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Understanding TPEs

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ISO 9001

Workshop Goals

1. Establish a definition
2. Understand how TPEs work
3. Classification & nomenclature
4. Performance
5. Compounded TPEs

Definition

ThermoPlastic Elastomer

"...Having the property of softening or fusing when heated and of hardening again when cooled..."

"...Any of various elastic substances resembling rubber..."

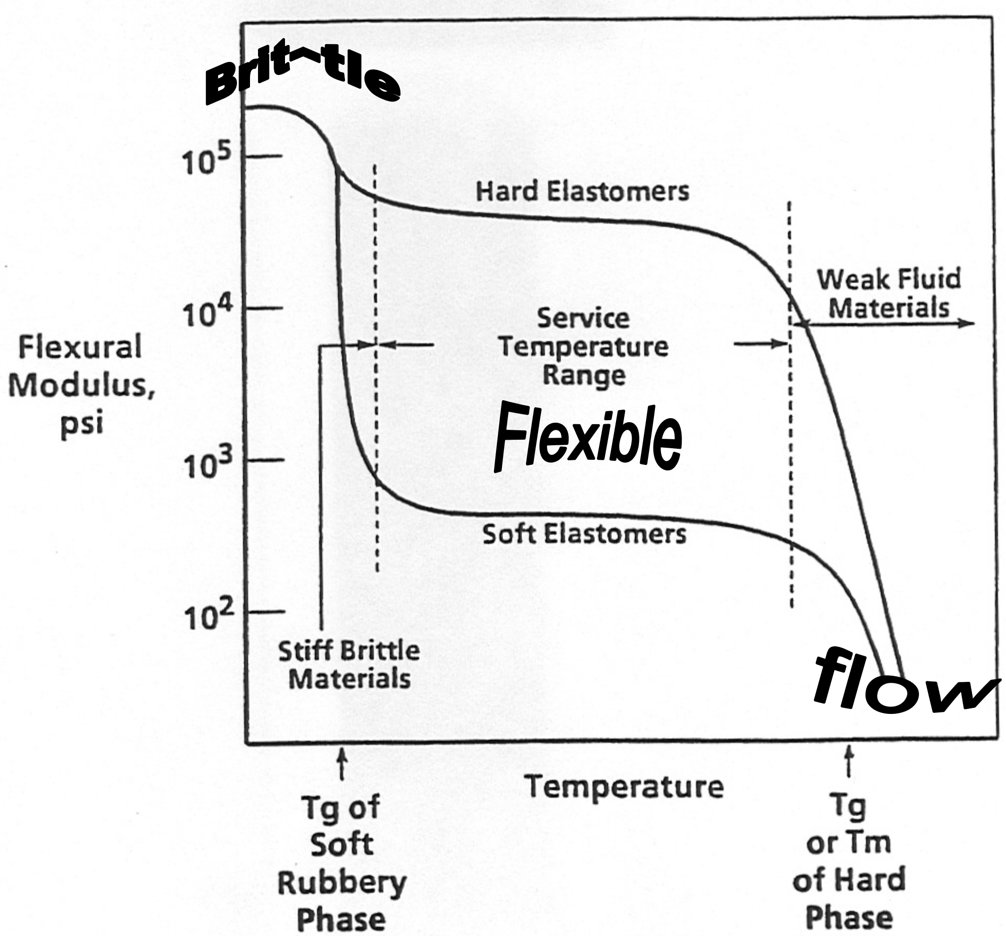
Int'l Inst. of Synthetic Rubber Producers (IISRP) definition:

"Polymers, polymer blends or compounds which, above their melt temperatures, exhibit thermoplastic character that enables them to be shaped into fabricated articles and which, within their design temperature range, possess elastomeric behavior without cross-linking during fabrication. This process is reversible and the product can be reprocessed and remolded."

TPEs are composed of hard and soft domains; they are multiphase materials in their solid state.

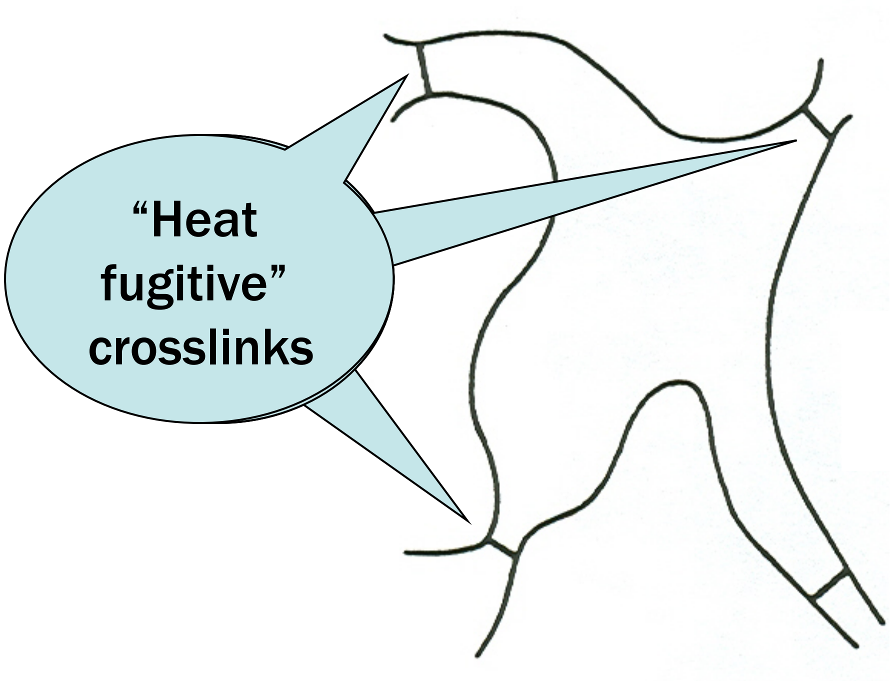
- **Hard phase contributes "plastic" properties such as:**
  - High-temperature performance
  - Thermoplastic processability
  - Tensile strength
  - Tear strength
- **Soft phase contributes "elastomeric" properties:**
  - Low-temperature performance
  - Hardness
  - Flexibility
  - Compression & tension set

But Why Are TPEs Rubbery?



The design temperature range of a TPE is bounded by the glass transition temperature of the rubbery phase and the glass transition or melt temperature of the hard phase.

So, How Can TPEs Be Melt Processable?



By raising the temperature of the TPE above the glass transition or melting temperature of the plastic phase.

So, How Can TPEs Be Melt Processable?

