The Use of Gamma Irradiation to Prepare Ureaformaldehyde/Acrylic Acid Copolymer Gypsum Composites for Use in Construction Applications

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ABSTRACT: Thermoset/thermoplast and gypsum copolymer composites were prepared as ureaformaldehyde (UF) copolymerized with acrylic acid monomer at various gamma radiation doses, where the latter monomer produced the greatest improvement in mold stability as cracks treatment, weight loss, hardness, and water absorption. This is due to water absorption showing an increase in water uptake for UF-gypsum composites containing high amounts of acrylic acid monomer copolymerized through the irradiation process, producing a hydrophilic mold able to retain water from evaporation and weight loss, thus obtaining an unshrinkable crackless mold. The influence of acrylic acid and the gamma irradiation process on water absorption, gelation time, weight loss, surface hardness, and compressive strength was studied. The results showed improvement of mechanical flexibility with a reduced sensitivity to cracks indicating the possibility of using these improved molds after mixing with gypsum in the field of construction as inner partition panels and tile seals. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4491–4498, 2006

Key words: irradiation; mechanical properties; copolymerization; FTIR

INTRODUCTION

Since 1870 when ureaformaldehyde resins (UF) were accidentally discovered, interest in these materials has steadily increased. Parallel with it, the production and consumption of resin grew from one thousand tons in 1930 to over one million tons today. Today, most of their uses are based on their unique availability, their low price, and their environmental compatability. Originally, the major proposed uses of UF were as molding resin [1]. Demands and requirements for UF reflect deep changes in lifestyle; it shows the depth of changes both in product demand and in the societal goals during the current adjustment to the recent industrial [2–5], electronic, and communication revolutions. UF-resins offer unique potential technical advantages in a variety of applications, in abundance unmatched in the competing product. Among those advantages are the above-mentioned low price, the nontoxicity of resin and resin products, and the environmental compatibility of resin bonded products, such as particleboard. Furthermore, UF-resins fit almost any purpose. A final advantage of UF-resins is that they are not as directly dependent on petroleum product user trends as are other resins, such as the phenol resins.

Study on UF resin modified with waste liquid (black liquid) in making pulp and production of strawboard,[6] preparation of thermally insulating urea resin foams with low shrinkage,[7] polyamine-modified UF-bonded wood joints, [8] and protecting UF-acrylic foams against destruction by rodents [9] were reported.

The use of gamma irradiation and acrylic acid monomer to improve the mechanical properties and prevent cracks of UF molds and products is of considerable practical and economic interest. This interest is due to the potential of acrylic acid to copolymerize UF through the gamma irradiation process for manufacture of conventional flexible polymer goods (e.g., inner partition panels, bricks, and articles) and especially, of UF/acrylic acid copolymers with unhydrous powder materials (e.g., gypsum and cement). To obtain improved mechanical properties of UF copolymer composites, there are some important aspects to be considered. The monomer added must be water-soluble and disperse well in the UF polymer solution, and then the unhydrous calcium sulfate (gypsum) is added to react with the water medium of the copolymer. However, by using gamma irradiation to create reactive species for grafting of unsaturated monomer [10] onto the UF mold, a more homogeneous mold may be obtained than by using the traditional UF acid curing technique.
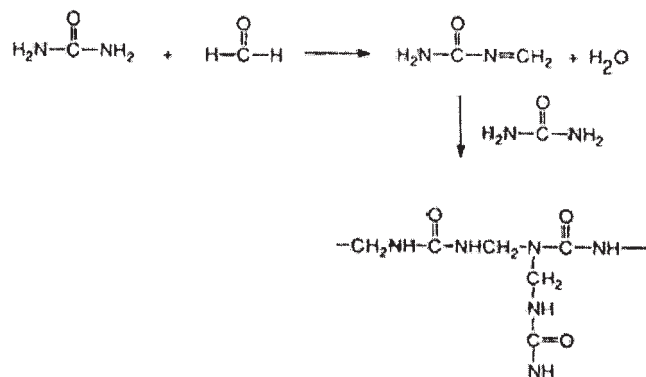
Scheme 1

EXPERIMENTAL

Materials

Urea and formaldehyde were supplied by El-Mansoura for Particle Wood and Resins Co., Egypt. Acrylic acid monomer was obtained from Aldrich Co., Germany. Unhydrous calcium sulfate was supplied by El-Nasr Phosphate Co., Egypt.

