Chemical Engineering Journal 155 (2009) 493–498

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Dispersibility in organic solvents of nanosized silica particles used in semiconductor package substrates

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ARTICLE INFO

Article history:
Received 31 March 2009
Received in revised form 27 June 2009
Accepted 2 July 2009

Keywords:
Dispersibility
Silane coupling agent
Silica nanoparticles
Methylisobutylketone
Cyclohexanone
Slurry

ABSTRACT

This study examined the influence of different types of silane coupling agents on the dispersion of nanosilica particles with diameters of ca. 10 nm and 25 nm in two organic solvents, methylisobutylketone (MIBK) and cyclohexanone (CXN). The nanosilicas were prepared by the sol–gel process, and the following coupling agents were used: 3-glycidylpropyltrimethoxysilane (EpoSi), N-phenyl-3-aminopropyltrimethoxysilane (AmiSi), 3-mercaptopropyltrimethoxysilane (MerSi), and alkyltrimethoxysilane (AlkSi). While the 25-nm silica particles displayed dispersibility similar to that of submicron silica particles (ca. 150 nm and 250 nm), the dispersibility of the 10-nm silica particles proved to be dependent on the combinations of the agents and solvents; for example, EpoSi and MerSi were found to be suitable agents for MIBK and CXN, respectively. The slurries were also subjected to heating at 40 °C for 24 h, which resulted in a considerably higher stability of the dispersion state when CXN was employed as the solvent, regardless of which silica coupling agents were used. FTIR measurement revealed the presence of unreacted free Si–OH at 3740 cm^{-1} for some nanosilicas. Combustion of the organic moieties introduced onto the silica surfaces also proved that the amount of organic groups present in a unit surface area of the nanosilicas were only 1/3 or 1/2 of that found on submicron silicas. From these observations, the low dispersibility of the nanosilicas was inferred to be due to the imperfect coverage of the silanol groups by the silane coupling agents.

1. Introduction

Flip-chip packaging is an innovative mounting technology that is increasingly replacing the conventional gold bonding wire technique used in the construction of semiconductor devices. The basic concept of the technology is to bind a semiconductor chip on its connection points with conduction bumps by flipping the chip over to face downward, then directly attaching it to the circuit on substrates (Fig. 1). The benefits of this technology are that it not only eliminates excess packaging, but also provides miniaturization, high-frequency operation, low parasitics, and a high I/O density [1,2]. Organic packaging (PKG) substrates employed for the flip-chip technique are normally composed of inorganic filler and thermosetting resin as the matrix. Of late, high thermal stability has been required for PKG substrates because of the increased reflow temperature mandated by the lead-free restrictions of the European Union's Restriction of Hazardous Substances (RoHS). The most serious issue is the mismatch in the coefficient of thermal expansion (CTE) between the chip and the substrates, which induces high thermal and mechanical stresses, and strain at the contact bumps. Such stresses and strain cause the joints to crack, which leads to the deterioration of the performance of the semiconductor devices.

To accommodate the organic PKG substrate to the advanced flip-chip technology, it thus becomes important to develop an organic PKG substrate with a low CTE of the order of several ppm K^{-1}. In order to realize such a substrate, an increase in the content of the inorganic filler has been studied [3,4]. At present, submicron silica particles are used as inorganic filler after coupling treatment, to increase adhesion performance and the dispersibility of particles [5,6]. To achieve the desired lower CTE for organic PKG substrates, one promising option could be to increase the contents of the inorganic filler. Nanosilica is a substance that we can expect increase the packing density of the inorganic filler, if these particles are mixed with conventional submicron silica [7–11].

The common process of manufacturing organic PKG substrates entails the following steps: (1) prepare a slurry of the silica particles whose surface is properly treated with silane coupling agents, (2) blend the slurry with a varnish containing thermosetting resin, and (3) insinuate a glass cloth into the varnish, followed by drying and

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1385-8947/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.cej.2009.07.025

press-molding. The achievement of an excellent dispersion state in step (1) is essential to the manufacture of high performance substrates; otherwise, the prepared substrates tend to have insufficient thermal stability due to the inadequate capturing of moisture in the body of the substrate.

