

Surface modification of polypropylene by the entrapping method using the short-chained stearyl-alcohol poly(ethylene oxide) ether modifier

Haofei Guo,¹ Juexin Huang,¹ Yuansong Ye,¹ Jian Huang,¹ Xiaolin Wang²

¹College of Material Science and Engineering, Nanjing Tech University, Nanjing 210009, China

²Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Correspondence to: J. Huang (E-mail: jhuang@njtech.edu.cn)

ABSTRACT: On the basis of the short-chained modifier of stearyl-alcohol poly(ethylene oxide) ether (AEO), an entrapping modification was carried out on the polypropylene (PP) surface for hydrophilic improvement. A swelling layer was confirmed locating in the amorphous region on the PP surface, from which the modifiers could penetrate into the surface. The AEO-8 modifier achieved the optimal hydrophilic modification on the surface with a contact angle of 20.6° and modifier coverage of 19.2%. A microphase separation was speculated to occur between the poly(ethylene oxide) (PEO) chain of AEO and the PP substrate in the entrapping surface, after which surface-enriched PEO chains could improve surface hydrophilicity, simultaneously, reserved stearyl chains in the surface could approach modifier fixation. Water immersion durability of the modified surface could be improved by establishing a covalent linkage in the surface-fixed structure. This work gives more comprehensive insights in the entrapping modification on the semi-crystalline PP surface based on the short-chained and block modifier. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43607.

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INTRODUCTION

Surface modification is the more effective way to render new surface functions on polymer surfaces, such as hydrophilicity, biocompatibility, adhesion, and lubrication, without influencing their bulk properties.^{1,2} The general modification strategies are to introduce functional groups onto the polymer surfaces by means of plasma treatment,³ UV radiation,⁴ chemical graft² or surface coating.⁵ In recent years, the entrapping modification method by embedding modifiers into the pre-swollen polymer surface has attracted much attention due to its convenient, effective, and low-cost characters.^{6–11} On the basis of the solid–liquid contact technique, the entrapping modification is especially suitable for surface modification of the porous polymer matrix like separation membranes.^{6–10} Benefiting from the pre-swelling technique, the entrapping modification can be potentially applied to the membrane surface modification during the membrane preparation, such as that by the thermally induced phase separation (TIPS) method.^{12,13}

The early studies in the entrapping modification were reported by Ruckenstein and Desai,^{14–16} who entrapped hydrophilic polymer modifiers, including poly(ethylene oxide) (PEO), poly(ethylene oxide-propylene oxide), and poly(*N*-vinylpyrrolidone-vinyl acetate), into hydrophobic polymer surfaces for biocompatible improvement. In their modification method, the polymer substrate was first immersed for a short time into an organic solution con-

taining the modifiers, and then introduced immediately into a container filled with the extraction solvent. Therein, the short contact with the organic solution allows an appropriate swelling on the substrate surface and is helpful for modifier implantation into the swollen surface. The subsequent contact with the extraction solvent allows a rapid deswelling to remove swelling agents from the swollen surface and fix the modifiers. Following this entrapping technique, some polymer modifiers, including polysaccharide, protein, chitosan, PEO, and poly(L-lysine), have been used in the biocompatible modification on the poly(lactic acid) surface.^{11,17–21}

In addition to the polymer modifiers, both Ruckenstein and Desai have attempted to entrap short-chained modifiers, namely sodium dodecyl sulfate, sodium dioctyl sulfosuccinate,¹⁴ and PEO with low molar mass,¹⁵ into the polymer surfaces. Nevertheless, any efforts from them were demonstrated unsuccessful. Desai indicated that the entrapping modification heavily depended on the chain length of the modifier.¹⁵ In their entrapping modification on the poly(ethylene terephthalate) (PET) surface, only the PEO modifier with the moderate molar mass of 18,500 could reach the maximum deposition amount. They thought that the PEO modifiers with the lower molar mass were easy to be leached out following swelling agents by the extraction solvent, and the PEO modifiers with the higher molar mass were difficult to penetrate into the swollen polymer surface.

In our group, however, some commercial and short-chained modifiers, such as stearyl-alcohol poly(ethylene oxide) ether (AEO),^{6–8} and perfluoroalkyl poly(ethylene oxide) ester,⁹ were confirmed feasible in the entrapping modification on surfaces of polypropylene (PP),^{6–8} polyethylene (PE),⁸ and poly(vinylidene fluoride) (PVDF).⁹ These modifiers were chosen because they are in the block structure, possessing a hydrophilic segment and a hydrophobic segment. Moreover, the hydrophobic segments should be compatible with the polymer substrates used in the entrapping modification. For these short-chained modifiers, a slower but simpler deswelling method of vacuum drying was adopted to remove the swelling agents for avoiding the great modifier leaching from the swollen surface, as mentioned by Desai in their deswelling by the solvent extraction method.¹⁵ On the basis of the compatibility of the hydrophilic segments of the block modifiers with the polymer substrates, there is less doubt that the entrapped modifiers in the surfaces would be repulsed by the substrate polymers during the slower deswelling. Nevertheless, significant chain repulsion tended to occur in the modified surface by the homopolymer modifier.^{15,16}

Although the short-chained and block modifiers were available in the entrapping modification, the detailed entrapping mechanism concerned with formation of the swelling layer, the hydrophilic–lipophile character of the block modifier, and hydrophilicity acquirement on the modified surface, has not been well clarified. By applying a series of AEOs with various PEO chain lengths as modifiers, this article deals with detailed investigation into the entrapping modification on the semi-crystalline PP surface. After which, an entrapping mechanism is proposed. On the basis of the short-chained modifier, hydrophilic durability of the modified surface is also evaluated.

