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# Crosslinked polyanhydrides for use in orthopedic applications: Degradation behavior and mechanics

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**Abstract:** High-strength, surface-eroding polymers were synthesized from methacrylated anhydride monomers of sebacic acid (MSA) and 1,6-bis(carboxyphenoxy) hexane (MCPH). These multifunctional monomers were photopolymerized using ultraviolet light to produce highly crosslinked polyanhydride networks. Through this approach, the crosslinking density of the resulting polymer network was used to control the final mechanical properties, while the degradation time scale was controlled by the chemical composition of the network. The combined hydrophobicity of the polymer backbone with the hydrolytically labile anhydride linkages led to surface-eroding networks, as confirmed by linear cumulative mass loss profiles as a function of degradation time for crosslinked polymer disks. By copolymerizing varying amounts of MSA and MCPH,

the degradation rate of the final network was controlled from 2 days to 1 year. The tensile modulus of crosslinked poly(MSA) (1.4 GPa) was nearly an order of magnitude larger than that of linear poly(sebacic acid). In general, the mechanical properties of the crosslinked polyanhydrides networks were within ranges of those reported for cortical and trabecular bone. However, unlike bulk degrading polyesters such as poly(lactic acid), these surface eroding networks maintained >70% of their tensile modulus with 50% mass degradation. © 1999 John Wiley & Sons, Inc. *J Biomed Mater Res*, 46, 271–278, 1999.

**Key words:** polyanhydride; photopolymerization; crosslinking; surface erosion

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## INTRODUCTION

Many orthopedic applications could benefit from the development of new high-strength, degradable polymeric materials. In general, treatment of bone fractures through fixation requires the use of materials with sufficient strength to allow fixation with restoration of regional mechanical properties to aid patient treatment and rehabilitation, good tissue–material compatibility, and facile molding (into potentially complex shapes) for easy placement by the surgeon. While metallic implants are widely used in many treatments,<sup>1</sup> current limitations of these systems include stress shielding during healing, chronic inflammation caused by corrosion, and fatigue and loosening of the implant. As a result, a second surgery is often required to remove the implant after healing, and the risk and expense to the patient of a second

surgery are significant. Thus, degradable polymeric materials provide an important alternative to metal implants for several reasons. First, degradable polymers eliminate the need for a second surgery and can prevent some of the problems associated with stress shielding during healing. Unlike metals, degradable polymer implants can also be used simultaneously to deliver therapeutic drugs to treat infections or growth factors to accelerate new bone growth.

Thus far, studies on high-strength, biodegradable polymers have focused on the family of polyesters, specifically poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(lactide-*co*-glycolide) (PLGA), and poly(*p*-dioxanon) (PDS). The advantages of these polymers are that they are biocompatible and bioresorbable, have been approved by the U.S. Food and Drug Administration (FDA) for clinical use, and have been used successfully in medical applications as suture materials. Cutright et al.<sup>2</sup> performed some of the first studies of these biodegradable polyesters—in particular, PLA—as fracture fixation devices and demonstrated the successful healing of mandibular fractures in monkeys and dogs. Since then, several researchers<sup>3–8</sup> have fabricated orthopedic screws and rods from PGA and PLA and studied their effects in animal models with varying degrees of success. However, the

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use of degradable polyesters for fixation under load often produces rather poor results, related to the polymers' bulk degradation mechanism. In particular, bulk degradation can cause significant and sudden losses in molecular weight early in the degradation process without accompanying losses in mass.<sup>9,10</sup> This behavior compromises the macroscopic structural properties of the polymer and leads to a majority of mass loss at the end of the degradation, which can elicit an inflammatory response because of the local burst of acid products.<sup>10,11</sup>

While the shortcomings of bulk degradation, particularly the potential for end-stage bursts of acid products leading to local inflammation, remain under debate, there is a need for new polymers that address the maintenance of mechanical properties with degradation and allow independent control of the mechanical properties and degradation time scale. Thus, as an alternative to the bulk degrading polyesters, polyanhydrides (from nonphysiological monomers) have been developed that are biocompatible, exhibit well-defined degradation characteristics, and were approved by the FDA in 1996 to deliver chemotherapy agents to treat patients with brain cancer.<sup>12</sup> These polymers have hydrophobic backbones and hydrolytically labile anhydride linkages that lead to surface degradation.<sup>13</sup> While this mechanism has proven to be beneficial in the delivery of drugs, we hypothesize that surface-eroding polymers might provide additional advantages in certain load-bearing applications such as orthopedics.

