

Title	Improvement of mechanical toughness of polypropylene by laminating with elastomer
Author(s)	Hachisuka, Ryosuke; Kobayashi, Toshiaki; Yamaguchi, Masayuki
Citation	Journal of Polymer Research, 26: 246
Issue Date	2019-09-12
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/16763
Rights	This is the author-created version of Springer, Ryosuke Hachisuka, Toshiaki Kobayashi, Masayuki Yamaguchi, Journal of Polymer Research, 26, 2019, Article number:246. The original publication is available at www.springerlink.com , https://doi.org/10.1007/s10965-019-1910-6
Description	

1
2
3
4
5
6 **Improvement of Mechanical Toughness of**
7 **Polypropylene by Laminating with Elastomer**
8
9

10 Ryosuke Hachisuka^{1),2)}, Toshiaki Kobayashi³⁾,
11 Masayuki Yamaguchi^{1)*}
12
13

14 1) School of Materials Science,
15 Japan Advanced Institute of Science and Technology
16 1-1 Asahidai, Nomi, Ishikawa 923-1292 JAPAN
17

18 2) Oral Care Research Laboratories, Research & Development Headquarters,
19 Lion Corporation
20 7-2-1 Hirai, Edogawa, Tokyo 132-0035 JAPAN
21

22 3) The Lion Foundation for Dental Health
23 (Public Interest Incorporated Foundation)
24 1-3-7 Honjo, Sumida, Tokyo 130-8644 JAPAN
25
26

27
28

* To whom correspondence should be addressed:
29 Phone +81-761-51-1621, Fax +81-761-51-1149
30 E-mail: m_yama@jaist.ac.jp

1 **Abstract**

2 We used three-point bending tests to investigate the effects of elastomer lamination on
3 the failure mode of bar-shaped products using isotactic polypropylene (PP). When a
4 thermoplastic elastomer sheet was laminated on PP, which was prepared by double-shot
5 injection molding, the specimen showed high mechanical toughness without signs of
6 stress whitening. Although rubbery materials have low tensile moduli, their bulk moduli
7 are comparable to those of plastics. Therefore, the laminated elastomer, located inside of
8 the bending deformation, prohibits sharp bending angles during the deformation.
9 Consequently, craze formation, which is the origin of stress whitening and leads to
10 brittle fracture, hardly occurs.

11

12 **Keywords:** Polypropylene; Elastomer; Lamination; Bending test

13

1 **Introduction**

2 Laminated polymeric materials are widely used in packaging; each film plays an
3 important role in terms of functionality and/or performance. Such factors include
4 rigidity, heat-sealability, gas-barrier property, and printability. Owing to various
5 industrial requirements, numerous studies have already been carried out on the
6 mechanical properties, adhesive strength, and processability of laminated plastic films.
7 In contrast, few studies have been reported on the properties of laminated products
8 obtained by injection molding—i.e., thick products—although double-shot injection
9 molding using two materials is a well-known technique [1-3]. Considering that
10 multi-layered products can show various functions [4-6], basic research using laminated
11 products prepared by double-shot injection molding should be performed more to
12 understand the mechanical properties and so on. In particular, the study on a plastic
13 laminated with a rubber, not blend, is practically important in industry.

14 In the present study, therefore, we evaluated the mechanical toughness and failure
15 mode of laminated products composed of a brittle plastic and a rubbery material using
16 specimens produced by double-shot injection molding. For products currently employed
17 in various applications such as stationery, toiletries, and automobile parts, the failure
18 mode is important for the safety of users [7,8]. Therefore, we investigated the
19 contribution to mechanical toughness of the laminated rubber. This was carried out
20 using bending tests, i.e., one of the most important deformation modes for bar-shaped
21 products in stationery and toiletries. The rubber lamination is usually carried out to
22 improve the tactile impression and to protect the surface from various damages. The

1 strength at a high strain rate and high frequency is known to be improved by rubbery
2 materials on surface due to their damping property, in which a rubber showing high
3 mechanical hysteresis is effective [9,10]. However, the failure mode at a slow
4 deformation rate has not been discussed in detail to the best of our knowledge except for
5 the lamination on textile [11] and lumber [12]. In general, the tensile stress, which is
6 predicted by the mechanical parallel model, is barely affected by the rubber lamination
7 because a plastic shows much higher tensile modulus than a rubber. In the case of
8 bending deformation, however, the situation is quite different because the volume
9 compression occurs inside of a specimen, as discussed by the beam theory [13]. This is
10 unfortunately unrecognized well for material design of double-shot injection molding.