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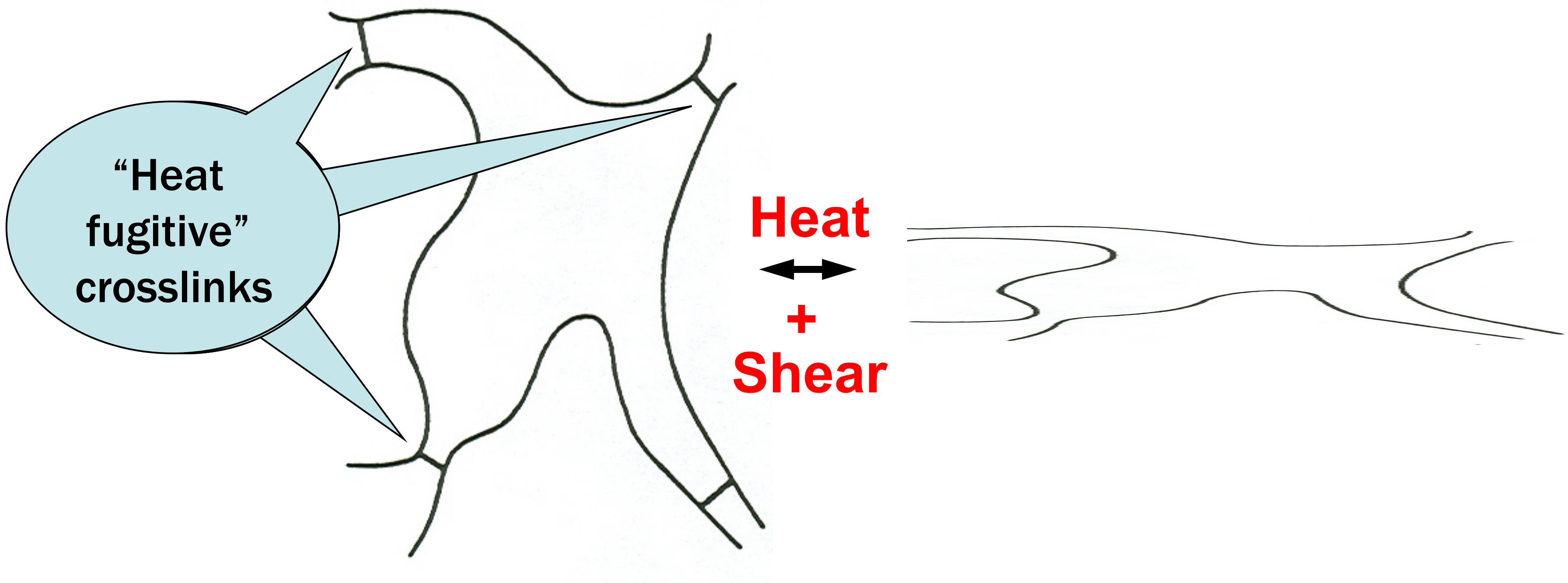
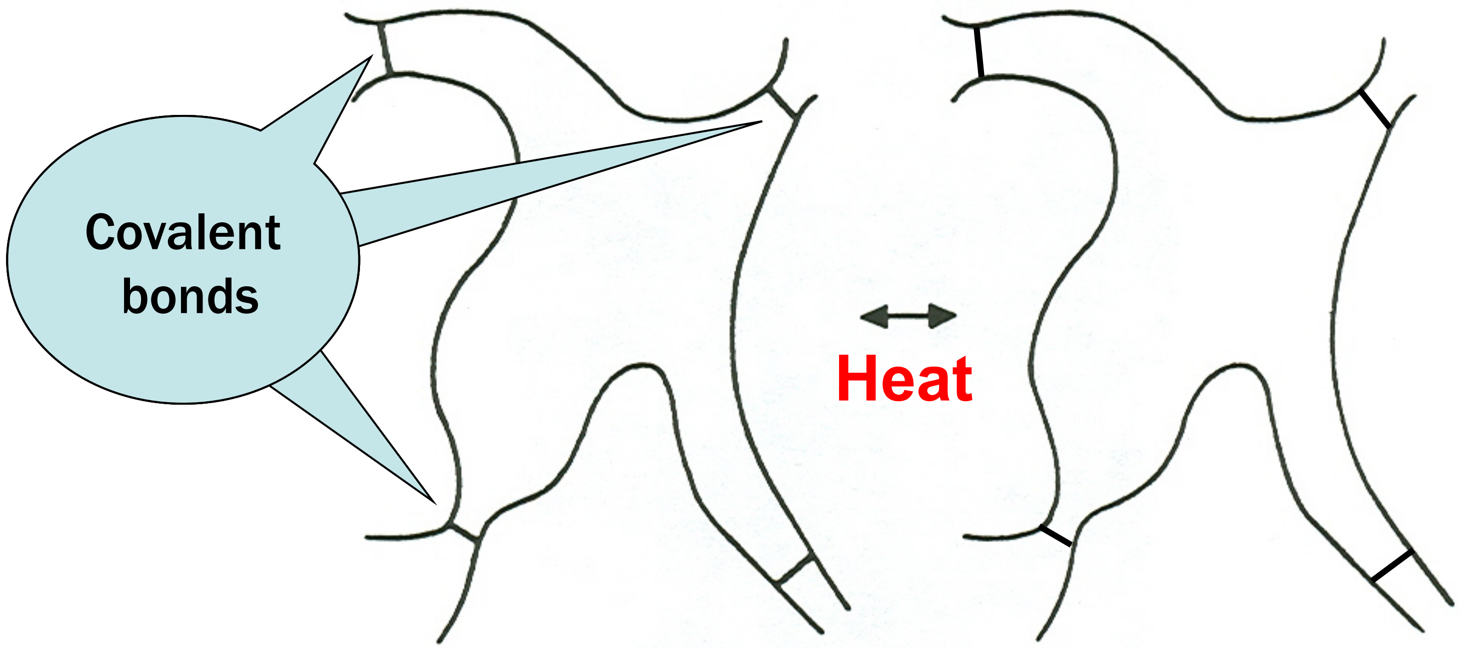


And applying shear forces typical of thermoplastic processes.

Unlike Thermoset Rubber…



By comparison, thermoset rubbers (TSRs) are single phase materials with non-reversible chemical (covalent) bond cross-links.

Unlike Thermoset Rubber...

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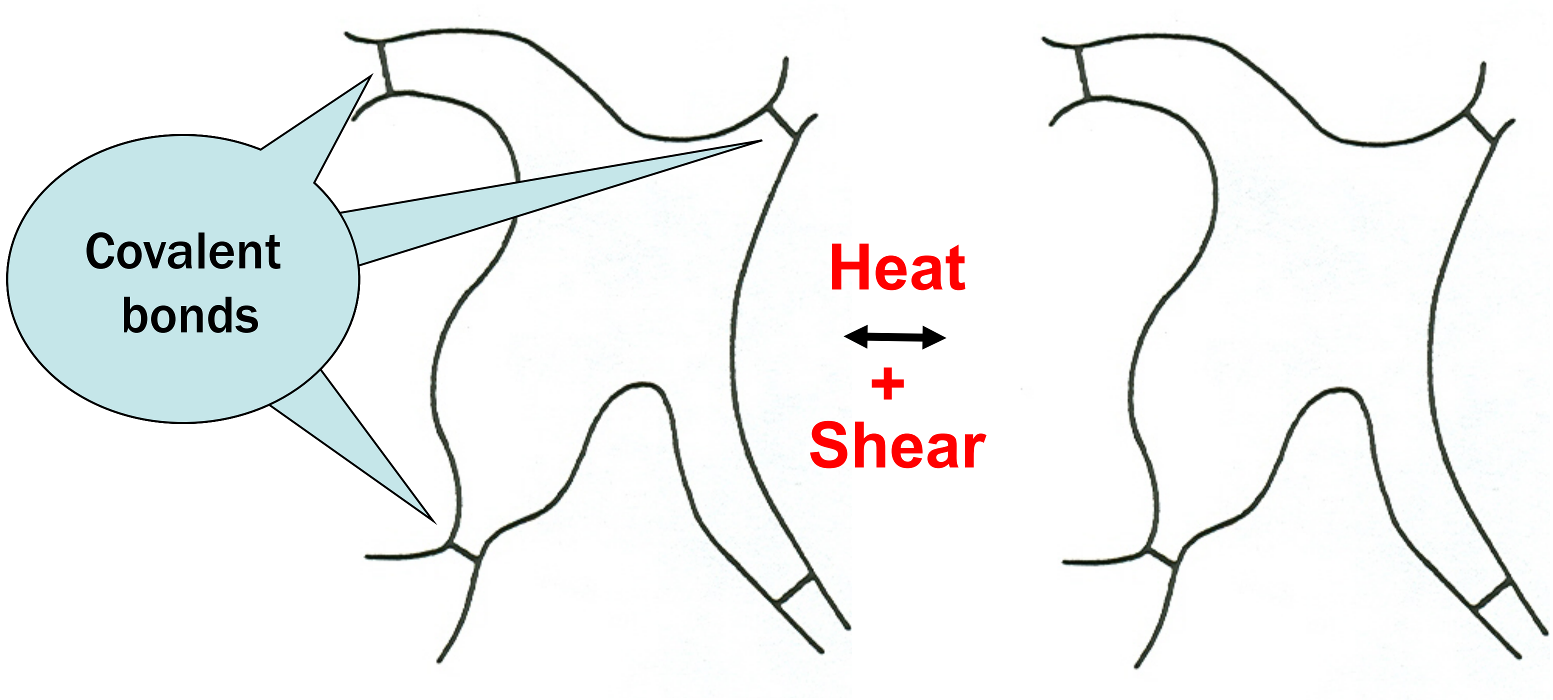

And are unaffected by shear forces.

Unlike Thermoset Rubber...

