

Graft Copolymerization of Methyl Acrylate onto Chitosan Initiated by Potassium Diperiodatocuprate (III)

Yinghai Liu, Zhenghao Liu, Yanzhe Zhang, Kuilin Deng

College of Chemistry & Environmental Science, Hebei University, Baoding 071002, China

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ABSTRACT: A novel redox system, potassium diperiodatocuprate [Cu (III)-chitosan], was employed to initiate the graft copolymerization of methyl acrylate (MA) onto chitosan in alkali aqueous solution. The effects of reaction variables such as monomer concentration, initiator concentration, pH and temperature were investigated. By means of a series of copolymerization reactions, the grafting conditions were optimized. Cu (III)-chitosan system was found to be an efficient redox initiator for this graft copolymerization. The structures and the thermal stability of chitosan and chitosan-g-poly(methyl acrylate) (PMA) were characterized by infrared spectroscopy (IR) and thermogravimetric analy-

sis (TGA). In this article, a mechanism is proposed to explain the formation of radicals and the initiation. Finally, the graft copolymer was used as the compatibilizer in blends of poly(vinyl chloride) (PVC) and chitosan. The scanning electron microscope (SEM) photographs and differential scanning calorimetry (DSC) thermograms indicate that the graft copolymer improved the compatibility of the blend. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2283–2289, 2003

Key words: potassium diperiodatocuprate [Cu(III)]; chitosan; chitosan-g-PMA graft copolymers; chitosan/PVC blends

INTRODUCTION

Basic theoretical research and its application to super-normal valence transition metals attracts more and more attention in chemical fields nowadays. It is no doubt that its feasibility in polymerization inspires thought and research. Some achievements have been made, to date, on vinyl monomer polymerization and graft copolymerization initiated by supernormal valence transition metals, such as Mn (VII), Cr (VI), V (V), Ag (III), Cu (III), etc.^{1–4} Experiments have demonstrated Cu (III) is an efficient and cheap initiator in grafting methyl acrylate (MA) or methyl methacrylate (MMA) onto macromolecular structures, such as poly(acrylamide), nylon1010, and starch.^{5–7}

Chitosan [B-(1,4)-2-amino-2-deoxy-D-glucose] is a natural polymer. It is prepared by the N-deacetylation of chitin, the second most abundant polysaccharide occurring in nature after cellulose. Due to its special biological, chemical and physical properties, chitosan and its derivatives have been applied in the fields of industry and agriculture. Chemical modification of chitosan to impart advantageous properties has attracted the attention of many researchers in recent years. Graft copolymerization of vinyl monomers on chitosan using redox initiators has been explored as a promising alternative method of developing natural/

synthetic polymer hybrid materials.^{8–14} In spite of the many graft copolymers of chitosan that have been synthesized, the grafting of methyl acrylate, an industrially important monomer, onto chitosan has only rarely been reported,^{15,16} and the use of Cu (III) as a cheaper initiator in this graft copolymerization has never been reported.

In this article, Cu (III) was employed as an oxidant and chitosan as a reductant in the redox system used to initiate the graft copolymerization of MA onto a chitosan backbone in an alkaline aqueous medium. The combined effects of the principal reaction variables on the copolymerization were investigated and the structures and properties of the grafted products were characterized by infrared spectroscopy (IR) and thermogravimetric analysis (TGA). The results showed that, compared to other initiators, Cu (III) was both an efficient and a cheap initiation system. The graft copolymer (chitosan-g-PMA) was used as the compatibilizer in blends of poly(vinyl chloride) (PVC) and chitosan. The scanning electron microscope (SEM) photographs indicate the graft copolymer improved the compatibility of the blend.

EXPERIMENTAL

Materials

A sample of pure chitosan was obtained as a gift from Yuhuan County Chemical Plant (Zhejiang Province). Its degree of deacetylation was at least 82%, and its molecular weight was in the range from 2.0×10^5 to

Correspondence to: Y. Liu.

3.0×10^5 . In accordance with a previous publication,¹⁷ the chitosan was ground into powder (>60 mesh) from flats and dried under vacuum at room temperature. MA from Beijing Yili Company was washed successively with aqueous sodium hydroxide solution and distilled water in order to get rid of inhibitor. Then it was dried over anhydrous sodium sulfate and finally distilled under vacuum. The middle fraction was used. Cu (III) was synthesized and measured according to the reported procedure.¹⁸ The other solvents (analytical grade) were used without any further purification.

