Improvement in the Water-Absorbing Properties of Superabsorbent Polymers (Acrylic Acid-*co*-Acrylamide) in Supercritical CO$_2$

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ABSTRACT: Superabsorbent resins prepared by ultraviolet radiation-inducing polymerization techniques with acrylic acid/acrylamide were treated with supercritical carbon dioxide (SC-CO$_2$). The water-absorbing properties of the treated resins were greatly improved. The water-absorbing properties of resins treated with SC-CO$_2$ in the pressure range of 10–35 MPa and the temperature range of 40–60°C were studied. The effects of the treatment time and depressurizing speed of CO$_2$ after treatment were also examined. Obviously, different results were found for particles of different sizes. Smaller particles were more efficient under the same treatment conditions. Samples were tested with differential scanning calorimetry. The results showed that the plasticizing effect of CO$_2$ reduced the glass-transition temperature of the polymer, and it was proposed that the plasticization effect might have led to polymer chain redistribution and better flexibility. Minor changes in the surface morphology of the particles were observed with scanning electron microscopy. The extraction of the unpolymerized monomers by SC-CO$_2$ was also studied. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2272–2278, 2002

Key words: superabsorbent resin; supercritical carbon dioxide; absorption; photopolymerization; poly(acrylic acid-*co*-acrylamide)

INTRODUCTION

Supercritical fluid has attracted the attention of chemical engineers for many years because of its adjustable solvent properties. Supercritical carbon dioxide (SC-CO$_2$) is a nonflammable, nontoxic, and relatively inexpensive environmentally benign fluid. It has moderate critical conditions (T_c = 31.1°C, P_c = 7.38 MPa) that make it convenient for many applications. In polymer engineering, SC-CO$_2$ can be used as a polymerization solvent and as a foaming agent. It also can be used to plasticize many polymers. There are many investigations concerning the effects of CO$_2$-treated polymers. Chen et al.[1] reported that the gas-transport and sorption properties of polycarbonate membranes could be changed after CO$_2$ treatment. Their study showed that the free volume of the membranes increased with an increase in the exposed CO$_2$ density. Mizumoto et al.[2] investigated how the crystalline stereocomplex of isotactic poly(methyl methacrylate) and syndiotactic poly(methyl methacrylate) could form, induced by high-pressure CO$_2$. For the CO$_2$-treated polymer, the average cell size decreased and the average cell density increased as the amount of the stereocomplex that was formed increased. Fourier transform infrared spectroscopy was used to investigate the interactions of CO$_2$ with carbonyl oxygen in polymers, as reported by Kazarian et al.[3] It was proposed that this interaction caused the CO$_2$ plasticizing effect.

Since the U.S. Department of Agriculture[4] reported the first superabsorbent polymer, there has been considerable interest in the preparation and properties of superabsorbent polymers. In a series of investigations, a number of preparation methods have been explored, including solution polymerization and inverse suspension polymerization.[5,6] Photopolymerization is a new method requiring less time and more moderate conditions. In all products, acrylic acid (AA)- and acrylamide (AM)-based superabsorbent polymers have received considerable attention in the last 4 decades.[7–9]

Because of the comprehension of the frame of the polymer networks and the interactions of CO$_2$ with polymers, it can be presumed that the water-absorbing properties are probably affected in SC-CO$_2$. In this work, the effects of SC-CO$_2$ on superabsorbent polymers were investigated under different treatment conditions. Differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were also used

for the determination of the mechanism of the phenomena.

EXPERIMENTAL

Sample preparation

The sensitizer benzophenone (BP; Shanghai Reagent Co., C.R.), AA (Beijing Yili Fine Reagent Co., A.R.), AM (Tianjin Reagent Research Laboratory, A.R.), and sodium hydroxide (Beijing Chemical Plant, A.R.) were all used as received, except that AA was partly neutralized with sodium hydroxide, and the neutralization ratio was 65%.

