

Effect of Mold Temperature and Additive on Scratch Behavior of TPOs at Elevated Temperatures

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- **Objective**
- **Model Systems**
- **Experimental description**
- **Effect of mold temperature & additive at elevated temperatures**
- **Tribometrics, human observation & LSCM analysis**
- **Effect of heat treatment by scratch testing at cooled back RT**
- **Summary**

- Two sets of model systems from **Advanced Composites**:
 - TPO containing 20% talc without scratch additive (TPO)
 - TPO containing 20% talc with scratch additive (TPO-A)
- Each material has 1% carbon black pigment
- Each model system was molded with mold temperatures at 40°C, 50°C, and 60°C

Crystallinity analysis (WAXD)

- Additive Effect: TPO vs. TPO-A
- Measurement incident angle 0.5°
- Crystallinity of the top 100 nm of the surface

Model system \ Mold temp.	Crystallinity (%)		
	40°C	50°C	60°C
TPO	46.8	50.3	52.1
TPO-A	42.4	48.3	51.4



*XRD equipment Bruker
D8 Discover

Interior temperature profile in automobile

➤ Experiment place: Arizona in June under shade & sun condition for 1 hr

Table 1. Heating trial (start and end times) by car type, day, and time, aligned with final surface temperature (T_{sf}) and cabin air temperature (T_{ac}) conditions in sun and shade.

Vehicle	Date	T_a (°C)	Trial	Time Start	Time End	SHADE				SUN						
						Final Interior Temperatures (°C)				Trial	Time Start	Time End	Final Interior Temperatures (°C)			
						Car T_{ac}	Dashboard T_{sf}	Wheel T_{sf}	Seat T_{sf}				Car T_{ac}	Dashboard T_{sf}	Wheel T_{sf}	Seat T_{sf}
Midsize Sedan	Jun-25	37.2	B	11:00	11:55	43.2	60.0	44.4	46.1	B	11:05	12:00	48.9	85.0	59.4	62.8
		41.5	C	12:30	13:25	42.0	76.1	48.9	45.6	C	13:00	14:00	49.5	76.1	61.1	60.0
		41.0	D	13:45	14:45	42.5	51.1	46.7	44.4	D	14:20	15:20	47.4	73.9	56.1	63.3
		40.8	E	15:05	16:00	39.9	42.8	42.8	42.8							
	Jun-26	32.8	A	10:20	11:20	35.3	41.1	37.8	37.8	A	10:00	11:00	40.2	76.1	47.2	56.1
		36.6	B	11:35	12:35	41.6	41.7	42.8	43.3	B	11:15	12:15	49.5	82.8	54.4	53.9
		38.0	C	13:00	14:00	39.9	40.0	40.6	42.2	C	12:40	13:35	48.7	54.4	56.1	52.2
		39.5	D	14:20	15:20	38.4	37.8	37.2	37.2	D	13:50	14:50	49.8	55.6	54.4	53.3
	Jul-11	36.3	A	9:40	10:40	37.6	39.6	37.3	37.0	A	9:45	10:45	45.5	76.1	53.3	51.1
		37.4	B	10:50	11:50	39.4	50.8	42.2	41.5	B	11:00	12:00	50.1	82.2	53.9	46.1
		38.4	C	12:10	13:10	40.9	62.2	43.9	40.6	C	12:30	13:30	51.3	82.2	75.0	51.1
		40.0	D	13:40	14:40	40.4	42.9	40.3	39.6	D	14:00	15:00	51.8	76.7	52.2	51.7
	Jun-25	40.3	E	14:50	15:50	41.1	44.3	41.0	39.0	E	15:20	16:20	51.4	63.9	55.6	45.6
		37.2	B	10:55	11:55	39.4	43.3	42.2	43.9	B	11:00	12:00	45.6	51.7	51.1	55.0
		41.5	C	12:30	13:30	38.9	56.1	43.3	43.9	C	12:50	13:50	45.7	54.4	56.7	55.6
		41.0	D	14:00	15:00	38.4	45.6	46.1	44.4	D	14:25	15:25	45.7	80.6	59.4	62.2
		40.8	E	15:20	16:20	41.4	43.3	43.9	43.9							
Economy Car	Jun-25	36.0	A	10:05	11:05	42.6	58.9	45.0	44.4							
		41.5	C	12:35	13:35	42.2	47.2	48.9	47.8	C	13:10	14:10	49.7	80.6	60.6	56.1
		41.0	D	14:05	15:00	41.2	47.8	45.6	45.0	D	14:50	15:40	45.6	54.4	58.3	53.3
		40.8	E	15:20	16:20	38.3	45.0	43.9	43.3	E	15:55	16:45	51.4	63.3	53.9	50.6
	Jun-26	36.6	B	10:20	11:20	39.7	68.9	38.3	41.1	B	9:55	10:55	45.4	46.7	49.4	48.9
		38.0	C	11:40	12:40	39.0	38.9	44.4	40.6	C	11:20	12:20	46.8	51.7	54.4	50.6
		39.5	D	12:50	13:50	40.5	42.2	42.8	41.7	D	12:50	13:30	47.5	78.3	56.7	58.9
		39.7	E	14:30	15:25	40.8	40.6	40.6	41.1	E	13:50	14:50	48.8	70.0	55.0	60.6
	Jul-11	36.3	A	9:40	10:40	36.5	40.6	37.8	37.2	A	9:35	10:35	42.5	79.4	53.9	53.3
		37.4	B	10:50	11:50	34.7	45.6	40.6	40.0	B	10:55	11:55	47.5	82.2	78.9	55.0
		38.4	C	12:05	13:05	38.1	61.1	43.3	40.0	C	12:20	13:20	49.2	81.1	76.1	52.2
		40.0	D	13:35	14:35	37.8	58.3	41.1	41.1	D	13:50	14:50	49.8	79.4	52.2	53.3
		40.3	E	14:55	15:55	38.9	45.0	41.1	41.7	E	15:30	16:30	46.0	63.3	54.4	52.2

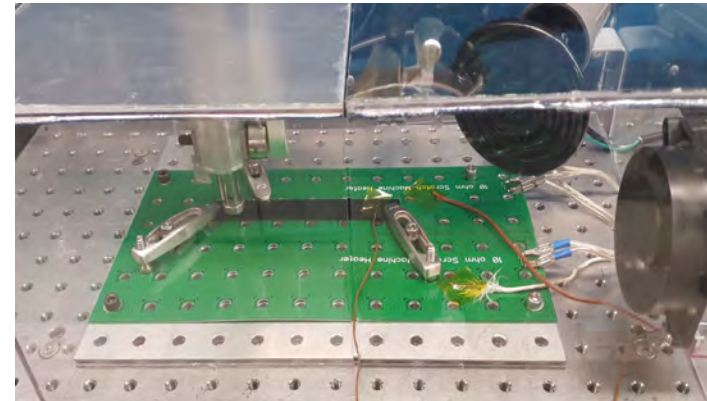
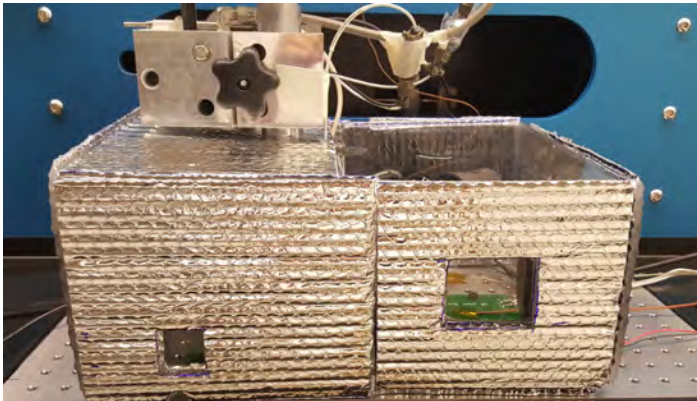
T_a : Ambient (outdoor) air temperature (°C); T_{ac} : Cabin air temperature (°C), T_{sf} : Surface temperature (°C)

Experimental – Scratch test

- 1 mm diameter stainless steel ball tip
- Normal load range: 2-50 N
- Scratch length: 100 mm
- Scratching speed:
 - 100 mm/s
- Three scratch tests per sample
- Testing temperatures @ 25 °C, 50 °C and 75 °C, and then back to 25 °C



