

Chemical Modification of Polypropylene Fibers Grafted Vinyl Imidazole/Acrylonitrile Copolymer Prepared By Gamma Radiation and Its Possible Use for the Removal of Some Heavy Metal Ions

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ABSTRACT: The chemical modification of polypropylene (PP) fibers by graft copolymerization with vinylimidazole (VIm) and acrylonitrile (AN) was carried out using γ -radiation. Preparation conditions, such as irradiation dose, comonomer concentration and composition and type of solvent, affecting the degree of grafting were investigated. The suitable diluent for obtaining reasonable graft VIm/AN copolymer yield was acetone. The higher grafted yield was achieved by increasing the amount of vinylimidazole in comonomer feed solution as well as irradiation dose. The derivatives of PP-g-P(VIm/AN) grafted fibers of different functional groups were obtained by treating the grafted fibers with various organic reagents containing reactive amino groups, such as sulpha-drug compounds,

aliphatic- and aromatic amines. Characterization of the obtained graft copolymers and their chemical treatments with different amines was also investigated. It was observed that the nitrile group in PP-g-P(VIm/AN) polymer undergoes simple addition reaction via nucleophilic interaction mechanism to produce the corresponding PP-graft-P(vinylimidazole/acrylomidine) derivatives. The ability of the grafted fibers and their treated forms to absorb some metal ions as Cd, Hg, and Pb from their individual and mixture solutions was evaluated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 11–18, 2009

Key words: polypropylene fiber; vinylimidazole; acrylonitrile; radiation grafting

INTRODUCTION

Polymers are considered as the ideal materials for their use as specialist materials in various fields such as ion exchangers,¹ biocompatible materials,² textile industries,³ and immobilization of bioactive materials.⁴ However, commonly available natural and synthetic polymers are not suitable for uses under hostile conditions which may include action of acids, bases, organic solvents and chemicals, action of high temperature, and exposure to various kinds of radiations. Growth of polymer science has led to the development of new materials in direct competition with the natural ones which have been in use since earlier times. A large variety of modifications have been devised to impart more desirable properties to existing synthetic polymers so that their material properties as well as application potential can be improved. Man-made fibers are those, which are produced in industrial conditions and mainly consist of organic carbon chain compounds; for example, polypropylene (PP) fibers. In the modern era,

the production of such fibers has been rapidly developed as well as their assortment has also been increased due to their regular properties such as specific surface area and strength.

Acrylonitrile (AN) based polymeric materials have been accepted in a broad way of applications that they exhibit high strength, stiffness and abrasion resistance. In addition, cyano groups of polyacrylonitrile are a suitable target for any several modifications that may improve the chemical and physical properties of the polymer substrate. On the other hand, *N*-vinylimidazole (VIm) and its derivatives have stimulated great interest due to the wide possibilities of the preparation of new materials, including the synthetic analogues of biopolymers with imidazole fragments in the macromolecules. These materials showed unique properties such as ion exchange and complexing behaviors, catalytic, biological and physiological activities, and heat resistance.^{5,6} Poly(VIm) ligands form multidentate complexation systems with Ag^+ and Cu^{2+} ions with two and four coordination numbers, respectively.^{7–14}

Radiation grafting is an easy and highly efficient procedure for modifying the properties of polymeric substrates of synthetic as well as natural origin. Radiation grafting offers some unique advantage

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over the conventional chemical grafting method.¹⁵ Extensive work on the fundamentals of radiation grafting of vinyl monomers onto various types of polymers has already been performed.

In this work, VIm and AN will be grafted onto PP fibers using ionizing radiation. The suitable preparation condition will be determined and the grafted fibers will be characterized spectrophotometrically and by studying their thermal behavior. To improve the chemical properties of the grafted fibers, they will be subjected to chemical treatment with different chemical reagents. The ability of the grafted PP fibers and their treated forms to absorb Cd, Hg, and Pb from their individual and mixture solutions will be evaluated.

