JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **11** (2000) 481–489

Thermal analysis studies of poly(etheretherketone)/hydroxyapatite biocomposite mixtures

B. J. MEENAN*, C. McCLOREY, M. AKAY
Northern Ireland Bio-Engineering Center (NIBEC), School of Electrical and Mechanical Engineering, University of Ulster, Shore Road, Newtownabbey, Co. Antrim, Northern Ireland, BT37 0QB, UK
E-mail: BJ.Meenan@ulst.ac.uk

Biocomposite formulations which have the potential to combine the proven mechanical performance of poly(etheretherketone) (PEEK) with the inherent bioactivity of hydroxyapatite (HA), may have a utility as load-bearing materials in a medical implant context. The effect of thermal processing on the relevant properties of the PEEK and/or HA components in any fabricated composite structure is, however, an important consideration for their effective exploitation. This paper reports the results of a detailed thermal characterization study of a series of PEEK/HA mixtures using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC). The TGA analyses show minimal weight loss for all of the mixtures and for a pure PEEK sample up to ≈530 °C. Above this point there is a sharp on-set of decomposition for the PEEK component in each case. The temperature at which this feature occurs varies for each mixture in the approximate range 539–556 °C. This observation is supported by the presence of exotherms in the corresponding DSC scans, in the same temperature region, which are also assigned to PEEK decomposition. The temperature at which the degradation on-set occurs is found to decrease with increasing HA contribution. The use of the modulated DSC technique allows a number of important thermal events, not easily identifiable from the data obtained by the conventional method, to be clearly observed. In particular, the glass transition temperature (T_g) of the polymer can now be accurately determined. Using these thermal analysis data, calculations of the % crystallinity of PEEK in the mixtures have been made and compared with that of a 100% polymer sample. From these studies it is evident that the presence of HA does not adversely affect the degree of crystallinity of the PEEK component in the mixtures of interest over the thermal range studied.

1. Introduction

Research into providing biomaterials with both improved mechanical performance and enhanced bio-functionality for use in a hard tissue load-bearing implant environment is of increasing importance [1–4]. The more so, since the replacement of prosthetic devices that have failed *in vivo* currently accounts for a significant proportion of expensive joint replacement operations [2]. Current emphasis of much of this research effort is directed towards the development of so-called ''second generation'' biomaterials which are bioactive and hence, specifically designed to ''enhance the restoration and repair of the body tissue function'' in a medical implant context [3, 4].

Bioceramic systems based on hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), are an important class of bioactive materials which can promote bone regeneration and hence can provide strong implant/host tissue interfacial fixation in medical and dental devices [5–9]. The use of HA in load-bearing orthopaedic devices is, however, restricted due to inadequate mechanical properties of strength and fracture toughness [5]. Conversely, polyaromatic materials, such as poly(etheretherketone) (PEEK, $(\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}CO\text{-})_n$), are polymers with excellent properties for a range of engineering applications [10–12]. PEEK is a semi-crystalline, high performance, linear thermoplastic polymer that exhibits excellent chemical resistance, has high thermal stability and superior mechanical properties. It has a glass transition (T_g) at ≈ 145 °C, a crystallization peak (T_c) at ≈ 160 °C and a melting point (T_m) of ≈ 343 °C [12]. The various chemical, physical and thermal properties of PEEK have been studied and reported in detail elsewhere [13–15].

---

*Author to whom all correspondence should be addressed.

0957–4530 © *2000 Kluwer Academic Publishers*

With regard to its potential as a biomaterial, PEEK is of particular interest since components can be readily formed using conventional thermoplastic molding and extrusion techniques. Moreover, the material can be repeatedly sterilized without marked deterioration of its high mechanical strength [16]. Carbon fiber-reinforced PEEK has been suggested for use in total hip replacement (THR) prostheses and several studies have addressed the optimization of the system for this orthopaedic application [17–20]. It has also recently been suggested as part of the retaining ring in an acetabular cup assembly of a THR system [21]. In addition to its superior mechanical performance, the biocompatibility of PEEK has been assessed [22–25]. In general, it is found that it is not cytotoxic and has a similar foreign body response to that observed for ultrahigh molecular weight polyethylene (UHMWPE) [23]. It has also been found to have a positive stimulatory effect on osteoblast protein content, which suggests that it may then encourage bone ingrowth in a hard tissue implant context [24].

In human cortical bone and associated hard tissues, HA and related minerals are present as one component of a biphasic composite with collagen fibers as the other. It is this relationship then, that gives bones their strength and flexibility. Hence, biocomposite formulations based on various bioceramic/polymer mixtures have been suggested for use in the manufacture of hard tissue implant prostheses to provide for improvements in load-bearing orthopaedic applications [25–27]. However, the success of this approach has, to date, been limited and only a very few systems have been shown to have significant benefit as implants *in vivo*. In particular, HAPEX^{TM}, based on a polyethylene/hydroxyapatite formulation, has been shown to be an effective biocomposite [28, 29]. However, the medical applications of this material have, to date, been limited to non-load-bearing situations such as orbital floor reconstruction and middle ear implants [30].

It is proposed here that the use of PEEK/HA composites may provide biomaterials with significantly enhanced properties for a range of orthopaedic implant applications. The presence of PEEK can provide the required mechanical strength and fracture toughness, particularly in major load-bearing situations. In addition, the use of HA with its proven bioactivity provides for the possibility of new bone growth, assuming that there is enough of this material at the surface and therefore at the implant/host tissue interface. The ceramic component may also provide some reinforcement to the polymer matrix, particularly if it can be presented in the form of fibrous ''whiskers''. In order to harness this potential, however, it is first necessary to understand the effects of thermal processing on polymer/bioceramic mixtures. In this way, the optimal formulation and accurate control of the relevant properties during subsequent thermal processing of these systems may be determined thereby allowing for their effective exploitation.