Measurements

A vicat apparatus was used for determination of the gelation time. Water absorption measurements were carried out using clean and dried samples of known weights, which were immersed in distilled water for 24 h; water absorption measurements were carried out at 25°C. The samples were removed, blotted with absorbent paper, and quickly weighed. Surface hardness was measured using shore A and D (Durometer tester). The surface morphology was indicated by scanning electron microscopy (SEM) technique; the micrographs were taken with a JSA-5400 (Jeol, Japan) instrument. Measurements of compressive strength were carried out using an Instron (model-1195, UK). A cobalt-60 source of gamma radiation manufactured by the Atomic Energy of Russia, at a dose rate of 10 kGy/90 min, was used.

Preparation of UF resin

Using the following amounts (urea, 2 g; formaldehyde, 8 g; and sulfuric acid, 0.1 mL), aqueous formaldehyde is added to solid urea and the mixture is stirred. A few drops of concentrated sulfuric acid were added to the clear solution. A white solid polymer was produced in a highly exothermic reaction. The reaction involves condensation between the nucleophilic nitrogen of urea with the electrophilic carbonyl of formaldehyde. A branched polymer was formed (see Scheme 1).[11]

RESULTS AND DISCUSSION

Modified resins

UF molds are always modified before their final use; unmodified resins are often too brittle and cracked due to the evaporation of water content, which consequently leads to mold shrinkage. In the present study, we have approached the problem of UF-mold cracking by using gamma irradiation to copolymerize the resin with acrylic acid monomer.

Preparation of UF/acrylic acid copolymer

Ureaformaldehyde (aqueous solution 60% solid content) with different ratios was mixed with acrylic acid monomer as the following percents:

| Urea-formaldehyde | 90 | 80 | 70 | 60 | 50 |
| Acrylic acid monomer | 10 | 20 | 30 | 40 | 50 |

The monomer should be mixed with UF with continuous stirring, and then left for solidification at room temperature (25°C).

Irradiation should be applied after mold solidification where, the acidic medium through the addition of acrylic acid monomer turns the state of UF liquid into UF-gel state then into UF-solid mould (as UV acid curing process).[1] At this stage, the UF mould may still contain the acrylic acid in a monomeric state which needs the irradiation process to initial polymerization process.

FTIR of UF/acrylic acid copolymer

Figure 1 represents the FTIR spectrum of UF/acrylic acid copolymer. The IR spectrum of the (UF) polymer is characteristic, with the following stretching vibration bands as N-H stretching vibration at 3400 cm^{-1}, which is confirmed by its bending band at 850 cm^{-1}, and the C-H stretching of the methylene group (CH$_2$) at 2950 cm^{-1}, which is confirmed by its bending band at 780 cm^{-1}. The carbonyl group (C=O) appeared at 1680 cm^{-1}, with some lower frequency due to some keto-enol toutomerizm structure with neighboring groups as the N-H group. Furthermore, C=N has a vibrational stretch at 1590 cm^{-1}. Single stretching vibration bands appear for C-O and C-N stretching at 1400 cm^{-1} and 1150 cm^{-1}, respectively.

The new copolymer produced by gamma induced radiation was proved by the IR spectrum to be due to grafting with acrylic acid. The sharp stretching band at 3450 cm^{-1} was characteristic for (OH) free of carboxylic groups; at this region of vibration, there are some introducing bands for (N-H) and (C-H) characteristic for a second amine and methylene groups at 3400 cm^{-1} and 3350 cm^{-1}, respectively. Moreover, the car-
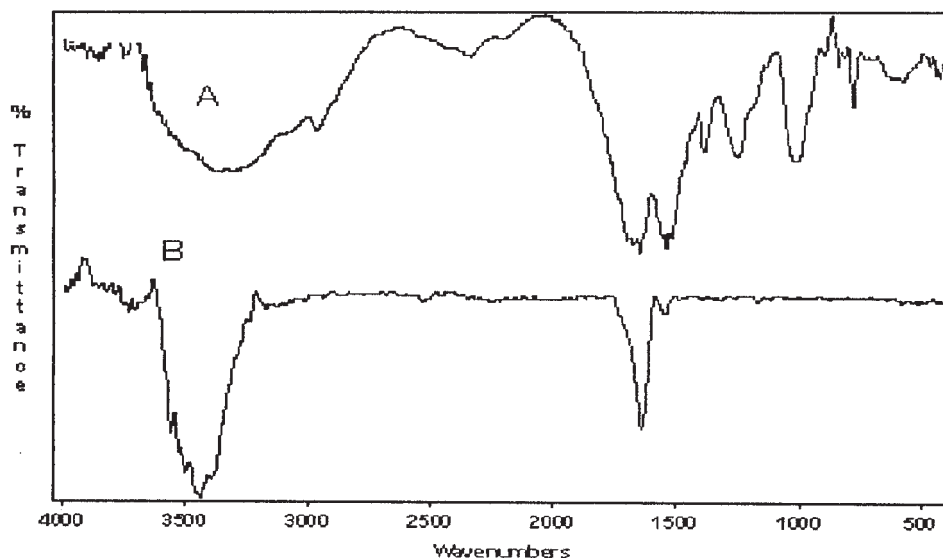
Figure 1 FTIR of (A) UF, and (B) UF/acrylic acid.

