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# Adsorption of calcium ions by graft copolymer of acrylic acid on biopolymer chitin

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The graft copolymer of acrylic acid on biopolymer chitin, with 45% grafting efficiency, was used to study the effect of the carboxylic group of the graft copolymer on the metal binding ability of calcium ions in aqueous solution as a function of pH, contact time and metal concentration. The adsorption equilibrium data correlate well with the Langmuir isotherm equation. The maximum adsorption capacities of graft copolymer and chitin were found to be $0.500 \pm 0.013$ and $0.195 \pm 0.005 \, \mathrm{mmol} \, Ca^{2+} \, g^{-1}$, respectively, suggesting the effective participation of the carboxylic group in $Ca^{2+}$ adsorption. The poly(acrylic acid)-grafted chitin is promising as a polymeric matrix to be used in the preparation of new glass ionomer cements.

(Keywords: grafted chitin; poly(acrylic acid); $Ca^{2+}$ adsorption)

## INTRODUCTION

Chitin, a biopolymer consisting of $\beta$-(1-4)-2-acetamido-2-deoxy-D-glucose units, is the second most abundant polysaccharide occurring in nature, after cellulose[1] (*Figure 1*). Although this polysaccharide is structurally similar to cellulose, it has less chemical versatility because of its strong crystal structure, and hence research on chitin is limited[2].

Graft copolymerization reactions of vinyl monomers on chitin, using redox initiatior and by a photoinduced method, have recently been explored as an interesting alternative chemical modification required to develop new natural/synthetic polymer hybrid materials[3,4]. These graft copolymers are of importance in view of new industrial applications such as water absorbents, ion exchangers, flocculants, membranes, modified electrodes and, principally, chelating agents[5-12]. However, graft copolymerization on chitin and chitosan has been scarcely reported in the literature, while on cellulose, starch, wool and cotton, it has been studied to a greater extent[2,7,13-20].

Recently, the ability of chitin, chitosan and derivatives to chelate metal ions such as $Cu^{2+}$, $Pb^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Zn^{2+}$, $Al^{3+}$ and $Mn^{2+}$ has ben studied, suggesting the possibility of using these polymers in the removal of metal ions in waste and natural water[21-27].

Glass ionomer cements are new polymer–glass composites in which glass particles, comprising an unreacted nucleus and a surrounding sheath of siliceous gel, are embedded in a matrix consisting of calcium and aluminium polyacrylates. Because of their highly ionic nature, these restorative dental materials have the ability to bond physicochemically to both enamel and dentin[28-30].

In the present paper, acrylic acid was grafted on chitin in order to verify the enhancement of calcium ion binding capacity by the presence of carboxylic groups in the graft copolymer. This work also examines the probable binding sites for the metal ions. The chemical combination of chitin and poly(acrylic acid) (PAA) by a grafting technique yields a new material which could be used as the principal component of alternative glass ionomer cements.

## EXPERIMENTAL

### Materials and methods

Chitin was isolated from shrimp shells according to the method described in the literature[31] and powdered (100 mesh) before use. The degree of deacetylation (*DA*) found by elemental analysis was about 15%.

Acrylic acid (Riedel) was used as received. Cerium ammonium nitrate (Riedel) was used to prepare the initiator solution, and was used without further purification. Calcium carbonate and ethylenediaminetetraacetic acid disodium solutions were prepared from analytical grade $CaCO_3$ (Merck) and EDTA (Sigma). Calcium carbonate in the presence of HCl (1:1) was used for preparing standard metal ion solutions. Other reagents were of analytical grade and were used without further treatment.

Purified chitin powder (1.00 g) was dispersed in 45 ml of deaerated water in a thermostatically controlled reaction flask at 60°C for 60 min. Ceric ammonium nitrate in 1 M nitric acid solution was then added with
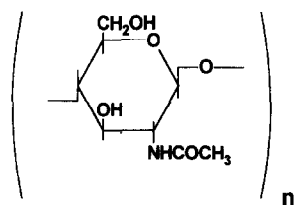
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**Figure 1** Structure of chitin

stirring and followed by a known weight of acrylic acid, with concentrations of $3.45 \times 10^{-3}$ M and $9.59 \times 10^{-1}$ M in the reaction mixture for the initiator and monomer, respectively.

Graft copolymerization was carried out at 60°C for 3 h in a nitrogen atmosphere under mechanical stirring. At the end of the graft copolymerization, the mixture was poured into 800 ml of distilled water and the copolymer precipitated out under strong stirring. The graft copolymer was filtered and washed with plenty of water. Purification of the graft copolymer was done by extraction of the homopolymer with distilled water at 60°C for 2 h under vigorous shaking. The solid obtained was filtered and dried at 60°C to constant weight.