1 mm diameter
stainless steel ball tip



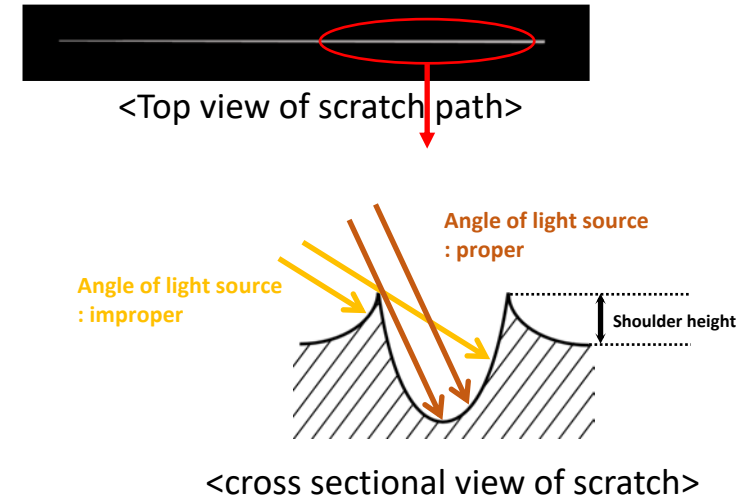
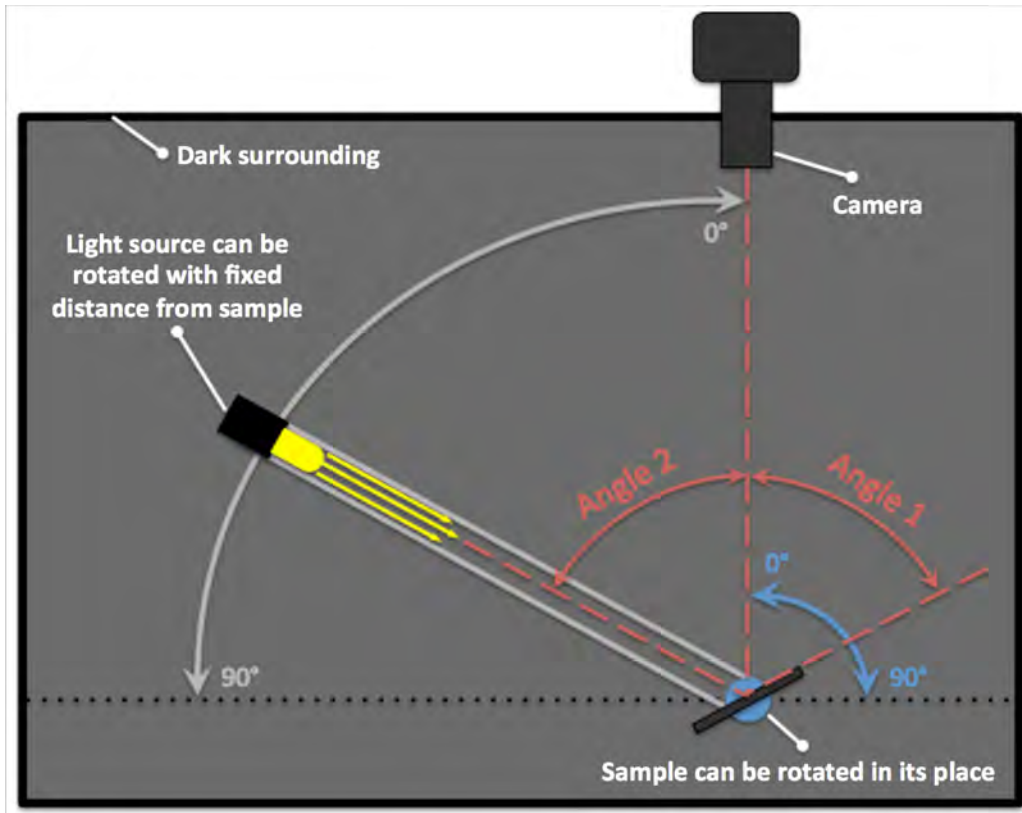
Chamber & equipment parts to elevate environmental temperature

Effect of mold temperature & additive at elevated test temperature

Experimental – Imaging Procedure

➤ Scratch Imaging and Analysis Procedure

- **Angle 1:** between camera and sample surface was 55°
- **Angle 2:** between camera and light source was 5°

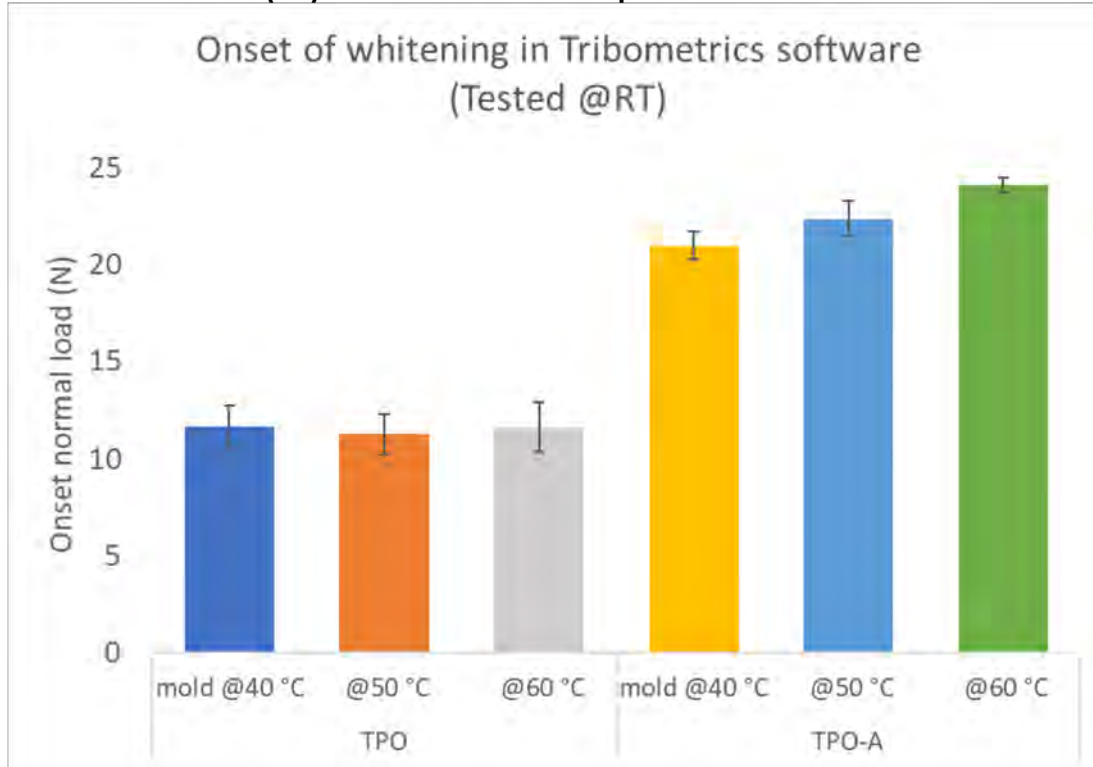


- The angles were chosen at 5° and 55° because the shoulder height is so high when tested @ 75°C .

- The captured images were analyzed with **Tribometrics** software package
- The method used was standard method (contrast: 3 %, continuity: 90 %)

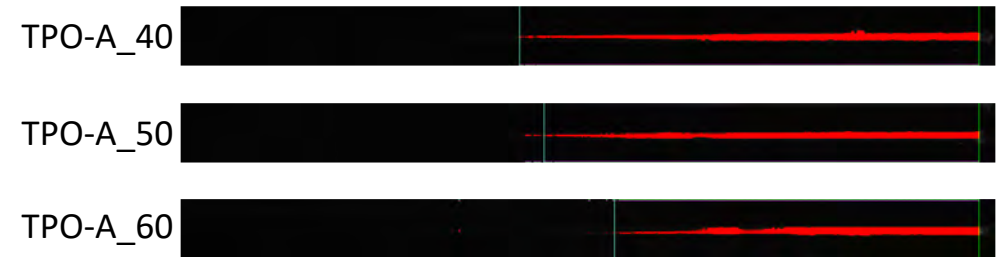
Scratch Testing @ RT (25 °C)

➤ Onset load (N) results on samples



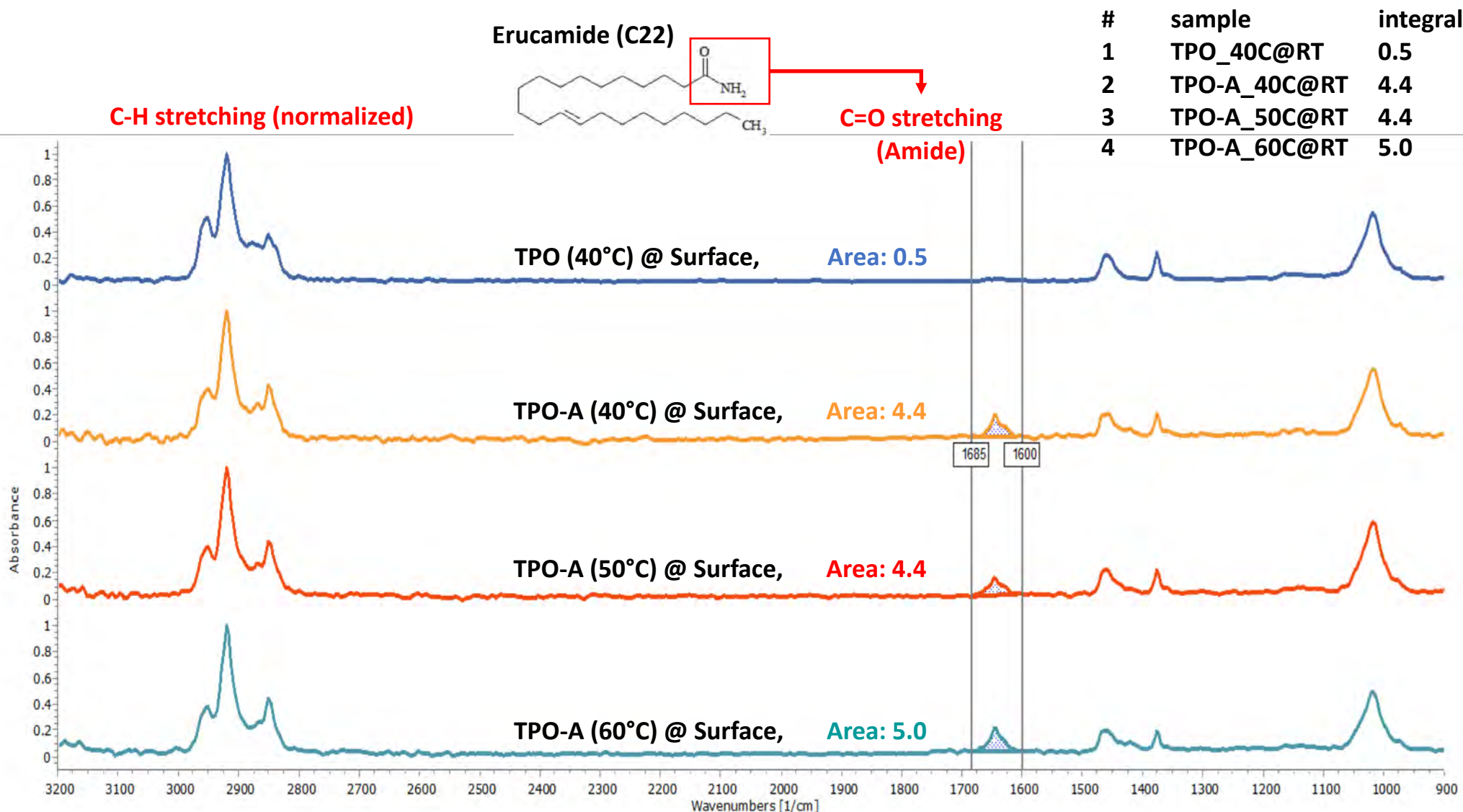
- In TPO, mold temperature effect is subtle.
- In TPO-A, mold temperature effect is more pronounced.
- Comparing TPO vs TPO-A, additive is effective, especially when molded @ 60 °C and tested at RT.

