Thermal Stability and Compressive Strength of Calcium-Deficient Hydroxyapatite−Poly[bis(carboxylatophenoxy)phosphazene] Composites

Carey S. Reed,[†] Kevor S. TenHuisen,[‡] Paul W. Brown,*[,‡] and Harry R. Allcock*[,†]

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and Intercollege Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

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We have examined the thermal stability and compressive strength of a composite material comprised of hydroxyapatite (HAp, $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$) and the polyphosphazene poly[bis(carboxylatophenoxy)phosphazene]. The HAp is synthesized in the presence of the polyphosphazene utilizing dicalcium phosphate dihydrate (DCPD), $CaHPO_4 \cdot 2H_2O$, and tetracalcium phosphate (TetCP), $Ca_4(PO_4)_2O$, as the inorganic precursors. Calcium from the inorganic precursors participates in the formation of a polymeric network via ionic cross-linking through the pendent carboxylate groups. The degree of cross-linking of the polyphosphazene and its bonding to the HAp increases the overall thermal stability and changes the mode of failure of the final composite material. The thermal behavior of the polyphosphazene in its protonated, sodium salt, and calcium cross-linked forms was examined utilizing (1) thermogravimetric analysis at temperatures between 50 and 1000 °C, (2) electron impact mass spectrometry up to 550 °C, and (3) isothermal thermolysis in a closed system. The thermal stability of the polyphosphazene was increased by sodium salt formation and was increased further by calcium cross-linking and by bonding to the HAp matrix phase. With heating, the polyphosphazene undergoes both cross-linking, to form a three-dimensional network, and random chain scission of the backbone. The compressive strengths of HAp and the composites constituted of (DCPD+TetCP)-to-polyphosphazene weight ratios of 20-to-1, 10-to-1, and 5-to-1 were examined. The reaction conditions were chosen to obtain a composite material with approximately 65% porosity. An increase in compressive strength, compared to that of HAp, was detected only for the 20-to-1 weight ratio. Further increases in polymer content decreased the compressive strength. In general, as the polymer content of the composite was increased, the composite strength decreased and the strain increased before failure. Thus the mode of failure changed from that of a brittle ceramic to that of a ductile composite.

Introduction

It is becoming increasingly important to develop new composite materials that combine the advantages of existing structural materials while minimizing their individual weaknesses. Biological systems have successfully accomplished this with naturally occurring composites such as bone which utilize hydroxyapatite (HAp) as the inorganic matrix with collagen as the binding and reinforcing phase. Bone has high strength, toughness, impact resistance, and chemical resistance while remaining a relatively lightweight material. However, even with these favorable properties, composites that utilize collagen for nonbiological applications, such as structural engineering materials, are limited in their technical applications due to the low thermal stabilities of proteins. In an attempt to overcome this inherent limitation, we have utilized synthetic polymers, such as polyphosphazenes, as the reinforcing phase that has a higher thermal stability than collagen.

Polyphosphazenes comprise a large class of macromolecules with the general formula $(NPR_2)_n$, with alternating phosphorus and nitrogen atoms in the backbone and a wide variety of organic, organometallic, or inorganic side groups.[1−2] The primary synthesis route, shown in Scheme 1, is through the thermal ring-opening polymerization at 250 °C of molten hexachlorocyclotriphosphazene (**1**) to form poly(dichlorophosphazene) (**2**).[3] The P−Cl bonds in this polymer are highly reactive and undergo substitution in the presence of a wide variety of organic and organometallic nucleophiles to form stable derivative macromolecules. The properties of polyphosphazenes, such as water-solubility and hydrothermal or thermooxidative stability, are determined mainly by the types of side groups present.

For example, the side groups influence the degradation mechanism of polyphosphazenes at elevated temperatures. Some polyphosphazenes undergo skeletal scission and a decrease in molecular weight, others depolymerize to form monomers or cyclic oligomers,

[†] Department of Chemistry.
[‡] Intercollege Materials Research Laboratory.
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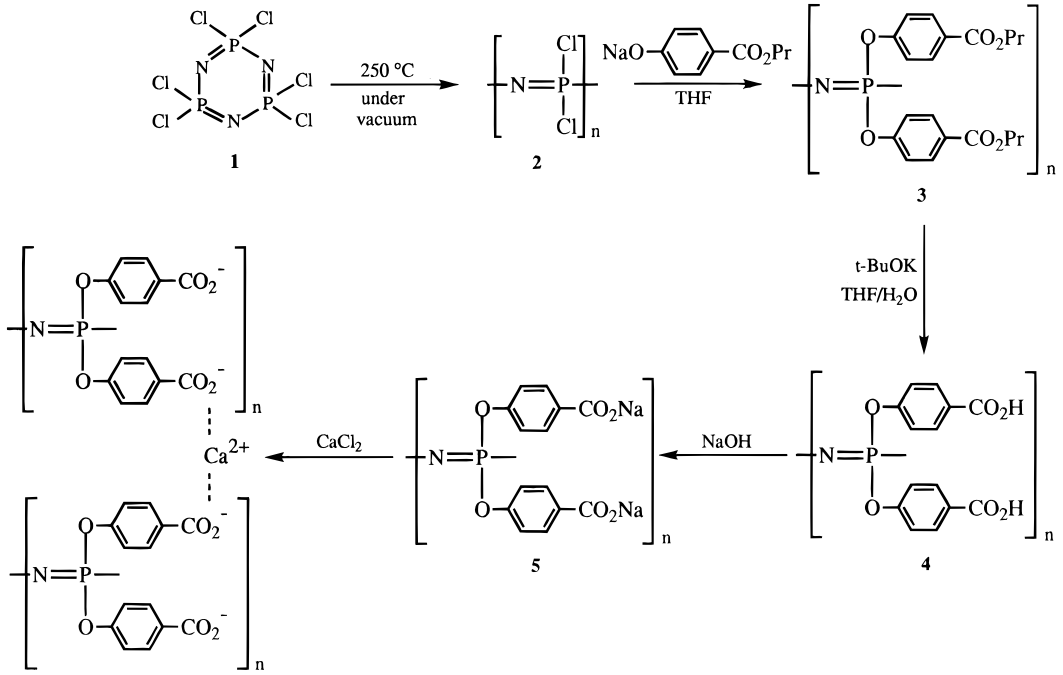
Scheme 1



