Thermoplastic Polyester Elastomers
2020
INTRODUCTION

Wide range of thermoplastic elastomers (TPE) are widely used owing to good formability and elasticity.

Double-injection technology, which combines more than two plastics, has been developed for united plastic products. Some TPEs are used to impart soft tactile properties or seal electric appliances or automotive parts. But alternative plastics are of limited use because of lower adhesion characteristics.

There is large demand in the field of food packaging for an adhesive resin to bind polyester with gas barrier resins. Polyester exhibits mechanical strength, high gloss and transparency, high heat resistance and good aroma retention, but polyester is difficult to bond. To maintain heat resistance during retort in the dry-lamination process, adhesive agents which contain much organic solvent are required. An adhesive resin which bind polyester to gas barrier resins even at elevated temperatures without using an organic solvent was developed. An acid anhydride-modified TPEE which bind polyester to gas barrier resins was made.

A new type of thermoplastic Polyester Elastomers (Copolyester elastomers (COPE) produced by Graft Polymer providing the stability of adhesion even after the double injection process. Using these alloys many new superimposed products can be produced easily even in double injection process.
The correct balance of TPEE and SBC in one package
Not only excellent compression set (Cs) and softness, but excellent adhesiveness to PS, ABS and PC.

The mechanical and adhesive properties of the alloy can be controlled by the type and amount of TPEE, SBC and extender oil.

- Excellent compression set (Cs) and softness
- Adhesion strength
GRAFTALLOY COPE-SB

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

The polymers which can be adhered to COPE-SB alloy are summarized in the table – along with PS families, PC and their alloys, as well as thermo-setting resin, such as phenol resin or unsaturated polyester resin. Polyesters such as PET and PBT also adhere to the COPE-SB alloy owing to the compatibility of the hard segment in COPE.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Original strength</th>
<th>Heat 80 °C 1000h</th>
<th>Heat shock test −40−80 °C 200 cycles</th>
<th>Humidity resistance 50 °C, 95% RH 1000h</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>230</td>
<td>160</td>
<td>150</td>
<td>210</td>
</tr>
<tr>
<td>PC</td>
<td>200</td>
<td>150</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

(Unit: N/cm)

TPEE/SBC alloy Shore A hardness score, 67.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate</td>
<td>PC</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>ABS, AES, AS, GPPS, HIPS</td>
</tr>
<tr>
<td>Polyphenylether</td>
<td>PPE/HP</td>
</tr>
<tr>
<td>Acrylate resin</td>
<td>PMM</td>
</tr>
<tr>
<td>Polyester</td>
<td>PET, PBT</td>
</tr>
<tr>
<td>Polymer</td>
<td>PC/ABS, PC/PET, PC/PBT</td>
</tr>
<tr>
<td>Thermosetting</td>
<td>Phenol Unsaturated polyester</td>
</tr>
</tbody>
</table>

(Tabulated data and table image)
Using *interactions* between PS and COPE, various things can be *formed easily* by double-injection molding, instead of by adhesive agents which take much time.

All samples are formed by ABS or PS injection first, and then COPE/SB alloy injection.

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

Water-proof cameras. COPE/SBC alloy on ABS. Seal-packing.

Goggles. COPE/SBC alloy on PC. Soft tactile properties

Grip of ball-point pens. COPE/SBC alloy on ABS. Soft grip.
Graftalloy COPE Grades

**Graftalloy COPE-TPO**
Based on COPE and thermoplastic polyolefin
Excellent compatibility with all PP and PE

**Graftalloy COPE-SB**
Based on COPE and styrene components
Excellent compatibility with PS, ABS, PC, PMMA and other styrene-based polymers

Tie layer for coextrusion of COPE and polyolefins soft component for over molding
The COPE (TPEE) with acid anhydride can solve the grafting problems in food packaging.

This modified COPE (TPEE) 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, COPE, which has less PTMG, cannot be grafted with sufficient adhesiveness.

A schematic adhesion mechanism is given on the picture. The compatibility of the PBT segment of COPE (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.

Examples of Modified COPE Usage:

Modified COPE may be used as an adhesive resin.

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

b) Multi-layered films
PS/modified TPEE/PET
PET/modified TPEE/EVOH
PET/modified TPEE/PVC
**PROPERTIES of GRAFTED COPE (TPEE)**

**Flexural Modulus and Impact Strength**

Picture shows the Izod impact strength of EVOH to increase in proportion to modified COPE, and the obtained resins soften with modified TPEE.

**Adhesion Strength of grafted COPE**

The modified COPE makes possible to produce materials 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.
PROPERTIES of GRAFTED COPE (TPEE)

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. Layered products consisting of metal and polyester can thus be produced.

Efficiency 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.

Morphology

The picture shows a TEM photograph of binary material composed of EVOH (32 mol % ethylene) and modified COPE (90/10). In contrast to unmodified TPEE in a picture, a finer dispersion at the submicron level can be seen. The grafted acid derivatives seem apparently reduce interface tension.

Other properties:

✓ Transparency and Oxygen Permeability
✓ Pinhole Defect Resistance
✓ Improvement in Formability
GRAFTALLOY COPE-SB/M

Based on COPE and polar component
Excellent compatibility with all polyesters, polyamides and other polar polymers

**Applications:**
- Tie layer for coextrusion
- Soft component for over molding

**Processing:**
GRAFTALLOY™ COPE-SB/M is processable on most thermoplastics processing equipment
Preferable for: Extrusion (Coextrusion), Over molding
It is recommended to avoid overheating above 320°C
Purge the equipment after a run is completed
SOCIAL APPLICATIONS

Reduction environmental loads

TPEE/SBC alloy and acid-anhydride-modified TPEE make possible reduction of the environmental loads.

- The double-injection method without adhesive containing organic solvent reduces VOCs
- 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 COPE is 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 10g/m² (conditions are based on the Japan Polyethylene Lamination Products Industrial Association report), and c) 2mm-thick modified COPE sheets are used to make co-extrusion film.

- Decrease in aluminum, which requires much energy to produce and has higher density than plastics, reduces environmental loads.
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 COPE (TPEE) with this adhesive, recycling efficiency should improve.

COPE/SBC alloy and modified COPE interact with various polymers and contain soft segments. They thus have high potential as recycling agents as impact modifiers.

Improvement in reliability

Remarkable reduction in pinholes in the multi-layer film promotes the reliability of film as food packing material.

Packing material made by double injection has higher reliability than that made by manually.

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.
WHAT MAKES GP UNIQUE

- Use **proprietary co-agents** and **redox initiating system** for grafting
- Use of **Nitroxide Mediated Polymerization** for controlled grafting reactions
- **Co-continuous nano-morphology** approach for creation polymeric alloys
- **Interpenetrating Polymer Networks (IPN)**
- **Thermo-Reversible Crosslinking polymers** and **Vitrimer**s
- **Smart Polymers**
  - **Self-Healing** polymers
- In-house synthesis of unique “nitroxide stable radicals” (TEMPO) for high-tech composite materials – proprietary process
To support its unique modification technologies, GP has built the R&D center including Laboratory and Synthesis facilities.

**INNOVATIVE TECHNOLOGIES**

- Flow induced crystallization
- Solid Phase Grafting
- Solution Grafting
- Fillers Treatments
- Powders Hybridization
- Hot ozonolysis/plasma modification
- Nitroxide Mediated Polymerization
- Micro/Nano Porous polymer carries

**SYNTHESIS**

**CROSSLINKING**

**POLYMERIC NANO ALLOYS**

**GRAFT / BLOCK POLYMERS**

**POROUS**
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