Super-Absorbent Resin Preparation Utilizing Spent Mushroom Substrates

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ABSTRACT: To find high value-added utilization for spent mushroom substrates (SMS), a series super-absorbent sample were prepared with SMS mass ratio between 0% and 100% based on acrylic acid plus SMS, heated with microwave. The maximum absorbency of the composite with 25% SMS ratio in water and saline corresponding to 0.3 wt % initiator is 458 and 61 g/g, respectively; the gel strength of the composite with 25% SMS is two times as high as that of the noncomposited polyacrylate. On SEM pictures, as SMS mass ratio increases the composites resin continuity was interrupted by SMS particles meanwhile some SMS particles are bare; microparticles of SMS uniformly dispersed in the acrylic resin forming submicroscopically homogeneous composites. IR spectra show that the composite has different chemical groups and structures from the mechanical mixture. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1098–1103, 2013

INTRODUCTION

Spent mushroom substrates (denoted by SMS for short hereafter), also called as spent mushroom composts, are the growth media left over after mushrooms are harvested. SMS are generally readily available since there are mushroom farms in most areas nearly of every country. SMS have been used as low value-added materials like fertilizers, or soil amendments in the production of certain crops.[1–4] SMS are expected to form super-absorbent resins through appropriate modification, since they are generally composed of such natural polymers as cellulose, protein, polysaccharides, and lignin, which can be grafted by acrylic acid (AA) and/or its derivatives.

Super-absorbent resins can absorb more water as much as thousand times of its original weight and the swelled can retain liquid even under some pressure.[5] They are widely used in hygiene, agriculture, horticulture, drug delivery, and food storage.[6,7] Most of them are synthetic polymers, which are derived from nonrenewable resources such as petroleum and poor in biodegradability to remain environmental problems.[8,9] In recent years, a variety of materials have been tried to avoid the environment problems and to enhance economic performance. Particularly, the natural polymers, such as starch, cellulose, proteins, and chitosan have attracted great attention due to their abundant resources and degradability.[9–11]

Microwave heating in chemical synthesis can significantly reduce reaction time and improve yield, selectivity, and purity of the product, as compared with conventional heating methods (such as water-bath heating) at the same temperature or even lower temperatures.[12] Microwave-assisted chemical synthesis has attracted more and more attention.[13,14] Microwave can break disulfide bonds in protein to induce subunit disaggregation, and also can improve the graft reaction selectivity.[15] In this article, SMS are mixed and reacted with AA under microwave electromagnetic energy and super-absorbents are synthesized.

EXPERIMENTAL

Materials

SMS was obtained from Zibo City Zhangdian Area, Shandong Province (China), which is fermented cotton seed hulls, and oyster mushrooms have cultivated four times. When just taken from mushroom-bed the SMS was thick slurry with water content about 80 wt %. The air-dried SMS is very crisp, easily crushed by our fingers into ultrafine powder, with a water content of 12 wt %. It was smashed and passed through a 100-mesh sieve before using. The composition of the SMS is listed in Table I, analyzed according to following technical specifications: (1) GB/T 6432-1994 "Method for the determination of crude protein in feedstuffs," (2) GB/T 6433-2006" Determination of crude fat in feedstuffs," (3) "GB/T 6434-2006" "Feeding stuffs-Determination of crude fiber content-Method with

Table I. Composition of the Spent Mushroom Substrate

Ingredient	Protein	Cellulose	Crude fat	Ash	Water
Content (wt %)	10.57	16.84	3.85	4.79	12.26

intermediate filtration," and (4) "GB/T 6438-2007"Animal feeding stuffs-Determination of crude ash."

According to related studies,[16,17] ingredients like lignin and semicellulose are possibly contained in SMS, which were not determined since we are lack of related conditions.

Acrylic acid (AA, A.R., purchased from Tianjin China), ammonium persulfate (APS, A.R., Xi'an Chemical Reagent Factory, Xi'an, China), and N,N-Methylene-bisacryl amide (MBA, chemically pure, Shanghai Chemical Reagent, Shanghai, China), were used as purchased. Other agents used were of analytical grade and all solutions were prepared with distilled water.

