Plasma press for improved adhesion between flexible polymer substrate and inorganic material

Mu Kyeom Mun, Doo San Kim, Dong Woo Kim, Geun Young Yeom

School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Kyunggi-do 16419, South Korea

ARTICLE INFO

Keywords:
Plasma press
Flexible device
Atmospheric pressure plasma
Atomic bonding
Surface activation

ABSTRACT

A novel adhesion process called “plasma press” has been investigated for achieving stronger bonding between two different materials. It was first developed to be applied in multilayer flexible printed circuit boards for next generation flexible mobile electronics. The plasma press is a hot pressing method employing plasma between the two materials in order to activate the material surfaces. Compared to the conventional hot-pressed sample, the plasma-pressed sample exhibited up to 130% higher adhesion strength. The stronger bond strength achieved in the plasma-pressed sample is attributed to the formation of active carboxyl functional groups and dangling bonds on the material surfaces by the presence of the plasma during the hot pressing process for bonding.

1. Introduction

In recent years, wearable electronic devices have come to be widely investigated as next generation mobile electronics. These next generation wearable electronics require not only the development of flexible electronic devices and sophisticated electrical components for specific wearable electronics, but also improved adhesion between the electrical components and flexible substrates, such as multilayer flexible printed circuit boards.

For multilayer flexible printed circuit boards, instead of electrical component mounting technologies such as Insert Mount Technology (IMT), the use of Surface Mounting Technology (SMT) and an Embedded Passive Substrate (EPS), where the semiconductor device is embedded in the multilayer flexible substrate, leads to significantly thinner and smaller electronic circuit boards [1–4]. For the formation of a multilayer flexible printed circuit board, a flexible adhesive substrate such as prepreg is required for the adhesion of the inorganic components to the flexible substrate. Prepreg is a resin containing flexible composite polymer substrate with woven fibers, such as glass fibers [5]. The resin is required for adhesion, and the glass fibers prevent thermal deformation during the hot pressing process for the bonding between the electrical components and prepreg to form EPS [6,7]. The chemical structure of the general phenol resin (thermosetting resin) used for prepreg resin can be found in the reference [8].

During the hot pressing to form EPS for flexible mobile electronics and wearable electronics, if the adhesion strength is not sufficiently high, delamination can easily occur at the interfaces between the prepreg and electrical components while the flexible and wearable electronics are being used [9,10]. The use of a higher hot press temperature to decrease the chance of this potential delamination problem occurring at the interfaces can increase the local adhesion strength, but it may also increase the thermal deformation of the flexible substrates, further increasing the chances of this local delamination problem occurring. In order to avoid such thermal deformation at higher temperatures, prepreg materials impregnated with carbon nanotubes, carbon nanofibers, etc. are also under investigation; however, the use of these materials tends to lead to other problems, with increased material costs and increased production costs being some examples [11,12]. The use of indirect heating methods such as induction heating has also been investigated, but no significant enhancement in adhesion strength has been reported through the use of such methods [13].

Plasma surface treatment methods have also been applied to improve the adhesion strength at lower temperatures, either by modifying the material surface or by cleaning the surfaces before beginning the hot press process [14–18]. When prepreg is processed under plasma, various functional groups such as –COOH, –OH, and –NH formed by the plasma can enhance the adhesion strength. In contrast, the surface atomic bonding of the prepreg can be easily broken by the plasma and cross-linked; the prepreg surface can thereby be easily hardened [19–21]. These plasma surface treatment methods are generally carried out prior to the hot pressing process for adhesion. Therefore, surfaces are generally stabilized before the hot pressing process begins, even though the surface atoms are modified to enhance adhesion, thus limiting the effect of plasma treatment in improving the adhesion between the surfaces.

In this study, we developed a novel plasma press method to improve...
the adhesion between the prepreg surface and the inorganic electronic component surface, such as BaTiO₃ (BTO). Moreover, the effect of this novel method on the adhesion strength between the prepreg and BTO was investigated. The plasma press is a hot press processing under a plasma environment. For the plasma press, the two heated materials to be hot pressed are positioned a certain distance apart, then a plasma is turned on between the material surfaces. While the plasma is on, the distance between the two materials is decreased until finally, the two materials contact each other for the hot press. The plasma between the two materials turns off by itself due to the lack of space between the two materials. The two materials are pressed to a certain load for a time for adhesion, then released. For the plasma press, up to the point that the two materials are in contact, the plasma exists between the two material surfaces, therefore the material surfaces could be activated by atomic dangling bonds on the material surfaces, in addition to the surface cleaning and modification because of the existence of the plasma during the hot press. In particular, in this study, atmospheric pressure plasma (APP) was investigated as the plasma condition for the plasma press owing to its ease of used in large area processing and roll-to-roll processing for flexible substrate processing, in addition to its low temperature and low cost processing for the fabrication of next generation flexible and wearable electronics [22-24].

