DMA Analysis of PVAc Latex Reinforced with Cellulose Nanofibrils

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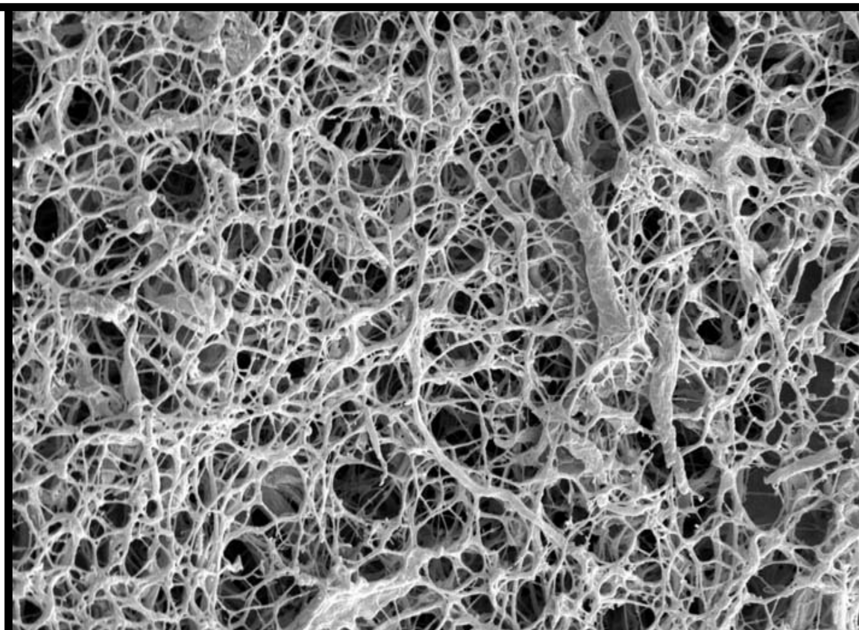
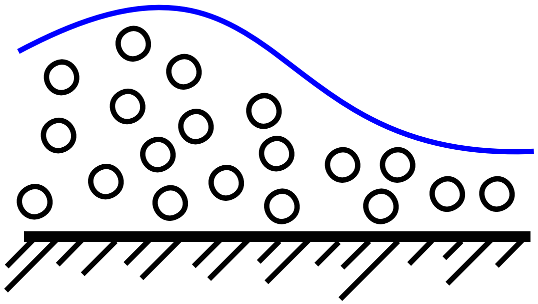
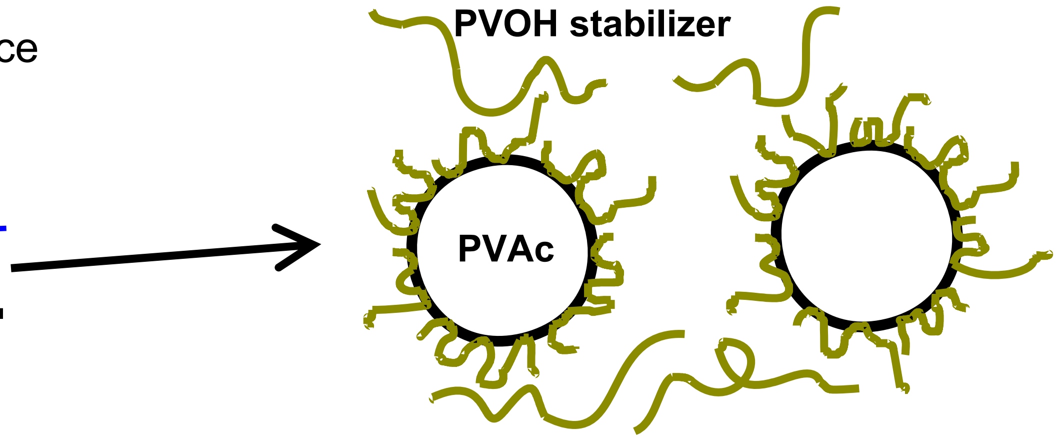


