

Oxidative Graft Polymerization of Aniline on the Modified Surface of Polypropylene Films

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ABSTRACT: A novel method for preparing electrically conductive polypropylene-graft-polyacrylic acid/polyaniline (PP-g-PAA/PANI) composite films was developed. 1,4-Phenylenediamine (PDA) was introduced on the surface of PP-g-PAA film, and then, chemical oxidative polymerization of aniline on PP-g-PAA/PDA film was carried out to prepare PP-g-PAA/PANI electrically conductive composite films. After each step of reaction, the PP film surface was characterized by attenuated total reflectance Fourier transform infrared spectroscopy. Static water contact angles of the PP, PP-g-PAA, and PP-g-PAA/PANI films were measured, and the results revealed that graft reactions took place

as expected. The morphology of the PP-g-PAA film and the PP-g-PAA/PANI composite film were observed by atomic force microscopy. The conductivity and the thickness of the PP-g-PAA/PANI composite films with 1.5 wt % PANI were around 0.21 S/cm and 0.4 μm , respectively. The PANI on the PP-g-PAA/PANI film was reactivated and chain growing occurred to further improve the molecular weight of PANI. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2442–2450, 2007

Key words: graft polymerization; polyaniline; modified surface

INTRODUCTION

In the past years, conductive polymers have been extensively studied for their promising applications in transparent electrodes, chemical and biological sensors, electrical conductive, optical materials, etc.^{1–6} In particular, polyaniline (PANI) is probably an important conducting polymer applied in industrial today due to its ease of synthesis, low cost, and relatively stable electrical conductivity. In recent years, a large number of excellent studies have been carried out to functionalize variety of substrates with PANI. Monolayer aniline is immobilized on the surface of inorganic materials, such as glass, silicon, quartz, SiO₂, metal, etc., through surface modification first, and then grafting polymerization of aniline on the materials' surface.^{7–13} PANI-aligned nanowire that is parallel to the surface of highly oriented pyrolytic graphite (HOPG) can also be fabricated by using adsorbed surfactants as templates.¹⁴ Surface modification of polymer via molecular design is a convenient and effective

means to improve the surface properties, such as hydrophilicity,¹⁵ biocompatibility,¹⁶ adhesion,¹⁷ and electrical conductivity.¹⁸ A large number of attentions is paid to functionalize the surface of polymer films^{18–24}; however, only few of them concerned the electrical conductivity of polymer films and the dissipation of electrostatic charges.^{18–23} The use of polymer substrates is increasing in importance owing to their light weight, flexibility, shock resistance, and low cost.²⁵ Unfortunately, it is difficult to directly prepare PANI on polymer surface because of the inertness and insulation in polymer surface. Recently, Kang et al. have published articles on preparing polytetrafluoroethylene (PTFE)/PANI composite films,¹⁹ in which aniline group was immobilized on the surface of PTFE, and subsequently, the oxidative graft polymerization of aniline was carried out. With this method, PTFE/PANI composite films were successfully obtained, and we have directly synthesized polymeric substrate/PANI conducting composite film by polymerization of aniline on the surface of PP-g-PAA film.²⁶

Here, we report a new method for preparing polypropylene-graft-polyacrylic acid/polyaniline (PP-g-PAA/PANI) composite conductive films, and the strategy is as follows: First, a layer of PAA was prepared on PP film's surface (PP-g-PAA) by simple photografting method, and then the above-mentioned PAA was reacted with thionyl chloride (SOCl₂) to form polyacryloyl chloride; subsequently, 1,4-phenylenediamine (PDA)

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was added and the reaction between them and polyacryloyl chloride took place to prepare PP-g-PAA/PDA films; finally, the PP-g-PAA/PDA films were immersed in a HCl aqueous solution containing aniline monomer to carry out oxidative polymerization, and the PP films so obtained were defined as PP-g-PAA/PANI composite films. In the present work, PDA was introduced and immobilized by chemical bond on the polymer film because PDA can be considered as a chain initiator to prepare PANI.^{11,27,28} The surface structure and properties of the PP-g-PAA/PANI composite films were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), UV-vis spectroscopy, static water contact angle measurement, atomic force microscopy (AFM), and electrical conductivity measurements.

EXPERIMENTAL

Materials

Commercial casting polypropylene (PP) films with 30 μm in thickness were cut into a rectangle shape of 3.0 cm \times 5.0 cm in size, and then subjected to Soxhlet extraction with acetone for about 36 h to completely remove the impurities and additives before use. Aniline was distilled twice under a reduced pressure. Thionyl chloride (SOCl_2) and acrylic acid (AA) were distilled under a reduced pressure. Petroleum ether (60–90°C) and chloroform were of analytical grade and dried with anhydrous calcium chloride. 1,4-Phenylenediamine (PDA), hydrochloric acid (HCl), acetone, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS), pyridine, *N*-methylpyrrolidinone (NMP), benzophenone (BP), NaOH, $\text{Na}_2\text{S}_2\text{O}_3$, ethyl ether, NH_4Cl , and $\text{NH}_3\cdot\text{H}_2\text{O}$ were all of analytical grade and used without further purification.

