INCORPORATION OF DEVULCANIZED RUBBER IN A TIRE RUBBER COMPOUND

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Outline

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

Introduction

- **Annual generation of Scrap tires :**

  World :1.6 billions

  USA: 299 millions

  Canada: 30 millions

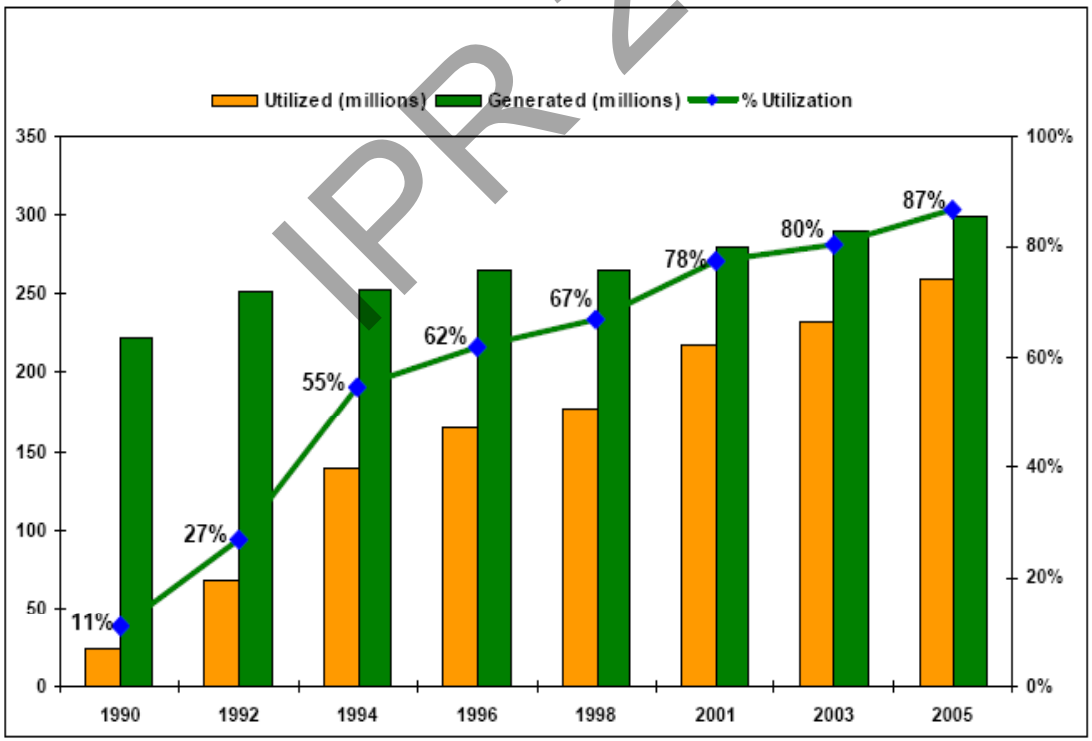
References:

