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Synthesis of nano ZrO_2-PPG complex and its spectroscopic and acoustic studies

C.V.Venkatakrishnan [a*], K.Venkatramanan [a]
[a] *Department of physics, SCSVMV university, Enathur, Kanchipuram*
** Corresponding Author: Email: cvvkrishnan@gmail.com*

Abstract:

Nanoceramic material-polymer complexes are a very interesting field of study as they are important as good dielectric materials, conducting polymers, sensors etc. Many applications are also in tribology. ZrO_2 nanoparticles prepared by reactive thermal plasma synthesis were dispersed in PPG 1000 polymer matrix by sonication. Size analysis and spectroscopic studies were done by XRD, SEM, EDX, FTIR and UV-VIS techniques. Ultrasonic parameters were calculated and significant variations in free length, free volume, acoustic impedance and internal pressure confirm the dispersion of nano ZrO_2 in PPG polymer matrix.

Keywords:

Nano ZrO_2, PPG 1000, XRD, SEM, EDX, Acoustic Parameters

Introduction:

Zirconia ZrO_2 is used in many ceramic composites, polymer composites, bio-composites apart from being used in pure form as nano sized powder. With the advantages in nanopowder form having large specific surface area [1] it has many oxygen vacancies on its surface [2]. It has high thermal stability [3] and comparatively low thermal conductivity [4] because of which it is used as thin film coating on tiles [5] and for high temperature applications [6]. It is unique as it exhibits both weak acidic and alkaline properties [7]. As it has good biocompatibility [8] it is used in dentistry. Having good oxygen sensing capability and oxygen conductivity and very low electronic conductivity, it is used in fuel cells [9]. It is used in microwave communication devices as resonator material [10]. To reduce wear and tear of moving parts of machines nano zirconia coating is popular [11]. Zirconia containing polymer pigments are used in paint manufacture [12]. Because of its high refractive index [13] it is useful from near UV to mid IR region where its absorbance is very low [14]. With these advantages it is necessary to stabilize the nano size of ZrO_2 nanoparticles. The polymer composites of it are hence of great utility. Many polymer composites of nano ZrO_2 have been synthesized [15]. Polypropylene glycol (PPG) of various molecular weights are very good for thermosetting of plastics, heat transfer [16], cosmetics [17], pharmaceuticals and electronics [18]. Dispersing nano ZrO_2 in PPG(low mol.wt) to form PPG-ZrO_2 membrane may support polymer electrolyte membrane fuel cell (PEMFC) [19]. Hence, dispersing ZrO_2 in PPG polymer will give advantages of both materials. It is also possible to include additional functionalities or enhance certain properties. Hence, in this work we have dispersed nano ZrO_2 in PPG1000 polymer matrix. Size and morphology of nano ZrO_2 was studied by XRD, SEM and EDX. ZrO_2 nanopowder was dispersed in PPG1000 by sonication. The dispersed ZrO_2-PPG complex was studied by acoustic studies and UV-VIS and FTIR spectroscopy.

Materials and Methods:

Synthesis of nano ZrO_2-PPG1000 complex:

PPG1000 analytical grade was obtained from Alpha Aesar and ZrO_2 nanopowder synthesized by reactive thermal plasma synthesis [20] was used for synthesis of nano material-polymer composite. 10 mg of ZrO_2 nanopowder was mixed with 1g PPG and the resulting mixture was dispersed in 100ml toluene. This solution was sonicated for 20 min and magnetically stirred for 4hrs at 30^{o}c. Viscosity studies were carried out using Brookfield viscometer at a speed of 75rpm. Acoustic studies were done on Digital ultrasonic velocity meter, Ultrasonic Instruments, at ultrasonic frequency of 2MHz. FTIR studies were performed on FTIR-ALPHA T BRUKER (400-4000 cm^{-1}) at SCSVMV. KBr pellet of ZrO_2 nanopowder was used for FTIR. PPG1000 and nano ZrO_2-PPG1000 complex were studied by Attenuated total Reflection (ATR) FTIR. UV-VIS absorption spectroscopy was performed on Specord 200/Plus Analytic Jena UV/VIS Spectrometer, at SCSVMV. Powder XRD, SEM and EDX studies were done at SAIF, IITM.

