Elastomer Technology & Engineering

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Plasma polymerization of Acetylene and Thiophene onto Silica - an Alternative to Improve Reinforcement of Silica in S-SBR and EPDM

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Contents

Introduction

Filler reinforcement

Filler dispersion depends on

Polymer:

- ð Type
- ð Molecular weight

Filler:

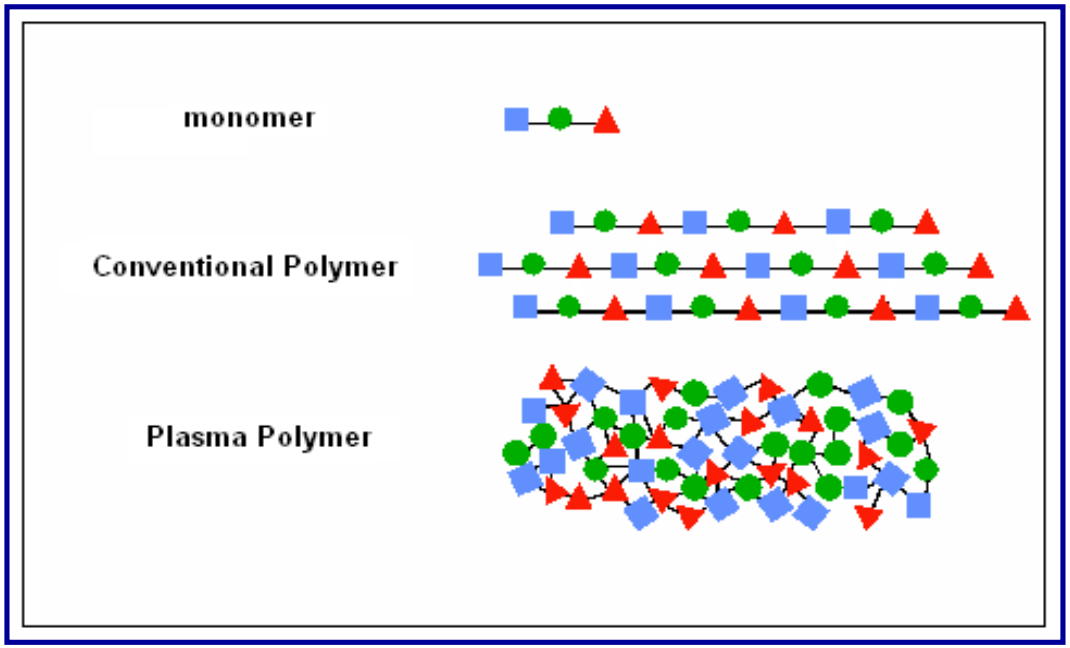
- ð Particle size distribution
- ð Structure
- ð Surface activity

è **Non-uniform dispersion influences the properties**

Introduction

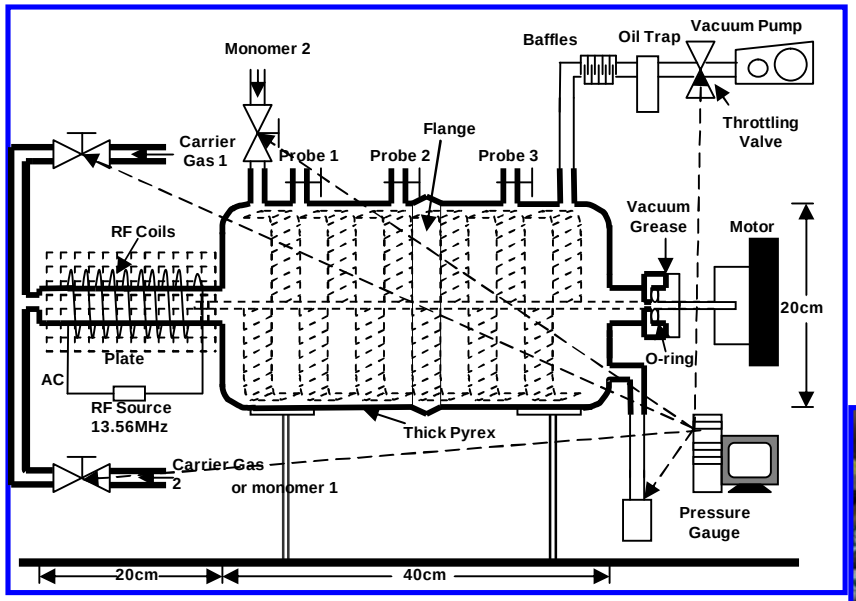
Plasma Polymerization

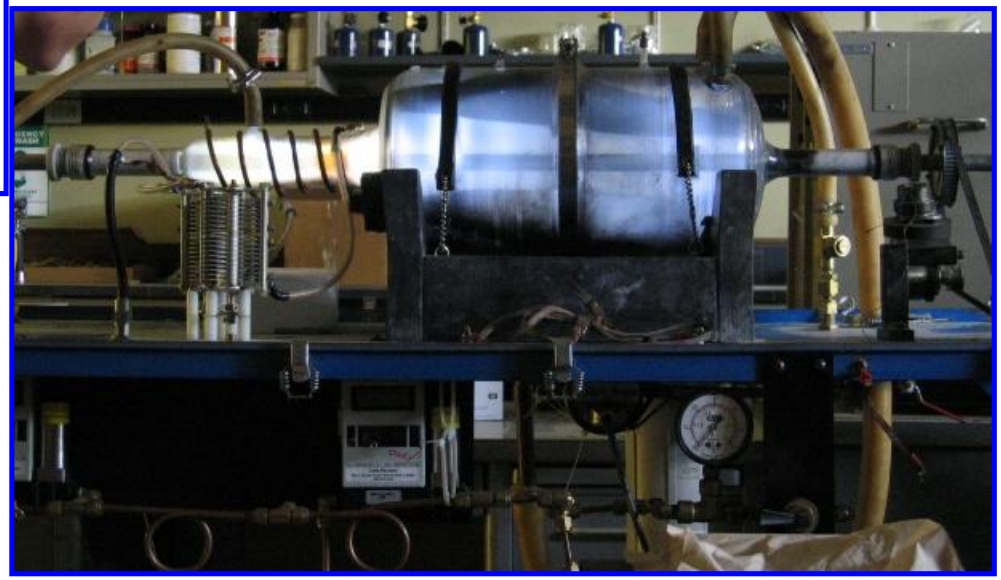
Monomer → **Plasma-Polymer**



- highly crosslinked
- disordered structure
- two-dimensional network
- thermally, chemically stable
- very adherent
- bulk properties preserved

Introduction
Plasma reactor





- RF (13.56MHz) plasma: very stable and reactive
- Tumbler reactor: 350 g capacity

Aim of the work

- Comparison of the effect of Plasma-thiophene and –acetylene coated silica in terms of their:

  - compatibility
  - wettability
  - dispersion

with S-SBR and EPDM

…achieved by surface modification by plasma polymerization process

Experimental
Materials

Polymers:

- S-SBR (Buna® VSL 5025-0 HM, Lanxess GmbH):

  25 wt% styrene, 75 wt% butadiene

- EPDM (Keltan® 4703, DSM Elastomers B.V.):

  9 wt% ethylidene norbornene, 48 wt% ethylene, 43 wt% propylene

Fillers:

- Precipitated silica (Ultrasil VN3, Degussa GmbH)

Plasma monomer:

-High purity acetylene (C_2H_2, Wright Brothers, Inc.)

