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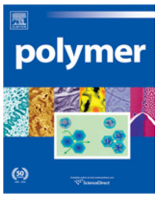

A thermally responsive, rigid, and reversible adhesive

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ABSTRACT

In this paper we present the development of a unique self-adhesive material that, unlike conventional adhesives, maintains a high degree of rigidity at the "adhesive" state while possessing the ability to easily de-bond upon heating. Consequently, the material is both a *rigid* and a *reversible* adhesive. The material is an initially miscible blend of poly(ε-caprolactone) (PCL) and diglycidyl ether of bisphenol-A/diaminodiphenylsulfone (DGEBA/DDS) epoxy, processed to a unique morphology via polymerization-induced phase separation (PIPS). The fully cured material features a biphasic, "bricks-and-mortar" morphology in which epoxy forms highly interconnected spheres ("bricks") that interpenetrate with a continuous PCL matrix ("mortar"). When heated to melt the PCL phase ($60\,^{\circ}\mathrm{C} < T < 200\,^{\circ}\mathrm{C}$), the epoxy bricks remain rigid due to the high epoxy T_g ($>200\,^{\circ}\mathrm{C}$) while PCL liquefies to become a melt adhesive. Moreover, the PCL liquid undergoes microscopic dilational flow to wet the sample surfaces due to its high volumetric expansion in excess to epoxy bricks expansion, a phenomenon we term "differential expansive bleeding" (DEB). Remarkably, the samples remain rigid at this state and their surfaces become covered by a thin layer of PCL now able to wet, and subsequently bond through cooling, to a variety of substrates. We observe high bonding strengths, which we attribute to a combination of good wetting and subsequent formation of a thin layer of crystalline PCL with high cohesive strength upon cooling. This adhesive layer can be melted again by heating ($T > T_m$) to easily de-bond and subsequent rebonding capacity was demonstrated, indicating repeated availability of PCL melt adhesive to the surface by the DEB mechanism.

1. Introduction

Conventional adhesives are materials that are applied as a low-viscosity liquid and transform into a strong, tough solid that bonds two surfaces together. This liquid–solid transformation can be either a chemical reaction, usually a non-reversible thermosetting polymerization that leads to a crosslinked network (thermoset adhesives), or a physical melting/crystallization process triggered by solvent evaporation or thermal (heating/cooling) cycling (thermoplastic adhesives). An emerging area of adhesives research is the development of reversible adhesives; i.e., adhesives that enable facile de-bonding and separation of the bonded surfaces when the adhesion is no longer needed [1]. Such a phenomenon has great industrial potential, as one can easily dissemble or selectively remove the components for repair or maintenance. Ideally this adhesive reversibility should be achieved with minimal sacrifice of adhesive strength in the bonded state, relative to the irreversible case.

One major strategy toward the achievement of reversible adhesives is to mimic the hierarchical structure of a Gecko foot [2,3] to produce micro- or nano-structured dry adhesive surfaces [4–10]. This has been reviewed in several recent articles [11,12]. Despite the intrinsic attractiveness of this biomimetic approach, the measured adhesive strengths have been relatively small compared to conventional adhesives, since they rely primarily on the relatively weak van der Waals interactions. Moreover, processing complexity is high due to the use of micro- and nano-fabrication processes. In order to overcome these restrictions, Lee et al. [8] took a unique biomimetic approach. In particular, they dip-coated a nano-structured surface with a copolymer containing 17% of dopamine methacrylamide (DMA), a synthetic mimic of the major amino acid 3,4-dihydroxy-L-phenylalanine (DOPA) found in the adhesive proteins of mussels, to produce a hybrid "geckel" adhesive and observed significantly enhanced adhesive strength both in air and in water. Another shortcoming of most synthetic gecko adhesives is that, unlike geckos themselves, a significant external peeling force is still required for the adhesive to de-bond. Recently, several

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researchers utilized shape memory effect to either induce a microscopic transition of surface topology [7,13] or a macroscopic change in geometry [14] as a means to “self-peel”. Alternatively, Aubert [15] developed a thermally removable adhesive using reversible Diels–Alder reaction.

In our prior publication [16], we reported on a new self-healing polymer blend composed of poly(ε-caprolactone) (PCL) and a diglycidyl ether of bisphenol-A (DGEBA) based high T_g epoxy. This system was found to undergo polymerization-induced phase separation (PIPS) during the crosslinking of epoxy and yield a “bricks-and-mortar” morphology in which epoxy exists as highly interconnected spheres (“bricks”) interpenetrating with a continuous PCL matrix (“mortar”). When heated ($T >$ PCL T_m), the material exhibited differential expansive “bleeding” (DEB) where molten PCL (the adhesive phase) undergoes a dilational flow process onto the surfaces while the material still remains a rigid solid, the latter due to the high T_g and mechanical dominance of the epoxy (the structural phase). The origin of DEB, as we analyzed, is the difference in volumetric expansion between the two (PCL and epoxy) phases, which generates a large transient pressure to drive the dilational/expansive flow of molten PCL. This phenomenon has been successfully utilized for self-healing of cracks. The net result of DEB is the coverage of samples by a thin layer of PCL on all free surfaces. We note that PCL-based polymers are known for their good adhesive properties and have been used for a number of industrial applications [17–20].

