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HOW TO COMBINE ELASTICITY WITH FIRE PROTECTION?
Progress in ceramifiable composites development

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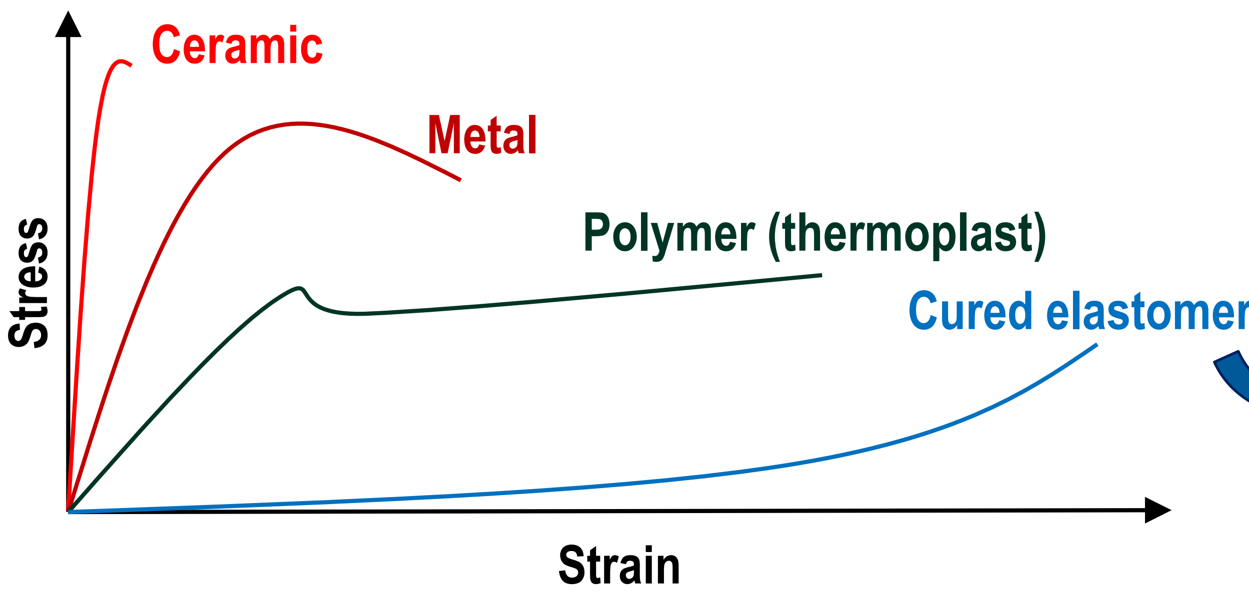
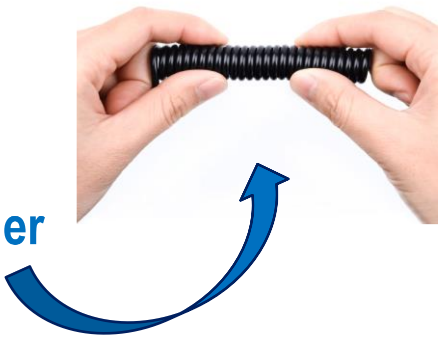
TENSILE PROPERTIES OF MATERIALS
THE UNIQUE PROPERTIES OF ELASTOMERS





- ✓ Elastomers exhibit an outstandingly high reversible deformation under relatively low stress.

