



GERMAN RUBBER CONFERENCE
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Educational Symposium

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THERMOPLASTIC ELASTOMERS – AN OVERVIEW

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Outline

- Introduction
- Structure principle of TPE
- Classification
- Structure and properties of most important TPE – classes
- Thermoplastic Vulcanizates
- Recent Developments
- Processing of TPE
- Outlook

TPE are one of the most versatile plastics

- Commercially introduced in the 1960s
- Block Copolymers TPU, Styrenic based SBS, etc.
- Cover a wide range of hardness (from low Shore A to Shore D)
- Use properties comparable with conventional elastomers
- Easy to process (as thermoplastics) and easy to recycle
- A great milestone was the development of TPV in 1980s
- High growth rates over the last decades



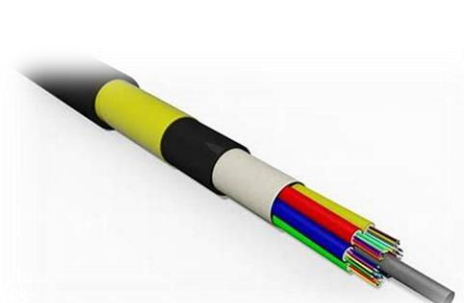
TPE cover a wide range of application areas



Automotive



Construction



Cable and wire



Sports and leisure



Consumer



Medical

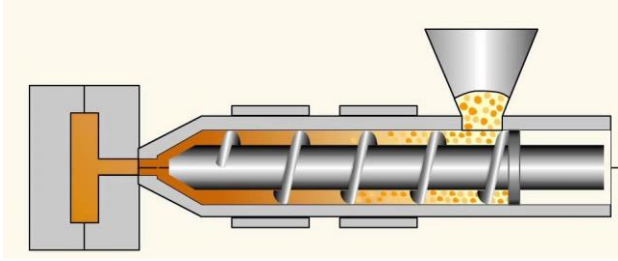


Electronics



Foot wear

TPE advantages



**Thermoplastic
processibility**

**Rubber elastic
use properties**



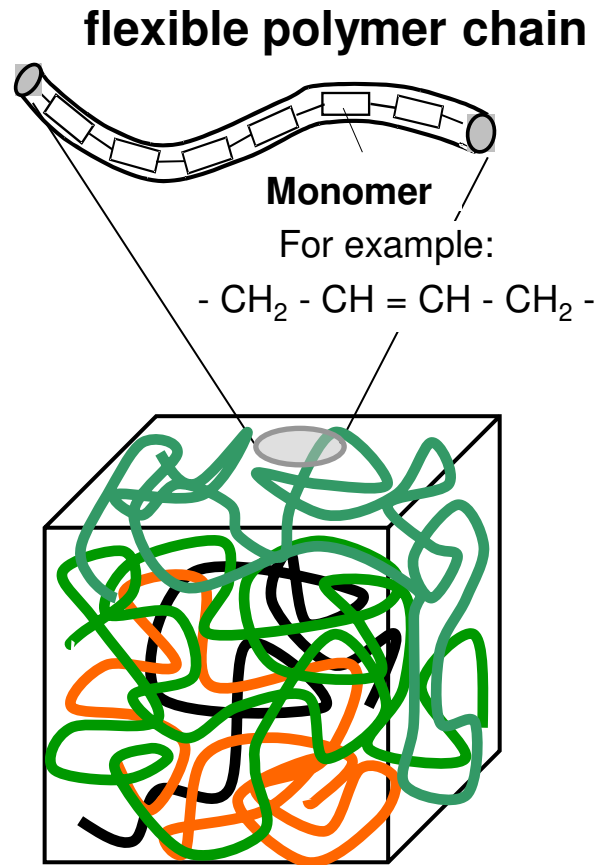
Recyclability

What makes the difference between TPE and conventional Elastomers ?



Structure and morphology

STRUCTURE OF RUBBER AND ELASTOMERS



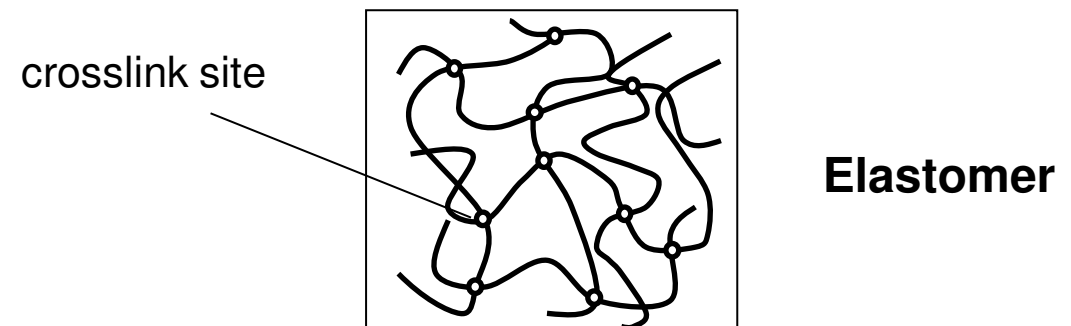
amorphous structure of raw rubber

Raw Rubber:

- amorphous polymers
- e.g. BR, SBR, EPDM, NBR
- high molecular weight
- glass transition temperature $T_g < 0\text{ }^\circ\text{C}$

Elastomers:

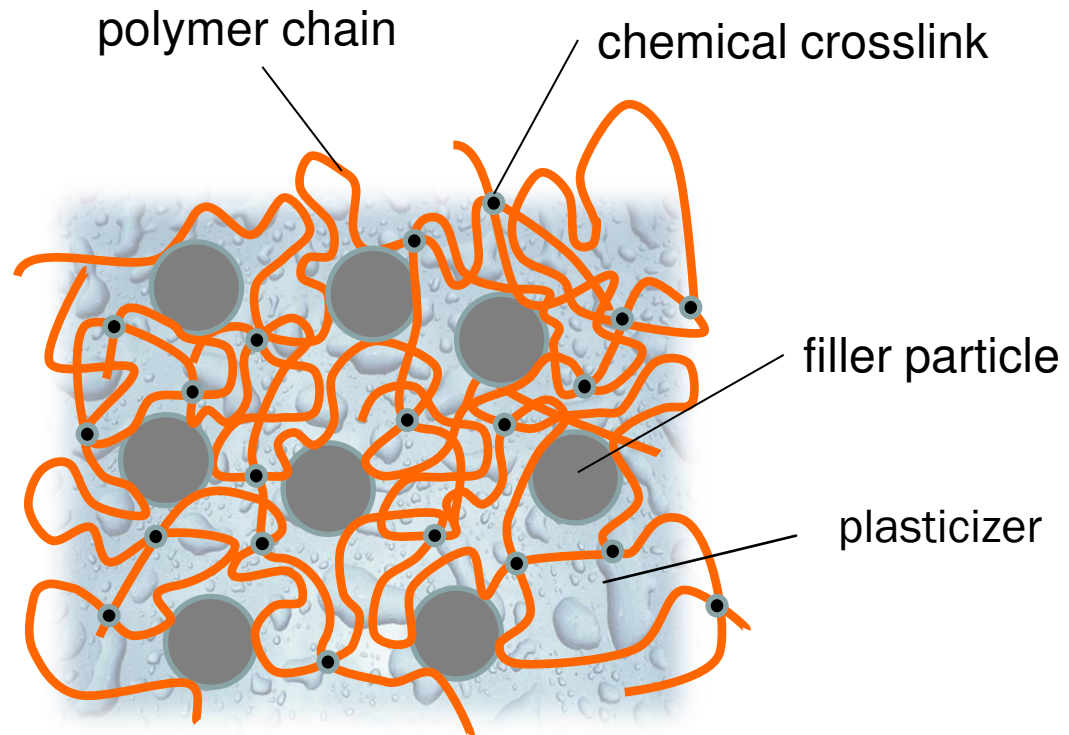
- crosslinked raw rubber
- contains additional ingredients
- fillers, plasticizer, curatives, antioxidants, etc.



crosslinked polymer chains

STRUCTURE MODEL OF FILLED ELASTOMERS (SYMPLIFIED)

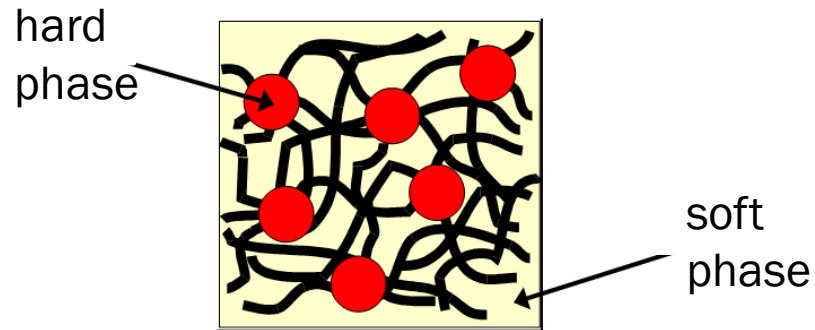
Conventional Elastomers



STRUCTURE PRINCIPLE OF TPE

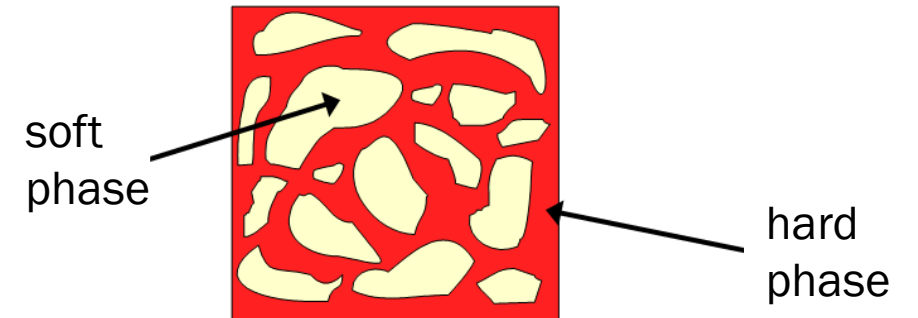
Combination of thermoplastic hard phase and rubbery soft phase

