Supplementary Material (ESI) for *RSC Advances*

Supporting Information

Novel photo-curable polyurethane resin for stereolithography

Experimental section

Materials

Poly(tetrahydrofuran) (PTH, M_n 2000 g/mol), hydroxyl terminated poly(dimethylsiloxane) (PDMS, M_n 550 g/mol), isophorone diisocyanate (IPDI), anhydrous tetrahydrofuran (THF), dibutyltin dilaurate (DBTDL), anhydrous 2-methyl-1-propanol and hydroxyethyl methacrylate (HEMA) were purchased from Sigma-Aldrich. Irgacure® TPO-L and orasol orange G were obtained from BASF. All chemicals were used as received.

Methods

Synthesis of polyurethane resin

A mixture of 2 g IPDI and 0.1098 g DBTDL (1wt%) in 10 mL of anhydrous THF was fed into a 100 mL three-neck flask. Nitrogen bubbling was carried out for 30 min to introduce inert environment. The mixture was heated to 60 ^oC. A mixture of 7.1981 g PTH and 0.494 g PDMS in 35 mL anhydrous THF was added slowly in 1 h to reaction flask. The reaction was carried out for another 2.5 h at 60 ^oC with Nitrogen flow. A mixture of 0.8197 g HEMA and 0.1996 g 2-methyl-1 propanol in 5 mL anhydrous THF was added and the reaction was continued for another 1 h. Solution of 0.2668g of 2-methyl-1-propanol in 1 mL anhydrous THF was added and stirred another 30 min to terminate polymerization reaction. Finally, anhydrous THF was evaporated by using a rotary evaporator and the liquid colorless resin was obtained after extraction with mixture diethyl ether and hexane at ratio 5:3 (v/v). The resin was stored in cool dark place to avoid crosslink reaction during storage.

Preparation of resin mixture for stereolithography

A weighted resin was fed into a dark colored vial fitted with a magnetic bar. Irgacure® TPO-L (0.1 wt%) and Orasol orange G (0.1 wt%) were added to the vial. The mixture was stirred for 24h to ensure the uniformity of the mixture.

Stereolithography fabrication

3D structures were fabricated by a self-made projection stereolithography (PSLA) system. The system was based on commercial video projector (Acer H6510BD, 1920*1080 pixels) that was used as a light projection device to project a dynamically defined mask images onto a photo-curable resin surface. The printing resolution of PSLA was 18 μm in x and y direction. Fabrications were carried out by using light wavelength of 400-500 nm, light intensity of 15000 $\mu W/cm^2$, layer thickness of 30μm, and curing time of 10s for each layer. In fabrications Orasol Orange G (0.1 wt-%) was used as a neutral absorber to control penetration depth of light into resin.

Characterizations

Gel permeation chromatography method was performed on a Water 717 Plus system using mixture of chloroform and 2 v% trimethylamine as eluent. ^{1}H-NMR method was carried out on an Ultrashield 400 Plus (Bruker). Viscosity of resin was evaluated on a Physica MCR 301 rheometer (Anton Paar) using cylinder cup geometry CC27 at a constant shear stress of 0.5 MPa. Differential scanning calorimetry (DSC) tests were performed on a TA instrument (Q2000) with temperature range from -80 ^{o}C to 250 ^{o}C at a heating rate of 10 ^{o}C/min. Dynamic mechanical analyses (DMA) were carried out by using the TA instrument (Q800) from -80 ^{o}C to 100 ^{o}C at a heating rate of 5 ^{o}C/min and frequency of 1 Hz. Mechanical properties of casted PU films were investigated on Instron 4204 universal testing equipment at 25 ^{o}C and relative humidity of 50%, with speed of 10 mm/min. The static elastic recovery properties were evaluated by using creep mode on the DMA system (Q800). In particular, the samples were applied with a constant stress of 0.25 MPa for 30 min at 30 ^{o}C. Then, the force was released to let the samples recover back to original position. The strain recovery (%) was recorded along with recovery time up to 120 min. The cytotoxicity of elastomer was evaluated by viability staining of fibroblast growing directly at the materials. The polyurethane elastomer substrates were cultured with the mouse fibroblast cell line (3T3). Cell viability was evaluated from fluorescence microscopy images of 3T3 cells growing on PU elastomer and negative control substrates stained after 4 days of testing with fluorescein diacetate (FDA, staining viable cells green fluorescent after intracellular esterase catalysed cleavage to fluorescein and acetate) and GelRed^{TM} (staining the nuclei of dead cells orange).

