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Research on preparation and properties of methacrylate grafted meltblown polypropylene nonwovens for oily wastewater treatment

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ABSTRACT

A kind of modified meltblown polypropylene nonwovens (BMA-g-MBPP and LMA-g-MBPP) was prepared by chemical grafting reaction with butyl methacrylate (BMA) or lauryl methacrylate (LMA) as monomer, benzoyl peroxide (BPO) as initiator, toluene, and Tween-80 as swelling agent. The structure of modified MBPP was characterized by FTIR, XPS, and SEM. And the absorbed property and mechanism of LMA-g-MBPP and BMA-g-MBPP to toluene or kerosene was analyzed. The results showed that the maximum saturated absorbency to toluene and kerosene was 14.5 and 15.4 g/g.

Keywords: Meltblown polypropylene nonwovens; Methacrylate; Grafting

1. Introduction

Oil spill into water resources has recently become one of the greatest causes of water pollution, and various technologies and materials have been applied to treat oil containing wastewater [1–4]. Meltblown polypropylene nonwoven (MBPP) is a typical hydrophobic material, having an excellent oil affinity for oil. The microfiber structure, large surface area, small pore size and high porosity of MBPP make it suitable for absorptive material. The density of MBPP is lower than water and it almost does not absorb water, so MBPP is usually applied as oil absorptive material to remove polluted oil in water. Wei [5] researched the structure and oil absorptive performances of MBPP by means of the environmental scanning electron microscope. Wei and Ling [6,7] analyzed the oil-absorbing characteristics of MBPP as oil-absorptive materials. But MBPP absorbed organic oil mainly by capillary action, which makes the saturated absorbency low and the absorbed oil was easy to leak out when pressured. Graft copolymerization is an effective method to introduce lipophilic group to the polymer chain and the oil adsorption properties of MBPP can be successfully improved. And grafting treatment on MBPP is a fast and effective way to prepare fibrous oil absorptive materials.

Methacrylate has a strong affinity to oily organic compound and it has been widely used in the high oil-absorbing material preparation. Jang [8,9] synthesized poly(styrene-acrylic) oil-absorbing resin by copolymerizing; Keenan [10,11] prepared synthetic oil-absorbing resin with methacrylic acid and methacrylate as monomers; Atta [12–15] made oil-absorbing resin with

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octene and methacrylate copolymer. Methacrylate is always used to prepare highly oil absorptive resins or fibers which have various applications in environment protection, industry and agriculture [16–21].

Graft copolymerization is an effective means of modification of polymer structure. At present, graft copolymerization technique is widely used in introducing lipophilic group in the polymer molecular chain to improve the adsorption performance. Said [22] grafted fatty acid acylation on bagasse, which greatly improved the hydrophobic property of bagasse. Chen. [23] synthesized polystyrene new oil-absorbing resin with grafting chlorinated paraffin on polystyrene molecule. Wei [24] prepared methyl acrylate grafted polypropylene fiber by ultraviolet radiation.

In this study, butyl methacrylate (BMA) and lauryl methacrylate (LMA) were used as monomer to modify the absorptive and retention properties of MBPP by grafting reaction. A novel oil absorptive material (MA-g-MBPP) was prepared by introducing an oil affinity group in the macromolecule of PP. The structure and oil absorptive property was characterized.

2. Experimental

2.1. Materials

Meltblown polypropylene nonwoven fabric was supplied by Jiang Shunhao Knitting Co., Ltd.; BMA and LMA were purchased from Tianjin Guangfu Fine Chemical Research Institute; Benzoyl peroxide (BPO), Tween-80 and toluene were analytical reagents from Tianjin chemical reagent company.

2.2. Preparation of graft-modified MBPP

MBPP was immersed in deionized water and boiled for 3 h to remove oil and impurities on the surface. A certain amount of deionized water was added into flask equipped with a stirring device and raised to a certain temperature at 60˚C. Then a mixture of initiator and swelling agent was added in. And the treated nonwoven fabric was placed into the flask and stirred at constant temperature at 75˚C. After a certain time of initiating reaction, BMA or LMA was added in with a dropping funnel. When the grafting reaction was finished after 90 min, the MBPP was washed with water and acetone several times to remove homopolymer and impurities.

