# 10- 4.- Structural Characterization of different Composites

# STUDY OF THE INFLUENCE OF IPPD ON THERMAL OXIDATION PROCESS OF NBR MATRIX NANOCOMPOSITES

# 10-1.- Structural Characterization of different Composites

# Elastomer properties

- Rubber-like
- Rapid processing technique
- Elasticity
- Softness
- Flexibility
- Resilience
- Amorphous
- All are insaturated
- Very low $T_g$

- Easyly oxidized
- Do not withstand abrasives
- They need to be :
  vulcanisated
  filled
  plasticisized
- 1% damage in the structure can stop working properly.

# How to improve elastomers?

Abrasion and rigidity:

- Addition of fillers as $SiO_2$, carbon, …
- Vulcanisation

Versus oxidizing :

- Antioxidants
- Preparing less unsaturated blends
- Preparing chlorinated blends

# Aim of this work ?

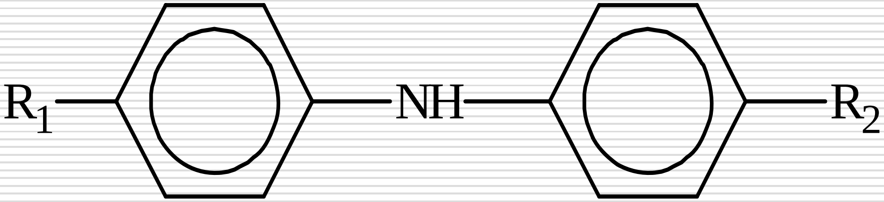
- To observe the behaviour of the antioxidant IPPD in the thermal oxidizing process at 140ºC of NBR-$SiO_2$ nanocomposite.
- To evaluate the effect of IPPD on chemical structure and mechanical properties of the composite during the degrading process

# Why use IPPD as antioxidant?

According to previous works antioxidants based in p-phenylendiamine is more effective.

## What is IPPD?

It is N-isopropyl-N’-phenyl-p-phenylendiamine



where $R_1 = H$ $R_2 = NH\text{-}CH(CH_3)_2$

# We propose

## to compare

Two nanocomposites of vulcanized acrylonitrilebutadiene rubber (<20%acrylonitrile) reinforced with fine $SiO_2$

## with / without

IPPD in a thermal-oxidizing atmosphere.

## exposed to

Thermal-oxidizing atmosphere in an air circulating oven at 140ºC for different periods of time (from 0 hours to 120 hours)

# materials

| | |
|---|---|
| **NBR** | (<20% acrylonitrile) |
| $SiO_2$ | (135 $m^2$/g) reinforcement |
| DOP | plasticizer |
| ZnO | catalyst of vulcanization |
| DPG | catalyst of vulcanization |
| Rheno | hexa |
| MBTS | vulcanization accelerator |
| S | vulcanization |
| IPPD | antioxidizer |

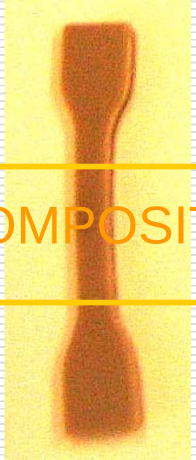
# preparation of nanocomposites

Vulcanization:

