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Superabsorbent Polymer of Poly[acrylamide-*co*-(acrylic acid)] by Foamed Polymerization. I. Synthesis and Water Swelling Properties

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Summary: Superabsorbent polymers of acrylamide and acrylic acid were synthesized by foamed polymerization, initiated by ammonium persulfate and N, N, N', N'-tetramethylenediamine. The crosslinking agent N, N'-methylenebisacrylamide, the foaming agent sodium bicarbonate, and a foam stabilizer, a triblock copolymer of polyoxyethylene/polyoxypropylene/polyoxyethylene, were used in the polymerization. The superabsorbent polymer synthesized with an acrylamide/(acrylic acid) ratio of 1:9 by mole at 250 rpm and 45°C for 30 min of polymerization time produced the highest water absorption of 2300 times its dried weight. This article describes the synthetic method and measurements of water absorption.

Introduction

Superabsorbent polymers containing hydrophilic vinyl monomers have been produced since the 1970s; the polymerization route is mainly radical chain polymerization, by various synthetic techniques. The extent of water absorption depends primarily on the types of hydrophilic monomers, the initiation system, the degree of crosslinking, the method used to precipitate the polymer, and the ionic strength of the test fluid.

Foamed polymerization has been found to be an alternative method for preparing superabsorbent polymers with enhanced absorption rate.[1-2] Ishizaki et al.[3] filed a patent for synthesizing water-absorbent resins by dispersing a solid blowing agent in an aqueous monomer having unsaturated monomers and a vinyl crosslinking agent. The water-absorbent resin was used for various applications in which a rapid absorption rate, high water retention and prevention of water leakage were required.

The present research focuses on the synthetic method and the characterization of

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properties affecting water absorption by superabsorbent polymers. High water absorption and a high water absorption rate were achieved.

Procedure

In this research, the foam formation reagents sodium bicarbonate (2g, Merck, Darmstadt, Germany) and 0.05% w v^{-1} Lutrol $F^{®}$127 (BASF, Ludwigshafen, Germany, analytical grade) were used. Lutrol $F^{®}$127 is a triblock copolymer of polyoxyethylene/ polyoxypropylene/polyoxyethylene, with molecular weight range 9800–14600 g mol^{-1} [2] which was used as a constant ingredient for the whole experiment. The effects of the crosslinker N,N'-methylenebisacrylamide (N-MBA), the initiator ammonium persulfate (APS)/N,N,N',N'-tetramethylenediamine (TMED) and the ratio of acrylamide (AM)/acrylic acid (AA) on water absorption of the polymer were studied. Swelling kinetics of the resulting superabsorbent polymer were studied.

Basic preparation technique

A mixture of 100-cm^3 aqueous solution containing acrylic acid (AA, 99% pure, Siam Resin & Chemicals, Thailand) and acrylamide (AM, 99% pure, Siam Resin & Chemicals, Thailand), N-MBA, and ammonium persulfate (APS, analytical grade, Merck, Hohenbrunn, Germany) was placed in a 250 cm^3 reaction flask. This round-bottomed flask, equipped with a mechanical stirrer set at 250 rpm, a spiral condenser, a thermometer, and an inlet tube for nitrogen gas, was immersed in a set temperature water bath. The ingredients were stirred by a small-bladed propeller for 5 min while heating at the desired temperature. After the set temperature of 318 K (45°C) was reached, 2 g of sodium bicarbonate powder was added. Lutrol $F^{®}$ 127 of 0.05% w v^{-1}, and TMED (analytical grade, Sigma, Aldrich, St Louis) were then added sequentially. The reaction between acrylic acid and sodium bicarbonate took place immediately to produce carbon dioxide bubbles, which floated upwards to the solution surface. Foam formation and solution polymerization continued for 30 min, after which the bubble production ceased and the reaction mixture became milky white. A fine powder then precipitated. The resulting polymer was filtered, washed several times with distilled water, dewatered with methanol, dried, and cut into small pieces, which were dried again at 323 K (50°C) for 24 h in a vacuum oven to a constant weight and then milled.

