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Synthesis of nano Al_2O_3 – Poly(o-toluidine) Composites and Investigations on the Additive Influences in its Characters

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Abstract: In the development of novel materials, observations on the influencing parameters altering the fundamental properties of a material plays a vital role. In the past few decades, development of nano hybrid materials has been enhanced and offers variety of multifaceted materials suitable for wide variety of applications. The nanocomposites consisting nano metal oxides and polymeric materials is one of a nano hybrid materials expected to exhibit unique behaviours. Poly(o-toluidine) (POT) is a polymer having exceptional behaviours in electrical conductivity and optical properties. Nano alumina is an important ceramic material offers high strength has wide applications in electronic ceramics and catalysts. In the present work, the composites of POT- nano Alumina (Al_2O_3), were prepared employing insitu chemical oxidative polymerization using precursors o-toluidine (OT) and nano aluminium oxide (n-Al_2O_3). Four different combinations of nano polymer composites were prepared by varying nano Al_2O_3 content as 10, 25, 50 and 75 weight percentage with poly-o-toluidine. Observations from UV-Vis. Spectra of all the samples shows two absorption bands in electronic spectra confirms both hyposochromic shift (π- π * transitions) and bathochromic shift (n- π * transitions). The obtained Scanning electron microscopic (SEM) and Atomic Force Microscopic (AFM) images confirmed the coalescence of nanocomposite particles when the incorporating content of nano Al_2O_3 is lower at 10 weight percentage. The resultant product is in the form of amorphous thin film result of coalescence. It evident that, an interdiffusion of additive molecule and polymer particles across the particle boundaries is resulted when the additive content is too low.
Keywords: Synthesis of nano Al_2O_3 – Poly(o-toluidine) Composites and Investigations on the Additive Influences in its Characters.

Introduction

In the recent decades, nanomaterials gained overwhelming lure mainly for their particle dimensional and structural dependent functionalities and properties which are entirely different from that of it's in bulk range. Present development of nanomaterials proven its ability that can be designed with tailor made properties such as physical, chemical, biological, etc. for specific applications. The current updates of materials research acknowledges the rapid growth of interfacing of two or more materials of different entities in single frame namely composite. This is to obtain a novel material with distinct properties different from their parent materials of the same chemical compositions but, attribute of these properties in nanoscale dimensions are still to be explored.

The emergence of nanocomposites open a new avenue for researchers of various disciplines since, these materials exhibiting newer properties which cannot be obtained from their individual components. Development of hybrid organic–inorganic nanocomposite materials is expected to be the state of the art since, it can be the extent of single entity comprising the properties of both inorganic as well as organic material. Polymer is an organic materials having unique features and it is proven well that its properties can be improved to any desired fashion by incorporating suitable inorganic nanomaterials. Earlier observations ensured that the dielectric properties of polymeric materials can be improved by heterogeneously incorporating certain nano metal oxides such as Al_2O_3, TiO_2, SiO_2, $BaTiO_3$, etc[1]. The nanoscale orientations and interactions within the nanocomposite materials are essentially to be characterised to understand their physico-chemical properties.

In the present work, a series of composite materials consisting of inorganic component nano alumina (n-Al_2O_3) at various amounts incorporated with organic material, poly(o-toluidine) (POT) is prepared employing insitu polymerization technique. POT is a derivative of polyaniline with $-CH_3$ group occupied in the ortho position of aromatic ring of aniline monomer[2]. Nano alumina (n-Al_2O_3) is well-known for its physical strength and stability and hence, the incorporation of n-Al_2O_3 with POT helps to obtain a composite materials with enhanced physical properties[3-8] and to overcome the limiting factors of polymeric materials. Still, the influence of additive material in the formation of nanocomposite materials is to be optimized. This work is to explore the role of additive in yielding the polymer nanocomposite material and its optical and morphological properties. The insitu formation of organic polymer- inorganic nanomaterials provides with an exclusive features in morphology and dimensions of the particle which were not resulted in any other techniques.

