

**DKT 2012**

**TPE Forum**



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**TPE versus Gummi:  
Freundlicher oder feindlicher Wettbewerb?**

**TPE versus Rubber:  
Friendly or unfriendly competition?**

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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**
- ➔ **TPE Versus Rubber**
  - **Compounds / Compounding**
  - **Forming**
  - **Property Description**
- ➔ **Summary**

# History of TPV

## Patent History

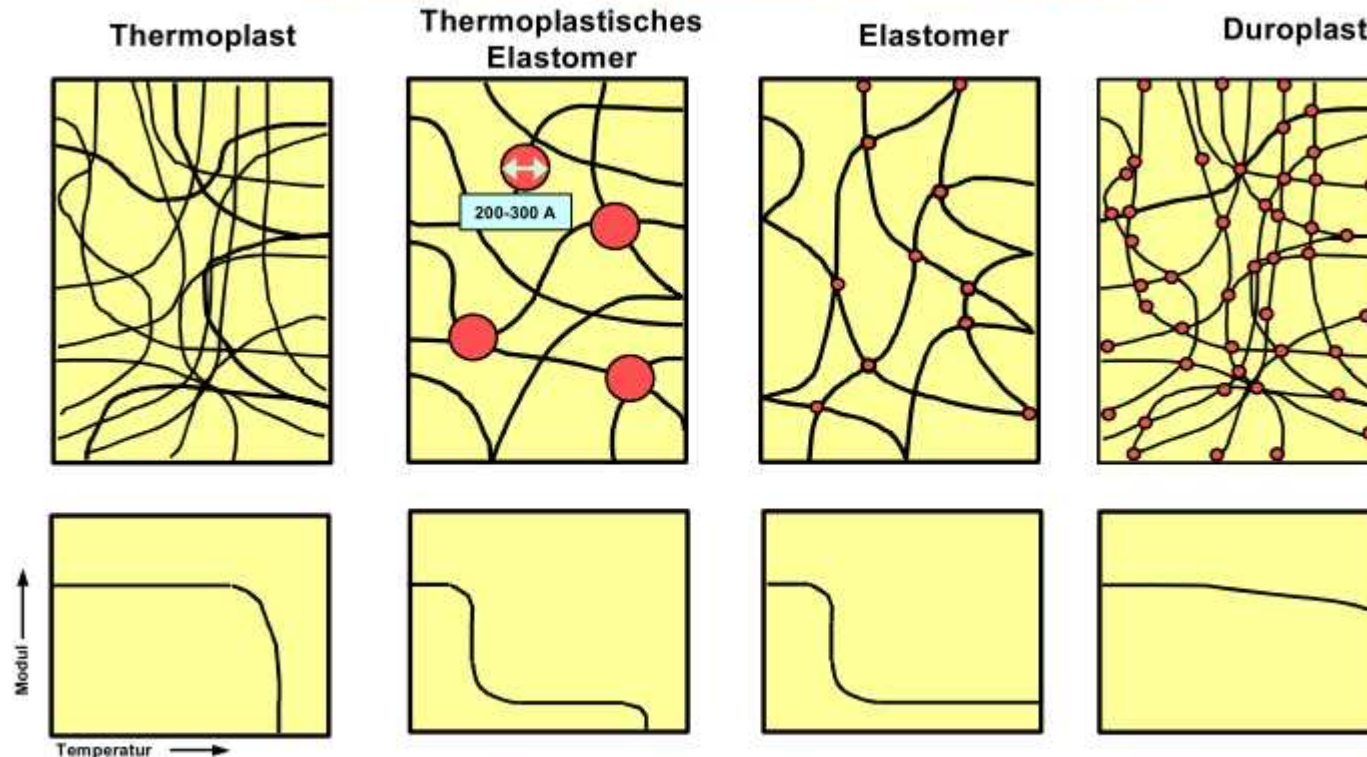


- ➔ **US 4,594,390 A is the Patent Base of Monsanto / AES on TPV**
- ➔ **Title: Process for the preparation of thermoplastic elastomers**
  - **Published 02.05.84**
- ➔ **US 4,803,244 Union Carbide on Silane crosslinked TPV**
  - **Published Nov. 16, 1987**
  - **Since then, the price has moved slightly downward, because of Korean Competitors, but not much.**
  - **But a lot of compounders are established today**
  - **Example: Allod – based on SEBS.**

# Uniqueness of TPE

Source: E. Osen, KHK 04

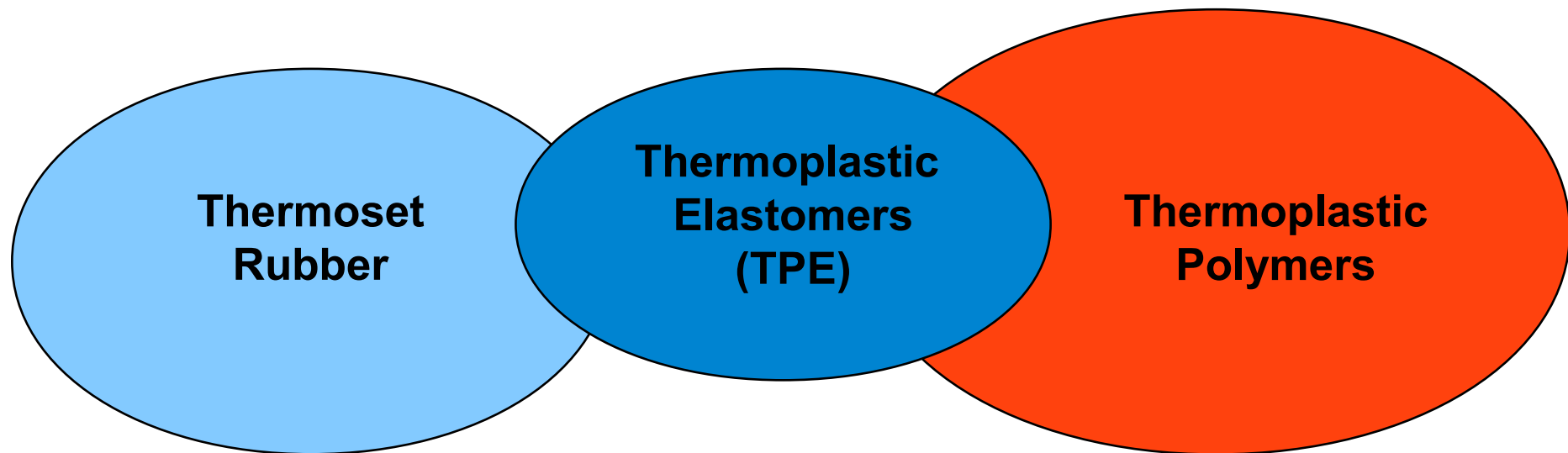
## Structure of TPE



Die Vernetzung makromolekularer Werkstoffe bestimmt u. a. den Modulverlauf.  
Thermoplastische Elastomere haben vernetzte Domänen.

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

# Uniqueness of TPE



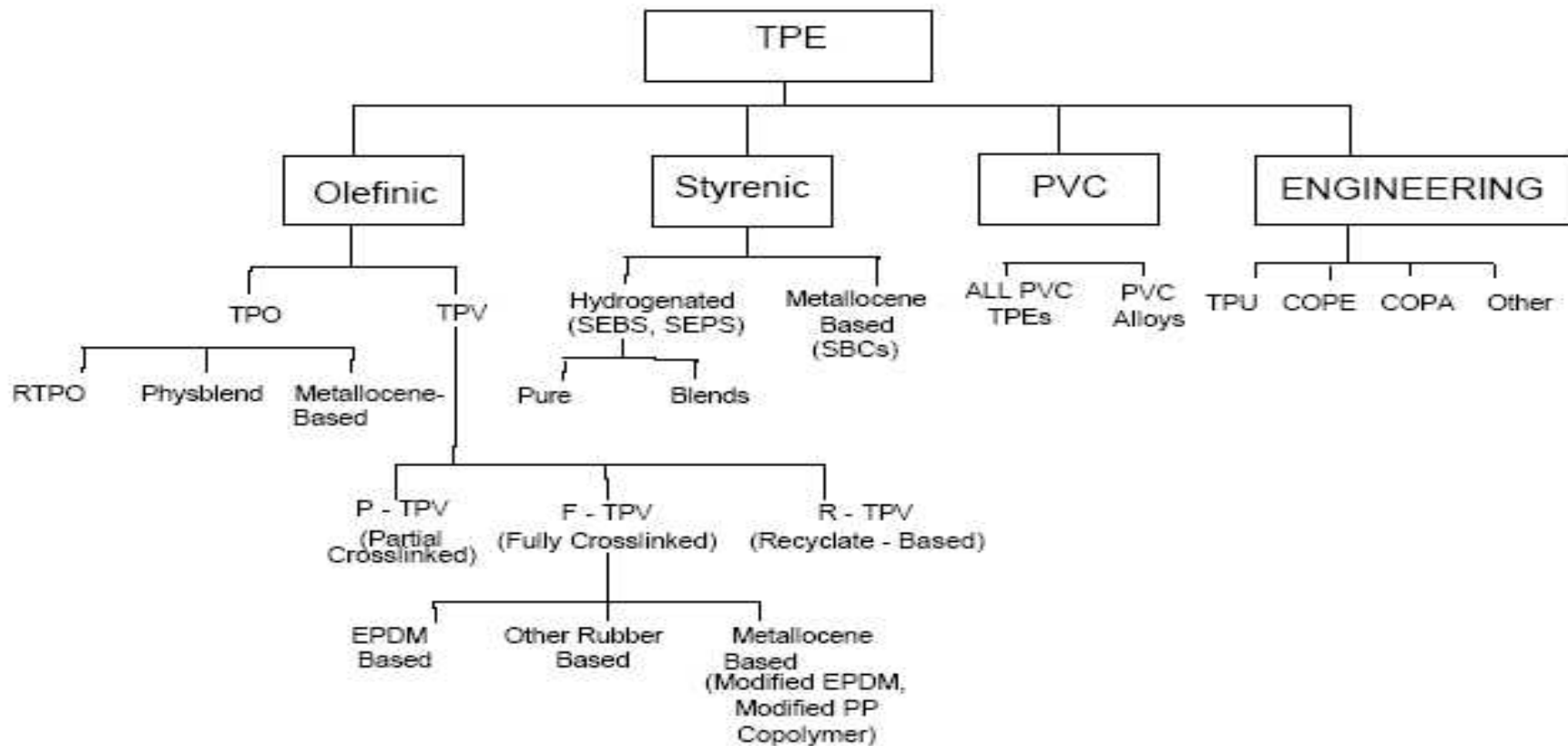
**Between Rubber and Thermoplastic:  
TPE is a “Dual Phase” material, which contains a  
thermoplastic continuous phase surrounding rubber droplets**

# Uniqueness of TPE

## TPE Family Tree

Source: R. Eller, TX, Feb. 2000

### TPE Families



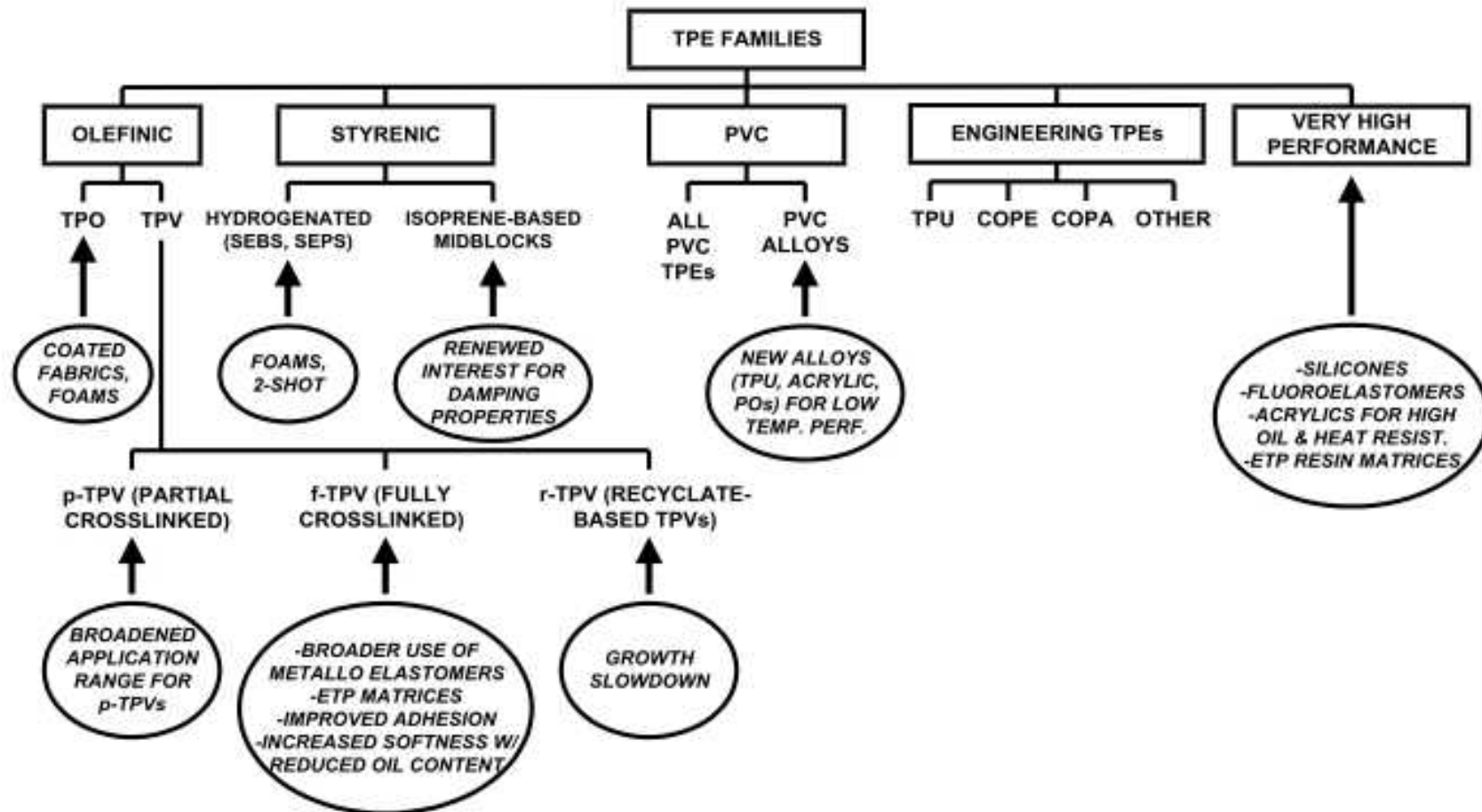
From: Rober Eller, "SPE Polyolefins 2000", Houston, TX, Feb 2000.

