

Supporting information

A stable amphiphilic hybrid nanoparticle compatibilizer constructed from polyhedral oligomeric silsesquioxane (POSS) for the immiscible thermoplastic polyurethane/methyl vinyl silicone elastomer (TPU/MVQ) blends

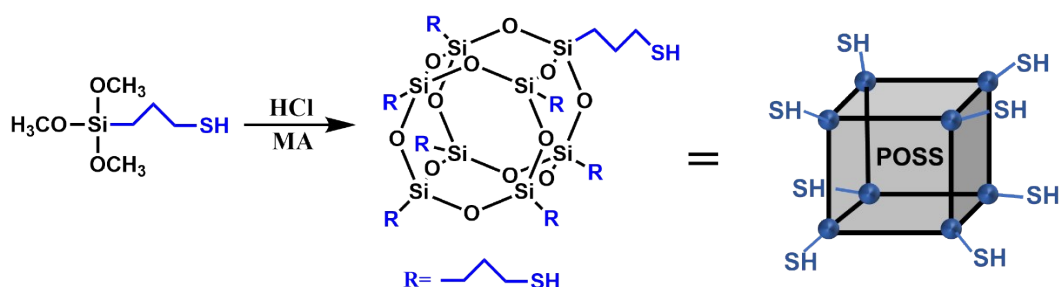
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Preparation of octa-mercaptopropyl polyhedral oligomeric silsesquioxane (POSS-SH) particles



Scheme S1 Synthesis route of POSS-SH.

POSS-SH was prepared by acid-catalyzed hydrolysis in the following synthesis steps: TPS (9.8 g, 0.05 mol) was dissolved in 400 mL of methanol and concentrated hydrochloric acid (30 mL) was added dropwise under stirring, and the mixture was refluxed at 90°C for 24 h.

After the reaction, the mixture was cooled to room temperature and white viscous liquid was precipitated. Then an appropriate amount of dichloromethane was added to dissolve the crude product, followed by the addition of methanol as a poor solvent to allow the product to precipitate. After equilibration for 2 h, the mixture was separated to obtain white viscous liquid. It was then dried in a vacuum oven at 60°C for 8 h to remove residual solvents, and finally the final product POSS-SH was obtained.

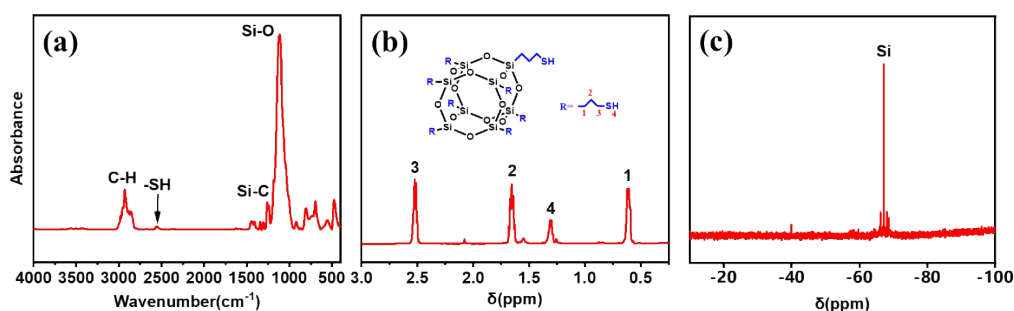


Figure S1 (a) FTIR spectrum of POSS-SH; (b) ¹H NMR spectrum of POSS-SH, with

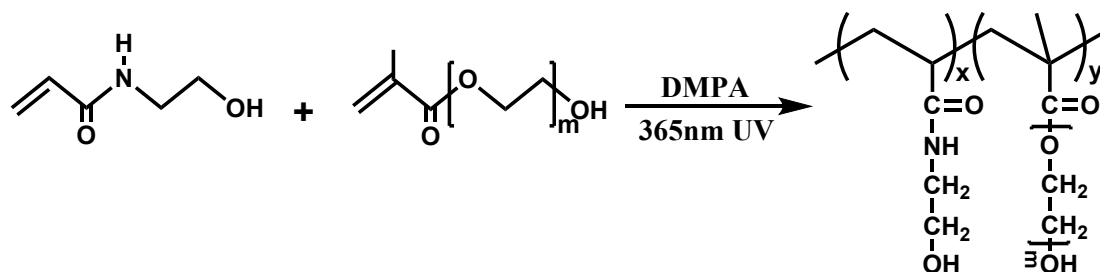
CDCl_3 as the solvent; (c) ^{29}Si NMR spectrum of POSS-SH.

In the FTIR spectrum (Figure S1(a)) of POSS-SH, the peak at 2550 cm^{-1} was attributed to the stretching vibration peak of S-H in thiol group, the peak at 1260 cm^{-1} , 1110 cm^{-1} , 2930 cm^{-1} belonged to the stretching vibration of Si-C, Si-O, C-H, respectively.

The ^1H NMR spectrum of POSS-SH was shown in Figure S1(b), the signals at 1 ($\delta=0.62\text{ ppm}$), 2 ($\delta=1.65\text{ ppm}$), 3 ($\delta=2.53\text{ ppm}$) were assigned to methylene protons on mercaptopropyl, which have an integration area ratio of 1:1:1. The signal at 4 ($\delta=1.31\text{ ppm}$) was attributed to the protons on thiol groups.

As shown in the ^{29}Si NMR spectrum of POSS-SH (Figure S1(c)), only a signal at -67.15 ppm indicating that TPS was fully hydrolyzed. According to the FTIR, ^1H NMR, and ^{29}Si NMR results, POSS-SH was successfully synthesized.

Preparation of poly (ethylene glycol) methacrylate and N-hydroxyethyl acrylamide copolymer [P(PEGMAA-r-NHEMAA)] with different segment ratios



Scheme S2 Synthesis route of P(PEGMAA-r-NHEMAA).