➤ Image analysis results of onset load (N) in Tribometrics software



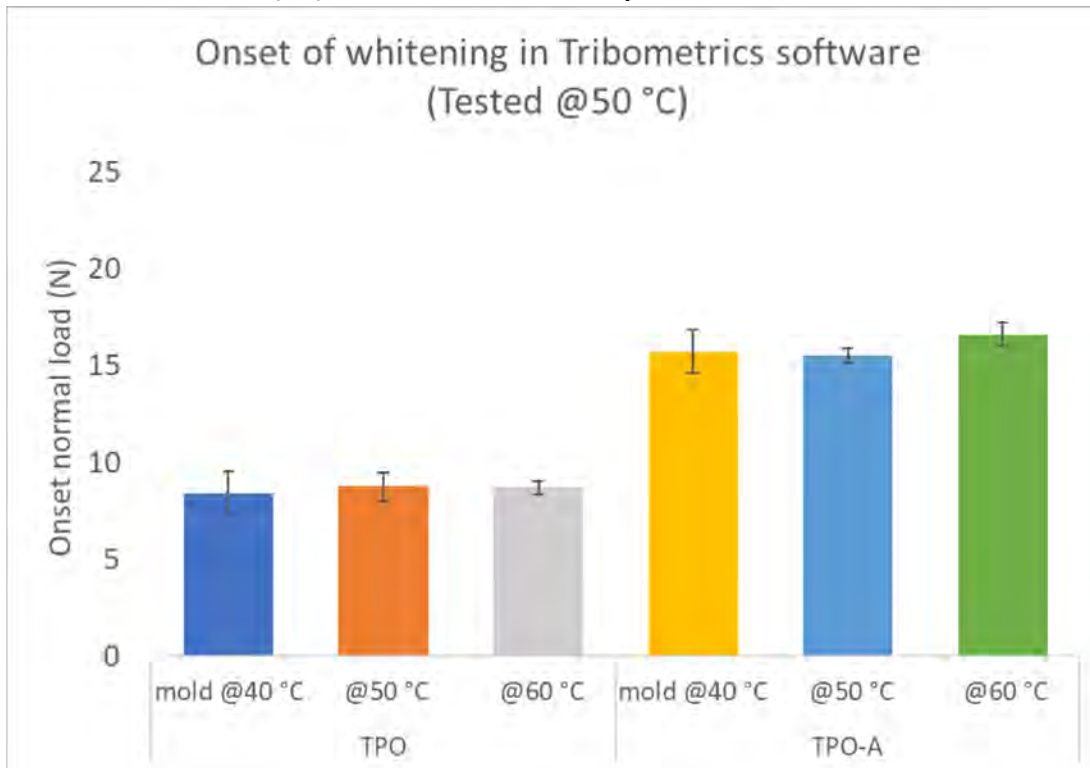
Mold temperature effect on additive (FTIR)

- Increase in mold temperature leads to migration of additive to the surface more readily



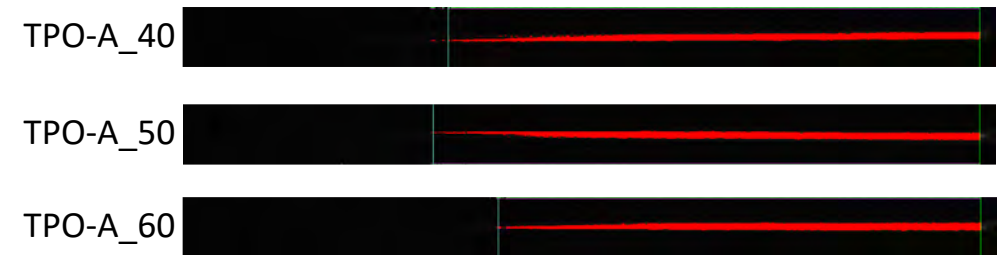
Scratch Testing @ 50 °C

➤ Onset load (N) results on samples



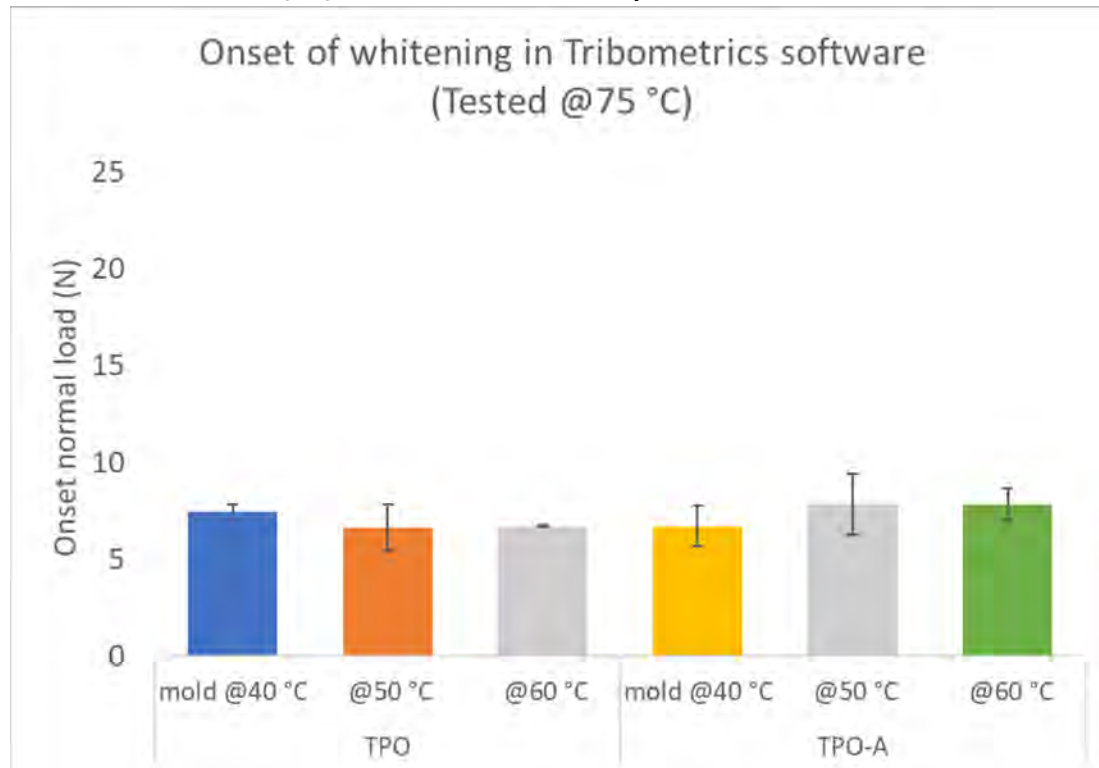
- In TPO, mold temperature effect is subtle.
- In TPO-A, mold temperature effect is also subtle.
- Comparing TPO vs TPO-A, additive is still effective when tested at 50 °C.