# Uniqueness of TPE

## TPE Family Tree

Source: R. Eller, TX, Feb. 2000

GROWTH AND VALUE OPPORTUNITIES IN THE TPE FAMILIES



SOURCE: ROBERT ELLER ASSOCIATES, INC., 2004

re/mydox/papers/tpebangkok-growth oppys tpe 04.vsd  
lg/myfiles/visio/tpebangkok-growth oppys tpe 04.vsd

# Uniqueness of TPE

## Basic Properties of TPE



Source: Franck/Biederbick,  
Kunststoff-Kompendium 88



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

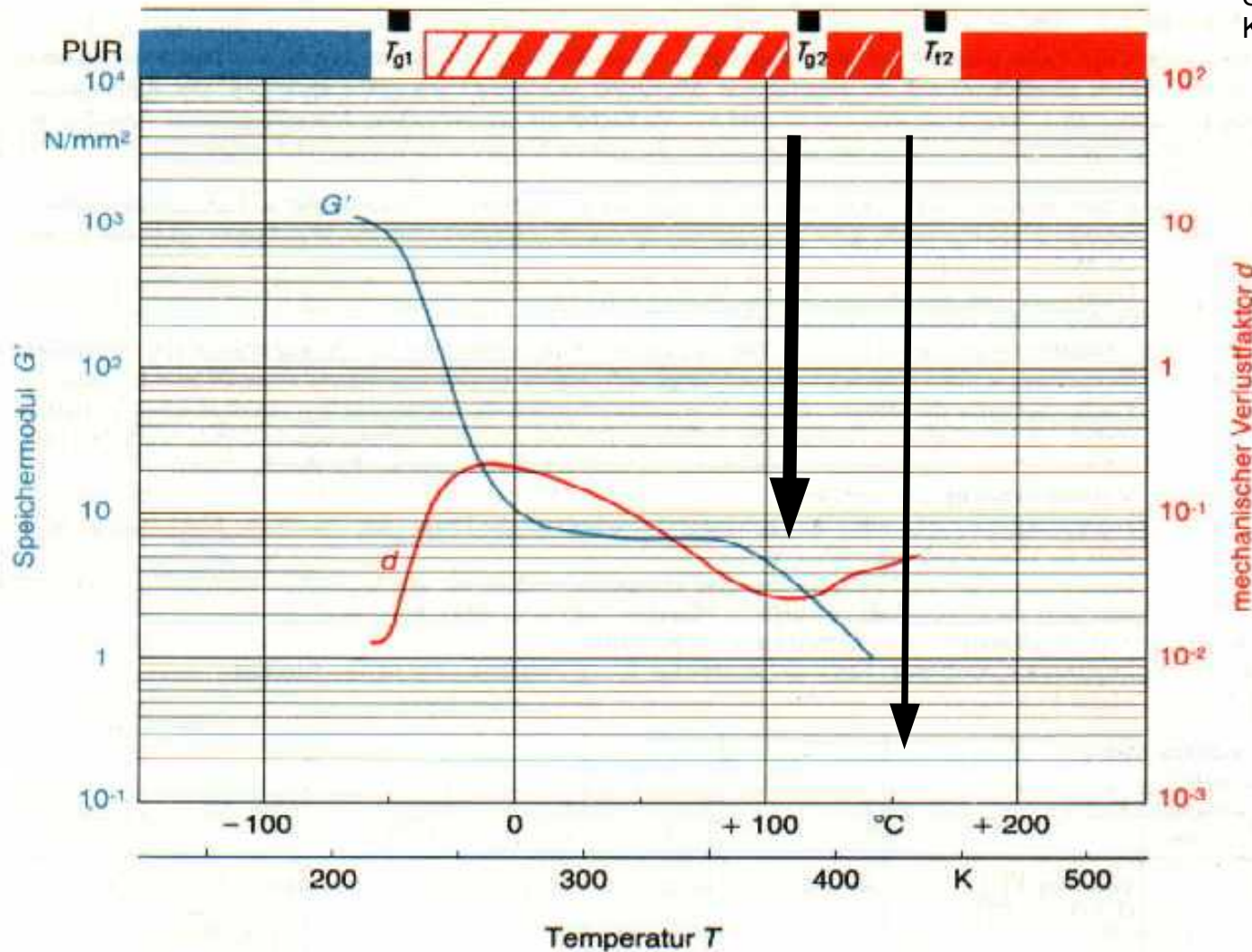


# Uniqueness of TPE

## Basic Properties of TPE

Source: Franck/Biederbick, Kunststoff-Kompodium 88

Storage Modulus  $G'$



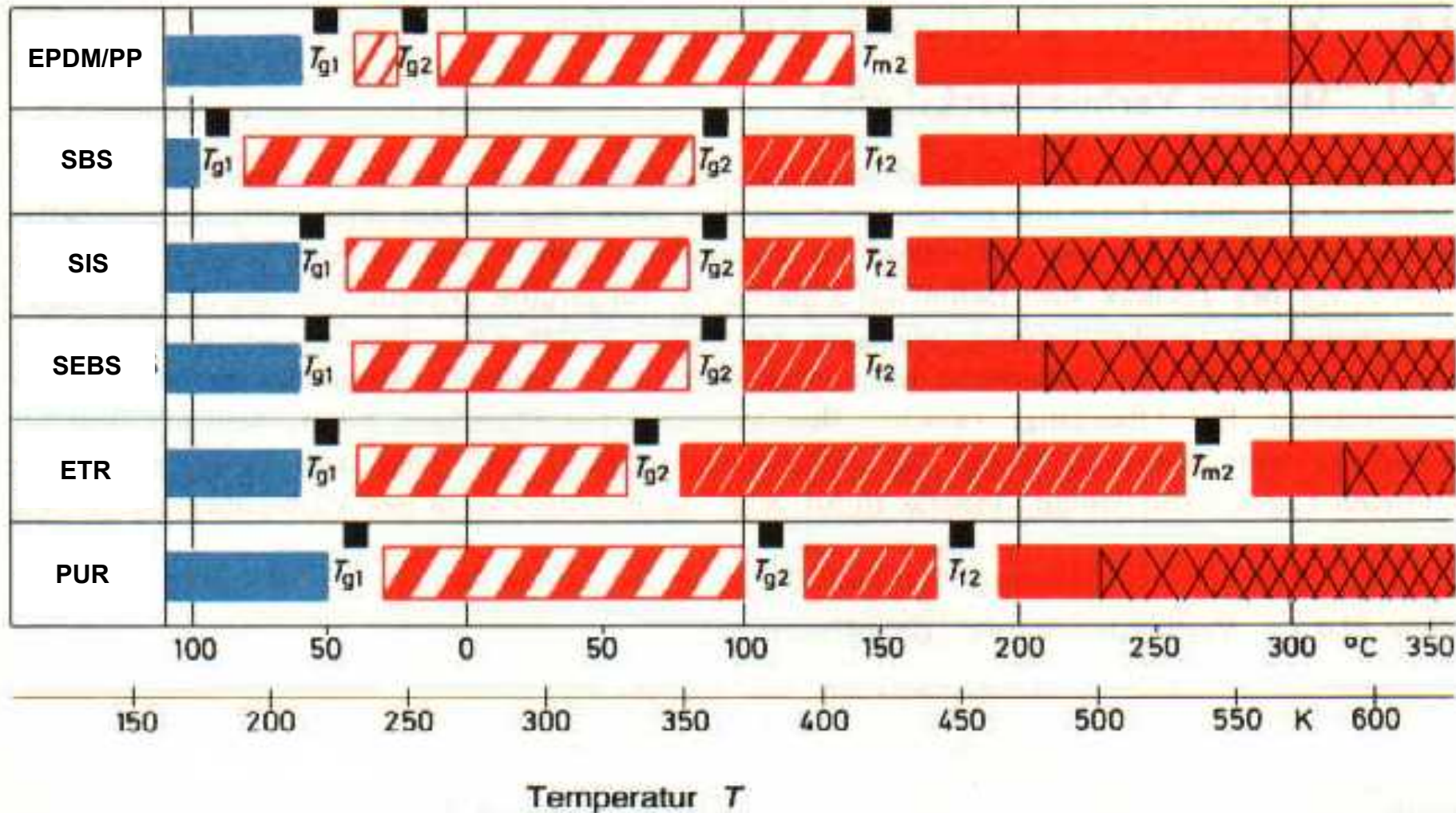
Mechanical loss Modulus  $d$

# Uniqueness of TPE

## Basic Properties of TPE



Source: Franck/Biederbick, Kunststoff-Kompodium 88



# Uniqueness of TPE

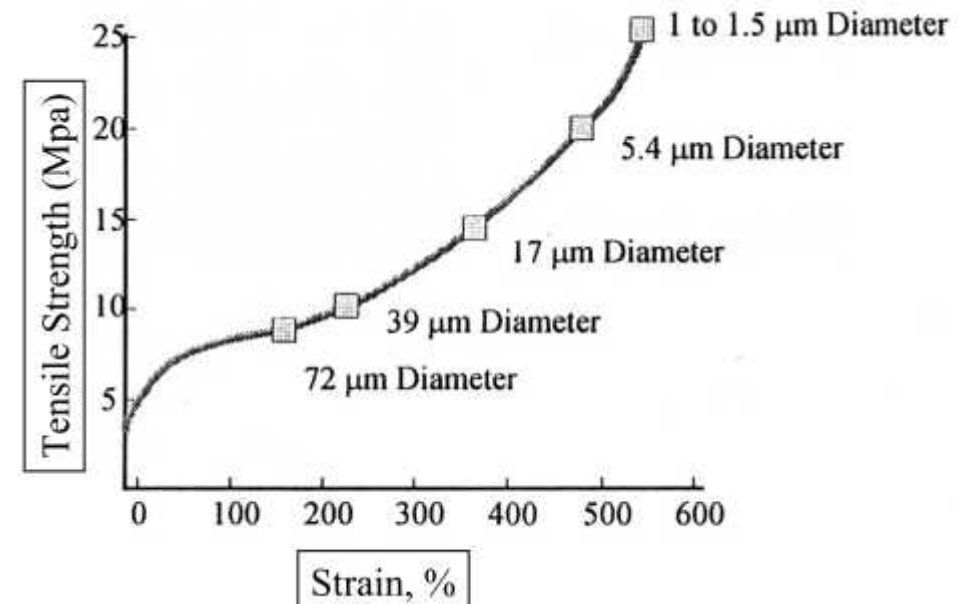
## Morphology - Property Dependency

Source: K. Walton, RCT 77

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



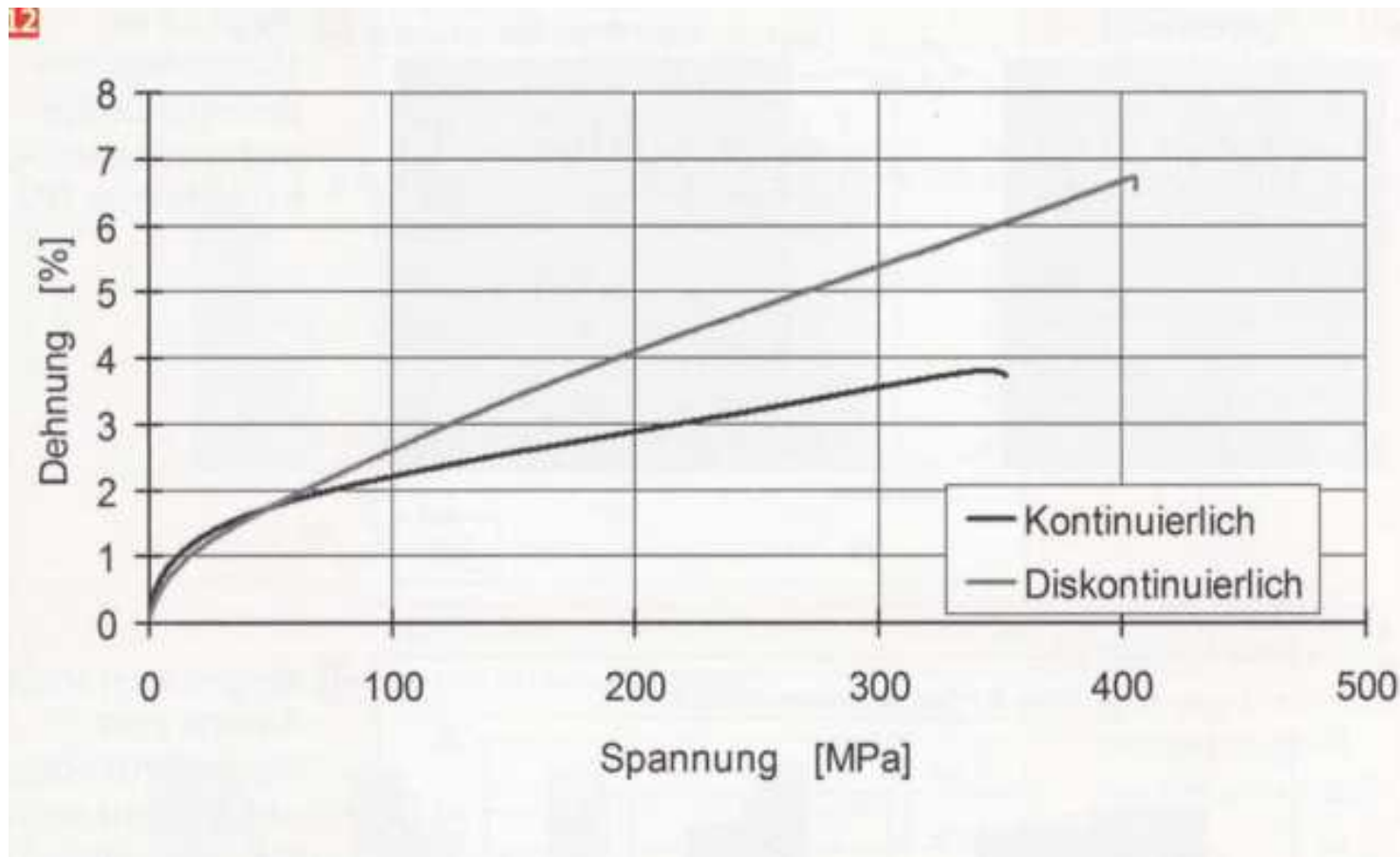
- Transmission electron microscopy (TEM) of PP/EPDM TPV. Dark areas are crosslinked rubber particles.



