

XRD STUDIES AND THEORETICAL MODELING ON POLYMER COMPOSITES OF FERROELECTRIC NANO CRYSTALLINE CERAMIC PbBaTiO_3

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Abstract: High temperature ferroelectric materials, like many other ceramics, are inherently brittle in nature and therefore pose problems in converting them into simple usable forms such as flexible wires, shapes, sheets etc. Composite materials are attracting much interest for technical applications and fundamental research. In this section the authors describes a method for the preparation of PbBaTiO_3 (PBT) - ferroelectric ceramic powder materials based on pre-calcinations of oxides. In order to show the viability of the proposed method, this ferroelectric powder was prepared in special furnace. By using the Classical polymer processing of converting raw polymeric materials into finished products of desirable shape and macromolecular structure, morphology, polymer is blended with ceramic ferroelectric material PbBaTiO_3 to form a new product. The results are analyzed by X-ray Diffraction (XRD), SEM, and EDX. This product is analyzed, characterized and property studies are done and found to be useful in many applications. Young's modulus of the composites is calculated by using different equations in theoretical modeling.

Keywords: Lead Barium Titanate (PBT), XRD, SEM, EDX, Debye Scherrer's formula, Young's modulus, Theoretical modeling.

1. Introduction

Today, ceramics may be defined as a product manufactured by the heat treatment of a material (or mixture of materials) which are inorganic and non-metallic [1]. The growth of ceramics is an important qualitative change in recent decades, based on deeper scientific understanding of the composition-structure-property correlations of ceramics. Ceramics is one of the oldest technologies, with a history of about 10,000 years behind our time. Ceramic materials showing ferroelectric and superconducting behavior are being used in many device applications in electronics and optics. Many advantages are foreseen by the use of the majority of ceramic devices in multilayer configurations and so a good amount

of work is expected in the development of newer innovative processing and fabrication techniques to improve the device performance and reduce the cost of production [2-4].

In spite of their chemical inertness, high temperature stability and abundance, ceramics have always been disqualified for structural applications due to their poor tensile strength and brittleness. These handicaps have to be overcome by several new approaches. In the development of material science, the drive for composites stems from the fact that the desirable properties could not be obtained from single phase materials such as ceramics or polymers. The requirement of each and every purpose can be optimized by combining the most useful properties of the two phases which do not ordinarily appear together [5-10]. The ceramic-polymer composites are made up of an active ceramic phase embedded in a passive polymer phase. Nano composites are a new class of polymer materials with ultrafine phase dispersion of the order of a few nanometers, which show very interesting properties often very different from those of conventional filled polymers [11-14]. Composites of polymers with particulate fillers have generated interest owing to their desirable improvement in certain properties for various applications. The performance of a composite material is strongly dependent on the combined effect of filler particle size, filler surface chemistry and volume fraction of the filler [15-18]. By principle polymer composite is a material created by the combination of two or more components, viz., selected filler or reinforcing agent and a compatible matrix in order to obtain specific characteristics and properties. Graded dielectrics with a wide range of dielectric properties can be prepared by using polypropylene matrices. The broader use of ceramic polymer composites as capacitors in dynamic random access memories (DRAMs) invokes an even greater interest in the family of materials. Development of electric devices working at high operating frequencies such as fast computers, cellular phones etc require a new high dielectric constant materials that combine good dielectric properties with both mechanical strength and ease of processing. In particular the high-K materials are required for making embedded capacitors for integrated electronic devices. Pure polymers are easy to process into mechanically robust components but generally suffer from low dielectric constant. On the other hand, typical high-K materials such as ferroelectric ceramics are brittle and require high temperature processing, which are often not compatible with current circuit integration technologies. The ideal solution would be high K-materials that is mechanically robust and procurable at ambient temperatures have to be incorporated with suitable polymers such as ceramic polymer composites that may combine desired properties of the components[19-21].

In this paper the authors describes a method for the preparation of PbBaTiO_3 -ferroelectric ceramic powder materials based on pre-calcinations of oxides and the prepared powder is mixed with polymer

material to form a new polymer composite in different compositions. The results were analyzed by X-ray diffraction (XRD), SEM and EDX. The particle size is calculated using Debye Scherrer formula. The SEM studies revealed that its particle size is in hundred nanometer range. The EDX spectrum of PBT gave the information on the elemental composition of the material. Young's modulus of the prepared polymer composites of different compositions are calculated by different equations in theoretical modeling.

2. Material and Methods

PBT has perovskite structure. The perovskite structure is adopted by many oxides that have the chemical formula ABO_3 [22]. The representative structure of perovskite compounds is cubic, the compounds in this family may possess some distortion. The orthorhombic and tetragonal phases are most common variants. The sample with the chemical formula $PbBaTiO_3$ is prepared by the conventional solid state reaction technique according to the molecular formula. For the prepared sample, the reagent grade chemicals of high purity (99.99%) Lead Oxide, Barium Carbonate and Titanium Oxide powders are used as the raw materials and weighed according to their molecular formula.