EXPERIMENTAL

Materials

PP fiber, produced by oriental waver, Egypt, 1-vinyl imidazole (Aldrich, Germany) of purity 99% and AN of purity 99% (Aldrich, Germany) were used as received. The other chemicals, such as solvents, inorganic salts, organic compounds, and other reagents were reagent grade and used without further purification.

Radiation grafting of PP fibers

PP fibers were washed with acetone, dried at 50°C in oven until constant weight is reached and then immersed in the comonomer-solvent mixture in glass tubes. The direct radiation induce grafting was used as a technique in nitrogen atmosphere. The glass tubes that containing the comonomer solution and the polymer substrate were subjected to ⁶⁰Co-gamma irradiation at dose rate 10.28 kGy/h. The irradiation facilities have been established by National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority (AEA), Nasr City, Egypt. The grafted fibers were removed and washed thoroughly with the proper solvent in order to remove homopolymer that may be formed, and then soaked overnight in dimethyl formamide (DMF) to extract the residual monomer and homopolymer, which may included in the grafted fibers. These grafted fibers were then dried in oven at 40°C for 24 h and weighed. The degree of grafting was calculated by using the following equation:

$$\text{Degree of grafting (\%)} = \frac{(W_g - W_o)}{W_o} \times 100$$

where W_o and W_g represent the weights of ungrafted and grafted fibers, respectively.

Chemical modification of the grafted fibers

The contained nitrile groups within the PP-g-P (VIm/AN) fibers was used as starting point for the introduction of new functional groups via nucleophilic addition of amino group containing chemical reagents such as, sulpha-drug, aliphatic and aromatic amines and amino acids to produce the corresponding acrylamidine derivatives. The chemical modification is carried out by refluxing of 1 g of the grafted fibers with an appropriate amount of corresponding chemical reagent in EtOH/EtO⁻ Na⁺ as a catalyst with few drops of (DMF) at 80°C for 72 h.¹⁶ The complete conversion of the nitrile groups was checked by following the intensity of its characteristic fourier-transform infrared analysis (FTIR) peak at 2240 cm⁻¹. The treated grafted fibers were thoroughly washed in hot DMF followed by ethyl alcohol, dried at 60°C for 6 h and kept in dry place.

FTIR measurements

Mattson 1000, Unicam, England in the range from 400–4000 cm⁻¹ was used to confirm the formation of graft copolymer and their treatments with different amines.

TGA

Shimadzu thermogravimetric analysis (TGA) system of Type TGA-50 under nitrogen atmosphere (50 mL/min) was used in this study. The temperature range was from ambient to 500°C at heating rate of 10°C/min.

Metal ion adsorption experiments

Metal ions adsorption experiments were carried out by shaking a 0.1 g dried samples of the metal adsorbing fibers with 25 mL aqueous solution for metal ions. The concentration of metal ions was detected by Optical Emission Spectroscopy (OES). The amount of metal ions adsorbed was calculated by the difference in the concentration of metal ions in the solution before and after adsorption.

RESULTS AND DISCUSSION

The graft copolymerization of VIm/AN binary comonomer system onto PP fibers was carried out by direct irradiation of PP fibers immersed in excess diluted comonomer solution. Simultaneous irradiation leads to the generation of monomer radicals and active sites on the backbone in the same reaction medium, so grafting can be initiated by the growth of monomeric radicals and from active sites on the backbone. The total dose of radiation, the monomer

