Graft Copolymerization of Methacrylamide onto Acrylic Fibers Initiated by Benzoyl Peroxide

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ABSTRACT: Acrylic fibers were graft copolymerized with methacrylamide in aqueous media, using benzoyl peroxide as a free-radical initiator. The grafting reactions were carried out within the 75–95°C temperature range, and the effect of initiator, monomer concentrations, and the amount of fiber on the graft yield were also investigated. The maximum graft yield was reached at the benzoyl peroxide concentration of 3.0×10^{-3} mol/L and the optimum temperature of 85°C. The activation energy of the reaction was found to be 33.8 kcal/mol at the temperature interval of 80–95°C. The grafted fibers were characterized with infrared spectroscopy, scanning electron microscopy, and thermogravimetry.

The thermogravimetric analysis results revealed that the degradation temperature of the acrylic fibers increased with grafting. The scanning electron photographs showed that the homogeneous appearance of the fiber surface changed and a shell-like heterogeneous structure occurred at the surface with an increasing degree of grafting. The moisture content and water absorption of grafted acrylic fibers was highly enhanced by grafting. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1519–1525, 2004

Key words: acrylic fibers; copolymerization; graft copolymer; methacrylamide; benzoyl peroxide

INTRODUCTION

Graft copolymerization is a well-established technique used to modify properties of natural[1–4] and synthetic polymers.[5–9] In this way, it is also possible to modify many different properties in the fibers, such as dyeability, ability to handle, thermal and chemical resistance, wash and wear characteristics, etc.

Among synthetic fibers, acrylic fibers seem to be an important fiber because of their potential applications in the textile industry particularly the manufacture of synthetic surgical threads and other implants.[10] However, some minor textile performances (thermal stability, crease recovery, and low moisture absorption) need to be improved.

Methacrylamide (MAA) has been widely applied in both laboratory and industry as a grafting agent for natural and synthetic fibers. It is one of the most important vinyl monomers for large polymer-add-ons can be easily obtained because of the hydrophilic nature of the MAA.[11] It is highly water soluble, relatively less toxic, polar, and less expensive than other vinyl monomers.

A literature survey reveals that much work has been reported on synthetic fibers such as poly(ethylene terephthalate) (PET),[5,7,8] Nylon,[12] etc. concerning the grafting of vinyl monomers but acrylic fibers seem to have been neglected. Thus, the present work deals with the grafting of MAA onto acrylic fibers using benzoyl peroxide (Bz_2O_2). The effects of various experimental conditions on grafting, such as initiator and monomer concentrations, amounts of fiber, polymerization time, and temperature were systematically studied. In addition, grafted acrylic fibers were characterized for thermal and morphological properties. Furthermore, moisture content and water absorption of MAA grafted acrylic fibers were also investigated.

EXPERIMENTAL

Materials and Methods

The experiments were carried out using multiflament acrylic fibers (semidull, 110 dTex) obtained from AKSA Co. (Yalova). The acrylic fiber samples in small bundles were Soxhlet-extracted with acetone for 24 h and dried at room temperature before being used. Reagent grade MAA (Merck) was used without further purification. Benzoyl peroxide (Merck) was recrystallized twice from the methanol and chloroform mixture. All other chemicals were of chemically pure grade.

Grafting procedure

A known weight of acrylic fiber and monomer dissolved in 29 mL water at a suitable concentration were

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placed in a 100 mL polymerization tube and Bz_2O_2, at a suitable concentration dissolved in 1 mL acetone was added to it. The mixture was vigorously mixed. The mixture was then placed in a water bath (Lauda D40 S, Germany) adjusted to the polymerization temperature. At the end of polymerization, the polymerization tube was taken from the water bath and fiber was treated by boiling water by changing the washing water at least three times for 4 h to separate the homopolymer from the grafted fiber. After the separation of homopolymer, the fiber sample was dried and weighed to a constant weight.

The percent graft yield ($G\%$) was calculated from the increase in the weight of the fibers by using the following equation:

$$G\% = (W_2 - W_1)/W_1 \times 100$$

where W_1 and W_2 are the weights of the original and grafted fibers, respectively.

