Bulk Grafting of Poly(styrene-*alt*-maleic anhydride) Onto Preirradiated Polyolefin Membranes in Supercritical Carbon Dioxide

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ABSTRACT: To take advantage of the property of supercritical carbon dioxide as both a solvent and swelling agent, the bulk grafting of poly(styrene-*alt*-maleic anhydride) [P(MAH-*alt*-St)] onto preirradiated polyolefin membranes was performed by a combination of γ-ray-preirradiation-induced graft copolymerization and supercritical fluid-swollen polymerization. The trapped radicals on the polyolefin backbones were uniformly distributed by γ-ray irradiation under a nitrogen atmosphere. Subsequently, these polymeric trapped radicals initiated the alternating copolymerization of styrene (St) and maleic anhydride (MAH) infused into the swollen polymer matrix with the aid of supercritical CO_2. It was important that the graft copolymers were relatively pure without any contaminants, including homopolymers, monomers, and initiators. The experimental results show that the degree of grafting could be easily controlled. In addition, St/MAH could synergistically promote the bulk grafting process and strongly effect on the alternating trend; this was confirmed by element analysis and differential scanning calorimetry. Soxhlet extraction, X-ray diffraction, and Fourier transform infrared spectroscopy indicated that the P(MAH-*alt*-St) was covalently bonded to the polymeric backbones. Scanning electron microscopy showed that the alternating graft chains were uniformly dispersed throughout the 5-mm thickness of the polymer membranes on the nanometer scale. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Graft copolymerization has been well known as an efficient method for the modification of the chemical and physical properties of various existing materials; it can be tailored to meet specific demands within a wide variety of compositions.[1–4] The properties of the graft copolymer depend not only on the grafted monomers, the degree of grafting, and the distribution of the grafted chain throughout the polymeric backbone but also on the initiation manner. Generally, γ-ray-radiation-induced graft copolymerization is an attractive and economical method for the chemical modification of preexisting polymeric materials without any initiators. Because γ-ray irradiation can penetrate thick polymeric materials to generate active sites, the irradiated polymers are allowed to react with vinyl monomers and then propagate to form side chains on the polymer main chains.[5] When the polymeric materials are first preirradiated in the absence of oxygen, trapped radicals are formed in the polymeric backbone and directly initiate the polymerization of vinyl monomers by a grafting-from technique. Alternatively, when polymers are irradiated in air or oxygen, macromolecular peroxides can be formed in the polymer chains and then thermally decomposed to initiate the graft copolymerization. Unlike the chemical initiation method, the radiation-induced process leaves no detrimental initiators.

The graft copolymerization of a binary monomer system onto parent polymers is of special importance in comparison with simple grafting of an individual monomer because the process has the advantage of introducing functional groups of different polymer moieties with different properties. During the past decade, extensive investigation has been carried out to prepare various graft copolymers based on styrene (St) and maleic anhydride (MAH) by means of solid-phase graft copolymerizaiton.[6–17] However, these methods suffer from several drawbacks, including the need for a high temperature, the lower degree of grafting, and the accompanying production of homopolymer and unreacted monomers. To overcome these limitations, in a previous study,[18,19] we designed a green and versatile process for bulk grafting polymerization with the individual monomer onto preirradiated polyolefins with the aid of a supercritical carbon dioxide swelling technique. It is generally known that the advantages of using supercritical CO_2 as a solvent and swelling agent include its adjustable solvent strength,[20–24] its ability to plasticize glassy

