ABSTRACT

The graft copolymerization of sodium acrylate onto chitosan in alkali medium was investigated, using redox system, potassium diperiodacuprate(III) (DPC) chitosan. The graft copolymer was characterized by Fourier transform infrared spectra analysis, X-ray diffraction analysis, differential scanning calorimetric, thermogravimetric analysis, and scanning electron microscopy techniques. A tentative mechanism is proposed to explain the generation of radicals and the initiation. The effects of reaction variables, such as the initiator concentration, the ratio of monomer to chitosan, and pH, as well as, reaction temperature and time were investigated, and the grafting conditions were optimized. Graft copolymer with high grafting efficiency was obtained, which indicated that DPC chitosan redox system is an efficient initiator for this graft copolymerization. The graft copolymer was used as the compatibilizer in blends of poly(methyl methacrylate) (PMMA) and chitosan. The scanning electron microscope micrographs indicated that the graft copolymer improved the compatibility of the blend. At the same time, the blend is expected to improve the biodegradability of the PMMA.

INTRODUCTION

Chitosan is a polyaminosaccharide, derived from the partial N-deacetylation of chitin, poly-β-(1,4)-N-acetyl-D-glucosamine, the most abundant natural polymer next to cellulose. Compared with other polymers, chitosan has additional important advantages, including biocompatibility, biodegradability, and nontoxicity [1-3]. Based on the unique molecular architectures with amino groups, sophisticated molecular designs became possible through controlled chemical modification of chitosan. Graft copolymerization, especially grafting of various vinyl monomers onto chitosan is one of the most effective and promising method, which can incorporate desirable functions,
affording novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. The resulting graft copolymers have found new potential applications in some fields including pharmaceuticals, biomaterials, water treatment, toiletries, agriculture as well as food processing. So far, graft copolymerizations of chitosan with vinyl monomers have been explored by various methods, performed typically with AIBN [4], \( \gamma \)-ray [5], and traditional redox systems including Ce(IV) [6-9], \( K_2 S_2 O_8 \) [10-13], \( Fe^{2+}-H_2 O_2 \) [14-16], etc. Among them, Ce(IV) is the most efficient initiator. However, the polymerization must be in the acid medium using ceric ion initiator and homopolymer percentage was also high, which lead to the generally low grafting efficiency. Besides, chitosan will degrade easily in acid medium. Compared with the above methods, graft copolymerization initiated by diperiodatocuprate (III), can take place in alkali medium, thus, this overcame the disadvantage of degradation of chitosan in acid medium. Furthermore, it has higher grafting efficiency than the other methods mentioned above. Based on our previous research on supernormal valence transition-metals [17-24], DPC was employed as oxidant and chitosan as reductant to make up the redox system to initiate the graft copolymerization of AA-Na onto chitosan in alkali aqueous medium.

The scanning electron microscope (SEM) micrographs indicated that the graft copolymer (chitosan-g-PAA-Na) could act as compatibilizer to improve the compatibility of the immiscible binary blend of PMMA and chitosan. The blend may be applied to biodegradation of PMMA. A tentative mechanism is proposed to explain the formation of radicals and the initiation.

**EXPERIMENTAL**

**Materials**

Chitosan, obtained from the Yuhuan County Chemical Plant, China. Acrylic acid (from the Fuchen Chemical Plant in Tian Jin, China) was obtained by distilling under reduced pressure and then dried over anhydrous sodium sulphate, at last the pure acrylic acid was stored at 4°C. Sodium acrylate, used in this work, was prepared in our laboratory. DPC was synthesized and measured according to the reported procedure [25]. The concentration of DPC was obtained by its absorption at \( \lambda = 405 \) nm using a Shimadzu UV-265 spectrophotometer (Japan). The other solvents were all of analytical reagent and used as received.

**Graft Copolymerization**

Graft copolymerization was carried out in a 50 mL four-necked flask equipped with thermometer, condenser, stirrer, and gas inlet, immersed into thermostat water bath. In a typical experiment, a required amount of chitosan and distilled water were added and the flask was degassed sufficiently by purging with nitrogen and equilibrated at required temperature with constant stirring. Then the required amount of monomer was added, followed by DPC aqueous solution and the total volume of the reaction mixture was made up to 20 mL with distilled water. After a required reaction time, the reactant was cooled and neutralized by aqueous acetate acid solution and then precipitated with acetone. The precipitate was filtered through a weighed sintered glass funnel, washed to neutral, and dried to a constant weight under vacuum at 60°C.

