Different Factors in the Supercritical CO_2-Assisted Grafting of Poly(acrylic acid) to Polypropylene

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ABSTRACT: The grafting of poly(acrylic acid) to polypropylene was realized with supercritical CO_2 as a substrate swelling agent and a monomer/initiator carrier. The effects of different supercritical CO_2-assisted impregnation conditions on the substrate mass increment and grafting efficiency were studied. The original isotactic polypropylene and the grafting product were characterized through IR spectroscopy, differential scanning calorimetry, and scanning electron microscopy. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4280–4285, 2006

Key words: graft copolymers; poly(propylene) (PP)

INTRODUCTION

Polypropylene (PP) is one of the most important general purpose polymers, and it is widely used in various fields, but its nonpolarity restricts its application. So, graft copolymerization by hydrogen abstraction from a tertiary carbon offers an effective approach for the introduction of some desirable properties and the expansion of its application. The grafting of polar compounds onto isotactic polypropylene (iPP) with conventional methods, such as the liquid solvent method,[1,2] UV radiation,[3] and cobalt-60 gamma radiation method,[4] have been studied. Recently, supercritical (SC) fluids, particularly for CO_2, have been widely used in materials chemistry. The advantages of with SC CO_2 have been listed elsewhere:[5,6] it is nonflammable, nontoxic, and inexpensive, and it a has high diffusivity, low viscosity, and an absence of surface tension. People have taken advantage of the properties of SC CO_2 to perform the grafting of polymers with various monomers and blend syntheses such as the maleation of iPP,[7] the grafting of *N*-cyclohexylmaleimide onto iPP,[8] and the synthesis of polystyrene/nylon 6 blends.[9] SC CO_2 is a desirable swelling agent for polymers and can dissolve many small molecules,[10–14] although it is a weak solvent for most polymers. In addition, because the density and solvent strength of SC CO_2 can be adjusted by a change in the pressure and temperature of the system, the degree of swelling in polymers and the partitioning of small molecules between the fluid phase and the substrate can be manipulated simply.

If the solute is a reactive monomer, the SC-CO_2-assisted impregnation can be followed by polymerizations, and so it is possible to prepare a massive composite[15–18] or a surface-modified organic polymer compound[19–21] or to induce the grafting of suitable polar monomers onto the polymer backbone.[22]

In this article, we describe the free-radical grafting of acrylic acid (AA) onto iPP with SC CO_2 as a carrier and swelling agent and discuss the effects of various factors, such as the pressure of CO_2, monomer concentration, and impregnation time and temperature, on the grafting level. We also focus attention on the effect of the forenamed factors on the grafting efficiency (introduced in the Experimental section). A relation between various factors and the grafting efficiency was found in this study, and this was due to complicated interactions among the additive (monomer and initiator)/SC CO_2/PP ternary system, as shown in Figure 1, which shows that there were at least four factors. The morphology and structure of the grafted and ungrafted polymer substrates were determined with scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

The iPP powder used in this study was supplied by the State Key Lab of Chemical Engineering in East
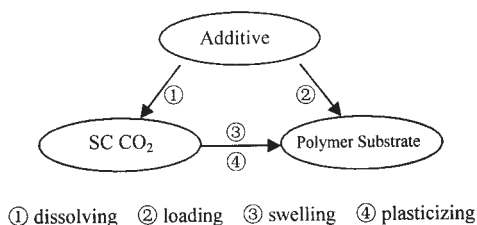
Figure 1 Complex interactions among the SC CO_2-assisted impregnation system.

China University of Science and Technology. The powder was Soxhlet-extracted from acetone for 8 h and dried in a vacuum oven at 60°C. The AA monomer (analytical grade) was produced by the Tianjin Fuchen Chemical Reagent Factory. Benzoyl peroxide (BPO) was purchased from Shanghai Sanpu Chemical Co., Ltd., and was used after recrystallization in chloroform. Acetone (analytical reagent grade) was provided by Kaifeng Chemical Reagent Factory. Carbon dioxide with a purity of 99.9% was obtained from Zhengzhou Shuangyang Gas Co. and was used as received.