Preparation of the Absorbents
The SMS, APS, water, AA and a solution of NaOH 40 wt % were added successively and proportionally into a hot-resistant bottle, forming a suspension with a total mass of 200 g; then the bottle was covered and placed into a microwave oven (Model MM721 AAU-PW, Midea Microwave Oven Manufacturing, Guangdong, China), heated for 8 min at low-grade-fire-power, forming a porous hydro-gel. The gel was spread on an aluminum plate and dried in a vacuum oven (model DZF-6050, Nanjing Wuhe Test Equipment, China) to water content not higher than 9 wt %. Then it was smashed and passed through a 20-mesh screen.

Measurement of Equilibrium Liquid Absorbency
A weighted quantity of the superabsorbent was immersed in distilled water or saline (0.9 wt % NaCl aqueous solution) at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtered over a 100-mesh screen. The equilibrium water absorbency Q (g/g) of superabsorbent was determined by weighing the swollen samples, and the Q of the samples was calculated using the eq. (1):

$$Q = (M_2 - M_1)/M_1 \qquad (1)$$

where M_1 and M_2 are the weights of the dry and the swollen sample (g), respectively.

Determination of Absorb-Speed
Add 90 mL distilled water into a 200 mL beaker with a 25 mm plastic-lined iron core stir. The beaker was placed on a magnetic stirrer (model 85-2, Jintan Sanhe Instrument in Zhejiang, China); the temperature is kept constant at 30°C. Stir the liquid at a speed of 600 ± 20 rpm; vortex can be seen in the flowing liquid. Then carefully add 0.900 g dry sample into the liquid meanwhile start timing; record the duration T (min) when the vortex just disappears. Ninety milliliter saline and 6.0 g dry sample was added to determine saline absorb-speed. Each sample was tested three times and the averaged duration was adopted to calculate the absorb-speed of the superabsorbent sample by eqs. (2) and (3); difference of three parallel determination result is not greater than 5%.

$$\text{Water absorb-speed} = 90/0.90/T \qquad (2)$$
$$\text{Saline absorb-speed} = 90/6.0/T \qquad (3)$$

Twenty-five gram gel resulted from every measure of the time T is used for viscosity measuring with NDJ-79 Rotational Viscometer.

Determination of Gel-Strength
Sixty gram gel resulted from the measuring of absorb-speed was put in the cell of a self-made gel-strength tester (Figure 1), the inside-radius of the cell is r (40 mm); record the initial gel height H_0, then put some weight on the weights plate and record the gel height H_i at 60 s after putting weight; the ratio of the weight mass to πr^2 was taken as stress; the stain was calculated through eq. (4). The slope of the stress–strain curve expresses the bulk modulus of the gel.[18]

$$\text{Strain} = 1 - H_i/H_0 \qquad (4)$$

Structure Characterization
The IR spectra of the absorbents were recorded using KBr pellets with a Thermo Electron's Nicolet 5700 Fourier Transform Infrared Spectrometer; SEM studies were carried out on a Dutch FEI Sirion 200 hot field emission scanning electron microscope after coating the sample with gold film using an acceleration voltage of 10 kV.

RESULTS AND DISCUSSION

Effects of the Ratio of SMS/AA on Absorbent Properties
In this preparation group, referring to related studies,[9,19,20] the weight ratio of APS and MBA were constant at 0.10 and 0.03%, respectively based on the total mass of the reacting liquid; the mole ratio of NaOH/AA is kept at 80/100; the total mass of SMS plus AA is 60 g; the SMS mass ratio based on the sum of SMS and AA was varied from 0 to 100%. The sample with 0% SMS is actually slightly crosslinked poly(sodium acrylate); the sample with 100% SMS is actually slightly crosslinked SMS.
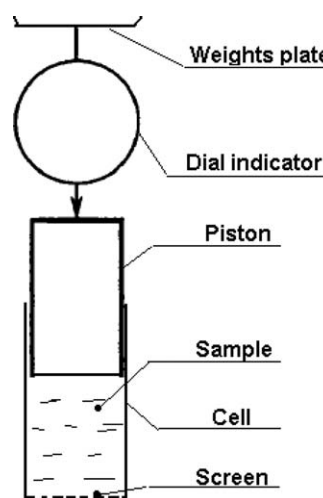

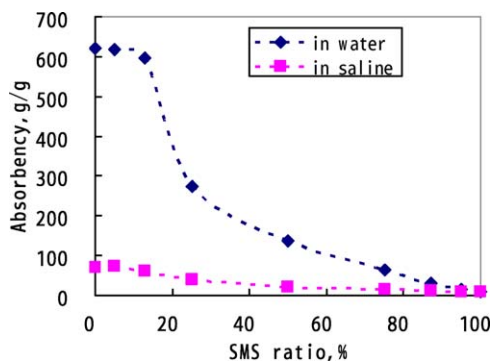**Figure 1.** Scheme of the gel-strength determination.

