PECULIAR MECHANICAL PROPERTIES AND MICROSTRUCTURE OF POLYAMIDE-CHLOROBUTYL RUBBER BLENDS BY DYNAMIC VULCANIZATION

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Objective

- Design a material that is elastic, and has chemical barrier properties
- Manufacturing requirements
  - Made from commercially available materials and processes
  - Thermoplastic processing techniques
  - Cost effective
- Applications
  - Protective gear
  - Equipment for aggressive environment
- "Good" mechanical properties

Background of Elastomeric Materials

Processing – +

- Vulcanized elastomers
  - Diene based
    - Natural rubber
    - Butadiene rubber
  - Silicone
  - Butyl rubber
- Thermoplastic elastomers (TPE)
  - Elastomeric Urethane Polymers
  - Ionomers
  - Certain block co-polymers
  - Plasticized polymers
  - Dynamically vulcanized polymer blends

Dynamically Vulcanized Polymer Blends

- Chlorobutyl rubber (CIIR)
  - Soft elastic material
  - High elongation at break
  - Good barrier properties for many chemicals
  - Low water absorption
  - Hardness: 30-80 Shore A
  - Specific gravity: 0.9
  - T_g: -40^{0}C
  - 1.26% chlorine

Exxon Chlorobutyl rubber 1068

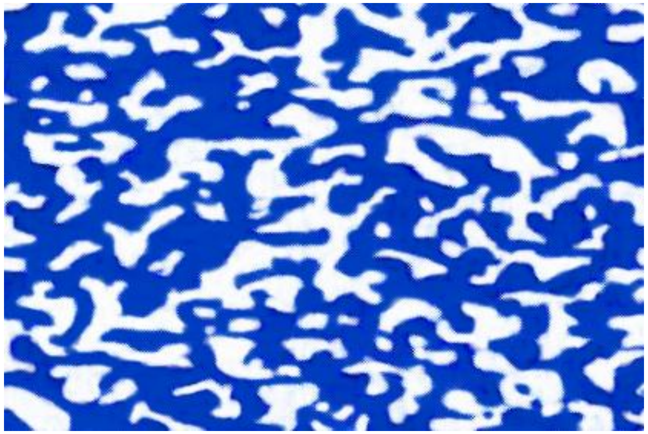
- Nylon 12 (Polyamide)
  - Hard engineering plastic
  - Excellent barrier properties
  - Low water absorption
  - Melt point: 178ºC
  - Hardness:73 Shore D
  - Specific gravity: 1.01
  - T_g: 66^{0}C

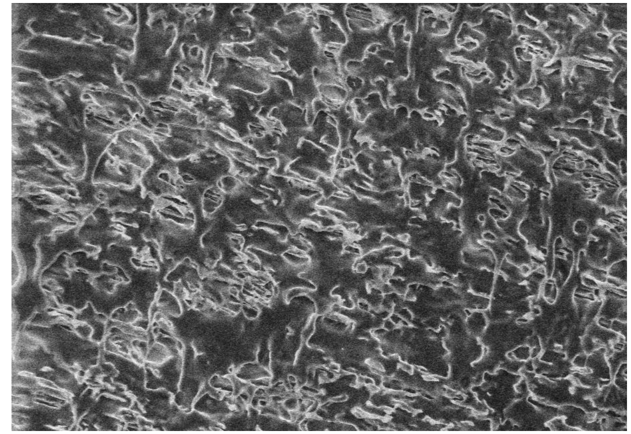
EMS- Grillimide PA 12 L16

- Challenges and Opportunities
  - Optimize with respect to barrier properties
  - CIIR and nylon have a $+\Delta G_{mix}$

