Acta Biomaterialia 7 (2011) 558–567

Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

Long-term toughness of photopolymerizable (meth)acrylate networks in aqueous environments

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ARTICLE INFO

Article history:
Received 6 July 2010
Received in revised form 27 August 2010
Accepted 1 September 2010
Available online 7 September 2010

Keywords:
Photopolymerizable
Toughness
Acrylate
Water
Glass transition temperature

ABSTRACT

Photopolymerizable (meth)acrylate networks are potentially advantageous biomaterials due to their ability to be formed in situ, their fast synthesis rates and their tailorable material properties. The objective of this study was to evaluate how immersion time in phosphate-buffered saline (PBS) affects the toughness of photopolymerizable methyl acrylate (MA)–co-methyl methacrylate–co-poly(ethylene glycol) dimethacrylate networks containing various concentrations of MA. Stress–strain behavior was determined by performing tensile strain to failure testing after soaking in PBS for different periods (1 day up to 9 months). In tandem, differential scanning calorimetry and PBS content measurements were undertaken at each time point in order to determine whether time-dependent changes in toughness were related to changes in T_g or PBS absorption. The effect of immersion time on network toughness was shown to be dependent upon composition in a manner related to the viscoelastic state of the polymer upon initial immersion in PBS. The results demonstrate that tough acrylate-based materials may not maintain their toughness after several months in PBS. In addition, decreasing the PBS content by changing the network hydrophobicity resulted in better toughness maintenance after 9 months. The results provide a possible means to toughen various amorphous acrylate-based implant materials that are being explored for load-bearing biomedical applications, beyond the systems considered in this work.

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1. Introduction

In recent years polymer-based biomaterials have been adopted for many orthopedic implant applications over metal or ceramic-based implants because their compliance aligns better with native biological tissues, thus reducing stress shielding effects and potential tissue degeneration [1]. In particular, photopolymerizable polymers offer additional advantages in that they can be formed in situ and into complex geometries rendering them useful for minimally invasive procedures [2]. Many photopolymerizable material platforms, such as (meth)acrylate networks, also possess readily tailorable material properties through changes in network chemistry and structure [3,4]. These materials have been proposed as cartilage tissue replacements [5], bone cements [6] and shape memory fixation devices [4]. Although acrylate-based materials are very versatile from a processing and surgical methods standpoint, "durability" in terms of mechanical properties are considerably less than alternative implant materials such as ultra-high molecular weight polyethylene (UHMWPE) or poly(ether ether ketone) (PEEK) [7], particularly when exposed to hydrated conditions. In this work we aim to better understand the toughness of a model acrylate system as a function of longer term exposure to aqueous solutions.

Besides having an appropriate elastic modulus, a key characteristic of a viable orthopedic biomaterial is its ability to withstand large mechanical loads and deformations for extended periods of time, requiring the material to be tough. Inherent toughness can be measured as the energy required to break a material and broadly reflects the ultimate stress and strain the material can withstand. Inherent toughness has also been correlated with other important properties of implant materials, including wear resistance, suggesting that toughness maybe an indicator of "overall" material durability [8]. Although acrylate-based materials have good wear resistance for dental applications, they achieve this through extremely high degrees of cross-linking [9,10], a mode of strengthening not available to applications that require open networks with an elastic modulus in the MPa to kPa range. Material durability or toughness is crucial in that premature mechanical failure of implants can lead to further tissue injury, pain and additional surgical procedures. Polymer-based biomaterials particularly are plagued with unsuitable toughness due to the inherent trade-off between a low modulus and toughness [7].

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1742-7061/$ - see front matter Published by Elsevier Ltd. on behalf of Acta Materialia Inc.
doi:10.1016/j.actbio.2010.09.001

Another prevalent issue with polymers implemented in biomedical load-bearing applications is loss of their mechanical properties, including toughness, after implantation, due to exposure to physiological conditions, particularly moisture [11,12]. This effect, termed plasticization, is typically driven by the presence of polar chemical groups in the network structure that thermodynamically drive water molecules into the network, resulting in increased chain mobility that reduces the strength and modulus of the material but increases its ductility [13,14]. This change in mechanical properties is associated with a reduction in the glass transition temperature (T_g) of the polymer. If the network is able to take up enough water its mechanical behavior will transition swiftly from glassy to rubbery, indicating that the amount of water absorption dictates the degree of change in T_g and, thus, the mechanical properties [12,14].

In a previous study the toughness of a (meth)acrylate-based network containing methyl acrylate (MA) and methyl methacrylate (MMA) cross-linked with poly(ethylene glycol dimethacrylate) (PEGDMA) was shown to increase significantly at 37 °C after 1 week immersion in phosphate-buffered saline (PBS) when the T_g was tailored to be close to body temperature by adjusting the co-monomer concentrations of MA to MMA. The optimal composition, 29MA–co-MMA–co-PEGDMA, exhibited a toughness several orders of magnitude higher than other compositions and had an elastic modulus (100 MPa) that aligned closely with many orthopedic soft tissues [12]. However, the effects of long-term exposure to PBS on the toughness of these materials have yet to be determined. Because it is desirable that implants maintain their function for years, the mechanical properties, including toughness, must be maintained throughout this period. Many studies have evaluated how moisture affects the mechanical properties of polymers after 24 h to 1 week exposure to moisture [12,13,15], but few studies have examined the effects of long-term exposure to water over many months on the toughness of photopolymerizable networks [16–18].

