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Dispersion behavior of laser-synthesized Si_3N_4 nanopowders in N-N-dimethylformamide

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Abstract

The dispersion behavior of Si_3N_4 nanopowders prepared by laser-induced gas-phase reaction in a non-aqueous solvent, N-N-dimethylformamide (DMF) was studied, and triethanolamine (TEA) was selected as a dispersant. One hundred and sixty-six-day sedimentation tests were used to study the stability of the suspensions. Photon correlation spectroscopy was employed to measure the sizes of aggregates and coagulation rates. TEA was proved an effective dispersant for nano-Si_3N_4 in DMF, presoaking treatment could enhance the effect of the dispersant. TEA 1.0 wt.% referred to Si_3N_4 and a 1-month-presoaking gave the best dispersion, the dispersion stability was improved from several minutes to several months, and the average size of the aggregates was reduced to about a twenty-fifth. The dispersion ability of TEA was believed being related to its strong affinities both to the powder surface and to the solvent.

Keywords: D. Si_3N_4; Dispersion; Nanopowders; N-N-dimethylformamide; Triethanolamine

1. Introduction

Nanosized ceramic powders have shown great potential in the preparation of ceramic and metallic nanomaterials and nanocomposites [1–3], whose mechanical properties were dramatically improved compared with common materials. Introduction of nanometric powders to polymers is also of great interest not only for the improved mechanical properties but also for some new functions [4]. However, nanometric powders are susceptible to aggregate, which will greatly deteriorate the properties of the materials, so it is essential to destroy the aggregation and gain stable powder dispersion during the process to guarantee uniform distribution in the matrix. Previous papers concerning the dispersion of nanopowders, especially of the non-oxide nanopowders are limited [5–8]. Much more studies are necessary to meet the specific processing conditions of the given materials.

Laser synthesized Si-based nanopowders include Si_3N_4, SiC and Si/C/N etc. which possess smaller sizes and higher purities than those obtained by other methods. The Si_3N_4 nanopowder owns special mechanical, optical and wave-absorbing properties, and it has been proved an interesting nanometric addition to the ceramics [2], metals [3] and macromolecule materials [4]. Studies on dispersion of nanometric Si_3N_4 powders in various solvents are of great importance. N-N-dimethylformamide (DMF) is a high-polarity and strong solvent for many organic polymers and is a widely used in industry, such as in textile industry etc. The present paper examines the dispersion behavior of laser-synthesized nanometric Si_3N_4 powders in DMF solvent.

2. Experimental procedure

The Si_3N_4 nanopowder used in the present investigation was produced via CO_2 laser-induced gas-phase reaction between silane (SiH_4) and ammonia (NH_3); the synthesis details were reported elsewhere [9]. The powders were collected in air and stored for about 1 year in double-sealed polyethylene package. The morphology of the powders was examined by transmission electron microscopy (TEM, Philips EM420). Diffuse reflectance infrared spectroscopy (DRIFT) was used to characterize

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the surface chemistry with Nicolet FTIR-51P spectrophotometer. The solvent, N-N-dimethylformamide (AR grade), was used without further purification. Screening tests for dispersants among Tween 80, Span 80, triethanolamine (TEA) and polyvinyl pyrrolidone were firstly carried out, triethanolamine (AR grade) showed the best dispersing ability, so it was selected as dispersant in further research. Si_3N_4 nanopowders (0.1 g) were added to 10 ml DMF with different amounts of dispersant from 0 to 10 wt.% referred to the solids and soaked for 1 h or 30 days then dispersed in 100 W ultrasonic bath for 20 min. The suspensions were poured into graduated test tubes and sealed with rubber stoppers. The suspensions separated into three parts during the rest: the upper clear solvent, the remained suspension and the lower sediment, the suspension volume and the sediment volume were recorded. The coagulation rates of nanosized Si_3N_4 in DMF were measured by photon correlation spectroscopy (PCS); the Z-average sizes of the aggregates were measured at different intervals after ultrasonication with a particle analyzer (Zetasizer 3000, Malvern Instruments, Malvern, UK). The suspensions prepared as earlier were diluted to optimize the solid concentration for the PCS measurement, at which the samples gave a count rate of about 100kcps in the instrument. The properties of N-N-dimethylformamide and TEA used in PCS measurements were listed in Table 1.