Graft copolymerization and treatment of copolymer

Graft copolymerization was carried out in a 50 mL four-necked flask equipped with thermometer, condenser, stirrer and gas inlet. In a typical reaction, 0.3 g chitosan and distilled water were added with constant stirring under nitrogen. The required amount of monomer was added, followed by Cu (III) aqueous solution and the total volume was increased to 20 mL. The graft copolymerization was performed under conditions of different pH, monomer concentration, initiator concentration and temperature. After completion of reaction, the reactant was cooled and neutralized with aqueous hydrochloric acid solution. Then it was filtered through a weighted sintered glass funnel, washed to neutral and dried to a constant weight under vacuum at 60°C. The homopolymer of methyl acrylate (PMA) was removed from the crude graft copolymer by exhaustive Soxhlet extraction with acetone for 48 h. The final copolymer was then dried to a constant weight under vacuum.

Measurements

Chitosan-g-PMA was characterized, after exhaustive Soxhlet extraction to remove PMA, by IR analysis using an FTS-40 spectrophotometer (BIO-RAD Co.) in potassium bromide pellets. The TGA of chitosan (4.32 mg) and its copolymers (4.07 mg) was carried out on a Shimadzu apparatus DGC-40 DTA-TG in a nitrogen-rich atmosphere at a heating rate of 10°C/min. A scanning electron microscope, AMKAY-1000B, was used to observe the morphologies of chitosan/PVC blends and those of chitosan/chitosan-g-PMA/PVC blends.

RESULTS AND DISCUSSION

The grafting parameters, such as grafting percentage ($P\%$), efficiency percentage ($E\%$) and total conversion percentage ($C\%$) were defined and calculated as follows: $C\% = (\text{total weight of PMA} \div \text{weight of MA charged}) \times 100\%$ $P\% = (\text{weight of PMA grafted}$

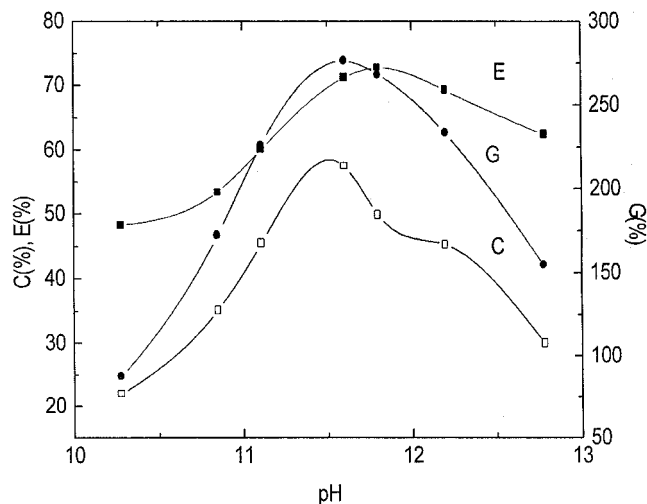


Figure 1 The effect of pH on grafting parameters. Reaction conditions: Cu (III): 1.92×10^{-3} mol/L, MA: 2.0 mL, T: 35°C, t: 1 h.

$$\div \text{weight of chitosan}) \times 100\% \quad E\% = (\text{weight of PMA grafted} \div \text{total weight of PMA}) \times 100\%$$

Effect of pH

The grafting parameters were evaluated under conditions of different pH, as shown in Figure 1. Aqueous hydrochloric acid solution or aqueous potassium hydroxide solution was added to the reaction system before Cu (III) was injected to change the pH, so the graft copolymerization was carried out at different pH values. The variation of pH causes changes in $C\%$, $P\%$ and $E\%$ because of the different complex forms of Cu (III) that occur under different pH conditions. In alkaline aqueous solution, the ratio of the concentration of $\text{H}_3\text{IO}_6^{2-}$ to $\text{H}_2\text{IO}_6^{3-}$ changes with pH,¹⁹⁻²⁰ leading to the different activity of the Cu (III) complexes, which directly influences the amount of radicals in the reaction system. The optimum pH for maximum grafting of MA onto chitosan is 11.6.

