

Quantitative measurement of physisorbed silane on a silica particle surface treated with silane coupling agents by thermogravimetric analysis

Ryota Yamazaki, Nozomi Karyu, Masayo Noda, Syuji Fujii, Yoshinobu Nakamura

Department of Applied Chemistry, Osaka Institute of Technology, 5-16-1 Ohmiya, Asahi-Ku, Osaka 535-8585, Japan

Correspondence to: Y. Nakamura (E-mail: nakamura@chem.oit.ac.jp)

ABSTRACT: We investigated a new method for estimating the amount of silanes physisorbed on a silica particle surface treated with silane coupling agents from a weight loss curve measured by thermogravimetric (TG) analysis. The silica particles were treated with 3-glycidoxypropyl trimethoxysilane (GPTMS) or 3-mercaptopropyl trimethoxysilane (MrPTMS) with both dry and wet treatment methods. In the TG curve for silica particles treated with GPTMS, the weight decreased in three steps: 100–170°C (first step), 170–250°C (second step), and 250–400°C (third step). The weight loss in the first step decreased with heating or acetone washing to remove the physisorbed molecules as the posttreatment. The three weight losses were found to be based on physisorbed monomeric silanes (first step), physisorbed polycondensed silanes (second step), and chemisorbed silanes (third step), respectively. The amount of physisorbed silanes on the silane-treated layer could be estimated from the TG curve without solvent washing to remove the physisorbed molecules. The amounts obtained were almost equal to those measured from a comparison of the weight losses for the treated particles before and after acetone washing. A similar tendency was observed for MrPTMS-treated silica. Thus, the amount of physisorbed silanes in silane-coupling-agent-treated silica particles was successfully estimated from the TG measurements. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43256.

KEYWORDS: adsorption; surfaces and interfaces; thermogravimetric analysis (TGA)

Received 13 September 2015; accepted 24 November 2015

DOI: 10.1002/app.43256

INTRODUCTION

Silane coupling agents are widely used for the surface modification of inorganic materials, where they are generally applied to inorganic substrates from dilute aqueous or nonaqueous solutions and then dried. They are also sometimes directly added to a polymer during processing.¹ Many researchers^{2–36} and our group^{37–43} have conducted investigations on the reactivity of silane coupling agents, the characterization of a silane layer formed on an inorganic surface, and the reinforcement effect in composites. Silane coupling agents react with inorganic surfaces as follows.¹ The hydrolysis reaction of silane coupling agents occurs in an aqueous phase to form silanol (SiOH) groups. Silanol groups can first form hydrogen bonds with the inorganic surface and then condense to a siloxane structure when they are dried and chemically bonded to the surface to form a chemisorbed layer. However, the polycondensation of silane coupling agents also occurs simultaneously in the solvent phase. Johansson *et al.*² reported that the probability that polycondensed silanes form chemical bonds with an inorganic surface is low but that polycondensed silanes are deposited on the chemisorbed layer as

physisorbed silanes. Naviroj *et al.*,³ Miller and Ishida,⁴ Culler *et al.*,⁵ and Ikuta *et al.*⁶ have indicated that multilayer silane coverage is more effective than monolayer coverage for the reinforcement of fiber-reinforced composites. In these studies, the interfacial layer was referred to as the interphase. The interphase is explained as follows. Polycondensed silanes formed in the solvent phase are deposited on the chemisorbed layer as physisorbed silanes. The physisorbed silanes can diffuse into the resin phase and copolymerize with the matrix resin. The resin can also penetrate into the chemisorbed layer and form an interpenetration layer. The resulting interphase has different characteristics from those of both the bulk polymer and the pure siloxane layer. The interdiffused chemisorbed siloxane layer significantly improves the mechanical properties of the composite. Physisorbed silanes diffused into the matrix improve the polymer properties, including the water absorption.⁷ The amount of chemisorbed silane chains should increase to make a well-entangled siloxane layer and, thereby, improve the mechanical properties of the composite. In addition, the ratio of chemisorbed silanes to physisorbed silanes has a strong effect on the composite properties.

The measurement of the amount of physisorbed silanes typically requires removal from the treated layer through washing with an organic solvent.⁸ It is also necessary to quantify the amounts of silanes before and after washing. The quantification of physisorbed silanes or confirmation of the chemisorption is a big unsolved subject, even now, and many studies have been done.

Marrone *et al.*⁹ confirmed the progress of chemisorption with Fourier transform infrared spectroscopy measurements. Triethoxysilane (TES) was adsorbed by vapor deposition onto the surface of a plate formed by pressing amorphous silica particles. The reaction of TES with the silica plate enhanced by heating from 100 to 500°C was investigated. The Fourier transform infrared results show that the peak of the ethoxy group in TES decreased, whereas that of the siloxane linkages increased with increasing heating temperature. Thus, the reaction of TES with the silica surface was promoted by the increase in temperature. It was also clarified that the formed siloxane linkage was stable at 500°C; that is, the thermal resistance of silane molecules was improved by reaction with an inorganic surface.

Yang *et al.*¹⁰ conducted a pyrolysis gas chromatography analysis of magnesium hydroxide and calcium carbonate surfaces treated with an acetone solution of 3-methacryloxypropyl trimethoxysilane. Two steps of thermal decomposition (first at 250°C and then at 600°C) occurred. The peaks for the physisorbed and chemisorbed silanes on the particles could be distinguished, and this indicated the possibility of estimating the ratio of physisorbed and chemisorbed silanes from the pyrolysis gas chromatography peak ratios.

Fujii and Uchimura¹¹ measured the pyrolysis products generated from phenyl triethoxysilane (PTES)-treated TiO₂ particles with laser ionization time-of-flight mass spectrometry. The molecular ion peak of PTES was detected for pure PTES. On the other hand, no PTES was observed, and benzene, as a decomposed material of PTES, was detected for the PTES-treated TiO₂ particles. In the case of PTES-treated glass filter paper, both molecular ion peaks of PTES and benzene were detected because the active sites were considerably smaller in glass filter paper than in TiO₂ particles. The study authors concluded that the laser ionization time-of-flight mass spectrometry method could be used to evaluate whether the silanes remained on the sample through physisorption or chemisorption.

