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Study of the effect of reaction variables on grafting of polyacrylamide onto chitosan

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Summary

The biopolymer chitosan was chemically modified by grafting polyacrylamide in a homogeneous aqueous phase by using potassium persulfate as redox initiator system and in the presence of N,N-methylene-bis-acrylamide as a crosslinking agent. The percentage of grafting was found to depend on the relative amount of monomer to chitosan, initiator and volume of the aqueous phase as well as the reaction temperature. By using optimized combinations of the reaction variables a grafting efficiency up to 88% and a percentage of grafting of nearly 220% were reached. Evidence of grafting was obtained from comparison of FTIR of the grafted and nongrafted chitosan as well as solubility characteristics of the products.

Introduction

Chitosan, (CHI), (poly-β-(1→4)-2-amino-2-deoxy-D-glucose) is obtained through partial deacetilation of chitin, (poly-β(1→4)-2-acetamido-2-deoxy-D-glucose, the second most abundant natural polysaccharide. To our knowledge few monomers have been grafted onto chitosan and the reactions had been mainly carried out in heterogeneous phase [1-6]. Recently CHI has attracted great attention since the range of its application has enormously expanded to medical, biotechnological, wastewater treatment and artificial membranes among other uses [5]. Thereafter, the modification of its structure appears to be interesting in order to expand the potential uses of this biopolymer. A useful approach in order to graft vinyl monomers onto polysaccharide macromolecules consist in creating radical sites by using appropriate initiators. A number of works regarding the grafting of chitosan have appeared recently [7-12].
In this paper we report the synthesis and the characterization of CHI grafted with polyacrylamide (PAAM). The grafting reactions were studied systematically in a homogeneous phase and by using potassium persulfate (KPS) as redox initiator.

Experimental

Materials

High molecular weight chitosan from Aldrich was used as received. An acetylation degree of 17.5% was estimated from ^{1}Hnmr spectroscopy as well as free amino group titration and its molecular weight was determined as 350000 by using the procedures described by Rinaudo et. al.[13,14]. Acrylamide (AAM) from Aldrich was used as received. Potassium persulfate (KPS) of analytical grade from BDH chemicals and N,N-methylene-bis-acrylamide from Fluka were used as received.

Instruments

FTIR spectra were taken by using a Bruker IFS-28 instrument. The samples were prepared as KBr pellets.

Graft copolymerization

Grafting reactions were carried out in 100ml polymerization flasks by first dissolving an exact amount of CHI in 2% acetic acid followed by the addition of a solution of monomer and N,N-methylene-bis-acrylamide, used as crosslinking agent. Finally a solution of the initiator (KPS) was added. The polymerization flask was closed and placed in a thermostated bath at desired temperature for 45 minutes. The reaction product was precipitated in acetone. The precipitate was filtered and then dried under reduced pressure to constant weight. The whole sample was extracted with water in a Soxhlet for 24 hours in order to remove the homopolymer formed during the grafting reaction and eventually non-reacted monomer. The remaining product after drying under reduced pressure was considered to be a graft copolymer.
The increase in weight of the original CHI after grafting and extraction and the weight of monomer was used to calculate the grafting efficiency (%E) using the relation [3,4] $\%E = W_2 - W_1 / W_3$, where W_2, W_1 and W_3 represents the weights of grafted chitosan, initial chitosan and monomer respectively.

Results and Discussion

The grafted CHI with PAAM was slightly soluble in dilute acetic acid contrary to pristine, nongrafted chitosan, which is very soluble in this medium. This solubility characteristic together with the increase in weight of the original chitosan and their FTIR spectra show that effectively the grafting has taken place. In order to obtain insoluble products potentially useful as hydrogel, a small amount of N,N-methylene-bis-acrylamide was added as crosslinking agent. The infrared spectra of CHI and grafted CHI with PAAM are shown in figure 1.
It can be seen that the amide-carbonyl absorption band from grafted chains appears at 1649 cm^{-1}. This band is located at 1670 cm^{-1} for polyacrylamide homopolymer. On the other hand, the most typical absorption bands of chitosan situated at 1558 cm^{-1} and 1661 cm^{-1} corresponding to amide I and amide II bands respectively, are not clearly visible since they are hidden by strong broad carbonyl absorption band of PAAM in

this spectral region. However, the CHI amide I absorption band can be observed as a shoulder at 1540 cm^{-1}. The shift of the carbonyl absorption band of PAAM and amide I band of chitosan to lower frequencies could be due to inter- and/or intramolecular interactions through hydrogen bonding. Naturally, the insolubility of PAAM grafted CHI samples, in spite of containing a large number of amide groups, is produced by the crosslinking. In a similar way as our previous studies [3,4,8], here also a marked effect of reaction variables on efficiency of grafting take place.