In the present work, we have exploited the thermally “activated” surfaces of our material for their ability to adhere to a variety of substrates in a rigid solid state, with adhesive strength primarily from the crystallization of PCL during subsequent cooling. Moreover, the structural rigidity as well as the physical nature of adhesion enable facile de-bonding upon a second heating treatment, mimicking the reversible adhesive behavior of a gecko foot. In what follows, we report on the details of sample preparation and basic characterization, adhesion testing methodology, and reversible adhesion findings.

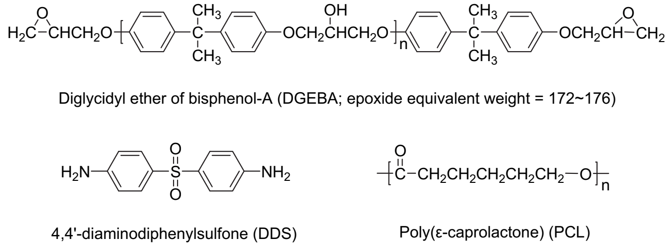
2. Experimental section

2.1. Materials

All raw chemicals, including diglycidyl either of bisphenol-A (DGEBA; epoxide equivalent weight = 172 ∼ 176), 4,4′-diaminodiphenylsulfone (DDS), and poly(ε-caprolactone) (PCL; $M_n \sim 42{,}500$ g/mol and $M_w \sim 65{,}000$ g/mol) were obtained from Sigma–Aldrich and used as received without any further purification. The chemical structures are shown in Scheme 1.

2.2. Material synthesis

We previously reported on the synthesis of PCL/DGEBA/DDS blends [16]. Here we describe the slightly modified process applied to the specific composition examined for adhesion studies. DGEBA (a viscous liquid) and PCL (pellets) in mass ratio of $m_{\mathrm{DGEBA}}{:}m_{\mathrm{PCL}} =$ 80:20 were first mixed in a three-neck reaction flask at 120 °C by continuous mechanical stirring using an Arrow 6000 stirrer with a Teflon blade, until a homogeneous clear mixture was obtained. Constant nitrogen flow was applied to minimize oxidation during mixing. The temperature was raised to 140 °C and a stoichiometric amount of DDS powder (molar ratio of DGEBA:DDS = 2:1) was quickly added to the mixture. The stirring lasted for another 20–30 min until the DDS had completely dissolved, and the nitrogen purge replaced with a light vacuum to remove the resulting air bubbles. The temperature was then reduced back to 120 °C and vacuum applied for another 1 h to completely remove air bubbles. Finally the mixture was poured into a pre-heated silicone rubber mold (PlatSil 73–34, Polytek Development Corp) and fully cured at 180 °C for 3 h in a convection oven (Fisher Scientific Isotemp 825F). The fully cured sample bars are both strong and tough, with a light yellow color. The final PCL wt% is 15.5% (considering the addition of DDS) in the blend and the fully cured material is referred to as *Epoxy/PCL(15.5)* hereafter.


Diglycidyl ether of bisphenol-A (DGEBA; epoxide equivalent weight = 172~176)

4,4'-diaminodiphenylsulfone (DDS)

Poly(ε-caprolactone) (PCL)

Scheme 1. The chemical structures of diglycidyl ether of bisphenol-A (DGEBA), 4,4′-diaminodiphenylsulfone (DDS) and poly(ε-caprolactone) (PCL).

2.3. Blend morphology and thermomechanical properties

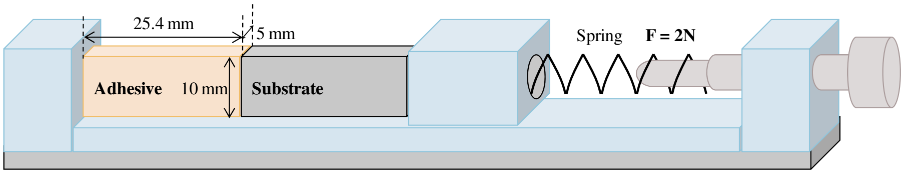
The bulk morphology of *Epoxy/PCL(15.5)* was studied using scanning electron microscopy (SEM) and polarized optical microscopy (POM). For the former, the fracture surface of a cryogenically fractured *Epoxy/PCL(15.5)* sample was sputter coated with gold and examined using a JEOL JSM-5600 SEM instrument. For the latter, a thin uncured mixture of *Epoxy/PCL(15.5)* was sandwiched between a glass slide and a cover slip, cured at 180 °C for 3 h and examined on an Olympus BX51 with polarizer and analyzer crossed for the imaging of birefringence exhibited by the crystallizable PCL component. The thermomechanical properties of *Epoxy/PCL(15.5)* were studied by dynamic mechanical analysis (DMA) using a TA Q800 dynamic mechanical analyzer. A rectangular bar with dimensions of 17.4 mm × 10 mm × 2.8 mm was loaded under single cantilever mode with an oscillatory deflection amplitude of 15 μm (corresponding to a tensile strain of 0.034%) at 1 Hz. The temperature was ramped from −90 °C to 280 °C at 3 °C/min, allowing observation of all significant mechanical relaxation events.

