

Effects of Structural Variables on AUL and Rheological Behavior of SAP Gels

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ABSTRACT: The swelling properties of superabsorbent polymers (SAPs) under real conditions are extremely important for selecting the material suitable for a given application, e.g. feminine napkin or agriculture. This new practical research represents deeper synthetic and physico-chemical studies on the structure–property relation in acrylic SAP hydrogels and composites. Thus, the values of saline-absorbency under load (AUL; a measurable simulation of the real circumstances of SAP applications, at pressures 0.3–0.9 psi) were measured for the SAP or SAP composite samples prepared under different conditions, i.e. type and content of crosslinker, type and concentration of initiator, percentage of inorganic filler (kaolin), and type and percentage of porosity generators. The samples were subsequently used to determine the rheological and mor-

phological characteristics. Dynamic storage modulus (G') measurements were carried out at constant strain in a wide range of frequency. Linear correlations were frequently found to be active between AUL and G' data over the rubber-elastic plateau. Thus, for a given SAP: $AUL = k_{total}G' + C$. The coefficient k_{total} is a function of (nature and content of crosslinker, initiator, inorganic component, particle morphology, etc.). Therefore, the easily measured AUL values could be simply correlated to the main synthesis variables and molecular structure of SAP gels through a rheological material function (G'). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3676–3686, 2009

Key words: superabsorbent; hydrogel; rheology; absorbency under load

INTRODUCTION

Superabsorbent polymer (SAP) hydrogels are well-known acrylic polymers with a three-dimensional lightly cross-linked hydrophilic network imbibing aqueous solutions up to hundreds of times their own weight.^{1–3} They are currently used in baby diapers, feminine napkins, agriculture, cosmetic, absorbent pads, sealing rubbers, and so on. The demand for SAPs worldwide is now over 1,483,000 metric tons per year.⁴

Three main functional features of SAPs are (a) high absorption capacity (b) high absorption rate, and (c) desirable swollen gel strength which is a measure of their real absorption capacity; saline-absorbency under load (AUL).^{5–7} However, as we have shown previously,^{5–11} it is very difficult to achieve a SAP which possesses all these factors simultaneously.

In nearly all academic literature, the swelling capacity values of superabsorbents are reported as free-swelling data, i.e. load-free swelling measured usually in distilled water. It is obvious that these swell-

ing conditions (i.e. distilled water and lack of pressure), and hence the resulting data, are not real, because in all applications of SAP (hygienic, agricultural, etc.) the swelling particles must absorb aqueous solutions while they are under pressure, e.g. the weight of baby, soil, etc. Conversely, a measurable imitation of the real conditions, i.e. AUL, is very rarely reported particularly in non-patent literature. Instead, the AUL data are usually given in the patent literature and technical data sheets provided by the commercial SAP manufacturers.

During many years of working on SAP materials, we used to empirically realize a straight relation between the AUL values and the strength of the swollen SAP. A SAP sample with good gel strength (rapidly identified by some qualitative indications in the swollen state such as lack of loose or slimy appearance and having a geometrically stable shape with sharp edges and corners) possesses definitely a high AUL. On the other hand, the usual measurement of the mechanical strength of “isolated uniformed gel particles” of the hydrogel is impossible because the commercially produced SAPs possess sugar-like particles with irregular randomized shapes. Therefore, we recently proposed a rheological method to quantitatively express the swollen gel strength of commercial SAP samples pre-swelled under the practical conditions.¹²

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It was shown that the rheological behavior of SAP swollen particles can be studied when they are subjected to sinusoidal shear oscillation at a fixed deformation on the gel body located between the plates of a parallel-plate arrangement.¹² The applied deformation should be chosen so that all measurements carry out in the linear viscoelastic (LVE) zone of the tested SAP (i.e. the complex shear modulus G^* is independent of the applied strain). The complex shear modulus can be calculated from the resulting torque.¹³ Applying complex oscillation equations can be resolved into its real (G') and imaginary (G'') components according to the following equation:

$$|G^*| = G' + iG'' \quad (1)$$

The real component is called the storage modulus which is a measure of the reversibly elastic storable deformation energy. The imaginary component called the loss modulus is a measure of the irreversible energy dissipated during flow.¹³

The properties of special SAPs are extremely important in the material selection for a given application.¹⁻³ There are many preparative factors that affect inherently the SAP properties including the monomer nature and content, comonomer, crosslinking agent, and initiator, reaction time and temperature, pH, filler type and content (for SAP composites), porosity generating method, the swollen-gel strength, etc.

In the present article, several preparative reaction variables (i.e. different crosslinker types and concentrations, different initiator types and concentrations, range of the content of an inorganic component, and various porosity generating agents) are studied while other factors are kept fixed in each series. Thus, as an attempt to further explore potential correlation between gels' structure and properties, we investigated the swollen-gel strength, the effect of some of the most important factors affecting the SAP gel AUL at different pressures and the swollen gel rheological properties.

EXPERIMENTAL

Materials

Sodium chloride (Merck, Germany) and kaolin (grade KSP, Kaolin Khorasan, Iran) were used as received. Other chemicals, all reagent grades, were purchased from Fluka.

SAP preparation

The laboratory prepared SAP samples, as previously reported,⁵⁻⁹ were similarly synthesized from partially (75 mol %) KOH-neutralized acrylic acid under appropriate experimental conditions. The SAP com-

posites⁷ and porous composites⁸ were prepared according to the previous papers. Ammonium persulfate (APS)/sodium metabisulfite (as a redox pair initiator; I1), APS/tetramethyl ethylenediamine (as initiator; I2), *N,N'*-methylenebisacrylamide (MBA), triethyleneglycol dimethacrylate (T) and polyethyleneglycol (MW 1000) diacrylate (P; a macro-crosslinker) were accordingly used to conduct the crosslinking polymerization reactions for preparing the SAP hydrogel samples.

Regardless the desired variable, a common procedure for all samples is as follows. The reaction variable studied in each series of experiments will then be given accordingly. Acrylic acid (30.0 g) was partially neutralized with KOH solution (20.33 g KOH + 17.1 mL H₂O). Then, appropriate amount of the desired crosslinker was added to the monomer solution.^{5,6} In the case of composite⁷ and porous composite samples,⁸ desired amount of kaolin was added to the mixture and allowed to completely disperse at room temperature. The appearance of the mixture changed from transparent to light brown as kaolin was added. Subsequently, APS, the desired porogen (if required), and the second component of the desired initiator were added. The viscosity and temperature were increased after addition of components until gelation occurred. A SAP composite with fixed kaolin content of 25% as well as different porous composite samples with various kaolin contents 1, 4, 11, and 22 wt % were prepared.

