Direct observation of particle dispersion patterns in non-aqueous slurries using an in-situ solidification technique

Hideo WATANABE, Aya TAMURA and Masayoshi FUJI

Ceramics Research Laboratory, Nagoya Institute of Technology, Honmachi 3–101–1, Tajimi, Gifu 507-0033

Characterization of particle dispersibility in slurry as raw materials for fabricating ceramics is very important since the dispersibility gives great effects directly on qualities of final ceramic products. In this study, a direct observation of particles dispersed in liquid media using an in-situ solidification technique, which has been developed by our group and examined only in aqueous systems so far, has been extended to non-aqueous systems. In this paper, radical polymerization with several combinations of monomer/cross-linker and initiator was attempted to find out gelling agent that was able to solidify slurry without any influence on particle dispersion. The direct observations of yttria or alumina particles in non-aqueous solvents were carried out with the selected gelling agent. The observations showed clearly dispersion patterns of the particles in the solvents such as pearl chain-like or island structures. The particles tended to be coagulated strongly in solvents with low dielectric constant, which agreed with results of conventional characterization methods such as apparent viscosity of the alumina slurries.

©2011 The Ceramic Society of Japan. All rights reserved.

Key-words: Particle dispersion, Coagulation, In-situ solidification, Non-aqueous slurry, Yttria, Alumina

1. Introduction

In powder forming processes using a mixture of fine particles and solvent, which is called colloid, suspension or slurry, such as slip casting or tape casting for fabricating green body of ceramics or spray drying to produce granules, control and characterization of particle dispersibility in liquid media are very important since the dispersibility gives great effects directly on properties of final products of ceramics or granules. The characterization of the particle dispersibility has been usually conducted by measurements of rheological properties, zeta potential, or particle size distribution.1-5 These are to measure properties relating to the particle dispersibility and hence are indirect characterization techniques. It is difficult in general for the indirect characterization techniques to figure out dispersion patterns perfectly. Therefore, a direct characterization technique has been desired to figure out the patterns of particle dispersion and coagulation in liquid media. A number of visual observations of slurries have been attempted using scanning electron microscopy (SEM)6,7 and CRYO-SEM.8,9 In these methods, however, removal of water is inevitable for preparing sample to be observed, which should affect dispersion patterns. We have developed a direct observation technique for particle dispersion patterns in ceramic slurries using solidification of the slurry due to radical polymerization, which is called in-situ solidification and does not require the removal of dispersion media to fix particle dispersion pattern.10-12

Figure 1 shows a schematic illustration of the in-situ observation technique. The slurry containing a chemical monomer and a cross-linker is solidified by addition of an initiator and a catalyst to facilitate radical polymerization. During the gelation particles in the slurry are entrapped with gel matrixes and are fixed in the original position. After drying the wet gel body under a controlled humidity, thin film of the body cut by using a microtome is observed with optical or electron microscopes.

1 Corresponding author: M. Fuji; E-mail: fuji@nitech.ac.jp

Microscopic observation with transmitted light or electron can visualize pseudo three dimensional structures of the particles formed in the slurry. The previous studies found the following knowledge: (1) it was confirmed by comparison with SEM observation of freeze-dried slurries that addition and polymerization of suitable chemical monomers hardly influenced original particle dispersion in slurries;11 (2) it was possible to figure out difference in dispersion patterns that was not able to be distinguished by measurement of apparent viscosity;10 (3) TEM observation of an ultra thin film sliced using an ultra microtome enabled to see dispersion patterns of nano-sized particles.12

