Tuning Mechanical Properties of Biobased Polymers by Supramolecular Chain Entanglement

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SUPPORTING INFORMATION

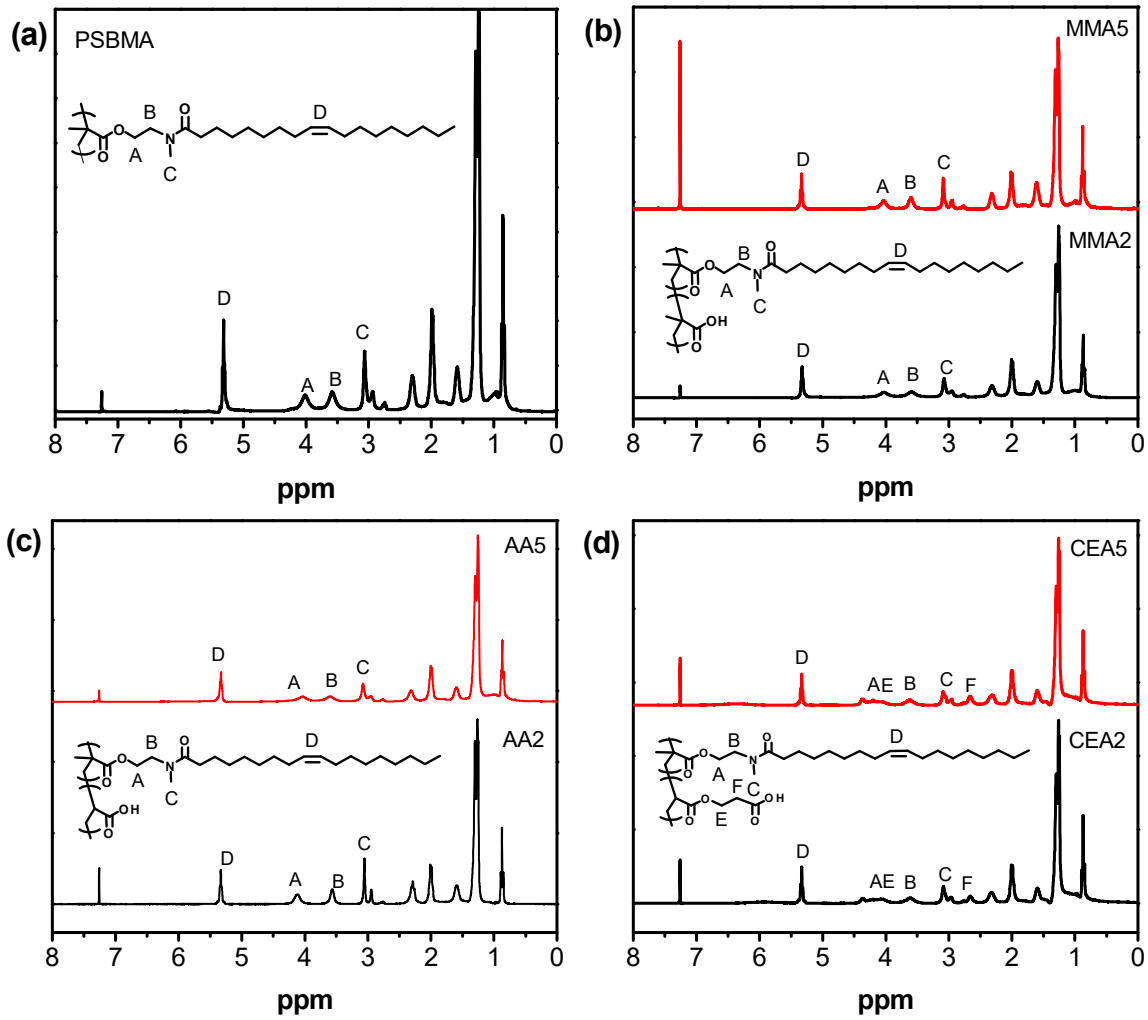


Figure S1. ^{1}H NMR spectra of homopolymer and P(SBMA-*co*-AA) copolymers: (a) homopolymer **PSBMA**, (b) copolymers **MAA2** and **MAA5**, (c) copolymers **AA2** and **AA5**, (d) copolymers **CEA2** and **CEA5**.

