Synthesis of butyl acrylate grafted polypropylene fibre and its applications on oil-adsorption in floating water

Feng Yuan,¹ 2 Jun-fu Wei, ¹ ² En-qi Tang,¹ ² Kongyin Zhao¹ ²

¹ Tianjin Municipal Key Lab of Fibre Modification and Functional Fibres, Tianjin Polytechnic University, Tianjin 300160, China. fax: +86 22 24528008; e-mail: jfwei@tjpu.edu.cn
² School of Material Science and Chemical engineering, Tianjin Polytechnic University, Tianjin 300160, China; fax: +86 22 24528054; e-mail: tjzhaokongyin@163.com

(Received: 15 October, 2008; published: 07 July, 2009)

Abstract: Polypropylene oil-absorption fibre (PP-g-BA) was prepared by radiation-induced graft polymerization of butyl acrylate (BA) onto polypropylene (PP) using divinylbenzene (DVB) as cross-linking agent. The original and grafted PP fibres were characterized by Fourier transform infrared (FT-IR) spectrometer and Scanning Electron Microscopy (SEM), and the result indicated that butyl acrylate was successfully grafted onto PP fibre. The factors that influenced the grafting degree of PP were discussed, such as the concentration of monomer and cross-linking agent. When the concentration of DVB was 2% and the concentration of BA was 10%, the maximum grafting degree reached 20.53%. The oil absorption properties of PP and PP-g-BA fibre were investigated and the results showed that the maximum adsorption capacity of PP-g-BA reached 19.74 g/g for toluene and 18.8 g/g for kerosene. Simulating absorption in the oil floating on the surface of water showed that the oil could be absorbed quickly and completely in three minutes. PP-g-BA exhibited quicker adsorption rate and higher adsorption capacity than PP fibre did.

Introduction

As one of the most important energy resources in modern world, oil is indispensable for everyone. However, there will be a risk of a spillage when oil is explored, transported, stored and used [1]. Recent major oil spills (the Braer in Scotland, 1993; the Sea Empress in Wales, 1996; and the Prestige in Spain, 2002) had contaminated thousand kilometres of coastlines and caused significant environmental impact. These spills can damage marine ecosystem and cause wide spread contamination of the surrounding environment. When these spills occur, human health and environmental quality are put at risk.

Once oil comes in contact with water, it forms emulsion that needs to be treated before it is disposed. The oil removal process usually involves emulsion destabilization, which is a difficult process. Various measures have been developed to remove oil from contaminated water so far [2]. Among which, using a specific adsorbent to recycle the spilled oil is the most economical and effective means. Some adsorbents had been widely researched, such as cotton grass fibre [3, 4], polypropylene (PP) [5, 6], wool-based non-woven [7], vegetable fibres [8], kapok [9], and Sugi Bark Adsorbent [10]. Of all these adsorbents, polypropylene adsorbents are...
ideal materials for oil recovery from the water surface given its hydrophobic property and its ability to selectively adsorb oil in the presence of water.

Wei et al. [5] evaluated the properties of PP non-woven as oil adsorbents in marine oil-spill recovery. Different forms of PP non-woven were evaluated in this study in terms of initial oil-adsorption capacities and oil-retention properties. The investigation revealed that the fibre diameter, adsorbent porosity and oil property are the most important factors in the oil-adsorption performance of PP non-woven. However, current materials for the treatment of oily wastewater remain unsatisfactory.

To graft PP with other monomer may be a good method to improve the oil-adsorption capacity of PP. Radiation-induced graft polymerization is a valuable method for the modification of the chemical and physical properties of polymer surfaces [11-15]. Some monomers such as acrylic acid [16], acrylonitrile [17], and styrene [18] have been successfully grafted onto PP. In order to improve the oil-adsorption capacity of PP, in this paper, polypropylene oil-adsorption fibre (PP-g-BA) was prepared by radiation-induced graft polymerization of butyl acrylate onto PP. The grafted fibre was characterized and its absorption properties for oil were investigated. Simulating absorption in the oil floating on the surface of water showed that the oil could be absorbed quickly and completely in three minutes.

Results and discussion

Fig. 1 shows the IR spectra of the original PP and the grafted PP fibre. There were strong bands at 1455 cm\(^{-1}\) and 1372 cm\(^{-1}\) in grafted PP, corresponding to the bending vibrations of CH\(_2\) for both PP and the grafted PP fibre. Compared to the original PP, the appearance of new band at 1733 cm\(^{-1}\) in the grafted PP was due to the stretching vibrations of C=O. The characteristic peak indicated that BA had been grafted onto the PP fibre by grafting polymerization.