Effect of Cu (III) concentration

The influence of the concentration of Cu (III) on the grafting parameters is shown in Figure 2. With increasing Cu (III), $C\%$ and $G\%$ increase sharply when the concentration of Cu (III) is lower, whereas, $E\%$ changes little. This behavior indicates that Cu (III) is primarily used to generate free radicals on the chitosan backbone for the initiation of graft copolymerization. As more macroradicals are generated, $C\%$ and $P\%$ increase. However, at higher concentrations of the initiator, the active sites for grafting may be increased on the chitosan backbone, but Cu (III) is able to participate in the termination reactions, which causes a decrease of $C\%$ and $G\%$. At the same time, the many

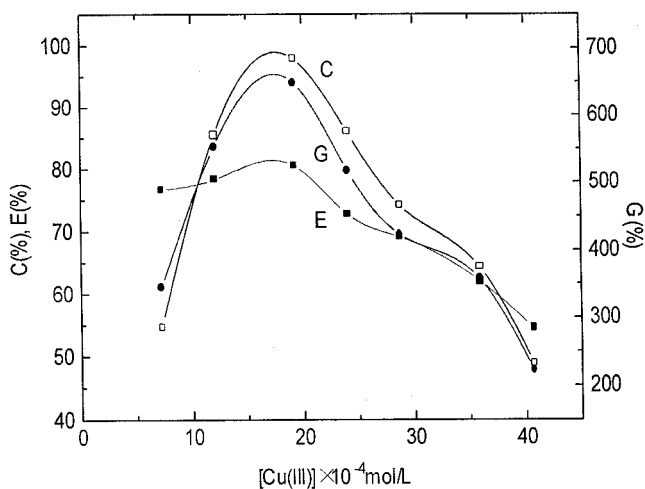


Figure 2 The effect of [Cu (III)] on grafting parameters. Reaction conditions: MA: 2.6 mL, T: 35°C, t: 1 h.

macroradicals could accelerate the chain transfer reaction, leading to the decrease of $E\%$.

Effect of ratio of MA to chitosan

By studying the influence of the ratio of MA to chitosan on the graft yields, as shown in Figure 3 it is found that $P\%$ and $C\%$ reach maximum values when the ratio of MA to chitosan is between eight and ten, and then the values fall gradually as the ratio increases further. Because of the limited solubility of MA in the reaction medium, when the ratio of MA to chitosan is low, the probability of interaction between chitosan and MA is small, so $C\%$ and $G\%$ are also low. With an increasing ratio of MA to chitosan, chitosan-g-PMA could bring into play self-emulsification so as to absorb more monomers on the chitosan surface, which considerably enhances the rate of the graft reaction;

therefore, $C\%$ and $G\%$ increase sharply. If the ratio of MA to chitosan exceeds 10, the adsorption of monomers onto chitosan is so great that it interferes significantly with the approach of both Cu (III) and chitosan, which is necessary for initiation; therefore, $C\%$ and $G\%$ decline. When the ratio of MA to chitosan is higher, the chain transfer reactions will be accelerated, which makes $E\%$ decrease gradually.

EFFECT OF TEMPERATURE

Figure 4 shows grafting parameters at different temperatures when other reaction conditions are held constant. In accordance with the general rule of radical polymerization, $E\%$ changes gradually and then levels off slightly. This may be due to the chance of chain transfer reaction speeding up with the increase of temperature that causes an increase in the homopolymerization of MA. Both $C\%$ and $P\%$ increase at first and then decrease rapidly. Lower temperatures benefit the initiating reaction and the chain propagation. When the temperature exceeds 40°C, the termination reaction of Cu (III) and radicals as well as the chain transfer reaction speeds up, so the grafting parameters decrease. The optimum temperature for maximum grafting is 35°C.

IR spectroscopy

The grafting was confirmed by comparing the IR spectra of chitosan with that of the grafted product. The results obtained are shown in Figure 5. The main difference observed is the appearance of a carbonyl absorption band at 1730 cm^{-1} corresponding to the carbonyl group of the PMA chains. Absorption bands at 840 cm^{-1} and 752 cm^{-1} are observed due to the rocking absorption of the methylene groups in PMA.

