Abstract—It is well known that enhancing interfacial adhesion between inorganic filler and matrix resin in a composite leads to favorable properties such as excellent mechanical properties, high thermal resistance, prominent electric insulation, low expansion coefficient, and so on. But it should be avoided that much excess of coupling agent is reacted due to a negative impact of their final composite’s properties. There is no report to achieve classification of the bonding state except for investigation of coating layer thickness. Therefore, the analysis of the bonding state of the coupling agent reacted with the filler surface such as BN particles with less functional group and silica particles having much functional group was performed by thermal gravimetric analysis and pyrolysis GC/MS. The reacted number of functional groups on the silane-coupling agent was classified as a result of the analysis. Thus, we succeeded in classifying the reacted number of the functional groups as a result of this study.

Keywords—inorganic filler, boron nitride, surface treatment, coupling agent, analysis of bonding state

I. INTRODUCTION

It is well known that the ability of alkoxysilanes added to a resin formulation to migrate to the substrate interface and improve their bonding. The hybrid chemicals with both organic and inorganic properties react with the polymer and mineral components, forming durable covalent bonds across the interface. It has been proposed that these bonds are both hydrolyzable and reformationable, and therefore provide a means of stress relaxation at the organic/inorganic interface. The results are given improvement on adhesion and durability [1]. The general reaction formula of alkoxysilanes shows two classes of moieties attached to the silicon atom:

\[ R_n-Si-X_{(4-n)} \]

R is a nonhydrolyzable organic moiety that can be either an alkyl, an aromatic, an organo-functional, or a combination of any of these groups. These groups provide the organic compatibility which allows the silane to react with the coating polymer. The X represents alkoxy moieties, most typically methoxy or ethoxy, which react with the various forms of hydroxyl groups and release methanol or ethanol. These groups can provide the linkage with inorganic substrates or filler to improve coating integrity and adhesion. The methoxy groups are also capable of reacting with hydroxy functional polymers such as Fig. 1 [1]-[2]. As shown in Fig. 1(1), the hydrolysis reaction formed a reactive silanol group. The silanol groups can condense with hydroxyl groups on mineral components (2) or with other silanol groups (3)-(4), to form siloxane linkages.

![Fig. 1 Reaction mechanism of alkoxysilanes as a coupling agent](image)

On the other hand, the heat dissipation problem in advanced microelectronic packaging and devices is becoming increasingly important as the demands in denser and faster circuits intensification. In order to improve the thermal conductivity of encapsulant or substrate, the incorporation of highly thermal conductive ceramic materials, such as aluminum oxide, aluminum nitride, silicon nitride, boron nitride, etc., in polymer composites has been studied [3]-[10]. As these ceramics have less interfacial adherence in the polymer composites, their surface modification is required [2]. Generally, a coupling agent or a surfactant was used for the surface modification, because hydrolysis of ceramics surface for producing much surface functional groups often obtain reduction of the crystallinity and the particle size resulting in decrease of thermal conductivity [11]. On the other hands, very
high content of the ceramics is required to achieve high thermal conductivity since the thermal conductivity of resin is much lower than the ceramics, but the high filler content in the polymer composites causes very high viscosity and degrading of mechanical properties. The surface modification of ceramics using a coupling agent improves the interfacial adherence and lowers the viscosity [12]. Many studies on the relationship between the amount of surface modification and mechanical properties has clarified that binding state of the modified surface is considered a major infection on the chemical and mechanical properties of polymer composites [13]-[15]. However, analyzing the chemical bonding state of the coupling agent on the modified particles is very rare; for instance, surface shape and hardness on the surface-treated silica beads by AFM were reported [16]. Furthermore, we could not find any reports concerning bonding state of alkoxysilanes with mineral components at starting this work.

