

Microwave-assisted polymerization: Superabsorbent polymer with improved properties

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ABSTRACT: Microwave-assisted polymerization was used as a promising technique to synthesize superabsorbent polymers. A small amount of thermal initiator was used to initiate the reaction, and the polymer's properties were evaluated at acid levels of 31–50% and degrees of neutralization of 68–75 mol %. The polymers were characterized with scanning electron microscopy, and properties such as the capacity and absorbency under a load were measured in a 0.9% sodium chloride solution. In addition, the extractable and residual acrylic acid contents were measured to determine the reaction's efficiency. In conclusion, the synthesis of the superabsorbent polymer via microwave heating reduced the time and cost of production and improved the physical properties of the polymer. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43325.

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INTRODUCTION

Superabsorbent polymers are generally produced with partially neutralized acrylic acid; this imparts a charge density to the polymer backbone. A small amount of crosslinker makes the polymer insoluble in water. This polymer absorbs over 100 times its own weight in aqueous liquid and retains it under moderate to high pressure.^{1–3} Superabsorbent polymers are mainly used in the hygiene industry,⁴ but they have also found commercial applications⁵ in other areas, such as agriculture, packaging, cables, firefighting, and medical industries.^{6–15} Free-radical solution polymerization is the current process of choice in the industry,⁸ but rising production costs and a constant quest to improve the polymer properties has necessitated the search for an improved method.

The free-radical solution polymerization method uses an acid content of 31–35%, and it requires a lot of energy, money, and time^{16,17} to rid itself of the water that is needed to dissipate heat in the polymerization step.⁸ Cheng *et al.*⁵ reported the synthesis of a novel superabsorbent polymer with microwaves, and Kretschmann *et al.*¹⁸ used microwaves to prepare a polymer based on poly(acrylic acid) in a short period of time. Microwave-assisted synthesis, in comparison to conventional heating, improves the reaction speed, reproducibility, and scalability. The electric charges present in the solutions are irradiated with microwaves, which end up converting electromagnetic energy into heat. This

results in an improved reaction rate. Bogdał *et al.*¹⁹ defines microwave heating as a noncontact energy transfer (instead of heat transfer) with a rapid startup and stop capabilities, or as Giachi *et al.*²⁰ puts it, microwave-assisted polymerization has turned from a scientific curiosity into a reliable polymerization technique. Also, an enhanced copolymer formation and a shorter polymerization time were reported by Menon *et al.*²¹ for the production of biodegradable polymers with microwave-assisted polymerization.

As Buchholz and Peppas⁸ describe in their book *Superabsorbent Polymers: Science and Technology*,⁸ the monomer concentration will affect the “properties of the polymer, the kinetics, and the economics of the polymerization process”. In this study, microwave-assisted polymerization was used for the production of superabsorbent polymers through the variation of the acrylic acid contents and the testing of crucial properties, such as capacity, absorbency under load (AUL), extractables, and residual acrylic acid (RAA) under these conditions.

EXPERIMENTAL

Materials

Glacial Acrylic acid was purchased from BASF. Potassium hydroxide, sodium chloride, hydrogen peroxide (H₂O₂), ascorbic acid (C₆H₈O₆), hydrochloric acid, 85% O-phosphoric acid, high performance liquid chromatography (HPLC)-grade methanol,



Figure 1. Weighing of the tea bag. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ultrapure water, and ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ were obtained from Aldrich, and ethoxylated trimethylol propane triacrylate were obtained from Sartomer. All of the chemicals were used without purification.

Equipment

The following equipment was used for polymerization: a Retsch ZM1000 instrument for milling, a RO-TAP model RX-29 equipped with a USA standard test sieve for sieving, a Heraeus Instrument Labofuge 400 for centrifuge retention capacity (CRC), a Thermo Scientific Lindberg Blue M laboratory oven for the drying of the polymer, an HPLC instrument from Waters with an UV detector, a Nucleosil column (C8, 120 Å 5 μm, 250 × 4.6 mm, with a mobile phase of 0.2 mL 85% O-phosphoric acid, 5.0 mL of HPLC-grade methanol, and 0.9948 L of ultrapure water), a Brinkmann 816 titration system for extractables, and a microwave from CEM.

