

Influence of surface hydroxyl groups on the direct joining of metal and polymer via injection molding

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Abstract

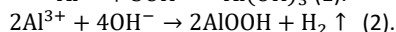
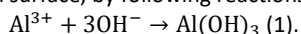
Demand for metal–polymer hybrids is increasing to achieve weight-reducing propose. Injection molded direct joining (IMDJ) is one of the promising direct joining methods. It involves firstly metal surface treatment and followed injection molding with polymer. Joining is achieved by the infiltration of polymer into the surface structures. Although IMDJ has high efficiency and precision, the lack of knowledge in its joining mechanisms, especially the influence of surface chemical conditions on the joining strength, impeded its application in industrials. In this paper, aluminum A5052 plates were used to make the direct joints with polycaprolactam (PA6) via IMDJ. Aluminum plates were treated by hot water treatment (HWT) which needs to immerse metal plates in hot water for several minutes. It produces mountain-like nano-structures consisting of aluminum hydroxide (Al(OH)₃), boehmite (AlOOH), and chemisorbed water on surface. The surface chemical conditions were changed by heating plates at 250 °C and 500 °C for 30 min after HWT. Thus, three different surface chemical conditions, HWT, HWT + 250 °C heating, and HWT + 500 °C heating, were studied. The surface chemical conditions were characterized by XPS. It shows that heating reduced the amount of hydroxyl group and chemisorbed water. This may make the amount of hydroxyl group free of chemisorbed water increase. At the same time, Al/PA6 joining strength increased with increase of heating temperature. It may indicate that the hydrogen bonding exists between hydroxyl groups free of chemisorbed water on metal surface and PA6. Due to the formation of hydrogen bonding, the joining strength increased after heating. On the other hand, the chemisorbed water can combine with the hydroxyl groups and inhibit the formation of hydrogen bonding.

Keywords: Metal-polymer direct joining, Injection molded direct joining, Hot water treatment, Hydroxyl group

1. Introduction

Light weight design now is pursued by automobile industrials to improve energy efficiency. Utilizing metal–polymer hybrid is one way to fulfil this pursue. Many methods have been developed to make metal–polymer hybrid. Among them, injection molded direct joining (IMDJ) is a promising one, due to its automation and high precision. It needs to treat the metal surface (Fig. 1(a)) and then form the polymer part via injection molding (Figs. 1(b) and (c)). The surface treatment is a key process for IMDJ, because the nano/micro-structures and/or surface chemical conditions greatly influence the final joining quality [1].

In our previous study [2], a simple and low-cost surface treatment method, called hot water treatment (HWT), was applied to join aluminium A5052 and polybutylene terephthalate via IMDJ. It treats the aluminum plate by immersing it in hot water, resulting in the formation of mountain-like nano-structures, as shown in Figure 2. The nano-structures consist of aluminum hydroxide (Al(OH)₃) or boehmite (AlOOH) on metal surface, by following reactions:



The nano-structure formed by HWT was well discussed in our previous research. This study focuses on the influence of surface chemical conditions, especially hydroxyl groups, since previous research shows that hydroxyl groups on the metal surface can form the hydrogen bonding with polymer to increase the joining strength [3].

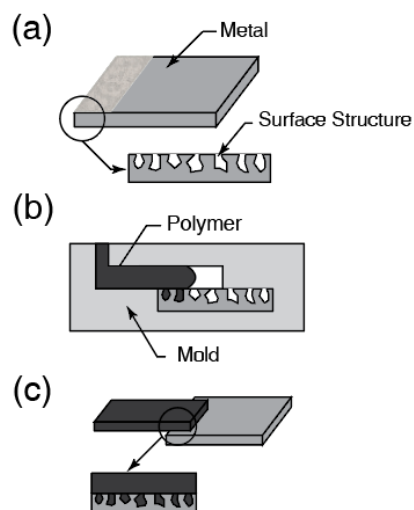


Fig. 1. Schematic illustration of the IMDJ process. (a) Treatment of the metal surface to create micro- or nano-structures. (b) Injection of the molten polymer onto the treated metal surface by injection molding. (c) Formation of the metal–polymer hybrid joint.