Preparation of PP-g-PAC films

Under UV light, the surface grafting polymerization of AA on PP films was carried out with BP as photoinitiator, and in two-step method as reported by Yang and coworkers.²⁴ First, 20- μL BP-acetone solution was filled between two PP films, and then, the prepared sandwich unit was irradiated under UV light (1 KW high pressure mercury lamp) for a given time at room temperature. After that, the films were separated and the unreacted BP was removed by extraction with acetone for 6 h. Second, the earlier PP films were reassembled again with AA solution filled between them, and then placed under the UV light for another irradiation. The PP films were extracted with deionized water for 24 h to remove the homopolymer. Following each step, the films were dried at room temperature to constant weight. The prepared PP-g-PAA films were subsequently immersed in 50-mL SOCl_2 containing several drops of pyridine for 5 h, then taken out, washed with petroleum ether three

times to remove SOCl_2 left on the film, and dried in a vacuum oven at 40°C for 24 h. The films prepared by this way were designated as PP-g-PAC films.

Synthesis of PP-g-PAA/PDA films

The PP-g-PAC films were immersed into chloroform containing 0.01M PDA at room temperature to fabricate PP-g-PAA/PDA films. After 12 h, the film samples were taken out, subsequently washed with chloroform and petroleum ether thrice, respectively, and then dried in vacuum at 30°C for 24 h.

Fabrication of PP-g-PAA/PANI films

Oxidative graft polymerization of aniline onto the PP-g-PAA/PDA films was carried out via the conventional method.²⁹ It was carried out in a 1M HCl solution containing both aniline (as the monomer varied in 0.01–0.1M) and APS (as the oxidant). The molar ratio of aniline to APS was kept unchanged. The polymerization of aniline to form emeraldine salt of PANI was allowed to proceed at 0 to 5°C for 5 h. The film samples were subsequently washed thrice with deionized water, methanol, and ethyl ether, respectively. Emeraldine salt of PANI on the surface of PP film was converted to the neutral emeraldine base (EB) by Soxhlet extraction with deionized water for about 48 h. The usually used base treatment with NaOH or NH_4OH was not adopted to avoid the decomposition of the amido group. The obtained PP-g-PAA/PANI films were immersed into a large volume of NMP at 80°C for at least 24 h to remove the physically adsorbed EM salt and subsequently washed with alcohol to remove the residual NMP, and then washed again with deionized water.^{7,9} Finally, the PP-g-PAA/PANI films were dried in vacuum for 24 h at 40°C. To determine the grafting percentage and grafting efficiency, the PP-g-PAA/PANI films were taken out of the reaction system at various intervals, and instantly washed with deionized water and dried in vacuum at 40°C for 24 h. The above-obtained reaction mixture was neutralized with a NaOH solution at various intervals and quenched with a $\text{Na}_2\text{S}_2\text{O}_3$ solution buffered with $\text{NH}_4\text{Cl-NH}_3/\text{H}_2\text{O}$ solution. The precipitate was washed with 1M HCl until the filtrate became clear and then dried in vacuum at 40°C for 24 h.

The grafting percentage (G_p) and grafting efficiency (GE) were obtained by a gravimetric method, and G_{P1} , G_{P2} , G_{P3} , G_{P4} , and GE were calculated according to the following equations:

$$G_{P1} = (W_1 - W_F)/W_F \times 100\% \quad (1)$$

$$G_{P2} = 90.5(W_2 - W_1)/18.5W_F \times 100\% \quad (2)$$

$$G_{P3} = 107(W_3 - W_1)/91W_F \times 100\% \quad (3)$$

$$G_{P4} = (W_4 - W_1)/W_F \times 100\% \quad (4)$$

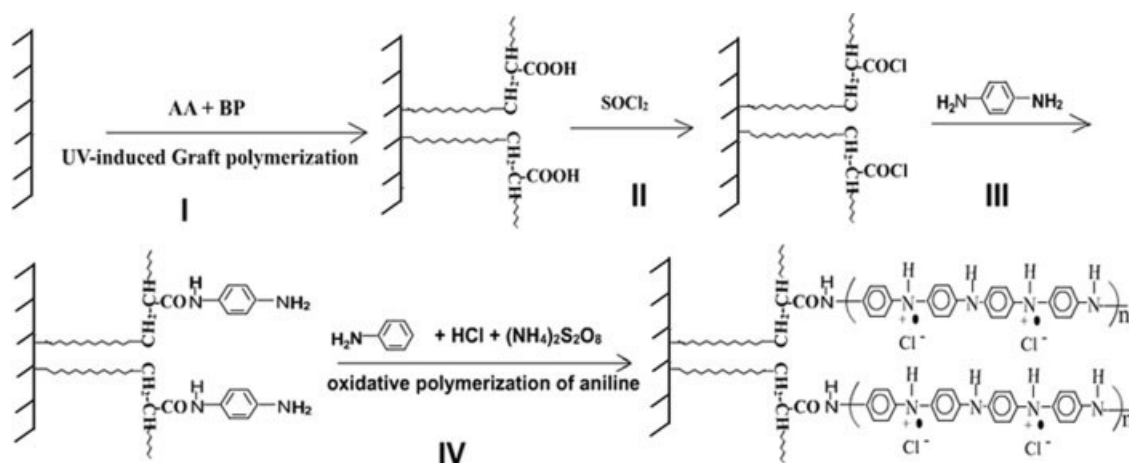


Figure 1 Schematic diagram illustrating the processes for grafting polymerization of aniline on the surface of PP film. AA, acrylic acid; BP, benzophenone.

$$GE = W_g / (W_{HP} + W_g) \times 100\% \quad (5)$$

where G_{P1} , G_{P2} , G_{P3} , and G_{P4} are the grafting percentage of PP-g-PAA, PP-g-PAC, PP-g-PAA/PDA, and PP-g-PAA/PANI films, respectively; W_F , W_1 , W_2 , W_3 , and W_4 are the weight of PP, PP-g-PAA, PP-g-PAC, PP-g-PAA/PDA, and PP-g-PAA/PANI films, respectively. GE is the grafting efficiency of PP-g-PAA/PANI films; $W_g = W_4 - W_1$; and W_{HP} is the weight of PANI homopolymer in reaction mixture.