CRC Measurements

The superabsorbent polymer sieved to 300–600 μm was added in amounts of 0.160 g to a teabag with dimensions of 63.5 × 76 mm². The teabag was fashioned from heat-sealable teabag paper from Dexter Alstrom (see Figure 1). The superabsorbent-polymer-containing bag and a blank bag with no polymer were sealed and soaked in a container with 2 L of 0.9% sodium chloride solution (see Figure 2). After 30 min, these were removed from the saline solution and centrifuged at 1600 rpm for 3 min to eliminate the interstitial/unbound liquid, and then, they were weighed. The CRC was calculated as follows:

$$\text{CRC (g/g)} = \frac{(\text{Weight of the centrifuged teabag with swollen polymer} - \text{Weight of the centrifuged blank teabag} - \text{Weight of the dry polymer})}{(\text{Weight of the dry polymer})}$$



Figure 2. Tea bags in a soaking solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 3. Different components of the AUL unit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

AUL Measurements

The superabsorbent polymer sieved to 300–600 μm was added in an amount of 0.160 g to a test cylinder with a flat-screen mesh at the bottom. The superabsorbent polymer granules were distributed evenly, and an acrylic spacer was inserted. This was followed by the appropriate piston to supply the required weight and pressure. The total dry weight of the assembly was measured and recorded. A glass frit was added to a soaking dish filled with a 0.9% sodium chloride solution to the top level of the glass frit. Filter paper was added to the frit, and then, the AUL assembly was placed onto the filter paper (see Figures 3–5). After 60 min, the AUL unit was removed and weighed. The following equation was used to calculate AUL:

$$\text{AUL (g/g)} = \frac{(\text{Weight of the AUL unit with superabsorbent after 1 h of absorption} - \text{Weight of the AUL unit with dry superabsorbent})}{(\text{Actual superabsorbent weight})}$$

Extractable Content

Into a 250-mL glass Erlenmeyer flask, 1 g of superabsorbent polymer was added to 200 mL of a 0.90% sodium chloride solution with stirring at 250 rpm. After 1 h, the resulting mixture was filtered by the use of a vacuum pump and a GF microfilter. Fifty grams of the filtered solution was placed into a 150-mL beaker. For a blank, 50 g of 0.90% sodium chloride solution was added to another 150-mL beaker. The calculation of the percentage of extractables consisted of a three-step, preset endpoint titration, which was done at pHs of 10.3, 10, and 2.7. Both the 0.90% sodium chloride solution and sample were titrated, and the following equation was used to calculate the percentage of extractables:

$$\text{Sample value(\%)} - \text{Blank value(\%)} = \text{Extractable polymer(\%)}$$



Figure 4. AUL unit in a soaking dish. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

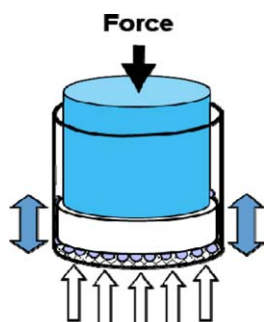


Figure 5. AUL unit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Monomer Solution

The monomer solution (620 g of acrylic acid + 675 g of potassium hydride + 628 g of deionized water for 31% acid content) was prepared by the addition of potassium hydroxide to the deionized water while it was cooled in an ice bath (the temperature was kept around 30 °C). In a separate beaker, the crosslinker, ethoxylated trimethylol propane triacrylate, was added to the acrylic acid, and then, this mixture was combined with the potassium hydroxide solution under constant stirring. The monomer solution for free-radical solution polymerization was cooled to 10 °C and was then purged with nitrogen for 5 min to remove dissolved oxygen. However, the monomer solution for microwave-assisted polymerization was kept at 30 °C and was not purged.

Microwave-Assisted Polymerization

The monomer solution was transferred to the polymerization vessel, which contained the required amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (see Figure 6), and was placed in the microwave cavity, which was equipped with a condenser. Gradient programming was used to do the polymerization under constant stirring in the microwave cavity. The wattage was 100, and the pressure was set to 0 bars. Programming consisted first of two cycles of heating for

2 min and cooling for 20 seconds. This was followed by heating for 1 min and cooling for another 20 s. The polymer was allowed to cool for 2 min and was then extracted from the polymerization tube. The sample was extruded, dried, milled, and sieved.

Free-Radical Solution Polymerization

The monomer solution was transferred to the polymerization vessel, and the required amounts of H_2O_2 , $\text{C}_6\text{H}_8\text{O}_6$, and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (see Figure 7) were used to initiate the polymerization. Because this was an open system, the temperature control was not possible. The polymer was extruded, dried, milled, and sieved.

