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Graft Copolymerization of Methyl Methacrylate onto Chitosan Initiated by Potassium Ditelluratocuprate(III)

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A novel redox system, potassium ditelluratocuprate(III) (DTC)–chitosan, was employed to initiate the graft copolymerization of methyl methacrylate (MMA) onto chitosan in alkali medium. The effects of reaction variables, such as the initiator concentration, ratio of monomer to chitosan, the pH value, as well as reaction temperature and time were investigated, and the grafting conditions were optimized. Graft copolymers with both high grafting efficiency (>90%) and percentage of grafting were obtained, and the rate of polymerization is higher, which indicated that the DTC–chitosan redox system is an efficient initiator for this graft copolymerization. The structures and the thermal property of chitosan and chitosan–g–PMMA were characterized by infrared spectroscopy (IR), X-ray diffraction and thermogravimetric analysis (TGA). A mechanism is proposed to explain the generation of radicals and the initiation. The graft copolymer was used as the compatibilizer in blends of terpolyamide and chitosan. The scanning electron microscope (SEM) photographs indicated that the graft copolymer improved the compatibility of the blend.

Keywords potassium ditelluratocuprate (Cu(III)), chitosan, methyl methacrylate, graft copolymerization, redox initiation, compatibility

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, allowing novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. The resulting graft copolymers have found new potential applications

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in some fields, including pharmaceuticals, biomaterials, water treatment, toiletries, agriculture, as well as food processing. So far, graft copolymerization of chitosan with vinyl monomers have been explored by various methods, performed typically with AIBN (4) and traditional redox systems, including Ce(IV) (5–9), $K_2S_2O_8$ (10–13), Fe^{2+}-H_2O_2 (14–16), etc. Among them, MMA is the most attractive monomer and Ce(IV) is the most efficient initiator. However, the grafting efficiency was generally low. Although Ce(IV) can initiate grafting polymerization with high grafting efficiency, the high price and acid reactant medium limited its broad application.

Nowadays, the basic theoretical research and application on super normal valence transitional metals have received considerable attention. In recent years, we have attained some achievements on the homopolymerization and graft copolymerization of vinyl monomers initiated by supernormal valence transition–metals, such as diperiodatocuprate(III) (17, 18), ditelluratocuprate(III) (19, 20), diperiodatonickelate(IV) (21, 22), as well as diperiodatoargentate(III) (23, 24) and ditteluratoargentate(III) (25). It has been demonstrated that DTC is an efficient and cheap initiator.

In our previous work, we have reported DPN-initiate grafting of MA (22) and AN (26) onto chitos, however, there is no literature on graft copolymerization of chitosan with MMA using DTC as initiator. In this paper, DTC was employed as an oxidant, and chitosan as a reductant to make up the redox system to initiate the graft copolymerization of MMA onto chitosan in alkali aqueous medium. The effects of the reaction variables on the graft copolymerization were investigated. The grafting efficiency and percentage of grafting, as well as the rate of polymerization is much higher. In addition, the structures and properties of the grafted products were characterized by infrared spectroscopy (IR) and X-ray diffraction and thermogravimetric analysis (TGA). The Scanning electron microscope (SEM) micrographs indicated that the graft copolymer, chitosan-g-PMMA, could act as compatibilizer to improve the compatibility of the immiscible binary blend of terpolyamide and chitosan. A tentative mechanism is proposed to explain the formation of radicals and the initiation.

Experimental

Materials

Chitosan was obtained from the Yuhuan County Chemical Plant. MMA, from Chemical Co. Ltd. (China), was washed successively with aqueous sodium hydroxide solution and distilled water, followed by drying over anhydrous sodium sulfate, and finally distilled under reduced pressure. DTC was synthesized and measured according to the reported procedure (27). The concentration of DTC was obtained by its absorption at $\lambda = 405\,\text{nm}$ using a Shimadzu UV-265 spectrophotometer (Japan). The other solvents were all of analytical reagent and used as such.

Graft Copolymerization

Graft copolymerization was carried out in a 50 mL four-necked flask equipped with thermometer, condenser, stirrer and gas inlet, immersed into a thermostat controlled water bath. In a typical experiment, a required amount of chitosan and distilled water were added into the reaction flask, with the contents deaerated sufficiently by sparging with nitrogen at the required temperature, along with constant stirring. The required amount of monomer was added, followed by the DTC 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 acetic acid solution and then 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 methacrylate (PMMA) 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 at 60°C. The above process was repeated for the different initiator concentration, monomer-to-chitosan ratio, pH value as well as temperature and time.

