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*Industrial Materials
Institute*

Polystyrenes with macro- intercalated organoclay

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Outline

- Introduction
- Objectives
- Preparation of organoclay COPS
- Materials and method of compounding
- XRD measurements
- SEM and TEM observations
- Rheological properties
- Mechanical properties
- Concluding remarks

Introduction

- Relatively easy exfoliation of clay platelets by polar polymers (PA) due to strong interaction, but much more difficult to exfoliate clays in non-polar polymers (PS, PP).
- Polymerization in presence of non-reactive organoclay:
 - Slow reaction;
 - Thermodynamically unstable exfoliation → re-aggregation during processing;
 - Process available only to resin manufacturer.
- Melt processing providing mechanical exfoliation:
 - Rapidity (< 10 min);
 - Controlled by thermodynamic interactions → no danger of re-aggregation;
 - Need to be miscible with PS and thermally stable organoclay.

(Hasegawa *et al.* 1999; Hoffman *et al.* 2000;
Yoon *et al.* 2001; Tanoue *et al.* 2004)

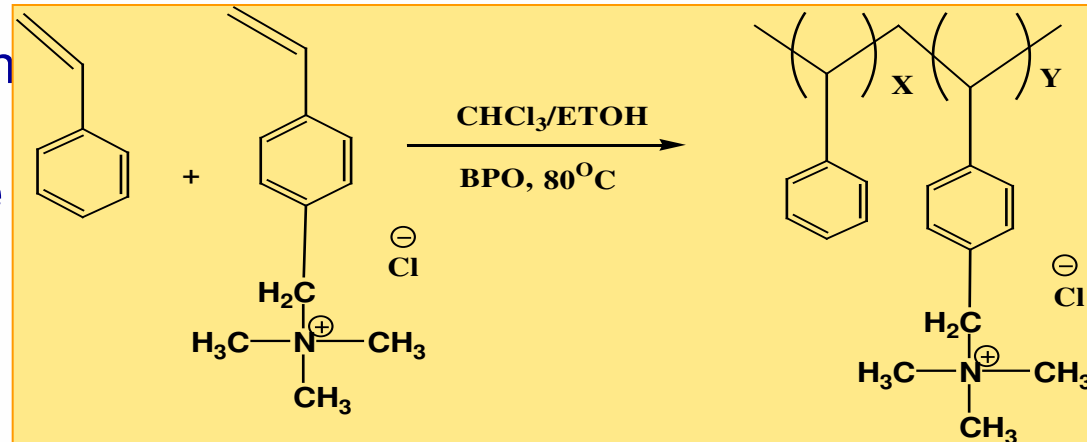
Objectives

- ▶ Prepare exfoliated PNC with PS as matrix.
- ▶ Investigate the degree of dispersion of COPS and the PNC performance.

Preparation of COPS

- ◆ COPS organoclay prepared with macromolecular intercalant.
- ◆ Preparation involved two steps:

- ◆ Free radical copolymerization of styrene with vinyl-benzyl 3-methyl ammonium chloride
- ◆ Na-MMT intercalation.



- ◆ TGA measurement from 30 to 700°C at a rate of $10^\circ\text{C}/\text{min}$ shows:
 - ◆ Volatile matter: 1.4-wt% loss at $T \leq 150^\circ\text{C}$;
 - ◆ Non-volatile matter (MMT): 21.7-wt%.

Materials and method of compounding

● Materials:

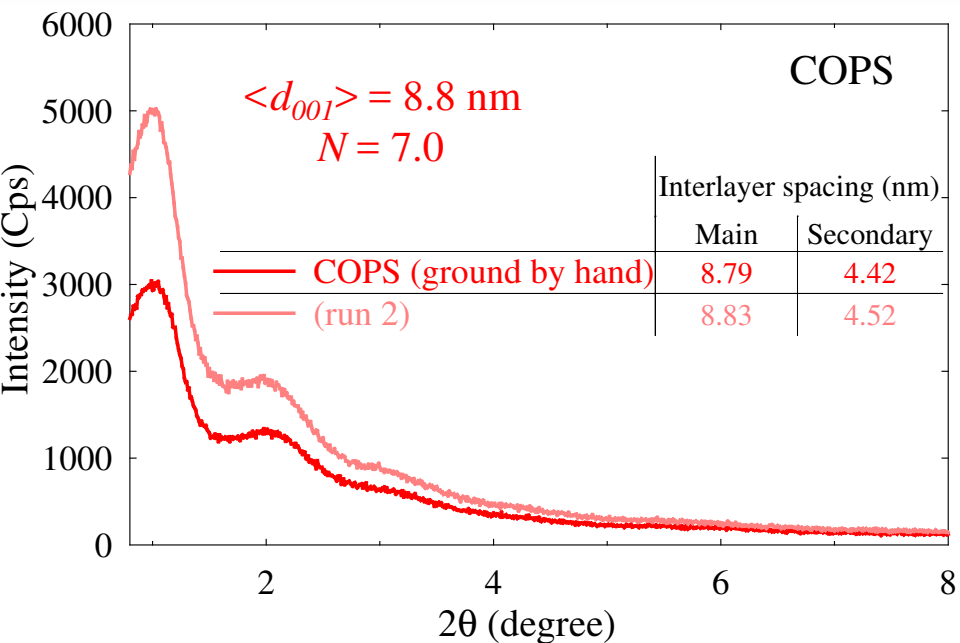
- PS1301 (Nova Chemicals, $M_w = 270$ kg/mol);
- PS20.3 (Delltec, $M_w = 116$ kg/mol);
- COPS organoclay dried for 15 d at 60 C;
- Cloisite 10A (C10A) dried for 24 h at 100 C.

● Method of compounding:

- Melt compounding with:
 - *MiniLab co- and counter-rotating micro-compounder (ThermoHaake)*
 - *Industrial co-rotating fully intermeshing TSE (Leistritz, TSE-34 mm, $L/D = 40$)*
- Solution blending of COPS and PS separately in toluene.