The obtained elastic gels were cut into small ($\sim 4 \times 4 \text{ mm}^2$) pieces. In the case of oven-dried samples, they were dried in an air-circulating oven (18 h at 80°C). In the case of methanol-dried samples, they were poured into 300 mL methanol to dewater for 72 h. Then, the non-solvent was removed by filtration and the sample was spread on aluminum foil to dry overnight at room temperature. Dried products were finally ground with a hammer-type mini-grinder, screened, and stored in a dry and cool place.

Characterization methods

The AUL test procedure in saline (NaCl 0.9% solution) was accomplished according to a previous report.¹² Briefly, weighed dried SAP sample ($0.9 \pm 0.01 \text{ g}$) was uniformly dispersed on the surface of a polyester gauze which had been located on a macro-porous sintered glass filter plate placed in a Petri dish. A cylindrical solid load (Teflon, $d = 60 \text{ mm}$, variable height) was put on the dry SAP particles while it could be freely slipped in a glass cylinder. Desired load (applied pressure 0.3, 0.6, or 0.9 psi) was placed on the sample. Then, 0.9% saline solution was added to the Petri dish. Whole of the set was covered to prevent surface evaporation and

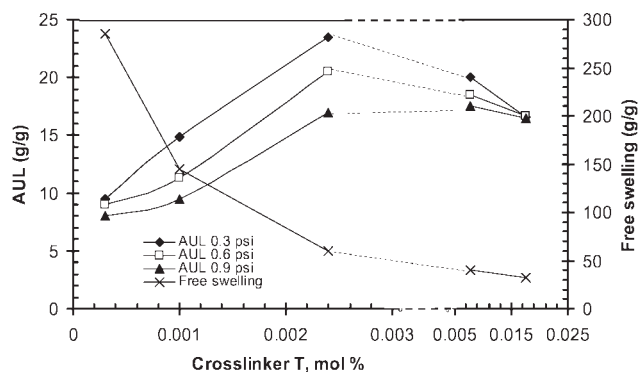


Figure 1 Dependency of AUL on the T-type crosslinker concentration for SAP samples swollen freely in distilled water, or in saline while they were under pressures 0.3, 0.6, and 0.9 psi.

probable change in the saline concentration. After 60 min, the maximally swollen particles were removed and re-weighed. AUL value was calculated via dividing the weight of absorbed saline by the initial SAP weight. The rheology of the samples swollen under load was subsequently studied.

The rheological measurements were performed on a Paar-Physica MCR300 rheometer using parallel-plate geometry with a plate diameter 25 mm and a gap height 3 mm. All experiments were conducted at 25°C. Various strain amplitude were checked to ensure that all oscillatory shear measurements were performed within the material's LVE regime, where dynamic storage modulus (G') and loss modulus (G'') of the tested material are strain-independent. The oscillatory measurements were carried out in 1–100 rad/s angular frequency (ω) range.

Morphology of dried SAP samples was studied by scanning electron microscopy (SEM). The samples powder were coated with a thin layer of palladium gold alloy and imaged in a SEM instrument (Cambridge S-360).

RESULTS AND DISCUSSION

The saline-AUL of acrylic SAP samples prepared under different physicochemical synthetic variables was firstly determined using an AUL tester under different pressures 0.3, 0.6, and 0.9 psi.¹² The same samples were subsequently used to determine the rheological properties.

The crosslinking agent

Crosslinker, the most effective synthetic variable affecting the SAP gel characteristics, is often introduced at the beginning of the polymerization reaction.^{5–11} This part of study includes both the nature and concentration of crosslinker while the initiator I1 has been employed.

Figures 1 and 2 show AUL and free swelling of acrylic superabsorbents synthesized using different crosslinker percentages and types (P and T stand for the long- and short-chain acrylic crosslinking agents, respectively). According to Figure 1, with increasing crosslink concentration up to 0.0025 mol %, all the AUL values increased intensely. This is mainly due to the increase in the mechanical strength of gels with a sharp slope. To typically demonstrate the destiny of AUL changes at much higher crosslinker concentration, two additional data are demonstrated in the right part of Figure 1. Higher crosslinker concentration results in AUL decrease with a mild slope. It is well understood that crosslinking density changes proportionally with crosslinking concentration,^{1,3} therefore, any changes in these SAPs' properties stem from this factor.

The extent of absorption in the absence of any load (i.e. free swelling) for the studied samples is also depicted in Figure 1. To be able to compare the free swelling and the swelling under load values for the samples, these measurements were carried out in distilled water instead of saline solution (indeed, upon increasing crosslinking density, decrease in free swelling in saline becomes too small to be able to study comparatively the effect of crosslinking density on the absorbency with and without external pressure). In the figure, beyond the crosslinker T concentration of 0.0025 mol %, any change in AUL is followed by a parallel change in free swelling. It means that both AUL and free-absorbency factors decrease as the crosslink density enhances. However, at a crosslinker concentration less than 0.0025 mol %, the extent of the free swelling exceedingly rises (from ~ 70 to ~ 300 g water/g sample), whereas the AUL values are diminished extremely with a sharp slope inversely similar to that of the free swelling. This is due to a decrease in the

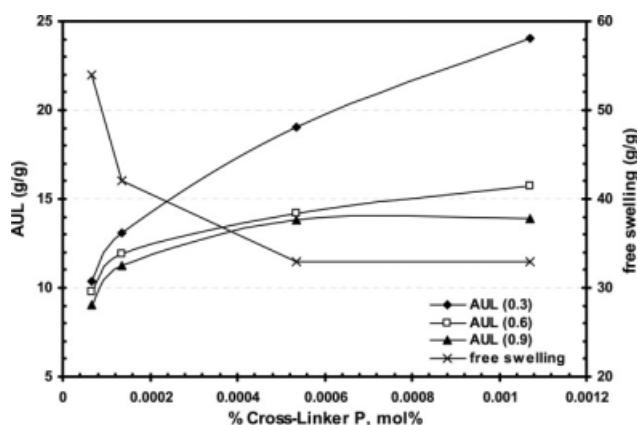


Figure 2 Dependency of AUL on the P-type crosslinker concentration for SAP samples swollen freely in distilled water, or in saline while they were under pressures 0.3, 0.6, and 0.9 psi.

mechanical strength of hydrogel's network at low crosslink densities. Overall, for this particular crosslinker and superabsorbent, it is concluded that 0.0025 mol % density is a critical value.

