

# Technology for Joining of Dissimilar Material with Thermoplastic Polymeric Resin Using Atmospheric Gas Phase Modification of Metal Surfaces

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## ABSTRACT

A technology was developed for metal surface modification treatment to be used on a car body production line for weld-joining parts made of thermoplastic resin with metal parts. A glass membrane with a high hydroxyl group density of  $1.4 \times 10^{-9}$  mol/cm<sup>2</sup> was successfully formed on an aluminum alloy surface by configuring the conditions for the atmospheric pressure plasma chemical vapor deposition process. The obtained surface was confirmed to have wettability to melted 6-nylon. In addition, an amorphous layer was observed to have formed near the interface portion of the thermoplastic resin thermally welded to it. The effect of these results was that a high level of join strength equal to that in existing items with roughened metal surface aiming for an anchor effect was achieved with items of dissimilar material joined by thermal welding.

## 1. Introduction

The recent rise in worldwide demand for improved fuel economy in automobiles is the context for increasing investigation of the application of composite materials for the purpose of achieving lighter-weight vehicle bodies. Among them are carbon fiber-reinforced thermoplastics (CFRTP), which are carbon fiber composite materials with a matrix of 6-nylon or other such thermoplastic resin. These CFRTPs are receiving attention for their high specific strength and specific rigidity as well as from the viewpoint of life cycle assessment<sup>(1)</sup>. In their application to vehicle bodies, there is concern about deterioration of the material's mechanical properties due to the environment of use, and about the cost of the material, so structures that combine CFRTPs with metal materials are frequently used. This involves the joining of dissimilar materials, for which the thermal welding ability of the thermoplastic resin that is the matrix material for CFRTPs is utilized to simplify the construction of parts and the process of manufacturing. Such simplification is desirable in terms of achieving lighter weight and reducing costs.

The technology for weld-joining dissimilar material with thermoplastic resin involves roughening by inscribing fine holes and grooves in the metal surface ranging from

several nanometers to several tens of micrometers in size. The pits are filled with melted thermoplastic resin by injection molding, which then solidifies by cooling, in the so-called anchor effect that provides a mechanical join. There have been many recent cases of application of this method. For example, there has been widespread use of technology for integrated forming of thermoplastic resin and light alloy plate using the anchor effect in the process of manufacturing components for compact mobile electronic equipment. However, these surface roughening treatments require chemical treatment by solution processes in which components are immersed in chemicals in order to form the holes and grooves on the metal surface. Due to the long time taken by the processes and the added complication of facilities for disposing of effluent and other such factors, these solution processes cannot readily be introduced to automobile body production lines. Furthermore, these solution processes are originally a technology intended for batch treatment of large numbers of relatively small parts simultaneously, and they are not well suited to localized treatment of only the necessary locations on the surface of large automotive parts. Applying a roughening treatment to the larger surface that includes portions not required for joining would necessitate the use of larger amounts of chemicals as well as larger treatment facilities. This would

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increase process costs, making this approach undesirable. One technique for roughening a metal surface without depending on solution processes uses laser machining equipment, but fine machining in three dimensions at high speed requires equipment with high power output and complex controls.

One conceivable method for achieving dissimilar material weld-joining in automotive parts other than by the mechanism of mechanical joining is by the application of chemical bonding force. In ordinary adhesive bonding, a hydrogen bond or a covalent bond is formed between the adhesive components and the solid surfaces. A join made by thermal welding of thermoplastic resins that does not involve a chemical reaction can make use of the chemical bonding force of the hydrogen bond.

In order to manifest the hydrogen bonding force, the presence of anisotropy functional groups such as hydroxyl groups or amide groups is necessary both on the solid surface and in the thermoplastic resin. A polyamide resin such as 6-nylon includes amide groups in the basic structure of the molecular chain, but anisotropy functional groups are not by their nature found on the solid surface of an inorganic material such as aluminum alloy. It is therefore necessary to place them there *de novo* by means of chemical modification of the surface.

This raises two issues. The first issue is raising the wettability of the solid surface with which the thermoplastic resin has fused thermally. To effectively manifest the chemical bonding force requires wettability to the solid metal surface, but the thermoplastic resin changes from the chainlike state of its molecular structure to a highly viscous fluid when it melts, so its wettability is diminished in comparison with a thermosetting adhesive that has a low molecular weight before it hardens.

