Fibrillated Cellulose and Block Copolymers as a Modifiers of Unsaturated Polyester Nanocomposites

Daniel H. Builes, Hugo Hernández, Laida Cano, Agnieszka Tercjak

andercol s.a.

DE NOVO
Centro de Desarrollo Tecnológico en Materiales Poliméricos y Renovables

Polymeric and Renewable Materials
Technological Development Center

Universidad del País Vasco
Euskal Herriko Unibertsitatea

Group "Materials + Technologies"

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Aim of this Work

To establish a pathway for mechanical isolation of cellulose nanofibrils from sisal fibers and to employ them as reinforcement of unsaturated polyester thermosets in order to produce a nanocomposite material with improved mechanical properties and high transparency

PARTS OF THE PRESENTATION

1. INTRODUCTION

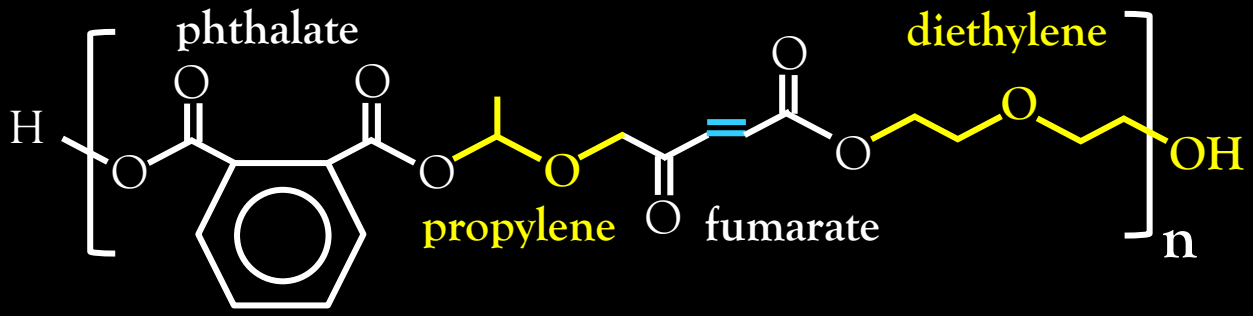
2. Modification of an unsaturated polyester matrix with the PEO-*b*-PPO-*b*-PEO block copolymer $E_{20}P_{69}E_{20}$ (EPE20)

3. Preparation of sisal microfibrillated cellulose (MFC)

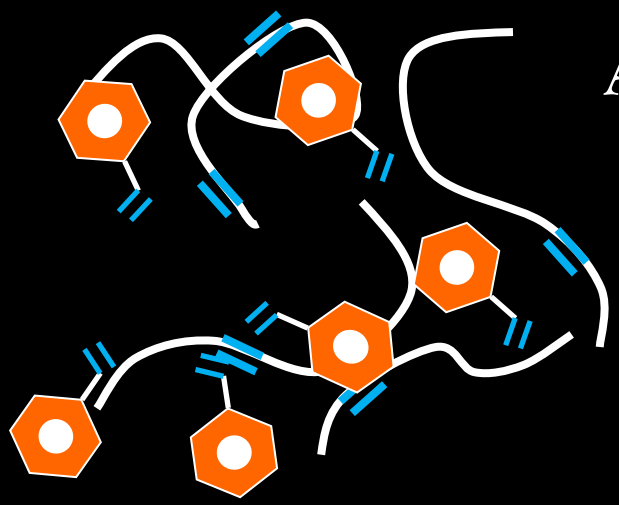
4. Nanocomposites based on unsaturated polyester and microfibrillated cellulose (MFC)

5. CONCLUSIONS

INTRODUCTION



Oligomer of Unsaturated Polyester (UPol)



Unsaturated Polyester Resin (UP)

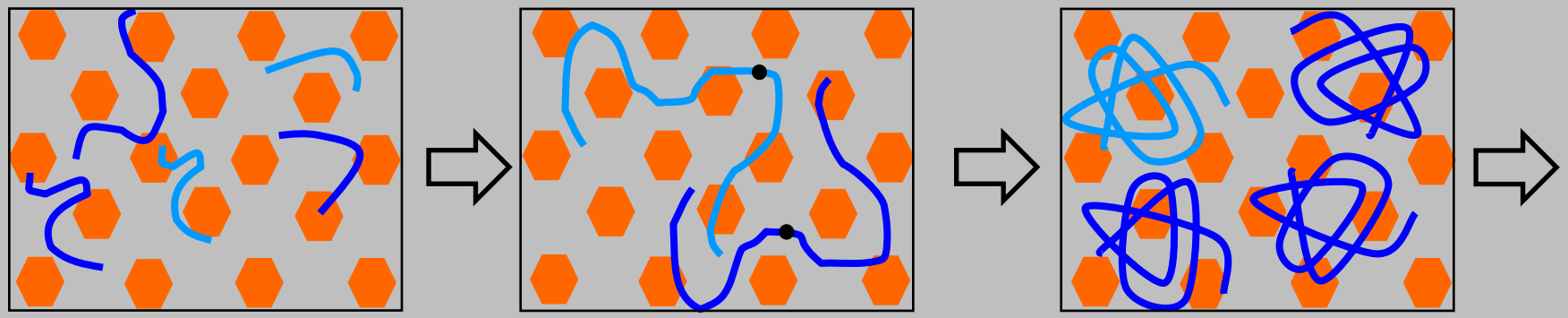
An UP resin is a mixture of UPol with styrene

Cristalán® 860: Orthophtalic UP resin with 36 wt % of St

Manufactured by Andercol S.A.

Curing Process

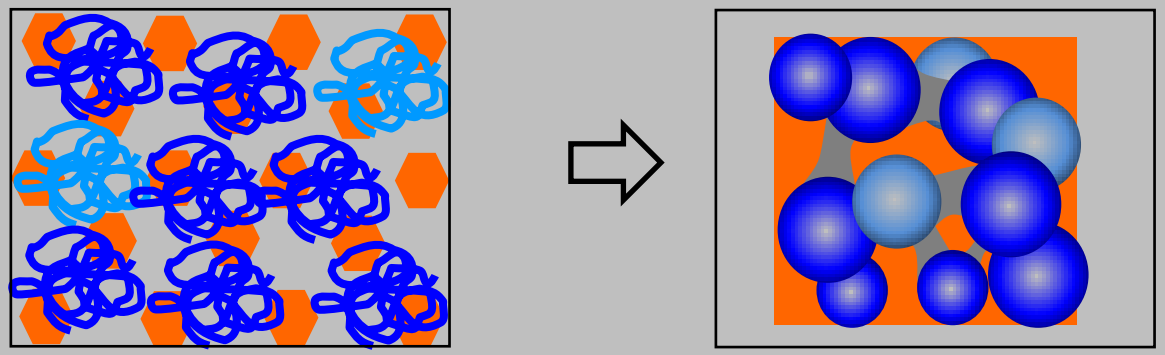
Curing process of UP resin is a free-radical chain polymerization, exothermic and inhomogeneous process



UP resin

Growth of chains

Cyclization of chains



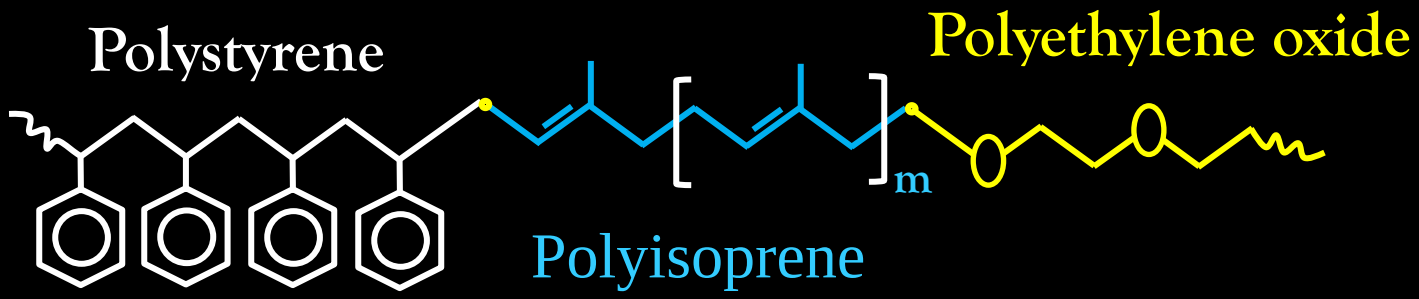
Phase separation
(microgels formation)

Microgel-Microgel
Crosslinking
(Percolation)

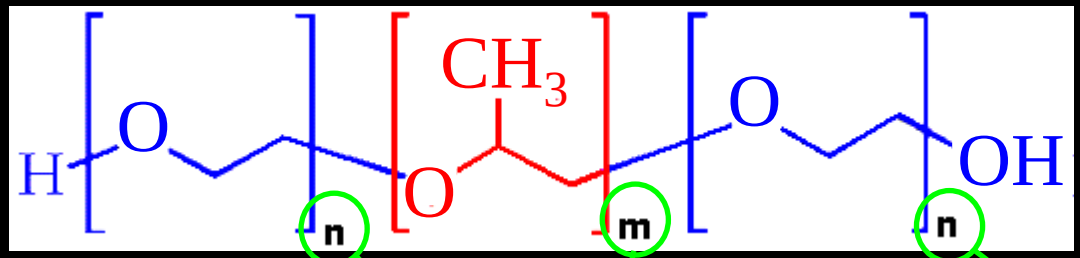
Block Copolymers (BCP)

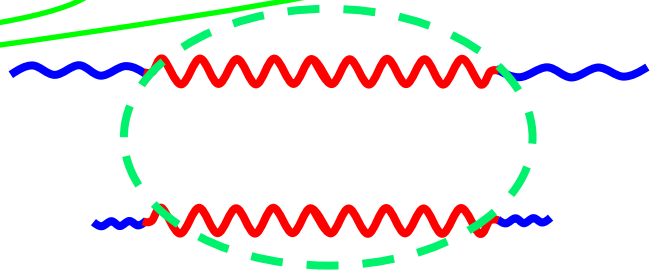
A BCP is produced linking by covalent bonds two or more homopolymers thermodynamically incompatible to create a novel macromolecule with hybrid properties

PS-*b*-PI-*b*-PEO triblock copolymer



PEO - *b* - PPO - *b* - PEO



Structure	Scheme	Name
$E_{20}P_{69}E_{20}$		EPE20
$E_5P_{68}E_5$		EPE5

PEO miscibility with UP resins is higher than the PPO miscibility

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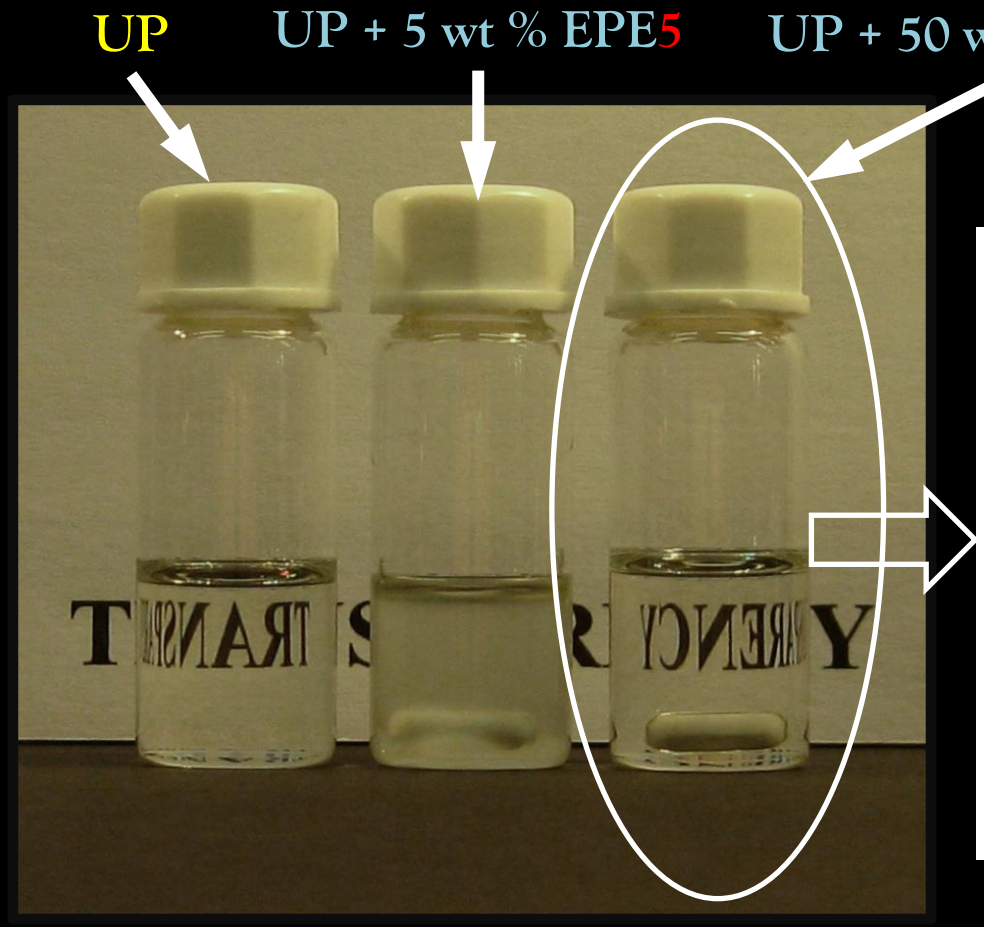
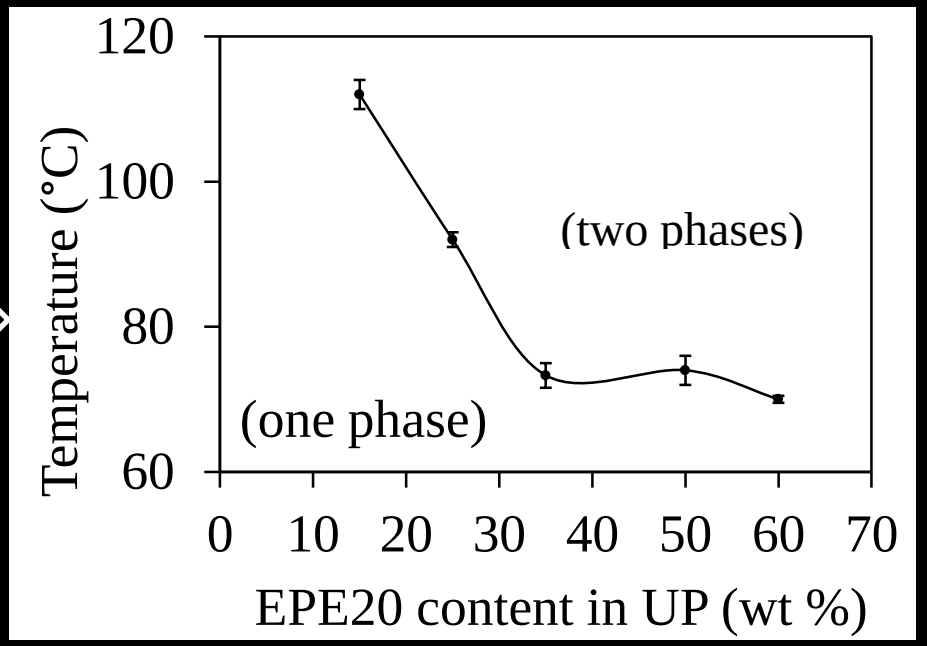
5. CONCLUSIONS

