

## INFLUENCE OF TiO<sub>2</sub> NANO FILLER ON THE PROPERTIES OF PVA<sub>x</sub>POM<sub>(1-x)</sub> POLYMER COMPOSITES

P. R. RAJKUMAR<sup>a\*</sup>, K. P. SUBHASHCHANDRAN<sup>b</sup>

<sup>a</sup>Research and Development centre, Bharathiyar University, Coimbatore-6410046

<sup>b</sup>Sri Vyasa NSS college, Thirussur, Kerala-680623

Nano filler dispersed conjugated polymer composites have zooming significance on account of their synergistic and hybrid attributes attained from the extensive gamut of modules. Pure and 2.5 mole % TiO<sub>2</sub> nanoparticle dispersed PVA<sub>x</sub>POM<sub>(1-x)</sub> polymer composite films for various x values ( x= 0 to 1 insteps of 0.25) were casted by means of simple solution casting technique ( SSCT). The casted films were characterized by structurally by X-ray diffraction method. Optical behaviour of the pure and TiO<sub>2</sub> dispersed films were tested using UV-Vis absorbance spectroscopy. The dielectric measurements were performed using an impedance analyzer (Agilent 4284 A LCR meter) covering a frequency range from 100 to 1×10<sup>6</sup>Hz.

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### 1. Introduction

Fabrication of polymer based nanocomposites has attracted much attraction because of their sterling characteristics and the variety of applications in the modern technology[1]. The doping of nanoscopic organic or inorganic materials into polymeric matrices represents a strategic route to improve the performance of material characteristics like structural, physical, chemical, optical, electrical, and mechanical properties. The relative nanocomposites belong to novel group of materials generated with nanosized fillers such as the metals, metal oxides, and so on. In the past few years, the polymer doped with metal oxide nanoparticles have been deeply investigated as optional materials for the optical applications, encompassing the planar waveguide devices and micro-optical modules [2-5].

Moreover, the effective properties of the composites are dependent upon the properties of constituents, the volume fraction of components, shape and arrangement of inclusions and interfacial interaction between matrix and inclusion[6]. With the recent development in the nanoscience and nanotechnology fields, the correlation of material properties with filler size has become a focal point of significant interest [7].

Further, the PVA has emerged as an outstanding polymer and a prospective material endowed with a lofty dielectric vigour, an excellent charge storage capability and doping-dependent electrical and optical qualities [6]. The hydroxyl groups existing in its central backbone are accountable for the strong intra- and intermolecular hydrogen bonds, blessing the PVA with various excellent qualities like the superior tensile strength, superb adhesive attributes, abrasion resistance, chemical resistance and gas barrier traits [7]. In the same way, the Poly-oxy-methylene (POM) otherwise called the Acetal is a superlative engineering polymer with elevated Crystallinity, modulus, and resistance to impact and weariness, which is effectively utilized as a weight-saving metal option[8]. In fact, there is a flood of literary works related to the enrichment of the PVA, POM with inorganic nano fillers [9-15].The TiO<sub>2</sub> nano filler has been widely used in a host of applications on account of its robust oxidizing power of the photo-generated holes, chemical

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\* Corresponding author: kumarpraj15@gmail.com

inertness, non-toxicity, insignificant expenditure, elevated refractive index and other beneficial surface traits [16].

Taking the relevant factors into consideration, in the current exploration, an earnest endeavour is made to generate the PVA/POM polymer blends with several mole ratios such as 100/0,75/25,50/50,25/75 and 0/100. Further, the overall impact of  $\text{TiO}_2$  nano particle as fillers in the suggested polymer blends is also deeply delved into. The pure and  $\text{TiO}_2$  dispersed films are casted by solution casting approach, which is cost-conscious and easy. Further the generated nanocrystals are dispersed by ex-situ polymerisation technique. The examination of the casted pure and  $\text{TiO}_2$  dispersed thin film is performed by means of the X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX), UV-Vis. spectroscopy, and the dielectrical analysis in that order.