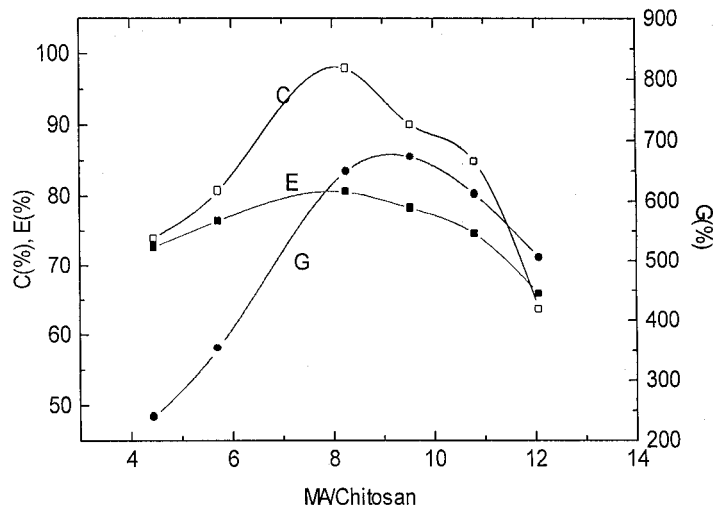


Figure 3 The effect of MA/chitosan on grafting parameters. Reaction conditions: Cu (III): 1.92×10^{-3} mol/L, T: 35°C, t: 1 h.

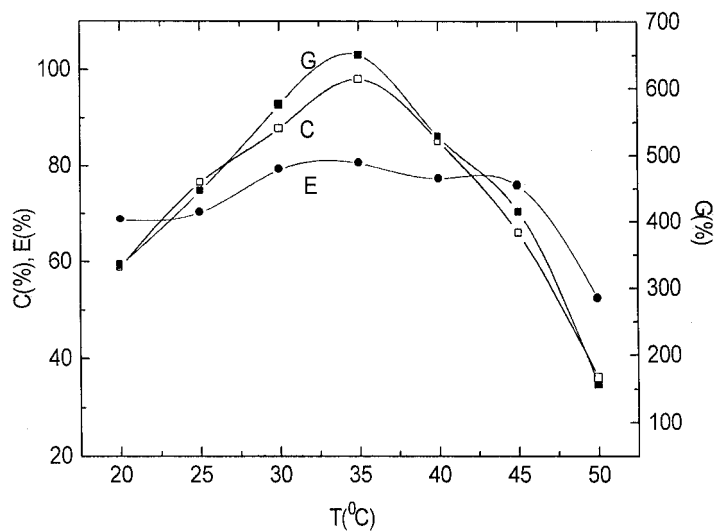


Figure 4 The effect of temperature on grafting parameters. Reaction conditions: Cu (III): 1.92×10^{-3} mol/L, MA: 2.6 mL, t: 1 h.

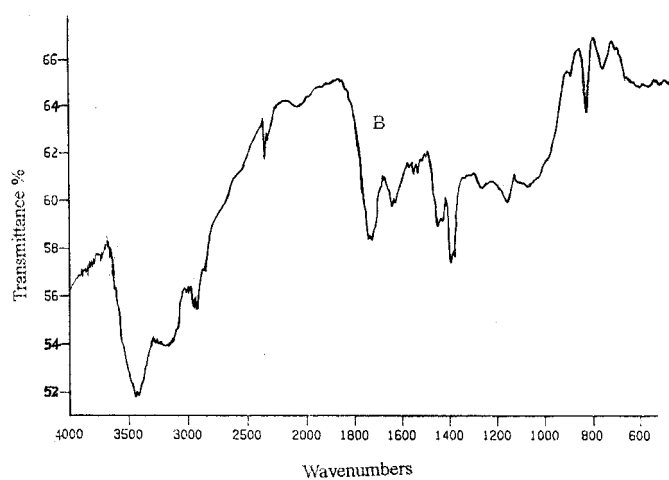
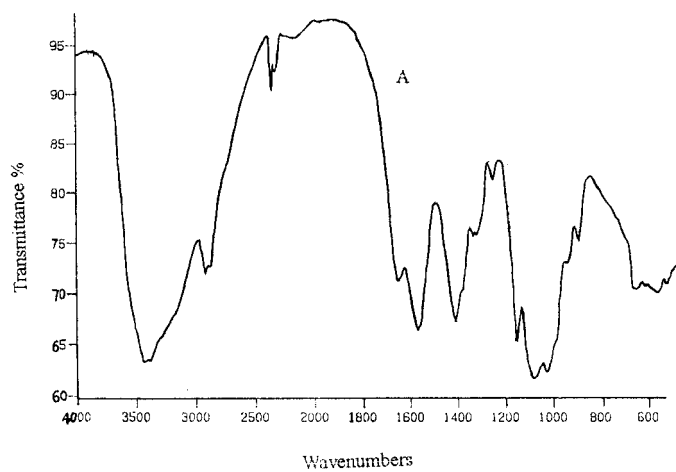