2.4. Observation of differential expansive bleeding (DEB)

To visualize the thermally induced DEB process, an *Epoxy/PCL(15.5)* sample bar was sputter coated with gold (to enhance optical contrast) and directly imaged using a Zeiss Discovery V8 stereo microscope. A controlled heating ramp at 2 °C/min was applied using a Linkam TST350 tensile stage (employing only the heating element). Images were taken at a constant frame rate of 2 frames/sec using a CCD camera (Q-Imaging QICAM Fast 1394) with a pixel density of 1392 × 1040 and 24 bit dynamic range.

2.5. Characterization of adhesive strength

The strength of the adhesive bond was characterized using a butt-joint test method. To eliminate the effect of surface roughness, the bonding surfaces of the metal substrates (aluminum and stainless steel) were polished in a consistent manner using 320-grit sand paper prior to bonding. An *Epoxy/PCL(15.5)* sample bar (25.4 mm × 10 mm × 5 mm) and a substrate of the same dimensions were first loaded on a custom made device (Scheme 2) with a controlled compressive force of 2 N. After heating in a convective oven isothermal at 150 °C for a prescribed bonding time, t_B, the device (with loaded specimen) was removed from the oven and allowed to cool to room temperature. All bonded specimens were kept at room temperature for at least 24 h before being tested on



Scheme 2. The custom made bonding device used to exert a compressive normal load of 2 N to the *Epoxy/PCL(15.5)* adhesive and the substrate.

a MTS 1122 universal mechanical tester. The specimen was loaded to complete fracture under tension at a constant displacement rate of 0.5 mm/min while recording the load vs. displacement data. The apparent pull-off strength, σ_{app}, was calculated from $\sigma_{app} = F_P/A$, where F_P and A represent the peak load and cross-sectional area (10 mm × 5 mm), respectively.

To demonstrate a typical thermal bonding cycle, an *in-situ* bonding experiment was conducted using a Linkam TST350 tensile stage with a 200 N load cell and a liquid nitrogen-based cooling system. An *Epoxy/PCL(15.5)* sample bar and an aluminum substrate, both of the same dimensions aforementioned, were clamped on the stage. A 2 N compressive force was applied to keep bonding surfaces in contact. The temperature was then ramped from 25 to 120 °C at 10 °C/min, kept isothermal at 120 °C for 20 min, and finally ramped back to 25 °C at 3 °C/min. A tensile test at a constant displacement rate of 0.5 mm/min was then performed immediately at 25 °C.

3. Results and discussion

3.1. Structural rigidity and differential expansive bleeding (DEB)

Fully cured *Epoxy/PCL(15.5)* is a strong, durable material with a room temperature elastic modulus close to pure epoxy and a much higher toughness due to the addition of PCL and the phase separated morphology. Fig. 1A and B show the bulk morphology of *Epoxy/PCL(15.5)* viewed under both POM and SEM. The POM image (Fig. 1A) shows dark spheres dispersed in a bright matrix (due to birefringence), allowing the identification of both phases to be composed primarily of amorphous epoxy and semi-crystalline PCL, respectively. A magnified SEM image of a cryogenically fractured specimen (Fig. 1B) reveals the fact that the epoxy spheres are highly interconnected in 3-D space. In fact, this interconnection is critical since it makes the epoxy phase more effective in load transfer, ensuring its dominance in determining the composite mechanical properties. The DMA result (Fig. 1C) shows the temperature-dependent storage modulus of *Epoxy/PCL(15.5)* comparabled to pure epoxy and PCL. *Epoxy/PCL(15.5)* shows two major transitions in the given temperature range that correspond to the melting of PCL (59 °C) and the glass transition of epoxy (203 °C), respectively, both transition temperatures being determined as the onset of E′ drop. Unlike pure PCL, which completely melts and becomes a low-strength viscoelastic liquid when heated above its T_m, *Epoxy/PCL(15.5)* displays only a minor softening above the T_m of PCL, and still behaves as a rigid solid with a relatively high modulus (several hundred MPa) for temperatures up to the epoxy T_g.

The thermally induced differential expansive bleeding (DEB) was reported and analyzed in a previous paper [16]. Here for the sake of completeness we present the phenomenon exhibited by the particular samples for adhesion studies (new results) and briefly describe its physical origin. Fig. 2A shows the surface of the *Epoxy/PCL(15.5)* subject to a heating ramp (a time-lapsed movie is available in Supplementary Information). One can clearly observe the formation and enrichment of liquid on the surface, while the bulk of the material still remains a rigid solid as evident from Fig. 1C. In fact the material is free of any macroscopic dimensional or shape change, and the DEB shown in Fig. 2A only occurs locally and microscopically on the surfaces. Physically, the DEB originates from the phase transition (melting) of the PCL matrix and the resulting difference in volumetric expansion of the two phases. When the temperature is increased from room temperature to a point between the T_m of PCL (*ca.* 60 °C) and the T_g of epoxy (>200 °C), the epoxy phase (interconnected spheres or the "bricks") shows a relatively small volumetric expansion typical for a glassy thermoset. However, the PCL phase (matrix or the "mortar") undergoes a large volumetric expansion due to (1) the transition from a semi-crystalline solid to a viscoelastic liquid during melting and (2) the large volumetric expansivity at the liquid state. The difference in volumetric expansion between the two phases can generate a large transient pressure which then drives the flow of molten PCL onto the surface. Fig. 2B and C compares