Measurements

The distributions of grafted chains on the surface of PP-g-PAA, PP-g-PAC, PP-g-PAA/PDA, and PP-g-PAA/PANI films were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). ATR-FTIR spectra were recorded on Nicolet NEXUS 670 with variable angle horizontal ATR accessory, on which a 45° rectangle ZnSe crystal was used. The UV-vis absorption spectra of PP-g-PAA-PANI films were recorded on GBC Cintra 20; the morphologies of the films were observed atomic force microscopy (AFM, Nanoscope IIIa, Veeco). Contact angles of the resulted films against water were measured by Dataphysics OCA 20. Conductivities of the films were measured using two-probe techniques by 2400 SourceMeter (Keithley).

RESULTS AND DISCUSSION

The processes of modifying PP films' surfaces via UV-induced graft polymerization of AA, reacting with SOCl_2 , amidating with PDA and oxidative polymerization of aniline are showed schematically in Figure 1. Each process is described and discussed in detail in the corresponding section below.

Preparation of PP-g-PAC films

AA was grafted onto the surface of PP films as reported previously by our group.²⁴ The grafting percentage of PAA (G_{P1}) could be obtained higher than 2 wt % by the method of UV-induced surface grafting polymerization for 1 min. The ATR-FTIR spectra of PP film and PP-g-PAA film are shown in Figure 2. In the spectra of PP-g-PAA film, the coexistence of the characteristic bands of PP and PAA was clearly observed; the band at about 1715 cm^{-1} was assigned to the carbonyl group C=O stretching vibration of PAA. In addition, from the AFM images of PP-g-PAA film [in Fig. 7(c,d)], it can be seen that the diameter of PAA spheres or particles on the PP film was about 45 nm. The corresponding graft percentage (G_{P1}) was about 1.1 wt %. The contact angle of the PP film surface decreased from 103° (pure PP film) to 41° (PP-g-PAA film). All the above-mentioned results demonstrated that PAA was grafted on the surface of PP film, and some of them are discussed in detail below.

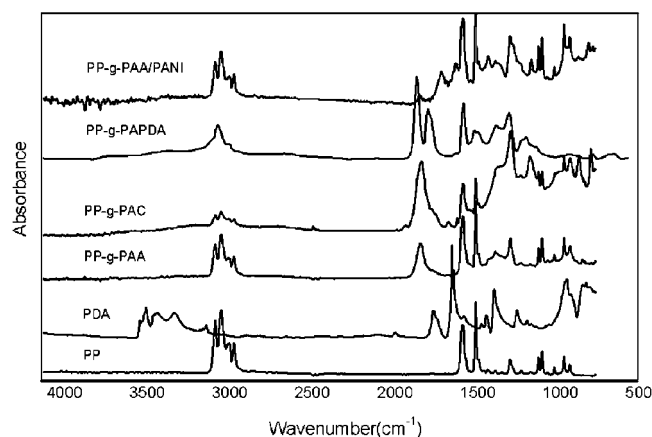


Figure 2 ATR-FTIR spectra of PP, PP-g-PAA, PP-g-PAC, PP-g-PAA/PDA, and PP-g-PANI films and PDA.

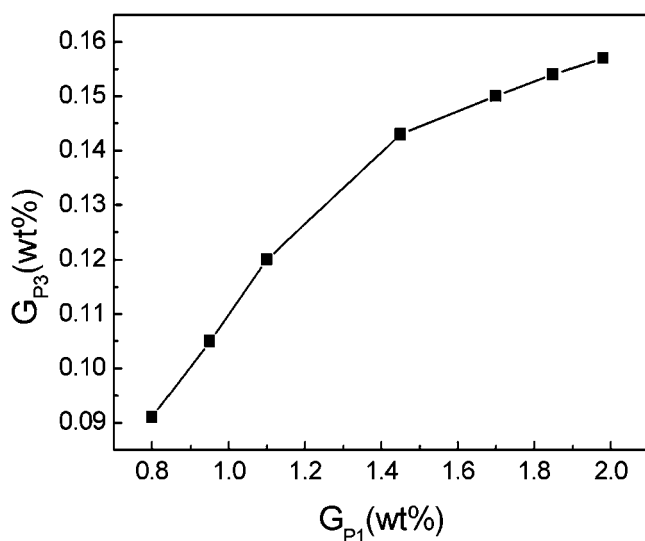


Figure 3 Effects of the amount of grafted AA (G_{P1}) on the grafting polymerization of PDA (G_{P3}). Concentration of PDA, 0.01M; reaction time, 12 h.

