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Production and evaluation of hydroxyapatite reinforced polysulfone for tissue replacement

M. WANG*, C. Y. YUE, B. CHUA
School of Mechanical and Production Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798
E-mail: mmwang@ntu.edu.sg

A variety of bioactive composites have been developed for tissue replacement over the last two decades. In this investigation, a new material consisting of hydroxyapatite (HA) and polysulfone (PSU) was produced and evaluated for potential medical applications. The HA/PSU composite containing up to 20 vol % of HA was studied at the initial stage. It was manufactured via a standardized procedure which included drying, blending, compounding and injection/compression molding. Defect-free composite samples (rectangular bars, discs and dumbbell specimens) could be obtained by injection molding. Thick composite plates could be made by compression molding. Both compounded materials and molded parts were assessed using a variety of techniques. It was found through scanning electron microscopy (SEM) that HA particles were well dispersed in the PSU matrix. Thermogravimetric analysis (TGA) verified the amount of HA in the composite. Differential scanning calorimetry (DSC) results indicated that the glass transition temperature (T_g) of the polymer matrix was not affected by the incorporation of HA. Rheological analysis revealed that PSU and the composite exhibited pseudoplastic behavior. For unfilled PSU, its viscosity decreased with an increase in temperature. The viscosity of HA/PSU composite increased with an increase in the HA volume fraction. It was shown through dynamic mechanical analysis (DMA) that the storage modulus of the composite was increased with an increase in HA volume percentage below T_g of the polymer, while tan δ was maintained at nearly the same level. It was established that water uptake reached an equilibrium after 7 days' immersion in distilled water for PSU and HA/PSU composite. After 7 days' immersion in distilled water, the storage modulus of the composite was decreased less than that of PSU.

1. Introduction

In the early 1980s, Bonfield *et al.* started the approach of using bioactive particles as the reinforcement in polymers to produce bone substitutes [1], considering the fact that bone itself at the ultra-structural level is a composite consisting of nano-size apatite crystals and collagen. Over the last two decades, a variety of bioactive composites having polymeric matrices have been developed [2–7] on the theory that the best material for replacing a body tissue should be identical or at least similar to that tissue [8, 9]. Furthermore, mechanical performance of these composites can be tailored by changing the type and amount of particulate bioceramics [10, 11] and enhanced by using suitable techniques that are readily available [12, 13]. One of the major advantages of using bioactive particle reinforced polymers for tissue replacement is that the problem of brittleness of monolithic bioceramics can be overcome while an *in vivo* bioactive response may be retained. It has been shown through *in vitro* and *in vivo* studies that bioceramic-containing composites do possess desired bioactivity [14] and can form strong bond with bone after implantation [15]. The successful clinical use of HAPEX™ [16, 17], i.e. hydroxyapatite (HA) reinforced high density polyethylene (HDPE), provides further stimulus for developing other bioactive composites for medical applications.

Polysulfone (PSU) is an amorphous polymer that has properties matching those of light metals. Its backbone aromatic structure leads to high glass transition temperature and resistance to thermal degradation. Favorable properties of polysulphone are high strength and stiffness, low creep rate, resistance to oxidation, excellent resistance to hydrolysis or reduction of molecular weight, stability in aqueous inorganic acids, alkalis and salt solutions, and bioinertness [18], which makes it a suitable candidate as the matrix of a bioactive composite. Furthermore, this polymer has high resistance to β-, γ-, X- and IR-radiation and can be steam-sterilized. In this investigation, particulate hydroxyapatite was

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*Corresponding author.

incorporated into a polysulfone and structure and properties of the resultant composite were evaluated.

2. Materials and methods

The hydroxyapatite used was grade P81B HA (Plasma Biotal, UK), which had a median size of 7.32 μm and was phase-pure HA according to previous analyzes [11]. The polysulfone used was Ultrason S2010 (BSAF Plastics, Germany) which had a medium viscosity and hence was suitable for injection molding. The production of HA/PSU composite followed a standardized procedure [19], with additional experimentation on injection molding. The as-received PSU pellets were first ground to powder using a Fritsch cutting mill. The PSU powder was then mixed with the HA powder in appropriate proportions and dried in an oven to remove moisture. Compounding of HA with PSU was conducted using a twin screw extruder (Haake Rheocord 90, Germany) with a maximum temperature of 360 °C. The residence time of materials in the barrel of the extruder was kept to a minimal to minimize polymer degradation. The extrudate was cooled in a water bath and pelletized through a Haake pelletizer. The composite pellets were subsequently dried and used for injection molding (Manumold 77/30, UK), with the maximum injection molding temperature being 360 °C. Defect-free rectangular bars, discs and dumbbell shaped samples were injection molded and thick composite plates were produced by compression molding. The manufacturing process is outlined in Fig. 1.