EXPERIMENTAL

Materials

The polypropylene (PP) film, with a thickness of 13 μm , was purchased from Shandong Deli Plastics Material Corporation, China. Both modifiers of stearyl-alcohol poly(ethylene oxide) ethers (AEO- n , n is the polymerization degree of poly(ethylene oxide) (PEO), $n = 4, 8, 16, 25,$ and 35) and poly(ethylene oxide) monooleate (OEO, with a PEO polymerization degree of 9) were kindly supplied by Nanjing Well Chemical Corporation, China. Xylene, cyclohexanone, and benzoin butyl ether were purchased from Shanghai Lingfeng Chemical Reagent Corporation, China, and used as received.

Entrapping Modification

The PP film was cleaned with acetone and dried before using. Mixed solvents of xylene/cyclohexanone in various ratios were prepared and their solutions containing 9 wt % AEO modifiers were adopted in the entrapping modification. Both xylene and cyclohexanone were selected due to the good solubility of xylene and poor solubility of cyclohexanone for PP. A mild swelling agent of PP could be prepared by mixing both solvents. By immersing the PP film into the modifier solution at temperatures from 70 to 115 $^{\circ}\text{C}$ for 15 min, both the surface swelling and modifier entrapment into the PP surface were simultaneously carried out. Subsequently, the sample was put inside the vacuum oven for surface deswelling, lasting 48 h at the temperature of 25 $^{\circ}\text{C}$ or 9 $^{\circ}\text{C}$. The

sample was washed with water and immersed in water for 2 h to remove adsorbed modifiers (not the entrapped ones) from the surface. For the OEO-9 modifier, the same entrapping technology was adopted except that 0.65 wt % photoinitiators of benzoin butyl ether were included in the solution. The photoinitiation reaction was carried out on each surface of the modified sample under the mercury lamp of 30 W for 30 min.

Characterization of the Modified Films

The morphological structure and crystalline structure of the swollen PP surfaces were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The swollen surfaces were prepared following the above entrapping technology except that the modifiers were absent in the swelling agents. The SEM was observed on the Scanning Electron Microscopy of JEOL JSM-5900 of Japan, with sample surfaces pre-deposited by gold. XRD spectra were recorded using a Rigaku D/MAX-RB Diffractometer of Japan, with Ni-filtered Cu K α radiation at 45 kV and 35 mA, in the Bragg Brentano reflection mode and 2θ range of 5–80 $^{\circ}$ under the counting rate of 5 $^{\circ}$ /min. Transition temperatures of the PP substrate, swollen PP, modified PP, and AEO-8 modifier were measured using a Perkin-Elmer Pyris 1 thermal analysis system of USA. In the differential scanning calorimetry (DSC) analysis, the sample mass used was about 14 mg. Scans were run from –50 to 250 $^{\circ}\text{C}$ at a heating rate of 20 $^{\circ}\text{C}/\text{min}$. Surface chemistries of modified surfaces by the AEO modifiers were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR) and X-ray photoelectron spectroscopy (XPS). The ATR FT-IR was measured using a Nicolet Nexus 670 Spectrometer of USA, equipped with a germanium crystal accessory. All spectra were acquired at 4 cm^{-1} resolution over 64 scans. XPS spectra were obtained using a VG ESCALB 250 electron spectrometer of United Kingdom, with a Mg K α X-ray source (1249 eV at 12 kV; 20 mA) at a pressure of 10^{-7} torr and an electron take-off angle of 45 $^{\circ}$. Water contact angles of the modified surfaces were measured by the sessile drop method using a Krüss Contact Angle Measurement System DSA-100, Germany, and the data were processed by an image analysis system. Contact angles were read within 10 s after 2 μL deionized water droplets were deposited on the surface. Each contact angle value was the average of seven values.

RESULTS AND DISCUSSION

Surface Swelling

PP, a semi-crystalline polymer, is known soluble in some non-polar solvents at higher temperatures. Surface swelling of PP is possible when its surface contacts a mild solvent at lower temperatures. The swelling can be limited in the amorphous region on the PP surface due to dissolution inhibition coming from the crystalline region. In this article, mixed solvents of xylene and cyclohexanone, a good and poor solvent for PP respectively, were selected as swelling agents for the surface swelling. After the surface swelling performed at 115 $^{\circ}\text{C}$ and concurrent modifier entrapment into the surface, water contact angles were detected to evaluate hydrophilicity of the modified surfaces, as results shown in Table I. The solubility parameter of the mixed solvents, a semi-quantitative index for estimating their miscibility with PP, is also shown. Evidently, the contact angles exhibited heave dependence on solvent ratios of the mixed solvents.

