Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Liquid amphiphilic polymer for effective airborne dust suppression

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Materials and Methods

Materials. Liquid poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) (PEO-PPO-PEO) triblock copolymer (Pluronic® L62 LF, BASF, NJ, USA), solid PEO-PPO-PEO (Pluronic® F-127, part # P305, Anatrace Products, OH, USA), liquid polyethylene glycol (PEG 200, catalog # B21918, Alfa Aesar, MA, USA) and liquid polypropylene glycol (P400, catalog # 81350, Sigma Aldrich, USA) were used in this research. Pluronic® L62 and F-127 are also known as poloxamer 182 and 407, respectively.[1,2]

Airborne dust sampling. Mine tailings, byproducts from mining processes, were obtained from a tailings storage facility (TSF) at a local copper mining company (Arizona, USA) and dried in an electric oven at 50 ^{o}C overnight to remove residual water. Then, the mineral particles were sieved with 140 US standard mesh (<106 μm) to obtain a reproducible airborne dust model.

Lab-scale air-blowing test. Polymer aqueous solutions were prepared by dissolving PEO-PPO-PEO, PEG and PPG liquid polymers, as well as solid PEO-PPO-PEO polymer, in deionized (DI) water at 1, 3, 5 and 7 v/v % or w/v %. Sample beds were prepared by measuring 30 g of mineral particles on an aluminum dish (Al dish smooth, catalog # 08732104, Fisher Scientific, MA, USA), pouring 15 mL of 1-7 v/v % or w/v % polymer aqueous solutions on top of the mineral particles and drying the samples in an electric oven at 50 ^{o}C for a week. Sample beds were placed on the lab-scale air-blowing closed chamber (dimensions: L x W x H = 25 x 22 x 12 cm) equipped with regulated compressed air and a laser dust sensor (SDS-021, Nova Fitness, China) with data acquisition using a Raspberry Pi (Raspberry Pi 3 Model B, Vilros, NJ, USA). To cause a significant disturbance, the strong wind was blown perpendicularly to the sample bed. Compressed air at 20 psi generated 20 m/s of wind, approximately twice as strong as the highest recorded wind speed (12 m/s) over the last decade at the field site, on the surface of the sample bed, measured by an anemometer (Fisherbrand™ Traceable™, catalog # 15078196, Fisher Scientific, MA, USA). After applying 20 m/s wind to the sample bed for 5 s, PM10 and PM2.5 concentrations were monitored and recorded every second. Using maximum values collected from three air-blowing tests, the average PM concentrations with standard deviations were calculated.

Pilot-scale field test. The pilot-scale field test was performed at an inactive TSF of a local mining company (Sahuarita, AZ, USA). Testing beds were prepared by installing wood frames (dimensions: L x W x H = 60 x 60 x 10 cm) on the top of the TSF surface, pouring a 3 L mixture of mineral particles and tap water at a 1:1 w/v ratio inside the wood frame and drying for 1 h under ambient conditions (19 °C with 14% humidity, sunny and 3 m/s wind speed). Each liquid polymer solution was prepared at 5 v/v % in water, then mixed with mineral particles at a 1:1 w/v ratio. On the surface of dried testing beds, 1 L of the mixture was discharged and covered by fabric mesh screens (dimensions: L x W = 70 x 70 cm) with 50 μm holes for two weeks under ambient conditions (16 ± 6.5 °C, 18 ± 9% humidity, sunny, and 3 ± 2 m/s wind speed; temperature, humidity and wind speed over the two-week testing period were expressed as the average ± standard deviation). To simulate the recorded strongest wind (12 m/s) since 2010 at the field site, the air-blowing test was performed with 10 m/s wind speed, generated by an electric blower. The wind speed was measured on the surface of the testing bed by an anemometer. The PM10 and PM2.5 concentrations were monitored and recorded every second for 1 min using a laser dust sensor with data acquisition using the Raspberry Pi. The average PM concentrations with standard deviations were calculated using maximum values obtained from five air-blowing tests in each testing bed.

Statistical data analysis. Lab-scale air-blowing tests were performed in triplicates and pilot-scale field tests were repeated 5 times. The maximum values of the recorded data in each PM measurement were utilized to calculate the average PM concentrations and standard deviations.