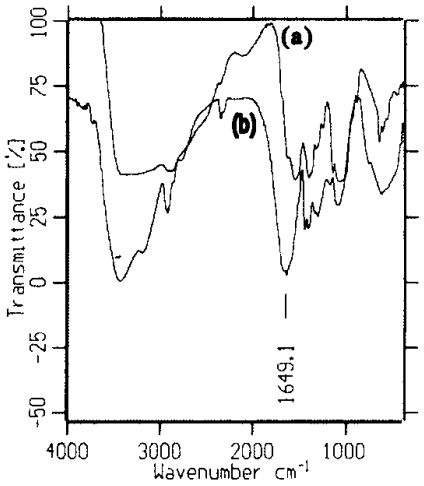

Figure 1. FTIR spectrum of chitosan (a) and chitosan grafted with polyacrylamide (b).

The influence of monomer, initiator and crosslinking agent concentrations, the total solvent volume used as well as reaction temperature on the grafting reaction was evaluated. The results are shown in figures 2 – 6. Following the results of preliminary experiments a restricted range of values for the variables was chosen for studying the grafting reactions. It was found that after 15 minutes the reaction was practically complete and then it can be considered that %E is unaffected by this reaction parameter. A reaction time of 45 minutes was considered as appropriate to be used in the following experiments. First the effect of reaction temperature on grafting was studied.

Reaction temperature

It can be seen from Fig. 2 that the major %E was found for 60 °C. For lower reaction temperatures the production of radicals necessary to form macroradical sites diminishes and by higher temperatures recombination reaction are important. Thereafter, this temperature should correspond to the best compromise between both tendencies. Sequentially, the set of conditions corresponding to the best values of grafting efficiency found for this variable was used for study the effect produced by the following reaction variable, and so on.
The series of results obtained can be considered as an optimization of the grafting reaction and also are useful in order to control its extent. In particular:

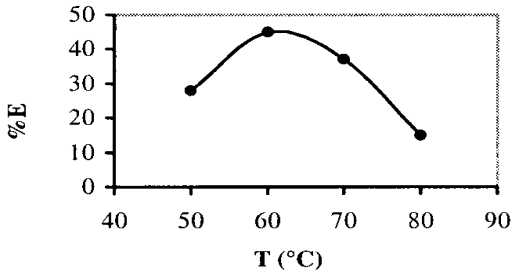

Figure 2. Effect of temperature on grafting efficiency (%E). Conditions: Chitosan, 0.8 g; AAM, 2.4 g; N,N-bis-AAM, 0.4%; [KPS], $2x10^{-2}$ M; Time, 45 min.; Solvent volume, 70 ml.

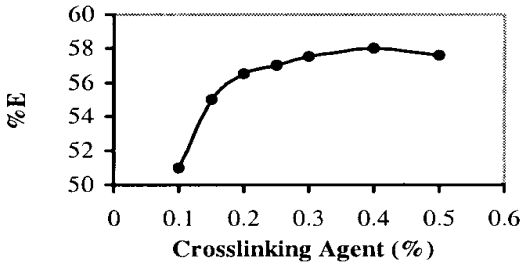

Figure 3. Effect of crosslinking agent on grafting efficiency. Conditions: Chitosan, 0.8 g; AAM, 2.4 g; [KPS], $2x10^{-2}$ M; Time, 30 min.; T =60 °C; Solvent volume, 70 ml

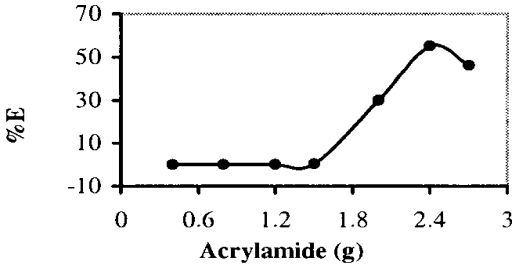

Figure 4. Influence of monomer on grafting efficiency. Conditions: Chitosan, 0.8 g; N,N-bis-AAM, 0.25%; [KPS], $2x10^{-2}$ M; Time, 30 min.; T=60 °C; Solvent volume, 70 ml.

