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Supporting Information for

Adhesive-less bonding of incompatible thermosetting materials

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1. Materials and Instrumentation:

Materials:

All chemicals were commercially purchased and were used as received without further purification. Bisphenol A diglycidyl ether (DER 332) (Epoxide equivalent weight, 172-176), Poly(dimethylsiloxane) diglycidyl ether (M_n = 800), 1,4-butanediol diglycidyl ether, poly-(propylene glycol) diglycidyl ether (M_n = 380), hexahydrophthalic anhydride (HHPA), 2-ethyl-4-methylimidazole, 4-(dimethylamino)pyridine (DMAP) and dimethyl aniline were purchased from Sigma-Aldrich. Nano-silica (AEROSIL-RX-200) was purchased from Evonik Opration GmbH.

Instrumentation:

Heat press: AS-ONE heat press machine was used to perform adhesive-less bonding, typically at 160°C for 4 hours and at a pressure of 200Kgf over 100mm^2 overlap area which corresponds to approximately 19.6 MPa pressure on the polymers.

Scanning Electron Microscopy (SEM) and EDAX analysis:

Low vacuum SEM analysis was conducted using TM 3000 (Hitachi High-Technologies Co., Japan). Carbon and silicon maps were generated using the in-built EDX gun.

Differential Scanning Calorimetry (DSC): A SHIMADZU DSC-60 plus instrument was used to monitor the thermal property and glass transition temperatures (T_g) of all polymers under nitrogen atmosphere in a temperature range was of -40 ^oC to 200 ^oC with a heating and cooling rate of 10 ^oC min^{-1}. Aluminium pans were used as sample holders. The T_g values were determined as the midpoint of the slope of phase transition.

Mechanical analysis:

Mechanical analysis of softer samples was performed with a Texture Analyser (Stable Micro Systems) with a load cell of 5N and that of harder samples was performed with a Shimadzu AG-X plus lap-shear tester with a load cell of 10kN.

Mechanical analysis of samples requiring higher loads was performed with a Shimadzu autograph AG-X plus instrument with a 10 kN load cell. The crosshead speed was 2 mm min^{-1} for all cases. The reported values are the average of four measurements with standard error for each study. The adhesive strength was determined using following equation:

Adhesive strength (MPa) = Load (N) / Area (mm^2)

Here, area = 10 mm x 10 mm =100 mm^2.

Contact angle: Water contact angles were measured using a contact angle meter (Kyowa Interface Science, Co Ltd., Japan, Model DMs-401). Distilled water (5 µL) was used as the probe liquid. The images were analyzed for the measurement of the contact angles in Surftens software version 4.5. The measurement of the contact angle was given by measurements of the diameter of the base of the drop and the height of the drop, where each drop was measured five times.

Three point bending tests:

Texture Analyzer (Stable Micro System, TA.XTplusC Texture Analyser) was used with a three-point probe with a 50N load cell for 3-point bending tests.

2. Experimental procedures:

a) Synthesis of BisA thermosetting polymer:

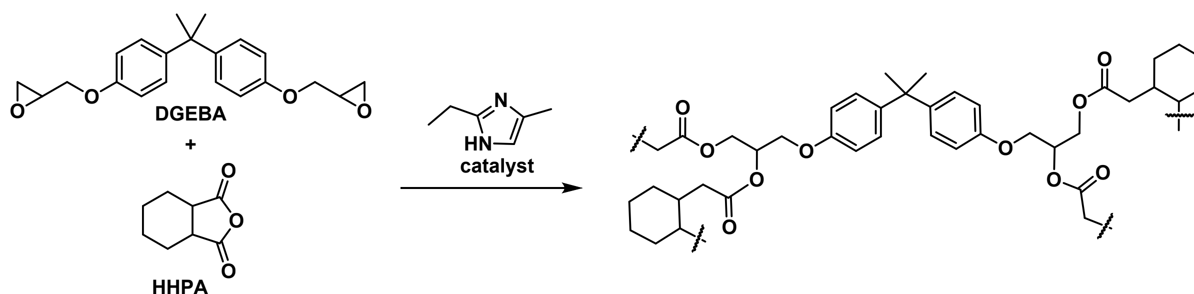

Figure S1. Scheme of the reaction for BisA thermoset curing.

9.0 g of epoxy resin and 7.5g of hexahydrophthalic anhydride (HHPA) were thoroughly mixed in a Teflon beaker with addition of 0.450 g of 2-ethyl-4-methylimidazole (5% by weight of epoxy resin) as a catalyst. This mixture was placed in a vacuum desiccator for 10 min to remove air bubbles. The mixture was then poured in a rectangular shaped PTFE mold. The thickness of the parts was kept at 2 mm (similar with industry standards). Curing conditions: 120 °C, 4 h.

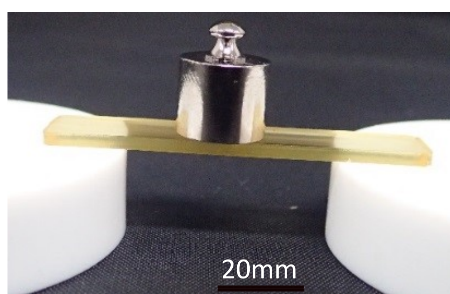

Figure S2. Photo of the BisA thermoset.

b) Synthesis of Bdiol thermoseting polymer:

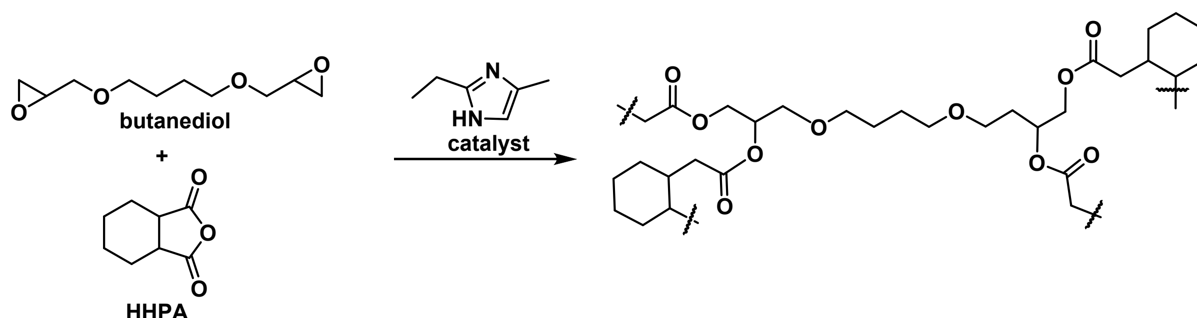

Figure S3. Scheme of the reaction of Bdiol thermoset curing.

5.0 g of epoxy resin and 7.5g of hexahydrophthalic anhydride were thoroughly mixed in a Teflon beaker with addition of 0.250 g of 2-ethyl-4-methylimidazole (5% by weight of epoxy resin) as a catalyst. This mixture was placed in a vacuum desiccator for 10 min to remove air bubbles. The mixture was then poured in a rectangular shaped PTFE mold. The thickness of the parts was kept at 2 mm (similar with industry standards). Curing conditions: 120 °C, 4 h.

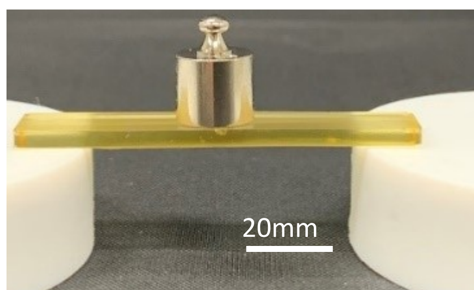

Figure S4. Photo of the Bdiol thermoset.

c) Synthesis of PPG thermosetting polymer:

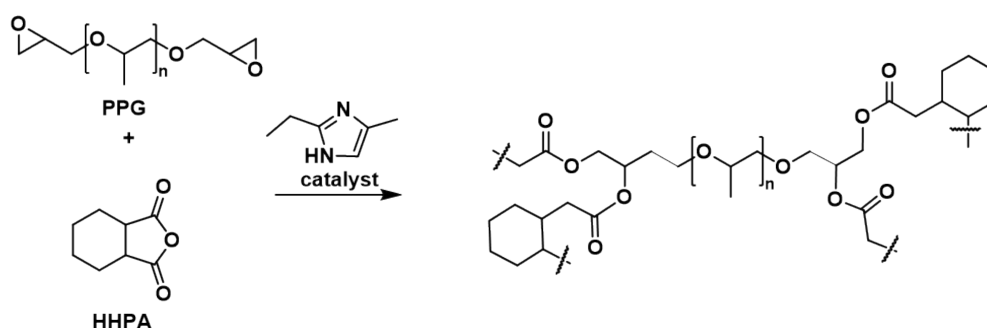

Figure S5. Scheme of PPG thermoset curing.