170ºC

15 min

1,96 MPa



COMPOSITES

mixing process was carried out in a two-roll mill at RT

# characterization

## Mechanical testing

- Tensile Strength
- Young’s Modulus
- Toughness
- Elongation at break

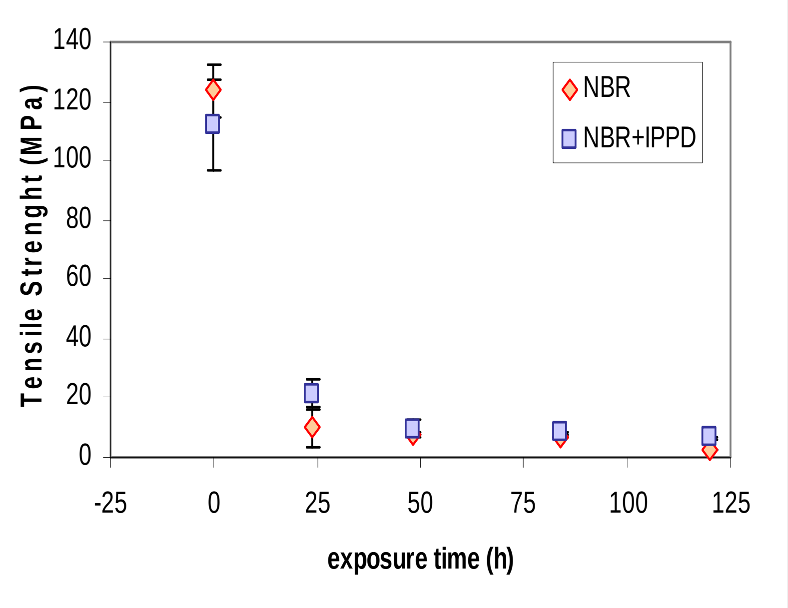
## Spectrophotometry FTIR-ATR

## Degree of cross-linking (Flory-Rehner equation)

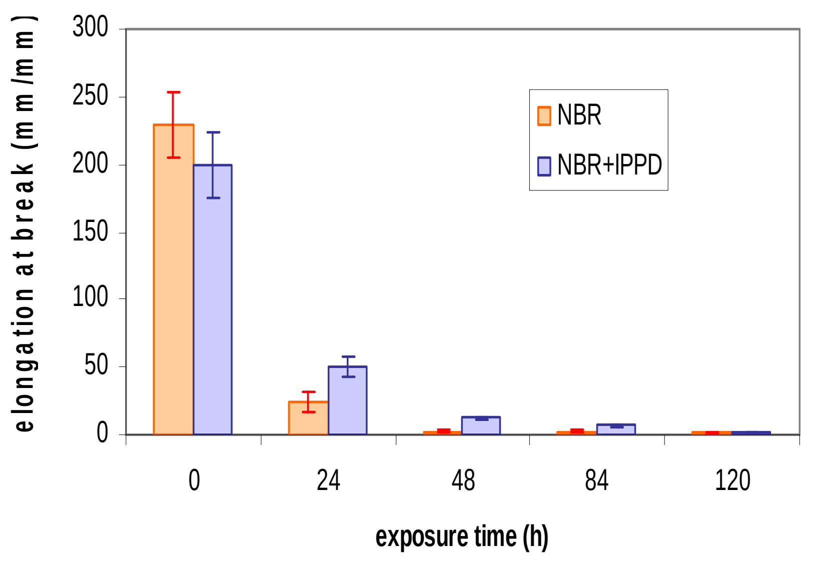
## Thermogravimetry

# mechanical properties

## Tensile strenght



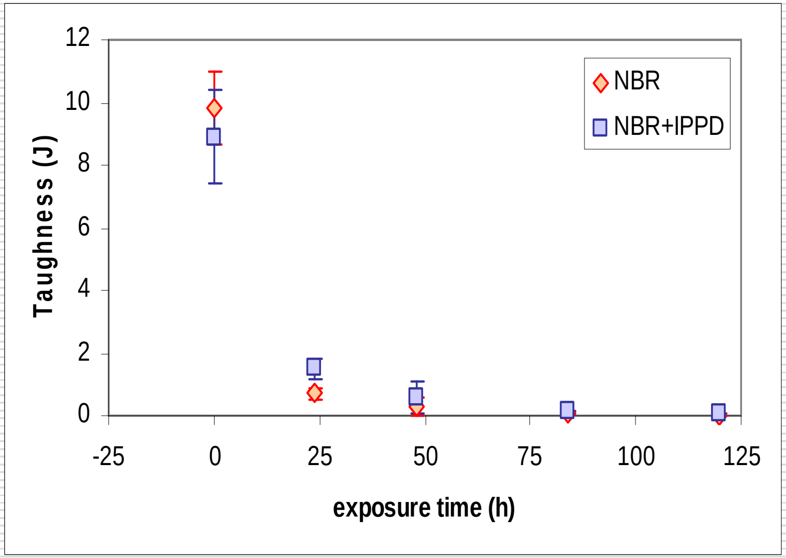
## Elongation at break



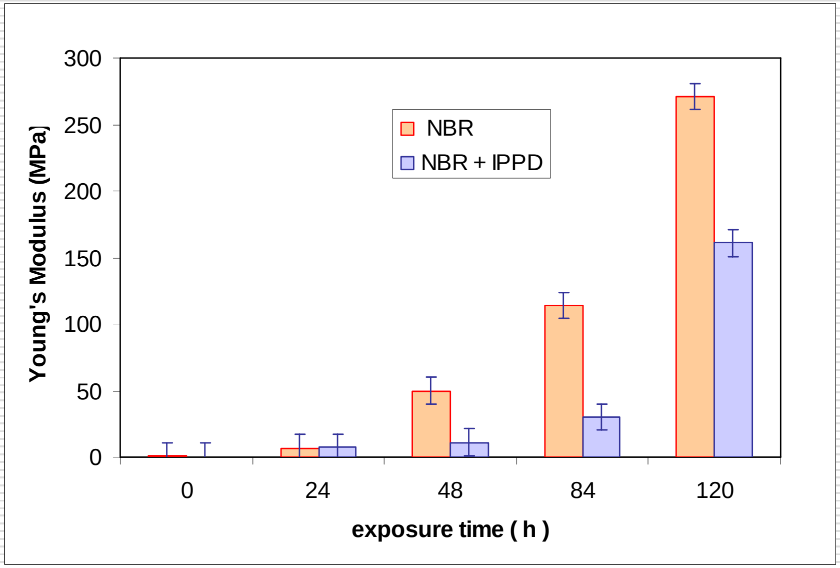
**From 48h the values of tensile strength are the same.**