ELASTOMER PROPERTIES

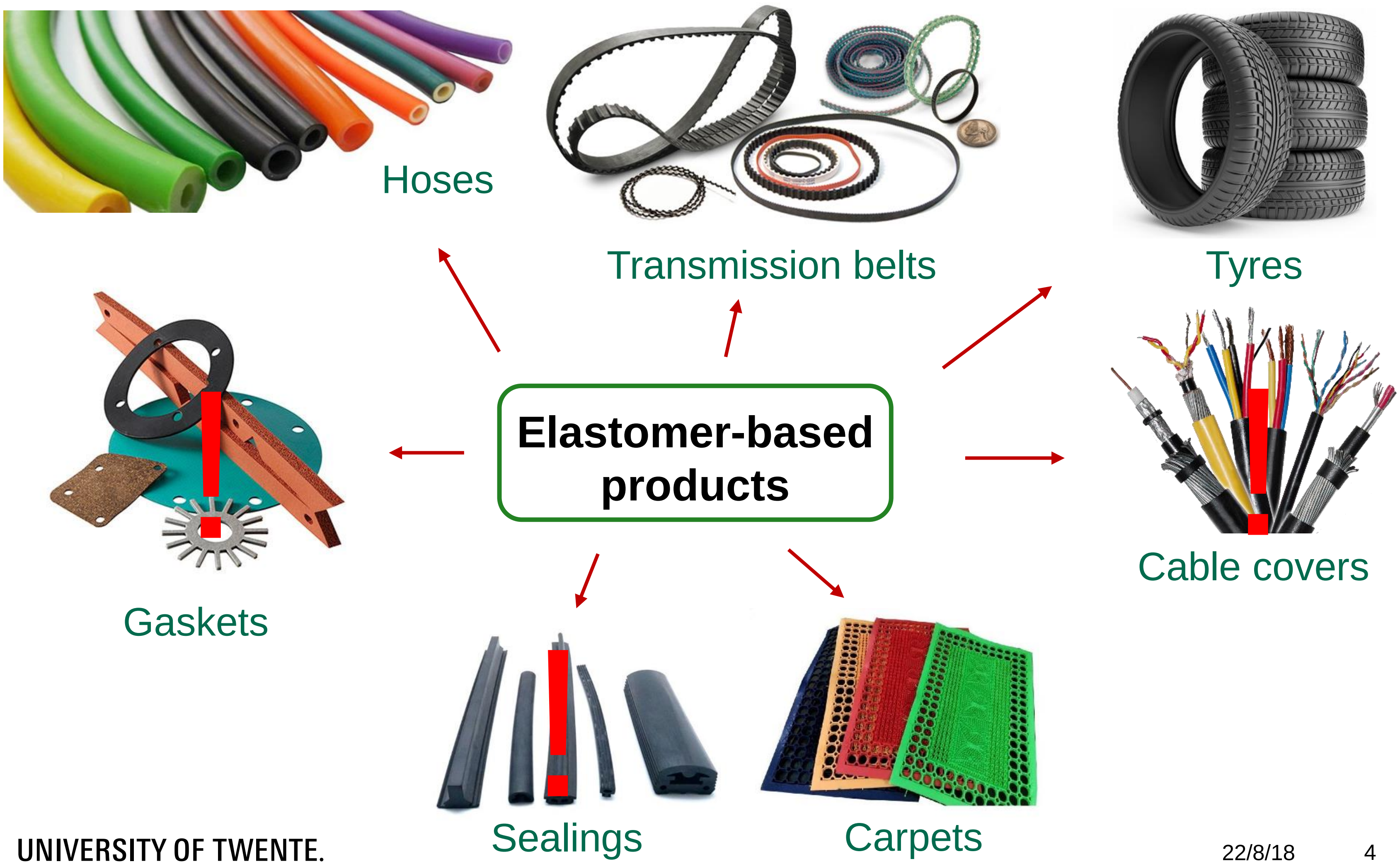
PROS & CONS

- Exceptional elastic, dynamic and dumping properties
- Relatively easy processing and forming even into complex shape
- Good mechanical properties/mass ratio
- Easy coloring
- Good chemical resistance
- Very good electrical resistance

- Limited UV and aging resistance
- Limited recyclability
- Worse mechanical durability then metals or ceramics
- **Low thermal stability and high combustibility**

APPLICATION OF ELASTOMER MATERIALS

THE UNIQUE PROPERTIES OF ELASTOMERS

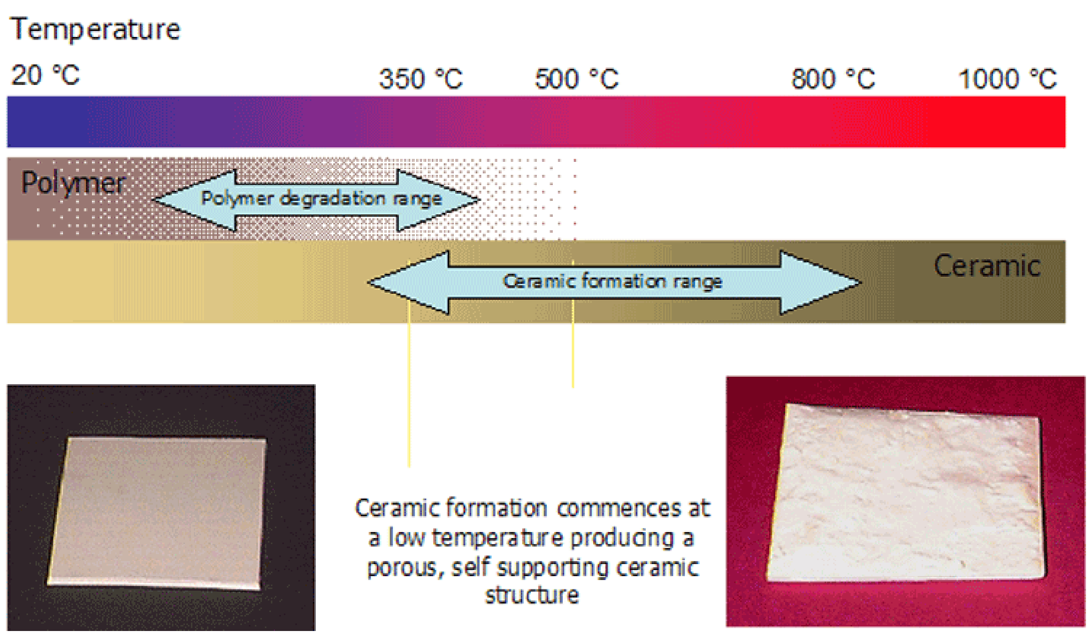


FLAME RETARDANCY OF POLYMER MATERIALS

TYPES OF FLAME RETARDANT ADDITIVES

Main mechanisms of polymer flame retardancy

- Deactivation of radicals
- Barrier-char formation
  - Ceramification (ceramization)
- Quenching and cooling of burning zone



http://www.hkc22.com/fireprotectionindustry_pressroom_ceram_polymerik.html

CERAMIFICATION (CERAMIZATION)

CHARACTERISTICS

A process leading to irreversible **transformation** from **viscoelastic** polymer composite to continuous, **rigid** ceramic structure, during exposition of the composite on fire and/or elevated temperature.