Another point that may be concluded from this comparative study is related to a technical measure for evaluation of SAPs. It is clear that for the cases where no load is applied during absorption or swelling, this is not a good criterion for superabsorbent quality at all. Because the values of swelling without load in distilled water medium, which are conventionally reported by researchers, are not real conditions. There is no practical application with the swelling medium of distilled water and/or without applying pressure. In reality, it is preferred to carry out AUL in saline solution, as a main criterion for SAP quality.

An additional point from the AUL change under different loads is convergences observed at AUL values lower and higher than the critical value 0.0025 mol % of the crosslinker T. Thus, it is obvious from Figure 1 that the AUL values are going to nearly level off at 0.0175 mol % of the crosslinker T. This means that, due to very high elastic force of the gel network at very high concentrations of the crosslinker, the AUL values become just about load-independent.

A series of superabsorbents synthesized using another different crosslinker (macro-crosslinker P series) were also experienced in the concentration range that was 10 times less than those of the T series. It is obvious from Figures 1 and 2 that the AUL in saline solution decreases with an increase in pressure from 0.3 to 0.9 psi.² According to Figure 2, an increase in the crosslinker concentration results in an increase in AUL values measured in saline. Meanwhile, the free swelling measured in the same medium expectedly decreases due to raising the crosslinking density. In addition, a comparison of Figures 1 and 2 implies that the macro-crosslinker P has higher performance than the crosslinker T in this system. For instance, using a crosslinker concentration of 0.001 mol % in the synthesis, the absorbency under pressure 0.3 psi for the T- and P-crosslinked SAP is ~ 9 and 24 g/g, respectively. The reason is not clear, though it may preliminarily be attributed to reactivity ratio difference of the crosslinkers. Again, a convergence trend in AUL values is observed with decreasing the P crosslinker concentration from 0.001 to 0.0001 mol % (Fig. 2).

The frequency dependency of storage modulus (G') for the SAP prepared at different concentrations of crosslinking agent T (T series) is depicted in Figure 3 under 0.9 psi at 25°C. According to these figures, the swollen gel strength increases with increasing the crosslinker T concentration. This is due to crosslinking density enhancement and devel-

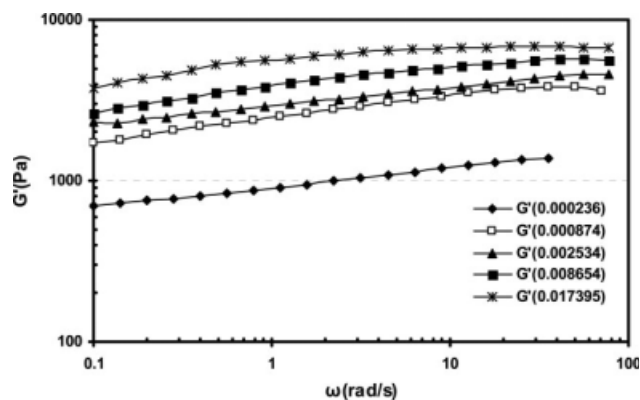


Figure 3 Frequency dependency of G' at constant strain (0.1%) for SAP samples prepared using T-type crosslinker (the numbers in parentheses are molar concentration of the crosslinker). The testing samples had already been swollen in saline while they were under pressure 0.9 psi.

opment of the network and mechanical stiffness. The increase in crosslinking concentration leads to an increase in gels' storage modulus through the following well-known rubber elasticity relationship:

$$G'_R = \frac{\rho RT}{\overline{M}_c} \quad (2)$$

where G'_R , ρ , R , T , and \overline{M}_c are the relaxed rubbery modulus, the density, the universal gas content, temperature, and the molecular weight of the polymer segment between two successive crosslinks, respectively. An alternative representation of eq. (2) is as follows:

$$G' = \nu RT \quad (3)$$

where ν is the number of crosslink sites per unit volume.

With increasing the crosslinker concentration (small \overline{M}_c), a dense network structure predominates and a G' enhancement is observed.^{13,14} Owing to transformation of viscous state to elastic one, SAP with low crosslinking mol % shows a gradual increase in G' curve with increasing frequency (Fig. 3), i.e. the storage modulus increases as the frequency increases. This is related to the fact that at low frequencies, enough time is available for disentanglements and extensive relaxation results in a low storage modulus. However, when a polymer sample is deformed at a high frequency, the entangled chains have not enough time to be relaxed, therefore, the modulus goes up. In the samples prepared using a high crosslinker concentration, the elasticity increases. So, at high levels of crosslinker the storage modulus increases with a non-sharp slope and levels off at higher frequencies. For these samples, the gel strength increases from 1000 to 8000 Pa with increasing crosslinking

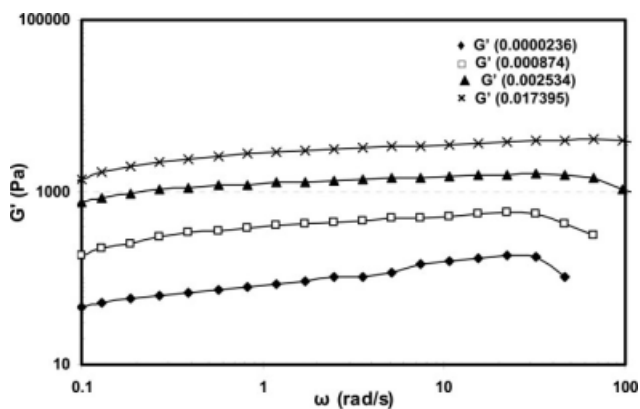


Figure 4 Frequency dependency of G' at constant strain (0.2%) for SAP samples prepared using T-type crosslinker (the numbers in parentheses are molar concentration of the crosslinker). The testing samples had already been swollen freely in distilled water.

concentration. Consequently, elastic modulus becomes crosslinking density independent. Another point is that with increasing the load, the storage modulus increases for each SAP sample.