3. Results and discussion

3.1. Powder characterization

Fig. 1 shows the TEM micrograph of nanometric Si_3N_4 powders, the powders were nearly spherical and the average particle size was about 17 nm, serious aggregation was observed. Fig. 2 shows the DRIFT spectra of Si_3N_4 nanopowder both as-synthesized and stored for about 1 year. During the storage, the absorption modes ascribed to Si–OH variation (1635, 3700 cm^{-1}) were strengthened, however the adsorption mode indicating the Si–NH vibration was weakened, this indicated that the N–H at the powder surface reacted with moisture and formed Si–OH as follows: [7, 10]

$$Si_x-NH_{3-x}+xH_2O=xSi-OH+NH_3$$

3.2. Sedimentation tests

In the sedimentation tests for 1 h-presoaking-time group (Fig. 3), the Si_3N_4 powders in pure DMF flocculated and settled quickly, large floccules appeared, this indicated that nanometric Si_3N_4 was poorly wetted in DMF. The addition of TEA to DMF led to the stabilization of the suspensions, and large floccules appeared no longer in the dispersion. Within 200 h duration, it

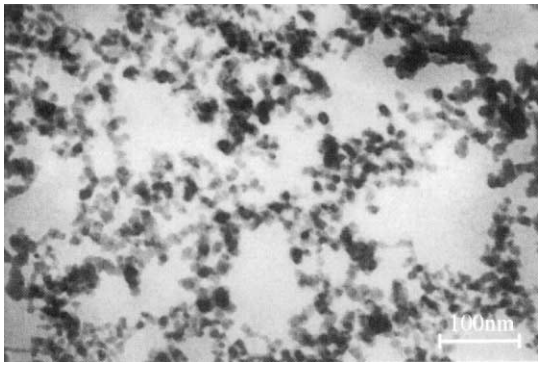

Fig. 1. TEM micrograph of Si_3N_4 nanometric powders.

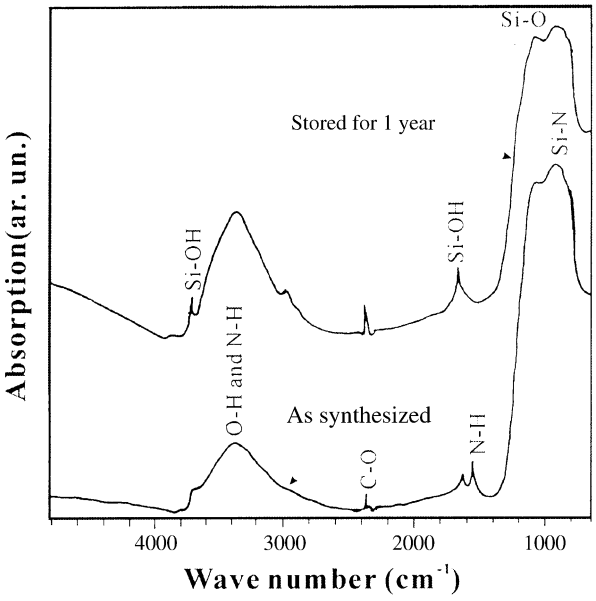

Fig. 2. DRIFT spectra of Si_3N_4 powders as-synthesized and stored for 1 year.

Table 1
Properties of DMF and TEA[a]

Substance	Structural formula	Density (g/cm^3)	Viscosity (cp)	Refractive index
DMF	$HCON(CH_3)_2$	0.948	0.82	1.4269
TEA	$(HOCH_2CH_2)_3N$	1.12		1.482

[a] DMF, N-N-dimethylformamide; TEA, triethanolamine.

seemed more dispersant would favor the dispersion, the suspensions containing no less than 4.0 wt.% TEA had perfect stability. However, moderate TEA concentration of 3.0 wt.% was favorable after 200 h duration. Figs. 4 and 5 show the sedimentation test results for Si_3N_4 powders pre-soaked for 1 month. Compared with the 1 h-soaking-time group, the stabilities of the suspensions were all further improved and showed more regularity. The Si_3N_4 in pure DMF is still unstable and soon settled down. With the addition of dispersant, the stability of the suspension was improved remarkably and got an extremum at 1.0 wt.%TEA content, which had a maximal suspension volume and a least sediment volume up to 4000 h, the dispersion stability showed some decline in the dispersant concentration range aside from this point.

