A Thermoplastic/Thermoset Blend Exhibiting Thermal Mending and Reversible Adhesion

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and Patrick T. Mather[1]*

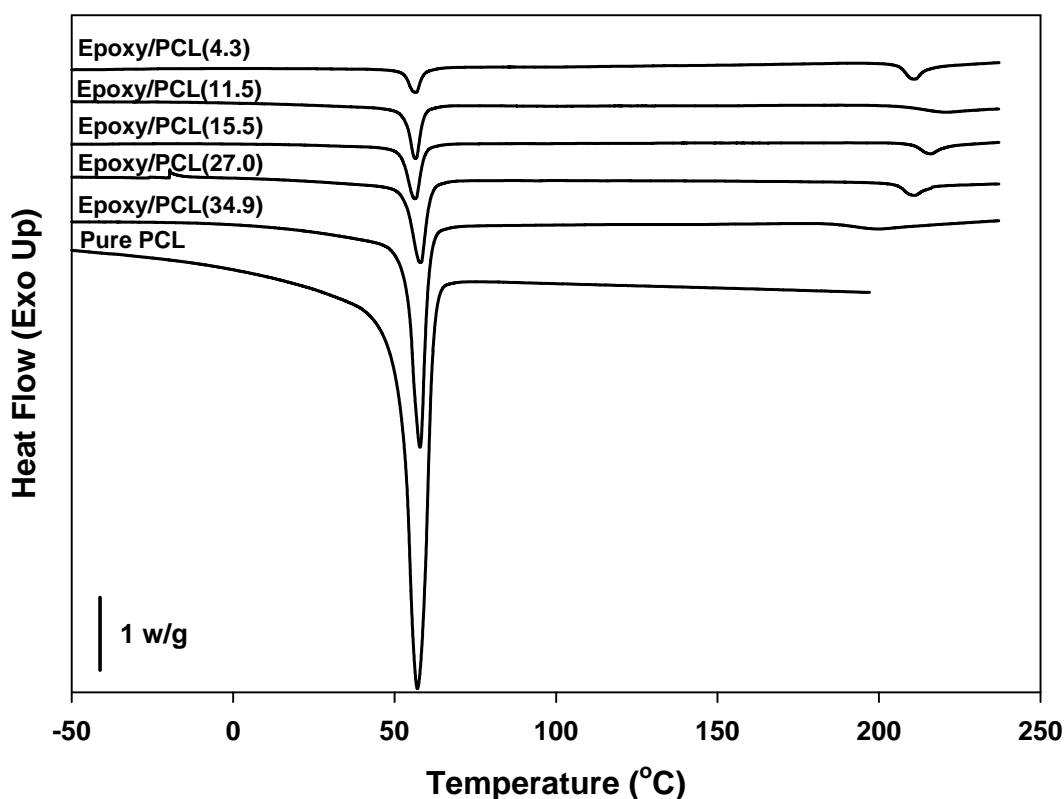**Supporting Information**

Figure S1. Differential scanning calorimetry (DSC) thermograms (2nd heating) of fully cured epoxy/PCL blends of different compositions.
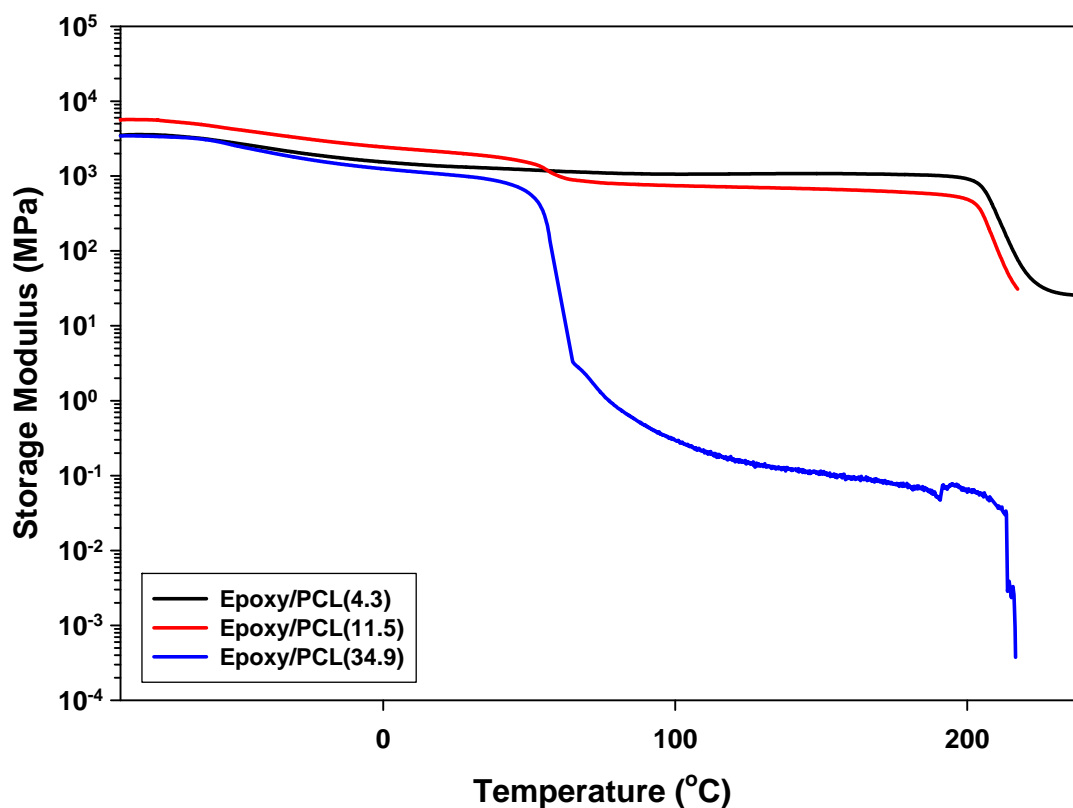
Figure S2. Dynamic mechanical analysis (DMA) results for **Epoxy/PCL(4.3)**, **Epoxy/PCL(11.5)** and **Epoxy/PCL(34.9)**.
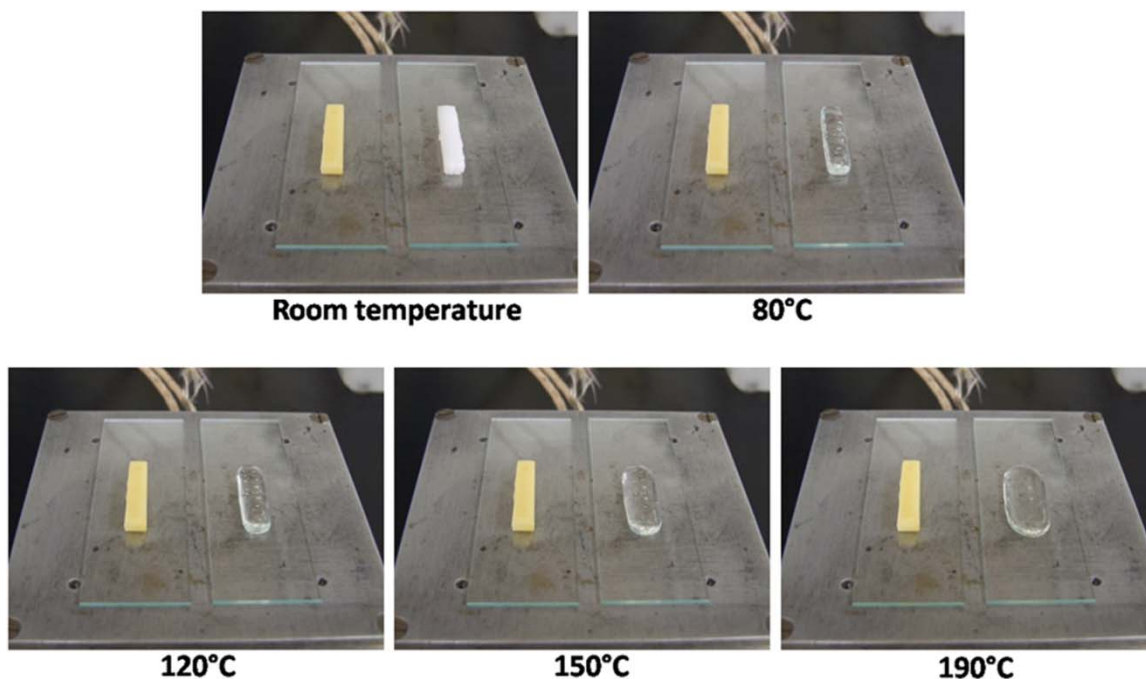

