Impact of Elevated Temperature on Surface Properties of Erucamide-containing Polyethylene Films

Rahul Sharma, Michaeleen L. Pacholski, Kenneth B. Laughlin, Johnpeter Ngunjiri, Justin Sparks, Vivek Kalihari and Mridula Kapur

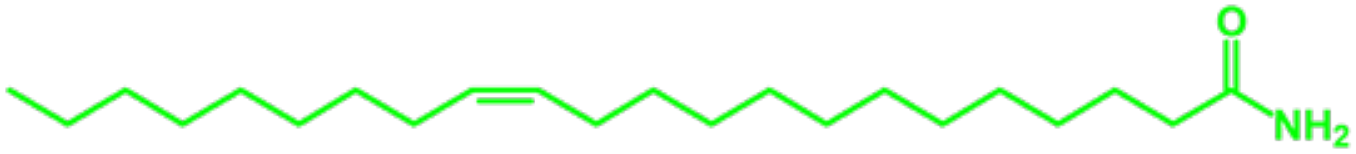
The Dow Chemical Company

SPE International Polyolefins Conference, Houston

February 27, 2017

Controlling the COF of PE Films

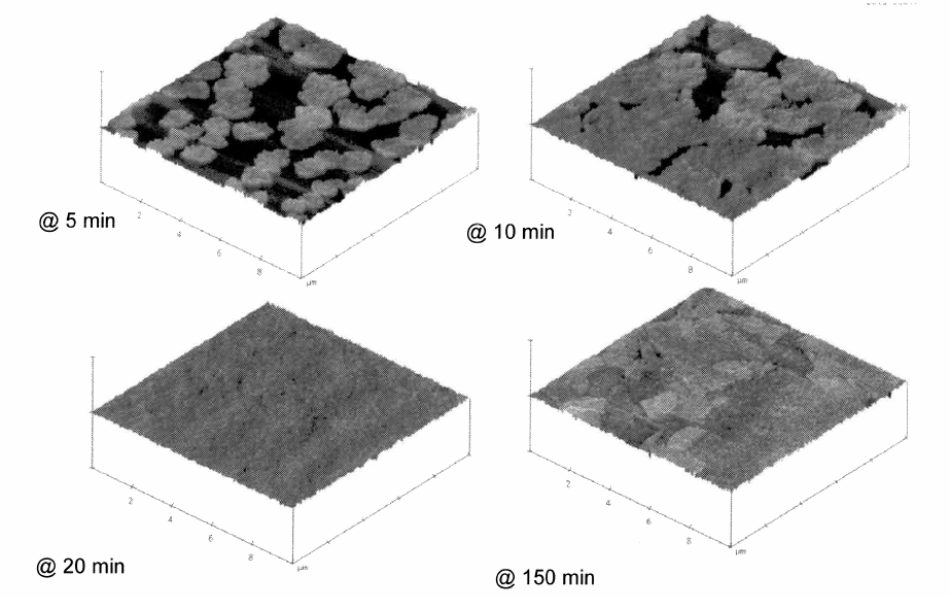
- Low COF, typically ≈0.2 or less, is needed for roll-to-roll processing of PE films
- Room temperature COF of PE films is typically >0.7
- Slip agents are added to bring the COF of PE films in the desired range
- One of the most common slip agents is **erucamide**



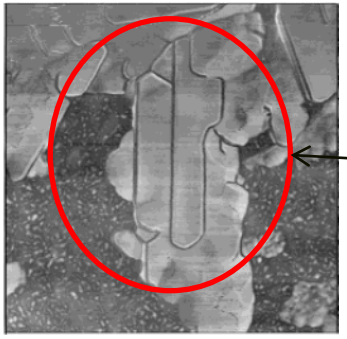
- Erucamide is either pre-mixed in the resin or blended in at the time of film manufacturing
- Usually ~100 – 1000 ppm loadings are sufficient to achieve COF <0.2
- Due to low loadings erucamide provides a cost-effective solution for reducing COF

How Erucamide Works

Erucamide spontaneously blooms to the surface as film cools at ambient conditions, and forms a layered structure of crystals at the surface