Rate measurement

The rate of grafting (Rg) was calculated as follows:[12,13]

$$\text{Rate of grafting } (Rg) = (W_2 - W_1/VtM) \times 1{,}000$$

where $W_2 - W_1$ is the weight of the grafted polymer, V is the total volume of the reaction mixture, t is the reaction time, and M is the molecular weight of MAA.

FTIR spectra

FTIR spectra in the form of KBr pellets of fiber samples were recorded on a MATTSON 1000 Model FTIR spectrophotometer.

Thermogravimetric analysis

The thermogravimetric analysis was run under nitrogen atmosphere with a flow rate of 200 mL/min using a Rheometric Scientific 1000+ Model thermal analyzer. The heating rate was 10°C/min and the temperature range studied was from the room temperature to 600°C.

Scanning electron microscopy

The surface morphology of grafted acrylic fibers was examined by means of a JEOL-JEM 100 CX II Model scanning electron microscope, after gold coating.

Moisture content

The weighted dry samples were conditioned at 25°C in medium having 100% humidity for 24 h for the
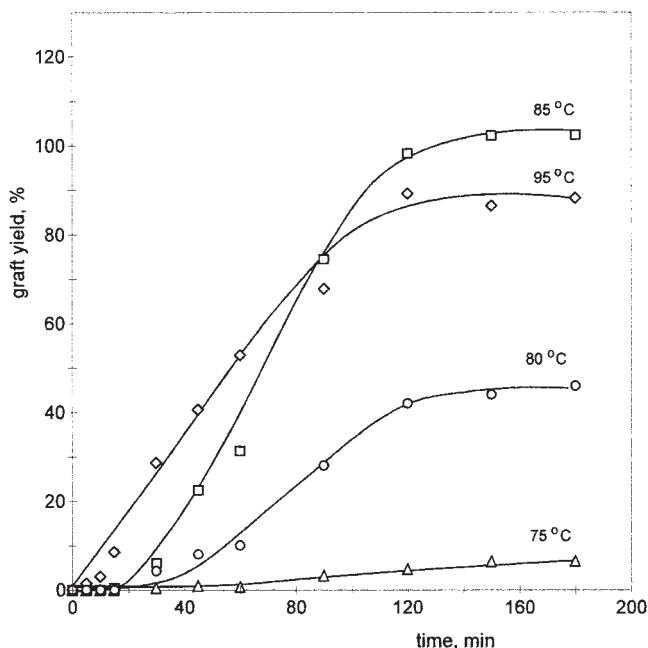

Figure 1 Change of the graft yield with temperature and the polymerization time: Bz_2O_2 concentration = 3.0×10^{-3} mol/L, MAA concentration = 0.39 mol/L, time = 180 min.

moisture content measurements. The moisture content was calculated from the difference between the weights of the conditioned and unconditioned samples.

Water absorption

The weight of samples was determined and then they were dried in a vacuum oven at 60°C overnight. After redetermining the weight of the dried samples, they were immersed in distilled water at room temperature for 24 h. The wet weights were determined after sandwiching the samples between the filter paper. The water absorption of the grafted samples was calculated from the weights of the wet and dry samples.

RESULTS AND DISCUSSION

Influence of reaction parameters

Effect of time and temperature on grafting

Figure 1 shows the effect of time and temperature upon grafting of MAA onto acrylic fibers between 75 and 95°C. It is seen that increasing time and temperature causes an increase in the grafting rate and graft yield. However, the saturation graft yield increased up to an optimum temperature of 85°C (102.4%) and then showed a decrease to 88.0% at 95°C owing to termination reactions predominate at higher temperatures.[2] No grafting was observed at temperatures

TABLE I
Values of the Rates of Grafting (Rg) at Various Temperatures[a]

Temperature (°C)	$1/T \times 10^3$	$Rg \times 10^6$ (mol L^{-1}s^{-1})	log Rg + 6
80	2.872	1.306	0.1158
85	2.792	1.959	0.2919
95	2.716	8.922	0.9505

[a] [Bz$_2$O$_2$] = 3.0×10^{-3} mol/L; [MAA] = 0.39 mol/L; time = 30 min.

below 75°C, even after a period of 180 min, due to the low rate of initiator dissociation and the difficulty of diffusion of the monomer into the fiber structure. The grafting remained at a very low level of 6.6% at 75°C after 180 min. There is also an induction period of 15 and 10 min observed at the temperatures used, namely, 75, 80 and 85°C. There was no induction period observed at 95°C. The maximum graft yield (102.4%) was observed at 85°C.