Mixtures Before Curing (non-reactive mixtures)



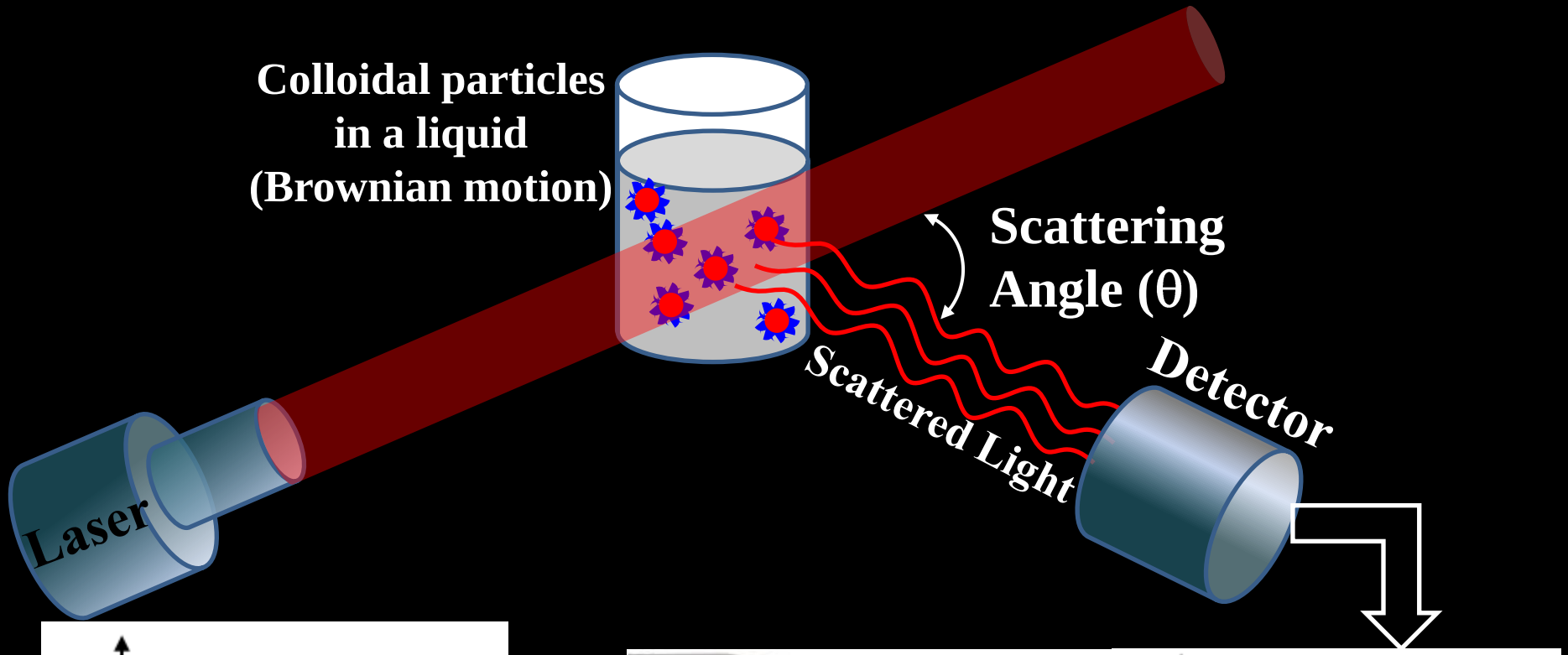
Visual appearance of non-reactive mixtures compared with neat UP resin at room temperature

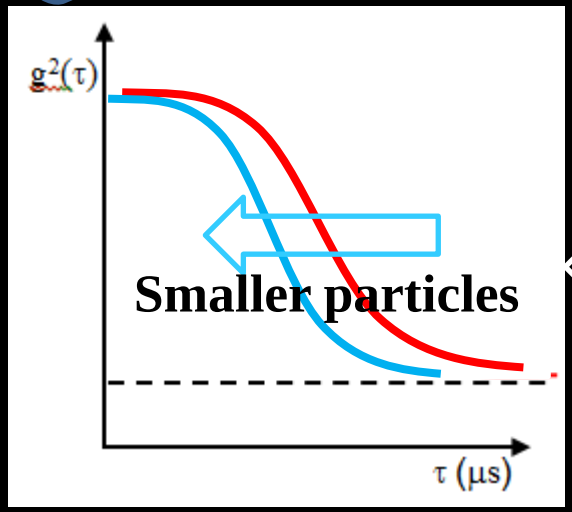


LCST behaviour of UP/EPE20 mixtures

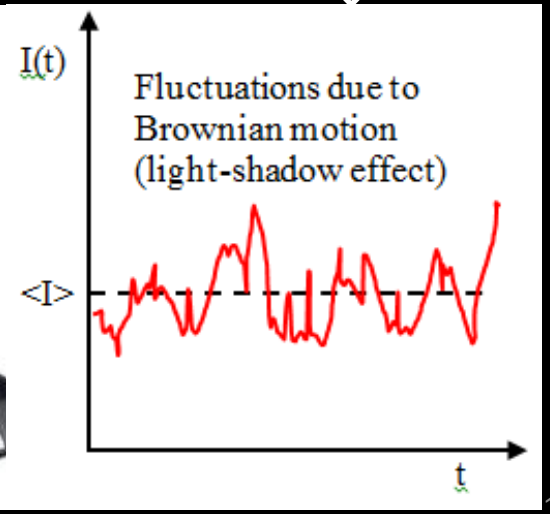
Builes, D. H. et al ***Polymer* 53, 3669 (2012)**

Dynamic Light Scattering (DLS)

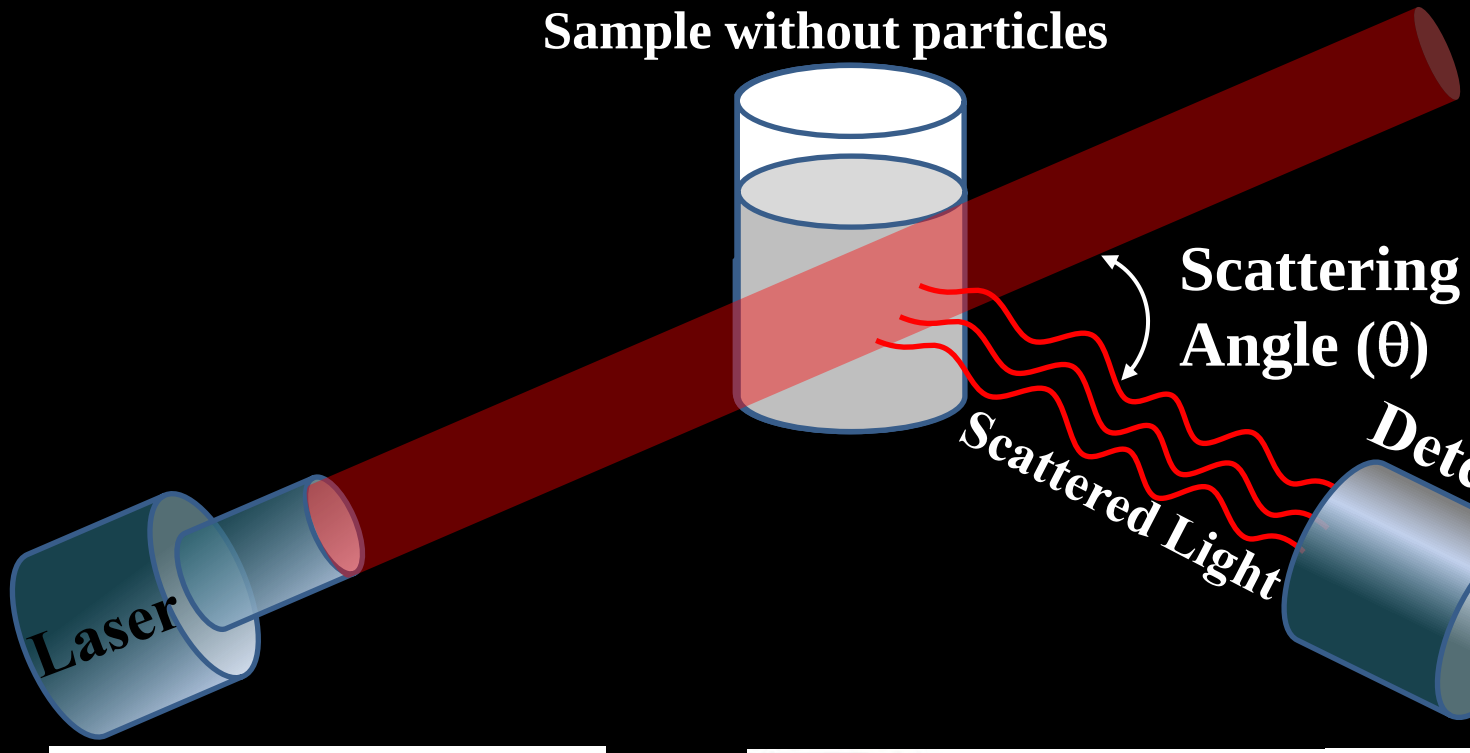


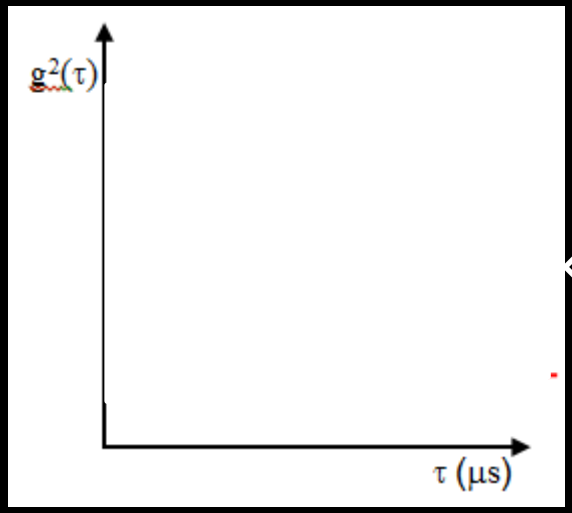


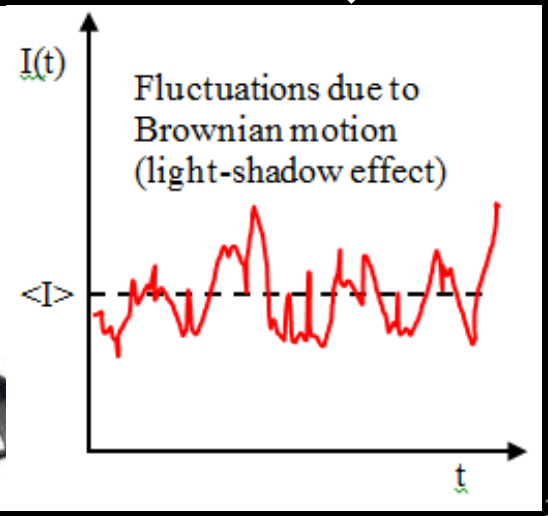
Autocorrelation function



Dynamic Light Scattering (DLS)



