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Superabsorbent polymer composites: does clay always improve properties?

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Abstract Clay is frequently incorporated to many materials including superabsorbent polymers (SAPs) to improve their properties. Superior properties have been reported for the SAP composite (SAPC) materials comparing to their clay-free counterparts. However, study of the effect of clay on some of very important requirements of superabsorbents, particularly the residual monomer (RM), has been unnoticed in the academic literature. Here, we report preparation of a series of SAPCs via a conventional solution polymerization of partially neutralized acrylic acid in the presence of common MMT clay (Na-montmorillonite). The products were characterized by FTIR spectroscopy, differential scanning calorimetry, thermogravimetric, thermomechanical, and rheometrical analyses. The RM content of the samples was determined by high performance liquid chromatography. It was found that the clay had unfavorable effects on the crosslinking polymerization process. This fact was observed as declining mechanical strength of the SAPCs in both dried and swollen states, increased swelling capacity, decreased gel fraction, and increased RM content. For instance, RM of clay-free sample was 740 ppm which was continuously increased with level of the clay incorporated. It surprisingly reached to ~34,000 ppm at clay content of 12%. The undesirable function of clay was attributed to inactivation and barrier effects of clay incorporated to the polymerization medium. These unwanted effects were more pronounced at high clay content. However, overall thermostability of SAPCs was improved comparing to the non-composite counterpart. It was concluded that such conventionally prepared SAPCs, in spite of the previously reported claims, could not be suitable candidates for hygienic applications, particularly those prepared with high clay percentages.

Introduction

Superabsorbent polymer (SAP) hydrogels are lightly crosslinked three dimensional networks with the ability of absorbing and retaining huge amounts of water and aqueous fluids [1, 2]. The applications of SAPs can be divided into hygienic and non-hygienic areas [2, 3]. The worldwide SAP production is ~1.5 million tons per year. Majority of the materials is consumed in hygienic uses such as baby diaper and feminine napkin [1, 2].

The practical features of an ideal SAP material can be stated as absorption capacity and rate, swollen gel strength (as a measure of the absorbency under load), non-toxicity, price, etc. [1, 2]. Meanwhile, particularly for the hygienic grade SAPs, high gel fraction and low content of the residual monomer (RM) acrylic acid is one of the most

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important requirements due to the monomer toxicity. During more than one decade research on SAP hydrogels, we realized that very scant studies have been reported on the later theme [1, 4, 5].

In the last decade, SAP composite (SAPC) [6–11] and nanocomposite [11–14] materials have been synthesized using different types of clay and hydrophilic monomers. The main reason for using clay is claimed to be reducing cost and improving mechanical properties. Improving of mechanical [15] and thermal [12, 15, 16] properties of superabsorbing composites and nanocomposites have been investigated in several articles.

The RM content of SAPs originates essentially from the basic reaction parameters (e.g., type and concentration of initiator and crosslinker, neutralization degree, reaction temperature, etc.). Research on this aspect of SAPs has been very rarely reported in the literature. Although numerous articles (more than 1,000) have been published about SAPs and superabsorbing composites and nanocomposites, however, there are only some reports about determination of the RM in these polymers. Recently, we studied the effect of two redox initiation systems on the RM content of the hydrogels [4]. We also investigated the effect of a two-step initiation strategy on the RM content [5]. These studies were carried out on non-composite SAPs.

To the best of our knowledge based on the extended experiences in the SAP area, we have ensured that there is no report about the clay effect on the RM and some of mechanical aspects of SAPCs [17]. Even for the non-composite (normal) SAPs, there are only some scattered reports involving RM just in the patent literature. Therefore, it is necessary to perform such study because the main use of the superabsorbent materials is covered by hygienic area, where the hydrogel is indirectly in touch with the human skin [1]. This is a preliminary work dealing with the synthesis of a series of SAPC based on partially neutralized poly(acrylic acid)–montmorillonite and investigation of the clay effect on the SAPC mechanical and chemical characteristics including RM.

Experimental

Materials

Sodium hydroxide (NaOH, Merck), ammonium persulfate (APS, Merck), sodium metabisulfite (SMBS, Merck), polyethyleneglycol diacrylate (PEGDA, MW 400, Rahn, Switzerland), and fine powder Na-montmorillonite (MMT, K10, Fluka) were used as received. Acrylic acid (AA, Sasol) was distilled under reduced pressure before use.