Bukleski and Ivanovski¹² succeeded in quantifying physisorbed and chemisorbed silanes in the 3-aminopropyl trimethoxysilane (APTMS)-treated silica gel by the diffuse reflectance infrared Fourier transform spectroscopy measurements. The dry toluene solutions of APTMS with various concentrations were prepared. The physisorbed silanes were removed by Soxhlet extraction. The relation between the intensity of the absorbance band versus the concentration of the treated APTMS solution was plotted, and the good linear relation was obtained, so quantification was possible. This relation was saturated above a certain concentration. They judged that the complete monolayer of APTMS was formed at this concentration. They also quantified the extracted physisorbed silanes. However, this method is a very time-consuming process. Therefore, it would be more convenient if an easier technique could be developed.

We previously reported³⁷ the preparation of polycondensed silane coupling agents with various organic functional groups, such as glycidoxy, mercapto, and amino groups. Thermogravimetric (TG) analysis of both the original and polycondensed silanes was performed. The results show that the temperature where the thermal decomposition of polycondensed silanes began was higher than that for the original silanes by not less than 100°C. Therefore, the thermal resistance of the silane coupling agent increased with the molecular weight.

In this study, a new simple method for quantifying the physisorbed silane on the treated layer with TG analysis was investigated. For this purpose, silica particles were treated with 3-glycidoxypropyl trimethoxysilane (GPTMS) or 3-mercaptopropyl trimethoxysilane (MrPTMS) and heated. In many of our studies,^{35–41} the characterization of the treated layer on the silica surface and the mechanical properties of filled rubber were investigated with MrPTMS and GPTMS. The influence of heating on the shape of the TG weight loss curve was analyzed with respect to the increase in the heat resistance of silane by reaction with the inorganic surface or by polycondensation.

EXPERIMENTAL

Materials

Spherical amorphous silica particles (FB-3SDX, Denki Kagaku Kogyo Kabushiki Kaisya, Tokyo, Japan) were used as received. GPTMS (KBM-403), MrPTMS (KBM-803), and 3-aminopropyl triethoxysilane (APTES; KBE-903) were used as received from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). Reagent-grade acetone was used as a solvent.

Characterization of the Silica Particles

The size and size distribution of the silica particles were determined with a laser diffraction particle size analyzer (Mastersizer 2000, Malvern Instruments, Ltd., Worcestershire, United Kingdom) equipped with a small volume sample dispersion unit (Hydro 2000SM; about 150 mL, including the flow cell and tubing), a HeNe laser (633 nm), and a solid-state blue laser (466 nm). The stirring rate was adjusted to 2000 rpm. The mean particle diameter was taken to be the volume mean diameter (D_v), which is mathematically expressed as follows:

$$D_v = \frac{\sum D_i^4 N_i}{\sum D_i^3 N_i}$$

where D_i is the diameter of the individual particles and N_i is the number of particles corresponding to the specific diameter. The resulting data are presented as the mean diameters with the standard deviations.

The specific surface area was measured with an automatic measurement apparatus for the specific surface area (Gemini VII2390a, Shimadzu Corp., Kyoto, Japan) by N₂ gas adsorption on the basis of the Brunauer–Emmett–Teller method.

The morphologies of the silica particles were observed with scanning electron microscopy (VE-8800, Keyence Corp., Osaka, Japan) with an acceleration voltage of 10 kV.

Surface Treatment

The surface treatment was conducted with both dry and wet treatment methods. The surface treatment and calculation of the amount of silane required for monolayer coverage of the

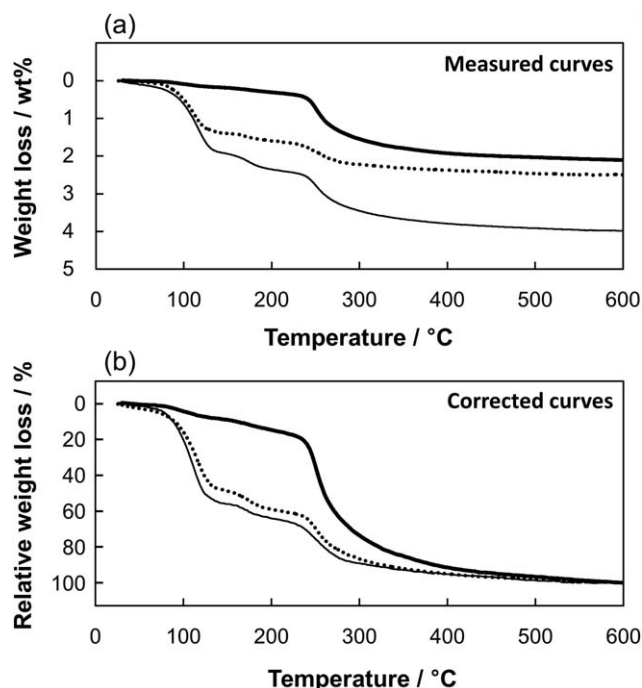


Figure 1. Schematic representation of the (a) measured weight loss and (b) relative weight loss curves by TG analysis.

silica particles has been described previously,^{37,38} where the area occupied by a single silane molecule (0.13 nm^2)¹³ and the specific surface area of the silica particles are used. The quantity of silane is given as surface coverage, which denotes the number of layers that cover the silica particle surface. Silane was added in a quantity to achieve a surface coverage of 5 layers for both the wet and dry treatments.

Wet Treatment. The silane and silica particles were mixed for 5 min in acetone. This was followed by the complete removal of the acetone with a rotary evaporator at 35°C for 30 min. All of the treated silica particles were left at room temperature for 24 h before the TG measurements.

Dry Treatment. The silane was added gradually to 100 g of silica particles in a polyethylene bag and mixed by hand from outside of the bag for 10 min. The mixture was then mixed for an additional 5 min with a mixer for home use. All of the treated silica particles were left at room temperature for 24 h before the TG measurements.

Removal of the Physisorbed Silane

The samples were washed with acetone to remove the physisorbed silane molecules. The surface-treated silica and acetone were mixed in a pear-shaped flask and stirred for 10 min with a rotary evaporator; this was followed by suction filtration with filter paper (No. 7, Toyo Roshi Kaisya, Ltd., Tokyo, Japan). The washed silica particles were left at room temperature for 24 h and then heated at 85°C for 3 h in an oven.

