INTERFACIAL STRUCTURE ANALYSES OF POLYMER LAMINATES USING SCANNING THERMAL MICROSCOPE, MICRO-BEAM X-RAY DIFFRACTION, AND NANO-RAMAN SPECTROSCOPE

C. Hongo[a,b*], M. Kotera[a,b], Y. Urushihara[c], D. Izumo[a], T. Nishino[a,b]

[a] *Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Rokko, Nada, Kobe 657-8501, Japan*
[b] *Organization of Advanced Science and Technology, Kobe University, Rokko, Nada, Kobe 657-8501, Japan*
[c] *Hyogo Science and Technology Association, Kouto, Shingu, Tatsuno, Hyogo*
**e-mail address of the corresponding author (chizuh@crystal.kobe-u.ac.jp)*

**Keywords:** Polymer Interface, Scanning Thermal Microscope, Raman Spectroscope, Micro-beam X-ray Diffraction.

Abstract

Polymer laminate interfaces were analyzed with high spatial resolutions using scanning thermal microscopy, synchrotron micro-beam X-ray diffraction, and confocal laser nano-Raman spectroscopy. For poly-α-olefin laminates, such as linear low density polyethylene (LLDPE)/deuterated polyethylene (D-PE) and, LLDPE/isotactic polypropylene (it.PP) combinations, the interfacial thickness was evaluated as several micrometer, which changed by annealing. The adhesive strength was found to be correlated with the interfacial thickness.

1. Introduction

Composite materials and laminates are composed of physically and chemically dissimilar materials, and hence, there exists an interfacial region (interface/interphase) between these dissimilar components [1]. The interfacial region plays an important role in the overall composite performance such as mechanical, thermal, electrical properties [2]. However, because of the relatively small volume of the interfacial region as compared to that of the bulk material, conventional analytical techniques are unsuitable for elucidation of the interfacial microstructure and properties. Many tools and methods have been proposed for surface analyses such as an X-ray photoelectron spectroscopy, a secondary ion mass spectroscopy, an attenuated total reflection of infrared, an atomic force microscopy and so on. They provide useful information on the surface characteristics and properties of the polymer composites. However, most of them cannot be utilized for the interface analyses, especially non-destructive evaluation method has been very limited. In addition, high spatial resolution will be needed because the interfacial region is localized between two substances.

We reported the use of synchrotron micro-beam X-ray diffraction (μ-X-ray) [3], scanning thermal microscopy (SThM) [4] and confocal laser nano-Raman spectroscopy (nano-Raman) [5] to evaluate the interfacial thickness of a poly-α-olefin laminates (Figure 1).
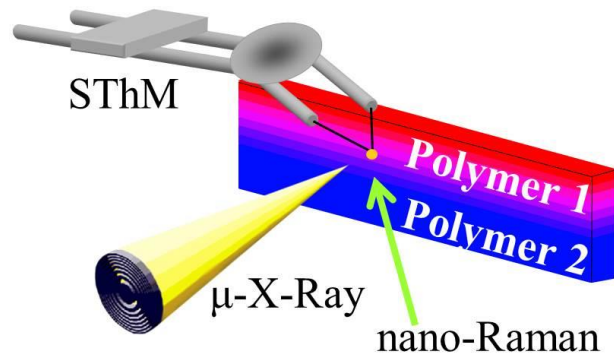
Figure 1. Schematic illustrations of scanning thermal microscope (SThM), synchrotron µ-beam X-ray diffraction (µ-X-ray) and nano-Raman scattering (nano-Raman) to investigate the interfacial region of the laminate.

In this study, we tried to adopt these methods for interfacial analyses of polymer laminates, such as linear low density polyethylene (LLDPE)/isotactic polypropylene (*it.*PP), and LLDPE/deuterated polyethylene (D-PE) combinations. We also investigated the effect of thermal treatment on the interfacial structure and peel strength, and attempted to correlate them to the interfacial thickness.

2. Materials and Methods
2.1 Sample Preparation
2.1.1 LLDPE/it.PP Laminate

Linear low density PE (LLDPE, Melting point (Tm): 107 °C) and deuterated PE (D-PE, Tm: 125 °C) films were laminated by a hot press at 125 °C and 6 MPa, and then quenched in ice water. The laminated film was then annealed at 90 °C for 2 h.

