

Swelling Study of Superabsorbent PAA-co-PAM/Clay Nanohydrogel

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ABSTRACT: A series of superabsorbent composites were prepared from acrylic acid (AA), acrylamide (AM), and Cloisite® 30B by aqueous solution polymerization technique using ammonium peroxodisulfate (APS) as initiator. The interaction of the organically modified nanoclay with PAA-co-PAM copolymer was verified by FTIR, whereas the morphology of the composite was studied by Scanning Electron Microscopy (SEM). The water absorbency in deionized water and saline water of the synthesized nanohydrogels was measured by calculating their percentage swelling ratio. The effects of copolymerization, monomer ratio, clay content, and temperature on the water absorbency were studied. The results indicated a considerable increase in swelling ratio by proper monomer proportion

and incorporation of optimum clay percentage into the copolymer matrix. It was found that the nanohydrogel acquired highest water absorbency with 2% clay loading. The reswelling ability and water retention capacity of the PAA-co-PAM hydrogel and PAA-co-PAM/clay nanohydrogel were also measured. The water absorbency was found to increase after each reswelling for which it may be useful as recyclable superabsorbent material. The results of water retention capacity of the nanohydrogel were also encouraging and find application in agriculture, especially in drought-prone areas. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1533–1538, 2011

Key words: hydrogel; morphology; swelling; copolymer

INTRODUCTION

Superabsorbent polymer-based hydrogels constitute a unique class of water absorbing materials. These are the polymeric networks that have the ability to swell by absorbing a large amount of water due to the groups on the main polymer chain, whereas its resistance against dissolving is because of cross grafts between polymeric chains.¹ The importance of these hydrogels lies not only in their high water intake capacity compared with the traditional water absorbing materials like cotton, sponge, etc. but also in their good water retention capacity, for which these are finding wide applications in agriculture,² coal dewatering,³ controlled release of drugs,^{4,5} and sealing.⁶

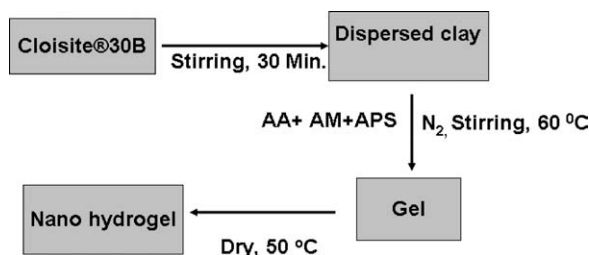
The water absorbing capacity of AA- and/or AM-based polymers/copolymers have been reported by some workers. Liu and Rempel⁷ reported about crosslinking acrylic acid-acrylamide copolymer, which absorbed about 900 g water/g dry copolymer. Raju et al.⁸ synthesized strongly water absorbing

polymers based on acrylamide, potassium acrylate, and magnesium methacrylate using *N,N*-methylene-bisacrylamide (MBA) as crosslinking agent. Some studies were also made on the effect of clay loading on swelling property of the hydrogels. Li et al.⁹ studied the effect of attapulgite on the water absorbency of polyacrylic acid and found that the composite with 10% clay content absorbed 1017 g water/g sample. Zhang et al.¹⁰ synthesized crosslinked sepiolite/poly (acrylic acid-co-acrylamide) hydrogel composites by solution polymerization and studied the effect of wt % of clay, crosslinking agent and initiator on their swelling behaviors. Zhang et al.¹¹ reported the comparative account of the swelling behaviors by incorporating different clays such as attapulgite, kaolinite, mica, vermiculate, and Na-MMT to polyacrylamide.

In this work, the nanohydrogels were synthesized with incorporation of the organoclay (Cloisite® 30B) into the poly (acrylic acid-co-acrylamide) matrix. Their water absorbencies were studied as a function of monomer ratio, clay loading, and temperature. The reswelling ability of the hydrogel/nanohydrogel was investigated by partial swelling-deswelling-reswelling technique. Interestingly, the swelling percentages were found to be increased with the number of reswelling times in contrast to the earlier studies.^{11–13} The water retention capacities of the hydrogel and nanohydrogel were compared.

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Scheme 1 Flow sheet for synthesis of PAA-co-PAM/clay nanohydrogel.