Continuos soft phase and dispersed hard phase



Micro-phase separated block copolymers with crystalline or glassy hard blocks

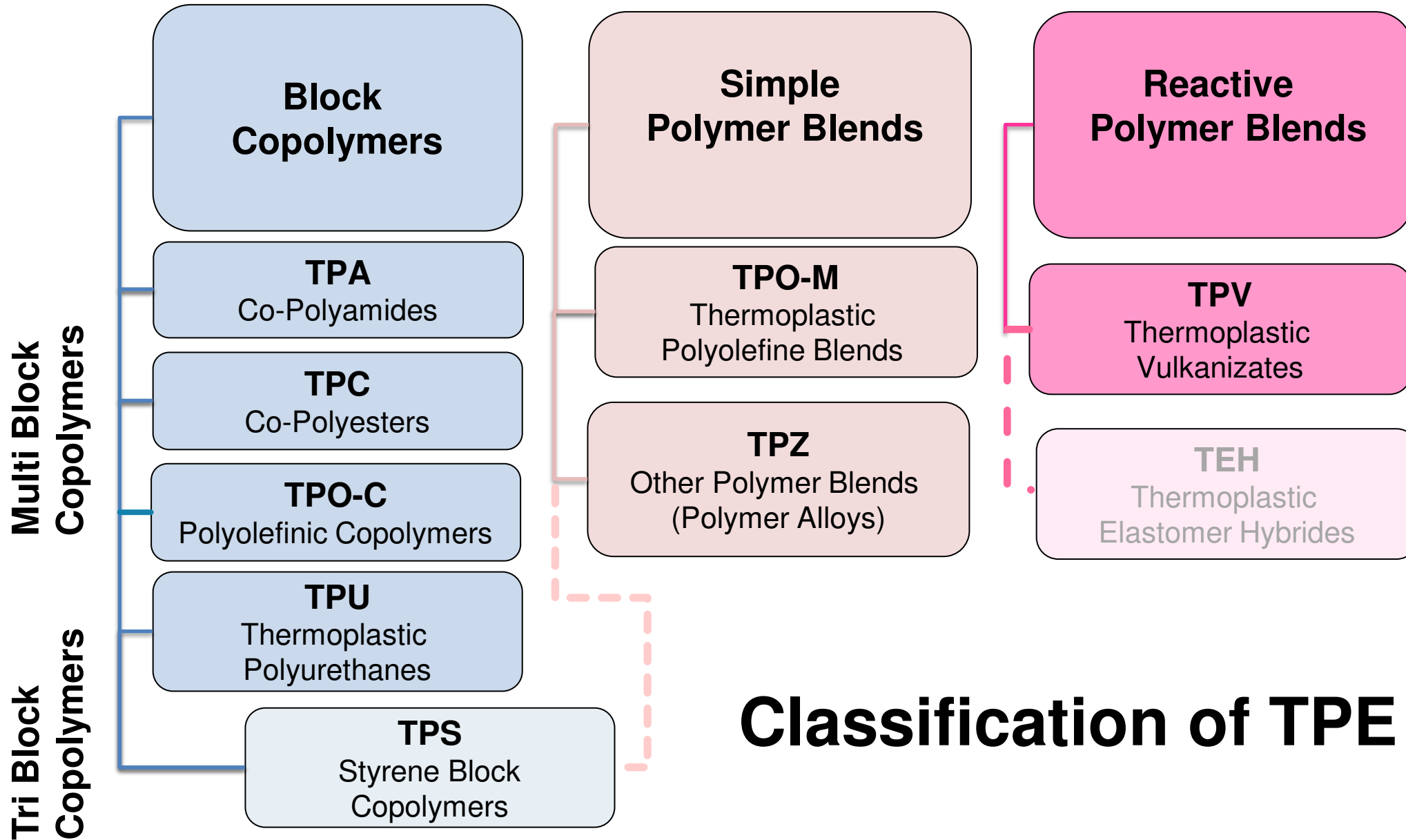
Continuos hard phase and dispersed soft phase



Heterogeneous polymer blends with island / matrix or co-continuous phase morphology

Nomenclature and abbreviated terms according to EN ISO 18064-2022

TPE Classes	Abbrev.	Sub Categories
Thermoplastic Polyamide Elastomer	TPA	TPA-EE, TPA-ES, TPA-ET, TPA-CE
Thermoplastic Copolyester Elastomer	TPC	TPC-EE, TPC-ES, TPC-ET, TPA-CE
Thermoplastic Olefine Elastomer	TPO	TPO-C; Block Copolymer TPO-M; Polymer mixture (e.g. TPO-M (PP+EPDM))
Thermoplastic Styrene Elastomer	TPS	TPS-H; fully-hydrogenated soft segment TPS-N; partially or non-hydrogenated soft segment
Thermoplastic Urethane Elastomer	TPU	TPU-ARES, TPU-ARET, TPU-AREE, TPU-ARCE, TPU-ALES, TPU-ALET, TPU-ALEE, TPU-ALCE
Thermoplastic Vulkanizate	TPV	TPV-(PP+EPDM), TPV-(PP+NBR), TPV-(PA+ACM), TPV-(TPU+QR)
Thermoplastic Elastomer of other Composition	TPZ	e.g. TPZ-(NBR+PVC)



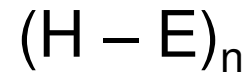
Classification of TPE

P
R
O
C
E
S
S
I
N
G

STRUCTURE AND PROPERTIES: MULTI BLOCK COPOLYMERS

General structure

structure formula

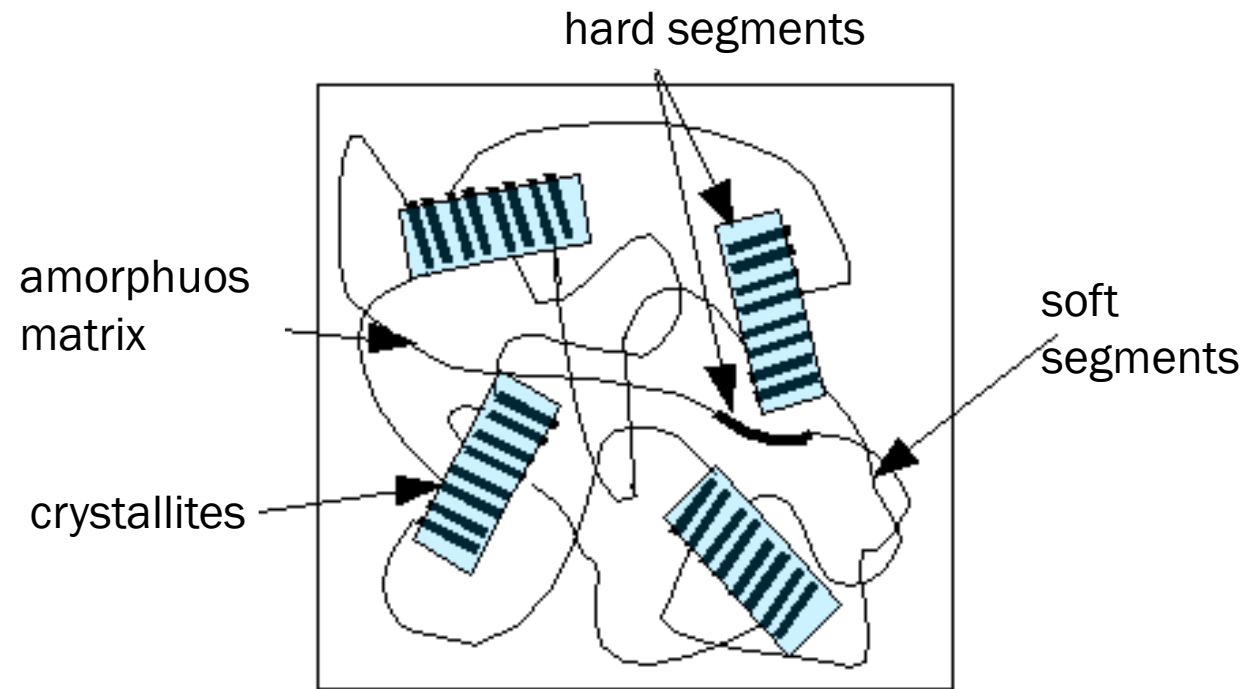


hard segments H

-A-A-A-A-A-A-A-A-
regular

soft segments E

-A-B-B-A-A-B-A-B-A-
irregular



Morphology (schematical)



STRUCTURE AND PROPERTIES: MULTI BLOCK COPOLYMERS

Hard Segments	Soft Segments	Abbreviations
Polyamides	Polyether/ester, Polyester or Polyether	TPA; TPA-EE; TPA-ES; TPA-ET
Polyesters	Polyether/ester, Polyester or Polyether	TPC, TPC-EE; TPC-ES; TPC-ET
Polyurethanes	Polyester or Polyether	TPU; TPU-ARES, TPU-ALES, TPU-ARET, TPU-ALET, etc.

Example: TPU-ARES


Aromatic hard segment Ester soft segment



EXAMPLE OF TPA: VESTAMID E®

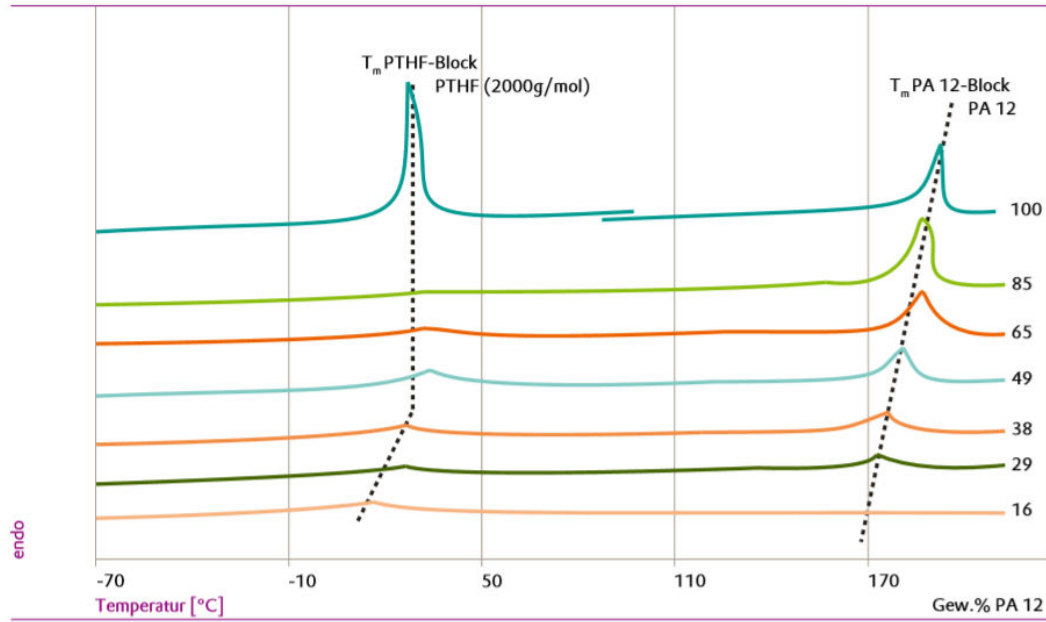
Typical Properties

Property	
Shore D	30 bis 72
Tensile modulus / MPa	45 bis 1500
Tensile strength / MPa	10 bis 45
Ultimate elongation / %	n.s.
Glass transition temp. / °C	-60 bis 0
Melting temperature / °C	ca. 175

Application example: foot wear



Abbildung 4: Aufschmelzdiagramme (DSC) von PA 12-Elastomeren mit Polytetrahydrofuran-Weichblöcken (PTHF); T_m = Schmelztemperatur



- The properties of TPA are determined by the phase morphology.
- Phase separation due to incompatibility of the polyamide and polyether blocks
- 4 Phases: 2 x crystalline; 2 x amorphous
- 2 x T_m und 2 x T_g

Phase morphology of TPA

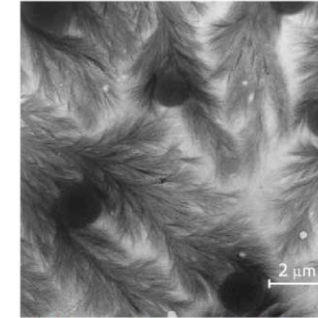


Abbildung 2: Aufnahme eines PA 12-reichen Elastomers mit dem Transmissions-Elektronenmikroskop