11 We used isotactic polypropylene (PP), which is currently utilized in various
12 stationery and toiletry products, as the brittle plastic component considering the effect
13 of thickness [14-18]. Because the double-shot injection molding becomes a
14 conventional processing method recently, the results obtained in this study, leading to
15 the improvement of safety for bar-shaped products, would have a great impact on the
16 industry.

17

18 **Experimental**

19 **Materials**

20 The polymeric materials used in the present study were two types of commercially
21 available isotactic polypropylene (PP) (Prime Polypro™ J-700GP and J108M; Prime
22 Polymer, Japan) with different molecular weights, denoted as PP_H and PP_L, respectively.

1 Both PP samples are propylene homopolymers, and their meso-pentad fraction is 96%.
 2 The number- (M_n) and weight-average (M_w) molecular weights of the PP polymers are
 3 provided in Table 1; they were determined by gel permeation chromatography
 4 (HLC-8321GPC/HT; Tosoh, Japan) with TSK-GEL GMH_{HR}-H(20)HT at 140 °C using
 5 1,2,4-trichlorobenzene as a solvent.

6

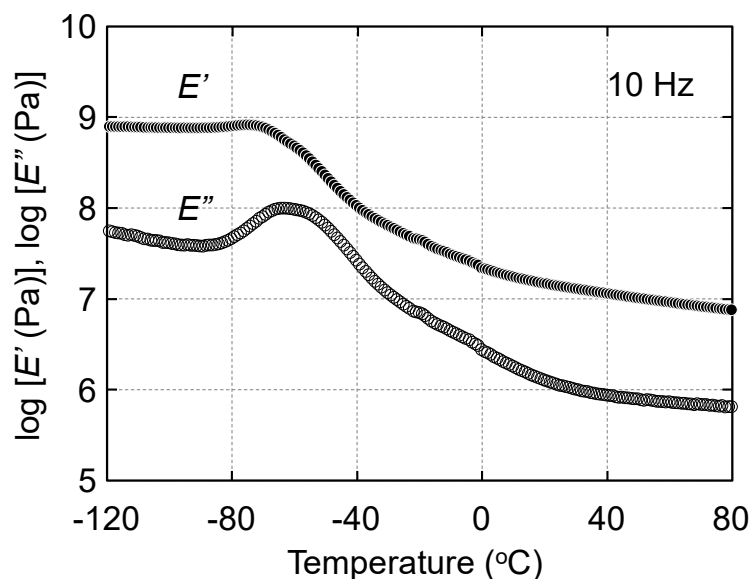
7 Table 1 Average molecular weights of the isotactic polypropylene (PP)

Sample	M_n	M_w	M_w/M_n
PP _H	4.9×10^4	2.5×10^5	5.1
PP _L	2.9×10^4	1.6×10^5	5.6

8

9 We also used a commercially available thermoplastic elastomer with a styrene
 10 block as hard segments (Leostomer® EFR9967P; Riken Technos, Japan). The density at
 11 23 °C is 890 kg/m³, and the shore A hardness is 61. Figure 1 shows the temperature
 12 dependence of dynamic tensile moduli, such as storage modulus E' and loss modulus
 13 E'' , at 10 Hz for the elastomer. The glass transition temperature, defined as the peak
 14 temperature of E'' , is around -63 °C. The storage modulus E' at room temperature is
 15 around 15 MPa, which is much lower than that of PP (> 1 GPa).

