471a Comparision of the Distributions of Glass Transition Temperatures in Thin and Ultrathin Films of Polystyrene and Polymethylmethacrylate

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A multilayer/fluorescence method has been used to determine the nanoscale distribution of glass transition temperatures (Tgs) in thin and ultrathin film of polystyrene (PS) and polymethylmethacrylate (PMMA) supported on silica substrates. Thus, each film has a free surface (polymer-air interface) and a polymer-substrate interface. When studied as single-layer films, PS and PMMA provide an interesting contrast as, in ultrathin films, the average Tg decreases with decreasing thickness in PS but increases in PMMA films. Using bilayer and trilayer films, where only one layer has a fluorescence dye labeled to the polymer (which reports the Tg of that layer), we show that the decreasing Tg in ultrathin PS films is due simply to a reduction in Tg associated with regions within ~ 30 nm of the free surface. Other regions of the film, including that next to the substrate exhibit bulk Tg. In constrast, bilayer and trilayer PMMA film studies reveal differences with PS films at both the free surface and substrate regions. A bilayer PMMA film consisting of a 25-nm-thick labeled layer next to the substrate and a bulk, unlabeled overlayer exhibits a substrate-layer Tg value that is 10 to 12 K higher than bulk Tg. This increase in Tg is associated with attractive polymer-substrate interactions, that is, hydrogen bond formation between surface silanol units on the substrate and the ester groups in the PMMA repeat unit. A bilayer PMMA film consisting of a 25-nm-thick labeled surface layer with a bulk underlayer exhibits a surface-layer Tg that is decreased relative to bulk, but only by 4 to 6 K instead of the 10 to12 K reduction observed in PS. Thus, while the free surface can lead to a Tg reduction in ultrathin films lacking attractive polymer-substrate interactions, when both a free surface and attractive-polymer substrate interactions are present, as with PMMA films supported on silica, the attractive polymer-substrate interactions will overwhelm the effect of the free surface, leading to a Tg increase. Possible reasons for the smaller free surface effect in PMMA as compared to PS as well as the implications of these studies for nanocomposites will be discussed.