



VARIATIONAL EFFECTS OF TiO₂ DOPING ON OPTICAL RESPONSE OF POLYMER BLEND NANOCOMPOSITES

Ismaila, A.^{1*} Ahmed, T. O.² and Ismail, H.¹

¹Department of Physics, Ahmadu Bello University, Zaria, Kaduna State, Nigeria

²Department of Physics, Federal University Lokoja, Lokoja, Kogi State, Nigeria

* Corresponding author Email: abdu.ismaila@gmail.com

ABSTRACT

Optical response of polymer-blend due to doping with titanium (iv) oxide nanoparticles was studied. The nanocomposites were prepared via solution-mixing technique; a two stage reaction involving the synthesis of TiO₂ nanoparticles and the subsequent mixing with the host polyvinyl (alcohol-co-acetate) matrix. Initial microstructural investigation of the TiO₂ nanoparticles reveals an almost spherical particles ($\geq 99.99\%$ phase purity) with diameters ~ 25 -40nm. Structural modifications due to TiO₂ doping on the host matrix were investigated using Fourier transform infrared spectroscopy and scanning electron microscopy. Optical properties were investigated using UV-visible spectrophotometer. Optical transparency decreased with the variation of TiO₂ concentrations from 1 to 4 wt. %. The nanocomposites were found to exhibit good properties of being excellent UV filters and good visible light absorbers with an optimum in the nanocomposite with 3 wt. % of TiO₂ nanofillers.

Keywords: Titanium (iv) oxide, nanocomposites, optical properties, optical band gap, nanofillers.

INTRODUCTION

The prospect of polymer blending has, in the last few decades, been compared to the alloying of metals as it requires little or no extra cost compared to the production of new polymers. This leverage has offered the possibility of producing a range of polymer materials with properties completely different from those of the blend constituents (Wanchoo & Sharma, 2003). These materials improve numerous favorable properties while maintaining the inherent properties of constituent polymer phases' such as ductility and optical transparency, etc. an advantage that is never achieved in the conventional polymer composites. Furthermore, at very low loading (< 5 wt. % of inorganic inclusions), tremendous property enhancements were recorded. This is, however, not achieved in the conventional polymer microcomposites in which particle loading ~ 25 -40 wt. % is required (Saujanya, 2001). The influence of semiconductive nanocrystals in property enhancement has attracted enormous research efforts which in turn led to a myriad of potential applications in engineering, medicine, biology, electronic and allied industries (Wu et al., 2019). Of the great number of inorganic nanocrystals used, TiO₂ attracts specific interest of researchers. This is due to the fact that TiO₂ has excellent chemical stability, resistance to photocorrosion, high photocatalytic activity, high refractive index, low cost and is non-toxic (Legrini et al., 1993; Sugimoto et al., 2003). Optical properties of properties of these nanostructured materials have been known to depend on the variation of chemical bonding structure and doping levels (Ismaila et al., 2015). In this work, the changes in optical transparency due to TiO₂ doping has been reported. It is found that the optical properties vary with the TiO₂ concentration. This is an indication that the material would have the advantage of tunable transparency which is dependent upon nanoparticles concentration.

Experimental Details

Polymer blend nanocomposites comprising of polyvinyl alcohol and polyvinyl acetate doped with TiO₂ nanoparticles were prepared via a two stage reaction. This involves the

synthesis of the TiO₂ nanoparticles from titanium (iv) chloride employing hydrothermal technique and the subsequent mixing of its functionalized form with the polymer blend dissolved in toluene via one-pot reaction. Four samples of the nanocomposites with different filler contents, (1-4 wt. %), were prepared by solution casting in petri dishes and oven-dried at a temperature below that of the blend's melting point. Each sample was hot-pressed to produce a relatively uniform films of the nanocomposites.

FTIR measurements were carried out using SHIMADZU 8400S spectrophotometer recorded in the frequency range 400 to 4600 cm⁻¹ to establish the spectral positions and intensities of the IR bands. EVOI (ZEISS) multipurpose scanning electron microscope was used to observe the surface morphology of the samples at 20kV employing secondary electrons at 500x magnification and the particles size distribution was deduced. For the optical characterization, a JENWAY 640S UV-visible spectrophotometer was used to study the absorption properties of the nanocomposites at wavelength range of 200 to 900nm.