Scanning electron microscopy (SEM) was performed on a JEOL 5600 SEM for examining the HA particle dispersion and distribution in the PSU matrix. Samples (extrudates and injection molded parts) were cold mounted, ground, polished and gold-coated before SEM examination. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA 7 machine at a heating rate of 10 °C/min and over a temperature range of 40–900 °C in a purified oxygen atmosphere. A plot of weight percentage against temperature was obtained, showing the weight loss of the PSU matrix in the composite as temperature was increased, which could be used for calculating the HA percentage in the composite after completion of the test. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC 7 thermal analysis system employing three thermal cycles between 50 and 300 °C. A heating/cooling rate of 40 °C/min and a sample weight of approximately 8 mg were maintained for all tests. The glass transition temperature (T_g) was taken to be the midpoint between the pre-transitional and post-transitional baselines. Rheological studies were performed on a Shimadzu CFT-500D capillary rheometer. Plots of true viscosity versus true shear rate and true shear stress versus true shear rate were obtained for the unfilled PSU at different temperatures (250–340 °C). For HA/PSU composite with different HA contents, tests were conducted at the processing temperature of 310 °C. Three dies of a fixed capillary diameter of 1 mm but with lengths of 1, 2 and 10 mm, respectively, were used. Results obtained with these three dies were used in the Bagley plot method to obtain true shear stress, true shear rate and true viscosity.

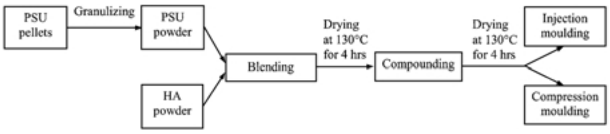

Figure 1 Manufacturing process for HA/PSU composites.

A preheat time of 300 s was used for ensuring full melting of the charge before tests commenced. For fluids showing pseudoplastic or quasi-plastic flow characteristics, the following equation applies:

$$\tau - \tau_y = k\acute{y}^n \qquad (1)$$

where τ is shear stress, τ_y the yield stress, $\acute{y}$ the shear rate, n, the flow behavior index and k a constant. For pseudoplastic flow, $n < 1$; for dilatant flow, $n > 1$.

Water absorption tests were conducted using distilled water at 37 °C. Samples of various HA contents but with the same dimensions (20 × 12.5 × 3 mm) were totally immersed in the water. They were taken from the incubator and weighed at regular intervals using a precision balance (AND HM 202, Japan; accuracy: 0.01 mg). As sample weight changes were more pronounced in the initial phase of water absorption, readings were taken at 10-min intervals for the first 1.5 h followed by hourly intervals for another 5 hours initially. The interval was then increased to one day. Water uptake was assumed to be weight increase of the sample. Dynamic mechanical analysis (DMA) was performed on a dynamic mechanical analyzer (GABO Qualimeter Eplexor®, Germany) with the three point bending configuration. Specimens were cut from injection molded bars and machined to the dimensions of 25 × 5 × 1 mm. A heating rate of 4 °C/min and a temperature range of 30–210 °C were used throughout this investigation. Tests were carried out with a maximum strain of 0.2% and at a frequency of 1 Hz. Furthermore, DMA was conducted on specimens that had been immersed in distilled water at 37 °C for 7 days. DMA was used to evaluate the viscoelastic properties of unfilled PSU and HA/PSU composite. For polymeric materials that obey Hooke's law, following equations exist:

$$E = \sigma/\varepsilon = E' + iE'' \qquad (2)$$

$$\tan\delta = E''/E' \qquad (3)$$

where E is dynamic modulus, E' the storage modulus, E'' the loss modulus and tan δ the loss tangent.