The homopolymer of sodium acrylate (PAA-Na) was removed from the crude graft copolymer by exhaustive Soxhlet extraction with alcohol for 48 h. The final copolymer was then dried to a constant weight under vacuum at 60°C. The above process was repeated for the different initiator concentration, monomer-to-chitosan ratio, pH as well as temperature and time. The grafting parameters, such as percentage of grafting (PG), grafting efficiency (GE) as well as the percentage conversion (PC) were defined and calculated as follows:

\[
PG(\%) = \left( \frac{\text{weight of grafted PMMA}}{\text{weight of chitosan}} \right) \times 100
\]

\[
GE(\%) = \left( \frac{\text{weight of grafted PMMA}}{\text{total weight of PMMA}} \right) \times 100
\]

\[
PC(\%) = \left( \frac{\text{weight of grafted polymer + homopolymer}}{\text{weight of monomer charged}} \right) \times 100
\]

**Characterization**

**FTIR Spectroscopy**

The FTIR spectra of the pure chitosan and chitosan-g-PAA-Na were recorded on a FTS 40 spectrometer (BIO RAD Co., USA) using potassium bromide pellets technique.
X-ray Diffraction
X-Ray diffractions of ungrafted and grafted chitosan were measured using a Y-4Q X-ray diffraction instrument (Dandong Ray Apparatus Corporation, China). The X-ray diagrams were made with Ni-filtered CuKa radiation at 30 kV and 20 mA.

Differential Scanning Calorimetry
The DSC Thermograms of chitosan and chitosan-g-AA-Na were obtained on Perkin Elmer differential scanning calorimetry (Perkin Elmer, USA) at a heating rate of 10°C/min in a nitrogen atmosphere.

Thermal Analysis
TGA Curves of chitosan and chitosan-g-AA-Na were carried out on a Perkin Elmer apparatus (Pyris 6 TGA) at a heating rate of 20°C/min in a nitrogen atmosphere.

SEM
Scanning electron microscope, AMKAY-1000B was used to observe the morphologies of chitosan/PMMA blend and those of chitosan/chitosan-g-PAA-Na/PMMA blends.

RESULTS AND DISCUSSION

Effect of Monomer-to-chitosan Ratio
The effect of monomer-to-chitosan ratio on graft copolymerization of AA-Na onto chitosan is depicted in Figure 1. There is an increase in percent conversion and percent grafting with an increase in ratio of AA-Na/chitosan at first, then a slightly decrease in grafting efficiency with further increase in AA-Na-to-chitosan ratio. This may be attributed to the chance of chain transfer reaction and homopolymerization of monomer increase with the increase of concentration of monomer, therefore, GE declines accor. The optimal monomer-to-chitosan ratio was 5.75.

Effect of Temperature
The grafting reactions were carried out at different temperatures between 20 and 40°C, keeping the other variables constant. As shown in Figure 2, it is found that PG and PC increase initially and then decrease to some extent with further increase in temperature. This is attributed to the fact that increasing the temperature favours the activation of macroradicals as well as accelerates the diffusion and mobility of the monomers from the aqueous phase to the backbone. However, a further increase in temperature decreases PG and GE parameters, which can be ascribed both to the acceleration of termination reaction and to the increased chance of chain transfer reaction, accounting for the increase in the amount of homopolymer. This observation indicates that the optimal reaction temperature is 30°C.

Figure 1. The effect of the monomer-to-chitosan ratio at: [DPC] = 1.67x10⁻³ mol/L, T = 60 min, pH = 12.7, and t = 30°C.

Figure 2. Effect of temperature at: [DPC]=1.67x10⁻³ mol/L, [AA-Na] = 1 mol/L, T = 60 min, and pH = 12.7.
Effect of Concentration of DPC
When the other factors are kept constant, the effect of DPC concentration on graft parameters is shown in Figure 3. With increasing DPC concentration the values of PC, GE, and PG increase. However, beyond the optimum DPC concentration of $1.67 \times 10^{-3}$ mol/L, they are found to decrease. This can be explained that a further increase in DPC concentration accelerates the reaction of DPC and radicals, which terminates the chain propagation reaction, hence decreasing grafting parameters.

Effect of pH
Figure 4 shows the effect of pH on graft parameters. GE keeps unchanged in the pH range studied. However, PC and PG increase initially and then decrease with increasing pH. This is due to DPC existing mainly in the form of $-(H_3IO_6^2)^-$ and $-(H_3IO_6^-)^-$.

In alkali aqueous solution, the ratio of the two forms changes with pH, which directly influences the amount of radicals produced in the reaction system. It is found that the optimum pH is 12.7.

Effect of Reaction Time
Figure 5 illustrates the influence of reaction time on grafting parameters. It can be seen that GE keeps unchanged during the course of the reaction, whereas PG and PC increase steadily with the reaction time prolonged up to 60 min, and then maintain a plateau, which is consistent with the general rule of conventional radical polymerization. Thus, the optimized reaction time is 60 min.

IR Spectroscopy
The grafting confirmation was obtained from the FTIR spectra of (a) pure chitosan and (b) chitosan-g-PAA-Na. As shown in Figure 6, in the spectrum of chitosan (a), it can be observed the characteristic absorption bands around 3420, 1658, and 1560 cm$^{-1}$. Owing to the grafting of the sodium acrylate onto the chitosan backbone...
(Figure 6b), there is a broad band in the range 1571-1409 cm⁻¹, which is the combined absorption of -COONa. These data confirm the formation of chitosan-g-PAA-Na effectively.