Additional Supporting Information may be found in the online version of this article.
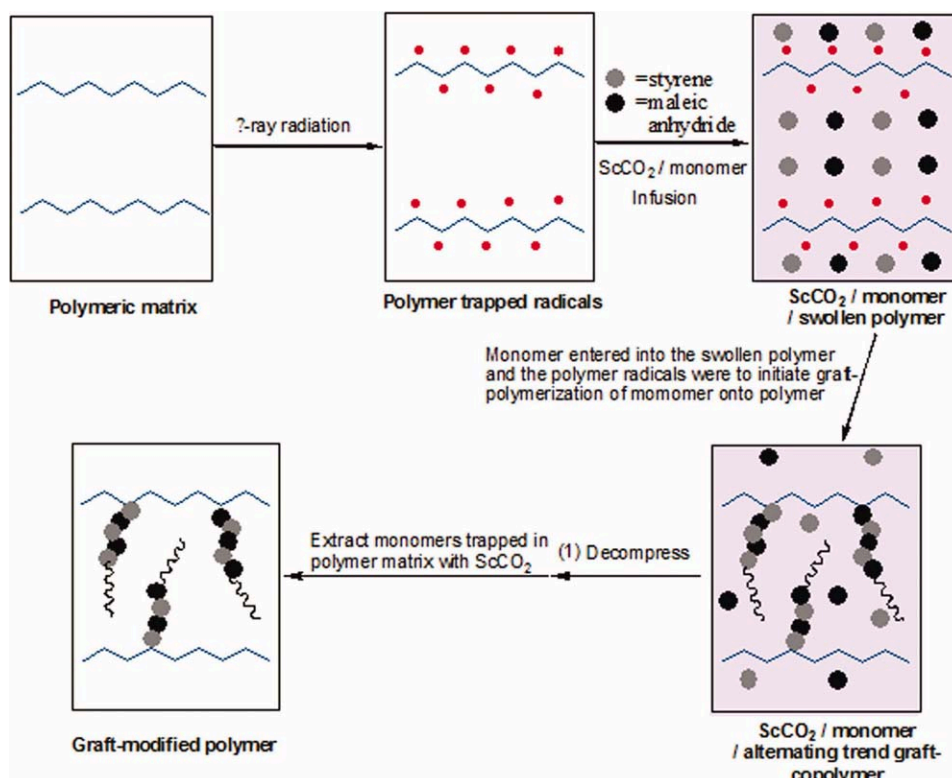
Figure 1. Schematic representation of the uniformly bulk alternating graft copolymerization of P(MAH-*alt*-St) to the γ-ray-activated preexisting polymer materials with supercritical CO_2 as both a solvent and swelling agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers, and the enhancement of the diffusion rate of the monomers.[25] It has been further noted that supercritical CO_2 can swell most polymers, including those generally considered to be solvent resistant.[23,26] Additionally, CO_2 is a gas at ambient temperature; hence, the solvent rapidly dissipates upon the release of pressure. Because of the unique properties of supercritical CO_2, supercritical CO_2-assisted graft polymerizations have been reported for the synthesis of bulk graft copolymers onto preformed membranes that involved supercritical CO_2-assisted infusion of reagents and initiators, and the subsequent graft polymerization was carried on within the organic polymer substrates.[27–31] However, the technique also requires a high temperature for the decomposition of initiators, yields a lower degree of grafting, and is accompanied by the production of homopolymer.

In this study, our strategy took advantage of the facts that well-defined alternating poly(styrene-*alt*-maleic anhydride) [P(MAH-*alt*-St)] can be synthesized in supercritical CO_2 and that γ rays have a high penetration depth in various polymers so that pure graft copolymers with an alternating trend can be obtained (Figure 1).[32] Radicals homogeneously trapped by means of γ-ray preirradiation were used to initiate the alternating graft copolymerization of St and MAH infused into the inner layer of polymer substrates with the aid of supercritical CO_2 at 45°C. After the polymerization reaction, the unreacted monomers were further extracted via supercritical CO_2 without any residue. Of importance, supercritical CO_2 did not interfere with the

chain-growth process during polymerization. Therefore, the binary grafting component could be easily obtained throughout the polymer matrix without any contaminants.

EXPERIMENTAL

Materials

Powders of polypropylene (PP; $\sim$ 65% crystallinity) and low-density polyethylene (LDPE) were obtained from Liaoyang Petrochemical Corp., Ltd. (Liao Yang, China), and the PP and LDPE membranes (thickness $\approx$ 5 mm) were pressed at 180–230°C. St was distilled from calcium hydride under reduced pressure. MAH was recrystallized from chloroform. Carbon dioxide (99.995%) was obtained from the Dalian Institute of Special Gases (Dalian, China) and was used as received.

