

Adhesion behavior of polymer networks with tailored mechanical properties using spherical and flat contacts

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Abstract

Four acrylate-based networks were developed such that they possessed similar glass transition temperature (~ -37 °C) but varied in material stiffness at room temperature by an order of magnitude (2–12 MPa). Thermo-mechanical and adhesion testing were performed to investigate the effect of elastic modulus on adhesion profiles of the developed samples. Adhesion experiments with a spherical probe revealed no dependency of the pull-off force on material modulus as predicted by the Johnson, Kendall, and Roberts theory. Results obtained using a flat probe showed that the pull-off force increases linearly with an increase in the material modulus, which matches very well with Kendall's theory.

Introduction

Normal adhesion testing is a widely used technique for determining adhesive contact between two surfaces. This testing technique most typically involves bringing a probe of known geometry in contact with a flat sample, applying a normal preload, and then retracting the probe until separation occurs.^[1–5] The most common approach is to utilize a hard, spherical probe to determine the adhesive properties of a soft, flat specimen.^[6–11] The spherical nature of the probe makes testing relatively insensitive to slight misalignment, although the increasing contact area with increasing preload complicates data interpretation. A theoretical solution of the contact between spherical objects was developed by Johnson, Kendall, and Roberts (so called “JKR” theory),^[3] and has been widely accepted to describe the adhesive behavior of a clean, smooth, elastic surface, showing no hysteresis in the loading–unloading paths.^[12]

Another commonly used probe geometry is a flat probe; the contact area beneath a flat probe is insensitive to the preload force, and the theory describing the adhesive behavior (often simply referred to as “Kendall” theory) is well-established.^[2] Unfortunately, flat probe testing is infrequently used relative to spherical probes because of the practical issues associated with probe alignment relative to the sample surface. However, recently some of the current authors have built a normal adhesion test set-up which allows control of probe–sample alignment within a fraction of a degree, allowing for more accurate testing.^[13]

The purpose of this work is to derive a deeper fundamental understanding of adhesive behavior by experimentally

characterizing normal adhesion behavior using spherical and flat probes, and comparing the results directly with well-established theories. Comparison of JKR and Kendall theory from a materials perspective reveals a strong relationship with surface energy; however, only flat probe adhesion is dependent on elastic modulus. Although these theories are well established, this has never been directly investigated; from a practical perspective it is difficult to change the elastic modulus without also changing the material and hence the surface energy. Our goal was to directly test a polymer network whose elastic modulus could be systematically varied independent of the surface energy. To accomplish this, we have derived an acrylate-based polymer system with tailorable mechanical properties. Specifically, four networks were fabricated with systematically varied crosslink molecular weight and mass fraction such that storage modulus can be varied over approximately an order of magnitude (2–12 MPa), while maintaining nearly constant glass transition temperature (T_g) (-37 °C) and surface energy (γ_s). These polymer networks are ideally suited for this fundamental study, as spherical adhesion testing is considered to be independent of material modulus, while flat probe testing is assumed to directly dependent on the square-root of modulus.

Experimental

The linear builder butyl acrylate (BA, number average molecular weight, $M_n \sim 128$), crosslinker poly(ethylene glycol) dimethacrylate (PEGDMA, $M_n \sim 750$), and the photoinitiator