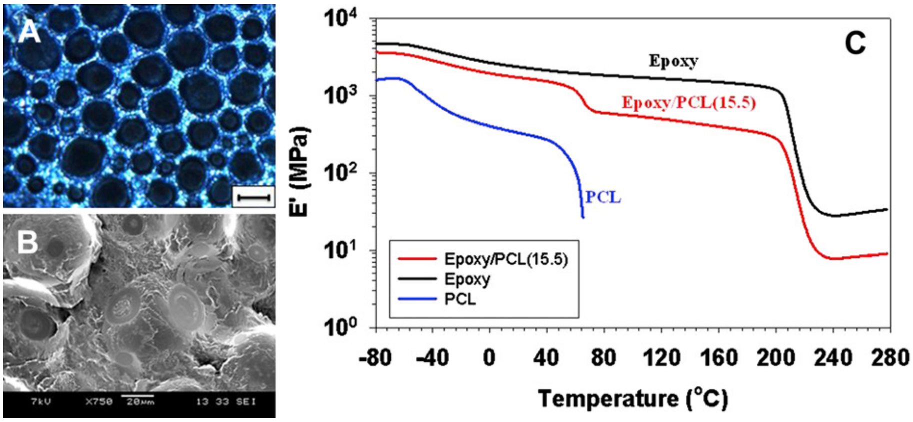


Fig. 1. The morphology and thermomechanical properties of the *Epoxy/PCL(15.5)* adhesive. (A) POM image of a thin *Epoxy/PCL(15.5)* film coated on a glass slide (the scale bar represents 50 µm), (B) SEM image showing a cryogenically fractured *Epoxy/PCL(15.5)* surface and (C) tensile storage modulus (E′) as a function of temperature for *Epoxy/PCL(15.5)*, compared with pure epoxy and PCL.

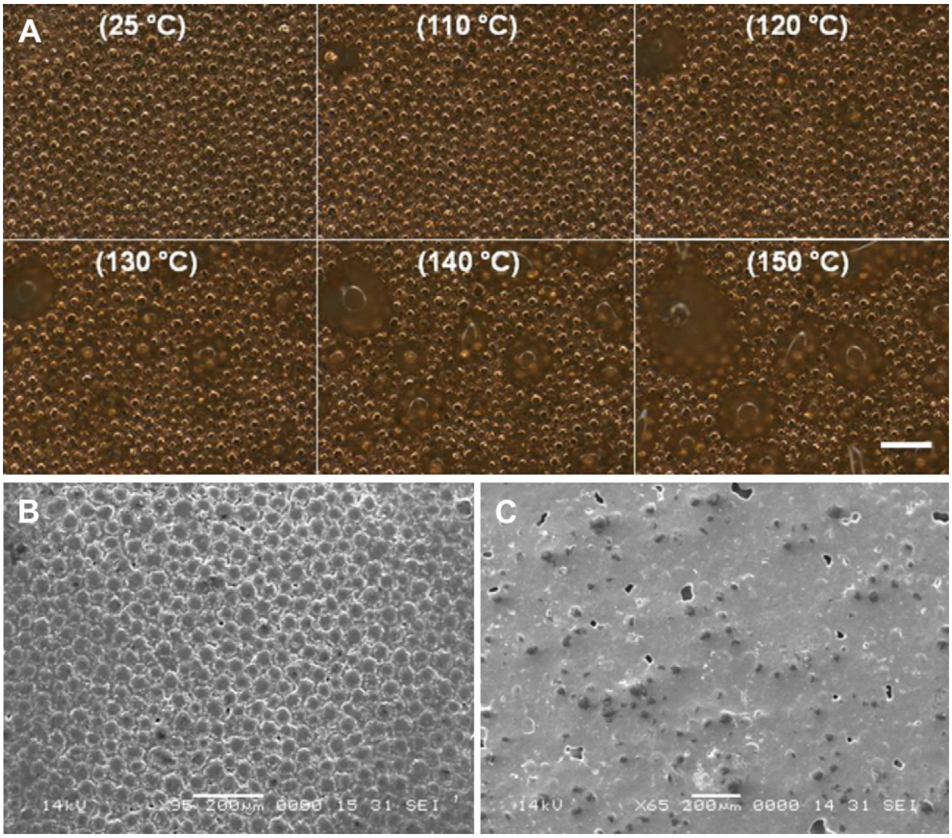


Fig. 2. Differential expansive bleeding (DEB) phenomenon. (A) stereo optical microscope images of the *Epoxy/PCL*(*15.5*) surface taken at various temperatures, and SEM images of the *Epoxy/PCL*(*15.5*) surface (B) before and (C) after heating.

the surface of *Epoxy/PCL*(*15.5*) before and after being heated at 150 °C for 20 min. The initially rough surface became quite smooth as a result of heating, due to the presence of a thin layer of "bled" PCL on the surface.

