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Preparation and Properties of Oligomeric Siloxane-Grafted Silica Nanoparticles in a Dry Surface Treatment System

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Abstract

For the purpose of the prevention of environmental pollution and the simplification of reaction process, the dry surface treatment system and carefully controlled synthesis of oligomeric siloxane (*oligo*-SiO) was investigated. The grafting of the *oligo*-SiOs onto the silica surface was successfully achieved. The *oligo*-SiOs made by both bifunctional silane and tetrafunctional silane contained many hydroxyl groups that led to the higher chemical grafting efficiency. By grafting of *oligo*-SiO containing moderate number of phenyl groups onto the surface, the silica was easily dispersed in mixed solvent of toluene/ethyl acetate. In addition, the *oligo*-SiO-grafted silica dispersed in a composite polyimide film had excellent adhesion ability to a silicon chip.

Key-words: Silica nano-particle, Grafting, Dry surface treatment, Oligomeric siloxane, Polyimide

1. Introduction

Accompanying the evolution of the information society, the adhesives for electronic materials are required to achieve high heat resistance and excellent reliability that matches the high density of electronics. The adhesives that have such higher heat resistance and excellent reliability include die bond films, semiconductor sealants and wiring board substrates. The development of adhesives now requires not only the development of new resins, but also the design of surface-modified inorganic particles.

In general, dispersing nanoparticles, such as silica or carbon black, uniformly into a polymer or an organic solvent is very difficult because of aggregation of these particles. We have pointed out that the dispersibility of silica nanoparticles and carbon black is greatly improved by surface grafting, namely, chemical binding of polymers, onto silica nanoparticle and carbon black surfaces¹⁾. We have also reported the grafting of various polymers such as vinyl polymer, polyester, polyether, poly(organophosphazene), poly(dimethylsiloxane) and poly(oxazoline) onto silica nanoparticle and carbon black surfaces¹⁾. Takano and his coworkers have reported that heat resistance and reliability of the adhesive were improved by controlled thickness of oligomeric siloxanes on the surface of nanoparticles²⁾.

However, scale-up production of polymer-grafted nanoparticles was still hardly achieved. The production

requires complicated procedures, such as centrifugation, filtration and solvent extraction, which results in the consumption of a lot of waste solvent. We have reported that the scale-up radical graft polymerization of vinyl monomers onto silica nanoparticle surface initiated by azo groups and peroxy carbonate groups previously introduced onto the surface in the solvent-free dry-system was effective to reduce the complicated procedures^{3,4)}. But there are certain disadvantages to these processes: they still take longer and cost more. It has been reported that several kinds of oligomeric siloxanes (*oligo*-SiOs) were effective to improve interfacial properties of inorganic material/polymer composites⁵⁾.

One purpose of this study is to make surface grafting of *oligo*-SiO onto silica nanoparticle by only one process. The grafting in a dry-system was successfully achieved by spraying solution of *oligo*-SiO (**Scheme 1**): the *oligo*-

Scheme 1 Preparation of *oligo*-SiO-grafted silica in a dry-system.

SiO-grafted silica nanoparticle was prepared by one-step reaction⁶⁻⁸⁾. In this paper the dispersibility of *oligo*-SiO-grafted silica nanoparticle into solvent and a polyimide film will be also discussed.

2. Experimental

2.1 Materials and reagents

Silica nanoparticle, Aerosil 300CF, was obtained from Nippon Aerosil Co., Ltd., Japan. The silica was dried in vacuum at 110 °C for 48 h before use. The specific surface area and particle size were 300 m²/g and 7 nm, respectively.

oligo-SiOs were synthesized by the hydrolysis and polycondensation of alkoxy silane monomers^{9,10)}. 3-Glycidypropyldimethoxymethylsilane was obtained from Sinetsu Chemical Co., Ltd., Japan. Dimethoxydiphenylsilane, dimethoxydimethylsilane and tetramethoxysilane were obtained from Tokyo Chemical Industry Co., Ltd., Japan. Special reagent grade methanol, toluene and ethyl acetate with 99.5% purity from Wako Chemical were used without further purification. Activated clay, Nikkanaito G-36, from Toshin Chemicals Co., Ltd., Japan and HCl from Wako Chemical were used as catalysts.

