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Influence of water temperature and existence of hydroxyl group on the strength of injection molded direct joining samples

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Abstract
Metal-polymer joining technique is highly needed for the weight reduction for automobile and electronic industrials. In this paper, hybrid joints of a 30% glass fiber reinforced polybutylene terephthalate (PBT) and an aluminum alloy A5052 plate are made by the Injection Molded Direct Joining (IMDJ). The metal surface is treated by a simple hot water treatment (boehmite treatment). We studied the influence of hot water temperature on the joining strength. In addition, in order to know whether boehmite (AlOOH) can produce chemical bonding with the polymer, we heat the hot water treated metal to a high temperature to decompose the AlOOH and test the strength change. Moreover, the treated metal surface is characterized by SEM and ATR-FTIR. It reveals that the boehmite treatment is a viable method for metal surface pretreatment. The highest joining strength is comparable to other surface treatment methods. The successful joining is due to the mechanical interlocking between nano structures on metal surface and the polymer.

Keywords: Metal-polymer Direct Joining, Injection Molded Direct Joining, Boehmite, Hot Water Treatment

1. Introduction

Nowadays, the automobile and smartphone industrials require the metal-polymer joining techniques to reduce the weight and facilitate the assembly. Conventionally, the joining of metals and plastics is achieved by mechanical joining and adhesive bonding by using screws and adhesive, respectively. However, these two methods are not suitable for high throughput production. The mechanical joining method requires holes to be made, while the adhesive bonding needs a curing process which takes hours.

Recently, direct metal-polymer joining methods, which means joining metal and polymer without screws and adhesives, like laser direct joining [1], friction direct joining [2], ultrasonic direct joining [3], and injection molded direct joining [4], have been developed. In this research, Injection Molded Direct Joining (IMDJ) is studied since this method excels compared with other direct joining methods when a complex-shaped or small polymer part is involved and has a large potential for industrial applications. For IMDJ, the metal surface is first treated to make micro or nano structures (Fig. 1(a)). Then the treated metal is put into the mold and the injection molding is carried out (Fig. 1(b)). The melted polymer is injected onto the treated metal surface and flows into the surface structures. After the polymer solidifies, the metal-polymer joints are formed (Fig. 1(c)).

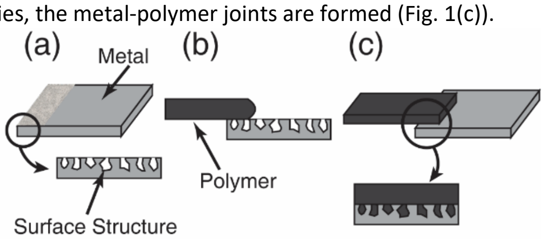

Fig. 1. Schematic illustration of the process for IMDJ.

Various surface treatments have been applied for IMDJ, including micro-blasting [5], laser [6], chemical etching [7]. The authors believe the joining between metal and polymer is due to the interlocking effect. They point out the importance of porous surface or small structures on the surface for the successful joining. Furthermore, some authors [7] emphasize the chemical state of the metal surface also have influences on the strength. Some polar groups, like hydroxyl and amide, are beneficial for strength improving.

Boehmite treatment [8], which can produce nano-sized porous surface and aluminum oxide hydroxide on the metal surface, seems to be a viable method for the surface pretreatment. In addition, it is economic, environmental-friendly, and easy to apply when compared with other treatments. Although there are some author applied boehmite treatment for adhesive joining [9, 10], no literature has reported about this treatment for IMDJ. Thus, the objective of this paper is to verify whether boehmite treatment can be used for IMDJ and to study the mechanisms for the successful joining.

The following section will introduce the materials, boehmite treatment process, injection molding conditions, and characterization methods. Lastly, results and discussions about joining mechanisms were proposed.

2. Experimental

2.1. Materials and sample size

Experiments were carried out with aluminum alloy A5052 plates and 30% glass fiber reinforced PBT (Toraycon 1101G-X54, Toray). The size of the joining sample is based on the ISO19095 (ISO 19095-2:2015) and its running system is shown in Fig. 2. The joining area is located at the end of the cavity where a temperature sensor and a pressure sensor are installed close to it.

