

**PREPARATION OF POLYSTYRENE-BASED POLYMERS FOR
CARRIER-MEDIATED HEAVY METAL ION-EXTRACTION**

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ABSTRACT

In the present work, different polymeric matrices have been prepared by incorporation of some phenolic compounds either through chemical modification of chloromethylated polystyrene or through physical blending with polystyrene (PS) and polyvinyl chloride (PVC). The blended products have been annealed to attain partial crosslinking. The incorporation of phenols into the polymeric matrix was investigated and followed up by using elemental and IR-spectroscopic analyses. It has been proved that the physically blended matrix can be used for metal ion extraction like the chemically modified one with some drawbacks that can be minimized through crosslinking after incorporation of the phenolic compounds. Carrier-mediated extraction of heavy metal ions was investigated using ferric ion as representative for the heavy metal ions while p-hydroxybenzaldehyde, vanillin, resorcinol and β -resorcylic acid were used as representatives for the phenolic compounds.

INTRODUCTION

The removal of metal ions from aqueous solutions can be achieved through two routes. The first is the metal transport between two phases resulting in the increase of the metal ion concentration in one phase which decreasing it in the other. This can be performed with the aid of membrane technology. The second one is the metal ion extraction

either through adsorption or chelate formation [Stevens et al, (1997); Slater et al, (1997) and Kaminiski et al, (1999)].

The above mentioned two routes based on utilization of functional groups able to interact with the target metal ions. Some functional groups can be introduced into the polymer matrix either through chemical modification reactions [Sarhan et al, (1998); Sarhan et al, (2002) and Abdelaal, (2000)] or physical blending [Abdelaal, (2001)]. The extraction or transport of metal ions using the physically blended matrix is known as a carrier-mediated process [Abdelaal, (2001)]. Many organic compounds can serve in a good way in this direction due to their expected ability to form metal chelates [Sobahi, (2003); Sobahi et al, (2003) and Sobahi (2004)].

The current work includes the utilization of some conventional phenolic compounds of known ability to interact with metal ions in a carrier-mediated metal ion extraction process.

RESULTS AND DISCUSSION

General considerations

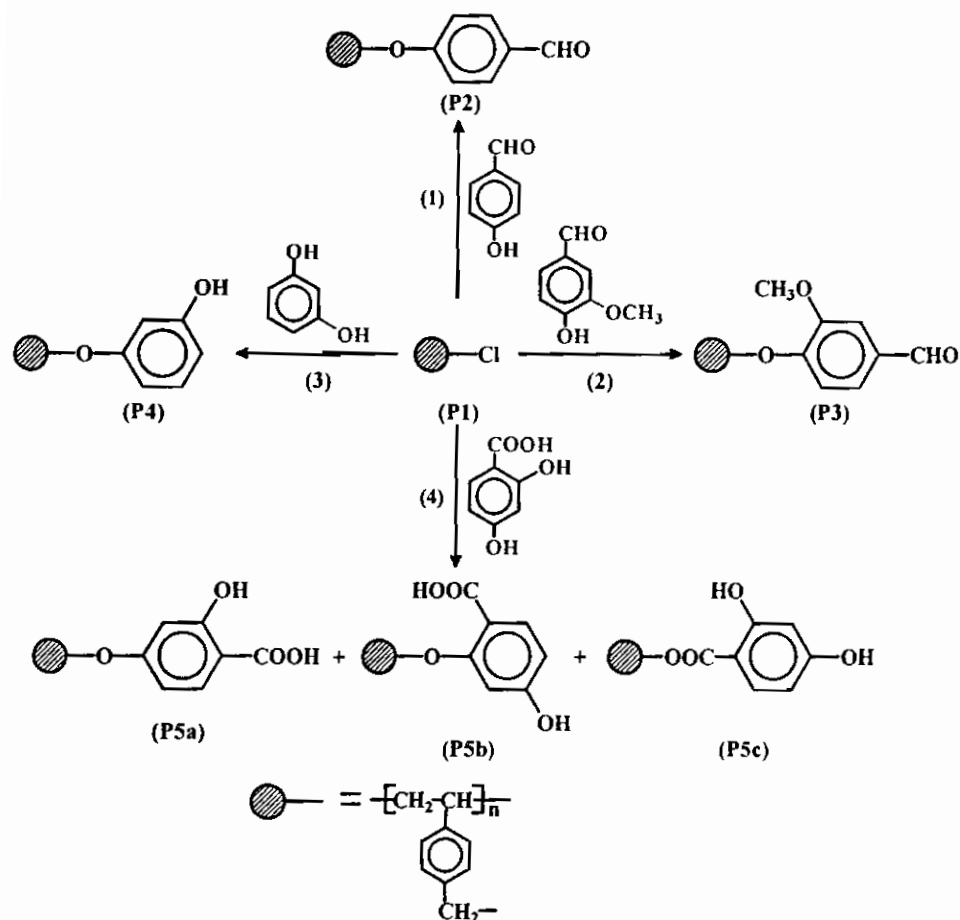
In the present investigation, different polymeric matrices have been prepared by incorporation of some simple organic compounds, namely, p-hydroxybenzaldehyde (1), vanillin (2), resorcinol (3) and β -resorcylic acid (4) into the polymeric matrix. This has been achieved either through chemical modification of chloromethylated polystyrene with such simple organic compounds or through physical blending of polystyrene (PS) with polyvinyl chloride (PVC) in THF as a common solvent in presence of the above mentioned simple organic compounds (1-4) followed by evaporation of the solvent while stirring. The blended products have been annealed at 75°C for 24 h in an oxygen atmosphere to attain partial crosslinking through the terminal double bonds present in PVC and those may be present along the PVC chains due to the dehydrochlorination reaction that probably occurs during annealing process.

