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# Preparation and characterization of bioactive composites and fibers for dental applications

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ABSTRACT

*Objectives.* The present study was carried out to create composites and fibers using polyurethane (PU) with hydroxyapatite (HA) that could be used for dental applications.

*Methods.* Composites with varying HA concentration were prepared by solution casting technique. Similarly, PU–HA fibers with varying PU hard and soft segments and fixed HA concentration were also prepared. Various characterization techniques, such as, X-ray diffractometry, differential scanning calorimetry, scanning electron microscopy and Fourier transform infrared spectroscopy in conjunction with photo-acoustic sampling cell were employed to study the composites and fibers for changes in their physicochemical properties before and after immersion in artificial saliva at 37 °C for up to 5 days.

*Results.* The results indicated formation of amorphous apatite layers with maximum amorphicity in composites containing highest amount of HA with 5 days of immersion in artificial saliva. Similarly, fibers with more PU hard segment resulted in better transformation of crystalline HA to its amorphous state with increasing immersion time thus confirming the bioactive nature of the HA–PU fibers.

*Significance.* Concentrations of HA and PU hard segment along with the duration of immersion in artificial saliva are two major factors involved in the modification of solid-state properties of HA. The amorphous apatite layer on the surface is known to have tendency to bind with living tissues and hence the use of optimum amount of HA and PU hard segment in composites and fibers, respectively could help in the development of novel dental filling material.



## 1. Introduction

In the recent past, the use of polymer composites for biomedical applications has gained massive recognition. Composites are popularly used as dental filling materials for restoration of tooth caries and are much preferred over other dental restorative materials due to their user friendly properties [1,2]. Properties of the composites, such as their biological and mechanical characteristics, can be tailored by changing type

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and ratio of the ingredients which may affect the interfacial adhesion at the interface where polymeric matrix comes in contact with the surrounding environment [2,3]. Therefore, it has always been of great significance to develop a correlation between in vitro and in vivo results regarding the changes in physical and chemical properties, stability, degradation, etc. of the composites.

Polyurethane (PU) polymers are widely used as biomaterials in clinical applications. Over the years, their morphology, mechanical properties, synthesis and chemical properties have managed to gain significant attention of researchers due to their excellent and easily alterable properties [2,3]. PU is comprised of different groups of polymers containing linkages of urethane within chains of each polymer. The fundamental parts of the polymer include the hard segments containing isocyanates and diols as chain extenders, and the soft segment containing polyols. All these monomers determine the properties of the resulting polymer [2]. Degradation of PU is known to be affected by pH and temperature and it is reported that the body temperature (37 °C) along with its aqueous environment is sufficient to degrade a number of polymers [2–4]. The process of hydrolysis and the rate of hydrolytic degradation for PU are related to the ester and ether linkages in the structure which are determined by the composition of hard and soft segments [2]. Some other factors involved in affecting the biostability of PU are synthesis, processing, fabrication, surface area, physiological environment, etc. [2,5].

Hydroxyapatites (HA) due to their biocompatibility have found wide variety of uses in the field of dentistry and medicine. HA can exist in both crystalline and amorphous forms and is able to transform from one form to the other during preparation [6,7]. The availability of HA in different forms has resulted in variable results in the respective fields and has caused some restrictions regarding its requirements by US Food and Drug Agency [6]. Crystalline forms of HA are known to have better bond strength and cohesive properties whereas amorphous forms of HA are known to have high dissolution [7]. The amorphous forms of HA when present on the outer surface of coating promote the growth of osseous tissue better than the crystalline form but do influence the stability of the implant or composite if present in excess or throughout the material [6,7]. It is therefore of utmost importance to evaluate a particular form before its application.

The stability of dental composites in an aqueous environment depends upon its adequate mechanical properties with non-porous and smooth surfaces because these properties are profoundly affected by the action of water [1]. It has also been reported that dissolution or degradation in surface layers may take place in materials that remain in contact with body fluids and some loss of unbound components is suspected may be along with fluid uptake into the basic structure. This fluid uptake in discrete zones of the material may exert unwanted residual pressure on the tissues thus resulting in softening, degradation or leakage of the materials [2,6,8].

The object of the present investigation is to prepare PU–HA composites and fibers with varying HA concentrations in composites and PU hard segments in fibers and study the effect of artificial saliva on their stability and solid-state properties with respect to time. This study would help in the development of composites and fibers of PU–HA with appropriate solid-state properties that could be used in the field of dentistry as novel obturating materials.

## 2. Materials and methods

### 2.1. Materials

Biomedical grade PU (Z3A1) was obtained from Biomer Technology Limited (Runcorn, UK), HA (sintered powder, Captal® S) from Plasma Biotal Limited (Buxton, UK) and tetrahydrofuran (THF) (99.99%) from Fisher Scientific Inc. (Loughborough, UK). Versalink® P-650 (oligomericdiamine) was procured from Air products and Chemicals, Inc. (Allentown, USA), methylene diphenyl diisocyanate from Biesterfeld (Hamburg, Germany) and Cil Release® (1812 E) spray from Chemical Innovations Limited (Preston, UK). Artificial saliva (Saliveze™, Wyvern Medical Limited, UK) was purchased from a local pharmacy.

### 2.2. Preparation of PU stock solution

A stock solution of 5% PU was prepared in THF. The solution was stirred on a magnetic stirrer for 24 h at room temperature, protected from light.

