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Synthesis of novel polypropylene-acrylate fiber sorbent and evaluation of the sorption properties for organic contaminants from water surface

Shaoning Li[a,b], Junfu Wei[a,c,*]

[a]*State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300387, China*
[b]*Department of Material Sciences, School of Material Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China*
[c]*School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, China*
Tel. +86 022 8395 5898; Fax: +86 022 8395 5451; email: jfwei@tjpu.edu.cn

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ABSTRACT

Treatment of organic matter spill remains a global concern due to its significant environmental impact. In this paper, a novel polypropylene-acrylate sorbent (PP-g-EA) has been prepared by grafting of ethylhexyl acrylate (EA) on the polypropylene (PP) fiber substrate using ultraviolet radiation method. The grafting degree could be controlled by adjusting the monomer concentration, photosensitizer (benzophenone [BP]) concentration, and the content of water in the solvent. This paper focused on the influencing factors on the sorption capacity of PP-g-EA for 1,4-xylene from water surface. The results showed that sorption capacity is mostly affected by sorption time, grafting degree of PP-g-EA, temperature, and pH. It could be concluded that the PP-g-EA fully took the advantages of both PP fibers and acrylate resins to overcome the shortcomings of each when used alone, such as fast saturation-sorption rate and high sorption capacity for organic contaminants.

Keywords: Polypropylene fiber; Grafting degree; Ethylhexyl acrylate; 1,4-Xylene; Sorption capacity

1. Introduction

Recently, the spill accidents of organic matter had caused a specific and serious environmental problem because of their toxicity and possible accumulation in the environment. Even a minor scale accident had contaminated 1,000 km of river banks and damaged the terrestrial habitats, resulting in a direct threat to the survival of human beings, animals, and agriculture [1–5].

The most urgent technique for elimination of organic matters spilled in water resources is by collecting thin layers from the water surface with the help of sorbent. Polypropylene (PP) fibers were chosen as an efficient sorbent because of their rapid saturation-sorption rate and high selectivity for the organic matters over the water [6–8]. Furthermore, it is convenient to graft many monomers on polypropylene fibers, which provided broad spaces for the improvement of sorption properties [8,9]. These features make PP fiber very attractive as an alternative sorbent compared with some other sorbents. However, the lower sorption capacity dramatically limited its practice in spill treatment [6,10].

Nowadays, grafting monomer onto polymeric substrate is widely used for the surface modification of

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*Corresponding author.

sorbents and usually enhancing sorption capacity of the sorbents [11–14]. In this paper, the PP fiber was modified through graft polymerization of ethylhexyl acrylate (EA) initiated by ultraviolet (UV) in isopropanol/water mixture solution, as a novel polymeric sorbent for organic contaminants from water surface. In order to investigate the applied scope of new sorbent, the aim of this study was to systematically evaluate the influencing factors through sorption capacity of polypropylene-acrylate sorbent (PP-g-EA). 1,4-Xylene was chosen as a model organic chemical, because it can be a serious environmental threat when being disposed or spilled. The results of this study can be considered in making decision, which adsorption conditions of PP-g-EA adsorbent can be efficiently applied for insoluble organic chemical removal in a real spillage treatment plant.

2. Experimental

2.1. Chemicals

The PP fiber was obtained from Haidexin Chemical Factory, Jiangsu, China, whose properties are presented in Table 1. EA and isopropanol were from Tianjin Chemical Reagent Institute. Photosensitizer benzophenone (BP) was obtained from Tianyi Chemical Factory, Tianjin, China. 1,4-Xylene was obtained from the company of Nan Jiang. All the chemicals were used as received.