Phase behavior

To measure the phase behavior of the $CO_2/AA/BPO$ system, a 50-mL optical stainless steel cell, a magnetic stirrer, a constant-temperature water bath, and a pressure gauge were assembled. The pressure gauge was accurate to 0.2 MPa in a pressure range of 0–40 MPa, and the temperature of the water bath was controlled by a Haake C10 controller.

In this experiment, a suitable amount of the AA/BPO solution was put into the optical cell, which was stabilized at desired temperature. Then, CO_2 was charged into the cell with a high-pressure pump until the solution in the cell changed from two phases to one phase with the increase of pressure and until this phase-indicated pressure could be obtained.

Grafting reactions

The pure PP films were placed into a 50-mL high-pressure stainless steel vessel together with the AA/BPO solution. The vessel was put into a heating jacket. The air in the vessel was replaced by CO_2, and then, CO_2 was compressed into the vessel to a desired pressure with the high-pressure pump. After an appropriate impregnating time, the fluid in the system was released. The impregnated film was transferred into another stainless steel vessel under the protection of N_2 for the grafting reaction at 100°C. After a reaction time of 2 h, the sample was taken out and weighed on an analytical balance with a sensitivity of 0.1 mg. Then, the sample was Soxhlet-extracted for 6 h with

acetone and dried at 60°C in vacuo to remove unreacted reagents and homopolymer.

The mass increment, grafting, and efficiency were calculated from the following relations:

$$\text{Mass increment (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

$$\text{Grafting (\%)} = \frac{W_3 - W_1}{W_1} \times 100 \quad (2)$$

$$\text{Efficiency (\%)} = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

$$= \frac{Grafting}{Mass\ increment} \times 100 \quad (3)$$

where W_1 is the weight of the original polypropylene, W_2 is the weight of the grafted polypropylene, and W_3 is the weight of the grafted polypropylene after washing by the Soxhlet extractor.

Characterization

IR spectroscopy experiments were performed with a Nicolet 460 FTIR spectrometer under standard operating conditions. A scanning electron microscope (AMRAY-1000B) at an accelerating voltage of 15 kV was used to observe the changes in the morphology of the samples. DSC measurements were conducted on a Netzsch 204 differential scanning calorimeter under a N_2 atmosphere at a heating rate of 10°C/min in a temperature range of 60–220°C.

RESULTS AND DISCUSSION

In this experiment, the impregnating processes were conducted under conditions at which CO_2, AA, and BPO existed as a single phase, which was known from the phase-behavior experiment. The mass uptake depended on the impregnating time, pressure, and temperature and the monomer concentration.

Effect of the impregnating time

The effect of the impregnating time is shown in Figure 2. Impregnating time was varied from 2 to 12 h at 60°C and 18 MPa. The original concentration of AA was 0.1 mol/L with 5 wt % BPO (based on the AA amount). The grafting reaction was carried out at 100°C for 2 h after the impregnating process. As shown in Figure 2(a), both the mass increment percentage and the grafting percentage increased with increasing impregnating time. Equilibrium was reached after an impregnating period of 10 h. When the impregnating time increased, the grafting efficiency was also enhanced,

as shown in Figure 2(b). However, the grafting efficiency could be enhanced continuously with time [Fig. 2(b)].