The second issue is achieving a stable bonded state. Thermoplastic resins that have crystallinity, such as 6-nylon, tend to separate or experience loss of join strength with solidification by cooling during the welding process or with subsequent changes in the temperature of the usage environment, so that they do not readily achieve stability in their bonded state. This is because, when the progressive crystallization of the melted nylon extends to the weld interface portion, its flexibility is lost so that it becomes unable to absorb the thermal stress in the weld interface that is caused by the difference in thermal expansion between the dissimilar materials. Technology has been given practical application to prevent interface separation. It involves coating the metal surface with a flexible non-crystalline resin to a thickness of approximately 100  $\mu\text{m}$ . Then a layer of thermoplastic resin is applied over that surface by injection molding, forming the shape of an integrally formed component. Finally, it is heat-treated and the non-crystalline resin is cross-linked to assure the join strength. This technology for creating a non-crystalline resin layer requires a special grade of resin material, in addition to which the process is complex and time-consuming.

## 2. Development Goals

In order to enable localized thermal welding of dissimilar materials with CF RTP components on the automobile body production line, a method for surface modification of metal parts in atmosphere was investigated.

The object was to utilize the chemical bonding force resulting from the hydrogen bond in the thermoplastic resin weld to obtain stable join strength equal to that of mechanical bonds obtained by the anchor effect. Attention was given to the following points:

- (1) Increase the hydroxyl group density at the bond interface;
- (2) Increase the thermoplastic resin wettability at the bond interface; and
- (3) Form a non-crystalline layer at the interface in order to increase the stability of the bond.

## 3. Method of Achieving Aims

In order to enable thermal welding of the thermoplastic resin, the introduction of high-density hydroxyl groups to the metal surface was adopted as the policy for investigation of surface treatment technology. The interaction between metal surface hydroxyl groups and the thermoplastic resin increased the wettability of the melted resin, which was noted above as the first issue, manifesting greater hydrogen bonding force so as to obtain greater join strength. The effect this interaction has of restricting polymer chain mobility was utilized to suppress the progressive crystallization of the thermoplastic resin in the weld interface portion. This formed a flexible and amorphous thermal stress relaxation layer, suggesting that stabilization of the bond, the second issue, could also be addressed.

As a method for introducing hydroxyl groups to the metal surface, the focus was placed on the atmospheric pressure plasma approach, which enables high-speed processing at atmospheric pressure.

Atmospheric pressure plasma processing ordinarily obtains a plasma gas flow by converting a portion of atmospheric gas to plasma by electric discharge or heat and directs that plasma gas flow onto the target object. This method causes oxidation-reduction or other such chemical processes to occur at atmospheric pressure<sup>(2)</sup>.

Siloxane or another such precursor is introduced into that plasma gas flow where it decomposes through the action of the plasma, and the highly chemically active substance that is generated is sprayed onto the target object and polymerized so that a membrane of glass or other substance is formed on the surface of the target object. This surface modification technology is the chemical vapor deposition (CVD) process<sup>(3)</sup>. The energy level of the excited species – meaning the atoms and molecules that were excited by the electrical discharge – will vary with the type of atmospheric gas. On the downstream side of the plasma gas flow, the energy level of the excited

species decreases as they undergo progressive relaxation or collide with molecules of oxygen, nitrogen, water, and so on in the atmosphere, causing excitation of those they collide with<sup>(4),(5)</sup>. By using this property, the atmosphere in which the precursor undergoes a decomposition reaction can be controlled so that a different degradation product can be obtained from the same precursor. As a result, glass membranes with different properties can be created for different purposes.

An example of existing research is the report from Ihde and others regarding the properties of two types of glass membrane formed on the surface of an aluminum alloy (Al 2024-T3) with hexamethyldisiloxane (HMDSO) as a precursor using the atmospheric pressure plasma CVD process<sup>(3)</sup>. The first was a highly homogeneous glass membrane with little organic residue from the precursor that was obtained when the processing conditions included the use of dry air as an atmosphere gas. This membrane has physical properties that suit it as an anti-corrosion coating for aluminum alloy. The second was created using the same apparatus with dry nitrogen (N<sub>2</sub>) as an atmosphere gas and with the location where the precursor is interfused with the plasma gas flow moved several millimeters downstream from the plasma source. The glass membrane obtained under these processing conditions has a chemical composition that includes approximately 2.5 times more organic constituents than the first membrane<sup>(3)</sup>. Research has also been done on the adhesion of coatings and adhesives to these glass membranes, and the first membrane in particular has been proposed for application as an adhesive primer for thermosetting urethane adhesive in automobile windshields<sup>(6)</sup>.

