Precipitation kinetics of PMMA sub-micrometric particles with a supercritical assisted-atomization process

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ABSTRACT

Sub-micrometric particles of PMMA were successfully prepared via a supercritical assisted-atomization (SAA) process using acetone as a solvent and supercritical carbon dioxide as a spraying medium. The effects of several key factors on the particle size were investigated. These factors included the concentration of polymer solution, temperature in saturator and volumetric flow rate ratio of carbon dioxide to polymer solution. The shape of the polymer's primary particles is spherical with the arithmetic mean size ranging from 82 nm to 176 nm and the mass-weighted mean size ranging from 127 nm to 300 nm. As evidenced from the experimental results, the lower concentrations of polymer solution, optimized volumetric flow rate ratios, and higher temperatures in saturator can effectively reduce the mean particle size. The precipitation kinetic parameters were determined from the particle size distributions with the aid of the population balance theory. This study found the primary nucleation to be dominant in the precipitation and diffusion may govern particle growth.

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1. Introduction

Over the previous decades, several supercritical fluid-assisted methods have been developed to prepare fine particles with unique characteristics in numerous industrial fields. These particulate processing techniques can be roughly classified, based on the function of supercritical fluids as: (a) a solvent, e.g., the rapid expansion of supercritical solution, RESS; (b) a solute, e.g., the particle from gas saturated solution, PGSS; (c) an anti-solvent, e.g., supercritical anti-solvent, SAS; (d) a spraying medium, e.g., supercritical assisted-atomization, SAA, and carbon dioxide assisted nebulization with a bubble dryer, CAN-BD. Reverchon and Antonacci [1] successfully developed a SAA process to produce micro- and nano-metric particles for pharmaceutical compounds, salts, dyes, catalyst, and superconductor precursors. The supercritical carbon dioxide was dissolved first in liquid solution containing water or organic solvents with solute. The mixed solution was then sprayed into a vessel via a nozzle at near atmospheric pressure under a flux of hot N_2. This process involves two steps of atomization. First, the primary droplets are formed at the exit of the nozzle by pneumatic atomization. Second, the secondary droplets are subsequently generated by rapidly releasing CO_2 inside of the primary droplets (decompressive atomization). Then, the ultra-fine parti-cles obtained by the evaporation of solvent and supersaturation of the solute.

Reverchon et al. [2] investigated micronization of Pigment Red 60 with both the SAS and SAA methods, and discovered that nano-metric particles could be formed using the SAS, with a low yield for SAS micronization. However, micro-metric particles were produced using SAA, thus, the yield of the SAA process was larger than 95%. The morphology of the resulting products using the supercritical anti-solvent (SAS) process is closely dependent on the phase regions where the precipitations are implemented. Micro-metric aggregated ball-like particles were produced as the SAS process passed by the vapor–liquid coexistence region, whereas nano-metric particles were obtained in the either supercritical or superheated vapor region [3,4]. Reverchon and Antonacci [1] micronized the PMMA particles using the SAA process. The experimental results indicated that the morphology, particle size and distribution of PMMA microparticles were dependent on the mass flow ratio of carbon dioxide to liquid solution. While increasing the mass flow ratio, the operating condition probably fell into the vapor–liquid coexistence region and resulted in the coalescence of particles collected in the precipitator. Wu et al. [5,6] have investigated the dispersion of 1 wt% of Pigment Red 177 and Violet 23 particles in propylene glycol monomethyl ether acetate (PGMEA) using a supercritical fluid-assisted dispersion process (SFAD). The SFAD process maintained at the supercritical state is effective in improving particle dispersion. As shown from these results, the phase behavior of mixtures in the high-pressure chamber is one of the crucial factors of the supercritical technology applied to particle

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Nomenclature

B^o	nucleation rate (no./s m^3)
C	mass concentration of polymer in the solution feed stream (kg/m^3)
$\bar{d}_{no}$	arithmetic mean particle size (nm)
$\bar{d}_{4,3}$	mass-weighted mean particle size (nm)
F_{CO_2}	volumetric flow rate of CO_2 at 276 K and 6.5 MPa (cm^3/min)
$F_{CO_2}(T_S)$	volumetric flow rate of CO_2 at the temperature in saturator and 6.5 MPa (cm^3/min)
F_l	volumetric flow rate of polymer solution (cm^3/min)
G	linear particle growth rate (nm/s)
i	order of growth rate in nucleation kinetics equation (Eq. (9))
K_N	constant in nucleation kinetics equation (Eq. (9))
k_V	volumetric shape factor
L	particle size (nm)
$\bar{L}$	arithmetic average size ranging from L_1 to L_2 (m)
ΔL	width of the size range (nm)
n	population density at size L (no./nm m^3)
n^o	population density of nuclei (no./nm m^3)
m_3	third moment of the population density distribution
M_T	suspension density (kg/m^3)
P	pressure (MPa)
R	volumetric flow rate ratio of CO_2 to polymer solution
R^2	square of correlation coefficient
T_S	temperature in saturator (K)
V_{mixing}	mixing volume in precipitator (cm^3)
w	mass of an individual particle
ΔW	weight fraction of particles in the size range L_1 to L_2
x_i	number of particles within a size range
τ	mean residence time of the mixed suspension (s)
ρ_C	density of polymer particle (kg/m^3)
ρ_{CO_2}	density of carbon dioxide (g/cm^3)