EMPA
Materials Science & Technology

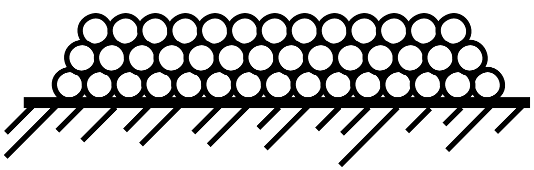
Film Formation in PVAc Latex Adhesives

1. Liquid latex spread on surface

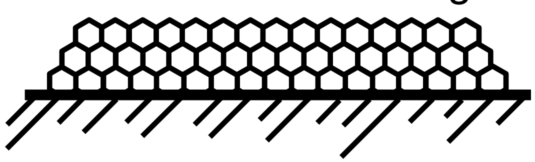


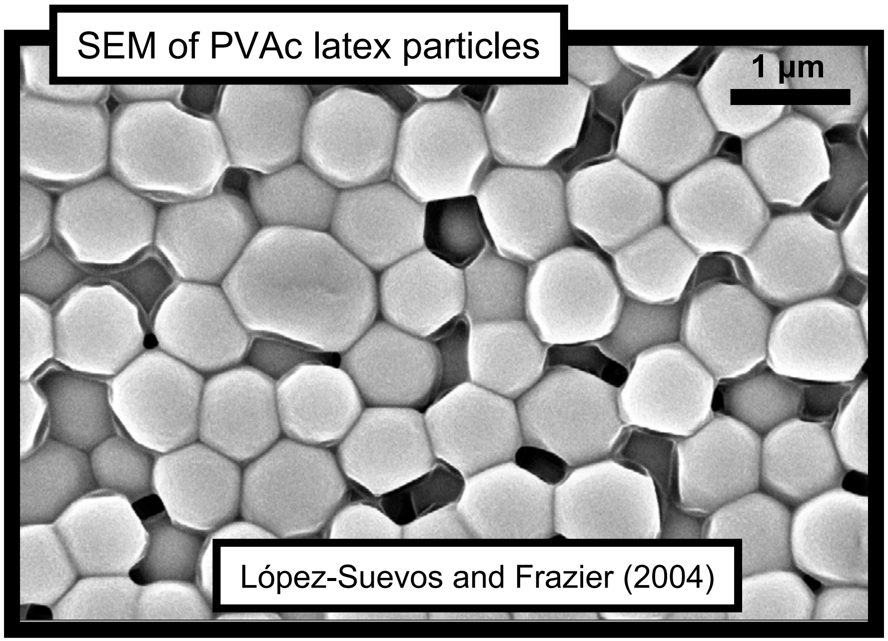


2. Water evaporation
...particle aggregation/packing



3. Particle deformation and
coalescence into a tough film



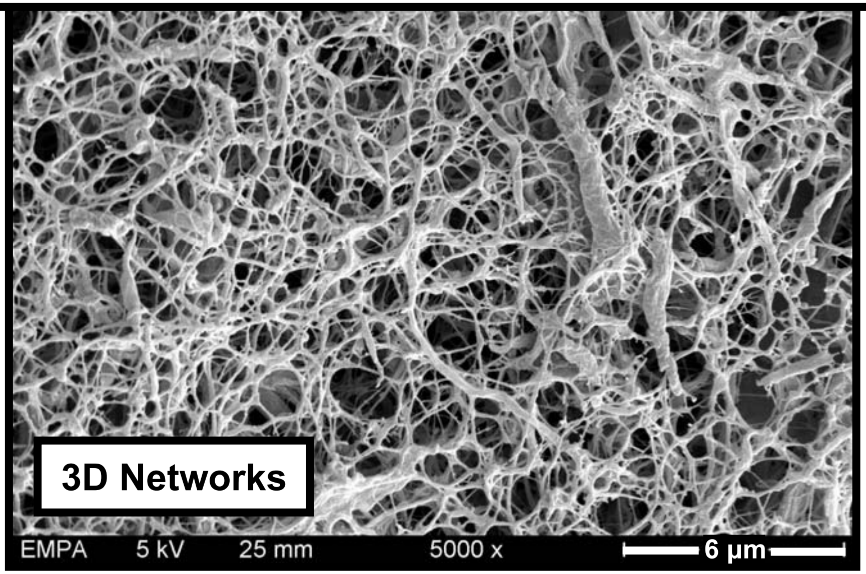


SEM of PVAc latex particles

López-Suevos and Frazier (2004)