3. Results

It was determined from TGA graphs (Fig. 2) that the degradation temperature of HA/PSU composite was around 490 °C. Volume percentages of PSU were converted to its weight percentages (using $\rho_{\mathrm{PSU}} = 1.24\ \mathrm{g/cm^3}$ and $\rho_{\mathrm{HA}} = 3.16\ \mathrm{g/cm^3}$) and nominal compositions of the composite were compared to the results deduced from the TGA analysis (Table I). It was evident that intended compositions had been achieved for the composite. The glass transition temperature T_g of the PSU matrix was obtained from interpolation of the DSC thermogram in the third heating cycle (Fig. 3). It can be

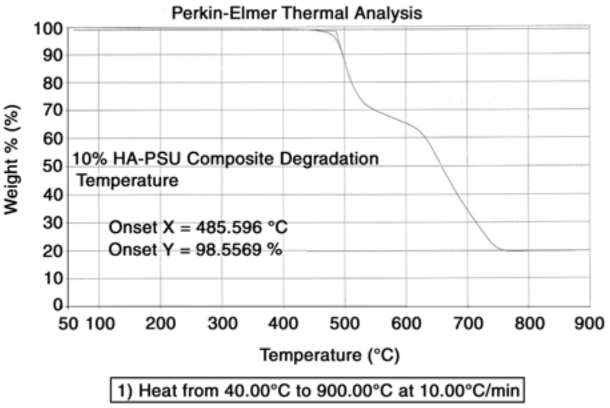

Figure 2 TGA graph of the HA/PSU composite (10 vol % of HA).

TABLE I Theoretical and actual composition of HA/PSU composite

Material	Theoretical PSU amount (wt %)	Actual PSU amount (wt %)	Difference (%)
Unfilled PSU	100.00	99.89	0.11
HA/PSU (5 vol% of HA)	88.18	88.02	0.18
HA/PSU (10 vol% of HA)	77.93	79.09	1.50

seen from Table II that T_g of PSU was not significantly affected by the incorporation of HA. SEM examination of polished samples revealed that HA particles were well dispersed in the PSU matrix for both compounded and injection molded materials (Fig. 4).

Rheological analyses showed that at a chosen processing temperature, with an increase in shear rate, the viscosity of PSU decreased while shear stress increased (Fig. 5). Over the temperature range of 250–340 °C, the higher the temperature, the lower the viscosity and the shear stress. Unfilled PSU exhibited pseudoplastic flow behavior. The incorporation of HA increased the viscosity of the system. At the processing temperature of 310 °C, the higher the HA content, the more viscous the composite (Fig. 6). For HA/PSU composite, with an increase in shear rate, the viscosity again decreased while the shear stress increased. Although the composite still exhibited pseudoplastic behavior, its flow behavior index n was significantly different from that of unfilled PSU.

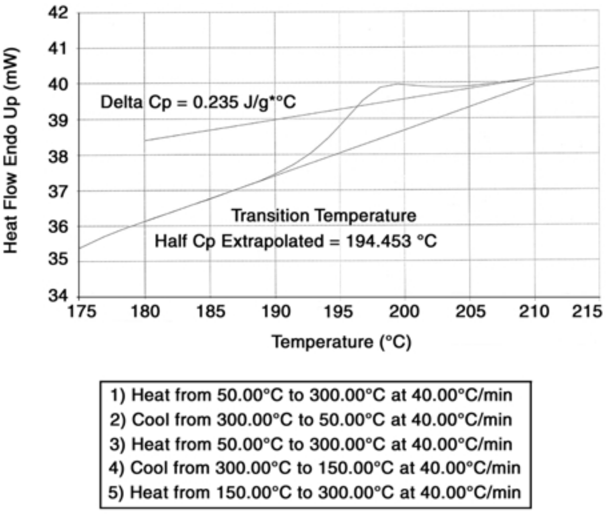

Figure 3 DSC thermogram of the HA/PSU composite (10 vol% of HA).

TABLE II Glass transition temperatures of PSU and HA/PSU composite

Material	T_g (°C)
Unfilled PSU	193.5
HA/PSU (5 vol % of HA)	193.2
HA/PSU (10 vol % of HA)	194.5

