Polymer-Based Metal Adsorbents via Graft Copolymerization of Polyvinyl Alcohol with Diaminomaleonitrile: A Green Chemistry Approach

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ABSTRACT: Synthesis, characterization, and amidoximation of diaminomaleonitrile-functionalized polyvinyl alcohol (PVA) grafts were studied. Ceric ammonium nitrate (CAN) was used as an initiator in an aqueous nitric acid medium under N_2 atmosphere. Optimum conditions for grafting were as follows: monomer concentration [DAMN] $= 1.4M$, [CAN] $= 16 \times 10^{-2}$ mol/L, $T = 50°C$, and $t = 2$ h. Water uptake of the PVA graft films increased with the increase of grafting yield. The imparted cyano group of the grafted PVA polymer chains (with degree of grafting up to 136%) was converted into amidoxime group by the reaction with hydroxylamine hydrochloride. The grafted polymers were characterized by FTIR spectroscopy, differential scanning calorimetry, and thermal gravimetric analysis. The grafted PVA films are more thermally stable than the ungrafted PVA membrane, because the grafted membrane showed a single degradation pattern despite having two components. A decrease in T_g values is observed as the grafting yield of copolymers increases indicating the incorporation of polydiaminomaleonitrile chains in amorphous copolymers with higher thermal stability. The prepared amidoximated DAMN136-g-PVA was investigated for its properties in removing heavy toxic metals, such as Pb^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, and Co^{2+} from water. The amidoximated film is characterized by a considerably greater binding ability with respect to heavy metals. The nature of the metal ion also has great importance in the amount binding to the polymeric material. The kinetics of the sorption/desorption process for Co^{2+}, Ni^{2+}, and Zn^{2+} were investigated. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2102–2109, 2012

Key words: graft copolymerization; polyvinyl alcohol; amidoximation; metal adsorbents

INTRODUCTION

Heavy metal ions resultants of the chemical process industries are pollutants that have received great attention of the governmental organizations, because they can be absorbed by plants and animals and then concentrated in the foods. It is well known that heavy metal ions released into the environment are highly toxic to the living organisms and change ecological balance by environmental cycling.[1] Chitin, its derivatives,[2] and modified cellulose[3] have been studied with respect to their ability to remove heavy metals from aqueous solution. Grafting of various monomers on plastic films can successfully solve the problem of preparation of polyfunctional sorbents and membranes.[4–6] The obtained materials are convenient for waste water treatment applications, because they are able to absorb various impurities very fast due to their chelation and/or complexation abilities through their reactive groups, such as car-boxylic acid, amine, amide, nitrile, oxime groups, and so on. In addition, these materials can be reused without lose of their sorption characteristics. Recently, the adsorbents based on natural products and their derivatives deserved particular attentions because of an increasing interest in the removal of heavy metal ions from waste water. For example, crosslinked amphoteric starch with quaternary ammonium groups can effectively remove Cr (VI), Cu (II), and Pb (II) ions in aqueous solution.[7–9] The ceric ion method is one of the most interesting methods to graft olefins on polymers presenting oxidizable functional groups.[10–12] Kinetics and mechanism of heterogeneous graft polymerization of acrylonitrile onto polyvinyl alcohol (PVA) initiated with ceric ammonium nitrate were investigated.[13] The capacities of Ni (II) adsorption using vinyl-2-pyrrolidone grafted chitin from aqueous solution have been measured. The graft copolymer VP-g-Ch shows an excellent ability for Ni (II) adsorption.[14] The newly-synthesized starch graft copolymers containing aminoethyl groups was used for removing Cu (II) and Pb (II) ions in the aqueous solution by the effective complexation of amine group with Cu (II) and Pb (II) ions.[15]

