

Dielectric Relaxation study of polypropylene and polypropylene nanocomposite with titanium oxide

Dharmvir Singh¹, Sharad Kumar Vaish²

¹Assistant Professor, Deptt. of Physics Nehru College Chhibramau, Kannauj(UP) India. ²Associate Professor, Deptt. of Physics N S C B Govt. Girls P.G. College Aliganj Lucknow(UP)

ABSTRACT

In the present study, the dielectric properties of Polypropylene and its nanocomposite with Titanium Oxide in anatase form (size less than 25nm) have been reported. Nanocomposites are prepared by solution casting method in different concentrations (5%.,10%, 15%). The XRD characteristics have been studied along with its dielectric properties such as capacitance, dielectric loss and dielectric constant at a large range of frequency (from 1Hz to 10^5 Hz). It has been observed that a high increment is found in these properties at low frequency of applied electric field with the increase in concentration of TiO2, but the values rapidly decrease and becomes almost constant towards the high frequency range.

Keywords- Nanocomposite, Nanofiller, XRD, dielectric loss, capacitance and dielectric constant.

1. INTRODUCTION

Polymer nanocomposites have gained much attention by scientific community for developing novel materials for various properties. Due to nanofillers, polymers change by its structural, mechanical, thermal and electrical properties [1-5]. Polymernanocomposites are the multiphase materials with nano sized filler particles dispersed in a polymer. Small loading of nano filler having larger surface area than the micrometer scaled fillers of the same volume fraction, can improve the strong interactions with the polymer matrix [6]. Polymers reinforced with clay, silica, rutile and alumina nanoparticles have been exhibiting excellent dielectric properties [7-8]. PMMA is an amorphous thermoplastic polymer possessing high strength, superior dimensional stability and excellent resistance to wear. Due to various properties of PMMA used in various applications, such as aircraft window, light house lances, and spectator protection in ice hockey rinks and special use of flexible PMMA films have been used as solar modules in solar cell industries. Various researchers [9-12] have worked on the molecular dynamics of PMMA. W Sun et al. [13] studied dynamics of PMMA/MMT (montmorillonite) nanocomposites. They found the effect of nanofiller on the dielectric permittivity. Even a small fraction of nanofillers contains a sufficiently large number of particles generating a considerable surface area to interact with a significant number of polymer chains in the nanocomposite. N Shubha et al [14] studied on solid polymer, when the solid polymer used as a electrolyte is a suitable material to replace the liquid electrolyte which is used in the energy storage devices. Zhang et al [15] studied the influence of surface modified polypropylene. E I Midany et al [16] have worked the effect of mineral filled surface nature on the mechanical properties of mineral filled polypropylene composites. They found that the mechanical properties of two mineral fillers such as silica and talc, differs in their surface properties Talc containing composite showed the better results in terms of Yong's modulus and impact strength, whereas the silica containing composites showed higher yield strength. Semko et al [17] studied the effect of TiO2 nanoparticles on the resistivity and gas sensing performance of poly(vinylchloride) expanded graphite composites. The graphite filler content composite shows a better electric properties in comparison to the talc fillered composites [18-19].

Rahima Nasrin et al (20)studied the behavior of polypropylene/TiO2 composite at different temperatures for various concentration and concluded that as the amount of TiO_2 increases, its surface smoothness decreases. The electrical conductivity increases rapidly with increase in the frequency but dielectric permittivity decreases and small change is found as temperature changes. A wide range of applications of nanocomposite [21] now days became very interesting in research area as given in flow chart





In this present paper we studied that how the dielectric properties (i.e. Capacitance, Dielectric loss, Dielectric constant) vary at same temperature when comes from pure polypropylene to polypropylene/TiO2 nanocomposite concentration increases with applied frequency of electric field.

2. NANOFILLERS

Nanofillers are understood, in essence, to be additives in solid form, which differ from the polymer matrix in terms of their composition and structure. Nanofillers are of the order of 100 nm or less in at least one dimension.

