Nano mechanical, Optical, and Microstructural analysis of PVA/NaCl/Cr_2O_3 Nano composites

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ABSTRACT

The metal oxide nano particles as fillers in the polymer matrix have exhibited remarkable changes in the physio-chemical properties of the polymer nano composites. The elastic modulus and hardness of the prepared polymer nano composites using solvent cast method were investigated using nano indentation. The different Raman modes have been studied for the prepared polymer nano composites. The optical absorption and band gap is studied by the diffused reflectance spectroscopy. The micro structural characterization has been performed using X-ray diffraction by whole powder pattern fitting method. The results indicated that nano mechanical properties like the elastic modulus and hardness of the prepared polymer nano composites were found to decrease compared to pristine PVA. The band gap of Cr_2O_3 nano particles estimated from the DR spectra was found to be 2.75 eV and 3.34 eV which was calculated using Kubelka - Munk function. The whole powder pattern fitting method was employed to determine micro structural parameters. This study implies the interfacial interactions between the nano particle and the PVA matrix which lead to the observed variation in the mechanical and optical properties.

Keywords: Micro structure, Nano composites, Nano indentation, Diffused Reflectance.

1. Introduction

Nanotech innovations are pioneered by nano materials by customizing the structure of materials at the nano scale. The unique functional materials with exclusively advanced properties could be engineered by curtailing the size and by ingraining the nano materials in a variety of pristine bulk materials. The intrinsic physical, optical, electrical and thermal properties for an accustomed material are modified [1-4] due to size, shape and composition of the nano materials.

Nano composites comprising of metal oxide nanoparticles distributed in the host polymer matrix present standalone properties, which essentially depend on the size and distribution of the metal oxide nano particles, but also on the pristine polymer nature and structure. Solvent casting method is versatile tool for the production of thin films. The advantages of this method is mainly uniform thickness distribution, drying without applying further mechanical or thermal stress, highest optical purity, excellent flatness[5]. PVA with its salient features of water solubility, biocompatibility, and non-toxicity makes an excellent host material. At the same time nanoparticles dispersed in PVA have been synthesized and studied for their excellent properties [6-7]. In the wide range of metal oxide nanoparticles synthesized using solution combustion method [8], which is economical, has short reaction time and offers chemical homogeneity; chromium oxide nanoparticles are outstanding optical material used as pigments, solar absorbers and colorant [9]. Nonetheless, there are constrained reports on chromium oxide nanoparticles as fillers in the PVA matrix and their microstructural characterization in the literature.

Conventionally, derived properties of the polymer nano composites are attributed to the inorganic-organic interfacial interactions between host polymer and metal oxide nanoparticles [10]. Henceforth the microstructural characterization of the prepared PVA/NaCl/Cr_2O_3 nano composites using X-ray diffraction is vital for understanding the emerging structure and properties of nano composites.

In this study, we have depicted the microstructure of PVA/NaCl/Cr_2O_3 nano composites using whole pattern fitting technique. The optical properties were investigated using UV-Vis Diffused Reflectance spectroscopy and Raman spectroscopy. The Nano indentation was used to measure the elastic modulus and the hardness of the prepared nano composites. The changes in microstructure have been correlated with optical and mechanical properties of the nano composites

"2. Experimental details"

2.1 *Materials*

PVA was procured from Fischer Scientific India and chromium nitrate from NICE chemicals, Kerala, India. All reagents and chemicals were used without purification as they were of analytical grade.

2.2 Synthesis of Cr_2O_3 nanoparticles and nano composite films

Employing chromium nitrate and oxalyl dihydrazide as precursors and utilizing solution combustion method, chromium oxide nanoparticles were synthesized. In an essential synthesis procedure 5g of chromium nitrate and 2.21g of oxalyl dihydrazide were dissolved in 25 ml of double distilled water in a petri dish. Furthermore, the reaction mixture was stirred well and placed in muffle furnace maintained at 300 ± 10^0C. The polymer nano composites of different weight percentages(2,4,6 and 8 wt%) were prepared by solution casting method[11] using sodium chloride salt as the spacer to prevent chromium oxide nanoparticles from aggregating.