while other species cross-link through the side groups. In a single-polymer system one or more of these mechanisms may occur. For example, in the class of polyphosphazenes of formula poly[bis-(*p*-R-phenoxy)phosphazene], it is known that the polarity of the R group influences the degradation mechanism. When R is a nonpolar group such as H or CH_3, the polymer initially undergoes chain cleavage above 100 °C followed by depolymerization to volatile cyclic oligomers when heated above 250 °C. This results in a 90% weight loss by 500 °C as determined by TGA experiments. However, when R is a polar group, the mechanism of degradation of the polymer is more complicated. For these polymers, a 50% weight loss occurs at 400 °C, after which the residue is stable up to 700 °C before further weight loss occurs due to condensation reactions that involve the side groups.[4−8]

One polyphosphazene that is of particular interest in the context of composite materials is poly[bis(carboxylatophenoxy)phosphazene] (**4**). Its synthesis is shown in Scheme 1. The sodium salt of propyl *p*-hydroxybenzoate displaces the chlorine atoms of compound **2** via a nucleophilic substitution reaction. The fully organo-substituted polymer is then subjected to ester hydrolysis to form the free carboxylic acid. The resultant polymer is soluble in basic aqueous media and can be cross-linked ionically by exposure to di- or trivalent cations. The degree of cross-linking of the resultant network or hydrogel can be controlled readily by variations in pH.[9−10] This characteristic is currently being utilized for the microencapsulation of biological materials such as liposomes, proteins, bacteria, and mammalian cells.[11−13] Compared to other synthetic polymers that bear carboxylic acid side units, polymer **4** has the advantage that it bears two carboxylic acid groups on every repeating unit. Thus, any effects that depend on ionic cross-linking are amplified in this system.

The inorganic matrix of interest in the present study, hydroxyapatite (HAp), does not have a fixed composition. Its composition is expressed as $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$, with a Ca/P mol ratio varying between approximately 1.33 ($x = 2$) and 1.67 ($x = 0$).[14] Stoichiometric HAp has a Ca/P ratio of 1.67, while calcium deficient HAp has a Ca/P ratio <1.67. Calcium-deficient HAp can be formed by reactions between basic and acidic calcium phosphates as shown in eq 1.

$$6CaHPO_4{\cdot}2H_2O + 3Ca_4(PO_4)_2O \Rightarrow 2Ca_9HPO_4(PO_4)_5OH \quad (1)$$

Tetracalcium phosphate (TetCP), $Ca_4(PO_4)_2O$, is the only calcium orthophosphate salt more basic than HAp. Conversely, a number of calcium phosphates more acidic than HAp can be utilized such as dicalcium phosphate, $CaHPO_4$ (DCP or monetite), dicalcium phosphate dihydrate, $CaHPO_4{\cdot}2H_2O$ (DCPD), and monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2{\cdot}H_2O$ (MCPM).[15−20] The

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specific acidic calcium phosphate used in this work is DCPD. This reaction, see eq 1, occurs at near physiological temperature and pH and results in a Ca/P ratio of 1.5. This is a difference of 1 mol of CaO from stoichiometric HAp (Ca/P = 1.67). The synthesis and characterization of several composite systems utilizing this route to HAp formation have been examined.[21−24]

In a previous paper we described the synthesis, solution chemistry, activation energy, and microstructure of a composite material comprised of calcium deficient HAp and poly[bis(carboxylatophenoxy)phosphazene].[24] In this paper we discuss first the thermal stability of the pure polymer, poly[bis(carboxylatophenoxy)phosphazene], in its protonated, sodium salt, and calcium cross-linked forms, followed by an examination of the polymer incorporated within the composite material. The compressive strength of this new composite is discussed in relation to that of pure HAp.

Experimental Section

Instrumentation. Solution-state NMR spectra were obtained in the quadrature mode at 294 K using a Bruker WM-360 NMR spectrometer resonating at 360.13 MHz for ^{1}H, 145.81 MHz for ^{31}P, and 90.56 MHz for ^{13}C. All NMR samples were prepared with deuterated chloroform (Isotec, 99.9%), deuterated dimethyl sulfoxide (Isotec, 99%), or deuterium oxide (MSD, 99.9%) as lock solvents. ^{1}H and ^{1}H-decoupled ^{13}C spectra were referenced to the residual ^{1}H and ^{13}C signals of the lock solvents respectively, and ^{1}H-decoupled ^{31}P spectra were referenced externally to a sealed capillary of 85% phosphoric acid. ^{31}P solid-state spectra were obtained at 120.38 MHz and 294 K with magic angle spinning (MAS) using a chemagnetics CMX-300 spectrometer. Spin rates were 3.5−4.0 kHz. Molecular weights of polymer **3** were estimated for solutions in THF using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1037A refractive index detector and a Polymer Laboratories PL gel 10 μm column calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Technology Laboratories, Watertown, MA. Samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium bromide in THF. Thermal weight loss measurements were made using a Perkin-Elmer TGA-7 thermogravimetric analyzer equipped with a PE 7500 computer. Testing was carried out under a stream of either nitrogen or air using compressed gases at a flow rate of 30 cm^3/min and a heating rate of 20 °C/min. Sample weights of 4−6 mg weight were analyzed. Analysis of the volatile pyrolysis products were performed using a Kratos MS 9/50 electron impact magnetic sector mass spectrometer (impact energy 70 eV) with an electron multiplier detector. Samples were heated over the temperature range 120−550 °C using a Kinderman probe. The materials morphology was examined utilizing an ISI-DS 130 dual stage scanning electron microscope. All samples were freeze-dried and coated with gold prior to imaging. Compression testing was performed with use of an Instron model TTBML utilizing a cross-head speed of 0.2 mm/mm and a 500 kg load cell interfaced with a PC for data collection.