Effect of mole fraction of APS/TMED

In this experiment, the mole ratio of AM:AA, percent of neutralization of AA, and the concentration of the crosslinking agent N-MBA concentration were fixed at 0.2, 40% and 6.30 x10^{-3} mol dm^{-3}, respectively. The same experimental procedure was carried out by varying the APS/TMED ratios (on a mol dm^{-3} basis) at: 1.5x10^{-3}/1.0x10^{-2}, 2.0x10^{3}/1.0x10^{-2}, 2.3x10^{-3}/1.0x10^{-2}, 3.0x10^{-3}/1.0x10^{-2}, 3.5x10^{-3}/1.0x10^{-2}, 4.4x10^{3}/ 1.0x10^{-2}, and 2.3x10^{-3}/2.0x10^{-2}.

Effect of mole fraction of acrylamide to acrylic acid and neutralization of acrylic acid

The same experimental procedure as described above was carried out, with varying mole fractions of AM to AA (0.1 to 0.9 with an increment of 0.1) and percent neutralization of acrylic acid; 0, 40, 60, 80, or 100%.

Effect of concentration of N, N'-methylenebisacrylamide

The mole fraction of AM : AA was fixed at 0.1 and the percentage neutralization of AA was at 40%. The concentration of crosslinking agent (in mol dm^{-3}) was varied from 1.0x10^{-3}, 1.5x10^{-3}, 2.0x10^{-3}, 2.5x10^{-3}, 3.0x10^{-3}, 3.5x10^{-3}, 4.0x10^{-3}, 4.5x10^{-3} and 5.0x10^{-3} and used for the preparation of superabsorbent polymer of poly[acrylamide-*co*-(acrylic acid)] or P(AM-*co*-AA) by following the basic preparation method.

Water absorption in distilled water

Distilled water (400 g) was added to 0.1 g of the dry copolymer in a 600-cm^3 glass beaker with a glass cover. The polymer was allowed to swell for 30 min. The fully swollen gel was then separated by filtering through a 100-mesh sieve aluminum screen for 2 h in a control room. The swollen gel was weighed and the water absorption was calculated by the equation as follows. Water absorption *(Q)* is *(B-A)/A* where *A* and *B* are the weights of the dry polymer (g), and the swollen polymer (g), respectively.

Swelling kinetics in distilled water

Distilled water (400 g) was added to 0.1 g of the dry copolymer in a 600-cm^3 glass beaker with a glass cover. It was allowed to swell for 10 min. The swollen gel was then separated by filtering through a 100-mesh sieve aluminum screen for 2 h in a control room. The swollen gel was weighed. A similar procedure was separately repeated at gel swelling times of 20, 30, 40, 50, and 60 min.

Results and Discussion

As mentioned above, superabsorbent polymers of P(AM-*co*-AA) were prepared by crosslinking polymerization of AM and AA monomers in the presence of gas bubbles. Carbon dioxide gas bubbles were generated by a reaction of sodium bicarbonate with acid solution. The amount of foam was governed by the amount of acid in the reaction mixture. We used an excess amount of sodium bicarbonate so that the foam size and amount were controlled by the amount of added acid, which was AA in this case. AA thus functions as a co-monomer and a foam accelerator. During the crosslinking polymerization, the viscosity of the medium increased gradually. The increased viscosity slowed down the bubble formation.

The foam stabilizer used in the present work is considered as one of the foaming materials with the best properties.[4] Polyoxyethylene/polyoxypropylene/ polyoxyethylene block copolymer (Lutrol® F 127), has the best foaming properties of most hydrophilic monomers; that is, it sustains the foam or bubbles for the longest period of time. In addition, it functions as a surface crosslinking agent, enhancing liquid permeability, improving the water absorption rate, and increasing water absorption capacity.[3]