3,5-Diaminobenzoic acid (DABA) and 4,4'-oxydiphthalic dianhydride (ODPA) were obtained from Sigma-Aldrich Japan. Ethoxylated bisphenol-A dimethacrylate, "BPE-100", as a radiation-polymerizable compound and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, "I-819", as a photopolymerization initiator were obtained from Shin-Nakamura Chemical Co., Ltd. and Ciba Specialty Chemicals Co., Ltd., respectively.

2.2 Synthesis of *oligo*-SiO

2.2.1 *oligo*-SiO (1)

The synthesis of *oligo*-SiO (1) was carried out by

Scheme 2 Synthesis of *oligo*-SiO (1).

Scheme 3 Synthesis of *oligo*-SiO (2).

polycondensation of dimethoxydiphenylsilane and tetramethoxysilane in the presence of water and activated clay as catalyst (Scheme 2). Into a 500 cm³ flask 0.5 mol of dimethoxydiphenylsilane, 0.5 mol of tetramethoxysilane, 100 g of toluene, 10.0 g of activated clay as catalyst and 26.0 g of water were charged. The reaction mixture was stirred with a magnetic stirrer at 75 °C. The weight-average molecular weight (*M_w*) of the obtained *oligo*-SiO (1) was determined by gel permeation chromatography (GPC) equipped with columns for THF solvent from Hitachi Chemical Co. (GL-A100). By adjusting the reaction time, the target *M_w* was made up to 2000. The activated clay was removed by filtration. After performing density adjustment by the addition of toluene, 50 wt% of *oligo*-SiO (1) solution was obtained. The concentration of *oligo*-SiO (1) solution was determined by the weight lost when *oligo*-SiO (1) solution was heated at 130 °C using thermoactive analysis and differential thermo-analysis (TG-DTA) (Shimadzu DTG-60/60H).

2.2.2 *oligo*-SiO (2)

The synthesis of *oligo*-SiO (2) was carried out by polycondensation of dimethoxydimethylsilane and tetramethoxysilane in the presence of water and acetic acid as catalyst (Scheme 3). Into a 500 cm³ flask 0.5 mol of dimethoxydimethylsilane, 0.5 mol of tetramethoxysilane, 30 g of methanol, 1.0 g of acetic acid and 26.0 g of water were charged. The reaction mixture was stirred with a magnetic stirrer at 60 °C. By adjusting the reaction time, the target *M_w* was made up to 2000 (Scheme 2). After performing density adjustment by the addition of methanol, 50 wt% of *oligo*-SiO (2) solution was obtained.

2.2.3 *oligo*-SiO (3)

The synthesis of *oligo*-SiO (3) was carried out by self

Scheme 4 Synthesis of *oligo-SiO (3)*. Scheme 5 Synthesis of *oligo-SiO (4)*.

polycondensation of dimethoxydiphenylsilane in the presence of water and activated clay as catalyst (Scheme 4). Into a 500 cm³ flask 1.0 mol of dimethoxydiphenylsilane, 100 g of toluene, 10.0 g of activated clay and 26.0 g of water were charged. The reaction mixture was stirred with a magnetic stirrer at 75 °C. *M_w* of the obtained oligomer was determined by GPC equipped with columns for THF solvent from Hitachi Chemical Co. (GL-A100). By adjusting the reaction time, the target *M_w* was made up to 1000 (Scheme 3). The activated clay was removed by filtration. After performing density adjustment by the addition of toluene, 50 wt% of *oligo-SiO (3)* solution was obtained.

2.2.4 *oligo-SiO (4)*

The synthesis of *oligo-SiO (4)* was carried out by self polycondensation of 3-glycidyloxypropyldimethoxymethylsilane in the presence of water and activated clay as catalyst (Scheme 5). Into a 500 cm³ flask 1.0 mol of 3-glycidyloxypropyldimethoxymethylsilane, 12.0 g of methanol, 10.0 g of activated clay and 5.0 g of water were charged. The reaction mixture was stirred with a magnetic stirrer at 60 °C. By adjusting the reaction time, the target *M_w* was made up to 1000. The activated clay was removed by filtration. After performing density adjustment by the addition of methanol, 50 wt% of *oligo-SiO (4)* solution was obtained.