# mechanical properties

## Toughness

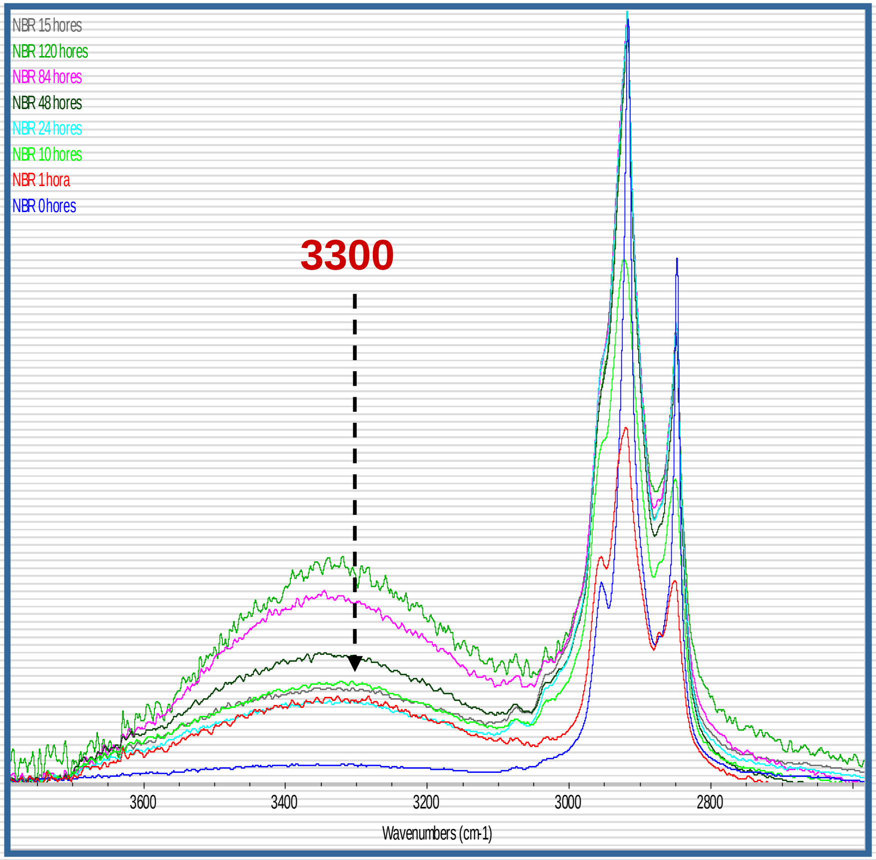


## Young’s modulus

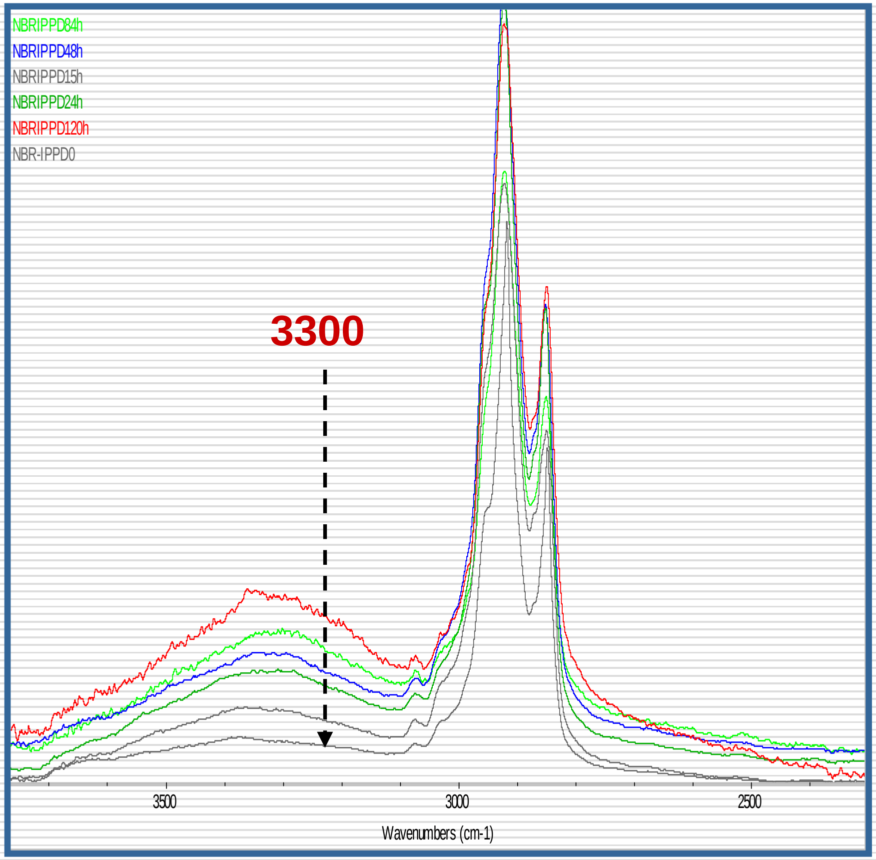


**From 48 h toughnes are almost the same.**

# FTIR/ATR hydroxyl region



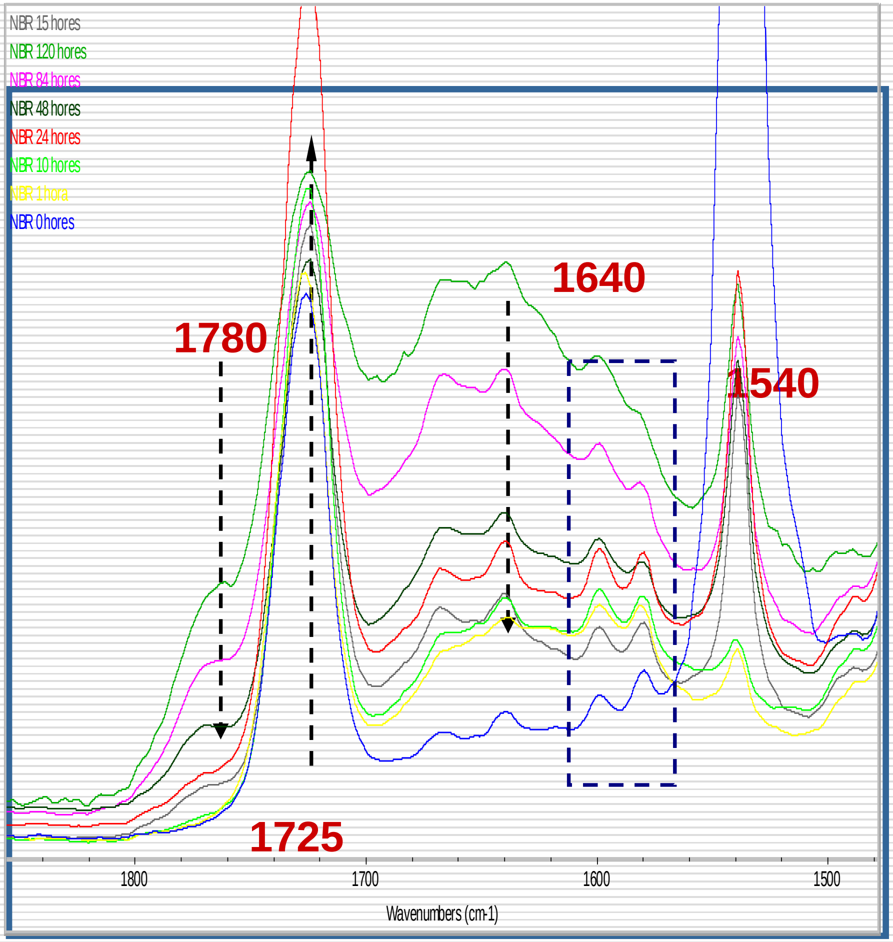
**NBR/SiO2**



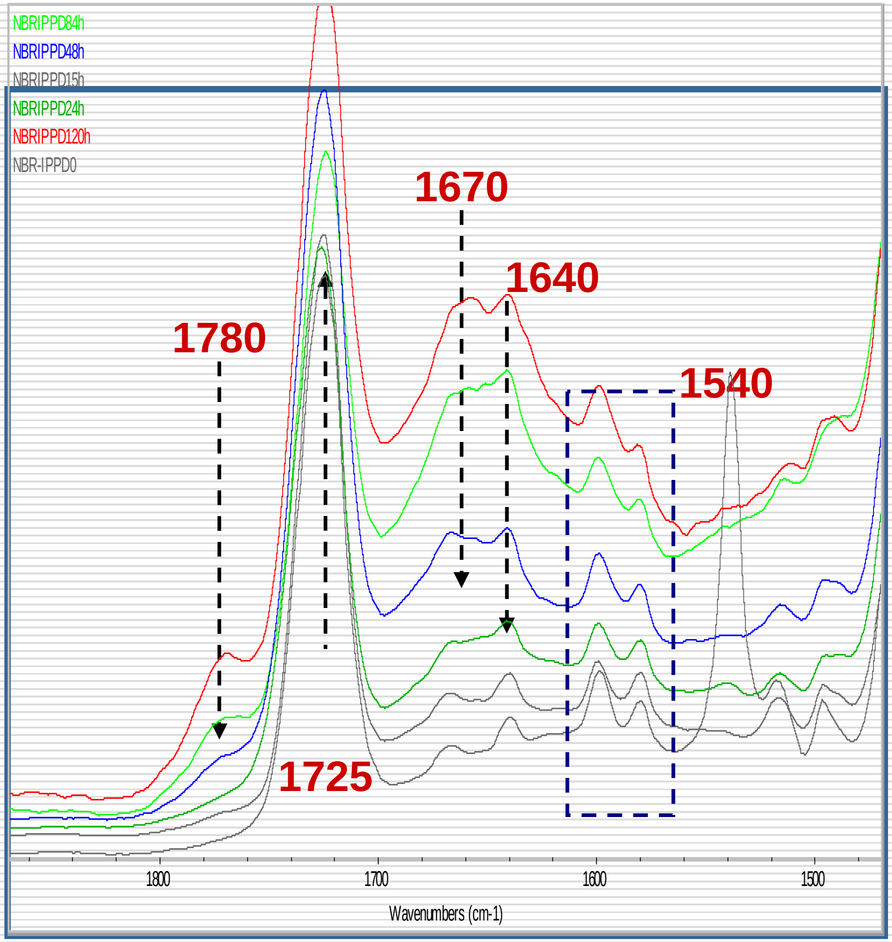
**NBRippd/SiO2**

Until 84hours **hydroxyl** increase faster in NBR/$SiO_2$.

# FTIR/ATR carbonyl region



**NBR/SiO2**



**NBRippd/SiO2**

**1780** cm$^{-1}$ is assigned to **CO** appeared by thermal-oxidizing. It is **higher in NBR** than in IPPD.

**1725** cm$^{-1}$ is assigned to oxygen bearing structures , mainly **CO** of **DOP** and aldehyde.

**1540** cm$^{-1}$ is assigned to **Zn carboxylates**.

# carbonyl region remarks

- **1725** cm$^{-1}$ allows following **DOP** evoution. It shoud be related with **1540** cm$^{-1}$

## NBR

| | 1725 | 1540 |