EXPERIMENTAL

Materials

The monomer Acrylic Acid (AA) and acrylamide (AM) were purchased from Merck, Darmstadt, Germany, which were used without any further purification. Ammonium peroxodisulfate (APS) was also a product of Merck, Darmstadt, Germany. The organically modified clay Cloisite®30B was supplied by Southern Clay Inc., Elmsford, NY, USA. The solutions of APS and AM were prepared with double distilled water.

Synthesis of PAA-co-PAM nanohydrogel

A calculated amount of the clay (Cloisite®30B) of 1%, 2%, 3%, or 4% by weight of the total monomer weight (AA + AM) are first dispersed in double distilled water by continuous stirring for 30 min. Then, the two monomers AA and AM and the initiator APS in a definite mole proportion were added. N₂ gas was allowed to bubble through the mixture for 15 min to expel dissolved oxygen and then it was stirred again with slow rise of temperature to 60°C till the formation of gel. The gel was washed repeatedly with double distilled water and then kept in a vacuum oven at 50°C till it is dried to a constant weight. A similar procedure was adopted to synthesize the PAA-co-PAM hydrogel without adding the clay. The flow chart for synthesis of PAA-co-PAM/clay nanohydrogel is illustrated as Scheme 1 and the experimental parameters for synthesis are discussed in Table I.

Characterization

1. The IR spectra of the materials were recorded on an Infrared Spectrophotometer (Perkin-Elmer Paragon 500) in the range of 400 to 4000 cm⁻¹ using KBr pellet. The KBr (0.5 g) and the sample (0.01 g) were grinded in a mortar to obtain a mixed powder. The mixed powder was compressed to prepare the pellet of diameter 10 mm and thickness 0.25 mm.
2. The surface morphology of the nanohydrogel was studied through the Scanning Electron

Microscope (SEM). The SEM micrographs of PAA-co-PAM/clay before and after swelling were characterized by Jeol, Japan (model 5200 Scanning Electron Microscopy with magnification of ×10,000).

Measurement of swelling properties

The water absorbency of the hydrogels/nanohydrogels was measured by calculating percentage swelling ratio. For this, a weighed amount (average mass of 0.1435 g) of the dried sample was immersed in excess of deionized water for a certain time interval or till equilibrium. The percentage swelling ratio was calculated by applying the formula as follows:

$$\text{Swelling ratio (\%)} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s is the weight of the swollen sample and W_d is the weight of the dry sample.

Reswelling ability was determined by calculating % swelling ratio of the same sample by repeating swelling-deswelling-reswelling process (i.e., keeping the sample in deionized water for 2 h to swell, then drying it completely, then again reswelling it).

Water retention capacity was measured in terms of the time taken by the fully swollen sample to lose water completely till constant weight. The loss of water was determined at 333 K in hot air oven and at room temperature, 303 K.

RESULTS AND DISCUSSION

Characterization of samples

FTIR analysis

The incorporation of clay into copolymer matrix was verified by FTIR (Fig. 1). This compared the IR spectra of PAA-co-PAM, PAA-co-PAM/clay, and Cloisite® 30B. The absorption bands at 3426 cm⁻¹

TABLE I
Synthesis of PAA-co-PAM and PAA-co-PAM/Clay Nanohydrogel at Different Conditions

Sample code	[AA] Mol dm ⁻³	[AM] Mol dm ⁻³	[APS] Mol dm ⁻³	wt % clay	Molar ratio AA : AM : APS
SH ₁	0.75	0	0.1875	0	4 : 0 : 1
SH ₂	0	0.75	0.1875	0	0 : 4 : 1
SH ₃	1.50	0.75	0.5625	0	8 : 4 : 3
SH ₄	0.75	1.5	0.5625	0	4 : 8 : 3
SH ₅	0.545	0.545	0.2725	0	2 : 2 : 1
SNH ₆	0.545	0.545	0.2725	1	2 : 2 : 1
SNH ₇	0.545	0.545	0.2725	2	2 : 2 : 1
SNH ₈	0.545	0.545	0.2725	3	2 : 2 : 1
SNH ₉	0.545	0.545	0.2725	4	2 : 2 : 1