The favorable effect of temperature (up to 85°C) on grafting could be ascribed to: (a) increase in the dissociation rate of Bz$_2$O$_2$, (b) enhanced diffusion of MAA into the fiber, (c) increase in the swellability and mobility of acrylic fibers, and (d) increase in the mobility of MAA molecules and their collision with acrylic fiber macroradicals.

The fact that graft yield remains constant after a certain time (saturation graft yield) also can be attributed to a decrease in initiator and monomer concentration with the progress of the reaction.[5,8]

The initial rates of grafting (Rg) calculated for the experimental temperatures are given in Table I. The slope of the log Rg versus $1/T$ graph shows that the activation energy for grafting is 33.8 kcal/mol within the 80–95°C temperature range (Fig. 2).

Effect of initiator concentration

The initiator concentration of Bz$_2$O$_2$ was varied from 0.125 to 7.0 × 10^{-3} mol/L to study the effect of Bz$_2$O$_2$ concentration on the graft yield, keeping the concentrations of all other conditions constant (Fig. 3). The graft yield increases with the Bz$_2$O$_2$ concentration at the beginning, reaching a maximum graft yield value (102.4%) at 3.0 × 10^{-3} mol/L. Thereafter a slow decrease in graft yield was observed at higher initiator concentrations. The increase of Bz$_2$O$_2$ concentration above 3.0 × 10^{-3} mol/L makes the radical concentration excessive in the medium, causing the rate of termination reactions to increase and graft yield to decrease.[7]

Effect of monomer concentration

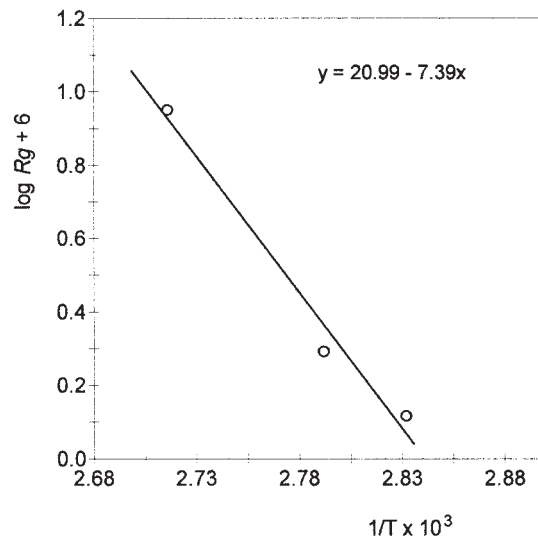The effect of MAA concentration was studied by varying its concentration from 0.20 to 0.78 mol/L (Fig. 4).

Figure 2 $1/T$ versus log Rg plot for grafting of MAA upon acrylic fibers using Bz$_2$O$_2$.

The saturation graft yield increases from 14.2% at a monomer concentration of 0.20 mol/L to 166.0% at a monomer concentration of 0.78 mol/L. An increase in the monomer concentration also increases the grafting rate. At MAA concentrations employed, namely 0.20, 0.39, 0.59, and 0.78 mol/L, grafting was not observed (induction period) within the first 15, 10, and 5 min, respectively. An increase in monomer concentration increases the number of MAA molecules diffused into acrylic fibers. This increases the probability of acrylic macroradicals and growing grafted side chains to find
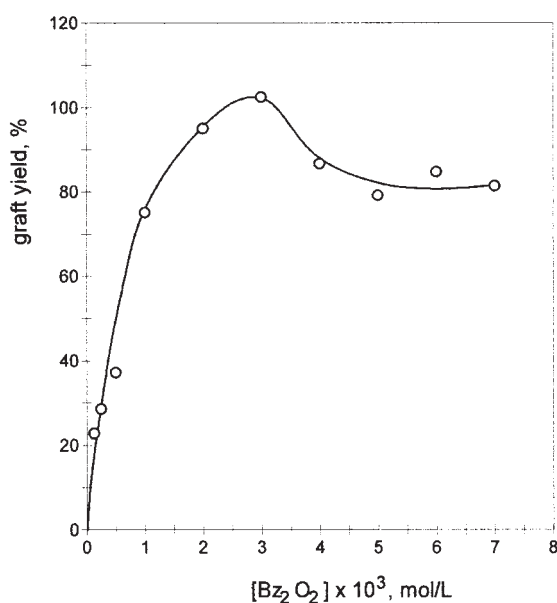