Measurements

The IR spectra of the pure chitosan and chitosan-g-PMMA were recorded on an FTS–40 spectrometer (BIO RAD Co. USA) using a potassium bromide pellets technique. X-ray diffraction of ungrafted and grafted chitosan was measured using a Y-4Q X-ray diffraction instrument (Dandong Ray Apparatus Corporation, China). The X-ray diagrams were made with Ni-filtered Cu Ka radiation at 30 KV and 20 mA. TGA curves of ungrafted and grafted chitosan were carried out on a Shimadzu apparatus (DGC-40 DTA-TG) at a heating rate of 10°C/min in a static air atmosphere. A SEM Scanning electron microscope, AMKAY-1000B was used to observe the morphologies of chitosan/terpolyamide blend and those of chitosan/chitosan-g-PMMA/terpolyamide blend.

Results and Discussion

The grafting parameters, such as percentage of grafting (PG), grafting efficiency (GE), as well as the rates of polymerization (Rp), graft copolymerization (Rg) and homopolymerization (Rh) were defined and calculated as follows:

$\mathrm{PG}/\% = (\text{weight of PMMA grafted}/\text{weight of chitosan}) \times 100$

$\mathrm{GE}/\% = (\text{weight of PMMA grafted}/\text{total weight of PMMA}) \times 100$

$\mathrm{Rp}\ (\mathrm{mol}\cdot\mathrm{L}^{-1}\cdot\mathrm{s}^{-1}) = \text{total weight of PMMA}/(\text{Mol. wt of MMA} \times \text{Reaction time(s)} \times \text{reaction volume (L)})$

$\mathrm{Rg}\ (\mathrm{mol}\cdot\mathrm{L}^{-1}\cdot\mathrm{s}^{-1}) = \text{weight of PMMA grafted}/(\text{Mol. wt of MMA} \times \text{Reaction time(s)} \times \text{reaction volume (L)})$

$\underline{\mathrm{Rh}}\ (\mathrm{mol}\cdot\mathrm{L}^{-1}\cdot\mathrm{s}^{-1}) = \mathrm{Rp}\text{-}\mathrm{Rg}$

Effect of Initiator Concentration

When the MMA-to-chitosan ratio, pH value, as well as reaction temperature and time are kept invariable, the effect of DTC concentration on graft parameters is shown in Figure 1. Percent grafting (PG), grafting efficiency (GE), rate of polymerization (Rp), rate of graft copolymerization (Rg), rate of homopolymerization (Rh) increase with increasing DTC concentration. However, beyond the DTC concentration of 3.3×10^{-3} mol/L, Rp, Rg, PG and GE are found to decrease. In the reaction system, the reduction of DTC involves the formation of chitosan radicals, which activate the backbone and monomer to initiate polymerization. This could be confirmed by the contrast experiment, in which no PMMA formed due to the absence of chitosan. And the primary radicals produced are mainly utilized for grafting copolymerization, thus resulting in all the parameters increase. However, a further increase of the DTC concentration accelerates the reaction of DTC and radical, which terminates the chain propagation reaction,