As far as the authors know, there have been no systematic investigations of the effects of surface treatments on nanosilica fillers on the dispersion stability in organic solvents such as the ketones commonly employed in industry: methylisobutylketone (MIBK) and cyclohexanone. Hence the objectives of the present study are to clarify the effects of factors such as particle size, coupling agent, and solvent on the dispersion stability of nanosized silicas, which would provide a fundamental understanding of the use of nanosized filler PKG substrates for years to come.

2. Experimental

2.1. Materials

All nanosilicas and submicron silicas used in our experiments were supplied by Admatechs Co., Ltd., Japan, after surface treatment with the different silane coupling agents described below. The nanosilicas, prepared by sol–gel syntheses, had two different particle sizes averaged over the volumetric distribution function obtained by a dynamic light scattering (DLS) apparatus (Nanotrac (UPA) 150, Nikkiso Co., Ltd., Japan); their diameters were $d_{\mathrm{init}} = 10.1$ nm (referred to as NSi10) and $d_{\mathrm{init}} = 24.1$ nm (NSi25). Transmission electron microscopic images are presented in Fig. 2(a) and (b), where a uniform size was observed even as the particles seemed to stick together, probably due to the drying process used to retrieve the solid material for the electron microscopic investigation.

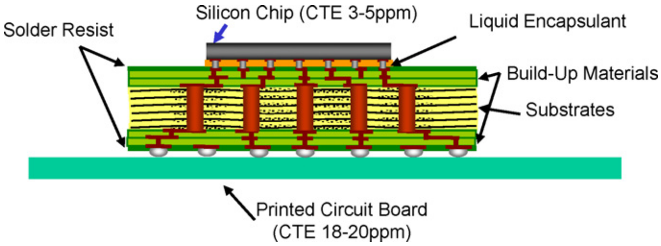

Fig. 1. Flip-chip PKG assembly materials. A PKG substrate consists of substrates, build-up materials, and solder resist.

Two submicron silicas were also employed to provide reference points for the results of testing on the nanosilicas. They were prepared by the vaporized metal combustion method invented by Admatechs Co., Ltd. The averaged particle sizes were $d_{\mathrm{init}} = 161.3$ nm (NSi150) and $d_{\mathrm{init}} = 251$ nm (NSi250), which were also calculated from the volumetric distribution curves measured by laser diffraction equipment (LA-750, Horiba Co., Ltd., Japan). As can be seen in Fig. 2(c) and (d), the variation in size seemed greater than that of previous nanosilicas; i.e., the ranges of variation in particle size were 30–190 nm and 40–400 nm for NSi150 and NSi250, respectively.

The silane coupling agents used in this study were 3-glycidylpropyltrimethoxysilane (epoxysilane: EpoSi, Shin-Etsu Chemical Co., Ltd.), N-phenyl-3-aminopropyltrimethoxysilane (aminosilane: AmiSi, Shin-Etsu Chemical Co., Ltd.), 3-mercaptopropyltrimethoxysilane (mercaptosilane: MerSi, Shin-Etsu Chemical Co., Ltd.), and alkyltrimethoxysilane (alkylsilane: AlkSi, Admatechs Co., Ltd.), whose chemical structures are presented in Fig. 3. These treatments were performed at the manufacturing site, and the samples were supplied as slurry containing two common industrial solvents: (1) methylisobutylketone (MIBK, relative permittivity = 13.11 (20 °C), Mitsubishi Chemical Corp., Japan); and (2) cyclohexanone (CXN, relative permittivity = 18.3 (20 °C), Kanto Denka Kogyo Co., Ltd., Japan). The concentration of the slurries was as follows: 30% for the particles of NSi10 and NSi25, 45% for the particles of NSi150, and 60% for the particles of NSi250, which