Figure 3 Change of the graft yield with initiator concentration: MAA concentration = 0.39 mol/L, temperature = 85°C, time = 180 min.
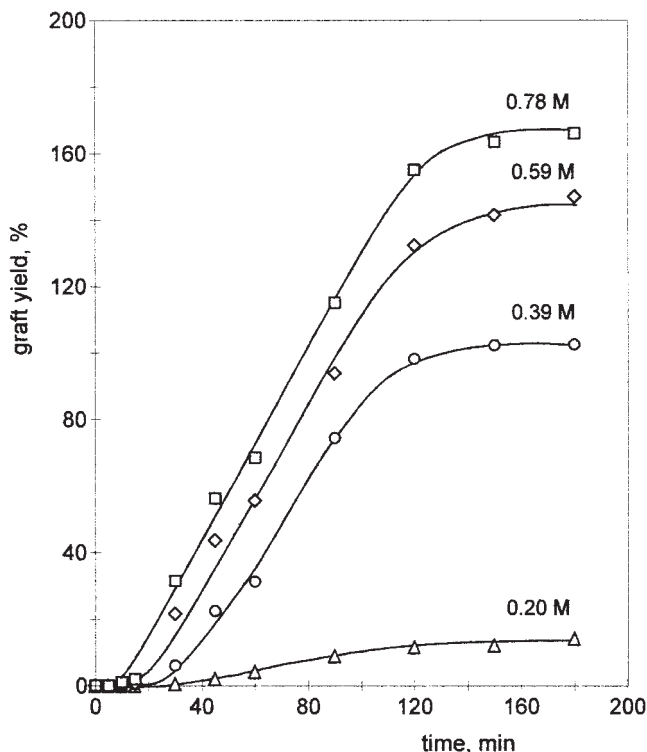
Figure 4 Change of the graft yield with monomer concentration: Bz_2O_2 concentration $= 3.0 \times 10^{-3}$ mol/L, temperature $= 85°C$, time $= 180$ min.
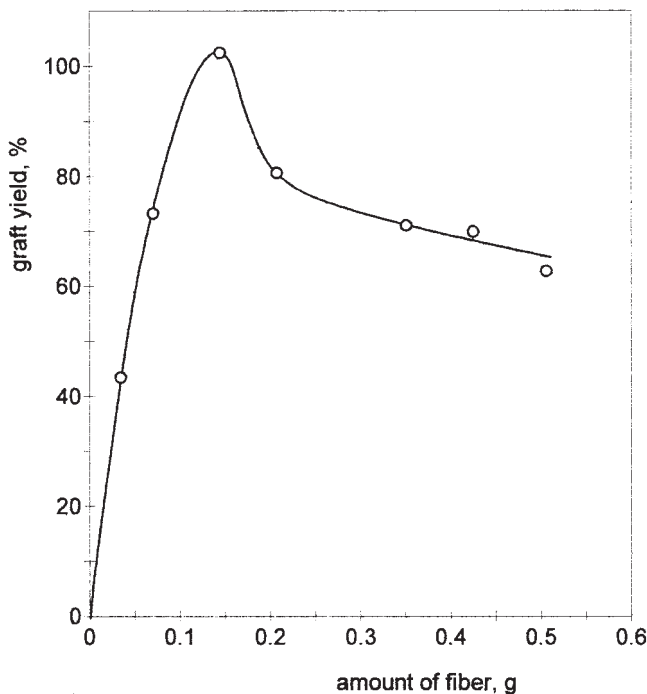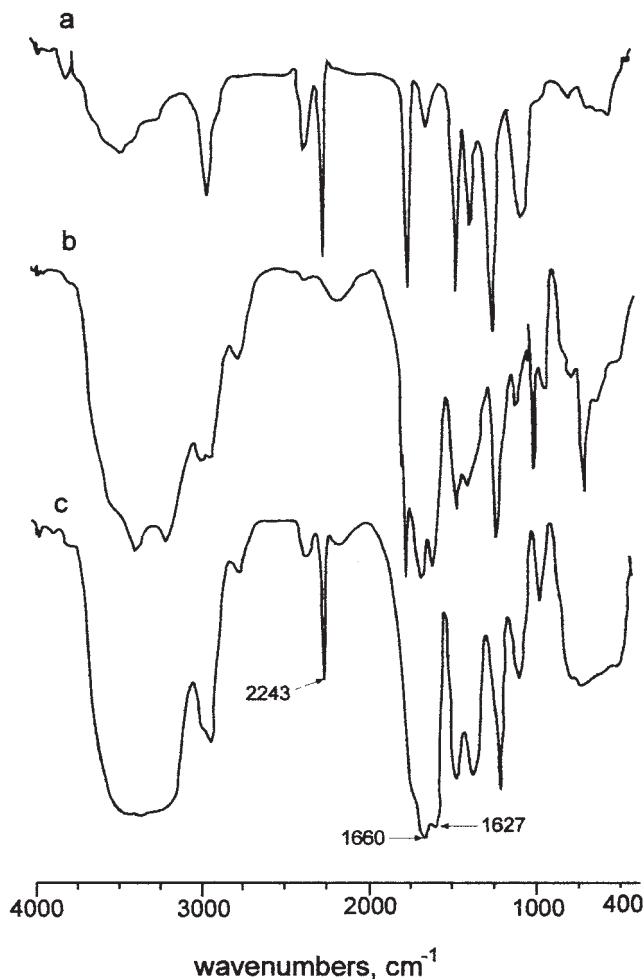