Therefore, we focused in the bonding state of the alkoxysilanes on inorganic particles and started to study the clarification of the bonding state such as reacted number of alkoxysilane groups predominantly, to form single-molecular layer. In order to make reaction of a hydroxy group on the inorganic particles by alkoxysilanes and one silanol group is so slow, we expected that this compound reacts with the particle surface functional groups predominantly, to form single-molecular layer. In order to make reaction of a hydroxy group on the inorganic particles with an alkoxysilane group of the trialkoxysilane, the reaction was attempted without a hydrolysis process of the alkoxysilane to generate silanols. A toluene solution of alkoxysilane added to the inorganic material and the toluene solvent was removed by drying on a heating plate at 40°C. The particles applied the alkoxysilanes were heated at 125°C in vacuum for 2h. After the particles rinsed by THF to remove excess alkoxysilane, the particles were homogenized in THF by ultrasonic and ultra-centrifuged for purification, furthermore the particles were rinsed by acetone and ultra-centrifuged and dried at 60°C in vacuum for 2h.

![Fig. 2 List of using alkoxysilanes](image)

C. Quantitative Analysis by Thermal Gravimetric Analysis (TGA) and Pyrolysis GC/MS (Py_GCMS)

TGA apparatus, Seiko Instrument Inc. EXSTAR TG/DTA 5200, Chiba, JAPAN, was used in 150 ml min$^{-1}$ of N$_2$ flow. Py$_{\text{GCMS}}$ is composed of Pyrolyzer (Frontier Labo. LTD., PY-2020D), Gas Chromatograph (Agilent Technology LTD., 7890A GC), and Mass Spectrometric Detector (Agilent Technology Inc., 5975C MSD). The operating conditions were as follows: Py temp., 600°C; ion source, 230°C; EI, 70 eV. A Frontier Lab. UA-5A column (30 m × 0.25 mm i.d., df ) 0.25 µm was used with the following temperature program: 50 °C (5min hold) raised at 10°C min$^{-1}$ to 300°C (10 min hold). The pyrolyzer temperature was 600°C. The mass spectrometer was operated in scan mode over a mass range from 10 to 550 amu.

D. Other Analysis

IR spectrometer (Nicolet 6700, Thermo Electron, Waltham, USA) equipped with a ZnSe ATR attachment was used for confirming existence of a functional group such as oxirane ring, S-H, or N-H. Wide-angle X-ray diffraction traces (WAXD) were scanned on a Rigaku X-ray diffractometer RINT-2500 (RIGAKU, Tokyo, Japan), 40 kV – 50 mA.

III. RESULTS AND DISCUSSION

A. Treatment of Ceramics Particles

The surface treatment of ceramic particles by alkoxysilanes was examined in accordance with methods of H. Hanagasaki et al. [17]. Applying alkoxysilane was performed in an anhydrous toluene without hydrolysis process and addition of water or alcohol. A vacuum heating achieved chemically bonded surface modification of alkoxysilanes.

B. Estimation of Real Coated Amount by TGA

Quantitative analysis of chemically bonded coupling agent by TGA was performed. A first weight loss based on the volatility of water adsorption at 100-150°C and main weight loss based on the pyrolysis of chemically bonded coupling agent at 400-560°C were observed. A quantitative result of the modified particles by TGA means the actual coated mass on the surface by the modification reaction.

C. Py_GCMS Analysis of Coated Particles

TGA can give the information of total coupling agent mass reacted with particle because the agent reacted with the particle surface is almost entirely removed by thermal decomposition. In contrast, Py$_{\text{GCMS}}$ for quantitative analysis of particles.
rather than total mass in response to the reacted coupling agent, provide the amount of the compound derived from the segment which the reacted agent was fragmented by pyrolysis. In other words, the information from Py_GCMS can give the actual concentration of the agent involved in the reaction.

