

TENSILE PROPERTIES OF POLYACRYLAMIDE-GELATIN/CALCIUM CARBONATE AND POLYACRYLAMIDE-CHITOSAN/ALGINIC ACID DOUBLE NETWORK HYDROGELS

NURUL ATIKA MOHD AMER, NUR FARIZAH AYUB, NUR AMANINA ABDUL KHALID, JAMARISLOZA JAMALUDDIN, NADIA ADRUS*

Department of Bioprocess and Polymer Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

**Corresponding author: nadia@cheme.utm.my*

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 with/without the presence of the second network pre-gel mixture i.e physically crosslinked gelatin-calcium carbonate (GCa) or chitosan-alginic acid (CAA). The mechanical properties of the hydrogels revealed that tensile strength, Young's modulus and elongation at break increased with increasing amount of second network component; i.e. GCa and CAA. These data could confirm that the DN hydrogels possessed 'stretchability' character. Overall, PAAm-GCa and PAAm-CAA 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.

Keywords: Double network, polyacrylamide hydrogel, gelatin-calcium carbonate solutions (GCa), chitosan-alginic acid (CAA)

INTRODUCTION

Hydrogels are hydrophilic polymer built-up of polymeric network crosslinking structure that allows water absorption until 90% of their own body mass [1]. For the hydrogel, it is insoluble in water due to chemical or physical crosslinking that was produced between the polymer chains. Moreover, when hydrogel in its fully swollen state, it possesses physical properties similar to living tissues [2].

Single network (SN) hydrogel can either be physically or chemically crosslinked. Although it has good water absorption property, SN hydrogels are soft and brittle [3] and has low mechanical properties [4]. The use of hydrogel nowadays is only limited to certain applications as they do not possess stretchability [5,6].

Double network (DN) hydrogels had been recently proposed as an alternative to increase the mechanical properties of the SN hydrogels [5]. These DN hydrogels are the combination of two networks and they usually have enhanced the mechanical properties over SN hydrogels. In the recent research done by Gong, she introduced that poly(2-acrylamido-2-methylpropane)(PAMPS)-PAAm DN hydrogels that possessed high fracture strength and low friction coefficient [5]. Another research was done 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. From both studies, the elastic modulus [6], tensile strength, hardness and also its toughness were investigated [5].

However, in those previous researches, hydrogels were prepared by using redox-polymerization and this technique has its own limitation. The limitations that were faced by this technique involved the use of organic solvent, temperature control and also uncontrollable free radicals formation [6,7]. Thus, in this research, photopolymerization technique was used instead of redox-polymerization that is much easier to be controlled.

This research highlights the effect of natural polymer as the second network on the SN hydrogel. The second network mainly used synthetic polymer such as PAMPS [5]. In this research, the effect of the natural polymer as the second network on the tensile properties was investigated so that it can be later applied in tissue engineering application.

EXPERIMENTAL

Materials

All chemicals were at least of analytical grade. AAm and MBAAm were purchased from Acros Organics (Belgium) and Sigma-Aldrich (USA), respectively. Type 1 photoinitiator for UV light; Irgacure 2959® was supplied by BASF-Ciba Chemicals (Germany) and another type of photoinitiator was Chivacure 300 purchased from Chitec technology corporation (Taiwan). Gelatin and calcium carbonate were purchased from Halagel Company (Malaysia) and Sigma-Aldrich (USA), respectively. Other chemicals were used without purification.

Synthesis of PAAm, PAAm-GCa AND PAAm-CAA 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 was 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 was dissolved in 15 mL of hot distilled water (80 °C). CaCO₃ solution with an initial concentration of 0.015 g/mL was added stepwisely into the gelatin solution. The addition of the CaCO₃ solutions was stopped before the GCa solution formed a gel.

The second network was prepared by dissolving 1g of chitosan in 50 mL of 0.01 M of acetic acid. In a separate vessel, 1 g of alginic acid was dissolved in 50 mL of distilled water. After that, both solutions were mixed to form the second network pre-gel solution.

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

Tensile Properties Characterization

Tensile test was done using EZ20KN LLYOD-20kN machine with tensile rate of 13 mm/min. The samples for this tensile test were cut according to the ASTM D638 Type 5. For each test, at least three measurements were performed and the average data were plotted.

