Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Characterization and Studies on Grafting of Methyl Methacrylate onto PAN Fibers

A. R. Bagheri[a]; M. Abdouss[a]; A. M. Shoushtari[b]; M. Javanbakht[a]; M. Zargaran[b]
[a] Department of Chemistry, Amirkabir University of Technology, Tehran, Iran [b] Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran

To cite this Article Bagheri, A. R. , Abdouss, M. , Shoushtari, A. M. , Javanbakht, M. and Zargaran, M.(2008) 'Characterization and Studies on Grafting of Methyl Methacrylate onto PAN Fibers', Journal of Macromolecular Science, Part A, 45: 7, 516 — 522

To link to this Article: DOI: 10.1080/10601320802100523

URL: http://dx.doi.org/10.1080/10601320802100523

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2008) **45**, 516–522

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320802100523

Characterization and Studies on Grafting of Methyl Methacrylate onto PAN Fibers

A. R. BAGHERI,[1] M. ABDOUSS,[1] A. M. SHOUSHTARI,[2] M. JAVANBAKHT,[1] and M. ZARGARAN[2]

[1]*Department of Chemistry, Amirkabir University of Technology, Tehran, Iran*
[2]*Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran*

Received November, 2007, Accepted December, 2007

The graft copolymerization of methyl methacrylate (MMA) onto commercial acrylic fibers (PAN) has been studied using Azobis(isobutyro)-nitrile (AIBN) as an initiator. MMA grafting initiated by radicals formed from thermal decomposition of AIBN. In this study, the effects of monomer and initiator concentration, time and temperature reaction on the grafting yield have been investigated.

The optimum conditions for this grafting reaction were obtained with an MMA concentration of 0.7 M, an AIBN concentration of 0.0073 M, a reaction temperature of T = 85°C and with a 60 min reaction time.

The fiber structure has been investigated by different experimental techniques of characterization such as Fourier transform infrared spectroscopy (FT-IR), calorimetric analysis (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), water absorption and the physical and mechanical properties has also been investigated in this study. The thermal analysis data showed that by increasing grafting yield, little changes have occurred in fibers samples up to 13.5% of grafting yield and the thermal transitions of grafted fibers have approximately the same behavior compared with the raw fibers sample. Grafting also slightly affected the fiber morphology. The experimental data of mechanical properties clearly show that by increasing grafting yield, max extension will decrease but this change up to 13.5% grafting yield is barely noticeable. Grafting of poly MMA improved water absorption.

Keywords: graft copolymerization; commercial acrylic fibers; thermal analysis; surface morphology; physical and mechanical properties

1 Introduction

The modification of polymers has received much attention in recent years. Among all the modification methods, grafting is one of the promising methods. In principle, graft copolymerization is an attractive method to impart a variety of functional groups to a polymer (1, 2). The grafting reaction involves copolymerization of the monomer onto the polymer backbone. The formation of copolymers of various synthetic and natural polymers via graft copolymerization has been extensively studied (3–5). Among synthetic fibers, acrylic fibers seem to be important fibers because of their potential applications in many industries (6). Acrylic fibers are synthetic fibers made from a polymer with a weight average molecular weight of ~100000. To be called acrylic, the polymer must contain at least 85% acrylonitrile (AN) monomer. Typical comonomers are vinyl acetate or methyl acrylate. The polymer is formed by free radical polymerization. End uses of acrylic fibers include sweaters, hand-knitting yarns, rugs, awnings, boat covers, and as a precursor for carbon fiber. It dyes very well and has excellent colorfastness. It is resilient, retains its shape and resists shrinkage and wrinkles. Acrylic is resistant to moths, oils, chemicals and is very resistant to deterioration from sunlight exposure. Grafting of PAN fibers with regard to its intensive effects on fiber properties such as thermal stability, swelling characteristics, physical and mechanical behavior, has been considered as one of the most important techniques for PAN fiber modification. Vinyl monomers such as acrylic acid, methacrylic acid and acrylamide can be grafted onto PAN fibers by chemical or radiation initiation (7, 8). Chemical methods are more advantageous, regarding to lower deterioration in the main polymer chains. This research reports the grafting of methyl methacrylate (MMA) onto PAN fibers by the use of azobis(isobutyro)nitrile (AIBN). In this research, the effects of various experimental conditions on grafting, such as initiator and monomer concentrations, polymerization time and polymerization temperature were systematically studied. In addition, grafted acrylic fibers were characterized for thermal, mechanical and morphological properties and water absorption.