3.2. Characterization of adhesive strength

When *Epoxy/PCL*(*15.5*) is heated, all the surfaces are covered by a thin layer of PCL as a result of DEB, while the bulk of the material is still a rigid solid, as dictated by the interconnected glassy epoxy spheres. This thin PCL "glue layer" can then be employed for adhesion. To depict the sequence of adhesion and adhesion testing, Fig. 3 shows a representative thermal bonding cycle, conducted using a Linkam TST350 miniature tensile testing stage. An *Epoxy/PCL*(*15.5*) sample bar and an aluminum substrate were clamped and a compressive of 2 N was applied. The temperature of this assembly was raised to 120 °C (PCL $T_m < 120\ ^\circ C <$ epoxy T_g) at a rate of 10 °C/min, held isothermally at 120 °C for 20 min to allow DEB to occur, then cooled back to 25 °C at 3 °C/min to fully crystallize the initially molten PCL. As expected, we observed the compressive force to increase during heating (to a maximum value of 30 N) and decrease during cooling (Fig. 3A), due to the corresponding thermal expansion and contraction of the test fixtures, respectively. With the specimen still in place, a tensile test was then conducted at a displacement rate of 0.5 mm/min (Fig. 3B). The result shows that a strong adhesive bond was formed and a peak force of 111.6 N was required to completely fracture the bond, which corresponds to an apparent pull-off strength of 223.2 N/cm^2 (2.232 MPa).

In order to obtain a more in-depth understanding of the adhesion, we characterized the adhesive strength (apparent pull-off strength) of *Epoxy/PCL*(*15.5*) samples bonded to different substrates for 3 consecutive bonding/de-bonding cycles. For this purpose, a custom made bonding device (Scheme 2) was used to bond each *Epoxy/PCL*(*15.5*) sample bar to a substrate of the same dimensions, with a small 2 N compressive force exerted by the spring. In particular, bonding was accomplished by heating the sample-loaded device in a convective oven at 150 °C. A higher temperature compared to the case of *in-situ* bonding (Fig. 3) was chosen to compensate for the slower rate of heat transfer associated with the convection heating oven in comparison with conductive heating of the Linkam cell. This bonding approach stands in contrast to the variable bonding force of Fig. 3 and offer the distinct advantage of simplicity amenable to high throughput testing. Fig. 4 shows the apparent pull-off strength for self-adhesion (adhesion between bars of the same composition) in which both the adhesive and the substrate are *Epoxy/PCL*(*15.5*) and rebonding was executed up to three total cycles. We observe quite large bond strength values and significant increase with each bonding cycle, up to a value exceeding 900 N/cm^2 for the third cycle.

For comparison, we prepared and tested specimens bonded by surface-application of the solvent, tetrahydrofuran (THF). In this case, a small amount of THF (1–2 drops) was applied on both bonding surfaces, rendering the surfaces tacky, qualitatively speaking. The samples were then loaded into the bonding device at room temperature and the force of 2 N applied for 10 min. We anticipated that the solvent would be able to swell the local PCL near the surface and promote the chain diffusion and entanglement across the interface when the bonding surfaces are brought into contact. From Fig. 4, in can be seen that the solvent-bonded specimens showed a bond strength almost unchanged through 3 bonding cycles, and with a magnitude comparable with the specimens that were thermally bonded at 150 °C for 9 min after cycle 1.

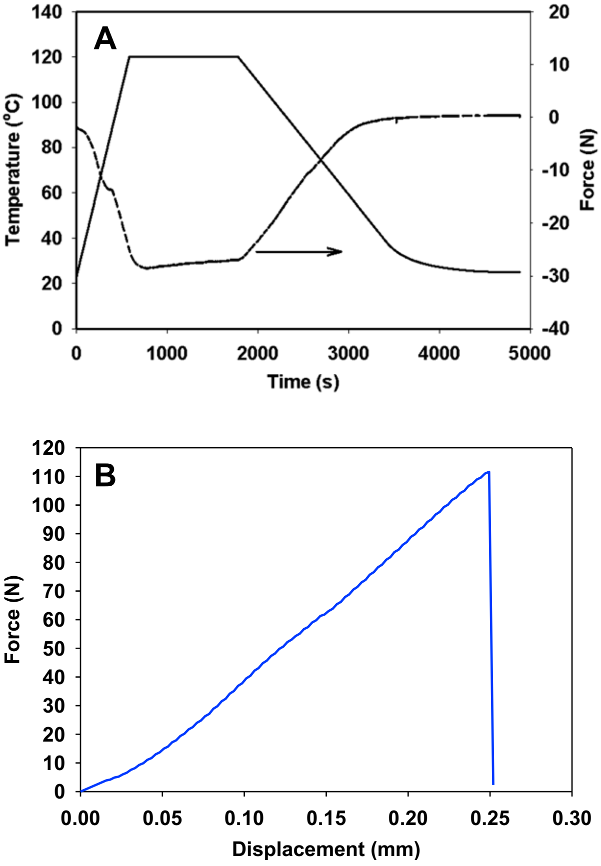


Fig. 3. A representative thermal bonding cycle and resulting bond strength testing. (A) The bonding process (negative force indicate compression) and (B) subsequent tensile test to completely fracture the adhesive bond.