2.3. Characterization of grafted MBPP

A Fourier transform infrared spectrometer (FTIR, Bruker TENSOR37 Germany) was used to examine the structure of grafted MBPP. The morphology of the grafted MBPP was observed by scanning electron microscope (SEM, FEI QUANTA200 Czech). An X-ray photoelectron spectroscopy (XPS, British Thermo Fisher K-alpha, the source is Al K 1486.6 eV, the analysis is 10 nm) was applied to analyze the structural change of grafted MBPP.

2.4. Oil absorptive performance of grafted MBPP

Oil absorbency was evaluated by ASTM (F726-81). About 0.1 g sample was put in a stainless steel mesh ($4 \times 4 \times 2$ cm). The sample was immersed in toluene or kerosene. The sample and the mesh were together picked up from oil, drained for 20 s, tapped with filter paper to remove excess oil from the bottom of the mesh, and then weighted. The oil absorbency (Q) was calculated by the following equation:

$$Q = \frac{W_1 - W_0}{W_0}$$

where Q was oil-absorbency of tested sample, W_1 was weight of sample after absorption; W_0 was weight of dried sample.

The saturated absorptive sample was put in a centrifuge. After centrifugal rotation with a speed of 1000 r/min and time of 1 min, the oil retention property was calculated using the following expression.

$$R = \frac{W_b}{W_a} \times 100\%$$

where W_b was the sample weight after centrifugal rotation; W_a was the sample weight before centrifugal rotation.

The oil mechanism of the grafted MBPP was also analyzed.

3. Results and discussion

3.1. FTIR analysis

Fig. 1 showed the infrared spectra of the BMA-g-MBPP sample before and after grafting. As shown in Fig. 1, the peak at 3,000~2,800 cm^{-1} was attributed to C–H group; the vibrational peak of $-CH_2$ group located at 1460 cm^{-1} and asymmetric bending vibration peak of $-CH_3$ group located at 1380 cm^{-1}. Meanwhile, the strong peak at 1,735~1,730 cm^{-1} of BMA-g-MBPP spectra was attributed to the stretching vibration of C=O, which indicated that the ester group has been grafted on the molecular structure of PP.

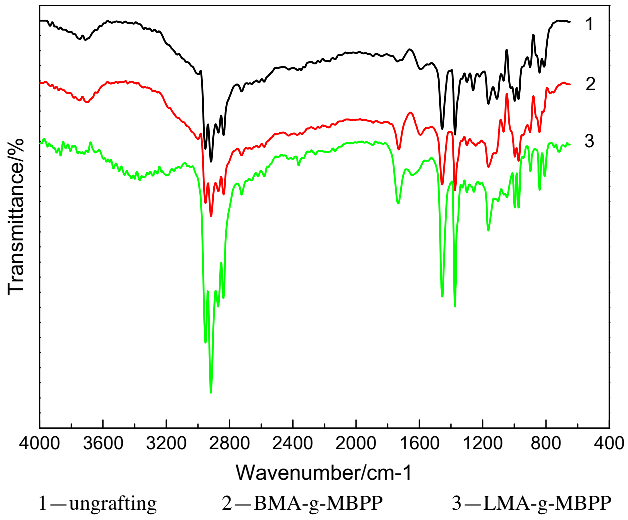


Fig. 1. FTIR spectra of samples.