Effect of the impregnating pressure

Figure 3 shows the effect of the impregnating pressure in the range 10–18 MPa. The original concentration of AA was 0.1 mol/L with 5 wt % BPO, and the impregnating time was 12 h. The graft reaction took place at 100°C for 2 h. As shown in Figure 3(a), there existed different inclinations for the mass increment and graft percentage with the change in pressure. There were two factors affecting the impregnation and grafting. They were as follows: (1) an increase in the pressure resulted in the increased solvent power of CO_2, which was not favorable for the partitioning of AA in the PP
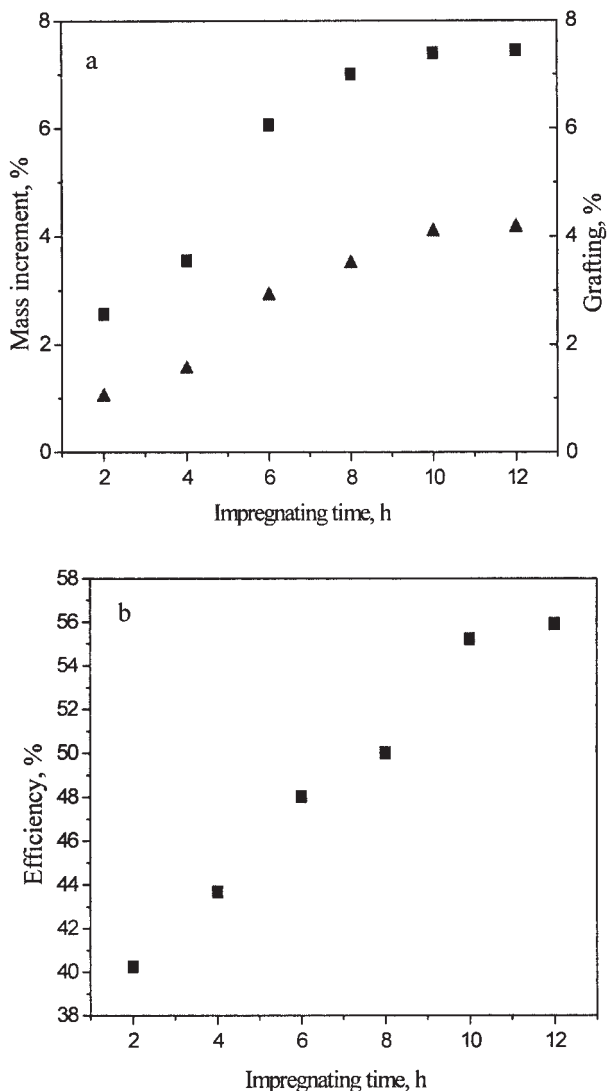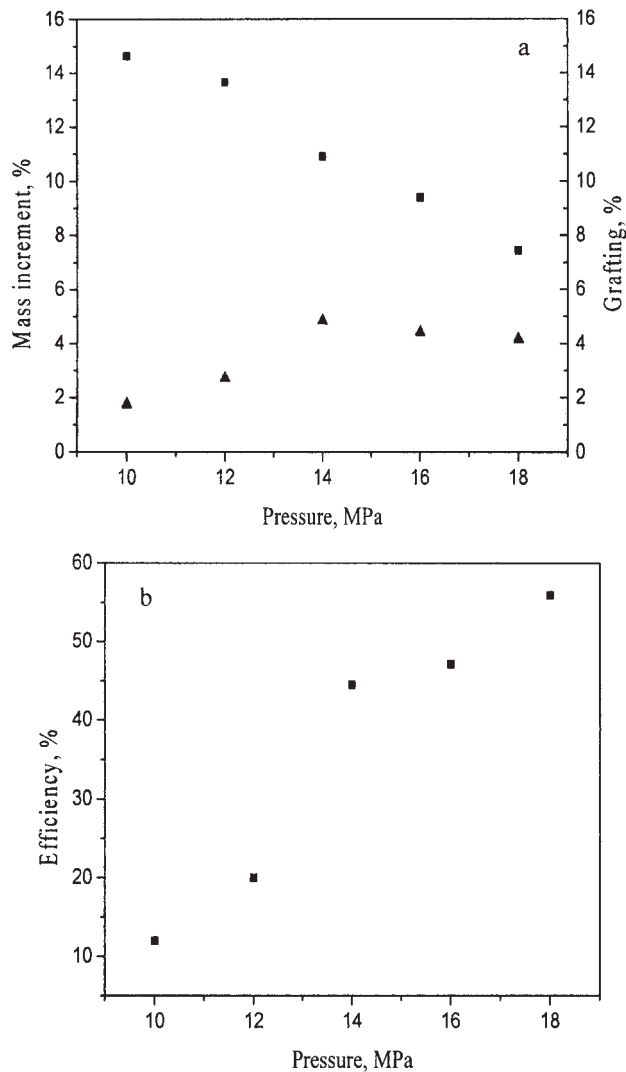