Figure 5 IR spectra of (A) chitosan and (B) chitosan-g-PMA.

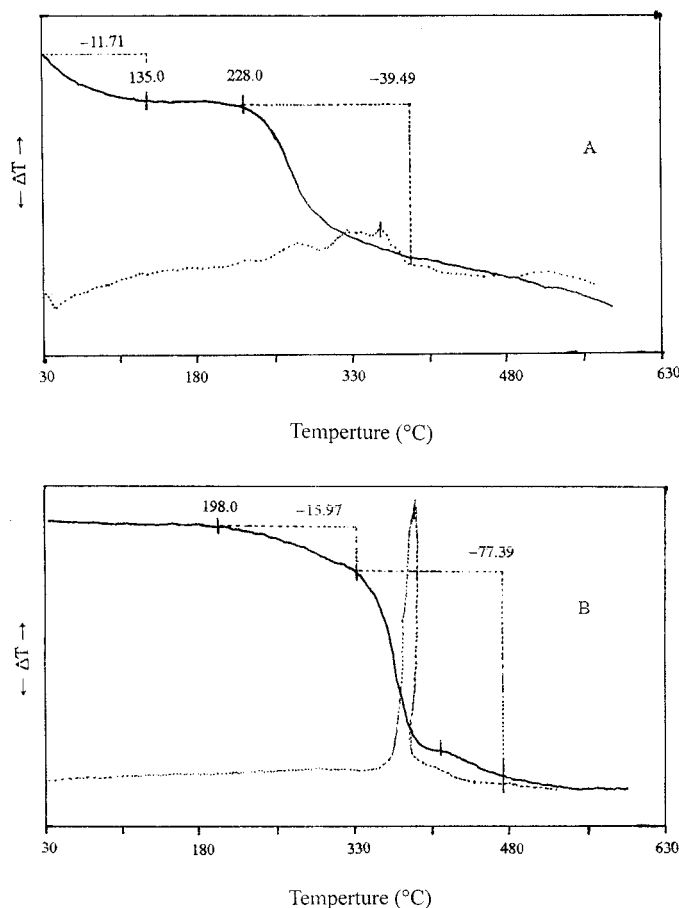


Figure 6 TGA curves of (A) chitosan and (B) chitosan-g-PMA.

All of these bands are absent in the IR spectra of pure chitosan. Moreover, the N—H bending vibration bands of the copolymer at 1660 cm^{-1} (I) and 1560 cm^{-1} (II) compared with those of pure chitosan are different. Owing to the results above, it could be proposed that Cu (III) may react with amino groups in chitosan to generate macroradicals first and then to initiate MA grafting polymerization. Obviously, as has been demonstrated, the final product is a graft copolymer of chitosan and MA.

Thermal analysis

Thermogravimetric analysis (TGA) of pure chitosan and the grafted copolymer is shown in Figure 6. The TGA of chitosan shows a weight loss in two stages. The first stage occurs between 30°C and 135°C and shows about 11.71% loss in weight. This may correspond to the loss of adsorbed and bound water. The second stage of weight loss starts at 228°C and continues up to 360°C , during which there is 39.49% weight loss due to the degradation of chitosan. The TGA of the grafted product is different from that of pure chitosan. It is observed that the former only has one stage of distinct weight loss, between 360°C and

414°C , with about 77.39% weight loss, attributed to the degradation of grafted polymer. From 198°C to 360°C , there is 15.97% weight loss, which may be caused by the degradation of part of the ungrafted chitosan. It is evident that grafting MA onto chitosan could augment the thermal stability of pure chitosan. Due to the presence of PMA, the copolymer exhibits enhanced hydrophobic character compared to pure chitosan.

