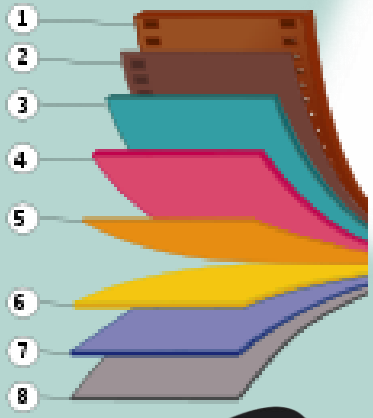
GRAFT POLYMER

COMBINE INCOMPATIBLE

Thermoplastic Polyester Elastomers

2020



INTRODUCTION

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

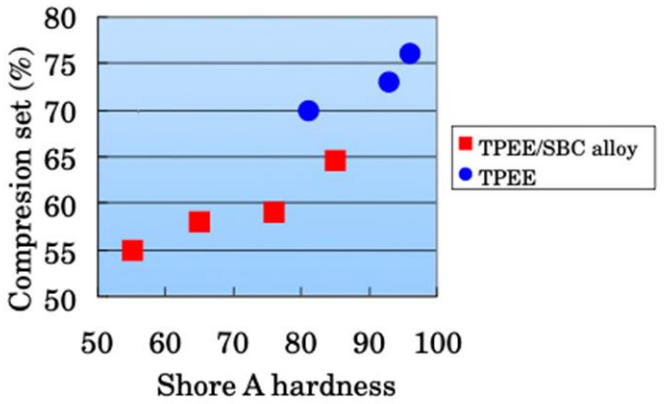
Double-injection technology, which combines more than two plastics, has been developed for united plastic products. Some TPEs are used to impart soft tactile properties or seal electric appliances or automotive parts. But alternative plastics are of limited use because of lower adhesion characteristics.

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.

GRAFTALLOY COPE-SB

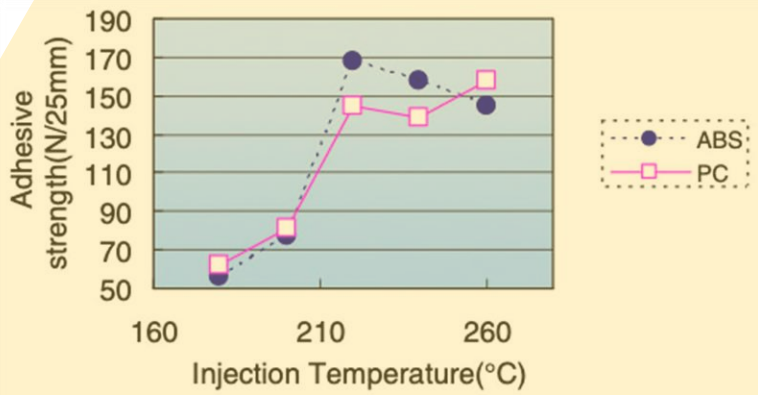
The correct balance of TPEE and SBC in one package
Not only excellent compression set (Cs) and softness, but excellent adhesiveness to PS, ABS and PC.



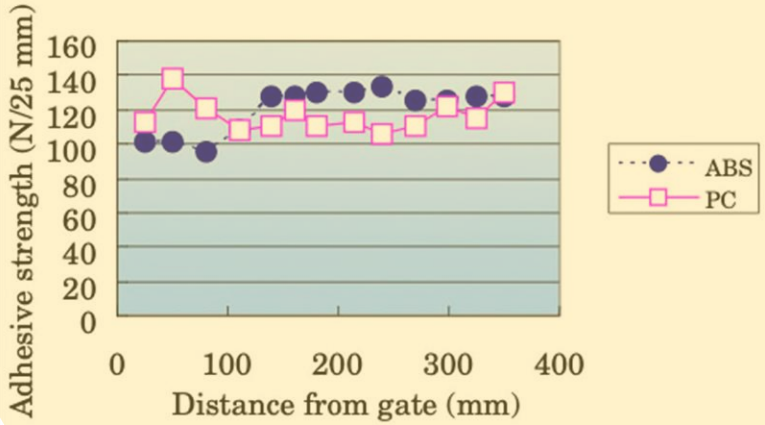
Balance of the compression set and the softness in comparison with that of pure TPEE. Conditions for compression measurement: 70 °C, 22 hrs.