XRD and TEM of COPS

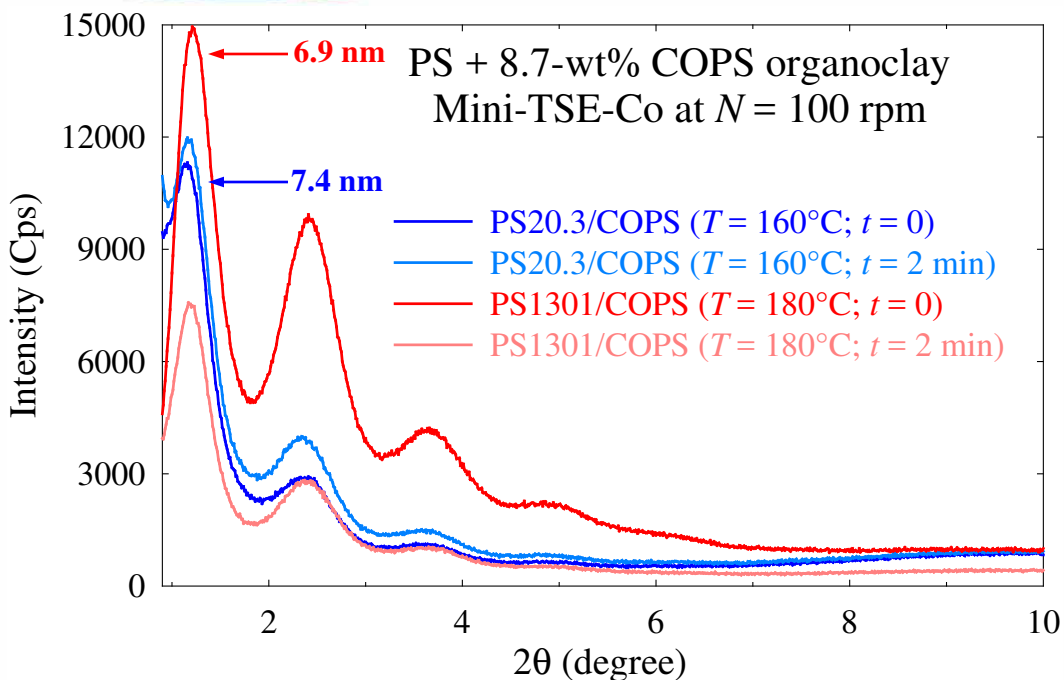
x 200k



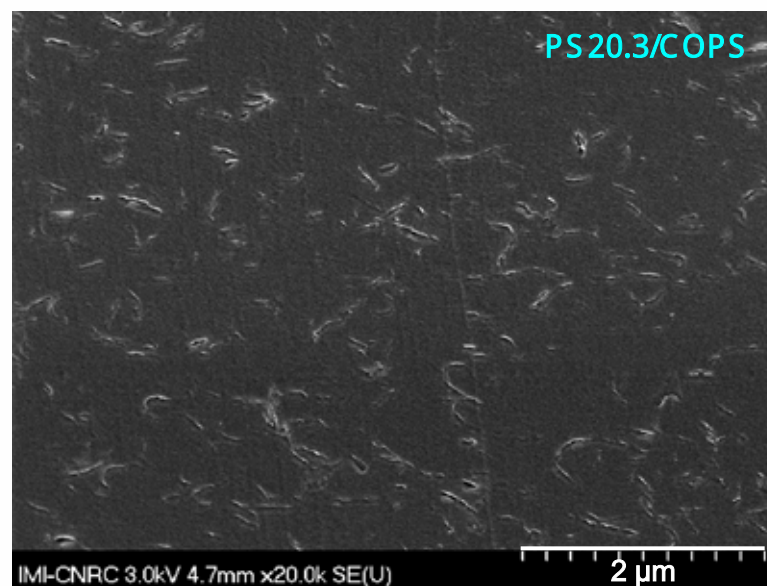
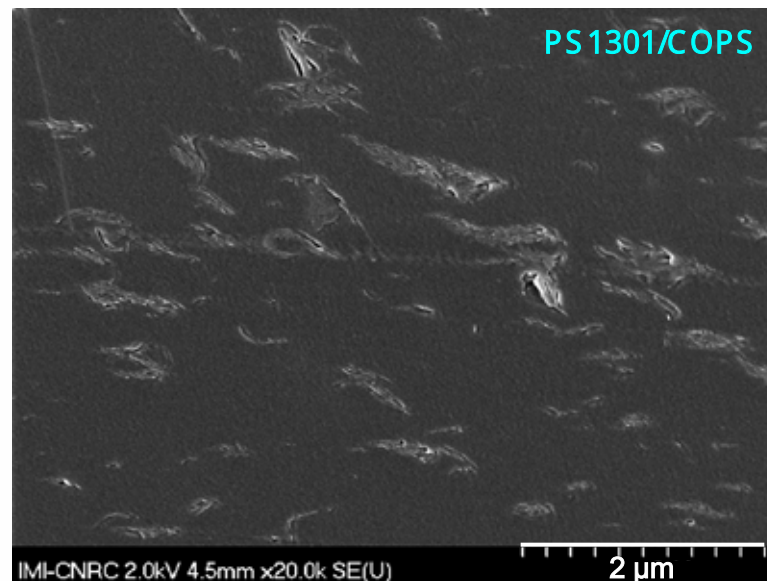
- XRD scans of COPS show two peaks: the first at $2\theta \leq 1^\circ$ ($d_{001} = 8.8 \text{ nm}$) and the second at $2\theta \approx 2^\circ$ ($d_{002} = 4.5 \text{ nm}$).
- TEM observation of COPS (compression molded then microtomed) confirm the XRD results of $d_{001} = 10 \text{ nm}$ (for 96 measures)

PS/COPS (Mini-TSE-Co)

