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Self-Healable bio-Based Polyurethane via Dynamic ES-Click Chemistry

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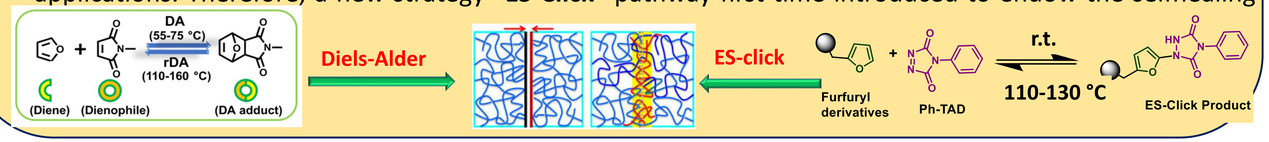
Abstract: Herein, furfuryl end-capped tri-arm PU prepolymer (FAPUs) were prepared by using polycaprolactone triol, 4,4'-methylene bis(phenyl isocyanate) and furfuryl alcohol in the presence of tin (II) catalyst. Cross-linked FAPUs were accomplished within 10 s under ambient conditions after reaction with bis-1, 2, 4-triazoline-3,5-dione (bis-TAD) via ES-Click chemistry. Differential scanning calorimetric (DSC) analysis revealed that TAD-derived FAPU elastomers were thermo-reversible at 110 °C and room temperature via ES-Click chemistry. Unlike pristine prepolymer with tensile strength (σ = 0.1 MPa), TAD-derived $FAPU_1$ polymer showed excellent tensile strength (σ = 34.68 MPa) with healing efficiency (Hσ = 83 %) with improved surface hydrophobicity without using any additive. These ES-clicked derived PU polymer materials showed excellent mechanical, self-healing, and hydrophobic characteristics and will be a potential candidate for advanced coatings, adhesives, and paint applications.

Introduction:

- Since the development of self healing materials via various mechanisms in early 2000, self-healing technology is one of the most important technologies declared by the World Economic Forum.
- Among these covalent bonded methods, the conventional furan-maleimide (4+2) cycloaddition DA reaction shows a promising approach due to its highly selective and easy synthetic methods under mild reaction conditions.
- However, the Diels-alder reaction pathway takes long time for preparation, processing and healing applications. Therefore, a new strategy "**ES-Click**" pathway first time introduced to endow the selfhealing

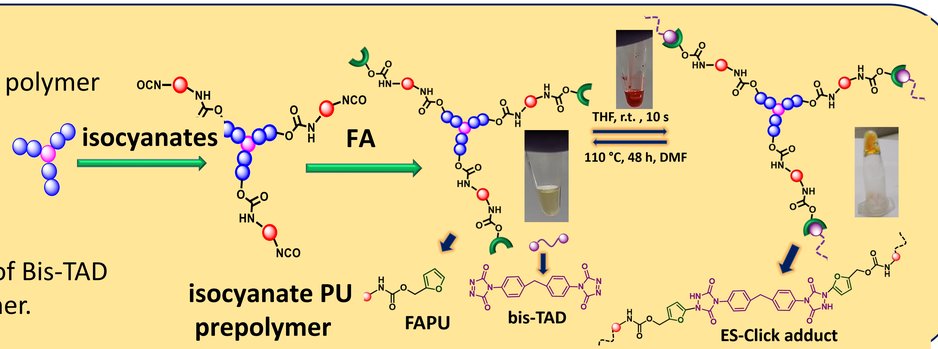


Objectives:

- Synthesis of trifunctional polyurethane with different molar ratio and crosslinked with TAD derivatives.
- Self-healing and reprocessing study of synthesized PU polymer via various characterisation.
- Mechanical and hydrophobicity study of the polymer

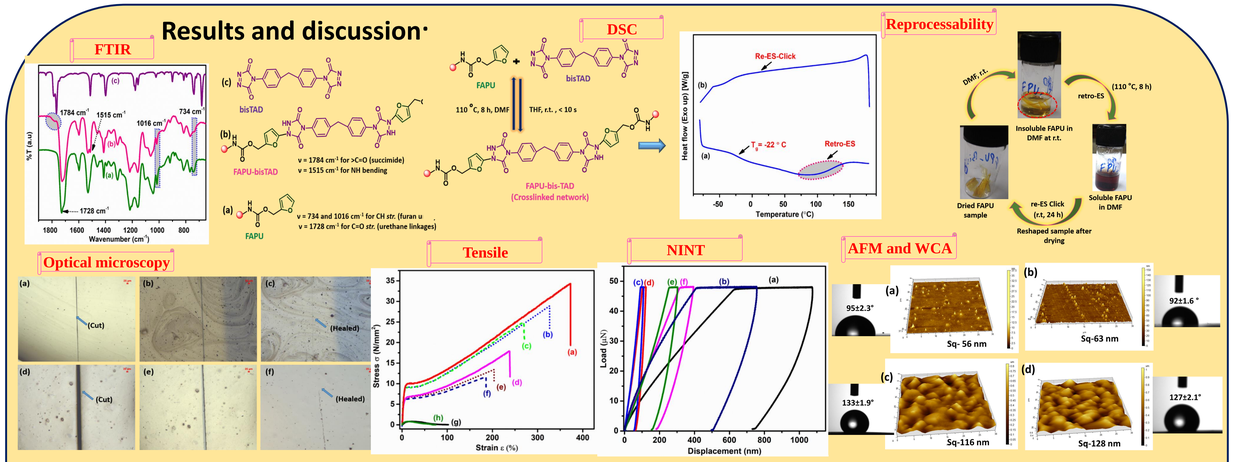
Synthesis:

- Synthesis of furan based polymer



- Controlled cross-linked of Bis-TAD with furan based polymer.

Results and discussion



- FAPU-TAD crosslink polymer synthesized within 10 s at ambient condition and confirmed by FTIR and NMR.
- DSC and reprocessing analysis revealed that FAPU-TAD was thermoreversible at 130 °C and shows self healing characteristics via ES-Click chemistry. Mechanical and hydrophobicity of cross-linked polymer was improved after crosslinking with TAD.

Conclusions:

- ES-crosslinked network was formed within 10 sec addition of bis-TAD at ambient condition via ES click chemistry.
- DSC shows that polymer is thermoreversible in nature and soluble in DMF at 130 °C.
- Optical microscopy confirms that the self healing nature of polymer occured ES-click temperature(130 °C and r.t)
- Tensile strength of FAPU-TAD was increased from 0.01 MPa to 34.6 MPa with healing efficiency of 83% .
- Surface hardness also significantly improved after crosslinking.
- WCA of cross-linked polymer was improved as surface roughness increases from 56 nm to 116 nm.
- This ultrafast derived polymer will have potential for coating, painting applications

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