All quantitative data from air-blowing tests were statistically analyzed by a one-way analysis of variance (ANOVA), hypothesis testing with a two-sample t-test and linear regression fitting using Origin Lab software (OriginPro 2016, OriginLab Co., MA, USA). A *p*-value ≤ 0.05 indicates significant differences between datasets. Table S1 summarizes the statistical values from ANOVA analysis for the lab-scale air-blowing test. In Figs. 1, S6, and S7, asterisks in each graph indicate *p*-values from two-sample t-tests. (Note: * is $p \leq 0.05$, ** is $p \leq 0.01$ and n.s. (not significant) is $p > 0.05$)

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy. Infrared (IR) spectroscopic analysis was carried out by ATR-FTIR spectroscopy (TENSOR 27, Bruker, USA). To analyze the characteristics of each polymer, 50 μL of liquid polymers or 0.5 g of solid PEO-PPO-PEO polymer was evenly covered on the ZnSe crystal plate. Moreover, to understand the interaction between mineral particles and each polymer, 1 g of the mineral particles were mixed with 1 mL of DI water or 1, 3, 5 and 7 v/v or w/v % of polymer aqueous solutions for 1 min. The mixtures were then dried in an electric oven at 50 ^{o}C for a week. The ZnSe crystal plate was evenly covered with 0.5 g of the dried mixture. Each sample was scanned at 4 cm^{-1} of resolution over a wavenumber range of 300-8000 cm^{-1}. The spectrums represented were obtained by averaging 64 scans.

Optical Microscopy and Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDS). Microstructure analysis was performed using an optical microscope (IX71, Olympus, Japan) and SEM-EDS (S-4800, Hitachi, Japan). Polymer aqueous solutions were prepared with 3 or 5 v/v % liquid PEG and PEO-PPO-PEO while DI-water was used as a control. These aqueous solutions were mixed with mineral particles at a 1:1 w/v ratio and dried in an electric oven at 50 ^{o}C for a week. The dried samples were analyzed by optical microscopy (Fig. 2) and SEM (Fig. S1 and S3).

UVA treatment. A UVP handheld lamp (UVGL-55, Analytik Jena, CA, USA) was used with a J-129 lamp stand (dimensions: L x H = 33 x 24.8 cm). For the sample preparation, 2 mL of liquid PEO-PPO-PEO polymer was transferred to each glass vial (Shell Vial, catalog # 60965D, Kimble®, USA). The vials were moved into a dark box (dimensions: L x W x H = 38 x 16 x 26 cm) and exposed to continuous 365 nm UVA (intensity of 950 μW/cm^2) light for 2, 4 and 8 weeks. The distance between the samples and UVA source was 15 cm.

Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry. MALDI-TOF mass spectrometer (Autoflex Speed, Bruker, USA) was used with a positive reflection method and a mass range of 700-3500 g/mol. The UVA treated-liquid PEO-PPO-PEO polymers were added to 1 v/v % of liquid PEG aqueous solution at a 1 v/v ratio. The samples were prepared at a 1:5 ratio of each polymer solution with the matrix, consisting of a saturated solution of CCA (α-Cyano-4-hydroxycinnamic acid) with ACN:H_2O at a 1:1 w/v ratio. Then, the dried droplet method was used to deposit 1 μL of each sample on a ground steel MALDI target plate. The laser power was 31% and 3000 shots were collected for each sample. To compare the UVA-treated PEO-PPO-PEO polymers to each other, the intensity of each UVA-treated polymer was normalized to the intensity of intact liquid PEG polymer, added in each UVA-treated sample before the MALDI-TOF sample preparation.

Viscosity measurement. The viscosity measurement of liquid PEO-PPO-PEO aqueous solutions was performed by Brookfield Rotary Viscometer(USS-DVT4, U.S. Solid, USA) with #1 rotor. The rotor speed was 60 rpm and temperature was at 20 ^{o}C during the measurement.

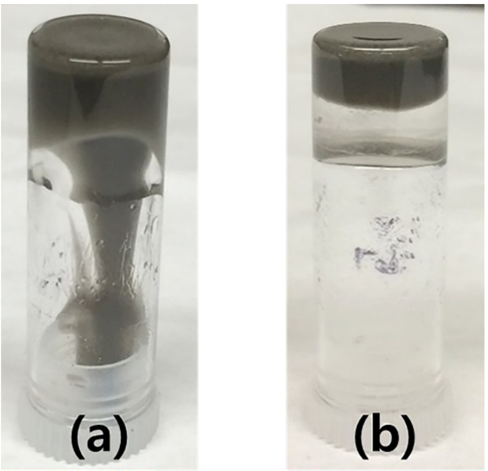


Fig. S1. Inversion tests of samples prepared by adding mineral dust into (a) 50 v/v % liquid PEG and (b) 50 v/v % liquid PEO-PPO-PEO aqueous solutions at a 1:1 w/v ratio. Before the inversion tests, the samples were dried without a lid at room temperature for two weeks.