Grafting Reaction

Membranes with dimensions of $30 \times 10 \times 5.0$ mm^3 were first put into a glass ampule under an inert atmosphere and irradiated in a cobalt 60 resource (Fuan Radiation Technology, Ltd., Dalian, China) at 100,000 Ci with a dose rate of 6 kGy/h for 10 h. In the preirradiation procedure, the substrate was first irradiated to generate relatively stable free radicals by cleavage at C—H. After irradiation, the samples were stored rapidly at low temperature of less than −20°C before the grafting reaction.

With St and MAH as comonomers, the graft copolymerization was carried out for PP and LDPE in a 60-mL stainless steel autoclave. The autoclave was charged with the irradiated

samples, St and MAH in a nitrogen atmosphere, respectively, and then, different weights of liquid CO_2 for the allotted pressure (e.g., 35 g of CO_2 normally reached 7.5 MPa, and 45 g of CO_2 normally reached 9.0 MPa at 45°C.). For the graft copolymerization, the autoclave was immediately heated to 45°C. At the end of the reaction, the samples were extracted to remove the unreacted monomers with fresh CO_2. With a Soxhlet apparatus, the grafted samples were further extracted by acetone for 48 h. Then, the samples were dried at 80°C *in vacuo*. The degree of grafting was calculated as follows:

$$\text{Degree of grafting (\%)} = (W - W_0)/W_0 \times 100\% \quad (1)$$

where W_0 and W are the sample weights before and after grafting, respectively.

Instrument and Characterization

Fourier transform infrared (FTIR) spectra of the polymers were recorded on a Nicolet NEXUS 430 FTIR spectrophotometer (Jasco Co. Tokyo, Japan).

The morphology of the polymer samples was observed with a KYKY-2800B scanning electron microscope (KYKY Technology Development, Ltd., Beijing, China) in the normal secondary electron imaging mode. The surfaces of the samples were coated with gold to prevent charging under the electron beam.

The thermal properties of the polymer membranes were determined on a Netzsch DSC 204 (Selb, Germany) instrument under a nitrogen atmosphere with a heating rate of 10 K/min.

The element analysis of the graft copolymer was performed on a Vario El III (Elementar, Germany), and the content of MAH units in the graft copolymer was determined. The precision of elemental analysis was less than 0.1%. The molar ratio for MAH/MAH+St (MAH/MAH + St) was calculated with the following equations:

$$\begin{aligned} \text{Degree of grafting(\%)} &= (W - W_0)/W_0 \times 100\% \\ &= (104m + 98z)/42n \times 100\% \quad (2) \end{aligned}$$

where m, z, and n are the molar repeating units of PP, polystyrene, and poly(maleic anhydride), respectively:

$$(96m + 48z + 36n)/(104m + 98z + 42n) = C \quad (3)$$

where C is the carbon content of the graft copolymer:

$$48z/(104m + 98z + 42n) = O \quad (4)$$

where O is the oxygen content of the graft copolymer:

$$G = [1/O_0 \times (C_0 - C_1)]/[C_0(1/O - 1/O_0) - (C - O)/O] \quad (5)$$

where G is the degree of grafting, C_0 and C_1 are the carbon contents of polystyrene and PP, respectively, and O_0 is the oxygen content of the poly(maleic anhydride) in the graft copolymer.

The dynamic contact angles (DCAs) of the specimens were measured at room temperature with the Wilhelmy plate method (CAHN Instruments, Inc., model DCA 322, Cerritos, USA) at 20°C. The samples were immersed in and drawn out of
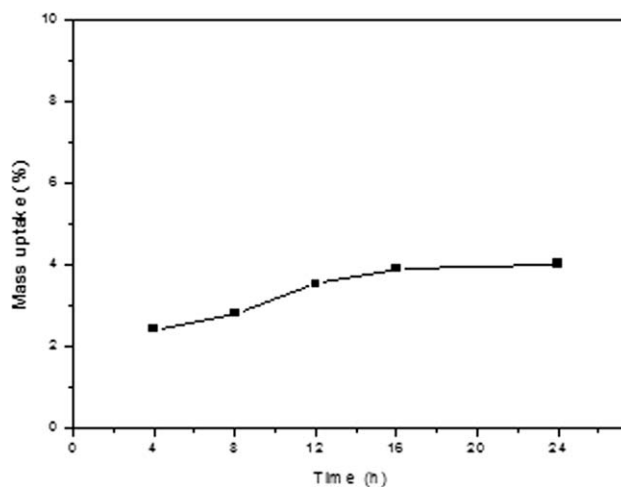
Figure 2. Absorption for St and MAH in PP from a 0.68 mol/L solution of St and MAH in CO_2 at 45°C and 10 MPa.

