Supplementary Information

Synthesis and characterisation

1. Synthesis and re-processing of SMPU-1s

A group of SMPU-1s were synthesized by varying the chemicals used, and the corresponding chemical re-processibility behaviours were studied. Polytetramethylene glycol (PTMG-2000) (polyether polyol), polybutylene adipate (PBA-U-2000) and polycaprolactone (PCL-2000) (both PBA-U-2000 and PCL-2000 are polyester polyols) were used as the soft segments to form the switching domains in SMPU-1s, while a combination of diisocyanates IPDI and MDI (isophorone diisocyanate and 4,4′-diphenylmethane diisocyanate) were used as the hard segments to synthesize the SMPU-1s. The molar concentrations ratios of MDI/(MDI+IPDI) were at 1, 0.68 and 0 to clarify the effect of diisocyanate type and concentration on the properties, as summarized in Table I.[23] 1,4-butanediol (BDO), being a chain extender, was used as part of the hard segment. PEG-200 was used as part of the hard segment for some SMPU-1s to clarify its role in the polymers and its effect on the SMPU properties. The concentrations were 58 and 42 % for the soft and hard segments respectively. Among the hard segment, the concentration is 4.2 wt% for BDO, and 11.5 wt % for PEG-200 if it was used (Diisocyanate : BDO : PEG = 26.3 : 4.2 : 11.5 % or Diisocyanate : BDO = 37.8 : 4.2 % if PEG-200 not used). Details of the synthesis process, the chemistry can also be found from our recent publication,[23] and sample parameters and test results are summarized in Table 1 (see below).

SMPU-1s have been trialled to react with various solvents including acetone, methanol, IPA and DMF to identify which solvents are suitable for reprocessing these materials. For reprocessing, the physically exhausted, fractured SMPU-1s were granulated or cut into small pieces, and added into various solvents (completely immersed) for reaction at the temperature of 110 °C. These exhausted samples have been used for various thermo-mechanical and cyclic tests until broken, and have been cleaned with IPA in ultrasonic for ~1min, then rinsed with DI water and dried by N_2 gas at room temperature. IPA and methanol were found to have no visible effect on the SMPU-1s after reaction for one hour, while acetone completely destroyed the SMPU-1s tested and no resin was formed. From these experiments, DMF was found to be the most suitable solvent for the designed reprocessible SMPU-1s.

The details of the final reprocessing method developed are as follows: DMF (50~100ml, depending on the amount of SMPU granules used) and SMPU granules were placed in a 250 ml three neck round bottom flask equipped with a mechanical stirrer and a thermometer to monitor the reaction temperature. The set up was immersed in a hot oil bath at 110 °C for reaction. The system was purged with a continuous flow of dry nitrogen during the reaction. The chemicals were allowed to react for one hour until the SMPU granules dissolved in DMF solution completely, forming a SMPU resin, ready for use. For polymerization, the SMPU resins were poured onto a PTFE coated glass mould, and baked at 60 °C for 12 hrs, followed by a further baking at 80 °C for 24 hrs, and then at 100 °C for another 8 hrs, all in a vacuum oven. The polymerization process was the same as those used for polymerising virgin SMPU-1s. The typical film thickness for all the samples was about ~1.0 mm after drying.

2. Characterisation

The following techniques were used to characterize the virgin and the reprocessed SMPU-1s.

(1) The thermal properties were measured using a differential scanning calorimeter (DSC) (Q-200, TA Instruments) purged with nitrogen gas. The specimens were scanned from 20 to 150 °C at a heating rate of 10 °C/minute. The weight of the specimens used for analysis was typically between 10.5–15.0 mg.
(2) Wide-angle X-ray diffraction (WAXD) was used to investigate the crystalline structure of the SMPU-1s with a scanning angle 2θ between 5 to 30° (D8 Discover X-ray diffractometer equipped with Goebel mirror and Cu Kα radiation with a wavelength of 1.542 Å) at 40 keV and 40 mA.
(3) Tensile and shape memory properties including stress-strain, tensile strength, shape recovery and shape fixity were measured using Instron Universal Tester (3369) with a heat chamber. Dumbbell-shaped specimens of 25 mm long and 7 mm width with average thickness about