Accordingly, this paper reports the results of a detailed thermal characterization study of a series of PEEK/HA mixtures using thermogravimetric and calorimetric techniques, namely thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC). It is suggested that these techniques can provide much important information on the thermally-induced behavior of each component in the presence of varying amounts of the other material. These data will then be of direct value in determining the optimum processing parameters necessary for the fabrication of suitable biocomposite structures with highly controled mechanical properties and enhanced bio-functionality.

2. Methodology

2.1. Preparation of PEEK/HA mixtures

A series of poly(etheretherketone) (450P standard viscosity grade, Victrex plc, UK) and hydroxyapatite, (bioceramics grade, Merck KGaA, Germany) mixtures with nominal % wgt/wgt compositions of 90/10, 70/30, 50/50, 30/70, and 10/90 % PEEK/HA were prepared from suitable amounts of the source powders. In each case, the combined powders were placed in a rigorously clean agate mortar and manually ground for approximately 20 min to provide for intimate mixing. In order to determine accurately the working composition of each of the mixtures, as presented as samples to the thermal analysis equipment, standard burn off (ashing) tests were carried out. A series of six 0.12 g samples were taken from each mixture, placed in vitreosil crucibles and each of the samples ashed in a tube furnace (Carbolite Ltd, UK) at 800 °C for 2 h. The residual weight of each sample, assumed to represent the ceramic content only, was determined post-processing, and the average percentage weight loss, taken to be the total polymer contribution, calculated appropriately. By way of direct comparison, samples of the pristine PEEK and HA powders were treated in the same way.

2.2. Thermogravimetric analysis (TGA)

The TGA scans for the various mixtures and individual component powders were recorded on a TA Instruments Model 951 Auto TGA system using platinum sample pans. In all cases, the purge gas used was a 60/40% nitrogen/air mixture at a flow rate of 100 cm^3/min. A heating ramp of 10 °C/min to a maximum temperature of 750 °C was used throughout.

2.3. Conventional and modulated differential scanning calorimetry (DSC)

For the studies reported here, the conventional DSC scans were recorded on a TA Instruments DSC 2000 system using aluminum sample and reference pans. During analysis, nitrogen gas was passed through the sample cell at a flow rate of 50 cm^3/min. The heating ramp applied was 10 °C/min to achieve a maximum temperature of 650 °C for the PEEK and PEEK/HA mixtures and 450 °C for the 100% HA material.

The Modulated DSC scans were recorded on a TA instruments MDSC 2920 system, again using aluminum pans. In this case, a nitrogen purge gas flow rate of 30 cm^3/min was employed. The heating ramp comprised an underlying rate of 2 °C/min overlaid with a sinusoidal oscillating temperature utilizing a 50 s period and an amplitude of ±0.265 °C, to a maximum temperature of

400 °C. An indium reference standard was used to calibrate the instruments used in both sets of calorimetric experiments.

3. Results and discussion

3.1. Determination of PEEK/HA mixture composition

As the PEEK/HA mixtures were prepared manually, burn off tests were used to confirm the actual % wgt/wgt compositions. Table I shows the nominal and experimentally determined (averaged) compositions of the mixtures of interest, after ashing the samples in air, at 800 °C for 2 h. It is clear from these data that the actual compositions get closer to the theoretical values as the % wgt of PEEK increases and, hence as the HA contribution decreases. In general, with the exception of the 25/75% PEEK/HA material, the other mixtures were found to be within ± 10–15% of their nominal values. Hence, this lowest PEEK content system was not fully characterized in the subsequent thermal analysis studies. Ashing of a 100% PEEK sample in air results in no measurable residue while the HA material shows $\approx$ 2% decrease in weight. These observations were taken into account when calculating the compositional values for the various PEEK/HA mixtures. It should be noted that carrying out the ashing studies at 1000 °C does not significantly change the compositional data obtained. Nor is there any significant variation in the data observed when the ashing duration is increased to four hours at either of the temperatures employed.

3.2. TGA, DSC and MDSC studies of PEEK and HA powders

In TGA, changes in the weight of a known amount of a material are monitored as a function of temperature (or time), while it is purged with an inert gas, normally nitrogen or a nitrogen/air mixture. In this way, TGA can provide quantitative information resulting from any processes that might cause detectable weight changes during the controled heating ramp. This enables the stoichiometry and kinetics of any thermally-induced reactions to be followed directly. The technique has been used here to study the nature of any interaction between HA and PEEK which might result on heating the mixtures, over the composition range of interest. The data have been directly compared to the scans originating from the individual component powders.

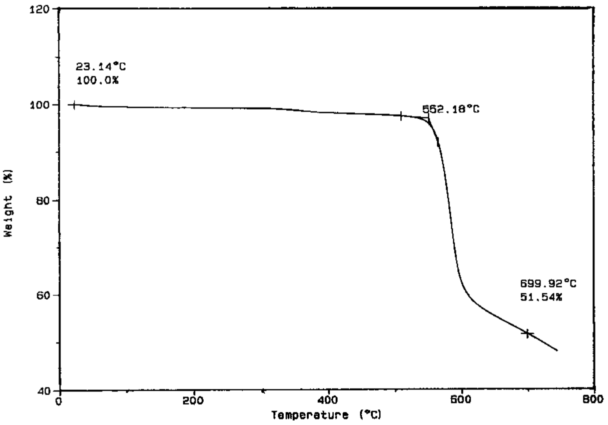

Figure 1 TGA scan (0–750 °C) for 100% PEEK, showing little or no weight loss until 552 °C after which a sharp on-set of degradation occurs resulting in 51.5% solid residues at 700 °C.