GPC

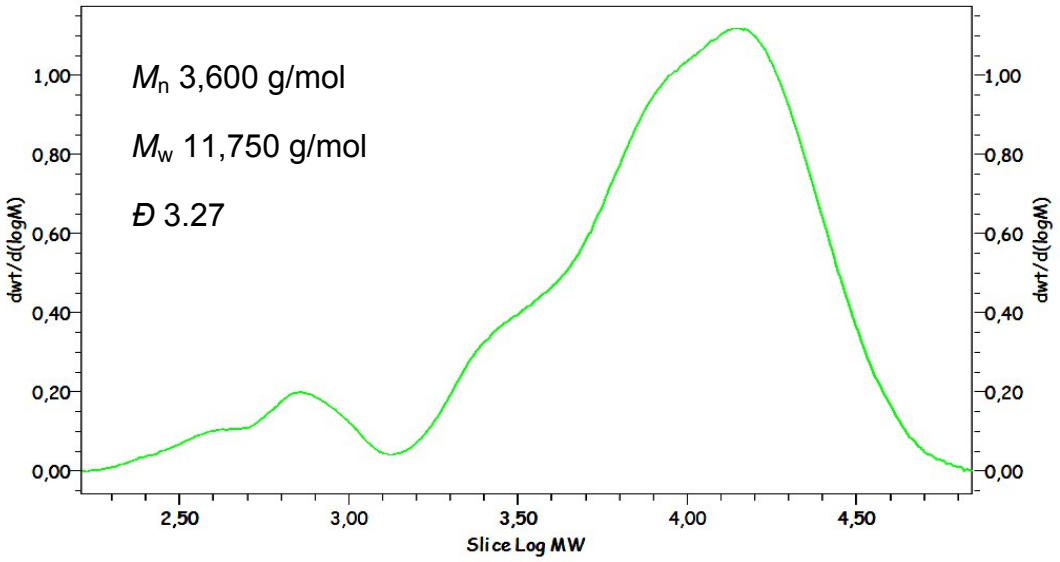

Fig. S1 GPC curve of photo-curable polyurethane resin.

^{1}H-NMR

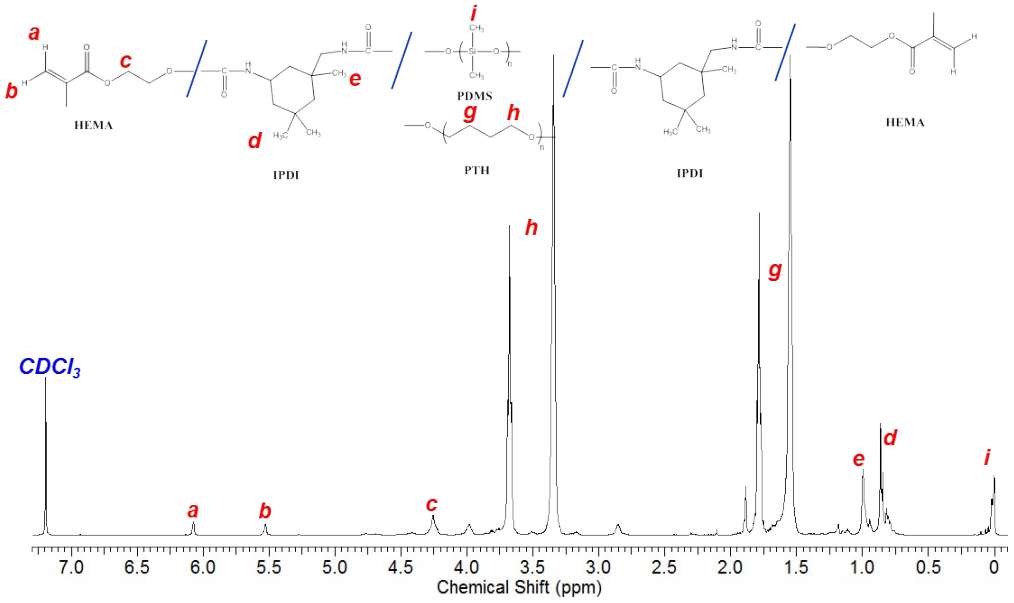

Fig. S2 ^{1}H-NMR of photo-curable polyurethane resin.

