SURFACE PROPERTIES OF HYDROSILYLATED POLYOLEFINS ANNEALED IN SUPERCRITICAL CARBON DIOXIDE

Shuihan Zhu and Costas Tzoganakis
Department of Chemical Engineering
University of Waterloo

Introduction

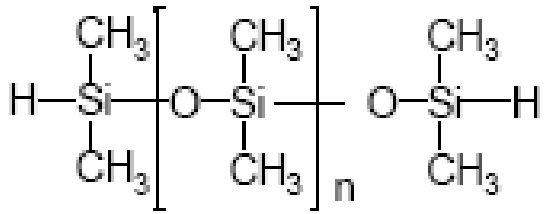
- Surface properties
  - adhesion/release properties, friction, gloss, scratch-resistance.
- Formation of surface layer
  - Driving forces: difference in the surface tensions of components
  - Benefits: small amount of surface materials; unaffected bulk properties; easiness of the process.
- Reactive polyolefin-PDMS compounds
  - No tacky surface
  - Permanent surface layer
  - Desired surface properties like friction and release capability

Objectives

- Fabricate hydrosilylated polyolefins in melts by reactive processing;
- Create PDMS-rich or SiO_2-covered surfaces on polyolefins;
- Develop a surface treatment method;
- Surface layer properties: chemical composition, contact angle, and the top layer thickness;
- Optimize the processing parameters.

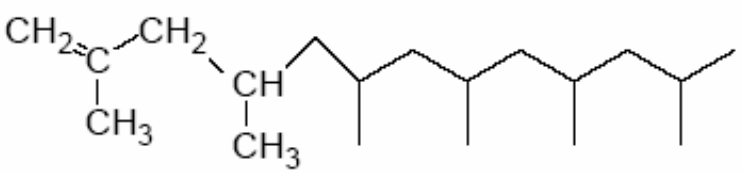
Schematic of hydrosilylation reaction schemes