The TGA scan for a 100% PEEK sample is given in Fig. 1 and shows little or no weight loss up to a temperature of $\approx$ 552 °C. However, immediately after this point is reached, on the heating ramp a sharp decrease in weight is observed and, by 700 °C, a total weight loss of almost 50% has occurred. This behavior is indicative of the thermal decomposition of PEEK as reported by Hay and Kemmish [31], who found that degradation occurred by random chain scission processes at the ether and/or carbonyl linkages in the oxy-1,4-phenylene-oxy-1, 4-phenylene-carbonyl-1, 4-phenylene repeat unit of the polymer chain and by the transfer reactions that can then occur. This results in the formation of volatile decomposition products, including furan containing oligomers, phenol and dibenzofuran. These workers also identified the presence of a black, non-volatile residual solid based on a poly(etherketone) backbone. It should be noted that the degradation studies of Hay and Kemmish were carried out in a flowing nitrogen gas environment as part of their thermogravimetric studies. Since, in the ashing studies for the pure polymer reported in this work, no non-volatile residues were observed, this suggests that the decomposition of PEEK in air is complete at 800 °C. This behavior has been confirmed by carrying out ashing studies for PEEK in a flowing nitrogen/air environment using conditions similar to those used for the TGA studies. This did indeed result in the formation of a non-volatile solid residue equivalent to $\approx$ 50% of the original weight. Hence, ashing PEEK at 800 °C for 2 h in a 100% (non-flowing) air environment leads to the complete thermal degradation of the material by oxidative decomposition with no detectable solid residue.

The corresponding TGA scan for the 100% HA powder sample is given in Fig. 2. The weight loss observed here is most pronounced up to $\approx$ 100 °C, after which there is a more gradual decrease to the upper heating limit. The solid residue content at 700 °C is $\approx$ 93% indicating the expected stability of this material over this temperature range. This relatively small weight loss is assigned to removal of adsorbed water between 80 and 120 °C and to the slow dehydroxylation of the HA material up to 700 °C [32].

In differential scanning calorimetry (DSC) the heat flow associated with transitions in materials are measured as a function of temperature (or time) in a controled atmosphere. In this way, quantitative information can be obtained about a number of key physical and chemical properties of the materials from changes in the measured heat capacity of the system. In conventional DSC, however, many of the transitions that would be desirable to monitor are complex and difficult to interpret due to inherent inadequacies in instrument sensitivity. Although it is possible to increase sensitivity, this requires a faster heating rate, which then reduces resolution.

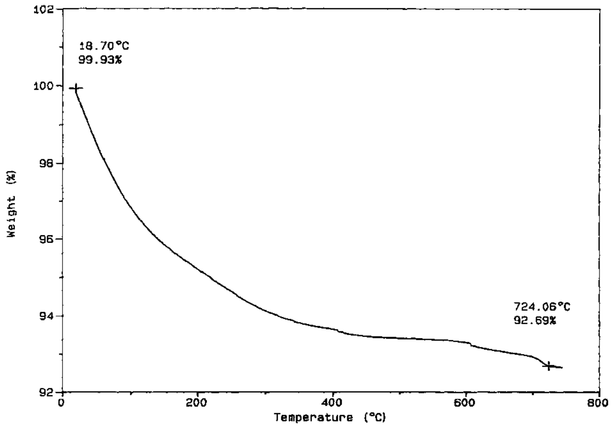

Figure 2 TGA scan (0–750 °C) for 100% HA showing a pronounced change in weight between 80 and 100 °C, which is assigned to the loss of adsorbed water. This is followed by a more gradual loss due to slow dehydroxylation to the upper temperature limit, giving 93% solids at 700 °C.

Modulated DSC is a new version of the technique, which can provide much additional calorimetric information. While the conventional method measures the sum of all thermal events, MDSC separates heat flow into reversing and non-reversing components. The reversing heat flow signal contains the heat capacity events such as the glass transition temperature (T_g) and the melting endotherm (T_m). The non-reversing heat flow trace indicates the kinetic events such as crystallization (T_c) and decomposition. In order to do this, a different heating profile is applied compared with that used in the standard DSC experiments. Specifically, a sinusoidal temperature oscillation is overlaid on the conventional linear heating or cooling ramp to yield a profile in which the average sample temperature continuously changes with time but not in a linear fashion. The net effect of imposing this more complex heating profile is the same as if two experiments were run simultaneously, one with the traditional linear heating rate and the other at the sinusoidal heating rate. This set of conditions thereby provides slow underlying heating, known to improve resolution, as well as faster instantaneous heating, which improves sensitivity. The combination of high resolution and sensitivity in the same experiment is one of the key benefits of MDSC. Additional advantages include increased sensitivity for detecting weak transitions, separation of complex thermal events, direct measurement of heating capacity and measurement of thermal conductivity.

