



Adhesion of blended polymer films



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ABSTRACT

In this work, the adhesion energies of two dissimilar polymer films after thermal bonding are studied. The films were formed from the emulsions of polycaprolactone (PCL) and nylon-6 (N6) spin-coated onto metal substrates. After that, the solidified blend polymer films on the metal substrates were faced with additional PCL films on metal substrates and thermally bonded to them. The surface structure of blend films was elucidated prior to thermal bonding by staining them using Rhodamine B. The dye stained only N6 leaving PCL undyed and the exposed structure was analyzed using digital photography, which revealed the surface concentration of PCL, as well as the N6 and PCL distributions over the surfaces. It was discovered that PCL-N6 domains would remain partially mixed, influencing the adhesion energy measured.

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1. Introduction

Polymer adhesion was previously studied in the framework of polymer physics, materials science, and technological applications [1–7]. Adhesion is a physical process of joining separate material surfaces together by means of quantum-mechanical, mechanical, chemical, or thermodynamic forces. This process is affected by polymer miscibility, and polymer blends with few exceptions tend to separate [1–7]. Accordingly, a rare miscibility or frequent immiscibility of polymers have a significant effect on the adhesive strength at the contact surfaces [1–7], typically causing a weak adhesion between two polymer surfaces. Note that several theoretical results on polymer-polymer adhesion linking it to polymer reptation through the interface are available, most notably [8–12].

Even with such weak adhesion, blended polymer systems are frequently employed for various technological applications ranging from the semi-conductor industry to the textile industry. In the semi-conductor industry, a process known as spin-coating is frequently used to create patterned polymer surfaces [13–15]. Similarly, in the development of optical devices, spin coating is used to create thin polymer blended films for anti-reflective

coatings [13,16–18]. In the textile industry, polymer blends are used to form fibers with desired properties [19,20]. Blended polymers are also used as protective coatings [21]. In all these applications, the immiscibility of polymers, solvent diffusion, interaction energies between the surfaces, wettability, etc., influence the final surface concentrations and morphologies of the polymer systems [15,22–24]. As a result, the surface concentrations of these mixed systems do not represent the bulk concentrations utilized. For example, in the case of spin-coating, the surface concentration of the thin films would not be equivalent to the bulk concentration of the spin-coated emulsions [15,22–24]. Frequently used methods to measure this surface concentration are often complicated and costly such as the X-ray photoelectron spectroscopy, Fourier transform infrared spectra, or atomic force microscopy [15,22–24].

In addition to the need to understand and properly measure the surface adhesion, and its dependence on the surface concentration of blended polymer films, the characterization of the surface morphology and homogeneity is crucial. Different properties such as optical reflectance and light transmission, as well as the adhesive strength would be severely influenced by the morphology and uniformity of the blended films. Thus, a means of quantifying such a uniformity becomes imperative. Various approaches are used to characterize the spatial uniformity in the ecological, geological, textile, nano-materials, etc. contexts [25–29].

The present work aims at measuring the adhesive energy

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between the blended polymer film and a monolithic polymer film consisting of one of the components. To facilitate characterization of the adhesive energy, a novel, efficient and straightforward method of characterization of the surface topography of blended polymer systems is introduced. This method employs selective staining of individual polymers at the surface.

2. Experimental methods

2.1. Materials

Two commercially available polymers were chosen for this work, PCL ($M_n = 80$ kDa) and N6 (molecular weight of each polymer repeat unit 104.83 Da [30]). The glass transition temperatures of PCL and N6 are -64 °C [31] and 62.5 °C, respectively, whereas their melting temperatures are 60 °C and 228.5 °C, respectively. The polymers were used as received without any further purification. Where not specified, properties were obtained from the manufacturer. The solvents that were used here were acetic acid (grade $99 \geq \%$) and formic acid (grade $\geq 95\%$). For the surface characterization and selective staining, Rhodamine B (basic violet 10) dye was utilized. All the materials were obtained from Sigma Aldrich.

2.2. Sample preparation

Sample preparation is depicted in Fig. 1. Spin coating was conducted as follows. Thin, rectangular copper wafer platelets of dimensions 60 mm \times 30 mm with a 3 mm hole at the center were used as the base for spin coating. Note that the copper wafers were polished with a 1000 grit sandpaper. After the copper wafers were polished, they were rinsed thoroughly with ethanol and exposed to open air for one day. This allowed them to develop an inert copper oxide layer on the surface which would minimize reactions between the copper surfaces and the solvents used during the following spin-coating process. The center hole in these wafers aimed the subsequent blister test where adhesion energy is to be measured. One opening of the hole in the copper wafers was covered with a tape prior to the wafer being placed into the spin-coating setup, taped side down, as shown in Fig. 1a.