Address correspondence to: M. Abdouss, Department of Chemistry, Amirkabir University of Technology, Tehran, Iran. E-mail: majidabdouss@yahoo.com

2 Experimental

2.1 Materials and Methods

The MMA used in this work was supplied by Merck Co. (Germany). PAN fibers (3.3 dTex) were obtained from Polyacryl Co. (Iran), and AIBN was obtained from Merck Chemical Co. (Germany). Acetone, methanol, dichloromethane were all of analytical grade and also supplied by Merck Chemical Co.

Methyl methacrylate (MMA) was washed three times with 5% NaOH, dried over $CaCl_2$ and finally distilled in vacuum at 46°C. MMA, freshly distilled throughout the study, was kept in the dark (9).

The experiments were carried out using multi-filament PAN fibers. The samples were prepared as a small hank (2 ± 0.01 gr) soxhlet-extracted for 3 h with dichloromethane, and dried at ambient temperature.

AIBN was recrystallized from the ethanol and dried in vacuum. The effects of various experimental conditions such as initiator and monomer concentrations, temperature and time on the grafting yield were investigated. A PAN fiber sample was placed in a 100 ml polymerization tube containing the required concentrations of monomer and initiator in 5 ml acetone. The volume of the polymerization mixture was increased to 50 ml with distilled water and then the mixture was immediately placed into a water bath at the polymerization temperature. After the desired polymerization time, the fiber sample was taken out of the tube and washed with boiling water for 3 h (changing the washing water 4 times) and then Soxhlet-extracted for 6 h. The washed fibers were dried at 50°C under vacuum.

Finally, the sample was dried until it maintained a constant weight (10–12). The percent graft yield was calculated from the increase in the weight of the original PAN after grafting:

$$\text{Grafting yield } (\%) = [(W_2 - W_1)]/W_1 * 100 \qquad (1)$$

Where W_1 and W_2 denote the weights of the original and grafted PAN, respectively.

To evaluate the chemical changes of fiber structure modified by grafting treatments, a Fourier transform infra red technique (FT-IR) using a Nicolet Nexus 670 spectrometer was employed. The spectra of PAN surfaces before and after grafting from 500 to 4000 cm^{-1} were recorded.

The calorimetric measurements were made with a DSC 2010 TA differential scanning calorimeter in a dry nitrogen atmosphere, and the decomposition temperature values, also by thermogravimetric analysis (TGA), were also investigated. Thermal data were obtained using a Labsys TGA thermobalance.

The physical and mechanical properties were investigated and measured by a tensile tester. The distance of jaws was 20 mm and the speed of increasing of jaws' length was 20 mm/min. Mechanical data were obtained using a Tex-Techno tensile tester.

The surface morphology of ungrafted and grafted fibers was investigated by scanning electron microscopy. Detailed images of PAN fibers surfaces were obtained using SEM (Philips XL30). The SEM samples were gold-sputtered before observations. The weight of samples was determined and then they were dried in a vacuum oven at 60°C overnight. After predetermining 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.

3 Results and Discussions

3.1 Effect of MMA Concentration

The effect of the methyl methacrylate concentration on grafting yield is presented in Figure 1. The experimental results show that the grafting yield increases when the MMA concentration is increased up to 0.7 M and then decreases. In fact, increasing MMA concentration increases the number of short chains and thus favors the diffusion of the polymer into the fiber. However, it can be noticed that the grafting yield does not exceed 90.5%. This is probably due to the saturation of radical sites present on the fibers by chains growing progressively. Beyond the value of 0.7 M, a decrease in the grafting yield is observed. This may be due to high homopolymer formation (termination by recombination or dismutation) in the reaction. Error of all reported grafting yield is 0.5% (Grafting yield (%) $\pm$ 0.5%).