Conventional DSC scans for the 100% PEEK and HA samples are shown in Figs 3(a) and 3(b), respectively. It should be noted that the DSC scan for HA was recorded to a temperature of 450 °C only, whilst that for PEEK was run to a maximum temperature of 650 °C. The DSC scan for the 100% PEEK shows the expected transitions associated with this semi-crystalline material, namely a crystallization exotherm (T_c) at $\approx 169\,^\circ\mathrm{C}$ and the melting endotherm (T_m) which can be seen at $\approx 348\,^\circ\mathrm{C}$. These values are slightly higher than the published data referred to earlier [12]. In addition, an intense exotherm can be observed at approximately $\approx 593\,^\circ\mathrm{C}$, which is indicative of the decomposition of the PEEK, as was also observed in the TGA data for this material in the same temperature range (Fig. 1). Although highly informative, the DSC scan does not allow the glass transition temperature (T_g), associated with PEEK to be clearly defined.

The most obvious feature in the conventional DSC scan for 100% HA (Fig. 3b), is the occurrence of a broad endotherm centered at $\approx 80\,^\circ\mathrm{C}$. As was the case in the corresponding TGA plot, this is due to the removal of adsorbed water from the HA crystal lattice. A second distinct, but much less intense feature is observed for this material at $\approx 324\,^\circ\mathrm{C}$. The origin of this exothermic peak is not immediately apparent, as no transitions are expected for HA at this temperature. It may therefore be assumed that it is caused by the presence of some contaminant species in the commercial HA material. Detailed Fourier transform infra-red (FTIR) spectroscopy and X-ray diffraction (XRD) studies (not shown here) of the commercial HA material used in this work have shown it to be a carbonated apatite with relatively poor crystallinity. This assessment of the Merck material is consistent with findings from Liu *et al.* who have used it as a component in a biocomposite system [27]. Hence, the additional feature noted in the DSC is assigned to the presence of the carbonate phase. This has subsequently been confirmed by studying DSC scans for calcium carbonate (Analar grade, Merck KGaA, Germany) and a

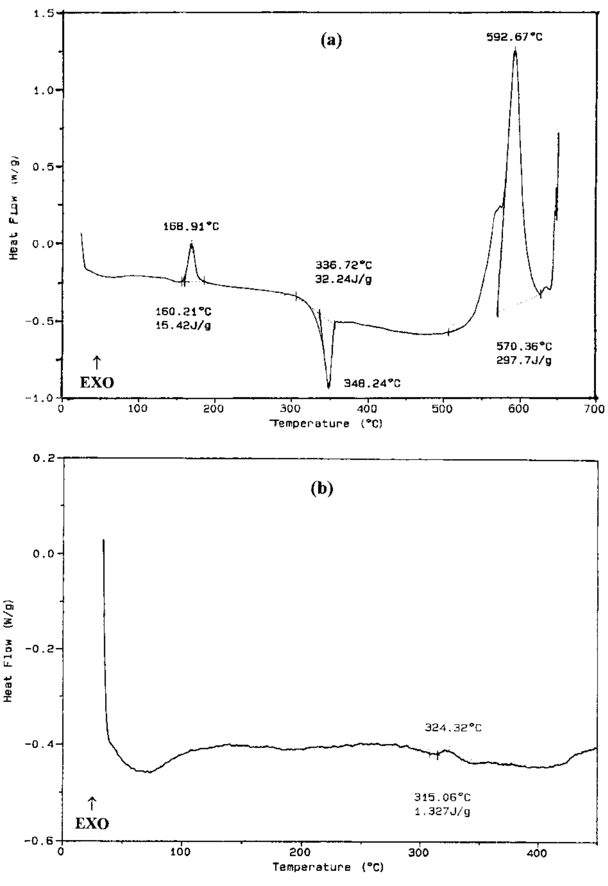

Figure 3 Conventional DSC for (a) 100% PEEK with $T_c \approx 169\,^\circ\mathrm{C}$, $T_m \approx 348\,^\circ\mathrm{C}$ and decomposition at $\approx 593\,^\circ\mathrm{C}$ and (b) 100% HA with a broad endotherm centered at $\approx 80\,^\circ\mathrm{C}$ due to water loss and an exotherm at $\approx 324\,^\circ\mathrm{C}$.

sample of laboratory synthesized HA that is known (from FTIR and XRD) to be highly crystalline. The data for the $CaCo_3$ sample clearly indicated the presence of an exotherm at $\approx 324\,°C$ while the ''pure'' HA did not. It should be noted that the MDSC scan for this HA material (not shown here) confirms the kinetic endothermic and exothermic activity described above. It is interesting to note that none of the DSC data recorded for the HA employed in this study showed the monoclinic to hexagonal phase transition reported by Suda *et al.* [33], which they observed as endo-and exothermic peaks at on-set temperatures of $\approx 207\,°C$ and $206\,°C$ during the heating and cooling of HA, respectively.

In the MDSC scan for PEEK, as given in Fig. 4, the total heat flow signal, represented by the solid line, shows all the information given by the conventional DSC. The (i) non-reversing (kinetic) and (ii) reversing (heat capacity) contributions are shown as a line broken by dots and a dashed line, respectively. The non-reversing signal identifies the PEEK crystallization at $T_c \approx 160\,°C$ and is followed by some re-ordering within the crystalline region immediately prior to the melt at $T_m \approx 349\,°C$. Whereas the values for T_m in both the DSC and MDSC studies of pure PEEK are more or less identical, the value for T_c is some nine degrees below that determined from the conventional DSC analyses. This difference is due to the fact that, as described earlier, the modulation technique uses a slow underlying heating rate with a simultaneous high instantaneous oscillating heating rate, thereby improving resolution without loss of sensitivity.

