Spin Coating Simulation of PMMA Solution on the Surface of SME NiTi

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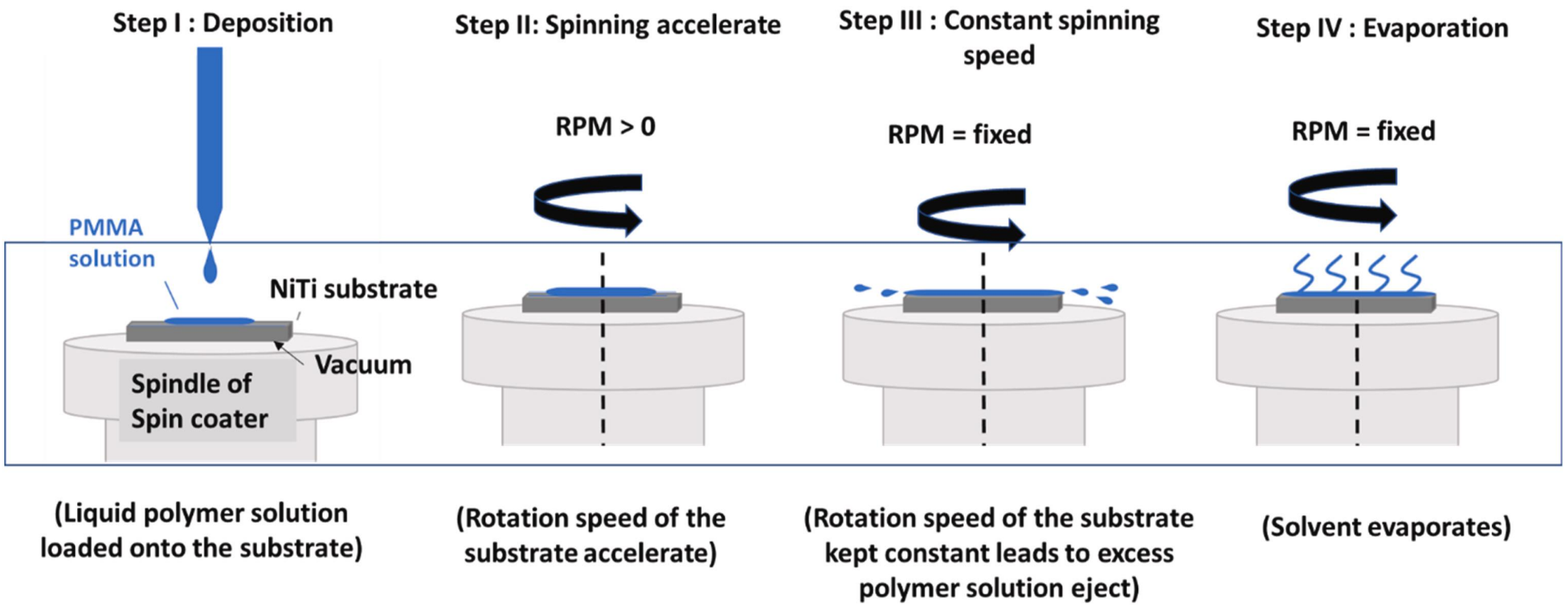
Contents

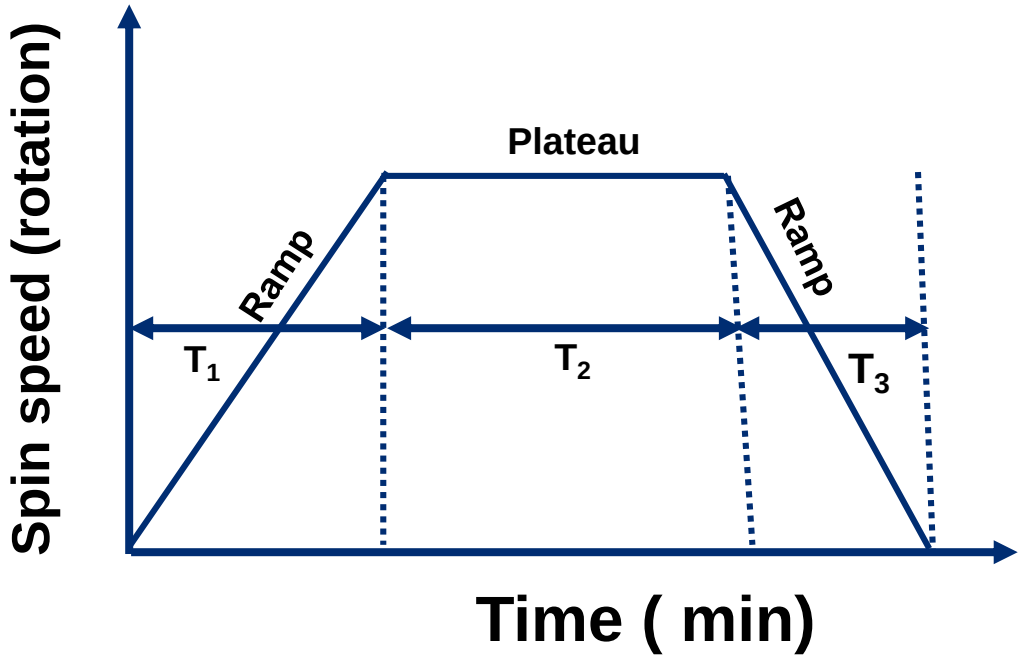
- Introduction about spin coating process
- Process parameters such as time, rotational speed for coating
- Profile behaviour of the coating process
- Internal parameters for simulation
- Model used the surface tension, density and viscosity
- Evaporation is ignored
- Results and discussion
- Conclusion

Overview : Spin Coating process



Surface feature of PMMA films on NiTi alloy substrate by the spin coating method, Ceramics International, Volume 49, Issue 14, Part B, 2023, Pages 24370-24378, ISSN 0272-8842, https://doi.org/10.1016/j.ceramint.2022.10.152.

Spin coating profile



A spin profile with steep ramps (short T1 and T3), and an adjustable short plateau (T2) to attain thicker and at the same time, more homogeneous films.

Table 1. shows Samples prepared by using various parameters for the spin coating method on shape memory NiTi surface.

