

Ground Particle Size Influence on the Swelling of a Copolymer of AA/AMPS in Water

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ABSTRACT: The influence of the ground particle size on the swelling behavior of a copolymer of AA/AMPS in water was observed to determine the best size considering water absorbency in view of fastest and highest equilibrium swelling. The copolymer gel, from acrylamide and 2-acrylamido-2-methyl-propanosulfonic acid and synthesized in the presence of *N,N*-methylene-bis-acrylamide, was obtained by a radical solution technique, and identified by FTIR spectroscopy. By grinding, various particle diameters were obtained, and then separated by sieves. Studies of dynamic and equilibrium swelling in deionized water at 20°C showed the influence of the particle size on the

kinetics of swelling and its equilibrium swelling capacity. A mathematical model for the absorption, including diffusion and relaxation modes, permitted to assess the absorption mechanism, and offered quantitative information about water diffusivity in the copolymer. The fastest swelling was obtained with diameters of 22.5–215 µm. Particle sizes ranging from 67.5 to 355 µm yielded the greatest equilibrium swelling, with mass ratios of about 1100. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3413–3418, 2008

Key words: particle size; swelling; AA/AMPS copolymer; absorption mechanism

INTRODUCTION

The control of the particle size of a swelling polymer is relevant regarding its many end uses, namely pharmaceutical, agricultural, and in other industries.^{1,2} In agriculture, the influence of particle sizes between 0.2 and 0.6 mm has been referred³ to affect efficiency in the use of fertilizers and herbicides. The swelling behavior is of great importance in the efficiency of the polymer to capture water, when used as water retention medium in the soil. If water absorption is slow, a significant drainage of water will occur, but if it is rapid, a higher efficiency in water retention is to be expected. The swelling of an absorbent polymer depends on various factors, mainly the particle size, the structure of its network, and the liquid to be absorbed.^{4,5} The structure is influenced by the technique of copolymerization and by several parameters adjustable during the synthesis, namely: concentration and type of the monomers,^{6–8} of the crosslinker^{9,10} and of the initiator,¹¹ reaction time, temperature, and pH.^{12,13} The technique of radical solution copolymerization was selected because of its advantage in avoiding further

purifications. It has been observed that the swelling depends on the liquid to be absorbed, water in this study, and the operating conditions (pH of the medium, nature and concentration of salts present in the liquid).^{14–16}

The objective of this work was, by grinding the copolymer synthesized, to find the best particle size to achieve a rapid swelling, i.e., a large solute-polymer diffusion coefficient, and a large amount of absorbed water. To obtain the copolymer gel to be used in the study, the monomers chosen were acrylamide (AA), 2-acrylamido-2-methyl-propanosulfonic acid (AMPS) and bis-acrylamide (BA), with the solution technique as the method of polymerization. The monomers were chosen due to the low cost of AA and, for AMPS, its compatibility with water and high tolerance towards divalent cations,¹⁷ thereby maintaining its capacity for propagation. The polymerization technique was chosen instead of the emulsion technique, which, although producing more regular particles, needs a further purifying step. To obtain suitable polymer particles, in the solution technique, the polymer must then be dried and ground to different particle sizes, so that the influence of this variable on the kinetic and equilibrium swelling may be studied, a range of its values being then considered.

The copolymer gel synthesized, whose structure is shown in Figure 1, was characterized by FTIR spectroscopic structure analysis, specific gravity, and granulometry. The equilibrium and the dynamic swelling of the copolymer synthesized were observed

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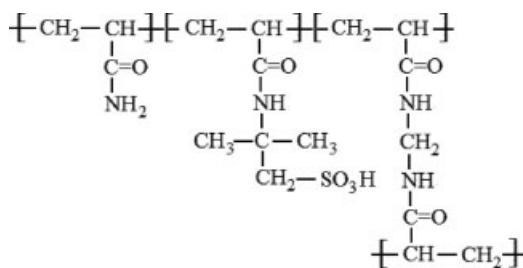


Figure 1 Structure of the repeating unit in the copolymer synthesized.

in deionized water at 20°C, at different particle sizes. It was considered that the final shape of the particles, which resulted from grinding the copolymer synthesized, was considered approximately spherical, an assumption underlying the application of a suitable mathematical model for the kinetics. The model adopted to describe the kinetics of swelling of the copolymer was proposed by Berens and Hopfenberg.¹⁸ This model considers both Fickian diffusion and the polymer relaxation, with good fit to data, as attested in the research of these authors. The dependence of the water diffusion coefficient on the particle size was then considered on the basis of that model, permitting to assess the diffusion-relaxation absorption mechanism and the values of the diffusion coefficients.