2. Experimental

2.1. Preparation of materials

For the adhesion test between the prepreg and inorganic materials, 5 × 5 mm² wide and 1 mm thick BTO fabricated by sintering ~10–100 nm-sized powders composed of barium 57.5%, titanium 6%, and oxygen 36.5% was used as the inorganic sample. Prepreg (a polymer substrate containing satin-weave-shaped glass fiber and resin for bonding at an elevated temperature) purchased from MUHAN Composite (GEP 224 black) was used as the flexible polymer substrate.

2.2. Plasma press equipment

A schematic diagram of the plasma press module used in this experiment is shown in Fig. 1. The plasma press module consists of two aluminum electrodes coated with 400 μm thick Al₂O₃ by the thermal spray method. An additional 1 mm thick Al₂O₃ plate was located on the bottom electrode in order to prevent possible arcing during the plasma operation, and the prepreg was loaded on top of the bottom electrode. BaTiO₃ attached to a 0.5 mm thick Teflon plate was located on the bottom of the top electrode. The distance between the prepreg and BTO before plasma ignition was 2.5 mm. The experiment was conducted while both electrodes were heated to 60 °C by flowing heated water to both electrodes. The plasma press module used in the experiment was home-made equipment, since it does not currently exist in the market.

Fig. 1. Schematic diagram of the plasma press module used in this experiment.

2.3. Plasma press process

The atmospheric pressure plasma was ignited for ~0–60 s by applying 60 kHz 6 kV AC voltage to the top electrode while flowing He (11 slm)/O₂(2 slm) between the prepreg and BaTiO₃. While the He/O₂ plasma was on, a load was applied to the top electrode in order to decrease the distance between the prepreg and BaTiO₃ as well as for hot pressing. When the prepreg and BaTiO₃ were in contact with each other, the plasma was turned off and the load was increased linearly to 38 kg/cm² for 20 s. The load was measured using a load-cell attached at the bottom electrode, as shown in Fig. 1. A load of 38 kg/cm² was maintained for 1 min, then decreased linearly to 0 for 15 s. All of the procedures of the plasma press were conducted at the same plate temperature of 60 °C. A schematic diagram of the plasma press procedure is shown in Fig. 2, and the time sequence of the plasma press is shown in Fig. 3. As can be seen in Fig. 2, the plasma press procedure was conducted in the following order: loading samples, plasma treatment between the samples, plasma hot press, and finally unloading. In addition, as shown Fig. 3, following the sample loading, the plasma was turned on for 25–60 s until the two electrodes were in contact. Then, after the plasma was turned off, a continuous increase of load up to 38 kg was applied for 20 s, and the load was removed for 15 s after 60 s of continuous hot pressing. In addition to the plasma press, a conventional hot press was conducted by applying the load to the top electrode without igniting the plasma. Moreover, the hot press was conducted with the BTO or prepreg, which were previously treated with He/O₂ plasma for 35 s prior to the hot press, in order to study the effect of plasma treatment alone on adhesion strength.

2.4. Specimen preparation for adhesion test

The adhesion test was conducted using a tensile strength tester (MECMESIN, Multi test 1-i) through the peeling-off technique. For the peel-off test, the plasma-pressed sample with BTO and prepreg was cut into an appropriate shape, as shown in Fig. 4, and attached on the glass holder using epoxy glue. The prepreg arm shown in Fig. 4 was connected to a strength gauge in the tensile strength tester, and the sample was pulled at a speed of 40 mm/min until it was completely peeled off. In order to ensure the accuracy of the data, data from 12 samples were collected, and their average value and standard deviation were calculated because there were many errors involved in the adhesion strength measurement.

2.5. Analysis and measurements

The contact angles of the BTO and prepreg measured before and after the plasma treatments and those of the hot-pressed samples were measured using a contact angle analyzer (SEO, phoenix 450). The chemical binding states of prepreg before and after the plasma treatments were measured by X-ray photoelectron spectroscopy (XPS, thermo VG SIGMA PROBE). The surfaces of BTO and prepreg before the bonding and the fracture surfaces after the peel-off test were observed using a scanning electron microscope (FE-SEM, HITACHI, s-4700).