Before ceramification:

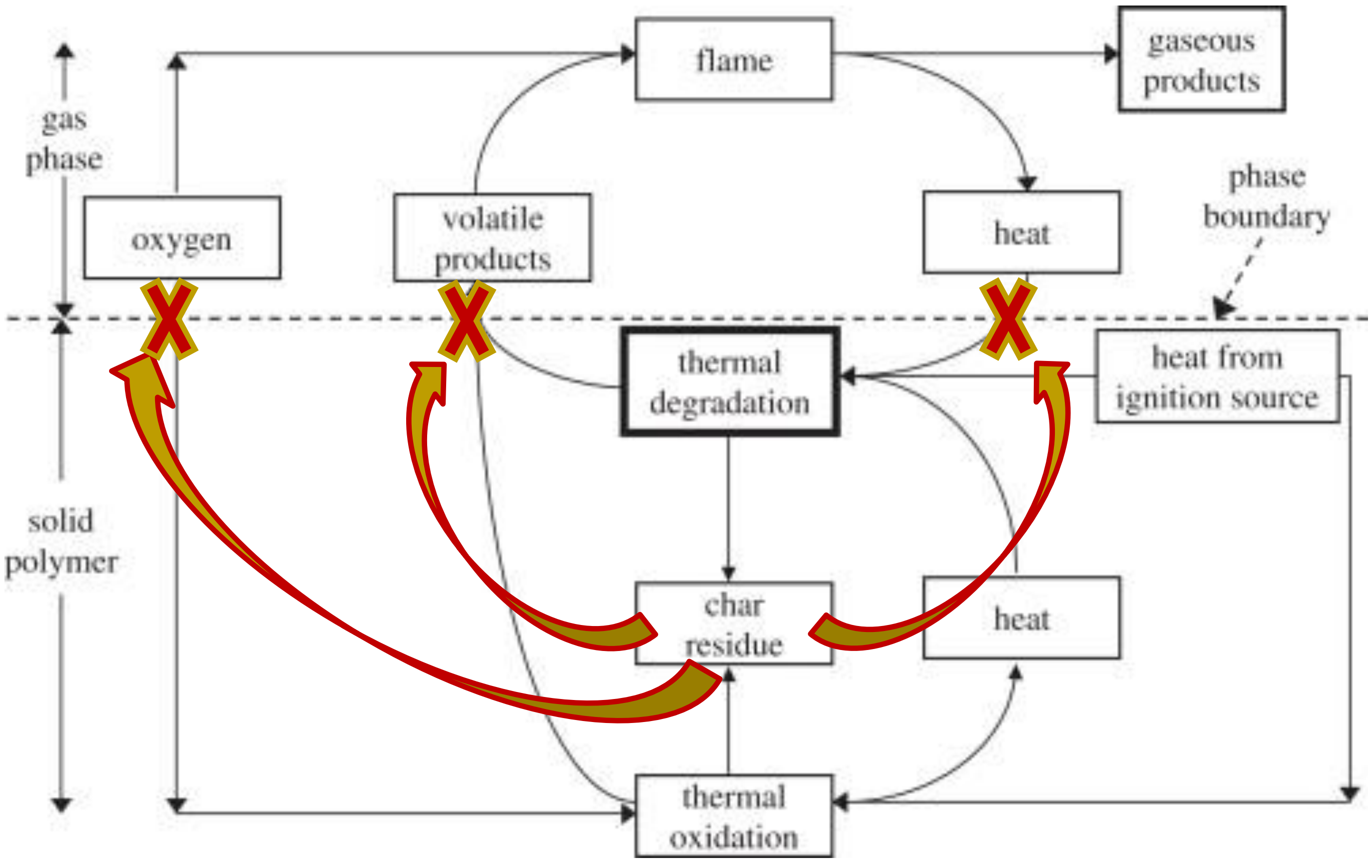
- ✓ Good processability
- ✓ Elasticity
- ✓ Facile colouring
- ❖ Combustibility
- ❖ Low thermal stability

After ceramification:

- ✓ Incombustibility
- ✓ Stiffness
- ✓ High porosity (thermal insulation)
- ✓ High thermal stability