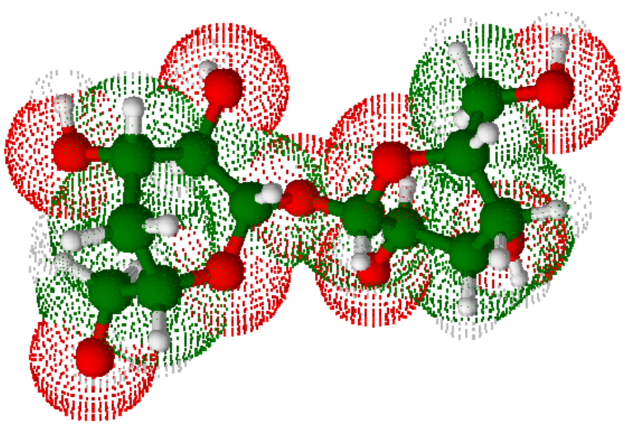
Cellulose Nanofibrils (CNF)

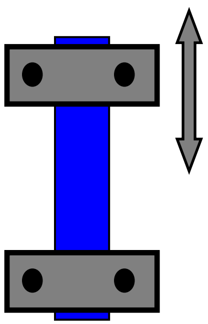
- Nano-sized crystalline biodegradable material
- Interesting physico-mechanical properties (high-strength, stiffness & hydrophilicity, low density, etc…)
- Huge progress in extraction, isolation & chemical modification
- Ideal for polymer reinforcement



Objective

To evaluate the reinforcing effect of different treated cellulose fibrils on the viscoelastic properties of PVAc composites by DMA





Tension Mode: Sinusoidal Oscillation

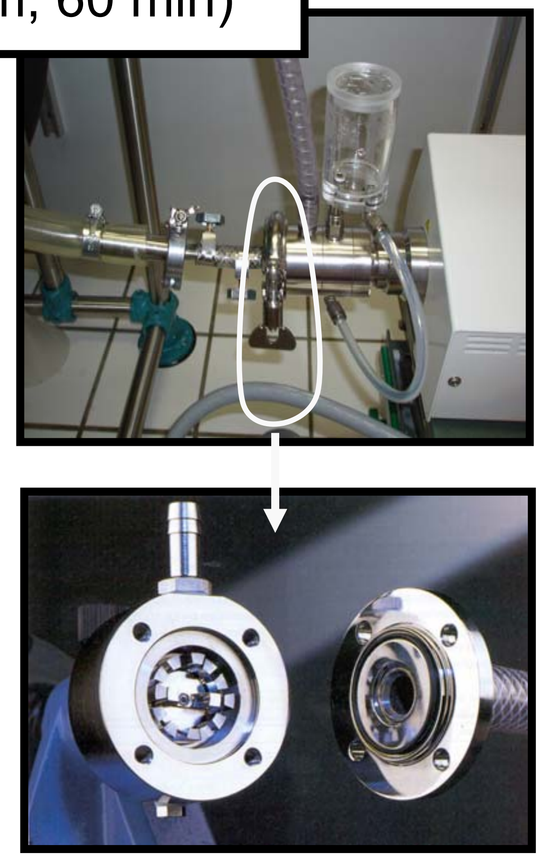
Experimental: Cellulose Fibrils

Refined and bleached wood pulp (RBP)

