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Swelling and mechanical properties of superabsorbent hydrogels based on Tara gum/acrylic acid synthesized by gamma radiation

Safaa G. Abd Alla^a, Murat Sen^b, Abdel Wahab M. El-Naggar^{a,*}

- ^a Radiation Chemistry Department, National Center for Radiation Research and Technology, Cairo, Egypt
- ^b Department of Chemistry, Hacettepe University, Beytepe, Ankara 06532, Turkey

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ABSTRACT

The main objective is to develop a new superabsorbent system especially for using in diaper applications. In this study, hydrogels based on Tara gum/acrylic acid (TG/AAc) were prepared by gamma irradiation, in the presence of N,N'-methylenebisacrylamide (MBAAm) as a crosslinking agent. The polymeric networks formed were characterized by FT-IR and evaluated by swelling studies as a function of MBAAm concentration, temperature and nature of the swelling medium. The swelling kinetics of the hydrogels was studied in terms of the diffusion exponent "n". The results showed that the water diffusion into hydrogels is a non-Fickian type. Mechanical measurements (stress-strain) curves of hydrogels were evaluated to calculate the shear modulus values and the average molecular weight between crosslinks (Mc). Moreover, the absorption under load at 37 °C of water and urea aqueous solutions (as a major component of urine) by TG/AAc hydrogels was determined.

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1. Introduction

Superabsorbent polymer (SAP) hydrogels, especially those based on natural polymers, can absorb large amounts of water, saline solutions or physiological fluids as high as 10-1000 times their own weight due to considerable hydrophilic groups in their structure (Chang, Duan, Cai, & Zhang, 2010; Chang, Zhang, Zhou, Zhang, & Kennedy, 2010; Pourjavadi, Eftekhar Jahromi, Seidi, & Salimi, 2010; Teli & Waghmare, 2010; Wang & Wang, 2010; Yang, Ma, & Guo, 2011; Yu, Yun-fei, Huan-lin, & Hui-min, 2010). The super swelling characteristics of SAP make them ideal for use as disposable diapers (Espinosa-Valdemar, Turpin-Marion, Delfin-Alcalá, & Vázquez-Morillas, 2011; Kosemund et al., 2009; Qu & de Varennes, 2010). Superabsorbents were also used in environmental applications for the removal of undesired heavy metal ions (Bao, Ma, & Li, 2011; Singh, Chauhan, Bhatt, & Kumar, 2006; Zheng, Hua, & Wang, 2010) and dyes (Dalaran, Emik, Güçlü, İyim, & Özgümüs, 2011; Dragan & Apopei, 2011).

The synthesis and characterization of superabsorbents based on natural gums have been reported by research works. In this regard, the synthesis and characterization of partially hydrolyzed graft copolymer (H-partially carboxymethylated guar gum-gmethacrylic acid) was reported (Yadav, Mishra, & Behari, 2011). Novel fast-swelling porous guar gum-g-poly(sodium acrylate-co-styrene)/attapulgite (GG-g-P(NaA-co-St)/APT) superabsorbent

hydrogels were prepared by simultaneous free-radical graft copolymerization reaction of guar gum (GG), partially neutralized AA (NaA), styrene (St) and attapulgite (APT) using N,N'-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator in aqueous solution and the surfactant self-assembling templating pore-forming technique (Shi, Wang, & Wang, 2011). Novel guar gum-g-poly(sodium acrylate)/rectorite (GG-g-PNaA/REC) superabsorbent nanocomposites were also prepared in aqueous solution using guar gum (GG), partially neutralized acrylic acid (NaA), acidified rectorite (H+-REC) and organified rectorite (CTA+-REC) by cetyltrimethylammonium bromide (CTAB) as raw materials, ammonium persulfate (APS) as initiator and N,N'-methylenebisacrylamide (MBA) as crosslinker (Wang & Wang, 2009). FT-IR spectra confirmed that NaA had been grafted onto GG chains and the OH groups of REC participated in polymerization reaction. Development of novel hydrogels by modification of sterculia gum through radiation cross-linking polymerization for use in drug delivery was studied (Singh & Vashishtha, 2009). Polymeric networks (hydrogels) thus formed were characterized with SEMs, FT-IR, TGA and swelling studies which were carried out as a function monomers concentration, radiation dose, amount of sterculia contents in the polymer matrix and nature of the swelling medium.

Tara gum is a low cost polysaccharide extracted from the Tara tree (*Caesalpinia spinosa*) by grinding the endosperm of the seeds. This polysaccharide is composed mainly of galactomannans. The principal component consists of a linear chain of β -(1–4) mannan (M) backbone with α -D-galactose (G) branches attached by (1–6) linkages; the ratio of mannose to galactose in Tara gum is

^{*} Corresponding author. Tel.: +20 2 22749298; fax: +20 2 22749298. E-mail address: ab_nagga@yahoo.com (A.W.M. El-Naggar).