The photopolymerization process includes three stages—excitation, initiation, and propagation—as shown in eqs. (1)–(3), respectively:

$$BP \xrightarrow{h\nu} [BP]^S \rightarrow [BP]^T \qquad (1)$$

$$(2)$$

$$(3)$$
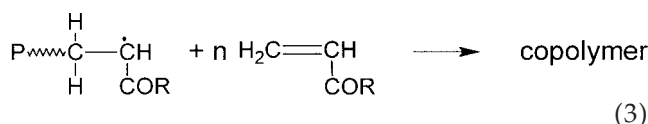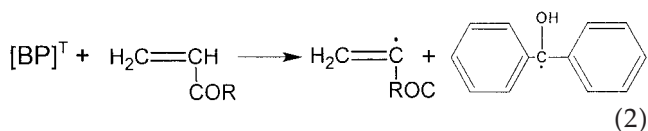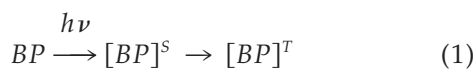
where the superscript S represents the singlet state, T represents the triplet state, and R represents the functional groups —OH, —ONa and —NH$_2$.

Weighed quantities of monomers and BP were dissolved in distilled water until saturation. The reaction medium was deoxygenated with nitrogen before being put into the reaction cell. A 4-mL solution was deposited onto the bottom of the cell. Then, a block of quartz glass was put onto the cell, and deoxygenation continued. The assembled unit (Fig. 1) was irradiated under UV irradiation from the top side at room tem-
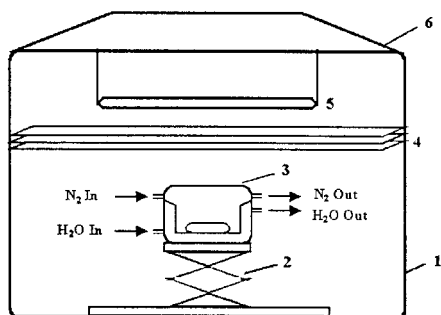
Figure 1 UV irradiation setup for polymerization: (1) obturator, (2) bracket, (3) jacketed vessel, (4) shutter, (5) UV irradiator, and (6) exhaust fan.
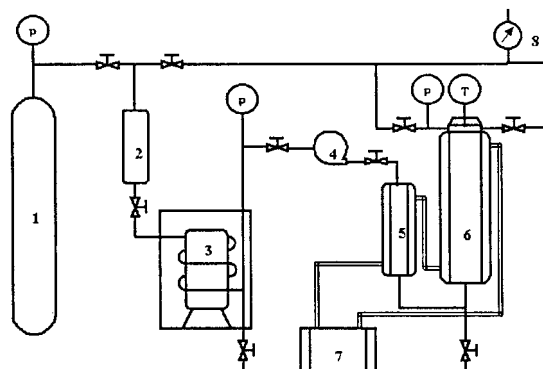
Figure 2 High-pressure apparatus used for treating the polymer samples: (1) CO$_2$ cylinder, (2) filter, (3) cooler, (4) pump, (5) water bath, (6) treatment autoclave, (7) temperature controller, and (8) pressure controller.

perature. The resulting product was cut into small pieces and vacuum-dried at 90°C to a constant weight.

SC-CO$_2$ treatments

As shown in Figure 2, a stainless steel pressure vessel with a jacket was designed for the process. First, the vessel was maintained at the desired temperature for a long time. The particles were put into a small beaker with a mesh cover. The beaker was then loaded into the vessel. The air was removed from the apparatus by CO$_2$ purging. CO$_2$ was pumped into the apparatus until it reached the desired pressure range. This condition was maintained for a given period of time. The CO$_2$ depressurization rate was controlled with a valve system.