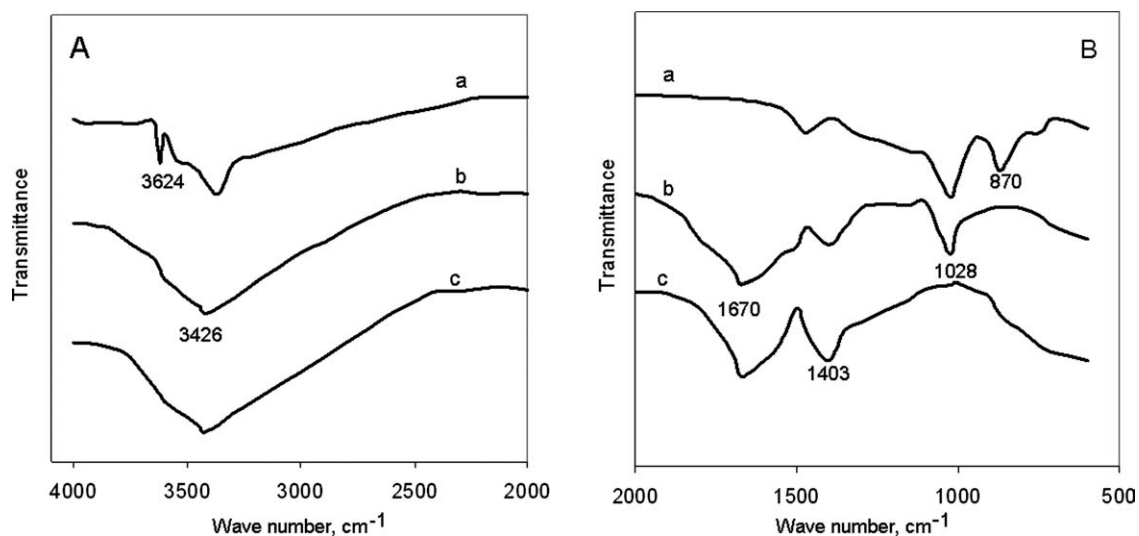


Figure 1 FTIR spectra in the region 4000 cm^{-1} to 2000 cm^{-1} (A) and 2000 cm^{-1} to 500 cm^{-1} (B) for clay 30B (a), PAA-co-PAM/clay (2%) (b), and virgin PAA-co-PAM (c).

in Figure 1A(b,c) corresponds to the stretching of $-\text{OH}$ or $-\text{NH}$ of PAA-co-PAM. The peaks at 3624 cm^{-1} of Figure 1A(a) and 870 cm^{-1} of Figure 1B(a) corresponding to $\text{Si}-\text{O}-\text{H}$ of the clay disappeared in Figure 1A(b) and Figure 1B(b). This indicated the esterification of carboxylic acid with silanol and the grafting of acrylic acid or acrylamide on the surface of the clay. It was assumed that the hydroxyl group on clay surface may react with acrylic acid followed by radical polymerization giving AA-AM branches on the clay backbone. The characteristic peaks at 1670 cm^{-1} is due to the carbonyl group ($>\text{C}=\text{O}$) of PAM, whereas that at 1403 cm^{-1} refers to symmetric $-\text{COOH}$ group in Figure 1B(b,c). The peak at 1028 cm^{-1} in Figure 1B(a) is due to the existence of $\text{Si}-\text{O}$ group, which is also observed in Figure 1B(b) but not in Figure 1B(c). It indicates the incorporation of the clay into the copolymer matrix.

SEM micrograph study

Surface morphology of PAA-co-PAM/clay nanohydrogel was studied by Scanning Electron Microscope (SEM) analysis (Fig. 2). The porous size of the nanohydrogel increased after the absorption of water [Fig. 2(b)] when compared with that of the same sample before swelling [Fig. 2(a)]. Furthermore, it was found that the porous size were not uniform. It may be due to local dispersion of nanoclay in the PAA-co-PAM copolymer matrix.

