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Preparation and characterization of hydroxyapatite doped PVP/PVA blend as bioactivematerial

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ABSTRACT

This system is focusing on characterization and spectroscopic studies of PVA and PVP blend and the blend filled with various mass fractions (2.5, 5 and 10%) of HAp because it has great potential for applications in the medical purposes. The films have been prepared by solution casting technique. The characteristic properties of the films were examined by FT-IR, X-ray, SEM, TGA and DSC techniques from room temperature to 300 °C. XRD scans revealed the semicrystalline nature of the prepared films and demonstrated that complexation between the blend and the HAp. SEM and thermal studies confirmed these results. Three main weight loss regions were observed in TGA thermograms that reveal reduction in the thermal stability of the prepared samples as HAp content increases. Three main transition peaks were observed in DSC with a single T_g which indicates a good miscibility of the films. So, the present work can be used in various bio-applications.

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KEYWORDS

Polymer blend;
HAp;
X-ray;
EDX;
Thermal stability.

INTRODUCTION

Poly(N-vinylpyrrolidone), PVP is used in wide variety of applications. It is also interesting for biological point of view, since it has structural feature similar to those of proteins and has great potential for applications in the medical domain. PVP is a bio- and hemocompatible polymer with very low toxicity, so that materials coated with this polymer can be used as medical devices intended for implanting in the human body^[1].

PVP/PVA interactions have been described in many papers because of interesting properties of the resulting blend, which combines the features of both polymers^[2].

Cassu et al.^[3] attributes the good blending of PVP and PVA to hydrogen bonding which may take place between the proton-accepting carbonyl moiety in pyrrolidone rings and the hydroxyl side group of PVA. Hydrogen bonding is also responsible for solubility of both PVP and PVA in water. PVP/PVA blend is mainly applied in medicine as a skin dressing component and electrochemical as membranes^[4].

In the past 30 years, hydroxyapatite (HAp) implants have attracted much attention as an alternative substance for autogenous free bone grafting. It is the most prominent bioactive material since it forms a chemical bonding to bone and is widely used and investigated. The

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synthesized hydroxyapatite with bone-bonding properties is widely used in hard tissue replacement due to biocompatibility properties^[5-8].

HAp has attracted considerable attention as a bone substitute because of its mechanical properties and the similarity with the mineral constituents of human bone and teeth^[9]. Additionally, synthetic HAp has also been extensively studied in the fields of drug storage/release and the reconstruction of damaged bone to their biocompatible, Non-toxic, osteoconductive, and non-inflammatory properties^[10]. Moreover, because of the high stability and flexibility of the apatite structure, a great number of substitutions, especially the composites resulting from the cationic substitution are of potential application in the fields of dental and bone pathologies, bioceramics, luminescence, water purification, and catalysis^[11].

HAp is used in composite form (HAp-polymer) to retain useful bioactive properties as well as enhancement in mechanical properties. However, in the composite materials synthesized based upon a simple physical mixture there is neither a morphological control nor there is any chemical interaction at the organic-inorganic interface. The mechanical properties of the composite systems prepared in this manner are inadequate for bone replacement applications^[12].

HAp/polymer blend have been developed as bone cements, dental implants or bone substitute material^[13]. In this work, we report the synthesis of pure HAp and HAp embedded in PVP/PVA blend to form a bioactive composite for bio-applications. After that, study the physical properties of the prepared composites films using FT-IR, X-ray, SEM, TGA and DSC.

EXPERIMENTAL

Preparation of pure hydroxyapatite

0.1M (where M is the molarity) of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) solution was prepared by double distilled water and stirred it on a magnetic stirrer about 6h at temperature 85°C to ensure that the calcium ions (Ca^{2+}) have been composed and then 0.06M of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) solution was added drop by drop to the solution with stirring about 6h at the same temperature with adding some drops of ammonia solution to adjust pH between 11 and 12. A

milky white coloration was observed which ensure the formation of hydroxyapatite. All mixture was leaved at room temperature about 24h to precipitate HAp and then separate the precipitated amounts using center fusion with washing it five times by the distilled water to remove any traces or impurities reaction and put it in the drier for 5hr at 80°C to remove the moisture.