Figure 3 Effect of impregnating pressure on the (a) (■) mass increment and (▲) grafting and (b) efficiency at 60°C with an impregnating time of 12 h ([AA] = 0.1 mol/L).

matrix, and (2) an increase in the pressure of CO_2 resulted in an increase in the swelling or plasticizing of the PP substrate, which made the diffusion of the monomer and initiator in PP easier; this was favorable to the grafting reaction. For the mass increment, the first factor was always predominant during the range of pressure. For the grafting percentage, the resulting maximum on the curve at 14 MPa indicated a balance of these two factors.

In addition, from the relation of the two curves shown in Figure 3(a), the grafting efficiency was enhanced with increasing impregnating pressure [as shown in Fig. 3(b)].

Effect of the impregnating temperature

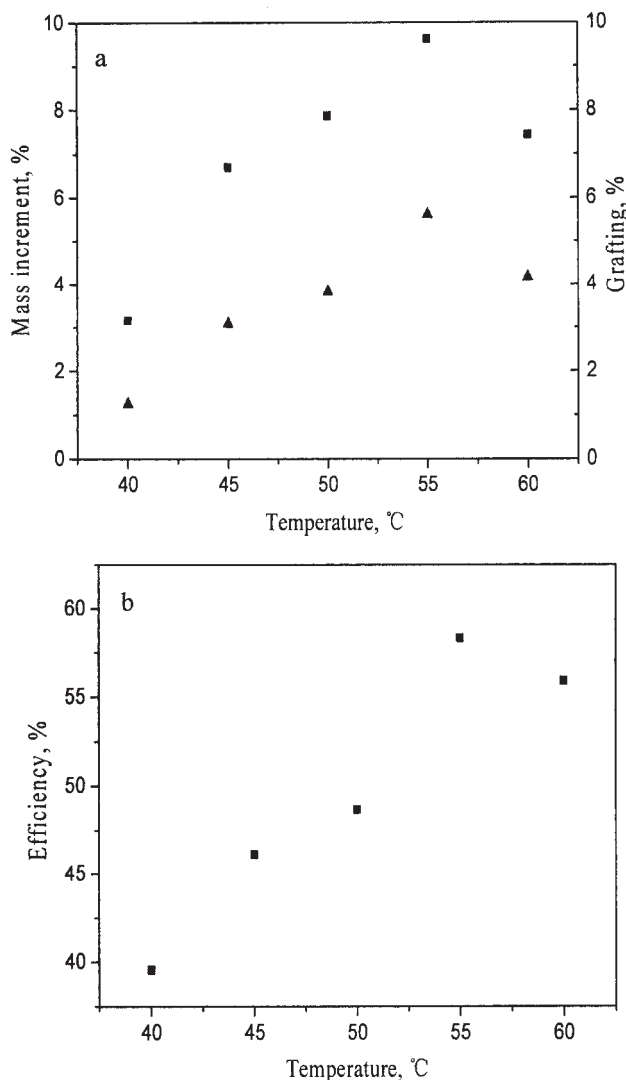Figure 4 shows the effect of the impregnating temperature in the range 40–60°C. The original concentration

Figure 2 Effect of impregnating time on the (a) (■) mass increment and (▲) grafting and (b) efficiency at 60°C and 18 MPa ([AA] = 0.1 mol/L).

Effect of the monomer concentration

A series of experiments were conducted at 60°C and 18 MPa in the impregnating process, with the AA containing 5 wt % BPO. The grafting reaction was performed at 100°C for 2 h after the impregnating process. Figure 5 shows the effect of monomer (AA) concentration on the percentages of grafting, mass increment, and efficiency.