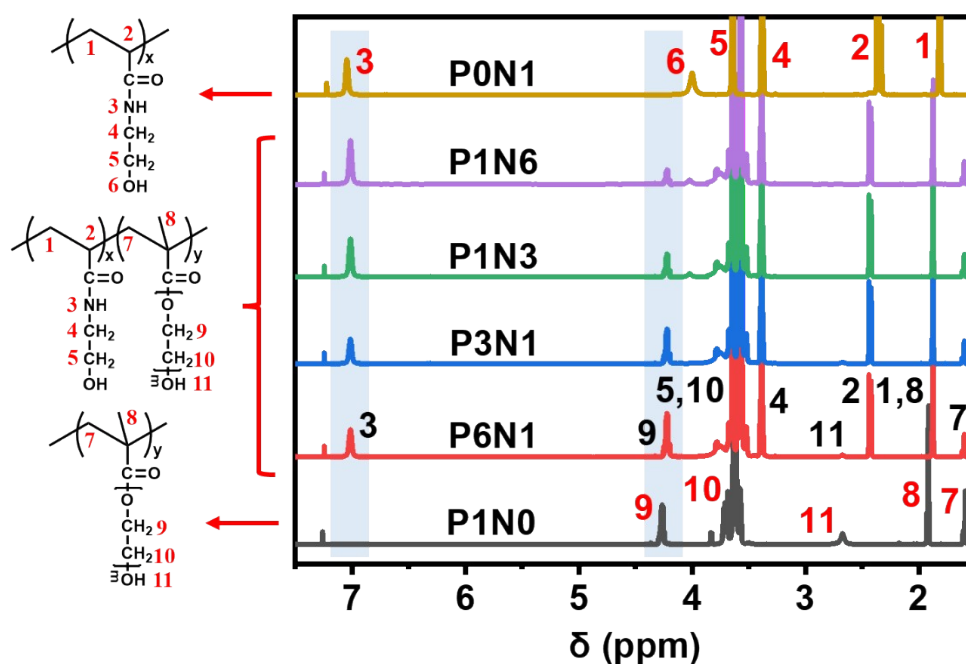


Figure S2 ^1H NMR spectra of P(PEGMAA-r-NHMAA) with different segment ratios, with CDCl_3 as the solvent.

As shown in Figure S2, the incorporation ratio of PEGMAA to NHMAA in the resulting copolymers (PUA) is verified by ^1H NMR, and compared with the theoretical feeding ratios. The actual structural unit ratio between PEGMAA and NHMAA can be calculated based on the integration peak area ratio of the protons (#9, $\delta=4.27\text{ppm}$) in $-\text{CH}_2\text{-O-CO-}$ of PEGMAA and the proton (#3, $\delta=7.10\text{ppm}$) in N-H of NHMAA. As shown in Table S1, there is a small difference between the experimental values and that in feeding, which may be related to the different reactivity ratios of these two monomers. However, the copolymerization reaction of PEGMAA and NHMAA is generally controllable.

The GPC data of resulting copolymers are used to evaluate the chain length and polydispersity of PUA chains, as shown in Table S1. However, it should be noted that

¹H NMR and GPC data cannot be regarded as the actual molecular weight and structural unit ratio of the polymer chains grafted from POSS particles, which can only be regarded as references.

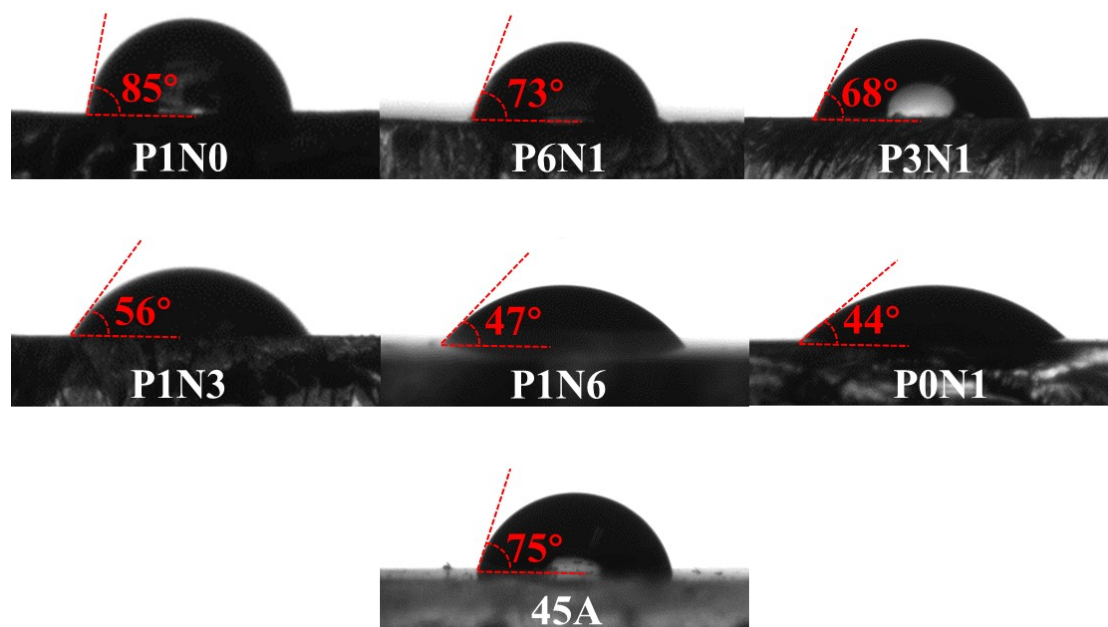


Figure S3 The contact angle of the P(PEGMAA-r-NHMAA) with different segment ratios and TPU (45A).

Table S1 The feeding ratio, ¹H NMR, GPC and contact angle data of P(PEGMAA-r-NHMAA) with different segment ratios. The actual structural unit ratio is obtained from the ¹H NMR integral area ratio.