Preparation of HAp/(PVP+PVA) composites

Poly(vinyl pyrrolidone), PVP, was obtained from SISCO Research Laboratory Ltd. (Mumbai, India) in the form of a white powder. Poly (vinyl alcohol), PVA was obtained from E-Merck (Germany) in the form of crystals with $M_w = 14000$.

Equal amount of PVP and PVA (50:50) by weight percent were added to double distilled water (30%) with stirring the solution at 80 °C to complete dissolution until a suitable viscous solution is formed and then leave the solution for 3h at the room temperature to avoid the formation of bubbles, after that the calcium nitrate solution was slowly added. The calcium nitrate - blend solution was stirred slowly for 6h at the same temperature and then the proper amounts (Ca/P molar ratio of 5:3) of ammonium dihydrogen phosphate solution were added drop by drop to the mixture. A milky white coloration was observed when adjusting the pH~11-12 to ensure the formation of the HAp inside the polymer blend. The different concentrations (2.5, 5 and 10 wt%) of HAp were prepared inside the polymer blend. The prepared samples were kept in a desiccator until used.

Measurements

FT-IR absorption spectra were carried out using the single beam Fourier transform-infrared spectrometer (FT-IR-430, JASCO, Japan). FT-IR spectra of the samples were obtained in the spectral range of 4000–400 cm^{-1} . X-Ray diffraction scans were obtained using DIANO corporation-USA equipped using $\text{Cu-K}\alpha$ radiation ($\lambda=1.540 \text{ \AA}$, the tube operated at 30 kV, the Bragg angle (2θ) in the range of 5–60°. Scanning electron micrograph of the studied samples was performed using SEM (JEOL-JSM 6100), operating voltage at 30KV accelerating voltage. Electron dispersion X-ray (EDX) unit coupled with a scanning electron microscope was used to provide a semi-quantitative analysis of the chemical composition of hydroxyapatite in the

HAp/polymer blend films. TGA was used to characterize the decomposition and thermal stability of prepared samples. The mass of the samples is recorded while temperature is increase at constant rate. Differential scanning calorimetry of the prepared samples were carried out using (DSC-50, Shimadzu, Japan) with measuring temperature range from room temperature 500°C and the heating rate was 10°C/min.

RESULTS AND DISCUSSION

FT-IR analysis

Figure 1 a-c shows FT-IR absorption spectra of the pure PVP, pure PVA and PVA/PVP (50:50 wt%) polymer blend doped with 2,5, 5 and 10 wt.% of HAp recorded at room temperature in the region 4000–400 cm^{-1} . The spectra exhibit bands characteristic of stretching and bending vibrations of the films.

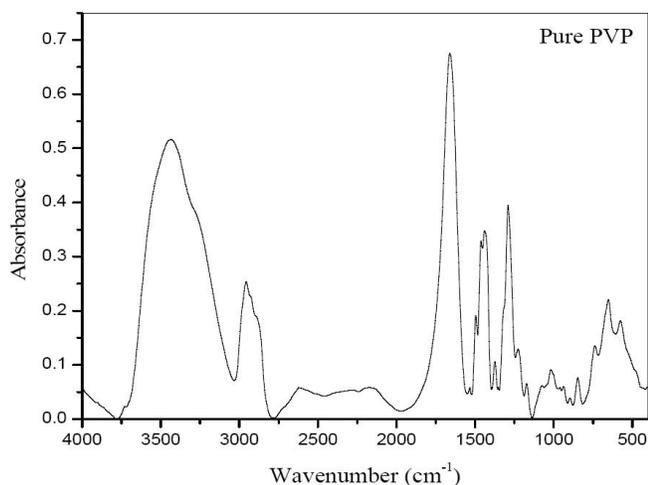


Figure 1a : FT-IR spectrum of pure PVP.