Subsequently, the PP-g-PAA film was immersed in SOCl_2 with a few drops of pyridine at 50°C for 5 h. Pyridine was used to neutralize the HCl yielded in the reaction between PAA and SOCl_2 . The ATR-FTIR spectra of PP-g-PAC film are shown in Figure 2. In the spectra, all the expected characteristic bands of the PP-g-PAC films could be clearly observed, and a new small band at about 1800 cm^{-1} was assigned to the carbonyl C=O stretching vibration of the PAC.

Synthesis and characterization of PP-g-PAA/PDA films

Wei²⁷ reported that in the aniline polymerization with PDA as the additive, both the molecular weight and polydispersity index (PDI) decreased with an increase in PDA concentration, and therefore PDA could be considered as the initiating dormant chain because of its lower oxidation potential (0.62 V vs. SCE) than that of aniline (1.03 V vs. SCE). In our study, PDA was introduced to initiate grafting polymerization of aniline on the surface of PP film. The PP-g-PAC films were immersed into chloroform solution with 0.01M PDA at room temperature for 12 h. The ATR-FTIR spectrum of the PP-g-PAA/PDA films was also shown in Figure 2. Comparing this spectrum with that of the PP-g-PAC films, the band at about 1800 cm^{-1} assigned to the carbonyl C=O stretching vibration of PAC disappeared, and simultaneously a new sharp peak at about 1670 cm^{-1} (including that at about 1650 cm^{-1} assigned to the N-H vibration of PDA) assigned to the carbonyl C=O stretching vibration of the amido group of PAA/PDA appeared. This suggested that PAC completely reacted with PDA on the PP films. Additionally, the grafting percentage of PDA was 0.12

wt % (G_{P3}) on the PP-g-PAA film with AA grafting percentage of about 1.1 wt % (G_{P4}). Theoretically, the grafting percentage of PDA should be higher than that of AA because the molecular weight of PDA ($M_w = 108$) is larger than that of AA ($M_w = 72$). The obtained result can be attributed to incomplete reaction between PAA and SOCl_2 . Furthermore, the mass of PDA increased with the increase of PAA on the film, which can be obviously observed in Figure 3.

Graft polymerization of aniline on PP-g-PAA/PDA films

The PP-g-PAA/PDA films were immersed into aniline aqueous solutions, where the aniline concentration was 0.1, 0.05, 0.025, and 0.01M, and then the graft oxidative polymerization of aniline was carried out in the conventional method. Figure 4(A,B) shows the effect of polymerization time on the graft percentage of PANI on the PP-g-PAA/PDA films with different concentrations of aniline. From Figure 4(A), the graft percentage (G_{P4}) of aniline increased rapidly at the first stage of the oxidative polymerization, reached a maximum value at about 1 h when the concentration of aniline was 0.1M, and then leveled off in the next 3 h [Fig. 4(A), a]. In addition, G_{P4} increased when the concentration of aniline increased; while the time reaching maximum values postponed when the concentration of aniline decreased. The results should be attributed to initiator efficiency correspondingly decreased with the concentration of initiator. Nevertheless, it seems that the graft polymerization finished within 90 min in any case. From Figure 4(C), grafting efficiency (GE) kept at nearly 100% within 5 min, which revealed that the graft polymerization proceeded smoothly, and the homopolymerization did not start yet during this period. Moreover, GE decreased when the aniline concentration increased or polymerization time elongated. These phenomena could be explained by the results in Figure 4(D), in which it is clearly shown that the yield of PANI in solution increased with the elongation of polymerization time and the increase of aniline concentration [Fig. 4(D)]; besides, PANI precipitation was not found within the first 5 min, which also indicated that the induction period for homopolymerization of aniline was over 5 min. The yield of PANI increased linearly with polymerization time, which suggested that the polymerization of aniline was autoaccelerated in the presence of PANI.³⁰ It seems that the PDA added on the modified PP film might shorten the induction period of aniline polymerization and serve as the "roots" for the subsequent graft polymerization of aniline. The reason is that it is much easier for PDA to be oxidized into radical cation than aniline under the same conditions since the oxidation potential of PDA (0.62 V vs. SCE) was lower than that of aniline (1.03 V vs. SCE). To further understand the

