Thermo-mechanical devulcanization of tire rubber crumb with supercritical CO_2: devulcanized rubber properties

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Outline

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- **Introduction**
  - ***Recycled Tires/ Rubber Crumb/***
  - ***Vulcanization & Devulcanization***
  - ***Background and Objectives***
- **Experimental**
  - ***Process/ Materials/ Scale up experiments/Characterization***
- **Results and Discussion**
- **Concluding Remarks**
- ***Current Efforts***

Introduction

- **Annual generation of Scrap tires :**

  World :1.6 billions

  USA: 299 millions

  Canada: 30 millions

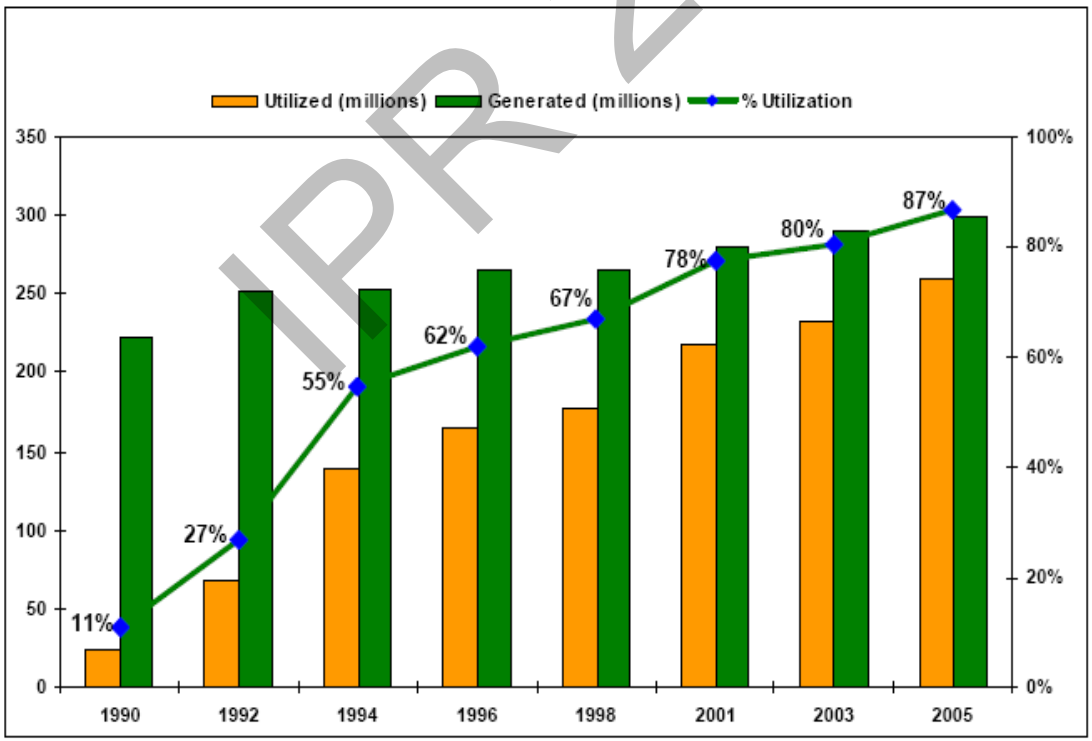
References:

- *"Scrap Tire Market in The United States" , Rubber Manufacturer Association, Nov 2006 ,page 15*
- *Sangari, S.S.; Kao, N.; Bhattacharya, S.N.; Pavel, D and Silva, K. Mechanochemical Devulcanisation of Elastomers, Rubber Div. ACS, Oct., 2001*
- *Schnekenburger, Michael, Tire Recycling in Canada-1999, Rubber Division, ACS, Paper No.166, Set.21-24, 1999*

Introduction

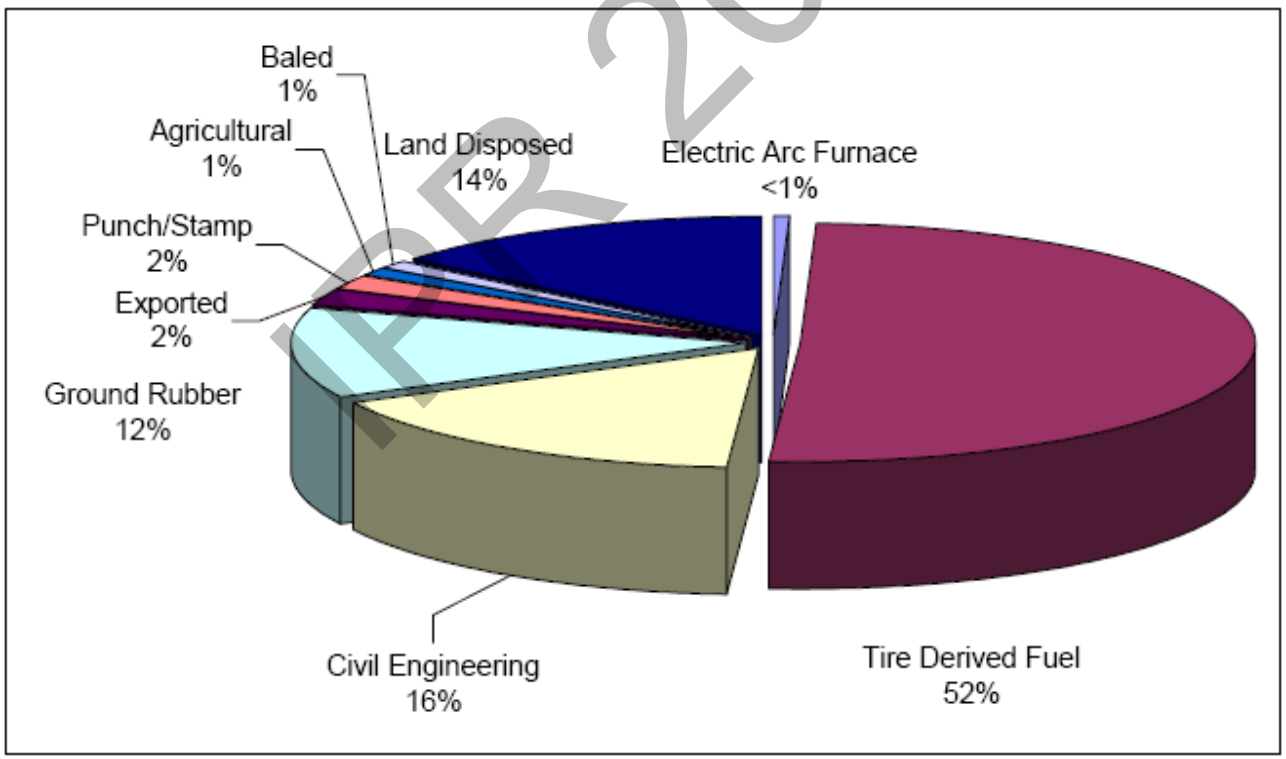
Tire Recycling

- Statistics in 2005 for the USA show that nearly 87% of scrap tires in the U.S. were used in end use market.
- Statistics show that there is an eight-fold increase in percentage of consuming of scrap tires by end use market annually since 1990.