- *"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

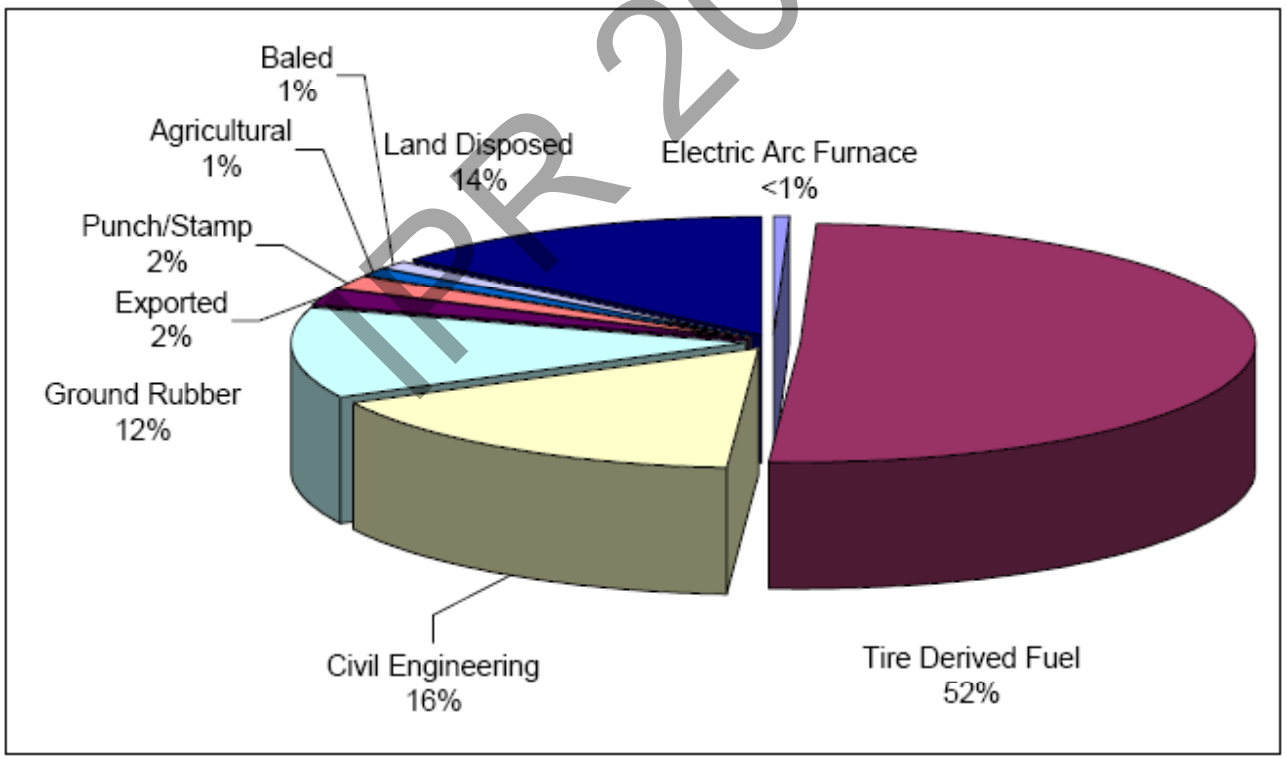
Tire Recycling

- 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

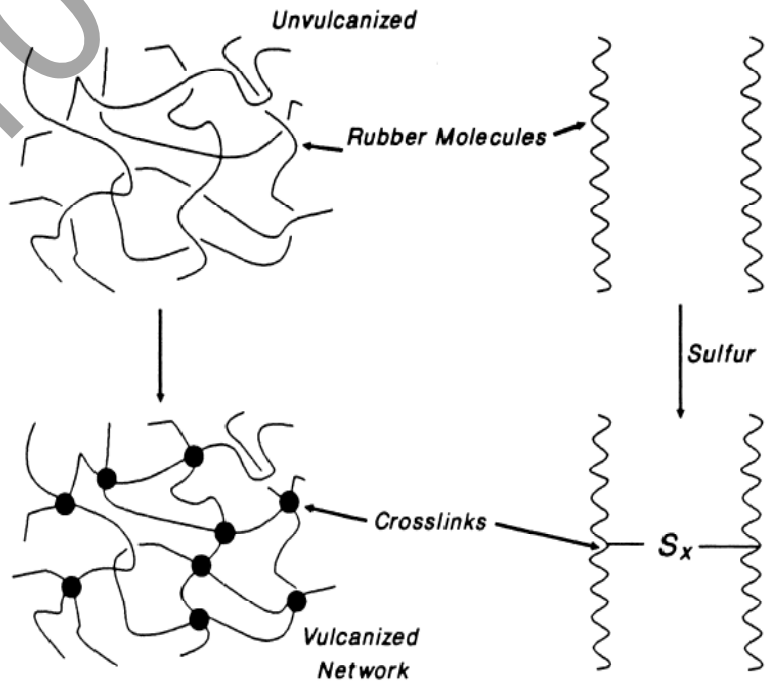
Introduction

- ***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

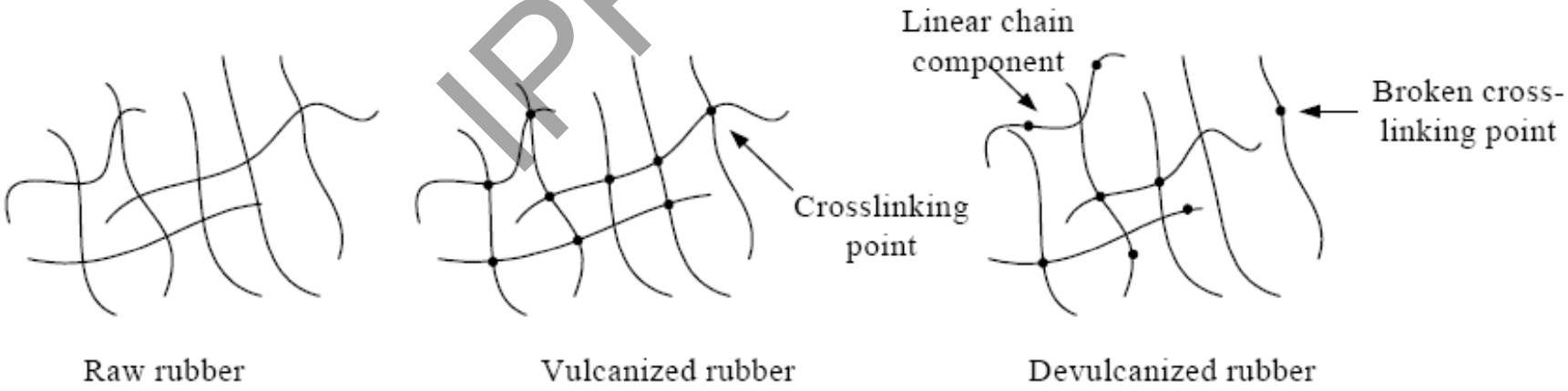


Introduction

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

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Advantages of breaking the 3D network :

(Devulcanized Rubber)