Sorption curve measurements

The dry gel prepared by photopolymerization was milled through 20–40-mesh screens. The dry gel (0.0900–0.1000 g) was immersed in water at room temperature. Swollen gel was then separated from unabsorbed water with a 200-mesh screen and weighed every minute. The water absorption in the first 5 min was designed to show the absorbing rate of the gel. Two days later, the equilibrium water absorption was measured. In this study, the water absorption was calculated with the swelling ratio (Q):[10]

$$Q = (W_s - W_d)/W_d \qquad (4)$$

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

Characterization

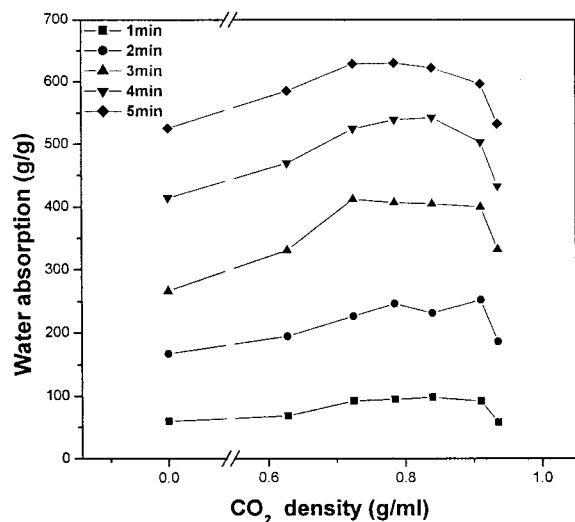A 2910 modulated differential scanning calorimeter from TA Instruments Co. was used to test the polymer

Figure 3　Effect of the CO_2 density on the absorbing properties of the samples treated for 3 h and depressurized slowly.

glass-transition temperature (T_g). The temperature was brought to 0°C with liquid nitrogen and was kept there for 5 min. The thermograms were recorded at a heating rate of 10°C/min. An SEM instrument (Hitachi S-520) was used to observe the polymer morphologies. The samples were prepared by gold sputtering. The acceleration voltage was 20 kV.

RESULTS AND DISCUSSION

Effect of the SC-CO_2 density on the absorbing properties of the polymer

The sample particles in the 300–450-μm range were immerged in CO_2 at a series of pressures and temperatures for 3 h. The pressures ranged from 6 to 35 MPa, and the temperatures ranged from 40 to 60°C. The depressurizing process, at a speed of 2–4 MPa/10 min, was slow. The CO_2 densities, which were calculated by the Peng–Robinson equation,[11] were correlated with the water absorption every minute. As shown in Figure 3, the water-absorbing rate increased with the CO_2 density increasing, up to 0.8 g/mL.

TABLE I
T_g Results of the Samples Tested by DSC

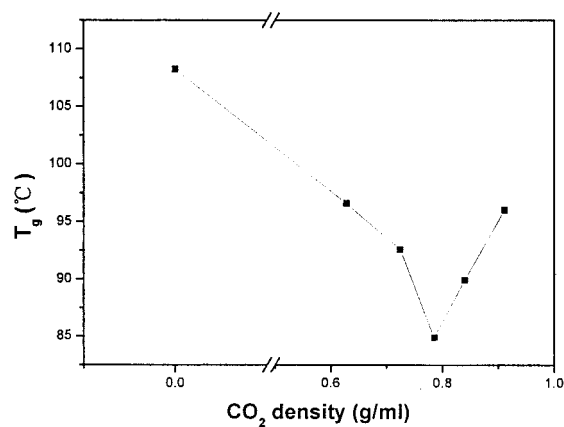| Sample	Temperature (°C)	Pressure (MPa)	Time (h)	T_g (°C)
d				108.26
d1	40.0	30.0	3.00	96.04
d2	40.0	20.0	3.00	89.92
d3	40.0	10.0	3.00	96.59
d4	40.0	20.0	1.00	98.98
d5	40.0	20.0	5.00	84.58
d6	50.0	20.0	3.00	84.92
d7	60.0	20.0	3.00	92.59

Figure 4　Effect of the CO_2 density on the T_g values of the samples treated for 3 h and depressurized slowly.

