

Open-cell polypropylene/polyolefin elastomer blend foams fabricated for reusable oil-sorption materials

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ABSTRACT: The fabrication of high-performance oil sorbents is of great significance for oil spill cleanup. The main objective of this study was to prepare open-cell polypropylene/polyolefin elastomer (PP/POE) blend foams for fabrication of reusable sorbents for oil sorption. Open-cell PP/POE blend foams were prepared via continuous-extrusion foaming using supercritical carbon dioxide as the blowing agent. The interconnected open-cell structure was characterized by scanning electron microscopy. The hydrophobicity and lipophilicity of PP/POE open-cell foams were revealed by tests of contact-angle measurement, water and cyclohexane sorption on the foam surface, CCl₄ and cyclohexane sorption in water, and oil/water separation. Further, the sorption tests indicated that PP/POE blend foams showed larger oil-uptake capacities than pure PP foams. In addition, cyclic compression tests showed that PP/POE open-cell foams had excellent ductility and significantly improved recoverability compared to pure PP foams. In cyclic sorption-desorption tests, the sorption kinetics was studied in terms of capacity and saturation time, showing that PP/POE foams kept larger sorption capacities for 10 cycles, with larger sorption rates and good reusability. Based on the high open-cell content, the good hydrophobic and oleophilic properties, the high oil-sorption capacity, the improved recoverability, the large sorption rate, and the good reusability in cyclic oil-sorption performance, the PP/POE open-cell foams have shown promise as potential oil sorbents in applications for oil spill cleanup. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, 133, 43812.

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INTRODUCTION

Offshore oil spills and the discharge of industrial waste oil have caused severe ecological and environmental problems. Oil cleanup has been an urgent task globally to protect the environment and to maintain sustainable development.^{1,2} The common cleanup methods include *in situ* burning, oil booms, bioremediation, oil dispersants, and oil sorbents.^{3–7} Among these methods, the application of oil sorbents has proven to be an effective and economical means of solving the problem.^{8,9}

Oil sorbents are classified as natural sorbents or synthetic sorbents. Natural sorbents include cotton,¹⁰ cattail fiber,¹¹ vegetable fibers,¹² corn stalks,¹³ and zeolites.¹⁴ These sorbents showed low oil-sorption capacities and could not be recycled. In addition, burning of the natural sorbents after usage might bring secondary pollution to the environment. Therefore, the conventional natural sorbents were gradually replaced by synthetic sorbents. The most commonly used synthetic sorbents were polyurethane (PU) foams and nonwoven polypropylene (PP) fabrics. The PU foams showed high oil-sorption capacity, but they showed low oil/water selectiv-

ity.^{15,16} The nonwoven PP fabrics showed good hydrophobic and oleophilic properties and a high rate of oil sorption, but they exhibited low oil-sorption capacities. Synthetic polyvinyl chloride/polystyrene fibers¹⁷ were also applied as oil sorbents and showed a high oil-sorption capacity up to 146 g/g. However, they could not be reused because of their poor physical recoverability.

Recently, open-cell polymer foams have been reported for use as oil sorbents. Park *et al.*¹⁸ reported that open-cell PP foams showed excellent oil-sorption capacities, and that an oil foam sorbent made of a PP copolymer showed better ductility and hence reusability in oil sorption than a PP homopolymer. However, PP copolymers are generally produced through more complex synthetic routes and usually are more expensive than PP homopolymers. Therefore, the fabrication of open-cell foam sorbents with high sorption capacities and low costs still remains a challenging task.

Several strategies have been applied to prepare open-cell foams in polymer blends, including crosslinking,¹⁹ semi-interpenetration,²⁰ and polymer blending.^{21,22} The basic concept was the same for these strategies: nonhomogeneity, that is, hard and soft regions in

Table I. Properties of the Oils and Organic Solvents Used in This Study

Oil samples	Viscosity (mPa s)	Density (g/cm ³)
Motor oil	140	0.814
Bean oil	47	0.875
Cyclohexane	0.888	0.779
Toluene	0.587	0.866
CCl ₄	0.965	1.595

polymer blends. Park *et al.*¹⁹ prepared open-cell foams in low-density polyethylene (LDPE)-based systems through partial crosslinking. Hard (crosslinking) and soft (noncrosslinking) regions were formed because of the nonhomogeneity of the polymer melts, with the soft regions facilitating cell opening. Ohshima *et al.*²⁰ prepared open porous structures in a semi-interpenetrating polymer network via batch foaming, and cell openings were inclined to form in the soft regions where the low-molecular-weight polymers were located. Yu *et al.*²¹ prepared open-cell structures in poly(lactic acid)/poly(butylene succinate) (PLA/PBS) blends, and cell openings were formed in PBS phases (soft regions) because of their relatively lower viscosity. Lee *et al.*²² produced open-cell foams in PP/LDPE blends through continuous-extrusion foaming. A critical factor that governs cell opening in a polymer blend during continuous-extrusion foaming is a dramatic crystallization temperature difference between the two components. LDPE crystallizes at a lower temperature than PP, and whereas PP had already crystallized as the blends were extruded from the die, LDPE could still remain in a molten state. Thus, the PP domains (hard regions) could hold the overall cell structure by preventing the cells from completely coalescing with each other. However, the gas could break through the LDPE domains (soft regions) in the cell walls during cell growth to form pores to interconnect cells, thus forming cell openings. In this study, polypropylene/polyolefin elastomer (PP/POE) blends could form open-cell structures through the same mechanism of nonhomogeneity because the POE phases could remain in a molten state after the PP crystallized as the blends were extruded from the die. Thus, the addition of POE could facilitate cell opening and increase the open-cell content compared to pure PP foams. The open-cell structure could facilitate a large oil-sorption capacity of PP/POE foams. In addition, POE has proved to be an excellent toughening agent for PP homopolymers,^{23,24} so the high elasticity of POE could enhance the recoverability of the foams, which would favor the reusability of PP/POE foams as oil sorbents. Moreover, the continuous-extrusion foaming makes it possible to produce large-scale open-cell foams to satisfy extensive and cost-effective uses as oil sorbents in practical applications. Therefore, based on these merits, it is highly expected that the PP/POE blend foams would have a high open-cell content and show excellent oil-sorption capacities and reusability.