### 2.3. Preparation of PU–HA composites by solution casting method

PU–HA composites were prepared in different ratios of 1:2, 1:4, 1:6, 1:8 and 1:10 by solution casting technique. From the stock solution, 10 ml of PU was taken out in a 25 ml conical flask and further stirred for 30 min. HA is insoluble in THF and forms a suspension when mixed with PU in THF solution. Therefore, each time HA powder was gradually added to the conical flask containing PU solution during stirring in order to obtain uniform dispersion. After adding all the HA powder of the desired ratio, the solution was further stirred for 30 min and then immediately poured in an aluminum mold. Before pouring of the suspension, the molds were sprayed with a mold releasing agent (Cil release®) in order to remove the composites easily from the mold. Slow evaporation of the solvent was achieved by covering the molds with a glass slide. Each set of composites was prepared in triplicate.

### 2.4. Preparation of PU–HA fibers by solution casting method

The composition of each type of fiber is given in Table 1. The fibers with varying amount of PU were prepared by thoroughly mixing Versalink® P-650 (PU-soft segment) and methylene diphenyl diisocyanate (MDI) (PU-hard segment) with HA powder to form a homogenous mixture before casting into a custom made aluminum mold. The mold was sprayed in the similar manner as described above to easily obtain the longitudinal fibers. Each set of fibers was prepared in triplicate.

**Table 1 – Compositions of PU–HA fibers.**

| Composition | PU | | HA (g) |
|---|---|---|---|
| | Versalink® P-650 (g) | MDI (g) | |
| 1 | 7.0 | 3.0 | 1.0 |
| 2 | 8.0 | 2.0 | 1.0 |
| 3 | 9.0 | 1.0 | 1.0 |
| 4 | 9.5 | 0.5 | 1.0 |

### 2.5. *Study of PU–HA composites and fibers in artificial saliva*

The dried samples (both composites and fibers) were carefully taken out from the molds and individually immersed completely in 5 ml of artificial saliva (Saliveze™). The saliva solution has a neutral pH and contains calcium chloride, magnesium chloride, sodium chloride, potassium chloride, dibasic sodium phosphate, carboxymethylcellulose, sorbitol, glycerol, methyl parabens, propyl parabens and mint flavor. Each sample was kept at 37 °C for 1, 3 and 5 days, respectively, mimicking natural oral environment.

### 2.6. *Characterization studies*

The effect of artificial saliva on the solid-state properties of composites and fibers was characterized by employing X-ray diffractometry, differential scanning calorimetry, scanning electron microscopy and Fourier transform infrared photoacoustic spectroscopy. Composites and fibers with no salivary exposure were used as controls and characterized in a similar manner. All the samples were stored in a desiccator during the course of characterization.

#### 2.6.1. *X-ray diffraction (XRD) analysis*

The change in the degree of crystallinity of samples was studied through XRD analysis using Philips PW 1830 diffractometer. The data were collected over the $2\theta$ range of 10–60° with a scan speed of 2°/min and processed by HBX software.

#### 2.6.2. *Differential scanning calorimetry (DSC)*

All the samples were analysed for their thermal behavior by using DSC 6 (PerkinElmer). Samples in an amount of $3.0 \pm 0.1$ mg were weighed accurately in an aluminum pinhole pan covered with a lid. An empty reference was also prepared in the same manner as that of the samples. Calibration of the instrument was carried out using standard zinc and indium. The sample along with the reference was heated from 30 to 350 °C with a rate of 10 °C/min and nitrogen was used as a purge gas with a flow rate of 20 ml/min. The data collected was processed using Pyris 7.0 software.

#### 2.6.3. *Scanning electron microscopy (SEM)*

In order to study the morphology of the prepared samples, SEM Inspect F (FEI, Holland) was employed with an accelerating voltage of 5 kV. The samples were mounted on 0.5 inch aluminum stubs using double-sided carbon adhesive tabs (12 mm) (Agar Scientific, UK). The stubs were made conductive with silver lining and then subjected to carbon coating using Speedivac carbon coating unit (Model 12E6/1598, UK). Several magnifications of the microscope were selected to obtain optimum details of the samples.