2.1.2 LLDPE/D-PE Laminate

LLDPE (Tm: 120 °C) and *it.* PP (Tm: 160 °C) films were laminated by a hot press at 150 °C and 6 MPa, and then quenched. The laminated film was then annealed at 100 °C for 2 h.

The cross-section of the laminate was cut into rectangular blocks using a microtome, and the interfacial region was investigated.

2.2 Measurements

An SThM probe, X-ray micro-beam, and laser beam for Raman scattering were scanned across the interfacial region of the poly-α-olefin laminate.

2.2.1 Scanning thermal microscope (SThM)

Thermal images of the laminate interface were taken by SThM (TA Instruments, 2990 Micro-Thermal Analyzer) with a contact mode. A scan speed of 320 mm/s, an applied constant force

of 40 nN at a constant probe temperature of 50°C for LLDPE/*it*.PP Laminate and 65 °C for LLDPE/D-PE Laminate were the conditions employed.

2.2.2 Synchrotron µ-beam X-ray diffraction analysis (µ-X-ray)

Micro-beam X-ray diffraction of the interfacial region was conducted using the synchrotron X-ray beam generated at SPring-8 BL24 XU in Japan [3]. The X-ray micro-beam (0.9µm (vertical) × 1.7 µm (horizontal)) formed using a phase zone plate was irradiated on the cross-section of the laminated films. By changing the sample Z-position in a stepwise manner, the X-ray diffraction pattern at each position was detected on an imaging plate (IP). The X-ray exposure time was 300 s for each pattern.

2.2.3 Nano-Raman scattering (nano-Raman)

Nano-Raman spectroscopy measurements were performed using a confocal laser Raman spectroscope (Tokyo Instruments, Inc.,Nanofinder 30) with an Ar laser at a wavelength of 514.5 nm and a space resolution of 400 nm. The laminated samples were irradiated by the focused laser beam with a power of 1.2 mW for 10 s, and the Raman scattering spectra with a resolution of 6 cm^{-1} were recorded. Raman mapping at the interfacial region for laminated films were performed by moving the sample X-Y piezo positioning stage at 234 nm/step. The exposure time was 1 s for each position.

2.2.4 T-peel strength

The peel strength of the laminated film was measured by using a tensile tester (Shimadzu, AutographAGS-1kND) at 25°C. The films (sample width of 5 mm) were T-peeled off at 180° at the rate of 50 mm/min.