EXPERIMENTAL

The synthesis of the copolymers reported was carried out by radical solution polymerization, and the copolymers obtained were studied regarding the particle size and its influence on swelling, both the equilibrium swelling and the kinetics of the absorption process.

The monomer AA and the crosslinking agent BA were supplied from Resiquímica, SA (Sintra, Portugal) and the monomer AMPS from Lubrizol Corporation (Wickliffe, OH), and the free-radical initiator potassium persulfate was supplied by Merck (Sintra, Portugal). Aqueous sodium hydroxide for adjustment of the pH of the monomer solution was supplied by Fisher Chemicals ("Garal," Lisbon, Portugal).

The following aspects are dealt with in this section: copolymer synthesis, characterization (FTIR spectroscopy, specific gravity, and granulometry), and measurement of equilibrium and kinetics of swelling.

Copolymer synthesis

The copolymerization of AA was carried out with cationic monomer AMPS, BA being the crosslinking

monomer. The copolymerization technique used was free radical solution copolymerization, having been carried out in aqueous solution at 50°C by using potassium persulfate as the free radical initiator. The copolymerization took place in a reactor equipped with a stirrer, a reflux condenser, a thermometer, a dropping funnel, and a gas inlet tube.

In the free radical solution copolymerization technique adopted, the monomers AA (itself a 50 wt % solution) and AMPS and BA as the crosslinker were dissolved in distilled water. The monomers, AA and AMPS, were in a molar ratio of 30 : 70, and BA in a molar ratio of 0.5% to the monomers. This aqueous phase was placed in the reactor at room temperature, and the pH value of the monomer solution was adjusted to 10 by drop-wise addition of aqueous sodium hydroxide.

A solution of potassium persulfate in distilled water was prepared. Prior to the injection of this solution, the reaction mixture was deaerated for 3 h. For this purpose, nitrogen was bubbled into the mixture at a slow rate while permanently stirring, and the mixture was heated to 50°C. The initiator solution of potassium persulfate was added by the top of the reactor. The reaction solution was then polymerized at 50°C, as mentioned, for a further 5 h, keeping the nitrogen flow. After the reaction completion, the copolymer was cooled to room temperature and isolated through precipitation of the product by mixing the solution with acetone. Finally the copolymer was dried in an oven at 60°C. The copolymer was then reduced to particles by grinding, as referred to below.

Characterization by FTIR spectroscopy

The copolymer synthesized was characterized by FTIR spectroscopy to confirm the copolymerization reaction, and to check the structure of the copolymer. FTIR spectra were recorded from a sample wafer of copolymer with KBr on a Perkin-Elmer 1600 Fourier transform infrared spectrophotometer. FTIR spectra of the monomers were included in a previous article¹⁹ and the one of the copolymer is shown in Figure 2. Typical peaks of primary amides, namely two N—H stretching, C=O stretching, and N—H deformation, were observed at about 3300, 1700, and 1550 cm⁻¹, respectively, which are characteristic.²⁰⁻²² The asymmetric and symmetric vibrations due to the SO₂ group in the sulfonic acid were also observed at about 1200 and 1000 cm⁻¹.²³ The absorption at 3000 cm⁻¹ appears to be characteristic of the stretching mode of OH groups bonded to SO₂. Most noticeable is that the C=C peak at 980 cm⁻¹ of the vinyl monomer is completely absent in the spectrum, which confirms evidence of the copolymerization of the monomers.