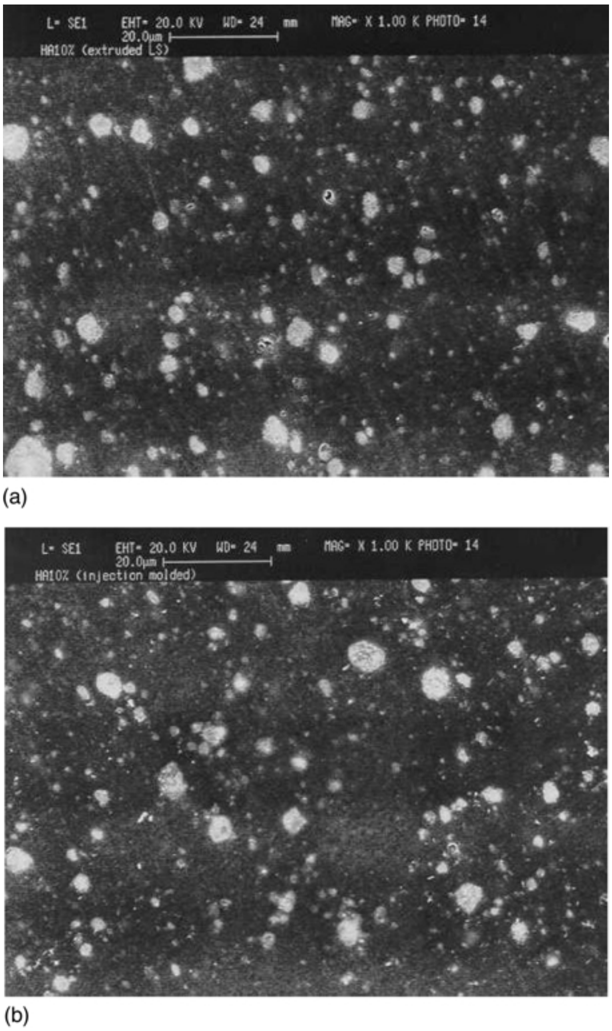

Figure 4 SEM micrographs of the HA/PSU composite (10 vol% of HA). (a) After compounding and (b) after injection molding.

It can be seen from Fig. 7 that water absorption reached an equilibrium after 7 days with a maximum water uptake of 0.4 wt % for the 10 vol % HA/PSU composite. DMA results revealed that the storage modulus of HA/PSU composite increased with an increase in the HA content and decreased with an increase in temperature (Fig. 8). Furthermore, water absorption by PSU and HA/PSU composite significantly reduced their modulus values. However, after 7 days' immersion in distilled water, the storage modulus of HA/PSU composite (containing 10 vol % of HA) was decreased less (from 4.64 to 3.98 GPa) than that of unfilled PSU (from 4.31 to 2.80 GPa). For PSU and HA/PSU composite, tan δ was maintained at nearly the same level (~ 0.02) up to 180 °C (Fig. 9), suggesting that the addition of HA did not reduce the damping ability of PSU.

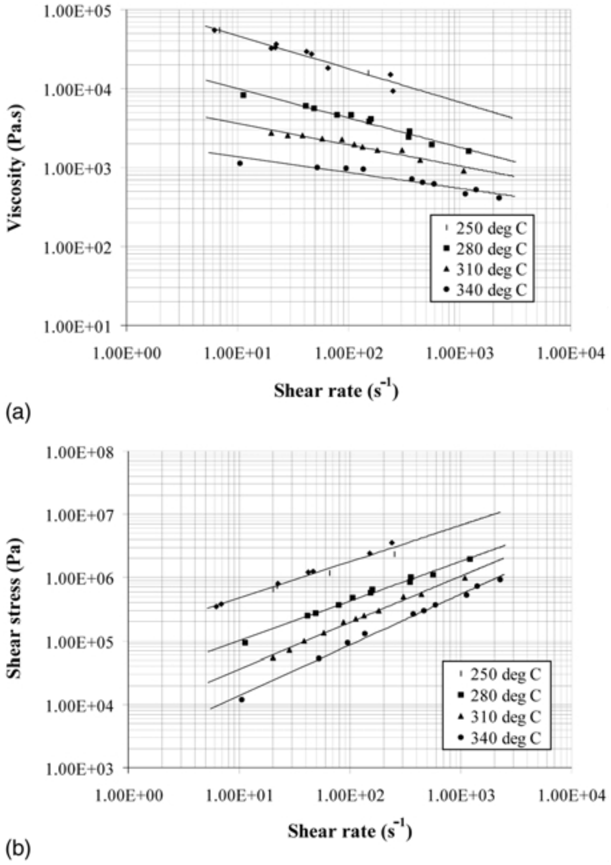

Figure 5 Rheological plots for unfilled PSU at different temperatures. (a) True viscosity vs. true shear rate and (b) true shear stress vs. true shear rate.