|---|---|---|
| **0h** | **medium** | **v.high** |
| **10h** | **high** | **v.low** |
| **24h** | **maximum** | **high** |
| **48h** | **medium** | **medium** |
| **84h** | **medium** | **medium** |
| **120h** | **medium** | **medium** |

**Zn Carboxylates volatilizes**

**In 10 min.disappears 1540**

**DOP of core migrates to the surface and volatilizes.**

**DOP plasticizer disappearance yields brittle and less elastic the composite from 10h to 84 hours.**

# carbonyl region remarks

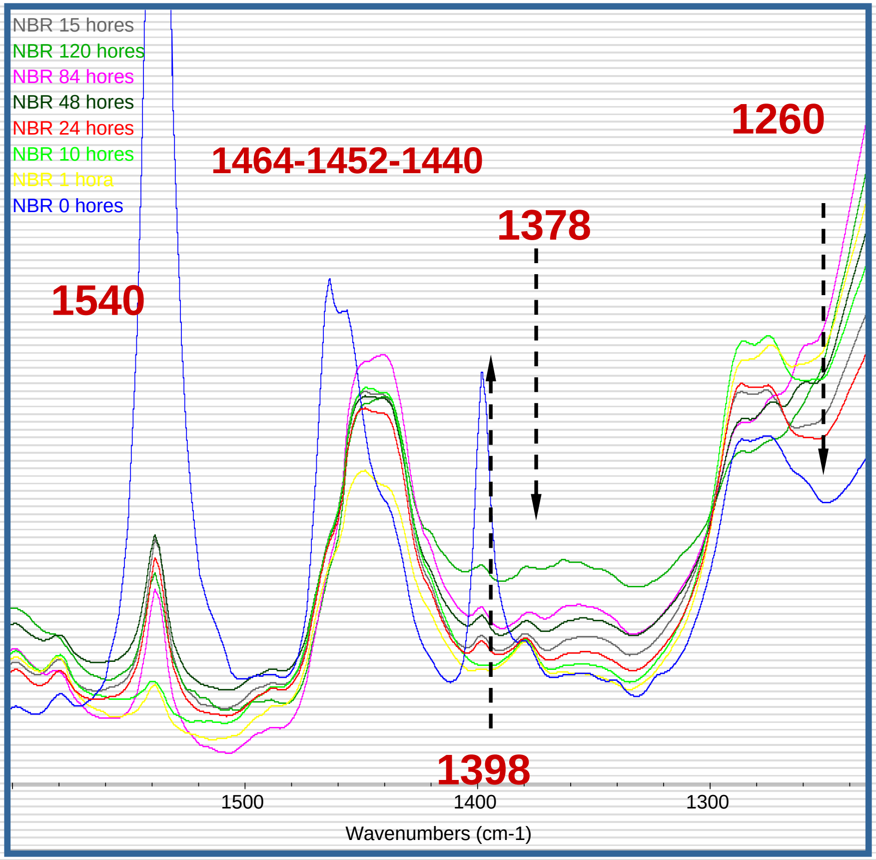
## NBR-IPPD

- Peak at **1540 cm$^{-1}$** disappears fastly, but for a very long time.
- Peak at **1725 cm$^{-1}$** increases continuously because of the loss of porosity.
- IPPD makes a surface layer that avoids the disappearance of DOP.
- Thus, elastomer keeps better elasticity until 84 hours.
- From 84 hours properties are the same because there is no IPPD.

