Trade Science Inc.

December 2007 Volume 2 Issue 3

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ 2(3) 2007 [100-106]

Studies on effects of grafting of acrylic acid onto commercial acrylic fibers on thermal and mechanical properties

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Received: 5th September, 2007 ; Accepted: 10th September, 2007

ABSTRACT

The graft copolymerization of acrylic acid(AA) onto commercial acrylic fibers(PAN) has been studied using azobis(isobutyro)nitrile(AIBN) as an initiator. AA 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 AA concentration of 1.67M, an AIBN concentration of 0.0097M, a reaction temperature of T=85^{0}C and with reaction time of 60 minutes. 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) and also in this study has been investigated the physical and mechanical properties. The thermal analysis data showed that increasing in grafting yield, decreases the thermal stability of fiber. Grafting also affected slightly the fiber morphology. The experimental data of mechanical properties show clearly that by increasing of grafting yield, max extension will decreased.

KEYWORDS

Graft copolymerization;
Acrylic fibers;
Fourier transform infrared spectroscopy;
Thermal analysis;
Surface morphology;
Physical and mechanical properties.

INTRODUCTION

The modification of polymers has received much attention in recent years. Among all the methods of modifications, 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]. Grafting reaction involves the copolymerization of monomer onto the polymer backbone. The formation of copolymers of various synthetic and natural polymers via graft copolymerization has been extensively studied[2,3,4]. Among synthetic fibers, acrylic fibers seem to be important fibers because of their potential applications in many industries[5]. 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(AA) 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, awning, 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 regarding 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. Chemical methods are more advantageous, regarding to lower deterioration in the main polymer chains. This research reports the grafting of acrylic acid(AA) 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 and morphological properties.

In this research could be conserved approximately the thermal transition of acrylic fiber showed in DSC thermograms up to 10 % of grafting yield but decomposition temperature of acrylic fibers decreased.

Grafting reaction was carried out by slight changes in morphological surface of fibers compared with other researches in this field[20,21].

MATERIAL AND METHODS

Reagents, solutions

The AA used in this work were 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.

EXPERIMENTAL

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

AIBN was recrystallized from the ethanol and dried in vacuum. Acrylic Acid (AA) was vacuum-distilled over a column filled with copper wires at 30^0C[6].AA freshly distilled throughout the study, was kept in the dark. 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 100ml polymerization tube containing the required concentrations of monomer and initiator in 5ml acetone. The volume of the polymerization mixture was increased to 50ml 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 warm distilled water and then washed with acetone and methanol mixture for 3h. Finally, the sample was dried until it maintained a constant weight[7,8,9]. Percent graft yield was calculated from the increase in the weight of the original PAN after grafting:

$$\textbf{Graft yield (\%)} = [(W2-W1)] / W1\times100 \qquad (1)$$

Where W1 and W2 denote the weights of the original and grafted PAN, respectively.

Fiber characterization

FT-IR

To evaluate the chemical changes of fiber structure modified by grafting treatments, 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.

Thermal analysis

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

Physical and mechanical properties

The physical and mechanical properties were investigated and measured by tensile tester. The distance of jaws was 20cm and the speed of increasing of jaws length was 20 mm/min.

Scanning microscopy

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.

RESULTS AND DISCUSSION

Effect of AA concentration

The effect of acrylic acid concentration on grafting yield is presented in figure 1. The experimental results show that the grafting yield increases when the AA concentration is increased up to 1.67M and then decreases. In fact, increasing AA 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 32%.This is probably due to the saturation of radical sites present on the fibers by chains growing progressively. Beyond the value of 1.67M, a decrease in the grafting yield is observed. This may be due to high homopolymer formation (termination by recombination or dismutation) in the reaction. Above results were in good agreement with other reports[1,10,11].

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 0.0097M leads to a significant enhancement in grafting yield, reaching 34.43%.Further increases in AIBN concentration decreases grafting yield. From grafting point of view, the increase of AIBN concentration acts similarly AA 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)[12,13].