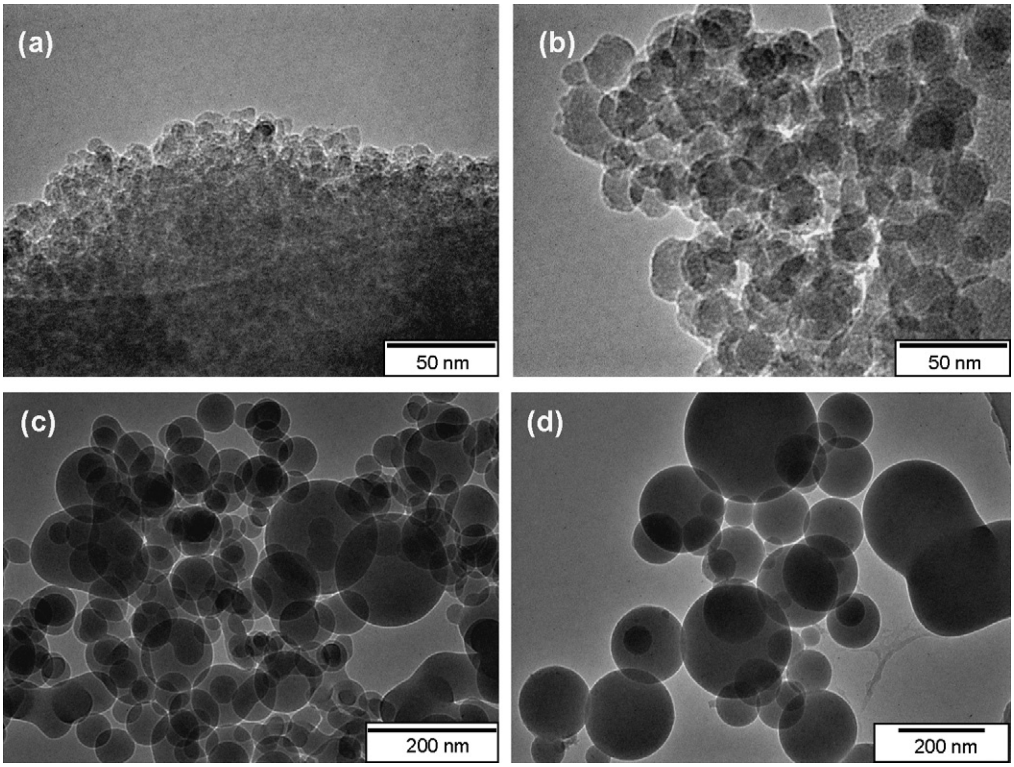

Fig. 2. Transmission electron microscope images of the silica particles: (a) NSi10, (b) NSi25, (c) NSi150, and (d) NSi250.

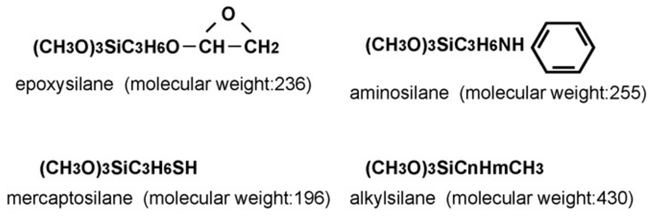

Fig. 3. Coupling agents used for the experiment.

were selected to produce the maximum concentration within a dispersible limit of each silica particle.

2.2. Characterization

Fourier transform infrared spectroscopy (FTIR) was used in obtain information as to what degree the intrinsic silanol groups were replaced by the coupling agents. This was performed on the dried silica by evaporating the slurry solvents by means of the diffuse reflectance method (Thermo Nicolet Coorporation AVATAR 370). Quantitative information was obtained by the combustion method, which is to combust the organic moieties introduced onto the silica surfaces by heating them in air at 800 °C, with the formed CO_2 then measured by an online infrared spectrophotometer.

2.3. Evaluation of dispersibility

The dispersion states of the slurries were evaluated by means of the dynamic light scattering method for the nanosilicas, and the laser diffraction method for the submicron silicas.

The long-term stability of the slurry is important for the actual application; hence the acceleration test was applied. The condition of the acceleration test was to measure the average sizes after leaving the slurries in a thermostatic oven set at 40 °C for 24 h, which is the standard method used in Hitachi Chemical Co., Ltd.