3.2g of epoxy resin and 1.54 g of hexahydrophthalic anhydride were thoroughly mixed in a Teflon beaker with addition of 0.160 g of 2-ethyl-4-methylimidazole (5% by weight of epoxy resin) as a catalyst. This mixture was placed in a vacuum desiccator for 10 min to remove air bubbles. The mixture was then poured in a rectangular shaped PTFE mold. The thickness of the parts was kept at 2 mm (similar with industry standards). Curing conditions: 120 °C, 4 h.

Figure S6. Photo of PPG Thermoset.

d) Procedure for synthesis of PDMS thermosetting polymer:

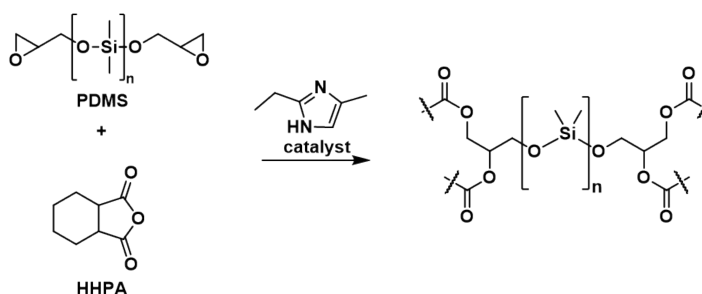

Figure S7. Scheme of PDMS thermoset curing.

8 gm of poly(dimethylsiloxane) diglycidyl ether and 3.2 gm of hexahydrophthalic anhydride were taken in a Teflon beaker with addition of 0.40 g of 2-ethyl-4-methylimidazole (5% by weight of epoxy resin) as catalyst. This mixture was placed in a vacuum desiccator for 30 min to remove air bubbles. The mixture was then poured in a rectangular shaped PTFE mold. The thickness of the parts was kept at 2 mm. Curing conditions: 140 °C, 4 h.

Figure S8. Photo of PDMS thermoset.

3. Contact angle measurements:

Water contact angle was used as a measure of hydrophobicity / hydrophilicity of the thermosetting polymeric networks. The measurement of the contact angle was given by measurements of the diameter of the base of the water drop and the height of the drop, where each drop was measured five time then averaged to obtain the value.

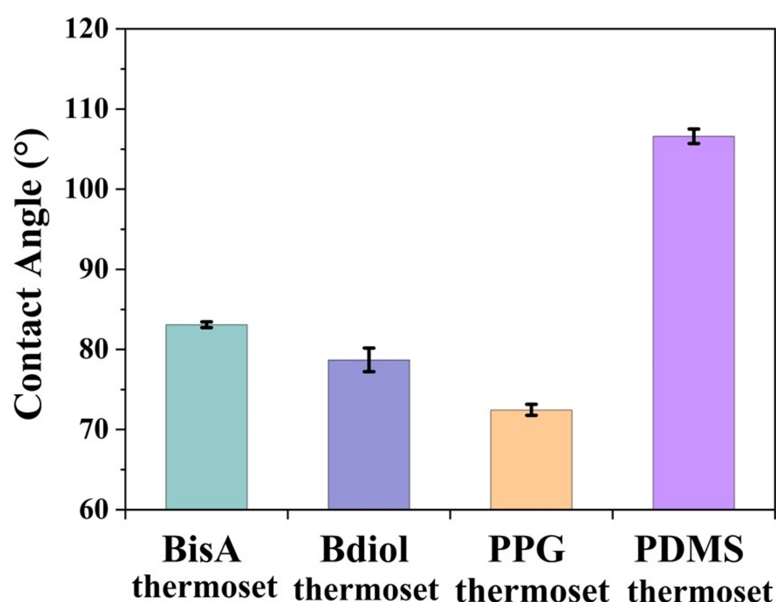

Figure S9. Water contact angles of the synthesized thermosetting polymers BisA (Equilibrium Contact Angle: 83.1°; Advancing Contact Angle: 82.7°; Receding Contact Angle: 80.3°), Bdiol (Equilibrium Contact Angle: 78.7°; Advancing Contact Angle: 79.3°; Receding Contact Angle:78.8°), PPG (Equilibrium Contact Angle: 72.46°; Advancing Contact Angle: 73.8°; Receding Contact Angle: 71.4°) and PDMS (Equilibrium Contact Angle: 106.6°; Advancing Contact Angle: 106.8°; Receding Contact Angle:105.4°).

4. Mechanical properties of thermosetting polymers

Parts were clamped between two grips and placed in the tensile testing apparatus. Parts were pulled apart with a load cell of (50 N for PDMS thermosetting polymers and 10k N for neat epoxy polymers) at a constant speed of 0.2 mm / min. The parts were pulled till failure and the force and extension at the breaking point were used and calculate the displacement with respect to tensile force:

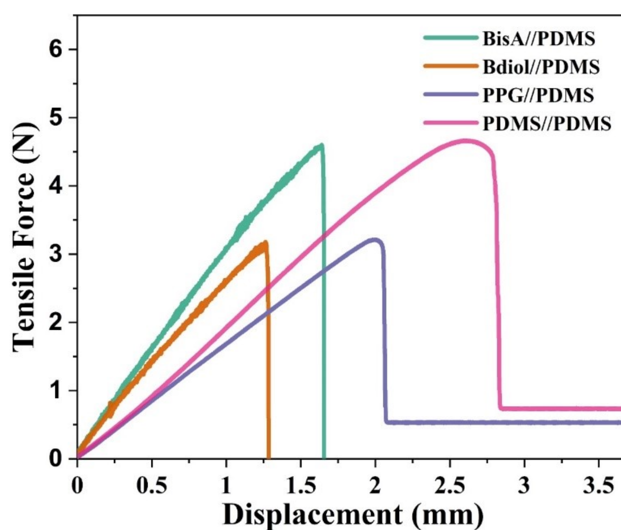

Figure S10. Tensile force at break for adhesion between PDMS thermoset and epoxy thermosets.

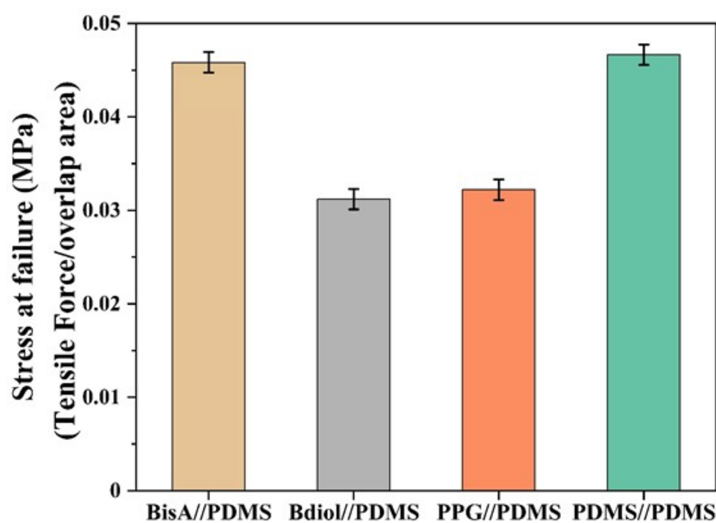

Figure S11. The stress at failure values of the four thermoset pairs are similar as, in each case, the substrate fails before failure of adhesion.