I

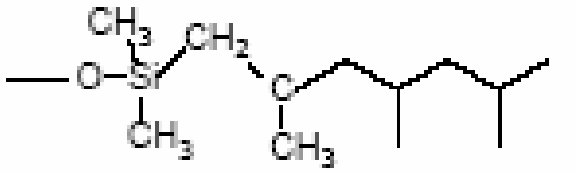


dH-PDMS

+

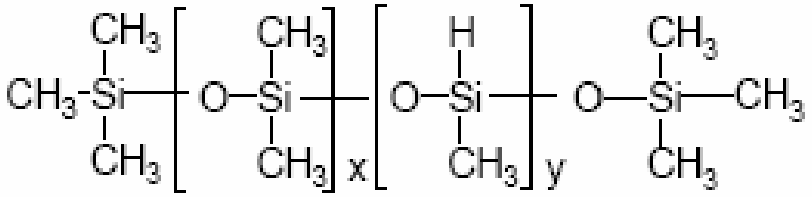


Degraded PP



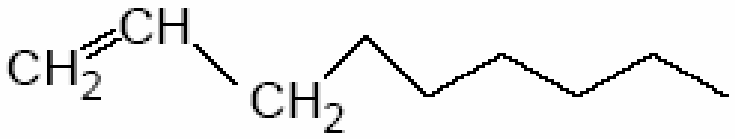
PP coupling

II

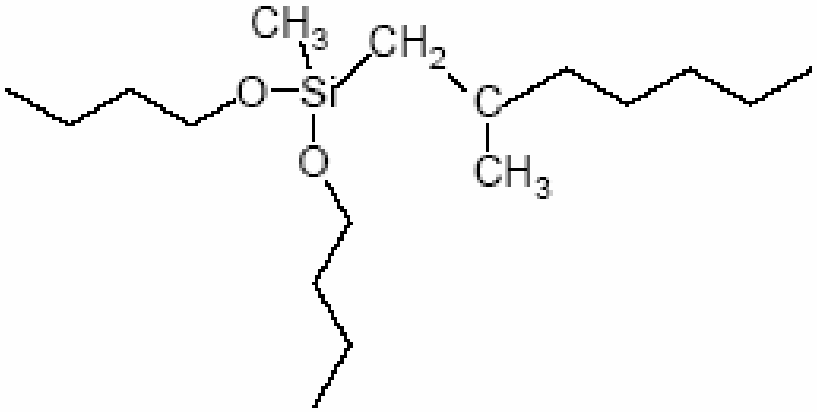


mH-PDMS

+

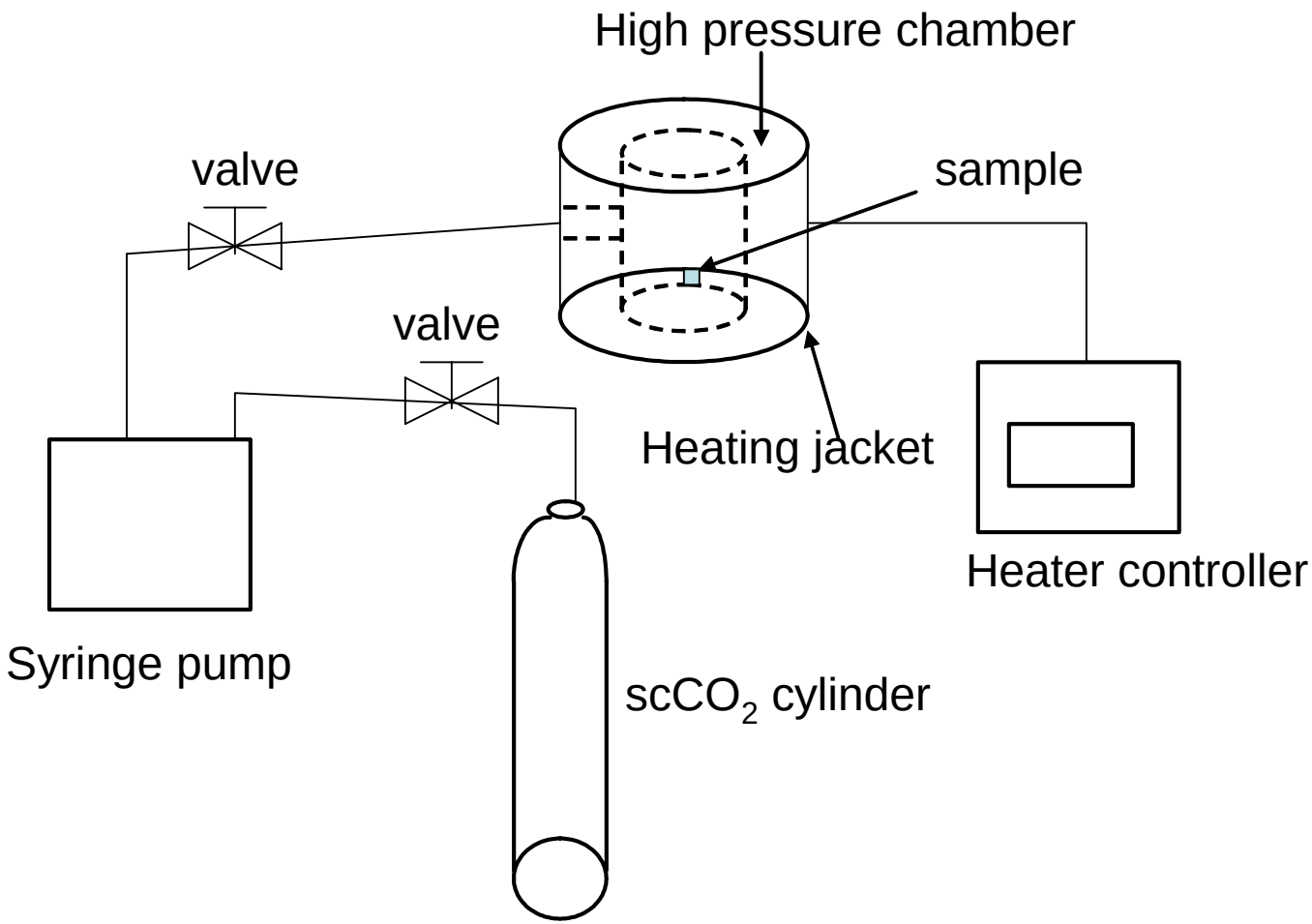


PE

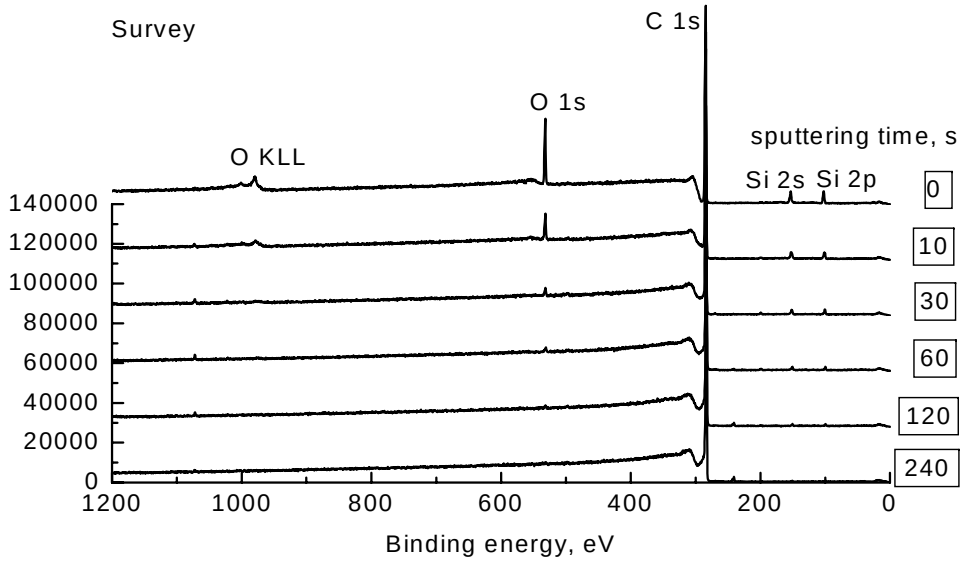


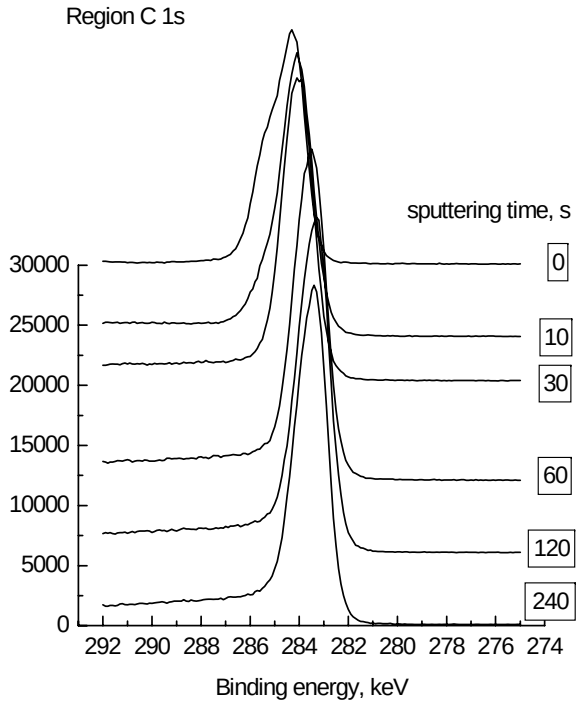
PE crosslinking

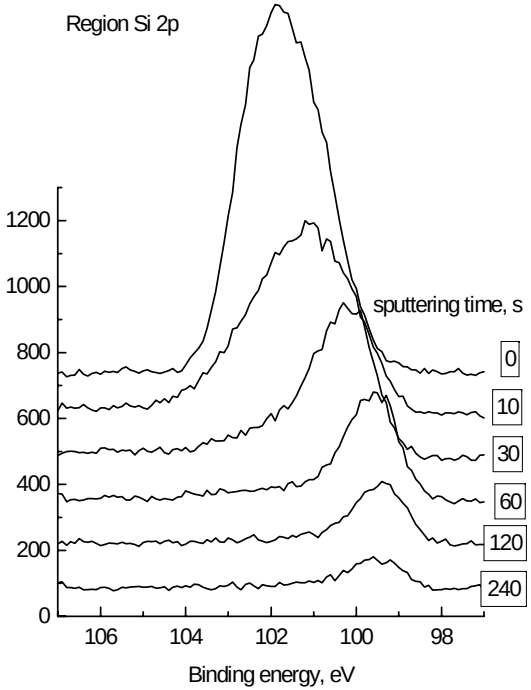
Apparatus for supercritical CO_2 ($scCO_2$) annealing process.

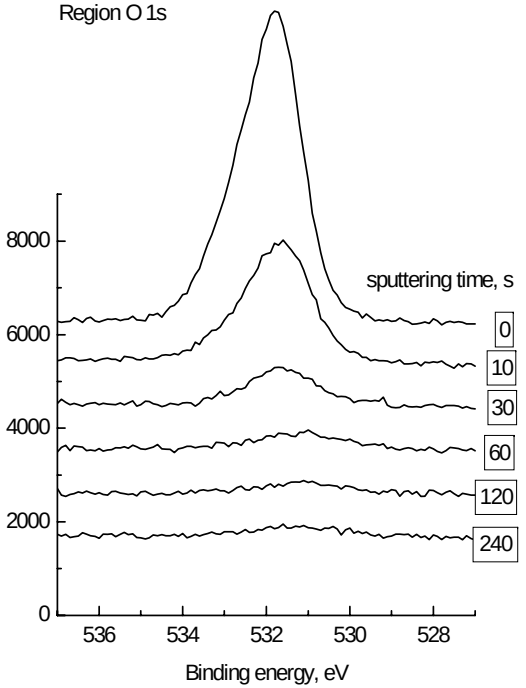


XPS spectra of PP/dH-PDMS sample before annealing.