The main objective of the present work was to prepare open-cell PP/POE blend foams for the fabrication of reusable sorbents for oil spill cleanup. Open-cell PP/POE blend foams were prepared via continuous-extrusion foaming with supercritical carbon dioxide (sc-CO₂) as the blowing agent. The cell structure of PP/POE blend foams was characterized by scanning electron

microscopy (SEM). The hydrophobic and oleophilic properties were studied with contact-angle measurements, the sorption of organic solvents on a foam surface and in water, and oil/water separation. The deformation and ductility of the blend foams were studied with cyclic compression tests. The oil-sorption capacities in weight and volume were studied for pure PP and for the blend foams with several oils and organic solvents. Further, the reusability of the open-cell PP/POE foams was studied with cyclic sorption-desorption. The kinetics of cyclic sorption was also extensively studied in terms of the capacity and the saturation time. Based on the results in this study, the PP/POE blend foams exhibited larger uptake capacities, excellent reusability, and larger oil-sorption rates in oil cleanup compared to the pure PP open-cell foams.

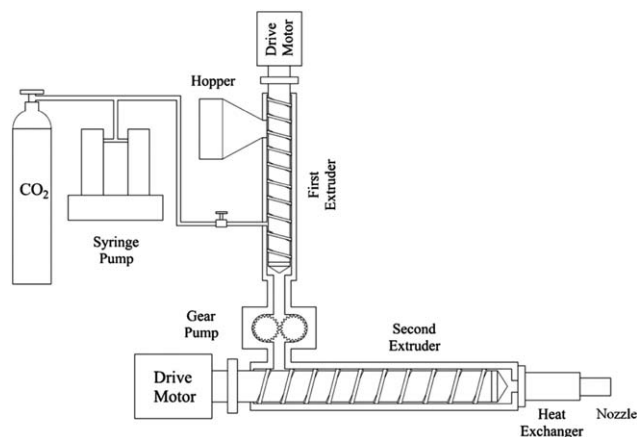
EXPERIMENTAL

Materials

The PP homopolymer (T03S) used in this study was provided by Sinopec Zhenhai Refining & Chemical (Ningbo, China), with a melt flow index (MFI) of 2.8 g/10 min at 230 °C/2.16 kg. Polyolefin elastomer (POE, Engage 8150) was provided by Dow Chemical Investment Co. (Shanghai, China), with an MFI of 0.5 g/10 min at 190 °C/2.16 kg. The physical blowing agent, CO₂ (99% purity), was obtained from Ningbo Wanli Gas Corporation (Ningbo, China). The oils used for sorption were motor oil and bean oil, and the organic solvents used were toluene, CCl₄, and cyclohexane. The oils and organic solvents were purchased from Sinopharm Chemical Reagent Co. (Beijing, China). The physical properties listed in Table I were provided by the manufacturer. Sudan IV (red dye) and Tween-80 (stabilizer) were also purchased from Sinopharm Chemical Reagent Co.

Open-Cell Foam Preparation

The open-cell PP/POE foams were prepared with a tandem extrusion system (Figure 1), which consists of two extruders, a syringe pump, a gear pump, a heat exchanger, and a die. A detailed description can be found in the previous paper.²⁵ For continuous-extrusion foaming, the first extruder is used to plasticize the polymers and to preliminarily mix polymer melts with sc-CO₂ at relatively higher temperatures. The second extruder is used to make a homogeneous polymer/sc-CO₂

**Figure 1.** Experimental setup of tandem extrusion system.

solution and to decrease the temperature, through which foaming with the desired cell structures is facilitated; otherwise, cell coalescence could happen at relatively higher foaming temperatures. In this study, the first extruder was driven by a 25-hp drive motor (SIMO, Xi'an, China, Z4-132-3), with a screw diameter of 45 mm and the temperature set at 190 °C. The second extruder was driven by a 40-hp drive motor (SIMO, Z4-132-3), with a screw diameter of 65 mm and the temperature set at 175–170 °C. A capillary die (a single hole) with a length of 40 mm and diameter of 1.5 mm was used, and the temperature was set to be the same as that of the second extruder. PP and POE pellets were first premixed by dry-blending in a bag, and then the premixed PP/POE blends were fed into the first extruder to plasticize and melt and to preliminarily mix with sc-CO₂. The CO₂ was injected into the polymer melts at the three-quarter point of the first extruder using an ISCO (Lincoln, USA) syringe pump. The pressure of CO₂ in the syringe pump was kept at 18 MPa, and its content was fixed at 10 wt %. Through mixing in the second extruder, a homogeneous PP/POE/sc-CO₂ solution was obtained. When the uniformly mixed PP/POE/sc-CO₂ solution passed through the capillary die, a sharp decrease in gas solubility in the PP/POE melts was induced by the rapid pressure drop. Consequently, numerous bubbles were nucleated in the PP/POE melts and the open-cell foams were generated. The PP/POE foam samples with similar foam diameters were collected for the foam structure study, cyclic compression, and oil sorption. In this study, a series of PP/POE blends with POE contents of 0, 10, 20, 30, and 40 wt % were prepared, and they were coded as PP/POE0, PP/POE10, PP/POE20, PP/POE30, and PP/POE40, respectively (Table II).

Cell Structure Investigation

The cell structures of open-cell PP/POE foams were observed using a Hitachi (Tokyo, Japan) TM-1000 SEM after the samples were freeze-fractured in liquid nitrogen and sputter-coated with gold. The cell sizes of the foams were determined from the SEM micrographs. Image analysis software (Image-Pro Plus, Media Cybernetics Inc., Bethesda) was used to determine the average cell size of at least 100 cells.

The mass densities of the samples before (ρ) and after (ρ_f) foaming were measured via water displacement according to ISO 1183-1987. Here, ϕ is the void fraction of the polymer foam, which can be calculated with eq. (1):

$$\phi = \left(1 - \frac{\rho_f}{\rho}\right) \times 100\% \quad (1)$$

The open-cell content of the PP/POE foams was estimated by a true densitometer (Ultrafoam 1000) according to ISO 4590. Five measurements for each sample were carried out until the error was less than 0.005%. The value of the open-cell content was the average of three samples.

Hydrophobicity and Lipophilicity Study

An OCA20 contact-angle system (Dataphysics, Buggenfeld, Germany) was applied to measure the contact angle of water and cyclohexane on the PP and PP/POE blend foams. Water was dropped onto the surface of the samples to measure the contact angle.

Table II. Compositions of PP/POE Blend Samples

Sample	PP (wt %)	POE (wt %)
PP/POE0	100	0
PP/POE10	90	10
PP/POE20	80	20
PP/POE30	70	30
PP/POE40	60	40

The hydrophobic and oleophilic properties of the PP/POE blend foams were studied via dropping water or cyclohexane labeled with Sudan IV onto the PP/POE blend foams to observe whether they would be absorbed by the foams.

The oil-sorption properties of the PP/POE blend foams were studied with CCl₄ (sinking in water) and cyclohexane (floating on water). CCl₄ and cyclohexane were both labeled with Sudan IV and were dropped in water. The PP/POE blend foams were put close to the testing oils to study the oil-sorption properties.