RESULTS AND DISCUSSION

The superabsorbent polymer was produced, as shown in Scheme 1. To render it water insoluble, 0.01 wt % ethoxylated trimethylol propane triacrylate was added to the monomer solution as a crosslinker. The degree of neutralization was in the range 68–75 mol %, and microwave-assisted polymerization was compared to free-radical solution polymerization at acrylic acid levels of 31, 35, 40, 45, and 50%. The first two levels, 31 and 35%, are currently in the range used in the production of superabsorbent polymers in industry with free-radical solution polymerization. The 40, 45, and 50% acid contents are beyond the grasp of the current polymerization methods, but one can produce a superabsorbent polymer at these levels with a microwave-assisted polymerization method. In general, the swelling of the superabsorbent polymer was the result of the osmotic pressure differences between network and solvent, electrostatic attraction based on ion–dipole interaction, and repulsion of the charged groups on the polymer. In fact, the swelling of the polymer continues until the expanding forces are in equilibrium with the restraining forces (stretching of the network chains and restriction of crosslinks). The degree of crosslinking and charges on the polymer are two primary factors that determine the strength of the polymer and also the amount of liquid it will absorb.

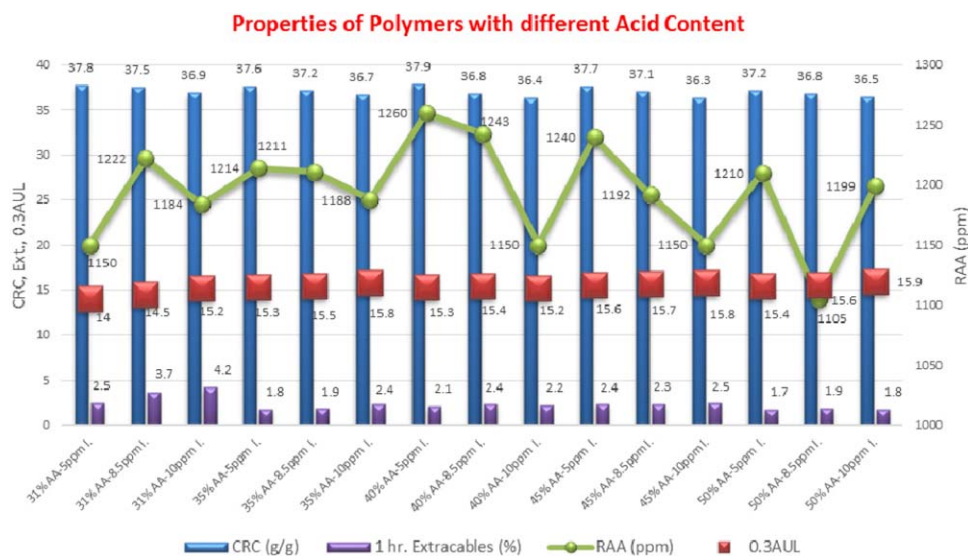


Figure 6. Measured polymer properties at different acid contents (microwave polymerization), where I indicates the initiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Properties of Polymers with Different Acid Contents



