Synthesis of Poly (Butyl Methacrylate/Butyl Acrylate) Highly Absorptive Resin Using Glow Discharge Electrolysis*

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Abstract A highly absorptive resin poly (butyl methacrylate (BMA)-co-butyl acrylate (BA)) was prepared by emulsion polymerization, which was initiated by glow discharge electrolysis plasma (GDEP). The effects of discharge voltage, discharge time, monomer ratio and the amounts of cross-linking agent were examined and discussed in detail. The chemical structure of the obtained resin was characterized by means of attenuated total reflectance Fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. The optimal conditions were obtained as: discharge voltage was 600 V, discharge time was 8 min, the ratios of BMA:BA being 2:1 for chloroform and 3:1 for xylene, with 2% N, N'-methylenebis. Under optimal conditions, the oil absorbency was 70 g/g for chloroform and 46 g/g for xylene. Moreover, the absorptive dynamical behavior of the resulting resin was also investigated.

Keywords: glow discharge electrolysis plasma, emulsion polymerization, resin

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(Some figures may appear in colour only in the online journal)

1 Introduction

As a result of the development of modern industry and human activities, the environmental pollution caused by organic substrates has become more and more serious. These substances entering into soil and water are endangering the human health as well as the health of other animals. Chloroform is the most common one of these pollutants. Chloroform is harmful to the central nervous system, liver and kidneys. Moreover, prolonged contact with chloroform will make the probability of cancer very high [1]. However, up to now, there has been no effective method to treat these contaminations. Therefore, their removal from the environment is still an urgent worldwide task. Highly absorptive resin has attracted a great deal of interest due to its many advantages, such as: it will only absorb oil and not water, it has good thermal stability, it is easy to store, and it is conveniently transported [2]. Based on monomers, highly absorptive resin can be divided into two types: one is acrylate system and the other is alkenes. Methacrylate is a commonly used monomer because of its extensive sources and cheap cost [3−5].

Plasma chemistry is a new subject that has attracted the interest of many researchers [6]. As an unconventional electrolysis, glow discharge electrolysis (GDE) occurs at the solution surface or under an aqueous solution when the applied voltage is beyond a critical value. A remarkable feature of GDE is that the chemical yield of the glow discharge electrode is several times higher than that calculated from Faraday’s law. Sengupta reported that the ·OH radical produced in the process of GDE is about 12 times that of the electrons of electricity [7]. So, GDE is regarded as a kind of non-Faradaic electrochemical process. The plasma produced in the process of glow discharge electrolysis is termed a glow discharge electrolysis plasma (GDEP). This process involves a lot of energetic species, such as ·OH, ·H, and HO2. These highly energetic species can provide energy for many chemical reactions in solution, and many unconventionality chemical reactions are easily initiated without breaking the structure of reactants [8,9]. Compared with the chemically initiated polymerization, glow discharge electrolysis plasma technology can be carried out in open systems. Not only does it initiate aqueous solution polymerization, but it also enables suspension polymerization and emulsion polymerization. This method has attracted considerable attention recently due to its simplicity of operation, no secondary pollution, and large numbers of high energy particles [10,11]. It has been applied successfully in the synthesis of polymers [12−15], organic wastewater treatment [16,17], and surface treatment [18,19].

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2 Experiment

2.1 Reagents and apparatus

All the chemicals used, such as N,N’-methylenebis (acrylamide) (MBA), butyl methacrylate (BMA), butyl acrylate (BA), OP-10, xylene, sodium hydroxide, chloroform, sodium dodecyl benzene sulfonate (SDBS), sodium sulfate, magnesium sulfate, are analytical grade. BMA and BA were washed with 5% sodium hydroxide solution and deionized water, in turn, until neutralization. They were then dried in magnesium sulfate and distilled at reduced pressure before use.

The power supply was a Model of LW100J2 DC (Shanghai LiYou Electrification Co., Ltd) providing a voltage of 0-1000 V and a current of 0-1 A. An attenuated total reflectance Fourier transform infrared spectrometer (FTS3000, DigiLAB Merlin, USA) was used to study the chemical structure. The morphological analyses were performed with scanning electron microscopy (SEM) (Model JSM-5600LV, JEOL, Japan) with an applied voltage of 20 kV. A thermogravimetric analyzer (Mettler Toledo, Switzerland, temperature range: 30°C-600°C, rate of temperature increase: 20°C·min⁻¹ under nitrogen flow rate of 50 mL·min⁻¹) was used to investigate the thermal stability of the resin.

