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Properties of silicious film on polycarbonate substrate prepared by vacuum ultraviolet irradiation: Effect of intermediate silane layer

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Abstract

We studied the effect of vacuum ultraviolet irradiation (VUV) on siliceous coatings of polycarbonate substrates derived by the sol–gel method, with the aim of improving the abrasion resistance of the substrate surface. The experimental conditions to insert an intermediate silane layer between siliceous film and polycarbonate substrate were examined in order to enhance the abrasion resistance and adhesion strength, using four kinds of silane coupling reagents, i.e., 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilne, phenyltriethoxysilne and ethyltriethoxysilane. After the formation of intermediate silane layer on the PC substrate, siliceous film was further prepared on it by VUV irradiation of the spin-coated sol solution containing methyltriethoxysilane and colloidal silica. Among the silanes examined in this research, 3-aminopropyltrimethoxysilne notably played a role as an appropriate intermediate layer for the enhanced abrasion resistance of siliceous-coated polycarbonate substrate. The average transmittance was kept as high as 70% even after abraded 140 turns.

Keywords: Sol–gel processes; Interfaces; Wear resistance; Silicate; Polycarbonate

1. Introduction

Currently, polycarbonate (PC)[1] is expected to be available as the alternative material for the glass windows of cars, based upon its lightness, transparency and impact resistance.[2] Nevertheless, the poor abrasion resistance, due to the low surface hardness, has to be overcome in order to practically use it for such windows of cars.

Previously, the present authors[3] examined the abrasion resistance of siliceous-coated PC substrate,[4] i.e., (i) the siliceous coating of PC substrate by sol–gel technique[5] in order to form the siloxane network, due to the hydrolysis of alkoxide, and (ii) the vacuum ultraviolet (VUV) irradiation[6–9] in order to remove the organic constituents and accelerate the densification and adhesion of film without heating at several hundreds of degrees Celsius. The adhesion strength between film and substrate could be enhanced by the simultaneous heating of siliceous-coated PC substrate while VUV irradiation. However, the heating of siliceous-coated PC substrate should be limited to the minimum, because the heating may damage the PC substrate even if the heating temperature is lower than the glass transition temperature of PC.[10] Then further chemical process seems to be needed in order to enhance the interfacial adhesion without the simultaneous heating. Previously, Li and Wilkes[11] reported that the adhesion between sol–gel coated layer and polymer substrate is chemically conducted by the hydrolysis of 3-aminopropyltriethoxysilane (3-APS) and subsequent condensation. Also, the adhesion between hybrid organic–inorganic silsesquioxane/silica based sol–gel coating and substrate appeared to be improved by treating the polymeric substrate with a solution containing 3-APS.[12,13] These facts suggest that the utilization of silane coupling agent as an intermediate layer is expected to enhance the adhesion strength between film and PC substrate. On the basis of such background, this paper describes the utilization of intermediate silane layer, as well as the VUV irradiation, in order to enhance the abrasion resistance and adhesion strength of siliceous-coated PC substrate.

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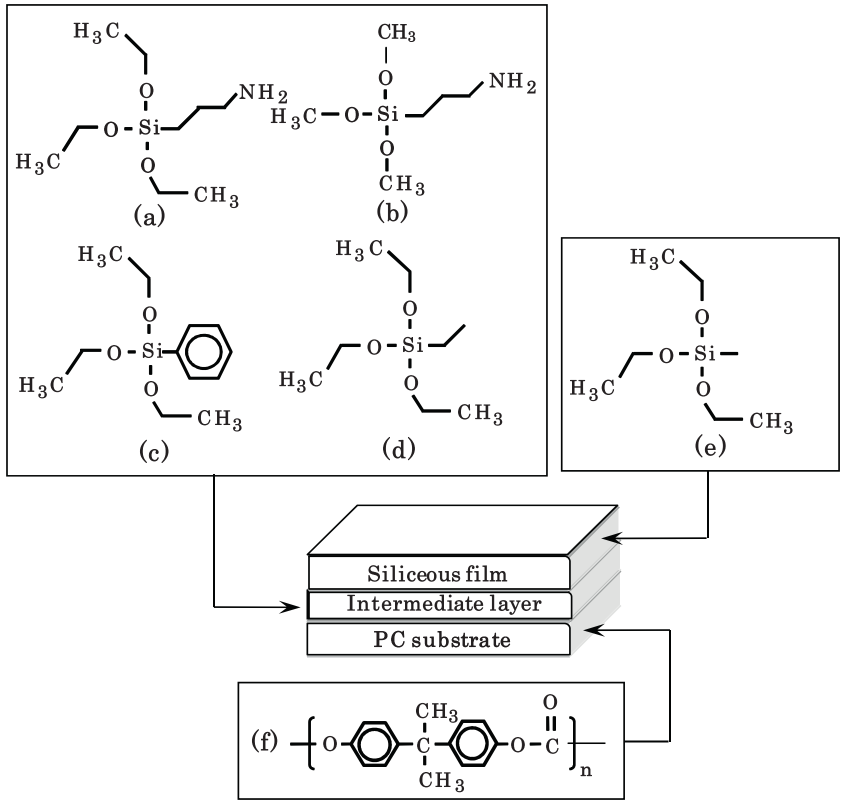

Fig. 1. Chemical structures of four kinds of silanes for the formation of intermediate layer and one silane for the formation of siliceous film used in this research: (a) 3-APS, (b) 3-APMS, (c) PTES, (d) ETES, and (e) MTES.