1. Mechanical disintegration
2. Chemical modification
3. Chemical modification + mechanical disintegration

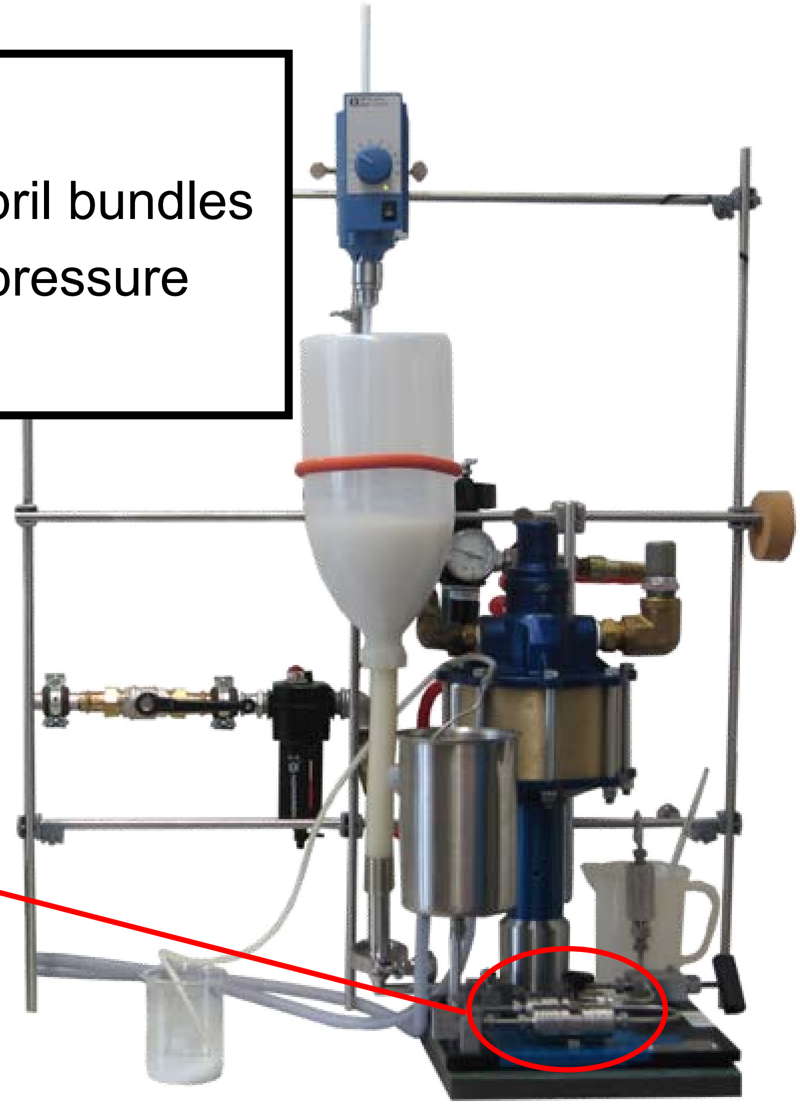
Experimental: Cellulose Fibrils

1. Mechanical Disintegration of RBP
   A. Homogenizer: Separation of fibril bundles from the cell wall by inline dispersing (20000 rpm, 60 min)



Experimental: Cellulose Fibrils

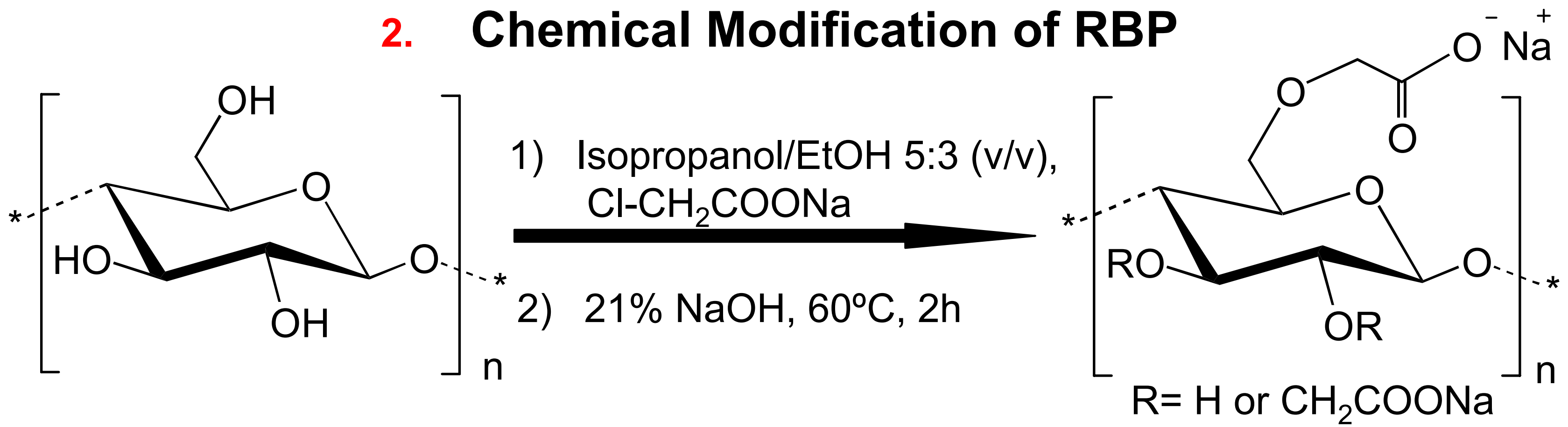
1. Mechanical Disintegration of RBP
   B. Microfluidizer: Disintegration of fibril bundles into cellulose nanofibrils by high-pressure dispersing (1500 bar, 6 cycles)