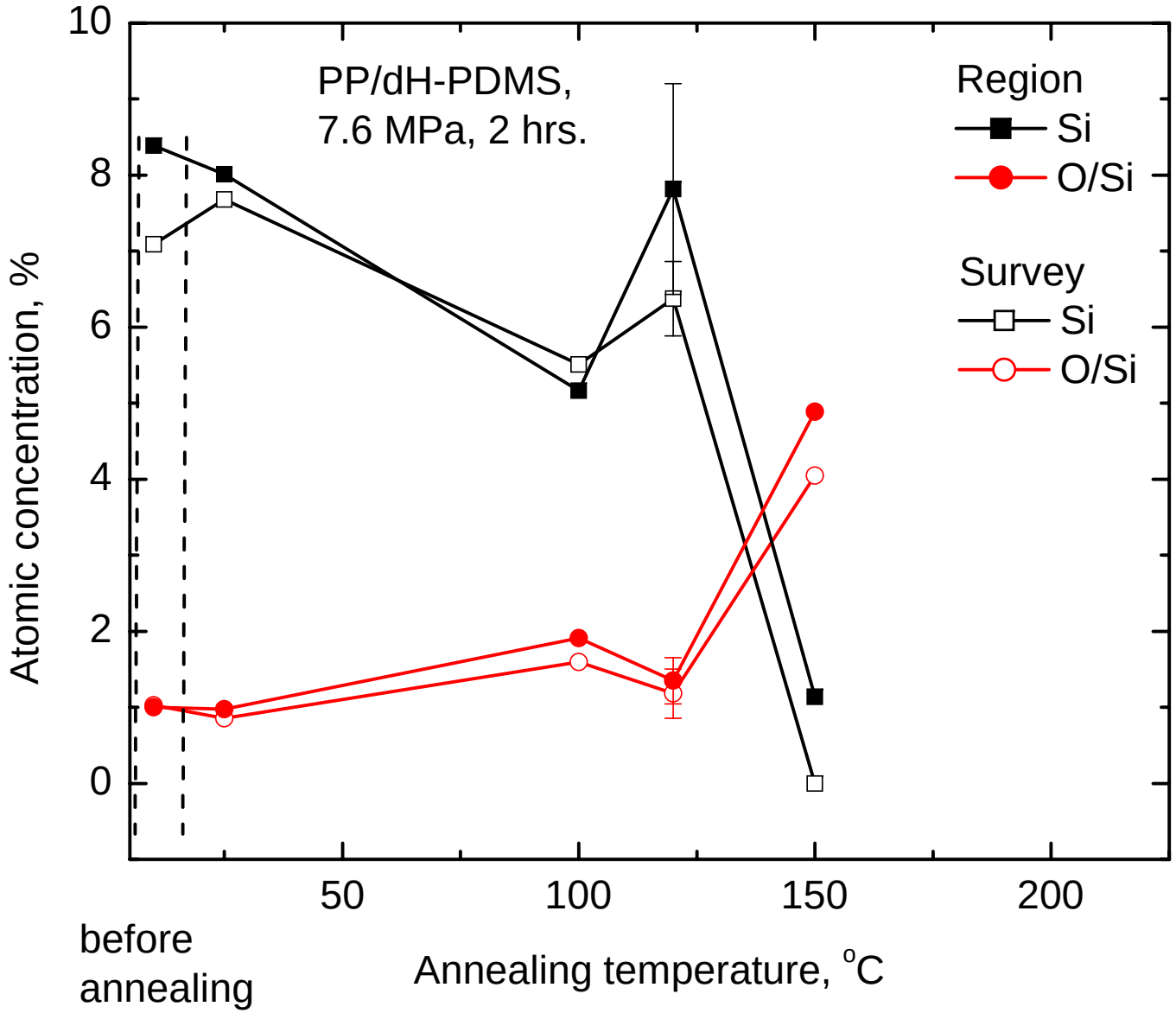




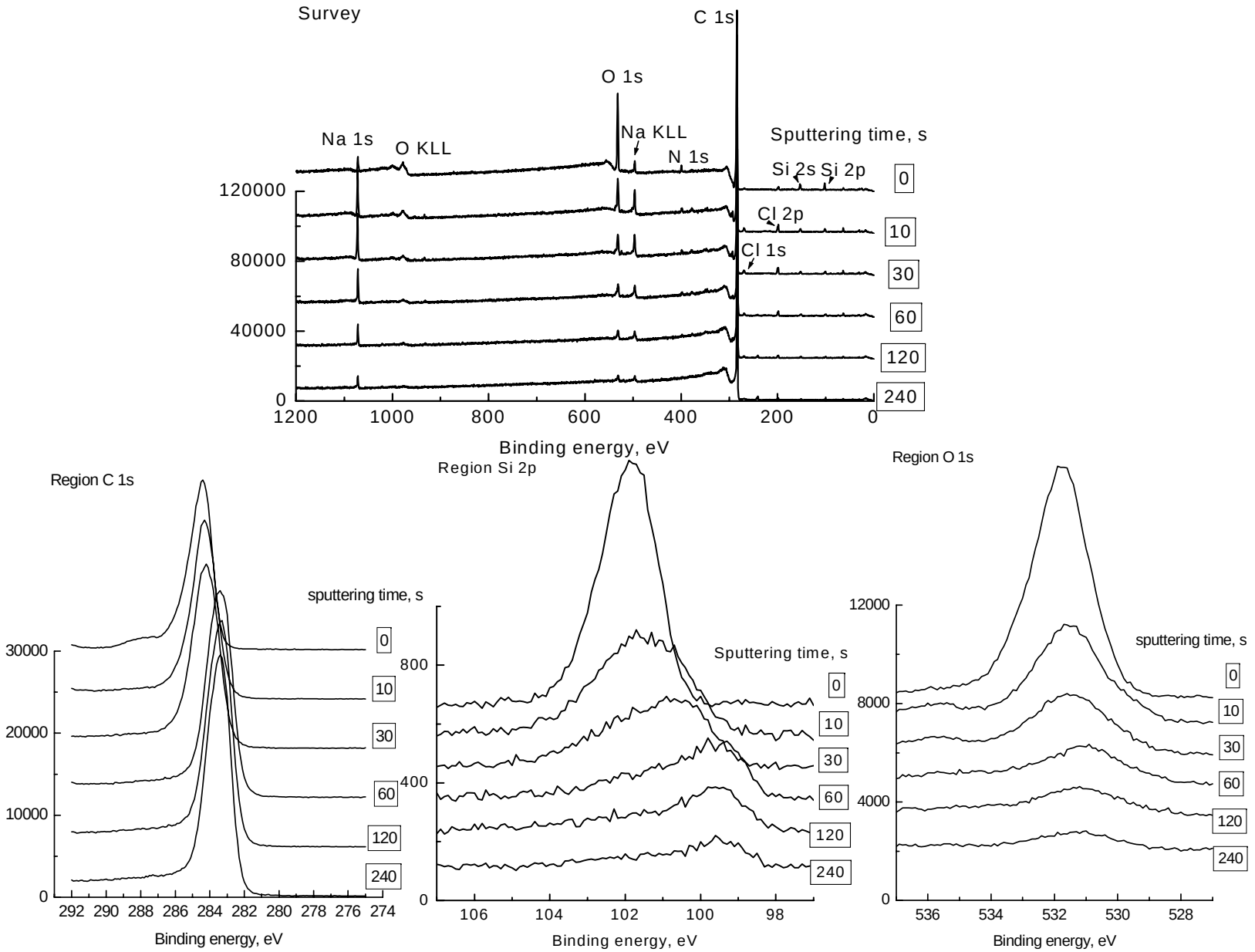




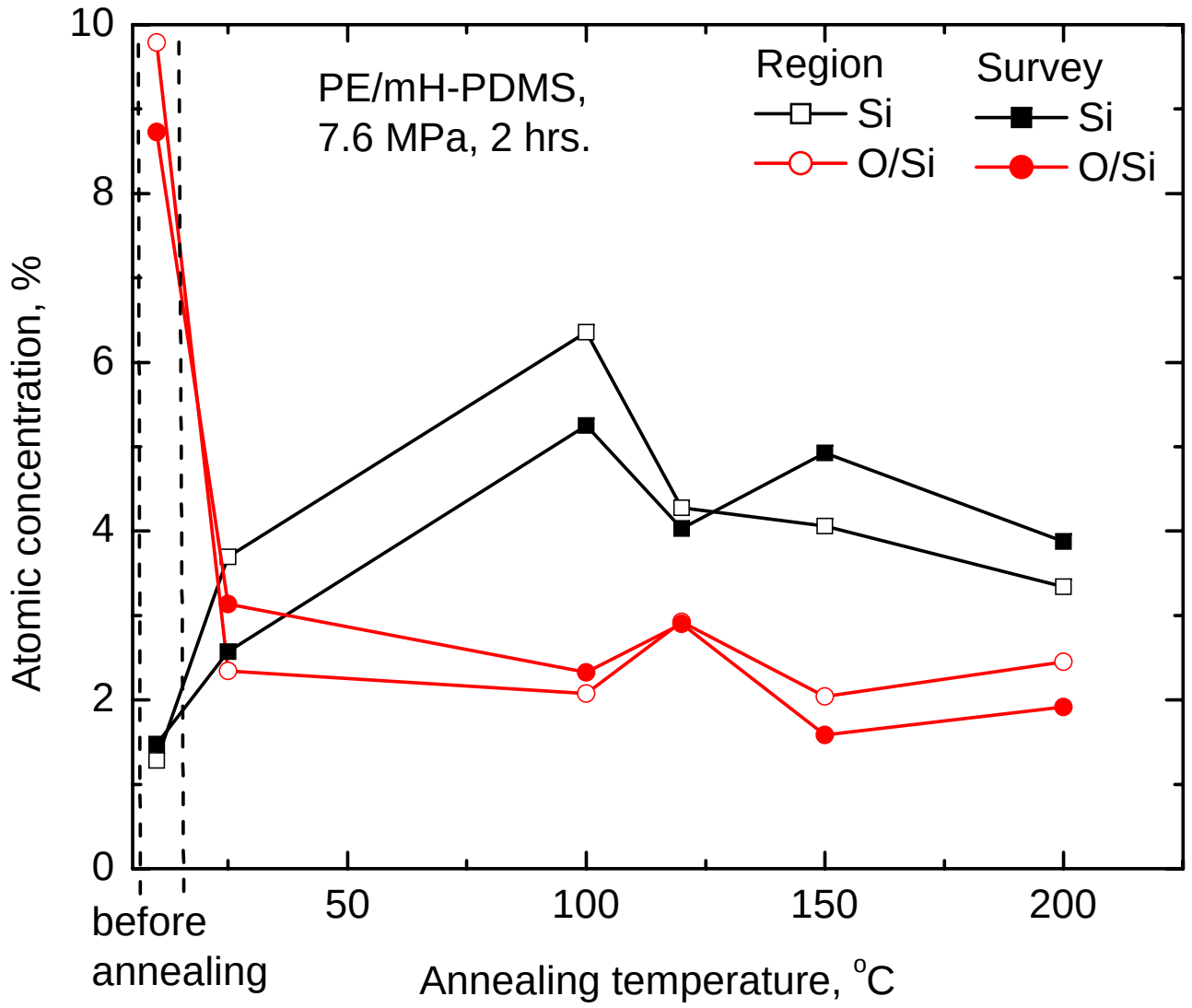
Effect of annealing temperature on the surface chemical compositions