2.3 Characterization methods

The Structural characterization of the synthesized nanoparticles and polymer nano composites using XRD, FTIR and SEM were reported earlier [11]. TEM measurements to determine particle size were done using Transmission Electron Microscope of PHILIPS (CM200S). The mechanical properties of the polymer nano composites were evaluated using Agilent made Nano indenter (Model G200). The hardness and elastic modulus values were calculated using Oliver Pharr method [12].The Raman spectrum was recorded with Peak Seeker Pro Raman system with in built 785nm wave length laser. The DRS measurement was performed using UV-Vis Spectrophotometer (Schimadzu 2600) over a wavelength range of 200 -800 nm at room temperature with a speed of 5nms^{-1}using $BaSo_4$ powder as the reference. Line profile analysis of X-ray diffraction data was performed to evaluate the microstructural parameters [11].

3. Results and Discussion

3.1 *Nano composite formation*

The figure 1 shows the EDS of the nano composite. The formation of nano composites is confirmed by the presence of Chromium (Cr) in the EDS spectrum

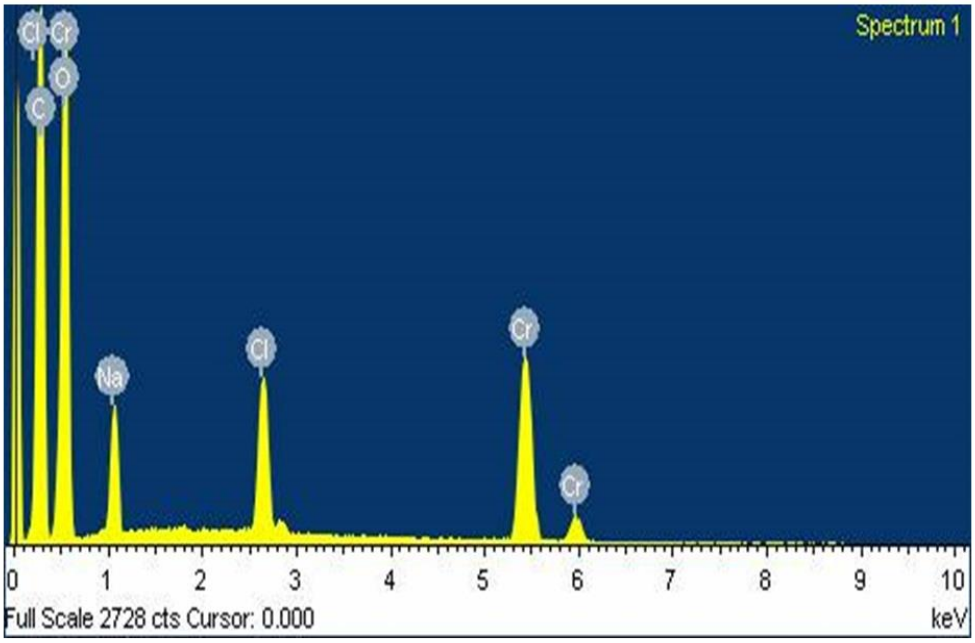

Fig 1. Elemental analysis using EDS spectra

3.2 *Morphological Studies*

The TEM images of the synthesized Cr_2O_3nanoparticles as depicted in Fig. 2,which illustrates that the particles formed are non-spherical with an average size of 25-45nm. The corresponding SAED pattern (figure2, inset) of the Cr_2O_3 nanoparticles demonstrate the poly crystallinity of the nanoparticles**.**

