Research on Butyl Methacrylate–Lauryl Methacrylate Copolymeric Fibers for Oil Absorbency

Y. Feng,[1] C. F. Xiao[2]

[1]School of Textile and Clothing, TianJin Polytechnic University, TianJin, China
[2]School of Materials Science and Chemical Engineering, TianJin Polytechnic University, TianJin, China

ABSTRACT: By adding hydroethyl methacrylate as potential crosslinker, the butyl methacrylate-lauryl methacrylate copolymeric (CPMA) fibers with oil-absorptive function were prepared using heat crosslinking technology after spinning. The effect of monomer feed ratio showed that by controlling the monomer ratio, crosslinker concentration, and crosslinking conditions, the maximum absorbencies of prepared fibers to different oil were 8 g (kerosene)/g (fiber), 15 g (toluene)/g (fiber), and 34.75 g (chloroform)/g (fiber). The structures of fibers were characterized by FTIR, DSC, and SEM. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1248–1251, 2006

Key words: butyl methacrylate; lauryl methacrylate; fiber spinning; post crosslinking; oil-absorptive characteristic

INTRODUCTION

Oil-absorptive particles were widely used in the fields of waste oil recovery and wastewater purification. Compared with traditional oil-absorptive materials, it has a three-dimensional network structure like water superabsorbent polymers. It gained excellent development prospect with the characteristics of good heat and cold resistance, large oil absorption capacity and convenient reclamation technology.[1–4] However, because of its shape limit, oil-absorptive particles have many disadvantages, such as smaller specific-areas, lower absorptive rate, and absorptive abilities, compared with fibrous material and this restricted its applications. Fiber has desirable properties, such as large absorptive area, outstanding mechanical anisotropies, *etc*. And it could be manufactured into various forms of products, such as nonwoven fabrics, so its using field was effectively widened. Then, it was important to research and develop oil-absorptive functional fibers no matter in learning or application field. But highly oil-absorptive resin now was synthesized with single chemical crosslinking agent such as divinylbenzene, and oil-absorptive resin prepared in this way had perfect crosslinked structure, which made it insoluble in proper organic solvent. So the resin was difficult to be span into fiber.[5,6] Although there were a lot of reports about oil-absorptive materials, the oil-absorptive fibers were still not successfully prepared and reported. The purpose of this research was to prepare fibers with oil-absorptive function. Methacrylate was used as monomer and hydroethyl methacrylate as potential crosslinker was put in polymerization system in this study. Resin synthesized by this method still kept a linear structure, which made it soluble in a solvent to prepare solution. After spinning, the fiber was heat-treated at certain conditions to form crosslinked structure in fiber molecule, which made the fiber have the properties of oil-absorption. And the effect of monomer ratio, concentration of potential crosslinking agent on properties, and structures of CPMA fibers was analyzed. A detailed study of the swelling properties of CPMA fibers was conducted and the structures were characterized through FTIR, DSC, and SEM.

EXPERIMENTAL

Materials

Butyl methacrylate (BMA), hydroethyl methacrylate (HEMA), and lauryl methacrylate (LMA) were distilled before use; Benzoyl peroxide (BPO, recrystallized); Poly (vinyl alcohol) (PVA); N,N-dimethylacetamide (DMAc).

Copolymer and fiber preparation

PVA was dissolved in a flask used as suspension stabilizer before copolymerization. A mixture of BMA, LMA, and BPO were added in it and reacted under a nitrogen atmosphere for 6 h. The products were dissolved in DMAc after drying in vacuum oven. Then, a

certain volume of HEMA and BPO were added in solution and the reaction was kept at 70–75°C for 3 h by stirring. The solution was coagulated with the addition of pure water. The precipitated CPMA fibers were heat-treated at certain temperature to obtain proper crosslinked structure.

Test and analysis of CPMA fibers

Oil absorbency

Oil absorbencies of fibers were measured by a weighing method.[7] A weighed quantity of fiber was immersed in oil, such as toluene, at room temperature until equilibrium was reached, and the residual oil was then removed by dropping for 10 min. The equilibrium was determined by measuring the oil absorbency at each time until it reached a limiting value. The oil absorbency, Q, was determined by weighing the swollen gel and calculated according to the following equation:

$$Q = (G_1 - G_0)/G_0$$

where, G_1 is weight of swollen gel and G_0 is weight of dried fiber.

