Two novel thermoplastic polyester elastomer (TPEE) were developed. One is an alloy of TPEE and SBC (styrene block copolymer). It exhibits a low compression set (Cs), high softness and high adhesiveness to PS (polystyrene), ABS (acrylonitrile butadiene styrene copolymer), PC (polycarbonate), etc. Adhesion after double injection is extremely stable and durable. By these alloys, many new superimposed products can be produced easily with double injection.

The other is TPEE modified by the grafting of an acid-anhydride group. It bonds polyester to PA (polyamide) or EVOH (ethylene vinylalcohol copolymer) with sufficient adhesion even at elevated temperatures (80–120°C). These properties have been used to create many new multi-layer products. This modified TPEE also improves properties of PA or EVOH, such as pinhole resistance.

These materials contribute to the reduction of environmental loads and enhance flexibility of superimposed article shape.

The SPSJ Award was given to mark the originality of this new adhesive elastomer and its contribution to producing superimposed articles.

KEY WORDS: Thermoplastic Polyester Elastomer / Styrene Block Copolymer / Polymer Alloy / Adhesion / Graft Polymer / Acid Anhydride /
F. J. Lu et al. reported\(^1\) that there is interaction between the ether group and aromatic ring of PS, based on the change in IR spectra of miscible and immiscible PS/PVME films.

Nemoto et al.\(^2\) calculated the diffusion coefficient and reported interaction between PS and PVME based on NMR analysis,\(^3,4\) suggesting that the phenyl ring is much closer to the methyl group of PVME than to the main chain carbons of PS.

H. Shimizu\(^5\) et al. observed the blend of PS and PVME to be a homogeneous structure when lower-Mn PS is used, while a nanoheterogeneous structure with high-Mn PS, according to TSDC (thermally stimulated depolarization current) and TEM findings.

From these reports on interactions between PS and PVME, comparable interactions may occur between PTMG and PS based on the analogical structures of PVME and PTMG.

There are several reports on interactions or miscibility between other polymers, such as PBT/PC or poly(alkylene ether)/PMMA. Detailed mechanisms of the interactions between other polymers are not clear, and significant interactions may exist between PBT or PTMG segments and other polymers to lead improvement in adhesion and miscibility.

### Morphology of the TPEE/SBC Alloy

Figure 2 shows a TEM photograph of the TPEE/SBC alloy. The PS domains are stained in black by RuO\(_4\). SBC domains were observed to be less than 1 micron in diameter, indicating a finely dispersed morphology. The lamellar structure of PBT segments in the matrix, the micro-phase separated structure of the SBC domain and irregularity along the interface of the matrix/domain were observed. The convex parts stained in black, which may indicate PS microdomains, were found to significantly interact with PTMG in the TPEE matrix.

### Properties of the TPEE/SBC Alloy

The mechanical and adhesive properties of the alloy can be controlled by the type and amount of TPEE, SBC and extender oil. Figure 3 shows the balance of softness and Cs.\(^6\) The TPEE/SBC alloy covers the region of higher softness and lower Cs than the softest TPEE. The softest alloy showed a Shore A hardness score of 55 and a Cs score of 55 (70°C, 22h).

Technical features:

a) Softness

The addition of softer TPEE (high content PTMG), softer SBC (suitable PS content and micro-structure of the mid-segment) and extender oil is desirable.

b) Low Cs

High-molecular-weight SBC is necessary.
c) Adhesion strength

More than the limited content of PTMG is required. The properties are controlled as described above. Controlling the viscosity of the matrix and domain and choosing the best processing conditions are important.

Adhesion Strength of the TPEE/SBC Alloy

The adhesion strength of specimens prepared by insert injection is measured as follows: a preformed sheet of ABS or PC, 2 mm in thickness, is inserted in the mold, and then a TPEE/SBC alloy sheet 2 mm in thickness of is injected into the mold at various temperatures. Peeling strength was measured at a peeling rate of 200 mm/min in the 180°C direction. Figure 4 indicates peeling strength even at injection temperature higher than 220°C to be over 100 N/25 mm, which would be difficult manually.

Deviation of the peeling strength was small across the length of flow from the gate to the end (350 mm), as shown in Figure 5.

Adhesion strength hardly decreased after 1000 h of heat resistance testing, 200 heat-shock cycles and 1000 h of humidity testing (Table I). Retention of adhesion strength after the humidity test indicated hydrogen bonding not to contribute to interactions between PS and TPEE.