As shown in Figure 5(a), with increasing monomer concentration, the amount of AA impregnated in the PP matrix increased continuously. On the other hand, the grafting increased initially with increasing monomer concentration up to 0.2 mol/L AA and then decreased with monomer concentration. The main reason for this was that at lower concentrations, most of the impregnated AA monomer was used by the available free-radical sites on the iPP backbone, so the
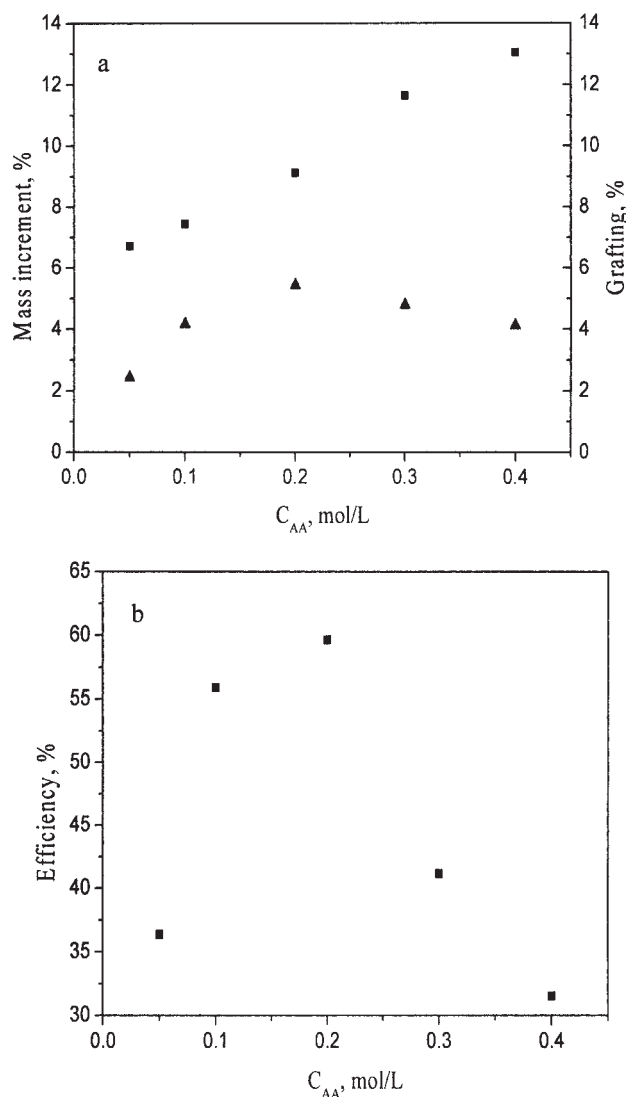
Figure 4 Effect of impregnating temperature on the (a) (■) mass increment and (▲) grafting and (b) efficiency at 18 MPa with an impregnating time of 12 h ([AA] = 0.1 mol/L).

of AA was 0.1 mol/L with 5 wt % BPO, and the impregnating time was 12 h. The graft reaction took place at 100°C for 2 h. The trends of the two curves in Figure 4(a) were similar. Both the mass increment and grafting percentage initially increased with increasing impregnating temperature and reached maximums at 55°C. An increase in the temperature resulted in decreased solvent power, and according to Figure 1, that is, on the premise that an adequate amount of AA was dissolved in the SC CO$_2$, the first factor in Figure 1 was lessened. So, comparatively, the dissolved AA was inclined to impregnate to PP. However, when temperature was increased to 60°C, the solvent power was too small, so it could not dissolve enough of the AA monomer; that is, in the completed impregnation and polymerization system, the first factor could not be granted.

Figure 5 Effect of monomer concentration on the (a) (■) mass increment and (▲) grafting and (b) efficiency at 60°C with an impregnating time of 12 h.

grafting amount increased. However, at higher concentrations, because of the limited number of free-radical sites available on the iPP backbone, the degree of homopolymerization increased, and so the grafting percentage decreased. As shown in Figure 5(b), the grafting efficiency also had a maximum point.

Characterization

IR spectroscopy measurements

The FTIR spectra of the pure iPP and the grafted sample (2.3 wt % grafting) in the wave-number range from 2000 to 500 cm^{-1} are shown in Figure 6. There was a new absorption at 1719 cm^{-1} for the carbonyl groups, which indicated that AA was grafted on to iPP.