To produce a highly porous superabsorbent polymer, polymerization and foaming processes had to take place simultaneously. Precise time control of the two processes was critical. Stabilizing a foam longer than a few minutes was rather difficult, because gelation had to start within this period just after the beginning of foaming resulting from the addition of sodium bicarbonate to the monomer mixture containing an acid component. We chose Lutrol® F 127, because it helps gel formation at lower reaction temperatures. The triblock copolymer of polyoxyethylene/polypropylene/polyoxyethylene is relatively polar and soluble in water and alcohol, which enhances stabilization of the bubbles and gelling and thickening of the copolymer. Normally, a fast gelation could be achieved by careful choice of monomers, initiators, temperature and solvent. In our case, gel formation was observed when a milky mixture resulted during the first 5 min after the addition of sodium bicarbonate, LF® 127, and TMED.

Crosslinking polymerization takes place in situ during and after formation of carbon dioxide gas bubbles, which acted as porogens. Toward the end of the foamed polymerization, the volume of the mass in the reaction vessel increased by 2 times. The polymerization was completed within 30 min. At the beginning of the crosslinking copolymerization, heat generated from the reaction was dissipated through the carbon dioxide bubbles. At this time, the reaction temperature was relatively constant, but it could increase as the reaction proceeded, which could lead to a decrease in viscosity of the reaction medium. Even though the reaction heat could be dissipated through the reaction solution, an autoacceleration or Trommsdorff effect (Norrish-Smith effect) was observed. The final superabsorbent polymers were thus of high molecular weight.

Effect of mole fraction of APS/TMED

The water absorbency of the crosslinked copolymers synthesized with various initiator (APS/TMED) concentrations for the solution polymerization is shown in Figure 1.

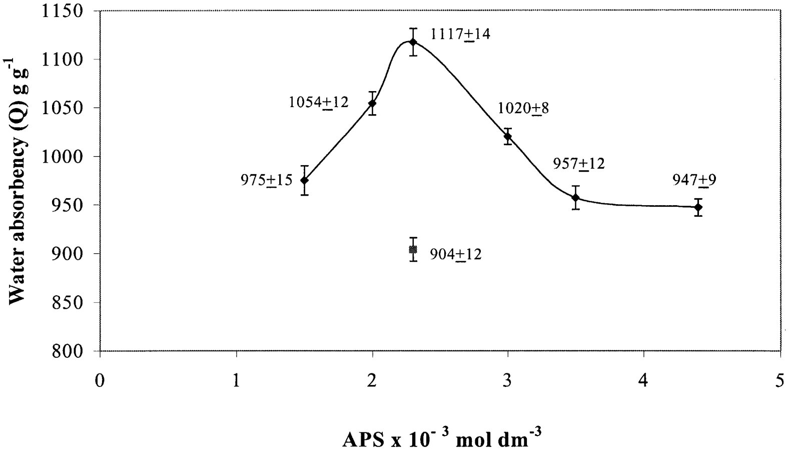

Figure 1. Effect of the initiator concentration on the water absorbency (Q) of the synthesized copolymers (♦ for TMED of 1 x 10^{-2} mol dm^{-3}, ■ for TMED of 2 x10^{-2} mol dm^{-3}).

Copolymers synthesized with APS (2.3×10^{-3} mol dm^{-3})/TMED (1.0×10^{-2} mol dm^{-3}) gave the optimum result, which has the highest water absorbency, 1117±14 g g^{-1}, compared with 904±12 g g^{-1} when twice the amount of TMED was used. Water absorbency increases linearly with an increase in the initiator ratio of APS:TMED at 0.23 and then decreases with increasing initiator ratio. As mentioned above, the rate of polymerization depended on the concentrations of monomers and initiator radicals in a bimolecular termination. When APS to TMED ratio is used as a redox initiator pair for the free radical polymerization, the free radical $[(CH_3)_2NCH_2CH_2(CH_3)N^{\bullet}CH_2)]$ is one of the initial free radicals responsible for the initiation of vinyl polymerization in addition to sulfate free radical ($^{\bullet}OSO_3H$).