2.2 Preparation of the highly absorptive resin

The reactions occurred in a 250 mL three-necked flask equipped with a reflux condenser, a magnetic stirrer, a platinum anode and a graphite cathode, as in our previous report [20]. The monomers BMA, BA, crosslinking agent MBA, and sodium sulfate solution were added into the reactor and then stirred at room temperature for 30 min. Then, the platinum anode and graphite cathode were immerged in the mixture with a distance of about 3 cm between them. The glow discharge electrolysis was executed to produce GDEP for a few minutes with an applied voltage of about 600 V. Then, the three-necked flask was rapidly moved into an oil bath at 90°C, a certain amount of SDBS and emulsifier OP-10 were added quickly and stirred for 24 h. The emulsion was treated with 95% alcohol solution, and a white resin was obtained, which was washed with distilled water for several times and dried under vacuum at 60°C until a constant weight was achieved.

2.3 Determination of oil absorbency

The dried sample was weighed and immersed into excess solvent at room temperature until equilibrium swelling was attained. It was then removed from the medium, wiped with a filter, and weighed immediately. The oil absorbency was calculated according to the following equation:

\[ W = \frac{m - m_0}{m_0} \]  

(1)

where \( m_0 \) (g) and \( m \) (g) are the masses of the dry sample and the swollen sample, respectively.

3 Results and discussions

3.1 Effects of discharge parameters on oil absorbency of the resin

When glow discharge electrolysis is used to initiate a reaction, discharge voltage and time become two important factors in the polymerization process. Since the applied voltage is lower than 500 V, there are not enough reactive particles for the polymerization reaction. As the voltage rises, the amount of energetic particles increases correspondingly. The effective network structure is then formed and the oil absorbency increases, as shown in Fig. 1(a). However, further increasing the applied voltage and discharge time would produce a large amount of free radicals and the reaction rate would be accelerated remarkably. The molecular weight of the resin decreased and the three-dimensional network structure was not stable because of implosion. As a result, the oil absorbency was decreased and the electrode melted. Therefore, the discharge voltage was selected as 600 V and the discharge time was 8 min (Fig. 1(b)).
3.2 Effect of MBA content on the oil absorbency

The cross-linking agent is one of the important factors that affect the structure of the resin. The effect of cross-linking agent on the oil absorbency of the resin was investigated, with the other conditions being constant. The result is shown in Fig. 2. The oil absorbency initially increases with the increase of the cross-linking agent, it then decreases. If the concentration of the cross-linking agent is 2% of the monomer concentration, the maximum oil absorbency is observed. The reason for this may be that the oil absorption capacity of the resin is controlled by the stretch capacity of its internal three-dimensional network structure. However, the concentration of the cross-linking agent mainly influences the network structure. Since the amount of cross-linking agent is too low, the three-dimensional network structure cannot form and the resin easily dissolves in organic solvents. With the increase of the cross-linking agent, the three-dimensional network structure forms entirely and the oil absorbency reaches a maximum. However, the cross-linking density and rigidity of the sample increases and the swelling capability decreases with a further increase of the cross-linking agent, so the oil absorbency decreased when an excess of cross-linking agent was added.

3.3 Effect of the ratio of monomers on the oil absorbency

Generally speaking, the size and quantity of its internal pores, and its selectivity to a solvent, are determined by the monomer structure. The absorbency for non-polar solvents is also affected by the carbon chain length of the monomers. The carbon chain of butyl acrylate is longer and the lipophilicity is better than other monomers commonly used. In addition, the number of pores inside increases when multiple branched monomers are used. Therefore, butyl methacrylate as another monomer is beneficial to form lots of micropores inside the resin. However, as the content of butyl methacrylate increases, the resin becomes harder and the swelling capability decreases, so the oil absorbency decreases apparently. It can be seen from Fig. 3 that the optimal value of BMA:BA varies with the oil absorbed because of its structure and size. In the present work, it is 2:1 for chloroform and 3:1 for xylene.