Quantitative Analysis of the Adsorbed Silane

The amount of adsorbed silane on the treated silica surface was measured with a TG/differential thermal analyzer (TG/DTA-6300, SII NanoTechnology, Inc., Chiba, Japan). The silane-

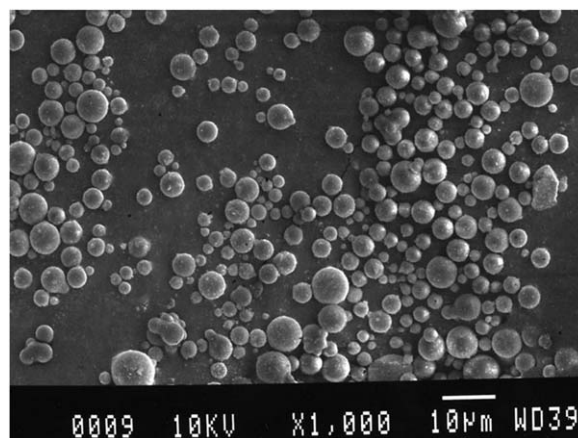


Figure 2. Scanning electron microscopy image of the silica particles.

treated silica particles were heated to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$ in an air atmosphere (flow rate = $300 \text{ mL}/\text{min}$). The amount of adsorbed silane was calculated according to the weight loss, as previously reported,^{37,38} and was determined by the surface coverage; this indicated the number of monolayers covering the silica surface.

The measured weight loss curve was corrected, as schematically shown in Figure 1, where Figure 1(a) shows the measured curves, and Figure 1(b) shows the corrected TG curves needed to achieve the same weight loss at 600°C ; these are referred to as the measured weight loss curve and the relative weight loss curve, respectively. The relative weight loss curve is convenient for the comparison of the TG curve shapes.

RESULTS AND DISCUSSION

Silica Particles

The scanning electron microscopy image and size distribution curve for the silica particles that we used are shown in Figures 2 and 3, respectively. The measured mean size was $3.4 \mu\text{m}$. The specific surface area measured on the basis of the Brunauer–Emmett–Teller method was $5.3 \text{ m}^2/\text{g}$. In our previous reports,^{37–43} this silica was widely used for the analysis of the

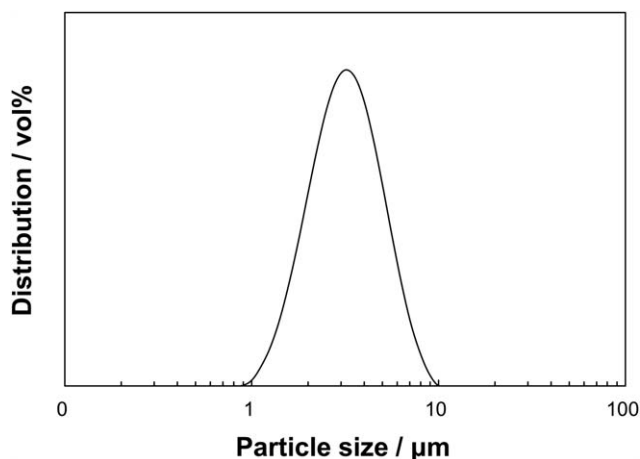


Figure 3. Particle size distribution curve of the silica particles.

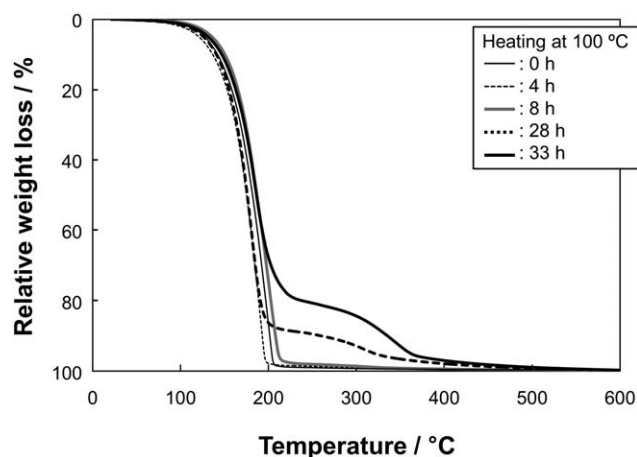


Figure 4. Relative weight loss curves for GPTMS heated at 100°C for various heating times.

silane-treated layer and the investigation of the mechanical properties of the filled rubber.

Glycidoxy Functional Silane

The starting temperature of the silane weight loss measured by TG analysis increased with polycondensation, as reported previ-

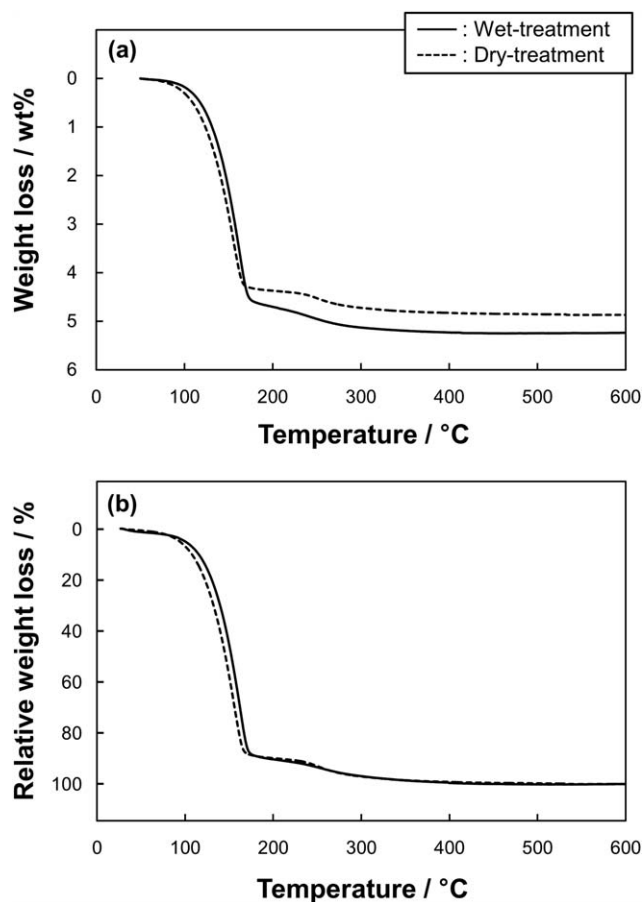


Figure 5. (a) Measured weight loss and (b) relative weight loss curves for the GPTMS-treated silica particles prepared by the wet and dry treatment methods without postheating.