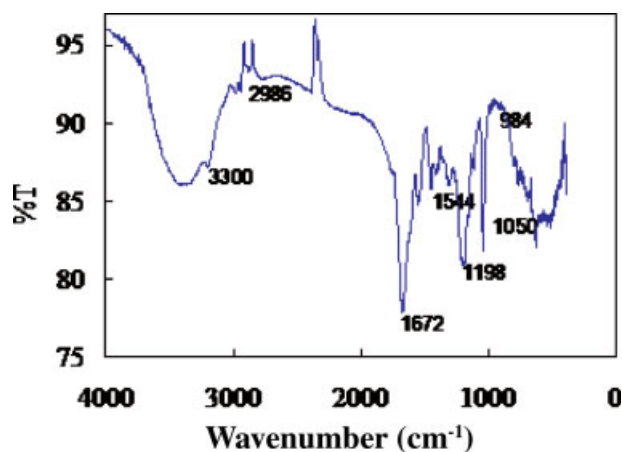


Figure 2 FTIR spectrum of the copolymer synthesized. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Characterization by specific gravity and texture

The specific gravity of the copolymer was determined by using a calibrated double-stem pycnometer. The calibration of the pycnometer was done with distilled water, and the volume of the pycnometer and all the measurements were accurately determined at $20^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$, the pycnometer being immersed in a controlled water bath.

With the exact volume of the pycnometer, the specific gravity of the copolymer was determined. Heptane is used as test liquid because the copolymer under measurement had shown no detectable solubility or swelling when immersed in this liquid. For the determination of the specific gravity, the copolymer sample was weighed dry and placed in the pycnometer, which was then filled with the test solution. Upon weighing again, the mass of heptane was calculated as the difference. As the specific gravity of the test solution is known, its volume is directly calculated leading to the volume corresponding to the dry polymer sample. The specific gravity is thus estimated as the quotient of the dry mass to the volume.

To observe texture, in an attempt of a better understanding of the swelling behavior, a fragment of the copolymer was taken before grinding and then viewed by electronic microscope photography, as shown in Figure 3, the surface presenting a nonporous, compact aspect.

Characterization by granulometry

As some absorption-related properties of the copolymers depend on the dimension and the superficial area of the particles they are composed of, a classification of the resulting particles according to their

size is needed. For a granulometric analysis, standard screens were used to classify the copolymer synthesized in different size ranges.

To obtain the copolymer as grains, it was placed in a small mill for some seconds to crush until it had a powder appearance. It was then passed through a sequence of 45–355 μm screens. The screens were, as usual, arranged serially in a stack, and the material was loaded at top and then shaken during 15 min. The mean particle diameter retained by a given screen is the arithmetic mean of the aperture of the screen on which the material is retained and the aperture of the next larger screen (with values 45, 90, 125, 180, 250, and 355 μm , the smallest one being considered half the first value).

Measurements of the swelling: Equilibrium and kinetics

Swelling of the copolymer in water was observed, regarding both the equilibrium swelling and the kinetics of absorption. The swelling ratio, s , of the copolymer was measured as ratio of the mass of absorbed water per unit mass of dry copolymer [$\text{g(w)}/\text{g(cop)}$], i.e., $s = \frac{m_t - m_0}{m_0}$, where m_0 is the initial mass (dry copolymer only) and m_t is the mass of wet copolymer, measured at time t . The swelling ratio was measured at time intervals (by the “tea bag” technique), by weighing granules of the copolymer, till equilibrium was reached. The granules were swollen in deionized water at 20°C .

