

Interface analysis of injection molded direct joining using surface nano-structures

Fuminobu Kimura¹, Shotaro Kadoya¹, Yukinaga Arai², Akitsu Shigetou², and Yusuke Kajihara¹

¹Institute of Industrial Science, The University of Tokyo

²National Institute for Materials Science

fuminobu@iis.u-tokyo.ac.jp

Abstract

Direct joining of metal and polymer structures is a promising technology for future industries. One of the means of the direct joining is an injection molded direct joining (IMDJ) that is based on two key processes: special surface treatment forming nano-structures on a metal surface and insert injection molding. The injection molded polymer structure is joined to the metal piece via the nano-structured surface. Since actual joining mechanism has not been revealed, the IMDJ has not been well applied to real industries. As one of revealing approaches, we carried out a basic observation/analysis of an interface of the IMDJ product in this study. We observed the cross section of the metal-polymer interface by a transmission electron microscope (TEM) and performed an electron energy-loss spectroscopy (EELS). The observation and the analysis results showed that the metal and polymer structures were not divided clearly at the interface: there was a reaction layer. This means that the joining is not caused by only anchor effects. This result will lead understandings of the actual joining mechanism.

Injection molding, Metal-polymer direct joining, Interface analysis

1. Introduction

By using a metal workpiece with a fine-structured surface, an injection molded polymer can be directly joined to the metal workpiece via the structured surface. This process is injection molded direct joining (IMDJ). The previous studies proposed a variety of surface structuring for the IMDJ by using abrasive blasting [1], laser processing [2], and chemical processing [3, 4] to form the nano/micro-scale sized structures. This study focuses on the nano-structures since the geometry limitation of the IMDJ product depends on the size of the surface structures; the smaller surface structures make the lower limitation.

The joining can be caused by a nano-anchor effect, intermolecular force, chemical coupling, and/or other effects; however the actual joining mechanism has not been revealed. To reveal the mechanism, in previous studies [5, 6], we have investigated how variations of processing conditions affect joining strength by mechanical tests. In addition to the mechanical tests, observations or analyses of joining interface are necessary for entire understanding of the IMDJ. Therefore, this report deals with the observation/analysis in nanoscale. From the results, we discuss elements at the interface affecting joining.

2. Sample preparation

2.1. IMDJ process

Figure 1 shows an overview of the IMDJ process that is composed of two key processes; (a) surface treatment of a metal workpiece and (b) insert injection molding of a thermoplastic. The surface treatment forms nano-structures on the metal workpiece. In the injection molding process, a melted polymer flows into the mold which the surface-treated metal workpiece is previously placed in. When the polymer cools and hardens, the molded polymer structure is joined to the metal piece via the treated surface. This process simultaneously

produces the joining as well as the formation of polymer structure.

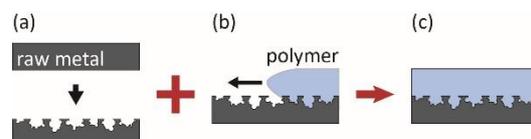


Figure 1. Overview of IMDJ process.

In this study, we utilized aluminum alloy (A5052) pieces as target metal workpieces and performed a chemical processing (NMT process, Taiseiplas [4]) for the surface treatment. This surface treatment provided porous structures on the surface of the metal workpieces as shown in Fig. 2: the size of each pore was approximately 20 nm. As a polymer material, we utilized polybutylene terephthalate (PBT: Toraycon 1101G-X54, Toray).

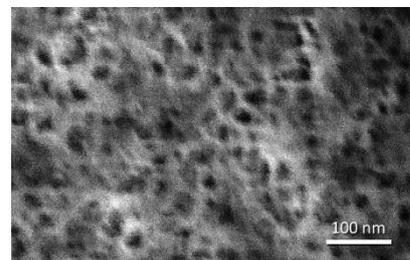


Figure 2. SEM image of the surface-treated metal workpiece.

Table 1 shows molding conditions. The condition values are not optimized for joining strength, which means that the strength of the samples used in this study were not the highest of our previous studies.

Table 1. Molding conditions.

Packing pressure	90 MPa	Injection rate	31.4 cm ³ /s
Holding pressure	60 MPa	Cylinder temp.	270 °C
Holding time	8 s	Mold temp.	140 °C

2.2 Slicing IMDJ sample

To observe and analyze an interface of the IMDJ sample by a transmission electron microscope (TEM) and an electron energy-loss spectroscopy (EELS), we prepared an ultra-thin specimen (thickness: < 50 nm), which contained cross-section of the metal-polymer interface, by slicing the molded bulk IMDJ sample. In this study, we utilized a focused ion beam (FIB) to make the ultra-thin specimen. A low-magnification TEM image of the sliced specimen is shown in Fig. 3.

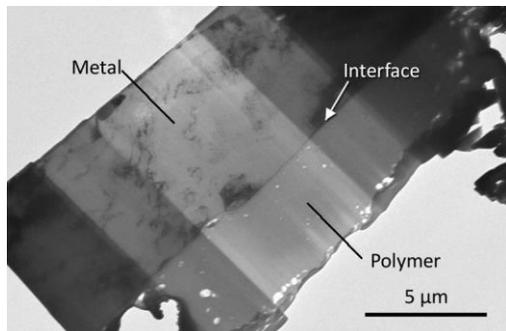


Figure 3. Ultra-thin specimen provided by a FIB.