Table S1. Stress at failure (MPa) (Tensile Force/overlap area) of the four thermoset pairs.

	Stress at failure (MPa) (Tensile Force/overlap area)				Error bars
Sample name	**1**	**2**	**3**	**Avarage**	**Std. Dev**
BisA//PDMS	0.0472	0.04543	0.04484	0.04582	0.00100
Bidiol//PDMS	0.03305	0.03017	0.03212	0.03178	0.00120
PPG//PDMS	0.03421	0.03237	0.03124	0.03261	0.00122
PDMS//PDMS	0.04738	0.04686	0.04468	0.04631	0.00117

5. Thermal properties of thermosetting polymers

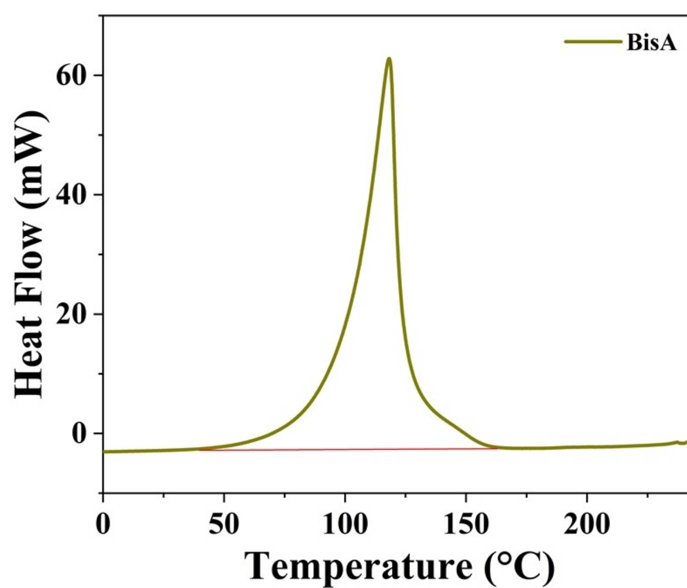

Figure S12. Dynamic DSC plot during curing of diglycidyl ether of bisphenol A (BisA) with HHPA and EMI as a catalyst.

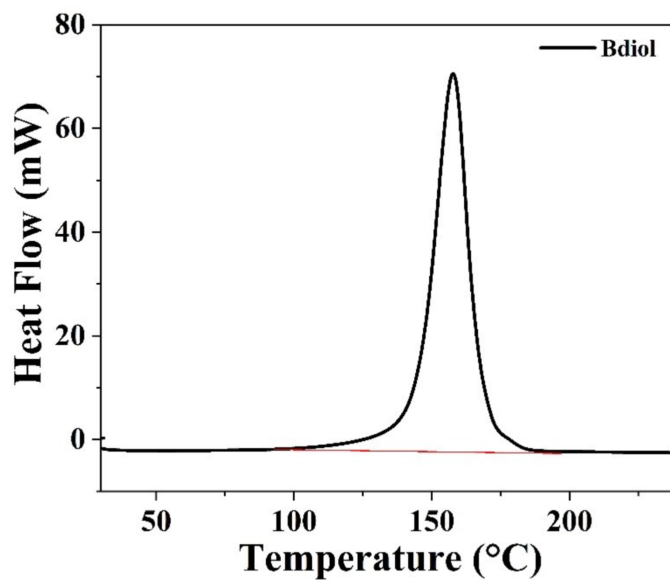

Figure S13. Dynamic DSC plot during curing of butane diol diglycidyl ether with HHPA and EMI as a catalyst.

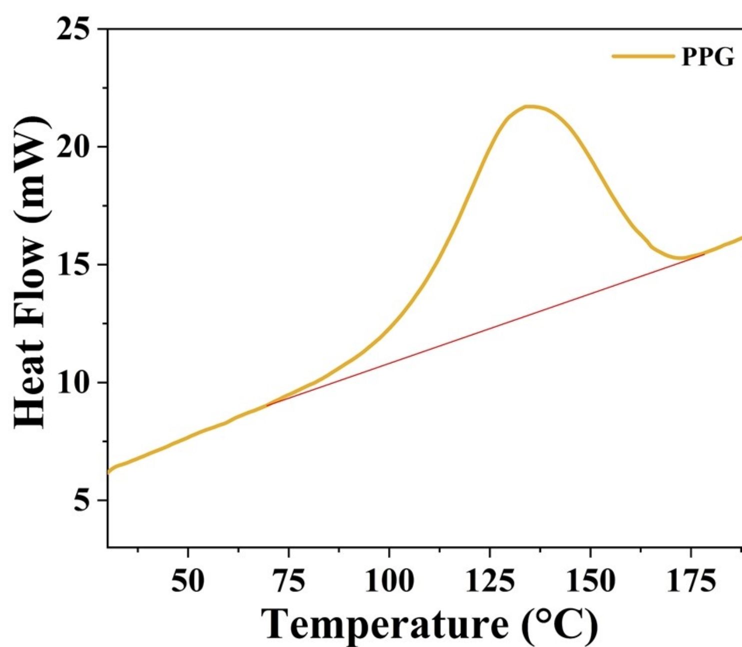

Figure S14. Dynamic DSC plot during curing of PPG diglycidyl ether with HHPA and EMI as a catalyst.

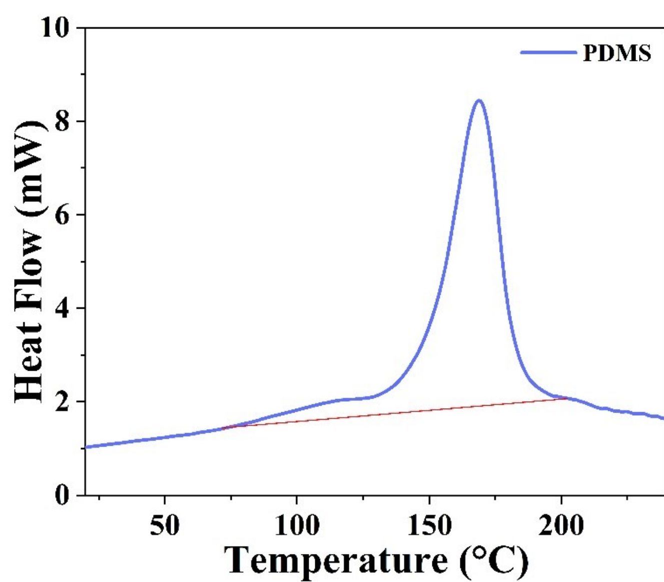

Figure S15. Dynamic DSC plot during curing of PDMS diglycidyl ether with HHPA and EMI as a catalyst.

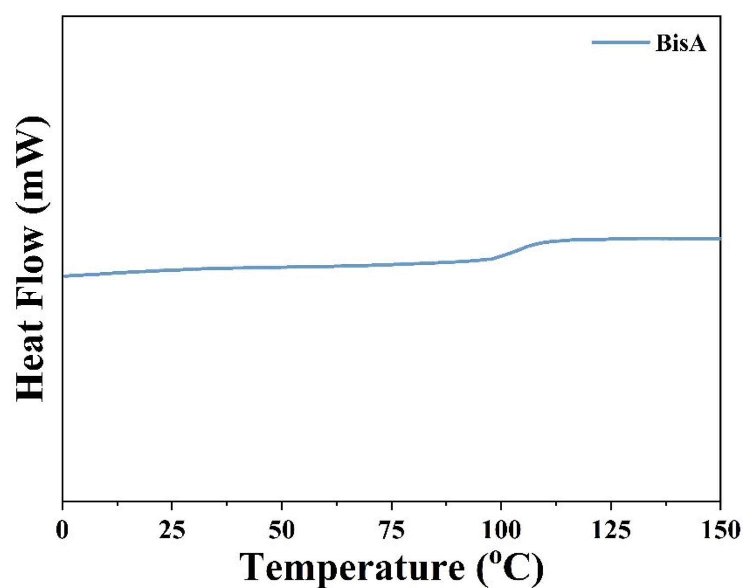

Figure S16. Glass transition temperature (T_g) of BisA thermoset.

