

ADHESIVE VISCOELASTIC RESPONSE TO SURFACES WITH TAILORED SURFACE CHEMISTRY

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ABSTRACT

Achieving weight reduction in lightweight structural and protection applications, multi-material assemblies are being proposed in several applications ranging from tactical wheeled vehicles, rotorcraft, and munitions. Adhesive bonding of dissimilar materials found in these systems is a critical technology in the production of lightweight energy absorbing structures. The design and control of the adhesive interfaces can contribute largely to overall performance to include structural load transfer as well as energy absorption during failure. Fundamental understanding of adhesive and interfacial mechanisms allows for the systematic design of multi-material assemblies with desired performance features. In this work, we present initial attempts to correlate adhesive viscoelastic parameters and interfacial bonding on the adhesion of urethane-acrylate adhesives to glass substrates.

1. INTRODUCTION

To achieve weight reduction in lightweight structural and protection applications, multi-material assemblies are being proposed in several applications ranging from tactical wheeled vehicles, rotorcraft, and munitions. Adhesive bonding of dissimilar materials found in these systems is a critical technology in the production of lightweight energy absorbing structures.

The design and control of the adhesive interfaces can contribute largely to overall performance to include structural load transfer as well as energy absorption during failure. Fundamental understanding of adhesive and interfacial mechanisms allows for the systematic design of multi-material assemblies with desired performance features.

The strength of an adhesive bond depends strongly on the viscoelastic properties of the adhesive and its chemical interaction with the substrate. Gent et al. has correlated the amount of energy, G , required to advance a fracture plane by unit area to the form of $G = G_0 [1 + f(R,T)]$ [1], where G_0 represents the minimum energy where failure occurs. This term (measured at low rates and high temperatures to minimize viscoelastic effects) is governed primarily by the amount of bonding of the adhesive to a surface. The second part of the equation, $f(R,T)$, represents the

contribution of adhesive viscoelastic properties to bonding strength. This function strongly depends on rate R and temperature T , which was shown to agree with rate-temperature effects described by Williams-Landel-Ferry (WLF) behavior.

In this work, we present initial attempts to correlate interfacial bonding and adhesive viscoelastic parameters on the adhesion of urethane-acrylate adhesives to glass substrates. Dynamic mechanical analysis (DMA) was utilized to obtain viscoelastic constants for the adhesive. These parameters were used to superimpose fracture energies at various rate and temperature conditions, thus generating a master curve for comparison purposes. Interfacial bonding was controlled through silane chemistry by treating the substrates with various ratios of reactive and non-reactive silanes. The work presented here shows the relationship between adhesion strength and surface reactivity at various strain rates at 0 °C and 25 °C. Future work will develop similar curves for different testing temperatures.

2. EXPERIMENTAL

2.1 Materials

The adhesives used in this work were free-radically curing thermosetting resins. The adhesive formulations contained 75 wt. % Ebecryl 270 (Cytec) as the urethane-acrylate crosslinker and 25 wt. % of a reactive monofunctional diluent (isobornyl acrylate (IBA, Sartomer) as shown in Figure 1. Each formulation was thermally cured using 1 wt. % Trigonox (Akzo Nobel) as the initiator and 1 drop of cobalt naphthenate (Aldrich) per 50 grams of resin as the catalyst.

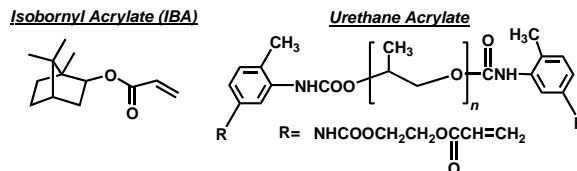


Fig. 1. The adhesive used in this work contains 25 wt. % isobornyl acrylate (IBA) and 75 wt. % urethane acrylate monomer.

2.2 Surface Treatments

Pyrex glass was purchased from Kaufman Inc. (New Castle DE) and pre-cut into 5.1 cm by 30.5 cm pieces with a thickness of 0.32 cm. To prepare the glass substrates for silane treatment, they were cleaned with a solution of 5:1:1 volumetric ratio of H₂O: H₂O₂: NH₃. The solution was brought to a boil and the glass pieces were placed in the solution for at least 5 minutes. Finally, the glass substrates were dried in a nitrogen stream.