Nylon/CIIR Rubber Blend

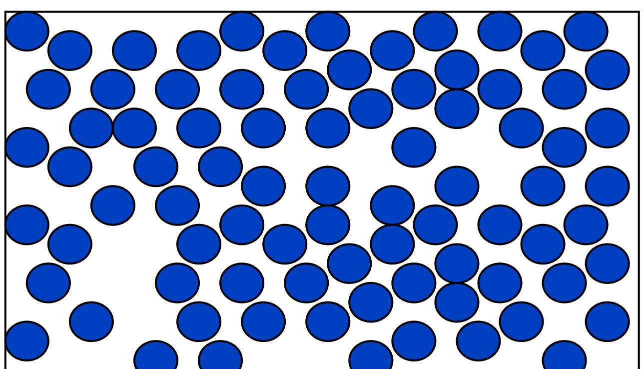
Regular Blending 50:50

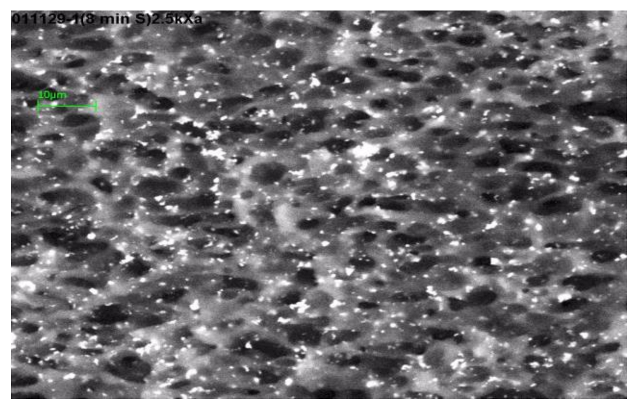




Strands form due to elongation during high shear

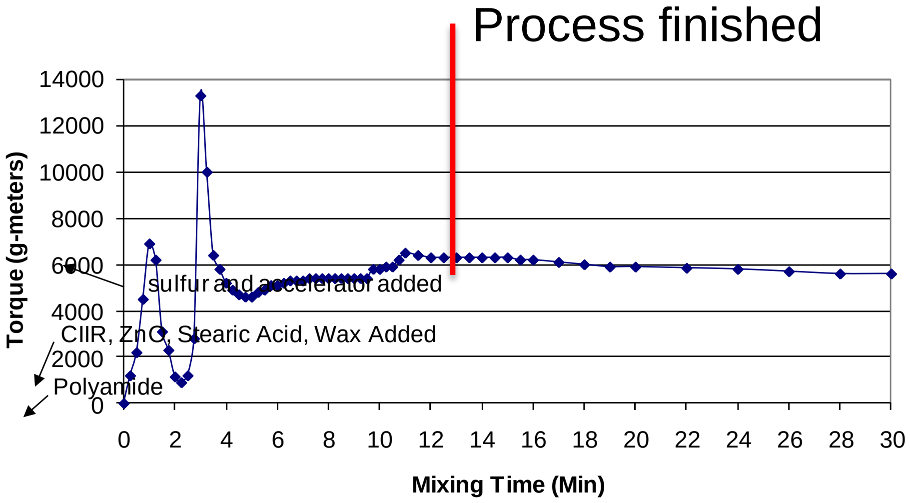
Dynamic Vulcanization 50:50





Rubber always dispersed phase

Preparation of Dynamically Vulcanized Elastomers



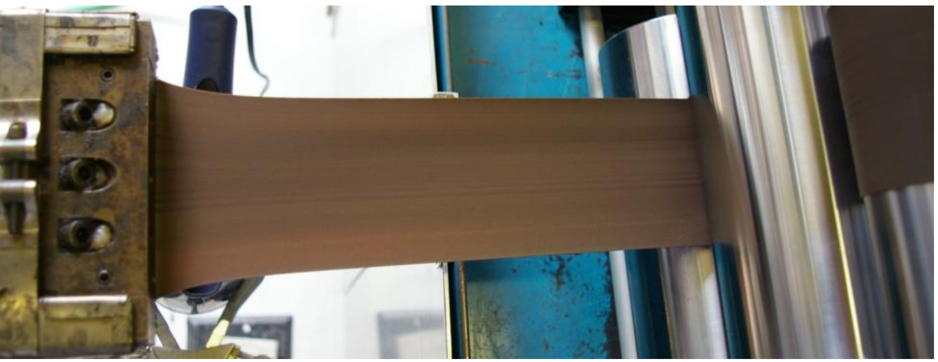
Batch mixing with high shear roller blades using Prep Mixer

- Nylon pellets (30-40%)
- CIIR (Rubber) (60-70%)
- ZnO, Stearic Acid, Wax
- Add sulfur to vulcanize system
- Pull out products when torque stabilizes (~12 minutes)
- Grind products

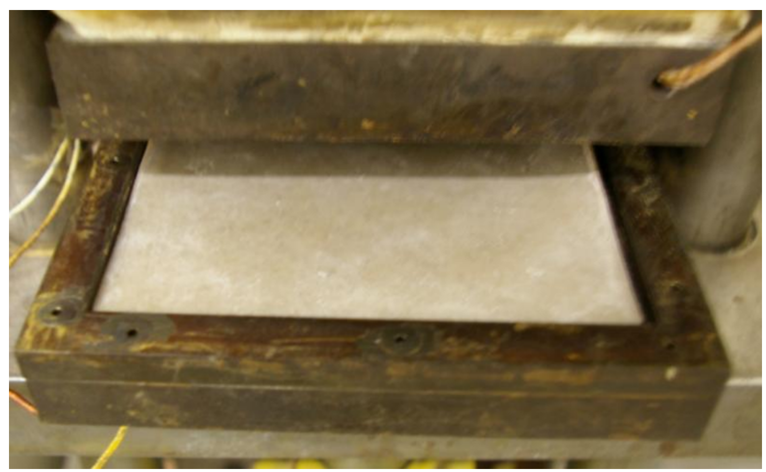
Samples Preparation

Injection moulding

Extrusion



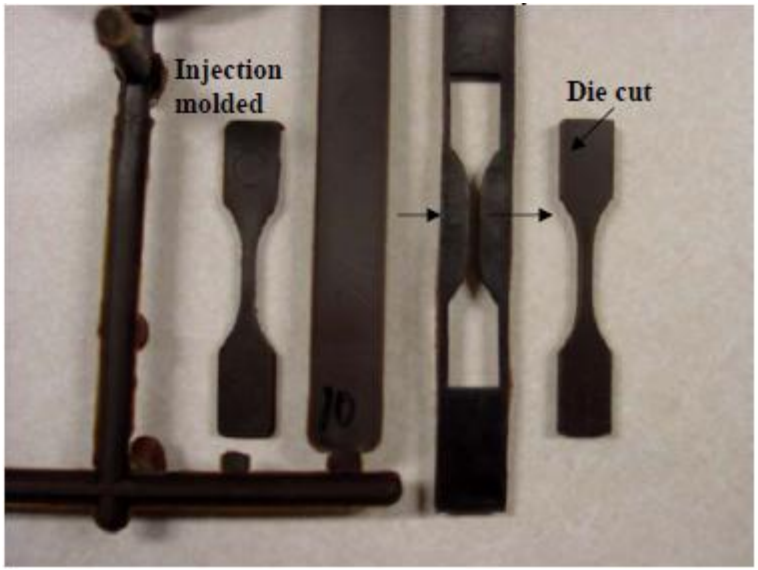
Compression moulding

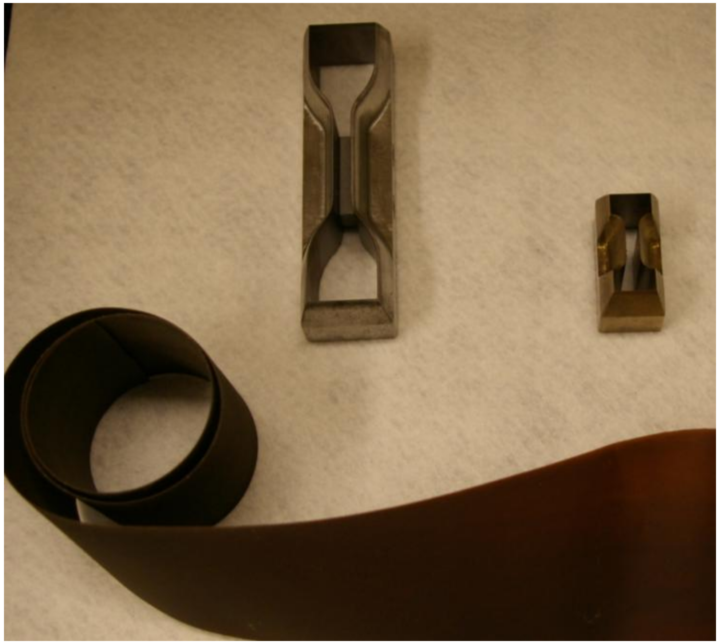


Specimen Preparation

- Injection moulding
  ASTM 638M
  (M1 and M3)

