

Supporting Information

Modified cassava starch/poly(vinyl alcohol) blend films plasticized by glycerol: Structure and properties

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FTIR assignments of non-degraded films

Table S1. Peak assignments in the FTIR spectra of pure PVA, pure starch, PVA/Gly and starch/Gly films.

Peak assignment	PVA ^a	PVA/Gly	NCS ^b	NCS/Gly	LCS ^c	LCS/Gly	HCS ^d	HCS/Gly	PCS ^e	PCS/Gly ^f
O-H (st)	3260	3264	3288	3284	3286	3283	3280	3283	3294	3282
-CH ₂ (st)	2937	2938	2925	2925	2926	2927	2925	2927	2927	2926
	2907	2909		2891		2888		2888		2885
-OH (b) (bound water)	1651	1651	1642	1647	1644	1646	1634	1645	1645	1647
CH ₂ (b)	1413	1415	1410	1413	1413	1412	1413	1413	1415	1410
CH ₂ OH (side chain) related mode	1237	1236	1241	1241	1242	1240	1243	1241	1240	1239
C-O (st) in C-O-H	1141	1142	1149	1150	1149	1150	1149	1150	1149	1150
	1086	1090		1077	1077	1078	1077	1077	1078	1079
C-O (st) (C-O-C glycosidic linkage)	-	-	990	994	991	994	991	994	990	994
C-O (b) (C-O-C ring vibration in starch)	-	-	759	760	759	760	760	760	759	759

^a PVA = poly(vinyl alcohol), ^b NCS = native cassava starch, ^c LCS = low-oxidized cassava starch, ^d HCS = high-oxidized cassava starch, ^e PCS = pregelatinized cassava starch, and ^f Gly = glycerol.

Table S2. Peak assignments in the FTIR spectra of PVA/starch/Gly blend films (Air side).

Peak assignment	3PVA/ 7NCS/ Gly	5PVA/ 5NCS/ Gly	7PVA/ 3NCS/ Gly	3PVA/ 7LCS/ Gly	5PVA/ 5LCS/ Gly	7PVA/ 3LCS/ Gly	3PVA/ 7HCS/ Gly	5PVA/ 5HCS/ Gly	7PVA/ 3HCS/ Gly	3PVA/ 7PCS/ Gly	5PVA/ 5PCS/ Gly	7PVA/ 3PCS/ Gly
O-H (st)	3288	3281	3264	3279	3274	3279	3288	3284	3269	3281	3279	3268
-CH ₂ (st)	2929	2932	2937 2907	2928	2934 2908	2935 2907	2928	2928 2890	2935 2907	2927	2936 2908	2938 2907
-OH (b) (bound water)	1646	1646	1646	1646	1647	1647	1645	1645	1648	1646	1646	1648
CH ₂ (b)	1414	1414	1416	1416	1415	1415	1414	1412	1415	1412	1415	1416
CH ₂ OH (side chain) related mode	1238	1237	1236	1239	1237	1236	1239	1239	1236	1238	1237	1236
C-O (st) in C-O-H	1147 1078	1145 1079	1142 1086	1149 1078	1143 1080	1142 1084	1148 1077	1149 1077	1143 1081	1148 1079	1143 1079	1142 1088
C-O (st) (C-O-C glycosidic linkage)	991	993	-	992	-	-	1000	1002	-	993	993	-
C-O (b) (C-O-C ring vibration in starch)	758	758	-	759	-	-	759	761	-	758	756	-

Soil burial test

1. Weight loss

Weight loss of PVA/Gly, starch/Gly, and PVA/starch/Gly blend films was determined after burial in soil for 15 and 30 days. At 15 days, NCS/Gly, HCS/Gly, and PCS/Gly films were completely consumed by soil microorganisms. The data are shown in Table S4 and weight losses in soil after 15 and 30 days are shown in Figure S1. At 30 days, all the starch/Gly films were completely consumed. The weight losses of PVA/Gly films at 15 and 30 days were 26 and 27 wt%, respectively. Since glycerol comprised 23 wt% of the film, we concluded that all the glycerol and some amorphous structure in PVA had been consumed after 15 days. Films of plasticized starches were much more biodegradable in soil than PVA/Gly film¹ and the resistance of PVA film to degradation in soil was due to the small amorphous phase in PVA.² Weight loss was affected by the composition of PVA and starch.³ The greatest weight loss occurred in 3PVA/7starch/Gly blends. These were the blends that contained the highest proportion of starch. The addition of PVA slowed the degradation process in the blends.⁴ At both 15 and 30 days, the blend films that lost the most weight were PVA/PCS/Gly blends. PCS-based blends also exhibited the most extreme swelling behavior after 24 hours in water (Figure S4(d)).