3. Results and Discussion
3.1 LLDPE/it.PP Laminate

Figure 2 shows the X-ray diffraction profiles of the laminated films for different sample Z-positions across the LLDPE/*it*.PP interface. For position (a), only diffraction peaks belonging to orthorhombic PE appeared. By changing the Z-position from the PE side to the *it*.PP side, the diffraction intensity belonging to α-form *it*.PP gradually increased, and finally, only diffraction peaks from α-form *it*.PP remained at the position of 4.69 µm apart from (a). The interfacial thickness obtained in this study was much greater than that reported by Chaffin *et al.* for PE/PP laminates (about 10 nm, by transmission electron microscopy image [6]). On the other hand, Ougizawa observed a very thick interface (of about 60 µm) between PP and ethylene-propylene rubber [7]. The X-ray microdiffraction method was performed under transmission geometry through the 50 µm sample thickness, so the value of the interfacial thickness may include the interfacial roughness or may be convoluted with the X-ray microbeam shape. We here defined the Z-distance with co-existence of the diffraction peaks both from LLDPE and *it*.PP crystalline regions as the thickness of interfacial region. According to the above results, the laminated film possesses an interfacial region of around 5 µm thickness. Judging from the diffraction peaks, crystallite size is almost same independent
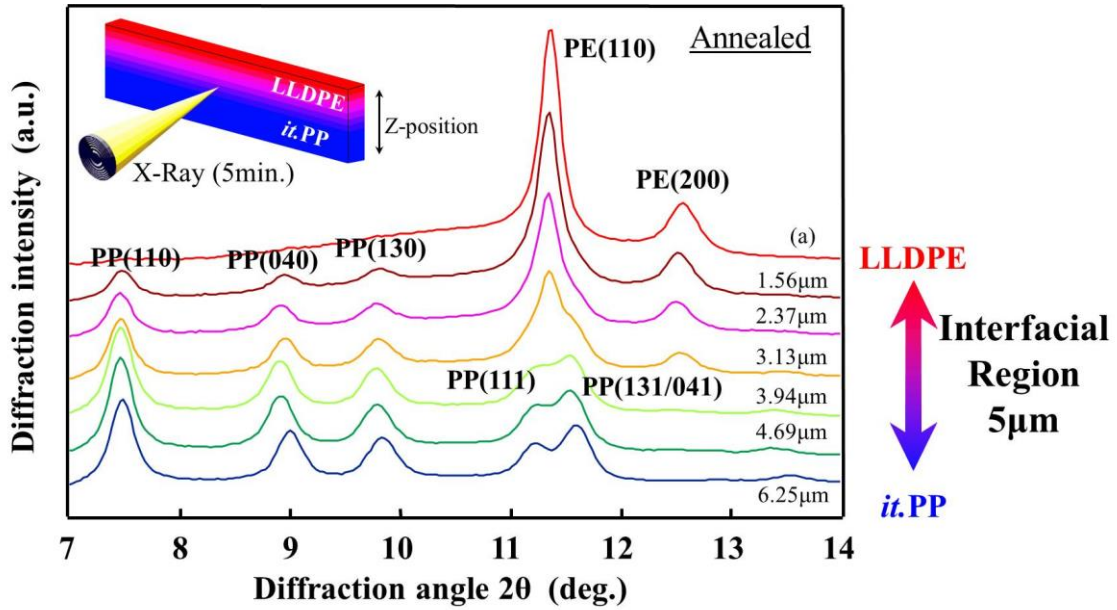
Figure 2. X-ray diffraction profiles of the laminated films by changing the sample Z-position across the PE/PP interfacial region.
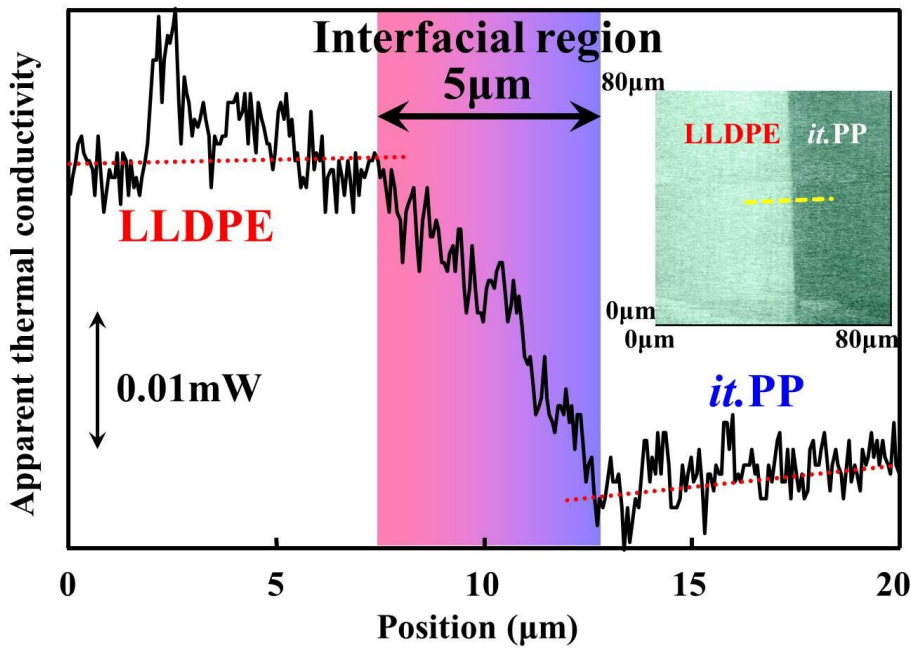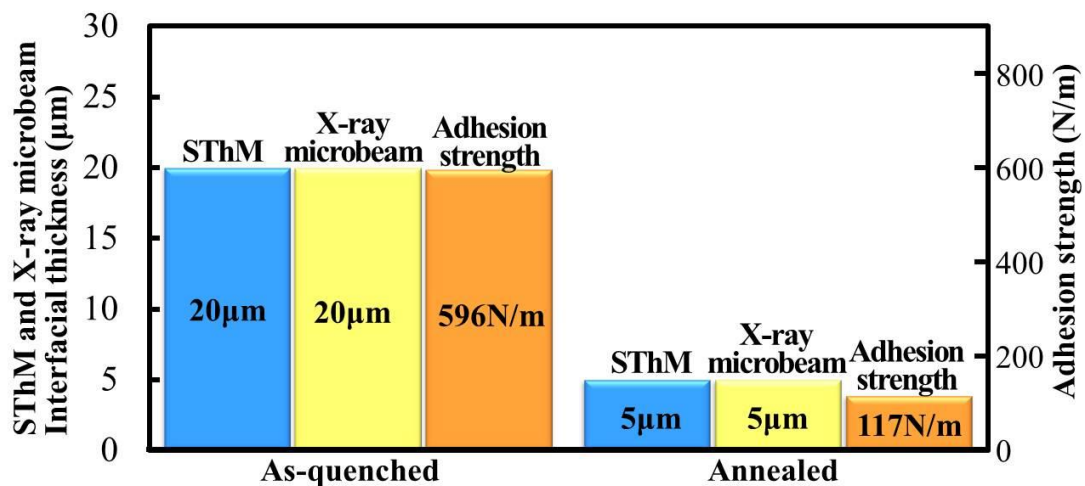