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp./Nippon Fine Chemical Co.) was purified by recrystallization from heptane and was sublimed at 50 °C (0.05 mmHg). Poly(dichlorophosphazene) was prepared as described previously.[3] Sodium hydride (60% dispersion in mineral oil, Aldrich), sodium hydroxide pellets (Aldrich), and potassium *tert*-butoxide (Aldrich) were used as received. Propyl *p*-hydroxybenzoate (Aldrich) was purified by recrystallization from methylene chloride. Tetrahydrofuran (Omnisolv) was dried over sodium benzophenone ketyl and was distilled under a nitrogen atmosphere. All reactions were performed under an atmosphere of dry nitrogen with standard Schlenk techniques. Reagent grade dicalcium phosphate and precipitated calcium carbonate were obtained from Fisher Scientific. Reagent grade calcium chloride was obtained from Baker.

Inorganic Precursor Synthesis. TetCP was synthesized by a high-temperature solid-state reaction between dicalcium phosphate and precipitated calcium carbonate ($CaCO_3$). These were mixed in equimolar quantities and were then milled to obtain a homogeneous mixture. The reactants were then fired at 1400 °C for 2 h to produce the product phase, TetCP, which was then milled to a mean particle size of 2−3 μm. Phase purity was confirmed using X-ray diffraction. DCPD was synthesized as described previously.[25] DCPD and TetCP were mixed in a 2-to-1 molar ratio to produce the calcium deficient HAp precursor powder.

Synthesis of Poly[bis(propyl 4-hydroxybenzoate)-phosphazene] (3). The sodium salt of propyl 4-hydroxybenzoate was prepared by the slow addition of propyl 4-hydroxybenzoate (93.16 g, 517 mmol) in THF (200 mL) to a suspension of sodium hydride (13.8 g, 60% dispersion) in THF (800 mL). The reaction mixture was stirred for 24 h. A solution of poly(dichlorophosphazene) (10.0 g, 862 mmol) in THF (1000 mL) was added slowly to the salt solution at reflux. The refluxing was continued for 72 h. The polymer was then purified by precipitation into deionized water (3 times), hexane (twice) and ethanol (once). $M_n = 2.59 \times 10^6$, $M_w = 3.40 \times 10^6$, pd = 1.31.

Synthesis of Poly[bis(carboxylatophenoxy)phosphazene] (4). Polymer **4** was prepared by a method reported previously.[9,10] A solution of potassium *tert*-butoxide (58.0 g, 517 mmol) in THF (750 mL) was cooled to 0 °C with an ice bath, and water (3.0 mL) was added slowly. A solution of polymer **3** (10.0 g, 24.8 mmol) in THF (750 mL) was then added slowly over 15 min. After 5 additional minutes at 0 °C, the reaction mixture was allowed to warm to room temperature and was stirred for 48 h. The polymer was purified by dialysis against deionized water (3 days). The polymer was then precipitated by acidification with hydrochloric acid and was collected by filtration.

Synthesis of Poly[bis(sodium carboxylatophenoxy)-phosphazene] (5). The purified polymer **4** was treated with sodium hydroxide to prepare the sodium salt which was itself purified by dialysis against deionized water to remove excess sodium hydroxide.

Calcium Cross-Linking of Polymer 5. Polymer **5** (1.0 g) was dissolved in 20 mL of deionized water. Calcium chloride (0.611 g, 5.55 mmol), dissolved in 10 mL of deionized water, was added rapidly to the polymer solution and this resulted in instantaneous precipitation. The mixture was stirred for 18 h then filtered through #5 Whatman filter paper. The cross-linked polymer was extracted three times with 100 mL of deionized water and was filtered off and washed with water. The resultant material was dried at 105 °C/760 mmHg.

Composite Sample Preparation. Composites with inorganic precursor (DCPD+TetCP)-to-polyphosphazene weight ratios of 20-to-1, 10-to-1, and 5-to-1 were examined. The relative amounts of deionized water and inorganic precursors were chosen to produce composites that contained approximately 65% porosity based upon density calculations (see Table 1). The required amount of polymer was dissolved in the corresponding weight of deionized water in a sealed stainless steel Sorvall container designed for high shear mixing and tissue fragmentation. Once the polymer was dissolved, the inorganic precursors were added to the polymer solution and

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Table 1. Precursor Weights Used To Produce Composites with Approximately 65% Porosity[a]

inorganic precursor-to-polyphosphazene weight ratio	wt of D.I. H_2O (cm^3)	wt of polyphos-phazene (g)	wt of Inorganic precursor (g)
pure mineral	10	0.000	22.67
20-to-1	12	1.193	23.86
10-to-1	13	2.301	23.01
5-to-1	15	4.742	23.71