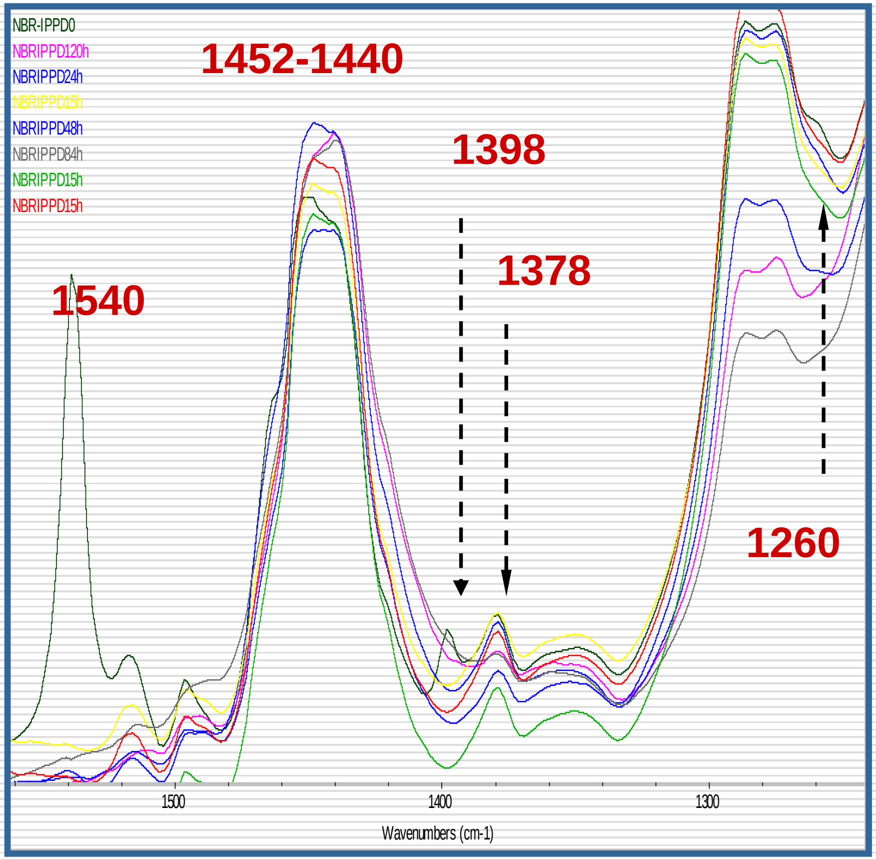
# unsaturated region remarks

- Band at 1640 $cm^{-1}$ of insaturations of PBD increase in both cases, but in relation to the weight.
- The increase is because of the breaking of chaines.
- The square: A doublet at 1598-1580 $cm^{-1}$. 1598 is assigned preferently to IPPD, and 1580 $cm^{-1}$ to other additives as DPG...
- From 84 hours the peaks of both composites are alike and mechanical properties do the same. So, IPPD corroborates that it is bound to mechanical properties.
- The band at 1598 $cm^{-1}$ (of IPPD) is bigger in short time, so mechanical properties are better.

# FTIR/ATR methylene region



**NBR/SiO2**



**NBRippd/SiO2**

# methylene region remarks

**They allow seeing as methylene groups are affected by other groups**

| **NBR** | **NBR-IPPD** |
|---|---|
| **•Bands at 1464-1440 cm$^{-1}$** | **•Bands at 1452-1440 cm$^{-1}$** |
| **•At 0h. there is a band at 1464 cm$^{-1}$ from DOP** | **•There is no band at 1464 cm$^{-1}$** |
| **•After 1h it is at 1452 cm$^{-1}$** | **•At 0h there is a band at 1452 cm$^{-1}$** |
| **•After 10 h it has been displaced to 1438 cm$^{-1}$** | **•Not before 48h has it been displaced to 1438 cm$^{-1}$** |

**IPPD has an effect on methylene band belonging to octyl group of DOP, and inhibits partially its appearance. Thus 1464 cm$^{-1}$ do not appear in IPPD.**

# Other remarks

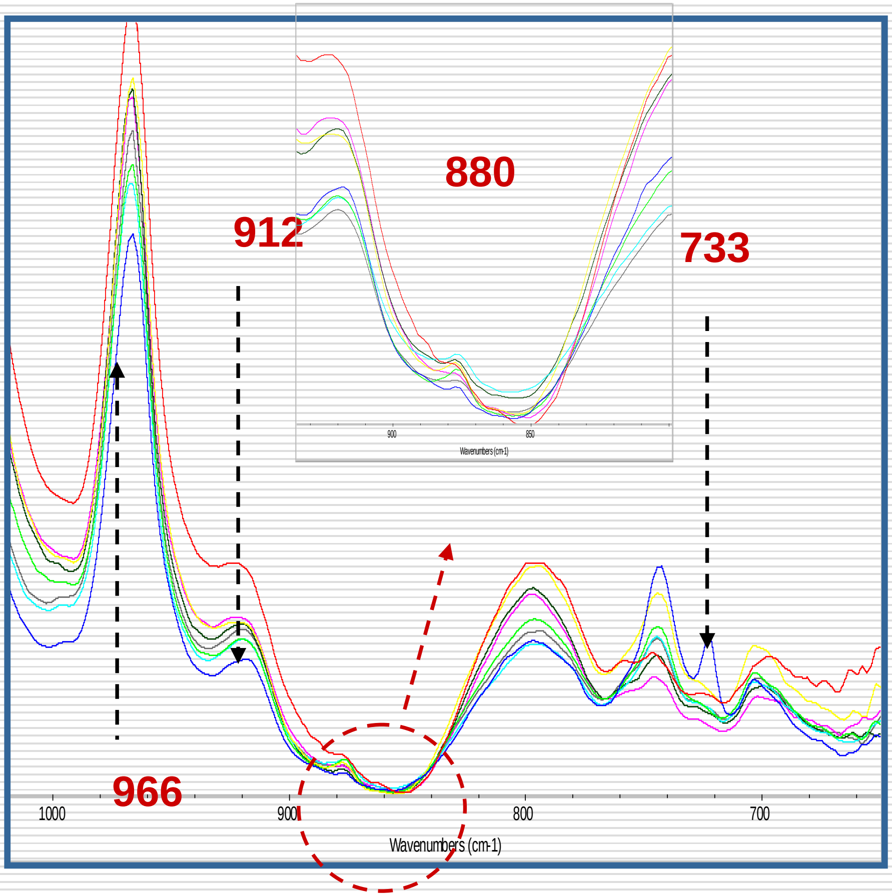
- 1378 cm$^{-1}$: methyl. Two cases
- NBR: this band is smaller and decrease with time.
- NBR-IPPD: this band is rather constant

