Supporting Information

Upcycling thermosetting polysiloxanes into thermoplastics via UV-induced surface photopolymerization of acrylates

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1. Materials

Methyl methacrylate (MMA, ≥ 99.5 %, CAS: 80-62-6) and 2-hydroxy-2-methylpropiophenone (1173, ≥ 99 %, CAS: 7473-98-5) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Bis[3-(triethoxysilyl) propyl] disulfide (Si75, ≥ 99 %, CAS: 56706-10-6) was obtained from Jiangxi Chenguang New Materials Co., Ltd. Hexamethyldisiloxane (MM, ≥ 99 %, CAS: 107-46-0) and tetraethyl orthosilicate (TEOS, ≥ 99 %, CAS: 78-10-4) were all supplied by Guangzhou Double Peach Fine Chemical Co., Ltd. All chemicals were used as received without further purification.

The opaque silicone waste used in this study was derived from a commercial neutral silicone sealant (Yin Peng Type 793, Guangzhou Xinjia Chemical Technology Co., Ltd.), which consisted of hydroxyl-terminated polydimethylsiloxane (~50 wt%), filler (~30 wt%), plasticizer (~5wt%), crosslinking agent (~5wt%), coupling agent (~1 wt%) and catalyst (~0.5 wt%). The transparent silicone waste was derived from a commercial transparent silicone structural sealant (Guibao Type 995, Chengdu Guibao Science and Technology Co., Ltd.), which consisted of hydroxyl-terminated polydimethylsiloxane (~48 wt%), fumed silica filler (~8 wt%), plasticizer (~6 wt%), crosslinking agent (~7 wt%), coupling agent (~1.5 wt%), catalyst (~0.5 wt%) and anti-yellowing additive (~1 wt%).

2. Preparation methods

2.1 Preparation of disulfide bond-containing thermosetting polysiloxanes

To simulate manufacturing waste resulting from runaway polymerization, a model thermosetting polysiloxanes containing disulfide bond was synthesized by reacting tetraethoxysilane (TEOS), hexamethyldisiloxane (MM), and bis(triethoxysilylpropyl)disulfide (Si-75). The mixture was maintained at 70 °C for 6 h, during which premature gelation occurred to form the targeted disulfide-containing solid waste. Resulting solid was subsequently pulverized into fine powders with a particle size of less than 0.85 mm using a high-speed crusher (BJ-150, Baijie Electrical Appliance Co., Ltd., China) for further grafting procedures.

2.2 Preparation of disulfide bond-containing industrial waste

To evaluate the feasibility for practical industrial applications, commercially available neutral silicone sealants (encompassing both transparent and opaque variants) were employed. Both post-consumer waste, followed by a surface modification with Si-75 at 70 °C for 6 h to introduce disulfide bonds onto the fragment surfaces. Both types of resulting solid materials were subsequently pulverized into fine powders with a particle size of less than 0.85 mm using a high-speed crusher (BJ-150, Baijie Electrical Appliance Co., Ltd., China) for further grafting procedures.

2.3 Surface grafting

UV-induced photopolymerization a measured amount of photoinitiator 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) was thoroughly mixed with the modified powders using a mechanical stirrer (OS20-S, DragonLab, China) according to the formulations in **Table S1**. The mixture was subjected to UV irradiation (MUA-165, MEJIRO Precision Inc., Japan) at an intensity of 10 mW/cm^2 for 5 min to generate sulfur free radicals through disulfide cleavage. Subsequently, methyl methacrylate (MMA) was added and exposed to UV irradiation for a predetermined period under continuous stirring to facilitate surface-initiated grafting (**Table S2**). The product was washed extensively with ethanol to remove unreacted MMA monomers and ungrafted homopolymers.

Table S1 Formula table for different photo initiators and monomer contents.