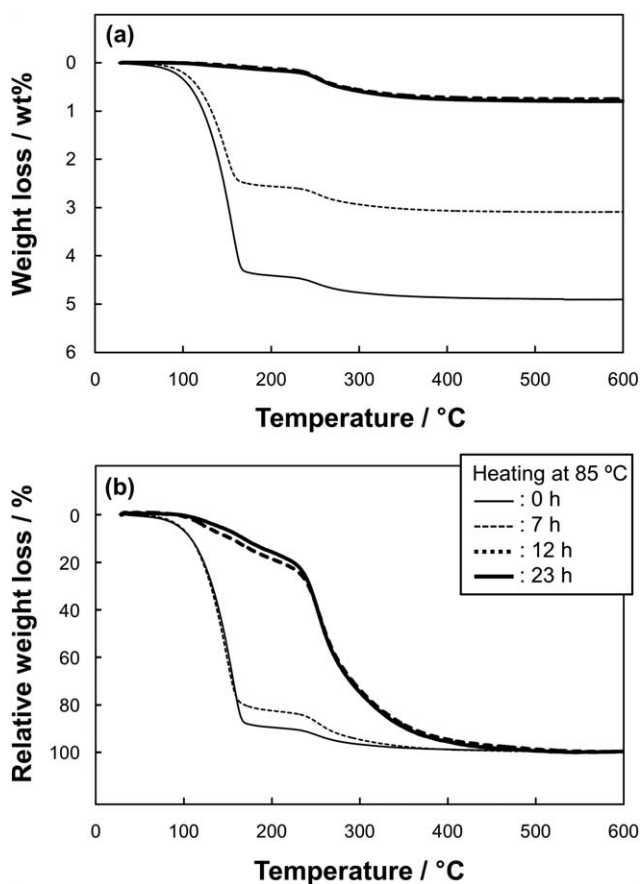


Figure 6. (a) Measured weight loss and (b) relative weight loss curves for the GPTMS-treated silica particles prepared by the dry treatment method and heated at 85°C for various heating times without acetone washing.

ously.³⁷ To confirm this, TG curves for the GPTMS heated at 100°C for various heating times were obtained and are shown in Figure 4. The weight loss of GPTMS started from about 100°C and ended at about 200°C for a heating time range of 0–8 h; there was no significant difference in the shape of the corrected TG curves. The gradual second-step weight loss appeared in the approximate range from 200 to 300°C, and the rapid third-step weight loss appeared in the approximate range from 300 to 400°C for a heating time of 28 h. The second-step weight loss became more significant for a heating time of 33 h. These results were due to the formation of polycondensed silanes by heating and increases in their molecular weight and quantity with heating time.

Figure 5 shows the measured and relative weight loss curves for the GPTMS-treated silica particles prepared by both wet and dry treatment methods without heating. There was no significant difference in the amount of adsorbed silanes with both treatment methods, as shown in Figure 5(a). The surface coverages were calculated to be 4.9 and 4.6 for the wet and dry treatments, respectively. The amount of added silane for surface treatment was equal to a surface coverage of 5; therefore, almost all of the added silane was present on the treated silica surface. In addition, there was no significant difference in the shape of the TG curves for the surfaces subjected to the wet and dry

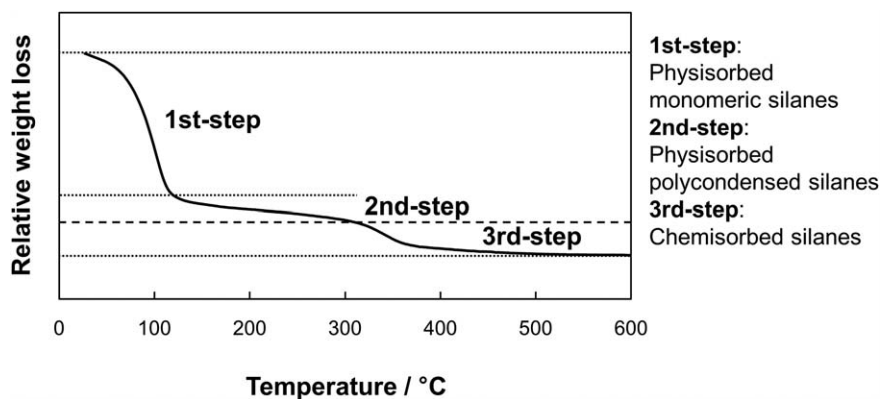


Figure 7. Schematic TG curve for the GPTMS-treated silica particles with three weight loss steps.

treatment methods [Figure 5(b)]. Three steps of weight loss were observed in the following temperature ranges: first step: 100–170°C, second step: 170–250°C, and third step: 250–400°C.

The first-step weight loss was considered to be due to monomeric physisorbed silanes. Figure 5 shows that there was a large amount of monomeric physisorbed silanes on the silica particles treated by both methods because no further heating or acetone washing were conducted after surface treatment.

GPTMS-treated particles prepared with the dry method were heated at 85°C with various heating times, and the measured TG curves are shown in Figure 6. The final weight loss and the weight loss between from approximately 100 to 170°C decreased with the heating step, as shown in Figure 6(a). There were significant differences between the relative weight loss curves for heating times of 0 and 7 h and 12 and 23 h, as shown in Figure 6(b). In the curves for 0 and 7 h, three weight loss steps were clearly observed, but most of the weight loss occurred in the first step. On the other hand, for heating times of 12 and 23 h, there was a very small weight loss in the first step. These results indicate that the monomeric physisorbed silanes were removed by heating.

The heated particles shown in Figure 7 were washed with acetone to remove the physisorbed silanes. As a result, only the third-step weight loss around 300°C was independent of the heating time, whereas the first- and second-step weight losses disappeared (the data are not shown). These results indicate that the first- and second-step weight losses were due to the physisorbed silanes, whereas the third step was due to the chemisorbed silanes. Furthermore, the first- and second-step weight losses were due to the losses of physisorbed monomeric silanes and physisorbed polycondensed silanes, respectively. The silane components in the treated layer that were considered to contribute to the three weight loss steps are schematically shown in Figure 7. The sum of the weight losses from steps 1 and 2 showed the amount of physisorbed silanes. The amount of physisorbed silanes was estimated as the ratio of this portion to the total weight loss in the vertical axis.

