Review   IJPSE

Preparation of PMMA Nanoparticles in Different Ways and Studying the Effect of Some Factors on Changing Its Properties

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Abstract
Poly(methyl methacrylate) (PMMA) is usually made with the help of radical polymerization, coordination polymerization, and methyl methacrylate acid esterification. Due to its hardness, PMMA is widely used in the medical sciences, optical materials, electronics, and automotive industries. The present study aims to fabricate PMMA nanoparticles using different chemical methods such as sol-gel polymerization, co polymerization, etc. Various aspects of the synthesis process will be changed, such as temperature, reaction time, initiator type, and monomer/water ratio. We aimed to study their effects on changing the properties of PMMA nanoparticles the morphology and structure of PMMA nanoparticles were investigated by scanning electron microscopy and X-ray diffraction.

Keywords: Poly(methyl methacrylate (PMMA), scanning electron microscopy (SEM), X-ray diffraction (XRD), polymerization

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a versatile polymer that has several applications outside of the construction industry. It has got remarkable qualities like low chromatic dispersion, high transmittance, high impact strength, high chemical stability, and high processing ability. Composite materials based on modified PMMA have found extensive use in recent years, particularly in the preparation of the dental and prosthetic foundation materials. These composites require a unique approach to preparation, as compared to the norm in the industry. After the prepolymer has been changed, composite materials are prepared using a room-temperature curing reaction process [1].

However, issues such as relatively weak mechanical characteristics and variable thermal properties are present in the composite materials created via a room-temperature curing procedure. Polymer matrix nanocomposites (PMMA NCMs) can be made by incorporating nanoparticles into the PMMA matrix to achieve the best of both natural and synthetic materials. Wang et al. [1], for instance, looked at how various nanoparticle shapes affected the characteristics of a PMMA-based composite material. Fortifying the dental material, Li et al. [2] employed complicated zirconia nanoparticles. When it comes to biocompatibility, mechanical characteristics, and thermal conductivity, the nanodiamond shines.

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Nanodiamond composites prepared using resin have been the subject of several research studies [3–5]. As far as we can tell, no one has ever tried incorporating nanodiamonds into PMMA-based composite materials before. As part of this study, PMMA prepolymer was infused with nanodiamonds that had been chemically changed using varying concentrations of a silane coupling agent. The PMMA/nanodiamond composites were then produced through a curing reaction at room temperature. Next, the characteristics of the resulting composite material were investigated, along with the dispersity characteristic of nanodiamonds in the PMMA matrix.

LITERATURE REVIEW
Synthesis of Poly(Methyl Methacrylate) Through Conventional Method
Due to their advantageously high surface area and proportion of molecules or atoms on the surface, nanosized polymer particles are anticipated to be employed and play a key role in different industries, such as medicine, the environment, agriculture, and catalysis [6]. The synthesis of nano polymer particles, and specifically the analysis of PMMA nanoparticles, has therefore garnered a significant deal of interest from scientists all over the world. Nano polymer particles, such as PMMA, are typically generated using mini- or micro-emulsion polymerization as opposed to chemical synthesis for inorganic nanomaterials. Micro-emulsions are thermodynamic systems that consist of a solvent, monomer, emulsifier, and, in certain cases, a co-emulsifier. Particles with sizes of 20 nm or less can be created using micro-emulsion polymerization, as has been reported in prior works. Nonetheless, a substantial amount of surfactant is necessary for the traditional micro-emulsion polymerization of nanoparticles. The use of surfactants like sodium dodecyl sulfate, which is both expensive and harmful to nano-sized polymer particles, is discouraged. As a workaround, researchers like Ming et al. [7] came up with their own methods of synthesis that required far less surfactant. In order to add MMA monomers to the reaction mechanism, just a tiny amount is added at a time, and the rest is supplied dropwise [7]. Stirring at a rate of 600 rpm is performed while a redox catalyst is utilized for initiation. The reaction was conducted at a temperature of 40°C using sodium dodecyl sulfate as the surfactant. A particle size of roughly 13 nm was achieved, and a surfactant/monomer ratio greater than 1:10 was achieved. Dodecyl trimethylammonium bromide was employed as the surfactant and potassium persulfate (PPS) was utilized as the initiator in the research conducted by Ming et al. [7]. In these tests, we used magnetic stirring and raised the reaction temperature to 60°C.

