博士論文（要約）

Studying on joining mechanisms of injection molded metal–plastic direct joining
（金属樹脂直接成形接合の接合メカニズムに関する研究）

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This thesis focused on revealing the joining mechanisms of injection molded direct joining (IMDJ). IMDJ is a promising metal–plastic direct joining method due to its high efficiency, integrated molding, and ability to form complex-shaped products. IMDJ has been used in the consumer electronics industry. However, the application of IMDJ is still limited in the automotive industry due to the uncleared joining mechanisms. Previous studies indicated two joining mechanisms for IMDJ, the mechanical interlocking and the intermolecular forces. The mechanical interlocking is produced by the anchoring between the surface structures and the infiltrated plastics, while the intermolecular forces are decided by the interaction between polar groups on the metal surface and functional groups in the plastic.

For the mechanical interlocking, many authors assumed that the infiltration depth (the depth of plastic flowed into surface structures) was decisive. However, experimental evidence was lacked. On the other hand, for the intermolecular forces, their existence is still under discussions for IMDJ. Making clear of the joining mechanisms is vital to promote the application of IMDJ in engineering fields. Therefore, the objective of this thesis was to reveal the joining mechanisms of IMDJ. Since the joining mechanisms of IMDJ include the mechanical interlocking and the intermolecular forces, two sub-objectives were set. The first objective was set to understand the infiltration process of the melted plastic and the relation between the infiltration depth and the joining strength. The second objective was set to verify the existence of the intermolecular forces.

According to the objectives, this thesis contained seven chapters.

In chapter 1, the increasing need for metal–plastic joining techniques in car manufacturing and consumer electronics industries was introduced. Conventional metal–plastic joining techniques and several metal–plastic direct joining techniques were reviewed. This thesis focused on injection molding direct joining (IMDJ), due to its high efficiency, integrated molding, and ability to form complex-shaped products. In order to make reliable joints and promote the application of IMDJ in industries, understanding the joining mechanisms of IMDJ is vital. IMDJ has two joining mechanisms, mechanical interlocking and intermolecular forces. According to previous studies, the uncleared points for these two joining mechanisms were defined. Aiming to reveal the joining mechanism of IMDJ, this thesis set two sub-objectives. one related to the mechanical interlocking, and the other related to the intermolecular forces. Four topics were developed.

(1) Studying the relation between infiltration depth and joining strength.

(2) Observing the infiltration during injection molding via the mold visualization technique

(3) Finding a suitable method for studying intermolecular forces

(4) Verifying the existence of intermolecular forces

The first two topics aimed to make clear of the infiltration, while the other topics focused on the verification of the existence of intermolecular forces.

In chapter 2, the first part related to the fabrication of metal–plastic joints. Materials were introduced. The metal was aluminum A5052, and the plastics were PBT and PA6. Then, chapter 2 introduced the surface treatments and explained the reasons for the selection of these treatment methods. Laser ablation was used for studying the mechanical interlocking, while hot water treatment and additional heat treatment were used for verifying the existence of intermolecular forces. After the surface treatments, aluminum plates were ready for injection insert molding. The injection molding machine and the mold were introduced. The surface of the treated aluminum plates and the joints were characterized by various methods to understand the joining mechanisms. The second part related to the mold visualization. The material (PS), the mold and setups for mold visualization, and characterization methods were introduced.

Chapter 3 related to the first topic. Aluminum plates with laser-treated surface dimples were used to join with PBT under various injection molding parameters. The infiltration depth was measured by dissolving the aluminum parts. Besides, the cross-section of the joint was observed to check the contact between metal and plastic. The effects of injection parameters on the infiltration depth and the contact were revealed. Among the injection parameters studied in this thesis, higher packing pressure and higher plastic temperature resulted in deeper infiltration. The influence of holding pressure and injection speed had a minor influence on the infiltration depth. Higher packing pressure, higher plastic temperature, applying holding pressure, and higher injection speed contributed to better contact. The positive correlations between the infiltration depth and the joining strength, and between the contact and the joining strength were found.

Chapter 4 focused on the second topic. The infiltration process of the melted plastic was observed via the mold visualization technique. The video taken by the high-speed camera showed that the melted plastic flowed into the holes by the flow-induced pressure before the cavity full. The infiltration was easier for larger-sized holes. At the moment of cavity full, the packing pressure pushed the melted plastics to a deeper position. Especially, for the small-sized hole, the packing pressure was important for full infiltration. After the cavity full, applying the holding pressure reduced the shrinkage of the plastic.