## 2. Synthesis of $\text{TiO}_2$ nanoparticle

In a classic synthesis process for the preparation of pure  $\text{TiO}_2$  nanocrystals, 0.6 mole urea ( $\text{CO}(\text{NH}_2)_2$ ) is dissolved in 50 ml ethylene glycol against dynamic stirring process for 1 hour at room temperature. Later on, 0.2 mole  $\text{TiCl}_4$  solution is poured in 50 ml ethylene glycol which is subsequently added gradually into the solution mentioned above. The resultant dissolved mixture is placed in a domestic microwave oven. The microwave irradiation is performed till the solvent is fully evaporated. The consequential product achieved in the form of colloidal precipitate is cooled to room temperature naturally and centrifuged many times with doubly distilled water and thereafter with acetone to eliminate the unreacted reactants and organic impurities existing in the colloidal precipitate. The attained powder is annealed at  $600^\circ\text{C}$  to achieve the clean phase of  $\text{TiO}_2$ .

## 3. Casting of pure and $\text{TiO}_2$ dispersed $\text{PVA}_x\text{POM}_{(1-x)}$ films

An easy Solution Casting Technique is effectively employed to cast the pure and  $\text{TiO}_2$  dispersed films. The compositions utilized for the generation of the undispersed  $\text{PVA}_x\text{POM}_{(1-x)}$  films are brilliantly brought out in Table 1. The requisite quantity of the PVA and POM are dissolved in the mixed solvent of the DMSO and water under nonstop stirring at a temperature of  $40^\circ\text{C}$ . The thin film is produced by means of the evaporation of the surplus solvent by pouring the solution in petri dish and drying it in sunlight. 2.5 Wt % of  $\text{TiO}_2$  is disseminated by way of stirring for the creation of the  $\text{TiO}_2$  diffused  $\text{PVA}_x\text{POM}_{(1-x)}$  films. The cut pieces of the generated films are effectively depicted in figure 1. The thicknesses of the films are evaluated at several locations with the assistance of the thickness evaluation unit model such as the US M probe Vis. spectroscopic reflectometer. It is clearly evident from the evaluated values at diverse locations that the film enjoys perfectly homogeneous thickness as illustrated in Table 1.



Fig. 1 Photograph of pure and  $\text{TiO}_2$  nanoparticle dispersed  $\text{PVA}_x\text{POM}_{(1-x)}$  films :From left: TOP Row PVA;  $\text{PVA}_{0.75}\text{POM}_{0.2}$ ;  $\text{PVA}_{0.5}\text{POM}_{0.5}$ ;  $\text{PVA}_{0.25}\text{POM}_{0.75}$ ; POM; Bottom row  $\text{TiO}_2$  dispersed films

Table 1: Amount of precursor used for casting the films and average measured thickness along with the measured values of Refractive index

Name of the sample	Amount of precursor (in g)		Thickness (nm)	Refractive index @ 500nm
	PVA	POM		
PVA	2.630	-	875.0	1.523
PVA <sub>0.75</sub> POM <sub>0.25</sub>	1.973	0.076	853.6	1.508
PVA <sub>0.5</sub> POM <sub>0.5</sub>	1.315	1.515	879.2	1.475
PVA <sub>0.25</sub> POM <sub>0.75</sub>	0.6575	2.272	923.4	1.362
POM	3.03	-	975.2	1.412
PVATi	2.630	-	864.2	1.756
PVA <sub>0.75</sub> POM <sub>0.25</sub> Ti	1.973	0.076	871.4	1.823
PVA <sub>0.5</sub> POM <sub>0.5</sub> Ti	1.315	1.515	883.1	2.112
PVA <sub>0.25</sub> POM <sub>0.75</sub> Ti	0.6575	2.272	942.4	1.785
POM Ti	3.03	-	953.7	1.563