DSC measurements

Figure 7 shows the DSC thermograms of pure iPP and the grafted samples with grafting percentages of 3.09 and 4.85 wt %, respectively. The melting temperature (T_m) and apparent enthalpy of melting (ΔH_m) obtained from the DSC curves in Figure 7 are listed in Table I. We regard T_{onset} as T_m in this work. All runs were made in a nitrogen atmosphere, and the temperature of the samples was raised from 30 to 220°C at a rate of 10°C/min.

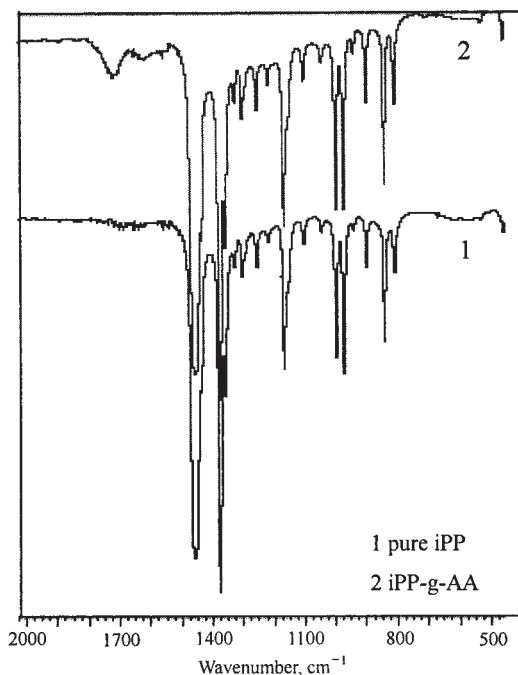The apparent crystallinity (C_a) of the iPP and the grafted iPP were calculated from the following equation:
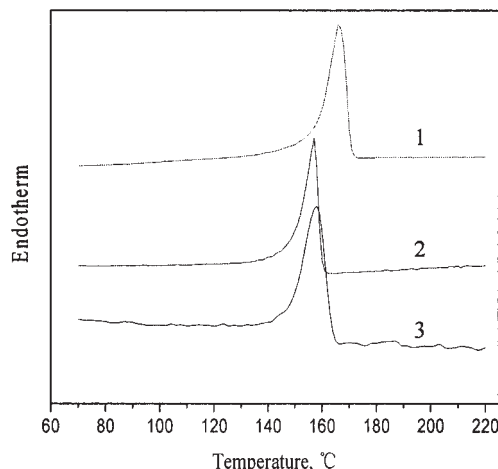

Figure 7 DSC thermographs for the (1) virgin PP, (2) 3.09% grafted iPP-g-AA specimen, and (3) 4.85% grafted iPP-g-AA specimen.

$$C_a\ (\%) = \Delta H_m/\Delta H^0 \qquad (4)$$

where ΔH^0 is the heat of fusion per gram of 100% crystalline iPP, which was 209 J/g.[23] As shown in Table I, C_a of the composites decreased as the grafting degree increased. This was probably due to the grafted branches, which disrupted the regularity of the chain structure and increased the spaces between the chains.

SEM measurements

SEM studies of the pure and grafted iPP allow us to assess the effect of grafting on morphology. The results are shown in Figure 8. After treatment with SC CO$_2$ and the grafting reaction, the surface morphology of the grafted iPP was no longer as even and homogeneous as that of virgin iPP. The grafted surfaces showed many poly(acrylic acid) microspheres formed and impregnated in the near surface region, and this made the surface dented.

CONCLUSIONS

AA and BPO were impregnated onto iPP films with SC CO$_2$ as the solvent and swelling agent, and then,

Figure 6 FTIR spectra of pure iPP and the grafted polymer (grafting = 2.3 wt %).