This redox initiation pair produces two radicals, which may be reasoned to be responsible for the fast polymerization. At the higher APS concentrations ($3x10^{-3}$ and $4.4x10^{-3}$ mol dm^{-3}), too many radicals were produced, resulting in an abundance of short kinetic chains, in which the superabsorbent polymers had lower molecular weights. This inevitably reduced the swelling capacity. Additionally, at constant APS concentration, higher concentrations of TMED ($1x10^{-2}$ and $2.0x10^{-2}$ mol dm^{-3}) hampered the efficiency of the initiators. The TMED accelerated the generation of a higher amount of free radicals to produce the shorter kinetic chains and/or radical recombination. The latter two effects led to the lower swelling superabsorbent polymers.

Effect of concentration of N, N'-methylenebisacrylamide

Water absorbency of the superabsorbent polymers, synthesized by a 0.1 mole fraction of AM with 2.3×10^{-3} mol dm^{-3} APS, 1.0×10^{-2} mol dm^{-3} TMED, 40% neutralization of AA, and various concentrations of the N-MBA crosslinking agent, is shown Figure 2.

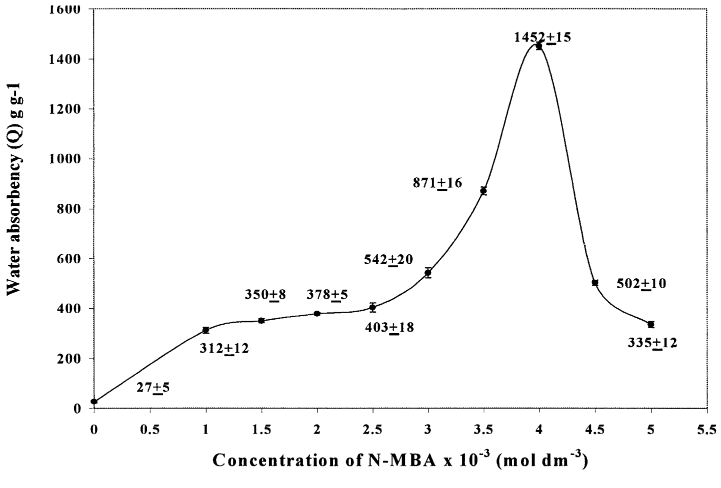

Figure 2. Effect of the concentration of crosslinking agent on the water absorbency (Q) of the synthesized copolymer.

The copolymer crosslinked with N-MBA at a 0.1 mole fraction of AM and 40% degree of neutralization of acrylic acid gave a water absorbency value of 1452±15 g g^{-1}, which is higher than the copolymer synthesized in the absence of the crosslinking agent (27±5 g g^{-1}). In the absence of the crosslinking agent, more soluble copolymers are produced that cannot absorb fluid effectively. Nonetheless, in the presence of high crosslinking agent concentrations, more crosslinks can also be formed to give rigid chains that reduce swelling of the gel as well.

Additionally, we did not extract the soluble part (non-crosslinked moiety) of the polymer before carrying out the water absorption experiment. The soluble portion is anticipated to interfere with the extent of water absorption in a negative way. Buchholz[5] reported that the solubility of a crosslinked agent depended on the extent of neutralization, which could exhibit different effectiveness in the crosslinked products. In general, crosslinking agents have been employed to improve the strength of the swollen gel but they very effectively reduce water absorbency if too high a crosslinking agent concentration is used.

Relatively small changes in crosslinker density can play a major role in modifying the properties of superabsorbent polymers. Figure 2 indicates the dependence of water absorption on the crosslinking agent concentration. It is clear that gel absorbency is diminished at low N-MBA concentration because of an increase in soluble polymers. A maximum water absorbency of 1452±15 g g^{-1} is obtained at the N-MBA concentration of 4.0×10^{-3} mol dm^{-3}. On the other hand, many branching points between two main vinyl backbones induce excessive crosslinking chains with rigidity, drastically decreasing the swelling ability of the superabsorbent polymer.[3,4] Moreover, a high concentration or high reactivity of the crosslinking agent usually leads to early depletion during polymerization. Polymer chains formed in a later stage of the polymerization lack the crosslinking agent, thus resulting in a more soluble polymer.