RESULTS AND DISCUSSIONS

Fourier transform infrared spectroscopy

It is an established fact that the fundamental vibrations of solids, so-called finger prints, are localized in the frequency region (< 1200 cm⁻¹) of the mid-range (400-4000 cm⁻¹) of the infrared spectrum [Ismaila et al., 2015]. Also, the Ti-O bond is clearly located in the range from 400-900 cm⁻¹ (Morterra and Magnacca, 1996). Here, the significant absorptions observed below 900 cm⁻¹ represent Ti bonds with vinyl groups, secondary alcohols, carbonyl groups and oxygen. From figs. 1(a-d), the functional groups appearing in the range 383.85 cm⁻¹ to 491.66 cm⁻¹ represent Ti-O bonds of the functionalized TiO₂ nanoparticles. The overall spectra of the nanocomposites reveal the additivity of polyvinyl acetate and polyvinyl alcohol with the modified TiO₂ nanoparticles. In the first two spectra (1a and 1b), most of the functional groups peculiar to the component reagents were observed. However, in figs. 1c and 1d, increased concentrations of the nanofillers from 2 to 4% are responsible for the extinction of the

functional groups due to oxidation and hydrolysis. This is in good agreement with the work of (Marques-Hueso et al., 2010).

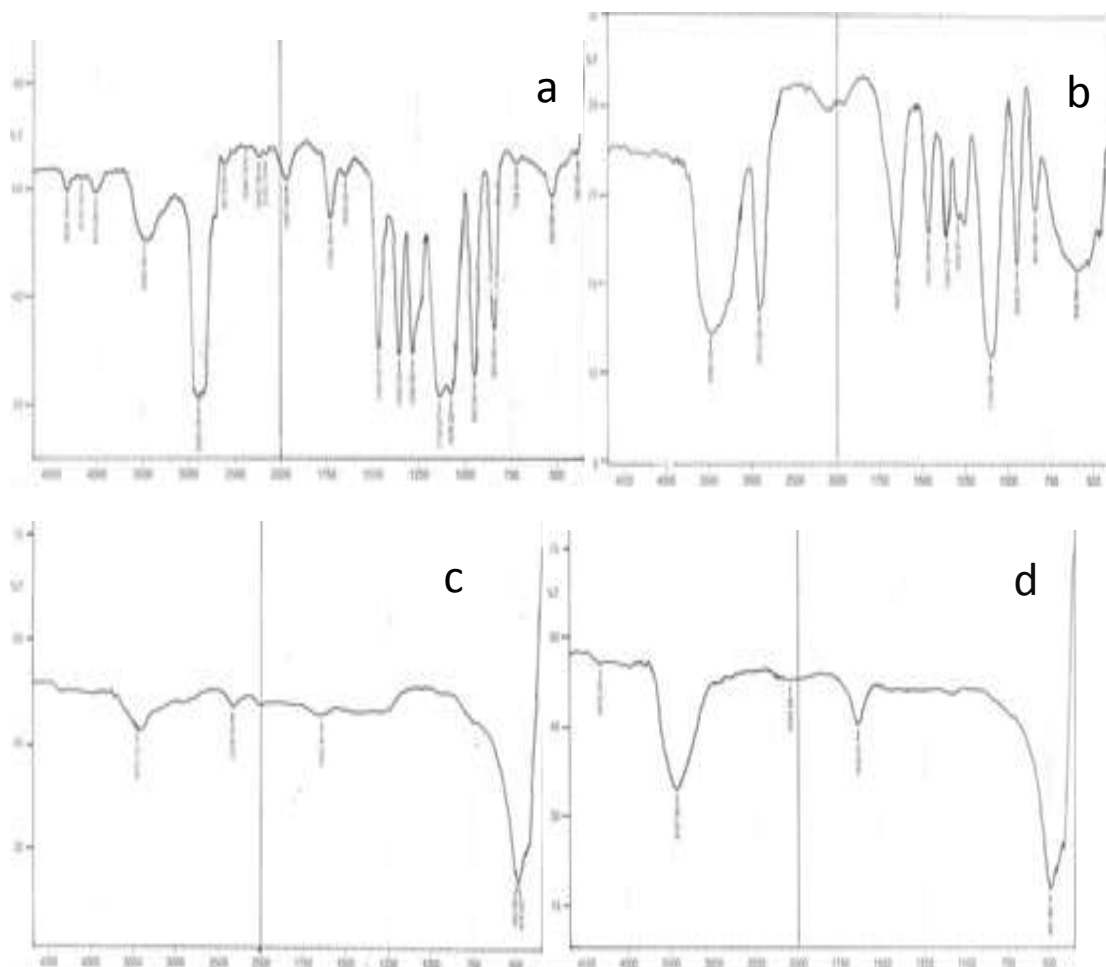
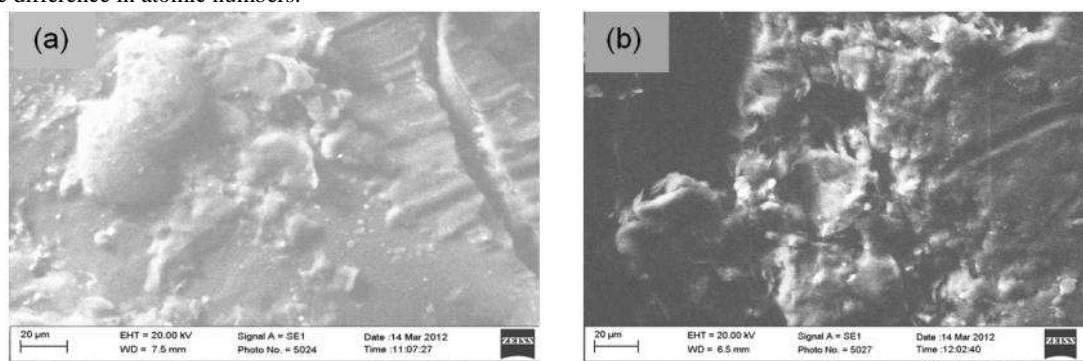