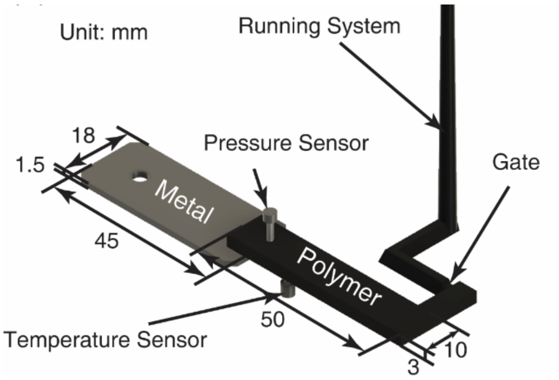

Fig. 2. Schematic illustration of the single lap joint and its running system.

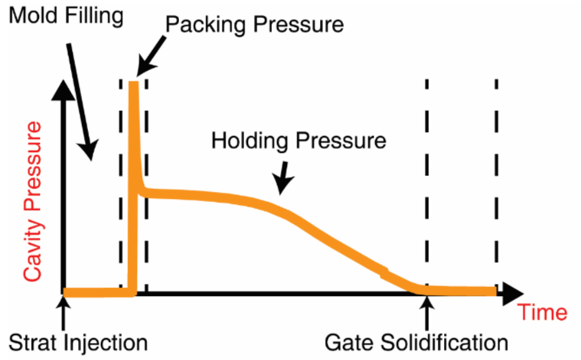

Fig. 3. Schematic illustration of pressure change during the injection process.

2.2. Boehmite treatment

We first performed the oxide removing for aluminum plates before the boehmite treatment. A two-step procedure was applied. Plates were firstly alkaline etched in a 5% sodium hydroxide solution for 1 min and then washed with DI water. Secondly, plates were dipped in a 30% nitric acid solution for 1 min and then washed with DI water. A nitrogen gas gun was used to blow out the water and dry plates. The oxide removed aluminum plates were kept carefully to avoid contamination before the boehmite treatment. As a reference for the oxide removing effect, some plates with only ultrasonic cleaning were prepared. The plates were ultrasonic cleaned in acetone, ethanol, and water in sequence for 3 min each.

We performed the boehmite treatment with a beaker in a constant temperature water bath by using DI water. The water temperature in the baker was measured by a thermocouple. Five water temperatures, including 55, 65, 75, 85, 95 °C, are studied in this paper. After the water temperature reached constant, the aluminum plates were immersed in the water for 5 min and then dried with a nitrogen gas gun.

As mentioned before, in order to know whether boehmite (AlOOH) has chemical effects with the polymer, we heated some 65 and 95°C hot water treated metal plates in an oven for 30 min. Two oven temperatures were used. Since the decomposition temperature of AlOOH is apporximately 450 °C, 500 °C was selected for decomposing the AlOOH, and 250 °C is selected as a comparison reference.

2.3. Injection molding process

The experiment was carried out with the injection molding machine (ROBOSHOT α-S100iA, FANUC corp.). Its joining process consists of mold filling, packing, holding, cooling, and ejection statues, which can be determined by cavity pressure change, as shown in Fig. 3. The packing pressure is defined as the instant cavity pressure produced just after the mold is filled up with melted polymer. The holding pressure is a constant pressure applied after the mold is full to reduce the shrinkage during the cooling process.

The injection molding was performed under the same parameters, shown in Table 1, for all metal plates:

Table 1. Injection molding parameters

Parameters	**Value**
packing pressure	100 MPa
holding pressure	50 MPa
injection speed	50 mm/s
polymer temperature	245 °C
mold temperature	140 °C

2.4. Characterization method

After the hybrid joints were heat treated under 130 °C for four hours, for each boehmite condition, five samples were used to perform the tensile shear tests with our home-made tester [11].

The metal surfaces after the cleaning, the oxide removing, and the boehmite treatment were analyzed with SEM (Hitachi High-Technologies S-4800) and ATR-FTIR (JASCO, FT/IR-6600) with a diamond and an incident angle of 45 ° to compare the effects of different temperatures. The plates heated in the oven were also analyzed with the same process. The ATR-FTIR spectrums were recorded with 4 cm^{-1} resolution and averaged over 16 scans in the wavenumber range of 4000cm^{-1}-400cm^{-1}.

3. Results and discussions

Figure 4 shows the results of tensile shear strength for samples made under different hot water temperatures. Error bar is the standard deviation of five measurements. It is clearly shown in the results the boehmite treatment can be a viable surface treatment method for IMDJ. The obtained joining strength is comparable to other surface treatment methods. For samples treated in 65 °C and 95 °C, the joining strength reached to 22.74 MPa and 21.2 MPa, respectively, indicating the most suitable hot water temperatures are 65 °C and 95 °C.

