Modification of Poly(Ethylene Terephthalate) Fiber by Grafting of Acrylic Acid/Acrylamid for Removel of Pb^{+2} from Aqueous Solutions

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ABSTRACT: *A new fibrous adsorbent was prepared by grafting Acrylic Acid /Acryl Amide (AA/AAm) co-monomers onto Poly(Ethylene Terephtalat) (PET) fibers. The resulting sorbent has been characterized by Fourier Transform InfraRed spectroscopy (FT-IR), Thermo Gravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and elemental analysis and studied for the preconcentration and determination of trace Pb^{+2} ion from water sample. The effects of reaction conditions such as monomer mixture ratio, grafting yield, polymerization. The time and temperature on grafting were investigated. Batch adsorption method was used for the pre concentration studies. Recovery of Pb^{+2} was 100.2% at optimum conditions. The adsorption capacity of the adsorbent was found 44.1mg/gforPb^{+2}.*

KEY WORDS: *Poly(ethylene terephtalat) (PET) fibers, Preconcentration, Elemental analysis.*

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INTRODUCTION

The modification of polymers has received much attention recently. Among the methods of modification of polymers, grafting is one of the promising methods. In principle, graft co-polymerization is an attractive method to impart a variety of functional groups to a polymer. The grafting reaction involves copolymerization of the monomer onto the polymer backbone. Poly(Ethylene Terephthalate) (PET) fibers are one of the most important synthetic fibers used in the textile industry and have superior fiber forming properties such as the easily packaging of polymer chains with orientation and resistance against microorganisms,

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erosion, stretching and acidic media. In addition to these properties PET has some drawbacks such as lower moisture regain and difficulty in dyeing due to lack of reactive functional groups [1-3].

One of the ways employed to improve these inferior properties of PET fibers or to give them new properties is graft copolymerization. A considerable number of studies on graft copolymerization of single monomers having different functional groups onto PET fibers have been reported. But, there are only a few studies on the grafting of multiple monomers onto PET fibers [1]. In recent years, grafted fibrous materials have widely used for the adsorption and preconcentration of metal ions. Fibrous reactive agents have shown many advantages. The large specific surface areas of the fibrous materials grafted with various vinyl monomers are other potential groups which can be used to adsorption of heavy metals. Although grafting is a well-known method for the modification of polymer structure, it has been used for adsorption only recently. In this work, we developed a new ion exchange chelating fiber by grafting Acrylic acid/Acryl amide on Poly(Ethylene Terephthalate) (PET) fibers for the preconcentration of Pb^{+2} from aqueous solution. The effects of various experimental conditions on grafting, such as monomer concentrations, polymerization time and temperature, mechanical and morphological properties were systematically studied [4-7].

EXPERIMENTA SECTION

Instruments

A flame atomic absorption spectrometer of the Varian, AA240, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 $L.min^{-1}$, respectively) and Inductively Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES), Varian, model Vista were used for measuring the concentration of metal ions. The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Infrared spectra were recorded on a Jasco Fourier Transform InfraRed spectrometer (FT-IR-410, Jasco Inc., Easton, Maryland). Elemental analysis was carried out on a Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer. Thermo Gravimetric Analysis (TGA) was carried out by using a TGA-50H (Shimadzu Corporation). The SEM micrographs were obtained on a SEM-PHILIPS XL30 scanning electron microscopy.

Reagents and solutions

Fiber PET (filaments: 130 and dtex 170) made in Faculty of Textile Engineering, Amir Kabir University of Technology Tehran, Acrylic acid, Acryl amide, benzoyl peroxide, acetone, $Pb(NO_3)_2$, NaH_2PO_4, Na_2HPO_4, CH_3COONa, HNO_3 were products of Merck (Darmstadt, Germany).

All the solutions were prepared in deionized water using analytical grade reagents.

The stock solution (1000 mg. L^{-1}) of Pb (II), were prepared by dissolving appropriate amounts of $Pb(NO_3)_2$, in deionized water. 10 mL, 0.1 M acetic acid - acetate buffer (pH 3 – 6.5), 0.01 M phosphate buffer (pH 6.5 - 9) were used to adjust the pH of the solutions, wherever suitable.