Synthesis and characterization of diaminomaleonitrile (DAMN)-functionalized polystyrene grafts for application in pervaporation separation were reported.[16] Synthesis, characterization, and amidoximation of DAMN-functionalized polyethylene terephthalate (PET) grafts were studied.[17] Azobisisobutyronitrile was used as an initiator. Separation of metal ions and chelating agents by nanofiltration explores the feasibility of nanofiltration for separating chelating agents from heavy metals, which would make it possible to reuse chelating agents.[18] Synthesis of porous acrylonitrile/methyl acrylate copolymer beads by suspended emulsion polymerization and their adsorption properties after amidoximation revealed an excellent adsorption capacities for Hg^{2+}, Ag^+, and Cu^{2+}, especially for Hg^{2+}, and it have good selectivity for Hg^{2+}. In addition, the equilibrium was established in 10 h through adsorption kinetics study.[19] Removal of uranium from mining industry feed simulant solutions using trapped amidoxime functionality within a mesoporous imprinted polymer material is successfully demonstrated.[20] Adsorption efficiency of a new adsorbent toward uranium and vanadium ions was synthesized by radiation-induced graft polymerization affording a new type of fibrous adsorbent with excess amidoxime groups.[21] Graft reaction of acrylamide and 4-vinyl pyridine onto ultra-low-molecular weight poly(vinyl alcohol) by ceric (IV) ion initiation had been systematically investigated.[22] Preparation of amidoxime-modified polyacrylonitrile (PANoxime) nanofibers and their applications to metal ions adsorption have been investigated intensively due to their potential applications in many areas especially in environmental applications for removal of heavy metals ions.[23] The aim of this work is to prepare DAMN-functionalized PVA grafts and amidoximation of grafted copolymer to investigate its properties in removing heavy toxic metals from waste water.

EXPERIMENTAL

Materials

PVA, fully hydrolyzed, ($M_w = \sim 145,000$) was purchased from Merck. DAMN (CAS 1187-42-4) was purchased from Hebei Furan International [Hebei, China (Mainland)]. The initiator, cerium ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]$, and the other reagents were Merck products, and they were used as received.

Characterization

FTIR spectroscopy of the grafted PVA was recorded with a Vector 22 Fourier Transform Infrared Spectrometer (Bruker). UV–vis spectra were obtained using Shimadzu UV2401PC spectrophotometer. ^{1}H-NMR spectra were obtained by using a Varian Gemini 200 instrument at 200 MHz. Differential scanning calorimetry (DSC) were carried out on a Perkin–Elmer DSC-2 for studying the melting and glass transition temperature behavior of the copolymers. DSC measurments were performed in temperature range of 20–450°C at the heating rate of 10°C/min in a N_2 atmosphere. Thermal gravimetric analysis (TGA) studies on ungrafted, grafted and amidoximated PVA films were carried out using Perkin-Elmer TGA-7. Thermograms were obtained in temperature range of 50–700°C. The heating runs were made at a constant heating rate of 10°C/min under N_2 atmosphere.

Synthesis of graft copolymers

DAMN (1.4 mol/L) was added with 2 g of PVA in water (10 mL) and left overnight. Next, 50 mL of dilute nitric acid (0.01N) was added at 80–90°C. After cooling to room temperature, the reaction mixture was transferred to a 100-mL three-necked flask equipped with a mechanical stirrer. The reaction mixture was purged with nitrogen gas for 30 min. Then the requisite amount of ceric ammonium nitrate (0.16M) was added rapidly, and the reaction was allowed to proceed for 30 min at 50°C to initiate the polymerization reaction. The reaction mixture was continuously stirred for 2 h and nitrogen gas was allowed to pass through the solution. At the end, the grafted PVA was removed and subjected to soxhlet-extraction for 6 h with methanol and distilled water, respectively, to remove the homopolymer. At the end of the grafting procedure, homopolymer formed in the grafting medium was precipitated by the addition of excess acetone, collected, and dried in an oven at 70°C. Grafting Yield (%) = [(dry wt. of grafted PVA – dry wt. of original PVA)/dry wt. of original PVA] × 100. Grafting efficiency (GE) was calculated as follows:

$$GE(\%) = [(\text{wt. of graft})/(\text{wt. of graft} + \text{wt. of}\}$$
$$\text{homopolymer})] \times 100.$$

Amidoximation of pendant nitrile groups

The obtained graft polymer, DAMN136-g-PVA, was reacted with the methanol solution of hydroxylamine hydrochloride $NH_2OH \cdot HCl$ at 80°C in the presence of triethylamine. During the amidoximation reaction, samples were taken from the reaction vessel at certain time intervals, and the conversion to amidoxime structure was followed by determining the changes in CN triple bonds of polymer from respective FTIR spectra. After amidoximation

reaction was completed, the amidoximated polymer taken from reaction vessel was washed with distilled water and then dried at 40°C in a vacuum oven.

Water absorption ratio

The polymer film was immersed in water for 48 h in room temperature. After treatment, the excess water on the surface was removed using a filter paper. Then the wet film was weighed and dried at 70°C in the oven to a constant weight. The water absorption (Wa) ratio was calculated according to Wa % = [(weight of wet grafted-PVA film – weight of dry grafted-PVA film)/weight of dry grafted-PVA film] × 100.