-High purity thiophene (C_4H_5S, Sigma-Aldrich, Inc.)

Silica coupling agent:

Bis-(triethoxysilylpropyl) tetrasulphide, TESPT (Si69, Degussa GmbH)

Experimental

Plasma polymerization

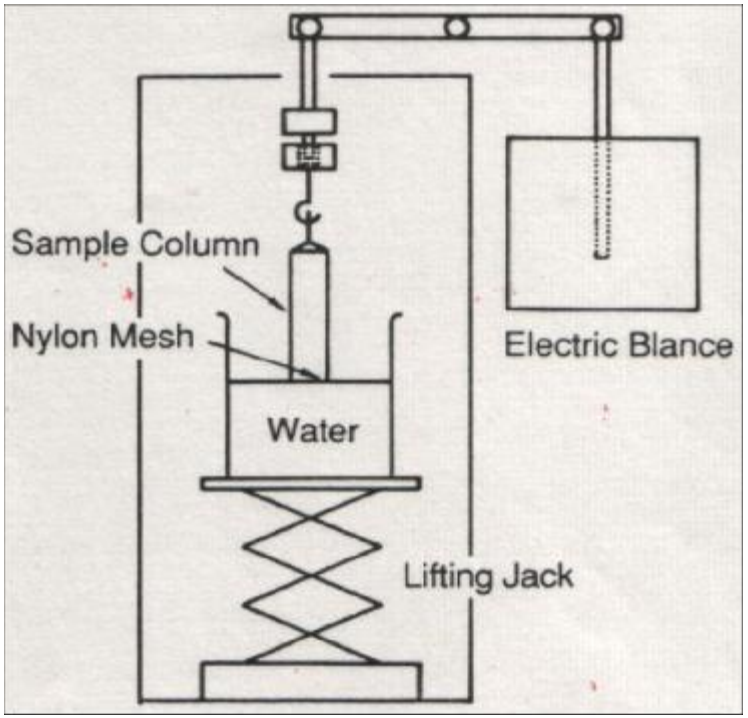
Monomers: - Acetylene

- Thiophene

Code	Power (W)	Monomer Pressure (Pa)	Time (minutes)
PA-Silica	100	53	90
PTh-Silica	100	20	90

Experimental
Filler characterization

ð Water penetration measurements



ð Thermo-Gravimetric Analysis

(TGA7, Perkin-Elmer; rate of heating 10°C/min.)

ð Time-of-Flight Secondary Ion Mass Spectrometry (ToF- SIMS)

Experimental

Compounding

Components	Samples							
	SU	SPA	SPTh	ST	EU	EPA	EPTh	ET
	phr	phr	phr	phr	phr	phr	phr	phr
S-SBR	100	100	100	100	--	--	--	--
EPDM	--	--	--	--	100	100	100	100
Silica	50	50	50	50	50	50	50	50
ZnO	2.5	2.5	2.5	2.5	5	5	5	5
Stearic acid	2.5	2.5	2.5	2.5	2.0	2.0	2.0	2.0
Silane (TESPT)	--	--	--	4	--	--	--	4
Sulfur	1.5	1.5	1.5	1.04	1.5	1.5	1.5	1.04
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DPG	1.5	1.5	1.5	1.5	--	--	--	--
TMTD	--	--	--	--	0.8	0.8	0.8	0.8
ZBEC	--	--	--	--	1.5	1.5	1.5	1.5

U: *Untreated;* ***PA:*** *Plasma acetylene coated;* ***PTh:*** *Plasma thiophene coated;* ***T:*** *Silanised with TESPT*

S: *S-SBR;* ***E:*** *EPDM*

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Experimental

Mixing procedure

Mixing: Brabender 350S

Step 1:	
Time (mins.)	**Action**
0	Filling of the chamber of the Brabender with gum rubber, lowering of the Plunger.
1	Raising of the plunger and adding ZnO, stearic acid, ½ silica and ½ silane (if the masterbatch preparation was with silane), lowering of the plunger.
2	Raising of the plunger and adding ½ silica and ½ silane (if the masterbatch preparation was with silane), lowering of the plunger.
4	Sweep
6	Dump of the masterbatch
Step 2:	
0	Load compound
5	Dump