Sample	Theoretical PEGMAA: NHMAA (mol/mol)	¹ H NMR PEGMAA: NHMAA (mol/mol)	M _n (×10 ³ g/mol)	PDI	Contact angle (°)
P1N0	1:0	1:0	19.07	1.56	85
P6N1	6:1	5.7:1	4.64	1.97	73
P3N1	3:1	2.8:1	3.41	1.54	68
P1N3	1:3	1:3.4	2.24	1.39	56
P1N6	1:6	1:6.5	1.60	1:73	47
P0N1	0:1	0:1	1.37	1.16	44
45A	/	/	/	/	75

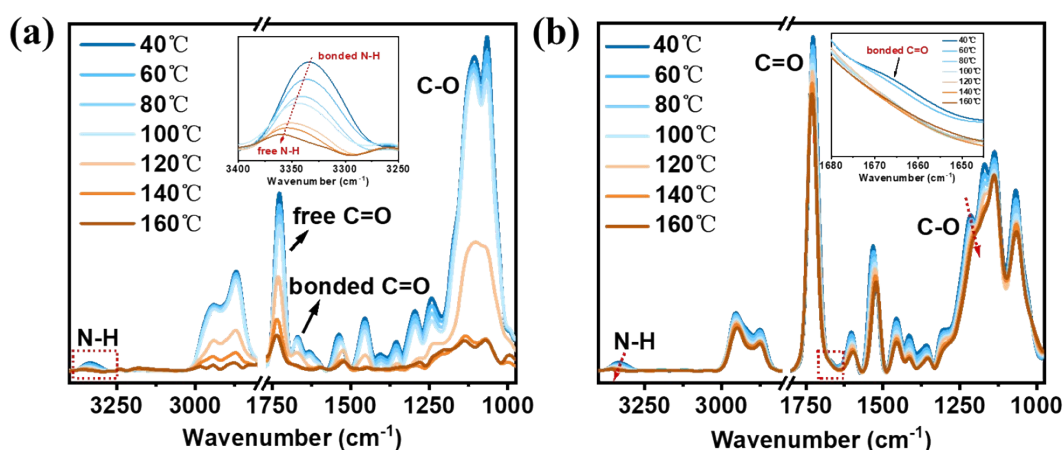
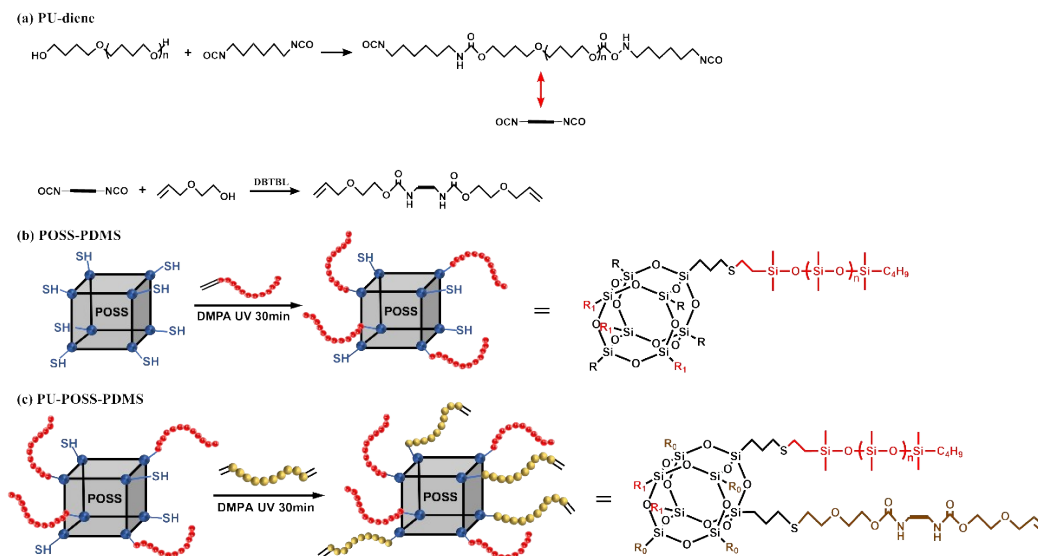


Figure S4 In-Situ FTIR spectrum at variable temperature of (a) P(PEGMAA-r-NHMAA)/TPU blends; (b) TPU.

As shown in Figure S4, a wide band at 3334 cm^{-1} is assigned to the stretching vibration of hydrogen bonded N-H, while the free N-H stretching vibration absorption appears on the high-frequency side of this band, with a wavenumber of 3360 cm^{-1} . The band at 1725 cm^{-1} is assigned to the free C=O stretch, while that at 1670 cm^{-1} is assigned to the hydrogen bonded C=O stretch. The hydrogen bonded N-H peak absorbance decreases at high temperature with a corresponding increase of the free N-H peak absorbance, and the maximum absorption wavenumber of the hydrogen bonded N-H band also shifts from 3334 to 3360 cm^{-1} with the increasing of the temperature from 40 to $160\text{ }^{\circ}\text{C}$. Similarly, the bonded C=O in the blends will be dissociated as the temperature increases, resulting in an increase in the intensity of free C=O, as observed in the Figure S4 (a). As shown in Figure S4 (b), the peak absorbances of the free and bonded N-H and C=O stretching bands of the TPU exhibit similar trends, but the ratio of bonded C=O at 1670 cm^{-1} is relatively less. Compared with pure TPU, the absorption of hydrogen bonding shifts in the blend, indicating that there is a hydrogen bonding

interaction between PUA chains and TPU phases.