Superscripts
calc	calculated value
expt	experimental value

formation and dispersion. Additionally, the investigators generally focused on discussing the effect of process parameters for preparing finely particles with narrow particle size distribution [1,3]. The precipitation kinetics for the SAS process has been studied from the particle size distribution with the aid of the population balance theory [7–9]. Reverchon and De Marco [10] organized the numerous SAS literature results to determine the precipitation mechanisms and particle morphologies. They proposed the possible particle formation mechanisms: liquid jet break-up and gas mixing at supercritical conditions in SAS process are in competition to produce spherical microparticles or nanoparticles. The formation of crystal with various habits and dimensions depends on the interactions with the liquid solvent used. Caputo et al. [11] used a laser diffraction method to investigate the atomization mechanism on the SAA process. Experimental data confirms that dissolved-gas atomization allows for the formation of micrometric droplets and produces fine-precipitates with controlled size and distribution. However, the modeling the precipitation kinetic for the SAA process is limited.

In the present study, poly(methyl methacrylate) (PMMA) was selected as a model polymer. Because it possesses excellent optical, electrical, and biocompatible properties, PMMA can be used as spacers for the fabrication of liquid crystal displays and as

substrates for drug delivery [12]. The precipitation experiments of PMMA particles in this study were conducted at various concentrations of polymer solution, and at the volumetric flow rate ratios of carbon dioxide to polymer solution over temperatures in saturator ranging from 313.2 K to 363.2 K. The collected samples were analyzed with a field emission scanning electron microscope (FESEM), and the particle size distributions and the mean particle sizes were then determined using image processing software. In addition to determining favorable conditions for small particle formation, the precipitation kinetic parameters were estimated by fitting the experimental results to the MSMPR population balance equation. Based on the correlated results, the mechanisms of nucleation and precipitation kinetics were then considered.

2. Experimental

2.1. Materials

Poly(methyl methacrylate) (PMMA, average MW = 15, 120, and 350 kg/mol) was supplied by Aldrich, USA. Acetone (99.9% purity, HPLC grade) was purchased from Tedia, USA. Carbon dioxide (99.9% purity) and nitrogen (99.9% purity) were purchased from Yung-Ping Gas Co., Taiwan. These chemicals were used without further purification.

2.2. Apparatus and operation

Fig. 1 is the schematic diagram of the SAA apparatus installed in the present study. The apparatus consists of three main chambers and feeding lines. The three chambers are: saturator (8), precipitator (10), and separator (14). The saturator is a high-pressure vessel (10 cm^3, Applied Separations, USA) loaded with protruded stainless steel packing (PRO-PAK$^®$ 0.16 inch protruded packing, Scientific Development Co., USA), assuring a large contact surface between the liquid polymer solution and CO_2. The solution obtained in the saturator was sprayed through a spray nozzle (9) (I.D. 130 μm, model: TP500004-TC, Spraying System Co., USA) into the precipitator. The saturator was circulated in a thermostatic water bath (5), which was regulated to within ±0.1 K. The water bath temperature was measured with a precision platinum RTD sensor (12) (model: 1560, Hart Scientific Co., USA) to an accuracy of ±0.02 K. A pressure transducer (13) (model: PDCR 4070, ranging 0–35 MPa, Druck, UK) with a digital display (model: DPI-280, Druck, UK) was used to measure the operating pressure in the saturator, accurate to ±0.1%. The precipitator (10) (volume, 3.14 dm^3) was immersed in a thermostatic air bath, which was regulated to within ±0.5 K. A 0.5 μm metal frit (11) was mounted at the outlet (bottom) of the precipitator to retain the polymer particles. A separator (14) followed the precipitator to separate the solvent and gas mixture at near atmospheric pressure. The flow rate and total volume of carbon dioxide and nitrogen passing through the precipitator were monitored using a wet test meter (15) (model: TG20, Ritter, Germany) to an accuracy of ±0.25%. Three feeding lines are a polymer solution (4), carbon dioxide and nitrogen. A HPLC pump (3) (model: PU-1580, JASCO, Japan) was used to deliver the polymer solution and another high-pressure liquid pump (2) (model: NPL-5000, Nihon Seimitsu Kagaku Co., Japan) for carbon dioxide. The N_2 flow was controlled using a mass controller (6) (model: 251-FKASBYAA, Porter, USA) from a cylinder, heated in an electric heat exchanger (7) (series 93, Watlow, USA) and sent to the precipitator to assist the liquid droplets evaporation.

The experimental procedure is described as follows. The saturator temperature (T_S) and the volumetric flow rate of carbon dioxide were at pre-set values. The precipitator temperature and N_2 were specified to 333.2 K and 0.8 Nm^3/h. As a steady-state was achieved,