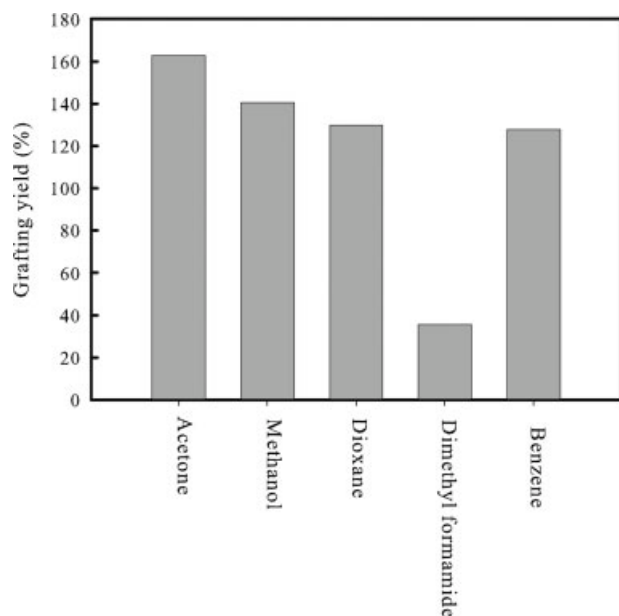


Figure 1 Effect of solvent type on the grafting yield of equimolar VIm/AN binary comonomer onto PP fibers. Irradiation dose; 20 kGy, comonomer composition; 50/50 mol % and comonomer concentration; 20 wt %.

concentration, and the type of solvent affect the extent and homogeneity of the grafting yields because these factors determine the relative number and distribution of the generated radical species.

Effect of preparation conditions on the grafting process

The use of suitable solvent would enhance the efficiency and uniformity of the grafting process by promoting the accessibility of the monomers to the active site located within the polymeric substrate. In this study, various solvents were tested as diluents for the grafting of VIm/AN binary comonomer on the PP fibers. Figure 1 shows that the highest grafting degree was achieved in acetone whereas the use of DMF as diluent resulted in the lowest grafting yield. The low grafting yield in DMF may be explained by the chain-transfer mechanism and bi-radical termination being more available in DMF.^{17,18} Whereas the low polarity of the acetone, which would be favorable for the swelling of the nonpolar polymeric substrate (PP), results in a high local concentration of the monomer around the active sites in the polymer substrate which consequently increase the grafting yield.

It is well known that the comonomer concentration as well as total irradiation dose play important roles in the grafting process that it may affect its kinetic parameters. Solvent may facilitate the diffusion of the monomers into the polymeric substrate

or reduce the propagation rate in case that it is more than enough. Also, depending on the solvent type and amount, gel effect which is directly proportional to the degree of homopolymerization of the monomer in the reaction medium, may be either enhanced or reduced.¹⁹ The total irradiation dose is responsible for the number of the generated free radicals which is directly related to the degree of grafting.

The effect of total irradiation dose on the grafting yield of VIm/AN copolymer onto PP fibers was investigated at different comonomer concentrations and shown in Figure 2. It is clear that the degree of grafting increases as the total irradiation dose as well as comonomer concentration increases. Such increase may be attributed to either the increase in the intensity of free radicals generated or the increase in the number of monomer molecules available to react with the free radical formed in the polymer backbone.²⁰ From these results it can be concluded that the degree of grafting is directly proportional to the comonomer concentration, which allows the selection of suitable concentration to obtain a reasonable grafting degree of suitable properties for the proposed practical application.

The use of binary comonomer system is mainly a pathway to enrich the functionality of an inert polymeric substrate by introducing two function groups of different chemical nature and behavior. Therefore, it is important to study the effect of the comonomer composition on the degree of grafting that the presence of more than one monomer may lead to the retarding or the enhancement of the grafting process. According to the physical properties of the reacting monomers; VIm which is a polar, electron-donor monomer with ($\pi' \rightarrow p \rightarrow \pi$) conjugated system characterized by a negative polarity of its vinyl double

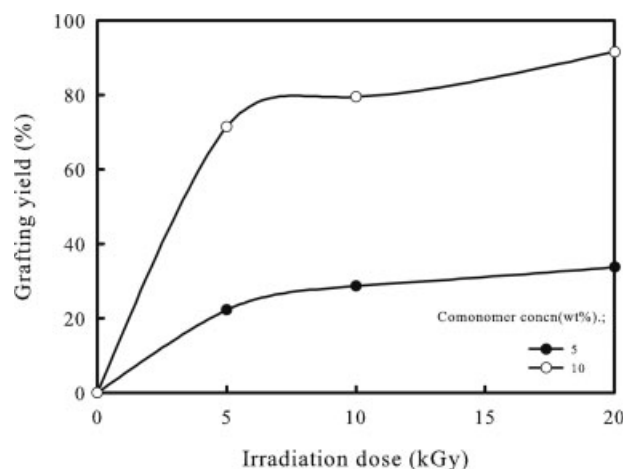


Figure 2 Effect of total irradiation dose on the grafting yield of equimolar VIm/AN binary comonomer onto PP fibers at different comonomer concentrations in acetone as a diluent; comonomer composition; 50/50 mol %.