➤ Image analysis results of onset load (N) in Tribometrics software



Scratch Testing @ 75 °C

➤ Onset load (N) results on samples

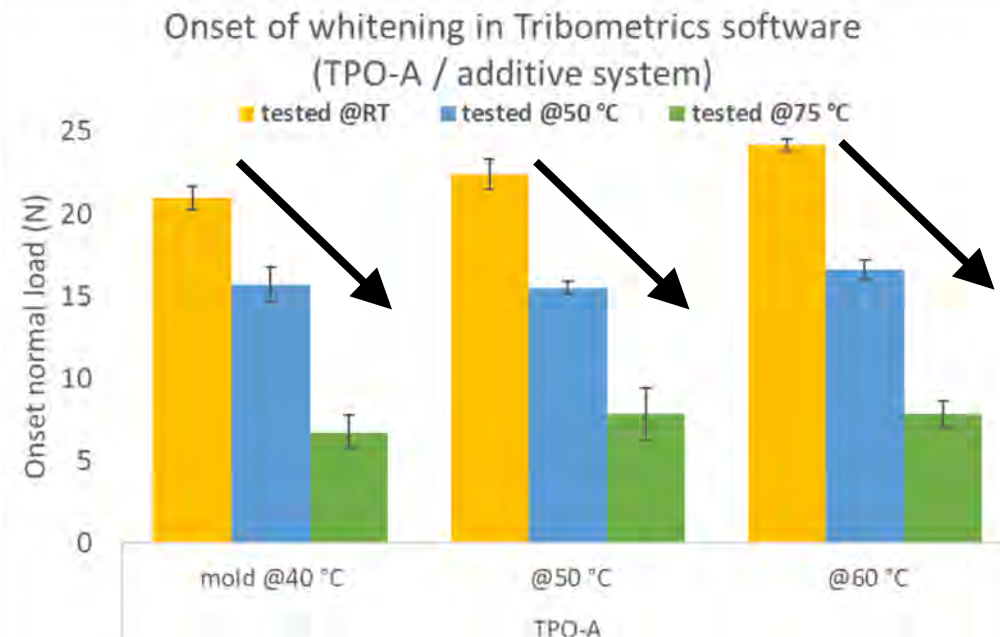
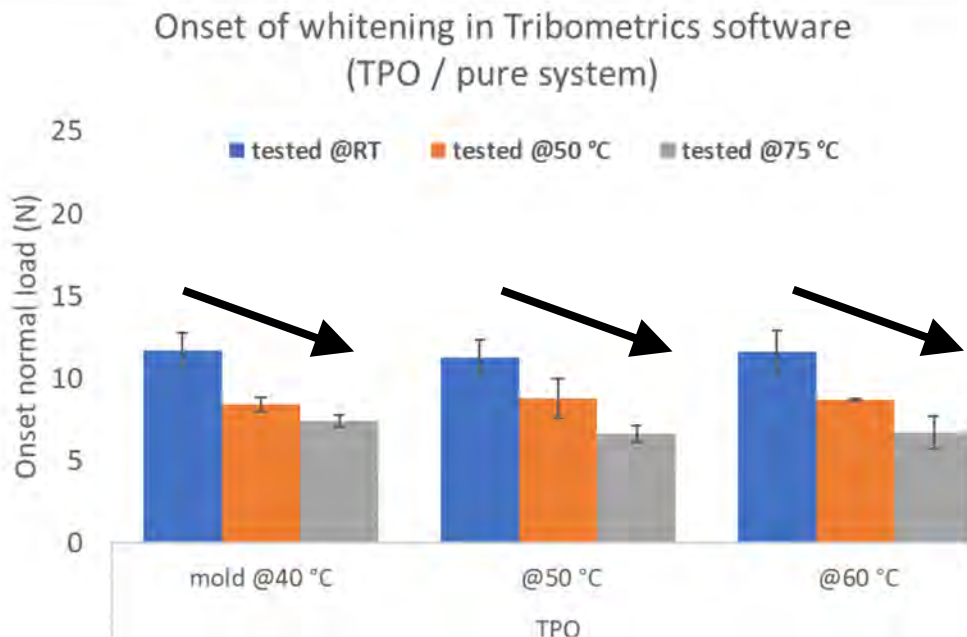


- There is no mold temperature effect.
- Additive is no longer effective.
- Both TPO & TPO-A have severe scratch damage onset.

➤ Image analysis results of onset load (N) in Tribometrics software



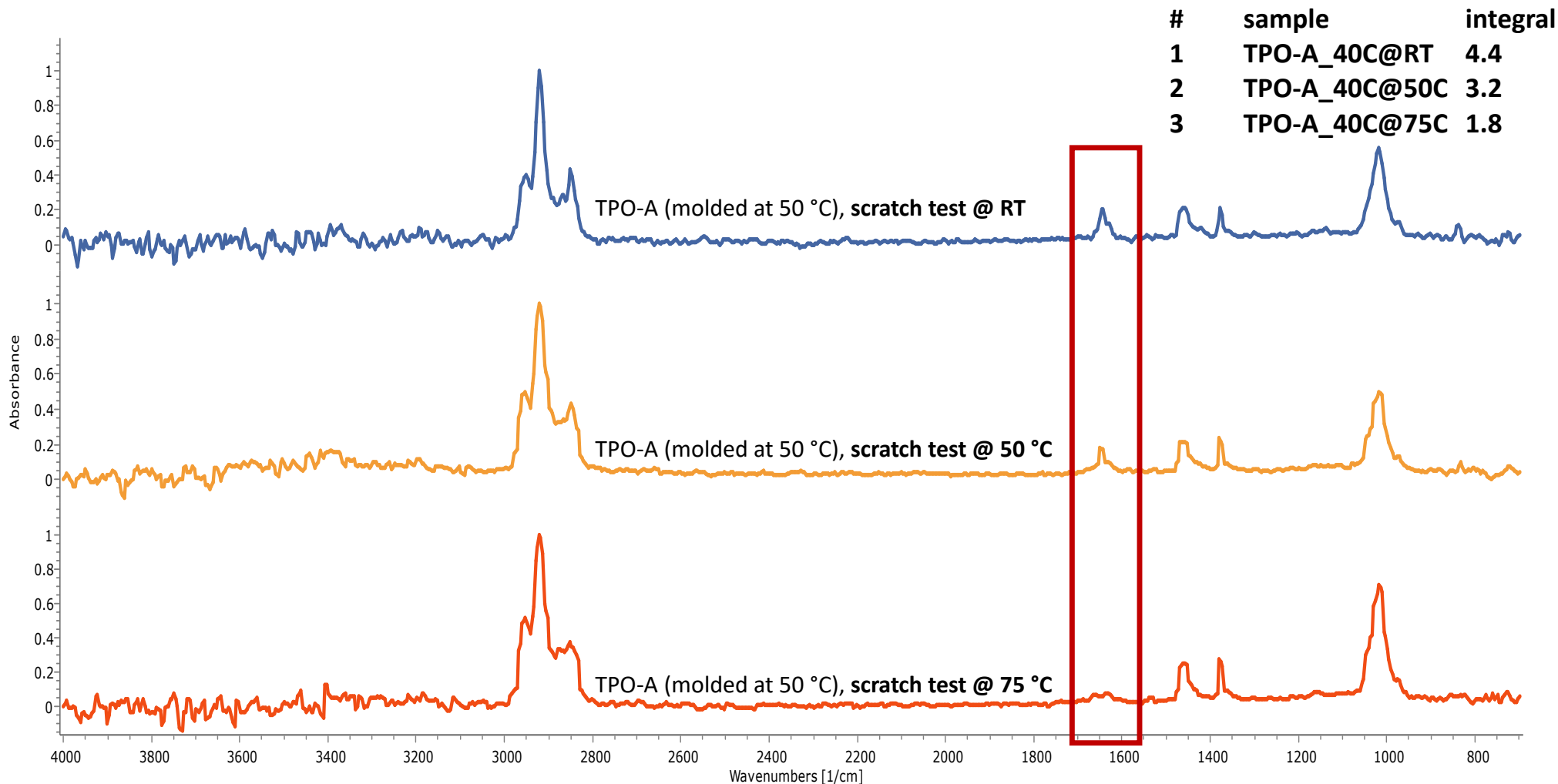
Effect of testing temperature



- As the testing temperature increases from RT to 50 °C and 75 °C, the onset of whitening takes place earlier and more readily.