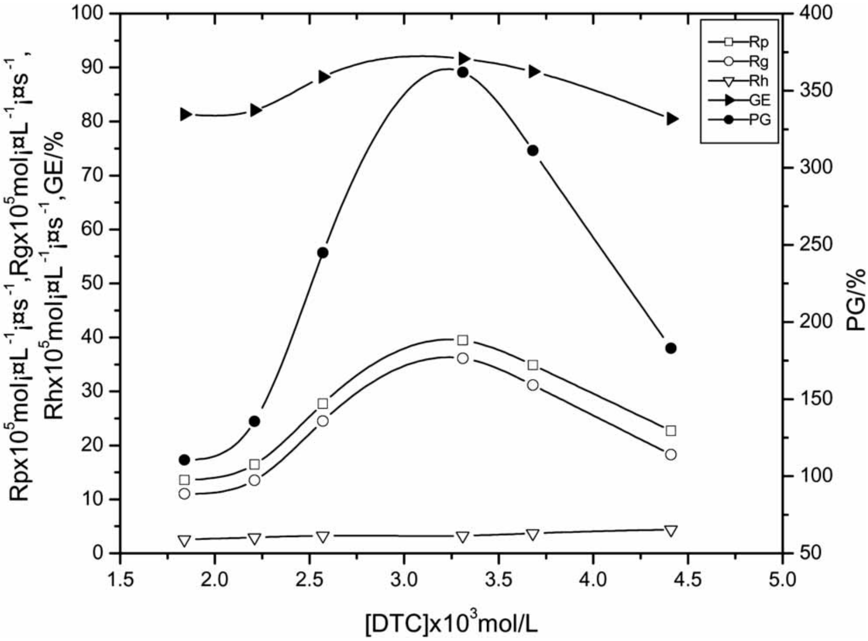


Figure 1. Effect of DTC concentration on graft parameters.

hence, decreasing Rp, Rg and PG. Meanwhile, at higher DTC concentration, the chance of chain transfer to monomer is enhanced, leading to the increase of Rh and decline in GE.

Effect of Monomer-to-Chitosan Ratio

The effect of monomer-to-chitosan ratio on graft copolymerization of MMA onto chitosan is depicted in Figure 2. MMA has little solubility in water, but GE is up to about 90%. This may be ascribed to the surface-activity and self-emulsifying properties of chitosan and chitosan-g-MMA, which assists in the proximity of monomer to the growing chains and active sites on the chitosan. With an increase in MMA-to-chitosan ratio, Rp, Rg and PG increase initially. However, beyond MMA/chitosan $(g/g) = 4.4$, Rg, PG and GE decline whereas Rh increase significantly. This may be explained as follows: with the total volume fixed, an increase in monomer-to-chitosan ratio means the higher DTC concentration in the water phase, in addition, chitosan-g-MMA can solubilize MMA in water. Thus, the chain transfer reaction of radicals to MMA is accelerated by the combined effect of the above factors. Moreover, when the MMA-to-chitosan ratio is higher, the adsorption of monomers onto chitosan reaches the point where it largely interferes with the approach of both DTC and chitosan, which is necessary for initiation. Therefore, the homopolymerization rate enhances and GE declines correspondingly.

Effect of Temperature

The grafting reactions were carried out at different temperatures between 30°C and 60°C, keeping the other variables constant, as is shown in Figure 3. It is found that PG, Rp and Rg increase initially and then decrease to some extent with a further increase in

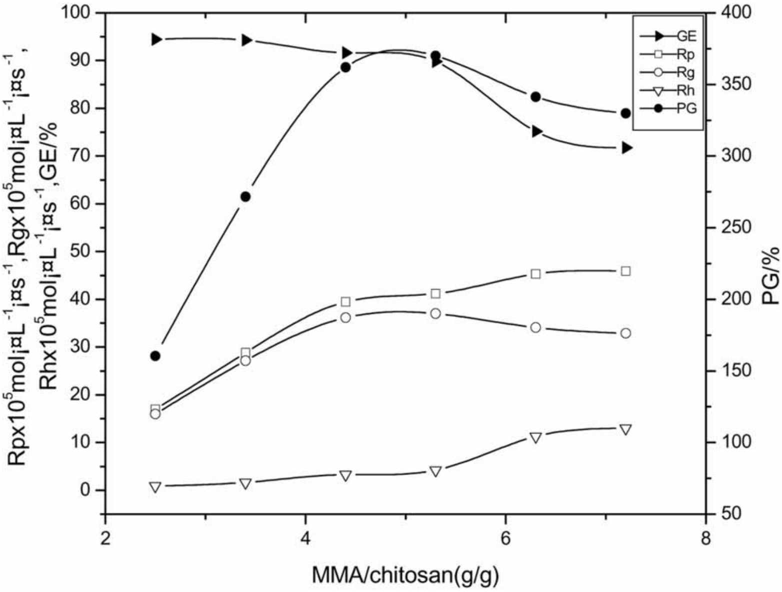


Figure 2. Effect of monomer-to-chitosan ratio on graft parameters.

temperature. This is attributed to the fact that increasing temperature favors the activation of macroradicals as well as accelerates the diffusion and mobility of the monomers from the aqueous phase to the backbone. Whereas a further increase in temperature decreases PG, GE, Rp, and Rg. This can be ascribed both to the acceleration of termination reaction through oxidation by DTC and to a increased chance of chain transfer reaction