Synthesis of Poly(Methyl Methacrylate) Through Polymerization
Chou and Stoffer [8] pioneered the use of ultrasound irradiation for MMA emulsion polymerization. The impact of molecular weight, as well as polymerization rate on a number of factors, were investigated, as were the effects of ultrasonic irradiation and cavitation. The MMA monomers are mixed with a surfactant (sodium dodecyl sulfate) ranging in concentration from 0.035 to 0.243 M in a slow process involving continuous stirring. The ratio of monomer to water (by volume) in the MMA monomers ranges from 1:19 to 1:5. The reaction was allowed to proceed at room temperature for 30 to 35 minutes with no chemical initiators. Intensity ranges from 6.8 to 14.4 W/cm^2 for an ultrasound with an input power of 34 to 72 W. The polymerization rate is very high, and the conversion rate can go as high as 70% under these conditions [8]. The outcomes are similar to those of tests conducted with a standard thermal initiator, although the polymerization and conversion rates are faster. It is found that considerable polymerization of MMA cannot be observed in the absence of persistent bubbling in the reaction system and that the presence of ultrasonic initiation is extremely relevant to the resonant cavitation. A higher ultrasound intensity results in a faster polymerization rate, which can be explained by a combination of factors including an increase in the number of free radicals produced by the ultrasound, a rise in temperature as a result of the ultrasound vibration, and a greater polymerization and gel impact as a result of an amplified cavitation bubble effect. Molecular weight often increases with increased ultrasonic intensity, and this is primarily due to the gel effect. Also, the polymerization rate was found to be affected by the argon flow rate that was added to the reaction mechanism for bubbling [9]. The enhanced gel effect is the primary reason for the marginal increase in rate with

increasing rate of flow [8]. It is also possible to speed up the polymerization process by increasing the concentration of the surfactant and the starting monomer [10].

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, containing 30 ppm MEHQ as an inhibitor, 99%, Sigma-Aldrich) was used unprocessed since it is a commercially accessible monomer. Water-Soluble potassium persulphate, 99%, and oil-soluble 2, 2-azobisisobutyronitrile, 98% were obtained from Sigma-Aldrich and used as initiators. The surfactant, on the other hand, was synthesized by dissolving sodium dodecyl sulphate 99%, which was supplied from Sigma-Aldrich, in deionized water.

Apparatus

During the polymerization experiments, the following instruments were used: a threeneck round-flask, hot plate equipped with a magnetic stirrer, peristaltic pump, ultrasonic cleaner, and ultrasonic probe/horn (Fisher Scientific Model 120 Sonic Dismembrator, 120 W, 20 kHz) with 1/8-inch probe.

Polymerization of Poly(Methyl Methacrylate)

PMMA was produced using three different methods: the "batch reaction method", the "pre-mixing separation method", and the "differential addition method". These three methods have been combined with five different emulsification techniques: "probe ultrasound," "ultrasonic bath," "and magnetic stirring combined with ultrasonic bath." In some of the studies, different temperatures, as well as varying amounts of surfactant and monomer at various concentrations, were investigated. Initiator-free testing was among the several kinds of trials that were carried out.

Characterization of Poly(Methyl Methacrylate)

The weighted gravimetric method was utilized to calculate the solid content (S%). Before and after oven-drying, a sample of 10 mL was weighed both before and after being removed. The following equation was used to compute S%:

$$S\% = W_1/W_2 \times 100 \dots\dots\dots \tag{1}$$

Where W_1 represents the weight of the PMMA particles after drying for a specific volume of latex specimen. Because the total quantity of the latex after the reaction, the volume of latex removed for specimen drying, and the actual quantity of SDS given to the system are all known, the total solid weight may be estimated by subtracting the weight of the surfactant from the total solid weight. W_2 represents the weight of a specific volume of latex that was collected as a sample. The conversion rate, denoted by X_m, is based on the same factor as the solid content and can be represented by Equation (2):

$$"X_m = \frac{W_1}{M_{(total)} \times \frac{l_1}{L}} \times 100\%" \dots\dots\dots \tag{2}$$

Where $M_{(total)}$ is the overall weight of MMA monomers that are being introduced to the reaction mechanism and the density of MMA is 0.9440 g/cm^3. The amount of latex that was used for the sample is denoted by l_1, and the amount of latex that remained following the reaction is denoted by L.

