Synthesis and Study on Thermal Stability of PMMA Microspheres by Emulsion Polymerization

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Abstract. Polymethyl methacrylate (PMMA) was prepared by emulsion polymerization using methyl methacrylate (MMA) as monomer, potassium per sulfate as initiator. Polymethyl methacrylate/mesoporous molecular sieve composite (PMMA/MCM-48) was synthesized via the addition of mesoporous molecular sieve MCM-48 silica nanomaterial. The synthesized samples were systematically characterized using XRD, SEM, TEM, FT-IR, and TG. The results showed that PMMA microspheres with a diameter of 80-110 nm were prepared by emulsion polymerization. Compared with pure PMMA, PMMA/mesopores molecular sieve MCM-48 composites have good thermal stability. Pure PMMA microspheres can be completely decomposed at a lower temperature (400°C), and the thermal stability of PMMA/MCM-48 composites were improved by the addition of mesoporous molecular sieves.

1. Introduction
Inorganic-organic nano hybrid materials combine the excellent characteristics of inorganic, organic and nano materials, and are widely used in electronics, chemistry, catalysis, biology, machinery and other fields [1-2]. In recent years, inorganic/polymer Nan composites have attracted wide attentions due to their unique properties and have become one of the hot topics in the field of materials research. It overcomes some of the defects in the performance of single materials and traditional composite materials, which combines the excellent characteristics of inorganic, organic and nanomaterial, and the inorganic nanoparticles are uniformly distributed in the form of nanoparticles in the polymer matrix. Composite materials have a wide range of applications in the fields of electricity, optics, optoelectronics and nonlinear optics, chemistry, catalysis, biology, and machinery.

Polymethyl methacrylate (PMMA) is an important transparent polymer material [3-4]. It has many excellent properties, such as good chemical stability, relatively balanced physical and mechanical properties, good processing properties, weather resistance and electrical insulation properties, excellent optical properties, and low density and good toughness, so it is widely used in aviation, construction, agriculture, Optical instruments and other fields. It has wide application prospects in bulletproof glass, window glass, instrument accessories, optical appliances, building materials, etc due to excellent electrical insulation and processing performance because of excellent electrical insulation and processing properties[4-8]. However, some disadvantages of PMMA itself, such as poor heat
resistance, abrasion resistance, and resistance to organic solvents, low use temperature, high water absorption, and easy burning, also limit its application range. Aiming at these shortcomings, this paper has carried out research on thermally stable modification. The modification of PMMA is to make certain adjustments and changes to the molecular chain structure, the aggregated state structure and/or the woven state structure of the polymer, so that certain properties of the material can be improved. From the perspective of practical application, the modification of PMMA mainly focuses on heat resistance, wear resistance, toughening, and flame retardancy.

Mesoporous molecular sieves have been one of the hotspots in the field of materials research in recent years [9]. Their unique structural characteristics and properties including long-range ordered, pore structure, narrow pore size distribution and adjustable pore size, large specific surface area and porosity. Taking advantage of the structural characteristics of mesoporous molecular sieves, it is dispersed as a nano-inorganic filler in the polymer, which strengthens and toughens the materials. At the same time, the interfacial area between the dispersed phase and the matrix phase is large. Greatly improve and change the various mechanical properties, optical properties, thermal properties and biological properties of materials.

In this work, mesoporous molecular sieve MCM-48 was used as an inorganic filler. Based on the unique structural characteristics of mesoporous molecular sieves and combining polymer filling modification principles, molecular sieve and polymer monomer MMA were used to prepare polymers mesoporous molecular sieve MCM-48 composites with different molecular sieve mass fractions by emulsion polymerization, and the thermal stability of the composites was studied.

2. Experimental

2.1. Reagents and Instruments
Methyl methacrylate (MMA), sodium lauryl sulfate (SDS), potassium per sulfate (K₂S₂O₈), and ethyl silicate (TEOS) are analytical reagents. JJ-1 timing electric mixer (Zhengzhou Du Fu Instrument factory), centrifuges, etc.

2.2. Synthesis of the PMMA
Polymethyl methacrylate (PMMA) microspheres were prepared according to the references[10-11]. A certain amount of methyl methacrylate monomer (MMA) was mixed with distilled water, the N₂ nitrogen gas was entered into the reaction flask at a certain flow rate, and then an appropriate amount of K₂S₂O₈ was added, and the temperature was raised to 70℃for 2 h. The microspheres were centrifuged for several hours, the supernatant was decanted, washed with distilled water, and dried at 60℃to obtain PMMA polymer microspheres.