#### 4. Characterizations made

Prior to the dispersion, the as-prepared nano particles of TiO<sub>2</sub> are characterized by EDAX. The casted films are analysed for their structural, optical and electrical properties by the deployment of suitable approaches. The crystalline trend of the films is established by the X-ray diffraction (XRD) with Cu K<sub>α</sub> radiation (PANalytical X-Pert Pro diffractometer,  $\lambda = 1.54056 \text{ \AA}$ ). The optical behaviour of the casted films are accomplished by UV-vis spectral analysis. The dielectric analysis is performed with a specified precision of  $\pm 1\%$  by employing the traditional two-probe method at room temperature for the frequency range 100-1MHz. [17].

#### 5. Results and Discussions

##### 5.1 Analysis of Bare TiO<sub>2</sub> nanoparticle

The X-ray diffraction pattern achieved for the bare TiO<sub>2</sub> nanoparticle is elegantly exhibited in Figure 1(a). The spectra exactly indexed to the tetragonal phase with space group *I4<sub>1</sub>/amd* which is similar to the pure TiO<sub>2</sub> (anatase) phase based on the JCPDS file no. 089-4921. The XRD spectra of bare TiO<sub>2</sub>, have no apparent stages of TiO<sub>2</sub> or impurity or metallic clusters, thereby indicating the excellent quality of the nano-crystalline material.

Moreover, the particle size of the samples is evaluated by means of the Debye –scherrer formula [18]. The estimated value of the particle (10.5nm) underscores the nano regime of the synthesized particles. The chemical composition of the synthesized sample is authenticated by the EDAX evaluation furnished in Figure 1(b).

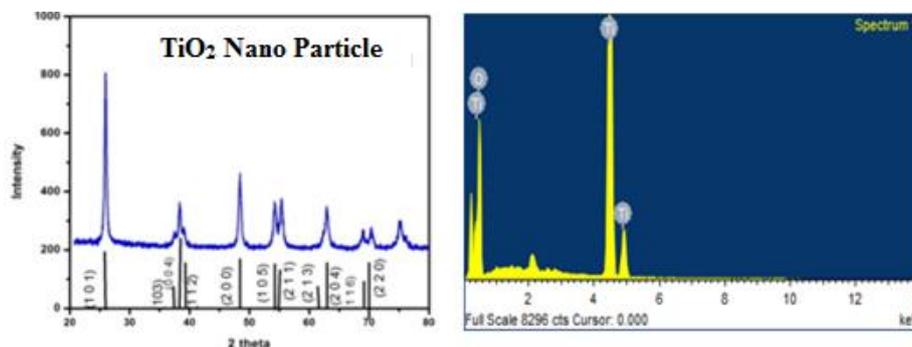


Fig. 2: a) PXRD pattern and b) EDAX spectra of Bare TiO<sub>2</sub> nanoparticles

## 5.2. Analysis of Pure and Nanoparticle dispersed $PVA_xPOM_{(1-x)}$ films

### 5.2.1 XRD analysis

The XRD patterns achieved in the current investigation for the pure and nanoparticle distributed films are elegantly exhibited in figures 2 a and 2 b. The XRD spectra of pure PVA and POM films are in perfect harmony with the reported spectra [19]. Further, the inclusion of the POM generates a small hump near the main peak of the PVA and is reinforced with added concentration of the POM. In view of the fact that POM represents a semi crystalline thermoplast, excessive concentration of the POM ultimately results in the decrease of the crystallinity. In addition the  $TiO_2$  addition in polymer blends, causes the build-up of new peaks which qualitatively match with the diffraction peak of the Bare  $TiO_2$  nanoparticles with negligible shift. The intensity of the peaks is likely to go up or down due to the interaction of the nanoparticles with the polymer chain. The nano fillers are endowed with such an elevated surface area that they are competent to incredibly interact with the polymer molecules, thereby resulting in the cross-linking of the polymeric network. This phenomenon goes a long way in the enrichment of the crystalline trend of the polymer composites.