3:1. Tara gum is listed as a food additive by the Codex Committee on Food Additives and Contaminants (CCFAC), with the INS (International Numbering System) as number 417 and with technical functions listed as thickener and stabilizer (Kounga & Aotearoa, 2006). Tara gum also has a synergistic effect when used in combinations with other gums (such as guar and locust bean gums) to produce improved gel and colloid stabilities and properties, Radiation synthesis of hydrogels has special technique advantages, not only for the strong interaction between chains through covalent bonds, but also it solves the problem of sterilization, and allows the fabrication of pure product non-contaminated with residuals of toxic initiators (Francis, Kumar, & Varshney, 2004; Francis, Mitra, Dhanawade, Varshney, & Sabharwal, 2009; Yang et al., 2011). Thus, the aim of this work is to prepare a new superabsorbent hydrogels based on the natural polysaccharide polymer Tara gum by gamma radiation to be used in diaper applications. These hydrogels are environmentally friendly materials.

2. Experimental

2.1. Materials and chemicals

Tara gum (TG) was obtained by Sigma–Aldrich, whereas the monomer acrylic acid (AAc) was obtained from Merck Chemical Company, Germany. N,N'-methylenebisacrylamide (MBAAm) as a crosslinking agent was obtained from B.D.H. (Poole, UK). Urea was provided from B.D.H. (Poole, UK). All the chemicals were used as received without purification or further treatment. Distilled water was used for the hydrogel preparation.

2.2. Preparation of TG/AAc hydrogels

The hydrogels were prepared by dissolving 2 wt% of TG gum and different weight fractions of acrylic acid (0.954, 0.913 and 0.840) in water (4 ml) with 2 or 4 wt% of N,N'-methylenebisacrylamide (based on the weight of acrylic acid). The homogenous viscous solutions were placed in PVC straw of 3 mm diameter and irradiated to 14.5 kGy in air at ambient temperature at a dose rate of 0.1 kGy/h. Irradiation was carried out in the Gamma cell 220 type, ⁶⁰Co gamma irradiator in Ankara, Hacettepe University. Hydrogels obtained, in long cylindrical shapes, were cut into pieces of 4–5 mm long and dried in air. The hydrogels were stirred for one day in distilled water to remove the unreacted materials.

2.3. Gel content determination

Sample of the prepared hydrogels were accurately weighed (W_0) and then extracted with distilled water using soxhlet system for 6 h. After extraction, the samples were removed and dried in vacuum oven at 80 °C to constant weight (W_1) . The gel content was calculated according to Eq. (1):

Gel content (%) =
$$\left(\frac{W_1}{W_0}\right) \times 100$$
 (1)

2.4. FT-IR spectroscopy

The infrared spectra of TG/AAc and pure AAc hydrogels were performed on a Mattson 5000 FT-IR spectrometer over the $500-4000\,\mathrm{cm^{-1}}$ range. Samples were ground to a very fine powder and mixed with a highly dried KBr powder, and then pressed to obtain transparent disks.

2.5. Swelling measurements

Dry weight of hydrogels (2-3 mm thickness, 3 mm diameter) was left to swell in different media [water, aqueous sodium chloride (0.5%, w/v) and aqueous urea (2%, w/v)] at room temperature and at $37\,^{\circ}\text{C}$. Swollen gels were removed from the swelling medium at regular time intervals and dried superficially with filter paper, weighed and placed in the same medium. The measurements were continued until a constant weight was reached for each sample. The swelling ratio was determined by using Eq. (2).

Swelling ration =
$$\frac{M_t - M_o}{M_o}$$
 (2)

where M_0 is the initial dry weight and M_t is the weight of a swollen gel at time t.

2.6. Compression measurements

Elastic properties and shear modulus of hydrogels, in the form of disks (3 mm in diameter and 5 mm in length), were determined by using a Universal Testing Instrument and uniaxial compression (Zwick Z010 model). The crosshead speed was 5 mm/min and 1 kN load cell. After adjusting the experimental parameters, each measurement was performed at less than 1 min to avoid the release of water from the hydrogel during the testing. The recorded results are the average of measurements (four times for each gel). Before measurements, the gels were maintained in water until equilibrium at room temperature and then dried with filter paper and put between the crosshead of the instruments. The magnitude of strain percentage at deformation was recorded and the stress values (σ) were determined by using Eq. (3) (De Paula & Rodrigues, 1995):

$$\sigma = \frac{F}{A} \tag{3}$$

where *F* is the force, and *A* is the cross-sectional area of the strained specimen. The parameters generated by the instrument are force and displacement. This information was then converted to elastic modulus (*G*), by the use of Eq. (4) (Ferruzzi, Pan, & Casey, 2000):

$$\sigma = \frac{G}{\lambda - \lambda^2} \tag{4}$$

where λ is relative deformation of the specimen, the $(\lambda - \lambda^2)$ is the strain and is calculated from Eq. (5) (Shultz, 1985).

$$\lambda = \frac{\Delta L}{L_0} \tag{5}$$

where ΔL is the deformation of the sample and L_o is the initial sample length.