Samples[*a]	PSI-Si75 [g]	MMA [g]	1173 initiator [%]
PSI-Si75-PMMA-25%-0.5%	5	20	0.5
PSI-Si75-PMMA-25%-1%	5	20	1
PSI-Si75-PMMA-25%-2%	5	20	2
PSI-Si75-PMMA-25%-3%	5	20	3
PSI-Si75-PMMA-16.7%-1%	5	30	1
PSI-Si75-PMMA-16.7%-2%	5	30	2
PSI-Si75-PMMA-16.7%-3%	5	30	3
PSI-Si75-PMMA-14.3%-3%	5	35	1
PSI-Si75-PMMA-14.3%-3%	5	35	2
PSI-Si75-PMMA-14.3%-3%	5	35	3

*(a)The graft polymer synthesized with different ratios of PSI-Si75 and MMA is named PSI-Si75-PMMA-X-Y, where X is the percentage by mass of PSI-Si75 to MMA, and Y is the percentage by mass of initiator to PSI-Si75.

Table S2 Formula table for different UV intensities and UV time.

Samples[*a]	Light intensity [mW/cm^2]	Reaction time [min]
PSI-Si75-PMMA-25%-3%-10mW-5min	10	5

PSI-Si75-PMMA-25%-3%-10mW-10min	10	10
PSI-Si75-PMMA-25%-3%-10mW-15min	10	15
PSI-Si75-PMMA-25%-3%-10mW-20min	10	20
PSI-Si75-PMMA-25%-3%-10mW-25min	10	25
PSI-Si75-PMMA-25%-3%-10mW-30min	10	30
PSI-Si75-PMMA-25%-3%-10mW-40min	10	40
PSI-Si75-PMMA-25%-3%-10mW-60min	10	60
PSI-Si75-PMMA-25%-3%-5mW-5min	5	5
PSI-Si75-PMMA-25%-3%-5mW-10min	5	10
PSI-Si75-PMMA-25%-3%-5mW-15min	5	15
PSI-Si75-PMMA-25%-3%-5mW-20min	5	20
PSI-Si75-PMMA-25%-3%-5mW-25min	5	25
PSI-Si75-PMMA-25%-3%-5mW-30min	5	30
PSI-Si75-PMMA-25%-3%-5mW-40min	5	40
PSI-Si75-PMMA-25%-3%-5mW-60min	5	60
PSI-Si75-PMMA-25%-3%-1mW-5min	1	5
PSI-Si75-PMMA-25%-3%-1mW-10min	1	10
PSI-Si75-PMMA-25%-3%-1mW-15min	1	15
PSI-Si75-PMMA-25%-3%-1mW-20min	1	20
PSI-Si75-PMMA-25%-3%-1mW-25min	1	25
PSI-Si75-PMMA-25%-3%-1mW-30min	1	30
PSI-Si75-PMMA-25%-3%-1mW-40min	1	40
PSI-Si75-PMMA-25%-3%-1mW-60min	1	60

*(a)The reaction of PSI-Si75-PMMA under different light intensities and reaction times is named PSI-Si75-PMMA-25% -3% - N-M, where N represents the corresponding light intensity and M represents the reaction time.

2.3 Hot-pressing recovery process

The samples were dried in an oven at 60 °C for 1 h until a consistent white powder was obtained. Finally, the dried powder was placed in a precision mold and subjected to thermal consolidation using a hot-pressing machine (BD230413, Dongguan Baoding Precision Instruments Co., Ltd., China) (**Table S3**).

Table S3 Formula table for different hot-pressing temperatures and time.

Samples*a	Hot-pressing temperature [°C]	Hot-pressing time[min]
PSI-Si75-PMMA-25%-10%-140-20	140	20
PSI-Si75-PMMA-25%-10%-160-20	160	20
PSI-Si75-PMMA-25%-10%-180-20	180	20
PSI-Si75-PMMA-25%-10%-160-30	160	30
PSI-Si75-PMMA-25%-10%-160-60	160	60
PSI-Si75-PMMA-25%-5%-160-20	160	20
PSI-Si75-PMMA-25%-10%-160-20	160	20
PSI-Si75-PMMA-25%-15%-160-20	160	20
PSI-Si75-PMMA-16.7%-15%-160-20	160	20
PSI-Si75-PMMA-14.3%-15%-160-20	160	20

*(a) PSI-Si75-PMMA prepared at different hot-pressing temperatures and times named PSI-Si75-PMMA-X-Y-L-Z. X and Y have been introduced, where L is the hot-pressing temperature and Z is the hot-pressing time.