# Uniqueness of TPE

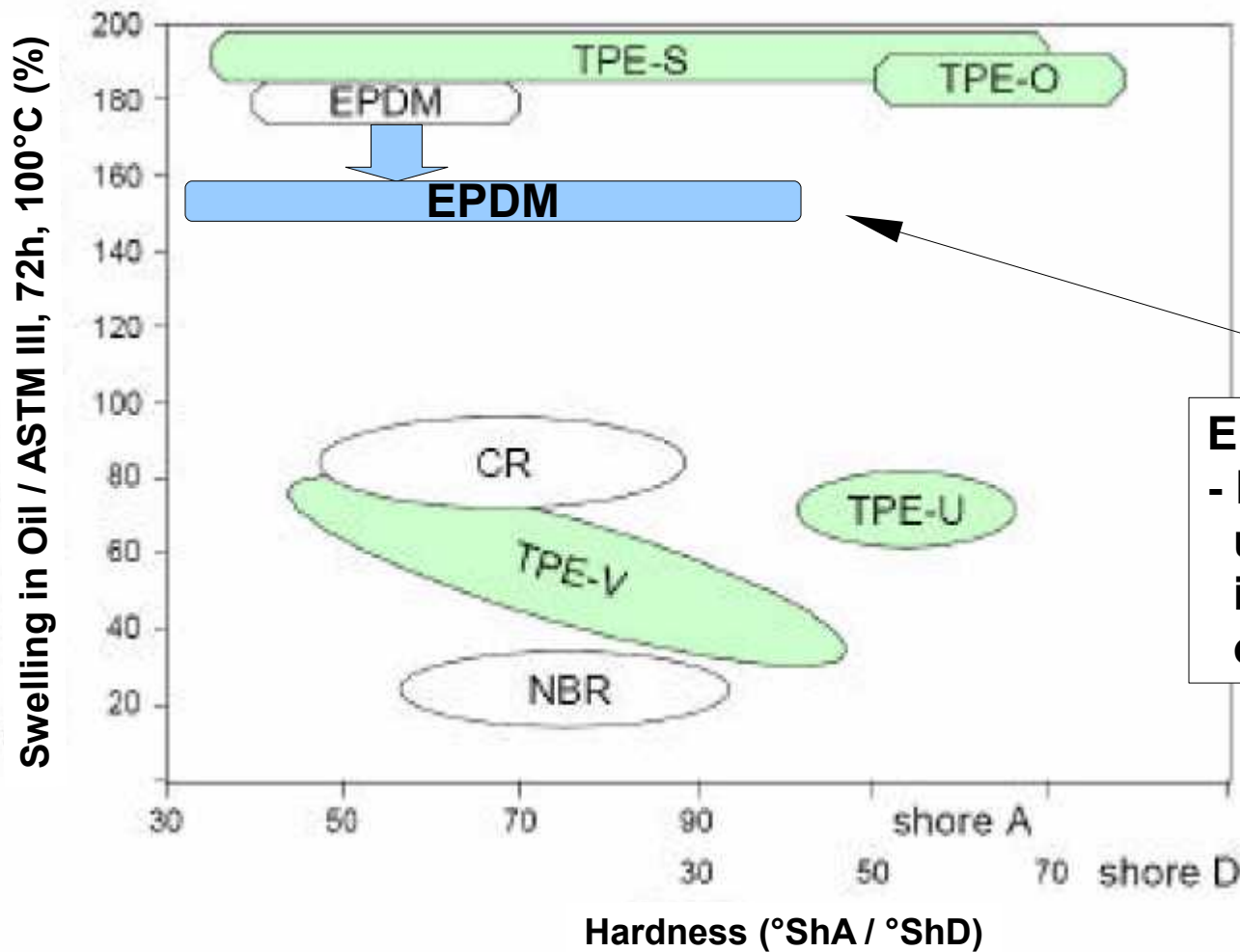
## Morphology - Property Dependency

Source: W. Michaeli et.al.  
KHK Sept. 2011



# Positioning of TPE Property Map

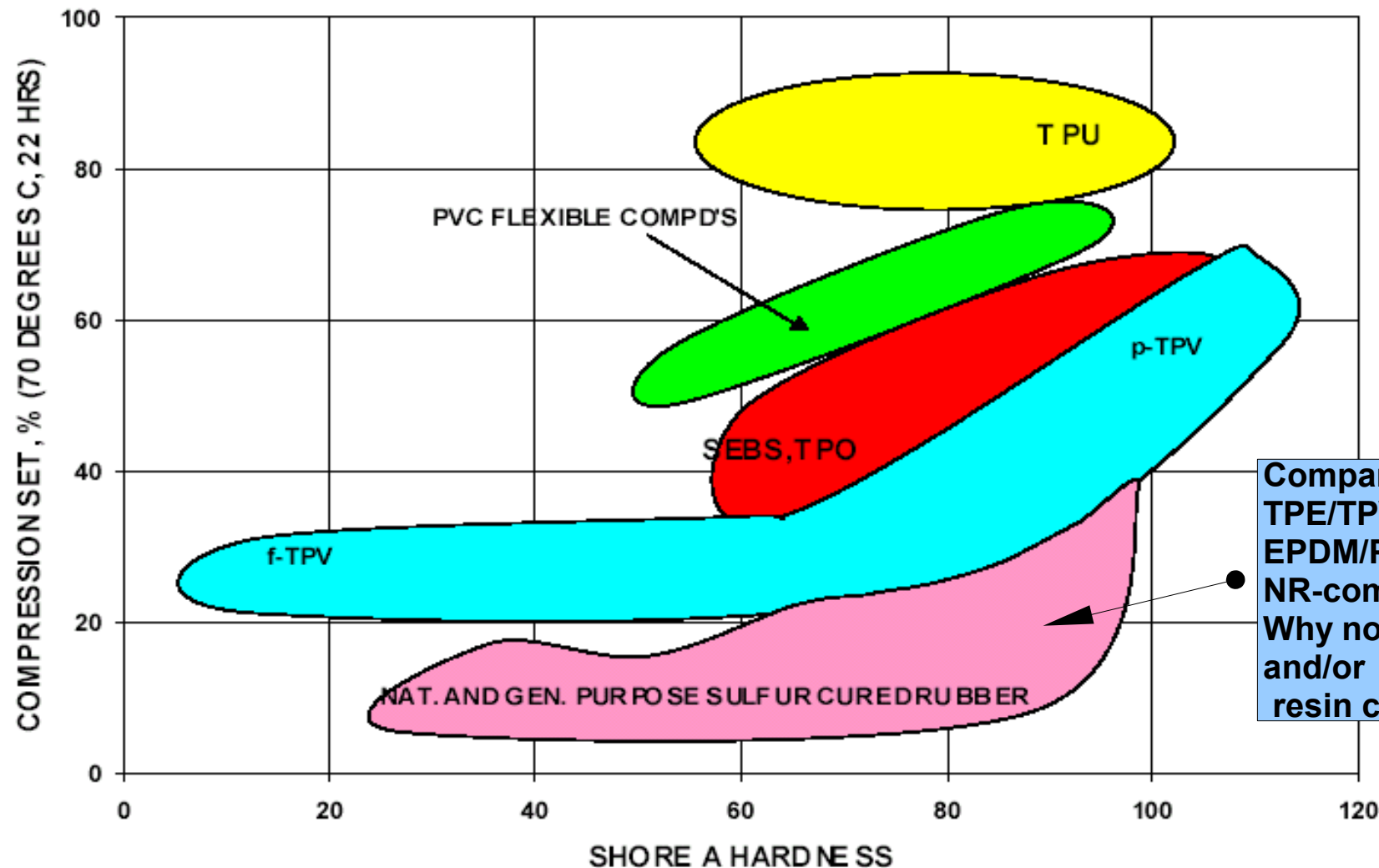
Source:Wittig, GAK 1997



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

# Positioning of TPE Property Map

Source: R. Eller, W. Klingensmith  
IISRP Annual Meeting 2001

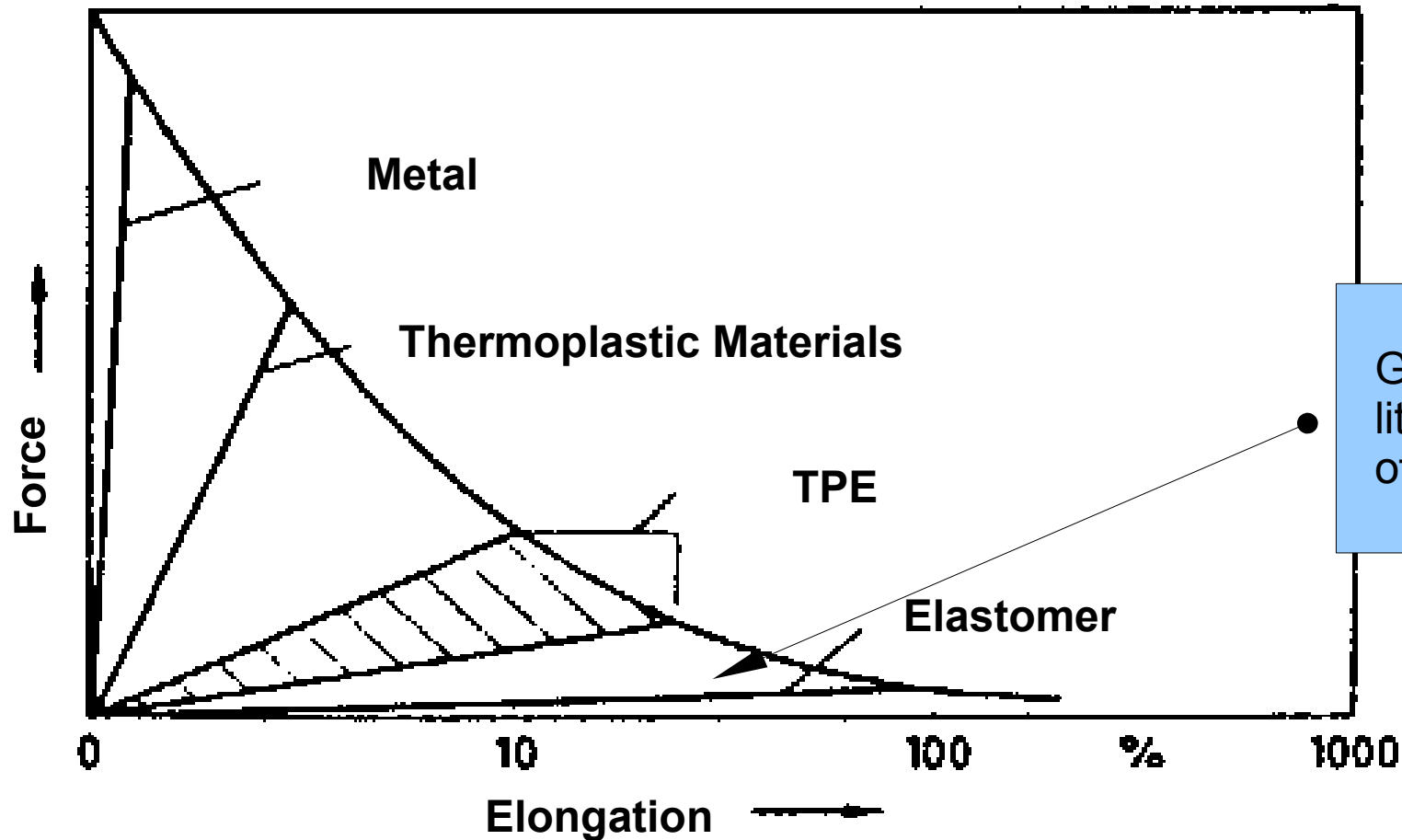


# Positioning of TPE

## Stress relaxation behaviour



Source: H. Dominghaus  
Plastverarbeiter 89



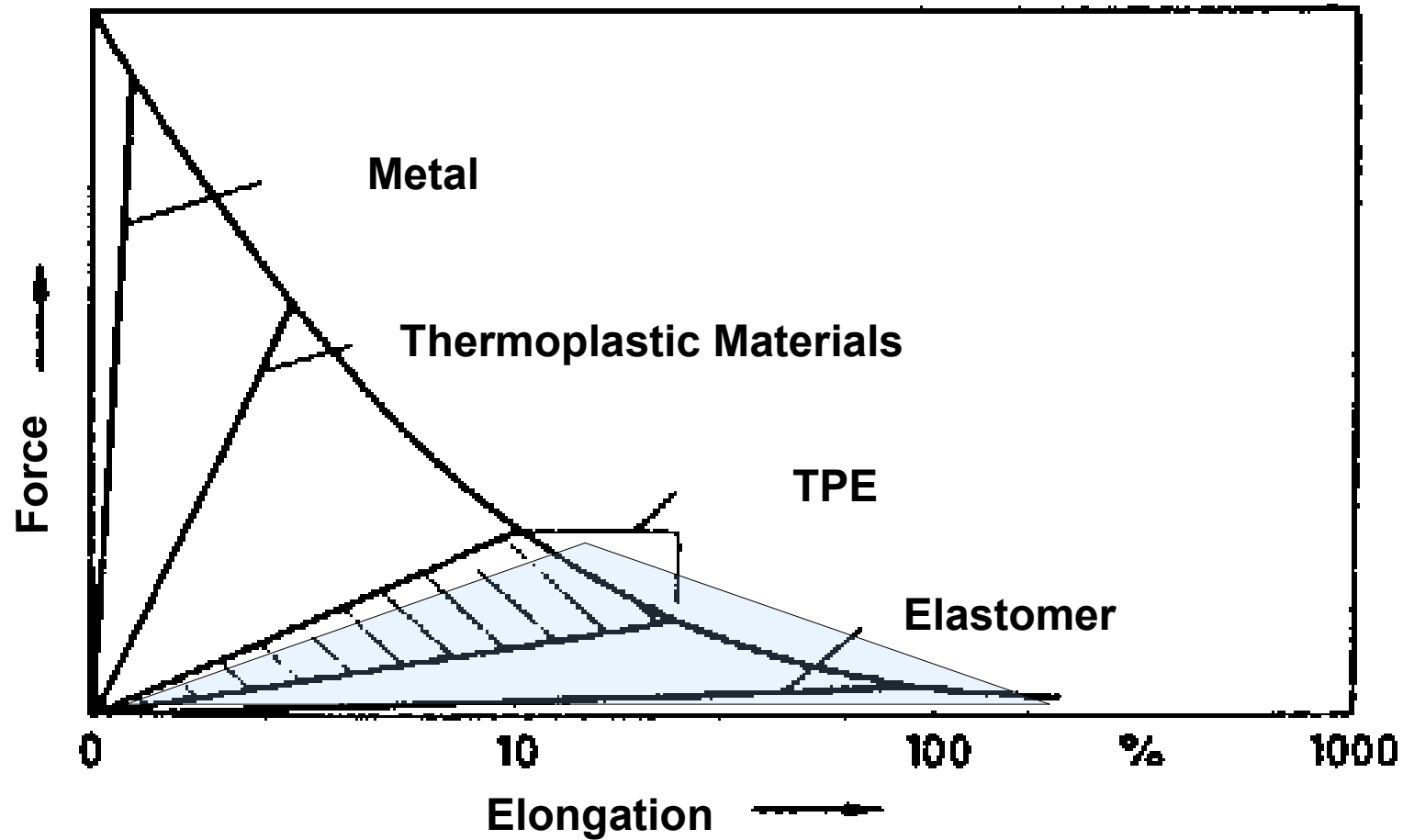