16

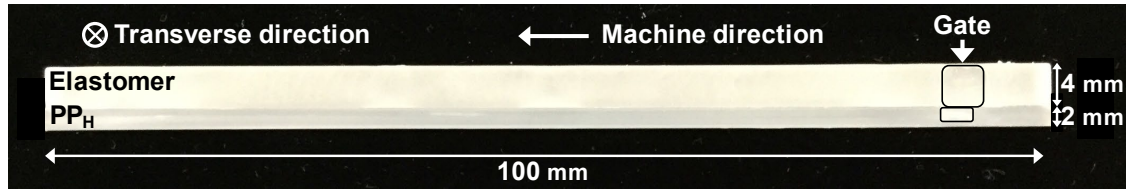


1
2 Figure 1 Temperature dependence of tensile storage modulus E' and loss modulus E''
3 for the elastomer. The measurements were performed at 10 Hz using a rectangular
4 specimen prepared by compression-molding. The heating rate was 2 °C/min.

6 Sample Preparation

7 PP pellets were fed into an injection molding machine (FNX-180III; Nissei Plastic
8 Industrial, Japan) to form rectangular specimens (100 mm in length and 5 mm in width)
9 with various thicknesses. The barrel temperature, injection pressure, mold temperature,
10 and cooling period were 220 °C, 6.4 MPa, 10 °C, and 7 s, respectively. The samples
11 were subsequently kept at 23 °C and 50% relative humidity (RH) for 72 h in a
12 temperature and humidity controller (IS400; Yamato Scientific, Japan) to promote
13 crystallization. We also prepared laminated rectangular specimens of the same length
14 and width by double-shot injection molding using PP and the thermoplastic elastomer.
15 An example of the molded product is shown in Figure 2. The total thickness was 6 mm,
16 and PP accounted for 2 mm of the thickness. The barrel temperature for the elastomer

1 was maintained at 200 °C, and for the PP it was maintained at 220 °C. The mold
 2 temperature was 10 °C. The PP was injected into the mold prior to the elastomer.



4
 5 Figure 2 Laminated specimen composed of PP_H and elastomer

6 7 **Measurements**

8 We carried out the three-point bending tests using a uniaxial tensile machine
 9 equipped with a bending test attachment (AGS-X, Shimadzu, Japan) at 23 °C and 50%
 10 RH. The load was applied over a 64-mm span at the midpoint of the specimen. All tests
 11 were performed at a crosshead speed of 100 mm/min. The stress σ and strain γ_b were
 12 calculated as follows:

$$13 \quad \sigma = 3FL / 2WH^2 \quad (1)$$

$$14 \quad \gamma_b = 6H\delta / L^2 \quad (2)$$

15 where F is the load, L is the distance between the supporting pins (64 mm), W is the
 16 sample width (5 mm), H is the sample thickness, and δ is the displacement. A schematic
 17 diagram of the measurements is shown in Figure 3.

18

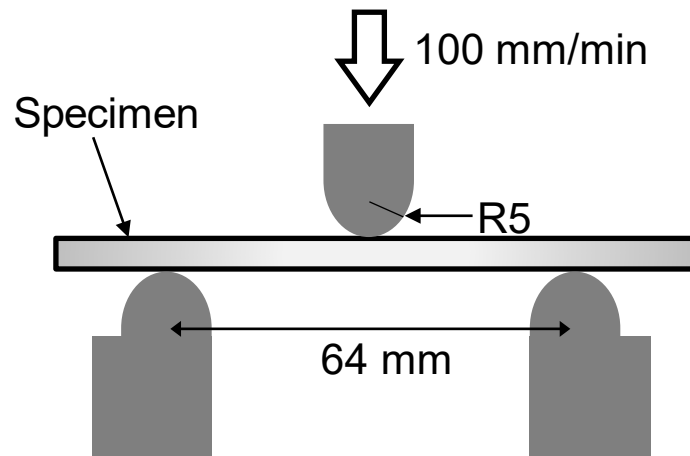


Figure 3 Schematic illustration of the three-point bending test

For some specimens, the crosshead was stopped when the vertical displacement of the midpoint reached 30 mm, to evaluate the time variation of the bending angle β after the cessation of the movement of the crosshead, as illustrated in Figure 4. The specimens were removed from the tensile machine after measuring the bending angle for 5 min. Then the surface morphology was observed by an optical microscope (VHX-2000; Keyence, Japan) to find the relationship between the bending angle and stress whitening behavior.