Since the initial mechanical properties of the linear polyanhydrides are significantly lower than that of ultrahigh-molecular-weight and highly crystalline PLA, Staubli et al.<sup>14</sup> and Urrich et al.<sup>15</sup> synthesized polyanhydrides with improved mechanical strength by incorporating imide groups in the polymer backbone. Polyimides have high thermal and mechanical stability, and several commercially available aromatic polyimides were evaluated and found to be biocompatible.<sup>16</sup> Urrich et al.<sup>15</sup> synthesized a series of poly-(anhydride-co-imides) in which the ratio of imide monomer to anhydride monomer was varied. For the imide monomers studied—for example, trimellitylimidoglycine (TMA-gly) or pyromellitylimidoalanine (PMA-ala)—the molecular weight of the polymer decreased with increasing imide content caused by the decreased mobility and backbone flexibility. In general, the mechanical and thermal stability of the materials were greatly increased by the incorporation of imide groups. Polymers of PMA-ala/CPH were the most promising materials, with initial compression strengths (36–56 MPa) in addition to long degradation times.<sup>15</sup>

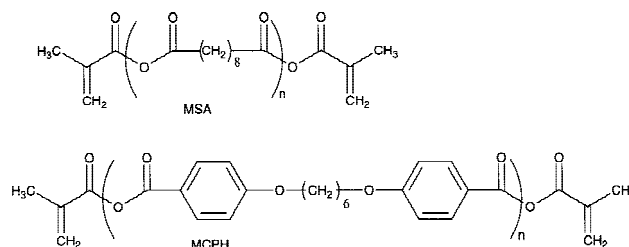
As an alternative approach, we recently developed a new class of anhydride monomers<sup>17–19</sup> that possess methacrylate end groups which are readily photopoly-

merized to produce highly crosslinked polyanhydride networks. Through this approach, the crosslinking density of the resulting polymer network can be used to control the final material properties, while the degradation time scale can be controlled by the chemical composition of the network. An additional benefit of this approach is the use of photopolymerization to form the crosslinked polymers. A system which could be photocured *in vivo* while possessing desired mechanical properties and degradation rates could lead to many newfound applications. For example, in an irregularly shaped trabecular bone defect, a viscous liquid monomer could be introduced into the defect and the system photopolymerized *in vivo* to provide a crosslinked, biodegradable polymer of the required dimensions. Flexible fracture fixation plates could be developed from partially reacted monomers (i.e., postgelation, but not completely reacted). The surgeon could contour these flexible plates *in vivo* and subsequently produce a rigid plate by exposing it to light to complete the crosslinking polymerization. The polymerization behavior of these monomers under a wide range of photoinitiation conditions has been presented elsewhere.<sup>19</sup>

The focus of this study was to examine the effect of polymer composition on the degradation rate and the influence of crosslinking density on the tensile and compressive moduli of the network. In addition, the influence of degradation on the structural and mechanical integrity of the crosslinked polyanhydrides was investigated.

## EXPERIMENTAL

Methacrylated sebacic anhydride (MSA) monomer (Fig. 1) was synthesized from sebacic acid and methacrylic anhydride. The MSA was prepared by converting the dicarboxylic acid to an anhydride by refluxing in 2.5M equivalents of methacrylic anhydride for 1 h. The product was subsequently isolated and purified by precipitation into petroleum ether from a methylene chloride solution. The methacrylated monomers were characterized with <sup>1</sup>H-nuclear magnetic resonance imaging (NMR) and Fourier transform infrared