↓

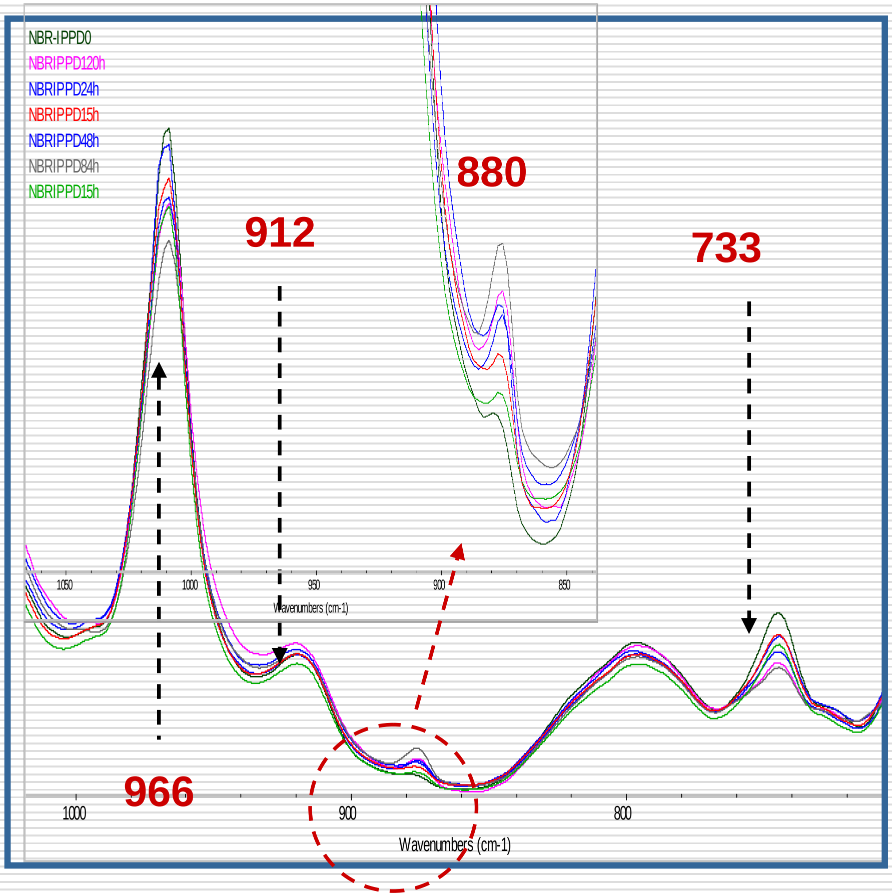
**NBR: There is a breaking of chaines until 84 hours.**

- Band at 1398 cm$^{-1}$ belongs to Zn carboxylates.
- Band at 1260 cm$^{-1}$: belongs to ether groups C-O-C . Do not appear in IPPD . Thus, there is more oxidation in NBR.

# FTIR/ATR configurational changes area



**$NBR/SiO_2$**



**$NBR_{ippd}/SiO_2$**

**880 $cm^{-1}$ of peroxydes: is higher in IPPD, so there is more cross-linking on the surface and thus, less diffusion of DOP across that layer.**

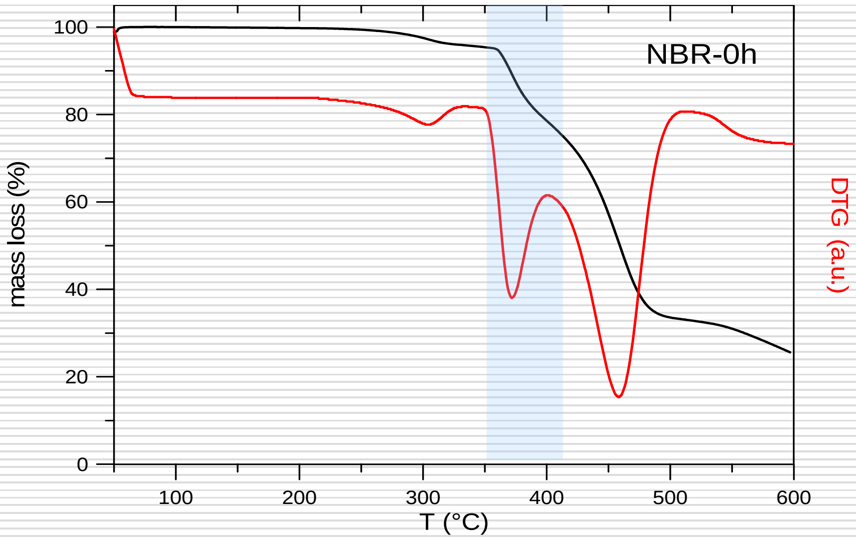
# configurational changes area remarks

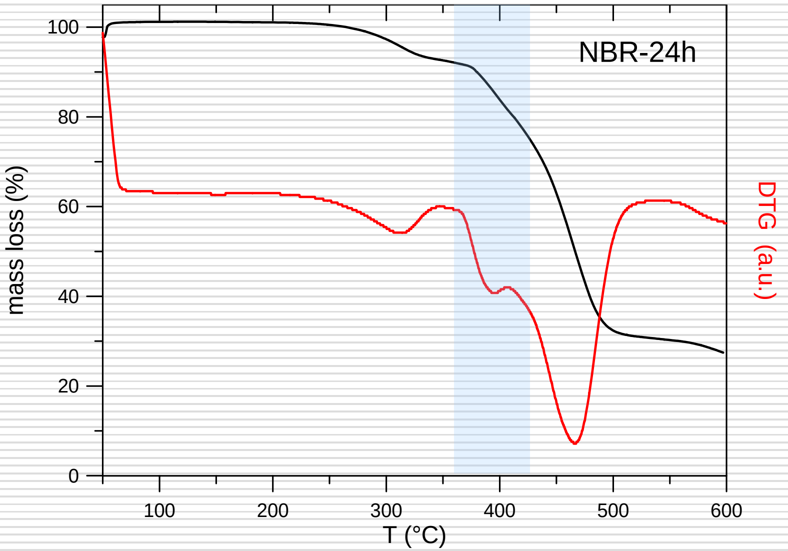
- **966 cm$^{-1}$ : trans 1,4-PBD**
- **912 cm$^{-1}$ : 1,2-vinyl-PBD**
- **733 cm$^{-1}$ : cis 1,4-PBD**