POLYMER COMBUSTION PHENOMENA

REQUIREMENTS FOR COMBUSTION MAINTAINING



G. Camino, et al. Polymer Degradation and Stability (1991) **33**: 131-154.

APPLICATION OF CERAMIFIABLE COMPOSITES

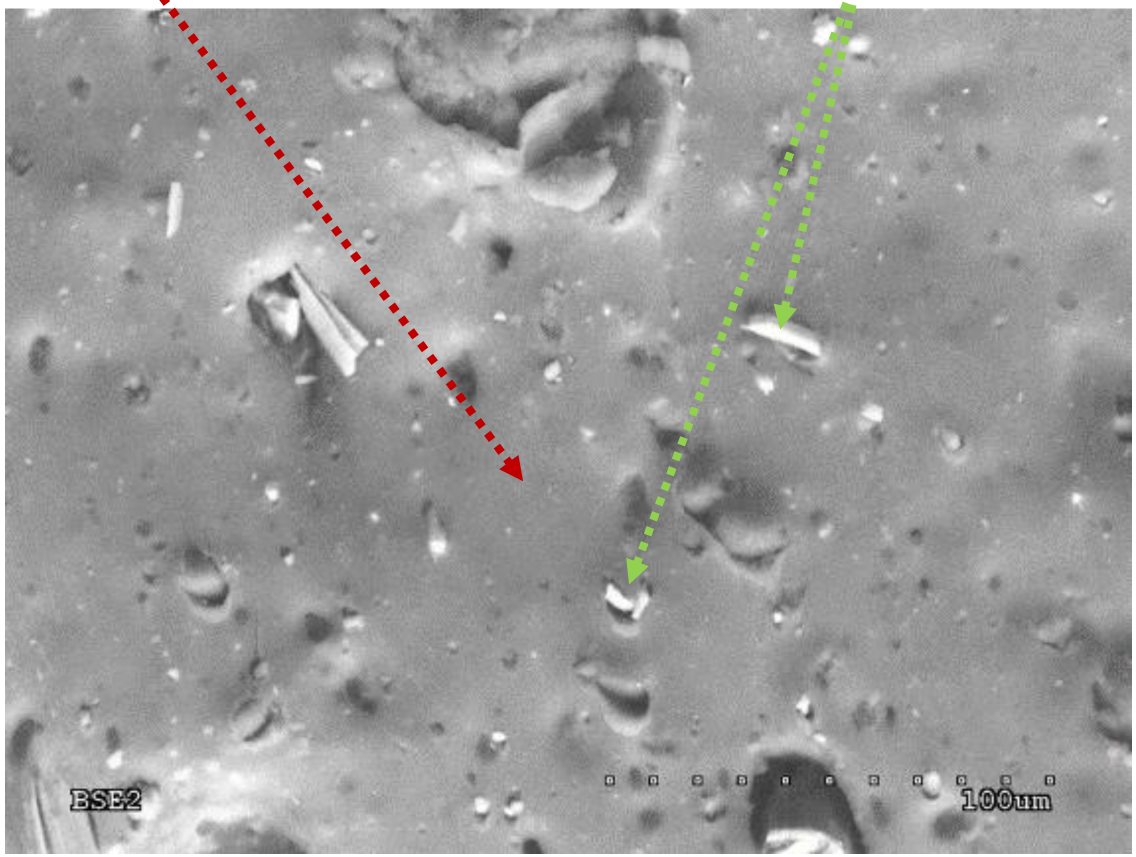
- **Cables assuring integrity of electrical instalation during a fire accident:** New standard for skyscrapers and specialist fireproof building applications
- **Fireproof glazing seal systems:** Cutting off oxygen supply into the fire zone
- **Protective coatings for steel structures:** Steel lose approx. 50% of its load bearing capability at around 500 °C
- **Anti-ablative composites for spacecraft and rocket structures:** Providing shielding effect in high-speed/high-temperature conditions