~1.0 mm were prepared. For shape recovery and shape fixity measurements, the strain for all the samples was fixed at 50 %. The tests were performed with a crosshead speed of 50 mm/min. A typical thermo-mechanical cycle routine as described by Tobushi et al[1] was used to characterize the behaviour of SMPU-1s. To measure the shape recovery ratio (R_r) and shape fixity (R_f), the samples were first extended at 60 °C, a temperature that is higher than the transition temperatures of all the samples. They were then cooled down to room temperature of ~20 °C and heated again above the transition temperatures. R_r and R_f were calculated by eq.(1) and eq.(2).

$$R_r = \frac{\varepsilon_m - \varepsilon_p(n)}{\varepsilon_m - \varepsilon_p(n-1)} x100\% \quad (1)$$

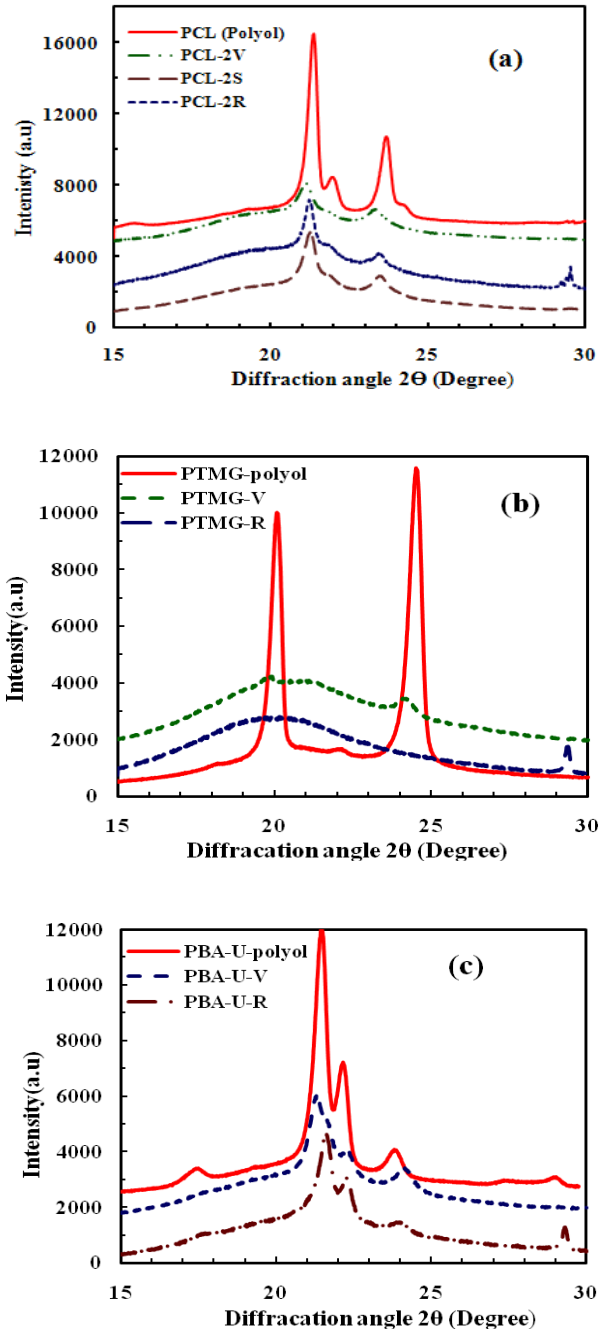
$$R_f = \frac{\varepsilon_u}{\varepsilon_m} x100\% \quad (2)$$

Where ε_m, e_u and ε_p are maximum strain, the relaxed strain at maximum stress and residual stress, n and n-1 refer to the nth and nth–1 cycle for cyclic testing. Three cyclic tests were used for all the samples.

