

# Probing the mobility of polymers grafted on cosmetic pigments using NMR and EPR

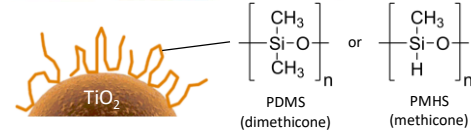
Poster ID: 269

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## Introduction:

Some cosmetic pigments (TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>) surface-treated with polymers



Solid pigments containing polymer = microplastics and banned from manufacture and sale in 2026 [1].

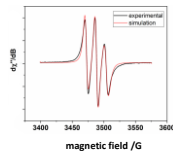
Exclusion: polymer is not solid.

Question: Are the PDMS and PMHS solid after grafting on TiO<sub>2</sub> pigment?

## Results & Discussion:

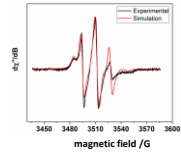
### EPR of TEMPO

in PDMS grafted on TiO<sub>2</sub>



narrow triplet:  
mobile chains

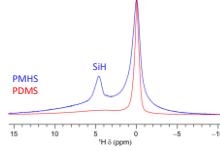
in PMHS grafted on TiO<sub>2</sub>



narrow and broad triplets:  
mobile and rigid domains

### <sup>1</sup>H solid-state NMR

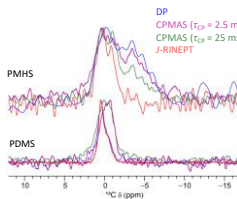
CH<sub>3</sub> (T<sub>2</sub>' = 2.4 ms) / CH<sub>1</sub> (T<sub>2</sub>' = 9.2 ms)



Based on integrated intensities,  
33% of SiH formed Si-O-Ti linkages

<sup>1</sup>H linewidth and T<sub>2</sub>' : PDMS < PMHS  
Mobility: PDMS > PMHS

### <sup>13</sup>C solid-state NMR



PDMS:  
DP ≈ J-RINEPT ⇒ most <sup>13</sup>C are mobile  
Small fraction of rigid segments seen in CP/MAS

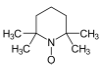
PMHS  
Broader spectra than PDMS ⇒ more rigid chains  
DP ≈ CP/MAS ⇒ most <sup>13</sup>C are rigid  
Small fraction of mobile segments seen in J-RINEPT

## Materials & Methods:

Sample: TiO<sub>2</sub> pigment grafted with PDMS or PMHS

### EPR at 9.81 GHz

TEMPO radical dissolved  
PDMS or PMHS/TiO<sub>2</sub>

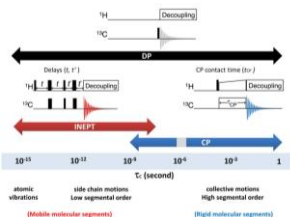


1D EPR spectra probe mobility of TEMPO and hence, grafted polymer.

### Solid-state NMR at 9.4 T (<sup>1</sup>H Larmor frequency of 400 MHz)

1D <sup>1</sup>H MAS NMR: mobility of protons

1D <sup>13</sup>C DP (all), <sup>1</sup>H → <sup>13</sup>C J-INEPT (mobile) and CP/MAS (rigid):  
mobility of <sup>13</sup>C [2,3]



## Conclusions:

- PDMS:** EPR as well as <sup>1</sup>H and <sup>13</sup>C solid-state NMR indicate that most segments are mobile and remain liquid-like at room temperature. The rigid fraction is small and correspond to PDMS rigid layer on TiO<sub>2</sub> surface (thickness ≈ 2 nm) [4]. **PDMS/TiO<sub>2</sub> is not microplastics according to REACH [1].**
- PMHS:** first study of the mobility of PMHS grafted on surfaces. EPR as well as <sup>1</sup>H and <sup>13</sup>C solid-state NMR indicate that the majority of segments are rigid. Higher rigidity stems from the formation of Si-O-Ti linkages. **PMHS/TiO<sub>2</sub> is a microplastics according to REACH [1].**

## Acknowledgements:

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## References:

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