Samples	Solution (mol. %)	Spin coating parameters	Post curing step	Coating thickness (mm)	Comments
Case *I*	8.3 (Dynamic Viscosity : 6)	Speed: 500 rpm, t: 30 s	RT, air	**0.376 ± 0.052**	Bubble trapped below surface in NiTi channels
Case II	8.3(Dynamic Viscosity : 6)	Speed: 100 rpm, t: 40 s Speed: 500 rpm t: 5 s	RT, air	0.232 ± 0.030	Rough surface with non-homogeneity of polymer
Case III	4.2(Dynamic Viscosity : 2)	Speed: 3200 rpm, 30 s	RT	0.230 ± 0.015	Non-homogeneity at surface
Case IV	4.2(Dynamic Viscosity : 2)	Speed: 500 rpm, 30 s	RT	0.305 ± 0.025	Best sample receive with minimum pin holes

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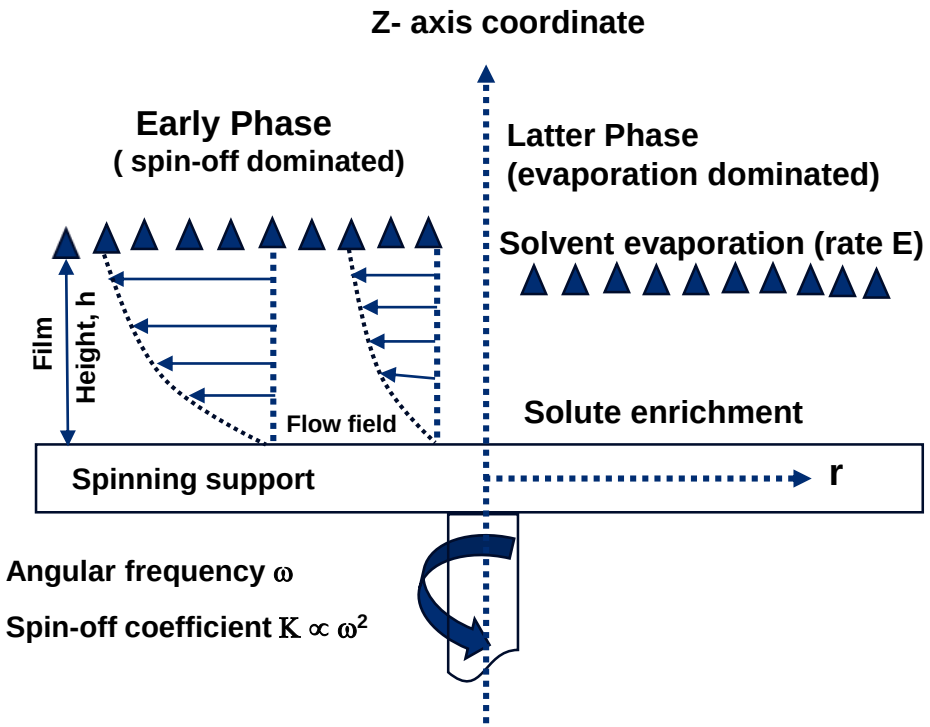
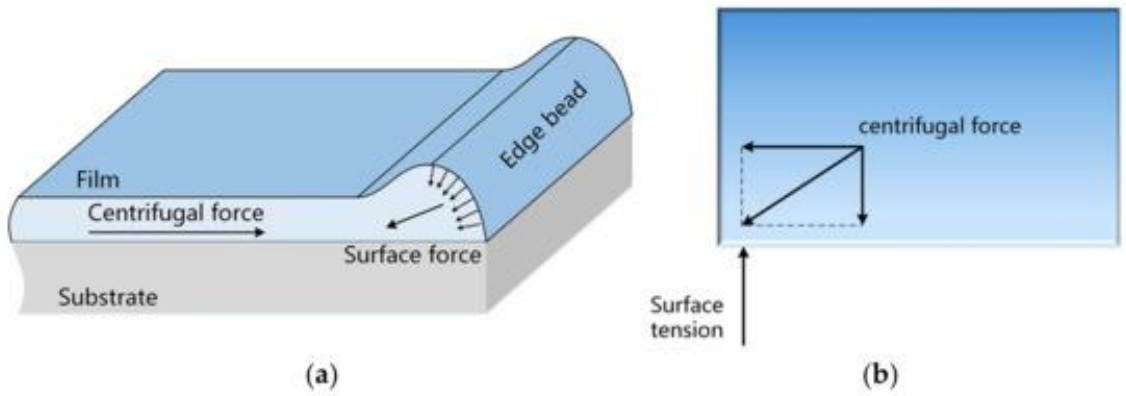
Stages of the spin coating process



Schematics of spin-casting with processes dominating early and late stages

Spin coating animation



The thinning of a Newtonian, volatile liquid film of thickness h on a rotating support is described by Meyerhofer (1978): $^{dh}/_{dt} = -2Kh^3 - E$ (1)

$K = {}^{\omega^2}/_{(3\gamma)}$, ω = rotational speed, ν= kinematic viscosity and E = evaporation rate.

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The total spin cast time for film thinning from h $\longrightarrow \infty$ to h = 0.

$$t_{sc} = \left({}^{2\pi}/_{3^{3}/_{2}}\right)\left(2E^{2}K\right)^{-1/3} \qquad (2)$$

E and K also determine the "transition height" h_{tr} , which identifies the film thickness of the transition from film thinning dominated by hydrodynamics to thinning dominated by evaporation

$$h_{tr} = \left({}^{E}/_{2K}\right)^{1/3} \qquad (3)$$

Because at thicknesses of less than h_{tr} film thinning is mostly due to evaporation, most of the solute, which is contained in the film of thickness h_{tr} (with a solute concentration approximately equal to the weighing in concentration x_0), is finally deposited on the substrate. This leads to the final film thickness

$$h_f = \chi_0 \frac{\rho_L}{\rho_S} h_{tr} = \chi_0 \left(\frac{3E\gamma}{2\omega^2}\right)^{1/3} \approx 0.8\chi_0 \left({}^{K}/_{E}\right)^{-1/3} \qquad (4)$$

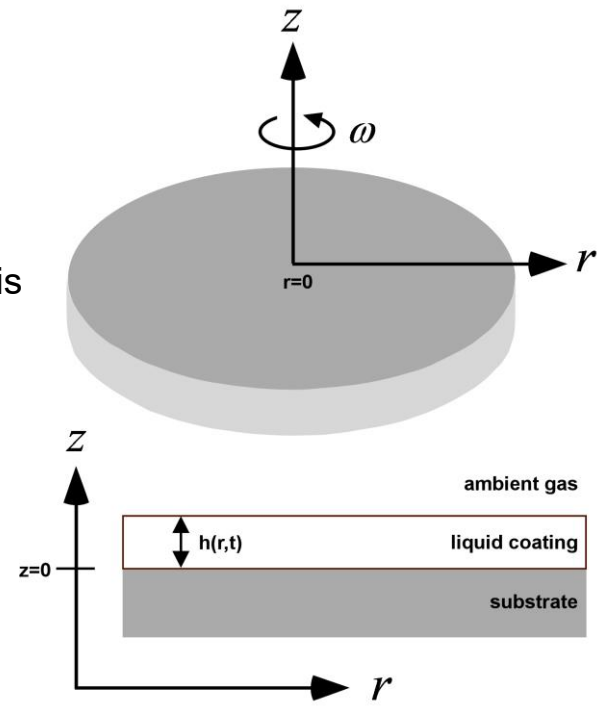
In general, the thickness of a spin coated film is proportional to the inverse of the square root of spin speed as in the below equation where ω is angular velocity/spin speed and h_f is final film thickness.