- **Re - Compoundable**
- **Re – Processable**
- **Re - Vulcanizeable**

Introduction

Devulcanization Methods

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

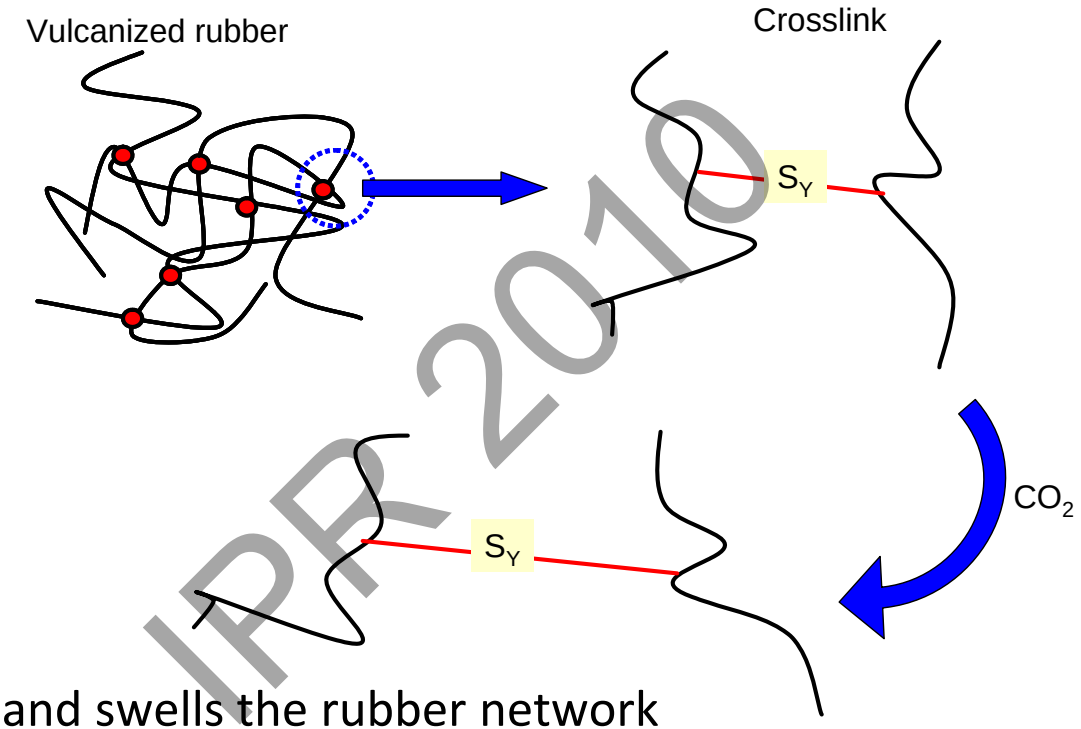
Introduction

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

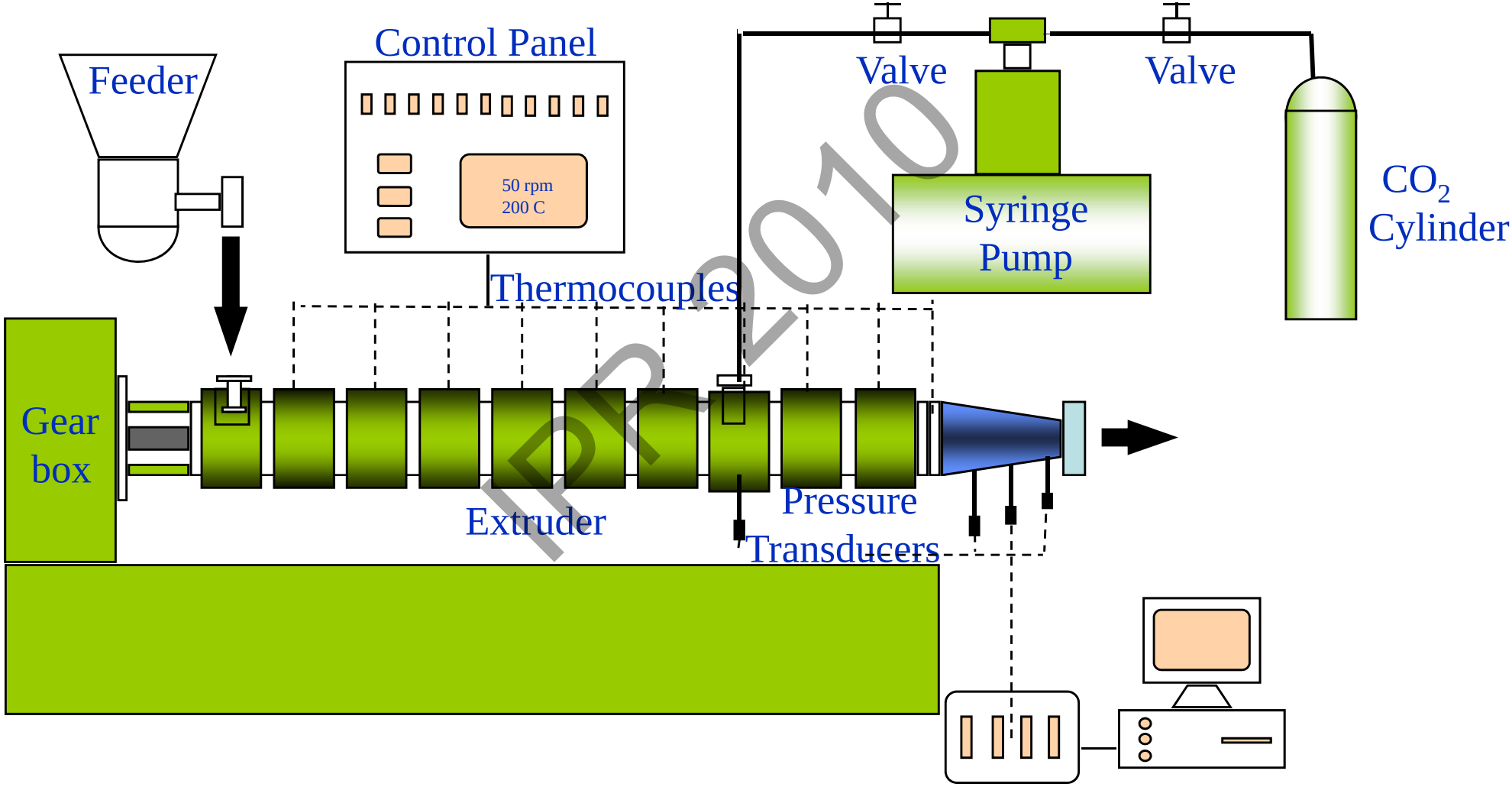
Introduction

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

Experimental

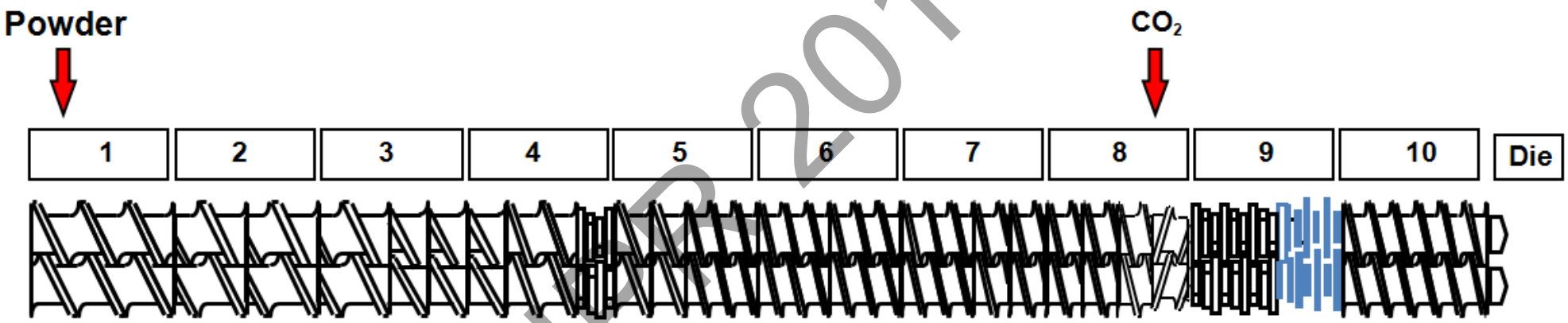


Experimental

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 (Edge Rubber co.)*

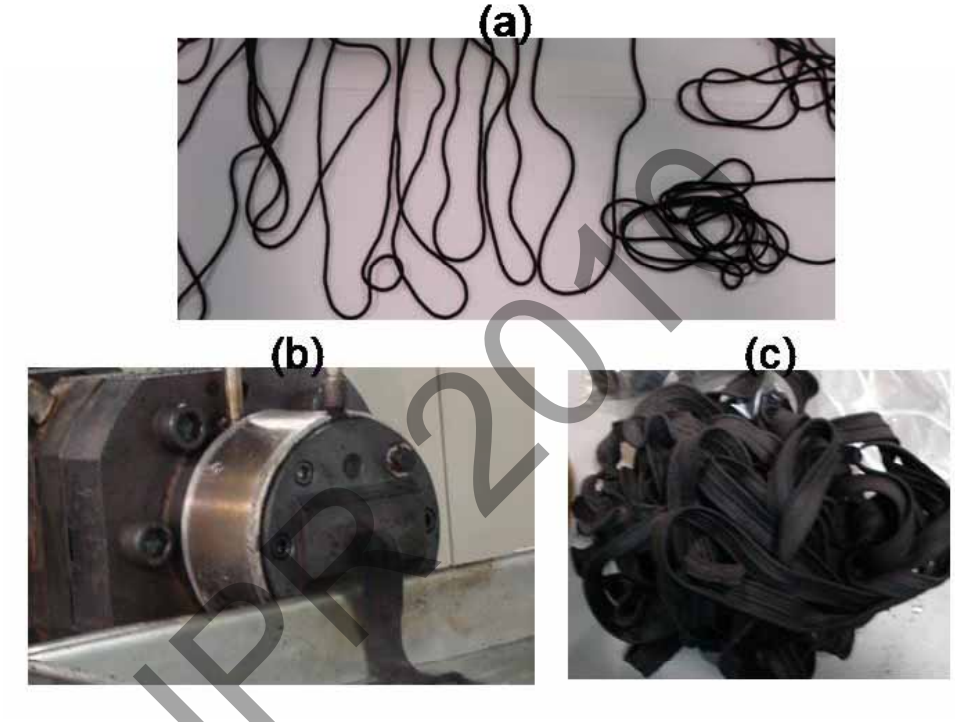
  Particle size :