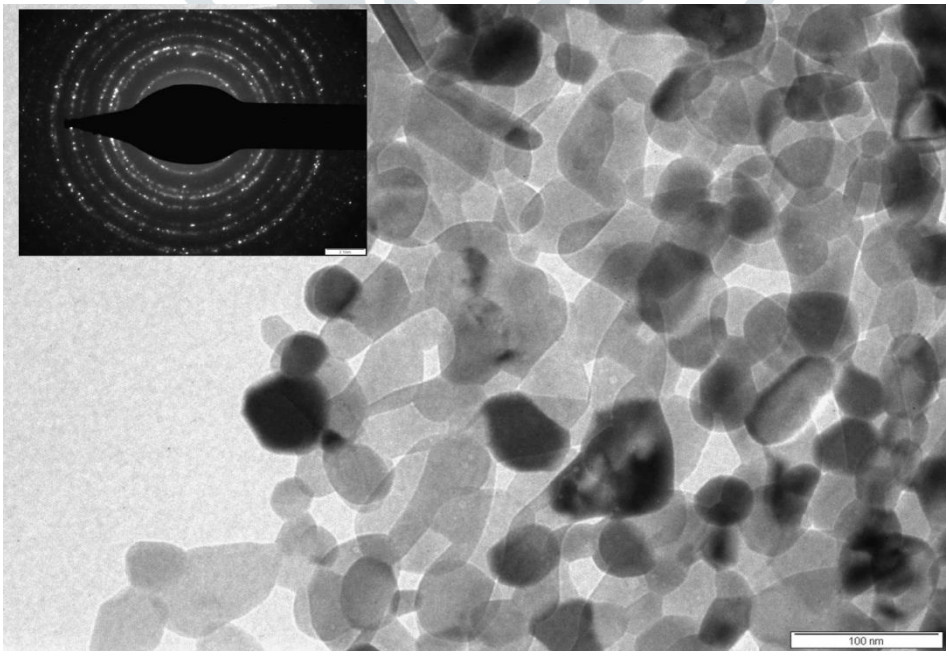

Fig.2. TEM image of the Cr_2O_3 nanoparticles with the inset SAED pattern

3.3Nanoindentation

The load displacement curves were investigated with the evaluation of elastic modulus E and hardness H from unloading curves using Oliver –Pharr method [12]by Nano indentation technique. The load displacement curves of pristine PVA and PVA/NaCl/ Cr_2O_3 nano composites are shown in the figure 3a. The analysis of loading and unloading curves indicate no fracture and increase in penetration depth at peak load with addition of nanoparticles which may be correlated to decrease in hardness. We observe significant differences in the load displacement curves. First, the maximum load drops to about 50% for the polymer nano composites when compared with pristine PVA .Second, the polymer nano composites withstand the load for larger indentation depth compared to host PVA matrix depicting more ductility of the polymer nano composites. Lastly the unloading curve of the polymer nano composites with different weight percentages does not show a trend similar to Pristine PVA unloading curve. On the other hand the maximum load is least for 6 wt% of polymer nano composites which is augmented by elastic modulus and hardness measurements as seen in figure3b and 3c.

The Fig. 3b and 3c, demonstrate the nonlinear variation of elastic modulus and hardness [13-15] as a function nanoparticle concentration. The elastic modulus and hardness values expressed in Fig. 3b and 3c, from Nano indentation in general way are the average values of 5 indents and error bars typifies the standard deviation of the mean values. It is evident from these plots that the elastic modulus of polymer nano composites decreases to 1.5GPa for 2 wt% of nanoparticle concentration compared to pristine PVA for which E_r values are 2.7GPa and 1.3GPa for 4 wt% of nanoparticle concentration and 0.8 GPa for 6 wt% of the nanoparticle concentration which is the lowest and again elastic modulus increases to 1.29 GPa for 8 wt% of the nanoparticle concentration. Similarly, there is a sharp drop in the hardness values of the polymer nano composites compared to the pristine PVA, the hardness value for pristine PVA is 0.12 GPa ,whereas the hardness value for 2wt%,4 wt% and 6 wt% is 0.03,0.03 and 0.029 GPa respectively. After 6 wt% of the nanoparticle loading the hardness value increases to 0.05 GPa for 8 wt% of the nanoparticle concentration.

Intriguing fact is that both the elastic modulus and hardness values decrease upto 6 wt% and above which there is an increase in the corresponding values but lower than the pristine PVA ,implying the interfacial

interactions between the nanoparticle and the host polymer matrix [16] for the observed variation in the mechanical properties.

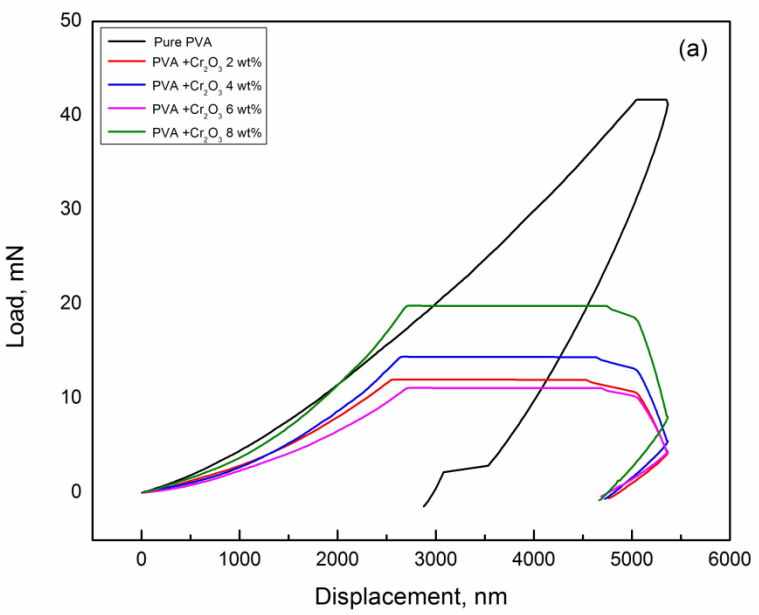

Fig. 3a. Load Displacement curves for Pure PVA and PVA / NaCl/Cr_2O_3 nano composites

