SUPPORTING INFORMATION

Self-healable and Ultra-hydrophobic Polyurethane-POSS Hybrids by Diels-Alder "Click" Reaction; A New Class of Coating Material

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^{1}H-NMR of chain extender (FA-FGE diol)

The ^{1}H-NMR spectra of furfuryl amine (FA), furfuryl glycidyl ether (FGE) and the product tri-furan containing chain extender (FA-FGE diol) are given in Figure S1. The complete disappearance of the -NH_2 resonance (designated as 'e' in Figure 1a) in the spectrum of FA-FGE diol (Figure S1C) indicates the successful reaction between FA and FGE. Further, the shifting of the resonances of the –C$\underline{H}_2$-NH_2 protons ('d' in Figure S1A) and the epoxy protons ('k' and 'l' in Figure S1B) to new positions (d_1 k_1 and l_1 in Figure 1C) also support the success of reaction between FA and FGE. In the ^{1}H-NMR spectrum of the product (Figure S1C), a broad peak at 3.2 ppm indicates the presence of hydroxyl groups which are formed by the reaction amine group of FA with the epoxy group of FGE. The resonances at 7.3-7.4 ppm (designated as 'a' and 'f' in Figure S1C) and 6.15-6.35 ppm (designated as b, c, g, h, and f in Figure S1C) indicates the presence of furan groups in the prepared chain extender (FA-FGE diol).