Figure 3. The apparent thermal conductivity image and one-dimensional profile along the broken line in the image around the interface of the annealed LLDPE/*it.*PP laminate.

of the Z-position in this study. As described before, interfacial structure of the LLDPE/it.PP laminated film will be influenced by annealing.

Figure 3 shows the two-dimensional apparent thermal conductivity image and one-dimensional apparent thermal conductivity profile along the broken line in the image around the interface of the annealed LLDPE/*it.*PP laminate. The apparent thermal conductivity gradually changes across the tapered interface between the two polymers. Here, the thickness of interfacial region is defined as the distance between the positions leave from the baseline of

the profile. According to this profile, the annealed LLDPE/*it.*PP laminate possesses an interfacial region with 5 μm thickness. Good reproducibility (±1 μm) of this value was confirmed by five measurements with the probe scan at different interface positions.

Figure 4 shows the interfacial thickness estimated by μ-X-ray and SThM analyses, together with the T-peel strength of as-quenched and annealed LLDPE/it.PP laminate. The interfacial region of the quenched sample was four times thicker than that of the annealed sample. The peel strength of the quenched sample was also about four times higher than that of the annealed sample. In both cases, the peeled position was always at the LLDPE/it.PP interfacial region. The quenched sample possesses a thicker interfacial region with entangled molecular chains of LLDPE and it.PP during processing. The entangled chains act as anchoring points between crystalline lamellae of both LLDPE and it.PP [3]. This is the reason that the quenched sample possesses high adhesion strength. However, LLDPE and it.PP are thermodynamically incompatible and form a non-reactive system. Thus, when the quenched sample is annealed at 100°C, further crystallization will be accompanied with phase separation[6]. These induced the decrease of the interfacial thickness, which is considered to be responsible for the decrease of the T-peel strength.


Figure 4. The interfacial thickness estimated by μ-X-ray and SThM analyses, together with the T-peel strength of as-quenched and annealed LLDPE/*it.*PP laminate.

3.2 LLDPE/D-PE Laminate

Figure 5 shows the two-dimensional apparent thermal conductivity image and one-dimensional apparent thermal conductivity profile along the broken line in the image around the interfacial region of the as-quenched LLDPE/D-PE laminate using SThM. The apparent thermal conductivity gradually changes across the tapered interfacial region between the LLDPE and D-PE. According to this profile, the as-quenched LLDPE/D-PE laminate possesses an interfacial region with a thickness of 3 μm. This estimated value should be a convolution of an interfacial thickness with the contact area of the thermal probe.