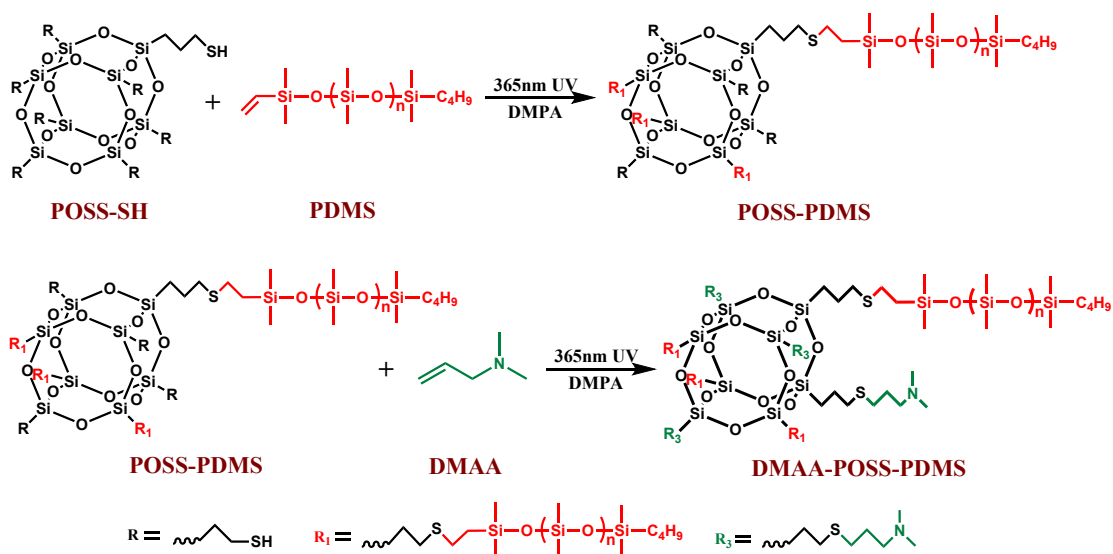
The expected preparation routes of PU-POSS-PDMS particles



Scheme S3 Synthesis routes of PU-POSS-PDMS.

As shown in Scheme S3, PU chains were grafted to POSS through the synthesized bifunctional PU chains, the -SH of POSS reacted easily with the double bonds in PU chains, and the multifunctional POSS-SH as cross-linker made PU form the cross-linking networks during the reaction in Scheme S3. Therefore, the method of grafting PU analogue chains was designed according to Scheme S5.

Preparation of modified POSS particles with small molecules of N, N-dimethylacrylamide on the surface (DMAA-POSS-PDMS) particles



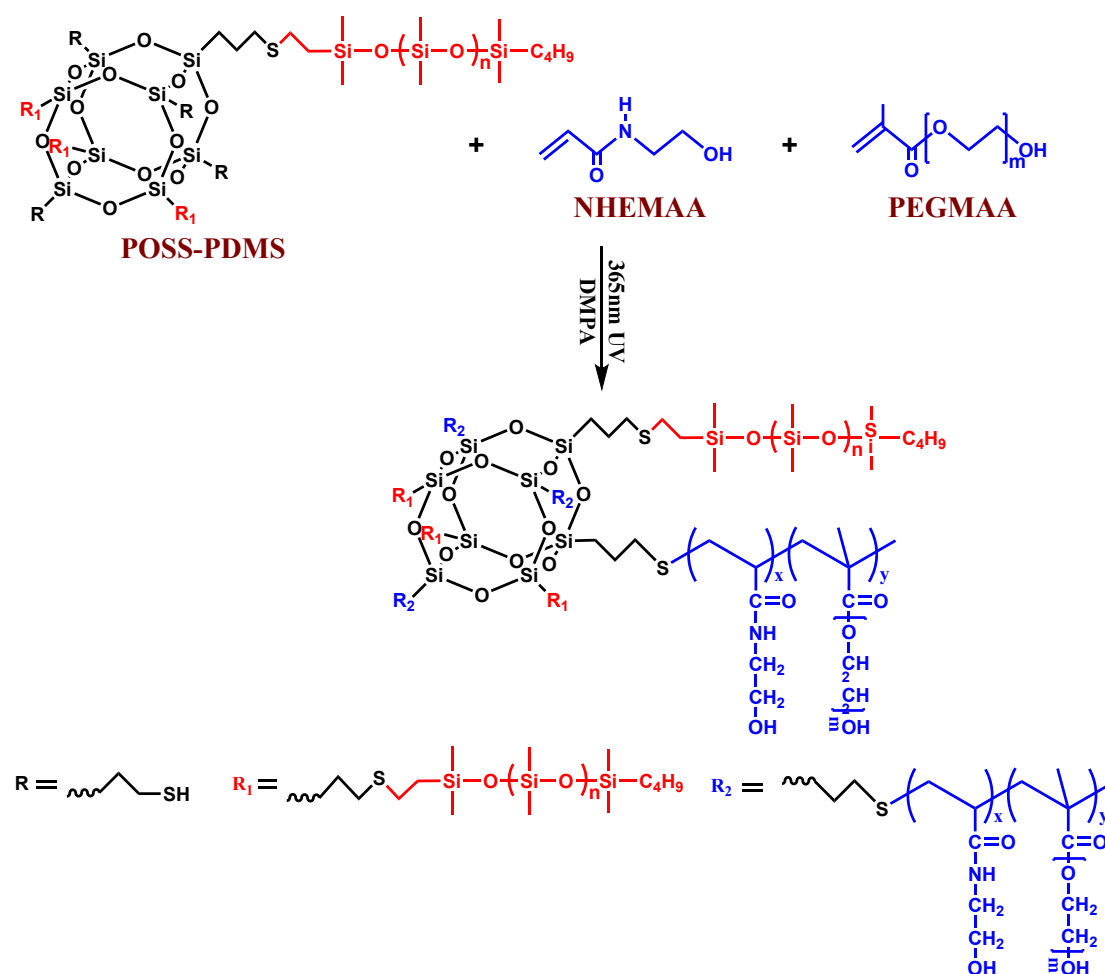
Scheme S4 Synthesis routes of DMAA-POSS-PDMS.

(1) The intermediate product POSS-PDMS was obtained by grafting PDMS chains onto the POSS-SH through a thiol-ene click reaction, as shown in Scheme S3(a). POSS-SH (1.016 g, 0.001 mol) was dissolved in 125 mL of THF in a conical flask, A-PDMS (24 g, 0.004 mol) and DMPA (0.24 g, 1 wt% of A-PDMS, photo-initiator) were successively added, then the mixture was stirred while being exposed to 365 nm UV irradiation for 30 min. Once the reaction was complete, the THF solvent was removed by rotary evaporation at 50°C. The resulting product was then dried in a vacuum oven at 60°C for 8 h to obtain the POSS-PDMS.