MICROMORPHOLOGY OF CERAMIFIABLE COMPOSITES

DISPERSSION TYPE OF COMPOSITES – POLIMER MATRIX + DISPERSSED MINERAL FILLERS

Polymer matrix

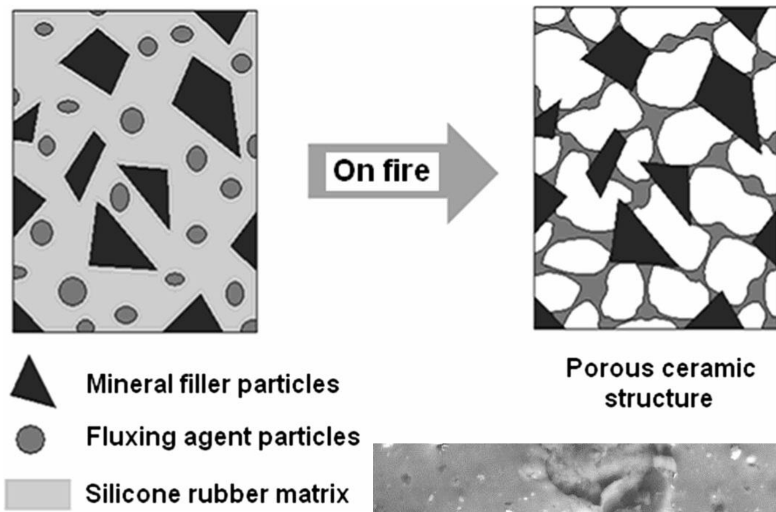
Disperssed mineral fillers

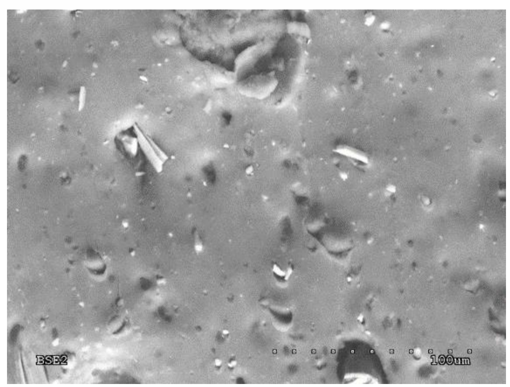


R. Anyszka, et al. Polymer Bulletin (2017) DOI 10.1007/s00289-017-2113-0

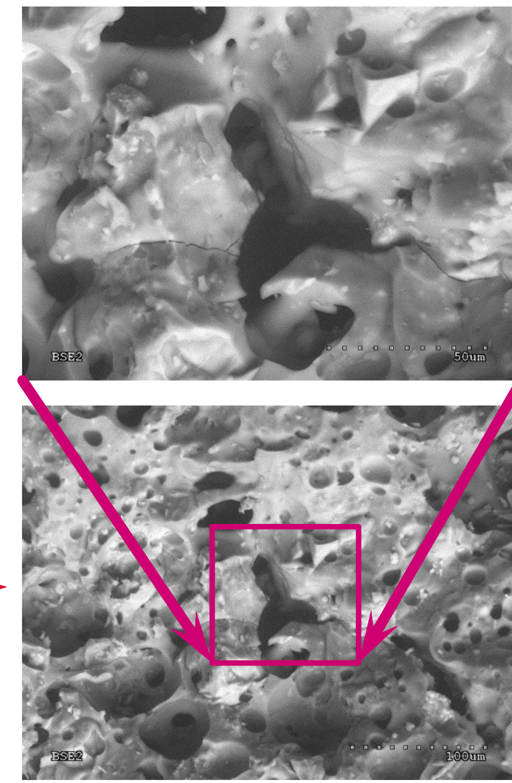
MECHANISMS OF CERAMIFICATION

LOW SOFTENING POINT TEMPERATURE GLASS-FRITS INITIATING CERAMIFICATION





Before ceramification



After ceramification

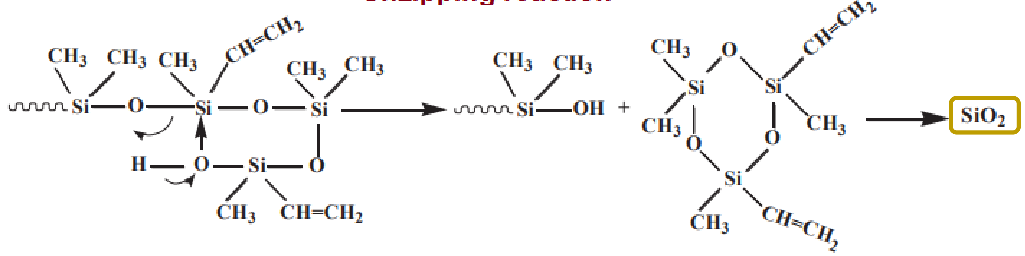
R. Anyszka, et al. Polymer Bulletin (2017) DOI 10.1007/s00289-017-2113-0

THERMAL DECOMPOSITION OF SILICONE RUBBER

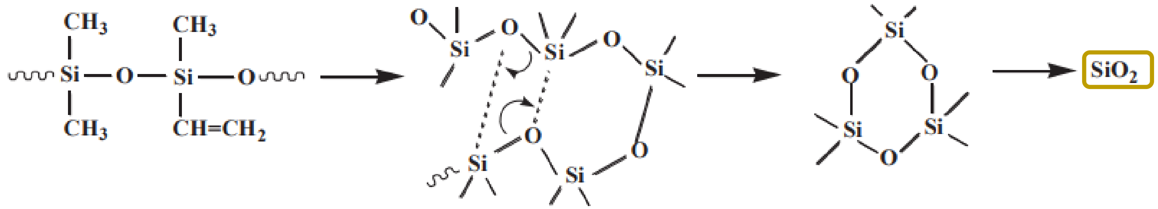
THE BENEFITS OF USING POLYSILOXANES

Thermal degradation mechanisms of PDMS in **presence** of **oxygen** results in formation of amorphous silica

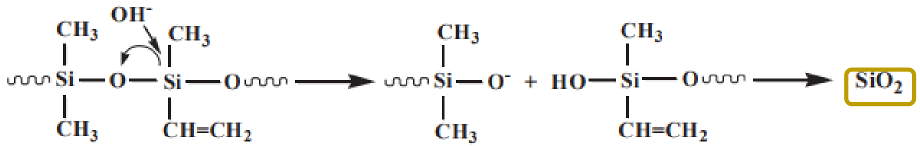
Unzipping reaction



Chain scission reaction

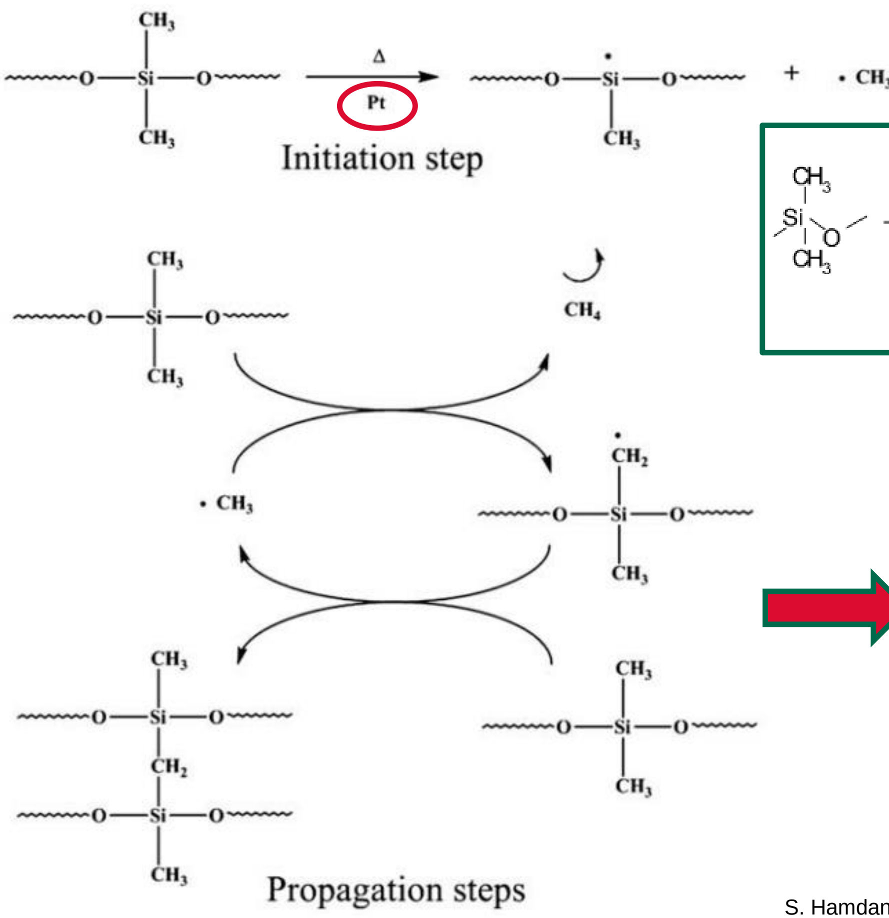


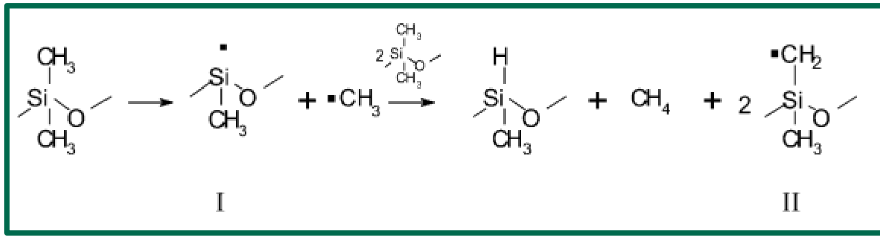
Externally catalyzed hydrolytic cleavage



