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Synthesis of SiO_2 Nano particles-Dimethyl Malonate Polymer

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Abstract

The goal of this research is synthesis of hybrid inorganic-organic microstructure to form a monolayer with anti-reflective properties. Dimethyl Malonate –Silica gel (DMM-SiO_2) composite were synthesized by chemical method from dimethyl malonate (DMM) and silica gel particles with a diameter ~34 nm. The anionic polymerization was applied for the preparation of composite. DMM as monomer polymerizes upon reacting with an initiator (OH^- in H_2O) and terminate by a terminator (H^+ in HCl). We modify the anionic polymerization reaction by adding silica gel nanoparticles before initiating polymerization. Variables including SiO_2 concentration, surfactant concentration, DMM/SiO_2 ratio, and pH of solution have been investigated. The optimal synthesis conditions were obtained by Box-Behnken design (BBD). The results show that reaction should be carried out at ambient temperature and pH 4.5. Sodium dodecyl sulfate (SDS) as surfactant concentration, SiO_2 concentration and DMM/SiO_2 ratio should be 5 mmol, 2 w.t% and 4.2g/1g, respectively. DMM-SiO_2 composite were characterized by Scanning Electron Microscopy (SEM), and Thermogravimetry Analysis (TGA).

Keywords: Silica gel nanoparticles, Dimethyl malonate polymer, Hybrid composite, Anionic polymerization.

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Introduction

Nanoscale inorganic materials have favorable properties that it can be incorporated into a microscale organic polymer to result a composite with enhanced macroscopic functionality. These composites are used for micro-optics [1], drug delivery systems [2], solar cells [3], self-cleaning, anti-corrosion [4] and coating technologies [5]. An anti-reflection (AR) coating is a type of optical coating applied to the surface of lenses, other optical elements, and photovoltaic cells to reduce reflection. It improves efficiency since less light is lost due to reflection. Reduction in reflections also improves the contrast of the image by elimination of stray light. A relatively wide wavelength range must be specified in coatings. Many coatings consist transparent thin film structures with alternating layers of contrasting refractive index. By using alternating layers of a low-index material like silica and a higher-index material, it is possible to obtain reflectivity as low as 0.1% at a single wavelength. Coatings that give very low reflectivity over a broadband of frequencies have be used, although these are complex and relatively expensive. The thickness and cost are limiting factors for the number of layers [6].

The refractive index (RI) depends on material through which the light passes. The angle of radiation, the wavelength of light and polarization are major factors related to anti- reflective property of a coating. A coating with anti-reflective properties should have broadband, omnidirectional and polarization insensitivity characteristics.

In previous research, anti-reflection coatings have been prepared by making different multilayer composites with different RI [7-9]. Typical anti-reflection coatings are silicon and titanium dioxide (TiO_2) films [10].

In addition, nanostructure materials may been placed on a substrate to form anti-reflective coatings such as a single layer of silica nanoparticles on a polymer substrate. Mesoporous silica nanoparticles were been mixed with tetraethyl ortho-silicate and then coated on a polycarbonate substrate. The formed coating has excellent resistance and anti-reflection properties [11]. The geometry of these nanostructures results in the variation of RI as a function of their height. The reflection in such nanostructure surfaces is about 1-4% of the total light [12].

Each phase in hybrid composition has a specific function. Organic phase provides the skeletal framework of microparticles and inorganic phase is used to impart functionality. The hybrid morphology can be obtained by encapsulating the inorganic nanoparticles in a polymer matrix. Various factors like surfactant concentration, monomer solubility, monomer concentration, pH, temperature, and initiator are responsible for synthesis of these composites [12]. Surfactant concentrations below the critical micelle concentration (CMC) give optimal encapsulation

results. Surface modification of inorganic species improves the encapsulation efficiency as the nucleation of the monomer occurs usually at the interface of the inorganic-organic phase. Slow rate of monomer addition (≈< 1 ml/h) into prevents homogenous nucleation of monomer molecules and enhances polymer dispersion in the solvent. Haga et al. synthesized TiO_2-polystyrene (PS), TiO_2-polymethyl methacrylate (PMMA) composite microparticles using free-radical emulsion polymerization. The encapsulation efficiency was evaluated by TGA [13]. Roebuck et.al demonstrated a versatile method to encapsulate calcium carbonate microparticles with methyl methacrylate (PMMA) polymer by conventional free-radical emulsion polymerization [14].