**Changes more significative in NBR**

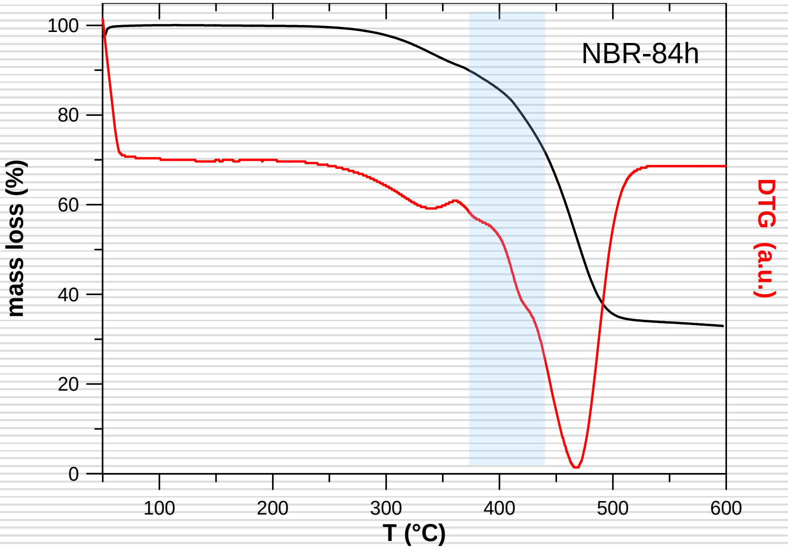
**IPPD has influence**

# Thermogravimetry analysis

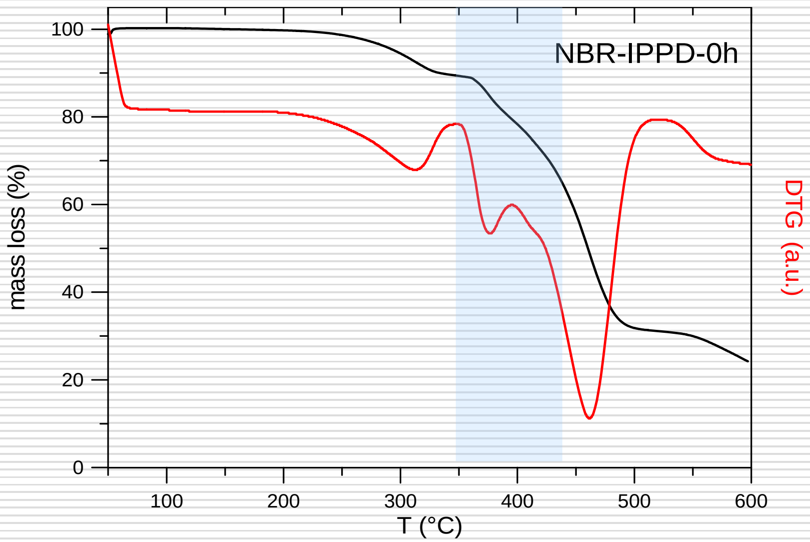


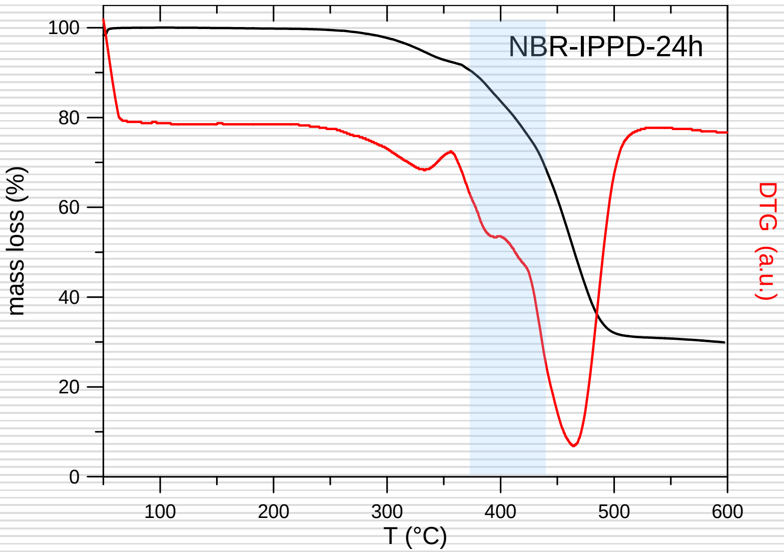


| NBR 0 | | NBR 24 | | NBR 84 | |
|---|---|---|---|---|---|
| T | loss (%) | T | loss (%) | T | loss (%) |
| 305 | 6.0 | 315 | 7.0 | 328 | 8.0 |
| 371 | 17.3 | 394 | 10.0 | 383 | 2.0 |
| 457 | 44.5 | 463 | 50.5 | 469 | 47.5 |
| | 32.2 | | 32.5 | | 43.0 |

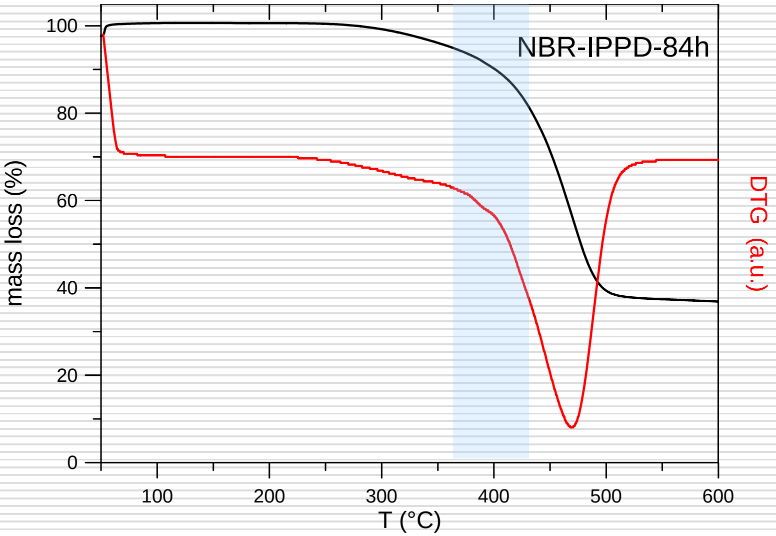


# Thermogravimetry analysis





| NBR$_{ippd}$ 0 | | NBR$_{ippd}$ 24 | | NBR$_{ippd}$ 84 | |
|---|---|---|---|---|---|
| T | loss (%) | T | loss (%) | T | loss (%) |
| 316 | 9.0 | 334 | 6.5 | 328 | - |
| 376 | 11.5 | 392 | 7.0 | 383 | 1.0 |
| 457 | 48.0 | 463 | 55.0 | 469 | 62.5 |
| | 31.5 | | 32.5 | | 37.5 |