Figure 2. Effect of SMS ratio on absorbency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Viscosity (Pa•s) of the Gel Just Resulted from Absorb-Speed Measuring

SMS ratio (%)	0	5	13	25	50
In water	4.7	4.5	4.6	4.5	4.4
In saline	5.3	5.4	5.2	5.3	5.3

Figure 5. Effect of APS dosage on absorbency of composites with 25% SMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
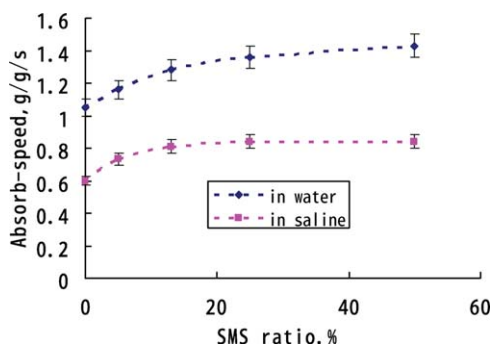

Figure 3. Effect of SMS ratio on absorb-speed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Determined results on the synthesized samples are shown from Figures 2–4.

Figure 2 shows that while the ratio of SMS is between 0 and 13%, the liquid absorbency only changes a little; with the ratio of SMS is from 13 to 87%, the liquid absorbency monotonically decreases. This may be due to the SMS has less swelling ability than chain-net of polyacrylic salt. The maximum absorbency in saline corresponds to SMS ratios around 5%, which is 74 g/g.

Figure 3 shows that the liquid absorb-speed of the absorbents increases precipitously with the SMS ratio increases from 0 to 25%, likely due for that the interfaces between SMS particles and chains of polyacrylic salt may include micro channels,
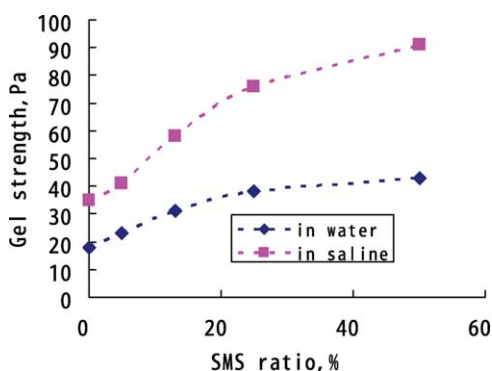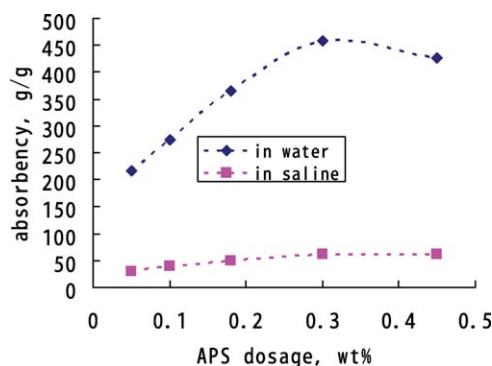
which can fastly absorbing liquid; this increasing slope turned gentle with further increase of the SMS ratio.

Similar to the curves of liquid absorb-speed (Figure 3), the gel strength of the swollen absorbents monotonically increases with increasing of the SMS ratios shown in Figure 4, which may be due to that SMS particles are less swollen thus are harder than swelled chains of polyacrylic salt, and due for the law of dispersed particles capable of improving the strength of the composite. The gel strength of the composite with 25% SMS is two times as high as that of the noncomposite polyacrylate.

The gel viscosity measured immediately after absorb-speed measuring listed in Table II varied in a small range, which may be due to that the differences of gel swelling degrees were not significant.