deionized water at a rate of 80 μm/s. Then, the advancing contact angle (θ_{adv}) and receding contact angle (θ_{rec}) were obtained. It is generally known that θ_{adv} indicates the hydrophobicity and θ_{rec} expresses the hydrophilicity of surfaces.

RESULTS AND DISCUSSION

Phase Behavior

To better determine how the graft copolymers were formed, the equilibrium uptakes of St and MAH for PP were determined under a given a set of processing conditions (45°C and 10 MPa). Smith et al.[33] reported that the swelling degree of PP was about 5% at 10 MPa in the presence of CO_2. Hence, the binary monomer mixtures could be quickly infused into the polymeric matrix with the aid of the supercritical CO_2. The concentrations of St and MAH in the fluid phase were 0.68 mol/L. The polymer samples were soaked for various lengths of time and were then vented. As shown in Figure 2, the mass uptake percentage of the samples increased with increasing impregnating time. The mass uptake of the equilibrium was found to be 4.0% after an impregnating period of 16 h.

Bulk Graft Polymerization without Homopolymers

Usually, the radiation-induced graft copolymerization of polymeric membranes is carried out in an organic solvent.[34,35] The addition of a good-swelling organic solvent probably results in bulk grafting in some cases. However, the polymer radicals will easily transfer to the monomers and solvent because of the high viscosity in the graft region, and thus, much more ungrafted homopolymers are produced. The major problem for widespread industrial development of graft copolymerization encountered is the simultaneous formation of homopolymer in the graft copolymerization.[36] On the contrary, because supercritical CO_2 offers some advantages as a solvent, such as a low solution viscosity, an effectively inert solution medium, and a tunable solvent strength, the propagation of polymer chain transfer to the solvent did not occur. Hence, we did not observe the formation of homopolymers in this graft copolymerization process. As expected, no observable loss in weight was found in the resulting products with a grafting degree of up to about

Table I. Free-Radical Polymerization of St and MAH from Various 5 mm Thick γ-Ray-Activated Polymer Membranes[a]

| Run	Polymer	Monomer ratio (MAH/St)	Time (h)	Pressure (MPa)	Degree of grafting (%)	MAH/(MAH + St) (%)[b]
1	PP	1 : 1	8	7.5	36.3	48.4
2	PP	1 : 2	8	7.5	32.8	36.7
3	PP	1 : 10	8	7.5	28.1	17.9
4	PP	1 : 1	20	7.5	154.3	47.3
5	PP	1 : 1	4	7.5	20.3	53.7
6	PP	1 : 1	8	15.0	8.4	—
7[c]	PP	—	8	7.5	24.8	—
8[d]	PP	—	8	75	2.7	—
9	PP	1 : 1	8	10.0	54.7	—
10	LDPE	1 : 1	4	75	13.4	46.6

[a]The graft polymerization was carried out with the use of St as a comonomer, and the St concentration was 0.68 mol/L. The membranes were irradiated in a cobalt 60 resource (Fuan Radiation Technology, Ltd.) at 100,000 Ci with a dose rate of 6 kGy/h for 10 h, [b]The molar ratio for MAH/MAH+St was calculated by element analysis, [c]Only individual St as a monomer, [d]Only individual MAH as a monomer.