Synthesis of SAP hydrogels

Acrylic acid (15.0 g) was neutralized partially (75 mol%) with sodium hydroxide solution (6.25 g NaOH in 20.0 mL H_2O). Crosslinker (PEGDA 0.40 g) and initiator (APS 0.075 g, SMBS 0.063 g) were kept unchanged. After addition of desired amount of MMT (0, 0.6, 1.2, 1.8, 2.4, and 3.0 g) to the monomer solution, aqueous solution of the initiator and the crosslinker were added and stirred at room temperature. Gelation point was observed in few minutes. After half an hour, the elastic gel product was removed from the reactor to cut into small pieces. It was dried in an air-drafted oven at 80 °C for 8 h. The dried gel pieces were pulverized by a hammer-type minigrinder, screened, and stored in a dry place.

Swelling measurements

A 0.20 g sample of dried polymer (mesh 35–100) was dispersed in an excess volume (200 mL) of distilled water and allowed to swell for 1 h to reach equilibrium swelling. The dispersion was filtered through polyester gauze to remove the excess water. Then, the swollen gels were weighted. Swelling capacity (g/g) was calculated via dividing the weight of the swollen gel by the initial dry sample. The experiments on the swelling rate were conducted using samples with particle size ranged 180–250 μm (mesh 60–80).

RM measurement

A system of high performance liquid chromatography (HPLC) was employed for the measurement. It was composed a model 510 computer-controlled HPLC pump, a model U6K injection valve equipped with a 20-mL sample loop, and a model 486 UV/vis detector all from Waters (Milford, MA, USA). Waters Maxima Software Model 820 was used for the system and data management. The separation was performed in isocratic mode at a 1.8 mL/min flow rate and ambient temperature on an analytical column containing the Tracer EXEL 120 ODSA stationary phase. The mobile phase was an aqueous 0.01% orthophosphoric acid. Sodium acrylate is converted to acrylic acid in this acidic medium. The UV–Vis absorbance over the 190–400 nm range was recorded and the wavelength used for quantification of the monomer acrylic acid was 200 nm [18].

A stock solution containing 10.0 mg/mL acrylic acid was prepared in the mobile phase and calibration standards were prepared by appropriate quantitative dilution from the stock solution with the mobile phase. Quantities of 100 mg of the hydrogel beads were extracted with the mobile phase (20 mL) through overnight stirring. The samples were centrifuged at 2000 rpm for 15 min and the supernatant was injected into the chromatographic system [18].

Fourier transform infrared spectroscopy

The FTIR spectra of dried samples as KBr tablets were recorded by an ABB-Bomem MB-100 FTIR spectrophotometer.

Thermal and thermomechanical analyses

Thermogravimetric analyses (TGA) of dried samples were performed using a TGA-PL England at nitrogen atmosphere with heating rate 10 °C/min. Differential scanning calorimetry (DSC) was conducted using a PL model system, England, at nitrogen atmosphere with heating rate 10°C/min.

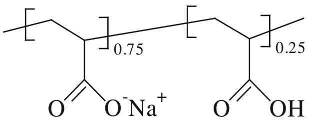
Dynamic mechanical thermal analysis (DMTA) of the dried powdery samples was performed using a Polymer Laboratories instrument. The experiments were carried out in the temperature range of 80–160 °C, heating rate 10 °C/min and frequency 1 Hz.

Rheometry

The samples were first swelled in a fixed volume of water which is 40% lesser than the volume of solvent absorbed by the least-swelling sample. Thus, 0.500 g of each sample was added to 15.0 mL distilled water. After full absorption of water (consuming time ∼40 min), the rheological measurement of the water-swollen gel was performed using a Paar-Physica oscillatory rheometer (MCR300, Germany) at 25 °C with parallel plate geometry (plate diameter of 25 mm, gap of 3 mm). The detailed procedure was previously reported [19].

Results and discussion

Conventional aqueous solution polymerization was employed to prepare the superabsorbent samples. A conventional redox pair APS–SMBS was used to initiate the polymerization at room temperature [20–24] in the presence of the crosslinker and the clay MMT. The general structure of hygienic grade SAP product is shown below.



It should be pointed out that the most conventional crosslinker *N*,*N*′-methylenebisacrylamide (MBA) was not preferred to be used for the crosslinking polymerization; instead, another water-soluble crosslinker, i.e., PEGDA, was employed. We recently established that MBA crosslinkages are thermo-hydrolytically cleaved upon heating during the oven-drying stage [25, 26] while PEGDA is a macromolecular bifunctional compound with more favorable characteristics including hydrolytic stability as well as rather non-toxicity and biocompatibility.