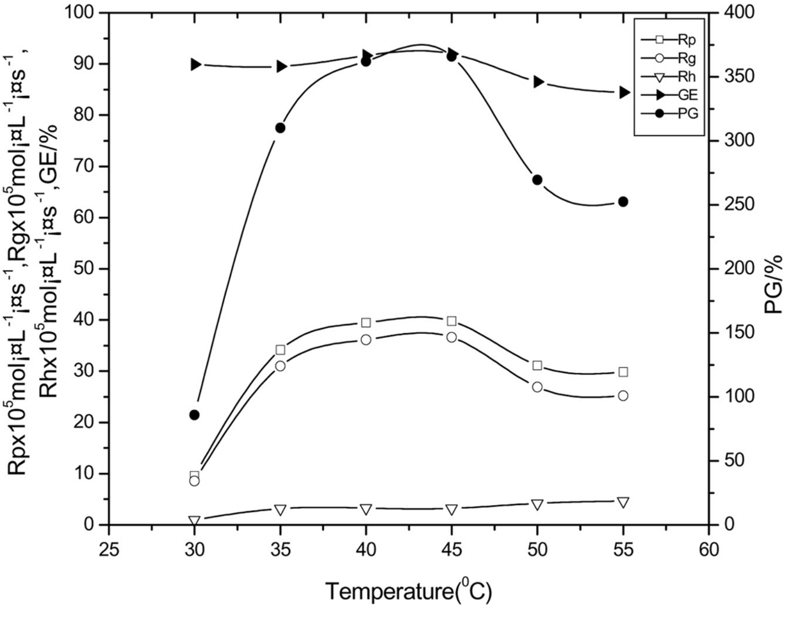


Figure 3. Effect of temperature on graft parameters.

to monomer. This also accounts for the increasing amount of homopolymer, and this is indicated by a steady increase in the rate of homopolymerization, Rh.

Effect of pH

Figure 4 shows the effect of pH on graft parameters. Potassium hydroxide and hydrogen chloride are employed to maintain the required alkalinity in the reaction solution. In the pH range studied, DTC exists mainly in the form of $(Cu(OH)_2(H_4TeO_6)_2)^{3-}$ and $(Cu(OH)_2(H_3TeO_6)_2)^{2-}$ (28). In alkali aqueous solution, the ratio of the two forms change with pH, which directly influences the amount of radicals produced in the reaction system. It is found that the optimum pH value is 12.50.

Effect of Time

Figure 5 illustrates the influence of reaction time on grafting parameters. It can be seen that GE remains unchanged during the course of the reaction, whereas PG increase steadily with the reaction time prolonged up to 25 min, and then maintains a plateau, which is inconsistent with the general rule of conventional radical polymerization. So the optimized reaction time is 25 min.

IR Spectroscopy

The proof of grafting was obtained from the IR spectra of pure chitosan and chitosan-g-PMMA after exhaustive Soxhlet extraction with acetone. As shown in Figure 6, in the

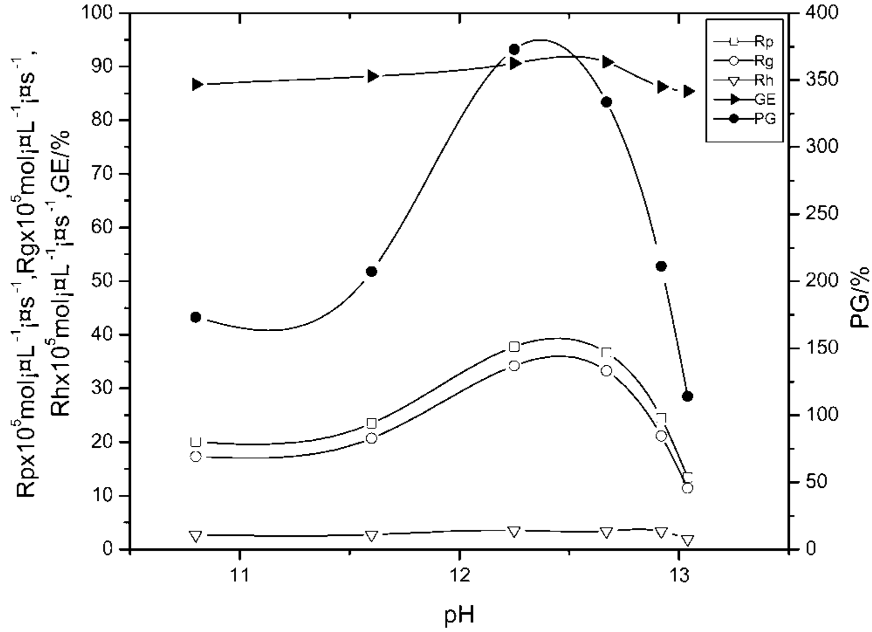


Figure 4. Effect of pH value on graft parameters.