**Figure 1.** Methacrylated anhydride monomers of sebacic acid (MSA) and 1,6-bis(carboxyphenoxy) hexane (MCPH).

spectroscopy (FTIR) to examine the extent of methacrylation. The presence of the methacrylate  $=\text{CH}_2$  protons was confirmed with  $^1\text{H-NMR}$  (VXR-300; Varian) at approximately  $\delta = 6.0$  and 6.5 parts per million (ppm), and with FTIR at approximately  $1637\text{ cm}^{-1}$ . Comparing the  $=\text{CH}_2$  protons to the internal methylene protons of the sebacic acid, the degree of oligomerization ( $n$ ) was calculated to be approximately three sebacic acid repeat units between the methacrylate end groups. Elemental analysis of the MSA monomer was C: 64.2, O: 27.7, H: 8.1 (calculated theoretical for  $n = 3$ , C: 64.6, O: 27.7, H: 8.2). All materials were stored under argon at subambient temperatures to prevent hydrolysis of the anhydride linkages before polymerization.

Dicarboxylic acids 1,6-bis(carboxyphenoxy) hexane (CPH) and 1,3-bis(carboxyphenoxy) propane (CPP) were synthesized as described elsewhere.<sup>20</sup> To facilitate methacrylation of the less soluble diacids, the acid groups were first acetylated by refluxing in an excess of acetic anhydride for several hours. The diacetylated products were isolated and purified by an ether wash and vacuum filtration. The acetylated CPH was end capped with methacrylate functionalities by refluxing in methacrylic anhydride for approximately 1 h. The dimethacrylated product (MCPH) (Fig. 1) was subsequently isolated and purified by precipitation in petroleum ether from a methylene chloride solution. As above, the presence of the methacrylate  $=\text{CH}_2$  protons was confirmed with  $^1\text{H-NMR}$  at approximately  $\delta = 6.0$  and 6.5 ppm, and with FTIR at approximately  $1637\text{ cm}^{-1}$ . Comparing the  $=\text{CH}_2$  protons to the aromatic protons of the CPH, the material was essentially monomeric ( $n = 1.1$ ). Elemental analysis of the MCPH monomer was C: 67.5, O: 25.8, H: 6.7 (calculated theoretical for  $n = 1$ , C: 68.0, O: 25.9, H: 6.1).

A linear polyanhydride, poly(CPP:CPH), was synthesized by a melt condensation of acetylated monomers.<sup>21</sup> The poly(CPP:CPH) was produced by a condensation polymerization of 50:50 acetylated CPP and CPH, in molar equivalents. The molecular weight of the polymer was estimated on a Perkin Elmer GPC system. The number average molecular weight was  $\sim 15,000\text{ g/mol}$ , and the copolymer composition was calculated as  $\sim 55:45$  poly(CPP:CPH) from NMR.

Samples were polymerized with either full-beam ultraviolet light (Ultracure 100SS; EFOS) or longwave ultraviolet light (Model B100AP; 115V, 2.5A Black-Ray) at various light intensities. Photopolymerizations were conducted at light intensities ranging between 1 and  $150\text{ mW/cm}^2$ . The ultraviolet initiator used was 2,2-dimethoxy-2-phenyl-acetophenone (DMPA), which is a standard photoinitiator used in many ultraviolet photopolymerization applications.<sup>22</sup> Sample formulations were prepared by dissolving 1.0 wt % of DMPA in the monomer being investigated. In general, the high concentration of double bonds in the system

and the multifunctional nature of the monomer (two double bonds per monomer molecule) led to the formation of a highly crosslinked polymer network.

Uniform disks ( $\sim 1.7\text{ mm}$  in thickness and  $16\text{ mm}$  in diameter) were prepared in Teflon molds to evaluate the degradation kinetics and mechanism. This disk thickness allowed easy handling, provided a high aspect ratio (diameter to thickness) to approximate one-dimensional (1D) degradation, and allowed high double-bond conversion as a function of sample depth.<sup>19</sup> Degradation studies were conducted in phosphate-buffered saline (PBS) solution under simulated physiological conditions, i.e., pH 7.4 and  $37^\circ\text{C}$ , with continuous orbital shaking at 80 rpm. The disks were degraded in 250 mL of buffer that was replaced when the pH dropped below 7.4. The solubility of SA in water is approximately  $1\text{ mg/mL}$ , and for CPH,  $0.1\text{ mg/mL}$ . Sink conditions were maintained throughout the degradation. Degradation rates were characterized by mass loss and dimensions of the degrading samples were monitored to evaluate further the surface degradation mechanism. The diameter of the disks did not change significantly with degradation.

