

Supporting Information

Catalyst Effect on the Self-Healing Properties of Bio-Based Diels-Alder Polyurethanes

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Keywords: self-healing polyurethane, Diels-Alder reaction, biobased, isocyanate trimer, catalyst, dynamic crosslink

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Determination of Swelling Degree and Gel Content

To measure the degree of swelling (Q) and gel content (G), 10x10x0.3 mm samples were submerged in 10 mL of toluene. This immersion occurred at room temperature within a sealed container for a 24-hour period. Following this swelling phase, the films were rinsed with toluene and then weighed to ascertain their swollen mass (ms). Subsequently, the films underwent a two-stage drying process at 35°C: first under atmospheric pressure, then under vacuum. The dried film weight (md) was recorded after this drying. Subsequently, the degree of swelling and gel content were computed using the following equations [1,2]:

$$Q = 1 + \frac{\rho_1}{\rho_2} \left(\frac{ms}{md} - 1 \right) \quad (1)$$

and

$$G(\%) = \frac{md}{m_{iso}} \cdot 100 \quad (2)$$

In these calculations, ρ_1 denotes the density of the solvent (toluene, with a density of 0.8669 g/cm³), while ρ_2 represents the density of the PU polymer. The variable m_d represents the weight of the dried sample after extraction, and m_{iso} represents the isolated weight of the sample before the extraction process began.

Table S1. Thermal properties derived from the DSC analysis of PU-DA synthesized with DBTDL and DBTDA catalysts

| Formula | T _{m-1} (°C) | T _{m-2} (°C) | T _c (°C) | ΔH _{m-1} (J/g) | ΔH _{m-2} (J/g) | ΔH _c (J/g) |
|--------------|-----------------------|-----------------------|---------------------|-------------------------|-------------------------|-----------------------|
| Pristine PEG | 65.14 | 61.11 | 21.5 | 182.33 | 158.33 | 136.97 |
| F1-DL | 55.58 | 57.02 | 27.65 | 94.56 | 79.05 | 74.75 |
| F2-DL | 55.13 | 61.97 | 23.77 | 87.59 | 85.64 | 80.99 |
| F3-DL | 47.69 | 52.46 | 11.11 | 74.33 | 71.69 | 58.92 |
| F4-DA | 54.40 | 56.84 | 28.41 | 100.99 | 91.64 | 140.42 |
| F5-DA | 57.40 | 61.23 | 21.49 | 111.06 | 99.04 | 114.31 |
| F6-DA | 58.52 | 59.53 | 27.84 | 104.43 | 93.01 | 104.98 |

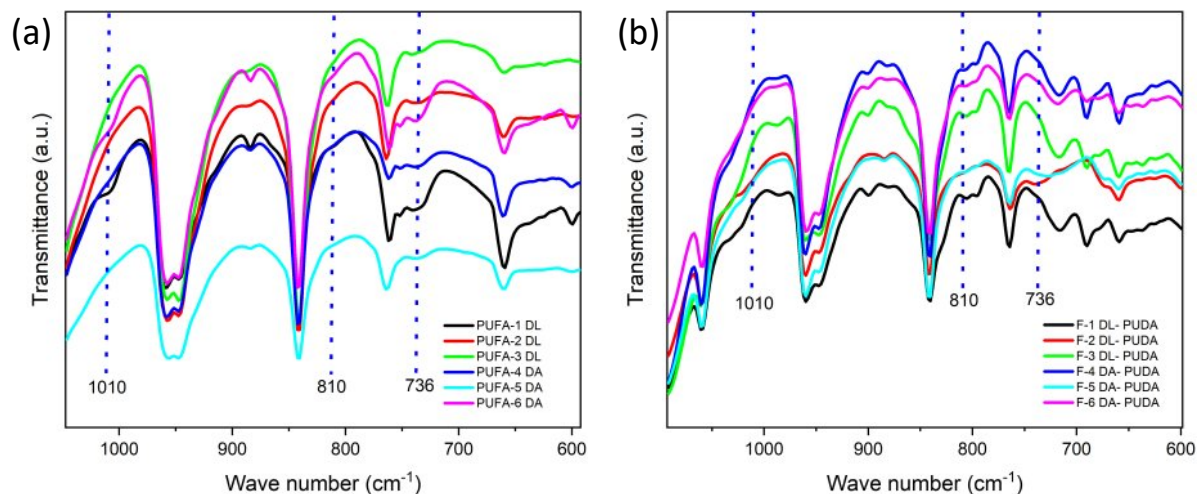


Figure S1. FTIR spectra illustrating (a) the characteristic absorption bands of the furan ring in PU–furan (PU–FA) and (b) the reduction in peak intensity associated with the furan ring following the Diels–Alder reaction.