$$h_f \propto \frac{1}{\sqrt{\omega}} \qquad (5)$$

Emslie, Bonner, and Peck Model

For a non-volatile, viscous fluid on an infinite rotating disk, Emslie's model as

$$\frac{\partial h}{\partial t} + \frac{\rho\omega^2 r}{\eta} h^2 \frac{\partial h}{\partial r} = -\frac{2\rho\omega^2 h^3}{3\eta} \qquad (6)$$



Here t is time since the start of the process, ω is angular velocity, r is the distance from the centre of rotation, ρ is the density, η is the viscosity and h is thickness of the fluid layer, (rather than the dry thin film). Here, ∂h/∂t represents the rate of change of thickness, and ∂h/∂r the rate of spreading.

If the film is considered initially uniform, this leads to a description of the fluid film thickness

$$h = \frac{h_0}{\left(1 + \frac{4\rho\omega^2}{3\eta} h_0^2 t\right)^{\frac{1}{2}}} \qquad (7)$$

Here h_0 represents the uniform thickness of the film at the start of the process (i.e. t=0). As this model does not account for evaporation, it cannot be used to calculate the exact thickness of the final dry film. An approximate dry thickness can be calculated from fluid film thickness by using the concentration of solute and solution density.

Meyerhofer Model

To include evaporation effects was published by Meyerhofer who modified the equations of Emslie, Bonner, and) with the inclusion of a solvent evaporation rate:

$$\frac{dh}{dt} = -\frac{2\rho\omega^2 h^3}{3\eta} - E \qquad (8)$$

Here *E* is the uniform solvent evaporation rate, in units of solvent volume evaporated per unit area per unit time.

Spin coating process, flow dominates the thinning process of the film (spin off); whereas later in the process (when the film is thinner and flow is slow), thinning is mainly due to evaporation. Meyerhofer also established that if the transition from fluid thinning to evaporation thinning is abrupt, then the film thickness can be estimated analytically – where it is assumed that the film is thin enough to ensure solvent concentration remains uniform through the depth of the film. This transition point will clearly be the point at which thinning by flow is equal to thinning by evaporation: The transition point between fluid thinning to evaporative thinning

$$E = \frac{(1-C)2\omega^2\rho h_0^3}{3\eta} \quad (9)$$

This gives the final film thickness as:

Where *C* is the volume fraction of solute in the film and h_0 is the film thickness at the transition between the two film-thinning regimes.

$$h_f = \left(\frac{3\eta_0 E}{2(1-C_0)\rho\omega^2}\right)^{\frac{1}{3}}$$

(10) for final dry film thickness from evaporation rate

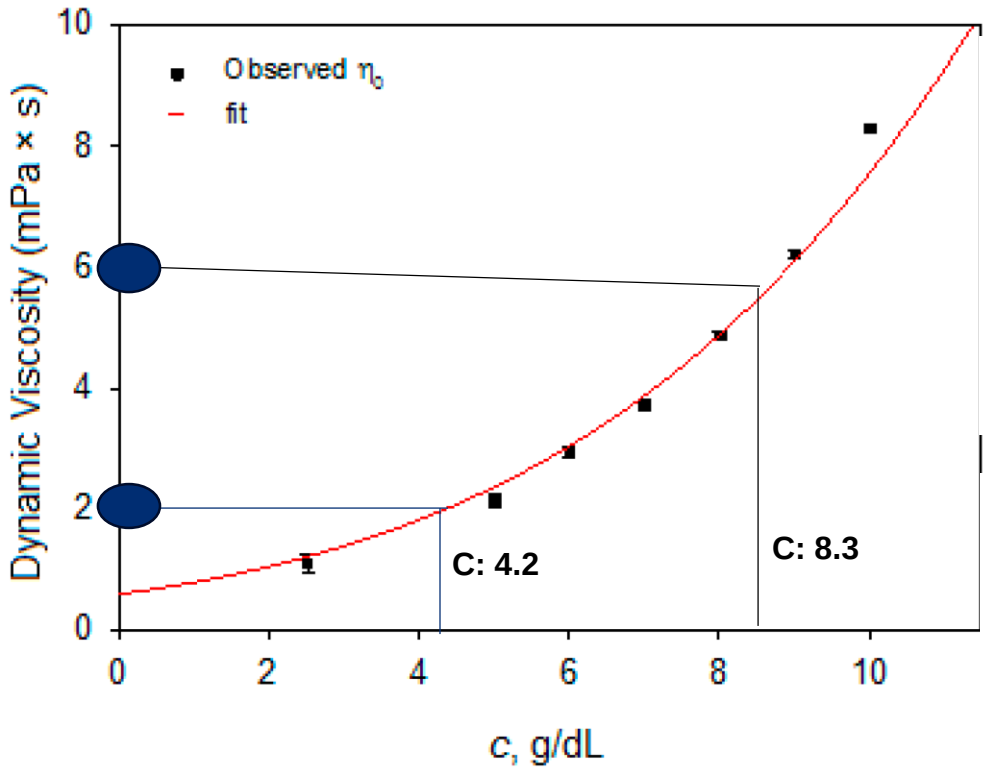
Where C_0 is the initial concentration of solute, and η_0 equates to $\eta(C_0)$. The concentration of solute is assumed to remain at C_0 until the transition of evaporation-driven thinning begins. Final spin coating film thickness can also be calculated without the solvent evaporation rate. This can be done by making several assumptions, including the assumption that air flow remains laminar during the process. This gives an overall equation as:

$$h_f = \left(\frac{3}{2}\right)^{\frac{1}{3}} k^{\frac{1}{3}} C_0 (1-C_0)^{-\frac{1}{3}} \rho^{-\frac{1}{3}} \eta_0^{\frac{1}{3}} \omega^{-\frac{1}{2}}$$