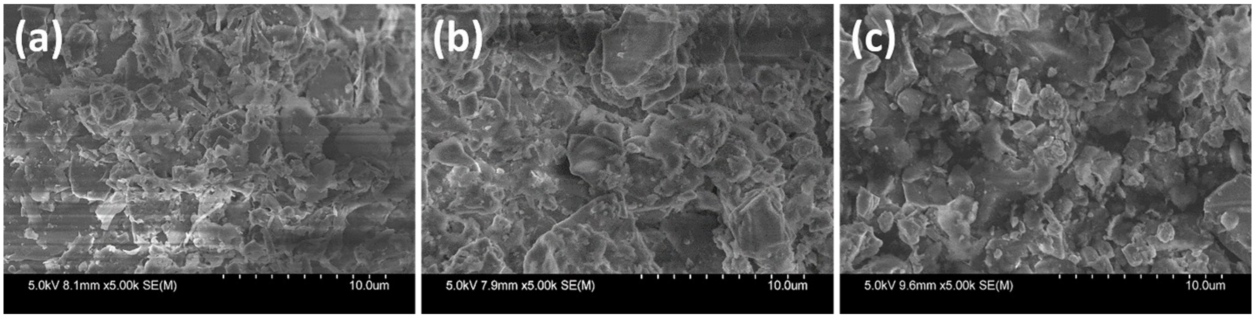


Fig. S2. Surface microstructure images obtained by SEM. Mineral dust was mixed with a 1:1 w/v % of (a) water, (b) 5 v/v % liquid PEG aqueous solution and (c) 5 v/v % liquid PEO-PPO-PEO aqueous solution. All mixtures were dried in an electric oven at 50 ^{o}C for a week.

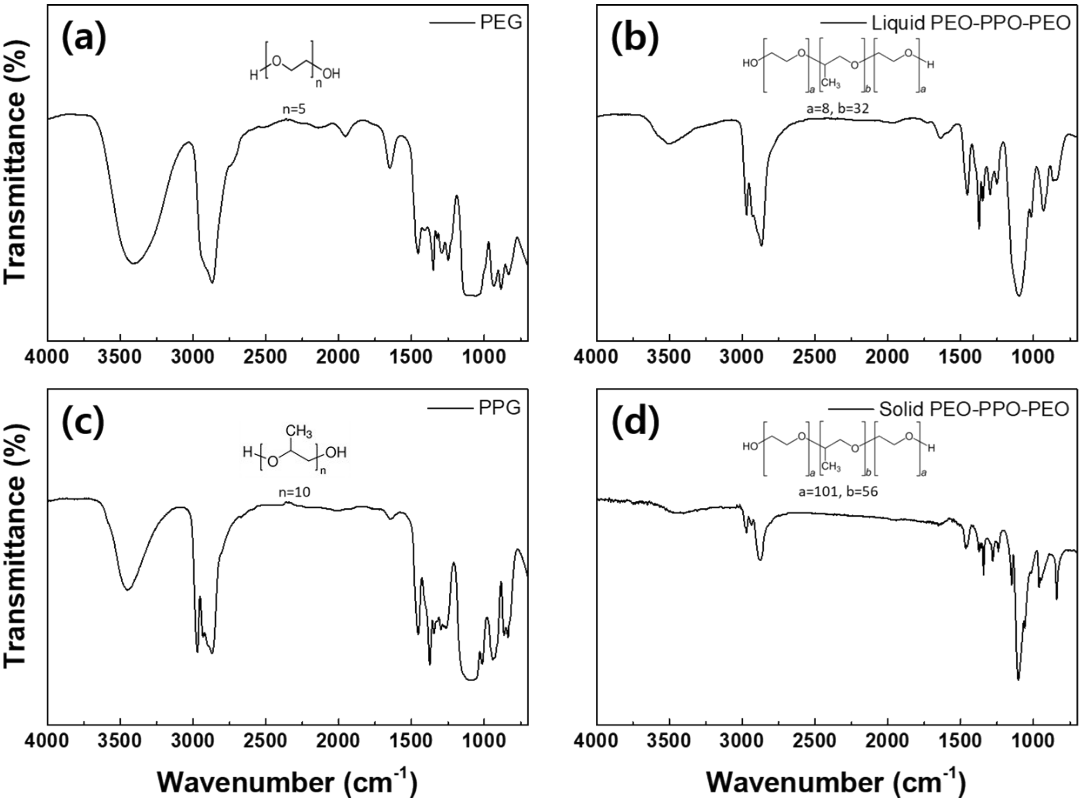


Fig. S3. ATR-FTIR analysis on (a) liquid PEG, (b) liquid PEO-PPO-PEO, (c) liquid PPG, and (d) solid PEO-PPO-PEO polymers. Representative peaks of each polymer are labeled on spectrums: C-O-C (1100 cm^{-1}), C-H (1350 and 1450 cm^{-1}), -CH$_2$ (2850 cm^{-1}), –CH$_3$ (2950 cm^{-1}) and -OH (3500 cm^{-1}) bonds.[3]