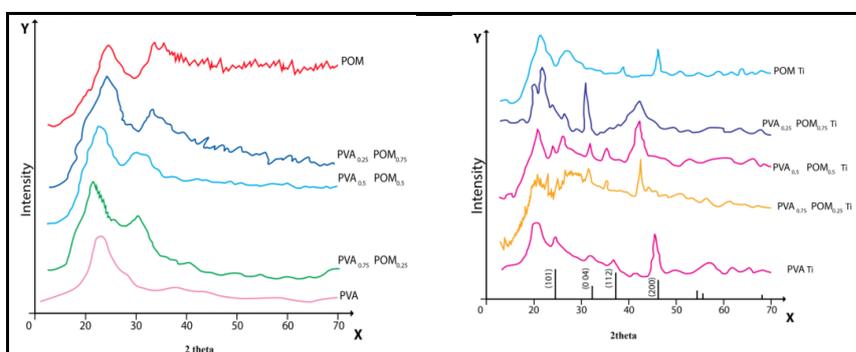


Fig. 3 : PXRD patterns of pure and  $TiO_2$  nanoparticle dispersed  $PVA_xPOM_{(1-x)}$  films

### 5.2.2 UV-Vis Spectral Analysis

A very small amount of guest nanoparticles, when dispersed uniformly in a polymer host drastically changes its electronic structure. In order to elucidate the effect of nano filler in  $PVA_xPOM_{(1-x)}$  polymer composites, UV-Vis absorbance spectra of the casted films were recorded in the range of 200-900nm and depicted in Figure 4. From the spectra it is clear that, Pure POM has a bit of absorption around 215nm, Whereas addition of PVA in POM significantly increases its absorbance also the absorption edge is shifted to higher wavelength except  $PVA_{0.5}POM_{0.5}$ . Moreover  $TiO_2$  presence produces a sharp absorption edge at lower wavelength except in the case of  $PVA_{0.5}POM_{0.5}$ .

The pure and  $TiO_2$  dispersed  $PVA_{0.5}POM_{0.5}$  films exhibit entirely different properties when compared with all other compositions. At this equimolar ratio, the absorption edge is redshifted with nano filler which in turn reduces a bandgap of this polymer composites. Redshift in absorbance of  $PVA_{0.5}POM_{0.5}$  films and blue shift in absorbance of all the other compositions with  $TiO_2$  addition may be explained with the interaction of  $TiO_2$  nano particles with Polymer host. This interaction occurs due to hydrogen bonding mainly between Ti ions and adjacent -OH group of PVA. This interaction increases with increasing concentration of PVA. Also the spectra predicted that the pure and  $TiO_2$  dispersed polymer composites shows excellent transparency in the visible region rather than its end members. It is a particular feature of the inorganic/polymer nanocomposite certainly at low concentration, when the aggregation of the nanoparticles is inhibited [20]. From the UV absorbance results, one can understand that we can tune the bandgap of  $PVA_xPOM_{(1-x)}$  composites by adjusting the molar ratio of PVA/POM and by adjusting the

concentration of Nano fillers. Due to the versatility in fine tuning the absorption windows of the resulting polymers, these casted films find its applications in solar cells to harvest more energy.