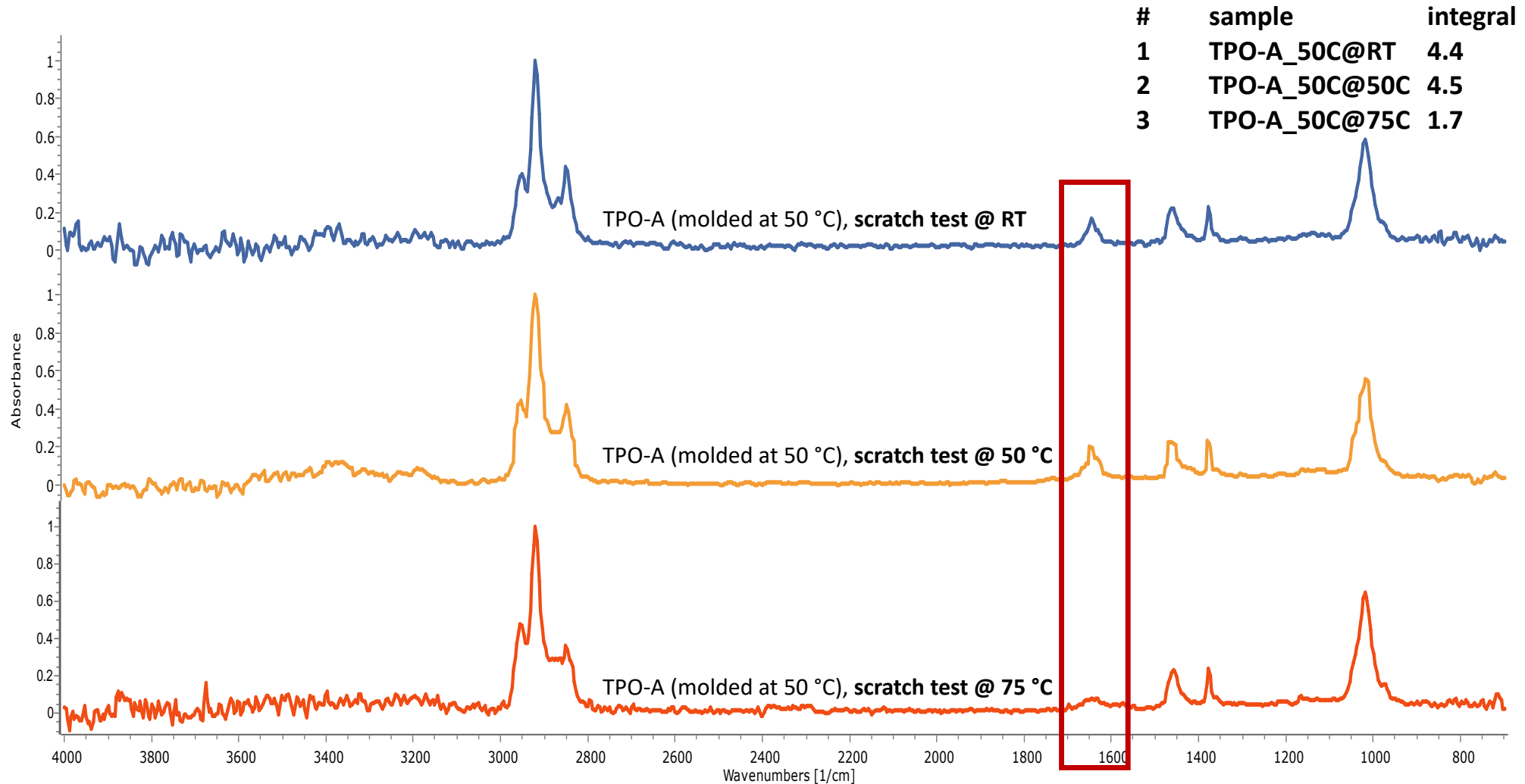
Elevated testing temperature effect

- **FTIR** (To determine the concentration of additive on the undamaged surface after scratch test)
- **TPO-A at 40 °C mold temperature**
- As the testing temperature goes up, the amount of additive decreases on the surface.



Elevated testing temperature effect

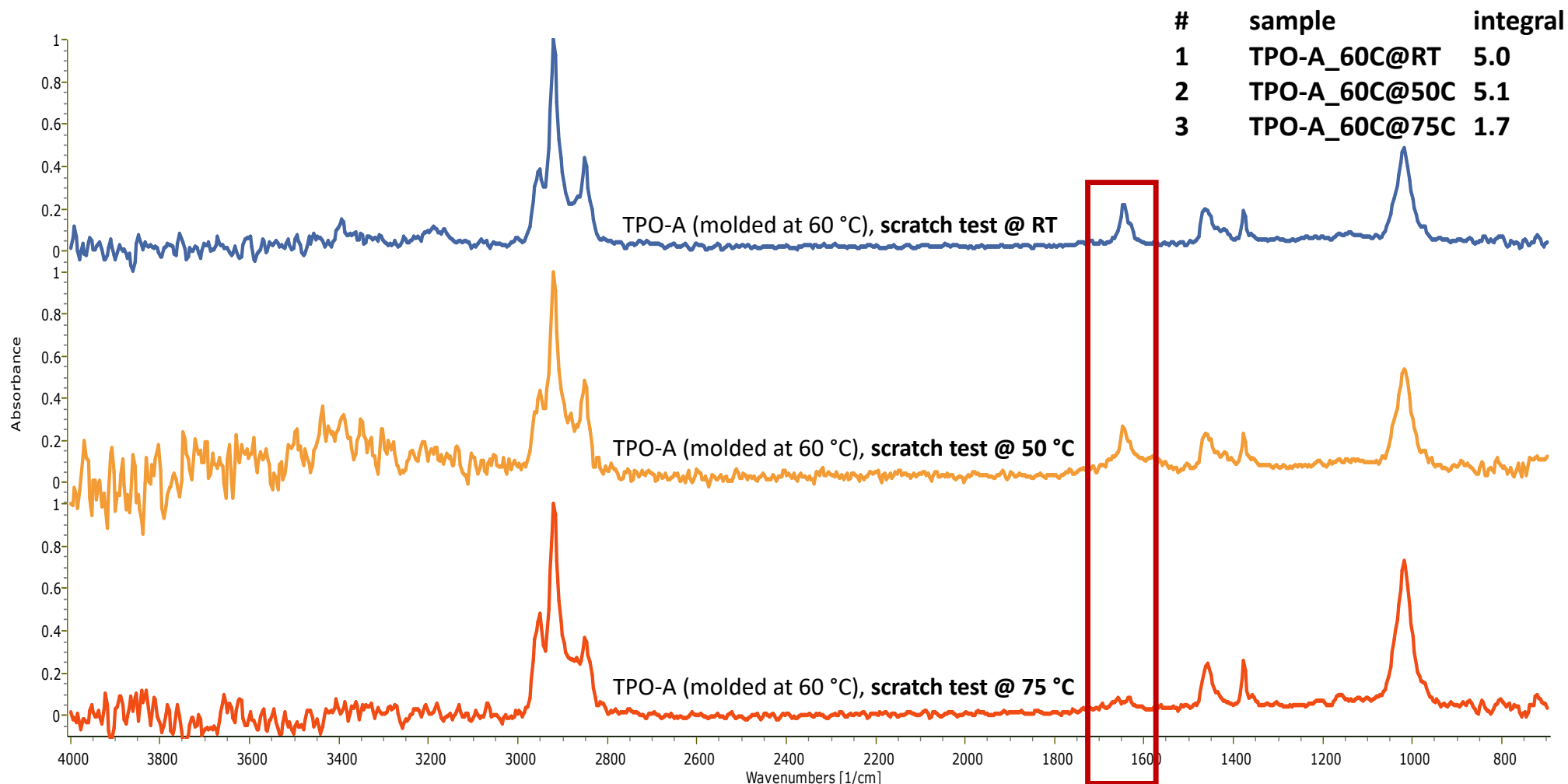
- TPO-A at 50 °C mold temperature
- As environmental temperature goes up, the amount of additive decreases on the surface



Elevated testing temperature effect

➤ TPO-A at 60 °C mold temperature

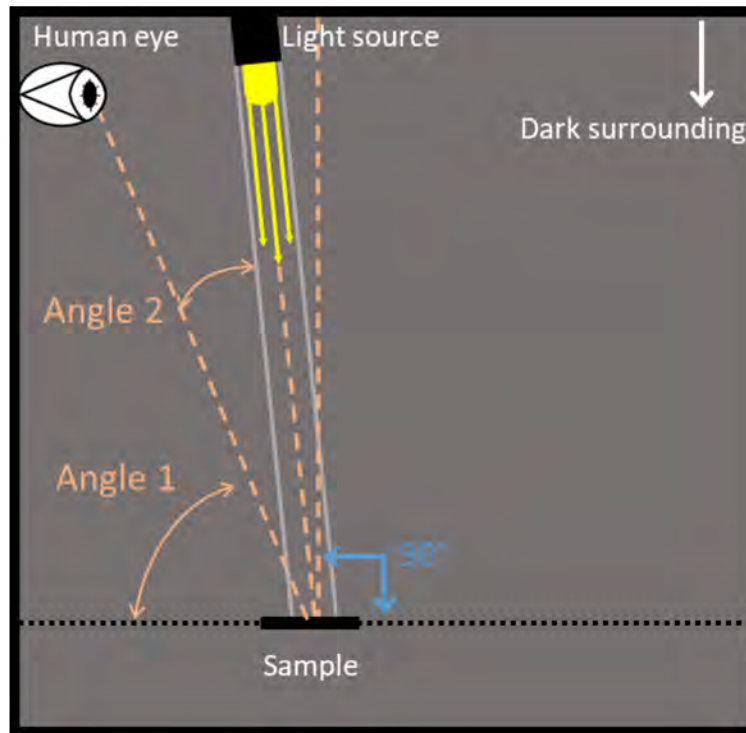
➤ As environmental temperature goes up, the amount of additive decreases on the surface.