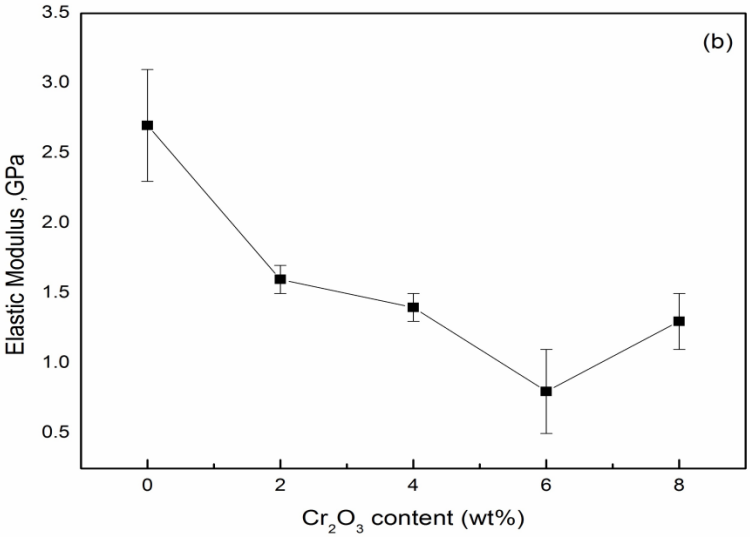

Fig. 3b. Variation of Elastic Modulus as a function nanoparticle concentration

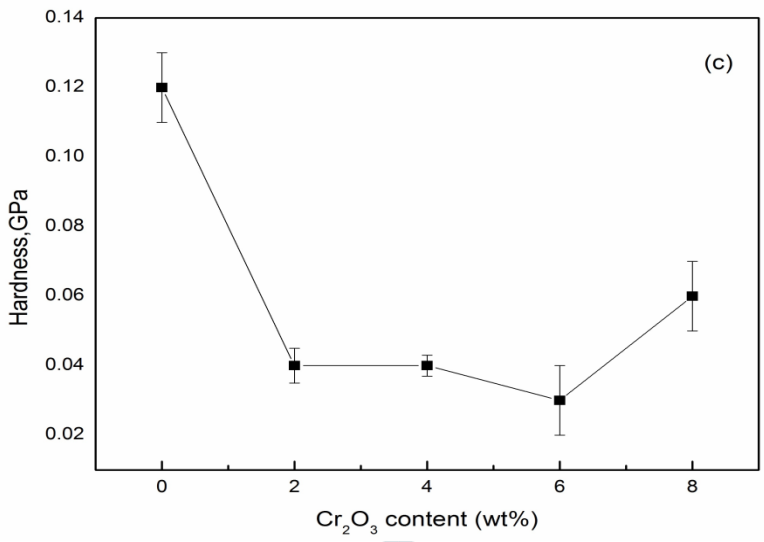

Fig. 3c. Variation of Hardness as a function of nanoparticle concentration

3.4 *Raman Characterization*

The Raman spectra of synthesized nanoparticles and polymer nano composites in the range of 300 cm^{-1} to 700 $cm^{-1}$are illustrated in the figure 4 .The figure 4 b shows the modes of vibration observed at 324cm^{-1},349cm^{-1},621cm^{-1} and 673cm^{-1} which corresponds to E_g modes and the one which observed at 526cm^{-1} and 553cm^{-1} corresponds to A_{1g} mode as reported in the literature[17,18].It is apparent from the Raman spectrum of polymer nano composites that the peaks at 621 cm-1 and 673cm-1 of Cr_2O_3 nanoparticles are red shifted which may be due to internal stress [19]

