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Harold Ade, Dept. of Physics, North Carolina State University, Raleigh, harald_ade@ncsu.edu

Tuning Substrate Surface Energies for Blends of Polystyrene and Poly(methyl methacrylate)

D.A. Winesett^{1,*}, S. Story¹, J. Luning² and H. Ade¹

¹Dept. of Physics, N.C. University, Raleigh, NC 27695-8202; ²Stanford Synchrotron Radiation Lab., P.O. Box 20450, MS 69, Stanford, CA 94309-0210, *permanent address: ExxonMobil Chemical Company, Baytown Polymers Center Baytown, TX 77520

We have developed and characterized three simple and inexpensive ways to make substrate surfaces that are neutral, i.e. that have the same interfacial energy, for polystyrene (PS), a common hard plastic, and poly(methyl methacrylate) (PMMA), a commercial plastic. In the first two of these surface treatment methods, two different high molecular-weight copolymers made of styrene and methyl methacrylate were absorbed onto hydroxylated silicon oxide. In another method, octyltrichlorosilane (OTS), a highly hydrophobic material, was covalently bonded onto hydroxylated silicon, a highly hydrophilic surface. A fourth method covalently attached hydroxyl-terminated, miscible, low molecular-weight homopolymers of PS and PMMA to the substrate. We found that the OTS treatment is advantageous because a gradient of continuous interaction can be created. Nonetheless, the principles of each method should be applicable to other polymer systems.

The ability to adjust the interactions between a material or a molecule and a substrate is desirable for a number of applications. This includes nano-patterning, sensing, and the dewetting and phase segregation in two-dimensional systems of polymer blends at elevated temperatures. In polymer blends, differences in interfacial energies, which reflect a preferential interaction, generally cause one polymer to segregate to the substrate or air interface. This segregation has to be avoided in a number of applications, and is prevented by tuning the polymer/substrate interfacial properties.

Homopolymer blends of polystyrene (PS) and poly(methyl methacrylate) (PMMA) of relatively low molecular weight (10,000 to 200,000 g/mol) make excellent model systems for a number of studies. Both polymers exhibit comparable glass transition temperatures (temperatures below which a polymer becomes hard and brittle) of approximately 102 to 120 degrees Celsius (°C)

and are readily codissolved in a common solvent. Moreover, for typical annealing temperatures (140°C to 180°C), the interfacial tension between PS and PMMA is larger than the absolute value of the difference between the surface energies of PS and PMMA. Hence,

neither polymer can spread onto the other at an air interface. A polymer-air interface might thus be one of two "neutral" interfaces that can be used to produce a two-dimensional system. A "neutral" substrate surface will provide the second defining interface.



Author (top, clockwise from left): Andy Winesett, Steve Story, Jan Luning and Harald Ade.

Thin polymer films are often cast on silicon substrates. At elevated temperatures, it is well established that the PMMA in a PS/PMMA blend will quickly segregate to the native silicon oxide (SiO₂) interface to form a wetting layer. In order to avoid and/or control this segregation, the effectiveness of several simple surface energy tuning methods has been tested. Using a standard UV/O₃ process, in which ultraviolet light is used to produce ozone and oxygen radicals in the air that removes carbon from surfaces, silicon substrates were cleaned and simultaneously activated to produce -OH groups on their surfaces. They were subsequently treated with either a commercial random copolymer,

P(S-*ran*-MMA), an alternation copolymer, P(S-*alt*-MMA), a partial or gradient n-octyltrichlorosilane (OTS) self-assembled monolayer, or a brush of a hydroxyl (-OH)-terminated low molecular-weight PS/PMMA blend with varying PS/PMMA composition. The relative effectiveness of all four methods was characterized using optical microscopy, Near Edge X-ray Absorption Fine Structure (NEXAFS) microscopy and spectroscopy, atomic force microscopy, and contact angle measurements.

The optical micrographs in **Figure 1** clearly show that very different morphologies develop, depending on the surface treatment. The P(S-*ran*-MMA)-treated surface shows a semi-bicontinuous

morphology, wherein the two material phases are partially continuous across the whole sample. However, the untreated SiO_x surface and the P(S-*alt*-MMA)-treated surface show large droplets. Therefore, the P(S-*alt*-MMA) treatment clearly failed. To verify that the P(S-*ran*-MMA) treatment was successful, NEXAFS microscopy (performed with the Stony Brook Scanning Transmission X-ray Microscope (STXM) at beamline X1A) was used to quantitatively map the thickness of the PS and PMMA phases on P(S-*ran*-MMA)-treated silicon nitride (Si₃N₄) membranes (**Figure 2**). The results show that the morphology is essentially two-dimensional in nature, with a relatively uniform film thickness and domains of PS and PMMA that span

the entire film thickness.

Our specific interests and studies on "neutral" surfaces were restricted to surfaces that would have the same interfacial energy for PS and PMMA. Hydroxy-terminated PS and PMMA is the most novel approach investigated. Except for the P(S-*alt*-MMA) treatment, all of the methods yielded neutral or near-neutral surfaces. The OTS treatment has the advantage that a gradient of continuous interaction ranging from preferential PMMA to preferential PS interactions can be created. However, the principles of all the methods developed should be applicable to other polymer systems.

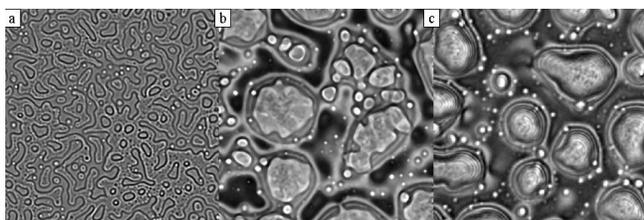


Figure 1. Optical micrographs of a PS_{21k}/PMMA_{22k} blend film, spun to a thickness of 500 nm and annealed in vacuum at 170°C for 250 minutes on three types of surfaces: a) SiO_x-OH surface treated with 270,000 g/mol P(S-*ran*-MMA), b) SiO_x-OH surface treated with 108,000 g/mol P(S-*alt*-MMA), c) Si-OH surface with no polymer treatment. The field of view in all three micrographs is 100 μm x 100 μm.

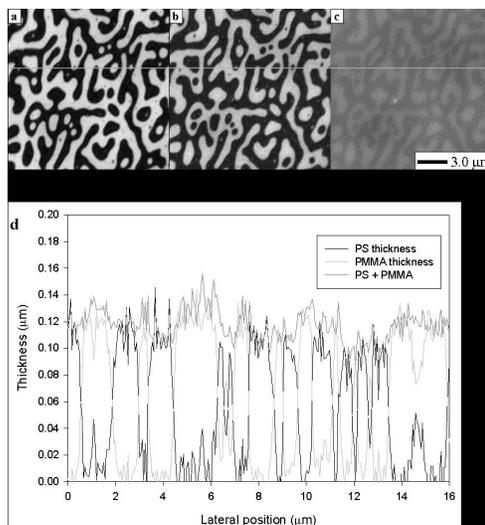


Figure 2. Quantitative STXM thickness maps of equal weight percent blend of PS_{21k}/PMMA_{22k} annealed at 153°C for 1 hour on Si₃N₄ treated with 270,000 g/mol P(S-*ran*-MMA). a) PS map b) PMMA map c) PS + PMMA map d) The line profile of the thickness maps.