2.7. Absorbance under load (AUL) measurements

A macro porous sintered glass filter plate ($d=100 \, \mathrm{mm}$, $h=7 \, \mathrm{mm}$) was placed in a Petri dish and the dry hydrogel sample was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid weight ($d=80 \, \mathrm{mm}$, variable height) which could slip freely in a glass cylinder was used to apply the desired load (applied pressure = $0.6 \, \mathrm{N/m^2}$) to the dry hydrogel particles as shown in Fig. 1. The sample was then covered by the solution such that the liquid level was equal to the height of the sintered glass filter. The dish and its contents were covered to prevent surface evaporation and probable change in the concentration. The swollen particles were weighed at regular time intervals and AUL was calculated by using Eq. (6).

$$AUL(g/g) = \frac{W_2 - W_1}{W_1} \tag{6}$$

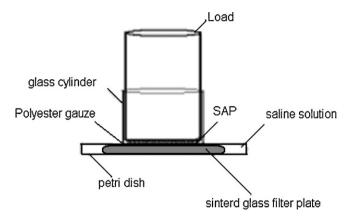


Fig. 1. Assembly of measurement of absorbency under load (AUL).

where W_1 and W_2 represent the weight of dry and swollen hydrogel, respectively.

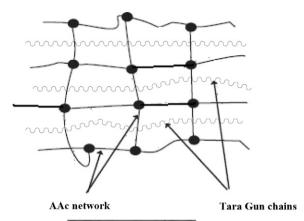
3. Results and discussion

3.1. Composition of TG/AAc networks

To increase the crosslinking density and avoiding the degradation of TG gum, N,N'-methylenebisacrylamide (MBAAm) as crosslinking agent was added to the mixture. The crosslinking enhancers during irradiation is reported, in which these materials do not directly enter into crosslinking reactions but enhance secondary reactions that lead to the formation of crosslink sites (Shultz, 1985). The secondary reactions involving the formation of free radicals due to the absorption of radiation of the unsaturated CH₂=CH₂ present in MBAAm molecule. These free radicals will enhance the formation of crosslinked sites on the different species in the mixture. When pure acrylic acid (AAc) monomer is irradiated with gamma rays, polymerization and subsequently crosslinking reactions took place. The total dose required for gelation was determined to be 14.5 kGy. When an aqueous solution of TG/AAc mixtures is exposed to gamma irradiation, free radicals are formed on the chains of both species. Also, the radiolysis products of water especially hydroxyl free radicals, are very effective in generating free radicals on both AAc monomer and TG gum polymer and the latter one can initiate the grafting of AAc onto TG chains. Therefore, AAc is polymerized and crosslinked in the presence of TG gum chains and leads to the formation of semi-interpenetrating network structure (semi-IPN). The semi-IPN type structure hydrogels formed, in which AAc is crosslinked and TG is physically included in the networks is illustrated schematically in Fig. 2. The hydrogels obtained in the presence of 2 and 4 wt% (MBAAm) were very stable and showed uniform swelling properties in all solvents. Fig. 3 shows the effect of weight fractions of AAc monomer and crosslinking agent (MBAAm) on the gel content of pure PAAc and TG/AAc hydrogels. It can be seen that the increase of AAc weight fractions or the crosslinking agent, in the initial feeding mixture, causes an increase in the gel content.

3.2. FT-IR spectroscopy

Fig. 4 shows the IR spectra of TG/AAc and pure AAc hydrogels with 2 wt% MBAAm. The intensity of absorption band at 2925 cm $^{-1}$ assigned to the C–H stretching of CH $_2$ groups, is increased in the IR spectrum of TG/AAc hydrogels due to the occurrence of crosslinking reaction. The broad absorption bands at 3412 cm $^{-1}$ due to –OH stretching of the hydroxyl group in pure AAc hydrogels were shifted towards lower wavelength in the TG/AAc hydrogels. This shift is



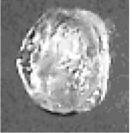


Fig. 2. Illustration of the semi-IPN type structure formation of AAc/TG hydrogels and a photograph of the obtained hydrogel.

attributed to the formation of inter/intra molecular hydrogen bonding. The absorption bands at $1730\,\mathrm{cm^{-1}}$ due to the C=O groups present in pure AAc hydrogels were observed with increased intensity in the spectrum of TG/AAc hydrogels. The absorption bands at 1169, 1247 and 1449 cm⁻¹ due to the stretching vibration of C=O in the rings, C=OH stretching, and stretching vibration of C=O=C in the repeating units of TG can be seen clearly in the spectrum of the hydrogel.