2. Experimental procedures

2.1. Preparation of coating solution and formation of layer/film

Five kinds of silane solutions were used for the coating of PC substrate as intermediate and siliceous films. The silane compounds used in this research are shown in Fig. 1. In order to prepare the intermediate layer on the PC substrate with the sizes of 30 mm × 30 mm × 0.5 mm (Iupilon® sheet NF-2000; Mitsubishi Engineering-Plastics, Tokyo), four kinds of silane coupling agents were used: 3-aminopropyltriethoxysilane (3-APS, Fig. 1(a)), 3-aminopropyltrimethoxysilne (3-APMS, Fig. 1(b)), phenyltriethoxysilne (PTES, Fig. 1(c)), ethyltriethoxysilane (ETES, Fig. 1(d)). Firstly, 0.1 cm^3 of each silane coupling agent was put on the PC substrate. Then the PC substrate was spin-coated under the conditions of 500 rpm for 10 s, followed by 1000 rpm for 50 s.

Furthermore, the silane sol solution for the formation of siliceous film was prepared by (i) mixing of 10.00 cm^3 methyltriethoxysilane (MTES; $CH_3Si(OC_2H_5)_3$, Aldrich, Fig. 1(e)), 16.44 cm^3 colloidal silica (CS, LUDOX®LS, Aldrich), 12.00 cm^3 de-ionized water and 0.1 cm^3 of acetic acid, (ii) addition of 40 cm^3 ethanol to the mixed solution for 24 h, (iii) heating of solution and condensation at 50 °C for 1.5–2 h while being stirred under a reduced pressure, and by (iv) addition of *iso*-butyl alcohol (IBA, $(CH_3)_2CHCH_2OH$, Wako, Tokyo) and 2-ethoxyethanol (EE, $(C_2H_5O)CH_2CH_2OH$, Wako, Tokyo). Firstly, 4–5 droplets of the sol solution prepared as above were put on the intermediate silane layer on the PC substrate. Then the PC substrate was spin-coated under the conditions of 500 rpm for 10 s, being followed by 1000 rpm for 50 s.

2.2. VUV irradiation and subsequent heat treatment

A xenon excimer lamp (USHIO UER 20H-172VB, Center wavelength: 172 nm, half bandwidth: 14 nm) was used for the irradiation to PC substrate under N_2 atmosphere. Eventually, with flowing N_2 gas, the specimen was irradiated with VUV at the irradiation distance of 1.4 cm. The effective light power density was about 10 mW cm^{-2} at the substrate surface. The heat treatment of the layer/film after the irradiation was conducted in a drying oven controlled at 90 °C.

2.3. Thin film characterization and mechanical testing

Abrasion test was conducted as previously reported.[3] After abrading specimen for the desired turns by an abrasion tester with steel wool #0000 on the tip under loading 1 kg, the transmittance of the abraded sample was measured with a UV–vis spectroscope (UV-Vis; JASCO V-550) in order to evaluate the abrasion resistance of each sample. The average transmittance was defined as the value that could be obtained by dividing total transmittance by the measurement number. Each abrasion test was conducted for three specimens and the results were shown as the graph with error bars with one standard deviation. For the tape test (grid tape method),[14] the film on the test specimen was gridironed so as for the cutting to reach the substrate surface, followed by removing the tape at once. The tape was peeled off from the substrate at once and the adhesion appearance of the film was observed.

The microstructure of coated surface after abrasion tests was observed using a scanning electron microscope (SEM; SU-8000, Hitachi High-Technologies, Tokyo) with an accelerating voltage of 5 kV. The Everhart–Thornley detector set on the specimen chamber wall (lower detector) was used for the observation. A dynamic ultra-microhardness tester (DUH-211, Shimadzu, Kyoto) was used for the measurement of the Martens hardness of the film.