Introduction

- TDF (tire derived fuel) application consumed about 52 % of total scrap tire in U.S
- Civil engineering market is another big consumer of scrap tires in U.S (16%)
- 12 % is consumed by ground rubber products



Introduction

Ground Rubber : Production Methods

- Ambient grinding process
- Cryogenic grinding process
- Wet grinding process
- Extrusion

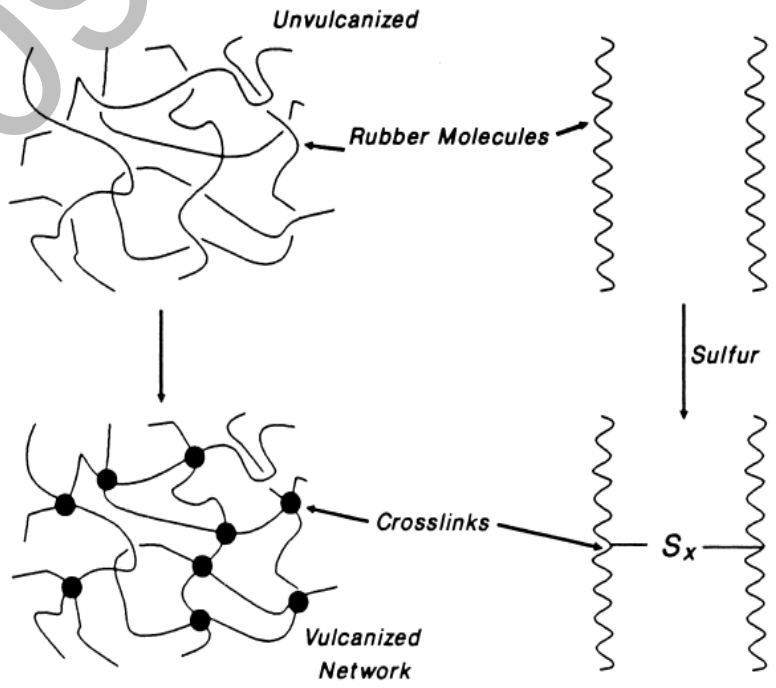
Introduction

- ***Rubber Crumb Applications***
  - **Sport Surfaces**
  - **Geotechnical/ Asphalt Applications**
  - **Rubber and Plastic Products**
  - **Automotive Industry**
  - **Adhesives and Sealants**
  - **Construction**
  - **Shock Absorption and Safety Products**

Introduction

Rubber Vulcanization

- Raw rubber is soft and sticky material with a low tensile strength and elasticity
- Atomic bridges composed of sulphur or carbon-carbon bonds link the polymer chains together
- First discovered by Charles Goodyear in 1839
- The vulcanized rubber is a thermoset material

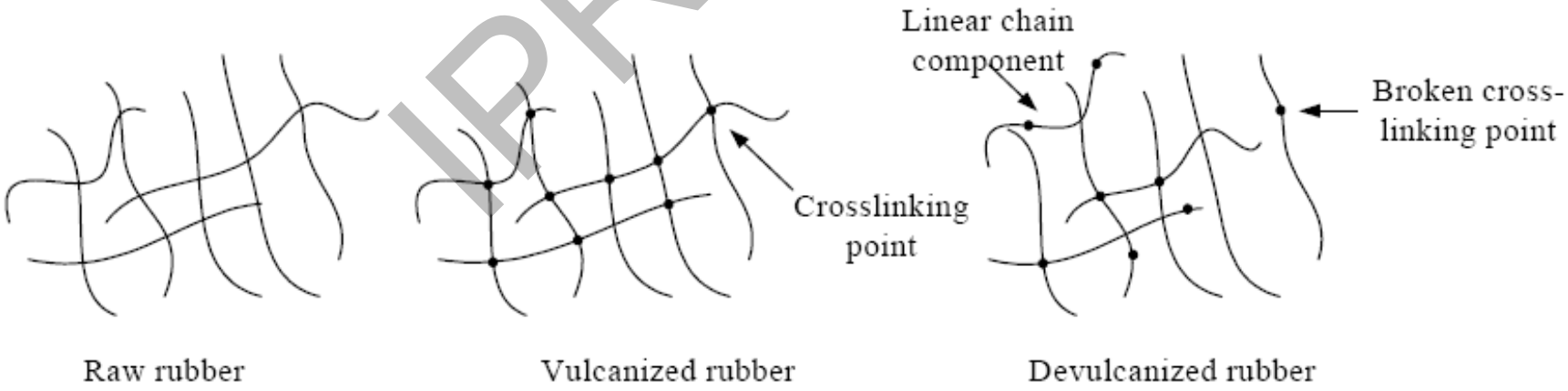


Introduction

Rubber Devulcanization

- Devulcanization refers to a process in which the crosslink bonds in the vulcanized rubber cleave totally or partially.