3.3. Swelling characters of hydrogels in water

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent.

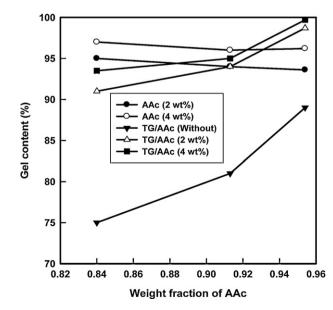


Fig. 3. Effect of weight fractions of AAc monomer and crosslinking agent (MBAAm) on the gel content of pure PAAc and TG/AAc hydrogels.

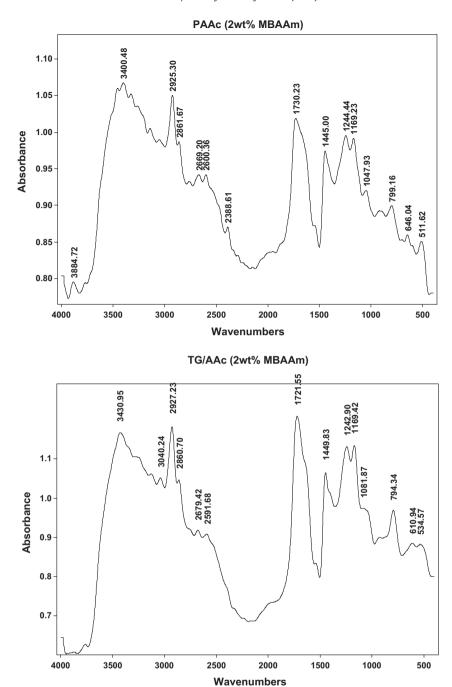


Fig. 4. FT-IR spectra of the hydrogels PAAc (2 wt% MBAAm) and TG/AAc (2 wt% MBAAm), all were prepared at the dose 14.5 kGy.

Figs. 5 and 6 show the swelling kinetics at room temperature and 37 °C for PAAc and TG/AAc hydrogels, prepared by gamma irradiation at a dose of 14.5 kGy, in the presence of different contents of the crosslinking agent MBAAm. The figures showed that the swelling increased with increasing time up to certain value and then tend to level off, especially at room temperature. It is clear that the swelling decreases with increasing MBAAm content and increases with increasing temperature. However, in all cases the PAAc hydrogel displayed higher swelling ratio than TG/AAc hydrogel, regardless of MBAAm content or temperature. This increase in the swelling with increasing temperature may be explained as follows. At higher temperatures, the free volume of the gels is increased resulting in increasing the mobility of chains and hence facilitates the diffusion of water molecules from the surroundings.

The decrease in swelling observed with increasing MBAAm content is due to the increase of crosslinking density which causes the structure more compact. The decreased swelling ratio with the introduction of Tara gum may be attributed to the blocking of active sites on PAAc chains through grafting reaction leading to decrease the hydrophilic groups.

Eq. (7) was used to determine the nature of diffusion of water into hydrogels (Peppas, Gurny, Doelker, & Buri, 1989).

$$F = \frac{M_t}{M_{\infty}} = kt^n \tag{7}$$

where M_t and M_{∞} denote the amount of solvent diffused into the gel at time "t" and infinite time (at equilibrium), respectively, "k" is a constant related to the structure of the network, and the

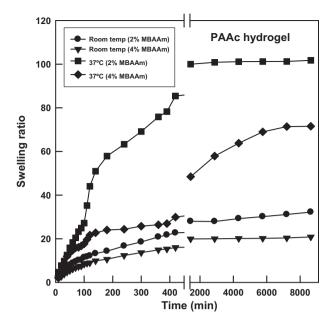


Fig. 5. Swelling kinetics in water at room temperature and 37 $^{\circ}$ C of PAAc hydrogels prepared by gamma irradiation at a dose of 14.5 kGy and in presence of different contents of the crosslinking agent MBAAm.

exponent "n" is a number determines the type of diffusion. Based on the relative rate of diffusion of water into polymer matrix and rate of polymer chain relaxation, swelling of polymers has been classified into three types of diffusion mechanisms (Ritger & Peppas, 1987a, 1987b). These mechanisms are Case I simple Fickian diffusion, Case II diffusion, and Case III Non-Fickian or anomalous diffusion. Simple Fickian diffusion is characterized by n=0.5, while Case II diffusion is characterized by n=1 and Non-Fickian diffusion is characterized by n=1 and 1.0. Eq. (7) was applied to the initial stages of swelling for the hydrogels based on pure

Table 1Kinetic parameters of swelling in water for pure PAAc and TG/AAc hydrogels prepared in the presence of different concentrations of the crosslinking agent MBAAm and at a dose of 14.5 kGy of gamma radiation.