Tensile properties

The mechanical test specimen of PVA and PVA copolymer was prepared by solution casting from chloroform. To obtain the copolymer film having the uniform thickness, about 0.5 g of sample was dissolved in 25 mL chloroform. The clear solution was poured into the aluminum dish. After chloroform was allowed to slowly evaporate at room temperature for 24 h, copolymer sample was kept in a vacuum oven at 35°C until its constant weight was attained. The tensile strength [σ (MPa)] and elongation (ε) of film sample were determined using Dumbbell-shaped specimen of 50-mm long with a neck of 28- and 4-mm wide (ASTM D882). The measurements of tensile strength and elongation at break point were recorded on an Instron 4203 instrument at temperature of 25°C and velocity of 100 mm/min.

Metal ion uptake measurements

Sample of amidoximated PVA film of known weight was soaked into $0.01M$ aqueous solution of the metal for 1 day until equilibrium was reached. The film was removed, dried in vacuum, and then weighed. The metal uptake, expressed in mmol/L was determined by measuring the increase in weight of the sample. The kinetics of the sorption/desorption processes of Co^{2+}, Ni^{2+}, Zn^{2+} ions were studied by photometric measurements at the wavelengths 240, 237, and 243 nm, respectively, using a Shimadzu UV2401PC spectrophotometer.

RESULTS AND DISCUSIONS

Effect of polymerization time on grafting yield

Grafting of PVA was carried out at various polymerization times, keeping the monomer, initiator, and temperature constant at $1.4M$, 16×10^{-2} mol/L, and
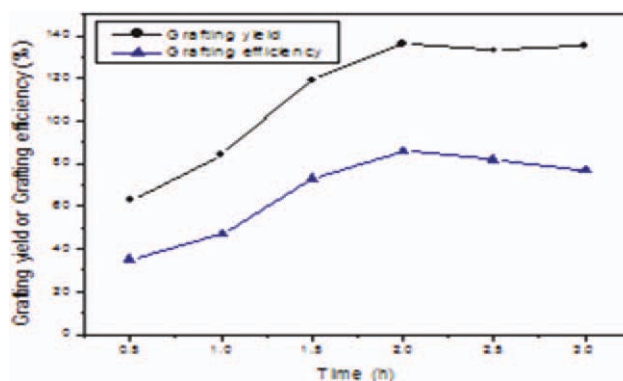
Figure 1 Effect of time on grafting yield and grafting efficiency. [CAN] = 16×10^{-2} mol/L. [DAMN] = $1.4M$. T = 50°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

50°C, respectively. As shown in Figure 1, grafting yield percentage first increased with increasing polymerization time; and then leveled off, reaching to a saturation grafting value of 136% at 2 h. As the polymerization time increases, the number of monomer and initiator molecules that diffuse onto PVA chains also increases, and this results in a higher grafting yield percentage. The leveling off of grafting may be attributed to less diffusion of the monomer as a result of the increase in the medium viscosity.

Effect of temperature on grafting yield

The effect of temperature on graft copolymerization of DAMN onto PVA was studied within the range of 30–60°C keeping monomer, initiator, and polymerization time constant (Fig. 2). As shown in the graph, a sharp increase in the grafting yield value of 136% was obtained and then leveled off. The enhancement in the grafting yield with increasing temperature may be attributed to the enhancement of PVA swellability, an increased rate of diffusion for the initiator and monomer from the solution phase to the PVA chains, an increasing number of active sites in the reaction medium and an increasing rate of initiation and propagation steps. The leveling off of the grafting yield at 50°C may be due to the increase in the formation of homo-polydiaminomaleonitrile as shown in the GE curve in Figure 2.