- The devulcanized rubber is able to be re-vulcanized and utilized again like a virgin rubber



Introduction

Devulcanization Methods

- **Mechanical**
- **Ultrasonic**
- **Chemical**
- **Microwaves**
- **Microorganisms**

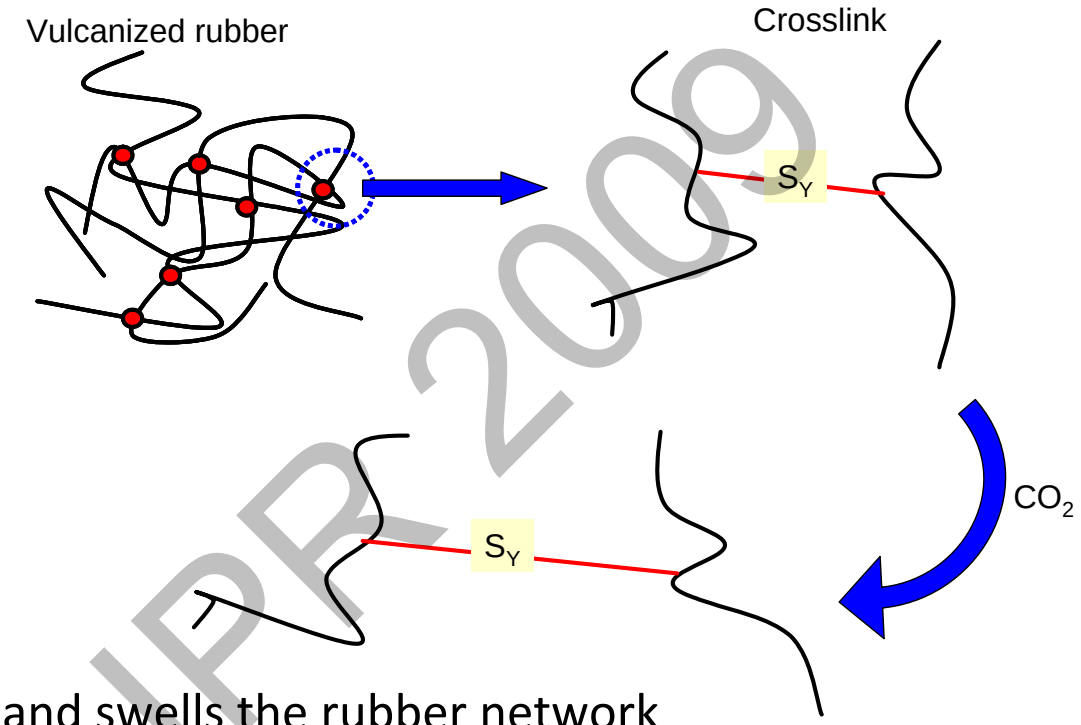
Introduction

Thermo-Mechanical Devulcanization Process with Supercritical CO_2

- A continuous devulcanization process which is carried out in a twin screw extruder
- No chemical agents
- $scCO_2$ acts as a plastisizer and facilitates the process
- US patent 7,189,762

Introduction

Devulcanization Mechanism



- ScCO2 diffuses and swells the rubber network
- Elastic constant (k) for S-S bonds is about 1/30 that for C-C bonds
- Selective cleavage of S-S bonds occurs

Introduction

Previous efforts

- *Lab-scale devulcanization process of rubber crumb using a twin-screw extruder has been established*

- *In scale-up trial, volatiles generated during devulcanization can blast out of the extruder die periodically*

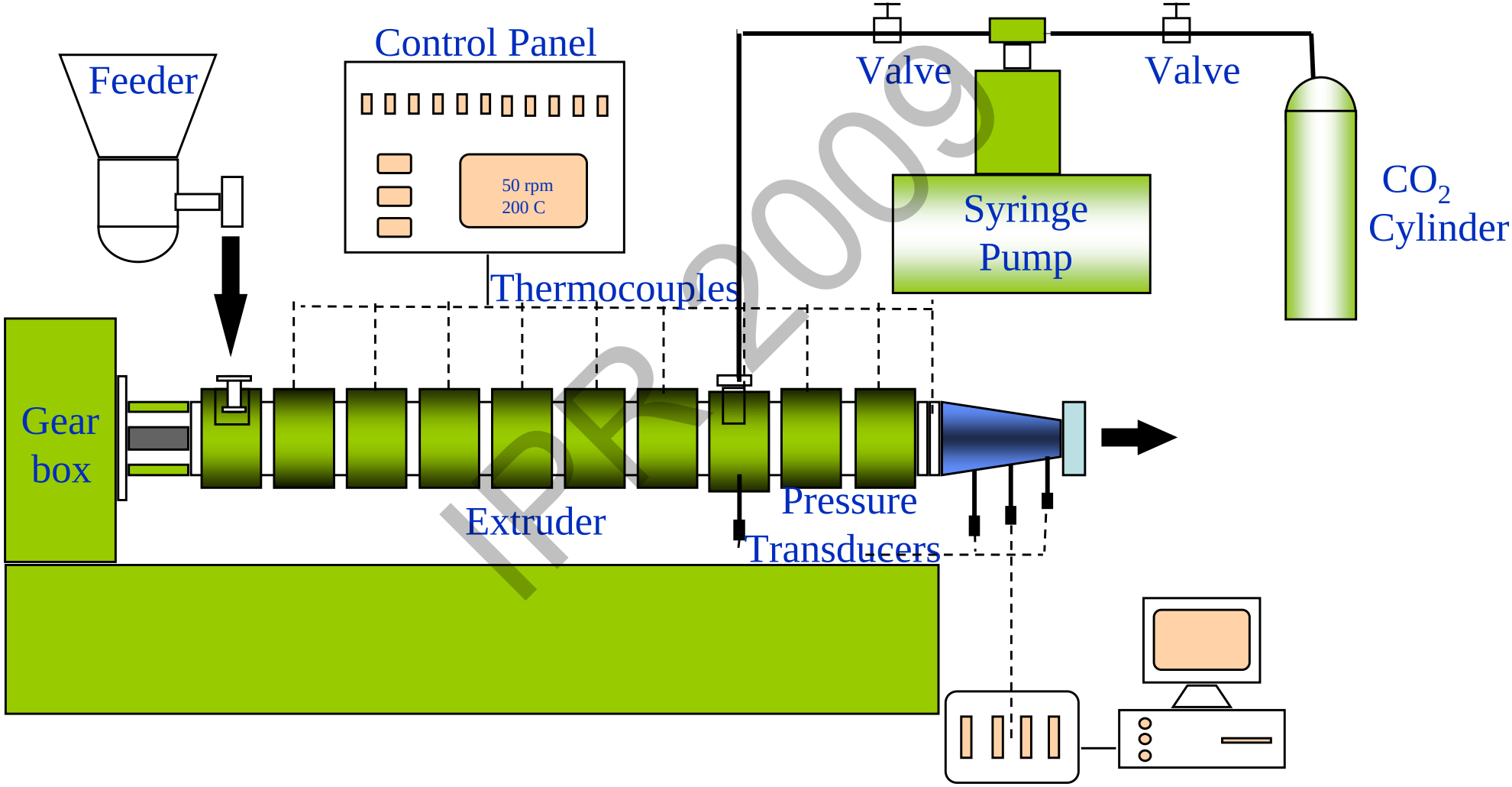
Objectives

- *To achieve a higher throughput of the devulcanized rubber for cost- reduction*