At 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.

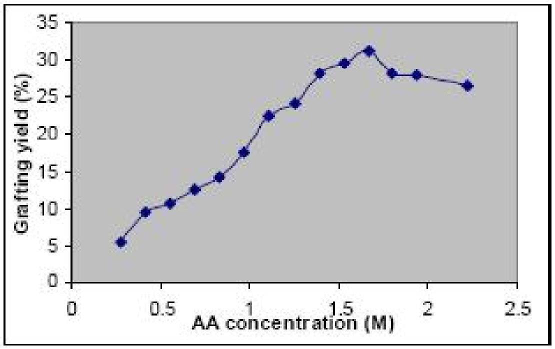

Figure 1 :Variation of the grafting yield vs. AA concentration. [AIBN]=0.0061M, temperature 85°C, time 60min

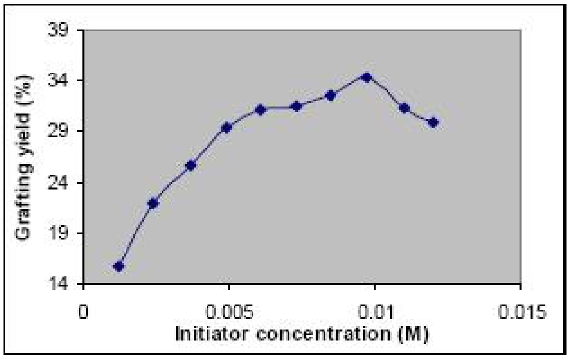

Figure 2: Variation of the grafting yield vs. AIBN concentration. [AA]=1.67M temperature 85°C,time 60min

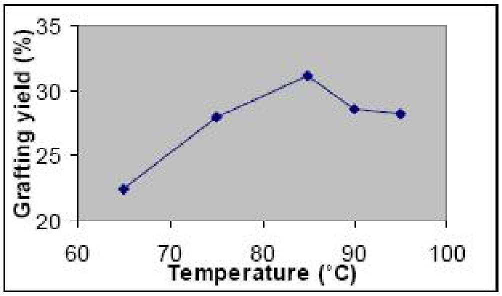

Figure 3: Variation of the grafting yield vs. temperature reaction.[AA]=1.67M, [AIBN]=0.0061M, time 60min

Effect of reaction temperature

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

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 beyond 85^{0}C, the grafting yield decreases. Probably this is because at higher temperatures, higher combination rates of monomer are obtained increasing

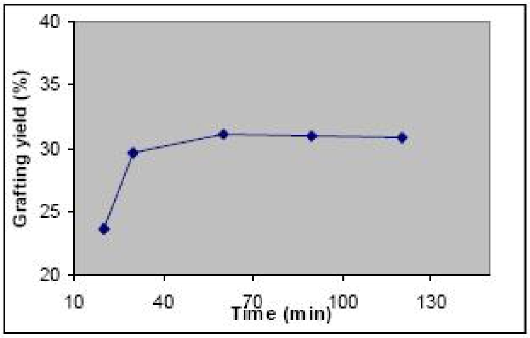

Figure 4:Variation of the grafting yield vs. time reaction. [AA]=1.67M, [AIBN]=0.0061M, temperature 85°C

homopolymerization reactions, which results in a decreased grafting yield. Similar observations for grafting methacrylic acid onto PET using benzoyl peroxide (BPO) as initiator have been reported[14].