Influence of initiator concentration

Figure 3 demonstrate that the graft yield increases with the increase in CAN concentration in the range from 4×10^{-2} to 16×10^{-2} mol/L and then decreases with further increase in the CAN concentration. The increase of grafting yield by increasing the CAN concentration to a certain limit prove that free-radical species produced by the dissociation of CAN molecules may participate essentially in the
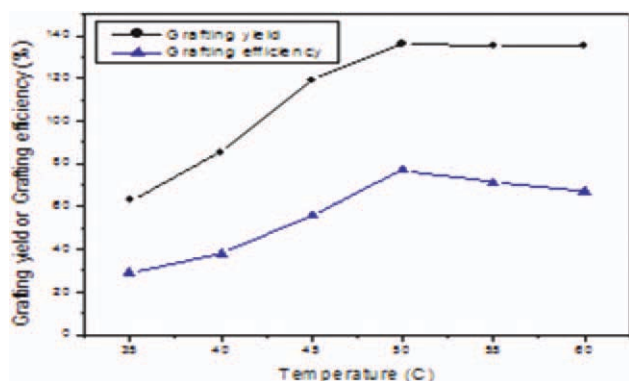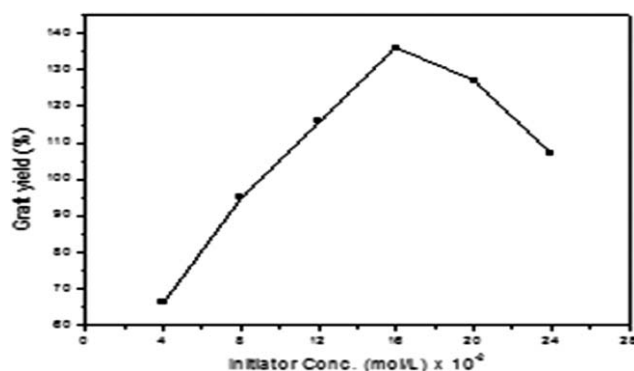
Figure 2 Effect of temperature on grafting yield and grafting efficiency. [CAN] = 16×10^{-2} mol/L. [DAMN] = 1.4M. t = 2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

abstraction of hydrogen atoms from the PVA backbone, yielding a PVA radical capable of initiating grafting. However, when the initiator concentration increased to 24×10^{-2} mol/L, termination reactions of the graft copolymerization takes place.

Influence of the monomer concentration

The effect of DAMN monomer concentrations on the grafting yield was investigated by carrying out polymerization at six different DAMN concentrations (Fig. 4) range from 0.8 to 1.8 mol/L.

The results showed that the grafting yield sharply rises with increasing DAMN concentration up from 0.8–1.4 mol/L, yielding 136% grafting yield, and then the grafting yield decreased with further increases in DAMN concentration. This may be attributed to the fact that when DAMN concentration rises, the diffusion of monomer into PVA surface increases enhancing the grafting yield. The decrease in the grafting yield at higher DAMN concentrations may be due to the adsorption of monomer on the PVA surface in excessive amounts, which prevents diffusion of the initiator molecules inside the PVA resulting in lowering the graft yield. It may

be also attributed to the increase of the homo-polymerization rather than grafting at these high monomer concentrations.

### FTIR Characterization of PVA grafts

Conversion of PVA into graft copolymer using DAMN as monomer in the presence of cerium ammonium nitrate initiator and further modification into amidoxime structure are shown in Scheme 1. The final step is the amidoximation of nitrile groups of grafted polymer. Nitrile groups were converted to amidoxime groups by using hydroxylamine hydrochloride in the presence of triethylamine. The unique advantage of this polymer is that it contains double amidoxime groups per repeating unit and an additional diethylene spacer unit between neighboring amidoxime groups in each monomeric unit. There are three attempts[24–26] of the preparation of resins with diamidoxime units per repeating unit so far all of which completely differ from our approach.
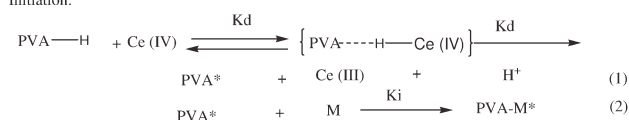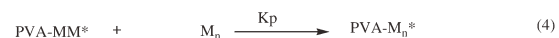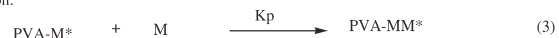

Mino et al. reported in literature[27] that the rate of reaction of ceric nitrate with the 1,2-glycol units and the alcohol units of PVA was determined at 20°C. It was found that the glycol units are oxidized much faster than the alcohol units even though they are outnumbered about one hundred to one in the polymer chain. Under the conditions studied, at least 83