3. Results

3.1. Characterization of surface-treated silicas

The FTIR spectra for each silica particle are shown in Fig. 4(a)–(d). The untreated silicas commonly showed absorption bands at 3740 cm^{-1}, 3660 cm^{-1} and 3400 cm^{-1}, which were assigned to free silanol, associated silanol and hydrogen bonding silanols [12,13]. This was probably caused by the high BET surface area of the nanosilicas, as shown in Table 1. Another interesting feature of the original silicas was their extremely sharp and intense absorption of the free silanol group at 3740 cm^{-1} in NSi150. This would have been caused by defects on the surface of this silica, since the preparation of smaller submicron silica by the vaporized metal combustion method tends to form such surface defects, according to the manufacturer.

Surface treatment with silane coupling agents commonly resulted in decreases in the intensity of the 3740 cm^{-1} absorption, as well as increases in the C–H stretching peaks at 3100–2840 cm^{-1}, which clearly demonstrated the reaction between the silane coupling agents and the silanol groups. The existence of residual free silanol groups was noted for the nanosilicas, as shoulders appeared at the high wavenumber ends of the hydrogen bonding silanol groups. This was observed for samples such as EpoSi–MIBK, MerSi–MIBK, EpoSi–CXN and MerSi–CXN. Only a trace of the residual free silanol peak was observed for AmiSi–MIBK and AmiSi–CXN, and almost no absorption was observed for AlkSi–MIBK and AlkSi–CXN. These observations indicate the difficulty involved in the surface treatment of the nanosilicas with silane coupling agents.

Table 1 shows the BET specific surface areas of the silicas. The surface areas of the untreated silicas are 295 m^2/g, 123 m^2/g, 30 m^2/g and 17 m^2/g for NSi10, NSi25, NSi150 and NSi250, respectively. We also calculated the surface areas by making the simple geometrical assumption that the silica particles are spherical, with diameters of d_{init}. An extremely high degree of agreement between the calculated and the measured surface areas was observed, which clearly indicates the absence of micropores, even on the high surface area of the nanosilicas. This point was also confirmed by inspecting the shape of the isotherms of the N_2 adsorption measurement, which indicated the presence of meso- and macroporosities.

Quantitative information on the amounts of the introduced agents was obtained by the combustion method, which measures the amount of the CO_2 produced during combustion in air at temperatures up to 850 °C. The amounts of the organic moieties thus obtained were expressed in terms of $\mu\mathrm{mol/m}^2$, which was obtained by normalizing the amount of the organic moieties by the BET surface area; the values are tabulated in Table 1.

Comparing the amounts of the coupling agents introduced onto the nanosilicas in contrast to the submicron silicas yields interesting insights. The density of the coupling agents was approximately 2.5–3 $\mu\mathrm{mol/m}^2$ while that of the submicron silicas was approximately 6 $\mu\mathrm{mol/m}^2$; this is consistent with the reported values for conventional silicas [14]. Thus, the surfaces of the submicron particles are almost completely covered with the coupling agents. If the surface density of the silanol group on the silica is the same, irrespective of particle size, there must be free silanol groups on the surface of the nanosilicas, which did not react with the coupling agents.

3.2. Effects of coupling agents and solvents on slurry dispersibility

No precipitation was observed on all sizes of the silica particles tested, when they were poured into MIBK or CXN after surface treatment with any of the types of silane coupling agents used. On the other hand, for silicas without surface treatment the formation of precipitates was observed. Surface treatment was thus found to be indispensable in the preparation of slurries.

In order to express the dispersion state of the slurries, we here introduce a parameter, the degree of aggregation, which is defined by the following formula:

$$\text{degree of aggregation} = 100 \times \left(\frac{[\text{slurry}\, d_{50}] - [d_{\mathrm{init}}]}{[d_{\mathrm{init}}]} \right),$$

where d_{init} is the particle size provided by the manufacturer and slurry d_{50} is the diameter measured for the actual slurry.

Fig. 5(a) and (b) shows the dependence of the degree of aggregation on particle size. The degree of aggregation of NSi10 varied widely, depending on the type of silane coupling agents, while silica particles larger than NSi25 showed similar trends for both MIBK and CXN. It is most noteworthy that the size effect of nanosilica occurs for NSi10 but not for NSi25, even as we expected that both nanosilicas would exhibit behavior different from that of conventional submicron silicas. Close inspection of the degree of aggregation of NSi10 revealed the following: (1) in the case of MIBK, both AmiSi and EpoSi exhibited higher dispersibility, though MerSi and AlkSi exhibited lower dispersibility; (2) in the case of CXN, only MerSi exhibited dispersibility superior to that of the other three silane coupling agents.