To compare superabsorbent strength during swelling under load and free swelling states, for example, the strength of SAPs (T series) freely swollen in distilled water was studied (Fig. 4). It is clear that the modulus increases upon increase in frequency. In these samples, the gel strength increases from 100 to 3000 Pa with increasing crosslinking concentration from 0.000236 to 0.017395 mol/L. The modulus values are less than that of the samples absorbed saline solution under load. The reason for this observation is less expansion of the network as compared with free swelling.

Figure 5 shows storage modulus curves versus frequency for the P series of SAPs having different crosslinking densities. It is obvious that the swollen

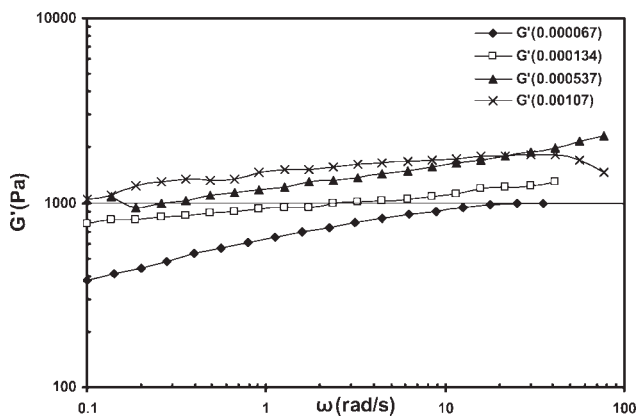


Figure 5 Frequency dependency of G' at constant strain (0.1%) for SAP samples prepared using P-type crosslinker (the numbers in parentheses are molar concentration of the crosslinker). The testing samples had already been swollen in saline while they were under pressure 0.9 psi.

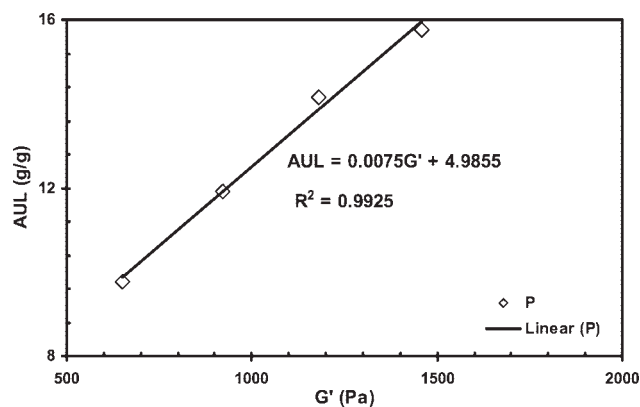


Figure 6 G' (at 1 rad/s) dependency of AUL for the P-crosslinked SAP samples absorbed saline under pressure 0.6 psi.

gel strength under load increases with increasing density of crosslinking. Of course, in these samples with increasing the crosslink density from 0.000067 to 0.00107 mol/L, gel strength rises from 800 to 1100 Pa.

Figure 6 sketches AUL versus the storage modulus at frequency 1 rad/s. A linear AUL- G' relation with a constant k is plotted for the P-crosslinked SAP that absorbed saline while pressurized under a load of 0.6 psi. The coefficient k_{cross} is a function of crosslinking density, network chemical structure, crosslinker reactivity, and so on.

$$\text{AUL} = k_{\text{cross}}G' + C \quad (4)$$

More research is needed to explore the nature of the coefficient k_{cross} . In general, this coefficient may be taken, by some means, similar to intrinsic viscosity, which symbolizes all structural parameters and intrinsic stipulations of the corresponding polymer, here, the hydrogel network.

The initiator

Initiator concentration, a reaction variable affecting the SAP gel properties, is necessary to start the polymerization reaction.¹⁻³ In this part of research, the effects of two redox initiators (I1 and I2) are investigated. The samples have been prepared using crosslinker P. Initiators I1 and I2 are experimentally differed by the index of gelation time in the reaction¹⁵; they stand for the short and long time of gelation, respectively.¹⁶

Table I gives AUL values of samples prepared employing various concentrations of initiator. The modulus decreases with increasing initiator concentration. This observation can be explained based on more network defects induced at higher initiator concentration. According to the free-radical polymerization concepts,¹⁷ increasing the initiator

TABLE I
AUL and Storage Modulus Values for the SAP Samples
differed by the Initiator Type and Concentration
Employed in Their Preparation

| Sample | Initiator type (molar concentration) | AUL (gram saline absorbed per gram sample located under pressure) | | G' (Pa) at 1 rad/s ^a |
|--------|--------------------------------------|---|---------|-----------------------------------|
| | | 0.3 psi | 0.9 psi | |
| 1 | I1 (0.000164) | 13.1 | 10.8 | 1890 |
| 2 | I1 (0.000219) | 12.5 | 10.5 | 1670 |
| 3 | I1 (0.000329) | 10.6 | 9.1 | 970 |
| 4 | I2 (0.000293) | 20.7 | 12.0 | 2470 |
| 5 | I2 (0.000439) | 14.5 | 11.7 | 2150 |
| 6 | I2 (0.000585) | 12.4 | 10.4 | 1880 |
| 7 | I2 (0.00430) | 11.6 | 9.9 | 1860 |

^a Storage modulus for the saline-swollen sample while it was under pressure 0.9 psi.

concentration results in decreasing the kinetic chain length (lower molecular weight) and, consequently, enhancing chain ends, which are known as defects in the gel network.¹⁶ The imperfections are developed by the chain end enhancement originated from the collision of the additional initiating free-radicals.⁹ It means that fewer junctions form between the chains and consequently the crosslink density and gel content are diminished. Decreased crosslink density leads to an enhanced load-free swelling and the swollen gel appears to be softer, quantified as the decreasing dynamic storage modulus (G'). The reduced modulus, as mentioned in the case of the crosslinker effect in this work, is practically appeared as the loss of AUL (Table I). It is evident that AUL values decrease with increasing the applied pressure.¹⁸

Another point from Table I is related to the differences of the initiators I1 and I2. Comparing the AUL or G' values for similar concentrations of the initiators, e.g. samples 2 and 4, it can be concluded that the initiator inducing the longer time of gelation produces the SAP gel with higher modulus and AUL values. This experimental fact is originated from the same phenomena mentioned above. At a specified concentration, an initiator with longer time of gelation (e.g. I2) gives rise to more opportunity for the growing macroradicals, monomer, and crosslinker molecules to react with each other. As a result, the chain ends and the imperfections of the gel network will reduce. More perfect network exhibits higher mechanical stiffness, i.e. higher G' and, therefore, higher AUL. In the contrary, a fast gelation, as observed in the case of the initiator I1, does not favor the formation of SAP gels with high stiffness and AUL.