Figure 3 Effect of initiator concentration on grafting yield. mol/L. [DAMN] = 1.4M. T = 80 °C. t = 2 h.
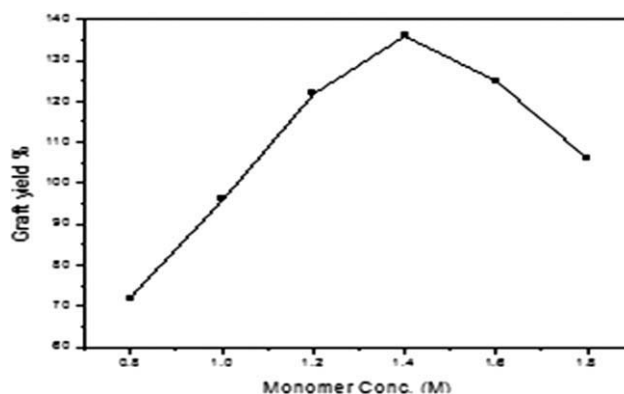
Figure 4 Effect of monomer concentration on grafting yield. [CAN] = 16×10^{-2} mol/L. T = 80°C. t = 2 h.
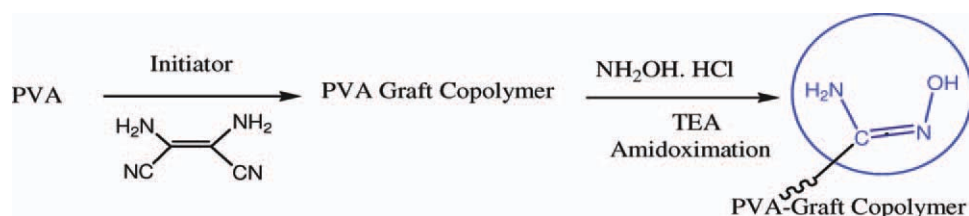
Scheme 1 Amidoximated polymer-based metal adsorbents via graft copolymerization of PVA with diaminomaleonitrile. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

glycol units reacted per 100 h oxidized. As the oxidation of the glycol units is accompanied by chain splitting, the free radicals are produced predominantly at the fragments at the end.

Grafting reaction between DAMN and PVA was confirmed by FTIR spectroscopy (Fig. 5), which showed a peak at 3324 and 2234 cm^{-1} assignable to (NH$_2$) and (CN) groups, respectively. A characteristic strong band appearing at around 3010 cm^{-1} corresponds to O—H stretching vibrations of the hydroxyl group of PVA. Presence of a peak assignable to CN group in the grafted PVA indicated high efficiency of grafting process. In addition, a peak at 2884 cm^{-1} assignable to CH stretching of CH$_2$ was found. According to Scheme 1, C≡N groups are expected to be replaced with H$_2$N—C=NOH groups at the end of amidoximation reaction. These results clearly show the disappearance of original nitrile groups in the amidoximated copolymer and formation of amidoxime groups through the treatment with hydroxylamine under specified reaction conditions.

Thermal analysis

Glass transition temperatures (T_g) for PVA, PVA grafts, and amidoximated PVA are presented in Table I. DSC measurements (Fig. 6) showed that there was only one T_g for each copolymer. The results indicated a decreasing trend of T_g as a function of increasing grafting yield. This is due to a variation of chain flexibility inherited from methylene length. A decrease in T_g values is observed as the grafting yield of copolymers increases indicating the incorporation of polydiaminomaleonitrile chains in amorphous copolymers with higher thermal stability. This might be due to an increase in their corresponding methylene length, which results in an increase in chain flexibility of the copolymer structure. Besides, the presence of side groups along the chains can also make the chains stand off from one another and lead to the increase of the distance of chains and free volume reducing T_g. This allows the polymer chains to become more flexible and move past one another easily at lower temperature. The effect of grafting on the thermal stability of the prepared copolymers was studied using TGA. All the degradation temperatures were measured from the

thermogram by onset extrapolation. Figure 7 shows TGA thermograms of ungrafted PVA, DAMN136-g-PVA, and Amidoximated PVA film. A continuous weight loss confined to a single-step degradation pattern has significantly comparable degradation temperature (T_d) at 370°C. The degradation temperature was found to vary as a result of grafting. For instance, the ungrafted PVA recorded a degradation temperature of 243°C. This temperature increased in the grafted PVA to 330°C. These results indicate that the incorporation of polydiaminomaleonitrile makes the PVA inalienable to thermal degradation. This
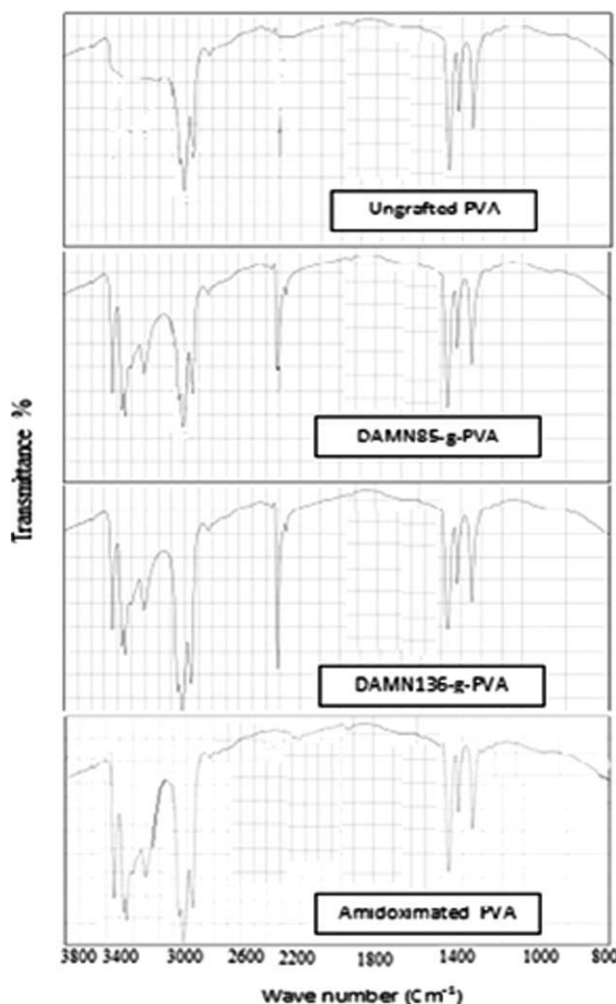
Figure 5 FTIR spectra of ungrafted-PVA, DAMN-g-PVA and amidoximated PVA.

