NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

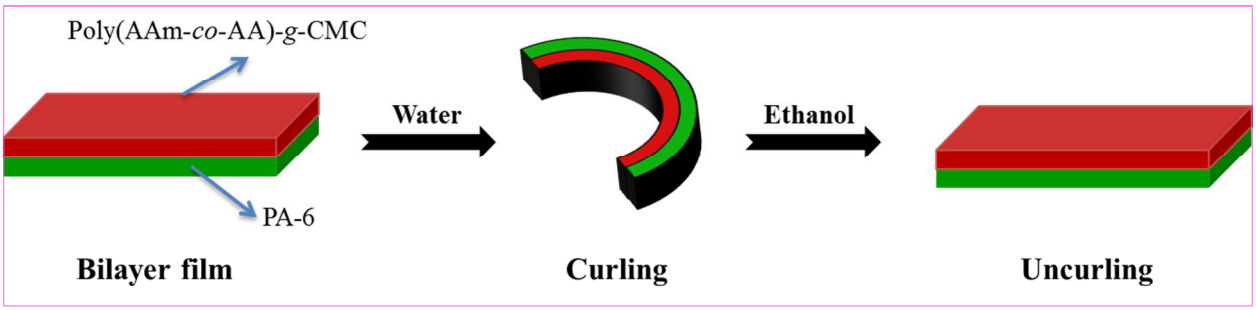
Graphical Abstract

Chemo-responsive bilayer actuator film: Fabrication, characterization and actuator response

Yuvaraj Haldorai, Jae-Jin Shim*

Supercritical Fluids and Nano Processes Laboratory, School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Republic of Korea

Tel: (+82) 53-810-2587; Fax: (+82) 53-810-4631; E-mail: jjshim@yu.ac.kr



A fast and stable curling/uncurling motion of bilayer actuator was prepared by photo-cross-linking poly(AAm-*co*-AA)-*g*-CMC onto PA-6.

New Journal of Chemistry Accepted Manuscript

Chemo-responsive bilayer actuator film: Fabrication, characterization and actuator response

Yuvaraj Haldorai, Jae-Jin Shim*

Supercritical Fluids and Nano Processes Laboratory, School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Republic of Korea

Tel: (+82) 53-810-2587; Fax: (+82) 53-810-4631; E-mail: jjshim@yu.ac.kr

Abstract

A chemo-responsive bilayer actuator was fabricated by cross-linking a polysaccharide based highly hydrophilic material with polyamide-6 (PA-6) substrate. The hydrogel material was prepared by grafting polyacrylamide (PAAm) and poly(acrylic acid) (PAA) copolymer onto carboxymethyl cellulose (CMC) [poly(AA-*co*-AAm)-*g*-CMC]. The successful grafting of the copolymer onto CMC was confirmed by Fourier transform infrared spectroscopy and thermogravimetric analysis. The swelling behavior of the poly(AA-*co*-AAm)-*g*-CMC hydrogel was examined at a range of pH and ionic strengths. Fabrication of the bilayer actuator was developed by drop casting a poly(AAm-*co*-AA)-*g*-CMC solution onto a PA-6 substrate followed by subsequent cross-linking under ultraviolet radiation. Cross-linking was performed to make the material readily swellable in water but prevent complete dissolution. The actuator response was measured in both water and ethanol.

1. Introduction

Hydrogels are high-performance water retentive and absorbent materials with a three-dimensional network structure connected by chemical and/or physical cross-links.[1,2] The excellent ability to hold or absorb a large amount of aqueous fluids by a hydrogel material

New Journal of Chemistry Accepted Manuscript

depends on the extent and content of hydrophilic units.[3] The hydrophilic units in a hydrogel make a relatively short time of absorbing water and can maintain a swollen state even under pressure. A large number of hydrogel materials are prepared for applications in agriculture,[4] waste water treatment,[5, 6] drug delivery systems,[7] and hygienic products.[8] Hydrogel materials have been produced based on polysaccharide-based natural polymers, such as cellulose, starch and chitosan, which can increase their biocompatibility, biodegradability and water uptake capacity, as well as decrease the toxicity.[9] Cellulose, which is abundant in nature, has been a major subject of academic and industrial research over the past few decades.[10] The material is quite difficult to dissolve in water but its derivatives, such as carboxymethyl cellulose (CMC) are soluble due to presence of the polar carboxyl groups on the backbone. Such polar groups also impart chemical reactivity and strong chelating capability which makes CMC economical in various water absorbent fields when modified.[11]

Previous research focused mainly on preparation methods using CMC as a hydrogel material by surface modification with range of polymers.[12] On the other hand, such hydrogels have rarely been used in the fabrication of actuators.[13] The first bigel actuator was reported in 1995 by Hu et al.[14] An actuator is a combination of active and inactive materials in the form of layers that show a motion response to external stimuli, such as heat, light, pH and chemicals.[15] The active material responds to external stimuli by changing its volume, whereas the inactive material remains unchanged owing to its inertness, resulting in a bending deformation of the actuator. Recently, water responsive actuators with a bilayer configuration have been used successfully to produce hinges and flytrap-like structures.[16] The cross-linked hydrogel material of poly(N-isopropylacrylamide-*co*-acrylic acid) (PNIPAM-*co*-PAA) was used as the active material bound to polyethylene oxide diacrylate as an inactive material.[16] On the other hand, PNIPAM-*co*-PAA

New Journal of Chemistry Accepted Manuscript

exhibits low mechanical properties, which is important for an actuator. Malachowski et al.[17] improved the modulus of PNIPAM hydrogel by combining with poly(propylene fumarate), which has three orders of magnitude greater than that of most hydrogels and has been previously used in bone tissue engineering. Considerable thought was given to the choice of materials for the hydrogels. We realized that many efforts have been made to synthesize CMC-based superabsorbents to improve the swelling capacity and mechanical property.[18-21] Therefore, we have chosen CMC-based hydrogel by grafting hydrophilic copolymer, polyacrylamide (PAAm) and poly(acrylic acid) (PAA) onto CMC; combining the high absorption capacity of PAA and fast swelling rate of PAAm.

