

## UV curable polyurethane-acrylate hybrids made by a prepolymer free process and free-standing polymer-metal oxide films made in a wholly water-based UV curing process

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### Experimental

#### Characterization

<sup>1</sup>H Nuclear magnetic resonance (<sup>1</sup>H NMR) measurements were recorded on Bruker UltraShield Avance 400 MHz FT-NMR instrument using deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) as solvent. Fourier transform infrared (FT-IR) spectroscopy was performed on a PerkinElmer Frontier NIR spectrometer in ATR mode from 400 to 4000 cm<sup>-1</sup>. The sample measurements were performed with 64 scans per spectrum with the resolution of 4 cm<sup>-1</sup>. Dynamic light scattering (DLS) was performed by using a Zetasizer Nano ZS Instrument (Malvern Instruments, UK) equipped with a He-Ne laser (633 nm) and with non-invasive backscattering (NIBS) detection at a scattering angle of 173°. The autocorrelation function was converted to intensity averaged particle size distribution using Dispersion Technology Software from Malvern Instruments. Each measurement was repeated at least three times, and the average result was reported as the final Z average diameter (nm). The measurements were performed at 25 °C. Scanning electron microscopic (SEM) images were observed using JEOL JSM-6700F Field Emission Scanning Electron Microscope. Thermal stability of polymers was determined by thermogravimetric analysis (TGA) on a TA instrument (SDT-TGA) at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere by heating the sample from 25 to 800 °C. Molecular weights were determined by gel permeation chromatography (GPC) on a Waters GPC system consisting of integrated solvent and sample delivery module. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 ml/min at 40 °C and molecular weight values were determined against Polystyrene standards. UV curing was performed using a UV Gel Nail Polish Dryer (Melody Susie brand) Model DR-5401 with input 110V – 120V and frequency 60 Hz. The power was 54W.

### Materials

Polyethylene glycol, M<sub>n</sub> 400 (PEG), Dibutyltin dilaurate (DBTDL), *N*-Methyl diethanolamine (MDEA), isophorone diisocyanate (IPDI), 1,4-butanediol (1,4-BD), acrylic acid (AA), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) were obtained from Aldrich. TiO<sub>2</sub> and SiO<sub>2</sub> were obtained from commercial sources. *N,N*-dimethyl formamide (DMF) was drawn from Glass Contour solvent purification system under nitrogen atmosphere. All other reagents were obtained from commercial sources and used as received.

### Synthesis of PU1 [MDEA-IPDI-PEG-BD]

PEG 400 (5.0 g, 0.013 mol) was dissolved in DMF (20 ml) in a 3 neck RB flask, equipped with N<sub>2</sub> flow. DBTDL (0.3 g, 0.0005 mol) and IPDI (7.0 g, 0.031 mol) were added and the resulting mixture was heated to 75 °C. After 2 h, a solution of MDEA (1.72 g, 0.014 mol) in DMF (10 mL) was added dropwise. Heating was continued at 75 °C for 3 h followed by addition of 1,4-BD (1.42 g, 0.016 mol). The mixture was stirred and heated further for 2 h and cooled to rt. Then the polymer solution was precipitated in water and dried under high vacuum to yield a white rubbery solid. Yield: 13.0 g, (86%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, δ ppm): 4.03 (b, -COO-CH<sub>2</sub>-, MDEA), 3.93 (b, -COO-CH<sub>2</sub>-, BD), 3.56 (b, -CH-, IPDI), 3.51 (s, -OCH<sub>2</sub>-CH<sub>2</sub>O-, PEG),

2.56 (b, N-CH<sub>2</sub>-, MDEA), 2.23 (s, N-CH<sub>3</sub>), 1.57 (b, -O-CH<sub>2</sub>-CH<sub>2</sub>-, BD), 1.43 (t, IPDI) and 1.11-0.79 (m, IPDI). GPC (Eluent: THF): M<sub>n</sub> = 10,100, PDI = 1.78.

#### Preparation of PU dispersion with Acrylic acid

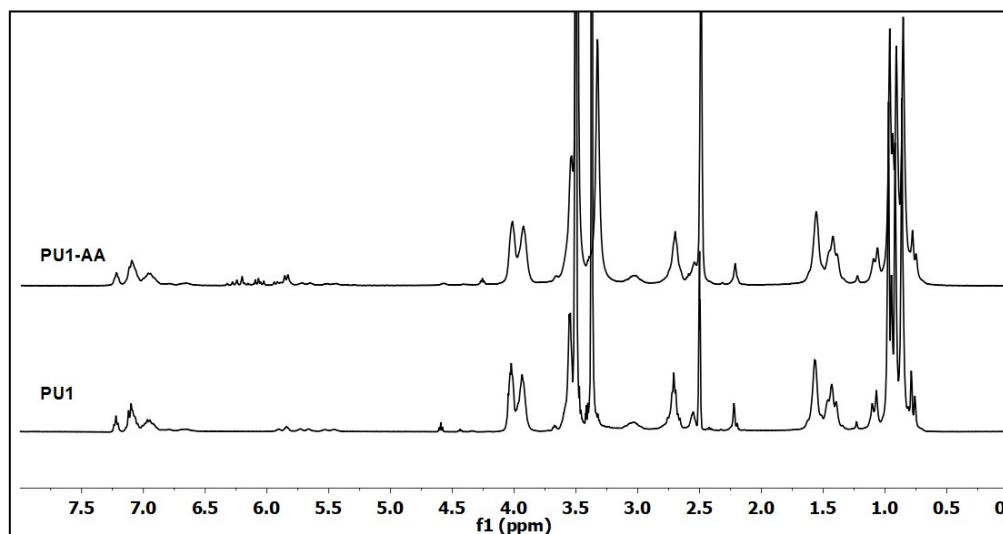
Acrylic acid (100 mol% with respect to amine content in the polyurethane) was added to **PU-1** suspended in 10 volume of water. Originally **PU-1** remained suspended in water. The polymer gradually dispersed in water upon stirring at ambient temperature for 6 h, making a 10 wt% aqueous dispersion of **PU1-AA**. A 15 wt% **PU1-AA** dispersion was also prepared and used in some cases.

#### UV curing experiments

To an aqueous dispersion of **PU1-AA**, photoinitiator, Irgacure 2959 (4 wt%) was added and was stirred at 1000 rpm for 30 mins before casting onto Teflon plate. Curing was facilitated by irradiating with UV lamp ( $\lambda = 365$  nm) for 45 - 60 mins. Water evaporation occurred during film formation. After the experiments, the cured film was peeled off, then rinsed with deionized water and dried.

#### UV cured film with TiO<sub>2</sub>

To an aqueous dispersion of **PU1-AA** (10 wt%), TiO<sub>2</sub> (5 – 10 wt%) (or SiO<sub>2</sub>, 5-10 wt%) and photoinitiator (4 wt%) were added with stirring at 1000 rpm. The white suspension was cured as described above for 1 h to obtain a free standing, flexible film. The stability of film in water was established by heating the film in water at 90 °C for 12 h. After the hot water treatment, the film shrank in size, however, did not disintegrate and was flexible as the original film.



**Figure S1.** <sup>1</sup>H-NMR spectra of **PU-1** and **PU1-AA** (solvent: *d*<sub>6</sub>-DMSO).