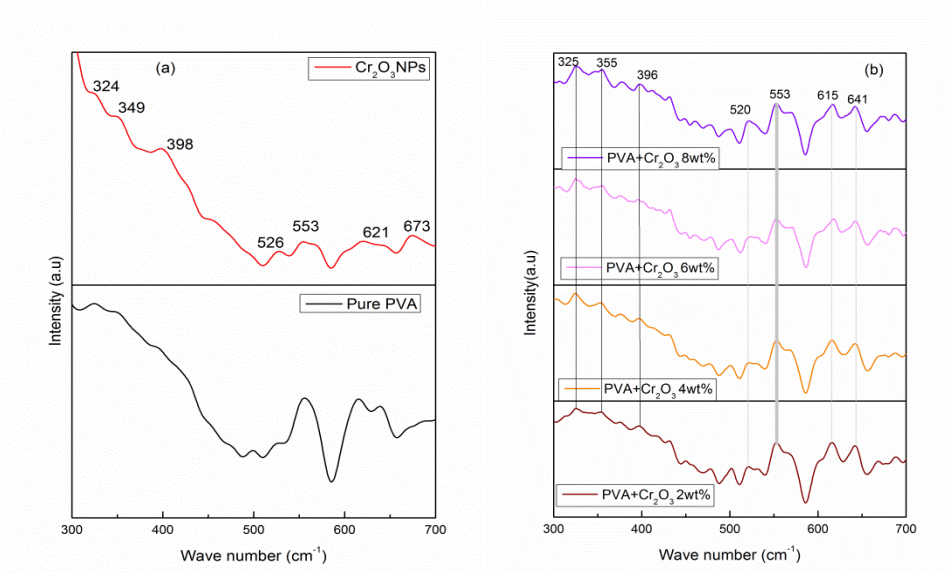

Fig .4.Raman Spectrum a) Pure PVA and Cr_2O_3 nanoparticles b) Polymer nano composites

3.5 Diffuse fuse Reflectance Measurement

The DR spectra were recorded in the wavelength range 200-800 nm using $BaSo_4$ powder as reference. It can be seen from the figure 5(a) that a sharp band is present at 250 nm for pure PVA which is also present in the nano composites, but absent in the Cr_2O_3 nanoparticles. On the other hand it can be observed from the figure 5(a) that a strong reflectance response between 400 -550 nm demonstrating potent absorption in the visible region. There are two maxima at 407 nm and 539 nm.

The band gap was determined using Kubelka–Munk function represented in equation (3)

$$F(R_\infty)=\frac{(1-R_\infty)^2}{2R_\infty}=\frac{K(\lambda)}{S(\lambda)}\propto \alpha=(h\gamma-E_g)^2/h\gamma \qquad (3)$$

The optical band gap energy can be obtained from the graphical plot between the square of the Kubelka–Munk function $F(R)^2$ and energy [20,21] as shown in figure 6. To attain the optical band gap, the linear part of $F(R)^2$ curve was deduced and converged to the energy axis.

The band gap of Cr_2O_3 nanoparticles estimated from the DR spectra was found to be 2.75 eV and 3.34 eV. The two absorption maxima [21] and two values of band gap may be attributed to the reduction of Cr^{6+} states to Cr^{3+} states [22-24]also it was observed from the diffused reflectance spectra that the band gap did not vary when the Cr_2O_3nanoparticles were blended in the Polymer matrix.

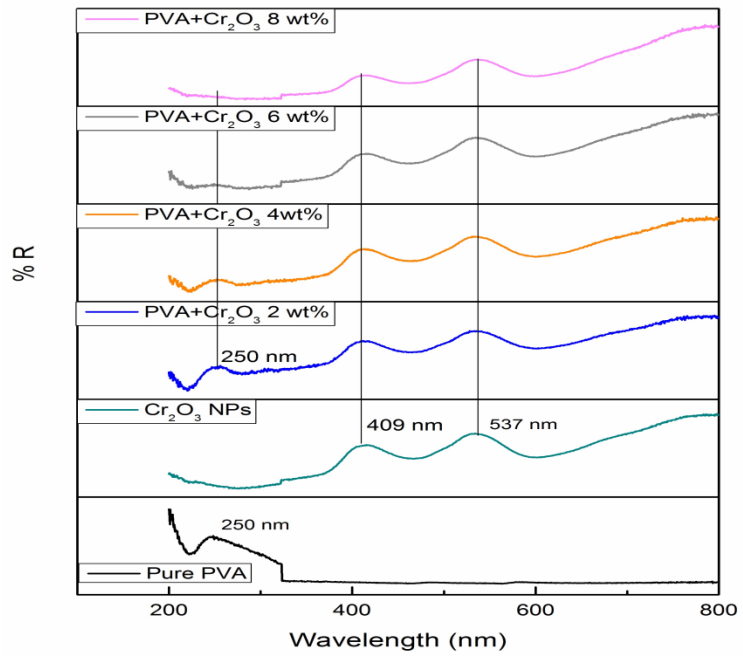

Fig .5.UV-Vis Diffuse Reflectance Spectra of Pure PVA and PVA /NaCl/ Cr_2O_3 nano composites