Figure 6 The FTIR spectra of (a) pure fiber, (b) pure polyMAA, and (c) 155.0% polyMAA-grafted fiber.

monomer units to add and, therefore, increases the graft yield.[3,14,15]

Effect of amount of acrylic fiber

The effect of the graft yield with variance of amount of acrylic fiber was investigated. Figure 5 shows the results obtained by changing the amount of fiber between 0 and 0.50 g while all other experimental conditions were constant. The graft yield is found to increase steadily with increase in the fiber amount and obtained a maximum graft yield at 0.15 g. By increasing the amount of acrylic fiber, the active sites on fiber surface are also increased and then the greater fiber surface area may be formed for better diffusion of the monomer. With a further increase in the fiber amount, the graft yield decreases. The decrease in the graft yield beyond the optimum amount of fiber may be due to the insufficient quantity of monomer for increasing the amount of fiber, hence giving minimal
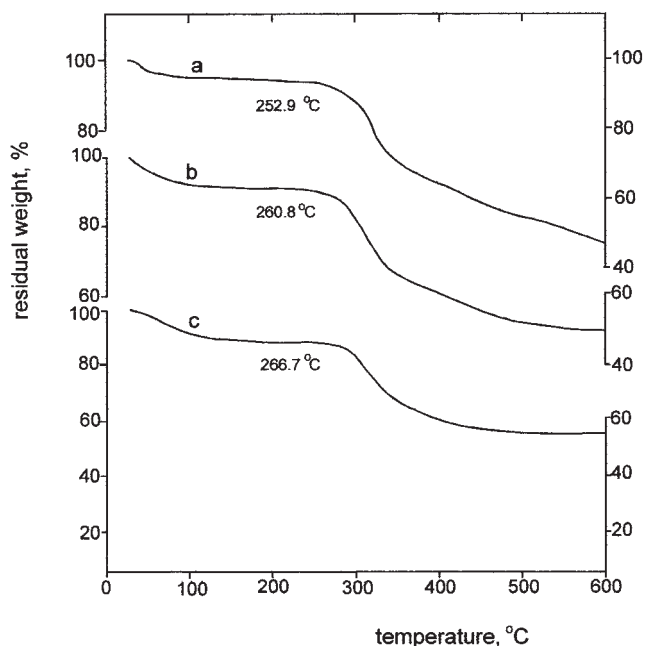

Figure 5 Change of the graft yield with amount of fiber: Bz_2O_2 concentration $= 3.0 \times 10^{-3}$ mol/L, MAA concentration $= 0.39$ mol/L, temperature $= 85°C$, time $= 180$ min.