Experimental

Chemicals of analytical grade were procured from Sigma-Aldrich used to synthesise the nano composite of n-Al_2O_3 incorporated poly(o-toluidine). Composition of the proposed samples shared with the contents of POT +n-Al_2O_3 in weight percentage. The sample codes are termed as POTA followed by the contributing quantity of n-Al_2O_3 in weight percentage for example, POTA25 contains 25 weight percentage n-alumina. The desired amount of o-toluidine as per its composition in weight percentage is taken and mixed with de-ionized water. The remaining part of the composition is filled with n-Al_2O_3, a desired amount is taken in weight percentage added directly with the o-toluidine solution. At the temperature of 5 °C, the chemical oxidation of o-toluidine in strong acidic medium (2.0 mol L^{-1} H_2SO_4) was carried out by adding one molar of ammonium peroxydisulphate ($(NH_4)_2S_2O_8$) solution drop by drop under continuous stirring. Stirring of the reaction mixture continues for further 24 hours of time to ensure the polymerization reactions. After then a series of filtration processes are carried out one by one with de-ionized water, Acetone and with Ammonia solution to ensure the changes to Emeraldine salt to base. Followed by the filtration processes, the obtained yield material was dried at the temperature of 50-60 °C, kept inside the vacuum oven for 90 minutes. The fine powder of nano alumina- poly(o-toluidine) composite was obtained grinding the product at last. The yield of the nanocomposite samples POTA25, POTA50 and POTA75 were obtained in granular form except, POTA10 has 10 weight percentage of additive derived in the form of thin film. XRD, SEM, AFM and UV-Vis spectra were obtained to characterise the prepared nanocomposite materials.

Results and Discussion

Poly(o-toluidine) is a polymeric base, the nano alumina is an inorganic material, and primary scope of the work is to explore the effects of this inorganic species incorporation into the organic polymeric matrix while employing insitu polymerization process. Hence, the content of the inorganic additive material varied in four different amounts as 10, 25, 50 and 75 weight percentage. Poly(o-toluidine) is organic substance and a derivative of polyaniline. Earlier observations[9], employing theoretical modeling and discusses the structural and bonding interactions between the similar organic and inorganic species in a composite material. This theoretical explanation reveals the possibility of strong bonding and interactions of the nano alumina particularly with dangling oxygen which are extends from the five membered ring of the polymer matrix. To explore the structural formation of the prepared POT-nAl_2O_3, the X-ray diffraction studies were carried out for all the prepared samples. Interestingly, the first one among the series of samples, POTA10 exhibits an amorphous nature rather other three samples. The XRD image of the POTA10 is shown in Fig.1.

It reveals the noisy reflections without any characteristic peaks confirmed the absence of crystallinity. It is obvious that POT is amorphous has no crystalline features in its base form $_2$. In polymer, particularly in POT, its quasi amorphous nature is the result of interchain spacing and interchain spatial coherence. In basic form of POT its interchain spacing is very large. Although POT is amorphous in base form, it exhibits crystalline nature when it is prepared with suitable additive components results in the form of composite material. It is obvious that incorporation of inorganic nanoparticles to polymeric material leads to modify its physical properties. The obtained XRD result shown in Fig.1 ensured that the incorporation of 10 weight percentage of n-Al_2O_3 is doesn't help to turn the crystalline features of POT as result of its incorporations. This may because of the lesser quantity of additive (10 weight percentage) used to incorporate is not enough to occupy the dangling oxygen sites and thereby unable to extend the conjugation which are essential for strong bonding interactions. The XRD result of other three samples exhibit well organized crystalline features.