Test of blending

Three grams of PVC, 0.3 g of chitosan and 0.1 g of chitosan-g-PMA ($G\% = 196.5\%$) were stirred completely in dichloromethane for 30 min. A film of chitosan/chitosan-g-PMA/PVC was obtained by casting the solution onto a glass surface. The solvent was allowed to evaporate under atmospheric pressure at 30°C for 2 days and in vacuum at 50°C for 24 h. A film of chitosan/PVC blends was prepared according to the same way. The surficial and sectional SEM micrographs of chitosan/PVC blends and those of chitosan/chitosan-g-PMA/PVC blends are shown in Figure 7. From A, B, C and D in Figure 7, it can be seen that the blend of chitosan/chitosan-g-PMA/PVC, compared with the blend of chitosan/PVC, has a different mor-

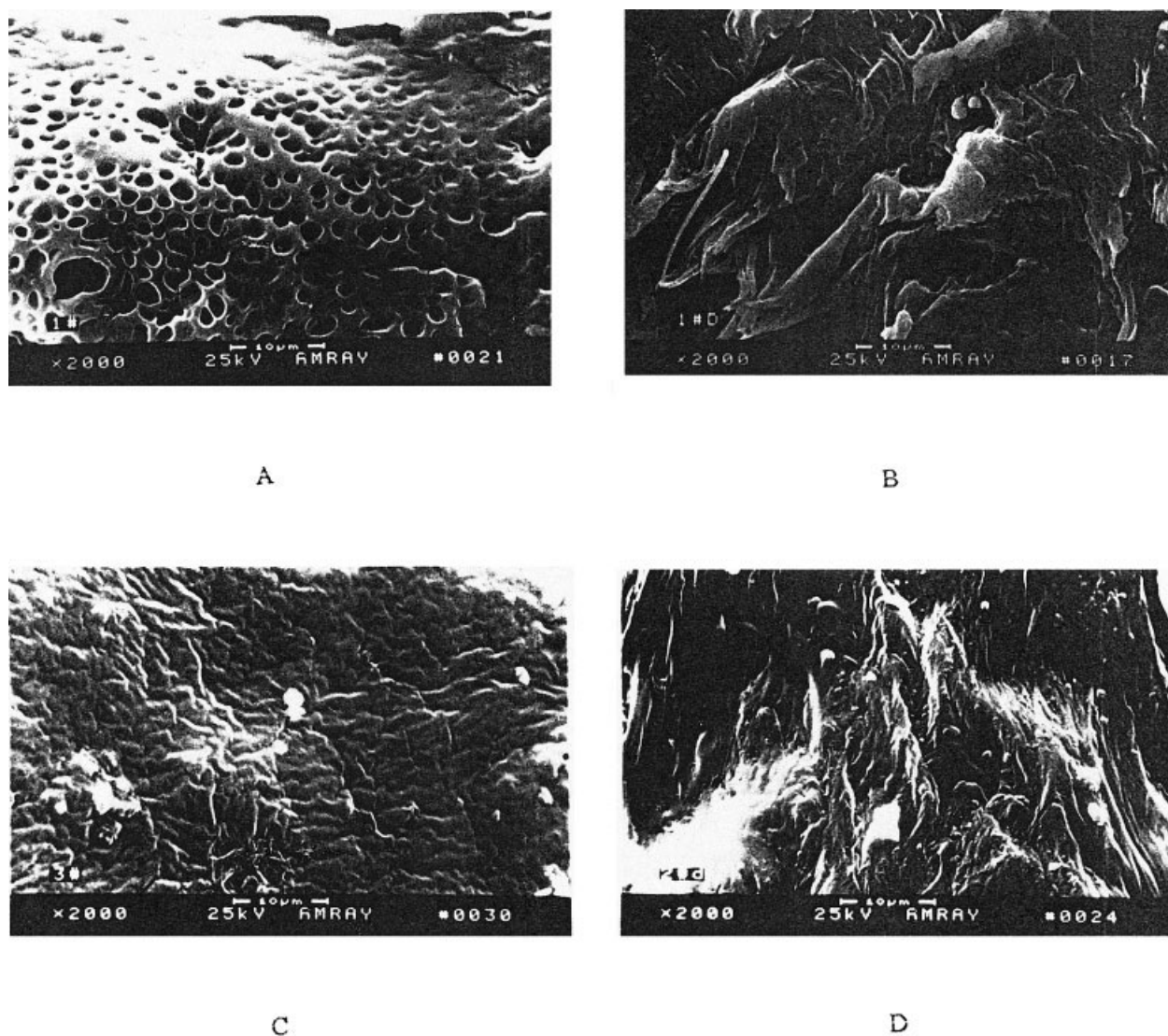


Figure 7 SEM micrographs of chitosan/PVC blends and of chitosan/chitosan-g-PMA/PVC blends. (A) Surficial SEM photographs of the film of chitosan/PVC blends; (B) Sectional SEM photographs of the film of chitosan/PVC blends; (C) Surficial SEM photographs of the film of chitosan/chitosan-g-PVC/PVC blends; (D) Sectional SEM photographs of the film of chitosan/chitosan-g-PVC/PVC blends.

phology. The addition of graft copolymer made the interface of two phases indistinct.

Figure 8 shows the DSC thermograms of PVC, chitosan/PVC blends, chitosan and chitosan/chitosan-g-

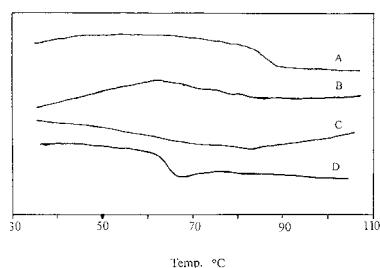


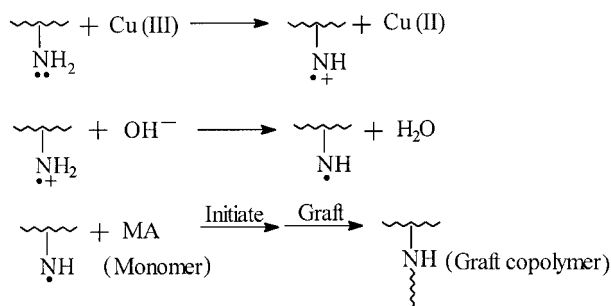
Figure 8 DSC curves of (A) PVC, (B) chitosan/PVC, (C) chitosan, and (D) chitosan/chitosan-g-PMA/PVC.

PMA/PVC blends. The cast film of PVC and chitosan containing the graft copolymer is homogeneous and reasonably transparent for miscible system, while the film of chitosan/PVC is heterogeneous and distinctly opaque, indicating immiscibility.²¹ The results of DSC analysis agreed with visual observations. Both PVC and chitosan/chitosan-g-PMA/PVC blends show a single T_g , and the T_g of the blends is obviously lower than that of PVC. However, a broad glass transition is observed in both chitosan and chitosan/PVC blend.