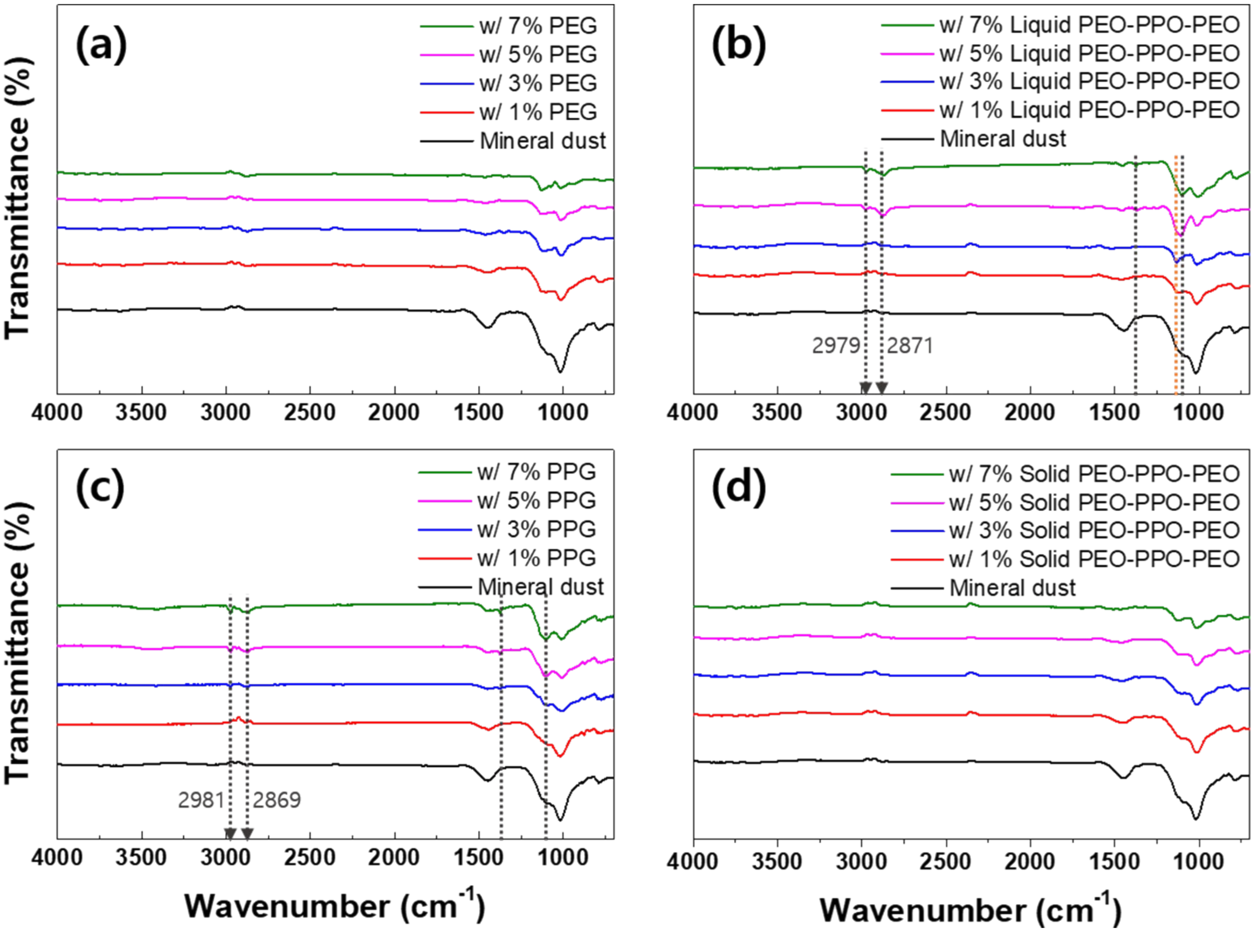


Fig. S4. ATR-FTIR spectrums from mineral dust treated by water alone (black solid lines) and various polymer aqueous solutions. The aqueous solutions were prepared by dissolving 1-7 v/v % of (a) liquid PEG, (b) liquid PEO-PPO-PEO, (c) liquid PPG and (d) solid PEO-PPO-PEO in water. Mineral dust was mixed with the aqueous solutions at a 1:1 w/v ratio and then dried in an electric oven at 50 °C for a week before the measurement.

