Transactions of the Materials Research Society of Japan 29 [1] 229-232 (2004)

Influence of annealing treatment on the Adhesion of Poly(butylene terephthalate) and its Interfacial structure

T. Izumi[1], R. Narita[2], K. Tanaka[3], A. Takahara[4], T. Kajiyama[5*]
[1]Joint Research Center for the Nanostructure Polymer Project, [2]Denso Corporation, [3]Department for Applied Chemistry, Kyushu University,[4] Institute for Materials Chemistry and Engineering, Kyushu University, [5*]Kyushu University,
Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, JAPAN
Tel: 81-92-642-3560, Fax: 81-92-651-5606, e-mail: kajiyama@cstf.kyushu-u.ac.jp

An annealing effect on the adhesion strength between additive free poly(butylene terephthalate) (PBT) surface and epoxy adhesive was studied. The atomic force microscopic observation of PBT surface revealed that the root-mean square roughness increased from 5.2 ± 0.5 nm to 9.6 ± 0.1 nm with annealing at 453 K for 1200 min. The tensile strength of adhesion was depended on annealing time, and the magnitude was decreased from 4.6 ± 0.8 MPa to 2.6 ± 0.4 MPa after annealing. The atomic force microscopic observation and X-ray photoelectron spectroscopic measurements revealed that the mode of failure was cohesive/interfacial mix-mode failure. Interfacial structure was observed with transmission electron microscopy. These results suggested that the rearrangement of the surface aggregation states of PBT, and the formation of weak boundary layer by annealing treatment.

Key words: poly(butylene terephthalate), surface structure, adhesion, annealing

1. INTRODUCTION

The development of modern technology and industry is closely related to the adhesion. It finds wide application and playing important role. Adhesion is frequently the most effective way of joining very different materials in ways that can be achieved using relatively simple equipment.

Mechanical strength of solid polymer/adhesive interface is closely related to aggregation states of the original two separate surfaces. In order to understand the mechanism of polymer adhesion, it is of important to characterize the original surface of the constituent polymer, especially, chemical composition, roughness and degree of crystallinity. Then, the relationship between interfacial adhesion strength and aggregation states of the original surface should be systematically discussed in detail. However, to the best of our knowledge, such a study has not been reported so far.

In this study, the authors choose poly(butylene terephthalate) (PBT) as a target material. PBT is a polyester that is rapidly gaining importance as an engineering thermoplastic due to its attractive mechanical properties, rapid crystallization rate, and good moldability. Then, PBT is one of popular polymeric material for inner components in automobiles. In addition, it is expected that PBT can be used for economical car due to its excellent mechanical properties and lightweight. Injection-molded PBT is supposed to be annealed at a temperature above the operating temperature so that the residual internal stress in it can be removed and the high-dimensional stability can be attained as well[1]. These give rise to the need for studying the structure and properties of this material. The crystalline structures of PBT have received considerable study[2-6]. In the industrial applications, it used as plastics, fibers or films involve one or more adhesion interface. Hence, an annealing effect on adhesion strength between additive free PBT and epoxy adhesive was studied.

2. EXPERIMENTAL

PBT used in this study was purchased from American Polymer Standards Corp. The number-average molecular weight, M_n, and the molecular weight distribution, M_w/M_n, where M_w is the weight-average molecular weight, of the PBT were 16k and 1.8, respectively.

The PBT was hot-pressed under compression at first and then immediately quenched to 273 K from the melt. The thickness was set to be approximately 20 μm. The PBT substrates and films made by hot-press were annealed at 453 K for 1200 min without constraint. Adhesive used in this study was Epikote 828 (Japan Epoxy Resin Co., LTD). The cure agent used was Epomate B002 (Japan Epoxy Resin Co., LTD).

The surface aggregation states of PBT were observed with Atomic Force Microscope (AFM, SPA300, Seiko Instruments Industry Co., LTD) with an SPI 3800 controller. The AFM observation of the surface aggregation states was operated under the constant force mode, in air at room temperature, using a 20mm x 20mm scanner. A cantilever with a bending spring constant of 0.12 Nm^{-1} was used.

The tensile strength of adhesion was measured at a crosshead speed of 50 mm min^{-1} using a push-pull gauge (DPX-50T, Imada Co., LTD) at 297 K. The schematic representation of the tensile adhesive strength test specimen is shown in Figure 1. To measure the tensile strength of adhesion, the specimens were clamped with flat-faced grip and applying stresses in the direction in Figure 1.