Figure 6 shows the nano-Raman spectra of (upper) LLDPE and (lower) D-PE in the range of 800-1400 cm^{-1}. Though both of them are polyethylene, the spectra were different each other. This reveals that polyethylene could be distinguished by deuteration using nano-Raman scattering. The scattering peak appears in the range of 1047-1107cm^{-1} is assigned as ν(C-C)T of LLDPE, and that of 962-1002cm^{-1} as δ(CD2) of D-PE, respectively [8-10]. By integrating
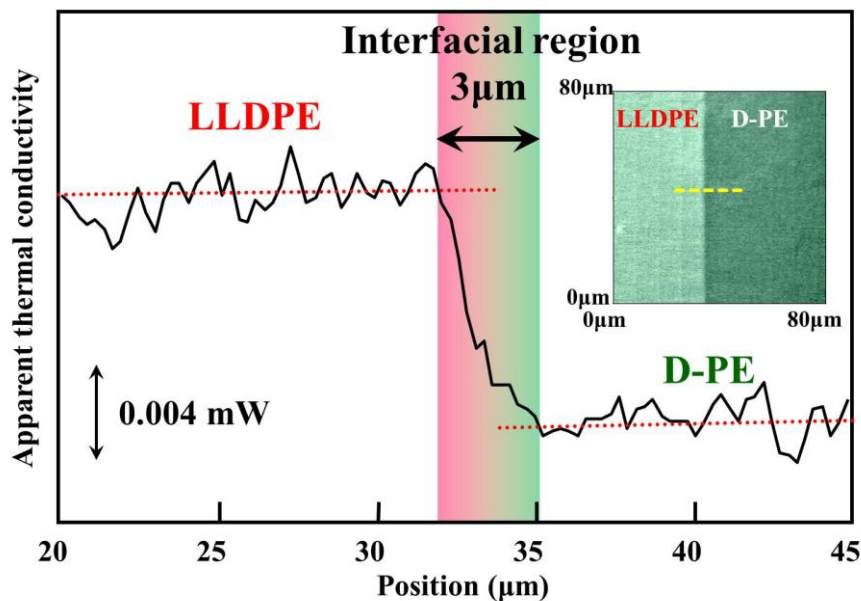
Figure 5. The apparent thermal conductivity image and one-dimensional profile along the broken line in the image around the interface of the as-quenched LLDPE/D-PE laminate
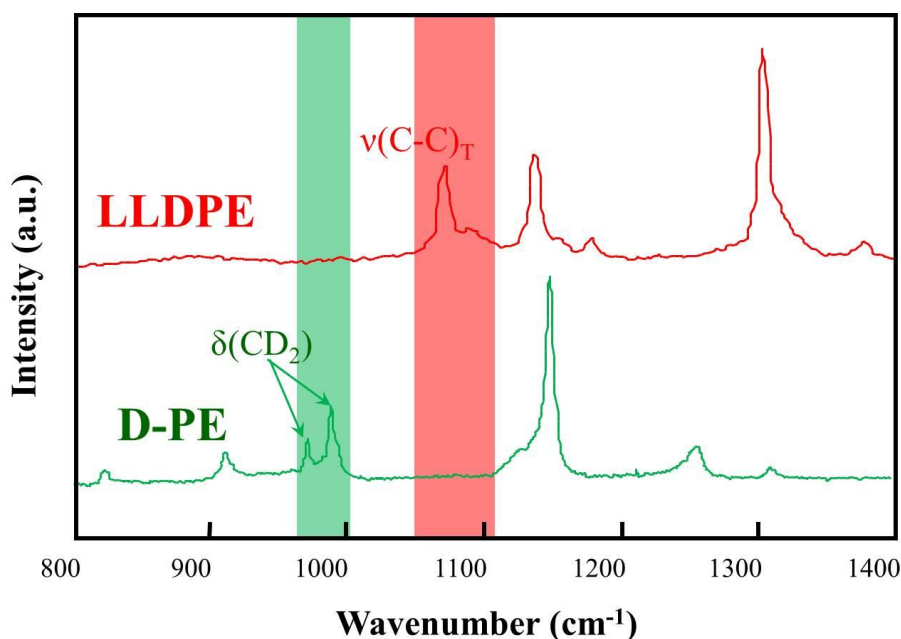
Figure 6. Nano-Raman spectra of (upper) LLDPE and (lower) D-PE in the range 800-1400 cm^{-1}.

the intensity of these scattering peaks, two dimensional distributions of LLDPE and D-PE are expected to be evaluated.