The powders of the required ceramics are mixed mechanically. Mechanical mixing is usually done by hand mixing in agate mortar for two weeks. Then ball milled with suitable balls for three months along with daily sieving and mixing to insure homogeneity. Then the material calcined at 900°C . After the furnace is off, on cooling the oxygen is allowed to flow into the furnace at intervals (Oxygen Annealing). A final furnace temperature of 900°C is maintained for the material. A temperature much higher than this will result in a material that is much harder to regrind. Temperatures above 1030°C may destroy the crystal structure.

The melt mixing technique is chosen for preparing the composites because it is a solvent free technique. By melting at high temperature, molten polypropylene can easily penetrate between filler particles which facilitate suitable mixing and allow avoiding air trapping into the composites. Consequently void free composites are obtained. Polypropylene-PBT composites are prepared in a Brabender Plasticorder which is a torque rheometer. The cavity for mixing in the instrument has a capacity of 40 grams and is fitted with two screw type rotors of variable speed [23]. Filling the internal cavity completely with mixing charges ensures a constant ram pressure and a good mixing. For mixing, the temperature of internal mixer is raised to 180°C and introduced the calculated amount of polypropylene into the cavity. Complete melting of polymer is ensured by a constant minimum torque and reattainment of the desired cavity temperature of 180°C . Filler particle is then added to the molten

polymer and mixed for about 6 minutes at a rotor speed of 60 rpm. This time is sufficient to generate a steady state torque response, indicative of uniform dispersion of the components. The compositions of the ceramic composites are 10%, 20%, 30%, and 40% by the volume fraction of the filler. The mixed samples are compression moulded into sheets of desired thickness by hydraulic press at a temperature of 180^o C and are used for different studies. The composites are named as PBT 10, PBT 20, PBT 30 and PBT 40 according to their percentage of ceramic component.

2.1 XRD Analysis

X-ray Diffraction pattern for the four compositions of the composites are taken using Bruker AXS D8 advance diffractometer. The diffractometer with radiations of wavelength 1.54184 Å having Nickel filter, equipped with X-ray generator 1140/90/96 having X-ray source KRISTALLOFLXE 780, KF, 4KE with wide angle goniometer PW1710/70 with single pen recorder pm 8203 and channel control PW1390 at 35kV, 10mA is used for the purpose. The scanning speed of the specimen is 2 degree/minute. From the XRD results, the obtained d values checked with the JCPDS (Joint Committee on Powder Diffraction Standards) file values and applied the EXPERT PRO software to analyze. This crystal is found to be in Tetragonal system:

$$a=b=3.761, c=11.942 \quad \alpha=\beta=\gamma=90^{\circ}$$

Here the authors studied the change of XRD spectrum of PBT at different ceramic filler compositions of the composites. The XRD spectrum of PBT- polypropylene composites for the four compositions are shown in **Fig.1**.

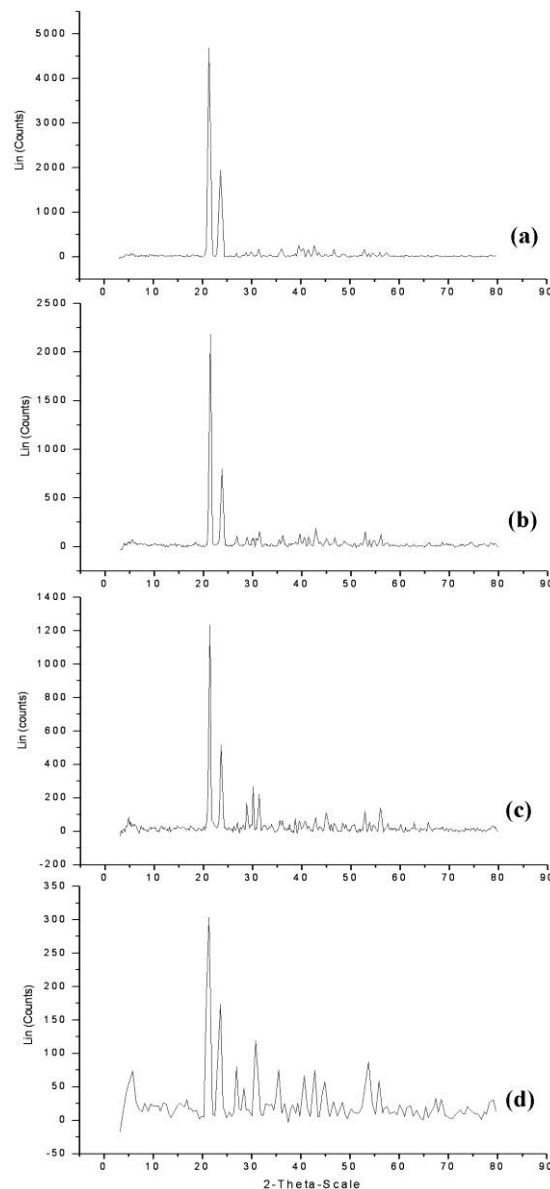


Figure.1. XRD of (a) PBT 40, (b) PBT 30, (c) PBT 20 and (d) PBT 10.