Free radical emulsion polymerization usually has been used for synthesis of composite microparticles [15]. However, this research work employs a novel malonate monomer with excellent coating properties by anionic polymerization. Anionic polymerization consist of the polymerization of monomers with an anionic group. A monomer polymerizes upon reacting with an initiator and generates a carbanion center. The active site propagates and grows along the polymer strand with the addition of more monomers until deliberately terminated by a terminator. This method is a well technique used to synthesize a wide variety of polymers [15]. We modify the anionic polymerization reaction by adding an inorganic pigment (silica gel nanoparticles) before initiating polymerization.

The goal of this research is synthesis of hybrid inorganic-organic microstructure to form a monolayer with anti-reflective properties. At first DMM as an organic matrix is placed on the surface of nanoparticles silica gel and nano SiO_2 -DMM composite has been synthesized. Optimal conditions in the preparation of the composite, confirmation of the structure of the composite and investigation of its anti-reflective properties are goals of this project.

Experimental

Anionic polymerization

At first SiO_2 nanoparticles (2 w.t%) were added to 10 ml water. After stirring for several minutes, 5 mmol sodium dodecyl sulfate (SDS) has been added as an anionic surfactant. For reactions under acidic conditions (pH 4.5), hydrochloric acid (HCl) was used. Finally, after pH adjustment, monomer (DMM) was added slowly (2 ml/h). The slow rate of addition minimizes the secondary nucleation of the monomer in the solution [12]. The reaction was carried out at room temperature for 6 hours at 500 rpm. The solution was transferred to a dialysis tube to separate undesirable components. Then the polymer particles separated from the unreacted compounds were used as a sample for analysis.

Design of Experiments

The reaction was performed at an ambient temperature of 25 ^{0}C. In order to study the role of each factor in the synthesis of nano SiO_2-DMM particles, we design a Box-Behnken design also known as BBD design, wherein each factor participating in the design is set to a high and low value. In this study, four main variables including SiO_2 concentration, surfactant (SDS) concentration, DMM/SiO_2 ratio, and pH of solution have been investigated. Each factor is set to two levels (low and high) leading to 16 combinations in the design (Table 1). Low and high values are determined by referring to the published literature on the synthesis of composite microparticles. The qualitative evaluation of the inorganic incorporation is performed by scanning electron microscopy (SEM).

Table 1. Box Behnken design of experiment.

Experiment No.	SiO_2 (Wt%)	DMM/SiO_2 (g/g)	pH	Surfactant (mmol)
1	2	4.2	7	5
2	2	4.2	7	8
3	2	4.2	4.5	5
4	2	4.2	4.5	8
5	2	1.5	7	5
6	2	1.5	7	8
7	2	1.5	4.5	5
8	2	1.5	4.5	8
9	1	7.5	7	5
10	1	7.5	7	8
11	1	7.5	4.5	5
12	1	7.5	4.5	8
13	1	4	7	5
14	1	4	7	8
15	1	4	4.5	5
16	1	4	4.5	8

Particle Characterization

The solution was transferred to a dialysis tubing and placed in SDS solution (9mM). The dialysis helps separate unreacted monomer and silica gel particles. It was conducted over three days by replacing the SDS solution daily. For further separate of unreacted constituents, dilution was done three times in a 20 ml vial with 9mM SDS.

100 µl of solution were diluted in 10 ml SDS for Light Microscopy Analysis (Nikon Ti2-Eclipse). The composite particle suspension were diluted (50 µl, 100 µl, 1000 µl in 10 ml SDS solution) for Scanning Electron Microscopy (SEM) analysis. The samples were placed on a silicon wafer attached to an SEM stub and placed in a desiccator for drying. TA instruments Q50 model was used for Thermogravimetry Analysis (TGA). Sample post-dialysis was decanted and settled residuum was dried in a vacuum oven at 60 ^{0}C. The dried material was transferred to the platinum pan for TGA analysis.