Compressive strengths of the crosslinked polyanhydrides were measured using a Static Material Tester on cylindrical samples with an aspect ratio of 2:1; An ASTM (F451-756) cylindrical Teflon die ( $8\text{ mm}$  in diameter,  $16\text{ mm}$  in length) was used. A Dynamic Mechanical Analyzer was used to measure the tensile modulus of the crosslinked polyanhydride strips ( $4 \times 1 \times 25\text{ mm}$ ) at  $37^\circ\text{C}$  and as a function of degradation. The values presented in this study were obtained using a three-point-bending probe at a frequency of 1 Hz.

## RESULTS AND DISCUSSION

### Degradation behavior

An implant system that demonstrates gradual and controllable, time-dependent, nontoxic degradation while maintaining mechanical integrity is highly desirable. It is necessary, however, for the degradation to be well characterized and flexible to fit varied applications. The degradation mechanism and erosion kinetics depend largely on the specific chemistry and morphology of the polymer, although the size and geometry of the implant, degradation environment (e.g., pH), and implantation site also contribute.

To this extent, salient degradation studies were performed to examine the erosion mechanism and rate of the newly developed crosslinked polyanhydrides. The effect of network composition on degradation behav-

ior was also investigated. Degradation rates, characterized by mass loss, of disks of poly(MSA), poly(MCPH), and MSA/MCPH copolymers were examined.

The cumulative degradation of crosslinked poly(MSA) disks in PBS at pH 7.4 and 37°C is plotted in Figure 2. The degradation of poly(MSA) was relatively rapid, with complete disappearance of a 16-mm-diameter and 1.8-mm-thick disk in approximately 54 h. In general, varying the rate of photoinitiation (e.g., changes in initiator concentration or light intensity) influenced the overall polymerization behavior of these crosslinking systems, and ultimately the extent of conversion and structural properties of the resulting network. However, the data in Figure 2 were collected from several disks polymerized at light intensities ranging from 1 to 150 mW/cm<sup>2</sup>, and the degradation behavior varied little from sample to sample, indicating little or no influence of the photoinitiation conditions on the macroscopic degradation behavior.

The degradation rate for poly(MSA) followed a linear trend ( $R^2 = .9964$ ), which further supports the surface erosion mechanism and is similar to previous observations in linear polyanhydrides.<sup>23–25</sup> However, the presence of crosslinks in these newly developed polyanhydride networks further limited the diffusion of water in the matrix and provided an effective means of extending the degradation time scale compared to linear polyanhydrides. For example, in disks of the same dimensions, compression molded disks of linear poly(SA) degraded in <24 h,<sup>25</sup> whereas the crosslinked poly(MSA) degraded in ~50 h, showing more than a twofold decrease in the degradation rate. Part of the differences in the degradation may also be attributed to the microporosity that can result in compression molded disks of the linear poly(MSA) that would not be present in the photocrosslinked system.

While these disks were fabricated to approximate 1D degradation, the mass degradation rate for a more

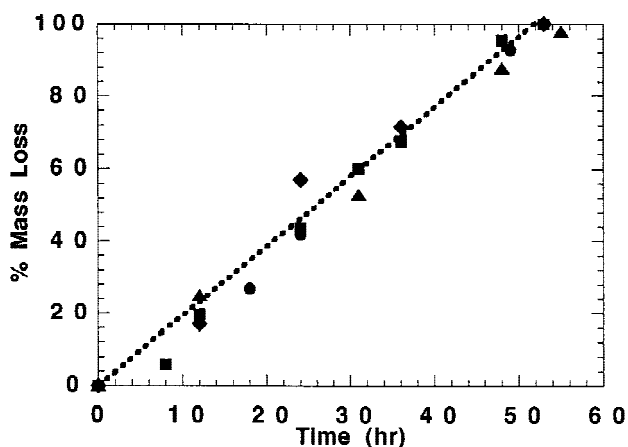


Figure 2. Cumulative percent mass loss as a function of degradation time for poly(MSA).