Swelling properties

Effect of copolymerization and mole proportion of monomers

The effect of copolymerization on the swelling ability can be observed from Figure 3. The swelling of

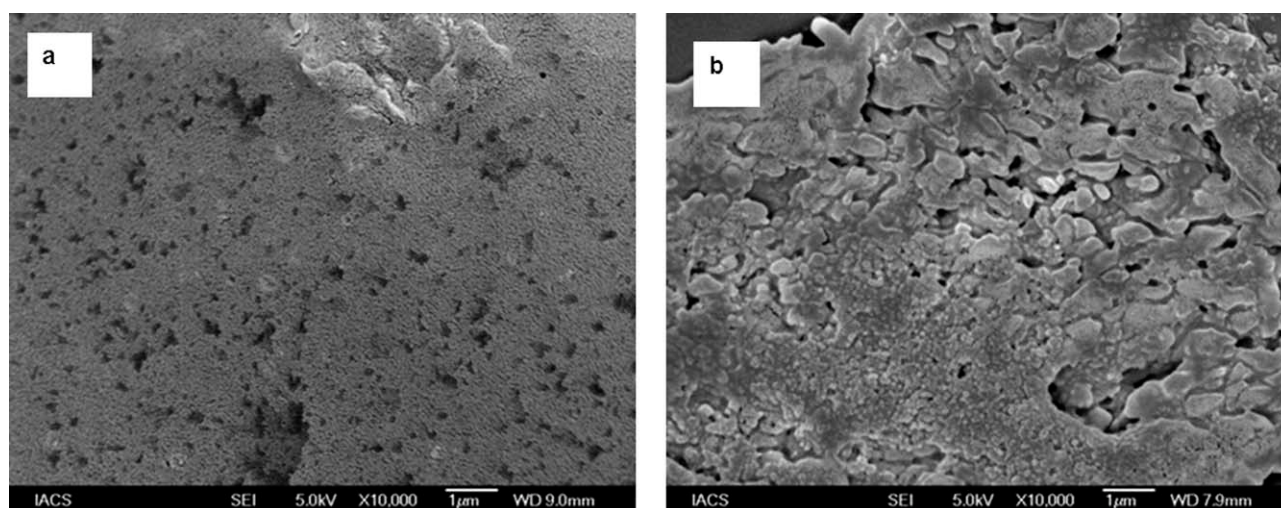


Figure 2 SEM micrograph of PAA-co-PAM/clay (2%) (a) before (b) after swelling.

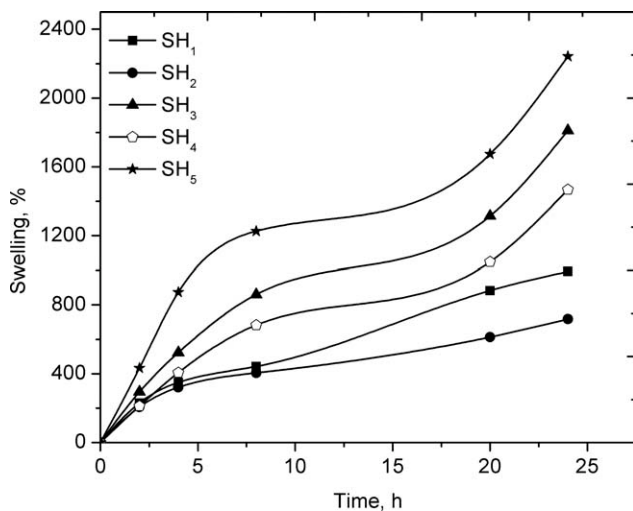


Figure 3 Percentage swelling of SH₁, SH₂, SH₃, SH₄, and SH₅ up to 24 h.

sample SH₁ (PAA) is higher than SH₂ (PAM). Furthermore, SH₃ with higher proportion of PAA has better absorbency than SH₄ having higher proportion of PAM. The explanation regarding the higher swelling behavior of copolymers (SH₃ and SH₄) when compared with homopolymers (SH₁ and SH₂) is due to the formation of extra voids because of grafting of AA with AM. This explanation is in agreement with the IR result of PAA-co-PAM/clay. However, the PAA-co-PAM of 1 : 1 mol proportion (SH₅) with initiator concentration of 0.2725 Mol dm⁻³ has superior swelling behavior when compared with SH₃ and SH₄. This outcome is in accordance with the result shown by Zhang et al.¹³

Effect of clay loading

The water absorbency of the copolymeric nanohydrogels with different clay loadings were investi-