Applicability of Stress/Strain on different Materials until elasticity limit, but with complete recovery after removing of the load

# Positioning of TPE

## Stress relaxation behaviour



Source: H. Domininghaus  
Plastverarbeiter 89



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

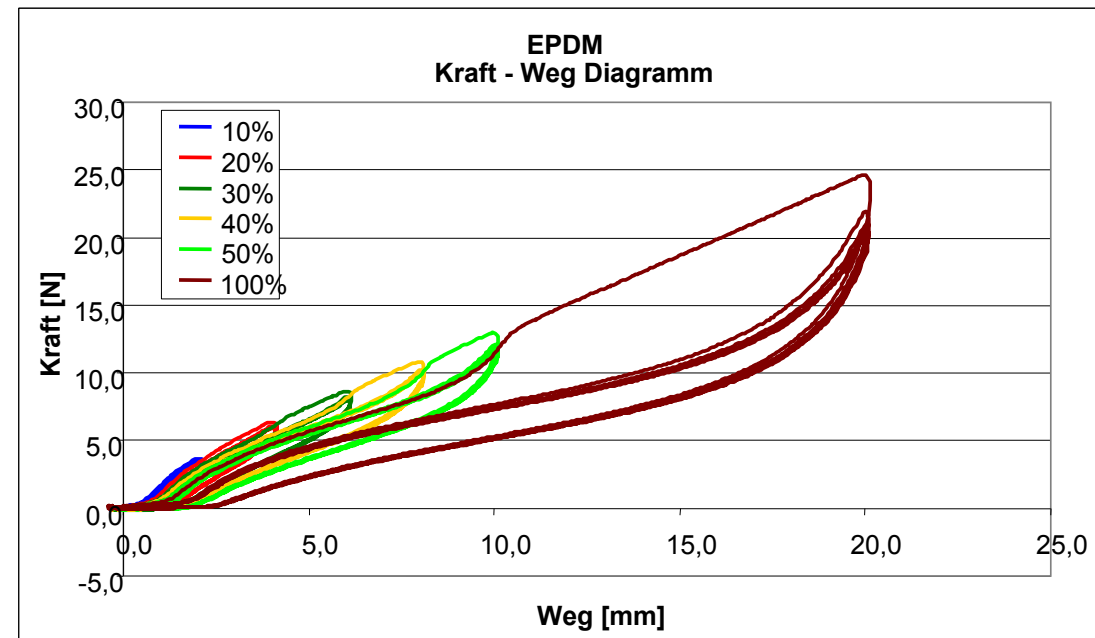
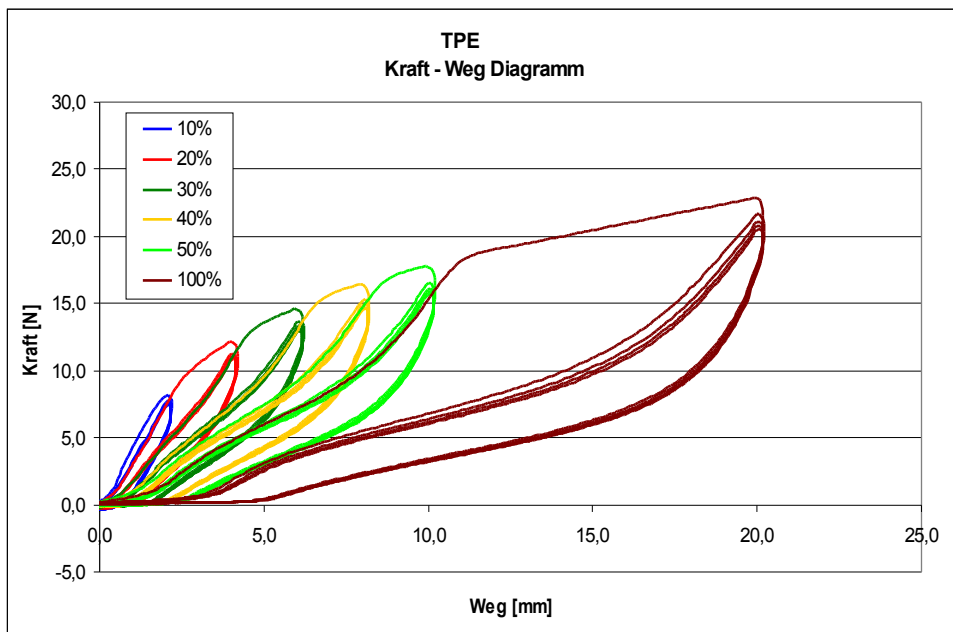


# Positioning of TPE

## Stress relaxation behaviour



Source: C. Thomas  
DIK TPE Seminar



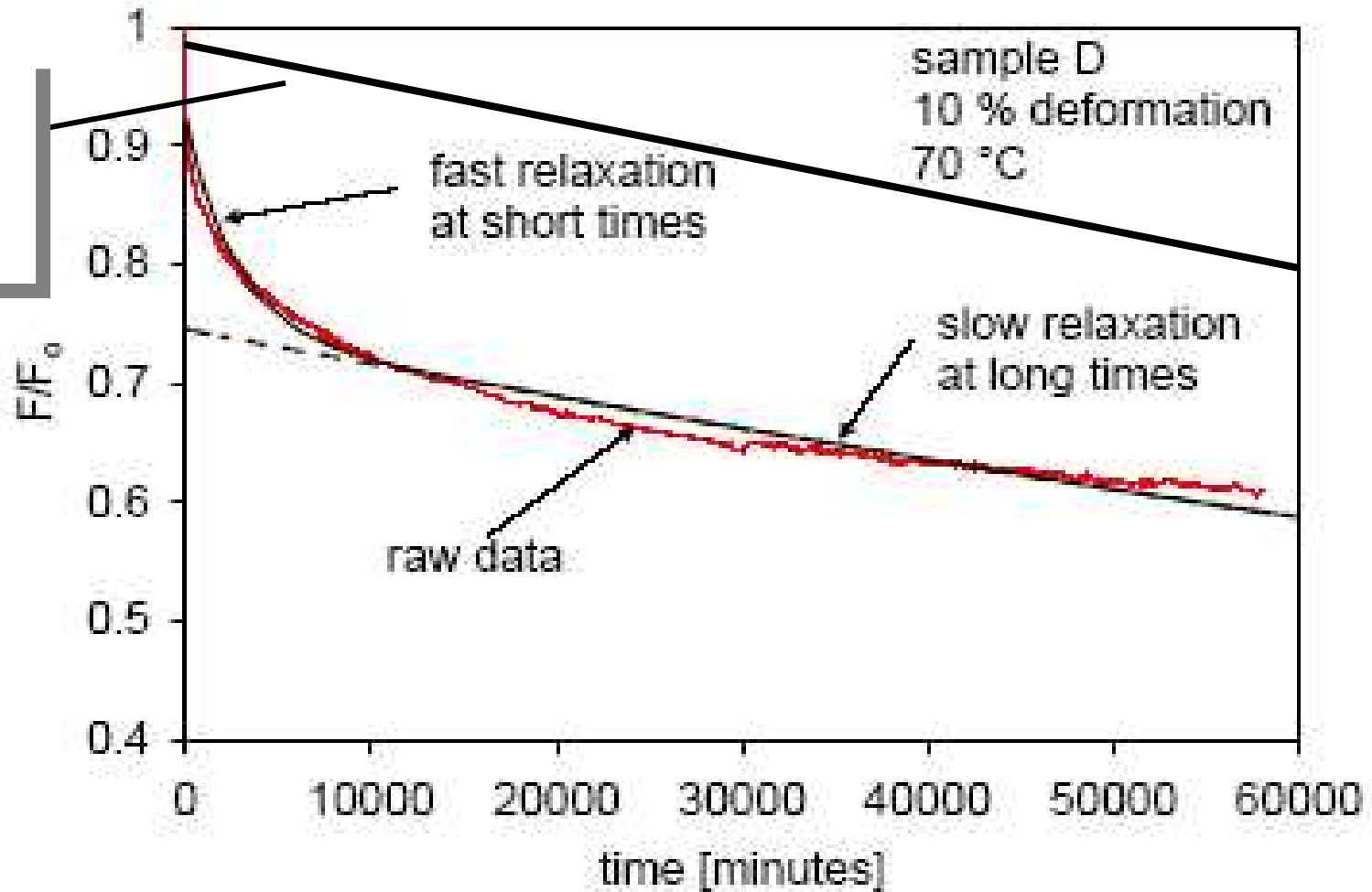
# Positioning of TPE

## Stress relaxation behaviour



Source: E. Jourdain,  
Autom.Elast.Conf. 04, Detroit

Compression load  
relaxation for  
Elastomers (typical  
behavior)