Curatives: added on a two roll mill

Curing: Wickert laboratory press WLP 1600/5*4/3 at 160°C, 100 bar

Experimental

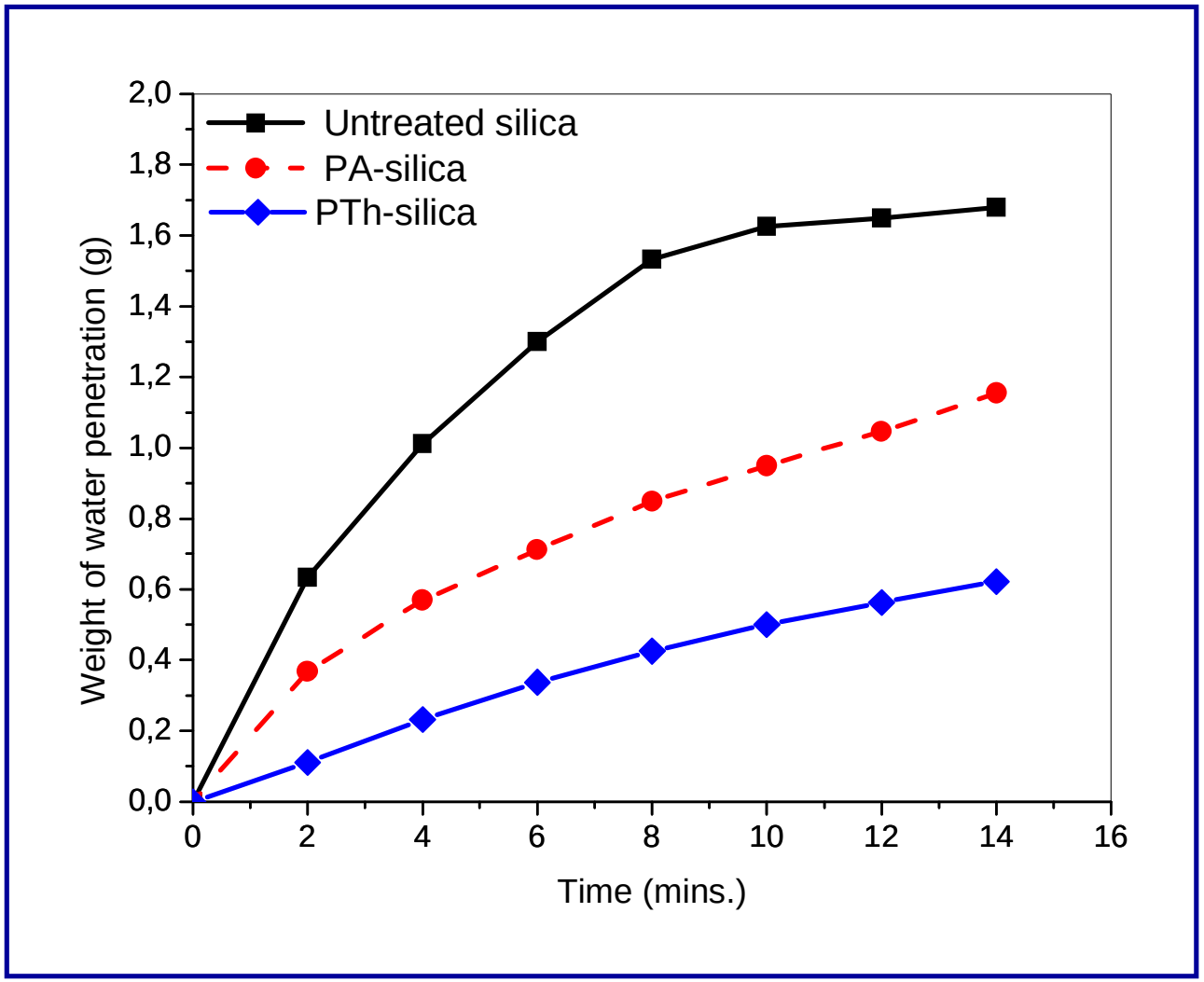
Compounds testing

- Payne effect (RPA 2000, Alpha Technologies)
- Bound rubber content
- Cure characteristics (RPA 2000, Alpha Technologies)
- Reinforcement parameter (α_F)
- Tensile properties (Zwick Z020)
- Relative ranking of cross-link density (1/Q)