  60 mesh

- *$scCO_2$ (Praxair)*

Sc Co2 injection system

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

Intruduction : Tire tread

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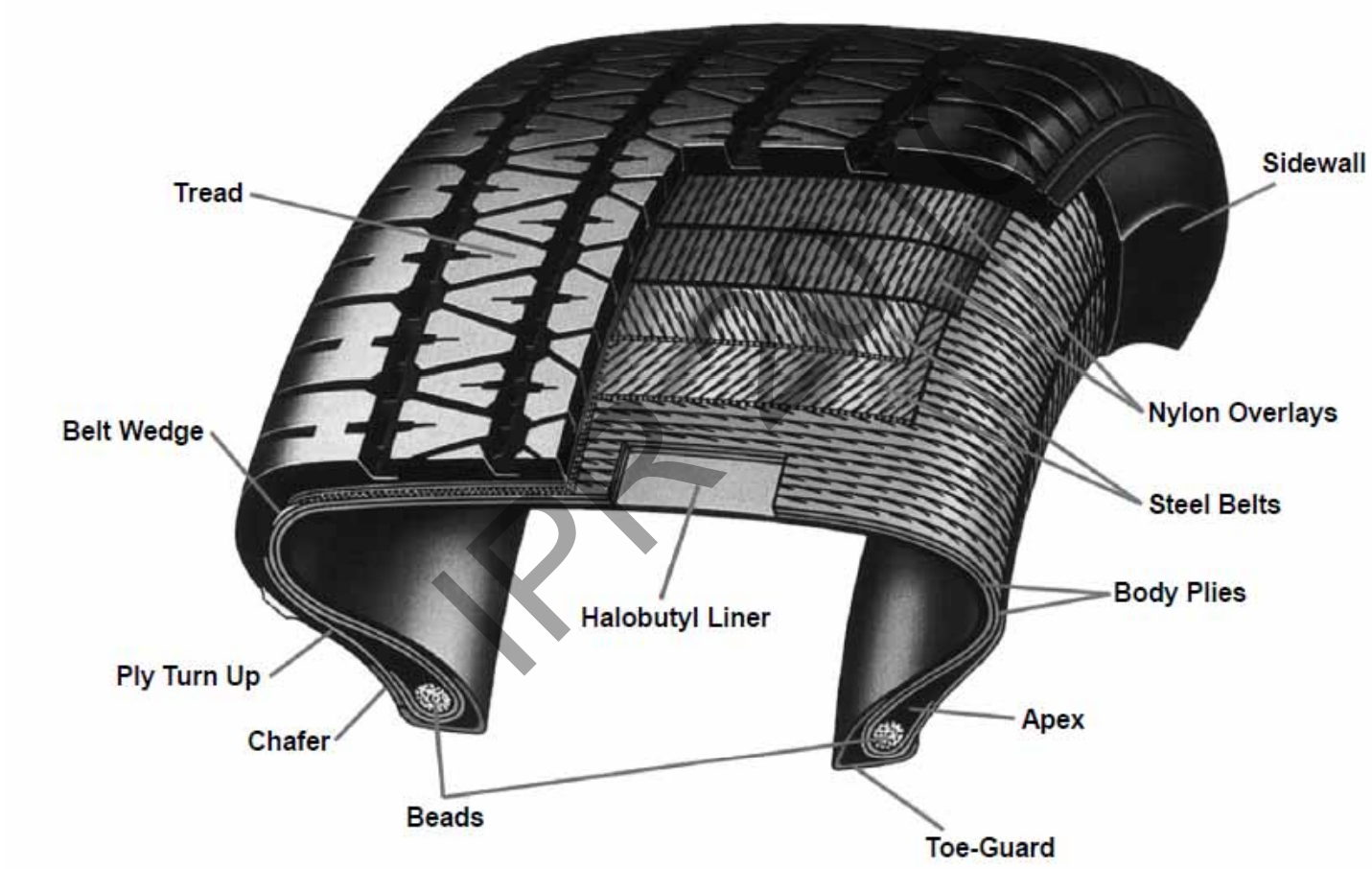
Tire Tread :

- Tread is the wear resistance component of the tire in contact with the road
- It must provide traction, wet skid, and also minimum noise generation and low heat buildup
- A blend of natural rubber, polybutadiene (BR),and styrene–butadiene rubber (SBR), compounded with carbon black, silica, oils, and vulcanizing chemicals

Why devulcanized rubber incorporation ?

- Lowering the cost of raw material
- Recycling of scrap tires

Intruduction : Tire tread



Cross-section of a high-performance passenger tire

Experimental

Compounding recipe for samples

Ingredients	*Control*	*10%*	*20%*	*30%*
Tread MB	194 phr	174 phr	155 phr	135 phr
Devulcanized rubber	-	20 phr	39 phr	59 phr
OBTS	1.25 phr	1.25 phr	1.25 phr	1.25 phr
PVI	0.3 phr	0.3 phr	0.3 phr	0.3 phr
Sulfur	1.95 phr	1.95 phr	1.95 phr	1.95 phr

- Tire tread MB is a compound of NR and BR plus carbon black, oil, anti ozonant, and etc.

- Tire tread MB was replaced by Devulcanized rubber in order to lower the cost of compound

Experimental

Sample preparation

- The virgin tire compound and devulcanized rubber were first mixed in a Banbury mixer
- Then curing chemicals were added during milling the compound on a two roll mill
- Appropriate curing time was determined using the MDR test data
- Samples were pressed and cured into standard testing specimens using a hot press

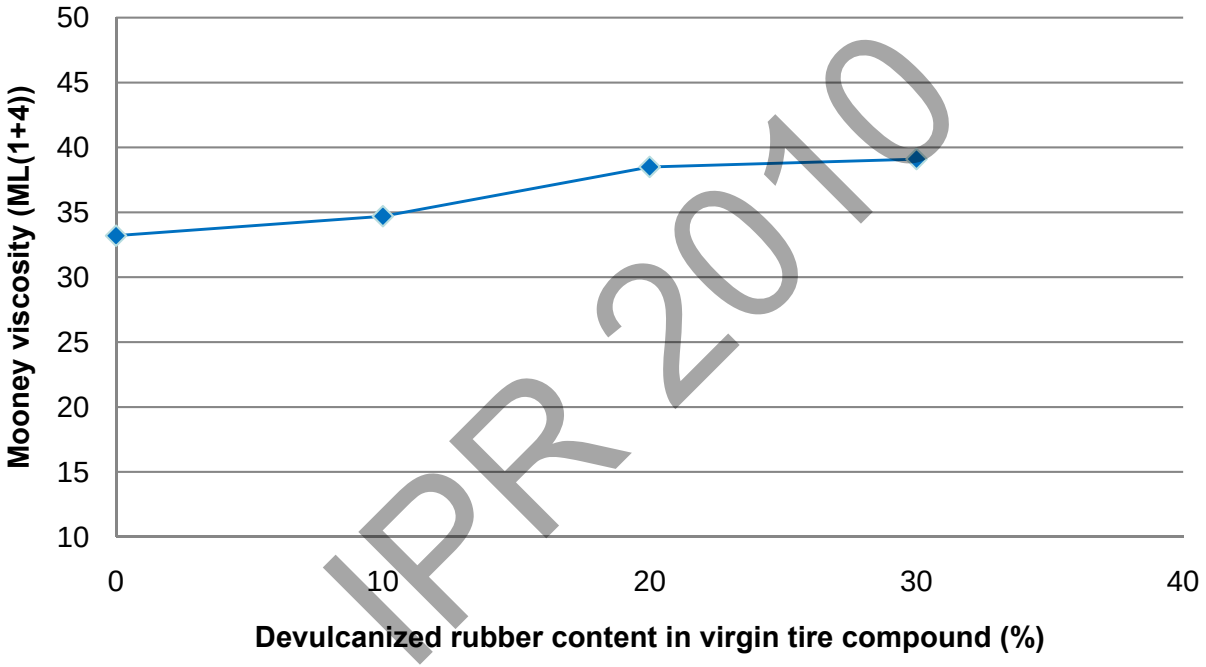
Experimental

Characterization

- *Mooney viscosity*
- *Curing Properties (MH, Ts_2, T_{90})*
- *Tensile properties (Tensile strength, Elongation at break, Modulus)*
- *Tear strength*
- *Hardness (shore A)*
- *Heat aging (72 hr @ 70 °C)*
- *Hysteresis (heat build up)*
- *Cut and chip (% of mass loss)*

