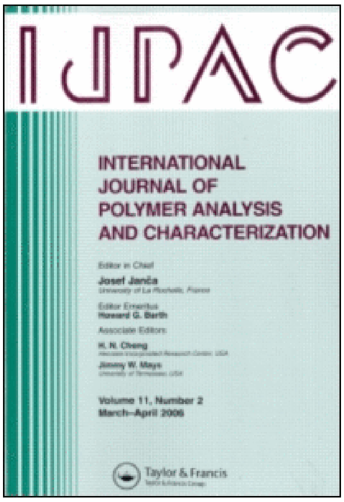

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Synthesis and Water Absorbency of Superabsorbent Copolymers

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Superabsorbent copolymers (SAPs) based on the monomers acrylamide, calcium acrylate, and potassium acrylate were prepared by copolymerization using ammonium persulfate (APS) as initiator and N,N′-methylene-bis-acrylamide (MBA) as cross-linking agent. The copolymers were synthesized by varying monomer, cross-linker, and initiator concentrations. The experimental results show that SAPs have good absorbency both in water and NaCl solutions. The copolymers were characterized by IR spectroscopy. The water retention capacity of the SAPs was carried out at 60° and 100°C.

Keywords: Superabsorbent copolymer; Acrylamide; Cross-linking agent; Water absorbency; Water retention

INTRODUCTION

Superabsorbents can absorb a large amount of water compared with general water-absorbing materials, and the absorbed water is hardly removable from them even under pressure. Because of their excellent

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Address correspondence to K. Mohana Raju, Synthetic Polymer Laboratory, Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur, AP 515 003, India. E-mail: Kmmohan@yahoo.com characteristics, superabsorbents are widely used in many products, such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine for drug delivery systems, and absorbent pads, where water absorbency or water retention is important[1-10]. Milimouk and coworkers[11] measured the swelling pressure and the diffusion coefficient in two series of salt-neutralized polyelectrolyte gels, one a poly(acrylamide-acrylic acid) copolymer, the other cross-linked potassium poly(acrylic acid). The incorporation of ionic groups in the copolymer backbone chain improves the water-absorbing capacity of superabsorbents. The authors have done work on the synthesis of superabsorbent copolymers and gels that have been evaluated for use in the growth of groundnut plants and croton plants[12–15].

In the present investigation, we report the synthesis of superabsorbent copolymers by polymerizing acrylamide (AM) with calcium acrylate (CA) and potassium acrylate (KA). The swelling behavior of the superabsorbent copolymers (SAPs) was studied, corresponding to cross-linker concentration, initiator concentration, and monomer ratios. Study of the water-retention capacity of SAPs was carried out at different temperatures.

EXPERIMENTAL

Materials

Acrylamide (AM) was purified by recrystallization from benzene. Ammonium persulfate (APS) was recrystallized from water. *N,N′*-methyl ene-bis-acrylamide (MBA) (chemically pure) was used as purchased. The compounds 1,4-butanediol diacrylate (BDA), ethylene glycol dimethacrylate (EGDMA), and diallyl phthalate (DP) were used as cross-linking agents after removing the stabilizer with 2% NaOH solution. Calcium acrylate (CA) and potassium acrylate (KA) were prepared in the laboratory, as described below. All the solutions were prepared with double-distilled water and all the solvents were distilled before use.

IR Spectra

The infrared (IR) spectra of the copolymers were recorded using Biorad WIN FTIR using KBr pellets.

Thermogravimetric Analysis

Thermal stability of the dry sample was investigated using a Universal V1, 12E thermogravimetric analyzer (TGA) instrument. The temperature range in the experiment was 50° to 800°C at a heating rate of 20°C/min using dry nitrogen at a flow rate of 50 mL/min.

Preparation of Calcium Acrylate

Calcium oxide (0.5 mol) was dispersed in methanol. Acrylic acid (0.1 mol) was added to a conical flask in dry ether and titrated against a calcium oxide solution. A white solid was separated out. The product was filtered under vacuum and dried in a vacuum.

$$2CH_2{=}CHCOOH + CaO \rightarrow [CH_2{=}CHCOO]_2Ca \downarrow + H_2O$$

Preparation of Potassium Acrylate

Potassium carbonate (0.5 mol) solution was prepared in distilled water and titrated against acrylic acid (0.1 mol) in a conical flask in dry ether. The white solid separated was filtered under vacuum and dried in a vacuum.

$$2CH_2{=}CHCOOH + K_2CO_3 \longrightarrow 2CH_2{=}CHCOOK \downarrow + H_2O + CO_2 \uparrow$$

Polymer Synthesis

All the reactions were conducted in a three-necked flask equipped with a mechanical stirrer, condenser, and nitrogen line. A weighed quantity of monomers along with cross-linking agent was dissolved in distilled water and added to the reaction vessel. After 15 min of stirring, ammonium persulfate was added to the reaction mixture; the temperature was then slowly raised to 80°C with effective stirring. After 2 h of reaction, the gel was formed. The gel was washed with ethanol and water and then dried in a vacuum oven at 60°C to constant weight. The dried gel was reweighed and milled through a screen. All the SAPs were transparent. The various copolymers prepared and the results are presented in Table I.

