

Preparation and swelling behavior of moisture-absorbing polyurethane films impregnated with superabsorbent sodium polyacrylate particles

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ABSTRACT: Moisture-absorbing composite films were prepared with superabsorbent sodium polyacrylate particles and solvent-type polyurethane for applications in fabrics. To study the effect of the particle size of sodium polyacrylates on the swelling capacity and deswelling behavior of the composite films, we prepared sodium polyacrylates with different particle sizes ranging from 277 μm to 485 nm. The rate of absorption and the swelling capacity of the composite films were generally observed to increase with decreasing sodium polyacrylate particle size—except that the water absorbency of the composite film containing the very smallest, 485-nm-size, sodium polyacrylate particles was lower than that yielded by the larger particles, perhaps because these very small sodium polyacrylate particles were impregnated inside the polyurethane matrix rather than on the surface. Meanwhile, the deswelling behavior was not significantly affected by the particle size. Differences in the ionic solutions also significantly affected the swelling capacity of the composite film and altered its swelling kinetics. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43973.

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INTRODUCTION

Superabsorbent polymers (SAPs) have attracted considerable attention because of their specific benefits such as their hydrophilic properties, high water absorbency, biocompatibility, and abundant availability.^{1–4} These hydrogels are composed of polyelectrolyte chains that are covalently cross-linked to form three-dimensional polymer networks that are capable of absorbing considerable amounts of water without dissolving itself when in contact with water, saline, or physiological fluid.⁵ Given these advantages, superabsorbent hydrogels can be applied to a wide range of industrial and commercial applications, such as agricultural potting soil, personal hygienic products, baby diapers, medical goods, adult incontinence products, composite materials, and adsorbents of marine pollutants.^{6–14} Absorbents with 70–80% swelling capacity were developed using polyvinyl alcohol (PVA) or acryl amide or polyethylene oxide (PEO), which have high affinities for water and are hydrophilic.¹⁵

The majority of present-day superabsorbent polymers are made from partially neutralized acrylic acid (AA) or acrylamide monomer (AM) and cross-linking agent, and have been demonstrated to provide the best ratio of performance to price. There are various methods to prepare superabsorbent polymers by solution polymerization^{16,17} and suspension polymerization.^{18,19} However, these type of traditional synthesis methods generally

require expensive equipment and need a long reaction time. Recently, new methods for producing superabsorbent polymers have been developed, and these methods include the use of γ -rays,²⁰ ultraviolet (UV) radiation²¹ or other high-energy radiation.^{22–27} Of these methods, that using UV radiation is simple, can be used to prepare the product with a shorter reaction time, and results in a superabsorbent polymer with an improved swelling capacity and swelling rate.

Hydrophilic polymers synthesized in particle or gel forms can be used in a variety of applications because of their large specific surface areas. Hydrophilic superabsorbent polymers have hydrophilic functional groups such as amides, carboxylic acids, and alcohols. The swollen equilibrium state results from balancing two opposing forces: osmotic forces related to the difference in the ion concentration between the inside and outside of hydrogel driving the swelling; and forces exerted by the polymer chains in resisting such expansion.²⁸ Wang *et al.*²⁸ prepared a very highly water-absorbent sodium polyacrylate with different particle sizes ranging from 10 to 50 μm by inverse suspension polymerization with Span 60 (dispersant) in cyclohexane. Here, the swelling capacity increased with reaction time; this relationship arises because longer reactions times yield smaller particles, which show a higher degree of absorption. Omidian *et al.*²⁹ investigated the dependence of absorption characteristics on

particle size and determined the particle size distributions of products made by carrying out inverse suspension polymerization. According to their results, as the particle size became smaller, the absorption rate and absorption capacity increased. Sohn *et al.*³⁰ prepared sodium polyacrylate polymer by performing inverse suspension polymerization and analyzed the effect of the polymer particle size using sieves and an optical microscope. The water adsorption of smaller particles was observed to be more rapid, and this relationship appears to be due to the larger specific surface areas (that is the larger surface areas per unit of polymer mass) of smaller particles. Therefore, the particles size of the superabsorbent polymer is very important in many applications. Desired features of superabsorbent polymers are high water absorbency, rapid swelling, short deswelling time, and the ability to maintain the swelled state for a prolonged time period. The majority of reported synthesized superabsorbent polymers have been evaluated for the swelling capacity of the particle, swelling rate, crosslinking density, deswelling time, and the effect of the cross-linker in certain applications such as agriculture, hygienic products, drug delivery systems, nonwoven fabrics, and additives in cement.^{1,5,18,31–33} Moreover, the superabsorbent polymer can be manufactured with various matrix (composites) to provide a number of advantages in related fields. To provide the optimal performance of moisture-absorbing composite films, we prepared polyurethane films impregnated with sodium polyacrylate particles for future applications such as sanitary products,^{11,15,23} medical bandages,^{1,23,24,27,34} water blocking products^{33,35,36} in the construction industry, liquid absorbers in food packaging products,³⁷ and fabric products such as car seats, shoes, and sport accessories (headbands, wristbands, etc.) to maintain comfortable circumstances by controlling the moisture absorption. We investigated their equilibrium swelling and deswelling behaviors in solutions such as deionized water, as well as the dynamics of the swelling and the amount of time these particles retained the swelled state. To study the effect of the particle size of sodium polyacrylates on the swelling behavior of the composite films, we used a ball mill to prepare sodium polyacrylates with different particle sizes, ranging from 277 μm to 485 nm. The particle size and concentration of aqueous NaCl solutions are also checked to study the effect on the water sorption kinetics of sodium polyacrylate particles.

