Laboratory X-ray reflectivity technique for negative thermal expansion study on polymer thin film

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The present paper presents the observation negative thermal expansion (NTE) in poly vinyl acetate (PVAc) ultra thin film of variety of thickness from 12 nm to 120 nm as shown in Figure 1 A, by laboratory X-ray reflectivity technique. In the previous research,[1] the same materials have been studied to determine the thermal expansion factors near the glass transition temperature (T_g, 31°C). The unusual thermal expansion coefficient has been confirmed with heating and cooling run and shifting of glass transition temperature has been found with the drastic change of thermal expansion coefficient in this thin film system. This time, with the latest improvement of the detector used in the present realtime X-ray reflectivity setup measurement, we have been able to obtain more accurate and detailed datasets. First of all, in the lower temperature side of T_g, the thickness is increasing even in cooling run, and is decreasing in the heating run. Second, it has been found that NTE in PVAc thin film system exhibits clear thickness dependence. In the ultra thin case such as around 12 nm, the thickness continuously decreases during the repetition of cooling and heating cycles. This can be explained by considering that the origin of NTE in polymer ultra thin film system is structure near the interface shown in Figure 1 B. Different to the general NTE in crystal materials which is explained as phase transition or transverse vibration, our proposing model is that two different layer parts contribute the observation of negative thermal expansion in PVAc film system. Bulk liked surface layer performs the normal thermal expansion with temperature, and the interface layer, which is greatly constricted by interface interaction, can shrink or recover with property change in glass transition.

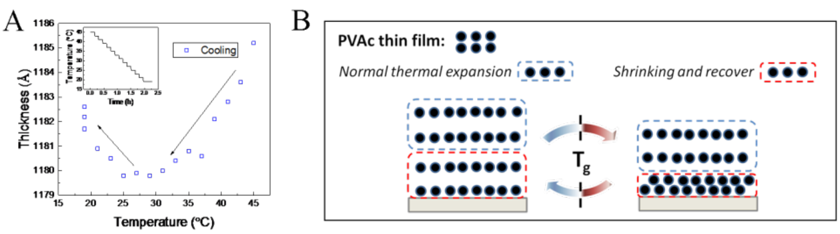

Figure 1. Negative thermal expansion of 120 nm PVAc thin film in cooling run (A), and contribution of interface layer with glass transition (B).

1) M. Mizusawa and K. Sakurai, *IOP Conf. Ser.: Mater. Sci. Eng.*, **2011**, *24*, 012013.