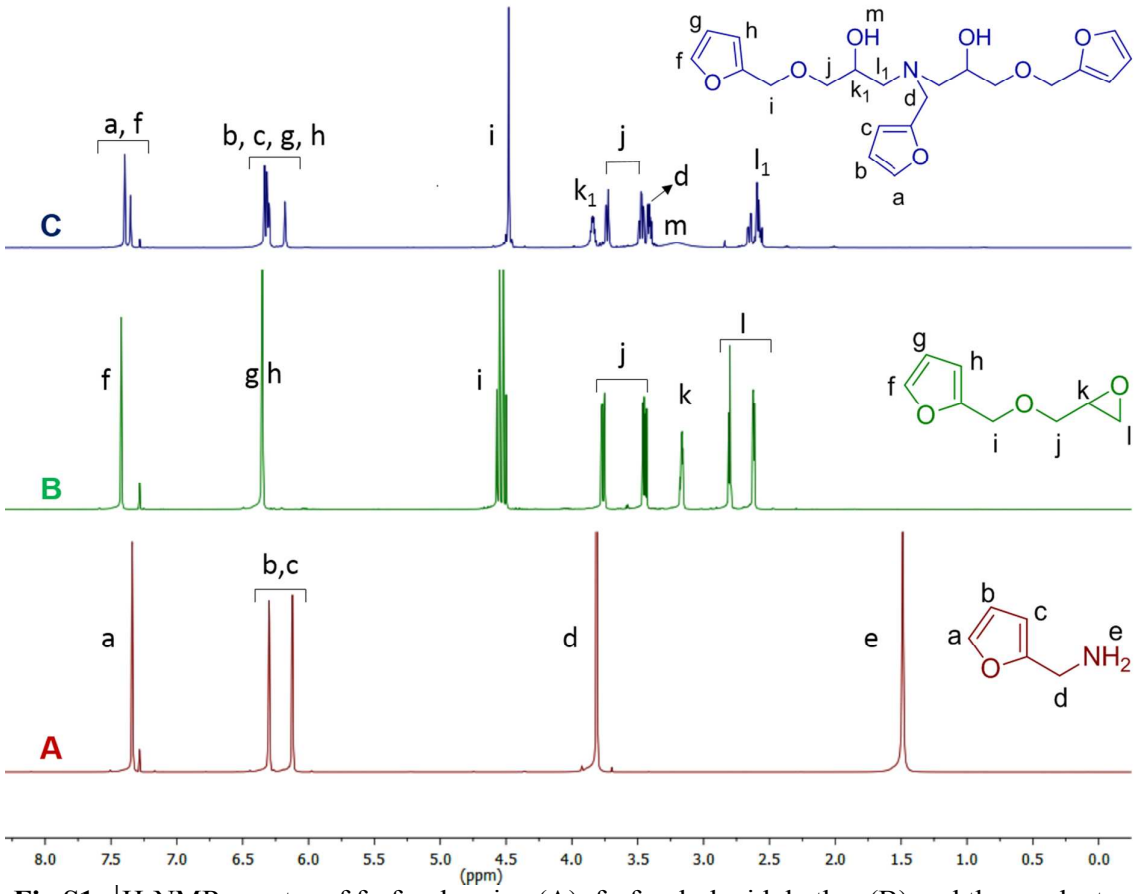

Fig S1: ^{1}H-NMR spectra of furfuryl amine (A), furfuryl glycidyl ether (B) and the product tri-furan containing chain extender (FA-FGE diol) (C) in $CDCl_3$.

MALDI-TOF analysis of chain extender (FA-FGE diol)

Chemical Formula: $C_{21}H_{27}NO_7$

Molecular Weight = 405.44

Exact Mass = 405.18

m/z for $[MH]^+$= 406.18 (Calculated)

m/z for $[MH]^+$= 406.19 (Experimental)

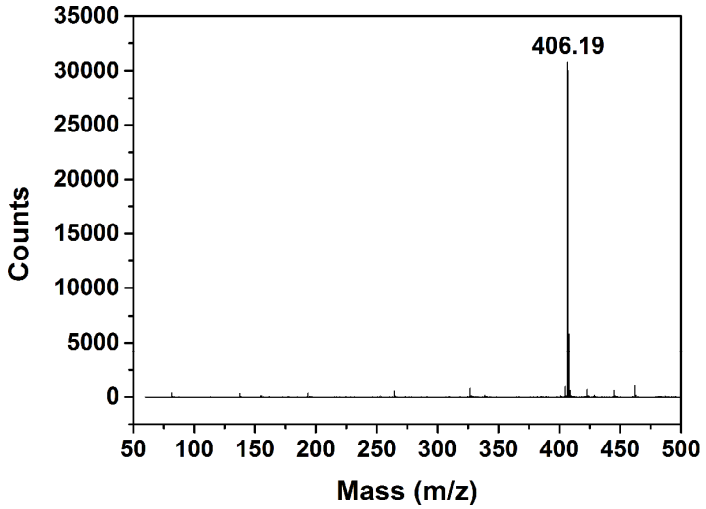

Fig S2: MALDI-TOF mass spectrum of FA-FGE diol.

FT-IR spectra of MDI, PCL-diol and furan containing polyurethane (FPU)

Figure S3 represents the FT-IR spectra of MDI, PCL-diol and the prepared furan containing PU (FPU). The absorption band at about 2265 cm^{-1}, corresponding to the stretching vibration of the -NCO group of MDI, has entirely disappeared in the spectrum of FPU. Furthermore, the FTIR spectrum of FPU shows an absorption band at 3300 cm^{-1}, which is due to the hydrogen-bonded -NH group of urethane linkages. The absorption band at 1728 cm^{-1} is assigned to free urethane carbonyl while the associate shoulder peak at 1707 cm^{-1} is due to hydrogen bonded carbonyl (Figure S4).[1] Absorption band observed around 1532 cm^{-1} is associated with the >N-H bending vibration of the urethane linkages. The absorption bands in the region 2862-2940 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of the aliphatic $-CH_2-$ groups.

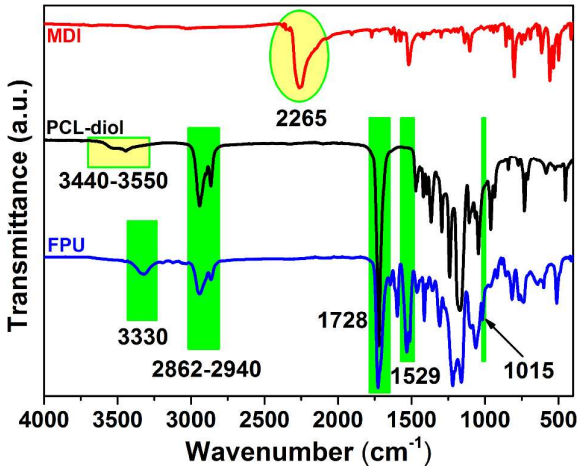

Fig S3: FT-IR spectra of MDI, PCL-diol and furan containing polyurethane (FPU)