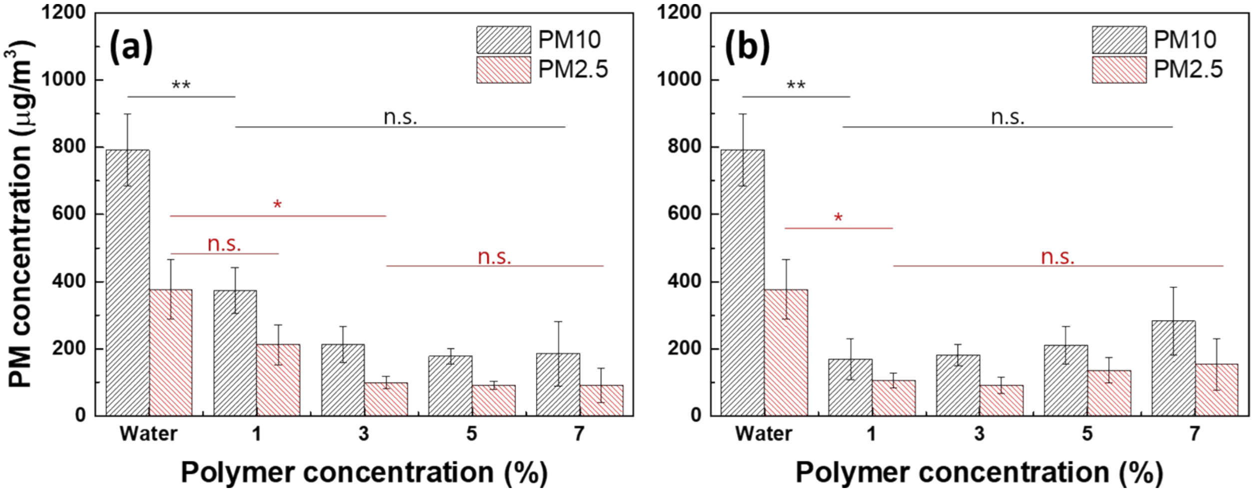


Fig. S5. PM10 and PM2.5 concentration measurements, generated from sample beds treated by 1-7 v/v % of (a) liquid PPG and (b) solid PEO-PPO-PEO polymer aqueous solutions. PM10 and PM2.5 concentrations were measured by applying compressed air on the sample surface (wind speed: 20 m/s). A one-way analysis of variance (ANOVA) determined significant differences in PM concentrations between conditions (Table S1). (Note: *n*=3; *p*-value ≤ 0.05 and ≤ 0.01 are denoted as * and **, respectively; n.s.: not significant)