•Die cutting of injection moulded M3 samples



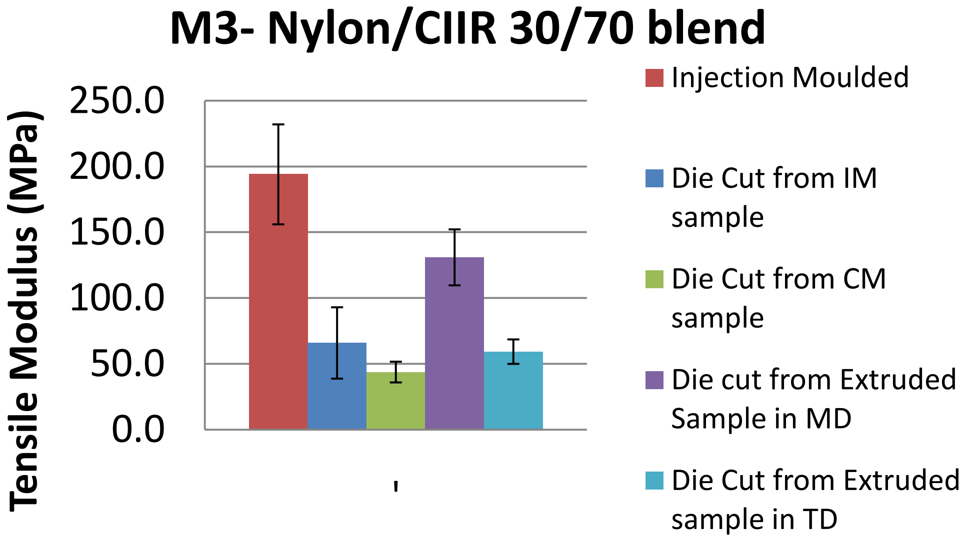


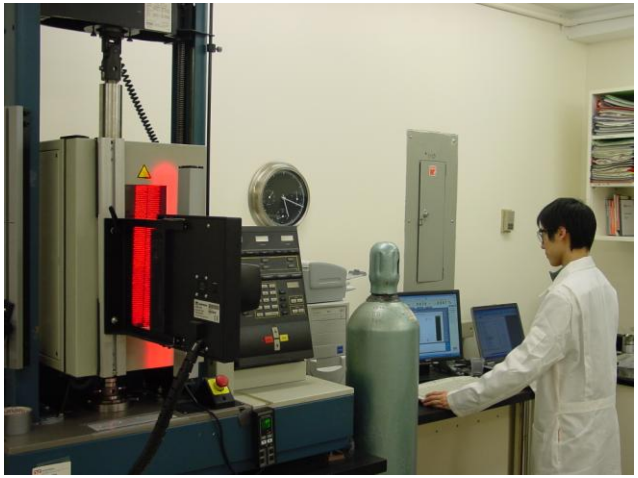
- Die cutting from extruded and compression moulded materials
- M2 and M3

RESULTS

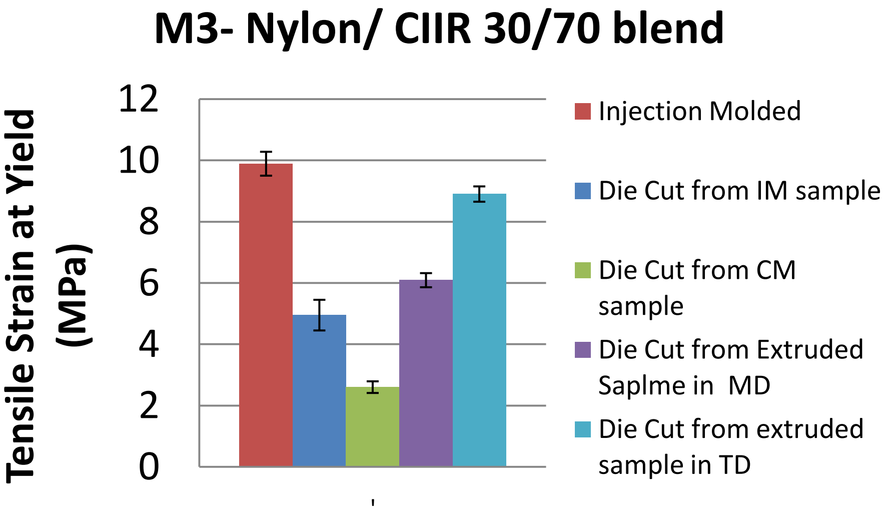
- Mechanical Testing
- DMA
- DSC
- SEM
- AFM-PFM

Mechanical Testing





Injection and MD extrusion moulding and has superior tensile at break properties than compression moulding due to alignment of nylon during flow.

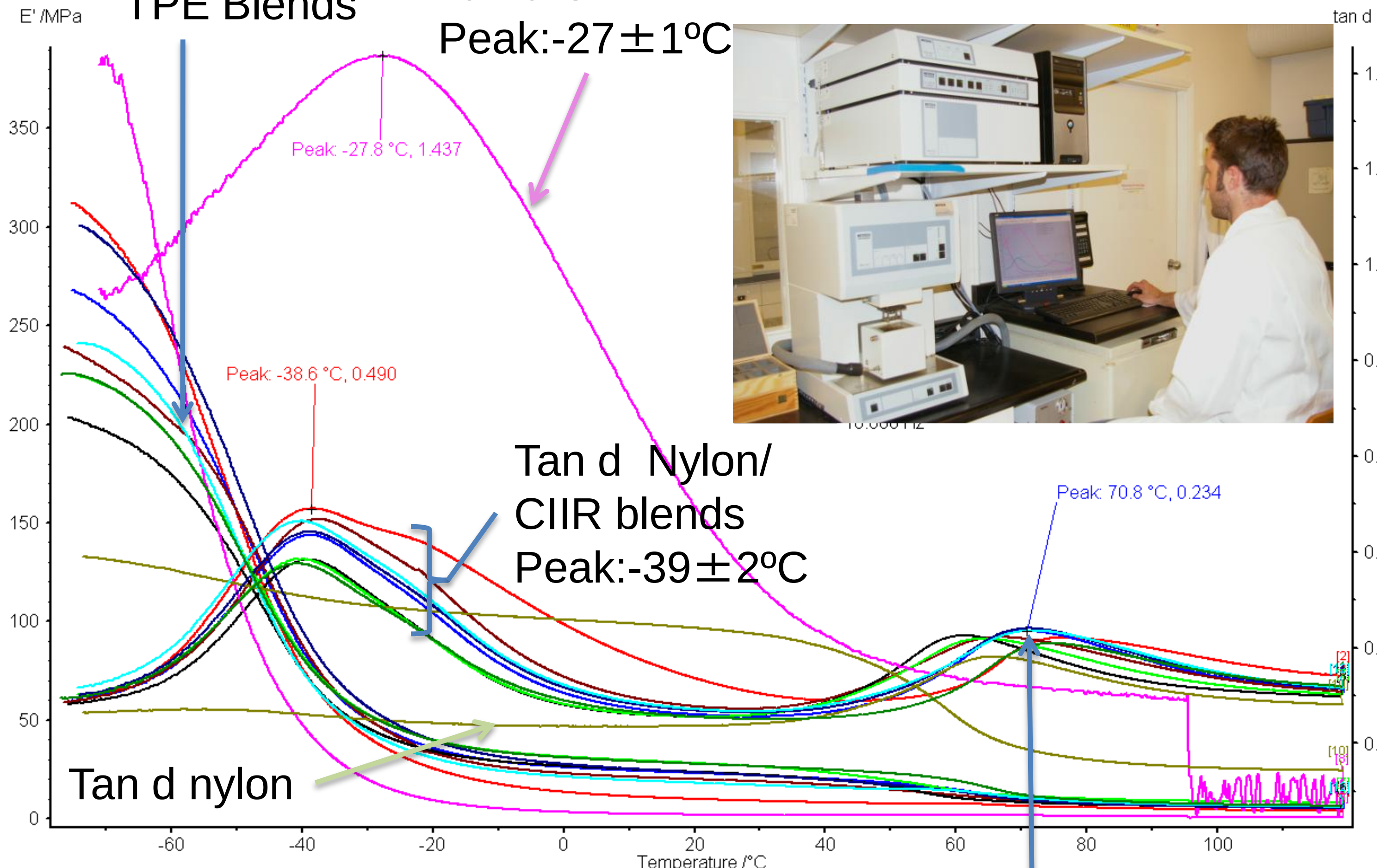


30/70 and 40/60 samples show similar trends but TS at yield increases with higher nylon content