Human assessment on onset of whitening

Experimental – human assessment

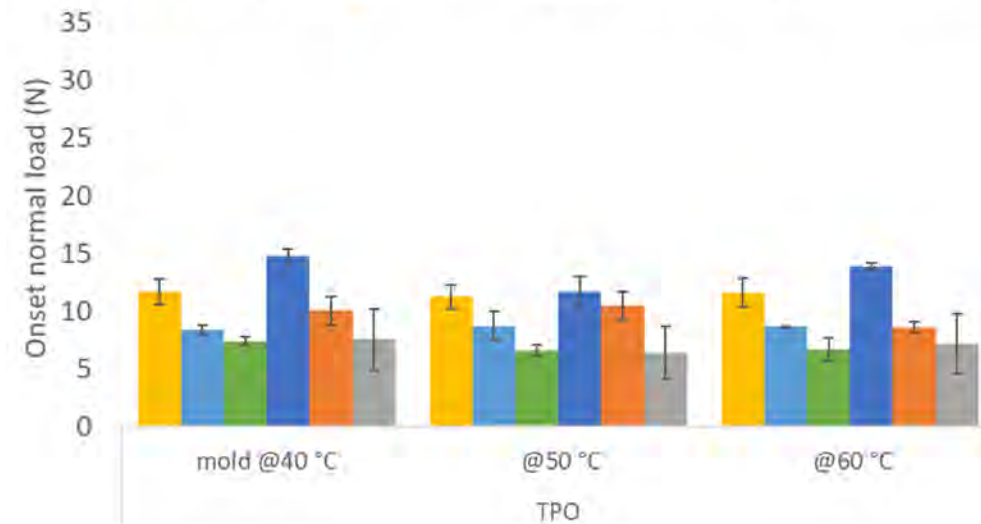
- To mimic the same environment of light diffraction with tribometrics analysis in black box, the angles were chosen as below.
 - **Angle 1:** between human eye and sample surface was 55°
 - **Angle 2:** between human eye and light source was 5°



- Four human observers measured the onset point of the whitening for each sample, then the distance was converted into the onset normal load.
- An average of four datapoints was reported as the onset of whitening for the human observation

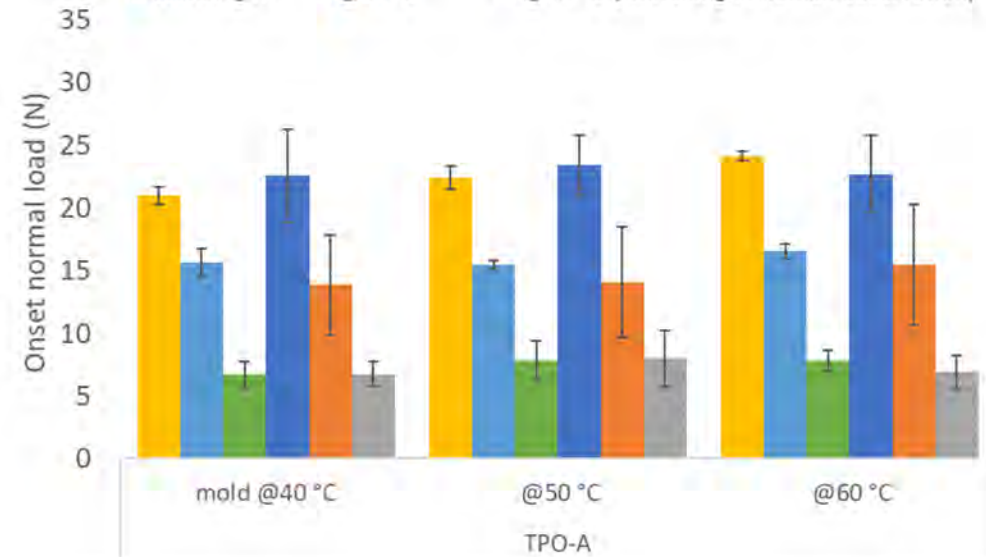
Onset of whitening in tribometrics & human observation
(TPO / pure system)

■ tested @RT ■ @50 °C ■ @75 °C (whitening in tribometrics)
■ tested @RT ■ @50 °C ■ @75 °C (whitening in human observation)



Onset of whitening in tribometrics & human observation
(TPO-A / additive system)

■ tested @RT ■ @50 °C ■ @75 °C (whitening in tribometrics)
■ tested @RT ■ @50 °C ■ @75 °C (whitening in human observation)



- The onsets of whitening between tribometrics analysis and human observation seem consistent.

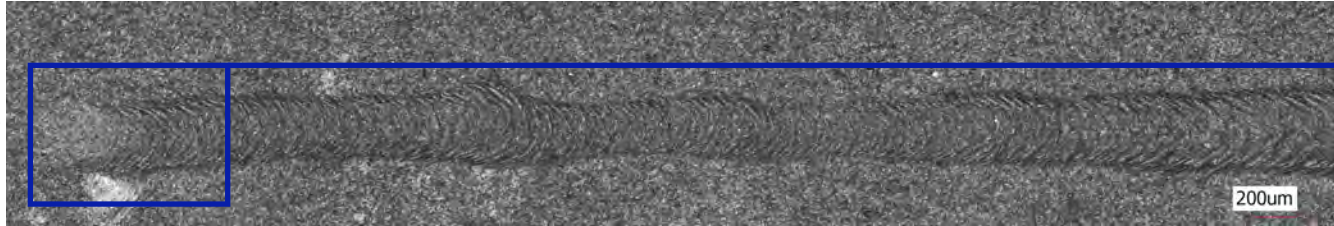
Observation of damage transitions using LSCM

Surface analysis using LSCM



➤ Surface analysis using A high-resolution KEYENCE VK-9700K laser scanning confocal microscope (LSCM)

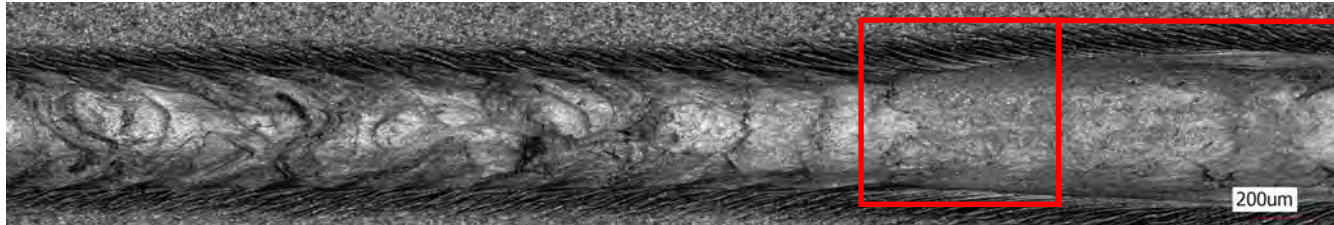
Onset: ~ 2 N



TPO tested @ RT
(molded @ 40 °C)

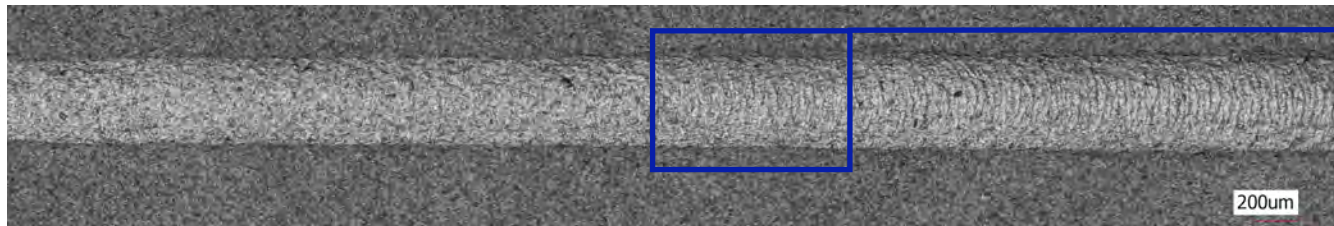


Onset: ~ 20.9 N



Transition 1
(fish-scale)

Onset: ~ 8.7 N



TPO-A tested @ RT
(molded @ 40 °C)



Onset: ~ 26.1 N



Transition 2
(plowing)

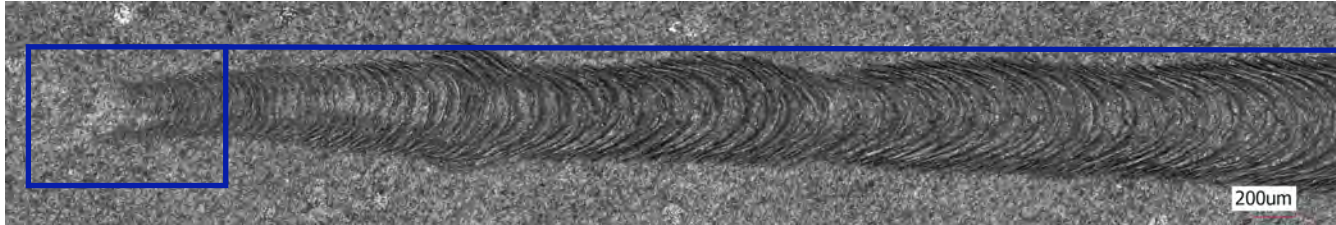
- Other TPO & TPO-A molded at different temperature but tested at same (RT) show a similar transition feature.