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. The sample was pulled until specimens 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].

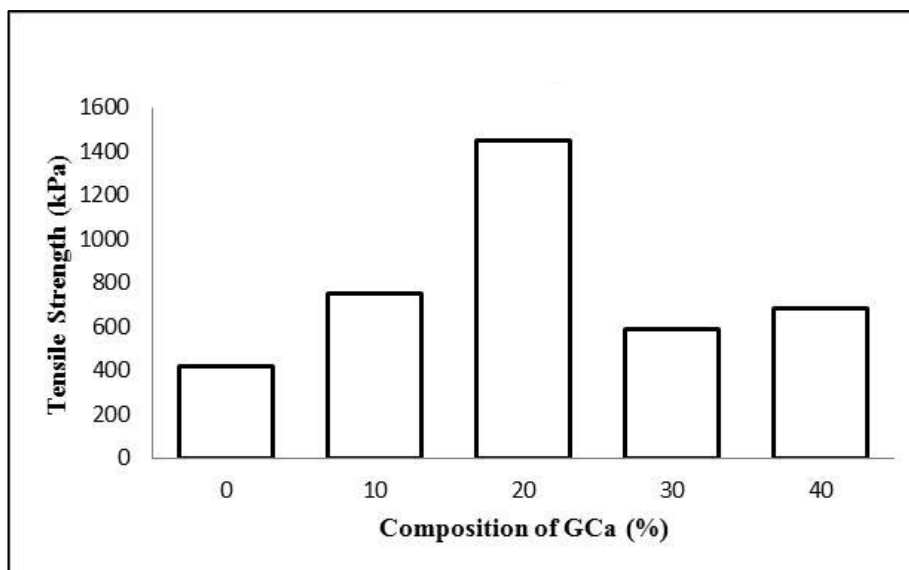


Fig. 1 Tensile strength of PAAm-GCa hydrogels

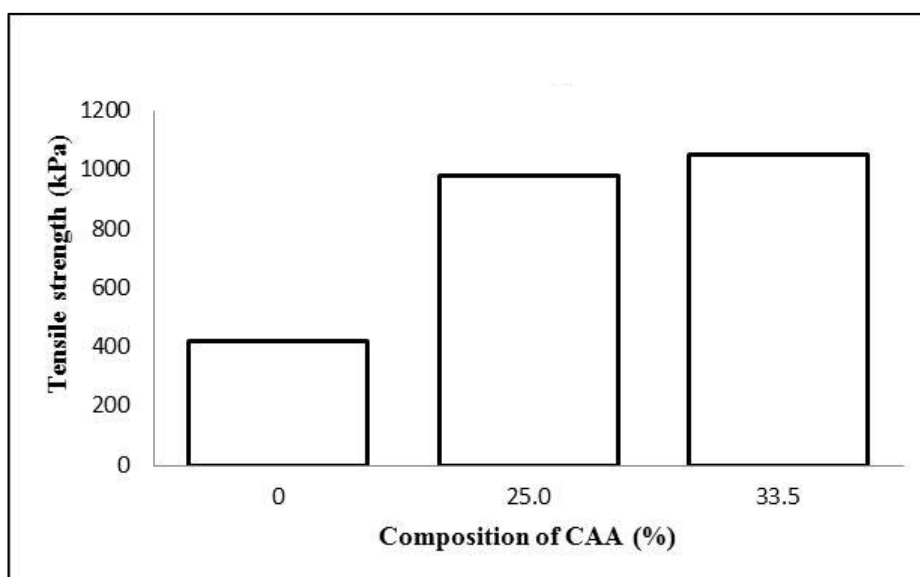


Fig. 2 Tensile strength of PAAm-CAA hydrogels

Based on Fig. 1 and Fig. 2 DN hydrogels exhibited an increase 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. The tensile strength of the PAAm hydrogels increased with increasing amount of the second networks. However, for the GCa second network 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 possibilities of the lower tensile properties [7]. As for the CAA second network the tensile strength of the PAAm was increased and reached 1050 kPa. Thus, it could be affirmed that the optimum tensile strength was obtained with 20 wt% composition of GCa in the PAAm-GCa hydrogel and also can be increased further in the PAAm-CAA hydrogels. Based on the research done by Haiyan Yin [4] it was discovered that the optimum conditions for second network to first network in the double network hydrogel was about 20 % for poly *N*-(carboxymethyl)-*N,N*-dimethyl-2-(methacryloyloxy) ethanaminium (PCDME) with PAMPS.