Plasma polymerization of acetylene and thiophene onto silica fillers

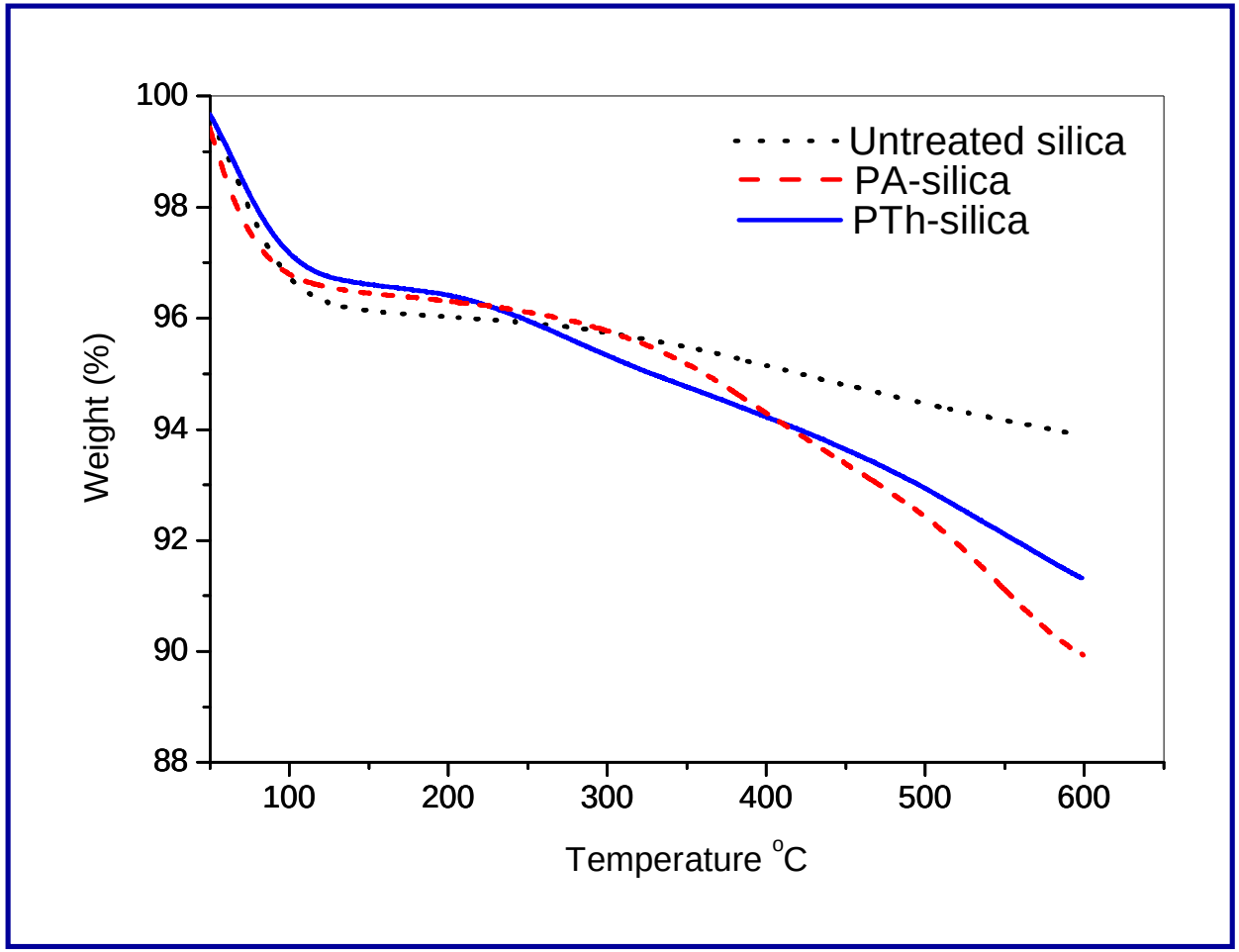
Results & discussion

Hydrophobicity: penetration



Results & discussion

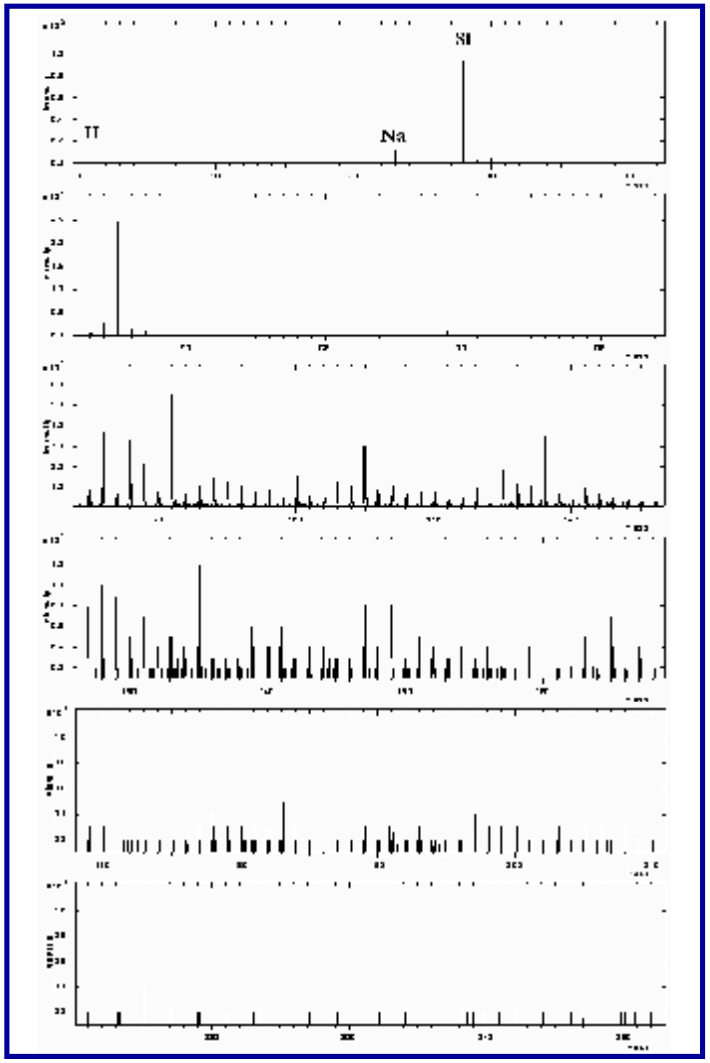
Weight loss (TGA)