This kind of investigation has not yet been carried out on the thermal welding ability of thermoplastic resin. In the present research, attention was focused on the methyl groups derived from the organic components in the surface of the second membrane, i.e., the HMDSO precursor.

The methyl groups that exist in the surface portion of the glass are known to be caused to alter into hydroxyl groups (silanol groups) by the oxidative reforming that is caused by the atmospheric pressure plasma process<sup>(7)</sup>.

It was reasoned that using the atmospheric pressure plasma CVD process to form a glass membrane with an abundance of methyl groups on the metal surface to start, and then to cause oxidative alteration of it by atmospheric pressure plasma processing, would yield a glass membrane with a high density of hydroxyl groups on its surface.

## 4. Tests

### 4.1. Surface Modification Treatment of Aluminum Alloy

An Openair plasma system (FG5001 plasma generator, PFW10-PAD/RD1004 plasma jet nozzle, and PAD1 polymer coating controller) made by Plasmatrete GmbH were used for the atmospheric pressure plasma CVD processing.

Figure 1 shows a schematic diagram of the device. The device is based on an atmospheric pressure plasma jet device. While atmospheric gas at atmosphere pressure is passed through a tube made of conductive metal, a high-voltage pulse is applied to an insulated electrode inside the tube to cause an arc discharge, and plasma is generated. The gas flow that includes this plasma is blown through the plasma nozzle at the tip of the tube and onto the surface of the target object. The device that does this is the atmospheric pressure plasma jet device. This plasma nozzle is installed with a cover nozzle that has a channel for liquid in it, as shown in Fig. 2. The precursor substance is injected through this channel into the plasma gas flow to mix with that flow, making it possible for the atmospheric pressure plasma CVD process to occur.

The metal substrate to which the atmospheric pressure plasma CVD process is applied is made using rolled aluminum alloy (Al 5052) material. This alloy surface is not cleaned using solvent or other such material. Instead a plasma gas flow generated using air as the atmosphere gas is blown against the surface so that oil or other contaminants adhering to it are oxidized and removed.

Next an atmospheric pressure plasma CVD process using HMDSO as the precursor substance is carried out and a glass membrane is formed on the substrate surface. The atmospheric pressure plasma CVD process is carried out under two sets of conditions that differ in the type of atmosphere gas and whether or not the nozzle has an extension. For each of those, another version is also made in which the process is applied post-oxidation with the

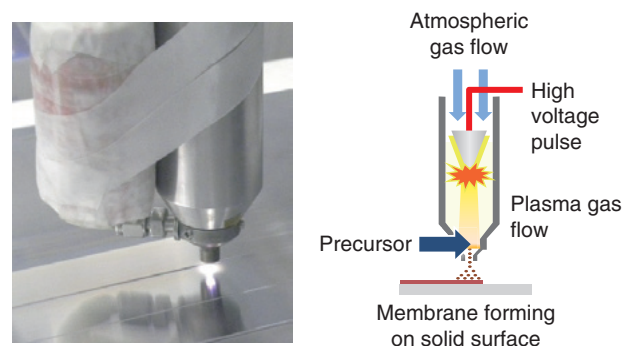


Fig. 1 Diagram of atmospheric pressure plasma CVD process principle

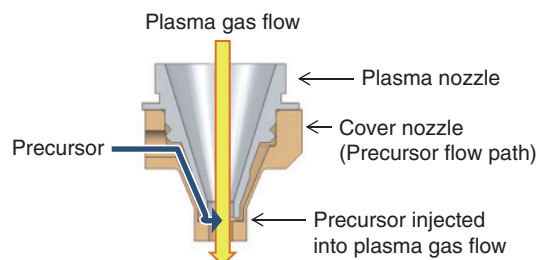


Fig. 2 Plasma CVD nozzle (original form)

Table 1 Atmospheric pressure plasma CVD process conditions

| Membrane type | Atmospheric pressure plasma CVD |                  | Post processing  |
|---------------|---------------------------------|------------------|------------------|
|               | Gas                             | Nozzle extension |                  |
| A             | Nitrogen                        | 4.5 mm           | -                |
| B             | Air                             | -                | -                |
| C             | Nitrogen                        | 4.5 mm           | Plasma oxidation |
| D             | Air                             | -                | Plasma oxidation |

atmospheric pressure plasma. In this way, a total of four types of glass membrane are created as shown in Table 1.