[a] Calculated values determined by density estimates utilizing HAp and polymer **5** densities of 3.16 g/cm^3 and 1.94 g/cm^3 respectively

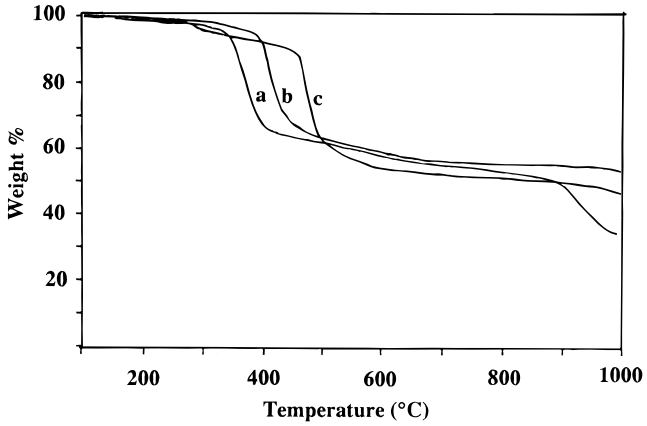

Figure 1. Loss in weight with temperature of poly[bis-(carboxylatophenoxy)phosphazene] in its (a) protonated, (b) sodium salt, and (c) calcium cross-linked forms.

mixed for 1.5 min. The resultant slurry was poured or intruded (depending on rheology) into a glass tube (measuring 170 mm in length and 10 mm in diameter) which was sealed with polyethylene end caps and wax, and the contents were allowed to react at 38 °C with heating supplied by a water bath. The resulting monolith was cut with a diamond edged blade to form cylinders with length-to-diameter ratios of 2-to-1 (20 mm × 10 mm) for compression testing.

Results and Discussion

General Overview. The ambient- or moderate-temperature formation of HAp in the presence of polymer **5** results in the intimate incorporation of the polymer into the inorganic matrix. This comes about through the cross-linking of the polymer via ionic linkages between the pendent carboxylic units and the calcium ions that are part of the HAp structure. The presence of this bound polymer strengthens the HAp matrix to a degree that may allow these composites to be used in biomedical or general engineering structural applications. A detailed report on the kinetics of formation of these composites will appear elsewhere.[24] Here we discuss the behavior of the reinforcing polymer, its calcium salt, and its HAp composites from the viewpoint of the reactions that occur when these materials are subjected to elevated temperatures.

Techniques Used for Thermal Analysis. Three experimental techniques were utilized to examine the thermal behavior of the polyphosphazene and the composite materials. The first made use of thermogravimetric analysis to examine the weight-loss pattern of the volatile thermolysis products as well as the weight fraction of nonvolatile material remaining at specific temperatures (Figures 1 and 8).

The second involved dynamic degradation experiments utilizing electron impact mass spectroscopy.

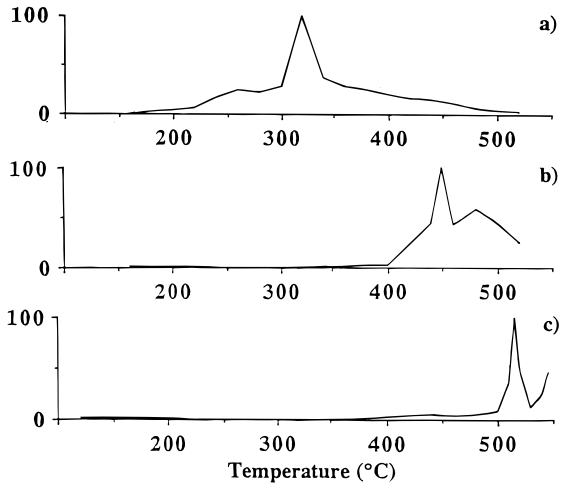

Figure 2. Electron impact mass spectrometric total ion current traces from the dynamic thermal degradation studies of poly[bis(carboxylatophenoxy)phosphazene] in its (a) protonated, (b) sodium salt, and (c) calcium cross-linked forms.

Dynamic degradation experiments provide important mechanistic information, but suffer from the drawback that the probe temperature does not accurately characterize the thermal stability of the material. This is due to a rapid heating rate, short measurement time, and the distillation rate of the degradation products out of the material. Also, the EI-MS experiments have a lower detection limit of *m*/*z* 28. However, the mass spectra obtained facilitated the identification of the volatile thermolysis products detected by TGA (Figure 2).

The third experimental technique involved the isothermal degradation of the polyphosphazene in sealed evacuated glass tubes. This prevented the loss of the volatile thermolysis products during the experiment and allowed them to contribute further to the reactions occurring during pyrolysis. The samples were held at various temperatures ranging from 50 to 500 °C for a period of 2 h in sealed glass tubes under vacuum. Residual products were analyzed by both solution and solid state ^{31}P NMR (Figures 3−7).

Polyphosphazene Thermal Stability. *(a) Carboxylic Acid Form.* The polymer $[NP(OC_6H_5COOH)_2]_n$ (**4**) undergoes both skeletal cleavage and cross-linking reactions when heated. However, polymer samples which had been heated isothermally at temperatures up to 150 °C remained completely soluble in DMSO with no difference evident in ^1H, ^{13}C, and ^{31}P NMR spectra compared to an untreated sample (Figure 3). Hence, matrix formation does not occur under these conditions.