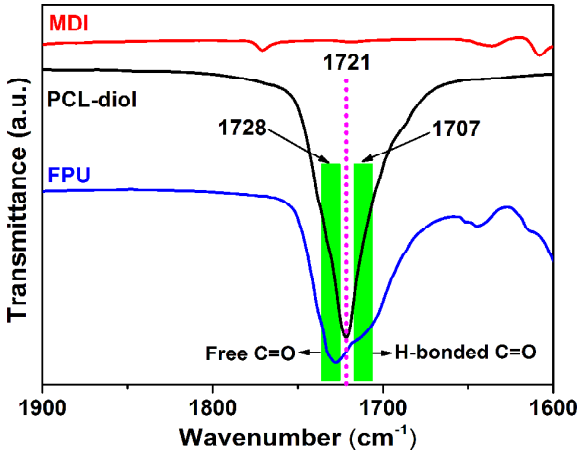

Fig S4: Amplified FT-IR spectra of MDI, PCL-diol and FPU in the frequency range 1600-1900 cm^{-1}.

^{1}H-NMR spectrum of furan containing polyurethane (FPU)

Figure S5 represents the ^{1}H-NMR spectrum of FPU prepared using MDI as diisocyanate, PCL-diol as soft segment and FA-FGE diol as chain extender. The resonances at 9.48-9.6 ppm (designed as 'a' in Figure S5) are due to the >N-H protons of the urethane linkages,[2, 3] which confirm the successful reaction between the –N=C=O groups of isocyanate and the –OH groups of PCL-diol and chain extender. Further, splitting of the >N-H resonance into two peaks indicates the presence of free as well as hydrogen bonded >N-H protons. The resonance at higher δ value (9.6 ppm) is due to the hydrogen bonded >N-H protons, whereas the resonance at lower δ value (9.48 ppm) is because of the free >N-H protons. The resonances at 6.25-6.35 ppm ('e' type proton) and 7.56 ppm ('b' type proton) indicate the presence of furan moieties in the prepared polyurethane. The presence of furan groups in the polymer was also evidenced by the presence of a resonance at 4.35 ppm corresponding to the –O-C$\underline{H}_2$- protons (denoted as 'f') as well as the resonance at 3.5 ppm for –N-C$\underline{H}_2$-furan protons (designated as 'k'). The resonances at 7.1 ppm and 7.3 ppm (proton 'c' and 'd' respectively) are due to the aromatic protons of the MDI. The resonance at δ value of 3.8 ppm corresponds to the –CH_2- protons of MDI. The resonances at 1.27, 1.53, 2.27, and 4.0 ppm

are due to the $–CH_2$- protons (i, m, n, o, p, q, and r type protons) of the polycaprolactone soft segment as represented in Figure S5. Further, the shifting of the >CH-OH resonance (δ = 3.8 ppm, designated as 'k_1' in Figure S1C) of the chain extender toward higher δ value in the polymer (δ = 4.95 ppm, designated as 'g' in Figure S5) also indicates the successful reaction between the –OH group of the chain extender with the –N=C=O group of the MDI.[4]

