PREPARATION AND CHARECTERISATION OF POLYMER-NANOCRYSTALS COMPOSITE

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Introduction

The development of new nanosized materials results in new materials having unique electronic and optical properties which are quite different from their bulk materials. Hence attempts have been made to grow and study such materials [1, 2]. Blending of a polymer with organic/inorganic material has given a new direction for developing such novel materials which is an easy and inexpensive method of modifying various properties of the composites. The incorporation of nanoparticles into various matrices will extend their utility in material and device applications. Such nanocomposites could exhibit novel optical properties as they are strongly affected by the surrounding matrix as well as closely spaced particles in matrices and can exhibit cooperative phenomena when interacting with light. The resulting properties of nanocomposites are, most of the time, a simple combination of the properties of inorganic and organic components.

In this paper, a novel technique of growing inorganic/organic crystals in a host polymer matrix is reported and the effects of the host polymer on the optical properties of the impregnated crystals have been studied. In the analysis, polyvinyl alcohol (PVA) is used as a host matrix and potassium dihydrogen phosphate (KDP) crystal as a filler. PVA (with a general formula $[\text{-CH}_2\text{CH(OH)-}]_n$) has been used as a host matrix as it is a well-known polymer for many technological applications and it forms a film with high aqueous solubility, transparency, very good flexibility and wide commercial availability.

Experimental

Research grade potassium dihydrogen phosphate (KDP) and polyvinyl alcohol (PVA) from Merck and co have been used. To prepare the PVA solution 10gm of PVA is dissolved in 20 ml of double distilled water. A homogeneous transparent solution of PVA is obtained after the solution is stirred continuously at room temperature for 6 hours. 10 ml of PVA solution is taken in a petri dish so that a film of a thickness around 0.5 mm is formed. Then that solution is allowed to settle for a day or two. Next a saturated solution of potassium dihydrogen phosphate (KDP) in doubled distilled water is prepared and filtered. The filtered solution (2 ml) is slowly poured over the polymer solution in the petridish. The petri dish is closed so that the rate of evaporation of the solution is low. To understand the growth of the filler crystals and their dispersion in the host polymer, two samples are prepared by keeping the PVA-KDP combine, at different temperatures. The sample PvKd2 is prepared at room temperature around 30^0C. The sample PvKd1 is prepared by keeping the PVA – KDP blend in a constant temperature bath maintained at 20^0C. The prepared samples are characterised by various spectroscopic techniques like X-ray diffraction (XRD), Fourier transform Infrared (FT-IR) spectroscopy and UV–Vis–Spectroscopy, to ascertain the incorporation of nanocrystals in the polymer matrix.

Characterisation studies, Results and discussions

(a) XRD analysis:

The XRD of KDP nanocrystals grown on PVA Polymer matrix are carried out using JEOL JD8p Visual XRD, (with automation software:VISX122D), with Cu K_α of $\lambda = 1.5405$ Å (30KV) as a source. XRD data has been recorded for pure KDP, PVA and KDP nanocrystals in a polymer matrix (for the samples PvKd-1 and PvKd-2). The diffractrographs (recorded with the angle of rotation between $0–50^0$) are shown in fig. 1.

In the fig. 1 the *X*-ray diffraction pattern for bulk KDP crystal shows presence of sharp peaks that indicate the crystalline nature and high degree of preferred orientation. The prominent peaks seen in the diffraction pattern of KDP are indexed as (200, 211, 301, 312). In the *X*-ray diffraction pattern of the PVA a hump is seen at 20^0. Moreover the XRD pattern suggests the amorphous nature of the PVA. The XRD pattern of the sample PvKd2 shows large number of prominent peaks and a hump. This ascertains the presence of KDP crystals in the host polymer matrix. In the diffraction pattern of the sample PvKd2, the increase in the intensity of the (211) peak, is due to preferred orientation. Also the partially amorphous and the partially crystalline nature of the sample are observed from the diffraction pattern. Though the XRD pattern of the

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sample PvKd1 does not show any sharp peak and appears amorphous, the SEM image of the sample PvKd1 (fig. 4,*a*) shows the presence of the KDP crystal. This ascertains the presence of crystals of smaller size in the host polymer in the case of the sample PvKd1. Overall, the structural integrity of both the PVA and the KDP are unaltered. The changes in the XRD pattern of those samples are due to the changes in the crystallite sizes in the host polymer [3–5].