Water Absorbency Measurement

A sample (100 mg) of the superabsorbent copolymer was immersed in water (or saline solution) at room temperature until equilibrium was reached. Absorbency was determined by weighing the swollen gel (the gel was allowed to drain on a sieve 10 min). The water absorbency is calculated using the following equation[16]:

$$\text{Water absorbency } Q(\text{g } H_2O/\text{g sample}) = \frac{M - M_o}{M_o}$$

TABLE I Influence of monomeric ratios on the water-absorbing capacity of cross-linked poly(AM-CA-KA) superabsorbents

Polymer code	Monomer in feed (mol/L) AM[a]	CA[b]	KA[c]	Water absorbency (Q)[d]
S_1	0.83	0.06	—	90
S_2	0.83	0.12	—	145
S_3	0.83	0.16	—	210
S_4	0.83	0.22	—	185
S_5	0.83	—	0.06	110
S_6	0.83	—	0.12	160
S_7	0.83	—	0.18	240
S_8	0.83	—	0.24	210
S_9	0.83	0.16	0.18	290
S_{10}	0.83	0.16	0.20	450
S_{11}	**0.83**	**0.16**	**0.22**	**600**
S_{12}	0.83	0.16	0.24	546
S_{13}	0.83	0.16	0.28	390

Reaction conditions: cross-linker [MBA]: 6.4×10^{-3} mol/L; initiator [APS]: 3.5×10^{-3} mol/L; temperature: 80°C ± 1; reaction time: 2 h.

[a] Acrylamide.

[b] Calcium acrylate.

[c] Potassium acrylate.

[d] gH_2O/g sample.

where M and M_o denote the weight of the water-swollen gel and the weight of the absorbent, respectively. Absorbency is expressed as the ratio of retained water in (g) the gel per gram of dried gel.

RESULTS AND DISCUSSION

IR Spectra

The IR spectra of the copolymers show peaks corresponding to the functional groups attached to the monomeric units. The peaks observed are 3454 cm^{-1}, corresponding to the NH stretching of the acrylamide unit; 1735 cm^{-1}, corresponding to the $\nu C=O$ of the acrylate unit; and 1658 cm^{-1}, corresponding to the carbonyl group of acrylamide unit. In addition to the above, peaks are also observed at 1239 and 1172 cm^{-1} corresponding to C–O–C stretching coupling interactions of ester groups. From the above IR analysis, it was determined that all the monomeric units, i.e., acrylamide, calcium acrylate, and potassium acrylate, are incorporated in the copolymer backbone.

Thermogravimetric Analysis

The completely dried powder sample (S_{11}) was used for thermogravimetric analysis. Due to its high water-absorbing capacity, there may be moisture present in the sample, measured below 100°C. The sample had significant weight loss starting at 200°C (11%) and at 300°C (24%). The major weight loss started at 306°C (31%) and continued up to 400°C, with a weight loss of 55%. This particular sample (S_{11}) had an initial decomposition temperature of 306°C.

INFLUENCE OF PARAMETERS ON WATER ABSORBENCY

The key properties of superabsorbent polymers are swelling capacity and the elastic modulus of the swollen cross-linked gel. Both of these properties are related to the cross-link density of the network. Table illustrates the absorbency of copolymers as a function of composition. Swelling increases with increasing ionic units in the polymer backbone chain, but an excess of ionic units leads to an increase in the solubility of the copolymer at a fixed cross-linker concentration. The S_{11} superabsorbent has a high water absorbency of 600 g H_2O/g sample.