Specifically, N<sub>2</sub> was used as the atmosphere gas for the atmospheric pressure plasma CVD process under the first set of conditions. In addition, as shown in Fig. 3, a shim and pipe-shaped extension part are added to the cover nozzle so that the location where the precursor is mixed together with the plasma gas flow is moved 4.5 mm downstream. Using this method, a sample in which glass membrane (A) had formed on the surface of the aluminum alloy was obtained.

In the second set of conditions, air was used as the atmosphere gas for the purpose of comparison. The atmospheric pressure plasma CVD process was carried out using the original specification nozzle, without extension parts, to create glass membrane (B). The above two processes were carried out with a plasma voltage of 283 V and plasma current of 13 A, distance from the nozzle tip to the substrate surface of 4 mm, and rate of nozzle movement in the horizontal direction of 20 mm/min as the plasma generating conditions.

After that, additional membranes (C) and (D) were created by generating a flow of plasma gas with air as the atmosphere gas and without introducing any precursor to it. The flow is respectively directed onto the surface of membrane samples (A) and (B), subjecting the organic residue constituents to post-oxidation treatment. This oxidation treatment was carried out with plasma voltage of 301 V and plasma current of 20 A, with distance from the nozzle tip to the substrate surface of 7 mm, and with rate of nozzle movement in the horizontal direction of 20 mm/min as the plasma generating conditions.

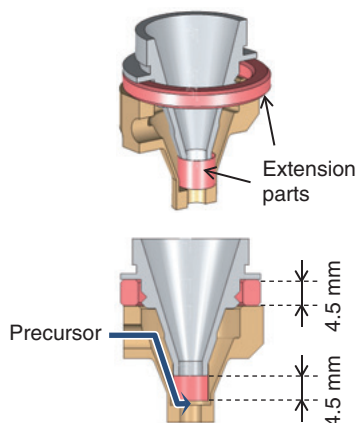


Fig. 3 Plasma CVD nozzle extension

#### 4.2. Glass Membrane Property Analysis

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to observe the glass membrane shape and to measure the roughness of the surface.

Positron annihilation lifetime measurement was conducted using the positron beam method to determine the average micropore radius distribution on the silicon oxide (SiO<sub>x</sub>) framework. A <sup>22</sup>Na-based positron beam was used as the positron beam source, and BaF<sub>2</sub> scintillator and photomultipliers were used as a gamma ray detector.

X-ray photoelectron spectroscopy (XPS) was used to measure the element existence ratio on the surface of the glass membrane. Monochromatic aluminum was used as the X-ray source with pass energy of 160 eV.

The ion chromatography method was used to measure hydroxyl group density on the surface of the glass membrane. Specifically, this involved thermal decomposition of a sample of a brominated silicon compound solution with hydroxyl groups on the surface subjected to derivatization treatment. The gas this generated was absorbed into an alkali aqueous solution and the amount of bromine in the solution was measured by ion chromatography. A per-surface-area figure for the hydroxyl group density was calculated from the substrate dimensions.

#### 4.3. Joining of Dissimilar Materials by Thermoplastic Resin Weld

A lap shear-strength test specimen was created using thermal welding to join the aluminum alloy subjected to the atmospheric pressure plasma CVD process with the CF RTP, and the strength of the join was measured. Aluminum alloy test specimens were prepared that were not subjected to the atmospheric pressure plasma process, that had membrane (C) formed on the surface, that had membrane (D) formed on the surface, and that had been subjected to metal surface roughening processes for the purpose of utilizing the already existing anchor effect. In the processes selected for metal surface roughening, an injection molding grade of 6-nylon was used to apply four types of process with surface roughness in different sizes to aluminum alloy. One of these used laser machining to inscribe grooves with a width and depth of approximately 50 μm with a pitch of 200 μm in a grid pattern. In the other three types, a chemical process applying an anodizing process, acid solution, or alkaline solution was carried out to apply finer sizes of roughening and to generate micropores.