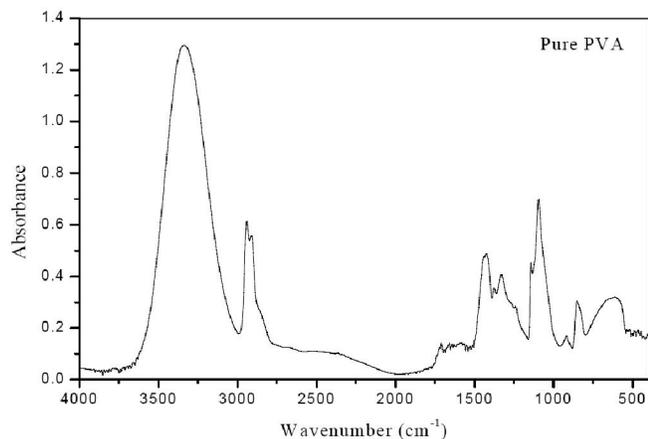


Figure 1b : FT-IR spectrum of pure PVA.

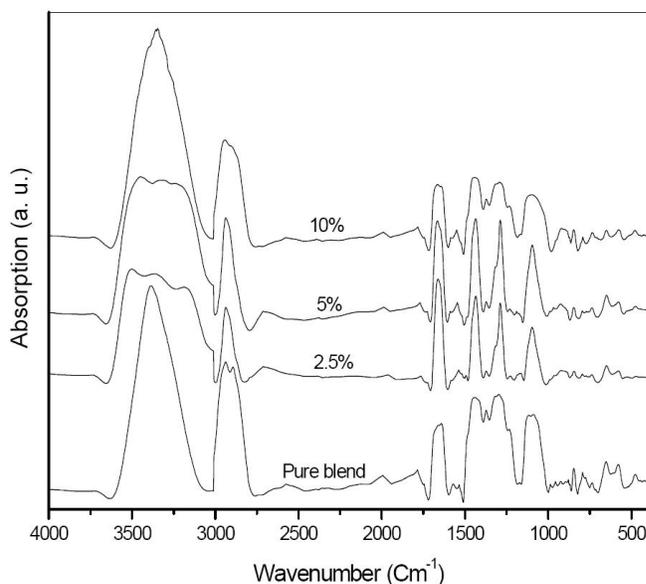


Figure 1c : FT-IR spectrum of PVP/PVA blend doped with 0, 2.5, 5 and 10 wt.% of HAp.

From the spectra, for pure PVP, very small absorption band at about 1539 cm^{-1} is assigned to the characteristic vibration of C=N (pyridine ring)^[14]. The absorption band at 962 cm^{-1} is assigned to the out-of-plane rings C–H bending^[15].

On the other hand, for pure PVA, the wide absorption band at about 3385 cm^{-1} is attributed to O–H stretching vibration of hydroxyl group. The band corresponding to CH₂ asymmetric stretching vibration occurs at about 2939 cm^{-1} . The band at about 1281 cm^{-1} corresponds to C–O stretching of acetyl groups present on the PVA backbone. Where appearing of C=O stretching is due to semicrystalline nature of the blends. The vibrational band at about 1647 cm^{-1} corresponds to C–O symmetric bending of PVA and PVP^[16,17].

It can be seen clearly from FT-IR spectra for HAp/polymer blend composite at different compositions of HAp fillers that the small characteristic band of HAp at 925 cm^{-1} is for PO₃; it was due to the P–O stretching^[18].

It can be seen that the intensities of some characteristic vibrational bands for those HAp/blend composite are decreased; it indicates that the amorphous regions in the composites polymer films are augmented.