Chemical modification of P1 with phenolic compounds 1-4

The chemical modification of chloromethylated polystyrene has been performed according to the methods described early [Sarhan et al (1998)] and has been proved through the elemental and FT-IR

spectroscopic analyses. The reaction conversion % and the overall reaction yield for the modified polymers have been calculated by using the elemental analysis data on the basis of mole fraction concept [Abdelaal & Elmorsy, (1995)]. It has been noticed that the reaction of **P1** with both of resorcinol and β -resorcylic acid was difficult and it needed lower reaction temperature and concentration of K_2CO_3 as well. The reaction between **P1** and p-hydroxybenzaldehyde (**1**), vanillin (**2**) and resorcinol (**3**) has been performed with the possibility for O-alkylation as well as C-alkylation while the reaction with β -resorcylic acid (**4**) was occurred through the oxygen atom of one of the two phenolic hydroxyl groups and/or through the oxygen atom of the carboxylic group resulting in formation of ether (**P5a,b**) and/or ester (**P5c**) link, respectively. Scheme 1 represents the chemical modification of chloromethylated polystyrene (**P1**) with the above mentioned phenolic compounds 1-4.

The calculations using the elemental analysis data showed that the chemical modification of **P1** has been achieved in a good conversion %. It ranges from about 65% for resorcinol (**3**) to about 80% for vanillin (**2**). In between, p-hydroxybenzaldehyde (**1**) and β -resorcylic acid (**4**) were reacted in about 69% and 75% conversion%, respectively. Elemental analysis data have been summarized in Table 1.



Scheme 1: Chemical modification of chloromethylated polystyrene with different phenolic compounds

Table (1): Reaction characteristics and elemental analysis for the chemically modified chloromethylated polystyrenes.