In this paper, poly(AAm-*co*-AA)-*g*-CMC hydrogel was synthesized as a high water uptake material. The swelling behavior of the hydrogel was examined at different pH and ionic strengths. The poly(AAm-*co*-AA)-*g*-CMC was then photo-cross-linked with PA-6 under UV-irradiation to form a bilayer. The actuation properties of the resulting bilayer in both water as and in ethanol were assessed. The solvent inactive material PA-6 has an affinity for amide groups of the poly(AAm), which ensures the durability of actuator and eliminates the likelihood of delamination.

2 Experimental

2.1 Materials

Acrylic acid (AA) and acrylamide (AAm), ammonium persulfate (APS), and thioxanthone disulfonate (TXS) and CMC were purchased from Sigma-Aldrich. All reagents were of analytical grade and used as received. De-ionized water with a pH 6.9 was used.

2.2 Preparation of buffers

Four stock solutions (200 mL each) at different pH (2.5, 4.8, 7.8, and 12.0) were prepared with

New Journal of Chemistry Accepted Manuscript

an ionic strength of 0.2 M using phosphate salts. The effects of ionic strength on the swelling of the hydrogel were examined by preparing additional buffers by the adding appropriate amounts of NaCl to 50 mL of the stock solution. Minimal coupling between the ionic strength and pH was anticipated because one value was approximately kept constant while the other varied.

2.3 Synthesis of poly(AAm-*co*-AA)-*g*-CMC

A CMC solution was prepared by the slow addition of 2 g of CMC powder to distilled water in a 250 mL three-necked flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen line. The solution was heated to 60 ℃, and after being purged with N_2 for 30 min, 0.15 g APS was added and kept for 5 min to generate free radicals. After cooling the reactants to 40 ℃, a mixture of 4 g AA (monomer), and 6 g AAm (monomer) were added to the flask. 5 g of AAm represents the mixture of 95% pure AAm and 5 % modified with N-(N_0-acryloyl-2-aminoethyl)-dimethylmaleimide. This modification was performed using the procedure reported by Seiffert et al. because it is necessary for further photo-cross-linking.[22] The temperature was then raised to 70 ℃ and maintained for 10 h to complete the polymerization process. The N_2 atmosphere was maintained throughout the reaction period. The resulting viscous product was precipitated in a large volume of acetone. The precipitated poly(AAm-*co*-AA)-*g*-CMC was dried and stored for further use.

2.4 Swelling ratio analysis

The poly(AA-*co*-AAm)-*g*-CMC solution was placed into a rectangular mold and photo-cross-linked using TXS as the cross-linker under UV-light. The cross-linked samples with a of thickness 1000 μm or less were peeled from the mold and washed well. The washed and dried cross-linked samples were placed in DI water for 30 min and then placed in the required solution. After equilibrating to the desired pH or ionic strength for 30 min, the hydrogels were weighed,

New Journal of Chemistry Accepted Manuscript

vacuum dried for 1 h, and weighed again. For each sample, the above mentioned strategies of weighing were accomplished in the same vial to minimize handling. The weights are recorded as weight of the wet or dry gel + vial, and all the vials were weighed before the swelling experiment. The average swelling ratio and standard deviation were determined from three samples placed in the same pH and ionic strength. The swelling ratio was calculated using the following equation.

$$\text{Swelling ratio} = (W_S - W_D/W_D) \times 100$$

where W_S is the weight of the swollen gel and W_D is the weight of the dry gel.

2.5 Fabrication of bilayer actuator film

The biaxially-oriented PA-6 film was used as a supporting and inactive material in this actuator. Poly(AAm-*co*-AA)-*g*-CMC with a 3 wt% TXS solution in water was drop casted on a PA-6 substrate and sheared gently to make a uniform layer. This assembly was then exposed to UV-irradiation to cross-link the poly(AAm-*co*-AA)-*g*-CMC onto PA-6. The bilayer film was then cut to the desired dimensions for further actuation analysis.

2.6 Characterization

The chemical structures were characterized by Fourier transform infrared (FTIR, Shimadzu) spectroscopy operating in the wavenumber range, 4000–500 cm^{-1}. Thermogravimetric analysis (TGA, TG/DTA EXSTAR 6000) of CMC and poly(AAm-*co*-AA)-*g*-CMC was performed on a series from room temperature to 800 ^{o}C at a heating rate of 10^{o}C/min under a nitrogen atmosphere. The morphology of the poly(AAm-*co*-AA)-*g*-CMC/PA-6 bilayer was evaluated by scanning electron microscopy (SEM, JEOL 6390). Prior to analysis, the sample was coated with platinum. Real time pictures during actuation of the bilayer film were captured using a Samsung DSLR. UV-inno cure 1000N was used to cure the CMC and monomers mixture for 15 min.

3. Results and Discussion

New Journal of Chemistry Accepted Manuscript

The polysaccharide-based hydrophilic material was synthesized by grafting the poly(AAm-co-AA) onto CMC. APS was used as a free radical initiator. Scheme 1 represents the reaction mechanism for grafting the copolymer onto CMC. In the first step, the APS initiator decomposes and generates sulfate anion-radicals upon heating the system. The radicals, when in contact with hydroxyl groups on the CMC, abstracts the protons, which results in the formation of active alkoxy radicals. The vinyl groups of the monomers, AA and AAm, close to the reaction sites become an acceptor of the CMC radicals resulting in the propagation of a new polymeric chain. Scheme 1 presents the reaction mechanism for the synthesis of poly(AAm-*co*-AA)-*g*-CMC.