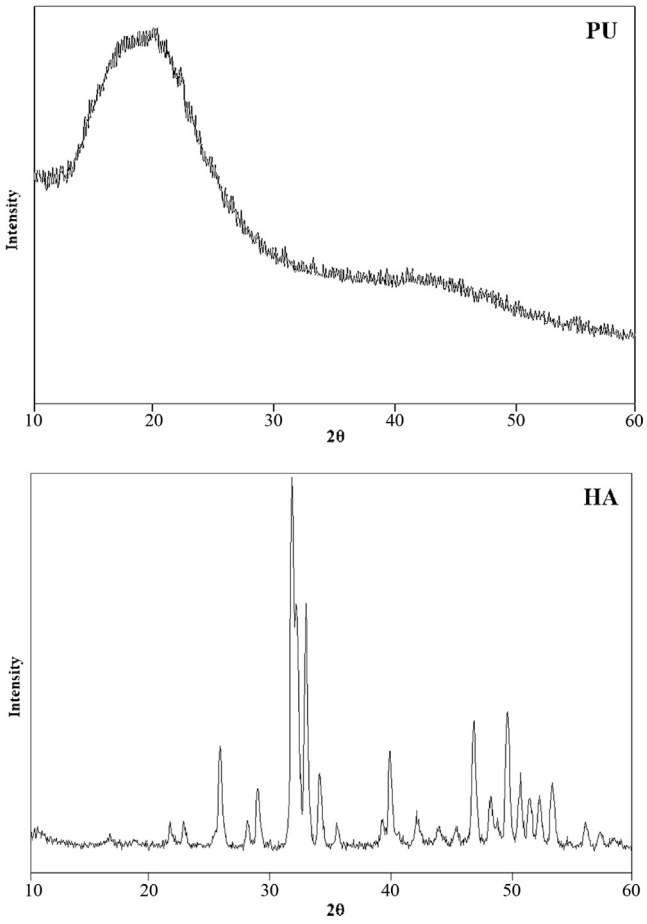


**Fig. 1 – XRD pattern of pure PU and HA.**

#### 2.6.4. *Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS)*

The structural properties of the composites and fibers were studied using a Thermo Nicolet Nexus FTIR spectrophotometer (Thermo Fisher Scientific Inc., USA) equipped with a photo-acoustic detector (MTEC Model 200, USA). Spectra were obtained at 8 $cm^{-1}$ resolution averaging 128 scans in the range 4000–400 $cm^{-1}$. The spectral data was processed using the OMNIC software version 7.4.

## 3. Results and discussion

### 3.1. *Formation of PU–HA composites and fibers*

In order to study the effect of increasing HA concentration on the physicochemical properties of the composites, the PU–HA composites were prepared in different ratios such as 1:2, 1:4, 1:6, 1:8 and 1:10. The slow evaporation of THF from the suspensions resulted in the formation of identical PU–HA composites with uniformly distributed surface properties. Similarly, the fibers also appeared identical except composition 4 (Table 1) which did not gain enough hardness on setting and hence,

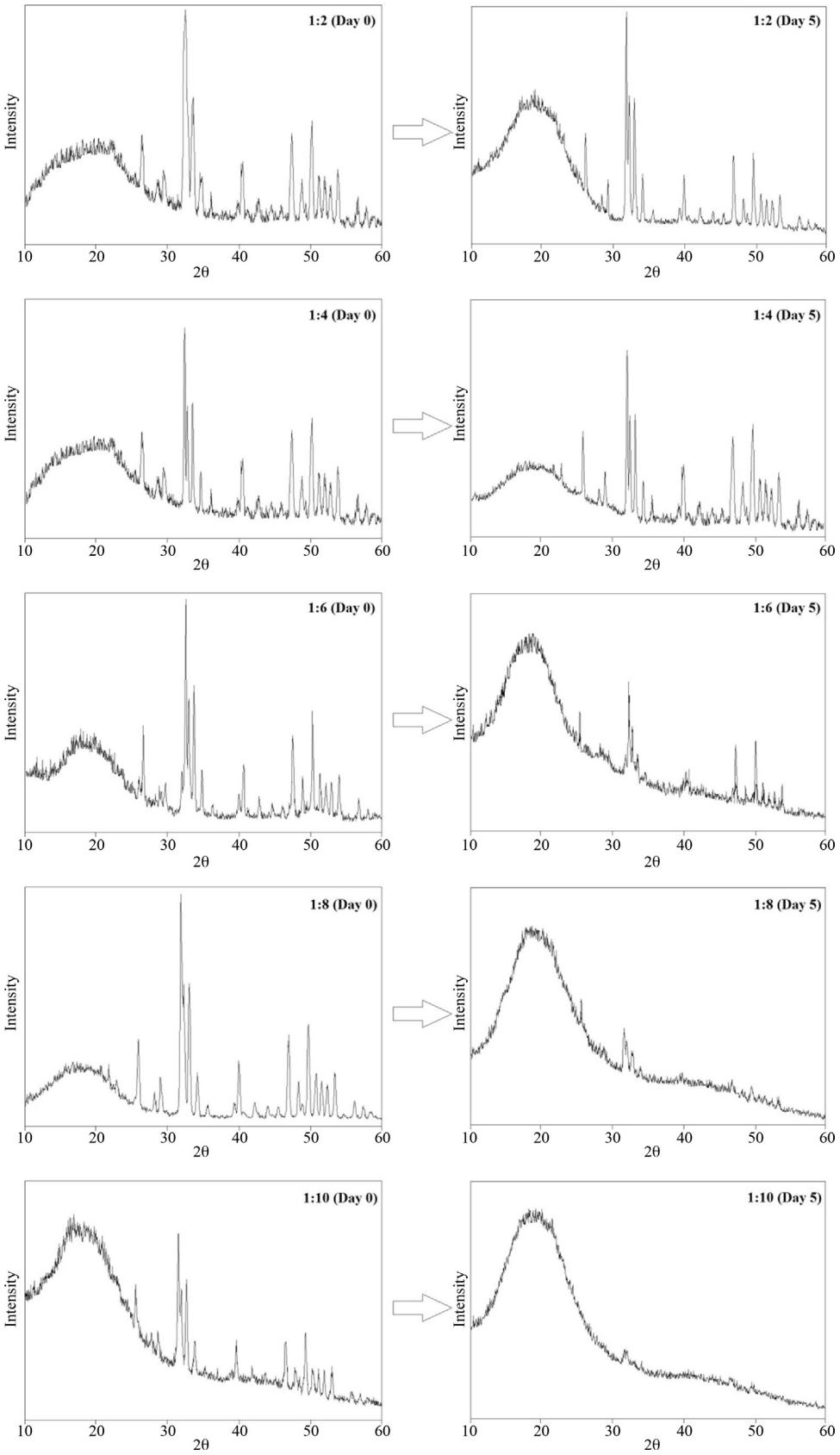


**Fig. 2 – XRD patterns of PU–HA composites (1:2–1:10) before (day 0) and after (day 5) immersion in artificial saliva.**