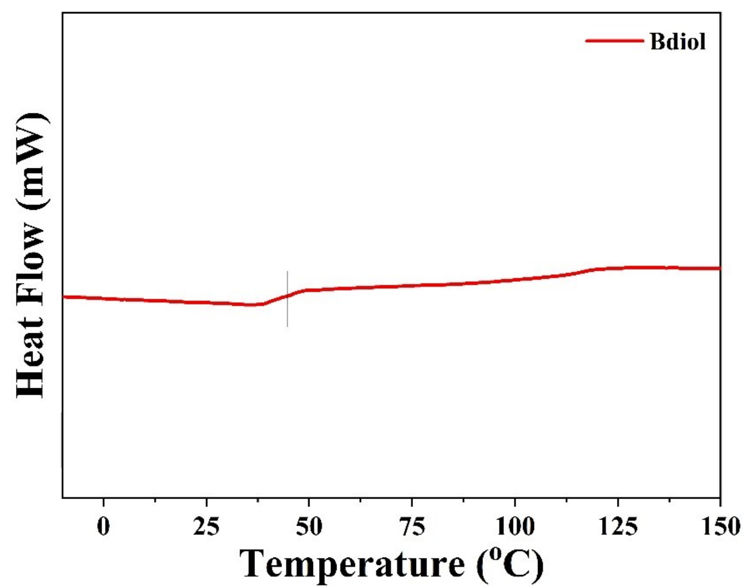

Figure S17. Glass transition temperature (T_g) of Bdiol thermoset.

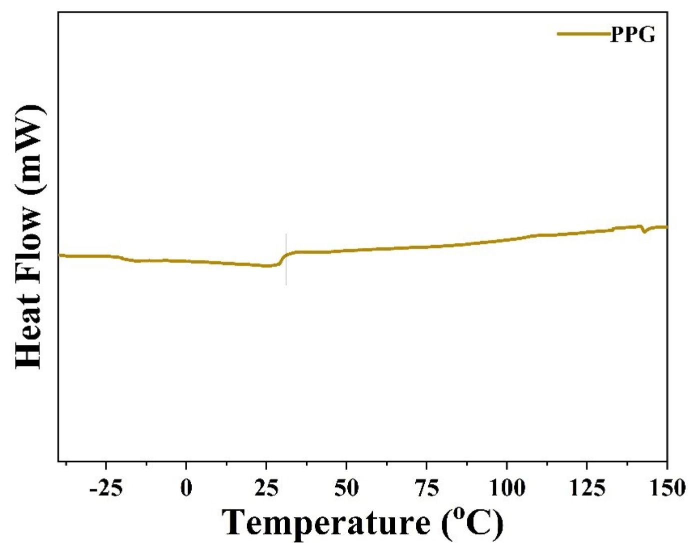

Figure S18. Glass transition temperature (T_g) of PPG thermoset.

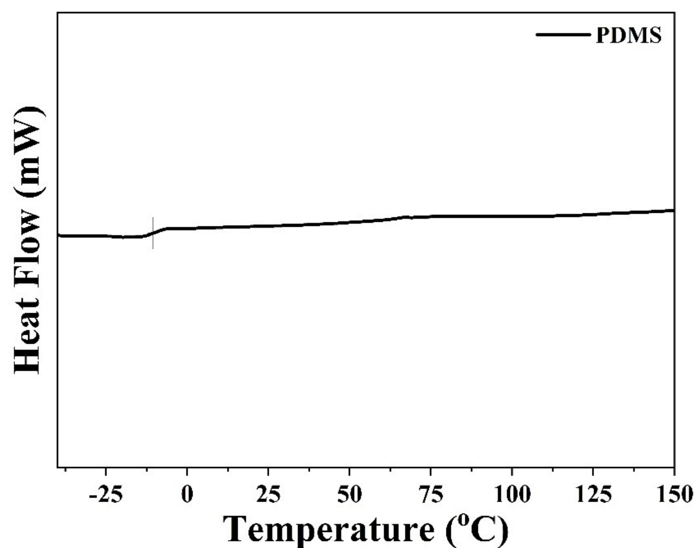

Figure S19. Glass transition temperature (T_g) of PDMS thermoset.

Procedure for DSC traces of the interfacial material:

Differential Scanning Calorimetry (DSC): A SHIMADZU DSC-60 plus instrument was used to monitor the thermal property and glass transition temperatures (Tg) of all polymers under nitrogen atmosphere in a temperature range was of -40 oC to 200 oC with a heating and cooling rate of 10° C min-1. Aluminium pans were used as sample holders. The Tg values were determined as the midpoint of the slope of phase transition.

To investigate the formation of a new material at the interface which results in strong adhesion, we fabricated thin films (100 to 50 microns) of all the materials and subjected these thermosetting polymeric films to the adhesive-less bonding procedure. The resulting materials were used as samples for differential scanning calorimetry (DSC). Thin films were used because thicker polymers would result in a lower interfacial area as a percentage of bulk polymers as compared to thin films.

Further evidence of extensive dynamic covalent exchange at the interface was provided by differential scanning calorimetry (DSC). When thin films (50 to 100 micrometers) of the two dissimilar polymers were bonded together using the typical adhesive-less bonding procedure, DSC traces (Figures S20, S21 and S22) show not just two glass transition temperatures (of the constituent polymers, i.e. the Tg for BisA thermoset is 115°C, and that of PDMS thermoset is -25°C), but also a third glass transition temperature (Tg = 27°C) occurring between the

individual Tgs. Similarly, new glass transition temperatures are observed in the case of Bdiol – PDMS thermoset as well as PPG – PDMS thermoset. Thus, the interfacial dynamic covalent exchange creates an exchange zone which is a new material at the interface with different thermal properties than those of the constituent polymers.

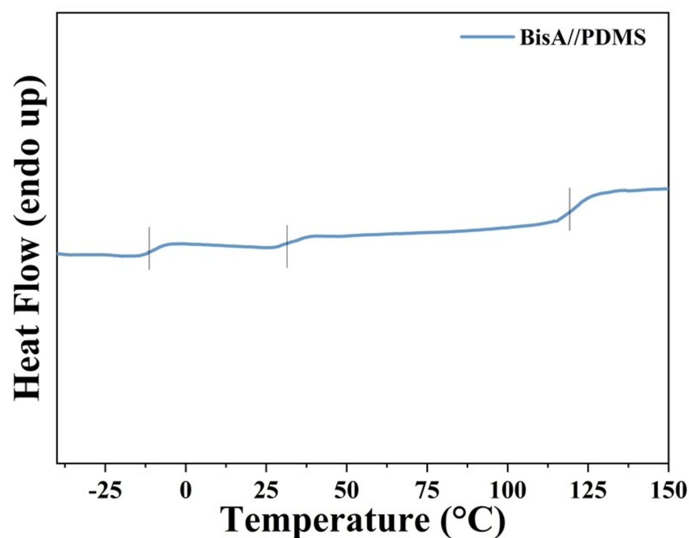

Figure S20. DSC traces of the BisA//PDMS show new glass transition temperatures due to creation of dynamic covalent exchange zones.

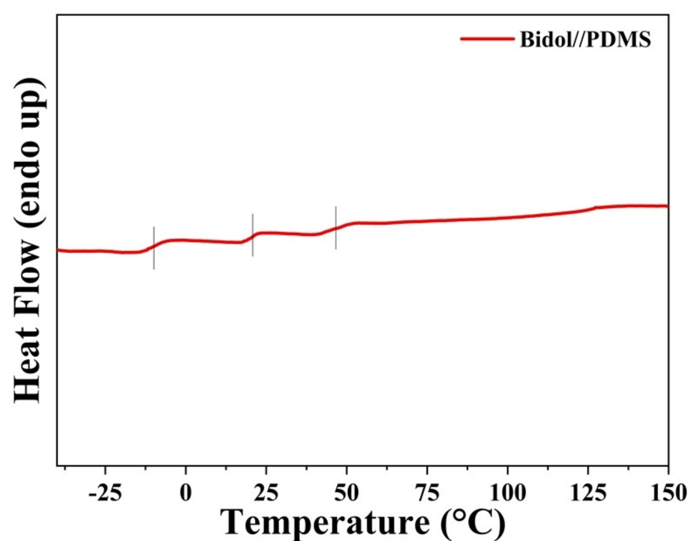

Figure S21. DSC traces of the Bidol//PDMS show new glass transition temperatures due to creation of dynamic covalent exchange zones.