Characterization of PVA, DAMN-g-PVA, and Amidoximated Films

Polymer film	Grafting yield (%)	Water uptake (%)	Breaking strength (MPa)	Strain at break (ε) %	T_g (°C)
PVA	–	23	24	4.7	83
DAMN85-g-PVA	85	38	33	6.4	74
DAMN136-g-PVA	136	63	42	7.3	58
Amidoximated polymer	–	72	45	7.8	53

means that the grafted PVA are more thermally stable than the un-grafted PVA, because the grafted PVA showed a single degradation pattern despite having two components. However, amidoximated PVA shows better thermal stability with a main degradation step taking place at 370°C. This thermal stability would make the amidoximated PVA film suitable for many practical applications.

Swelling properties of PET grafts

The effect of grafting percentage on water uptake ratios for PVA, PVA grafts, and amidoximated PVA films at 25°C is shown in Table I, which reveals that an increase in the water uptake ratios with the increase of grafting percentage. Clearly, the swelling behavior of the film depends on the amount of the grafted branches. Under the same conditions, amidoximated resultant graft copolymer shows water uptake value of 72%.

Mechanical properties

Table I illustrates the effect of grafting on some mechanical properties of ungrafted PVA and copolymer films. Based on the data listed in this table, one can conclude the following: Breaking strength increased continuously with an increase in grafting

yield. The behavior of elongation is the same as that of breaking strength. The grafted and amidoximated samples showed a higher increase in breaking strength as compared with ungrafted film. The result obtained in this study agreed closely with the conclusion of Rink,[28] who reported that in the toughening of ABS resin, the impact strength increased as grafting ratio increased. A typical stress to strain curve is illustrated in Figure 8.