Both the SEM micrographs and the DSC thermograms indicate that the graft copolymer is an efficient way of improving the compatibility of chitosan and PVC. Chitosan-g-PMA has a good practical foreground in the synthesis of degradable plastics.

Initiation mechanism of grafting reaction

IR spectra and TGA illustrate that MA has been grafted onto chitosan. It can be concluded the single electron transferred in changing Cu (III) into Cu (II) is able to initiate the grafting process. The IR spectrum above has characterized the structure of the graft copolymer, chitosan-g-PMA. The initiation mechanism may be shown as follows:



CONCLUSION

The feasibility of grafting MA onto chitosan by using Cu (III)-chitosan as the redox initiator has been demonstrated by this work. Cu (III) obtained from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is cheaper than other initiators; hence, it is suitable to popularize application. Graft copolymers with high graft efficiency and grafting percentage have been produced. Cu (III)-chitosan is an efficient redox initiator for the graft copolymerization of chitosan and MA. Moreover, because the activation energy of the reaction employing Cu (III)-chitosan as the initiator is low, the graft copolymerization is able to be carried out at a mild temperature of 35°C and in alkali aqueous medium, which makes it superior to other initiators. Therefore, Cu (III)-chitosan is thought to be practical as an initiator and shows promise for future research.

The grafted product shows augmented thermal stability and is a good compatibilizer for the chitosan/

PMA blending system. Changes of morphology between chitosan/PVC blends and chitosan/chitosan-g-PVC/PVC blends were obvious. Further work is being carried out.

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