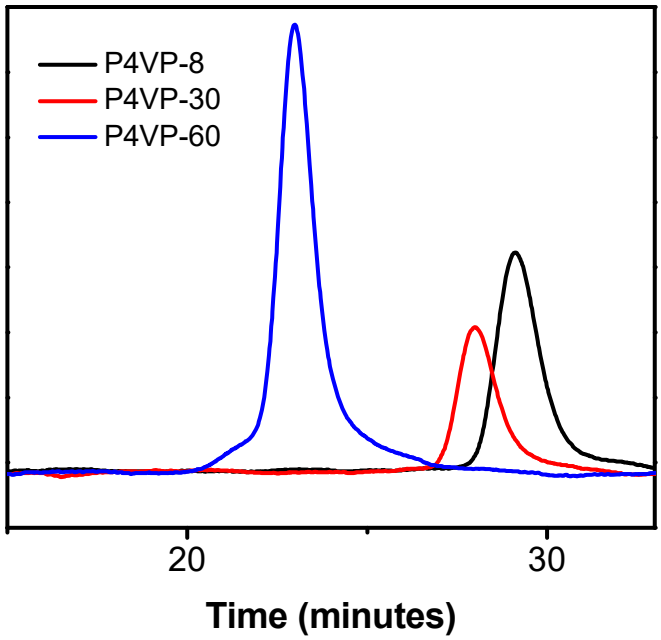


Figure S2. Gel permeation chromatography traces of P4VP homopolymers (**P4VP-8**, **P4VP-30**, and **P4VP-60**).

