

Reversible adhesion between chemically heterogeneous switchable polymeric brushes and an elastomeric adhesive

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Introduction

Adhesion at polymer / polymer and polymer / solid interfaces is of great importance for numerous applications from microelectronics to aircraft industry. It is essential, for permanent as well as for reversible adhesion, that the chemical composition and morphology of the materials at the interfaces are perfectly controlled.

The purpose of the present work is to aim at the development of a new generation of adaptative surfaces, based on chemically heterogeneous switchable thin polymer films, which are covalently bonded to the solid substrates, modifying therefore their surface chemistry in a well-controlled and reproducible way. Such films were fabricated from two incompatible end-functional homopolymers, terminally tethered from one of their ends to the substrate (mixed polymer brushes) by using "grafting to" methods¹ of polymer deposition. Those mixed (binary) brushes undergo phase segregation depending on environment resulting in a remarkable switching of morphology and surface energetic state. This investigation aims to study the influence of the switching phenomenon of mixed brushes on the strength of the interface which such a surface can form with an adhesive. The surfaces are particularly useful to tune the adhesive properties of soft adhesives. This class of adhesives is gaining increasing interest in industry and medicine for its low toxicity and ease of use. Knowing the main requirements for such adhesives provides the capability to generate reversible, fast and easy adhering bonds to different substrates in a controlled environment.

Experimental

Materials. The adhesives are blends of 40% polystyrene – polyisoprene – polystyrene (SIS) triblock copolymer (ExxonMobil Chem., trade name Vector® 4100, $M_w=154$ kg/mole with 15.1 %wt styrene) and 60% C-5 hydrogenated resin (ExxonMobil Chem., trade name Escorez® 5380) completely miscible with the isoprene phase. The glassy films consist of various ratio mixtures of end functional polystyrene (PS-COOH, $M_w=50$ kg/mole) and polyvinyl-pyridine (P2VP-COOH, $M_w=50$ kg/mole) macromolecules (Polymer Source Inc.), tethered on silicon wafers or glass slides, covered by a ultra thin poly(glycidyl-methacrylate) (PGMA, $M_n=84$ kg/mole, PDI=3.4) layer.

Sample Preparation. The solid substrates (glass or silicon) were first cleaned in ultrasonic organic solvent baths for 30 minutes, placed in a boiling 25% NH_4OH / 25% H_2O_2 / 50% distilled H_2O solution for 30 - 45 minutes and then rinsed several times with highly purified water. For the deposition of the ultra thin PGMA layer (3 - 7 nm thickness) on the substrates the spin coating technique has been chosen. $CHCl_3$ solutions (C=0.05% - 0.2%) of PGMA left under stirring for several hours and then spin coated on the wafers and annealed (100 °C, 1 hour). In order to graft the binary PS / P2VP brush layer we spin coated separately the two polymers on the substrates by using the appropriate solvents. Starting always with the PS, we annealed the layer (150°C, 75 minutes) and rinsed the excess ungrafted polymer with solvent, then spin-coated the P2VP layer, annealed it (150°C, 22 hours) and rinsed the excess again. The ~100 μm adhesive layer was prepared by casting the SIS / C-5 resin mixture, dissolved in toluene, on a standard microscope slide, which

was then left to evaporate for 24 hours and then placed at 45 °C under vacuum for 2 days to approach an equilibrium state.

Probe test experiments. We performed probe test experiments on our custom-designed apparatus, built on an MTS 810 hydraulic testing machine.² A typical probe test can be divided into three stages (figure 1). In the first stage, a flat, stainless steel probe with a wafer coated with the binary brush film, glued on its end, approaches a ~100 μm thick adhesive layer deposited on a microscope glass slide at a constant velocity 30 $\mu m/s$. When the contact pressure of 1 MPa is reached, the probe stops during a contact time of 10 seconds. The probe is then removed during stage 3 with a constant debonding velocity 10 $\mu m/s$.

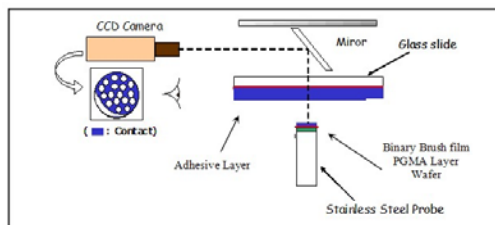


Figure 1. Schematic of the experimental setup for the probe test.

During this test, all experimental parameters are well controlled. The contact pressure, the contact time and the debonding velocity are independent parameters of the test and the contact area is measured with the video acquisition which also allows the detailed analysis of the debonding mechanism.

Contact Angle Measurements. The contact angle data were obtained by means of the Drop Shape Analysis system DSA 10 (Kruss GmbH) and the sessile drop method.³ During the measurement of the advancing contact angles the needle remains inside of the drop. The droplet is monitored by a CCD camera and analyzed by Drop Shape Analysis software (DSA Version 1.0, Kruss). The complete profile of the sessile droplet is to be fitted by the tangent method to a general conic section equation. The derivative of this equation at the baseline gives the slope at the three phase contact point and thus the contact angle as shown in figure 2. In this way the contact angles are determined both on the right and on the left side and therefore reproducibility is within 0.5°.

