Synthesis and characterization of modified PVC waste with different diamines for Hg(II) removal

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Abstract: PVC waste, after removing contamination (P1), was cross-linked with 1,3-diaminopropane, hexamethylenediamine and 1,4-diaminonaphthalene (P2, P3 and P4). The cross-linked PVC was characterized by FTIR, SEM and CHN elemental analysis. The influence of the type of crosslinking agent on the thermal properties and swelling of PVC was also investigated. P3 was characterized by the highest water absorption, and P4 had the best thermal stability. All cross-linked polymers showed good effectiveness in removing Hg(II) ions, especially PVC modified with hexamethylenediamine.

Keywords: PVC waste, crosslinking, diamines, swelling parameters, thermal properties, Hg(II) ion removing.

Synteza i charakterystyka odpadów modyfikowanego PCV z różnymi diaminami do usuwania Hg(II)

Streszczenie: Odpady PVC po usunięciu zanieczyszczeń (P1) sieciowano 1,3-diaminopropanem, heksametylenodiaminą i 1,4-diaminonaftalenem (P2, P3 i P4). Usieciowany PVC scharakteryzowano za pomocą FTIR, SEM i analizy pierwiastkowej CHN. Zbadano także wpływ rodzaju środka sieciującego na właściwości termiczne i pęcznienie PVC. P3 charakteryzował się największą absorpcją wody, a P4 najlepszą stabilnością termiczną. Wszystkie usieciowane polimery wykazały dobrą skuteczność w usuwaniu jonów Hg(II), zwłaszcza PVC modyfikowany heksametylenodiaminą.

Słowa kluczowe: odpady PVC, sieciowanie, diaminy, parametry pęcznienia, właściwości termiczne, usuwanie jonów rtęci(II).

Preparing of smart and ecofriendly polymers having environmental benefits has attracted the attention and interest of many researchers [1, 2]. Polyvinyl chloride (PVC), flexible and rigid, could be considered as one of the most important polymers that has many applications in various fields; for instant, agricultural foil, pipes, frames, packing, coating, hoses, floor covering, window blinds, joints, cables and wires, medical tubing and blood bags [3–5].

The importance of PVC derived from its suitable properties, such as easy recyclability, slow degradation, and high compatibility with additives. On the other hand, the huge production, and uses of plastic polymers such as PVC and polyethylene cause many environmental problems due to their durability [6, 7]. To reduce the problems caused by these pollutants, polymers waste should be recycled to useful materials that can be employed in many applications, such as oil/water separation, heavy metals removal, construction and building, drug delivery release, and gases separation [8-11]. To ensure the success of using PVC waste as heavy metals removal, its chemical structure should be modified by introducing functional groups containing high electron density atoms such as oxygen and nitrogen due to the ability of such atoms to form strong coordination bonds with heavy metals ions [12]. Many researchers have reported the modification of PVC and their different applications. Tooma *et al.* have reported the modification of PVC by grafting with ethyl acrylate monomer that showed superior performance for vacuum membrane distillation (VMD) application [13]. In another study achieved by Siekierka *et al*., pentaethylenehexamine and diethylenetriamine have been successfully grafted onto PVC to prepare membranes can be used as anion-exchange to remove chromium ion from wastewater [14]. Bierbrauer *et al*. observed that chlorine atoms in PVC chains can be partially replaced with pentafluorothiophenol, 3,4-difluorothiophenol, and 4-fluorothiophenol. The modified polymers were used to prepare membranes for methane, carbon dioxide, oxygen, nitrogen, and hydrogen separation [15]. Despite the importance of reducing pollution caused by polymers, there are a few studies reported on recycling PVC waste and convert it to useful material.

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The main goal of this work was to purify and modify PVC waste by using several types of diamines as cross-linking agents. The influence of the type of cross-linking agent on the properties of modified PVC waste and its ability to remove mercury(II) ions from industrial wastewater was also examined.