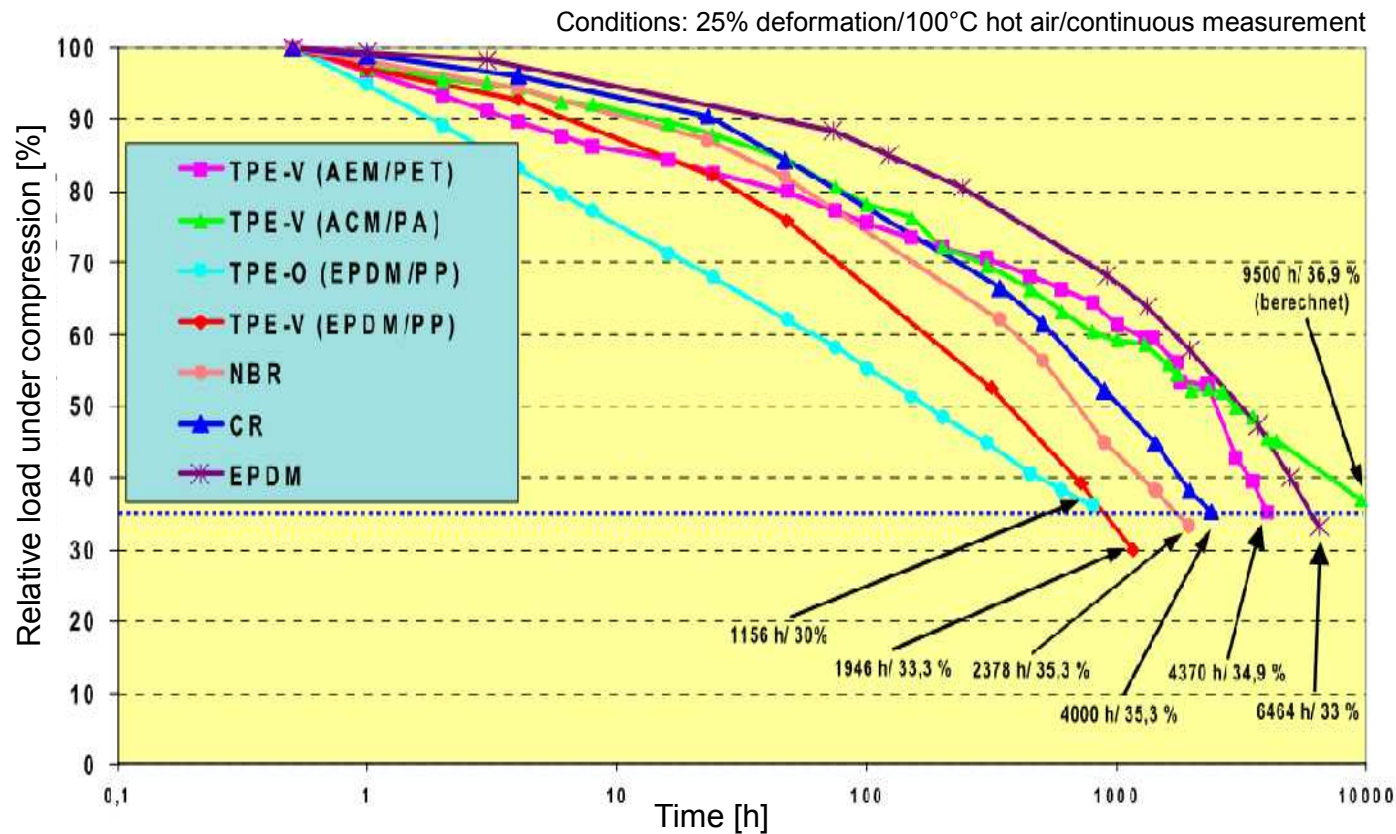
# Positioning of TPE

## Stress relaxation behaviour



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

Source: E. Osen  
KHK 2006



# 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)

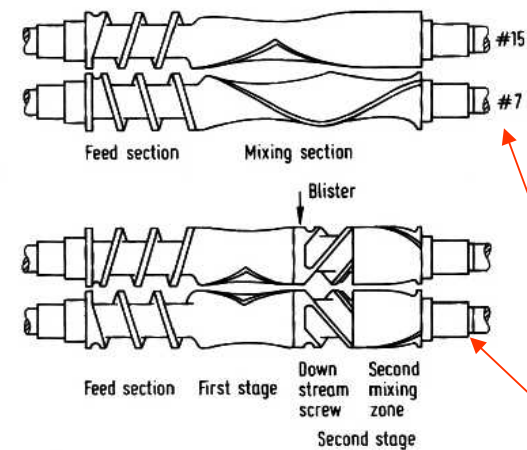
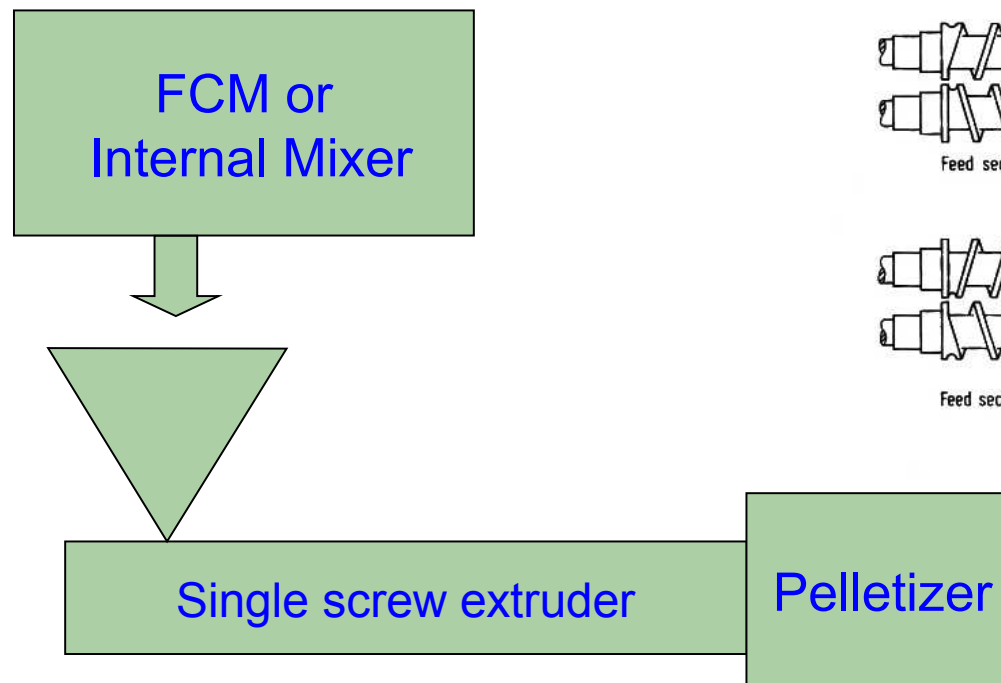
# TPE versus Rubber Compounds / Compounding