Sample No.	C %	H %	Cl %	Conversion %	Overall Yield %
P1	79.88	6.66	13.46	—	—
P2	88.22	6.98	3.44	68.8	33
P3	80.71	6.50	2.10	79.2	38
P4	82.63	6.68	4.04	64.6	31
P5	77.77	6.05	2.52	75.0	36

FT-IR spectroscopic analysis proved also such chemical modification of **P1** as **P2** and **P3** showed absorption at $\nu = 3500\text{cm}^{-1}$ corresponding to the phenolic OH group, at 1720cm^{-1} corresponding to C=O of the aldehyde group and at 1050cm^{-1} corresponding to C–O–C bonding of p-hydroxybenzaldehyde (**1**) and vanillin (**2**), respectively. This means that these organic compounds have been attached through C-alkylation and O-alkylation. Also, **P4** showed absorption at 1050cm^{-1} corresponding to the phenolic hydroxyl group and the ether linking, respectively. **P5** showed also absorptions at $\nu = 1050\text{cm}^{-1}$, 1715cm^{-1} and 1730cm^{-1} corresponding to C–O–C bonding, COOH group and COO-ester bonding, respectively, in addition to the absorption at the range of $\nu = 3300\text{cm}^{-1} - 3400\text{cm}^{-1}$ corresponding to the phenolic hydroxyl group. FT-IR spectroscopic analysis data have been summarized in Table 2.

Table (2): FT-IR spectroscopic analysis data of the chemically modified polymeric products P2-P5 (P1 is the starting polymer).

Sample No.	Characteristic absorption peaks ν in cm^{-1}
P1	690 (C–Cl); 1590 (C=C aromatic)
P2	690 (C–Cl); 1070 (C–O–C); 1590 (C=C ar.); 1715 (C=O); 3400 (O–H)
P3	690 (C–Cl); 1070 (C–O–C); 1590 (C=C ar.); 1715 (C=O); 3300 (O–H)
P4	690 (C–Cl); 1100 (C–O–C); 1590 (C=C ar.); 3400 (O–H)
P5	690 (C–Cl); 1120 (C–O–C); 1590 (C=C ar.); 1720 (C=O); 3300 (O–H)

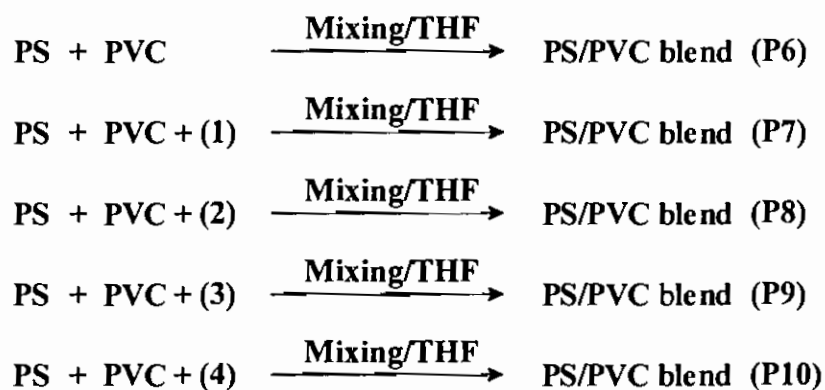
The chemical modification products have not been completely characterized in the light of determination of the extent of O-alkylation and C-alkylation in case of **P2** – **P4** as well as the extent of ether binding and ester linking in case of **P5**.

Physical blending of PS blends with phenolic compounds 1-4

The aim of the present work is to investigate the ability of such polymeric products to be employed for metal ion extraction based on the known ability of the employed simple organic compounds to be useful through chelation with it. The introduction of such simple organic compounds has been performed *via* chemical attachment and *via* physical

blending through dissolution/evaporation technique. The incorporated compounds have been compared with each other in the light of their availability for metal ion extraction. Iron (III) ions have been selected as a representative for the metal ions as it easily forms intense colors with those phenolic derivatives.

For this target to be achieved, different blends of PS and PVC have been prepared in presence of the investigated simple organic compounds. It has been considered that composition of the final blends would have the same loading ratio to the chemically loaded polymeric products or slightly higher. All the physically blended samples have been annealed at 75°C for 24h to give the opportunity for the linear chains of PVC to be lightly crosslinked. This would help of course to prevent, or at least to hinder, the blooming of the entrapped simple organic compounds from the bulk of the matrix onto the surface. Hence, the problems that arise from dissolution of such organic compounds and consequently their chelation products with the investigated metal ions can be avoided to a great extent. The physically blended samples have schematically represented in Scheme 2.