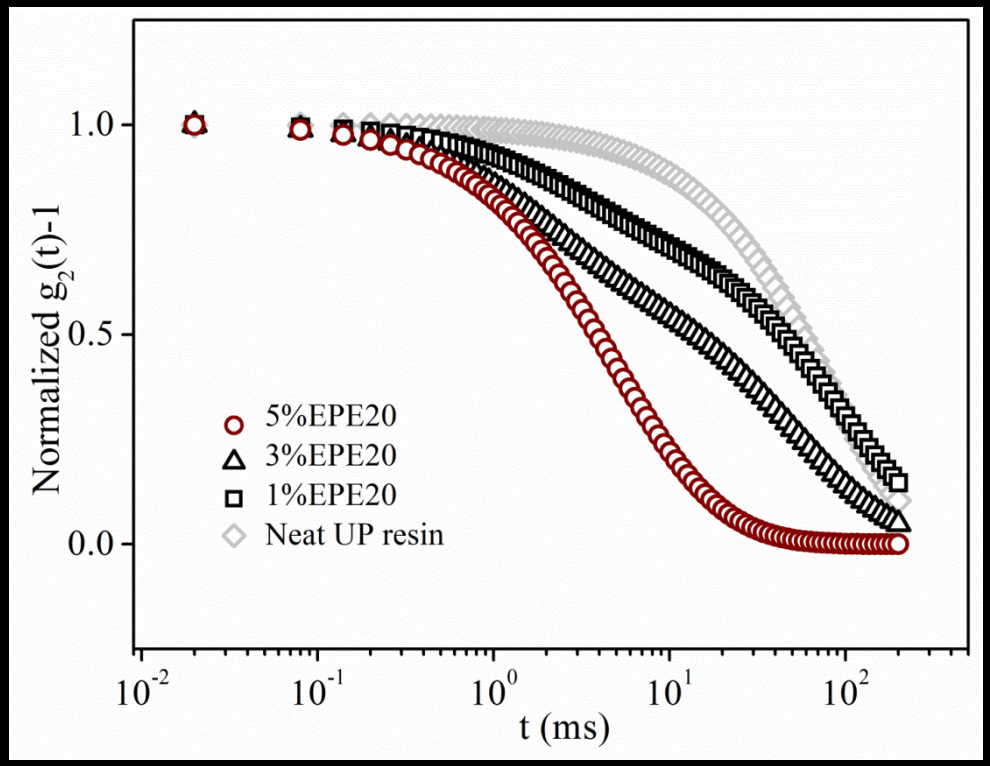




No autocorrelation function

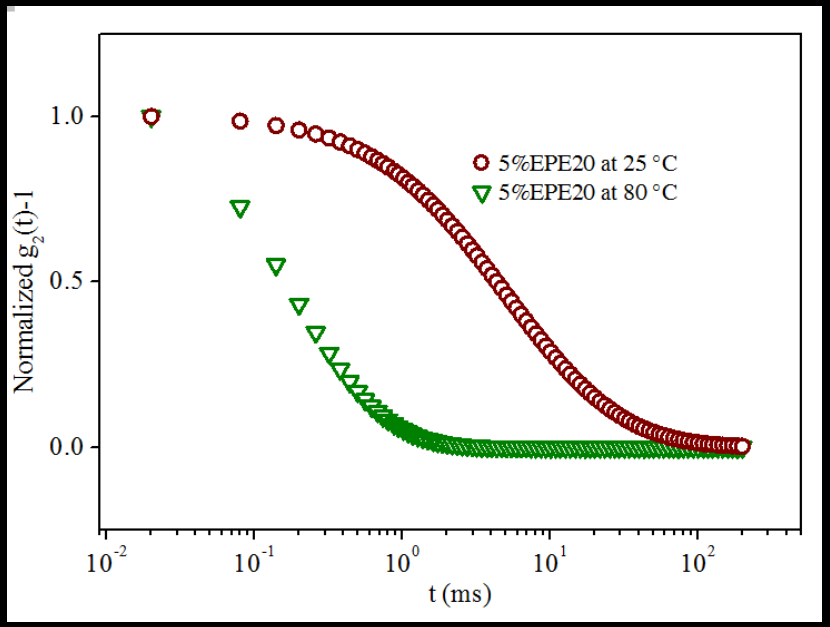
Dynamics of Nonreactive Mixtures (DLS)

Mixtures of UP + EPE20



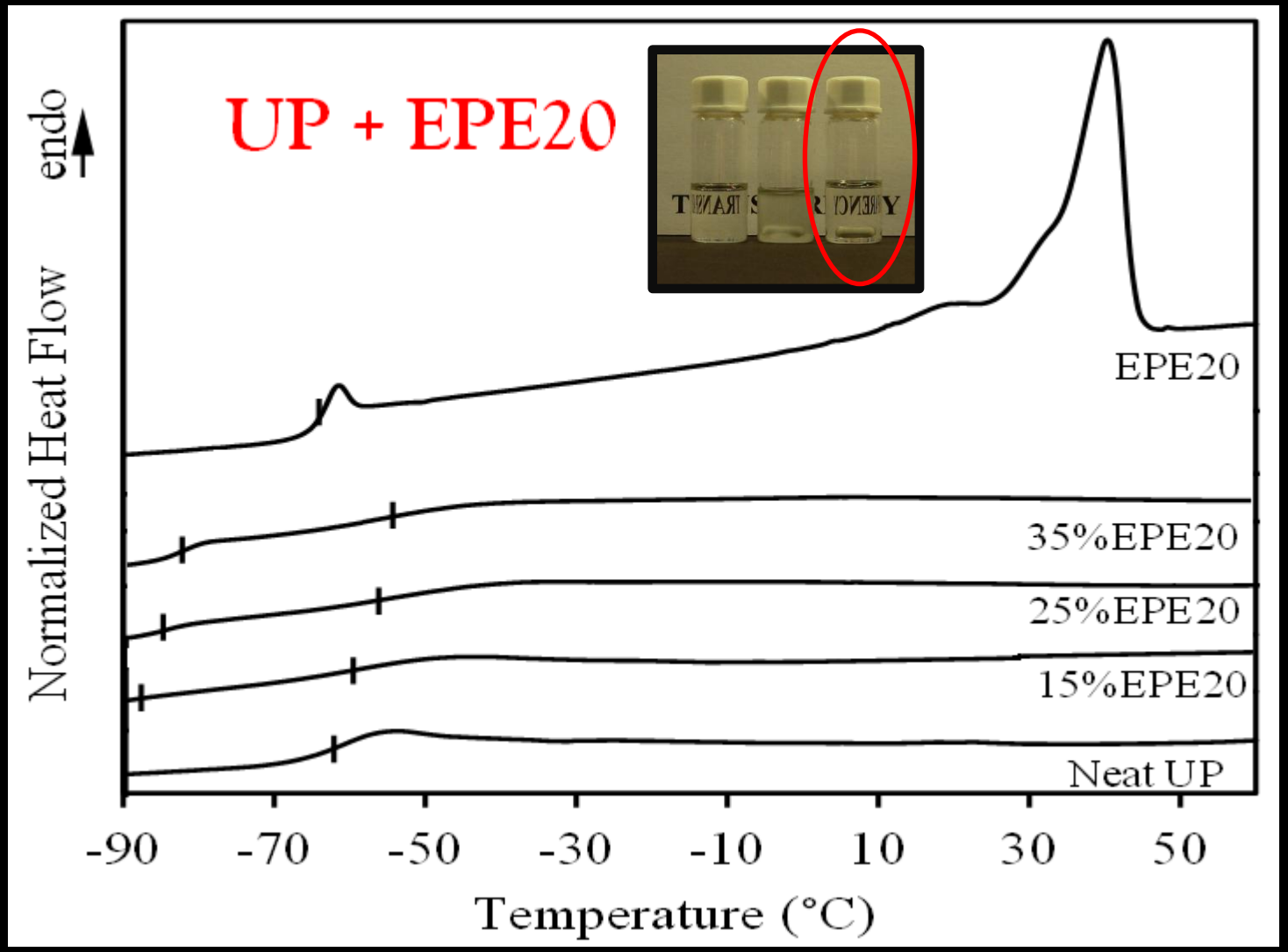
Autocorrelation fuction vs EPE20 content

Autocorrelation fuction vs Temperaure



Differential Scanning Calorimetry (DSC)

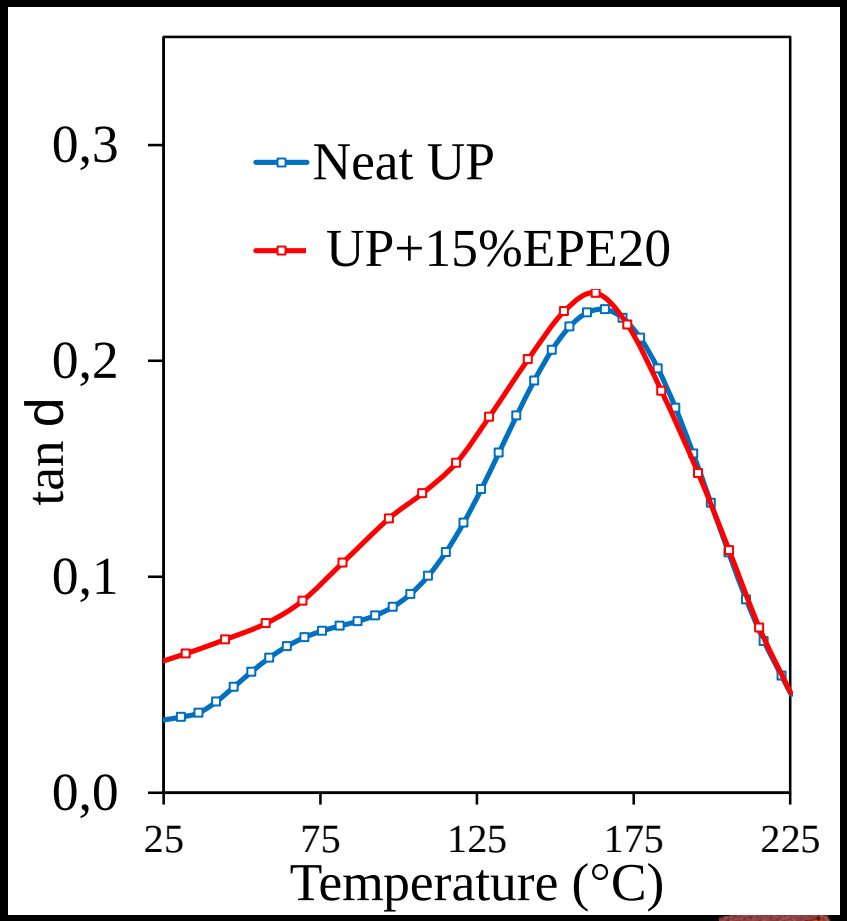
Nonreactive mixtures of UP + EPE20



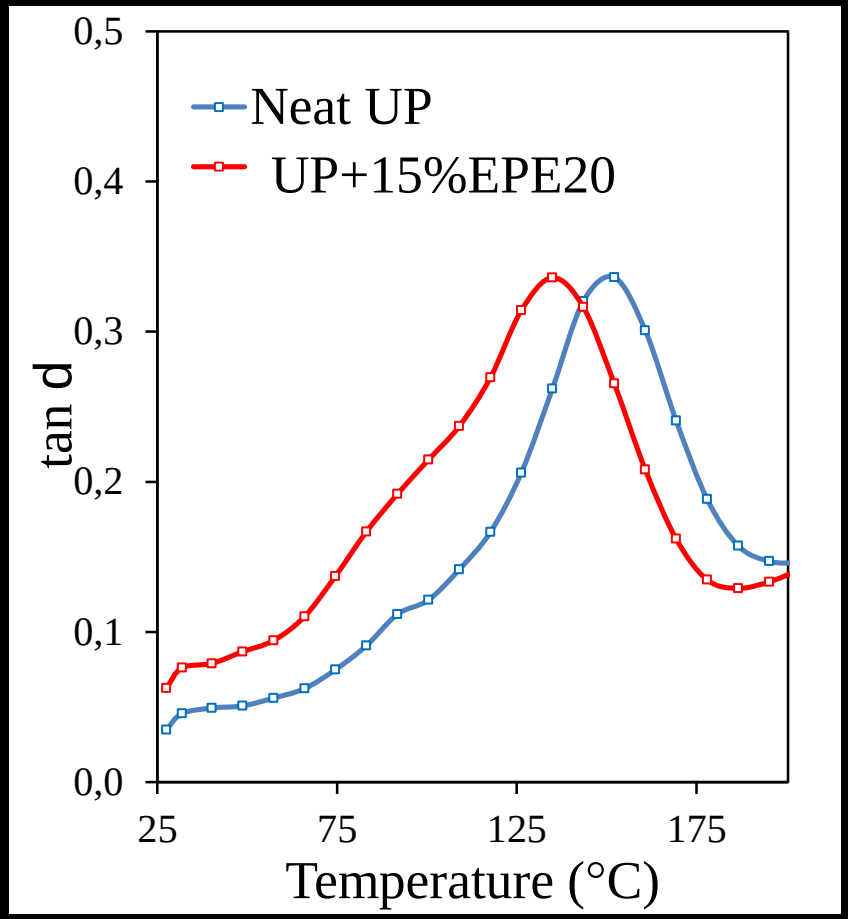
Cured Mixtures

Dynamical Mechanical Analysis (DMA)