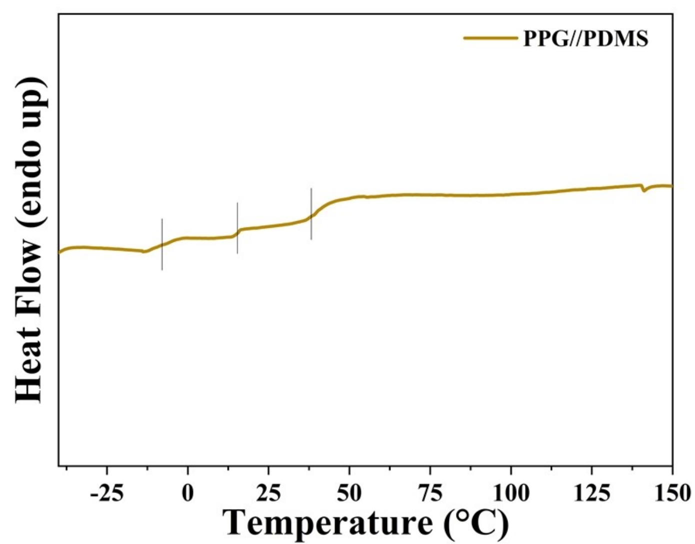

Figure S22. DSC traces of the PPG//PDMS show new glass transition temperatures due to creation of dynamic covalent exchange zones.

6. Dynamic covalent exchange experiments:

A polar thermosetting polymeric part (60 mm x 10 mm x 2 mm) was kept in contact with the PDMS-based non-polar thermoset with an overlap area of 10mm x 10mm. Both the polymers were slightly abraded with a sandpaper (Abrasive Sand Polish Paper PL28C60) to improve interfacial contact. This system was placed in a heat-press between two steel plates with 200Kgf over 100mm^2 overlap area at 160°C for 4 hours. The systems were then removed from the hot-press and allowed to cool to room temperature and used for further characterization.

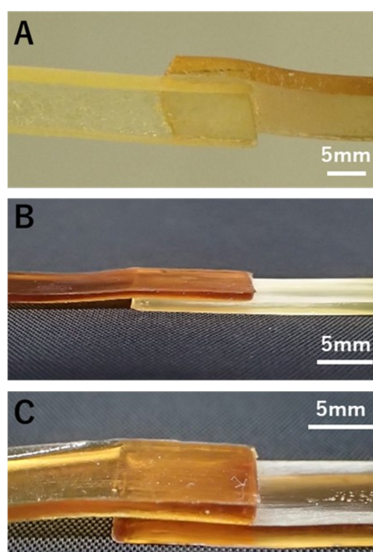

Figure S23. Photos of (A) BisA thermoset and PDMS thermoset after bonding (B) Bdiol thermoset and PDMS thermoset after bonding and (C) PPG thermoset and PDMS thermoset after bonding.

7. Influence of catalysts:

To investigate whether the catalyst used while curing of the epoxy resin has an influence over dynamic covalent exchange at the interface of the two polymeric networks, we compared 3 catalysts – (1) ethyl methyl imidazole (2) DMAP (3) dimethyl aniline. In all cases, we observed strong adhesion via dynamic covalent exchange at the interface. Hence, we conclude that this dynamic covalent exchange is independent of the catalyst used to cure the polymers.

Synthesis of epoxy thermosets with amino-catalysts: The epoxy monomer (1 mole equivalent) and the curing agent, hexahydrophthalic anhydride (1 mole equivalent), were taken in a Teflon beaker with addition of 0.5 weight % of epoxy resin as a catalyst. This mixture was kept in a desiccator under vacuum for 10 min to remove air bubbles. The mixture was then

poured in a rectangular PTFE mold. The thickness of the parts was kept at 2 mm (similar with industry standards). Curing conditions: 120 °C, 4 h.

Polar epoxy thermosets and non-polar PDMS thermosets were subjected to adhesive-less bonding via dynamic covalent exchange using a procedure reported in section 7 in the SI.

Table S2. Adhesion strengths of BisA thermoset with PDMS thermoset using different catalysts.

Resin 1	Resin 2	Curing agent	Catalyst	Adhesion Strength, Lap shear* (MPa)
BisA	PDMS	HHPA	*EMI*	0.045
BisA	PDMS	HHPA	*DMAP*	0.04
BisA	PDMS	HHPA	*DMA*	0.03

* Strictly speaking, this value is not the adhesion strength of the adhesion as the soft substrate (PDMS) fails before the dynamic covalent adhesion.

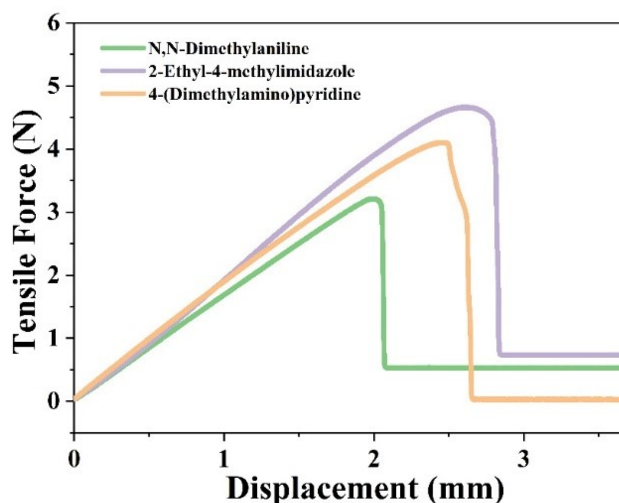

Figure S24. Force-extension curves of the bonded BisA thermoset and PDMS thermoset using different catalysts for curing of the polymers.

8. SEM/ EDX analysis:

Interfacial characterization of epoxy//PDMS by SEM-EDX: On keeping the two dissimilar materials in contact at elevated temperatures under pressure, transesterification reactions between the two components leads to strong adhesion, giving rise to a covalently bonded composite consisting of a soft PDMS part and a hard epoxy part. Carbon / silicon ratios obtained by SEM – EDX studies confirm the penetration of silicon in the carbon rich polymeric region. SEM images indicate "annealing" at the interface of the two materials, and a diffused interface is clearly visible.

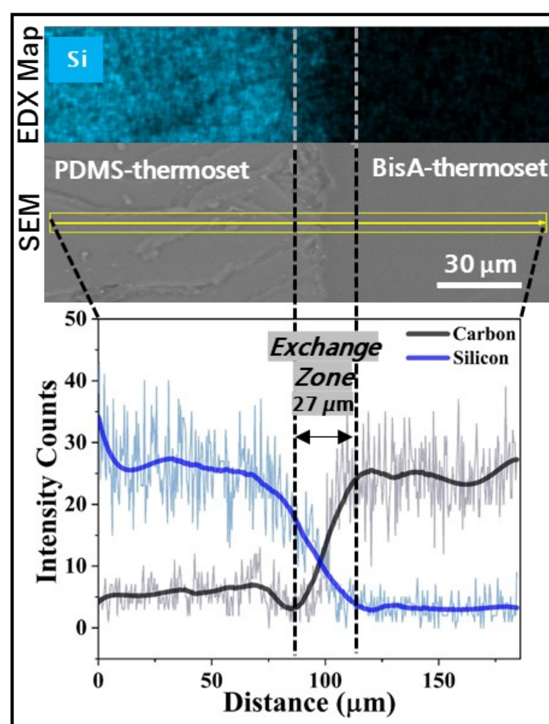

Figure S25. (*top*) SEM Image & elemental mapping of silicon using EDX of adhesion between BisA thermoset and PDMS thermoset. (*bottom*) Spatial distribution of carbon and silicon in the SEM/EDX image. Distribution of the elements is given across the horizontal yellow line. As can be clearly seen, an exchange zone of approximately 20-30 µm created which is responsible for strong adhesion between the thermosetting polymers.