The curves were recorded at 25°C. The straight line between points A→C, A→D, and A→E represents the interval used by the integrated software to calculate the elastic of Young's modulus of the samples DAMN85-g-PVA, DAMN136-g-PVA, and amidoximated PVA, respectively, whereas the straight line between points A → B represents the elastic of Young's modulus of ungrafted PVA film where the true stress and true strain vary linearly, and then followed by a yield drop at the elastic limit. Points M, X, Y, and Z represent the break points of the samples and the approach to failure. In the case of ungrafted PVA, the mechanical behavior shown in Figure 8 is typically that of a hard and brittle material, but this may be transformed to hard and strong or hard and tough through structural modification by grafting or amidoximation.
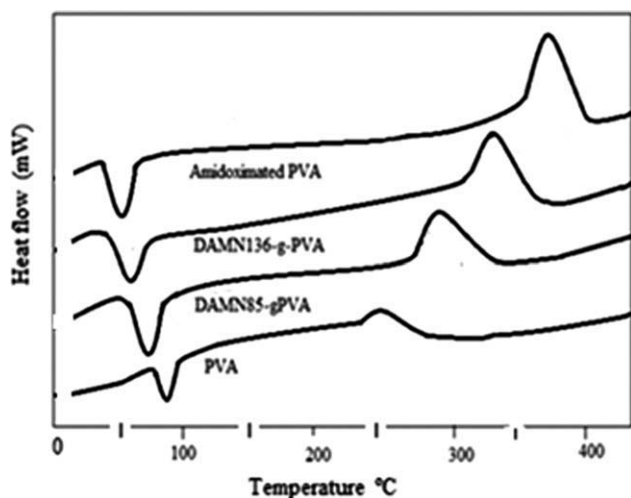
**Figure 6** DSC thermograms of ungrafted PVA, DAMN-g-PVA and amidoximated PVA.
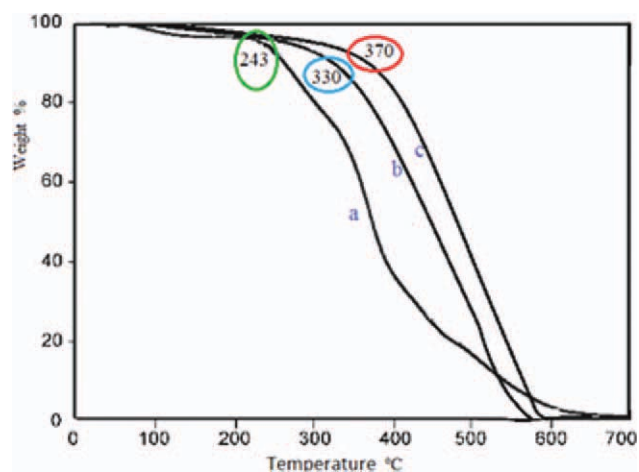
Figure 7 TGA thermograms of ungrafted PVA (a), DAMN136-g-PVA (b) and amidoximate PVA (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
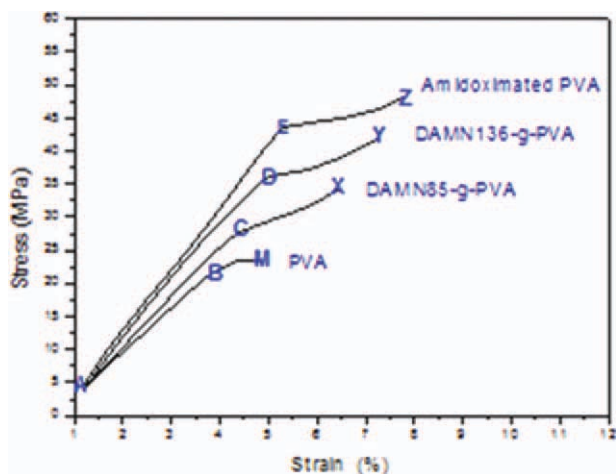
Figure 8 Typical stress/strain curve showing the linear elastic regions A-B, A-C, A-D, and A-E and brittle failure point at M, X, Y, and Z. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

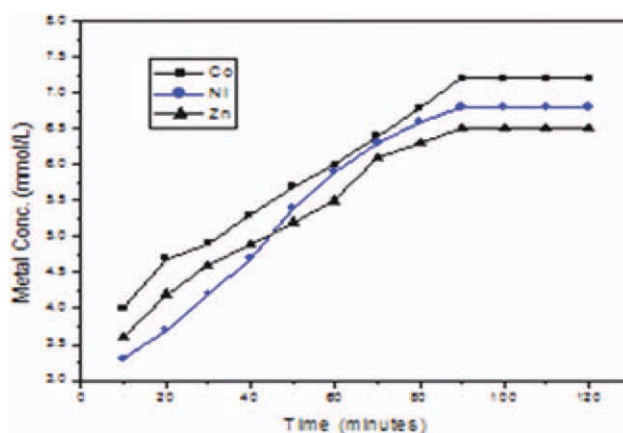## Sorption of transition metals by amidoximated PVA