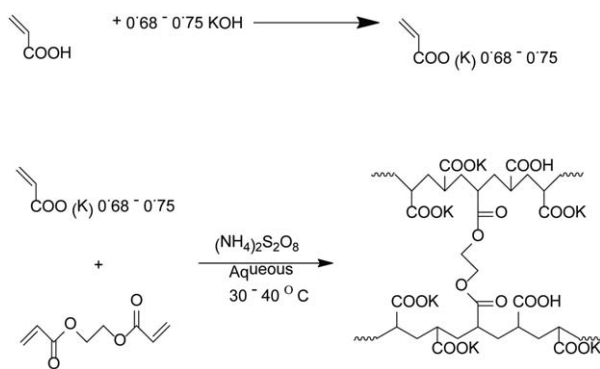
Figure 7. Measured polymer properties at different acid contents (free-radical solution polymerization). The conditions for AA-1 were 150-ppm H_2O_2 , 150-ppm $\text{C}_6\text{H}_8\text{O}_6$, and 75-ppm $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The conditions for AA-2 were 175-ppm H_2O_2 , 175-ppm $\text{C}_6\text{H}_8\text{O}_6$, and 100-ppm $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The conditions for AA-3 were 225-ppm H_2O_2 , 225-ppm $\text{C}_6\text{H}_8\text{O}_6$, and 125-ppm $(\text{NH}_4)_2\text{S}_2\text{O}_8$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conventional free-radical solution polymerization uses redox coupling (e.g., $\text{C}_6\text{H}_8\text{O}_6$ and H_2O_2) to initiate the polymerization, and the addition of a radical/thermal initiator, such as sodium or $(\text{NH}_4)_2\text{S}_2\text{O}_8$, is necessary to reduce RAA in the final product. However, only small amounts of thermal initiator are needed for microwave polymerization [5–10 ppm $(\text{NH}_4)_2\text{S}_2\text{O}_8$]. Higher amounts of initiator result in a higher percentage of extractables. Minimizing these small, linear polymer chains will translate into a product with better properties. Conventional free-radical solution polymerization requires a large amount of initiators to start and propagate the chain. However, higher amounts of initiators also will produce higher percentages of extractables. As the level of initiator increases, they have tendency to bump in to each other; this will result in chain termination and, obviously, shorter chains. Additionally, larger amounts of initiator increase the polymer nucleation points, and this will also result in more, shorter chains. Longer polymer chains have two advantages over shorter ones: (1) physical entanglement becomes more likely, and this hinders the migration of any free chains outside of the polymer matrix, and (2) statistically, a longer chain is more likely to have incorporated crosslinker

molecules and, thereby, be attached covalently to the polymer matrix.

In the microwave-assisted process, polymerization can be done without an initiator, but the polymer becomes too sticky, and the processing of this type of polymers is not very practical on a larger scale. In this study, 5–10-ppm $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was used as a radical/thermal initiator, and redox coupling became unnecessary. Conversely, the conventional free-radical solution polymerization used 300–400-ppm redox coupling and 75–150-ppm radical/thermal initiators. In the microwave-assisted polymerization, the extractables stayed under 5% in all of the formulations, and the RAA levels were around 1200 ppm for the non-surface-coated polymer. The lower percentage of extractables was attributed to the lower amounts of initiator used in the microwave-assisted polymerization. Surface coating was used as a means to impart gel strength to the polymer without the sacrifice of significant amounts of the absorption capacity. Most superabsorbent polymers in the market today have extractables levels of greater than 10% and RAA contents of less than 1000 ppm for the finished product. Extractables have a tendency to leach out of the polymer network once the polymer is swollen; this affects the superabsorbent properties both by the loss of superabsorbent mass and by the osmotic competition of extractables against the insoluble polymer matrix. Additionally, the lower RAA content that results from microwave-assisted polymerization is desirable for safety reasons.

Microwave polymerization makes the oxygen purging of the monomer solution unnecessary. It is just possible that the nature of heating in microwave-assisted polymerization (energy transfer instead of heat transfer) minimizes the effect of oxygen on the propagating monomer chains. In conventional free-radical solution polymerization, the purging of the monomer solution with nitrogen is necessary to speed up the reaction through the elimination of dissolved oxygen.^{22,23} Molecular oxygen, with its biradical structure and high reactivity toward electron-rich groups, participates in chemical reactions and, to



Scheme 1. Generic schematic representation of the polymerization of acrylic acid by microwave polymerization.

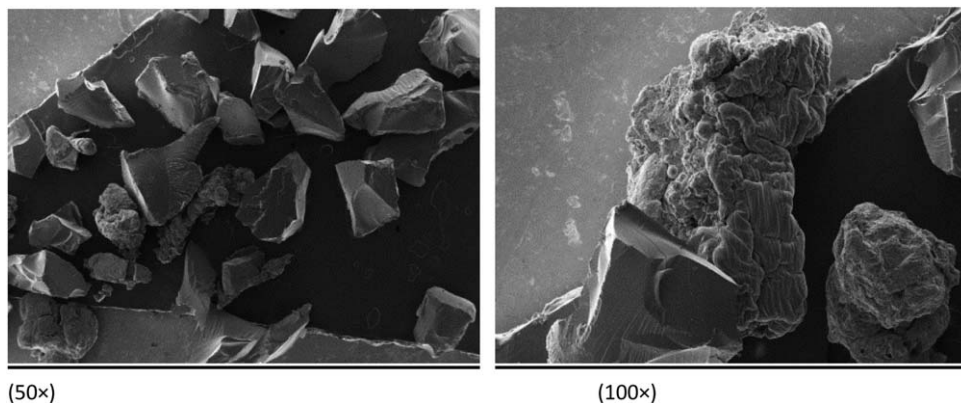


Figure 8. Scanning electron microscopy images of the polymer particles from microwave polymerization.