At 200 °C, an initial condensation and cross-linking of the side groups was detected and this resulted in a small weight loss by TGA (Figure 1). The main fragments identified by EI-MS corresponded to benzoic acid and *p*-hydroxybenzoic acid as well as carbon dioxide and phenol. It can be assumed that water, which is below the detectable limits of the EI-MS experiments, was also a byproduct of condensation between carboxylic acid units. At this point, a clear gel was formed when a suitable solvent, such as DMSO, was added, and this is an indication of cross-linking. The phosphorus chemical shifts in solution ^{31}P NMR spectra suggested the presence of small molecules (Figure 3) indicating that polymer chain cleavage had also occurred. The appear-

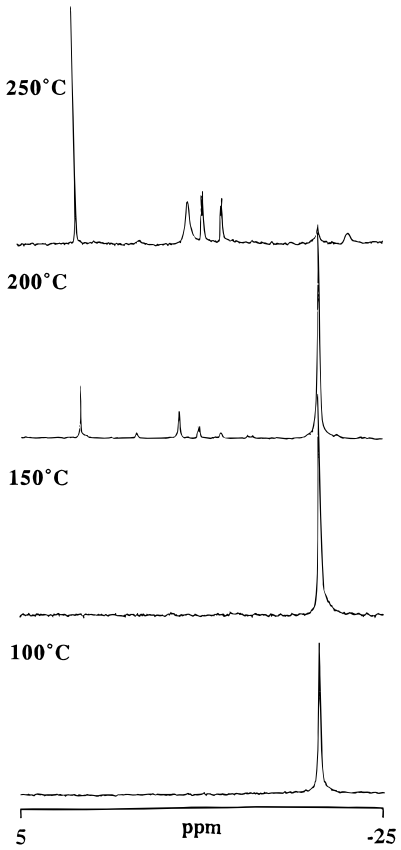

Figure 3. Solution-state ^{31}P NMR spectra of the soluble fractions obtained after isothermal degradation of poly[bis(carboxylatophenoxy)phosphazene] at the indicated temperatures.

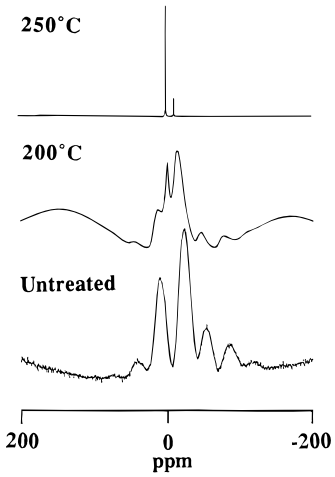

Figure 4. Solid state ^{31}P MAS NMR spectra of poly[bis(carboxylatophenoxy)phosphazene] obtained before heat treatment, shows the typical spectrum for a polyphosphazene below its T_g and after isothermal degradation at the indicated temperatures.

ance of a new resonance at −1.3 ppm in the solid-state ^{31}P MAS NMR spectrum (Figure 4) was consistent with this hypothesis. However, no evidence was found for the tri- and tetrameric cyclic oligomers that are typically formed by the clean depolymerization of polyphosphazenes. This is in agreement with previous reports that polyphosphazenes with polar para substituents on phenoxy side groups typically do not depolymerize into small rings.[4]

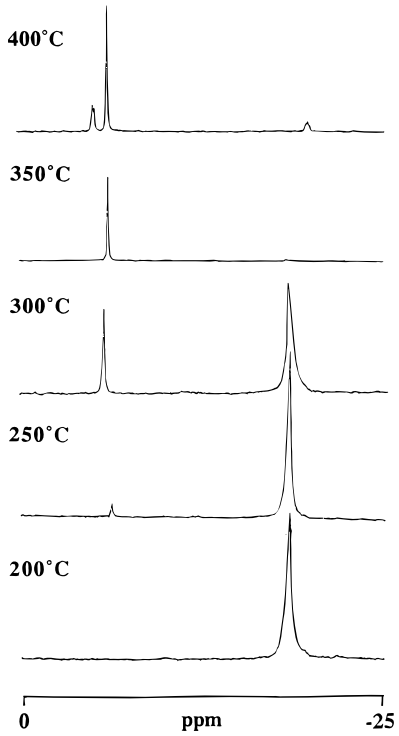

Figure 5. Solution-state ^{31}P NMR spectra of the soluble fractions obtained after isothermal degradation of the sodium salt of poly[bis(carboxylatophenoxy)phosphazene] at the indicated temperatures.

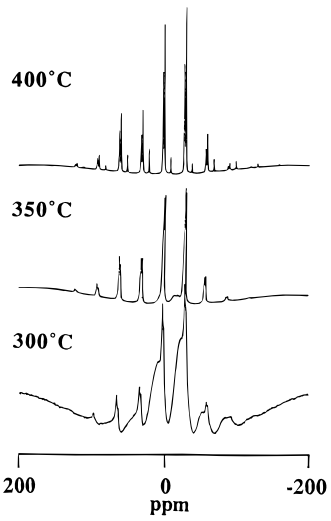

Figure 6. Solid-state ^{31}P MAS NMR spectra of the sodium salt of poly[bis(carboxylatophenoxy)phosphazene] after isothermal degradation at the indicated temperatures.