(11) for final dry film thickness without evaporation rate

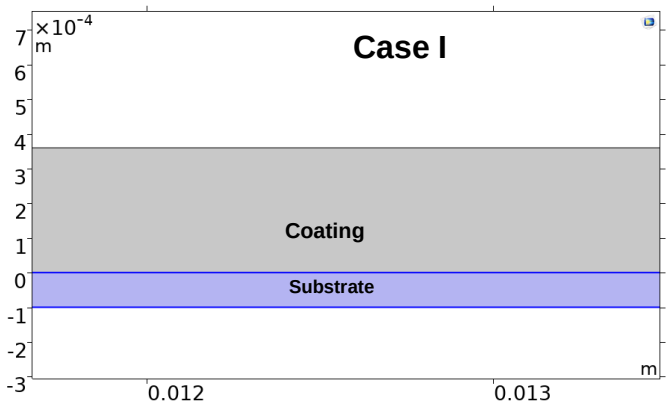
Meyerhofer's equation for final dry film thickness without evaporation rate . Where *k* is a constant specific to the coating solvent and for typical spin coating solvents $k \approx 1^{(-5)} cm/s^{(-1/2)}$

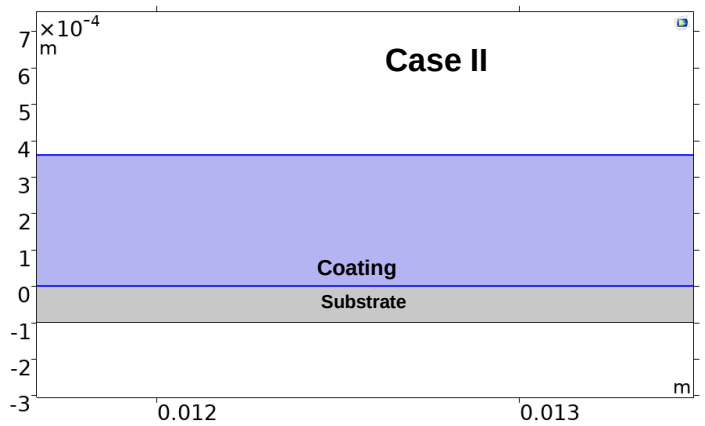
Dynamic viscosity as a function of spin-coating solution concentration

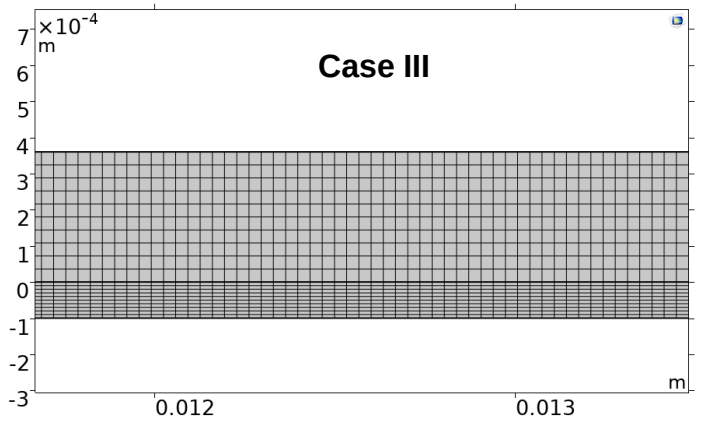


Input Parameters

Mu	2, 6[mPa*s]	0.002 -0.006Pa·s	Dynamic viscosity
Rot	100, 500, 3200[rpm]	1.6-8.3333 1/s	rotational speed
dsubstrate	4[in]	0.1016 m	NiTi diameter
sigma	0.07[N/m]	0.07 N/m	Surface Tension
rho0	1150[kg/m^3]	1150 kg/m³	Density
h0	360[um]	3.6E-4 m	Initial thickness
h1	100[um]	1E-4 m	SME Thickness







2D axisymmetric
Two-phase flow, moving mesh
- laminar flow
  - Turn on *Swirl flow* and set the rotating speed of the wafer
- Moving mesh
  - *Free surface*, surface tension 0.07 N/m, contact angle 90 degrees

Substrate (NiTi) diameter is 4 inches, initial thickness of PMMA is 205-360um
Parametric scanning
- Rotate Speed: 100/500/3200 [rpm]
- dynamic viscosity: 2/6 [mPa · s]

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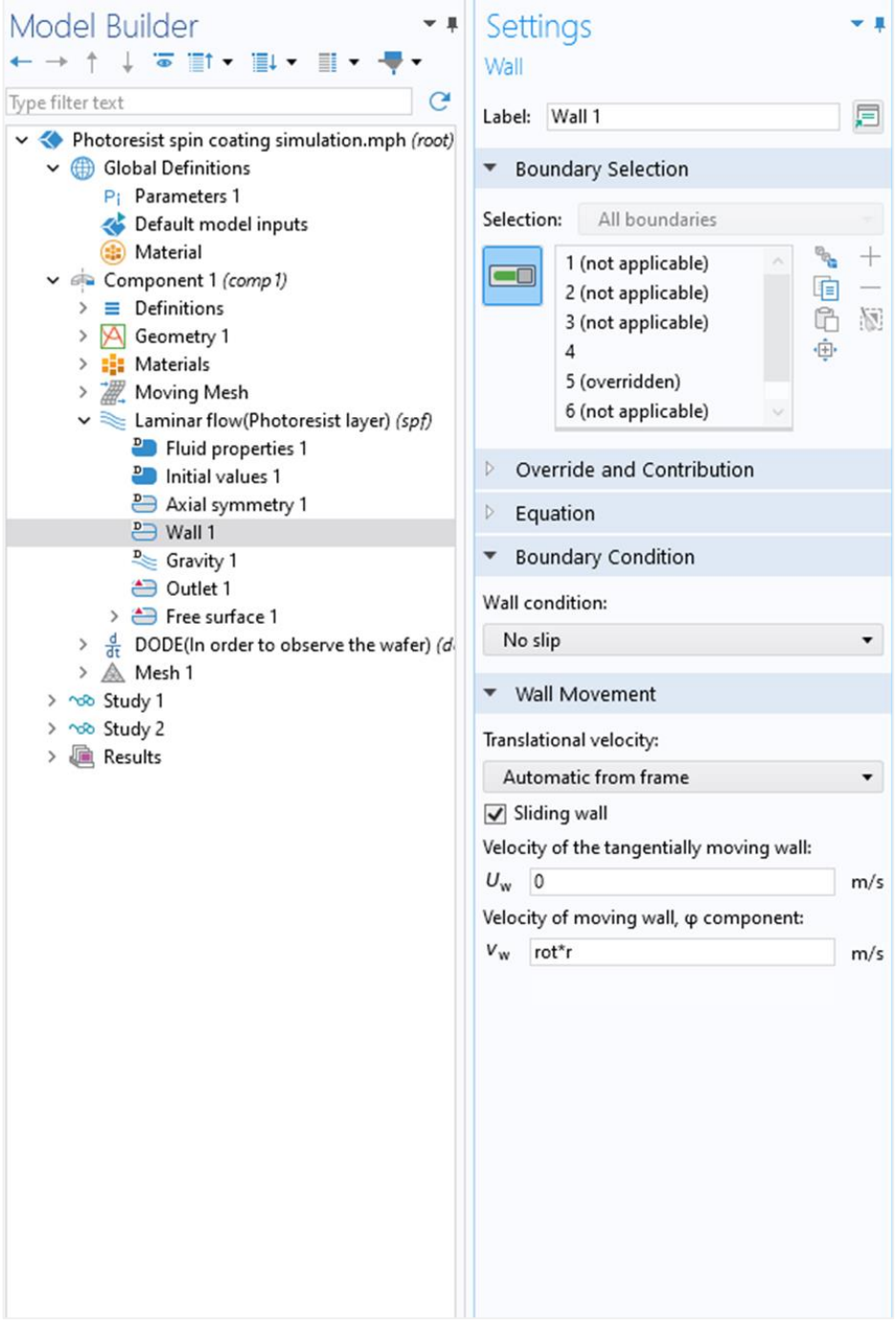