DMA Scans

Modus of TPE Blends

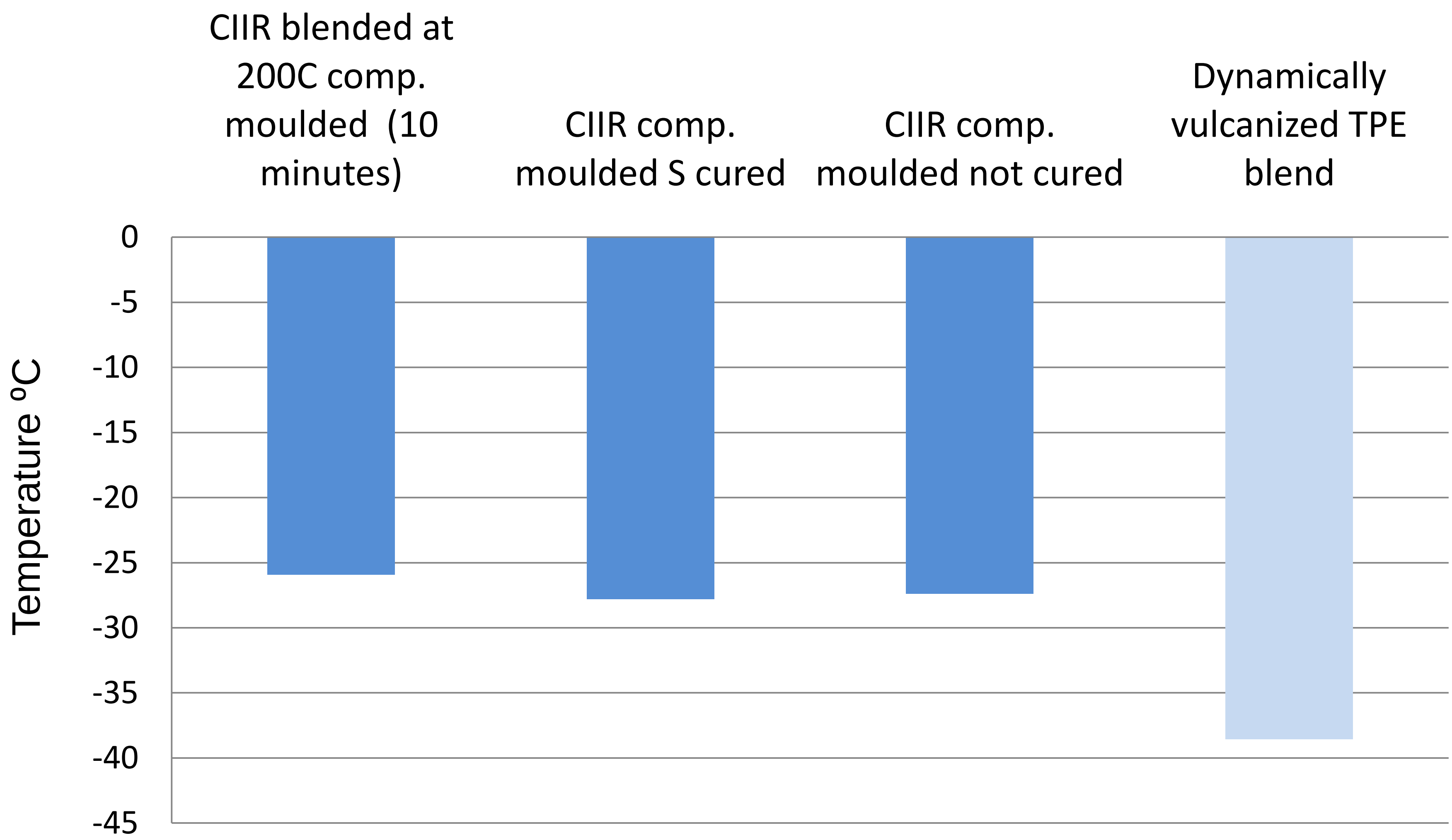
Tan d CIIR Peak:-27±1ºC



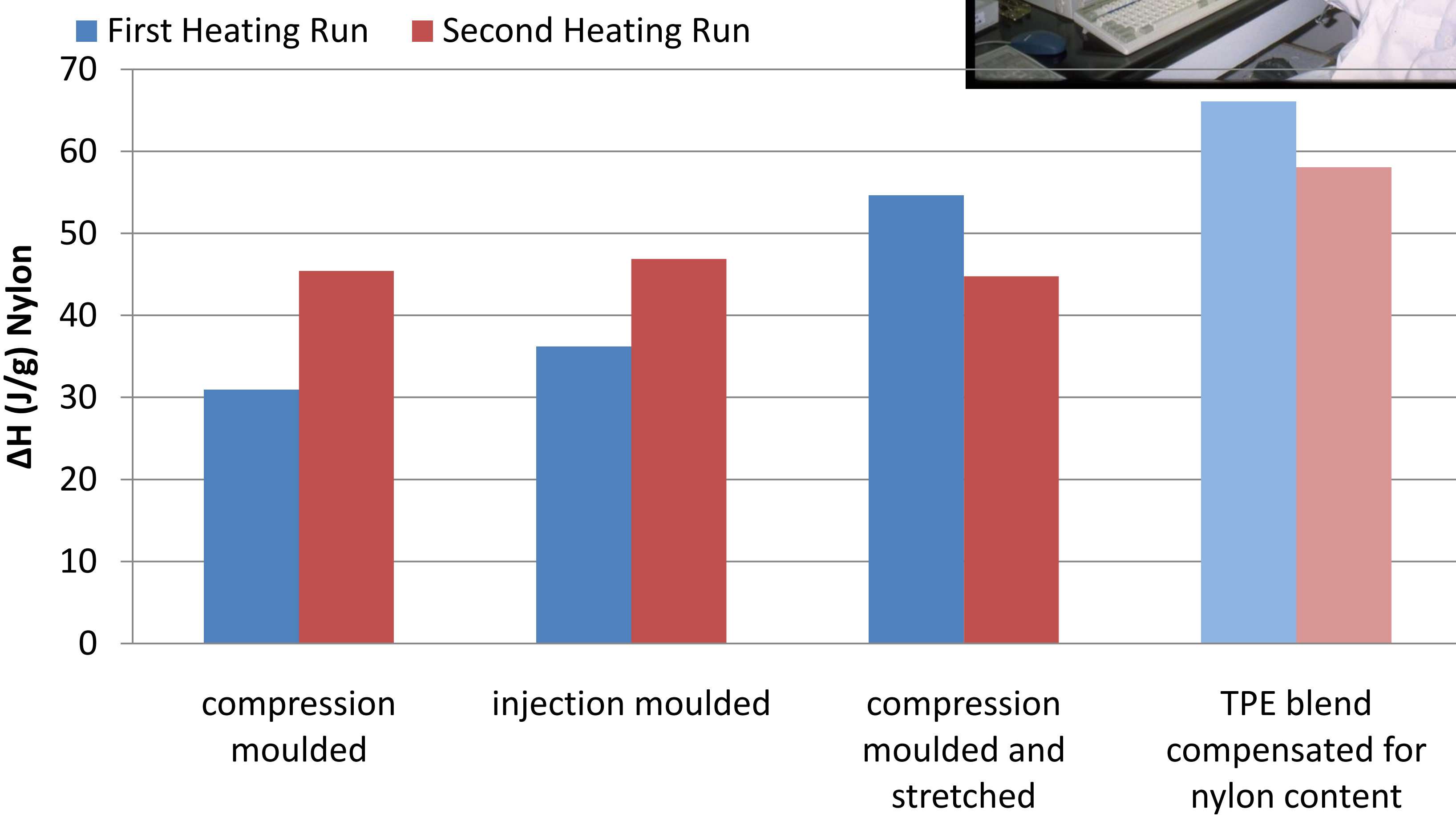