Results and Discussions:

Powder XRD: X-ray diffraction pattern of ZrO_2 nanoparticle is shown in Fig.1. Table.1. shows the prominent peaks enlisted. Typical peaks of ZrO_2 and (h k l) index observed in the powder XRD pattern are enlisted in Table.1 [21]. This confirms the tetragonal phase of the ZrO_2 nanoparticles (compare JCPDF 37.1484) [22].

Fig.1. XRD Pattern of ZrO_2 nano particle

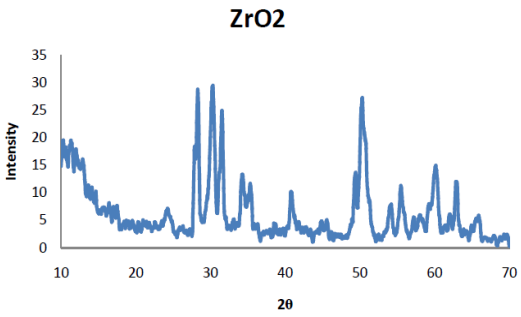


Table.1. XRD Pattern of ZrO_2 nano particle

2θ	(h k l)
30.2^o	101
34.5^o	110
50.3^o	200
60.0^o	211

SEM and EDX: The SEM micrography of ZrO_2 nano particle is shown in Fig.2. The average size of the nanoparticles was found to be 26.7nm. EDX clearly shows ZrO_2 composition as per stoichiometric ratio of the two elements.

Fig.2. SEM micrograph of ZrO_2 nano particle

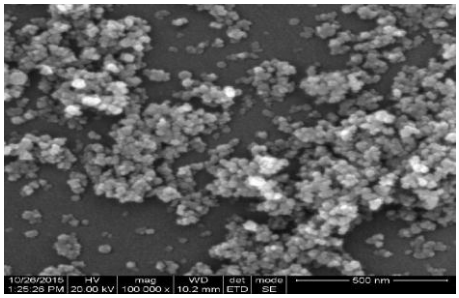


Fig.3. EDX analysis of ZrO_2 nano particle

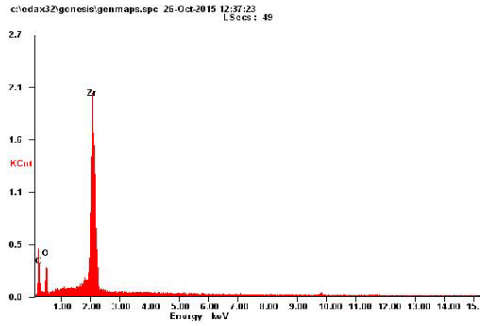


Table.2. Elemental Analysis by EDX

O K	**14.44**	**18.35**
Zr L	**42.97**	**9.57**
Matrix	**Correction**	**ZAF**

FTIR Spectrum: FTIR Spectrum of ZrO_2 shown in Fig.4 shows the signature of 744.86 cm^{-1} assigned to Zr-O-Zr asymmetric stretching, 537.22 cm^{-1} assigned to Zr-O stretching as at 404.84 cm^{-1} also [23]. The band due to non-bridging OH groups in zirconia is observed at 1383cm^{-1} in ZrO_2 and at 1371 cm^{-1} in the nano ZrO_2-PPG complex. Fig.5 shows the FTIR spectrum of PPG1000 with clear stretching vibrations of PPG identified at 2917.73 cm^{-1} and 2867.46 cm^{-1} due to C-H stretching mode and weak peaks around 3500 cm^{-1} due to –OH stretching mode.