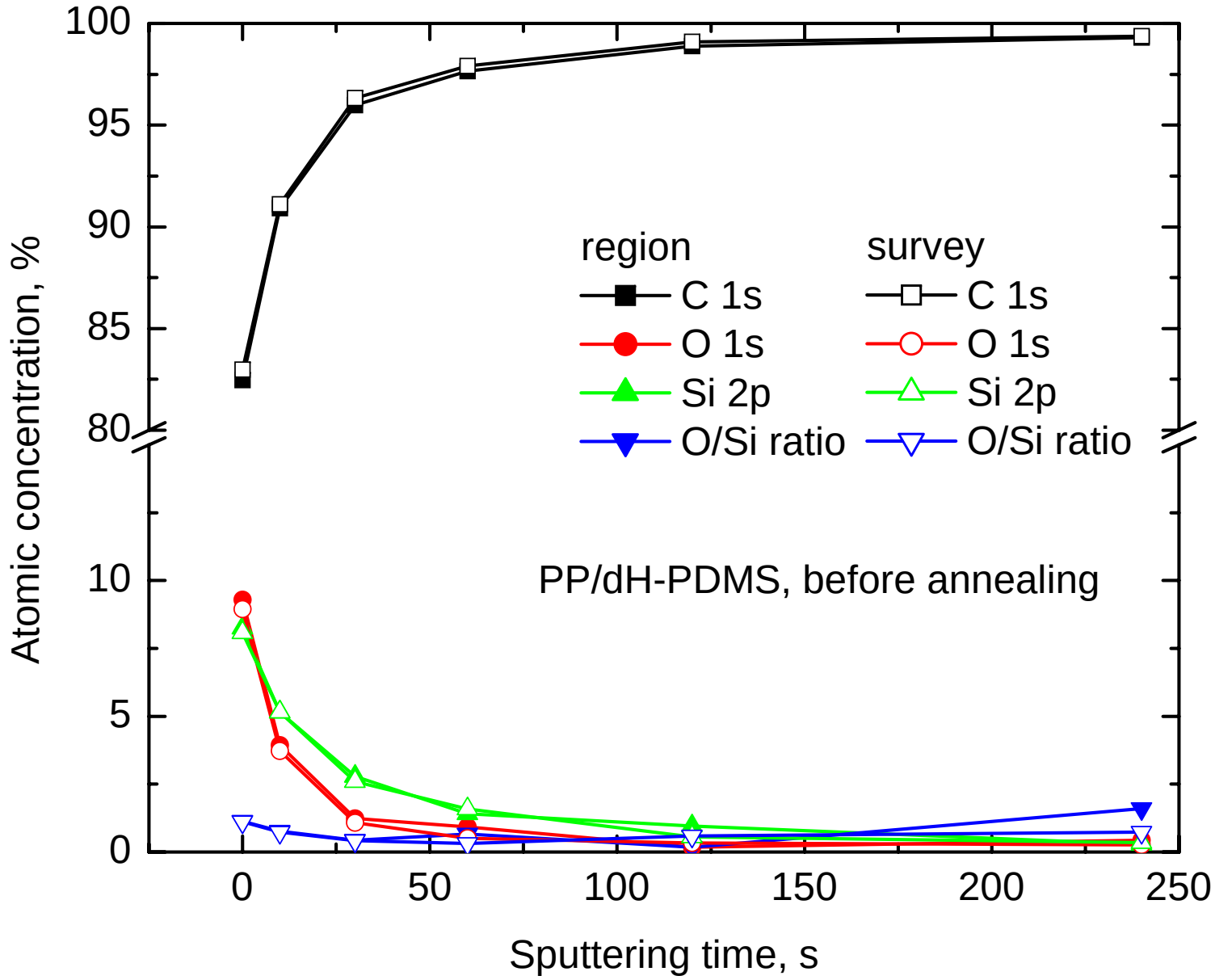
XPS spectra of PE/mH-PDMS sample before annealing



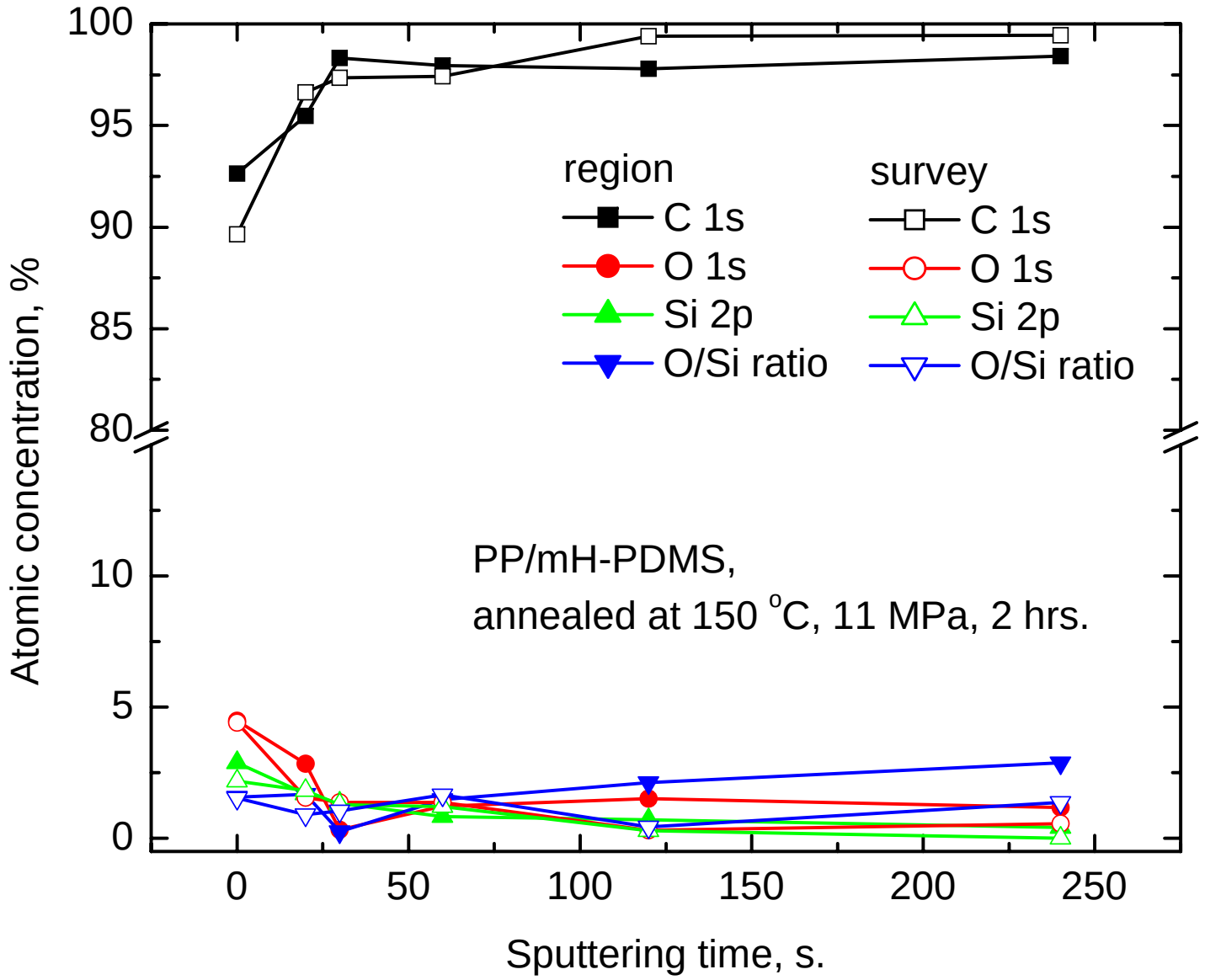
Effect of annealing temperature on the surface chemical compositions