Effects of the Initiator Dosage on Absorbent Properties
Above results shows that the higher absorbency values are reached with very low quantities of SMS. To investigate whether higher absorbency values can be reached with high SMS ratio, a group composite samples with 25% SMS ratio and different APS dosage were prepared and measured for properties. The results are shown in Figure 5 and Table III. With the APS dosage increases from 0.05 to 0.30, the water and saline absorbency increase from 216 to 458 g/g, and from 29 to 61 g/g,

Table III. Effect of APS Dosage on Absorb-Speed and Gel Properties of Composites with 25% SMS in Water

APS (wt %)	0.05	0.10	0.18	0.30	0.45
Absorb-speed (g/g/s)	1.29	1.36	1.41	1.45	1.44
Gel viscosity (Pa•s)	4.3	4.5	4.6	4.5	4.6
Gel strength (Pa)	37	38	40	41	42

Figure 4. Effect of SMS ratio on gel strength. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
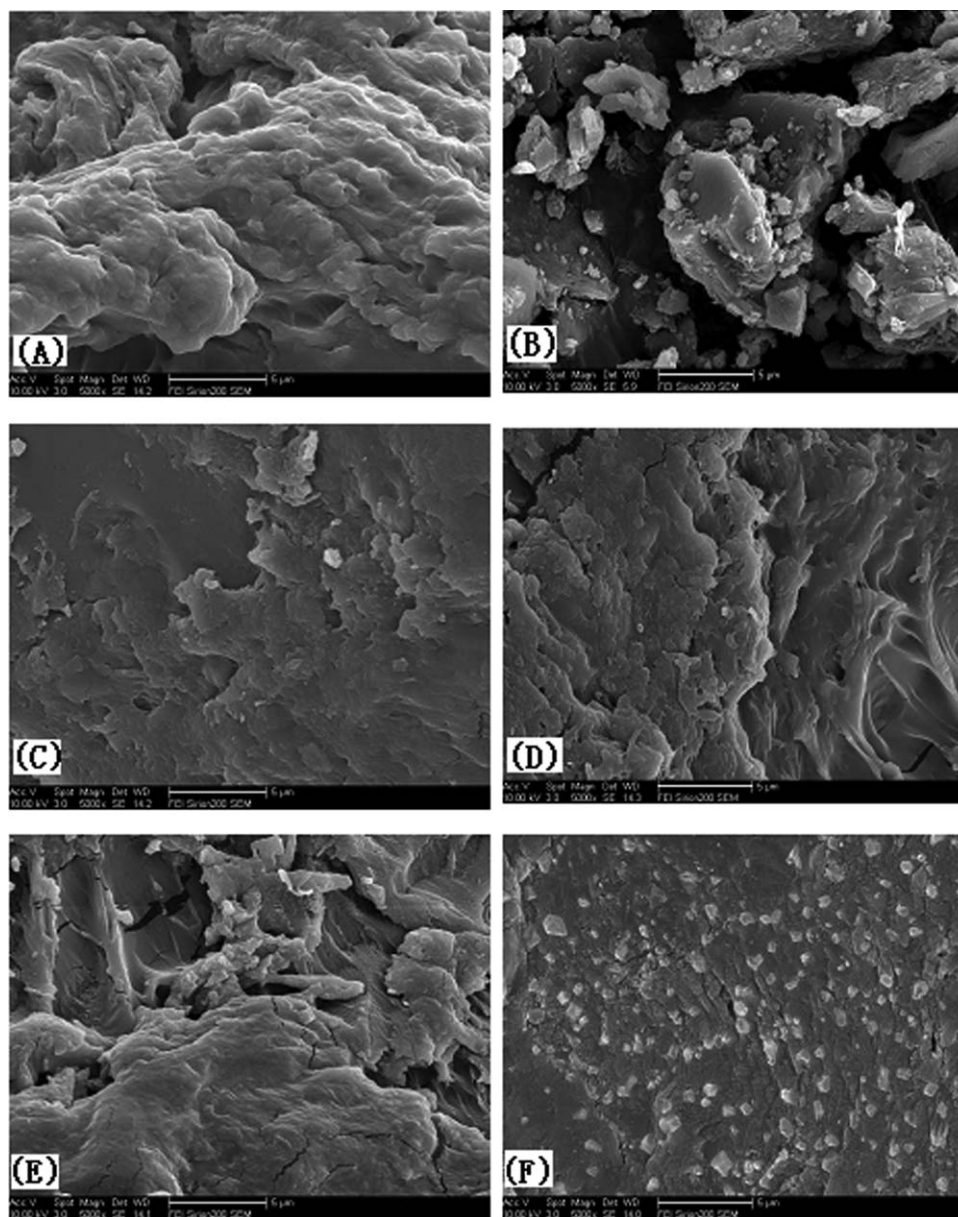
Figure 6. SEM pictures of dry with SMS ratio of: (A) 0%; (B) 100%; (C) 13%; (D) 25%; (E) 50%; and (F) 75%.