Nanofillers are often added to enhance one or more of the properties of polymers. Inactive fillers or extenders raise the quantity and lower the cost price, while active fillers bring about targeted improvements in certain mechanical or physical properties. Common nanofillers include calcium carbonate, ceramic nanofillers, carbon black, carbon nanotubes (CNTs), carbonnanofibres, cellulose nanowhiskers, nanoclays, gold particles, kaolin, mica, silica, silver nanoparticles, titanium dioxide, etc. Because of their impressive intrinsic mechanical properties, nanoscale dimensions and high aspect-ratio, nanofillers such as CNTs or nanoclays are among the most promising due to the fact that small amounts (less than 5 %) of them can provide the resulting nanocomposite material with significant property improvements.

(3) Experimental Details

(3.1) Materials- The polypropylene in powder form procured from Sigma Aldrich containing high proportion of isotactic configuration with average molecular weight of 12.000amu. The physical properties of polypropylene have been shown in table-1. The nanoparticle TiO2 used in anatase form and procured from Sigma Aldrich. Particle size of TiO2 is less than 25 nm with high purity of 99.7% and molecular weight 79.87gm/mol with melting point $1825^{\circ}C$ and density 3.9gm/ml at $25^{\circ}C$.

Physica lproperties of Polypropylene ^[22]					
Properties	Values	Properties	Values		
Molecular weight	12amu	Heat of combustion	44 kJg ⁻¹		
Melting point	157 ⁰ C	Heat of Fusion	21Jg ⁻¹		
Density	0.9g/ml	Softening Point	40^{0} C		
Specific heat	$1.6 Jg^{-1}$	Tg	40^{0} C		

Table-1

(3.2) Methods- Variation of capacitance has been studied with varying frequency. Similarly dielectric loss and dielectric constant have been investigated at different frequency using HIOKI EE CORPORA IM3590 at NIT Kurukshetra Haryana with varying concentration of TiO2 in polypropylene nanocomposite.

(3.3) **Preparation of PP/TiO2 nanocomposite**- Polypropylene/TiO2 nanocomposites were prepared by using solution casting method. In this method physically mixing the PP and TiO2 at different particle concentration i.e. 5%, 10%, 15% have been done. Table-2 shows the samples prepared at different concentration. All these compositions have been separately dissolved in 2ml of Xylene solvent with stirrer and baked at 200^oC for 20 minutes.

Preparation of PP-TiO2 nanocomposites				
PP(gm)	TiO2 (gm)	Wt%		
1.9	0.1	5%		
1.8	0.2	10%		
1.7	0.3	15%		

Table-2



(3.4) **Preparation of Pallets**- To dielectric study of pure PP and its nanocomposites, pallets were prepared as given dimensions in table-3

Table-3

Polypropylene/TiO2 Nanocomposite pallets					
TiO2%	Pallet diameter (mm)	Pallet Thickness(mm)	Area(mm ²)		
0	6	1.4	28.26		
5	6	3.65	28.26		
10	6	2.98	28.26		
15	6	2.90	28.26		

(4)Results and Discission XRD Analysis-



Figure-(1a)^[23]



Figure-1b

(20)

The powder XRD patterns of prepared composites (TiO₂-PP) is shown in Figure 1. All diffraction peaks are corresponded to single phase pure tetragonal anatase structure with lattice parameters a=b = 3.7794 Å and c = 9.4984 Å (JCPDS card No: 89-4921). A large intensity peak at (101) is mainly due to the agglomeration of crystallites along the c axis. Slight increasing trends were noticed in the lattice parameters after doping of PP from 5% to 15%. Few secondary peaks were detected indicating the PP of the prepared composites. The extra peaks such as peaks namely (111) and (041) is corresponded to PP. This is observed only when doping concentration is increased to 15%. This slight variation proves that PP is perfectly mixed into the TiO₂for doping concentration of PP at 5%. It is worthy to observe that the peaks are slightly narrowed with an increase in the doping concentration. This is due to change in the grain size. The lattice constants a and c, and the average crystallite sizes (d) were calculated using following Eqs. (1) and (2):