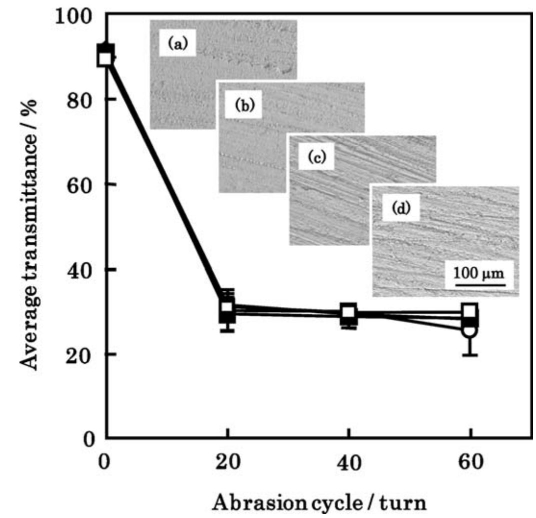

Fig. 2. Changes in average transmittance of silane-coated PC substrate with increasing abrasion cycle, together with typical SEM micrographs (abrasion for 60 turns). Note that the PC substrate was coated once with four kinds of silanes, followed by the VUV irradiation for 5 min and then the heat treatment at 90 °C for 30 min. (a) 3-APS (●)-coated PC substrate; (b) 3-APMS (○)-coated PC substrate; (c) PTES (■)-coated PC substrate; (d) ETES (□)-coated PC substrate.

3. Results and discussion

3.1. Effect of silane layer formed on PC

Prior to checking the effect of intermediate silane layer on the adhesion between siliceous film and PC substrate, the PC substrate was coated with four kinds of silane layers. These silanes were coated onto the PC substrate and VUV was irradiated for 5 min, followed by heat treatment at 90 °C for 30 min. Firstly, we tried to measure the thickness of intermediate silane layer through the beating behavior of UV–vis spectra. However, the beating was too small to calculate the thicknesses of intermediate silane layers.[3] Instead, we assumed the thickness of <0.5 µm on the basis of the depth of indentation conducted in order to evaluate the Martens hardness. The changes in average transmittance with increasing abrasion cycle of the PC substrate having the individual silane layer are shown in Fig. 2, together with typical SEM micrographs. The overall trend revealed that the average transmittance was reduced with abrasion cycle to 20 turns but that it remained unchanged with increasing abrasion cycle from 20 to 60 turns. The SEM micrographs showed that the scratches were formed in a linear fashion, irrespective of the kinds of silanes. Thus, the abrasion resistance of PC substrate appears to be independent upon the kind of silane.

Since the silane layer could be successfully formed on the surface of PC substrate, we checked the adhesion strength between the PC substrate and the silane layer by the grid tape test. Fig. 3 shows the typical SEM micrographs of the surfaces of the silane-coated PC substrates after the tape test. The fashion for the

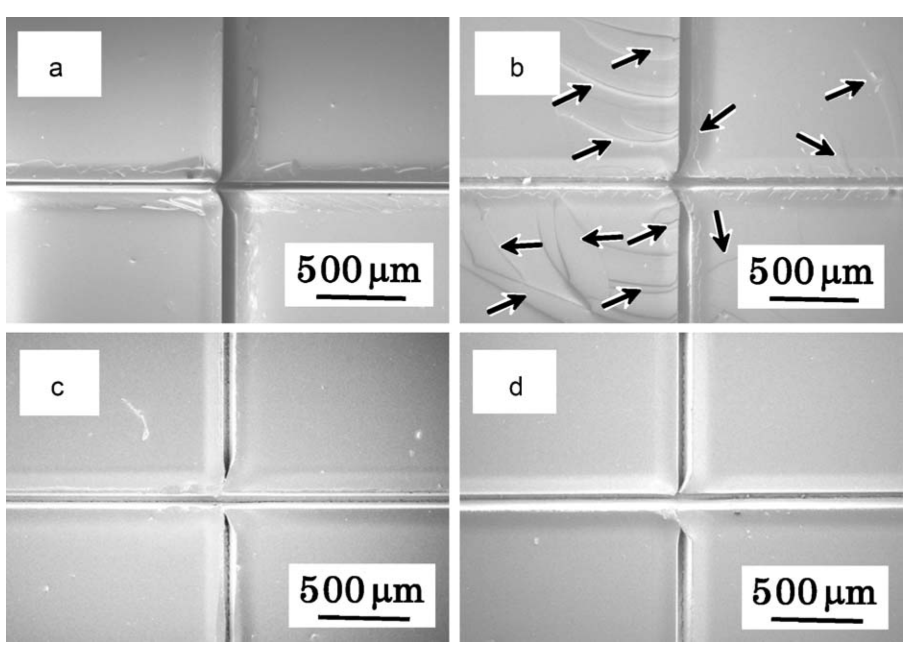

Fig. 3. SEM micrographs of the surfaces of silane-coated PC substrates after the tape test. Note that each PC substrate was coated once by silane, followed by the VUV irradiation of 5 min and heat treatment at 90 °C for 30 min. (a) 3-APS-coated PC substrate; (b) 3-APMS-coated PC substrate; (c) PTES-coated PC substrate; (d) ETES-coated PC substrate.

