Synthesis and Characterization of an Ionic Liquid Enhanced High Oil Absorption Resin of P (BMIm-MMA-BA) and Its Oil Absorption Performance

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Abstract: A novel oil highly absorptive resin was prepared by a suspension polymerization using 1-butyl -3- (2- methacryl) ethyl imidazolium hexafluorophosphate $(BMIm)PF_6^-$, methyl methacrylate (MMA), and butylacrylate (BA) as monomers, azobisisobutyronitrile as initiator, N, N methylenebis (acryl amide) (MBA) as crosslinking agent and polyvinyl alcohol (PVA) as dispersant and characterized by Fourier-transform infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). The effects of different polymerization technological parameters, such as the mass ratios of the monomers, the addition amounts of the initiator, the cross-linker and the dispersant, the polymerization temperature and time, on the oil absorbency of the high oil absorption resin P (BMIm-MMA-BA) copolymer were examined in detail. Under the optimal condition, the oil absorbency was about 25.6 g/g for benzene, 22.6 g/g for xylene, 32.3g/g for chloroform, and 30 g/g for carbon tetrachloride, respectively. The kinetic investigation indicated the oil absorption obeyed the pseudo-first-order kinetic equation.

Keywords: Ionic Liquids Monomer, Suspension Polymerization, High Oil-Absorption Resins, Oil Absorbency

1. Introduction

Environmental pollution is becoming more and more serious at present; in particular, deterioration of water quality of ocean, river and lake polluted by oil and oil-like organic solvents is one of the most calamities for human, animal, halobios, and plant. Various materials, including natural absorbents and synthesized polymeric materials, have been developed to deal with oil pollution hazards and recover the spilled oils [1-7], and oil-absorbing resin have been used widely to absorb oil spilled on water. High oil-absorption resin, different from ordinary oil-absorbing materials, is a new self-swelling oil-absorbing material with many virtues of absorbing large quantity and variety of oils, only absorbing oil from oil/water mixture and high capacity for oil retention, and has a promising future. Synthesis and applications of high oil-absorption resins have very important practical significance for environment protection [8].

The highly absorptive resin, perhaps, could catch a part of contaminations to decrease the pollution and recovery the solvents [9-11]. Acrylic has been widely used as monomer to prepare porous high-oil-absorbing resins. Xu et al. [12] used methyl methacrylate (MMA), butyl methacrylate (BMA), and hydroxyl ethyl methacrylate (HEMA) as monomers to synthesize an oil-absorbing resin through a suspension polymerization. This kind of resin mainly contained physical crosslinking instead of chemical crosslinking. The absorbency of the resin to toluene was 12.59 g/g. Gao et al. [13]used methyl methacrylate (MMA), butyl acrylate (BA), as monomers to prepare high-oil-absorbing resins by a glow-discharge electrolysis plasma

initiated suspension copolymerization, and N, N-methylenebis (acrylamide) as crosslinking agent, and polyvinyl alcohol as dispersant and a high absorbency to chloroform was obtained 38.1 g/g.

Copolymerization of acrylic derivatives can be employed to prepare high oil absorption resins by various methods such as emulsion polymerization and suspension polymerization. However, the resins obtained by the above methods universally have some defects of compact structure [14-17].It is very important to select suitable monomers so as to introduce appropriate functional groups improving oil sorption for synthesizing high-oil-absorption resins.

Room temperature ionic liquids (ILs) are desirable green solvents for a wide range of separation and reaction media applications and they have good affinity to various organic compounds [18]. Interestingly, poly (ionic liquid) could retain partially or completely the intrinsic performances of the ionic liquid monomers [19, 20].

In this study, we used the ionic liquid as monomer to obtain a high-oil-absorption resin of ternary copolymerized network polyacrylate BIMm-MMA-BA by a suspension polymerization. The removal performance of the prepared high oil absorption to several organic compounds (oil contaminations) was examined and the influencing factors on the oil absorbency of the high-oil-absorption resin were studied in detail including the monomers mass ratio, water/oil mass ratio, amounts of the cross-linking agent and initiator, type and amount of dispersing agent, and polymerization temperature.

2. Experimental

2.1. Materials

1-butylimidazole (Aldrich; 98%), ammonium hexafluorophosphate (Aldrich; 98%), 2-chloroethanol (Aldrich; 95%), methacryloyl chloride (Aldrich; 97%), acetonitrile (anhydrous, 99.8%), triethylamine (Aldrich; 99.5%), methyl methacrylate (MMA), butyl acrylate (BA), polyvinyl alcohol (PVA), N, N'-methylene bisacrylamide (MBA, chemical pure), azobisisobutyronitrile (AIBN, 97%) were used without further purification. Sodium sulfate, anhydrous magnesium sulfate, tetrahydrofuran (THF), xylene, toluene, benzene, carbon tetrachloride, and chloroform were of analytical reagent grade.