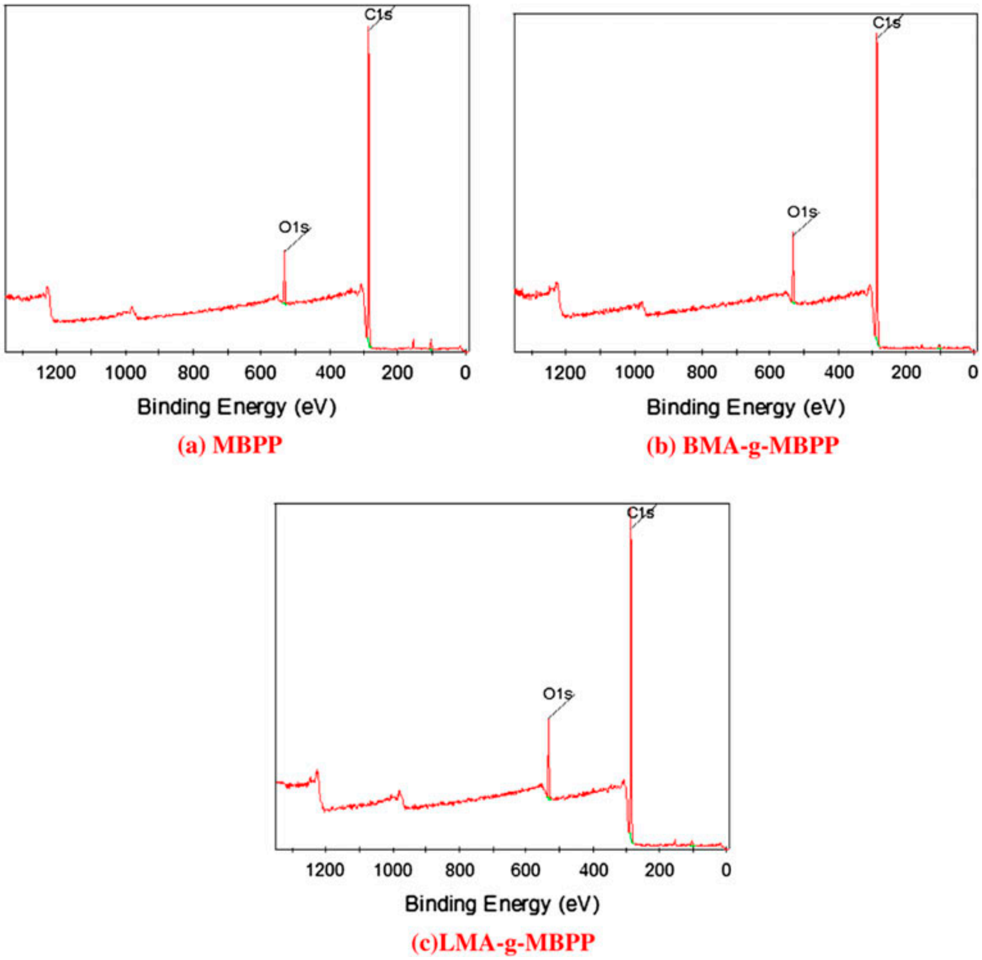
This proved that BMA has been successfully grafted onto the polypropylene matrix.

3.2. XPS analysis

The XPS spectra of MBPP and grafted MBPP were shown in Fig. 2. The O1 peak after grafting was improved, indicating the introduction of new group containing O element. The O1 peak in the spectrum of MBPP (shown in Fig. 2(a)) might be the absorption O from air. The calculating results of the surface elemental composition and the relative content were shown in Table 1. As shown in Table 1, after grafting treatment, the C element content on the surface of the MBPP decreased and the O element content increased.

Table 1
Element content before and after grafting

Sample	Element content (%)	
	O	C
Ungrafted	5.91	90.97
BMA-g-MBPP	8.50	89.50
LMA-g-MBPP	10.07	87.46



(a) MBPP

(b) BMA-g-MBPP

(c)LMA-g-MBPP

Fig. 2. XPS spectra of MBPP and grafted MBPP.

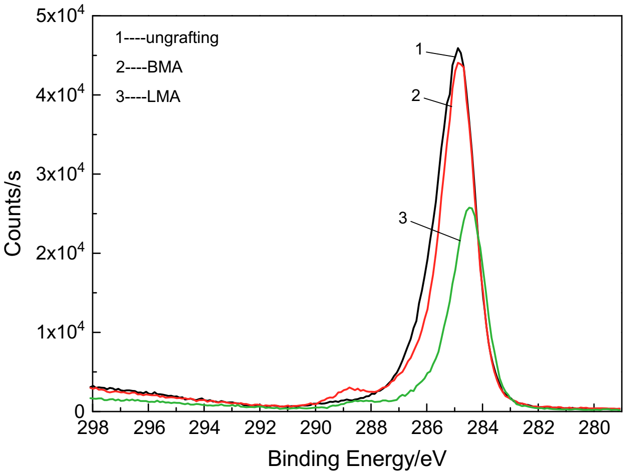


Fig. 3. Local amplified spectra of samples.