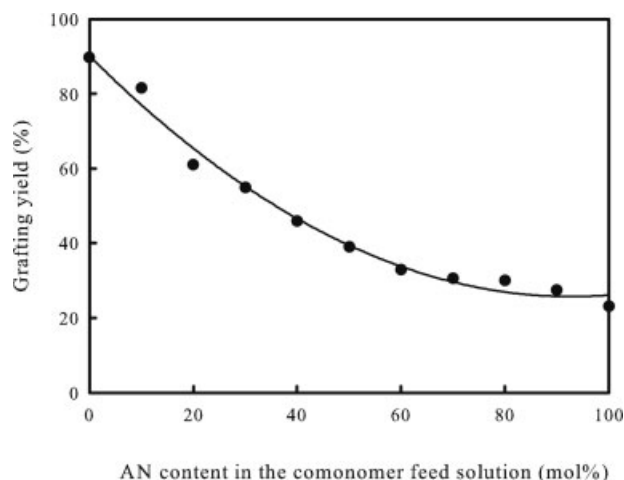


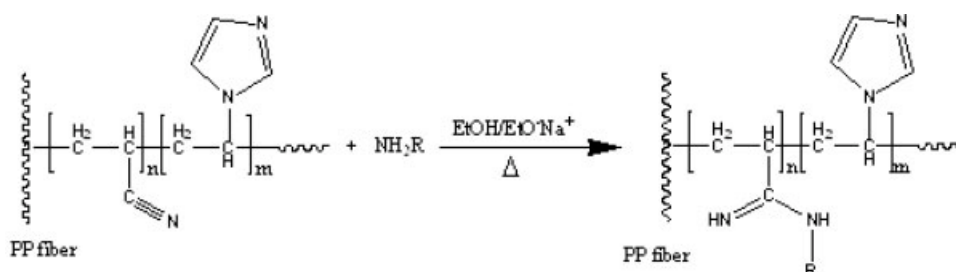
Figure 3 Effect of comonomer composition on the grafting yield of VIm/AN binary comonomer onto PP fibers. Irradiation dose; 20 kGy, comonomer concentration; 5 wt % in acetone.

bond ($e_1 = -0.61$)²¹ and AN which is also polar monomer, but an electron-acceptor monomer with a positive charge on its vinyl β -carbon atom ($e_2 = 1.23$)²². Higher activity and some tendency to alternating the monomer units in copolymer chains was expected to take place during the graft copolymerization of this donor-acceptor monomer system.

Figure 3 shows the effect of comonomer composition on the grafting yield of VIm/AN binary comonomer onto PP fibers. The data unexpectedly show a clear decrease in the grafting yield by increasing in the AN content in the comonomer feed solution. Such result can be explained in the light of the nature of the AN-based copolymer in the diluent used for the copolymerization process; acetone. It is well known that AN as well as AN rich copolymers forms precipitating homo- or copolymer in acetone. Such precipitation exclude the AN rich macroradical from the grafting medium which as a results reduce the degree of grafting.

Chemical modification of the functionalized PP fibers

Polyacrylonitrile and AN copolymers are particularly appropriate due to the reactive nitrile groups within the polymer chains. The chemical modification of AN-based copolymer has been the object of numerous studies since these modification lead either to the improvement of the physico-mechanical properties or to the obtaining of polymers with new properties. The mechanism of such treatment is extensively studied.^{23,24} Figure 4 shows schematic diagram for the chemical modification of PP-g-P(VIm/AN) fibers with different amines.