Joining by thermal welding was carried out using the metal insert injection molding method. The molding used a specialized metal mold with a cavity in which an aluminum alloy test specimen in strip form and 100 × 25 × 2.0 mm in size could be set, as shown in Fig. 4. The remaining space inside the cavity was shaped in strip form so as to overlap by 12.5 mm longitudinally with the test specimen. Pellets of CF RTP grade 6-nylon containing 15 wt% carbon fiber (CF) were injection-molded into that space with a cylinder temperature of 260°C and a mold temperature of from 160

to 180°C under dwelling pressure of 30 MPa. This injection molding yielded an aluminum alloy plate and 6-nylon plate joined by thermal welding for use as a lap shear-strength test specimen.

All the test specimens were fabricated to a single standard with  $n = 5$  and were used for lap shear-strength testing.

SEM and energy dispersive X-ray spectrometry (EDX) were used to examine the fracture surface and perform qualitative analysis of the constituent elements in order to identify the rupture locations.

#### 4.4. 6-Nylon Analysis of Thermal Welding Interface Portion

The crystallization state of the 6-nylon was examined by grazing incidence X-ray diffraction (GIXD) using the multi-axis X-ray diffractometer manufactured by Huber Diffraktionstechnik GmbH & Co. KG that is located in BL46XU Hutch No. 1 at the Spring-8 large synchrotron radiation facility. The sample was fabricated by forming a 6-nylon membrane layer on the substrate surface by the solution spin coating method, thermally fusing it, then resolidifying it. Since surface unevenness caused by the aluminum alloy substrate rolling process diminishes measurement accuracy, a smooth Si wafer was used for the substrate. The strength profile relative to the diffraction angle was separated into crystallized constituents and non-crystallized constituents to calculate the degree of crystallization.

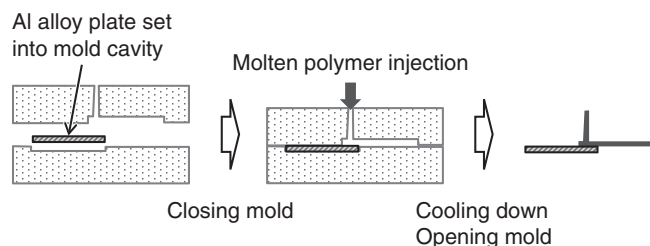


Fig. 4 Process of joining by metal insert polymer injection molding method

## 5. Results and Discussion

### 5.1. Property Analysis of the Reformed Surface

First the glass membranes (A) and (B) were analyzed and the physical properties of their respective glass frameworks were compared. Figure 5 shows an SEM image of the membrane (A) and (B) surfaces. Figure 6 shows the result from AFM observation of the membrane (A) surface. Positron annihilation lifetime measurement of the two types of membrane was conducted using the positron beam method. Figure 7 shows a comparison of the average micropore distributions on the SiOx molecular framework of the glass obtained in this way.

Membrane (B) has a homogeneous membrane structure

with a smooth surface and the micropore distribution on the SiOx framework shows a sharp peak. The structure was composed of microparticles approximately 20 nm in size, which is the mean square root value of the surface roughness measured by AFM on membrane (A). The glass frame of membrane (A) showed an irregular and broad distribution of SiOx pore diameters. This suggested that it had a frame structure that was irregular by comparison with membrane (B). In macro terms, this membrane structure has a large surface area, and in micro terms, it is characterized by an irregular molecular structure and instability. It can be inferred, therefore, that the structure is likely to undergo change in its chemical composition due to oxidative reforming.