Fig. 1 shows the FTIR spectra of CMC and poly(AAm-*co*-AA)-*g*-CMC. The spectra of CMC and poly(AAm-*co*-AA)-*g*-CMC were similar because both presented the characteristic absorption bands of cellulose, such as absorption at approximately 3400 cm^{-1} (H-bonded hydroxyl), 2905 cm^{-1} (methylene), and 1060 cm^{-1} (1,4-glycosidic bond).[23] For poly(AAm-*co*-AA)-g-CMC, new absorption bands were observed compared to pure CMC. The characteristic bands intensities at 1033–1162 cm^{-1} were weakened after polymerization, indicating the participation of hydroxyl groups of CMC in the chemical reaction. The new absorption band at 1670 cm^{-1} appeared for poly(AAm-*co*-AA)-*g*-CMC which was attributed to the superposition of C=O in amide I (1659 cm^{-1}) and C=O in COOH (1718 cm^{-1}). In addition, the band at 1552 cm^{-1} was assigned to C=O asymmetric stretching in the carboxylate anion. This was reconfirmed by bands at 1456 and 1408 cm^{-1}, which were related to symmetric stretching of the carboxylate anion. Therefore, the superabsorbent hydrogel comprises a structure of CMC with a side chain of poly(AAm-*co*-AA).

The thermal stability of a polymeric material depends on the strength of the covalent bond between the atoms. The reported dissociation energies for different covalent bonds, -C-H, C-C,

New Journal of Chemistry Accepted Manuscript

C-O, C=O, O-H and N-H were reported to be 414, 347, 351, 741, 464 and 412 kJ/mol, respectively. Based on these values, the expected average complete dissociation energy of poly(AAm-*co*-AA)-*g*-CMC should be higher than CMC. Fig. 2 shows the TGA curves of CMC and poly(AAm-*co*-AA)-*g*-CMC. CMC has a major weight loss over the temperature range, 200-420 ℃, which was due to the degradation of saccharide rings, the breaking of C-O-C bonds in the CMC chain and the elimination of CO_2 from the polymeric backbone.[24] On the other hand, poly(AAm-*co*-AA)-*g*-CMC degraded steadily between 200-610 ℃ due to grafting of the copolymer onto CMC. The difference in the weight loss above 600 °C between CMC and poly(AAm-*co*-AA)-*g*-CMC suggested that the amount of poly(AAm-*co*-AA) grafted onto the CMC was approximately 20 wt%. Therefore, the successful grafting of PAAm and PAA onto CMC imparted higher thermal stability compared to pure CMC.

The swelling behavior of the poly(AA-*co*-AAm)-*g*-CMC was recorded after performing a swelling ratio test. The samples for the swelling ratio test were prepared by the photo-cross-linking of poly(AA-*co*-AAm)-*g*-CMC aqueous solution with a 3 wt% TXS in a rectangular shape mold. Fig. 3 shows the effects of the pH and ionic strength on the swelling ratio of hydrogel. Hydrogels containing pH-sensitive moieties swell in response to pH changes due to the charge density of the material. On the other hand, P(AAm) did not show any changes in the equilibrium mass with the pH of the external medium, whereas for the samples containing acidic or basic moieties, the equilibrium mass increased/decreased with pH of the swelling solution. The pH-independent swelling behavior of the P(AAm) was attributed to the polymer matrix being purely non-ionic in nature, and not containing any ionizable groups. Therefore, variations in the pH of the swelling media did not produce any changes in the swelling capacity of the P(AAm).

New Journal of Chemistry Accepted Manuscript

Fig. 3a shows the effect of pH on the swelling of as-synthesized hydrogel was measured at different pH ranged from 2.5-12. Acidic hydrogel, such as poly(AA-*co*-AAm)-*g*-CMC, swells in solution with a pH above the pKa of the hydrogel. Swelling occurs due to the ionization followed by subsequent dissociation of the AA groups present in the hydrogel.[25,26] Under acidic pH (≤ 4), most of the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently swelling values are decreased. At higher pH (4-8), some of carboxylate groups are ionized and the electrostatic repulsion between COO^- groups causes an enhancement of the swelling capacity. The largest increase in swelling occurs between pH 4.8 and 7.8 which is consistent with the pKa value of AA (4.25).[27] The reason for swelling-loss in the basic solutions (pH > 8) is "charge screening effect" of excess Na^+ in the swelling media, which shields the carboxylate anions and prevents effective anion-anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems.[28-31]

Fig. 3b shows the effects of the ionic strengths at different pH. A general trend of decreasing swelling ratio for poly(AA-*co*-AAm)-*g*-CMC hydrogel with increasing ionic strength was observed at various pH (2.5, 4.8, 7.8 and 12). Driven by the Donnan equilibrium, an osmotic pressure proportional to the difference in the mobile ion concentration is generated between the inside and outside of the hydrogel.[32] The Debye screening lengths of hydrogels is changed by altering the ionic strength,[33] causing volume changes (swelling or de-swelling) due to the different degrees of self-repulsion of the hydrogel moieties. As the ionic strength of the solution increased from 0.2 to 1.2 M, the swelling ratio decreased from 1514 to 775 at pH 7.8. 50 % shrinkage was readily achieved at a single pH condition (7.8) with increasing ionic strength. Overall, the hydrogel was sensitive to changes in ionic strength, specifically showing a decrease in swelling with increasing ionic strength. This can be attributed to the similarity of mobile ion

New Journal of Chemistry Accepted Manuscript

concentration inside and outside of the hydrogel.[34] Swelling ratio analysis showed that the hydrogel material can be swollen readily in water at pH ~ 7.8 and an ionic strength of 0.2 M.

Fig. 4a shows the fabrication process of the bilayer actuator. poly(AAm-*co*-AA)-*g*-CMC with a 3 wt% TXS aqueous solution was drop casted on the PA-6 substrate and irradiated with UV-light for photo-cross-linking. Fig. 4b shows a cross-sectional SEM image of a bilayer film where the two layers were well adhered to each other. The thickness of poly(AAm-*co*-AA)-*g*-CMC and PA-6 was found to be 34 and 43 μm, respectively. As the poly(AAm-*co*-AA)-*g*-CMC is highly soluble in water, the uncross-linked hydrogel can be removed easily from PA-6 by water. Photo-crosslinking adheres the poly(AAm-*co*-AA)-*g*-CMC layer well to the PA-6 layer due to the formation of covalent bonds between the amide groups of both layers. In addition, cross-linking prevents the complete dissolution of poly(AAm-*co*-AA)-*g*-CMC in water but it imparts swelling propertied to this layer. In a bilayer soft matter system, when a single layer swells more than another adhered layer, the system bends. Curling deformation is achieved when the swelling is high.