182.4% after further extraction for 48 h. However, without the aid of the supercritical carbon dioxide, the grafting polymerization only occurred on the surface of the polymer membranes, and many homopolymers were produced in accordance with our previous studies.[18,19]

**Alternating Graft Copolymerization with St and MAH onto Polyolefin**

With the PP membrane as the model substrate, the degrees of grafting of individual St, individual MAH, and St/MAH binary monomers were investigated. The results are listed in Table I. It can be seen that the degree of grafting for the St/MAH binary monomers was much higher than that of St or MAH alone under the same conditions. The results indicate that the St/MAH binary monomers could synergistically promote the bulk grafting process. In addition, the carbonyl groups had specific interactions with CO_2, which were beneficial to the enhancement of plasticization and swelling for the polymer membranes so that the monomers were easily transported into the grafting samples.[37] Furthermore, the effect of the St/MAH molar ratio on bulk grafting was examined. Apparently, the maximum of degree grafting could be always attained at a 1 : 1 molar feed ratio of MAH to St; this indicated that charge-transfer complexes (CTCs) between the binary monomers were formed. Thereby, this result confirms that apparently the effect of CTC was a key factor contributing to the facile alternating graft copolymerization. Moreover, the experimental parameters, such as pressure and time, all played crucial roles in determining the grafting rate. These were investigated with respect to the degree of grafting. An increase in the pressure resulted in a maximum degree of grafting (Table I, run 1, 6 and 9). This behavior was ascribed to the changing solubility parameter of supercritical CO_2. At a higher pressure, the CO_2 solution could swell the PP well so that the infusion of monomers was quicker. However, because the fluid phase was a better solvent, St and MAH partitioned more preferentially in the fluid phase. This was not favorable for the absorption of St and MAH into the polymer matrix. Hence, the maximum of the degree of grafting occurred with a balance of the competing factors.

There was a strong tendency toward the formation of CTCs in the donor–acceptor monomer system between St and MAH, and consequently, these pairs underwent alternating copolymerization. The extensively CTC-forming monomer pairs were studied by the combination of St and MAH, which could be alternatively copolymerized under ordinary free-radical-initiating techniques in supercritical CO_2.[32] When the molar ratio of St to MAH was altered within the range of 1 : 10 to 2 : 1 (Table I, runs 1–3), the degree of grafting was highest when the proper monomer ratio was 1 : 1. The element analysis demonstrated that the ratio of the polystyrene to poly(maleic anhydride) was calculated to be approximately 1 : 1 (runs 4 and 5). It is well known that MAH does not homopolymerize in the presence of St; instead, it forms a complexomer with St and reduces the chance of St homopolymerization.[38] In addition, the glass transition of the alternating graft copolymer was examined by a differential scanning calorimetry (DSC) profile (Figure 6, shown
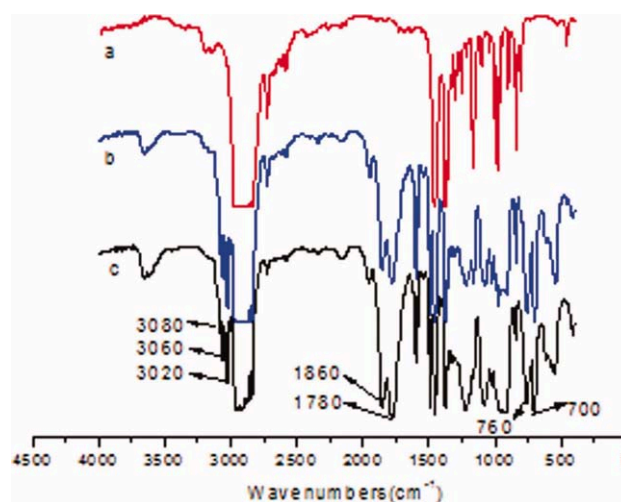
Figure 3. FTIR spectra of the (a) original PP and (b) inner and (c) outer layers of a typical PP-*g*-P(MAH-*alt*-St) sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
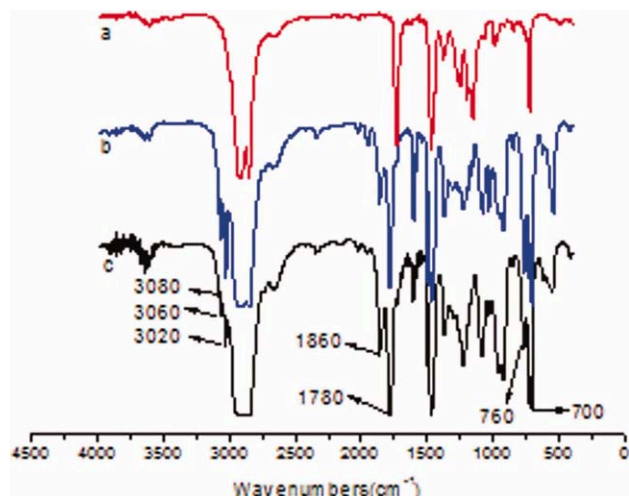
Figure 4. FTIR spectra of the (a) original LDPE and (b) inner and (c) outer layers of a typical LDPE-*g*-P(MAH-*alt*-St) sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