Table S4. Weight loss (%) of degraded PVA/Gly and starch/Gly films was determined after burial in soil for 15 and 30 days.

sample	Weight loss (%)	
	15 days	30 days
PVA/Gly	26.44 ± 0.29	27.40 ± 0.38
NCS/Gly	n.a.	100
LCS/Gly	Small amount	100
HCS/Gly	n.a.	100
PCS/Gly	n.a.	100

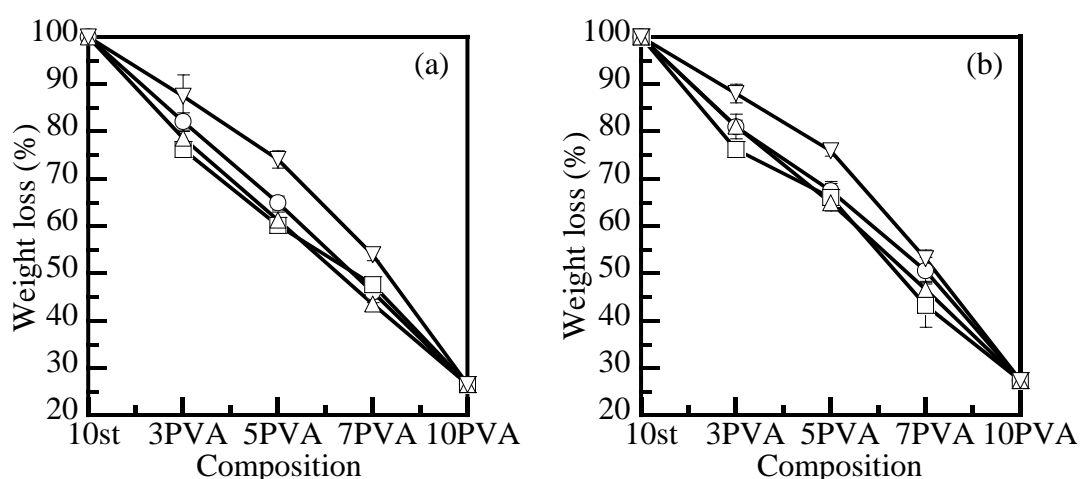


Figure S1. Weight loss was determined after burial in soil for (a) 15 and (b) 30 days. (○) PVA/NCS, (□) PVA/LCS, (△) PVA/HCS, and (▽) PVA/PCS.

References

1. Azahari, N. A.; Othman, N.; Ismail, H. J. *J. Phys. Sci.* 2011, **22**(2), 15.
2. Tudorachi, N.; Cascaval, C. N.; Rusu, M.; Pruteanu, M. *Polym. Test.* 2000, **19**, 785.
3. Siddaraamaiah Raj, B.; Somashekar, R. *J. Appl. Polym. Sci.* 2004, **91**, 630.
4. Mao, L.; Imam, S.; Gordon, S.; Cinelli, P.; Chiellini, E. *J. Polym. Environ.* 2000, **8**, 205.