Model Setup

2D axisymmetric, laminar model

Two-phase flow, moving mesh

laminar flow

Turn on *Swirl flow* and set the rotating speed of the substrate

Moving mesh

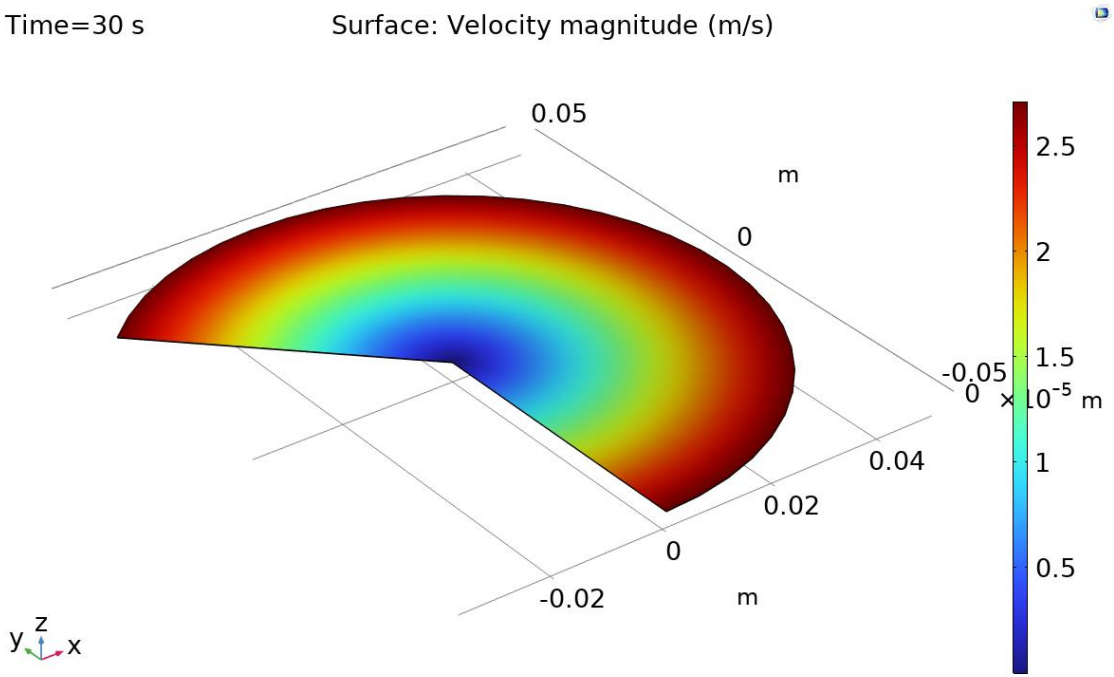
***Free surface*, surface tension 0.07 N/m, contact angle 90 degrees**

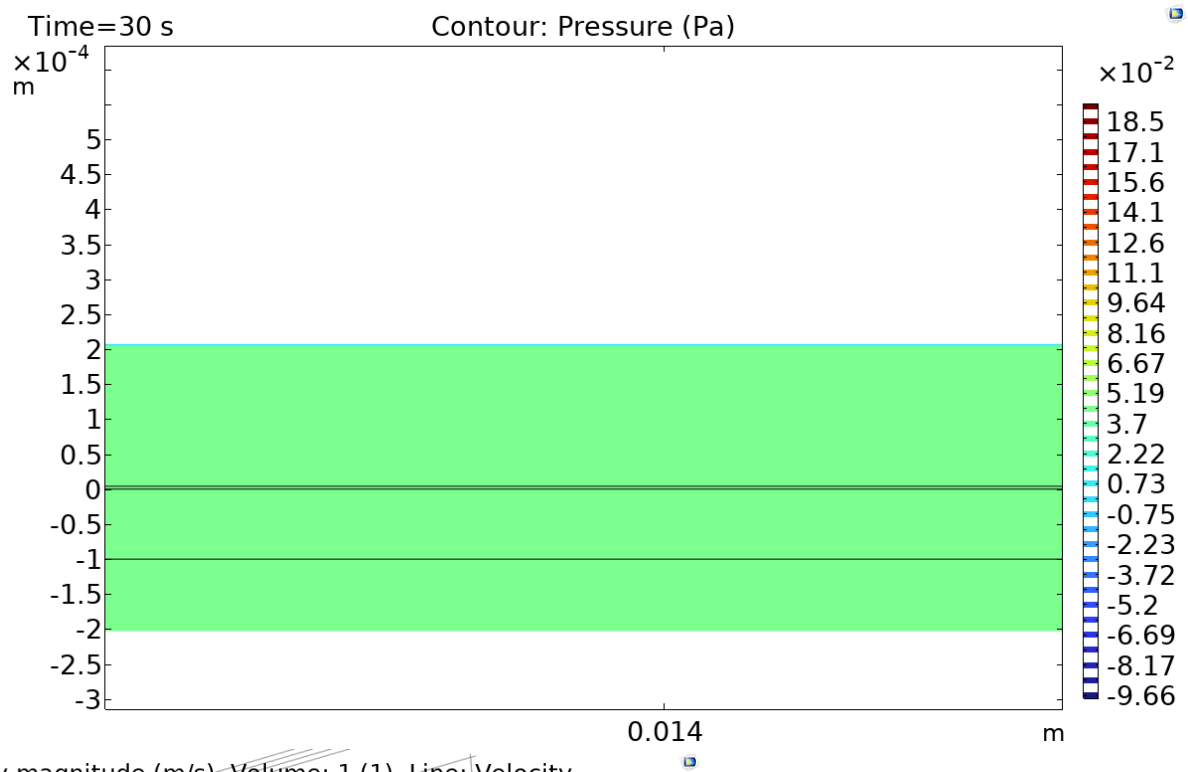
Substrate diameter is 100 μm, initial thickness of coating is 320 um