X-ray photoelectron spectroscopy (XPS) was used to determine the modifications produced in the outermost (5-10nm) treated surface. The surface chemical composition of failed interface was investigated on the basis of XPS (AXIS-Ultra, Kratos Analytical Co., LTD). X-ray source was monochromatic AlK_{α}, operating at 15keV with an emission current of 20mA. Pressure inside the analysis chamber of the instrument was kept below $6.6x10^{-5}$ Pa during the course of the analysis. Rectangular sample pieces (5mm x 5mm) were used, although the dimension of the analyzed area on the samples was 0.4 mm x 0.4 mm. Binding energies of all peaks were referenced to the C_{1s} peak position for C-C and C-H species at 248.5eV.

Transmission electron microscopy (TEM) was applied for investigating interface between PBT and epoxy resin. PBT films for TEM observation were embedded in epoxy resin. The ultra-thin sections of 60 nm thickness were cut with the ultramicrotome. Then, sections were collected on a grid for TEM instrument. For TEM observation, a 200 kV scanning transmission electron microscope (LEO922, Carl Zeiss SMT AG) was used.

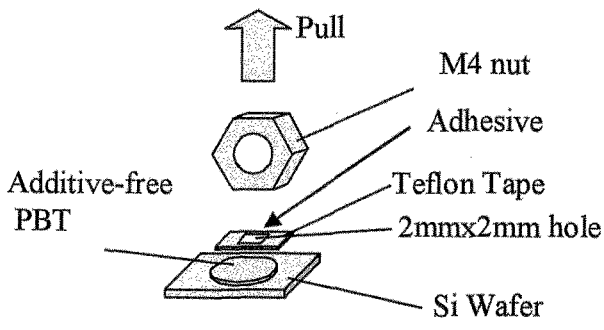

Figure 1. Schematic representation of tensile adhesive strength test.

3. RESULT AND DISCUSSION

3.1 AFM observation

It has been recognized that surface roughness was an important factor in adhesive joint. Figure 2 shows the AFM images of investigated PBT surface before and after annealing treatment at 453 K for 1200 min. On the reference surface with annealing for 0 min, the root-mean square roughness was 5.2 ± 0.5 nm. Later on, the root-mean square roughness was increased to 9.6 ± 0.1 nm with annealing for 1200 min. The increase in root-mean square roughness with the annealing treatment indicates the change in surface aggregation states of PBT. Also, the surface might become poorly wettable against adhesive liquid with high viscosity.

3.2 Tensile adhesive strength

Figure 3 shows the annealing time dependence of tensile adhesive strength for jointed PBT substrate. The average tensile adhesive strength from experimental is calculated by dividing the failure load by the jointed area. The magnitude of tensile adhesive strength was decreased from 4.6 ± 0.8 MPa to 2.6 ± 0.4 MPa after annealing. The path of failure was almost parallel to the joint and the fracture surfaces were visually smooth. In general, an increase in root-mean square roughness means increase in the effective adhesive area and the number of anchor sites, intermolecular bonds and keying for mechanical adhesion which enhanced the adhesion strength. In this case, an increase in the root-mean

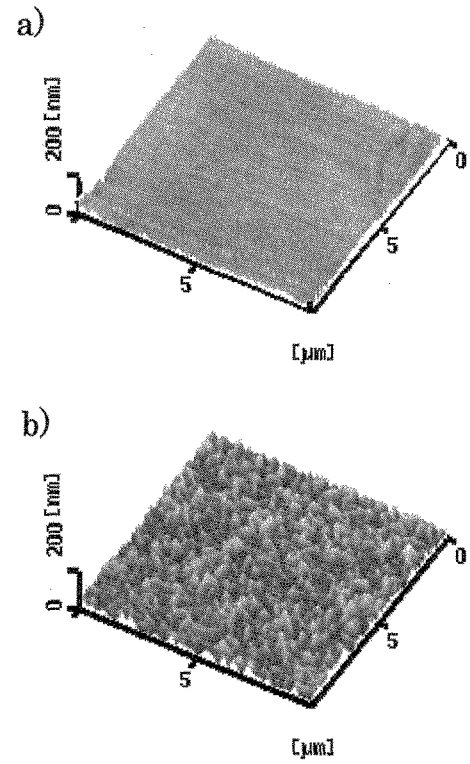

Figure 2. AFM images of PBT surface a) original and b) after annealing at 453 K for 1200min.

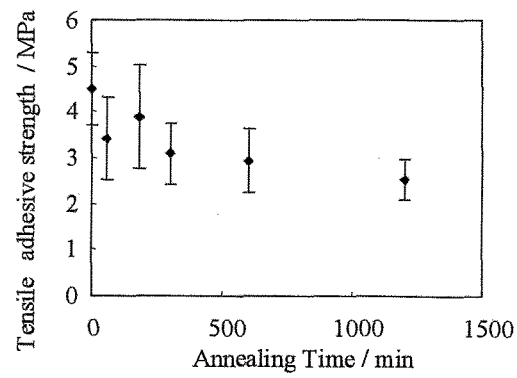

Figure 3. The tensile adhesive strength of annealed PBT with epoxy resin.

square roughness of PBT surface does not reflect to tensile adhesive strength. The relation ship between roughness and adhesion is not very simple[7, 8].