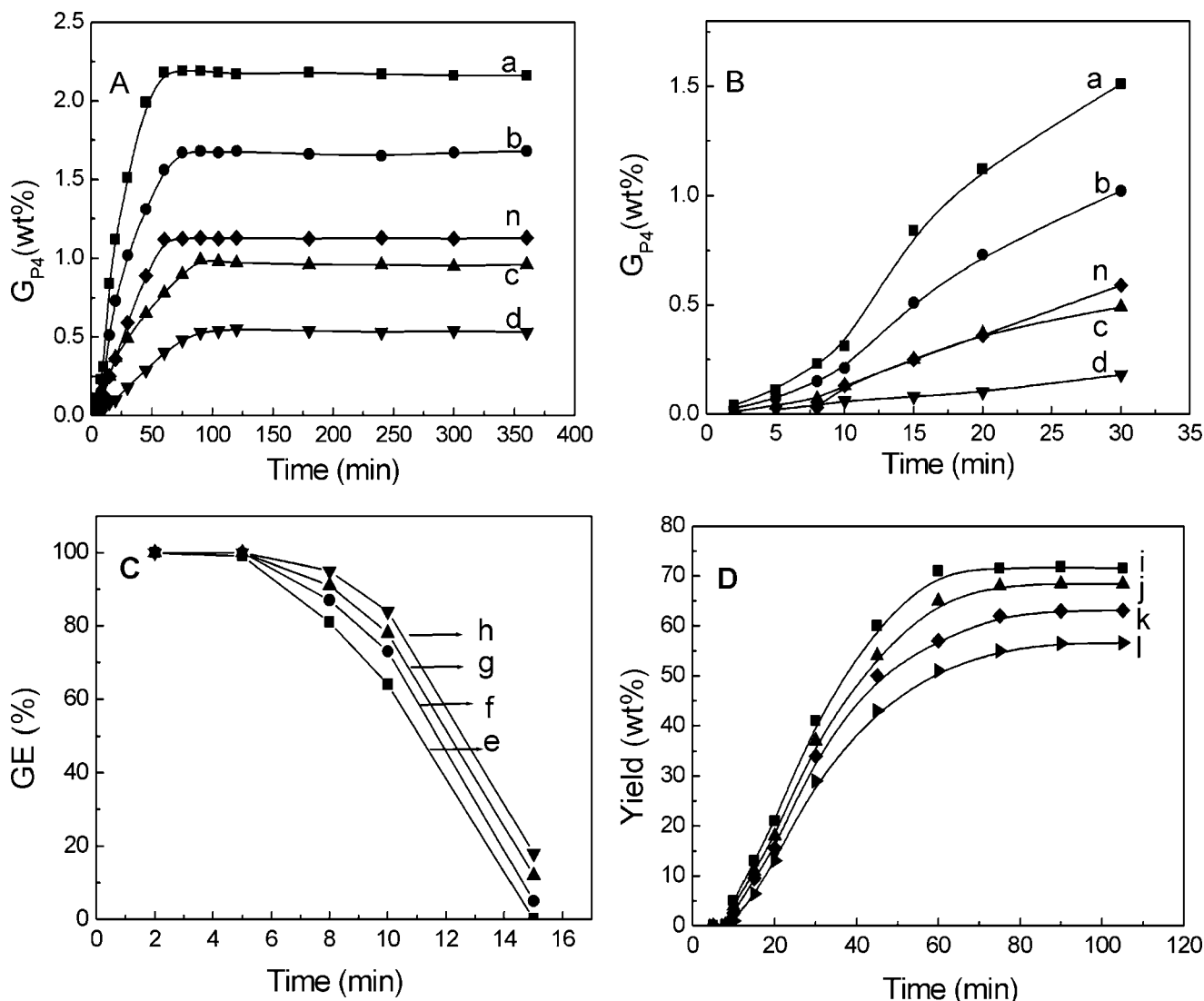


Figure 4 Effect of polymerization time on grafting polymerization of aniline. A: grafting percentage with various aniline concentrations, (a) 0.100, (b) 0.050, (c) 0.025, and (d) 0.010M; (n) PP-g-PAA-aniline film, aniline concentration, 0.1M. B: Part of A (polymerization time, 0–30 min) to make A more clear. C: grafting efficiency on PP-g-PAA/PANI films with various aniline concentrations (G_{P3} , 0.16 wt %), (e) 0.100, (f) 0.050, (g) 0.025, and (h) 0.010M. D: PANI yield in solution with various aniline concentrations, (i) 0.100, (j) 0.050, (k) 0.025, and (l) 0.010M.

effect of PDA, aniline was employed to take the place of PDA to form the PP-g-PAA-aniline films and then the oxidative graft polymerization of aniline was induced on PP-g-PAA-aniline films with aniline concentration of 0.1M. It is clearly found that oxidative graft polymerization of aniline on the surface of PP-g-PAA-aniline films had an induction period because the weight of PP-g-PAA-aniline films did not increase in the first 5 min [in Fig. 4(B), n]; in addition, G_{P4} of PP-g-PAA-aniline films was clearly lower than that of the corresponding PP-g-PAA/PDA film [Fig. 4(A,B)]. This result further supported the conclusion that PDA on the modified PP film might serve as the “roots” for the subsequent graft polymerization of aniline.

Figure 5 shows the effect of the amount of grafted PDA on the grafting polymerization of aniline on PP-

g-PAA/PDA films. It is found that the more the amount of PDA on the PP-g-PAA films, the higher the graft percentage of PANI on the corresponding PP-g-PAA/PDA films, which might further confirm that PDA was the “roots” of PANI chains. Another point worth noting is that the weight difference of the PP-g-PAA/PANI films was small by drying the resulted films in vacuum after washing with deionized water than immersing them into NMP. This result revealed that PANI deposited on the PP-g-PAA/PANI films was easily washed off with water.

The ATR-FTIR spectra of the PP-g-PAA/PANI films obtained above are also shown in Figure 2. Three characteristic bands of PANI at 1581 (C=C stretching vibration of quinoid rings), 1489 (C=C stretching vibration of benzenoid rings), and 1300 cm^{-1} (C—N