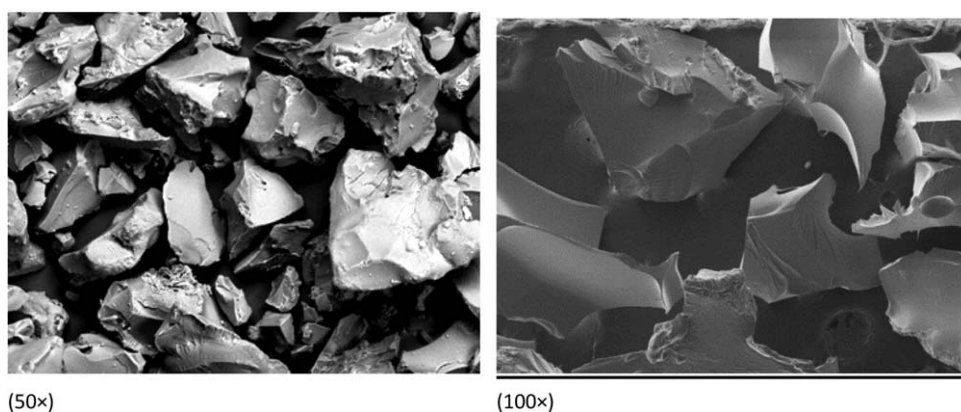


Figure 9. Scanning electron microscopy images of the polymer particles from free-radical belt polymerization.

some degree, determines the ultimate outcome of these reactions. Oxygen will significantly reduce the polymerization rate and will ultimately affect the polymer properties.

Another necessary but time-consuming step is the cooling of the monomer solution. In industry, a tremendous amount of time and money is being wasted to cool the monomer solution to 10 °C; again, this step could be eliminated by the switch to microwave-assisted polymerization.

In this study, sodium hydroxide was replaced with potassium hydroxide to resolve the solubility issues of sodium hydroxide

at higher acid contents. After polymerization, the polymer was extruded and dried in a conventional laboratory oven at 165 °C for an hour. The dried polymer was milled and sieved. The particle size of the final product was in the range 106–810 μm . The acrylic acid content of the current free-radical solution polymerization was in the range 31–35%. Water acts as a heat sink in the polymerization step, but in the drying step, one has to waste lots of energy to eliminate it. The acid content of the microwave-assisted polymerization was increased to 50%. The financial implications of the extra 10–15% acid addition in the polymerization step are huge, and this could add millions of



Figure 10. Images of a polymer made with 31% acrylic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



5 ppm initiator

8.5 ppm initiator

10 ppm initiator

Figure 11. Images of a polymer made with 35% acrylic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



5 ppm initiator

8.5 ppm initiator

10 ppm initiator

Figure 12. Images of a polymer made with 50% acrylic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dollars to the bottom line. The properties of the polymers with 50% acid were similar to those with 31% acid (Figure 6), and the time that it took to do the polymerization did not change when the acid level was increased. Superior network formation during the polymerization step could be one reason for this improvement. Conversely, with free-radical solution polymerization, the degradation of the polymer's properties became obvious when the acid content passed 35% (Figure 7), and the polymerization became very explosive at acid levels of 40, 45, and 50%. It was very hard to get reproducibility from one run to the next at these levels, and the reported properties are based

on small polymer amounts that were collected from several polymerization runs. Although the polymer produced with a lower acid content had better properties, economic realities have forced companies to increase their acid contents past 31%.

As stated before, partial neutralization adds charge density to the polymer network; this is necessary for better liquid absorption. In the microwave-assisted polymerization in this study, optimal properties were obtained with 73 mol % neutralization.