respectively; absorb-speed in water increases from 1.29 to 1.45 g/g/s, as the APS dosage increased further, the water absorbency and absorb-speed began to decrease and the saline absorbency did hardly very. These results are likely due for that SMS contains som reducing groups, which can consume oxidizing substance such as APS to a certain extent. Obvious regularity is not seen about the effect of APS dosage on gel-viscosity and gel-strength as shown in Table III, which indicate that these properties are much strongly affected by SMS ratio than by APS dosage.

It can be seen from above figures that an absorbent with certain SMS ratio and initiator dosage will meet the needs of certain occasions. For example, the absorbent with 25% SMS and 0.30 wt % APS has absorbency of 458 g/g in water, such properties

are thought suitable to plant aquasorb; the absorbent with 95% SMS having absorbency about 10 g/g in saline may be suitable as per liter. The weight ratio of SMS here as a biomass is comparable to that of another biomass—chemically modified pulverized wheat straw (CMPWS) in acrylic salt based super-absorbent[21] and in the super-absorbent polymer based on AA, acrylic amide (AM), and dimethyl-diallyl ammonium chloride[22]; the reagent cost and energy consumption are reduced than utilizing modified wheat straw.

SEM Analysis of Dry Absorbents
The SEM pictures magnified 5000 times of the dry absorbents with different SMS ratio are seen in Figure 6(A) being nearly pure poly(sodium acrylate) appears as continuous resin, on which bare particle of SMS did not appear; (B) is SMS modified
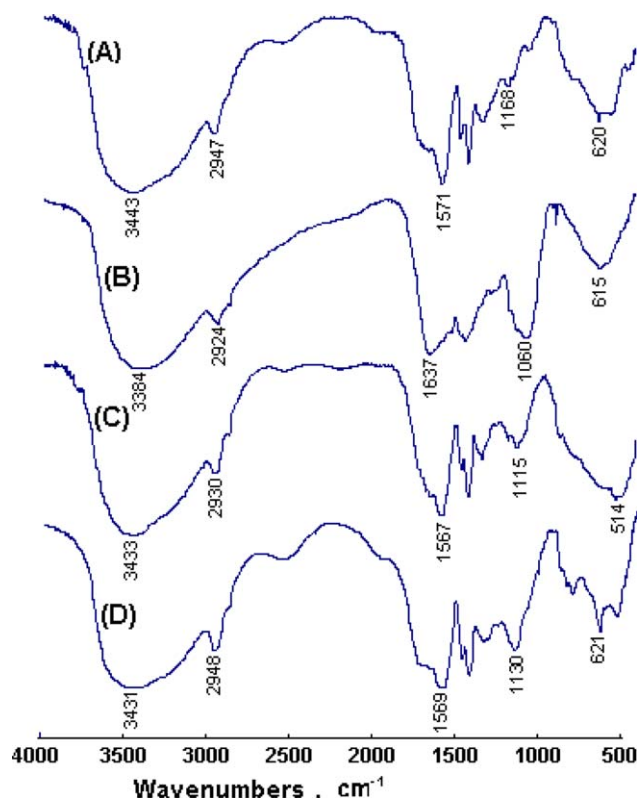
Figure 7. FTIR spectra of the dry absorbents with SMS ratio as: (A) 0%; (B)100%; (C) 13%; (D) is of the mechanical mixture consisting of (A) 8.7 g and (B) 1.3 g. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

only with a little APS and less MBA, appearing as multilayered clumps or particles so loose as to being easily smashed into pieces with edge length much less than 1 micron.