Graft copolymerization PET-AA/AAm fiber

Fiber samples (0.100 ± 0.001 g) were placed in a 100 mL polymerization tube and calculated amount of AA(96-770 µl) and AAm(0.2-1g) were added to it. Then Bz_2O_2(0.2g) dissolved in 5 mL acetone was added to tube. The mixture was made up to 50 mL with deionized water and placed into a water bath at the polymerization temperature 85±1 ºC. The fiber samples taken at the end of polymerization were freed from homopolymer or copolymers by washing with boiling water and acetone for 1h (changing the washing water four times). The washed fiber was dried at 50 ºC under vacuum [8]. The methodology used to synthesize modified PET is summarized in Fig. 1. The percentage of grafting (G%) was calculated as follows:

$$G\% = \frac{Wg - W\circ}{W\circ} \times 100$$ Where

- Wg, Dry weight of the PET-g-(AA/AAm) (g)
- Wo, Dry weight of the PET (g)

RESULTS AND DISCUSSION

Characterization of the grafted fibers

IR Spectrum

The IR spectrum of PET-AA/AAm is compared with free PET. There are 2 additional bands at 2096-3078 and 1787 cm^{-1} which appear to originate due to NH_2 amidic C=O and acid.

Elemental Analysis

The elemental analysis for PET (found: C, 62.08; H, 8.20; N, 0%, calculated for ($C_{10}H_8O_4$): C, 62; H, 8.69; N, 0%)

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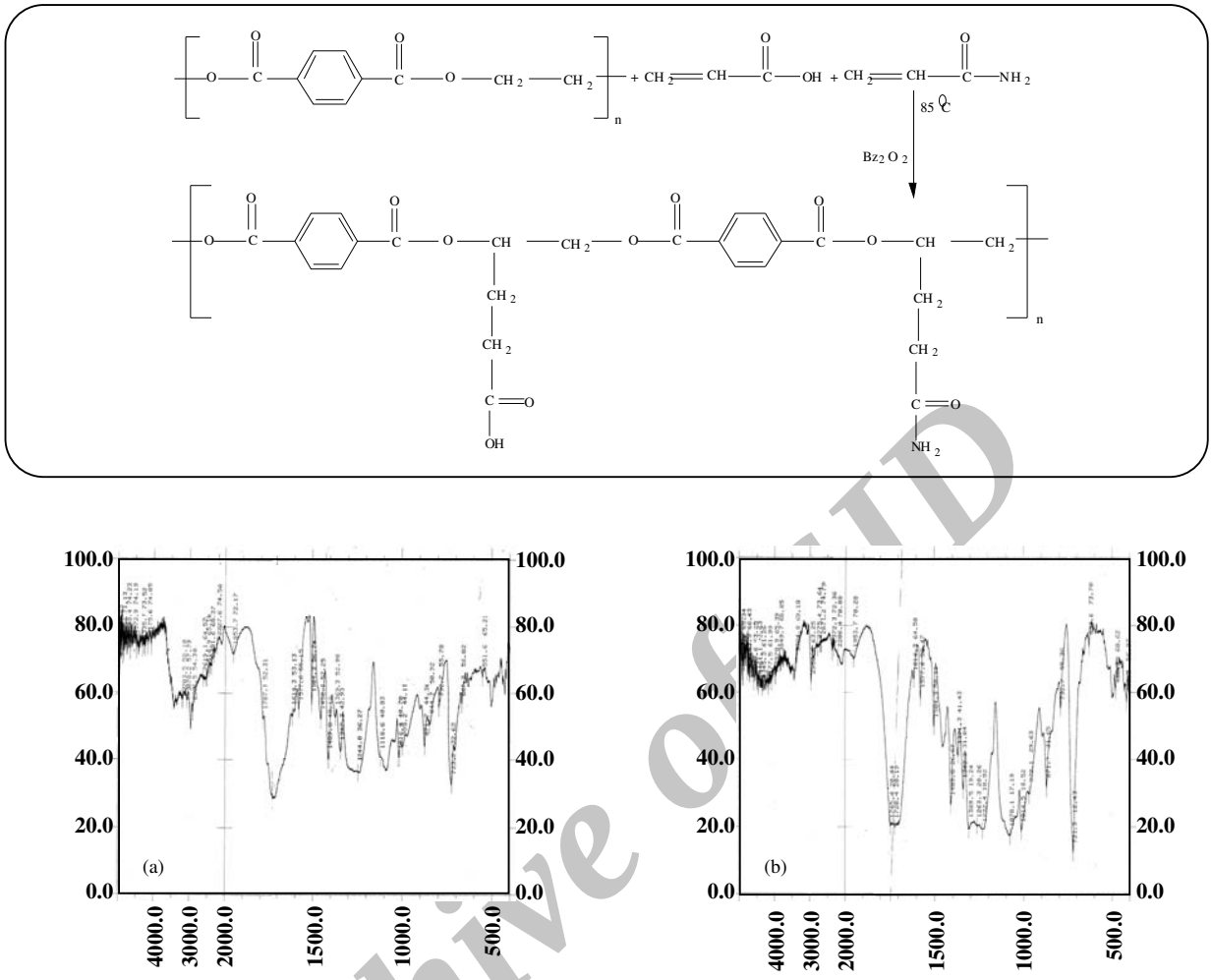