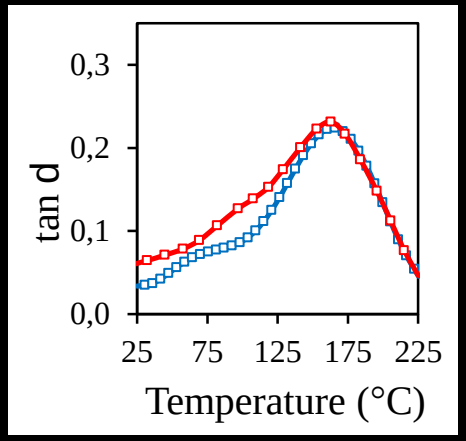
Cured at 80 °C

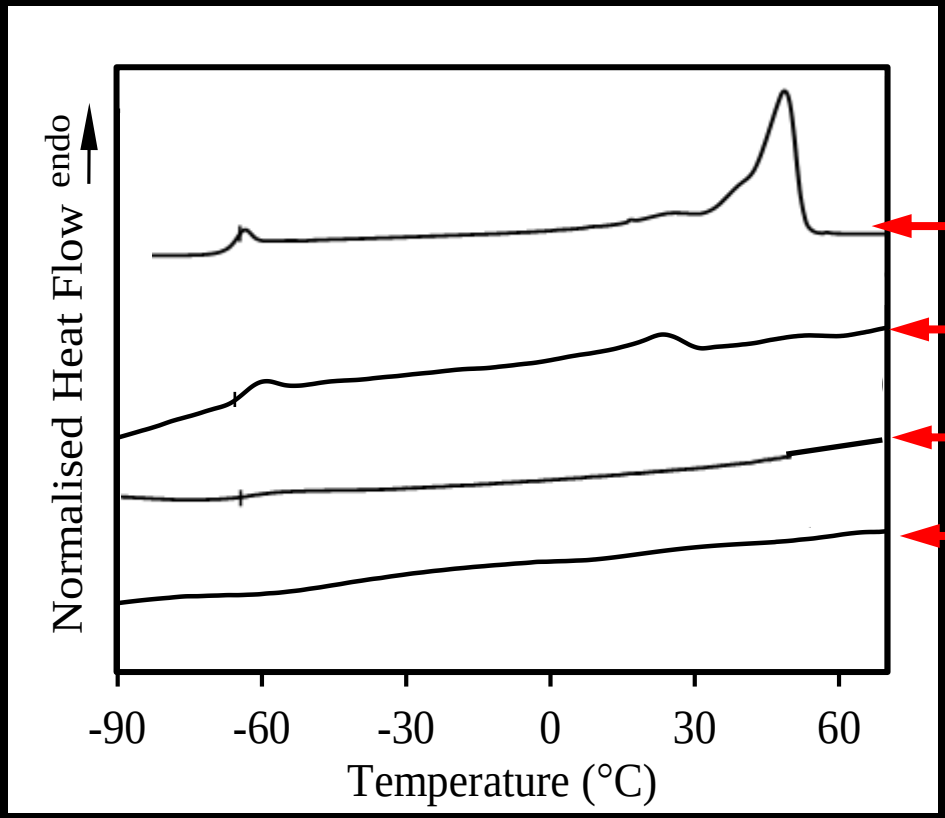


Cured at 25 °C



DSC





EPE20

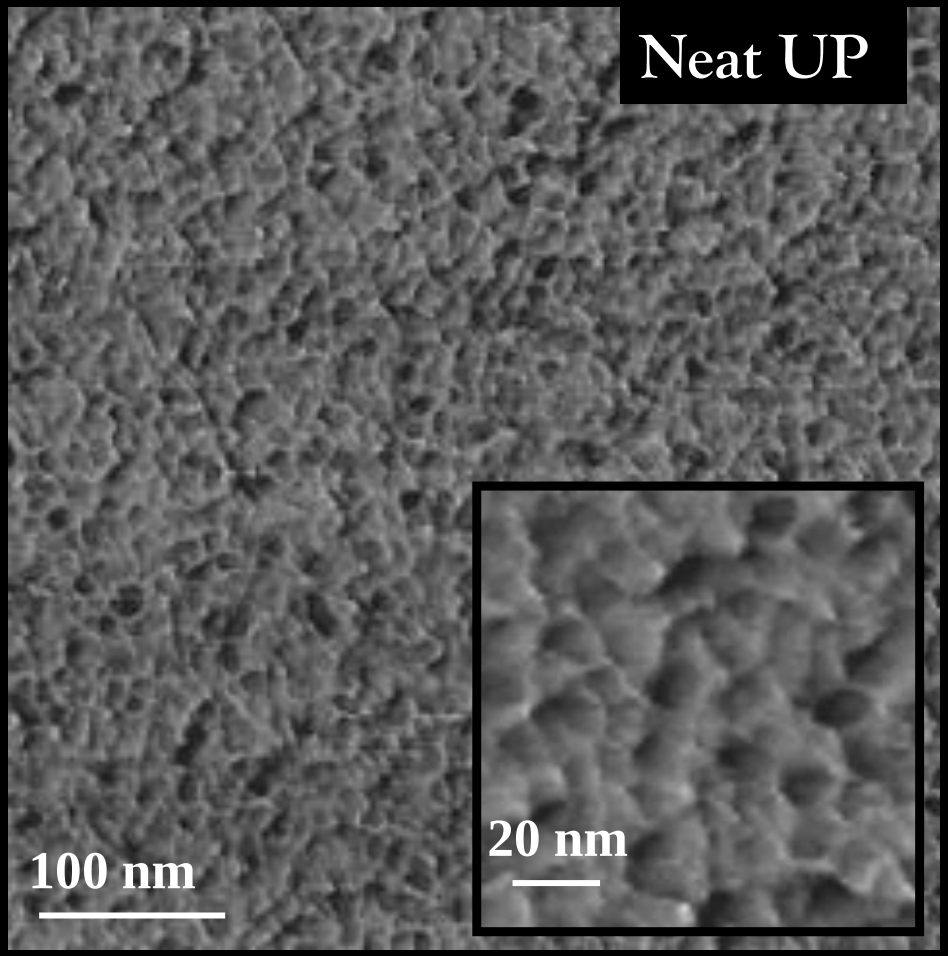
UP + 15%EPE20 (80 °C)

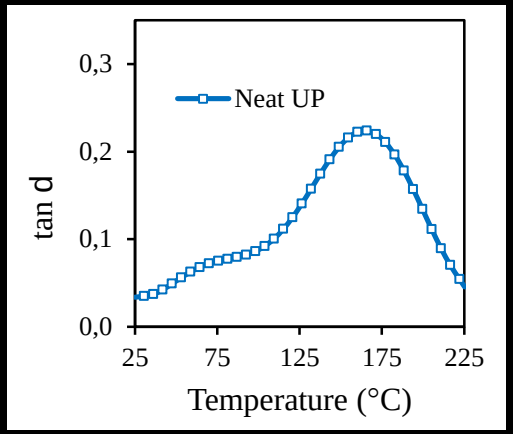
UP + 15%EPE20 (25 °C)

Neat UP

Neat UP Morphology

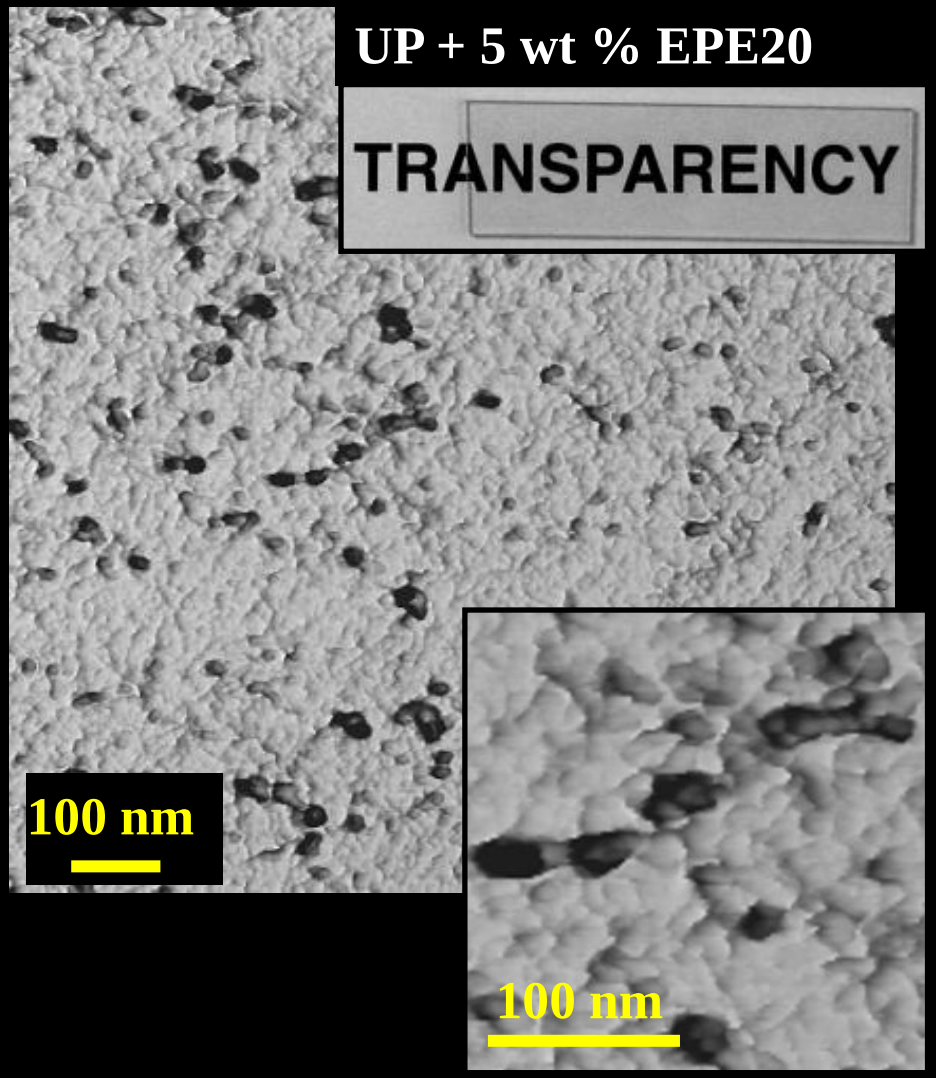
(AFM)

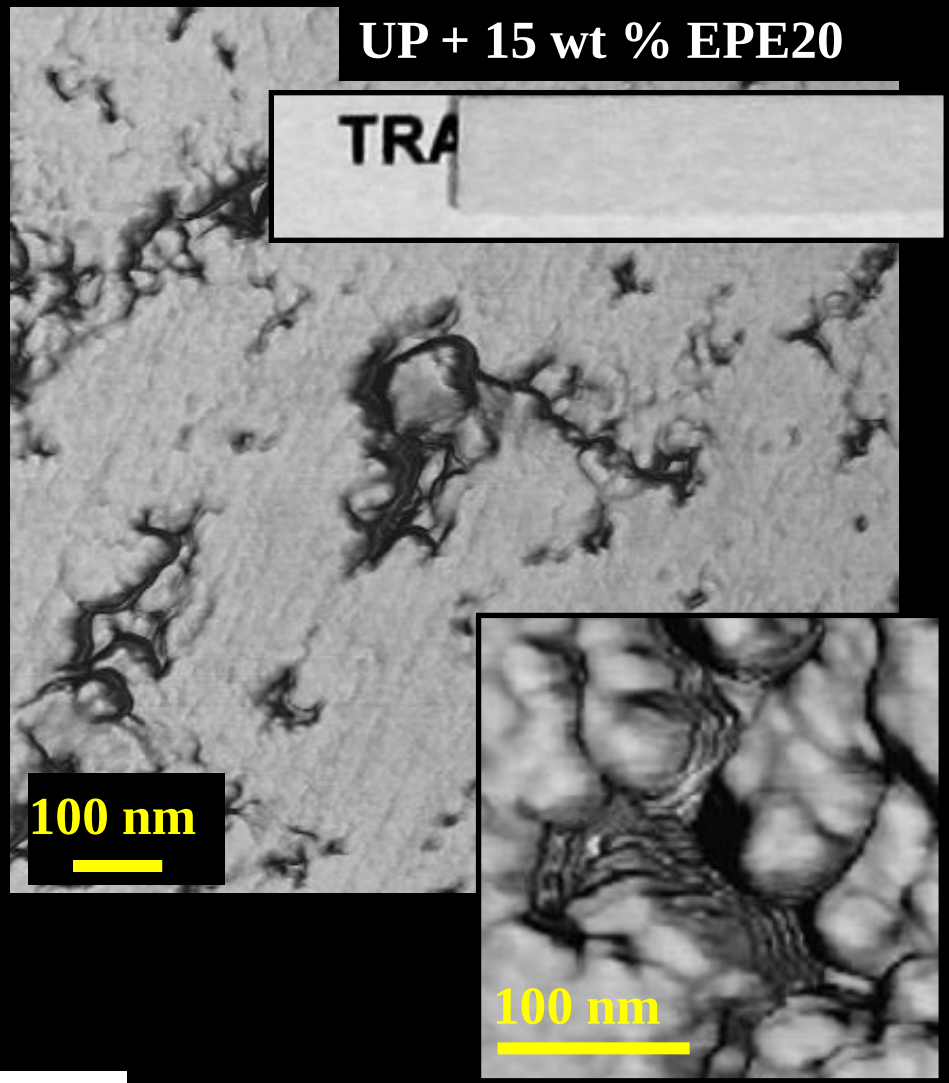




Mixtures
Morphology (AFM)