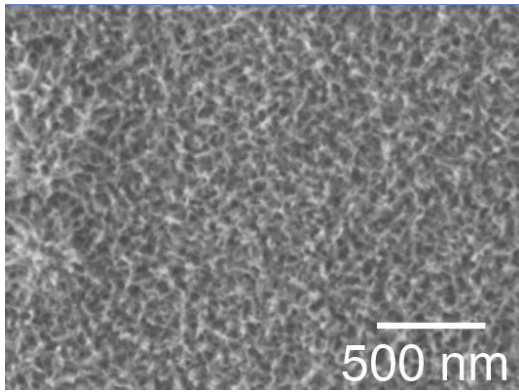


Fig. 2. SEM image of nano-structures formed by HWT on aluminum surface.

Thus, the objective of this research is to reveal the influence of hydroxyl groups on the joining strength. We compare the joining strength between aluminum A5052 plates with three different surface chemical conditions and polycaprolactam (PA6). We change the surface chemical conditions by heating plates at 250 °C and 500 °C for 30 min after HWT. Thus, three surface conditions are HWT, HWT + 250 °C heating, and HWT + 500 °C heating. Heating can change the amount of hydroxyl groups. The change is characterized by X-ray photoelectron spectroscopy (XPS). After that, we discussed the relation between the chemical condition change and the joining strength.

2. Experimental

Metal–polymer direct joints were fabricated by using A5052 aluminum alloy plates and 30% glass fiber-reinforced PA6 polymer (Amilan CM1011G-30, Toray). Figure 3 shows the geometry of a direct joint based on the ISO 19095-2 [4]. The joining area had a size of 5 mm × 10 mm.

The aluminum was first treated to remove the contaminated oxide layer and then immersed in hot water at 65 °C for 5 min, according to our previous research [2]. We changed the surface chemical conditions by an additional heat treatment after the HWT. Some plates were rapidly heated by directly putting them in an oven at high temperatures (250 °C and 500 °C) for 30 min and then cooled in air. The change of surface chemical conditions was characterized by XPS (PHI 5000 VersaProbe, ULVAC-PHI, Inc.). The heating only changed the chemical conditions. The surface roughness and the number of nano-structures were not changed [2]. In our previous, it is found that the joining strength of HWT treated plates was highly correlated to both the surface roughness and the number of nano-structures.

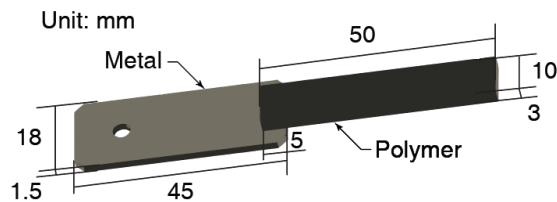


Fig. 3. Geometry of a metal–polymer direct joint.

The treated plates were used to make direct joints with PA6 via injection molding. Figure 4 shows the top-view and side-view of the mold used for injection molding. The injection molding conditions are listed in Table 1. We measure the joining strength after annealing the direct joints at 85 °C for 4 h.

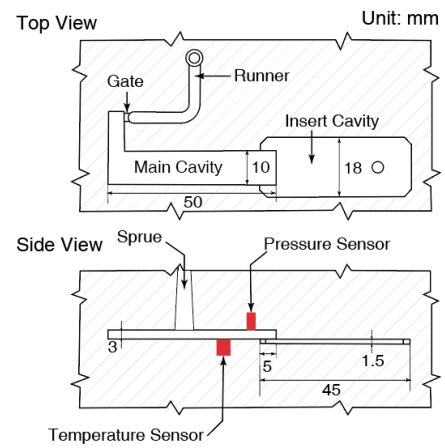


Fig. 4. Top- and side-views of the mold used for injection molding.

Table 1. Injection molding conditions.

Mold Temperature	Injection Speed	Packing Pressure	Holding Pressure	Polymer Temperature
130 °C	10 mm/s	100 MPa	50 MPa	260 °C

3. Results and discussion

The surface chemical conditions were characterized by XPS to show the difference among the surfaces treated by HWT, HWT + 250 °C heating, and HWT + 500 °C heating.

Figure 5 shows the fitted XPS O1s spectrums of the surfaces treated by HWT, HWT + 250 °C heating, and HWT + 500 °C heating. The O1s spectrum shows three peaks due to O in chemisorbed water (533.10 eV), O in hydroxyl groups (531.90 eV), and O in crystal structures (530.50 eV) [5].