Surface analysis using LSCM



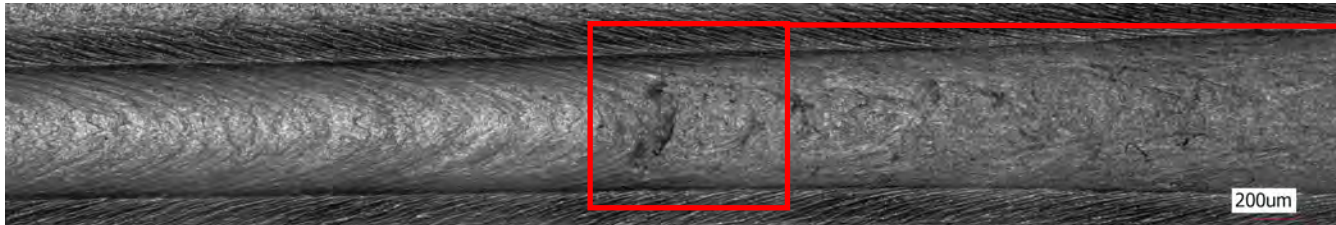
- Surface analysis using A high-resolution KEYENCE VK-9700K laser scanning confocal microscope (LSCM)

Onset: ~ 2 N



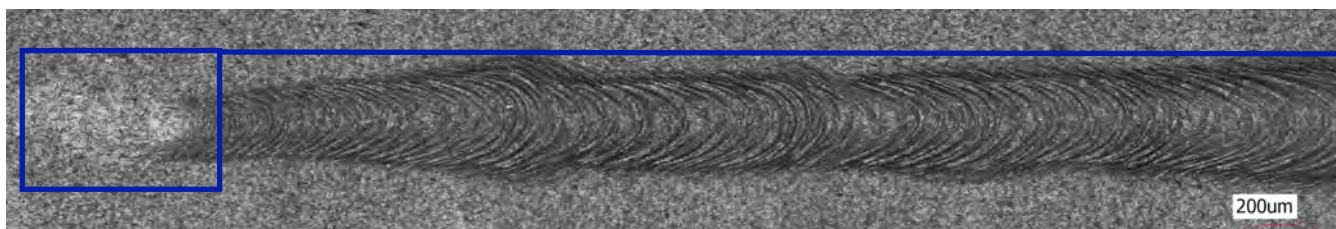
TPO tested @ 75 °C
(molded @ 40 °C)

Onset: ~ 12.1 N



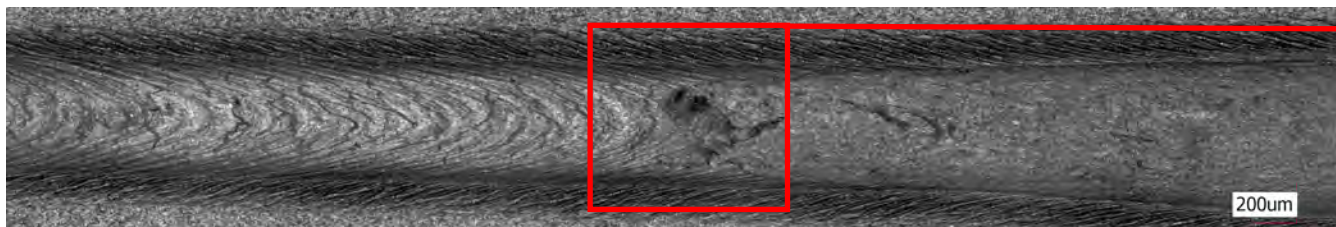
Transition 1
(fish-scale)

Onset: ~2 N



TPO-A tested @ 75 °C
(molded @ 40 °C)

Onset: ~ 11.9 N

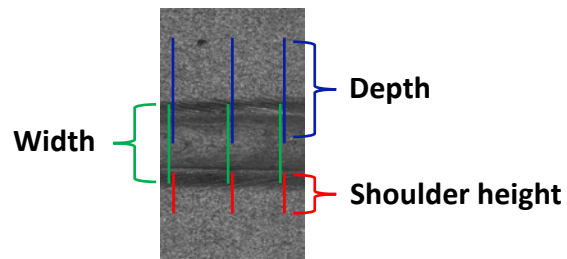
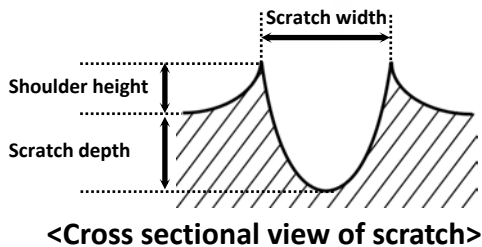
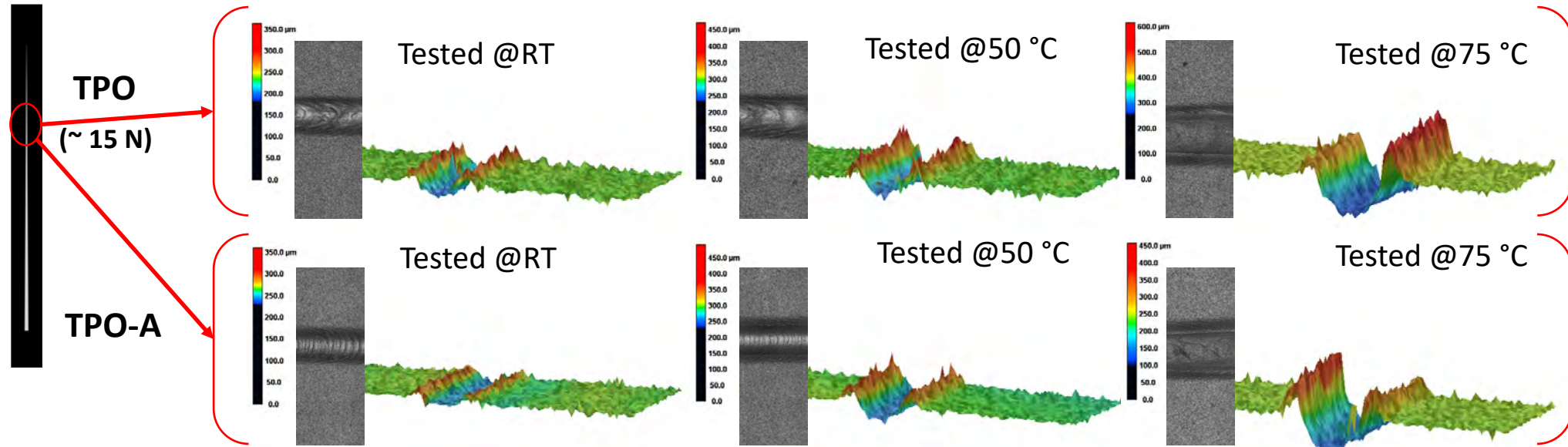


Transition 2
(plowing)

- Other TPO & TPO-A molded at different temperature but tested at same (75 °C) have similar transition phenomena nothing but their different location.

Surface analysis using LSCM (3D)

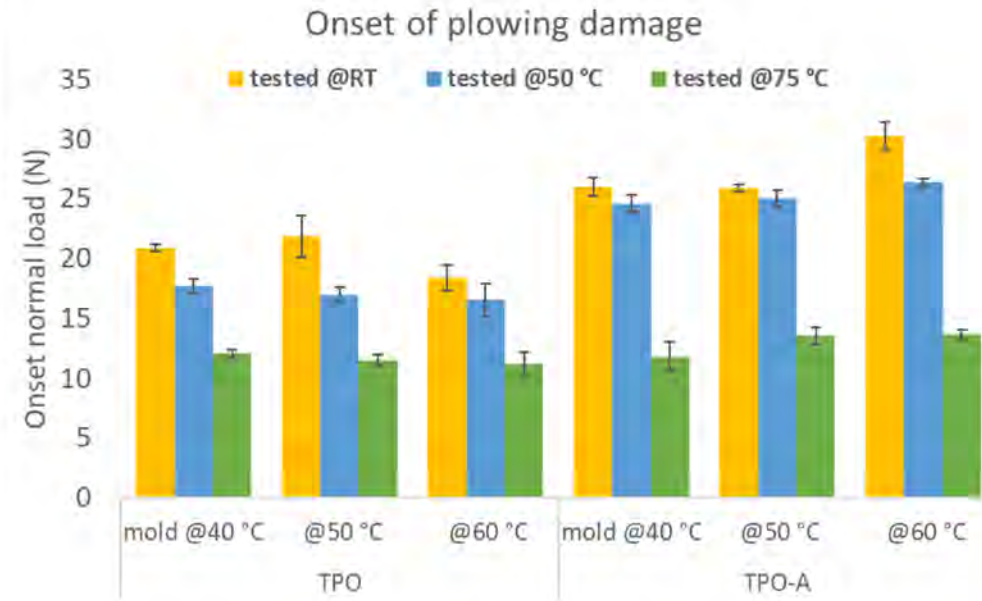
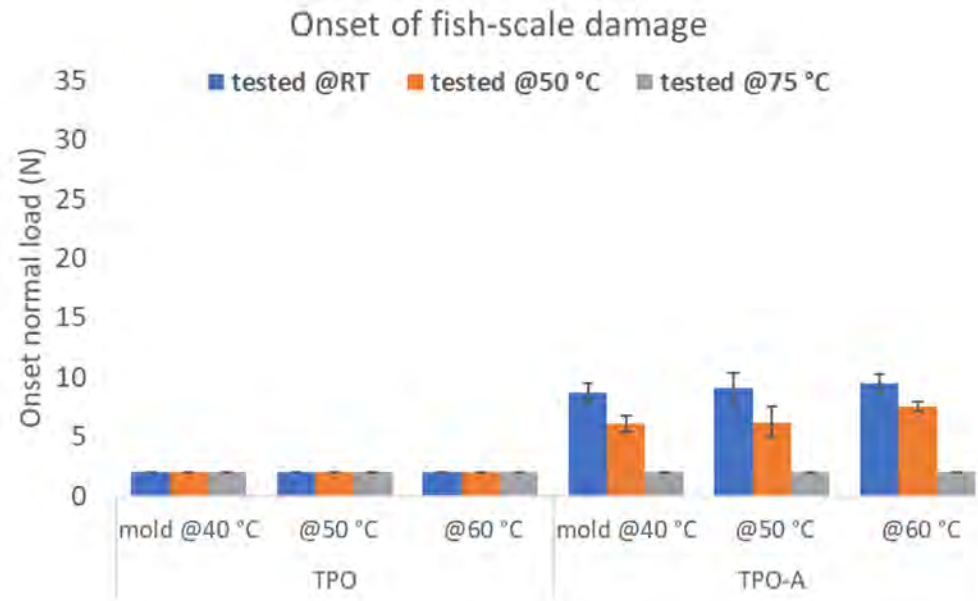
- 3D profiles of the position at ~ 15 N for TPO & TPO-A (molded at 40 °C) at different testing temperature