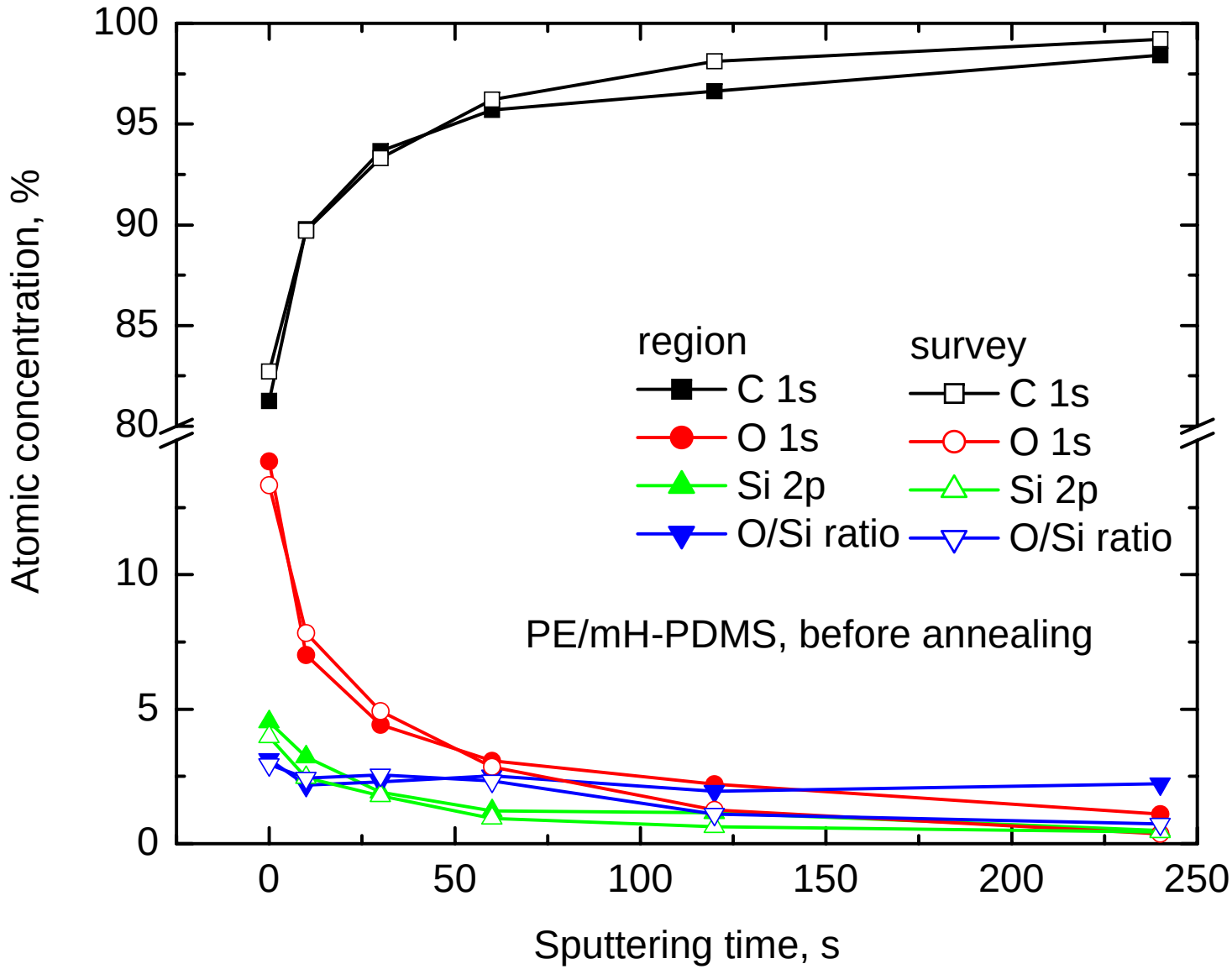
Depth profile of PP/dH-PDMS sample before annealing.



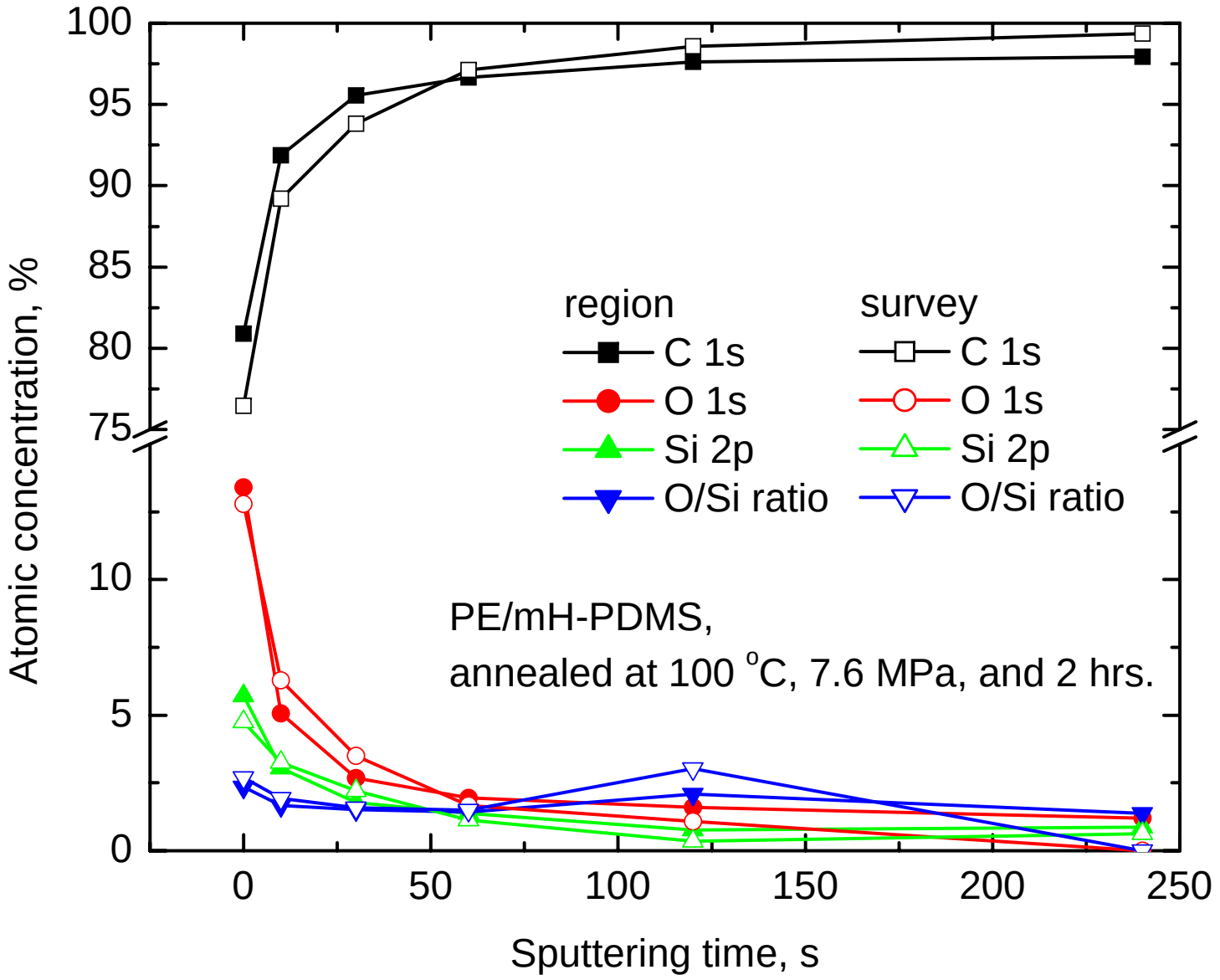
Depth profile of PP/dH-PDMS sample annealed in $scCO_2$.



Depth profile of PE/mH-PDMS sample before annealing.