2.2. Preparation of PP-g-EA sorbent

A homogeneously mixed solution was obtained by dissolving a certain amount of EA and BP in isopropanol/water solution under stirring. Then, the PP fiber was immersed in the mixed solution. After injecting bubbling nitrogen gas for 5 min, UV radiation with a wavelength of 312 nm was adopted to initiate the graft polymerization for 1 h at room temperature. The grafted PP fiber was taken out and washed with ethanol to remove the unreacted monomer. A typical graft polymerization recipe is shown in Table 2. The grafting degree (G) of PP-g-EA was calculated as:

Table 2
The recipe for preparation of PP-g-EA

	Monomer concentration (%, v/v)	BP concentration (wt‰)	Water content (%)
Typical recipe	3.75	0.625	70
Parameters	1.25–11.25	0–2.5	10–95

$$G(\%) = [(W_1 - W_0)/W_0] \times 100\% \qquad (1)$$

where W_0 and W_1 are the weight of original and grafted PP fiber, respectively.

Table 1
Physical properties of PP fiber

Sample	Fiber diameter (μm)	Initial modulus (cN/dTex)	Density (g/cm^3)
PP fiber	19–21	26.51	0.91

2.3. Materials characterization

High-energy-resolution XPS analyzes were performed on a Kratos AXIS 165 spectrometer using monochromatic Al Ka X-rays. Infrared spectra were obtained with fourier transform infrared spectra (VECTOR22, BRUKER Co.) and the measurements were carried out in a range of 3,000–1,000 cm^{-1}. Specific surface area of the original PP and PP-g-BA is measured by BET method on TriStar 3,000 V6.08 A. All samples were degassed for 4 h at 473.15 K.

2.4. Methodologies of sorption experiments

In the sorption experiments, 30 g 1,4-xylene was added into a 100 mL beaker containing 50 g water. Then, the test fiber sample (0.05 ± 0.01 g) was gently placed onto the organic layer. The fibers samples after sorbed were removed using a nylon net collector and allowed to drain for about 10 min. Then, the sorbed fibers were weighed. The sorption properties of PP-g-EA were evaluated by the sorption of 1,4-xylene from water body and the scope of influencing factors is shown in Table 3.

3. Results and discussion

3.1. Characterization of the PP and PP-g-EA

Compared to the original PP fiber, an additional peak can be observed at 287.0–288.9 eV (Fig. 1(b))

Table 3
The scope of influencing factors of PP-g-EA

Influencing factors	Grafting degree (%)	sorption time (s)	Temperature (℃)	pH
Typical recipe	16.21	5	15	10
Scope	0–78.84	1–8	5–40	1–10

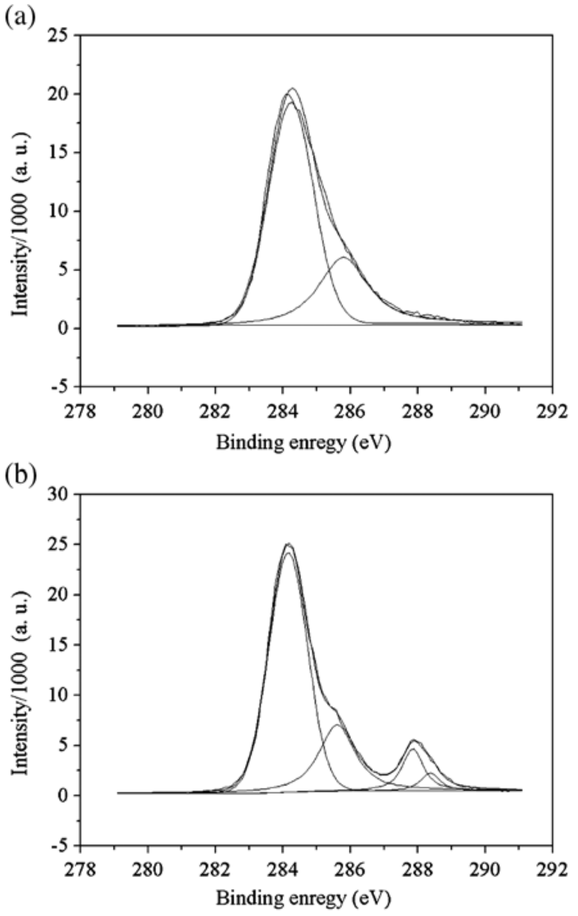

Fig. 1. XPS spectra of original (a) PP fiber and (b) PP-g-EA fiber with grafting degree of 16.21%.