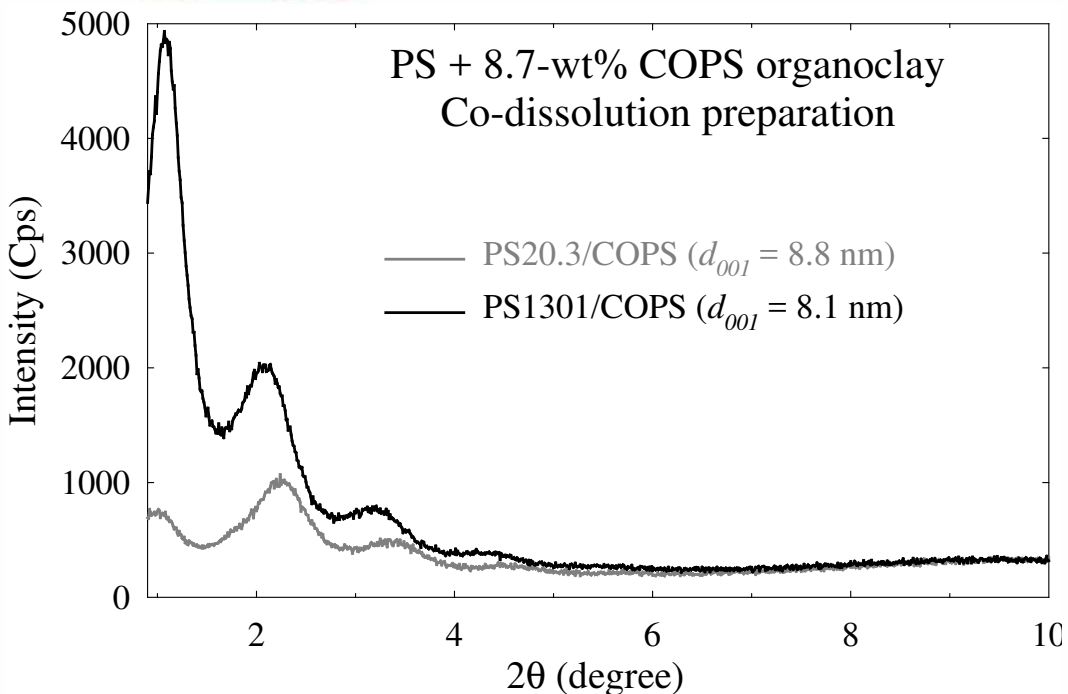
x 20k



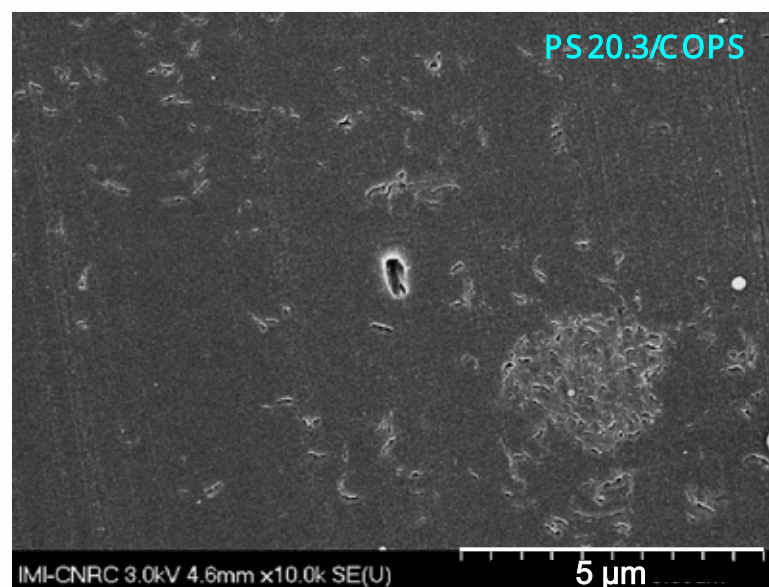
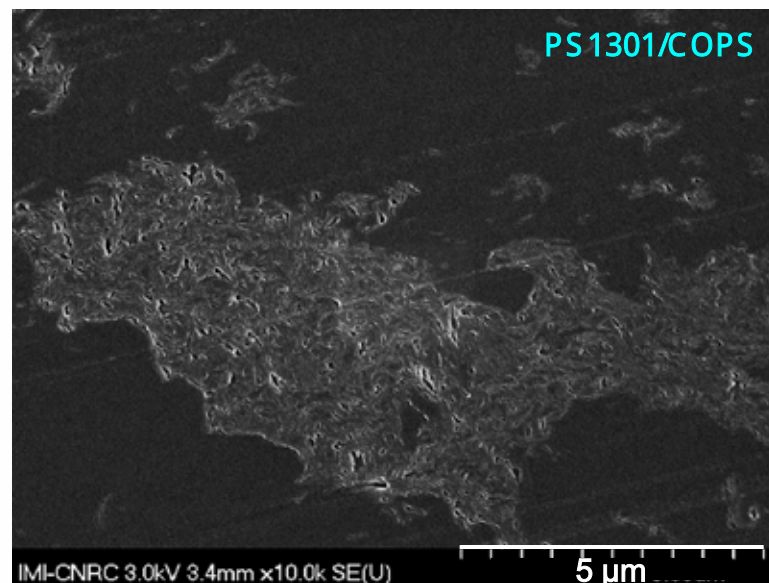
- Decrease of d_{001} of COPS from 8.8 to 7.4 and 6.9 nm for melt processed PS/COPS;
- Decrease of d_{001} with increasing T and/or intensity of mixing conditions;
- Smaller aggregates of COPS in PS20.3.



PS/COPS (co-dissolution) x 10k



- d_{001} of COPS remains in PS/COPS prepared with co-dissolution;
- However large aggregates of COPS were observed in PS (smaller for PS20.3).