Particle size distribution and TEM observation indicated the presence of particles with 30–40 nm in the submicron silicas,

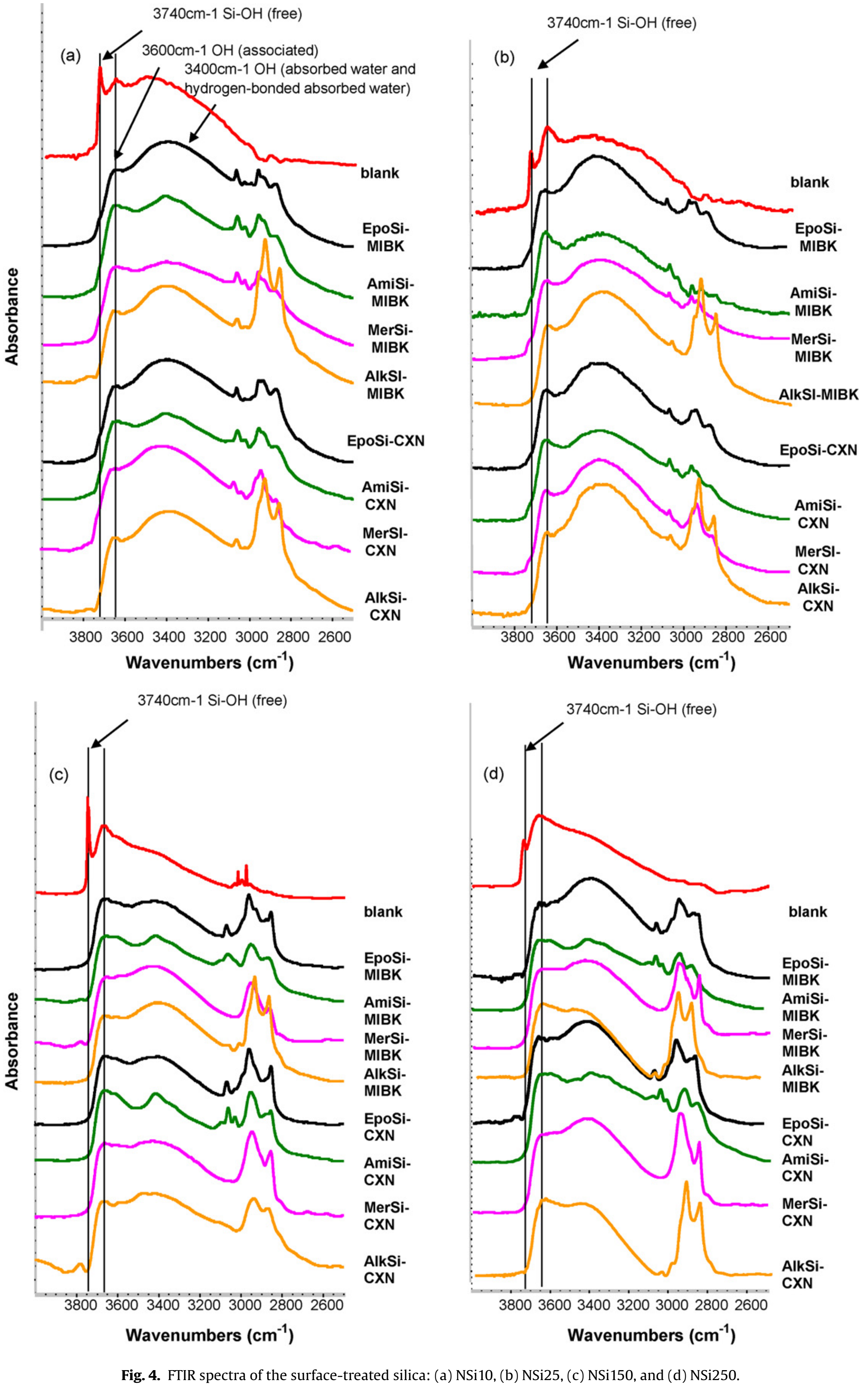

Fig. 4. FTIR spectra of the surface-treated silica: (a) NSi10, (b) NSi25, (c) NSi150, and (d) NSi250.

