₃ via an electromagnetic field introduces an interfacial compressive stress onto its surrounding rigid (fully cured) epoxy that enhances the toughness of the nanocomposite via suppressing the coalesce of inherent or process induced microcracks in the epoxy. The

mechanism provides an effective route for mechanical property tailoring, specifically toughening of thermoset composites, under an electric field. The in-situ Tensile and Raman (during the stimulation) along with the materials characterisation (post stimulation) provides a unique quantitative framework for design of a toughening mechanism.

Keywords: Epoxy resin, Barium titanate, Electric field, Induced strain, Toughness, Extrinsic strains

1. Introduction

Fibre-reinforced polymer (FRP) composite materials are widely used materials because of their superior specific strength and modulus [1]. A FRP composite consists mainly of thermoset resins such as epoxy with a highly cross-linked structure to achieve optimum mechanical properties and thermal stability. Despite its beneficial properties, epoxy has the disadvantage of having intrinsic brittleness and therefore the tendency to fail at relatively low fracture energy, particularly under the transversal direction or when it is exposed to high strain rate or impact loading [2-4]. Additionally, it is difficult to tailor the properties (e.g. toughening) of the fibre during the composite's fabrication process. To overcome these property-driven drawbacks, several research studies have been carried out for property enhancement by modifying the epoxy with the inclusion of numerous micro-and nano-fillers as a second phase. These include rubber tougheners [5], silica particles [6], carbon nanoparticles [7], clay [8] and fibre coating [9]. It was observed that rubber tougheners are the most efficient ones, having significantly increased the fracture toughness [10] of a brittle epoxy by multiple orders of magnitude, though a reduction in strength and stiffness have also been observed [11]. It is noted by several studies that a threshold exists above which the particles are prone to agglomerate and trigger a deterioration in mechanical properties [12]. Thus, the use of coupling agents for surface treatment of particles has been introduced to accomplish a superior interfacial bonding between particles and the matrix [13]. Despite the outstanding performance of particle-toughened epoxy composites, loss in elastic modulus, tensile strength, and glass transition temperature have been additionally described by other studies [14]. Nevertheless, the drawback of this method is that the control of the toughening process is highly difficult due to the poor thermal conductivity of the polymer that hinders the material's response, mechanically. The toughening via volume dilation of embedded fillers was first proposed in a study by Ho Sung et al. It is accomplished by pre-stressing the epoxy matrix by expandable hollow microspheres under heating [15]. This idea was based on mimicking the toughening effect of the phase changing ceramics in the vicinity of the crack. Phase-transition toughening has been extensively studied in the past years as one of the most efficient toughening mechanisms for ceramics [16]. It has been observed experimentally that the stress-induced martensitic phase transition of a second phase at a crack tip, such as a tetragonal Zirconium dioxide change to a monoclinic phase, can result in volume expansion and forming a compressive stress field around the crack tip to prevent its propagation [17]. Thus far, there are no attempts made to investigate the strain behaviour of embedded fillers in rigid polymer composites under an in-situ electric field. Therefore, a novel active toughening effect based on radiation field-induced strains has been investigated and presented here, by incorporating ferroelectric crystals (BaTiO₃) that show an electro-strain under an applied electric field. Our research group has already conducted a quantification phase of extrinsic strain variations induced by domain walls movement as a result of subjected to electromagnetic radiation in BaTiO₃-epoxy nanocomposites using fibre bragg

grating technique, presented in Li et al. (2022). The current paper presents data from *in-situ* and real-time Raman and tensile testing of the same material equipped with an electric field, *in situ*.

2.1 Materials and Methods

The epoxy used in this study was Araldite LY1564, and was supplied by Huntsman, UK. The coupling agent for surface functionalisation selected in this study, 3-glycidoxypropyl trimethoxysilane (3-GPS), the hydrogen peroxide (H₂O₂, 30%) and the acetic acid (C₂H₄O₂, 99.9%) used as functionalisation aids were all supplied by Sigma-Aldrich, UK. The ethanol (C₂H₆O, 99.9%) used for BaTiO₃ dispersion was by Fisher Scientific International, Inc., UK. BaTiO₃ powders were supplied by Nanostructure & Amorphous Materials Inc., US.