PS = Polystyrene; PVC = Polyvinyl chloride

Scheme 2: Physical blending of PS with PVC in presence of different phenolic compounds

Table 3 summarizes the amount of Fe(III) extracted into the chemically modified chloromethylated polystyrene or into the physically blended matrices either those thermally treated or the untreated samples.

Table (3): Concentration of the extracted Fe(III) into the polymeric samples in mmole/g polymer

Sample No.	Fe(III) concentration
P1M	1.8
P2M	5.9
P3M	6.8
P4M	5.5
P5M	6.4
P6M*	1.9 (2.1)
P7M*	3.8 (5.7)
P8M*	4.5 (7.0)
P9M*	3.6 (5.8)
P10M*	4.2 (6.6)

*: Concentrations in parentheses are for the thermally treated samples.

It has been previously reported that such systems can give some mobility chances for the entrapped low molecular weight fraction with which the metal ions can either extracted or transported using different carrier-mediated polymeric membranes [Abdelaal, (2001); Stevens et al, (1997); Slater et al, (1997) and Kaminiski et al, (1999)]. Therefore, a comparison between the thermally treated samples with those untreated samples concluded that the dissipated amount of the low molecular weight organic compounds into the aqueous solution of the investigated metal ion was much higher for the untreated samples than in case of the thermally treated ones. This can be explained by the post-crosslinking that may be occur during the thermal treatment due to the presence of unsaturation either at the chain terminals or along the PVC chains. This light crosslinking hinders the mobility of both the polystyrene (PS) and PVC chains in addition to the low molecular weight organic compounds entrapped within this coiled and entangled matrix. Polystyrene itself can take part in crosslinking through the tertiary hydrogen but it can be neglected relative to that caused by PVC.

Interaction of polymeric products (P1-P10) with Fe(III) ions

The modified polymeric materials have been interacted with ferric chloride in a slightly acidic solution. The color has been changed into violet to reddish violet color in all cases reflecting a positive interaction leading to metal extraction or enrichment in the polymeric solid phase. In all cases also, the absorption peaks of OH groups of the phenolic compounds have been shifted due to the effect of chelation. In a comparison between the two routes of the polymer modification, it can be concluded that physical blending of PVC with PS in presence of the investigated phenolic compounds resulted in formation of a more efficient matrix able to extract Fe(III) than that formed through the chemical modification. This can be explained by the fact that through physical blending one can incorporate more chelating compounds such as the phenolic compounds in the current investigation. On the other hand, chemical modification can be considered as better as physical blending and this can be attributed to the higher stability of the phenolic compounds in the polymeric matrix due to the chemical attachment.

As the phenolic compounds are physically distributed within the polymeric matrix in case of physical blending, the ability of such molecules and/or their chelates to be dissolved in the contacting solution may lead to dissipation of the phenolic compounds as a consequence of leaching process into the solution. This may enhance the undesirable results such as toxicity in addition to the inefficiency to extract Fe(III). This has been proved through the colorization of Fe(III) solution in case of the physically blended matrix due to leaching of the phenolic compound from the matrix which has not been occurred for the chemically modified polymers. This reflects the difficult regeneration of the polymer matrix in case of the physical blending compared with the chemically modified matrix. This drawback for the physically blended matrix can be minimized through crosslinking of the polymeric matrix. This was found to be the case and the change in color of Fe(III) solution was not too high as in the above mentioned case.

In conclusion, the current investigation proved the ability of the physically blended matrix to be used for metal ion extraction like the chemically modified matrix but there are some important drawbacks to be considered to eliminate, or at least to decrease, their negative characteristics mainly through crosslinking after incorporation of the chelating compounds such as phenolic compounds in the current study.