Table 1
The introduction density and individual number density of silanol groups obtained by the combustion method.

Nanosized silica particles NSi#	Coupling agent-solvent	BET specific surface area (m^2/g)	Geometric specific surface area (m^2/g)	Quantity of coupling agent (%)	Surface density of coupling agent ($\mu mol/m^2$)
10	EpoSi–MIBK	295	273	11.6	2.0
10	EpoSi–CXN	295	273	14.6	2.6
10	AmiSi–MIBK	295	273	11.6	2.0
10	AmiSi–CXN	295	273	12.7	2.2
10	MerSi–MIBK	295	273	16.6	2.9
10	MerSi–CXN	295	273	27.4	4.8
10	AikSi–MIBK	295	273	14.1	2.5
10	AlkSi–CXN	295	273	13.7	2.4
25	EpoSi–MIBK	123	109	7.1	3.0
25	EpoSi–CXN	123	109	7.0	2.9
25	AmiSi–MIBK	123	109	6.4	2.5
25	AmiSi–CXN	123	109	8.6	3.3
25	MerSi–MIBK	123	109	10.1	5.3
25	MerSi–CXN	123	109	11.7	6.2
25	AikSi–MIBK	123	109	13.1	2.8
25	AlkSi–CXN	123	109	10.5	2.2
150	EpoSi–MIBK	30.2	27	3.5	6.0
250	EpoSI–MIBK	17	9	1.5	4.5
250	EpoSi–CXN	17	9	1.6	5.1
250	AmiSi–MIBK	17	9	1.8	5.1
250	AmiSi–CXN	17	9	1.8	5.1
250	MerSi–MIBK	17	9	2.2	8.4
250	MerSi–CXN	17	9	2.5	9.6
250	AlkSi–MIBK	17	9	1.8	2.7
250	AlkSi–CXN	17	9	2.2	3.4

NSi150 and NSi250. As far as the results shown in Fig. 5(a) and (b) are concerned, no influences are introduced by the presence of such smaller particles. Specifically, the combinations of EpoSi and MIBK, as well as MerSi and CXN, effectively achieve states of high dispersion.

The effect of temperature on the state of dispersion of the slurry was also investigated. Taking into account the standard conditions for an acceleration test, the slurry was stored at 45 °C for 24 h. The degree of aggregation of the slurry was evaluated by applying the same formula shown above; the results are presented in Fig. 6(a) and (b). The most striking changes in dispersion state were observed for the variation of NSi10; i.e., the large variation observed in Fig. 5 became smaller except for the silica treated with MerSi, where gelation took place. Higher dispersibility was observed for NSi10 when CXN was used as the solvent, regardless of which type of coupling agents were used.

4. Discussion

In previous sections, we shared some impressive features of nanosilicas that we discovered; i.e., the difficulty encountered attempting to achieve complete coverage of the silanol groups with silane coupling agents; the great tendency toward aggregation of NSi10 but not of NSi25; and the improved dispersibility of NSi10, especially for CXN, after heating at 45 °C for 24 h. In this section we discuss the factors that determine dispersibility, which are crucial to the achievement of higher dispersibility of nanosilicas.

The dispersion of particles in liquid media is controlled by the relative magnitudes of the particle–solvent and particle–particle interactions. When the former interactions are stronger than the latter, the dispersion state is expected to be stable. The solvents used in the present study were MIBK and CXN, whose relative permittivities were 13.11 and 18.3, respectively. The interactions expected