10g BaTiO₃ nanoparticles were added into a 230mL solution of H₂O₂ in a round bottom flask. The mixture was then sonicated in an ultrasonic bath for 30 min and then refluxed at the boiling temperature of 30% H₂O₂ solution at 108°C at 100 rpm using a mechanical stirrer for six hours to facilitate the process by heating without losing H₂O₂. The nanoparticles were retrieved by centrifuging the resulting solution at 4500 rpm for 15 min and washed three times with deionized water. The achieved BaTiO₃ nanoparticles refluxed suspensions were dried in an oven at 80°C for 24 hours, as shown in Figure 1.

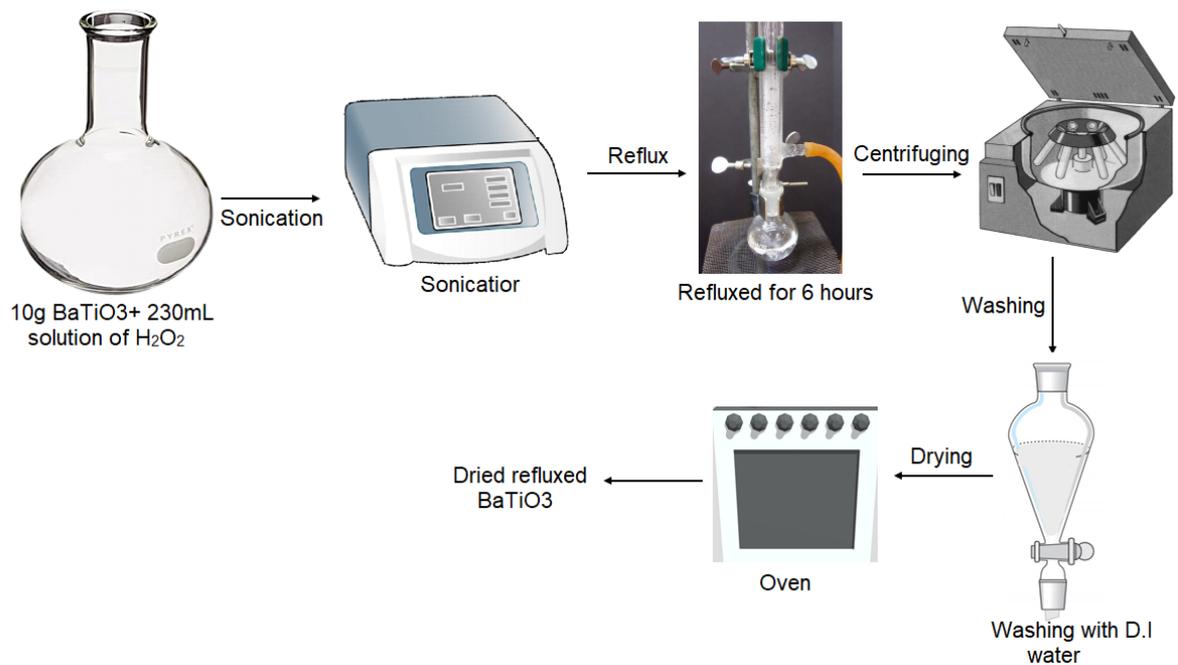


Figure1. Schematic diagram of the refluxing process of BaTiO₃ nanoparticles.

3-glycidoxypropyl trimethoxysilane (3-GPS) was then applied to BaTiO₃ nanoparticles refluxed to improve the processability and filler dispersion in nanocomposites; the solution of 1 wt.% of 3-glycidoxypropyl trimethoxysilane (3-GPS) with respect to BaTiO₃ refluxed was prepared. 150mL aqueous solution of ethanol and deionized water (9:1) was firstly mixed in a beaker. Adding the acetic acid drops using a pipette and stir vigorously after each drop until the pH value of 3.5-4 measured by a METTLER TOLEDO pH meter was reached, stirred vigorously again for 3mins to form a clear solution. The low pH values of the solution facilitate the silane functionalisation process [92]. After the addition of the 0.1g 3-GPS solution to the acidified

solution using a pipette, the mixture was left in an ultrasonic bath for 30mins to form a homogenous solution. 10g hydroxylated BaTiO₃ powders was then added to the silane solution, and mixed under ultrasonic bath for 10mins for better filler wetting. Finally, the mixture was refluxed at the boiling temperature of ethanol, 78°C [93], at 100 rpm using a mechanical stirrer for six hours using a silicone oil bath over a hotplate. After refluxing, the BaTiO₃ was washed three times with deionized water and retrieved using centrifugation at 4500 rpm. The silane treated BaTiO₃ (Si-BaTiO₃) 19 powders were dried at 110°C for 24 hours to avoid any condensation of silanol groups at the surface, as shown in Figure 2. In the end, the powders were crushed in a mortar and pestle for the nanocomposites preparation.