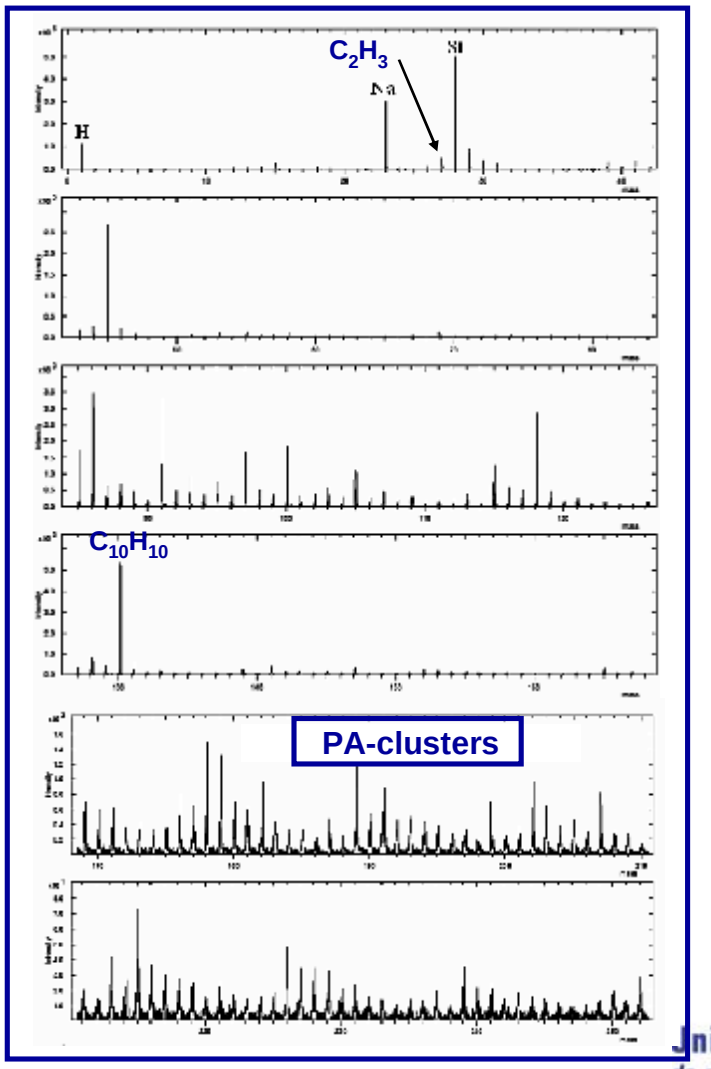
Results & discussion

Chemical composition of the surface: ToF-SIMS

Untreated



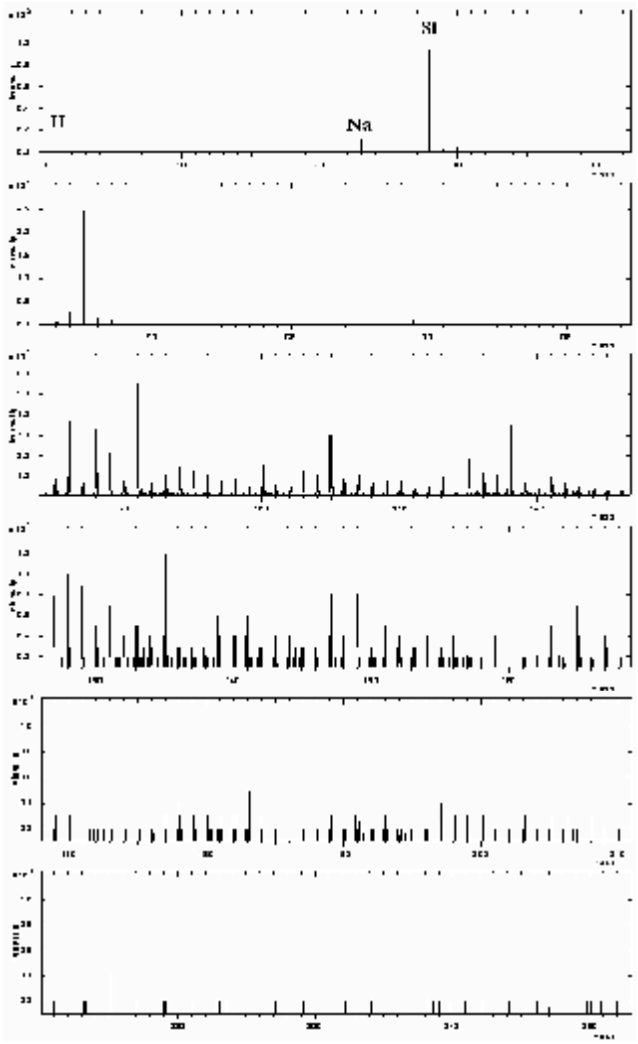
PA-treated



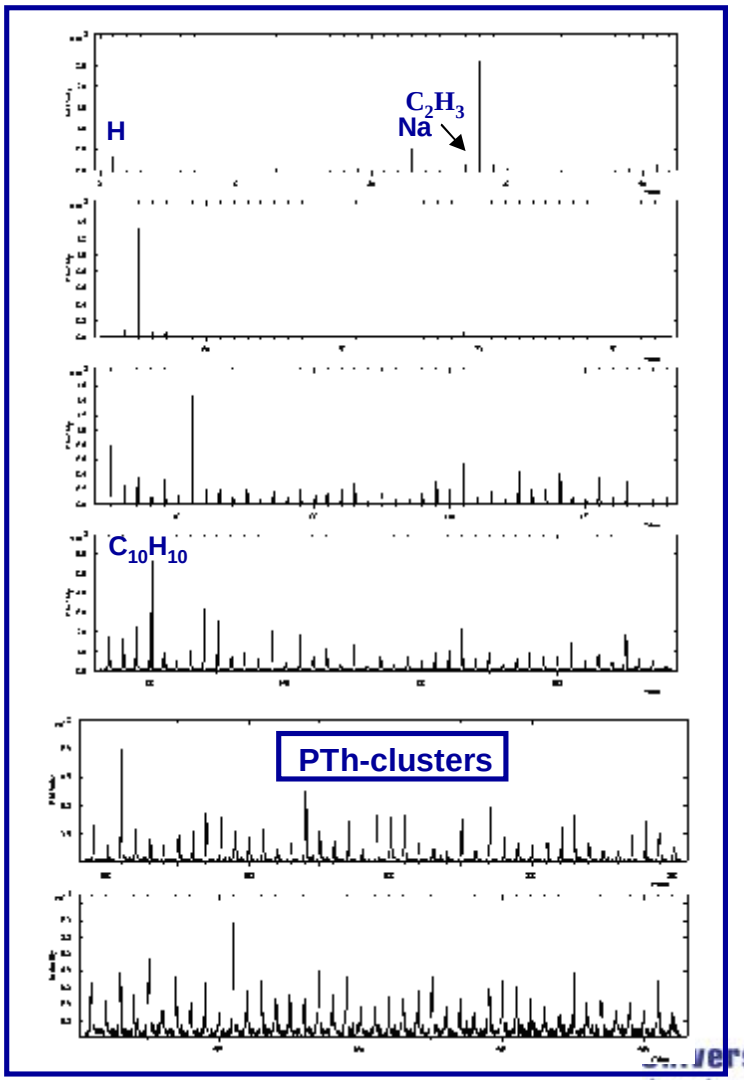
Results & discussion

Chemical composition of surface: ToF-SIMS