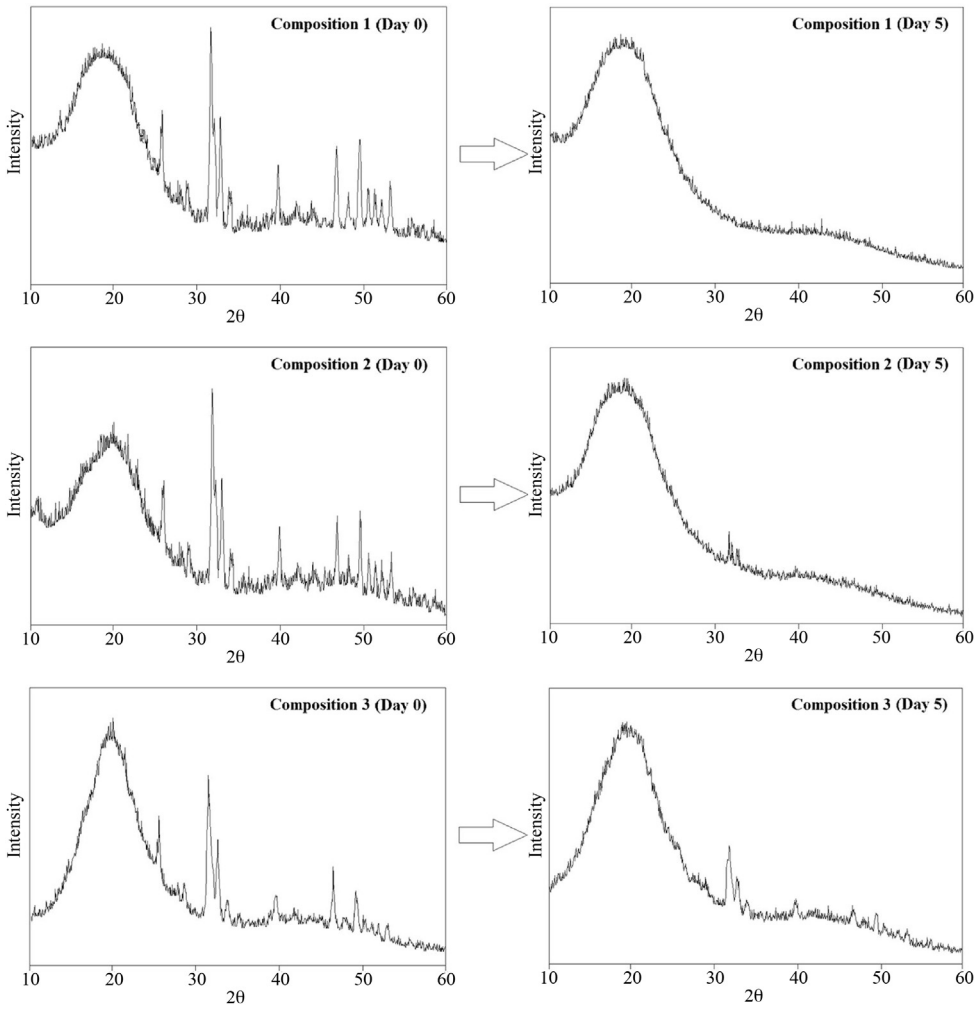


**Fig. 3 – XRD patterns of PU–HA fibers before (day 0) and after (day 5) immersion in artificial saliva.**

excluded from the study. The outcome of this composition made it obvious that the increment in the presence of hard segment of PU is crucial in making fibers of desired hardness. It appears that the interaction of HA with the hard segment of PU plays a pivotal role in obtaining good quality fibers. This may be due to the intra-urethane bonding that exists within the polymer backbone and its interaction with the hydroxyl or/and phosphate groups results in increasing the mechanical strength of the fibers.

### 3.2. *Effect of artificial saliva on PU–HA composites and fibers*

It is reported that interface adhesion between polymer and HA plays an important role as far as the properties of composites are concerned [9,10]. At times, the mechanical bond between the filler and polymer is weak which leads to cavitations [11] and thus softening or degradation of the material occurs. Similarly, particle size (nano or micrometer) is also known to affect the performance of HA. In a study performed by Domingo et al. [1], it was observed that water deleteriously affected the nature of few nano and micro sized composites of HA attributing to surface damage, softening, removal of portions of polymeric matrix and hydrolytic degradation, thus making the composition inadequate for the dental use.

In the present study, softening of surface layer has been observed in the PU–HA composites and fibers in artificial saliva incubated at 37 °C. The softening has increased with increasing HA concentration and the time of incubation i.e. 1:10 PU–HA composites at day 5 showed maximum changes, whereas comparatively fewer changes have been observed in composites of 1:2 ratios at day 5. This pattern of softening of composites in artificial saliva with increasing HA concentration indicates the formation of amorphous apatite layers on the surface of the composites, which due to the fluid uptake in the discrete zones has resulted in the softening of the composites.

