TPE versus Gummi:
Freundlicher oder feindlicher Wettbewerb?

TPE versus Rubber:
Friendly or unfriendly competition?

H.-J. Graf (SP), WOCO GmbH, Bade Soden Salmünster, (D)
H. Magg, Lanxess Deutschland GmbH, Leverkusen (D)
E. Osen, Freudenberg Sealing Technologies GmbH, Weinheim, (D)
C. Thomas, Meteor Gummwerke GmbH, Bockenem (D)
Introduction

- History of TPE
- Uniqueness of TPE
  - TPE Family Tree
  - Basic Properties of TPE
  - Morphology – Property dependency
- Positioning of TPE
  - Property Map
  - Stress Relaxation
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  - Compounds / Compounding
  - Forming
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History of TPV
Patent History

⇒ US 4,594,390 A is the Patent Base of Monsanto / AES on TPV
⇒ Title: Process for the preparation of thermoplastic elastomers
  • Published 02.05.84

⇒ US 4,803,244 Union Carbide on Silane crosslinked TPV
  • Published Nov. 16, 1987

• Since then, the price has moved slightly downward, because of Korean Competitors, but not much.
• But a lot of compounders are established today
• Example: Allod – based on SEBS.
Uniqueness of TPE

Structure of TPE

Crosslinks of polymer materials determines their modulus
Thermoplastic elastomers have crosslinked domains only

Dr. Hans-Joachim Graf
Uniqueness of TPE

Between Rubber and Thermoplastic: TPE is a “Dual Phase” material, which contains a thermoplastic continuous phase surrounding rubber droplets.
Uniqueness of TPE
TPE Family Tree

TPE Families

- Olefinic
  - TPO
  - Physblend
  - Metalloocene-Based
    - RTPO

- Styrenic
  - TPV
    - Hydrogenated (SEBS, SEPS)
    - Blends
      - Pure
      - Metallocene-Based (SBCs)

- PVC
  - PVC TPEs
  - PVC Alloys
    - TPU
    - COPE
    - COPA
    - Other

- ENGINEERING

Uniqueness of TPE
TPE Family Tree

GROWTH AND VALUE OPPORTUNITIES IN THE TPE FAMILIES

OLEFINIC
- TPO
- TPV
- COATED FABRICS, FOAMS
- p-TPV (PARTIAL CROSSLINKED)
- BROADENED APPLICATION RANGE FOR p-TPVs

STYRENE
- HYDROGENATED (SEBS, SEPS)
- ISOPRENE-BASED MIDBLOCKS
- FOAMS, 2-SHOT
- f-TPV (FULLY CROSSLINKED)
- -BROADER USE OF METALLO ELASTOMERS
- -ETP MATRICES
- -IMPROVED ADHESION
- -INCREASED SOFTNESS W/ REDUCED OIL CONTENT

PVC
- ALL PVC TPEs
- PVC ALLOYS
- NEW ALLOYS (TPU, ACRYLIC, POs) FOR LOW TEMP. PERF.
- r-TPV (RECYCLATE-BASED TPVs)
- GROWTH SLOWDOWN

ENGINEERING TPEs
- TPU
- COPE COPA OTHER

VERY HIGH PERFORMANCE
- SILICONES
- FLUOROElastomers
- ACRYLICS FOR HIGH OIL & HEAT RESIST.
- ETP RESIN MATRICES

SOURCE: ROBERT ELLER ASSOCIATES, INC., 2004

Source: R. Eller, TX, Feb. 2000
Uniqueness of TPE
Basic Properties of TPE

- Hard-elastic, brittle
- Hard elastic, tough
- Tough, still too hard for application as Elastomer
- Soft-elastic, area of application
- Very soft, not applicable for service
- Viscous melt, forming area
- Chemical aging and decomposition

Source: Franck/Biederbick, Kunststoff-Kompendium 88
Uniqueness of TPE
Basic Properties of TPE

Source: Franck/Biederbick, Kunststoff-Kompendium 88
Uniqueness of TPE
Basic Properties of TPE

Source: Franck/Biederbick, Kunststoff-Kompendium 88
Uniqueness of TPE
Morphology - Property Dependency