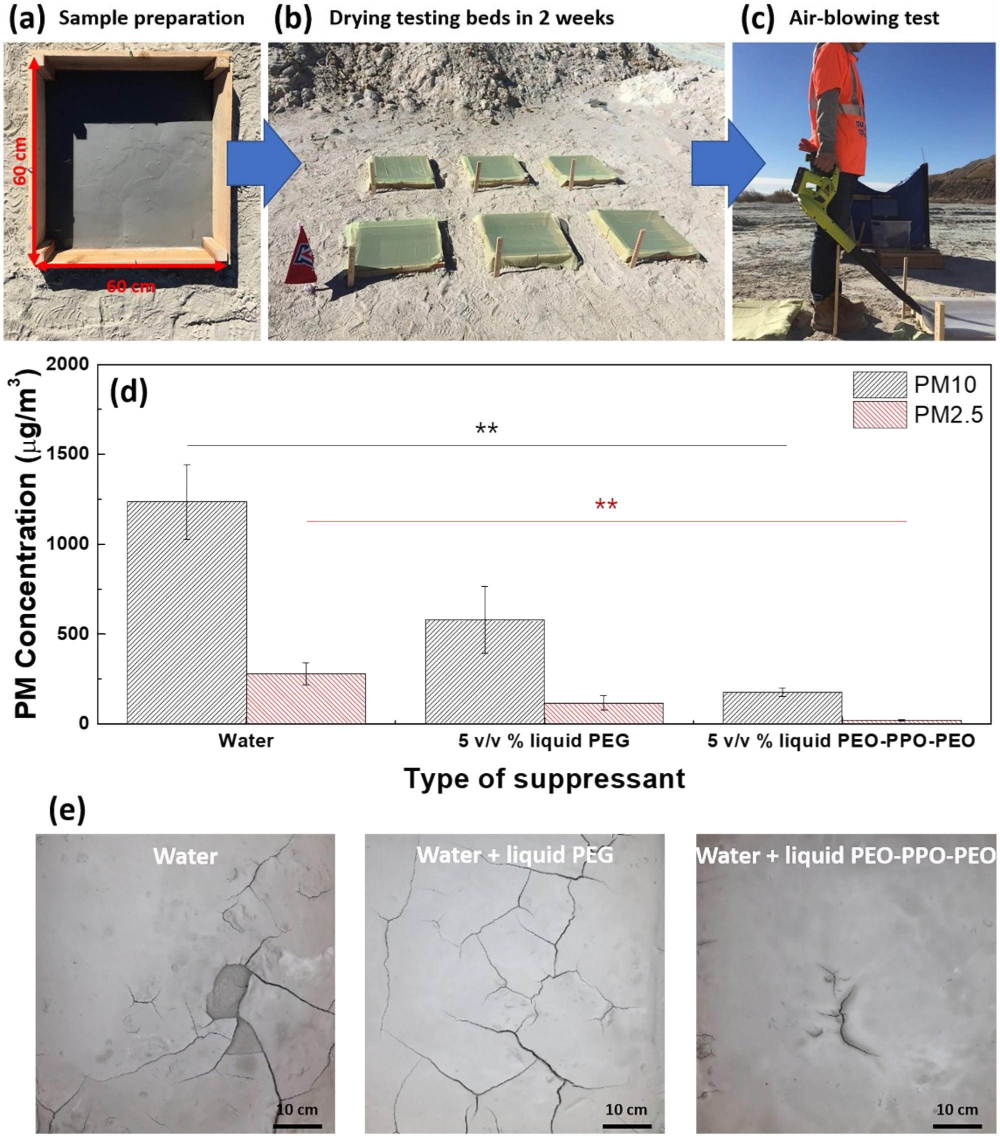


Fig. S6. Dust suppression comparison among water, liquid PEO-PPO-PEO polymer and liquid PEG polymer at an inactive TSF. (a) Testing beds were prepared with water and each polymer aqueous solution for the pilot-scale field test.; (b) To minimize dust deposited from outside of the testing beds, testing beds were covered by fabric mesh screens with 50 μm hole size; (c) After two weeks, air-blowing tests were performed with 10 m/s wind speed.; (d) PM10 and PM2.5 concentrations were measured by a SDS-021 dust sensor (*n*=5; $p \leq 0.01$); (e) Surface images of testing beds after the air-blowing test.

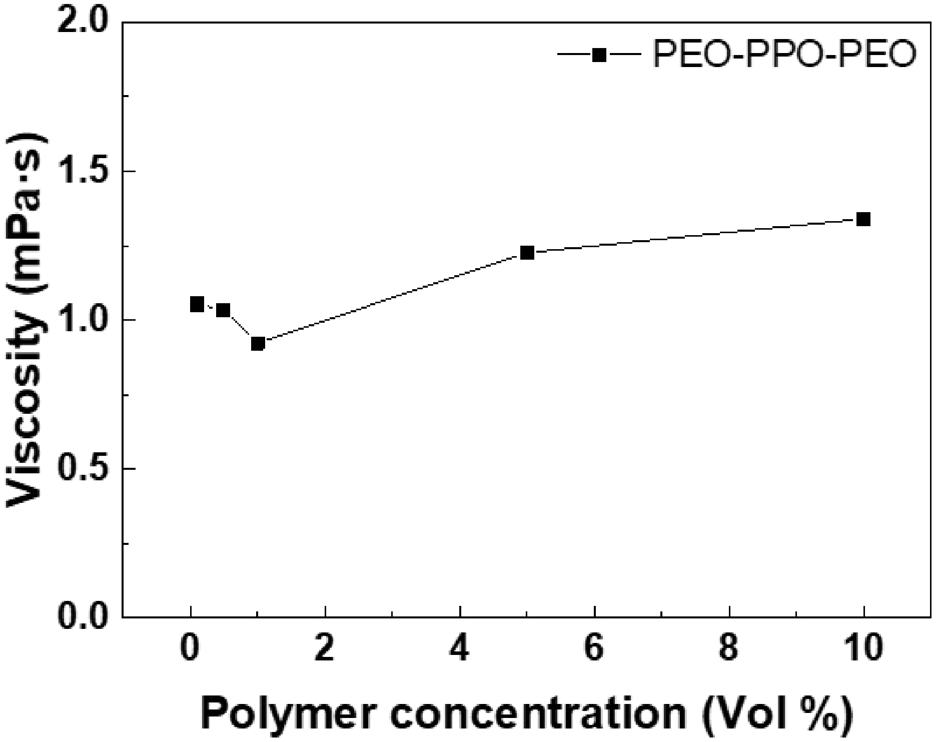


Fig. S7. The viscosity behavior of PEO-PPO-PEO aqueous solutions as a function of polymer concentrations at 20 °C.