There is a demand for ultra-permeable polymer of good thermal and chemical stability. The study of materials that possess voids of molecular dimensions is an area of nanoscience with technological applications.[29] Microporous materials are defined as solids that contain interconnected pores of less than 2 nm in size. Single tetrahedral carbon atom shared by hydroxyl and side chain in aminoximated PVA film, besides, the formation of six-membered rings along, side chains through hydrogen bonds between amino and hydroxyl groups, make the chains nonlinear that would inhibit cofacial association and prevent structural relaxation to a dense and rigid solid (i.e., provide a site of contortion). These polymer chains trap a considerable amount of excess free volume
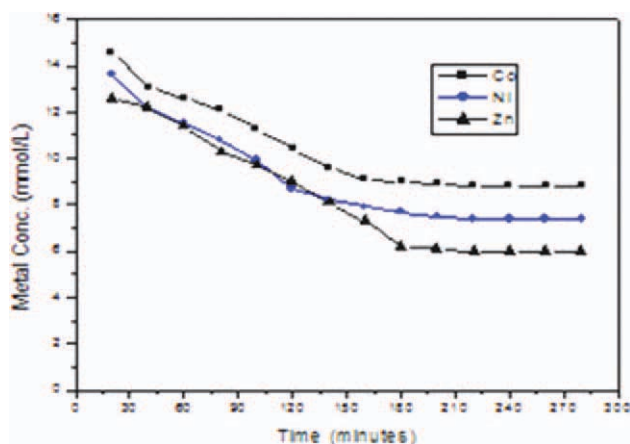
elements, which are connected to give a micropore structure.[30] Thus, the maximum metal uptake is very dependent on the type of metal ion and its coordination, as well as the ionic size of the metal, all of which affect the permeability and diffusion of these metals through the porous ionic films. The latter parameter is mainly dependent on the polarity, electronic configuration, and ionic radii of these metal ions. The possibility of using the obtained materials was evaluated over several sorption/desorption cycles. Kinetics of sorption/desorption of metal ions could not be followed by gravimetric studies because that requires removal and drying of the samples periodically, which affects the accuracy of the results. Thus, a spectrophotometric technique was applied. With this technique, it is easy to determine the absorbed/desorbed amounts of metal ions without removing and drying the samples. As the amidoximated PVA film is immersed into a metal salt solution, it starts to absorb metal ions. Therefore, the concentration of metal ions in solution decreases with the sorption process and this decrease was monitored using a spectrophotometer. The metal sorption increases with time and reaches a maximum after about 3 h (Fig. 9), when the chelating sites of the film are saturated. The maximum amount of absorbed metal salt was determined spectrophotometricaly and expressed in mmol/L. The recovery and separation of absorbed metals can be easily carried out by treating the films with $0.01M$ HCl for 1.5 h. Figure 10 shows the kinetics of the desorption process for Co^{2+}, Ni^{2+}, and Zn^{2+} ions. The desorbed metal ion concentration increases in HCl solution with time and then reaches a maximum when the desorption process is complete. The regenerated films are once again effective for resorption.

The ability of the amidoximated PVA film to absorb various heavy metals in order to evaluate the
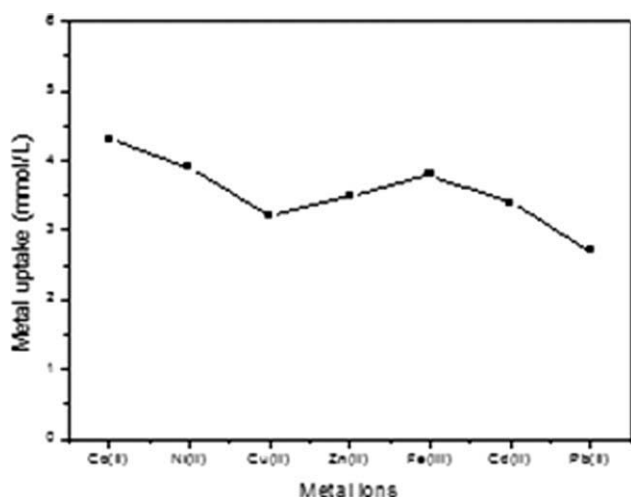

Figure 9 Kinetics of sorption process for Co, Ni, and Zn ions by amidoximated PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10 Kinetics of desorption process for Co, Ni, and Zn ions from amidoximated PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 11 Sorption of different heavy metals using amidoximated PVA film.

possibility of their use in waste water treatment has been studied. A diagram showing the capacity of the films for metal uptake is shown in Figure 11. It can be seen that the amidoximated film is characterized by a considerably greater binding ability with respect to heavy metals. The nature of the metal ion also has great importance in the amount binding to the polymeric material. The results showed by Figure 11 suggest that the sorption depends on the nature of the metal ion, being that, for example, the affinity of Co^{2+} to be absorbed in the amidoximated film is apparently higher than that observed to Pb^{2+}. The results pertaining to the affinity of this new adsorbent against vanadyl and uranyl ions in batch and continuous adsorption process and will be the subject of another publication.

CONCLUSIONS

Ceric ammonium nitrate (CAN) was used as an initiator in an aqueous nitric acid medium under N_2 atmosphere. Optimum conditions for grafting were as follows: monomer concentration [DAMN] = 1.4M, [CAN] = 16×10^{-2} mol/L, $T = 50°C$, and $t = $ 2 h. Water uptake of the PVA graft films was found to be increasing with the increase of grafting yield. The results indicate that amidoximated product of the obtained graft copolymer DAMN136-g-PVA film is a potentially powerful ion exchanger that can be employed for heavy metals removal from waste water effluents.

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