X-ray Reflectivity Evaluation of the Thermal Cycling Effects in Methylcellulose Thin Films

Vallerie Ann Innis-SAMSON[1] and Kenji SAKURAI*[1,2]

[1]University of Tsukuba, Tsukuba, Ibaraki, JAPAN
[2]National Institute of Materials Science (NIMS), Sengen, Tsukuba, Ibaraki, JAPAN
Fax: 81-029-859-2821, e-mail: sakurai@yuhgiri.nims.go.jp

Changes in the layer thickness and roughness of as-prepared methylcellulose (MC) films with thermal cycling were studied using the X-ray reflectivity technique. It was found that thermal stress induced by rapid and slow thermal cycling brings no apparent changes in the surface and interface roughness after thermal cycling. On the other hand, some reduction of layer thickness was observed. With rapid thermal cycling, the relative shrinkage of the films is much higher at a maximum of 5% change at 15 cycles. With slow thermal cycling, it remains at a maximum of 3.6% even after 20 thermal cycles. Such film shrinkage is highly dependent on the initial film thickness and the amount of absorbed water molecules in the film.
Key words: thermal stability, thermal cycling

1. INTRODUCTION

Methylcellulose (MC) is a chemical compound derived from cellulose and exhibits temperature-related inverse solubility and gelation behavior in aqueous solution. It is also known to exhibit thermoreversible volume phase separation in water at a lower critical solution temperature (LCST) of ~70°C [1]. At the LCST, polymer chains undergo a coil to globule transition in solution due to increased hydrophobic dehydration. In thin film geometry, some previous reports [2,3] have pointed out that water molecules are still trapped/absorbed in an MC thin film at room temperature because of the hydrophilic nature of the polymer and its low moisture vapor transmission rate. The amount of such water remaining in the film is extremely important, because it can affect the property of the MC thin film, particularly with regard to the temperature dependence of the surface and the interface.

On the other hand, the thermal stability of the film structure is of great importance, because thermal stress can be induced due to the difference in thermal expansion coefficient between the polymer layer and the substrate. It is also possible to modify or enhance certain properties such as alignment of polymer chains along a certain direction and electrical conductivity [4,5]. We have previously reported the thermal stability of MC thin films heated at the supposed phase transition temperature for volume phase separation in solution, 70°C, then quenched to room temperature [6]. X-ray reflectivity (XRR) measurements before and after the heating process showed no significant change, indicating that the MC thin film is quite stable in terms of the parameter obtained from XRR, i.e., the density, the layer thickness, the roughness of the surface and the interface between the polymer layer and the substrate. However, the next question is what happens when heating and cooling are repeated.

In the present study, we applied thermal cycling to the MC thin films to investigate further the thermal stability of the films if subjected to thermal stress brought about by thermal cycling and also to ascertain if thermal cycling can contribute to desorption of the water molecules in the film. Thermal cycling of MC films was done at both slow and rapid heating/cooling rates for different numbers of cycles and the films were measured by XRR.

2. EXPERIMENTAL

Analytical grade MC polymer powder (with degree of substitution (DS): ca. 1.6-1.9 and molecular weight (MW): 4×10^4 gmol^{-1}) from Sigma-Aldrich Inc. was used without further purification. An MC solution with a concentration of 0.5% w/v was prepared in distilled water via hot water dispersion and cold water dissolution. 60 μl of the solution (with a temperature of ~10°C) was pipetted onto a clean Si substrate and spin-coated at a final speed of 5000rpm for 30 seconds. The prepared MC thin films were stored in a dessicator for 24 hours prior to measurement by XRR to obtain data before thermal cycling. Thermal cycling was done by heating the films to 80°C at a specified ramp rate, kept at 80°C for 10 minutes, then cooled down to 25°C and kept at 25°C also for 10 minutes before starting the next cycle. Thermal cycling was done continuously for each film between 25°C-80°C. Slow thermal cycling was done in a vacuum oven (AS ONE AV0-250N), without a vacuum, at a heating rate of ~1°C/min while the cooling rate was ~1°C/3min. Vacuum heating was not done in order to facilitate comparison with rapid thermal cycling, which was done in open air with the use of a home-built Peltier-controlled heating stage. The heating and cooling rate was ~10°C/min.

XRR measurements of the films were done after thermal cycling (that is back to 25°C) using a home-built X-ray reflectometer with a θ-2θ geometry and Cu as the target. The incident X-ray energy used was Cu-Kα₁ monochromatic X-rays 8.048keV (λ=1.541Å). The data analysis was done based on least-squares fitting [7,8] to

Parratt's theoretical reflectivity. Further details of the procedure are described elsewhere [6].