2.2. Methods

2.2.1. Synthesis of the Ionic Liquid Monomer (BMImPF$_6$)

The synthesis of the ionic liquid monomer BMImPF$_6$ was shown in fig 1. The reaction of 2-chloroethyl methacrylate with 1-butylimidazole yielded the imidazolium chloride salt. The metathesis reaction of imidazolium chloride with ammonium hexafluorophosphate yielded the metathesis monomer.
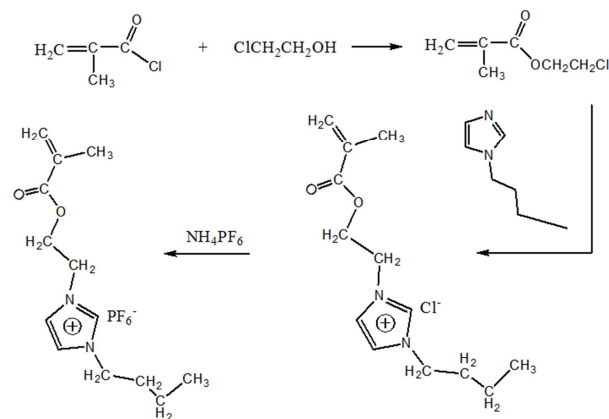

Fig. 1. *Synthesized procedure of ionic liquid monomer 1-butyl -3- (2-methacryl) ethyl imidazolium hexafluorophosphate (BMImPF$_6$).*

A typical synthesis procedure is as follows:

To a solution of 14.0 g (0.11 mol) of 2-chloroethanol in 50 mL of methylene chloride, a solution of 10.4 g (0.10 mol) of methacryloyl chloride in 10 mL of methylene chloride was added gradually for 10 min at 0°C. After the addition, the reaction mixture was continuously stirred for 30 min. Then, 11.0 g (0.11mol) of triethylamine in 10 mL of methylene chloride was added dropwise for 15 min at 0°C. The solution became slurry after several minutes. The reaction mixture was stirred overnight at room temperature and then filtered. The filtrate was washed thoroughly with 100 mL of distilled water three times and was dried with anhydrous magnesium sulfate. The solvent was removed *in vacuo* at less than 30°C. The product 2-chloroethyl methacrylate (CEMA) was obtained in an 80.0% yield. And the[1]H-NMR data of CEMA are: δ: 6.1 ppm (1H, s, =CH$_2$*cis*), 5.6 ppm (1H, s, =CH$_2$*trans*), 4.3 ppm (2H, broad s,–COO–CH$_2$–), 3.7 ppm (2H, broad s, –CH$_2$–Cl), 1.96 ppm (3H, s, CH$_3$–C=C).^{1}H NMR spectra of the compound is shown in Fig. 2a.

