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Poly(vinyl alcohol)–acrylamide hydrogels as load-bearing cartilage substitute

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ABSTRACT

Poly(vinyl alcohol) (PVA) has been advanced as a biomaterial for the fabrication of medical devices to be used as synthetic articular cartilage because of its viscoelastic nature, high water content, and biocompatibility. Key material requirements for such devices are high creep resistance to prevent mechanical instability in the joint and high water content to maintain a lubricious surface to minimize wear and damage of the cartilage counterface during articulation. The creep resistance of PVA hydrogels can be increased by high temperature annealing; however this process also collapses the pores, reducing the water content and consequently reducing the lubricity of the hydrogel surface [Bodugoz-Senturk H, Choi J, Oral E, Kung JH, Macias CE, Braithwaite G, et al. The effect of polyethylene glycol on the stability of pores in polyvinyl alcohol hydrogels during annealing. Biomaterials 2008;29(2):141–9.]. We hypothesized that polymerizing acrylamide (AAm) in the pores of the PVA hydrogel would minimize the loss of lubricity during annealing by preventing the collapse of the pores and loss of water content. Increasing AAm content increased porosity and equilibrium water content and decreased the coefficient of friction, tear strength, crystallinity, and creep resistance in annealed PVA hydrogels.

1. Introduction

Degenerative joint diseases and trauma lead to cartilage lesions that are most often accompanied by pain and disability. With shallow lesions, the healing capacity of cartilage is much better than when the lesions extend to the subchondral bone. Osteochondral defect repair in human joints has been a challenging task due to the poor self-healing nature of articular cartilage; if left untreated, most of these lesions could lead to osteoarthritis [2–4]. A number of biological treatment options, such as periosteal flaps, microfracture, autologous chondrocyte implantation, osteochondral transplantation, are available today [5–7]. In the short term, outcomes show functional improvement and reduction in pain [7–10]; however, the quality of the repaired tissue is often inferior to that of native hyaline cartilage [11–16].

An alternative treatment option is the use of a synthetic articular cartilage material either by filling the lesion or in the form of a hemiarthroplasty counterface or interpositional device to alleviate pain and/or correct joint deformity. Poly(vinyl alcohol) (PVA) is a candidate material, which was first advanced as a synthetic articular cartilage material by Bray and Merrill in 1973 [17]. Since then, a number of approaches have been utilized to demonstrate the utility of PVA hydrogels [18–23]. The basic premise was that the high water content of a crystalline PVA hydrogel and its biphasic nature (water and solid PVA) would suffice to act as a synthetic articular cartilage. However, PVA hydrogels in their as-gelled form lack the strength and toughness to serve as a cartilage substitute material [24–26]. Researchers have reduced the water content by annealing to strengthen the hydrogel [1,25,27,28]. While thermal annealing increased strength, we found that it also decreased the lubricity of the hydrogel because of the collapse of the pores and the ensuing reduction in equilibrium water content [1]. This is of particular concern as counterface cartilage is likely to be damaged with an increase in coefficient of friction.

One method to prevent the collapse of the pores during annealing is to add poly(ethylene glycol) (PEG), which fills and protects the pores during annealing [1]. However, upon rehydration PEG diffuses out leaving behind pores occupied by water, which then reduces the strength of the hydrogel. We hypothesize that another approach to minimize water loss after the necessary step of annealing is to add polymers of high hydrophilicity permanently bound to the PVA network to increase water uptake and hence increase lubricity; and we postulate that the new polymer will replace the water in the pores of the hydrogel and further increase the strength. We advance the use of poly(acrylamide) (PAAm) as