Next, a comparison was made of the chemical

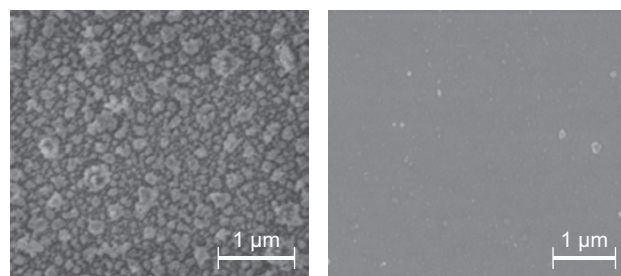


Fig. 5 SEM image of membrane A (left) and membrane B (right) surfaces

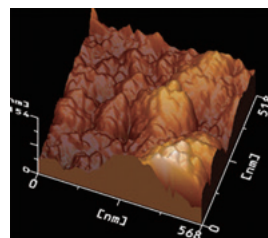


Fig. 6 AFM image of membrane A

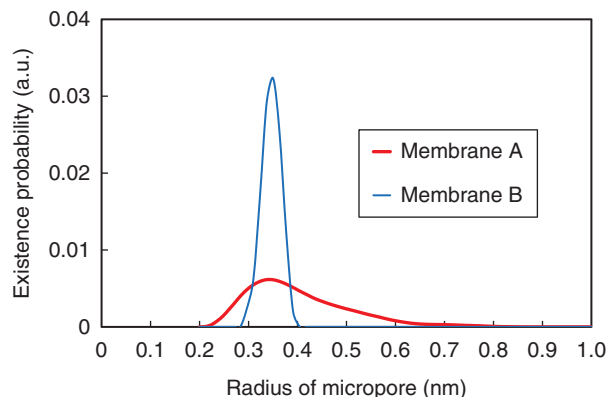


Fig. 7 Positron annihilation lifetime spectroscopy of atmospheric pressure plasma CVD glass membrane

Table 2 Property of atmospheric pressure plasma CVD glass membrane surface

| Membrane type | Process conditions          |          |                 | Membrane properties              |                         |                                               |
|---------------|-----------------------------|----------|-----------------|----------------------------------|-------------------------|-----------------------------------------------|
|               | Atmospheric pressure plasma |          | Post processing | C/Si content (atomic %/atomic %) | Water contact angle (°) | Hydroxyl group density (mol/cm <sup>2</sup> ) |
|               | Gas                         | Nozzle   |                 |                                  |                         |                                               |
| A             | Nitrogen                    | Extended | -               | 1.3                              | 160                     | Unmeasured                                    |
| B             | Air                         | Normal   | -               | 0.8                              | 80                      | Unmeasured                                    |
| C             | Nitrogen                    | Extended | Oxidation       | 0.3                              | 2.5                     | $1.4 \times 10^{-9}$                          |
| D             | Air                         | Normal   | Oxidation       | 0.6                              | 43                      | $2.6 \times 10^{-10}$                         |

composition and properties of the surfaces of membranes (A), (B), (C), and (D). The fabrication conditions of the various membranes, analysis of their chemical composition by XPS, water contact angle, and surface hydroxyl group density are shown in Table 2.

As shown by the C/Si content ratio data, membrane (A) contained approximately twice as much carbon from HMDSO methyl groups as membrane (B). The change in chemical composition from membrane (A) to (C) – namely, the extent of the reduction in carbon atoms – that is due to the oxidation resulting from atmospheric pressure plasma processing, was relatively greater than the corresponding change from membrane (B) to (D). It appears likely that this is because membrane (A) has a larger surface area and the glass framework was more susceptible to oxidation. As a result, the surface hydroxyl group density of membrane (C) was greater than that of membrane (D) by a factor of five or more.

As shown by the water contact angle data, membrane (A) displayed super water repellency through the synergistic effect with a physical surface form composed of fine irregularities. On the other hand, membrane (C), which was obtained by oxidation of this surface, displayed superhydrophilic properties. As shown by the photographs in Fig. 8, a similar change in wettability was also displayed with respect to thermally melted 6-nylon.

## 5.2. Evaluation of Thermoplastic Resin Weld Strength

A join was not obtained by injection molding of 6-nylon using the metal mold for insert injection molding so that the 6-nylon would be in contact with an unprocessed

aluminum alloy substrate surface and membrane (D). When the mold was released, those two elements would come out as separate pieces. On the other hand, a test specimen with a satisfactory weld join, as shown in Fig. 9, was obtained when the membrane (C) treatment was applied to the aluminum alloy substrate. The test specimen also achieved a join when the metal surface roughening process was applied to the aluminum alloy substrate plate in order to make use of the anchor effect. Figure 10 shows a comparison of results from lap shear-strength testing of these specimens.