The amount of physisorbed silanes measured by TG analysis (Figure 6) is shown as white circles in Figure 8. At heating times of 0 and 5 h, the amount of physisorbed silane was about 90%; however, this decreased to 20–40% for heating times over

12 h. The amounts of physisorbed silane calculated from a comparison of the weight losses before and after acetone washing of the treated silica particles are shown as black circles in Figure 8. There was no significant difference in the amount of physisorbed silane measured with the two methods. These results show that TG analysis is a generally and widely useable method for the quantitative measurement of physisorbed silanes.

Figure 9 shows the surface coverage of the GPTMS-treated silica particles by the dry treatment method with various heating times before and after washing with acetone, as measured by TG analysis. The GPTMS added for surface treatment had a surface coverage of 5. The silanes detected without a heating step had a surface coverage of 4.6; this almost corresponded to the amount of added silanes. The silanes present on the silica surface (before washing) decreased, whereas the chemisorbed silanes (after washing) increased with the heating time. Almost all of the silane was present as chemisorbed silane for heating times over 12 h. However, the amount of chemisorbed silanes on the treated silica prepared by the method used in this study

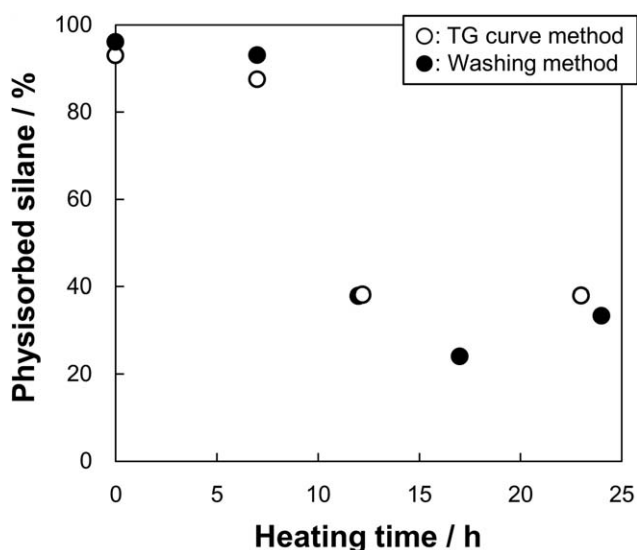


Figure 8. Amount of physisorbed silane in the GPTMS-treated layer on silica particles prepared by the dry treatment method or the acetone washing method and heated at 85°C for various heating times.

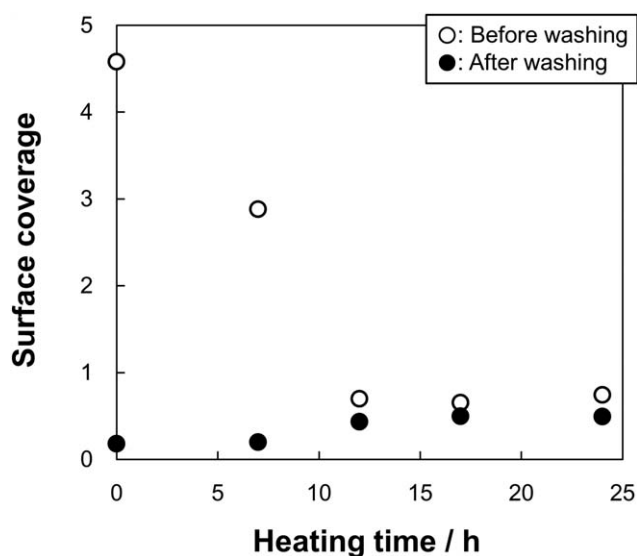


Figure 9. Surface coverage of the GPTMS-treated silica particles prepared by the dry treatment method and heated at 85°C for various heating times before and after acetone washing.

was very small. Heating at 85°C increased the amount of chemisorbed silane; however, the increase was very small.

Amino-Functional Silane

Figure 10 shows TG curves for APTES heated at 100°C for various heating times. The weight loss began below 100°C and was completed below 200°C for the sample that was not heated. These temperatures were lower than those for GPTMS shown in Figure 4. The weight loss over 200°C began to increase for heating times over 4 h and increased significantly for heating times of 28 h or greater; the same tendency was observed for GPTMS (Figure 4). However, the weight loss over 200°C was far larger for APTES than for GPTMS; this indicated that the amount of polycondensed silanes formed by heating was larger for the APTES-treated silica than for the GPTMS-treated silica. Salon *et al.*¹⁴ reported that the polycondensation rate for amino-functional silanes was far larger than those for other functional silanes. The polycondensation rate on the treated particles was

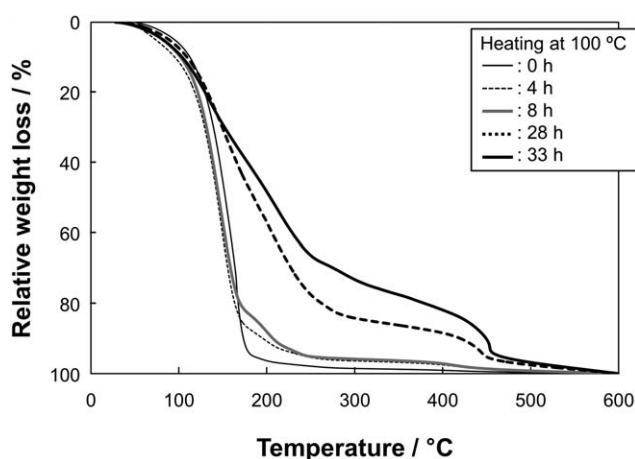


Figure 10. Relative weight loss curves for APTES heated at 100°C for various heating times.

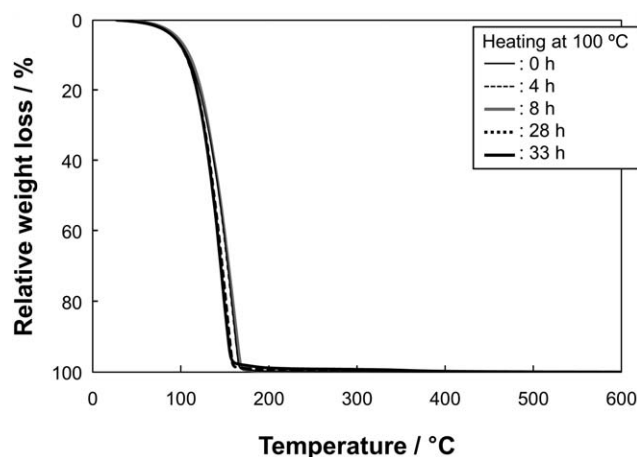


Figure 11. Relative weight loss curves for MrPTMS heated at 100°C for various heating times.

thus also expected to be larger for treatment with amino-functional silane, and this will be discussed in a future report.