Source: K. Walton, RCT 77

Source: A.Y. Coran, R.P. Patel
Thermoplastic Elastomers 96

Transmission electron microscopy (TEM) of PP/EPDM TPV. Dark areas are crosslinked rubber particle.
Uniqueness of TPE
Morphology - Property Dependency

Source: W. Michaeli et.al.
KHK Sept. 2011
Positioning of TPE
Property Map

EPDM Compounds:
- Hardness from 20°ShA up to 95°ShA is possible, opposite to original slide

Source: Wittig, GAK 1997

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Positioning of TPE Property Map

Comparison of a TPE/TPV based on EPDM/PP with a NR-compound. Why not peroxide and/or resin cured rubber?
Positioning of TPE
Stress relaxation behaviour

Graph suggests little performance of vulcanized rubber

Applicability of Stress/Strain on different Materials until elasticity limit, but with complete recovery after removing of the load
Positioning of TPE

Stress relaxation behaviour

Applicability of Stress/Strain on different Materials until elasticity limit, but with complete recovery after removing of the load

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Positioning of TPE
Stress relaxation behaviour

TPE Kraft - Weg Diagramm

EPDM Kraft - Weg Diagramm

Source: C. Thomas
DIK TPE Seminar

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Positioning of TPE
Stress relaxation behaviour

Compression load relaxation for Elastomers (typical behavior)

Source: E. Jourdain, Autom.Elast.Conf. 04, Detroit
Positioning of TPE
Stress relaxation behaviour

Compression Stress Relaxation of different rubbers compared with Standard and high performance TPE.

Source: E. Osen
KHK 2006

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TPE versus Rubber Compounds / Compounding

**TPE**
- Continuous Matrix
  - PP
  - PO
  - TP Polar Polymers
  - Developments mostly on Heat / Media resistant TPE
- Suppliers
  - Since 2000 numerous suppliers established similar to the TP-Industry

**Rubber (TSR)**
- Material developments are seldom
- Developments for improvement
  - Machines
  - Compounding to meet specifications
- Material replacement during life cycle is difficult:
  - Expensive testing
  - Customer declines
  - Economical restrictions (Ownership of mixing equipment)
Two stage compounding

- FCM (Farrel Continuous Mixer)
- Internal mixer
- Discharged to single-screw extruder and then pelletized

Source: HF Mixing
Former Farrel

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TPE versus Rubber Compounds / Compounding

Twin Screw Extruder Production Unit

- Feeding ports
- Underwater pelletizer
- Pellets/water separator
- Pellet drier
- Classifier
(a) Vulcanized rubber

Gum Rubber
Chemicals
Filler
Others

Mixing ➔ Shaping ➔ Vulcanization ➔ Finished product
Scrap ➔ Scrap ➔ Scrap

(b) Thermoplastic elastomer

Thermoplastic Rubber
No mixing required?

Recycle of scrap

Part goes "hot" in the bin.
No cooling required??
**TPE versus Rubber**

**Forming**

### Processing of TPE
Physical Crosslinking

- **Material**: TPE-Granules
- **Forming**: (Inj. Molding, Extrusion, compression)
- **Part**
- **Reuse of Scrap**

### Processing of Rubber
Chemical Crosslinking

- **Raw Materials**: Rubber, Filler, Ingredients
- **Compounding**
- **Forming**: (Inj. Molding, Extrusion, compression)
- **Vulcanization**
- **Part**
- **Scrap**
- **Scrap**

Source: J. Stemper
Plastverarbeiter 84

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TPE versus Rubber Forming

Source: Wittig, GAK 1997

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TPE versus Rubber
Forming

Source: Wittig, GAK 1997
PP content is increased to achieve hardness, which improves flow.