The oils used in this research were toluene, kerosene, and chloroform.

Gel fraction

A weighed quantity of fiber was put in Soxhlet extractor and continuously extracted for 8 h, using butanone as solvent because of its low boiling point and its ability to dissolve methacrylate. After extracting, the fiber was dried in vacuum at 60°C for 3 h and weighed. The gel fraction, R, was calculated according to the following formula:[7]

$$R = \frac{G_b}{G_a} \times 100\%$$

where, G_b is the weight of dried fiber after extraction and G_a is the weight of dried fiber before extraction.

FTIR analysis

The infrared transmission spectra of CPMA fibers were recorded on a Bruker Vector-22 spectroscopy.

DSC analysis

The glass transition temperatures (T_g) of various uncrosslinked polymers were determined using an instrument PerkinElmer DSC7. Measurements were performed on 5 mg samples, with a scanning rate of 10°C/min. The T_g was taken as the midpoint temper-
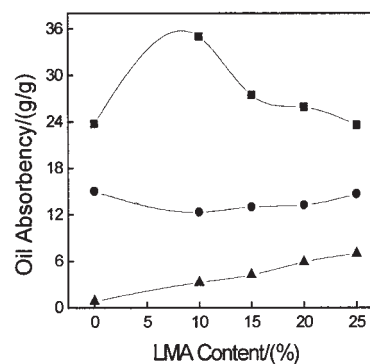
Figure 1 Relation between oil absorbency and LMA content of CPMA fibers —■—chloroform, —●—toluene, —▲—kerosene.

ature, that is, the temperature where half of the increment in specific heat had occurred.

Morphology of CPMA fiber

The cross section (breaking in liquid nitrogen) and surface morphologies of CPMA fibers were observed on a Philips XL 30 scanning electronic microscope (SEM).

RESULTS AND DISCUSSION

Effect of LMA content on oil absorbencies

The copolymerizing ratio had an important influence on oil-absorptive properties of CPMA fibers because the oil-absorptive functions came from the good affinity of groups on CPMA molecules to oil. Figure 1 showed the relationship between saturated absorbency of CPMA fibers and copolymerizing monomer composition. It demonstrated that with increasing LMA content, the chloroform absorbency got peak value and the toluene absorbency only had a small change, but the kerosene absorbency had improved rapidly. It was reported that the longer the side chain on copolymers, namely, the amount of C was more on the carbon chain of monomer, the higher the nonpolar oil absorbency, such as kerosene.[7] The kerosene absorbency of CPMA fibers improved from 0.83 to 8.00 g/g with the LMA content increasing from 0 to 25% [volume ratio, $V_{LMA}/(V_{LMA} + V_{BMA})$]. So the kerosene absorbency could be effectively improved by additional of LMA. We also noticed that if the LMA content was higher than 25%, it was impossible to dissolve the copolymer to obtain stable spinning solution. So the LMA content was determined at 25% in this research.

Effect of HEMA concentration on oil absorbencies and gel fractions

Figure 2 presented the relation between saturated absorbencies and gel fractions of CPMA fibers with
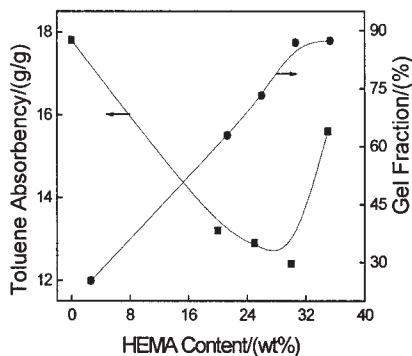
Figure 2 Relation between toluene absorbency or gel fraction and HEMA content of CPMA fibers.