Table I. Water Contact Angles on Modified PP Surfaces by AEO-8 after Surface Swelling and Modifier Entrapment in Mixed Solvents of Xylene and Cyclohexanone

Solvent ratios of xylene/cyclohexanone (wt %)	Solubility parameters (MPa ^{1/2}) ^a	Swelling temperatures (°C)	Contact angles (°)
100/0	18.0	115	101.0
90/10	18.2	115	65.4
80/20	18.4	70	97.2
80/20	18.4	90	89.8
80/20	18.4	110	86.4
80/20	18.4	115	20.6
70/30	18.6	115	60.0
60/40	18.9	115	62.7
50/50	19.1	115	63.6
0/100	20.3	115	97.7
PP substrate	17.2		97.7

^aThe solubility parameters of the mixed solvents (δ_{mixture}) were taken as the sum of the products of the component solubility parameters (δ_i) with their volume fractions (Φ_i): $\delta_{\text{mixture}} = \sum \delta_i \Phi_i$.²²

Both modified surfaces by the good solvent of xylene (100/0) and the poor solvent of cyclohexanone (0/100) showed less hydrophilic improvement relative to the original PP surface. The optimal hydrophilic improvement was achieved by the mixed solvent of 80/20 xylene/cyclohexanone, when the lowest contact angle of 20.6° was reached on the modified surface. These contact angle results reveal that a mild solvent with a medium solubility parameter value is suitable for the surface swelling and subsequent modifier entrapment into the surface.

Apart from the solvent ratio, the swelling temperature is also an important factor for affecting the swelling level on the surface. Several swelling temperatures lower than 115 °C, on the basis of the swelling agent of 80/20 xylene/cyclohexanone, were tested in the entrapping modification. In result, the swelling temperature of 115 °C was proved the optimal one in the entrapping modification, as seen in contact angle results of Table I. For the PP substrate, a lower swelling temperature than 115 °C could present an insufficient swelling level, whereas a higher swelling temperature could induce serious etch on the PP surface. In some degree, a lower swelling temperature may need a stronger swelling agent to reach the same swelling level.

Surface morphologies of swollen PP without modifier entrapment are shown in Figure 1. Many granules were seen on both swollen surfaces by the 80/20 mixed solvent and xylene. These granules are apparently representations of the crystalline region of PP because amorphous PP is apt to be etched by the swelling agents. Relative to pure xylene, the 80/20 mixed solvent gave more crystal granules on the surface and exhibited obscurer appearance of the crystal granules. This great discrepancy confirms the weaker solvation ability of the 80/20 mixed solvent and suggests considerable reservation of amorphous PP on its crystal surfaces. Considering the good hydrophilicity reached by the 80/20 mixed solvent, as shown

in Table I, it is assumed that a steady swelling layer composed of amorphous PP is generated on the swollen surface, and will provide embedding sites for the entrapped modifiers. As for xylene, a good solvent of PP, both amorphous and crystalline PP tend to be etched and constantly peeled off from the surface so that the swollen surface showed fewer crystal granules and clearer appearance of the crystal granules. In result, fewer chances could be offered for modifier entrapment and the modified surface exhibited poorer hydrophilicity.

Crystalline structures of both swollen surfaces were analyzed by XRD, as spectra shown in Figure 2. Four characteristic peaks emerging at 14.20°, 17.04°, 18.66°, and 25.64° indicated the α -crystalline lattice on the PP substrate surface.^{23,24} After both solvent treatments, however, three new peaks were found emerging at 16.22° (shoulder peak), 21.38°, and 22.20° on the swollen surfaces, indicating production of the β -crystalline lattice.^{25,26} Crystalline degrees were calculated from the XRD spectra and 65.7%, 27.7%, and 22.4% of crystalline degrees were obtained on the PP substrate surface, swollen surface by the 80/20 mixed solvent and swollen surface by xylene, respectively. This crystalline degree order reveals that both swelling agents can invade the crystalline region of PP to decrease the crystalline degrees. The higher crystalline degree reached by the 80/20 mixed solvent than by xylene also confirms the weaker solvation ability of the 80/20 mixed solvent due to dissolution inhibition coming from cyclohexanone.

Block Structures of AEO Modifiers

In our modification strategy, block AEO equipped with a hydrophilic PEO segment and a hydrophobic stearyl segment was used as the modifier. The stearyl segment is believed to be compatible with the PP substrate due to both similar chain structures,²⁷ however, the polar PEO segment is believed to be incompatible with the PP substrate.²⁸ A series of AEOs with PEO polymerization degrees ranging from 4 to 35 were adopted in the entrapping modification. After the entrapping modification in the 80/20 mixed solvent and surface deswelling at 25 °C, water contact angles were detected on the modified surfaces, as results shown in Table II. Hydrophilic–lipophile balance (HLB) values of the AEO modifiers are also shown for estimating their hydrophilic–hydrophobic characters. In result, all AEO modifiers could improve hydrophilicity on the PP surface with contact angles below 63°. Nevertheless, AEO-8 achieved the optimal hydrophilic modification on the surface with a contact angle of 20.6°.