Results & Discussion

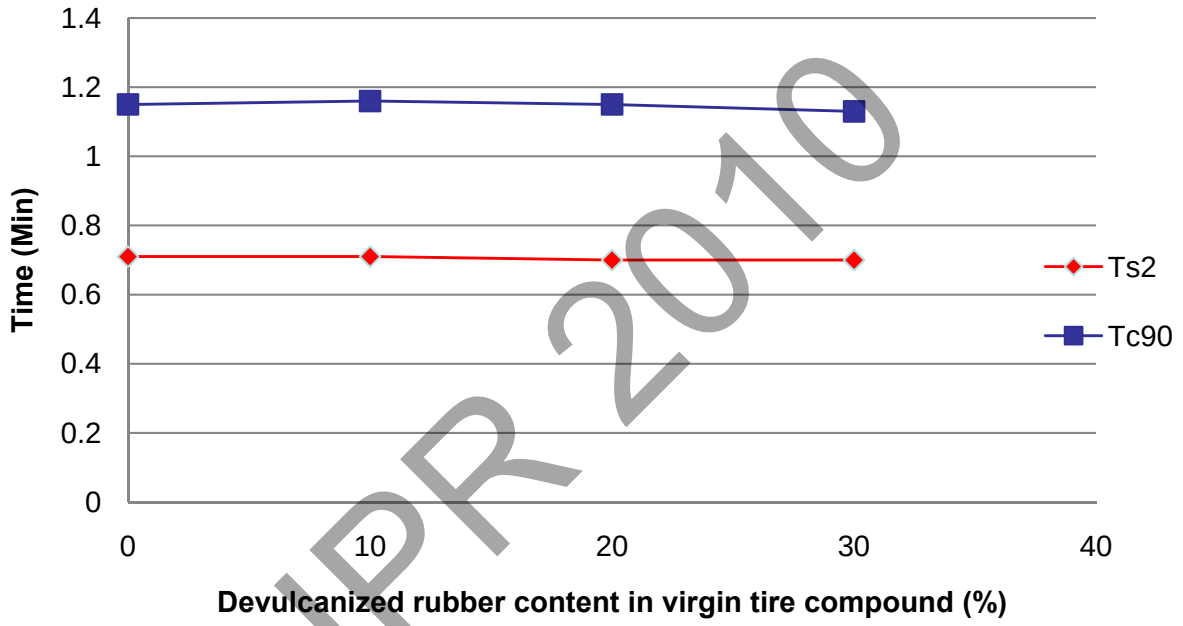
Mooney Viscosity



- *A slight increase for Mooney viscosity can be observed when the percent of devulcanized rubber in virgin rubber compound increases*
- *Presence of remained cross-link bonds could be the reason for the Mooney viscosity increasing*

Results & Discussion

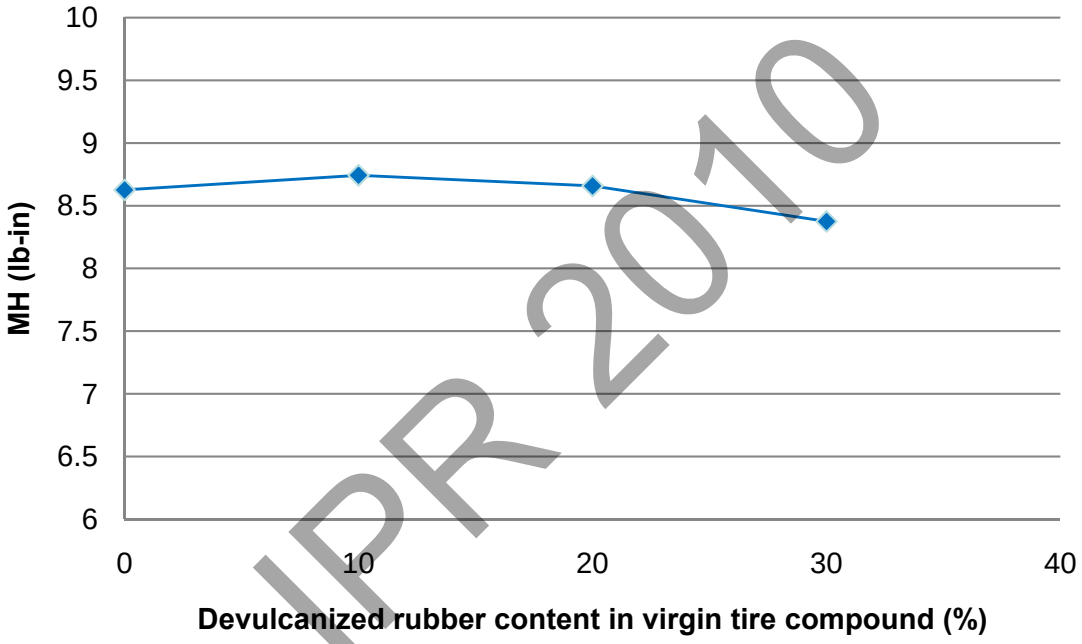
Curing characteristics (Ts2 & Tc90)



- *Scorch time (Ts2) and optimum cure time (Tc90) do not change by incorporation of devulcanized rubber into a tire tread compound up to 30 %.*

Results & Discussion

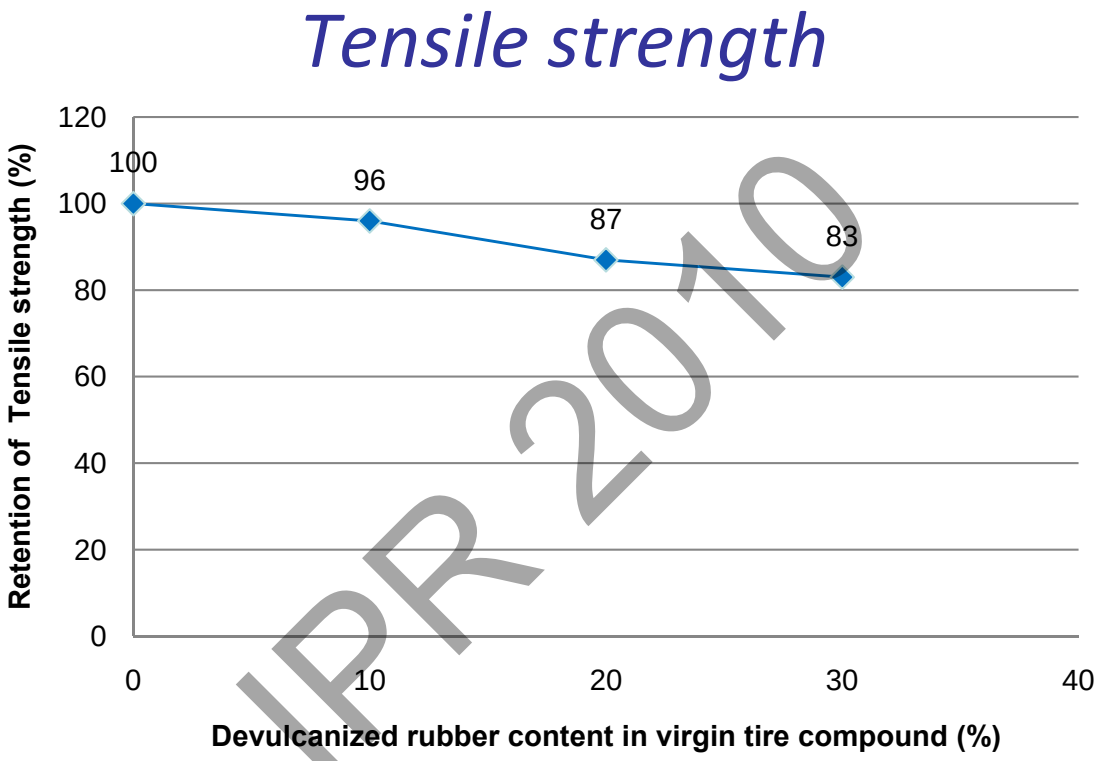
Curing characteristics (MH)