Results and discussion

In this research, SiO_2 nanoparticles as inorganic part and dimethyl malonate (DMM) as organic part has been employed. Sodium dodecyl sulfate (SDS) an anionic surfactant has been used to uniformly disperse SiO_2 nanoparticles and initiate polymerization at the particle surface. The surfactant acts as a colloidal stabilizer by inducing charge at the silica gel surface. A stronger surface charge leads to a monomer polymerization at the surface sites. Surfactant concentration is set to lower or equal to the critical micelle concentration (CMC) value. If the surfactant concentration is higher than the CMC value, it causes the agglomeration of hybrid particles. This is caused due to formation of micelles that entrap monomer molecules in their nonpolar core which results in secondary nucleation leading to agglomeration.

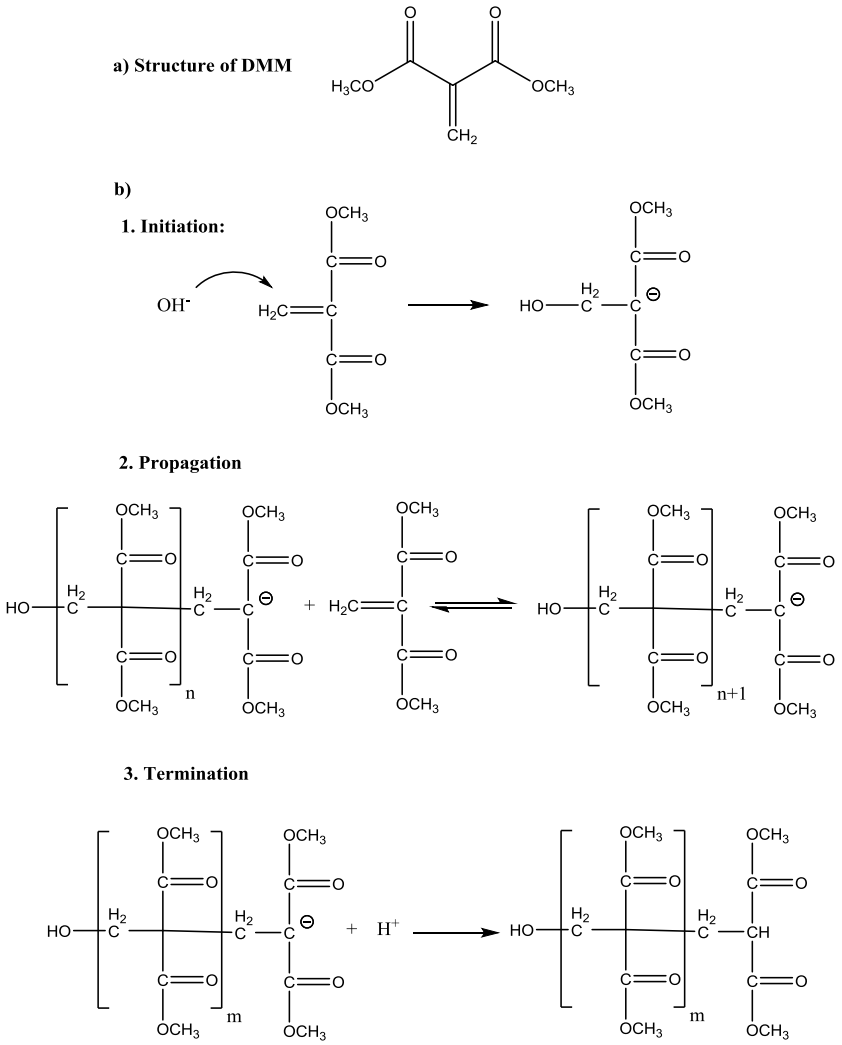

Figure 1. (a) Chemical structure of DMM (b) Polymerization mechanism

Structure of DMM and polymerization mechanism is shown in Figure 1. Hydroxide ions (OH^-) in water could initiate DMM, and DMM could polymerize in water at pH 4 or greater without adding any additional initiators. The hydroxyl group (OH^-) in water play the role of the anionic initiator, while protonic hydrogen ions (H^+) act as the terminator to stop polymerization. Experiments were performed at different pH and visually, the production of an emulsion occurred at pH values lower than 6 (Figure 2). At pH values of 6 and 7, white cotton-like polymer separated from the emulsion, which indicated the formation of a higher molecular weight polymer.