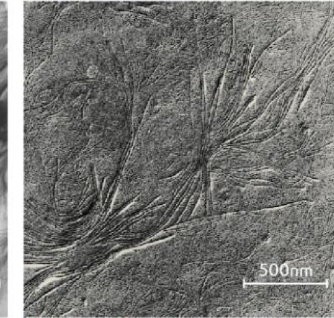
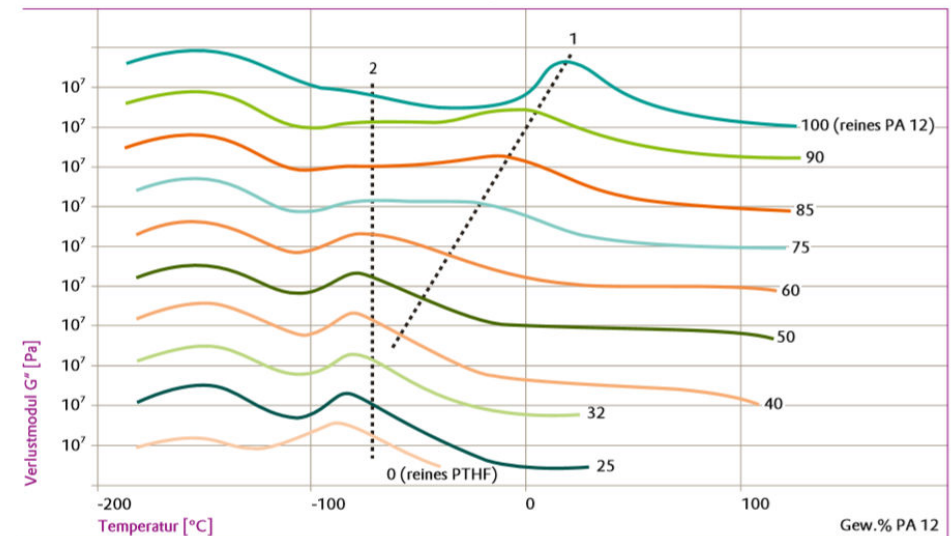


Abbildung 3: Aufnahme eines Polytetrahydrofuranreichen PA 12-Elastomers mit dem Transmissions-Elektronenmikroskop

Abbildung 5: Verlustmodulkurven aus Torsionsschwingungsanalysen von PA 12-Elastomeren mit Polytetrahydrofuran-Weichblöcken (PTHF); T_g = Glasübergangstemperatur



1 Tg der PA 12-reichen Mischphase (Matrix), 2 Tg der PTHF-reichen Mischphase

EXAMPLE OF TPC: HYTREL®

Typical Properties

Property	
Shore D	20 to 80
Flexural modulus / MPa	20 to 1200
Tensile strength / MPa	10 to 50
Ultimate elongation / %	200 to 900
Glass transition temp./ °C	-60 to 0
Melting temperature / °C	150 to 220

Application example: Axle boots



EXAMPLE OF TPU: DESMOPAN®

Typical properties

Property	
Shore	60 A to 80 D
Tensile modulus / MPa	n.s.
Tensile strength / MPa	25 to 80
Ultimate elongation / %	300 to 900
Glass transition temp./ °C	n.s.
Melting temperature / °C	n.s.

Application example: TPU foil for Interior



2

Foto: Covestro



Styrene Tri – Block - Copolymers

Combination of Polystyrene – and Elastomer – Blocks

T_g	$\sim 100\text{ }^{\circ}\text{C}$	$\sim -60\text{ }^{\circ}\text{C} \dots -90\text{ }^{\circ}\text{C}$
	hard	soft

General structure of Styrene – Block – Copolymers $(S - E)x_n$

Functionality n of junction point x

$n = 1$

S – E

di – Block-

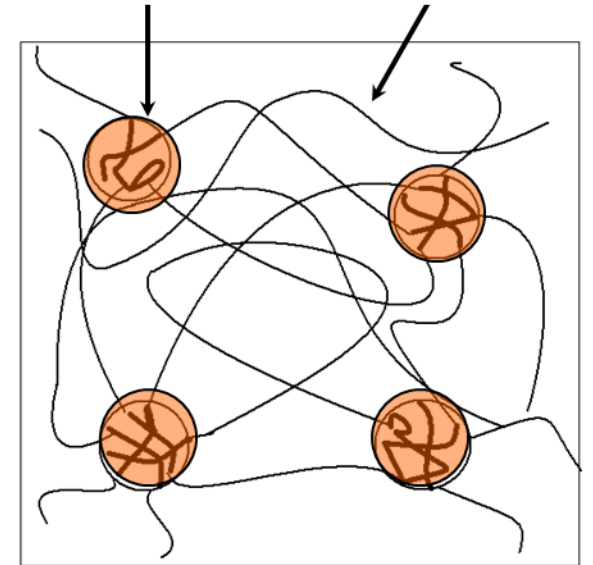
$n = 2$

S – E – x – E – S

tri – Block - Copolymers

und

Styrene domain Soft segments



Morphology (schematically)



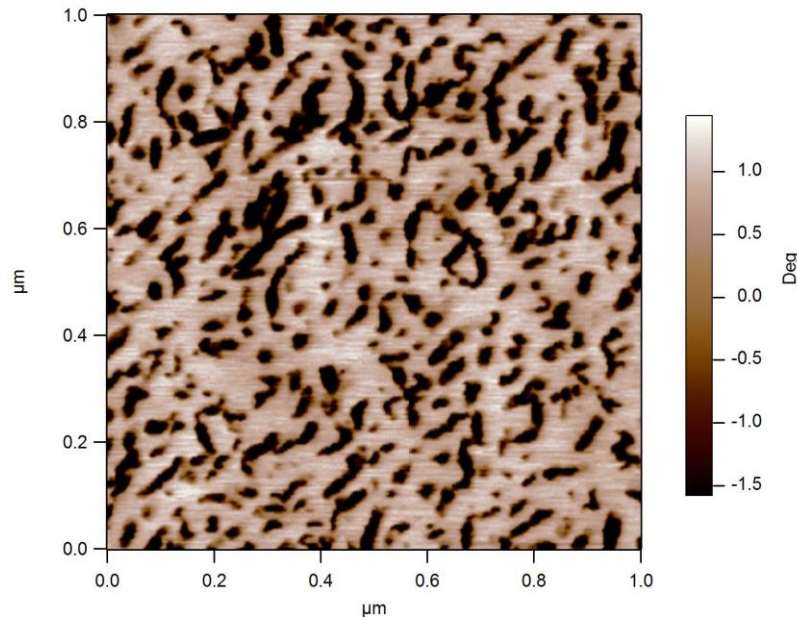
Different Types of Styrene – Tri – Block - Copolymers

Abbreviation	Soft segments	Relative stiffness	Stability
SBS	Butadiene	1	sufficient
SIS	Isoprene	0,5	sufficient
SEBS	Ethylene-Butylene	2	excellent
SEPS	Ethylene-Propylene	2	excellent
SiBS	Isobutylene	0,3	excellent



Morphology of plasticized SEBS

SEBS + plasticizer



AFM image: SEBS compound containing 100 phr plasticizer

Ref.: Barbe et al; Poly. Eng. Sci. 45 (2005) pp. 1498 – 1507

2 phase system

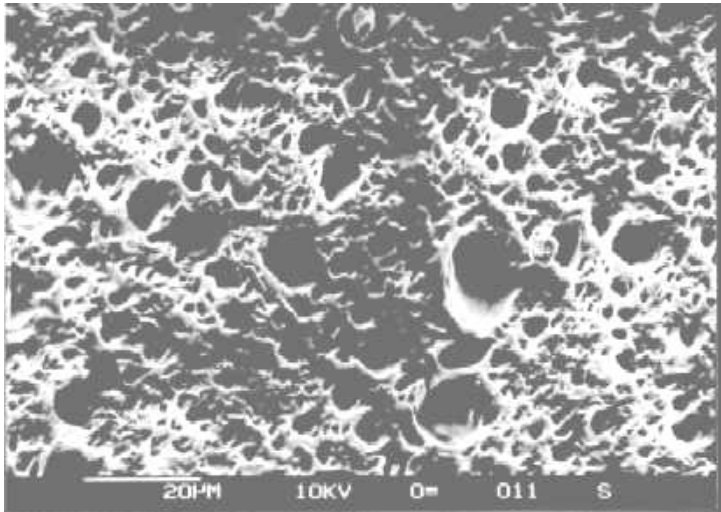
- PS - blocks form spherical domains dispersed in the soft phase
- PS – domains act as physical crosslinks and additionally as filler particles
- Plasticizer is mainly located in the soft phase



Morphology of plasticized SEBS/PP - blend:

Multi phase system

SEBS/PP (100/60) – blend + plasticizer



REM micrograph of co-continuous PP Phase, SEBS has been selectively dissolved and removed from the surface

- Commercial TPS usually contain an additional thermoplastic polymer (mostly PP)
- Thermoplastic polymer (PP) und Block Copolymer generate a 3-dimensional co-continuous phase morphology
- At least **4 phases**:
- Amorphous and crystalline phase of PP
- Amorphous hard phase and amorphous soft phase of SEBS

EXAMPLE OF TPS: THERMOLAST K®

Typical Properties

Property	
Shore Hardness	< 10 A to 70 D
Tensile Modulus / MPa	n.s.
Tensile strength / MPa	2 to 50
Ultimate elongation / %	300 to 800
Glass transition temp./ °C	-90 to -60 (soft phase) +80 to +100 (hard phase)
Melting temperature / °C	ca. 160 to 165 (PP - phase)

Application example:

Directly injected TPS sealing of a drilling machine



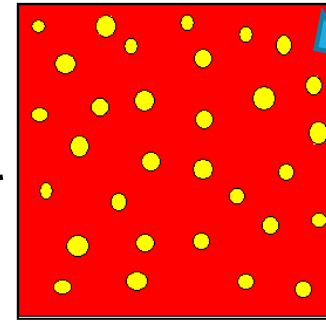
Foto: Kraiburg TPE



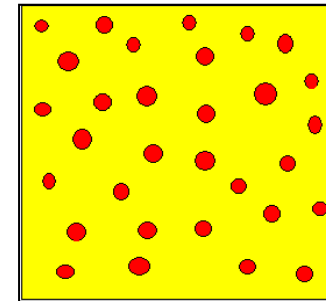
Simple Polymer Blends

Three possible phase morphologies:

1. Rubber phase dispersed in the thermoplastic hard phase (matrix)
2. Hard phase dispersed in the soft rubber phase
1. Co-continuous phase morphology of thermoplastic hard phase and rubbery soft phase



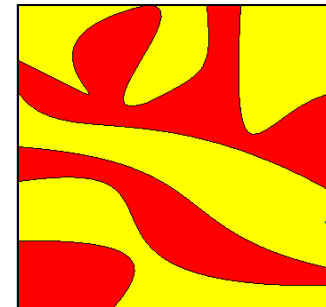
Impact modification of brittle thermoplastics (e.g. HIPS)



hard phase



soft phase



TPO - Thermoplastic Polyolefine Blends

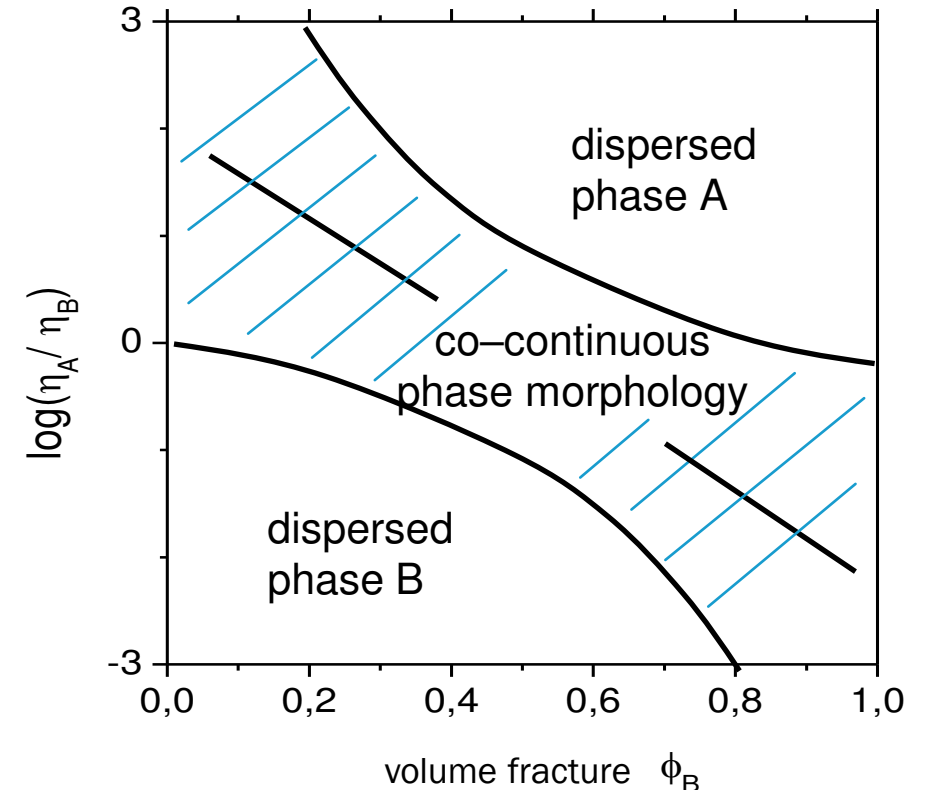


Simple Polymer Blends

Thermoplastic Elastomers based on simple blends exhibit co-continuous phase morphology