(2) Then, a portion of DMAA was grafted onto the POSS-PDMS through the thiol-ene click reaction between the remaining thiol groups on POSS-PDMS and C=C in DMAA, as shown in Scheme S3(b). The POSS-PDMS was dissolved in 125 mL of THF in a conical flask and DMAA (0.341 g, 0.004 mol) and DMPA (0.24 g) were added. The mixture was stirred using a magnetic stirrer until complete dissolution. Subsequently, the mixture was irradiated on 365 nm UV for 30 min. The THF solvent

was removed by rotary evaporation at 50°C, and the product was dialyzed against water in a dialysis bag (MWCQ=7000) for 3 d, and the solvent water was changed every 6-8 h to remove unreacted DMAA. The product was dried in a vacuum oven at 60°C for 8 h to obtain the functional group modified DMAA-POSS-PDMS compatibilizer.

Preparation of PUA-POSS-PDMS particles



Scheme S5 Synthesis route of PUA-POSS-PDMS.

(1) The preparation of intermediate product POSS-PDMS was the same as the synthesis process of DMAA-POSS-PDMS.

(2) Then, a portion of the polymer chain synthesized by copolymerization of PEGMAA

and NHEMAA was grafted from the remaining thiol groups of POSS-PDMS through the photoinduced radical polymerization reaction, as shown in Scheme S4. The POSS-PDMS was dissolved in 125 mL of THF in a conical flask and PEGMAA (14.76 g, 0.041 mol), NHEMAA (0.806 g, 0.007 mol), and DMPA (0.24 g) were added. The subsequent synthesis steps were similar to the synthesis of DMAA-POSS-PDMS.

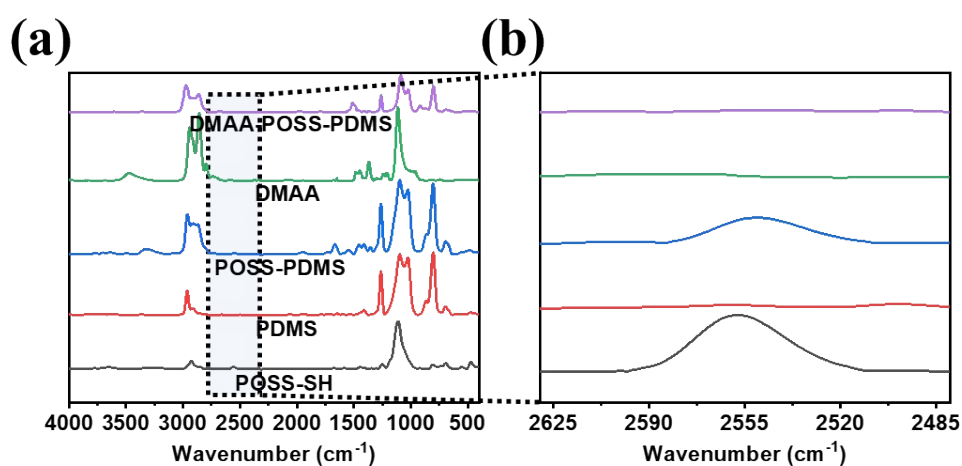


Figure S5 (a) FTIR spectra of raw materials and the product DMAA-POSS-PDMS; (b) The enlarged FTIR spectra of 2630 cm⁻¹-2480 cm⁻¹.

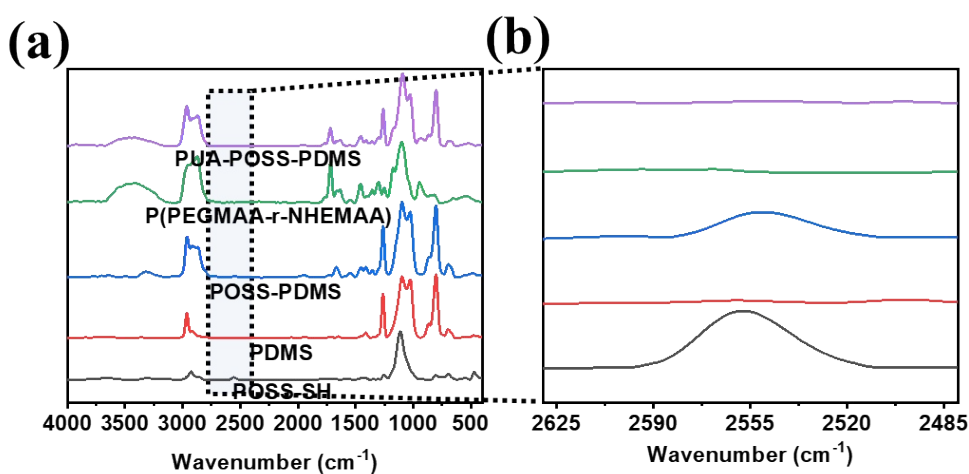


Figure S6 (a) FTIR spectra of raw materials and the product PUA-POSS-PDMS; (b) The enlarged FTIR spectra of 2630 cm⁻¹-2480 cm⁻¹.

The FTIR spectra of DMAA-POSS-PDMS and PUA-POSS-PDMS were shown

in Figures S5 and S6. The absorption peaks observed at 3450 cm^{-1} , 2975 cm^{-1} , 2560 cm^{-1} , 1645 cm^{-1} , and 1100 cm^{-1} were attributed to the O-H stretching vibration of -OH groups on PEGMAA and NHEMAA, the C-H stretching vibration on $-\text{CH}_3$, the S-H stretching vibration on the periphery of POSS, the C=C double bonds stretching vibration, and the stretching vibration of Si-O-Si bonds in POSS and PDMS, respectively. After grafting the periphery of POSS with PDMS, the S-H stretching vibration peak on the POSS surface at 2560 cm^{-1} became weaker (Figure S4b), and a new peak appeared at 2975 cm^{-1} , which was attributed to the C-H stretching vibration of $-\text{CH}_3$ on PDMS, indicating that the -SH groups on the POSS particles have reacted with the C=C bonds in PDMS. Upon grafting DMAA or P(PEGMAA-r-NHEMAA), the S-H stretching vibration peak at 2560 cm^{-1} disappeared, indicating that the remaining -SH groups on the POSS surface have also reacted completely. All these FTIR results confirmed the successful synthesis of DMAA-POSS-PDMS and PUA-POSS-PDMS.