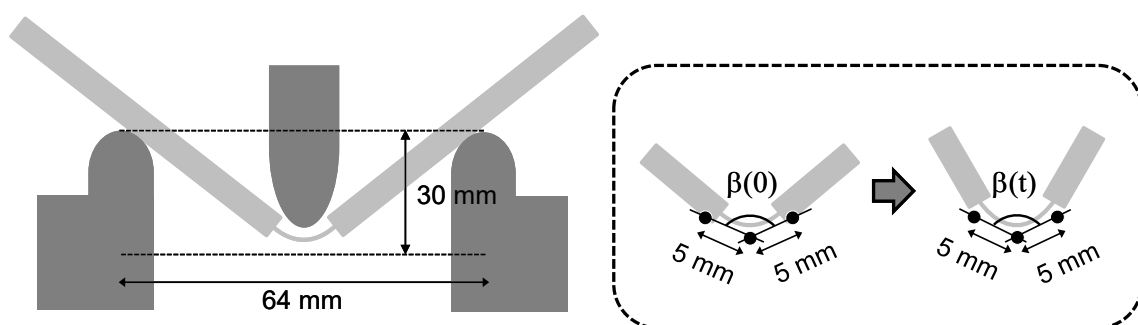


Figure 4 Schematic illustration of bending angle measurements

The stress whitening behavior at the bending deformation was examined also by an

1 Izod impact testing machine (DG-1B; Toyoseiki, Japan) using a 2.75 J pendulum
2 hammer at 23 °C and 50 % RH. The injection-molded specimens with 1, 2, and 3 mm
3 thicknesses and the laminated specimens of PP_H (2 mm thickness) and the thermoplastic
4 elastomers (4 mm thickness) were set without giving notch. All the sample specimens
5 were not broken at this experiment because of thin thickness. After striking the
6 specimens by the pendulum, the surface morphology of the specimens was observed by
7 the optical microscope to confirm the stress whitening behavior.

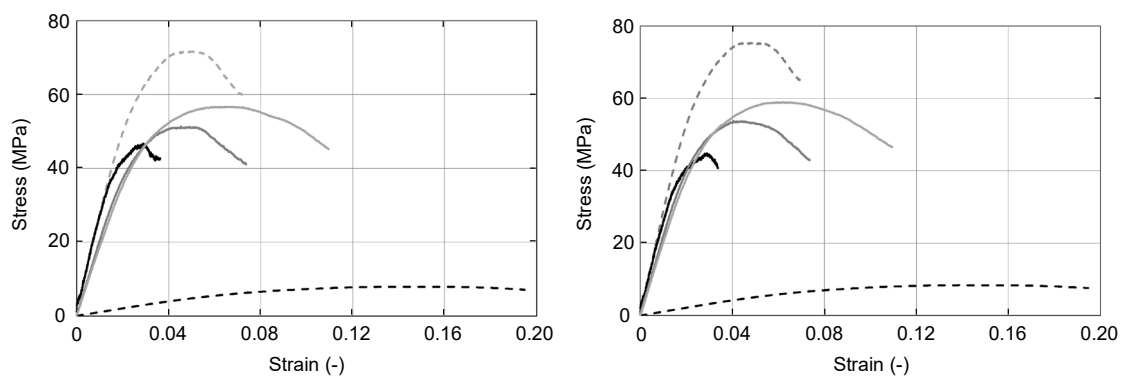
8

9 **Results and Discussion**

10 Figure 5 shows the stress–strain curves resulting from the bending tests on the PP
11 specimens with various thicknesses (solid lines), and the laminated specimens with the
12 thermoplastic elastomer (black dotted lines). As shown in the figure, the initial modulus
13 of PP increased with decreasing the sample thickness, and was independent of the
14 molecular weight of the PP. This was as expected because the molecular orientation is
15 enhanced in thin specimens owing to the increase in the fraction of the skin layer
16 [19,20]. The strain at maximum stress—i.e., the yield strain—increased greatly with
17 increasing PP specimen thickness. Consequently, the thick specimens had high flexural
18 strength, as reported previously [21,22]. In the laminated specimens—denoted by black
19 dotted lines in Figure 5—the initial modulus was low because of the low modulus of the
20 elastomer. In fact, the stress of pure elastomer with 4 mm thickness, prepared by
21 compression molding, is too low to be measured (lower than 2 MPa) in the strain region.
22 The gray dotted lines in the figure represent the stress–strain curves calculated assuming

1 a thickness of 2 mm, i.e., the thickness of the PP. If the elastomer sheet did not produce
 2 any stress, the curves would have been the same as those of the 2-mm-thick PP
 3 specimen. However, the initial modulus and yield stress were higher than those of the
 4 pure PP. This result demonstrates that the elastomer on PP surface plays an important
 5 role in stress generation, as discussed later.