Beyond 0.8 g/mL, there was a decrease in the water-absorbing rate with the CO_2 density increasing.

As shown in Table I, the DSC results indicated that T_g's of the treated samples decreased. These results proved that the free volume of the treated samples increased. As a good plasticizing agent, SC-CO_2 mobilized the polymer chains of the samples. The more flexible chain framework improved the water-absorbing properties of the polymer. We correlated T_g with the density of CO_2, and the result is shown in Figure 4. The equilibrium absorption results are shown in Figure 5. In comparison with Figure 3, Figure 4 shows a decreasing trend for T_g the corresponds to the increasing trend for the water-absorbing rate. The lowest T_g occurred at the CO_2 density of 0.8 g/mL in Figure 4, and the water-absorbing rate of the polymer was most rapid at the same treatment density. This result reflected the relationship between the free volume, which reflected the chain flexibility of the polymer, and its water-absorbing rate. That is, the more flexible the polymer chains are, the more rapid the water-absorbing rate is for the polymer.
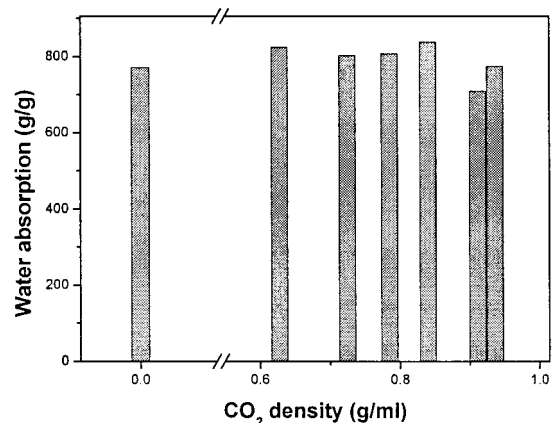

Figure 5　Equilibrium absorption capacity of the samples treated for 3 h and depressurized slowly.
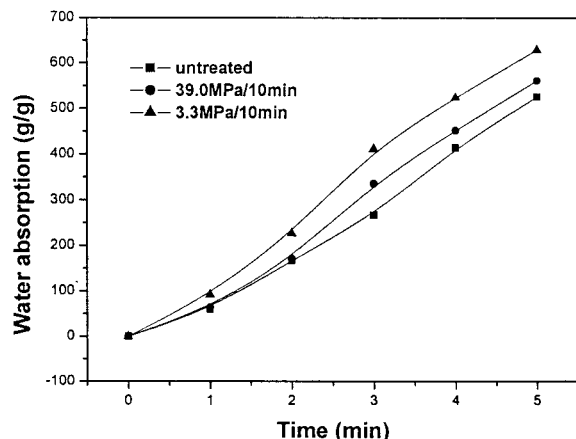
Figure 6 Effect of the depressurizing speed on the absorbing curve for the samples treated at 60°C and 20 MPa for 3 h.