The motor oil labeled with Sudan IV was first mixed with surfactant (Tween-80) at a ratio of 9/1 (oil/surfactant, w/w). Then the mixture was added in a beaker to mix with deionized water. The mixture of motor oil, water, and surfactant were emulsified for 6 h with magnetic stirring to obtain a stable emulsion. The prepared oil/water emulsion remained stable within 10 h at room temperature. Oil/water separation was carried out with a sand core funnel, with three-quarters of its volume being filled with open-cell PP/POE foams. The prepared oil/water emulsion was poured into the sand core funnel manually, and a paper cup containing water was placed above the foams to prevent the foams from floating. Oil was absorbed by the foams, and water flew into the suction flask.

Cyclic Compression Tests

To study the mechanical deformation and recoverability, cyclic compression tests were carried out on the PP/POE blend foams. The dimensions of all the foams used were kept the same: about 6 mm in length and 6 mm in diameter. The compression test was performed for 10 cycles for each sample on an Instron 4465 universal mechanical testing machine at room temperature. For the cyclic compression, the maximum strain was set at 70% with a compression rate of 0.5 mm/min.

Sorption Experiments

The procedure for the oil-sorption experiments can be found in the previous literature.^{26,27} The sorption experiments were performed at room temperature with open-cell foams of about 6 mm in both diameter and length. The open-cell foams were first weighed and then immersed in a 100-ml beaker with an external force. After saturation, the foams were taken out of the oil and quickly weighed. The oil-sorption capacities in weight and volume for these sorbents were obtained based on the following equations:

$$\text{Oil sorption (g/g)} = \frac{m_s - m_0}{m_0} \quad (2)$$

where m_0 is the weight of the dry open-cell foam sample, and m_s is the weight of the open-cell foam sample after saturated sorption of the target oil.

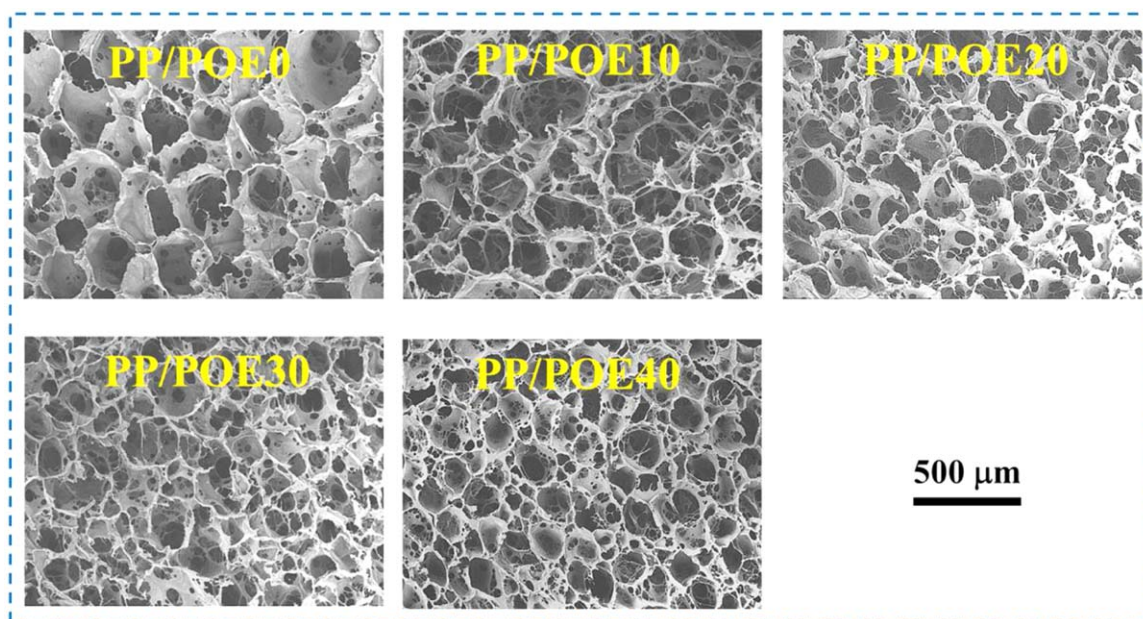


Figure 2. Cell morphologies of PP/POE blend foams. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\text{Oil sorption (ml/ml)} = \frac{m_s - m_0}{\rho_s} \bigg/ \frac{\phi m_0}{\rho_0} \quad (3)$$

where m_0 is the weight of the original dry open-cell foam sample, m_s is the weight of the open-cell foam sample after saturated sorption of the target oil, ρ_s is the density of the target oil, ρ_0 is the density of the original foam, and ϕ is the void fraction of the original foam.

The cyclic sorption process is described as follows. The open-cell PP/POE foams were cut into pieces with a length of about 6 mm and then were weighed as m_0 . After that, the foams were immersed in oil to absorb oil to saturation and then were weighed as m_1 . The sorption capacity $[(m_1 - m_0)/m_0]$ was obtained for the first sorption. Subsequently, the oil was squeezed out of the foams as much as possible, and then the foams were weighed as m'_1 , and the restored capacity $[(m'_1 - m_0)/m_0]$ was obtained for the first desorption. The sorption and desorption for the subsequent cycles (second to tenth) were performed in the same way, and the corresponding uptake capacity and restored capacity were obtained.

The sorption kinetics of PP/POE0 and PP/POE30 foams absorbing cyclohexane was studied. The foams were first weighed and then were put on cyclohexane in a beaker to absorb the organic solvent gradually. During the sorption, the weight of the foams was measured. When the weight did not increase any more, the saturation time was marked for the first cycle. This procedure

was repeated for the following cycles, and the saturation time was marked accordingly.

RESULTS AND DISCUSSION

Cell Morphology of PP/POE Foams

The foamed filaments with a diameter of about 6 mm were prepared with the tandem extrusion system. The cell morphologies of open-cell PP and PP/POE blend foams are shown in Figure 2, and the corresponding foam properties are shown in Table III. The foam density and the void fraction for all the specimens were around 0.040 g/cm³ and 95.0%, respectively. It was found that the average cell size of the pure PP foams was about 260 μm, and their open-cell content reached 80.3%, which was higher than that reported in other literature.²² This could be attributed to the following three reasons. First, the PP used in this study was a linear polymer, which showed lower melt viscosity and thus favored formation of an open-cell and interconnected structure.^{28,29} Second, the die temperature in this study was set in a proper range of 170–175 °C. If the die temperature were set above this temperature range, the melt strength of the PP melt would be too low to hold the gas and would result in cell coalescence and cause collapse, while if it is below this temperature range, the cell walls would be too hard for the gas to break, thus resulting in a closed-cell structure. Third, a high gas content was used in this study to achieve high open-cell contents. Based on the published literature,³⁰ the cell densities

Table III. Characteristics of PP/POE Blend Foams

Characteristics	PP/POE0	PP/POE10	PP/POE20	PP/POE30	PP/POE40
Foam density (g/cm ³)	0.040	0.041	0.041	0.039	0.042
Void fraction (%)	95.6	95.5	95.5	95.7	95.3
Open-cell content (%)	80.3	92.4	92.1	93.7	91.6

would be significantly increased with increased gas content, and the increase in cell densities could lead to a decrease in thickness of the cell walls, which would be easier for the gas to break, thus forming an open-cell structure.