because of the presence of carboxylic group at the grafted fiber. The PP-g-EA grafted fiber could be fitted well by introducing two new oxidized carbon species, the new peaks at 287.8 and 288.6 eV, corresponding to the carboxyl carbon (–C=O–O–) and ketone carbons (–C=O–), respectively. Further characterization of PP-g-EA fiber was carried out by FT-IR spectra analysis. Infrared spectra of the original PP and PP-g-EA are illustrated in Fig. 2. In addition to the characteristic bands of original PP, a new absorption peak can be observed in the spectrum of the copolymer. The new peak at 1,738 cm^{-1} came from the vibrating absorption of carbonyl group (C=O) in the grafted PP fibers [9]. The characteristic stretching vibration showed that EA had been grafted onto the PP substrate. The XPS and FT-IR spectra suggested the surface grafting modification of PP fiber had been successfully achieved.

3.2. *Graft polymerization of PP-g-EA*

The graft polymerization was carried out by direct irradiation immersed in monomer solution. Several factors would contribute to obtain considerable grafting degree. As shown in Fig. 3, the grafting degree increased with the increase of the monomer concentration, the presence of high concentration of EA provided a greater availability of monomer molecules to contact with the surface free radical onto PP substrate, leading to a higher grafting degree [15]. The grafting degree of PP-g-EA prepared with different photosensitizer (BP) concentrations and content of water in the solvent is shown in Figs. 4 and 5, respectively. The grafting degree increased with the increase of the BP concentration within the limits of this study (0–0.625‰). BP captured hydrogen from the PP substrate to generate surface radicals and semipinacol radicals, which were combined to form surface photoinitiators in the absence of monomer solution. However, the higher BP concentration would terminate the graft polymerization reaction, then the grafting degree decreased sharply as the concentration further increased [16]. Previous study

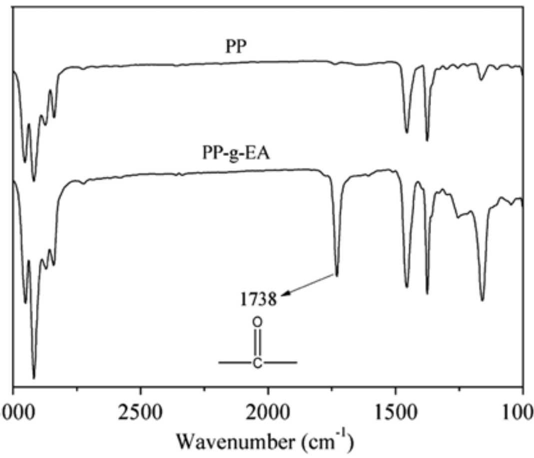

Fig. 2. FT-IR spectra of original PP and PP-g-EA.

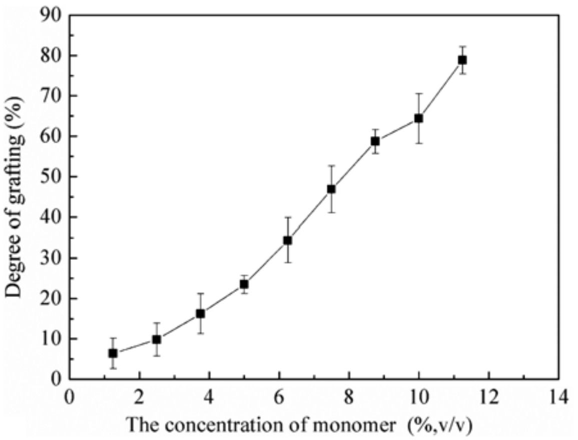

Fig. 3. Effect of monomer concentration (v/v) on grafting degree (BP concentration: 0.625‰, water content: 70%).