2,2-dimethoxy-2-phenylacetophenone (DMPA) were procured from Sigma Aldrich (Sigma-Aldrich, St. Louis, MO). The other crosslinker poly(ethylene glycol) dimethacrylate (PEGDMA, $M_n \sim 1000$) was procured from PolySciences Inc. (Warrington, PA). A crosslinker solution (XLS) was created by mixing 88% PEGDMA 1000 with 12% PEGDMA 750. Note that all % values are wt%. The XLS solution was chosen based on preliminary testing to yield a constant T_g when copolymerized with BA, regardless of the XLS weight fraction. The BA-co-XLS networks were thoroughly mixed and then solidified by UV-induced free-radical polymerization using 0.1% DMPA photoinitiator.^[14–18] The low-strain thermo-mechanical properties of the samples were characterized by dynamic mechanical analysis (DMA, TA Instruments Q800DMA, New Castle, DE). These samples were thermally equilibrated at $-80\text{ }^\circ\text{C}$ for 5 min and heated to $40\text{ }^\circ\text{C}$ at a rate of $2\text{ }^\circ\text{C}/\text{min}$ while subjected to a 0.1% dynamic tensile strain at 1 Hz. T_g was defined as the peak of the tan delta curve.^[19] The rubbery modulus, E_r' , was defined as the storage modulus at $22\text{ }^\circ\text{C}$.

Contact angle measurements were performed using the EasyDrop Goniometer (Krüss Scientific, KRÜSS GmbH, Hamburg, Germany) to characterize the surface energy of the samples, γ_s . Water and hexadecane were chosen as polar and non-polar liquids. The γ_s was estimated using the Owens and Wendt model^[20]:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1)$$

$$\gamma_l(1 + \cos \theta) = 2\sqrt{\gamma_s^d \gamma_l^d} + 2\sqrt{\gamma_s^p \gamma_l^p} \quad (2)$$

where θ is the measured contact angle, γ_l is the total surface tension of the liquid used, and superscript d and p denote the dispersive and polar components. A white light interferometer (Zygo NewView 5000, Zygo Corporation, Middlefield, CT) was used to obtain an estimate of the roughness of the probe and samples. The probes exhibited roughness on the order of $5\text{ }\mu\text{m}$, while it was in the average range of $18\text{--}48\text{ nm}$ for samples of all crosslinking densities. The adhesion measurements were performed on the samples using a custom-made macroscopic adhesion measurement device built by Kroner et al.^[11,13] The sample surface was cleaned with water and the probe surface was cleaned with high-purity ethanol before adhesion measurements. To measure adhesion the probe was brought in contact with the sample. After compressive preloading the probe was retracted at a constant rate until pull-off occurred. The loading/unloading velocity was kept constant at $10\text{ }\mu\text{m}/\text{s}$. The preloads tested were 5000 , $10,000$, and $20,000\text{ }\mu\text{N}$ for spherical probe testing while only one preload of $5000\text{ }\mu\text{N}$ was used for flat probe testing, as flat-probe adhesion measurements are preload independent. Thirty measurements were performed for every sample to obtain statistically relevant data. The environmental temperature was recorded to be in the range of $25.5\text{--}27.0\text{ }^\circ\text{C}$, while relative humidity was always in the range of $27\text{--}42\%$. Data collection

was performed using LabView software (National Instruments Corporation, Austin, TX) package. The spherical and flat probes were made of borosilicate glass having a diameter of 3 and 2 mm , respectively.

Results and discussion

Thermo-mechanical testing

Representative data obtained from low-strain thermo-mechanical tests are summarized in Fig. 1. Figure 1(a) shows that tan delta increases with temperature, reaches a peak value at temperatures ranging from -37 to $-39\text{ }^\circ\text{C}$ (used to define the T_g), and decreases with further increase in temperature. The tan delta peak scaled inversely with mass fraction of XLS. At $22\text{ }^\circ\text{C}$, where adhesion measurements were performed, all materials exhibit very low tan delta values ($0.001\text{--}0.004$) indicative of small time-dependent contribution. Figure 1(b) shows that independent of the crosslinking density, all samples demonstrate a sharp transition from glassy to rubbery state. With increasing temperature the modulus drops significantly at around T_g for all crosslinking densities and reaches