Mercapto-Functional Silane

Figure 11 shows TG curves for MrPTMS heated at 100°C for various heating times. The weight loss began below 100°C and was completed below 200°C for the sample that was not heated.

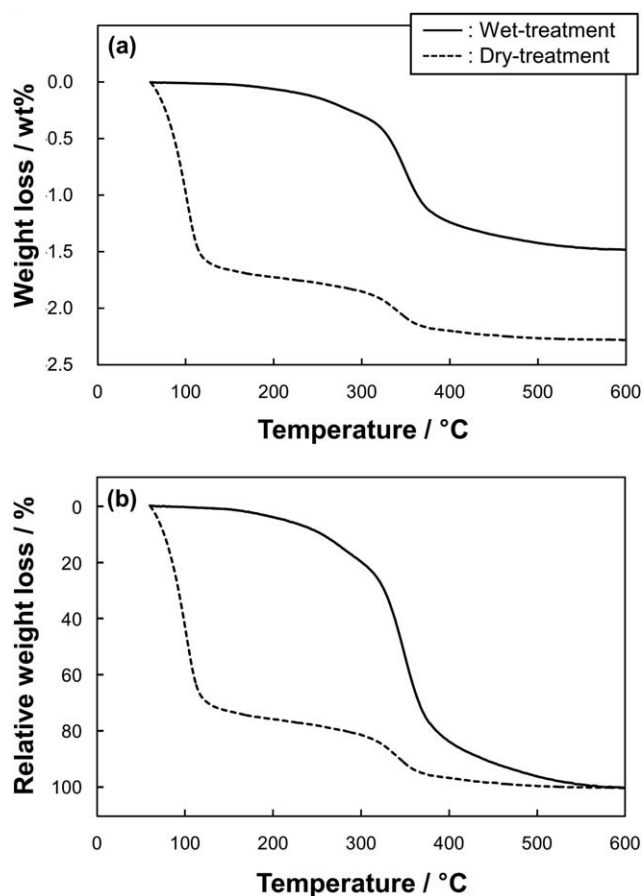


Figure 12. (a) Measured weight loss and (b) relative weight loss curves for MrPTMS-treated silica particles prepared by the wet and dry treatment methods without postheating.

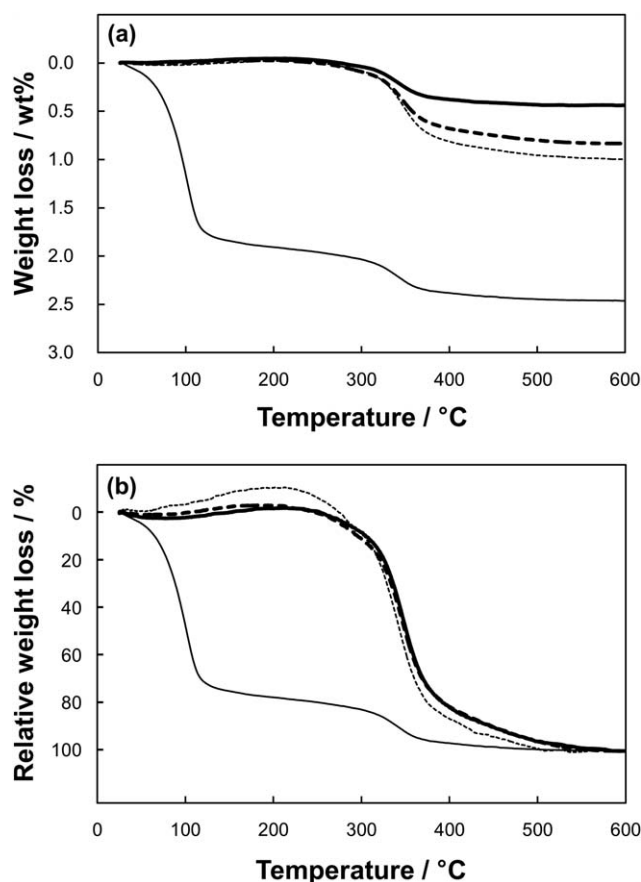


Figure 13. (a) Measured weight loss and (b) relative weight loss curves for MrPTMS-treated silica particles prepared by the dry treatment method and heated at 120°C for various heating times without acetone washing.

However, no weight loss was observed over 200°C, even for heated MrPTMS; this was quite different from those observed for GPTMS (Figure 4) and APTES (Figure 10).

Figure 12 shows the measured weight loss and relative weight loss curves for the MrPTMS-treated silica particles by both the wet and dry treatment methods without heating. There was large difference in the TG curves between the wet and dry treatment methods. Three weight loss steps were observed for the silica treated by the dry method. The approximate temperature ranges were as follows: first step: 80–120°C, second step: 120–310°C, and third step: 310–500°C. This tendency was the same as that observed for the GPTMS-treated silica (Figure 5); however, the temperature ranges were different. The MrPTMS added for surface treatment was equivalent to a surface coverage of 5. The detected silanes had a surface coverage of 4.3; this was almost the same as the surface coverage of the added silanes. In contrast, only two weight loss steps were observed for the silica treated by the wet method, where the first weight loss step was absent. The detected silanes had a surface coverage of 2.6; this was far smaller than that obtained with the dry treatment method. In the wet treatment method, acetone was evaporated with a rotary evaporator at 35°C for 30 min under decompression. Therefore, some of the MrPTMS may also have evaporated with the acetone during this process. In addition, Figure 11

showed no evidence that the polycondensed silanes were formed by the heating step.

Figure 13 shows the measured weight loss and relative weight loss curves for MrPTMS-treated silica particles prepared by the dry treatment method and heated at 120°C for various heating times. The first-step weight loss disappeared for the samples that were heated, and the total weight loss (adsorbed silanes) decreased with the heating time [Figure 13(a)]. Three weight loss steps were observed for the MrPTMS-treated silica that was not heated. However, only the third weight loss step was observed for heating times in the range from 7 to 24 h. The shape of the relative weight loss curves were similar [Figure 13(b)]; this indicated that the physisorbed monomeric silanes were not changed to polycondensed silanes with heating.