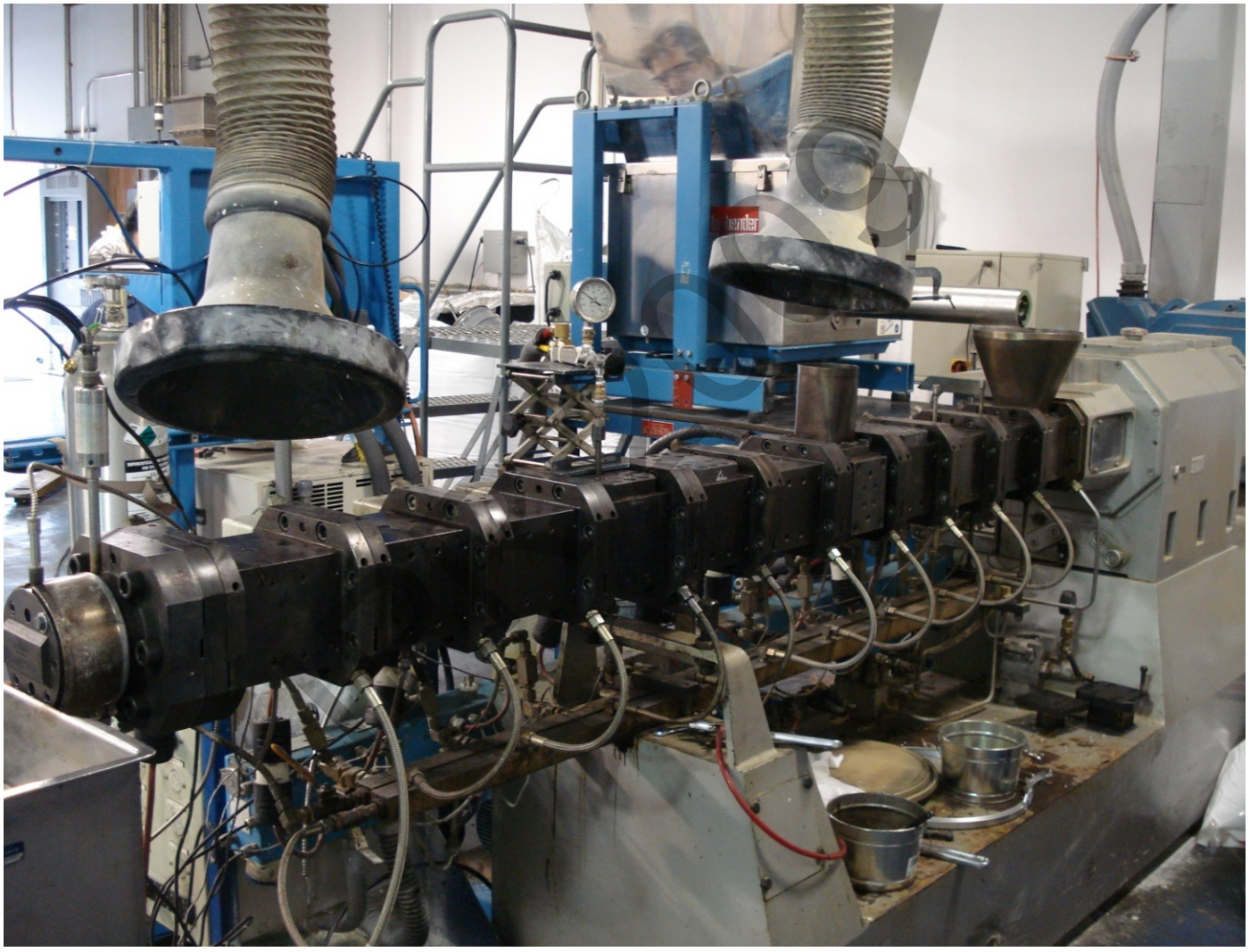
- *To maintain the degree of devulcanization in the scaled-up process*

- *To optimize the process and find out the processing window to avoid the volatile blast-off*

Experimental



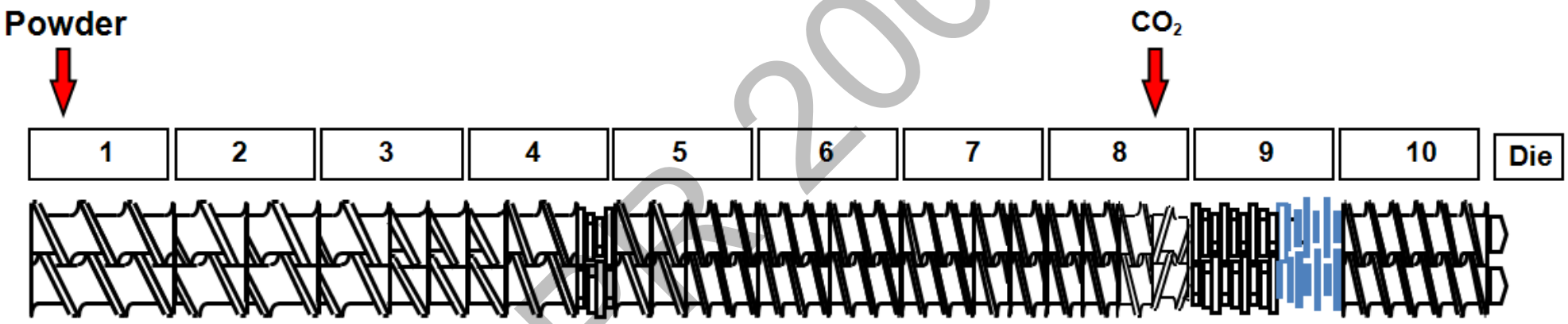
Experimental



50 mm twin screw extruder (American Leistritz, NJ)

Experimental

Screw configuration



- In the first zone the crumb rubber is heated to the devulcanization temperature
- Kneading elements after injection of CO_2 give the CO_2 and rubber crumb a good mixing and enough shearing and stretching

Experimental

- *Rubber Crumb (Permalife co.)*

Particle size :