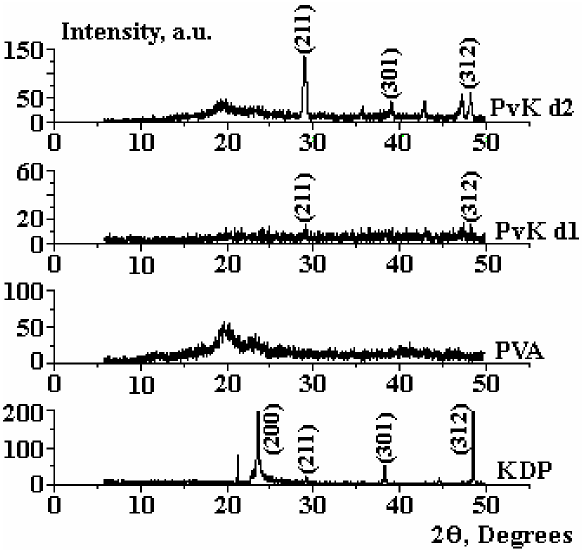

Fig. 1. X-ray diffractrograph of KDP-PVA polymer nanocomposites

(b) FT-IR Studies

The FT-IR analysis for the two samples has been carried out using Nicolet AVATAR 330FT-IR spectrophotometer in the wave number range of 400 cm^{-1}-4000 cm^{-1}. Fig. 2 shows the FT-IR of KDP incorporated in the PVA polymer matrix.

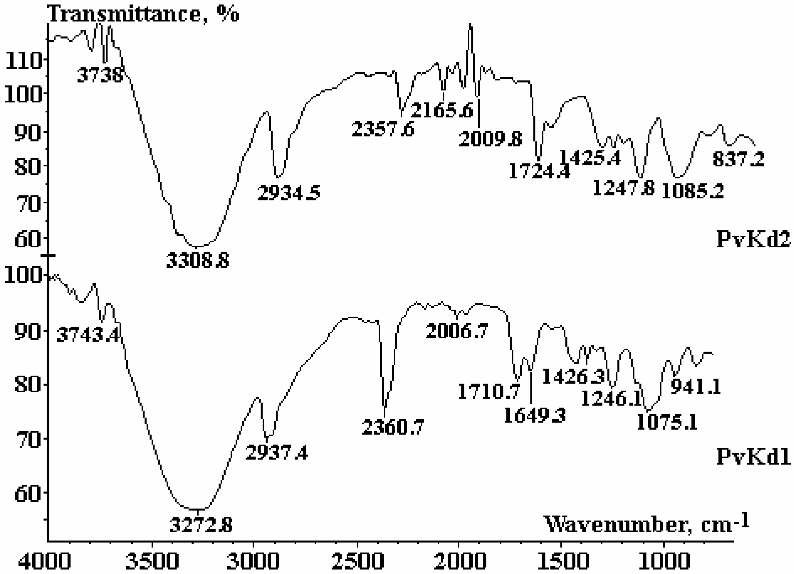

Fig. 2. FTIR spectra for the samples (PvKd1 and PvKd2)

In the FT-IR analysis of pristine KDP, the peaks are P-OH stretching at 3743 cm^{-1}, P-O-H bending at 2365.1 cm^{-1}, P=O stretching at 1630 cm^{-1}, P-O-H stretching at 1279 cm^{-1}, and HO-P-OH bending at 915 cm^{-1} [6, 7]. For pure PVA, some of major absorbance peaks associated with (PVA) are 1723 cm^{-1} due to C=O, C-H broad alkyl stretching band at 3350 cm^{-1}, and typical strong hydroxyl bands of free alcohol at 2850–3000 cm^{-1} and a hydrogen bonded band 3200–3570 cm^{-1}. The peak at 1142 cm^{-1} is an important assessment tool of the PVA structure. Fig. 2 of KDP incorporated in the PVA matrix depicts major peaks of both KDP and PVA. This confirms the presence of KDP nanocrystals in the PVA polymer matrix. There are changes in intensity, shift in positions and broadening of peaks and it is attributed to the interaction between the PVA support and KDP nanocrystals [8, 9].

(c) UV-Vis spectral analysis

Shimadzu UV-Vis – NIR Spectrophotometer model 3101 PC has been employed to investigate the optical properties of KDP nanocrystals incorporated in the PVA polymer matrix. The spectra recorded in the wavelength region of 200–3000 nm for the samples grown under different temperature conditions are depicted in fig. 3.