Using a "dynamic light scattering" device manufactured by Brookhaven Instruments Corporation at an angle of 90° and a temperature of 20°C, the mean particle size and the polydispersity (PD) were calculated. The hydrodynamic diameter, also known as the z-average diameter and effective diameter, is the particle size that may be measured using this device. Equation (3) gives us a definition of the magnitude of PD.

$$"PD = \frac{\mu}{\Gamma^2}" \dots\dots \tag{3}$$

Where • corresponds to the standard deviation of the intensity-weighted diffusion coefficient, and Γ varies according to the adaptability of the intensity variation of diffused light. A smaller value for PD indicates that there is a smaller variation of particle size, and PD will be equal to zero in a circumstance where there is no difference in distribution.

RESULTS AND DISCUSSION

Experiments were conducted in order to discover practical methods for the synthesis of tiny and uniform nanoparticles and for the manufacturing of PMMA in large quantities. As a result of the fact that numerous types of polymerization approaches and emulsifying methods were tried out in an effort to find the best way to achieve the goal, the results have been categorized according to the methods that were used for the synthesis, and some comparisons will be made to determine the differences between them. During the polymerization process, three basic methods will be used including "batch reaction", "pre-mixing separation", and "differential addition". Because some of the obtained results by the "batch reaction method" and the "pre-mixing separation method" approaches are the primary goals of this study, additional experiments were carried out in order to obtain more specific information. Although the "batch reaction method" is the most suitable method for mass manufacturing, a "pre-mixing separation method" has an advantage that other methods do not have, which is the formation of fine and uniform particles. Other variables, such as the ratio of monomers to water, the concentration of the surfactants, and the type of initiator, were investigated for those procedures that provide meaningful outcomes.

Batch Reaction Method

The simplest method for producing polymer particles with a nanoscale size is to use a batch process. In the course of a batch reaction, the initiators, surfactants, monomers, and solvents are all emulsified and mixed together according to the protocol that has been laid down. In the glass flask with three separate necks, reactions may be seen taking place (Table 1). The standard recipe is as follows.

As part of this batch approach, the reaction system was subjected to a variety of emulsifying procedures, and the variations between these procedures can be observed in the results. After the reaction is complete, ice water was used as a cooling strategy. The typical reaction duration is 1 hour and 15 minutes, which includes 15 minutes for the temperature to rise before the reaction begins and 1 hour for the reaction itself. The temperature of the batch reaction was regulated at 70°C.

Pre-mixing Separation Method

PMMA nanoparticles have been created by the process of differential addition in the research laboratory. Utilizing a peristaltic pump allowed for the MMA monomer to be introduced into the reaction mechanism in a differential method. In order to obtain very fine particles, monomers are carefully dissolved in the SDS solution (Table 2). This allows very small particles. However, it does not function effectively and the instructions for using it are difficult to understand. The recipe is identical to the one that was used for the batch reaction, with the exception that an initiator has been added.

Figure 1. Components in batch reaction method.

Initiator (PPS or AIBN)	Solvent (Water)	Monomer (MMA)	Surfactant (SDS)
0.16 g	120 mL	14 mL	1.4 g

Table 2. Components in pre-mixing separation method.

Initiator (PPS or AIBN)	Solvent (Water)	Monomer (MMA)	Surfactant (SDS)
0.16 g	120 ml	14 ml	1.4 g

After that, a particular emulsifying procedure is used to combine the solvent, the monomer, and the surfactant. When it comes to this procedure, a great number of investigations have demonstrated that the various approaches to emulsifying do not have an impact on the outcomes of the mixing and separating processes. The emulsion, once it has been put into a separation funnel, will, after a period of time and regardless of how the components are combined, separate into two distinct layers. The layer on top is clear because the MMA that makes it up is dissolved in water, while the layer below is opaque because the MMA that makes it up is soluble in water. In this scenario, the bottom layer can be thought of as a saturated MMA solution. It is separated out in order to carry out the reaction, and when the separation procedure is complete, 0.16 g of PPS are added to the mixture in the role of an initiator.

The major goal of such a procedure is to produce an environment that is "starved" for the purpose of polymerization. In this scenario, the underlayer solution only consists of micelles and monomers that have been dissolved in water. In contrast to traditional emulsion polymerization, there are no droplets of monomer in the underlayer solution. When the supply of MMA monomers is stopped, it is possible to produce particles that are of small size and have a restricted dispersion.