Two necessary conditions for the formation of a co-continuous phase morphology:

1. The viscosity ratio of the blend polymers have to be in a certain range
2. Thermodynamic conditions of (partial) miscibility have to be fulfilled



Reference: G.E. Holden; Thermoplastic Elastomers



Simple Blends based on Polyolefines (TPO-M) / Summary

- TPO-M made of PP+EPDM are widely used in many applications.

Advantages:

- Low density
- Hardness range Shore 65 A to 50 D
- Relatively low material costs

Disadvantages:

- At low hardness deterioration of mechanical properties
- Poor relaxation and creep behavior



TPO-M Application examples

- Bumper
- Instrument panel
- Airbag cover
- Interior panels
- Flooring
- etc.



Other Polymer Blends (Polymer Alloys) TPZ

NBR/PVC - Blends

- PVC hardphase; Nitrile rubber (NBR) soft phase
- Usually, high content of plasticizer and filler
- Typical composition
 - 100 parts PVC
 - 33 parts NBR
 - 75 parts plasticizer
 - 20 parts filler



Foot mats

Rear light housing



Other Blends

- Melt Processable Rubber (e.g. ALCRYN®)
- Polyurethane/PVC
- Polyester/PVC

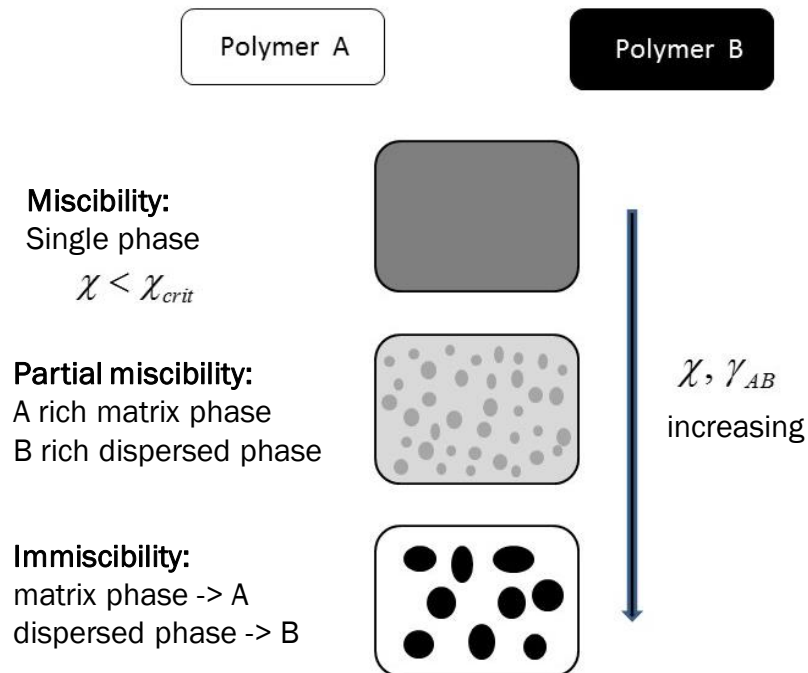


Keyboard

REACTIVE POLYMER BLENDS

Polymer blends

Simple blends:
Physical mixtures

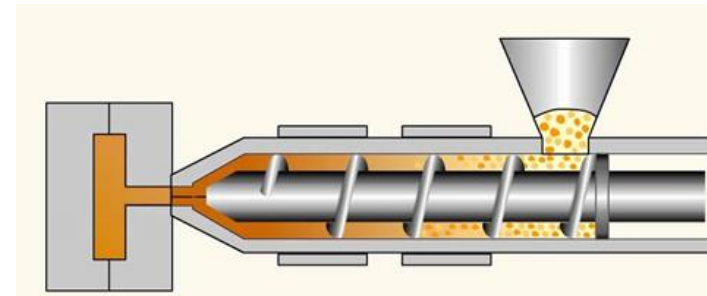


Reactive Blends

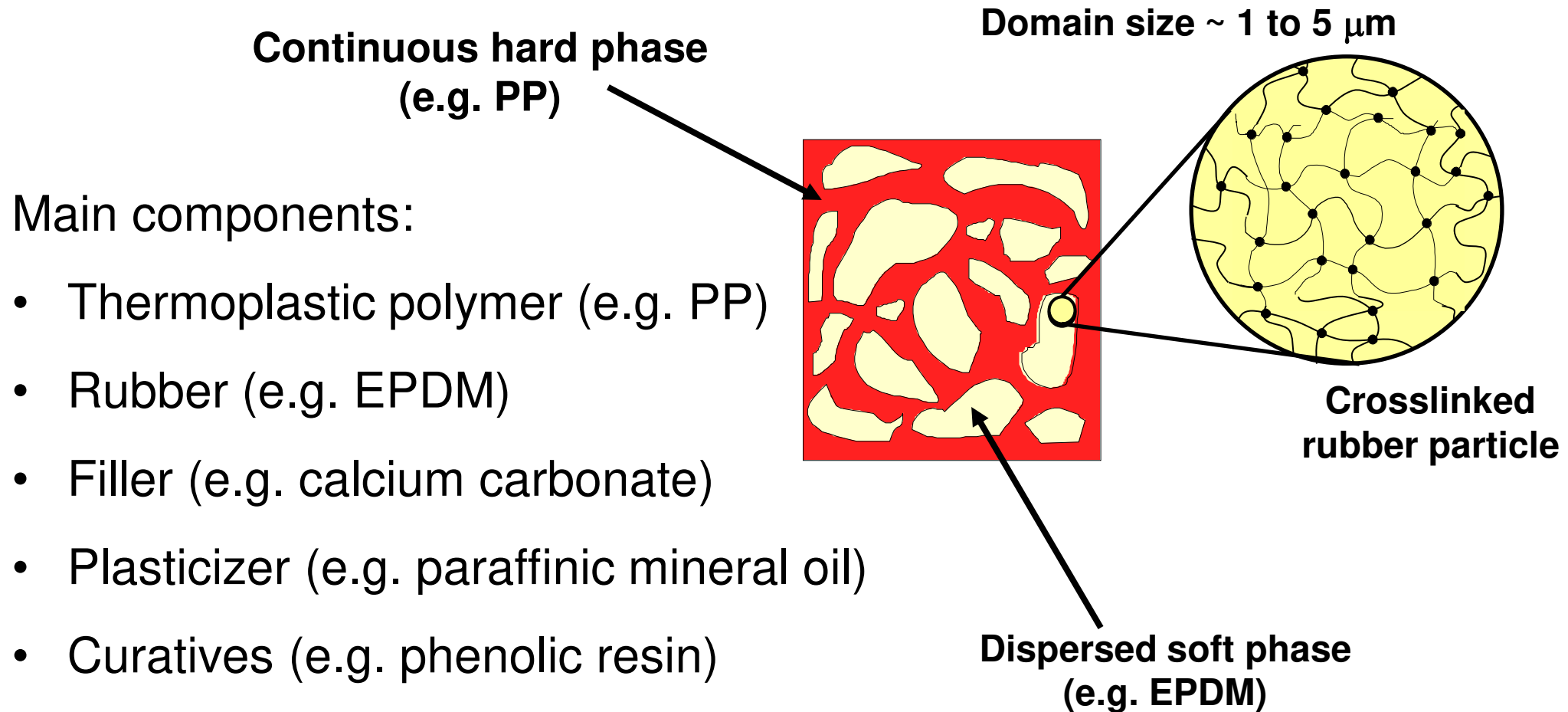
Chemical modifications during mixing process

e.g.

- Graft reactions
- Silanization
- **Dynamic Vulcanization**



COMPOSITION AND STRUCTURE OF TPV

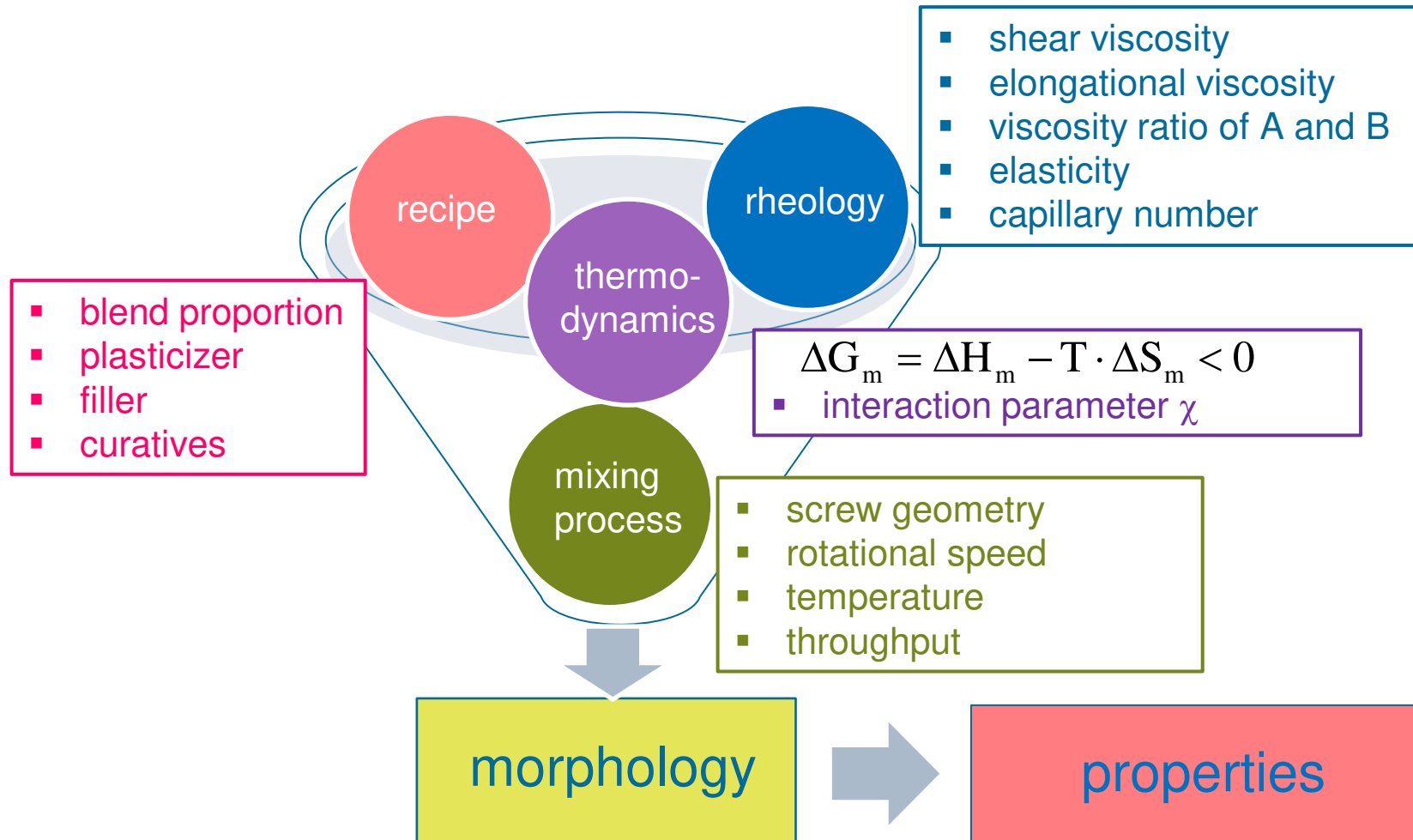


COMPOSITION AND STRUCTURE OF TPV

- TPV consist of thermoplastic polymer A and rubber B
- Partial miscibility of A and B is needed
- Micro phase seperation occurs during mixing
- Formation of hard and soft phase
- Thermoplastic matrix and finely dispersed rubber phase
- Formation of morphology occurs during mixing process
- Dynamic vulcanization
- Production of TPV by means of twin screw extruders or internal mixer