The spectral and thermal analyses

Figure 1 shows comparatively FTIR spectra for typical purified samples clay-free SAP and a SAPC containing 12.7% MMT. The main peaks assigned in the figure are convincing evidences about the acrylic structure shown in the above formula. The PEGDA crosslinks (and probable MMT–polymer linkages) are not appeared in spectra because in a SAP these bonds are very infrequent [1, 2] and without due consideration.

The spectral bands of two spectra are nearly identical except for the characteristic peaks of MMT parts. The stretching vibration of Si–O and Al–O are appeared at 1035 and 512 cm^{-1}, respectively, [27]. Peaks of the organic part have been assigned elsewhere in detail [5, 28].

Figure 2a shows TGA thermograms for the SAP and SAPCs containing 7.7 and 12.2% clay. The SAPC has slightly higher thermal stability than its clay-free counterpart. In this relation, char yield for SAP and SAPC-12.2% is 47 and 53%, respectively. This can be attributed to the presence of inorganic filler in the structure of the SAPC sample. Thermal stability improvement for a superabsorbent composite based on kaolin–poly(sodium acrylate) has been reported previously [7].

The DSC thermograms of the same samples are exhibited in Fig. 2b. They verify that the non-composite SAP, SAPC-7.7%, and SAPC-12.2% have not been thermally

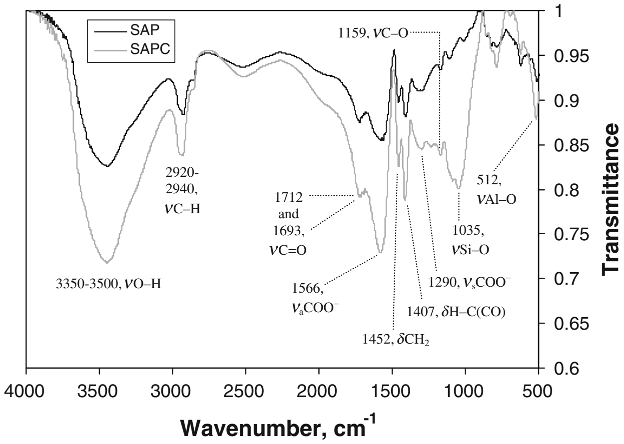


Fig. 1 FTIR spectrum for clay-free sample (SAP) and a typical SAPC sample (containing 12.2% MMT)

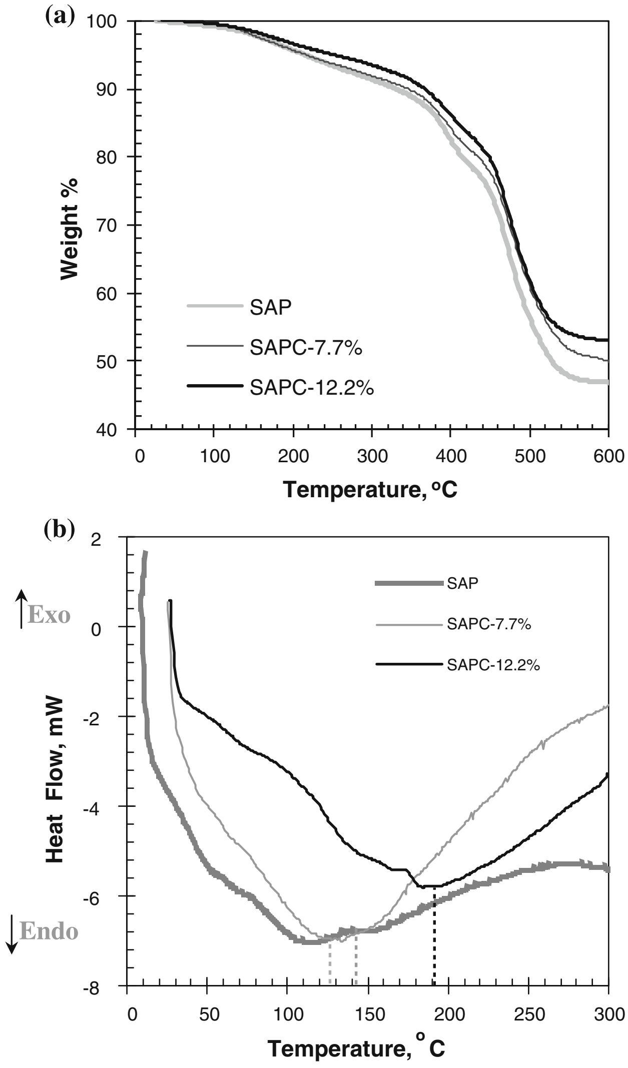


Fig. 2 Representative thermograms **a** TGA and **b** DSC for the SAP and two SAPC samples containing 7.7 and 12.2% MMT