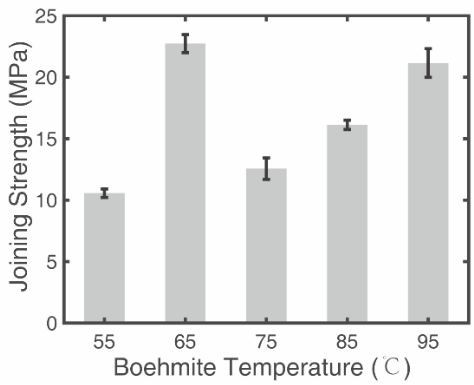

Fig. 4. Tensile shear strength results for sample treated with different water temperature.

Figure 5 shows the results of SEM images for an untreated sample, an oxide removing sample and samples treated under different hot water temperatures. From Fig.5(a) and (b), we can see that the oxide removing process removed the polluted oxide film produced during the manufacturing process, and a new cleaned oxide film formed on the metal surface. Grain boundaries can be clearly seen in Fig.5(b). Fig.5(c) shows that some small and thin convex structures formed on the surface after the metal was treated in the 55 °C hot water for 5 min. Fig.5(d) indicates a much clear hot water treatment effect. A two-level nanostructure was formed on the surface. One level regards to the convex cellular structure consisting of sharp rims. These sharp rims are only 10 nm wide. The second level structure is the deep circular pores surrounded by sharp rims. The diameter of the hole is around 30 nm. Fig.5(e) shows that for 75 °C hot water treatment, the number of sharp rims reduced and its edge became wider and more like plates. As for 85 °C hot water treatment, as shown in Fig.5(f), the cellular rims develop into distinct plates and they became wider than that in Fig.5(e). The circular pores became much clear and wider. The diameter of the holes reached to above 50 nm. As shown in Fig.5(f), the plate structures kept and some small new plates were formed in the holes, which made the hole diameter reduced to around 40 nm.

SEM results indicate that the mechanical interlocking can take effect. It is highly possible that the melted polymer flowed into the nanostructures during the injection molding process, which resulted in the joining between metal and polymer. The results also show that the two-level nanostructure formed at 65 °C and dense plate structure formed at 95 °C are most suitable for high joining strength. This resulted from the fact more nano rims and nano plates were formed under these two temperatures. Thus, we assumed that the more rims or plates, the higher the joining strength. However, a quantitative measurement is needed in the future.

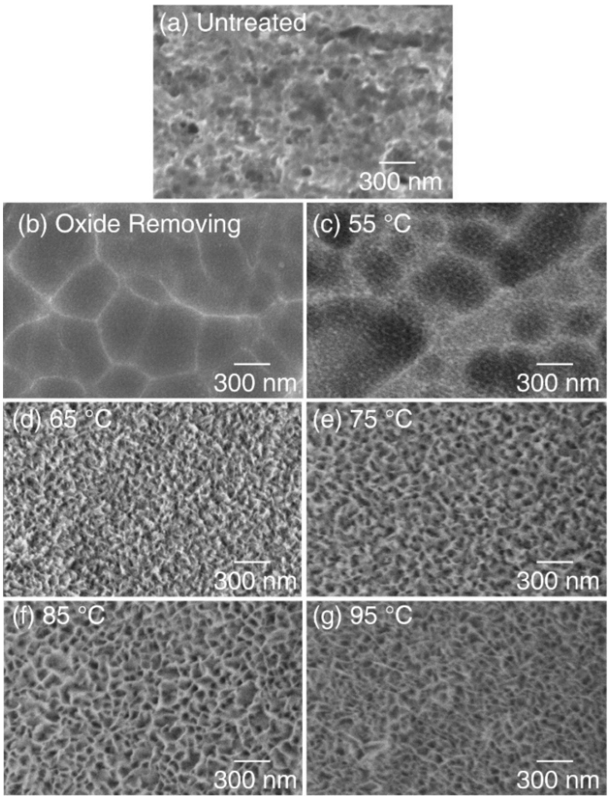

Fig. 5. The SEM images of (a) untreated sample; (b) oxide removing sample; (c) 55 °C hot water treated sample; (d) 65 °C hot water treated sample; (e) 75 °C hot water treated sample; (f) 85 °C hot water treated sample; (g) 95 °C hot water treated sample.