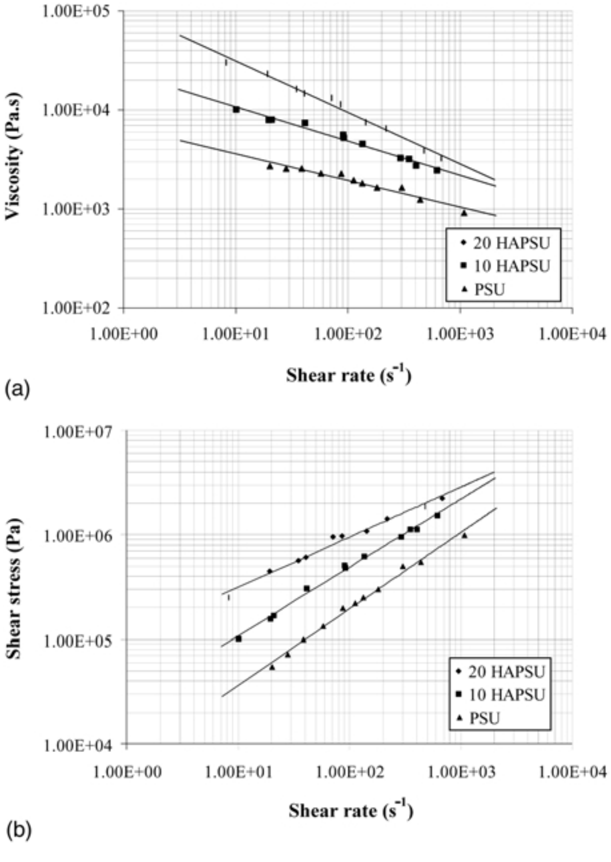

Figure 6 Rheological plots for HA/PSU composite at 310 °C. (a) True viscosity vs. true shear rate and (b) true shear stress vs. true shear rate.

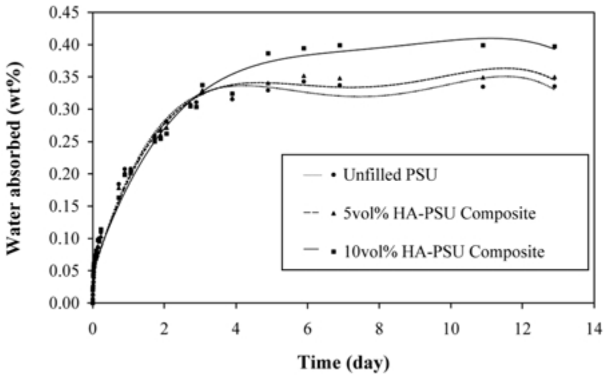

Figure 7 Water absorption of PSU and HA/PSU composite.

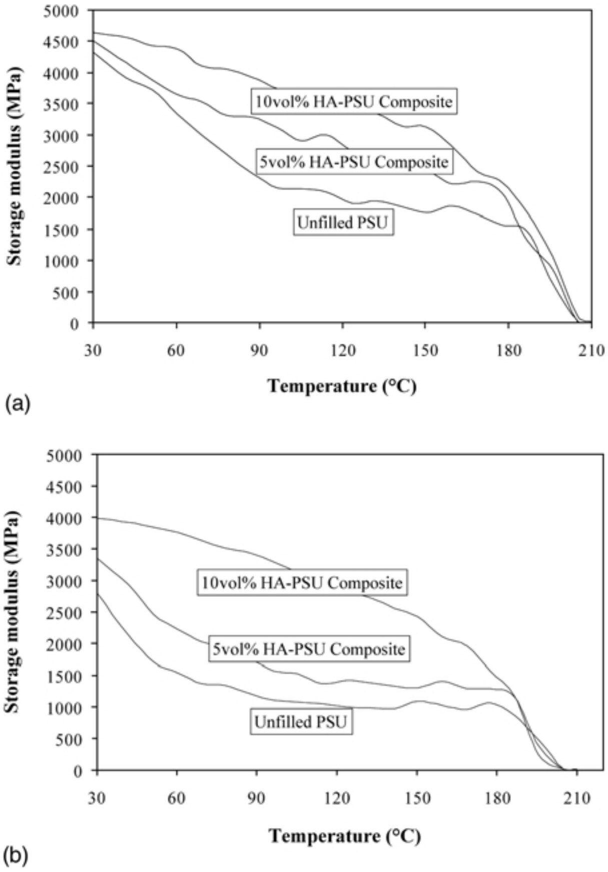

Figure 8 Effects of filler content and water absorption on the storage modulus of PSU and HA/PSU composite. (a) Before immersion and (b) after 7 days immersion in distilled water at 37 °C.