bonyl group (C=O) has a stretching vibration band at 1730 cm^{-1} without any toutomerizm effect, while most of the C=N at 1590 cm^{-1} was mainly reduced due to the effect of grafting by introducing acrylic acid (compensation of the toutomerizm). On the other hand, the bending bands of (C-H) and (N-H) at 780 cm^{-1} and 850 cm^{-1} disappeared.

Preparation of UF/acrylic acid/gypsum as copolymer composite

Urea-formaldehyde (90%)/acrylic acid (10%) as liquid copolymer was added with different ratios with gypsum (calcium sulfate anhydrous) as the following percents:

Ureaformaldehyde/acrylic acid copolymer (10% conc. AAc)	90	80	70
Gypsum (calcium sulphate anhydrous)	10	20	30

UF should be mixed with acrylic acid and gypsum with continuous stirring for one minute, then left for molding (solidification) at room temperature, then irradiated using gamma irradiation.

Physical properties of the prepared modified UF-resin

Water absorption

Figures 2 and 3 show the effect of acrylic acid on UF in both irradiated and nonirradiated conditions, and also the difference between UF as an acid curing technique with acrylic acid and the copolymerization with irradiation technique. When acrylic acid adds to UF solution as a resin hardener, part of the acrylic acid reacts directly with the UF, producing UF mold as acid hardener, and the residual amount of acrylic acid will be
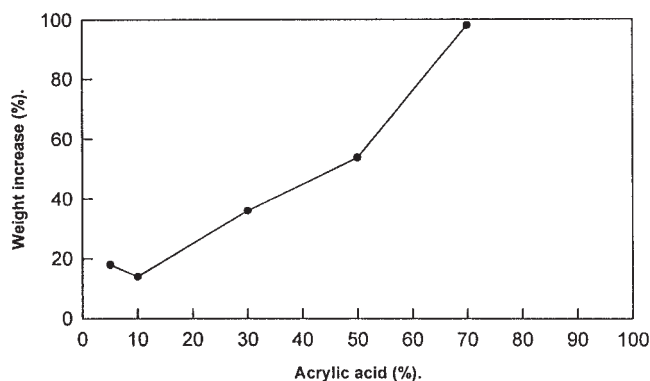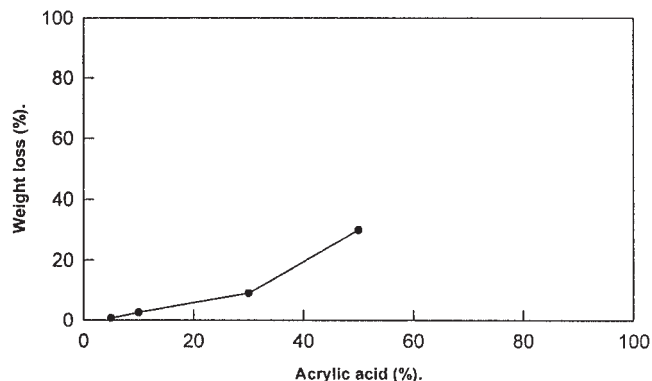

Figure 2 Effect of acrylic acid percent (%) on weight increase (water absorption) % of UF/acrylic acid mold (after 15 days) of irradiated mold.

