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Preparation of monodispersed PMMA particles and composite particles containing pigment green 36 by dispersion polymerization

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ABSTRACT

Monodispersed PMMA (polymethyl methacrylate) particles were prepared *via* a dispersion polymerization process using methanol as the dispersive medium, azobisisobutyronitrile (AIBN) as initiator, and polyvinylpyrrolidone (PVP) as steric stabilizer. This study applied the Taguchi experimental design to determine an optimized formulation for preparing monodispersed PMMA particles at a stabilizer molecular weight of 360 kDa, a concentration of 8.0 wt.%, a monomer concentration of 5.0 wt.%, and an initiator concentration of 0.05 wt.%. The addition of water to the dispersive medium alters the dispersive medium solvency, causing a reduction in size of the monodispersed particles, which could be as small as 0.40 μm diameter under our experimental conditions. We used pure methanol as dispersive medium, and successfully prepared spherical monodispersed composite particles containing pigment green 36 and PMMA by dispersion polymerization in the presence of pigment green 36. The experimental results show that the arithmetic mean size of composite particles decreased, and pigment content in composite particles increased after increasing the amount of pigment in the polymerization process.

1. Introduction

Polymer particles are applied in many fields such as cosmetics, toner, and biomaterials. Preparations methods include emulsion polymerization, suspension polymerization, and dispersion polymerization. The dispersion polymerization approach provides monodispersed, sub-, or micrometric particles in a single step [1–3]. Typically, dispersion polymerization is conducted in either polar or nonpolar liquid media, involving the use of a steric stabilizer. Unlike emulsion and suspension polymerization, the reaction mixture for dispersion polymerization is a single-phase homogeneous liquid, consisting of a solution containing the monomer, initiator, and steric stabilizer in a solvent that does not dissolve the product polymer. During the polymerization process, free radicals formed by initiator decomposition grow in the continuous phase until reaching a critical chain length, thus forming nuclei. These nuclei adsorb the stabilizer and aggregate to form mature polymer particles. The mature particles can capture radicals and nuclei in the continuous phase, resulting in the formation of monodispersed particles. Thus, dispersion polymerization is a relatively complex process that involves several factors, including composition of the polymerization medium, the type and molecular weight (MW) of steric stabilizer, and concentrations of monomer, initiator, and steric stabilizer [4].

Shen *et al.* [5] prepared PMMA particles with diameters ranging from 2 to 10 μm by dispersion polymerization. They investigated the effects of various polymerization parameters on size and monodispersity of the resulting polymer particles, and found that PMMA particle size increased with increasing polymerization temperature, increasing initiator concentration, decreasing MW of stabilizer, and decreasing stabilizer concentration. The sizes of the resulting polymer particles also varied with the solvency of the dispersive medium. Using a water and methanol mixture instead of pure methanol yielded a reduction in particle size with increasing water content. Particle size distribution remained narrow up to a water content of 45 wt.%. Yabuuchi *et al.* [6] proposed a dispersion polymerization method for producing printing toner with narrow particle size distribution, and that contained a uniformly dispersed pigment therein. Horák *et al.* [4] prepared colored monodispersed polymer particles by dispersion copolymerization of a system containing styrene, butyl methacrylate, and non-polymerizable dyes; the polarity of the ethanol–water dispersion medium had a significant influence on the size of the polymer–dye composite particles.

Our previous study [7,8] reported that a supercritical fluid-assisted dispersion process (SFAD) could substitute for

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conventional grinding apparatus to prepare 1 wt.% C.I. Pigment Red 177 and Violet 23 dispersions. However, the mean size of the resulting dispersoids increased with time, indicating that wet-type pigment dispersion is un-stable and does not store well. Encapsulated pigments can help overcome this shortcoming; they are employed in the manufacture of cosmetics, inks, and paints to improve the stability of the encapsulated product, aiding both storage and transport.

In this study, PMMA was selected as a model polymer because it possesses excellent optical and electrical properties and can be used a spacer in the fabrication of liquid crystal displays and as a binder for preparing photo resists. Fine PMMA particles were prepared by dispersion polymerization, using methanol as the dispersive medium, azobisisobutyronitrile (AIBN) as the initiator, and polyvinylpyrrolidone (PVP) as the steric stabilizer. The parameters of dispersion polymerization process included the MW of stabilizer, and concentrations of monomer, stabilizer and initiator. Taguchi's orthogonal experimental design [9] was employed to search the optimal conditions for fine polymer particles with narrow size distribution (monodispersed). We also verified the effect of adding water to the dispersive medium on polymer particle size. The model material in preparation of composite particles was C.I. Pigment Green 36. The composite particles containing pigment green 36 and PMMA prepared by dispersion polymerization in presence of pigment green 36, using pure methanol as dispersive medium because water is disadvantage for pigment dispersion. The effects of the mass ratio (*R*) of monomer to pigment on the mean particle size, pigment content and monodispersity of the composite particles were investigated in this study.