At this juncture, the relationship between AUL and storage modulus data can also be plotted for these SAP samples (Fig. 7). As before, linear relations with different slopes are explored for different initiators [eq. (5)].

$$AUL = k_{\text{init}}G' + C \quad (5)$$

The k_{init} parameter is inherently dependent on the initiator chemical structure, reactivity, concentration, etc.

The SAP composites

Other series of acrylic SAP composite gels in which mineral filler (kaolin) was introduced during polymerization (initiator I1, crosslinker MBA) were studied. Figure 8 represents the AUL data versus the filler weight percentage (1–22 wt%). The AUL values decrease logically with the load increase.

According to our previous work,⁸ free-swelling of kaolin-free sample in distilled water (i.e. 294 g/g) was reduced to ~ 250 g/g when 10–15% of kaolin was incorporated. As usual, based on the data

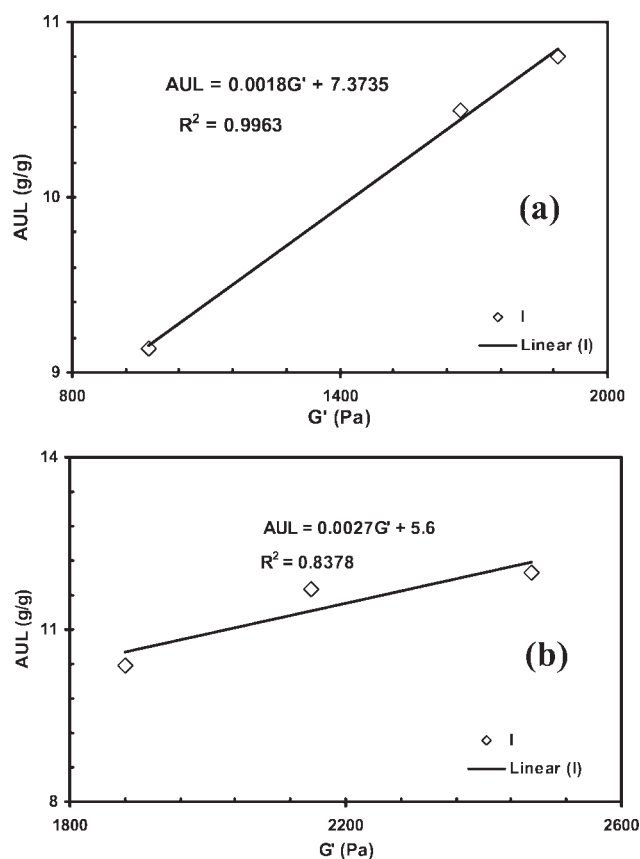


Figure 7 G' (at 1 rad/s) dependency of AUL for SAP samples prepared using the initiator I1 (a) and I2 (b). The testing samples had already been swollen in saline while they were under pressure 0.9 psi.

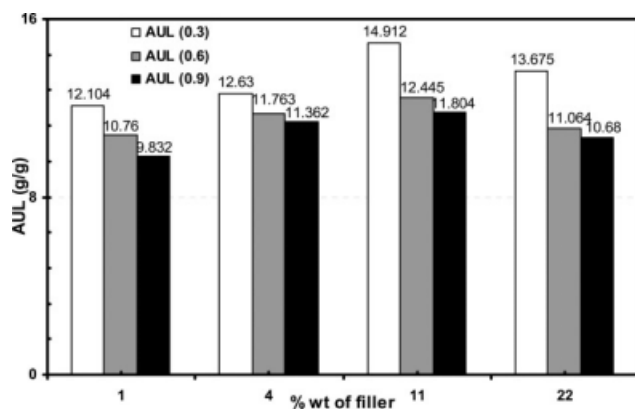


Figure 8 AUL-inorganic filler (kaolin) dependency for SAP composites swelled in saline under pressures 0.3, 0.6, and 0.9 psi.

obtained from free-swelling in distilled water, optimum kaolin content was determined to be $\sim 25\%$. This value, however, is not valid under actual conditions, e.g. saline media while the sample is under external pressure (i.e. the conditions applied in the AUL testing).

The AUL data (Fig. 8) reveals that at low weight percentages of filler (from 1 to 11%) AUL value increases, but it slightly decreases at higher content of filler ($>20\%$). The AUL loss can be attributed to several reasons. We have already established that the functional group of the filler particle surface involved an esterification reaction with the carboxylic groups of the acrylic chain in the SAP composite.⁷ It implies that the filler particles take action like multi-functional crosslinker¹⁹ or crosslink points^{20–22} inherently driving the network toward a higher density of crosslinking. Another possible reason may be related to some non-homogeneity within the polymerization mixture with high filler level partially hindering a full network formation. On the other hand, high content of inorganic particles in SAPs relatively reduce the overall hydrophilicity per unit volume leading to a loss of absorbency. Some preliminary rheological measurements have already verified these results.⁷

Storage modulus (G') variation versus frequency was recorded at constant strain 0.2% for the SAP gel composites swollen under different loads. Figure 9 shows the rheological curves. It can be concluded from this figures that with increasing the filler content (around 12%), the storage modulus increases. The storage modulus is actually the swollen gel strength, therefore, a higher gel strength results in a higher AUL, as mentioned above (Fig. 8). On the other hand, once the filler content rises to about 22%, the modulus decreases due to the foresaid reasons related to the AUL loss. In these series, the samples swollen under load in saline solution, the

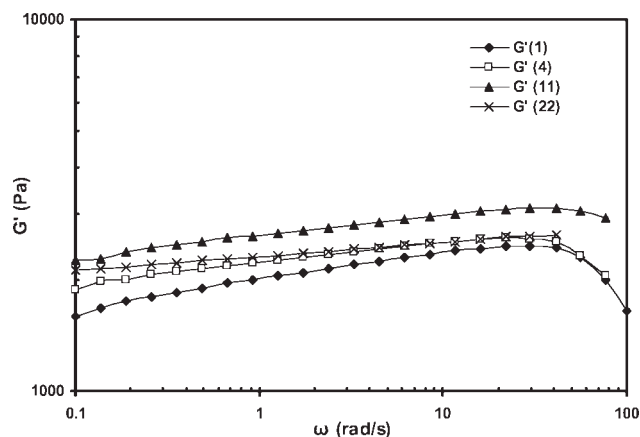


Figure 9 Frequency dependency of G' at constant strain (0.2%) for SAP composites with different levels of inorganic filler (kaolin; 1, 4, 11, and 22 wt%) swelled in saline under pressure 0.9 psi.

modulus rises from ~ 2000 to ~ 3000 Pa (filler content 1–11%) and thereafter it declines to 2600 Pa for the gel with filler content 22%.