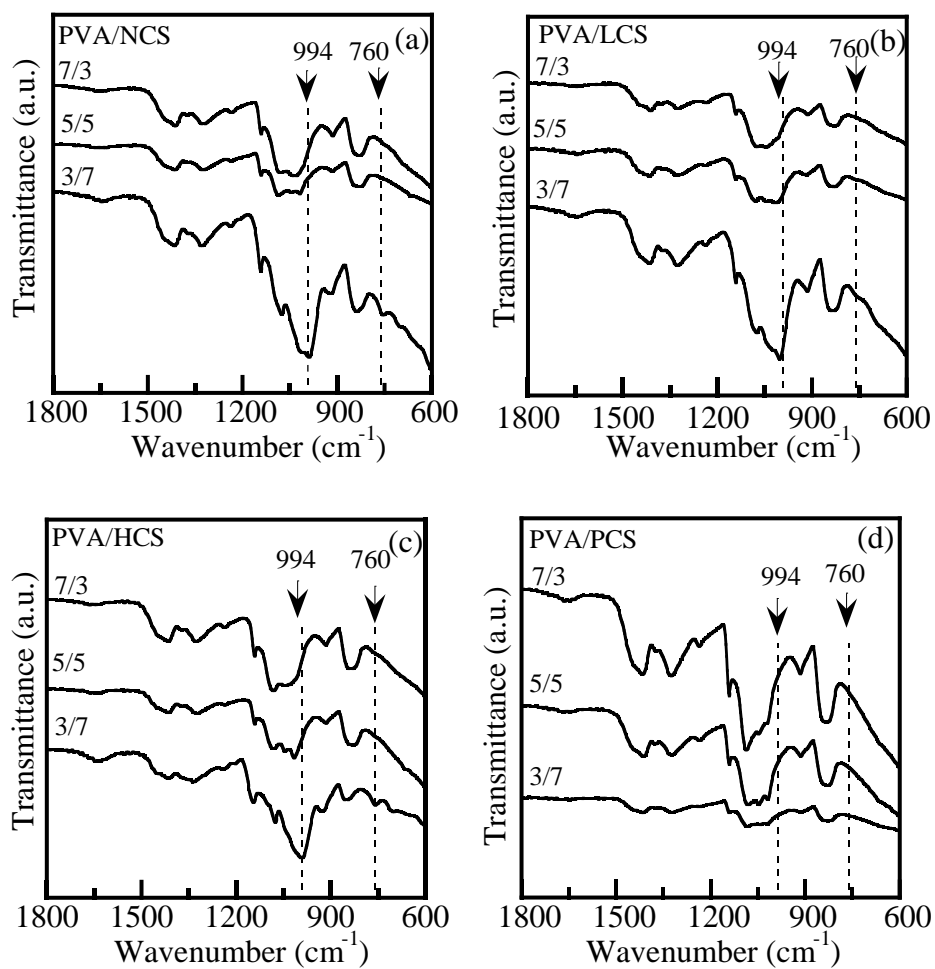


Figure S2. FTIR spectra were obtained from degraded (a) PVA/NCS/Gly, (b) PVA/LCS/Gly, (c) PVA/HCS/Gly and (d) PVA/PCS/Gly films after burial in soil for 15 days. The ratios of PVA/starch are indicated.

Morphology

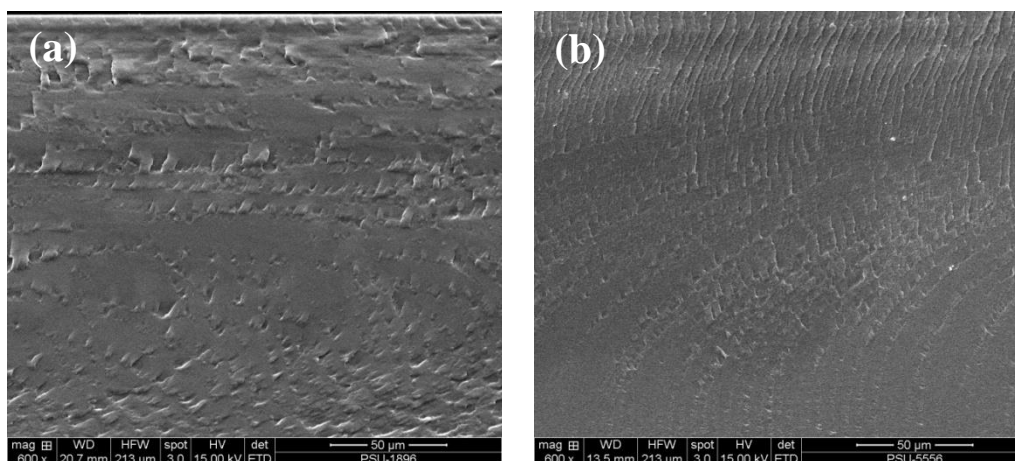


Figure S3. SEM micrographs of cryo-fracture surfaces of (a) pure PVA and (b) PVA/Gly films.