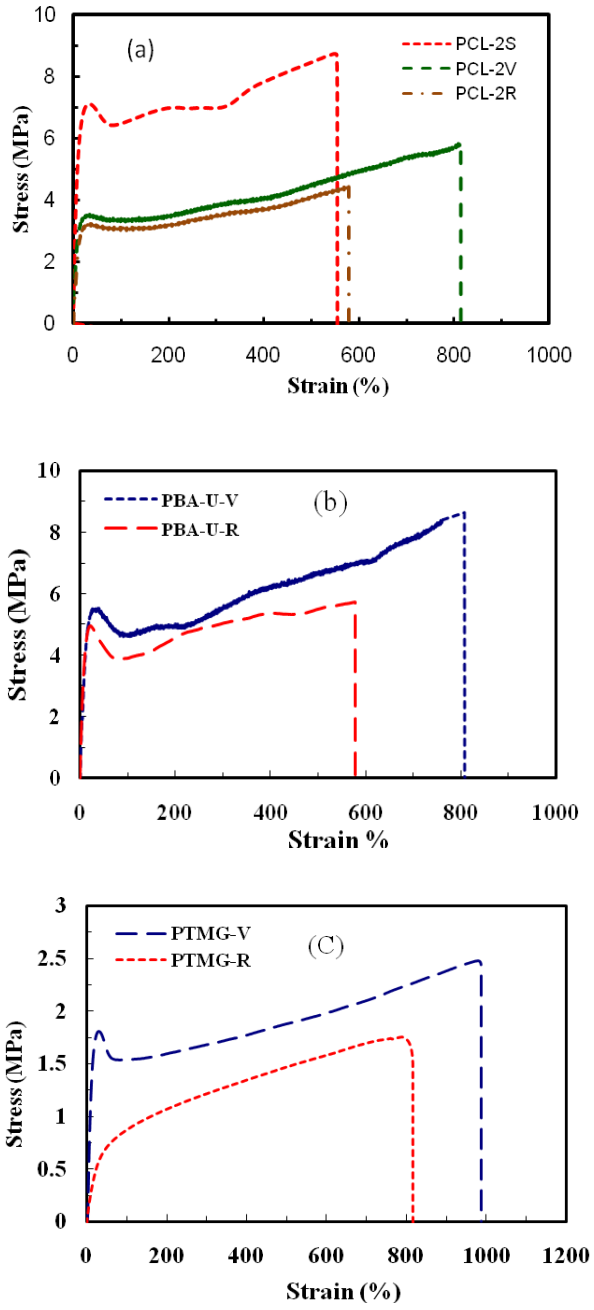
SI Table 1: Summary of the synthetic conditions used for making the polymers.

	MDI/(MDI+IPDI)	PEG-200 Concent	Virgin/ Reproc.	Tm (°C)	ΔH_f (Jg^{-1})	Stress at break (MPa)	Strain at break (MPa)	Solubility in DMF
PCL-polyol	N/A	N/A	N/A	53.03	65.27	N/A	N/A	N/A
PCL-1S	1	**No**	V	43.95	11.10	9.32	755	**No**
PCL-2S	0.68	**No**	V	40.03	13.79	8.45	546	**No**
PCL-3S	0	**No**	V	44.55	17.53	9.75	345	**No**
PCL-1V	1	11.5%	V	43.06	7.68	6.8	945	Yes
PCL-1R	1	11.5%	R	43.5	14	5.9	850	Yes
PCL-2V	0.68	11.5%	V	40.03	13.79	5.64	814	Yes
PCL-2R	0.68	11.5%	R	45.42	23.84	4.32	556	Yes
PCL-3V	0	11.5%	V	41.06	28.47	5.35	~45	Yes
PCL-3R	0	11.5%	R	42.8	25	3.8	~40	Yes
PTMG-2000	N/A	N/A	N/A	25.03	91.94	N/A	N/A	N/A
PTMG-V	0.68	10%	V	15.77	7.27	2.47	985	Yes
PTMG-R	0.68	10%	R	17.66	2.43	1.75	815	Yes
PBA-U-2000	N/A	N/A	N/A	53.77	51.61	N/A	N/A	N/A
PBA-U-V	0.68	10%	V	42.81	18.64	8.55	810	Yes
PBA-U-R	0.68	10%	R	49.36	23.14	5.77	577	Yes