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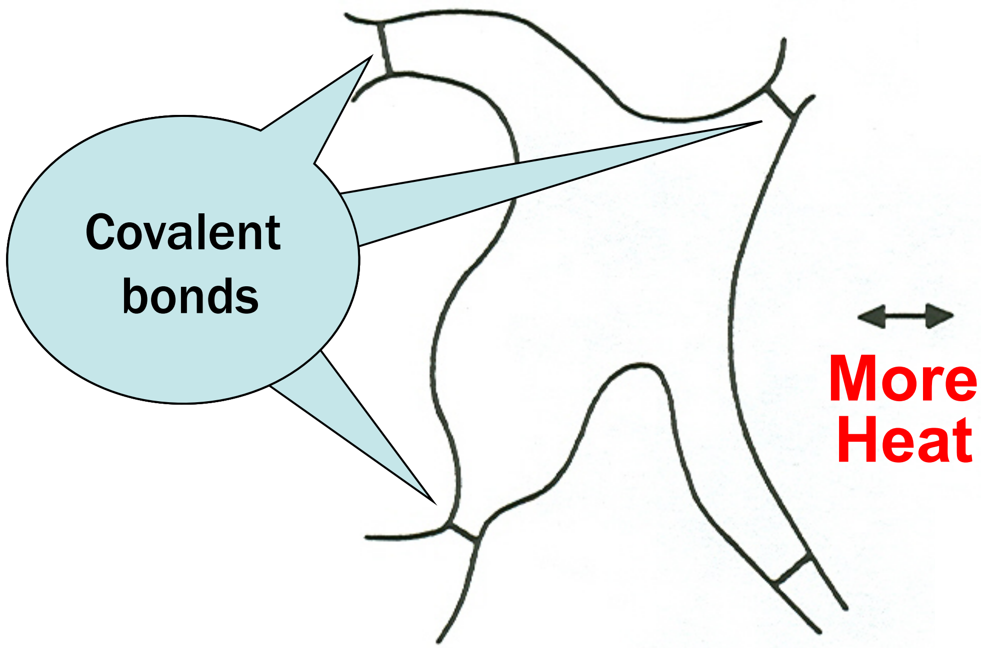

Or increasing heat...

Classification & Nomenclature

- Performance (heat & oil resistance following ASTM, SAE, etc.)
- Chemistry (styrenic, olefinic, urethane, etc.)
- Structure
  - Block copolymers
  - Blends & alloys
  - Dynamic vulcanizates

Architecture of Block Copolymers

- Polymers – molecular chains of repeating units

a-a-a-a-a-a-a-a

- Copolymers – polymer made up two or more different units along the chain

a-b-a-b-a-b-a-b

- Block copolymers – copolymers in which the different units congregate in clusters or blocks

a-a-a-a-b-b-b-b-a-a-a-a-b-b-b-b

Block Copolymers - Mechanism

- Block copolymer based TPEs are made of polymers that have both hard (semi-crystalline or glassy) blocks and soft (amorphous) blocks along the backbone

s-s-s-s-s-h-h-h-h-h-s-s-s-s-s-h-h-h-h-

- In the bulk, as they cool from the melt, the hard blocks will coalesce into crystalline or glassy domains creating physical crosslinks
- The soft blocks are left to form amorphous rubbery domains that provide the elastomeric bridges between the crystalline domains

Block Copolymers - Morphology

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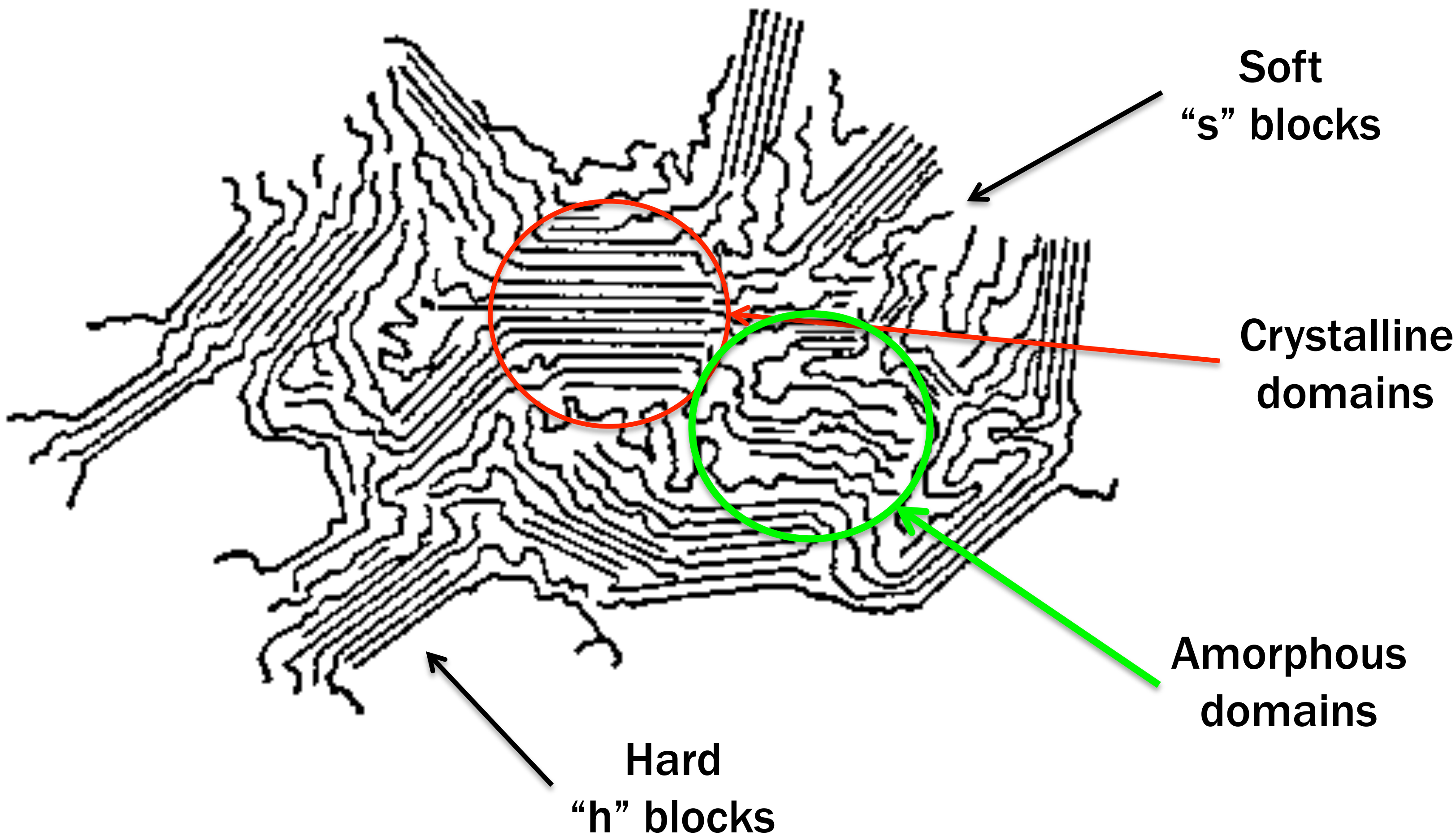


Block Copolymers - Examples

- **Styrenic block copolymers “SBC”**
  - SBS, SEBS, SIS, SIBS, SEEPS
  - Rarely used in their neat form
- **Polyolefin elastomer “POE”**
- **Reactor thermoplastic olefins “r-TPO”**
- **Thermoplastic urethane “TPU”**
- **Copolyether-ester “COPE”**
- **Polyether-block-amide “COPA” or “PEBA”**

Blends of:

- **Homopolymers and/or**
- **Copolymers**
  either of which may be the elastomeric component
- **Plasticizers**
- **Fillers**
- **Compatibilizers**

Blends & Alloys - Mechanism

- One of polymers has a melting or glass transition temperature well above room temperature
- In the bulk, as it cools from the melt, it will coalesce into crystalline or glassy domains creating physical crosslinks
- The other polymer forms the rubbery domains that provide the elastomeric character of the blend
- Fillers and plasticizers are generally excluded from the crystalline domains
- Compatibilizers - if used - concentrate at the interface of the crystalline & amorphous phases

Blends & Alloys - Morphology

- Discrete hard domains in a sea of soft elastomeric polymer
- Discrete soft elastomeric domains in a sea of hard polymer
- Co-continuous (interpenetrating) network of hard polymer entangled with soft elastomeric polymer
- What you get is a function of the relative surface energy of the polymers, volume fraction, and relative viscosity during mixing

[ref: Jordhamo, et.al., “Phase Continuity and Inversion in Polymer Blends and Simultaneous Interpenetrating Networks”, Polymer Engineering and Science, April 1986, Vol. 26, No. 8]