3.3. Coagulation rates

The Z-average sizes ($D_{Average}$) for Si_3N_4 powders pre-soaked for 1 month in DMF with different TEA content were measured as a function of coagulation time (Fig. 6). The $D_{Average}$ just after the ultrasonication, i.e. minimum average size, and that while $d(D_{Average})/dt$ was zero-most, i.e. stabilized average size, were showed in Fig. 7. Si_3N_4 nanopowders in pure DMF solvent coagulated quickly after ultrasonication (Fig. 6a), the average size reached 4280 nm in 12 min and 7827 nm in 22 min, and then the average size decreased due to the sedimentation of large aggregates. For Si_3N_4 powders in TEA solution, the average sizes experienced a rapid increase in the first tens of minutes then stepped into a relatively stable period. Even with only 0.1 wt.%TEA addition, the dispersibility and stability of nano-Si_3N_4 in DMF was dramatically improved compared with those in the pure DMF. With further increasing TEA content in DMF up to 1.0 wt.% TEA, both the minimum and stabilized average size were gradually decreased to 166.7 and 171.8 nm, respectively, above this limit, the both parameters were gradually increased, which showed the optimal addition of TEA was about 1.0 wt.% for Si_3N_4 powders pre-soaked for 1 month, this is consistent with the sedimentation results.

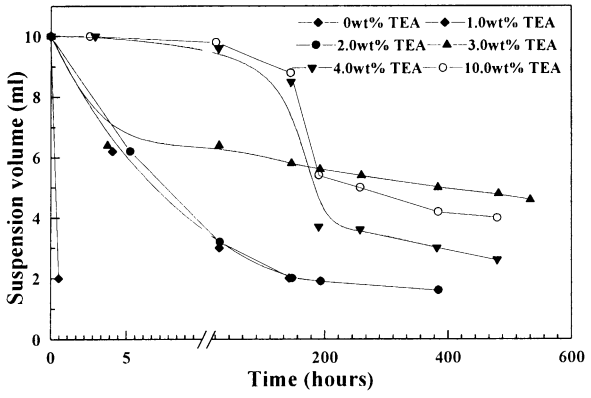

Fig. 3. Suspension volume vs. coagulation time for Si_3N_4 presoaked for 1h in DMF with different TEA content.

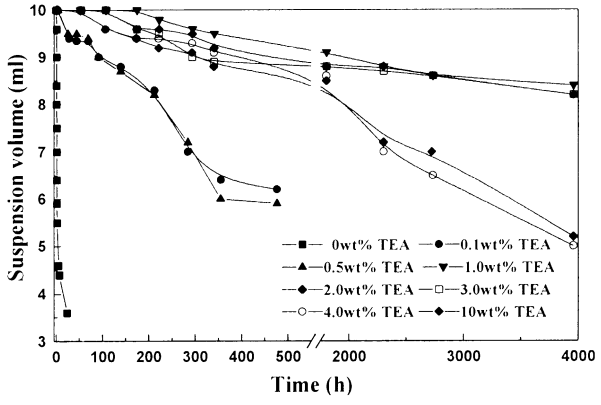

Fig. 4. Suspension volume vs. coagulation time for Si_3N_4 presoaked for 1 month in DMF with different TEA content.

3.4. Discussion

Both the sedimentation tests and size measurement proved that TEA is an effective dispersant for laser-synthesized Si_3N_4 nanopowder in N-N-dimethylformamide. Longer pre-soaking time seems to be beneficial to the effect of TEA. The dispersing ability of TEA for nano-Si_3N_4 in DMF is believed to be related to the affinities both to the powder surface and to the solvent, viz., its amphoteric adsorption characteristics. The Si–OH group on the nano-Si_3N_4 exposed to moisture has a weak affinity to the DMF, however, it will probably hydrogen bond to aliphatic alcohol [11], such as the –OH group of TEA. The high solvency of DMF to TEA shows the strong affinity between them, so the TEA can act as an intermedium between the Si_3N_4 particle and the solvent, which improves the wettability. The aliphatic chains of TEA may also act as steric barrier between two particles and improve the dispersion stability. Owing to the three –OH groups of one TEA molecule,

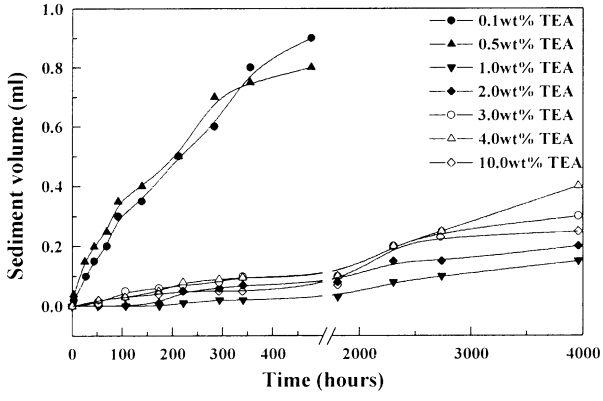

Fig. 5. Sediment volume vs. coagulation time for Si_3N_4 presoaked for 1 month in DMF with different TEA content.