Figure 3 Effect of acrylic acid percent (%) on weight loss (monomer release) % of UF/acrylic acid mold (after 15 days) of nonirradiated mold.
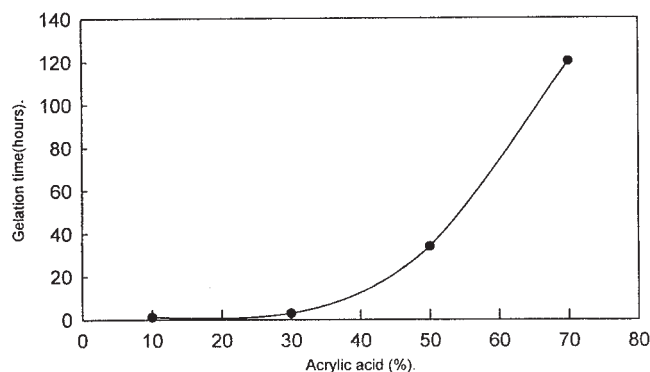
Figure 4 Effect of acrylic acid percent (%) on gelation time (hours) of UF/acrylic acid mold.

still free and releases if the mold is immersed in water and the mold will decrease in its weight. On the contrary, with the irradiated mold where acrylic acid reacts well with UF through the polymerization process, the excess amount of acrylic acid monomer, which may be present as a free monomer, will be also polymerized in the form of fine poly acrylic acid particles impeded in the mold.

Gelation time

The gelations are preceded by an incubation period during which the resin viscosity usually changes little, or even drops, and the solidification process takes place within a few seconds. Figure 4 shows the gelation time for resin, which was modified by a stepwise increase in the acrylic acid amount. The Figure shows how sensitive the gelation time is to the chemical nature of the hardener. As the molecular weight continues to increase and the "turning point" or hydrophobe point is reached, the mixture becomes cloudy. At this point, the mixture is still homogenous, but the high molecular fraction is no longer soluble in dilute solution and thus precipitates upon dilution with water. The gelation of resin occurs at low pH, and the process can be induced by any method that lowers the pH. The best pH value is 2–4 since below pH 2 the resin degrades rapidly. Acrylic acid monomer is a weak organic acid added to the UF solution without any dilution. The process takes place normally at room temperature to form a mold in such a time related to the acrylic acid amount added. The acrylic acid in this case stays in the monomeric state miscible in the UF solution, but in the case of the irradiation process the monomer tends to polymerize, forming a copolymer with UF through a grafting process. The gelation time (molding time) depends mainly on acidifying the UF solution; as a result of the pH change in the media, the solution turns into a hard mold. The excessive amount of acrylic acid in more than the

amount required for forming a mold leads to a free soluble monomer in the UF solution in which the delaying of molding and mold formation at room temperature will occur.

Radiation plays the main role for controlling the amount of water absorbed via the UF mold at any ratio of acrylic acid monomer added; consequently, the different ratios of acrylic acid (10, 30, and 50) added to UF make a copolymerization reaction with UF at 10 kGy, increasing the hydrophilic[12] properties until a certain value. After that, the amount of water absorbed will slightly decrease as the irradiation dose increases. Figure 5 shows the effect of the irradiation dose on the UF/acrylic acid monomer (at different ratios added of acrylic acid to UF) where acrylic acid is considered as the UF crosslinker by the radiation process.

Weight loss normally occurred via water evaporation leaving cavities, and this slightly causes surface cracks. However, in the case of irradiated samples, the chemical linking between UF and acrylic acid as a copolymerization reaction leads to binding UF, water, and acrylic acid all together in a crosslinked series with a large molecular weight; this exactly helps to decrease the water free (the water of UF content which is susceptible to evaporate) and trap them through the chemical linkage through the process of irradiation whatever the ratio of acrylic acid added to the UF mold. As shown in Figure 6, the irradiated mold was noted to be more resistant to weight loss as shown in all ratios of acrylic acid added to UF at the interval times of 5, 10, 15, 20, and 25 days.