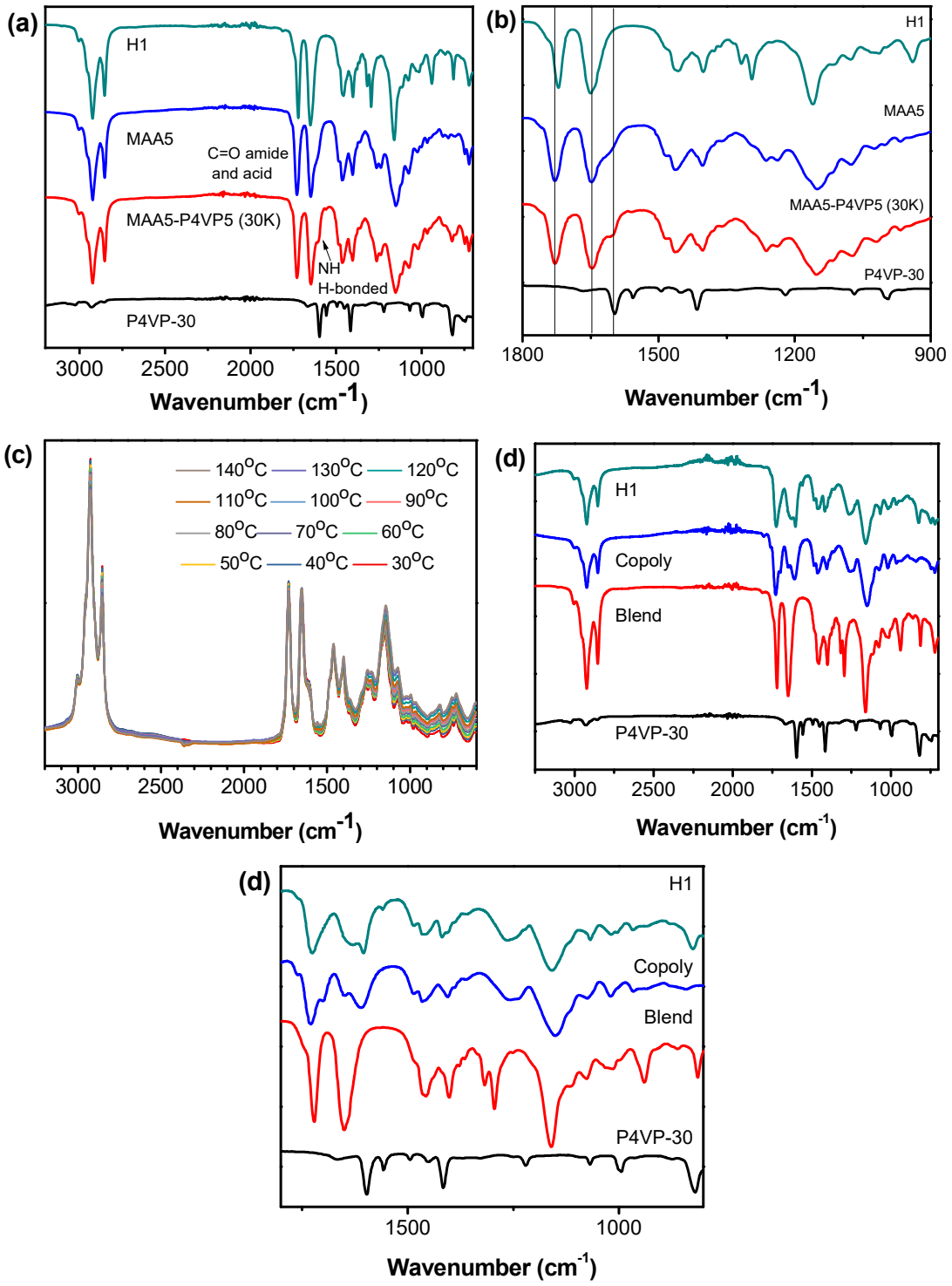
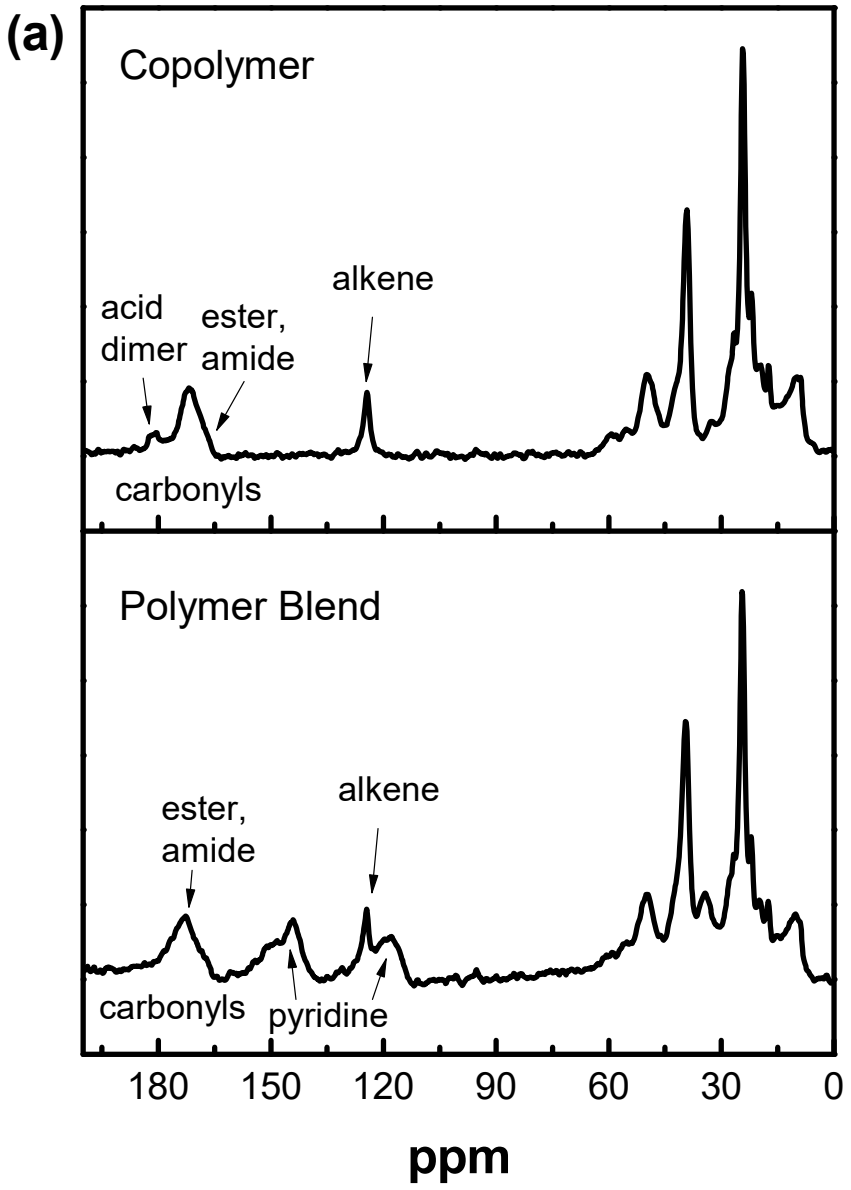