Synthesis of PMMA/MCM-48: MCM-48 was also synthesized according to the references [12]. The method of PMMA/MCM-48 was the same as that of PMMA. When the solution temperature rised to 70℃, the prepared MCM-48 sample is directly added to the polymer emulsions at a certain ratio, and finally the PMMA/MCM-48 was obtained.

2.3. Characterization of the synthesized samples
The microstructure of PMMA particles was observed with a JEM-2100 transmission electron microscope. The XRD test was performed using a Japanese science TTR type III target X-ray diffract meter. The test conditions were: Cu target, KA wire, tube voltage 40 kV, tube current 200 mA, scanning speed 10°/min. Thermo gravimetric analysis was performed on the STA449F3 integrated thermal analyzer. In addition, analytical tests such as the SEM was detected with FEI's Inspect F50 field emission scanning electron microscope, Infrared spectrum test was performed on PE Frontier.
3. Results and discussion

3.1. XRD analysis of samples

Figure 1. XRD image of PMMA polymers and MCM-48

The XRD spectra of mesoporous molecular sieves MCM-48 (a) and PMMA/MCM-48 (b) are shown in Figure 1. It can be seen from Figure 1(a) that in the range of $2\theta=2^\circ$–$6^\circ$, there are two distinct characteristic diffraction peaks, indicating that the synthesized silica has a highly ordered cubic mesoporous structure, which is consistent with the literature reported [9, 12]. In Figure 1(b), there are no characteristic peaks below $2\theta=10^\circ$, and the characteristic peaks of MCM-48 have completely disappeared. This is mainly due to the relatively small amount of mesoporous molecular sieve MCM-48 added in the PMMA matrix. The characteristic diffraction peaks of molecular sieves could not be highlighted. In addition, in the wide angle range of $2\theta=10^\circ$–$40^\circ$, there are two large gimmick peaks (broad peaks), which indicates that the composite materials PMMA / MCM-48 is amorphous.

3.2. SEM analysis of PMMA

Figure 2 is a scanning electron microscope (SEM) picture of PMMA colloidal crystals obtained by centrifugal sedimentation. Some pores are also seen in the SEM image Figure2 (a). On the one hand, it may be related to the reaction depth and temperature control, resulting in a large number of bubbles; on the other hand, it may be related to centrifugal sedimentation. In the process of centrifugal sedimentation, superimposed slowly, there will be a large gap in the middle. The final prepared PMMA microspheres are not neatly arranged in a long range, and are in a three-dimensional irregular close-packed form. At the same time, it can be seen from Figure 2 (b) that the size of the microspheres is not uniform, the surface is rough and not smooth, and there are a large number of flaky blocks. This may be related to the synthesis factors [13]. Since the synthesis of the microspheres is proceeding under heating conditions, and the reaction is a typical exothermic reaction. In the entire mixed reaction system, a large amount of heat may be locally accumulated by the reaction released energy during the synthesis, which leads to the temperature of reaction system suddenly rise, and result in the polymer pellets connecting with together one by one to form a large block.
3.3. TEM analysis of PMMA

Figure 3 is a transmission electron microscope (TEM) picture of PMMA microspheres obtained by centrifugal sedimentation. It can be seen from Figure 3 (a) and Figure 3 (b) that the size of the microspheres is uniform, the microspheres and microspheres are interconnected with each other, and the dispersion is not very good, which may be in agreement with the control of the reaction conditions [3, 13]. The TEM images of Figure 3 (c) and Figure 3 (d) show that the diameter of PMMA microspheres prepared by the emulsion method is about 80-110 nm.

3.4. FT-IR analysis of PMMA

FT-IR spectra of PMMA and PMMA-SiO$_2$ polymers are shown in Figure 4. Figure 4 (a) is the infrared spectrum FT-IR chart of PMMA. From the figure, the characteristic absorption peak can be clearly found. The wide and strong bands around 2995cm$^{-1}$ is corresponded to the bending vibration
absorption peak of the C-H bond and also 2950 cm\(^{-1}\) is assigned to the stretching vibration absorption peak of C-H bond, and the absorption peak of 1750 cm\(^{-1}\) is the vibration absorption peak of C=O double bond. Bending vibration peak of water is around 1500 cm\(^{-1}\). The characteristic absorption peaks throughout the figure indicate the presence of methyl (-CH\(_3\)), carbon-oxygen double bond (C=O), and carbon-oxygen bond (C-O) in the polymer [3].