According to the entrapping method described above, both surface swelling and modifier entrapment into the surface occurred simultaneously. The AEO modifiers would be randomly blended with PP in the swollen surface before swelling agents were removed. Poor hydrophilicity could be endowed by the modifiers on the surface. The surface hydrophilicity would be presented merely after a microphase separation of the block modifiers in the surface, when hydrophilic PEO chains were oriented towards the outmost surface. On the basis of the great incompatibility between PEO and the PP substrate, a microphase separation between both chains could be expected in the entrapping surface after swelling agents were removed. In result, the oriented PEO chains on surface could improve the surface hydrophilicity, simultaneously, the

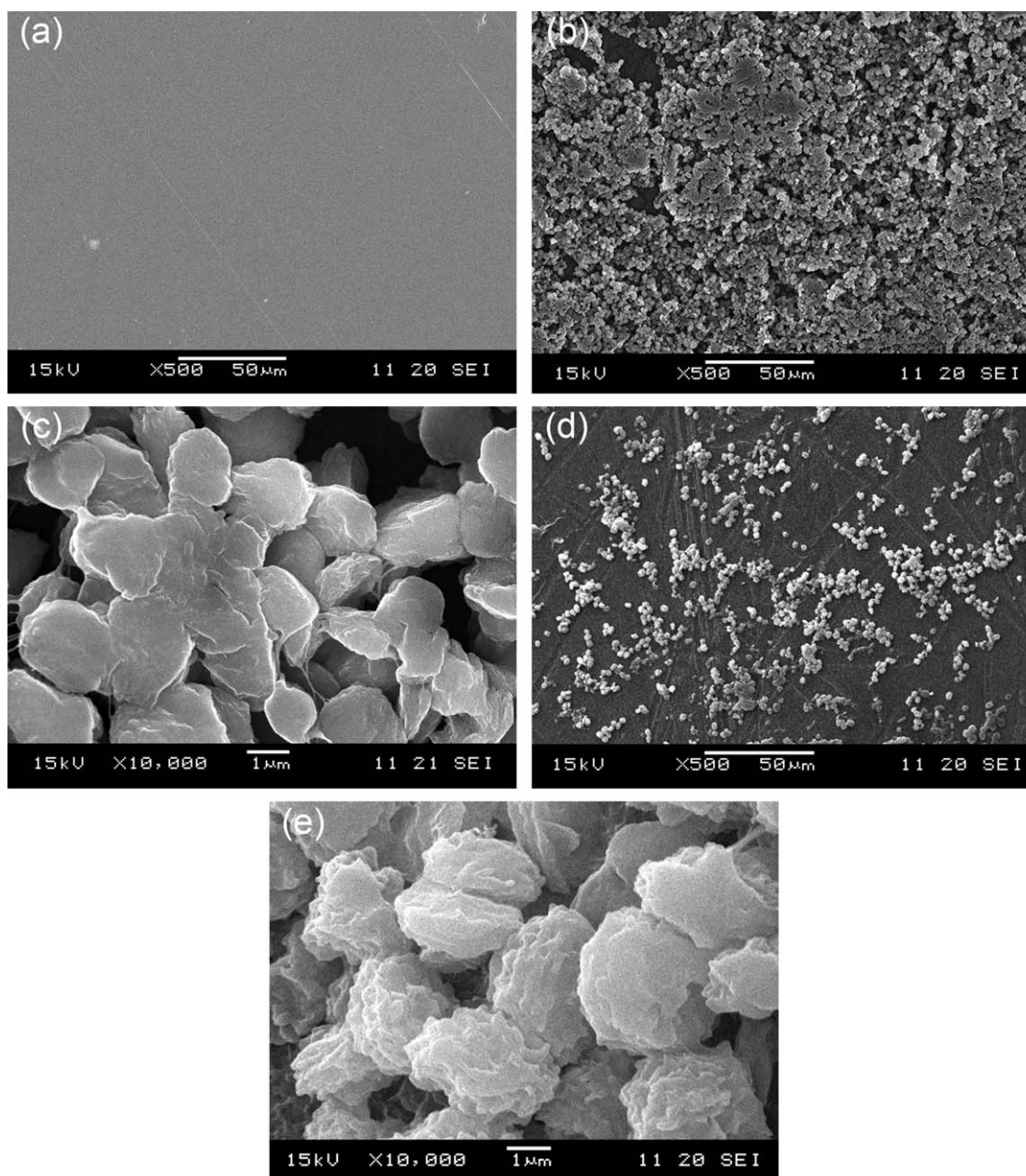


Figure 1. SEM images of swollen PP surfaces without modifier entrapment: (a) PP substrate, (b) 80/20 xylene/cyclohexanone ($\times 500$), (c) 80/20 xylene/cyclohexanone ($\times 10,000$), (d) xylene ($\times 500$), (e) xylene ($\times 10,000$).

reserved stearyl chains in the surface could achieve modifier fixation.

Generally, the microphase separation tendency of PEO heavily depends on its chain length, that is to say, a longer PEO chain is inclined to produce a stronger microphase separation from the incompatible polymer.²⁷ For AEO-4, with a shorter PEO chain, only a weaker microphase separation could be induced and poorer surface hydrophilicity was offered. Although AEO-16, AEO-25, and AEO-35 possess longer PEO chains and could induce stronger microphase separation, the stearyl segment in the modifiers is relatively short so that weaker modifier fixation could be provided. In result, these AEO modifiers with longer PEO chains had great

tendencies to be leached out of the surfaces by ambient water in the water washing procedure (seeing EXPERIMENTAL). Hence, AEO-8 could achieve the optimal hydrophilic modification benefiting from its medium PEO length and the appropriate HLB value.