Rheology

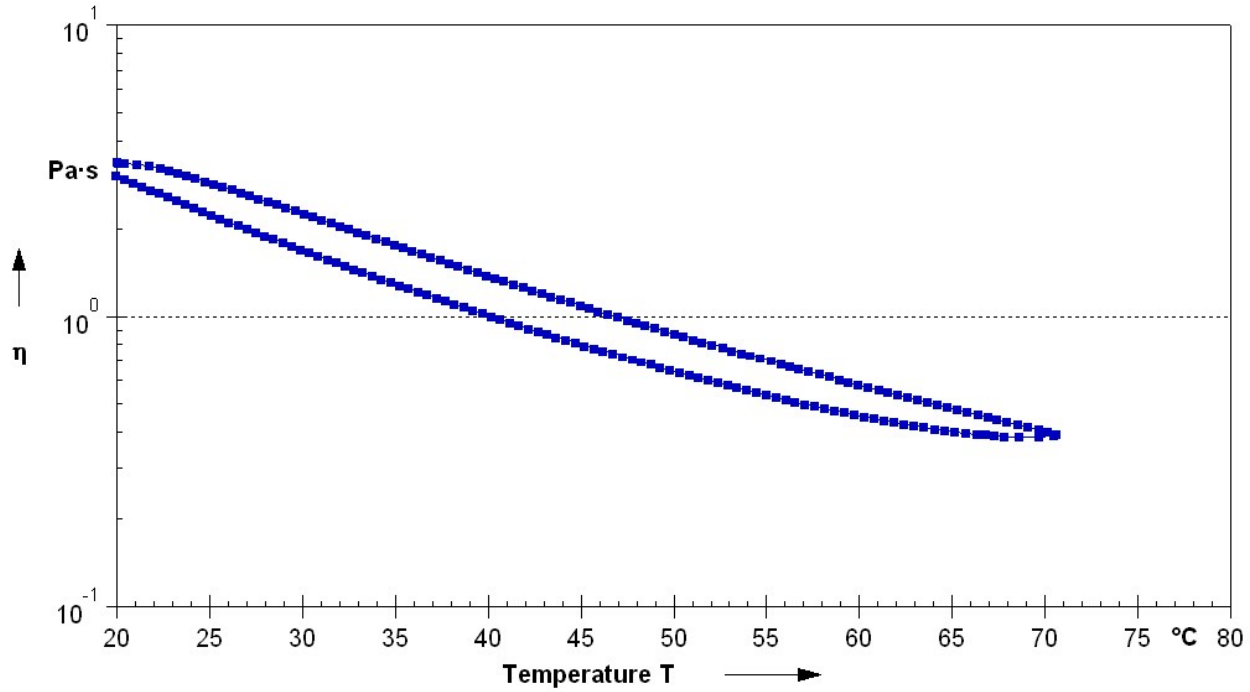

Fig. S3 Viscosity of photo-curable polyurethane resin.

Mechanical strength

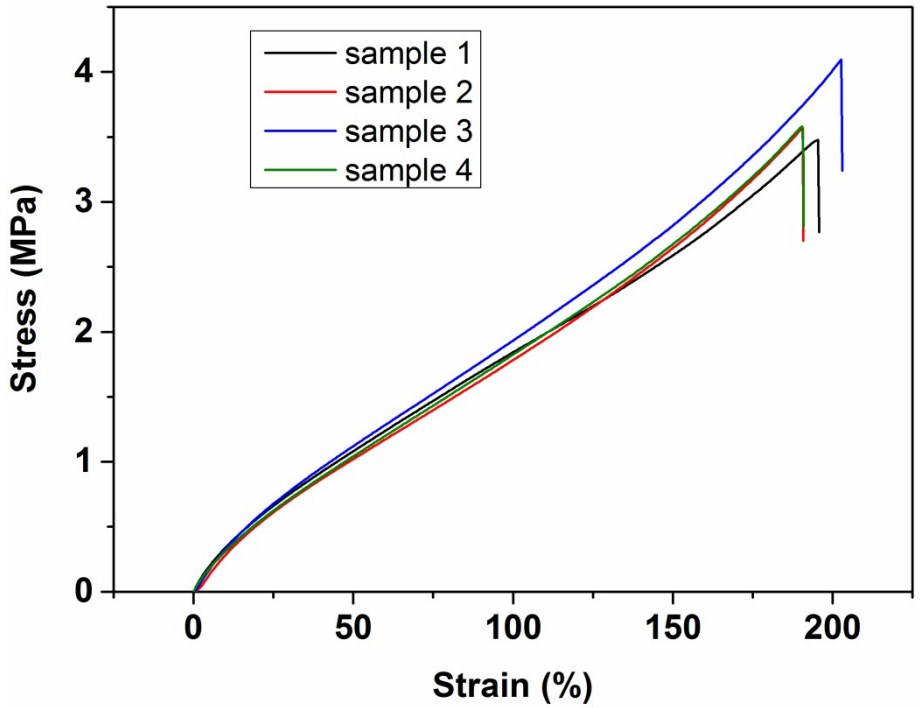

Fig. S4 Stress-strain curves of resultant elastomer.