Figure S3. (a) Complete FTIR spectra comparing homopolymers (**PSBMA** and **P4VP-30**), copolymer (**MAA5**), and polymer blend (**MAA5-P4VP5 (30K)**). (b) Zoom-In of FTIR spectra from 1800-800 cm^{-1}. (c) Variable temperature FTIR of polymer blend

MAA5-P4VP5 (60K). (d) Complete FTIR spectra comparing homopolymers (**PSBMA** and **P4VP-30**), copolymer (featuring 1:1 mole ratio of SBMA: MAA) and polymer blend (featuring 1:1:1 mole ratio of SBMA: MAA: 4VP). (e) Zoom-In of FTIR spectra from 1800-800 cm^{-1}.



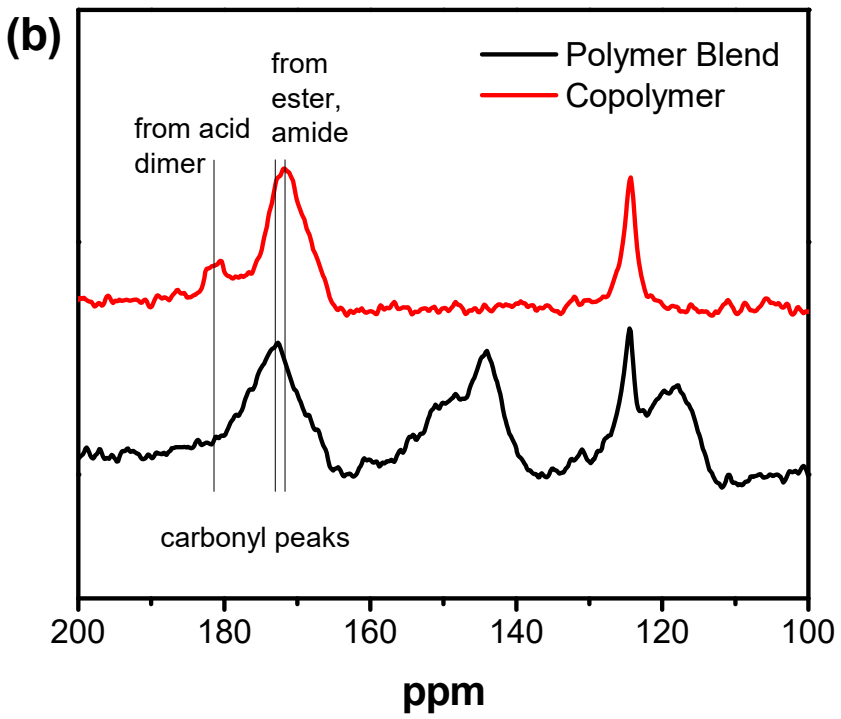


Figure S4. (a) ^{13}C solid-state NMR spectra of P(SBMA-*co*-AA) copolymer (1:1 molar ratio of SBMA: MAA) and polymer blend (1:1:1 molar ratio of SBMA: MAA: 4VP); (b) magnified spectra from 100-200 ppm.