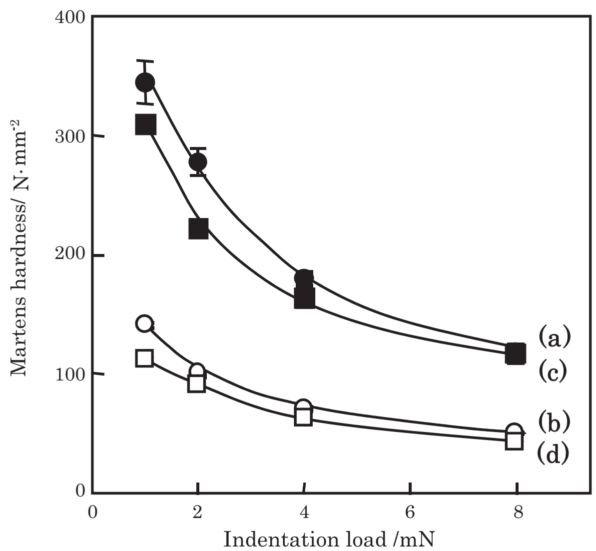

Fig. 4. Changes in Martense hardness of silane-coated PC substrate with increasing indentation load. Note that the PC substrate was coated once by a silane, followed by the VUV irradiation of 5 min and the heat treatment at 90 °C for 30 min; (a) 3-APS-coated PC substrate; (b) 3-APMS-coated PC substrate; (c) PTES-coated PC substrate; (d) ETES-coated PC substrate.

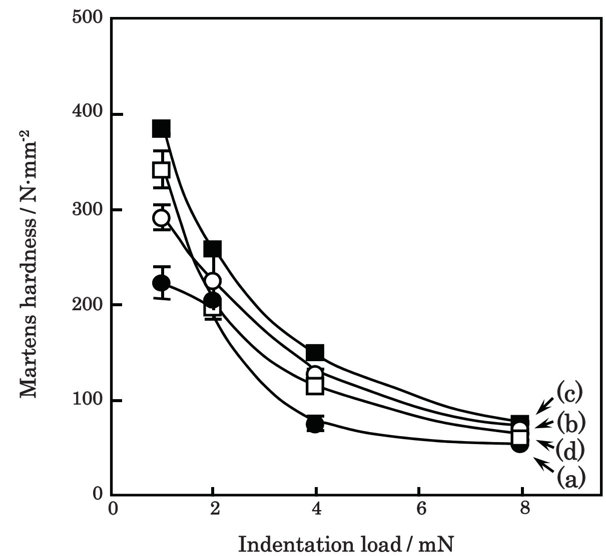

Fig. 5. Changes in Martens hardness of PC substrate having siliceous film and intermediate silane layer with increasing indentation load. Note that the PC substrate was coated by silane, followed by the VUV irradiation for 5 min: the siliceous film was further coated onto this substrate, followed by the irradiation for 5 min; finally, the heat treatment was conducted at 90 °C for 30 min. The kinds of silanes used for the formation of intermediate layer: (a) 3-APS, (b) 3-APMS, (c) PTES, and (d) ETES.

exfoliation of silane layer from the PC substrate was differed, being dependent upon the kinds of silanes. When 3-APS was used as the coating layer, the resulting layer was exfoliated along the grid lines (Fig. 3(a)). Similar exfoliation was observed when PTES and ETES were used as the silane layers (Fig. 3(c) and (d)). The noted exfoliation was observed when 3-APMS was used as the coating layer; the exfoliation was observed not only in the places along the grid lines but also within the square places (Fig. 3(b); see arrow marks). Since 3-APMS is sensitive to the moisture, such difference in exfoliation behavior may be attributed to the hydrolysis of 3-APMS. Details will be discussed later.

Furthermore, the Martens hardness values of silane-coated PC substrates were measured, because the surface hardness, as well as adhesion strength, may also be a key factor for the practical use. Fig. 4 shows the relationship between indentation load and Martens hardness of the silane-coated PC substrates. The overall trend revealed that the Martens hardness of the PC substrate decreased as the indentation load increased from 1 to 8 mN. When 3-APS was used as the coating layer, Martens hardness decreased from 345 to 119 N mm^{-2} with increasing the indentation load from 1 to 8 mN (Fig. 4(a)). The behavior similar to the case of 3-APS was observed, i.e., from 311 to 118 N mm^{-2}, when PTES was used as the coating layer (Fig. 4(c)). On the other hand, Martens hardness values of 3-APMS and ETES-coated PC substrates were reduced from 142 to 51 N mm^{-2} and from 113 to 44 N mm^{-2}, respectively, with increasing indentation load from 1 to 8 mN (Fig. 4(b) and (d)).

The above results show that the Martens hardness values of 3-APS and PTES-coated PC substrates are higher than those of 3-APMS and ETES-coated PC substrates. Details of not only such Martens hardness but also other as-mentioned phenomena will be discussed again in the next section.