Where NH_2R :

- Anthranilic acid.
- 4-Aminopyridine.
- Glycyl-L-leucine.
- 6-p-Amino-phenyl-4 anisyl pyridazine-3-(2H)one.
- 4-Amino-2, 6-dihydroxy pyrimidine.
- 1-Naphthyl amino-4-sulphonic acid.
- 4-Amino diphenyl amine.
- o-Amino phenol.
- 4-amino-N(5-methoxy pyrimidinyl)benzene sulphonamide.

Figure 4 Schematic diagram for the chemical modification of PP-g-P(VIm/AN) fibers with different amines.

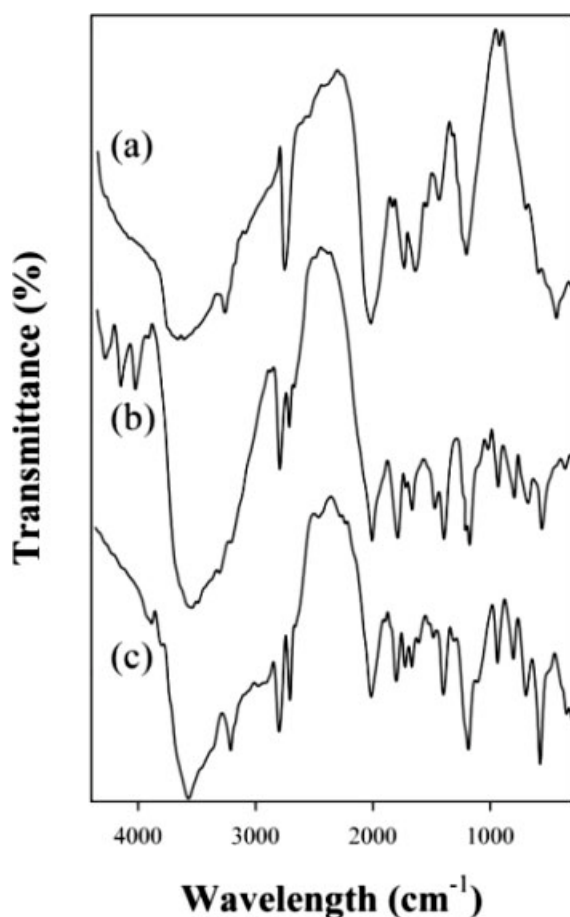


Figure 5 FTIR spectra of PP-g-P(VIm/AN) of different AN content (mol %); (a) 100, (b) 80 and (c) 20.

Characterization of the prepared functionalized polymer

FTIR analysis

Figure 5 shows the FT-IR spectra of PP-g-P(VIm/AN) prepared using comonomer solutions of different AN content; 100, 80, and 20 mol %. The pure AN grafted PP fibers shows the characteristic nitrile stretching band at 2241 cm^{-1} . The introduction of imidazole moieties to the grafting process leads to the appearance of new characteristic bands at 1650 cm^{-1} for C=C (ring) stretching vibrations, 667 cm^{-1} for the possible C—N (ring) in PVIIm ring and at 1500 cm^{-1} for the characteristic C=N (ring) stretching vibrations. The figure also shows that the increase in imidazole content in the copolymer feed solution increases the intensities of its characteristic peaks in the grafted fibers.

On the other hand, Figure 6 shows the FTIR spectra of the PP-g-P(VIm/AN) fibers treated with different reagents as examples to verify the occurrence and completeness of the treatment of the nitrile group of the VIm/AN copolymer grafted to the PP fibers. The spectra of the samples under investiga-

tion show complete disappearance of the characteristic nitrile group at 2241 cm^{-1} and instead other characteristic peaks appeared corresponding to the treating agent. For grafted PP treated with anthranilic acid, the spectrum shows the peaks characteristic for NH, OH, C=O of carboxylic acid, HN=C imine, C=C aromatic, and C—N amino at 3413 , 3236 , 1700 , 1620 , 1558 , and 1230 cm^{-1} , respectively, where as treatment with glycyl-L-leucine shows the peak characteristic for OH and C=O of carboxylic groups, HN=C imine, methyl group and C—N amino acid at 3116 , 1670 , 1620 , 1375 , and 1230 cm^{-1} , respectively. The FTIR spectrum of the grafted fiber treated with 4-amino pyridine shows the reach characteristic NH, HN=C imine and C—N at 3300 , 1620 , and 1230 cm^{-1} , respectively. The characteristic peaks of FTIR as a result of the treatment of the PP-g-P(VIm/AN) fibers with the rest of reagents were summarized in Table I.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to investigate the thermal stability of the grafted fibers and the effect of the comonomer composition and the influence of the nature of treating agents on the