Figure S3. Comparison of dimensional stabilities of **Epoxy/PCL(15.5)** and pure PCL. **Epoxy/PCL(15.5)** (left) and pure PCL (right) sample bars were placed on a hot-stage with a stepwise increase of temperature. Images were taken at different temperatures after stabilizing at the temperature for several minutes. Pure PCL showed the melting and flow behavior, while no macroscopic flow or obvious dimensional changes were observed for **Epoxy/PCL(15.5)**.
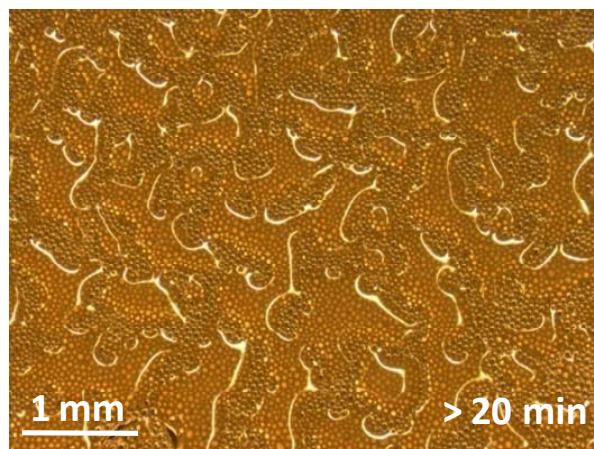
Figure S4. Stereo optical micrograph showing the heated surface of **Epoxy/PCL(15.5)** after the bleeding reached steady-state (> 20 min).
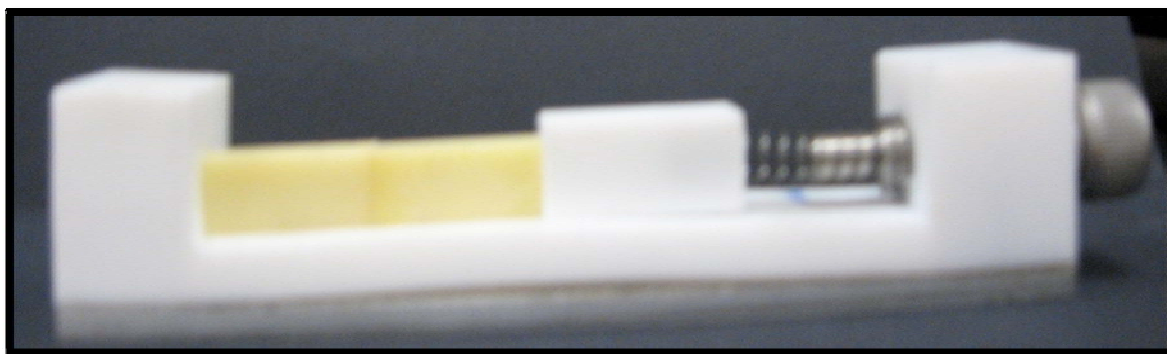

Figure S5. A photograph of the spring based device used for bonding. The spring (with known spring constant, k) can be compressed by adjusting the screw to control the force exerted on the samples.