Effect of mole fraction of acrylamide to acrylic acid

The results on water absorbency of the copolymers synthesized by crosslinking polymerization of various mole fractions of acrylamide (AM) are shown in Figure 3. The synthesized copolymers of acrylamide (AM) and acrylic acid (AA) are swollen in water on account of the hydrophilic pendants (amide and carboxylic groups) in their structure. The synthesized copolymer with the mole fractions of AM and AA at 0.1 and 0.9, respectively, at 40% degree neutralization of acrylic acid and 4.0×10^{-3} mol dm^{-3} N-

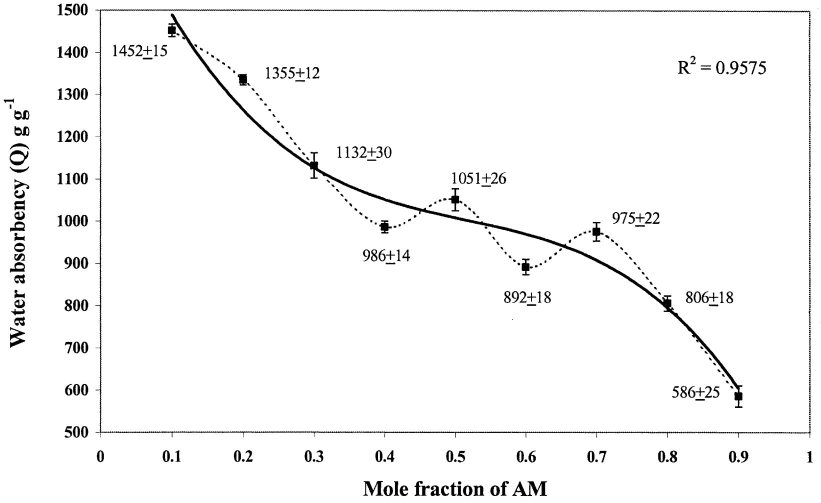

Figure 3. Effect of the mole fraction of AM on the water absorbency (Q) of the synthesized copolymers.

MBA crosslinking agent, produced a high water absorbency value of 1452±15 g g^{-1}. Water absorption capacity decreased with increasing mole fraction of AM, because chain transfer to the polymer increased with monomer concentration. In particular, at mole fraction 0.9 of AM, the water absorbency value was only 586±25 g g^{-1}. The chain transfer reaction, which results in increasing amounts of branching chains, and self-crosslinking reactions of imidization, by the amide moiety, affects the product's properties.[6] The critical mole fraction of AM at 0.1, with no pre-neutralization of acrylic acid, produced the superabsorbent polymer with the highest water absorption; this result indicated that one of the side reactions could be crosslinking of the copolymer with an appropriate crosslinking agent whose concentration is 4.0×10^{-3} mol dm^{-3}. Actually, the structure of the copolymer consists of more acrylamide units than acrylate units owing to the higher hydrophilicity of the carboxylate group, although the reactivity of AM is lower than that of sodium acrylate, because the copolymerization reactivity ratios of acrylamide and sodium acrylate are 0.355 and 2.852, respectively.[5] In contrast, if the flexibility of polymer chain were another important factor, the water absorbency should have been decreased with increasing concentration of acrylate units in the polymer chain, since the glass transition temperature (T_g) of sodium acrylate, 194°C (467 K), is higher than that of acrylamide, 165°C (438 K).[7] The water absorbency of the crosslinked copolymers synthesized with various mole fractions of AM and the degree of neutralization of acrylic acid are shown in Figure 4.