Either a 0.5 mL drop of the 15 wt% PCL solution or a drop of an emulsion of PCL in N6 was placed at the center of a copper wafer on the spin-coater. The 15 wt% PCL solution used was prepared by dissolving PCL in a $1:1$ ratio (by weight) mixture of the acetic acid and formic acid. Similarly, three separate emulsions of PCL in N6 were prepared for spin coating. The first emulsion contained 70 wt% PCL and 30 wt% N6; the second emulsion contained 60 wt% PCL and 40 wt% N6; and the third emulsion contained 40 wt% PCL in 60 wt% N6. These emulsions were prepared by mixing the 15 wt% PCL solution with a 20 wt% N6 solution prepared in the same $1:1$ ratio (by weight) mixture of the acetic and formic acid. After thoroughly mixing, the polymer solutions were left for 30 min before spin-coating, permitting spinodal decomposition of the co-dissolved polymers and formation of clearly visible droplets of PCL in N6 matrix, or N6 in PCL matrix, i.e. the emulsion formation similarly to [32].

After depositing a 0.5 mL droplet on the copper wafers on the spin-coater, they were spun at 2700 rpm to form thin films from 70 wt% PCL spin-coated substrates using the 70 wt% PCL to 30 wt% N6 emulsion, or 60 wt% PCL spin-coated substrates using the 60 wt% PCL to 40 wt% N6 emulsion, or 40 wt% PCL spin-coated substrates using the 40 wt% PCL to 60 wt% N6 emulsion. In addition, monolithic thin films on copper wafers were spin-coated from the 15 wt% of PCL. It should be emphasized that after spin-coating, the pre-drilled holes in the copper wafers were not filled with polymer solutions or emulsions despite being exposed to the solution during spin-

coating. The samples were then left for two days for the solvents to fully evaporate. The process resulted in the approximately 0.1 mm thick blended (PCL with N6) films (substrates) adhering to the underlying copper wafers (cf. Fig. 1b).

The samples thus prepared were characterized using two methods. First, images of the resultant surface topography of the blended polymer substrates were obtained using the novel staining method. Namely, N6 at the surface of the blended polymer films was selectively stained. Images were then obtained of these selectively stained films, and through an image analysis described in detail in subsection 2.5, the surface topography was evaluated. These polymer films were also used in the blister tests to measure the adhesion energy, as described in detail in subsection 2.4.

The monolithic PCL films used to measure adhesion energy were formed by spin coating. An aluminum petri dish (53 mm in diameter) was uniformly coated by 2 mL of the 15 wt% PCL solution. The PCL solutions in such petri dishes were left on a hotplate at 45 ± 2 °C to facilitate evaporation and formation of the PCL films. The films were left for two days for the solvent to fully evaporate. After that, these monolithic PCL films were removed from the petri dishes and located onto the spin-coated substrates, forming a sandwich that was heat-treated at 55 ± 2 °C, below the glass transition temperature of N6, 62.5 °C. As described in the following subsection 2.3, adhesion would not occur between PCL and N6 at this temperature. The spin-coated blended substrates which were thermally adhered to the monolithic PCL films consisted of 100% PCL, 70% PCL, 60% PCL, and 40% PCL (with the rest being N6).

To further observe the effect of heat treatment on the adhesion between PCL and N6 and to characterize the surface structure by the selective staining with Rhodamine B, additional thin PCL films and N6 films were formed. These monolithic thin films were formed by spinning pure PCL or pure N6 solutions on the spin-coating setup shown in Fig. 1. In this case, a sheet of aluminum foil acting as the substrate was placed onto the spin-coating setup (instead of the copper platelet), and 1.5 mL of the 15 wt% PCL solution was used to form monolithic PCL films. Alternatively, a 20 wt% N6 solution was used to form monolithic N6 films. In both cases the solvent was a $1:1$ ratio (by weight) of acetic acid and formic acid. These solutions were spun for 30 s at 170 rpm. The aluminum foil with the thin film of polymer solution was then removed from the spin coater and placed onto a hotplate for 2 days to facilitate evaporation. In the case of PCL, the hotplate was set at the temperature of 45 ± 2 °C, while in the case of N6, it was set at the temperature of 60 ± 2 °C. It should be emphasized that formation of N6 films by a simple evaporation method in an aluminum petri dish is not robust and yields non-uniform films. After these monolithic PCL and N6 films were solidified, they were removed from the hotplates and used to evaluate their adhesion energy to one another at temperatures below the glass transition of N6. These films were also used in the staining experiments described in subsection 2.5.

2.3. Sample heat-treatment

The spin-coated substrates containing either monolithic PCL or the PCL and N6 blends were placed (with the attached copper wafer down), onto a hotplate at 55 ± 2 °C. Then, the monolithic PCL films were placed onto the polymer side of the substrates, and a copper block pre-heated to the same temperature as the hotplate was placed onto these films, applying a low constant pressure of 0.01 MPa to facilitate an initial adhesion. The samples were heated for 180 s in this sandwich-like configuration, shown in Fig. 2.

After the 180 s heat treatment, the pre-heated copper block was removed, and a steel roller of radius 30 mm was pressed to the substrates and rolled manually to remove air bubbles and facilitate

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