EXPERIMENTAL PART

Materials

1,3-diaminopropane ($C_3H_{10}N_2$, M = 74.12 g/mol, 99%), hexamethylenediamine ($C_6H_{16}N_2$, M = 116.20, 98%), 1,4-diaminonaphthalene ($C_{10}H_{10}N_2$, M = 158.20 g/mol, 98%), acetone (99%), tetrahydrofuran (98%), dimethylformamide (98%), chloroform (99%), methanol (98%) and ethanol absolute were all collected from Merck (Darmstadt, Germany).

Preparing of purified PVC

100 g of PVC waste (pipe) was cut and converted into sawdust-like form, and then carefully washed at 30°C using 500 ml of distilled water. To remove any industrial additives such as alcohols and pigments, 10 g of PVC pieces was placed in conical flask with 100 ml of acetone, closed and heated for 48 hours at 65°C. The samples were then filtered, and the purification process was repeated three times to make sure that all impurities were completely removed. The presence of chlorine in the chemical structure of purified PVC was confirmed by Bilstein test and FTIR spectroscopy (Perkin Elmer 1650, Waltham, MA, USA), the band observed at 599 cm^{-1} was attributed to C-Cl band.

Modification of purified PVC

After purification, the PVC waste was cross-linked using 1,3-diaminopropane (hereinafter referred to as P2), hexamethylenediamine (P3) and p-phenylenediamine (P4). The procedure was carried out as follow: mixture of recycled PVC (2 g, 32 mmol), diamino derivatives (16 mmol) and potassium iodide (0.05 g, 0.26 mmol) were dissolved in 75 ml of tetrahydrofuran. The mixture was then transferred into round bottom flask and heated under nitrogen atmosphere at 70°C with continuous stirring for two days. After cooling, bulky crosslinked PVC was filtered, washed with tetrahydrofuran/methanol mixture, and dried at 65°C for 72 hours. The synthesis process of crosslinked PVC from purified PVC and different amines is shown in Figure 1. The solubility of prepared modified PVC was evaluated by using different solvents; the polymers were soluble in DMF and insoluble in most of solvents such as toluene, benzene, methanol, chloroform, ethanol, and water. However, the polymers swell in most of mentioned solvents which confirms forming of crosslinked PVC.

Methods

The chemical structure of modified PVC was analyzed using a Perkin Elmer-1650 Fourier spectrophotometer (Waltham, MA, USA). Infrared spectra were recorded using the potassium bromide in the wave number range from 400 to 4000 cm^{-1}. Elemental analyzer Leco Chns-932 instrument (St. Joseph, Michigan, USA) was employed to determine nitrogen wt% in the polymers. The concentration of Hg^{2+} in the solutions, before and after adsorption by polymers, was determined by using flame atomic absorption spectrophotometer, Shimadzu AA-7000 (Kyoto, Japan). TGA Perkin Elmer (USA) was used to analyze the thermal stability of sample under nitrogen atmosphere, in the range of 0°C to 800°C with 10°C/min heating rate.

The swelling procedure was conducted by putting 50 mg of dry polymer in deionized water and weighing the sample at regular times until reaching to constant weight, the sample was dried at 40°C for two days, and then the equilibrium water content (EWC) was calculated as follow [16]:

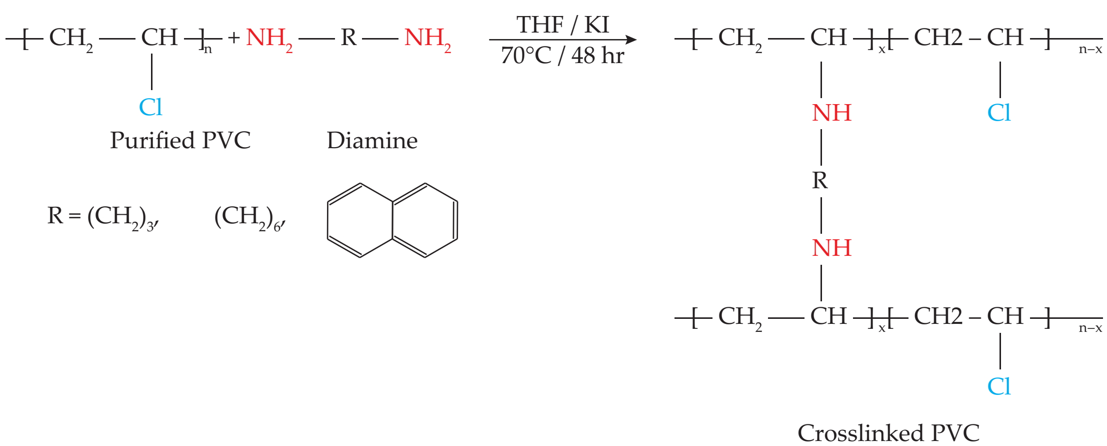


Fig. 1. Schematic synthesis of crosslinked PVC from purified PVC and different diamines