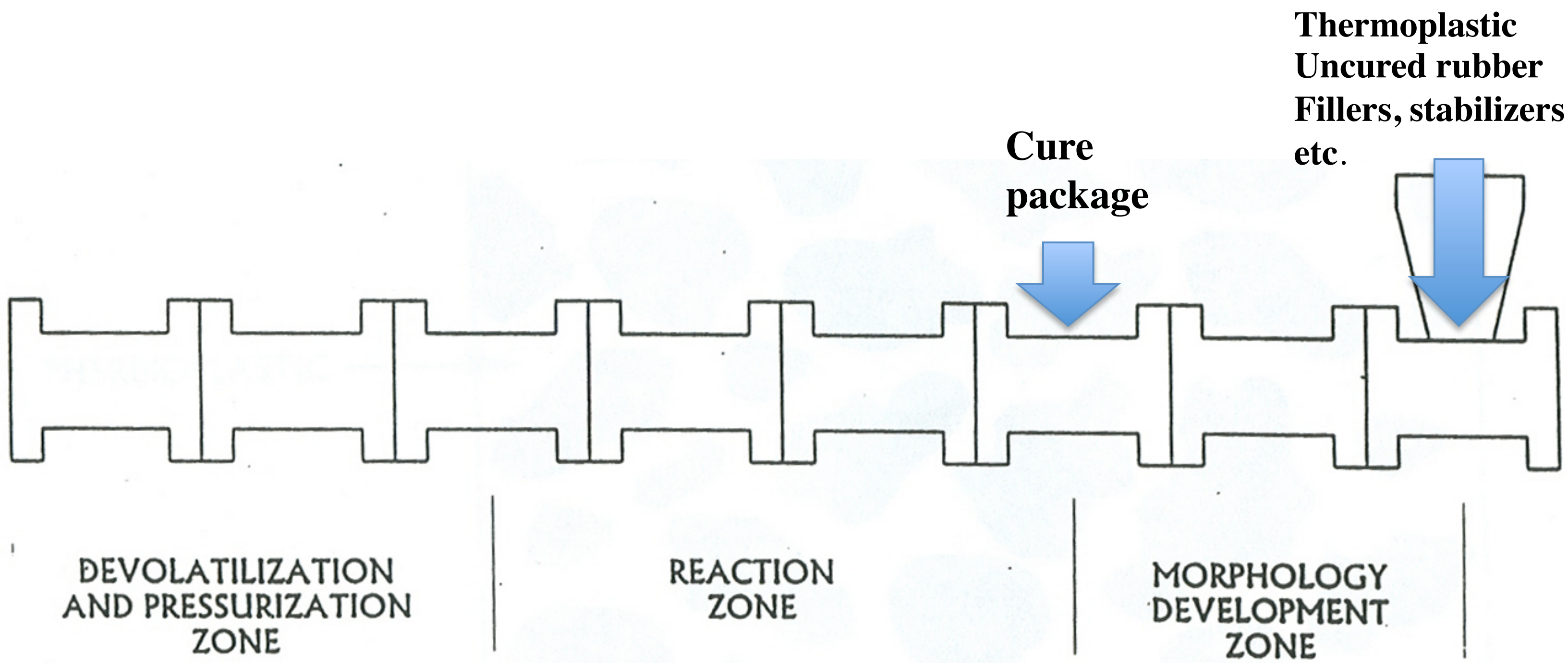
Blends & Alloys - Examples

- **Styrenic block copolymers "SBC"**
  - SBS, SEBS, SIS, SIBS, SEEPS
  - Most frequently compounded with PP, PE, or POE
- **Thermoplastic olefins "TPO"**
- **PVC / NBR blends**
- **Melt processable rubber "MPR"**

Dynamic Vulcanizates - Architecture

- Dynamic vulcanization is a process by which a cross-linkable material is cured in-situ during a melt mixing process
- The result is a dispersion of micron scale particles of cross-linked rubber dispersed in a polymer matrix
- With significant entanglement of the matrix polymer into the surface of the cured particles

Dynamic Vulcanizates – the process



- Final product is process dependent
- Two phase morphology on a micro-scale

Dynamic Vulcanizates - Morphology

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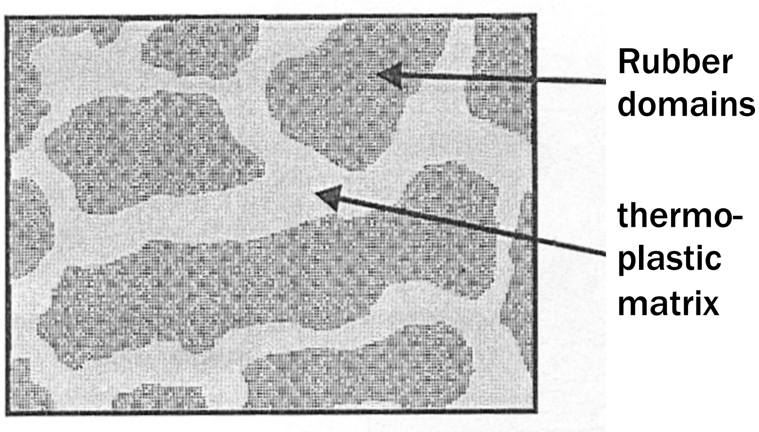
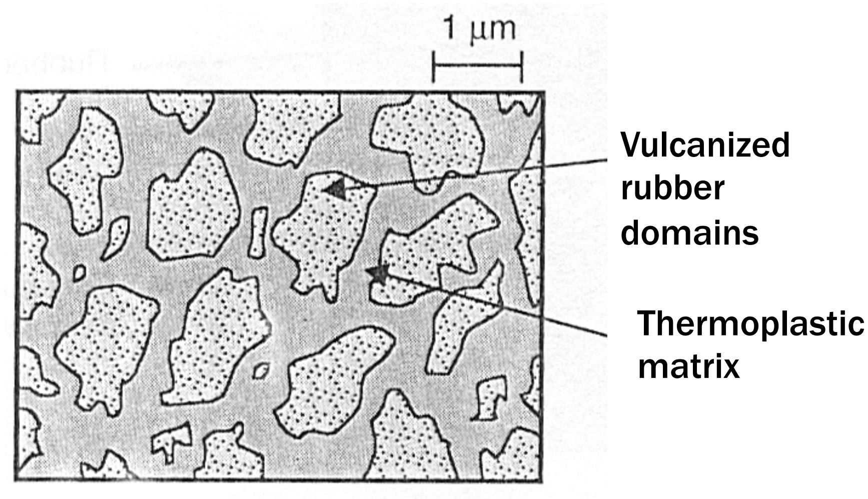
Simple melt-mixing



Coarse *morphology - TPO*

Dynamic vulcanization



Fine *morphology - TPV*

Dynamic Vulcanizates - Mechanism

- The thermoplastic polymer matrix has a melting or glass transition temperature well above room temperature but conducive to thermoplastic processability
- The concentration and modulus of the cured rubber particles is such that they impart the elastomeric character to the solid
- Entanglement of matrix material into the surface of the cured particles enables stress transfer between the phases

Dynamic Vulcanizates - Examples

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- **PP / EPDM**
- **PP / NBR**
- **PA / ACM**
- **Silicone**
  - PA matrix
  - TPU matrix
- **COPE / ACM**
- **PVDF / FKM**

Lineage (Alphabet Soup)