Figure 7 shows the two dimensional nano-Raman images of as-quenched LLDPE / D-PE interfacial region from the integral intensity in the range of (a) 1047-1107cm^{-1}, (b) 962-1002cm^{-1}, respectively, and (c) the line profile of the intensity across the interfacial region. The intensity of 1047-1107 cm^{-1} peak was higher for the LLDPE region in Fig.6 (a). In contrast, the intensity of 962-1002cm^{-1} peak was higher for the D-PE region in Fig.6 (b). The intensity profiles in Fig.6 (c) crossed each other with the tapered curves, from which the thickness of the interfacial region can be evaluated as 1.7 μm.
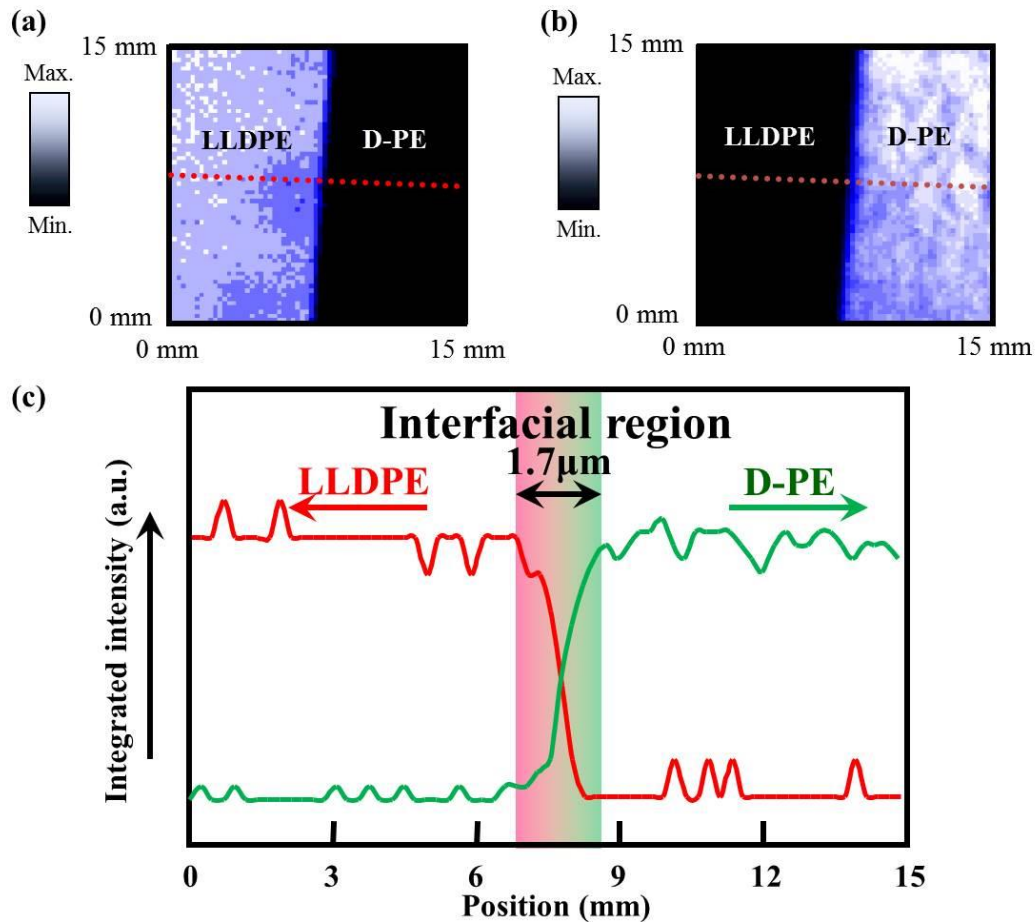
Figure 7. Two dimensional Raman images of as-quenched LLDPE / D-PE interfacial region from the integral intensity in the range of (a) 1047-1107cm-1, (b) 962-1002cm-1, and (c) the line profile of the integrated intensity across the interfacial region.

Figure 8 shows the interfacial thickness by SThM, nano-Raman and T-peel strength of quenched and annealed LLDPE/D-PE laminates. The interfacial thickness, evaluated from the thermal conductivity image by SThM, increased with annealing. This increase corresponds to the thickness increase measured by nano-Raman. The increase of the interfacial thickness suggests the chain diffusion across the interface was stimulated for the LLDPE/D-PE laminate, which is considered to bring the increase of the T-peel strength by annealing.

The thickness of the interfacial region evaluated by SThM is twice compared with that by nano-Raman. Intrinsically, the difference of the principle for these methods contributes to the difference of the absolute thickness. Especially, the effect of thermal diffusion on the SThM cannot be ignored, which will be the reason for the thicker interfacial region.