**X ray Diffraction**
The X ray diffraction spectra of pure chitosan (a) and chitosan-g-PAA-Na (b) were analyzed, as shown in Figure 7. The spectrum of chitosan is more convex than that of copolymer. The crystallinity of ungrafted and grafted chitosan was calculated as 54.6% and 38.4%, respectively. This indicated that the incorporation of PAA-Na had impaired the crystallinity of chitosan, which may provide some useful information.

**Thermal Analysis**
The TGA of chitosan and the grafted copolymer is shown in Figure 8. The TGA of chitosan shows a weight loss at three stages. The first stage ranges between 41 and 230°C and shows about 11% loss in weight. This may be attributed to the loss of adsorbed and bound water. The second stage of weight loss starts at 230°C and continues up to 339°C. There is about 42% of weight loss due to the degradation of the polysaccharide. The last stage, 339-671°C, shows a weight loss of 41.26%, as a result of carbonization.

The TGA of chitosan-g-AA-Na undergoes a weight loss in three stages. During the first stage which starts from 42°C and continues up to 217°C, there is about 10% weight loss, corresponding to the loss of adsorbed and bound water. In the second stage which ranges between 217 and 328°C, there is about 22% weight loss. This may be due to the degradation of chitosan in the graft copolymer. In the last stage, weight loss continues up to 688°C with about 31% of the weight random chain scission. At 690°C the weight loss of chitosan-g-AA-Na is 63%, while the weight loss of chitosan is 96%. The TGA data clearly indicate that the stability of chitosan has been improved by grafting with sodium acrylate and it is truly grafted onto chitosan.

**Differential Scanning Calorimetry**
Figure 9 shows the DSC thermograms of chitosan (a) and chitosan-g-PAA-Na (b). The first exothermic peak in (a) at 91.8°C is the glass transition temperature ($T_g$) of chitosan. However, the glass transition temperature of
chitosan-g-PAA-Na has appeared at 90.0°C (Figure 9b). This may be explained that sodium acrylate grafting onto chitosan lowered the $T_g$ of chitosan. The second exothermic transition of chitosan is at 301°C, which may correspond to the decomposition of the polysaccharide. Compared with 283°C, which is the second exothermic transition temperature of chitosan-g-PAA-Na, it indicates that the degradability of chitosan has been improved through grafted sodium acrylate.

Scanning Electron Microscopy

Figure 10 shows the SEM micrographs of (a) chitosan/PMMA blend and (b) chitosan/chitosan-g-PAA-Na/poly(methyl methacrylate) blend. Figure 10 a provides direct evidence that phase separation occurred in chitosan/PMMA blend. This sample has a distinct two-phase morphology, i.e., a continuous PMMA phase with a dispersed chitosan phase indicates poor interfacial adhesion between terpolyamide and chitosan phases. However, with the addition of compatibilizer, chitosan-g-PAA-Na, the morphology of fractures surface changes dramatically. The photograph in Figure 10 b shows that the cast film of chitosan/chitosan-g-PAA-Na/PMMA blend is homogeneous and continuous.

It is well known that chitosan has the good ability of degradation. Therefore, PMMA interfered with chitosan can improve its biodegradability. Chitosan-g-PAA-Na plays an important role in enhancing the compatibility of chitosan and PMMA.

The Initiation Mechanism of Grafting Reaction

IR Spectra, X ray diffraction, DSC, and TGA show that PAA-Na has been grafted onto chitosan. Thus, a tentative initiation mechanism based on a single-electron-transfer process of DPC is shown in Scheme I.

CONCLUSION

Graft copolymerization was employed as an important technique to obtain a chemically modified natural polysaccharide, chitosan. Sodium acrylate was successfully grafted onto the chitosan backbone in an aqueous alkaline medium initiated by diperiodatocuprate (III) (DPC).

Compared with other methods, DPC can initiate...
Grafting copolymerization of sodium acrylate and chitosan in alkali medium, which decreases the degradation of chitosan during reaction. There are higher graft percentage and lower homopolymer formation. The grafting process was confirmed by IR analysis and X-ray diffraction.

Based on the TGA and DSC results, it was found that the grafted chitosan was more thermally stable than ungrafted one due to the incorporation of PAA-Na, which may broaden the range of chitosan application. In addition, the SEM micrographs indicate that the graft copolymer is efficient to improve the compatibility of binary blend of chitosan and PMMA, which will be respected to be applied in the degradation of PMMA.

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SYMBOLS

DPC: Potassium diperiodacurate(III)
AIBN: 2,2'-Azobis-isobutryronitrile
DPN: Potassium diperiodatonickelate(IV)
DTC: Potassium ditelluratocuprate(III)
MA: Methylacrylate
MMA: Methyl methacrylate
AA-Na: Sodium acrylate
PAA-Na: Poly(sodium acrylate)

PG: Percentage of grafting
GE: Grafting efficiency
PC: Percentage conversion

REFERENCES

12. Yazdani Pedram M., Retuert J., Homogeneous graft-