Pure Nylon T_g=66.4

Nylon blend T_g Peak 70±6ºC

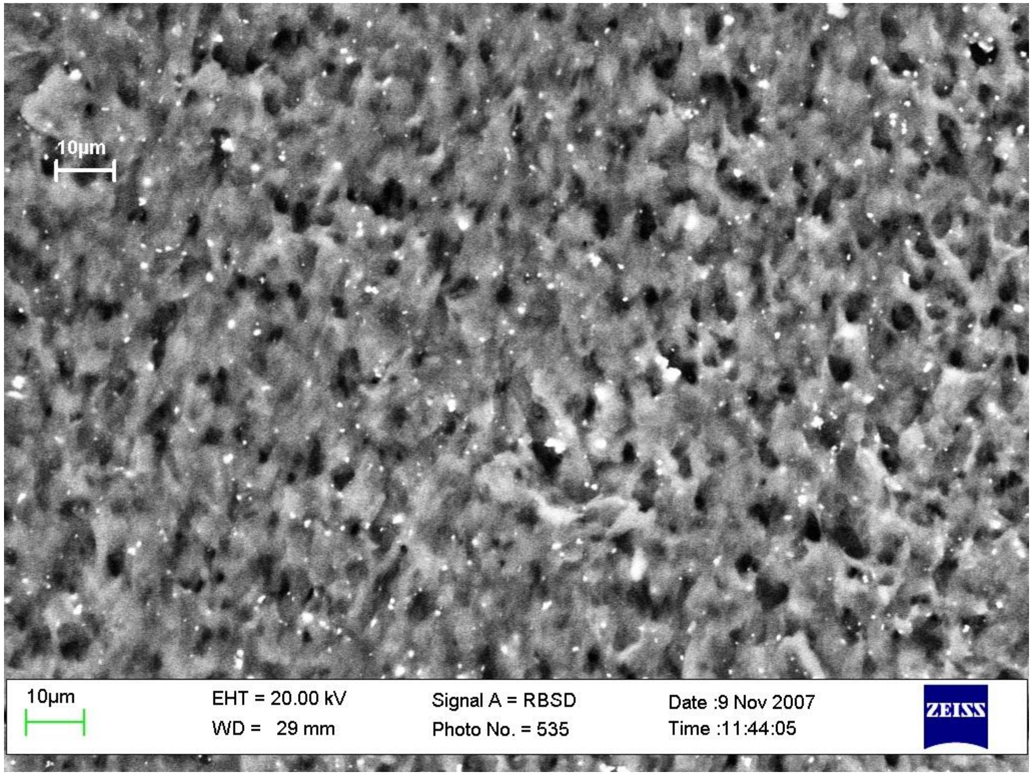
T_g Shift of CIIR Phase as Measured by DMA