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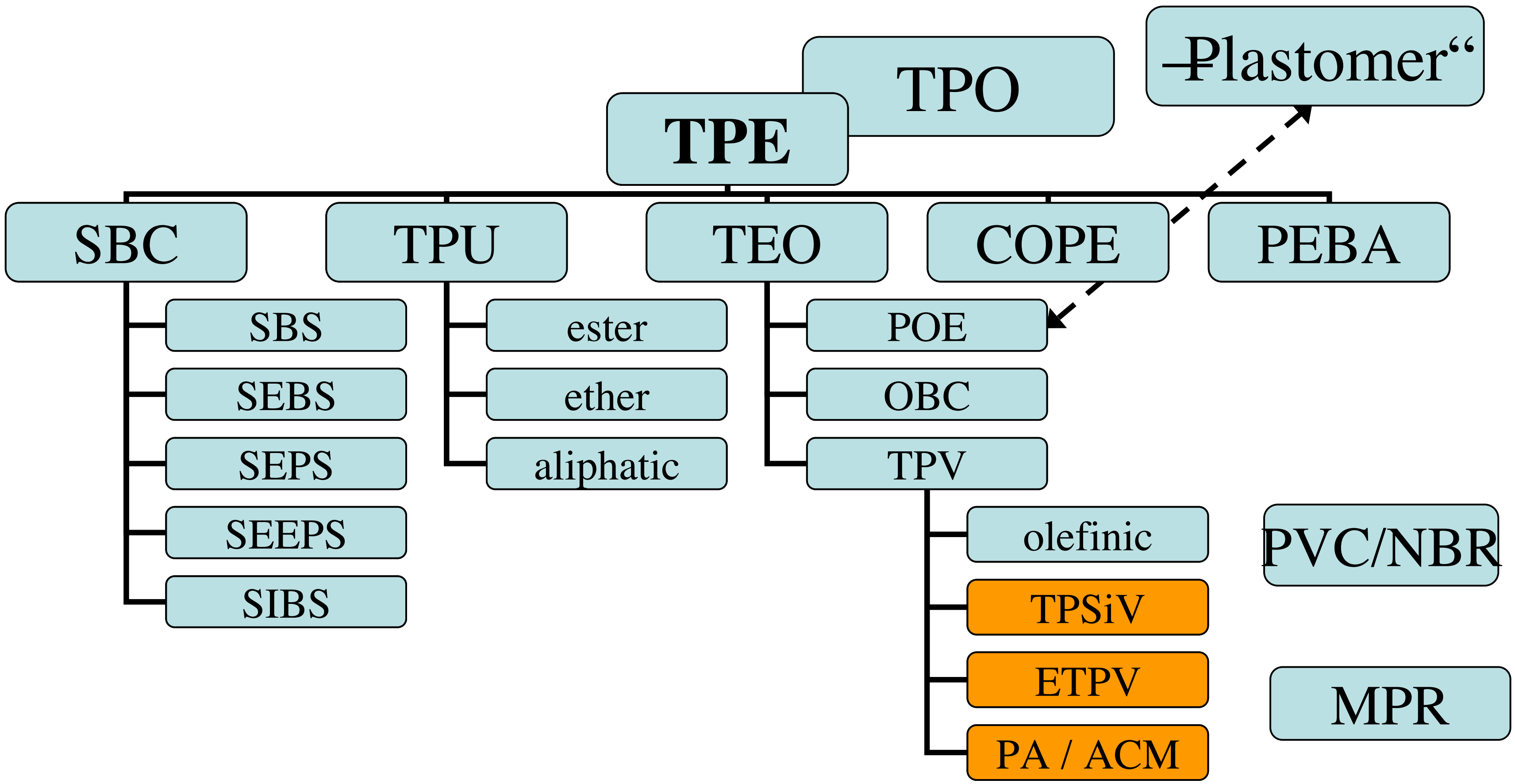

Performance

- TPEs “possess elastomeric behavior” not thermoset rubber properties
- Performance should be considered in terms of part function, not material specification

Relative Value of TPEs

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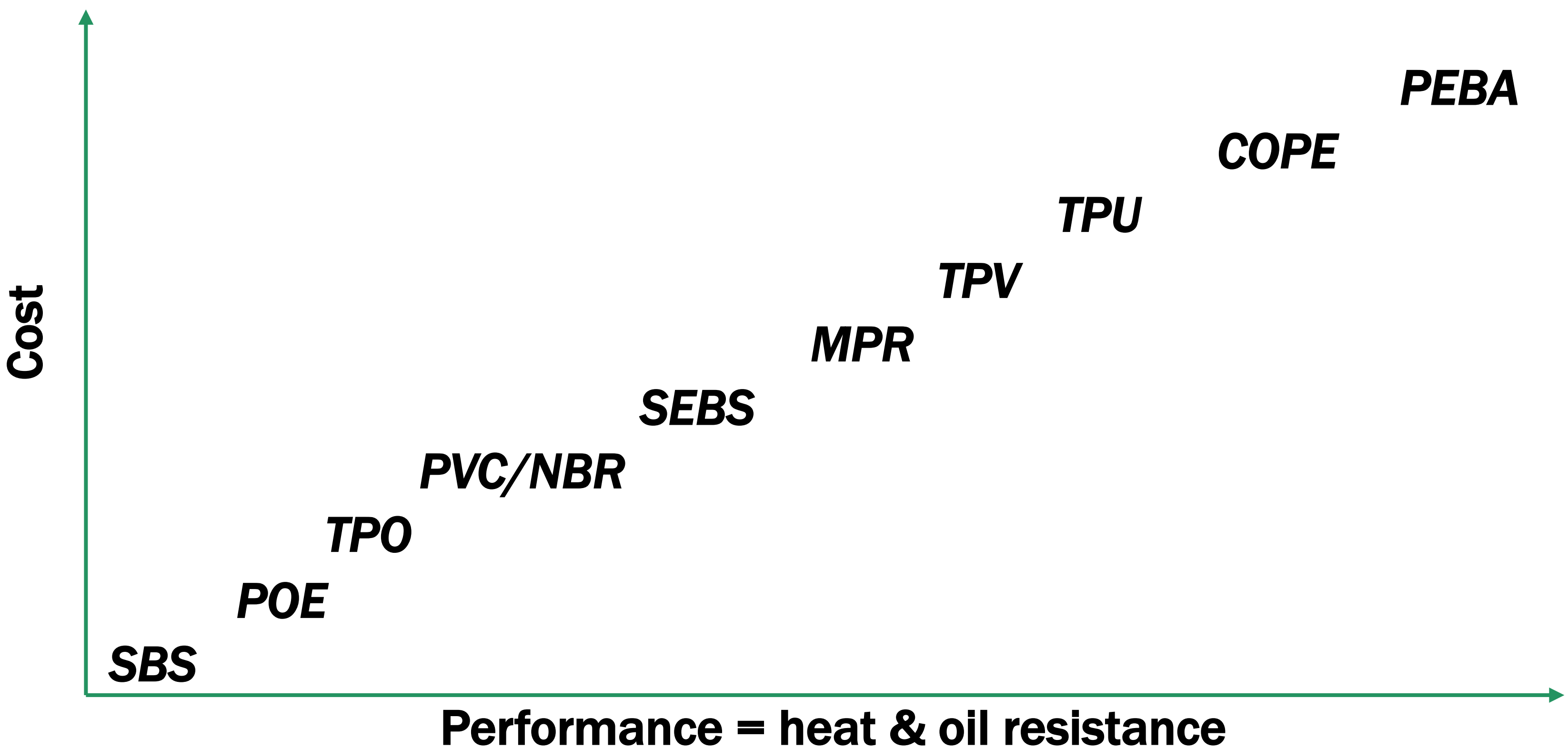
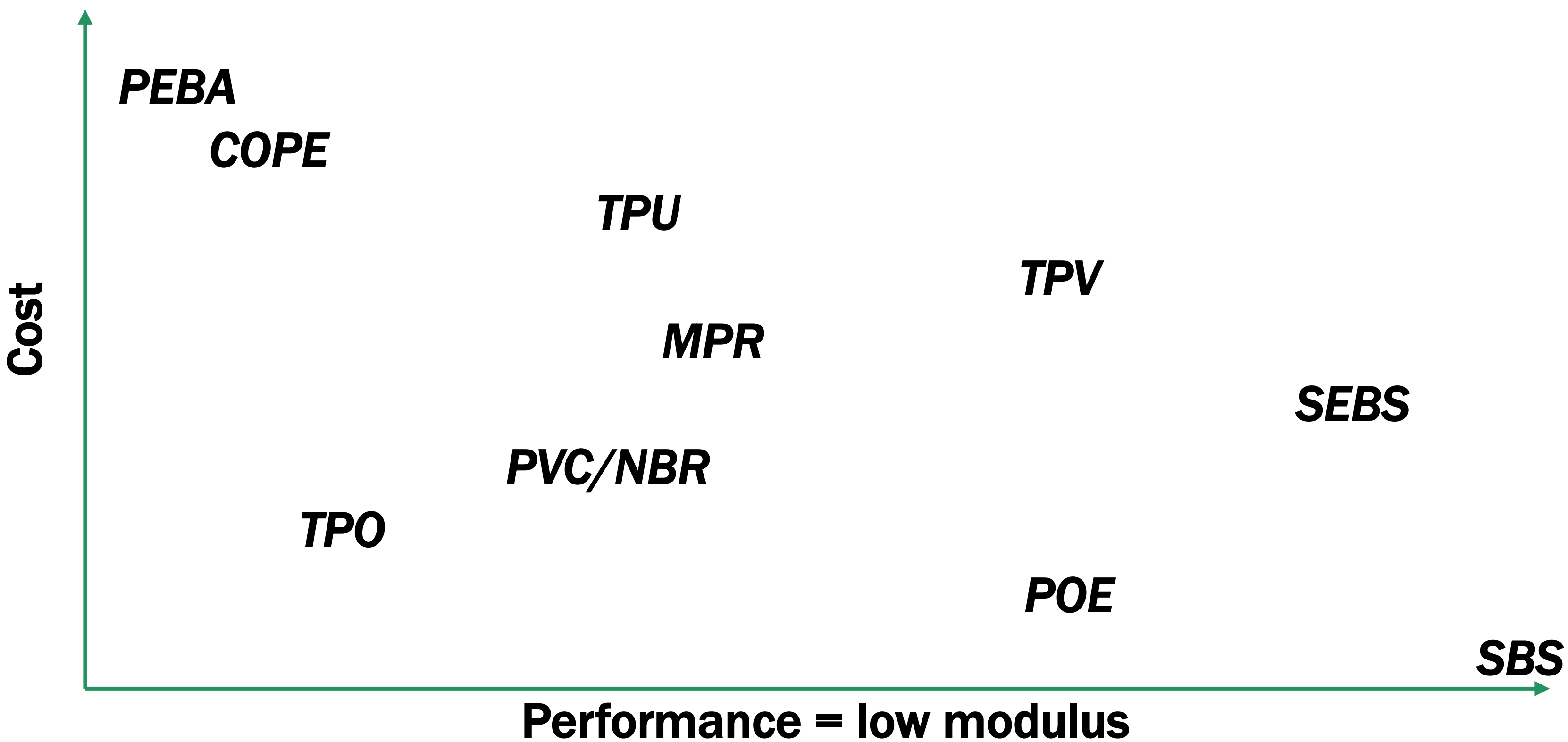