The remaining product after drying to constant weight was considered to be a graft copolymer with 45% efficiency of grafting, calculated by the equation:

$$\% \text{ grafting efficiency} = W_2 - W_1/W_1 \times 100 \quad (1)$$

where $W_1$ and $W_2$ denote the weights of chitin and grafted chitin after water extraction, respectively.

Infra-red spectra were obtained on KBr pellets on an *FT* i.r. Perkin–Elmer 1600 spectrophotometer.

*Optimization of adsorption pH*

To reaction flasks thermostatically maintained at $25.0 \pm 0.5$°C were added 100 mg of chitin or chitin-*g*-PAA and 50 ml of an aqueous solution of 1 mM calcium ions. The reaction mixtures were adjusted to different pH ranges, and the systems were maintained under magnetic stirring. After 1 h the mixtures were filtered and the amounts of adsorbed metal ion (mmol) were determined by titration with 0.01 M EDTA using murexyde as indicator. The amount of metal ion adsorbed per gram of polymer was calculated by the difference between the initial and final numbers of mmol in the solutions.

*Optimization of adsorption time*

The times required for the solid–liquid system to attain equilibrium conditions were determined by placing 100 mg of chitin or chitin-*g*-PAA and 50 ml of an aqueous solution of 1 mM calcium ions containing 0.02 M Tris–HCl buffer (prepared at the optimum pH for each material) in a reaction flask maintained at $25.0 \pm 0.5$°C. The reaction mixtures were stirred for different times and then the supernatants separated by filtration. The amounts of metal ion adsorbed were determined according to the above procedure.

*Adsorption isotherms*

The adsorption isotherms were determined in aqueous solution at $25.0 \pm 0.5$°C. Solutions of metal ions in the concentration range 0.25–3.30 mM were shaken for 60 min with 100 mg of chitin or chitin-*g*-PAA. The

supernatant was separated by filtration and the amounts of metal ion adsorbed were determined.

## RESULTS AND DISCUSSION

Poly(acrylic acid)-branched chitin was prepared by the grafting reaction with cerium(IV) as redox initiator according to the well established mechanism of graft copolymerization of vinyl monomers on polysaccharides such as cellulose, starch, wool and cotton[14-17,19,20]. Thus, the carboxylic group grafted to the chitin surface can offer an additional metal ion binding site.

The influence of pH on the $Ca^{2+}$ binding ability of chitin and chitin-*g*-PAA with 45% grafting efficiency was investigated. It was observed that the amount of bound $Ca^{2+}$ ions increases with increasing pH, showing a maximum value at pH 7 and pH 6 for chitin and grafted chitin, respectively.

Adsorption properties of such a copolymer may be different from those observed for homopolymers. These results showed that the metal ion binding capacity of chitin is markedly increased by the presence of acrylic acid grafts, which provide additional metal ion binding sites. Since the hydroxy groups on chitin are highly hydrated and are known not to be adsorption sites, the acetamido and amino groups on chitin and the carboxylic group on the graft copolymer are the sites responsible for calcium ion adsorption. There is practically no influence of pH on the adsorption of these ions by chitin, while for chitin-*g*-PAA, the adsorption is strongly dependent on pH. A major adsorption of $Ca^{2+}$ was found at around pH 6, which is ascribed to the deprotonated carboxylic group.

The effect of time on the metal binding capacity was studied for chitin and the graft copolymer, where the relatively rapid initial rate of adsorption is seen to decrease during the first minutes of interaction, and after 100 min a gradual approach to the limiting adsorption is observed. Both polymers achieved adsorption equilibrium after 10 min, as shown in *Figure 2*.

The adsorption capacities of chitin and the graft copolymer for calcium ions from aqueous solutions were investigated using the Langmuir isotherm. In *Figure 3*, it can be seen that the adsorption capacity increases as the concentration of calcium ions increases.
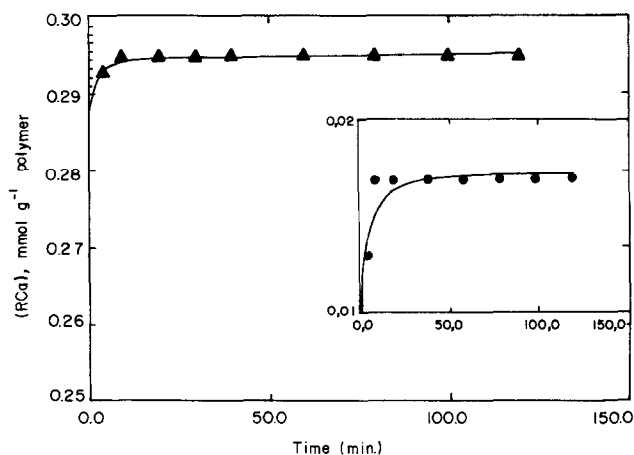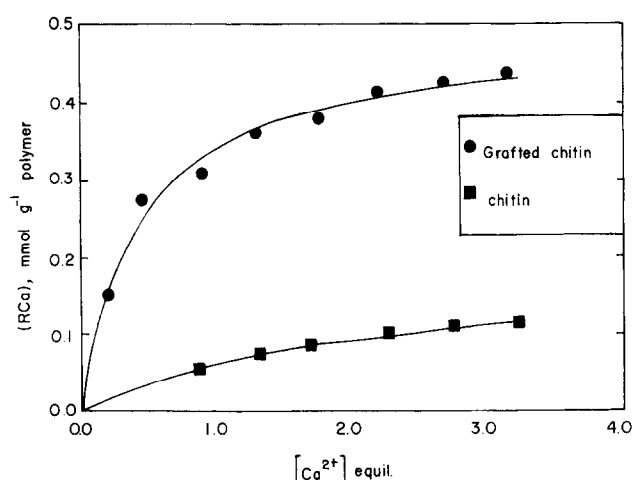