(cured at T ≥ 60 °C)

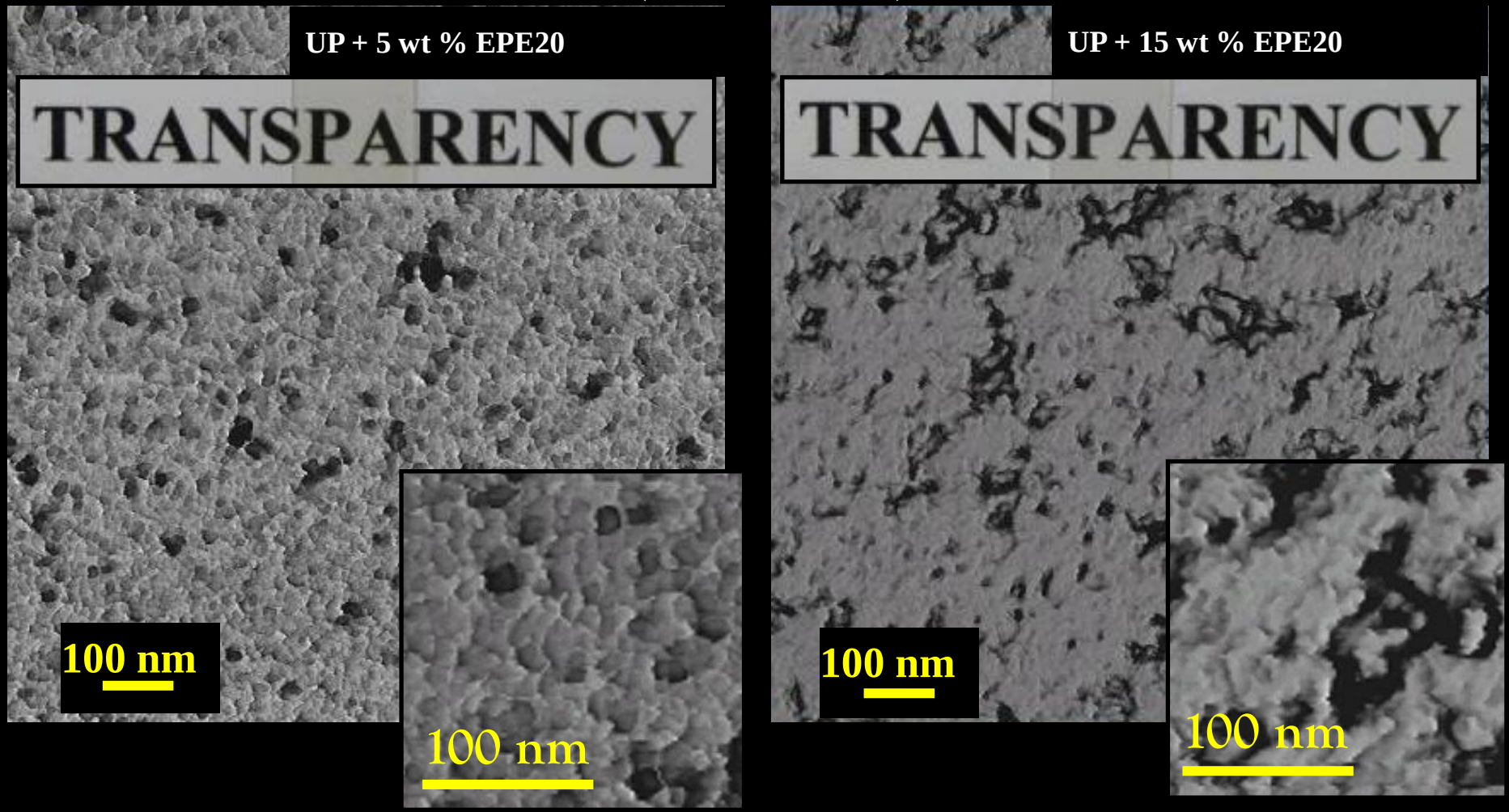




Builes, D. H. et al ***ACS Appl Mater Interfaces* 6, 1073 (2014)**

Mixtures
Morphology (AFM)

(cured at 25 °C)



Builes, D. H. et al ***J Phys Chem C*** **117, 3563 (2013)**

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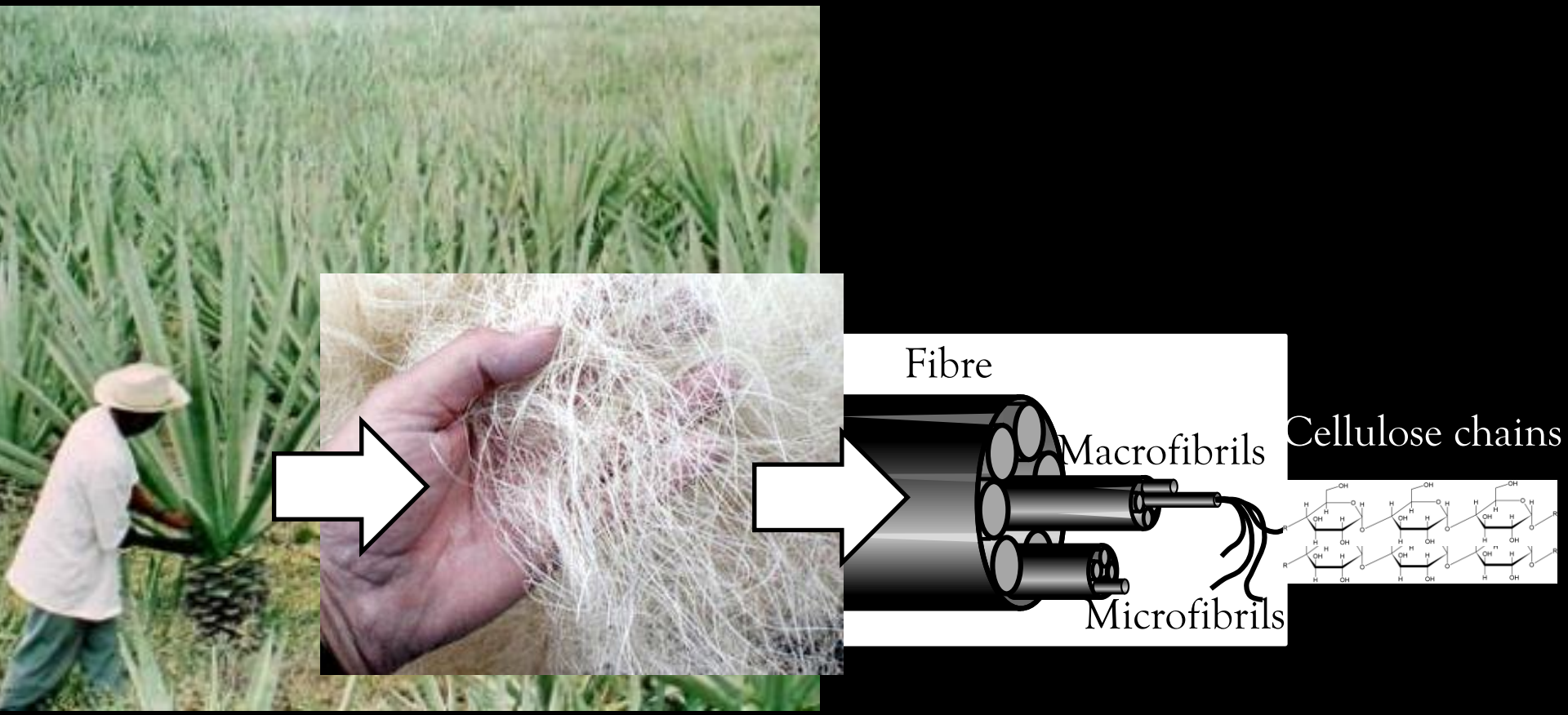
5. CONCLUSIONS

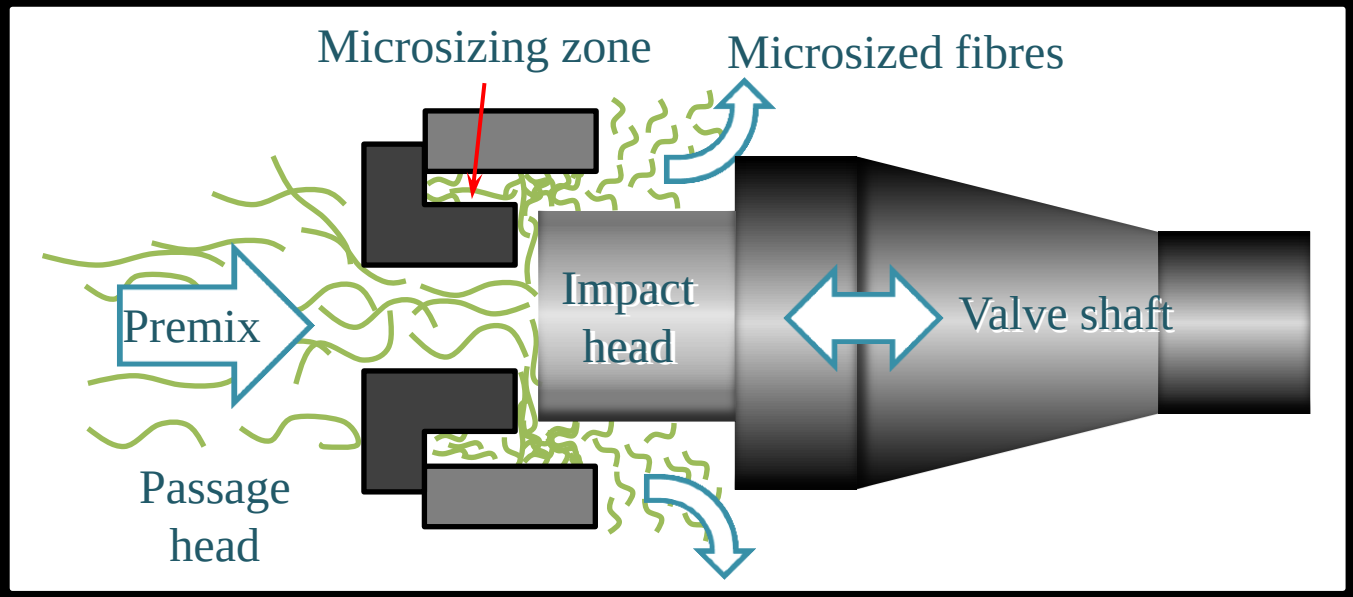
Cellulose Fibers as Reinforcement

- Sustainability
- Hierarchical structure
- Low density
- Recyclability
- Biodegradability
- Good mechanical properties: (elastic modulus from 130 to 250 GPa in the crystalline regions)
- Renewability