The results of ATR-FTIR for oxide removing and sample treated under different water temperature are shown in Fig.6. For cleaned and oxide removing samples, low intensive peaks can be found in 1090 cm^{-1} and 940 cm^{-1}, which indicates hydroxyl bending vibration and Al-O vibrations, respectively. For sample treated by hot water, a broad peak was found around 3300 cm^{-1}, which represents the existence of hydroxyl stretching mode. In addition, the peak for hydroxyl bending vibration became more intense as the increase of hot water temperature and shited to 1060 cm^{-1}. Al-O vibration shifted to 550-650 cm^{-1}, indicating a crystal structure change[12].

Further characterizations are needed to confirm the hot water treatment product in our experiment. However, based on previous publications [8, 13] and the measured hydroxyl stretching and bending vibration peaks, it is highly possible that boehmite (AlOOH) was formed in our case. The hydroxyl group was introduced on the metal surface. In addition, the change of vibration mold of Al-O indicates a much thicker oxide layer was formed during hot water treatment.

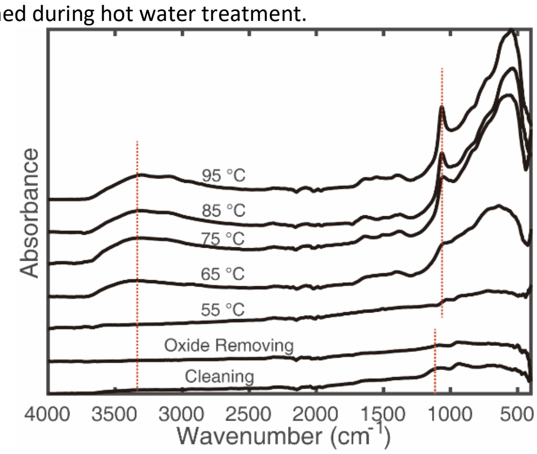

Fig. 6. The ATR-FTIR results of untreated,oxide removing, 55, 65, 75, 85, 95 °C hot water treated samples.

Figure 7 shows the results of tensile shear strength for samples heated in the oven. Error bar is the standard deviation of five measurements. It shows the joining strength dropped when sample heated in 250 °C. However, no obvious strength difference was observed between 250 °C and 500 °C. From this results, it shows the heating is disadvantageous for the joining strength. In addition, the hydroxyl groups seem to have no effect or very little effect for the joining strength between aluminum A5052 and PBT, because the decomposition of AlOOH under 500 °C heating almost had no effects on joining strength.

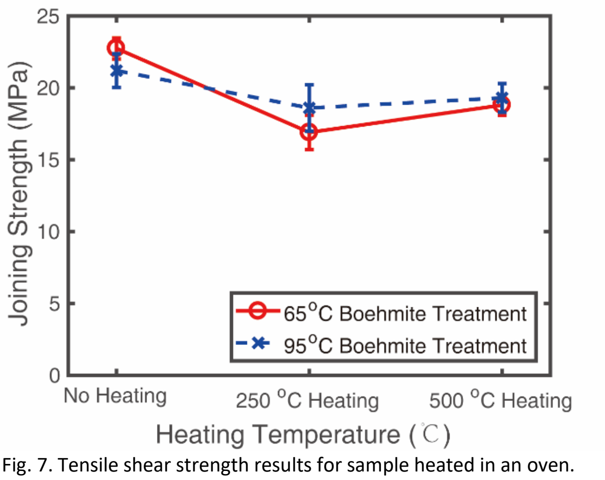

Fig. 7. Tensile shear strength results for sample heated in an oven.

Figure 8 shows the SEM images of samples after heated in an oven. From Fig.8(b) and (e), we can see that the sharp rims of the cellular structures became thicker for 65 °C boehmite treated samples and some plate edges were connected for 95 °C boehmite treated samples. Fig.8(c) and (f) shows that increasing oven temperature to 500 °C does not have an obvious influence on boehmite structures when compared with 250 °C heating.

The SEM results may explain the strength drop after heating under 250 °C. The thickening and connection of rims and plates reduced the number of rims and plates, which was detrimental for mechanical interlocking effect.

Figure 9 (a) and (b) show the results of ATR-FTIR spectrums for 65 °C and 95 °C boehmite treated samples, respectively. It shows the peak of hydroxyl stretching (3300 cm^{-1}) and bending (1060 cm^{-1}) vibration can be found for the sample without heating and the sample heated in 250 °C. The stretching and bending peaks disappeared after heating in 500 °C. This trend exists for both 65 °C and 95 °C boehmite treated samples. The results confirmed that the AlOOH was decomposed and only aluminum oxide existed after 500 °C heating.