2.2 Particle size measurements

X-ray diffraction profile may be used to measure the average crystal size in the sample provided the average diameter is less than 200\AA . The lines in a powder diffraction pattern are of finite breadth but if the particles are very small, the lines are broaden than usual. The broadening decreases with the increase in particle size. The particle size for PBT is calculated from X-ray diffraction profiles of strong reflections with intensity % by measuring the full width at half maximum (FWHM). The Debye Scherrer equation for calculating the particle size is given by [24].

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where K is the Scherrer constant, λ is the wavelength of light used for the diffraction, β is the ‘full width at half maximum’ of the sharp peaks and θ is the angle measured. The Scherrer constant (K) in the above formula accounts for the shape of the particle and is generally taken to have the value 0.9.

2.3 SEM

Morphology has been analyzed from Scanning Electron Microscope (SEM). The SEM analyses the surface of solid objects, producing images of higher resolution than optical microscopy. It produces representations of three dimensional samples from a diverse range of materials. **Fig.2** and **Fig.3** are the surface morphology and fracture surface morphology of PBT respectively. The particle size measurement through SEM reveals its maximum dimensions always less than 100 nm.

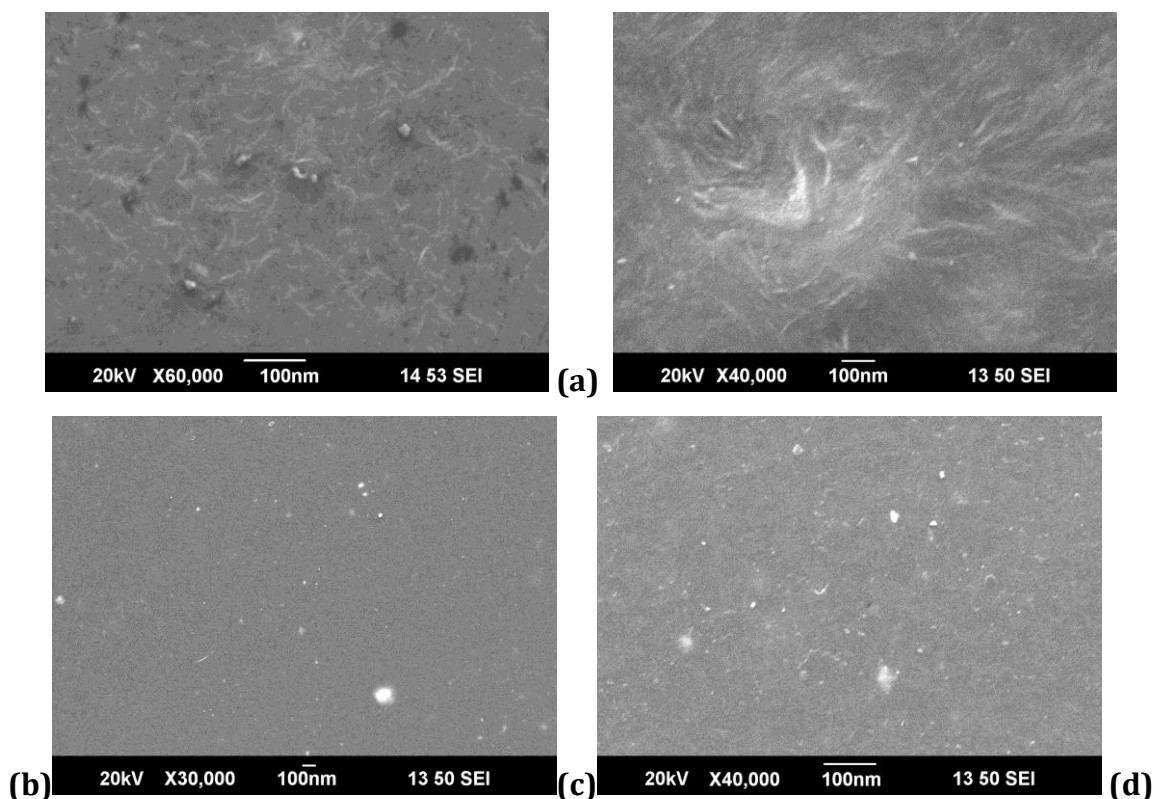


Figure. 2. Surface view of (a) PBT10, (b) PBT20, (c) PBT30 and (d) PBT40.