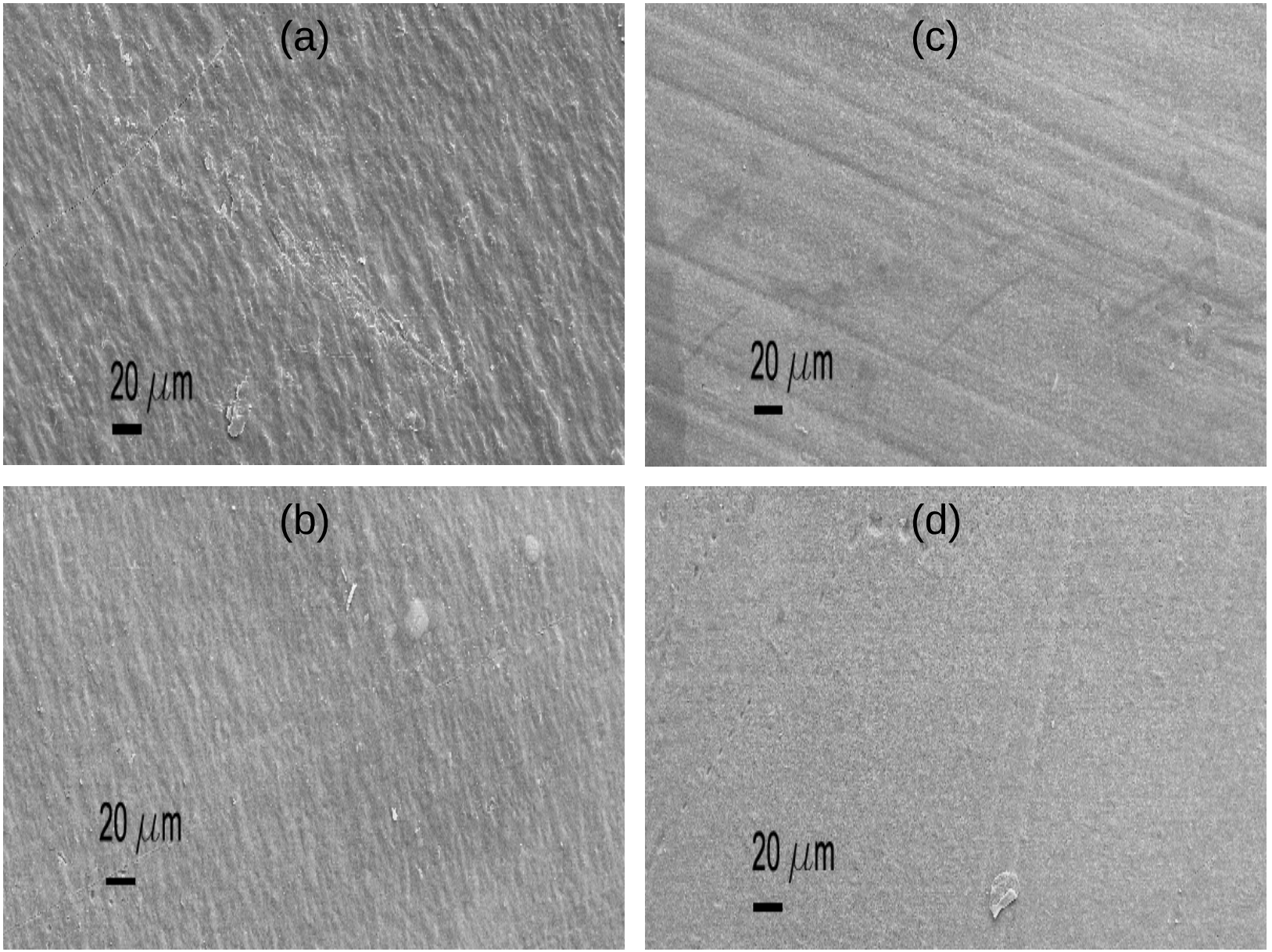


Depth profile of PE/mH-PDMS sample annealed.



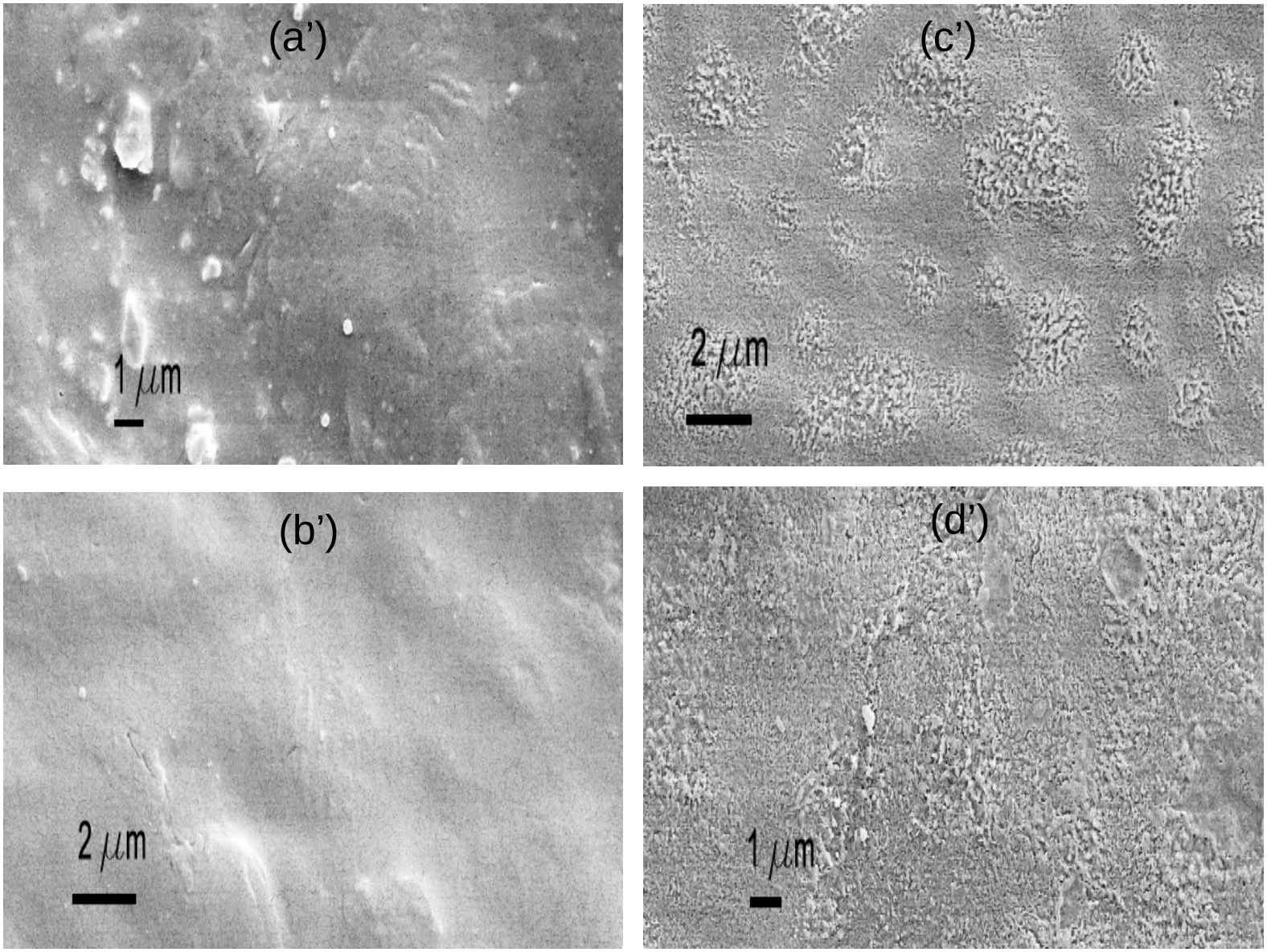
Surface morphology of PP/dH-PDMS sample

(a) before annealing; (b) 100 ^{o}C, 7.6 MPa, 2 hrs;
(c) 150 ^{o}C, 11 MPa, 1 hrs; (d) 150 ^{o}C, 11 MPa, 2 hrs.