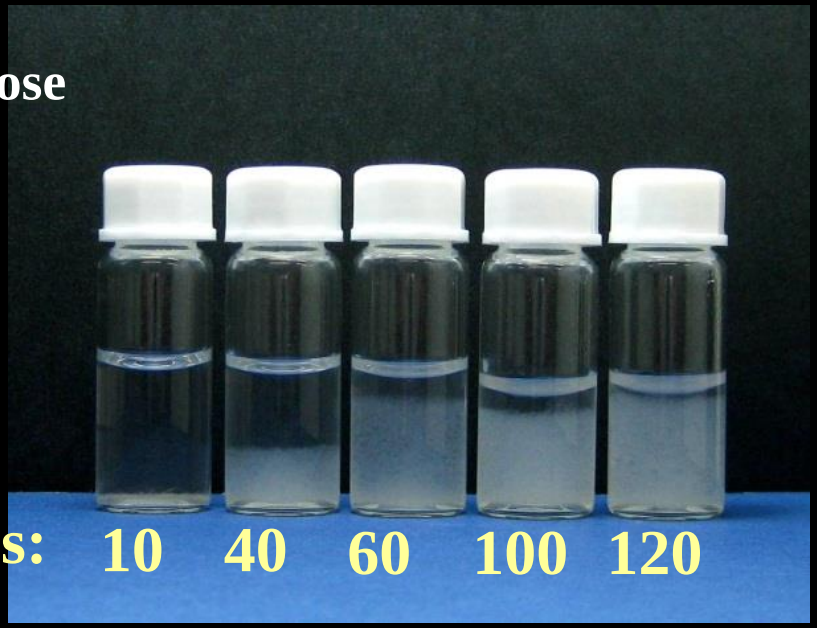
Hierarchical Structure



Homogenization Technique

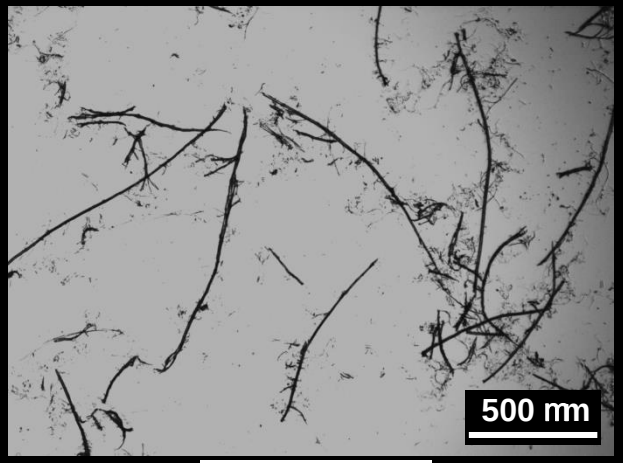


Aqueous suspensions sisal cellulose fibers during homogenization process after several passes

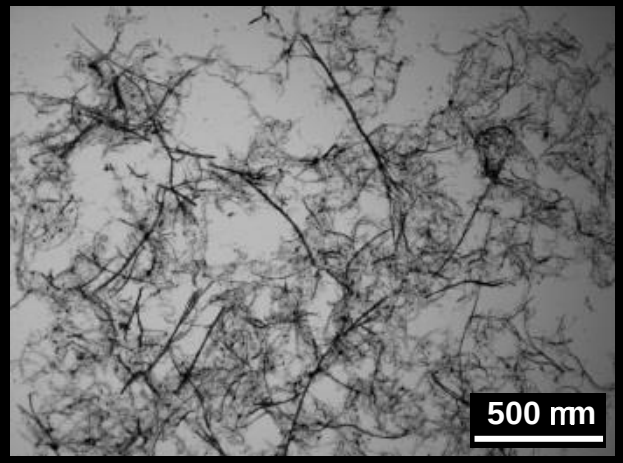


Size Monitoring (Optical Micrographs)

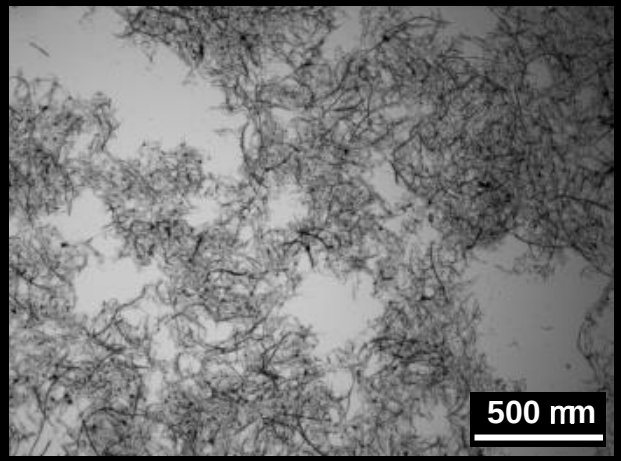
Cellulose fibers during mechanical homogenization process



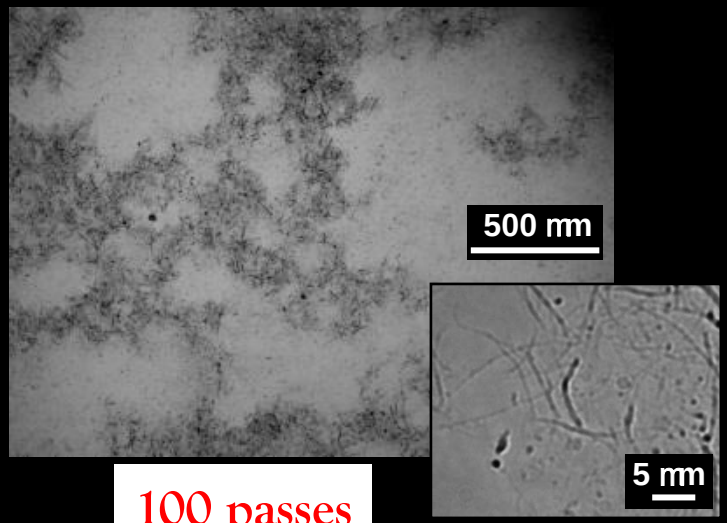
10 passes



40 passes



60 passes

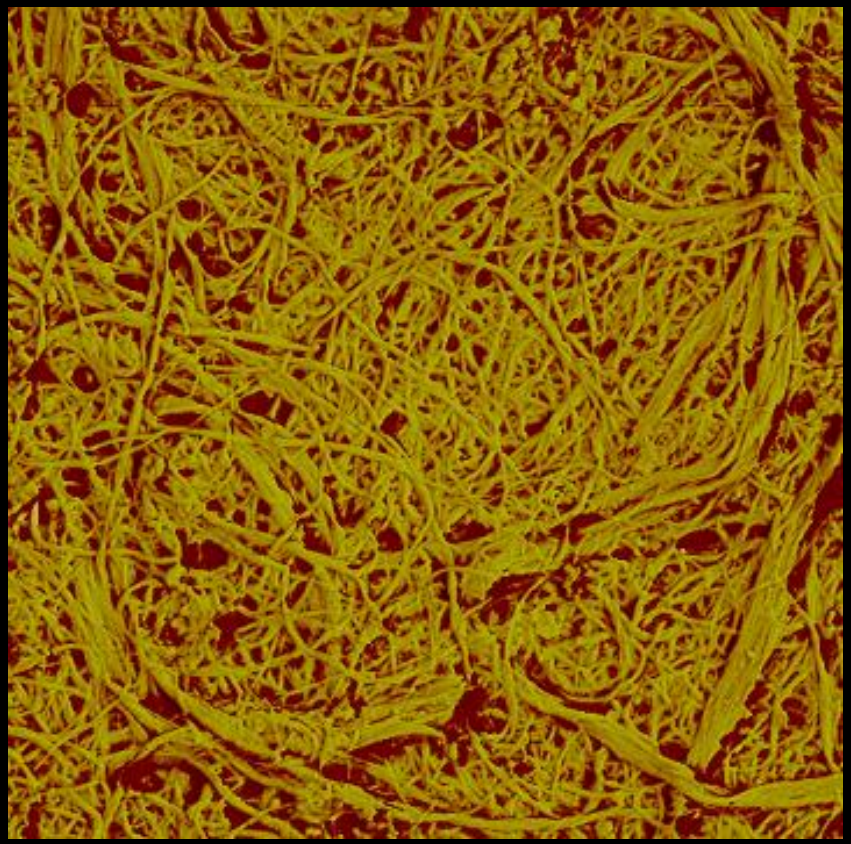


100 passes

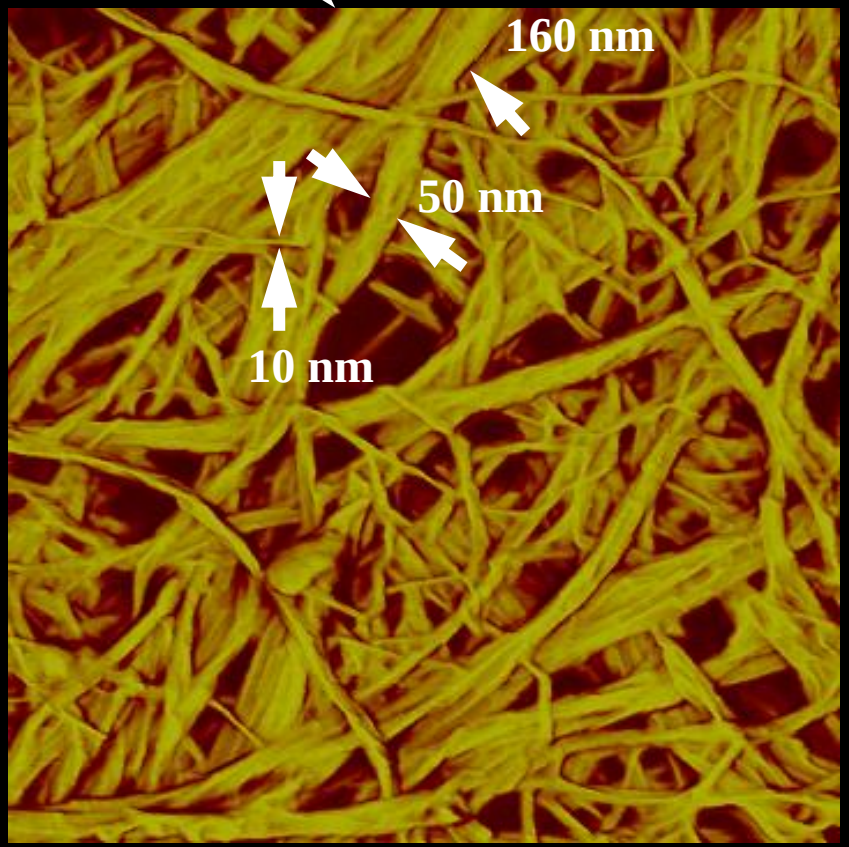
Builes, D. H. t al ***Compos Sci Technol* 89, 120 (2013)**

Microfibrillated Sisal Fibers

(AFM)