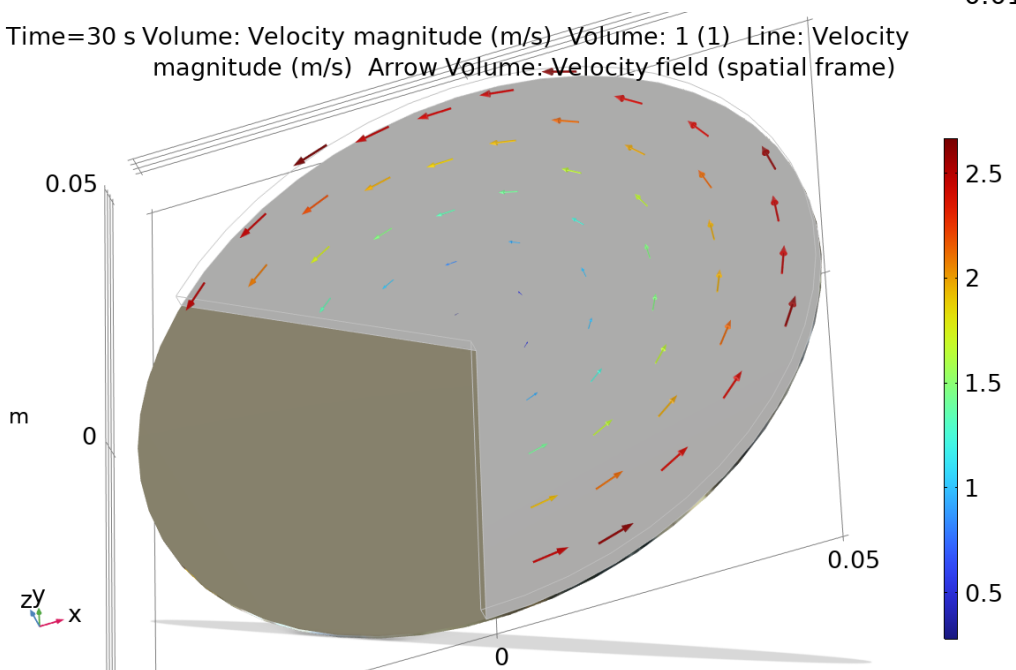
Parametric scanning

Rotate Speed: 100/500/32000 [rpm]

dynamic viscosity: 2/6 [mPa · s]







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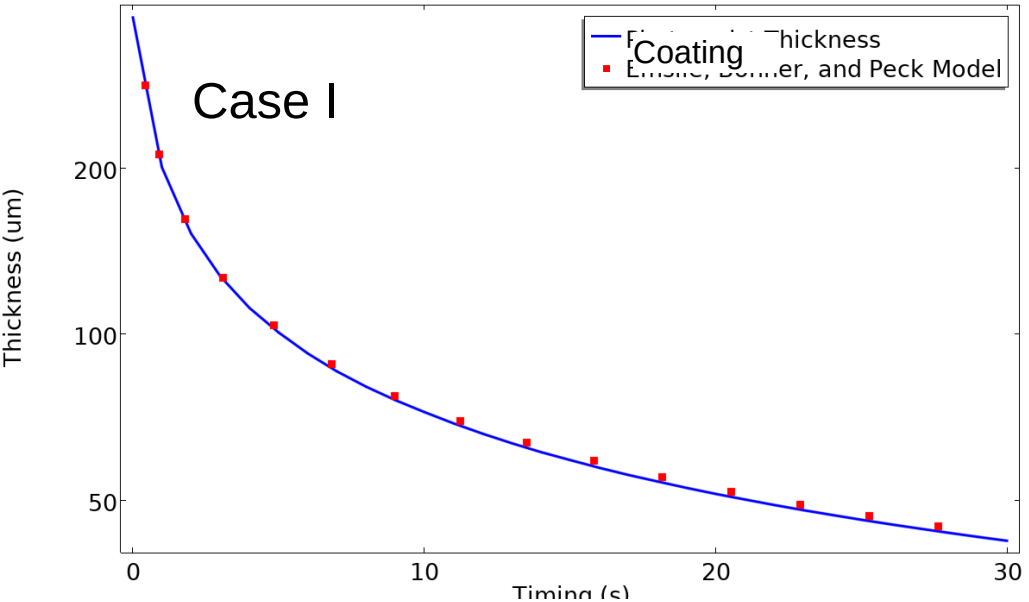