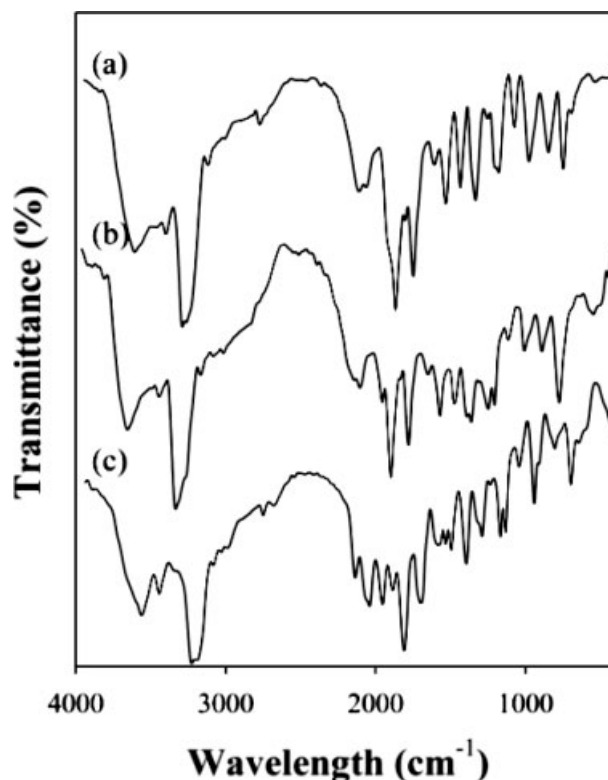


Figure 6 FTIR spectra of PP-g-P(VIm/AN) of composition 50/50 (mol %) treated with different amines. (a) Anthranilic acid (b) Glycyl-L-Leucine (c) 4-Aminopyridine.

TABLE I
FTIR Data of PP-g-P(VIm/AN) Fibers Treated with Different Reagents

Treating agents	Group	Wavelength cm ⁻¹
4-Amino-2, 6-dihydroxy pyrimidine	OH	3300
	C=C	1680
	C=N(imine)	1580
6-p-Amino-phenyl-4 anisyl pyridazine-3-(2H)one	NH	3421
	C=O	1700
	C=C(Ar)	1649
	C=N(imine)	1542
1-Naphthyl amino-4-sulphonic acid	NH	3442
	C=C (Ar)	1647
	C=N(imine)	1562
	SO ₃ H	1376
4-Amino diphenyl amine	NH	3240
	C=N(imine)	1590
	C=C	1500
o, Amino phenol	OH	3445
	N=C(imine)	1650
	C=C (Ar)	1560
	C-N (amine)	1233
	NH	3500
4-amino-N(5-methoxy pyrimidinyl) benzene sulphonamide	NH	3500
	C=C (Ar)	1670
	C=N(imine)	1610
	-SO ₂ -	1325

grafted fibers stability. Figure 7 shows the thermogravimetric curves of the grafted PP fibers of different AN content. It is clear that the VIm rich grafted fibers possess higher thermal stability than AN rich grafted fibers. The higher thermal stability of the VIm rich grafted fibers can be attributed to the stability of the PVIm which start to decompose at 459°C. The decrement in the thermal stability of the grafted fibers by the increase in the AN content is a direct result for the low stability of PAN which start to decompose at 285°C.²⁵ The absence of a sharp degradation in the derivative thermogram at 285°C indicates that AN moieties in the copolymer structure are not present in blocks or in segments and rather distributed randomly on the main chain.