X-ray diffraction

To obtain some information about the structural and crystalline of the prepared samples under investigations, X-ray diffraction scans were studies. Figure 2 represents

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the X-ray diffraction of pure PVA/PVP (50/50) blend and blend with 2.5, 5 and 10 wt.% of HAp. The figure shows small peaks with some ripples and relatively sharp peak centered at $2\theta \sim 20^\circ$ reveal the semicrystalline nature of the blend contains crystalline and amorphous structure. This peak corresponds to (110) reflection, which are consistent with the values in the standard card (JCPDS file No. 41-1049). Small peak at $2\theta \sim 10^\circ$ is observed for pure PVP, as reported in reference^[19,20]. It can be seen that, the peak intensity at $2\theta \sim 20^\circ$ decreased and the band width increased with increasing the concentrations of HAp. This is because the interaction between HAp and blend lead to a decrease in the intermolecular interaction between the polymer chains. These results indicate that the composites become more amorphous.

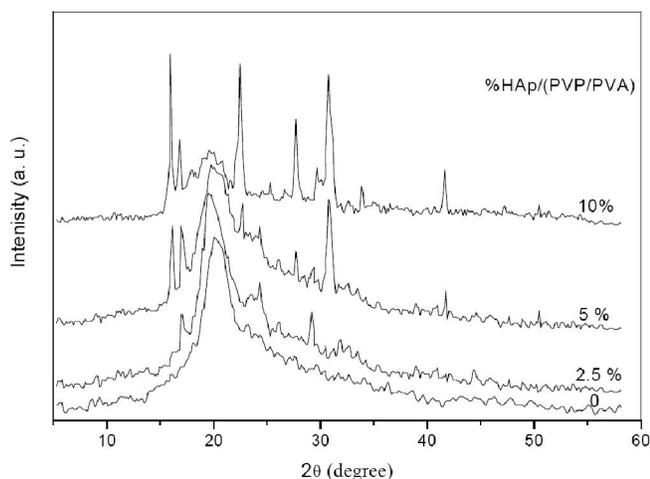


Figure 2 : X-ray diffraction scans of pure PVP/PVA blend films filled with 2.5, 5.0 and 10 wt% of HAp

Also may be there is a significant motion of polymer blend chains in the amorphous region or may be there are some defects existing at an interface between the polymer chain and the HAp filler.

For 5 and 10 wt.% of HAp, it is reveals that the crystallinity is increased and the sharp peaks appears at 16.88° , 22.52° , 27.71° , 30.68° and 41.55° are corresponding to (101), (111), (210), (300) and (400), respectively,^[21]. These peaks may indicate that the basic apatite phase is decomposed into different crystalline phases, these phases may be classified to α - $\text{Ca}_3(\text{PO}_4)_2$, β - $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_4(\text{PO}_4)_2$ and $\text{Ca}_4\text{P}_2\text{O}_3$ which identified among the original apatite^[22].

Scanning electron microscope

To investigate fully the effect of HAp content, the

prepared films were studied by scanning electron microscope. Figure 3a-d shows SEM micrographs of pure blend and HAp/(PVP+PVA) composite films with different concentrations of HAp. It is observed that most the prepared samples are translucent and homogeneous. For pure blend; image (a) shows a uniform surface morphology revealing a rather smooth surface. After adding a small concentration of calcium phosphate (2.5 wt% image (b)) an aggregation of the calcium phosphate particles or chunks that are randomly distributed on the top surface is observed. This indicates that the calcium phosphate particles fillers were completely dispersed-well within the polymeric matrix.