3.2 Effect of AIBN Concentration

The effect of azobis(isobutyro)nitrile concentration on grafting yield was studied at different AIBN concentrations. These results are shown in Figure 2. It is seen that increasing the AIBN concentration up to 0.0073 M leads to a significant enhancement in grafting yield, reaching 94%. Further increases in AIBN concentration decreases the grafting

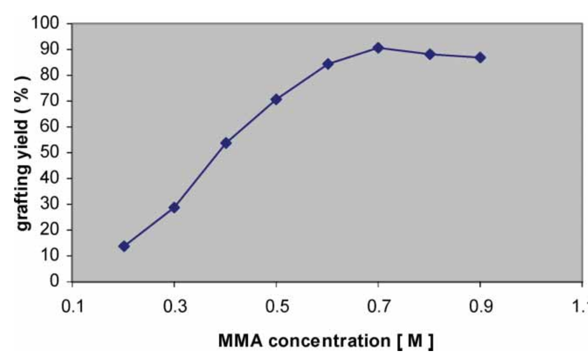

Fig. 1. Effect of the grafting yield vs. MMA concentration. [AIBN] = 0.0061 M, temperature 85°C, time 60 min.

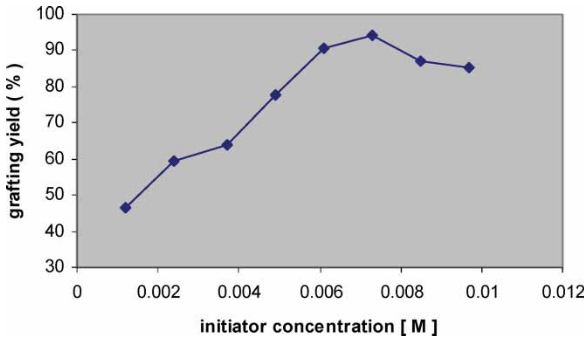

Fig. 2. Effect of the grafting yield vs. AIBN concentration. [MMA] = 0.7 M, temperature 85°C, time 60 min.

yield. From grafting point of view, the increase of AIBN concentration acts similarly to the MMA concentration. We propose the similar explanation mentioned previously. Similar results were reported for grafting acrylic acid/methyl methacrylate on polyethylene terephthalate) (PET) fibers and grafting acrylic acid on poly(ethylene terephthalate) (13, 14).

At a higher AIBN concentration, an abundance of free radicals is expected. As a result, participation of the free radicals in a termination process with growing polymer chains and PAN macroradicals, would be favored over grafting, thus decreasing it.

The free radical concentration of AIBN molecules in the polymerization medium increases with increasing AIBN concentration. In addition, the increase in AIBN concentration increases the number of radicals' species, such as active poly MMA chains. These active polymeric chains undergo chain transfer reaction with PAN macromolecules which causes the formation of a higher number of active sites on the PAN backbone. However, the increase of AIBN concentration above a critical value of 0.0073 M makes the radical concentration excessive in the polymerization medium. Thus, the rate of termination reactions increases and grafting yields decrease. The error of all reported grafting yield is 0.5% (grafting yield (%) ± 0.5%).

3.3 Effect of Reaction Temperature

The effect of temperature on the grafting yield was studied and represented in Figure 3.

The grafting yield is affected by temperature. In fact, an increase up to 85°C increases the grafting yield. This can be related to the increase of the initiation and propagation rates of graft copolymerization, the swellability of PAN fibers, and the mobility of the reactive species. But above 85°C, the grafting yield decreases. This is probably because at higher temperatures, higher combination rates of monomer are obtained increasing homopolymerization reactions and also the decrease in the grafting yield at temperatures above 85°C may be attributed to the increase in the rates of termination reactions. Similar observations for grafting methacrylic acid onto PET using benzoyl peroxide (BPO) as initiator have been reported (15). Error of all reported grafting yield is 0.5% (Grafting yield (%) ± 0.5%).