3.4 Infrared spectra analysis

The obtained resin was extracted with THF for 24 h in Soxhlet extractor and then dried under vacuum to remove homo-polymer. The FTIR spectrum of the resin is presented in Fig. 4. As can be seen from Fig. 4, the peaks at 2931 cm\(^{-1}\) and 2856 cm\(^{-1}\) are attributed to the -CH\(_2\) asymmetric and symmetric stretching vibration peaks, respectively, and the absorption at 1452 cm\(^{-1}\) is attributed to -CH\(_3\) bending vibration peak. The peaks at 2958 cm\(^{-1}\) and 2880 cm\(^{-1}\) are attributed to the asymmetric and symmetric stretching C-H vibration in the CH\(_3\) group. The absorption at 1730 cm\(^{-1}\) is attributed to the C=O stretching vibration, whereas the absorptions at 1068 cm\(^{-1}\) are assigned to the C-O stretching vibration. The absorption peak of C=C at 1650 cm\(^{-1}\) did not appear while recording the spectrum. These results show that the highly absorptive resin contains butyl methacrylate and butyl acrylate segment.
3.5 Morphology analysis

The surface morphology of the highly oil absorptive resin was evaluated, and is shown in Fig. 5. There are many deep pores in the surface and inside of the resin. These pores can help oil spread into the resin internally. In addition, the oil molecules cannot easily exude from the three-dimensional cross-linked resin. This improves the oil absorbency. Therefore, glow discharge electrolysis plasma initiating polymerization technique is favorable to the formation of pores in the resin.

![Fig. 5 SEM of the resin](image)

3.6 Thermal stability of the resin

The thermal stability of the resin was also assessed and the thermogravimetric (TG) curve is shown in Fig. 6. From the TG curve it can be seen that the sample has a very little weight loss before 100 °C, which is mainly caused by a small amount of moisture evaporating. The polymer chain is broken after 340 °C, and the sample weight loss ratio reaches 49.91% at 395 °C. Therefore, the highly oil absorbent resin obtained has good thermal stability and can be used at high temperatures.

![Fig. 6 The TG curves of the resin](image)

3.7 Absorption kinetics of the resin

The absorption rate of the sample was tested at room temperature as follows: the sample was immersed in excess solvent for one hour and then taken out to weigh. This operation was repeated ten times, at last it was immersed for 24 h and weighed.

As can be seen from Fig. 7, the oil absorbency increases quickly with increasing immersion time at the beginning. The results show that the driving force at this stage of the process is the van der Waals force between the lipophilic groups of the resin and the oil molecules. According to the principle of “like dissolves like”, there was a strong tendency to build an equilibrium between the resin and oil. When this process reached equilibrium, the slope became smaller and smaller. Consequently, the absorption rate reached saturation after 10 h.

![Fig. 7 Absorption rate of the resin](image)

The absorption kinetic model of obtained resin was studied by the absorption of chloroform. As described by Yao and Zhou [21], the swelling rate of the first-order model can be described by the following experimental formula:

\[
\frac{dQ}{dt} = k_1 (Q_{\max} - Q_t),
\]

where \(Q_t\) is the oil absorbency at time \(t\) and \(Q_{\max}\) is the maximum oil absorbency. \(k_1\) is the swelling constant.

The integration of Eq. (1) yields

\[-\ln(Q_{\max} - Q_t) = k_1 t + c,\]

where \(c\) is the integration constant and \(k_1\) is the absorption rate constant.

According to Eq. (3), a plot of \(-\ln(Q_{\max} - Q_t)\) against \(t\) with a straight line was obtained by the least square fit, as shown in Fig. 8. The correlation coefficient is \(R^2=0.9928\). So, it is indicated that the first-order absorption kinetics is more reasonable to describe the absorption process.
3.8 Retention after absorption

Retention after absorption is an important evaluation factor for highly oil absorptive resin. The accurately weighed highly oil absorption resin was immersed into the test oil. After the adsorption equilibrium, the resin was taken out of the oil and weighted. The resin was transferred to the plastic centrifuge tube quickly and it underwent centrifugation for 5 min at 5000 r/min, the resin was then weighed again. The retention after absorption was calculated according to the following equation:

\[ K(\%) = \frac{m}{m_0}, \]

(4)

\( K(\%) \) is the retention, \( m_0 \) (g) is the quantity of resin after adsorption but before centrifugation, while \( m \) (g) is the quantity after centrifugation.

The results indicate that the retention after absorption of the resin initiated by glow discharge electrolysis plasma is high: 90.1% for chloroform and 89.5% for xylene. The high retention is favorable for practical applications.

4 Conclusion

Poly (butyl methacrylate/butyl acrylate) highly oil absorptive resin was synthesized by GDEP-initiated emulsion polymerization. The results show that the resin has higher oil absorbency, oil absorption rate and retention. The pores in surface of the resin were beneficial to oil absorption. The absorption kinetic results indicate that the first-order absorption kinetics model can accurately describe the absorption process. Such highly oil absorptive resin could be used in the treatment of pollution caused by organic solvents.

References

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