DSC Study of Changes in Nylon ΔH_f



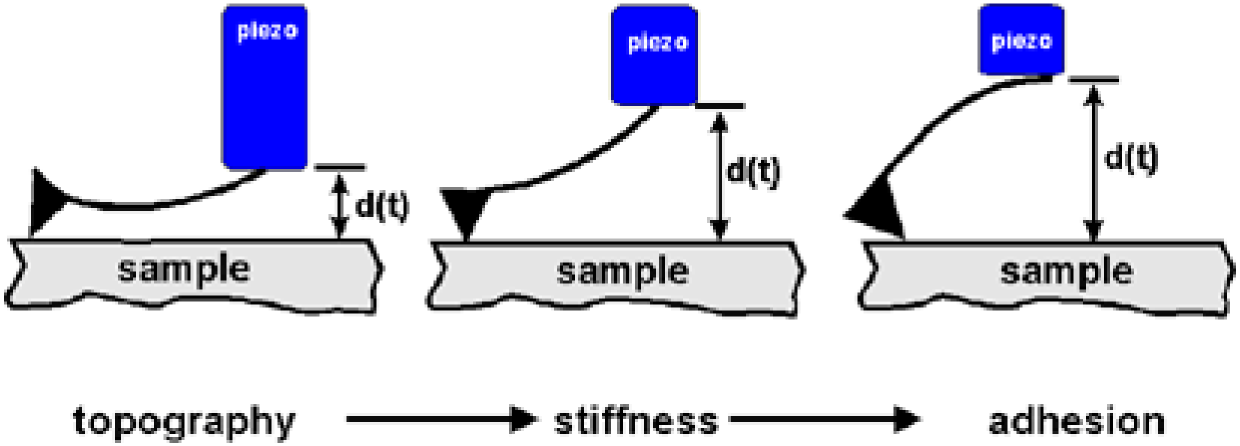
SEM 40/60 Blend

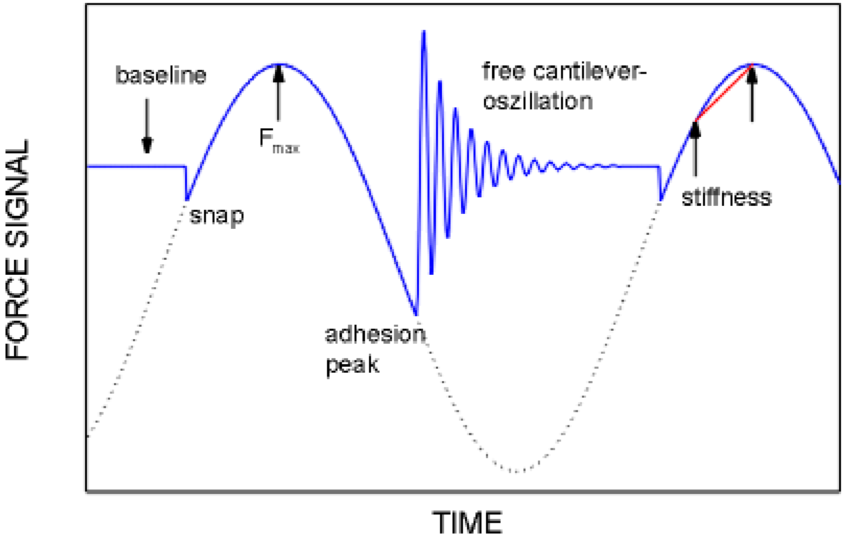


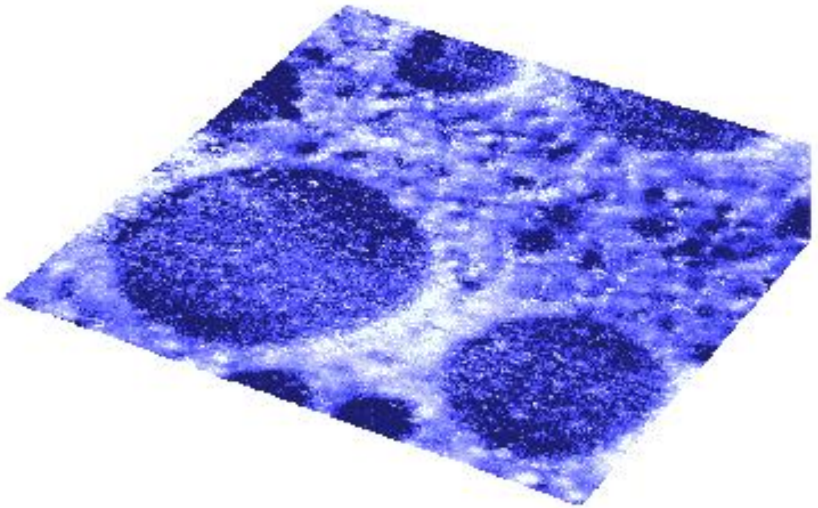
• 4mm particles reduced to 1-3µm by blending process
• No obvious alignment of rubber particles due to extrusion or injection moulding

AFM-Pulse Force Mode (PFM)

(Source: Witec and Topometrics webpage)







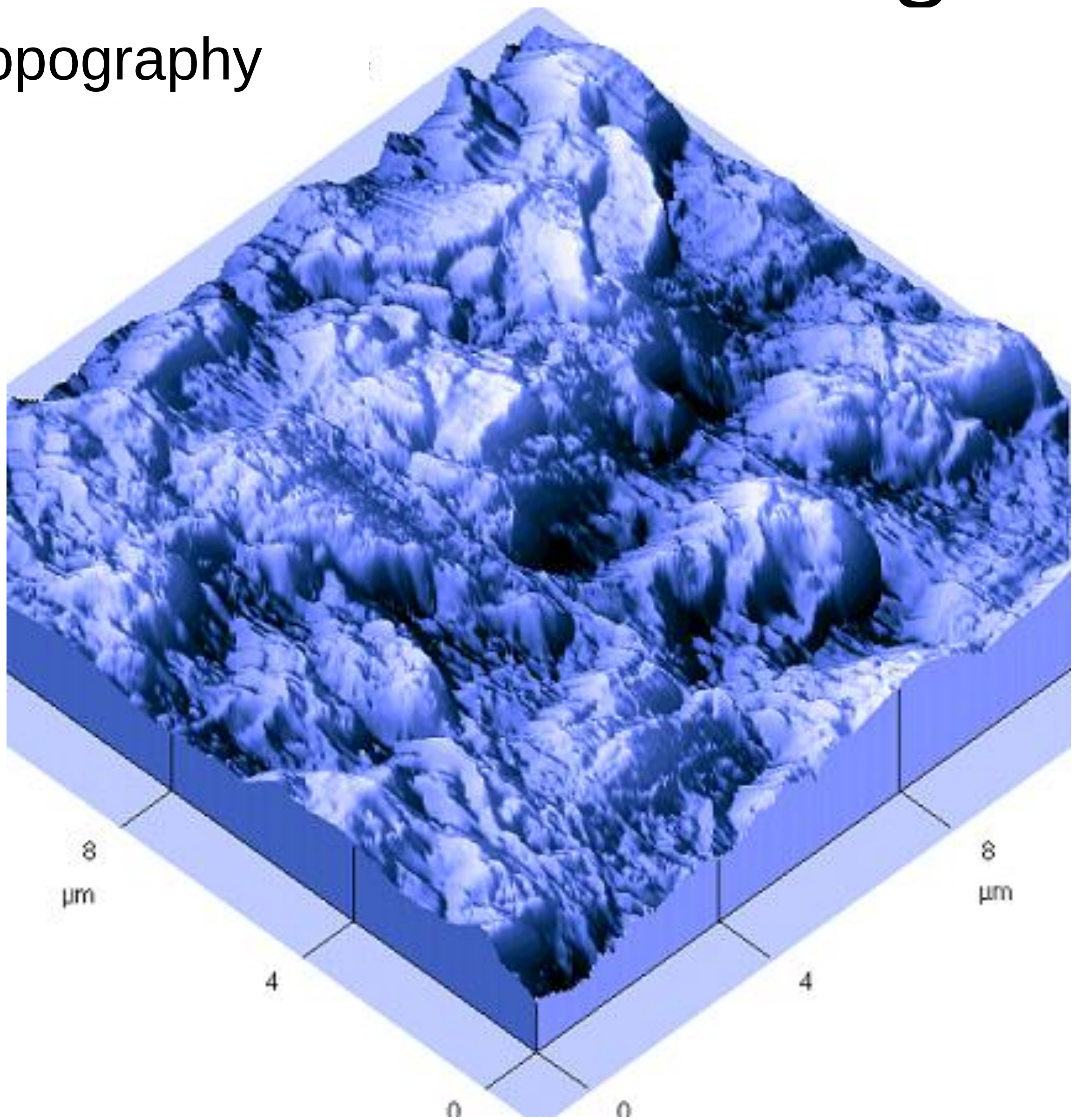
Adhesion Image

(Bodyguard adhesive tape)

https:/.../student/en/media/11707/parkafm.jpg

AFM Images

Topography



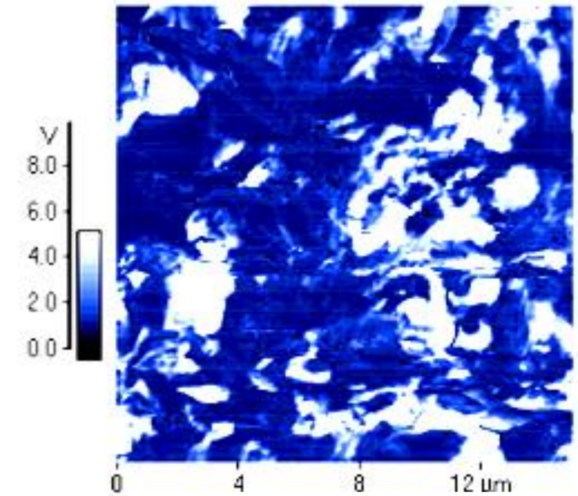
- 70/30 Rubber/Nylon
- Cut sample
- 15µm scan