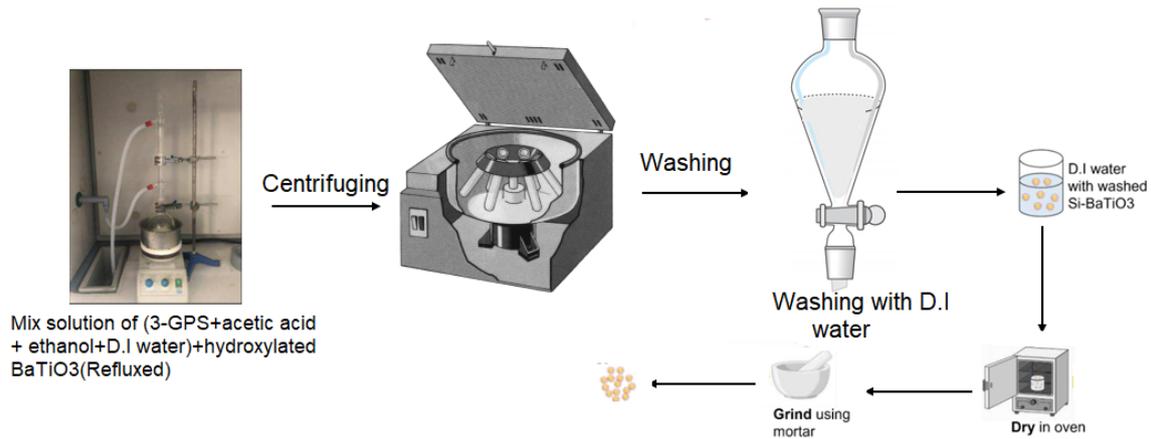


Figure.2. Schematic diagram of the functionalisation process of BaTiO₃ with 3-GPS. The epoxy nanocomposite fabrication process including Si-BaTiO₃ functionalisation is schematically illustrated. The epoxy resin nanosuspension with 1, 5, 10, wt.% Si-BaTiO₃ nanoparticles and 5, 10wt.% untreated BaTiO₃ nanoparticles were prepared as follows: Firstly, the weighed amount of BaTiO₃ powders was added to ethanol and sonicated with an ice water bath for 2 min with a 10s pulse to form a homogenous solution. Then a weighed amount of epoxy was added to the solutions which were stirred using a mechanical stirrer at 300 rpm and 80°C overnight under the fume hood to gradually remove the ethanol without precipitation of the particles. The epoxy mixtures were weighed before and after the evaporation of the solvent to ensure the complete removal of ethanol. The curing agent was then added to the mixture with a weight ratio recommended by the company and stirred for a further 3mins. Finally, the mixture was placed in the vacuum oven at 30°C for 1 hour to remove air bubbles at 29 inHg and achieve complete removal of ethanol. The whole mixture was poured into a mould made of two pieces of glass clamped with a 3 mm silicone gasket in-between, as shown in Figure 1 This set-up assured that a uniform thickness of samples was achieved. The samples were then cured in the oven for 8 hours at 80°C as recommended by the manufacturer, then cooled down to room temperature. The final samples were of size 100 × 20 × 0.3 mm³, and cut to different sizes using a precision cut-off machine BRILLANT 220.

2.2. Electric Induced Characterisations

The Tensile vs elongation and tensile modulus were measured by Instron tensile tester under an in-situ electric field with varying voltages of 0 V, 6 V, 9 V and 24 V. The electric component of the electric field and set up for tensile testing performed *in-situ* are illustrated in Figure 2. Figure

2a shows that before testing the sample was covered with an insulating tape at both ends where it was clamped and was coated with a silver paste to assure electrical contact for the in-situ electric field. Figure 2b shows the full setup for the tensile tests. Figure 2c shows the fractured sample after testing. A change in voltage introduces a corresponding change in the electric field. These tests aimed at observing a significant difference in the tensile strength, elongation and modulus results in presence and in absence of an electric field with a varying degree of intensity, the dimension of sample was $65 \times 10 \times 5 \text{ mm}^3$.