PS20.3/COPS

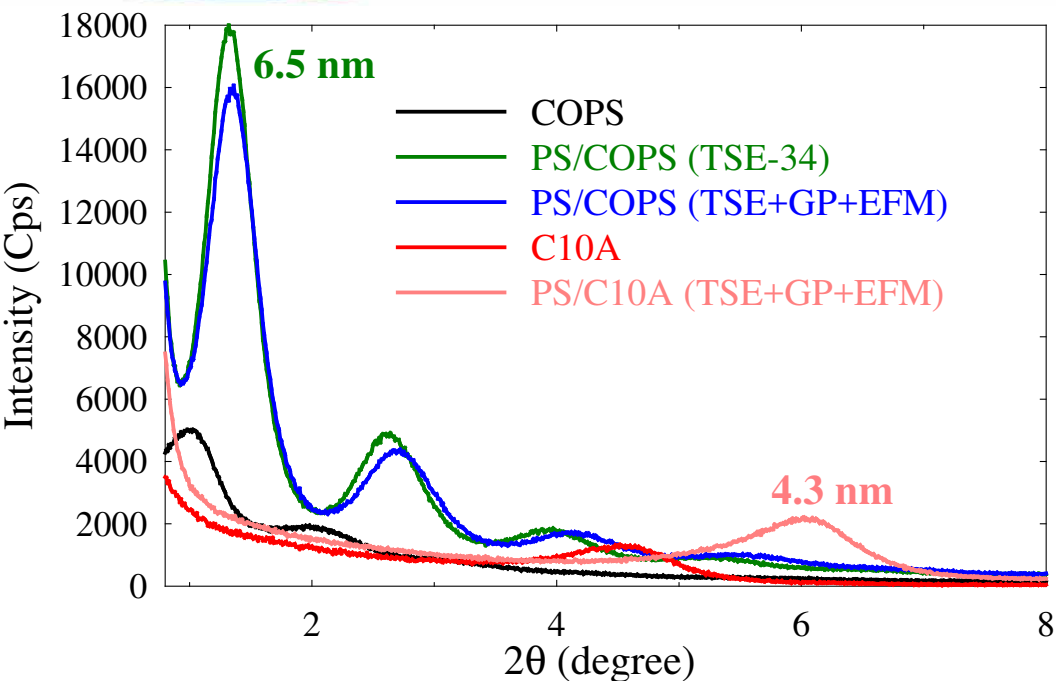
x 80k



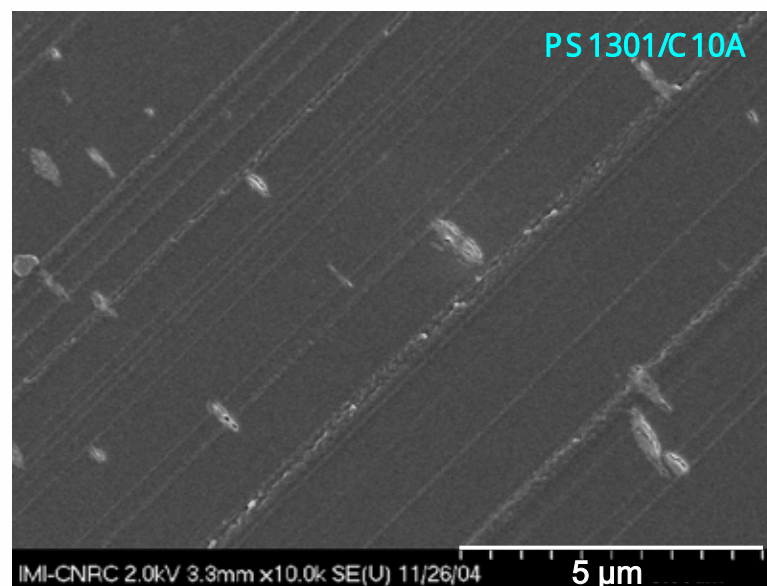
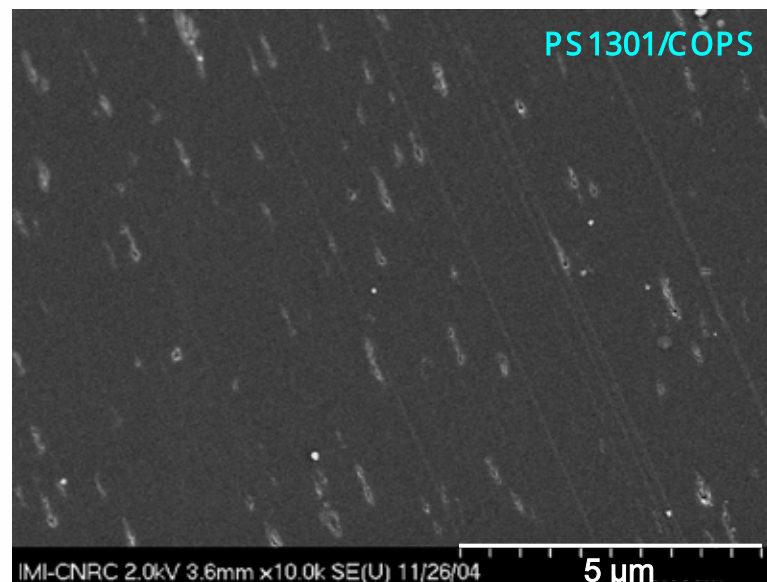
- Small aggregates of COPS have 10 to 15 platelets;
- Individual (exfoliated) clay platelets may be seen also, which are more frequent for co-dissolution prepared blend.

PS/Clay (TSE+GP+EFM)

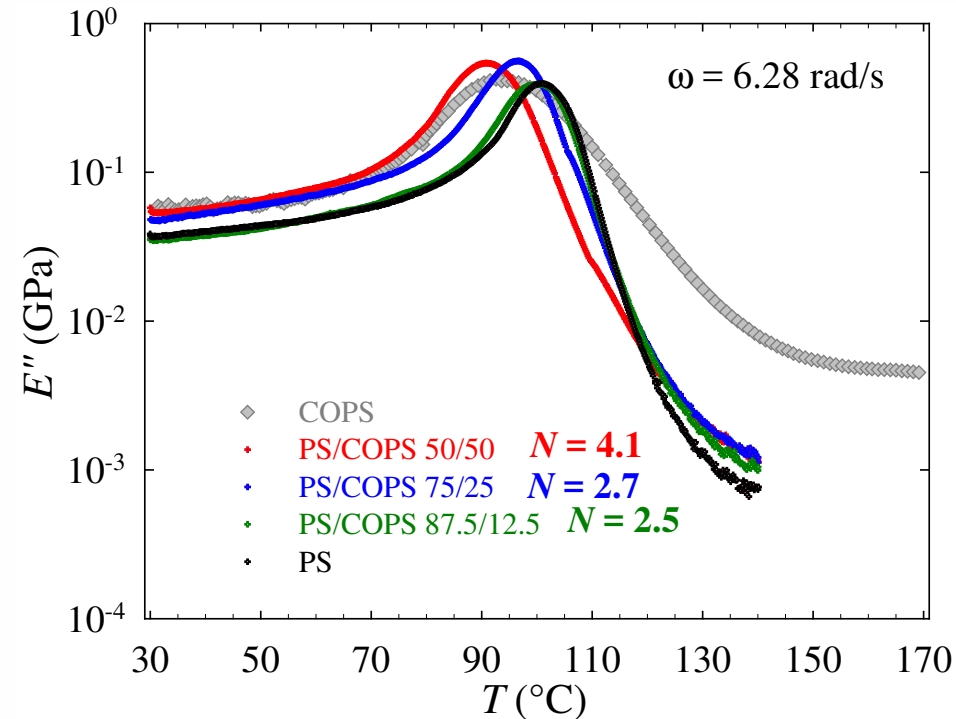
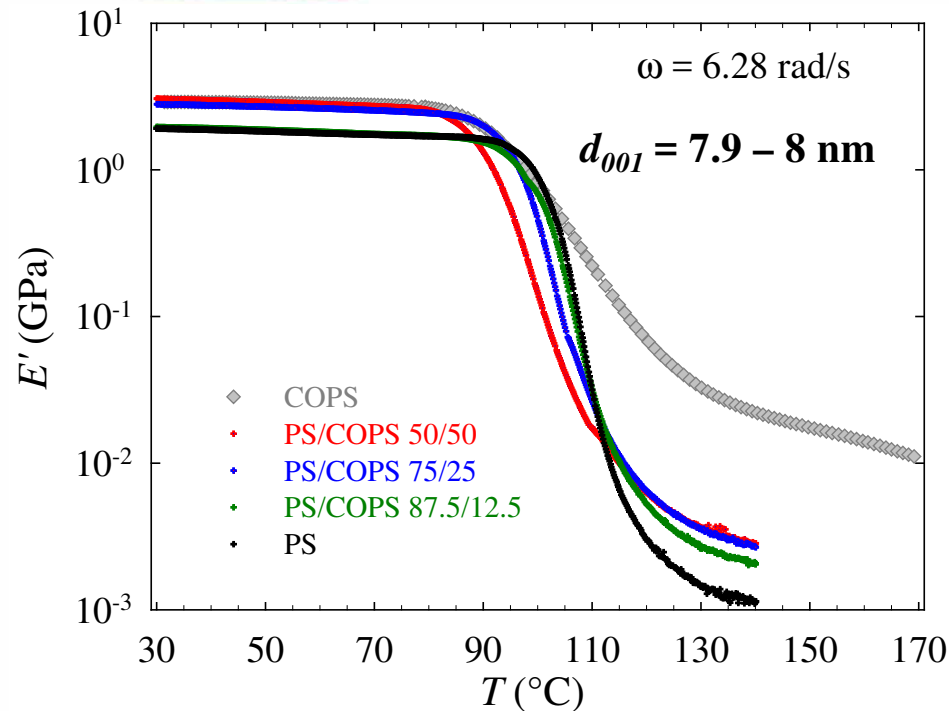
x 10k



- PS/COPS prepared with TSE-34 with or without EFM show decrease in d_{001} of COPS from 8.8 to 6.5 nm;
- Larger aggregates of C10A in PS in comparison with PS/COPS.