![FT-IR spectra of PP and PP-g-BA.](image)

Fig. 1. FT-IR spectra of PP and PP-g-BA.

Fig. 2 shows the SEM micrograph of the original PP and the grafted PP fibre (PP-g-BA). It is found in Fig. 2 that the diameter of fibre increased obviously after grafting.
polymerization. The smooth surface of PP became rough after grafting. The branch of polyacrylate grafted onto the PP randomly during the irradiation and most of them were vertical to the axis of fibre. A heterogeneous grafting layer structure was formed on the surface of fibre after grafting, resulting in the thickness and coarse of PP fibre. It is proved that BA had been grafted onto the PP fibre by γ-irradiation induced polymerization.

![SEM micrograph of original and grafted PP fibre.](image)

**Fig. 2.** SEM micrograph of original and grafted PP fibre.

The effect of cross-linking agent concentration on the degree of grafting is given in Fig. 3. Divinylbenzene is used as the cross-linking agent and the concentration of monomer is 10%. It was found that the grafting degree initially increased with the increase of concentration of divinylbenzene (DVB), and then reached the maximum. However, with further increase of DVB concentration, there was an obvious drop in the grafting degree of PP.

![The degree of grafting with different concentration of cross-linking agent.](image)

**Fig. 3.** The degree of grafting with different concentration of cross-linking agent. (The monomer concentration is 10%)
When the concentration of DVB reached 2% the maximum grafting degree was 20.53%. This was a typical behaviour observed in grafting processes occurring via chain transfer mechanism. With the increasing amounts of DVB, more monomer reacted and grafted with PP, leading to a higher grafting degree, a further increase in DVB did not improve the degree of grafting. Self-polymeric reactions of monomer and cross-linker in higher DVB concentration may decrease the relative degree of grafting.

Fig. 4 shows that the degree of grafting increased with the increase of monomer concentration, and then decreased slightly with the sequential increase of monomer concentration. When the monomer concentration reached 10% the degree of grafting reached the maximum, with a value of 20.53. The higher concentration of monomer increased the probability of monomer that reacted with PP. So in a low concentration the degree of grafting increased with the increase of monomer. However, when the monomer is over a critical concentration, it will cause phase separation of homopolymer and PP matrix, which is a disadvantage to the grafting of PP. So the degree of grafting increased fast within the concentration of 10%, and when the concentration of monomer exceeded 10%, the degree of grafting decreased.

![Fig. 4](image_url)

**Fig. 4** The degree of grafting with different monomer concentration. (The cross-linking agent concentration is 2%).

Fig. 5 shows the oil-adsorption capacity of PP-g-BA with different concentration of cross-linking agent. It is found that the absorption capacity for toluene and kerosene increased initially but decreased subsequently with the increase of cross-linking agent. And when the concentration was 1.5%, the oil-adsorption of PP-g-BA reached the maximum. The absorption capacity for toluene and for kerosene was 19.74 g/g and 18.8 g/g, respectively. When the concentration of cross-linking agent is too low, the network structure of grafting chain cannot form, so the absorption capacity of oil increased initially. But with the subsequent increase of cross-linking agent, the self-polymeric reactions between monomers also increased, which resulted in the compactness of grafted network and the decrease of adsorbent porosity. So the oil-adsorption capacity decreased with the subsequent increase of cross-linking agent.
Fig. 6. shows the effect of grafting degree on the absorption capacity of oil. It is found that the absorption capacity for toluene and kerosene increased with the increase of grafting degree. And when the grafting degree was 14.95%, the highest absorption of PP-g-BA for toluene was reached with a value of 19.18 g/g. Similarly when the graft degree was 15.88%, the highest absorption for kerosene was got with a value of 17.6 g/g.

Fig. 5. The oil-adsorption capacity with different concentration of cross-linking agent.

Tab. 1 shows the absorption properties of PP and PP-g-BA for toluene floating on the water. It can be seen that the absorption rate of the grafted PP was quicker than the original PP fibre, and PP-g-BA exhibited higher absorption capacity than original PP.