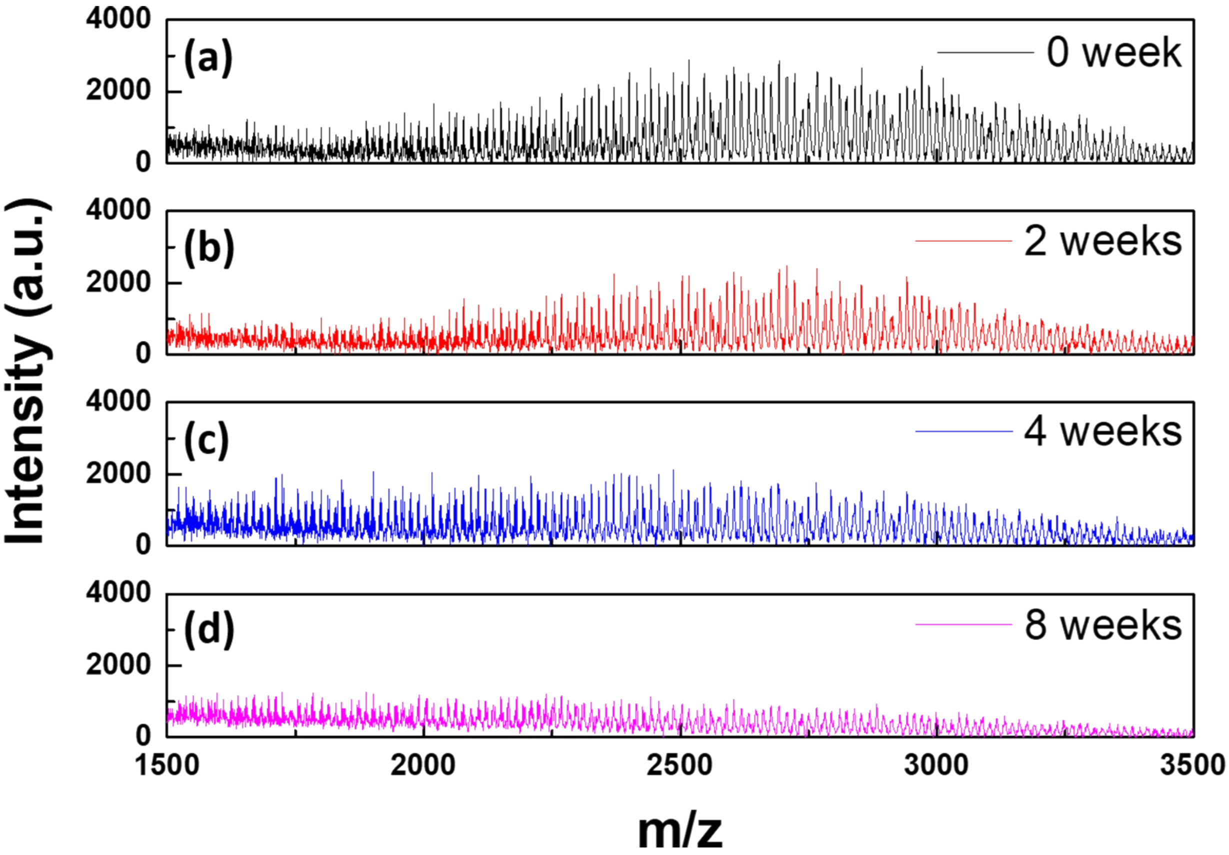
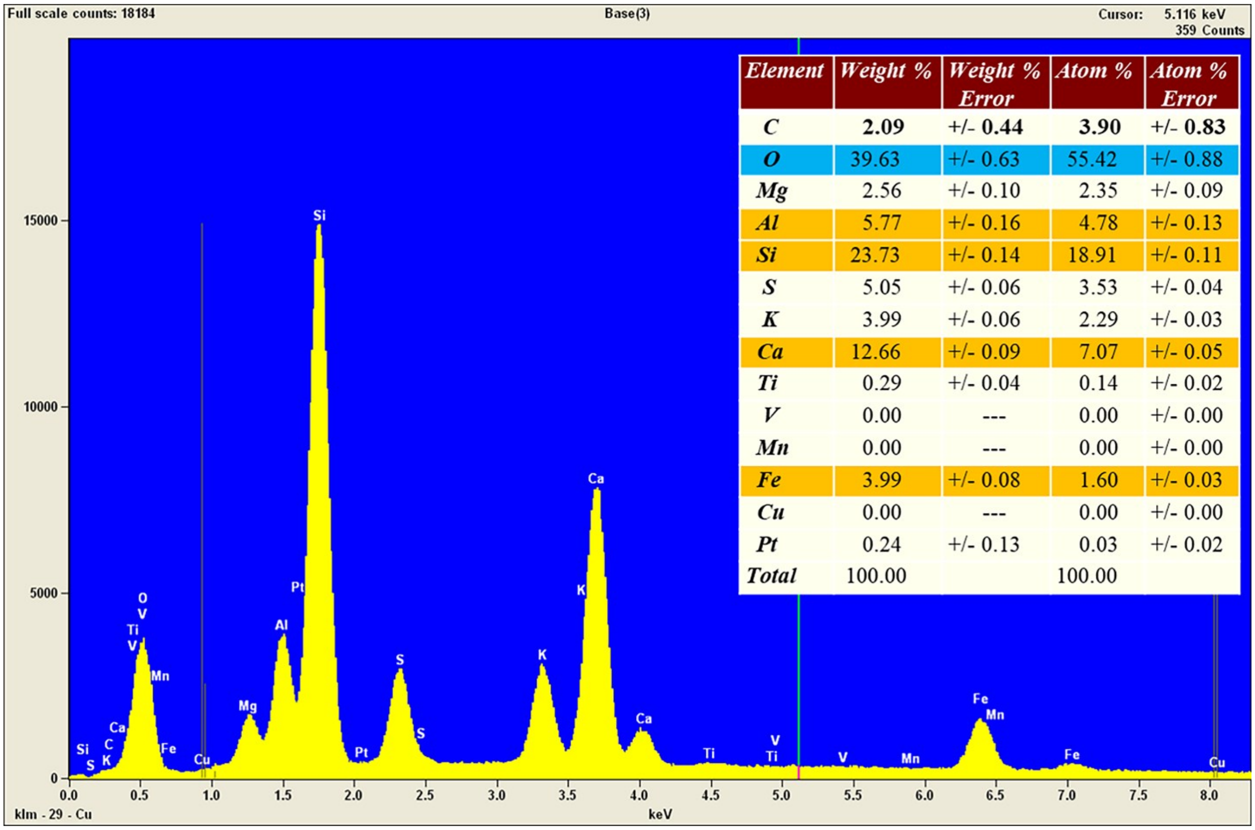