In addition to the melting peak, the reversing signal (Fig. 4 (i)) indicates the presence of a glass transition peak (T_g) at $\approx 142\,°C$. This is indicative of the amorphous phase of the PEEK coupled with imperfectly crystallized polymer and is not seen with any certainty in either the total heat flow (solid line) or non-reversing (Fig. 4 (ii)) traces. The observation and quantification of these data from different parts of the same experimental run allow integration of the crystallizing and melting phenomena to be done independently, thereby increasing the accuracy and precision in determining the resultant crystallinity.

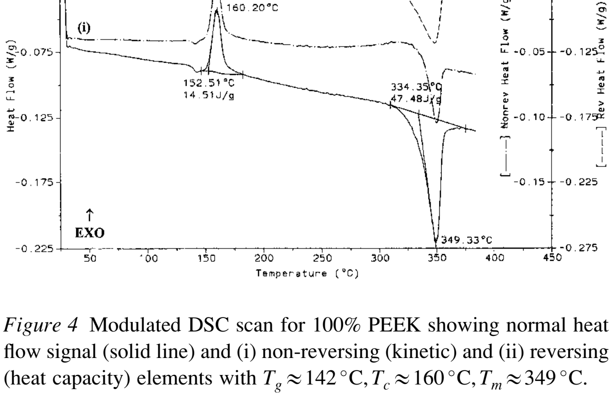

Figure 4 Modulated DSC scan for 100% PEEK showing normal heat flow signal (solid line) and (i) non-reversing (kinetic) and (ii) reversing (heat capacity) elements with $T_g \approx 142\,°C, T_c \approx 160\,°C, T_m \approx 349\,°C$.

3.3. TGA, DSC and MDSC studies of PEEK/HA mixtures

Thermal analyzes of the various PEEK/HA mixtures have been carried out under conditions identical to those used to study the component powders. In general, the TGA data for the higher PEEK content samples are similar in form to those recorded for the 100% PEEK sample (Fig. 1), in that, there is no significant weight loss until $\approx 530\,°C$ where upon a very sharp decrease in weight occurs. TGA scans for the 74/26% and 37/63% PEEK/HA mixtures are shown in Figs 5(a) and 5(b), respectively. Table II shows the decomposition on-set temperature for each of the mixtures and the resultant % residue detected at 700 °C. These data show that, with the exception of the 25/75% PEEK/HA mixture, the temperature at which decomposition commences decreases as the amount of HA in the mixture increases. Not surprisingly, the total solid residue at $\approx 700\,°C$ also increases with the addition of HA since this material is extremely stable at this temperature.

The conventional DSC scans for the 74/26% and 37/63% PEEK/HA mixtures are shown in Figs 6(a) and 6(b), respectively. These plots show all the characteristics expected for the PEEK component. However, there is also evidence for a broad endotherm, centered at 80 °C, which is again associated with loss of adsorbed water from the HA component and, as such, is found to be more prevalent with increasing HA contribution to the mixture. For the higher HA content samples this feature

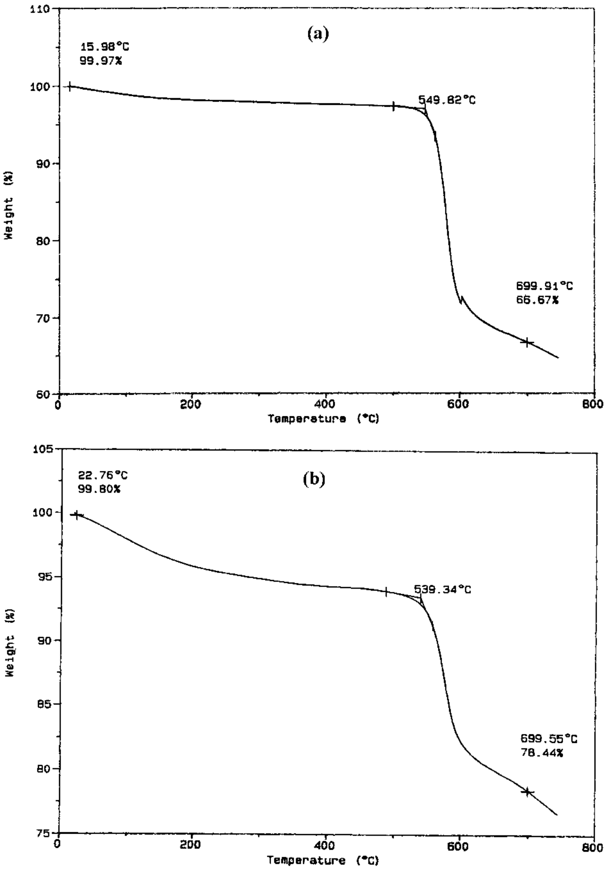

Figure 5 TGA scans for (a) 74/26% PEEK/HA with on-set of decomposition at $\approx 550\,°C$ and 67% solid residues at 700 °C and (b) 37/63% PEEK/HA showing on-set of decomposition at $\approx 539\,°C$ and 78% solid residues at 700 °C.