Relative Value of TPEs



Performance – Hardness

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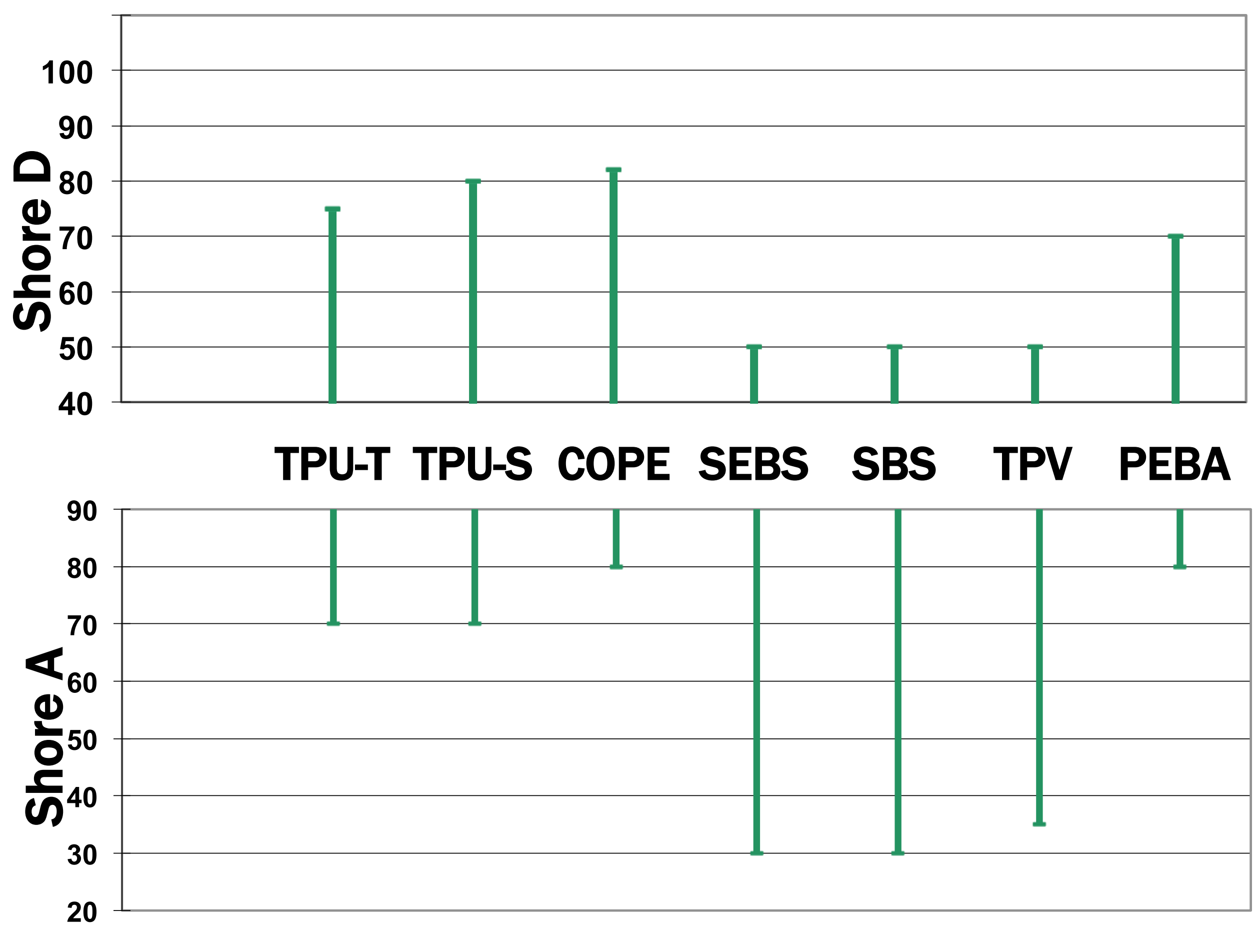

The Problem with Hardness

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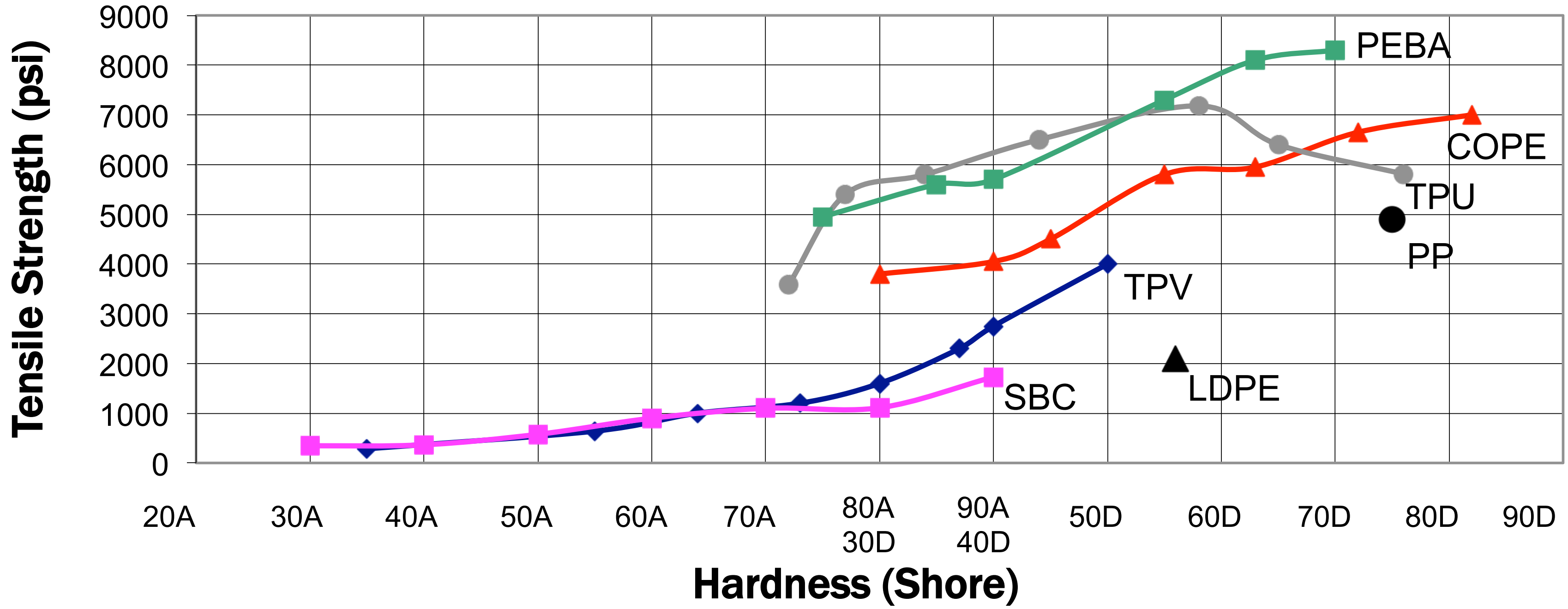
TPE Strength and Hardness Comparison