3. Results and discussion

The adhesion strength of the plasma-pressed BTO/prepreg sample measured as a function of plasma exposure time is shown in Fig. 5. The BTO and prepreg were exposed to atmospheric pressure plasma for 25, 35, and 60 s just before the hot pressing at 60 °C, and they were hot-pressed under the plasma, which was generated by applying 60 kHz 6 kV AC voltage to the top electrode, while flowing He (11 slm)/O₂(2 slm) between the prepreg and BTO. In order to compare the plasma press with the conventional hot press, the BTO and prepreg were also hot pressed at 60 °C without the plasma. In addition, for the purpose of comparing the plasma press with the hot press on the
plasma-treated samples, the samples were hot pressed with the BTO or the prepreg treated with the He/O2 plasma for 35 s. Therefore, in these cases, BTO or prepreg was hot pressed after the plasma treatment rather than during the plasma treatment. As shown in Fig. 5, the adhesion strengths of the plasma-pressed BTO/prepreg samples for 25–60 s were generally higher than that of the hot-pressed BTO/prepreg sample. In particular, the plasma-pressed BTO/prepreg sample treated with the plasma for 35 s exhibited approximately 130% higher adhesion strength than the hot-pressed sample. The sample hot pressed after the BTO plasma treatment for 35 s showed a slightly (∼34%) higher adhesion strength than the hot-pressed sample, but the sample hot pressed after the prepreg plasma treatment for 35 s exhibited a very low adhesion strength close to 0 gf/mm. This exceedingly low adhesion strength of the sample hot pressed after the prepreg plasma treatment was attributed to the hardening of the prepreg surface by the exposure to the He/O2 plasma.

In order to understand the increase in the adhesion strength of the plasma-pressed BTO/prepreg sample, first, the effects of He/O2 plasma treatment on the surfaces of BTO and prepreg were investigated by measuring the contact angles of the BTO and prepreg as a function of plasma treatment time, and the results are shown in Figs. 6 and 7, respectively. The contact angles of the as-received BTO and prepreg as well as those of the BTO and prepreg after the exposure to a high temperature of 60 °C for 60 s were also included. As shown in Fig. 6, regarding BTO, the hot temperature-treated BTO sample and the as-received BTO sample showed a similar contact angle of ∼73°. However, after the plasma treatment, the BTO samples showed a lower contact angle of ∼15°, regardless of the plasma treatment time up to 60 s, indicating a higher surface energy after the plasma treatment but no differences in surface energy for different plasma treatment times. Regarding prepreg, as shown in Fig. 7, the prepreg exposed to a high
A temperature of 60 °C for 60 s showed a contact angle of 64°, and the as-received prepreg showed a contact angle of 60°. Therefore, no significant change in the surface energy was observed after the exposure to a hot temperature. After the He/O₂ plasma treatment, the contact angle decreased, indicating an increase in the surface energy similar to that in the BTO exposed to the plasma. However, as shown in Fig. 7, the prepreg treated with He/O₂ plasma for 25, 35, and 60 s showed contact angles of 36°, 34°, and 47°, respectively. Therefore, the plasma-treated prepreg showed the lowest contact angle at 35 s with increasing plasma treatment time, and further increases in the plasma treatment time increased the contact angle. The initial decrease in the contact angle with increasing plasma treatment time up to 35 s is attributed to the increased modification of the prepreg surface, specifically the improved adhesion to the BTO. However, the increase in the plasma treatment time accelerated the hardening rate of the resin on the prepreg by the cross-linking of polymers on the resin surface. Therefore, the contact angle increased with increasing plasma treatment when the plasma treatment time was higher than 35 s [25,26].

The changes in the contact angles after the plasma treatment observed in Figs. 6 and 7 for both BTO and prepreg are believed to be related to the change in the adhesion strength of the BTO/prepreg sample, shown in Fig. 5. For the plasma press, the highest adhesion strength at 35 s of plasma treatment time appears to be related to the lowest contact angle for the prepreg at 35 s. When the plasma treatment time during the plasma press exceeded 35 s, the adhesion strength decreased in a manner similar to the increase in the contact angle of prepreg with increasing plasma treatment time, because of the hardening of the prepreg by the cross-linking of the resin surface. The higher adhesion strength of the BTO/prepreg sample hot pressed after the plasma treatment of BTO for 35 s (and after no plasma treatment for prepreg) was also related to the high surface energy of BTO by the plasma treatment. However, the nearly zero adhesion strength of the BTO/prepreg sample hot pressed after the plasma treatment of prepreg for 35 s (and after no plasma treatment of BTO) was related to the rapid hardening of prepreg after the plasma treatment. Moreover, when the plasma treatment time was higher than 1 min during the plasma press, because of the hardening of the prepreg, it was also difficult to achieve bonding between BTO and prepreg.