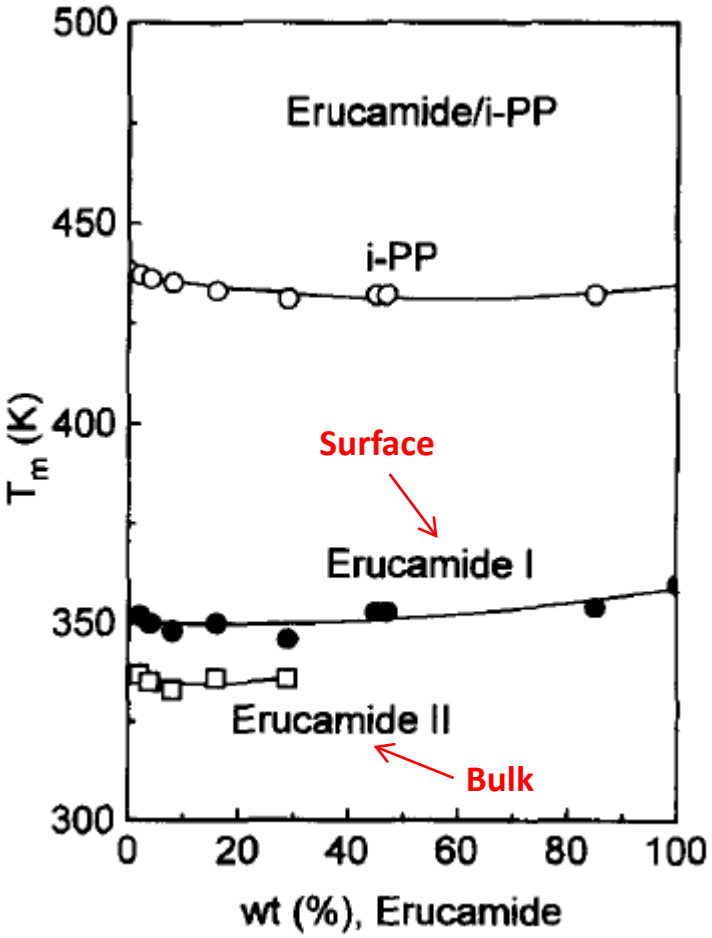


J. Vac. Sci. Technol. (2007) 25, 886-892



Nano Letters (2002) 2, 9-12

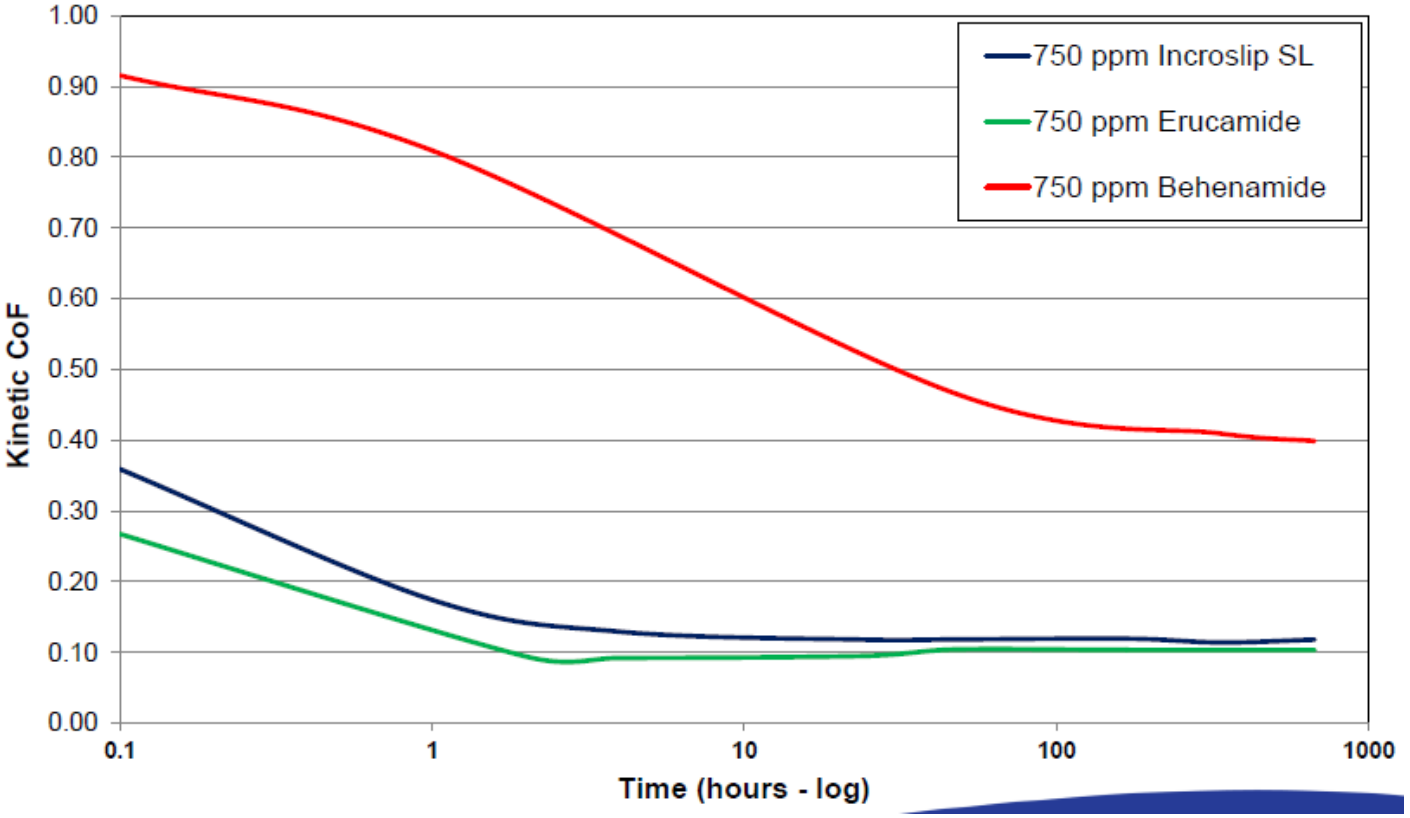
Polymer (1997) 38, 5125-5135



How Erucamide Works

- It is believed that the crystal-crystal slip provides the lubrication effect needed for reducing the COF

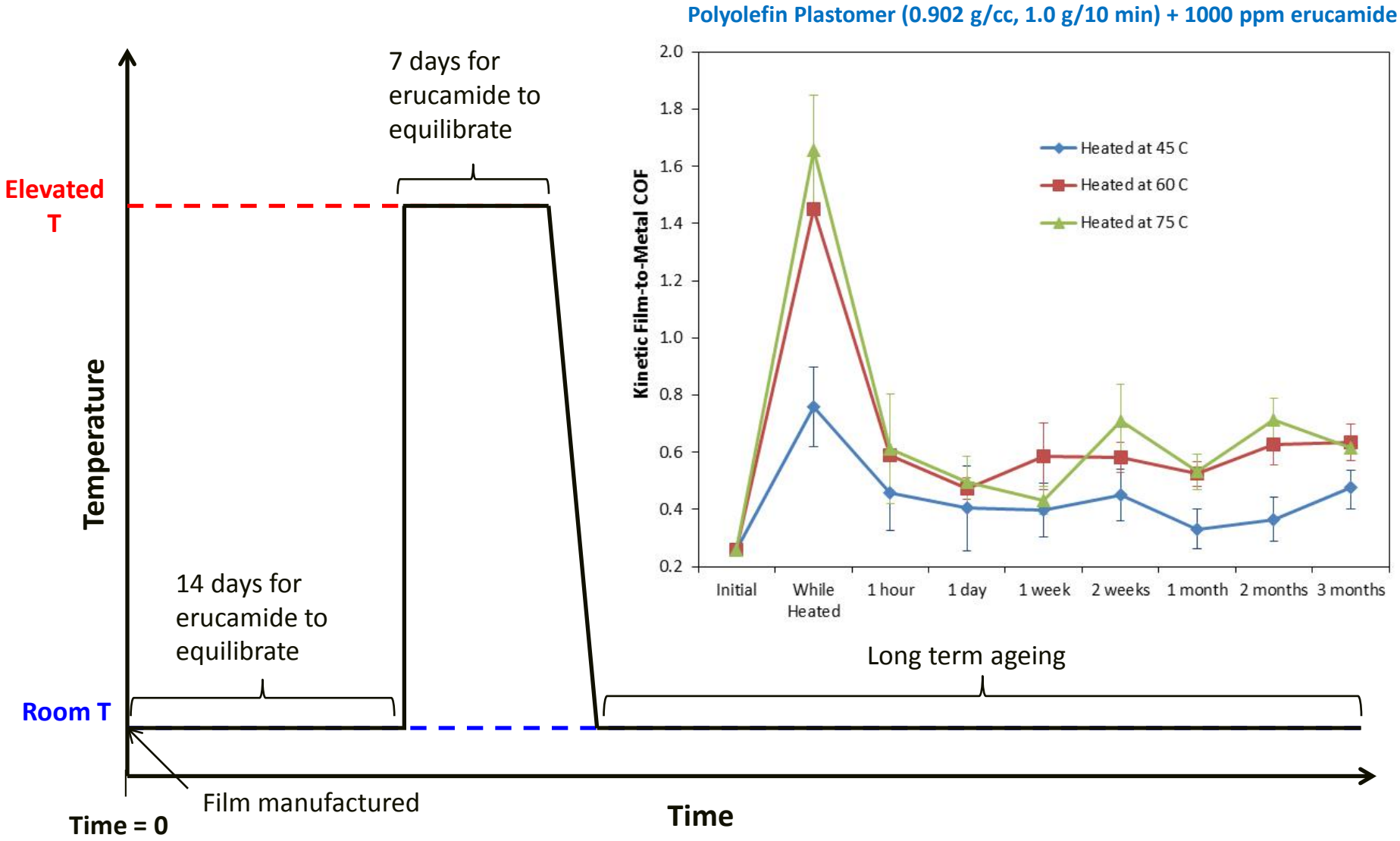
- COF takes few days to stabilize but equilibrates to a low value which is fairly stable at room temperature