8.69 g (0.07mol) of 1-butyl imidazole was added to 13.51 g (0.07mol) of 2-chloroethyl methacrylate. And then the mixture was stirred at 40°C in water bath for 24 h and yielded a viscous liquid. The liquid was dissolved in 40 mL of anhydrous acetonitrile. The solution was mixed with 11.1 g (0.1mol) of NH$_4$PF$_6$in 80 mL of anhydrous acetonitrile. After the mixture was stirred for 48 h at room temperature, the sodium chloride precipitate was removed by filtration, and the filtrate was concentrated. The concentrated filtrate was diluted with methylene chloride (200mL) and filtered through a silica gel column. The removal of methylene chloride yielded the ionic liquid monomer1-butyl -3- (2- methacryl) ethyl imidazolium hexafluorophosphate (BMImPF$_6$) as viscous oil. The[1]H-NMR data BMImPF$_6$ are: ^{1}H NMR (400 MHz, DMSO) δ7.71 (s, 1H, N−CH−N), 7.00 (s, 1H, N−CH=CH−N), 6.93 (s, 1H, N−CH=CH−N), 6.06 (s, 1H, CH$_2$=CCH$_3$), 5.22 (m,1H, CH$_2$=CCH$_3$), 4.31 (m, 2H, COO-CH$_2$-CH$_2$-N), 3.93 (t, 2H, COO-CH$_2$-CH$_2$-N), 3.66 (m, 2H, N-CH$_2$-C$_3$H$_7$), 1.86 (m,3H, CH$_2$=CCH$_3$), 1.71 (m, 2H, N-CH$_2$-CH$_2$C$_2$H$_5$), 1.26 (m, 2H, N-C$_2$H$_4$-CH$_2$-CH$_3$), 0.86 (t, 3H, N-C$_2$H$_4$CH$_2$-CH$_3$) and corresponding 1H NMR spectra is given in Fig.2.
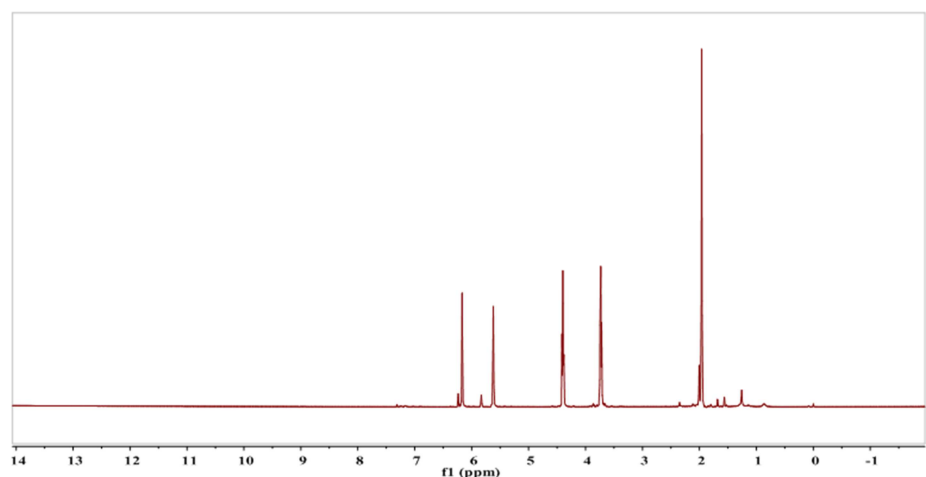
(a)
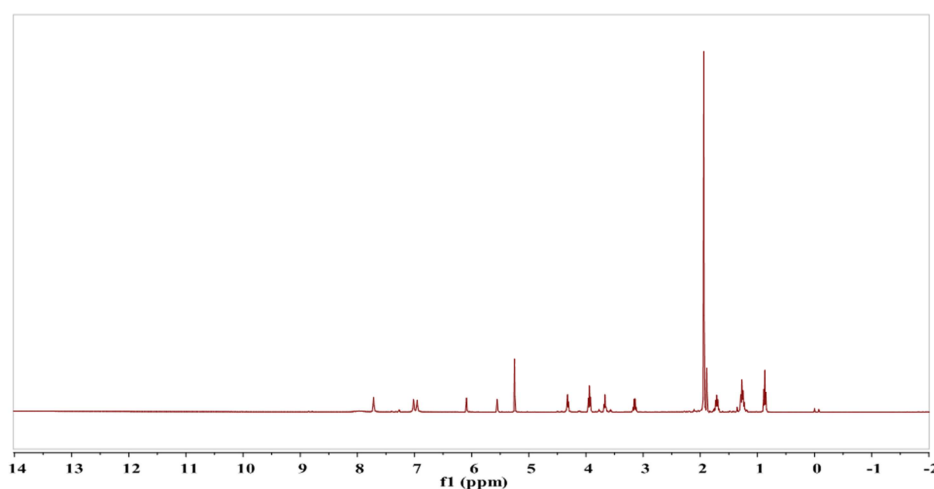
(b)

Fig. 2. *1H NMR spectra of (a) CEMA and (b)BMImPF$_6$.*

2.2.2. Preparation of Oil-Absorbing Resin

Copolymerization of BMIm, MMA and BA was carried out in a 250-ml three-necked flask equipped with a stirrer, condenser. 1.5ml of 0.8% PVA, 0.03 g of MBA, 7 mL of MMA, 10 mL of BA, 3mL of BMIm, deionized water and 0.5g of AIBN were added in the order. Then, the mixture was stirred at 30°C for 30 min to disperse homogeneously, while nitrogen was also bubbled to remove oxygen. After rising the temperature of oil bath to 90°C to react for 2h under N$_2$ atmosphere, the reaction finished. The product was cooled, washed with hot water of 60°C, extracted with THF for 24 h in Soxhlet extractor and then dried under vacuum at 60°C until a constant weight. Obtained product was named as BMIm- MMA- BA high oil absorption.

2.3. Materials Characterization

2.3.1. Fourier Transforms Infrared

The attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectra were collected by using a Nicolet NEXUS 670 FT-IR single-beam spectrometer (USA) with a 4 cm^{-1} resolution and a 45°C angle maintaining constant contact pressure between the Ge crystal and the specimens.

2.3.2. Thermogravimetric Analysis

Thermal stability measurements were performed on a Metter Toledo TG apparatus (Switzerland) from 30 to 800°C, with a heating rate of 10°C/min under a nitrogen flow rate of 50 mL/min.

2.3.3. Scanning Electron Microscopy

The morphological analyses were carried out through a scanning electron microscopy (SEM) (JSM-5600LV, Japan), using an applied voltage of 20 kV. Before SEM observation, all samples were fixed on copper stubs and coated with gold.