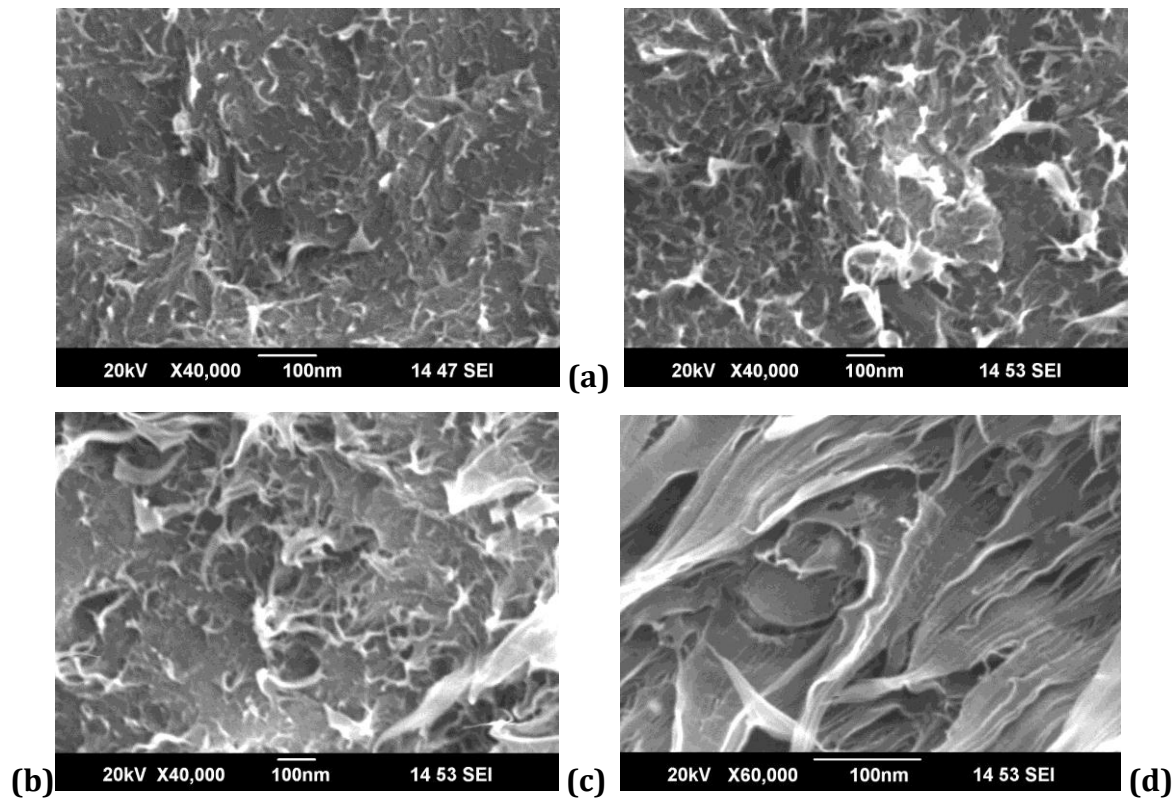


Figure.3. Fracture surface view of (a) PBT10, (b) PBT20, (c) PBT30 and (d) PBT40.

2.4 Energy Dispersed X-ray Spectrograph (EDX)

EDX shows the composition details of the prepared ceramic powders. The instrument used for this measurement is ISIS Link Oxford Instrument UK. This technique generally associated with Scanning Electron Microscope (SEM). In this technique an electron beam of 10-20 KeV strikes the surface of a sample which causes X-ray to be emitted from point of incidence. The energy of the X-ray emitted depends on material under examination. The energy of the characteristic X-ray emitted from the different elements is different and thus it gives the unavoidable signature of the particular element. When an X-ray strikes the detector, it will generate a photoelectron which in turn generates electron-hole pairs. A strong electric field attracts the electrons and holes towards the opposite ends of the detector. The size of the pulse thus generated depends on the number electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. In this method however elements with low atomic number are difficult to be detected. The detector which is lithium doped silicon (SiLi) is protected by a beryllium window and operated at liquid nitrogen temperatures. The absorption of the soft X-rays by the beryllium decreases the sensitivity below an atomic number of 11.

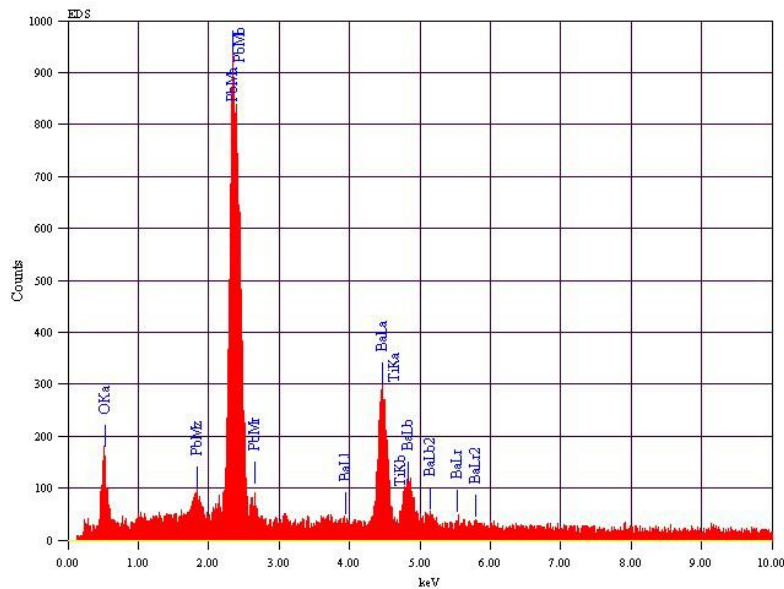


Figure.4. EDX of PBT

3. Theory/calculation

3.1 Theoretical modeling

The mechanical properties of two-phase composites made up of particulate filled polymer phase have been studied in great detail. The modeling and simulation of polymer based composites has become an important topic in recent times because of the need for the development of these materials for engineering applications [25]. The mechanical properties of particulate filled composites are affected by a number of parameters such as filler orientation, particle size of the filler and filler/ matrix adhesion etc. Several theories have been proposed to model the Young's modulus of the non-interactive composite materials in terms of different parameters. Among the most prominent, historically and technically are those developed by Einstein[26], Guth [27], Quemeda [28], Thomas [29], Kerner [30] and Sato and Furukawa [31]. These theoretical predictions are graphically represented in Fig.5 and Fig. 6.