The reason was that the ester group has been introduced on the chain of PP, which resulted in the increase of O element content. Fig. 3 was a local amplified spectrum of C1s peak in the vicinity of 285 eV of MBPP before and after grafting treatment. As can be seen from Fig. 3, the C–H peak of the sample before grafting was symmetrical, but the peak became asymmetrical and the acromion at 288~289 eV increased after grafting BMA or LMA on the MBPP while the binding energy of the main peak decreased. This could be attributed to the introduction of the ester group, which resulted in the presence of C–O and C=O structure in the surface of the MBPP.

3.3. Morphology analysis

The morphology before and after grafting was shown in Fig. 4. It could be seen that before grafting, the fiber surface of MBPP was smooth and even; after grafting reaction, the nonwoven fabric remained as the fibrous structure, but the fiber surface became rough. This indicated that the branched chain had been grafted on the surface of the polypropylene fibers and the introduction of a lipophilic group enhanced the adsorptive capacity of the resulting grafted product.

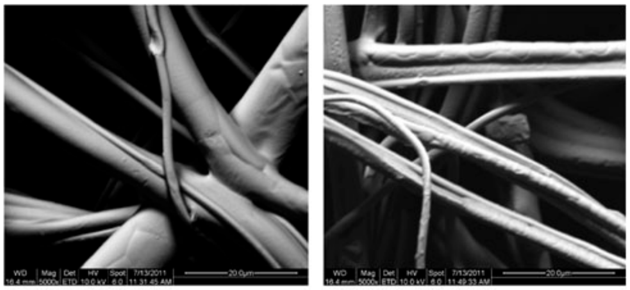

(a)MBPP (b)LMA-g-MBPP

Fig. 4. SEM figures of samples.

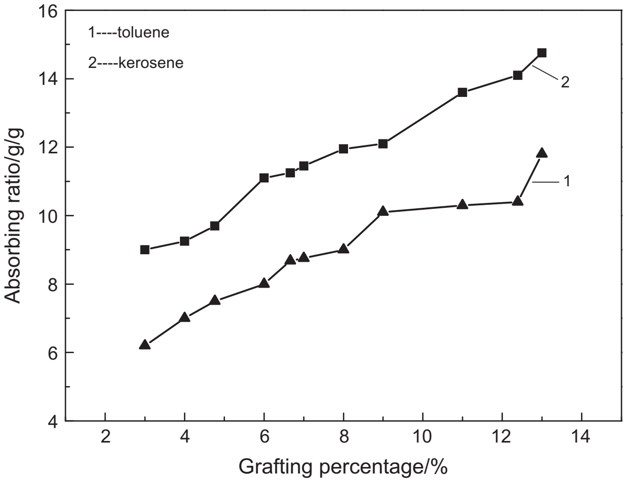


Fig. 5. Oil absorbency of LMA-g-MBPP.

3.4. Oil absorptive property of grafted MBPP

Toluene and kerosene were used as organic oil to measure the oil absorbency and oil retention property of LMA-g-MBPP and the results were shown in Figs. 5 and 6. The saturated oil absorbency of MBPP and grafted MBPP were tested and the results were shown in Table 2. The original MBPP without grafting adsorbed oil mainly by capillary action of the pores and gaps of the nonwoven structure. But graft reaction introduced oil affinity group on the PP chain, which significantly improved the chemical affinity between the oil and fiber chain. Then, van der Waals' force played a dominant role in the adsorption process. The modified MBPP absorbed oil both by chemical affinity