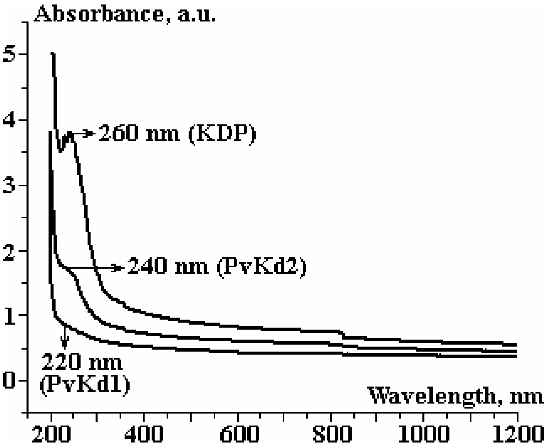

Fig. 3. UV-Vis spectra of KDP crystals in the PVA polymer matrix

From the UV absorption spectra, it is evident that the samples exhibit strong absorption peaks. The bulk KDP crystal exhibits an absorption peak at about 260 nm. The addition of the PVA polymer host environment to the KDP causes growth of nanocrystals, which is realized in a strong absorption peak at 220 nm, in the sample PvKd1. This suggests a blue shift with respect to the bulk KDP. For the sample PvKd2 an absorption peak is seen at 240 nm. A sharp peak in the absorption curve for the sample of PvKd1 is not observed. This is attributed to the broadening of the peak. A shift in the absorption edge of the spectra towards blue or red end of the spectrum is attributed to the crystal size in the polymer matrix. The observed blue shift (for the samples PvKd1 and PvKd2) and broadening of the peak (for the sample PvKd1) indicates the decrease in crystal size [10, 11]. Energy gap increases with decrease in particle size.

(d) Scanning Electron Microscopy (SEM) analysis

To observe the sizes and morphologies of KDP crystals in the PVA matrix, SEM analysis of the samples PvKd1 and PvKd2 have been carried out using JEOL JSM-5800 LV scanning electron microscope. The SEM micrograph images (fig. 4) reveal the growth of crystals of varying sizes in the PVA polymer matrix. The growth of nanocrystals of varying sizes in the host polymer matrix, confirmed through various spectroscopic techniques, is ascertained from the SEM images of the samples. Fig. 4,*b* shows crystals of larger sizes and spherical shapes compare to fig. 4,*a*.

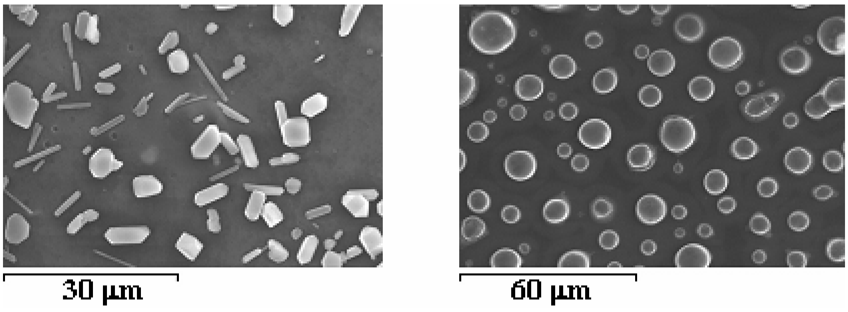

Fig. 4,a. PvKd1 *Fig. 4,b. PvKd2*

Fig. 4. SEM images of crystals grown in PVA Polymer matrix

In the SEM image of the sample PvKd1 (fig. 4,*a*), elongated crystals are seen. These variations in sizes and shapes may be tendency of nanocrystallites to agglomerate and form clusters, which results in non uniform distribution of the crystals in the polymer matrix. The crystals grown are of 300 nm in size. For the sample of PvKd2, the SEM image shows well defined spherical crystals. This is owing to the growth of crystals of bigger sizes. It is also seen that the crystals are mono dispersed in the PVA matrix. From the SEM images (fig. 4,*a* and fig. 4,*b*) it is evident that the filler particle dispersion and the crystallite sizes are different for the samples of PvKd1 and PvKd2, which are prepared at different temperatures. This implies that the temperature has a strong influence in the growth of the KDP crystals of varying sizes in the PVA polymer matrix. Other studies on the particle size determination using UV absorption spectrographs, XRD and SEM are in progress. Also, the grown samples will undergo the second order nonlinear efficiency studies.

Conclusions

Nanocrystals of KDP have been incorporated in to a PVA polymer matrix by using slow evaporation technique. By adjusting the temperature of the sample solution, it has been possible to achieve the growth of the crystal of different sizes in the prepared samples. Analysis of spectrographs confirms the presence of KDP nanocrystals in the polymer matrix. Moreover, the SEM analysis has ascertained the growth of KDP nanocrystals in the host PVA polymer matrix. The blue shift in the absorption edge of one of the samples shows the increase in band gap and decrease in the crystal size.

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Summary

Nanosized particles have become the focus of attention of researchers due to their outstanding optical properties as compared to those of bulk materials. The optical properties can be tuned or tailored if these nanocrystals of right materials are grown on a suitable host matrix. In this paper, a novel method of incorporating inorganic/organic crystals in a polymer matrix and the study of their optical properties are presented. By controlling the level of saturation of the solution and the rate of evaporation, an attempt has been made to incorporate nanocrystals in the host polymer. Inorganic material Potassium di-hydrogen phosphate (KDP) has been chosen because of its versatile properties and applications. Polyvinyl alcohol (PVA) is the host matrix since it has good aqueous solubility and exceptional transparency. The prepared samples, thin nanocrystals in a polymer sheet, have been characterised by various spectroscopic techniques such as X-ray diffraction (XRD), UV-vis spectrometer, Fourier Transform Infrared Spectroscopy (FT-IR) and scanning electron microscopy (SEM).