In this experiment, chitosan was not easily dispersed in alginate acid as compared to gelatin and calcium carbonate. This could contribute to greater tensile strength of PAAm-GCA than PAAm-CAA double network hydrogels. Even though no data to support this observation, it is

foreseen that the interaction between chitosan and alginic acid was higher than that of gelatin and calcium carbonate. Thus in order to break the ionic interaction, CAA second networks require more energy and thus and make it less elastic when compared to GCA hydrogel.

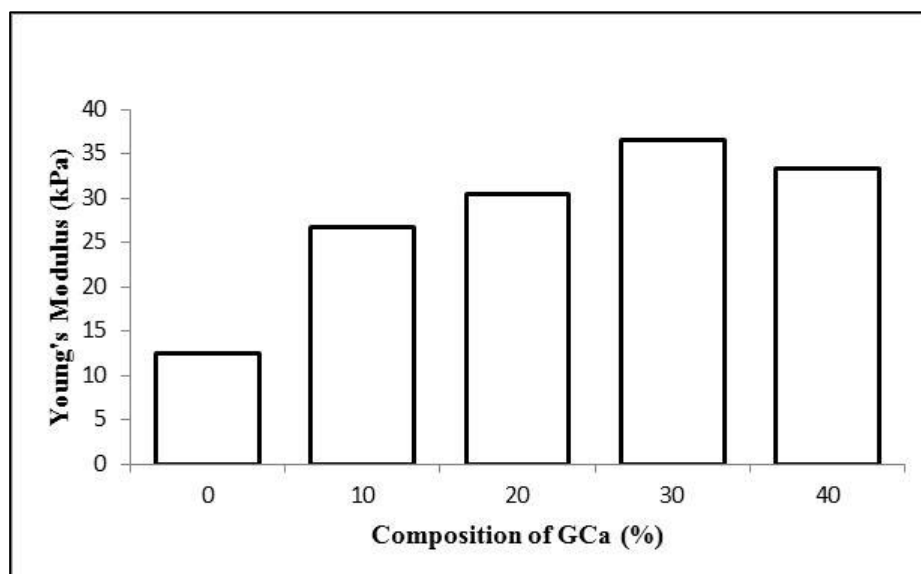


Fig. 3 Young's modulus of PAAm-GCa hydrogels

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. From Fig. 3 and Fig. 4, it can be observed that when 30% of second network was added into the PAAm single network it reaches the highest Young's modulus. Thus, this observation was associated with the synergistic mechanism of entangled PAAm with GCa or CAA DN hydrogels [5]. The entanglement of DN hydrogels allowed for faster and higher energy dissipation within the network [8]. Overall, incorporation of second network into the DN hydrogels has imposed on superior stiffness and elasticity than pure PAAm hydrogels.