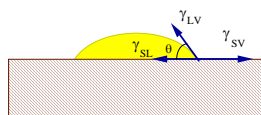


Figure 2. Schematic of an equilibrated sessile drop, γ_{SL} , γ_{LV} and γ_{SV} are the solid-liquid, liquid-vapor and solid-vapor interfacial tensions, satisfying Young's equation: $\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$.

Results and discussion

Switchability of binary polymer brushes. Systematic contact angle measurements of distilled water droplets, after exposing the model surfaces to selective and non-selective solvents have proven the switchability and reversibility of the surfaces due to self-organization. The binary system of a hydrophobic (PS) / hydrophilic (P2VP) polymer mixture is allowed to sense the environment and reorganize in order to minimize its total free energy. In table 1, we demonstrate the water contact angle measurements for samples with various PV/P2VP ratios after exposing to selective (toluene, acid water pH=2) and non - selective ($CHCl_3$) solvent vapor for 15 minutes. The more P2VP a sample contains, the more pronounced, the hydrophobic – hydrophilic transition appears, when the sample has been left in the appropriate environment. In figure 3 we schematically propose a

molecular picture of a binary hydrophobic / hydrophilic polymer brush, consistent with the different water contact angles which are measured.

Table 1. Water contact angles of various PS/P2VP mixed brushes after exposure to selective and non-selective solvents

Sample (PS/P2VP)	CHCl ₃ exposed	pH 2 water exposed	Toluene Exposed
P2VP-100%	62°	35°	60°
P2VP-69%	70°	55°	72°
P2VP-50%	60°	60°	82°
P2VP-25%	80°	70°	85°
PS-100%	88°	86°	88°

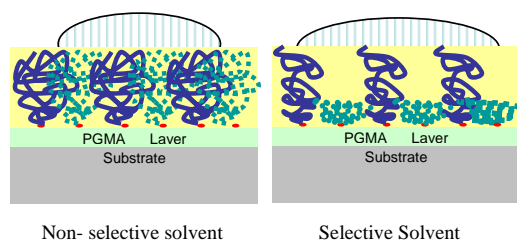


Figure 3. Binary brush layer reorganization due to exposure in selective and non-selective solvents

Probe tests. For the probe experiments, in order to estimate the effect of the surface switchability on the brush / elastomer adhesion we have chosen to test a roughly symmetric PS/P2VP mixture. Four types of environmental treatments have been performed, 1st exposure to toluene and dry, 2nd exposure to water, dry then exposure to toluene and dry again, 3rd exposure to water and dry and 4th exposure to toluene, dry then exposure to water and dry again. All the results are presented in figure 4.

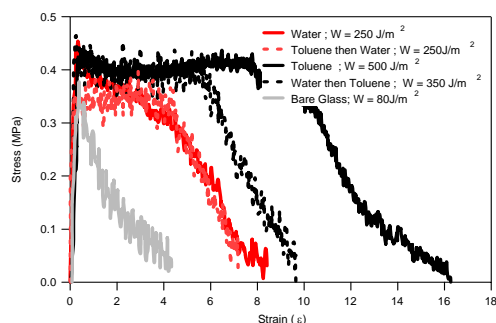


Figure 4. Stress / Strain measurements of a symmetric PS / P2VP brush layer in contact with an adhesive layer. The brushes film has been exposed in different solvent vapors before the testing.

Several information can be obtained from these preliminary results. The maximum stress at which the plasticization of the adhesive layer starts (by cavitation) is more or less identical for all the cases. This is a typical result for such an adhesive and depends only on its bulk properties. The lack of peak is due to the fairly rough surface resulting from the sample preparation method. The maximum extension at detachment (or the adhesion energy W , given in the inset) is the real adhesion information. The regime where the stresses remain roughly constant is the regime where a foam of fibrils is formed and extended

in the tensile direction. Since the elastic properties of the adhesive fibrils are the same, the longer the fibrils extend before detaching, the higher are the local stresses necessary to detach them.⁴ The exposure of the mixed binary brushes to toluene, results in a very high adhesion, the double exposure (water then toluene) is slightly worse implying that it is relatively difficult to reverse an exposure into water. On the other hand, the direct exposure to water is exactly equivalent to an exposure in toluene then water (the two red curves are superimposed). These preliminary results are very promising and the effect is really obvious, justifying the relevance of more detailed and systematic tack experiments.

Conclusion

Our work up to know has confirmed the switchable character of the binary PS/P2VP model surfaces when they are exposed to appropriate environments. Preliminary adhesion experiments have shown that the re-organization of the binary brush on the surface has also a marked effect on its adhesive properties with a typical block copolymer based hydrophobic pressure-sensitive-adhesive (PSA), as characterized by its adhesion energy. A detailed series of experiments is planned to investigate the interfacial adhesion as a function of the molecular characteristics of a glassy polymer / elastomer interface. While the surface tension of the glassy surface is important,⁵ a low Flory-Huggins interaction parameter χ between the glassy and the elastomeric material may favor partial chain interpenetration⁶ and interfacial slippage certainly plays a major, yet poorly understood, role in practical adhesion.⁷

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