Effect of the depressurizing speed after treatment on the absorbing properties

In the experiment, we controlled the depressurizing speed with a valve system. There were some differences in the polymer absorbing curves for different depressurizing processes. Particles that were in the depressurizing speed range of 20–40 MPa/10 min and particles that experienced the same treatment conditions and a different depressurizing speed range of 2–4 MPa/10 min were compared. Figures 6 and 7 show that the water-absorbing speed of the particles treated by the higher speed depressurizing process was degraded. A coherent phenomenon for the particles could be observed in the high depressurizing speed process. In this process, the sudden release of CO$_2$ from the polymer induced the abrupt shrinkage of the swelling particles. It was assumed and proposed that the high depressurizing speed process of CO$_2$ could induce a decrease in the flexibility of the polymer chains like the thermal annealing process. A thermal annealing process can make a polymer
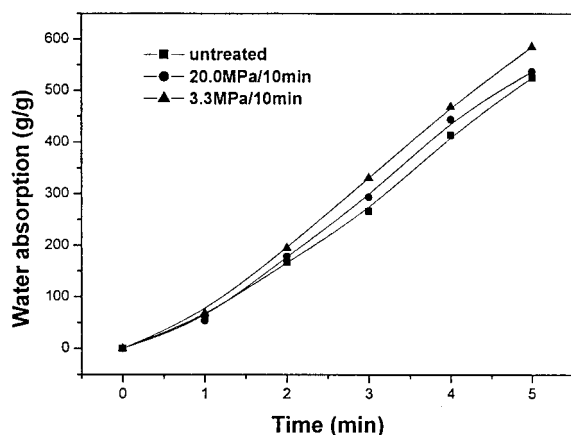

Figure 7 Effect of the depressurizing speed on the absorbing curve for the samples treated at 40°C and 10 MPa for 3 h.
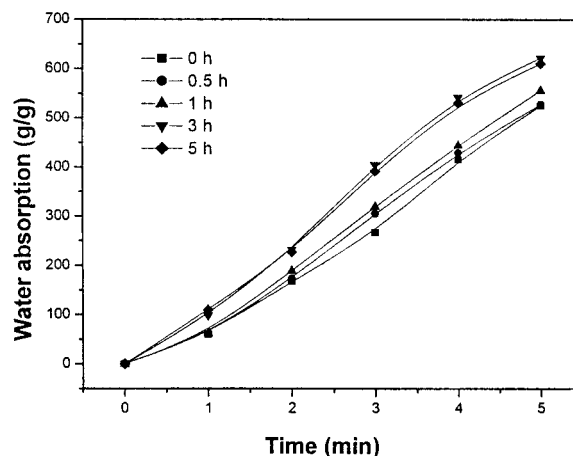

Figure 8 Effect of the CO$_2$ treatment time on the absorbing properties of the samples treated at 40°C and 20 MPa and depressurized slowly.

crisp, and so it would affect the water-absorbing properties of the polymer. Therefore, a slow depressurizing process was necessary for the whole experiment.

In Figure 3, the water-absorbing rate of the samples is shown decrease with a CO$_2$ density greater than 0.8 g/mL. This can be attributed to a relatively rapid depressurizing process after the treatment. It was harder to control the release speed of the higher density CO$_2$ for most valve systems during the initial depressurizing process. Therefore, selecting a proper CO$_2$ density and a corresponding depressurizing speed was an important step for better absorption properties.

Effect of the treatment time on the absorbing properties of the polymer

The effects of the CO$_2$ treatment time on the water-absorbing properties are shown in Figure 8. The depressurizing process was slow. The water absorption of the samples obviously increased with the increasing treatment time in the first 5 min. A higher degree of swelling in CO$_2$ could be attained with a longer swelling time. It would lead to polymer chain redistribution and better chain flexibility. With the treatment time extended, the swelling degree would reach an upper limit.

Different effects on polymer particles of different sizes

Figures 9 and 10 show the water absorption of the samples with diameters of 300–450 μm and less than 300 μm at 20 MPa and 40°C. The water-absorbing curves of the smaller particles are very different from those of the bigger particles. The water-absorbing rate of the smaller particle was faster, and it reached absorption equilibrium in a shorter period of time. Com-
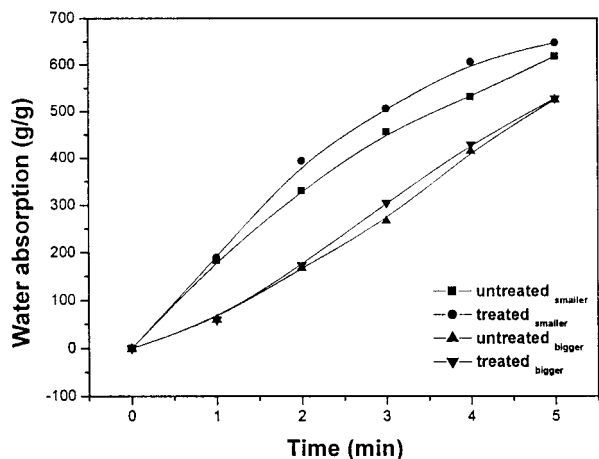
Figure 9 Effect of the particle size on the absorption properties of the samples treated at 40°C and 20 MPa for 0.5 h and depressurized slowly.