Table 2 shows the relative percentage of chemisorbed water (H₂O), O in hydroxyl groups (OH), and O in crystal structures (O²⁻) by calculating the peak intensity in Fig. 5. The O 1s signal from O²⁻ consists of contributions from both AlOOH and Al₂O₃.

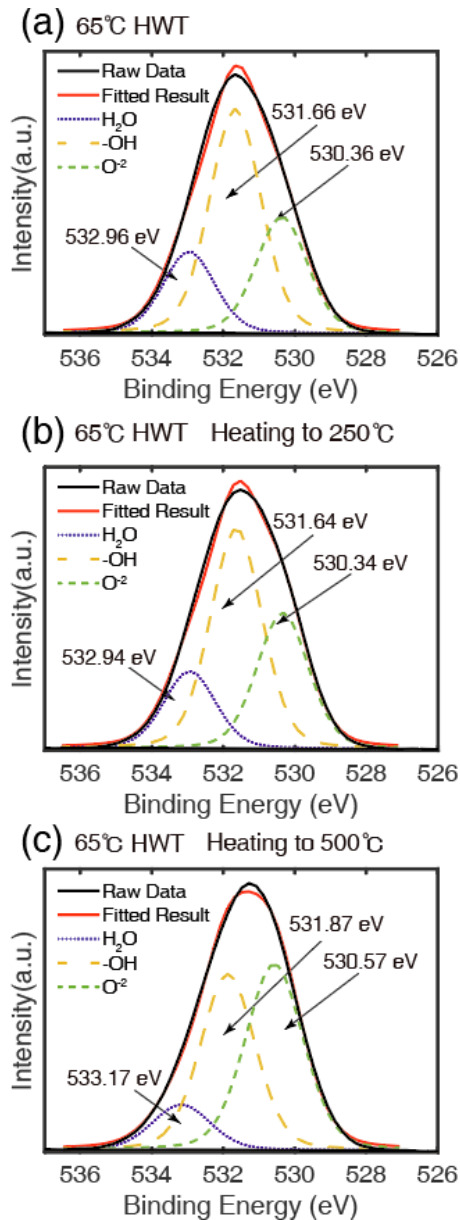


Fig. 5. XPS spectrums of O1s for the aluminum plates treated by (a) HWT; (b) HWT + heating to 250 °C; (c) HWT + heating to 500 °C.

Table 2. The relative percentage of chemisorbed water (H₂O), O in hydroxyl groups (OH), and O in crystal structures (O²⁻).

Conditions	chemisorbed water (H ₂ O)	O in hydroxyl groups (OH)	O in crystal structures (O ²⁻)
HWT	19.3%	53.2%	27.6%
HWT + heating to 250 °C	17.8%	50.8%	31.4%
HWT + heating to 500 °C	11.4%	41.9%	46.8%

For Al(OH)₃, AlOOH, and Al₂O₃, the ratio OH to O²⁻ should be equal to infinite, 1, and 0 based on their compositions.

For the HWT surface, the ratio of OH to O²⁻ is 1.93. This indicates that not only AlOOH but also Al(OH)₃ exist on the surface. This agrees with the previous research [6], which shows that both Al(OH)₃ and AlOOH were produced for aluminum plate treated by HWT at low water temperature. In addition, the percentage of Al₂O₃ on the surface is thought to be small, since immersing in hot water can highly hydroxylate the aluminum surface.

For the surface treated by HWT + 250 °C heating, it shows that OH reduced and O²⁻ increased compared with unheated samples. Al(OH)₃ has a decomposing temperature near 300 °C. It mainly decomposes to AlOOH under fast heating conditions [7].

Based on the results, we suggest that heating at 250 °C caused a very small percentage of Al(OH)₃ to decompose to AlOOH.