Fig. 6. The oil-adsorption capacity with different degree of grafting.
Fig. 7 shows the pictures of toluene floating on the water before absorption, after being adsorbed by PP and PP-g-BA, respectively. In order to observe the difference of oil-adsorption capacity of PP and PP-g-BA, some methyl orange was dissolved in toluene. It is found that toluene was absorbed completely by PP-g-BA fibre within 3 minutes and the solution was colourless. There is a little toluene in the beaker where PP adsorbent was added and the colour is buff. PP-g-BA exhibited quicker adsorption rate and higher adsorption capacity than PP fibre did.

**Tab. 1.** Floating toluene absorption of PP and PP-g-BA.

<table>
<thead>
<tr>
<th>Fibres</th>
<th>PP</th>
<th>PP-g-BA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grafting degree</td>
<td>0</td>
<td>9.3%</td>
</tr>
<tr>
<td>Toluene absorption (g/g)</td>
<td>13.6</td>
<td>19.29</td>
</tr>
<tr>
<td>Absorption time (min)</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>The remaining toluene</td>
<td>a little</td>
<td>none</td>
</tr>
</tbody>
</table>

(a) toluene before absorption  (b) adsorbed by PP  (c) adsorbed by PP-g-BA

**Fig. 7.** The toluene absorption of PP and PP-g-BA in floating water.

Tab. 2 shows the absorption properties of PP-g-BA under different mass of toluene. It is found that with the increase of toluene on the surface of water, the absorption time became longer and the saturation absorption capacity was about 17.54 g/g. The oil had been absorbed completely by the fibre before its saturation absorption capacity within three minutes.

**Tab. 2.** Absorption properties of PP-g-BA under different mass of toluene.

<table>
<thead>
<tr>
<th>The initial toluene (g)</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption time (min)</td>
<td>3</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>The remaining toluene</td>
<td>none</td>
<td>a little</td>
<td>some</td>
</tr>
</tbody>
</table>

The fibre with the degree of 9.3% was used and the mass of fibre was 0.5700 g.
The PP fibre was obtained from Shijiazhuang Cigarette Factory, Hebei, China. Butyl Acrylate (BA) was from Tianjin Chemical Reagent Institute and used without any further purification. Divinylbenzene (DVB) was obtained from Tianlian Chemical Factory, Shanghai, China, and used as received. All the other chemicals were analytical grade and were used without any further purification.

The graft polymerization of BA onto PP fibre was carried out by co-irradiation method using a $^{60}$Co gamma radiation source. A homogenously mixed solution was obtained by dissolving a certain amount of BA and DVB in deionized water under stirring. The mixture solution was joined into the glass tube, and a certain amount of PP fibre was marinated into the solution. Then the mixtures in the glass tube were aerated by bubbling nitrogen gas for 5-7 min. The graft polymerization was performed by co-irradiation for 30 h with the total radiation dose of 30 kGy. Then the PP fibre was taken out and washed with ethanol and acetone for 24 h to remove the homopolymer and unreacted monomer. The graft degree (G) was calculated as follows:

$$G (%) = \frac{(W_g - W_0)}{W_0} \times 100\%$$

where $W_g$ and $W_0$ is the weights of initial and grafted PP fibre, respectively. The grafted or non-grafted PP were dried in a vacuum oven for 8 h at 333 K and weighed to get $W_g$ and $W_0$.

The structure of polypropylene fibres were characterized by VECTOR22 IR-spectrometer (Germany, Bruker Co.) and their surface morphology was observed by a QUANTA200 scanning electron micron microscope (Holand, FEI Co.).

To detect the oil-adsorption properties of original PP and grafted PP, 20 g oil (kerosene or toluene) was put into a beaker. A certain amount of fibre (about 0.5 g) was added and sealed in the beaker for 24 h at room temperature. Then the fibre was picked out and weighed to determine the oil-adsorption. The oil-adsorption capacity (W) was calculated as follows:

$$W = \frac{(G_2 - G_1)}{G_1}$$

where $G_1$ and $G_2$ represents the weights of the dried fibre and the fibre with oil, respectively.

In order to observe the difference of oil-adsorption capacity of PP and PP-g-BA, about 9.5 g toluene dissolved in some methyl orange was suspended in 200 ml water in a 250 ml beaker. Then 0.5 g PP or PP-g-BA fibre was added in to the beaker at room temperature. The oil-adsorption was observed by the reduction of colour in toluene and the process was pictured by a digital camera.

Acknowledgements

The authors thank the Special Program for Key Research of Chinese National Basic Research Program (2008CB417202), Tianjin Colleges Science and Technology Development Fund (2006ZD40) and the Specialized Research Fund for the Doctoral Program of Higher Education (20050058001) for supporting this research work.

References