2.3.4. Removal of Oil

The oil absorbency was determined by a weighing method. A quantity of 0.04- to 0.1g dried sample was immersed in excess solvent at room temperature. After 24 h, the sample was filtered and weighed immediately. The oil absorbency

was calculated by the following formula:

$$Q_{eq} = \frac{m - m_0}{m_0}$$

Where m_0 (g) is the weight of the dry sample and m (g) is the weight of the swollen sample.

3. Results and Discussion

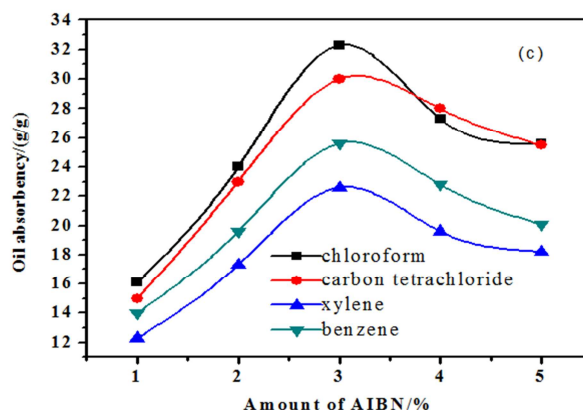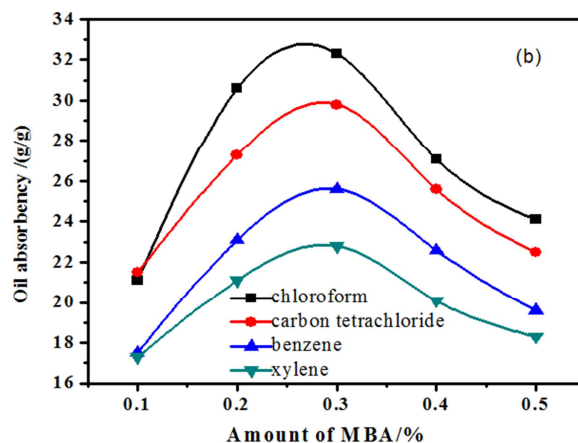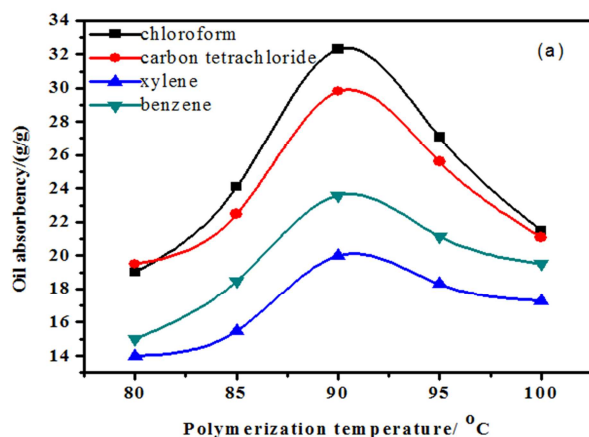## 3.1. Optimization of the Polymerization Conditions

3.1.1. Effect of Polymerization Temperature on Oil Absorbency

Fig. 3 (a) shows the effect of polymerization temperature on oil absorbency. The reaction temperatures were kept at 80, 85, 90, 95 and 100°C, respectively. The oil absorbency of the resin increased with increasing polymerization temperature up to 90°C.If the temperature continually increased from 90°C, the decomposition rate of the initiator would increase to produce too many polymerization active centers, which would cause formation of the low molecular weight of high-oil-absorption resins and decrease in the oil absorption.