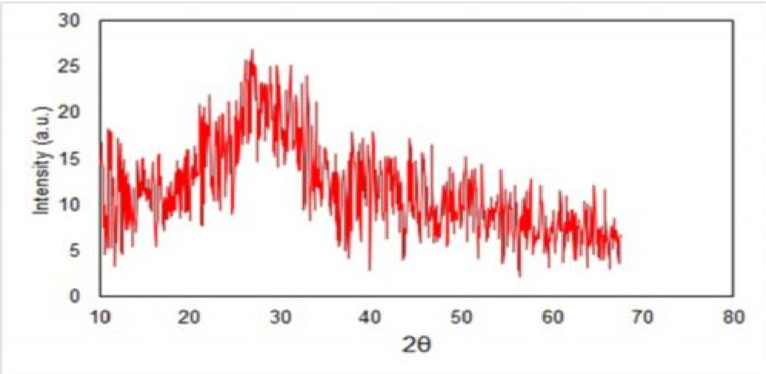

Fig.1. X-ray diffraction pattern of POTA10

The morphological features of the samples are one of the key parameters help to characterise the material property. Among the obtained four samples, POTA10 is an only yield in the form of film, rather than any other three (POTA25, POTA50 and POTA75) which are derived in the form of granule. Fig.2 is used to exhibit the morphological feature of the film deposited as a resultant product of POTA10. The images obtained using the techniques Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) are used to explore the surface morphology of the prepared samples. In Fig.2a, the SEM image doesn't depict any characteristic features except few dark and white spots. The AFM image used to explore the three dimensional observation on the deposited film of POTA10 as shown in Fig.2b. The recorded height variations on the sample surface is within 0.5 μm approximately in the entire scanned area of 50 μm^2.

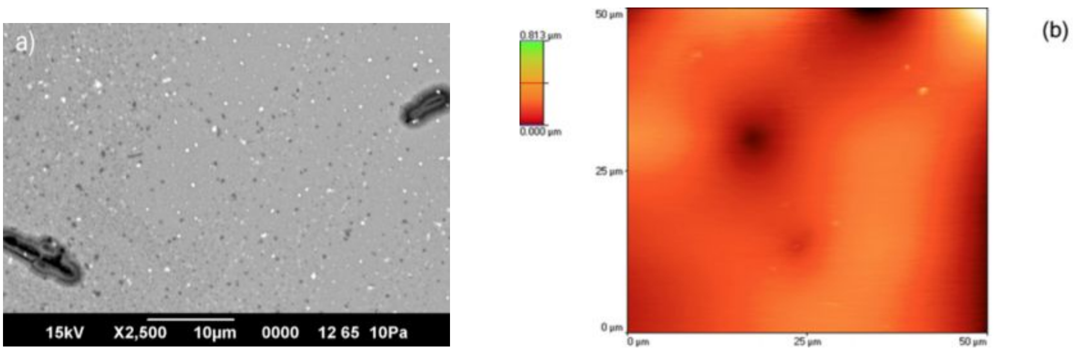

Fig. 2. a) SEM of POTA10 **b) AFM image of POTA10**

The crystalline features were emerged in the same combination of organic and inorganic materials while increasing the additive content above or equal to 25 weight percentage and decreasing the composition of polymeric matrix less than or equal to 75 weight percentage. The yield of other three samples such as POTA25, POTA50 and POTA75 were able to obtain in the form of granule. Both the pure polyaniline and its derivative POT usually exhibits the granular form of yield without uniformity[10]. These granular formation and thereby emergence of crystallinity is possible obtained only if the incorporated n-Al_2O_3 get occupy into the network of

POT polymeric matrix as an active component. The earlier studies[9] explored that the connectivity between the polymer chain and incorporated n-Al_2O_3 is possible through the labile oxygens such as in ether linkages available in the polymeric network. These oxygens are responsible to interact with the nano alumina species which are all in its vicinity.