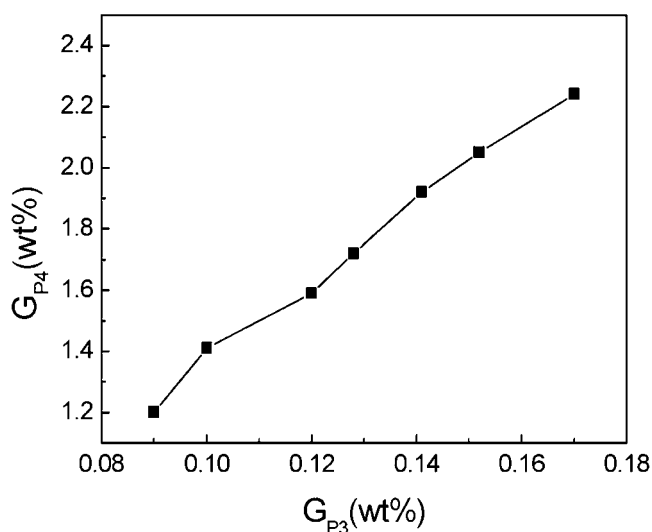


Figure 5 Effect of PDA quantity on the amount of PANI grafted on PP-g-PAA/PANI films. Aniline concentration, 0.1M; polymerization time, 5 h.

stretching mode) appeared in the spectrum of PP-g-PAA/PANI films. The surface water contact angle of PP-g-PAA/PANI films increased from 41° (before) to 80° (after PP-g-PAA films being grafted with PANI). These results might further provide evidence for the conclusion that the emeraldine salts of PANI were grafted on the PP-g-PAA films. It can be seen that, as presented in Figure 6, UV-vis absorption spectra of the above-prepared PP-g-PAA/PANI films exhibited a strong absorption peak at 320 nm, a shoulder peak at about 420 nm and a broad peak at 800 nm with a tail assigned to the polaron transition [Fig. 6(a)], which are identical to those of the emeraldine salt form of PANI.^{31,32} When the PP-g-PAA/PANI films were treated with NMP [Fig. 6(b)], only two peaks at 320 and 630 nm could be observed in their UV-vis absorption spectrum, which are the same as those of the emeraldine base form of PANI treated with NMP.⁷

The AFM images of the involved PP films are presented in Figure 7(a–f). The pure PP film surface was relatively smooth [Fig. 7(a,b)]. A layer of sphere with an average diameter of about 45 nm was observed on the PP-g-PAA film surface [Fig. 7(c,d)]; after graft polymerization of aniline, the film surface was obviously covered with PANI particles. The size of most PANI particles was about 150 nm in diameter with G_{P4} of 1.4 wt %; moreover, the particles were closely piled [Fig. 7(e,f)]. Nevertheless, the roughness of the PP-g-PAA/PANI film surface was obviously higher than that of PP-g-PAA films, which might result from the PANI chain's growth on the basis of grafted-PAA particles.

As to the PP-g-PAA/PANI films with the thickness about 0.4 μm and G_{P4} about 1.5 wt %, the conductivity

was about 0.21 S/cm at room temperature. The high conductivity of the PP-g-PAA/PANI films could be attributed to the ordered high-density structure of the surface layer in which PANI chains were tightly piled. The conductivity of the composite film was similar to that of the 1- μm PANI grafted on glass surface,⁷ but lower than that of PANI grafted on single-crystal undoped Si, (100) where the conductivity was 23 S/cm with H_2SO_4 as dopan.¹² We assume that the following points might make contributions to our results. From the AFM image [Fig. 7(b)], it is found that commercial casting PP film was flexible, but its surface was not very smooth; consequently PANI grafted onto the PP film was rougher than that grafted onto the other smooth solid substrates. In addition, from the AFM images [Fig. 7(c,d)], PAA grafted on PP film mainly existed in spheres or particles, and therefore the surface of the PP-g-PAA/PANI films was rougher than that of aniline grafted onto the other smooth substrates. Besides, PANI might be not very uniform because the commercial casting PP films contained some cracks.

Polymerization of aniline again on PP-g-PAA/PANI film to prepare PP-g-PAA/PANI/PANI film

In the presence of PANI, the polymerization of aniline exhibited autoacceleration feature because PANI had lower oxidation potential than aniline.^{30,33} In the presence of oxidant agent APS, the PANI dormant chains can be reactivated and the obtained reactive species might attack a neutral aniline monomer, which was followed by deprotonation to afford a new dormant species of higher molecular weight. Repeating this process led to the formation of PANI with higher molecular weights.²⁷ In the current research, new aniline was added and further polymerized on PP-g-PAA-

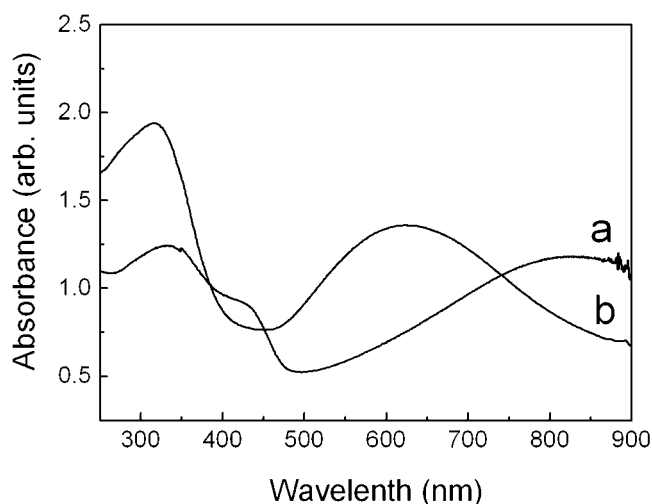


Figure 6 UV-vis spectra of (a) PP-g-PAA/PANI films; (b) PP-g-PAA/PANI films treated with NMP.