Fig.1 FTIR spectra of polymer blend with (a) 1% TiO₂ (b) 2% TiO₂ (c) 3% TiO₂ and (d) 4% TiO₂ nanoparticles.

Scanning electron microscopy

The SEM images, figs. 2(a-d), depict the microstructure of the nanocomposites showing two distinct phases; the light functionalized TiO₂ nanoparticles and the dark bulk polymer blend matrix. The observed contrast in the images was as a result of the difference in atomic numbers.



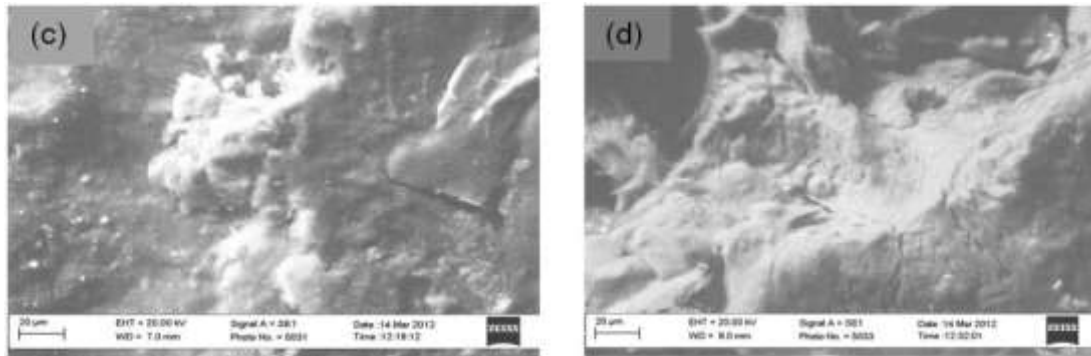


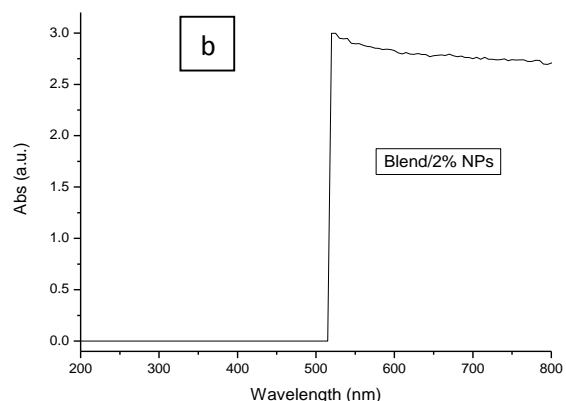
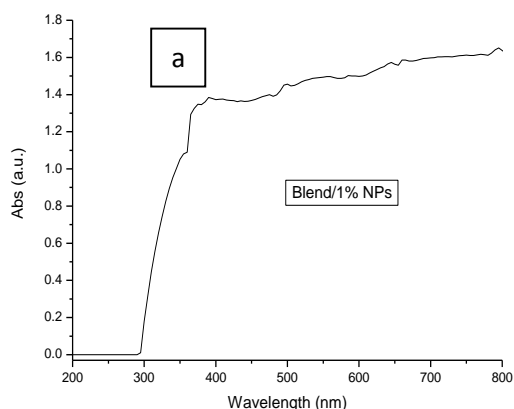
Fig. 2. SEM images of the polymer blend containing (a) 1% TiO₂ (b) 2% TiO₂ (c) 3% TiO₂ and (d) 4% TiO₂ nanoparticles.

This is due to the fact that phases within a material depend upon back scattered electron yield and the corresponding atomic numbers of substituent atoms within different phases. Hence, the nanoparticles appear light because their atoms are of higher atomic numbers compared to those in the matrix phase and consequently a higher back scattered electron yield (Patterson, 1939). These lighter modified nanoparticles, with spherical shapes, are evenly dispersed over the bulk polymer blend matrix.