Effect of Cross-Linking Agent

Figure 1 shows the water absorbency of the cross-linked poly(AM-CA-KA) (S_{11}) as a function of cross-linker concentration. The water absorbency increases as MBA concentration proceeds from 1.8×10^{-3} to 6.4×10^{-3} mol/L and decreases considerably when MBA concentration is higher than 6.4×10^{-3} mol/L. This is due to a decrease in the distance between the copolymer chains as the cross-linker concentration increases. The water absorbency increases as BDA concentration proceeds from 1.8×10^{-3} to 8.1×10^{-3}mol/L and decreases considerably when BDA concentration is higher than 8.1×10^{-3} mol/L. The swelling capacity increases as EGDMA concentration proceeds from 1.8×10^{-3} to 5.9×10^{-3} mol/L and decreases considerably when EGDMA concentration is higher than 5.9×10^{-3} mol/L. The swelling capacity increases as DP concentration proceeds from 1.8×10^{-3} to 7.6×10^{-3} mol/L and decreases considerably when DP concentration is higher than 7.6×10^{-3} mol/L. The cross-linking concentration of maximum absorbency of the copolymer depends upon the nature of the cross-linking agent. Maximum absorbency is found when MBA is used as the cross-linking agent. This may be caused by the more polar nature of

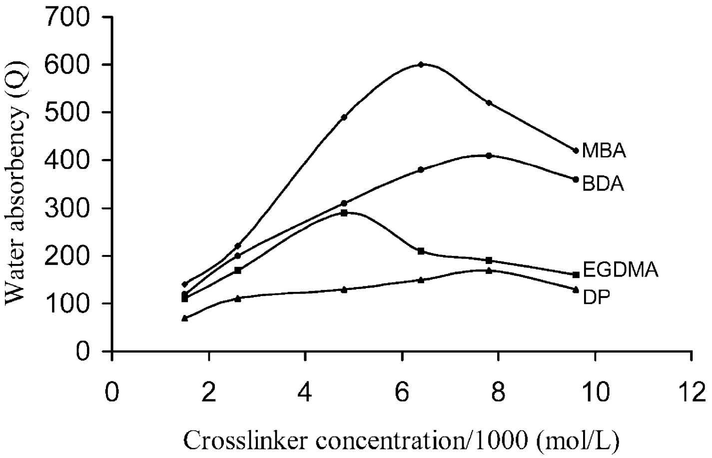

FIGURE 1 Influence of cross-linker concentration (mol/L) on water absorbency (Q) in deionized water of poly(AM-CA-KA) (S_{11}); MBA— *N,N'*-methylene-bis-acrylamide, BDA—1,4-butanediol diacrylate, EGDMA—ethylene glycol dimethacrylate, DP—diallyl phthalate.

N, N'-methylene-bis-acrylamide (MBA). Polarity of the cross-linking agent increases the swelling capacity due to polar end-groups, which attract water molecules. As the concentration of the cross-linking agent increases, the swelling capacity increases up to a certain level, and with higher cross-linker concentration, the water absorbency decreases drastically.

Effect of Salt Solution

Figure 2 shows the effect of NaCl concentration on water absorbency of copolymer S_{11}. As NaCl concentration increases, water absorbency decreases. At swelling equilibrium, the chemical potential of water in the polymer is equal to that of the water surrounding the polymer. The ionic strength in saline solution is larger than that in the deionized water. Therefore absorbent polymers cannot imbibe as much saltwater as in pure water alone.

Swelling Kinetics

The time required to reach maximum swelling capacity of the copolymers was studied and the results are presented in Figure 3. An amount of 100 mg of SAP was immersed in 200 mL of deionized water, and the water absorbency was measured every 10 min. The results indicate that the SAPs absorb maximum water within 40 min.

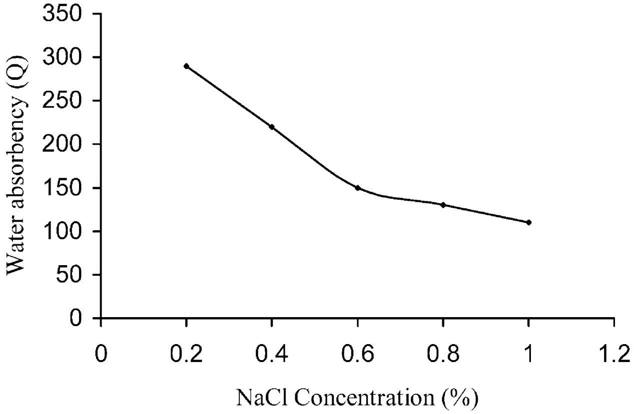

FIGURE 2 Influence of NaCl concentration (%) on water absorbency (Q) in deionized water of poly(AM-CA-KA) (S_{11}).