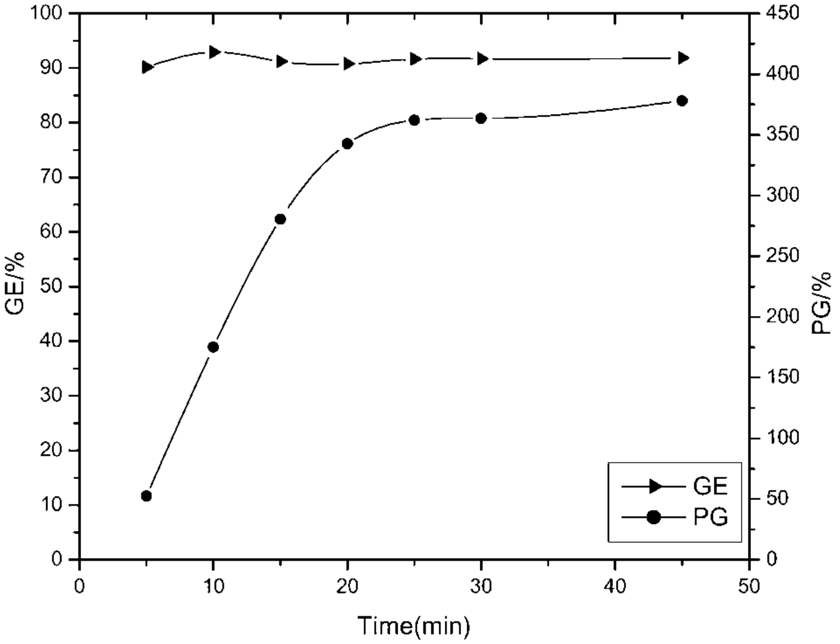


Figure 5. Effect of time on graft parameters.

spectrum of chitosan, the characteristic absorption bands around 3420 cm^{-1}, 1650 cm^{-1} and 1560 cm^{-1} can be observed. Compared with pure chitosan, graft copolymer has an additional peak at 1732 cm^{-1}, attributed to the ester carbonyl group of PMMA, which confirmed the formation of chitosan-g-PMMA effectively.

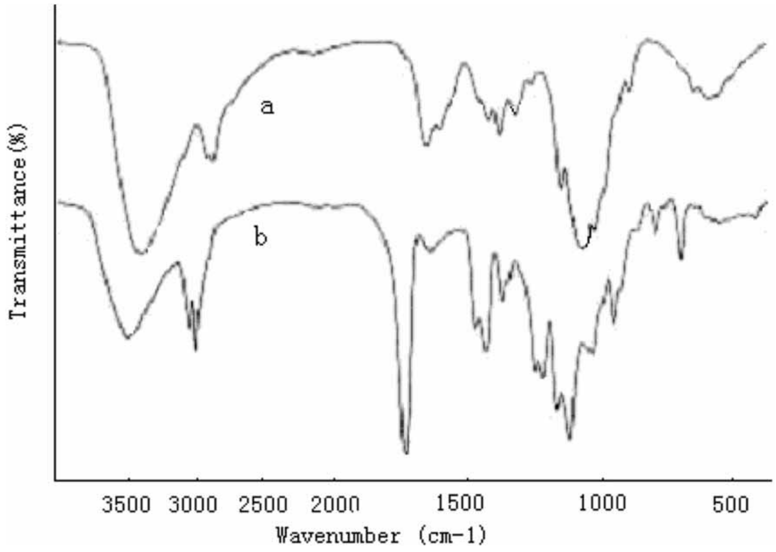


Figure 6. IR spectra of chitosan (a) and chitosan-g-MMA (b).