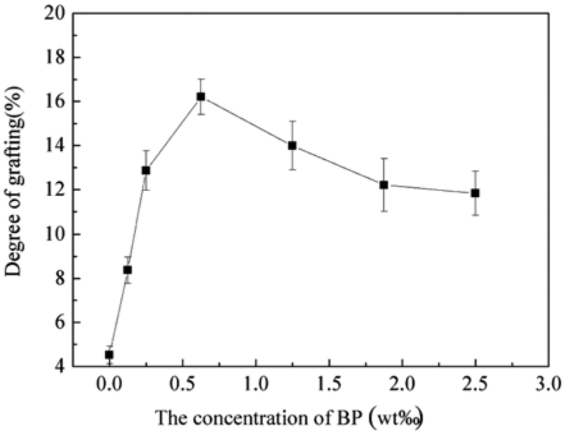

Fig. 4. Effect of BP concentration (wt‰) on grafting degree (monomer concentration: 3.75%, water content: 70%).

suggested that the content of water also played an important role on grafting degree. The appropriate water content of a grafting solution can yield a homogeneous and compatible grafting solution, so that it is necessity to approach the backbone active sites and as a result chain transfer reactions taking place [17]. According to the results of this study, the optimal photosensitizer (BP) concentration and content of water were 0.625‰ and 70%, respectively, for a moderate grafting degree. When the monomer concentration was 3.75%, the grafting degree of PP-g-EA under the optimal conditions was 16.21%.

3.3. *Influence factors of grafted fiber sorption for 1,4-xylene from water surface*

3.3.1. *Sorption time*

It was found that sorption time is a determining factor in the sorption of 1,4-xylene on grafted fiber. To determine the optimal sorption time at which organic chemicals were effectively sorbed on the prepared sorbent, the sorption experiments were carried out at different sorption times ranging from 1.0 to 8.0 s. As it can be seen in Fig. 6, the sorption of 1,4-xylene from water surface using the grafted fiber continuously increased with time until reached equilibrium after 5 s. The sorption capacity of grafted fiber was not substantially increased with sorption time increased. The results indicated that the graft polymerization still reserved the fast sorption rate of original PP fiber. Therefore, this obtained equilibrium time of 5 s was selected for the next sorption experiments.

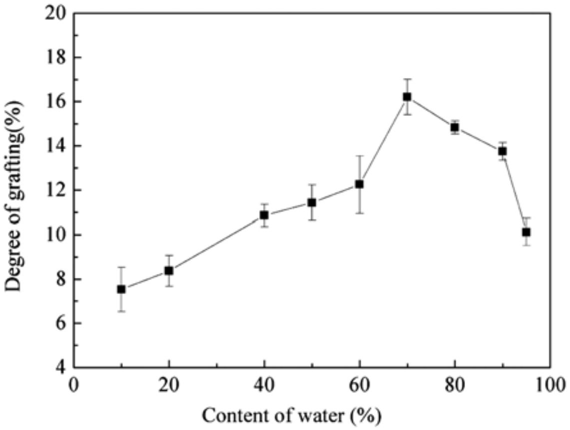

Fig. 5. Effect of water content (%) on grafting degree (monomer concentration: 3.75%, BP concentration: 0.625‰).

3.3.2. *Grafting degree of PP-g-EA*

The influence of grafting degree on sorption capacity of PP-g-EA for 1,4-xylene from water surface was investigated, and the results are shown in Fig. 7. It was concluded that with the increase of grafting degree at first, the sorption capacity of grafted fiber was improved significantly. When the grafting degree was 16.21%, the sorption capacity reached a maximum value of 18.17 g/g which was 2.21 times as lager as that of original PP fiber. The tendency of specific surface area with grafting degree was much similar with that of sorption capacity. The PP-g-EA surface became rougher and the specific surface area value reached a maximum of 0.94 m^2/g at the grafting degree of 16.21% after graft polymerization. The specific surface area played an important role on the sorption capacity for 1,4-xylene, because the rough surface promoted formation of capillary bridges between 1,4-xylene molecular and surface of PP-g-EA. Therefore, the acceptable explanation for the trend was that graft