The change in the surface composition of prepreg and the change in the binding state of carbon on the prepreg surface after the heat treatment at 60 °C for 60 s and after the He/O₂ plasma treatment for 25, 35, and 60 s were investigated, with the results shown in Table 1 and Fig. 8, respectively. The as-received prepreg surface was mostly composed of carbon (82%) and oxygen (18%) on the surface (hydrogen should also exist on the prepreg surface, but XPS could not measure any hydrogen on the surface), and this surface became slightly oxygen-rich.
after the heat treatment. However, after the plasma treatment, nitrogen emerged, and its percentage increased with increasing plasma treatment time from 0.4% for the as-received to 23% for 60 s, and the carbon percentage further decreased from 82% for the as-received to 51% for 60 s. In the case of oxygen, it increased with increasing plasma treatment time from 18% for the as-received to 28% for 35 s, and a further increase in the plasma treatment time to 60 s slightly decreased the oxygen percentage to 26%. The observed increase in the nitrogen percentage with increasing plasma treatment time is believed to be caused by the atmospheric pressure plasma in the air environment (N$_2$/O$_2$ = 4:1), and may be related to the hardening of prepreg, because of the cross-linking of carbon in the resin with the nitrogen atoms formed in the plasma. In addition, the highest oxygen percentage at 35 s of plasma treatment appears to be related to the highest adhesion strength shown at the same plasma treatment time. For further investigation, the carbon narrow scan data in Table 1 were examined as shown in Fig. 8, and carbon binding peaks related to C–C bonding (285 eV), C–O/C–N bonding (287 eV), and CO$_x$ (x = 2, 3, 289.7 eV) were observed, and increased plasma treatment time increased not only the C–O/C–N peak but also the CO$_x$ (x = 2, 3) peak [27,28]. In the case of the plasma process, unlike heat treatment, not only could single bonds be formed between carbon and oxygen, but double bonds could be formed as well [29,30]. Therefore, it is believed that functional groups such as > C=O and –COOH increased the binding between BTO and prepreg.

In fact, the contact angles and XPS data in Figs. 6–8 were measured after the heat treatment. However, after the plasma treatment, nitrogen emerged, and its percentage increased with increasing plasma treatment time from 0.4% for the as-received to 23% for 60 s, and the carbon percentage further decreased from 82% for the as-received to 51% for 60 s. In the case of oxygen, it increased with increasing plasma treatment time from 18% for the as-received to 28% for 35 s, and a further increase in the plasma treatment time to 60 s slightly decreased the oxygen percentage to 26%. The observed increase in the nitrogen percentage with increasing plasma treatment time is believed to be caused by the atmospheric pressure plasma in the air environment (N$_2$/O$_2$ = 4:1), and may be related to the hardening of prepreg, because of the cross-linking of carbon in the resin with the nitrogen atoms formed in the plasma. In addition, the highest oxygen percentage at 35 s of plasma treatment appears to be related to the highest adhesion strength shown at the same plasma treatment time. For further investigation, the carbon narrow scan data in Table 1 were examined as shown in Fig. 8, and carbon binding peaks related to C–C bonding (285 eV), C–O/C–N bonding (287 eV), and CO$_x$ (x = 2, 3, 289.7 eV) were observed, and increased plasma treatment time increased not only the C–O/C–N peak but also the CO$_x$ (x = 2, 3) peak [27,28]. In the case of the plasma process, unlike heat treatment, not only could single bonds be formed between carbon and oxygen, but double bonds could be formed as well [29,30]. Therefore, it is believed that functional groups such as > C=O and –COOH increased the binding between BTO and prepreg.