complex geometry (e.g., plates, screws, and pins used in fracture fixation) was a function of the surface area to volume of the implant. For these cases, characterization of the 1D degradation kinetic constant is useful, as it can be used to model and predict the mass loss from other 3D geometries. Thus, the degradation kinetic constant ( $k$ ) was obtained from crosslinked disks of varying composition by calculating the slope of the erosion profile and multiplying this by the thickness of the disk (i.e., the direction of the 1D degradation front). For the degradation studies, the surface area remains nearly constant throughout the degradation, so  $k$  was readily calculated. The average  $k$  value was computed from several duplicate experiments for poly(MSA) and found to be approximately  $3.47 \times 10^{-2}$  mm/h.

To control the degradation rate, more hydrophobic monomers were incorporated into the network. For example, MCPH with its aromaticity (two phenyl rings per molecule) and its long hydrocarbon backbone is a more hydrophobic anhydride monomer than MSA. As illustrated in Figure 3, the rate of erosion in the poly(MCPH) system was much slower than those measured for poly(MSA). The reported compositions are in weight percentage for each of the monomers. Even after 2160 h (90 days), the system reached only ~30% mass loss. Extrapolating a linear erosion profile, this disk would require approximately 1 year to degrade completely. The degradation kinetic constant was  $2.16 \times 10^{-4}$  mm/h, approximately two orders of magnitude lower than the value computed for the crosslinked homopolymer of MSA. Thus, by copolymerizing MSA and MCPH, networks were formed with degradation times spanning ~2 days to ~1 year, and these results are shown in Figure 3. For example, if we extrapolate the curves to 100% mass loss, the 50:50 (MSA:MCPH) copolymer degrades in ~10 days,

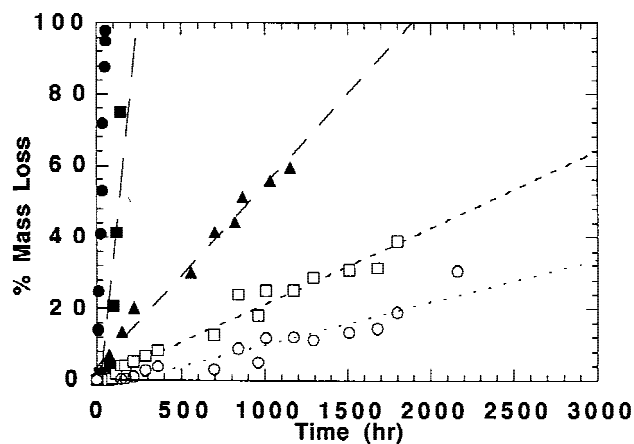


Figure 3. Cumulative percent mass loss as a function of degradation time for crosslinked polymers of varying composition: poly(MSA) (●), 50:50 poly(MSA:MCPH) (■), 40:60 poly(MSA:MCPH) (▲), 25:75 poly(MSA:MCPH) (□), and poly(MCPH) (○).

the 40:60 copolymer in ~79 days, and the 25:75 copolymer in ~195 days.

The degradation kinetic constants calculated for each of the copolymer compositions were  $8.29 \times 10^{-3}$  mm/h (50:50),  $9.19 \times 10^{-4}$  mm/h (40:60), and  $3.85 \times 10^{-4}$  mm/h (25:75). These data are plotted in Figure 4 along with the results for the crosslinked homopolymers. These results indicate the sensitivity of the degradation rate to the overall composition. In general, a slight decrease, approximately fourfold, in the degradation kinetic constant was seen as the network composition approached 50 wt % MCPH. Then, beyond this threshold composition, the kinetic constant depended more strongly on the MCPH content and decreased by a factor of 40 as the network composition approaches 100 wt % poly(MCPH). These results indicate the ability to tailor the copolymer compositions to produce implants that degrade over a wide range of time scales.