decomposed up to around 120, 140, and 190 °C. The endothermic transitions below these temperatures are attributed to the removing of the absorbed moisture (as free water) as well as bound water upon heating. Beyond the temperatures, exothermic transitions are started due to beginning of the thermal decomposition. The exothermic transition starts obviously at higher temperatures for the composite samples comparing to the non-composite sample.

This DSC evidence also reconfirms that thermal stability improvement for SAPC samples is more noteworthy in comparison with the non-composite SAP counterpart. Clay layers may be mostly intercalated and exfoliated in the SAPC which causes to increase surface area of clay. Several reasons, such as shielding and inactivation effects, are reported for the role of clay in the thermal stability improvement [29, 30].

The water absorption and gel fraction

The maximum water absorption (swelling capacity) and gel fraction versus clay content of SAPC samples are exhibited in Fig. 3a. Swelling capacity is 52 g/g for SAP which is increased to 66 g/g at 5.25 MMT%. It is enhanced with increase of clay content up to 98 g/g at 12.7% of the clay. Gel fraction is slightly increased to around 0.9 at low clay content up to ~5% clay, but it is decreased at clay content higher than 5%. It is known that clays can possess both crosslinking role and inhibiting role in a polymerization medium. Crosslinking is more prominent at low clay content which mostly increases gel fraction and decreases swelling capacity. It is reported that clay can act as a multifunctional crosslinker in hydrophilic gels [31]. In some cases, even in the absence of a chemical crosslinker, a polymer network may be originated just from the clay-based crosslinks [31].

At high clay content, inhibiting effect of clay dominates over the crosslinking role. The high concentration of clay increases the polymerization mixture viscosity, so the mixing process is not as efficient as before. The molecular collision is decreased while the chain transfer to the clay

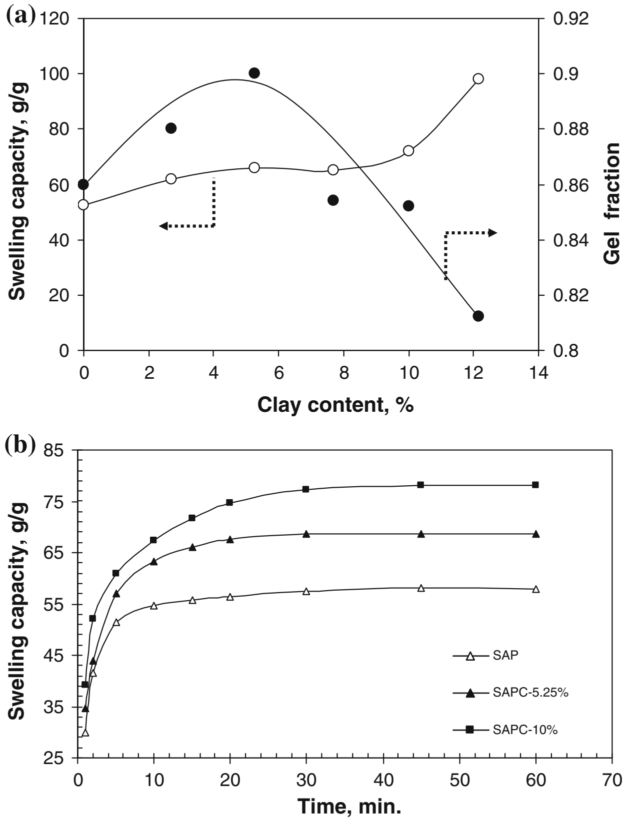


Fig. 3 **a** Effect of clay percentage on the swelling capacity and gel fraction of the SAPC products. **b** Swelling kinetics for representative superabsorbing samples in distilled water

particles will be potentially high [32]. Therefore, it can be seen that clay interferes the polymerization process. As a result, a lesser amount of crosslinker and monomer molecules can be participated in the crosslinking polymerization [6, 7, 10]. This clay inhibiting effect results in lower available crosslinker leading to (a) swelling capacity increase and (b) gel fraction decrease which are both obvious from Fig. 3a.

