Mechanical Properties of the ‘Stretchable’ Polyacrylamide-Gelatin Double Network Hydrogel

Nadia Adrus¹,a, Nur Farizah Ayub¹,b, Nurul Atika Mohd Amer ¹,c and Jamarosliza Jamaluddin¹,d

¹Polymer Engineering Department, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, UTM Skudai, Johor, MALAYSIA
²nadia@cheme.utm.my, ³farizahayub@yahoo.com, ⁴akitalurun91@gmail.com, ⁵jamarosliza@cheme.utm.my,

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Abstract. Double network (DN) hydrogels have drawn considerable attention as innovative materials possessing both high water content as well as improved mechanical properties. In this study, DN hydrogels were formed from a combination of two hydrogel networks. The first network composed of acrylamide (AAm) and N',N'-methylenebisacrylamide (MBAAm). AAm and MBAAm were covalently crosslinked via photopolymerization simultaneously with/without the presence of the second network pre-gel mixture; physically crosslinked gelatin-calcium carbonate (GCa). The mechanical properties characterization of the hydrogels revealed that tensile strength, Young’s modulus and elongation at break increased with the increasing amount of second network component; i.e. GCa. These data could confirmed that the polyacrylamide (PAAm)-GCa DN hydrogels possessed ‘stretchability’ character. Overall, PAAm-GCa DN hydrogels had shown better mechanical strength than the PAAm single network hydrogels. We foreseen that DN hydrogels are highly potential to be developed as artificial muscles.

Introduction

Hydrogels are hydrophilic polymer built-up of polymeric network crosslinking structure. They have unique properties that allow for water absorption until 90 % of their own body mass [1]. Hydrogels have a high water attraction, but are insoluble in it due to the chemical or physical bonds produced between the polymer chains. Fully swollen hydrogels have physical properties that are typical to living tissues [2].

Single network (SN) hydrogels can either be chemically or physically crosslinked. Despite of their good water absorption property, SN hydrogels are soft and brittle materials [3] and also have low mechanical properties [4]. Most of SN hydrogels do not possess stretchability. This has imposed the limitation hydrogels applications in certain area only [5, 6].

Recently, double network (DN) hydrogels are proposed as an alternative in order to increase their mechanical strength and toughness [5]. DN hydrogels are the combination of two single networks and they usually have good mechanical properties as compared to SN hydrogels. Gong introduced PAMPS-PAAm DN hydrogels that possessed high fracture strength and low friction coefficient [5]. Here, PAMPS stands for poly(2-acrylamido-2-methylpropane sulfonic acid). Another research conducted by Nakayama also proposed similar idea of producing DN hydrogels [6]. The stiff and brittle first network was combined with soft and ductile second network [14]. From both of these studies, the elastic modulus [6], tensile strength, hardness and also its toughness was investigated [5].

However, in those previous studies, hydrogels were usually prepared via redox-polymerization. This technique has its own limitation such as involving organic solvents,
uncontrolled free radicals and temperature to be conducted. Therefore, the synthesis of DN hydrogels was carried out using photopolymerization in this study.

**Experimental Part**

**Materials**

All chemicals used for hydrogel preparations were at least analytical grades. AAm and MBAAm were purchased from Acros Organics (stock from Belgium) and Sigma-Aldrich (Malaysia), respectively. “Type I” photoinitiator; Irgacure 2959® was supplied by BASF-Ciba Chemicals (stock from Germany). Gelatin used in this experiment was purchased from Halagel Company. The calcium carbonate (CaCO₃) was obtained from the laboratory. Others chemicals were used without further purification.

**Synthesis of PAAm and PAAm-GCa Hydrogels**

The PAAm pre-gel solutions were firstly prepared. 7.5 g of AAm was stirred in 50 mL of distilled water for about 5 min. Then, 5 wt% of MBAAm (crosslinker) relative to AAm were added into the solution. The solution was further stirred for 20 to 25 minutes. Next, the photoinitiator was added to the monomer solution. The mixture was stirred until completely dissolved at ambient temperature.

In a separate glass container, 1.6 g of gelatin were dissolved in 15 mL of hot distilled water (80 °C). CaCO₃ solution with initial concentration of 0.015 g/mL were stepwisely into the gelatin solution. The addition of the CaCO₃ solutions was stopped before the GCa solution formed a gel.