3.2. Combined effects of siliceous film and intermediate silane layer formed on PC

In this section, some experimental conditions were checked in order to enhance the adhesion strength between siliceous film and PC substrate having an intermediate silane layer. Note that VUV was irradiated for 5 min to the specimen, followed by the heat treatment at 90 °C for 30 min. As mentioned before, the thickness of silane layer was estimated to be less than 500 nm, whereas the film thickness of the siliceous film was approximately 2 μm (beat method[3] on the basis of UV–vis spectra). Fig. 5 shows the Martens hardness of the siliceous-coated PC substrates, using intermediate silane layer. The overall trend revealed that Martens hardness of the PC substrate having an intermediate silane layer, together with siliceous film, decreased with increasing indentation load from 1 to 8 mN.

When only silane layer was formed on the PC substrate, the Martens hardness value was varied, according to the kind of silane, i.e., 3-APS and PTES-coated PC substrate > 3-APMS and ETES-coated PC substrate. When the siliceous film was further prepared on the silane layer, no marked difference in Martens hardness was observed, regardless of higher Martens hardness values of 3-APS and PTES-coated PC substrates rather than those of 3-APMS and ETES-coated PC substrates. Here the Martens hardness was measured at and near the surface of PC substrate having the siliceous film and intermediate silane layer. Since the thickness of siliceous film (approximately 2 μm) was larger than that of intermediate layer (less than 0.5 μm), it would appear that the thin intermediate layer does not affect the Martens hardness but chiefly affects the adhesion strength.

We further checked the abrasion resistance of PC substrate with siliceous film, inserting the intermediate layer. Fig. 6 shows

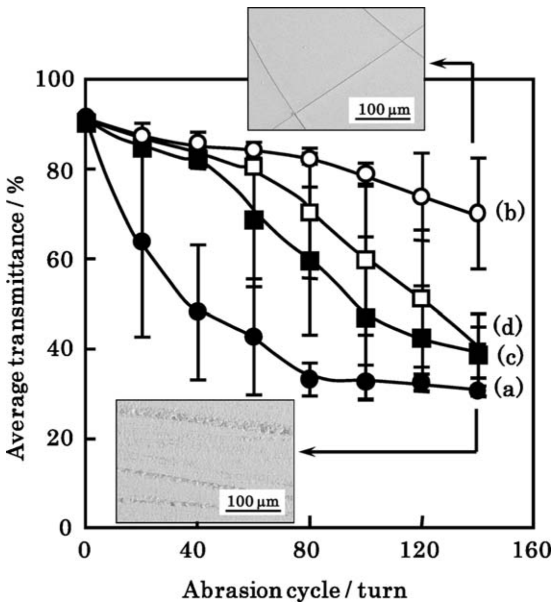

Fig. 6. Changes in average transmittance of the PC substrate having siliceous film and an intermediate silane layer with increasing abrasion cycle, together with typical SEM micrographs. Note that the PC substrate was coated by a silane, followed by the VUV irradiation for 5 min; the siliceous film was further coated onto this substrate, followed by the irradiation for 5 min; finally, the heat treatment was conducted at 90 °C for 30 min. The kinds of silanes used for the formation of intermediate layer: (a) 3-APS, (b) 3-APMS, (c) PTES, and (d) ETES.

the changes in average transmittance of the PC substrate having the siliceous film and an intermediate layer with increasing abrasion cycle, together with typical SEM micrographs. When 3-APS was used as an intermediate layer, the average transmittance decreased down to below 30% after 140 turns of abrasion (Fig. 6(a)). When PTES and ETES were used as the intermediate layers, the average transmittance kept being 38% and 39% after abraded for 140 turns (Fig. 6(c) and (d)). The average transmittance was reduced down to around 70% after abraded for 140 turns when 3-APMS was used as intermediate layer (Fig. 6(b)). The average transmittance of PC substrate having intermediate layer and siliceous film after 140 turns of abrasion may be classified, according to the kind of silane used for intermediate layer, i.e., approximately 70% for 3-APMS > 40% for ETES and PTES > 30% for 3-APS. Among the convex and concave curves shown in Fig. 6, the concave curves show the poor abrasion resistance (i.e., the utilization of intermediate silane layer prepared using 3-APS and PTES), whereas the convex curves indicate the excellent abrasion resistance of siliceous film (i.e., the utilization of intermediate silane layers prepared using 3-APMS and ETES). Thus the excellent abrasion resistances of PC substrates having siliceous film, which were achieved by the utilization of intermediate layers prepared using 3-APMS and ETES, appear to be affected by the Martens hardness of 3-APMS and ETES-coated PC substrates (see Fig. 4).

On the SEM micrographs, many scratches were observed all over the film surfaces when 3-APS was used as the intermediate layer, whereas the film surfaces of abraded specimen having the 3-APMS intermediate layer showed the noted appearance, i.e., the presence of some cracks. Such cracks seem to come from the strains introduced by the abrasion test, instead of the resistance to the scratches.