Courtesy A. Maltby, Croda

Problem with Erucamide

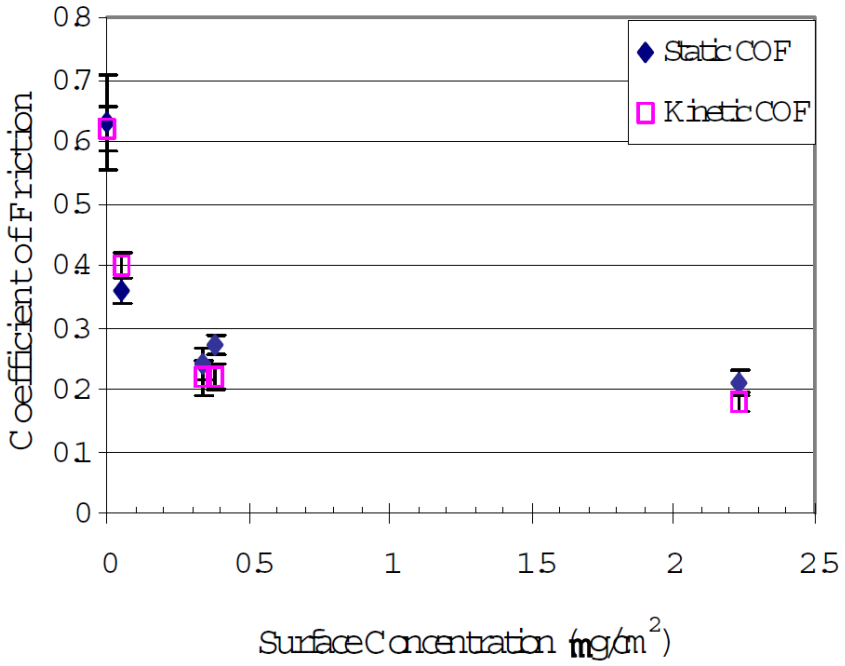
COF increases irreversibly if the films get exposed to elevated temperatures during storage and transport



Factors Affecting COF

(1) Surface concentration of erucamide

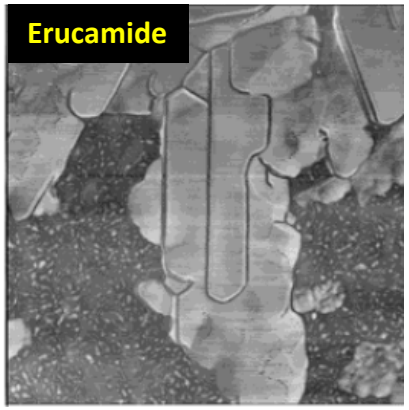
SPE ANTEC Proceedings (2000) 2873-2876



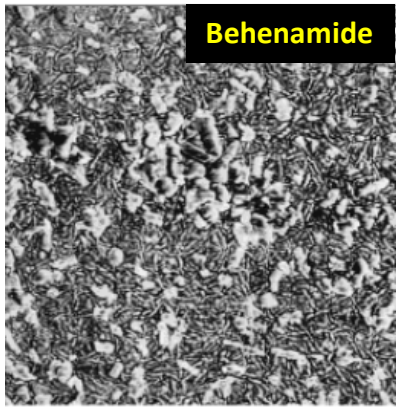
- COF decreases with increasing surface concentration
- A threshold concentration needed to achieve equilibrium COF

(2) Stacking of crystals

Nano Letters (2002) 2, 9-12



Stacked crystals
(Low COF)

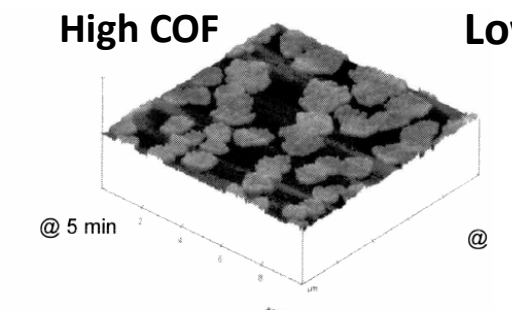


No clear stacking
(High COF)