5 mm x 5 mm



1 mm x 1 mm

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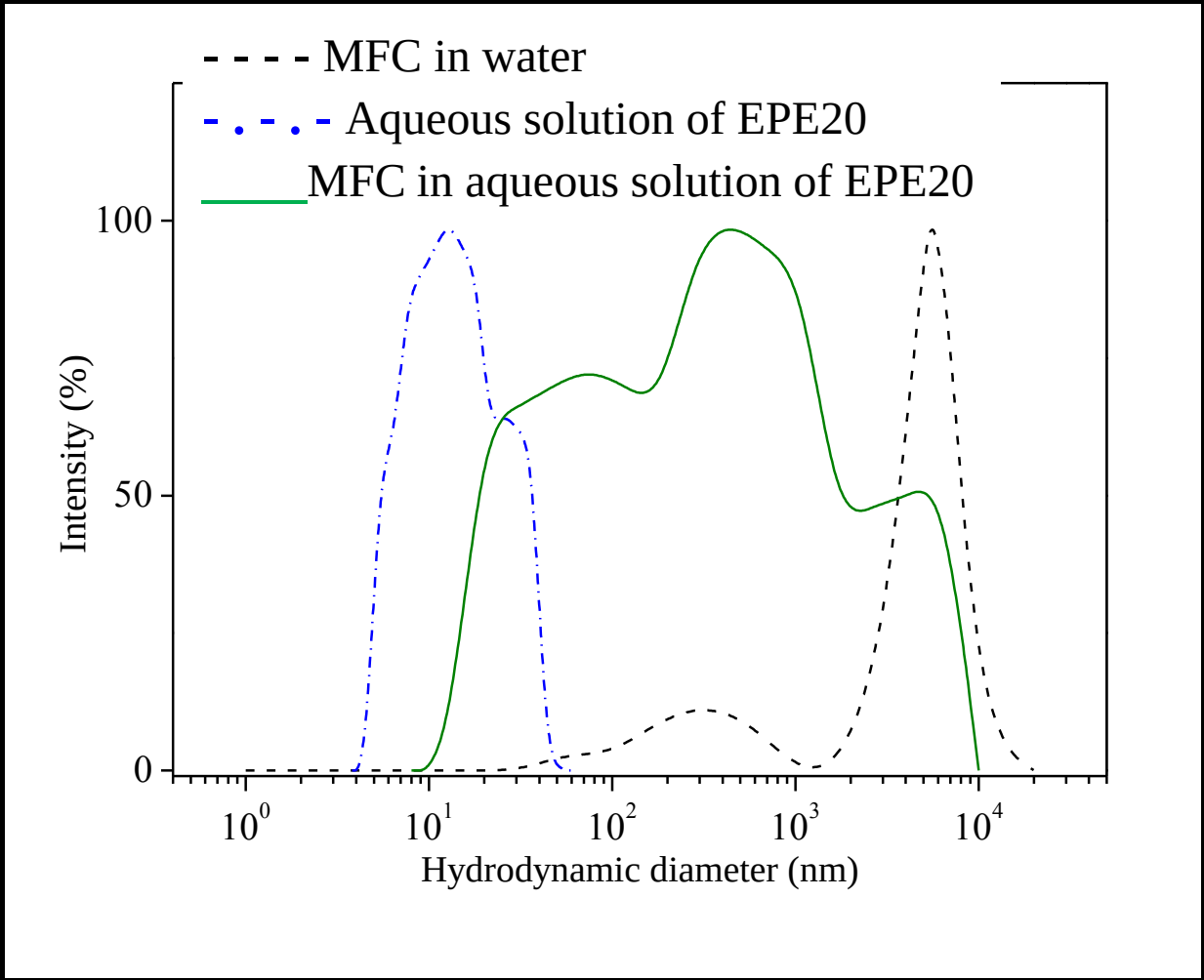
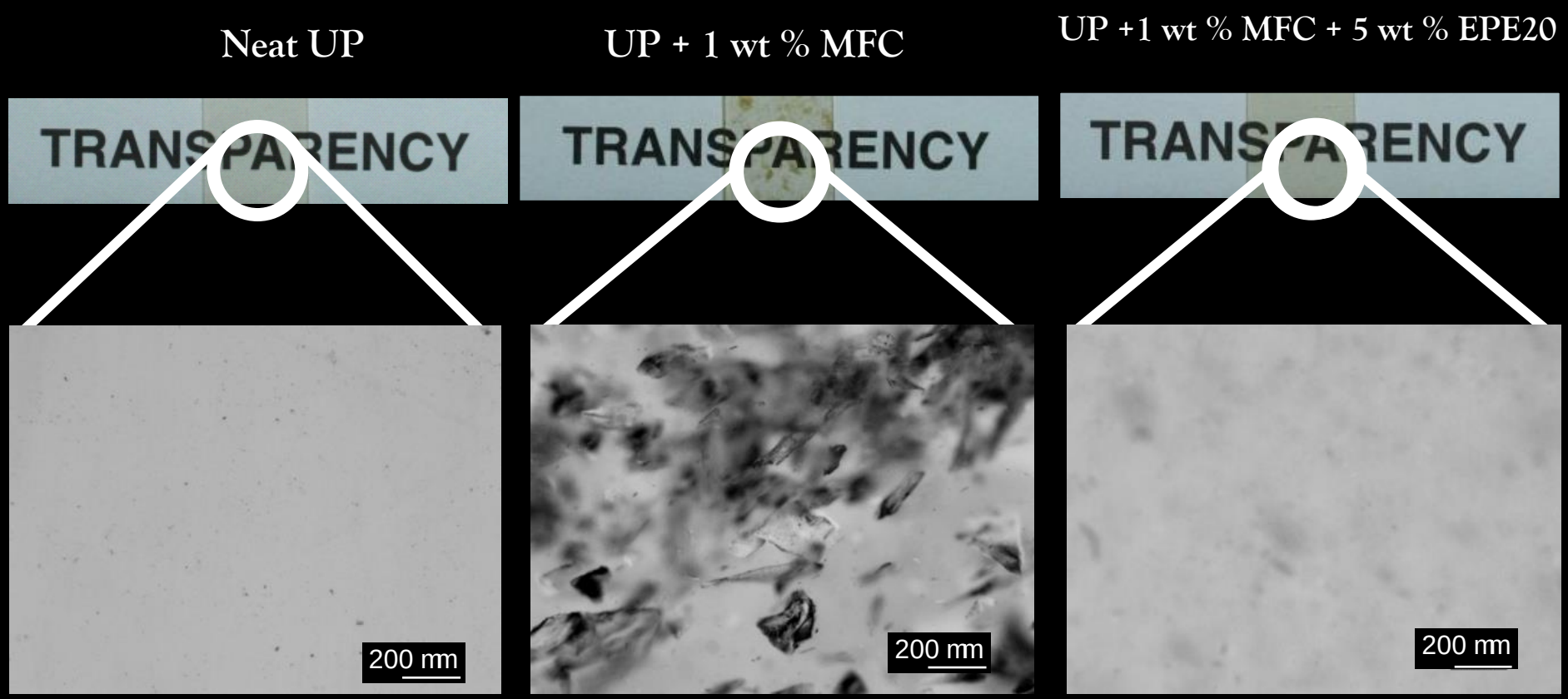
Hydrodynamic Diameter (DLS)



Two different thermosetting systems based on UP resin were prepared:

1. UP + 1 wt % MFC
2. UP + (1 wt % MFC + 5 wt % EPE20)

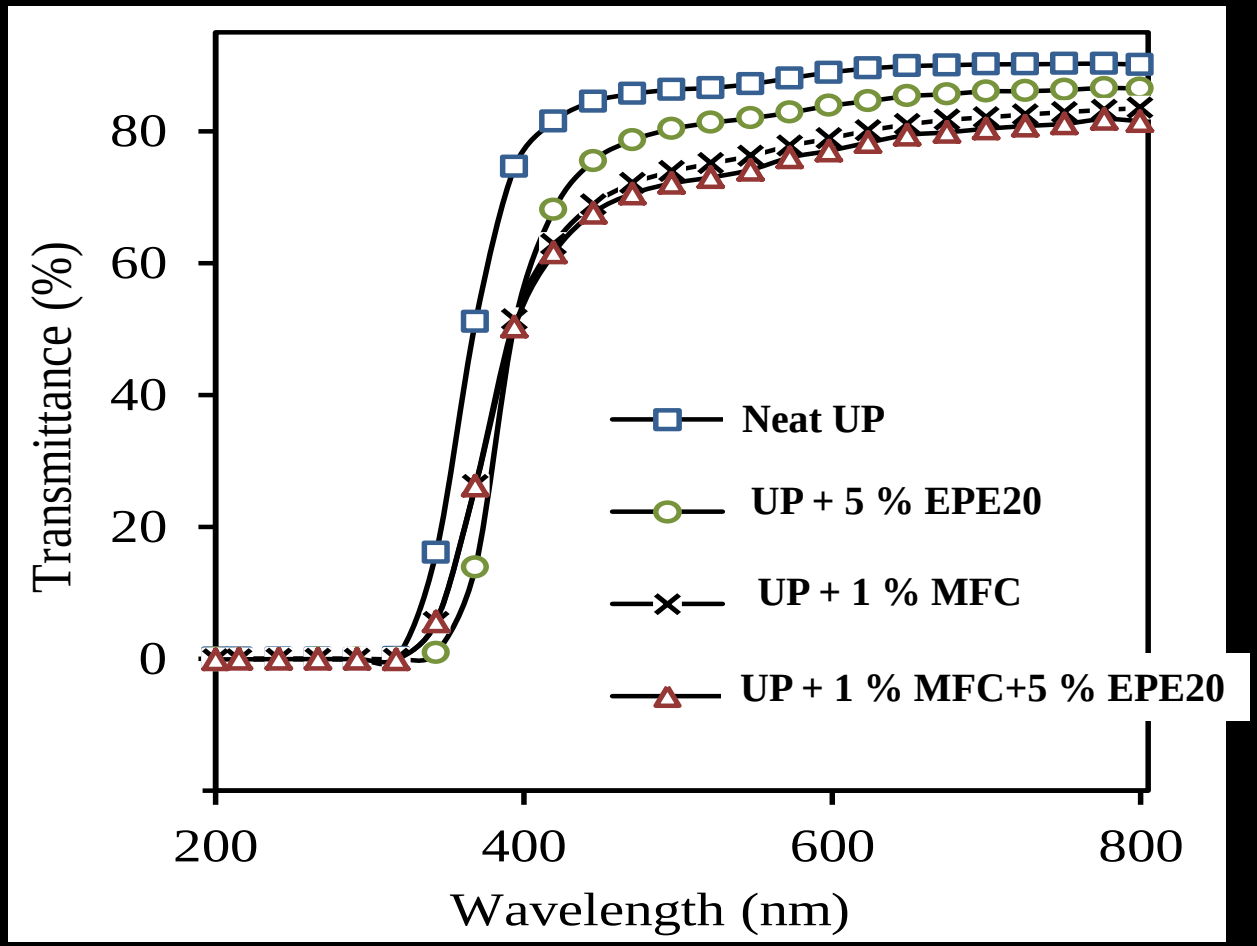
UP+MFC



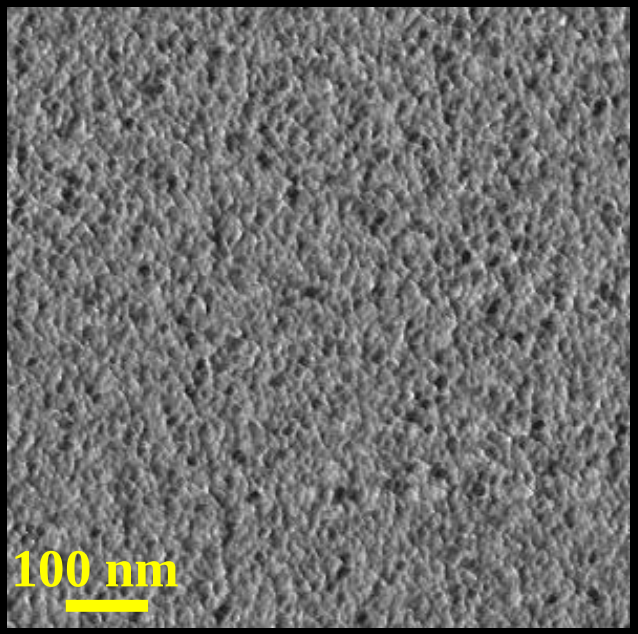
Optical Micrographs of Cured Samples

Transparency

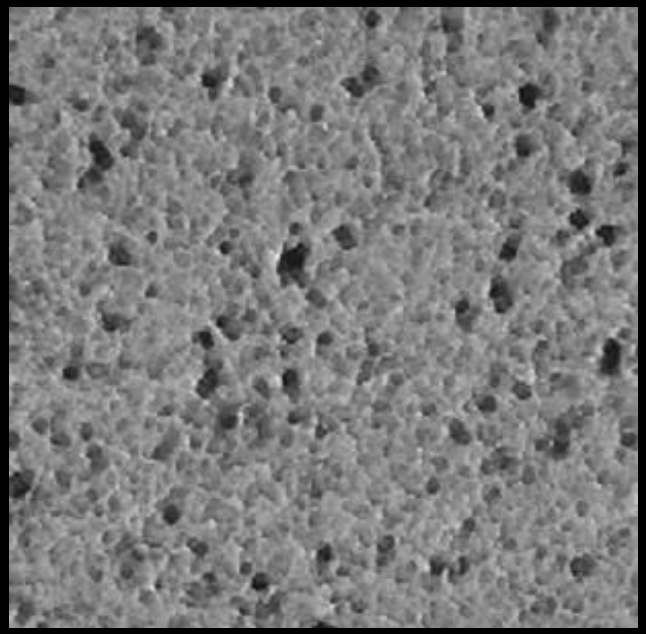
Ultraviolet-visible Spectroscopy (UV-vis)



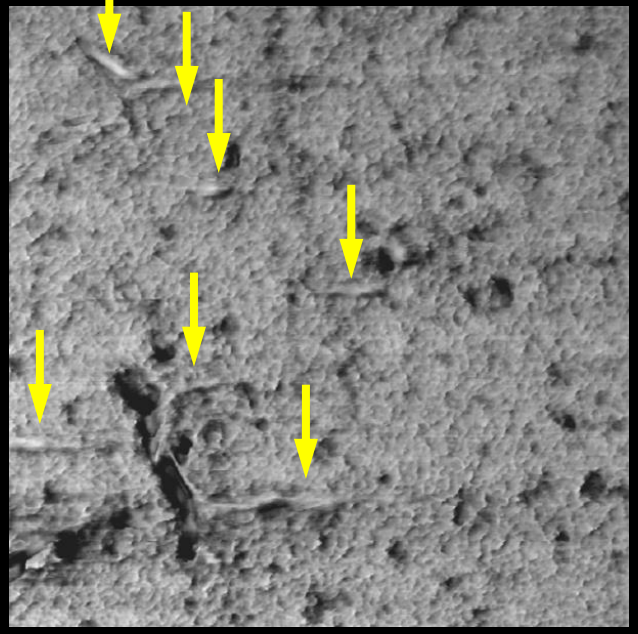
Morphology (AFM)