The above results show that the silane layer does not contribute to the Martens hardness but enhances the abrasion resistance. Among four kinds of silanes used as the intermediate layers, 3-APMS has a noted effect on the enhancement of abrasion resistance.

Since the abrasion resistance could be enhanced by inserting the 3-APMS layer between PC substrate and siliceous film, we further checked the adhesion strength with tape test. Fig. 7 shows the typical SEM micrographs of film surfaces after the tape test. In the case of 3-APS as an intermediate layer, the exfoliation occurred along the grid lines and the exfoliated films were present along the grid lines (Fig. 7(a); see arrow marks). In the case of 3-APMS as intermediate layers, the exfoliation was observed along the grid lines, while the cracks were observed over the film surfaces (Fig. 7(b); see arrow marks).

After the tape test, the Si mapping on the surfaces of PC substrate with silane intermediate layer and siliceous film was conducted by using EDX. Typical results are shown in Fig. 8, together with the SEM micrographs and EDX/SEM images after the tape test. SEM micrograph and EDX results of the PC substrate having 3-APS as intermediate layer and siliceous film showed that the film and intermediate layer were exfoliated along the grid lines, but that the silane layer and/or siliceous film remained on the PC substrate (Fig. 8(a)). On the other hand, when 3-APMS was used as intermediate layer, the EDX results showed that the silane layer, as well as the siliceous film, was exfoliated from some parts but both layer and film remained in square parts (right bottom side; Fig. 8(b)). It is therefore proved that the 3-APMS has noted adhesion to the PC substrate than the case of siliceous film. The exfoliation behavior, as well as the adhesion properties of siliceous layer with intermediate silane layer, seems to be varied, according to the functional group of intermediate silane layer. It would be probable that the condensation rate of 3-APMS with methoxy group may be higher than the case of silane layers with ethoxy group, thereby showing the exfoliation due to the rapid volume changes.

On the basis of the results shown above, we considered the probable reaction mechanisms among 3-APMS, PC and MTES. The overall reaction scheme predicted by the molecule structures is shown in Fig. 9. Based upon the previous report regarding the reactivity between 3-APS and PC,[11] the bonding reaction between 3-APMS and PC substrate seems to occur by the formation of urethane group (see the squared region), due to the donation of lone electron pair on the nitrogen atom of 3-APMS to the carbonyl group in PC (Route (i)). When the siliceous film formed by the sol–gel reaction of MTES was further coated onto the 3-APMS-coated PC substrate, the hydrolysis and condensation of MTES and 3-APMS may be repeated by the conversion of silanol group (Si–OH) to siloxane group (Si–O–Si), resulting in the formation and enhancement of bonding between 3-APMS and MTES (Routes (ii)).

As shown in this paper, the intermediate layer of 3-APMS plays an important role in the enhanced adhesion and noted abrasion resistance. Although the Martens hardness of 3-APMS layer

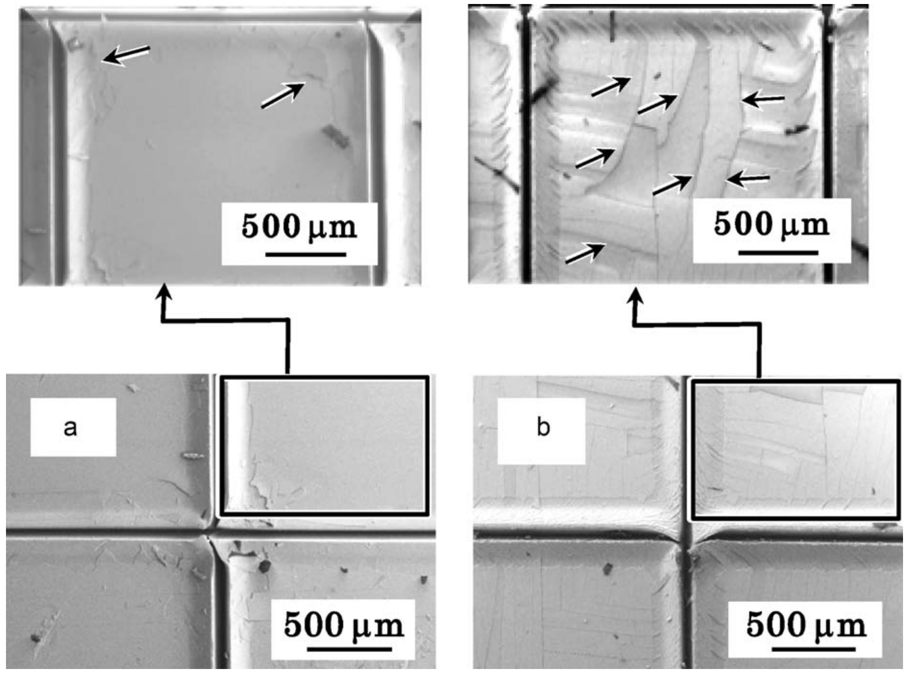

Fig. 7. Typical SEM micrographs of the film surfaces of the PC substrate having siliceous film and intermediate silane layer after the tape test. Note that the PC substrate was coated once by silane, followed by the VUV irradiation for 5 min; the siliceous film was further coated onto this substrate, followed by the irradiation for 5 min: finally, the heat treatment was conducted at 90 °C for 30 min. The kinds of silanes used for the formation of intermediate layer: (a) 3-APS and (b) 3-APMS; note that the arrow marks indicate the typical presence of cracks.