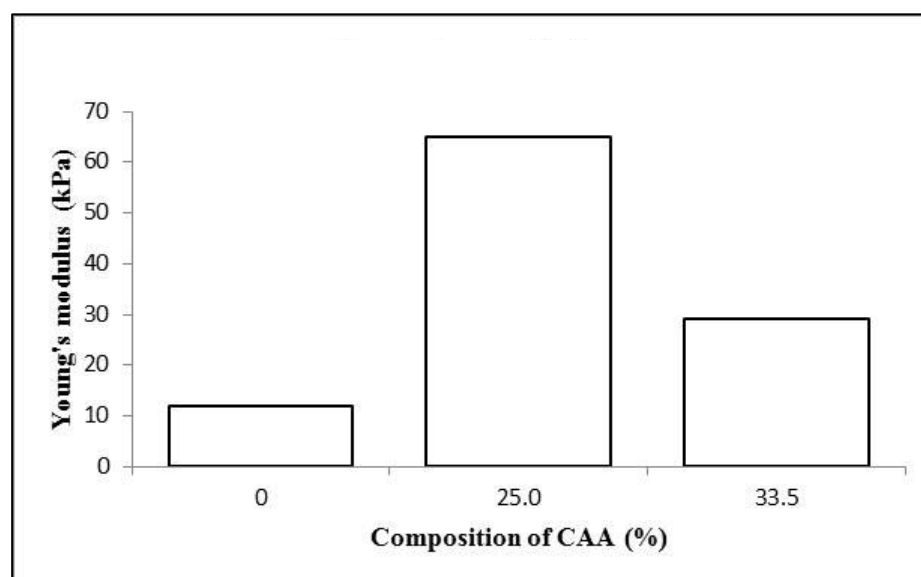


Fig. 4 Young's modulus of PAAm-CAA hydrogels

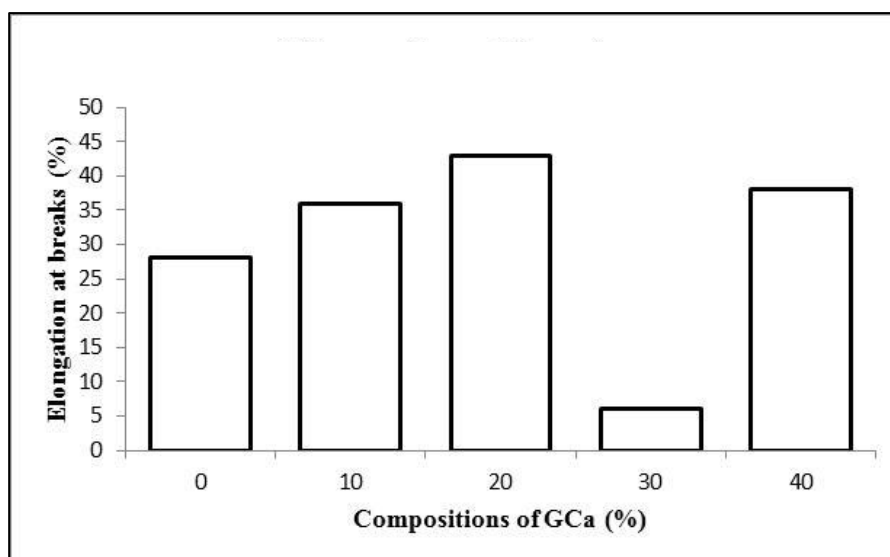


Fig. 5 Elongation at breaks\ for PAAm-GCa hydrogels

Fig. 5 and Fig. 6 show the effect of GCa and CAA composition on PAAm-GCa and PAAm-CAA DN hydrogels for elongation at break, respectively. The DN hydrogels revealed that they have improved the elongation at break as compared to that of the SN PAAm itself. Moreover, the elongation at break increased when the composition of the GCa or CAA was increased. For PAAm-CAA hydrogels at 25% of CAA composition the elongation at break was lower than the PAAm as it might be due to the agglomeration of CAA network in the PAAm. Agglomeration makes the hydrogel stiffer and thus lowering the elongation at break. The increase in the elongation at break was also due to the sliding effect [9].

Instead of continually increased over the increase of GCa, the elongation at break was slightly decreased at 30 and 40 % of GCa. This similar trend was also observed from the tensile and Young's modulus of both the PAAm-GCa and PAAm-CAA hydrogels. From these results, it could only be postulated that the agglomeration of the second network had affected the PAAm mechanical properties. Eventually, by comparing the SN and DN hydrogels, the elongations at break of both PAAm DN hydrogels had improved from the original SN PAAm.

In addition, the DN hydrogel showed highest elongation for both DN hydrogels. An increase of about 30 % to 50 % in elongation at break was obtained under this optimum composition. Thus, the elongation at break data could confirm that DN hydrogels are comparatively more stretchable than SN hydrogels.