paring the water-absorption curves before and after treatment, we find that the effect on the smaller particles was more efficient than that on the bigger particles in the same treatment progress. A possible explanation was the rule of solvent transport in polymers. Lin et al.[12] studied the transport phenomenon of solvent–penetrant systems in spherical glassy polymers, and they found that the penetration time for different radii could be predicted. This study indicated that the penetration of SC-CO_2 in the polymer particles was affected by the particle size. In the same treatment time, it could penetrate smaller particles more completely and thereby improve the particle absorbing properties more efficiently.

Morphologies of the polymers by SEM

The photomicrographs in Figure 11 show that the particles were irregular in shape, just like the particles from solution polymerization reported by Omidian et
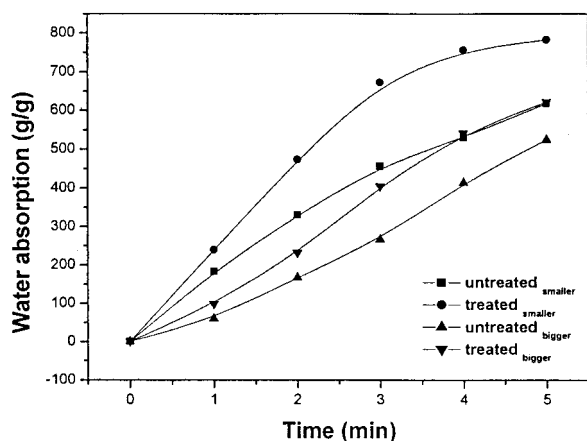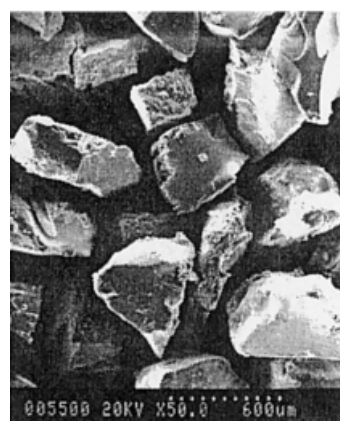

Figure 10 Effect of the particle size on the absorption properties of the samples treated at 40°C and 20 MPa for 3 h and depressurized slowly.

(a)

(b)

Figure 11 Morphologies of the particles by SEM, amplified 50 times: (a) untreated and (b) treated at 40°C and 20 MPa for 3 h and depressurized slowly.

al.[5] This occurred because that the particles were ground in a mortar. The representative particles 300–450 μm in size were photographed, as shown in Figures 12 and 13. It can be observed in Figure 12 that there were some eyelets on the surfaces of the treated samples. The swelling of SC-CO_2 in the polymer formed these defects. These were similar to the defects on the polycarbonate membrane formed by the rapid removal of absorbed CO_2 from the membrane matrix, as reported by Chen et al.[1] There were rougher surfaces on the particle rupture region by abrasion, as shown in Figure 13. The swelling imprint can be observed in the SEM micrographs also. These changes in the sample surface can lead to a slight increase in permeability. However, these minute changes were not enough to affect the absorbing properties of the polymer so efficiently.

Effect of SC-CO_2 extraction on the polymer

The extraction of the unpolymerized monomers by SC-CO_2 was studied by a gravimetric method.