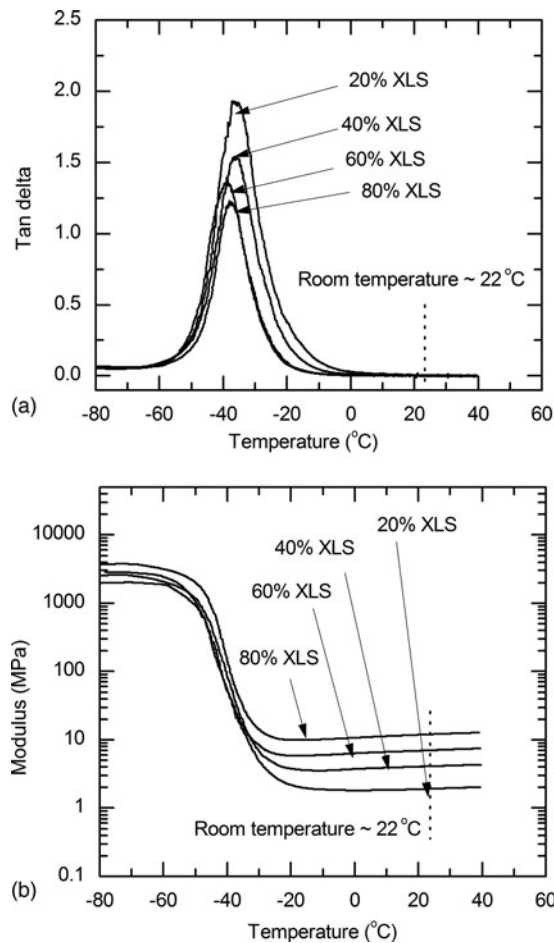


Figure 1. Representative DMA curves of the developed samples.

Table I. Summary of thermo-mechanical properties obtained from DMA analysis. Also presented are the crosslinking density and surface energy at room temperature.

| % XLS | Crosslinking density, ν (mol/m ³) | Glass transition temperature, T_g (°C) | Modulus at room temperature, E_r' (MPa) | Surface energy of material, γ_s (mN/m) |
|-------|---|--|---|---|
| 20 | 257.8 | -37.0 ± 0.4 | 2.1 ± 0.2 | 24.3 ± 1.0 |
| 40 | 552.1 | -37.1 ± 1.0 | 3.7 ± 0.6 | 25.3 ± 0.9 |
| 60 | 947.6 | -39.3 ± 0.3 | 7.1 ± 0.2 | 24.2 ± 1.4 |
| 80 | 1622.5 | -39.0 ± 1.5 | 11.9 ± 0.1 | 25.9 ± 1.1 |

a plateau well above T_g . For temperatures above T_g , the segmental rotations are relatively free and the polymer chains can slide past each other.^[21] Under these conditions, the crosslinking density dominates the material stiffness, thus, E_r' of the samples increases with an increase in the crosslinking density [Fig. 1(b)]. Accordingly, for an elastomeric network above T_g , it has been well established that the crosslinking density, ν , is related to E_r' through the following relation:

$$E_r' = 3\nu RT \quad (3)$$

where R is the gas constant and T is the absolute temperature at which E_r' is measured.^[22] The ν values along with the thermo-mechanical properties of all samples obtained from DMA are presented in Table I.

Contact angle testing

The values for γ_s obtained using the contact angle measurements, for all samples at 22 °C, are also presented in Table I. It can be seen that γ_s does not change significantly with the amount of XLS. A previous study by some of the authors demonstrated that oligomers can be pulled out from the sample during adhesion testing and transferred to the probe surface, thereby reducing the surface energy of the probe.^[23] This leads to a gradual change from glass surface energy to sample surface energy. To quantify this effect, contact angle measurements were performed on a pristine piece of glass cleaned with acetone, ethanol, and isopropanol, which gave average values of 47° for water and 0° for hexadecane. The same piece of glass was brought in contact with a 20% XLS sample 100 times and average contact angles were measured to be 75° for water and 11° for hexadecane. Using Eqs. (1) and (2), the surface energy of pristine glass and sample-contacted glass was calculated to be 53 and 33 mN/m, respectively. A significant decrease in the surface energy of glass towards the surface energy of the material (~25 mN/m) was observed. It can be assumed that the glass surface energy will approach the sample surface energy after a few hundred measurements. Therefore, the samples were indented 1000 times to stabilize the probe surface energy, before the actual adhesion measurements were obtained. All theoretical calculations were performed assuming the probe and the polymer samples were of equal surface energy.