Fig. 1: FT-IR spectra of (a) raw fibers and (b) grafted fibers.

and PET-AA/AAm fiber (found: C, 61.37; H, 4.31; N, 1.16%, calculated for $(C_{10}H_8O_4)_5(C_3H_5O_2)_m(C_3H_6ON)_n$: on condition that m=n=1: C, 61.36; H, 3.74; N, 1.27%) show that on an average one Acrylic acid /Acryl amide molecules are present in each 5 repeat unit of the polymer.

Thermal Analysis

The thermal behavior of the PET-AA/AAm fiber in comparison with raw PET fibers was studied by thermogravimetry and differential thermogravimetry (TG-DTG) analysis. The thermal decomposition of PET-AA/AAm fiber and raw PET proceed in three steps. For PET-AA/AAm decomposition, temperatures corresponding to the maximum rate of the mass loss are 408.8, 429.5 and 451.7 °C and total mass loss is 89.7 wt%. The same values for the raw PET are 410.2, 432.7, 465.1°C and 88.8 wt%. The beginning and end temperature in each decomposition steps of PET-AA/AAm are 350-425, 375-460 and 450-470 °C**.** The values for three steps of raw PET are 355-436.1, 380-465 and 455-475 °C. The overall mass loss in the PET-AA/AAm and raw PET samples were similar. The thermogravimetric data indicate that the initial thermal stability of PET-AA/AAm are lower than that of raw PET due to joined of the AA and AAM onto PET (shown in Fig. 2).

Scanning electron microscopy

Scanning Electron Microscopy (SEM) was used to examine the external surface of the fiber after modification

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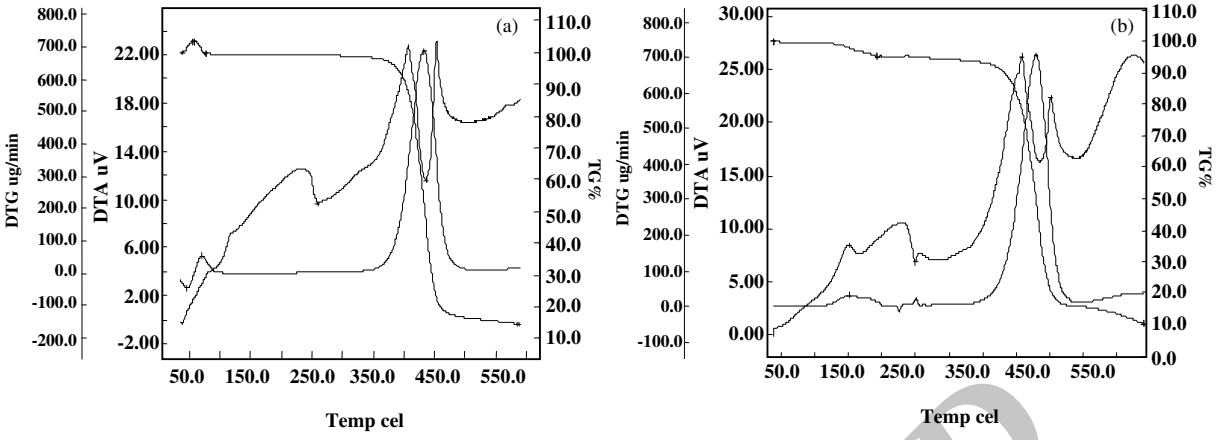