An additional strategy for controlling the degradation time scale of the final polymer network was investigated in these studies: the formulation of semi-IPNs (semi-interpenetrating polymer networks). The semi-IPNs were fabricated by combining the MSA monomer with a linear copolymer of CPH and CPP, poly(CPP:CPH). The MSA was photopolymerized to produce a crosslinked polymer network while the linear polymer remained chemically independent and physically entangled. The purpose of selecting a semi-IPN was twofold. First, the hydrophobic fragments of poly(CPP:CPH) should further hinder the penetration of water into the semi-IPN, increasing the overall hydrophobicity in the degrading network by reducing the concentration of the more hydrophilic degradation products [e.g. poly(methacrylic acid) and sebacic acid]. Second, the incorporation of an unreactive linear polymer in the MSA reduces the volume shrinkage and heat evolution that occurs when the system is photocrosslinked.

The semi-IPN examined consisted of 50 wt % MSA

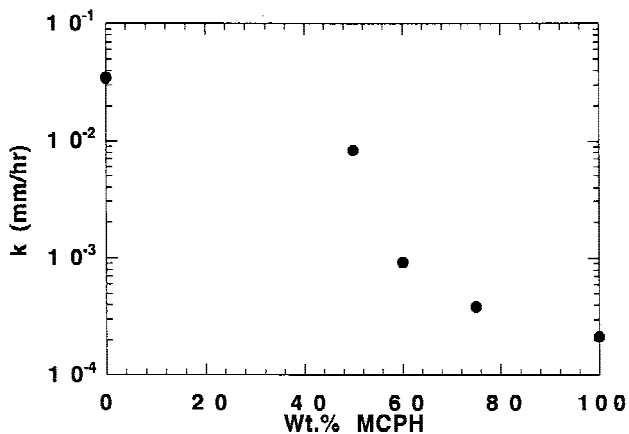


Figure 4. Degradation kinetic constants,  $k$ , as a function of weight percent MCPH in the polymer network.

and 50 wt % poly(CPP:CPH), and the mass degradation resulting as a function of time are plotted in Figure 5. The erosion rate was significantly reduced compared to the crosslinked homopolymer of MSA. For example after 48 h, the semi-IPN was only 1% degraded, while the MSA homopolymer was nearly completely degraded. The slope of the degradation curves varied by more than a factor of 30. Thus, in addition to composition variations in the crosslinked networks, incorporation of linear polymers to form semi-IPNs provides another mechanism to control the degradation rate while simultaneously providing further advantages with respect to polymerization issues.

### Mechanical properties

For fracture fixation, a desirable material should provide initial mechanical strength to the injured area, induce or allow new bone growth, and degrade systematically into nontoxic, resorbable compounds to circumvent surgical removal of the device. The focus of this study was to examine the initial mechanical properties of the proposed photocrosslinkable polyanhydride systems and assess their ability to maintain structural and mechanical integrity with degradation.

Table I provides ranges for the strength and moduli of cortical and trabecular bone.<sup>26–28</sup> The bone properties reported are ranges for the human femur, fibula, tibia, humerus, radius, and ulna. In general, the vertebrae and skull have less stringent requirements and can be up to an order of magnitude lower. For comparison, crosslinked polymers of MSA and MCPH were prepared and tested to measure the compressive strength, the initial tensile modulus, and the tensile modulus as a function of degradation. The results are summarized in Table I.