Spherical probe adhesion measurements

Hertz investigated the contact between elastic spherical bodies and proposed a theory that agrees quite well for a contact between rigid materials. However, it fails to describe the behavior of soft materials, as it does not take into account adhesion.^[1] Thus, Johnson, Kendall, and Roberts extended Hertz's theory taking adhesive interactions into consideration, resulting in the well-known JKR theory.^[3] The JKR theory derives an expression for the pull-off force, P , at which separation of the two spheres will occur, as

$$P = -\frac{3}{2}\pi\gamma R^* \quad (4)$$

where R^* is the reduced radius given by $1/R^* = 1/R_1 + 1/R_2$, with R_1 and R_2 being the radii of curvature of the bodies in contact and γ is the work of adhesion per unit area. From Eq. (4) it can be seen that the pull-off force only depends on γ and R^* , and is independent of the elastic modulus. Figure 2 shows the

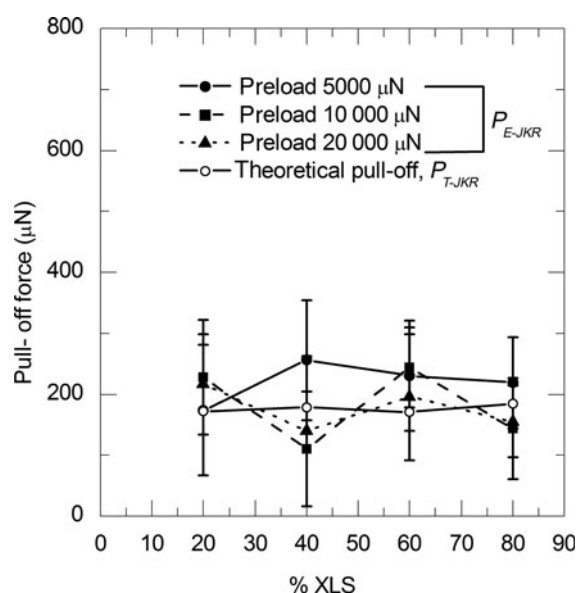


Figure 2. Experimental and theoretical JKR pull-off forces at room temperature as a function of %XLS. Experimental pull-off forces are independent of the amount of XLS in the range from 20% to 80% XLS.

experimental JKR pull-off force, P_{E-JKR} values obtained from adhesion testing at 22 °C for three different preloads of 5000, 10,000, and 20,000 μN . P_{E-JKR} followed a similar trend for all tested preloads. Following the oligomer transfer argument, theoretical pull-off forces were also obtained by using γ_s straight in Eq. (4) instead of γ and are termed P_{T-JKR} . P_{T-JKR} matches quite well with P_{E-JKR} for all samples tested, thereby justifying the oligomer transfer argument. The data from Fig. 2 indicate that the pull-off force is independent of the amount of XLS and accordingly of the elastic modulus for a large range of tested samples, which is in agreement with the JKR theory. The scatter shown in Fig. 2 might be related to the relatively high stiffness of the material, which causes low adhesion. As a consequence, slight variations in surface topography and inhomogeneities in the material properties result in a broad variation of the data.