6



7

8 Figure 5 Stress–strain curves at the bending tests: (left) PP_H and (right) PP_L samples
 9 with different thicknesses. The solid lines denote the curves of PP specimens: (black) 1
 10 mm, (gray) 2 mm, and (light gray) 3 mm. The dotted lines denote the curves of the
 11 laminated specimens (black) calculated with a thickness of 6 mm, and (gray) calculated
 12 assuming a thickness of 2 mm.

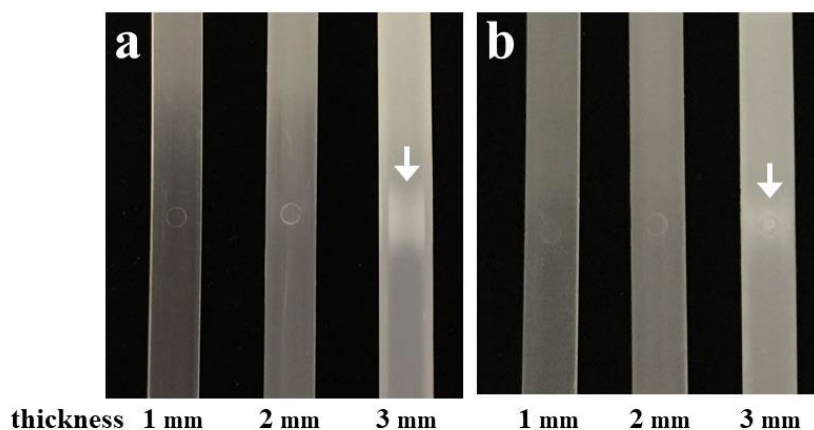
13

14 The pure PP specimens after the three-point bending tests are shown in Figure 6.

15 Although there was intense stress whitening in the 3-mm-thick specimens of both PP_H
 16 and PP_L , we did not observe stress whitening in the 1-mm- or 2-mm-thick PP specimens,
 17 suggesting that thinner specimens were in the plane stress condition in this experiment.

18 In contrast, thick specimens were in the plane strain condition, leading to a rapid

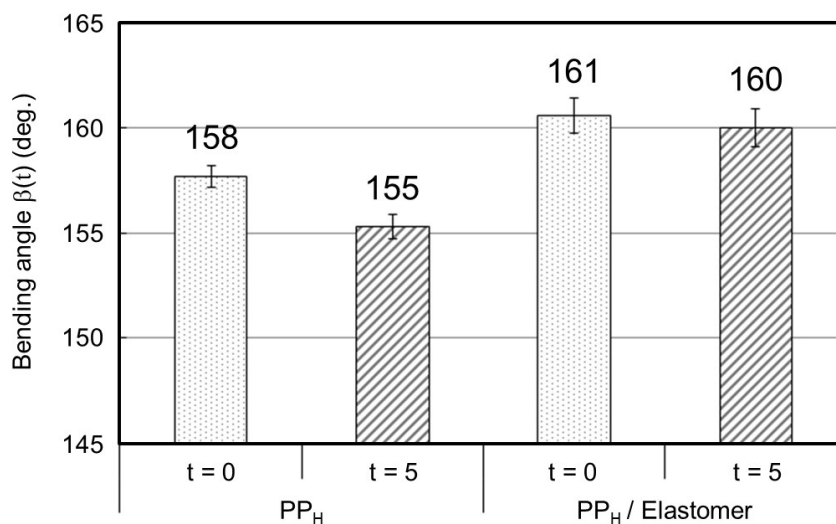
1 increase in the dilatational stress at the outside of the bent specimens. As a result, void
 2 opening leading to crazing occurred, which was the origin of stress whitening [23-28].