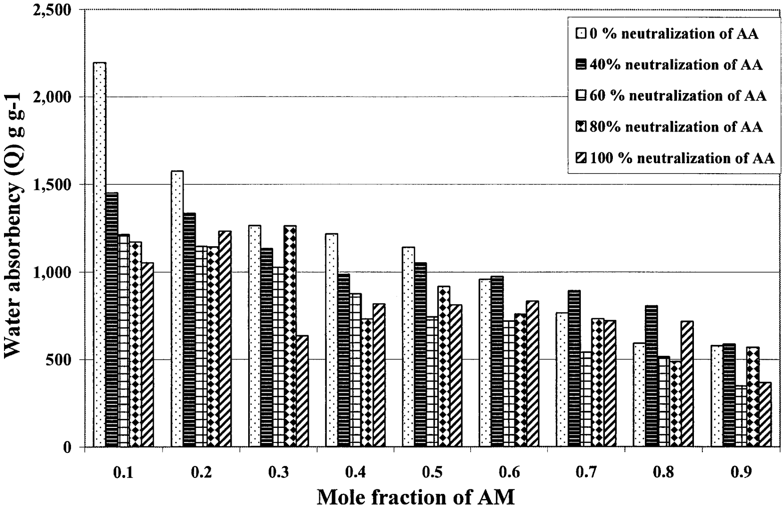

Figure 4. Water absorbency (Q) of the synthesized copolymers vs. mole fraction of AM and the degree of neutralization of acrylic acid.

Water absorbency decreases with increasing degree of neutralization of AA. Partial neutralization of acrylic acid before polymerization did not give the highest water absorption, compared with the non-neutralized AA. Surprisingly, the non-preneutralized AA gives the highest water absorption. However, in the presence of the blowing agent ($NaHCO_3$), the AA portion was eventually neutralized by the concentration of the sodium ion in the solution. Likewise, the preneutralized AA could probably be further neutralized. The presence of 0.1 mole fraction of AM is considered important similarly to the effect of crosslinking agent. Without both of them, the swelling ratio may exceed 2000, possibly compromising gel strength. The gel might then behave just like slightly viscous water, or it may not hold water effectively.

We found that the superabsorbent polymer is a viscous gel. We anticipated that AM could contribute to chain stiffness due to its relatively hydrophobic nature compared to that of sodium acrylate; the association of the amide function groups may also take place. The hydrophobicity of AM contributes to the gel strength of the superabsorbent polymer. Also, N-MBA provides the crosslinking reaction to acrylate portion. We needed to mention that the pre-neutralization of acrylic acid was performed before polymerization, owing to the ease of neutralization of the liquid monomer. As a drawback, sodium acrylate polymerizes less readily than acrylic acid, because ionized monomers react more slowly in the propagation step of polymerization. Higher percentages of soluble polymer and higher residual monomer concentrations in the final product can result. Because an excess amount of sodium bicarbonate was used as a foaming agent, one must consider that there is sodium bicarbonate left in the reaction solution, which can neutralize AA to become sodium acrylate, which is very water soluble.[9]

Flory described the mechanism of swelling of an ionic network.[10] If the polymer chains making up the network contain ionizable groups, the swelling forces may be greatly increased as a result of the localization of charges on the polymer chains. When the crosslinked copolymer is neutralized with sodium hydroxide, the negatively charged carboxyl groups attached to the polymer chains set up an electrostatic repulsion, which tends to expand the network. The concentration of sodium ions also increases with an increase in the degree of neutralization of AA. Sodium ions, which screen the negative charges of carboxyl groups, reduce the electrostatic repulsion tremendously, leading to the decrease in water absorption.

The water absorbency of synthesized copolymer depends not only on the degree of neutralization of AA, but also on the mole fraction of AM, because the electrostatic repulsion may be decreased with an increase of the mole fraction of AM, resulting in decreased water absorbency (Q).