The procedure used for following the sorption kinetics experiments was to place weighed samples of dry copolymer in a glass with an excess of deionized water. The temperature of the penetrating liquid was controlled to within 0.01°C by using a thermostat unit. Periodically, the copolymer was

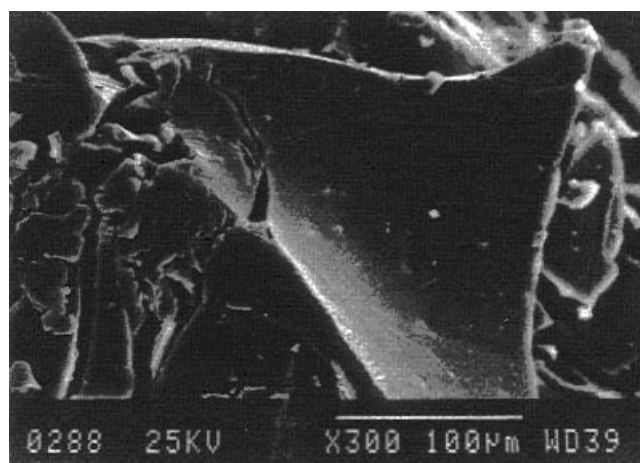


Figure 3 Electronic microscope photography of the synthesized copolymer AA/AMPS/BA in solution.

TABLE I
Equilibrium Swelling^a of the Copolymer AA/AMPS/BA of Different Particle Sizes in Water

Particle size (μm)	22.5	67.5	107.5	215.0	302.5	355.0
Equilibrium swelling	660	1000	1200	1250	1200	1100

^a Wet mass per dry mass.

removed from the water and weighed, after the excess water was removed from the sample. From the dry and the wet mass values, the water content was calculated, the swelling ratio being defined as mentioned above (wet mass divided by dry mass).

The swelling measurements were performed in triplicate to reduce the experimental error.

RESULTS AND DISCUSSION

From the copolymer characterization, it was concluded that the reaction took place, by the observation of the FTIR spectrum, as referred. The specific gravity was 1.3 (with measurements in the range 1.27–1.32), and the copolymer presented a solid aspect under observation by electronic microscopy.

To reveal the effect of the particle diameter of the copolymer on the swelling behavior, swelling experiments were conducted with the AA/AMPS/BA copolymer at a temperature of 20°C. The swelling behavior of the copolymers was characterized by measuring both the kinetics of swelling and the equilibrium swelling reached, for a sequence of six diameters.

The equilibrium swelling data are shown in Table I, with each value being the average of three determinations, with deviations from the average not exceeding 5% (mostly 2–3%) and standard deviations in the range 13–16 (or coefficients of variation in the range 1–2.5%). Among the diameter values used for the measurements, the swelling ratio was found to average about 1100 (in the range 1000–1250) g(w)/g(cop), not including the smallest diameter. This diameter, 22.5 μm , yields a swelling ratio of only 660, deviating from the other ratios. This is possibly due to agglomeration, more likely to occur in small particles, leading to significant diameter heterogeneity and hindrance to water intake to the absorbent material. Besides this smallest particle diameter, the variation of the surface to volume ratio, expected to favor smaller particles, did not affect the equilibrium swelling significantly, in the range of diameters studied.

The other aspect of the swelling behavior to be considered here is the kinetics of swelling. A mathematical model selected to explain the absorption kinetics will be shown later in this article.

In Figure 4, the experimental points and the corresponding curves calculated by the model are shown,

two plots being used for a better visualization, each with a subset of the diameters tested. The fraction swelling in water, r , of the copolymer, for these diameters, is represented versus \sqrt{t} , as usual, with the advantage of revealing the Fickian behavior, if prevalent, through the presence of an initial straight line (usually considered till at least about 50% swelling). Because of the rapidity of the beginning of swelling, this initial section cannot be clearly