Figure 7 TGA curves of (a) pure fiber, (b) 11.5% polyMAA-grafted fiber, and (c) 155.0% polyMAA-grafted fiber, obtained in nitrogen atmosphere at heating rate of 10°C/min. The decomposition temperatures are indicated within the figure.

diffusion of the monomer; an another factor is the active sites present in the backbone polymer may interact with each other and lead to termination of side chains.[12,16,17]

Characterization of grafted acrylic fibers

FTIR spectra

To confirm the changes in the chemical structure of the polyMAA-grafted acrylic fiber, FTIR spectroscopy measurement was carried out. Figures 6(a)-(c) give the FTIR spectra of pure fiber, pure polyMAA, and 155.0% polyMAA-grafted acrylic fiber, respectively. The spectrum of the grafted fiber showed a N–H stretching band at 3,200–3,450 cm,$^{-1}$ CO amide peaks at 1,660 cm,$^{-1}$ and a CN resonance peak at 1,627 cm,$^{-1}$ coming from the grafted polyMAA, and, at 2,243 cm,$^{-1}$ a peak due to the presence of C≡N groups coming from pure fiber.

Thermogravimetric analysis

The thermal behavior of ungrafted fiber and poly-MAA-grafted fiber was examined by TGA analysis under N_2 atmosphere at a heating rate of 10°C min^{-1}. The TGA curves for the thermal degradation of pure fiber and 11.5% and 155.0% polyMAA-grafted acrylic fiber are presented in Figure 7. The initial weight losses observed in the cases of pure and polyMAA-grafted fibers are due to the loss of moisture. The weight loss of the ungrafted acrylic fiber started at 252.9°C and reached a value of 52.55% at 600°C. The weight loss of 11.5 and 155.0% polyMAA-grafted fibers reached values of 50.00 and 44.65% at 600°C, respectively.

At higher graft yield values, the decomposition temperature of polyMAA-grafted acrylic fibers was observed to increase. This indicates that grafting increases the thermal stability of acrylic fibers perhaps due to new crosslinkages formed after grafting.[15,18]
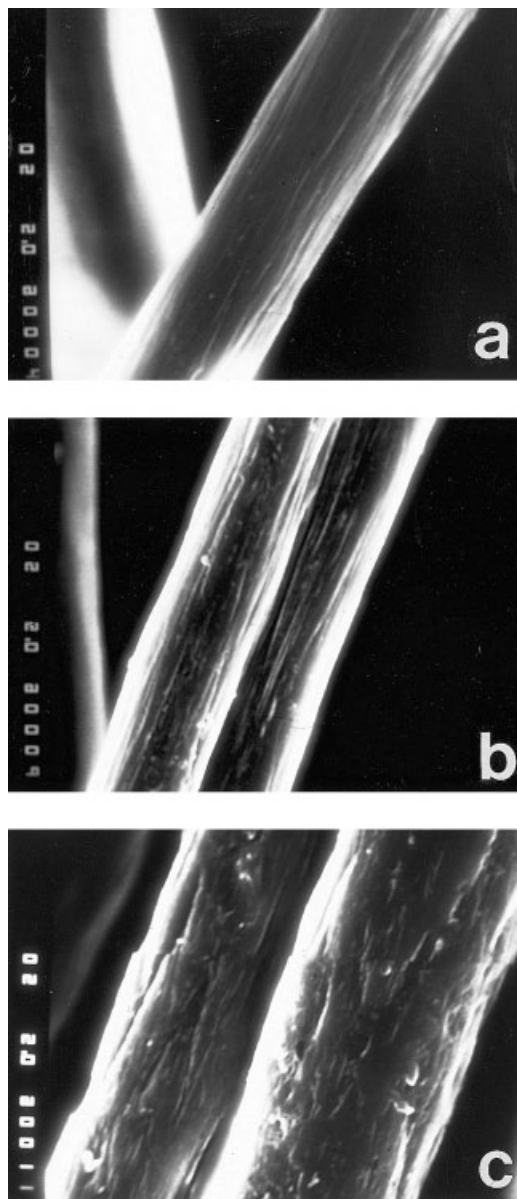

Figure 8 SEM photographs of polyMAA-grafted fiber at a magnification of ×2,000: (a) pure fiber, (b) 11.5%, and (c) 155.0% polyMAA-grafted fiber.