This stands in contrast with the bond strength of the thermally bonded specimens that, as mentioned above, increased dramatically from cycle 1 to cycle 3, and became more than four times as large as the solvent-bonded specimen at cycle 3. Thus, thermal bonding and solvent-initiated bonding are substantially different. In the latter case, the solvent could only mobilize those PCL chains present near the free surface; therefore, the amount of polymer "recruited" for adhesion is limited. In thermal bonding, however, heat can trigger much more PCL mass transfer via DEB to completely wet the surface (Fig. 2C) therefore significantly promote the adhesion. Notwithstanding this mechanistic difference, the convenience of room temperature solvent-bonding coupled with reasonably high bond strengths (>200 N/cm^2, or > 2.00 MPa) may render this an attractive alternative from a practical point of view.

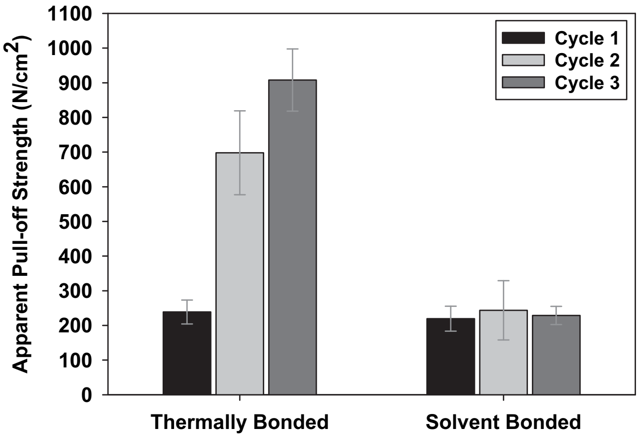


Fig. 4. The apparent pull-off strength for thermally and solvent-initiated (heat free) self-adhesion.

The bonding of *Epoxy/PCL*(*15.5*) to aluminum and stainless steel substrates was more demanding than the case of self-adhesion. A general observation was that longer bonding times were needed to achieve adequate adhesion. Considering that the metal substrate blocks (aluminum and stainless steel) have substantially higher thermal diffusivities than the adhesive blocks (*ca*. 0.157 mm^2/s for epoxy [21] and 97 mm^2/s and 4.2 mm^2/s for aluminum and stainless steel [22], respectively), heat transfer cannot explain our observations. However, the amount of adhesive agent (PCL) delivered to the interface upon bonding to metal substrates is only half of that in the case of self-adhesion and further requires wetting of the metal surface to occur. Together, these considerations may explain the longer times may be required to allow effective DEB to happen. Fig. 5 shows the adhesive strength for bonding times of 20, 30 and 40 min up to 3 bonding cycles. Similar to self-adhesion, for each bonding time the bond strength was observed to increase with bonding cycle, with the only exception being bonding to stainless steel for 20 min. The apparent pull-off strength also increased with increasing bonding time. This appears to be a discrepancy from our previous observation that DEB is accomplished in a relatively short time scale due to the large bulk modulus (small compressibility) of PCL, and can possibly be attributed to some slow structural relaxation, chain dynamics and delayed heat transfer which were not captured in our previous microscopy experiments and simplified

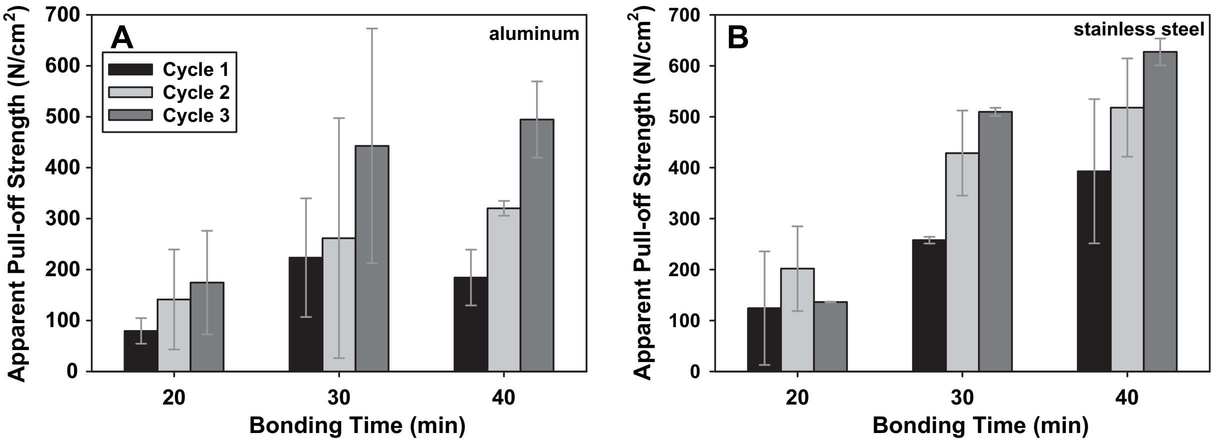


Fig. 5. The apparent pull-off strength as a function of both bonding time and bonding cycles for (A) aluminum substrate and (B) stainless steel substrate.