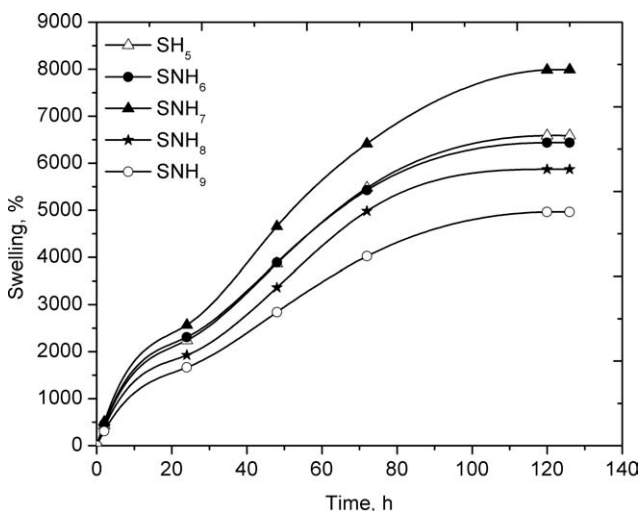


Figure 4 Percentage swelling of SH₅, SNH₆, SNH₇, SNH₈, and SNH₉ at different intervals of time up to equilibrium.

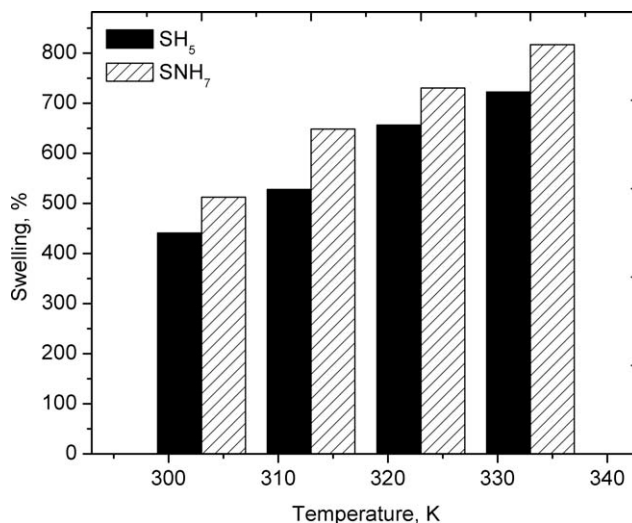


Figure 5 Percentage swelling of SH₅ and SNH₇ with variation of temperature for period of 2 h.

gated (Fig. 4). The absorbency increased with clay loading up to 2% and then decreased. The nanohydrogel with 2% clay loading (SNH₇) was found to swell by about 8000% compared with 6589% in case of the virgin hydrogel (SH₅) till equilibrium. This can be explained in the light of Flory's theory,¹⁴ according to which, water absorbency of a gel is dependant on ionic osmotic pressure, crosslinking density, and polymeric network. In low concentration (2%), the clay is easily ionized and dispersed into the polymeric gel, which enhances its hydrophilicity and makes it absorb more water.¹⁵ However, the reduction of the absorbance with clay loading more than 2% may be due to the fact that a higher amount of clay results in the generation of more crosslink points, thereby increasing crosslinking density.⁹

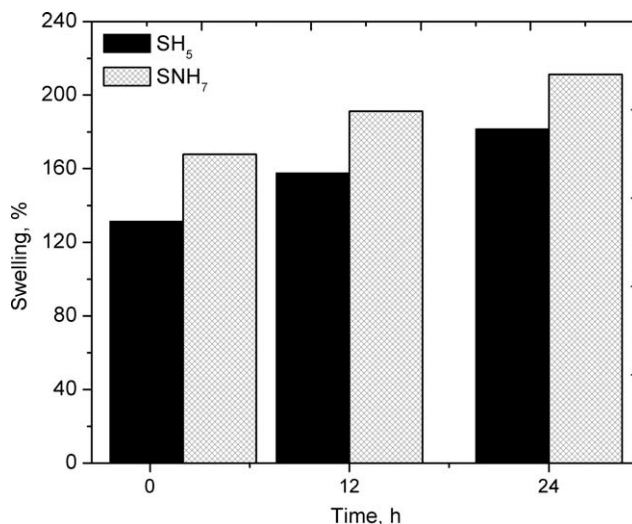


Figure 6 Percentage swelling of SH₅ and SNH₇ in saline water (1% aq. NaCl) at different intervals of time.