TABLE I
Parameters of iPP and the Composites

Sample[a]	ΔH_m (J/g)	T_m (°C)	C_a(%)
iPP	89.36	157.4	42.8
Sample A	83.63	150.5	40.0
Sample B	79.80	148.7	38.2

[a] The grafting degrees of samples A and B were 3.09 and 4.85%, respectively.
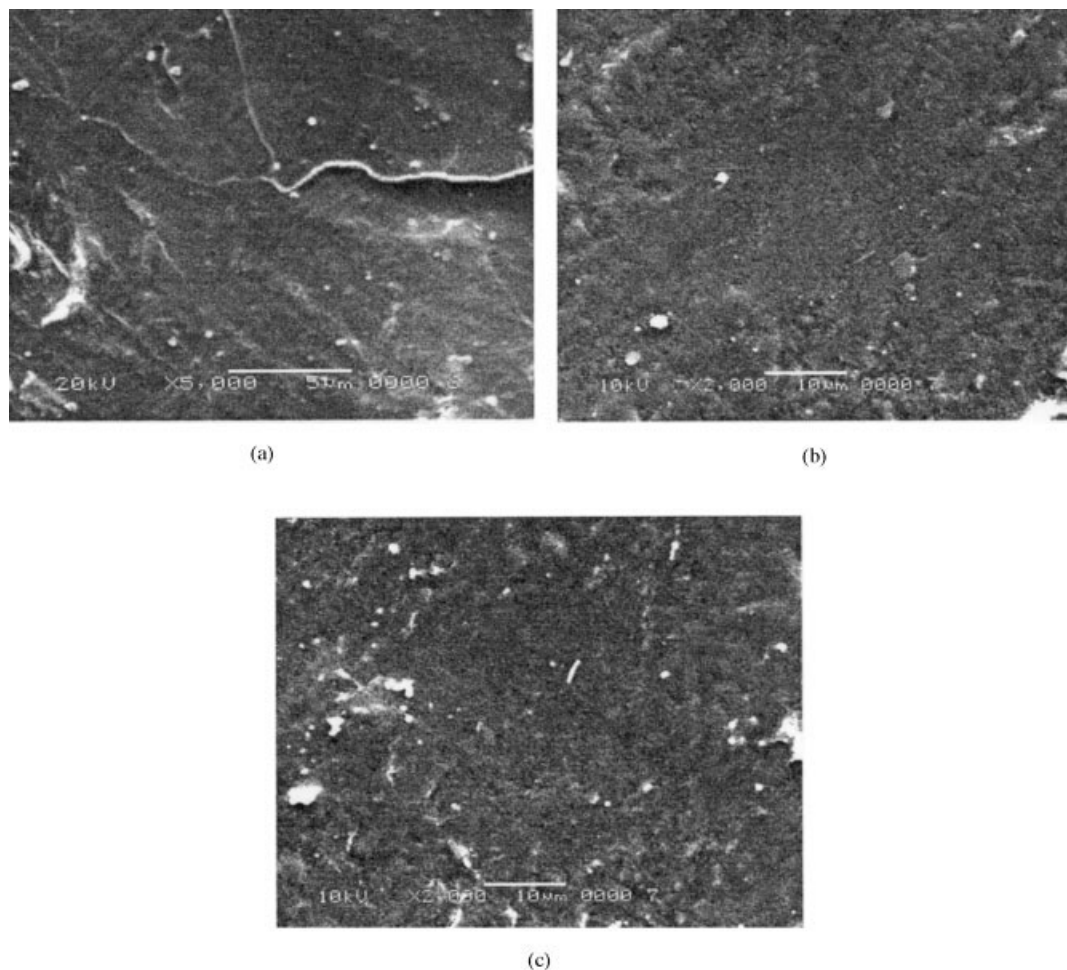
Figure 8 SEM images of the (a) virgin iPP, grafting iPP at (b) 1.55, and (c) 3.83%.

AA was grafted on iPP at higher temperatures. The different experimental conditions, including impregnating time, temperature, and pressure and monomer concentration, acted on the mass increment, grafting percentage, and grafting efficiency. DSC measurements were performed, and the results show that T_m of the grafted sample was lower than that of pure iPP and that C_a decreased with increasing grafting percentage. The SEM studies of the pure iPP and grafted iPP showed a dented structure in the grafted AA.

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