To examine the effect of filler in the absence of the external load and lack of the salinity of the swelling medium, the same samples were freely tested in distilled water (Fig. 10). Obviously, much higher fluid was absorbed and, as a result, the highly swollen gels expectedly showed loss in modulus. Again, as can be seen from Figure 10, with increasing filler from 1 to 12%, the modulus clearly rises (from 300 to 800 Pa), and still, very high amount of the active filler disfavors the gel modulus. Therefore, it can be preliminarily concluded that the observed differences in the filler-originated behavior is not dependent on the composition of swelling medium and level of the external pressure.

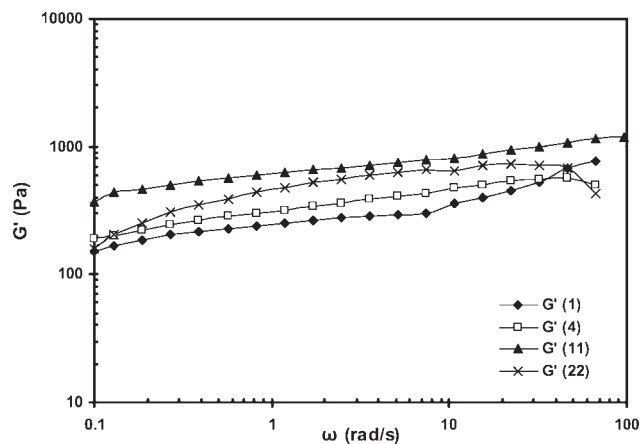


Figure 10 Frequency dependency of G' at constant strain (0.05%) for SAP composites with different levels of inorganic filler (kaolin; 1, 4, 11, and 22 wt%) swelled in distilled water freely.

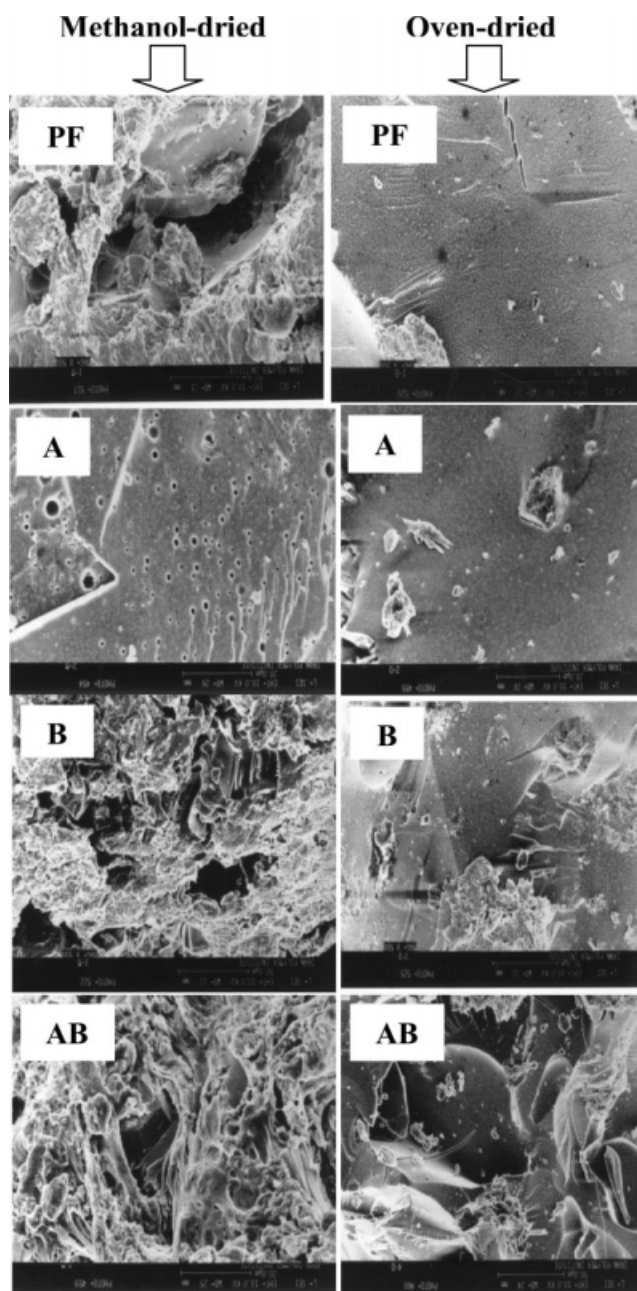


Figure 11 SEM pictures of oven- and methanol-dried SAP composites pored by means of porogens A, B, and AB. PF demonstrates the samples prepared without porogen. Magnification $\times 500$.

Porous SAP composites

The swelling rate, one of the main features of SAPs, has been recognized to be influenced by several physicochemical factors including particle size¹⁴ and porosity.⁶ In the latter approach, to create voids and channels in the structure of superabsorbents, porosity generating materials (porogens) are usually employed in the course of the synthesis. As a result, the rate of water absorption increases. In this study, acetone (A), bicarbonate (B), and their combination

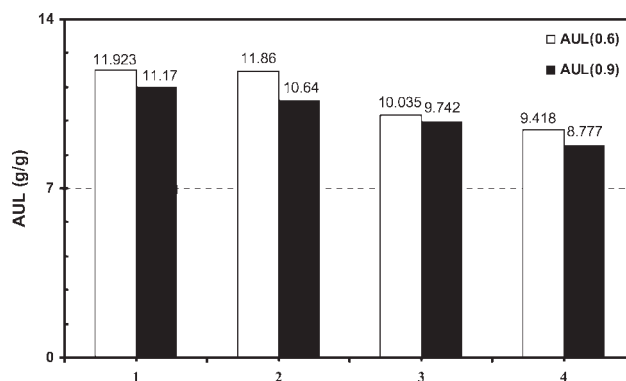


Figure 12 AUL (at 0.6 and 0.9 psi)-porosity dependency of SAP composites dried in oven. Number 1 represents sample prepared under porogen-free conditions. Numbers 2–4 are samples prepared by employing the porogens A, B, and AB, respectively.