Similarly, the fiber with more PU-soft segment becomes much softer with respect to time. No significant correlation has been found between the weight of samples before and after incubation, therefore, the data related to this has not provided significant values. In order to understand both the physical and molecular level changes, the composites and fibers were characterized by using XRD, DSC, SEM and

FTIR-PAS. The details of the results obtained by these techniques are discussed as follows:

### 3.3. XRD studies

Solids may be either crystalline or non-crystalline (i.e. amorphous) or a crystalline substance may occur in different polymorphic forms. XRD is a widely used technique to study the diffraction patterns of such materials. The crystalline materials show strong diffraction peaks whereas amorphous substances exhibit diffuse and halo diffraction patterns [12–14]. The XRD pattern of pure PU is given in Fig. 1 showing no defined peaks thus indicating the amorphous nature of the polymer. On the other side, the diffractogram of pure HA exhibited characteristic sharp peaks for the crystalline material (Fig. 1).

The composites of PU–HA show the combined pattern similar to their individual diffractograms at day 0 (Fig. 2) demonstrating the presence of both materials in their original forms. Comparison of the XRD results of the composites immersed in artificial saliva for 1, 3 and 5 days shows a marked effect of both HA concentration and immersion time period. Initially, very little or no change has been observed at day 0 and 1 in all the composites but with the passage of time a marked decrease have been observed at day 5 in the diffraction peaks of composites containing HA in a ratio of 1:6–1:10. Fig. 2 represents the diffraction patterns for the composites initially and after 5 days of immersion in artificial saliva, where a clear decrease in peak intensity of HA can be observed with almost no peak in the 1:10 ratio composites. The decrease in peak intensities with increasing HA concentration indicates the conversion of crystalline HA into its amorphous form. The transformation rate of HA in the composites with respect to immersion time period in artificial saliva is much faster than those previously observed in deionised water and phosphate buffer solutions (pH 7.4) at 37 °C [2]. Thus, the dissolution media along with the ratio of PU–HA complex plays an important role in converting crystalline HA to its amorphous form.

The diffraction patterns of the fibers after immersion in artificial saliva also show marked changes in their crystalline nature. Complete absence of peaks has been observed in composition 1, whereas a considerable decrease in the intensity has also been noted for compositions 2 and 3 (Fig. 3). These results suggest the transformation in the physical state properties of HA in presence of saliva with respect to increasing hard segment (MDI) quantity (Table 1).

No changes have been observed in the controls, which indicate the significance of artificial saliva in the modification of solid-state properties of the composites and fibers. The conversion of crystalline HA to its amorphous form might have occurred due to the formation of apatite layer on the surface of the composites, which happens due to the bioactive nature of the HA, facilitated by artificial saliva. Bioactive layer formed on the surface of the PU–HA composites is amorphous to start with and is known to recrystallize with time [15]. However, in this study no signs of recrystallization were observed in both composites and fibers for up to one week, which were stored in a desiccator.

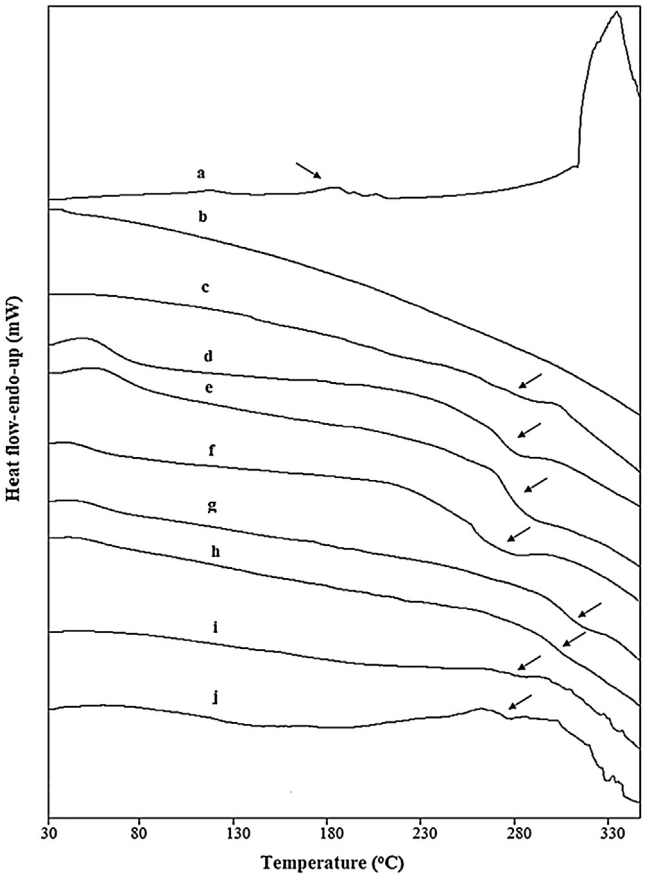


**Fig. 4 – DSC thermograms showing the change in $T_g$ (arrows indicating the change) in PU–HA composites and fibers. (a) PU; (b) HA; (c) PU–HA composite at day 0. Composites immersed in artificial saliva for 5 days of ratios (d) 1:2; (e) 1:4; (f) 1:6; (g) 1:8 and (h) 1:10. Fibers immersed in artificial saliva for 5 days of (i) composition 1 (j) composition 2.**