Figure 2. Schematic illustration of the *in-situ* electric field induced tensile test measurement: a) Sample before testing, b) Testing setup, c) Sample after testing.

2.3. Results

The research has aimed at obtaining the electro-induced stress vs strain behaviour in the surrounding matrix of the BaTiO₃ particles under different voltages. Consequently, the electrical polarisation of the sample introduced contributes to the improvement in tensile strength, elongation and modulus.

2.3.1. Scanning Electron Microscope (SEM)

In this study, the BaTiO₃ particles were modified using the silane coupling agent 3-GPS to produce a finer dispersion in the epoxy resin. The SEM was used to characterise the dispersion and distribution of the nanoparticles at different loadings in the epoxy to see if it was effective. There were several levels of aggregation events due to higher particle weight fractions and improved dispersion due to surface functionalisation: SEM images of the cracked cross-section of silane functionalised as well as non-functionalised BaTiO₃ epoxy composites at different weight % can be seen in Figure 3(a)-(c). SEM images of the cracked cross-section of non-functionalised BaTiO₃ epoxy composites at 10 wt % can be seen in Figure 3(d). With the use of surface functionalisation, the nanoparticles are uniformly dispersed. The silane-treated particles have the same size of 200 nm as the pure BaTiO₃ particles, as depicted in Fig 3(a). There is no obvious aggregation of Si-BaTiO₃ particles until small-scale clusters appear owing to nanofiller agglomeration, as shown in Figure 3. (c). When compared to the untreated particles, the majority of the Si-BaTiO₃ particles were finely distributed. The effectiveness of the silane functional group is consistent with previous research [21].

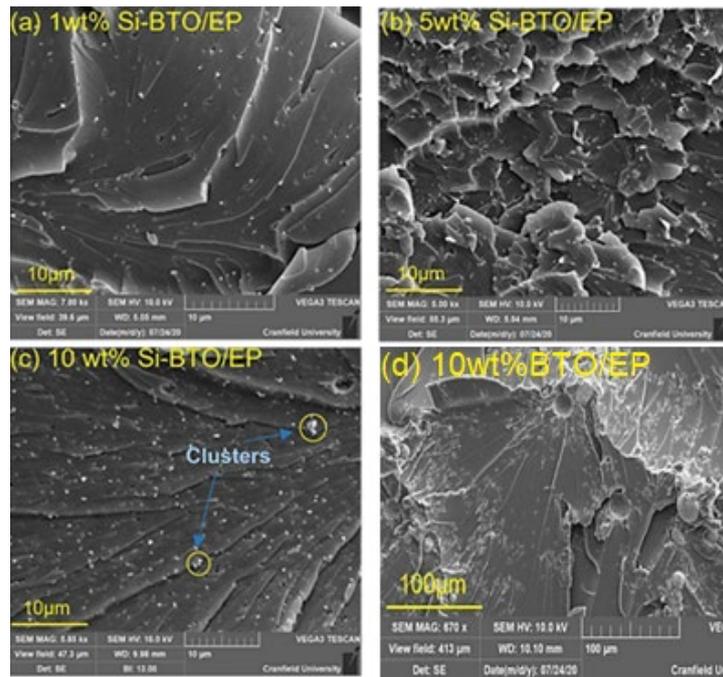


Figure.3. SEM images of fracture cross of epoxy nanocomposites with BaTiO₃ at different weight loading, (a)-(c) images of 1 wt.%, 5 wt.% and 10wt%Si- BaTiO₃, (d) untreated 10wt% BaTiO₃ Li et al. (2022).