Interaction/friction chambers

Experimental: Cellulose Fibrils

2. Chemical Modification of RBP



- Degree of Substitution = 0.156 ± 0.028, n=3
- Powdered CM-RBP is redispersable in water

3. Chemical Modification + Mechanical Disintegration of RBP

1) CM-RBP redispersed in water (ca. 2.5% wt.) with high-shear blender
2) Mechanical disintegration as previously described (CM-MD-RBP)

Experimental: Cellulose Fibrils

Summary

1. Refined and bleached wood pulp (**RBP**)
2. Mechanical disintegration of RBP (**MD-RBP**)
   - Homogenizer + Microfluidizer
3. Chemical modification of RBP (**CM-RBP**)
   - Carboxymethylation of ~5% of Cellulose –OH groups
   - The CM-RBP powder is redispersable in water
4. Chemical modification + mechanical disintegration of RBP (**CM-MD-RBP**)

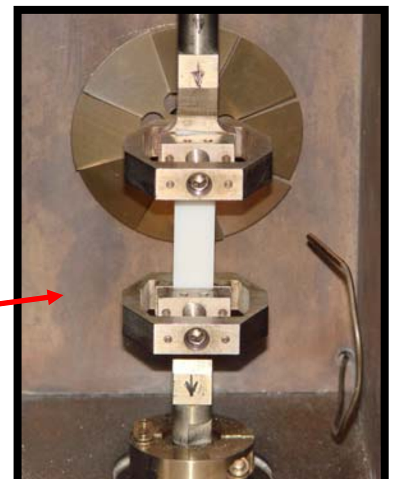
Experimental: PVAc–Fibrils Composites

- **PVAc-Cellulose fibril formulations (0, 5, 10, 20 & 30% wt.):** High-shear blended (12000 rpm, 1 min), degassed under vacuum, casted onto silicon molds & dried under ambient conditions.
- **Size:** 45 (length) x 10 (width) x 0.6-0.7 (thickness) mm
- Samples **dried** over silica gel under vacuum for at least 3 days prior to DMA analysis