Calculation of Flow Time, t_{flow}, for Differential Expansive Bleeding (DEB)
1. The model

For simplicity the expansive flow is treated as a two-step process (shown below for flow in one direction). During the first step the material is heated to a high temperature, but without any flow or volume change. A hydrostatic pressure is generated within the material due to the fact that the material is tending to expand (or resistant to be compressed; imagining a compressive pressure equal to the "expansive" pressure is applied onto the 1material all the time to keep its volume constant). During the second step, the "compressive pressure" is released and an "expansive flow" takes place while the temperature is held constant (isothermal). The expansive flow is driven by the hydrostatic pressure generated in step one. The flow completes when the pressure drops to atmospheric pressure.

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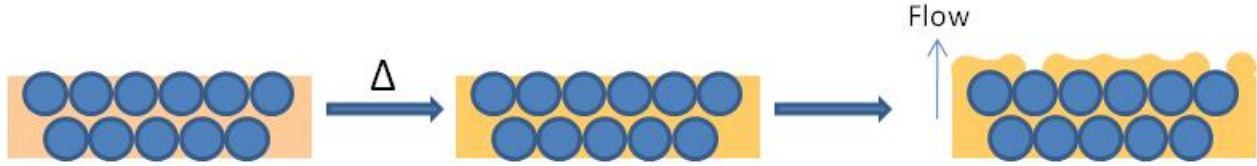
Based on this simple model the expansive pressure can be calculated (Section 2.1). This can subsequently be used to estimate the flow time, by assuming a pressure driven flow process through a porous medium. Comparison between calculated flow time and experimental observation would lead to a better understanding of the "expansive bleeding" process.

2. Determination of expansive pressure, P

2.1 Determination of K (bulk modulus)

Given the Tait equation (the most common empirical equation of state (EOS) to fit polymeric PVT data)

$$V(P,T) = V(0,T)\left\{1 - Cln\left[1 + \frac{P}{B(T)}\right]\right\} \quad (1)$$

Where the coefficient C is usually taken to be a universal constant equal to 0.0894.

For PCL (*Journal of Applied Polymer Science*, **48**, 1061-1080, 1993) in the temperature range of 100-148 °C:

$$V(0,T)\,(cm^3/g) = 0.9049\,exp\left(6.392 \times 10^{-4}T\,(°C)\right)$$

$$B(T)\,(bar) = 1890\,exp\left(-3.931 \times 10^{-3}T\,(°C)\right)$$

Considering T = 130 °C (the measured surface temperature for a particular experiment):

$$V(0,130°C)\,(cm^3/g) = 0.9049\,exp\left(6.392 \times 10^{-4} \times 130(°C)\right) = 0.9833\,(cm^3/g)$$

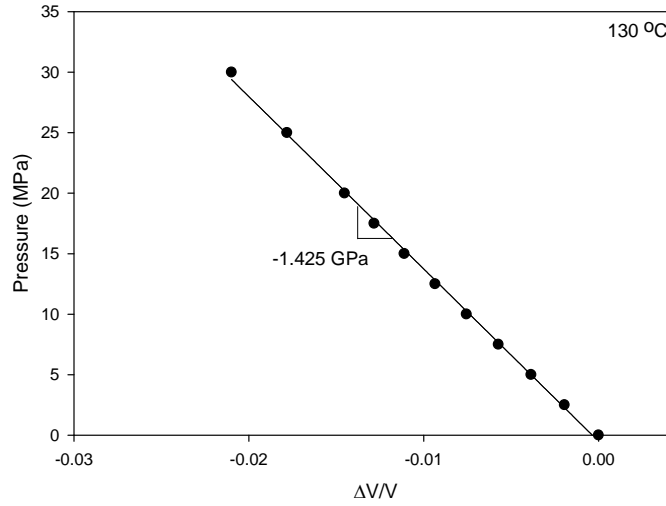$$B(130°C)\,(bar) = 1890\,exp\left(-3.931 \times 10^{-3} \times 130\,(°C)\right) = 1133.768\,(bar)$$

Eqn (1) can be rewritten as

$$\frac{V(P,T) - V(0,T)}{V(0,T)} = \frac{\Delta V}{V} = -Cln\left[1 + \frac{P}{B(T)}\right]$$

and at 130°C we have:

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$$\frac{\Delta V}{V} = \frac{V(P,T) - 0.9833}{0.9833} = -0.0894 ln\left[1 + \frac{P(bar)}{1133.768}\right]$$

Plotting $\frac{\Delta V}{V}$ vs. P:

Since $P = K\frac{|\Delta V|}{V}$, the slope of the above plot gives the bulk modulus (compressibility^{-1}) at 130 °C and

$$K = 1.425 \times 10^3 \, MPa = 1.425 \, GPa$$

2.2 Determination of $\Delta V/V$, the volume change of PCL from room temperature to 130 °C

The specific volume of PCL at room temperature (from Aldrich)

$$V = \frac{1}{\rho} = \frac{1}{1.145} = 0.8734 \, cm^3/g$$

The specific volume of PCL at 130 °C, as calculated from Tait equation (assuming 1 bar)

$$V(1bar, 130°C) = 0.9833 \times \left\{1 - 0.0894 ln\left[1 + \frac{1}{1133.768}\right]\right\} = 0.9832 \, cm^3/g$$

Therefore the change in volume is,

$$\frac{\Delta V}{V} = \frac{0.9832 - 0.8734}{0.8734} = 0.1257 = 12.57\%$$

2.3 Calculation of the expansive pressure

By using $P = K\frac{\Delta V}{V}$ again, the transient hydrostatic pressure generated can be calculated as,

$$P = 1.425 \times 10^3 \times 12.57\% = 179.1225 \, MPa$$

We noticed that a large transient pressure (~1791 atmospheric pressure) is generated by heating the material to 130 °C. This is not surprising given the relatively large bulk modulus of PCL, which behaves nearly as an incompressible fluid.

3. Determination of flow time, t_{flow}

The hydrostatic pressure P due to this "compression" (essentially an increase in temperature) can drive the subsequent expansive flow. The expansive flow can be treated as pressure driven flow through porous media (beds of solid spherical particles), where *Darcy's law* and *Kozeny-Carman* equation apply. It is assumed that flow through a bed of solid particles is equivalent to flow through a set of channels having an equivalent channel diameter, D_{eq}. The total surface area and void volume of the channels should match those of the bed.

The overall *Kozeny-Carman* equation for calculating the flow time, t, is given by

$$t = \frac{L}{\bar{\bar{V}}} = \frac{150\eta(1-\varepsilon)^2 L^2}{\Delta P \Phi_s^2 D_p^2 \varepsilon^2}$$

Where ΔP, D_p and Φ_s are particle size (estimated to be 50 μm from Figure 1(a)) and sphericity (assumed to be 1), respectively. L is the length of the channel and is estimated to be 2 mm, half of the sample "thickness" (normal to the observed surface). ε is the porosity (void fraction) and can be calculated based on the weight fractions and densities of epoxy and PCL. For epoxy/PCL(15.5):

$$\varepsilon = \frac{\frac{\omega_{PCL}}{\rho_{PCL}}}{\frac{\omega_{PCL}}{\rho_{PCL}} + \frac{\omega_{epoxy}}{\rho_{epoxy}}} = 14.5\%$$

Where ω_{PCL} = 15.5% (known), ω_{epoxy} = 1 - ω_{epoxy} = 84.5%, ρ_{PCL} = 1.145 g/cm^3 (Aldrich) and ρ_{epoxy} = 1.06 g/cm^3 (www.matweb.com).

Finally, η, the viscosity of PCL melt was measured by a dynamic rheological experiment and η = 772.3 Pa*s at 130 °C.

Based on these values and *Kozeny-Carman* equation the flow time t_{flow} was calculated to be **35.98 s**. This means the expansive flow completes in about half a minute, consistent with our experimental observation that the "bleeding" behavior shows very little time dependence and is mainly controlled by temperature. Because this time is comparable or shorter than heat transfer time (Figure 3a), we can safely conclude that the rate of DEB is dominated by heat transfer, not by viscous flow.