



Original Research Paper

Surface modification of fumed silica by photo-dimerization reaction of cinnamyl alcohol and cinnamoyl chloride



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ABSTRACT

The surface modification of silica particles by an organic functional group has been intensively studied, and the modified structure can be analyzed by various experiments and simulations. Cinnamyl alcohol and cinnamoyl chloride are well known for their photo-dimerization reactions. By introducing them on the fumed silica surface, it is possible to create a functional silica which can be aggregated by cross-linking under optical irradiation. For surface modification of the fumed silica, an autoclave method was used with the cinnamyl alcohol, while the reflux method was used for the cinnamoyl chloride. Fourier Transform Infrared Spectroscopy (FT-IR), a thermogravimetric analysis (TG) and the Brunauer–Emmett–Teller (BET) method were used to evaluate the surface structure of the modified silica. In the case of modification with cinnamyl alcohol, the maximum amount of the modifier groups was 1.7-OR/nm², and the modification degree could be controlled by varying the initial concentration of the modifier in the reaction. On the other hand, the maximum amount of the modifier groups was 0.33-OR/nm² with cinnamoyl chloride, but it could be increased to 0.69-OR/nm² when pyridine was used as the catalyst during the modification. The reaction process was evaluated by the MOPAC simulation, and the ultraviolet (UV) absorption based on the structure was calculated by ZINDO. In the photo-irradiation experiment, which used an extra high pressure mercury lamp as a spectral source, it was confirmed that the modifier on the silica surface formed α and β -dimer, the structure of which was decided by the intermolecular distance. In this study, it was confirmed that the cross-linking occurs on interparticle based on the results of the simulation and measurement of the UV absorption. However, a moderate density of the modifier is essential for initiating the interparticle cross-linking.

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1. Introduction

In recent years, the 3D printer has been begun to be used in various fields [1–3]. The 3D printer could create structures by read out of the three-dimensional data generated by Computer Aided Design (CAD) [4,5]. The start of that technology was acquisition of a patent on 3D stereo lithography [6,7] by Chuck Hull who was an American engineer in 1987. His first working 3D printer was created in 1984. He published a number of patents on the concept of 3D printing, many of which are used in today's additive manufacturing processes [8–10]. In addition to the foregoing, based on the invention of various molding method technologies, Fused Deposition Modeling [11–13], Inkjet [14–17] and Selective Laser Sintering [18–22] are also applied to the 3D printer [23].

Following the evolutional of development of the technology and price reduction of the 3D printer, the 3D printer market is rapidly growing. Along with this development, the demands of resins for each manufacturing method have been rapidly rising and technical development has proceeded. A UV curing resin with an acrylic resin base and a thermoplastic resin with an acrylonitrile–buta diene–styrene resin base are primarily used in the 3D printer material. In current industry, based on the inkjet printer becoming mainstream because it can be further reduced in size, the market share growth of UV curing resin is significantly expanding on a global scale [24]. Using the UV curing resin has attracted attention in recent years from the viewpoint of a small environmental burden because it provides reducing the volatile organic compound (VOC) due to its instant formation of the cure coating film by UV irradiation [25]. As a conspicuous feature of the UV resin, it doesn't need a drying process for removing the solvent which makes it possible to shorten the working hours.

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In the past decade, nanosilica particles have been widely introduced into polymers to provide functionalities which has never existed before [26]. There are some reports that the nanosilica contained in UV cured resin provided new functions for the polymers. Nanosilica particles are used as the filler of UV acrylate paint and it provided the function to crosslink and cure the silica and UV curing resin by UV irradiation [27]. However since the amount of silica powder to be added to a UV resin is limited, it is difficult to obtain a UV resin containing a large amount of the inorganic material. If the material included an inorganic material in greater amount than the organic polymer, the 3D printing process may be possible to be more environmentally friendly. Additionally, one of the optical shaping methods requires a step of excessive resin removal, thus it can reduce the surplus resin and increase of efficiency due to shorter processing time. If it is possible that the inorganic material can function between itself by photo-irradiation, it can increase its content rate and can function in the polymer.

There are two kinds of photo-dimerization functional groups, which are the cinnamoyl based and cinnamylidene based groups. Many compounds functionalized with these groups, such as activated ethylene and polycyclic compounds, are able to perform the photo-dimerization reaction, developing a reaction of the intermolecular cross-linking bond in the polymer. As cinnamoyl groups develop the [2+2] cyclization by the photo-dimerization reaction, polyvinyl cinnamate, which was made by the esterification reaction of the cinnamoyl groups and PVA, becomes insoluble depending on the photo-crosslinking [28]. Therefore, polyvinyl cinnamate applied as the negative photoresist is one of the representative examples of the photo-sensitive resin. Inspired by the photo-reaction of polyvinyl cinnamate, photo-functional groups might be introduced on the surface of the fumed silica, creating functional particles having the properties of photo-crosslinking by optical irradiation, and developing the nano-sized inorganic functional materials which are difficult to be obtained by modern technology [29,30].