Curvature is commonly used to describe the curling actuation system quantitatively. The curvature is defined mathematically as K = 1/R, where K is the curvature and R is the radius of the actuator at a specific stage. R is represented schematically in Fig. 5a. Fig. 5b shows the digital photographs taken at a time interval of 102 s when clamped poly (AAm-*co*-AA)-*g*-CMC/PA-6 film was dipped in water. A straight film curled and closed upon dipping in water after 330 s. In the curled state, the outer layer was poly(AAm-*co*-AA)-*g*-CMC which upon immersion in water, swells and transforms the initial straight film to a curled state. Fig. 5c shows a series of pictures of a poly(AAm-*co*-AA)-*g*-CMC/PA-6 film after dipping in ethanol. Ethanol naturally dissolves water very well. Therefore, when the closed/curled film was dipped in

New Journal of Chemistry Accepted Manuscript

ethanol, the water from poly(AAm-*co*-AA)-*g*-CMC layer migrated into the ethanol due the excellent miscibility of both solvents. As a result, de-swelling of the poly(AAm-*co*-AA)-*g*-CMC layer occurred and the initial straight configuration of the poly(AAm-*co*-AA)-*g*-CMC/PA-6 film was restored. The curvature (K) as a function of time when the bilayer film was dipped in water and ethanol is shown in Fig. 5d & 5e. The K values increased from 0.05 to 0.30 upon film exposure to water in 530 s. On the other hand, K values decreased from 0.24 to 0.05 in 330 s after immersing the same film in ethanol. The curling time of the actuator was longer in water than the un-curling time in ethanol. This is due to the fact that when the dried film was dipped in water, it uptakes water slowly. Whereas, the water absorbed film was further dipped in ethanol, it releases water very fast due its good miscibility with ethanol. This is because hydrogel layer contains CMC and PAA units which may impart good mechanical stability and pH dependant actuation. These topics are beyond the scope of this study and will be mediated in a separate publication.

Conclusions

A hydrogel material with a high water uptake was synthesized by grafting the copolymer, poly(AAm-*co*-AA) onto the CMC. FTIR and TGA confirmed the preparation of poly(AAm-*co*-AA)-*g*-CMC. The super absorbent hydrogels exhibited high sensitivity to pH, so that, several swelling changes of the hydrogel were observed *in lieu* of pH variations in a wide range (2.5-12). Ionic repulsion between charge-groups incorporated in the hydrogel matrix by an external pH modulation could be assumed as the main driving force responsible for such swelling changes. The poly(AAm-*co*-AA)-*g*-CMC hydrogel showed a maximum swelling at pH 7.8 and an ionic strength of 0.2 M. Reversible curling/un-curling actuation was shown for the poly(AAm-*co*-AA)-*g*-CMC/PA-6 bilayer film in both water and ethanol due to the expansion and contraction of

New Journal of Chemistry Accepted Manuscript

the polymer layer in the respective solvents. By utilizing biocompatible polymer and hydrogel, the actuator has potential across the biological and medical fields in the areas of drug delivery and implantable tools.

Acknowledgement

This study was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012009529).

New Journal of Chemistry Accepted Manuscript

Notes and references

1. J. Kuang, K. Y. Yuk and K. M. Huh, *Carbohydrate Polymers*, 2011, **83**, 284-290.

2. H. Dai, Q. Chen, H. Qin, Y. Guan, D. Shen, Y. Hua, Y. Tang and J. Xu, *Macromolecules*, 2006, **39**, 6584-6589.

3. D. Arunbabu, H. Shahsavan, W. Zhang and B. Zhao, *The Journal of Physical Chemistry B*, 2012, **117**, 441-449.

4. L. Wu, M. Liu and L. Rui, *Bioresource Technology*, 2008, **99**, 547-554.

5. D. R. Kioussis and P. Kofinas, *Polymer*, 2005, **46**, 9342-9347.

6. D. R. Kioussis, F. W. Wheaton and P. Kofinas, *Aquacultural Engineering*, 1999, **19**, 163-178.

7. D. Sivakumaran, D. Maitland and T. Hoare, *Biomacromolecules*, 2011, **12**, 4112-4120.

8. K. Kosemund, H. Schlatter, J. L. Ochsenhirt, E. L. Krause, D. S. Marsman and G. N. Erasala, *Regulatory Toxicology and Pharmacology*, 2009, **53**, 81-89.

9. C. Chang and L. Zhang, *Carbohydrate Polymers*, 2011, **84**, 40-53.

10. R. J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Youngblood, *Chemical Society Review*, 2011, **40**, 3941-3994

11. T. Heinze and A. Koschella, *Macromolecular Symposia*, 2005, **223**, 13–40.

12. R. Reeves, A. Ribeiro, L. Lombardo, R. Boyer and J. B. Leach, *Polymers*, 2010, **2**, 252-264.

13. N. Bassik, A. Brafman, A. M. Zarafshar, M. Jamal, D. Luvsanjav, F. M. Selaru and D. H. Gracias, *Journal of American Chemical Society*, 2010, **132**, 16314–16317.

14. Z. Hu, X. Zhang and Y. Li, *Science*, 1995, **269**, 525-527.

15. J. Guan, H. He, D. J. Hansford and L. J. Lee, *Journal of Physical Chemistry B*, 2005, **109**, 23134-23137.

16. N. Bassik, B. T. Abebe, K. E. Laflin and D. H. Gracias, *Polymer*, 2010, **51**, 6093-6098.

New Journal of Chemistry Accepted Manuscript

17. K. Malachowski, J. Breger, H. R. Kwag, M. O. Wang, J. P. Fisher, F. M. Selaru and D. H. Gracias, *Angewandte Chemie International Edition*, 2014, **53**, 1 – 6.