EXPERIMENTAL

Materials

Sodium polyacrylate powder (PANa, MW: 20,000–70,000, Wako Pure Chemical Industries, Japan) was used without any purification as a starting material to prepare the composite films, and solvent-type polyurethane was used as purchased from Samsung Chemical, Korea. Toluene, methyl ethyl ketone (MEK), and dimethylformamide (DMF) were purchased from Sigma-Aldrich and used to reduce the viscosity of the solvent-type polyurethane. Others materials used were of analytical grade. In addition, to study the effect of the sodium polyacrylate particle size on the swelling behavior of the composite films, we used a ball mill machine (MSK-SFM-3, MTI Corporation, Richmond, VA, USA) to prepare sodium polyacrylates with different particle sizes ranging from 277 μm to 485 nm.

Preparation of Polyurethane Films Impregnated with Sodium Polyacrylate

To prepare polyurethane films impregnated with sodium polyacrylate, MEK, DMF, and toluene were added to a reactor under stirring at room temperature in order to control the polyurethane viscosity. The content of polyurethane was 15%, and this polyurethane was used as a stock solution for preparing the polyurethane films impregnated with sodium polyacrylate. The sodium polyacrylate particle sizes ranged from 277 μm to 485 nm, and samples containing 0.01–0.05% sodium polyacrylate were added to 15% polyurethane and mixed to obtain homogeneously dispersed solutions. Each solution was poured into a spherical mold with a diameter of 5 cm at room temperature and kept in the mold until it solidified, after which it was placed in an oven at a temperature of 150 $^{\circ}\text{C}$ and kept in the oven for 5 min to obtain the polyurethane film impregnated with sodium polyacrylate.

Measuring Water Absorbency and Deswelling at Various Time Points

The swelling-deswelling characteristics of the prepared polyurethane films impregnated with sodium polyacrylate were measured by carrying out gravimetric analyses. Composite films were immersed in 500 mL of distilled water at room temperature for different durations (t ; 5–300 min). The swollen sample was weighed after removing excess water from the composite film with a paper towel. The water absorbency of the film samples (Q_t ; g/g) was calculated by using the equation

$$Q_t = (m_t - m_o) / m_o \quad (1)$$

where m_o (g) and m_t (g) are the weights of the samples in the dry state and the swollen state, respectively, at a certain time. Q_t is defined as the water absorbency when swelling reached equilibrium. Using the same method, water absorbency values of these films were also determined when they were immersed in salt solutions of various concentrations. All experiments were performed three times, and the results were averaged.

Characterization

The sodium polyacrylate particles sizes were measured by using a particle size analyzer (LS 13 320) as powders. The surface and overall morphology of the polyurethane films impregnated with sodium polyacrylate were imaged using a scanning electron microscope (SEM, Hitachi, S-570, Japan).

RESULTS AND DISCUSSION

Effect of Concentration of Sodium Polyacrylate

One set of composite films was made by combining the contents of 15% solvent-type polyurethane and different concentrations of sodium polyacrylate not subjected to any grinding. Note that the average particle size of such sodium polyacrylate before grinding was about 277 μm . A film was also manufactured using 15% solvent-type polyurethane but without sodium polyacrylate. All of these films were prepared by heating them at 150 $^{\circ}\text{C}$ for 5 min. The swelling capacities of these films immersed in deionized water for various reaction times are shown in Figure 1. There was no change in weight with increasing reaction time when the solvent-type polyurethane film without sodium polyacrylate was immersed in deionized water. The composite films containing sodium polyacrylate, however, did quickly absorb water. For

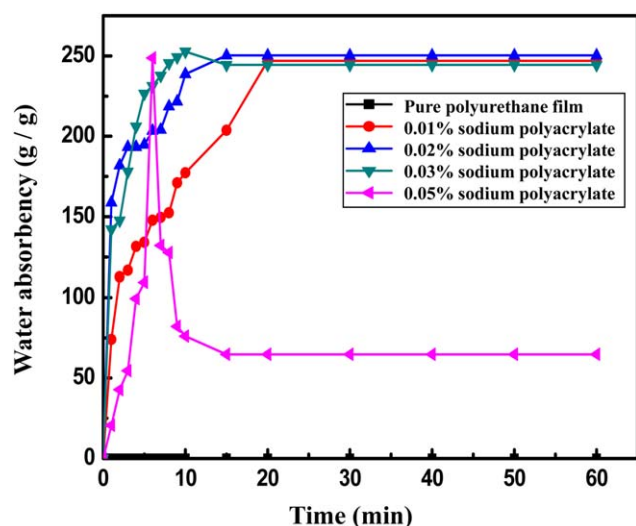


Figure 1. Water absorbency values as a function of absorption time of various concentrations of sodium polyacrylate impregnated in polyurethane films immersed in deionized water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