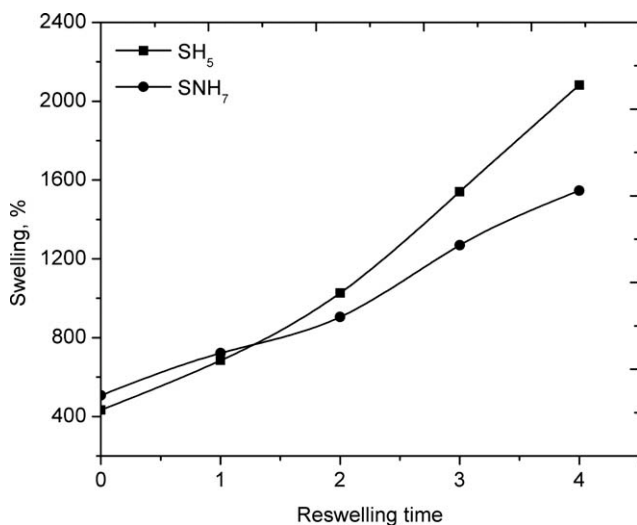


Figure 7 Percentage swelling of SH₅ and SNH₇ as a function of reswelling time.

Effect of temperature

The swelling abilities of the two superabsorbing materials such as the hydrogel (SH₅) and the nanohydrogel (SNH₇) were examined by raising the temperature of the deionized water to be absorbed. In both the materials, the % swelling ratios were found to be increased with increase in temperature (Fig. 5). This may be either due to easy movement of the copolymer chains with rise in temperature^{7,16} or because of kinetic effect.

Absorbance in saline water

The absorbance of SH₅ and SNH₇ was tested in saline water (1% NaCl solution). The swelling %ages for both of them in saline water were found to be much less in comparison to those in deionized

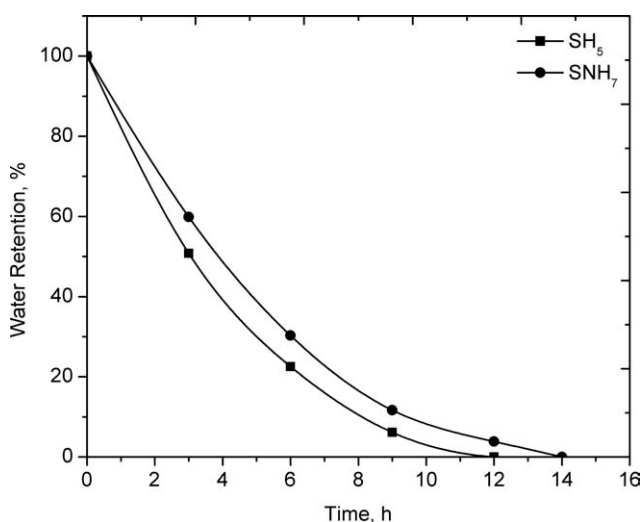


Figure 8 Water retention capacity of SH₅ and SNH₇ at 333 K.

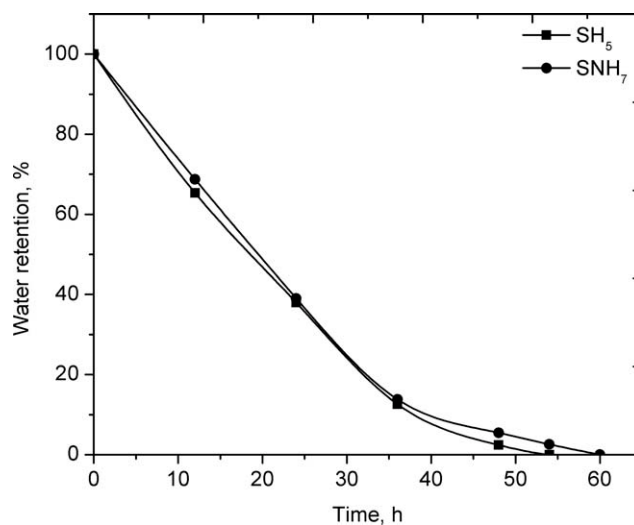


Figure 9 Water retention capacity of SH₅ and SNH₇ at 303 K.