$$EWC\% = \frac{\text{weight of fully hydrted sample} - \text{weight of dried sample}}{\text{weight of fully hydrted sample}} \quad (1)$$

1000 mg of prepared polymers were put in 50 ml of wastewater collected from Tigris River (Iraq), near battery factory. The optimum conditions for the adsorption were adjusted as pH 7 at 30°C for 12 hours. The following equation was used to determine the adsorption capacity [17]:

$$\text{Adsorption capacity } (AC) = \frac{(\text{initial ion conc.} - \text{ion conc. after adsorption}) \cdot \text{volume solution}}{\text{weight of dry polymer}} \quad (2)$$

To check the surface morphology of purified and modified PVC by using ZEISS EVO scanning electron microscopy (Oberkochen, Germany), polymer films were prepared by casting a solution composed of 5 mg of polymer dissolved in 500 ml DMF on a glass plate by using 100 μm casting knife. The films were dried at 50°C for 48 h in an oven and then washed with ethanol to ensure removing all the solvent.

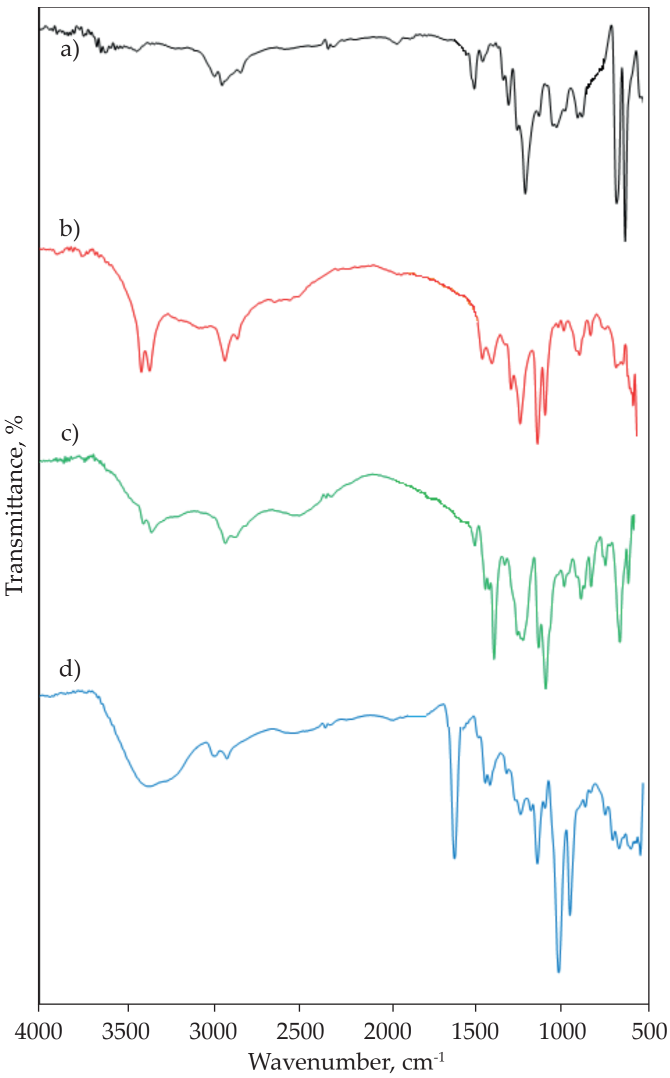


Fig. 2. FTIR spectra: a) P1, b) P2, c) P3, d) P4

RESULTS AND DISCUSSION

The percentage of nitrogen determined by elemental analysis for polymers P1, P2, P3 and P4 was 0, 7.4, 5.1, and 3.8, respectively. These results indicate the successful incorporation of the diamines compounds between purified PVC chains as crosslinkers. Similar findings have been obtained by Mbarki *et al*. [18] when PVC was grafted with p-methoxyaniline.