Herein, it was introduced that the cinnamoyl chloride has a cinnamyl group ($C_6H_5-CH=CH-CH_2-$) and cinnamyl alcohol has cinnamoyl group ($C_6H_5-CH=CH-CHO-$) on the fumed silica surface because their terminal substituted by $-Cl$ and $-OH$ has a high reactivity with the silanol groups. Furthermore, it was determined that the corresponding interparticle photo-dimerization process of the cyclobutane ring formed with the photo-functional groups on the modified silica surface.

2. Experimental

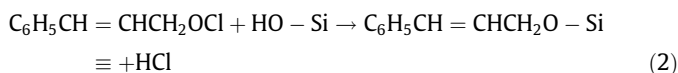
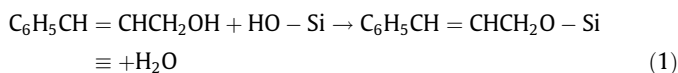
2.1. Materials and surface modification

Fumed silica powder, Aerosil® OX50 (OX50), was obtained from Nippon Aerosil Co., Ltd. Cinnamyl alcohol and cinnamoyl chloride with photo-functional groups were used as the modifier, and the physical properties of the two photo-functional groups are shown in Table 1. As both photo-functional groups can initiate a reaction when exposed to natural light, these experiments were carefully carried out in the dark. For the surface modification with cinnamyl alcohol, the autoclave method was performed at 270 °C, and 30 atm for 1 h with hexane used as the solvent [31,32]. An additional amount of modifier was then changed from 0.25 to 20 number of modifiers per nm^2 on the modified silica surface related to the specific surface area of 2 g of OX50. After the reaction, the sample was dried in a nitrogen atmosphere at above 70 °C. For the modification with cinnamoyl chloride, the reaction was carried out by the reflux method [33]. OX50 (2.0 g) was dispersed in 62.5 mL of hexane and a certain amount of cinnamoyl chloride was then dissolved. The additional amount of cinnamoyl chloride

Table 1
Physical properties of cinnamyl alcohol and cinnamoyl chloride.

Modifier	Cinnamyl alcohol	Cinnamoyl chloride
Formula	$C_9H_{10}O$ ($C_6H_5CH=CHCH_2OH$)	C_9H_7ClO ($C_6H_5CH=CHCOCl$)
Molecular weight	134.18	166.6
Melting point	33 °C	35–36 °C
Boiling point	250 °C	256–258 °C
Manufacture	Kanto Chemical Co., Inc	Kanto Chemical Co., Inc

was changed the same as for the modification using cinnamyl alcohol. The suspension was heated to reflux for 1 h at 68 °C, then the modified OX50 was washed with 80 mL of hexane 3 times and separated by pressure filtration, followed by drying under reduced pressure. Surface modification was carried out by the reactions of the cinnamyl alcohol and cinnamoyl chloride molecules with the hydroxyl groups on the silica surface according to the following equations:



2.2. Characteristics of silica surface

Qualitative analysis of the modifier on the surface of the modified OX50 was evaluated by FT-IR (Jasco FT/IR-620 spectrometer, Jasco Corporation), and the purpose of this characterization was to determine the decrease in the hydroxyl groups and presence of the $Si-O-C$ spectral peak. It is regarded that the spectral peak of $Si-O-C$ was attributed to chemisorption of the modifier on the silica surface, thus the processing of the modified reaction can be confirmed by observing this peak. The FT-IR measurement was done at a resolution of 4 cm^{-1} between 400 and 4000 and the scan number was 200. The sample was molded into a pellet and it was then placed in a vacuum measuring cell [34].

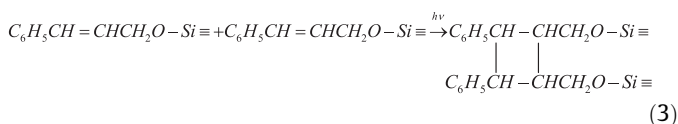
The surface modifier density was estimated from the amount of modifiers and the specific surface area. Quantitative analysis of the modifier groups was obtained from the TG/DTA performed using a Rigaku Thermo plus TG8120 (Rigaku Corporation) from 30 °C to 550 °C at the heating rate of 20 °C/min in flowing air at 250 mL/min.

2.3. Determination of hydrophilic/hydrophobic

In order to determine the hydrophobic or hydrophilic properties of the modified silica surface, the sample powders were dropped into the water, while the floating nature was judged by visual observation. The hydrophilic powders sank in the water, while the hydrophobic ones floated [35,36].

2.4. Simulation

The modified silica forms a dimer structure through the cyclobutane-ring with $C=C$ bonds by optical irradiation due to the photo-irradiation reaction described as follows:



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