water. However, the nanohydrogel (SNH₇) was found to have more ability to absorb saline water than virgin copolymer (Fig. 6). The decrease of absorbance in saline water can be explained in the light of polyelectrolyte effect.¹⁷ In pure water, the polymer containing charged groups (carboxylic anions) along its backbone will have the tendency to expand its dimensions to minimize repulsion. However, in the presence of NaCl (electrolyte), the oppositely charged ions (Na⁺) move into the polymeric network and neutralize its charge to a great extent, thereby decreasing its tendency to expand.

Reswelling

Swelling percentage of PAA-co-PAM hydrogel (SH₅) and PAA-co-PAM/clay nanohydrogel (SNH₇) were measured as a function of reswelling times as explained in Figure 7. It was observed that water absorbency of both the hydrogel and nanohydrogel gradually increased with reswelling time. On fourth time reswelling, the sample was found to absorb about five times more water when compared with the initial time (Fig. 7). This is due to increase in the porous size after each swelling and deswelling as evident from Scanning Electron Micrographs (Fig. 2). Unlike the earlier studies,¹¹⁻¹³ the increasing tendency of water absorbency with reswelling time may be considered as an interesting and important result of this work. Consequently, the hydrogels/nanohydrogels may assume useful as recyclable superabsorbent materials.

Water retention capacity

Water retention capacities of both the two superabsorbing materials were measured in hot air oven at

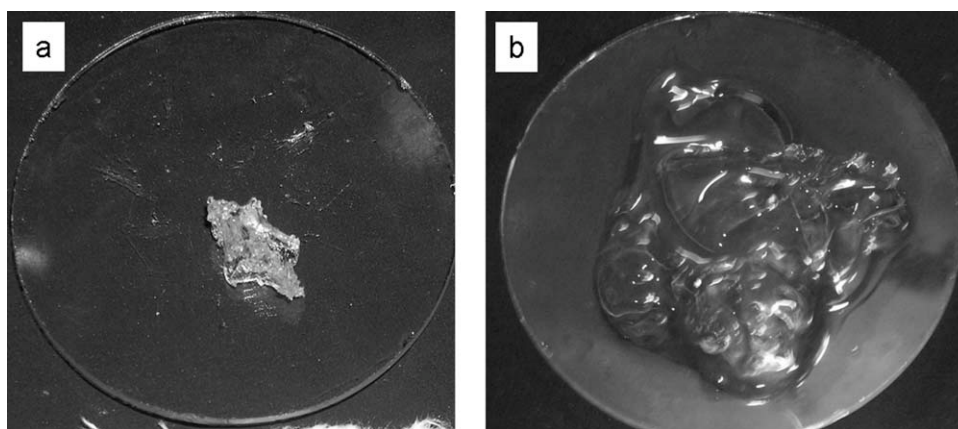


Figure 10 Photograph of SNH₇ nanohydrogel (a) before and (b) after swelling.

333 K (Fig. 8) and in room condition, 303 K (Fig. 9). Both of them exhibited good retention capacity, though the nanohydrogel is better retainer. In hot air oven at 333 K, the nanohydrogel could retain the absorbed water up to 14 h compared with 12 h in the case of the virgin hydrogel. At room condition, the retention times were 60 h and 54 h for the nanohydrogel and hydrogel, respectively. The photographs of the superabsorbent nanohydrogel (SNH₇) in dry and swollen states are represented in Figure 10(a,b), respectively. The size of the swollen sample was observed to be several times bigger than the dry sample.

CONCLUSIONS

In this work, novel hydrogel and nanohydrogel were synthesized by low-cost aqueous solution polymerization method without using any crosslinking agent. The swelling, reswelling, and water retention abilities of the materials were extensively studied. Incorporation of optimum percentage of the organo-clay Cloisite® 30B raised the swelling ability to a remarkable extent. In addition to this, it also increased the water retention capacity. However, the reswelling test gave the most interesting result. The material was found to be reswelled more even after initial swelling. The enhanced reswelling ability and significant water retention capacity would make the materials highly applicable in the field of agricul-

ture, horticulture, and forestry, especially in dry areas.

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