# TG remarks

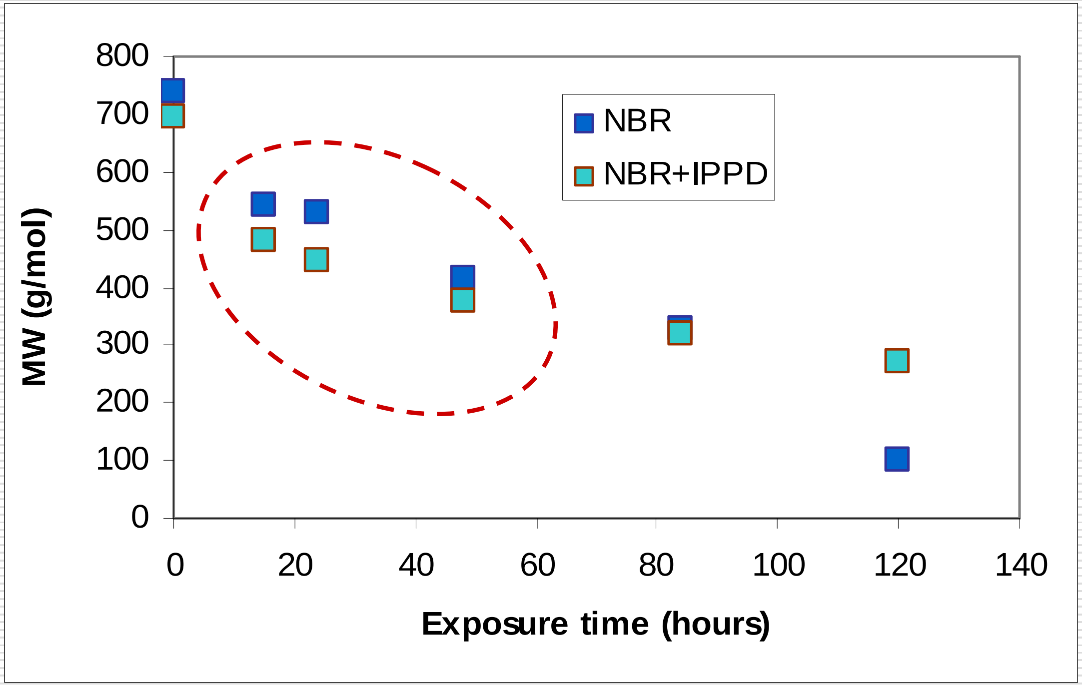
**NBR looses 7,3% in 24 hours. And 8% more between 24 and 84 hours.**

**IPPD looses a 4,5% and 6%, respectively.**

- **NBR looses more ZnO and DOP than IPPD.**
- **Cross-linked layer on the top when there is IPPD avoids the permeation of volatile Zn carboxylates.**

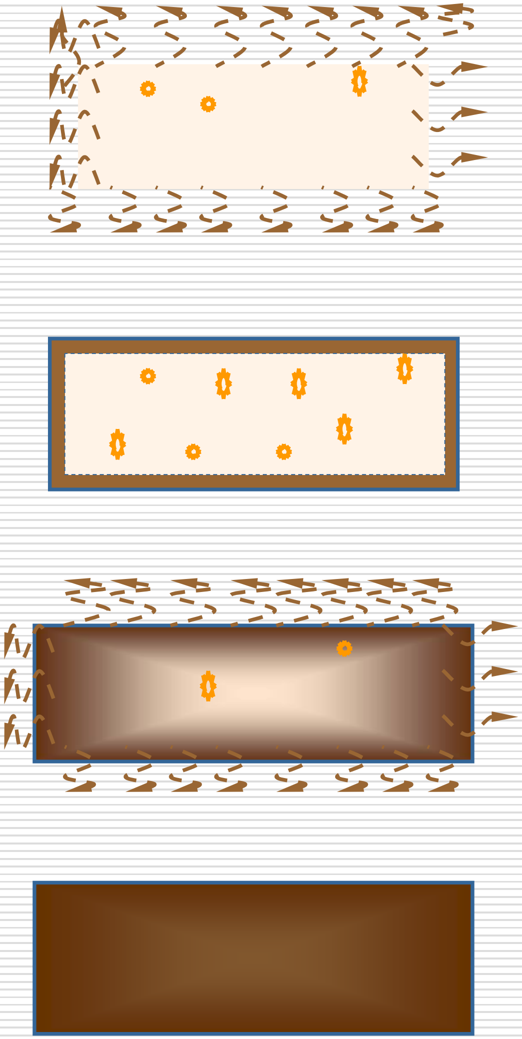
**$\mathrm{NBR}_{\mathrm{IPPD}}$ has more DOP in the core, thus it has better mechanical properties.**

# cross-linking



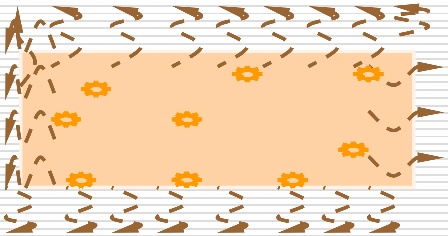
**When there is IPPD molecular weight between knots become bigger because of the smaller cross-linking .**

# NBR degradation’s process schem

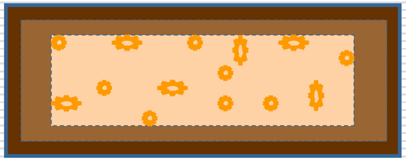


- **Volatile organic Zn salts by means the reaction between carboxylic group of DOP and ZnO until 10 minutes.**
- **From 10 minutes to 10 hours the amount of Zn salts decrease drastically. A low crosslinking surface appears that avoid the loss of DOP.**
- **From 10 hours to 84 hours appear the band at 1540. That means, another time, the volitzation of Zn salts and a progressive drecrease of DOP.**
- **Finally the NBR appear absolutely cross-linked**

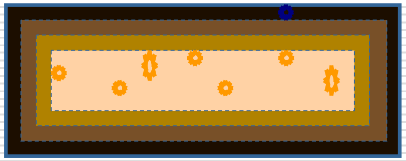
# NBR$_{ippd}$ degradation's process schem



- Volatile organic Zn salts by means the reaction between carboxylic group of DOP and ZnO until 3hours



- From 3 hours very thin concentric layers are made . They avoid the permeation of Zn carboxylate.



- From 48h is difficult to avoid permeating the Zn carboxylate and thus its amount is decreasing.

- From 84 hours the amount of DOP has been disappeared absolutely and the NBR$_{ippd}$ appear cross-linked completely.

# Conclusions (1)

- IPPD improves the endurance to thermal-oxidizing but not for a long time treatment.
- After 84 hours thermal-oxidation , elasticity and tensile strength decreases significantly because of the disappearance of IPPD.
- Unsaturated groups increases with thermal-oxidation.
- According the evolution of carbonyl group there are thermal migration processes to the surface.

# Conclusions (2)

- Those unsatured points are sites of developing rigidity by means cross-linking.

- Rigidity increases as DOP disappears from the composite matrix and as it cross-links making a tridimensional network.

- Molecular mass results indicate a lower degree of cross-linking when there is IPPD. This is in concordance with ATR that show a slower decrease of methylene and methyl groups of the NBR matrix.