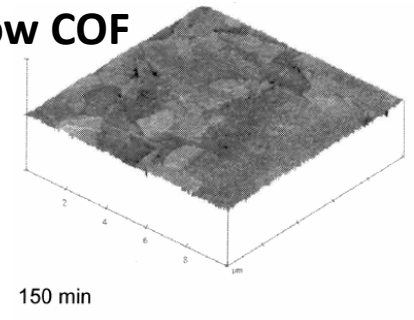
(3) Erucamide surface coverage

J. Vac. Sci. Technol. (2007) 25, 886-892

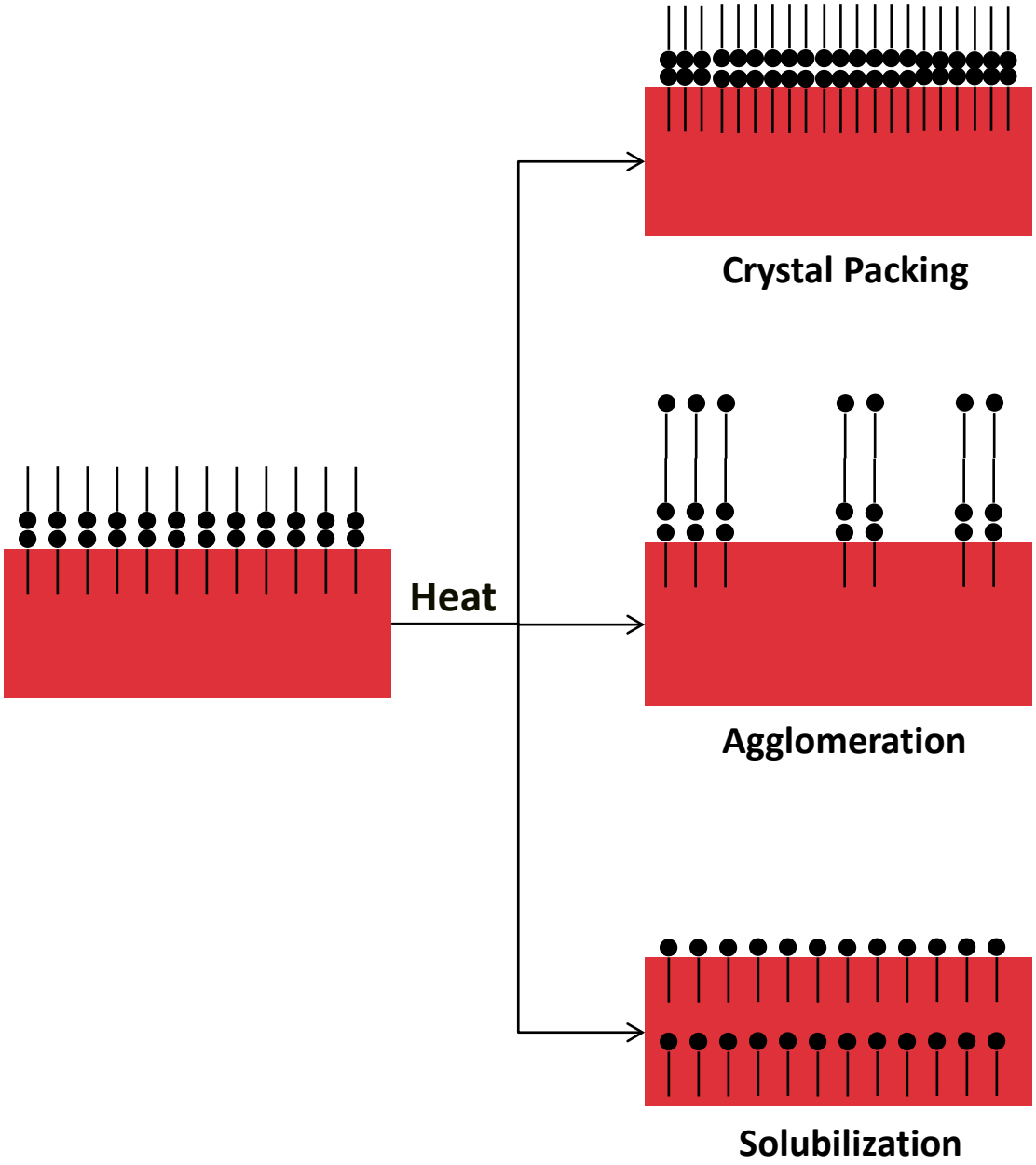
High COF



Low COF



Hypotheses Tested



- Higher temperature affects crystal packing
- The new crystal structure inhibits slip

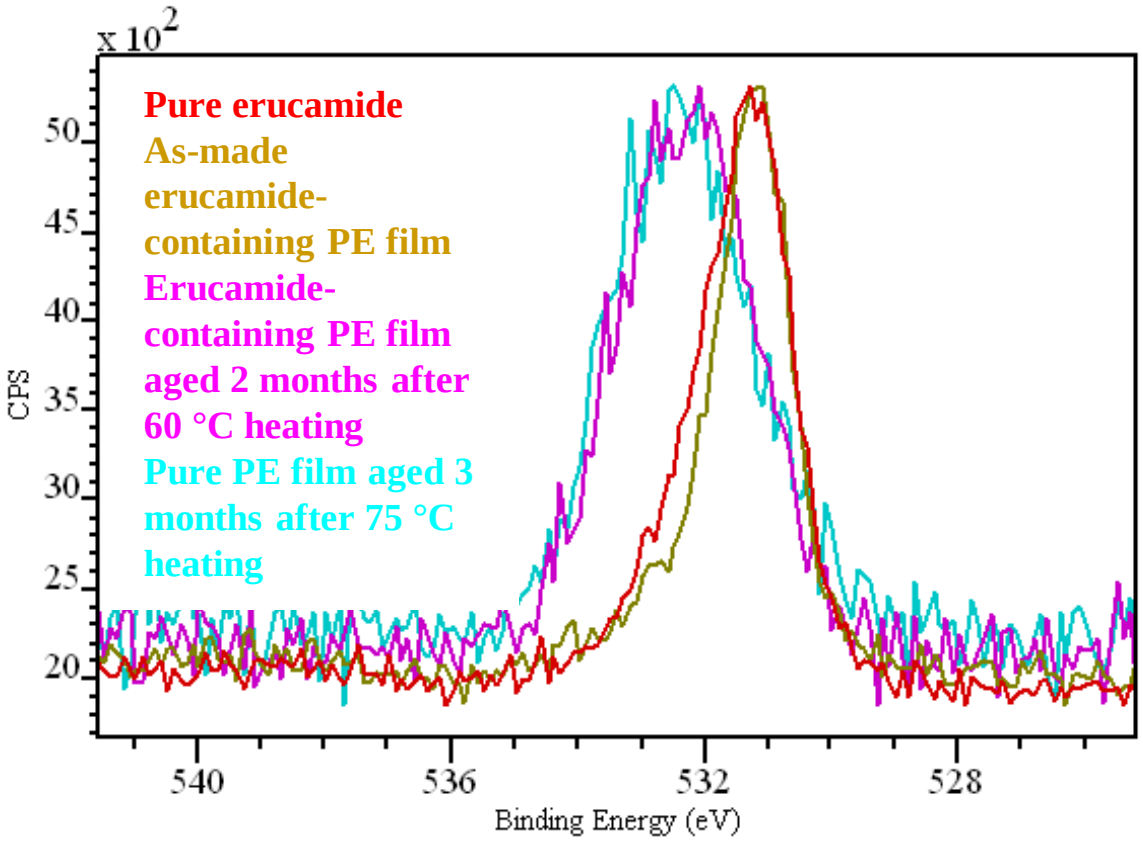
- Higher temperature causes agglomeration
- The bare film surface exposed during agglomeration leads to higher COF

- Erucamide becomes more soluble in the polymer at higher temperature
- Lower surface concentration of erucamide causes higher COF