2.3.2. In-situ Tensile Test

The *in-situ* tensile test was performed under different voltage conditions (e.g.0V,6V,9V,24V) and the tensile strength, elongation and modulus seemed to vary both by changing the content of BaTiO₃ and the voltage. The overall tensile strength and elongation of the 1 wt.% BaTiO₃- epoxy nanocomposites were relatively smaller compared to those of the 5 wt.% and 10 wt.% BaTiO₃- epoxy nanocomposites under the applied voltage conditions. The tensile strength and elongation of the nanocomposites increased with increasing the voltage, as shown in Figure 4a-c. The increasing tensile strength and elongation with increasing the content of BaTiO₃ and voltage confirm the toughening effect of epoxy, as shown in Figure 4a-c. The results confirm that the voltage has a profound effect on the elongation and tensile strength of the nanocomposite due to the polarisation of BaTiO₃. The change in tensile strength and increase in elongation confirm the increment in toughness of the epoxy.

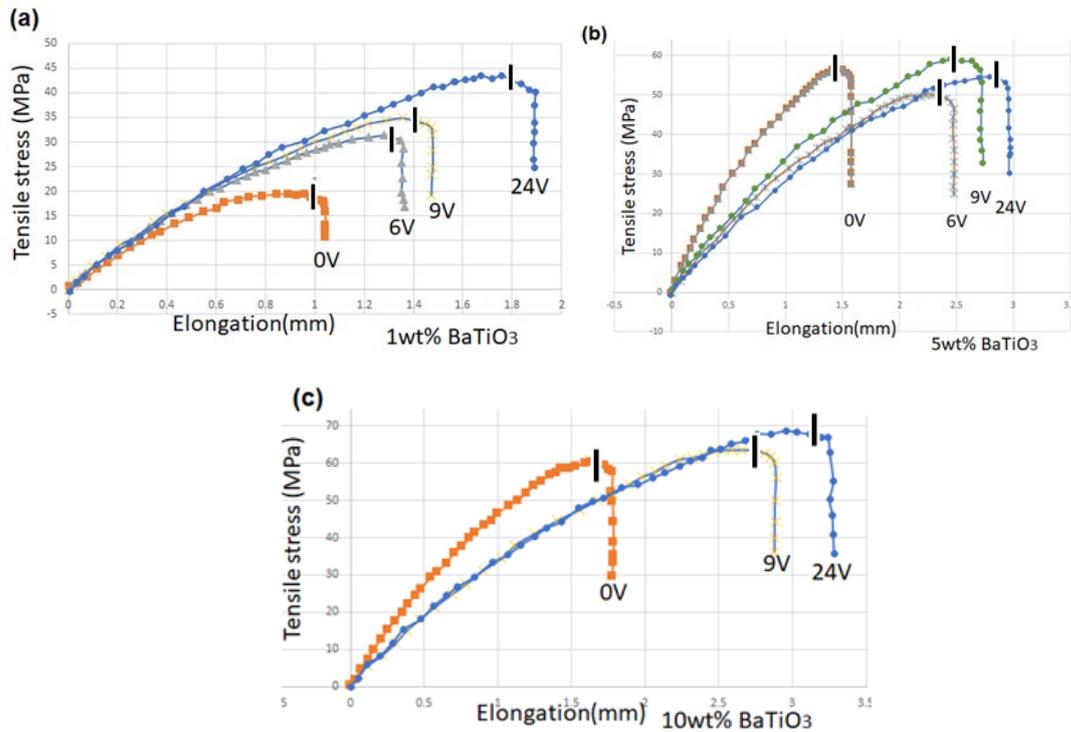


Figure.4. Evolution of tensile strength vs elongation curves under increasing electrical voltage.

It is well known that the elastic modulus is strongly dependent upon the nanofillers content and matrix. The *in-situ* tensile tests were performed under different voltage conditions (e.g., 0V, 6V, 9V, 24V) and the tensile modulus was measured both when varying the content of BaTiO₃ and the voltage. The results showed that in the case of 1wt% BaTiO₃ the tensile modulus increased while increasing the voltage, as shown in Figure 5a. On the other hand, in the case of 5wt% and 10wt% BaTiO₃ the tensile modulus seemed to decrease while increasing the voltage, as shown in Figures 5b and 5c. Also, it was noted that elongation at break was increased with increase in the percentage of BaTiO₃ with respect to increase in voltage, however, tensile modulus decreased with increase in voltages for 5wt% and 10wt% BaTiO₃, which confirm the was decreased of stiffness with increasing the voltages for 5wt% and 10wt% BaTiO₃. It is owing to the decreasing the stiffness of nanocomposites concerning voltage and content of BaTiO₃, in other hand, elongation has been increased with voltage and content of BaTiO₃. It proves the toughening effect of BaTiO₃ concerning the voltage and content of BaTiO₃. Hence, the induced electric field has a positive effect on the scenario of improving the toughness of nanocomposites.