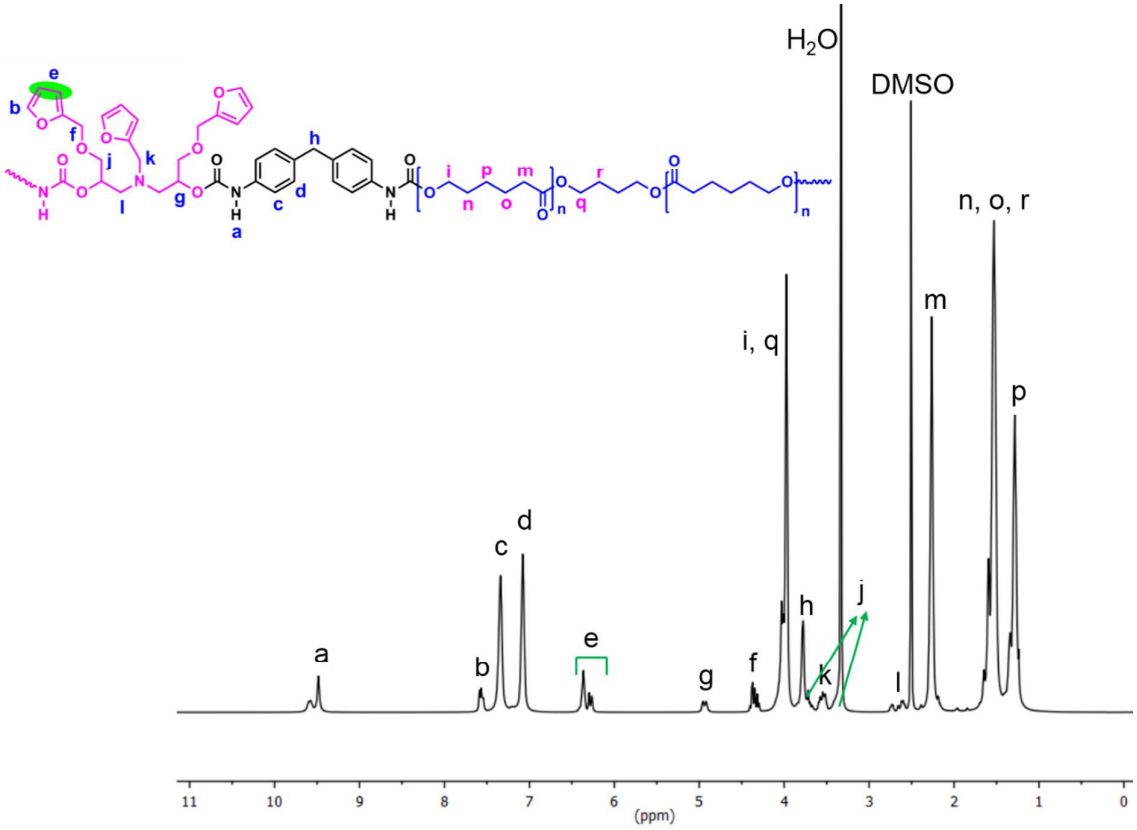

Fig S5: ^{1}H-NMR spectrum of furan containing polyurethane (FPU)

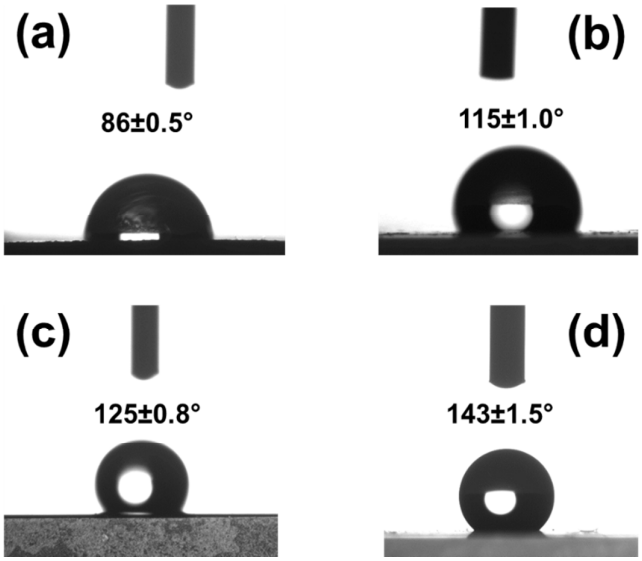

Fig S6: Images of water droplets on (a) FPU, (b) FPU-POSS-M6, (c) FPU-POSS-M12, and (d) FPU-POSS-M36 surfaces after heating above rDA temperature (130 °C) followed by keeping them at 70 °C for 15 h.