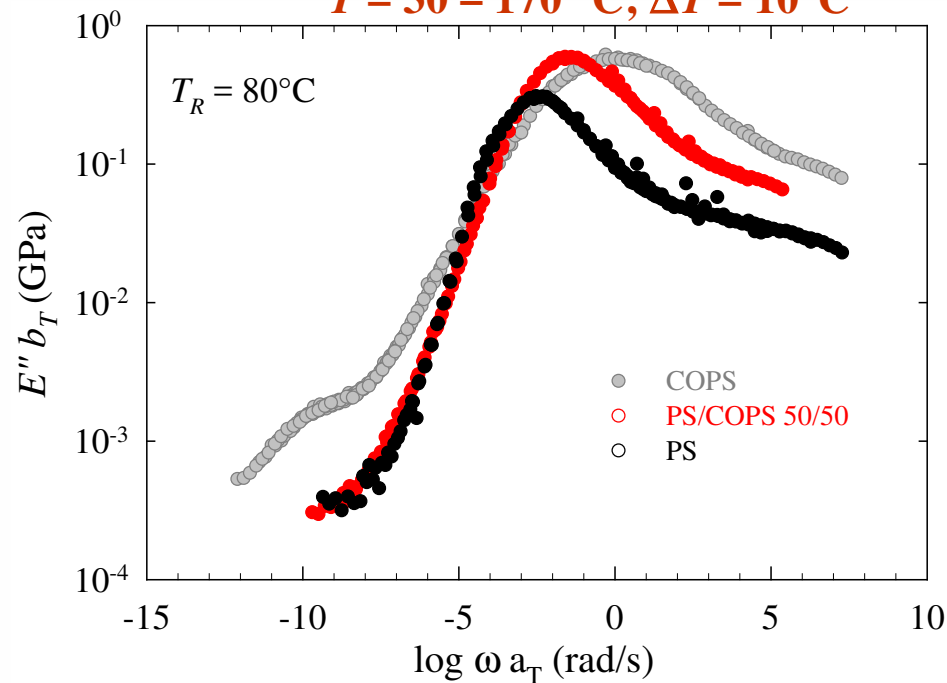
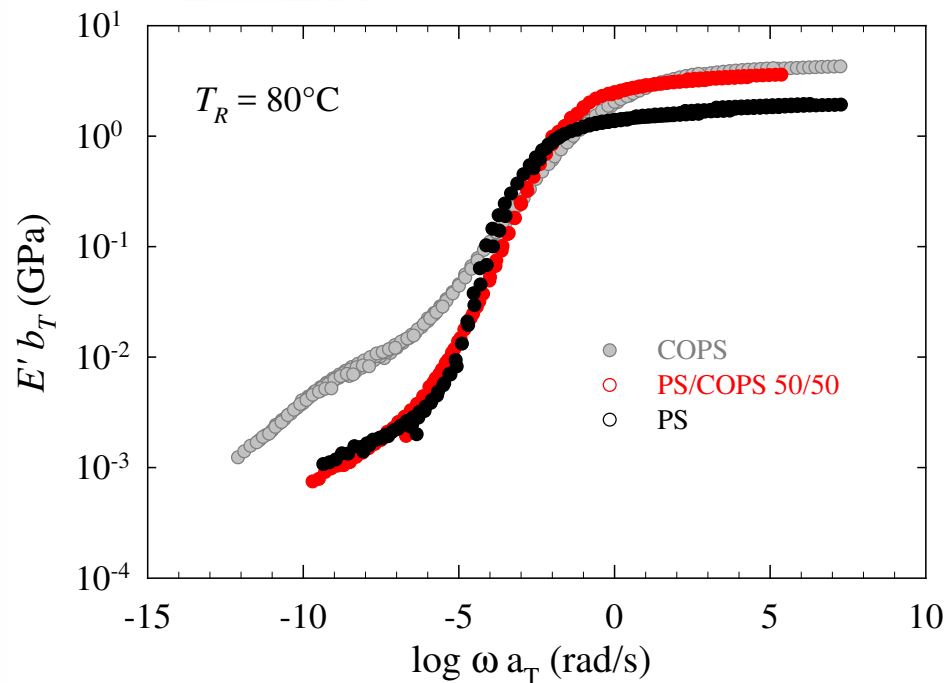


Temperature sweep with DMTA



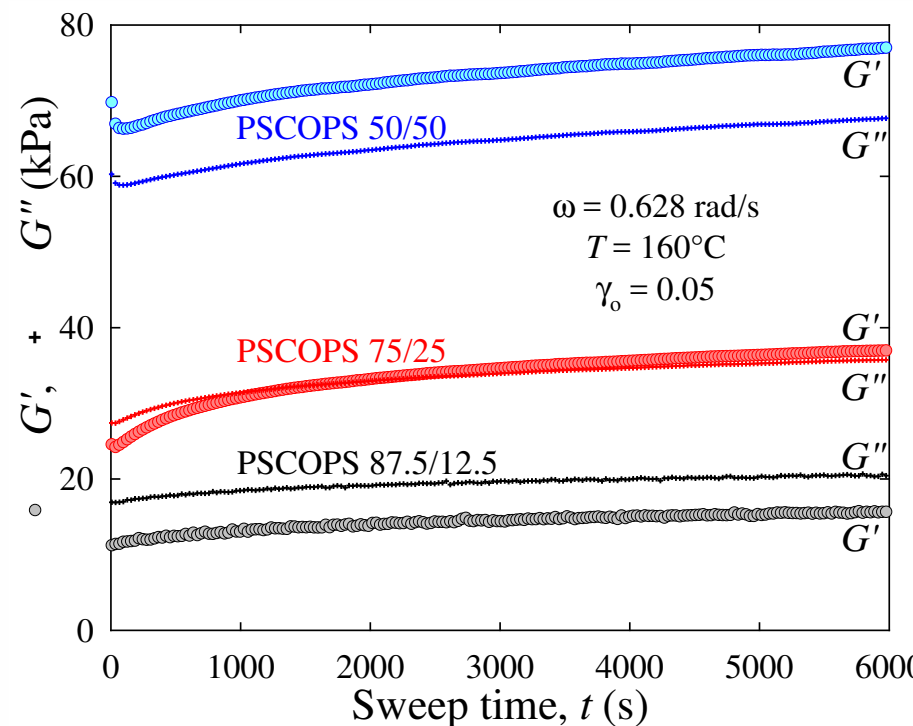
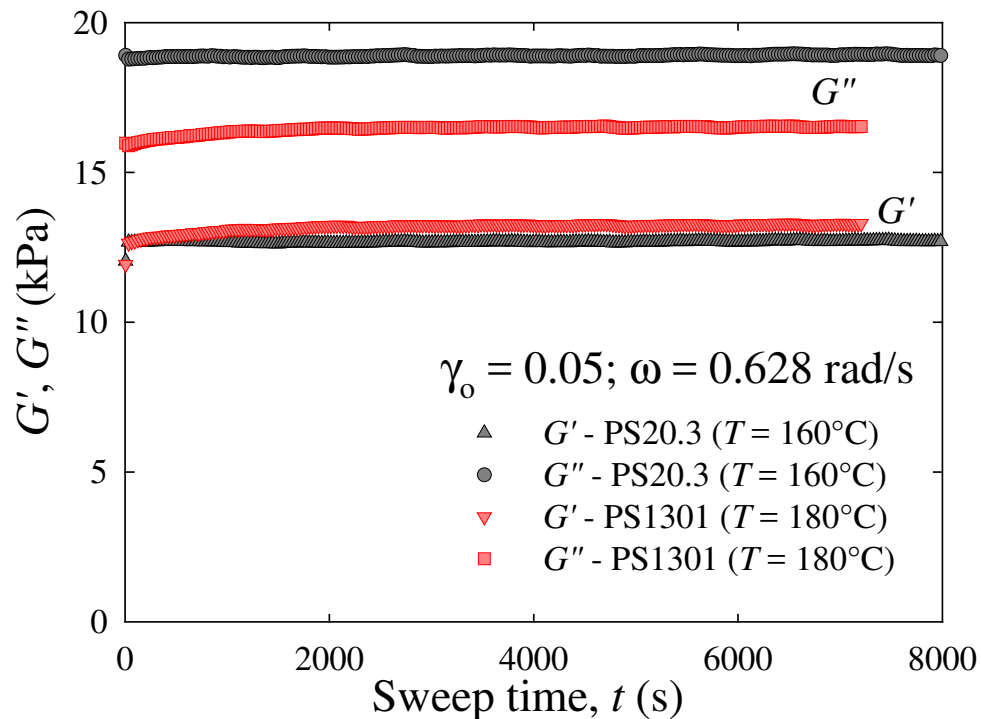
- The peak of loss modulus (T_g) of PS broadening by adding COPS and shifts to lower temperature.
- At low T , two categories can be distinguished, one for COPS ≤ 12.5 -wt% and another one for higher concentrations.
- At high T , the moduli of neat COPS are much higher than those of PS and PS/COPS compounds and show secondary plateaus.