The Problem with Hardness

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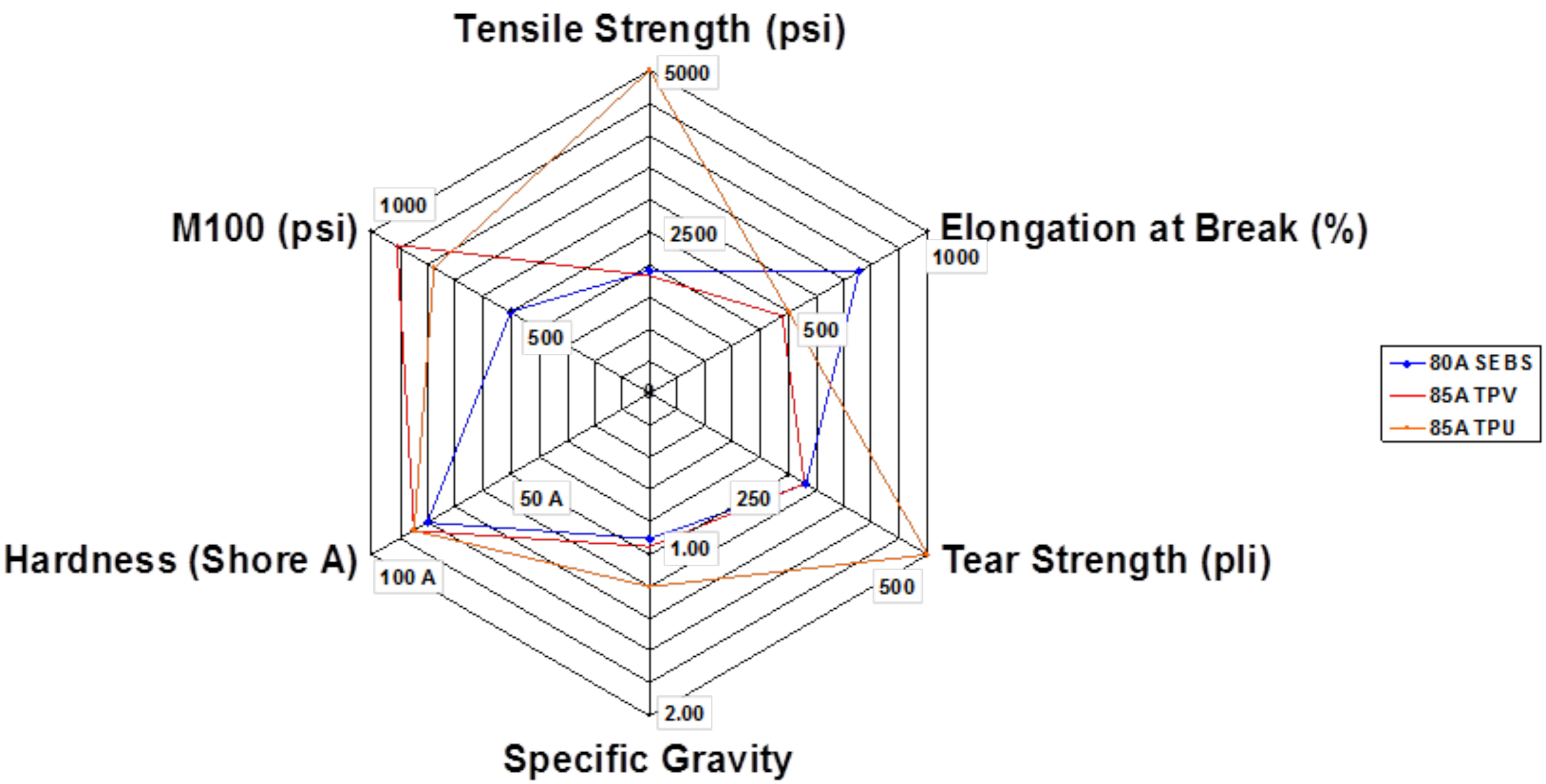

(Static) Use Temperature

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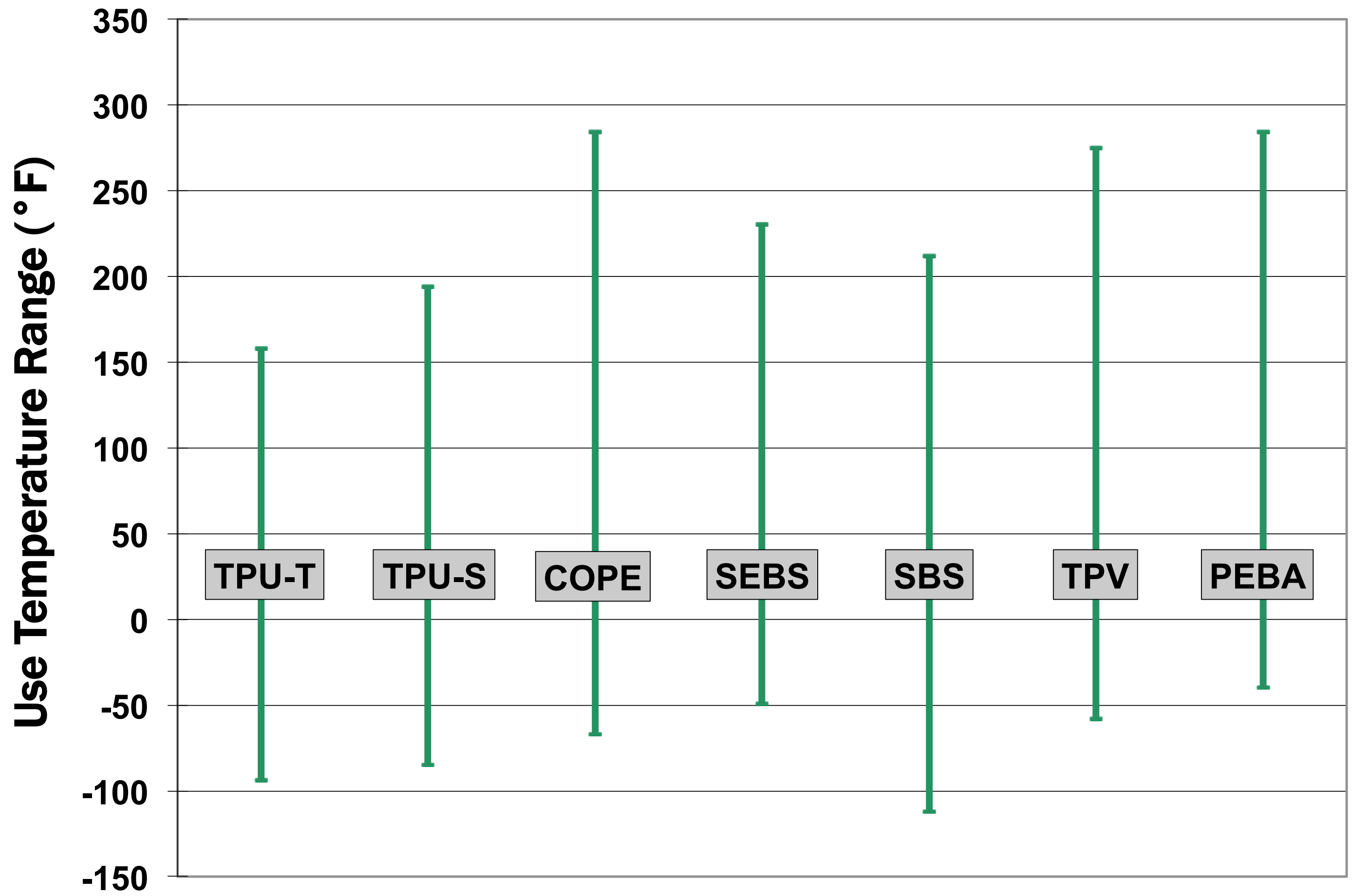

Performance - SBC

- **Hardness range: Shore 00 (gels) – 40D**
  - SBC-based TPEs used in molded or extruded articles are compounds of SBC, olefin, oil, and (often) mineral filler
- **Strengths**
  - Lowest Tg of any TPE
  - Very soft and low stiffness compounds possible
  - Very high elastic limit and elongation at break
  - Translucency/clarity possible
- **Weaknesses**
  - Low continuous use temperature (210 - 230°F)
  - Poor chemical resistance (organic solvents/oils)