3.4 Effect of Reaction Time

Grafting yield increases with an increase in reaction time. The graft copolymerization yield increases to a maximum value after 60 min of reaction time (Figure 4). Similar observations were reported such as grafting acrylic acid/methyl methacrylate on PET fibers and grafting acrylic monomers such as acrylamide and glycidyl methacrylate on polyamide fibers using other initiators (13)160. The error of all reported grafting yield is 0.5% (grafting yield (%) ± 0.5%).

3.5 FT-IR Spectroscopy

The IR spectra of PAN fibers before and after grafting are shown in Figures 5 and 6. Spectroscopy of grafted fibers also indicates an increase of the peak intensity of the carbonyl group in $\sim$1732 cm^{-1} as a function of the grafting yield. This peak can pertain to ester group as a yield from the addition of methyl methacrylate. Because of existence of some comonomers with ester group (-COOR) such as vinyl acetate and methyl acrylate in raw commercial acrylic fibers, a peak environs 1730 cm^{-1} in the raw fiber's spectrum

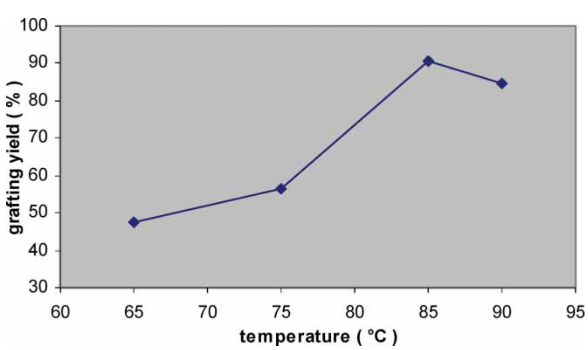

Fig. 3. Effect of the grafting yield vs. temperature reaction. [MMA] = 0.7 M, [AIBN] = 0.0061 M, time 60 min.

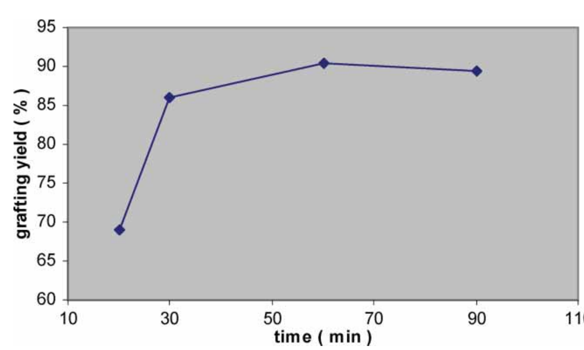

Fig. 4. Effect of the grafting yield vs. time reaction. [MMA] = 0.7 M, [AIBN] = 0.0061 M, temperature 85°C.

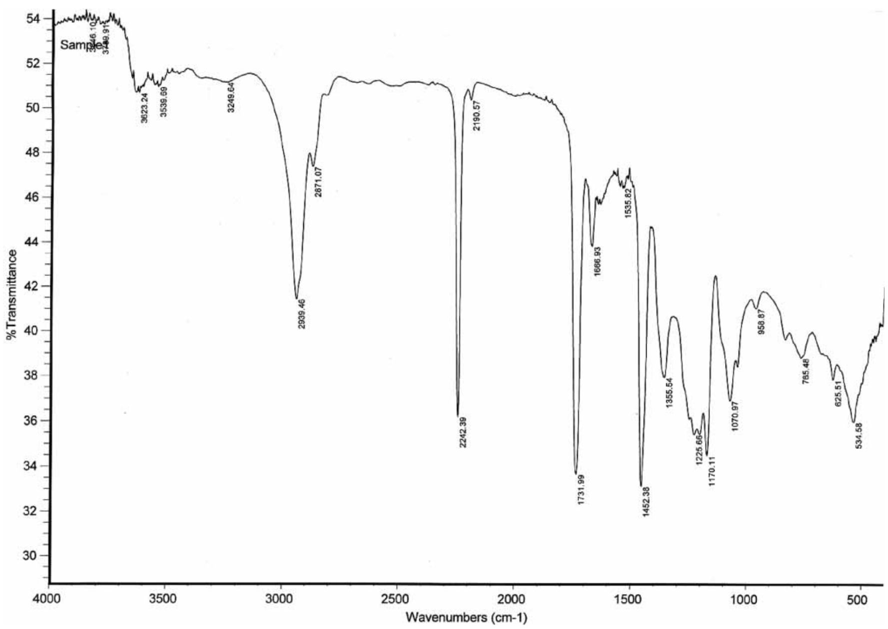

Fig. 5. Infrared spectrum of ungrafted PAN fibers.