Figure 7 shows the influence of time on weight loss of the irradiated and nonirradiated UF mold samples at different ratios of acrylic acid (10, 30, and 50%). From the Figure it can be seen that the crosslinked mold leads to a decrease in the amount of water absorbed. This is one reason, and the other is that the irradiation process keeps the mold through the time (aging) from dissolving or the acrylic acid releasing
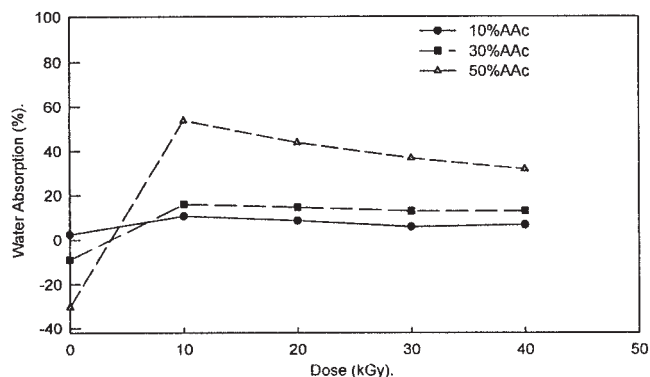

Figure 5 Effect of irradiation dose (kGy) on water absorption of UF mold at different percentages of acrylic acid added (after 15 days).
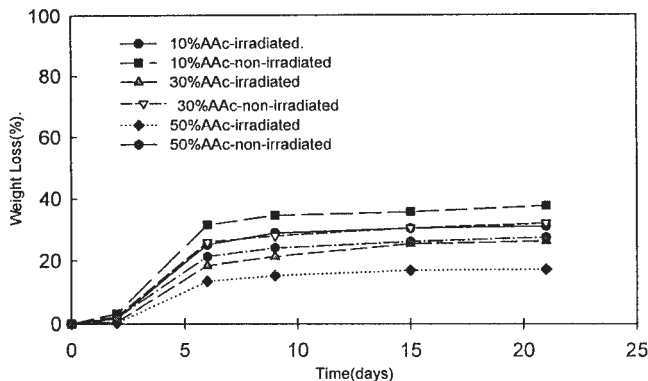
Figure 6 Effect of time (days) on weight loss of UF mold at different ratios of acrylic acid added (in both conditions: irradiated and nonirradiated molds).
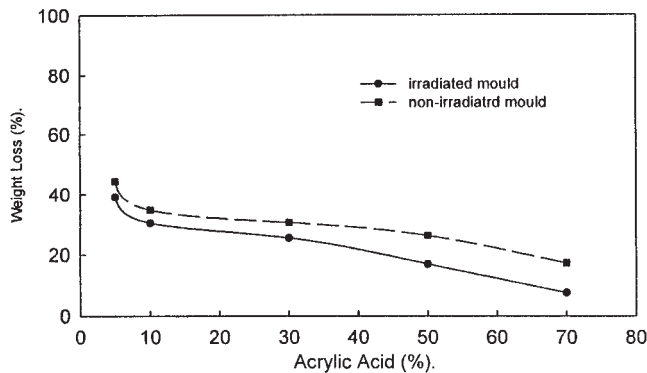

Figure 8 Effect of acrylic acid on weight loss of irradiated and nonirradiated UF/acrylic acid copolymer mold after 15 days at irradiation dose = 10 kGy.

from the formed mold, due to the copolymer formation. On the contrary, nonirradiated samples were susceptible to releasing the excess amount of acrylic acid in water above the ratios required for initiating the molding process. All the samples, which have been applied through the irradiation process, have improved and stabilized towards water attack or immersing, where no release of acrylic acid was observed.

Weight loss

Figure 8 shows the effect of acrylic acid concentration on weight loss of the irradiated and nonirradiated UF/acrylic acid copolymer. In the case of irradiated samples, the weight loss value decreases with increasing acrylic acid content in the mold more than the nonirradiated one. Also, the irradiated samples showed that a complete reaction between acrylic acid, UF, and water content helps the irradiated mold to retain water, leads to preventing water evaporation, and consequently leads to a decrease in weight loss.
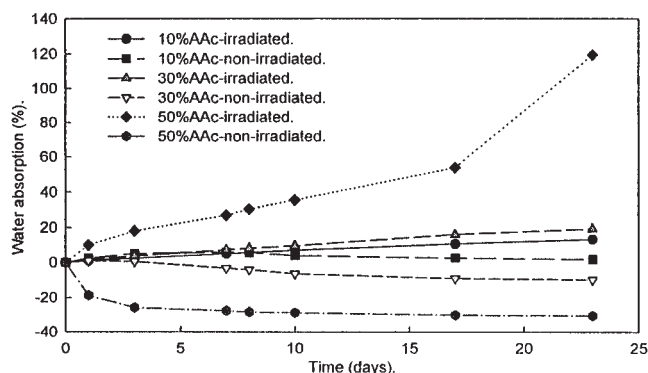
This behavior was much more than in the nonirradiated samples.