Applications - SBC

- Toothbrush handles & pen grips
- “Cause” bracelets & produce bands
- Injection molded synthetic wine corks
- Appliance knobs
- Light duty gaskets
- Vibration damping
- Gel inserts for shoes

Performance – Olefinic TPV

- **Hardness range: 35 Shore A – 50D**
- **Strengths**
  - Best balance of properties of all TPEs
  - Most rubber-like surface feel of all TPEs
  - Highly shear-thinning flow behavior provides an added dimension of process control
- **Weaknesses**
  - Opaque
  - Shear-thinning behavior yields process sensitivity
  - Crosslinked rubber domains are unavailable for additives incorporation

Applications – Olefinic TPV

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- Automotive isolation systems -
- Extruded synthetic wine corks
- Industrial Power Tools
- Automotive sensors & airflow ducts
- Light duty power transmission belts
- Gaskets
- Rack and pinion boots
- Automotive weather seals
- Electric power transmission connectors & switch gear

Performance - TPU

- **Hardness range: 70 Shore A – 70D**
- **Strengths**
  - Best abrasion and tear resistance of all TPEs
  - Very high strength vs. other TPEs of similar hardness
  - Excellent rebound & impact resistance
- **Weaknesses**
  - Processability
    - Drying is required
    - Hydrolysis, shear & thermal stability & tackiness can be problematic
    - Long cycle times
  - Peak performance is achieved by annealing the molded part (look at the hard blocks that haven't made it into the crystalline domains…)

Performance - TPU

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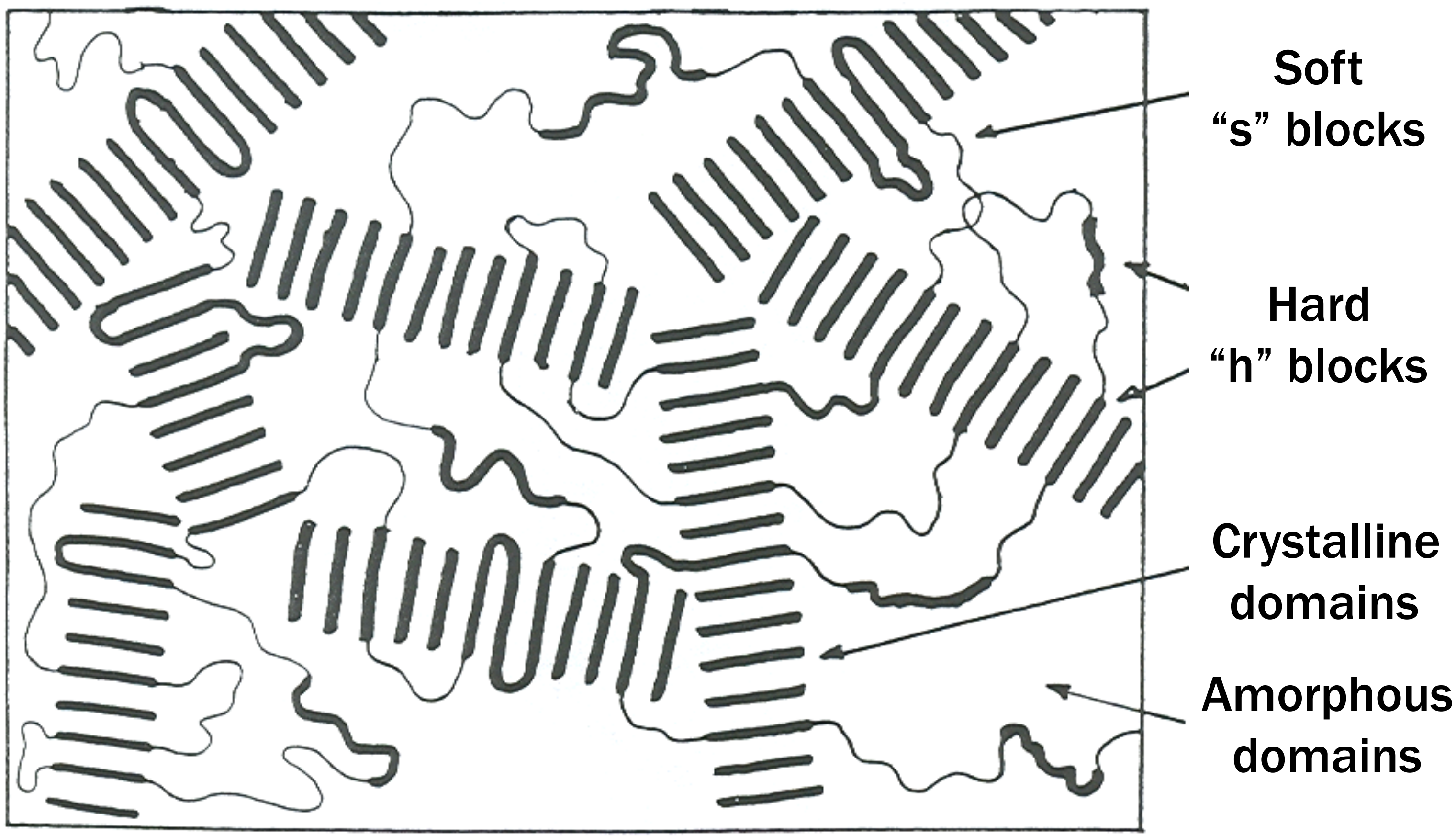

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Applications - TPU

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- Athletic shoe uppers and arches
- Roller blade & caster wheels
- Conveyor belts
- Ball joint boots
- Livestock ear tags
- Synthetic fletchings
- Medical tubing
- Prosthetic fingers
- Automotive shifter handle

Performance - COPE

- **Hardness range: 75 Shore A – 75D**
- **Strengths**
  - Highest use temperature of the most common TPEs
  - Excellent flex life
  - Easier to process than TPU
- **Weaknesses**
  - Generally stiffer than any other TPE of similar hardness
  - Lowest elastic limit of any TPE
  - Solvent / grease resistance is hardness dependent

Applications - COPE

- Semi truck wiring harness
- Constant velocity joint boots
- Coiled pneumatic tubing
- Light duty low noise gears
- Boxed wine & detergent dispensers
- Ski and snow shoe bindings
- Automotive clean & charged airducts (cold side)
- Gas cap tether
- Automotive mounting clip

Performance - PEBA

- **Hardness range: 75 Shore A – 70D**
- **Used in specialty applications (catheters, ski bindings, breathable films, high-speed belting) where cost-performance is justified**
- **Strengths**
  - Excellent flex life w/ low hysteresis
  - Good oil resistance at higher temperatures
- **Weaknesses**
  - Arguably not a TPE at all
  - Best properties correspond w/ highest hardness grades

Compounded TPE's

- **Modification / customization of properties**
  - Strength / stiffness (hardness)
  - Compression set / stress relaxation
  - Tear strength
  - Puncture resistance

- **Aesthetics**
  - Color effects (color, glow-in-the-dark, sparkle)
  - Laser marking effects
  - Feel (rubbery, soft & silky)

- **Processability**
  - Viscosity adjustments
  - Two shot or overmolding adhesion
  - Cycle time improvements

- **Value-added**
  - Electrical conductivity (anti-stat, ATEX, EMI shielding)
  - Flame retardant (halogen free, RoHS compliance)
  - Abrasion & wear resistance / coefficient of friction
  - Specific gravity tuning
  - Structural reinforcement

The Future of TPES

- **TPEs are growing at double the rate of TP market**
  - "demand for TPEs to rise 5.5% per year through 2017"
    - Freedonia market study, "World Thermoplastic Elastomers", published August 2013
- **Key areas of growth continue to be:**
  - Rubber replacement through innovative design
  - Bondable TPE's for overmolding
- **The winners will be**
  - Rubber part suppliers who learn to process thermoplastic elastomers and
  - Thermoplastic part suppliers who learn to incorporate TPEs into part designs

What Does RTP Bring To The Table?

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The broadest offering of TPE chemistries –

- Styrenics
- Olefinics
  - Co-polymers &
  - Vulcanizates
- Thermoplastic urethanes
- Co-polyetheresters
- Co-polyamides
- Custom Alloys to fit an application

In conjunction with the most comprehensive slate of specialty additives around –

- Color effects
  - Edge glow
  - Laser mark
- Conductives
- Anti-stats
- Abrasion and wear resistance
- Flame retardants
- High gravity fillers

What to take away from today.

- What is the operating temperature range for my application?
- What chemical and/or environmental exposures might there be?
- What are the key performance requirements for the application (beyond just shore hardness)?

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Questions?

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