- *A very slight increase at the beginning can be observed for the M_H value and then it starts to decrease*

- *The difference is very low so one can say the M_H value remains almost constant.*

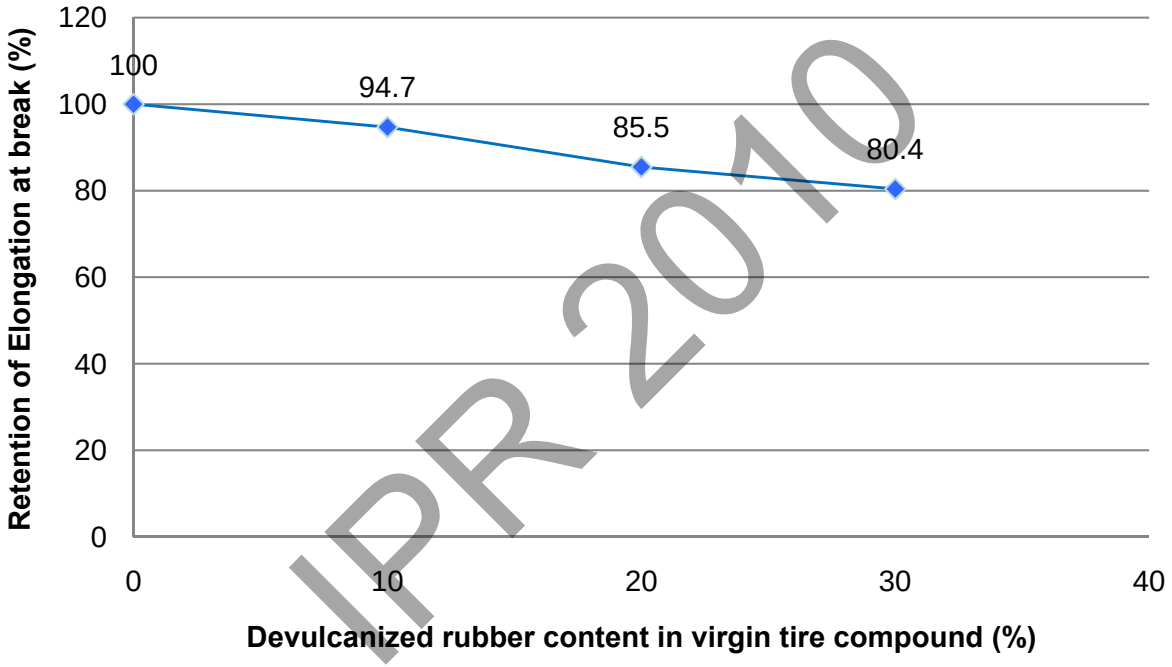
Results & Discussion



- *Tensile strength decreases as devulcanized rubber content increases*
- *Sample with 30 % devulcanized rubber shows an 83% retention of tensile strength*

Results & Discussion

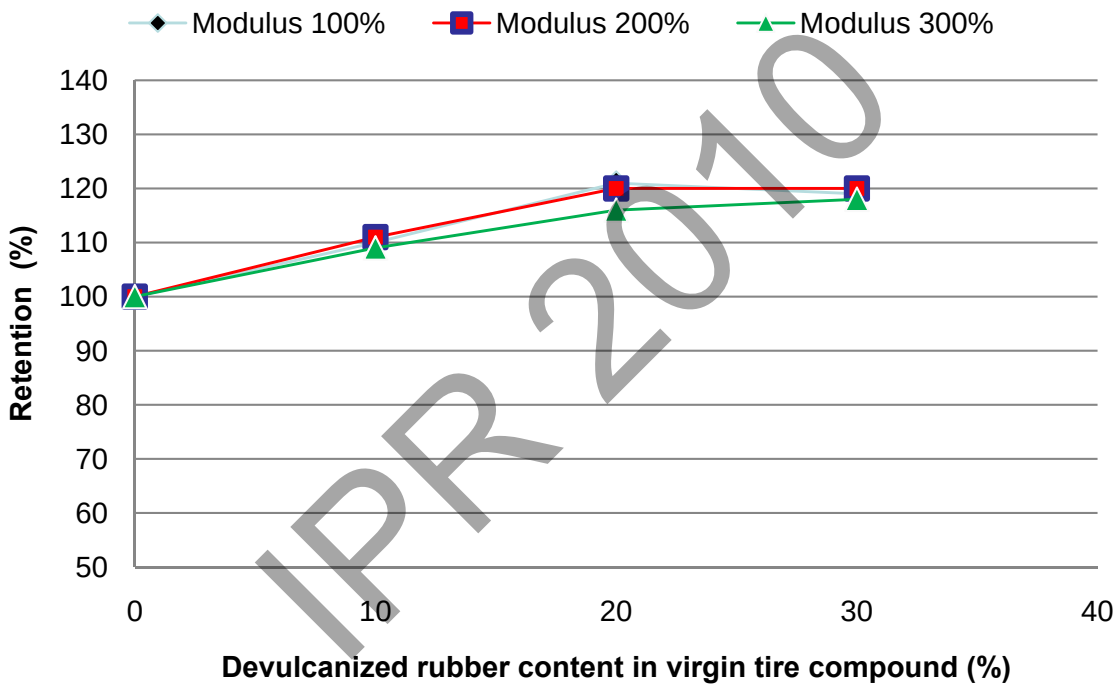
Elongation at break



- *Elongation at break decreases as devulcanized rubber content increases*
- *Sample with 30 % devulcanized rubber shows an 80.4% retention of elongation at break*