Effect of reaction time

Grafting yield increases with an increase in reaction time. The graft copolymerization yield increases to a maximum value after 60min of reaction time(see figure 4). Similar observations were reported such as grafting acrylic acid/methyl methacrylate on PET fibers and grafting acrylic monomers such as acrylamide and

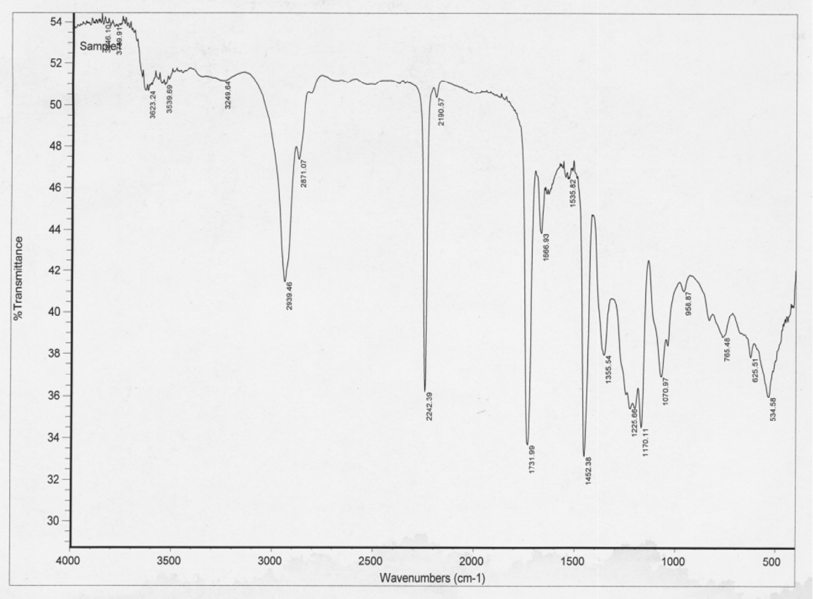

Figure 5 : Infrared spectrum of ungrafted PAN fibers

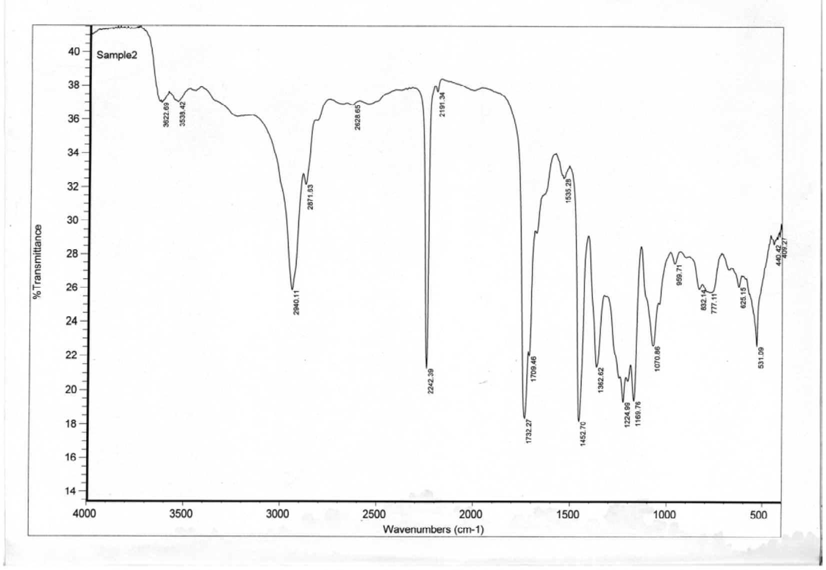

Figure 6 : Infrared spectrum of grafted PAN fibers

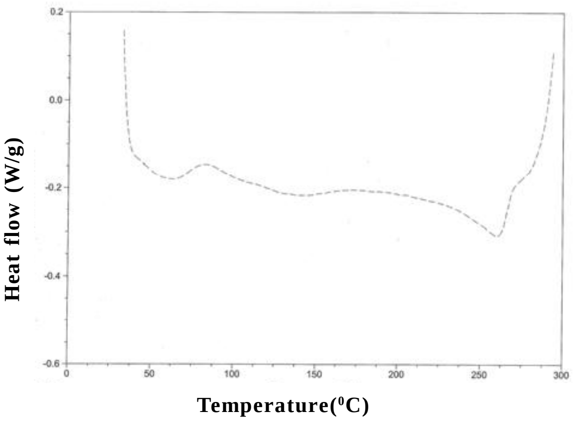

Figure 7 : DSC thermogram of ungrafted PAN fibers

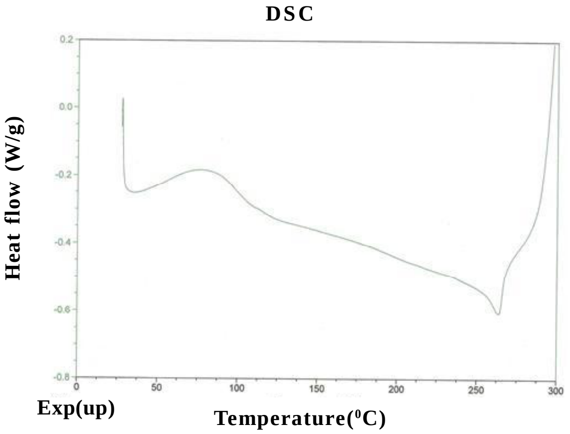

Figure 8: DSC thermogram of grafted PAN fibers

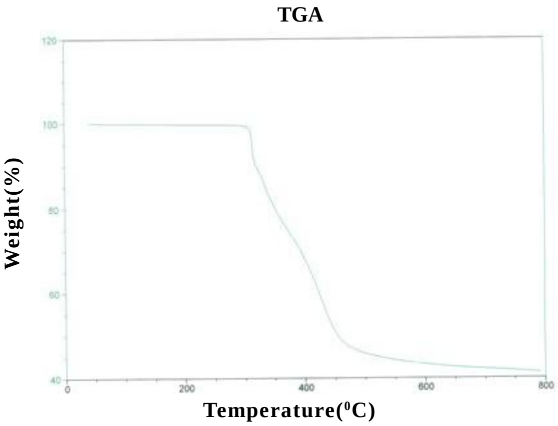