As shown in Figure 13(b), there were some curves in which the weight appeared to increase by heating. However, as shown in Figure 11(a), the weight loss at 600°C of these curves was very small, and these curves were greatly expanded in the vertical axis direction, as shown in Figure 13(b), and only gave the appearance of a weight gain.

Figure 14 shows the measured weight loss and relative weight loss curves for the MrPTMS-treated silica particles prepared by the dry treatment method and heated at 120°C for various heating times after acetone washing to remove the physisorbed

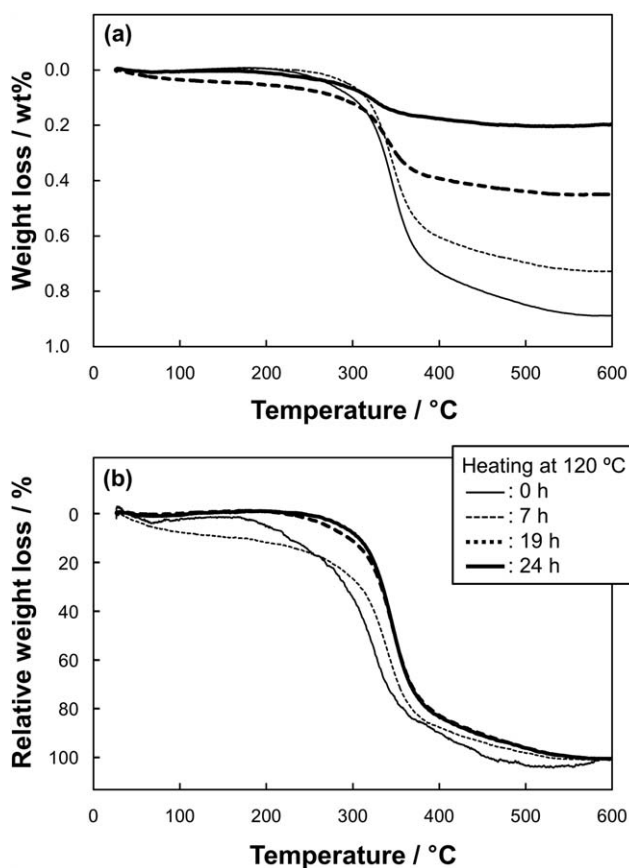


Figure 14. (a) Measured weight loss and (b) relative weight loss curves for MrPTMS-treated silica particles prepared by the dry treatment method and heated at 120°C for various heating times after acetone washing.

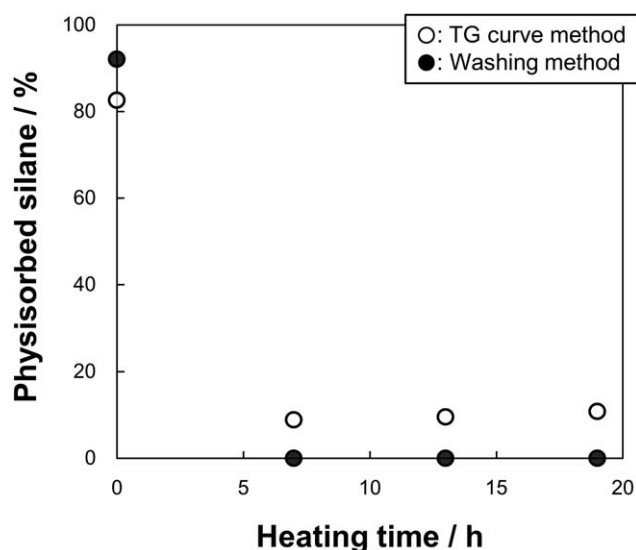


Figure 15. Amount of physisorbed silane in the MrPTMS-treated layer on silica particles prepared by the dry treatment method and the acetone washing method and heated at 120°C for various heating times.

silanes. The first-step weight loss was absent because of the acetone washing step [Figure 14(a)]. All of the relative weight loss curves were almost the same, regardless of the heating time [Figure 14(b)].

Figure 15 shows the amount of physisorbed silanes for the MrPTMS-treated silica particles prepared by the dry treatment method and heated at 120°C for various heating times. The amounts calculated from TG analysis [Figure 13(a)] are shown as white circles in Figure 15. The amount of physisorbed silanes was about 80% for the sample that was not heated. However, this decreased to below 10% for heating times over 7 h. The amount of physisorbed silanes calculated from a comparison of the weight losses before and after acetone washing of the treated silica particles are shown as black circles in Figure 15. The results from the two different methods were in good agreement; this confirmed that the amount of physisorbed silanes could be estimated from TG curve measurements of the treated particles. The surface coverage of the sample that was not heated was 4.2; however, the surface coverage of those samples with heating times greater than 7 h was approximately 1 or less; this indicated very small amounts of adsorbed silanes.

CONCLUSIONS

We investigated a new method for the estimation of the amount of physisorbed silanes in the silane-treated layer on silica particle surfaces from weight loss curves measured by TG analysis. Silica particles were treated with GPTMS or MrPTMS with both dry and wet treatment methods. The following results were obtained:

1. In the GPTMS-treated system, the TG curve showed weight losses with three steps: 100–170°C (first step), 170–250°C (second step), and 250–400°C (third step). These were attributed to physisorbed monomeric silanes, physisorbed polycondensed silanes, and chemisorbed silanes, respectively. A similar tendency was observed for the MrPTMS-treated system.

2. The amount of physisorbed silanes in the silane-treated layer were measured from the TG curve for the treated silica. The values obtained were almost equal to those measured from a comparison of the weight losses for treated particles before and after acetone washing as a conventional general technique. Thus, we confirmed that the amount of physisorbed silanes could be measured easily from the TG curves for treated particles. Furthermore, the amounts of physisorbed monomeric silanes and physisorbed polycondensed silanes could be measured separately by our new method.
3. There was no significant difference in the weight loss curves for the GPTMS-treated silica particles prepared by the dry and wet treatment methods. However, there was a large difference for the MrPTMS-treated silica. In the latter samples, there were greater amounts of monomeric MrPTMS; these could easily be removed during the evaporation process of the wet treatment method.

ACKNOWLEDGMENTS

The authors are grateful to Denki Kagaku Kogyo Kabushiki Kaisya (Tokyo, Japan) and Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan), for their kind donations of silica particles and silane coupling agents, respectively.