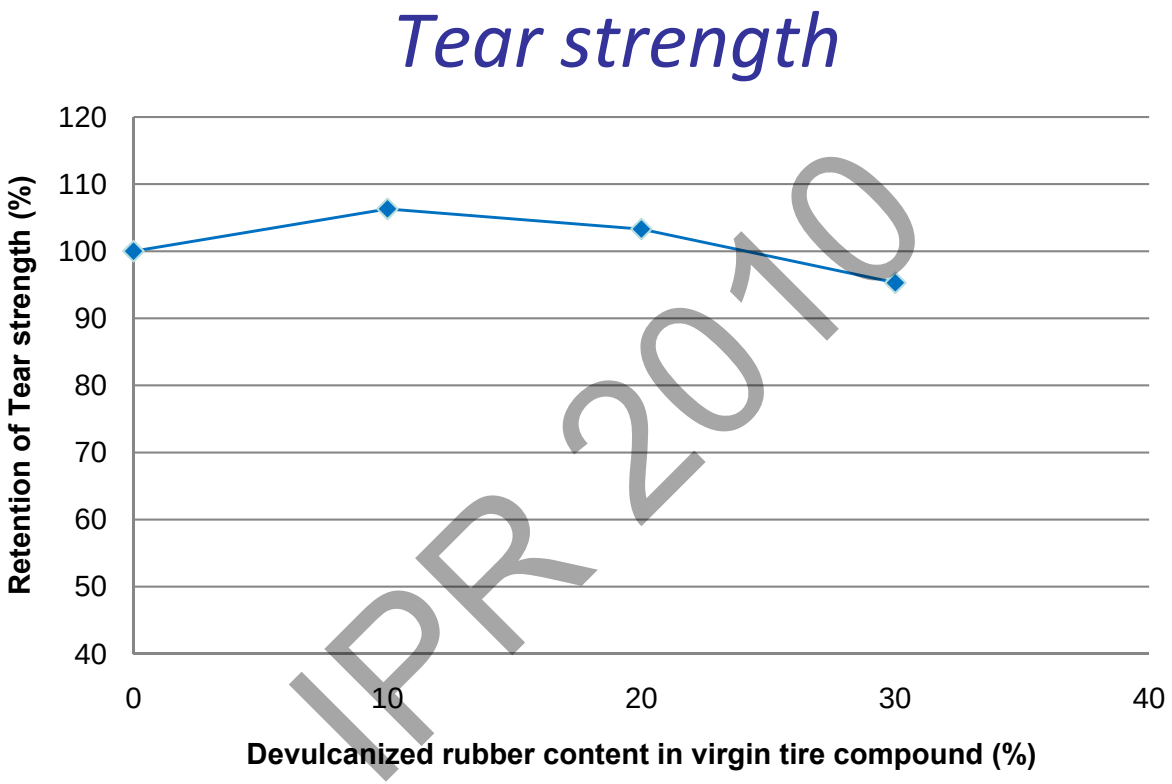
Results & Discussion

Tensile Modulus



- *Modulus increases as the content of devulcanized rubber increases in the tire tread compound*

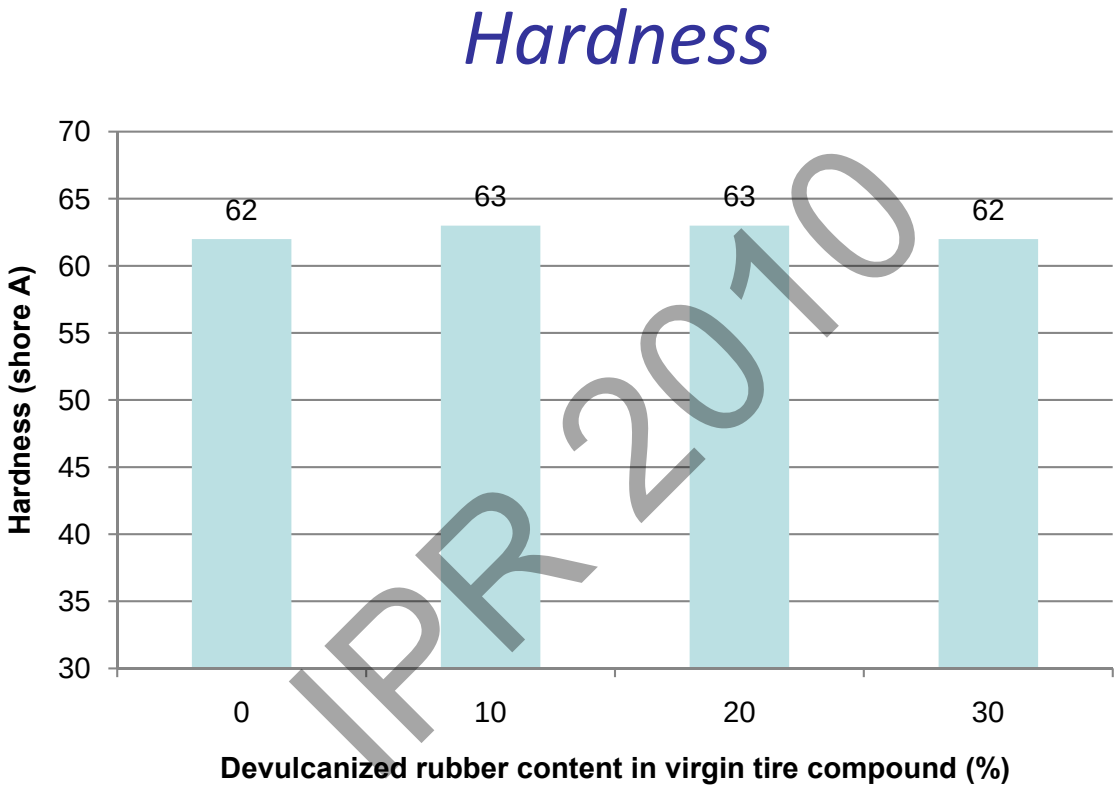
Results & Discussion



- *Tear strength increases by 7% at the beginning (when 10 % devulcanized rubber is added) and then starts to decrease*

- *Compound containing 30% devulcanized rubber shows around 95 % retention of tear strength*

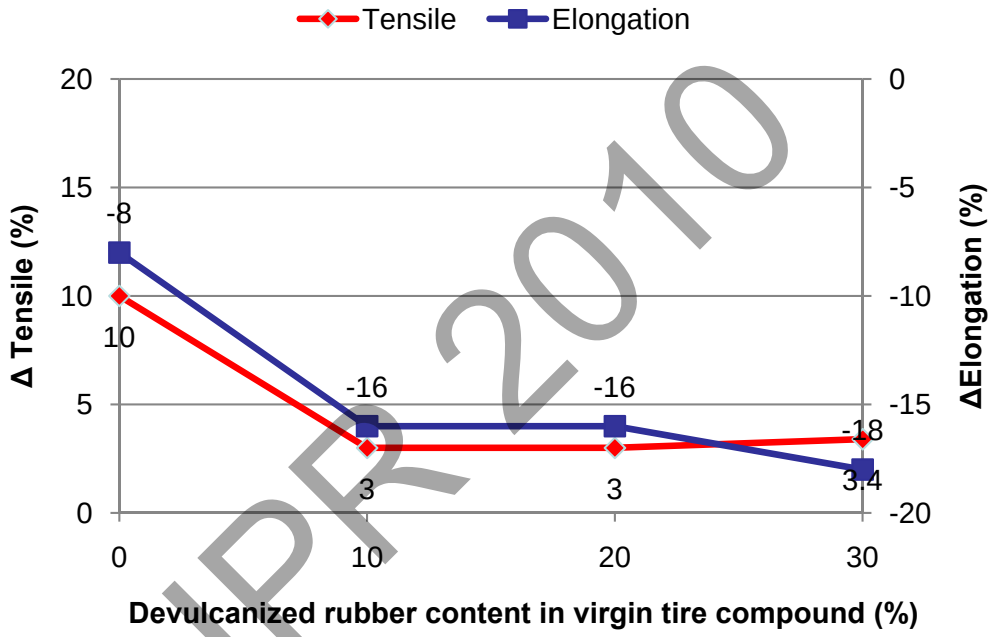
Results & Discussion



- *Addition of devulcanized rubber does not change the hardness of tire tread compound*