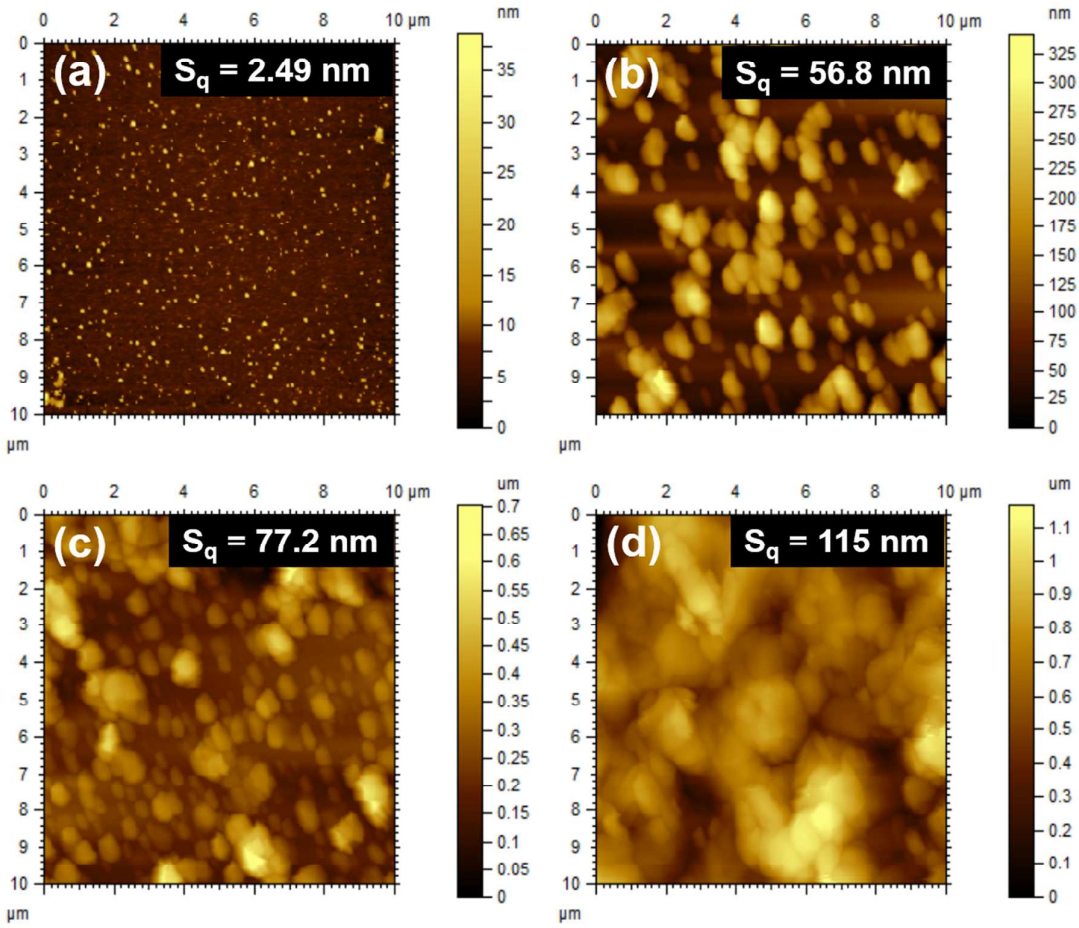

Fig S7: AFM 2D images of (a) FPU, (b) FPU-POSS-M6, (c) FPU-POSS-M12, and (d) FPU-POSS-M36

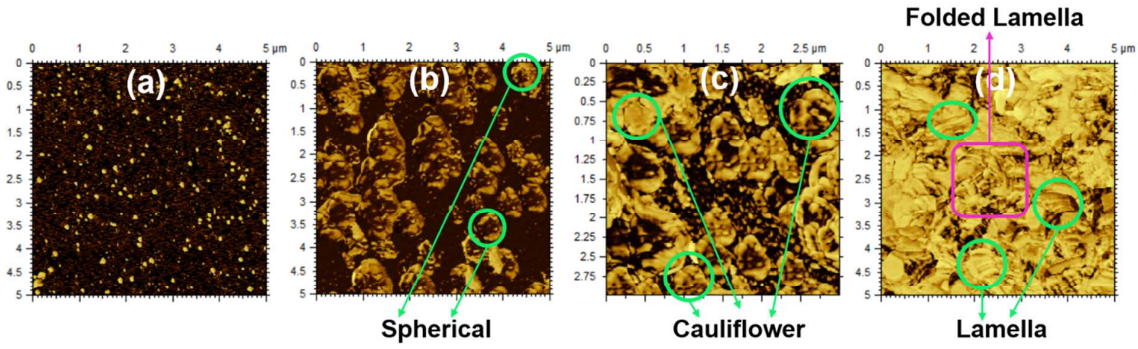

Fig S8: AFM phase images of (a) FPU, (b) FPU-POSS-M6, (c) FPU-POSS-M12, and (d) FPU-POSS-M36