## ➔ Two stage compounding

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

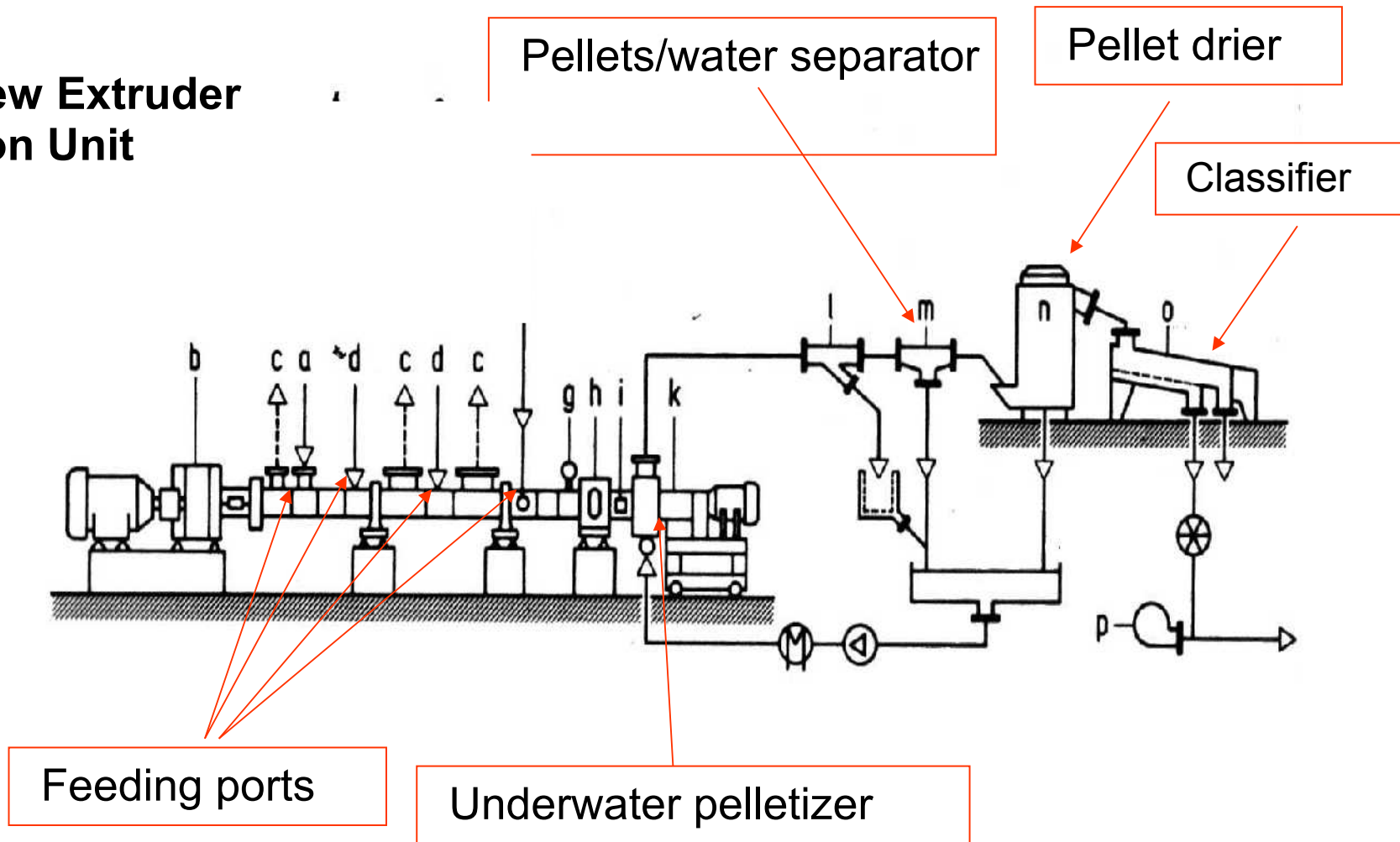
Source: HF Mixing  
Former Farrel



FCM Rotors

# TPE versus Rubber Compounds / Compounding

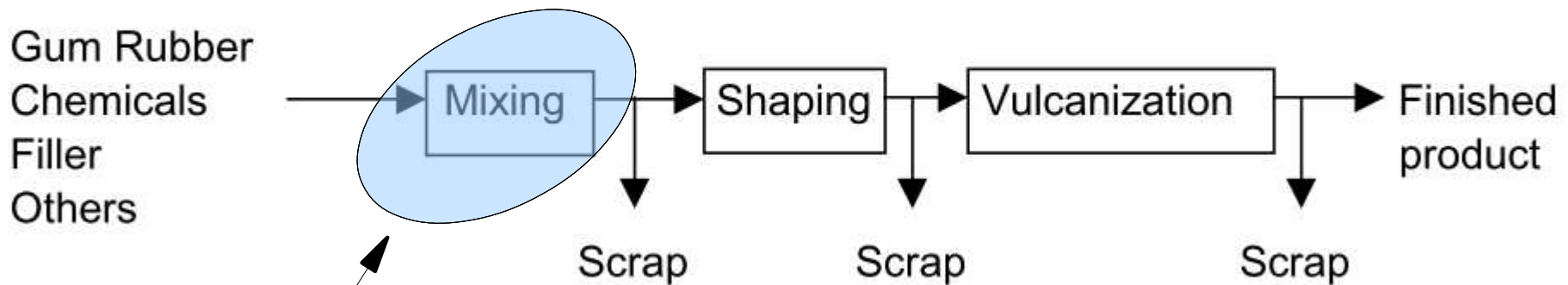
## Twin Screw Extruder Production Unit



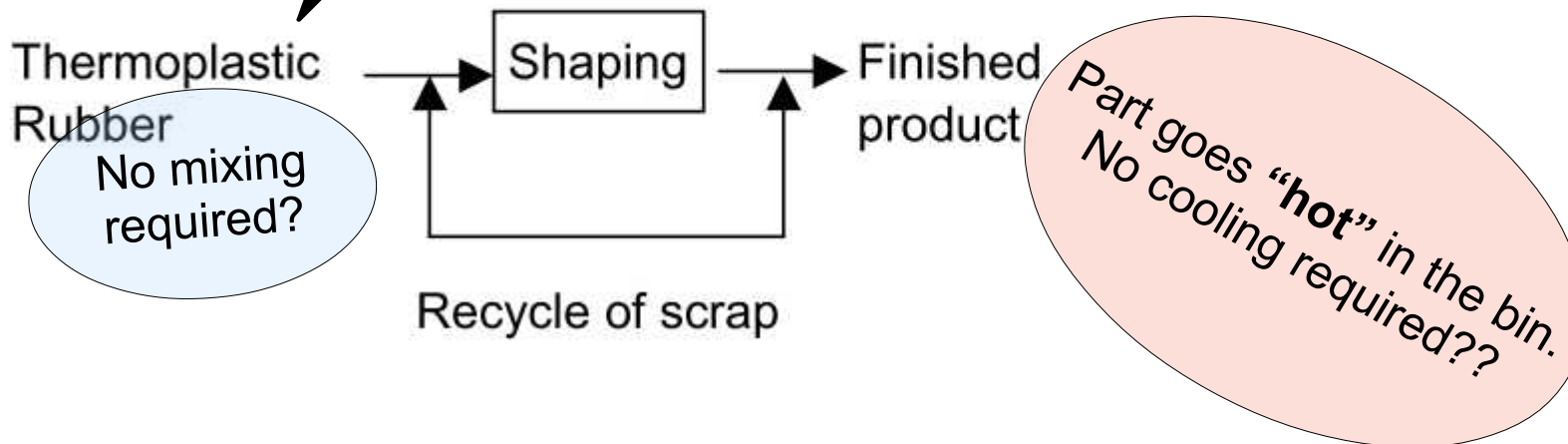
# TPE versus Rubber Forming

Source: K Naskar  
Diss. U. of Twente 2004

(a) Vulcanized rubber



(b) Thermoplastic elastomer

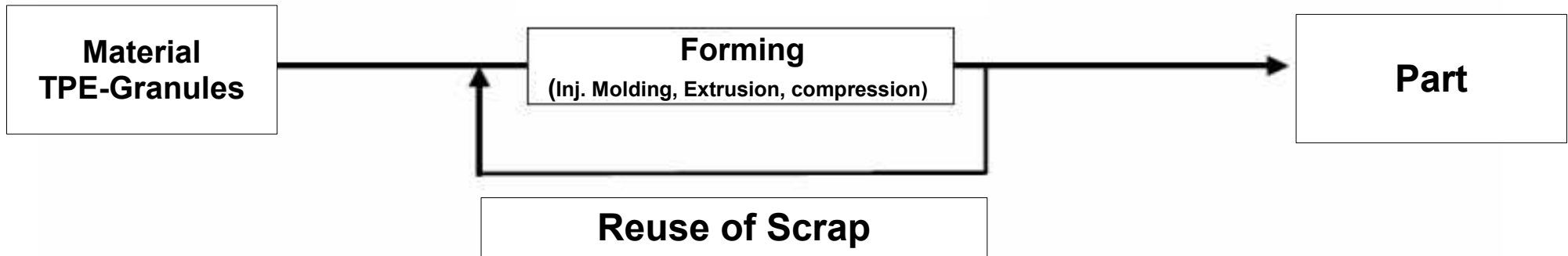


# TPE versus Rubber Forming

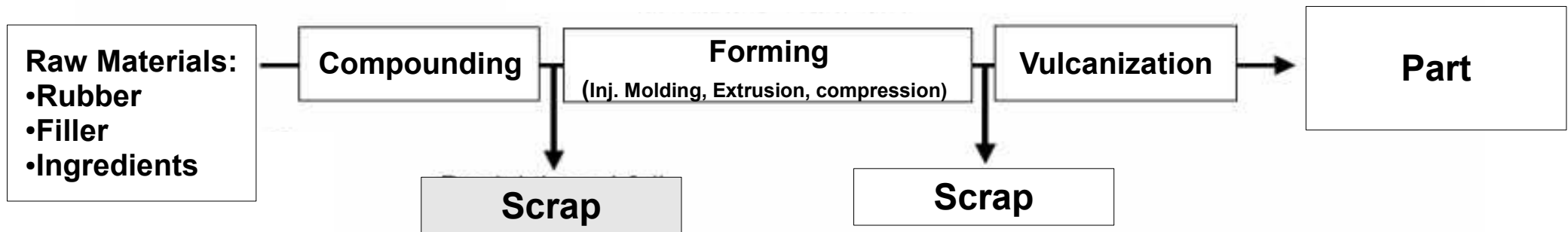


Source: J. Stemper  
Plastverarbeiter 84

## Processing of TPE Physical Crosslinking



## Processing of Rubber Chemical Crosslinking



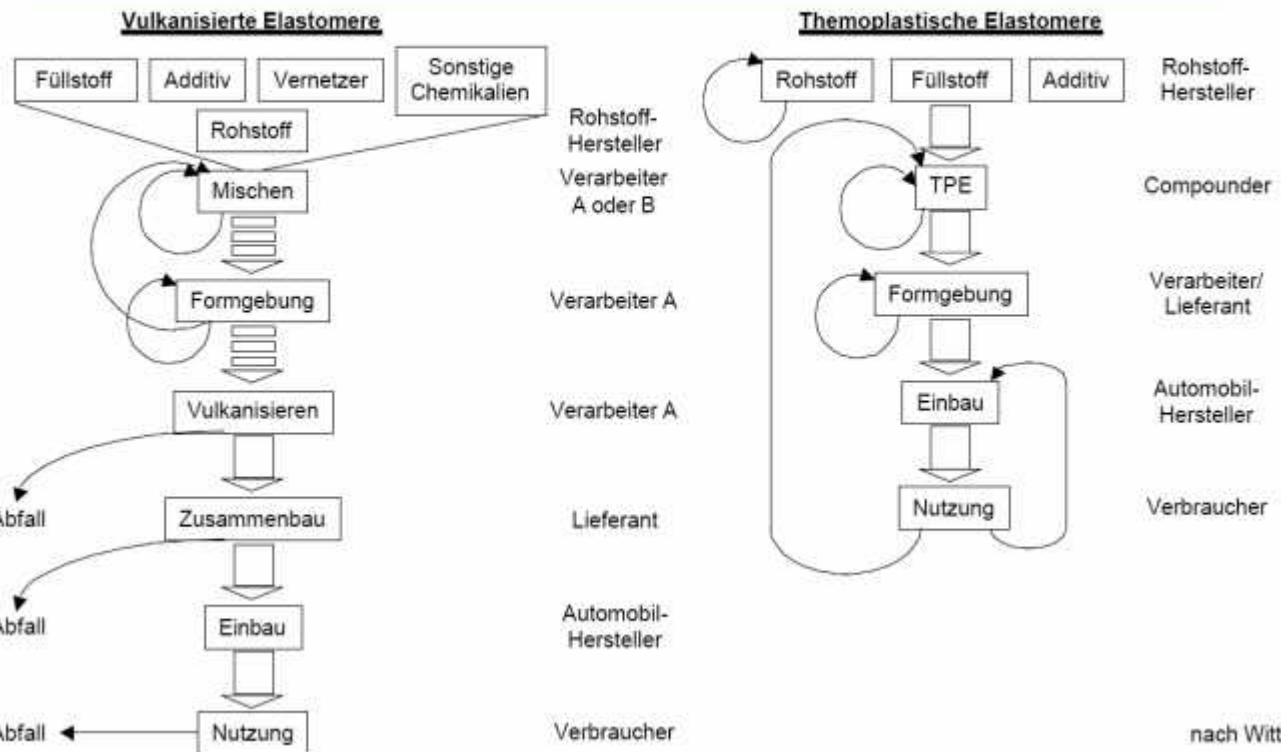


# TPE versus Rubber Forming



Source: Wittig, GAK 1997

## Fertigungsabläufe



Polymer  
Form  
Scrap  
Scrap

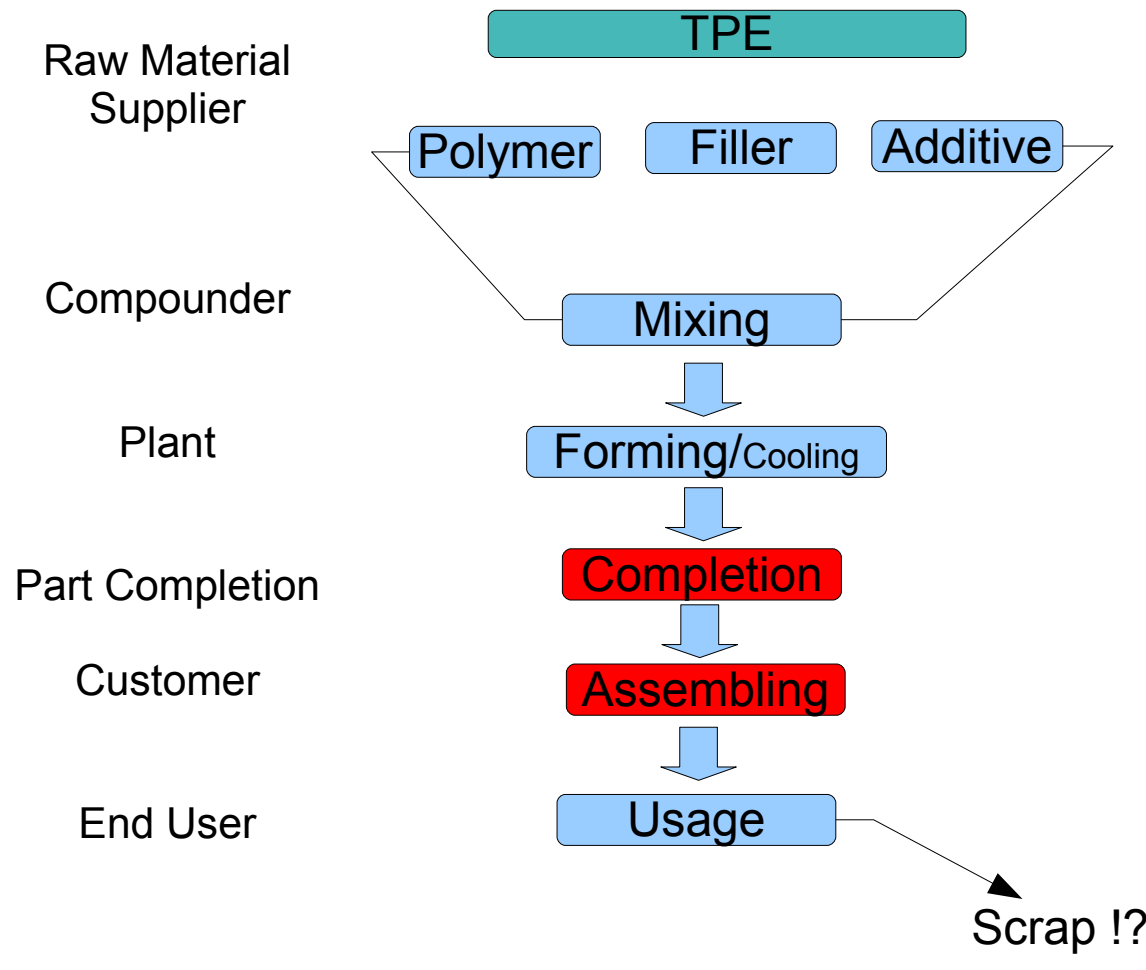
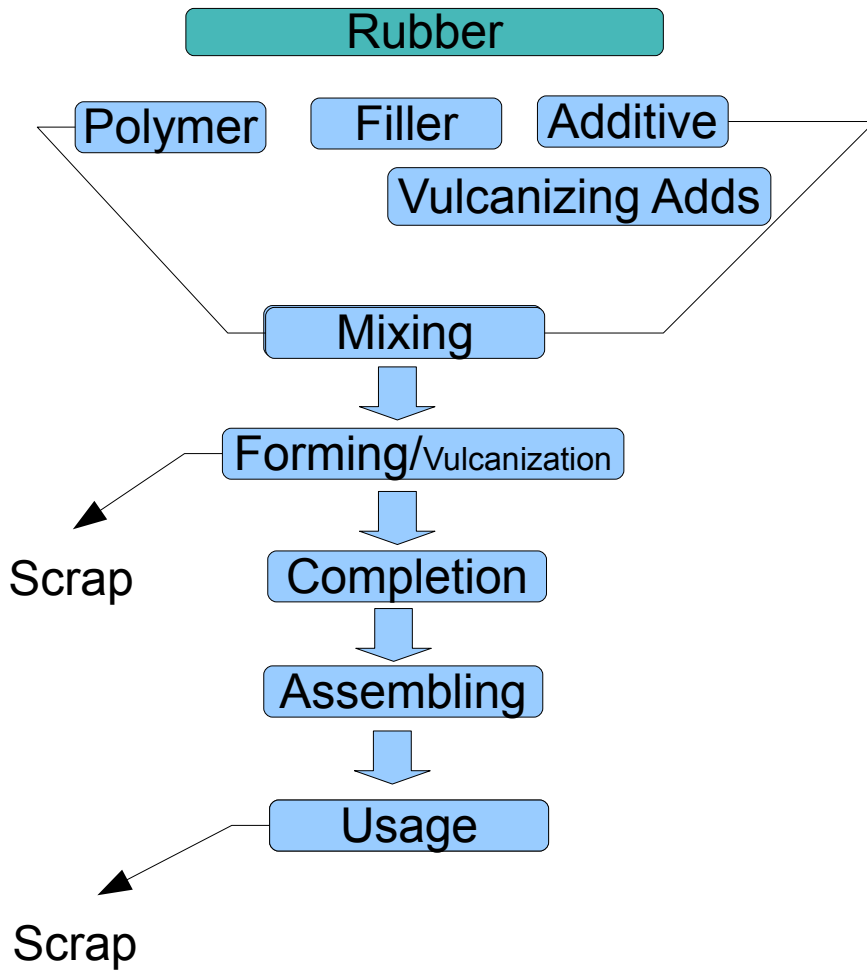
Additive  
g  
Scrap !?