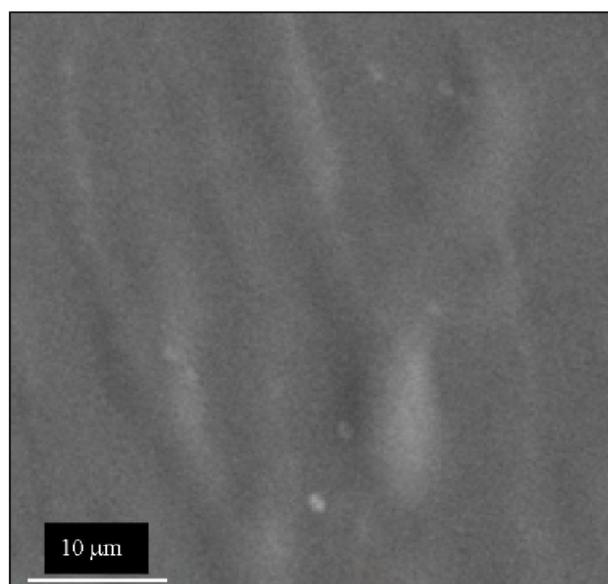


Figure 3a : Morphology of pure PVP and PVP polymer blend.

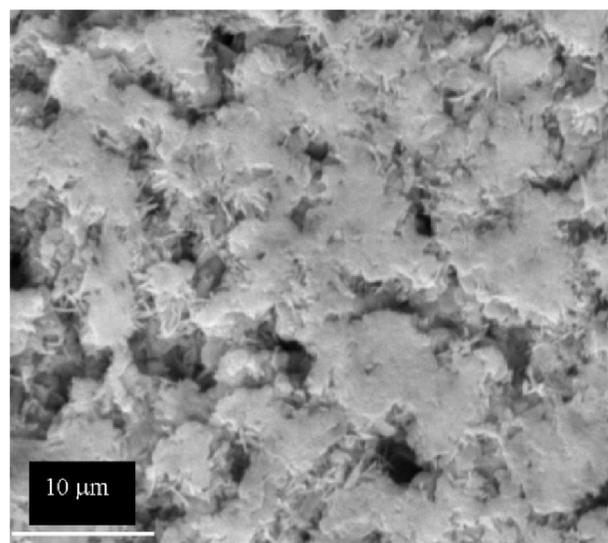


Figure 3b : Micrographs of PVP/PVA blend doped with 2.5 wt.% of HAp at 10000X.

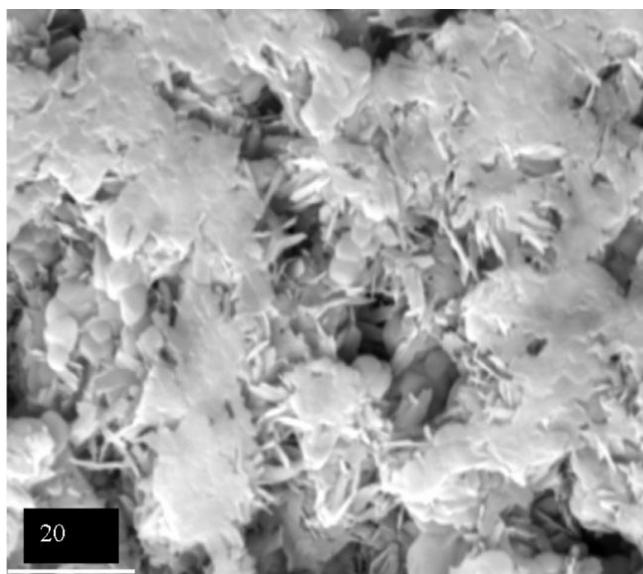


Figure 3c : Micrographs of PVP/PVA blend doped with 5 wt.% of HAp at 10000X.