formed on the PC substrate is rather insufficient (see Fig. 4), compared to the case of 3-APS and PTES, this fact may be explained in terms of the combined effects of the interactions among 3-APMS, siliceous film (derived from MTES) and PC. When 3-APS and 3-APMS were used as the intermediate silane layer, each PC substrate with siliceous film showed the different properties. This fact suggests that the different abrasion resistance and exfoliation behavior reflect the steric effect of the ethoxy group and the methoxy group. In addition, reactivity of the 3-aminopropyl group is affected by the difference in electron

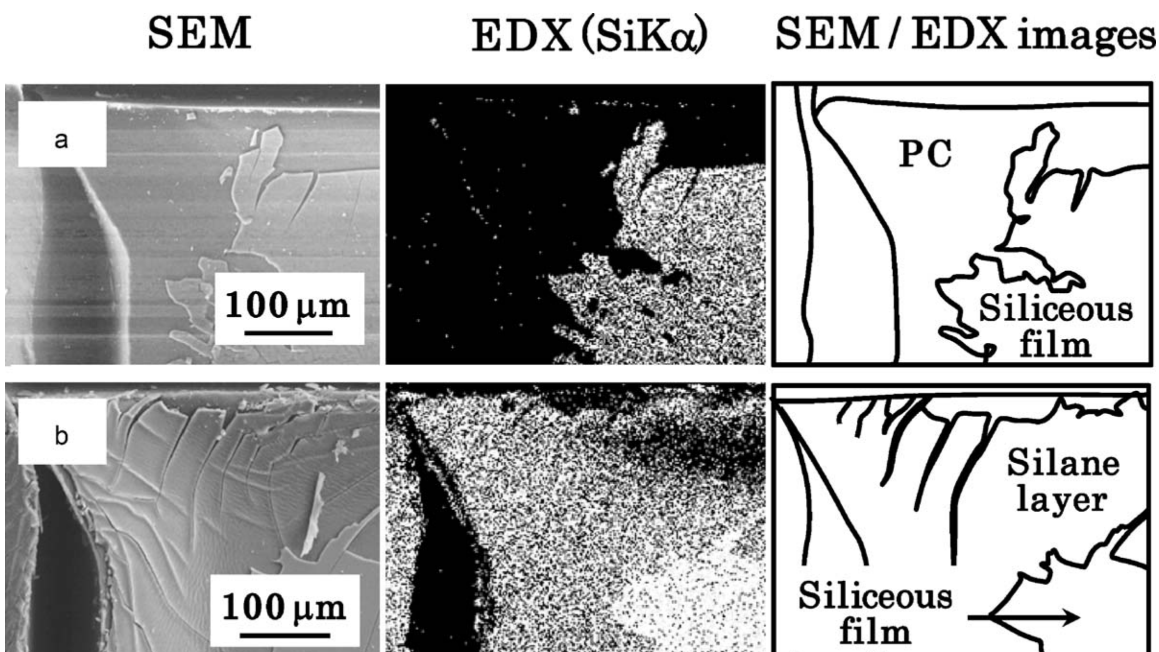

Fig. 8. SEM micrographs and EDX SiKα mapping (EDX) of the surfaces of PC substrate having siliceous film and intermediate silane layer after the tape test, together with the typical overviews. Note that the PC substrate was coated once by silane, followed by the VUV irradiation for 5 min; the siliceous film was further coated onto this substrate, followed by the irradiation for 5 min; finally, the heat treatment was conducted at 90 °C for 30 min. The kinds of silanes used for the formation of intermediate layer: (a) 3-APS and (b) 3-APMS.