3.3 XPS measurement

In order to examine the surface chemical composition of fracture surfaces and investigate the failure mechanisms, XPS measurement was carried out. XPS was used to analyze both side of fracture surface and reference materials to identify the true path of failure.

Figure 4 and Figure 5 shows C_{1s} and N_{1s} spectra of the epoxy resin surface after tensile adhesive strength test. A C_{1s} peak was observed corresponding to carbonyl carbon atoms resulting from PBT at 288.7 eV on fracture surface, both nut and PBT substrate side. The presence of carbonyl carbon atoms on both sides of the fracture surface, suggested that the fracture is cohesive failure of PBT. Furthermore, a clear N_{1s} peak resulting from epoxy cure agent was only observed on nut side fracture surface. From the presence of nitrogen, the mode of failure was interfacial. These fracture surfaces showed that there was a possible mix-mode failure mechanism, some cohesive failure around the PBT surface and some interfacial between PBT and epoxy resin. The path and the mode of failure were unchanged by annealing time.

3.4 TEM

TEM observation of epoxy PBT/adhesive layer can reveal the aggregation structure of the interface. Figure 5 shows the TEM images of the cross-section view around epoxy adhesive/PBT interface, where the upper side is the epoxy adhesive layer and the lower side is the PBT. In the case of 1200min annealed PBT (Figure 5 (b)), it is apparent that the low density layer with the thickness of approximately 1 μm in the central part of image was formed, which is not present in the high tensile strength specimen (Figure5 (a)). The presence of this layer indicates that the surface structure of annealed PBT was different from the original surface, which might lead to the poor tensile adhesive. This means the interfacial phenomena are more important than the bulk structure and rearrangement of the PBT molecule by annealing at the surface may involve the low cohesive strength of the surface. In this case, the top of PBT surface was transited by annealing to low cohesive strength region, so called weak boundary layer[9, 10].

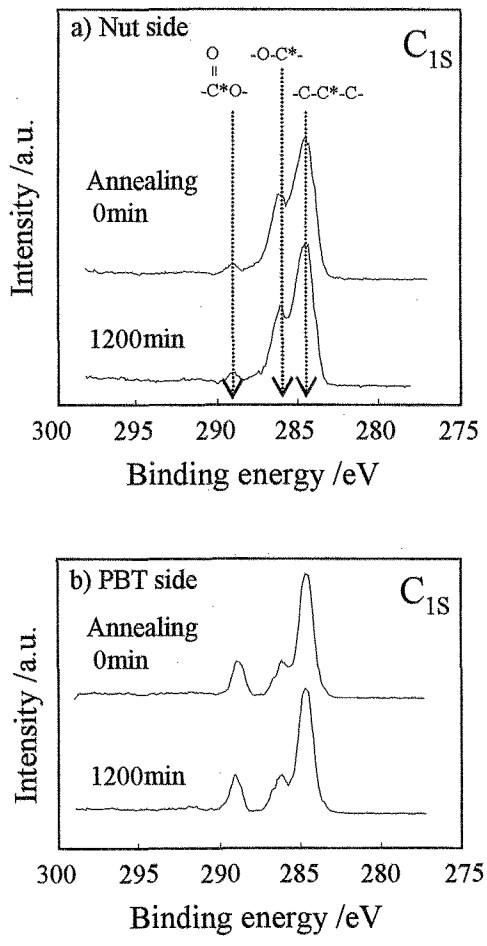

Figure 4. C_{1s} spectra of fracture surface.