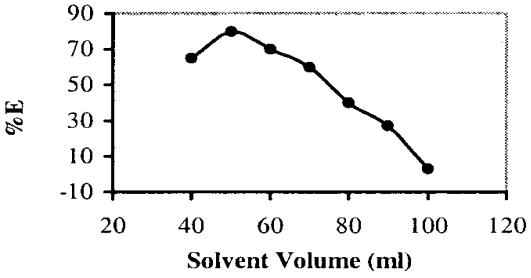

Figure 5. Effect of solvent volume on grafting efficiency. Conditions: Chitosan, 0.8 g; AAM, 2.4g; N,N-bis-AAM, 0.25%; [KPS], $2x10^{-2}$ M; Time, 30 min.; T=60 °C.

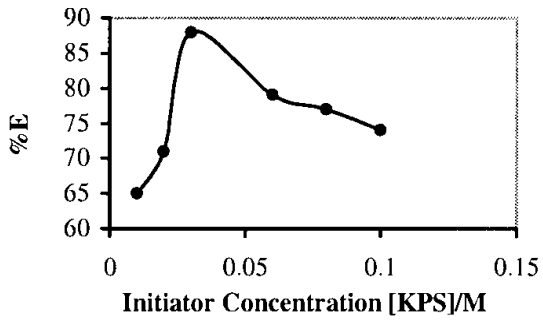

Figure 6. Influence of initiator concentration on grafting efficiency. Conditions: Chitosan, 0.8 g; AAM, 2.4g; N,N-bis-AAM, 0.25%; Time, 30 min.; T=60 ºC; Solvent volume, 50 ml.

Crosslinking agent

N,N-methylene-bisacrylamide was used as a crosslinking agent due to the solubility of the grafted products obtained in the absence of this agent. Fig.3 shows that %E remains practically constant for concentrations of N,N-methylene-bisacrylamide greater than 0.25% respect to the weight of acrylamide. Thereafter, this concentration was considered as the minimum necessary to insolubilize the grafted product.

Acrylamide

It can be observed in Fig.4 that for lower amounts than 1.5g of monomer the %E is nearly 0; what indicates that no grafted product was produced. By starting with more acrylamide, the %E grows sharply to a maximum by 2.4g and then tends to decrease. This could be attributed to the consumption of monomer to form homopolymer, before reaching the CHI chains, with a maximum of 1.5g, or to a short life of the macroradicals due to recombination reactions. Both possible events are related with diffusion problems. Related directly with diffusion is the combination of factors such as CHI/AM ratio and total aqueous volume. It is apparent from Fig.4 that by further increase of the relative amount of monomer the %E increases markedly due to larger availability of monomer for grafting. Once the maximum number of monomer units has been added, an excess of monomer only can change the optimum volume, affecting the diffusion controlled nature of the reaction, which is governed by the dilution extent.

Solvent volume

As was suggested, the combination of CHI/monomer ratio and the total liquid volume are very important for the results of the grafting reaction due to the diffusion-controlled nature of these reactions. The importance of the effect of this variable is visible from Fig. 5. A dramatic reduction in percentage of grafting was obtained until reaching practically zero grafting by increasing the total volume of the reaction to the double of the optimum amount. These results are in accord with the above discussion

Initiator concentration

By keeping constant all other reaction variables, the amount of KPS used was varied

Initiator concentration

By keeping constant all other reaction variables, the amount of KPS used was varied between 10^{-3} and 10^{-1} M. It can be observed from Figure 6 that %E increases sharply reaching to a maximum of ≈ 90% at a KPS concentration of 10^{-2} M; thereafter grafting decreases to a somewhat lower and nearly constant value for the range studied. The lowering of %E from its optimum value is due to the possible combination of the chitosan macroradicals with the existing excess of primary free radicals present in the reaction medium and also the termination of propagating polyacrylamide grafted chains.

Conclusions

The grafting of acrylamide onto chitosan, in the absence of N,N-methylene-bisacrylamide as crosslinking agent, leads to slightly soluble products. When N,N-methylene-bisacrylamide was used as crosslinker insoluble grafted chitosan was obtained which could be easily separated from the reaction medium and purified. Moreover, the insoluble grafted chitosan showed characteristics of a hydrogel material. The swelling behavior of the hydrogel in different media is currently under study.

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