2.3 Grafting of *oligo-SiOs* onto silica nanoparticle surface in dry-system

The grafting of *oligo-SiO (1)*, (2), (3) and (4) having silanol group was achieved by the dry-system^{3,4}. For example, silanol groups of *oligo-SiO (1)* easily react with surface silanol groups of silica nanoparticle by direct condensation in the presence of acetic acid as catalyst (Scheme 1). Using a 200 ml four-necked flask, as shown in Fig. 1, which contained 1.0 g silica nanoparticle, 1.0 g of 50 wt% *oligo-SiO* methanol solution was sprayed and

Fig. 1 Reaction apparatus for the preparation of *oligo-SiO*-grafted silica in the dry system.

the silica was agitated at 120 rpm at 120 °C under N₂. After 2 h, residual toluene or methanol was removed under high vacuum. After 6 h *oligo-SiO*-grafted silica was obtained.

2.4 Determination of percentage of grafting efficiency

In order to determine chemical grafting and chemical grafting efficiency, *oligo-SiO*-grafted silica was dispersed in THF, and the dispersion was centrifuged at 1.8×10^4 rpm. The silica precipitated was dispersed again in THF and centrifuged. The procedures were repeated until no more ungrafted polymer could be detected in the supernatant solution. Chemical grafting (%) and chemical grafting efficiency (%) were determined by the following equations:

$$\text{Chemical grafting (\%)} = (A/B) \times 100,$$

$$\text{Chemical grafting efficiency (\%)} = (A/C) \times 100.$$

Where *A* is weight of grafted *oligo-SiO* after washing, *B* is weight of silica used, and *C* is weight of *oligo-SiO* used. The weight of *oligo-SiO* grafted onto the silica surface was determined by the weight lost when *oligo-SiO* grafted silica was heated at 900 °C using thermo active analysis and differential thermo-analysis (TG-DTA) (Shimadzu DTG-60/60H).

2.5 Preparation of *oligo-SiO*-grafted silica dispersion in mixed solvent

In this study, mixed solvent of toluene/ethyl acetate (50 vol%/50 vol%) was used for the dispersant. The grafted silica was pre-dispersed in the mixed solvent by ultrasonic wave irradiation using a US-150E (Nippon Seiki Co, Ltd., 20 KHz 150 W). Then further mixing was conducted by rotation and revolution using an independent mixer ARE-400TWIN (Thinky Co, Ltd.) for 30 min. Finally, a high-pressure wet jet mill, NM2-L200AR (Yoshida Kikai co., Ltd), was used. As shown in Fig. 2, the aggregates of silica were pulverized by the high-pressure in the pulverizing processor. The maximum processing pressure was 200 MPa and the maximum running speed in the orifice of the

pulverizing processor was 280 m/s.

2.6 Size distribution of *oligo*-SiO-grafted silica in the organic solvent

The size distribution of 0.1 wt% *oligo*-SiO-grafted silica in the mixed solvent was measured by dynamic light scattering using a Zetasizer ZS (Malvern Co, Ltd).

2.7 Preparation of *oligo*-SiO-grafted silica/polyimide composite

2.7.1 Preparation of polyimide

The preparation of polyimide was carried out as follows. Into a flask equipped with a stirrer, a thermometer and nitrogen purge, 50 g of DABA, 102.3 g of ODPa and 450 ml of NMP were charged. Then the reaction mixture was stirred at 50 °C. After 5 h, a reflux condenser with a water receptor was fitted to the flask. Then 450 ml of *m*-xylene was added to the reaction mixture and the reaction temperature was elevated to 180 °C. After 5 h, the reaction mixture was cooled to room temperature and poured into large excess of distilled water. The resulting precipitate was filtered and dried in a vacuum dryer. The weight average molecular weight of the polyimide was 72,000.

2.7.2 Preparation of *oligo*-SiO-grafted silica/polyimide composite

The preparation of *oligo*-SiO-grafted silica/polyimide composite was carried out as follows. 50.0 g of the polyimide, 20.0 g of ethoxylated bisphenol-A dimethacrylate, as radiation-polymerizable compound, 3.0 g of bis(2,4,6-trimethyl benzoyl) phenylphosphine oxide, as photopolymerization initiator, and *oligo*-SiO-grafted silica were uniformly mixed in 350 ml of toluene/ethyl acetate mixed solvent. The varnish thus obtained was coated on a PET film with mold release silicone, and dried to form an adhesive composite polyimide film with a thickness of 40 μ m.

2.8 Evaluation of adhesive force between composite polyimide film and silicon chip

Silicon, 400 μ m thickness and 6 inches in diameter, was laminated by the above adhesive composite polyimide film. Then the adhesive film was irradiated by 1000 mJ/cm² of

ultraviolet light. After the PET film was peeled off, the dicing tape of the pressure-sensitive was laminated to the adhesive composite polyimide film. Then the silicon chip with the adhesive film was cut into 3.0 mm $\times$ 3.0 mm pieces.