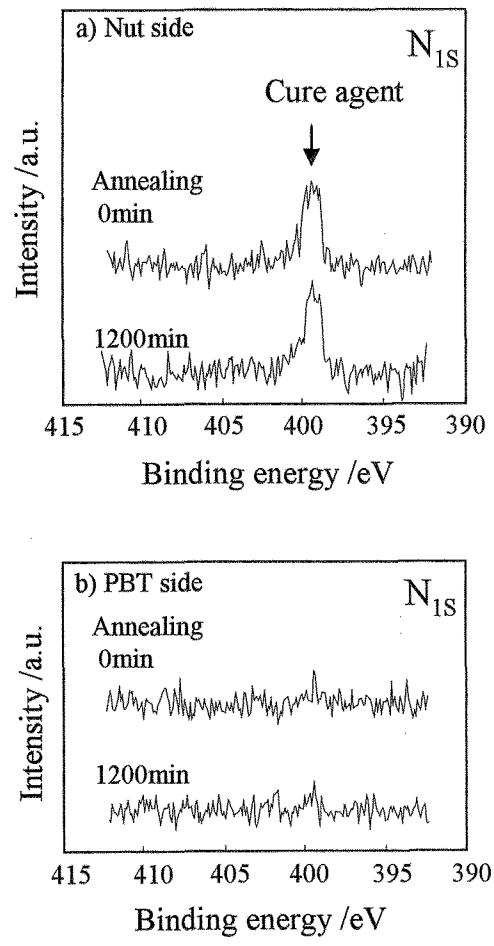

Figure 5. N_{1s} spectra of fracture surface.

It maybe concluded that a weak boundary layer, the region of low cohesive strength was formed at PBT surface by annealing.

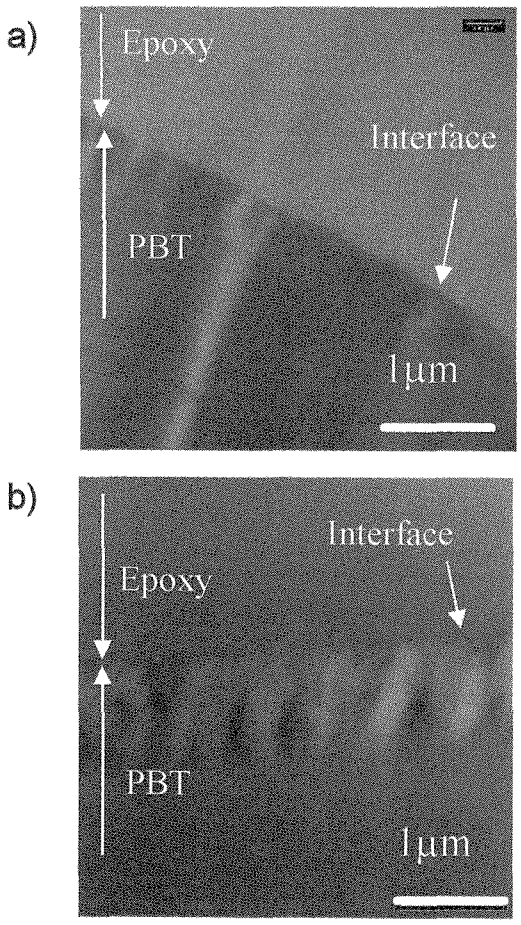

Figure 6. TEM images of the interface between epoxy adhesive and PBT a) original and b) after 1200 min annealing.

4. CONCLUSION

An annealing effect on the adhesion behavior between PBT surface and epoxy adhesive was studied.

The surface roughness of PBT was measured by AFM. The surface roughness of PBT increased with annealing time. It was claimed that the effective adhesive area was enlarged, however, the tensile adhesive strength between PBT surface and epoxy adhesive decreased with annealing time.

The mode of failure was cohesive/interfacial mix-mode failure before and after annealing.

From these results obtained above, it maybe concluded that a weak boundary layer was formed at PBT surface by annealing treatment.

5. ACKNOWLEDGEMENT

This study is carried out as 'Nanostructure Polymer Project' (partially) supported by NEDO (New Energy and Industrial Technology Development Organization) launched in 2001

6. REFERENCES

[1] D. Chauhan, V. Hauk, *Materialwissenschaft und Werkstofftechnik*, **23**, 309-324, (1992).
[2] I. M. Ward, M. A. Wilding, *Polymer*, **18**, 327-335, (1977).
[3] A. Misra, SN. Garg, *Journal of Polymer Science Part C-Polymer Letters*, **20**, 121-125, (1982).
[4] M. Yokouchi, Y. Aakakibara, Y. Chatani, H. Tadokoro, T. Tanaka, K. Yoda, *Macromolecules*, **9**, 226-273, (1976).
[5] K. Tashiro, Y. Nakai, M. Kobayashi, H. Tadokoro, *Macromolecules*, **13**, 137-145, (1980).
[6] S. Y. Hobbs, C. F. Pratt, *Journal of Applied Polymer Science*, **19**, 1701-1722, (1975).
[7] M. Shahid, S. A. Hasim, *International Journal of Adhesion and Adhesives*, **20**, 235-244, (2002).
[8] J. P. Sargent, *International Journal of Adhesion and Adhesives*, **14**, 21-30, (1994).
[9] J. J. Bikerman, *Industrial and Engineering Chemistry*, **9**, 40, (1967).
[10] M. Stehr, I. Johansson, *Journal of Adhesion Science and Technology*, **14**, 1211-1224, (2000).

(Received October 29, 2003; Accepted November 25, 2003)