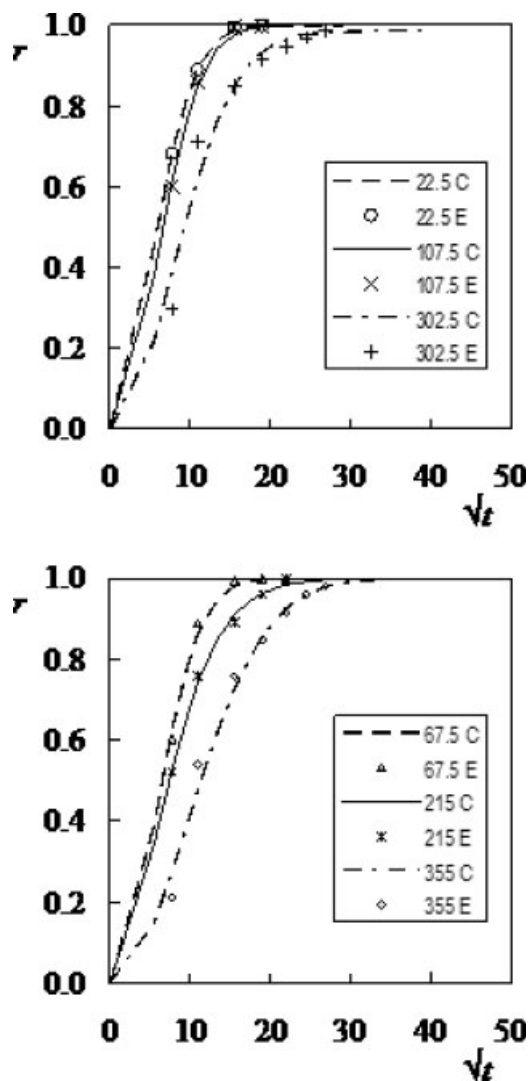


Figure 4 Fraction swelling in water, r , versus \sqrt{t} ($\text{s}^{1/2}$), with varying particle diameters (range 22.5–355 μm , alternately distributed in the two figures): experimental points (E) and calculated curve (C).

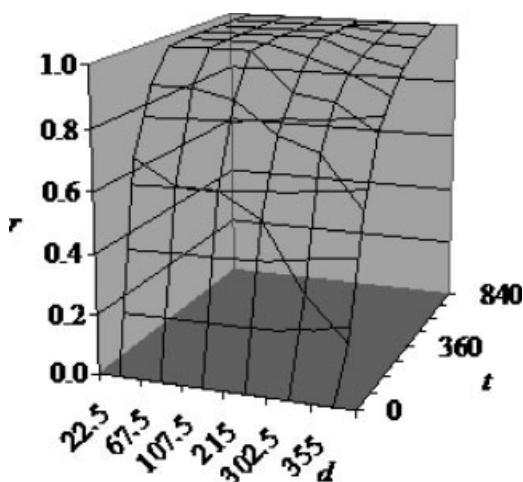


Figure 5 Fraction swelling, r , versus time, t (s) and diameter, d (μm).

observed experimentally, the conclusions coming from the model. For the largest particles (in both graphs), points with $r < 0.5$ can be observed, these plots showing a shape nearer to the sigmoid type, as is characteristic of the predominance of the relaxation mode of absorption. Observing the water absorption curves, it is found that the absorption rate of the copolymer was, as expected, fastest for the smaller particles, and the swelling reached equilibrium in a time of about 480 s ($\sqrt{t} = \sqrt{480} \approx 22$ in the plot).

In Figure 5 the joint effect of the two variables, diameter and time, on the swelling ratio is shown. For all the diameters, the swelling equilibrium is reached at least at about 480 s; and for a given time, it can be viewed that for the smaller diameters the greater swelling ratios are obtained, irrespective of the absolute swelling obtained (Table I).

To verify if there is a significant influence of the particle size on the swelling kinetics, some diameter values were tried, particle sphericity being admitted. This approximation is shown below to be reasonable, as far as the agreement with experimental data is concerned. In the interpretation of the absorption kinetics experiments, the following model, proposed

by Berens and Hopfenberg for the swelling fraction,¹⁸ $r(t)$, was chosen, as already mentioned:

$$r(t) = w_F \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 k_F t) \right] + w_R [1 - \exp(-k_R t)] \quad (1)$$

In this equation, t is time along which swelling takes place, w_F and w_R (with $w_F + w_R = 1$) are the Fickian and relaxation contributions, and k_F and k_R are the rates of diffusion and relaxation, respectively (with n summation index). In the latter term, only one term contribution is retained (instead of a possible weighted sum of contributions).²⁴