Surface Deswelling

After the surface swelling and modifier implantation into the surface, a surface deswelling is necessary for removing swelling agents from the surface and fixing the modifiers. In the entrapping modification described by Ruckenstein and Desai,¹⁴⁻¹⁶ a rapider deswelling way of solvent extraction was adopted for relieving great chain repulsion between the polymer modifier and the incompatible

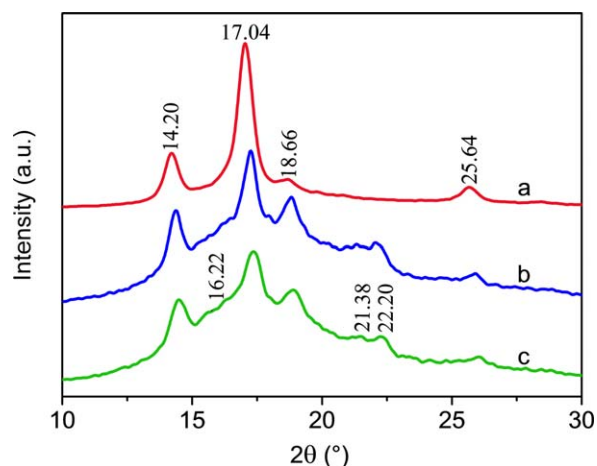


Figure 2. XRD spectra of swollen PP surfaces without modifier entrapment: (a) PP substrate, (b) 80/20 xylene/cyclohexanone, and (c) xylene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

substrate polymer in the entrapping surface. In this work, however, a block modifier of AEO was adopted, which possesses a compatible stearyl segment with the PP substrate. Therefore, less chain repulsion should occur between both chains in the entrapping surface. A slower but simpler deswelling way of vacuum drying, instead of the solvent extraction, should be available in the entrapping modification.

The surface deswelling by the vacuum drying method was performed at both temperatures of 25 °C and 9 °C. Effects of the deswelling temperatures on surface hydrophilicity of the modified surfaces are shown in Table II. It was interesting to find that all modified surfaces could approach lower contact angles at the deswelling temperature of 25 °C than those they did at 9 °C. That is to say, the higher deswelling temperature of 25 °C was suitable for the entrapping modification, whereas the lower deswelling temperature of 9 °C was unsuitable.

For interpreting the great discrepancy endowed by the deswelling temperatures, transition temperatures of modified PP were measured using a DSC method, when the surface deswelling was performed at 9 °C. Figure 3 shows DSC thermograms for

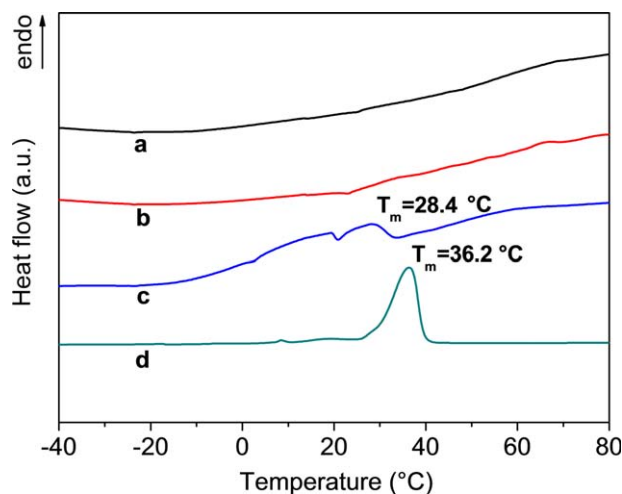


Figure 3. DSC thermograms for (a) the PP substrate, (b) swollen PP, (c) modified PP by AEO-8, and (d) AEO-8 modifier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PP substrate, swollen PP, and modified PP by AEO-8 and AEO-8 modifier. Both the PP substrate and swollen PP exhibited indistinct glass-transition temperatures (T_g) in the DSC traces because of their higher crystalline degrees (the crystalline degree 27.7% from Figure 2 mainly reflected that of the shallower layer of the swollen surface by the 80/20 mixed solvent). After modifier implantation into the surface, however, modified PP gave an apparent T_g transition at -2.8 °C concerned with PP. The melting temperature (T_m) emerging at 28.4 °C for modified PP was ascribed to the entrapped stearyl segment of AEO-8, although the value was lower than the T_m of 36.2 °C of pure AEO-8. The apparent T_g transition and significant decline of the T_m value for modified PP revealed chain interaction between PP and the stearyl segment in the entrapping surface, for which both crystallizations of PP and the stearyl segment could be restrained. In view of the T_g of -2.8 °C for modified PP, a value near the deswelling temperature of 9 °C, chain motion of PP tended to be limited during the surface swelling. In result, the microphase separation of the block modifier was inclined to be inhibited in the entrapping surface so that poorer surface hydrophilicity could be provided by the modifier. The great discrepancy endowed by the deswelling temperatures reveals that the microphase separation of the block modifier prefers to occur in the period of surface deswelling.