Next, the synthesis of DN hydrogel was done by mixing the PAAm with the various amount of GCa pre-gel solutions. The solutions containing first and second networks in their pre-gel solution states were then poured into glass plate (210 mm x 270 mm x 0.2 mm). The mixture was exposed to UV Mercury (UV Hg) lights source (Hönle AG, Germany) for 15 min. Then, the hydrogels were cut into small sample for further test. The synthesis of PAAm single network hydrogels were done in a similar manner in the absence of GCa pre-gel solution.

**Mechanical Properties Characterization**

Tensile test was done using EZ20KN LLYOD-20kN machine with tensile rate of 13 mm/min. Samples for the tensile test was cut according to the ASTM D638 Type 5. Young's modulus E was also determined as the slope at the 0–0.1 strain range from the stress–strain curve. Measurements were performed at least three times for each sample.

For elongation at break, the specimen was clamped in the testing machine. No more tension was applied to the specimen during clamping. The masking tape was used to cover the end of the sample’s neck in order to enhance the gripping of the sample. Crosshead was started in motion at a rate of 10 mm/s, until the specimen ruptures.

**Results and discussions**

The tensile strength measurement has shown that PAAm SN hydrogel alone has low mechanical strength. This is attributed to the brittleness and softness of the SN hydrogels [4, 5]. As shown in Figure 1, the DN exhibited an increment in tensile strength when compared to SN hydrogels. The high tensile strength of the hydrogel may arise from the entanglement and synergistic mechanism of the rigid but brittle covalently crosslinked first network and the soft but ductile physically crosslinked second network. Upon stretching the hydrogel the ionic interaction within GCa restored larger deformation of the PAAm network and resulted in higher tensile strength.

Based on Figure 1, the tensile strength of the PAAm hydrogels increased with the increasing amount of GCa. However, the tensile strength dropped when the composition of GCa was 30%.
The agglomeration of second network within the entire hydrogel network could be one of the possibility of the lower tensile properties [7]. Thus, it could be affirmed that the optimum tensile strength was obtained with 20 wt% composition of GCa in the PAAm-GCa hydrogel. These results were in agreement with the previous research done by Haiyan Yin [4]. Accordingly, she discovered that the optimum conditions of second network to first network in a double network hydrogel was about 20 % for poly N-(carboxymethyl)-N,N-dimethyl-2-(methacryloyloxy) ethanaminium (PCDME) with PAMPS.

Young’s modulus or tensile modulus is a measure of stiffness for an elastic isotropic material. The Young’s modulus of PAAm-GCa DN hydrogels was even more notable when compared to PAAm SN hydrogels. Similarly, this observation was associated to the synergistic mechanism of entangled PAAm and GCa DN hydrogels. The entanglement of DN hydrogels allowed for faster and higher energy dissipation within the network [8]. Overall, incorporation of GCa into the DN hydrogels has imposed on superior stiffness and elasticity than pure PAAm hydrogels.

Figure 3 shows the effect of GCa composition on PAAm-GCa DN hydrogels for elongation at break. PAAm-GCa DN hydrogels revealed significantly improved elongation at break in contrast to the PAAm itself. Moreover, the elongation at breaks increased when the composition of the GCa increased. It could be envisioned that entanglement between the first and second network resulted in the stretchability of the DN hydrogels. The previous study reported that an increase in elongation at break was due to sliding effect [9].

Instead of continually increased over the increment of GCa, at 30 and 40 % of GCa the elongation at break was slightly decreased. The similar trends were also observed for tensile strength and Young’s modulus. Subsequently, it could only be postulated that the agglomeration of the second network has an influence towards the slight fluctuations in the mechanical properties. Further investigations are in progressed. Eventually, by comparing the SN and DN hydrogels, the
integration of GCa into the DN hydrogels has improved the overall elongation at break. This result clearly indicated the the SN PAAm has relatively low elongation at break.

In addition, the DN hydrogel showed a highest elongation at 20 % composition of GCa network PAAm. An increment of 50 % in elongation at breaks was obtained under this optimum composition. Thus, the elongation at break data could confirmed that DN hydrogels are highly stretchable.

Conclusion

Overall, PAAm-GCa DN hydrogels showed an overall enhancement of mechanical properties as compared to their SN counterparts. Tensile strength, Young’s modulus and elongations at breaks increase gradually with the increasing of GCa compositions. There was a slight decrease in these properties beyond 20 % of GCa composition. Thus, future works need to be carried out to further scrutinize the underlying mechanism and proof-of-concept. Ultimately, the DN PAAm-GCa hydrogels were highly stretchable and suitable as candidate for artificial muscle applications.

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References