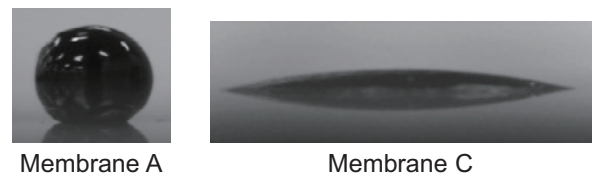


Fig. 8 Molten polyamide 6 behavior on CVD glass membrane surface



Fig. 9 Specimen of joined CFRTP and Al alloy

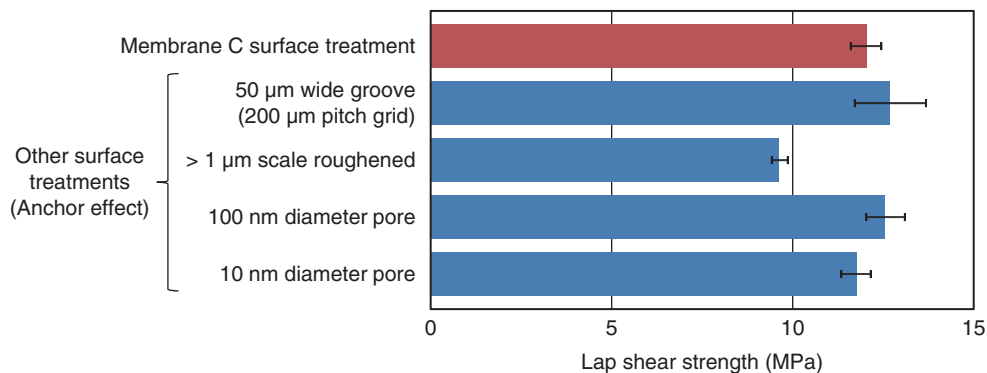


Fig. 10 Joining strength of Al alloy and CFRTP joined by insert injection molding

This confirms that the membrane (C) treatment realized weld join-strength equal to that with the physical anchor effect.

Figure 11 shows the SEM photograph of a weld joining test specimen that fractured in the lap shear-strength testing. The aluminum alloy surface was observed to have fragments of CF RTP adhering to it. EDX analysis also confirmed that carbon from the CF RTP and silicon from the CVD glass membrane were present on the fracture surface on the aluminum alloy side. These observations indicate that the rupture in the weld joint portion was not a separation of the weld interface portion or a rupture of the glass layer, but rather occurred as a material rupture within the CF RTP portion. In other words, this indicates that a thermal welding strength had been obtained that was equal to or greater than the interlaminar strength of the CF RTP.

### 5.3. Analysis of 6-Nylon Crystallization State in the Thermal Welding Interface Portion

A more detailed analysis was made of the mechanism of thermoplastic resin thermal welding on the membrane (C) treatment surface.

The GIXD method is capable of measurement and evaluation of the extent of crystallization in the thermoplastic resin in the weld interface region and in the bulk region, and this method was used to evaluate the crystallization state of the 6-nylon. The results this yielded are shown in Fig. 12. The horizontal axis of the graph shows the thickness of the 6-nylon membrane from the substrate surface to the measurement position. The vertical axis shows the ratio of observed X-ray crystal diffraction intensity to total scattering intensity, and a larger figure signifies a higher degree of 6-nylon crystallization in that portion. In the case of 6-nylon thermal-welded to an untreated Si wafer surface, crystallization had advanced to

the vicinity of the contact interface with the wafer. In the case of the membrane (C) treated surface, on the other hand, there was confirmed to be a layer of amorphous 6-nylon that extended to a thickness of several hundred nanometers from the interface.

### 5.4. Confirmation of Thermoplastic Resin Weld Stability

A weld-joined object was placed in an environment that cycled repeatedly between cooling and heating in which it was exposed to atmospheric temperatures of  $-30^{\circ}\text{C}$  and  $80^{\circ}\text{C}$  for 30 minutes each for 200 cycles. As shown in Fig. 13, the join strength was not found to change. A sample of thermal-welded 6-nylon plate was also subjected to a compound cycle test of exposure to a 5% neutral salt solution spray at  $35^{\circ}\text{C}$ . Each cycle also included exposure in a dry atmosphere at a temperature of  $60^{\circ}\text{C}$  and humidity of 25% RH, and exposure in a humid atmosphere at  $50^{\circ}\text{C}$  and 98% RH. After testing for 60 cycles, no separation was observed in the weld portion.