Aqueous slurries were used in the previous studies of the in-situ observation, but no study for non-aqueous slurry has been conducted yet. Non-aqueous slurry is often used especially in tape casting, whereas sifting to the use of aqueous slurry is a recent trend to meet with demands to reduce environmental burden. Also in chemical surface modification treatment for controlling particle dispersibility, non-aqueous solvents are commonly used.13 Therefore, characterization of particle dispersibility in non-aqueous solvents is still of great interest. For non-aqueous system, applicability of conventional indirect characterization techniques mentioned above should be limited as compared to aqueous system. Zeta-potential is no longer valid since surface charge of particle in non-polar solvents is too low to disperse particles by electrostatic repulsive force. Measurement of particle size distribution based on light diffraction or scattering should prefer to use solvents with high transparency, so that some organic solvents and inclusion of some other component like polymer binder or plasticizer may cause problems on the measurement. Measurement of rheological property such as apparent viscosity of slurry is used traditionally in the field of ceramics, since the viscosity is important not only for relating to particle dispersibility but also for accessing casting behaviour of the slurry in slip casting or tape casting. The viscosity measurement can be used as a characterization technique for particle dispersibility in non-aqueous slurries but is indirect method.
In this study, we have intended to apply the direct observation technique for non-aqueous ceramic slurries. In this paper firstly, radical polymerization with combinations of monomer/cross-linker and initiator was attempted to find out gelling agent that was able to solidify non-aqueous slurry without any influence on particle dispersion patterns. The direct observations of yttria or alumina particles in non-aqueous solvents were carried out with using selected gelling agent. The results of the observation were compared to measurement of viscosity as a conventional method for characterizing particle dispersibility in slurry.

2. Experimental procedure

2.1 Materials

Yttria powder with average particle size around 3.0–5.0 μm (Nippon Yttrium Co. Ltd., Japan) and alumina powder with average particle size around 0.5 μm (Showa Denko Co. Ltd., Japan) are used as sample powders. Ethanol, 1-propanoal and ethyl acetate (Kanto Chemical Co., Inc., Japan) were used as sample solvents of non-aqueous slurry. All the combinations of monomer/cross-linker and initiator listed in Table 1 were tested for radical polymerization in non-aqueous slurry to be solidified.

2.2 Direct observation of non-aqueous slurries by using in-situ solidification technique

In order to find out an appropriate gelling agent for the direct observation of non-aqueous slurry, radical polymerization with all the combinations of monomer/cross-linker and initiator listed in Table 1 was attempted with three kinds of solvents. A type of monomer/cross-linker was mixed with a solvent and a certain amount of sample powder (solid loading of 2.7 vol%), where monomer/cross-linker content was 20% to mass of the solvent. Ball milling of the slurry was carried on for 24 h at 25°C for facilitating particle dispersion. An initiator was added into the slurry, where the amount of the initiator was 0.0048% to mass of the monomer in the slurry. For the initiator of AIBN or BPO, the mixture of slurry and initiator put into a sealed container was heated in a water bath at 50°C for facilitating radical formation.

For the initiator of HPCK, ultraviolet light of which wave length was 245 nm at the peak was illuminated to the slurry in a container to facilitate radical polymerization. The UV illumination for one hour at room temperature resulted in solidification of the slurry to be wet-gel green body. The obtained wet gel body was dried at 25°C with controlling humidity from 90 to 60% with decreasing 5% a day. A small piece of the dried body was embedded in an epoxy resin and thin sections of the resin including the dried body were prepared by using an ultra mikromot (RM EM UC6, Leica Microsystems). The thickness of thin sections was typically 5 μm. The optical microscopic observation of the thin section was conducted with a transmitted light mode.

2.3 Viscosity measurement of non-aqueous slurries

Viscosity measurement was carried out for the prepared non-aqueous slurry after defoaming by a rotation and revolution type mixer (MX-201, THINKY) for 2 min at 2000 rpm. Apparent viscosity of the slurry was measured using a rheometer (RS 600, Thermo Hakke) at temperature of 25°C. Apparent viscosity as a function of shear rate was obtained as derivative value of shear stress with respective to shear rate.

3. Results and discussion

3.1 Selection of gelling agents for in-situ solidification of non-aqueous slurry

To select an appropriate gelling agent is very important for the direct observation by using in-situ solidification technique. For attempting radical polymerization with all the combinations of monomer/cross-linker and initiator listed in Table 1, the combinations which can solidify the slurry are shown in Table 2 with the time required for the solidification. Type I monomer and cross-linker listed in Table 1 was often used for gel casting as well as in-situ solidification for aqueous slurry,10(11) but was found to be not suitable for non-aqueous slurry: actually alumina slurry with 1-propanoal or ethyl acetate with type I monomer/
cross-linker could not be solidified with use of any initiators listed in Table 1. Therefore, we have attempted to use other sets of monomer and cross-linker such as Type II and III. It was experimentally confirmed that the polymerization of the both yttria and alumina slurry took place for all the combinations shown in Table 2. However, increase in viscosity of the slurry by adding monomer/cross-linker occurred except for 1,6-hexanediol diacrylate (Type III in Table 2). The increase implied that the coagulation occurred owing to interactions between the particles and chemical molecules. Actually, microscopic observation of slurries solidified by monomers apart from Type III verified obvious coagulation of particles, which was apparently different from that of the slurry solidified by Type III monomer. In the range of present study, therefore, it has been found that the combination of 1,6-hexanediol diacrylate as a monomer and HCPK as an initiator is most suitable to solidify the non-aqueous slurries with the three organic solvents for the direct observation of the particle dispersion.