Hydrogels	n	K(×100)	$D(\times 10^8 \mathrm{m^2 min^{-1}})$
PAAc (2 wt% MBAAm)	0.65	1.79	4.01
PAAc (4 wt% MBAAm)	0.63	2.15	4.30
TG/AAc (2 wt% MBAAm)	0.64	2.46	5.07
TG/AAc (4 wt% MBAAm)	0.56	1.91	2.83

AAc and TG/AAc mixtures, in which plots of $\ln M_t/M_\infty$ versus $\ln t$ yield straight lines. The exponent "n" and "k" were calculated from the slope and the intercept of the lines as shown in Table 1. The values in this table show that the values of "n" are between 0.56 and 0.65 and that the lower the crosslinking density the more non-Fickian swelling behavior of the hydrogels. This can be explained as the dominance of solvent diffusion rate is over the relaxation rate of polymer chains in between crosslinking sites, i.e. the slow relaxation rate of the hydrogel.

3.4. Swelling in urea solutions

The swelling kinetics of the hydrogels based on TG/AAc and pure AAc in urea aqueous solution at different temperatures and by using different concentrations of crosslinking agent is shown in Figs. 7 and 8. The figures show that the swelling increases continuously with time due to superabsorbent character of these hydrogels, in which the samples almost reached the equilibrium state after 9000 min. In this regard, the highest swelling (%) for TG/AAc (2 wt% MBAAm) at 37 °C in urea solution is \sim 7500%, while for pure PAAc (2 wt% MBAAm) at 37 °C is \sim 27,000%. This big difference in the swelling (%) is due to the higher hydrophilicity and lower crosslinking density of pure AAc hydrogels than that of TG/AAc hydrogels. It should be noted that pure AAc hydrogels after this time ruptured and cannot be controlled, which is most probably due to increase of the inhomogeneous distribution of crosslinks within the hydrogel.

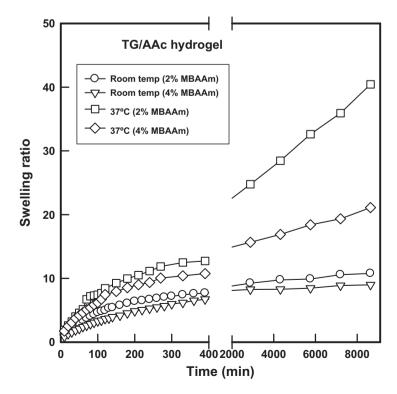


Fig. 6. Swelling kinetics in water at room temperature and 37 °C of TG/AAc hydrogels. Preparation conditions as in Fig. 5.

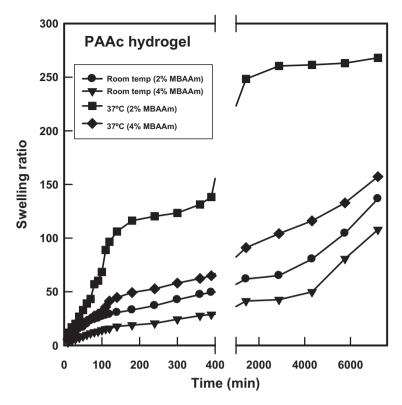


Fig. 7. Swelling kinetics at room temperature and 37 °C of PAAc hydrogels in aqueous urea solution (2% w/v). Preparation conditions as in Fig. 5.

The internal pressure developed upon swelling of homogeneous network structure may be responsible for the poor mechanical properties of pure AAc hydrogels. On the other hand, the values of the swelling (%) of TG/AAc and pure AAc hydrogels in urea solution are higher than the swelling (%) of the hydrogels in water. The highest swelling (%) for TG/AAc (2 wt% MBAAm) at 37 °C in water was ~4000%, while in urea solution reaches ~7500%. Also, the highest swelling (%) for pure AAc (2 wt% MBAAm) at 37 °C in water was

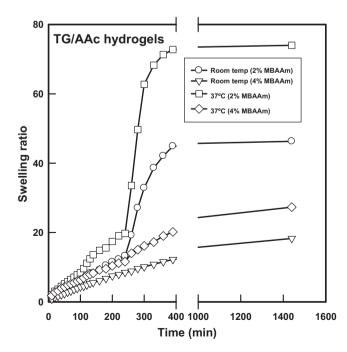


Fig. 8. Swelling kinetics at room temperature and $37\,^{\circ}$ C of TG/AAc hydrogels in aqueous urea solution (2% w/v). Preparation conditions as in Fig. 5.

10,000%, while in urea \sim 27,000%. The reason for this difference is the hydrophilic character of urea molecules could be due to the urea is an effective reagent for breaking the hydrogen bonds in gels.