Hardness

As shown in Figure 9, gelation takes place once the acid was added but it takes a longer time to harden. The hardness depends on several factors, including whether the process was applied in room temperature condition or through the irradiation process as well as the amount of acrylic acid added, water, and the solid content of UF as time passes. At first, the major factor affecting the hardness is the amount of UF polymer reacted; then the water loss values, secondary, acrylic acid acts as a hardening agent and also possessing flexible character for the formed mold due to thermoplastic properties of poly-acrylic acid formed through the co-polymerization via gamma irradiation.

Figure 10 shows the effect of time (days) on weight loss of the UF/acrylic acid copolymer at different concentrations of acrylic acid added in two conditions (low and high dose rate). The irradiation dose in a low state leads to trapping (binding) the amount of water
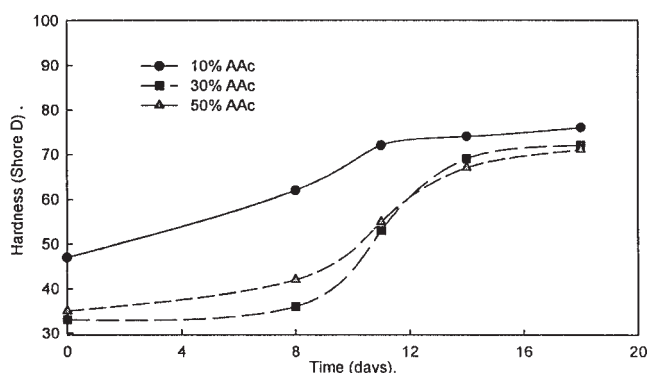

Figure 7 Effect of time on water absorption of UF mold at different ratios of acrylic acid added (irradiated and nonirradiated molds).

Figure 9 Relationship between time (days) and the hardness of gamma irradiated UF/acrylic acid copolymer with different percentages of acrylic acid.
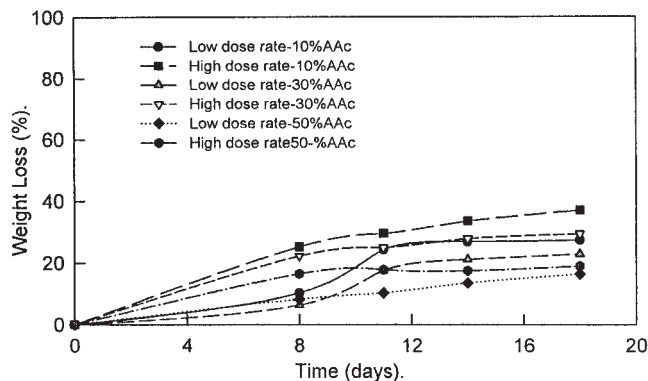
Figure 10 Relationship between time (days) and the weight loss (%) of gamma irradiated UF/acrylic acid copolymer at different dose rates (irradiation dose = 10 kGy).

Figure 12 Relationship between time (days) and the weight loss (%) of gamma irradiated and nonirradiated acrylic acid/UF/gypsum.

free in the compound more than the high dose rate, where the time is not sufficient for the water to be reacted and evaporated, yielding more cracks and loss in weight.

Compressive strength

Figure 11 shows that the compressive strength decreases by increasing the acrylic acid concentration, where thermoplastic properties are responsible for increasing the rate of compacting, leading to increasing the elasticity of the mold to break down (highly impact), and the mold becomes more flexible and has less compressive strength.