30 mesh

- *$scCO_2$ (Praxa*

Sc Co2 injection system

Experimental

Scale-up of devulcanization process

- Material : 30 mesh rubber crumb (Permalife Inc)
- Temperature was fixed at 200℃
- Equipment : 50 mm twin screw extruder (leistritz)

Screw Configuration	Feeding rate (lb/hr)	Screw speed (rpm)
Screw a, b, c d, e, f	50	50
	50	100
	100	50
	100	100

Experimental

Example of an unstable process

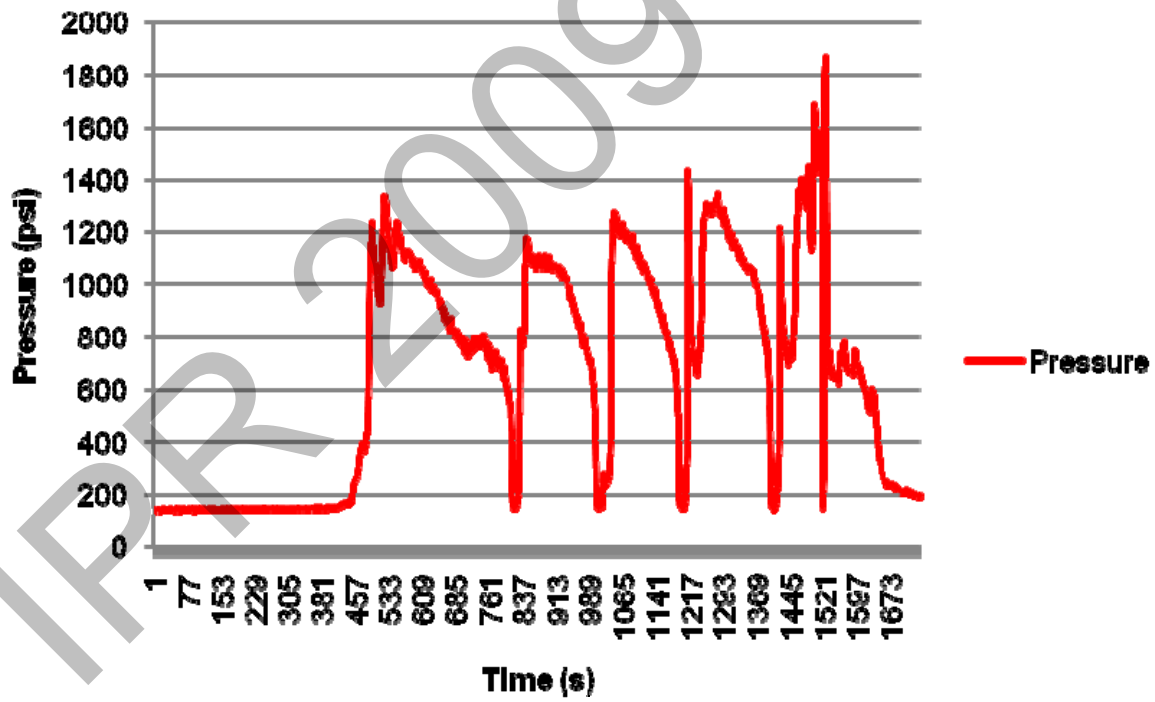
Process conditions:

Temperature: 200 °C

Screw Speed: 100 rpm

Flow Rate: 100 lb/hr.

Screw : d



- Unstable process
- Material and gases blasted out from the die exit periodically

Experimental

Stable process

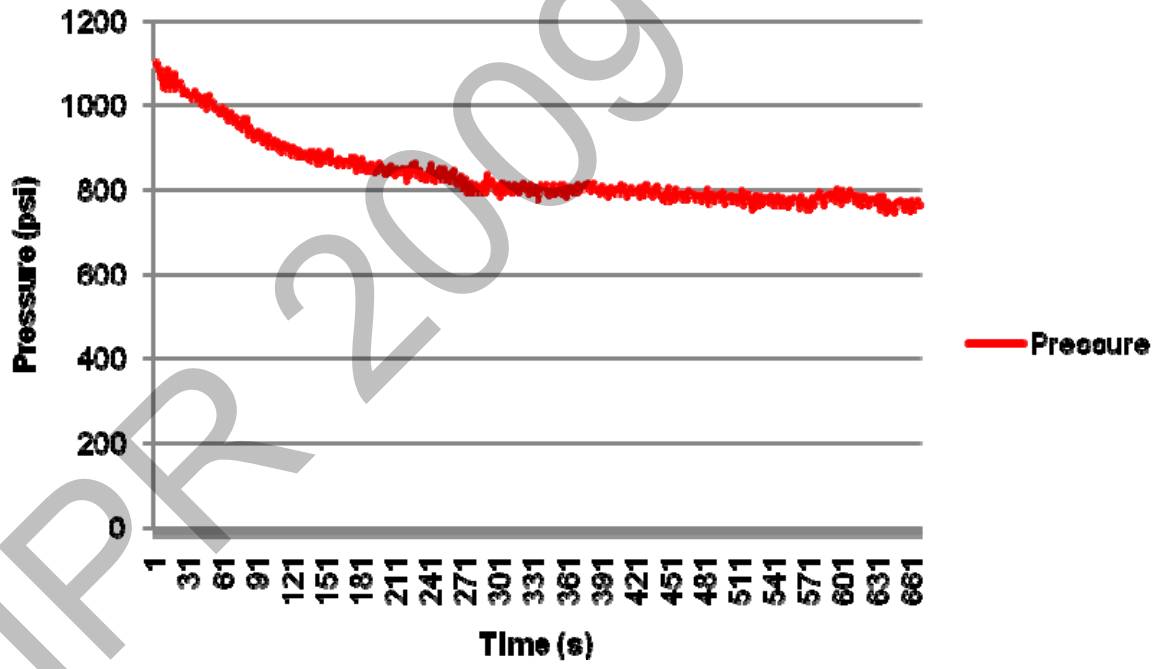
Process conditions:

Temperature: 200 °C

Screw Speed: 100 rpm

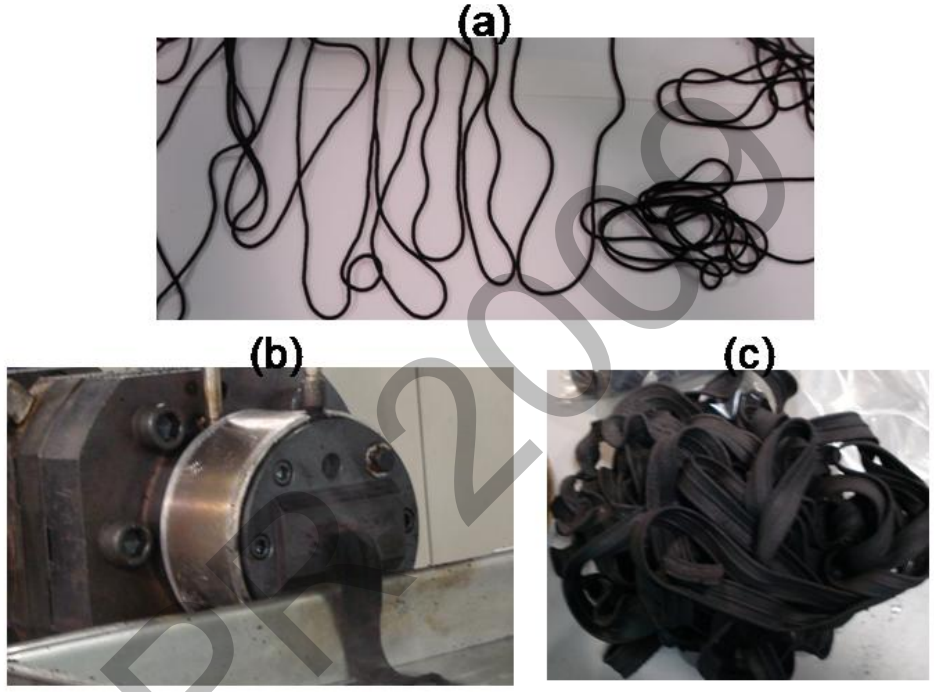
Flow Rate: 100 lb/hr.

Screw : e



- Stable process
- Material was coming out from the die exit in a continuous manner

Experimental



Typical devulcanized samples :

a)Samples of devulcanized rubber in strand shape

b)Devulcanized rubber ribbons exiting the die;

c)Samples of devulcanized rubber in ribbon shape

Stable process

Experimental

Compounding recipe for samples

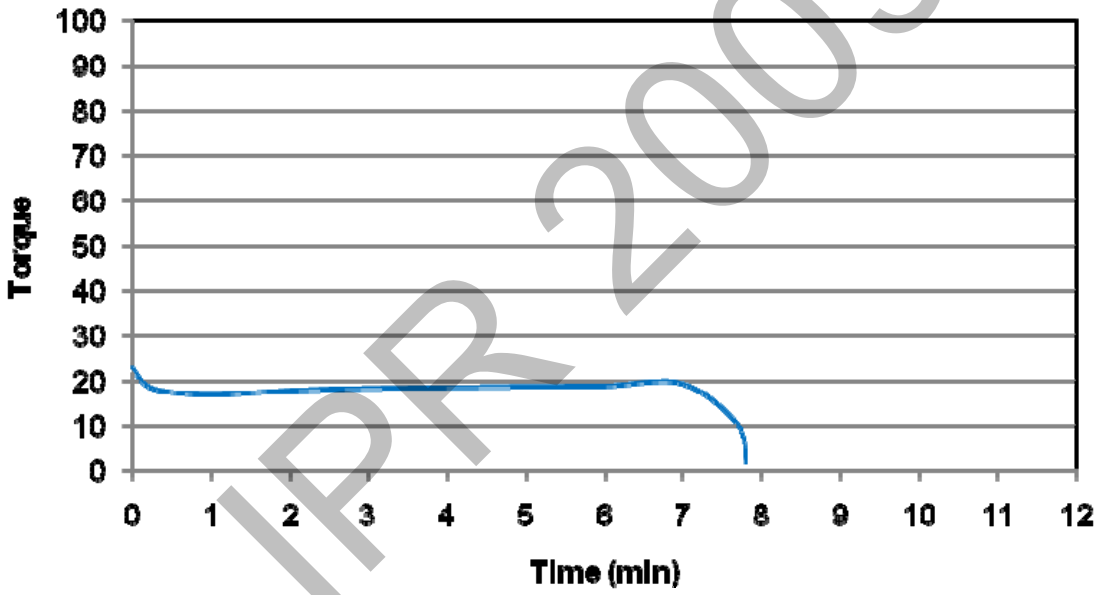
Ingredients / Samples	Devulcanized rubber	Virgin rubber compound	Curing agents
1	100 phr	-	-
2	100 phr	-	10 phr
3	-	100 phr	10 phr
4	30 phr	70 phr	10 phr
5	50 phr	50 phr	10 phr
6	70 phr	30 phr	10 phr

- Virgin rubber compound (typical NR/SBR compound)
- Curing system (St. A, ZnO, TBBS, TMTD, S)