3.5. Molecular weight between crosslinks

For the characterization of the network structure and determination of molecular weight between crosslinks (Mc) of the prepared hydrogels, the swelling in water experiments were continued until a constant value of swelling was reached. The weight of the swollen hydrogels was used to calculate the polymer volume fraction in swollen gel (ν_{2m}) by using Eq. (8).

$$\frac{1}{\nu_{\rm 2m}} = \left[\frac{1+\rho}{\rho_{\rm W}(1/W-1)} \right] \tag{8}$$

where ρ and ρ_W are the densities of dry gel and water, whereas W is the weight of the hydrogel at equilibrium. The values of ν_{2m} for TG/AAc and pure AAc hydrogels are listed in Table 2. At the end of the swelling experiments, uniaxial compression was applied on the swollen gel. Typical stress–strain curves of hydrogels are given in Fig. 9. As can be seen from the figure, the magnitude of stress was increased with increasing MBAAm ratio in the initial feeding solution of hydrogels at a given strain. Also, the magnitude of stress of TG/AAc hydrogels is much higher if compared with that of pure AAc hydrogels. Shear modulus values of hydrogels were calculated by using the elastic deformation theory and Eq. (3). When Eq. (3) is applied to the initial stages of deformation, the plots of stress

Table 2Structural properties of PAAc and TG/AAc hydrogels.

Hydrogels	ν_{2m}	ν_{2r}	ρ	G (kPa)	Мс
PAAc (2 wt% MBAAm)	0.3062	0.0604	1.02	8.9	29,600
PAAc (4 wt% MBAAm)	0.2207	0.0611	1.04	14.8	16,400
TG/AAc (2 wt% MBAAm)	0.0996	0.0554	1.05	30.2	5800
TG/AAc (4 wt% MBAAm)	0.0551	0.0280	1.02	45.7	1950

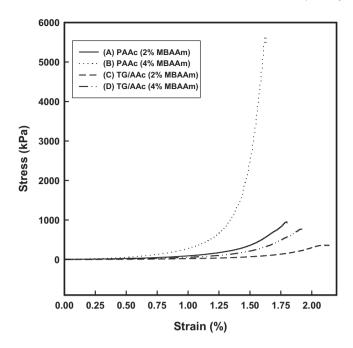


Fig. 9. Strain versus stress curves of pure PAAc and TG/AAc hydrogels. The swelling (%) for A, B, C and D hydrogels are 3223, 2083, 1078 and 898, respectively.

versus $(\lambda - \lambda^{-2})$ give straight lines as shown in Fig. 10. The G value was calculated from the slope of the lines as shown in Table 2. By using G values and other relevant experimental parameters, the average molecular weight values were calculated by using Eq. (9) and listed in Table 2.

$$G = \frac{\rho}{(\bar{M}c)RT v_{2r}^{2/3} v_{2m}^{1/3}}$$
 (9)

where ρ is the polymer density, R is the universal gas constant, T is the temperature and ν_{2r} is the polymer volume fraction in the relaxed state, i.e. after crosslinking but before swelling as shown in Table 3. The average molecular weight between crosslink ($\bar{\text{Mc}}$) of TG/AAc and pure AAc hydrogels was decreased with increasing the

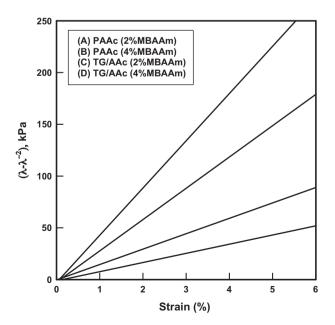


Fig. 10. $(\lambda-\lambda^{-2})$ versus stress curves of pure PAAc and TG/AAc hydrogels. The swelling (%) for A, B, C and D hydrogels are the same as in Fig. 9.

Table 3Rate of AUL for TG/AAc (2 wt% MBAAm) hydrogel swelled in water and urea solution at 37 °C under 0.6 N/m² pressure and free load.

Medium	Pressure (0.6 N/m²)	Rate
Water	Free load Load	0.44 0.46
Urea	Free load Load	0.27 0.23

ratio of MBAAm. The TG/AAc hydrogels have $(\bar{M}c)$ lower than that of pure AAc hydrogels.