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



Injection temperature dependency of adhesive strength. TPEE/SBC alloy Shore A hardness score, 67.



Adhesive strength at various distances from gate. TPEE/SBC alloy Shore A hardness score 67.

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.

Durability of adhesion strength under various conditions

Resin	Original strength	Heat 80 °C 1000 h	Heat shock test −40–80 °C 200 cycles	Humidity resistance 50 °C, 95% RH 1000 h
ABS	230	160	150	210
PC	200	150	200	200

(Unit: N/cm)

TPEE/SBC alloy Shore A hardness score, 67.

Polymers which can be adhered

Resin	Example
Polycarbonate	PC
Polystyrene	ABS, AES, AS, GPPS, HIPS
Polyphenylether	PPE/HIP
Acrylate resin	PMM
Polyester	PET, PBT
Polymer	PC/ABS, PC/PET, PC/PBT
Thermosetting	Phenol Unsaturated polyester

GRAFTALLOY COPE-SB

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

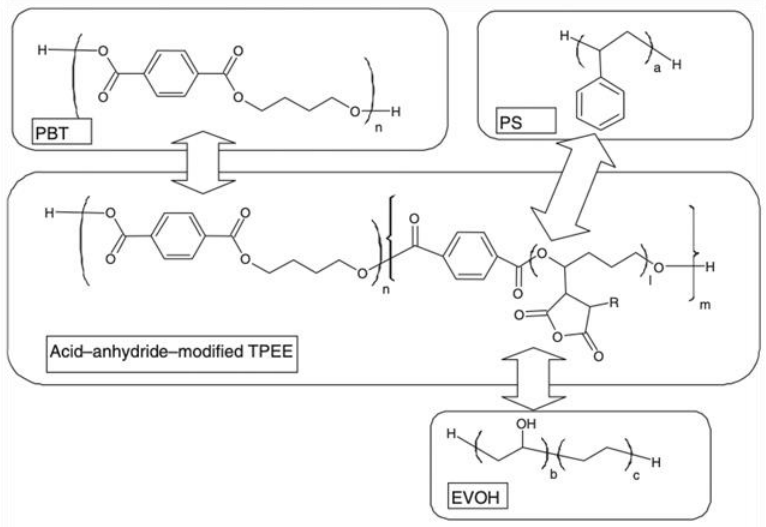
Tie layer for coextrusion of COPE and polyolefins soft component for over molding

GRAFTED COPE (TPEE)

The COPE (TPEE) with acid anhydride can solve the pgraftedroblems 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.



Schematic interactions between modified TPEE and other polymers.

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

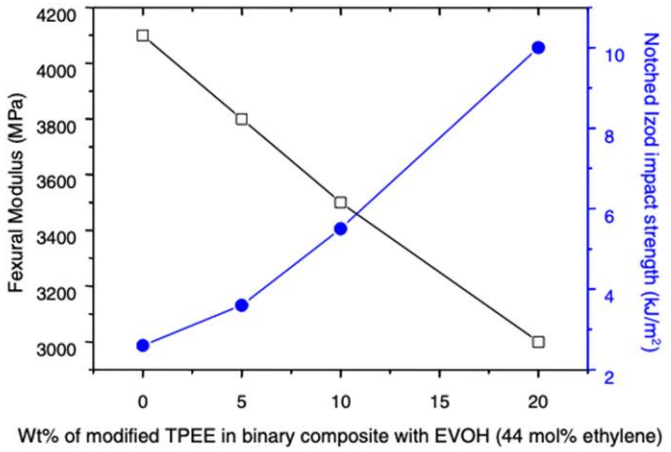
PET/modified TPEE/EVOH

PET/modified TPEE/PVC

PROPERTIES of GRAFTED COPE (TPEE)