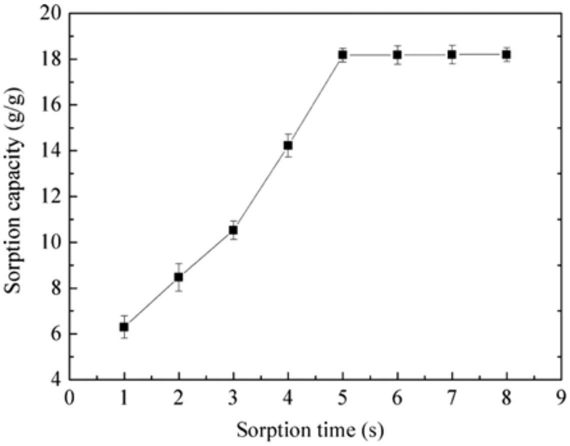

Fig. 6. Sorption capacity of PP-g-EA for1,4-xylene depending on sorption time ($t = 15$℃, grafting degree = 16.21%, and pH = 10.00).

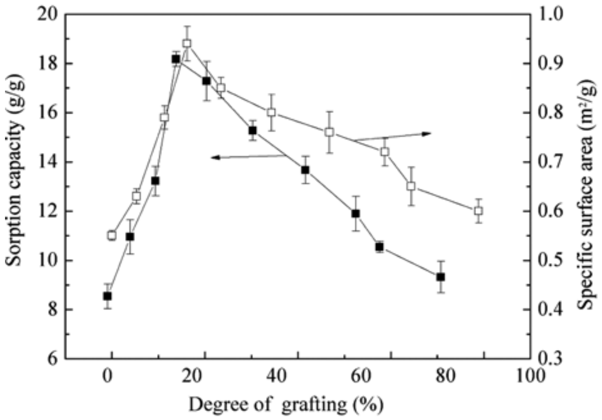

Fig. 7. Sorption capacity of PP-g-EA for1,4-xylene depending on grafting degree and specific surface area of grafted fiber ($t = 15$℃, sorption time = 5 s, and pH = 10.00).

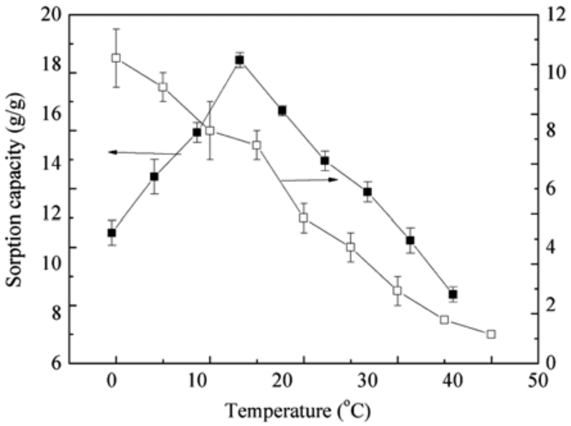

Fig. 8. Sorption capacity of PP-g-EA for 1,4-xylene depending on temperature and viscosity (pH = 10.00, sorption time = 5 s, and degree of grafting = 16.21%).

polymerization induced the highest specific surface area coupled with sufficient hydrophobicity and surface microroughness at grafting degree of 16.21%. It was expected that the introduction of EA segment would increase the sorption capacity for 1,4-xylene with the increasing of grafting degree. However, when the grafting degree was over 16.21%, the much more space between fiber monofilaments occupied by acrylate branch, leads to the specific surface area continuous decrease from 0.94 to 0.59 m^2/g with the grafting degree increasing from 16.21 to 78.84%, which attached to a minimum capillary for 1,4-xylene and affected the sorption capacity of grafted fiber consequently [9].