Thus, the primary objective of this study was to evaluate how immersion time in PBS affects the toughness of MA–co-MMA–co-PEGDMA networks containing various concentrations of MA. The tensile mechanical properties were determined by performing tensile strain – failure testing after soaking in PBS for different periods of time (1 day to 9 months). In addition, the T_g and PBS content were assessed in order to determine if time-dependent changes in toughness were related to changes in T_g or PBS absorption. This study has shown that PBS absorption affects network toughness in a manner that differs from short-term conditions and that a polymer with suitable initial toughness in PBS can eventually lose its toughness after long-term exposure. These results have ramifications on the toughening of the materials considered in this study (MA–co-MMA–co-PEGDMA) and possibly other acrylate systems being considered for biomedical applications, such as in situ cured acrylates [19–21] and shape memory polymer acrylates [3,4].

2. Materials and methods

2.1. Materials

MMA, MA, dodecane dioldimethacrylate (DDDA) and PEGDMA with a molecular weight of M_n = 750 kDa were obtained from Sigma–Aldrich and used as received. 2,2-Dimethoxy 2-phenylacetophenone (DMPA) was used as the photoinitiator and was also purchased from Sigma–Aldrich. UHMWPE was obtained as 1 mm thick sheets from McMaster-Carr Inc. (Atlanta, GA). The chemical structures of the monomers are shown in Fig. 1.

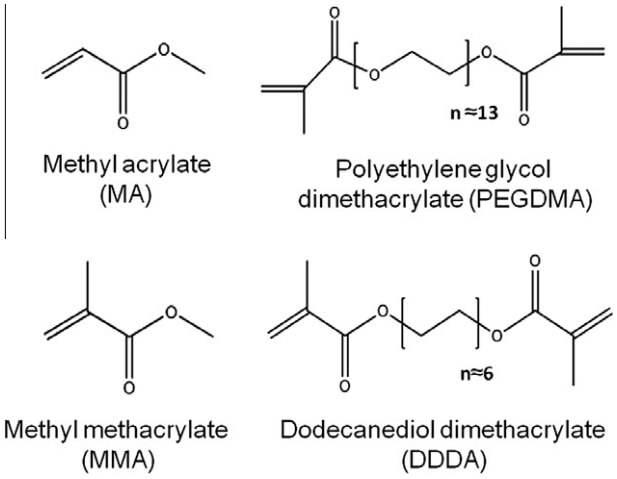

Fig. 1. Chemical structures of the monomers.

2.2. Synthesis

MA–co-MMA–co-PEGDMA solutions were prepared by combining ratios of MA and MMA by weight percentage with 10 wt.% PEGDMA and 1 wt.% DMPA. Four compositions with varying MA concentrations were used for further testing. A MA–co-MMA–co-5%DDDA network consisting of 50%MA and 45% MMA (50MA) was created in the same manner. Each solution was mixed manually in a glass vial and injected between two Rain-X-coated glass slides using a glass pipette. Slides were separated with two 1 mm glass spacers. To prevent leakage of the MA–co-MMA–co-PEGDMA solution all four sides of the slides were taped. The samples were placed in a UV chamber (model CL-1000L ultraviolet cross-linker, λ = 365 nm, energy = 2000 × 100 μJ cm^{-2}) for 30 min.

2.3. Characterization

Test samples of each composition were incubated in PBS (Sigma–Aldrich) at either room temperature or 37 °C for up to 9 months and then subjected to the following regime at various time points.

2.3.1. Tensile testing

To determine the stress–strain behavior of each network the polymer sheets were laser cut into ASTM D638 Type IV dumb-bell shapes and strained to failure in tension mode at a strain rate of 5% strain s^{-1} using a MTS Insight 2 with a 2 kN load cell. Before testing the edges were sanded to remove any defects due to the laser cutting and the width and thickness of the gauge section were measured using digital calipers. All tests, except for the dry experiments, were performed in an environmental chamber filled with PBS heated to 37 °C. Samples were allowed to equilibrate at the testing temperature for 10 minutes before initiating the test. Only samples that broke in their gauge length (at least 90% of total samples tested) were used for property calculations. Toughness was calculated as the area under the stress–strain curve in units of MJ m^{-3}. The elastic modulus was calculated as the slope of the initial linear portion of the stress–strain curve for each test as previously described (n = 4) [7,12].

2.3.2. Differential scanning calorimetry

The T_g of each network was determined by differential scanning calorimetry (DSC) (TA Instruments Q100, Newcastle, DE) in a