3. Results and discussion

3.1 TEM image

Figure 4 shows a high-magnification image of the metal-polymer interface observed by a TEM. From this image, we can see a reaction layer (approximately 100 nm in width) whose contrast is different from that of metal area nor polymer area. It seems there were compounds made from reaction of the aluminum and the PBT polymer.

We cannot see any void spaces in the reaction layer. No void space means that the melt polymer fully flows into the surface nano-structures. Our previous studies [5, 6] discussed that joining strength was affected by how much nano-structures were filled with the polymer: the higher filling ratio provided the higher joining strength. Although there was no void spaces in the sample, joining strength was not the highest as described in the section 2.1. This fact indicates the joining is caused by not only anchoring to the nano-structures but also aluminum-PBT chemical reactions.

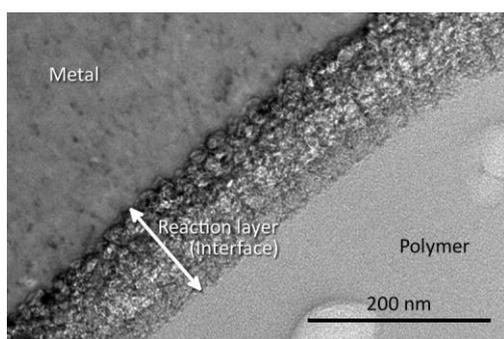


Figure 4. High-magnification TEM image of metal-polymer interface.

3.2 EELS result

Three points of the ultra-thin specimen were analyzed by an EELS; a polymer area, a reaction layer, and a metal area. The distances of measured points of the polymer and metal areas from the reaction layer were a few μm. Figure 5 shows energy-loss spectra. The graph also shows reference data of aluminum oxide (Al_2O_3) and pure aluminum (Al) obtained from a material database. To see clearly, the intensity shown in this graph was normalized and shifted by adding offsets.

Since all rising edges of both measured and reference spectra appeared in similar level of energy loss, aluminum elements could exist in all points. It indicates aluminum ion could diffuse in the polymer region. The spectra of the metal area and Al_2O_3 reference behave similar curves, which means that the major

element of metal area is Al_2O_3 (the aluminum of the metal area was possibly oxidized after the FIB process). In addition, the spectrum in the reaction layer behaves differently from both the reference spectra. Thus, the element in the reaction layer was neither pure aluminum nor Al_2O_3 . It is possible that Al-organic compounds exist in the reaction layer, which will be confirmed in future work.

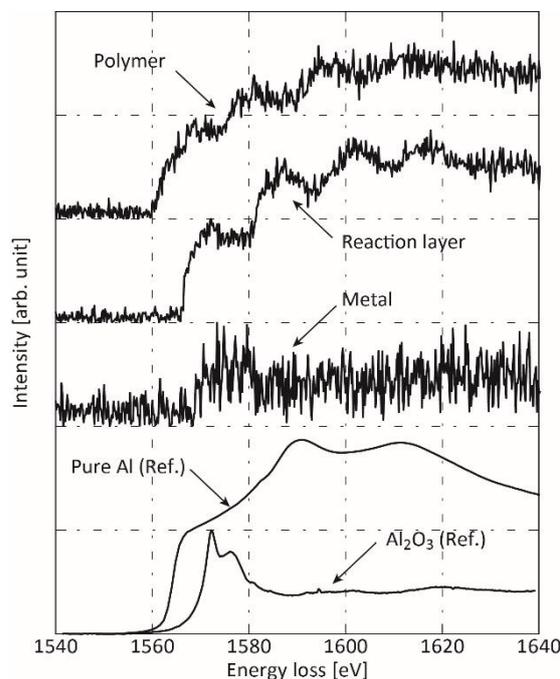


Figure 5. Energy-loss spectra provided by an EELS.

4. Conclusion

In this study, we dealt with the observation and analysis of the interface of the metal-polymer direct joining produced by the IMDJ process using surface nano-structures. To make ultra-thin specimens from the bulk IMDJ samples, this study performed a FIB process. We observed and analyzed the interface of the ultra-thin specimen by using a TEM and an EELS. Resultantly, we found that three types of layers, metal, polymer, and reaction layers, exist at the interface. In addition, the EELS result indicated that aluminum ion could diffuse in the polymer region and the reaction layer. The diffused aluminum ion could provide unknown compounds in the reaction layer. In future work, we will investigate effects of processing conditions of the IMDJ upon the interface appearances or elements by using the technique shown in this study.

Acknowledgements

This work was supported by JSPS KAKENHI (#15K17946) and Foundation for the Promotion of Industrial Science, Japan. Parts of the experiments were supported by "Nanotechnology Platform" of the Ministry of Education, Culture, Sports, Science and Technology and Yokoi group, the University of Tokyo, Japan.

References

- [1] Ramani K and Moriarty B 1998 *Polym. Eng. & Sci.* **38** 870-7
- [2] Taki K, Nakamura S, Takayama T, Nemoto A and Ito H 2016 *Microsyst. Technol.* **22** 31-8
- [3] Fabrin P A, Hoikkanen M E and Vuorinen J E 2007 *Polym. Eng. & Sci.* **47** 1187-91
- [4] Naritomi M and Andoh N 2010 *US Patent* 12/669,143 (2010-Jul-29)
- [5] Kimura F, Kadoya S and Kajihara Y 2015 *Proc. MATADOR 2015* pp. 154-158
- [6] Kimura F, Kadoya S and Kajihara Y 2015 *Proc. LEM21 2015* 2507