Figure 12 shows that no significant differences were found between the ratios of weight loss through time with and without irradiation after two days. The weight loss decreased as the irradiation dose increased, as shown in the Figure. Where, the amount of water, which may evaporate through the ureaformaldehyde mould reacted with acrylic acid through the irradiation process preventing the cracks that may
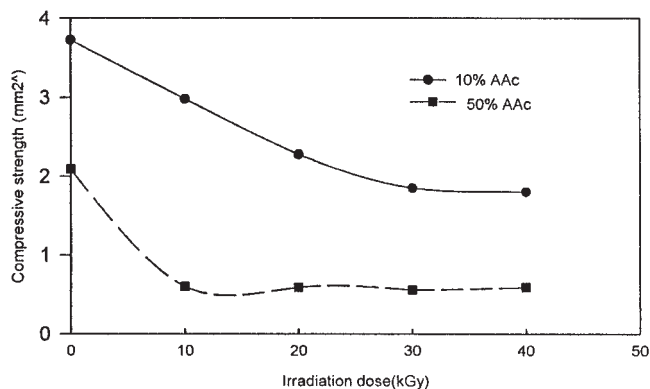
occur due to water evaporation through the mold. This leads to the weight loss being stable with time. This supports the idea that the well-trapped free water in the mold (through the combination of water with acrylic acid and calcium sulfate) helps the mold to avoid weight loss, shrinkage, and cracks.

Figure 13 shows the relationship between time and the swelling of nonirradiated and gamma irradiated acrylic acid/UF/gypsum at room temperature. The irradiation dose affects directly the swelling of the mold, that is, increasing the irradiation dose increases the swelling. This is due to the combination that happened between acrylic acid, UF, and calcium sulfate. Acrylic acid—a hydrophilic polymer—through the γ-irradiation process turns the hydrophobic UF to a hydrophilic state through the polymerization process.

Surface morphology

The surface morphology of the irradiated and nonirradiated materials is shown in Figure 14. In micro-

Figure 11 Relationship between irradiation dose (kGy) and the compressive strength of gamma irradiated UF/acrylic acid copolymer at different acrylic acid rates.
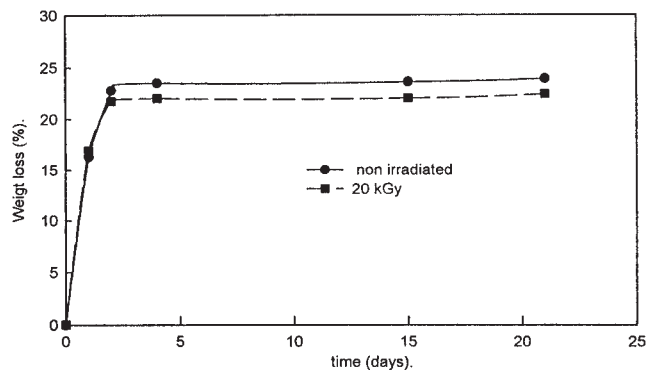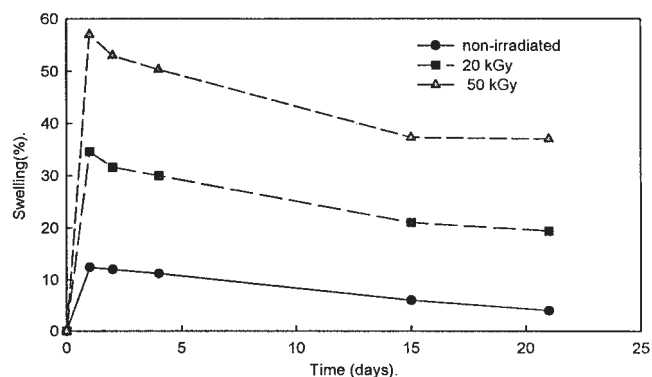

Figure 13 Relationship between time (days) and the swelling of nonirradiated and gamma irradiated acrylic acid/UF/gypsum at room temperature.

(A)Non-irradiated ureaformaldehyde resin (Blank)