3. Characterization methods

Molecular weights were determined by gel permeation chromatography (GPC) on a Waters 1515 instrument (Waters Corporation, USA). For MMA copolymers, dimethylformamide (DMF) was used. Polystyrene standards were used for calibration. Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet iS50 spectrometer (Thermo Fisher Scientific, USA) using the attenuated total reflection (ATR) technique or solution-flowed film method. Scans were performed from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans per sample. Raman spectra were obtained using a LabRAM HR Evolution Micro Confocal Raman Spectrometer (HORIBA Scientific, France) with a 785 nm excitation laser (100% energy), a scanning time of 60 s, and 50× magnification. Scanning Electron Microscopy (SEM) images of the fractured surfaces were acquired using a Hitachi SU8010 microscope (Hitachi Ltd., Japan). Samples were gold-sputtered prior to observation. Thermogravimetric Analysis (TGA) was performed on a TGA/SDTA851e analyzer (METTLER-Toledo, Switzerland). Samples (10–15 mg) were heated from 30 to 800 °C at a rate of 10 °C /min under a nitrogen flow of 20 mL/min. Tensile properties were evaluated according to ASTM D412 using dumbbell-shaped specimens (total length: 50 mm; parallel width: 4 mm). Tests were conducted on a universal testing machine (STD500, Guangdong Lugong Precision Instruments Co., Ltd., China) at a crosshead speed of 10 mm/min at room temperature. Five replicates were tested for each condition.

Grafting kinetics were studied by monitoring the mass change over time under varying UV intensities. Three samples were tested per condition, and the average value was recorded. The grafting rate was calculated as follows:

$$\text{Grafting Rate (\%)} = \frac{m_t - m_p}{m_t} \times 100$$

where m_t is the mass of the final product and m_p is the mass of the Si75-modified silicone rubber.

4. Results

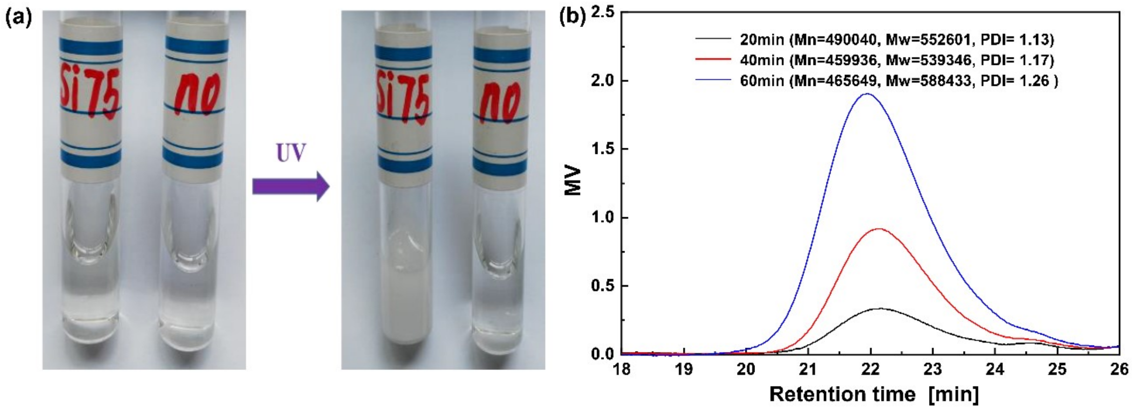

Figure S1 (a) Mixtures of methyl methacrylate (MMA) with or without 3 wt% Si-75 before and after UV irradiation within 30 min. (b) GPC curves of the MMA mixture with Si75 after UV polymerization as a function of reaction time.