2. Experiment

2.1. Materials

Methyl methacrylate monomer (99%, Aldrich, USA) was distilled before use and the initiator (AIBN, 99%, Showa, Japan) re-crystallized before use. The stabilizers polyvinylpyrrolidone (PVP-10, MW = 10 kDa; PVP-40, MW = 40 kDa; PVP-360, MW = 360 kDa, 99%, Sigma), methanol and acetone (99%, Aldrich, USA) were used without further purification. Deionized water with a resistivity of 18 MΩ cm at 25 °C was obtained with a Millipore Milli-Q water purification system. C.I. Pigment Green 36 (Cu-phthalocyanine, halogenated) was supplied by Ciba Special Chemicals Co., Hong Kong; its chemical structure is shown in Fig. 1. The pigment green 36 primary particle size was approximately 50 nm in diameter.

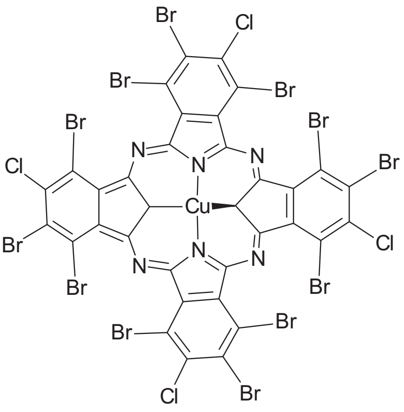

Fig. 1. Chemical structure of pigment green 36.

2.2. Procedures

Table 1 shows the L_9 Taguchi orthogonal array, listing the formulations used in this study. The total weight of each formulation was 20 g (except pigment). All reagents were weighed and mixed in 50 ml glass serum vials, purged with nitrogen, and then sealed. The vials were placed in a shaking water bath (B603D, FIRSTEK, Taiwan) at 60 °C and 50 rpm, and dispersion polymerization was allowed to run for 24 h. Addition of inhibitor solution (0.4 g hydroquinone in 2 ml methanol) terminated the polymerization reaction. The product PMMA particles or pigment–PMMA composite particles were washed with methanol under repeated sedimentation–dispersion cycles. The yield (wt.%) of polymer particles was estimated by the mass ratio of the reagents and product polymer particles. Samples

Table 1
Taguchi orthogonal array L_9 (3^4) and experimental results of PMMA particles prepared by dispersion polymerization.

Run	Stabilizer MW	Monomer wt.%	Stabilizer wt.%	Initiator wt.%	d_{no}[b] μm	d_w[c] μm	*PDI* d_w/d_{no}	PMMA MW
1[a]	PVP-10	5.0	4.0	0.05	5.98 ± 0.55	8.23	1.4	58,900
2[a]	PVP-10	10.0	8.0	0.1	9.47 ± 0.81	14.4	1.5	90,300
3[a]	PVP-10	15.0	12.0	0.2	10.7 ± 0.91	15.5	1.4	90,300
4[a]	PVP-40	5.0	8.0	0.2	1.56 ± 0.14	9.02	5.8	38,700
5[a]	PVP-40	10.0	12.0	0.05	2.19 ± 0.19	2.23	1.0	214,800
6[a]	PVP-40	15.0	4.0	0.1	6.68 ± 0.59	7.92	1.2	114,200
7[a]	PVP-360	5.0	12.0	0.1	3.77 ± 0.33	18.9	5.0	63,600
8[a]	PVP-360	10.0	4.0	0.2	4.47 ± 0.40	4.60	1.0	65,500
9[a]	PVP-360	15.0	8.0	0.05	2.32 ± 0.19	2.35	1.0	263,000
10[d]	PVP-360	5.0	8.0	0.05	1.90 ± 0.14	1.93	1.0	83,600
11[e]	PVP-360	5.0	8.0	0.05	0.36 ± 0.04	0.38	1.0	268,000

Factors	Low level	Middle level	High level
Type of stabilizers	PVP-10	PVP-40	PVP-360
Monomer (wt.%)	5.0	10.0	15.0
Stabilizer (wt.%)	4.0	8.0	12.0
Initiator (wt.%)	0.05	0.1	0.2

[a] Selected conditions in Taguchi's design.
[b] The arithmetic mean size, $d_{no} = \sum d_i / N$.
[c] The mass-weighted mean size, $d_w = \sum d_i^4 / \sum d_i^3$.
[d] The optimal formulation.
[e] The optimal formulation of run #10 in a 1:1 water–methanol dispersion medium.