Fig. 2: TG-DTG cruve of (a) raw fibers and (b) grafted fibers.

and metal ions adsorption. The SEM images are presented in Fig 3. The surface of ungrafted PET has a smooth and highly homogeneous appearance. As shown in Fig. 3. (a),(b), in comparison with the surface of the grafted PET, surface of raw PET were less coarse and groovy because PET-AA/AAm fiber have grafted chains containing AA and AAM. As seen in Fig. 3(c), surface debris on the fibers after metal cation impregnation were observed. This image shows that ion adsorption increases the surface roughness. There is also increase diameter of the modified fibers. This can be related to the swelling phenomenon.

Mechanical properties of modified fibers

In this study, possibility of break to the used PET fiber so in order to measuring the amount of damage the vibromat set was used and the changes of properties such as tenacity -elongation at break and initial moduls were investigate . So in the whole test samples of the distance jaws in phonograph of 20cm and rate elongation 20mm/min has been selected. The mechanical properties of samples were presented in Table 1. Though some reduction in mechanical properties of all modifical samples in comparison with raw fibers were observed, still the properties are at acceptable levels [9].

The effect of the monomer mixture ratios on grafting percentage

To investigate the effect of monomer mixture ratios on the grafting, the graft copolymerization was carried out at different w/v percentage ratios of AA/AAm co monomers by using Bz_2O_2. The experimental results are shown in Fig. 4. As seen from Fig. 4, when AA was grafted alone on PET fibers the maximum grafting percentage was found to be as low as 6.94%. This suggests that AA is not sufficiently reactive toward PET macro radicals. Thus, the amount of AA in PET structure is lower. The use of AAm co monomer in grafting caused an increase in grafting percentage (9.98%). The grafting percentage was highly dependent on the monomer mixture ratio, and the maximum grafting percentage (16.34%) was reached at a AA/AAm ratio of 30:70. On the fibers grafted with the AA/AAm mixture, the side chains contained structural units coming from both AAm and AA.

Effect of Reaction Time

Grafting yield increases with an increase in reaction time. The graft co polymerization yield increases to a maximum value after 120 min of reaction time (Fig. 5). The error of all reported grafting yield is 0.5% .

Effect of reaction temperature

The effect of temperature on the grafting yield was studied and represented in Fig. 6. The grafting yield is affected by temperature .In fact , an increase up to 85 increases the grafting yield. this can be related to the increase of the initiation and propagation rates of graft co polymerization, the swellability of pet fibers, and the mobility of the reactive spaces. But after 85 ºC, the grafting yield decreases. This is probably because

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Table 1: Mechanical properties of modified fibers.

sample	% graft	Tenacity Cn/tex	Elongation at break	Work at repture Cn/tex	Initial muduls Cn/tex
1	0	24.39	55.01	8.89	131.12
2	16.34	17.8	50.8	7.81	128.4
3	10.39	19.2	52.3	8.1	129
4	8.38	20.21	52.9	8.3	129.8
5	7.9	21.4	53.3	8.37	130