The average cell sizes of the PP/POE10, PP/POE20, PP/POE30, and PP/POE40 foams were about 250 μm , 220 μm , 200 μm , and 190 μm , respectively, decreasing with increasing POE content. The open-cell contents of the PP/POE foams were about 92%, which was higher than that of the pure PP foam. This might be attributed to the following two reasons. First, according to the heterogeneous nucleation mechanism,^{22,23} the addition of POE to the PP matrix would increase the cell nucleation density, which would lead to a decrease in both cell size and thickness of the cell wall, thus favoring cell opening. Second, the POE phase might still remain in a molten state when the PP matrix had been stiff after extrusion from the die of the extruder. Thus, the cell walls in the POE phase could be easily broken by the diffusion of CO_2 during the cooling process. This mechanism for cell opening can be found elsewhere.^{19,31}

Based on the discussions above, it is expected that, compared to pure PP foams, the PP/POE blend foams would show higher oil-uptake capacities, arising from the higher open-cell contents. In addition, based on the previous literature about PP toughening, POE is an excellent toughening agent for PP, and PP/POE blends would show better ductility under mechanical deformation and thus better recoverability after the deformation.^{23,24} Therefore, it is expected that higher sorption rates would be favored in oil sorption for PP/POE foam compared to the PP counterpart, arising from the better mechanical recoverability for the former. Moreover, according to the reported study on PP toughening,³² the addition of 30% POE in PP would induce the brittle-ductile transition under ambient conditions and would thus lead to dramatically improved flexible and ductile behaviors in the PP/POE30 blend compared to pure PP. Therefore, the PP/POE30 foam was taken in particular as an example in many tests in this study to compare with the pure PP foam to investigate the effect of the addition of POE on the cell structure, sorption property, and reusability of the PP/POE foams as oil sorbents.

Hydrophobic and Oleophilic Properties of Open-Cell PP/POE Foams

Ideal oil-sorption materials should possess the following properties: high oil/water selectivity, high oil-uptake capacity, buoyancy, a large sorption rate, excellent reusability, and low costs.^{33,34} The commercial PP-based oil-sorption materials include PP nonwoven mats and PP fibrous mats, which show excellent hydrophobic and oleophilic properties.¹ Based on the good properties of these PP-based materials in oil sorption, it is highly expected that the PP/POE open-cell foams would also show excellent hydrophobic and oleophilic properties. In this study, cylindrical PP/POE blend open-cell foams were prepared [Figure 3(a)] of about 6 mm in diameter and about 6 mm in length. The hydrophobic properties [Figure 3(b)] of the PP/POE foams were studied, showing that neither PP/POE0 nor PP/POE30 was wetted by water, whereas the contact angle was larger than 140° , indicating good hydrophobicity of the foams.

Based on the published literature,^{35,36} the wettability of a solid surface is determined by the surface microstructure and chemical composition. Thus, the excellent hydrophobic properties of the PP/POE foams were probably due to the roughness of the foam surface and the lack of polar groups. The hydrophobic and oleophilic properties of the open-cell PP/POE30 foams were further revealed by studying the sorption of distilled water and cyclohexane (labeled with Sudan IV) applied to the foam's surface, respectively [Figure 3(c)]. The water droplet stayed firmly on the foam surface, while the cyclohexane was immediately absorbed by the foam.

As the PP-based foams showed excellent hydrophobic and oleophilic properties, it is highly expected that they could show good oil-sorption properties in applications. Two organic solvents were used to test the oil-sorption properties of PP/POE30 foams. Figure 3(d) shows that CCl_4 (labeled with Sudan IV) sinking in water was quickly absorbed by the open-cell PP/POE30 foam. Similarly, Figure 3(e) shows that cyclohexane (labeled with Sudan IV) floating on water was also quickly absorbed. These results indicated that PP/POE30 foams showed good oil-sorption properties in water. In addition, the foams still float on water after sorption of organic solvents CCl_4 or cyclohexane, which is probably due to the low density of the PP/POE foams and the good oil/water selectivity during sorption. Thus, the floating characteristic of the foams makes them easy to collect and recycle after sorption of oils in real applications.

Considering that PP/POE30 foams showed good oil-sorption properties in water, it is expected that they could be used for oil/water separation. Motor oil/water emulsions (labeled with Sudan IV) stabilized by Tween-80 were used as test solvents. Oil/water separation by open-cell PP/POE30 foams was carried out with a sand core funnel. Figure 3(f) shows that, after filtration, the liquid flowing to the conical flask was changed from red to colorless. This was because the motor oil labeled with Sudan IV was absorbed by the PP/POE30 foams, while the water flowed along the interstices among the foams into the conical flask. This demonstrated that open-cell PP/POE30 foams could be used in the application of oil/water separation. Thorough and systematic studies on the kinetics of oil/water separation of open-cell PP/POE foams with different oils and organic solvents are still ongoing and will be presented in the future.

Oil-Sorption Capacity

The oil-sorption capacities in weight and volume of PP/POE0 and PP/POE30 foams were extensively studied, with different oils of different density and viscosity. Based on the previous literature,³⁷ the main factors that influence the oil-sorption capacities are the density and the viscosity of the testing oils or organic solvents. The oils or organic solvents with a lower viscosity and a larger density could be more easily absorbed by the open-cell foams and hence show a larger uptake capacity. In comparison, it could be imagined that the oils with a large viscosity would be hard to absorb and thus would lead to a smaller sorption capacity.