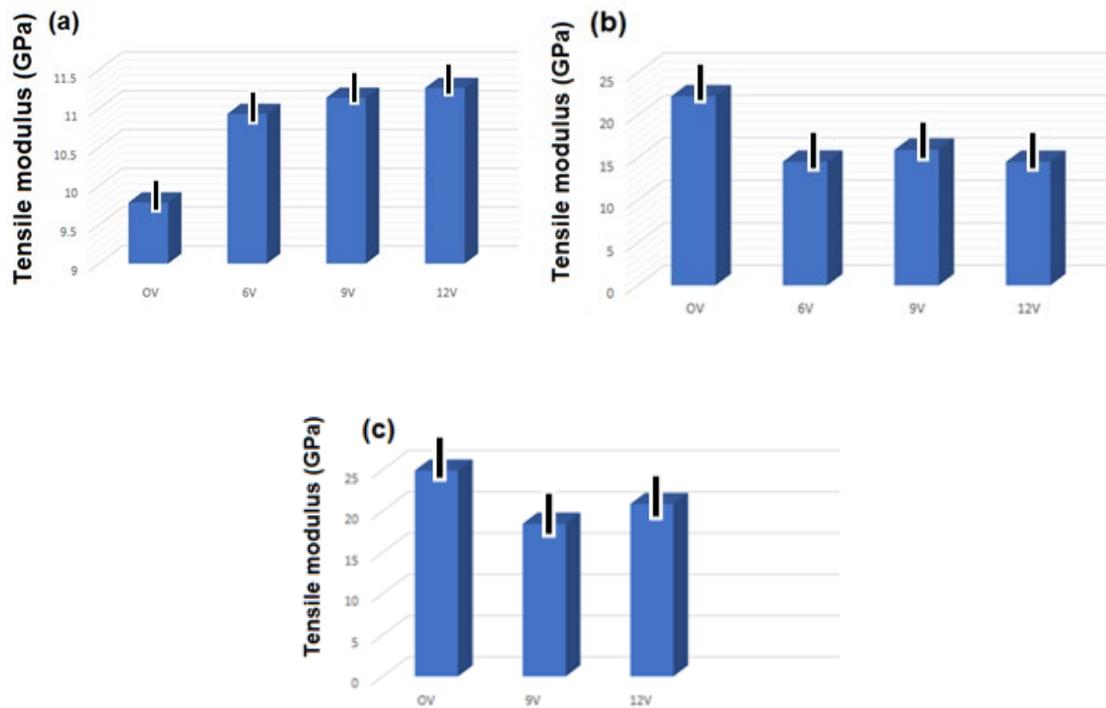


Figure.5. Measurement of tensile modulus under different electrical voltage, (a)-(c) Tensile modulus of nanocomposites with varying content of 1 wt.%, 5 wt.% and 10wt% respectively.

2.4. Conclusions

The in-situ electrical field-nanocomposite interaction was conducted to study the ferroelectric (BaTiO₃) materials' response in a high-performance (rigid) epoxy composite that offers a synergic effect on the dielectric phase-based nanocomposites by the electric field. The results have presented a pioneering investigation as no investigations have been reported, thus far, on the electric field response of ferroelectric materials in polymer under external electric fields. The research has characterised the mechanical properties of ferroelectric nanoparticles (BaTiO₃) modified polymer (epoxy) at weight loadings up to 10 wt.%, and subsequently investigated the toughening induced by the BaTiO₃ nanoparticles' dipole displacements onto their surrounding epoxy. Silane surface functionalisation of the nanoparticles was used to uniformly disperse and improve interfacial particle-matrix bonding quality. The electrical electrode-based technique was employed, *in-situ* with the electric field exposure, for monitoring the tensile stress and elongation response of the nanocomposite subjected to different voltages and induced electric field. In-situ electric field and the Raman measurements are under investigations.

2.5. Acknowledgements

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