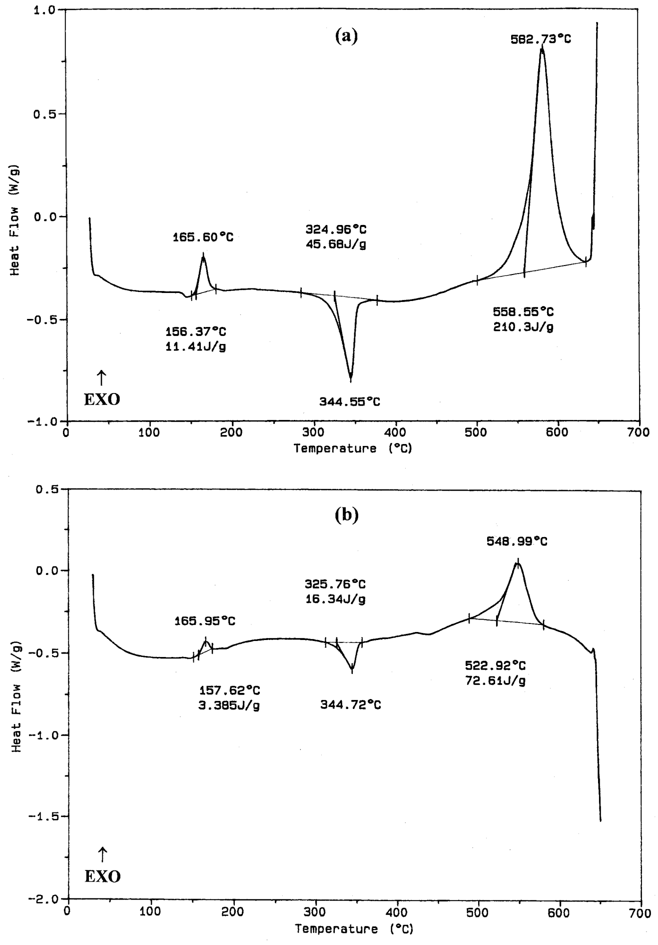

Figure 6 Conventional DSC scans for (a) 74/26% PEEK/HA with $T_c \approx 166\,^{\circ}\mathrm{C}, T_m \approx 345\,^{\circ}\mathrm{C}$ and decomposition at $\approx 583\,^{\circ}\mathrm{C}$ and (b) 37/63% PEEK/HA with $T_c \approx 166\,^{\circ}\mathrm{C}, T_m \approx 345\,^{\circ}\mathrm{C}$ and decomposition at $\approx 545\,^{\circ}\mathrm{C}$.

dominates this region of the scan. It should be noted that any evidence for the exothermic feature detected at $\approx 324\,^{\circ}\mathrm{C}$ for the HA (Fig. 3b), is masked by the melting endotherm of the PEEK at $\approx 345\,^{\circ}\mathrm{C}$.

As was the case for the 100% PEEK sample, the MDSC method provides the resolution necessary to observe and quantify the temperature at which the glass transition occurs for each of the mixtures of interest. Figs 7(a) and 7(b) show the MDSC scans for the 74/26% and 37/63% PEEK/HA mixtures, respectively, with T_g occurring at $\approx 141\,^{\circ}\mathrm{C}$ in each case as determined during the reversing (heat capacity) component. The water loss endotherm from the HA contribution, centered at 80 °C, is again evident and, for the higher HA content sample, dominates this region of the scan. Table III gives the thermal analysis data obtained from the DSC and MDSC analyzes of the various mixtures. The enthalpies of crystallization (ΔH_c) and melting (ΔH_m), determined from the area under curves associated with the exo- and endotherms, respectively, in the MDSC analysis, are also included. It is evident from these data that the T_g value for each sample, as determined by MDSC, is unaffected by the level of HA present. Likewise, the values for T_c and T_m are also highly reproducible from mixture to mixture and very similar to that for the 100% PEEK material. As expected, the ΔH_c and ΔH_m data associated with PEEK show a decrease in value with increasing HA contribution to the mixtures.

The % crystallinity of the PEEK component present in each of the mixtures has been calculated from the MDSC data given in Table III by comparing the enthalpy of crystallization with that determined from the subsequent melting endotherm. This has been done by using a value of 130 J/g as the heat of fusion of totally crystalline PEEK [11, 34], and making the assumption that the heat of fusion is the same as the heat of crystallization. The values obtained are presented in Table IV and have been normalized to the 100% PEEK sample equivalents. The additional crystallization that occurs during the MDSC experiment has been determined by calculating the % crystallinity from the melting endotherm, i.e. that which has occurred after further crystallization of any amorphous phase and imperfectly crystallized contributions. The difference between these two values is then taken to be the % crystallization induced by the thermal processes in the MDSC experiment. It is apparent from these data that the % crystallinity of PEEK in the mixtures, as determined from ΔH_c and ΔH_m values, respectively, show a gradual decrease as the HA contribution increases. The % crystallinity of the PEEK source material calculated for these data is 25.5%, which is