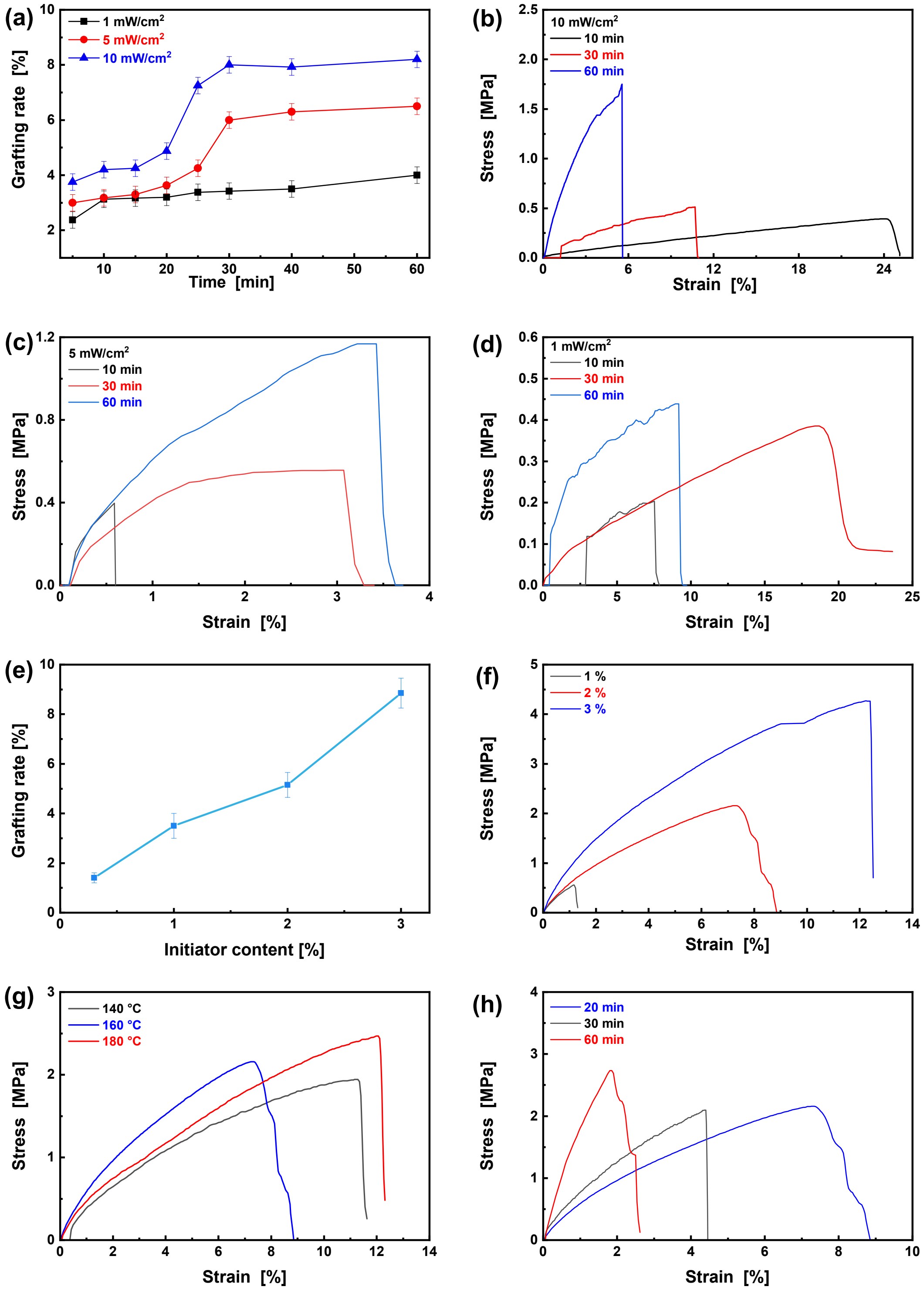

Figure S2 Characterization of recycled polysiloxanes under various conditions. (a) Grafting efficiency and (b-d) evolution of mechanical properties as a function of UV irradiation parameters; effects of photoinitiator dosage on both (e) grafting rates and (f) mechanical strength; optimization of (g) hot-pressing temperature and (h) duration.