The silicon chip was placed on a glass substrate of 10.0 mm $\times$ 10.0 mm $\times$ 0.55 mm thickness in which the adhesive film was sandwiched and heated for 10 sec with the pressure of 500 gf at 120 °C. Then it was heated for 3 h at 160 °C. The adhesive force was measured at 260 °C by Dage 4000, which was made by Dage Corporation with the measuring speed of 50 μ m/s.

3. Result and discussion

3.1 Synthesis of *oligo*-SiO

Table 1 shows the molecular weight of *oligo*-SiO (1), (2),

Table 1 The molecular weight of oligomeric siloxanes just after synthesis.

<i>oligo</i> -SiO	Molecular Weight	
	Weight average (M_w)	Number average (M_n)
<i>oligo</i> -SiO (1)	1876	1291
<i>oligo</i> -SiO (2)	1980	1359
<i>oligo</i> -SiO (3)	998	712
<i>oligo</i> -SiO (4)	1093	765

Fig. 3 Relationship between weight average molecular weight (M_w) and elapsed time after synthesis of *oligo*-SiOs.

Fig. 4 Relationship between number average molecular weight (M_n) and elapsed time after synthesis of *oligo*-SiOs.

Fig. 2 Diagram of the jet wet mill system.

(3) and (4) after the synthesis. These *oligo*-SiOs having many hydroxyl groups were unstable. Due to this instability, further reaction easily occurred even at a lower temperature. **Figs. 3** and **4** show the relationship between molecular weight and elapsed time after synthesis of *oligo*-SiO (1), (2), (3) and (4). The storage temperature was 5 °C. The *oligo*-SiOs made by both bifunctional silane and tetrafunctional silane (*oligo*-SiO (1) and (2)) contained many hydroxyl groups that led to higher reactivity. Even with low storage temperature, the weight average molecular weight of *oligo*-SiO (2) after 30 days exceeded up to 10,000. In this study, grafting was carried out within two days of the synthesis of the *oligo*-SiOs.

3.2 Grafting of *oligo*-SiOs on the silica nanoparticle in a solvent free dry system

The grafting of *oligo*-SiOs onto the silica nanoparticle in a dry system was investigated. The *oligo*-SiO-grafted silica was a white powder. **Fig. 5** shows the picture of *oligo*-SiO (1)-grafted silica.

Table 2 shows the chemical grafting and the chemical grafting efficiency after washing of *oligo*-SiO-grafted silicas. There were significant differences with the chemical grafting of the 4 samples.

It was found that the amount of hydroxyl groups in oligomeric siloxane played a major role in the chemical grafting and chemical grafting efficiency result. It is considered that the reaction between silanol groups on silica and hydroxyl groups in *oligo*-SiO is proceeded by

Fig. 5 Photograph of *oligo*-SiO (1)-grafted silica.

Table 2 The chemical grafting and chemical grafting efficiency of *oligo*-SiO on silica surface.

Silica	Chemical Grafting (%)	Chemical Grafting efficiency (%)
Untreated	Trace	—
<i>oligo</i> -SiO (1)-grafted	9.0	18.0
<i>oligo</i> -SiO (2)-grafted	15.3	30.6
<i>oligo</i> -SiO (3)-grafted	2.7	5.4
<i>oligo</i> -SiO (4)-grafted	3.8	7.6

the dehydration condensation¹¹⁾. With a small amount of hydroxyl groups, the chemical grafting of *oligo*-SiO (3) and *oligo*-SiO (4) onto the surface was lower than those of *oligo*-SiO (1) and *oligo*-SiO (2). On the other hand, *oligo*-SiO made by both bifunctional silane and tetrafunctional silane had many hydroxyl groups, the large amount of hydroxyl groups led to a higher chemical grafting efficiency of *oligo*-SiO (1)-grafted and *oligo*-SiO (2)-grafted silica.

Steric hindrance made a substantial difference in the chemical grafting of *oligo*-SiO (1) and *oligo*-SiO (2), resulting to a smaller value for *oligo*-SiO (1) compared to *oligo*-SiO (2). *oligo*-SiO (1) including phenyl groups has a low reactivity to silica compared to *oligo*-SiO (2) including methyl groups.

