*Advanced Powder Technol.*, Vol. 16, No. 6, pp. 639–648 (2005)

Also available online - www.vsppub.com

*Original paper*

# Surface modification of silica particles with polyimide by ultrasonic wave irradiation

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Received 24 December 2004; accepted 6 February 2005

**Abstract**—Spherical silica particles were dispersed in a polyamic acid varnish (PAAV) solution, and ultrasonic wave irradiation resulted in high-speed condensation of conversion to polyimide and in coating of the silica particles. The imidization reaction was verified by Fourier transform IR analysis, thermogravimetry, gel-permeation chromatography and moisture analysis. In addition, the particle coating was observed by transmission electron microscopy. Adsorption of polyimide acid onto the surface of the silica particles while achieving an imidization reaction by ultrasonic wave irradiation has been clearly shown to enhance the rate of the imidization reaction.

*Keywords*: Spherical silica particle; polyimide; imidization; coating; surface modification; ultrasonic irradiation.

## 1. INTRODUCTION

Recently, the idea of green chemistry, otherwise known as environmentally friendly chemical technology, has attracted considerable attention in the professional community. One aspect of green chemistry is that it utilizes little energy in efficient and selective ways to induce desired reactions. Sonochemistry [1–5] is a technique that utilizes ultrasonic wave irradiation to effect chemical transformations and is becoming a method of choice for some green chemistry applications [6]. Examples are the coating of $TiO_2$ with pigment [7]. Abe and Ojima [8, 9] have uniformly coated the surface of polymer particles with ferrite. Nishida *et al.* [10] succeeded in using ultrasonic wave irradiation on silica particles dispersed in commercial polyimide

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varnish to be coated with polyimide within 4 minutes. The varnish used in this latter research was composed of preformed polyimide resin dissolved in a solvent.

In the present study, a varnish [polyamic acid varnish (PAAV)] was composed of a polyamic acid dissolved in a solvent. Silica particles were dispersed in this solution and a polyimide was formed *in situ* with ultrasonic irradiation. The imidization reaction was monitored by Fourier transform analysis (FT-IR), gel-permeation chromatography (GPC) and an analysis for water generated by the conversion of polyamic acid to polyimide. In addition, morphology of the coated silica particles was observed by transmission electron microscopy (TEM). Using these methods it was confirmed that polyimide was generated from PAAV and simultaneously coated the suspended silica particles.

## 2. EXPERIMENTAL

### *2.1. Materials*

All chemicals were of reagent grade quality. Tetraethyl orthosilicate (TEOS), ammonium hydroxide (28%), 2-propanol, *N*-methyl-2-pyrrolidone (Kishida Chemical) and PAAV solution were purchased from UBE Industries (U-varnish type S) and used as received.

### *2.2. Preparation of $SiO_2$ particles*

Uniform spherical silica particles, 0.4 $\mu$m in diameter, were prepared in a 500-$cm^3$ round bottom flask, in which 390 $cm^3$ 2-propanol, 57.6 $cm^3$ distilled water and 78.6 $cm^3$ ammonia were thoroughly mixed and equilibrated for 1 h at 40°C [11]. The solids formed were repeatedly washed with water and dried in a vacuum oven before use. The polyimide varnish was properly diluted with *N*-methyl-2-pyrrolidone (NMP) and used in the experiments.

### *2.3. Ultrasonic wave irradiation*

*2.3.1. Imidization reaction.* An aliquot of 50 $cm^3$ of 0.2 wt% PAAV solution was irradiated by ultrasonic waves of 600 W (20 kHz) using a US-6000CCVP apparatus (Nihonseiki) (0.2 wt% PAAV means polyimide of 0.2 wt% is present in the NMP solution). A sample without ultrasonic wave irradiation was used for comparison. The ultrasonic probe was always placed at the same position in the glass cell (1 cm above the bottom of the glass cell). The ultrasonic wave irradiation time was 1, 2, 4 and 10 min. After the ultrasonic wave irradiation, the sample, was dried in a vacuum oven at 60°C and then evaluated using FT-IR analysis. Moisture analysis was evaluated by the Karl Fisher moisture titration method using an MKC-210 (Kyoto Electronic Manufacturing). Molecular weight was analyzed with GPC using HLC-8220 (Tosoh).