3.6. Absorbance under load (AUL)

Desired features of superabsorbents are swelling capacity, high swelling rate and strength of the swollen gel. The majority of reports on superabsorbents cover the first and second factors. However, there are few studies on the swollen gel strength consideration (Mahmudi, Sen, Rendevski, & Güven, 2007; Sen & Sari, 2005). When the superabsorbents are under load, the swelling capacity is decreased. So, another parameter, i.e. absorbency under load (AUL) is important since AUL is logically changed in proportion to mechanical strength of the swollen gel. AUL can be considered as a measure of the gel strength of SAP. The properties of specific SAP are extremely important for selecting a material for a given application. The properties are highly dependent on the environmental swelling conditions. It is imperative that SAP properties are precisely determined under conditions as close to the real circumstances as possible. To determine the swollen gel strength, we used TG/AAc (2 wt% MBAAm) hydrogel to absorb water and urea solution under 0.6 N/m² load and without load at temperature 37 °C as shown in Fig. 11. As can be seen from the figure the AUL of hydrogels in water or urea, under 0.6 N/m² load, is lower than the AUL in free pressure. However, the AUL in water is greater than in urea solution. It is interesting to notice that the rate of the initial values of AUL in urea, in absence and presence of pressure, is relatively higher than in water in the absence of pressure as shown in Table 3. On the other hand, the effect of pressure is relatively low in urea solution due to abruptly swelling of hydrogels in this solution.

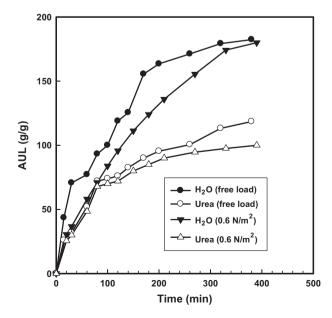


Fig. 11. Time dependence of the AUL values for TG/AAc (2 wt% MBAAm) hydrogel swelled in water and urea solution at 37 °C under 0.6 N/m² pressure and free load.

4. Conclusions

Superabsorbent disposable diapers are products that provide many benefits including convenience, comfort, exceptional leakage protection, improved hygiene and skin care benefits compared with cloth diapers. To design a hydrogel for diaper applications, three factors should be considered; firstly the layer of absorbent material must be light in weight and thin, secondly the quantity of urine released from body must be absorbed to keep the contact skin dry and the most important the absorption rate of fluids must be efficient enough to absorb urine. A new superabsorbent hydrogel based on Tara gum and acrylic acid was synthesized by gamma irradiation. The swelling behavior in water and aqueous urea solutions of the prepared hydrogels was studied. Results of mechanical properties showed that the presence of Tara gum with acrylic acid in the hydrogel was accompanied by an increase in the crosslink density. The increase in the crosslink density appears in the increase in the elastic modulus, which is inherent to the more rigid structure. Consequently, due to high mechanical properties and anomalous swelling the natural/synthetic hybrid hydrogel systems can be considered as potential absorbents for body fluids such as urine and blood and may be used especially as diapers. The swelling capacity of TG/AAc hydrogel (absorbed water and aqueous urea solution under pressure of 0.6 N/m²) at 37 °C showed that the pressure did not change the swelling capacity of hydrogels up to 6 h in urea solution, which is the major component of urine. The overall quality performance of PAAc/TG and PAAc as superabsorbent polymer (SAP) hydrogels evaluated from the swelling rates indicated that the prepared SAP is more or less comparable with commercial products.

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References

- Bao, Y., Ma, J., & Li, N. (2011). Synthesis and swelling behaviors of sodium carboxymethyl cellulose-g-poly(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel. Carbohydrate Polymers. 84(1), 76.
- Chang, C., Duan, B., Cai, J., & Zhang, L. (2010). Superabsorbent hydrogels based on cellulose for smart swelling and controllable delivery. *European Polymer Journal*, 46(1), 92.
- Chang, C., Zhang, L., Zhou, J., Zhang, L., & Kennedy, J. F. (2010). Structure and properties of hydrogels prepared from cellulose in NaOH/urea aqueous solutions. Carbohydrate Polymers, 82(1), 122.
- Dalaran, M., Emik, S., Güçlü, G., İyim, T. B., & Özgümüş, S. (2011). Study on a novel polyampholyte nanocomposite superabsorbent hydrogels: Synthesis, characterization and investigation of removal of indigo carmine from aqueous solution. *Desalination*. 279(1–3). 170.
- De Paula, R., & Rodrigues, J. (1995). Composition and rheological properties of cashew tree gum, the exudate polysaccharide from *Anacardium occidentale* L. *Carbohydrate Polymers*, 26, 177.
- Dragan, F. S., & Apopei, D. F. (2011). Synthesis and swelling behavior of pH-sensitive semi-interpenetrating polymer network composite hydrogels based on native