Scanning electron microscopy

The effect of MAA grafting upon the surface morphology of fiber was investigated by SEM. The SEM photographs of pure fiber and 11.5% and 155.0% polyMAA-grafted fiber at a magnification of ×2,000 are shown in Figure 8. The photographs demonstrated that the surface of 11.5% polyMAA-grafted acrylic fiber was as smooth and homogeneous as that of pure fiber. On the other hand the surface morphology of 155.0% polyMAA-grafted fiber completely changed and the smooth and homogeneous structure was destroyed and a shell-like structure was observed due to the chemically and/or physically bonded polyMAA on the fiber.[18,19]

Properties of grafted acrylic fibers

Moisture content and water absorption

The behavior of moisture content and water absorption as a function of grafing is shown in Figures 9 and 10. PolyMAA-grafted acrylic fibers exhibited a marked increase of moisture content and water absorption.

The values of moisture content of polyMAA-grafted acrylic fibers increased almost linearly in low graft yields (up to 70%) and then a tendency to attain a saturation value at higher graft yields was observed (Fig. 9).

The water absorption values of grafted acrylic fibers increased within an initial narrow range of graft yield (0–80%), thereafter decreasing very slowly due to the grafting process blocking the water attracting groups on the acrylic fiber chains[4] (Fig. 10).

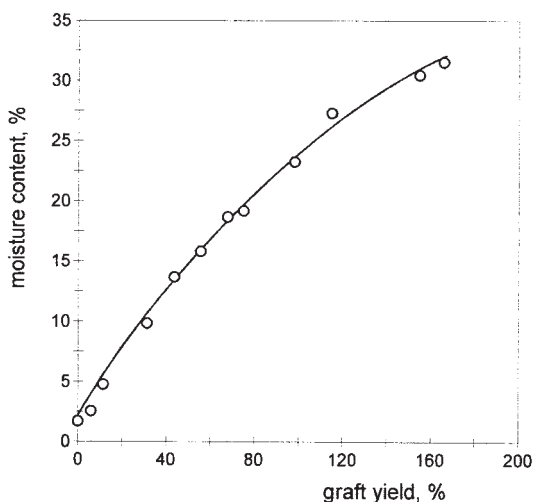These results confirm the grafting of MAA increased the moisture content and water absorption of
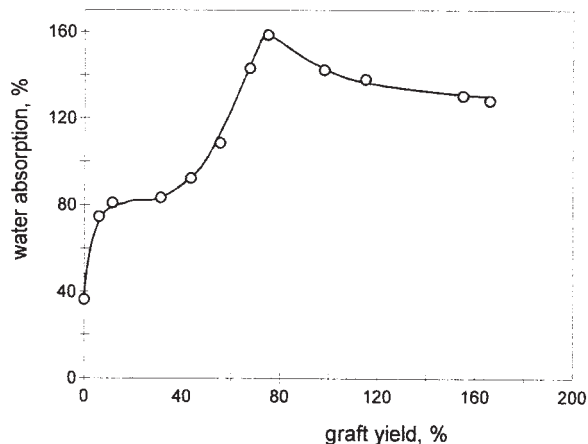

Figure 10 Relationship between water absorption and graft yield %.

acrylic fibers due to polyMAA being hydrophilic in nature and enhancing moisture absorption. This behavior has been recognized to play a positive role in improving the comfort of acrylic fibers.[19–22]

CONCLUSION

In this study MAA-grafted acrylic fibers with a high graft yield (up to 166.0%) can be obtained by means of the conventional reaction system (chemical initiation with Bz_2O_2 in aqueous medium). The optimum initiator concentration is 3.0×10^{-3} mol/L and the optimum temperature is 85°C to obtain a higher graft yield. No optimum value for the monomer concentration was found. The graft yield was observed to increase with the monomer concentration. Grafting of polyMAA improved the thermal stability, moisture content, and water absorption of fiber. Grafting also affected the fiber morphology. This is assumed to establish strong interactions between acrylic fiber and polymer by means of physical and/or chemical bonds.

Figure 9 Relationship between moisture content and graft yield %.

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