Concern About Erucamide Oxidation

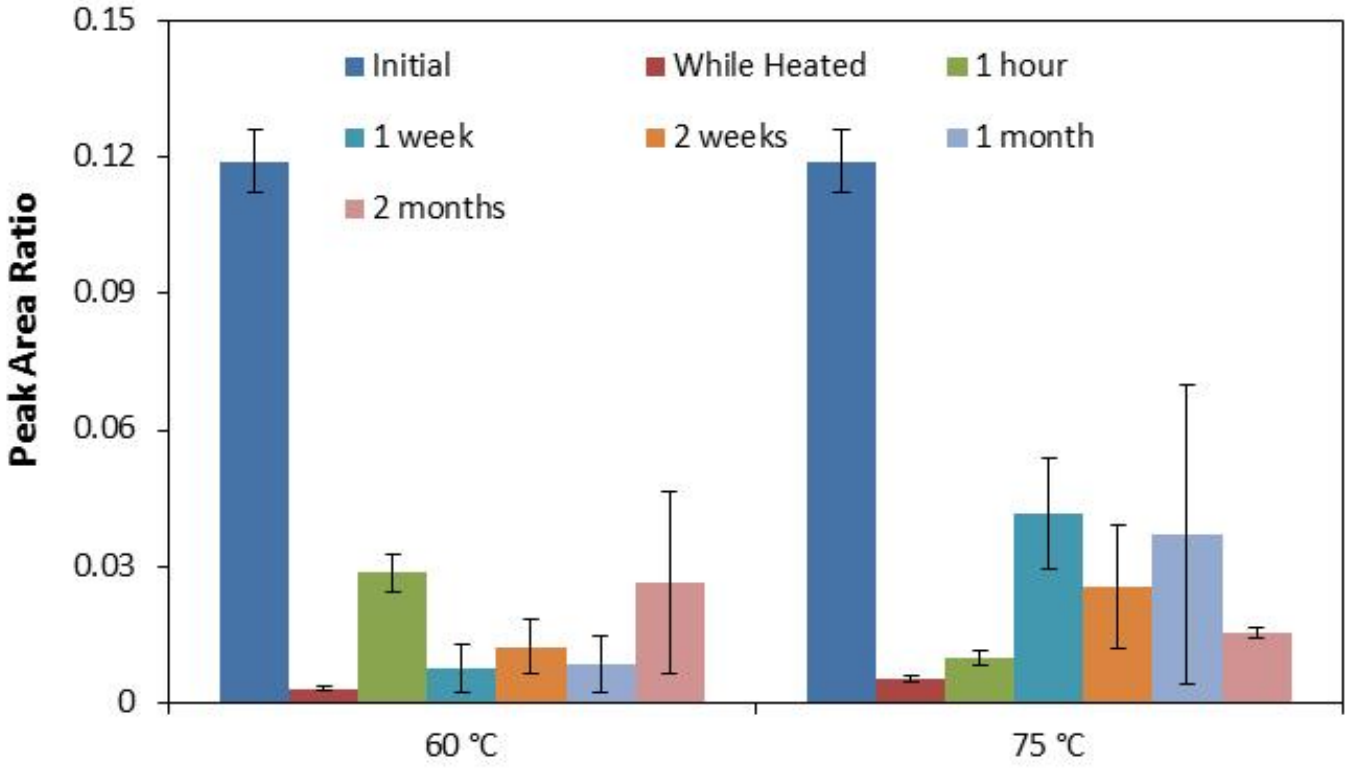
- Schuler et al. (Polym. Eng. Sci., 44, 2247) reported that erucamide oxidizes when exposed to elevated temperature

- No significant degradation of erucamide observed in the conditions employed in this study



Changes in Surface Concentration

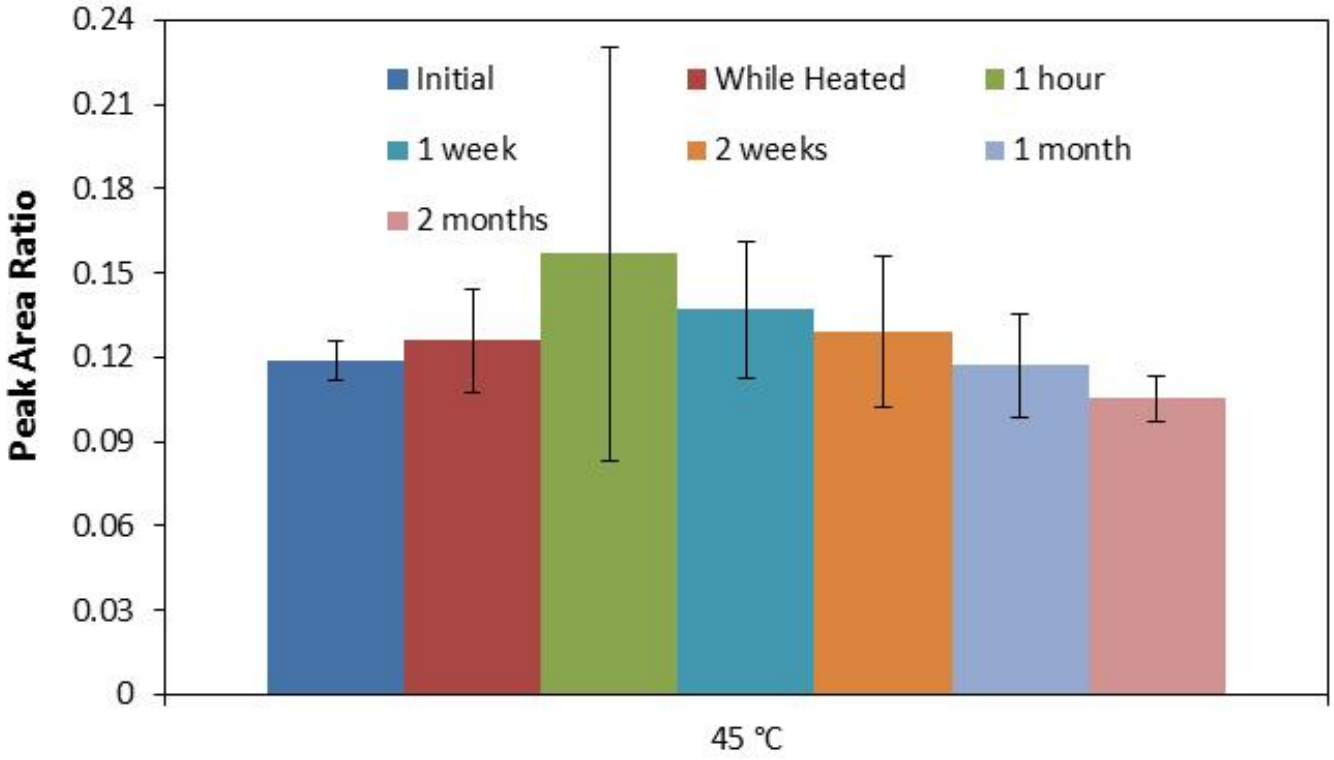
- Surface concentration monitored by ATR IR – penetration depth ≈1 µm
- Films heated at 60 and 75 °C