those films prepared with 0.01 to 0.03% sodium polyacrylate, the water absorbency reached an effective plateau of about 250 g/g within approximately 20 min. For the composite film made with 0.05% sodium polyacrylate, the same 250 g/g water absorbency was reached in less than 10 min, but the water absorbency then decreased with longer reaction times, eventually stabilizing at about 70 g/g. Note also that the initial swelling rate was observed to increase for composite films as the concentration of sodium polyacrylate was increased up to 0.03%. The distinct profile observed for the composite film that contained 0.05% sodium polyacrylate may have been due to it forming a gel caused by the loss of particles in contact with water. Therefore, the maximum water absorbency was reduced and weight loss occurred because of weakening of cohesion of the polyurethane film and the gelled sodium polyacrylate.

Effect of Sodium Polyacrylate Particle Size

In addition to using the sodium polyacrylate before grinding, with its average particle size of about 277 μm , we also ground the sodium polyacrylate to obtain smaller particles. By varying the grinding condition, we were able to produce particles with average sizes ranging between 20 and 136 μm as shown in Table I. Also, to obtaining nanosized sodium polyacrylate particles, samples No 4 and No 5 were reground for different durations to prepare sodium polyacrylate particles with average sizes of 5.34 μm and 485 nm, respectively. A different solvent-type polyurethane-based composite film was prepared from each of the different-sized sodium polyacrylate particles in order to study the effect of the particle size of sodium polyacrylate on the water absorbency of the composite film.

Figure 2 shows the water absorbency from deionized water of each of the 15% solvent-type polyurethane films impregnated with a different particle size of 0.02% sodium polyacrylate. The initial swelling rate was observed to increase as the average sodium polyacrylate particle size decreased from 277 to 5.34

Table I. Particles Sizes of Sodium Polyacrylate for Various Grinding Conditions

Sample No.	Grinding conditions	Particle size (μm)
1	Not grinding	277.7
2	Grinding 15 min	136.06
3	Grinding 20 min	52.10
4	Grinding 40 min	20.78
5	Regrind sample No. 4, 30 min	5.34
6	Regrind sample No. 5, 30 min	0.485

μm . In other words, a decrease in sodium polyacrylate particle size in this range in general led to faster absorption, and the particles with average sizes of 20 and 5.34 μm reached swelling equilibrium in only about 2 min after they were immersed in deionized water. However, it took significantly longer amounts of time for the larger particles of this range to reach swelling equilibrium: 5 min for the 52 μm -size particles, and 10 and 15 min for the 136 μm -size and 277 μm -size particles, respectively. Also, in this range, the equilibrium water absorbency that was reached (and maintained) also tended to increase as the particle size decreased in this range. The equilibrium water absorbency was about 250 g/g for the particles with average dimensions of 277 μm , 275 g/g for the 136 μm -size particles, 475 g/g for the 52 μm -size particles, and 550 g/g for the 20 μm - and 5.34 μm -size particles. We suggest that the smaller particles (in this range of sizes) displayed both faster absorption and increased equilibrium levels of water absorbency because their larger specific surface areas present larger contact areas for absorbing water. These trends, however, reversed as the average sodium polyacrylate particle size was decreased below 5.34 μm down to 485 nm,

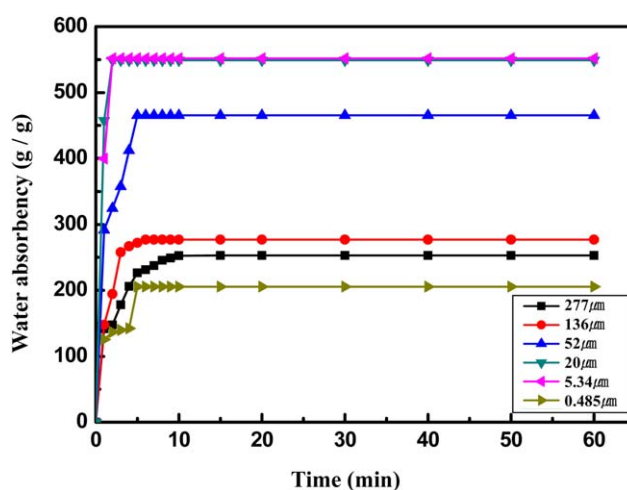


Figure 2. Water absorbency values of polyurethane films impregnated with sodium polyacrylate of different particles sizes and immersed in deionized water. These films were prepared by combining 0.02% sodium polyacrylate and 15% solvent-type polyurethane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