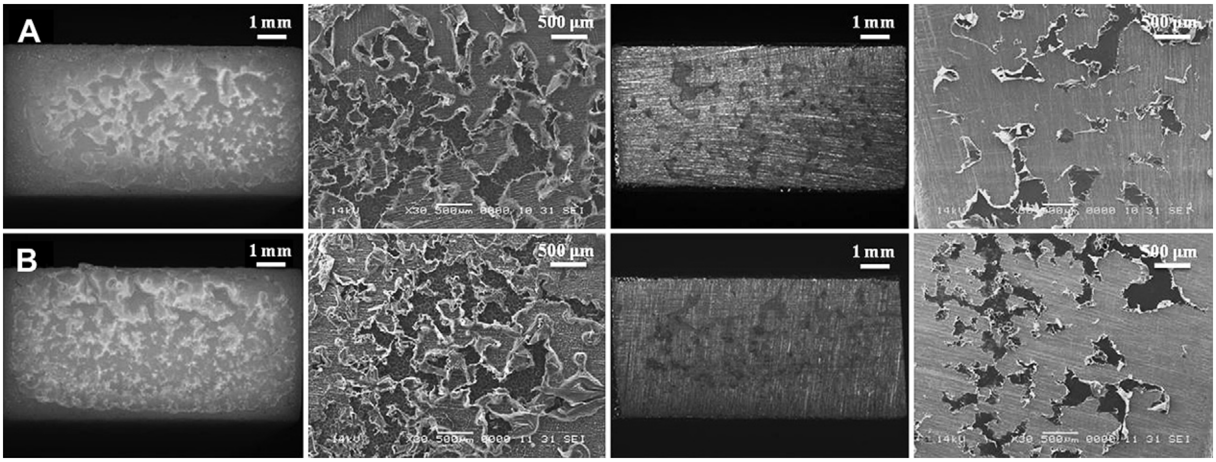


Fig. 6. Morphologies of fractured surfaces for representative (A) aluminum bonded specimen and (B) stainless steel bonded specimens. Both were bonded for 40 min and observed after cycle 3. For each row, the first two and last two images show the *Epoxy/PCL*(*15.5*) adhesive surface and the metal substrate surface, respectively. The first and third columns are optical micrographs while the second and fourth columns are higher magnification SEM images. The scale bar in the top left stereo optical micrograph represents 1 mm.

calculations. Overall, the adhesive strength of *Epoxy/PCL*(*15.5*) to aluminum and stainless steel falls in the range of several hundred N/cm^2 (or several MPa), which is larger than reported "gecko-foot" reversible adhesive systems, which typically give a pull-off strength in the range of 1–30 N/cm^2 [11], and comparable to many conventional liquid adhesives [23].

We further examined the fractured bonding surfaces of *Epoxy/PCL*(*15.5*) and the metal substrates (Fig. 6) to reveal the nature of bond fracture as well as the underlining structural changes associated with bonding and fracturing processes. On the *Epoxy/PCL*(*15.5*) surfaces, the fractured PCL adhesive layer can be clearly observed. The whitening zones on the stereo micrographs and the rough morphology on the SEM images suggest a high degree of plastic deformation of the "bled" PCL layer, which may facilitate energy dissipation and potentially results in a tough bond, although the toughness is not quantitatively addressed here. The stereo