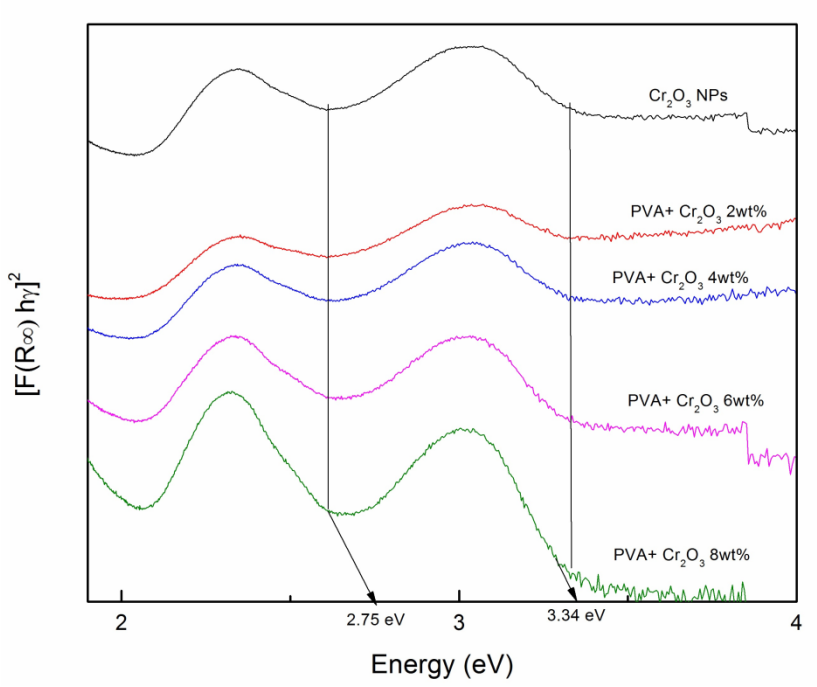

Fig .6.Kubelka-Munk transformed reflectance spectra of pure PVA and PVA /NaCl/ Cr_2O_3 nano composites

3.6 *Microstructure analysis*

The experimental and simulated x-ray profiles with different weight percentage composition of PVA/NaCl/Cr_2O_3 nano composites using whole powder pattern technique is shown in figure 7. There is conformity between experimental and simulated X-ray intensity profiles as the standard deviation is about

5%.The microstructural parameters evaluated are shown in Table 1for pristine PVA and PVA/NaCl/Cr_2O_3 nano composites using exponential column length distribution. From Table 1 we observe that the average crystallite area increases for 2wt% and decreases upto 8 wt%. The crystallite shape ellipsoid was obtained as shown in figure 8.

