ISGC 2022

N°257 / OC
TOPIC(s) : Polymers or composites / Clean reactions

Greener Silicone Hydrogels Crosslinked with Protein: Synthesis and Degradation Studies

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PURPOSE OF THE ABSTRACT

Protein hydrogels are increasingly important synthetic biomaterials that mimic aspects of human physiology. They have been proposed, for example, as load-bearing composites and for use in drug delivery. Silicone polymers - known for their biocompatibility and low surface energy - are used in the form of hydrogels in contact lenses, where they function to facilitate oxygen delivery to the cornea. We reasoned that the exploitation of silicon chemistry could lead to protein-based silicone hydrogels with better properties, while also increasing the value of (essentially) waste proteins, such as whey. Herein, we report the systematic study of the formation of protein-silicone conjugates exploiting both formaldehyde and aza-Michael cure protocols.

Classic methods to crosslink proteins to increase their long-term stability frequently exploit amine reactions with aldehydes, such as formaldehyde. Aminosilicones undergo these reactions rapidly and spontaneously, both in air and underwater (Figure 1A).[1] In control studies, the reaction of aminoalkyl silicones with formaldehyde yielded white opaque gels that, after about 1 hour, became clear as water was spontaneously extruded from the gel. Based on these studies, formaldehyde was chosen as the curing agent in the same system, into which aqueous protein solutions of casein, soy and whey were added in various concentrations to give protein hydrogels (Figure 1B). The physical properties of composites derived from casein or soy were poor, while whey led to mechanically strong gels; a difference that is attributed to the relatively high lysine content in whey (7-9%)[2] that can react with the aldehyde or acrylate. It was straightforward to tune the mechanical properties by balancing crosslinker concentration (from H_2CO) and the ratio of silicone / protein; with whey, hydrogels comprised of 75% protein could be prepared. The gels are robust materials that, after dehydration using lyophilization or low temperature ovens, became tough elastomers resistant to rehydration that, at their interface, exhibited low surface energies typical of silicones.

While effective as a crosslinker, formaldehyde in these systems could possibly be problematic because of its toxicity, even though a large stoichiometric excess of amine was used to ensure complete consumption. An alternative rapid reaction was needed to make analogous silicone protein conjugates, but without the accompanying toxicity. The reaction of amines with silicone acrylates is efficient, particularly when a hydroxy group is proximal to the acrylate.[3] The native amine groups on whey were thus directly reacted with telechelic and pendent silicone acrylates of varying molecular weights as a dispersion in water/alcohol mixtures to create protein hydrogels (Figure 1C).

When hydrated, the enzymatic degradation of the protein hydrogels is relatively facile on demand using inexpensive enzymes like bromelain. The dehydrated composites underwent decomposition much more slowly. These studies exhibit routes to new, sustainable protein hydrogels that boast desirable properties ascribed to the inclusion of silicone. Studies of the physical properties of these materials, including hardness, swelling behaviour,

thermostability and enzymatic degradation are currently underway.

FIGURES

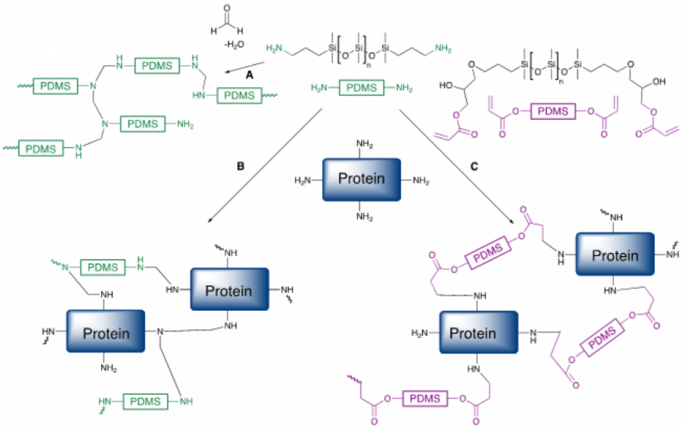

FIGURE 1

Routes to protein-silicone hydrogels

Formaldehyde cured A) silicone elastomers and B) Silicone / protein hydrogels. C) Aza Michael-cured silicone protein hydrogels.

FIGURE 2

KEYWORDS

protein hydrogel | biodegradable | silicone | amine grafting

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