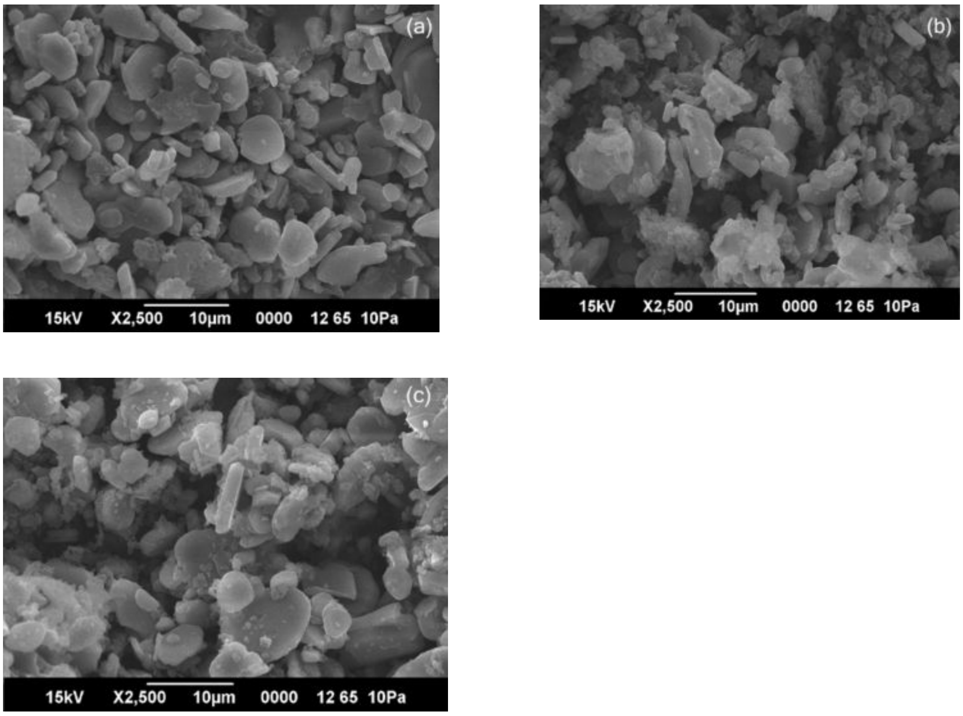

Fig. 3 SEM images of a) POTA25, b) POTA50 and c) POTA75 ensured the granular yield

An induced electrostatic attraction on the negatively charged oxygen in the polymeric network results a strong interaction with the positively charged Al of the nano alumina available in its proximity and thereby extends connectivity. The SEM images shown in Fig. 3 exhibits the granular form of yield of the three samples POTA25, POTA50 and POTA75 ensured the modifications in its molecular structural features as result of n-alumina incorporations above 25 weight percentage. It ensured that the incorporated n-Al_2O_3 occupied in the POT network lattice distributions.

The optical investigation plots of the prepared series of POT-nAl_2O_3 samples were obtained employing UV-Vis absorption spectra as shown in Fig.4. The spectral absorption particularly in the range of ultraviolet - visible of electromagnetic radiation is a versatile tool of research mainly helps to analyse the key functions of certain compounds or nanoparticles. While irradiating a species with UV-Vis radiation, the absorption leads to the transition between electronic energy levels. This transitions also includes the transition of vibrational energy levels and hence, results in a merging of more number of closely spaced bands provides a broad absorption band.

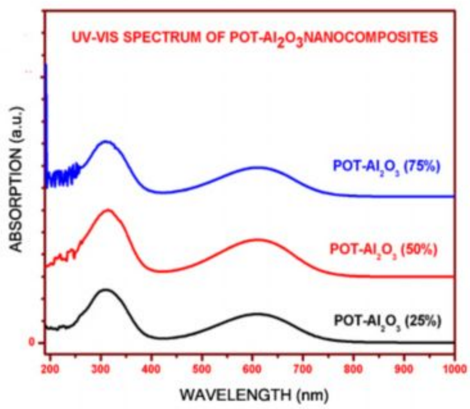

Fig. 4. UV-Vis spectrum of POT- n-Al_2O_3 samples of different compositions

All the three samples exhibited similar fashion of absorption bands centered almost on 300 and 600 nm with little bit differences. The emergence of absorption bands attributed to the excitation of electrons by the photon of known energy value from the topmost occupied molecular orbital to the lower most unoccupied molecular orbital corresponds to an absorption edge. The first absorption band in the range of 309 – 316 attributes to the transition $\pi - \pi$ * relative to the bond of conjugation between the neighboring phenylene rings of the polymer network.

This band of absorption ensured the hypsochromic shift assigned to POT result of synergistic effect of substituent on the electrochemical behaviour of polyaniline[11]. It also reveal the steric effect of $-CH_3$ groups and thereby reduction in the conjugation length of POT. The next absorption band located around 600 nm is corresponds to **n** – π * transitions also attributed to the exciton band as result of inter band charge transfer associated with the shifting of electrons from benzenoid ring to quinoid ring. Absorbance around 600 nm is inferred mainly because of the quinoid structure of the base form of POT. It is evident the bathochromic shift. It can be described more specifically, the absorption band at 600–650 nm is mainly attributes to the transition from a localized benzenoid highest occupied molecular orbital to a quinoid lowest unoccupied molecular orbital[12], that can be termed as an excitonic transition from benzenoid to quinoid[13].