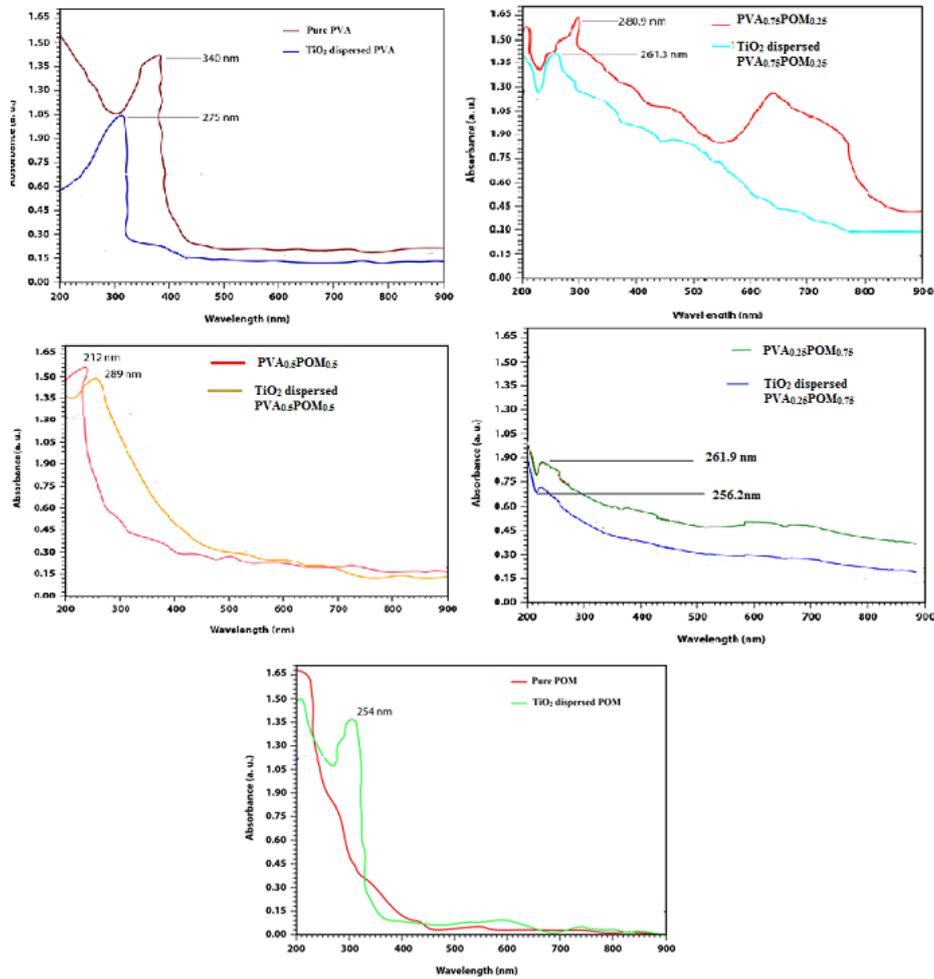


Fig. 4. UV-Vis spectra of pure and  $\text{TiO}_2$  filled  $\text{PVA}_x\text{POM}_{(1-x)}$  composites

### 5.2.3 Dielectric Studies

Dielectric spectroscopy is perceptive to the mixed system and can provide insights into the structures and electrical properties of the materials at molecular and macroscopic levels [21]. The dielectric constant and dissipation (dielectric loss) factor are vital factors required in the design of electronic and other related electrical devices and in addition, as a function of temperature or frequency, they reveal much information on the chemical or physical state of the polymer [22]. Agilent 4284 A LCR meter) covering a frequency range from 20 to  $1 \times 10^6$  Hz was employed to measure the dielectric parameters of the casted film samples which were cut into circular pieces of diameter 13 mm and coated with silver paste and mounted between the electrodes of the parallel plate capacitor. The real part of the dielectric constant was calculated using the relation [23]

$$\varepsilon' = \frac{C}{C_0}$$

where  $C$  and  $C_0$  are the capacitance values with and without sample, respectively;  $C_0 = [(0.08854 \text{ A})/d] \text{ pF}$ , where  $A$  ( $\text{cm}^2$ ) is the area of the electrode and  $d$  (cm) is the thickness of the film sample. The imaginary part of the dielectric constant was calculated using the relation

