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### **Mechanics of polymer interfaces<sup>1</sup>**

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Although size-dependent effects of constraint and deformation volumes on elastoplastic mechanical behavior of metallic and ceramic structures are increasingly well-studied, relatively little is known about how the deformation of polymers depends on microstructural and physical length scales. In particular, it is not yet clear how the structural and mechanical properties of amorphous (glassy) polymers differ at free surfaces, at rigid interfaces, and within the bulk. Such understanding is important in that free surface and interface properties dominate the mechanical behavior of (bio)polymeric thin film and nanocomposite applications. Recent experiments have demonstrated as much as a 50% depression in the glass transition temperature  $T_g$  within  $\sim 100$  nm of the free surface in amorphous polystyrene (PS) and poly(methyl methacrylate) (PMMA) thin films [1-3]. This indicates possible differences in the amorphous topology and/or macromolecular mobility that induce a mechanical response quite different from that indicated via bulk or  $\mu\text{m}$ -scale testing, even at room temperature, within 100 nm of the free surface. Here, we employ spherical nanoindentation experiments and analytical models to determine the indentation elastic moduli  $E_i$  of three well-characterized, amorphous polymer surfaces (PS, PMMA, and polycarbonate or PC) for maximum contact depths ranging from 5 nm to 250 nm. Over this range, we observe a 200% increase in  $E_i$  with respect to the bulk  $E_i$ . We demonstrate that this apparent stiffening of the polymeric surfaces cannot be attributed to experimental artifacts such as surface roughness, assumptions of indenter contact area, or loading rates. Further, we consider this effect as a function of monomer structure for a given molecular weight, molecular weight for a given monomer structure, processing routes (injection and compression molded, and spin coating), and physical environment (temperature and humidity). We propose a model for the physical basis of and length scale of this surface stiffening with respect to the structural length scales of these macromolecules, and discuss the implications of this effect in terms of mechanical performance for synthetic and biological polymeric nanocomposites

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