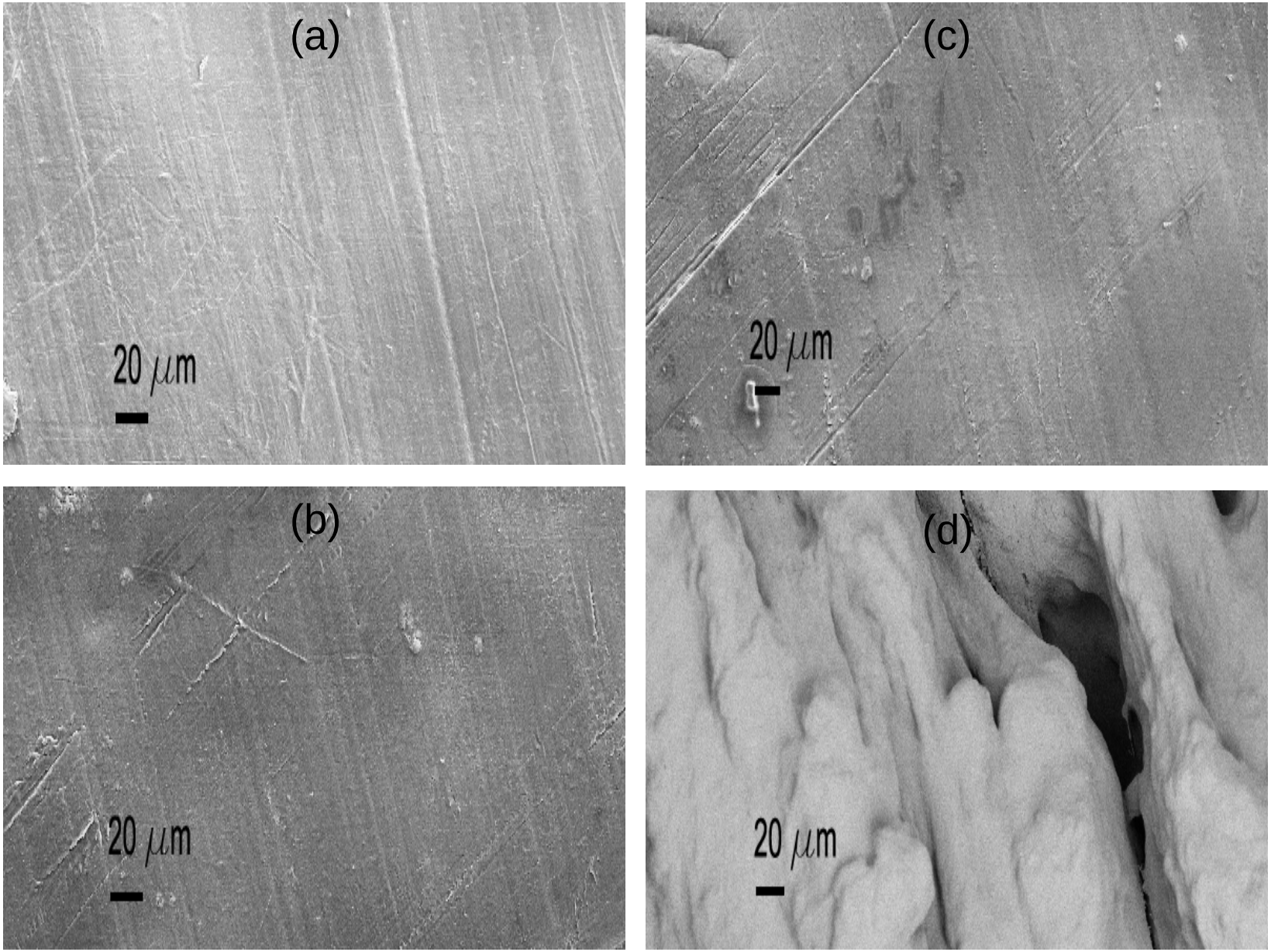
Surface morphology of PP/dH-PDMS sample (cont')

(a) before annealing; (b) 100 ^{o}C, 7.6 MPa, 2 hrs;
(c) 150 ^{o}C, 11 MPa, 1 hrs; (d) at 150 ^{o}C, 11 MPa, 2 hrs.



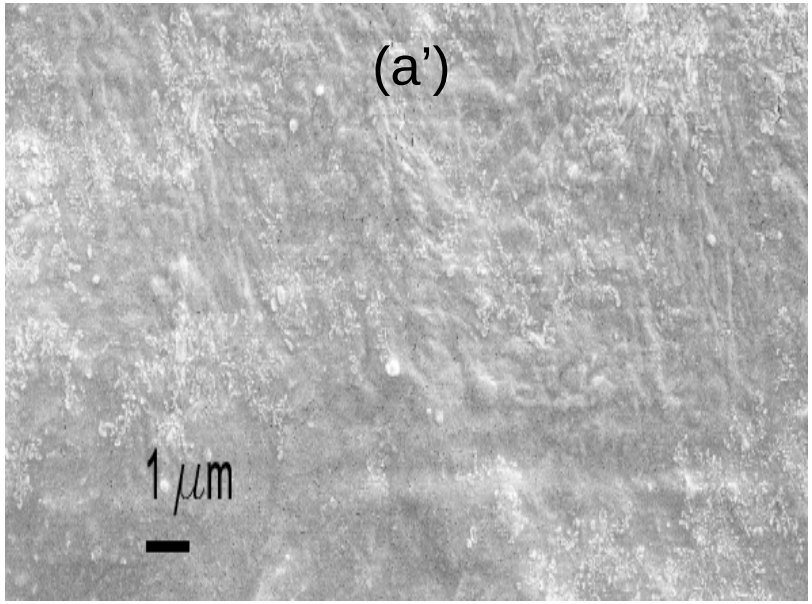
Surface morphology of PE/mH-PDMS sample

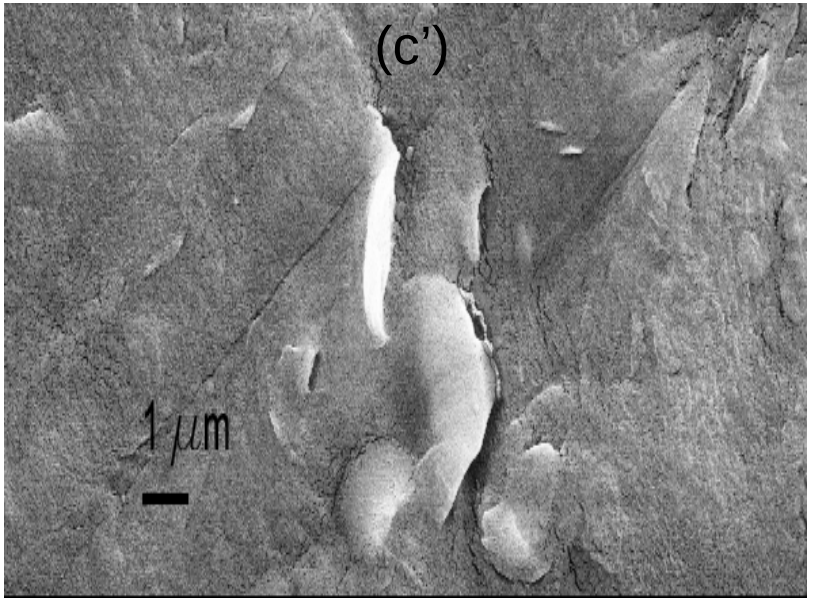
(a) before annealing; (b) 100 ^{o}C, 7.6 MPa, 2 hrs;
(c) 120 ^{o}C 7.6 MPa,2 hr.; (d) 150 ^{o}C, 7.6 MPa, 2 hrs.