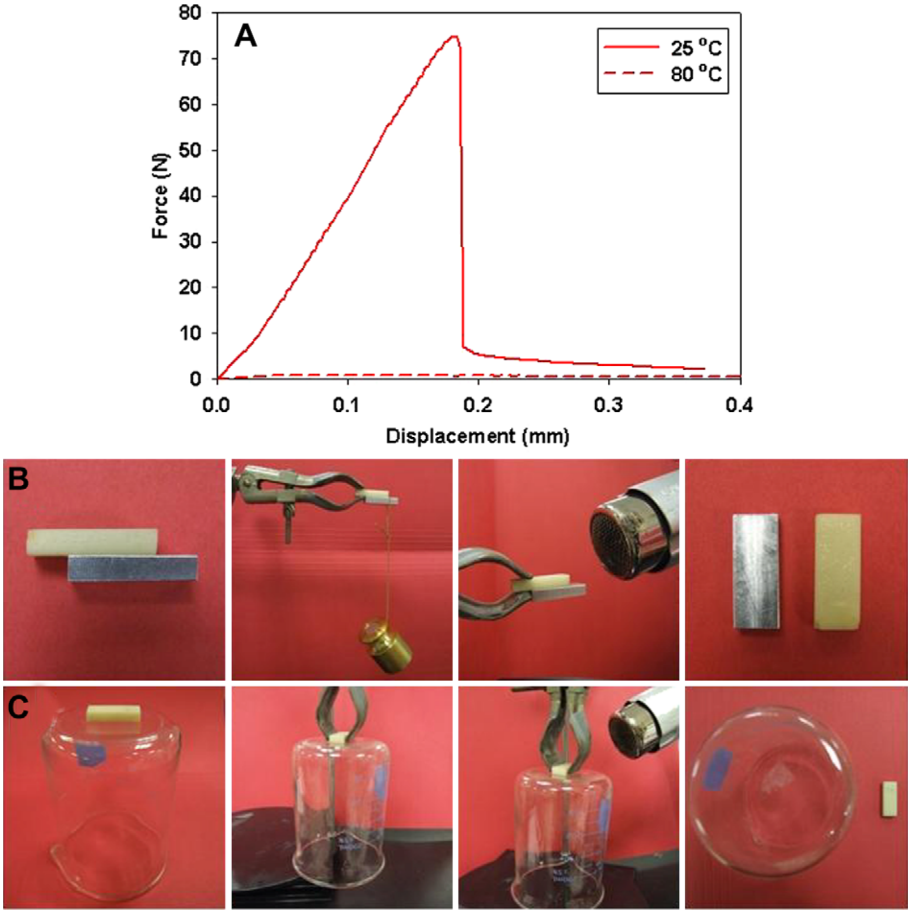


Fig. 7. The reversibility of adhesion. (A) The tensile testing results of two aluminum bonded specimens both prepared by heating at 150 °C for 20 min but tested at two different temperatures of 25 °C and 80 °C. (B) and (C): Demonstrations of the reversible adhesive property of *Epoxy/PCL*(*15.5*).

micrographs of the metal surfaces indicate that a small amount of PCL residue was left on the metal substrates. The corresponding SEM images corroborate this finding and reveal, more particularly, that a thin film of PCL was deposited on the metal surfaces (reference polished metal surfaces prior to bonding are available in Supplementary Information), and this occurs for both aluminum and stainless steel. We conclude that the PCL adhesive layer underwent a cohesive failure at the microscopic level. Therefore the bond strength is mainly determined by the cohesive strength of the bled PCL layer, which is in turn determined by its semi-crystalline structure. Such findings are consistent with the observed large adhesive strength values.

3.3. *Reversibility of adhesion*

So far, we have shown that by a simple heating/cooling cycle *Epoxy/PCL(15.5)* can be induced to adhere firmly to itself and metal substrates including aluminum and stainless steel, with bond strengths derived primarily from the cohesive strength of the semi-crystalline PCL layer induced by DEB. With this understanding of the physical nature of the bond, we utilized heating ($T > T_{\mathrm{m}}^{\mathrm{PCL}}$) to melt the PCL layer and therefore diminish its cohesive strength as a simple mechanism for on-demand adhesion removal. The result can be seen in Fig. 7A, which shows the tensile testing results of two aluminum bonded specimens, each prepared by heating to 150 °C and holding for 20 min, but tested at different temperatures. The specimen tested at 25 °C showed a reasonably large peak force of 75 N (or an apparent pull-off strength of 150 N/cm^2) whereas the other specimen tested at 80 °C showed no tangible adhesion at all (all force values were below 1 N). A similar de-bonding capability was observed for all other bonded specimens.

The reversible adhesive property of *Epoxy/PCL(15.5)* is further elucidated, qualitatively, in Fig. 7B and C. In the first case, an *Epoxy/PCL(15.5)* sample bar was heated to 150 °C and held for 20 min while being pressed onto an aluminum substrate of the same dimensions as shown in the first photograph of Fig. 7B. After cooling, a strong bond was formed and this bond could withstand a 200 g standard weight hanging at one end. The *Epoxy/PCL(15.5)* adhesive and the aluminum substrate could then be easily de-bonded by moderate heating with a standard laboratory heating gun to approximately 100 °C. In the second case, an *Epoxy/PCL(15.5)* adhesive was simply put on the bottom of an inverted 200 ml Pyrex™ lab beaker. The beaker and the adhesive were then placed in an oven at 150 °C for 20 min before being taken out to cool. During the whole heating and cooling processes no external force was applied. The generated adhesive bond was strong enough to support the weight of the beaker and the adhesive/beaker was easily de-bonded by heating with a standard laboratory heating gun, as described above.

The demonstrated adhesive capability suggests excellent potential for *Epoxy/PCL(15.5)* in applications where temporary adhesion, or an on-and-off switch of the adhesion is required. For example, strong and reversible adhesion to glass indicates potential use for the coupling of glass tubing and the adhesive chucking of glass components for polishing. Further, reversible adhesion of this type can enable assembled structures to be easily self-disassembled for repair, recycling or upgrade. The unique structural rigidity, superior mechanical properties and good processibility can further be utilized to produce reversible adhesive blocks useful for the assembly or prototyping of complex structures. Given the large adhesive strength, we envision the materials being integrated into a device that can be used to grab and move heavy or hazardous objects (currently achieved with electromagnetic or suction-cup devices), similar to what Fig. 7C shows.

4. Conclusions

To briefly conclude, we have extended the applicability of differential expansive bleeding (DEB) seen in an epoxy/PCL blend from thermal mending to solid, reversible adhesion. We have found that the material can bond strongly to a variety of substrates with apparent pull-off strength values generally in the range of 100–1000 N/cm^2 (1–10 MPa). Compared to the existing reversible adhesives, our material system has a number of advantages including (1) low raw material and manufacturing cost, (2) high adhesive strength, (3) easy on-demand removal of the adhesion and (4) superior mechanical properties and durability. We anticipate applicability of the new materials ranging from structural adhesives to prototyping, assembly, and manufacturing. Future studies may include the performance of the new adhesive system in creep (constant applied load), as well as interfacial fracture toughness.

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