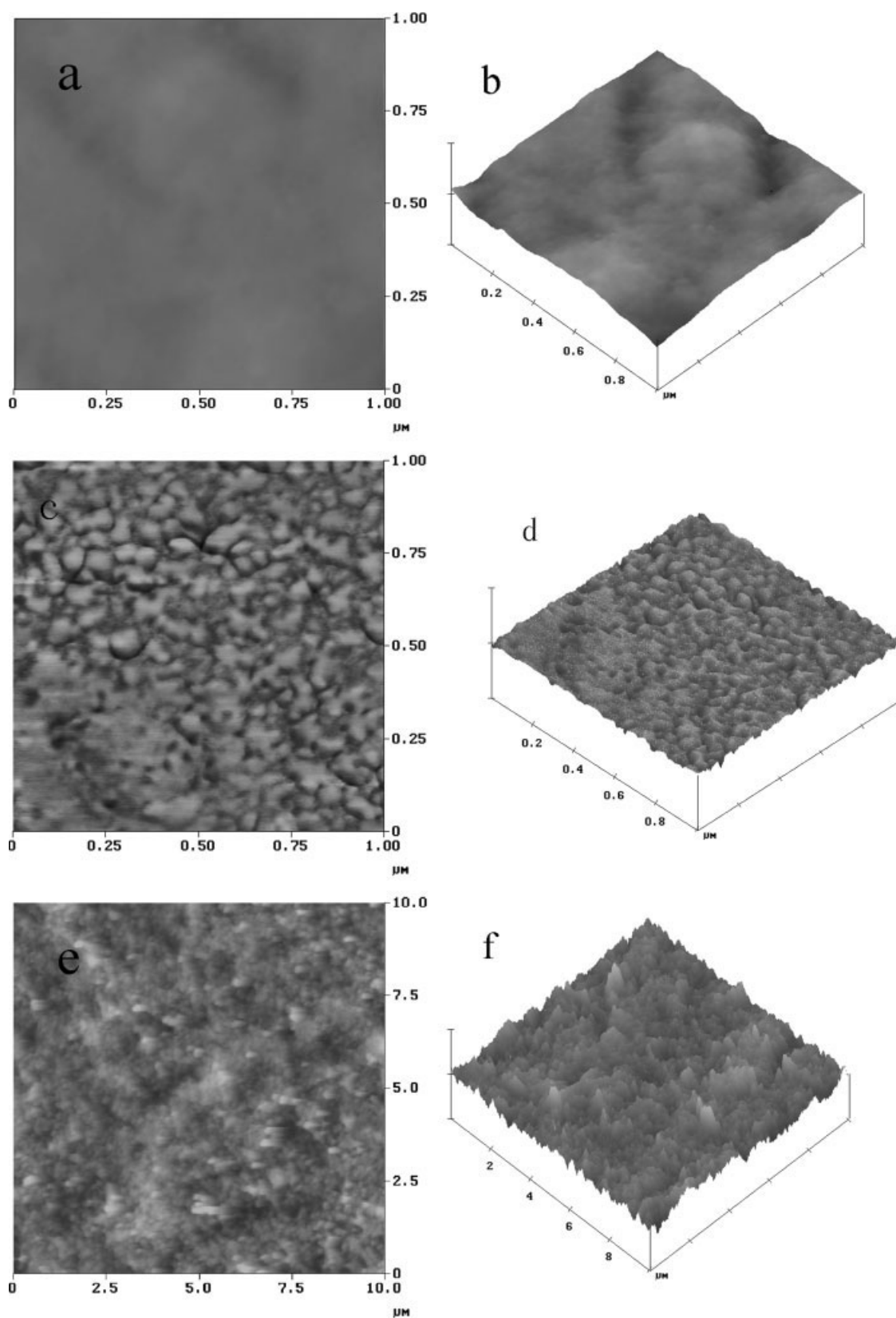


Figure 7 AFM images for (a) and (b) PP film; (c) and (d) PP-g-PAA film, G_{P1} , 1.10 wt %; (e) and (f) PP-g-PAA/PANI film, G_{P4} , 1.40 wt %.