In equation (1), h is the diffraction angle, k is incident wavelength (k = 1.54056 Å) and h, k and l are Miller's indices. Figure 1a, 1b and its inset figure shows the change in lattice parameters, a and c, of all the samples with doping concentration. In equation (2), d is the mean crystallite size, K is the shape (0.89), k is the X-ray wavelength of Cu-K α radiation (k = 0.154056 nm), b is the full-width-at-half-maximum (FWHM). The experimental results showed that the anatase has a broader peak width than the rutile. Using Scherrer method the crystalline size of Pp/TiO2 have been calculated and found to be 23 nm for [101] of anatase ... The XRD pattern is showing that (101) of anatase is the highest intense peak, thus it can be assumed that these are the mostly exposed facets of the materials for any catalytic reaction. The decrease in particle size is due to the decrease in diffusion and growth rate as the dopant ions are situated near the boundary of TiO₂nanoparticles and dopants incorporated in the interstitial positions in the TiO₂ lattice. Figure 2 and its inset figures shows the change in lattice parameters, a and c, of all the samples with doping concentration.











(4.2) Dielectric analysis-













From the graphs (figures-3 to figure-5) frequency versus capacitance, dielectric loss and dielectric constant. The variation of capacitance of polypropylene and its nanocomposites with TiO_2 showed that at 400Hz frequency of electric field, capacitance is 18.1PF for pure polypropylene but as concentration increase capacity increases up to 65.8PF and frequency increases capacitance slightly decreases for all concentrations. The dielectric loss of the nanocomposite is increases as concentration of TiO_2 increases at low frequency but this loss becomes approximately constant at higher frequency The dielectric constant of pure polypropylene is low but increases the concentration, is increases This is notable that dielectric constant becomes same in large concentration then 5% (at 10 &15%). Dielectric constant is large at very low frequency and becomes low and constant at very high frequency.

CONCLUSION

The lattice constants (a&c) of polypropylene/TiO₂ nanocomposite increases as concentration of TiO₂ increases due to these reason capacitance of the nanocomposites is large at low frequency and becomes approximately constant at high frequencies. The dielectric loss is large at low frequency but becomes constant at high frequency. Hence polypropylene/TiO₂ nacomposite provide more strength and loss of energy very low and constant. This is also concluded that the concentration of Nano-filler increases the dielectric constant increases. At very low frequency its values is very large, therefore at low frequency and high concentration nanocomposites devices can store more memory.