DSC

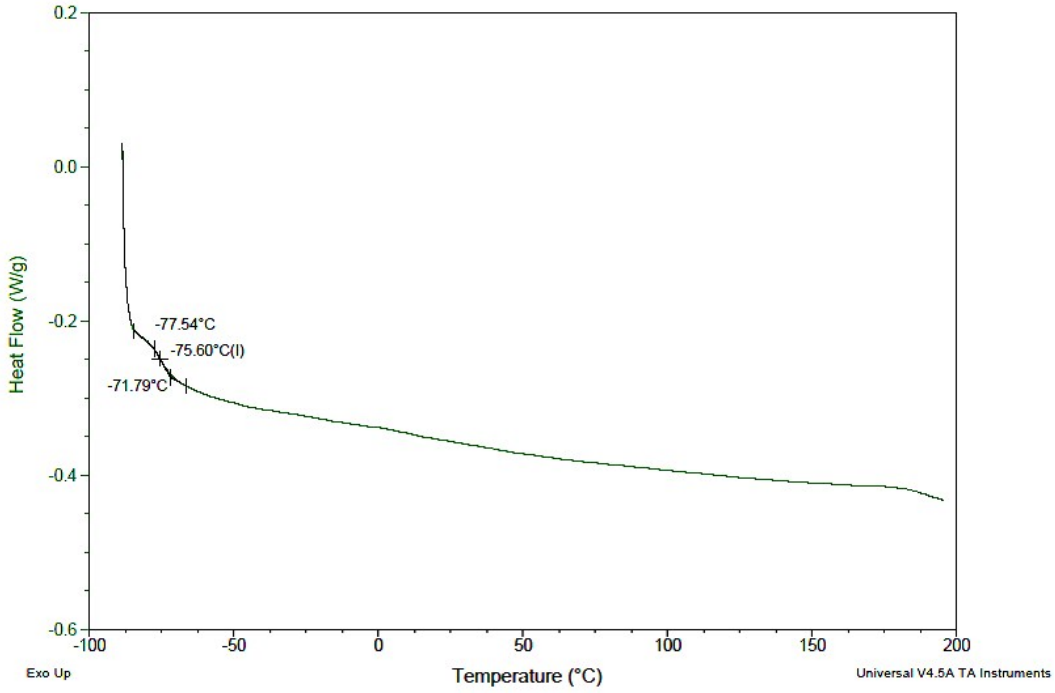

Fig. S5 DSC diagram of resultant elastomer.

DMA

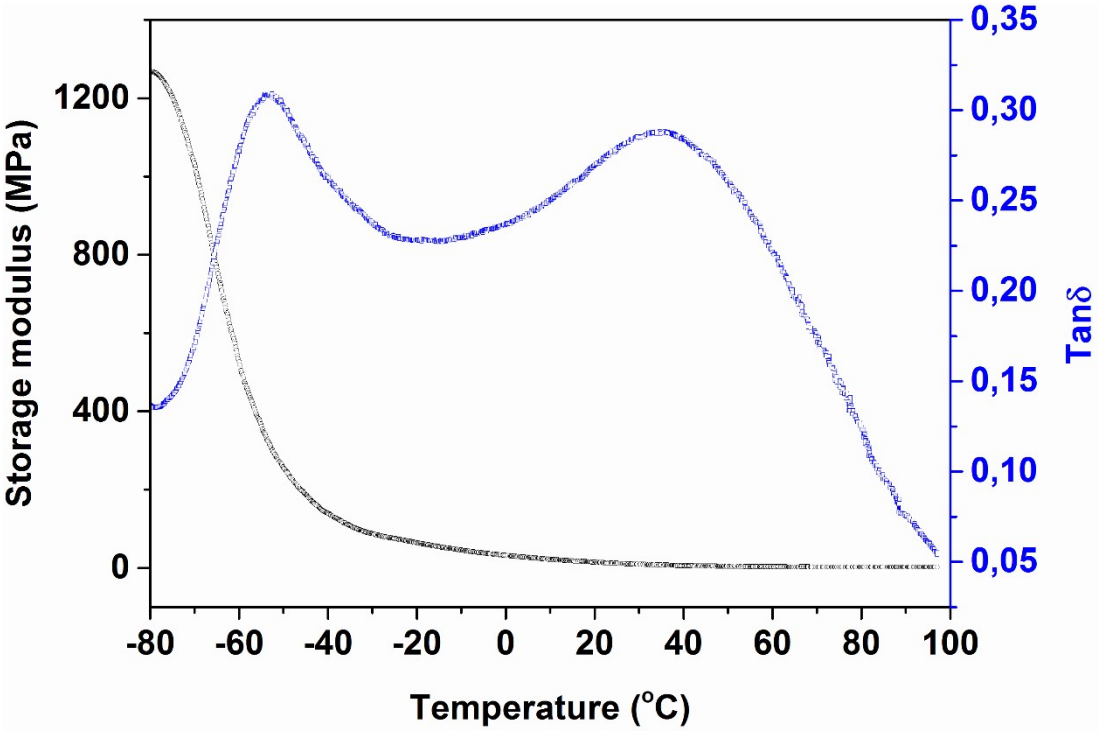

Fig. S6 Storage modulus and tanδ plots of resultant elastomer.