REFERENCES

1. Plueddemann, E. P. *Silane Coupling Agents*, 2nd ed.; Plenum: New York, 1991.
2. Johansson, U.; Holmgren, A.; Forsling, W.; Frost, R. L. *Clay Miner.* **1999**, *34*, 239.
3. Naviroj, S.; Koenig, J. L.; Ishida, H. *J. Adhes.* **1985**, *18*, 93.
4. Miller, J. D.; Ishida, H. *Langmuir* **1986**, *2*, 127.
5. Culler, S. R.; Ishida, H.; Koenig, J. L. *J. Colloid Interface Sci.* **1986**, *109*, 1.
6. Ikuta, N.; Maekawa, Z.; Hamada, H.; Ichihashi, M.; Nishio, E. *J. Mater. Sci.* **1991**, *26*, 4663.
7. Graf, R. T.; Koenig, J. L.; Ishida, H. *J. Adhes.* **1983**, *16*, 97.
8. Ishida, H.; Miller, J. D. *Macromolecules* **1984**, *17*, 1659.
9. Marrone, M.; Montanari, T.; Busca, G.; Conzatti, L.; Costa, G.; Castellano, M.; Turturro, A. *J. Phys. Chem. B* **2004**, *108*, 3563.
10. Yang, R.; Liu, Y.; Wang, K.; Yu, J. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 413.
11. Fujii, T.; Uchimura, T. *Anal. Methods* **2015**, *7*, 2611.
12. Bukleski, M.; Ivanovski, V. *Maced. J. Chem. Chem. Eng.* **2014**, *33*, 267.
13. Hozoji, H.; Horie, O.; Ogata, M.; Numata, S.; Kinjo, N. *Kobunshi Ronbunshu* **1990**, *47*, 483.
14. Salon, M. C. B.; Bayle, P. A.; Abdelmouleh, M.; Boufi, S.; Belgacem, M. N. *Colloids Surf. A* **2008**, *312*, 83.
15. Griswold, C.; Cross, W. M.; Kjerengtroen, L.; Kellar, J. J. *J. Adhes. Sci. Technol.* **2005**, *19*, 279.
16. Miller, J. D.; Hoh, K. P.; Ishida, H. *Polym. Compos.* **1984**, *5*, 18.

17. Suzuki, N.; Ishida, H. *Compos. Interfaces* **2005**, *12*, 769.
18. Krasnoslobodtsev, A. V.; Smirnov, S. N. *Langmuir* **2002**, *18*, 3181.
19. Miller, A. C.; Berg, J. C. *Compos. A* **2003**, *34*, 327.
20. Benkoski, J. J.; Kramer, E. J.; Yim, H.; Kent, M. S.; Hall, J. *Langmuir* **2004**, *20*, 3246.
21. Abel, M. L.; Allington, R. D.; Digby, R. P.; Porritt, N.; Shaw, S. J.; Watts, J. F. *Int. J. Adhes. Adhes.* **2006**, *26*, 16.
22. Jensen, R. E.; Palmese, G. R.; McKnight, S. H. *Int. J. Adhes. Adhes.* **2006**, *26*, 103.
23. Rattana, A.; Abel, M. L.; Watts, J. F. *Int. J. Adhes. Adhes.* **2006**, *26*, 28.
24. Castellano, M.; Conzatti, L.; Turturro, A.; Costa, G.; Busca, G. *J. Phys. Chem. B* **2007**, *111*, 4495.
25. Abdelmouleh, M.; Boufi, S.; Belgacem, M. N.; Dufresne, A. *Compos. Sci. Technol.* **2007**, *67*, 1627.
26. Dohi, H.; Horiuchi, S. *Langmuir* **2007**, *23*, 12344.
27. Liu, X.; Zhao, S. *J. Appl. Polym. Sci.* **2008**, *108*, 3038.
28. Han, J.; Zuo, C.; Gu, Q.; Li, D.; Wang, X.; Xue, G. *Appl. Surf. Sci.* **2008**, *255*, 2316.
29. Garcia, N.; Benito, E.; Guzman, J.; de Francisco, R.; Tiemblo, P. *Langmuir* **2010**, *26*, 5499.
30. Stockelhuber, K. W.; Svistkov, A. S.; Pelevin, A. G.; Heinrich, G. *Macromolecules* **2011**, *44*, 4366.
31. Zhao, Z.; Zhao, X.; Gong, G.; Zheng, J.; Liang, T.; Yin, C.; Zhang, Q. *Polym. Plast. Technol. Eng.* **2012**, *51*, 268.
32. Liu, J.; Wu, S.; Dong, E. *J. Appl. Polym. Sci.* **2013**, *128*, 2337.
33. Suzuki, N.; Yatsuyanagi, F.; Ito, M.; Kaidou, H. *J. Appl. Polym. Sci.* **2002**, *86*, 1622.
34. Demjén, Z.; Pukánszky, B.; Földes, E.; Nagy, J. *Polymer* **1999**, *40*, 1763.
35. Blagojević, S. L.; Kovačević, V.; Leskovac, M.; Vrsaljko, D.; Volovšek, V.; Nover, C. *e-Polymers* **2004**, *4*, 384.
36. Altmann, S.; Pfeiffer, J. *Monatsh. Chem.* **2003**, *134*, 1081.
37. Nakamura, Y.; Yamazaki, R.; Fukuda, T.; Shitajima, K.; Fujii, S.; Sasaki, M. *J. Adhes. Sci. Technol.* **2014**, *28*, 1895.
38. Fukuda, T.; Fujii, S.; Nakamura, Y.; Sasaki, M. *Compos. Interfaces* **2013**, *20*, 635.
39. Nakamura, Y.; Honda, H.; Harada, A.; Fujii, S.; Nagata, K. *J. Appl. Polym. Sci.* **2009**, *113*, 1507.
40. Nakamura, Y.; Nishida, Y.; Honda, H.; Fujii, S.; Sasaki, M. *J. Adhes. Sci. Technol.* **2011**, *25*, 2703.
41. Nakamura, Y.; Nishida, Y.; Fukuda, T.; Fujii, S.; Sasaki, M. *J. Appl. Polym. Sci.* **2013**, *128*, 2548.
42. Fukuda, T.; Yamazaki, R.; Fujii, S.; Nakamura, Y.; Sasaki, M. *J. Adhes. Sci. Technol.* **2013**, *27*, 1641.
43. Fukuda, T.; Fujii, S.; Nakamura, Y.; Sasaki, M. *J. Appl. Polym. Sci.* **2013**, *130*, 322.