Figure 3 DSC thermograms of BMA-LMA copolymer with different LMA content.
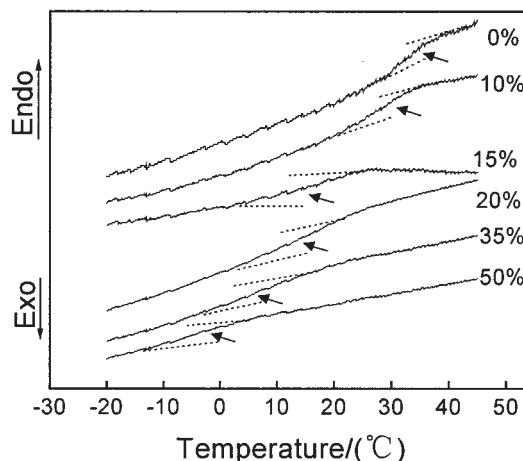
HEMA content, while other conditions were kept constant, and we used toluene as tested oil. Gel fraction was commonly used as a parameter representing the degree of crosslinking of a polymer material. From Figure 2, it could be seen that when HEMA content was zero in polymerization system, the toluene absorbency was large, but the gel strength was too low to use and the gel fraction value was only about 25%. As HEMA amount increased, the degree of crosslinking and the interaction in the polymer networks also increased, and this restrained the chain extending of polymer molecule. So the toluene absorbency decreased while the gel fraction continuously went up. But when LMA content was lower than 25%, the supporting performance of network in CPMA fibers were still too infirm, which lead to disadvantage of recovery and reduced its usage value, so the minimum value of LMA concentration was 25%. It should be noted that when HEMA content reached 35%, the toluene absorbency of oil-absorptive fiber contrarily increased because the hydrophobic ester group on HEMA molecular chain could not only act as crosslinking agent in the fiber, but also could absorb oil itself. So the oil-absorptive fibers also had high absorbency even in high gel fraction.

DSC analysis

Copolymerization often brings about drastic changes in the mechanical and physical properties of the polymer. The most important physical property to be affected is T_g. Fox predicted the changes of the copolymer T_g according to its composition with the Fox equation:[6]

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{\dot{W}_B}{T_{gB}}$$

where W_A and W_B are the weight fractions of the monomers A and B in the copolymer, and T_{gA} and

T_{gB} are the respective T_g of the homopolymers A and B.

However, this equation is very simple and many systems deviate from this. Theoretical values predicted from the Fox equation and experimental values were shown in Figure 3 and 4. As shown in the figures, the theoretical values from the Fox equation somewhat deviated from the experimental values. This should be due to the difference of copolymers compositions or sequence distribution in the polymer chain.

FTIR analysis

Figure 5 indicated IR spectra of poly (butyl methacrylate) (PBMA) and CPMA fibers (LMA content 25%). It showed —OH peaks at 3410 cm^{-1}; The peaks at 2910, 2860, 2840 cm^{-1} were due to stretching vibration of CH$_3$, CH$_2$, and CH bond; the peaks at 1481, 1438,1386
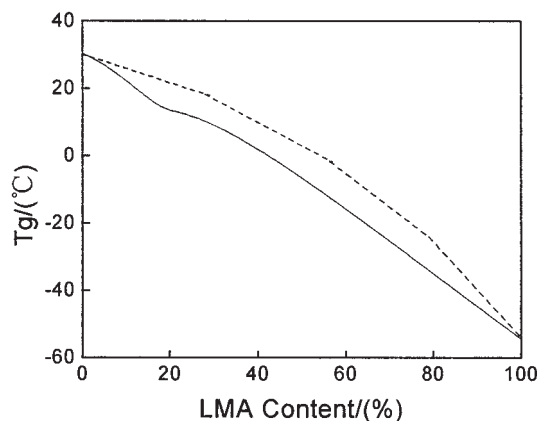

Figure 4 Variation of T_g as a function of fraction of LMA for the BMA-LMA copolymer ——Experimental curve; - - - - Prediction curve by Fox's equation.

cm^{-1} were due to scissoring and bending of C—H; The very strong peak at 1724 cm^{-1} was attributed by the C=O stretching in methacrylate; and the less intense peak at 1271 cm^{-1} was designated to the C—O—C stretching in methacrylate.[6] Figure 5 expressed that additional of LMA had little effect on chemical structure of PBMA fiber, although the oil absorbency could be greatly changed.