MECHANISMS OF CERAMIFICATION

CROSS-LINKING OF **PDMS** LEADING TO **SiOC** CERAMIC FORMATION



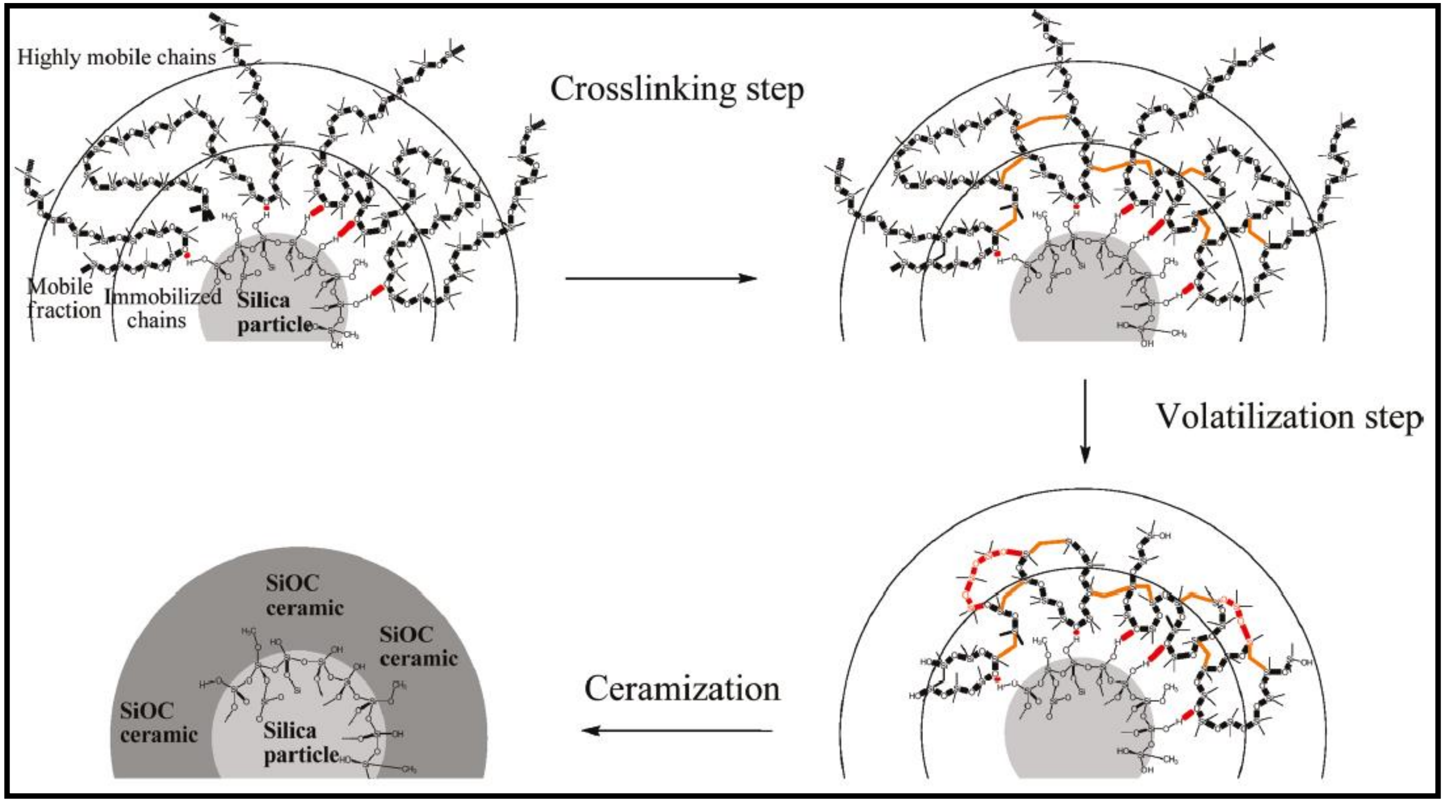


SiOC – silicon-oxycarbide ceramic formation via silicone rubber cross-linking in high temperature

S. Hamdani, et al. Polymer Degradation and Stability (2009) **94**: 465-495.
G. Camino, et al. Polymer (2002) **43**: 2011-2015.
G. Camino, et al. Polymer (2001) **42**: 2395–2402.