Frequency sweep with DMTA $\omega = 0.0628 - 62.8$ rad/s; $\gamma = 0.0004$ $T = 30 - 170$ °C; $\Delta T = 10$ °C



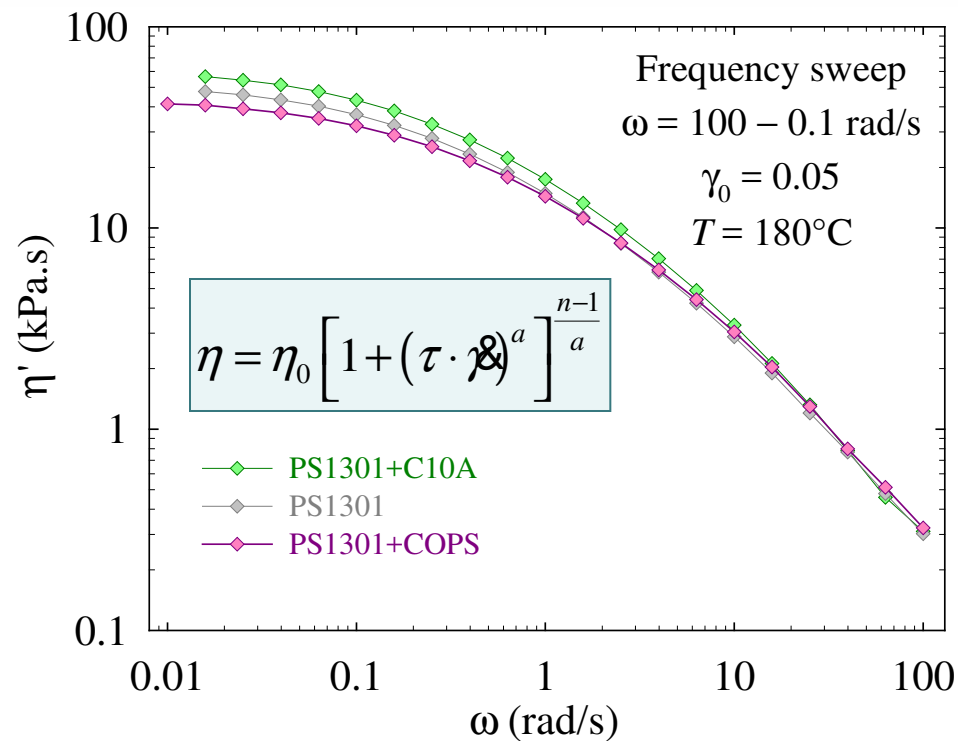
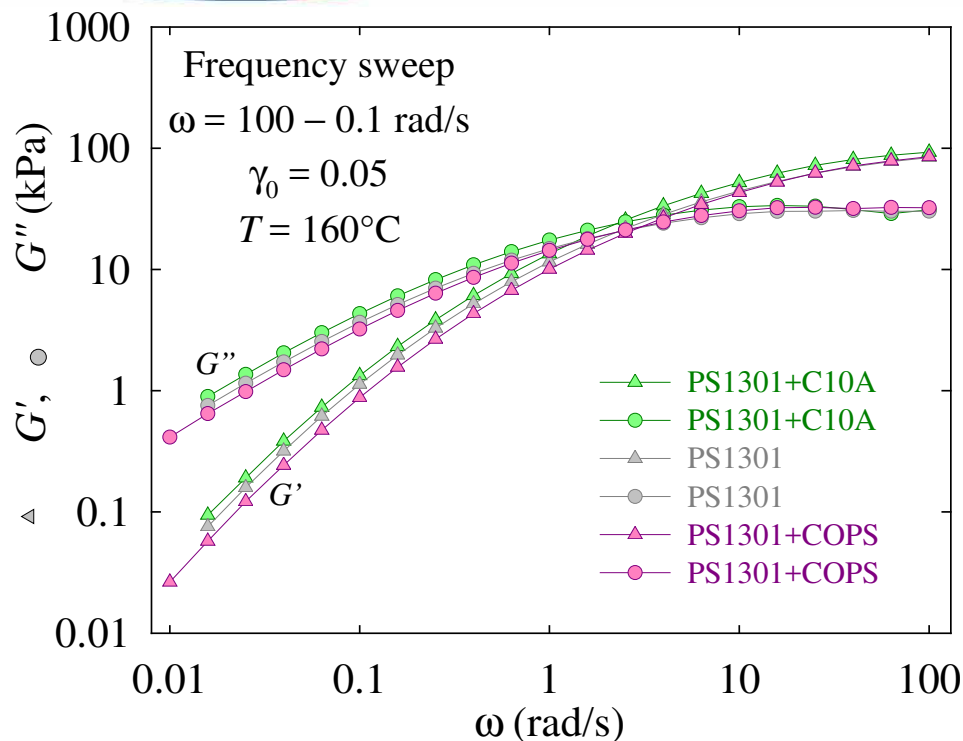
- At high frequency (low T), E' of PS/COPS 50/50 superpose COPS E' .
- At high T ($T > T_g$), the COPS moduli show small peaks, similar to what has been observed for crosslinked systems.
- Considering E'' peaks indicates transitions, the secondary peak may originate in the breakup of the ammonium ion pairs or clusters.