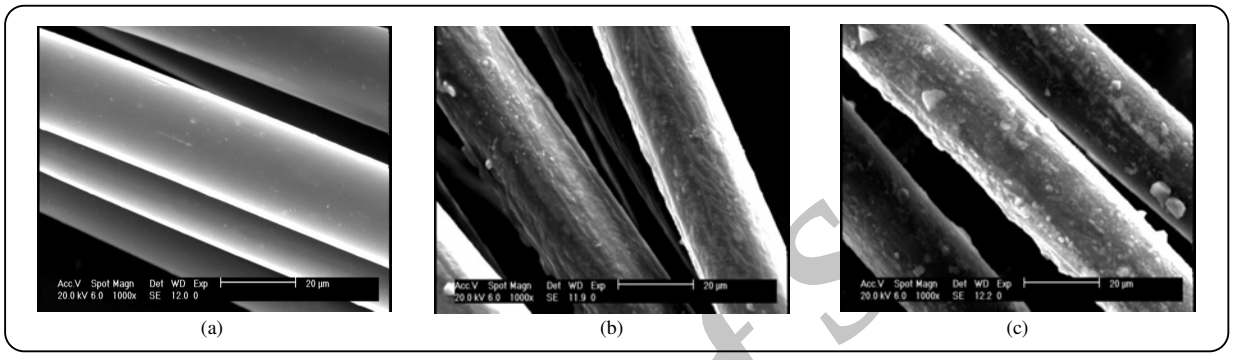

Fig. 3: SEM image of (a) the raw fibers (b) grafted fibers (PET-g-AA/AAm) and (c) grafted PET contianing pb^{+2} cations.

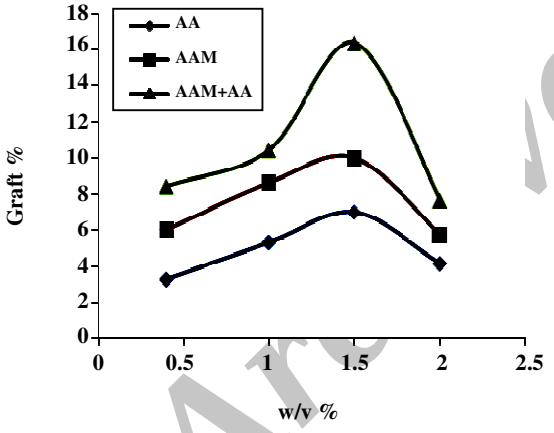

Fig. 4: Amount of monomer in the reaction mixture(W/V).

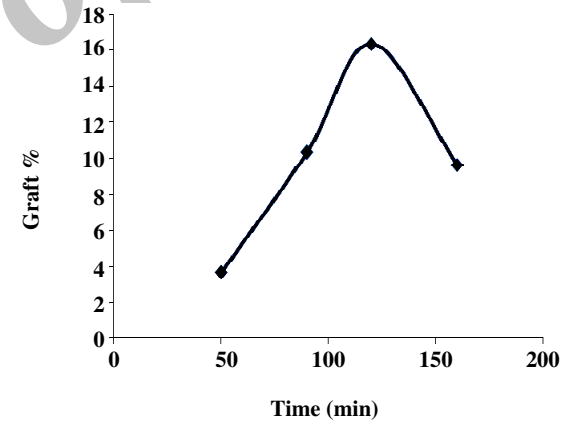

Fig. 5: Effect of the grafting vs time reaction.

at higher temperatures, higher combination rates of monomer are obtained increasing homopolymerization reactions and also the decrease in the grafting yield at temperatures after 85±1ºC may be attributed to the increase in the rate of termination reaction [8].

Effect of AIBN and BZ_2O_2

The effect of Azobis(Isobutyro)Nitrile (AIBN) and benzoyl peroxide (BZ_2O_2) on grafting yield was studied at different Acrylic acid/Acryl Amid(AA/AAm) concentrations. these results shown in Table*. According to the results, grafting yield with BZ_2O_2 was increased.