$$\varepsilon'' = \varepsilon' \tan \delta$$

Real part of dielectric constant decreases with increasing fraction of PVA content.  $\text{TiO}_2$  addition increases the value of  $\epsilon'$  and  $\epsilon''$ . Similar results were reported by Rathod et al for  $\text{TiO}_2$  doped PVA/CN-Li nano composite [24]. Higher value of  $\epsilon'$  at lower frequency is due to space charge polarization and enhancement of  $\epsilon'$  with addition of  $\text{TiO}_2$  in polymer not only due to the electronic and atomic contribution but also due to the space charge contribution. At higher frequency, the dielectric constant and loss become almost frequency independent indicating the rotational motion of the polar molecules of the dielectric is not sufficiently rapid for the attainment of equilibrium with the field. Moreover, increasing the effective dielectric constant must be achieved without an unacceptably large increase in dielectric loss (i.e., energy dissipation). Low dissipation factor confirms the lower size and narrow distribution of  $\text{TiO}_2$  filler. Thus these casted films with high dielectric constant and low loss factors are more useful in embedded capacitor applications.

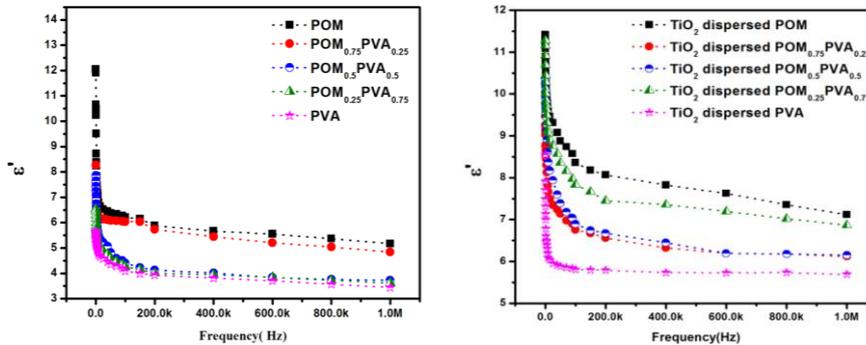


Fig. 5. Variation of real part of dielectric constant with frequency for pure and  $\text{TiO}_2$  dispersed  $\text{PVA}_x\text{POM}_{(1-x)}$  films

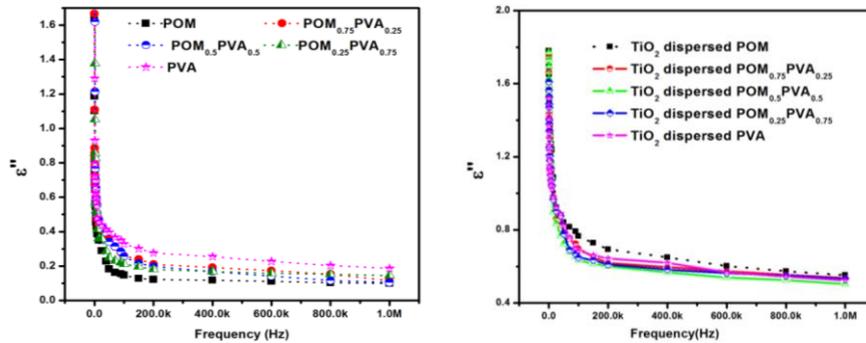


Fig. 6. Variation of imaginary part of dielectric constant with frequency for pure and  $\text{TiO}_2$  dispersed  $\text{PVA}_x\text{POM}_{(1-x)}$  films

## 6. Conclusions

Pure  $\text{PVA}_x\text{POM}_{(1-x)}$  films are generated by means of solution casting method. The homogeneously sized, untainted anatase phase  $\text{TiO}_2$  nano particles are prepared by microwave assisted solvothermal technique and is disseminated under the ex-situ polymerization approach. The impact of nano filler on the qualities of the  $\text{PVA}_x\text{POM}_{(1-x)}$  films are examined with the XRD, UV-Vis, and dielectric measurements.

The X-ray diffraction pattern signify well-configured  $\text{TiO}_2$  dispersed  $\text{PVA}_x\text{POM}_{(1-x)}$  nanocomposites.  $\text{TiO}_2$  addition increases the absorbance of hosted films and enhances the dielectric parameters. Enhancement in dielectric parameters leads to increment in AC conductivity and also these novel materials are more useful in embedded capacitor applications.