UV-visible spectrophotometry

The incorporation of impurities in the form of atoms or nanoparticles into a pure matrix (semiconductor, metal, polymer, etc.) brings about changes because their environment is neither inert nor isotropic. By exposing the anisotropic nanocomposite materials to electromagnetic radiation, resonant coupling between the light photons and the collective modes (electronic transitions/excitations) of the nanocomposites occurs. Such interaction gives rise to polarization of the matrix in form of variations in the degree of absorption and or transmission as a function of wavelength (Abarques et al., 2009). The observed variation in the light absorbance of the nanocomposites over wavelength range of 200 to 900 nm is attributed to the TiO₂ content in each of the samples. Figs. 3(a-d) showed the UV-Visible spectra of the nanocomposites. Nanocomposite containing 1 wt. %

TiO₂(fig. 3a) transmits in the UV range up to about 290 nm before a significantly rapid absorption with a maximum at 390 nm. This absorption appreciates reasonably through the visible range indicating that the material is a good filter at a low UV wavelength ranges (<300 nm) and a good light absorber at higher wavelengths of the UV range, 300 – 400 nm, and through the visible light wavelength ranges. The remaining three samples displayed almost similar spectra with slight variations in the onset of absorption. As can be seen in figs (3b-d), all the samples filter the whole UV light through lower wavelengths of visible radiation. Absolute transparency to ultraviolet radiation through a visible wavelength of about 510 nm was observed for the 2 wt. % of TiO₂ nanocomposite. Slightly above the onset, a much significant absorption was recorded with maximum of about 3.0 a.u. after which it decreases slightly within almost the same absorption range with minimum absorption at ~ 2.7 a.u. The onsets for the samples containing 3 and 4 wt. % of TiO₂ (figs. 3c & d) were recorded at wavelengths of 580 nm and 550 nm respectively. Above these wavelengths, the absorptions increase rapidly in a similar trend with the previous one (2% TiO₂). Both samples have maximum absorptions in the same range of 3.0 to 2.7 a.u. within the visible radiation wavelengths.



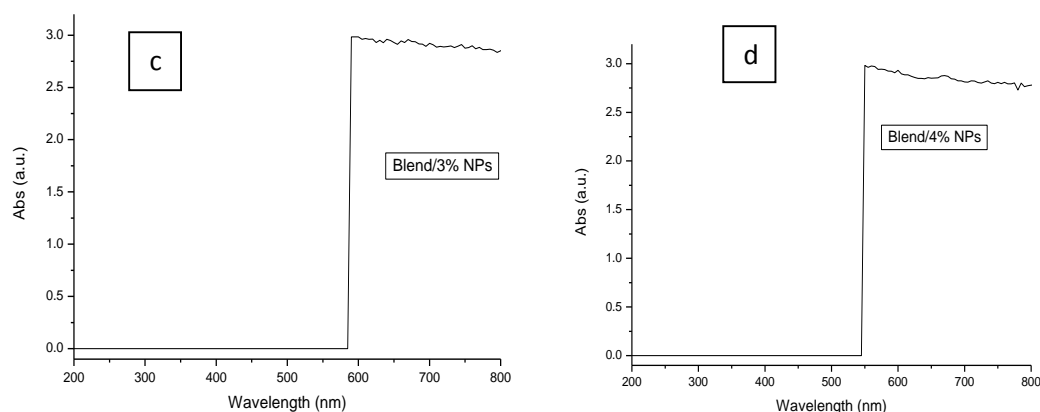


Fig. 3. Optical absorption spectra of the polymer blend nanocomposites containing (a) 1% TiO₂ (b) 2% TiO₂ (c) 3% TiO₂ and (d) 4% TiO₂ nanoparticles.

Furthermore, the last three samples containing 2, 3 and 4 wt. % of TiO₂ nanocrystals are all excellent UV filters and very good visible radiation absorbers. The shifts in the onset of absorptions, as shown by (Hamadani & Majedi, 2010) were due to higher concentrations of the TiO₂ because the nanofillers are transparent to UV-Visible light.

CONCLUSION

TiO₂ doped polymer-blend nanocomposites were developed via a two-staged experiment involving the synthesis of the TiO₂ nanoparticles and modifying it to create functional sites and to improve dispersion when mixed with host polymer matrix. FTIR spectra revealed excellent additivity of the polymer blend with the TiO₂ nanofillers. SEM images of the nanocomposites showed uniform dispersion of the TiO₂ nanocrystals having good adhesion with polymer domains. Optical spectroscopic analysis revealed that nanocomposites with relatively higher concentrations of TiO₂ nanofillers were optically transparent indicating potential applications as good UV filters and visible radiation absorbers.

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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