later). These results provided valuable information that strongly proved the alternating graft copolymerization with St and MAH onto polyolefin.

Graft Copolymer Characterization

Figures 3 and 4 show the FTIR spectra of raw PP, PP-*g*-P(MAH-*alt*-St), raw LDPE, and LDPE-*g*-P(MAH-*alt*-St) at the outer and inner layers, which were turned on a lathe (Figure 6 in the Supporting Information) according to the required thickness. In contrast to the FTIR spectrum of raw polyolefin, the appearance of new absorbance peaks at 1780 and 1860 cm^{-1}, which corresponded to the symmetric and asymmetric stretching of carbonyl groups, and more peaks at 3060 and 760 cm^{-1} (the characteristic absorption of the grafted St) indicated that the St and MAH were successfully introduced onto PP and LDPE.

The homogeneity of the bulk graft modification was evaluated by comparison with the characteristic absorption bands of the side graft chain at the outer and inner layers of the grafted samples. To do this, the FTIR spectra were taken at the edge and at the center. It was confirmed that the bulk graft modification was uniformly achieved by the similar intensity of the absorption band from St and MAH of the grafted polymer at the outer and inner layers. Moreover, the content and distribution of the graft component could be controlled by adjustment of the reaction parameters and the monomer ratio in the supercritical fluid.
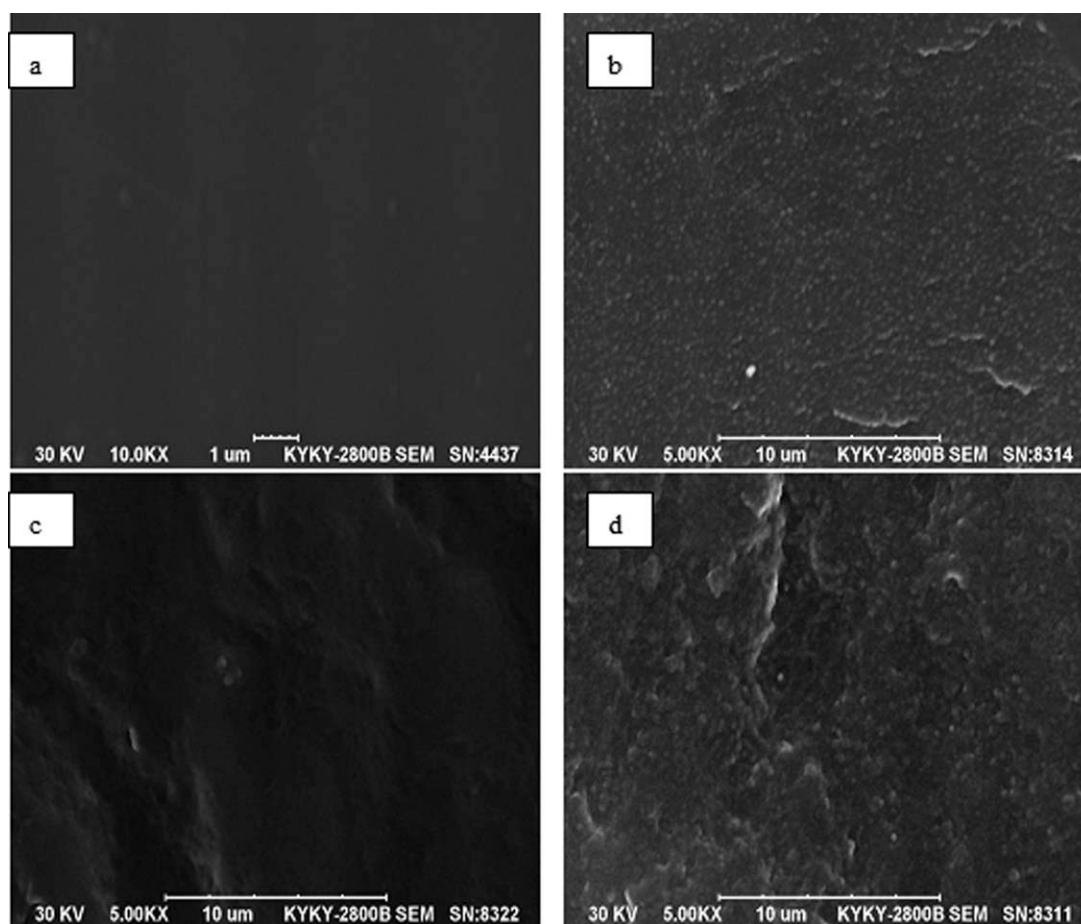