Neat UP

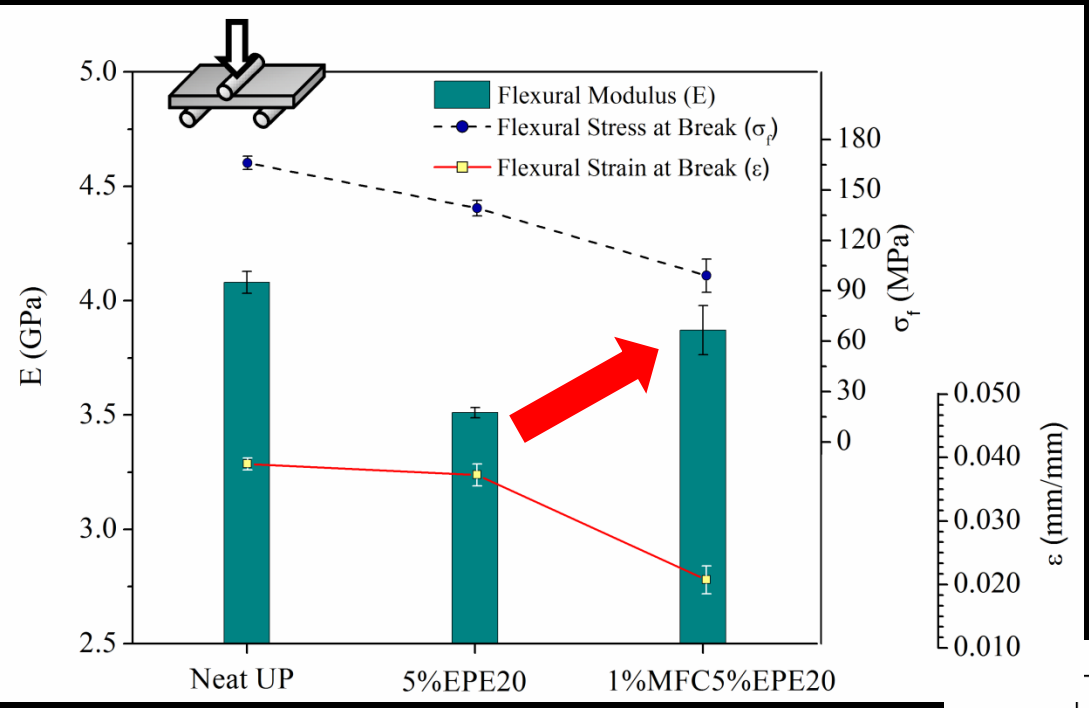


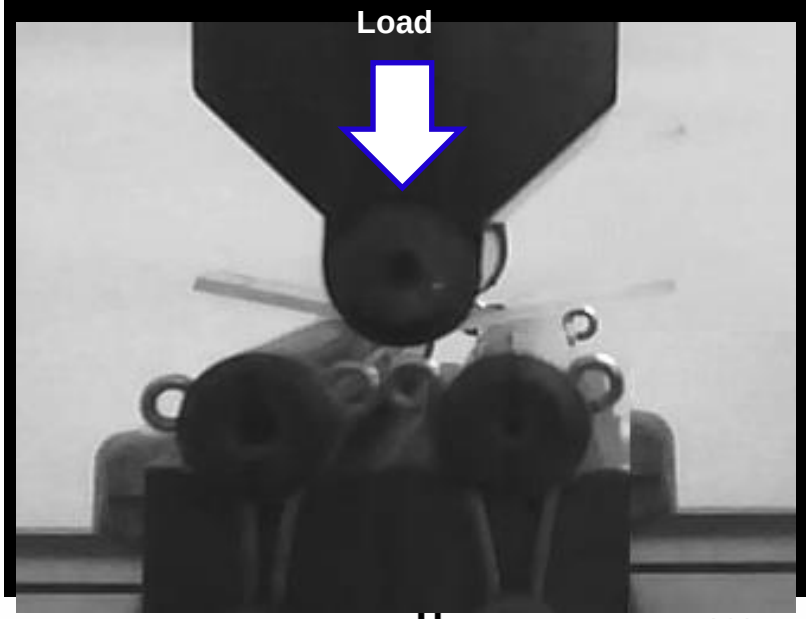
UP + 5 wt % EPE20

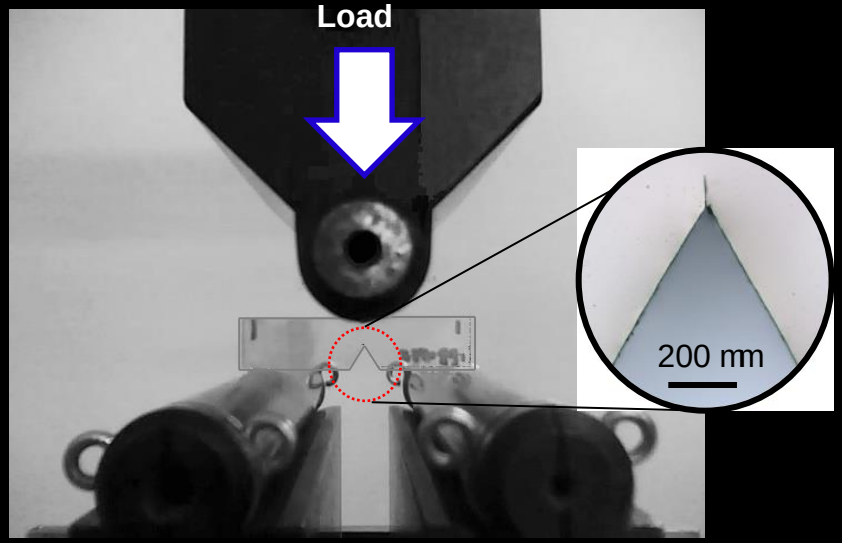


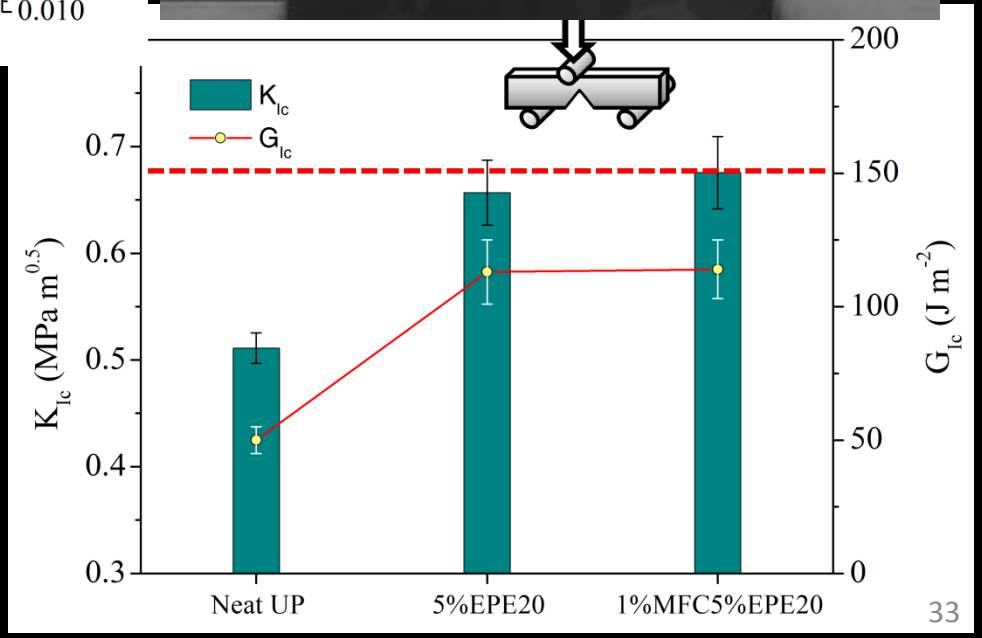
UP + 1 wt % MFC + 5 wt % EPE20

Mechanical Properties

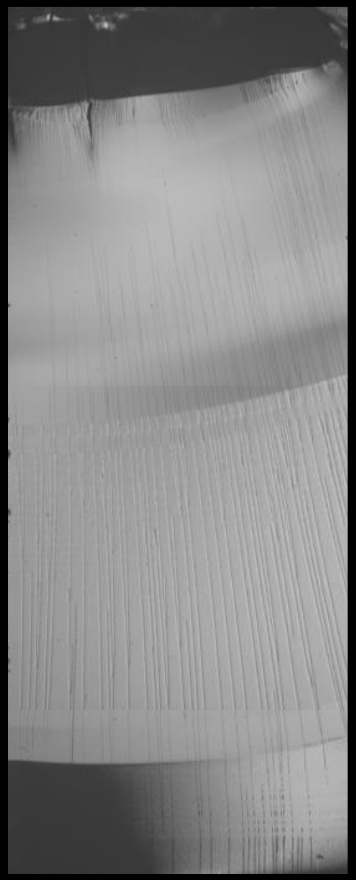






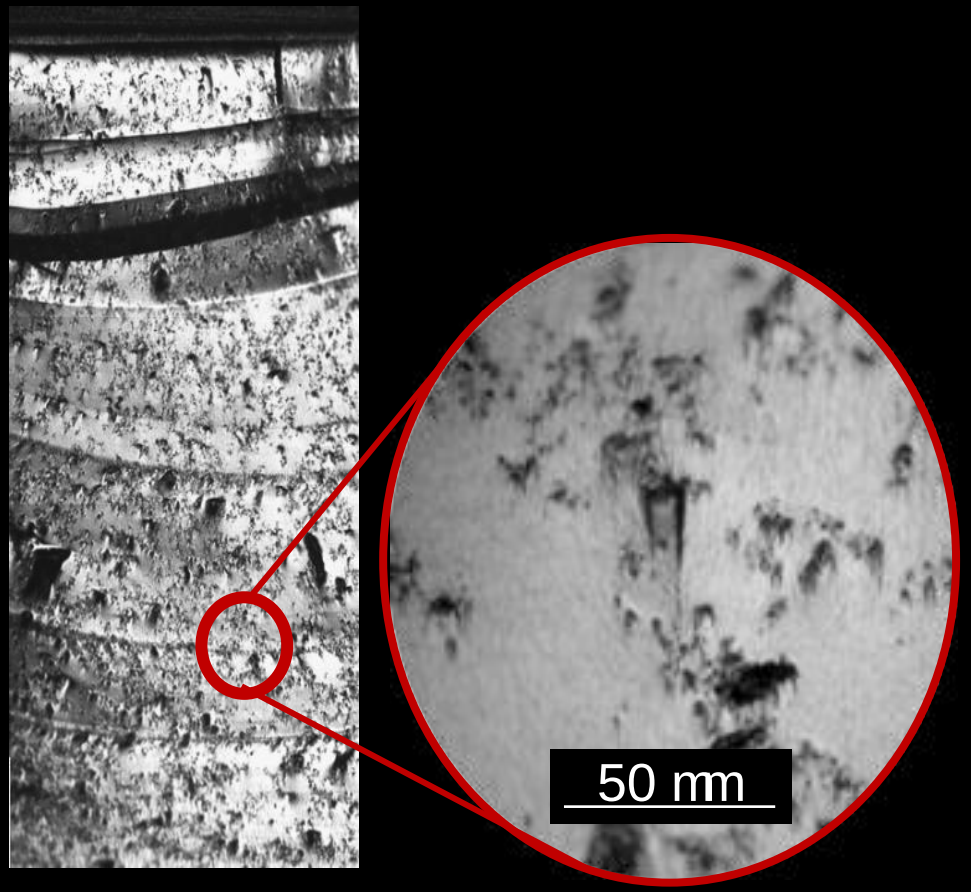


Fracture Surface



Neat UP

UP+ 5 wt % EPE20



UP + 1 wt % MFC +
5 wt % EPE20

APPLICATIONS

Transparency is not required

Transparency is required

CONCLUSIONS

- **A block copolymer with structure $E_{20}P_{69}E_{20}$ (EPE20) was used as an effective nanostructuring agent to increase the toughness of a commercial UP resin**

- **Self-assembly mechanism was responsible for the nanostructuration of the UP resin modified with EPE20 block copolymer**

- **A new pathway to fabricate nanocomposites of UP/MFC/EPE20 was developed by means of a controlled nanostructure achieving an appropriate reinforcement/transparency balance**

ACKNOWLEDGMENTS

- To Andercol S.A.

- To Group 'Materials + Technologies' (GMT) University of the Basque Country (UPV/EHU)

Publications

- Builes, D. H.; Tercjak, A.; Mondragon, I.
  ***Polymer* 53, 3669 (2012)**
  "Nanostructured Unsaturated Polyester Modified with Poly[(ethylene oxide)-*b*-(propylene oxide)-*b*-(ethylene oxide)] Triblock Copolymer"

- Builes, D. H.; Hernández, H.; Mondragon, I.; Tercjak, A.
  ***J Phys Chem C* 117, 3563 (2013)**
  "Relationship between the Morphology of Nanostructured Unsaturated Polyesters Modified with PEO-*b*-PPO-*b*-PEO Triblock Copolymer and their Optical and Mechanical Properties"

- Builes, D. H.; Labidi, J.; Eceiza, A.; Mondragon, I.; Tercjak, A.
  ***Compos Sci Technol* 89, 120 (2013)**
  "Unsaturated Polyester Nanocomposites Modified with Fibrillated Cellulose and PEO-b-PPO-b-PEO Block Copolymer"

- Builes, D.; Hernández-Ortiz, J. P.; Corcuera, M. A.; Mondragon, I.; Tercjak, A.
  ***ACS Appl Mater Interfaces* 6, 1073 (2014)**
  "Effect of Poly(ethylene oxide) Homopolymer and Two Different Poly(ethylene oxide-b-poly(propylene oxide)-b-poly(ethylene oxide) Triblock Copolymers on Morphological, Optical, and Mechanical Properties of Nanostructured Unsaturated Polyester"

Thank you!

daniel.builes@andercol.com.co

Group "Materials + Technologies"