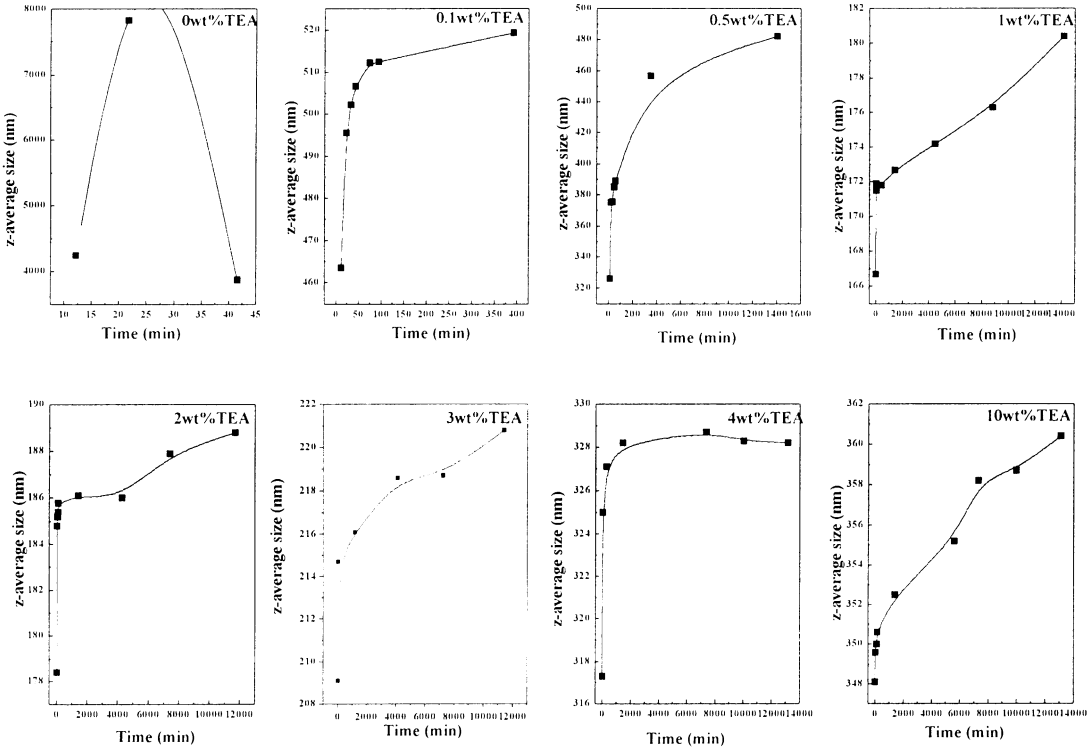

Fig. 6. Z-average sizes vs. coagulation time for suspensions with different TEA content and 1 month-presoaking.

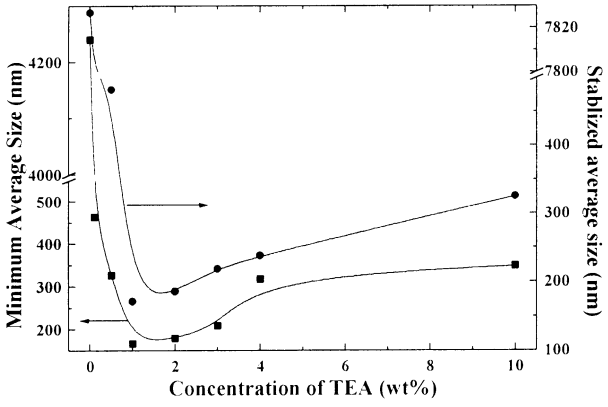

Fig. 7. Minimum and stabilized average sizes of Si_3N_4 powders in DMF with different amount of TEA and 1 month-presoaking.

excessive TEA addition may led to the bridging between two particles and go against the dispersion. The adsorption of TEA on Si_3N_4 surface to equilibrium may be a time-consuming process; long time presoaking can result in a full coverage of TEA on the Si_3N_4 surface so better dispersion can be gained with lower TEA content.

4. Conclusion

Triethanolamine was proved to be an efficient dispersant for laser-synthesized Si_3N_4 nanopowders in a non-aqueous solvent, dimethylformamide. Presoaking the Si_3N_4 powders in the media containing dispersant for 1 month is beneficial with the dispersion compared with the 1 h-presoaking, the optimal concentration of TEA in the suspension is about 1.0 wt.% referred to the solids, which ensured that the pre-soaked Si_3N_4 suspension in DMF had an extremely good stability within 4000 h duration and had a smallest aggregate size. The effect of TEA is related to the affinity both to the powder surface and to the solvent.

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