appears. This peak was noticed in raw fibers in 1731.99 cm^{-1}. By grafting of methyl methacrylate onto fibers increased this peak's intensity because the content of ester group increases.

3.6 Differential Scanning Calorimeter (DSC) Analysis

Scanning was carried out from 25°C to 300°C under nitrogen atmosphere at a heating rate of 10°C/min. The DSC thermograms of ungrafted and grafted fibers (are presented in Figure 7) showed little change in thermal transitions (17). However, it is clear that DSC thermograms of commercial acrylic fibers are very complicated because of including other comonomers such as vinyl acetate and methyl acrylate with unknown mass fraction. With grafting of MMA to fibers, the thermal transitions have been conserved.

The DSC thermograms of ungrafted and grafted acrylic fibers in this research were used only for comparing changes in thermal transitions between ungrafted and grafted fiber.

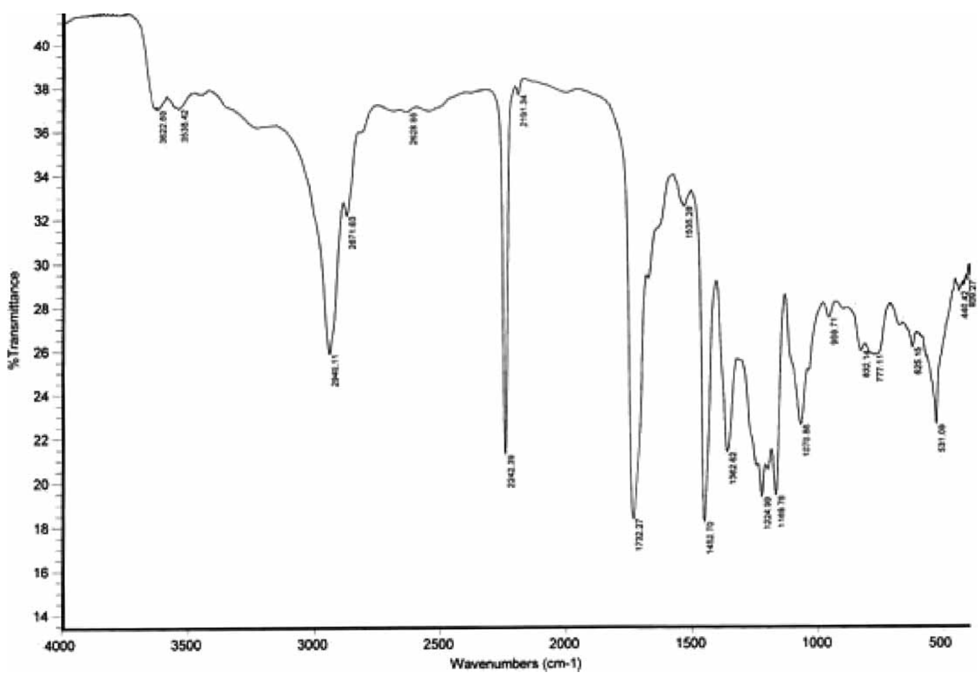

Fig. 6. Infrared spectrum of grafted PAN fibers.