Thermal stability



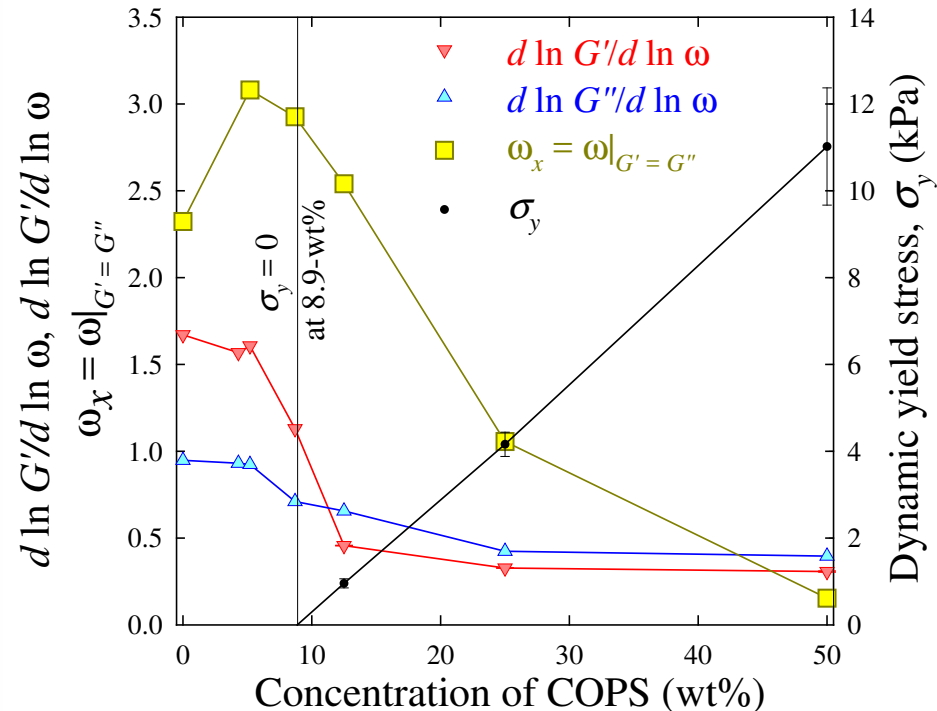
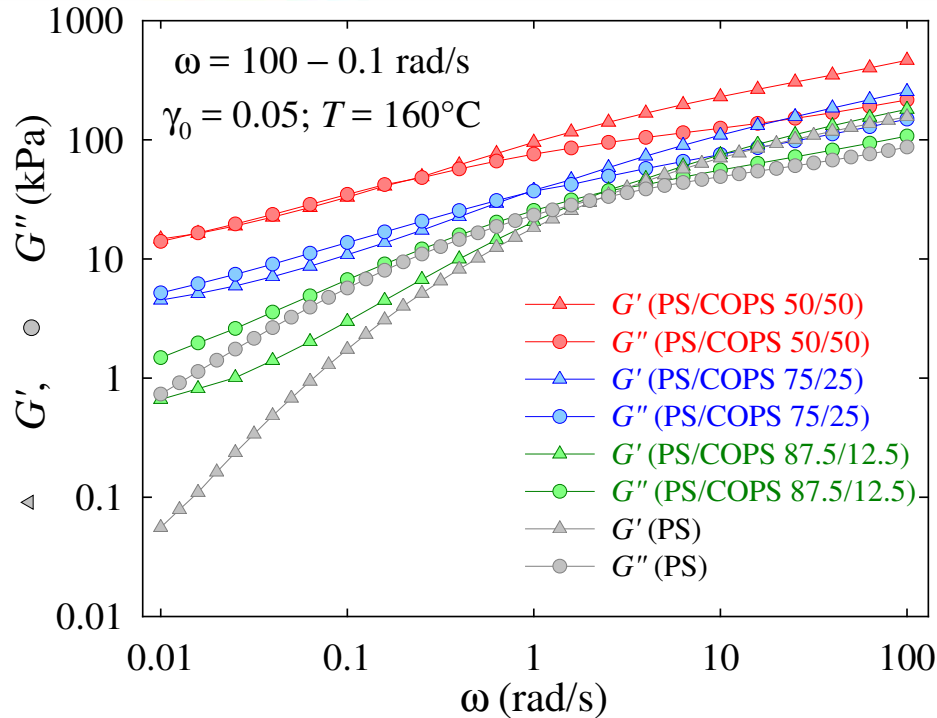
- PS20.3 remains stable during 2 h but the moduli of PS1301 increase by 4.4% ($t < 2000$ s) then remain stable.
- Dynamic shear moduli of PS/COPS increase by 14 – 35% during 6000 s, which can be due to the presence of volatile materials.

Rheological properties of low clay content blends



- Melt structure not affected by the presence of organoclays.
- Absence of G' plateau confirming the XRD and TEM results (not exfoliated COPS).
- Increase of G' and G'' by adding C10A to PS (1.2-wt% MMT) due to presence of solid particles, but their decrease in PS/COPS (1.1-wt% MMT) caused by the presence of extractable oligomers.

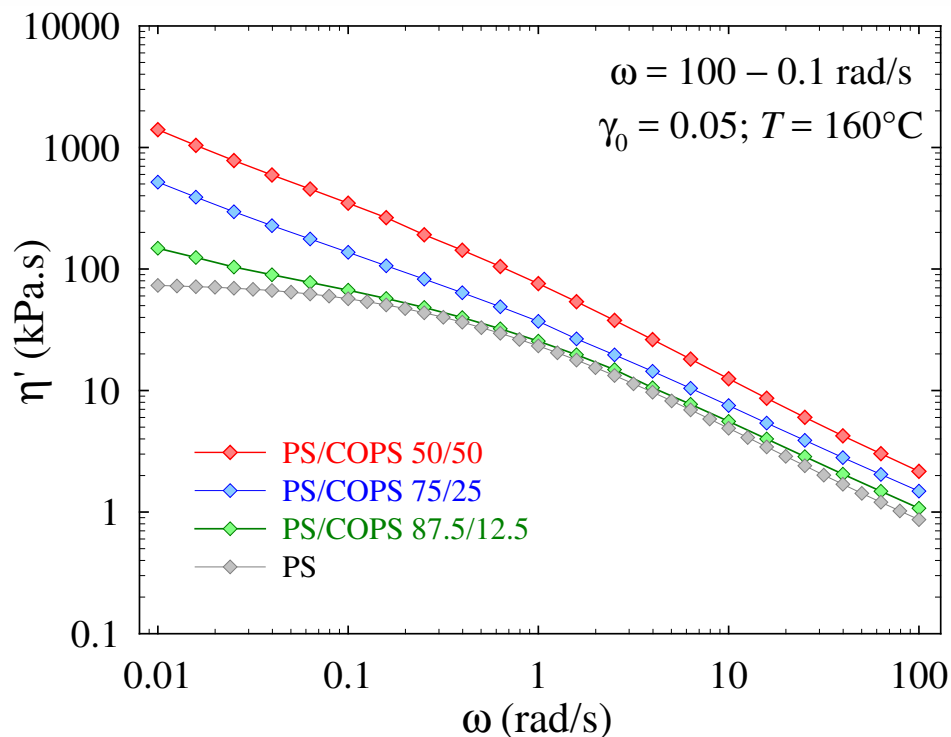
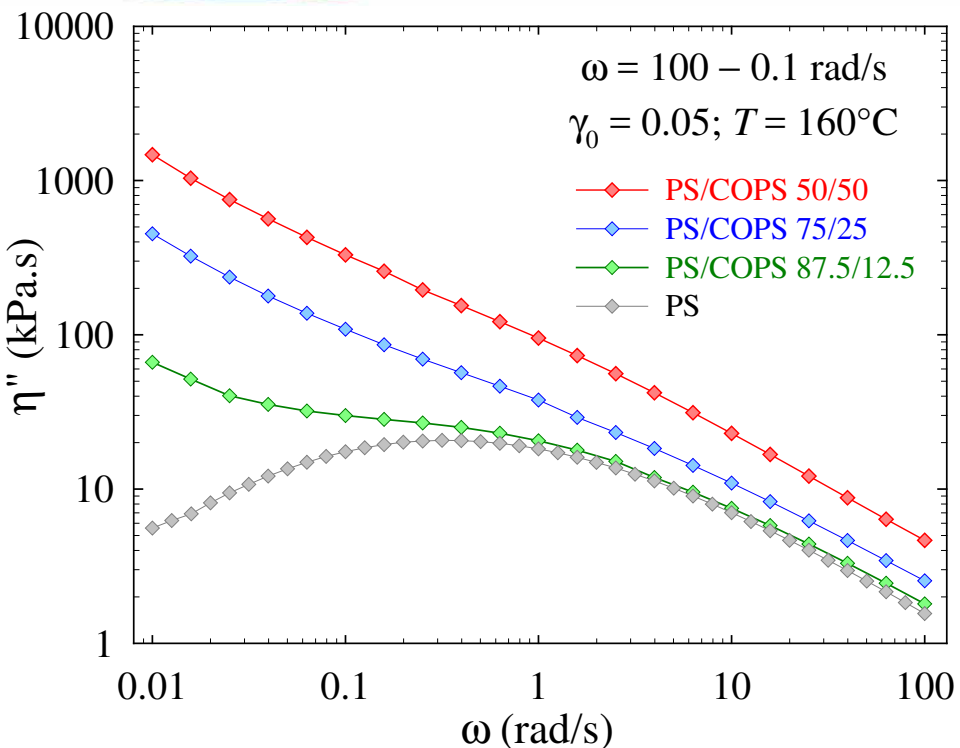
Rheological properties of high clay content blends