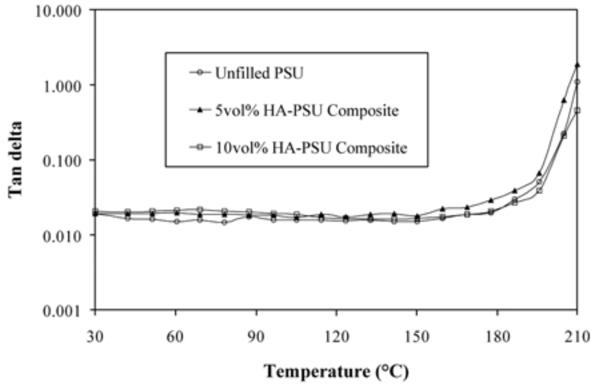

Figure 9 Loss tangent of PSU and HA/PSU composite.

4. Discussion

SEM and TGA results have indicated that good quality HA/PSU composite of intended compositions can be produced through the established manufacturing route. Glass transition temperature of the PSU matrix is not significantly affected by the incorporation of HA.

Capillary flow is a good measure of material behavior during flow through a nozzle into a mold [20]. Shear rates between 100 and $1000\,s^{-1}$ have often been used, as this is the typical range required for ceramic injection molding [21]. In this investigation, a shear rate range of $10\text{–}1000\,s^{-1}$ and a temperature range of 250–340 °C were used for rheological studies of PSU and HA/PSU composite. For unfilled PSU, the higher the temperature the lower the viscosity. PSU shows pseudoplasticity which is suitable for injection molding [20]. The HA/PSU composite also exhibited pseudoplasticity. Dilatant flow was not observed during the tests, which can occur when a critical level of shear rate is exceeded, causing the particulate filler to separate from the molten polymer. The viscosity of the HA/PSU composite at 310 °C is relatively high for injection molding. Higher temperatures need be explored together with possibly using a range of particle sizes of HA so as to reduce the viscosity of HA/PSU composite. However, due to polymer degradation at higher temperatures, a compromise has to be made for composite processing. Residence time is another important factor for consideration for extrusion and injection molding of filled polymers, which is affected by the processing temperature. Viscosity may also be decreased by using specific blend ratios of filler particle sizes [22].

Water absorption tests revealed that water uptake reached an equilibrium after 7 days immersion, with composite containing a larger amount of HA exhibiting greater water uptake. In composite materials, liquid penetration is generally through the diffusion process. In this system, diffusion of water occurred through both the PSU matrix and the HA-PSU interface. The greater the HA volume percentage, the greater the number of penetration sites (i.e. interfacial areas) for liquid diffusion. Therefore, composite with higher filler contents absorbed more water.

DMA results showed that an increase in HA content led to an increase in the storage modulus of HA/PSU composite. Storage modulus is the ability of a material to store energy and resist deformation. Therefore, HA particles act not only as a bioactive phase but also as a reinforcement in the composite. The incorporation of HA into PSU stiffens the system. This trend was also observed for the HA/HDPE composites [11]. After immersion in distilled water at 37 °C for 7 days, the storage modulus of both PSU and HA/PSU composite was reduced, but with the composite showing better resistance to reduction in stiffness. Composites have exhibited reductions in storage modulus because the interface between the HA particle and the polymer matrix allows water uptake thus reducing their mechanical properties. For unfilled polymer and composites containing lower amounts of HA, the uptake of fluid molecules tends to ease the mobility of polymer chains, leading to an increase in susceptibility to deformation. The loss tangent ($\tan\delta$) was maintained at ~ 0.02 until just below the T_g of PSU, showing that the damping ability of PSU is not significantly affected by the addition of HA particles. Water absorption does not affect the damping ability of HA/PSU composite either.

5. Conclusions

1. A processing route has been established for producing HA/PSU composites. HA particles are well dispersed in the PSU matrix and intended compositions of the composite can be achieved.
2. T_g of the polymer matrix is not affected by the incorporation of HA. Water absorption of PSU and HA/PSU composite reaches an equilibrium after 7 days' immersion in distilled water and water uptake can be up to 0.4 wt %.
3. Both PSU and HA/PSU composite exhibit pseudoplastic flow behavior. Viscosity and shear stress decrease with an increase in temperature. Increasing the HA content in the composite leads to increases in viscosity and shear stress.
4. The storage modulus of the composite is increased with an increase in HA content while $\tan\delta$ is maintained at nearly the same level below T_g of PSU. After 7 days' immersion in distilled water, the storage modulus of HA/PSU composite is decreased less than that of unfilled PSU.

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