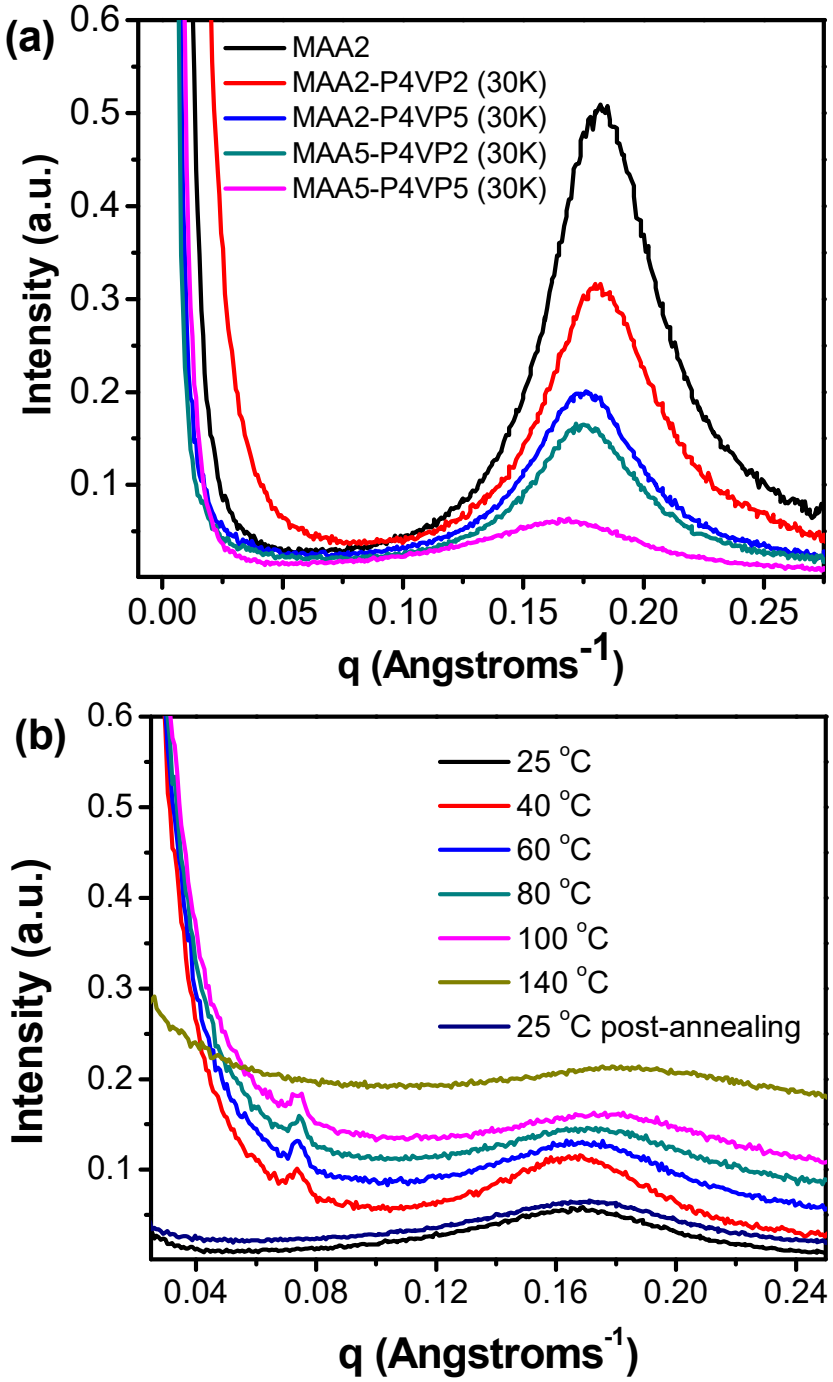


Figure S5. SAXS profiles of (a) copolymer (**MAA2**) and polymer blends containing P4VP and P(SBMA-*co*-MAA) copolymers at 25°C; (b) polymer blend **MAA5-P4VP5 (60K)** at various temperature.