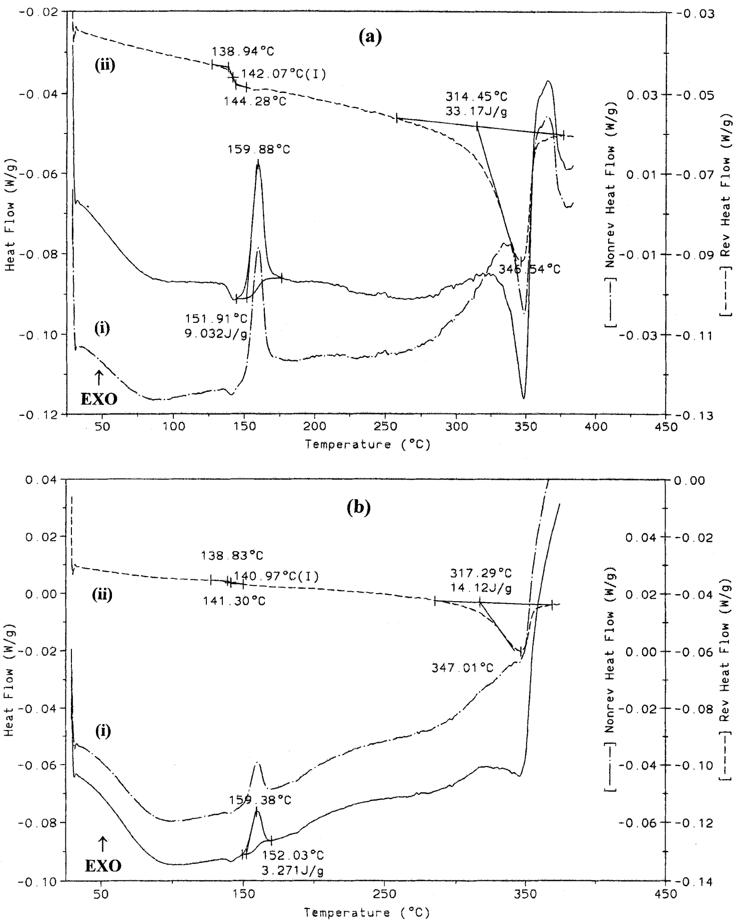

Figure 7 Modulated DSC scans for (a) 74/26% PEEK/HA with $T_g \approx 142\,^{\circ}\mathrm{C}, T_c \approx 160\,^{\circ}\mathrm{C}$ and $T_m \approx 347\,^{\circ}\mathrm{C}$ and (b) 37/63% PEEK/HA with $T_g \approx 141\,^{\circ}\mathrm{C}, T_c \approx 160\,^{\circ}\mathrm{C}, T_m \approx 347\,^{\circ}\mathrm{C}$. In both plots the total heat flow signal (solid line) has been split into (i) the non-reversing (kinetic) and (ii) reversing (heat capacity) components.

slightly below the nominal value of 30% specified for this grade of the polymer. The inherent % crystallinity of the PEEK in the various mixtures, changes only slightly compared to that recorded for this 100% PEEK material. The variation in these latter values is found to be commensurate with the error associated with the ashing studies used to determine the PEEK contribution in each of the mixtures. This relatively small change in

TABLE I Theoretical and actual (averaged) compositions of PEEK/HA mixtures as determined from ashing studies at 800 °C

Theoretical PEEK/HA composition		Actual (averaged) PEEK/HA composition	
% PEEK	% HA	% PEEK	% HA
90	10	87	13
70	30	74	26
50	50	57	43
30	70	37	63
10	90	25	75

TABLE II Decomposition on-set temperatures and % non-volatile solid residues at 700 °C, as determined by TGA, for PEEK/HA mixtures

Actual (averaged) PEEK/HA composition		Temperature of decomposition on-set (°C)	% Solid residue @ 700 °C
% PEEK	% HA		
100	0	552	51
87	13	556	59
74	26	550	67
57	43	547	71
37	63	539	78
25	75	550	87
0	100	—	97

TABLE III Calorimetric data, as determined by DSC and MDSC studies, for PEEK/HA mixtures

Actual (averaged) PEEK/HA composition		Thermal analysis data							
%PEEK	%HA	DSC (°C)			MDSC				
		T_c	T_m	T_{decom}	T_g(°C)	T_c(°C)	ΔH_c(J/g)	T_m(°C)	ΔH_m (J/g)
100	0	169	348	593	142	160	14.5	349	47.5
87	13	167	345	590	141	160	12.1	349	36.9
74	26	166	344	582	142	160	9.0	346	33.2
57	43	167	345	565	142	160	6.4	346	27.4
37	63	166	345	549	141	160	3.3	347	14.1
25	75	—	—	550	—	—	—	—	—

TABLE IV Determination of % crystallinity for PEEK/HA mixtures from MDSC thermal analysis data

Actual (averaged) PEEK/HA composition		% Crystallinity at T_c	% Crystallinity at T_m	% Crystallinity of sample
% PEEK	% HA			
100	0	11.1	36.5	25.5
87	13	10.7	32.6	21.9
74	26	9.3	34.5	25.2
57	43	8.6	37.0	28.4
37	63	6.9	29.3	22.4
25	75	—	—	—

the % crystallinity, even at high HA loading, is an important observation, as it suggests that the addition of increasing percentages of HA to PEEK, does not adversely effect this critical property of the polymer.

4. Conclusions

The effect of thermal processing on the properties of a series of PEEK/HA mixtures has been studied using thermogravimetric (TGA) and calorimetric (DSC and MDSC) methods. The TGA results suggest that increasing the HA content of the mixtures has the effect of decreasing the on-set temperature of PEEK degradation by up to 13 °C for a sample containing 37% PEEK. The contribution of the ceramic component is clearly seen for the samples to which it provides a higher contribution and results from water loss at lower temperatures (80–120 °C) and a slow dehydroxylation of the HA as the temperature increases over the range 200–750 °C.

Conventional DSC analyses for these materials allow the values for the PEEK crystallization (T_c) and melting (T_m) temperatures to be readily determined. The on-set of thermal decomposition has also been examined with this technique and again found to decrease with increasing HA content in the sample. Using the modulated version of the DSC technique, it is possible to separate the heat flow into reversing (heat capacity) and non-reversing (kinetic) components which provide a dramatic improvement in resolution and allow the glass transition temperature (T_g) for PEEK to be clearly observed. The values obtained for T_c and T_m are also determined more accurately and, furthermore, are found to be highly reproducible. This improvement in accuracy has allowed for a more reliable calculation of % crystallinity of the PEEK component present in the various mixtures of interest. These data show that the % crystallinity induced by the analysis technique, which is indicative of that which would occur during thermal processing, is not adversely affected by the presence of the HA, even at relatively high loading of 43 and 63%. Hence, the ceramic component does not cause a significant change to the PEEK in this critical molding temperature region. This has important implications for the fabrication of composite structures based on PEEK/HA formulations.