Swelling kinetics in distilled water

Swelling rates were measured for the superabsorbent polymer prepared with AM/AA ratio of 1:9 and without neutralization. This gel absorbed distilled water up to 1628±14 g per gram dry weight of the polymer within 10 min. After 20 min, water absorption rate reached a plateau and remained constant afterwards. The factor determining the swelling time of the dried porous superabsorbent polymer is the time needed for water to enter into the gel matrix and cover most of the surface of the pores. We can determine them by the effectiveness of the capillary action and wettability of the pore surface. The swelling kinetics of superabsorbent polymer can be studied by application of a first-order kinetic expression based upon Fick's second law of diffusion,[9] where C is concentration of the diffusing species, D is the diffusion coefficient of C, and r is the diffusion path length. For a spherical particle, the diffusion equation reduces wherein the rate of swelling is first-order in the amount of swelling capacity remaining unswollen at any time, as given by Equation 1. The values of Q_{max} and Q are the swelling capacities at equilibrium and at the any time t. The first-order rate constant, k, depends on particle radius and on the diffusion coefficient[9] as shown in Figure 5.

$$Q(t) = Q_{\max}(1 - e^{-kt}) \qquad (1)$$

In this model of the dynamic swelling processes, the structural features of the polymer and system affect the maximum swelling capacity Q_{max}. In practical applications, not only a higher swelling capacity, but also a higher swelling rate is required for the absorbent. The synthesized copolymer is also characterized by its rapid swelling kinetics as presented in Figure 5.

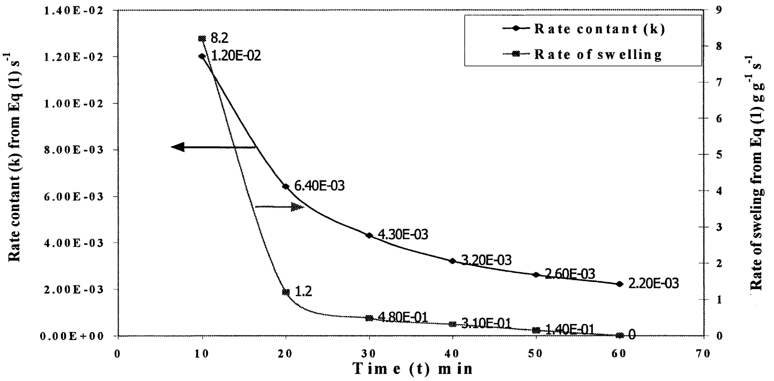

Figure 5. Swelling kinetics of the synthesized copolymer

From the plot of Q vs. time, one gets a slope of the swelling kinetics of 27 g $g^{-1}s^{-1}$. One can also calculate the rate constant of swelling (k) from the first-order kinetics at any time, t, and the k value decreases steadily with time. The k value depends on the diffusion coefficient and the particle radius. We found that the rate of swelling decreased with increasing swelling time. The swelling rate became stable or constant within 20 min, with a rate constant for swelling of 6.4 x 10^{-3} s^{-1}, and a swelling rate of 1.2 g g^{-1} s^{-1}. The faster swelling was then accompanied by a higher degree of swelling.

Conclusions

Superabsorbent polymers of poly[acrylamide-*co*-(acrylic acid)] were synthesized through a crosslinking copolymerization of acrylamide and acrylic acid in the presence of N, N'-methylenebisacrylamide crosslinker under the influence of carbon dioxide gas bubbles, stabilized by a triblock copolymer of polyoxyethylene/polyoxypropylene/ polyoxyethylene stabilizer, from the chemical reaction of acrylic acid and sodium carbonate. The resulting superabsorbent polymers have water absorption values as high as 2300 times their dry weight and much faster volume change kinetics than the non-porous absorbent polymers. The polymer made of the non-preneutralized acrylamide/acrylic acid with a ratio of 1:9 (by mole fraction) gave the highest water absorption with a swelling rate constant and swelling rate of 6.4 x 10^{-3} s^{-1} and 1.2 g g^{-1} s^{-1}, respectively. The non-ionic moiety of acrylamide yielded lower water absorption, but the ionic moiety of acrylic acid has higher water absorption. This research further indicates that the high mole fraction of acrylic acid or ionic part of the poly(acrylic acid) moiety in the copolymer contributes significantly to the high absorption values in distilled water, while the acrylamide portion decreased water absorption due to its less hydrophilicity. The soluble portion of the superabsorbent imposes a negative effect on water absorption, which is caused by both of the amount of sodium bicarbonate and excessive amount of highly reactive crosslinking agent of N, N'-methylene bisacrylamide.

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