In fact, the contact angles and XPS data in Figs. 6–8 were measured...
after the plasma treatment, not during the plasma treatment. Therefore, they do not reflect the actual surface characteristics of BTO and prepreg during the plasma pressing process. The fracture surfaces of BTO and prepreg after the peel-off test were observed through SEM in order to understand the surface statuses of BTO and prepreg during the plasma pressing process. Fig. 9 shows the fracture surfaces of BTO and prepreg for both the hot-pressed BTO/prepreg sample ((c) BTO and (d) prepreg) and the plasma-pressed BTO/prepreg sample (Plasma treatment for 35 s, (e) BTO and (f) prepreg) after the peel-off test. The surfaces of the as-received BTO and prepreg samples ((a) BTO and (b) prepreg) were included for comparison. As shown in Fig. 9(c) and (d), the SEM images of BTO and prepreg for the hot-pressed BTO/prepreg sample showed that the fractured surfaces are the interfaces of BTO and prepreg, when compared to the surfaces of the as-received BTO and prepreg in Fig. 9(a) and (b). In contrast, the fracture surfaces of the BTO and prepreg for the plasma-pressed BTO/prepreg sample were covered with broken BTO particles (composed of spherical particles tens to hundreds of nanometers in size), indicating fracturing of the BTO inner surface, not the interface between the BTO-attached prepreg surface, as shown in Fig. 9(e) and (f). Therefore, it is believed that for the plasma-pressed sample, strong bonding occurred at the interface between BTO and prepreg by breaking the BTO material rather than breaking the BTO/prepreg interface during the peel-off test. The strong BTO/prepreg interface observed during the plasma pressing process is believed to be partially related to the existence of the dangling atomic bonds on the surfaces of BTO and prepreg during the bonding in the presence of He/O2 plasma, in addition to the surface modification allowing for functional groups such as > C=O and –COOH on the prepreg surface. The dangling atomic bonds existing on the BTO and prepreg surfaces during the bonding could have formed strong atomic bonds between the atoms on the BTO and prepreg surfaces, thus generating a strongly bonded interface.

Fig. 10 shows cartoons explaining the differences between the hot pressing and plasma pressing processes during the pressing (a), after the bonding (b), and after the peel-off test (c). During the plasma pressing process, dangling bonds with and without oxygen atoms are formed, thus activating the surfaces by the existing plasma on both the BTO and prepreg surfaces, while during the hot-pressed process, the surfaces are not activated. Therefore, the surface atomic bonding is saturated. After the bonding, atomic bonding occurs between the BTO atoms and prepreg atoms in the plasma-pressed sample, while no atomic bonding occurs between the BTO atoms and prepreg atoms in the hot-pressed sample. During the peel-off test, for the plasma-pressed sample, because of the strong atomic bonds between the BTO atoms and prepreg atoms, fracturing started and propagated at the sintered BTO inner surface rather than at the interface between BTO and prepreg, because of the strong atomic bonds at the interface, whereas for the hot-pressed sample, the fracturing started and propagated along the BTO/prepreg...
interface, because the interface has a weak bonding.

4. Conclusions

In this study, in order to ensure strong adhesion between inorganic electric components and multilayer flexible printed circuit boards, a novel plasma press method (hot pressing while a He/O2 plasma is on) was developed. In addition, its effect on the adhesion strength between a flexible substrate (prepreg, a flexible composite polymer substrate containing woven fibers and resin for hot press) and an inorganic component material (BaTiO3, BTO) was investigated and compared to that of a conventional hot press method. APP was specifically investigated as the plasma condition for the plasma press because it is more applicable for the fabrication of next generation flexible and wearable electronics. The adhesion strength of the plasma-pressed BTO/prepreg sample was generally higher than that of the hot-pressed BTO/prepreg sample, and it was also higher than that of the BTO/prepreg sample hot pressed with the BTO or that of the prepreg previously treated with He/O2 plasma. In particular, the plasma-pressed BTO/prepreg sample treated with the He/O2 plasma for 35 s exhibited ~130% higher adhesion strength than the hot-pressed sample. The surfaces inspected after the adhesion test showed that the fracture surface was the BaTiO3 internal surface, not the interface between the BaTiO3 and prepreg for plasma press, indicating substantially stronger bonding at the interface than at the BaTiO3 material itself. The stronger bonding for the plasma-pressed sample is believed to be related to the formation of functional groups such as > C=O and –COOH and dangling bonds on the material surfaces under the plasma operation during the pressing. Even though the adhesion between BTO and prepreg was investigated in this study, similar increases in adhesion strength between various polymer substrates and inorganic materials, which are required for next generation flexible mobile electronics and wearable electronics, could be achieved by the plasma press technique.

Acknowledgments

This research was supported by Nano Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012M3A7B4035323).

References