18. S. Kuwabara and H. Kubota, *Journal of Applied Polymer Science*, 1996, **60**, 1965-1970.

19. M. Yoshinobu, M. Morita and I. Sakata, *Journal of Applied Polymer Science*, 1992, **45**, 805-812.

20. H. Kubota and S. Kuwabara, *Journal of Applied Polymer Science*, 1997, **64**, 2259-2263.

21. A.Suo, J. Qian, Y. Yao and W. Zhang, *Journal of Applied Polymer Science*, 2007, **103**, 1382–1388.

22. S. Seiffert, W. Oppermann and K. Saalwächter, *Polymer*, 2007, **48**, 5599-5611.

23. F. Wu, Y. Zhang, L. Liu and J. Yao, *Carbohydrate Polymers*, 2012, **87**, 2519-2525.

24. Y. Bao, J. Ma and N. Li, *Carbohydrate Polymers*, 2011, **84**, 76-82.

25. S. -K. Ahn, R. M. Kasi, S. -C. Kim, N. Sharma and Y. Zhou, *Soft Matter*, 2008, **4**, 1151-1517.

26. P. Somasundaran, in *Encyclopedia of Surface and Colloid Science*, CRC Press, Boca Raton, New York, 2006. vol. 5.

27. *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, FL, 75th edn., 1994, pp. 8-45.

28. A. Pourjavadi, M. Sadeghi and H. Hosseinzadeh, *Polymers for Advanced Technologies*, 2004, **15**, 645-653.

29. S. E. Park, Y. C. Nho, Y. M. Lim and H. Kim, *Journal of Applied Polymer Science*, 2004, **91**, 636-643.

30. S. Lu, M. Duan and S. Lin, *Journal of Applied Polymer Science*, 2001, **79**, 1665-1674.

31. A. Pourjavadi, M. S. Amini-Fazl and H. Hosseinzadeh, *Macromolecular Research*, 2005, **13**, 45-53.

New Journal of Chemistry Accepted Manuscript

32. S. -K. Ahn, R. M. Kasi, S. -C. Kim, N. Sharma and Y. Zhou, *Soft Matter*, 2008, **4**, 1151-1157.

33. K. Kratz, T. Hellweg and W. Eimer, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2000, **170**, 137-149.

34. X. Liu, Z. Tong, O. Hu, *Macromolecules*, 1995, **28**, 3813-3817.

New Journal of Chemistry Accepted Manuscript

Figure captions

Scheme 1. Reaction mechanism of the synthesis of poly(AAm-*co*-AA)-*g*-CMC.

Fig. 1. FTIR spectra of (a) CMC and (b) poly (AAm-*co*-AA)-*g*-CMC.

Fig. 2. TGA curves of CMC and poly(AAm-*co*-AA)-*g*-CMC.

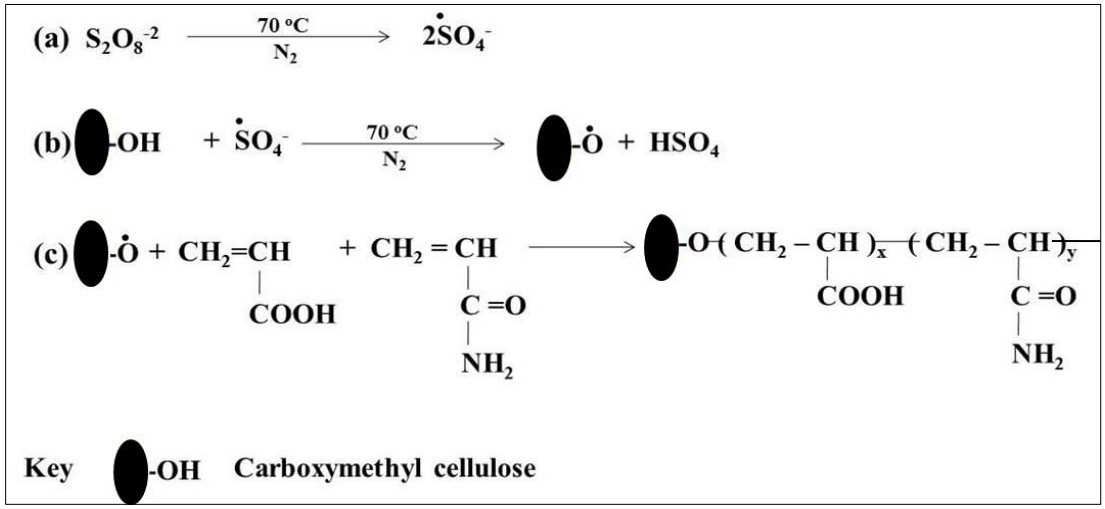
Fig. 3. Swelling behaviour of poly(AA-*co*-AAm)-*g*-CMC hydrogel at different (a) pH and (b) ionic strength.

Fig. 4. (a) Schematic diagram of the steps followed for the fabrication of poly(AAm-*co*-AA)-*g*-CMC/PA-6 bilayer film and (b) cross-section SEM image of the bilayer film.

Fig. 5. (a) Schematic representation of the process for measuring the R for curvature, (b-c) digital photographs of actuator in water for curling ((i) to (vi), every 102 s) and ethanol for uncurling ((i) to (vi), every 66 s) and (d, e) corresponding curvature as a function of time in water and ethanol.