3.3.3. Temperature

In order to consider possible relation between temperature and sorption capacity of grafted fibers, further attempts should be focused on the variation of the viscosity of 1,4-xylene. As shown in Fig. 8, with the increase of temperature at first, the sorption capacity of grafted fiber was significantly increased and the maximum sorption capacity reached 18.17 g/g at 15℃, when the temperature was over the critical value of 15℃, the sorption capacity of grafted fiber decreased. In order to consider possible relation between temperature and sorption capacity of PP-g-EA, further attempts should be focused on the variation of the viscosity of 1,4-xylene. When the viscosity of 1,4-xylene is remarkably affected by the temperature, it exhibited an decrease from 10.5 to 1 Pa s with the temperature increased from 0 to 40℃ in steps of 5℃. However, we believed that the variation of viscosity was not the sole factor for the sorption capacity increased from 0 to 15℃. It should be emphasized that molecules sorption is Braunian motion which is constant motion, and when they are very close to the surface of grafted fiber, they get attached and connected with the surface of fiber sorbent following the increase of temperature, also attributed to the increase of sorption capacity for 1,4-xylene. The 1,4-xylene with a high viscosity leads to an easier adherence on the surface of the grafted fiber, but the high viscosity significantly affects the capillary penetration of 1,4-xylene molecular into monofilament space between PP-g-EA, which leaded a dissatisfactory sorption capacity for 1,4-xylene. When temperature interval was from 0 to 15℃, the increase of temperature will cause the decrease of viscosity of 1,4-xylene excessively, the 1,4-xylene molecular quickly moves into the PP-g-EA as well as on to the surface, and resulted in a significant increase of the sorption capacity. Over this period, the sorption capacity of PP-g-EA is substantially reduced with the temperature further increased [18,19]. Therefore, the optimum temperature of 15℃ was selected for the sorption experiments in this study.

3.3.4. pH of water

In this study, the effect of organic-over-water solution pH on the sorption capacity of grafted fiber was studied by varying the pH between 1.00 and 10.00. As shown in Fig. 9, the sorption capacity of PP-g-EA (with a grafting degree of 16.21%) was more sensitive to pH change than original fiber, which exhibited a increase from 9.31 to 18.17 g/g with the pH value increasing from acidic to alkali medium, the maximum amount of sorption capacity was obtained at pH 10.0, and minimum sorption capacity exhibited when

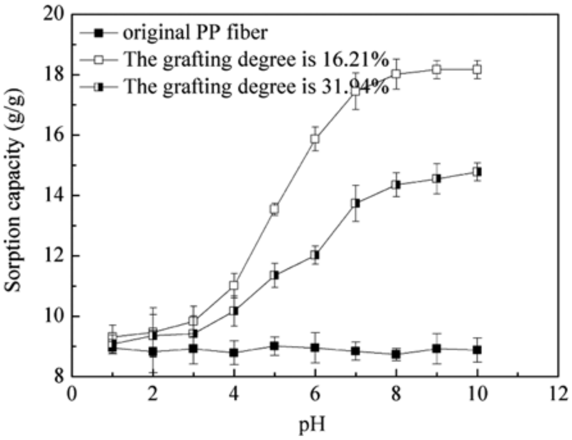

Fig. 9. Sorption capacity of PP-g-EA for 1,4-xylene depending on the pH of water ($t = 15$℃, sorption time = 5s, and degree of grafting = 16.21%).

pH value was 1.00. Furthermore, the PP-g-EA with different grafting degree was also showed the same trend. This trend would be due to the acrylate grafting chains hydrolysis in acidic medium, the variation of pH can affect the surface charge of the PP-g-EA and may be attributed to the completion behavior between hydrogen and active group (–CO–CH_2–) on grafted fiber surface [20–23].

Based on all the consideration above, the sorption capacity of organic contaminant from water by PP-g-EA is highly dependent on the pH. Optimal pH range for PP-g-EA was from 8.00 to 10.00 and thus all sorption experiments in the present study were carried out at initial pH 10.0.

4. Conclusions

In this work, a polymeric PP-g-EA has been prepared and successfully employed as a new sorbent material for 1,4-xylene from water surface. From the experimental data, it is evident that the sorption capacity of PP-g-EA is strongly influenced by the factors such as sorption time, grafting degree of grafted fiber, temperature, and pH values of water. When 1 g of PP-g-EA sorbent with a grafting degree of 16.21% was used at 15℃, the grafted fiber sorbent can sorb 18.17 g of 1,4-xylene in 5 s (the pH value was 10.0). This novel sorbent combined the advantage of PP fiber with acrylate resin, which exhibited higher sorption capacity compared with original PP fiber and made it feasible for the treatment of large-scale organic spilling.

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