3.3 Dispersibility of *oligo*-SiO-grafted silica in a mixed solvent of toluene/ethyl acetate

Taking industrial cost into consideration, it is better to use unwashed *oligo*-SiO-grafted silica than washed *oligo*-SiO-grafted silica. Unwashed *oligo*-SiO-grafted silica was dispersed in mixed solvent of toluene/ethyl acetate by the ultrasonic irradiation, followed by mixing procedure and the pulverizing processor. **Fig. 6** shows the distribution of the particle size of *oligo*-SiO-grafted silica determined by dynamic light scattering in a mixed solvent of toluene/ethyl acetate.

oligo-SiO (1)-grafted silica could be dispersed in the mixed solvent of toluene/ethyl acetate without aggregation. Although *oligo*-SiO (2)-grafted, *oligo*-SiO (3)-grafted and *oligo*-SiO (4)-grafted silica made smaller aggregates, they were not easily dispersed in the mixed solvent of toluene/ethyl acetate as compared to *oligo*-SiO (1)-grafted silica. *oligo*-SiO (1) did not only have moderate number of phenyl groups, which had high solvent affinity, but also moderate number of hydroxyl groups, which had high reactivity to silica.

3.4 Properties of *oligo*-SiO-grafted silica/polyimide composite

When the surface treatment of the silica is insufficient, aggregation of the silica in the solvent occurs. In that case, it is impossible to disperse a large amount of silica in polyimide film. **Table 3** shows the appearance evaluation results of several kinds of silica/polyimide composites. By using *oligo*-SiO (1)-grafted silica, it was possible to increase the amount of silica in the polyimide film up to 30% without aggregation.

Fig. 7 shows the adhesive strength of the *oligo*-SiO (1)-grafted silica/polyimide composite against to silicone chip. It can be seen that the adhesive strength increased in accordance with the increasing amount of *oligo*-SiO (1)-grafted silica. By uniformly dispersing the *oligo*-SiO-grafted silica in polyimide film, it was possible to produce film that had excellent adhesion to the silicone chip.

Fig. 6 Particle size distribution of *oligo*-SiO-grafted silica in mixed solvent of toluene/ethyl acetate.

Table 3 The Appearance evaluation of *oligo*-SiO/polyimide composite film.

Silica	Silica content (vol%)			
	5 vol%	15 vol%	30 vol%	50 vol%
<i>oligo</i> -SiO (1)	Good	Good	Good	Very Poor
<i>oligo</i> -SiO (2)	Good	Good	Poor	Very Poor
<i>oligo</i> -SiO (3)	Good	Poor	Very Poor	Very Poor
<i>oligo</i> -SiO (4)	Good	Poor	Very Poor	Very Poor

Good - No problem with the appearance of the film

Poor - Poor appearance by particle aggregation

Very Poor - Film formation difficult

Fig. 7 Adhesive strength of polyimide film using *oligo*-SiO (1)-grafted silica and the chip.

4. Conclusion

1. The grafting of *oligo*-SiOs onto the silica surface was successfully achieved.
2. *oligo*-SiOs made by both bifunctional silane and tetrafunctional silane contained many hydroxyl groups that led to a higher chemical grafting efficiency.
3. *oligo*-SiO-grafted silica containing moderate number of phenyl groups was easily dispersed in mixed solvent of toluene/ethyl acetate.
4. By dispersing the *oligo*-SiO-grafted silica in polyimide film, it was possible to produce the film that had excellent adhesion to the silicon chip.

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ドライ表面処理システムによるシリコンオリゴマー被覆シリカ粒子の製法およびその特性

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要 旨

環境対応ならびにプロセスを簡略化する目的で, ドライシステムによる表面処理とシリコンオリゴマーの合成方法の検討を行った。その結果, シリコンオリゴマーをシリカ上に被覆できることがわかった。2官能ならびに4官能のシランによって合成されたシリコンオリゴマーを用いることで高いグラフト効率が得られることがわかった。さらにフェニル基を有するシリコンオリゴマーを用いることで, トルエン/酢酸エチル混合溶媒に容易に分散することがわかった。そしてシリコンオリゴマー被覆シリカ粒子を添加したポリイミドフィルムはシリコンチップとの接着性が高くなることがわかった。

キーワード: シリカナノ粒子, グラフト, 無溶媒表面処理, シリコンオリゴマー, ポリイミド