Untreated



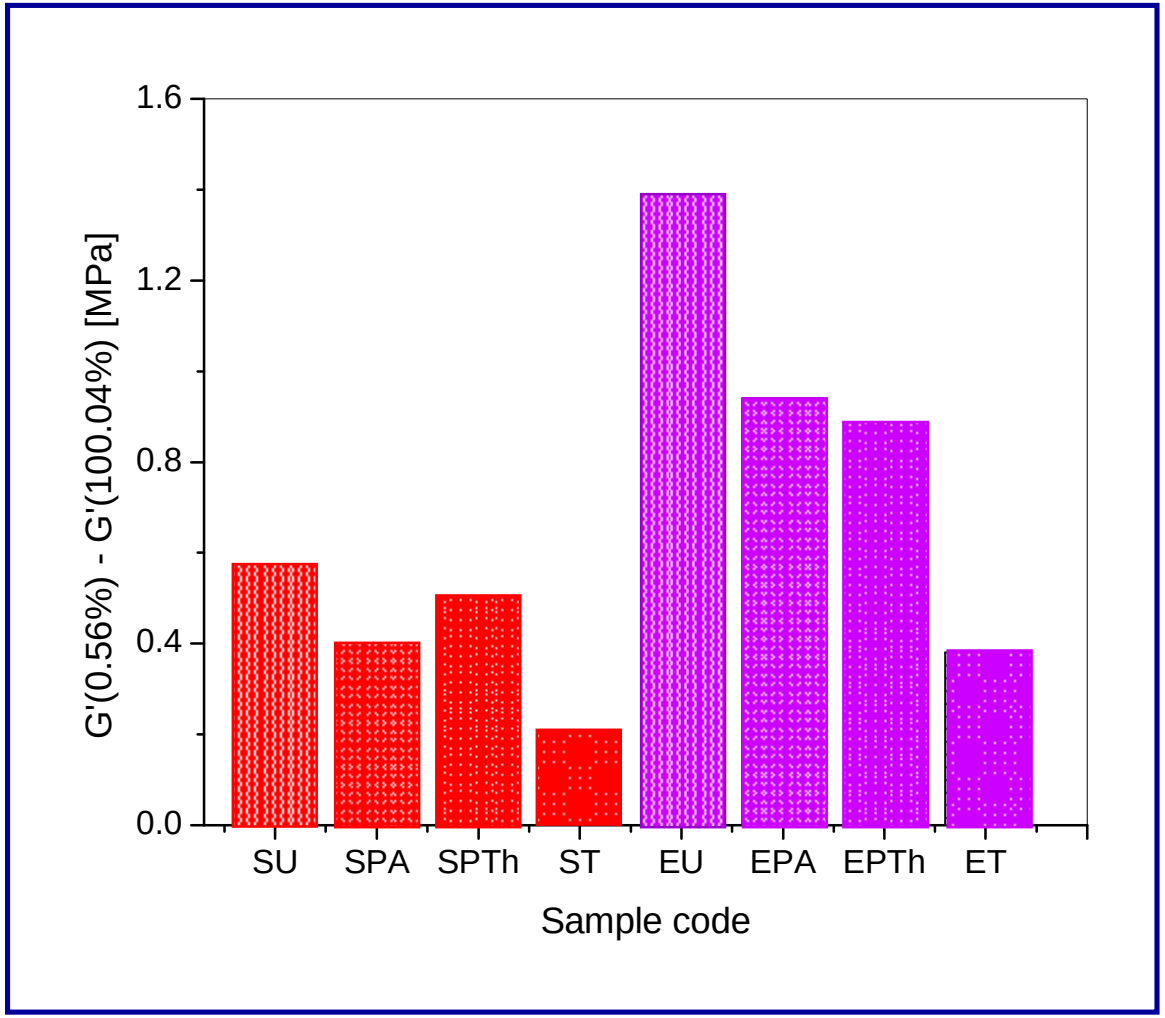
PTh-treated



Plasma-acetylene and -thiophene silica reinforced S-SBR and EPDM

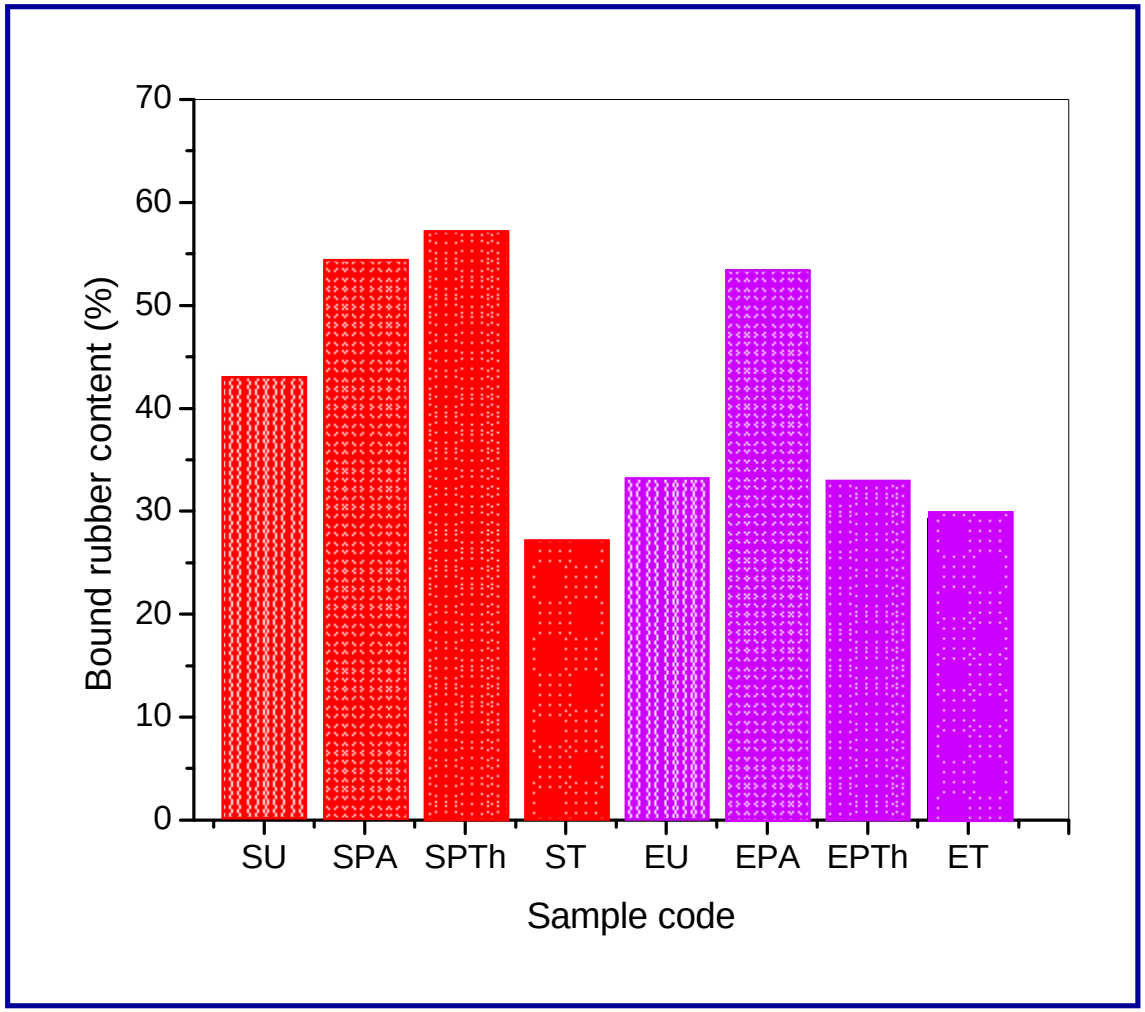
Results & discussion

Payne effect (Filler-filler interactions)