- and modified potatoes starch as potential sorbent for cationic dyes. *Chemical Engineering Journal*, 178, 252.
- Espinosa-Valdemar, R. M., Turpin-Marion, S., Delfín-Alcalá, I., & Vázquez-Morillas, A. (2011). Disposable diapers biodegradation by the fungus *Pleurotus ostreatus*. *Waste Management*, 31(8), 1683.
- Ferruzzi, G., Pan, N., & Casey, W. (2000). Soil Science, 165, 778.
- Francis, S., Kumar, M., & Varshney, L. (2004). Radiation synthesis of superabsorbent poly(acrylic acid)-carrageenan hydrogels. *Radiation Physics and Chemistry*, 69(6), 481-486.
- Francis, S., Mitra, D., Dhanawade, B. R., Varshney, L., & Sabharwal, S. (2009). Gamma radiation synthesis of rapid swelling superporous polyacrylamide hydrogels. *Radiation Physics and Chemistry*, 78(11), 951–953.
- Kosemund, K., Schlatter, H., Ochsenhirt, J. L., Krause, E. L., Marsman, D. S., & Erasala, G. N. (2009). Safety evaluation of superabsorbent baby diapers. Regulatory Toxicology and Pharmacology, 53(2), 81.
- Kounga, T. M., & Aotearoa, A. (2006). Food standards Australia New Zealand, final assessment report.
- Mahmudi, N., Sen, M., Rendevski, S., & Güven, O. (2007). Nuclear Instruments and Methods in Physics Research B, 265, 375.
- Peppas, N. A., Gurny, R., Doelker, E., & Buri, D. (1989). Modelling of drug diffusion through swellable polymeric. *Journal of Membrane Science*, 7, 241.
- Pourjavadi, A., Eftekhar Jahromi, P., Seidi, F., & Salimi, H. (2010). Synthesis and welling behavior of acrylatedstarch-g-poly (acrylic acid) and acrylatedstarchg-poly (acrylamide) hydrogels. Carbohydrate Polymers, 79(4), 933.
- Qu, G., & de Varennes, A. (2010). Use of hydrophilic polymers from diapers to aid the establishment of Spergularia purpurea in a mine soil. *Journal of Hazardous Materials*, 178(1-3), 956.
- Ritger, P. L., & Peppas, N. A. (1987a). A simple equation for description of solute release. I. Fickian and non-Fickian release from non-swellable devices in the form of slabs, spheres, cylinders or discs. *Journal of Controlled Release*, 5, 23–36
- Ritger, P. L., & Peppas, N. A. (1987b). A simple equation for description of solute release II. Fickian and anomalous release from swellable devices. *Journal of Controlled Release*, 5, 37–42.
- Sen, M., & Sari, M. (2005). European Polymer Journal, 41, 1304.
- Shi, X., Wang, W. B., & Wang, A. Q. (2011). Effect of surfactant on porosity and swelling behaviors of guar gum-g-poly(sodium acrylate-co-styrene)/attapulgite superabsorbent hydrogels. Colloids and Surfaces B: Biointerfaces, 88(1), 279
- Shultz, A. R. (1985). (1st ed.). Crosslinking with radiation in EPST, pp. 398-414.
- Singh, B., Chauhan, G. S., Bhatt, S. S., & Kumar, K. (2006). Metal ion sorption and swelling studies of psyllium and acrylic acid based hydrogels. *Carbohydrate Polymers*, 64(1), 50.
- Singh, B., & Vashishtha, M. (2009). Development of novel hydrogels by modification of sterculia gum through radiation cross-linking polymerization for use in drug delivery. Nuclear Instruments and Methods in Physics Research Section B. Beam Interactions with Materials and Atoms, 266(9), 2009.
- Teli, M. D., & Waghmare, N. G. (2010). Synthesis of superabsorbents from Amaranthus starch. *Carbohydrate Polymers*. 81(3), 695.
- Wang, W., & Wang, A. (2009). Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite. Carbohydrate Polymers, 77(4), 89.
- Wang, W., & Wang, A. (2010). Synthesis and swelling properties of phsensitive semi-IPN superabsorbent hydrogels based on sodium alginate-gpoly(sodium acrylate) and polyvinylpyrrolidone. Carbohydrate Polymers, 80(4), 1028.
- Yadav, M., Mishra, D. K., & Behari, K. (2011). Synthesis of partially hydrolyzed graft copolymer (H-partially carboxymethylated guar gum-g-methacrylic acid): A superabsorbing material. Carbohydrate Polymers, 85(1), 29.
- Yang, L., Ma, X., & Guo, N. (2011). Synthesis and properties of sodium alginate/Na⁺rectorite grafted acrylic acid composite superabsorbent via ⁶⁰Co(irradiation. Carbohydrate Polymers, 85(2), 413.
- Yu, C., Yun-fei, L., Huan-lin, T., & Hui-min, T. (2010). Study of carboxymethyl chitosan based polyampholyte superabsorbent polymer I: Optimization of synthesis conditions and pH sensitive property study of carboxymethyl chitosan-g-poly(acrylic acid-co-dimethyldiallylammonium chloride) superabsorbent polymer. Carbohydrate Polymers, 81(2), 365.
- Zheng, Y., Hua, S., & Wang, A. (2010). Adsorption behavior of Cu²⁺ from aqueous solutions onto starch-g-poly(acrylic acid)/sodium humate hydrogels. *Desalination*, 263(1-3), 170.