a. Einstein equation

According to Einstein equation,

$$E_c = E_m(1 + 1.25\xi_p)$$

where E_c and E_m are the Young's modulus of composite and matrix, respectively and ξ_p is the mass ratio of the particle given by the equation,

$$\xi_p = \frac{m_p}{m_m + m_p}$$

Where m_m and m_p are the mass of the matrix and mass of the filler particle respectively. Einstein's equation is applicable only for materials filled with low concentrations of non interactive fillers. The equation also assumes that the filler is denser than the polymer matrix.

b. Guth equation

According to Guth equation,

$$E_c = E_m(1 + 2.5\xi_p + 14.1\xi_p^2)$$

where E_c and E_m are the Young's modulus of composite and matrix, respectively and ξ_p is the mass ratio of the particle. Guth's equation is an expansion of Einstein, to account for the interparticle interactions at higher filler concentrations.

c. Quemeda equation

According to Quemeda equation,

$$E_c = E_m \frac{1}{(1 - 0.5k\xi_p^2)}$$

where E_c and E_m are the Young's modulus of composite and matrix, respectively and ξ_p is the mass ratio of the particle. K is a constant normally 2 for non-interactive fillers. This variable coefficient is introduced to account for the interparticle interactions and difference in particle geometry.

d. Thomas equation

According to Thomas equation,

$$E_c = E_m \{1 + 2.5\xi_p + 10.05\xi_p^2 + 0.00273\exp(16.6\xi_p)\}$$

where E_c and E_m are the Young's modulus of composite and matrix, respectively and ξ_p is the mass ratio of the particle. Thomas equation is an empirical relationship based on the data generated with dispersed spherical particles in polymer matrices.

e. Kerner equation

According to Kerner equation,

$$E_c = E_m \left[1 + \frac{15\xi_p(1-r)}{(1-\xi_p)(8-10r)} \right]$$

where E_c and E_m are the Young's modulus of composite and matrix, respectively ξ_p is the mass ratio of the particle and r is the Poisson's ratio of the matrix. For expansible polymers incorporating rigid spherical particles featuring some adhesion, the Kerner equation can be used to estimate the modulus.

f. Sato and Furukawa equation

Sato and Furukawa have developed an expression for the modulus for the case where the adhesion is termed as the main parameter, the equation is,

$$E_c = E_m \left[\left(1 + \frac{\xi_p^{2/3}}{2 - 2\xi_p^{1/3}} \right) (1 - \psi_j) - \frac{\xi_p^{2/3} \psi_j}{(1 - \xi_p^{1/3}) \xi_p} \right]$$

Where, $\psi = \left(\frac{\xi_p}{3} \right) \frac{1 + \xi_p^{1/3} - \xi_p^{2/3}}{1 - \xi_p^{1/3} + \xi_p^{2/3}}$, E_c and E_m are the Young's modulus of composite and matrix,

respectively ξ_p is the mass ratio of the particle and j is the adhesion parameter, $j=1$ for poor adhesion, $j = 0.5$ for medium adhesion and $j=0$ for perfect adhesion.

4. Results and Discussion

The XRD patterns of polymer composites of PBT obtained for various compositions of filler and matrix are shown in **Fig.1**. The emergence of characteristic diffraction lines and their gradual sharpening increased with filler content and for the last composite PBT40, almost all the characteristic peaks of PBT are present. It is confirmed that the fillers did not react with the polymer [32]. The chemical non reactivity of the filler and the polymer at the processing temperature is another important factor in the preparation process. It is found that the composites showed no extra intensities due to the formation of impurity phases, but only the characteristic peaks of the fillers. This revealed that PBT showed no chemical reaction with polypropylene. Characterization of the composites by XRD allows identification of the crystalline components. The lattice parameters of the constituent phases are almost the same in all composites. The average particle size is estimated from these XRD lines, by Scherrer's equation and no noticeable change in particle size is observed. The results reveal that the particle size is 25.99 nm i.e., less than 100 nm. All the peaks of the composites are identified. No other additional peak is observed apart

from the parent material. This confirms the successful preparation of the two-phase composite material. The humps in the diffraction pattern characterize the amorphous nature of polypropylene. They gradually gave way to discrete lines with the increment in filler content. It is observed that the characteristics peaks with high intensity are found to increase with increasing proportion of the filler.