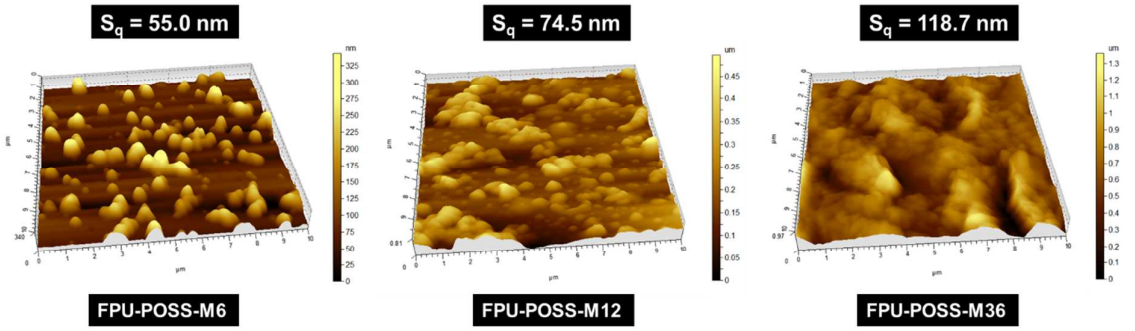

Fig S9: AFM 3D images of FPU-POSS-M hybrid materials after heating above rDA temperature (130 °C) followed by keeping them at 70 °C for 15 h.

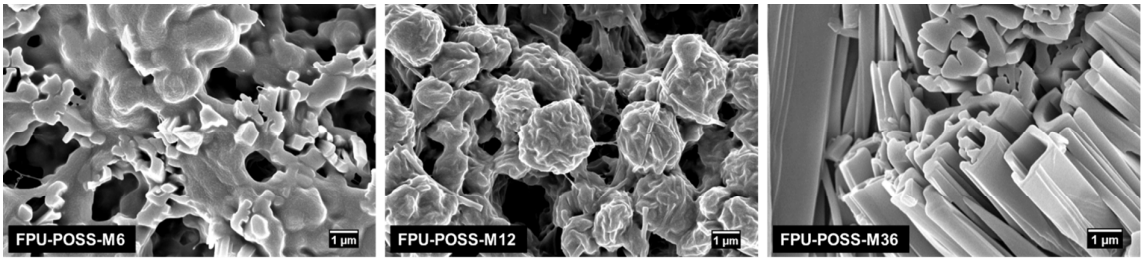

Fig S10: FESEM images of FPU-POSS-M hybrid materials after heating above rDA temperature (130 °C) followed by keeping them at 70 °C for 15 h.

Nanoindentation experiment

Table S1: Surface hardness and contact depth of FPU, FPU-POSS-M6, FPU-POSS-M12, and FPU-POSS-M36.

Sample	Hardness (GPa)	Contact depth (nm)
FPU	0.0023±0.0002	838±28
FPU-POSS-M6	0.0052±0.0003	586±31
FPU-POSS-M12	0.0080±0.0005	473±24
FPU-POSS-M36	0.0345±0.0021	248±15