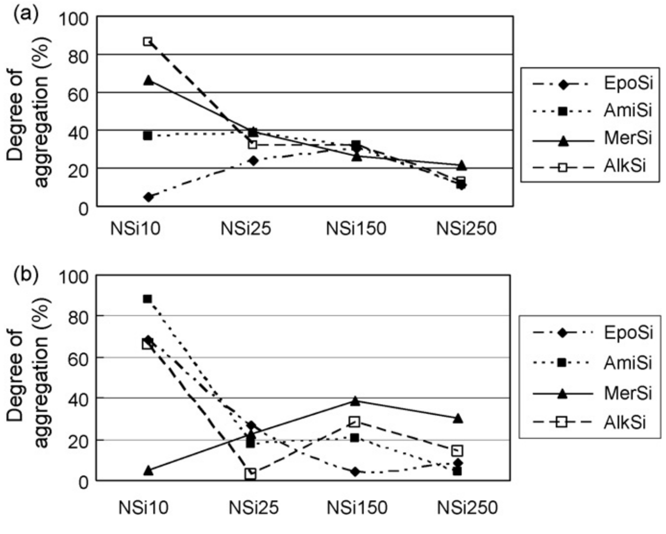

Fig. 5. Dependence of the degree of aggregation on the particle sizes of silica in (a) MIBK and (b) CXN.

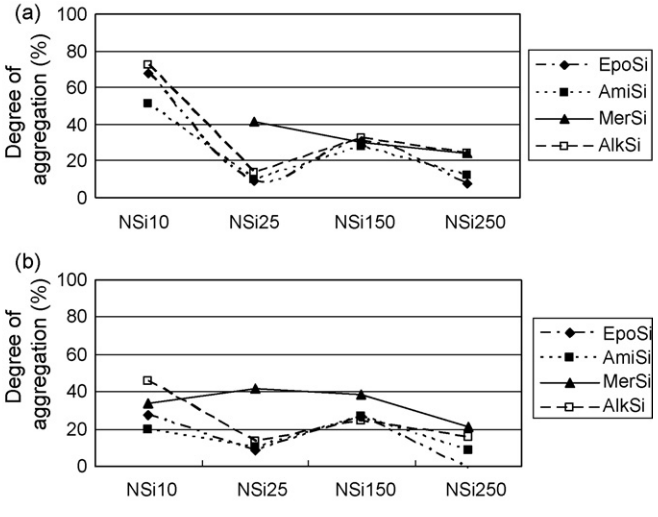

Fig. 6. Dependence of the degree of aggregation on the particle sizes of silica after the acceleration test was performed in (a) MIBK and (b) CXN.

for the solvents are the London interaction and the dipole–dipole interactions including the carbonyl groups in the solvent molecules.

On the other hand, the surface-modified silicas are host to interactions generated by the organic moieties that are introduced, as well as residual silanol groups, as evidenced by the aforementioned FTIR and combustion study. According to the manufacturer, the silica particles used in the study adsorbed water molecules of approximately 100 ppm by weight, even for surface-treated silicas. Thus, there still remained an attractive force originating from the hydrogen bonding that was active among the silica particles via several layers of water molecules [15,16]. To achieve an excellent state of dispersion it is critical that this attractive force is in some way overcome.

As mentioned in the previous sections, unreacted silanol groups remain on the nanosilicas even after surface treatment, which indicates a lower reactivity of the silanol groups with the silane coupling agents. The presence of the surface group and the adsorbed water molecule would result in aggregation. We must at this point highlight an important experimental result, namely that higher dispersion was achieved in the more polar solvent, CXN, when the slurry was heated at 40 °C for 24 h. This can be understood in terms of high polarity, as well as the tendency of thermal agitation to separate aggregated individual silica particles.

5. Conclusion

The present study investigated the effects of surface treatments and the selection of solvents on the dispersibility of nanosilicas when utilized as fillers for the organic packaging substrate in advanced flip-chip technology. Silane coupling treatment proved difficult for nanosilicas, resulting in the presence of unreacted silanol groups, as evidenced by both FTIR and combustion analysis. The aggregation tendency of NSi25 was the same as that found for conventional submicron silicas; however, the aggregation tendency of NSi10 varied, depending on the types of silane coupling agents used. This variability diminished when slurries of NSi10 were heated at 40 °C for 24 h, at which point a great improvement in dispersibility was observed for CXN in opposition to MIBK. These results were sought in order to understand the silanol groups that remained on the surfaces of nanosilicas even after surface treatments. The complete substitution of free silanol groups by the silane coupling agents and the use of polar solvents are critically important to the achievement of high dispersibility; in addition, heating of the slurry proved effective.

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