Confirmed 1-3µm rubber particles

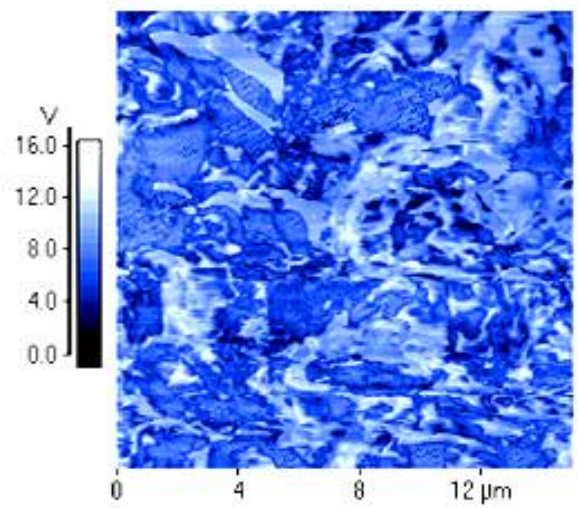
AFM Images of Adhesion and Stiffness

- Rubber: low stiffness, high adhesion
- Nylon: high stiffness, low adhesion

- Lighter colors indicate exposed rubber
- 70% of nylon is exposed in this cross section even though 30% by volume in blend
- This indicates substantial cohesive failure in nylon
- High adhesion between nylon and rubber phases despite chemical incompatibility



Adhesion



Stiffness

Conclusions

- Mechanical properties depend on sample preparation method
- DMA: shift down in T_g of blended CIIR component
- DSC: increased ΔH_f increase in nylon phase of TPE blends indicating high orientation due to rubber balls in shear with nylon during processing
- SEM: 1-3μm CIIR particles and no significant alignment due to flow
- AFM: significant failure in nylon phase indicating strong adhesion between CIIR and nylon and the cut is occurring in a harder phase which is unexpected
- Properties of nylon dictate physical properties of the blend as seen by the increase in tensile strain at yield and break of the 40/60 blend in comparison to the 30/70
- Morphology failed to explain mechanical properties

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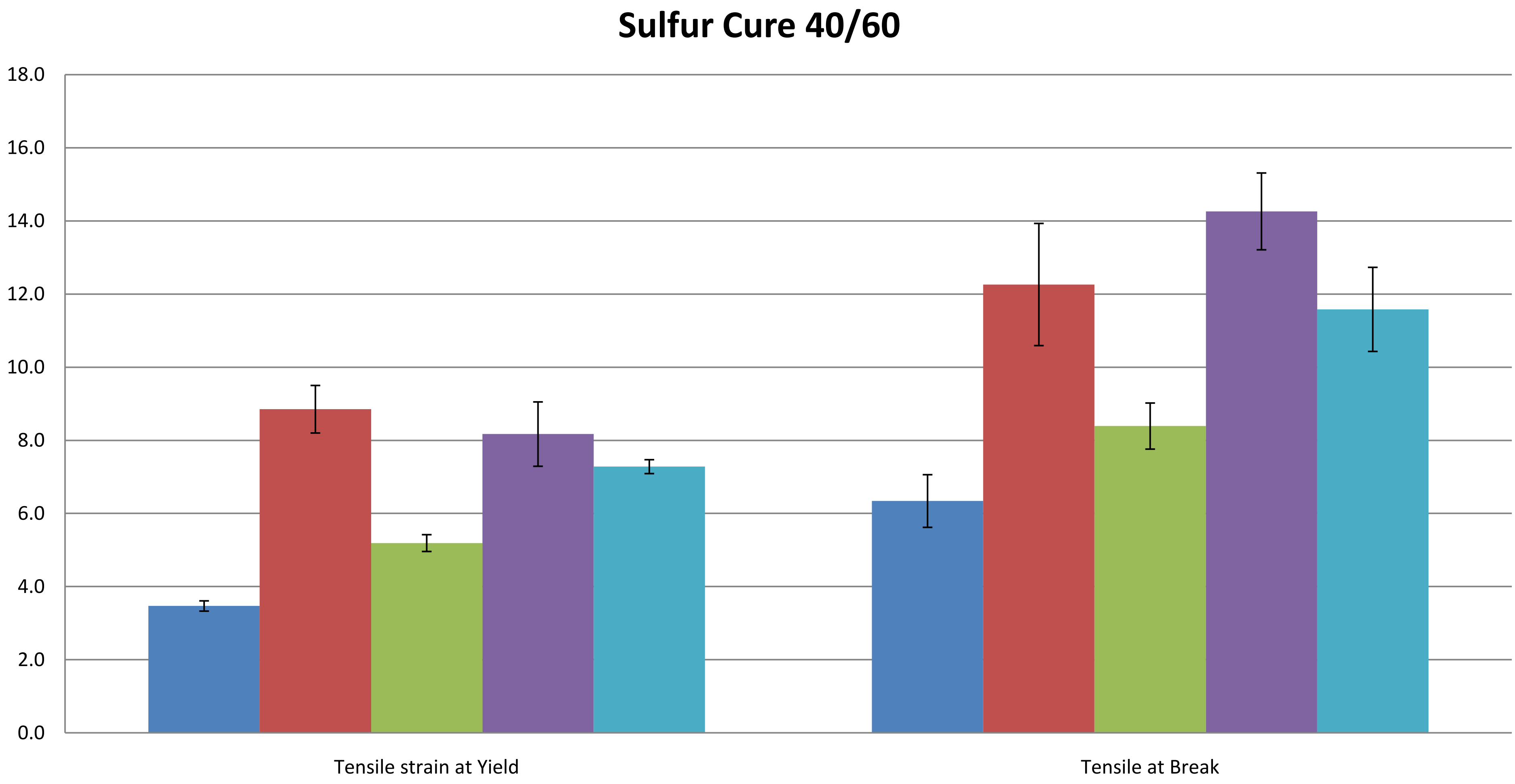
- John Berg – University of Washington in Seattle
- DRDC Canada (funding and contribution to project)

About PEC

- Based in Vancouver, BC. Canada
- Privately owned consulting company
- Testing and analysis
- Designing materials for unique polymer applications
  - Specializes in polymer technology
    - Plastic materials
    - Coatings
    - Paints
    - Adhesives
    - Rubbers