Polymers Which Can Be Adhered to the TPEE/SBC Alloy

The polymers which can be adhered to TPEE/SBC alloy are summarized in Table II along with PS families, PC and their alloys, as well as thermo-setting resin, such as phenol resin or unsaturated polyester resin. Polymers such as PET and PBT also adhere to the TPEE/SBC alloy owing to the compatibility of the hard segment in TPEE.

The mechanism of adhesion to PC is not clear, but possibly may be interacted between the aromatic ring and ether, as in the case of PS and PTMG.

TPEE/SBC Alloy Usage

Using interactions between PS and TPEE, various articles can be formed easily by double-injection molding, instead of by adhesive agents which take much time. Example samples are shown in Figure 6.

All samples were formed by ABS or PS injection first, and then TPEE/BC alloy injection.

Using TPEE/SBC alloy packing materials to seal interior, operation buttons on precision components, compact appliances and tools were made.

ACID-ANHYDRIDE-GRAFTED TPEE

The TPEE/SBC alloy adheres to many plastics though not polyamide (PA) and ethylene-vinyl alcohol copolymer (EVOH).

To solve problems in food packaging, we grafted acid anhydride onto TPEE by reactive processing using peroxide in the molten state.7,8 This TPEE modified with acid anhydride bind polyester to PA and EVOH. It is not unusual to graft acid anhydride onto polyolefin. But it seems impossible to graft acid anhydride onto polyester; in fact, TPEE, which has less PTMG, cannot be grafted with sufficient adhesiveness.

A schematic adhesion mechanism is given in Figure 7. The compatibility of the PBT segment of TPEE with polyester makes possible bonding between TPEE and polyester. The acid-anhydride group binds modified TPEE with gas barrier
resins by chemical bonds or through chemical interaction. Obviously, strong adhesion to PS is maintained.

Modified TPEE features:
1) content of the PTMG segment in TPEE should be larger than 50 wt %.
2) molecular weight slightly smaller than that of the original polymer.
3) acid-anhydride grafting point possibly the α-position of the PTMG segment in TPEE. The grafting point is the α-position when reacting maleic acid anhydride with poly-THF using peroxide.9

Modified TPEE has been registered as a new chemical substance in the Law Concerning the Examination and Regulation of Manufacture, etc. of Chemical Substances (Japan), as well as in the positive list approved by the Japan Hygienic Olefin and Styrene Plastics Association.

Adhesion Strength of TPEE Modified with Acid Anhydride
A three-layer film consisting of PBT, adhesive resin and PA6 or EVOH (32/8/32 μm) was produced by cast co-extrusion, and adhesion strength between the adhesive resin and PA6 or EVOH was measured. The adhesive resin as reference was a commercially available resin for the co-extrusion of PET/EVOH, composed of olefinic elastomer and tackifier. At ambient temperature, modified TPEE had much greater adhesiveness than the reference, as shown in Figure 8. At 80 or 120 °C, the temperatures corresponding to the boiling and the retort, respectively, the reference lost its adhesion strength, whereas the modified TPEE retained adhesion strength at more than 1 N/cm, which is sufficient for food packaging film.11,12

The modified TPEE makes possible to produce materials for multi-layered film by co-extrusion, without releasing VOCs (volatile organic compounds) as in the dry lamination method or extrusion lamination using AC (anchor coat) agent.

ESCA Analysis of the Adhesion Interface
The chemical structure of the interface between EVOH and modified TPEE was analyzed by ESCA (electron spectroscopy for chemical analysis). Figure 9 shows typical C1s ESCA signals of the surface. Each signals was assigned using a database.13 Three major binding energy peaks at 286, 290 and 292 eV were attributed to C1s electron adjacent to carbon, oxygen and the carbonyl C1s electron, respectively. On the surface of EVOH after the peel-off, a COO-attached carbon peak (292 eV), not observed in the original EVOH, appeared. The peak area ratios of oxygen-attached carbon (290 eV) to the hydrogen-attached carbon (286 eV) became larger than in the original EVOH. Cohesive failure of the modified TPEE thus occurs and it partially covers the surface of EVOH.

Adhesiveness of the Modified TPEE to Metal
The modified TPEE adheres to many metals, such as SUS304, zinc-galvanized sheet iron or aluminum, as summarized in Table III. Layered products consisting of metal and polyester can thus be produced.