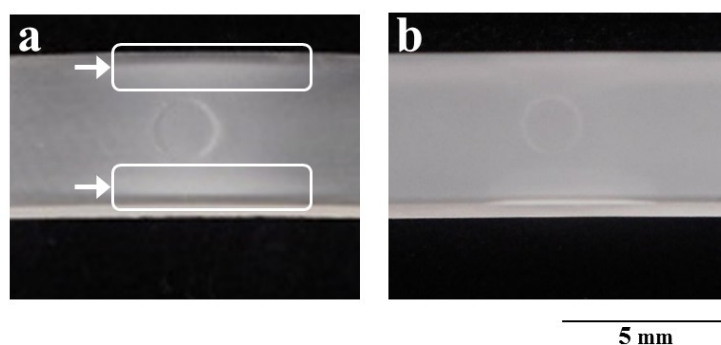
4 Figure 6 Photographs of the PP specimens of (a) PP_H and (b) PP_L after the three-point
 5 bending tests. The loads were applied from the opposite side of the samples. The white
 6 arrows indicate the stress whitening regions.

8 We examined the increase in the bending angle after the cessation of the crosshead
 9 movement during the three-point bending tests on PP_H and PP_H laminated with the
 10 thermoplastic elastomer. The PP_H was 2 mm thick and the elastomer was 4 mm thick.
 11 The compression force was applied from the elastomer side of the laminated specimen.

12 Figure 7 shows the bending angle β immediately after the cessation of the
 13 crosshead movement ($t = 0$) and after 5 min, for both samples. In the case of PP_H, the
 14 bending angle decreased from 158° ($t = 0$) to 155° ($t = 5$). Stress whitening was obvious
 15 on the surface during the measurement, as shown in Figure 8, although we did not
 16 detect it at the beginning of the measurement, i.e., $t = 0$.



1

2 Figure 7 Bending angle β , as defined in Figure 4, for the 2-mm-thick PP_H specimens,3 and the laminated specimens comprising 2-mm-thick PP_H and 4-mm-thick elastomer.

4

5 Figure 8 Photographs of the sample surfaces after the cessation of the crosshead

6 movement at three-point bending tests ($t = 5$) for (a) 2-mm-thick PP_H specimen and (b)7 the laminated specimen comprising 2-mm-thick PP_H and 4-mm-thick elastomer. The

8 loads were applied from the opposite side of the samples. The white arrows indicate the

9 stress whitening regions.

10

11 In contrast, the bending angle of the laminated specimen barely changed over 5 min.

12 Moreover, we detected no stress whitening at all during the measurement,

13 demonstrating that elastomer lamination affects the plastic deformation behavior.

1 The bulk modulus of a rubbery material is comparable with that of a plastic,
 2 although the tensile and shear moduli are much lower than those of plastics [29].
 3 Therefore, the results shown in Figures 5 and 7 must be attributed to the high bulk
 4 modulus of the elastomer. When the laminated specimen was bent, the elastomer on the
 5 inside of the bending deformation supported the large compressive stress without
 6 volume shrinkage. As a result, the bending angle of the PP_H layer in the laminated
 7 specimen was not sharp compared with that without the elastomer layer, leading to
 8 weak stress concentration at the bending point without stress whitening. The large
 9 bending angle and its stability over a long period will be of great benefit for avoiding
 10 brittle fractures in products.

11 Such discussion suggests that even the pure elastomer avoids sharp bending, which
 12 was confirmed by further experiments using the pure elastomer specimen. Figure 9
 13 shows the photographs after the cessation of the crosshead movement ($t = 5$) at the
 14 bending test. It was clarified that the bending angle of the pure elastomer (4 mm
 15 thickness), shown in the left picture, was almost the same with that of the laminated
 16 specimen of PP and elastomer, shown in the right picture.

17

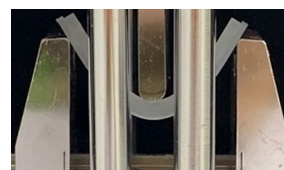
18

19

20



Figure 9
 the three-point



Photographs after
 bending tests ($t =$

1 5). (left) Elastomer specimen with 4 mm thickness and (right) laminated specimen of
 2 2-mm-thick PP_H and 4-mm-thick elastomer.