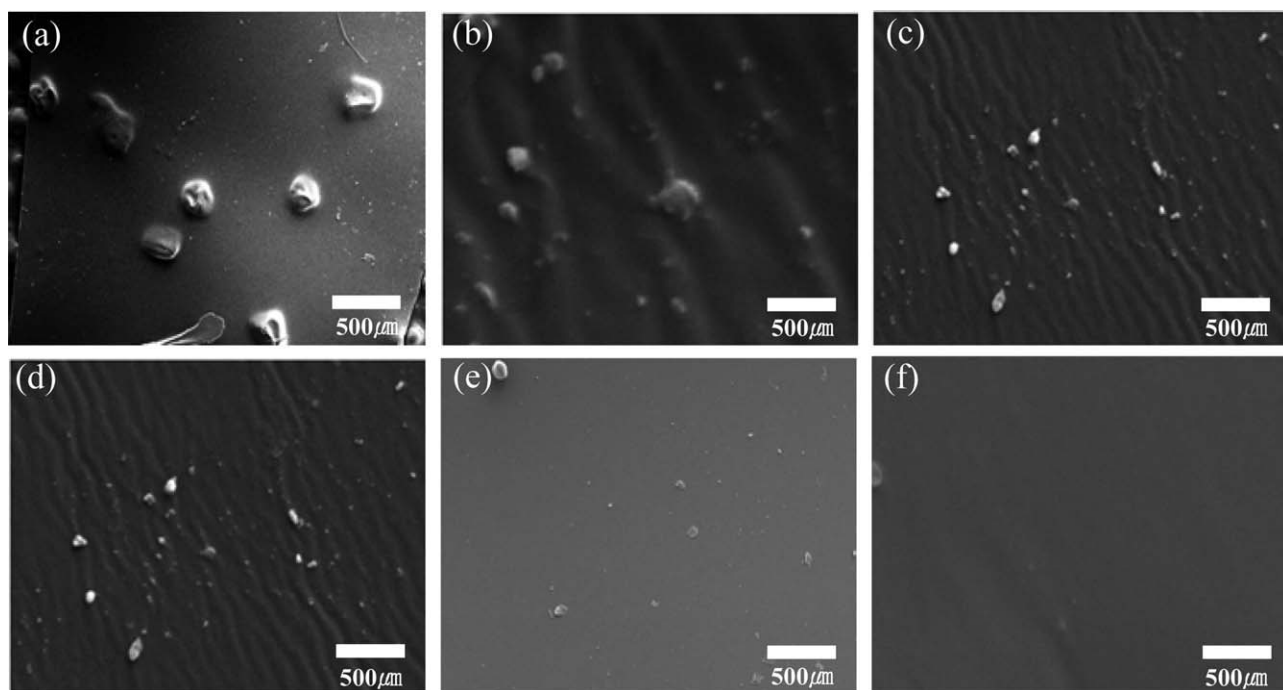


Figure 3. SEM images of polyurethane films impregnated with sodium polyacrylate of different particles sizes: (a) 277 μm , (b) 136 μm , (c) 50 μm , (d) 20 μm , (e) 5 μm , and (f) 0.485 μm .

at which size the time to reach swelling equilibrium time was increased to about 5 min, and the swelling ratio was decreased to about 200 g/g, a value lower than for any of the other particles sizes tested.

To explain these phenomena, we acquired SEM images of surface and the cross-section (shown in Figures 3 and 4) of polyurethane films impregnated with different particles sizes of sodium poly-

acrylate, which were obtained from combining 0.02% sodium polyacrylate and 15% solvent-type polyurethane. These films were all observed to be uniformly impregnated with sodium polyacrylate particles—except when the particle size was 485 nm, in which case the film appeared smooth compared with other samples. These very small sodium polyacrylate particles (essentially powders) apparently became impregnated inside the polyurethane matrix