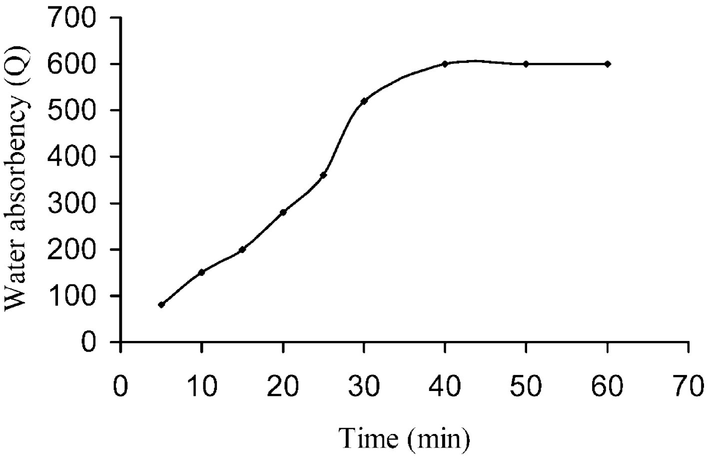

FIGURE 3 Swelling kinetics of poly(AM-CA-KA) (S_{11}).

Water-Retention Capacity

Investigation of the water retention capacity of the SAPs was carried out at 60° and 100°C in a hot air oven; the maximum water absorbency of copolymer was selected for this study. The results are presented in

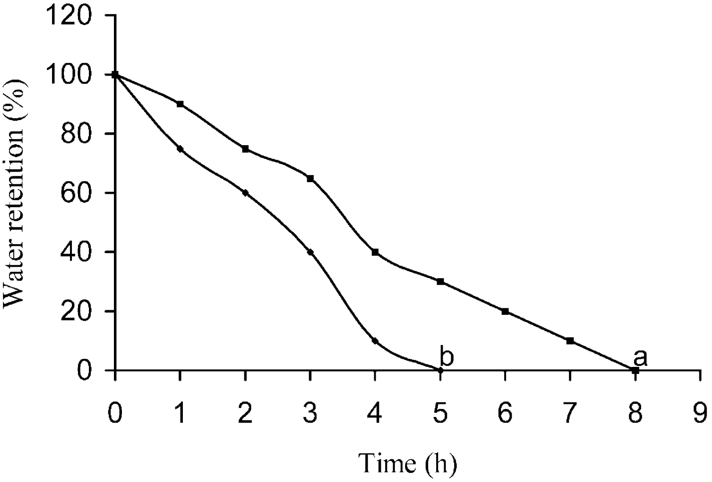

FIGURE 4 The water retention capacity of poly(AM-CA-KA) (S_{11}) at (a) 60°C and (b) 100°C.

Figure 4. From the results of above study, the SAPs have good water retention capacity. The photographs of the dry and swollen states of superabsorbent copolymers are presented in Figure 5.

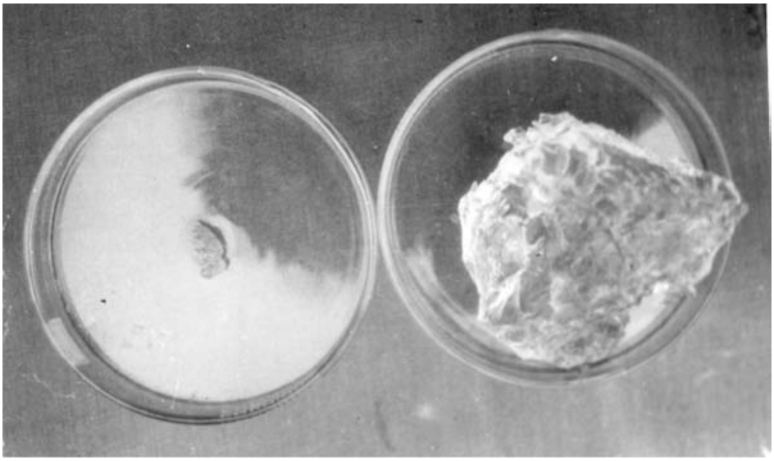

FIGURE 5 Dry and swollen superabsorbent copolymers (S_{11}).

CONCLUSION

A number of superabsorbent copolymers were synthesized in an aqueous solution by copolymerization of acrylamide, calcium acrylate, and potassium acrylate with either *N,N′*-methylene-bis-acrylamide, 1,4-butanediol diacrylate, ethylene glycol dimethacrylate, or diallyl phthalate as cross-linking agents and ammonium persulfate as initiator. The water absorbency of the copolymers is maximum when MBA is used as cross-linking agent. The synthetic variables (monomer feed ratios and cross-linker concentration) were also studied. The copolymers were characterized by IR, and thermal properties were studied by TGA. The absorbency of the SAPs was measured in both water and NaCl solutions. One superabsorbent sample, S_{11}, had a high-water absorbency ($Q_{max} = 600\,g\ H_2O/g$ sample). Investigation of the water retention capacity of the SAPs was carried out at 60° and 100°C. The results of the present work indicate that the SAPs have good water retention capacity, which could find application in agriculture, especially in drought-prone areas.

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