(AB) were used as porogens during the polymerization using initiator I1 and crosslinker MBA to prepare porous SAP composites containing 25% kaolin.⁸ The samples were dried through different approaches, i.e. oven heating (O) and methanol dewatering (M) to study some additional effects of the drying method. These samples have already been synthesized in our laboratory.⁸ Morphologies of samples are shown in Figure 11.

Figures 12 and 13 show AUL curves based on the porogen type. It is clear that, the incorporation of each porosity agent decreases AUL values. Meanwhile, AUL is decreased with changing the porogen from A to B. According to SEM pictures (Fig. 11), the porogen agent B makes the polymer structure more porous than the porogen A does. Whenever two types of porosity agents are used together (AB), a synergistic effect is observed and the superabsorbent structure becomes even more porous.⁶

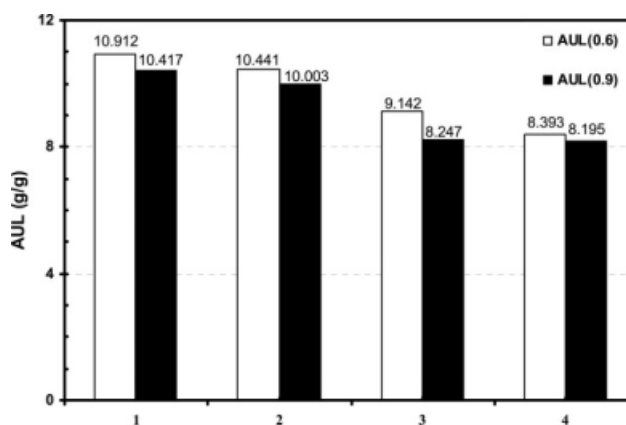


Figure 13 AUL (at 0.6 and 0.9 psi)-porosity dependency of SAP composites dried in methanol. Number 1 represents sample prepared under porogen-free conditions. Numbers 2–4 are samples prepared by employing the porogens A, B and AB, respectively.

Consequently, a decrease in AUL is observed along with an increase in the absorption rate, which is in agreement with that observed highly porous morphologies.⁸

The procedure of gel drying also affects the swollen gel strength. Comparison of Figures 12 and 13 (AUL at 0.6 and 0.9 psi load at 25°C) shows that the samples dried by the methanol method have a smaller AUL than that of the same samples dried in oven. In the oven method, enough energy is available for the polymer chains of the samples for a better packing during hydrogel dehydration process at 80°C, therefore, the free volume of polymer decreases. But in the samples dried in methanol, a lower test temperature (room temperature) prevents any movement of large and crosslinked chains. The chains and microscopic layers are stabilized in their positions, i.e. the chains have not enough energy to change their conformations or move. In other words, the free volume of the samples does not decrease. As a result, the samples dried in oven have a less free volume than that of the samples dried in methanol. This difference has also been evidenced by the morphological studies.⁸

Figures 14 and 15 show the storage modulus versus frequency for samples dried via the methanol and oven methods, respectively. It can be concluded that the swollen-gel strength of the samples without porogen is higher than that of the samples with porogens A and B. Comparison of the curves of Figures 14 and 15 shows that the swollen gel strength in the samples dried in oven is higher than that of the same samples dried in methanol.

Figure 16 shows modulus changing versus type of porogen, measured at 1 rad/s. According to this figure, because the oven-dried samples have less free volume in their structure, they exhibit higher swollen gel strength than that of the samples dried in

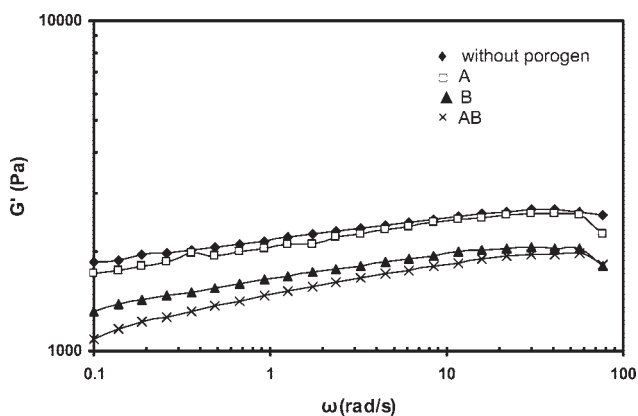


Figure 14 Frequency dependency of G' at constant strain (0.1%) for methanol-dewatered SAP composites prepared employing no porogen, and using porogens A, B, and AB. The testing samples had been swollen in saline while they were under pressure 0.9 psi.

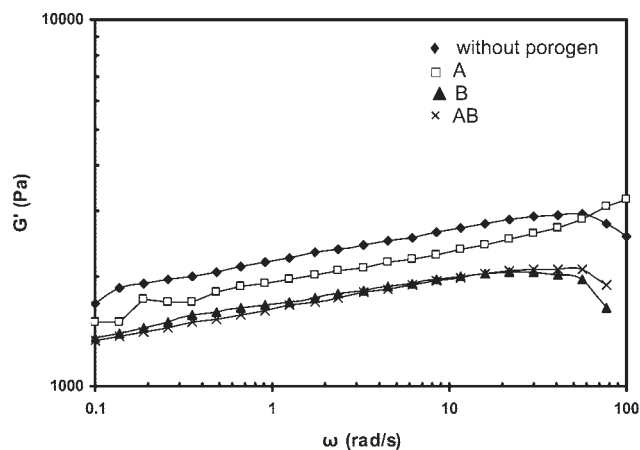


Figure 15 Frequency dependency of G' at constant strain (0.1%) for oven-dried SAP composites prepared employing no porogen, and using porogens A, B, and AB. The testing samples had been swollen in saline while they were under pressure 0.9 psi.

methanol. This is confirmed by AUL data as well (Figures 12 and 13).