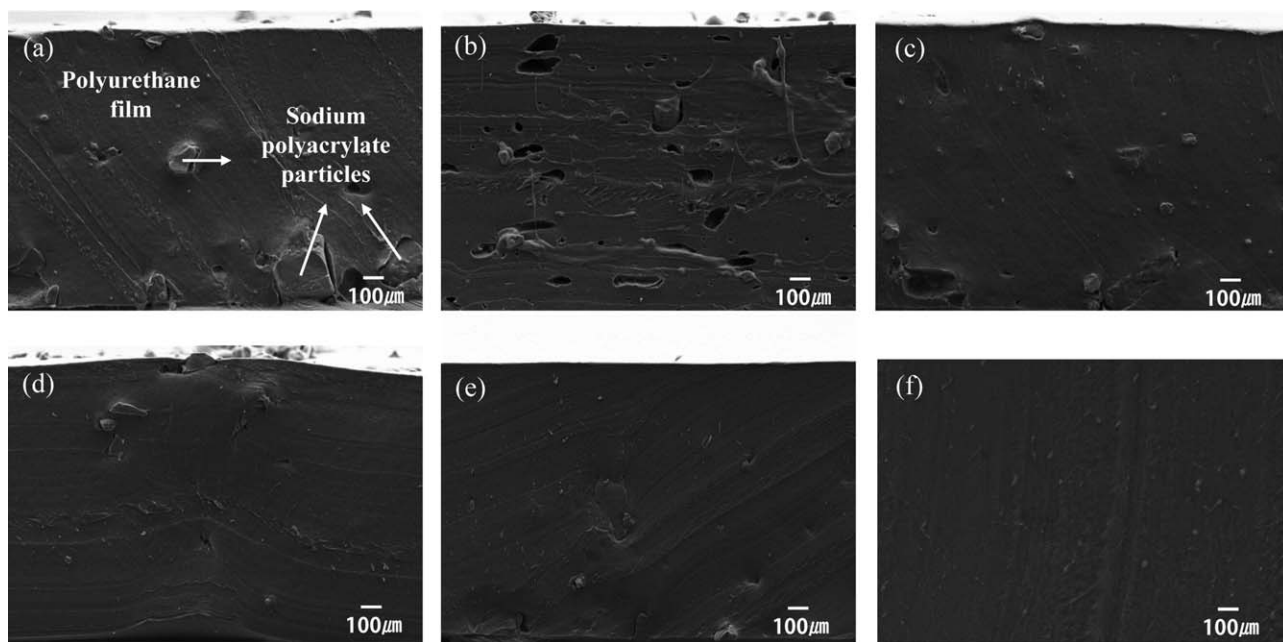


Figure 4. The cross-sectional SEM images of polyurethane films impregnated with sodium polyacrylate of different particles sizes: (a) 277 μm , (b) 136 μm , (c) 50 μm , (d) 20 μm , (e) 5 μm , and (f) 0.485 μm .

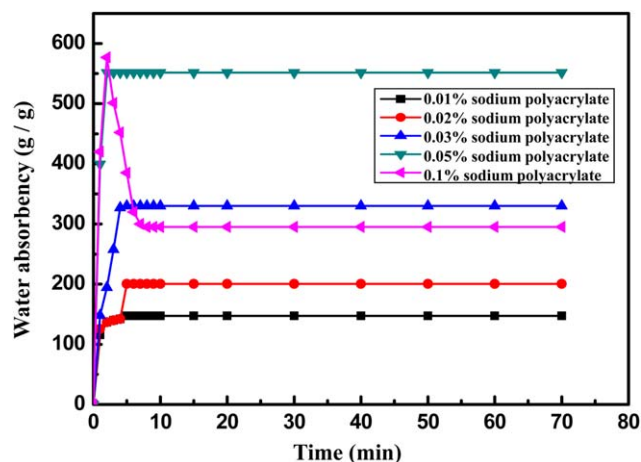


Figure 5. Water absorbency of composite films that were prepared by combining 15% solvent-type polyurethane with various concentrations (0.01–0.1%) of sodium polyacrylate with an average particle size of 0.485 μm . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

rather than on the surface of the film, which would explain its aberrantly low water absorption.

According to Jensen and Hansen,³⁵ the small particles have decreased water absorbency because their surfaces are less active for water absorption than is the bulk of the SAP. This suggestion combined with the impregnation of the 485-nm-size sodium polyacrylate particles inside the polyurethane may explain the decreased water absorbency of these powders.

To further test these ideas, we prepared the polyurethane films (using 15% solvent-type polyurethane) with various concentrations, from 0.01 to 0.1%, of 485 nm-size sodium polyacrylate particles (powders) with the aim of determining the optimal concentration for water absorbency. We immersed these composite films in deionized water and measured their swelling capacities as a function of reaction time (Figure 5). The water absorbency was observed to increase from about 145 g/g to about 557 g/g as the concentration of sodium polyacrylate was increased from 0.01 to 0.05%. The equilibrium swelling time, however, was less than 5 min regardless of the concentration of sodium polyacrylate in this range. In contrast, when the concentration of sodium polyacrylate was increased further, to 0.1%, the swelling capacity increased dramatically in about 2 min but then decreased for longer immersion times.

Figure 6 shows SEM images of polyurethane films impregnated with sodium polyacrylate, which were prepared by combining 15% solvent-type polyurethane with various concentrations (0.01–0.1%) of sodium polyacrylate with an average particle size of 485 nm. As the concentration of this sodium polyacrylate powder was increased up to 0.05%, increasing amounts of sodium polyacrylate powder were observed to be impregnated into the surface of the polyurethane film. However, sodium polyacrylate at a concentration of 0.1% lost its particle form and formed a gel. Therefore, taken together, 0.05% sodium polyacrylate with an average particle size of 485 nm optimized the water absorbency of the film in our tests.