- Dramatic reduction in concentration while films were at 60 and 75°C
- Some recovery when films return to ambient conditions but concentration still significantly lower than initial

Changes in Surface Concentration

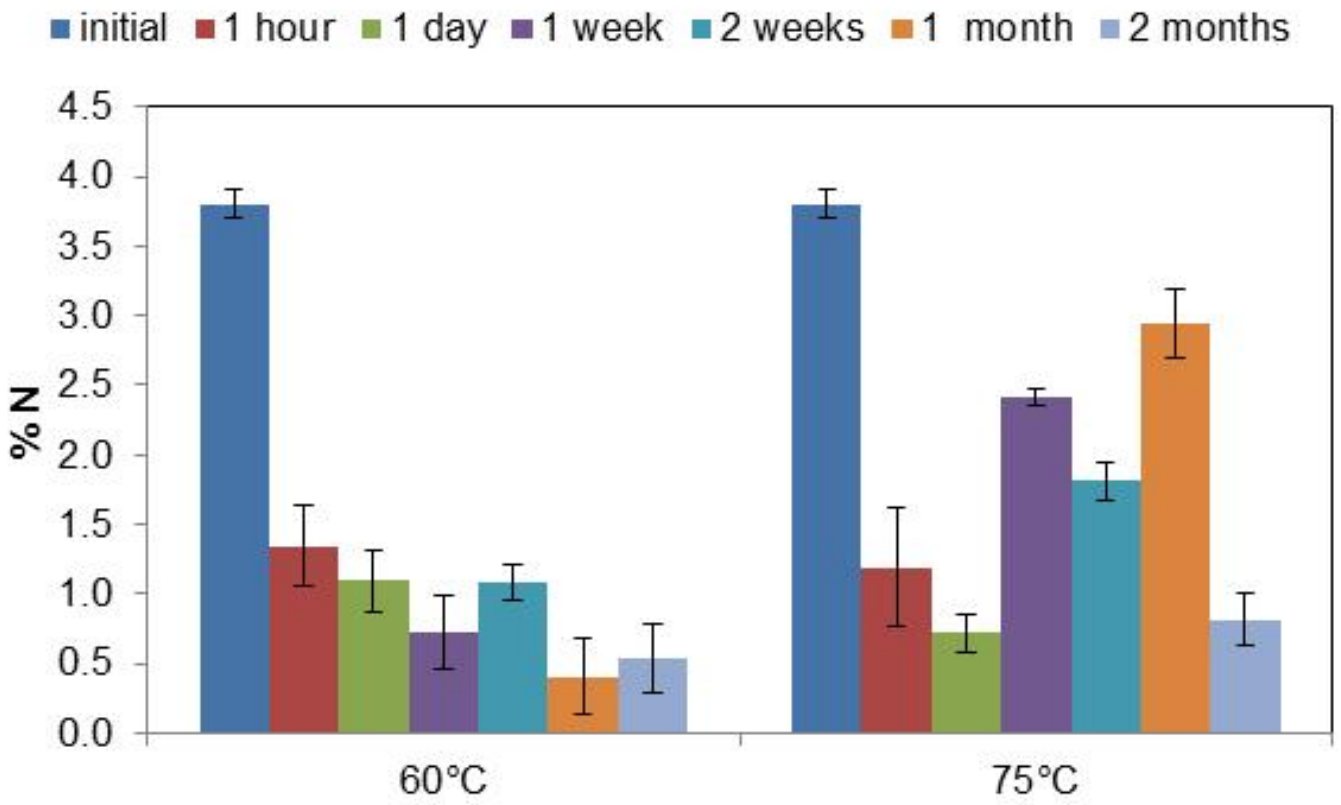
- Films heated at 45 °C



- Virtually no change in concentration even while the films are at 45 °C
- Concentration stays similar to initial over long term aging
- COF increase not correlated to change in surface concentration

Changes in Surface Coverage

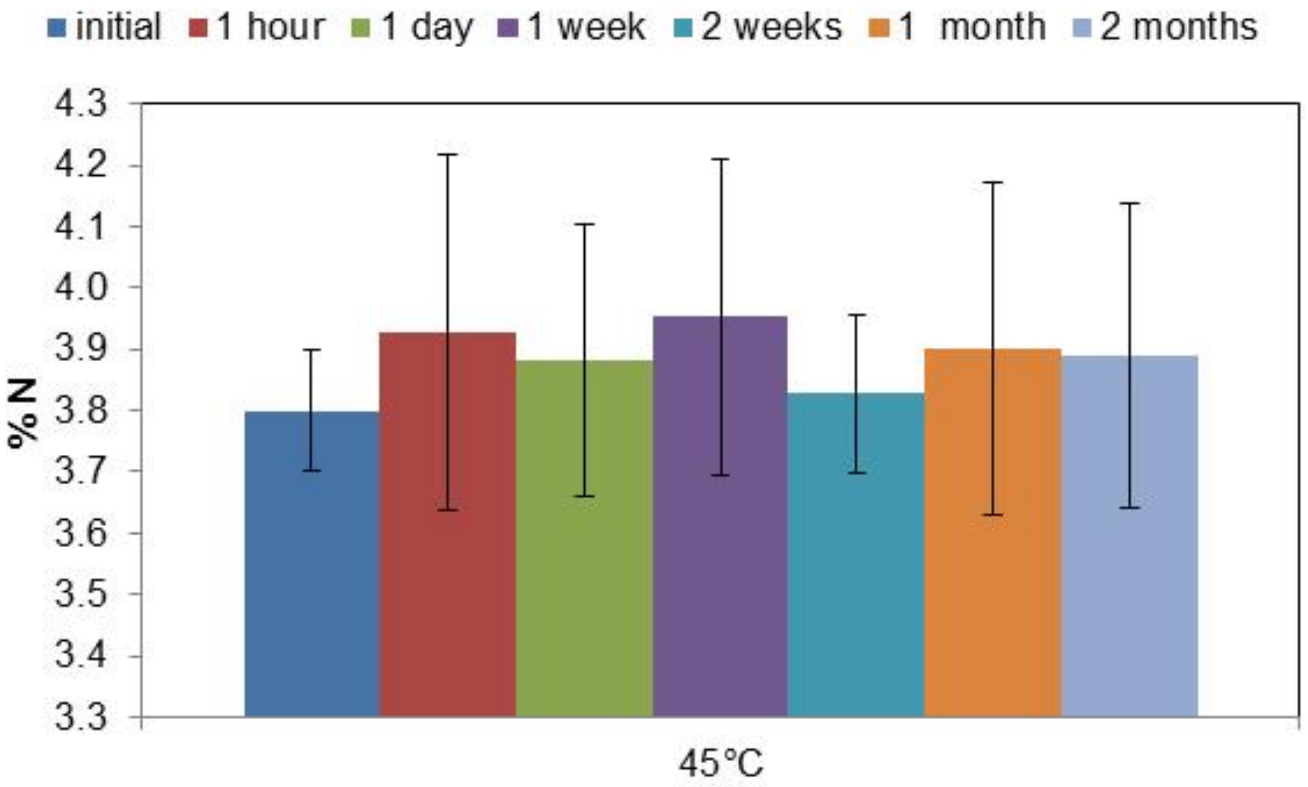
- Surface coverage monitored by XPS – penetration depth ≈10 nm
- %N ≈ 4.0 for complete coverage