3. RESULTS AND DISCUSSION

Shown in Figure 1 are the XRR profiles of MC thin films subjected to slow heating/cooling cycles for 5, 10, 15, 20 and 25 cycles. Thermal cycling for the specified number of cycles was done on a different film and not continuously on the same film because of the hygroscopic nature of the polymer. In the data fitting of all the XRR profiles, a simple single-layer model on top of the substrate was used. The thin native oxide layer, SiO_2, and some possibly contaminated layers on top of the substrate were neglected, because it was found that finally obtained results are not affected by such layers. The critical angle of MC was observed at around 2.2 mrad, and it agrees well with that calculated from the reported density value of the MC, 1.31 g/cm³. As the angular spread of the present reflectometer is nearly 0.1 mrad (this is mainly limited by the energy resolution of the monochromator), the precision in determining the critical angle at 2.2 mrad will be around 5 %. In our case, detailed simulation to see the shape of the curve in addition to the position of the critical angle indicates that a density value of 1.31 ± 0.06 g/cm³ is reasonable in order to explain all the experimental data obtained in this study. In other words, the density change during thermal cycling at the 25°C-80°C range is not significant, being within 5 %.

The summarized thickness and interface roughness parameters derived from the curve fitting are shown in Table 1 for the slow heating/cooling cycle before and after thermal cycling. In the model fit of the XRR profiles, as previously mentioned, a single-layer model was used and the native SiO_2 layer was entirely neglected. We can assume that the SiO_2 layer does not change with heating at 80°C, which is too low for silicon oxide to grow in an ordinary environment. Polymer films prepared by spin-coating are described as being in a metastable state owing to the fast evaporation of the solvent during spin-coating which leads to frozen-in non-equilibrated chain conformations of the polymer [9]. Thickness changes associated with solvent loss can occur at room temperature over time and ultra-slow structural relaxation is expected [9, 10]. As seen from Table 1, the decrease in the layer thickness of the polymer after 5-10 thermal cycles for MC films is so small that we can just interpret this as no change in layer thickness with this number of thermal cycles. Actually, layer thickness changes of less than 5Å are likely in polymer systems because of the constant absorption/desorption of water molecules or other gas over time.
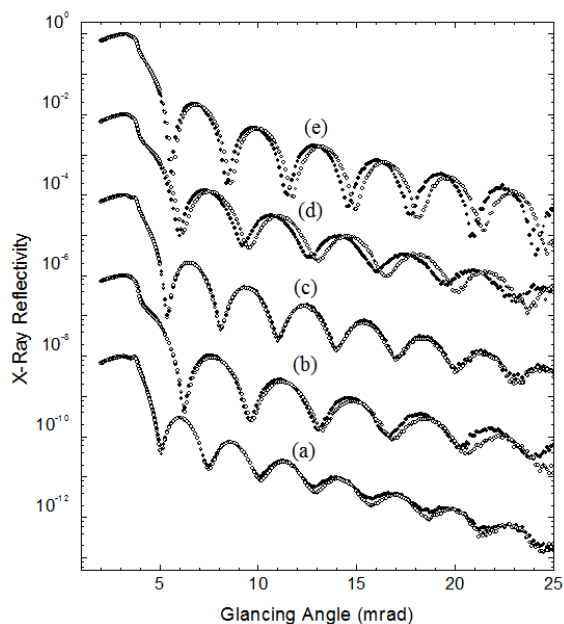

Fig.1   XRR profiles of MC thin films before (closed shapes) and after slow thermal cycling (open shapes): (a) 5 cycles (b) 10 cycles (c) 15 cycles (d) 20 cycles (e) 25 cycles. For clarity, all curves are shifted in the intensity scale.

Significant film thickness change begins only from 20 and 25 thermal cycles which have 3.6% and 2.5% film contraction respectively. The change in thickness of the MC films can be due to desorption of absorbed water molecules in the thin film with heating and structural relaxation of the non-equilibrated polymer chain conformations. The amount of film shrinkage in the slow thermal cycling does not show a systematic dependence on the number of thermal cycles in our study because of the variability of the initial film thickness. The thin films were all spin-coated at the same spin speed and spin time but the final film thickness value varies around 250Å ±15%. Film shrinkage appears to be easily observed in thinner films. This phenomenon has also been described in other polymer thin film systems which can be due to the early onset of structural relaxation in thinner films [11, 12]. The variability of film thickness shrinkage may also be due to the amount of water molecules actually absorbed in the thin film such that the amount desorbed during heating also varies. It is important to note though that MC films do not show significant film contraction

Table 1: Layer thickness d and interface roughness σ_{int} parameters for the XRR profiles of the MC thin films before and after slow thermal cycling.