Figure 9: TGA thermogram of ungrafted PAN fibers

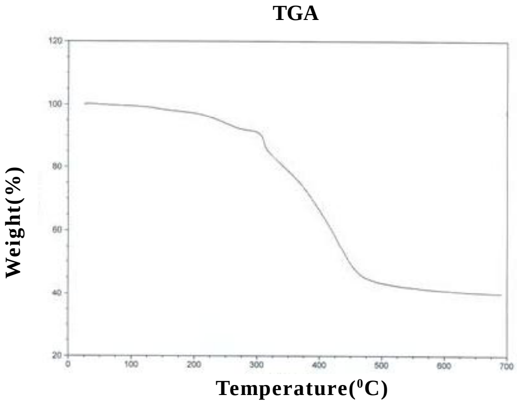

Figure 10: TGA thermogram of grafted PAN fibers (10.63 % grafting yield)

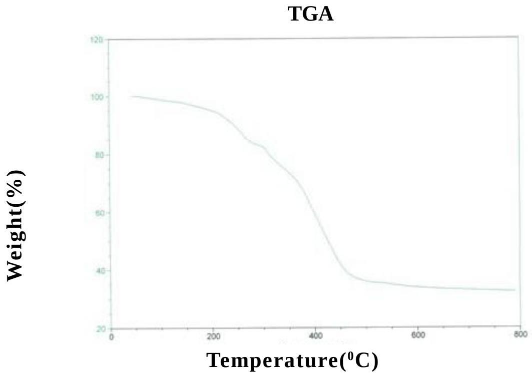

Figure 11: TGA thermogram of grafted PAN fibers (17.46 % grafting yield)

glycidyl methacrylate on polyamide fibers using other initiators[11,15,16,17].

FT-IR spectroscopy

The IR spectra of PAN fibers before and after grafting are shown in figure 5 and figure 6. These results reveal clearly the grafting reaction with the appearance of a new bond , located at ~1709cm^{-1}, characteristic of the carboxylic acid (-COOH) group of AA[18].

Moreover, spectroscopy of grafted fibers indicates also an increase of the peak intensity of the carbonyl group as a function of the grafting yield.