Table 2. Combination of solvent, monomer/cross-linker and initiator that can be solidified due to radical polymerization and time required for solidification

<table>
<thead>
<tr>
<th>solvent</th>
<th>monomer/cross-linker</th>
<th>initiator</th>
<th>time for solidification</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>Type I</td>
<td>HCPK</td>
<td>1 h</td>
</tr>
<tr>
<td></td>
<td>Type II</td>
<td>BPO</td>
<td>3.5 h</td>
</tr>
<tr>
<td></td>
<td>Type III</td>
<td>HCPK</td>
<td>1 h</td>
</tr>
<tr>
<td>1-propanol</td>
<td>Type III</td>
<td>HCPK</td>
<td>1 h</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>Type III</td>
<td>HCPK</td>
<td>1 h</td>
</tr>
</tbody>
</table>

3.2 Observation of non-aqueous slurry of yttria and alumina

The transparent optical microscopic images of in-situ solidified yttria slurries (2.7 vol%) with either ethanol, 1-propanol or ethyl acetate are shown in Fig. 2. The dispersion or coagulation pattern of the particles can be clearly seen in these images. Thus, a relatively good dispersion of the particles can be seen in ethanol, and partial coagulation including pearl chain-like structures can be seen in 1-propanol, and large coagulates like an island structure can be seen in ethyl acetate. Figure 3 shows the optical microscopic images of in-situ solidified alumina slurries (2.7 vol%). It should be noted that observed particles are coagulated ones since primary alumina particle with 500 nm in size can not be seen by optical microscope. In the both yttria and alumina slurries, the order from dispersion to coagulation agrees with the order of dielectric constant of the solvents, which are under the name of solvent in Figs. 2 and 3. Electrostatic repulsive force works for dispersing particles in aqueous systems, but does not work for non-aqueous systems because electrostatic charge on the particle surface decrease with decreasing dielectric constant of medium between particles. Therefore, the observation results obtained here are pretty reasonable.

3.3 Apparent viscosity of the alumina slurries

Figure 4 shows relative viscosity, which is defined as a ratio of apparent viscosity of slurry to that of solvent itself, as a function of shear rate for the 2.7 vol% alumina slurry with solvents of ethyl acetate, 1-propanol or ethanol. For all the curves in this figure the relative viscosity decrease with increasing shear rate, which is so-called shear thinning behavior. The relative viscosity at a certain shear rate is highest for the slurry with ethyl acetate.
acetate, second for 1-propanol, and lowest for ethanol. This order of the viscosity agrees with degree of coagulation shown in Fig. 3. It has been concluded that direct observation of particle dispersion patterns in the slurry with in-situ solidification technique is verified by the viscosity measurement as a conventional method and is useful to characterize particle dispersibility in non-aqueous solvents.

4. Conclusions

Direct observations for dispersion patterns of yttria and alumina particles in non-aqueous solvents have been conducted by means of in-situ solidification technique with the use of monomer of 1,6-hexanediol diacrylate and initiator of 1-hydroxycyclohexyl phenyl ketone, which are found in this study to be most suitable for radical polymerization in ethanol, 1-propanol and ethyl acetate. The transparent optical microscopic images of thin section of solidified slurry reveal that both yttria and alumina particles tend to be coagulated strongly when dielectric constant of solvent decreases, which is presumably due to decrease in electrostatic repulsive force. This trend agrees with results of relative viscosity of the slurry. The direct observation of particle dispersion patterns using in-situ solidification technique is indeed useful to characterize particle dispersibility in non-aqueous solvents.

References