**Figure 2** Adsorption equilibria of $Ca^{2+}$ by poly(acrylic acid)-grafted chitin and chitin in aqueous medium at 25°C

**Figure 3** Adsorption isotherms of $Ca^{2+}$ by poly(acrylic acid)-grafted chitin and chitin in aqueous medium at 25°C

The adsorption of metal ions on polyfunctional macromolecules can be correlated with the equilibrium formation of a surface complex[21].

$$RH_n + Ca^{2+} \xrightarrow{K} RCa^{(2-n)} + nH^+ \qquad (2)$$
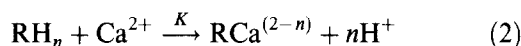
If the charges on the species are omitted, the equilibrium constant for a given pH is represented by:

$$K_L = \{RCa\}/(\{RH_n\}[Ca]) \qquad (3)$$

where $\{RCa\}$ and $\{RH_n\}$ are, respectively, the metal and protons adsorbed on the polymers as $mmol\,g^{-1}$. The experimental results (*Figure 3*) and equation (3) above can be adjusted to the Langmuir isotherm [equation (4)], which provides a good fit to the equilibrium adsorption data for $Ca^{2+}$ ions on the chitin and graft copolymer:

$$\{RCa\} = K_L\{R_t\}[Ca]/(1 + K_L[Ca]) \qquad (4)$$

Linearization of the above equation yields:

$$[Ca]/\{RCa\} = 1/K_L\{R_t\} + [Ca]/\{R_t\} \qquad (5)$$

By using equation (5), the maximum adsorption capacities $(R_t)$ of the graft copolymer and chitin were found to be $0.500 \pm 0.013$ and $0.195 \pm 0.005\,mmol\,Ca^{2+}\,g^{-1}$, respectively (*Figure 4*).
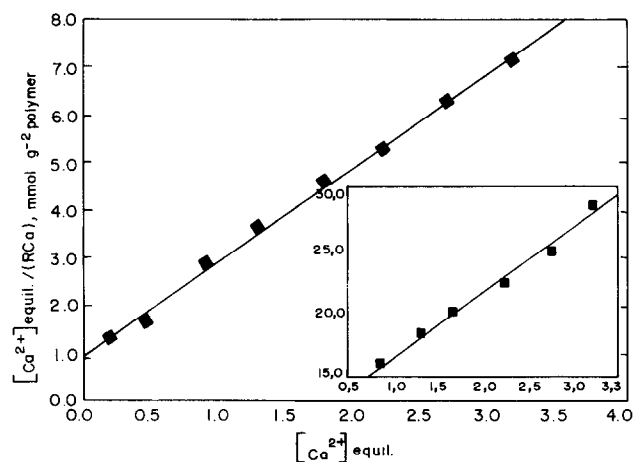
**Table 1** Adsorption capacities for chitin ($DA$: 15%), chitosan ($DA$: 97%), insolubilized chitin phosphate (Insol-P-chitin), insolubilized chitosan phosphate (Insol-P-chitosan) and chitin-*graft*-poly(acrylic acid) (chitin-g-PAA) (grafting efficiency: 45%)

| Polymer | Adsorption ($meq\,g^{-1}$) |
|---|---|
| Chitin[a] | 0.4 |
| Chitosan[b] | 1.4 |
| Insol-P-chitin[b] | 1.4 |
| Insol-P-chitosan[b] | 1.5 |
| Chitin-g-PAA[a] | 1.0 |

[a] In this work
[b] Nishi et al.[18]

Recently, Nishi and co-workers reported the adsorption of calcium ions on chitosan and insolubilized chitin phosphate[18]. The corresponding adsorption capacities in $meq\,g^{-1}\,Ca^{2+}$ are compared in *Table 1* with those for chitin and chitin-g-PAA. The results of adsorption experiments for $Ca^{2+}$ ions obtained by Nishi et al.[18] for phosphorylated chitin, which has 100% substitution, are comparable to the results obtained in this work for chitin-g-PAA which has a grafting efficiency of 45%. By considering that this grafting efficient can still be improved, it will be expected that the maximum adsorption capacity can also be increased.