3.1.2. Effect of the Amount of Crosslinking Agent on Oil Absorbency

Fig. 3 (b) shows the effect of the used amounts of the crosslinking agent on oil absorbency. The used amount of the crosslinking agent determines the crosslinking density of the resultant resin. The linear resin can dissolve easily in organic solvents without swelling, whereas the network resin can swell after oil absorption due to the presence of network. Such property was closely related to the used amount of MBA. Just as shown in Fig. 3 (b), if the amount of MBA was not enough, a well three-dimensional network structure cannot form, leading to the oil absorbency declined. On the other hand, when the addition amount of MBA was too much, both the crosslinking density and rigidity were too big, which would decrease the swelling capability of the copolymer resin and correspondingly decreased the oil absorbency. Thus, 3% of MBA was chosen as the optimum.
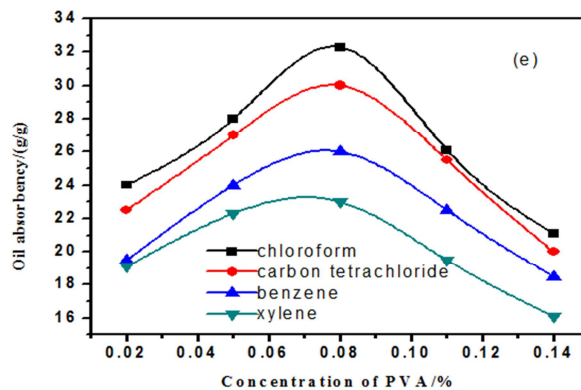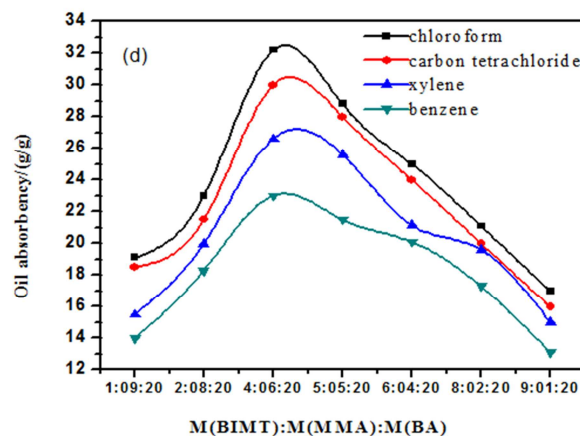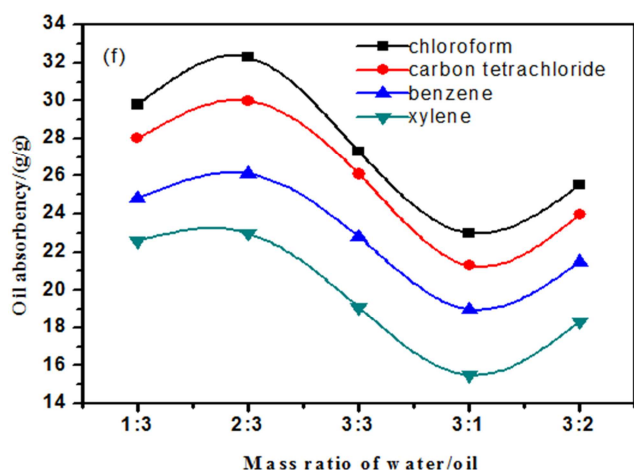
Fig. 3. Effects of the polymerization conditions.

(a) Polymerization temperature, m_{water}/m_{oil} = 3:2, m_{BMIm}: m_{MMA}: m_{BA} = 4:6:20, 3% AIBN, 0.06 wt% PVA, t =2hr;
(b) the amount of crosslinking agent, m_{water}/m_{oil} = 3:2, m_{BMIm}: m_{MMA}: m_{BA} = 4:6:20, 3% AIBN, 0.06 wt% PVA, t = 2hr, T = 90°C;
(c) the amount of initiator, m_{water}/m_{oil} = 3:2, m_{BMIm}: m_{MMA}: m_{BA} = 3:7:20, 0.3 wt % MBA, 0.06 wt% PVA, T = 90°C and t = 2hr;
(d) the monomer feed ratio, m_{water}/m_{oil}=3:2, 0.3 wt % MBA, 3% AIBN, 0.06 wt% PVA, T = 90°Cand t =2hr;
(e) PVA concentration, m_{water}/m_{oil} = 3:2, m_{BMIm}: m_{MMA}: m_{BA} = 3:7:20, 0.3wt % MBA, 3% AIBN, T = 90°Candt = 2hr; (f) the water/oil ratio, m_{BMIm}: m_{MMA}: m_{BA} = 3:7:20, 0.3 wt % MBA, 3% AIBN, 0.08wt% PVA, T = 90°C and t = 2hr.

3.1.3. Effect of the Amount of Initiator on the Oil Absorbency

Fig.3 (c) shows the changes of the oil absorbency depending on the different amounts of initiator. With increasing AIBN concentration, the oil absorbency at first increased and then decreased. It was apparent that the oil absorbency reached the highest when the amount of initiator was 3wt %. In the reaction system, the concentration of the initiator remarkably in fluencies on the reaction rate, the molecular weight of the resins and the crosslinking degree. Appropriate amount of the initiator can enhance polymerization speed, but more initiator will generate more active centers in order to increase the conversion and the gel fraction and decrease the length of the basic chain in polymer systems. As a result, the chain length between crosslinking points of the network decrease and the crosslink density increase with the increase of the initiator concentration. Therefore, the final result was a decrease of the oil absorbency. In practice, both growth and transfer of polymer chains should be considered simultaneously. When the polymerization temperature was 90°C and reaction time was 8h, 5wt% AIBN (based on the total monomer weight) was optimal.