Fig. 3 is a typical pyrogram (pyrolysis gas chromatogram) of BN particle (010T) modified by 50wt% of the coupling agent 103. The outside window and inside window how a total ion chromatogram (TIC) and an ion 78 chromatogram extracted from the TIC, respectively. The peaks in the TIC were identified as gases from air, water, benzene, toluene, unknown compound and biphenyl. The C-Si bond in reacted coupling agent 103 on the particle is cleaved and the benzene moiety is vaporized by the thermal decomposition as the main product due to its lower bonding energy than others. Heating treatment at 200°C for 15 min in Argon flow reduced most of the water and certain amount of the toluene and the unknown compound without the influences in other peaks.

Fig. 3 Typical programs of modified BN particle (010T) by the coupling agent 103

Fig. 4 Coat amount calculated from GCMS results and actual coat mass measured by TGA

The integral value of the peak area on ion 78 chromatogram on the measurement was used for quantitative calculation because of its simple shape suitable for accurate integration. These results are common to both of the particles modified by the agent 103. Two compounds corresponding to benzene and aniline were mainly detected by pyrolysis of the particles modified by agent 573. As in the case of agent 103, the concentration of both compounds were determined from each ion chromatogram (ion 93 and 78) corresponding to each main ion of them. In the chromatographs of modified particles applying other coupling agents, many peaks derived from pyrolysis of their coating layer were detected. Unfortunately, quantitative analysis could not execute due to almost impossible of exact quantitative analysis in much complex chromatograms.

Comparison of the actual amount of the reacted agent and their coat mass gives interesting information as shown in Fig. 4 (a)-(d). Because quantitative GCMS analysis gives only the true amount of the reacted agent, the actual coated mass cannot get by the analysis directly. However, it is possible to calculate
the coat mass depending on the reacted number of functional
groups, since the actual coat mass varies with changes in the
molecular weight corresponding to the reacted number of
functional groups. The curves in the graphs are fitting curves
of coating amount calculated from those values (Fig. 4). The
actual coat masses estimated by TGA are plotted as circular or
square dots in the graphs. The dots in Fig. 4(a) and (e) are
located almost on the curve when one ethoxy group reacts with
the particle surface, and they are saturated at about 3.2wt% and
7.7wt% showing as gray arrow positions (→). This fact
would indicate that the modified BN is covered with agent 103
which one ethoxy group reacts with a functional group on the
particle. Consequently, we expect that one functional group
of the agent with three functional groups reacts with nearly all of
the surface functional groups. Moreover, it suggests that SP2
has less functional group which can react with the coupling
agent 103, since saturated coat amount of the 010T was
approximately four times that of the SP2. In contrast, the dots in
Fig. 4(b) and (d) move from the curve of one alkoxy reacted
estimation to the curve of three alkoxy reacted estimation with
increase of addition amount. Similarly, the dots in Fig. 4(c)
shift from the curve of one alkoxy reacted estimation to the
curve of two alkoxy reacted estimation. These results will
suggest that the agent preferentially reacted with particle
surface at low concentrations until 5 or 10% and then the homo
reaction between the agents predominantly occurred with
increasing concentration of the agent. The coat amount of
reagent 103 was not more than the saturation value even if
increasing the addition amount, but the coat amount of reagent
573 increased with increasing added amount. This result will
cased by differences in ease of homo-condensation reactions,
i.e., the difference would be due to tendency of
self-condensation progress under basic of the self amino group.