In the entrapping modification with the PEO homopolymer as the modifier, a temperature dependency was also reported.¹⁶ The modified surface could keep hydrophilicity at storage temperatures below the T_g of the PET substrate, whereas lost the hydrophilicity at storage temperatures above the T_g . The authors have ascribed this hydrophilic instability to the thermodynamically unstable surface-fixed structure of their modified surface. The PEO modifier was inclined to be repulsed by incompatible PET in the modified surface at higher temperatures. For the block AEO modifier used in this work, however, the surface-fixed structure is believed thermodynamically stable due to compatibility between the stearyl segment and the PP substrate. Less worry should remain in case that the AEO modifiers were repelled by

Table II. Contact Angles on Modified PP Surfaces by AEO-*n* after Surface Swelling and Modifier Entrapment in 80/20 Xylene/Cyclohexanone

AEO- <i>n</i> modifiers	HLB ^a	Contact angles (°)	
		Deswelling at 9 °C	Deswelling at 25 °C
AEO-4	8.7	99.3	61.9
AEO-8	11.9	96.0	20.6
AEO-16	14.8	96.6	50.5
AEO-25	16.3	99.3	58.6
AEO-35	17.2	99.3	62.8

^aHydrophile-lipophile balance (HLB) was calculated according to Griffin.²⁹

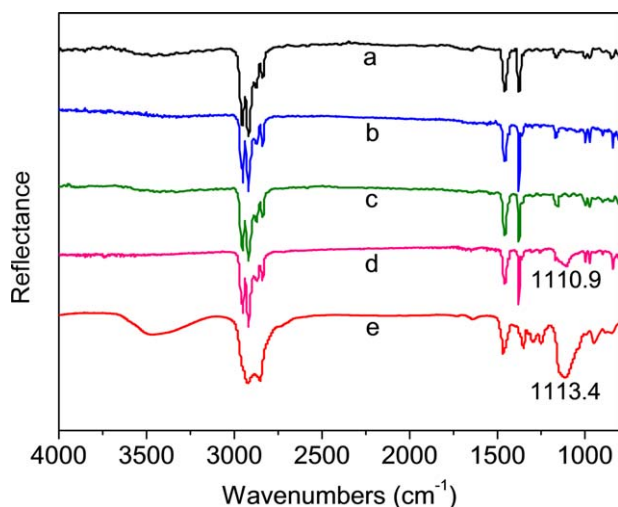


Figure 4. FT-IR spectra of swollen, coated, and modified PP surfaces: (a) PP substrate, (b) swollen by 80/20 xylene/cyclohexanone without modifier entrapment, (c) coated by AEO-8 in solution of 80/20 xylene/cyclohexanone at the room temperature, after water rinsing, (d) modified by AEO-8 after surface swelling and modifier entrapment in 80/20 xylene/cyclohexanone at 115 °C, and (e) AEO-8 modifier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

substrate PP in the entrapping surface. Hence, the modified surface could keep the hydrophilic stability at storage temperatures whether below or above the T_g of the PP substrate.

Surface Chemistries

Surface chemistries of the modified surfaces were analyzed by Fourier transform infrared spectroscopy (FT-IR), as spectra seen in Figure 4. Both the swollen surface by the 80/20 mixed solvent and the PP substrate surface showed similar spectra, implying that few chemical changes occurred after surface swelling. The entrapping modification was proved by the new band at 1110.9 cm^{-1} on the modified surface, a stretching vibration of C–O–C of the AEO modifier.³⁰ Another evidence for the entrapping modification was absence of the band at 1110.9 cm^{-1} on the coated surface by AEO-8, when the coating was carried out following the standard entrapping technique except that a room temperature was adopted in solution treatment for avoiding surface swelling. This difference between the entrapping surface and the coated surface proves that the modifier entrapment into the surface is not a simple analogy to the modifier coating on the surface.

Surface chemistries of the modified surface were also analyzed by XPS, as spectra shown in Figure 5. Both spectra of the modified surface by AEO-8 and the PP substrate surface exhibited the same C1s peak at 285.0 eV, which was assigned to C-CH_2 of PP.¹⁵ However, a weak shoulder peak emerged at the higher binding energy near 285.0 eV on the modified surface, suggesting a new-produced group. This new group could also be confirmed by the increased O/C ratio of 0.049 on the modified surface from that of 0.023 on the PP substrate surface. By a peak separation treatment, a C1s peak at 286.4 eV assigned to O-CH_2 ¹⁵ of AEO-8 was obtained on the modified surface, as seen in the fitting line of Figure 5(b). From these separated