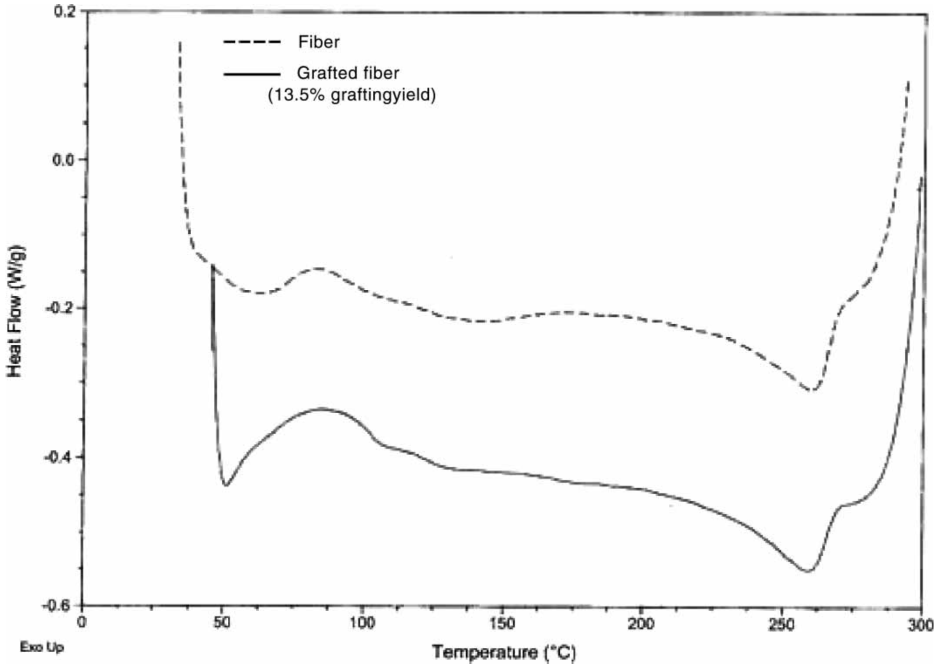

Fig. 7. DSC thermograms of ungrafted and grafted PAN fibers.

3.7 *TGA Analysis Results*

The thermal behavior of ungrafted fiber and poly MMA-grafted fiber was examined by TGA analysis under nitrogen atmosphere at a heating rate of $10^{\circ}C\ min^{-1}$. Figure 8 illustrates the experimental TGA curves before and after grafting reaction.

By increasing the degree of graft copolymerization, the thermal stability decreases.

But up to 13.5% of grafting yield, this decrease is very slight. In other words, the decomposition temperature of grafted fibers up to 13.5% of grafting yield compared with raw acrylic fibers has been conserved approximately.

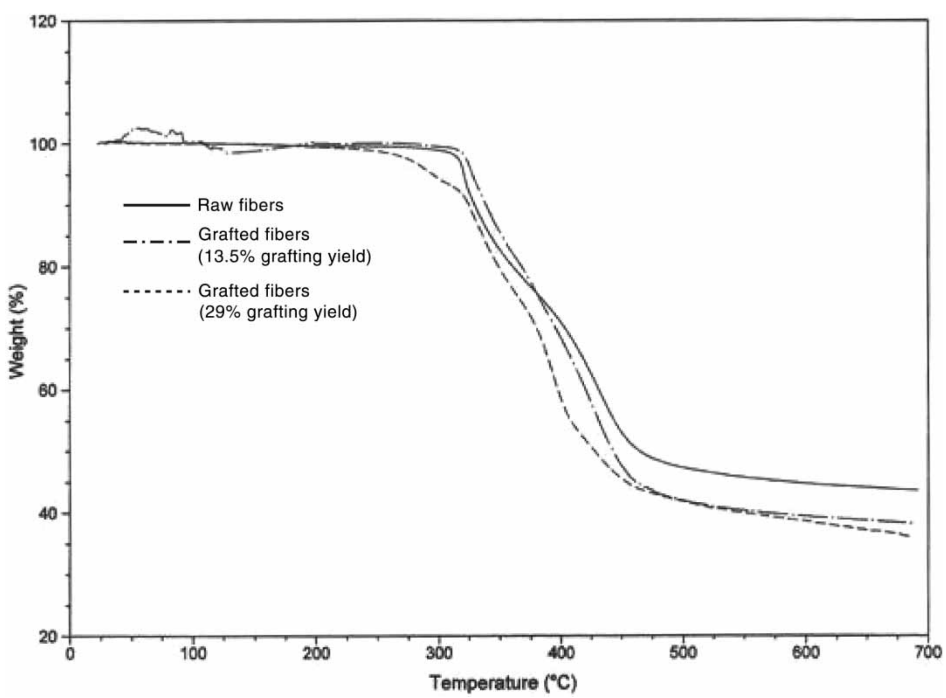

Fig. 8. TGA thermograms of ungrafted and grafted PAN fibers.