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TPE versus Rubber Forming

Calculation of TPE glass run channel solution versus EPDM

Cost estimation

<table>
<thead>
<tr>
<th></th>
<th>EPDM</th>
<th>TPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion</td>
<td>0.110 $/ft</td>
<td>0.130 $/ft</td>
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<tr>
<td>Flocking</td>
<td>0.020 $/ft</td>
<td>N/A</td>
</tr>
<tr>
<td>Slipcoat</td>
<td>N/A</td>
<td>0.020 $/ft</td>
</tr>
<tr>
<td>Molding</td>
<td>1.350 $/unit</td>
<td>0.270 $/unit</td>
</tr>
<tr>
<td>Total</td>
<td>1.480 $/unit</td>
<td>0.420 $/unit</td>
</tr>
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</table>

Source: S.Z. Yu, H.-J. Graf

Source: Internet
In an experiment with a production scale twin screw extruder to study the manufacturing process of TPE the following formulation was used (Note the large amount of oil in this formulation):

**65 SHORE A FORMULATION**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>100</td>
<td>30.42</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>30</td>
<td>9.13</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>50</td>
<td>15.21</td>
</tr>
<tr>
<td>Oil</td>
<td>130</td>
<td>39.55</td>
</tr>
<tr>
<td>SP 1045</td>
<td>10</td>
<td>3.04</td>
</tr>
<tr>
<td>Stannous Chloride (dihydrate)</td>
<td>1.7</td>
<td>0.52</td>
</tr>
<tr>
<td>Processing aid</td>
<td>5</td>
<td>1.52</td>
</tr>
<tr>
<td>ZnO</td>
<td>2</td>
<td>0.61</td>
</tr>
</tbody>
</table>

**Totals** 328.7 100.00
TPE versus Rubber
Property Description

Source: G. Williams
Autom. Elastomer Conf. 03
TPE versus Rubber
Property Description

Source: G. Williams
Autom. Elastomer Conf. 03

Dr. Hans-Joachim Graf
Reason, why most OEM suppliers not satisfied with TPE-V today

Dr. Hans-Joachim Graf

Source: G. Williams
Autom. Elastomer Conf. 03
## TPE versus Rubber

### Property Description

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness - °ShA</th>
<th>Tensile – Mpa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Confirmation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>longitudinal</td>
</tr>
<tr>
<td>TPE 1</td>
<td>55</td>
<td>3.8</td>
</tr>
<tr>
<td>TPE 2</td>
<td>60</td>
<td>5.4</td>
</tr>
<tr>
<td>TPE 3</td>
<td>60</td>
<td>4.5</td>
</tr>
<tr>
<td>TPE 4</td>
<td>60</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Reason, why most customers not pleased with suppliers today

Dr. Hans-Joachim Graf
Comparison of Continuous Stress Relaxation for EPDM and TPV Lips at Varying Temperatures

Load (N)

Time (min)

Chambre Temperature (°C)

Source: S.Z. Yu
Cooperstandard Automotive
TPE versus Rubber Property Description

Figure 12: view of profile cross section in A pillar, (old profile)
Disadvantages of TPE compared to Rubber

- Resistance against Temperature falls short. Even a short period at a temperature beyond softening changes the shape irreversibly.
- Limited usage, because of high creep under load, if exposed to higher temperatures.
- Limited resistivity against media compared to special rubbers
- Process adjustments not possible
- High material costs
- Little to none protection of know how for development engineers
Processing of thermoplastic elastomers

ือน Opposite to Rubber processing, which is a cold/hot process, TPE are manufactured in a hot/cold process.
ือน Most TPE materials need a smaller flight depth than rubber compounds in case of injection molding, which requires machine investment.
  ■ For TPE Screws with longer L/D of 15 and a flat flight screw are preferred like similar used for PVC processing
ือน TPE parts can be manufactured in all processes typical for TP, like extrusion, blow molding, injection molding and thermo forming.
Conclusion

► Competition is not always friendly
TPE should be offered with more reliable data to support the manufacturer, who is responsible for the part.
To achieve this, we should have more
  ● Round robin tests
    not only for more reliable data, but also to benefit from the standards in rubber manufacturers laboratory practice.
  ● Possibly define better test standards

► Manufacturers Material departments have to increase their attention at TPE.
It is insufficient to leave it in the hands of the development engineers.

► More intense cooperation between material specialist at manufacturer and supplier will be beneficial for further developments and market penetration of TPE.