Fig.2&Fig.3 showed SEM image of PBT polymer composites for various compositions. The SEM photograph revealed maximum dimensions of the particles to be always less than 100nm. This is an experimental proof of the theoretical calculation of particle size by Debye Scherrer equation from XRD data. SEM analysis supported the reinforcement of fillers in the composites. The filler particles are uniformly distributed in all the composites and the particles are almost spherical in shape with irregular boundaries. The results give a true picture of how the fillers interact with polypropylene matrix that effect the overall properties of the composites. The most fascinating property is the uniform dispersion of the fillers in the matrix. The surface view and fracture surface view of PBT-polypropylene composites revealed the dispersion of the particles in the composites (**Fig.2& Fig.3**). The particle dispersion and particle-matrix reinforcement play vital roles for both tensile and elongation properties of the composites. The ceramic particles are dispersed homogeneously with the interspaces filled with polypropylene, and large defects are not observed in the fracture surface view of the composites [33]. The fractured surface of the composites showed a dense microstructure as in **Fig.3(a-d)**. SEM photographs are used to determine the size of the dispersed particle and the particle size distribution.

Fig.4 shows EDX spectrum of PBT. The EDX spectrum of PBT gave the information on the elemental composition of the material. This technique is generally associated with SEM. The percentage of the elemental composition as in **Table.1** agrees with the stoichiometric relations of $PbBaTiO_3$. From the EDX spectrum, the four dominant peak positions at 2.342keV, 4.465keV, 2.307keV, 0.525keV correspond quite well to the energy pattern of the corresponding materials (Pb, Ba, Ti, and O) reported in the EDAX international chart, giving the evidence that Pb and Ba are dominant in PBT samples.

Table 1. Material Content (EDX)

Material	Content (%)
Pb	70.07
Ba	24.53
Ti	3.35
O	2.05

The mechanical properties such as Young’s modulus of two-phase composites made up of particulate filled polymer phase have been studied in great detail by using different equations. It can be seen that in most conventionally filled polymer systems the modulus increases linearly with the filler volume fraction as shown in the **Fig. 5**. The increase of modulus is mainly governed by the particle size of the filler. The explanation is based on the assumption of a special morphology of the polymer matrix around the filler particles. When a thermoplastic is cooled down from the melt a solidification process will take place. During cooling from the processing temperature of the composites (180°C) to room temperature the filler particles are assumed to act as sites where thermal contraction is particularly favored, which should cause the special morphology. If it is assumed that the polymer adjacent to the embedded particles contract in an earlier stage of process because of the difference in thermal conductivity of the polymer (0.1–0.2 W/m/K) and that of ceramics ($\sim 1-40$ W/m/K), a zone with a higher density (high modulus) will be formed around the filler particle. Because of the heat transportation processes, a depletion zone with relatively low density (low modulus) will be created surrounding the high-density zone. It is essentially due to the different thermal expansion of polymer ($50 \times 10^{-6} \text{ K}^{-1}$ to $300 \times 10^{-6} \text{ K}^{-1}$) on one hand and ceramics ($0.5 \times 10^{-6} \text{ K}^{-1}$ to $15 \times 10^{-6} \text{ K}^{-1}$) on the other hand [34]. Fig.6 shows the Theoretical modeling of the tensile modulus of PBT filled polypropylene composites with different adhesion parameters.

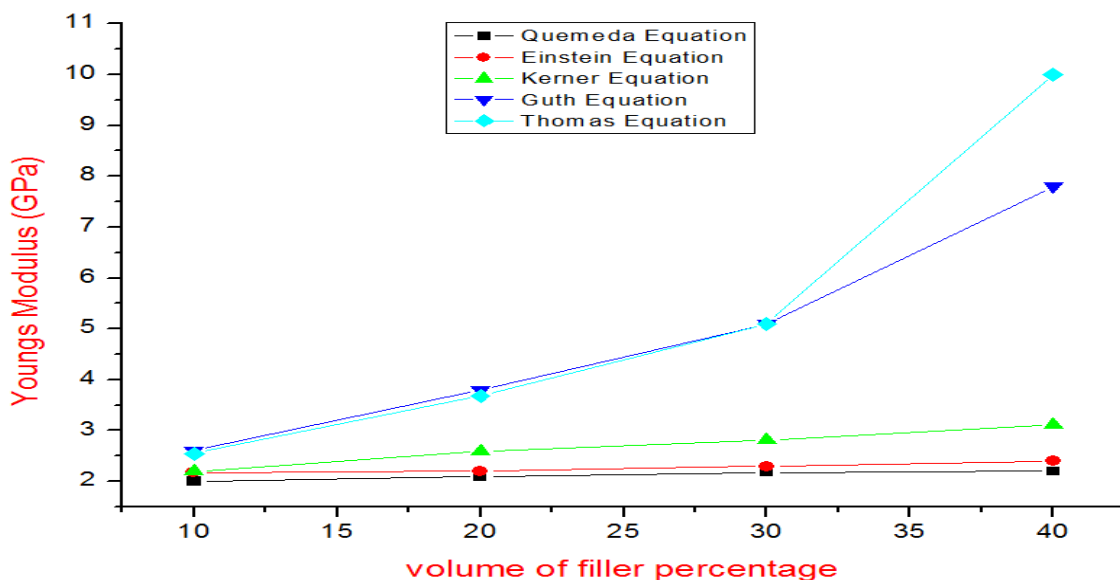


Fig. 5. Theoretical modeling of the tensile modulus of PBT filled polypropylene composites.