Figure 5. Scanning electron micrographs of the (a) virginal PP membrane, (b) PP-*g*-P(MAH-*alt*-St) membrane with a degree of grafting of 158%, (c) virginal LDPE membrane, and (d) LDPE-*g*-P(MAH-*alt*-St) membrane with degree of grafting of 92%.
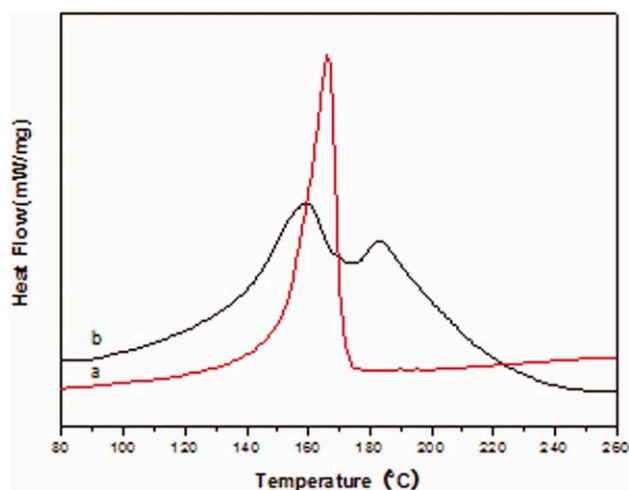
Figure 6. DSC curves of (a) PP and (b) PP-*g*-P(MAH-*alt*-St) with a degree of grafting of 154.3%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The fractured cross-sectional morphology of the PP and LDPE samples was measured by scanning electron microscopy before and after grafting. As shown in Figure 5, the cross-sectional structures of membranes were significantly different from those of the ungrafted substrates. The gray continuous regions correspond to the graft component with different sizes, spreading from 100 to 300 nm in diameter, and appear as islands in Figure 5(b,d). A well-proportioned dispersion of P(MAH-*alt*-St) particles in the PP and LDPE matrix was formed throughout the entire samples because of the low viscosity and high diffusivity inherent to supercritical CO_2 and a uniform distribution of trapped radicals throughout the thickness of the irradiated samples due to γ-ray penetration.