Differential Addition Method

The main goal of this study is to improve the differential addition method to produce PMMA nanoparticles, to achieve this goal ultrasound is applied to the reaction system. Specifically, the goal was to make the process significantly more effective. The recipe is identical for each of these three different approaches.

The initiator, the surfactant, and the water were all combined at the very beginning of this procedure, and then the mixture was heated to a temperature of 70°C. A peristaltic pump was utilized in order to add the monomer to the reactor in a drop-by-drop fashion. After the dropping step process was completed, the reaction should be left for 15 to 30 minutes to ensure that the reaction is finished. The total time required for the dropping process is 1 hour. Following this step, ice water was utilized in a cooling process that is fed to the reaction system (Table 4). However, when compared to the other two techniques of emulsifying with the help of an ultrasound helper, the differential addition approach does not perform as well as the other two methods, which is why additional research was not conducted on this method.

The findings and occurrences of the experiments indicate that, in contrast to the batch reactions, in According to Table 4, it can be seen that the majority of monomers incorporated in the reaction

Table 3. Components in differential addition method.

Initiator (PPS or AIBN)	Solvent (Water)	Monomer (MMA)	Surfactant (SDS)
0.16 g	120 ml	14 ml	1.4 g

Table 4. Results of differential addition method.

Effective diameter (nm)	PD	Percentage of probe ultrasound amplitude	Probe ultrasound power (W)	Agitation speed (rpm)	Reaction time
211.0	0.232	80%	~13.8	N/A	15 min
178.0	0.177	80%	~13.8	200	15 min
126.8	0.206	80%	~13.8	N/A	15 min
135.1	0.190	80%	~13.8	200	15 min
144.8	0.186	80%	~13.8	200	30 min

Reaction condition: 120 mL water, 1.4 g sodium dodecyl sulfate (SDS), 0.16 g potassium persulfate (PPS), 14 mL methyl methacrylate (MMA); dropping time =1 h; temperature = 70°C; reaction time =15/30 min.

mechanism were not converted into PMMA. Moreover, the conversion rate is also found to be relatively low. This is because the batch reactions take place in a separate container. No matter what kind of emulsifying method is used, the particle size produced by this approach is always significantly larger than the particle size produced by the other two methods. Because of the low conversion, it is more likely that the diameter that was obtained represents the diameter of micelles and droplets found in the latex. The differential addition approach offers no advantages over the other two polymerization methods while the batch reaction can produce enough PMMA nanoparticles with small sizes and limited particle shape in the same process that takes 1 hour and 15 minutes.

CONCLUSION AND RECOMMENDATIONS

Microemulsion polymerization with the assistance of ultrasound can produce PMMA particles on the nanoscale. It has been demonstrated that batch reaction is the easiest and quickest method of synthesizing such particles. However, the pre-mixing separation method is capable of producing sometimes smaller particles with a limited size distribution, despite the fact that the solid content produced by this method is lower (3%) than that obtained from the batch reaction (10%). A study is required since the differential addition approach is not as productive as the other ways, and there is a need for more research to be done.

Only by using probe ultrasound emulsifying can one achieve tiny particles with a small size distribution and a high conversion (100%) using the batch reaction approach. At an amplitude of 40%, the probe ultrasonic achieves its optimum level of intensity. Methods of emulsifying that are too powerful have a tendency to increase particle sizes due to rapid polymerization and a gel effect that is amplified by foams that are created during the emulsifying process. The inclusion of more monomers would result in an increase in the particle size as well as the rate of polymerization, whereas the addition of fewer monomers will have the opposite effect. The polymerization period can be lengthened to make the particles more homogenous, and a high conversion rate could be attained in a relatively short amount of time.

According to the findings, this approach is very well suited for the mass production of PMMA nanoparticles thanks to its high polymerization rate and high conversion rate, as well as its fair particle size and size dispersion. Eliminating big monomer droplets is one of the steps involved in the pre-mixing separation procedure. This step serves to cut off the monomer supply. When compared to the results of the batch reaction, the particles that were formed here are finer and more homogeneous. Emulsifying with an excessive amount of power, in a manner analogous to the batch reaction approach, will result in huge particles, and the stringent cooling method is accountable for a significant amount of precipitation. More research is needed since the differential addition method is not as effective as the other two methods. These experiments should require altering the variables for the reaction and researching the mechanism behind differential emulsion polymerization with the assistance of ultrasound. According to the findings, this technology seems to be more appropriate for synthesising small and homogenous particles than producing a large quantity of something.

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