### 3.4. DSC studies

Glass transition temperature ($T_g$) is the temperature at which a polymer goes from a hard glass like state to a rubber like state and is considered as a method of characterization for polymeric materials. In DSC thermograms, $T_g$ usually appears as a step transition and not as a melting peak. The $T_g$ of PU is known to be at around 190 °C [16,17]. However, in the present study the composites show an increase in the $T_g$ of PU with a value of about 270 °C, which is further enhanced with increasing HA concentration to around 300 °C. Fig. 4 represents the DSC data for pure PU, HA and their composites and fibers at day 5 along with a typical thermal pattern of PU–HA composite at day 0. A melting peak of pure PU has been observed around 340 °C and its $T_g$ at around 190 °C. No $T_g$ has been observed in pure HA in the studied region of temperature. The DSC pattern of all three compositions of fibers exhibited decomposition of the polymer after 300 °C due to presence of higher amount of soft segments. Compositions 1 and 2 showed a $T_g$ effect at around 280 °C whereas no $T_g$ has been observed for

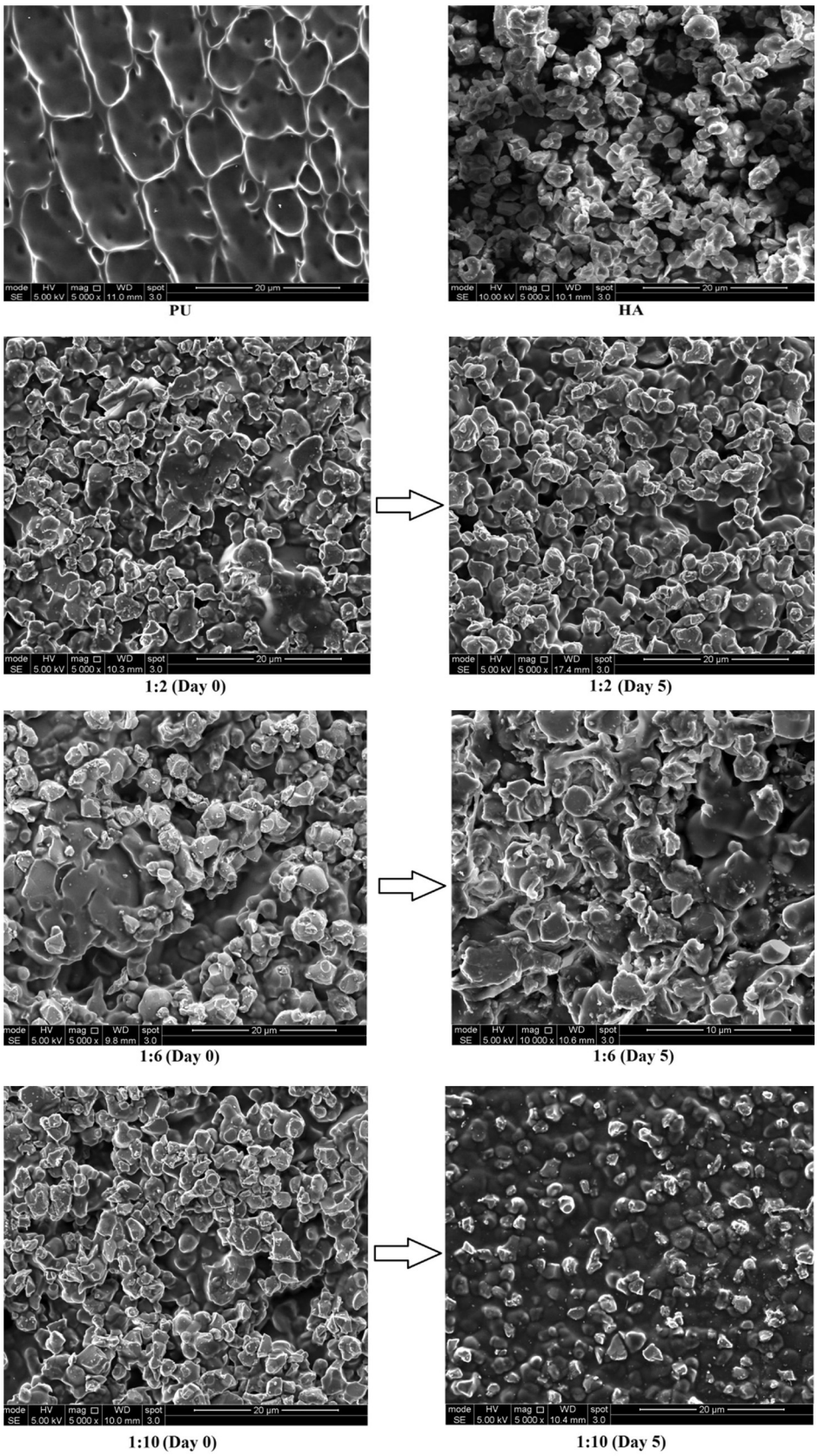


**Fig. 5 – SEM images of PU, HA and their composites before and after immersion in artificial saliva.**

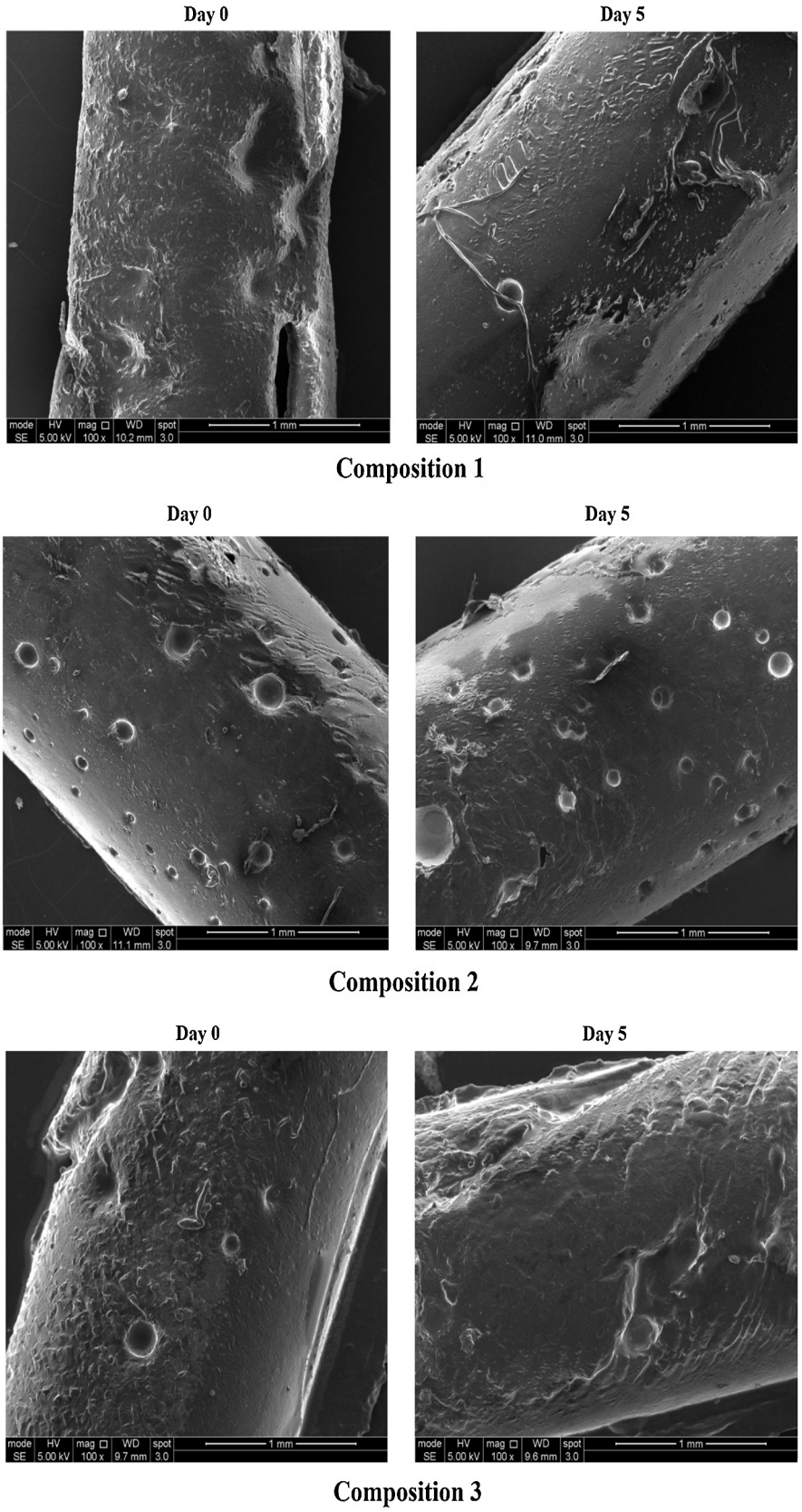


**Fig. 6 – SEM images of PU–HA fibers of compositions 1, 2 and 3 before and after immersion in artificial saliva.**

composition 3 of fiber due to higher degree of dissolution in the artificial saliva.

HA is made up of phosphates which are good glass formers [6] and polymers are known to form stable amorphous solid dispersions depending upon the glass forming ability of other substance [18]. This change in the $T_g$ of the molecular blend with increasing HA concentration indicates the complexation and conversion of crystalline HA into its amorphous form. These findings thus support the results of XRD, where increasing concentration of HA in PU–HA composites and fibers indicated the presence of its amorphous form in artificial saliva.

### 3.5. SEM studies

SEM was used to study the morphological changes in the PU–HA composites and fibers before and after incubation in artificial saliva. The HA particles with increasing concentration at day 0 appears almost identical in all composites. The gradual transformations in the appearance of all samples have been observed from day 0 to day 5 (Fig. 5). Negligible changes can be observed in composites with a PU–HA ratio of 1:2 after 5 days of immersion in artificial saliva. On the contrary, moderate modification in the particles can be noted in 1:6 ratio composites. A higher degree of transformation in the HA particles can clearly be seen after 5 days of incubation in 1:10 ratio composites (Fig. 5). The images with increasing HA concentration also reveal the presence of unbound HA particles on the surface of the composites at day 5 and further justifies the results of XRD and DSC.