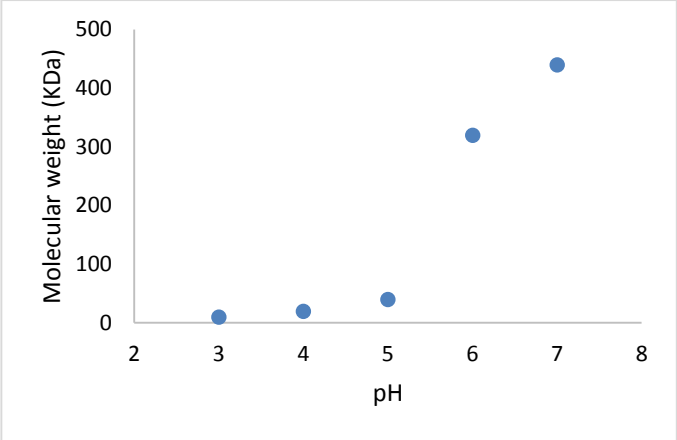

Figure 2. Variation of the molecular weight of poly (DMM) with pH.

The anionic polymerization reaction has been modified by adding an inorganic part (SiO_2 nanoparticles) before starting polymerization. The surfactant acts as a colloidal stabilizer by inducing charge at the silica gel surface. A stronger surface charge leads to a monomer polymerization at the surface sites. Surfactant concentration is set to lower or equal to the critical micelle concentration (CMC) value. If the surfactant concentration is higher than the CMC value, it causes the agglomeration of hybrid particles. This is caused due to formation of micelles that entrap monomer molecules in their nonpolar core which results in secondary nucleation leading to agglomeration.

Silica gel nanoparticles have a particle size of about 34 nm with no surface functionalization. Nano silica gel particles were prepared in laboratory by sol-gel method [16]. Silica gel is the most widely used white pigment because of its brightness and very high refractive index. Silica gel crystal size is ideally around 220 nm (measured by electron microscope) to optimize the maximum reflection of visible light. Silica gel nanoparticles show a strong degree of agglomeration due to low surface charge and particle size (34 nm). A pigment (SiO_2) concentration from 0.1 to 10 wt% is generally employed for the synthesis of composite particles to minimize agglomeration of inorganic nanoparticles. The organic to inorganic ratio is critical because a high ratio may result free polymer formation. Temperature for anionic polymerization is reported to be ranging from 25 ^{0}C to 40 ^{0}C [17]. Therefore, we carry the reaction at an ambient temperature of 25 ^{0}C. The desirable range of pH for synthesis is from 4 to 7. The range of nano silica gel concentration varied from 0.1-5% weight percent.

The particle size of microparticles for each of 16 experiments in BBD design were conducted Via SEM. When surfactant concentration and monomer to inorganic ratio were at a low level,

we measured particle size of about 520-680 nm for pH of 4.5 and about a micron (1000 nm) for a pH of 7.2 (Figure 3).

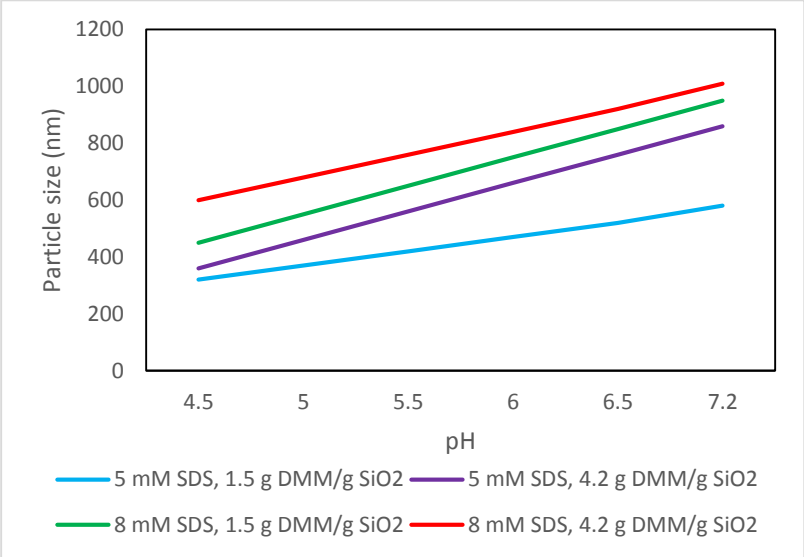

Figure 3. Effect of pH on composite particle size.