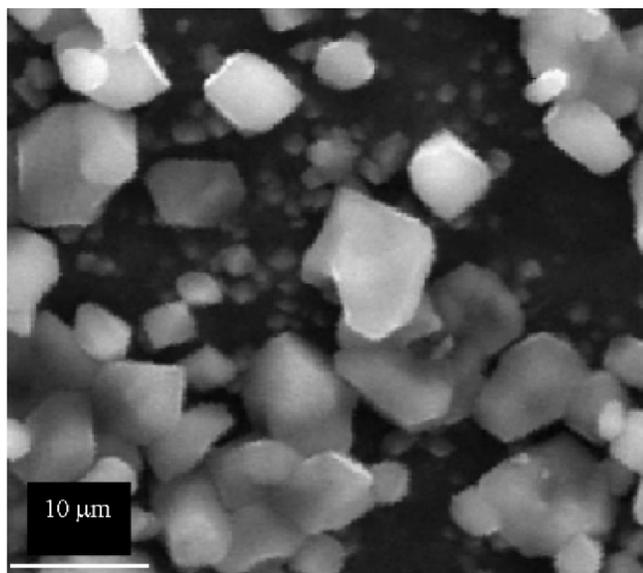


Figure 3d : Micrographs of PVP/PVA blend doped with 10 wt.% of HAp at 10000X.

It is revealed that there is more than one form of HAp such as plates, needles and bundles which are also observed with spherical form (5 wt.% image c). These results reveal that the polymer and the calcium phosphate are compatible and HAp is then formed which will be confirmed further with the EDX analysis. The surface of image d, 10 wt.%, is composed of relatively regular crystal and the crystals have strong tendency to aggregate.

EDX analysis

Another elemental composition analysis has been

used which is Energy Dispersive X-ray analysis (EDX), from which we can get qualitative and quantitative analysis about the specimen, i.e we can know each element in the sample and its concentration. In the present work as shown in Figure 4, calcium and phosphate had been detected in the samples where the concentration of the calcium is more than the phosphate as the peak of the calcium is much higher than the phosphate one with ratio Ca/P is 1.65 which confirm the formation of hydroxyapatite were the Ca/P ratio in human bone is 1.67^[23]. Thus the EDX analysis works as an integrated feature of SEM and for the present work, it is a confirmation for the composition of hydroxyapatite.

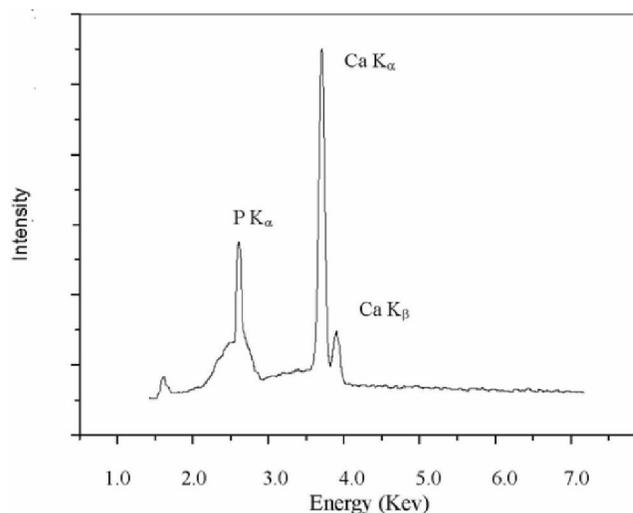


Figure 4 : EDX analysis for HAp/polymer blend composite of concentration 10 wt% of HAp

Thermogravimetric analysis

The thermogravimetric analytical measurements (TGA) of the HAp/polymer composite with various HAp compositions with constant heating rate (10 °C/min) are recorded in Figure 5. TGA curves in the figure reveal three main weight loss regions. The explanation of these regions as follows: a) The change of mass in the first region at temperature 50-100 °C could be attributed to the partial removal of physically and chemically adsorbed water and possibly lattice water. the total weight loss corresponding to this stage was about 3.77 wt.%, b) The second transition region (main region) from 280-435°C is due to the degradation temperature of the polymer blend^[24] with weight loss about 70 to 80 wt%; and c) The third stage at 440 °C is due to the cleavage backbone of polymer blend or so-called carbonation and the total weight loss was about 95-97 wt.%.