- Dramatic reduction in the initial surface coverage (within 1 hour)
- Inconsistent trend of coverage change as the films subsequently aged at ambient conditions

Changes in Surface Coverage

- Films heated at 45 °C

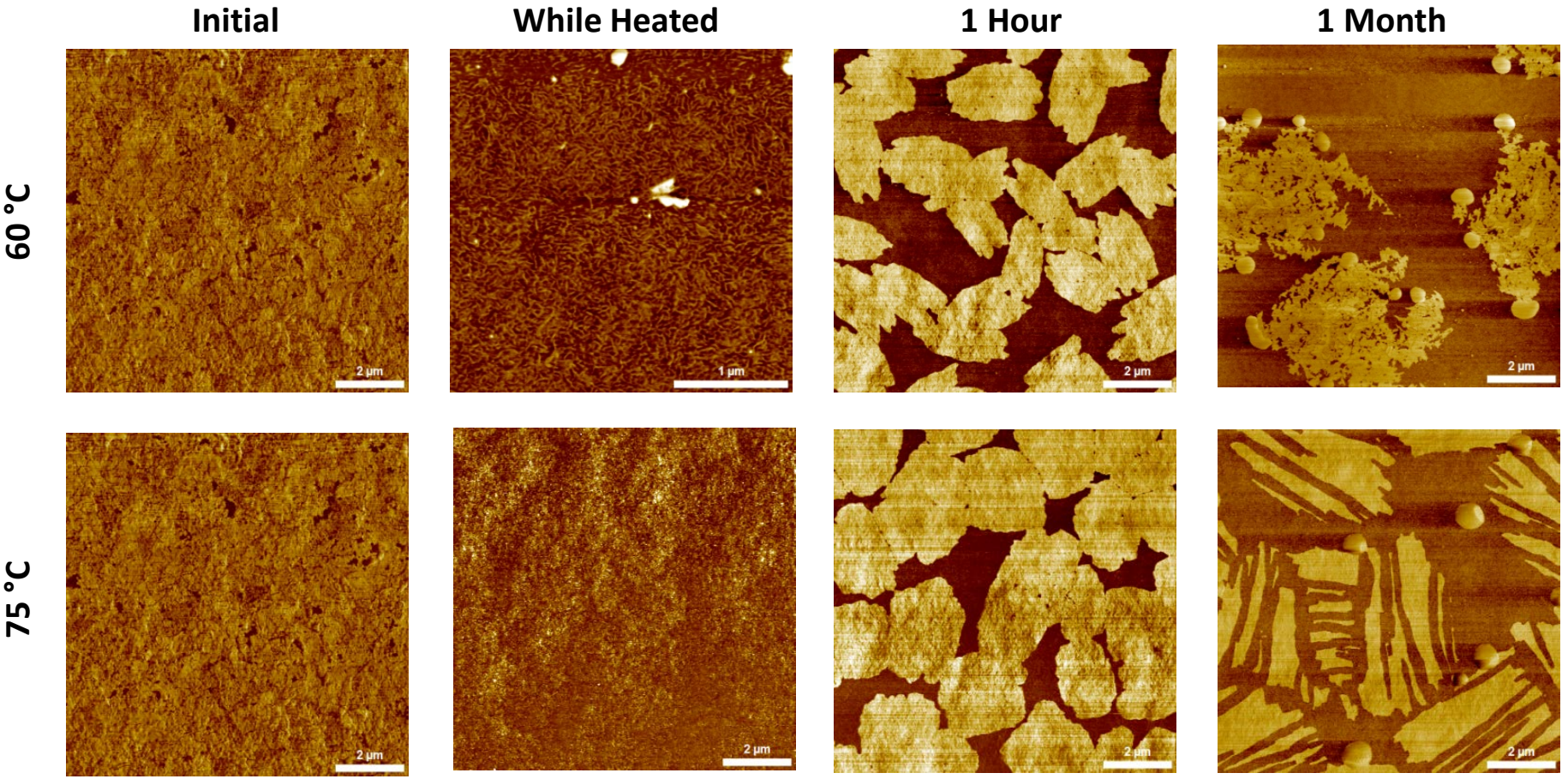


- Virtually no change in surface coverage at any time point

- No correlation of COF increase with surface coverage irrespective of the heating temperature