The differential infra-red spectra for chitin-g-PAA and $Ca^{2+}$-loaded chitin-g-PAA copolymers were investigated to obtain information about the functional groups participating in binding of $Ca^{2+}$. *Figure 5* shows that absorption bands at around 1720 and $1413\,cm^{-1}$, assigned to the axial deformation of carboxylic groups, were shifted due to the binding of $Ca^{2+}$ ions (*Figure 6*). Other changes in the absorptions due to the amide group at around $3260\,cm^{-1}$ (axial deformation of NH), $1655\,cm^{-1}$ (amide I) and $1550\,cm^{-1}$ (amide II) were also observed. All of these results can be interpreted only by supposing that the high binding ability is achieved by the cooperative action of plural functional groups including the acetamido group, although in small proportion.

In biological systems in general, calcium ions are believed to bridge two negatively charged molecules, especially those containing carboxylates or phosphates,



**Figure 4** Linearization of Langmuir isotherms by poly(acrylic acid)-grafted chitin and chitin
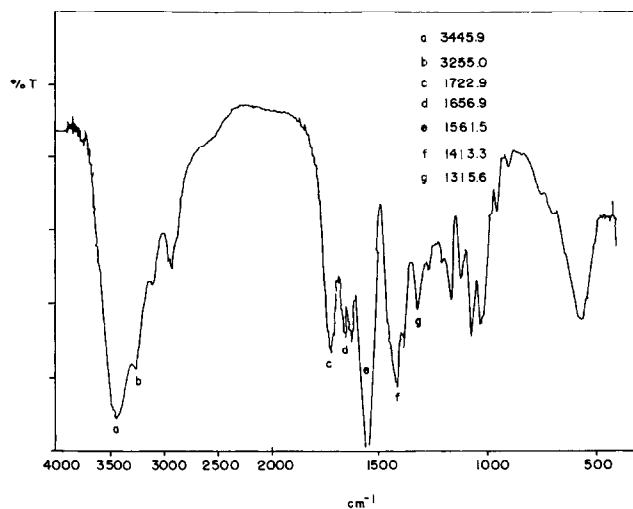


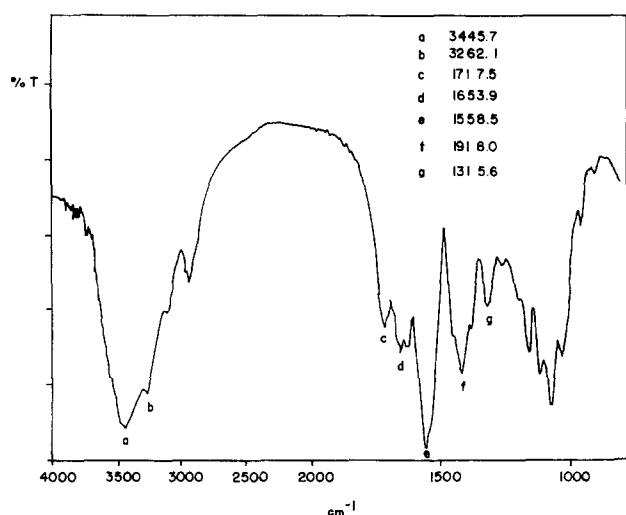**Figure 5** Differential infra-red spectra for chitin-g-PAA copolymer

Figure 6 Differential infra-red spectrum for $Ca^{2+}$-loaded chitin-*g*-PAA copolymer

thus functioning as an adhesive between molecules[32]. In this sense, the adhesion mechanism of calcium ions to enamel and dentine in the dental structure is verified by reaction with the carboxylic group of poly(acrylic acid), and thus chitin-*g*-PAA could be used as a new polymeric material for glass ionomer cement[30].

## CONCLUSIONS

Poly(acrylic acid)-branched chitin was prepared by the grafting reaction with cerium(IV) as redox initiator. Carboxylic groups grafted to the surface of chitin can readily be used to adsorb calcium ions from aqueous solution. The high metal binding ability is achieved by cooperative action of the plural functional groups including the carboxylic and acetamido groups. The adsorption of calcium on chitin can be correlated well with equilibrium formation of a surface complex. The $Ca^{2+}$ binding ability corresponding to the poly(acrylic acid)-chitin graft copolymer suggests its use in the preparation of a new glass ionomer cement.

## ACKNOWLEDGEMENTS

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