Morphologies observed by SEM

SEM was used to observe the cross section and surface morphologies of CPMA fibers, as shown in Figure 6. We could clearly see micropore structure formed by the diffusion of solvent-coagulation in fiber formation [Fig. 6(a)] and the fiber surface was loose, through which the oil molecule could be easily diffused into internal space of CPMA fiber. However, the sustaining ability of net structure was bad when the fibers were not heat crosslinked. So the network could not keep its shape after oil molecule diffused in it, which represented viscous state lack of intensity. The fiber chains were rearranged and aggregated through motion when heat crosslinked [Fig. 6(b)]. Some micropores closed and the structure of CPMA fibers became tighter, but still some pores with smaller diameter remained that provided channels for oil molecules to diffuse in. Moreover, the sustaining ability of net structure increased because of more perfect network in fibers, and the fibers fully swelled in oil but did not dissolve. If crosslinked temperature was too high or crosslinked time was too long, the absorptive ability of fiber obviously decreased while the mechanical properties of fibers improved. So the key factor to preparing fiber with high oil-absorbency was choosing proper crosslinked conditions that made the fiber have three-dimensional network structure and micropores with proper size and quantity.
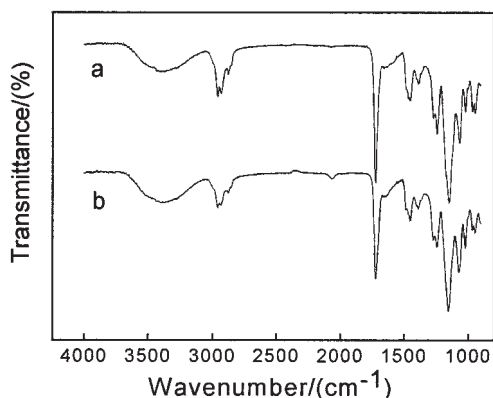
Figure 5 FTIR spectra of PBMA and CPMA fiber (a) CPMA fiber; (b) PBMA fiber.

(a-1) (×200)   (a-2) (×2000)

(b-1) (×200)   (b-2) (×2000)
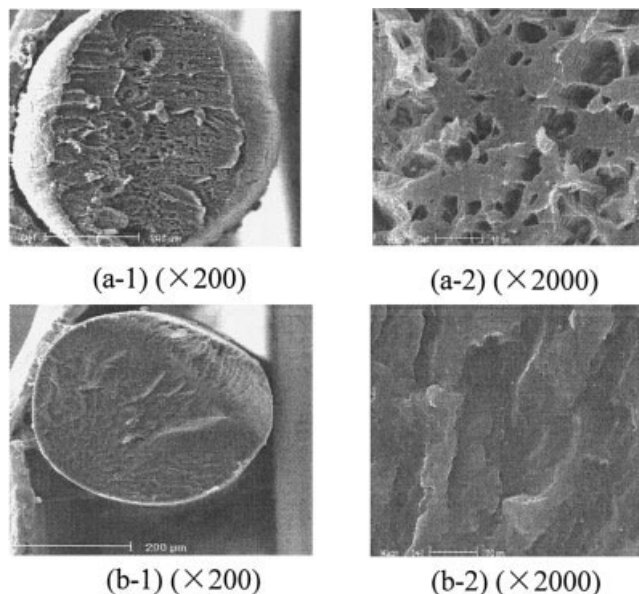
Figure 6 Cross section and surface morphologies of BMA-LMA oil-absorptive fibers (a) uncrosslinked fiber; (b) crosslinked fiber.

CONCLUSIONS

The following conclusions could be drawn from this study:

1. The butyl methacrylate-lauryl methacrylate copolymeric(CPMA)fibers with oil-absorptive function were prepared using heat crosslinking technology, after spinning by adding hydroethyl methacrylate as potential crosslinker.
2. Monomer ratio directly affected the absorbencies of fibers, especially the absorbencies to aliphatic oil. When LMA content was 25%, the kerosene absorbency could get 8.00 g/g.
3. HEMA content was a main factor affecting absorptive properties of CPMA fibers, and the HEMA content was not less than 25% in this study;
4. The highest absorbency of CPMA fiber to various oil was 15 g (toluene)/g (fiber), 34.75 g (chloroform)/g (fiber), and 8 g (kerosene)/g (fiber), respectively.

References

1. Zhou, M. H.; Cho, W.-J. J Appl Polym Sci 2002, 85, 2119.
2. Blaney, C. A. U.S. Pat. 5,834,385 (1998).
3. Hansell, D.; Huizinga, H. In Proceedings of the AESF Annual Technical Conference; Cincinnati, OH, 1999.
4. Berrigan, M. R. U.S. Pat. 5,763,083 (1998).
5. Thucha, H. Jpn. Pat. 05–209217 (1993).
6. Jang, J.; Kim, B.-S. J Appl Polym Sci 2000, 77, 903.
7. Jang, J.; Kim, B.-S. Appl Polym Sci 2000, 77, 914.