Flat probe adhesion measurements

The indentation of a flat punch on an elastic half-space is proportional to the applied load, while the contact area stays constant, independent of the preload.^[2] Kendall^[2] showed that the value of P , the critical pull-off force can be obtained from fracture mechanics and thermodynamic arguments. Using this approach, P was obtained as

$$P = -\sqrt{8\pi a^3 E^* \gamma} \quad (5)$$

where a is radius of the probe, $1/E^*$ is the reduced elastic modulus given by $(1 - \nu_1^2)/E_1 + (1 - \nu_2^2)/E_2$, where E_1 and E_2 are the elastic moduli of the two materials in contact and ν_1 and ν_2 are their respective Poisson's ratios. Consequently, P depends

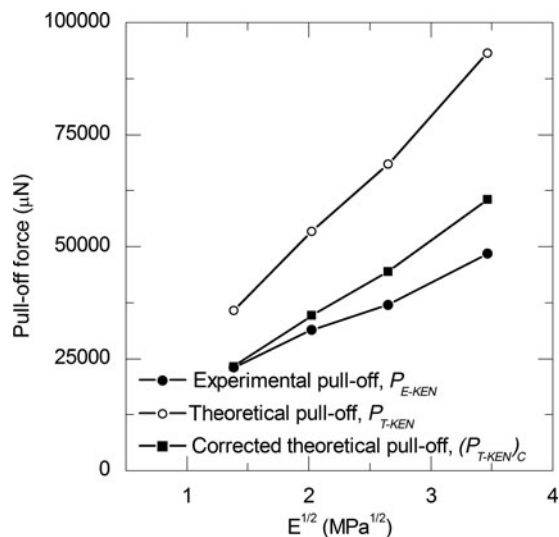


Figure 3. Experimental and theoretical Kendall pull-off forces at room temperature as a function of square root of material modulus. Pull-off force increases as a function of elastic modulus. The error bars are very small and lie within the symbols (on the order of 200 μN).

on the probe size, the surface energy of the materials, and their elastic moduli.

The experimental Kendall pull-off force, P_{E-KEN} , obtained from the adhesion measurements is presented in Fig. 3. P_{E-KEN} was observed to increase linearly as a function of the square root of the elastic modulus, as expected from Eq. (5). Theoretical pull-off forces, P_{T-KEN} were calculated as before and were also seen to increase as a function of the square root of the elastic modulus. As surface energy and probe size are constant, this is an effect of the change in elastic modulus. However, the P_{E-KEN} values are lower than P_{T-KEN} values by a factor of 1.5–2.

The reason for this difference was that the probe used in this study did not have a perfectly flat surface. White light interferometry of the probe showed a variation of approximately 5 μm in surface roughness close to the edge. Therefore, the surface roughness of the rigid probe was dominant over the surface roughness of the soft samples during adhesive contact formation. This variation in surface roughness was predominantly seen to exist in the annulus of width 250 μm from the edge of the probe. However, the rest of the probe surface (diameter ~ 1.5 mm) was relatively flat, showing a variation in roughness to a fraction of 1 μm . Therefore, a perfectly flat adhesive Kendall contact occurs over a diameter of 1.5 mm instead of 2 mm of the probe size, thereby explaining the P_{T-KEN} values being higher than the P_{E-KEN} values. The corrected P_{T-KEN} values corresponding to a flat probe diameter of 1.5 mm ($(P_{T-KEN})_C$) are also shown in Fig. 3 and matches fairly well with the experimental results. Despite the absolute values differing from each other, the observed general trend follows the prediction of the Kendall model. These experiments highlight that adhesion against a flat probe can be controlled by tuning the crosslinking density and therefore the elastic modulus.

Conclusion

Acrylate networks with T_g (~ 37 °C) and varying elastic modulus (2–12 MPa) were developed such that the effect of modulus on pull-off force measurements can be studied. For spherical testing, the experimental pull-off forces showed no modulus dependency as expected from the JKR theory. It is proposed that the transfer of free oligomers from the sample to the probe surface causes a decrease in probe surface energy during repeated measurements. The theoretical pull-off forces calculated considering this effect were in good agreement with the experimental pull-off forces for all samples tested. Flat probe testing revealed an increase in pull-off force as a function of elastic modulus, which is in agreement with Kendall's theory. The experimental values were lower than the theoretical values owing to probe geometry allowing for reduced contact and causing detachment at lower pull-off forces.

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