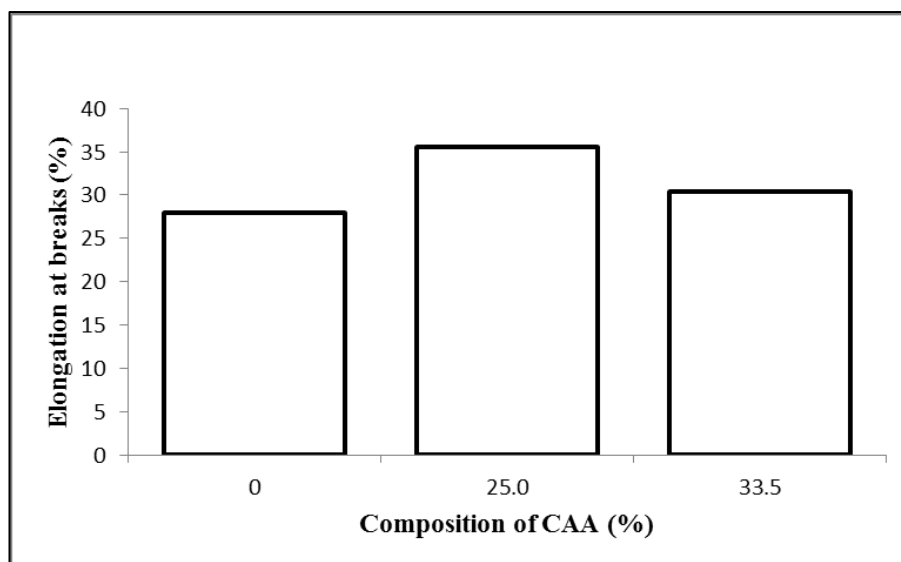


Fig. 6 Elongation at break for PAAm-CAA hydrogels

CONCLUSION

PAAm-GCa and PAAm-CAA DN hydrogels showed an overall enhancement of mechanical properties as compared to their SN PAAm counterpart. Tensile strength, Young's modulus and elongations at break increase gradually with the increasing amount of second component. There were some compositions that show low properties in comparison to the SN PAAm. Thus, future works need to be carried out to further optimize the underlying mechanism and proof-of-concept. Ultimately, the DN PAAm-GCa and PAAm-CAA hydrogels were highly stretchable and suitable as a candidate for artificial muscle applications.

ACKNOWLEDGEMENT

The authors thank Universiti Teknologi Malaysia for Research University Grants (Vot. No: 06H99) and Ministry of Higher Education Malaysia FRGS (Vot. No: 4F624)

REFERENCES

1. Okay, O. G. Gerlach and K.F Arndt, Editors. General Properties of Hydrogel, 2009, Springer-Verlag Berlin Heidelberg: Berlin. 1-14.
2. Geever, L.M., Devine, D.M., Nugent, M.J.D., Kennedy, J.E., Lyons, J.G., Hanley, A. And Higginbotham, C.L. Lower Critical Solutions Temperature Control and Swelling Behaviour of Physically Crosslinked Thermosensitive Copolymers Based on *N*-Isopropylacrylamide, *Eur. Polym. J.*, (2006) 42: 2540-2548.
3. Hinkley, J.A., Morgret, L.D. and Gehrke, S.H. Tensile Properties of Two Responsive Hydrogels, *Polymer*, (2004) 45(26): 8837-8843.
4. Yin, H., Akasaki, T., Sun, T. L., Nakajima, T., Kurokawa, T., Nonoyama, T., Taira, T., Saruwatari, Y., and Gong, J.P. Double Network Hydrogels from Polyzwitterions: High Mechanical Strength and Excellent Anti-Biofouling Properties, *J. Mater. Chem.*, (2013) 1(30): 3685-3693.
5. Gong, J.P. Why are Double Network Hydrogels So Tough?, *Adv. Mater.*, (2010) 6(12): 2583-2590.
6. Nakayama, A., Kakugo, A., Gong, J.P., Osada, Y., Takai, M., Erata, T. and Kawano, S. High Mechanical Strength Double-Network Hydrogel with Bacterial Cellulose, *Adv. Funct. Mater.*, (2004) 14(11): 1124-1128.
7. Rosiak, J.M. and Yoshii, F. Hydrogels and Their Medical Applications, *Nucl. Instrum. Methods Phys. Res., Sect. B: Beam Interactions with Materials and Atoms*, (1999) 151: 56-64.
8. Sun, J.Y., Zhao, X., Illeperuma, W.R.K., Chaudhuri, O., Oh, K.H., David, J.M., Vlassak, J.J. and Suo, Z. Highly Stretchable and Tough Hydrogels, *J. Nat.*, (2012) 489: 133-136.
9. Tanaka, Y., Gong, J.P., and Osada, Y. Novel Hydrogels with Excellent Mechanical Performance, *Prog. Polym. Sci.*, (2005) 30(1): 1-9