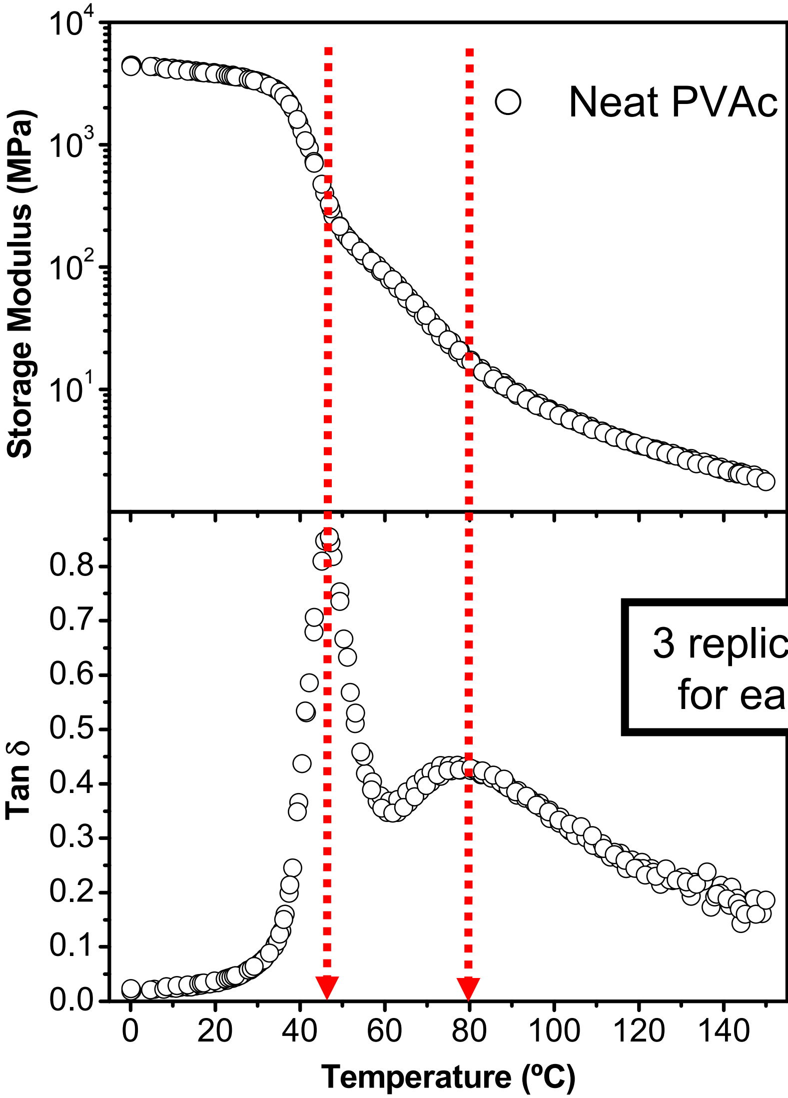
Experimental: DMA Experiments

- Dynamic heating scans:
  - Isothermal at 0ºC for 5 min
  - 0 to 150ºC at 2ºC/min and 10 Hz
  - 0.1 N Contact force, 0.3 % Static strain, 0.03% Dynamic strain
  - Three analyses for each sample


GABO-eplexor DMA 800


Tension Mode

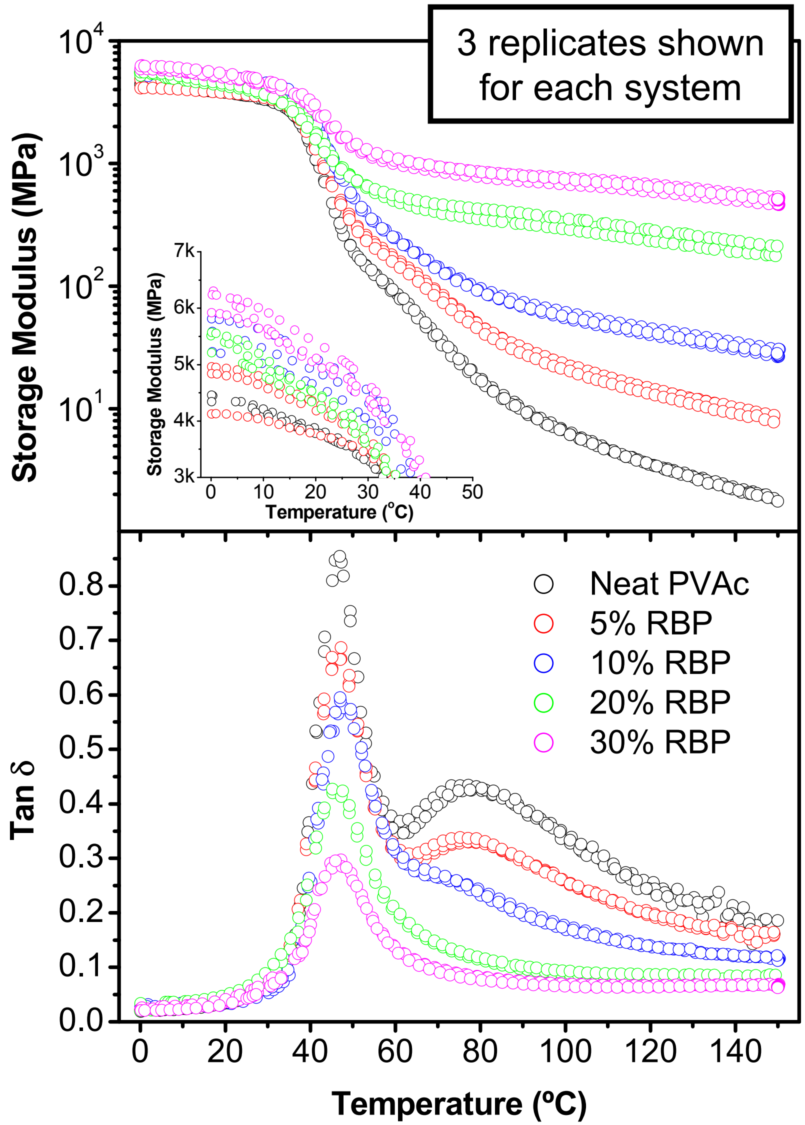
Results: DMA of Neat PVAc Films



- Excellent reproducibility
- PVAc Tg (Tan δ peak) ~ 45ºC
- PVOH Tg (Tan δ peak) ~ 80ºC
- > 3 decade drop in Storage Modulus