Figure 4 (b) shows the infrared spectrum of a PMMA / SiO\(_2\) hybrid material. It can be seen from the figure that the sample has the characteristic absorption of MMA (C=O at 1737 cm\(^{-1}\), -CH\(_3\) at 2950 cm\(^{-1}\), etc.); the absorption peak of PMMA / SiO\(_2\) at 3000 cm\(^{-1}\) is weaker than that of pure PMMA, and the absorption of PMMA/SiO\(_2\) shifted slightly toward the long wavelength direction. The absorption peak of the hybrid materials near 3454 cm\(^{-1}\) is attributed to the vibrational absorption of hydroxyl groups on the surface of the channel, which indicates that there are a large number of hydroxyl groups on the surface of the channel of the mesoporous silica. The absorption peak is broadened due to the large hydroxyl concentration and the presence of intermolecular hydrogen bonds, so the absorption peak appears as a broad absorption peak with strong intensity, which is consistent with that reported in the literature [3, 4, 12]. The absorption peak of Si-O-C bond is at 1137 cm\(^{-1}\), and the absorption peak of Si-O-Si bond is at 470 cm\(^{-1}\). The above results indicate that covalent bonds are formed between SiO\(_2\) and PMMA in the hybrid materials.

Figure 4. FT-IR image of PMMA and PMMA-SiO\(_2\) polymers

3.5. TG analysis of PMMA

The thermal stability of PMMA and PMMA-SiO\(_2\) materials were investigated by thermal weight. Figure 5 (a) is a thermal weight loss curve TG diagram of pure polymer PMMA. As shown in the figure, thermal decomposition begins at a temperature of about 180°C, and completely decomposes at 400°C. It can be seen from the figure that the thermal decomposition of the PMMA copolymer is divided into three stages, which are the head-to-head joint fracture of the main chain, the end of the vinyl-induced fracture and the random break of the main chain. At 180°C, the weight loss of the sample is about 1%, which may be the residual moisture in the sample. At 180-250°C, the weight loss of the sample is about 5%, and it may be that various bonds (C-H, C=O, C-O, etc.) in the sample begin to break. The 250-420°C sample lost 100% of its weight, all the bonds in the sample were broken and oxidized, and the decomposition was complete, which produce simultaneously a large amount of carbon dioxide gas and water vapor [3].

Figure 5 (b), Figure 5 (c), and Figure 5 (d) are the thermal weight loss curves TG of 0.5%-SiO\(_2\)-PMMA, 1%-SiO\(_2\)-PMMA, and 2%-SiO\(_2\)-PMMA, respectively. The results are shown in Figure 5, the
initial mass loss temperatures of pure PMMA and PMMA/MCM-48 composites are comparable, both around 180°C. However, when the temperature rises to 250°C, the weight loss rates of the composites 0.5%-SiO₂-PMMA, 1%-SiO₂-PMMA, and 2%-SiO₂-PMMA are 9.7%, 8.5%, and 5.5%, respectively, while the weight loss rates of pure PMMA are 10%. With the increase of temperature, especially after 350°C, the weight loss rates of composite materials decreases obviously, and the mass of the composites (0.5%-SiO₂-PMMA, 1%-SiO₂-PMMA, 2%-SiO₂-PMMA) is constant when the temperature is over 450°C, 460°C, 500°C successively, while the mass of pure PMMA remains the same (that is to say, complete decomposition for PMMA) at 420°C. The above analysis results show that the thermal stability of composites is superior to that of pure PMMA, which is mainly attributed to the fact that MCM-48 acts as a cross-linking point in PMMA system, and hinders the thermal decomposition of composites. These results are consistent with XRD and FT-IR characterization of the sample [3, 12], and a certain valence bonds are formed between SiO₂ and PMMA. It can be seen that the loading of SiO₂ varies the thermal behavior of the composite material, which indicates that the formation of an inorganic phase and an organic phase network in the composite material enhances the cross-linking between organic segments and inhibits the molecular chain movement of the polymer. Their weight loss rates by calculation were 89.4%, 86.8%, and 72.2%, respectively. The thermal stability of PMMA materials was improved by adding mesoporous molecular sieves.

![TG image of PMMA polymers](image)

**Figure 5.** TG image of PMMA polymers

4. Conclusion
PMMA materials and PMMA/MCM-48 composites were prepared by emulsion polymerization. TEM analysis showed that the prepared PMMA microspheres had a diameter of 80-110 nm, and the microspheres were relatively uniform in size and they were arranged in three-dimensional periodic close array in long range. The mesoporous molecular sieves MCM-48 was introduced into PMMA, The FT-IR and XRD analysis showed that MMA polymerized inside and outside the three-dimensional channel of MCM-48, and some covalent bonds were formed between SiO₂ and PMMA as a result of interaction of each other. The results of TG showed that the thermal stability of the PMMA/MCM-48 composites was improved owing to the addition of mesoporous molecular sieve MCM-48.
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