COMPOSITION AND STRUCTURE OF TPV



MAIN PARAMETERS OF INFLUENCE

- hardness
- stiffness
- tensile strength
- compression set
- etc.



POSSIBLE POLYMER – COMBINATIONS FOR TPV

- In principle many combinations are possible
- e.g. NR/HDPE; NBR/PVC; NBR/PP; ENR/PP, etc.
- But, only few combinations are useful and commercialized
- Most important are TPV based on EPDM/PP
- Introduction into market ~ 1980 by Monsanto under tradename Santoprene™
- Until now strong growth occurred and additional producers appeared on the market
- New developments of high oil and high temperature resistant TPV
- e.g. TPSiV™ => Silicon/TPU
- Zeotherm™ => ACM/PA6



THERMODYNAMIC CONDITIONS

Necessary condition for miscibility

$$\Delta G_m = \Delta H_m - T \cdot \Delta S_m < 0$$

Flory – Huggins - Equation

$$\Delta G_m = R \cdot T \left[\frac{\phi_1}{P_1} \cdot \ln \phi_1 + \frac{\phi_2}{P_2} \cdot \ln \phi_2 + \chi \cdot \phi_1 \cdot \phi_2 \right] < 0$$

Condition for **single phase** polymer blends

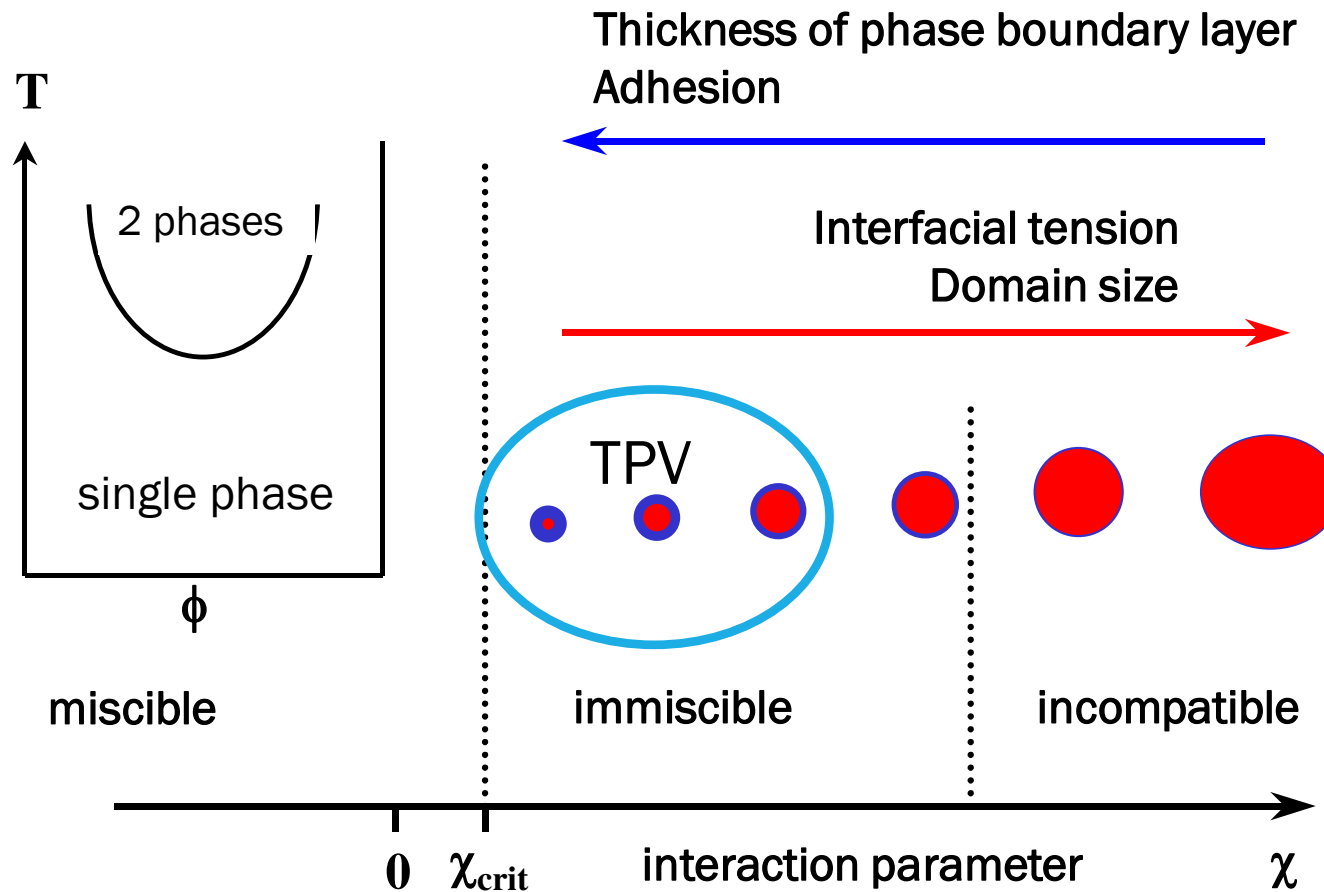
$$\chi < \chi_{\text{crit}}$$

But, for TPO and TPV a single phase mixture is not desired!

Aim: Co-continuously micro phase separated blend morphology.

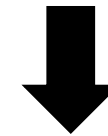


THERMODYNAMIC CONDITIONS



χ depends on solution parameters δ_1 and δ_2

$$\chi \sim (\delta_1 - \delta_2)^2$$

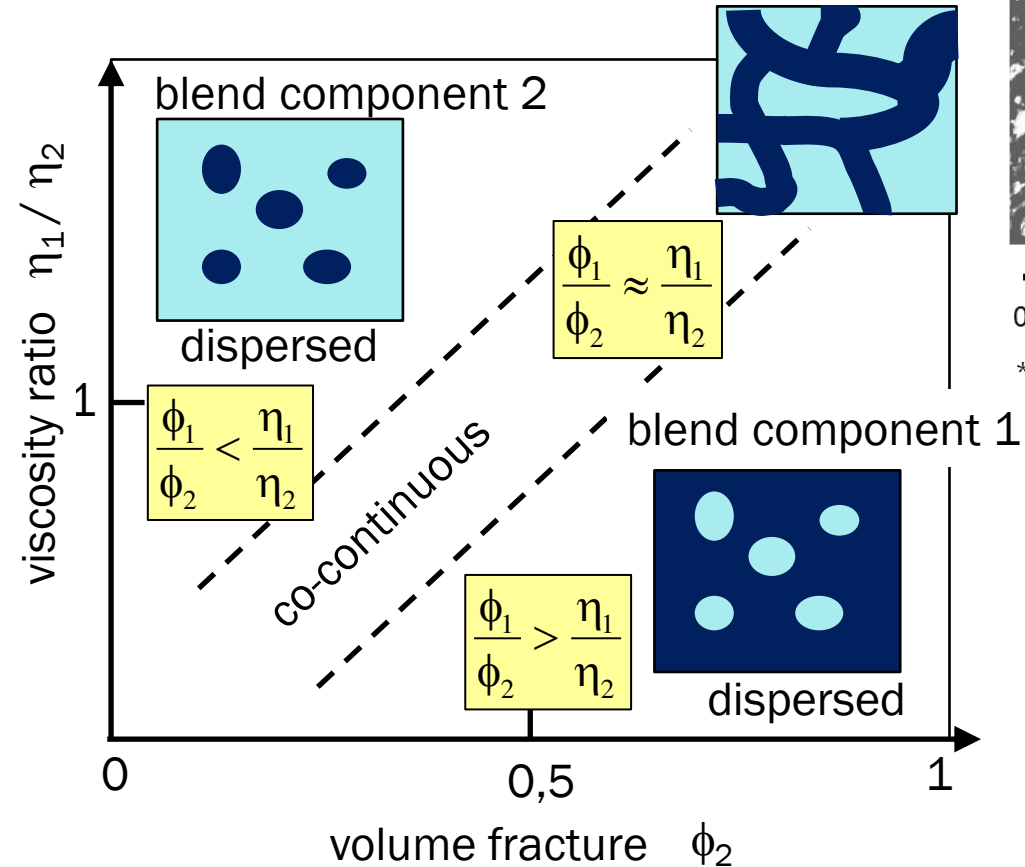


Domain size

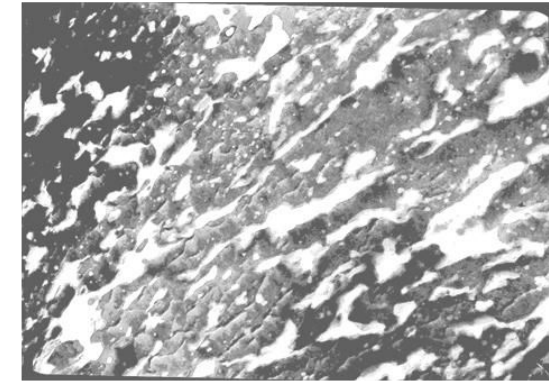


RHEOLOGICAL CONDITIONS

- co-continuous phase morphology exists only under certain conditions
- viscosity ratio and volume fracture are determining parameters