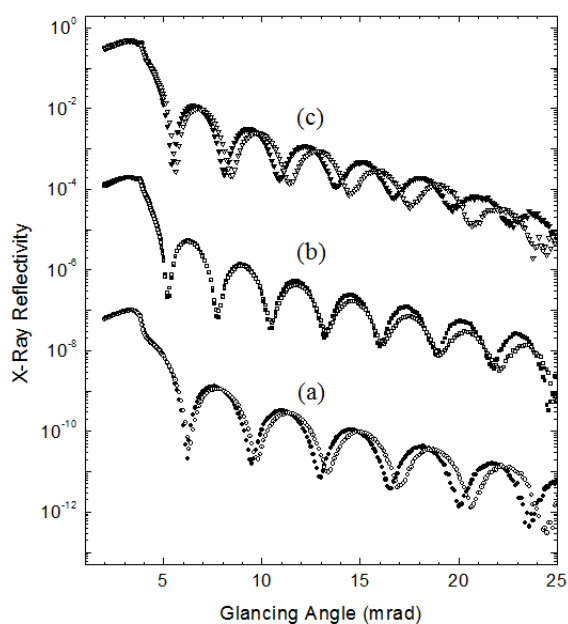| Number of thermal cycles	Before heating		After thermal cycling		Absolute shrinkage	Relative shrinkage
	d_i (Å)	σ_{int} (Å)	d_f (Å)	σ_{int} (Å)	($\Delta d = d_i - d_f$) (Å)	($\Delta d_{rel} = (d_i - d_f) \times 100/d_i$) (%)
5	280	17	278	15	2	0.7%
10	229	15	226	12	3	1.3%
15	254	10	254	10	0	0%
20	221	14	213	12	8	3.6%
25	243	5	237	5	6	2.5%

Fig. 2 XRR profiles of MC thin films before (closed shapes) and after rapid thermal cycling (open shapes): (a) 5 cycles (b) 10 cycles (c) 15 cycles. For clarity, the curves are shifted in the intensity scale.

for 5-15 thermal cycles which means that they retain the solvent (water) and the bound water is not easily removed from the polymer structure. In Table 1, we have included the values for absolute shrinkage and relative shrinkage of the thin films. Absolute shrinkage relates to the solvent loss of the film while relative shrinkage relates to the solvent loss per unit of thickness. Relative shrinkage for the slow thermal cycling even after 20 and 25 thermal cycles is less than 5%. Such thermal stability and very slow solvent loss in the MC thin film is ideal for applications that require moisture retention but slow desorption of the absorbed water molecules.

Surface roughness for all the as-prepared films was between 2Å -5 Å. This surface roughness corresponds to a smooth film surface and subsequent evaporation of the solvent with the heating/cooling cycle did not roughen the surface. Surface roughness is dependent on the evaporation of the solvent on the film [13]. Interface roughness is expected to change more with thermal cycling because of the thermal stress generated. However, there appears to be no marked difference in the interface roughness of the film before and after thermal cycling as shown in Table 1. Even with films that have higher interface roughness mainly due to film preparation differences, interface roughness does not become any greater after thermal cycling. This suggests that there is no formation of holes or dewetting centers that will lead to film rupture. This can be interpreted as good thermal stability between the interface of the polymer and the substrate even with accumulated thermal stress due to temperature rise and the difference in thermal expansion between the oxide layer of the Si substrate and the polymer.

In the case of rapid heating/cooling cycles, the change in film thickness is more rapid as shown in Figure 2. The

values for thickness parameter, absolute and relative shrinkage are summarized in Table 2. Change in thickness is more apparent at the 5 and 15 cycle films which have thinner initial film thickness. For the 5 and 15 cycle thin films, relative thickness change is 2.8% and 5% respectively. The slow thermal cycle only showed a maximum relative thickness change of 3.6% at 20 cycles. This means that rapid thermal cycles decrease film thickness earlier than slow thermal cycles. This is because of rapid solvent loss and minimal reabsorption of water molecules in air because of the fast heating and cooling rate. Since measurement after thermal cycling was done at T=25°C, we can say that the contraction with heating is irreversible, which means that the contraction is mostly due to solvent loss. In the study of Orts et. al [14], which reported similar contraction of polystyrene (PS) films upon heating below the glass transition temperature, T_g, the contraction was reversible, that is the films returned to their original thickness at room temperature. The PS films studied were annealed at 90°C to remove all the solvent prior to thermal cycling. Such contraction was attributed mainly to the weakening of the polymer network with moderate heating, which contracts the film. After cooling, the network strengthens again and the original film thickness is regained [9]. In our case, the MC films were not heated to remove all the solvent prior to thermal cycling. This step was omitted in the MC film preparation because prior experiments showed that drying at 80°C for 12 hours or 100°C for one hour did not significantly decrease the film thickness. Only with thermal cycling was significant change in layer thickness observed, especially rapid thermal cycling. The increased thermal stress in the film due to the higher heating rate and the sequential heating and cooling may have dissociated the intermolecular and intramolecular H-bonds within water molecules and/or between water/MC interactions, which resulted in the faster desorption of the bound water molecules in the film.