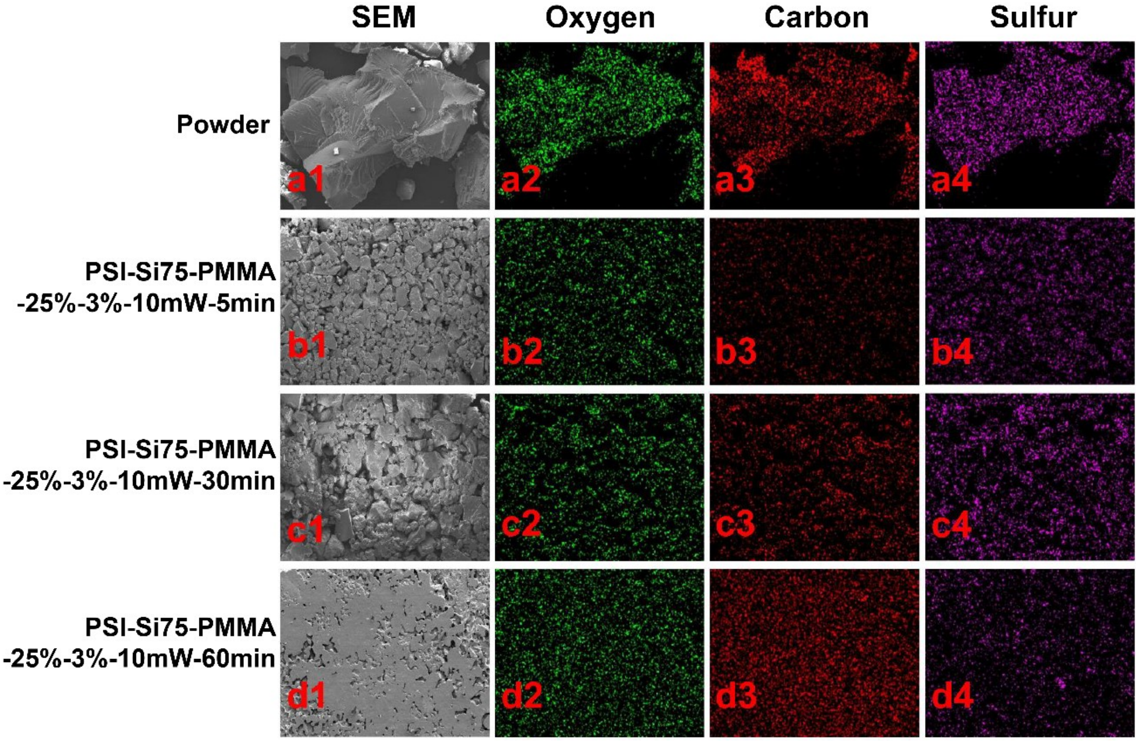

Figure S3 (a1–d1) SEM images, (a2–d2) oxygen content, (a3–d3) carbon content, and (a4–d4) sulfur content of PSI-Si75-PMMA powder and sheets with different grafting durations.

Figure S4 Recovery process of opaque silicone waste.

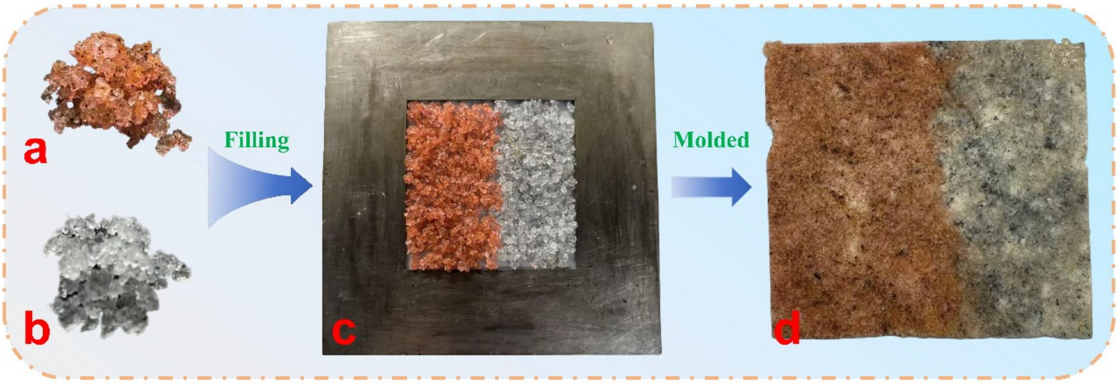

Figure S5 Fabrication of recycled thermoplastic sheet from pigmented wastes. (a, b) Images of red and light blue PSI-Si75-PMMA powders; (c) distribution of powders in the mold, and (d) the resulting consolidated sheet after hot-pressing.