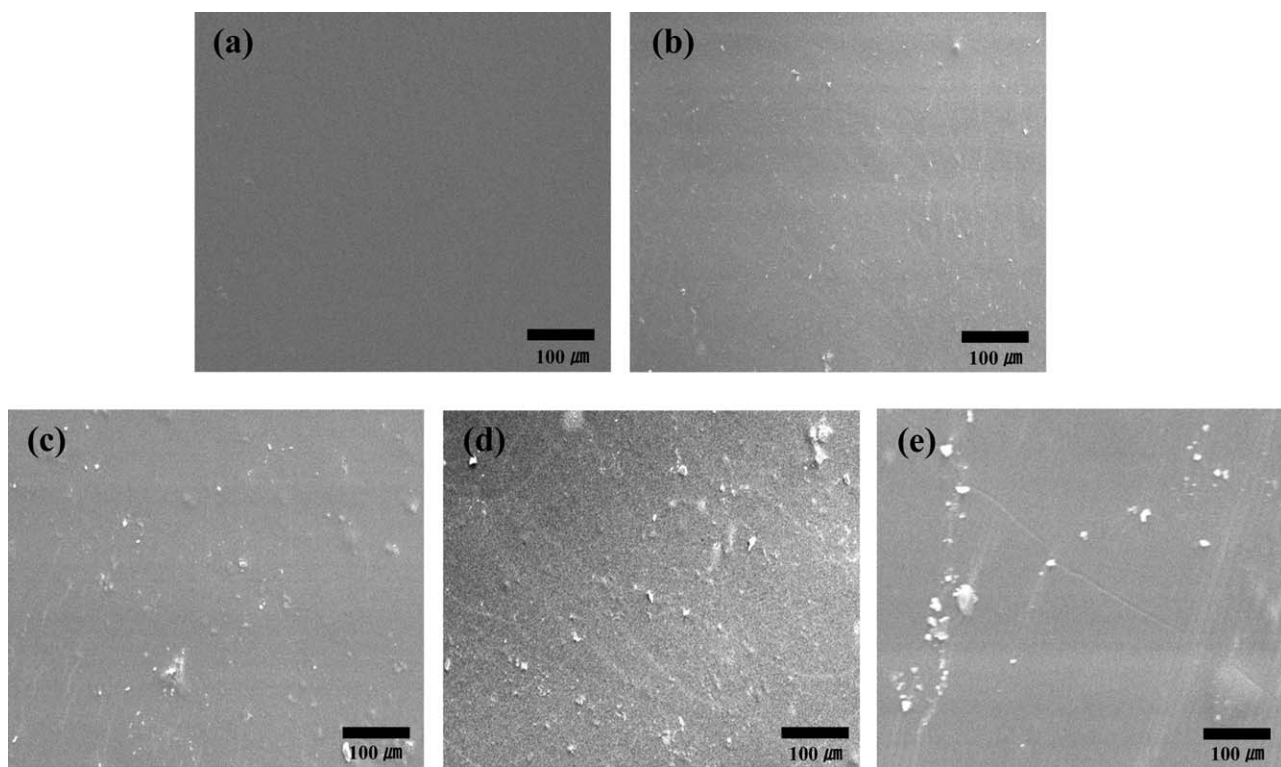


Figure 6. SEM images of composite films that were prepared by combining 15% solvent-type polyurethane with various concentrations (0.01–0.1%) of sodium polyacrylate with an average particle size of 0.485 μm . (a) 0.01%, (b) 0.02%, (c) 0.03%, (d) 0.05%, and (e) 0.1% sodium polyacrylate.

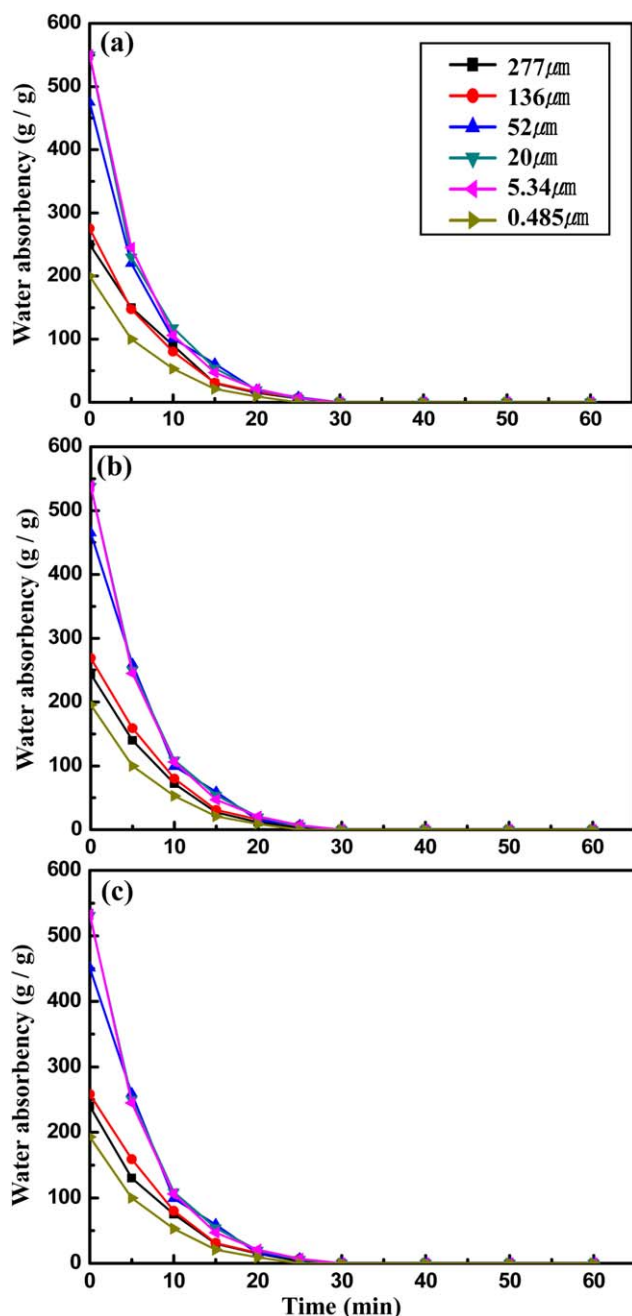


Figure 7. Deswelling behavior of sodium polyacrylate impregnated in a polyurethane film at 35°C. (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle tests. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Deswelling Behavior