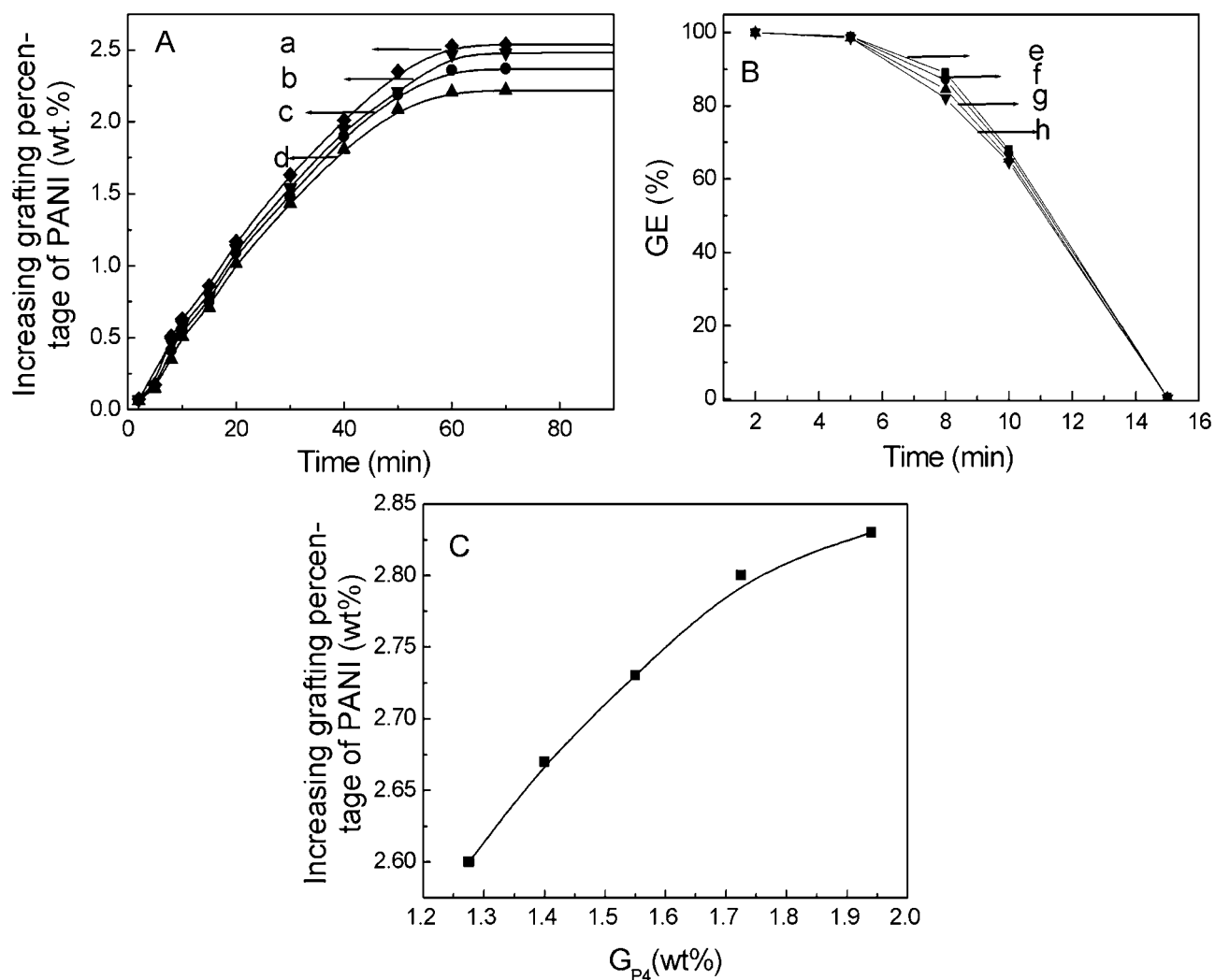


Figure 8 Effect of polymerization time on graft percentage. A: with various ahead-grafted PANI: (a) 1.5, (b) 1.0 (c) 0.5, and (d) 0.3; grafting efficiency. B: on PP-g-PAA/PANI films with various ahead-grafted PANIs: (e) 1.5, (f) 1.0, (g) 0.5, and (h) 0.3; grafting efficiency. C: relationship between the increasing grafting percentage of PANI and ahead-grafted PANI (G_{P4}). Aniline concentration, 0.1M.

PANI film via the above mechanism to improve the molecular weight of grafted PANI. Figure 8(A) shows the relationship between polymerization time and the increasing grafting PANI on the PP-g-PAA/PANI films with G_{P4} of 0.3, 0.5, 1.0, and 1.5 wt %. It was found that the quantity of grafted PANI increased with polymerization time from 2 to 60 min, and whereafter the grafting PANI quantity kept nearly constant. This result followed the mechanism of non-classical chain polymerization.²⁶ From Figure 8(B), GE increased with increasing the ahead-grafted PANI quantity and decreased with polymerization time. GE kept nearly 100% in the first 5 min showed that homopolymerization did not take place during this period. Figure 8(C) shows the direct relationship between the increased quantity of PANI on the PP-g-PAA/PANI film and the quantity of PANI previously grafted on the PP-g-PAA film. It was found that the difference in the amount of regrafted PANI was small on the PP-g-

PAA/PANI films with different G_{P4} , which resulted from the same G_{P3} and PANI chains previously grafted, and different length of PANI chains can have approximately same oxidation potentials. This result was originated in the first-obtained PANI chains grafted on PP-g-PAA film that could be reactivated again, and thus grew further upon the addition of new aniline to generate PANIs with higher molecular weights. Consequently, PP-g-PAA-PANI film with high conductivity was obtained. It is therefore reasonable to conclude that the quantity of PANI grafted on the surface of PP film and the conductivity of the composite films could be controlled by different polymerization time and/or different polymerization times.

CONCLUSIONS

The electronically conductive PP-g-PAA/PANI composite films were first synthesized by photograft poly-

merization of AA and then the oxidative polymerization of aniline on PP-g-PAA films. It was found that the PDA immobilized by chemical bonds on the film might act as "roots" for the polymerization of aniline and might shorten the induction period of the grafting polymerization of aniline due to the lower oxidation potential of PDA than that of aniline. The graft percentage of PANI could be enhanced with increasing the graft percentage of PDA on the films. PANI grafted on the PP-g-PAA film could be reactivated for the further propagation of PANI chains. The quantity of PANI grafted on the surface of PP films and the conductivity of the obtained composite films could be controlled by different polymerization time and/or different polymerization times. The PANI chains on the conducting composite films existed mainly in particles with a diameter of about 150 nm. The conductivity and the thickness of the resulted film with 1.5 wt % of PANI were about 0.21 S/cm and 0.4 μm , respectively.

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