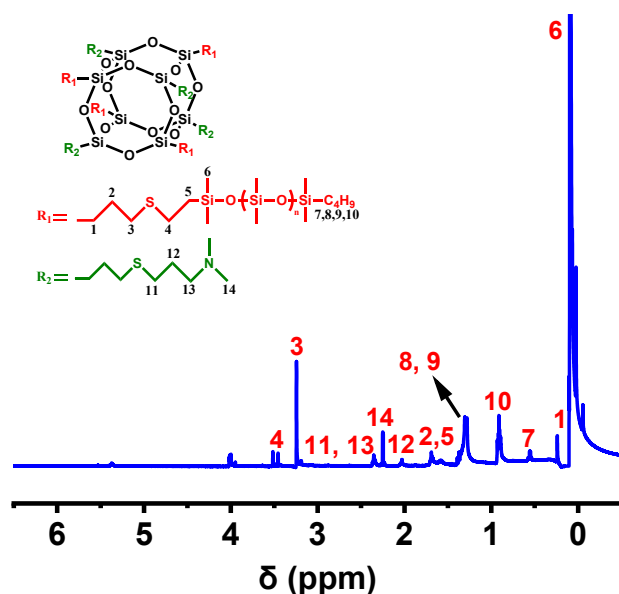


Figure S7 ^1H NMR spectrum of DMAA-POSS-PDMS, with CDCl_3 as the solvent.

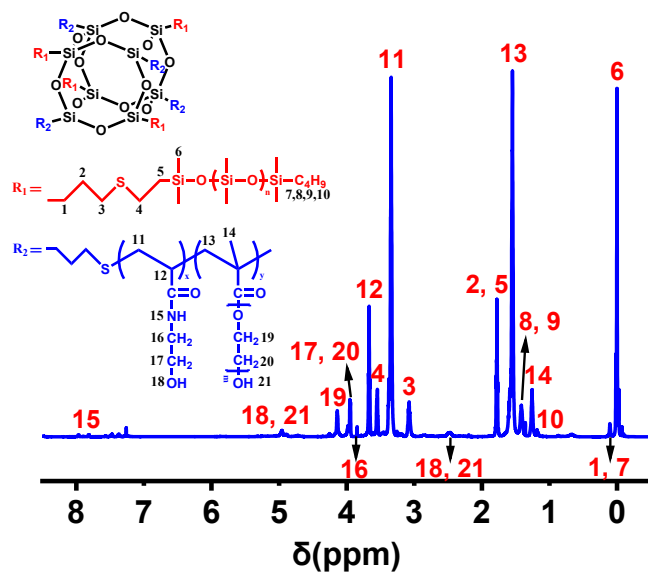


Figure S8 ^1H NMR spectrum of PUA-POSS-PDMS, with CDCl_3 as the solvent.

The ^1H NMR spectrum of the products DMAA-POSS-PDMS and PUA-POSS-PDMS were shown in Figures S7 and S8. The proton signals on the $\text{C}=\text{C}$ with a chemical shift between 5.0 ppm and 6.1 ppm disappeared and the proton signals of DMAA or P(PEGMAA-*r*-NHEMAA) appeared, indicating the successful grafting and polymerization reactions.

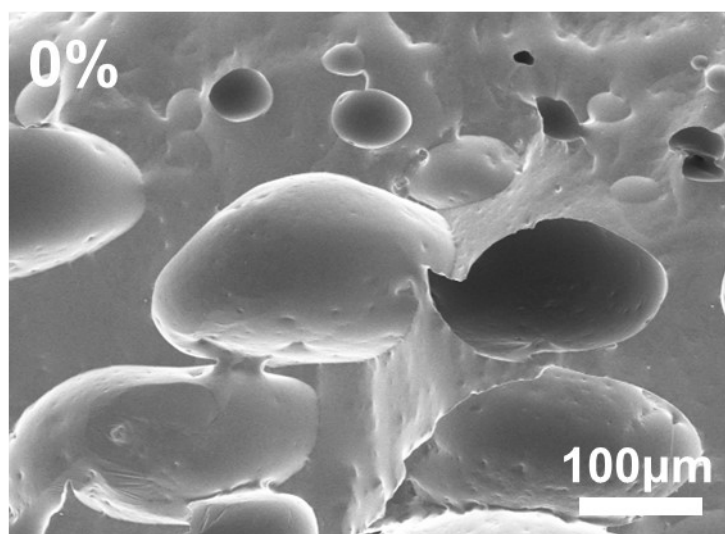


Figure S9 The SEM micrograph obtained for blending of TPU/MVQ without any compatibilizers.