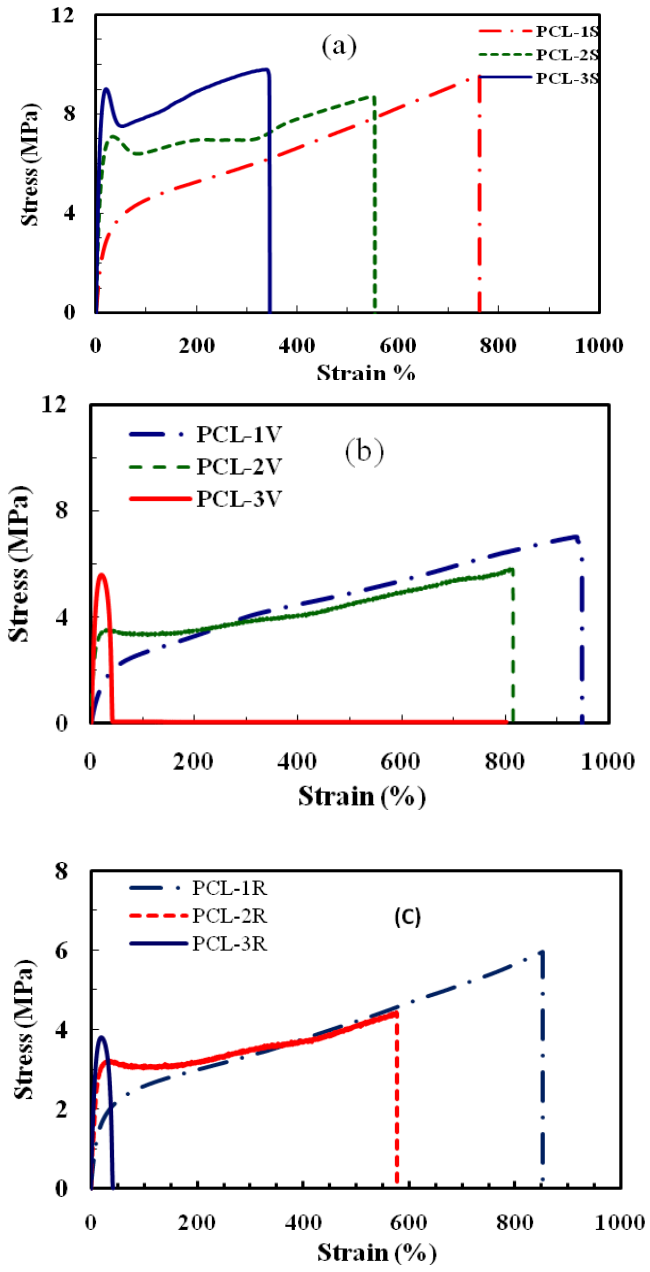
Note: S represents samples without PEG-200, V and R represent virgin and reprocessed SMPU-1s with PEG-200.



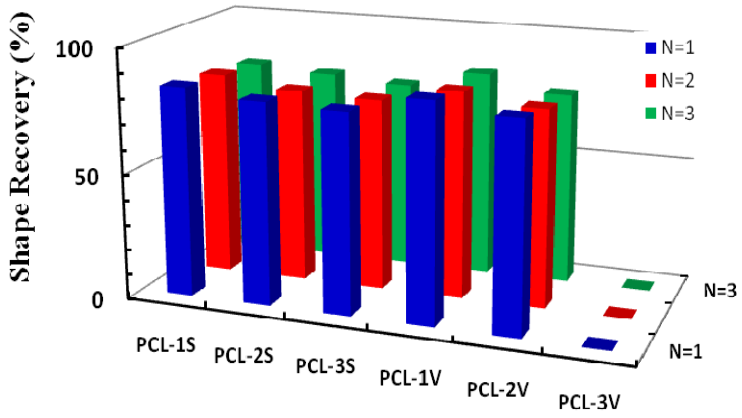
SI Figure 1. Comparison of WAXD curves of virgin and reprocessed SMPU-1s. (a) is for PCL based SMPU-1s, (b) for PTMG-based ones, and (c) for PBA-U-based ones.