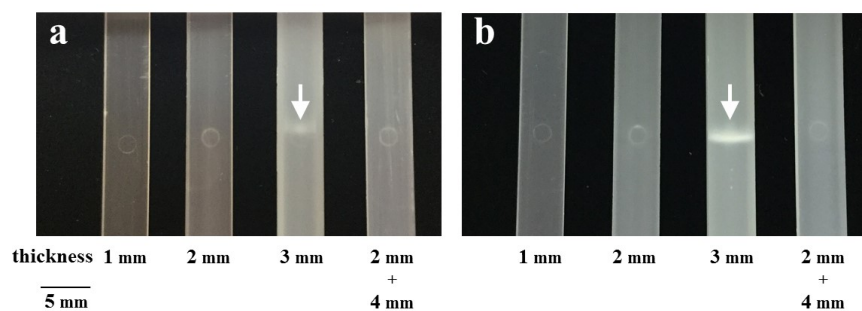
3

4 The stress whitening behavior was also evaluated using the Izod impact tester.

5 Although all the specimens used in this study exhibited no break due to the thin
 6 thickness of the specimens, the stress whitening behavior was obviously different.

7 Figure 10 shows the photographs of the specimen struck by a pendulum. For the

8 laminated specimens, the impact force was applied from the PP side.



10 Figure 10 Photographs after striking by a pendulum. (a) The sample specimens using
 11 PP_H and (b) those using PP_L. The right sample in each figure represents the laminated
 12 specimen comprising 2-mm-thick PP and 4-mm-thick elastomer. The white arrows in
 13 the picture denote the stress whitening region.

14

15 As similar to the bending tests, stress whitening was not detected for the specimen
 16 with 1 and 2 mm thicknesses, whereas the intense stress whitening was observed clearly
 17 on the 3-mm-thickness specimens irrespective of the molecular weight. In the case of
 18 the laminated specimen, no stress whitening appeared, suggesting that the elastomer
 19 lamination avoids void opening leading to the brittle fracture.

1

2 **Conclusions**

3 We investigated the failure mode of PP at bending deformation using bar-shaped
4 specimens with various thicknesses produced by injection molding, and laminated
5 specimens comprising PP and a thermoplastic elastomer obtained by double-shot
6 injection molding. The specimen laminated with an elastomer showed a large bending
7 angle without stress whitening. Furthermore, the bending angle was stable even after the
8 cessation of the deformation, although that of the PP without the elastomer lamination
9 increased with time with the appearance of stress whitening. These results demonstrated
10 that the elastomer sheet eliminates acute bending due to the large bulk modulus,
11 although the elastomer has low modulus in the tensile deformation. Furthermore, the
12 large bending angle of the laminated specimen, which resulted in the decrease in the
13 stress concentration of PP, was responsible for plastic deformation without void opening.
14 Consequently, the brittle fracture is avoided by the elastomer lamination, leading to the
15 safety of a product. Considering that the double-shot injection molding is widely
16 available in industry, the elastomer lamination technique will be employed more for
17 various applications in bar-shaped goods that require safety.

18

19 **References**

- 20 1. Isayev, A.; Hung, K. M.; Co-Injection molding of polymers, in Injection molding,
21 Eds. Kamal, M.; Isayev, A.; Liu, S. Chap. 21; Hanser: Munich, **2009**.
- 22 2. Kazmer, R. O.; Injection mold design engineering, 2nd ed.; Hanser: Munich, **2016**.