3.1.4. Effect of the Monomer Feed Ratio on the Oil Absorbency

The sort and ratio of the monomers can affect the oil affinity of resulting resins and the effective network volume, which can further influence the oil absorption process [21].

In this chapter, a high oil-absorbing resin was prepared by a suspended polymerization with BMIm and MMA and BA as monomers. The influence of the BIMm to MMA and BA molar ratio on the oil absorbency of the crosslinking polymers was investigated. Fig. 3 (d) exhibits the relation between the monomer molar ratio and the oil absorption. It can be seen that with the amount of BMIm increasing, the oil absorbency of the resultant polymer resin increased until the mass ratio of BMIm to MMA reached 4:6. Maybe that is because the introduction of BMIm chain segment into the polymer increases the affinity of the resulting polymer to oil. But excess amount of BMIm would bring too many branched chains, which was disadvantageous for the formation of the proper network structure. When the polymerization was carried out at 90°C for 8h in the presence of 0.3wt% MBA, 5wt% AIBN and 0.08% PVA, the optimum BIMm: MMA: BA ratio was 4:6:20.

3.1.5. Effect of PVA Concentration on Oil Absorbency

The dispersant used in the suspension polymerization has direct effects on the molecular weight of the resins. Just as shown in Fig. 3 (e), when the amount of dispersant used was low, the oil absorbency increased with its addition amount increasing, but the addition exceeded the critical amount of 0.08%, the oil absorbency started to decrease. That is because when the concentration of PVA was too low, the product tended to form large particles and hardly absorbed oil. However, because PVA could increase the viscosity of water, excess of PVA would cause a decrease of the resulting resin. Thereby, in this study, 0.08% of PVA was used as a suitable amount.

3.1.6. Effect of the Ratio of the Water/Oil on Oil Absorbency

Water, acting as a dispersed phase, was suspended in the continuous monomer phase in the suspension polymerization where the initiator, crosslinking agent, and monomers were an oil-soluble. When the amount of water was lower, with the water/oil mass ratio increasing, the oil absorbency increased, resulting from the increased availability of space of the oil-absorption resins. But the water/monomer mass ratio influenced the particle size of the polymer, so too much water would cause a decrease of oil absorbency. Fig. 3 (f) displayed the variation of the oil absorbency relative to different water/monomer mass ratio. A suitable water/oil mass ratio of 2:3 was chosen in this work.

3.2. Characterization of the Oil Absorption Resin

3.2.1. FTIR Spectra of the High oil Absorption Resin

FTIR spectrum of BMIm-MMA-BA copolymer was shown in Fig. 4 it could be seen that in the IR spectrum of the copolymer appeared characteristic peaks of ionic liquid segment. The absorption peak at 1638 cm^{-1} was attributed to C= N stretching vibration and the absorption peak appearing at 849 cm^{-1} was assigned to the stretching vibration of PF_6^-, where as the frequency at 875 cm^{-1} was assigned to the P–F bond.

The peak at 1762 cm^{-1} was saturated C=O stretching vibration absorption, which indicated the entire C=C functional groups in the monomers had been polymerized. The peaks at 1247, 1252 and 1195, 1155 cm^{-1} were respectively assigned to asymmetrical and symmetrical stretching vibrations of C–O–C bonds [22] and the peak at 988 cm^{-1} was assigned to the stretching vibration of CH$_3$-O bond [23]. The peaks appeared at 2996cm^{-1} and 2882 cm^{-1} respectively resulted from the C-H asymmetric and symmetric stretching vibration of –CH$_2$CH$_3$, where as the frequencies at 1439 and 1384 cm^{-1} were respectively assigned to the symmetrical and non-symmetrical in-plane bending vibrations of C-H groups. No absorption peak in the range of 3000 – 3100 cm^{-1} indicated absence of unreacted monomers. The wide peak appeared at 3462 cm^{-1} was attributed to the -OH stretching vibration, which might come from the residual PVA molecules in resin [13]. The absorption peak at 3648 cm^{-1}assigned to the stretching vibration of N–H in BMImPF$_6$ was shielded by strong and wide –OH stretching vibration peak.
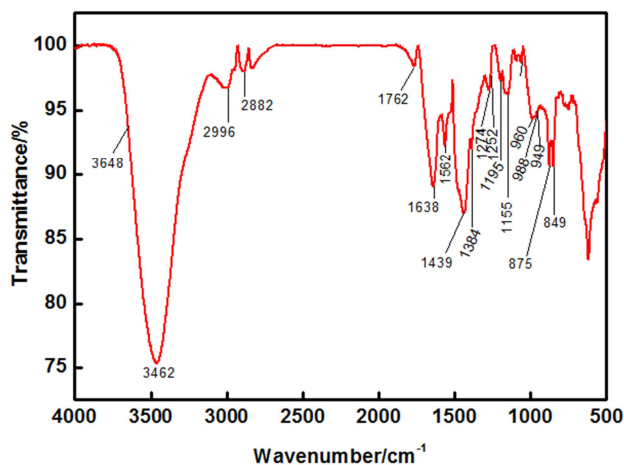

Fig. 4. *ATP-FTIR spectra of the resin.*

3.2.2. Morphology Analysis

As we know, the morphology of a crosslinked resins will influence the rate of oil absorption [24]. Fig. 5 displays SEM microphotographs of the resin prepared by different polymerization. It was apparent that there were many large deep holes randomly distributed in the surface and inside of the resin. These holes would support large surfaces in the polymeric network.