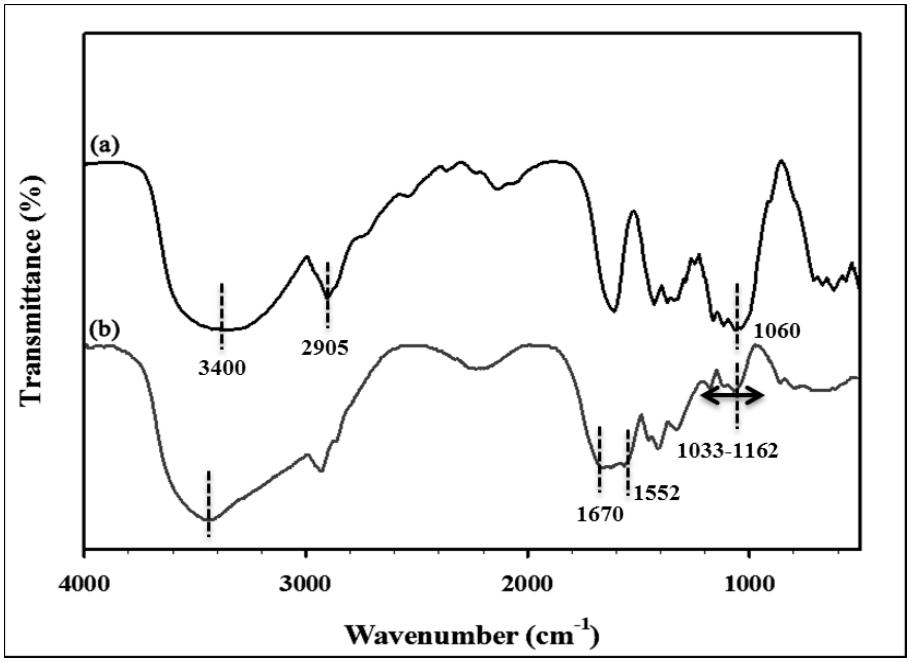
New Journal of Chemistry Accepted Manuscript

Scheme 1



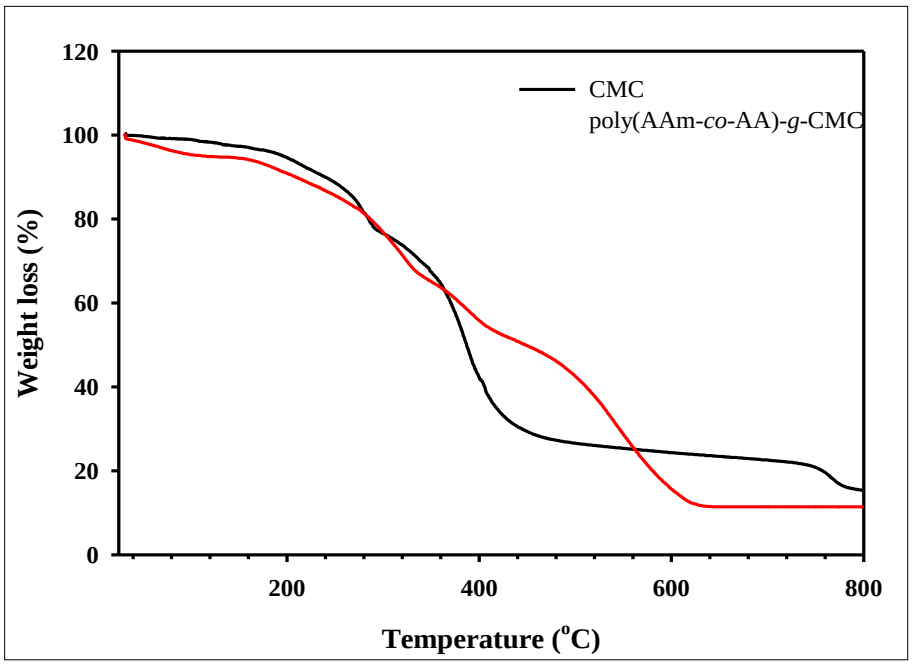
New Journal of Chemistry Accepted Manuscript

Fig. 1



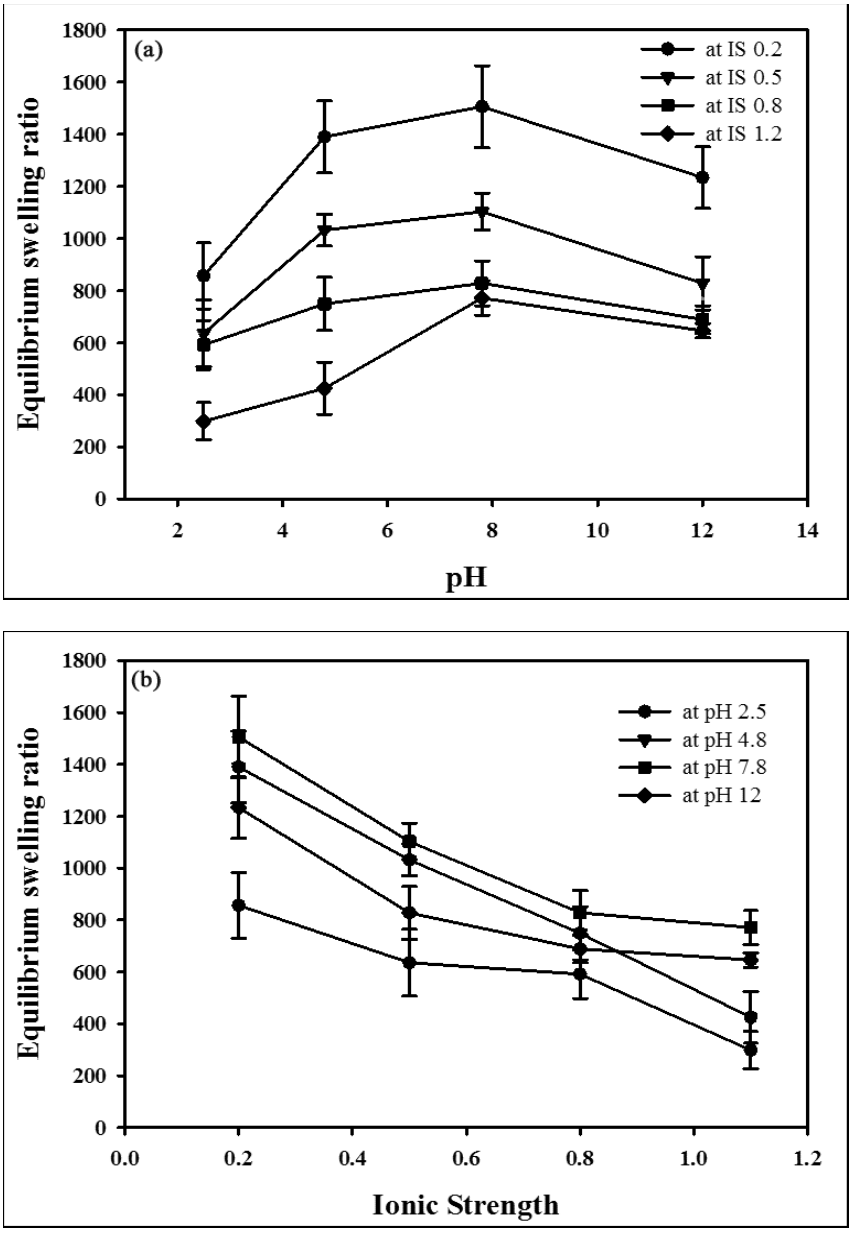
New Journal of Chemistry Accepted Manuscript