Efficacy of Polymer Modification
Gas barrier resins usually have high modulus and brittleness, because their molecules are densely packed. Certain properties of EVOH could be improved by adding modified TPEE.

Flexural Modulus and Impact Strength.
Figure 10 shows the Izod impact strength of EVOH to increase in proportion to modified TPEE, and the obtained resins soften with modified TPEE.

Morphology.
Figure 11b shows a TEM photograph of binary material composed of EVOH (32 mol % ethylene) and modified TPEE (90/10). In contrast to un-modified TPEE in Figure 11a, a finer dispersion at the sub-micron level can be seen. The
grafted acid derivatives seem apparently reduce interface tension.

Transparency and Oxygen Permeability. Modified TPEE was so finely dispersed that transparency was not significantly influenced and nor did barrier properties much. Increase in oxygen permeability was limited since modified TPEE was dispersed into small separate domains in the EVOH matrix, as shown in Figures 12 and 13.

Pinhole Defect Resistance. Remarkable pinhole defect resistance was observed in the Gelboflex tester. By adding only 5 wt% modified TPEE to EVOH, the number of pinholes was reduced without significant change in the gas barrier and transparency, as shown in Figure 14.

Improvement in Formability. Improvement in EVOH formability was confirmed by cup-shape SPPF (solid-phase pressure forming). The shaded portion in Figure 15 shows the moldable area without cracks. Although EVOH forms only at a certain temperature, the moldable temperature range is enhanced with increase in modified TPEE.

Example of Modified TPEE Usage

Modified TPEE may be used as an adhesive resin.

a) Tubes composed of PET/modified TPEE/EVOH/adhesive resin/PE.

Tubes for transferring juice must have good aroma retention and so PET is used as the inner layer. Whitening occurs in the case of conventional adhesive resins due to low adhesive strength, but tubes lined with modified TPEE can be bent without whitening.

b) Multi-layered films

In films modified TPEE is used owing to superior adhesion, high transparency, and absence of gel formation.
Table III. Adhesion strength of modified TPEE on various metals

<table>
<thead>
<tr>
<th>Press temperature (°C)</th>
<th>160</th>
<th>180</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SUS304</td>
<td>1.5</td>
<td>7</td>
<td>29</td>
</tr>
<tr>
<td>Zinc-galvanized sheet iron</td>
<td>10</td>
<td>31</td>
<td>46</td>
</tr>
<tr>
<td>Aluminum</td>
<td>15</td>
<td>36</td>
<td>39</td>
</tr>
</tbody>
</table>

(UNIT: N/cm)

Pressing conditions: heating time, 7 min without pressure and 3 min at 1 MPa. Measurement conditions: 180° peel at 20 mm/min.

Figure 9. C1s spectra, as found by ESCA. (a): Original EVOH. (b): Original modified TPEE. (c): EVOH surface after peel-off.

Figure 10. Impact strength and softness of EVOH improved by addition of modified TPEE. Flexural modulus and Izod impact measured at 23°C, 50% RH (relative humidity). Content of soft segment in modified TPEE: 60 wt %.

Figure 11. Morphology, as found by TEM. (a): EVOH/unmodified TPEE = (90/10). (b): EVOH/modified TPEE = (90/10).
Further applications of modified TPEE are expected.

SOCIAL APPLICATIONS

1) Reduction environmental loads.
   TPEE/SBC alloy and acid-anhydride-modified TPEE make possible reduction of the environmental loads.
   (1) The double-injection method without adhesive containing organic solvent reduces VOCs.
   (2) Co-extrusion laminated films reduce VOCs considerably, compared to the dry-lamination method.
   VOC can be reduced is about 3.5 times that of modified TPEE used, as a rough estimation, assuming that a) the solid content of the adhesive for dry lamination is 30 wt %, b) the amount of adhesive used is 10 g/m² (conditions are based on the Japan Polyethylene Lamination Products Industrial Association report), and c) 2 µm-thick modified TPEE sheets are used to make co-extrusion film.
   (3) Decrease in aluminum, which requires much energy to produce and has higher density than plastics, reduces environmental loads.

Recycling
(1) Silica-coated PET film serves as a gas barrier comparable with that of aluminum foil, but it is difficult to adhere to other materials. However, it can be a good substitute for aluminum if an efficient adhesive is used. This adhesive is modified TPEE with this adhesive, recycling efficiency should improve.
(2) TPEE/SBC alloy and modified TPEE interact with various polymers, and contain soft segments. They thus have high potential as recycling agents as impact modifiers.