The original material of the SMS used here are cotton seed hulls, in which the cellulose support frames are disbanded by biological fermentation during cultivating mushrooms, therefore this biomass is easier to become ultrafine, allowing various molecules or functional groups in this biomass having more chances to contact with the acrylic monomers.

In Figure 6 from (C–E) the SMS mass ratio is from 13 to 50%, resin continuity was interrupted by SMS particles meanwhile a little SMS particles are bare; in picture (F) a lot of SMS particles are bare, according to the fact that the SMS content is higher than acrylic resin in this composite. Differences of these four composite samples to (B) is that the SMS particles are lined and/or bonded with acrylic resin, which manifest that micro-particles of SMS uniformly dispersed in the acrylic resin forming submicroscopically homogeneous composites. These

appearances supported the above discussions that the uniformly dispersed SMS microparticles improved the liquid absorb-speed and the gel strength of the super-absorbents.

FTIR Analysis of Dry Absorbents
From the FTIR spectra of the four dry samples (Figure 7), the absorptions were observed around 3380 cm^{-1} (hydroxyl stretch influenced by hydrogen bond), 2930 cm^{-1} (H—C—H stretch), 1400 cm^{-1} (carbonyl stretch), and 1060 cm^{-1} (1,4-glycosidic bond),[21–23] which is characteristic absorptions of cellulose included in the SMS. In the spectrum (D) of the mechanical mixture consisting of 8.7 g sample with 0% SMS and 1.3 g sample with 100% SMS, there are less changes of absorption peaks than the sample with 13% SMS; between 600 and 800 cm^{-1} in spectra (C) and (D), there are three sharp peaks in spectrum (D) for the mechanical mixture, but only one wide peak for the composite, which suggest that the composite has different chemical groups and structures from the mechanical mixture.

Comparison of IR absorption peaks of samples with different SMS ratio; there are a little changes of IR absorption, which suggested that the serial compositions of SMS had changed due to the reaction with AA. In the spectrum (B), the absorption peak at 1451 cm^{-1}, which resulted from the symmetrical extension vibration of —COO was lager than those in the SMS. According to related reports,[21,22] indicating that cellulose in pre-treated wheat straw can graft-copolymerize with acrylic monomers under experimental conditions similar to this article, these IR absorptions indicate that the AA have been grafted on such molecules as cellulose in SMS. The absorption peak between 1060 and 1120 cm^{-1} indicated the existence of C—O—C bonds, which was wide and deep in the spectrum (B) of SMS but narrowed and shorted in the spectrum (C) of the composite with 13% SMS. It suggested that the C—O—C bonds in the SMS were fractured. A schematic diagram for grafting to fractured C—O—C bonds is shown in Figure 8.

CONCLUSION

The maximum absorbency of the composite with 25% SMS ratio in water and saline corresponding to 0.3 wt % APS dosage is 458 and 61 g/g, respectively; absorb-speed and gel strength increase with increasing of SMS ratio. The gel strength of the composite with 25% SMS is two times as high as that of the noncomposited polyacrylate. Absorb-speed, gel-viscosity, and gel-strength are much strongly affected by SMS ratio than by APS dosage. On SEM pictures, SMS appears as multilayered and loose particles; as SMS mass ratio increases the composites resin continuity was interrupted by SMS particles meanwhile some SMS particles are bare. In composite samples the SMS particles are lined and/or bonded with acrylic resin, which manifest that microparticles of SMS uniformly dispersed in the
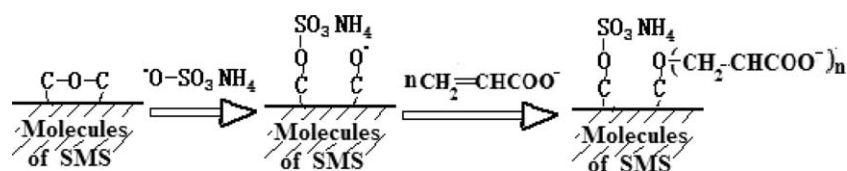

Figure 8. Scheme of acrylate grafting onto SMS molecules.

acrylic resin forming submicroscopically homogeneous composites. IR spectra show that the composite has different chemical groups and structures from the mechanical mixture.

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