Changes in Surface Morphology

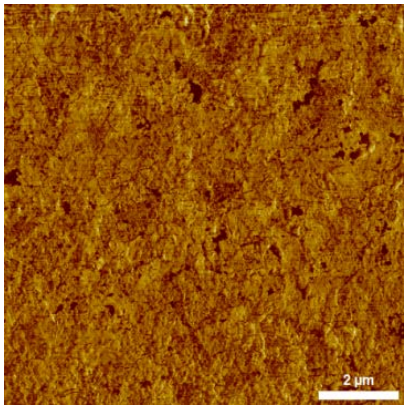
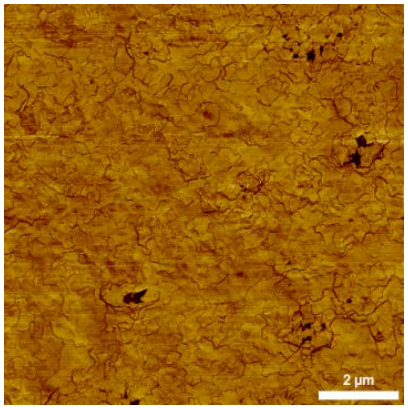
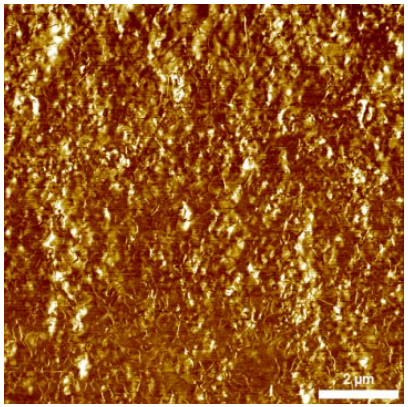
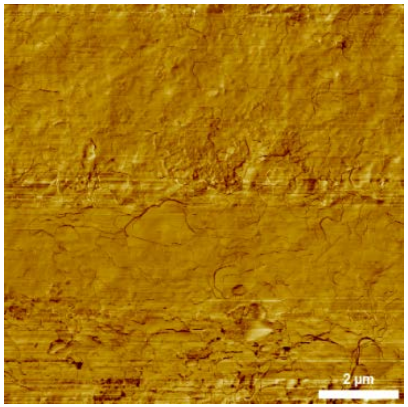
- AFM phase images of films heated at 60 and 75 °C



- Transition from stacked crystals to bilayers – possible factor for COF increase

Changes in Surface Morphology

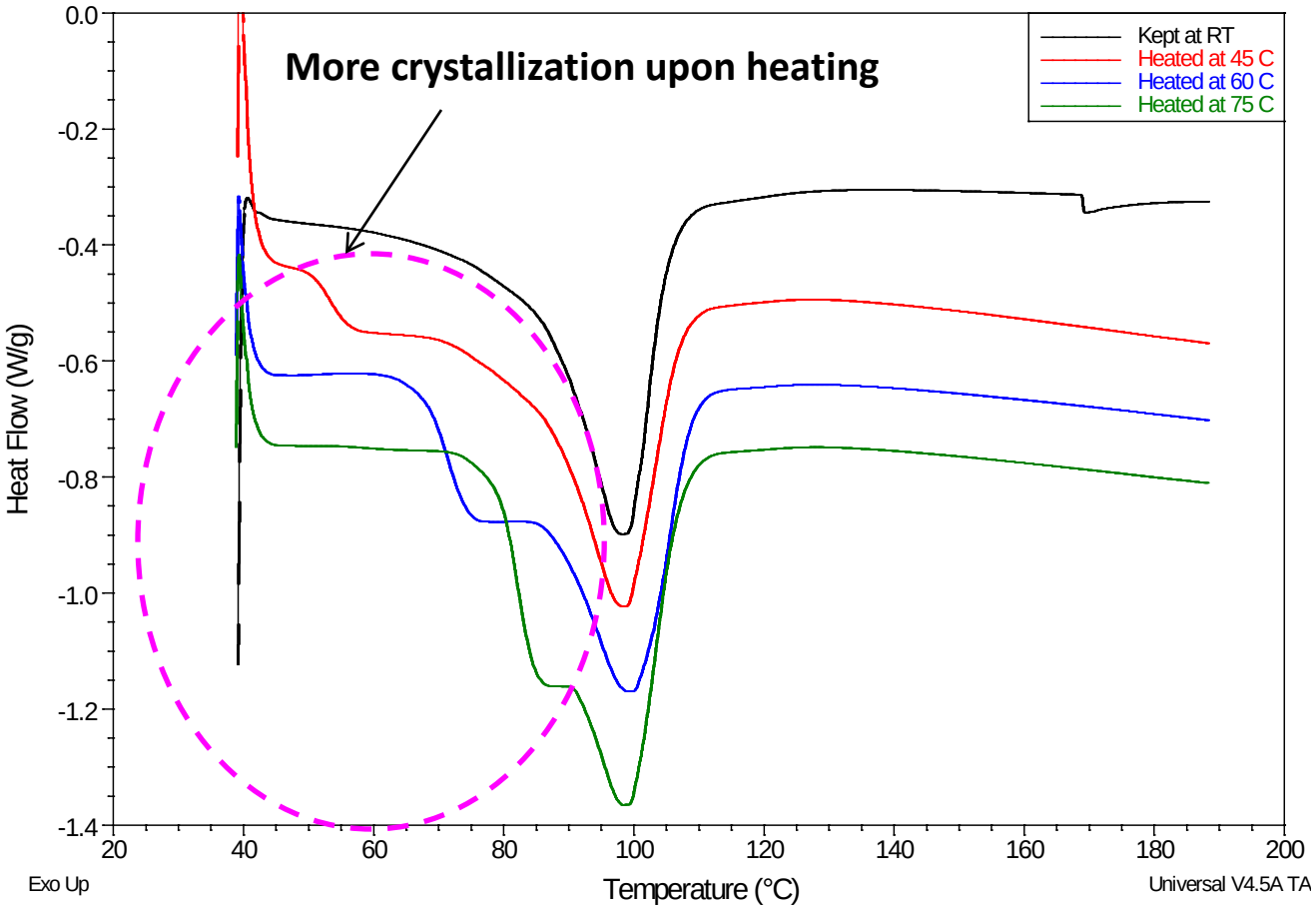
- AFM phase images of films heated at 45 °C

	Initial	While Heated	1 Hour	1 Month
45 °C				
	Stacked Crystals (Height ≈ 50 nm)	**Stacked Crystals**	**Stacked Crystals**	**Stacked Crystals)**

- Stacked crystals are maintained even when the film is at 45°C and subsequently at ambient conditions too

- Change in crystal stacking cannot explain increase in COF when films are heated at 45 °C

Changes in Crystallinity of Base Resin



T (°C)	%Crystallinity
Ambient	20.7
45	24.0
60	25.4
75	25.6

- Base resin crystallinity increases when the films are heated
- Unclear as to how this affects the COF

Conclusions

- **In films heated at 60 and 75 ° C**
  - Temperature induces an irreversible reduction in surface concentration of erucamide and transition of crystal morphology from stacks to bilayers
  - Both these changes can contribute to the increase in COF observed post heating
- **In films heated at 45 °C**
  - No significant change in surface concentration of erucamide, its stacking or its surface coverage
  - More work needed to understand the reason for COF increase
- **Surface concentration appears to be a more dominant factor in affecting COF than surface coverage**
- **Heating also affects the crystallinity of the base resin**
  - Could also be a contributing factor to changes in COF
  - More work needed to understand the changes in crystal structure and size