By 250 °C, the polymer had developed a brown color and was no longer swellable when brought into contact with organic liquids. This is consistent with the presence of a highly cross-linked ultrastructure. After two hours at 250 °C, the polymer had also undergone extensive chain cleavage as deduced from the solid state ^{31}P MAS NMR spectrum. Peaks were detected at −1.3 and −12.4 ppm (Figure 4). By 300 °C, the residue was a black char. Continued pyrolysis resulted in a further 35% weight loss at 340 °C followed by a steady loss of benzoic acid up to 850 °C, at which point the overall weight loss was 50%. A final 20% weight loss between 850−1000 °C resulted in an ultrastructure material which comprised 34% of the original weight. The EI-

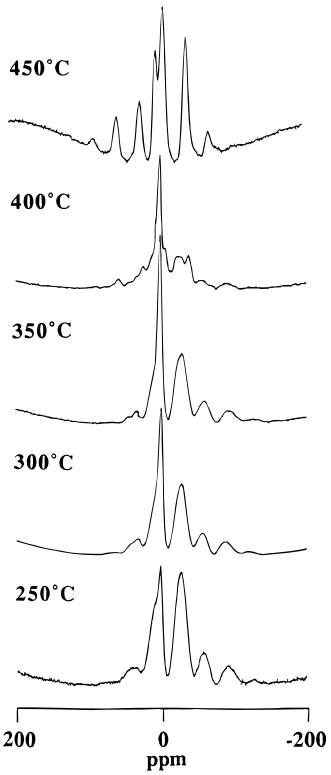

Figure 7. Solid-state ^{31}P MAS NMR spectra of the calcium cross-linked poly[bis(carboxylatophenoxy)phosphazene] after isothermal degradation at the indicated temperatures.

MS (Figure 2) obtained from the dynamic degradation experiments agreed fairly well with the results from the TGA and NMR experiments.

(b) Sodium Salt Form. Conversion of the polymer into its sodium salt or calcium cross-linked forms resulted in substantial increases in the thermal stability as is evident from Figures 1 and 2. For the sodium salt and calcium cross-linked forms, the onset of the 35% weight loss occurred at higher temperatures, from 340 to 400 and 470 °C, respectively. The 20% weight loss detected at 880 °C for the protonated form is absent or shifted beyond the range of the TGA experiments for the sodium salt and calcium cross-linked forms. The remaining pyrolysis product consisted of 53% and 49% of the original weight for the sodium salt and calcium cross-linked forms, respectively.

The sodium salt form of the polyphosphazene is completely stable up to 250 °C with no evidence of depolymerization, chain scission, or thermal cross-linking. The solution state ^{31}P NMR spectrum showed a singlet at −18 ppm which corresponded to the unchanged polymer (Figure 5). TGA and EI-MS data showed no weight loss or molecular fragments (Figures 1 and 2). Furthermore, no change occurred in the solubility of the polyphosphazene, and this indicated that substantial cross-linking had not occurred.

After the polymer sodium salt had been heated at 250 °C, the solution-state ^{31}P NMR spectrum contained a peak at −6.3 ppm which indicated the onset of chain scission (Figure 5). This is a major difference from the behavior of the protonated form which, as discussed, undergoes chain scission to yield small molecules below 250 °C. These observations illustrate the higher thermal stability of the sodium salt. TGA experiments showed a continuous, slight weight loss above 200 °C; however, EI-MS still did not provide any evidence for the volatilization of small molecular fragments.

After the 300 °C heat treatment, the polymer remained completely water-soluble. TGA experiments still showed the continuous, slow weight loss of volatile molecules which were not detectable by EI-MS. Solid-state ^{31}P MAS NMR spectra contained two new resonances at 2.3 and 0.5 ppm with associated spinning sidebands (Figure 6). The single resonances seen in the solid-state spectra for the protonated form had become two resonances which indicated that two slightly different phosphorus environments existed. The presence of the spinning sidebands indicate a highly rigid structure in the solid state.

By 350 °C substantial cross-linking had started to occur, with very little polymer remaining soluble in water. A small, continuous weight loss was detected by TGA and was identified by EI-MS as the loss of carbon dioxide during the condensation of the side groups. At 400 °C, a doublet appeared at −5.2 ppm in the solution-state ^{31}P NMR spectrum of the soluble portion. According to solid-state ^{31}P MAS NMR, no evidence was found for resonances associated with the high polymeric material, and a singlet appeared at −8.6 ppm with its associated sidebands. Between 400 and 500 °C no observable change occurred in the spectra. According to the EI-MS data, the main fragment initially lost is carbon dioxide, followed by a partial loss of the residual phenol until a temperature of 420 °C was reached, at which temperature other fragments were detected and these accounted for the weight-loss detected by TGA.

(c) Calcium Salt Cross-Linked Form. The calcium cross-linked form was not examined by solution-state NMR due to its general insolubility. As with the sodium salt, the calcium cross-linked species had a higher thermal stability than the protonated form. By solid-state ^{31}P MAS NMR (Figure 7), no change was evident until the material had been heated to 250 °C, at which point a singlet appeared at 2.5 ppm, which shifted to 1.8 ppm at higher isothermal degradation temperatures as the percentage of remaining polymer decreased. This suggested that chain scission had begun to occur in this temperature range. By 400 °C, the resonance pattern associated with the polymer had almost disappeared concurrently with the appearance of a new splitting pattern with the isotropic peak at −9.3 ppm. By 450 °C, no evidence remained of the polymer from the solid-state spectra. EI-MS indicated that carbon dioxide was the only detectable fragment evolved below 510 °C, at which point phenol and other side group fragments were eliminated.