3.2.3. Thermogravimetric Analysis

The thermal stability is an important parameter to assess a material. Fig. 6 shows the thermogravimetric (TG) curve of the oil-absorptive resin. It could be seen that from the curve of (BMIm-MMA-BA) copolymer presented a little mass loss before 100°C possibly caused by evaporation of residual water in the resin. A rapid mass loss emerged after 302°C resulted from the break of resin chain and decomposition of alkyl acrylate. The sample mass loss was about 58.4% at 399°C. The results showed that the highly oil-absorptive
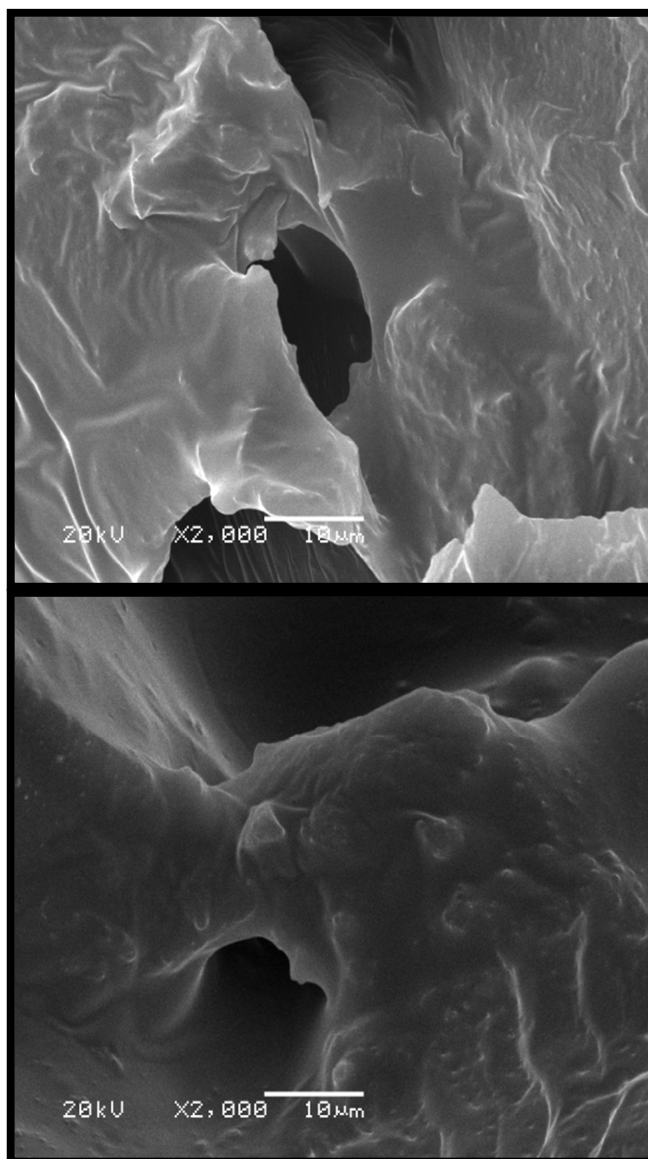
resin had a good thermal stability.

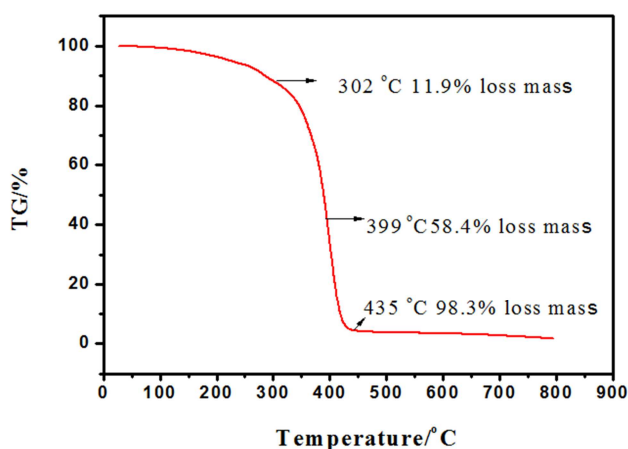***Fig. 5.*** *SEM of the resin prepared by different polymerization.*