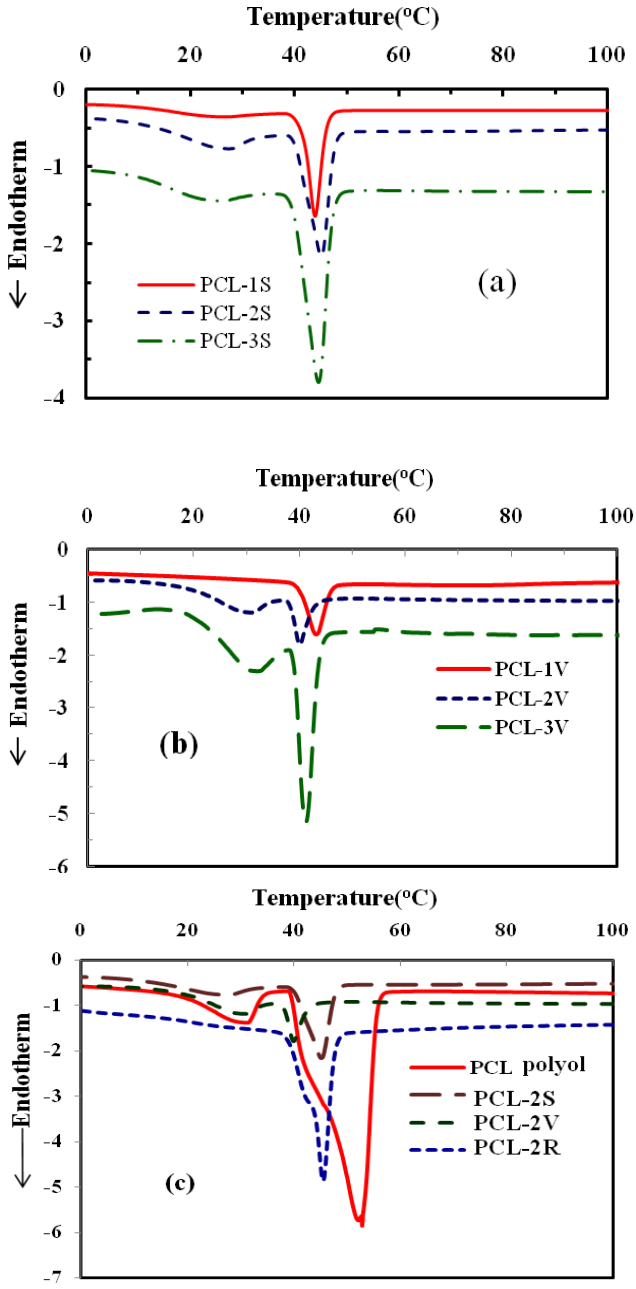
SI Figure 2. Stress vs. strain relationship for (a) PCL-based SMPU-1s, (b) PTMG-based ones, and (c) PBA-U-based ones at ambient temperature. The result of PCL-2S (without PEG-200) is also shown in (a) for comparison. This polymer cannot be reprocessed.



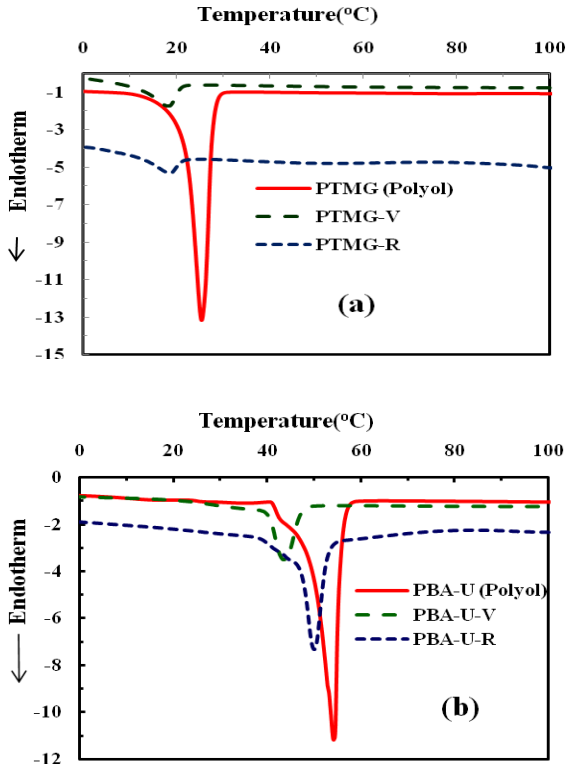
SI Figure 3. Stress vs. strain relationships for PCL-series without (a), and with PEG-200 component (b), and the subsequently reprocessed ones (c), respectively, at the ambient temperature.



SI Figure 4. Shape recovery ratio for SMPUs and SMPU-1s. The samples with similar hard segment molar ratios have similar recovery ratios except for PCL-3V which has 100 % IPDI diisocyanate and does not possess shape memory effect. N (=1, 2, 3) is the number of the cyclic tests.



SI Figure 5. DSC curves of PCL-based SMPUs and SMPU-1s of various soft to hard molar ratios. Please refer to SI Table 1 for details of the synthetic conditions used for each polymer.



SI Figure 6. DSC curves of the virgin and reprocessed (a) PTMG and (b) PBA-based SMPU samples. PTMG-R shows an identical curve to the virgin one, while PBA-U-R shows a curve in between the polyol and the virgin one.