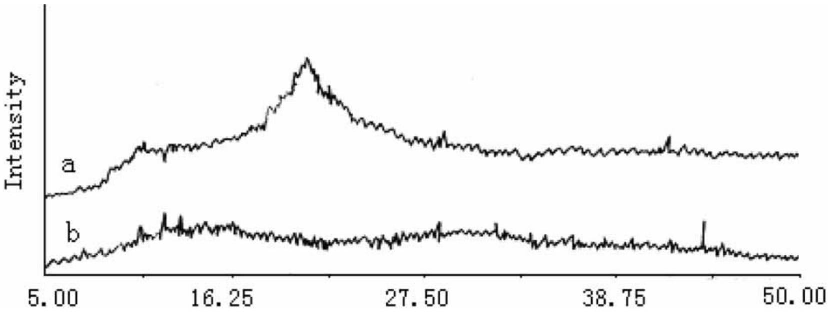


Figure 7. X-ray diffraction patterns of chitosan (a) and chitosan-g-PMMA (b).

X-Ray Diffraction

The X-ray diffraction spectra of pure chitosan and chitosan-g-PMMA were analyzed, as shown in Figure 7. The chitosan figure is more convex than that of the copolymer. The crystallinity of ungrafted and grafted chitosan was calculated as 53.6% and 38.1%, respectively. This indicated that the incorporation of PMMA has decreased the crystallinity of chitosan, which suggested that the crystal region was also involved in the grafting reaction besides the amorphous region.

Thermal Analysis

The thermogravimetric analysis (TGA) of pure chitosan and the grafted copolymer is shown in Figure 8. It is evident that the TGA of pure chitosan shows a weight loss in three stages. The first stage ranges from 42.2°C to 105.3°C and shows about 7.24% weight loss, corresponding to the loss of residual or absorbed moisture. No such inflexions are observed in the TGA curve of chitosan-g-PMMA. This reveals that graft copolymer is resistant to moisture absorption owing to the incorporation of hydrophobic PMMA chain.

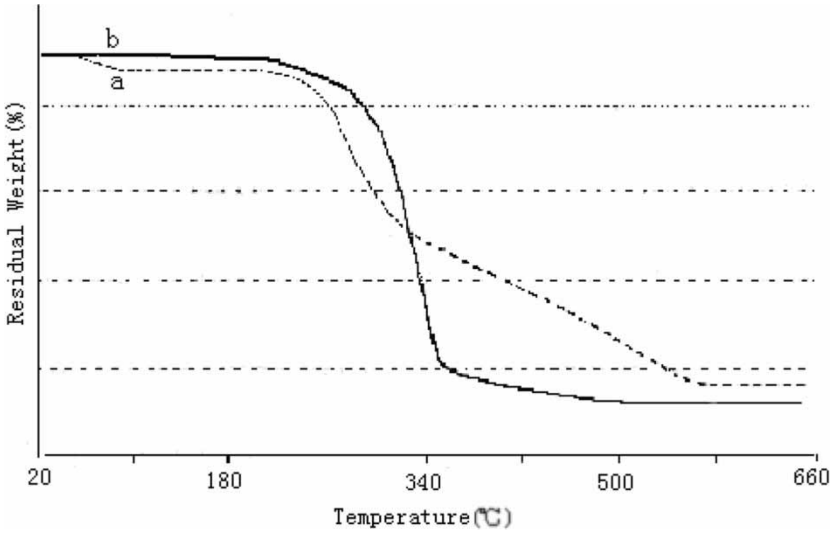


Figure 8. Thermal analysis of chitosan (a) and chitosan-g-PMMA(b).

The second stage referred to as pyrolysis starts at 224.2°C and continues up to 438.3°C, during which time there is a 46.33% weight loss, which may be due to the decomposition of polysaccharide in chitosan. The last stage, from 438.3°C to 531.0°C, shows a weight loss of 41.26%, as a result of carbonization, while the thermogram of the grafted copolymer shows a single stage of distinct weight loss between 261.1°C and 434.1°C. In addition, it is also evident from the TGA curve that the temperature at about 50% weight loss of grafted copolymer is 384.0°C, higher than that of pure chitosan (at 357.1°C). It shows that the grafted copolymer has a distinct difference in thermal properties, compared to pure chitosan.