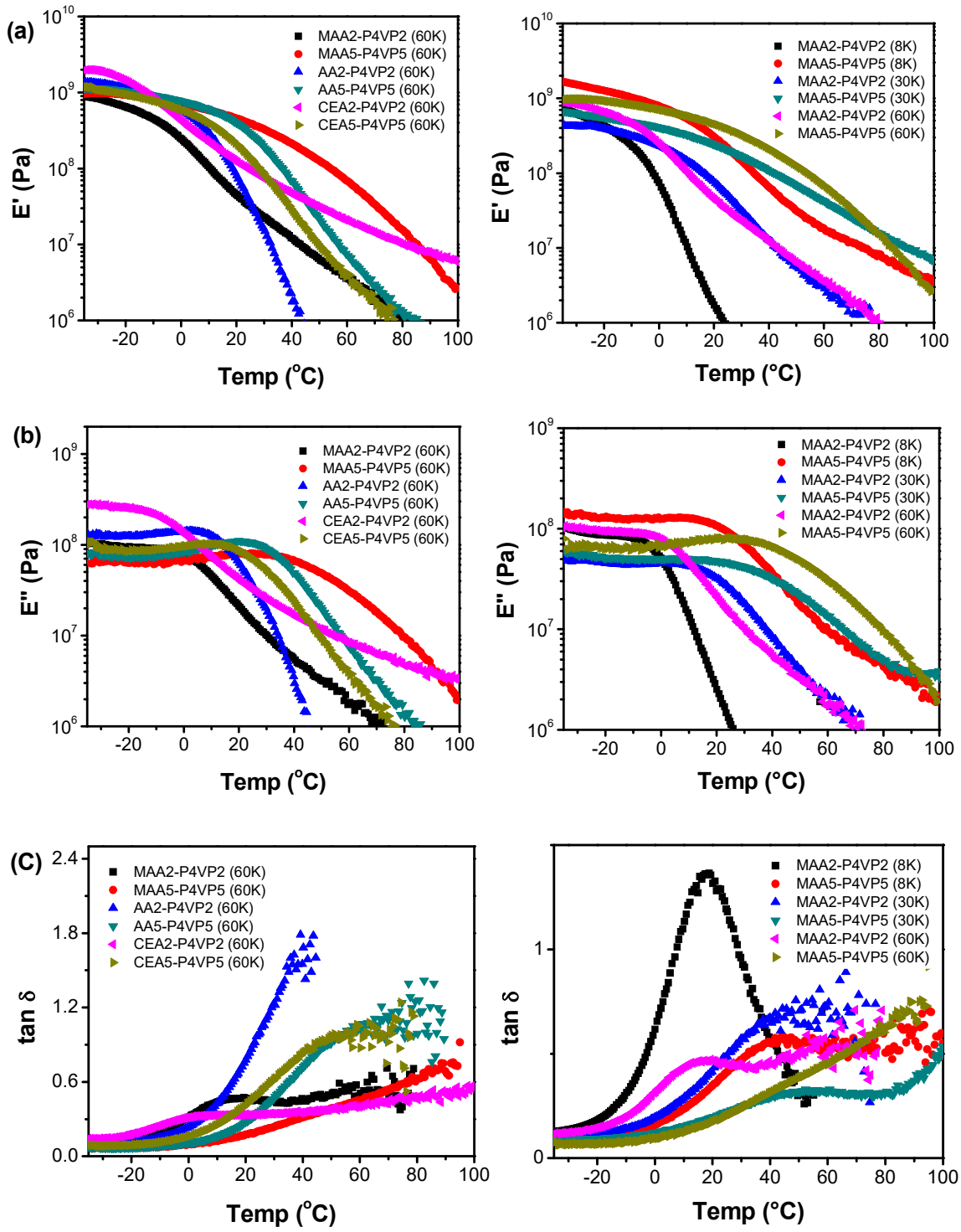


Figure S6. DMA curves of polymer blends with various compositions of copolymers and P4VP: (a) storage modulus; (b) loss modulus; (c) tan delta.

Table S1. Weight and molar fractions of all components in polymer blends containing P4VP and SBMA copolymer (**MAA2**, **MAA5**, **AA2**, **AA5**, **CEA2**, and **CEA5**).

Sample code (wt% in Number)	Weight Fraction (wt %) [a]			Molar Fraction (mol %) [a]		
	Acid	4VP	SBMA	Acid	4VP	SBMA
MAA2-P4VP2[b]	2	2	96	7.2	6.8	86.0
MAA2-P4VP5[b]	2	5	93	7.7	15.7	76.6
MAA5-P4VP2[b]	5	2	93	16.6	7.6	75.8
MAA5-P4VP5[b]	5	5	90	15.1	14.3	70.6
AA2-P4VP2 (60K)	2	2	96	7.8	6.7	85.5
AA2-P4VP5 (60K)	2	5	93	8.1	16.3	75.6
AA5-P4VP2 (60K)	5	2	93	17.1	8.0	74.9
AA5-P4VP5 (60K)	5	5	90	15.9	15.1	69.0
CEA2-P4VP2 (60K)	2	2	96	6.8	7.0	86.2
CEA2-P4VP5 (60K)	2	5	93	7.2	15.4	77.4
CEA5-P4VP2 (60K)	5	2	93	16.5	7.0	76.5
CEA5-P4VP5 (60K)	5	5	90	14.1	14.9	71.0

[a]Weight and molar fractions of MAA and CEA were calculated via ^{1}H NMR. [b]Fractions are the same for these blends, regardless of the molecular weight of P4VP.