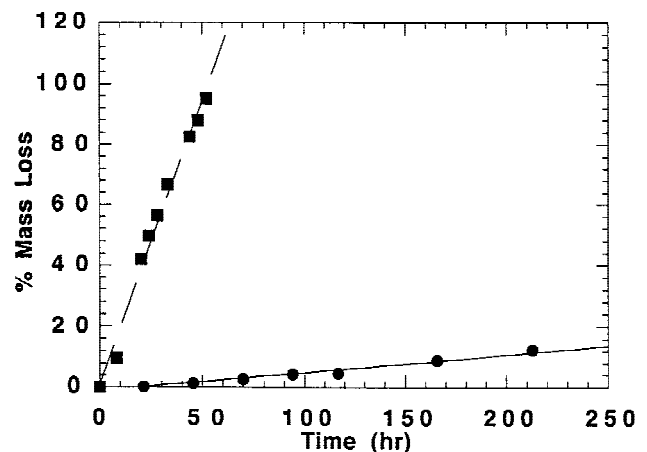


Figure 5. Cumulative percent mass loss as a function of degradation time for a semi-IPN (●) composed of 50 wt % crosslinked MSA and 50 wt % linear poly(CPP:CPH) as compared to the crosslinked homopolymer of MSA (■).

TABLE I  
Mechanical Properties of Bone 26–28 as Compared to the Mechanical Properties of Crosslinked Homopolymers of MSA and MCPH

Bone	Modulus		Strength	
	Tensile	Flexural	Tensile	Compressive
Cortical	17–20 GPa	3 GPa	80–150 MPa	130–220 MPa
Trabecular	50–100 MPa	50–100 MPa	5–10 MPa	5–10 MPa
Polymer composition	Compressive Strength			Tensile Modulus
Poly (MSA)	40 ± 10 MPa			1400 ± 120 MPa
Poly (MCPH)	32 ± 2 MPa			640 ± 80 MPa

In general, the mechanical properties of the crosslinked polyanhydrides were intermediate between those of trabecular and cortical bone. Interestingly, the tensile modulus of poly(MSA) was significantly greater than that of poly(MCPH) at 37°C. One possible explanation for the difference in the tensile modulus between the two networks may be related to the molecular weight of the monomer. During the synthesis of the methacrylated monomers, oligomerization can occur,<sup>18,19</sup> which produces a higher molecular weight starting material ( $n = 5$ ). In particular, the oligomerization occurs to a greater extent during the MCPH synthesis, which can lead to a lower degree of crosslinking in the network. In addition, both systems were photopolymerized under identical reaction conditions (i.e., light intensity, initiating wavelength, and initiator concentration); however, MCPH polymerizes more slowly than MSA and light attenuation occurs to a greater degree in MCPH when polymerized with ultraviolet light.<sup>19</sup> Both of these factors can lead to a lower maximum double-bond conversion in the poly(MCPH) network compared to the poly(MSA) network. The presence of unreacted double bonds not only reduces the crosslinking density, but can plasticize the network and reduce its mechanical properties.<sup>29</sup>

In comparison to their linear polymer counterparts, the tensile modulus of the crosslinked polyanhydrides was greatly improved. While crosslinking is widely known to enhance mechanical properties, relatively few degradable polymers are readily crosslinkable. Thus, one of our objective was to design materials that were readily photocrosslinkable and formed highly crosslinked degradable networks. For example, the tensile modulus of linear poly(SA) has been reported at 100 MPa; hence, crosslinking leads to more than an order of magnitude increase in the modulus.<sup>30</sup> Other approaches to increasing the mechanical strength of linear polyanhydrides have focused on incorporating imide groups into the polymer backbone. These materials have good compressive strengths (ranging from ~30 to 60 MPa),<sup>11,12</sup> but they are relatively brittle and lack tensile strength. Finally, currently used orthopedic fracture fixation devices of PLA have good initial

tensile and compressive strengths, between 30 and 50 MPa, which can be further increased by self-reinforcement techniques.<sup>31,32</sup> However, the efficacy of polyesters such as PLA and PGA in many orthopedic applications is limited by their bulk degradation, which can lead to dramatic losses in mechanical strength early during the degradation process.<sup>33</sup> For example, one study<sup>34</sup> examined the bending strength of self-reinforced PGA rods following subcutaneous implantation in rabbits. Results showed approximately 36% mechanical loss after 1 week, and close to 70% loss in bending strength following 2 weeks of implantation. Similar losses have been reported for various devices composed of PGA and PLA *in vitro* as well.<sup>5</sup>

In contrast, Figure 6 shows the effect of mass degradation on the tensile modulus of crosslinked poly(MSA) and a crosslinked copolymer of MSA and MCPH. In both systems, the polymers maintained their structural integrity and >70% of their tensile modulus at 50% mass degradation. Thus, the photopolymerizable and crosslinkable polyanhydrides provide not only great flexibility in placement and processing of orthopedic implants, but also enhance mechanical properties of the resulting polymer, particularly as the sample degrades.