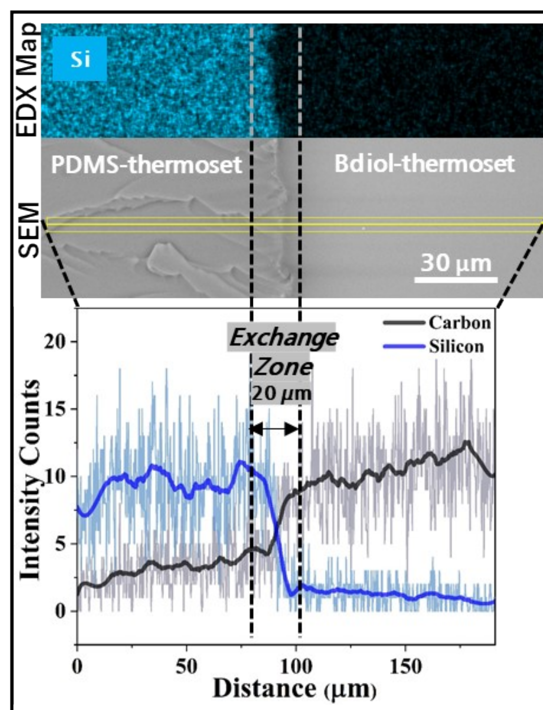

Figure S26. (*top*) SEM Image & elemental mapping of silicon using EDX of adhesion between Bdiol-thermoset and PDMS thermoset. (*bottom*) Spatial distribution of carbon and silicon in the SEM/EDX image. Distribution of the elements is given across the horizontal yellow line. As can be clearly seen, an exchange zone of approximately 20 µm created which is responsible for strong adhesion between the thermosetting polymers.

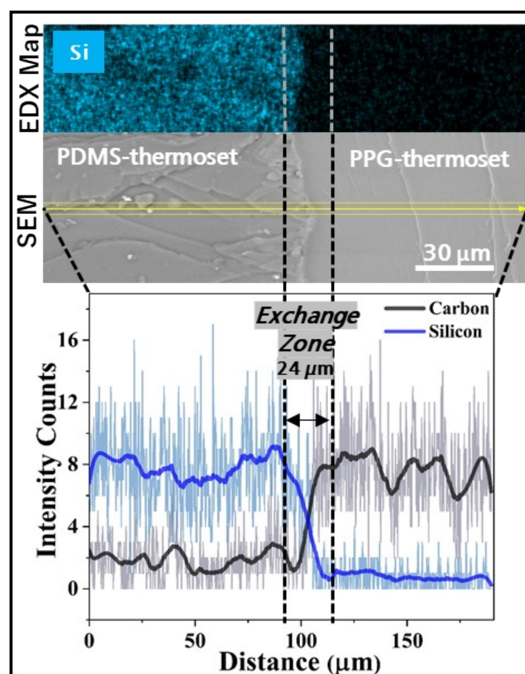

Figure S27. (*top*) SEM Image & elemental mapping of silicon using EDX of adhesion between PPG-thermoset and PDMS thermoset. (*bottom*) Spatial distribution of carbon and silicon in the SEM/EDX image. Distribution of the elements is given across the horizontal yellow line. As can be clearly seen, an exchange zone of approximately 20-30 μm created which is responsible for strong adhesion between the thermosetting polymers.

9. Control Experiments

a) Bonding of epoxy thermoset to a commercial polysiloxane (Sylgard 184)

As a control experiment, we investigated whether there is any adhesive bonding between the anhydride cured epoxide polymer and a commercial polysiloxane polymer, Sylgard 184, which does not contain ester bonds. We did not observe any adhesion between these polymeric networks.

b) Bonding of PDMS thermoset to an amine-cured epoxy polymer

As another control experiment, we investigated whether there is any adhesive bonding between the anhydride cured PDMS polymer and an amine cured epoxy polymer which does not contain ester bonds. We used the commercially available curing agent Jeffamine D230 as the amino crosslinker which crosslinks the epoxide network via tertiary amino linkages. In this case as well, we did not observe any adhesion between these polymeric networks.

10. Synthesis and mechanical properties of thermosets with nano-silica reinforcement

Each epoxy monomer (1mole equivalent) and the curing agent, hexahydrophthalic anhydride (1 mole equivalent) were taken in a Teflon beaker with addition of 0.450 gms of 2-Ethyl-4-methylimidazole (5 % by weight of epoxy resin) as the catalyst followed by addition of nano-silica (1 % by weight of the mixture). The mixture was vigorously stirred and kept in a desiccator under vacuum for 10 min to remove air bubbles. The mixture was then poured in a rectangular PTFE mold. The thickness of the parts was kept at 2 mm. Curing conditions: 120 °C, 4 h.

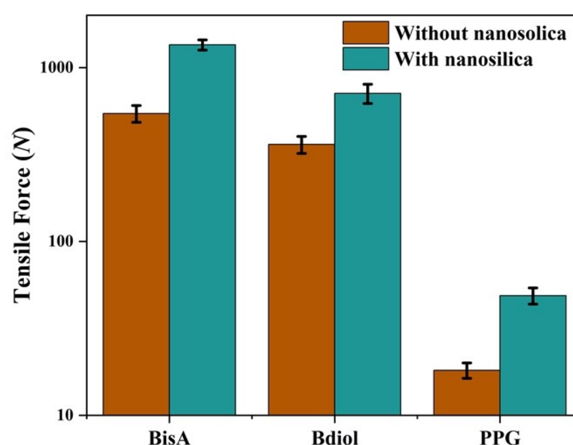

Figure S28. Tensile strength of the thermosetting materials with and without nano-silica as reinforcement.

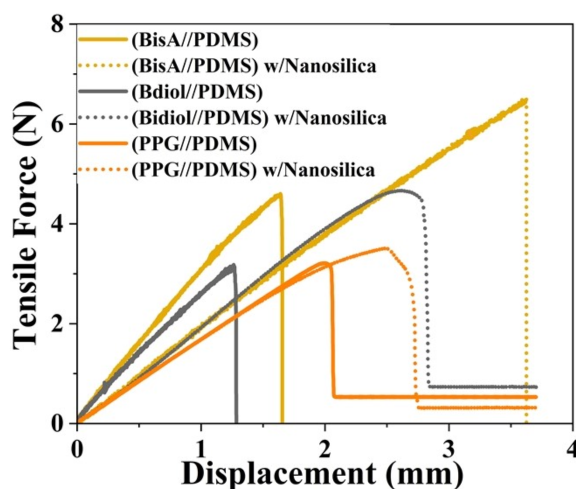

Figure S29. Force - displacement curves of adhered thermosets with and without nano-silica (1% by weight as a filler). Thus, this adhesive-less bonding technique can be applied to reinforced polymeric materials as well.

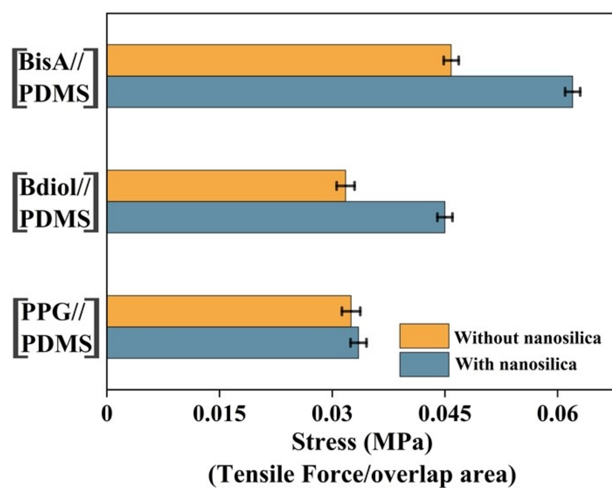

Figure S30. Addition of nano-silica reinforces the polymeric networks, and the bonded materials fail at higher stress as compared to the unreinforced polymeric networks.