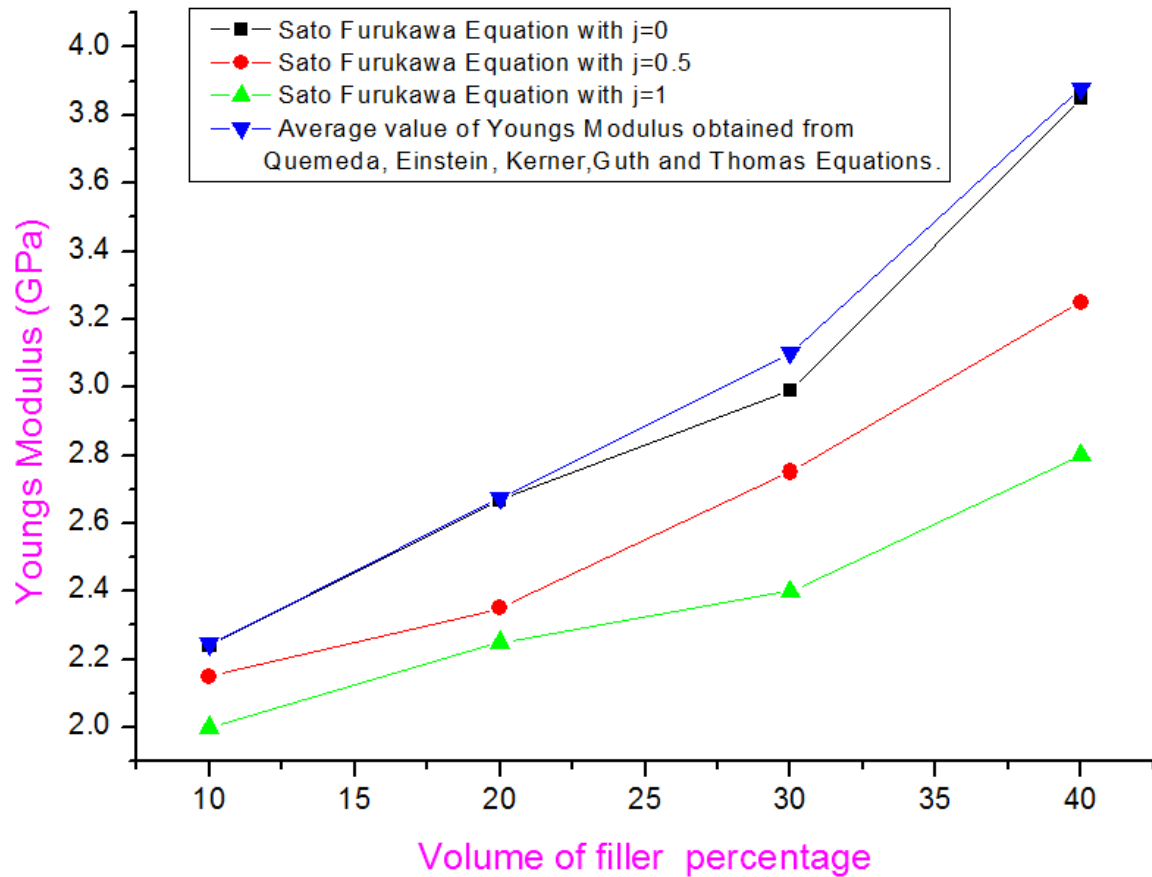


Fig 6. Theoretical modeling of the tensile modulus of PBT filled polypropylene composites with different adhesion parameters.

According to Van Krevelan [35] Young's modulus (E) is proportional to the seventh power of density (ρ). This means that the starting zones, which have a higher density, have a higher Young's modulus, and the depletion zones, which have a lower density, have a lower modulus. The filler particles can act as initiation sites of the solidification process, and for this reason they could be surrounded by an enriched layer of polymer with an increased modulus (high modulus layer), around which a zone of material with a lower modulus is found [36]. The effect of this morphology on the Young's modulus of the filled polymer with respect to the filler particle size will cause a combination of both effects. Two extremes are treated: a polymer filled with very small particle (nano particle), and a polymer filled with very large particles (size $> 10\mu\text{m}$). Of course, an intermediate particle size will cause a combination of both effects. In the case of composite material filled with nanoparticles, the inter particle distance is so small and by the abundance of number of particles there is a huge number of starting points for thermal contraction process, so that a homogeneous matrix material of 'high modulus' polymer is assumed to be created

around the filler particle (**Fig.7 & Fig.8**). For a large filler particle the thickness of high modulus layer is very small compared to the diameter of the filler particle. With Sato and Furukawa relations, Young's modulus can be calculated with an adhesion parameter $j = 1$ for poor adhesion, $j = 0.5$ for medium adhesion, and $j = 0$ for good adhesion (Fig.6). The data for various volume fractions of PBT is found to be less than that with the case of $j = 1$ and the results obtained with adhesion parameter $j=0$ are fully satisfied as in Figure 6. This type of perfect adhesion is due to the formation of the high modulus layer around the PBT particles.