Tensile Strain at Yield Versus Break



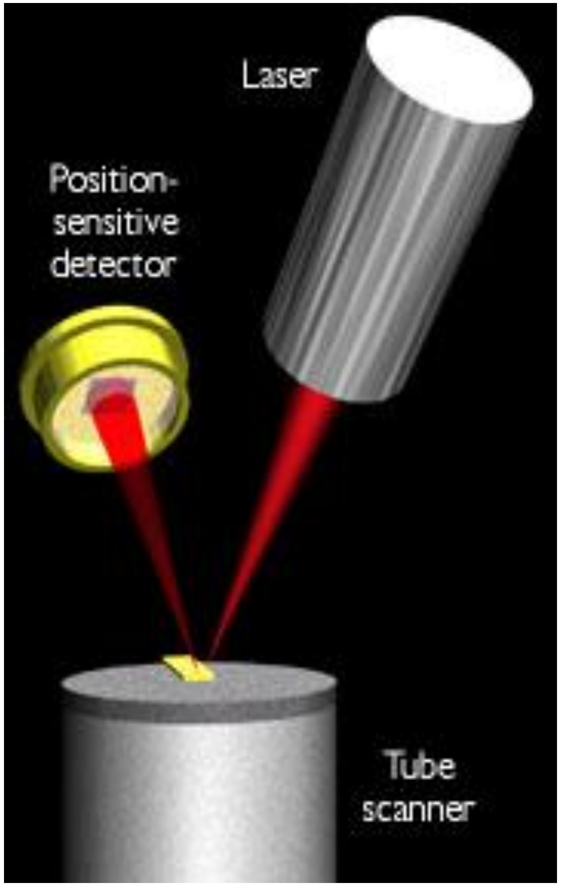
Mechanical Properties Summary Table

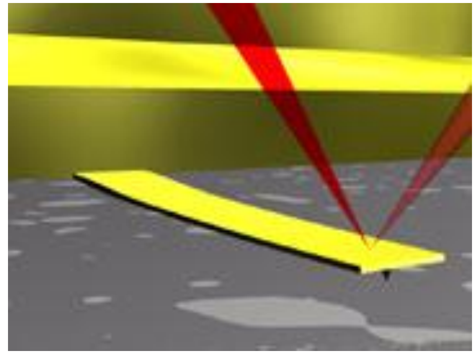
Cure Method and nylon rubber ratio	Process Method	Specimen Type	Sample ID	Description	Tensile strain at Yield		Tensile Stress at yield		Modulus 1.1-1.8%		Axial Strain		Tensile at Break	
					MPa	stdev	%	stdev	MPa	stdev	%	stdev	MPa	stdev
Sulfur 30/70	IM	M1	060724-1	As moulded	6.0	0.6	4.9	0.1	113.0	10.0	178.0	12.0	8.3	0.3
		M3	060724-1	As moulded	6.7	0.6	9.9	0.4	194.0	38.0	172.0	17.0	14.3	0.7
		M3	060724-1	Die Cut from Impact bar	11.8	5.0	5.0	0.5	65.8	27.1	197.0	40.0	7.9	0.9
	Compres	M2	060724-1	Die Cut from Sheet	9.8	1.4	2.6	0.1	39.6	8.2	85.0	27.0	1.3	0.3
		M3	060724-1	Die Cut from Sheet	10.3	2.2	2.6	0.2	43.7	7.9	132.0	19.5	5.4	0.4
	Extrusion	M2	060802-1	Die Cut MD	5.9	1.2	5.1	0.6	65.5	16.8	161.6	11.3	8.8	1.1
		M3	060802-1	Die cut MD	7.3	2.3	6.1	0.2	130.9	21.3	194.5	20.8	11.7	0.3
		M3	060802-1	Die cut TD	8.9	2.0	3.5	0.3	59.2	9.3	190.4	10.7	6.3	0.2
Sulfur 40/60	IM	M1	060717-1	As moulded	5.0	0.6	8.9	0.1	266.8	31.6	219.8	22.4	12.3	0.7
		M3	060717-1	As moulded	5.7	0.7	14.3	0.7	298.4	128.2	244.0	3.3	20.2	1.7
		M3	060717-1	Die Cut from Impact bar	6.3	1.3	8.2	0.2	188.4	60.4	278.8	4.0	13.3	0.6
	Compres	M2	060717-1	Die Cut from Sheet	5.3	0.2	5.2	0.1	129.3	26.3	98.4	15.9	8.4	0.5
		M3	060801-1	Die Cut from Sheet	5.5	0.4	5.6	0.2	77.2	20.5	149.5	24.4	9.5	0.6
	Extrusion	M2	060801-1	Die Cut MD	8.1	2.0	8.2	0.5	229.0	124.3	314.6	17.1	14.3	1.1
		M3	060801-1	Die Cut MD	8.8	3.6	7.4	0.9	134.1	22.1	340.6	45.3	14.9	1.1
		M3	060801-1	Die Cut TD	6.2	1.4	7.3	0.2	105.3	50.9	261.2	59.9	11.6	1.2
100% Nylon	IM	M1	100129	As moulded	5.0	0.2	41.6	0.6	974.0	47.2	332.7	64.4	41.6	10.4
		M3	100129	As Moulded	4.4	0.3	44.5	0.3	1044.2	140.9	439.7	15.8	74.6	4.4
		M3	100129	Machined from Impact Bar	5.3	0.6	44.5	1.6	1369.5	497.8	338.1	36.7	45.2	4.5
100% rubber	CM	M2	060717-1	Die Cut from Sheet					0.6	0.1	517.7	24.6	2.1	0.2

Tools

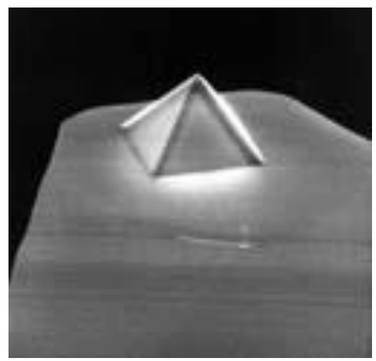
- Instron – mechanical properties
  - Elongation at break
  - Tensile strength
- DMA (Dynamic Mechanical Analysis) Netzch DMA 242
  - Modulus, tan delta
- DSC (Dynamic Scanning Calorymetry) Perkin Elmer DSC7
  - Crystallinity
- FTIR (Fourier Transform InfaRed Spectrum) Thermo-Nicolet 370
  - Changes in chemistry of the rubber during mixing
- SEM (Scanning Electron Microscope) Hitachi N3000S
  - Imaging
- AFM/PFM (Atomic Force Microscope/Pulsed Force Mode) Park Scientific Autoprobe CP
  - Imaging- mechanical differentiation between rubber and nylon

Atomic Force Microscopy
(AFM)





Laser reflects off the back of the cantilever



AFM tips (3μm tall)
Tip radius <10nm

Source: http://stm2.nrl.navy.mil/how-afm/how-afm.html#General%20concept