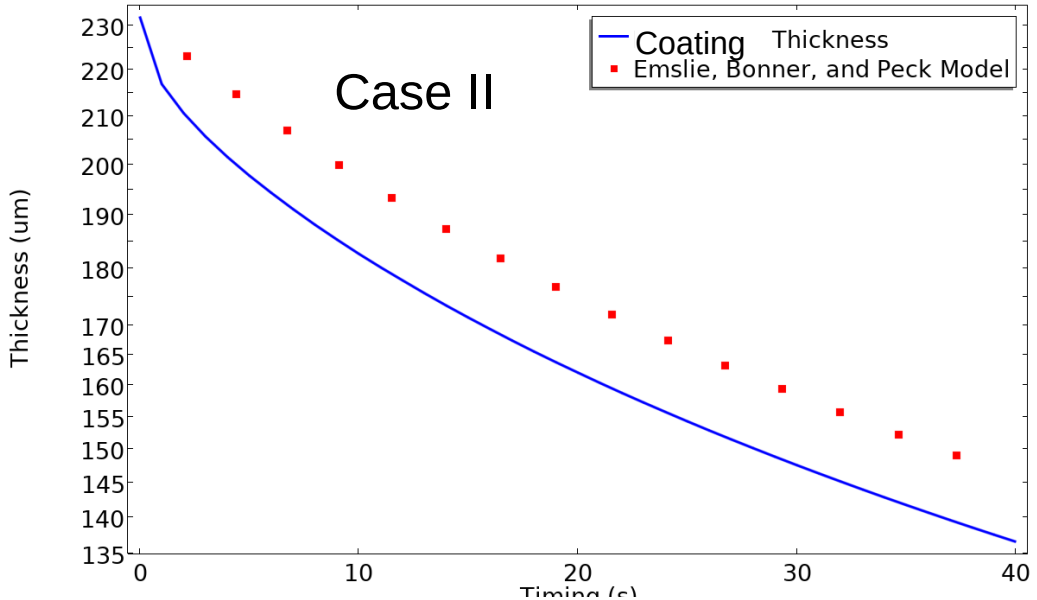

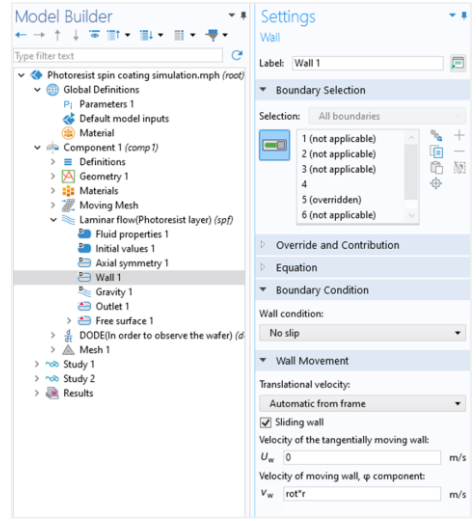

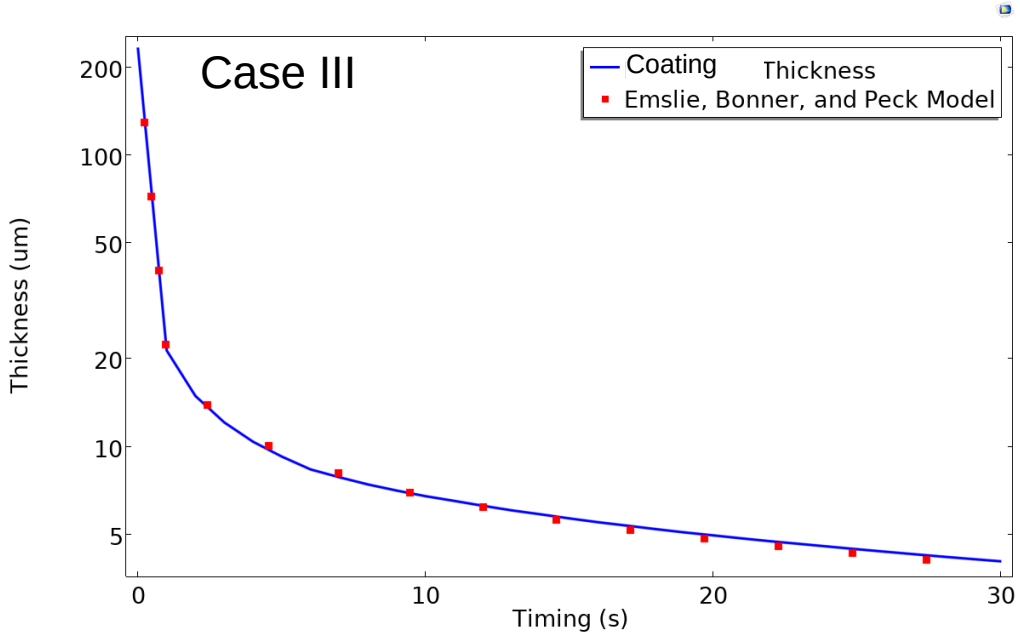

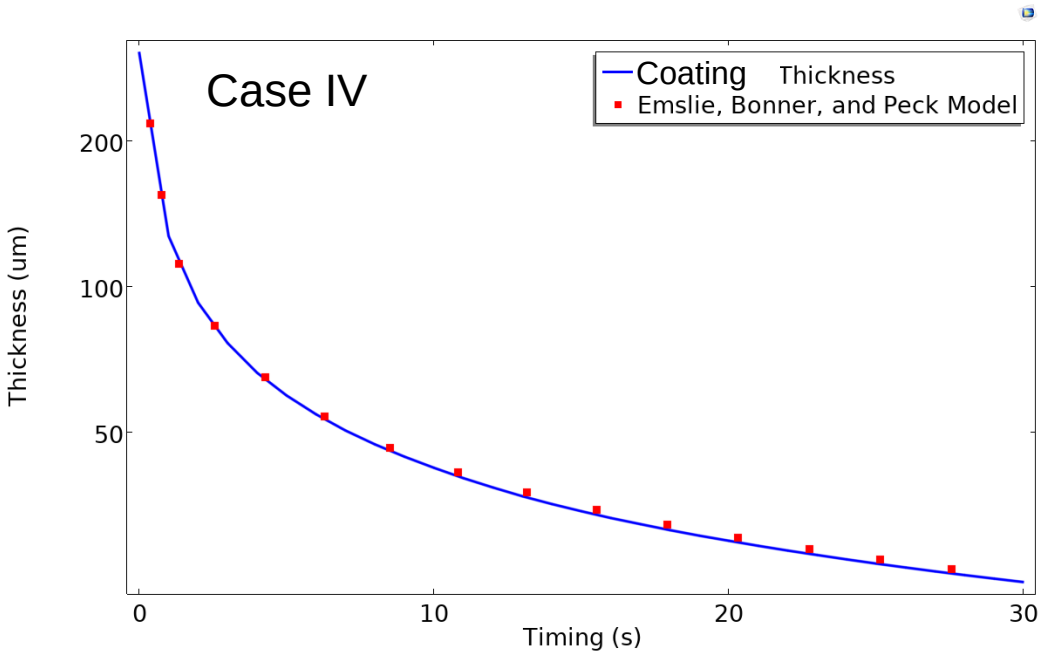

As the substrate rotates, the solution is thrown out from all around, and the thickness of the coating layer gradually becomes thinner
Consistent with theoretical results

Emslie, Bonner, and Peck *

$$h = \frac{h_0}{\left(1+\frac{4\rho\omega^2}{3n}h_0^2 t\right)^{\frac{1}{2}}}$$

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Summary

- Simulated PMMA spin coating process by laminar flow and moving mesh in COMSOL
- PMMA layer gradually becomes thinner with rotation, consistent with experimental results
- The smaller the viscosity, the faster the rotational speed, and the thinner the coating layer such as case III (Dynamic viscosity 2 and rotation : 3200 rpm, thickness of 230 μm. The optimum is at
- PMMA with toluene solution is treated as a Newtonian fluid without considering shear thinning/thickening effects and the influence of temperature.
    - If there is a non-Newtonian effect, a non-Newtonian constitutive should be used.
- The evaporation of solvent has not been considered.
    - If necessary, an evaporation flux should be added to the free surface.