The oil-sorption capacities in weight of different oils for PP/POE0 and PP/POE30 foams are shown in Figure 4(a). It was

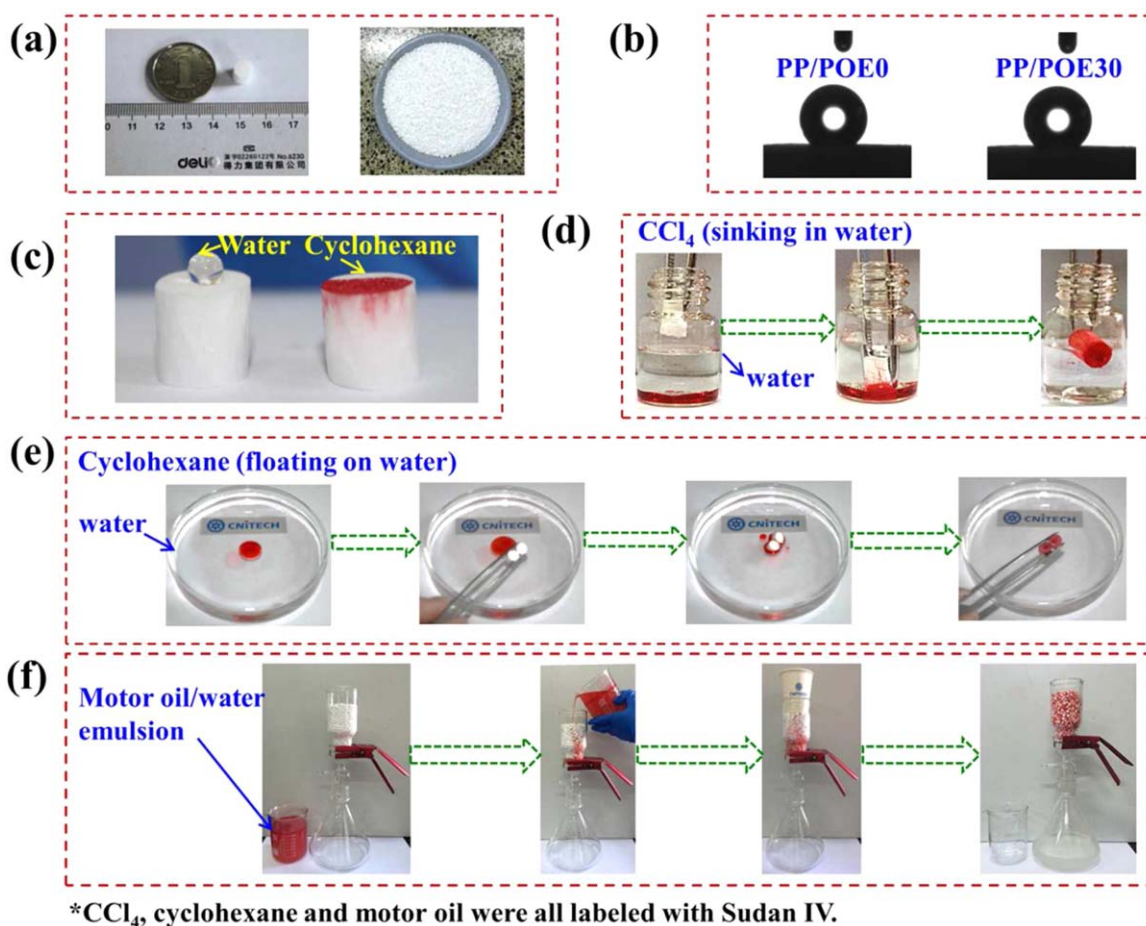


Figure 3. (a) Open-cell foams with a diameter of about 6 mm; (b) hydrophobicity of PP/POE0 and PP/POE30 foams; (c) hydrophobic and oleophilic properties of PP/POE30 foams testing with water and cyclohexane drops; (d) sorption of CCl₄ (sinking in water) with PP/POE30 foam; (e) sorption of cyclohexane (floating on water) with PP/POE30 foam; (f) motor oil/water emulsion separation with PP/POE30 foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

found that the maximum oil-sorption capacity of motor oil, bean oil, cyclohexane, toluene, and CCl₄ for the PP/POE0 foams was 15.1, 19.9, 24.5, 26.1, and 43.8 g/g, respectively, while it was 19.3, 25.3, 29.1, 32.3, and 52.1 g/g for the PP/POE30 foams, respectively. This indicates that the PP/POE30 foams possessed higher oil-sorption capacities than pure PP foams because of

the higher open-cell content for the former foams. Moreover, the PP/POE30 foam showed the highest sorption capacity of CCl₄ because of the relatively low viscosity and the high density of CCl₄ relative to other oils or solvents (see Table I). In comparison, for motor oil and bean oil, which have high viscosity, the sorption capacity of PP/POE30 foam was relatively low.

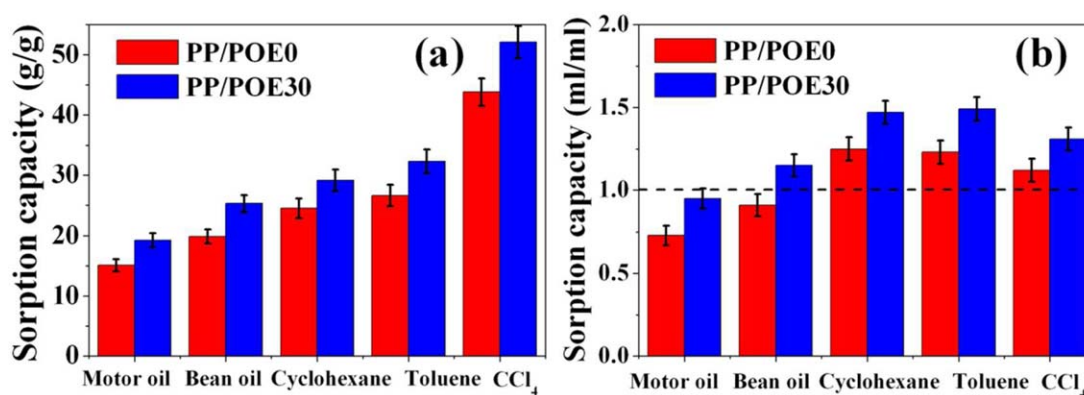


Figure 4. Sorption capacities of PP/POE0 and PP/POE30 foams with different oils and organic solvents in (a) weight and (b) volume. The dashed line in (b) represents the value of 1.0. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