For samples heated at 500 °C, the OH is further reduced, indicating the decomposition of Al(OH)₃ to AlOOH. Since the heating temperature of 500 °C is much higher than the decomposition temperature of Al(OH)₃, we believe that nearly all of the Al(OH)₃ decomposed to AlOOH after heating at 500 °C. Under fast heating temperature, AlOOH was reported to decompose at 730 °C [7]. Thus, the heating temperature of 500 °C can hardly decompose AlOOH. The final ratio of OH to O²⁻ is 0.90 after heating at 500 °C, which is near the ratio of OH to O²⁻ of AlOOH. This means the final composition of the surface mainly consists of AlOOH. The existence of a small percentage of Al₂O₃ makes the ratio less than 1, which may come from the decomposition of AlOOH and/or Al(OH)₃ [7]. In summary, with the increase of heating temperature, the percentage of OH on the surface is reduced.

Figure 6 shows the joining strength of the samples treated by HWT, HWT + 250 °C heating, and HWT + 500 °C heating. The joining strength increases slightly after heating at 250 °C, and increase greatly after heating at 500 °C. This trend means that using the surface containing less hydroxyl groups produced higher joining strength. This is in contrast with previous evidence [3], in which the higher joining strength was obtained with samples having higher percentage of hydroxyl groups.

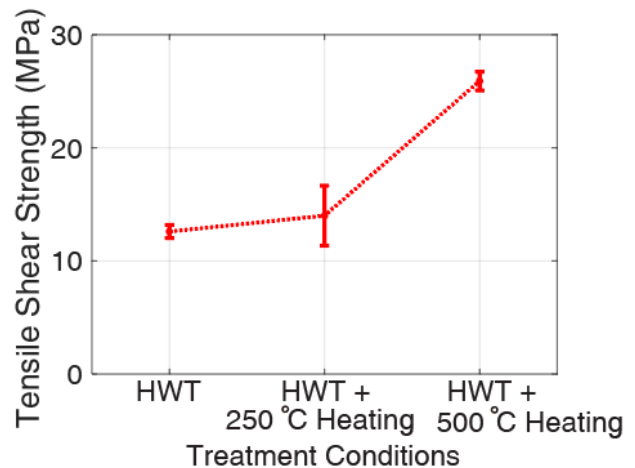


Fig. 6. The joining strength of the samples treated by HWT, HWT + 250 °C heating, and HWT + 500 °C heating

This contradiction should be caused by the negligence of the chemisorbed water. Actually, a lot of water exists on the hot water treated surface, as indicated by the high percentage of H₂O for the HWT surface in table 2. This water is reported to inhibit surface reactivity by blocking hydroxyl groups [8]. For the HWT surface, although many hydroxyl groups exist, a large amount of them are bonded with chemisorbed water and unable to have hydrogen bonding with PA6.

For HWT + 250 °C heating condition, the amount of chemisorbed water and hydroxyl groups only slightly changed, which explained the small increase of the joining strength after 250 °C heating.

For HWT + 500 °C heating condition, the amount of hydroxyl groups was also reduced. At the same time, the amount of chemisorbed water was also reduced. It is assumed that the hydroxyl groups free of the chemisorbed water produced hydrogen bonding with the functional groups in the PA6. The HWT + 500 °C heating samples are assumed to have more hydrogen bonding with PA6 than that of the HWT samples. Thus, the joining strength increased obviously after heating at 500 °C.

Based on the results, we proposed that hydrogen bonding exists between aluminum A5052 and PA6. The hydroxyl groups free of the chemisorbed water on the aluminum surface can combine with the functional groups in PA6. On the other hand, the chemisorbed water can combine with the hydroxyl groups and inhibit the formation of hydrogen bonding.

4. Conclusions and future work

In this work, we studied the influence of hydroxyl groups on the joining strength. Aluminum plates treated by HWT, HWT + 250 °C heating, and HWT + 500 °C heating were used to make the direct joints with PA6. The joining strength increased from 12.6 MPa to 25.9 MPa with the increase of heating temperature, which could result from the hydrogen bonding between the the hydroxyl groups free of the chemisorbed water and the functional groups in the PA6. The chemisorbed water can combine with the hydroxyl groups and inhibit the formation of hydrogen bonding. Understanding the effect of the hydroxyl group and the chemisorbed water is important to make strong joints for the industrials. In future work, we will try to use other surface treatment methods, like plasma treatment, to introduce hydroxyl groups on aluminum surface without the chemisorbed water. HWT is performed in hot water, which may make water easily attach to hydroxyl groups. It is difficult to remove the chemisorbed water and keep the hydroxyl groups at the same time. With other surface treatment method, we hope the strength can increase further.

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