EXPERIMENTAL

All chemicals and pure solvents were used without further purification as purchased by Aldrich, USA. Porous chloromethylated polystyrene-co-DVB (**P1**) was supplied by Fluka. It has about 4 mmole chlorine/g polymer. β -Resorcylic acid has been prepared according to method reported before [Schwetlick, (1986)]. The polymeric products were dried under vacuum at 40°C for 24h and subjected to FT-IR spectroscopic analysis that has been performed using Perkin Elmer FT-IR spectrophotometer while elemental analysis was performed at the Micro-analytical Unit, King Abdulaziz University, Saudi Arabia. Fischer melting point apparatus was used for the determination of melting point of the simple organic compounds.

Reaction of P1 with phenolic compounds 1-4

Chloromethylated polystyrene (**P1**) (1.7g) corresponding to 5.2 mmole of the chloride functionality was swollen in 10 ml DMF for 48h. About 0.2 mmole of benzyltriphenylphosphonium chloride (BTTPC), 10 mmole of K_2CO_3 was dissolved in 10 ml of water and 4 mmole of the investigated phenolic compounds were added. The reaction mixture was stirred magnetically for 9h at 90°C in water bath. The reaction mixture was filtered off and the modified polymers (**P2-P5**) were characterized with the aid of elemental and FT-IR spectroscopic analyses.

Synthesis of blended polystyrene with phenolic compounds 1-4

A solution of 5g polystyrene (**PS**) in 50 ml THF was added to 5g polyvinyl chloride (**PVC**) dissolved also in 50 ml THF. To the mixture of both solutions, 25 mmole of the target organic compound (**1-4**) dissolved in the least amount of THF was added and mixed well with shaking. After a homogeneous solution has been formed, the solvent has been removed completely by evaporation while stirring. The residual material has been dried at 40°C under vacuum for 24h and after that has been grinded into fine powder. A half amount of each polymeric blend has been annealed in an oven for 6h at 75°C. All the polymeric products (**P7-P10**) have been subjected to FT-IR spectroscopic analysis. Parallel to this process, a blank sample of PS/PVC blend (**P6**) has been prepared without loading any of the investigated organic compounds.

Interaction of the polymeric products P1-P10 with Fe(III).

Each polymeric product either chemically modified (P1-P5) or physically blended (P6-P10) (1g) has been treated with stirring for 1h with 100ml of 0.5M aqueous solution of ferric chloride. The medium has been adjusted to pH of about 6-6.5. The mixture was filtered off and the concentration of Fe(III) has been determined in the filtrate. The separated polymeric products (P1M-P10M) have been subjected to FT-IR spectroscopic analysis.

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تحضير بلمرات بأساس بولي إسترين لاستخلاص أيونات
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في هذه الدراسة تم تحضير مواد بوليمرية مختلفة بإدخال بعض مركبات الفينول من خلال التحوير الكيميائي لكلوروميثيل بولي إسترين وكذلك التوليف الفيزيائي بالخلط مع بولي إسترين وبي في سي. تمت معالجة نواتج الخلط الفيزيائي حرارياً للحصول على تشابك جزئي للسلاسل وتمت دراسة وتتبع إدخال الفينولات في البوليمر بالتحليل الكمي للعناصر والتحليل الطيفي بالأشعة تحت الحمراء. وقد ثبت إمكانية استخدام نواتج الخلط الفيزيائي مثل نواتج التحوير الكيميائي في استخلاص أيونات بعض المعادن الثقيلة بالوسيط الحامل مع بعض العيوب التي يمكن أن تقل بتشابك السلاسل بعد إدخال الفينولات في البوليمر. أيضاً تمت دراسة استخلاص أيونات المعادن الثقيلة بالمواد الحاملة باستخدام أيونات الحديد كنموذج لأيونات المعادن الثقيلة بينما تم استخدام ٤-هيدروكسي بنزالدهيد، فانيلين، ريزورسينول و حمض بيتا-ريزورسيليك كنماذج للمركبات الفينولية.