- 1 3. Geminger, T.; Jarka, S. Injection molding of multimaterial systems, in Specialized
2 injection molding techniques, Chap. 4, Ed. Heim, H. P.; Elsevier: Amsterdam, **2016**.
- 3 4. Arayachukiat, S.; Doan, V. A.; Murakami, T.; Nobukawa, S.; Yamaguchi, M. *J. Appl.*
4 *Polym. Sci.* **2015**, *132*, 42008.
- 5 5. Sako, T.; Nobukawa, S.; Yamaguchi, M. *Polym. J.* **2015**, *47*, 576-579.
- 6 6. Sako, T.; Ito, A.; Yamaguchi, M. *J. Polym. Res.* **2017**, *24*, 89.
- 7 7. Yamaguchi, M.; Irie, Y.; Phulkerd, P.; Hagihara, H.; Hirayama, S.; Sasaki, S.
8 *Polymer* **2010**, *51*, 5983-5989.
- 9 8. Phulkerd, P.; Hirayama, S.; Nobukawa, S.; Inoue, T.; Yamaguchi, M. *Polym. J.* **2014**,
10 *46*, 226-233.
- 11 9. Mills, N. J.; Zhang, P. S. *J. Mater. Sci.* **1989**, *24*, 2099-2109
- 12 10. Xie, M.; Zhang, Y.; Krasny, M. J.; Rhead, A.; Bowen, C.; Arafa, M. *Mech. Sys. Sign.*
13 *Proc.*, **2018**, *107*, 429-438.
- 14 11. Fedorko, G.; Molnar, V.; Honus, S.; Belusko, M.; Tomaskova, M. *Eng. Failure Anal.*,
15 **2018**, *94*, 145-156.
- 16 12. Han, J.; Lv, J.; Zhan, X.; Huang, R.; Xu, X. *Bioresources*, **2016**, *11*, 6677-6691.
- 17 13. Staab, G. H. *Laminar Composites*, 2nd ed.; Elsevier: Amsterdam, **2016**.
- 18 14. Kausch, H. H. *Polymer Fracture*, 2nd ed.; Springer-Verlag: Berlin, **1986**.
- 19 15. Narisawa, I.; Kuriyama, T.; Ojima, K. *Macromol. Symp.* **1991**, *41*, 87-107.
- 20 16. Lazzeri, A.; Bucknall, C. B. Recent developments in the modeling of dilatational
21 yielding in toughened plastics, in *Toughening of plastics*, Eds., Pearson, R. A.; Sue,
22 H. J.; Yee, A. F. Chap. 2; American Chemical Society: Washington DC, **2000**.

- 1 17. Argon, A. S. The physics of deformation and fracture of polymers. Chap.12;
2 Cambridge Univ. Press: Cambridge, **2013**.
- 3 18. Kinloch, A. J.; Young, G. J.; Fracture behavior of polymers; Springer: Berlin, **2013**.
- 4 19. Tenma, M.; Yamaguchi, M. *Polym. Eng. Sci.* **2007**, *47*, 1441-1446.
- 5 20. Yamaguchi, M.; Irie, Y.; Phulkerd, P.; Hagihara, H.; Hirayama, S.; Sasaki, S.
6 *Polymer* **2010**, *51*, 5983-5989.
- 7 21. Felekoglu, B. *Civil Engineering.* **2014**, *58*, 279-291.
- 8 22. Folkes, M. J.; Hardwick, S. T.; *J. Mater. Sci.* **1990**, *25*, 2598-2606.
- 9 23. Bucknall, C. B.; Smith, R. R. *Polymer*, **1965**, *6*, 437-446.
- 10 24. Brown, N.; Ward, I. M. *J. Mater. Sci.*, **1983**, *18*, 1405-1420.
- 11 25. Chiu, H. T.; Shiau, Y. G.; Chiu, W. M.; Syau, S. S. *J. Polym. Res.* **1995**, *2*, 21-29.
- 12 26. Liu, Y.; Kennard, C. H. L.; Truss, R. W.; Calos, N. J. *Polymer* **1997**, *38*, 2797-2805.
- 13 27. Yamaguchi, M.; Nitta, K. *Polym. Eng. Sci.* **1999**, *39*, 833-840.
- 14 28. Hegde, R. R.; Bhat, G. S.; Spruiell, J. E.; Benson, R. *J. Polym. Res.* **2013**, *20*,
15 323-335.
- 16 29. van Krevelen, D. W.; Te Nijenhuis, K. Properties of Polymers. 4th ed.; Elsevier:
17 Amsterdam, **2009**.
- 18 30. Ramsteiner, F. *Polymer* **1979**, *20*, 839-842.
- 19 31. Jang, B. Z.; Uhlmann, D. R.; van der Sande, J. B. *Polym. Eng. Sci.* **1985**, *25*,
20 98-104.
- 21 32. Faulkner, D. L. *J. Appl. Polym. Sci.* **1999**, *36*, 467-480.
- 22 33. van der Wal, A.; Mulder, J. J.; Thijs, H.A.; Gaymans, R.J. *Polymer* **1998**, *39*,

1 5467-5475.