Table 1. Mechanical test results of ungrafted and grafted PAN fibers

	Max extension (%)	Extension at max load (%)
Ungrafted fibers	24.89	23.73
Grafted fibers (13.5% grafting yield)	21.95	20.12
Grafted fibers (29% grafting yield)	20.41	19.37

Thermograms of ungrafted and grafted fibers indicate that thermal decomposition temperatures of the fibers decrease after grafting yields more than 13.5%. Similar results have been obtained by grafting of acrylic acid/methyl methacrylate mixture onto PET fibers (13, 17).

3.8 Mechanical and Physical Properties Results

The experimental results obtained by the series of mechanical tests made on the ungrafted and grafted PAN fibers are presented in Table 1. Increasing the grafting yield decreases max extension and extension at maximum load. This is probably because of changes which resulted in molecular structure of raw fibers through radical polymerization. Statistical results have been done more than 20 times in this research. C.V. % of all of the mechanical data is under 8%.

3.9 Surface Morphology of the Ungrafted and Grafted Fibers

The effect of MMA grafting upon the surface morphology of fiber was investigated by SEM. The SEM photographs of raw (ungrafted) fiber and 29% poly MMA-grafted fiber at a magnification of 1500 are shown in Figures 9 and 10. It is clear that little changes have occurred in the morphology of the fiber but photographs demonstrated that the surface of 29% poly MMA-grafted acrylic fiber was approximately as smooth and homogeneous as that of raw fiber. This can be related to lower grafting yield due to chemically bonded poly MMA on the fiber (7, 8).

Fig. 9. SEM photograph of ungrafted PAN fibers (Magnification of 1500).

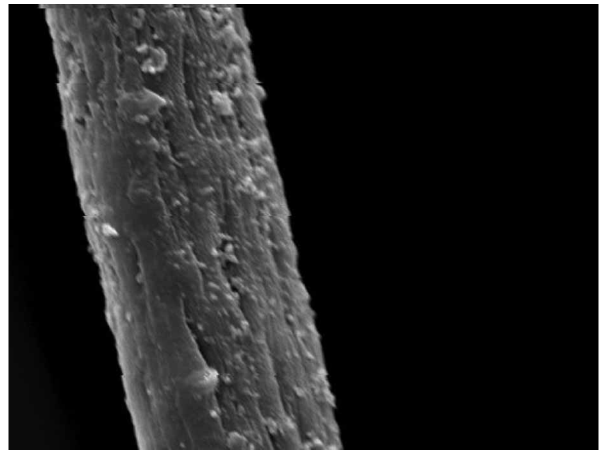

Fig. 10. SEM photograph of grafted PAN fibers (29% grafting yield) (Magnification of 1500).

3.10 Water Absorption

The behavior of water absorption as a function of grafting is shown in Figure 11. 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 (Fig. 11).

These results confirm the grafting of MMA increased water absorption of acrylic fibers due to the enlargement of the fiber structure due to grafting process. The enlargement of the fiber structure will also have effect on the increase of water absorption.

This behavior has been recognized to play a positive role in improving the comfort of acrylic fibers (18–20).

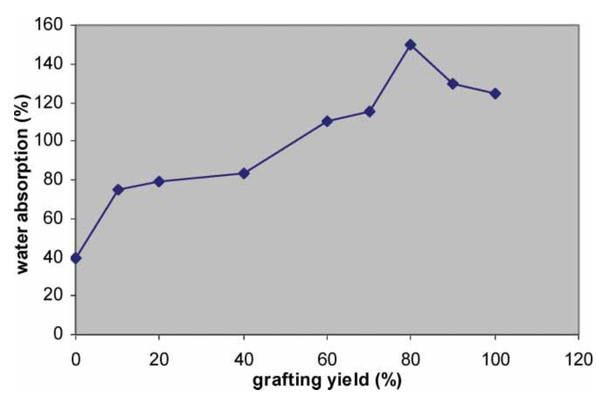

Fig. 11. Relationship between water absorption and grafting yield.