Figure 2 shows the FTIR spectra of PVC before and after modification. The bands at about 3250–3300 cm^{-1} and 1100–1220 cm^{-1}, which appear in the spectrum of P2, P3 and P4, belong to N-H and C-N stretching vibrations, respectively, while these bands are not seen in the spectrum of unmodified PVC (P1) which support accruing crosslinking of polymers with diamines. The band at about 1600 cm^{-1} in polymer P4 is attributed to the aromatic C=C of naphthalene rings. In addition, it can be clearly observed that the multiple bands at about 600–800 cm^{-1}, which belong to C-Cl group of PVC did not disappear completely in the FTIR spectra of P2, P3 and P4 because Cl atoms in the purified PVC were partially substituted with amino groups of diamines.

Thermal properties

Thermal properties of purified PVC, before and after modification with diamines, were studied using TGA, and the results are shown in Figure 3. Thermal stability of modified PVC increased compared with unmodified PVC because diamines form bridges as crosslinking agent between polymer chains. This effect of crosslinker on thermal properties of polymers has already discussed by many other researchers [19–21]. Moreover, type of used diamine has also an effect on thermal properties of modified polymers; thus, P4 is more stable than P2 and P3 due to the presence of aromatic rings in 1,4-diaminonaphthalene. In all cases, the polymers start the first stage of decomposition at 150–160°C and end at 400–500°C, the total weight loss in this region is between 5–40%.

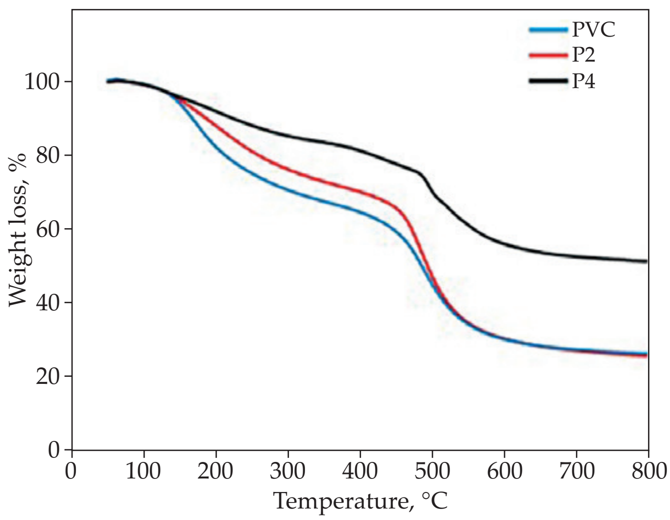


Fig. 3. TGA of unmodified and modified PVC

The major decomposition occurs at the range 500–600°C when the total weight loss is 75% for PVC and P2. No difference has been observed between thermal stability behavior of P2 and P3; hence, TGA curve of P3 is not shown in Figure 3.

Swelling behavior

Swelling characteristics, equilibrium water content and weight loss of polymer during swelling, were also studied due to their effect in determining the applications of polymers; the results are listed in Table 1. It can be easily observed that unmodified PVC has the lowest EWC compared with P2, P3 and P4. Since all modified polymers have the same number of the hydrophilic amino groups, the length and hydrophilicity of crosslinkers determine the ability of polymers for swelling in water. Thus, P3 has higher EWC than other modified polymers because of the length of hexamethylenediamine structure allows the easiest diffusion of water molecules among polymer chains. The low values of weight loss of polymer during swelling can be attributed to the limited number of linear hydrophilic polymer chains and high crosslinking density. Noor *et al*. obtained similar findings when the effect of crosslinker on swelling properties of phenyl acrylamide was studied [22].