MECHANISMS OF CERAMIFICATION

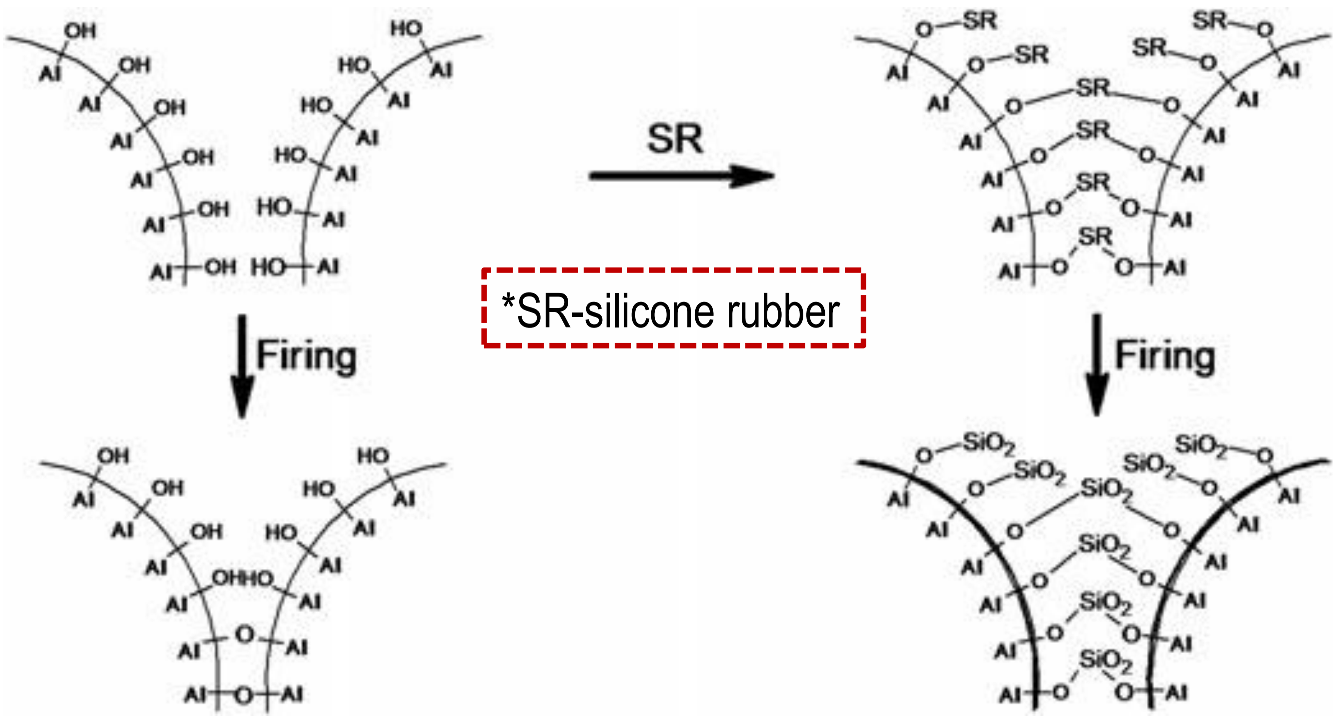
CROSS-LINKING OF **PDMS** LEADING TO **SiOC** CERAMIC FORMATION



E. Delebecq, et al. ACS Applied Materials & Interfaces (2011) **3**: 869-880.

MECHANISMS OF CERAMIFICATION

SINTERING OF MINERAL FILLERS PARTICLES



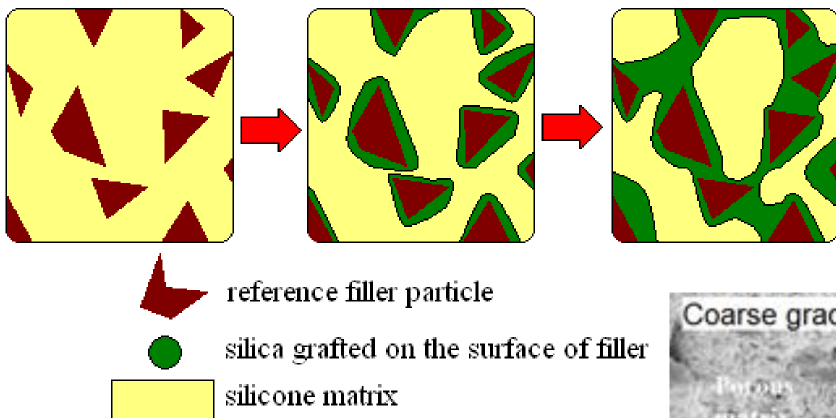
*SR-silicone rubber

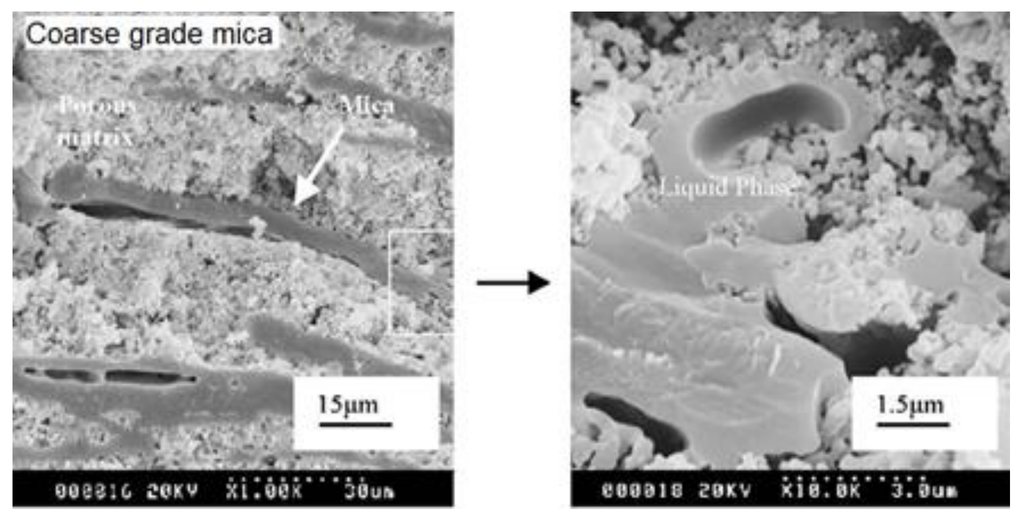
Y. Xiong, et al. Fire and Materials (2012) **36**: 254-263