One of the most fascinating outcomes of the microwave-assisted polymerization was its AUL. Preproducts (products without

Table 1. Reproducibility Study of the Polymer with Acid Contents of 31, 35, and 40%

| Sample | Acid content/initiator level | CRC (g/g) | 0.3 AUL | RAA (ppm) | 1-h extractables (%) |
|--------|------------------------------|-----------|---------|-----------|----------------------|
| 1 | 31% AA/5-ppm initiator | | | | |
| | Average | 37.9 | 14.3 | 1180 | 2.3 |
| | Standard deviation | 0.2 | 0.3 | 23.3 | 0.2 |
| 2 | 35% AA/5-ppm initiator | | | | |
| | Average | 37.5 | 15.6 | 1191 | 2 |
| | Standard deviation | 0.3 | 0.2 | 18.6 | 0.2 |
| 3 | 50% AA/5-ppm initiator | | | | |
| | Average | 37.2 | 15.6 | 1175 | 2 |
| | Standard deviation | 0.4 | 0.3 | 8.2 | 0.2 |

AA, acrylic acid.

surface coating) produced with free-radical solution polymerization are very weak and cannot be used in a diaper or other applications as they are. To impart robustness to these polymers, a long and expensive surface crosslinking step is necessary. Base polymers produced with conventional solution polymerization have AUL values under 10 g/g (Figure 7), but this value is increased to more than 14 g/g for polymers produced with microwave-assisted polymerization (Figure 6). As one could imagine, the surface crosslinking step will be much shorter for this type of polymer. In our microwave-assisted polymerization, RAA stayed under 1300 ppm for all of the acid levels, whereas the extractable concentrations were less than 5% (Figure 6).

In free-radical solution polymerization, higher amounts of initiator (over 300 ppm) are needed to initiate the polymerization. These polymers had extractable values higher than 10% (Figure 7). The RAA values were under 1300 ppm, and this was the direct result of the use of a large amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (75 ppm) in the polymerization step. When the amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was increased from 75 to 125 ppm, the RAA levels decreased for all five acid content levels.

Scanning electron microscopy images of the free-radical solution polymerization showed a relatively homogeneous polymer with straight edges, whereas heterogeneity (increased surface area) was apparent for the polymer made with microwave-assisted polymerization (Figures 8 and 9). An increased surface area usually manifests itself in the liquid absorption speed. This had a direct effect on the length of time that it took for the polymer to absorb a particular amount of liquid. Two grams of polymer made with microwave-assisted polymerization absorbed 50 mL of 0.9% sodium chloride solution in less than 30 s, whereas it took more 50 s for the one made with free-radical solution polymerization to accomplish the same task. At a given particle size, a polymer with a greater surface area has a tendency to absorb liquid at a much faster rate than a polymer with a smaller one. The same rule applies for polymers with a porous structure. Peaks and valleys were more pronounced in the surfaces of some particles produced with microwave-assisted polymerization, and it was not surprising that the increased surface area produced a faster absorption.

In the microwave-assisted polymerization, as the acid level increased from 31 to 50%, the polymers became less glassy and more opaque in appearance (Figures 10–12). Immediately following polymerization, the percentage of water in the polymer with 31% acid was measured at 21%, whereas those made with 50% acid stayed at 9%. This had very little effect on the CRCs.

To the contrary, a drop in CRC in the range of 1–1.5 g/g was observed as the amount of initiator was increased from 5 to 10 ppm at each acid level. At a constant initiator level, CRC remained nearly unchanged as the acid content was increased from 31 to 50%. The trend was not the same for the polymers made with free-radical solution polymerization. CRC increased by about 0.3–2.5 g/g as the amount of initiator was increased, whereas the acid contents (31–50%) raised the capacity by 1.3–4.1 g/g. The percentages of water were 23 and 11% for acid levels of 31 and 50%, respectively. The total amount of initiator used in the free-radical solution polymerization was much

higher at all three levels (375 vs 5 ppm, 450 vs 8.5 ppm, and 575 vs 10 ppm).

The reproducibility of the polymers made with microwave-assisted polymerization was surprisingly good. Because the polymerization process was so rapid, reproducibility was one of the major concerns. Table 1 summarizes some of the results (performed in triplicate in each case) with favorable standard deviations.

CONCLUSIONS

Microwave-assisted polymerization could potentially reduce production costs by increasing the solid content, reducing the polymerization time, and eliminating the purging step. On the basis of our results, the acid content could be increased to 50% without affecting the polymer's properties. In addition, 0.3 AUL of the base polymers was about 5 g/g higher than those of the conventional products, whereas the extractables stayed under 5% (>10% for the current polymers). The initiation temperature was kept at 30 °C.

In the next phase of this work, nanoclay and a comonomer will be added to the monomer solution, and the properties of the surface-coated polymers will be investigated.

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