Results & Discussion

Curing behavior of devulcanized rubber

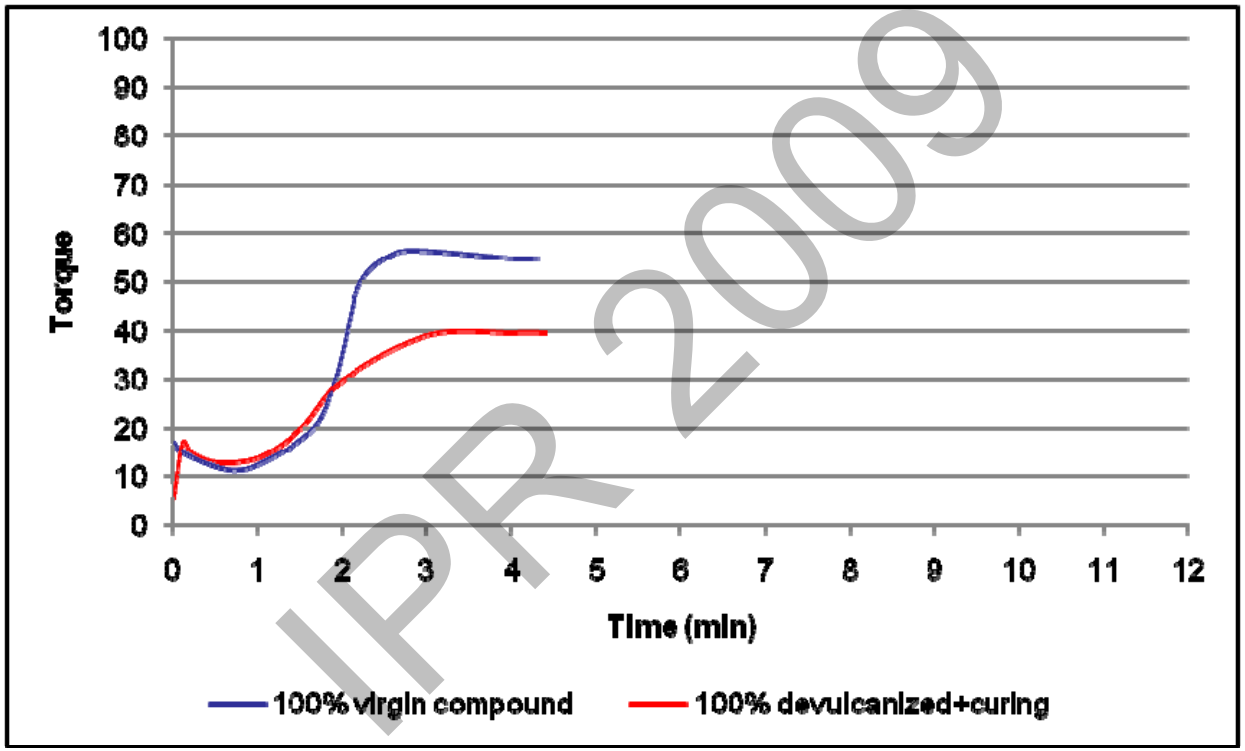
(sample 1 ,No curing agent)



- *No rise in torque was observed ,confirming that no crosslinks form*
- *No active sulfur component and curing agents is remained in devulcanized rubber.*

Results & Discussion

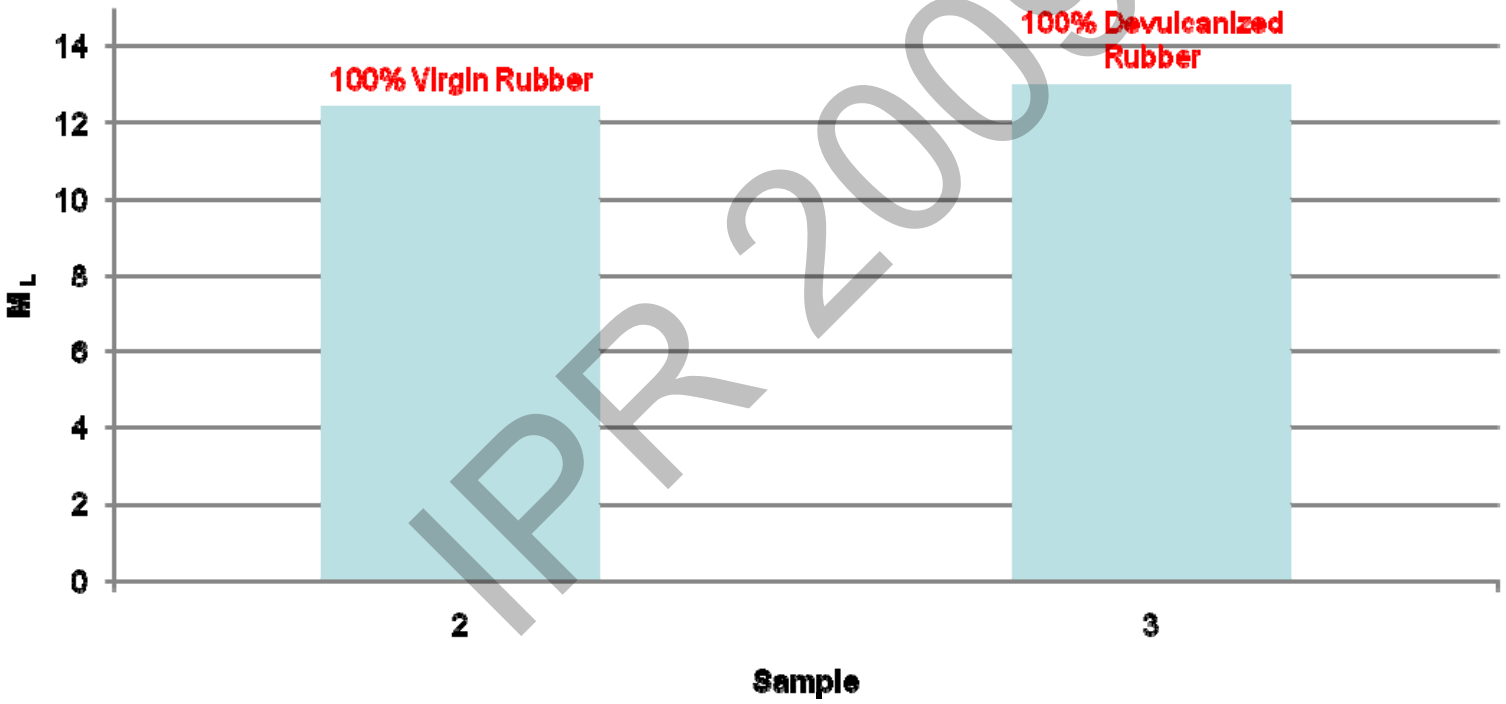
Curing behavior of revulcanized samples



- *The devulcanized rubber can be revulcanized by adding curing agents*
- *The maximum torque for the revulcanized sample is lower than the virgin compound*