Figure 3b exhibits the swelling rate experimental results for some representative superabsorbent samples. The water absorption rate can simply be calculated based on the slope of the curves at the initial minutes of absorption. As it is obvious from the figure, higher MMT leads to elevated rate of water absorption, so that the swelling rate for the samples SAP, SAPC-5.25%, and SAPC-10% is determined to be about 10.3, 11.4, and 12.2 g/g min, respectively. This behavioral trend is expectable, because higher level of the clay in the hydrogel favors both capacity and rate of swelling. Based on the chemistry mentioned above, the presence of the clay particles eventually favors the lower crosslink density leading to improved absorbency [10, 32].

Some aspects related to the clay unfavorable effect were confirmed by DMTA, rheology, and HPLC (the following sections).

The thermomechanical properties

The thermomechanical properties of dried SAPs were studied by DMTA (Fig. 4). Storage modulus is higher for SAP in comparison the SAPC containing 12.2% clay. Storage modulus is directly related to the crosslink density (v) stated by Eq. 1.

$$G' = \rho R T v, \qquad (1)$$

where G' is the relaxed rubbery modulus, ρ is density, R is the gas constant, and T is temperature [33].

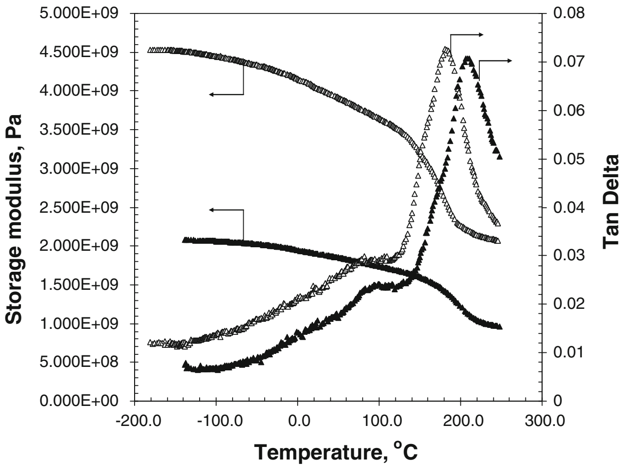


Fig. 4 Dynamic mechanical thermal analysis for dried samples of SAP (*open symbols*) and SAPC containing 12.2% MMT (*filled symbols*)

Higher storage modulus indicates that SAP has higher crosslink density in comparison with SAPC. As the crosslinker content is identical for both samples, the higher crosslink density of SAP can be attributed to more efficient involvement of the crosslinker in the crosslinking polymerization. High clay content (12.2%) can act as a barrier during polymerization. The probability of diffusion of monomer and crosslinker is reduced due to increased viscosity of the reaction mixture. As a result, some reactants are remained unused. Increased unreacted crosslinker means decreased crosslink density which results in reducing storage modulus.

As exhibited in Fig. 4, glass transition temperature (T_g) of the samples can also be provided from tan δ curves. Therefore, T_g for the non-composite SAP and the SAPC with 12.2% MMT was determined to be 182 and 210 °C, respectively. The T_g value for non-crosslinked poly(acrylic acid) has been reported to be $\sim$130 °C [34–36]. Here we have a crosslinked poly(sodium acrylate-co-acrylic acid) network, so T_g is increased to 182 °C due to both the crosslinks and the possible metal cation aggregates. In the latter cause, the counterion Na^+ has high potential to be aggregated (via the so-called process of counter ion binding) to form ionic clusters leading to increased T_g [37].

In the SAPCs sample, the presence of inorganic particles in the network enhances T_g to 210 °C. The enhanced T_g is attributed to the polymer segments local motion restricted by the dispersed MMT at the organic–inorganic interface [38]. Similar observation has been reported by Ren et al. [39]. On the other hand, the overall trend and appearance of tan δ curves is nearly identical for the SAPC and non-composite SAP, i.e., there is no phase separation in the composite sample. It implies that SAPC has not been composed of a simple physical mixture of SAP and clay; it is an integrated acrylic network chemically bounded with the clay particle surface [7, 10, 40].