Composites. Our HAp standard gave a TGA curve (Figure 8) typical of that reported previously.[26−29] The TGA gave a continuous but variable weight loss between 100 and 600 °C followed by a plateau region before a well-defined step at 700−800 °C. It is generally accepted that weight losses detected when HAp is heated are due to four mechanisms: (1) evolution of absorbed

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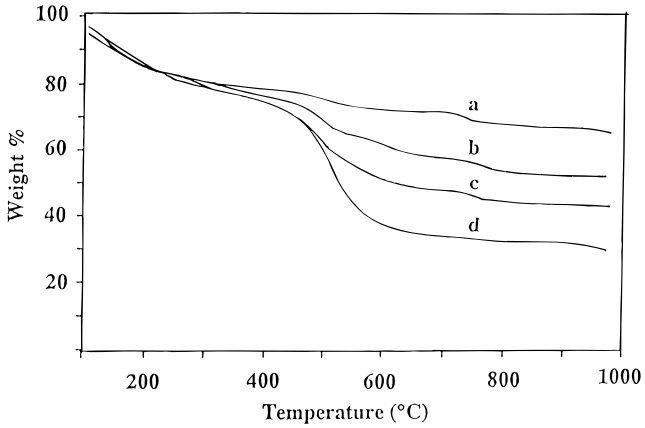

Figure 8. Loss in weight with temperature of (a) calcium-deficient hydroxyapatite and composites with inorganic precursor (DCPD+TetCP)-to-polyphosphazene weight ratios of (b) 20-to-1, (c) 10-to-1, and (d) 5-to-1.

water at 100−200 °C; (2) evolution of lattice water at 200−350 °C; (3) condensation of HPO_4^{2-}, $2HPO_4^{2-} \Rightarrow P_2O_7^{4-} + H_2O$, at 300−650 °C; (4) hydrolysis of $P_2O_7^{4-}$, $P_2O_7^{4-} + 2OH^- \Rightarrow 2PO_4^{3-} + H_2O$, at 700−900 °C. Mechanisms 3 and 4 do not occur in stoichiometric HAp ($Ca_5(PO_4)_3OH$) since no protonated orthophosphate anions are present in the structure. Conversely, calcium deficient HAp undergoes weight loss by all four mechanisms due to the presence of HPO_4^{2-} in its lattice. The relative amount of HPO_4^{2-} present increases as the Ca/P ratio decreases. At a Ca/P = 1.5, HAp can be completely converted to tricalcium phosphate ($Ca_3(PO_4)_2$) through the above weight loss mechanisms.

The TGA curves of the composite samples showed several features of interest (see Figure 8). The first is the extent of the weight losses associated with the polymer between 400 and 470 °C. The composite with the lowest polymer content of 20-to-1 (inorganic precursors-to-polyphosphazene) underwent a ∼2.5% weight loss. As the polymer content was doubled and quadrupled to 10-to-1 and 5-to-1 the weight losses increased correspondingly to ∼5% and ∼10%, respectively. The weight loss mechanism between 400 and 500 °C associated with the polymer probably occurs by the same route found for both the sodium salt and calcium cross-linked forms, i.e., the initial loss of CO_2 followed by the loss of phenol. The second feature of interest is the temperatures at which the weight losses occurred. As discussed above, the main loss from the sodium salt is at 400 °C while that for the calcium cross-linked form was at 470 °C. The main weight losses associated with the polymer in the 20-to-1, 10-to-1, and 5-to-1 composites were located at 445, 440, and 417 °C, respectively, which indicated varying degrees of calcium cross-linking.

This trend is consistent with the results from solution chemistry we reported previously.[24] It was found that *partial cross-linking and precipitation of the polymer by calcium ions is a prerequisite for significant HAp formation*. However, insufficient free calcium is present to result in the complete precipitation of the polymer. Therefore, as the polymer content is increased, the degree of calcium cross-linking is decreased and this leads to the observed trend in the weight losses associated with the differing polymer contents of the composites. This can also be used as an indication of the

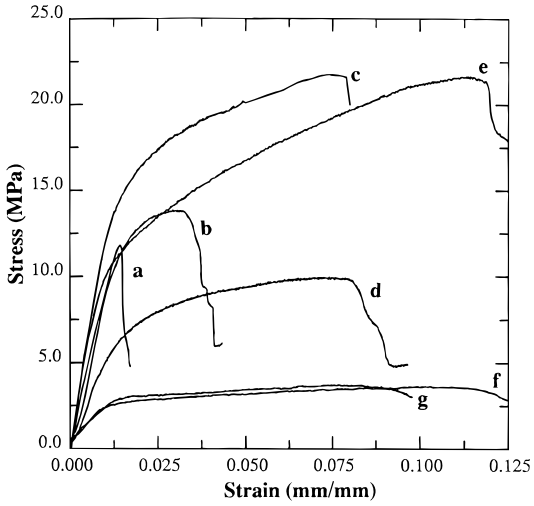

Figure 9. Stress-strain curves obtained from compression testing of (a) calcium deficient hydroxyapatite and composites with inorganic precursor (DCPD+TetCP)-to-polyphosphazene weight ratios of (b) 20-to-1 without cycling, (c) 20-to-1 with cycling, (d) 10-to-1 without cycling, (e) 10-to-1 with cycling, (f) 5-to-1 without cycling, and (g) 5-to-1 with cycling.

percentage of the polymer that is intimately bound into the HAp structure. It is this degree of intimate binding that will have a major effect on the mechanical properties of the composite material.