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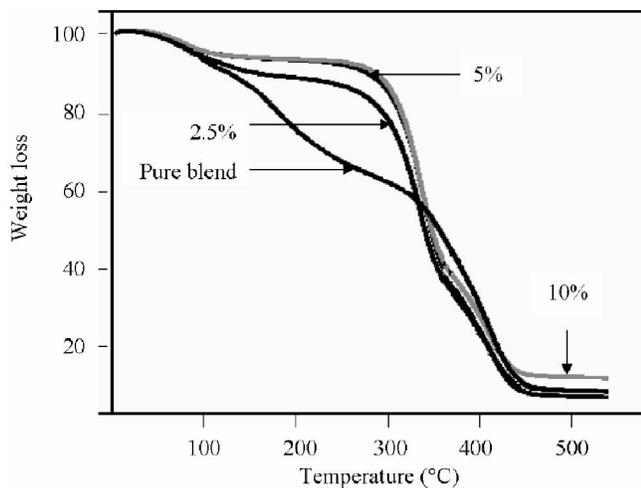


Figure 6 : Plotting $-\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$ against $1000/T$ (K^{-1}) for each sample.

Otherwise, the degradation peaks of the polymer HAp/blend composite samples are less intense and shift towards higher temperatures in the temperature range of $100\text{ }^\circ\text{C} < T < 440\text{ }^\circ\text{C}$ and also, we see that, pure polymer blend shows larger weight loss in this temperature range with improve of thermal stability due to the additive effect of the HAp filler and the chemical reactions between the blend and HAp.

Determination of activation energy

The activation energy for the thermal decomposition for TGA measurements of the present samples, which depends on the residual mass, can be calculated using integral equation of Coats and Redfern^[25]:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2}\right] = \log\left[\frac{R}{\Delta E}\left[1-\frac{2RT}{E}\right]\right] - \frac{1}{2.303} \frac{E}{RT}$$

where T is the absolute temperature, E is the activation energy in J/mol, R is the universal gas constant (8.3136 J/mol K), n is the order of reaction and α is the fractional weight loss at that particular temperature calculated as:

$$\alpha = \frac{w_i - w_t}{w_i - w_f}$$

where w_i is the initial weight, w_t is the weight at given temperature and w_f is the final weight of the sample.

For $n \neq 1$, Eq.2 reduces to:

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\left[\frac{R}{\Delta E}\left[1-\frac{2RT}{E}\right]\right] - \frac{1}{2.303} \frac{E}{RT}$$

By plotting $-\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$ against $1000/T$ for each sample, we obtain straight line as shown in figure 6. The value of activation energy (E) was calculated from the slope of the plot as:

$$E = 2.303R \times \text{slope}$$

The values of calculated activation energies of the samples are decreased from 64.25 to 30.21 KJ/mole with increasing the hydroxyapatite content which indicates that the HAp is intensively affects the polymer.

Differential scanning calorimetry

DSC measurements have been carried out to get some information about transition temperatures of the prepared samples and it is one of the most convenient methods to determine miscibility and thermal properties of polymer blend^[26].

The DSC thermograms obtained for pure polymer blend and the blend with different concentrations of HAp are depicts in Figure 7. All samples were heated from room temperature to $380\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere. From this figure, the observed thermal transitions can be assigned as follows: The broad exothermic peak (T_w) at about ~ 48 to $100\text{ }^\circ\text{C}$ for all samples could be due to a small amount of moisture present in them unless it is carefully vacuum dried.