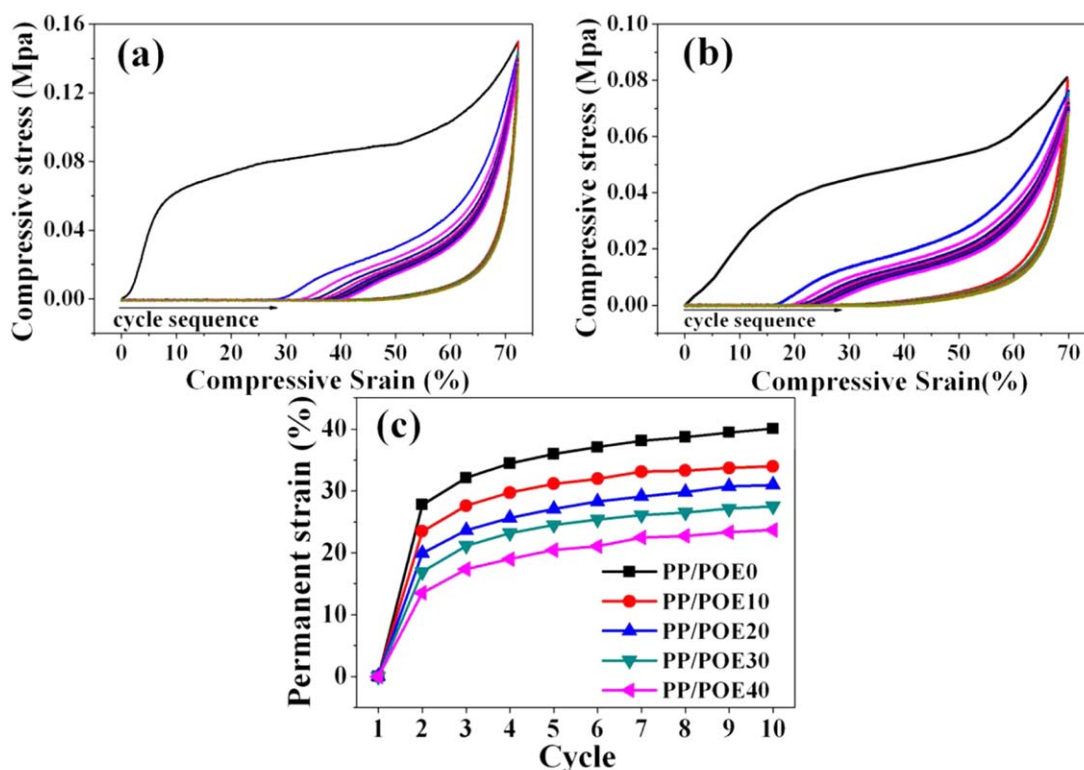


Figure 5. Cyclic compression behaviors of open-cell PP/POE blend foams for 10 cycles: (a) PP/POE0 and (b) PP/POE30; (c) permanent strain for PP/POE blend foams as a function of cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The oil-uptake capacities in volume for PP/POE0 and PP/POE30 foams were also investigated, and the results are shown in Figure 4(b). Actually, the uptake capacity in volume was calculated based on the ratio of the volume of the absorbed oil to the volume of the voids in the foam [see eq. (3)]. If the uptake capacity was smaller than one, it would mean that the voids in the foam had not yet been completely occupied by the oil, probably due to the large viscosity of the oil. In comparison, if the uptake capacity was larger than one, it would mean that the cell walls of the foam were swelled by the oil. Figure 4(b) shows that the oil-sorption capacity of motor oil, bean oil, cyclohexane, toluene, and CCl_4 for the PP/POE0 foams was 0.73, 0.91, 1.25, 1.23, and 1.12 ml/ml, respectively, while it was 0.95, 1.15, 1.47, 1.49, and 1.31 ml/ml for the PP/POE30 foams, respectively. By comparison, it was found that the volume uptake capacities of various oils for PP/POE30 foams were also higher than those for the PP/POE0 foams. Moreover, the maximum volume uptake capacities of motor oil and bean oil for the PP/POE0 foams and the capacity for motor oil for PP/POE30 foams were lower than one, probably due to the relatively high viscosity of motor oil and bean oil. In comparison, the maximum volume uptake capacities of cyclohexane, toluene, and CCl_4 for PP/POE0 foams and the maximum volume uptake capacities of bean oil, cyclohexane, toluene, and CCl_4 for PP/POE30 foams were larger than one. This means that the volume of these absorbed organic solvents or oil were higher than the geometric volume of the voids in the original foams, thus indicating that the foams were swelled by the organic solvents or oil. In addition, the swelling of PP/POE30 foams was more

obvious than that of PP/POE0 foams, probably due to the decreased crystallinity of the former with the addition of POE. As previously reported,³⁸ the oil-sorption mechanism of PP fibrous mats was only a surface phenomenon, a capillary action through bridges of the voids between fibers, due to the high crystallinity of the PP fibrous mats. However, the oil sorption of the PP/POE foams in this study could involve capillary action as well as swelling of the foams by the oils or organic solvents. Therefore, the higher sorption capacity of the PP/POE30 foams relative to the PP/POE0 foams should be attributed to its higher open-cell content and the swelling behavior.

Recoverability and Reusability of PP/POE Foams

Recoverability was considered an important factor for PP/POE open-cell foams as oil sorbents. If the foams showed good recoverability after compression deformation, it would facilitate the foam recovering and absorbing oils in the following cycles. Consequently, the foams could keep showing large sorption capacities and hence good reusability. Thereby, cyclic compression was carried out with PP/POE0 and PP/POE30 open-cell foams to study their recoverability after compression (See Figure 5). Ten cycles of compression were applied to the foams with a maximum strain of 70%. The stress-strain curves of the cyclic compression in Figure 5(a,b) show that the maximum stress for PP/POE0 and PP/POE30 foams was about 160 kPa and 90 kPa, respectively. This indicates that the PP/POE30 foams were less rigid than the pure PP foams, which is attributed to the elastic component in the blend. In addition, after the first compression, the permanent strain for PP/POE0 and PP/POE30 foams