The actual coat masses on modified BNs (010T or SP2) by
agent 403, estimated by TGA, are plotted in Fig. 5(a). The coat
mass of 010T increased with increase of the addition amount
and reached saturation in the 2.4wt% coat at supplemented with
10%. The coat mass of 010T was increased by little more than 20%
addition amount again. The maximum coat mass of 3.4wt% at
50wt% addition coincides the calculation results of saturated
coating mass with respect to that of modified particle by
applying 103 in Table I. On the other hands, the coat mass of
SP2 increased with increasing addition amount and reached
saturation in the 8.8wt% coat at the 50% supplement (Fig. 5(a)).
It was expected that the surface functional groups of SP2 are
less than those of 010T from Fig. 4, but the coating amount of
the SP2 was more than that of 010T in this case. The reason for
this result would be attributed to the formation of many
homo-polycondensate because the broad peak (around $2\theta =
21^\circ$) derived from silica was observed in the WAXD pattern of
modified SP2 by 50wt% of 403 whereas no peaks exist in that
of modified 010T, as shown in Fig. 6. In case of modified BN
by 903 (Fig. 5(b)), the coat masses of BNs increased
proportionally with increase of the addition amount due to
self-condensation progress under basic of the self amino group.
It should be avoided that much excess of coupling agent is react
with the less functional group on their surface due to reducing
their final composite’s properties such as bending strength,
impact strength, electric insulation, low expansion, and so on [18].

Actual coat masses reacted with surface functional groups of the particles are summarized in Table II. In comparing between the calculated coat masses (Table I) and measured actual coat masses (Table II), those for SP2 (BN) do not match at all, although the two coating masses for 010T (BN) are approximately consistent without the cases of no saturation. This fact means that the reaction between 010T and each coupling agents (103 and 403) would progress with condensation of one alkoxy group in three ones of the agents coupling agents (103 and 403) would progress with approximately consistent without the cases of no saturation. Although the two coating masses for 010T (BN) are masses (Table II), those for SP2 (BN) do not match at all, the particles are summarized in Table II. In comparing between the final composite’s properties. There is no report to achieve much excess of coupling agent is reacted due to reducing their expansion coefficient, and so on. But it should be avoided that high thermal resistance, prominent electric insulation, low inorganic filler and matrix resin in a composite lead to showing contrary functionalities simultaneously, by controlling the nanometer size structure”.

**REFERENCES**


**IV. CONCLUSION**

It is well known that enhancing interfacial adhesion between inorganic filler and matrix resin in a composite lead to favorable properties such as excellent mechanical properties, high thermal resistance, prominent electric insulation, low expansion coefficient, and so on. But it should be avoided that much excess of coupling agent is reacted due to reducing their final composite’s properties. There is no report to achieve classification of the bonding state excepting investigation of coating layer thickness.

### Table I

**Calculation Results of Saturated Coating Mass Relative To That Of Modified Particle By Applying Agent 103**

<table>
<thead>
<tr>
<th>Agent</th>
<th>010T (BN) (wt%)</th>
<th>SP2 (BN) (wt%)</th>
<th>Silica gel (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>103</td>
<td>3.2</td>
<td>0.84</td>
<td>7.7</td>
</tr>
<tr>
<td>403</td>
<td>3.4</td>
<td>0.89</td>
<td>8.1</td>
</tr>
<tr>
<td>573</td>
<td>3.7</td>
<td>0.96</td>
<td>8.8</td>
</tr>
<tr>
<td>903</td>
<td>2.4</td>
<td>0.63</td>
<td>5.8</td>
</tr>
</tbody>
</table>

### Table II

**Actual Results of Saturated Coating Mass of Modified Particles**

<table>
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<tr>
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</tr>
</tbody>
</table>

* no saturation

Therefore, comparison of silane-coupling treatment between for BN particles with less functional group and for silica particles having much functional group was investigated. The analysis of the bonding state of the coupling agent reacted with the filler surface was performed by TGA and Py_GCMS, because TGA and Py_GCMS can estimate the agent mass concentration and the agent mole concentration reacted with the functional groups of filler surface, respectively. Thus, we succeeded in classifying the reacted number of the functional groups as a result of this study.

**ACKNOWLEDGMENT**

Some parts of this investigation achievement were the research result obtained by performing New Energy and Industrial Technology Development Organization (NEDO) project, “Development of the technology of the materials showing contrary functionalities simultaneously, by controlling the nanometer size structure”.

## Table II

<table>
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<tr>
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* no saturation