Table S3. Stress at failure (MPa) (Tensile Force/overlap area) of the three thermoset pairs.

Sample name With Silica	**Stress at failure (MPa) (Tensile Force/overlap area)**				**Error bars**
	1	**2**	**3**	**Avarage**	**Std. Dev**
BisA//PDMS	0.06145	0.06164	0.06386	0.06232	0.00109
Bidiol//PDMS	0.04614	0.04538	0.04369	0.04507	0.00102
PPG//PDMS	0.03389	0.03452	0.03207	0.03349	0.00104

11. Non-polar PDMS thermoset as an adhesive for polar epoxy thermosets

A 400-micron thin film of PDMS thermoset was used as a hydrophobic, thermosetting adhesive film for bonding of polar epoxy thermosets. A 10mm x 10mm area of this film was sandwiched between polar epoxy thermosets and kept at 160°C for 4 hours at 200Kgf over 100mm^2 overlap area which corresponds to approximately 19.6 MPa pressure.

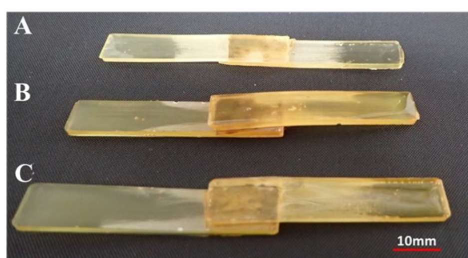

Figure S31. Pictures of thermosetting polymers adhered using a siloxane-based thin film. A non-polar PDMS thermoset film was used as a dry adhesive for polar epoxy thermosets between (a) two BisA thermosets (b) two Bdiol thermosets and (c) two PPG thermosets.

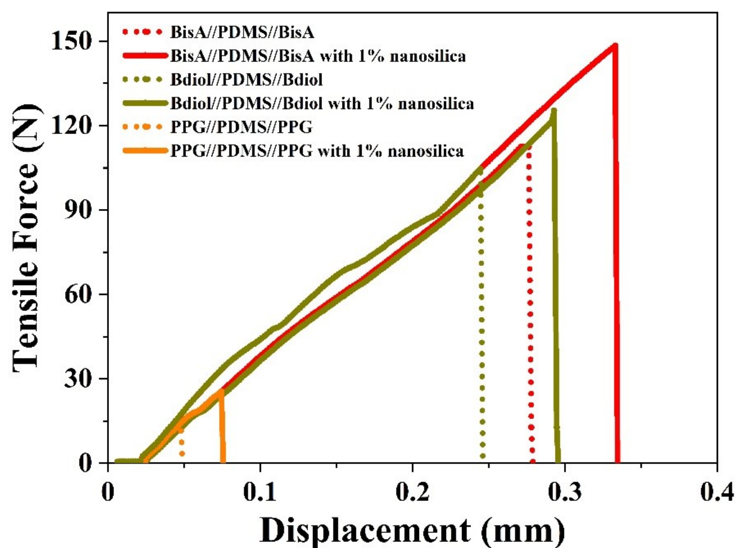

Figure S32. Force extension curves for use of PDMS-thermoset as an adhesive film for bonding of polar epoxy polymers. Addition of 1% w/w of nano-silica dramatically improves the mechanical properties of the thermosets and hence, requires greater force to break the adhesion between the polymers.

12. Re-adhesion of the polymers after first failure

In this dynamic covalent bonding system with a soft PDMS polymer as an adhesive film, failure of adhesion leads to cracks within the soft polymer. As this ester exchange is dynamic in nature, this failed adhesive can be reused to form an adhesive bond between the polymeric parts once again. The failed parts are kept in contact with each other and reheated under pressure, where covalent bond exchange again leads to adhesion between the polymers.

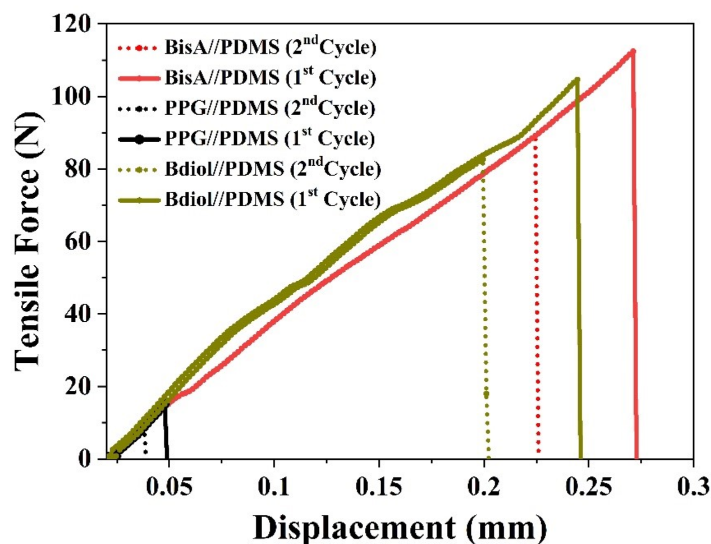

Figure S33. Force-extension curves for adhesion between polar epoxy thermosets using a non-polar PDMS thermoset. The de-bonded polymers can be re-bonded when subjected to the same dynamic covalent exchange conditions.

13. Sandwich structures of incompatible thermosetting materials

This dynamic covalent exchange strategy can lead to many interesting mechanical structures where, for example, a soft, non-polar polymer is sandwiched between two hard, polar polymers or vice versa.

a) **Fabrication of BisA//PDMS//BisA sandwich structure:** A 2 mm thick PDMS polymer in the shape of a dog-bone was placed between two 2 mm thick epoxy thermosetting polymers, also in the shape of a dog-bone. This system was then placed in the hot-press at 160°C for 4 hours at 200 Kgf over 100 mm^2 overlap area which corresponds to approximately 19.6 MPa pressure. This sample was further used for three-point bending tests.

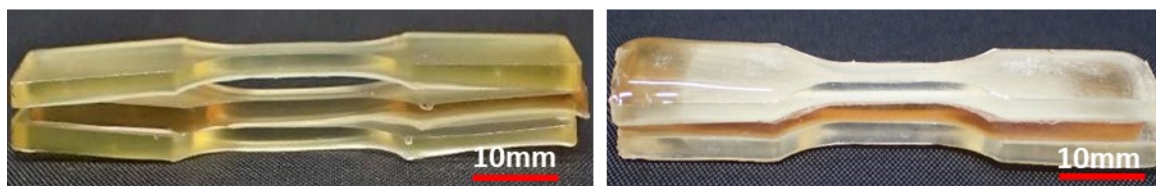

Figure S34 (*left*) Sandwitch BisA//PDMS//BisA thermoset before adhesive-less bonding. (*right*) Sandwitch BisA//PDMS//BisA thermoset after adhesive-less bonding.

b) PDMS//BisA//PDMS thermoset: A 2 mm thick epoxy thermoset polymer in the shape of a dog-bone was placed between two 2 mm thick PDMS thermosetting polymers, also in the shape of a dog-bone. This system was then placed in the hot-press at 160°C for 4 hours at 200 Kgf over 100 mm^2 overlap area which corresponds to approximately 19.6 MPa pressure. This sample was further used for three-point bending tests.