The rheological study

In all application areas of SAPs, the terms swelling or absorbency are often used without specifying its conditions. It implies uptake of water while the sample swells freely, i.e., no load is put on the testing sample. However, in practice (e.g., in a baby diaper), the SAP has to absorb urine while it is under pressure of the baby load. This is why the absorbency under load (AUL value) is sometimes reported in the patent literature and technical data sheets by industrial SAP manufacturers (when a SAP is under load, the swelling capacity is decreased to some extent in comparison with its swelling capacity without load).

Practically, it is recognizable that a SAP with higher AUL is more stiffened in its “water-swollen” state in comparison with an analogous SAP with lower AUL. This swollen gel stiffness can be felt when its particles are pressured between the fingers. We have already introduced a rheometrical method to quantify the *swollen gel stiffness* as the dynamic storage modulus (*G*’) [19, 41]. In this method, the comparable samples are swelled in a fixed volume of water. This solvent volume is less than the volume required for the equilibrium swelling, so that for a desired sample series, the solvent volume has to be 40% lesser than that of solvent absorbed by the least-swelling sample. Then, the water-swollen samples are measured rheometrically.

Figure 5 shows storage modulus of the water-swollen form of the samples versus angular frequency obtained from rheological measurements.

The modulus is decreased with increase of clay content. According to many reports, clays typically lead to improved modulus [7, 11, 17, 42, 43] particularly at low levels of clay content. For instance, it has been reported that the hydrated modulus of poly(2-acrylamido-2-methylpropane sulfonic acid)–chitoMMT was increased with the clay content up to 6%. This positive function of clay is often attributed to its possible role of crosslinking [7, 40] which causes to increase crosslink density and modulus. At higher clay content, however, another parameter is involved to determine final crosslink density SAPCs and nanocomposites. This parameter can be known as inhibiting effect of clay [15]. As mentioned before, viscosity of the reaction mixture is increased at high clay content. This parameter decreases the probability of collision of monomers and crosslinker to the reactive growing polymer chain. As a result, the remained monomer and crosslinker is increased. At low clay content (mostly up to ~6%), crosslinking role of clay dominates the inhibiting effect. This results in increased modulus for the hydrated SAPCs comparing to the non-composites [15]. At higher clay content, inhibiting role of clay against the polymerization progress dominates and leads to decreased crosslink density and, in turn, the storage modulus. In this study, the inhibiting effect of clay for samples containing 7.7 and 12.2% clay dominates the crosslinking role of clay (Fig. 5), therefore, a reduced storage modulus is observed.

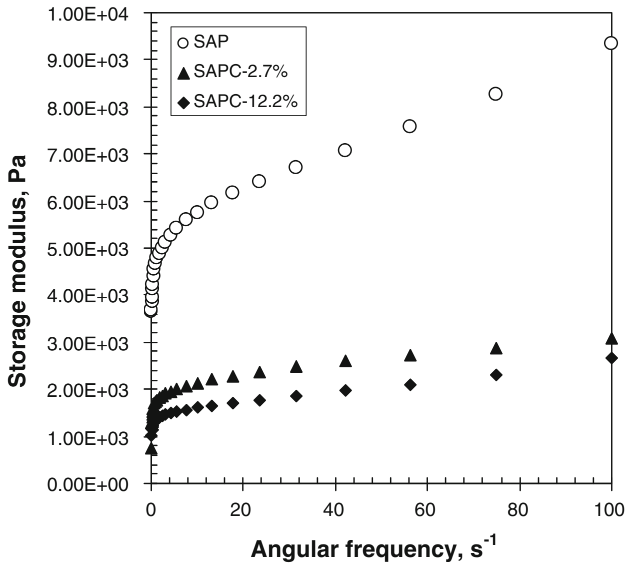


Fig. 5 Rheological analysis of water-swollen samples of SAP, SAPC containing 2.7% MMT, and SAPC containing 12.2% MMT

The RM content

Among more than 1,000 non-patent articles on superabsorbents published during last three decades, none of them investigated effect of fundamental parameters on the SAP RM content as a key characteristic particularly for those used in hygienic, medical, pharmaceutical, and food packaging applications. Recently, we published two articles focused on the effect of the initiating system type and concentration on the RM content of SAPs [4, 5]. We could minimize the RM content up to ~210 ppm using an innovative approach of initiation [5]. Now, there is an inquiry in the SAPCs: does not clay favor the RM content?