For the thicker 10-cycle film, relative thickness change is only 1.1%. As previously mentioned, this non-uniform response to thermal cycling might be due to the initial film thickness and the actual absorbed water molecules in the thin film. The 10-cycle thin film was the thickest among the three samples used and thus film response with temperature might be different from the thinner films. For other polymer systems, as-prepared thicker films expand when heated below the glass transition temperature, similar to bulk properties [12]. This might also be the case for thicker MC films for which film expansion can occur instead of film contraction with heating at temperatures below T_g.

Comparing relative shrinkage values for slow and rapid thermal cycling, values for rapid cycling are higher than those for slow cycling. With slow thermal cycling, the time elapsed during the cooling process may have allowed the films to reabsorb water molecules in the surrounding air and thus film shrinkage proceeds at a slower rate. With rapid thermal cycling, films contract easily with rapid evaporation and minimal reabsorption of water molecules in air.

Because of variability in the initial thickness of film used in this study, further investigations into the correlation of film thickness with thermal cycling needs to be done.

Table 2: Layer thickness d and interface roughness σ_{int} parameters for the XRR profiles of the MC films before and after rapid thermal cycling

Number of thermal cycles	Before heating		After thermal cycling		Absolute shrinkage	Relative shrinkage
	d_i (Å)	σ_{int} (Å)	d_f (Å)	σ_{int} (Å)	$(\Delta d = d_i - d_f)$ (Å)	$(\Delta d_{rel} = (d_i - d_f) \times 100/d_i)$ (%)
5	214	6	208	5	6	2.8%
10	270	7	267	9	3	1.1%
15	257	10	244	9	13	5.0%

4. CONCLUSION

The influence of rapid and slow thermal cycling of MC thin films was studied in order to investigate further thermal stability and possible atomic-scale changes due to thermal stress. It was found that MC thin films exhibit only small changes in surface and interface roughness after thermal cycling. On the other hand, due to solvent evaporation and structural relaxation, some clear thickness changes were observed after 20 thermal cycles. In addition, with rapid thermal cycling, relative shrinkage of the films is higher than with slow thermal cycling. A 5% relative thickness change was observed after only 15 thermal cycles. This is because of rapid solvent loss in the film and minimal reabsorption of surrounding water molecules in air. The increased thermal stress in the film due to the higher heating rate and sequential heating and cooling may have dissociated the intermolecular and intramolecular H-bonds within water molecules and/or between water/MC interactions, which resulted in the faster desorption of the bound water molecules in the film. Film shrinkage is highly dependent on the initial film thickness and the actual absorbed water molecules in the film such that there is no clear trend observed with the number of thermal cycles and the magnitude of film shrinkage.

References:
[1] M. Takahashi, M. Shimazaki, J. Yamamoto. *J. Polym. Sci.* B **39**, 91-100 (2001).
[2] A. Gomez, G. Cruz, M.O. Polo, *J. Appl. Phys.* **89** (10), 5431-5437 (2001).
[3] S. Lin, S. Wang, Y. Wei, M. Li, Surface Science **601**, 781-785 (2007).
[4] H. Nomura, M. Asano, *Jpn. J. Appl. Phys.* **34**, 6143-6148 (1995).
[5] S. Lopez, E. Santiago, M. Rojas, D. Contreras, *J. Phys. Conference Series* **167**, 012059 (2009).
[6] V.A.I. Samson and K. Sakurai. *X-ray. Spec.* **38** (5), 376-381 (2009).
[7] K. Sakurai, A. Iida. *Jpn. J. Appl. Phys.,* **31**, L113-L115 (1992)
[8] K.Sakurai and A.Iida, *Adv. in X-ray Anal.* **35**, 813-818 (1992).
[9] G. Reiter, P.G. de Gennes. *Eur. Phys. J.* E **6**, 25-28 (2001).
[10] H. Richardson, C. Carelli, J.L. Keddie, M. Sferrazza. *Eur. Phys. J.* E **12**, 437-441 (2003).
[11] T. Kanaya, T. Miyazaki, R. Inoue, K. Nishida. *Phys. Stat. Sol.* (b) **242** (3), 595-606 (2005).
[12] T. Miyazaki, K. Nishida, T. Kanaya. *Phys. Rev.* E **69**, 022801 (2004).
[13] K. Strawhecker, S. Kumar. *Macromolecules* **34**, 4669-4672 (2001).
[14] W.Orts, J. van Zanten, W. Wu, S. Satija. *Phys. Rev. Lett.* **71**, 867-870 (1993).