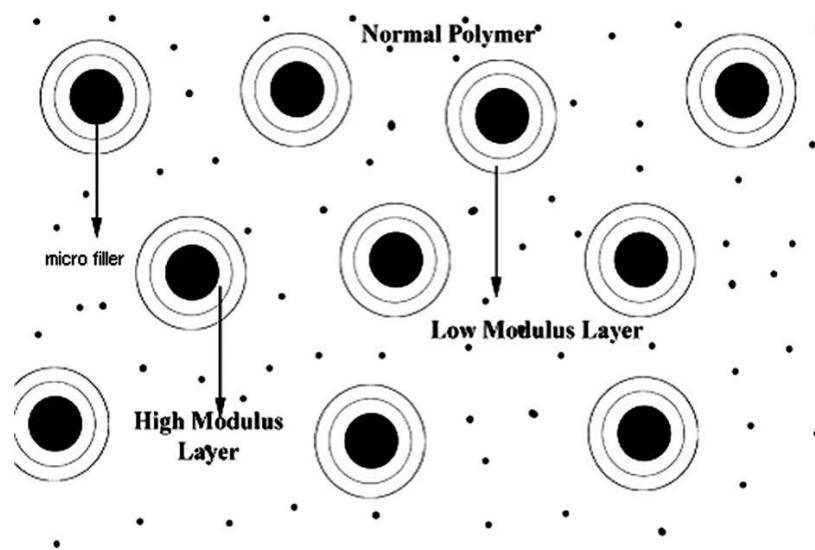


Figure 7. Proposed morphology of the polymer matrix with micro size filler particles.

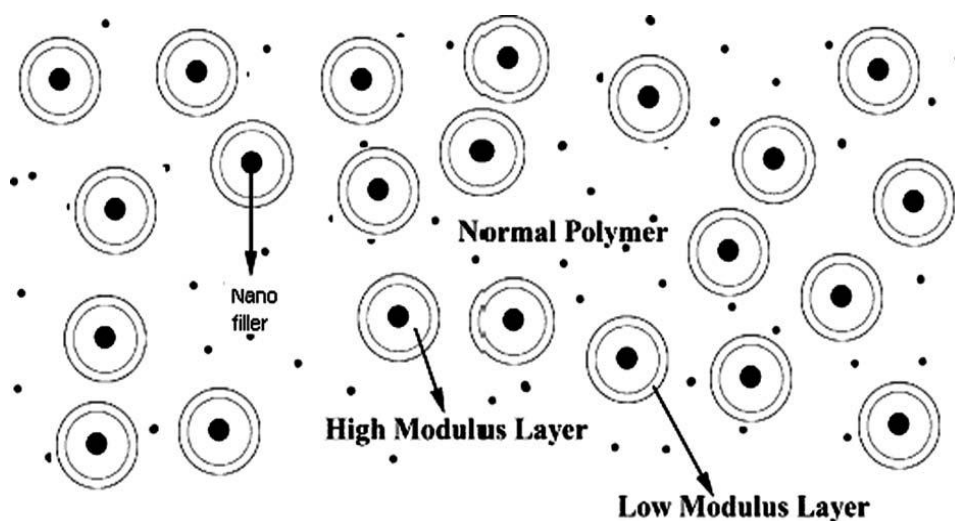


Figure 8. Proposed morphology of the polymer matrix with nanosize filler particles.

From the above discussions it could be argued that the particle size play an important role in Young's modulus value. Generally, the elastic modulus increases with augmenting filler volume fraction, while all other tensile properties such as the ultimate stress and strain at break decreases with increasing filler volume fraction [37]. However, many investigations showed that the effect of solid fillers on the tensile strength of polymers might be positive or negative, depending on such factors as filler size and shape, internal stresses, surface nature, and aspect ratio. In the prepared composites, the interaction between filler and polymer is expected to be physical. The polymer matrix is, however, stiffened by the particulate. The particles restrict the mobility and deformability of the matrix by introducing a mechanical restraint, the degree of which depends on the particulate spacing and the properties of the particle and the matrix. Restriction in polymer molecular diffusion is seen in the presence of solid particles. The most important feature that affects the interfacial adhesion is believed to be the mechanical stresses, chemical interactions, and physico-chemical weak boundary layers.

5. Conclusion

In this work, PBT ceramics are prepared successfully by the conventional solid state reaction technique and polypropylene composites are prepared by the melt mixing technique. The composites are prepared for different compositions and analyzed by XRD, SEM and EDX. The mechanical properties such as Young's modulus of two-phase composites were calculated using different equations in theoretical modeling and plotted graphically.

SEM results revealed a true picture of how the fillers interact with polypropylene matrix that affects the overall properties of the composites. In all composites filler particles are clearly embedded in the polymer matrix. The surface view and fracture surface view of PBT –polypropylene composites revealed the dispersion of the particles in the composites. The EDX analysis indicates that the elements existing in the sample and it agree with the stoichiometric relations of the prepared compound. Theoretical modeling for calculating Young's modulus of the different compositions of composites revealed that the value of Young's modulus increases with the filler volume fraction.

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