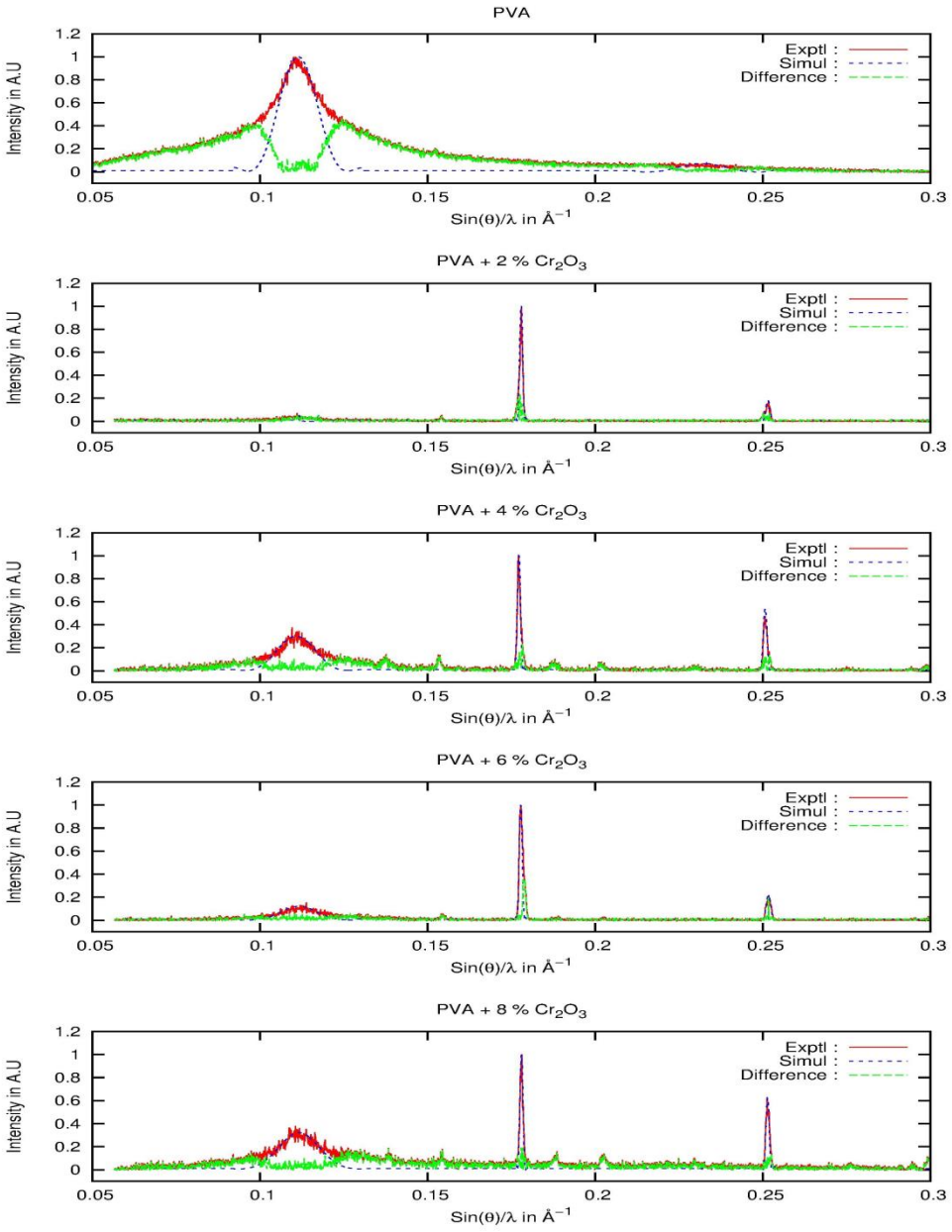

Fig.7. Experimental and simulated X-ray diffraction pattern of PVA / NaCl/Cr_2O_3 nano composites by whole powder pattern fitting technique

