

EFFECT OF INTERFACES AND ADHESION ON THE CREEP COMPLIANCE OF THIN POLYMER COATINGS

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Introduction

For thin polymer coatings, stresses within the polymer film transfer to the interface, requiring robust adhesion to maintain performance and reliability. Indentation techniques have been widely used to study thin films, quantifying the material properties of both bulk and heterogeneous materials. Models generally account for interfacial effects using static ideal cases of perfect adhesion (bonded) or perfect slip at the interface. These two cases show a dramatic difference in the indentation contact area, since the former restricts motion at the interface, while the latter allows polymer translation.^{1,2} The interfacial strength also dictates available relaxation modes and can influence the overall viscoelastic response of the polymer film.³ In this work, we use a static load creep indentation experiment to probe time-dependent interfacial responses at the buried interface between a polymer film and a rigid substrate. These additional relaxations at the buried interface were strongly dependent on the extent that the substrate surface moieties could hydrogen bond with the hydroxyl groups present on the polymer chain.

Experimental

Equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by NIST, nor does it imply the materials are necessarily the best available for the purpose.

Hydroxypropyl cellulose (HPC, number average relative molecular mass of 100 000 g/mol) was chosen for this study due to the potential for hydrogen bonding between pendant hydroxyl groups on the backbone and the substrate. Chemical functionalities developed on glass substrates were strong hydrogen bonding groups, non-hydrogen bonding groups, or a mixture of both types. A description of the chemistry at the interface is shown in Figure 1.

To form these interfaces, glass slides were cleaned with ethanol and water, dried, and then exposed to ultraviolet ozone (UVO) cleaning for 500 s. This formed silanol (hydroxyl) groups on the glass substrate that are able to hydrogen bond with HPC. Subsequent silane treatments of octyl dimethylchlorosilane and tridecafluoro-1,1,2,2-tetrahydrooctyl) dimethylchlorosilane created alkyl and fluoroalkyl groups at the glass surface, that cannot hydrogen bond with HPC. The final chemical moiety was pro-

duced through UVO exposure of an alkyl surface to create carboxylic acid groups. The reaction caused by UVO exposure was slow enough to control the relative density of carboxylic acid moieties to alkyl moieties at the glass substrate by varying the exposure time. Water contact measurements were used to confirm uniform coverage. HPC films were flow-coated from ethanol onto glass slides and annealed for 24 h in a dry oven before use.⁴

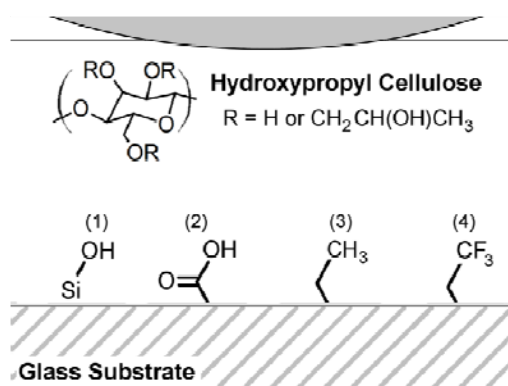


Figure 1. Chemical structures present at the interface. Hydroxyl (1) and carboxylic acid (2) groups can hydrogen bond with hydroxypropyl cellulose, while the alkyl (3) and fluoroalkyl (4) surfaces cannot.

To measure compliance, static load indentation was performed using 12.7 mm diameter chrome steel spheres, arranged in a row on $4.4 \mu\text{m} \pm 0.2 \mu\text{m}$ thick HPC films. The set of spheres was placed on the surface simultaneously through the use of a vertical motion stage. The indentation contact areas were imaged for 10 000 s using an inverted optical microscope, with post-image processing to detect the contact radii utilizing edge detection and circular Hough transforms.³ Indentations on ≈ 1 mm thick polymer films were also performed to obtain the bulk viscoelastic response. From contact radii, the compliance of the polymer layer could be calculated from models describing the indentation of a heterogeneous substrate.¹ Models used in this study define a perfectly bonded interface to calculate the compliance of the polymer layer. Uncertainty in this work is displayed as standard deviation at a 95 % confidence interval.

Results and Discussion

Bulk viscoelastic measurements were used as a reference to determine if any deviations occurred from a per-

fectly bonded interface. During this static load indentation, the contact radii will increase due to bulk polymer relaxations and also increase from any relaxations at the interface. If the interface remains perfectly bonded, the compliance results from the model should match bulk viscoelastic measurements. Since the model does not account for these interfacial relaxations, the perfectly bonded model will over-predict the compliance if interfacial relaxations occur.

Both the carboxylic acid and hydroxyl interfaces exhibited statistically insignificant deviations from the bulk compliance over the course of the experiment. Both the alkyl and fluoroalkyl interfaces showed significant deviations, with the fluorinated interface exhibiting the largest increase in modeled compliance. The interfacial failure caused significant differences in the contact area at equivalent indentation times. At 1800 s, the contact radii for the alkyl interface was $48.4 \mu\text{m} \pm 0.4 \mu\text{m}$, in comparison to the carboxylic acid surface at $42.9 \mu\text{m} \pm 0.4 \mu\text{m}$. The alkyl interface has no hydrogen bonding sites, resulting in polymer translation and a correspondingly larger contact area. Conversely, the carboxylic acid surface could hydrogen bond with hydroxyl groups in the HPC chain, resulting in an interface which behaved like the ideal perfectly bonded interface.

To confirm the trend seen in the indentation experiments, the interfacial strength was measured using cantilever peel. Fracture toughness was calculated from the separation of the HPC film from the treated glass substrate under an applied load. As in the thin film indentation technique, fracture toughness was lowest for the fluorinated surface. Both hydrogen bonding interfaces were stronger than the measurement technique, which supports the result of an interface close to perfectly bonded.

Since the alkyl and carboxylic acid functionalities could be presented on the surface simultaneously, a mixture of the two chemical moieties was tested to determine if there was a critical density of hydrogen bonding sites which would allow for perfectly bonded conditions to be maintained. When mixed interfaces were measured, the deviation from the bulk response was not removed, but the extent of deviation was reduced as hydrogen bonding sites increased. The calculated compliance remained statistically equivalent to the bulk compliance for up to 1000 s. Even though mixed interfaces systems improved as compared to the pure alkyl substrate, complete coverage of the glass substrate with hydrogen bonding groups was optimal.

Conclusions

Thin film indentation experiments on viscoelastic materials allowed for the deconvolution of the bulk compliance from interfacial responses at the buried interface. This technique could discriminate both large changes in the interfacial strength due to different chemical moieties and interfaces with varying densities of multiple chemical moieties. Indentation results correlated with cantilever peel measurements, with systems showing limited interfa-

cial relaxations having higher fracture toughness. While the interfacial strength can be measured through techniques which cause complete separation of the interface, this indentation technique provided time-dependent results and does not cause delamination of the polymer film. More complex geometries and interactions can be explored with further modifications to the polymer-glass interface, providing a route to study and design robust interfacial regions for improved performance.

Acknowledgements

P.M.J. and J.A.H. would like to thank the NIST/National Research Council for Postdoctoral Fellowship Program for funding.

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