REFERENCES

- [1]. Z. Liu, M.J, Gilbert, "Structure and properties of talc-filled polypropylene: effect of phosphate coating", J. Appl. Polym. Sci., 59(7), 1087–1098, (1996).
- [2]. Y. J. Lee, M. I. Zloczower, D. L. Feke, "Analysis of titanium tioxide agglomerate dispersion in linear low density polyethylene and resulting properties of compounds", Polym. Eng. Sci., 35(12), 1037–1045, (1995).
- [3]. S. H. Mansour, S. L. Abd-El-Messieh, "Electrical and mechanical properties of some polymericcomposites", J. Appl. Polym. Sci., 83, 1167–1180, (2002).
- [4]. A. S. Luyt, J. A. Molefi, H.Krump, "Thermal, mechanical and electrical properties of copperpowder filled low-density and linear low-density polyethylene composites", Polym. Degrad. Stab, 91,1629–1636, (2006).
- [5]. Y.Zhou, V. Rangari, H. Mahfuz, S.Jeelani, P. K. Mallick, "Experimental study on thermal and mechanical behavior of polypropylene, talc/polypropylene and polypropylene/clay nanocomposites", Mater. Sci. Eng., 402, 109–117, (2005).
- [6]. T. Tanaka, "Dielectric nanocomposites with insulating properties" IEEE Trans. Dielectric Electric Insul. 12, pp.914-928 (2005).
- [7]. J.W. Gilman, T. Kashiwagi, J.D. Lichtenhan. Nanocomposites: a revolutionary new flame retardant approach. SAMPE J., 33, pp. 40–46 (1997).
- [8]. F. Bellucci, D. Fabiani, G.C. Montanari, L. Testa. The processing of nanocomposites. J.K. Nelson (Ed.), Dielectric Polymer Nanocomposites, Springer, New Yor, k p. 31 (2010).
- [9]. R. Bergman, F. Alvarez, A. Alegria, J. Colmenero. The merging of the dielectric alpha- and beta-relaxations in poly(methyl methacrylate). J. Chem. Phys., 109, pp. 7546–7555(1998).
- [10]. M.S. Ardi, W. Dick, J. Kubat. Time-domain dielectric-relaxation of poly(methyl methacrylate) and nitrile rubber. Colloid Polym. Sci., 271, pp. 739–747 (1993).
- [11]. J. Colmenero, A. Alegria. Methyl group dynamics in glassy polymers by neutron scattering: from classical to quantum motions. Adv. Funct. Mol. Polym., vol. 2, pp. 271–294(2001).
- [12]. V.M. Boucher, D. Cangialosi, A. Alegria, J. Colmenero, J. Gonzalez-Irun, L.M. Liz-Marzan. Physical aging in PMMA/silica nanocomposites: enthalpy and dielectric relaxation. J. NonCryst. Solids, 357 pp. 605–609 (2011),.
- [13]. W. Sun, Li Li, E.A. Stefanescu, M.R. Kessler and N. Bowler," dynamics of polymethylmathacrylatemontmorillonite nanocomposites: ADielectric Study", Journal of Non-Crystalline Solids, 410, pp. 43-50 (2015).
- [14]. N. Shubha, R. Prasanth, H.H.Hoon, M. Srinivasan, Plastic crystalline-semi crystalline polymer composite electrolyte based on non-woven poly(vinylidene fluoride-co-hexafluoro propylene) porous membrane for Lithium ion batteries, Electrochim Acta. 125, pp. 362-370 (2014).
- [15]. L. S. Semko, Ya. I., Kruchek, Yu. A., Shevlyakov, P. P.Gorbik, E. I.Oranskaya, "Effect of TiO2nanoparticles on the resistivity and gas-sensing performance of poly(vinyl chloride)-expanded graphite composites" Inorg. Mat. 43,358– 363, (2007).
- [16]. H. Zhang, H. Park, X. Zhu, "Influence of surface- modified TiO2nanoparticles on fracture behavior of injection molded polypropylene", Front. Mater. Sci. 2(1), 9–15, (2008).
- [17]. E. Midany, A. Ayman, Ibrahim, S. Suzan, "The effect of mineral surface nature on the mechanical properties of mineral-filled polypropylene composites", Polym. Bull., 64, 387–399, (2010).



- [18]. S. Afroze, K. Humayun and M. Rahman, "Elastic and electrical properties of graphite and Talc filler reinforced polypropylene (PP) composites" Inter J. Basic Appl. Sci, 12, 13-16. (2012).
- [19]. L. Shengtao, Y. Guilai, N.Fengyan, B.Suna, L. Jianying, T. Zhang "Investigation on the dielectric properties of nanotitanium dioxide-low density polyethylene composites" International Conference on Solid Dielectrics, Potsdam, Germany, July 4-9, (2010).
- [20]. R Nasrin, S Seema, M A Gafur, A H Bhuiyan; American Journal of Materials Synthesis and Processing, 3(4),56-61 (2018)
- [21]. S Gowri, L Almeida, T Amorin, N Carneiro A S Peedro, and M F Esteves; Polymer nanocomposites for Multifunctional Finishing of Textiles- a Review, Textile Research Journal, 80,1290-1306 (2010).
- [22]. K. Sen; Polypropylene Fibres, in "Manufacture Fibre Technology" edited by V B Gupta and V K Kothari, Chapman and Hall, London, 457-479 (1997).
- [23]. M Sarkar, K Dana, S Ghatak, A Banerjee,"Polypropylene-clay composite prepared from Indian bentonite" Bull. Mater. Sci., vol.31, No. 1, pp. 23-28 (2008).