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Suppression of the Tg-Confinement Effect in Thin Polymer Films by the Presence of an Anti-Plasticizer SOYOUNG KIM, MANISH MUNDRA, CONNIE ROTH, JOHN TORKELSON, Northwestern University — The effect of film thickness on the glass transition temperature (Tg) of poly(vinyl acetate) supported on silica was studied via ellipsometry for films that were in the bone-dry state and also with several weight percent water sorbed into the film. The presence of water resulted in a decrease of the Tg of bulk poly(vinyl acetate) films but an increase in the density of the films. This combination of effects indicates that water acts as an anti-plasticizer in poly(vinyl acetate). We demonstrate that the bone-dry poly(vinyl acetate) films exhibit a significant reduction in Tg with decreasing film thickness below about 50 nm. In contrast, the poly(vinyl acetate) films containing several weight percent water exhibited no reduction in Tg relative to bulk Tg with decreasing film thickness down to a thickness of about 10 nm. These results are in accord with recent theoretical analysis (Riggelman et al., PRL 97, 045502 (2006)) indicating that the presence of anti-plasticizers leads to a suppression of confinement effects on the behavior of polymer films and indicate that caution should be employed when studying confinement effects in polymer systems that may sorb significant levels of water from the atmosphere.

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