According to elastic modulus and AUL data of two series of superabsorbents, AUL and G' data can be correlated (Fig. 17). These figures show that AUL is increased with augmenting modulus. It is worth noting that there is a linear relation between AUL and G' values, in which k_{poro} is dependent on porosity or density of the dry superabsorbent, soluble particles, voids morphology, etc.

$$\text{AUL} = k_{\text{poro}}G' + C \quad (6)$$

This equation expresses that a higher elasticity results in a higher AUL and vice versa. The other important point is that one is able to evaluate AUL

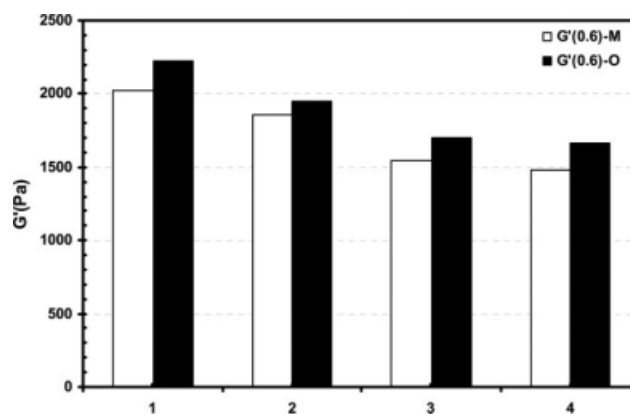


Figure 16 Dependency of G' (at 1 rad/s) on the porosity generating techniques. The as-synthesized SAP composites were prepared without porogen (sample 1) or with porogens A (sample 2), B (sample 3), and AB (sample 4), and then dried in methanol (M) or oven (O). The testing samples had been swollen in saline while they were under pressure 0.6 psi.

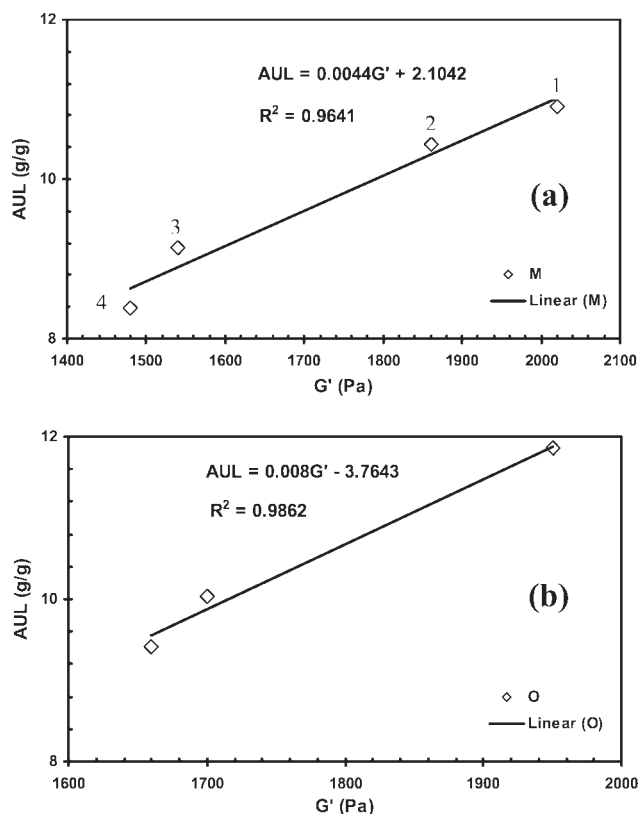


Figure 17 G' (at 1 rad/s) dependency AUL for porous SAP composites dried in methanol (a) and oven (b). The testing samples had already been swollen in saline while they were under pressure 0.6 psi. Numbers 1–4 denote the porogen type as introduced in Figure 2 caption.

data using the well-established rheological measurements and correlate it to the developed theory of rubber elasticity.

CONCLUSION

Saline-AUL can be taken as a simple measurable simulation of the real circumstances of the applications of SAP gels.

In the preparation of SAPs, increased crosslinker concentration leads to an enhancement of the swollen gel strength and, consequently, an AUL improvement. The crosslinker nature is also of a significant importance. For instance, at similar concentrations, polyethyleneglycol diacrylate produces SAP gel with higher storage modulus and AUL, in comparison with triethyleneglycol dimethacrylate.

The initiator nature and concentration also affect the mechanical and swelling characteristics of the SAP gels. Overall, under a faster reaction, more defects are formed in the gel network leading to loss of storage modulus and AUL.

Increasing filler content (kaolin) improves both modulus and AUL, however, beyond a certain value ($\sim 12\%$), it disfavors the mechanical and AUL prop-

erties of the SAP composites. Porosity generation disfavors AUL and the swollen gel strength of the SAP composites. The drying method plays also a major role in this regard. For instance, SAP samples dried in oven possess higher AUL and gel strength than those dewatered in methanol.

It is proposed that the saline AUL is proportionally dependent on the rubbery-plateau storage modulus (G') of the swollen gel. Thus, for a given SAP with a specified repeating unit, AUL can be varied with the molecular weight average between crosslinks, \bar{M}_c [eq. (2)], and many other inherent factors originated from the chemistry of reactants and the preparative circumstances [eqs. (7) and (8)].

$$\text{AUL} = k_{\text{total}}G' + C \quad (7)$$

$$\begin{aligned} k_{\text{total}} &= k_{\text{cross}} + k_{\text{init}} + k_{\text{poro}} + \dots \\ &= f(\text{crosslinker structure and reactivity,} \\ &\quad \text{crosslinking density, initiator chemistry} \\ &\quad \text{and reactivity, initiator concentration,} \\ &\quad \text{nature and content of inorganic component,} \\ &\quad \text{gel porosity, morphology of porosity, } \dots) \end{aligned} \quad (8)$$

In this regard, physico-chemical approaches (particularly surface crosslinking as post-treatment) established to improve the SAP gel strength and AUL of SAPs, can also be studied.

Overall, the easily and rapidly measured experimental values of AUL can be simply correlated to the preparative variables and molecular structure of SAP gels just through rheological measurements. This correlation can be taken as a commencement for studying the SAP gel structure deeper than before. In general, the present work can be construed as a research for expanding our knowledge of the SAP gel structure–property relationship.

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