Figure 8 shows the TGA thermogram of PP-g-P(VIm/AN) fibers treated with 4-amino pyridine, anthranilic acid, and glycyl-L-leucine. It is clear that the treatment with all the reagents acquire the grafted fiber higher thermal stability. The figure shows that the acquired stability was in the following order: glycyl-L-leucine < Anthranilic acid < 4-amino pyridine. The higher stability of anthranilic acid and 4-amino pyridine over glycyl-L-leucine may be attributed to their aromatic structure which acquires the grafted chains higher stability whereas the higher stability of 4-amino pyridine over the anthranilic acid might be attributed to the higher degree of substitution in anthranilic acid.

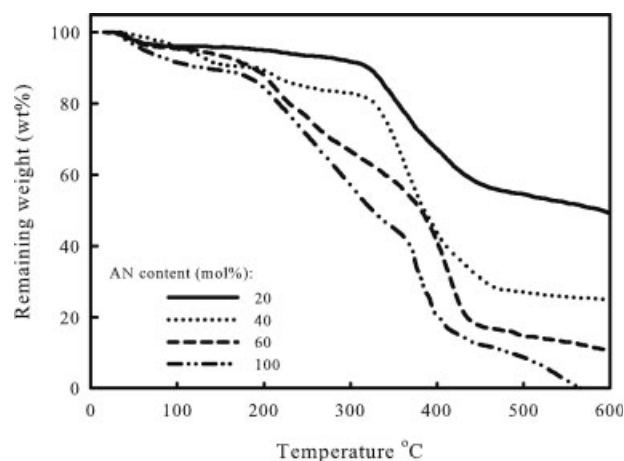


Figure 7 TGA thermogram of PP-g-P(VIm/AN) of different AN content.

Adsorption of metal ions on PP-g-P(VIm/AN) fibers and their chemical treatments

The contamination of water resources by industrial effluents become a serious issue. Metal ion toxicity has increased substantially because of the use of metal ions as catalysts in industry and as semiconductor in electric and electronic devices.

Figure 9 shows the effect of the composition of (VIm/AN) graft chains on the efficiency of the grafted fiber in the removal of Pb, Hg, and Cd from their individual solutions. The figure shows that, for all compositions, there is a very weak affinity towards Cd which might be referred to its relatively low electronegativity.²⁶ On the other hand, the prepared grafted fibers of all graft chains compositions show considerable affinity towards Pb and Hg. Such affinity increases by increasing the AN content in the graft chain composition to reach maximum at graft chain of VIm/AN of composition 50/50 mol %.

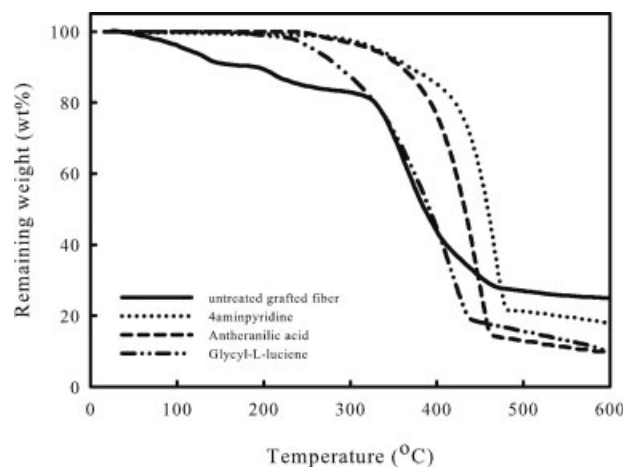


Figure 8 TGA thermogram of PP-g-p(VIm/AN) treated with different amines.

Any further increase in the AN content results in a reduction in the amount of adsorbed metal ions. The data revealed that there is some kind of synergism between AN and VIm to maximize the amount of adsorbed metal ions.