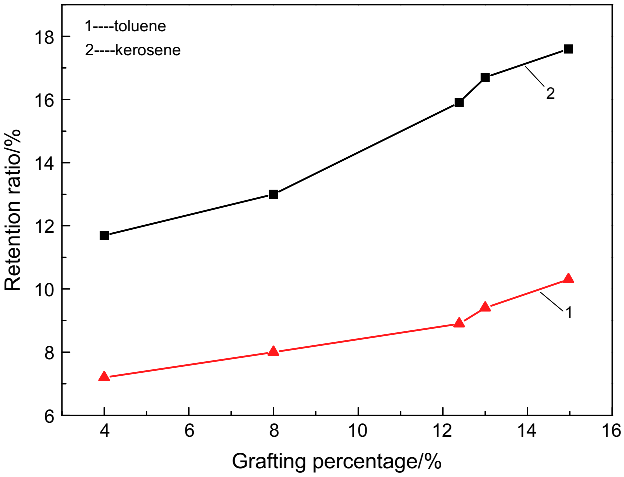


Fig. 6. Oil retention of LMA-g-MBPP.

Table 2
The saturated oil absorbency of MBPP and grafted MBPP

Sample	Saturated oil absorbency (g/g)	
	Toluene	Kerosene
MBPP	5.3	10.5
BMA-g-MBPP	14.5	11.7
LMA-g-MBPP	12.9	15.4

force and physical capillary action. So, the saturated oil absorbency increased. The research showed that the longer the side chain, namely, the amount of C was more on the carbon chain of monomer, the higher the nonpolar oil absorbency, such as kerosene. So the saturated oil absorbency of LMA-g-MBPP to kerosene was successfully improved and the saturated oil absorbency of BMA-g-MBPP to toluene was increased compared with ungrafted MBPP. And because of the existence of chemical affinity between ester group and oil molecule, the oil retention also increased.

The oil absorptive mechanism of LMA-g-MBPP was studied with kerosene as tested oil. Assume that the absorptive behavior of LMA-g-MBPP to kerosene could be represented by the following expression:

$$Q = A + Bx$$

where Q was the saturated oil absorbency of the sample; x was the content of oil affinity group; A was the contribution of the pores to oil absorbency; B was the contribution of the oil affinity group to oil absorbency.

The absorptive experimental result of LMA-g-MBPP was linear regressed by the above formula, as shown in Fig. 7.

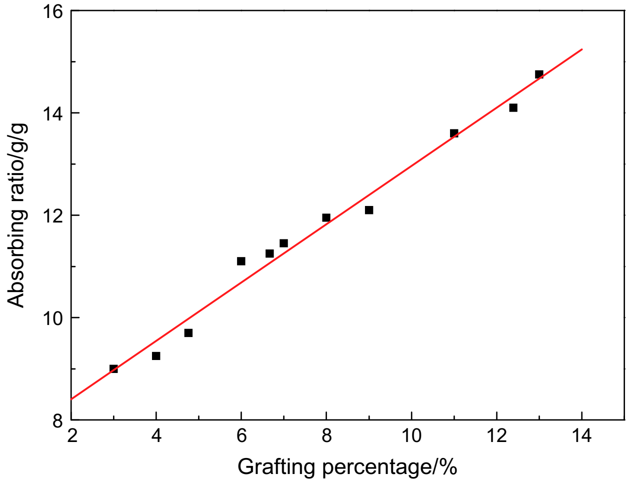


Fig. 7. The linear regression result of LMA-g-MBPP.

The calculation formula of Q was:

$$Q = 7.26717 + 0.56961x$$

The Correlation coefficient R was 0.99217. The result showed that the oil absorbency of LMA-g-MBPP was proportional to the content of oil affinity group. The more the oil affinity group, the greater the amount of adsorption was.

4. Conclusions

BMA-g-MBPP and LMA-g-MBPP were successfully prepared with benzoyl peroxide as an initiator by the method of chemical grafting. The saturated oil absorbency of LMA-g-MBPP to kerosene was 15.4 g/g and the oil absorbency of LMA-g-MBPP was proportional to the content of oil affinity group. The graft reaction introduced oil affinity group on the PP chain, which significantly improved the chemical affinity between the oil and fiber chain.

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