The melting endotherms were determined with DSC for the PP and a PP-*g*-P(MAH-*alt*-St) samples with a degree of grafting
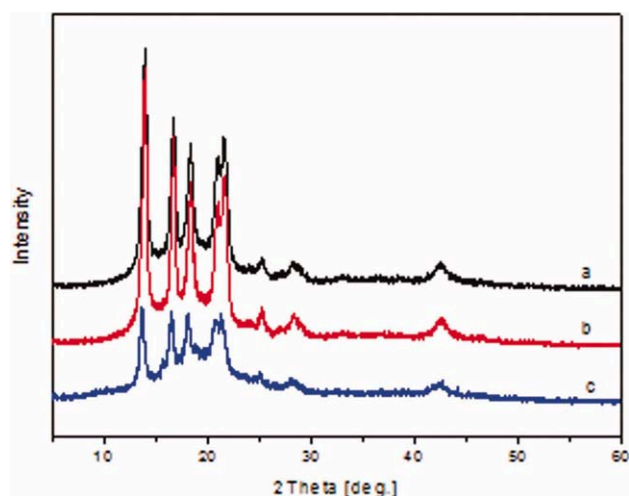
Figure 7. XRD spectra of (a) original PP, (b) irradiated PP, and (c) PP-*g*-P(MAH-*alt*-St) sample with the degree of grafting about 69.4%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
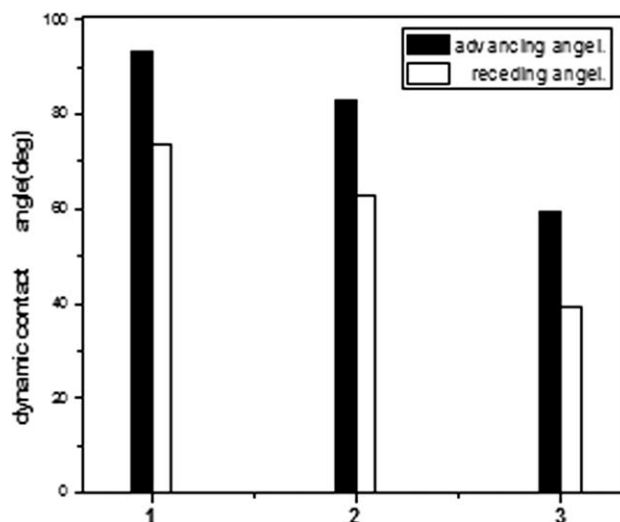
Figure 8. DCAs for (1) PP, (2) PP-*g*-P(MAH-*alt*-St) with a degree of grafting of 121.6%, and (3) PP-*g*-P(MAH-*alt*-St) with a degree of grafting of 158.8%.

about 154.3% (Figure 6). The St/MAH alternating copolymers often showed a single phase transition for the glass transition, which corresponded to the glass transition of St at about 100°C and ranged from 160 to 202°C.[32] The final graft copolymer possessed only one glass-transition temperature for P(MAH-*alt*-St) (a grafting chain) at 177.6°C and another melting peak for the PP substrate at 159.5°C. This also strongly supported the conclusion that an alternating graft copolymer was achieved.

To verify whether or not the grafting process induced changes in the crystallinity of PP, X-ray diffraction (XRD) measurements were carried out for the PP, irradiated PP, and PP-*g*-P(MAH-*alt*-St) samples with a degree of grafting of about 69.4% (Figure 7). The results clearly show that there was no change or shift in the positions of the peaks; this indicated that no change occurred in the crystalline form of the original PP and grafted samples. The properties of the original PP were similar to those of the irradiated PP samples. The grafting of St and MAH onto PP reduced the intensity of the peaks, but the crystallinity of the PP portion of the grafting sample remained almost unchanged, mainly because the graft predominately occurred in an amorphous part of the PP substrate.

DCA analysis was used for the measurement of θ_{adv} and θ_{rec}. For the graft copolymer, a decrease in θ_{adv} and θ_{rec} was compared to those of the original PP. It is generally accepted that θ_{rec} indicates the hydrophilicity of surfaces, whereas θ_{adv} represents the hydrophobicity. Both θ_{adv} and θ_{rec} were determined for the grafted polymer, and the mean values of at least three measurements are shown in Figure 8. Hence, these values were significantly lower and reflected the hydrophilic species present at the surface.

CONCLUSIONS

In this study, the alternating graft copolymerization of St and MAH onto preirradiated PP and polyethylene was performed with supercritical CO_2 as both the solvent and swelling agent under mild conditions. The grafting components were

uniformly distributed throughout the bulk polyolefin membrane. Moreover, this method also could be applied to prepare similar graft copolymers with a variety of binary monomer systems into preformed polymeric matrices with high viscosity or limited solubility. The grafting process was not accompanied by any solvent or by the formation of ungrafted homopolymers far from contamination; this indicated potential application in the medical industry.

ACKNOWLEDGMENTS

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