To develop the capability and selective adsorption properties of the prepared fibers, The PP-g-P (VIm/AN) fibers, of graft chains composition 50/50 mol %, were subjected to further chemical treatment using several chemical reagents. The effect of the introduction of different chemical treating agents on the selective adsorption behavior of the PP-g-P(VIm/AN) fibers towards Hg from its equimolar binary mixture with Pb compared with that of the untreated grafted fibers was investigated and shown in Figure 10. The figure shows that there is a general reduction in the amount of total adsorbed metal ions in mg except that in case of the grafted fibers treated with glycyl-L-leucine. The results also show that the selectivity toward Hg was reduced as a result of chemical treatment except that in case of treatment with 4, 5-dichloro aniline. On the other hand, the most interesting results showed by the grafted fibers treated with anthranilic acid and p-toluidine. Such treatments inverse the selective adsorption behavior of the grafted fibers i.e. the grafted fibers treated with both anthranilic acid and p-toluidine become more selective towards Pb ions.

CONCLUSION

New metal adsorbing fibers were prepared by radiation induced grafting of AN and VIm onto PP fibers. The conditions of the grafting process were optimized and the grafted fibers were characterized using spectroscopic and thermal analysis techniques. The grafted fibers received further improvement by

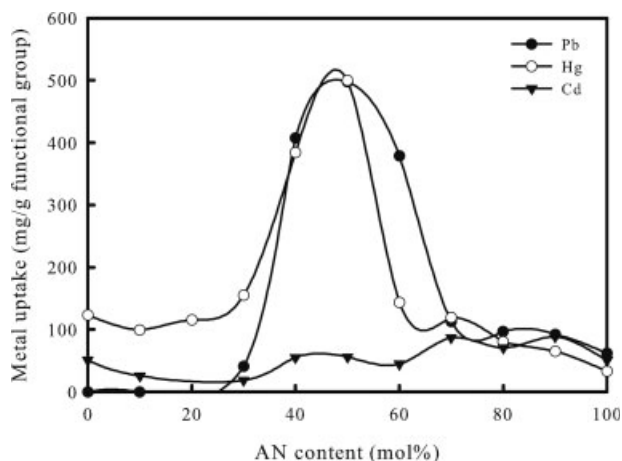


Figure 9 Effect of the composition of (VIm/AN) graft chains on the efficiency of the grafted fiber in the removal of different metal ions.

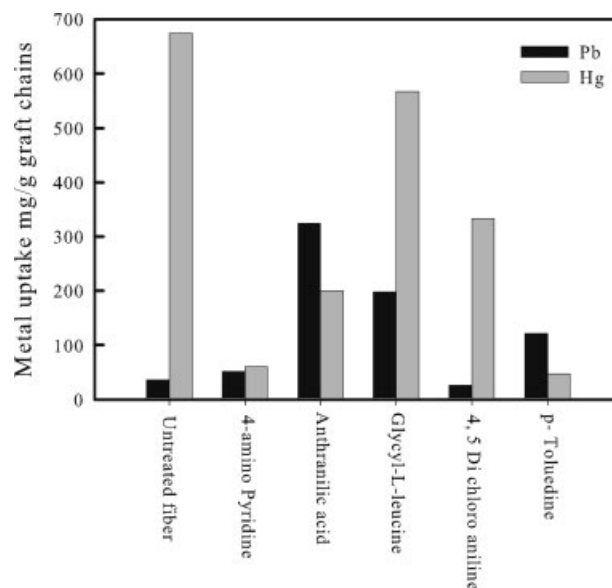


Figure 10 Selective adsorption behavior of the chemically treated PP-g-P(VIm/AN) fibers towards Hg from its equimolar binary mixture with Pb in comparison with untreated grafted fibers.

chemical treatment of the included cyano groups with different treating agents. The metal adsorption properties of the grafted fibers of different comonomer composition and the chemically treated grafted fibers were examined. The results show that the grafted fibers of graft chain composition 50/50 mol % not only achieved the highest adsorbing property but it also possessed high selectivity towards Hg. Even though the chemical treatment had a limiting effect on the metal adsorption property of the grafted fibers, the treatment with anthranilic acid and p-toluidine inverse the selectivity of the prepared grafted fibers.

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