T a b l e 1. Swelling characteristic of unmodified and modified PVC

Polymer	EWC, wt%	Weight loss, wt%
P1	9.5	3.5
P2	18.4	2.7
P3	25.2	3.6
P4	16.8	2.3

Scanning electron microscopy

The top surface of PVC film, before and after modification with hexamethylenediamine, is illustrated in Figure 4. Pores can be seen on the top of the smooth surface of P2, P3 and P4 films as it is shown in Figure 4b), c) and d), whereas Figure 4a) shows more pores distributed on the top surface of P1 film. The difference in the results can be attributed to the difference in the viscosity of the polymers solutions [23, 24]. The viscosity and density of any polymer solution increase as the crosslinking density increases, and thus all polymers' solutions having the same concentration, however, P2, P3 and P4 are more viscos than P1 because these polymers are crosslinked with diamines.

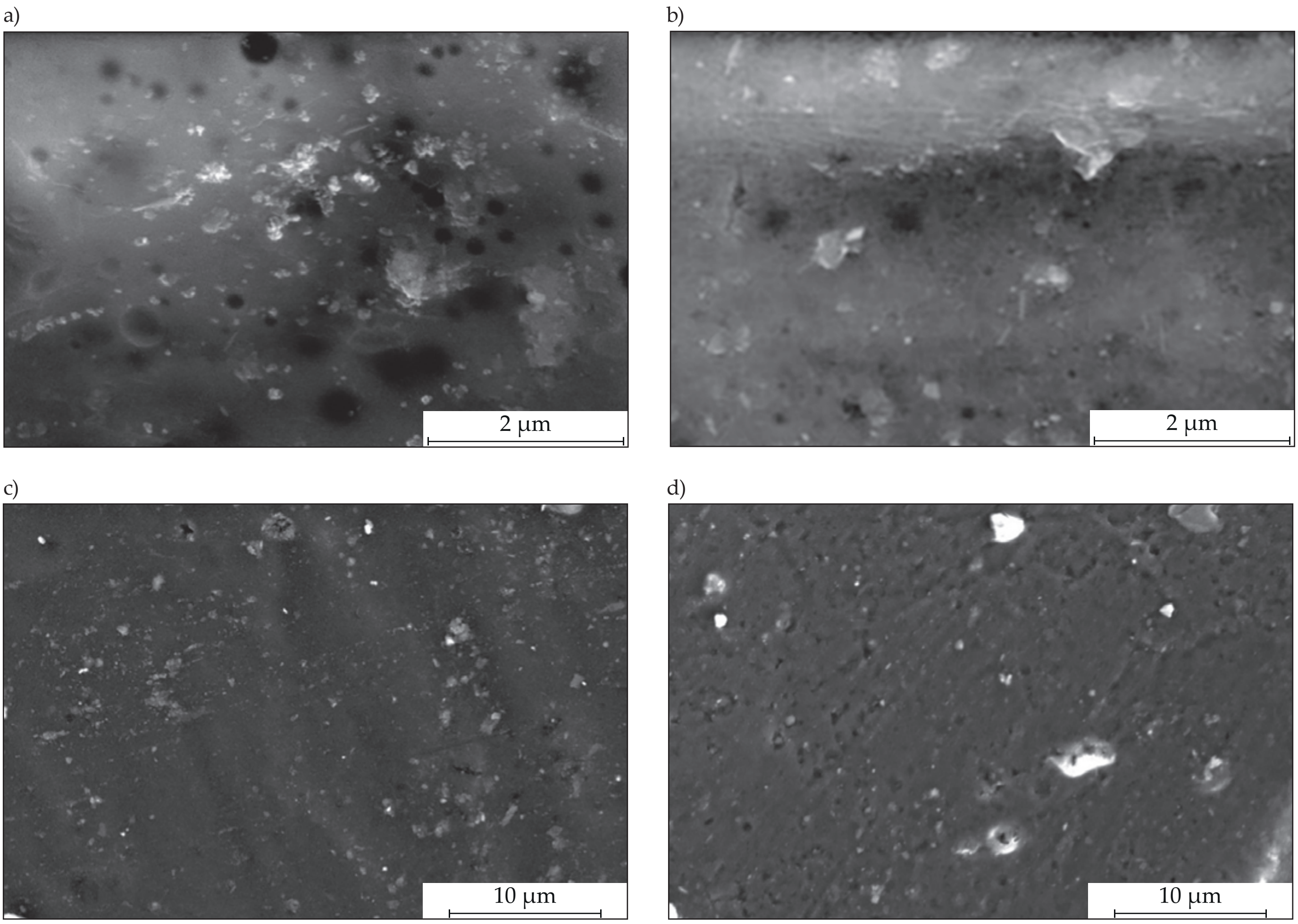


Fig. 4. SEM images: a) P1, b) P2, c) P3, d) P4

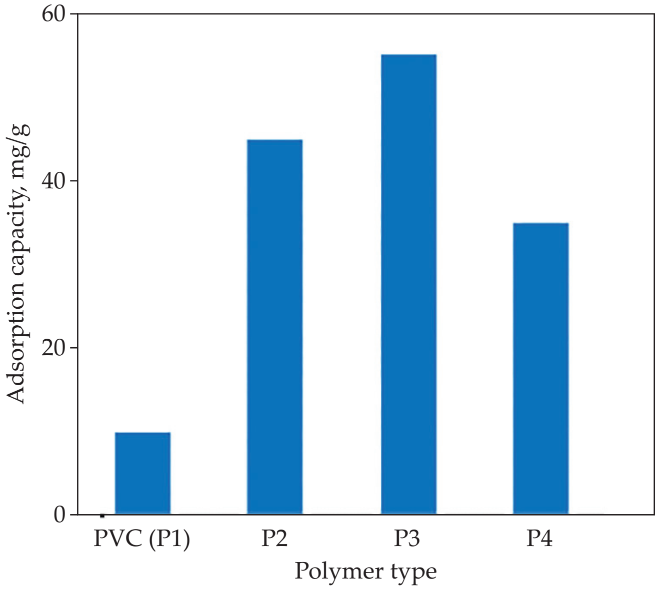
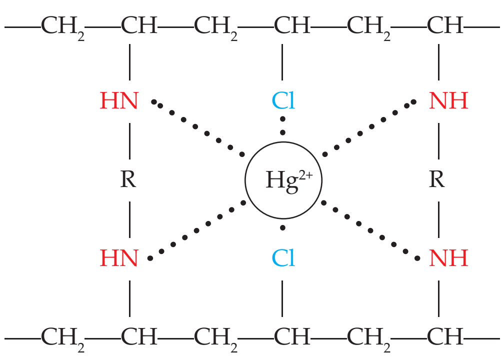


Fig. 5. Effect of polymer type on its adsorption capacity for Hg^{2+} from wastewater

Removing of Hg^{2+} from industrial wastewater

The prepared polymers were also examined for removing Hg^{2+} from wastewater collected from Tigris River (Iraq), near battery factory. The collected samples were first analyzed to determine the concentration of Hg^{2+} by using atomic adsorption technique. The results revealed that the industrial wastewater contains