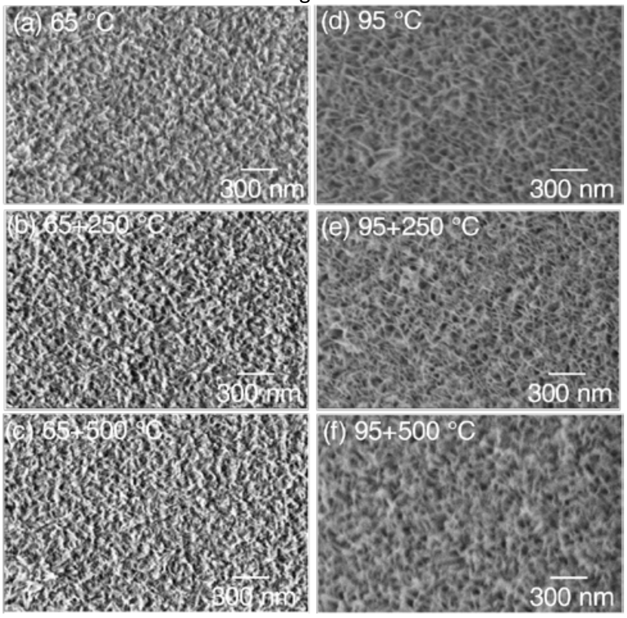

Fig. 8. The SEM images of (a) 65 °C hot water treated sample; (b) 65 °C hot water treated sample heated in 250 °C ; (c) 65 °C hot water treated sample heated in 500 °C; (d) 95 °C hot water treated sample; (e) 95 °C hot water treated sample heated in 250 °C; (f) 95 °C hot water treated sample heated in 500 °C.

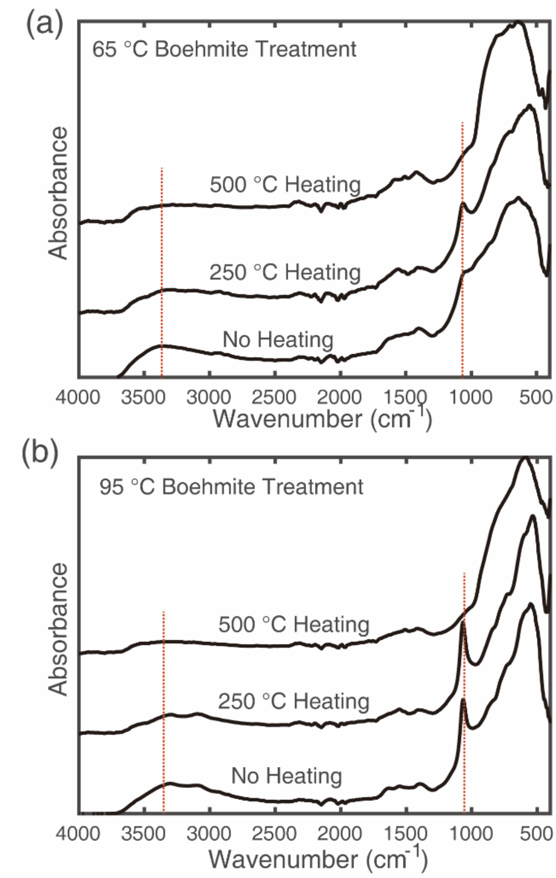

Fig. 9. The ATR-FTIR results of (a) 65 °C hot water treated and oven heated sample; (b) 95 °C hot water treated and oven heated sample.

4. Summary and future work

The hot water treated aluminum plates were successfully joined with PBT by IMDJ. 65 and 95 °C are most suitable temperatures for hot water treatments, which can obtain a strength of 22.74 MPa and 21.2 MPa, respectively. The successful joining is mainly due to the mechanical interlocking. The more nano rims and plates, the higher the strength. In addition, the existence of hydroxyl group has no effect or very litter effect on the joining between aluminum A5052 and PBT. The strength drop after oven heating results from the reduced number of rims and plates, rather than the disappearance of the hydroxyl group. In the future, more characterizations, like AFM and XPS, will be applied to quantitatively study the mechanical interlocking effect and chemical reactions.

Acknowledgements

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