nach Wittig 97

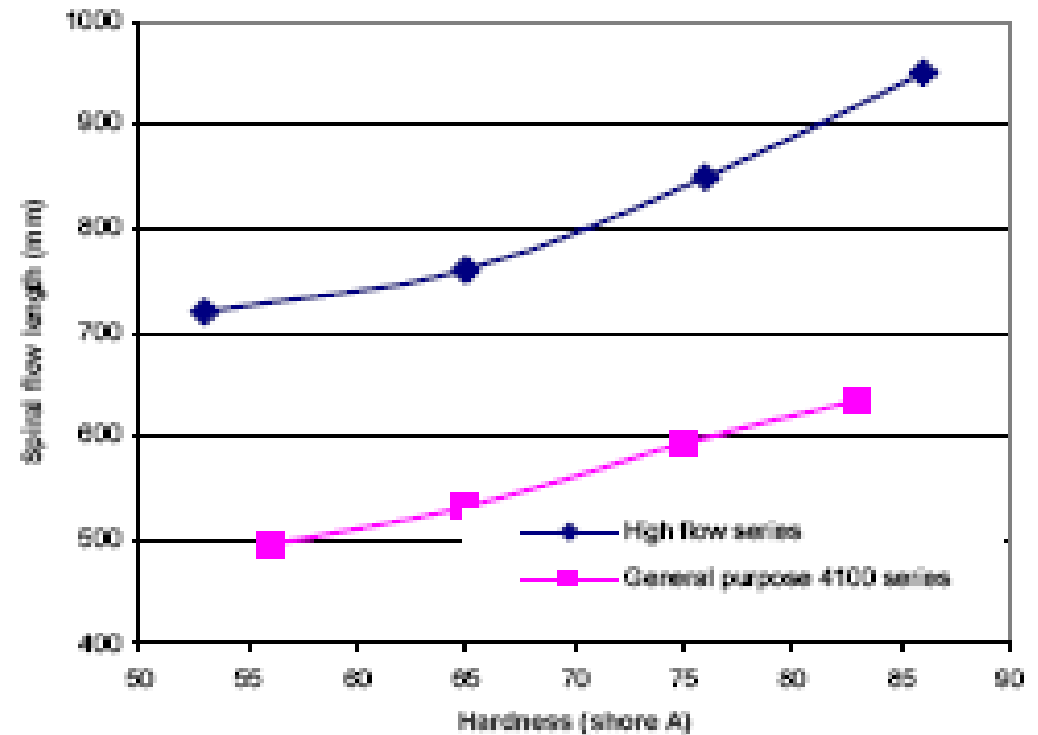
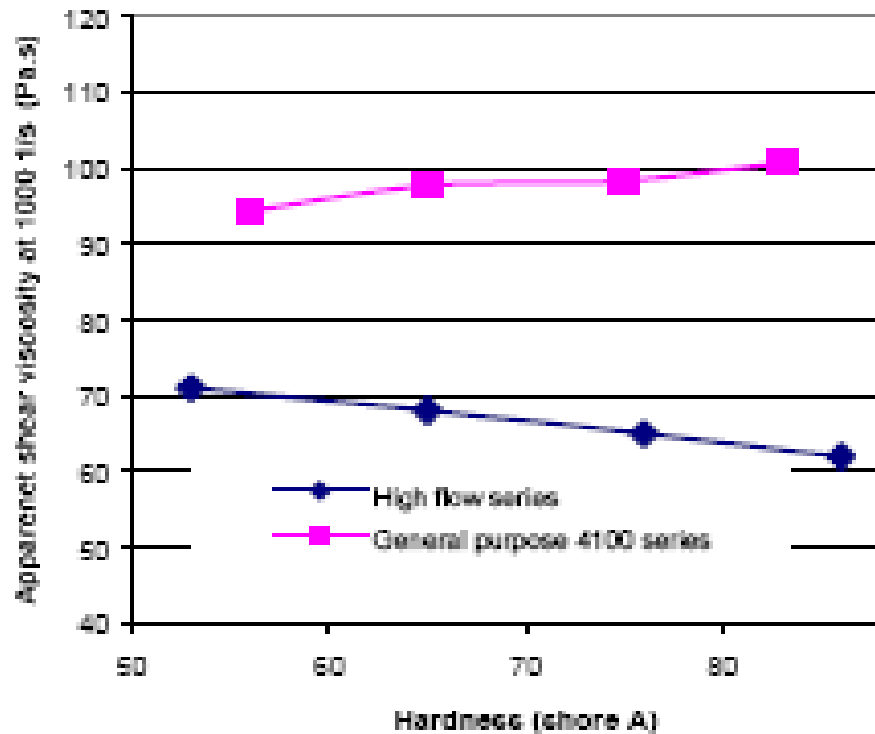
# TPE versus Rubber Forming



Source: Wittig, GAK 1997



# TPE versus Rubber Forming



**PP content is increased to achieve hardness, which improves flow.**

# TPE versus Rubber Forming

Source: S.Z. Yu, H.-J. Graf  
Standard Products priv. Comm.

- ➔ **Calculation of TPE glass run channel solution versus EPDM**
- ➔ **Cost estimation**

	EPDM	TPE
Extrusion	0.110 \$/ft	0.130 \$/ft
Flocking	0.020 \$/ft	N/A
Slipcoat	N/A	0.020 \$/ft
Molding	1.350 \$/unit	0.270 \$/unit
<b>Total</b>	<b>1.480 \$/unit</b>	<b>0.420 \$/unit</b>



Source: Internet



Source: G. Williams  
Autom. Elastomer Conf. 03

# TPE versus Rubber Property Description

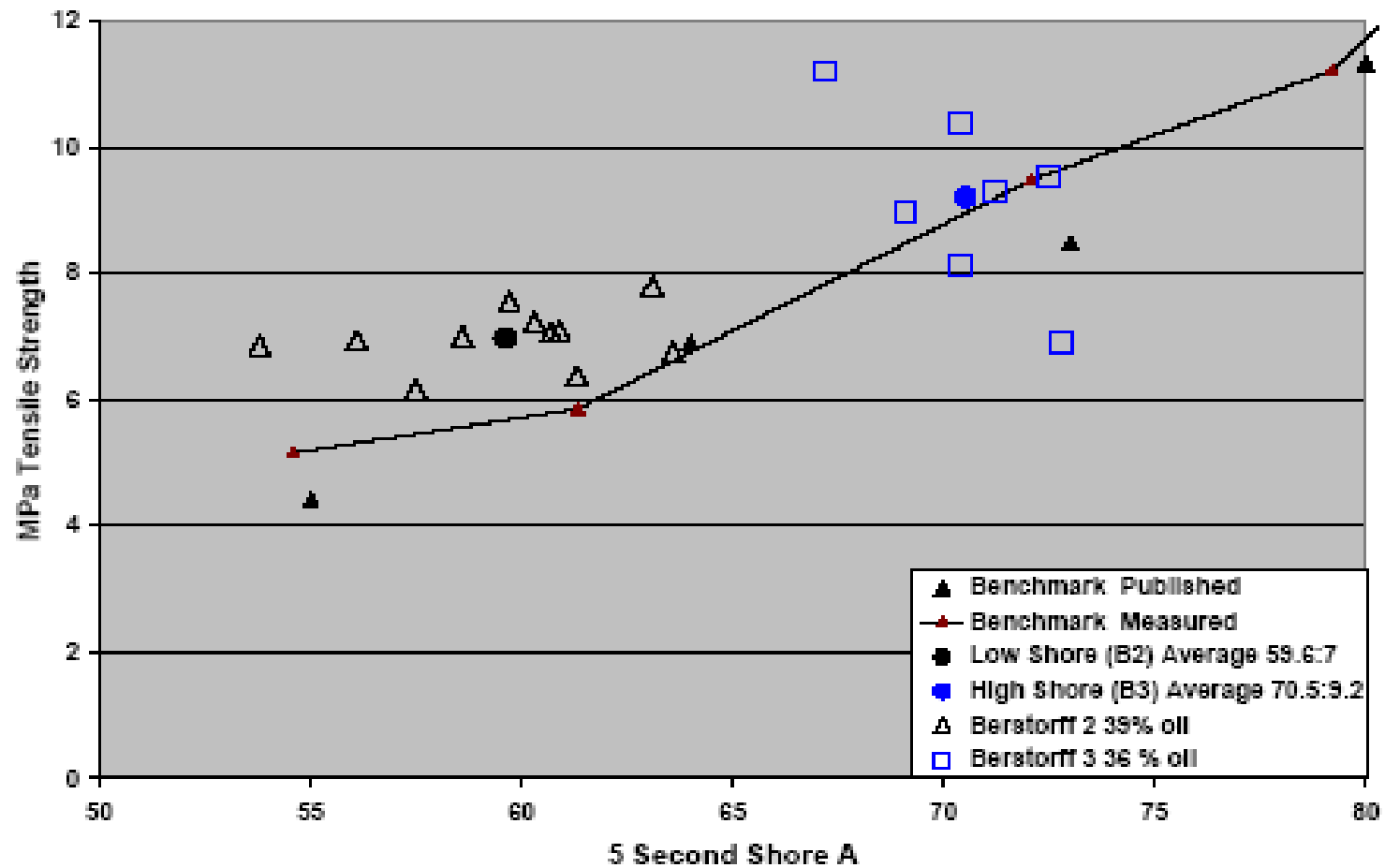
In an experiment with a production scale twin screw extruder to study the manufacturing process of TPE the following formulation was used (Note the large amount of oil in this formulation):

## 65 SHORE A FORMULATION

	phr	Wt%
EPDM	100	30.42
Carbon Black	30	9.13
Polypropylene	50	15.21
Oil	130	39.55
SP 1045	10	3.04
Stannous Chloride (dihydrate)	1.7	0.52
Processing aid	5	1.52
ZnO	2	0.61
<b>Totals</b>	<b>328.7</b>	<b>100.00</b>

# TPE versus Rubber Property Description

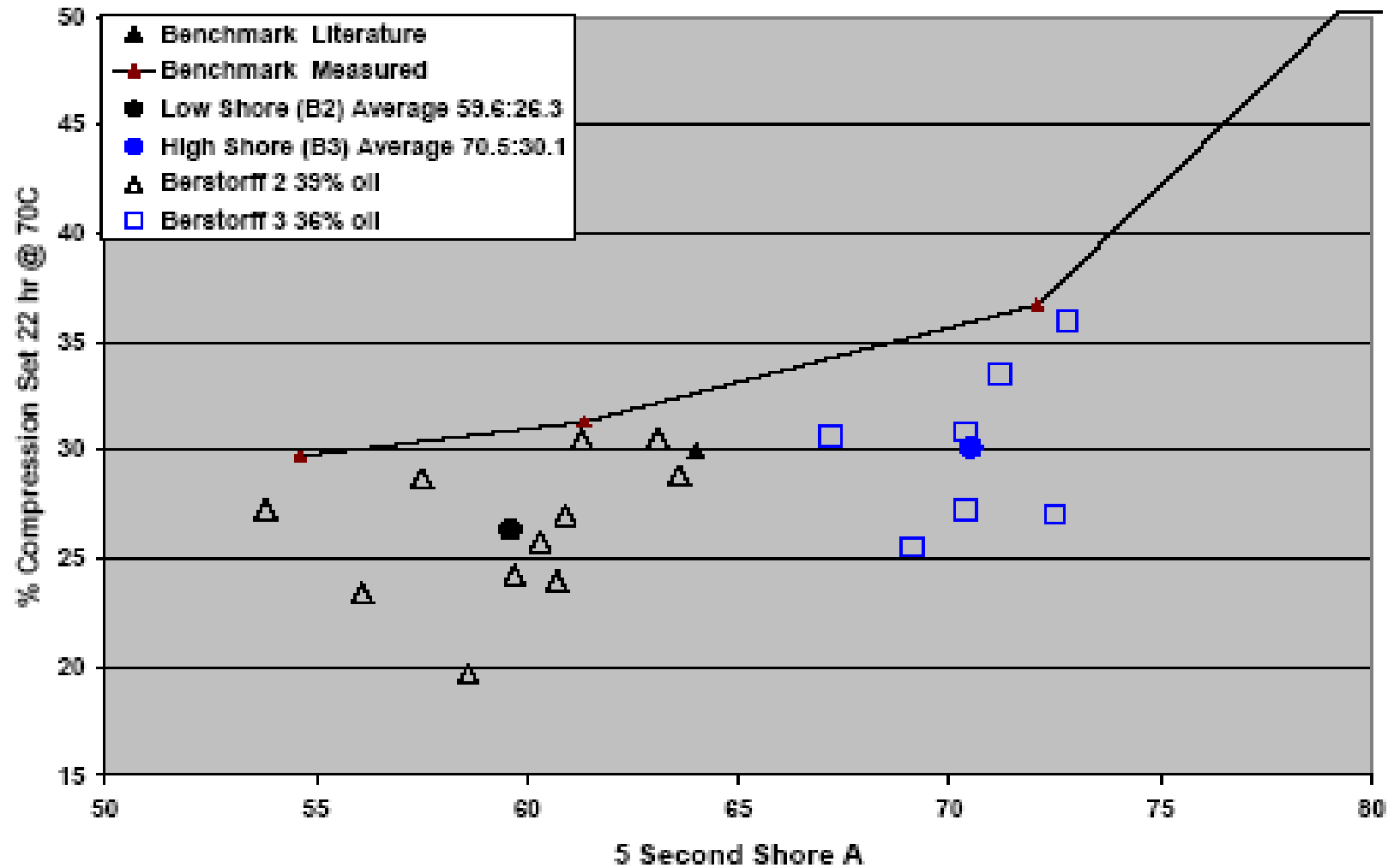
Source: G. Williams  
Autom. Elastomer Conf. 03