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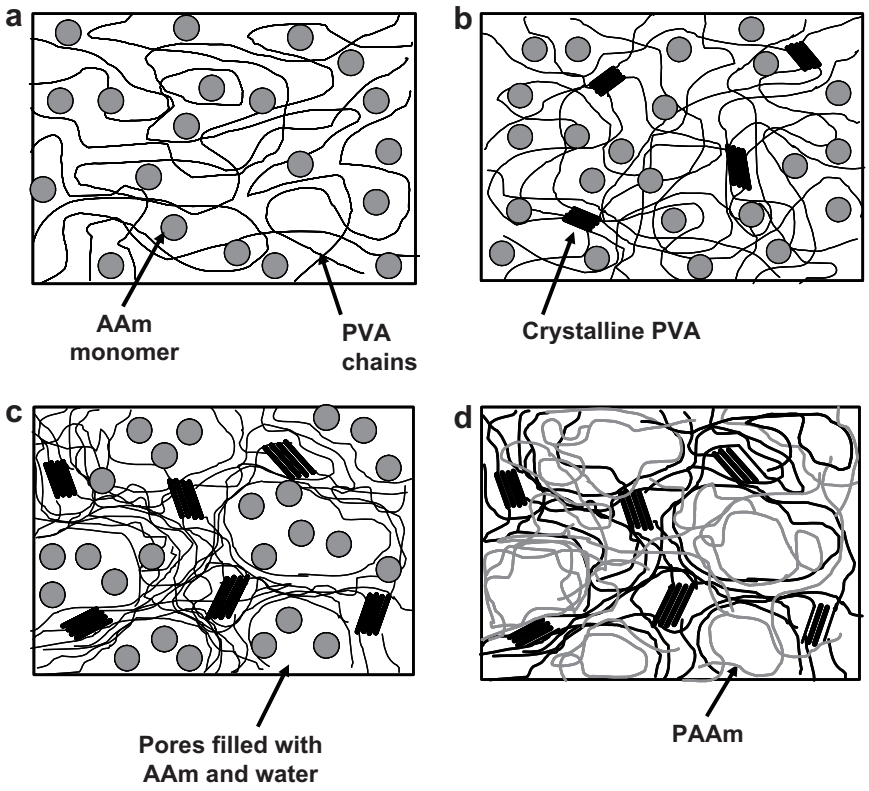

Fig. 1. Schematic of PVA–AAm gel formation: (a) PVA–water mixture at 90 °C is a uniform solution; (b) as the solution is cooled down phase separation begins and forces the PVA to form crystalline domains; (c) with further cooling to near room temperature phase separation results in the formation of pores containing water and AAm monomer surrounded by PVA-rich regions; and (d) the gels are heated to polymerize the PAAm in the semi-crystalline PVA host network.

the hydrophilic compound added to PVA where the former is permanently bound to the PVA network and also fills the pores.

PVA is a non-toxic and non-immunogenic polymer [25,29]. The vast number of hydroxyl side groups in PVA not only makes it hydrophilic but it also allows this polymer to form a semi-crystalline structure through intramolecular hydrogen bonding. PVA can be made into a hydrogel by either chemical or physical crosslinking. Chemical crosslinking can be achieved using functional crosslinking agents, such as glutaraldehyde, or by using ionizing radiation [30,31]. Physically crosslinked PVA-based hydrogels in water can be prepared by the so-called 'freeze–thaw' method, where microphase separation of PVA chains from water is achieved by taking the solution below freezing temperature of water and thawing to above freezing temperature of water in repeated cycles [32,33]. Alternatively, phase separation and gelation can be achieved by using a theta-solution for PVA at low temperatures [1,34,35]. In this method, the addition of a gelling agent, such as low molecular weight poly(ethylene glycol) (PEG), to PVA solution reduces the quality of the solvent upon cooling to room temperature, forcing the PVA to phase-separate and crystallize without the need of a freeze–thaw cycle, again forming a physically crosslinked hydrogel network.

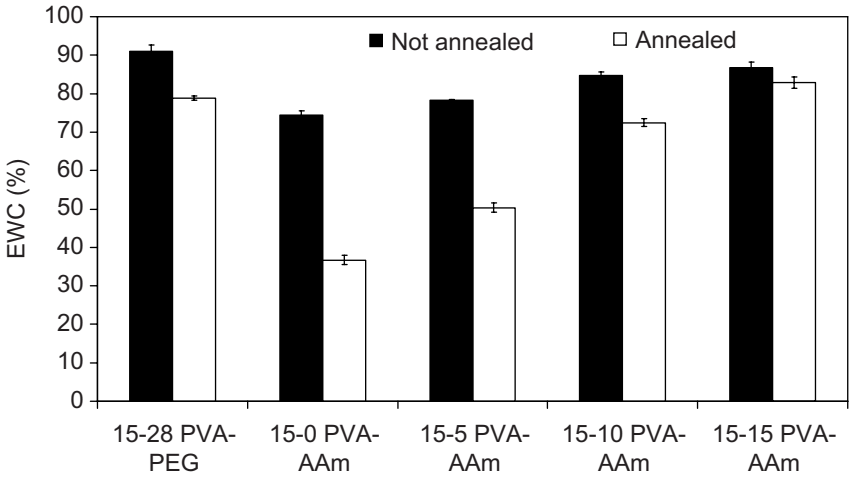

Fig. 2. Comparison of EWC values of PVA–AAm gels and PVA–PEG hydrogels before and after annealing.