The images for PU–HA fibers reveal interesting observations for the three different compositions (Fig. 6). Composition 1 shows slight surface changes at day 5 indicating mild effect of artificial saliva. On the contrary, compositions 2 and 3 appeared with pits or micro-fissures and the surface becomes comparatively rough and cracked at day 5. This indicates the composition and media effect, as an increase for PU-soft segment resulted in the alteration of the surface anatomy of the fibers in the presence of artificial saliva (Fig. 6). The SEM images give a clear indication that amorphous HA layer has been formed on the surface. This further confirms the deposit of amorphous apatite layer on the composite, which is due to the bioactivity of HA particulate.

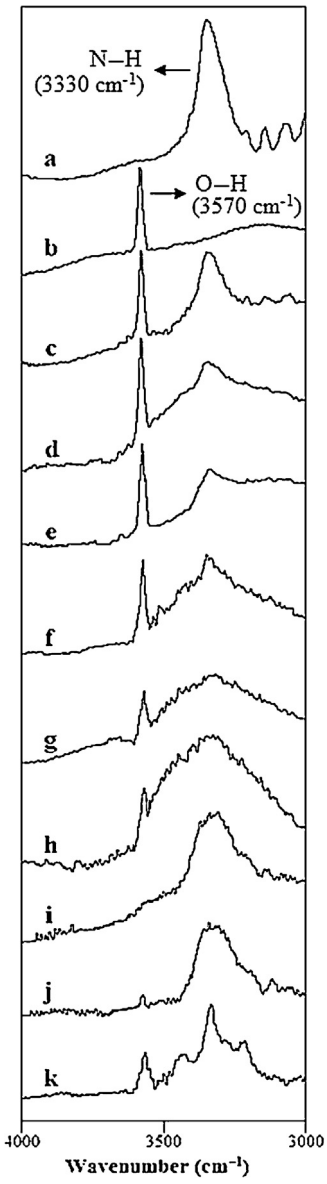


**Fig. 7 – FTIR spectra of (a) PU; (b) HA; (c) PU–HA composite at day 0; composites and fibers immersed in artificial saliva for 5 days of ratios (d) 1:2; (e) 1:4; (f) 1:6; (g) 1:8; (h) 1:10; (i) composition 1; (j) composition 2 and (k) composition 3.**

### 3.6. FTIR-PAS studies

FTIR-PAS was employed in the present study to identify the possible molecular interactions between PU and HA at different concentrations in artificial saliva for 0, 1, 3 and 5 days. PU is a polymer that contains N—H and C=O groups as electron donating sites which are responsible to form hydrogen bonds during complexation. However, the ether linkage (C—O—C) also contains oxygen atom as a proton acceptor and is involved in hydrogen bonding between hard–hard and hard–soft segments [2,19–21]. HA is a weak base and on dissociation ($pK_a \sim 7$) produces hydroxyl (OH) and phosphate ($HPO_4^{2-}$) ions that are capable of accepting protons. These OH and $HPO_4^{2-}$ moieties are thus merely responsible for any possible interaction during complexation [22].

The spectral study of PU–HA composites and fibers further confirms the effect of saliva, time of immersion and HA concentration on the physical state properties of the samples. The complexation between PU and HA could be identified most prominently in the region of N—H stretching at 3330 $cm^{-1}$ that exhibits broadening and change in the peak height intensity with increasing HA concentration (Fig. 7). However, the ether group of PU at 1110–950 $cm^{-1}$ shares the same region of peak for its phosphate moiety of HA, whereas no significant changes have been observed in the region of C=O group (1735–1700 $cm^{-1}$).

In the case of pure HA, the stretching band for O—H group could be observed at 3570 $cm^{-1}$ (Fig. 7). The conversion of crystalline HA to its amorphous form can be correlated with

lower hydroxyl content with variable porosity as a hydroxyl deficient material is reported to give rise to an amorphous phase [6,7,23]. Similar observations were noted in this study, where a decrease in the peak height of OH group at 3570 $cm^{-1}$ resulted with an increase in HA concentration with respect to duration of immersion of composites and fibers in artificial saliva (Fig. 7). The OH liberation could be due to the effect of saliva pH (i.e. neutral) and dissociation constant ($pK_a$) of HA, which is also around 7, thus resulting in the dissociation of hydroxyl content and formation of amorphous form of HA. These findings are in agreement with the results of XRD, DSC and SEM, where similar effect of increasing HA concentration with respect to immersion time in artificial saliva leads to changes in the crystallinity of HA in the composites and fibers.

## 4. Conclusions

The in vitro interaction studies between biomaterials and human body fluids are simple, effective and much more economical as compared to culturing cells and using animals and are also helpful in foreseeing the in vivo activity. The physicochemical behavior of PU–HA composites and fibers in artificial saliva has been monitored and the changes occurred are characterized through various techniques. Bioactive composites produced in this study and fibers fabricated indicate a strong interaction between PU and HA. The pre and post immersion results clearly indicated the transformation of crystalline HA to its amorphous state with an increase in HA concentration along with the duration of immersion in artificial saliva. The crystalline form of HA offers better bond strength and cohesive properties whereas on the contrary, its amorphous forms are known to provide better clinical effect than crystalline forms but they do pose a problem in the stability of the material which is also evident from the results of this study. The ratio of hard and soft segments of PU is also very important as excess amount of soft segment results in the softening of the fiber. The employed characterization techniques confirm the presence of unbound HA particles in composites thus forming apatite layer on their surface. The amorphous apatite layer is known to have tendency to bind with living tissues therefore the composites and fibers with optimum HA concentration and appropriate PU hard segment can be employed for dental applications after further clinical investigations.

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