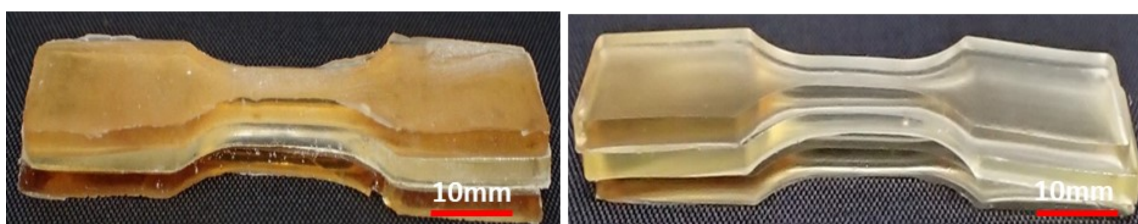

Figure S35. (*left*) Sandwitch PDMS//BisA//PDMS thermoset before adhesive-less bonding. (*right*) Sandwitch PDMS//BisA//PDMS thermoset after adhesive-less.

14. Three-point bending analysis of sandwich structures:

Dynamic covalent exchange between anhydride cured epoxides of significantly different mechanical properties gave rise to sandwich structures. These structures have unique mechanical properties, as exemplified by their three-point bending analysis data, where a programmed collapse of a heterogenous structure is desired.

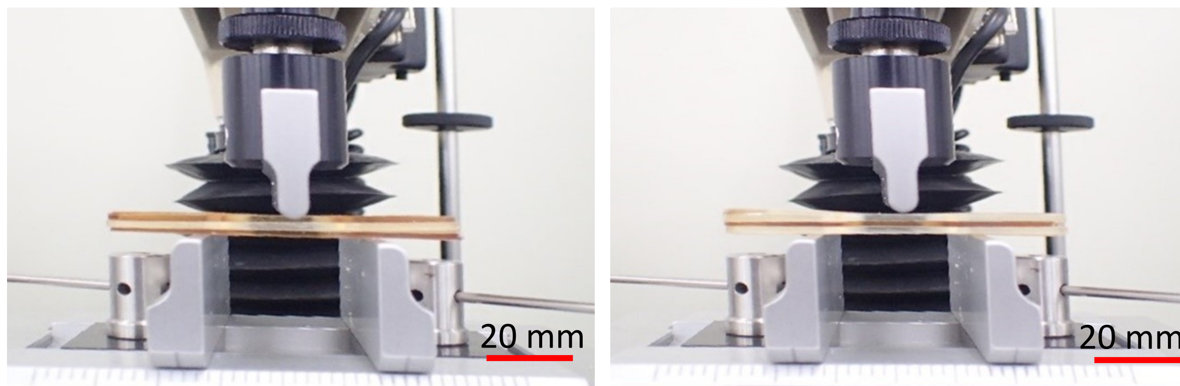

Figure S36. (left) Three-point bending analysis of PDMS-BisA-PDMS thermoset and (*right)* BisA-PDMS-BisA thermoset.

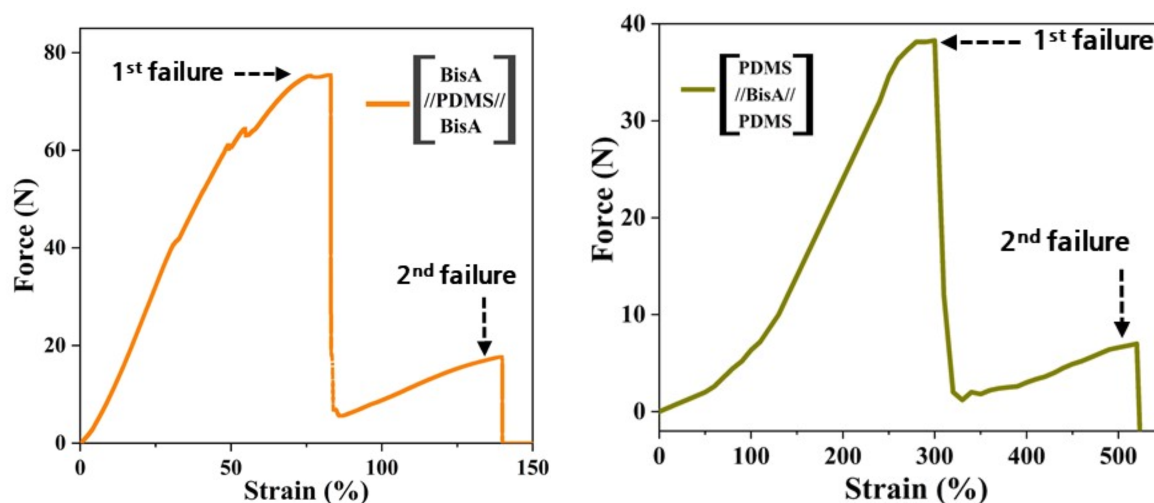

Figure S37. Force – extension traces of BisA-PDMS-BisA sandwich structure (*left*, provided in the manuscript Figure 5) and PDMS-BisA-PDMS sandwich structure (*right*). In both these cases, the composite structure shows a "tuneable" failure mode, depending on the constituents used to make the structure.

15. FTIR Analysis

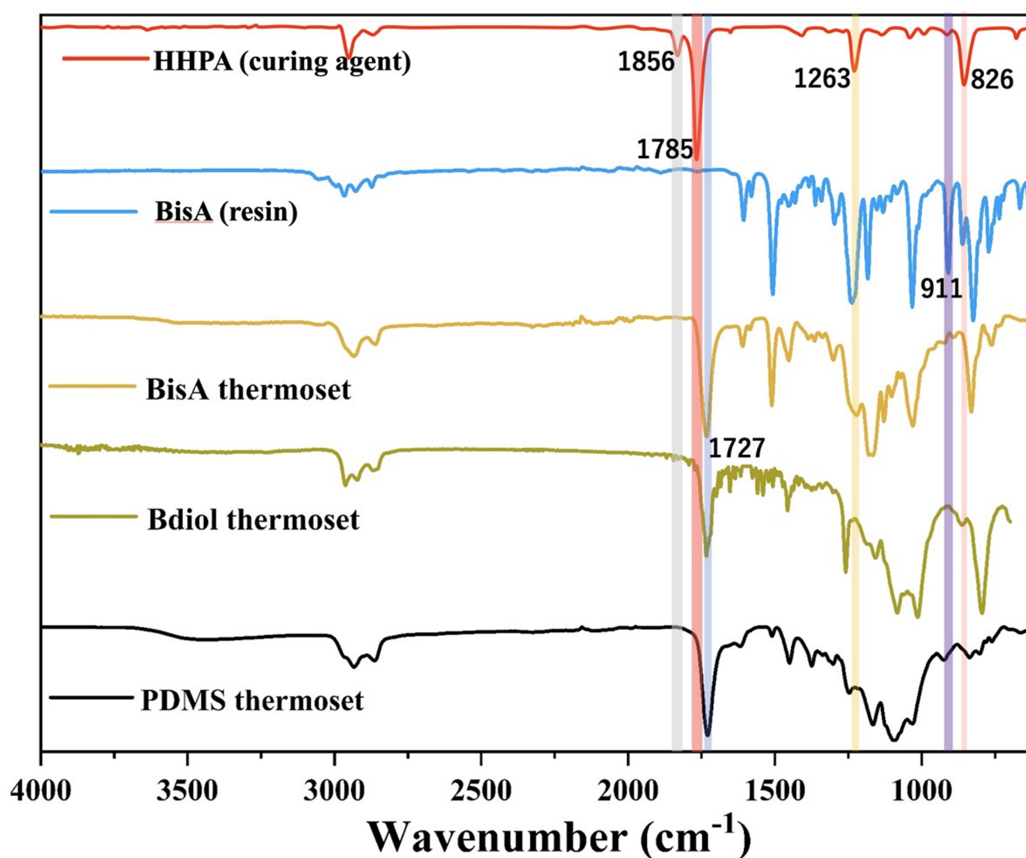

Figure S38. FTIR spectra comparisons of the starting materials (HHPA curing agent and BisA resin, top two traces) and the cured polymers (BisA thermoset, Bdiol thermoset and PDMS thermoset, bottom three traces). As seen from the spectra, the cured polymers do not contain unreacted anhydride or epoxide functional groups, and thus, are fully cured. Thus, the bonding observed between the thermosetting polymers is indeed a dynamic covalent exchange, rather than due to reaction of unreacted functional groups.