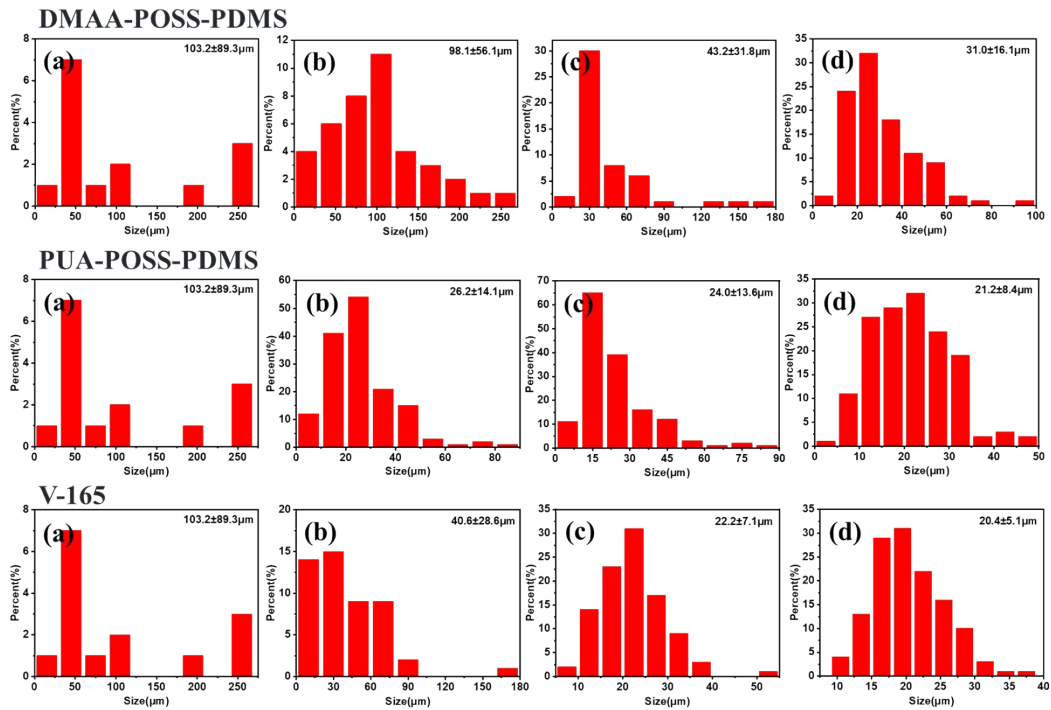
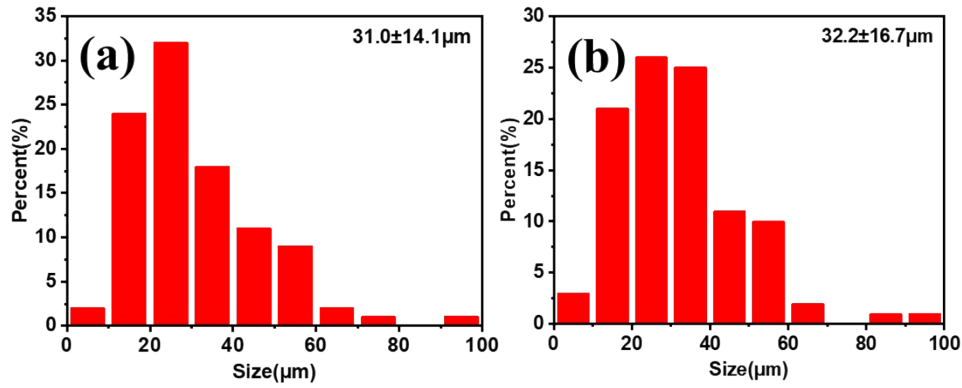
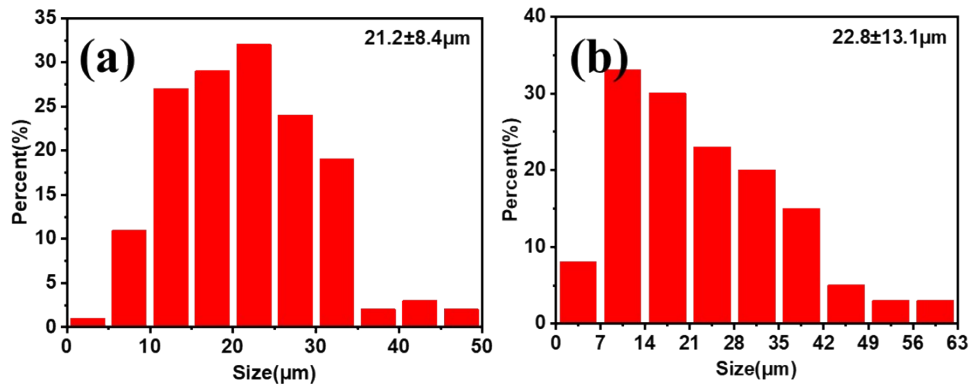


Figure S10 The MVQ phase size distribution of TPU/MVQ blends compatibilized by the compatibilizers of different content: (a), (b), (c), and (d) represent the addition amount of compatibilizers is 0 wt%, 1 wt%, 5 wt%, and 10 wt%, respectively. The blends were obtained by solution blending.

DMAA-POSS-PDMS



PUA-POSS-PDMS



V-165

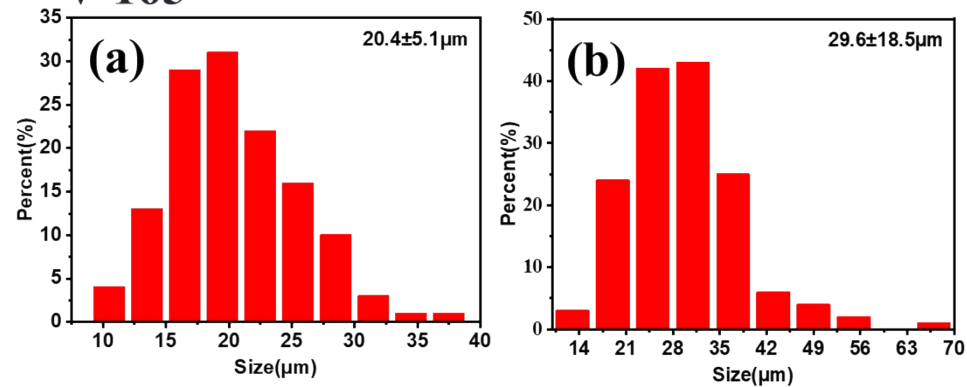


Figure S11 The MVQ phase size distribution of TPU/MVQ blends compatibilized by the compatibilizers with an additive content of 10 wt%: (a) and (b) represent before and after annealing at 180 °C for 6 h, respectively. The blends were obtained by solution blending.