(B) Irradiated ureaformaldehyde with 3% acrylic acid

(C)Irradiated ureaformaldehyde with 50% acrylic acid

(D)Irradiated urea formaldehyde-acrylic acid copolymer-gypsum composite.
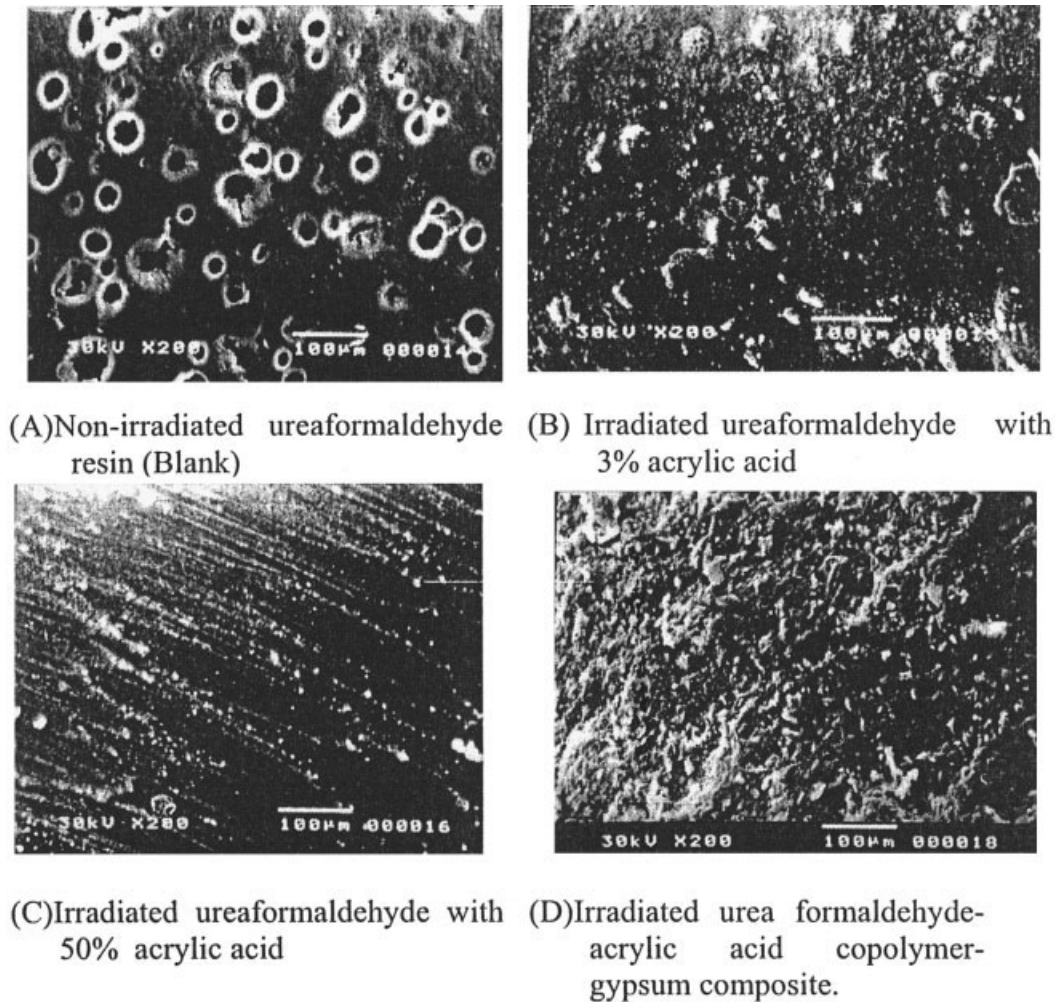
Figure 14 SEM of nonirradiated and irradiated UF with acrylic acid and gypsum.

graph A, the whole space is filled with randomly positioned spherules, indicating clearly that longitudinal cracks had run through the UF matrix after drying. In micrographs B and C, the addition of acrylic acid monomer causes a great increase in the elasticity; this is attributed to the presence of grafted species at the interface between the two polymers decreasing the inner cavities and cracks, where spherical domains disappeared and a smooth matrix appeared. Moreover, the addition of gypsum to the UF/acrylic acid mixture is useful for retaining the water content of the mixture from further evaporation; in turn, shrinkage will be prevented, protecting the mold against cracks occurring, as shown in micrograph D.

CONCLUSIONS

The results presented confirm that modifying UF with acrylic acid monomer using a gamma irradiation process turns the UF mold to a hydrophilic state, thus decreasing water evaporation and weight loss; therefore, the modified mold exists for a long time without deterioration. High improvement in surface hardness was obtained with a decrease in compressive strength due to the flexibility, which may have occurred related to the amount of reacted acrylic acid and the applied irradiation dose. The results determined in this study are comparable with those using the unmodified and traditional methods for UF mold preparation.

UF-acrylic acid-gamma irradiation modified molds are optimized to provide the needed balance of properties for their use as inner partition panels and tile seal applications, where they provide high stiffness, impact resistance, dimensional stability, and outstanding functional flexibility. They also possess an excellent surface for painting and resistance to cracks. Gamma irradiation and acrylic acid protect the UF panel mold from damage, which can occur particularly when the panels are accidentally dropped during transportation.

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