Chapter 5 focused on the third topic. a surface treatment method, hot water treatment (HWT), was introduced. HWT produced nanostructures consisting of aluminum hydroxide ($Al(OH)_3$) and boehmite (AlOOH) on the aluminum surface via aluminum–water reaction. HWT conditions, including water temperature and treatment time, were optimized. The highest joining strength was obtained with aluminum plates treated at 65 °C for 5 minutes. Besides, the relation between the surface nanostructures and the joining strength was discussed. The joining strength correlated with both surface roughness (*Sa*) and the number of nanostructures (*Nn*).

Chapter 6 concentrated on the fourth topic. The aluminum plates treated by hot water at 65 °C for 5 minutes were used to verify the existence of the intermolecular forces. Additional heat treatment was used to prepare aluminum plates with different surface chemical conditions. The surface conditions were characterized by SEM, AFM, XPS, contact angle measurement. A layer system model that consist of a contamination layer, a chemisorbed water layer, a hydroxide layer, and metal substrate was proposed. Aluminum plates were joined with PBT and PA6. The joining strength and the interface of the metal–plastic joints were analyzed to provide evidence for the existence of the intermolecular forces. Results showed that the additional heating did not change the nanostructures. However, the thickness of the chemisorbed water layer was reduced. The number of hydroxyl groups was reduced due to the decomposition of aluminum hydroxide ($Al(OH)_3$) to boehmite (AlOOH). The joining strength between aluminum and PA6 increased after heating due to the formation of hydrogen bonding between the hydroxyl groups on the aluminum surface and the peptide group (-CONH) in PA6. In AFM-IR spectrums, the formation of hydrogen bonding caused the relative intensify change and the peak formation/reduction. On the other hand, the joining strength between aluminum and PBT did not change because the hydroxyl groups on the surface did not form hydrogen bonding with the ester group (-COO-) in PBT.

Chapter 7 summarized the whole thesis. The obtained results are listed as follows.

- Revealed the relation among injection parameters, infiltration depth, and joining strength

Not only the infiltration depth but also the contact between metal and plastic influenced the joining strength. Deeper infiltration depth and better contact between metal and plastic resulted in higher joining strength. The infiltration depth and the contact were influenced by the injection parameters. Among the injection parameters studied in this thesis, higher packing pressure and higher plastic temperature were conducive to the deeper infiltration. Holding pressure and injection speed had a minor influence on the infiltration depth. Higher packing pressure, higher plastic temperature, applying holding pressure, and higher injection speed contributed to better contact.

- Revealed the infiltration process via mold visualization

After the melted plastic passed the holes on the metal surface, it flowed into the holes by the flow-induced pressure. The infiltration was easier for larger-sized holes. With the packing pressure, the melted plastic was pushed to a deeper position. For the full infiltration of small-sized holes, applying packing pressure was important. Applying the holding pressure compensated for the shrinkage of the plastic.

- Optimized the hot water treatment (HWT)

HWT produced complex nanostructures on the aluminum surface via the aluminum-water reaction. The highest joining strength was obtained with aluminum plates treated at 65 °C for 5 minutes. The joining strength correlated with both surface roughness (*Sa*) and the number of nanostructures (*Nn*). A surprising finding is that high joining strength between aluminum and PBT was obtained with just hot water treated aluminum plates. The oxide removing in the pretreatment process was decisive for obtaining high joining strength. HWT showed huge potentials for industries.

- Verified the existence of intermolecular forces

Additional heat treatment on hot water treated aluminum plates did not influence the nanostructures on the surface, but it changed the chemical conditions of the surface. The thickness of the chemisorbed water layer was reduced, and $Al(OH)_3$ was decomposed to AlOOH. A layer system model that consist of a contamination layer, a chemisorbed water layer, a hydroxide layer, and metal substrate was proposed to describe the aluminum surface. For the aluminum/PA6 joint, the joining strength increased by the additional heat treatment, especially after heating at 500 °C. The increased joining strength was believed to result from the hydrogen bonding between C=O/N-H in -CONH and the hydroxyl groups on the aluminum surface. On the other hand, the joining strength did not change for the aluminum/PBT joint, which indicates that the hydroxyl groups on the aluminum surface did not produce hydrogen bonding with -COO- in PBT.

The obtained results show that the objectives were well attained. The results provide valuable information for industries. At first, the thesis shows that intermolecular forces influence the joining strength between metal and plastic. In practical applications, manufacturers should pay attention to not only the surface structures but also the chemical conditions of the surface. Besides, the selection of a suitable pair of metal and plastic is also vital for achieving high joining strength due to the existence of intermolecular forces. Furthermore, for the direct joining between metal plates with micro-sized surface structures and plastics, high packing pressure, high plastic temperature, high injection speed, and applying holding pressure are recommended.