Acknowledgments

The authors wish to thank: Mr Andrew Wells of TA Instruments, Surrey, UK, for assistance with MDSC analysis; Mr Maurice Jamieson, SEME, University of Ulster, for help with the TGA studies and Victrex plc for PEEK samples. Access to the TA 2000 DSC at the Material Science Laboratory, via an award from the Research Unit for Surfaces, Transforms and Interfaces (RUSTI) CCLRC, Daresbury Laboratory, UK, is gratefully acknowledged. One of the authors (CMcC), wishes to thank the Department of Education for Northern Ireland (DENI) for the award of a postgraduate studentship.

References

1. A Review of the UK Research Base in Biomaterials (Royal Academy of Engineering, London, 1998).
2. R&D Priorities for Biomaterials and Implants (Department of Health, London, 1996).
3. Technology Foresight - Materials Panel Report (Office of Science and Technology, HMSO, London, 1995).
4. Materials Technology Foresight in Biomaterials (Institute of Materials, London, 1995).
5. A. RAVAGLIOLI and A. KRAJEWSKI (Eds) "Bioceramics: Materials Properties Applications", (Chapman & Hall, 1992).
6. L. L. HENCH, *J. Amer. Ceram. Soc.* **81** (1998) 1705.
7. W. N. CAPELLO, J. A. D'ANTONIO, M. T. MANLEY and J. R. FEINBERG, *Clin. Orthop. and Related Res.* **355** (1998) 200.

8. M. OGISO, *J. Long-Term Effects of Medical Implants* **8** (1998) 193.
9. K. A. HING, S. M. BEST, K. E. TANNER, P. A. REVELL and W. BONFEILD, *Proc. Instn. Mech. Engrs, Part H-J. Engin in Med.* **212** (1998) 437.
10. P. C. DAWSON and D. J. BLUNDELL, *Polymer* **21** (1980) 577.
11. D. J. BLUNDELL and B. N. OSBORN, *ibid.* **24** (1993) 953.
12. R. B. RIGBY, in ''Plastics Engineering No. 8'' (Marcel Dekker Inc., New York, 1985) p. 299.
13. M. DAY, J. D. COONEY and D. M. WILES, *Polym. Enging Sci.* **29** (1989) 19.
14. *Idem. J. Appl. Polym. Sci.* **38** (1989) 323.
15. *Idem. Thermochim. Acta* **147** (1998) 189.
16. T. E. ANDRES and I. GRIFFITHS, Proceedings of 1998 SPE Annual West Regional Meeting, Anaheim, CA (Soc. Pet. Eng. Richardson, TX, USA, 1998) pp. 203–7.
17. S. L. EVANS and P. J. GREGSON, *Biomater* **19** (1998) 1329.
18. M. SPECTOR, E. J. CHEAL, R. D. JAMISON, S. ALTER, N. MADSEN, L. STRAIT, G. MAHARAJ, A. GAVINS, D. T. REILLY and C. B. SLEDGE, in Proceedings of 22nd National SAMPE Technical Conference (1990) 1119.
19. M. AKAY and N. ASLAN, *Proc. Instn. Mech. Engrs; Part H-J. Enging in Med.* **209** (1995) 93.
20. *Idem. J. Biomed. Mater. Res.* **31** (1996) 167.
21. A. CHOPRA, European Patent Application: 0 790 044 A3 (Howmedica Inc., New York, NY, 10017, USA 14/01/98).
22. D. F. WILLIAMS, A. MCNAMARA and R. M. TURNER, *J. Mater. Sci. Lett.* **6** (1987) 188.
23. K. A. JOCKISCH, S. A. BROWN, T. W. BAUER and K. MERRITT, *J. Biomed. Mater. Res.* **26** (1992) 133.
24. C. MORRISON, R. MACNAIR, C. MACDONALD, A. WYKMAN, I. GOLDIE and M. H. GRANT, *Biomaterials* **16** (1995) 987.
25. I. B. SEVOSTIANOV, *Composite Structures* **43** (1998) 109.
26. A. M. RADDER and C. A. VAN BLITTERSWIJK, *J. Mater. Sci.: Mater. Med.* **5** (1994) 320.
27. Q. LIU, J. R. DE WIJN and C. A. VAN BLITTERSWIJK, *J. Biomed. Mater. Res.* **40** (1998) 490.
28. K. E. TANNER, R. N. DOWNES and W. BONFIELD, *Brit. Ceram. Trans* **93** (1987) 104.
29. M. WANG, R. JOSEPH and W. BONFIELD, *Biomaterials* **19** (1998) 2357.
30. J. L. DORNHOFFER, *Laryngoscope* **108** (1998) 531.
31. J. N. HAY and D. J. KEMMISH, *Polymer* **28** (1987) 2047.
32. A. J. RUYS, M. WEI, C. C. SORRELL, M. R. DICKSON, A. BRANDWOOD and B. K. MILTHORPE, *Biomaterials* **16** (1995) 409.
33. H. SUDA, M. YASHIMA, M. KAKIHANA and M. YOSHIMURA, *J. Phys. Chem.* **99** (1995) 6752.
34. P. CEBE and S.-D. HONG, *Polymer* **27** (1986) 1183.

Received 27 April 1999
and accepted 17 November 1999