Thank you

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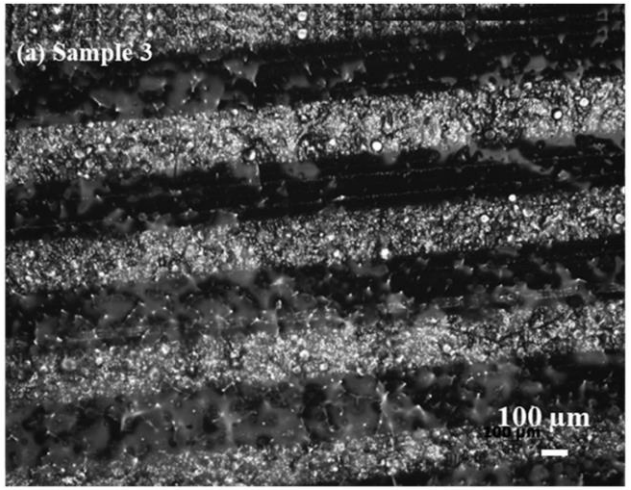
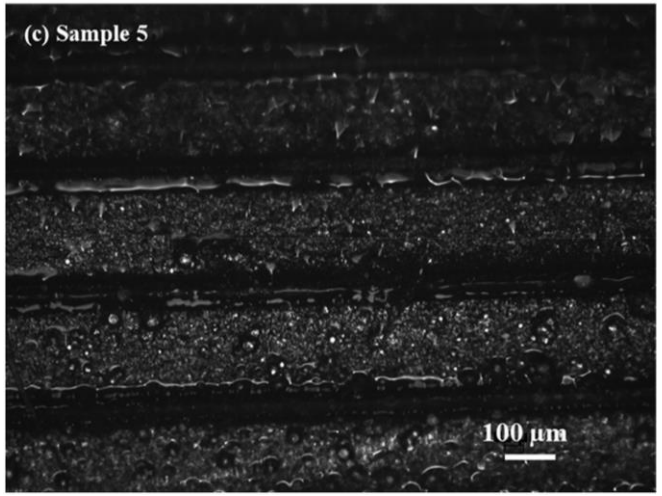
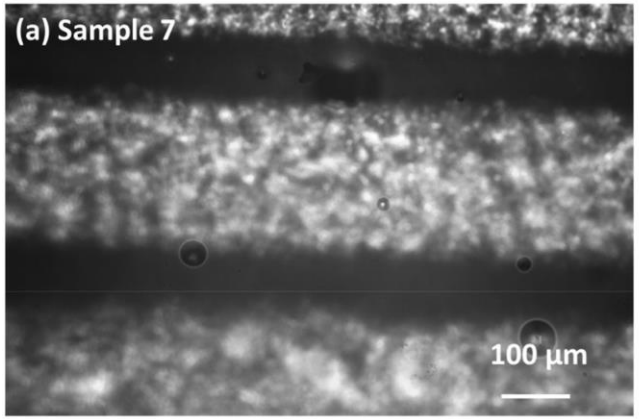
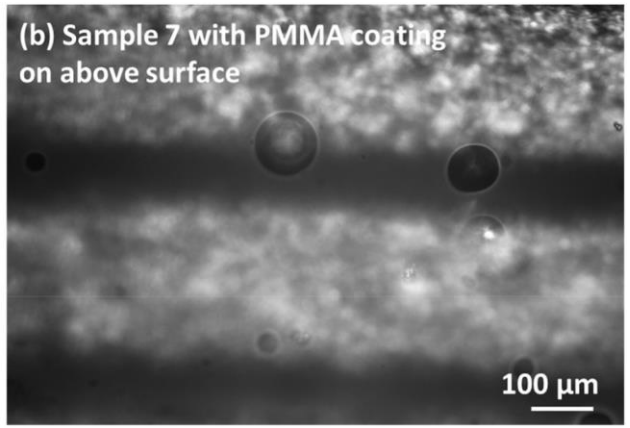
PMMA-coated NiTi surface with 8.3 mol. % solution at RT

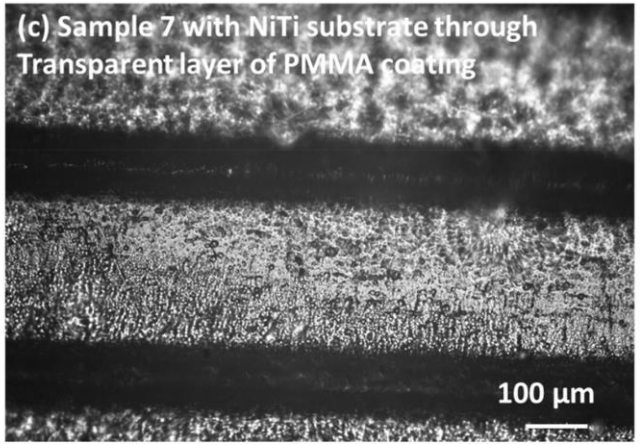


PMMA coated NiTi surface with laser lines at 4.2 mol % at RT









(a)PMMA coating on NiTi surface (b) PMMA coating with some pin hole on the top surface (c) NiTi surface through a transparent layer of PMMA coating (4.2 mol. %), 500 rpm.

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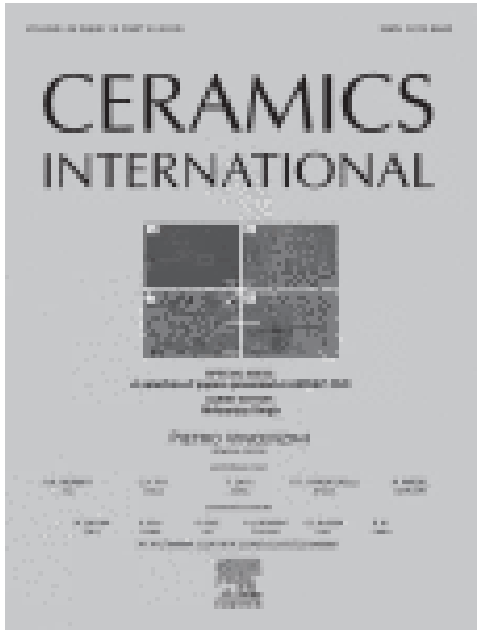

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Surface feature of PMMA films on NiTi alloy substrate by the spin coating method

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Abstract

Polymethylmethacrylate (PMMA) films are deposited on NiTi shape memory alloy by using the spin coating method. Different ratios of PMMA powder to Toluene were mixed with magnetic stirrer for a duration of 12 h. The various concentrations of solution (mol. %) were used for the spin coating method on the substrate NiTi to produce thin films. The samples were cured in various environment from room to furnace temperature. The surface features of PMMA films were investigated by using an optical microscope. Thermal and mechanical behavior of the NiTi substrate and composites was and studied in the paper. The spin coating and post-processing conditions determined the surface morphology that is featureless or dominate by pinholes and other surface defects. The spin-coated coating at 200 rpm improved film surfaces with 4 mol % PMMA solution. Surface defects in the form of pinholes appear on the surface of the film obtained by spin-coating at 3200 rpm from 8 mol % solution and post-baked at 80 °C for 60 min on a hot plate in an oven inside a vacuum chamber. Different coating properties depends on the preparation parameters by spin coating and thermal and microstructural, mechanical properties are explained and discussed in the paper.