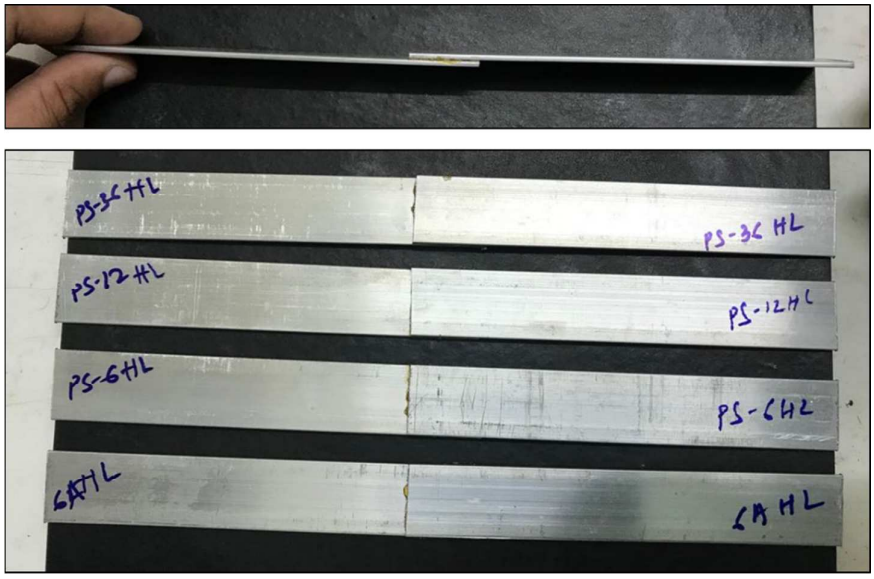

Fig S11: Single-lap joint specimens for adhesion test

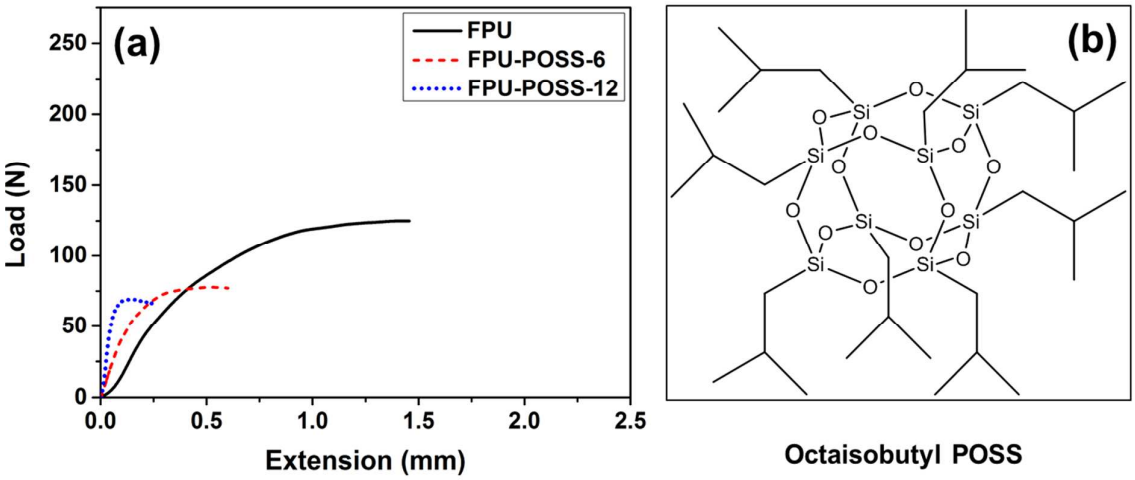

Fig S12: (a) Typical single-lap joint load-displacement response for FPU, FPU-POSS-6 and FPU-POSS-12 prepare using octaisobutyl POSS. (b) Structure of POSS molecule (octaisobutyl POSS) without maleimide functionality.

References

(1) Gurunathan, T.; Mohanty, S.; Nayak, S. K. Effect of reactive organoclay on physicochemical properties of vegetable oil-based waterborne polyurethane nanocomposites. *RSC Adv* **2015,** 5, 11524-11533.

(2) Mou, Z.; Feng, S. K.; Chen, E. Y. Bio-based difuranic polyol monomers and their derived linear and cross-linked polyurethanes. *Polym. Chem.* **2016,** 7, 1593-1602.

(3) Mahapatra, S. S.; Yadav, S. K.; Yoo, H. J.; Ramasamy, M. S.; Cho, J. W. Tailored and strong electro-responsive shape memory actuation in carbon nanotube-reinforced hyperbranched polyurethane composites. *Sens. Actuators, B* **2014,** 193, 384-390.

(4) Gaina, C.; Ursache, O.; Gaina, V.; Varganici, C. Thermally reversible cross-linked poly (ether-urethane) s. *Express Polym Lett* **2013,** 7.