4 Conclusions

In this study, the grafting of methyl methacrylate (MMA) monomer onto PAN fiber was performed by free-radical polymerization using AIBN as an initiator. The maximum grafting yield in this research was 94%. The optimum conditions were 0.7 M methyl methacrylate concentration, 85°C temperature and 60 min reaction time. The chemical changes of modified PAN fibers were examined by FT-IR. DSC measurements showed approximately same thermal transitions in MMA grafted acrylic fibers compared with raw acrylic fibers and also TGA measurement data showed primarily the approximate same thermal behavior such as decomposition temperature and thermal stability in grafted fiber compared with raw fiber (up to 13.5% of grafting yield) but by increasing grafting yield, decreases thermal stability clearly. In terms of mechanical properties, experimental results have shown a decrease in final extension and extension at max load by an increase of grafting yield. Grafting also slightly affected the fiber morphology. Grafting of poly MMA improved water absorption.

5 References

1. Celik, M. and Sacak, M. (2002) *J. Appl. Polym. Sci.*, **86**, 53–57.
2. Mohanty, K., Tripathy, P.C., Misra, M., Parija, S. and Sahoo, S. (2000) *J. Appl. Polym. Sci.*, **77**, 3035–3043.
3. Celik, M. and Sacak, M. (1996) *J. Appl. Polym. Sci.*, **59**, 609–617.
4. Sacak, M. and Celik, M. (1996) *J. Appl. Polym. Sci.*, **59**, 1191–1194.
5. Tsukada, M., Imai, T., Freddi, G., Lenka, S. and Kasai, N. (1998) *J. Appl. Polym. Sci.*, **69**, 239–246.
6. Buchenska, J. (1997) *J. Appl. Polym. Sci.*, **65**, 1955–1966.
7. Celik, M. (2004) *J. Appl. Polym. Sci.*, **94**, 1519–1525.
8. Makhlouf, C., Marais, S. and Roudesli, S. (2007) *J. Appl. Surf. Sci.*, **253**, 5521–5528.
9. Buchenska, J. (2001) *J. Appl. Polym. Sci.*, **80**, 1914–1919.
10. Osipenko, I.F. and Martinovicz, V.I. (1990) *J. Appl. Polym. Sci.*, **39**, 935–942.
11. Sacak, M. and Oflaz, F. (1993) *J. Appl. Polym. Sci.*, **50**, 1909–1916.
12. Sacak, M., Bastug, N. and Talu, M. (1993) *J. Appl. Polym. Sci.*, **50**, 1123–1129.
13. Azizinejad, F., Talu, M., Abdouss, M. and Shabani, M. (2005) *Iran. Polym. J.*, **14(1)**, 33–38.
14. Okoniewsko, M., Sogka, J. and Ledakowicz, S. (1988) *J. Appl. Polym. Sci.*, **35**, 1241–1249.
15. Saihi, D., El-Achari, A., Ghenaim, A. and Caze, C. (2002) *J. Polym. Test.*, **21**, 607–612.
16. Sanli, O. and Pulet, E. (1993) *J. Appl. Polym. Sci.*, **47**, 1–6.
17. Coskun, R. (2007) *Euro. Polym. J.*, **43**, 1428–1435.
18. Freddi, G., Massafra, M.R., Beretta, S., Shibata, S., Gotoh, Y., Yasui, H. and Tsukada, M. (1996) *J. Appl. Polym. Sci.*, **60**, 1867.
19. Tsukada, M., Freddi, G., Massafra, M.R. and Beretta, S. (1998) *J. Appl. Polym. Sci.*, **67**, 1393.
20. Chen, Y., Zhang, G. and Zhang, H. (2001) *J. Appl. Polym. Sci.*, **82**, 400.