Weight-change data for samples were measured immediately after the treatment process in CO_2. In Table II, we find that the weight changes were very slight under all conditions. A similar experimental method
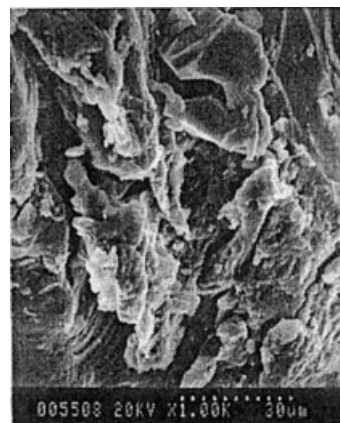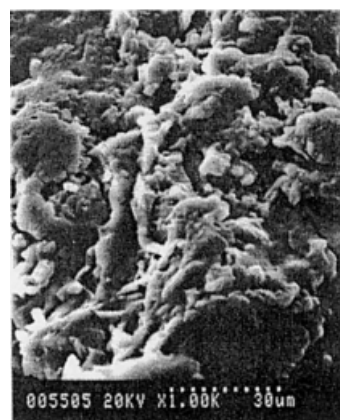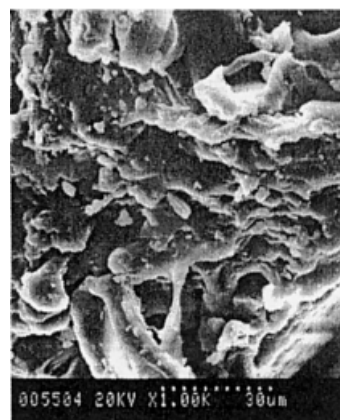

(a)

(b)

(c)

Figure 12 Morphologies of the polymer surfaces by SEM, amplified 1000 times: (a) untreated, (b) treated at 40°C and 20 MPa for 3 h and depressurized rapidly, and (c) treated at 40°C and 20 MPa for 3 h and depressurized slowly.

(a)

(b)

(c)

Figure 13 Morphologies of the polymer surfaces on the particle rupture region by SEM, amplified 1000 times: (a) untreated, (b) treated at 40°C and 20 MPa for 3 h and depressurized rapidly, and (c) treated at 40°C and 20 MPa for 3 h and depressurized slowly.

was introduced in McHardy and Sawan's book.[13] This demonstrates that the extraction of the unpolymerized monomers by SC-CO_2 was very slight, and it was not the main factor affecting the water-absorbing speed under the experimental conditions.

TABLE II
Weight Changes of Samples Treated
with SC-CO$_2$ for 3 h

Sample	Temperature (°C)	Pressure (MPa)	Weight Change (%)
d1	40.0	30.0	0.10
d2	40.0	20.0	−0.21
d3	40.0	10.0	−0.08
d6	50.0	20.0	0.04
d7	60.0	20.0	−0.14

CONCLUSIONS

Superabsorbent polymer samples prepared by ultraviolet radiation-inducing polymerization techniques were treated with SC-CO$_2$.

The effects of CO$_2$ treatment on the water-absorbing properties of the polymer were assessed. It was shown that a proper CO$_2$ density range enhanced the absorbing properties of the samples. A longer treatment time and a slower depressurizing process were also beneficial.

Comparing the water-absorbing properties before and after treatment, we found that the effects on smaller particles were more efficient than those on bigger particles with the same treatment progress. This can be explained by the rules of solvent transportation in polymers.

The DSC results showed that the plasticizing effect of CO$_2$ reduced T_g of the polymer. It was proposed that the plasticization effect could lead to polymer chain redistribution and better flexibility. Minute changes in the surface morphology of the particles were observed with SEM. These changes were not enough to affect the absorbing properties of the polymer very much. The extraction of the unpolymerized monomers by SC-CO$_2$ was very slight and could not affect the water-absorbing speed under the experimental conditions.

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