Results & Discussion

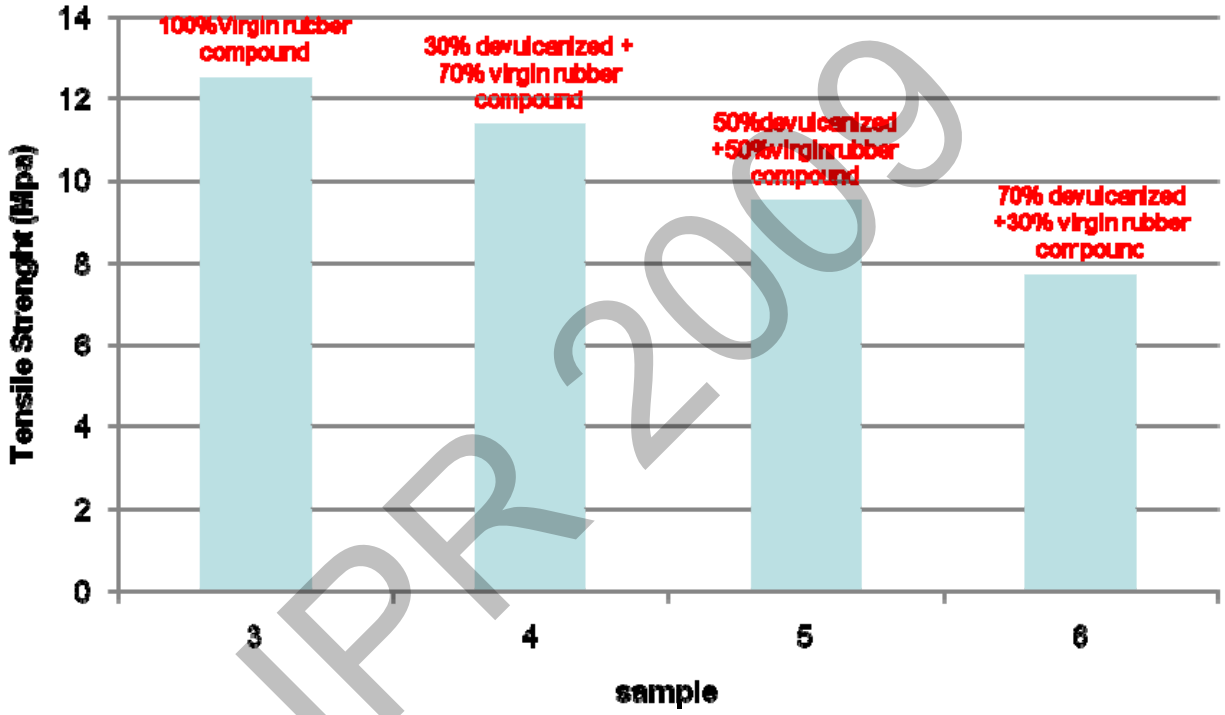
M_L (Mooney Viscosity)



- *The Mooney viscosity of devulcanized rubber is very close to the virgin rubber showing good processability*

Results & Discussion

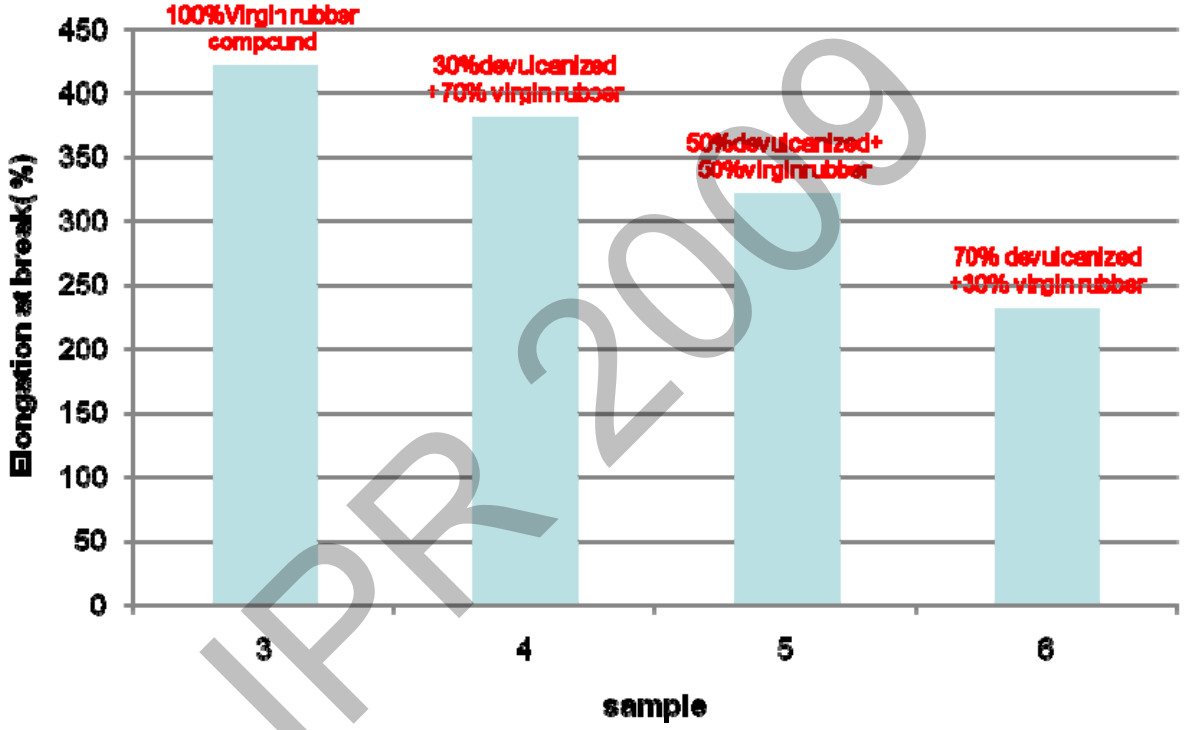
Tensile strength



- *Increasing of devulcanized rubber content in a virgin /devulcanized compound will decrease the tensile strength of the compound*
- *Tensile strength reduction for sample having 70% devulcanized rubber is about 35%*
- *Adding 50 percent devulcanized rubber to a virgin rubber compound decreases the tensile strength only up to 25 %.*

Results & Discussion

Elongation at break



- *Elongation at break reduction for sample containing 70% devulcanized rubber is about 35%.*
- *Adding 50 percent devulcanized rubber to a virgin rubber compound decreases the percent of elongation at break only up to 10 %*

Concluding remarks

- *Devulcanization of ground tire rubber crumbs under stress in the twin screw extruder with supercritical CO_2 is a continuous, cost-effective, and environmentally friendly process*

- *A reasonably high throughput of devulcanized rubber has been obtained in the scale-up devulcanization process in a twin screw extruder, which is stable*

- *The volatiles generated during extrusion can be controlled and screw configuration, feeding rate and the screw speed are the key parameters to control the process stability*

- *The devulcanized rubber can be revulcanized again by adding curing agents, and it shows a reasonable physical and mechanical properties*

Current Efforts

- *Investigation of effects of different process parameters on crosslink density and percent of devulcanization*
- *Improvement of physical and mechanical properties of devulcanized rubber*
- *Preparation of TPV material by using the devulcanized rubber*

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