Flexural Modulus and Impact Strength

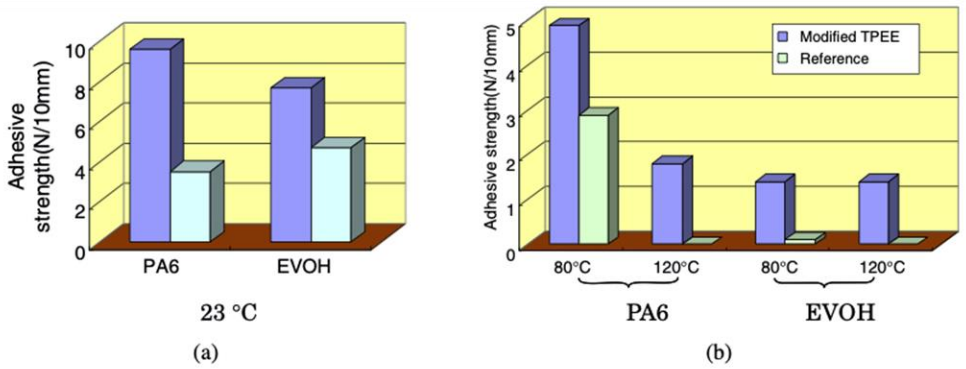
Picture shows the Izod impact strength of EVOH to increase in proportion to modified COPE, and the obtained resins soften with modified TPEE.



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 %.

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.



Adhesion strength of modified TPEE against PA6 or EVOH. (a) Ambient temperature, (b) elevated temperatures. Peeling rate: 100 mm/min. Peeling direction: MD (machine direction).

PROPERTIES of GRAFTED COPE (TPEE)

Adhesion strength of modified TPEE on various metals

Metal	Press temperature (°C) 160	180	200
SUS304	1.5	7	29
Zinc-galvanized sheet iron	10	31	46
Aluminum	15	36	39

(Unit: N/cm)

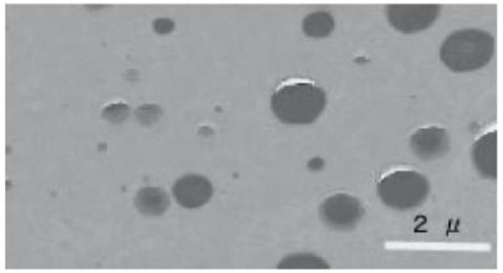
Pressing conditions: heating time, 7 min without pressure and 3 min at 1 MPa. Measurement conditions: 180° peel at 20 mm/min.

Adhesiveness of the Modified TPEE to Metal

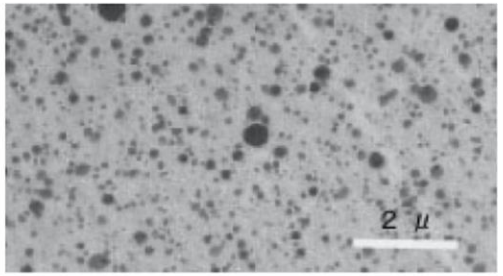
The modified TPEE adheres to many metals, such as SUS304, zinc-galvanized sheet iron or aluminum, as summarized in Table. Layered products consisting of metal and polyester can thus be produced.

Other properties:

- ✓ Transparency and Oxygen Permeability
- ✓ Pinhole Defect Resistance
- ✓ Improvement in Formability



(a)



(b)

Morphology, as found by TEM. (a): EVOH/unmodified TPEE = (90/10). (b): EVOH/modified TPEE = (90/10).

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.

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

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.

SOCIAL APPLICATIONS

RECYCLING

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 **Vitrimers**
- **Smart Polymers**
  Self-Healing polymers
- In-house synthesis of unique "**nitroxide stable radicals**" (TEMPO) for high-tech composite materials – proprietary process

BUSINESS MODEL: INNOVATIONS

GRAFT / BLOCK POLYMERS

POLYMERIC NANO ALLOYS

CROSSLINKING

POROUS

SYNTHESIS

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

To support its unique modification technologies, GP has built the **R&D** center including **Laboratory** and **Synthesis facilities**

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