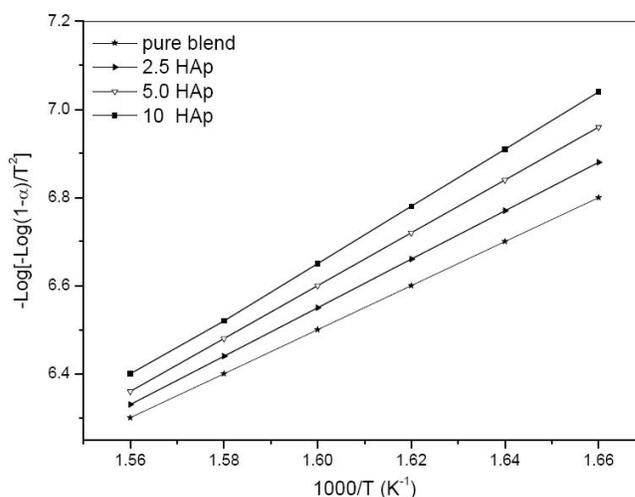


Figure 7 : DSC thermographs of (PVP+PVA) as a host material with 2.5, 5 and 10 wt%. of HAp.

The glass transition temperature (T_g) of pure PVA is about $84\text{ }^\circ\text{C}$ and $130\text{ }^\circ\text{C}$ for pure PVP^[27,28]. Pure PVA/PVP blend curve shows a small single transition at about $98\text{ }^\circ\text{C}$ attributed to T_g relaxation process re-

sulting from micro-Brownian motion of the main chain backbone^[29]. In general, DSC curve of a miscible polymer blend system shows a single T_g or melting peak, because the component polymer molecules would interact with each other^[30]. This interaction would affect the crystallization and glass transition temperature of the blend. The presence of this single T_g indicates miscibility of the blend. This miscibility should be promoted by hydrogen bonding formation between hydroxyl groups of PVA and carbonyl groups of PVP.

The exothermic peak centered at about 166 °C was attributed to α -relaxation associated with the crystalline regions^[31]. The position of α -relaxation temperature (T_α) was slightly shifted toward lower temperature and its intensity decreased with increasing the mixed filler content. The change in the position of T_α might mainly have been due to the effect of HAp on the orientation of crystals, crystallinity and microstructure of the samples^[32]. It is observed that it was disappeared at 10 wt%.

Sharp endothermic peaks observed at about 256 °C is assigned to melting temperature (T_m) and that at about 342 °C is assigned to decomposition temperature (T_d). The double endothermic peaks (for 2.5 and 5 wt.%) at about 330 °C may be assigned to second decomposition temperature (T_{d2}). It is clear that, the melting temperature decreased with the increase of HAp content. This decrease of T_m (from 256 °C to 223 °C) suggests a large influence of the intercalation treatment of the polymer blend matrices.

The position of T_d shifts toward lower temperatures from 342 °C to 307 °C indicating the formation of an intermolecular interaction between the polymer blend and mixed HAp. This confirms the results obtained by X-ray, FT-IR and SEM studies.

CONCLUSIONS

➤ PVA/PVP polymer blend pure and filled with different mass fractions of HAp have been prepared using solution casting technique. For XRD, it is revealed that the crystallinity is increased. Some sharp peaks indicate that the basic apatite phase is decomposed into different crystalline phases, these phases may be classified to α - $\text{Ca}_3(\text{PO}_4)_2$, β - $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_4(\text{PO}_4)_2$ and $\text{Ca}_4\text{P}_2\text{O}_3$ which identi-

fied among the original apatite.

- SEM for blend shows a homogenous smooth structure but for blend/HAp reveals that there is more than one form of HAp such as plates and needles. EDX analysis confirms the formation for the composition of hydroxy apatite.
- TGA thermographs reveal that the degradation temperature of polymer was shifted to lower temperatures and the thermal stability is reduced due to the chemical reactions between the polymer and HAp. DSC study confirmed miscibility of the blend due to the presence of single glass transition temperature. The magnitude of thermal degradation temperature suggested that addition of HAp to the blend films decreases the thermal stability; therefore, HAp molecules greatly affected the polymer structure.
- Hence, PVA/PVP polymer blend filled with HAp looks desirable and promising for fabrication of various bio-applications.

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Full Paper

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