Thermal Properties. All polymer blends and copolymers showed excellent thermal stability. The degradation temperature was similar to previously reported soybean homopolymers, T_d >300 ºC at ~5% weight loss (**Figure S7**). According to the derivative TGA curves, there were two maximum degradation temperatures for the polymer blends, seen around 360-380 and 420 ºC. Alternatively, the copolymer samples only had one maximum degradation temperature around 370 ºC. The second degradation observed in the polymer blends is consistent with the degradation of P4VP, indicating that at these extreme temperatures, our blends become immiscible.

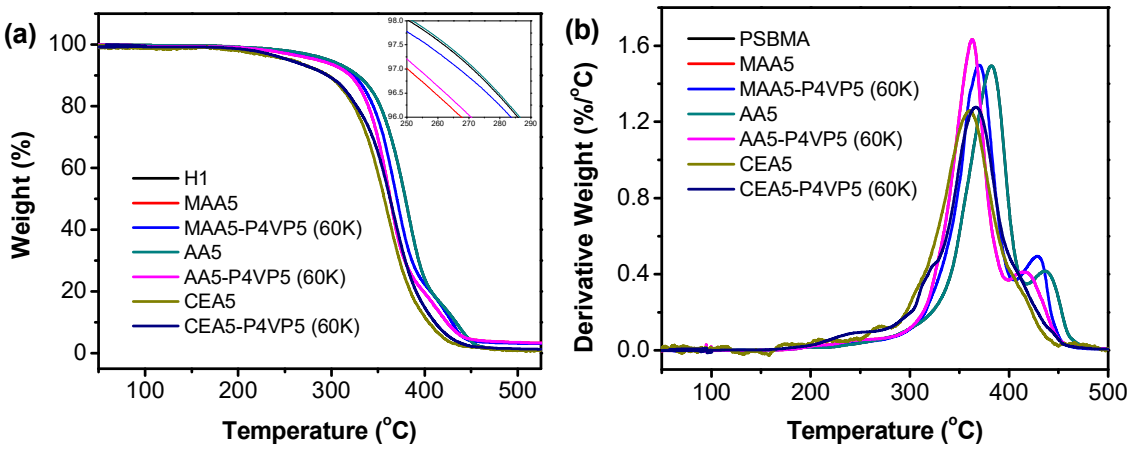


Figure S7. TGA curves of **PSBMA**, **MAA5**, **MAA5-P4VP5 (60K)**, **AA5**, **AA5-P4VP5 (60K)**, **CEA5**, and **CEA5-P4VP5 (60K)**. All polymers and polymer blends showed similar degradation behaviors.

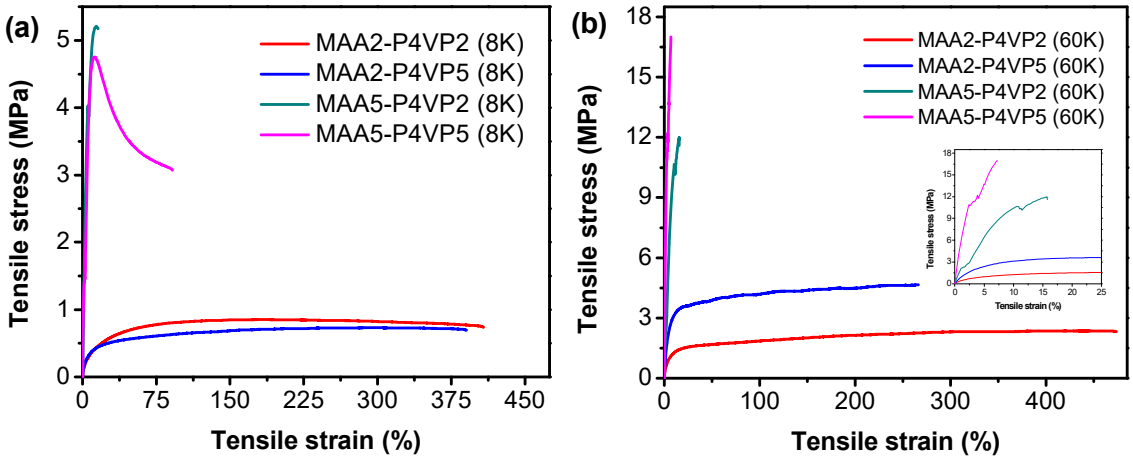


Figure S8. Stress-strain curves of polymer blends using P(SBMA-*co*-MAA) (**MAA2** and **MAA5**): (a) blended with **P4VP-8** and (b) blended with **P4VP-60**.