Silane treatments comprised a 99 weight percent 90:10 (v:v) ethanol:H₂O mixture, and 1 weight percent of either 3-methacryloxypropyltrimethoxysilane 97% (MPS, Avocado Research Chemicals Ltd) or n-propyltrimethoxysilane (PTMO, Degussa Corporation). Each silane solution was given one hour to hydrolyze by adjusting pH to 4.5 with acetic acid. The solutions were mixed to achieve a desired MPS:PTMO ratio and the substrates were dipped in the solution for one minute. After treatment, the substrates were dried in a nitrogen stream and placed in an oven at 100°C to allow for full condensation. A schematic representation of the mixed silane treatments is given in Fig. 2. By blending adhesive-reactive and adhesive-nonreactive silanes, the surface reactivity can be controlled.

2.3 Mechanical and Thermal Testing

Tear strength was measured for the adhesive according to ASTM D624 – 98. Thin sheets of adhesive were cast, thermally cured, and cut out using a chevron-shaped die (Die C from the ASTM). The specimens were placed in an Instron 4505 equipped with a 1 kN load cell and loaded in tension at a strain rate of 8.47·10⁻³ m/s. Tear strength was reported as the maximum force recorded. Tensile properties were measured according to ASTM D412-98a. Dynamic mechanical analysis was performed using a TA Instruments DMA Q800 to determine the storage modulus (E') and the loss modulus (E'') in a multiple-frequency sweep at temperatures from -100 °C to 50 °C. The sample was equilibrated at a temperature of -100 °C for 5 minutes, then incremented in steps of 3 °C to a final temperature of 50 °C. At the initiation of each isothermal step the instrument was allowed to equilibrate for 5 minutes prior to recording a frequency sweep. A frequency sweep of 0.1, 0.3, 1, 3, 10, and Hz was then conducted. At each temperature and frequency, E', E'', and tan δ were recorded.

The peel test specimens were tested using a 90° flat roller peel apparatus according the ASTM D6862-04. The adhesive was pulled from a non-stick tape starter crack to initiate peel and loaded into an Instron 4505 equipped with a 1 kN load cell. The adhesive was then peeled from the substrate at various strain rates and temperatures. The thermal chamber used for temperature control was a Plexiglas box (40 cm x 46 cm x 100 cm)

with insulating foam adhered to the interior. Two air circulation vents attached the chamber to a refrigeration unit to ensure environmental control in the testing chamber. The refrigeration unit provided continuous feedback to ensure constant hot or cold temperatures, ranging from -60°C to 80°C. This temperature range is ideal for many polymers because it allows testing below and above T_g. Two thermocouples were also used to measure the temperature of the sample while testing.

3. RESULTS AND DISCUSSION

3.1 Adhesive Properties

The T_g, tear force, and tensile properties of the adhesive used in this work is given in Table 1. In addition to these properties, viscoelastic properties play an important role in adhesion strength. Gent et al. observed that the viscoelastic behaved according to the WLF equation (Equation 1). To fully characterize the viscoelastic properties of the material in the frequency domain using linear viscoelastic theory, multiple-frequency sweeps with DMA were performed.

Table 1. Summary of Adhesive Properties

Property	Value
T _g (°C) DMA @ 1Hz	-22.0
Tear Strength (kN/m)	20.7 ± 1.3
Tensile Strength (MPa)	7.6 ± 0.7
Young's Modulus (MPa)	23.5 ± 1.3

To fully characterize the viscoelastic properties of the material in the frequency domain using linear viscoelastic theory, multiple-frequency sweeps with DMA were performed. The adhesive was analyzed with DMA in a multiple-frequency sweep at temperatures from -100 °C to 75 °C. The sample was equilibrated at a temperature of 100 °C for 5 minutes, then incremented in steps of 3 °C to a final temperature of 50 °C. At the initiation of each isothermal step the instrument was allowed to equilibrate for five minutes prior to recording a frequency sweep. A frequency sweep of .01, 0.3, 1, 3, 10, and 30 Hz was then conducted. At each temperature and frequency, E', E'', and tan δ were recorded. Figure 2 and Figure 3 show E' and E'' spectra, respectively, for the adhesive obtained from the multiple-frequency sweeps.

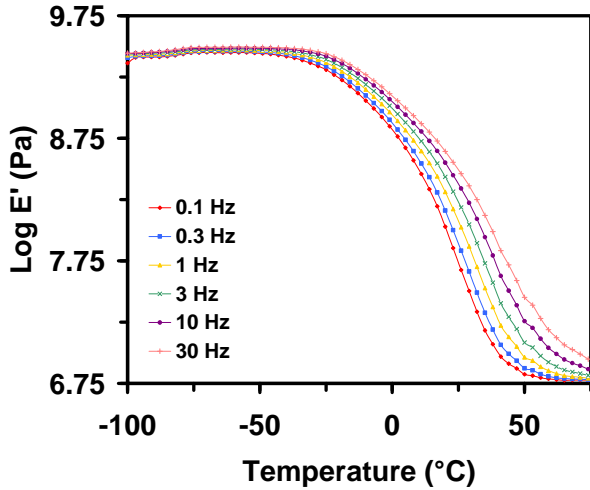


Fig. 2. DMA E' curves for the 25 wt. % IBA, 75 wt. % UA adhesive as a function of temperature and frequency.