Fig.4. FTIR Spectrum of ZrO_2 nanoparticle

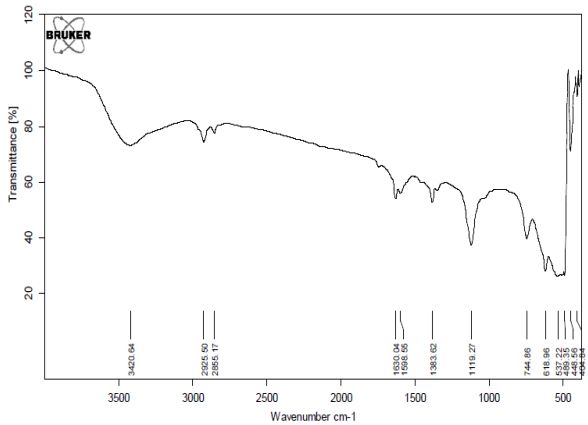


Fig.5. FTIR Spectrum of PPG100

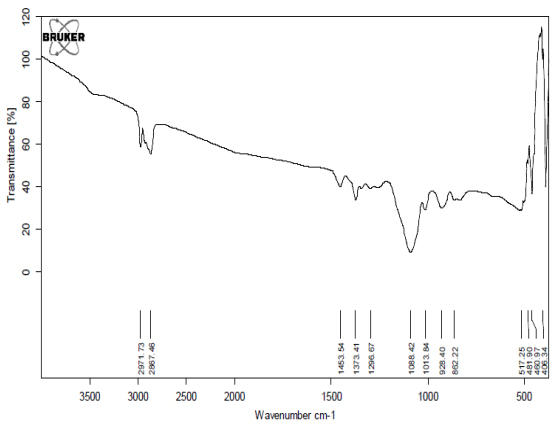
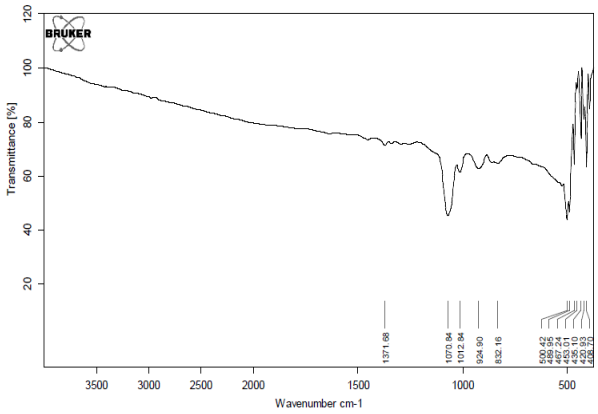


Fig.6. FTIR Spectrum of nanoZrO_2-PPG complex



UV-VIS Spectrum: The UV-VIS absorption spectrum of PPG and ZrO_2-PPG complex are shown in Fig.7 and Fig.8. It is evident from the spectra that both PPG and ZrO_2-PPG complex have very low absorbance in the 300-800nm region indicating their high transparency in this region of the electromagnetic spectrum. Also, the comparison shows that there is no significant change in the absorbance in the UV region.

Fig.7. UV-VIS Absorption Spectrum of PPG1000

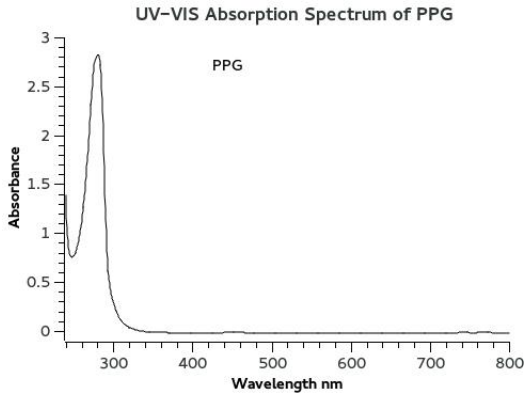
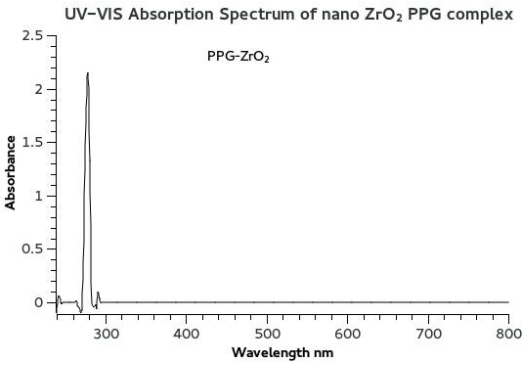