Results & Discussion

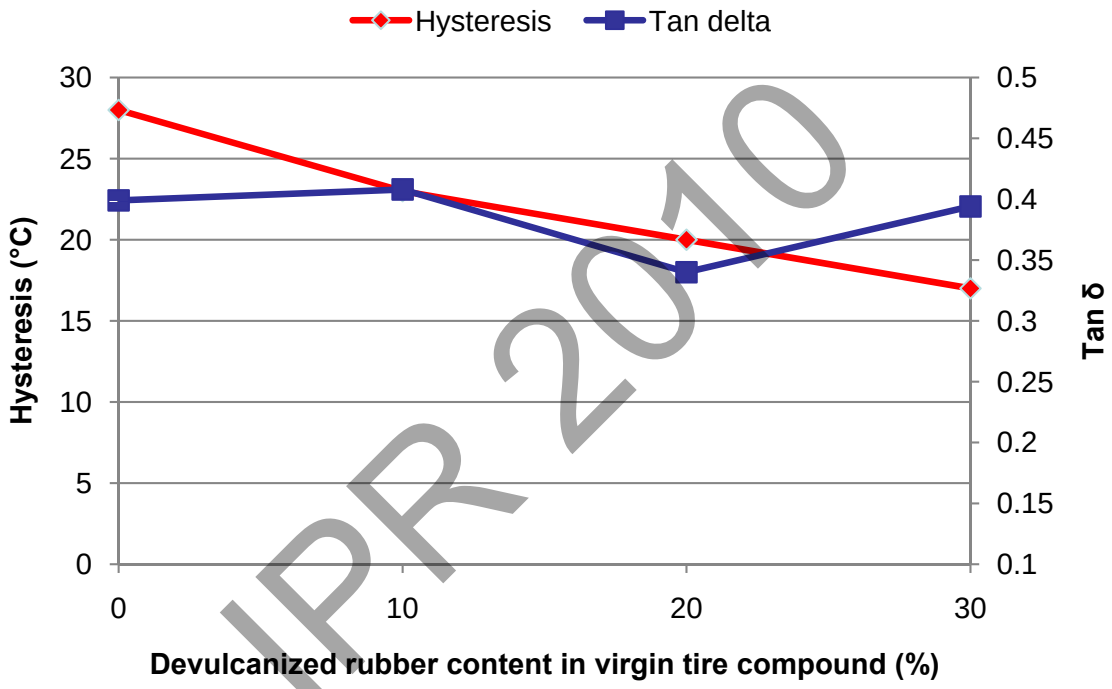
Heat aging (72 hr @ 70 °C)



- *Tensile strength increases around 10% after aging for the control compound, this value for the compounds having devulcanized rubber is around 3 %*
- *Elongation at break decreases by 8 % for control compound while for samples 10 & 20 this value is 16%. For sample having 30 % devulcanized rubber elongation decreases by 18% after aging process*

Results & Discussion

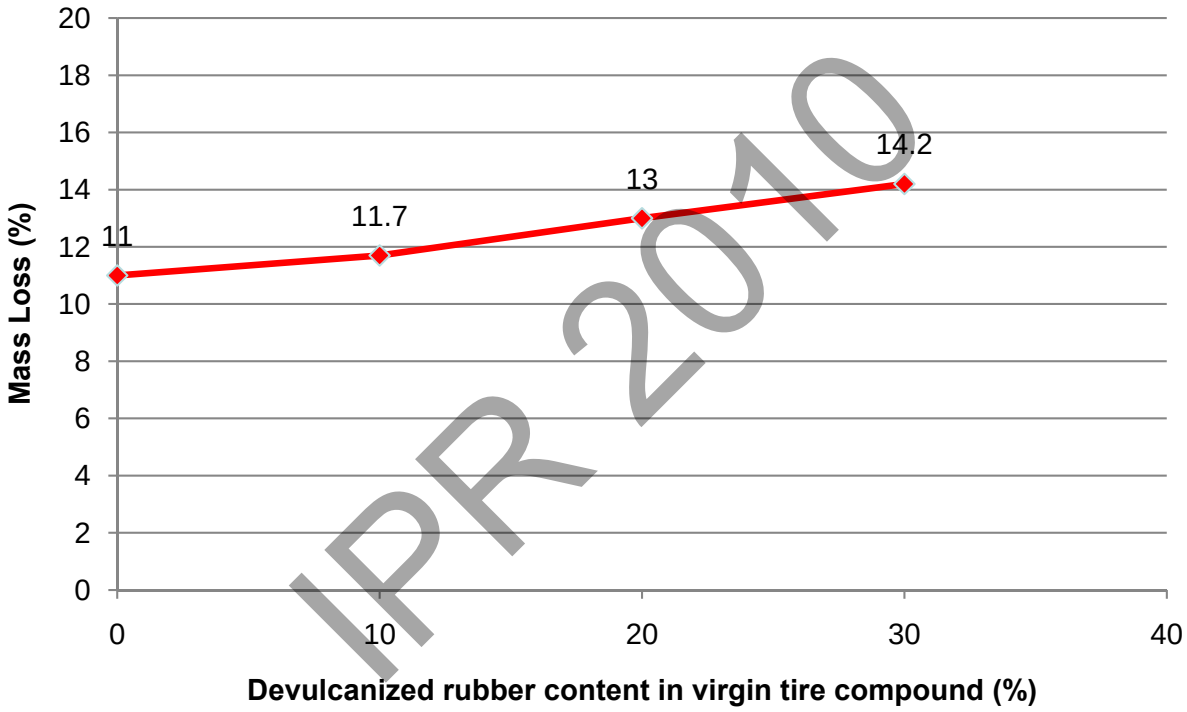
Damping and Hysteresis



- *Specimens were subjected to a dynamic load for 25 min at 148 °C using a flexometer*
- *Hysteresis (heat build up under dynamic stress) decreases as content of devulcanized rubber increases in tire tread compound*
- *Tan δ (damping) does not show a distinguishable trend and fluctuates from 0.332 to 0.408*

Results & Discussion

Mass loss in cut & chip test



- *This test shows the service performance of tire treads*
- *Percent of mass loss in a cut and chip test increases as the percent of devulcanized rubber increases in a tire tread compound*

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 devulcanization process in a twin screw extruder, which is stable*
- *Devulcanized rubber obtained from our devulcanization process was incorporated in a virgin tire compound and the results show that by addition up to 30 % of devulcanized rubber the Mooney viscosity, Hardness, tear strength and curing properties does not change significantly. Tensile strength and elongation at break decrease up to 15 % and 20%, and heat build up improves.*
- *These results show that devulcanized rubber can be incorporated in a tire compound in order to lower the price without significant deterioration of compound properties. However, additional experiments are required to further optimize the tire compound properties*.

Current Efforts

- *Optimization the properties of the tire tread and devulcanized rubber compound*
- *Incorporation of devulcanized rubber in a conveyor belt compound*
- *Devulcanization of EPDM scrap rubber*
- *Preparation of TPV material by using the devulcanized rubber*

Acknowledgements

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