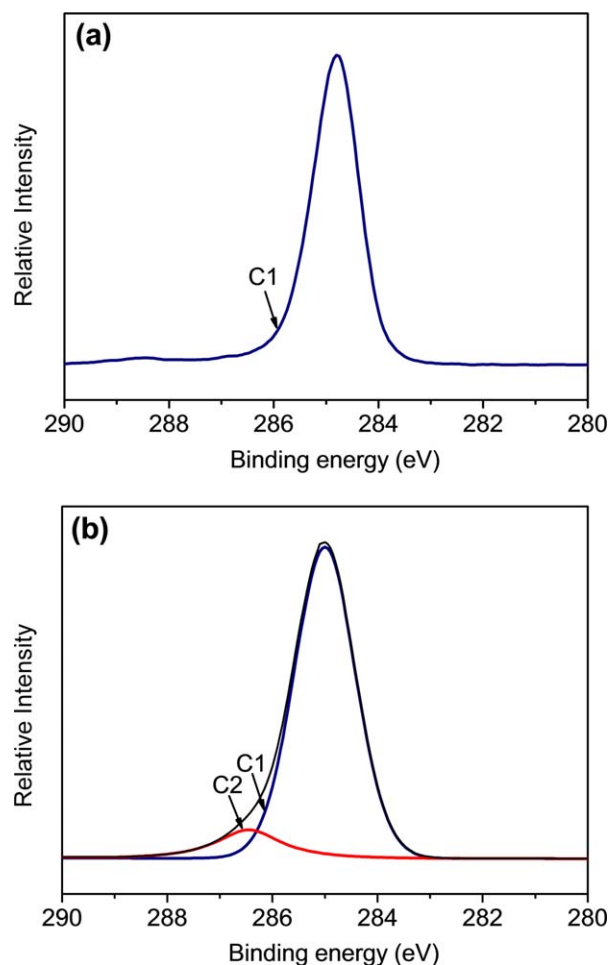
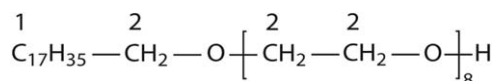


Figure 5. XPS spectra of the modified PP surface by AEO-8 after surface swelling and modifier entrapment in 80/20 xylene/cyclohexanone: (a) PP substrate, and (b) modified surface by AEO-8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peaks, modifier coverage on the surface, defined as the carbon atom ratio of AEO-8 to the modified surface, could be calculated following eq. (1):

$$\text{Modifier coverage} = \frac{C_{\text{AEO-8}}}{(C_{\text{PP}} + C_{\text{AEO-8}})} \times 100\% \quad (1)$$



AEO-8

As seen in the molecular formula of AEO-8, the peak at 286.4 eV is contributed by both C2 from stearyl alcohol and PEO. Certainly, the peak at 285.0 eV is contributed by both C1 from stearyl alcohol and the PP substrate. Hence $C_{\text{AEO-8}}$ and C_{PP} in eq. (1) could be calculated following eqs. (2) and (3), respectively:

$$C_{\text{AEO-8}} = C_2 + C_2 \times 17 / (2 \times 8 + 1) \quad (2)$$

$$C_{\text{PP}} = C_1 - C_2 \times 17 / (2 \times 8 + 1) \quad (3)$$

In result, modifier coverage of 19.2% was reached on the PP surface after the entrapping modification by AEO-8.

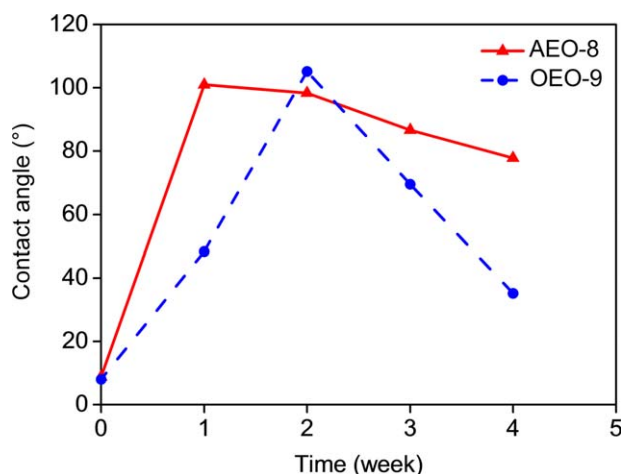


Figure 6. Contact angle changes on modified surfaces by AEO-8 and OEO-9 during water immersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water Immersion Durability

For the modified surface by the AEO modifier, the modifier is believed to be fixed in the surface via physical entanglement between the short-chained stearyl segment and substrate PP. It is possible that the entrapped modifiers could be leached out of the surface by ambient water under the strong water orientation effect on the hydrophilic PEO chains. Therefore, durability against water contact of the modified surface is an interesting question. The durability was evaluated by periodical contact angle measurements on the modified surface, which was kept immersed in water at the room temperature. As shown in Figure 6, the contact angles on the modified surface by AEO-8 were seen to increase sharply from 20.6° to 101.0° after one week of water immersion, and then went down slowly to 77.8° after four weeks of water immersion. This rapid increase in contact angles can be ascribed to water leaching of modifiers from the shallower layer of the entrapping surface. Subsequently, under water orientation on the hydrophilic PEO chain, the entrapped modifiers in the deeper layer would sustainably migrate towards the outmost surface to decrease the contact angles. These contact angle results prove that the water immersion durability of the entrapping surface is insufficient on the basis of the short-chained AEO modifier.