As mentioned before, the decrease of the interfacial thickness was observed for the LLDPE/*it*.PP laminate by annealing. In this case, crystallization accompanied with phase separation and disentanglement will induce the decrease of the interfacial thickness, which is considered to be responsible for the decrease of the T-peel strength. This is very in contrast with the case for LLDPE/D-PE, where both of the interfacial thickness and the adhesion strength increased by annealing. LLDPE and D-PE possess the chemically same polyethylene backbone. Thus, when the as-quenched sample is annealed, interdiffusion of each polymer chain and/or interlocking of the crystalline lamellae will be accompanied with chain
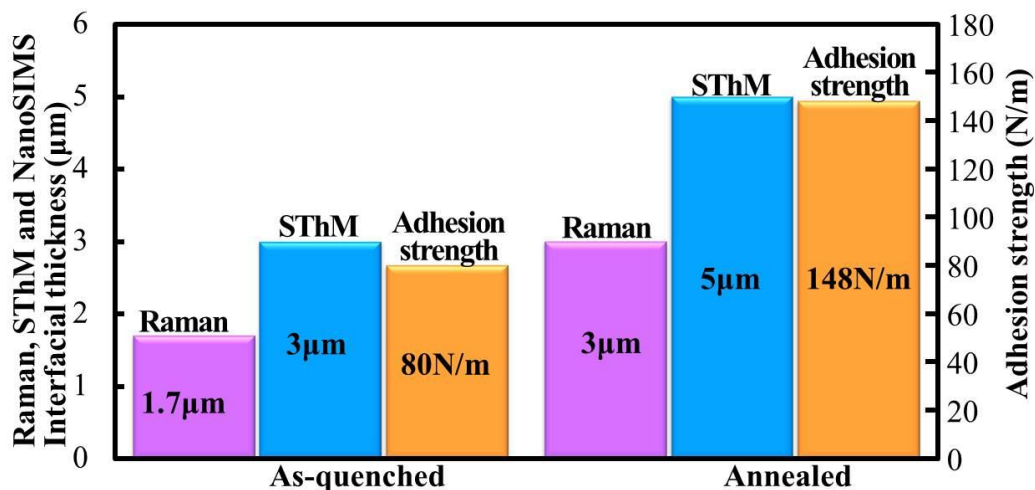
Figure 8. The interfacial thickness estimated by nano-Raman and SThM analyses, together with the T-peel strength of as-quenched and annealed LLDPE/D-PE laminate.

entanglement. These result in the increase in the interfacial hickness, which is responsible for the increase in the peel strength. Thus, single polymer composites are expected to have high interfacial strength due to their good molecular compatibility. Compatibility of chain molecules are considered to play important roles at the interfacial region of polymer laminate.

4. Conclusions

The interfacial region of the poly-α-olefin laminate was analyzed using SThM, μ-X-ray and nano-Raman. For the laminate, the interfacial thickness can be evaluated as several μm, which are very thick compared with those already reported. Upon annealing, the thickness increased for the all-polyethylene laminate, LLDPE/D-PE, but it decreased for the LLDPE/*it.*PP laminate. The T-peel strength could be correlate to the interfacial thickness. Micro-Themal, X-ray and nano-Raman analyses, such as SThM, μ-X-ray and nano-Raman are found to be effective tools to investigate the polyolefin interface quantitatively, and non-destructively.

References
[1] D. Hull, T. W. Clyne, *An Introduction to Composite Materials*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1996.
[2] M. Stamm, in: M. Stamm (Ed.), *Polymer Surfaces and Interfaces*, 1–16, Springer, Berlin,. 2008.
[3] M. Kotera, T. Nishino, T. Taura, M. Saito, A. Nakai, T. Koyama and Y. Kagoshima. *Composite Interfaces*, **14**: 63-72, 2007.
[4] M. Kotera, Y. Urushihara, D. Izumo and T. Nishino. *Thermochim. Acta*, **531**: 1-5, 2012.
[5] M. Kotera, Y. Urushihara, D. Izumo and T. Nishino. *Polymer*, **53**: 1966-1971, 2012.
[6] K. A. Chaffin, J. S. Knutsen, P. Brant and F. S. Bates, *Science,* **288**: 2187–2190, 2000.
[7] T. Ougizawa, *Proc. Intern. Rubber Conf. 2005*, Yokohama, Japan, 26-G3-05, 2005.
[8] R. L. Morgan, M.J. Hill, P.J. Barham, A. Pol, B.J. Kip, R. Ottjes, *et al.*, *Polymer* **42**: 2121-2135, 2001.
[9] H. Sato, M. Shimoyama, T. Kamiya, T. Amari, S. Sasic, T. Ninomiya, *et al.*, *J. Appl. Polym. Sci.* **86**: 443-448, 2002.
[10] Z. Liao, J.E. Pemberton, *J. Phys. Chem. A.* **110**: 13744-13753, 2006.