Sample	TPO			TPO-A		
Test temp.	RT	50 °C	75 °C	RT	50 °C	75 °C
Shoulder (μm)	65	142	313	45	110	239
Depth (μm)	-	-	135	-	-	112
Width (μm)	607	660	861	551	622	840

- Each value is the average of three data points measured in different positions.
- Measuring depth at RT & 50 °C has huge fluctuations due to fish scales.

The onset of fish-scale & plowing damage

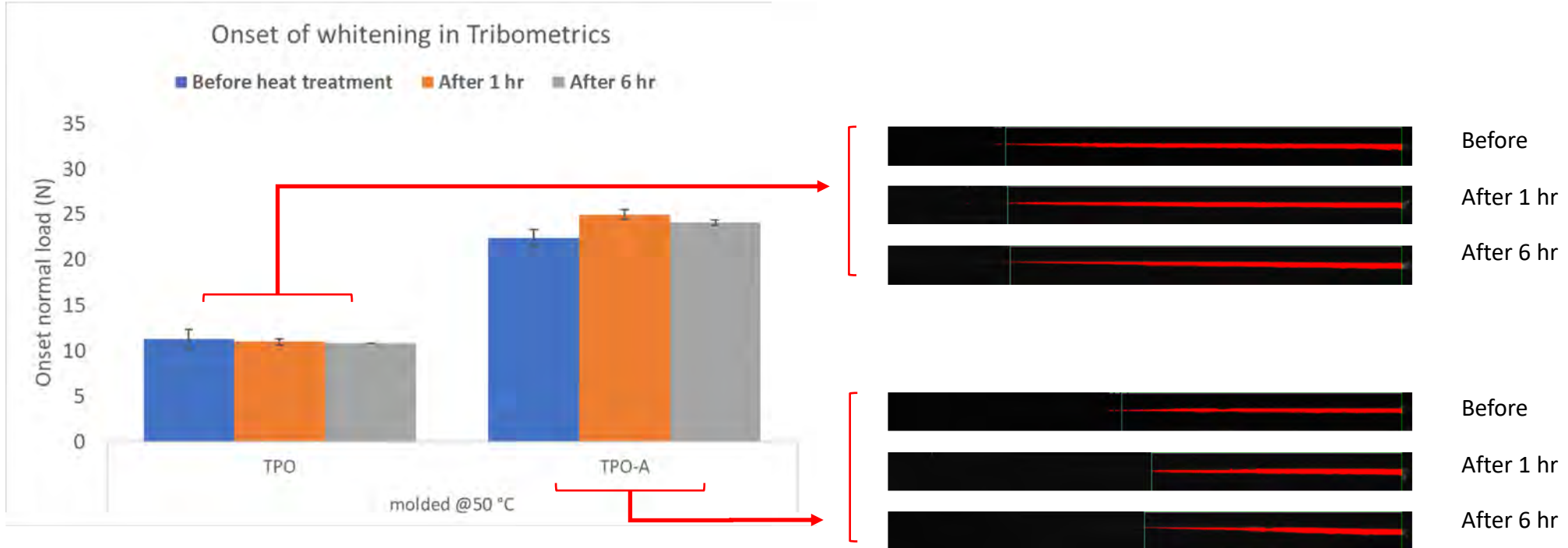


- All TPO samples showed subtle fish-scale damages from the beginning of scratch.
- In TPO-A samples tested at RT & 50 °C, the onset of fish-scale was delayed. However, when tested at 75 °C, the fish-scale damage appeared from the beginning of the scratch.
- In terms of plowing damage, onset loads decreased as the test temperature increased from RT to 75 °C for both TPO and TPO-A systems.

Scratch-resistance of TPO & TPO-A
tested in cooling back to room
temperature after heat treatment

Heat treatment effect (50 °C) for TPO & TPO-A

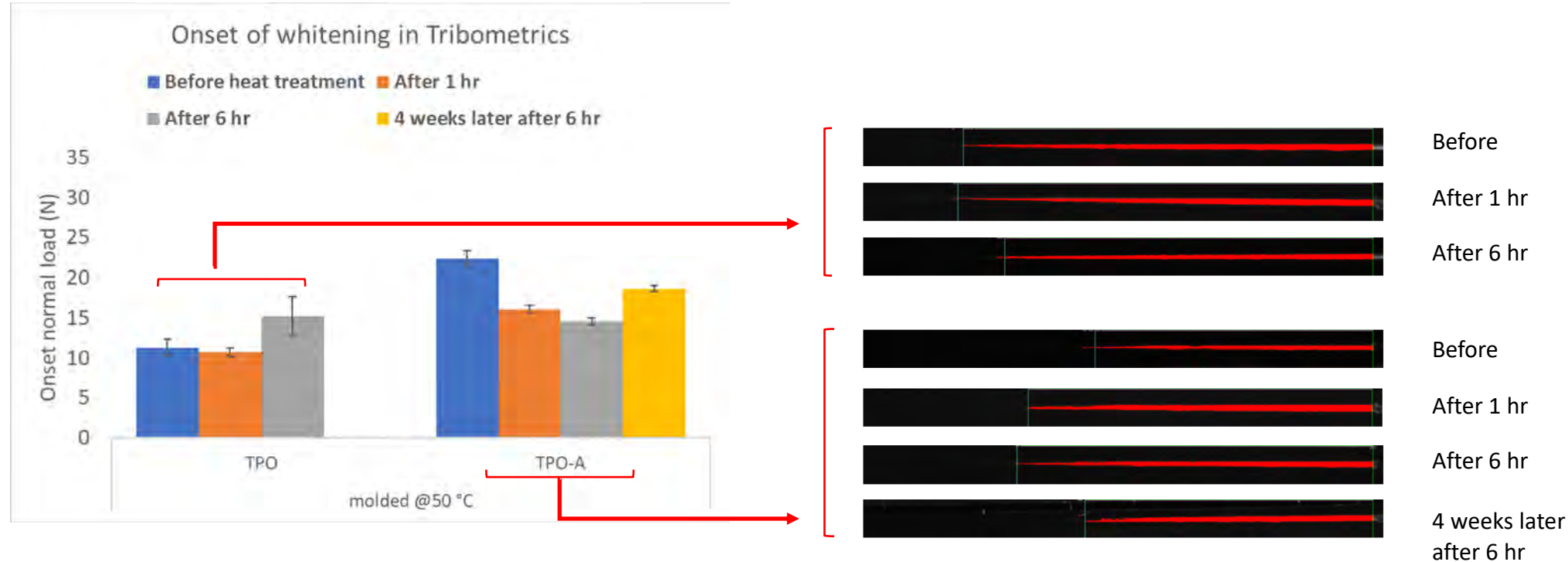
- **Heating process:** Both TPO & TPO-A were aged in oven at 50 °C for 1 hr and 6 hr, respectively
- **Scratch tested at RT**



- Only model systems molded at 50 °C were tested for TPO & TPO-A.
- Onset of whitening in TPO-A after heat ageing for 1hr was increased and slightly decreased after heat ageing for 6 hrs.
- This improvement might be attributed to migration of Erucamide to the surface.
- For TPO, there is no difference before and after heat ageing at 50 °C.

Heat treatment effect (75 °C) for TPO & TPO-A

- **Heating process:** Both TPO & TPO-A were aged in oven at **75 °C** for **1 hr** and **6 hr**, respectively
- **Scratch tested at RT**



- Only model systems molded at 50 °C were tested for TPO & TPO-A.
- Onset of whitening in TPO-A after heat ageing for 1hr is significantly decreased and became even worse after heat ageing for 6 hrs.
- For neat TPO, there is an annealing effect after heat ageing for 6 hr. The onset of whitening is improved.
- Despite the fact that the scratch-resistance of TPO-A becomes worse after heat treatment for 1 hr, it is still better than TPO without heat-ageing.

- Mold temperature does not affect the scratch visibility of neat TPO in this study.
- Increase in mold temperature leads to migration of additive to the surface more readily, and thus delayed (improved) onset of fish-scale & plowing formation when tested at RT and 50 °C. However, at 75 °C, the additive is no longer effective.
- Tribometrics analysis and human observation for the onset of whitening are consistent with each other.
- Based on FTIR-ATR analysis, slip-agent migration is greatly influenced by heat treatment at different temperatures.