TPO

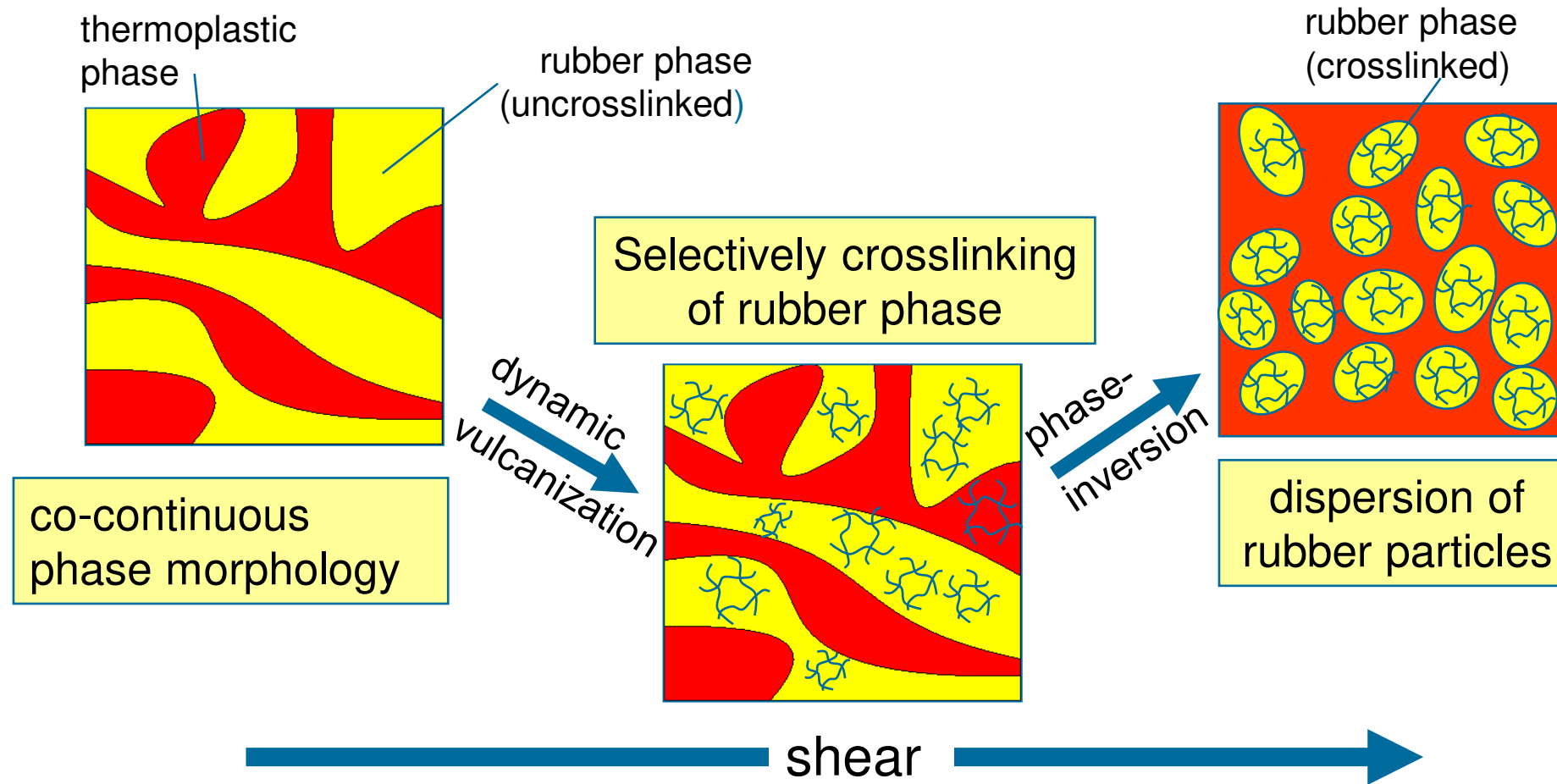


0.85 μm EPDM/PP *)

*) N.Vennemann et al., Macromol. Symp. 2006, 245-246, 641-650



Dynamic Vulcanization

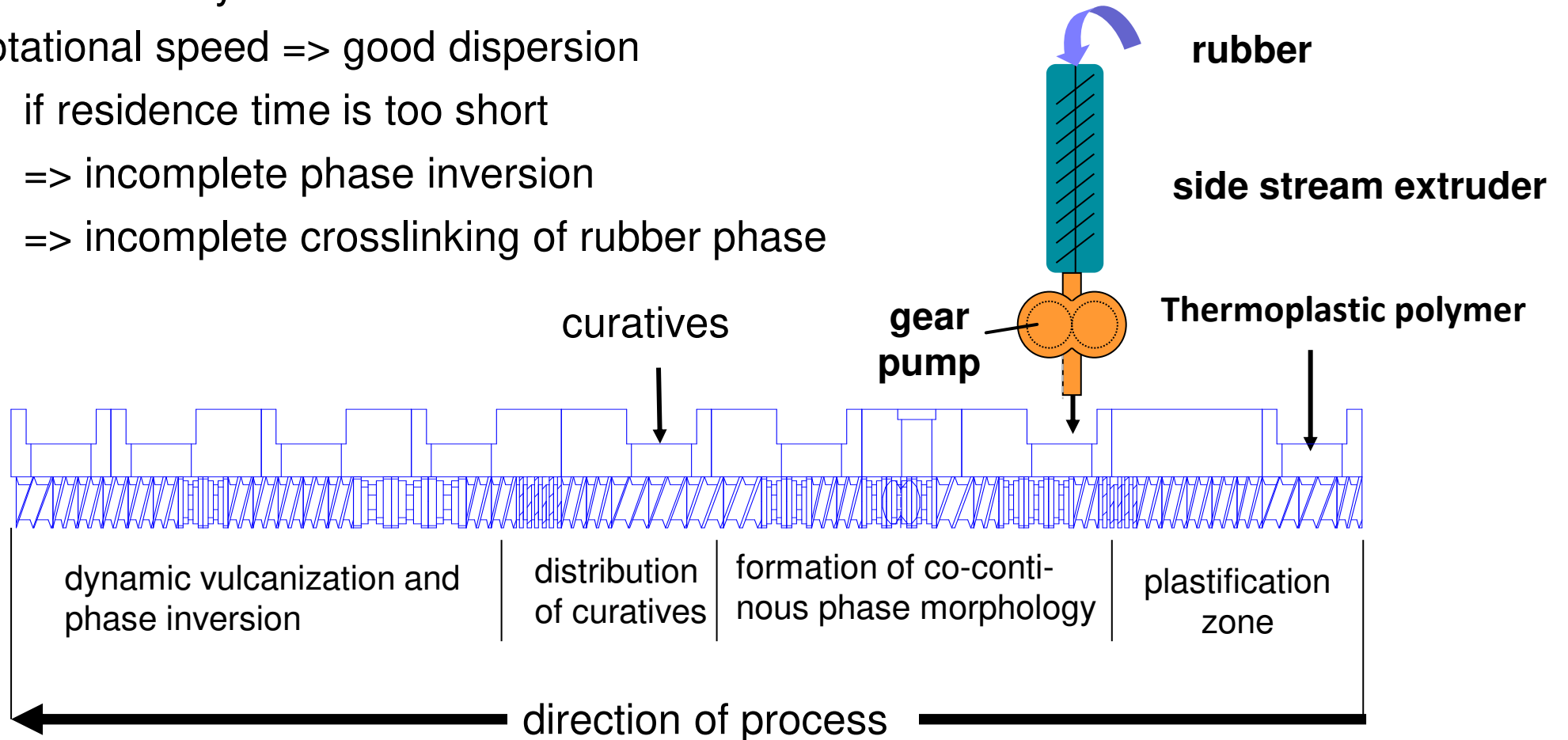


Production of TPV via twin screw extruder

$L/D > 54$ necessary / residence time $\sim 40 - 80$ s

High rotational speed $\Rightarrow$ good dispersion

But: if residence time is too short
 $\Rightarrow$ incomplete phase inversion
 $\Rightarrow$ incomplete crosslinking of rubber phase



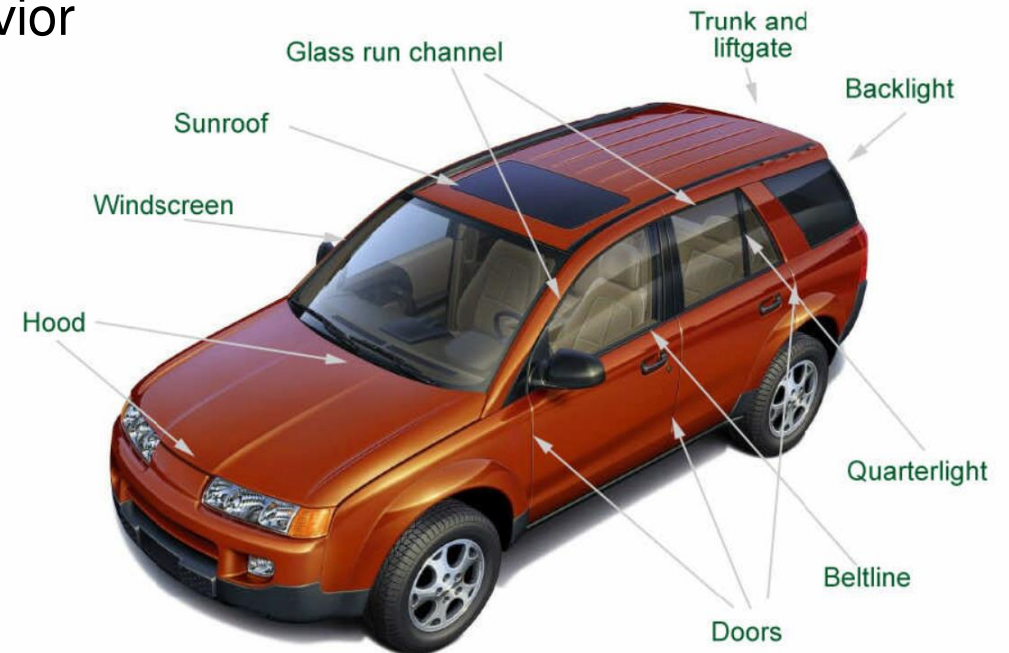
PROPERTIES AND APPLICATIONS OF TPV

Advantages in comparison to simple blends

- Good mechanical properties even at low hardness
- Improved relaxation and compression set behavior
- Improved oil resistance