- The partially crosslinked COPS domains are expected to be deformable, the the apparent yield stress can be calculated by:
- The extrapolation to zero determines the critical COPS concentration at 8.9-wt%: the percolation threshold, where the soft gel domains interact. $\phi = 0.089 < 0.156$ shows that the domains have $p > 1$.

$$\sigma_y = \sigma_y^0 \left[1 - \exp(-\tau_y \cdot \gamma) \right]^u$$

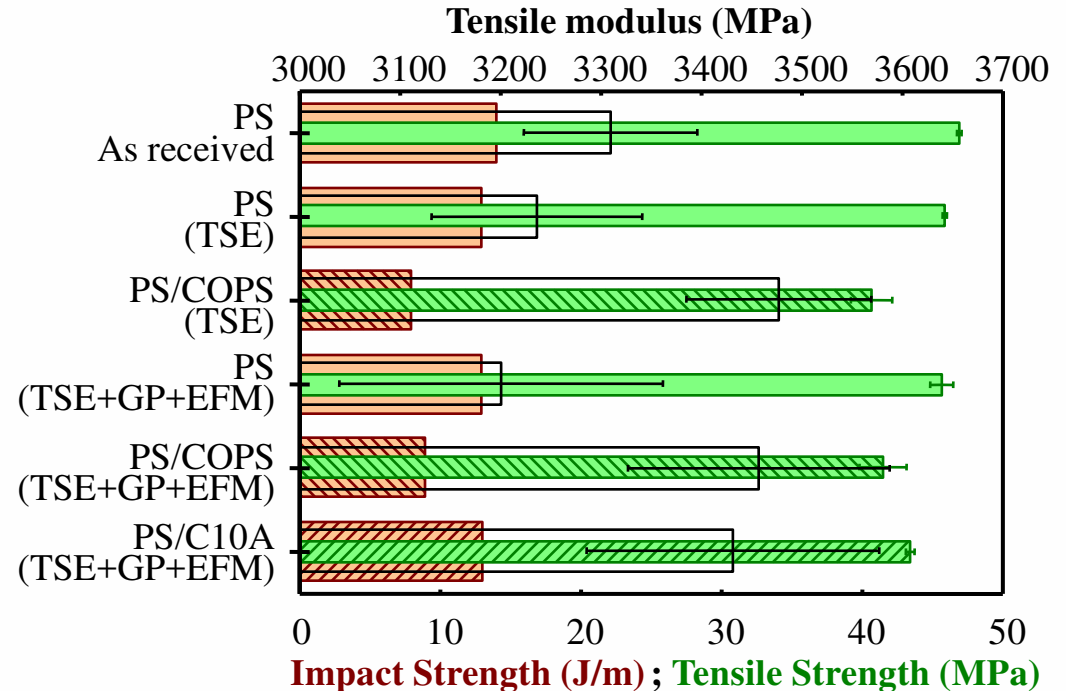
Rheological properties of high clay content blends



- The η' and $G'\omega$ plots vs. frequency make the structural changes of the melt more evident, the elasticity is in the same level of viscous loss.
- The immiscible COPS domains start to interact after the concentration of 8.7-wt% ($\phi_{\text{threshold}} = 8.9\%$).

Mechanical performance

- Reinforced effect restricted to dispersed domains;
- The dispersed domains act as partially solid with low aspect ratio, having low reinforcing effect;
- Plasticating effect of extractable low Mw from COPS.



Specimen	Reference	Δ Tensile strength	Δ Tensile modulus	Δ Flexural strength	Δ Flexural modulus	Δ Impact strength
Error of measurements (%)						
PS (TSE)	PS (as received)	-2.0	-2.2	-0.6	1.1	-7.1
PS (EFM)	PS (as received)	-2.5	-3.2	0.1	1.3	-7.1
PS/COPS (TSE)	PS (TSE)	-11.3	7.4	-37.4	7.3	-38.5
PS/COPS (EFM)	PS (EFM)	-9.1	8.0	-35.3	6.1	-30.8
PS/C10A (EFM)	PS (EFM)	-5.1	7.2	-16.3	3.6	0

$$\Delta(\%) = 100 \left[\frac{Y_{specimen}}{Y_{reference}} - 1 \right]$$

Concluding remarks 1

- COPS organoclay with macromolecular intercalant was prepared in two steps: the free radical copolymerization of styrene with vinyl-ammonium compound followed by Na-MMT intercalation.
- Melt compounding of COPS with PS, instead of exfoliation engendered a two-phase dispersion.
- The co-dissolution method was also unsuccessful.
- The statistic of random copolymerization indicates that a significant proportion of copolymer molecules would have two ammonium groups, statistically capable of bridging the gap between the adjacent clay platelets. The bridging forms clay/oligostyrene network immiscible with PS.

Concluding remarks 2

- The time sweeps indicated an increase of dynamic shear moduli, due to the presence of volatiles in materials containing COPS.
- The incorporation of 2-wt% C10A increased the zero-shear viscosity by 20% but that of 5.2-wt% COPS (same amount of MMT) reduced it by 18%, which can be caused by the presence of extractable oligomers in COPS.
- The addition of 12.5-wt% COPS increased the system elasticity as the same level of viscous loss and the material with 50-wt% COPS behaves in the non-linear VE region. These materials behave like partially crosslinked system.
- At high temperatures $T > T_g$, E' and E'' of COPS show a secondary plateau, similar to what has been seen for crosslinked systems.
- The performance of PS/COPS was slightly inferior of that of PS/C10A.

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