# TPE versus Rubber Property Description



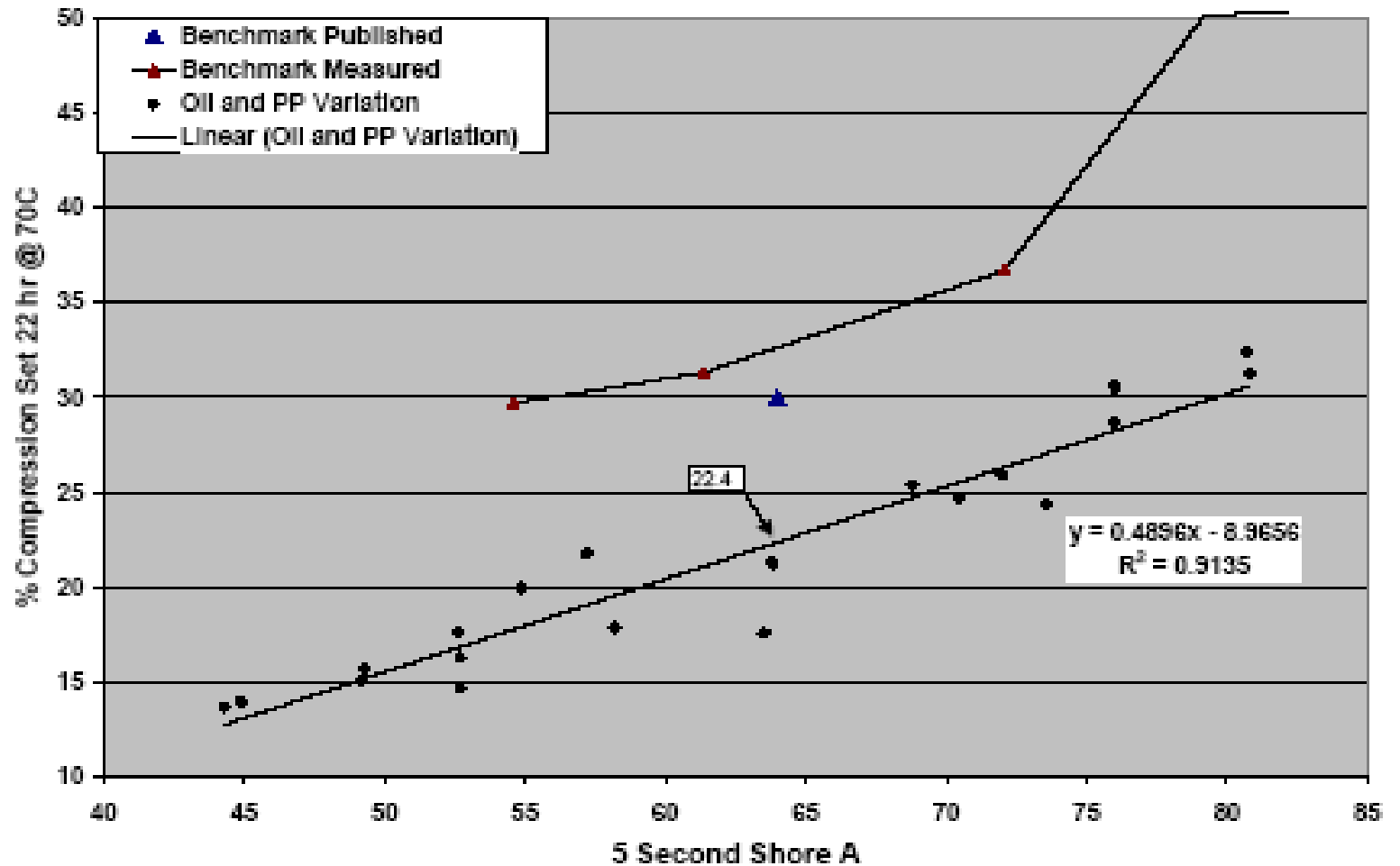
Source: G. Williams  
Autom. Elastomer Conf. 03



# TPE versus Rubber Property Description



Source: G. Williams  
Autom. Elastomer Conf. 03



Reason, why most  
OEM suppliers not  
satisfied with TPE-V  
today



# TPE versus Rubber Property Description



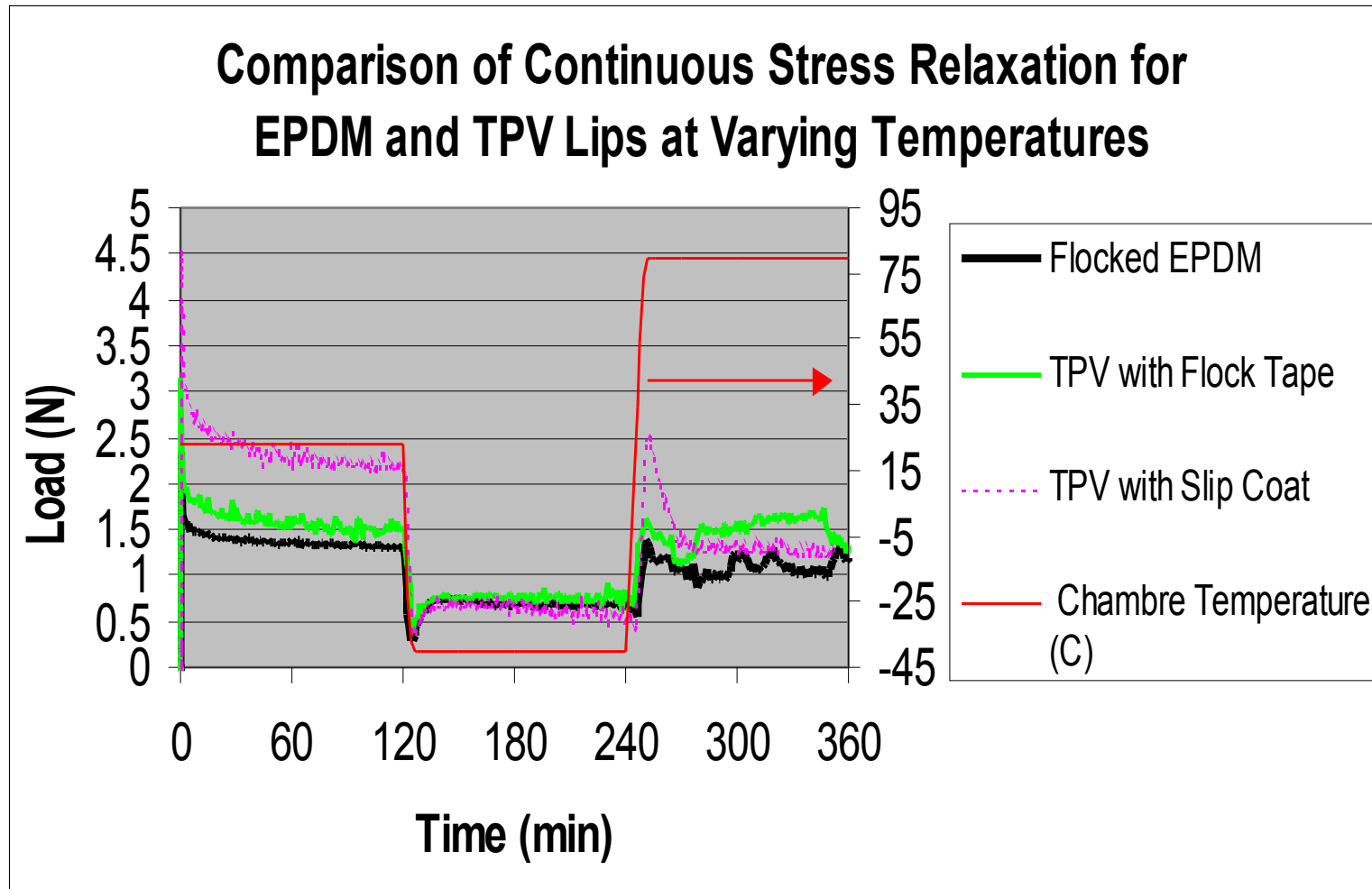
Material	Hardness - °ShA	Tensile – Mpa			
		Confirmation		Supplier data sheet	
		longitudinal	perpendicular	longitudinal	perpendicular
TPE 1	55	3.8	<u>7.5</u>	3.3	8.6
TPE 2	60	5.4	<u>5.5</u>	5.4	7.4
TPE 3	60	<u>4.5</u>	<u>5.5</u>	5.4	6.4
TPE 4	60	3.8	5.4	5.8	

Reason, why most customers not pleased with suppliers today

# TPE versus Rubber Property Description



Source: S.Z. Yu  
Cooperstandard Automotive



# TPE versus Rubber Property Description



Source: J.E. Pfeiffer  
RDoACS Oct. 2002 No.8

## Stress-Strain Curves

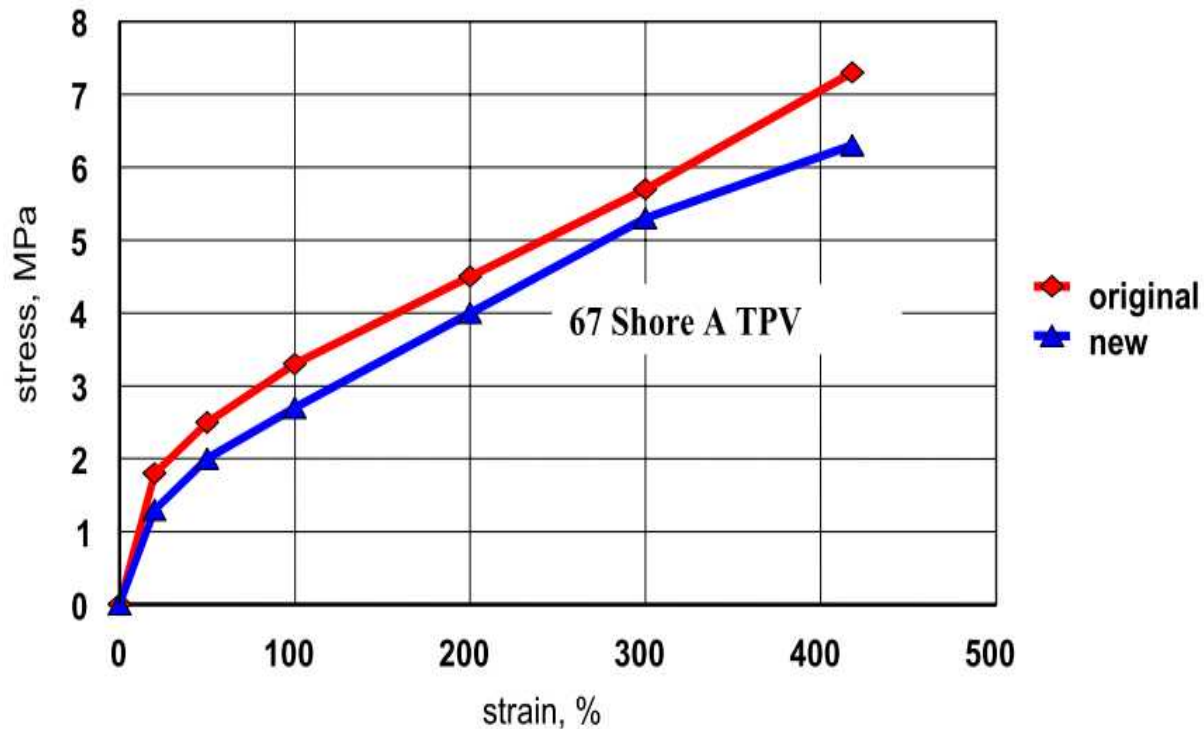


Figure 12: view of profile cross section in A pillar, (old profile)

# Summary

## ➔ **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**

# Summary

## ➔ Processing of thermoplastic elastomers

- **Opposite to Rubber processing, which is a cold/hot process, TPE are manufactured in a hot/cold process.**
- **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**
- **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.**