Figure 6 shows the effect of clay content on the RM acrylic acid. RM for the clay-free sample is 740 ppm. Surprisingly, clay has an undesirable effect on the RM content. RM is increased to 1,260 ppm at 2.7% clay content. It has an ascending power law trend with clay content enhancement. It finally reached to 34,090 ppm at 12.2% clay content.

There are two possible reasons for negative effect of clay on the polymerization progress. The first, as mentioned above, is the barrier effect of clay which can reduce the probability of collisions of the free radicals to monomers. The second is the inactivation effect of clay. Free radicals can be reacted with clay surface and become inactive. Inactivation effect of free radicals is reported in thermal studies. It has been reported that clay may reacted with free radicals produced during thermal degradation and inactivate them [30]. Clay surface can comprise similar effect on free radials during polymerization. Another consequence of these circumstances will be the crosslinker insufficiency, particularly in high clay concentration. Inactivation of free radicals is increased with increase of clay content which results in increased RM.

This study indicates that clays are not suitable for using in hygienic-grade superabsorbent preparation in a conventional manner like we used here. The allowed RM content for the hygienic SAP is less than 300 ppm. In many

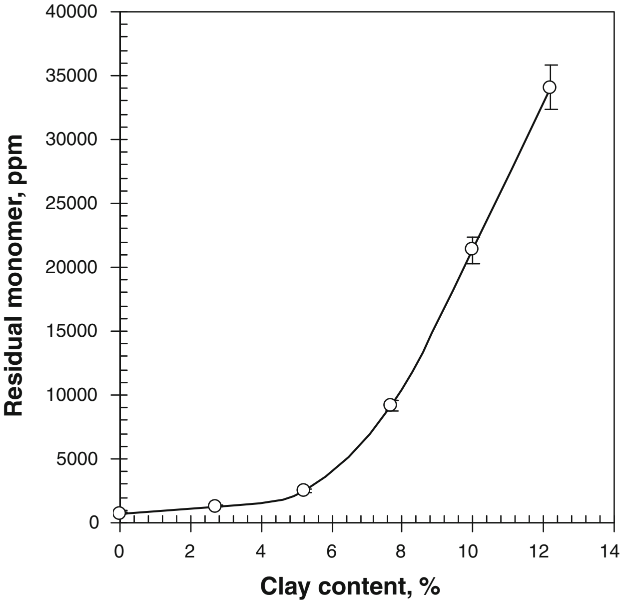


Fig. 6 Dependency of the RM content and the clay MMT wt% incorporated in the SAPC products

research studies, high clay amounts (as high as 40–50%) are reported to be incorporated [44, 45]. This study shows that clay incorporation in the synthetic systems like ours is unacceptable for even low-clay SAPC. The RM at 2.7% clay content is 1260 ppm which is yet fourfold more than the allowed content. Therefore, it is really necessary to evaluate and minimize the RM content of the SAPCs; the polymer composites which has frequently been studied and reported with nothing about the RM factor.

Conclusions

In the academic literature, RM measurement has been a forgotten aspect in SAPs particularly in SAPCs. Although some SAPC properties such as thermostability and stiffness are improved in comparison with those of the non-composite SAP samples, clay can induce some negative effects on progress of the conventional crosslinking polymerization for preparing SAPC. In the polymerization reaction initiated by the APS–SMBS redox pair at room temperature, clay disfavors the reaction via both barrier and inactivation effects. A polymerization mixture with high clay content possesses high viscosity. In such thickened medium, the probability of free radicals collision to monomer (and crosslinker) is decreased due to inactivation effect leading to limited progression of polymerization. As a result, in comparison with the non-composite counterpart, the SAPCs consist of inferior mechanical strength (in both dried and water-swollen states) as well as higher content of RM. These undesirable effects are particularly observed at high clay content; e.g., the RM is increased up to around 34,000 ppm when ~12% MMT is incorporated.

According to the results of this study and our experiences based on the polymerization reaction viewpoint, we can preliminarily suggest some general synthetic operational factors favoring the SAPC properties: incorporating low amounts of clay (<2 wt%), employing initiators with slow rate of dissociation (e.g., pair of APS–tetramethyl ethylenediamine), employing thermal initiators (e.g., APS alone), diluting the reaction medium (i.e., lowering monomer concentration) to an optimum extent, heating the reaction mixture, extending the reaction time, etc.

Overall, in spite of many claims, these kinds of conventionally prepared SAPCs are not proper candidates for hygienic, medical, and pharmaceutical uses, mainly due to high RM content.

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