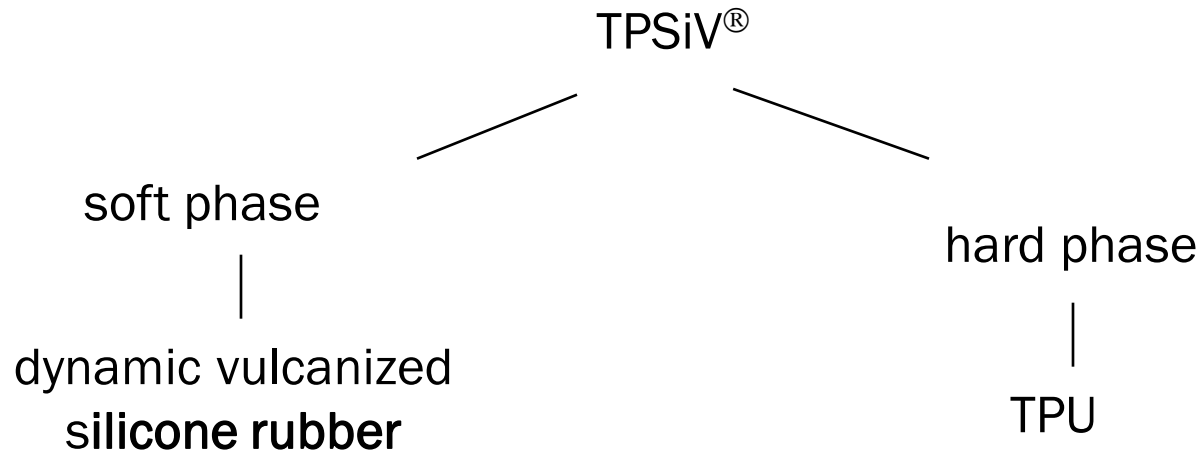
Disadvantages

- Complex production process
- Higher material costs



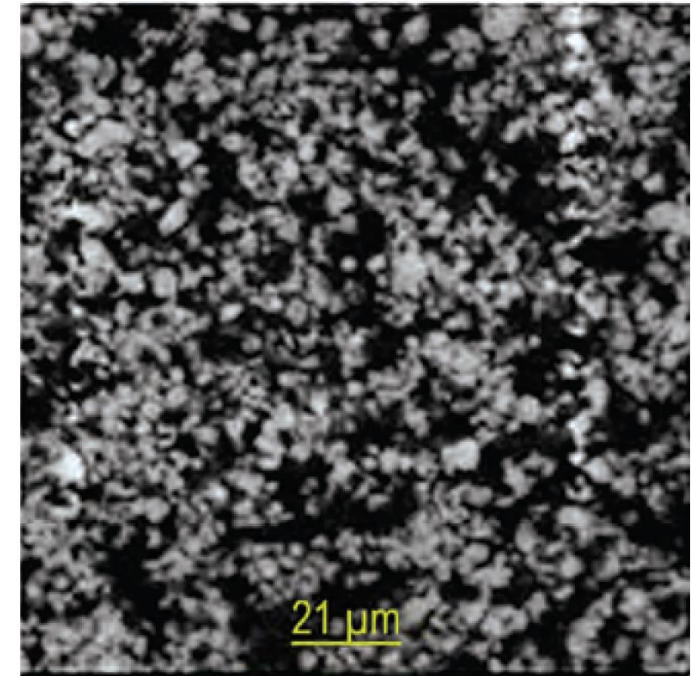
NEW DEVELOPMENTS: SUPER TPV

- TPSiV® / Dow Corning – Multibase



- Hardness range from 50 Shore A to 60 Shore D
- Usage temperature up to 150 °C
- Good oil resistance
- Silky touch

Morphology



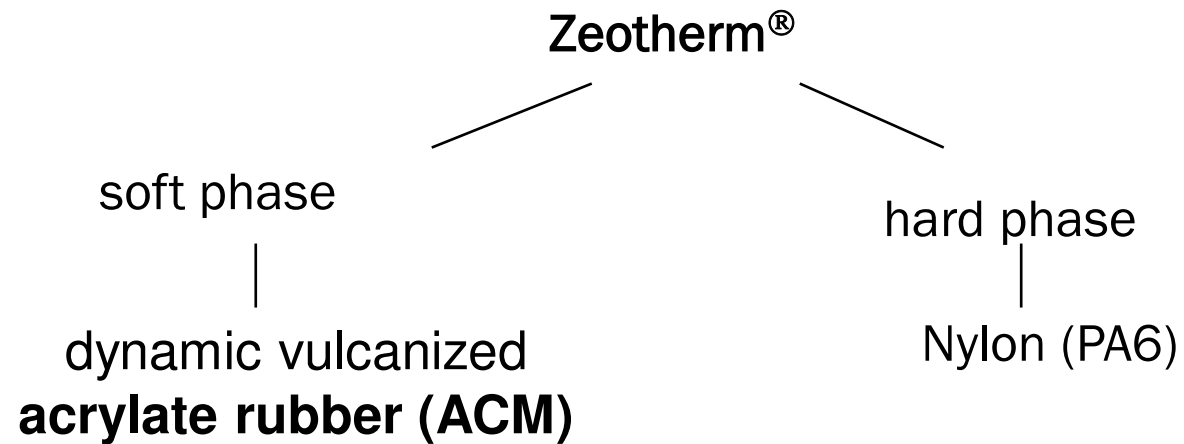
Dispersion of the silicone internal phase in TPSiV® (TEM micrograph)

Source: Dow Corning 2015



NEW DEVELOPMENTS: SUPER TPV

Zeotherm® / Zeon Chemicals



- Usage temperature 150 °C – 175 °C
- Good oil resistance
- Good adhesion to Nylon

Application example:
Axle boots

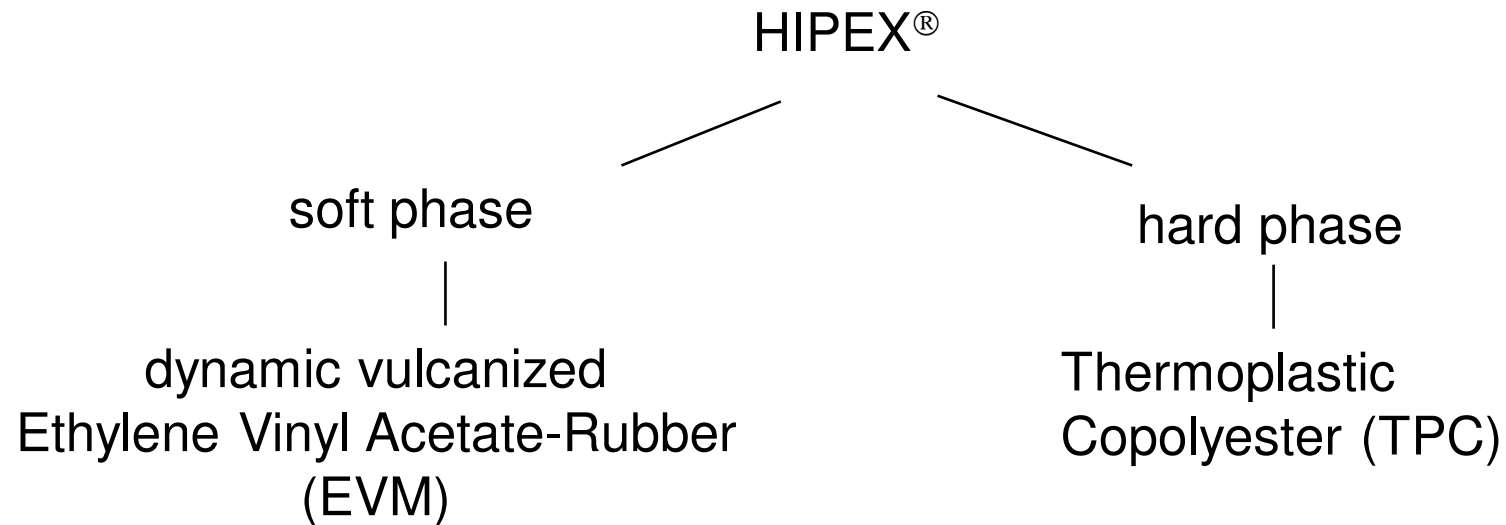


J. Dykerhoff, KGK 10/2006, S. 504



NEW DEVELOPMENTS: SUPER TPV

HIPEX® / Kraiburg TPE



- Usage temperature up to 150 °C
- Good oil resistance
- Low density

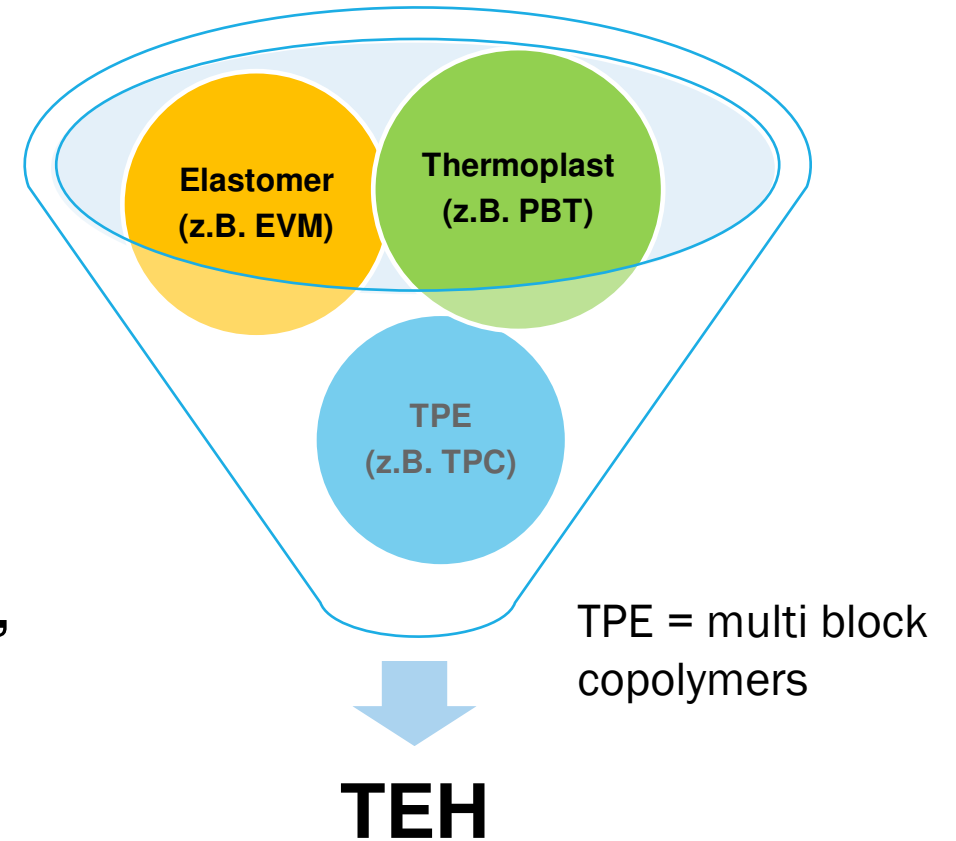
Application example:
Cylinder cover gasket