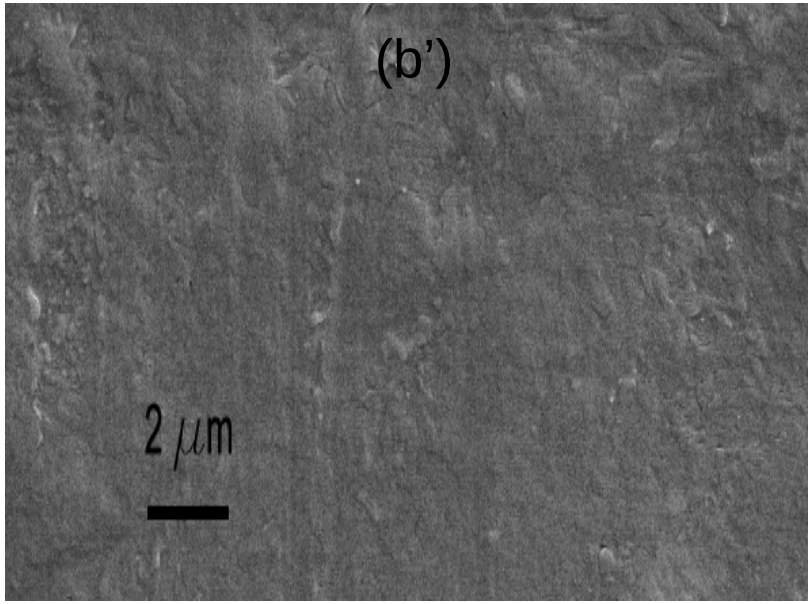


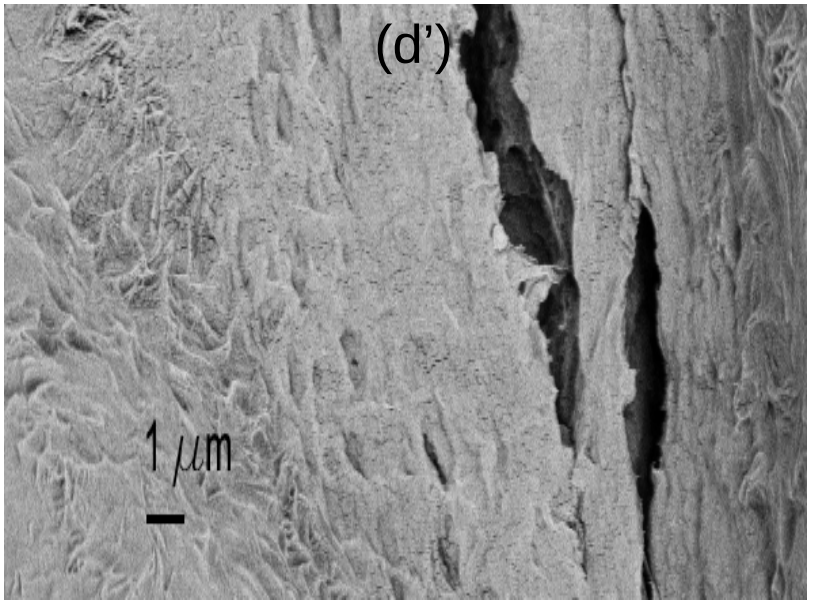
Surface morphology of PE/mH-PDMS sample (cont')

(a) before annealing; (b) 100 ^{o}C, 7.6 MPa, 2 hrs;
(c) 120 ^{o}C, 7.6 MPa, 2 hr.; (d) 150 ^{o}C, 7.6 MPa, 2 hrs.









Effect of annealing temperature on the contact angles of PP/dH-PDMS and PE/mH-PDMS samples

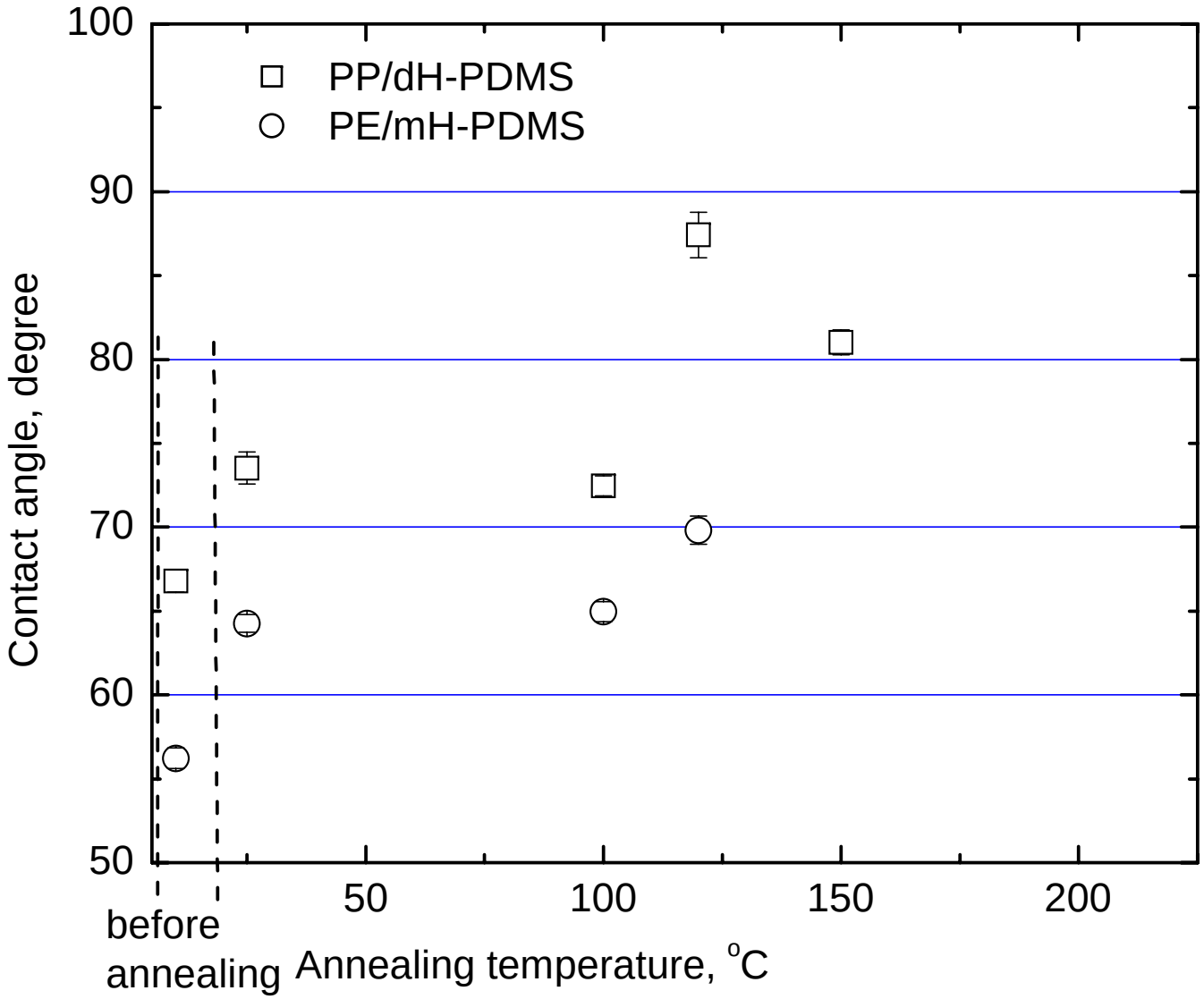


Table 1 Effect of annealing time on the surface properties of PP/dH-PDMS sample

11 MPa; annealing T: 120 ^{o}C

	Contact angle, degree	XPS modes	C	O	Si	F	O/Si
Ref.*	66.8±0.7	survey	84.3	8.6	7.1	-	1.0
		region	83.2	8.4	8.4	-	1.0
t =1 hr.	94.1±1.0	survey	95.0	3.5	1.5	--	1.9
		region	94.6	3.6	1.8		2.0
t = 2hrs.	98.4±1.8	survey	89.6	4.4	2.2	3.8	1.5
		region	92.6	4.5	2.9		1.6

* Before annealing

Table 2 Effect of $scCO_2$ pressure on the surface properties of PP/dH-PDMS and PE/mH-PDMS samples

120 ^oC; time: 2 hrs.

	PP/dH-PDMS							PE/mH-PDMS					
	Contact angle, degree	XPS modes	C	O	Si	F	O/Si	Contact angle, degree	C	O	Si	F	O/Si
Ref.*	66.8±0.7	survey	84.3	8.6	7.1	-	1.0	56.2±0.6	85.6	12.9	1.5	-	8.7
		region	83.2	8.4	8.4	-	1.0		86.2	12.6	1.3	-	9.8
P= 7.6 MPa	81.0±0.7	survey	95.4	4.6	0	-	4.0	69.8±0.8	84.3	11.7	4.0	-	2.9
		region	93.3	5.6	1.1	-	4.9		83.2	12.5	4.3	-	2.9
P= 11 MPa	98.4±1.8	survey	89.6	4.4	2.2	3.8	1.5	60.0±0.6	78.3	10.3	5.1	6.3	2.0
		region	92.6	4.5	2.9	-	1.6		84.4	9.5	6.1	-	1.5

* Before annealing

CONCLUSIONS

- Two hydrosilylated polyolefin compounds are obtained by reacting PP and PE with di-functional and multi-functional hydride-terminated PDMS in melts: PP/dH-PDMS and PE/mH-PDMS. The Si concentration on PP/dH-PDMS sample before the annealing is higher than PE/mH-PDMS sample.
- The Si concentration on the PP/dH-PDMS sample surface changes little up to 120 ^{o}C, drops at 150 ^{o}C, where the SiO_2 particles appear. On PE/mH-PDMS sample, the Si concentration has a maximum value at 100 ^{o}C. Contact angle increases with annealing temperature on both samples.
- The SiO_2 particles on the PP/dH-PDMS surface form patterned clusters at a shorter time and spreads all over the surface at a longer time.
- An increase in $scCO_2$ pressure induces higher Si concentrations on both samples, a larger value of contact angle on PP/dH-PDMS surface, but the opposites PE/mH-PDMS sample.

Acknowledgement

- Funding from NSERC
- Dr. Anle Xue and Ms. Mercy Bulsari in sample preparation