2) Improvement in reliability
(1) Remarkable reduction in pinholes in the multi-layer film promotes the reliability of film as food packing material.
(2) Packing material made by double injection has higher reliability than that made by manually.
3) Increase in shape flexibility
Flexibility in the shape of the superimposed article greatly
increases by double injection. This should help satisfy the demand for diversification in various material application.

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We thus greatly appreciated our many customers and their suggestions, and the many people in the Departments of Production, Analysis and Patents, and in the Laboratory of the Mitsubishi Chemical Corporation.

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Junji Mayumi was born in Mie Prefecture, Japan in 1955. He received his Bachelor’s degree in 1978 and his Master’s degree from the Faculty of Engineering of Nagoya University in 1980. In the same year, he joined Mitsubishi Chemical Corporation, and started his R & D work at the Polymer Development Laboratory. He has been mainly engaged in the R & D of polymer materials, such as paintable polypropylene, paint for plastics, cross-linkable polypropylene, etc. He is currently a group leader of the Performance Polymers Laboratory, and his current research interests include new adhesive thermoplastic polyester elastomers. He is a recipient of the Award of the Society of Polymer Science, Japan (2006).

Atsushi Nakagawa was born in the Tokyo Metropolitan area, Japan in 1976. He received Master’s degree from the Department of Electronic Chemistry of the Tokyo Institute of Technology in 2001. In the same year, he joined Mitsubishi Chemical Corporation, and started his R & D work at the Polymer Development Laboratory. He has been mainly engaged in the R & D of polymer materials, such as cross-linkable polymers and adhesive polymers for polyester. He is a recipient of the Award of the Society of Polymer Science, Japan (2006).

Keiko Matsuhisa was born in Gifu Prefecture, Japan in 1969, and received her Bachelor’s degree from the Faculty of Engineering of Nagoya University in 1992. In the same year, she joined Mitsubishi Chemical Corporation, and has been mainly engaged in the analysis and R & D of various modified polyolefins and thermoplastic elastomers. She is a recipient of the Award of the Society of Polymer Science, Japan (2006).
Hideki Takahashi was born in Fukushima Prefecture, Japan in 1964. He received his Bachelor’s degree in 1988 and his Master’s degree from the Department of Industrial Chemistry of the Tokyo University of Science in 1990. In the same year, he joined Mitsubishi Chemical Corporation and started his R & D work at the Polymer Development Laboratory. He has been engaged in the R & D of many kinds of thermoplastic elastomers (polyester, polystyrene and polyolefin) (1990–2002). He is currently a senior manager of the Performance Polymers Department. He is a recipient of the Award of the Society of Polymer Science, Japan (2006).

Hiroshi Takahashi was born in Tokyo, Japan in 1947. He received his Bachelor’s degree in 1970 and his Master’s degree in 1972 from the Department of Applied Chemistry, the School of Science and Engineering of Waseda University. In the same year, he joined Mitsubishi Chemical Corporation. He was engaged in the process development of poly-propylene at the Yokkaichi Factory (1972–1975), material design and marketing of specialty plastics and engineering plastics at the Research Center (1975–1994), and business planning of specialty plastics and specialty chemicals at Headquarters (1994–2002). He was transferred to Hokkaido University in 2002. He manages the research strategy of CRIS (Creative Research Initiative “SOUSEI”) as a director of Strategy Planning Office. He is a recipient of the Award of the Society of Polymer Science, Japan (2006).

Michihiro Iijima was born in Hokkaido, Japan, 1972. He received his Doctor’s degree (Doctor of Engineering) in 1999 from the Tokyo University of Science under the supervision of Prof. Masao Kato, Prof. Kazunori Kataoka and Prof. Yukio Nagasaki. The title of his thesis was “Synthesis and applications of novel end-reactive polymers for medical applications.” He joined the Specialty Polymers Laboratory of Mitsubishi Chemical Corporation from 1999 to 2000. He has mainly been studying new thermoplastic adhesive polyester elastomers. In 2000, he moved to Oyama National College of Technology as a research associate in the Department of Materials Chemistry. In 2006, he was promoted to lecturer. His current research interests are the synthesis and applications of end-reactive polymers and stimulus-sensitive polymers.