From the application of the kinetic model, a good agreement of the model with the experimental data was obtained. A plot with the experimental and the calculated points is given in Figure 4. The data obtained from the kinetics of swelling of the different particle sizes were fitted into eq. (1) to find the best values of the rates of Fickian diffusion and of relaxation. These values are shown in Table II. Diffusivity is estimated from its relation to the Fickian rate of diffusion, k_F , through the expression $D = k_F d^2 / (4\pi^2)$, from the underlying diffusion theory.²⁵

The results of the effect of the particle diameter on the swelling behavior indicate that for the smaller diameters, till 107.5 μm , the diffusion and relaxation rates are of the same order of magnitude, or even similar, $k_F \approx k_R$; and that for the larger diameters, the diffusion rates become smaller than the relaxation rates, $k_F < k_R$. The two contributions were detectable, but of different weights, and in the larger particles the greater effect is from relaxation, as seen from the form of the kinetics curves (Fig. 4). In the cases described, when the diameter increases, the diffusion rate k_F is smaller (more difficult advancement of the penetrant, water). Some estimated values of diffusivity are affected by the minute contribution of the Fickian absorption (Table II). The values of diffusivity of water in the copolymer particles approximate $1.0 \times 10^{-8} \text{ cm}^2/\text{s}$, values deriving from the diffusion rate and the particle diameter.

TABLE II
Effect of the Particle Diameter on the Swelling of the Copolymer:
Calculated Constants^a

d , μm	22.5	67.5	107.5	215	302.5	355
w_F	0.18	~ 0	~ 0	0.38	0.03	~ 0
w_R	0.82	1	1	0.62	0.97	1
k_F , (s^{-1})	1.8E-02	2.1E-02	1.6E-02	5.6E-03	3.7E-04	9.9E-04
k_R , (s^{-1})	1.8E-02	1.6E-02	1.6E-02	1.3E-02	8.4E-03	5.4E-03
D , (cm^2/s)	2.3E-09	2.4E-08	4.6E-08	6.1E-08	8.6E-09	3.2E-8

^a $D = k_F \frac{d^2}{4\pi^2}$.

CONCLUSIONS

The swelling behavior of a superabsorbent copolymer was investigated for different particle sizes, the particles being considered approximately spherical. The particle diameter of the ground superabsorbent was found to affect the swelling rate and equilibrium swelling capacity.

By comparing the equilibrium swelling in the set of diameters studied, we found that the smallest particle, sized 22.5 μm , was the least efficient, as the equilibrium swelling capacity reached was 660 g of water per gram of copolymer. This capacity was not substantially affected by the particle diameter for all the other diameters studied. For the copolymer synthesized, the data obtained indicate that the suitable diameters for a good swelling capacity are greater than 67.5 μm , leading to about 1100 g(w)/g(cop).

Measurements of the rate of swelling of the superabsorbent in water showed rates depending on the diameters of the particles. The fastest swelling was attained in particles with a diameter in the range 22.5–215 μm .

A good fit to the kinetics of swelling was obtained using the Berens–Hopfenberg model. This model can explain the characteristic curve shapes for absorption of water in this superabsorbent, in the two basic absorption modes considered, diffusion and relaxation. Namely, based on the diameter 215 μm , which provided the largest swelling ratio, the values of the diffusion and relaxation rates are $k_F = 5.6\text{E-}3 \text{ s}^{-1}$ and $k_R = 1.3\text{E-}2 \text{ s}^{-1}$, respectively, with a diffusivity of $D = 6.1\text{E-}8 \text{ cm}^2/\text{s}$. For the remaining diameters, these parameters vary, having nevertheless values in the same orders of magnitude.

This study has implied that the particle size is a parameter to be considered when the swelling of this kind of polymers is addressed.

NOMENCLATURE

D	diffusivity, cm^2/s
d	particle diameter, cm or μm
k_F	diffusion rate constant, s^{-1}
k_R	relaxation rate constant, s^{-1}

Indices

F	index for Fickian diffusion
M_t	mass of copolymer (dry or wet), as a function of time, t , g (m_0 initially)

R	swelling fraction (current swelling ratio, s , over its final value)
s	swelling ratio
t	time, s
w_F, w_R	contributions for swelling: F , Fickian, R , relaxation
R	index for relaxation

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