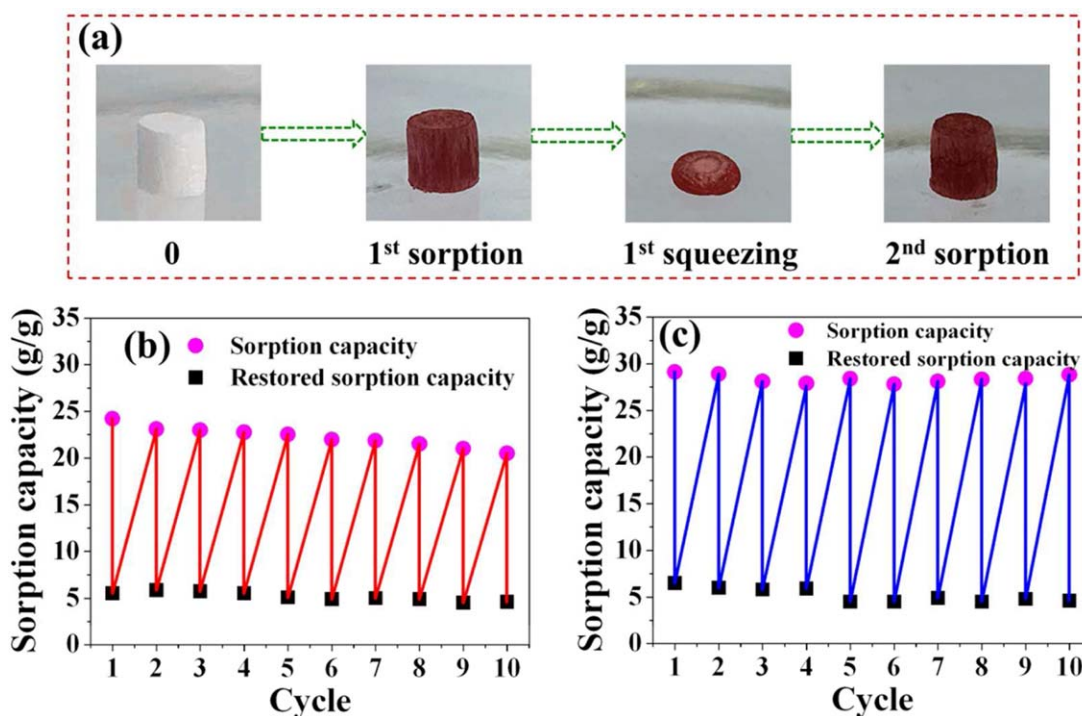


Figure 6. (a) Photographs of cyclic sorption and squeezing processes of PP/POE30 open-cell foam with cyclohexane dyed with Sudan IV. Sorption and restored sorption capacities of PP/POE open-cell foams with cyclohexane: (b) PP/POE0 and (c) PP/POE30. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was about 30% and 15%, respectively. This indicates that the latter foams were more ductile and recovered more easily after compression. With more cycles of compression applied to PP/POE0 and PP/POE30 foams, the permanent strain was increased for both foams, with less for the latter. The permanent strain for the PP/POE foams with different contents of POE after different cycles is summarized in Figure 5(c). It was found that the permanent strain was increased with number of cycles, while it decreased with the POE content. Therefore, this indicates that the addition of POE in the PP/POE blends facilitates the recoverability of the foams after compression deformation. Thus, compared to pure PP foams, it was highly expected that the recoverability of PP/POE foams would be improved after mechanically squeezing out oils in their application as oil sorbents.

Good reusability is a desired key factor for oil sorbents that saves costs in practical oil-cleanup applications. If the PP/POE blend foams keep showing high capacities in cyclic sorption-desorption tests, they would possess the characteristics of good reusability as oil sorbents. Figure 6(a) shows the sorption and squeezing process of PP/POE30 open-cell foam in the application of cyclohexane labeled with Sudan IV. For the first sorption, PP/POE30 open-cell foam absorbed cyclohexane to saturation. During the mechanical squeezing, most of the cyclohexane was squeezed out. During the second sorption, the foam absorbed cyclohexane to saturation, recovering its original size. This indicates excellent reusability for the PP/POE30 foams. The cyclic sorption-desorption properties of the PP/POE0 [Figure 6(b)] and PP/POE30 [Figure 6(c)] foams were quantita-

tively studied with cyclohexane. Figure 6(b) shows that PP/POE0 foam exhibited a sorption capacity of 24.5 g/g for the first sorption and a slight decreased capacity for the following cycles, probably due to the mechanical deformation of the foam. For the desorption of each cycle, the absorbed cyclohexane could not be completely removed under a mechanical pressure (1 MPa), and a restored capacity of about 5.0 g/g still remained in the foam after squeezing. In comparison, the PP/POE30 foam showed a relatively higher sorption value of 29.1 g/g for the first sorption and still possessed a high sorption capacity of around 28.0 g/g after 10-cycle sorption and desorption. In a comparison of the PP/POE0 and PP/POE30 foams, the larger sorption capacity and better reusability make the latter foams better potential oil sorbents, which was considered to be related to the addition of POE.

A larger sorption rate and a shorter saturated sorption time are desired properties for materials to be used as oil sorbents. The sorption kinetics of PP/POE0 and PP/POE30 foams for cyclohexane was investigated in terms of the saturated sorption time (Figure 7). For the first cycle, it was found from Figure 7(a) that the sorption capacities were gradually increased with time up to saturation. The saturated sorption time was about 40 min and 30 min for the PP/POE0 and PP/POE30 foams, respectively. The faster sorption of cyclohexane for the PP/POE30 foam could be related to the increased open-cell content and the improved ductility and recoverability with the addition of POE in PP/POE blend foams. The saturated sorption times for the PP/POE0 and PP/POE30 foams for 10 cycles are shown in Figure 7(b). It was found that, for the first four cycles, the

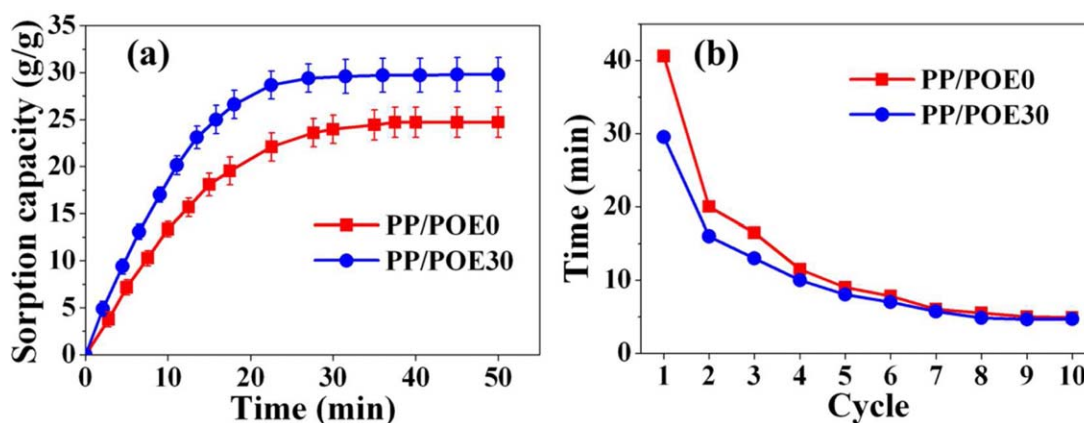


Figure 7. (a) The first sorption curve of PP/POE0 and PP/POE30 open-cell foams with cyclohexane. (b) The saturated sorption times of the cyclic oil sorption of PP/POE0 and PP/POE30 open-cell foams with cyclohexane for 10 cycles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

saturation time of the PP/POE30 foams was prominently shorter than that of the PP/POE0 foams. This indicates that the PP/POE30 foams were quicker to achieve saturated oil sorption, which might be related to the higher open-cell content and the better mechanical recoverability with the addition of POE in the blends. Moreover, it was found that the saturation time was decreased with the cycles, both for PP/POE0 foams and PP/POE30 foams, which might be due to the following two aspects. First, the restored oil within the cell walls could possibly facilitate the wetting and sorption of the oil in the subsequent cycles. Second, some cell walls could be broken during mechanical deformation of the foams, which would increase the open-cell content and thus accelerate the subsequent sorption rate and shorten the saturation time. Thus, the saturation time from the seventh cycle to the tenth became similar for PP/POE0 foams and PP/POE30 foams. The possible two reasons are still under study and need to be verified by ongoing work.