Scanning Electron Microscopy

Figure 9 shows the SEM micrographs of chitosan/terpolyamide blend (a) and chitosan/chitosan-g-PMMA/terpolyamide blend (b). Figure 9(a) provides direct evidence that phase separation occurred in the chitosan/terpolyamide blend. This sample has a distinct two-phase morphology, i.e., a continous terpolyamide phase with a dispersed chitosan phase. All the spheres and holes have smooth surfaces, indicating poor interfacial adhesion between terpolyamide and chitosan phases. However, with the addition of compatibilizers, chitosan-g-PMMA, the morphology of fractures surface changes

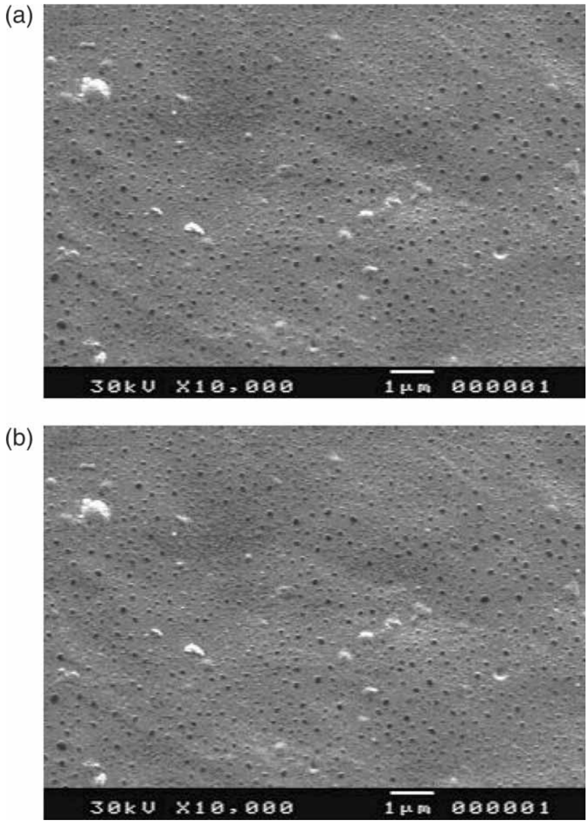


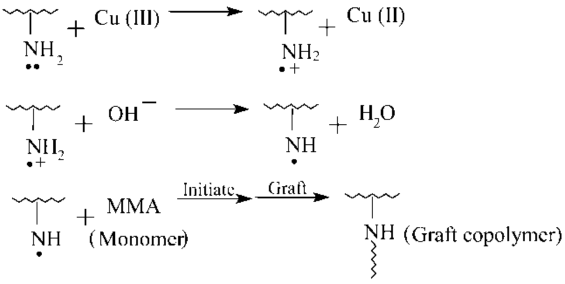
Figure 9. SEM micrographs of (a) chitosan/terpolyamide blend and, (b) chitosan/chitosan-g-PMMA/terpolyamide blend.

dramatically. The photo in Figure 9(b) shows that the cast film of chitosan/chitosan-g-PMMA/terpolyamide blend is homogeneous and continuous.

It is well established that the phase morphology of immiscible chitosan/terpolyamide blend can be controlled by the addition of compatibilizer, chitosan-g-PMMA, which act as interfacial agents. Furthermore, the addition of properly selected compatibilizer to an immiscible binary blend should (1) reduce the interfacial energy between the phases; (2) permit finer dispersion during mixing; (3) provide stability against gross segregation and, (4) result in improved interfacial adhesion, so that it enhances mechanical properties.

Grafting Reaction Initiation Mechanism

IR spectra, X–ray diffraction and TGA shows that PMMA was grafted onto chitosan. A tentative initiation mechanism, based on a single-electron-transfer process of DTC, is proposed as follows:



Conclusions

Graft copolymerization of MMA onto chitosan in an aqueous alkaline medium initiated by DTC can be carried out successfully. The proof of grafting was obtained from IR analysis and X-ray diffraction. Based on the TGA results, it was found that the grafted chitosan was more thermally stable than the ungrafted one due to the incorporation of PMMA, 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 the immiscible binary blend of chitosan and terpolyamide.

During this research work, graft copolymers with high graft efficiency ($>$ 90%) and grafting percentage have been obtained. A DTC-chitosan system is found to be an efficient redox initiator for this graft copolymerization. Furthermore, because the activation energy of the reaction is low, the graft copolymerization can be achieved at a mild temperature and in an aqueous alkali medium, which is superior to other initiators. Thus, a DTC–chitosan redox system is considered to be a practical initiator and has a good foreground. Further work is being carried out.

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