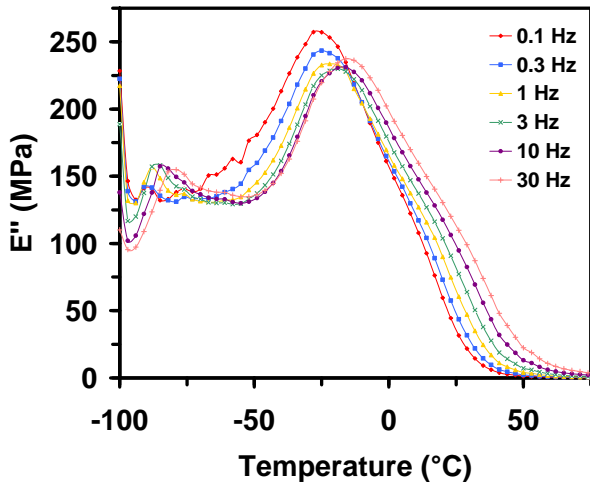


Fig. 3. DMA E'' curves for the 25 wt. % IBA, 75 wt. % UA adhesive as a function of temperature and frequency.

From the multi-frequency E' curves, the data from each isotherm can be plotted and horizontally shifted into a single master curve. This single curve represents a much wider frequency range at a single reference temperature. This temperature reduction of the storage modulus is performed by multiplying the storage modulus, E', by (T/T_0) , where T_0 is the reference temperature and T is the temperature of the isotherm, and plotting against $\omega a_T T$, where ω is the frequency and a_T is the horizontal shift factor [2]. This creates a single curve in which all of the data is reduced to the reference temperature, T_0 . Figure 4 shows the unshifted isothermal E' data for the adhesive comprising 25 wt. % IBA and 75 wt. % UA crosslinker. The reference temperature, T_0 , for horizontal shifting was set to the glass transition temperature, $T_0 = T_g = -22^\circ\text{C}$, determined from the peak of the loss modulus at 1 Hz. By horizontally shifting the isotherms along the frequency axis and visually aligning

each with OriginPro software [3], the individual isothermal data can be assembled into one continuous master curve, as shown in Figure 5.

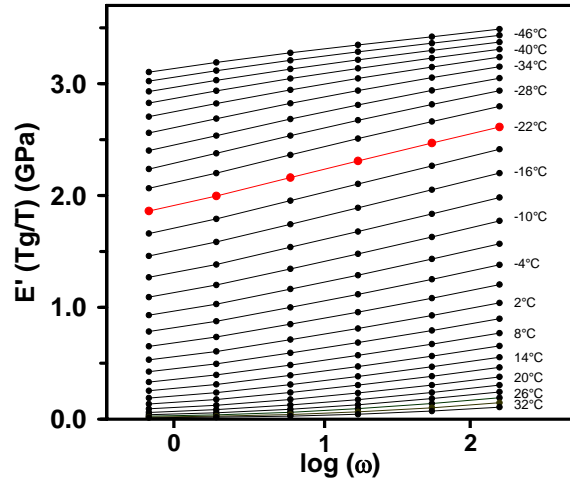


Fig. 4. Unshifted E' isotherms for the 25 wt. % IBA, 75 wt. % UA adhesive.

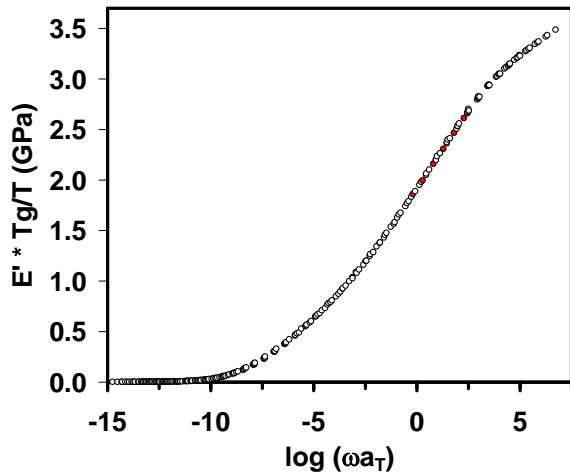


Fig. 5. Frequency domain E' mastercurve for 25 wt. % IBA, 75 wt. % UA adhesive, $T_0 = -22^\circ\text{C}$ (in red).