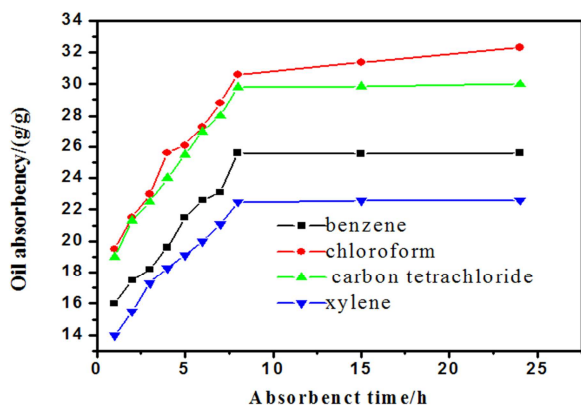***Fig. 6.*** *The TG curve of the prepared high oil absorption resin.*

Fig. 7. Influence of absorption time on oil absorbency of the resin.

3.3. Absorption Kinetics

To test the absorption rate, the sample was immersed in excess solvent at room temperature for different time. It was taken out and weighed every 1 h. The operation was repeated for ten times. Finally, it was immersed in excess solvent for 24h and weighed. Influence of absorption time on oil absorbency of the resin is shown in Fig. 7.

Xylene was chosen to study the oil-absorbing rate and absorption kinetics. It can be seen from Fig. 8 that the oil absorbency increased with increasing immersion time until the absorption rate reached saturation after 8h. According to Yao and Zhou [14], if oil absorption process obeys the first-order model, the swelling rate can be described by the following experimental formula:

$$-\ln(q_e - q_t) = k_1 t + c_1 \tag{1}$$

Where q_t and q_e are the oil absorbency (g/g) at time t (h) and the equilibrium oil absorbency (g/g) respectively, k_1 is the first-order swelling kinetic constant and c_1 is integration constant.

According to the Eq. (1), a plot of -ln (q_e - q_t) against t could be obtained by the least square and is shown in Fig. 8 (a).

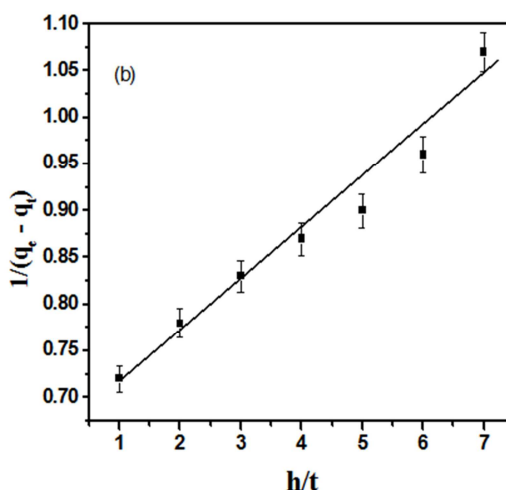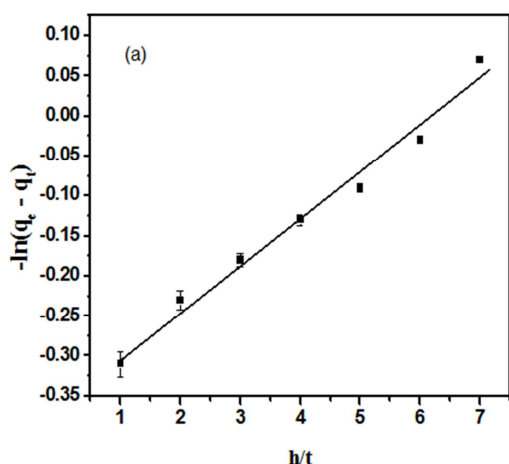Similarly, according to the second-order model:

Fig. 8. Kinetic fitting curves using the first-order model (a) and the second-order model (b).

$$\frac{1}{q_e - q_t} = k_2 t + c_2 \tag{2}$$

A fitting plot of 1/ (q_e − q_t) against t was obtained in Fig. 8 (b). Clearly, the correlation coefficient for the first-order model ($R^2 = 0.983$) is better than the second-order model ($R^2 = 0.966$), indicating that the first-order absorption kinetics was more suitable to describe the absorption process.

4. Conclusion

In this chapter, an ionic liquid enhanced high-oil-absorption resin of copolymerized (BMIm-MMA-BA) was prepared by suspension polymerization. The highest oil absorbency was about 25.6 g/g for benzene, 22.6 g/g for xylene, 32.3g/g for chloroform, and 30 g/g for carbon tetrachloride respectively under optimal conditions. And the oil absorption obeyed the pseudo-first-order kinetic equation.

Acknowledgments

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