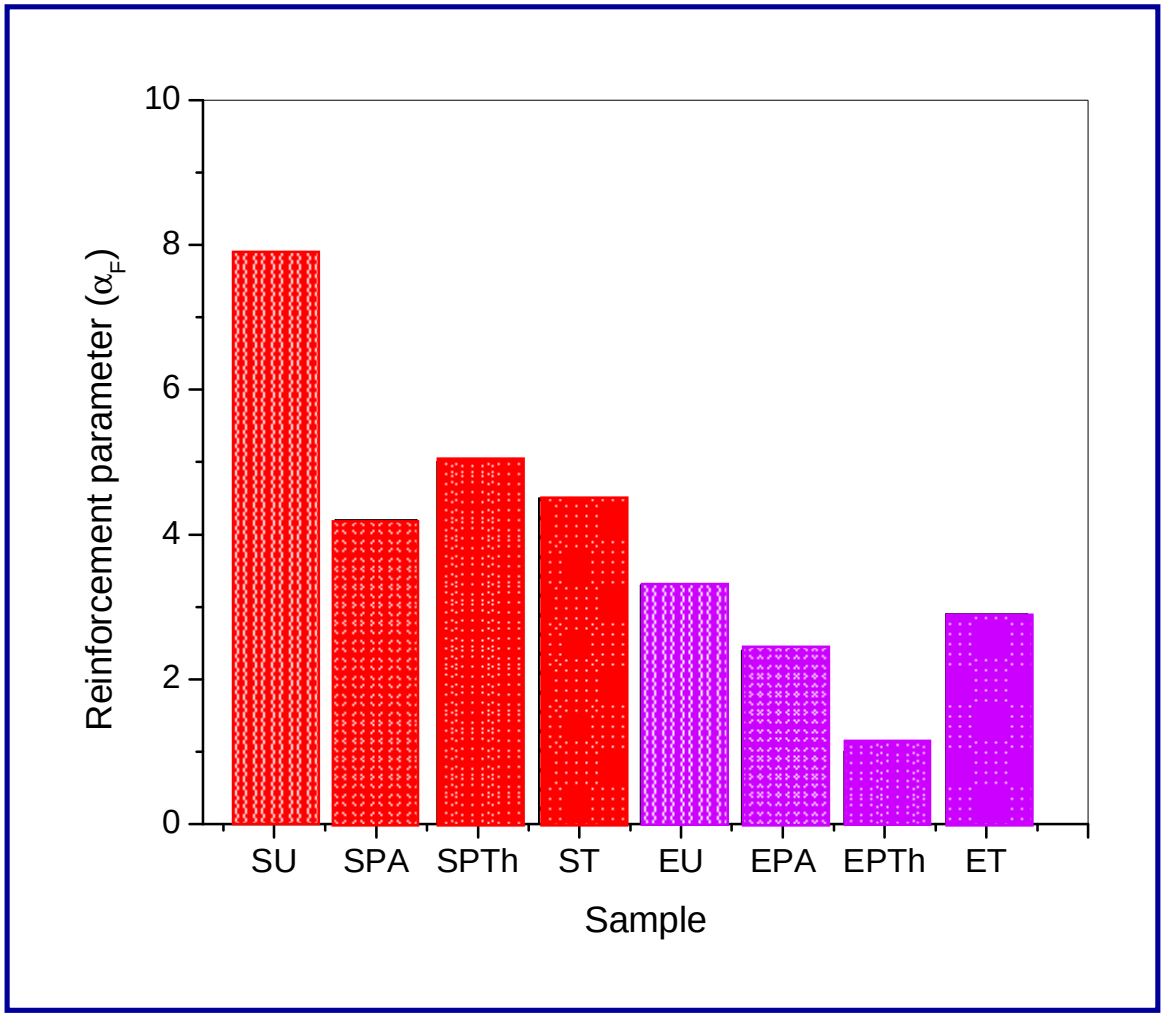
Results & discussion

Bound rubber content



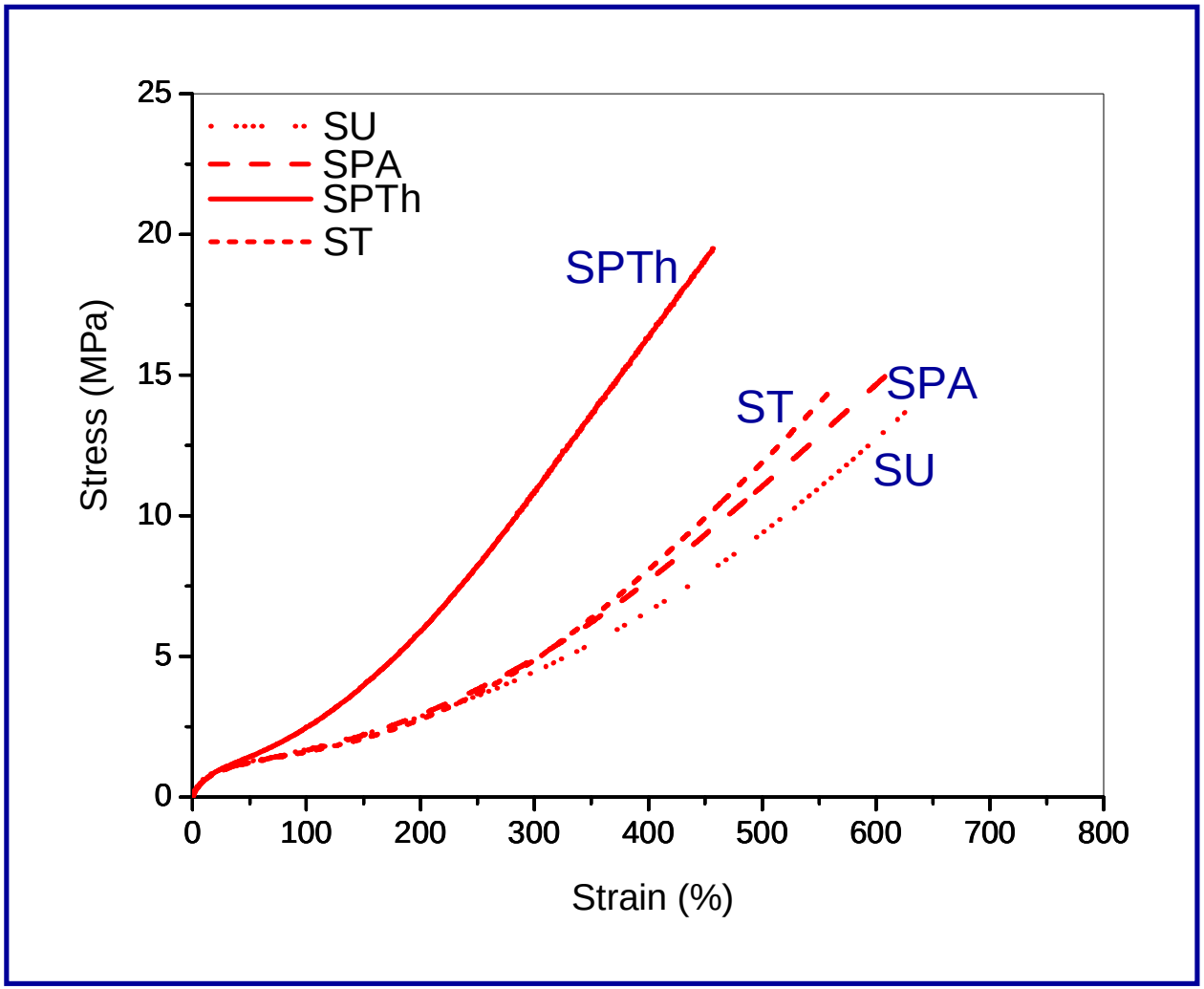
Results & discussion

Reinforcement parameter



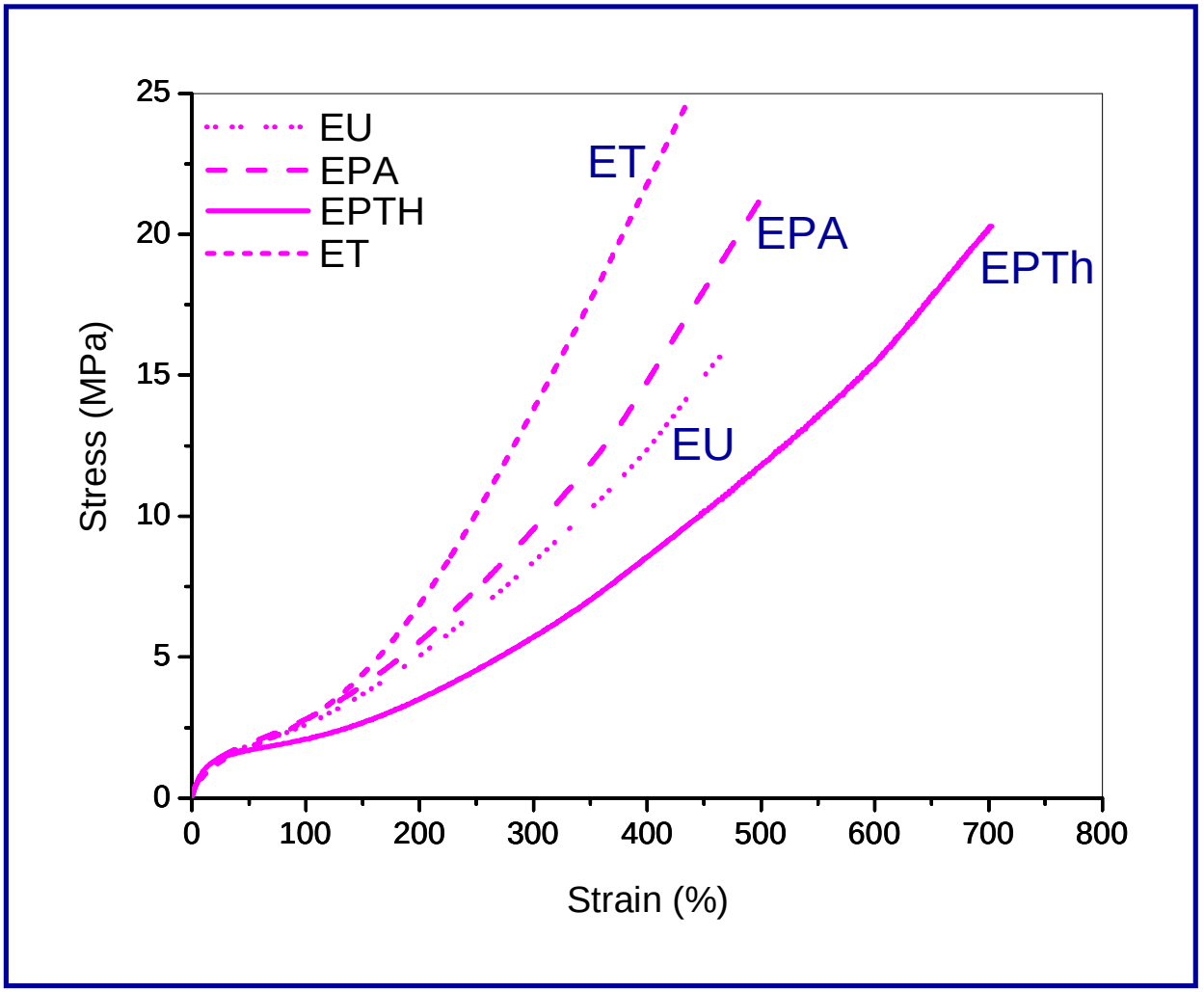
Results & discussion

Stress-strain behavior: S-SBR



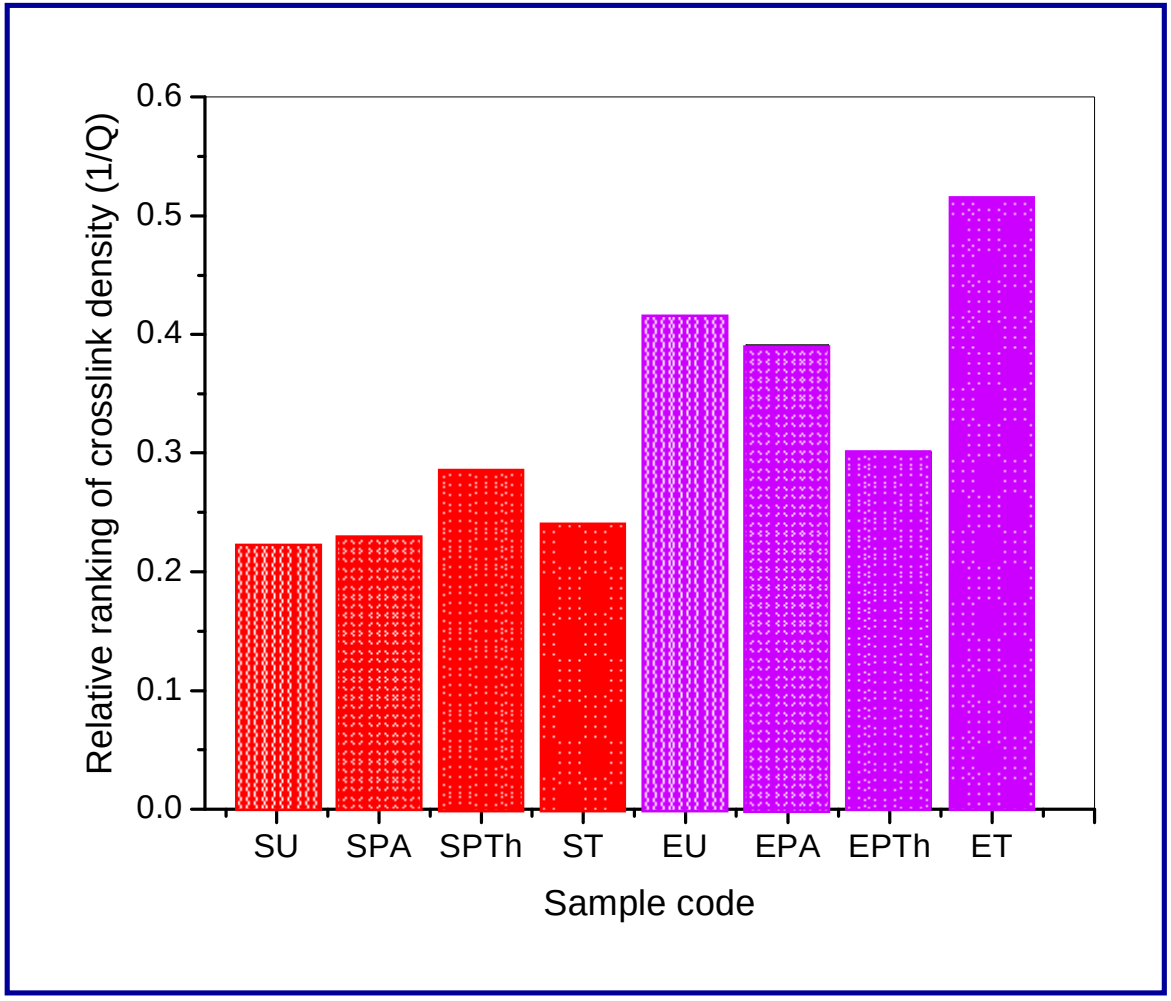
Results & discussion

Stress-strain behavior: EPDM



Results & discussion

Relative ranking of cross-link density



Summary

Acetylene and thiophene plasma coating:

- Silica is coated successfully by plasma acetylene- and thiophene-treatment
- Reduced polarity of the silica due to plasma coating

Comparison of acetylene and thiophene plasma treatment in S-SBR:

- Higher reduction in filler-filler interaction (Payne effect) due to PA-silica
- PTh-silica shows highest bound rubber content
- Dispersion is improved in the case of PA-silica
- Compared to PA-silica, PTh-silica shows the best tensile properties which correlates with the relative ranking of cross-link density

Summary

Comparison of acetylene and thiophene plasma treatment in EPDM:

- **PTh-silica shows higher reduction in filler-filler interaction (Payne effect)**
- **Bound rubber content is highest in PA-silica**
- **PTh-silica shows the best dispersion**
- **PA- and PTh-silica shows improved tensile properties but PA-silica shows higher moduli at 100% and 300%**
- **Tensile properties are in correlation with the relative ranking of cross-link density**
- **PA-silica shows improved compatibility and interaction of fillers with EPDM**

Acknowledgements