CONCLUSIONS

In this paper, open-cell polypropylene/polyolefin elastomer (PP/POE) blend foams were prepared via continuous-extrusion foaming using supercritical carbon dioxide as the blowing agent. It was found that the PP/POE foams showed an interconnected open-cell structure with a high open-cell content. The open-cell PP/POE foams exhibited excellent hydrophobic and oleophilic properties and higher oil-sorption capacities. In addition, compared to pure PP foams, the addition of POE enhanced the ductility and recoverability of PP/POE blend open-cell foams, improved their reusability as oil sorbents, and also increased their sorption rates. Based on this study, PP/POE open-cell foams have shown promise as potential oil sorbents in applications in oil/water separation, industrial wastewater treatment, and oil cleanup on the sea.

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REFERENCES

- Wei, Q. F.; Mather, R. R.; Fotheringham, A. F.; Yang, R. D. *Mar. Pollut. Bull.* **2003**, *46*, 780.
- Gui, X.; Li, H.; Wang, K.; Wei, J.; Jia, Y.; Li, Z.; Fan, L.; Cao, A.; Zhu, H.; Wu, D. *Acta Mater.* **2011**, *59*, 4798.
- Atlas, R. M. *Int. Biodeterior. Biodegrad.* **1995**, *35*, 317.
- Buist, I.; Potter, S.; Nedwed, T.; Mullin, J. *Cold Reg. Sci. Technol.* **2011**, *67*, 3.
- Lewis, A.; Trudel, B. K.; Belore, R. C.; Mullin, J. V. *Mar. Pollut. Bull.* **2010**, *60*, 244.
- Zahid, M. A.; Halligan, J. E.; Johnson, R. F. *Ind. Eng. Chem. Process. Des. Develop.* **1972**, *11*, 550.
- Muttin, F. *Appl. Ocean Res.* **2008**, *30*, 107.
- Choi, H. M.; Cloud, R. M. *Environ. Sci. Technol.* **1992**, *26*, 772.
- Al-Majed, A. A.; Adebayo, A. R.; Hossain, M. E.; Hossain, M. E. *J. Environ. Manage.* **2012**, *113*, 213.
- Carmody, O.; Frost, R.; Xi, Y.; Kokot, S. *J. Colloid Interface Sci.* **2007**, *305*, 17.
- Cui, Y.; Xu, G.; Liu, Y. *J. Ind. Text.* **2012**, *43*, 330.
- Annunciado, T. R.; Sydenstricker, T. H. D.; Amico, S. C. *Mar. Pollut. Bull.* **2005**, *50*, 1340.
- Hussein, M.; Amer, A. A.; El-Maghraby, A.; Hamedallah, N. *J. Anal. Appl. Pyrolysis* **2009**, *86*, 360.
- Adebajo, M. O.; Frost, R. L.; Klopogge, J. T.; Carmody, O.; Kokot, S. *J. Porous Mater.* **2003**, *10*, 159.
- Duong, H. T. T.; Burford, R. P. *J. Appl. Polym. Sci.* **2006**, *99*, 360.
- Yang, J. S.; Cho, S. M.; Kim, B. K.; Narkis, M. *J. Appl. Polym. Sci.* **2005**, *98*, 2080.
- Zhu, H.; Qiu, S.; Jiang, W.; Wu, D.; Zhang, C. *Environ. Sci. Technol.* **2011**, *45*, 4527.
- Rizvi, A.; Chu, R. K. M.; Lee, J. H.; Park, C. B. *ACS Appl. Mater. Interfaces* **2014**, *6*, 21131.
- Park, C. B.; Padareva, V.; Lee, P. C.; Naguib, H. E. *J. Polym. Eng. Sci.* **2005**, *25*, 239.

20. Kohlhoff, D.; Ohshima, M. *Macromol. Mater. Eng.* **2011**, 296, 770.
21. Yu, P.; Mi, H. Y.; Huang, A.; Geng, L. H.; Chen, B. Y.; Kuang, T. R.; Peng, X. F. *Ind. Eng. Chem. Res.* **2015**, 54, 6199.
22. Lee, P. C.; Wang, J.; Park, C. B. *Ind. Eng. Chem. Res.* **2006**, 45, 175.
23. McNally, T.; McShane, P.; Nally, G. M.; Murphy, W. R.; Cook, M.; Miller, A. *Polymer* **2002**, 43, 3785.
24. Pang, Y.; Dong, X.; Zhao, Y.; Han, C. C.; Wang, D. *Polymer* **2007**, 48, 6395.
25. Wang, K.; Wu, F.; Zhai, W.; Zheng, W. *J. Appl. Polym. Sci.* **2013**, 129, 2253.
26. Deschamps, G.; Caruel, H.; Borredon, M. E.; Bonnini, C.; Vignoles, C. *Environ. Sci. Technol.* **2003**, 37, 1013.
27. Radetic, M. M.; Jovic, D. M.; Jovanc, P. M.; Petrovic, Z. L.; Thomas, H. F. *Environ. Sci. Technol.* **2003**, 37, 1008.
28. Park, C. B.; Cheung, L. K. *Polym. Eng. Sci.* **1997**, 37, 1.
29. Zheng, W. G.; Lee, Y. H.; Park, C. B. *J. Appl. Polym. Sci.* **2010**, 117, 2972.
30. Lee, P. C.; Naguib, H. E.; Park, C. B.; Wang, J. *Polym. Eng. Sci.* **2005**, 45, 1445.
31. Lee, P. C.; Li, G.; Lee, J. W.; Park, C. B. *J. Cell. Plast.* **2007**, 43, 431.
32. Yang, J.; Zhang, Y.; Zhang, Y. *Polymer* **2003**, 44, 5047.
33. Ceylan, D.; Dogu, S.; Karacik, B.; Yakan, S. D.; Okay, O. S.; Okay, O. *Environ. Sci. Technol.* **2009**, 43, 3846.
34. Sonmez, H. B.; Karadag, K.; Onaran, G. *J. Appl. Polym. Sci.* **2011**, 122, 1182.
35. Zhang, X.; Li, Z.; Liu, K.; Jiang, L. *Adv. Funct. Mater.* **2013**, 23, 2881.
36. Barthlott, W.; Neinhuis, C. *Planta* **1997**, 202, 1.
37. Zhu, Q.; Chu, Y.; Wang, Z.; Chen, N.; Lin, L.; Liu, F.; Pan, Q. *J. Mater. Chem. A* **2013**, 1, 5386.
38. Choi, H. M.; Kwon, H. J.; Moreau, J. P. *Text. Res. J.* **1993**, 63, 211.