Fig.8. UV-VIS Absorption Spectrum of ZrO_2-PPG complex



Acoustic Parameters: Acoustic parameters calculated are listed in Table.4. A decrease in adiabatic compressibility (0.12%) is indicative of adhesive force of attraction between PPG and ZrO_2 which brings the two molecules closer that makes the nanopolymer matrix stable and confirms steric surface adhesion. Decrease in free length (0.34%) and free volume (3.2%) together imply penetration of nano ZrO_2 into the polymer matrix; further that PPG sufficiently isolates the nanoparticles preventing agglomeration which is necessary and conducive to stabilization of the ZrO_2 nanoparticle. Increase in relaxation time (2.26%) signifies that apart from zirconia being colloidally dispersed in the polymer matrix the acoustic wave disturbance persisits for hundreds of femtoseconds in the matrix. Increase in ultrasonic velocity (0.14%), increase in molarsound velocity (0.23%) and decrease in acoustic impedance (3.99%) together indicate that nanosized zirconia has sufficiently dispersed in the PPG matrix volume wise homogenously. Because the nanoparticles have greater surface area, when dispersed in polymer matrix it results in an increase in Gibbs free energy. Here also it is observed that the Gibbs free energy has increased (0.91%). The relative association of nano ZrO_2 particles on PPG matrix is 0.998 which indicates strong association.

Table.4. Acoustic parameters

Density		PPG1000: 859.876 (Kg/m^3)		nanoZrO_2-PPG complex: 858.521 (Kg/m^3)	
Relative Association		0.99796			
S.No	**Parameter**	**PPG1000**	**nanoZrO_2-PPG complex**	**Nature of Change**	**Percentage change**
1.	Viscosity	0.84 (cP)	0.86 (cP)	Increase	2.4
2.	Ultrasonic Velocity	1286.75 (ms^{-1})	1288.54 (ms^{-1})	Increase	0.14
3.	Adiabatic Compressibility	$7.0239x10^{-10}$ ($Kg^{-1}ms^{-2}$)	$7.0154x10^{-10}$ ($Kg^{-1}ms^{-2}$)	Decrease	0.121
4.	Free Length	0.5258 (Å)	0.5255 (Å)	Decrease	0.34
5.	Free Volume	$1.9237x10^{-7}$ (m^3mol^{-1})	$1.8610x10^{-7}$ (m^3mol^{-1})	Decrease	3.2
6.	Internal Pressure	$3.8408x10^8$ (Pa)	$3.8801 x10^8$ (Pa)	Increase	1.05
7.	Relaxation Time	$7.8667x10^{-13}$ (s)	$8.0443 x10^{-13}$ (s)	Increase	2.26
8.	Acoustic Impedance	$1.1065x10^6$ ($Nm^{-2}s$)	$1.0624 x10^6$ ($Nm^{-2}s$)	Decrease	3.99
9.	Molar Sound Velocity	$3.8842x10^{-3}$	$3.8932 x10^{-3}$	Increase	0.23
10.	Gibbs Free Energy	$-6.7057x10^{-21}$ (KJ mol^{-1})	$-6.767 x10^{-21}$ (KJ mol^{-1})	Increase	0.91

Conclusion: XRD, SEM micrograph and EDX analysis confirm the nanocrystalline structure of ZrO_2 of average size 26.7nm of tetragonal structure well formed as per stoichiometric ratio. FTIR studies confirm the formation of PPG-nanoZrO_2**,** nano material-polymer complex and further acoustic studies estimating the acoustic parameters reaffirm successful formation of nanoZrO_2-PPG complex. The optical characteristics of the ZrO_2 nanoparticles are not modified by the polymer matrix on dispersion as is evident from the UV-VIS absorption studies. Thus PPG1000 is a good dispersant matrix for the stabilization of ZrO_2 nanoparticles that preserves the optical functional properties of zirconia nanoparticles.

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