## References

- [1] Balazs AC, Emrick T, Russell TP, Science 314 **1107**, ( 2006) .
- [2] R. W. Boyd. J. Korean Physical Society 43, (2003).
- [3] J.Yang, X.Zhang, P.Wang, H.Ming, Y.Wu, J.Xie, Zang , Chinese Optics Letters 3, (2005) .
- [4]P. Rejania , B. Beena, Indian Journal of Advances In Chemical Science 2 (**3**), (2013) .
- [5] Atheel Alwash1 , Ameer A Ameer , Mohammed Abdul Nabi , Ahmed Ahmed , Yip-Foo Win And Emad Yousif, IJRPC4 (**2**), ( 2014).
- [6]Andrea Dorigato, Alessandro Pegoretti, Colloid and Polymer science 290(**4**), (2012).
- [7] S. Matsumura, N. Tomizawa, A. Toki, K. Nishikawa, K. Toshima, 32 (**23**) , (1999).
- [8] K. Mohan Babu And M. Mettilda, Journal Of Applied Chemistry (2014)
- [9] N. B. Rithin Kumar, Vincent Crasta, Rajashekar F. Bhajantri, And B. M. Praveen, Journal of Polymers 7, (2014).
- [10] Kodge Anil Kumar, Kalyane Sangshetty, Lagashetty Arun Kumar , Journal Of Metallurgy And Materials Science 53 (**4**), (2011) .
- [11] Chivukula Srikanth, Chakradhar Sridhar B, B.M.Nagabhushana And R.D.Mathad,, Int. Journal Of Engineering Research And Applications ,4(**10**), (2014).
- [12] W. Shirbeeny, M. Hafez Andwaleed E. Mahmoud,, Polymer Composites 34( **4**), (2013) .
- [13] Anna Llordes, Aaron T. Hammack, Raffaella Buonsanti Ravisubhash Tangirala, Shaul Aloni, Brett A. Helms and Delia J. Milliron, J. Mater. Chem., 21, (2011).
- [14] S. Clara Anthoniamma and, H. Gurumallesh Prabu, Journal of Environmental and Applied Bioresearch, 205(**3**), .
- [15]Afshin Zamani Zakaria1 and Karim Shelesh-Nezhad1, Nanomater Nanotechnol ,4(**17** ),(2014).
- [16] Satyajeet Chaudhari, Tasnim Shaikh and Priyesh Pandey., IJERA,3(**5**),(2013).
- [17] R.Divya, M.Meena , C.K.Mahadevan and C.M.Padma , International Journal of Research in Engineering and Technology (IJERT) , 3(**7**),(2014) .
- [18] V. S. Vinila, Reenu Jacob, Anusha Mony, Harikrishnan G. Nair, Sheelakumari Issac, Sam Rajan, Anitha S. Nair4, Jayakumari Isac, Crystal Structure Theory and Applications, 3,(2014)
- [19] G. Attia and M.F.H. Abd El-kader, Int. J. Electrochem. Sci., 8, (2013).
- [20] A.M.Shehap and Dana S.Akil, Int. J. Nanoelectronics and Materials 9, (2016) .
- [21] N.Ni, K.Zhao, Journal of Colloid and Interface Science 312, (2007).
- [22] F.H.Abd El-kader, W.H.Osman, K.H.Mahmoud, M.A.F.Basha, Physica B: Condensed Matter 403 (**2008**).
- [23] R.Divya, M.Meena, C.K.Mahadevan, and C.M.Padma, IJERA,4(**7**) ,(2014).
- [24] Sunil G. Rathod & R. F. Bhajantri & V. Ravindrachary & T. Sheela & P. K. Pujari & Jagadish Naik & Boja Poojary, J Polym Res, ) 22(**6**), (2015).