The horizontal shift factors (a_T) shift factors from each isotherm can then be used to determine the C_1 and C_2 constants in the WLF equation, where C_1 is dimensionless, and C_2 has units of Kelvin (K).

$$\text{Log } a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (1)$$

The WLF constants for the 25 weight percent IBA, 75 weight percent UA adhesive were calculated to be $C_1 = 33.8$ and $C_2 = 122.3$ K. These values slightly deviate from the universal constants of 17.4 and 51.6 K, respectively.

3.2 Adhesion Studies

One of the goals of this work was to relate interfacial bonding of the adhesive with the substrate. The surface of glass substrates contains many hydroxyl groups that can be utilized to control surface reactivity through organofunctional silane treatments. Figure 6 gives a schematic representation of how silanes can be used to control surface reactivity. The two silanes used in this work are propyltrimethoxysilane (PTMO) and methacryloxypropyltrimethoxysilane (MPS). PTMO has a propyl functionality that does not react with the free radical curing adhesive, while the methacryl group of the MPS does. By varying the ratio of these two silanes during condensation onto the glass surface, the surface reactivity can be designed to have a strong or weak bond with the matrix.

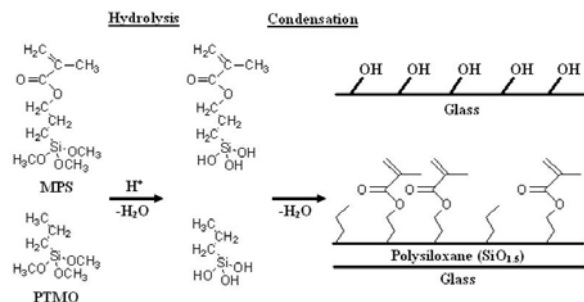


Fig. 6. Interfacial bonding of the adhesive with the substrate was controlled through organofunctional silane treatments of propyltrimethoxysilane (PTMO) and methacryloxypropyltrimethoxysilane (MPS).

When the strain rate was reduced by an order of magnitude (0.254 cm/s), the adhesive behavior changed significantly. The overall peel force reduces. Instead of reaching a plateau at a specific surface reactivity, it was observed that there was a direct relationship between the amount of reactive groups applied to the surface of the glass and peel force. As more reactive groups are added, the peel force increases, thus indicating a stronger bond. Additionally, no cohesive failure was observed for these strain rates. When the strain rate is further decreased (0.0254 cm/s), the peel force again reduces and the effect of surface reactivity is more prevalent than for higher strain rates.

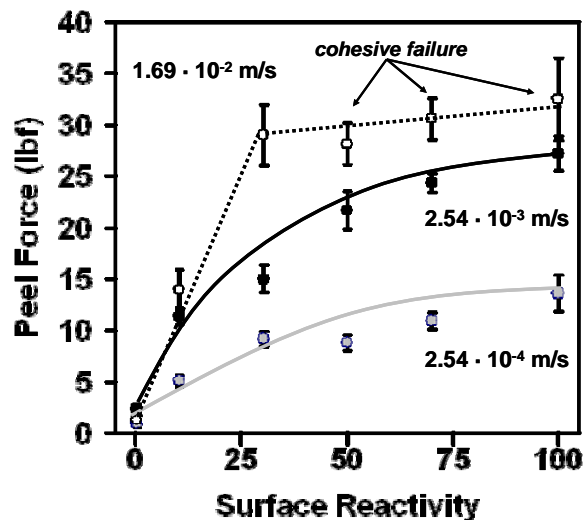


Fig. 7. The adhesive used in this work contains 25 wt. % isobornyl acrylate (IBA) and 75 wt. % urethane acrylate monomer.

4. CONCLUSIONS

The goal of this work was to investigate the bonding of urethane acrylate adhesives onto glass substrates with controlled surface chemistry. Viscoelastic properties (WLF constants) of the adhesive were obtained utilizing DMA and will be used to superimpose rate-temperature effects obtained in the future. The dependence of strain-rate and surface coverage on bond strength was obtained at ambient conditions. High strain rates showed a plateau in peel force at relatively low surface reactivity (25 %) and exhibited cohesive failure above 50 % reactivity. When strain rate was reduced, the effect of interfacial bonding was more prevalent.

In this work, we presented results obtained at ambient conditions. Future work will investigate various temperatures to further develop master curves with respect to rate-temperature and surface reactivity. Another potential area of interest in this work is to investigate the effects of adding surface reactivity in a preferential pattern. The surface reactivity in this work was randomly applied to the surface through silane treatment. If one could control the geometry and length scale of the reactive groups on the surface, could further benefits in adhesive bonding be achieved?

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