For strengthening modifier fixation to improve the durability, a covalent bond linkage should be established in the surface-fixed

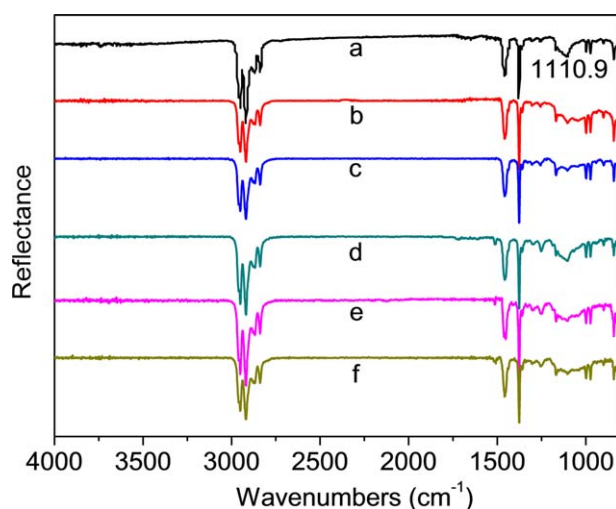
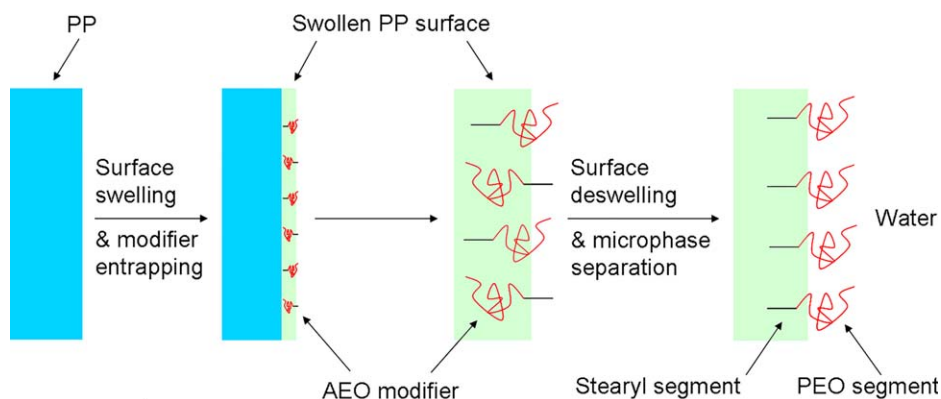


Figure 7. FT-IR spectra of modified surfaces by AEO-8 and OEO-9 during water immersion: (a) AEO-8, before water immersion; (b) AEO-8, after 2 weeks of water immersion; (c) AEO-8, after 4 weeks of water immersion; (d) OEO-9, before water immersion; (e) OEO-9, after 2 weeks of water immersion; and (f) OEO-9, after 4 weeks of water immersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure. OEO-9, with a similar structure to AEO-8 except a double bond equipped in the hydrophobic segment, was adopted in the entrapping modification. After a radical initiation, the entrapped modifier is anticipated to be covalently linked with the PP substrate. Contact angle results of the modified surface by OEO-9 are also shown in Figure 6. By comparing with results of AEO-8, the peak contact angle of OEO-9 was evidently delayed to the second week and lower contact angle values were exhibited after that. These contact angle results prove improvement of the water immersion durability of the modified surface by OEO-9.

Water immersion durability of the modified surfaces by AEO-8 and OEO-9 could be else illustrated by their FT-IR spectra, as shown in Figure 7. The modified surface by OEO-9 presented the similar spectrum to that by AEO-8, revealing that both modifiers have behaved analogously in the entrapping modification due to their similar chain structures. After two weeks of water immersion, both modified surfaces exhibited similar peak



Scheme 1. Entrapping modification on the PP surface by the short-chained and block AEO modifier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decrease at 1110.9 cm^{-1} , indicating the modifier leaching from the shallower layer of the entrapping surface. After four weeks of water immersion, however, the modified surface by OEO-9 only showed slighter peak decrease at 1110.9 cm^{-1} relative to that of AEO-8. These FT-IR results coincided with the above contact angle results that the OEO-9 modifier could improve the water immersion durability of the entrapping surface.

In summary, the entrapping modification by the short-chained and block AEO modifier can be depicted in Scheme 1. Initially, a swelling layer was formed on the PP substrate surface and would offer implanting sites for entrapped modifiers. Under both solvation inhibitions from the poor solvent of cyclohexanone and the crystalline region of PP, the swelling could be limited in the amorphous region on the PP surface. In the entrapping surface before surface deswelling, the block AEO modifier preferred to randomly blend with substrate PP. Nevertheless, on the basis of incompatibility of the PEO chain with substrate PP, a microphase separation of the block modifier was inclined to occur in the entrapping surface. In result, the surface-enriched PEO chains could improve the surface hydrophilicity, simultaneously, the reserved stearyl chains in the surface could achieve modifier fixation.

CONCLUSIONS

Utilizing AEO with various PEO chain lengths as the modifiers, this article describes an entrapping modification on the PP surface for hydrophilic improvement. The entrapping technique concerned with surface swelling, surface deswelling, and block structures of AEO was investigated in detail. After that, an entrapping mechanism was proposed. Both analyses of SEM and XRD confirmed formation of the swelling layer in the amorphous region on the PP surface, from which the modifiers could penetrate into the surface. On the basis of an appropriate HLB value, the AEO-8 modifier achieved the optimal hydrophilic improvement on the surface with a contact angle of 20.6° and modifier coverage of 19.2%. A microphase separation of PEO from PP tended to occur in the entrapping surface during surface deswelling, after which the surface-enriched PEO chains could improve the surface hydrophilicity, simultaneously, the reserved stearyl chains in the surface could approach modifier fixation. The modifier fixation could be reinforced by adopting the OEO-9 modifier, when a covalent linkage was established in the surface-fixed structure.

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