Based on the water absorbency and swelling rate of the polyurethane films impregnated with sodium polyacrylate (0.02%), the deswelling behavior was investigated. In fact, the polyurethane films impregnated with different particle sizes of sodium polyacrylate were subjected to three cycles of swelling and deswelling, with the swelling occurring in distilled water at 25°C for 30 min, and the deswelling effected by placing the film in a vacuum oven at 35°C. The deswelling behavior is shown in

Figure 7. The deswelling time was about 30 min for all of the samples regardless of the sodium polyacrylate particle size. Also, the water absorbency of the composite film was slightly reduced, by 2.00–2.18%, from one cycle of swelling and deswelling to the next regardless of the particle size. The sodium polyacrylate particle size thus does not appear to be of great importance for the deswelling rate and deswelling time.

Swelling Behavior in NaCl Solutions

The superabsorbent polymer, while important for the absorption of water in order to be used for a nonwoven fabric, is also important for the absorption of concentrated ionic solutions. The prepared composite film containing different particles sizes of sodium polyacrylate (0.02%) was immersed in various concentrations of aqueous sodium chloride. As shown in Figure 8, the swelling kinetics of the composite films immersed in these sodium chloride solutions was observed to differ from the behavior of the films immersed in distilled water.

All of the composite films containing the sodium polyacrylate and immersed in a NaCl solution yielded an obvious peak of water absorbency at a short immersion time, but no such peak was observed for the pure polyurethane film. These peaks indicated rapid swelling of composite films immediately followed by deswelling or release of fluid from the sample. In addition, the water absorbency values of the composite films were observed to decrease for all samples as the sodium ion concentration of the swelling solution was increased from 0.1 to 1.0%. For example, for the composite films containing sodium polyacrylate particles smaller than or equal to 52 μm and that were immersed in 0.1% aqueous sodium chloride solution, the water absorbency reached 520 g/g within the first 10 min, while the water absorbency values of the composite films immersed in 1.0% aqueous sodium chloride only reached 250 g/g. The deswelling after the peak absorbency was rapid regardless of NaCl concentration for these composite films. The other samples, that is, those films containing sodium polyacrylate particles larger than 52 μm , exhibited the same overall tendency, but after reaching maximum water absorbency, these films exhibited a more gradual decrease in swelling capacity with immersion time than did the films with the smaller particles. The deswelling was also observed to become more gradual as the concentration of the sodium chloride was increased, and this relationship was found regardless of particle size. Taken together, the amount of time it took for an equilibrium level of water absorbency to be attained, that is, the equilibrium swelling time, was greatest for the films that contained the largest tested sodium polyacrylate particles and that were immersed in the highest tested concentration of sodium chloride. Finally, the equilibrium level of water absorbency that was reached was observed to be about 200 g/g in the 0.1% sodium chloride solution, about 100 g/g in the 0.3% sodium chloride solution, about 45–48 g/g in the 0.5% sodium chloride solution and 0 g/g in the 1.0% sodium chloride solution, and these equilibrium levels did not vary with sodium polyacrylate particle size.

Generally for superabsorbent polymers (SAPs) immersed in a sodium chloride solution, water absorbency has been found to increase initially and after certain amount of time attain a