When monomer to inorganic ratio factor and surfactant concentration factor were set to a high level, we recorded the least particle size, ranging from 300-350 nm for a pH 4.5 and 550-600 nm for a pH 7. Surfactant concentration and pH factors had main role in particle size of composite nano SiO_2-DMM microparticles. The lower pH corresponds to a higher concentration of H^+ ions that are responsible for chain termination of poly (DMM). The presence of an acidic environment results in polymer chains of lower molecular weight and lower particle size. Another reason for the reduction of particle size at a lower pH is the difference in polarity between inorganic surface and solvent that minimize aggregation between inorganic particles.

The images of SEM show the incorporation of the inorganic phase in the organic matrix. Silica gel nanoparticles can be seen inside the polymer matrix (Figure 4).

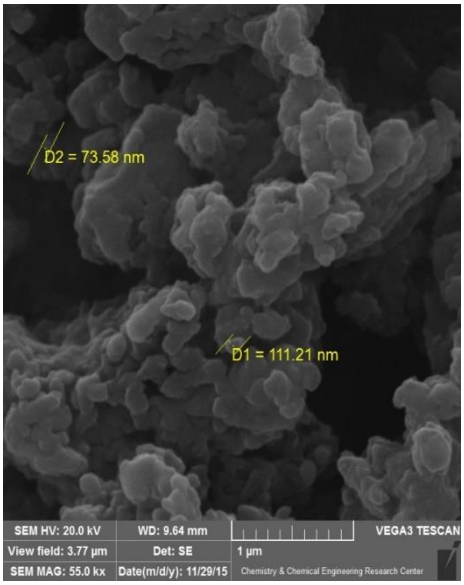

Figure 4. SEM images of hybrid SiO_2-DMM.

The residual weight fraction was evaluated by TGA analysis for all samples. The temperature range is 25^0 C to 500 ^{0}C at rate of 25 ^{0}C/min. DMM polymer has a boiling point ranging from 250-300 ^{0}C. The silica gel has a boiling point above 1000 ^{0}C. We observe a sudden decrease in weight percent after passing DMM boiling point, as shown in Figure 5.

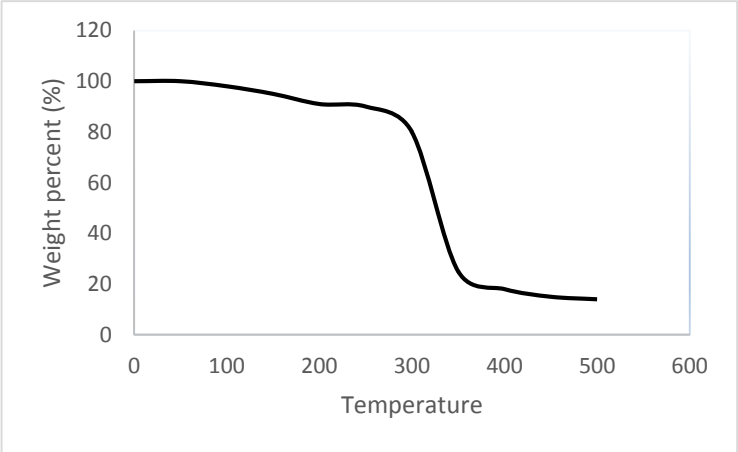

Figure 5. TGA analysis of DMM-SiO_2 composite**.**

Conclusion

A new composite of SiO_2-DMM microparticles has been synthesized. The composite particles are characterized by SEM and TGA methods. The hybrid microparticles were formed by modifying anionic polymerization of DMM to silica gel nano particles. The particle composition are controlled by setting the variables. The most important effective factors are pH and surfactant concentration. Optimal conditions in the preparation of the composite, confirmation of the structure of the composite and investigation of its anti-reflective properties are goals of this project.

Acknowledgements

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