Fig. S8. The degradability of liquid PEO-PPO-PEO polymer under continuous UVA (~360 nm) exposure. UVA-treated liquid PEO-PPO-PEO polymers at each time point were collected and analyzed by using MALDI-TOF mass spectrometry. (a)-(d) UVA non-treated liquid PEO-PPO-PEO polymer and liquid PEO-PPO-PEO polymer treated by continuous UVA light for two, four and eight weeks. The degradation amount for each time point was calculated by integrating the area of intensities in the range of 2300-2700 m/z based on the average molar mass (2500 g/mol) of liquid PEO-PPO-PEO polymer.



Element	*Weight %*	*Weight % Error*	*Atom %*	*Atom % Error*
C	**2.09**	+/- **0.44**	**3.90**	+/- **0.83**
O	39.63	+/- 0.63	55.42	+/- 0.88
Mg	2.56	+/- 0.10	2.35	+/- 0.09
Al	5.77	+/- 0.16	4.78	+/- 0.13
Si	23.73	+/- 0.14	18.91	+/- 0.11
S	5.05	+/- 0.06	3.53	+/- 0.04
K	3.99	+/- 0.06	2.29	+/- 0.03
Ca	12.66	+/- 0.09	7.07	+/- 0.05
Ti	0.29	+/- 0.04	0.14	+/- 0.02
V	0.00	---	0.00	+/- 0.00
Mn	0.00	---	0.00	+/- 0.00
Fe	3.99	+/- 0.08	1.60	+/- 0.03
Cu	0.00	---	0.00	+/- 0.00
Pt	0.24	+/- 0.13	0.03	+/- 0.02
Total	100.00		100.00	

Fig. S9. The elemental analysis of mineral dust using EDS.

Table S1. ANOVA results for comparing PM concentrations between polymers in lab-scale and pilot-scale air-blowing tests (Figs. 1, S6 and S7).

Type of test		PM10			PM2.5		
		F-value	*p*-value[a]	R^2	F-value	*p*-value[a]	R^2
Lab-scale test	Liquid PEG	F(4, 10) = 29.45	1.64x10^{-5}	0.92	F(4, 10) = 9.20	2.20x10^{-3}	0.79
	Liquid PEO-PPO-PEO	F(4, 9) = 61.63	1.55x10^{-6}	0.96	F(4, 9) = 16.18	3.84x10^{-4}	0.88
	Liquid PPG	F(4, 9) = 20.61	1.49x10^{-4}	0.90	F(4, 9) = 9.08	3.19x10^{-3}	0.80
	Solid PEO-PPO-PEO	F(4, 10) = 23.65	4.4x10^{-5}	0.90	F(4, 10) = 8.37	3.13x10^{-3}	0.77
Pilot-scale test	5 v/v % liquid PEG	F(1, 8) = 4.47	6.74*10^{-2}	0.36	F(1, 8) = 3.92	8.32x10^{-2}	0.33
	5 v/v % liquid PEO-PPO-PEO	F(1, 8) = 20.74	1.86x10^{-3}	0.72	F(1, 8) = 14.39	5.29x10^{-3}	0.64

[a] significance level is ≤ 0.05

Table S2. Linear regression fitting data from measured PM concentrations in Figs. 1b and 1c.

Type of polymer	**PM10**			**PM2.5**		
	Intercept	Slope	Adj. R^2 [a)]	Intercept	Slope	Adj. R^2 [a)]
Liquid PEG	552.42 ± 17.53	-64.77 ± 3.44	0.99	356.32 ± 13.18	-43.17 ± 2.17	0.99
Liquid PEO-PPO-PEO	34.32 ± 100.00	18.31 ± 26.50	-0.21	61.99 ± 30.96	-2.79 ± 9.63	-0.44

[a)] Adj. R^2 = adjusted R-squared.

References

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3 George Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons, New York, 3rd edn., 2004.