Differential scanning calorimeter (DSC) analysis

Scanning was carried out from 25^{0}C to 300^{0}C under nitrogen atmosphere at a heating rate of 10^{0}C/min. The DSC thermograms of ungrafted and grafted fiber(are presented in figure 7 and figure 8) showed a little changes in thermal transitions. But it is clear that the interpretation of DSC thermograms of acrylic fibers is very complicated because of including other comonomers such vinyl acetate with unknown mass fraction in structure of commercial acrylic fibers.

TGA analysis results

The thermal behavior of ungrafted fiber and poly AA-grafted fiber was examined by TGA analysis under nitrogen atmosphere at a heating rate of 10^{0}Cmin^{-1}.

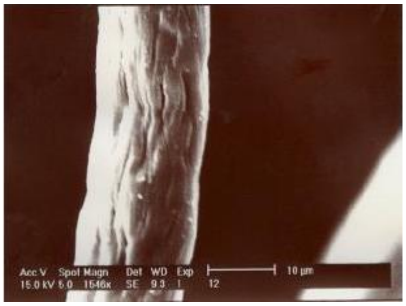

Figure 12 : SEM photograph of ungrafted PAN fibers

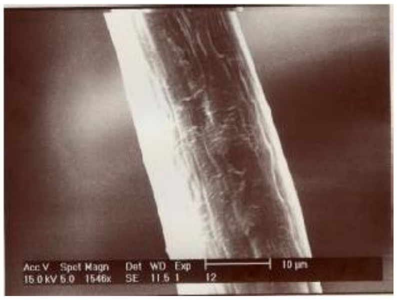

Figure 13: SEM photograph of grafted PAN fibers (17.46% grafting yield)

TABLE 1 : Mechanical and physical test results of ungrafted and grafted PAN fibers

	Max extension(%)
Ungrafted fibers	24.89
Grafted fibers (10.63 % grafting yield)	20.12
Grafted fibers (17.46 % grafting yield)	18.17

Figure 9, figure10 and figure11 illustrate the experimental TGA curves before and after grafting reaction.

By increasing the degree of graft copolymerization, the thermal stability decreased. Thermograms of ungrafted and grafted fibers indicate that thermal decomposition temperatures of the fibers decrease after grafting treatment. Similar results have been obtained by grafting of acrylic acid/methyl methacrylate mixture onto PET fibers[12,19].

Mechanical and physical properties results

The experimental results obtained by the series of mechanical and physical tests made on the ungrafted and grafted PAN fibers are presented in TABLE 1. By increasing of the grafting yield decrease in the max extension was noticed. Probably this is because of the decrease in nitrile group content and changes resulted in molecular structure of ungrafted fibers through radical copolymerization.

Surface morphology of the ungrafted and grafted fibers

The effect of AA grafting upon the surface morphology of fiber was investigated by SEM. The SEM photographs of pure (ungrafted) fiber and 17.46 % poly AA-grafted fiber at a magnification of 1500 are shown in figure12 and figure13. As it is clear, it has been occurred some little changes in the morphology of the fiber but photographs demonstrated that the surface of 17.46% poly AA-grafted acrylic fiber was as smooth and homogeneous as that of pure fiber. This can be related to lower grafting yield due to the chemically and physically bonded poly AA on the fiber[20].

CONCLUSION

In this study, the grafting of acrylic acid (AA) monomer onto PAN fiber was performed by free-radical polymerization using AIBN as an initiator. The maximum grafting yield was 34.43%. The optimum conditions were 1.67M acrylic acid concentration, 85°C temperature and 60 min reaction time. The chemical changes of modified PAN fibers were examined by FT- IR. DSC measurements showed and also TGA measurement showed the decrease in thermal stability. In terms of mechanical properties, experimental results have shown decrease in final extension with an increase of grafting yield. Grafting also affected slightly the fiber morphology. This is assumed to establish strong interactions between acrylic fiber and polymer by means of physical and chemical bonds, but by 17.46% of grafting yield little changes in fibers surface can be observed.

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