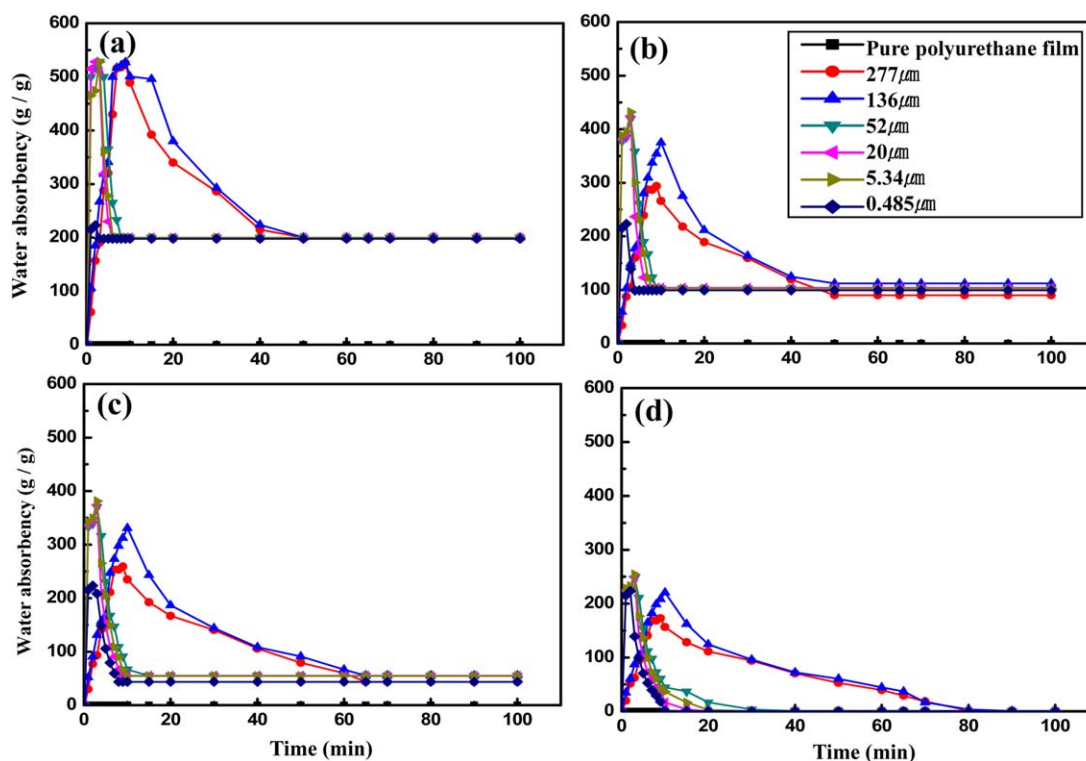


Figure 8. Swelling behavior of various particle sizes of sodium polyacrylate impregnated in polyurethane film and immersed in solutions with various concentrations of NaCl. (a) 0.1% NaCl solution, (b) 0.3% NaCl solution, (c) 0.5% NaCl solution, and (d) 1.0% NaCl solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

constant equilibrium swelling.^{1,3,6,10,13,19,20,33} These studies, in contrast to ours, did not report any tendency for the water absorbency level to decrease after the maximum swelling was attained. An explanation for the decrease in the water absorbency level in our study after an initial peak was obtained may be related to our observation described above that the overall swelling capacity decreased with an increasing concentration of sodium chloride, which has been determined to be caused by a concentration gradient between the ion concentration inside of the film containing sodium polyacrylate and the ion concentration outside of the film in the sodium chloride solution.³⁴ Therefore, when the polyurethane film impregnated with sodium polyacrylate was immersed in the 1.0% sodium chloride solution, the swelling capacity increased initially, but then decreased slowly with reaction time until there was no change in swelling capacity. It can be confirmed that sodium polyacrylate absorbs water was the dehydration by the external ion concentration to maintain the equilibrium concentration depending on the reaction time. In general, the driving force for swelling, that is, osmotic pressure, is related to the difference between the ion concentration inside and outside of the composite film, referred to as the ion concentration gradient. Thus, the higher specific surface area for absorption yielded by polyurethane films impregnated with smaller sodium polyacrylate particles explains the increased water absorbency at short immersion times for the composite films immersed in the same swelling medium, such as deionized water or aqueous sodium chloride solution. However, as mentioned above and shown in Figure 3, the water absorbency of the composite film containing polyur-

ethane and 485-nm-size sodium polyacrylate particles was decreased because these nanosized sodium polyacrylate powders impregnated deep into the polyurethane film.

Overall, the water absorbency of a given composite sample directly depended on the ion concentration of the immersion solution. As seen in Figure 2, the water absorbency was higher for all of the composite films immersed in deionized water than in any aqueous sodium chloride solution. This relationship was further confirmed by the experimental results described above, and shown in Figure 8, in which swelling was observed to decrease for all composite films immersed into aqueous sodium chloride as the concentration of the sodium chloride was increased. Water absorbency of sodium polyacrylate has been previously described to be strongly influenced by ionic strength.^{33,34} Thus, the results can be particularly used in pharmacy or medical applications to check the swelling behaviors in NaCl containing fluids.

CONCLUSIONS

In this study, moisture-absorbing composite films were prepared with superabsorbent sodium polyacrylate particles and solvent-type polyurethane. By weighing these samples, we investigated their equilibrium swelling and deswelling behaviors in solutions such as deionized water and aqueous NaCl, as well as the dynamics of the swelling and the amount of time these particles retained the swelled state. To study the effect of the average particle size of sodium polyacrylates on the swelling behavior of the composite films, we prepared sodium polyacrylates with different particle

sizes ranging from 277 μm to 485 nm. The swelling capacity of the composite films was generally observed to increase with decreasing sodium polyacrylate particle size—except that the swelling capacity of the composite film containing the very smallest, 485-nm-size, sodium polyacrylate particles was significantly and aberrantly decreased. Meanwhile, the deswelling behavior was not significantly affected by the particle size. The water absorbency of polymer particles in solutions was affected not only by the particle size, but also by the saline concentration of the aqueous medium. In summary, the water absorption ratio of polyurethane films impregnated with sodium polyacrylate was found to generally increase with decreasing sodium polyacrylate particle size and with decreasing ionic concentration in the bulk solution.

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