It was confirmed from the above that a stable weld-join was obtained by the effect of thermal stress relaxation in the flexible amorphous layer formed in the weld interface.

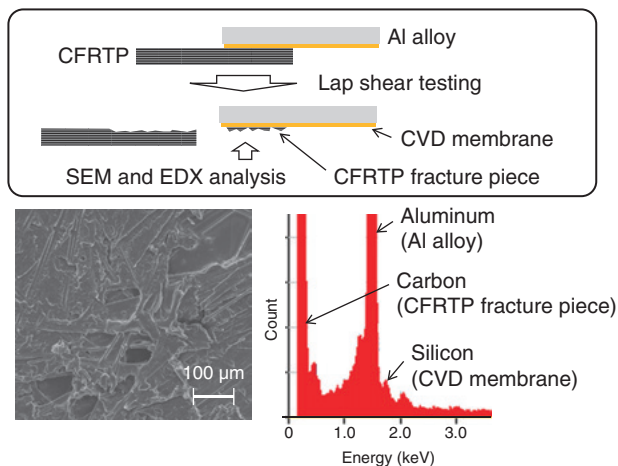


Fig. 11 SEM image (left) and EDX spectrum (right) of CF RTP fracture piece on Al alloy substrate

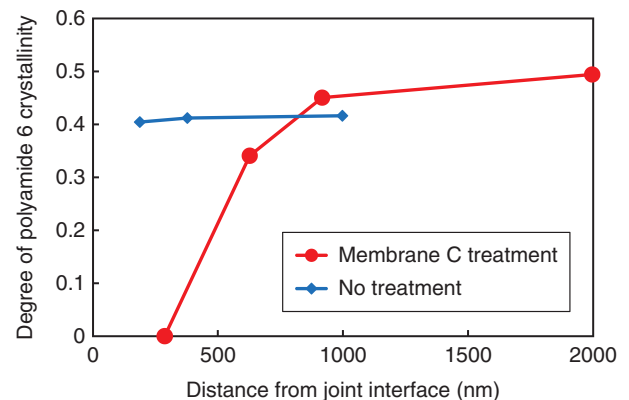


Fig. 12 Suppression of polyamide 6 crystallization by CVD membrane surface effect

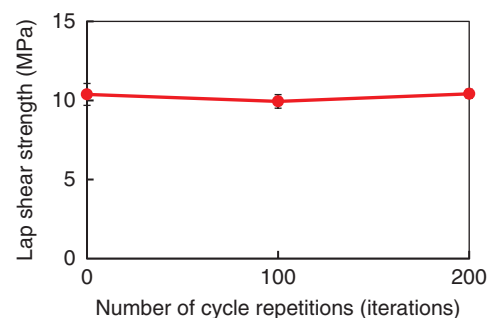


Fig. 13 Joining strength after cooling and heating cycle

## 6. Conclusion

A surface modification was carried out that formed a glass membrane layer on an aluminum alloy surface by a gas phase process in atmosphere. The properties of the obtained surface and the quality of the weld with thermoplastic resin were evaluated.

- (1) In the atmospheric pressure plasma CVD process, a glass membrane that contains organic constituents was formed by modification of the atmosphere in which the plasma decomposed the precursor substance. This membrane was subjected to oxidative alteration by atmospheric pressure plasma processing, yielding a membrane layer with a high hydroxyl group density on the surface.
- (2) On this surface, the melt state of 6-nylon had high wettability and the hydrogen bond could be used effectively so that a thermal welding join could achieve high join strength on a par with the mechanical anchor effect.
- (3) An amorphous layer of 6-nylon was formed in the vicinity of the weld interface portion. This was due to the effect of suppression of crystallization caused when the mobility of polymer chains of thermally fused thermoplastic resin was inhibited by interaction with solid surface hydroxyl groups. The amorphous layer, which possessed greater flexibility than the crystallized bulk portion, absorbed and relaxed the thermal stress between the dissimilar materials so that separation from the metal surface was prevented and the thermal welding join was stabilized.

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