Compression Testing. The results of compressive strength analysis of HAp and the composites constituted at 5-to-1, 10-to-1, and 20-to-1 ratios are shown in Figure 9. In general, as the proportion of polyphosphazene was increased, the amount of strain prior to failure during compression increased. The compressive strengths of four polymer-free HAp cylinders ranged from 10.8 to 11.8 MPa. These samples showed very little deformation before failure, as is typical with ceramic materials. With the incorporation of the polymer in the 20-to-1 ratio, the compressive strength increased to 13.5−13.9 MPa (six cylinders). This increase is attributed to the high degree of calcium cross-linking and the resultant binding to the HAp phase. Due to the low percentage of polymer and high degree of bonding to the inorganic phase, the samples underwent only slightly more deformation before failure than did the pure HAp. This is a consequence of the plasticizing influence of the polymer. However, further increases in polymer content resulted in a decrease in the compressive strength of the composite with an increase in the amount of deformation which occurred before failure. Thus, as the polymer content was increased to the 10-to-1 ratio, a decrease occurred in the compressive strength to 9.1−9.9 MPa (four cylinders) and a further decrease to 3.4−3.7 MPa (four cylinders) at the 5-to-1 ratio. These decreases are a result of the decreasing cross-linking density of the polymer, and this yields a more flexible polymeric phase which contributes to the plasticizing effect, i.e., it acts as a lubricant between inorganic particles. Under the conditions specified for the compression testing, the samples still contain a high percentage of water, which allows the polymer to undergo plastic flow during compression testing. Thus, as the cross-linking density decreases, the polymer shows more plastic flow and this results in increased deformation and lower ultimate compressive stresses upon failure.

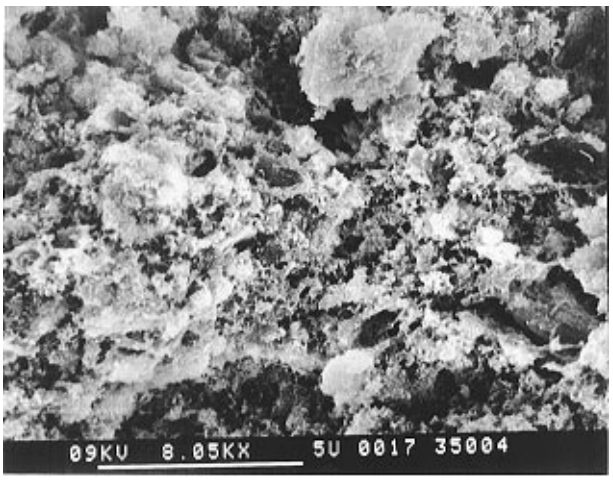

Figure 10. Scanning electron micrographs of the fracture surface after compression testing of a 5-to-1 (DCPD+TetCP)-to-polyphosphazene at a magnification = 8.05k×, bar = 5 μm.

The effect of cyclic loading on the compressive strength of the HAp-polyphosphazene composites was also investigated. Cycling increased the compressive strength of the 20-to-1 ratio to 21.8 MPa (after being cycled 10 times to 13 MPa) and that of the 10-to-1 ratio to 20.8−23.2 MPa (after being cycled 10 times to 8 MPa). This increase is due to the plasticizing effect of the polymer which allows particle rearrangement and densification of the highly porous composite material. The 5-to-1 ratio (after being cycled 10 times to 3 MPa) did not exhibit a difference in the compressive strength. However, it underwent failure at lower strain.

Microstructure. Figure 10 is a scanning electron micrograph of the 5-to-1 composite after compression testing and shows the general microstructure of the fracture surfaces. Aspects of the microstructure of these composites have been discussed previously.[24] The microstructures of all samples were relatively homogeneous with pore sizes ≤ 1 μm. The polyphosphazene-containing composites exhibited two main microstructural features. The microstructure is characterized by particulates on the order of 5 μm or less dispersed among and bound to a mineralized polymeric network. Homogeneity and uniformity in pore size distributions are critical for control of the mechanical properties of these materials. While porosity reduces the overall mechanical strength, the values can be both maximized and reproduced at a given bulk density provided large pores are minimized. Although compressive strength is less sensitive to critical flaw sizes than flexural strength, the reproducible ultimate compressive strengths found for our composites and the microstructure at a given composition indicate a relatively homogeneous system.

Conclusions

We have developed a method to overcome the inherent limitation in the thermal stability of bone, which limits its potential nonmedical applications, by the substitution of a polyphosphazene for the collagen reinforcing phase. Thermogravimetric analysis, isothermal, and dynamic degradation studies were used to examine the thermal stability of poly[bis(carboxylatophenoxy)phosphazene] in its protonated, sodium salt, and calcium cross-linked forms as well as in composites that utilize hydroxyapatite as the inorganic phase. Unlike poly[bis(phenoxy)phosphazene],[4] poly[bis(carboxylatophenoxy)phosphazene] showed no evidence of depolymerization but instead underwent elimination of the side groups in a variety of fragments. The main fragments initially lost from the protonated form of the polymer are benzoic acid and *p*-hydroxybenzoic acid together with carbon dioxide and phenol. This does not preclude the possibility that other volatile molecules are formed below the detection limit of the EI-MS experiments. It was found that conversion of the polyphosphazene from the protonated form to its sodium salt substantially increased its thermal stability. A further increase was evident following conversion to the calcium cross-linked form. The thermal stability of the polyphosphazene incorporated into the composite varied according to the (DCPD+TetCP)-to-polyphosphazene weight ratio and the degree of intimate bonding between the two phases.

The compressive strength of the HAp−polyphosphazene composites was also examined. It was found that, at a 20-to-1 weight ratio, an increase occurred in the compressive strength due to the high degree of cross-linking and binding of the polymer to the inorganic phase. However, further increases in polyphosphazene content resulted in a decrease in the compressive strength. This decrease is a result of the decreasing cross-link density as the polymer content is increased and thus allows the polymeric phase to undergo plastic flow. Also, as the polyphosphazene content was increased, there was a corresponding increase in the strain before failure due to the plasticizing effect of the polyphosphazene.

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