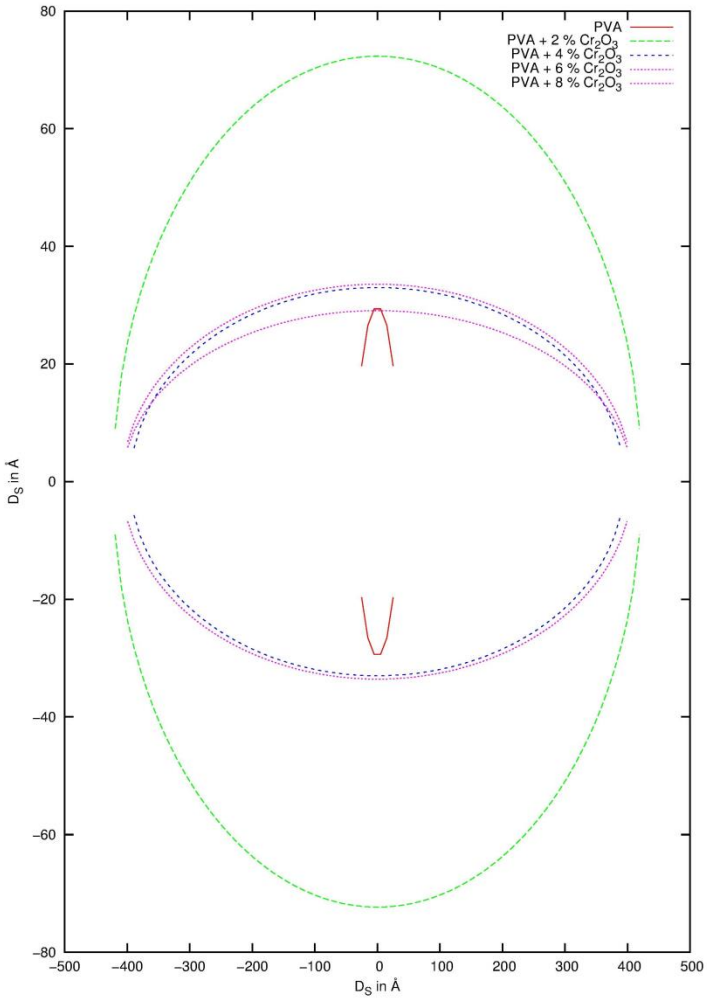

Fig.8. Variation of crystallite shape ellipsoid for Pure PVA and PVA/NaCl/Cr_2O_3 nano composites by whole powder pattern fitting technique

"Conclusions"

The aim of this study was to determine the microstructural properties of the PVA/ Cr_2O_3 nano composites and to correlate with the mechanical and optical properties. For this purpose, X-ray line profile analysis, diffuse reflectance spectroscopy and nano indentation was performed.Nano indentation studies implied a concentration gradient for nanoparticle loading at 6 wt% for which the elastic modulus and hardness is minimum and above 6wt% both the mechanical parameters showed an increased trend which may be

substantiated by further studies. The red shift was observed for E_g modes in the Raman spectrum and band gap was estimated using DRS studies. The microstructural parameters were evaluated using whole pattern fitting method. The prepared nano composites will be investigated for antibacterial and in vitro biocompatibility studies.

Acknowledgments

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Table 1.Microstructural parameters and stacking faults for PVA /NaCl/Cr_2O_3 using exponential distribution function

Samples	Peaks	2θ (deg)	α	g (%)	d_{hkl} (Å)	<N>	D_s (Å)	α^d	β	delta (E-03)	Crystallite area (Å^2)
PVA	1 2	19.7 41.91	2.302 3.413	0.5 0.5	4.502 2.153	7.5 13.8	33.7 29.7	3.38E-7 3.10E-5	7.21E-5 8.54E-5	3.04	1000
PVA + 2 % Cr_2O_3	1 2 3 4	19.79 31.81 45.59 56.59	6.382 1.852 0.731 5.133	0.5 0.5 0.5 0.5	4.482 1.852 2.795 1.625	16.14 150.5 150.8 260	72.33 278.7 421.4 422.5	1.55E-6 3.12E-6 3.16E-8 5.61E-9	1.40E-6 6.08E-6 9.07E-9 6.02E-9	0.249	30559
PVA + 4 % Cr_2O_3	1 2 3 4	19.67 31.69 45.43 56.46	1.384 1.569 0.442 0.553	0 0 0 0	4.509 2.821 1.994 1.628	7.32 140.0 168.7 183.4	33.00 394.9 336.3 298.5	3.03E-5 5.49E-6 2.43E-6 2.75E-6	3.52E-6 3.29E-6 5.64E-6 4.59E-6	0.497	13031
PVA + 6 % Cr_2O_3	1 2 3 4	19.75 31.79 45.62 56.67	0.809 1.541 1.518 1.797	0 0 0 0	4.476 2.812 1.986 1.622	7.5 144.9 140.1 154	33.57 407.4 278.2 249.7	8.44E-6 1.00E-6 9.24E-6 5.15E-6	8.28E-6 4.47E-6 9.78E-6 2.87E-5	0.357	13676
PVA + 8 % Cr_2O_3	1 2 3 4	19.79 31.83 45.57 56.60	0.805 1.644 1.456 0.949	0 0 0.5 0	4.474 2.809 1.989 1.624	6.5 145.0 190.4 196.2	29.08 407.3 378.7 318.6	4.28E-6 4.96E-6 8.67E-6 1.98E-9	1.27E-6 1.09E-5 9.83E-6 1.12E-8	0.705	11844

Figure Captions

Fig 1. Elemental analysis using EDS spectra

Fig.2. TEM image of the Cr_2O_3 nanoparticles with the inset SAED pattern

Fig. 3a. Load Displacement curves for Pure PVA and PVA /NaCl/Cr_2O_3 nano composites

Fig. 3b. Variation of Elastic Modulus as a function nanoparticle concentration

Fig. 3c. Variation of Hardness as a function of nanoparticle concentration

Fig .4.Raman Spectrum a) Pure PVA and Cr_2O_3 nanoparticles b) Polymer nano composites

Fig .5.UV-Vis Diffuse Reflectance Spectra of Pure PVA and PVA /NaCl/ Cr_2O_3 nano composites

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