In crystalline material, the absorption edges directly relates to the direct or indirect band gap that is conduction band and valence band. The absorption process is initiated with the supplied photon of known energy. Using the result of UV-Vis absorption spectra of the prepared samples, the optical parameters such as, absorption coefficient (α), band gap (E_g), etc. have been determined.

Employing Tauc relation[14], the optical band gap exist in the prepared samples are derived. The fundamental relation is:

$\alpha h\nu = B(h\nu - E_g)^n$ ------(1)

where α is the absorption coefficient, hν the energy of absorbed light, n = ½, 3/2, for direct allowed transition and n = 1,2,3,…for non-direct transitions respectively. B is proportionality constant. Energy band gap (Eg) values can be obtained by plotting $(\alpha h\nu)^{1/2}$ versus hν and extrapolating the linear portion of $(\alpha h\nu)^{1/2}$ to zero. Using one-electron theory of Bardeen et al[15], the details of direct and indirect band gap relates with the data can be observed. As described elsewhere[15,16], for high absorption coefficient $\alpha > 10^3$ cm^{-1}, the inter band transition referred to direct transition. As per the above statement, the present system obeys the role of non-direct transitions, since the measured $\alpha < 10^3$ cm^{-1} and hence the relation of $(\alpha h\nu)^{1/2}$ with incident optical energy E (eV) can help to derive the optical band gap (Eg) value as shown in Fig.5. These observations gain significance since it can explore the variations of LUMO-HOMO of resultant composite material in which the nano alumina influenced within polymer matrix[17].

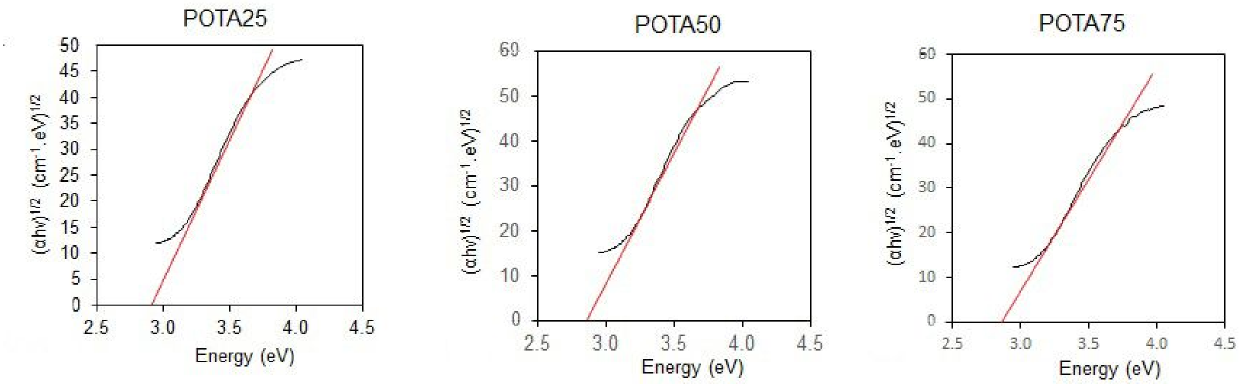

Fig. 5. Tauc's plot for obtaining optical energy band gap values in prepared samples

The measured band gap values doesn't reveal any considerable difference among the nanocomposite materials of different compositions. The observed band gap (E_g) values of POTA25, POTA50 and POTA75 respectively are 2.88, 2.86 and 2.85 eV as shown in Fig. 5. It reveals that the incorporated nano alumina species doesn't make any significant changes in the electronic band structure although, it occupies in the lattice of polymeric structure.

Conclusion

A series of four different nanocomposite samples consists of various amount of poly(o-toluidine) with nano Al_2O_3 has been prepared employing insitu polymerization technique. The yield of nanocomposites is in the form of film without any crystalline features when the content of nano alumina is below 25 weight percentage. The samples having 25, 50 and 75 weight percentage of n-Al_2O_3 records the products in the granular forms. The observed UV-Vis spectroscopic results helps to determine the optical parameters such as absorption coefficient (α), optical band gap (E_g), etc. It depicts the present system has non-direct band transitions. The measured optical energy gap value employing Tauc's plot exhibit no characteristic changes among the samples of different compositions.

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