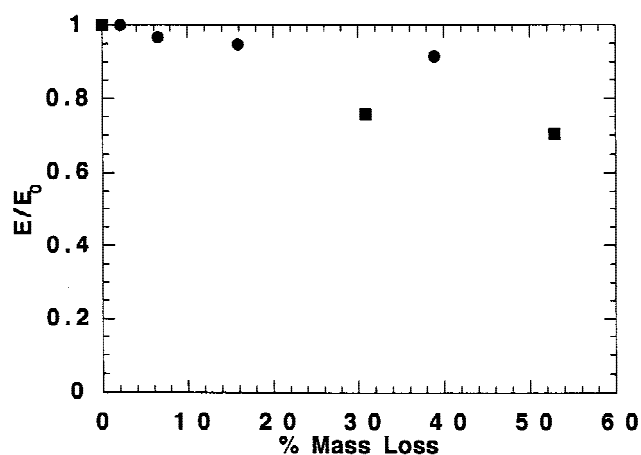


Figure 6. Tensile modulus normalized by the initial tensile modulus during the degradation of poly(MSA) (●) and poly(MSA:MCPH) 25:75 (■).

In future work, the initial mechanical properties of these crosslinked networks will be further controlled and optimized by changes such as the rigidity of the monomer units, incorporating fillers in the polymer network, varying the crosslinking density, and optimizing the polymerization conditions (e.g., light intensity and initiator concentration) to increase the maximum functional group conversion. For example, an inorganic filler such as hydroxyapatite<sup>35</sup> can improve the compressive strength of the polymer while simultaneously imparting osteoconductive properties to the composite. In addition, linear polymers can be incorporated to form semi-IPNs that not only alter the degradation behavior of the implant, as illustrated in this work, but may potentially improve the tensile strength of the network. For example, bone cement consists of a linear poly(methyl methacrylate) powder that is mixed with a liquid methyl methacrylate monomer and subsequently polymerized with redox or thermal initiators to produce a material with good compressive (70–90 MPa) and tensile (20–50 MPa) strengths.<sup>1</sup> Fillers such as these not only serve to impart desired mechanical properties, but also act as a heat sink for *in vivo* polymerizations and reduce the concentration of double bonds to help minimize shrinkage.

## CONCLUSIONS

Anhydride monomers end capped with methacrylate functionalities were photopolymerized to produce highly crosslinked, surface-eroding polymers. Specifically, the two monomers studied were MSA and MCPH, which is relatively more hydrophobic than MSA. The hydrolytic degradation of polymer disks of varying composition was characterized *in vitro* in PBS at 37°C. In general, the cumulative mass loss from these crosslinked polyanhydrides was linear with degradation time, demonstrating the surface controlled erosion mechanism. Furthermore, the degradation time scale could be controlled by variations in the network composition from ~2 days for poly(MSA) to ~1 year for poly(MCPH).

Characterization of the mechanical properties of these crosslinked polyanhydrides (i.e., tensile modulus and compressive strength) showed that in comparison to linear polyanhydrides, the tensile modulus and compressive strength were greatly improved. Typically, the polymer mechanical properties were intermediate between those of cortical and trabecular bone. However, unlike bulk degrading polyesters, these surface-eroding polymers maintained their structural and mechanical integrity with degradation. Studies indicated that crosslinked networks maintained >70% of their tensile modulus beyond 50%

mass degradation. The maintenance of mechanical integrity during degradation could provide many advantages in load-bearing applications such as orthopedics.

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