MECHANISMS OF CERAMIFICATION

IN-SITU SILICA-BRIDGES FORMATION DURING **PDMS** DEGRADATION

Amorphous silica adsorbs on surface of a mineral filler particles forming connecting bridges between them





S. Hamdani, et al. Polymer Degradation and Stability (2009) **94**: 465-495.
R. Anyszka & D. M. Bieliński. Analysis and Performance of Engineering Materials: Key Research and Development. (2015) *Apple Academic Press*

MECHANISMS OF CERAMIFICATION
SILICONE RUBBER VS. ORGANIC RUBBERS

Ceramization mechanism/parameter	Silicone rubber	Organic rubbers
Sintering of mineral filler particles	Yes	Yes
Fluxing agent application	Yes	Yes
Deposition of silica on mineral filler surface	Yes	?
Sintering of mineral fillers accompanied with bonded silicone rubber	Yes	No
Creation of SiOC ceramic via cross-lining of silicone rubber	Yes	No
Creation of SiOC ceramic on surface of silica particles	Yes	No
Price	High	Various
Processability	Good	Various
Maximal capacity of filler	~100 phr	≤ 500 phr
Mechanical properties after addition of high amount of filler	Low	Avarage

POLYMER MATRICES APPLIED FOR CERAMIFIABLE COMPOSITES

References	Polymer matrix
♠ Hamdani S, et al. (2010) *Polym Degrad Stabil* **95**:1911–1919; ♠ Hamdani-Devarennes S, et al.. (2011) *Polym Degrad Stabil* **96**:1562–1572; ♠ Hamdani-Devarennes S, et al. (2013) *Polym Degrad Stabil* **98**:2021–2032; ♠ Hamdani S, et al. (2009) *Polym Degrad Stabil* **94**:465–495; ♠ Mansouri J, et al. (2007) *J Mater Sci* **42**:6046–6055; ♠ Mansouri J, et al. (2005) *J Mater Sci* **40**:5741–5749; ♠ Mansouri J, et al. (2006) *Mat Sci Eng A* **425**:7–14; ♠ Hanu LG, et al. (2004) *J Mater Process Tech* **153–154**:401–407; ♠ Hanu LG, et al. (2006) *Polym Degrad Stabil* **91**:1373–1379; ♠ Hanu LG, et al. (2005) *Mat Sci Eng A* **398**:180–187; ♠ Wang J, et al.. (2015) *Polym Degrad Stabil* **121**:149–156; ♠ Xiong Y, et al. (2012) *Fire Mater* **36**:254–263; ♠ Pedzich Z, et al. (2013) *J Mat Sci Chem Eng* **1**:43–48; ♠ Pędzich Z, et al. (2014) *Key Eng Mat* **602-603**: 290-295; ♠ Imiela M, et al. (2016) *J Therm Anal Calorim* **124**:197–203; ♠ Anyszka R, et al. (2015) *J Therm Anal Calorim* **119**:111–121; ♠ Anyszka R, et al. (2014) *Przem Chem* **93**:1291–1295; ♠ Anyszka R, et al. (2014) *Przem Chem* **93**:1684–1689; ♠ Anyszka R, et al. (2017) *Polym Bull* **75**: 1731-1751; ♠ Delebecq E, et al.(2011) *ACS Appl Mater Interfaces* **3**:869–880; ♠ Gardelle B, et al.(2014) *J Fire Sci* **32**:374–387; ♠Lou F, et al. (2017) *J Therm Anal Calorim* **130**:813–821; ♠ Guo J, et al. (2018) *Polymers* **10**:388	**Silicone rubber (PDMS)**
♠ Di H-W, et al. (2015) *RSC Adv* **5**:51248–51257; ♠ Gong X, et al. (2017) *Sci Eng Compos mater* **24**:599-608; ♠ Li Y-M, et al. (2018) *Polym Degrad Stabil* **153**:325-332; ♠Zhao D, et al. (2018) *Polym Degrad Stabil* **150**:140-147	**Poly(ethylene-co-vinyl acetate) (EVA)**
♠ Ferg EE, et al. (2017) *Polym Composite* **38**:371–380	**EVA/PDMS blend**
♠ Shanks RA, et al. (2010) *Express Polym Lett* **4**:79–93	**Poly(vinyl acetate)**
♠ Pei Y, et al. (2016) *Materials Science and Environmental Engineering*, Taylor & Francis 197-200; ♠ Anyszka R, et al. (2017) *High Temp Mater Proc* **36**:963-970	**Ethylene-propylene-diene rubber (EPDM)**
♠ Wang T, et al. (2010) *Adv Compos Lett* **19**:175–179	**Polyethylene (PE)**
♠ Anyszka R, et al. (2016) *Materials* **9**:604	**Styrene-butadiene rubber (SBR)**
♠ Shanks RA, et al. (2010) *Adv Mat Res* **123–125**:23–26	**Polyester**
♠ Fan S, et al. (2017) *Acta Mater Compos Sinica* **34**:60-66; ♠ Shi M, et al. (2018) J Wuhan Univ Technol, Mater Sci Edition **33**:381-388; ♠ Wang F, et al. (2017) *High Perform Polym* **29**:279-288	**Boron phenolic resin**
♠ Rybinski P, et al. (2018) *J Compos Mater* **52**:2815-2827	**Acrylonitrile-butadiene rubber (NBR)**

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22 August 2018,
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Thank you for your kind attention!

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