about 3.2 mg/l of Hg^{2+}. From Figure 5, it could be concluded that performance of P3 for removing Hg^{2+} from industrial wastewater is better than performance of P1, P2 and P4. The results could be explained in term of that amount of adsorbed Hg^{2+} is directly affected by EWC and hydrophilicity of polymers, the amount of adsorbed Hg^{2+} increases as EWC of polymer increases, this fact is further supported by other studies in the literature [25]. In case of P4, the electron pair of nitrogen atoms might get delocalized into naphthalene rings resulted in decreasing the hydrophilicity of polymer; thus, low adsorption of Hg^{2+} by this polymer was observed. Scheme 1 shows the suggested mechanism of removing process.



Scheme 1. The suggested mechanism of removing Hg^{2+} from waste water

CONCLUSIONS

In this study, PVC waste was purified from impurities and additives, and crosslinked with 1,3-diaminopropane, hexamethylenediamine, and 1,4-diaminonaphthalene. The obtained polymers were characterized by elemental analysis, FTIR and SEM. Swelling and thermal properties of obtained polymers were also studied and found that P3 has higher EWC than other modified polymers; whereas P4 showed good thermal stability compared to P2 and P3. The adsorption capacity of prepared polymers for removing Hg II from wastewater of Tigris River (Iraq), near battery factory, was determined, the promising performance was assigned to P3.

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