Foto: Kraiburg TPE GmbH

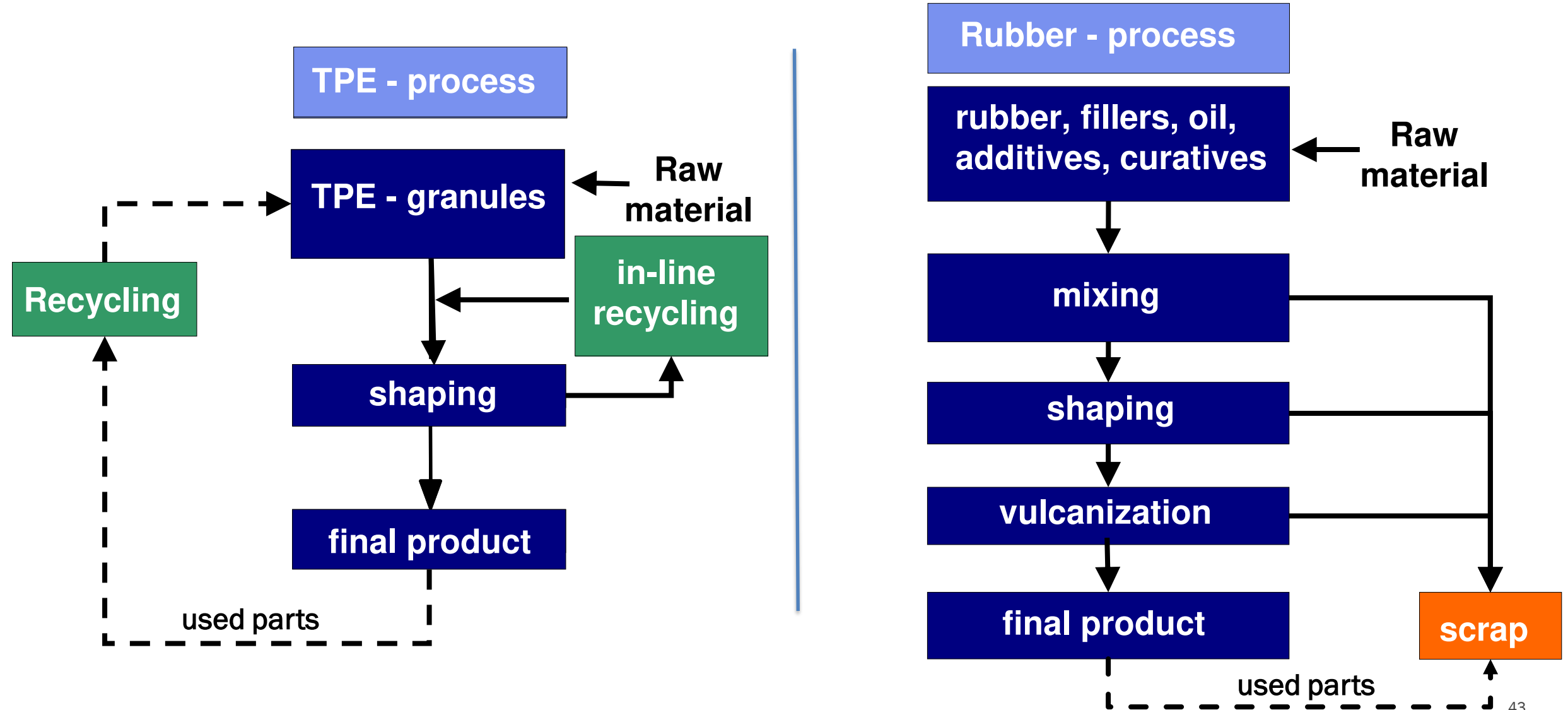
VERY NEW: THERMOPLASTIC ELASTOMER HYBRIDE TEH^{*)}

- Further development of **HIPEX**[®] from Kraiburg TPE
- Extended raw materials selection
- Patented method for production of soft TPE without deterioration of mechanical properties
- TPV are based on a binary combination of **two** polymers (Thermoplastic and Rubber)
- TEH consist of at least **three** different polymers (**TP, TPE, EL**)
- Material properties very close to elastomers



^{*)} Reference: F. Vielsack and D. Butschkau; Kunststoffe 1/2019, S. 71 - 73

Processing of TPE in comparison to rubber



Processing (general aspects)

TPE

- Ready to use
- Thermoplastic processibility
 - ✓ Injection moulding
 - ✓ Extrusion
 - ✓ Blow moulding
 - ✓ 2C (hard/soft)
- Short production cycles
- Re-use of scrap is possible
- Recycling of used parts

Conventional Elastomers (rubber)

- Mixing of raw materials
- Rubber processing methods
 - CM, TM, IM
 - Extrusion of semifinished parts
 - Vulcanization is required
 - 2C parts difficult to produce
- Long production cycles
- Scrap cannot be re-used
- Recycling of used parts is impossible



Material properties (general aspects)

TPE

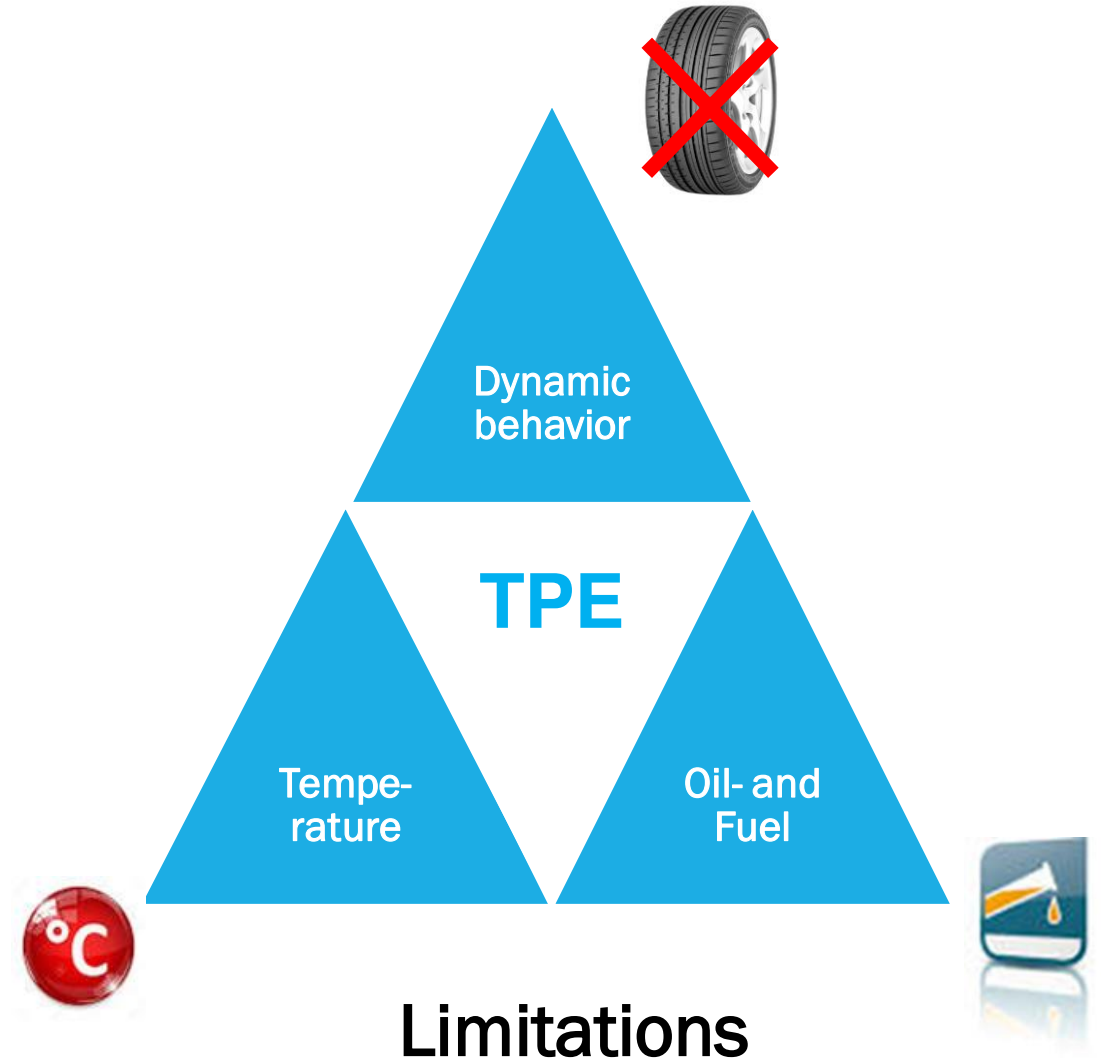
- Less rubber elasticity
- Higher irreversible deformation after cyclic loading
- High compression set at elevated temperature
- Poor long term creep behavior
- Stronger limitations with respect to upper service temperature
- Overheating very critical (even short term)
- Higher material costs

Conventional Elastomers (rubber)

- Excellent rubber elasticity
- Very good reversibility of deformation
- Low compression set at elevated temperature is possible
- Excellent creep behaviour
- Less temperature limitations with use of suitable polymers
- Short term overheating not critical

Concluding remarks

- Thermoplastic Elastomers are a novel and interesting class of polymer materials
- Those may be used to replace conventional vulcanized rubber, but ...
- ... also open new fields of applications
- TPE offer a lot of opportunities, but limitations should be considered

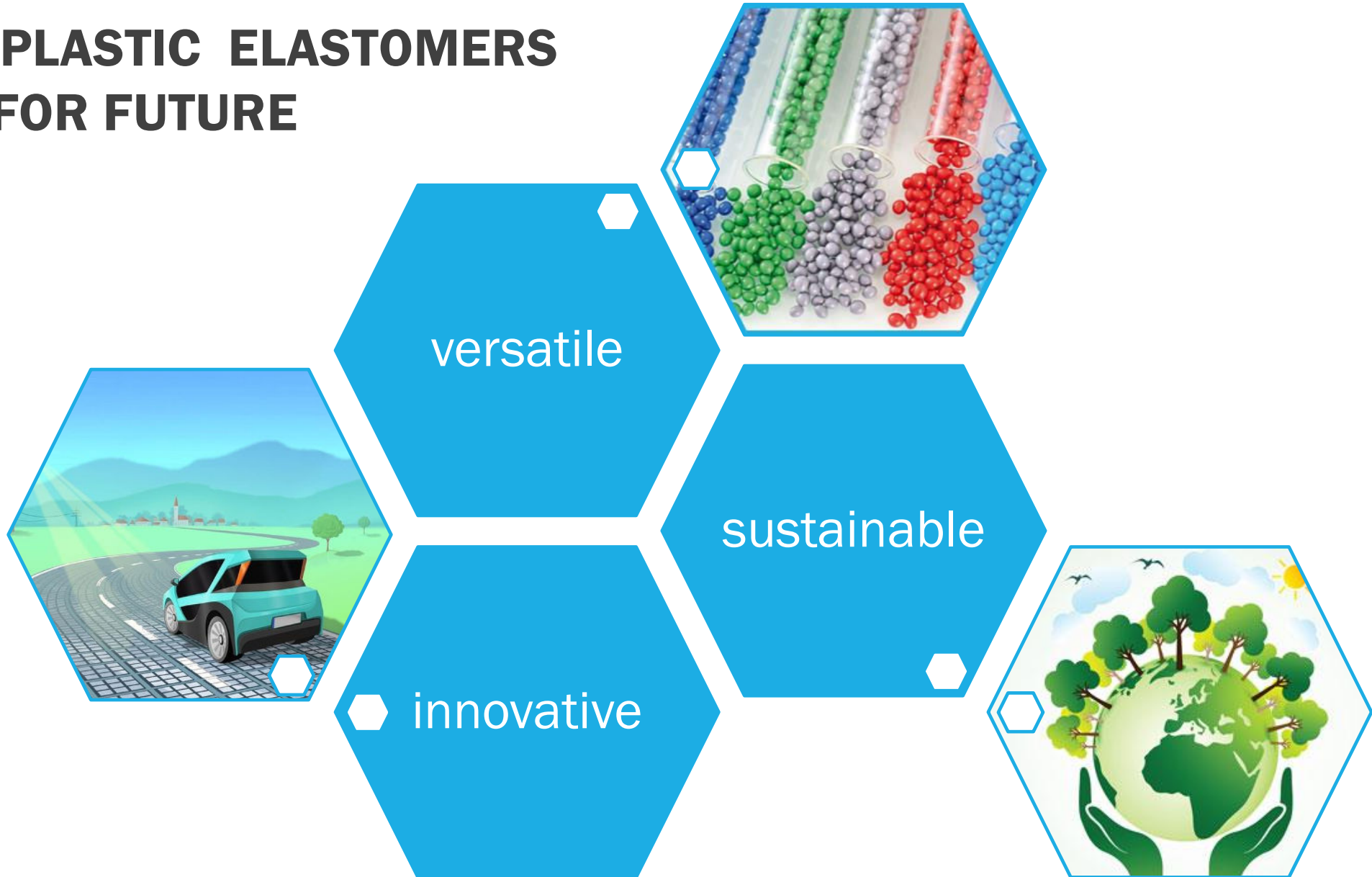


OUTLOOK

- New technologies pose new challenges for TPE
- Most important requirements result from
 - E-mobility
 - Hydrogen and fuel cell technology
 - Alternative synthetic fuels
 - Autonomous driving technology
 - Novel processing methods, e.g. additive manufacturing
 - Sustainability and circular economy

Demand of further development of TPE results from future technologies

THERMOPLASTIC ELASTOMERS ARE FIT FOR FUTURE





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UNIVERSITY OF APPLIED SCIENCES



Thank you very much for your kind attention