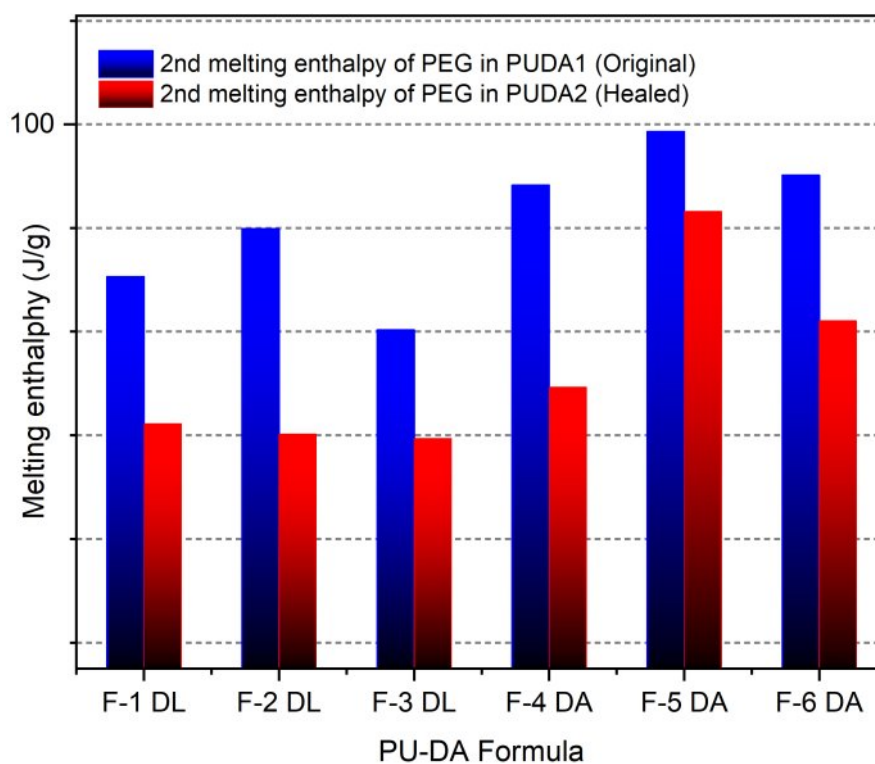


Figure S2. The melting enthalpy of PEG during the second heating (ΔH_{m2}) measured by DSC for PU–DA1 and PU–DA2 samples with DBTDL and DBTDA catalysts.

Table 2. Tensile Strength, Elongation at Break, Elastic Modulus, and Self-Healing Efficiency of PU-DA Samples Before and After Healing

| PU-DA Formula | Tensile strength of PU-DA ₁ (MPa) | Tensile strength of PU-DA ₂ (MPa) | Elongation at break PU-DA ₁ (%) | Elongation at break PU-DA ₂ (%) | Elastic modulus of PU-DA ₁ (MPa) | Elastic modulus of PU-DA ₂ (MPa) | Healing efficiency (%) ^a |
|---------------|----------------------------------------------|----------------------------------------------|--------------------------------------------|--------------------------------------------|---------------------------------------------|---------------------------------------------|-------------------------------------|
| F-1 DL | 0.83 ± 0.39 | 6.45 ± 0.30 | 28.44 ± 8.44 | 50.20 ± 4.11 | 4.02 ± 0.73 | 27.00 ± 9.13 | 776.55 |
| F-2 DL | 1.36 ± 0.10 | 7.49 ± 0.37 | 39.27 ± 5.83 | 48.72 ± 7.03 | 3.98 ± 2.36 | 23.49 ± 2.19 | 552.54 |
| F-3 DL | 3.56 ± 0.56 | 9.91 ± 0.40 | 56.29 ± 1.72 | 57.15 ± 3.96 | 6.83 ± 1.43 | 20.50 ± 2.81 | 278.41 |
| F-4 DA | 1.85 ± 0.62 | 5.16 ± 1.12 | 59.13 ± 12.50 | 62.97 ± 8.17 | 4.64 ± 0.68 | 8.94 ± 0.93 | 278.55 |
| F-5 DA | 1.11 ± 0.38 | 4.50 ± 0.24 | 51.50 ± 9.87 | 59.14 ± 3.42 | 3.72 ± 0.26 | 11.05 ± 2.12 | 407.08 |
| F-6 DA | 0.58 ± 0.07 | 3.37 ± 0.62 | 18.15 ± 2.08 | 40.86 ± 5.69 | 4.58 ± 0.44 | 9.92 ± 0.62 | 581.23 |

^a A self-healing efficiency of 100% is defined by the complete recovery of tensile strength in a PU-DA sample following a two-step thermal healing process—initial heating at 130 °C for 2 hours, followed by post-treatment at 70 °C for 24 hours—such that the healed sample matches the mechanical performance of the original undamaged, material. In this study, PU-DA₁ refers to the pristine polyurethane, whereas PU-DA₂ denotes the corresponding sample after the healing process.

References

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2. C. Lakatos, K. Czifrák, J. Karger-Kocsis, L. Daróczy, M. Zsuga, and S. Kéki, *J. Appl. Polym. Sci.* **133**, (2016).