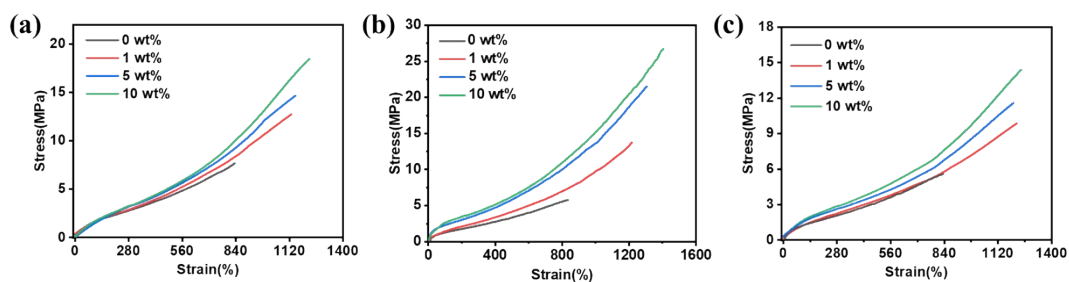


Figure S12 The stress-strain curves of TPU/MVQ blends compatibilized by different compatibilizers: (a) DMAA-POSS-PDMS; (b) PUA-POSS-PDMS; (c) V-165.

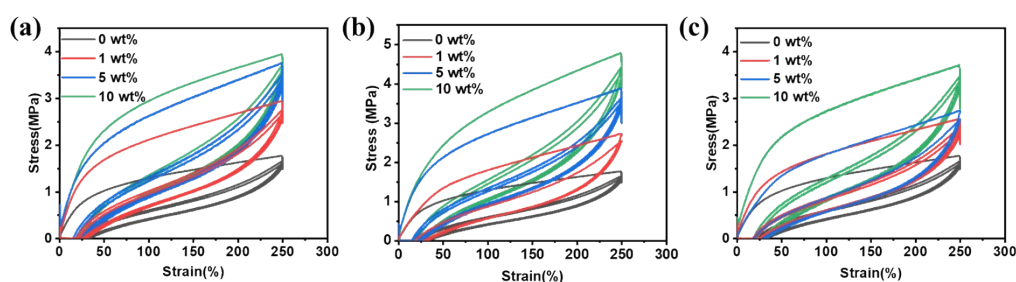


Figure S13 The tensile recovery curves of TPU/MVQ blends compatibilized by different compatibilizers: (a) DMAA-POSS-PDMS; (b) PUA-POSS-PDMS; (c) V-

165.

Table S2 The mechanical properties of TPU/MVQ blends compatibilized by different compatibilizers.

Compatibilizer	Content of compatibilizer (wt%)	Tensile strength (MPa)	Elongation at break (%)	Permanent deformation (%)
/	0	5.8±1.6	834±46	15.4
DMAA-POSS-PDMS	1	12.7±1.3	1130±38	12.9
	5	14.6±1.0	1151±35	12.1
	10	18.5±1.2	1225±30	11.3
	1	13.7±1.2	1218±33	13.8
PUA-POSS-PDMS	5	21.5±1.1	1306±26	11.1
	10	26.7±0.7	1405±22	10.9
	1	9.9±1.4	1215±37	13.5
V-165	5	11.6±1.5	1200±35	13.9

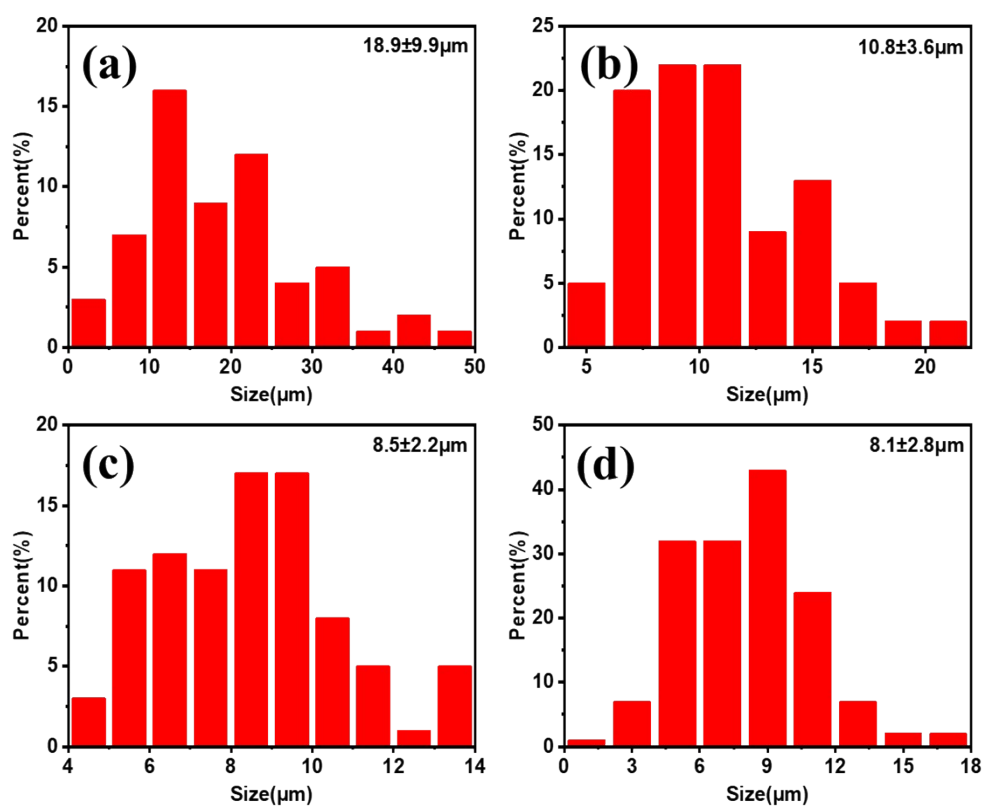


Figure S14 The MVQ phase size distribution of TPU/MVQ blends compatibilized by PUA-POSS-PDMS: (a), (b), (c), and (d) represent the addition amount of compatibilizers is 0 wt%, 1 wt%, 5 wt%, and 10 wt%, respectively. The blends were obtained by melting blending.