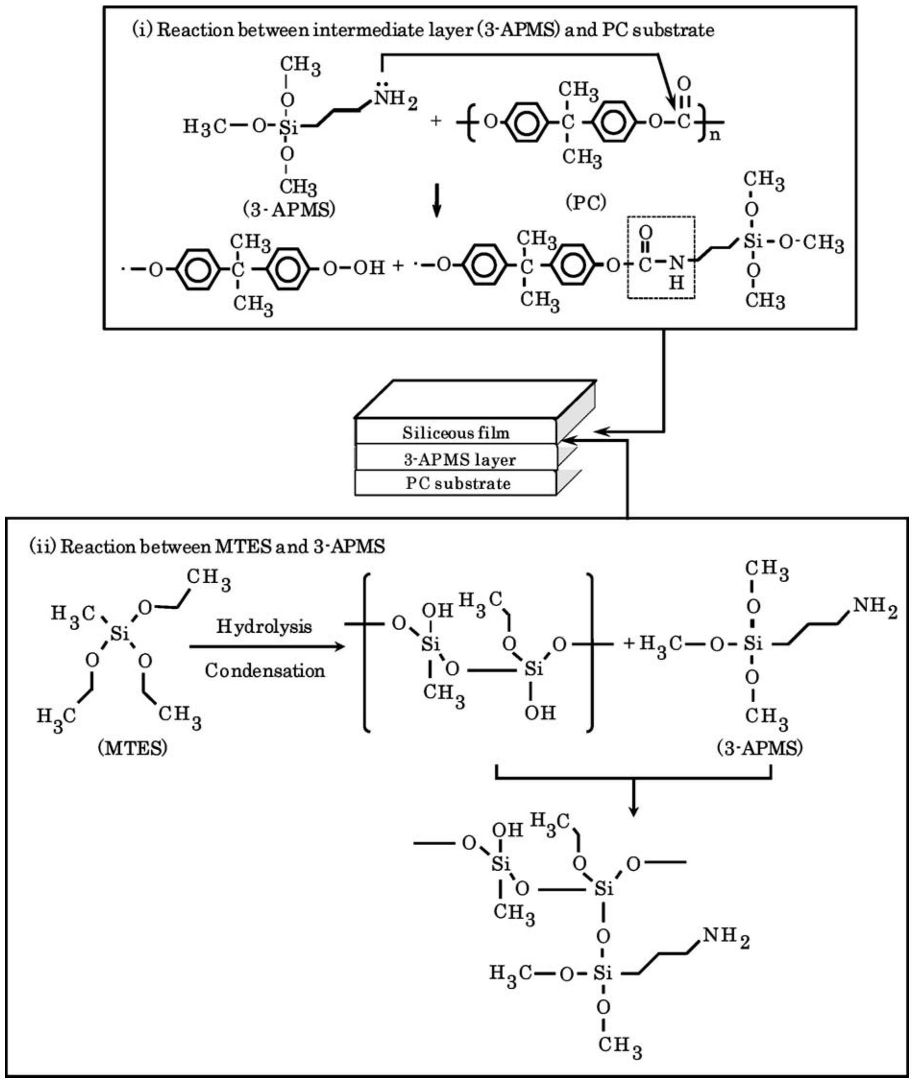

Fig. 9. Expected reaction routes between 3-APMS and PC and between 3-APMS and siliceous film derived from MTES.

affinity of the methoxy group and the ethoxy group. It is interesting that the 3-amionopropyl group is effective for the interfacial reaction between the PC substrate and the siliceous film, while its effect is influenced by the kinds of the alkoxy group.

The overall evaluation of the properties of abrasion resistance, adhesion strength and Martens hardness of the PC substrate having siliceous film and intermediate silane layer is listed in Table 1. The noted effects of abrasion resistance and adhesion strength were found when 3-APMS was used as an intermediate layer. This fact indicates that the chemical bonding may be effectively formed among PC, 3-APMS and siliceous layer.

Table 1
Effect of intermediate silane layer on the abrasion resistance, adhesion strength and Martens hardness of the PC substrate having siliceous film.

Kind of silane	Abrasion resistance	Adhesion strength	Martens hardness
3-APS	−	±	±
3-APMS	+	+	±
PTES	±	±	±
ETES	±	±	±

+, significant effect; ±, no significant effect; −, poor effect.

4. Conclusion

In this study, four kinds of silanes, i.e., 3-APS, PTES, ETES and 3-APMS, were inserted between PC substrate and siliceous film in order to enhance the abrasion resistance and adhesion strength. The siliceous film was prepared by the sol–gel technique using MTES and CS as starting materials. Simultaneously, the VUV irradiation was conducted to both siliceous film and silane layer. The results obtained were summarized as follows:

(1) Although the silanes were coated onto the PC substrate with VUV irradiation, no enhancement of abrasion resistance was found in any silane; 3-APS, 3-APMS, PTES and ETES. The Martens hardness of PC substrate was enhanced by the coating of 3-APS and PTES. On the other hand, no marked difference in Martens hardness of PC substrate was

achieved by the coating of 3-APMS and ETES. The tape test revealed that the silane layers of PTES and ETES showed the noted adhesion to the PC substrate, compared to the case of 3-APMS and 3-APS.

(2) When the siliceous film was coated on the PC substrate having silane layer, the abrasion resistance of the substrate was significantly enhanced. When 3-APMS was used as the intermediate layer, the average transmittance was especially kept being higher, compared to the case of other silanes, and was over 70% even after abraded for 140 turns.

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