3 replicates shown for each system

Results: DMA of PVAc/RBP Composite



Higher amounts of RBP fibrils leads to:

<u>Glassy region:</u>

- Slight increase in Storage modulus (SM)

<u>PVAc glass transition:</u>

- Reduction in Tan δ intensity (0.85 to 0.3)
- ~ 1 decade increase in SM
- Tg unaltered (45 ± 2ºC, Tan δ peak)

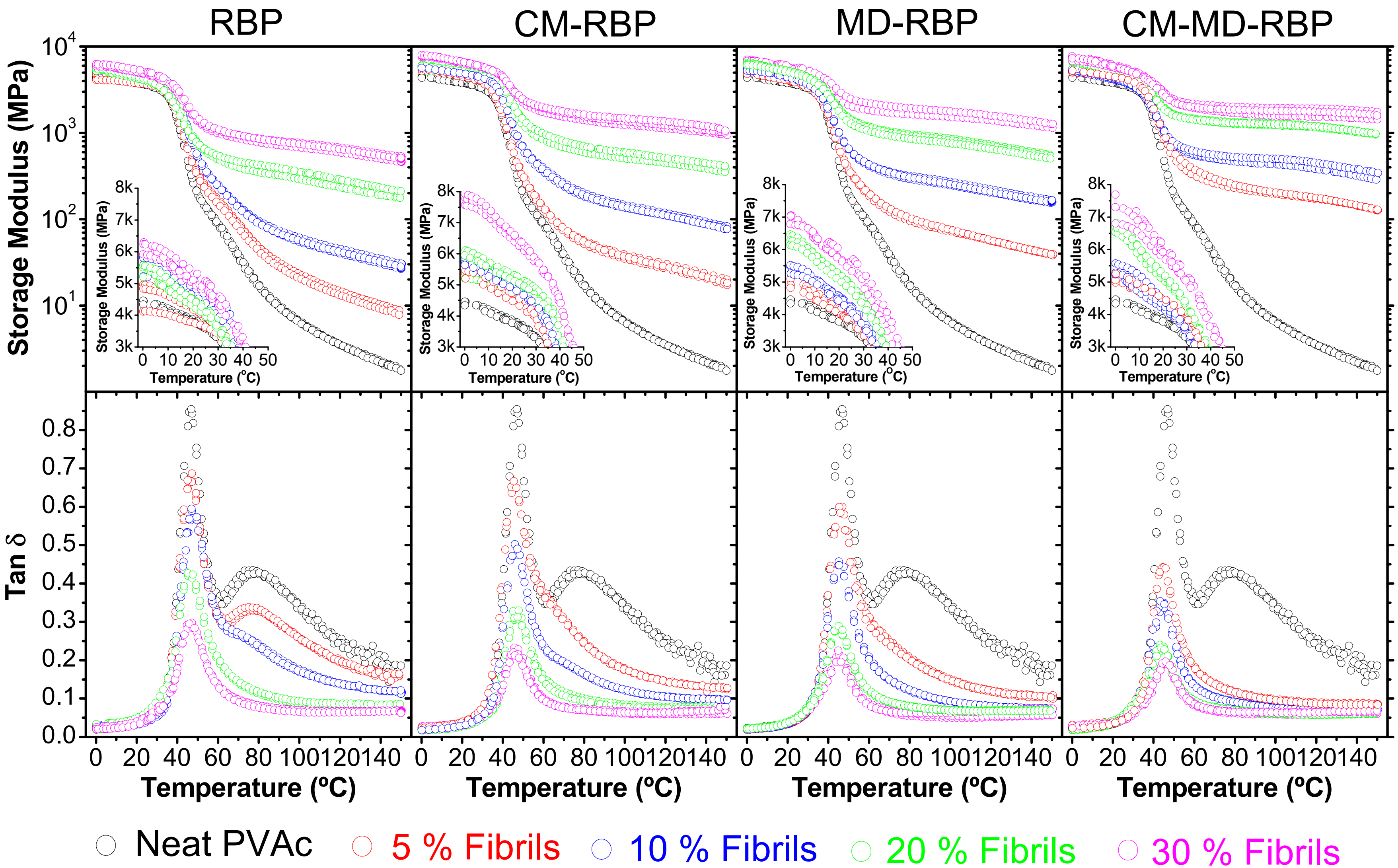
<u>PVOH glass transition:</u>

- Gradually dissapears
- Fibrils act at the particle boundaries

<u>Rubbery plateau</u>

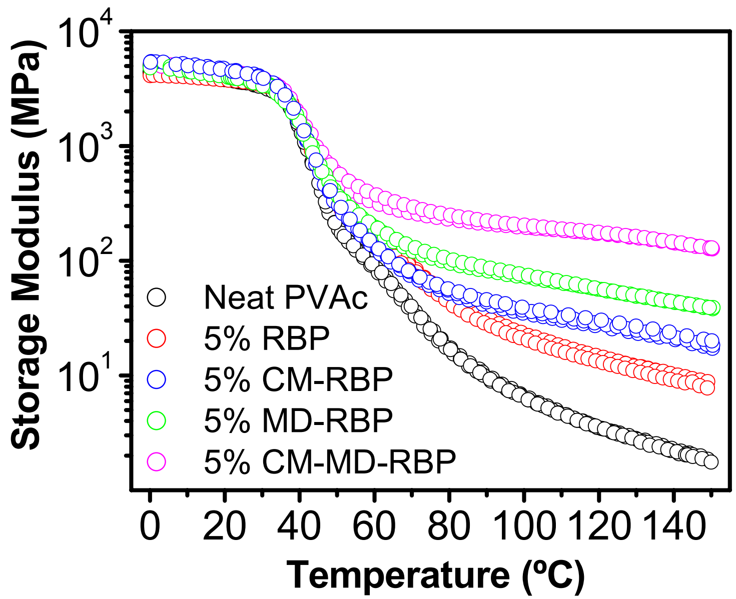
- SM increases >> 2 decades @ 150ºC

Results: DMA of all PVAc-Composites

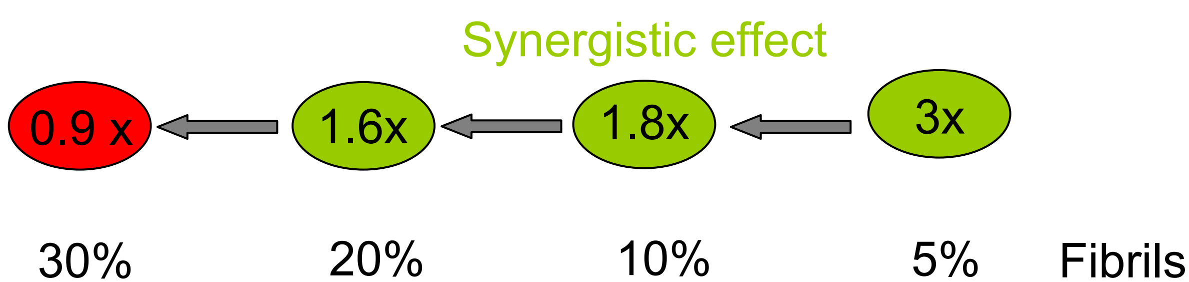


Results: Synergistic effect

Synergy: Treatments acting together > Sum of treatments acting independently



5% Fibril	Storage Modulus @ 150ºC (MPa)	Reinforcement by treatment
RBP	8.5	n/a
CM-RBP	18.3	9.8
		+
MD-RBP	39.2	30.7
		^
CM-MD-RBP	129.5	121



Conclusions

- Addition of Untreated/treated RBP fibrils remarkably altered the viscoelastic properties of PVAc composites in the studied temperature region
- Reinforcing effect: RBP < CM-RBP < MD-RBP < CM-MD-RBP
- Effective reinforcement especially above the glassy state
  - Remarkable increase in the Storage Modulus
  - Dramatic reduction of PVAc & PVOH transitions (Tan δ)
  - Unaltered PVAc Tg
- Synergistic effect between treatments
  - CM-MD-RBP >> CM-RBP + MD-RBP (up to 3x larger)

Acknowledgements

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