Pb^{+2} Ion ADSORPTION STUDIES on to GRSFTED PET

The adsorption capacity of the grafted PET for pb^{+2} ion were investigated using the batch method. Dried samples (0.1 g) each of reactive fiber were added into

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Table 2: Effect of initiations AIBN and BZ_2O_2 .

(AAm : AA) %	% grafting By BZ_2O_2	%grafting by AIBN
20:80	8.38	1.79
50:50	10.39	3.2
70:30	16.34	7.4
90:10	7.6	4.1

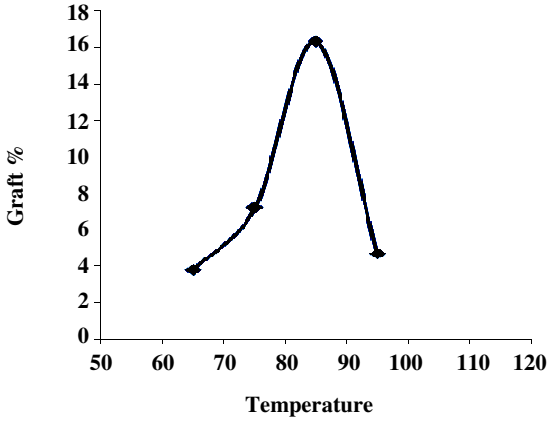

Fig. 6: Effect of temperature on the grafting.

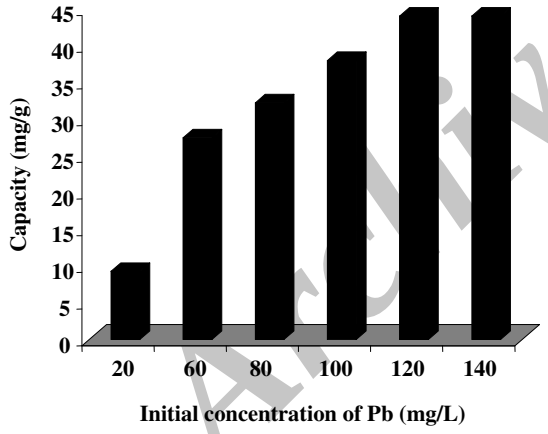

Fig. 7: Capacity adsorption fibers.

100 mL Erlenmeyer containing volume of 20-40-60-100-120-140 ppm of each metal ion solution and adjusted to desired pH(pH=8). The mixture solution was stirred at 20 ◦C temperature. The flask were agitated on shaker for 4h. After filtration of the solution, the ion concentration of the filtrates was analyzed with an atomic adsorption spectrophotometer. The adsorption amount was calculated (44.1mg/g) as follows:

$$q = \frac{C_\circ - C_t}{G} \times V$$

where q is the adsorption amount (mg/g), G the weight of there active fiber (g), V the volume of solution (l), and C1 and C2 are the concentrations (mg/L) of each ion before and after adsorption, respectively. The metal ions adsorbed on the grafted PET were then removed by placing o.1 g of the metal loaded fiber in 10 mL of 0.5 M HNO_3 solution for 4 h [9].

CONCLUSIONS

As seen from the experimental results, Acrylic acid/Acryl Amid (AA/AAm) monomer mixture can be grafted onto PET fiber by free-radical polymerization using Bz_2o_2 as an initiator. The maximum grafting yield in this research was 16.34%. The optimum condition were 30:70 (w/v%) AA/AAm concentration, 85 °C temperature and 120 min reaction time. The chemical changes of modified PET fibers were examined FT-IR, TGA, SEM, CHN. TGA measurement data showed primarily the approximate same thermal behavior such as decomposition temperature and thermal stability in grafted fiber compared with raw fiber but by increasing grafting yield. 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. This is probably because of changes which resulted in molecular structure of raw fibers through radical polymerization. Adsorption of Pb^{+2} ion from aqueous solutions onto modified PET fiber were studied. Adsorption capacity of modified PET surface was found to be 44.1 mg/g for Pb^{+2} in the pH=8. A recovery of 100.2% was obtained for Pb^{2+} with 0.5M nitric acid as eluting agent.

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