Fig. 2



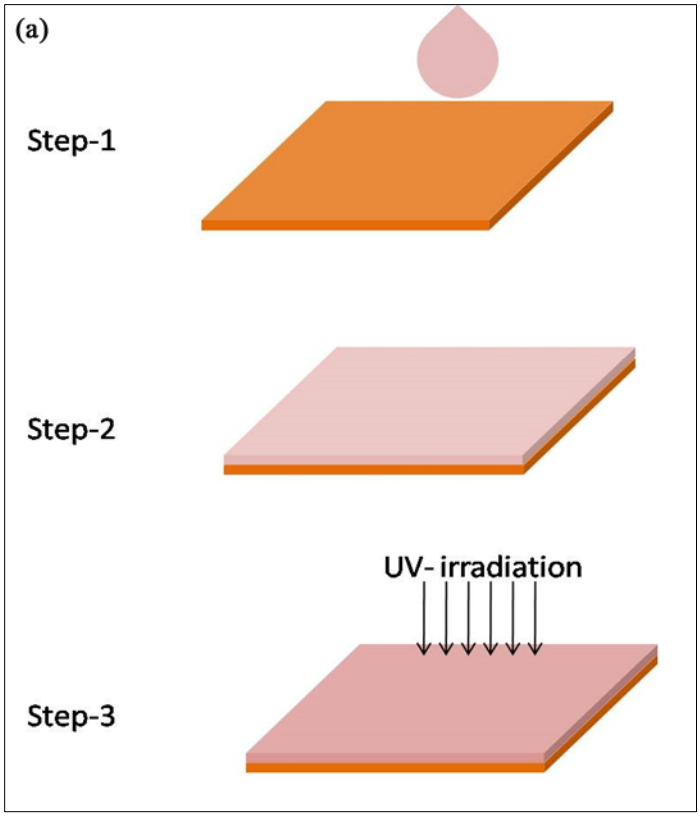
New Journal of Chemistry Accepted Manuscript

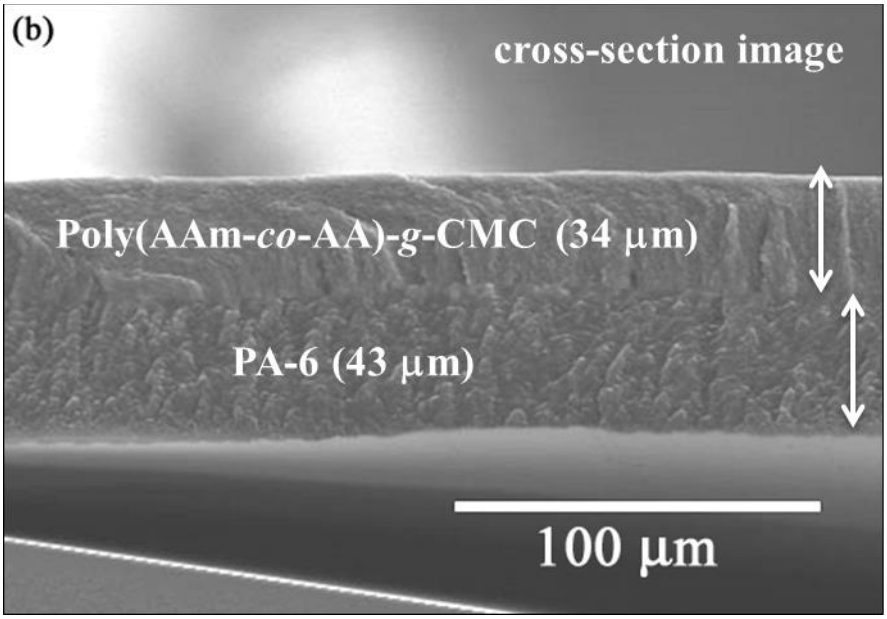
Fig. 3



New Journal of Chemistry Accepted Manuscript

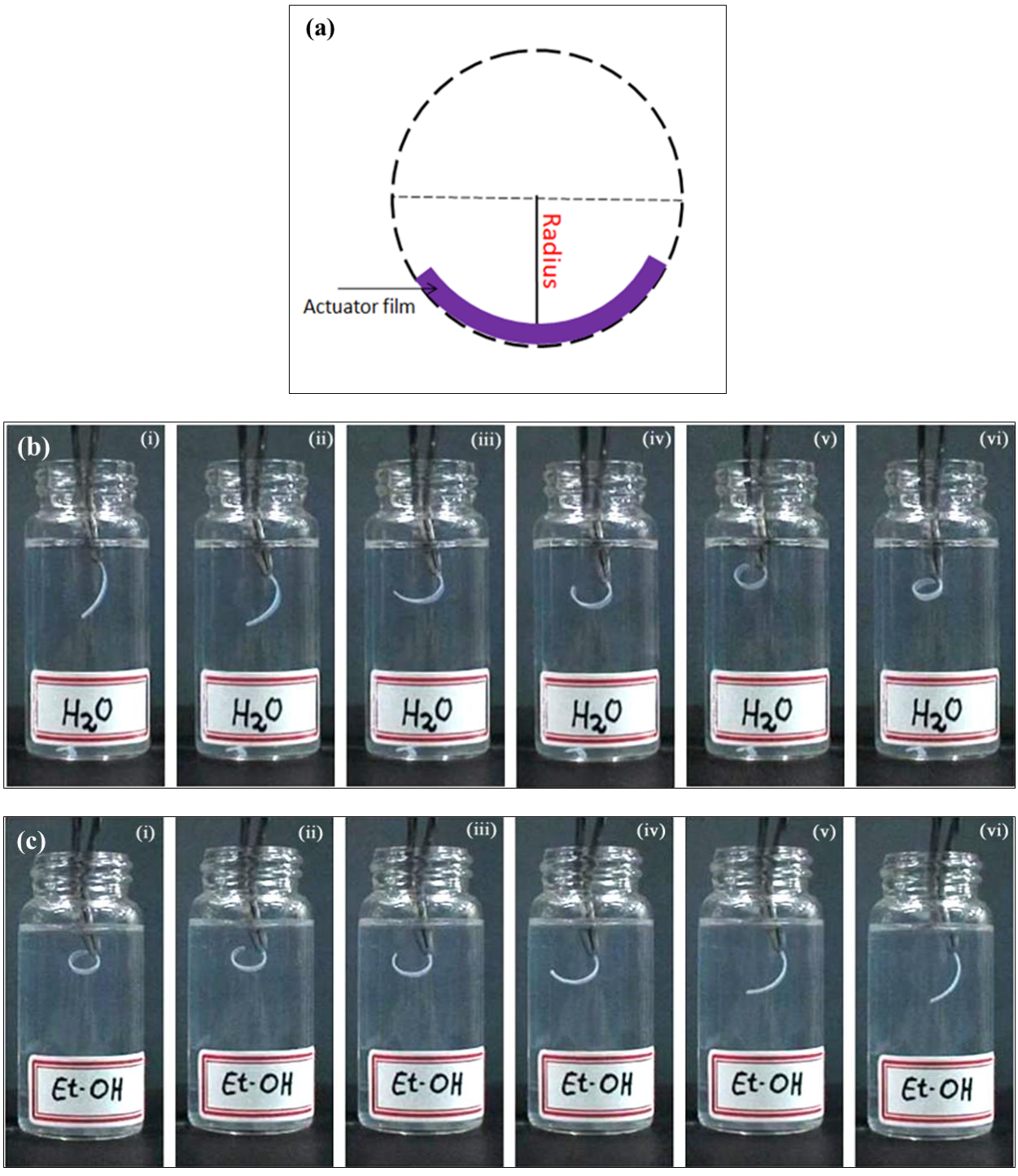
Fig. 4



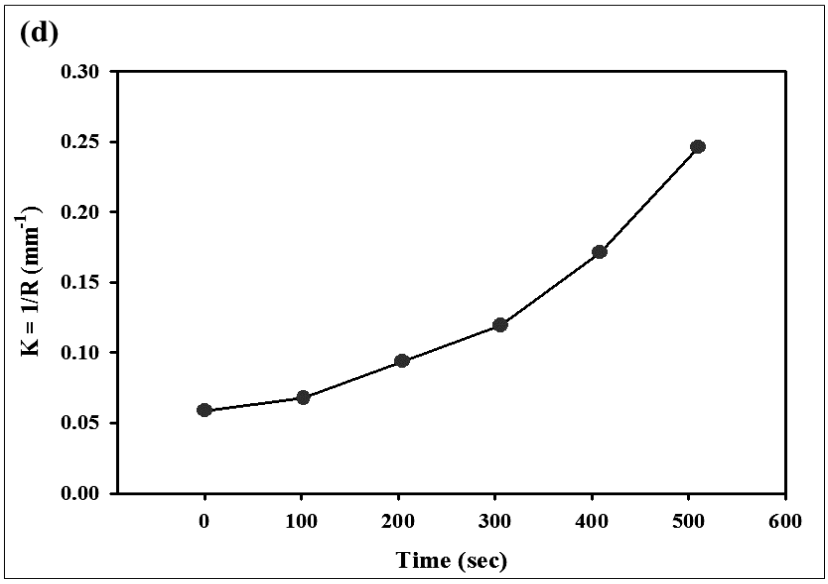


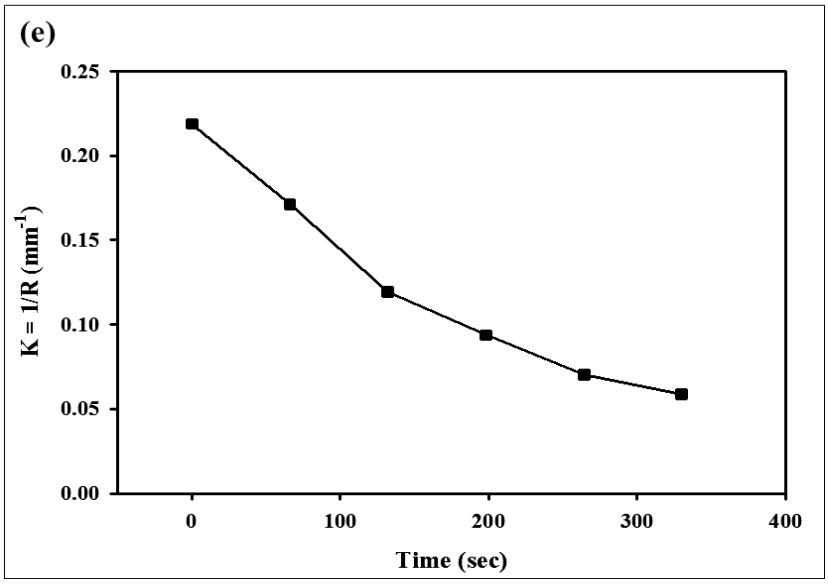
New Journal of Chemistry Accepted Manuscript

Fig. 5



New Journal of Chemistry Accepted Manuscript





New Journal of Chemistry Accepted Manuscript