Swelling test

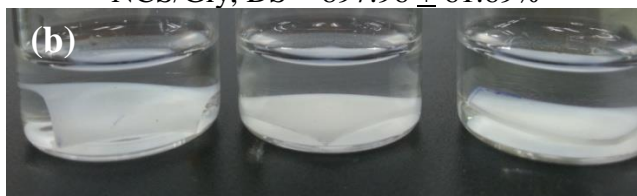
Samples (15 mm×15 mm) were dried in an oven at 60 °C for 24 h. The dried samples were immersed in 5 mL water at room temperature and kept in darkness for 24 h. When placing the blend samples in the vials, care was taken to place the surface that was in contact with the polystyrene plate during the casting process in contact with the bottom of the vials. When the samples were removed from the vials, moisture on the surface of the sheets was removed with filter paper. Six samples were determined per formulation. The degree of swelling (DS) was determined from eq. (1):¹

$$DS = (w_e - w_0) \times 100 / w_0 \quad (1)$$

where w_e was the weight of the sample at the absorbing equilibrium and w_0 was the dry weight of the sample. Photographs of NCS/Gly, LCS/Gly, HCS/Gly and PVA/Gly are shown in Figure S4. The blend films of PVA/HCS/Gly and PVA/PCS/Gly are shown in Figure S5.



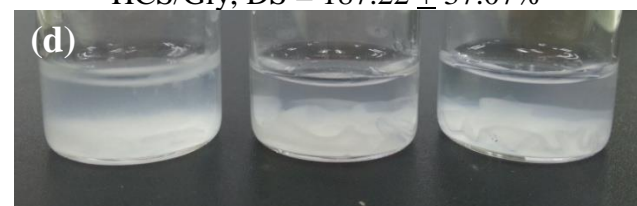
NCS/Gly, DS = $897.96 \pm 61.69\%$



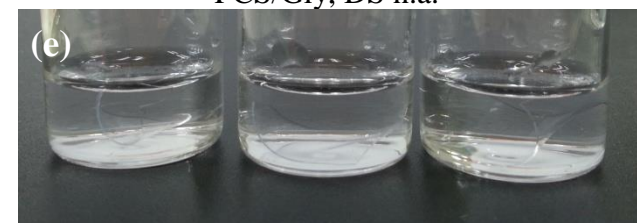
LCS/Gly, DS = $245.76 \pm 2.51\%$



HCS/Gly, DS = $187.22 \pm 37.07\%$

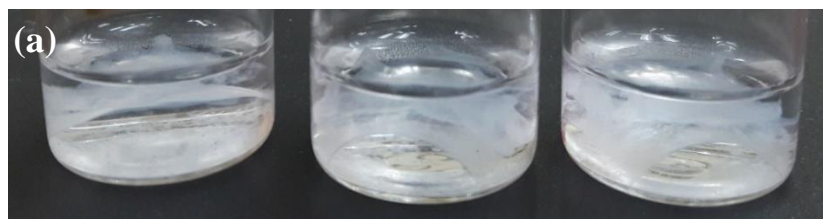


PCS/Gly, DS n.a.

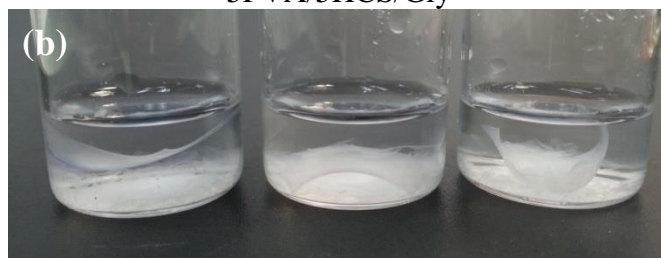


PVA/Gly, DS = $81.51 \pm 1.84\%$

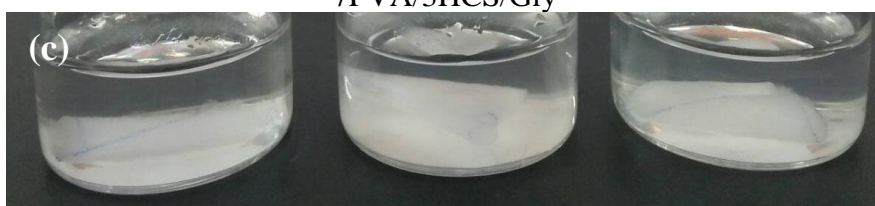
Figure S4. Photographs were taken of (a) NCS/Gly, (b) LCS/Gly, (c) HCS/Gly, (d) PCS/Gly, and (e) PVA/Gly film samples after immersion in water for 24 hours. The degree of swelling (DS) is indicated as a percentage. The DS of PCS/Gly could not be determined due to the gel-like condition of the film sample after immersion in water.



5PVA/5HCS/Gly



7PVA/3HCS/Gly



5PVA/5PCS/Gly



7PVA/3PCS/Gly

Figure S5. Photographs were taken after immersion in water for 24 hours of (a,b) PVA/HCS/Gly and (c,d) PVA/PCS/Gly blend films.

Reference

1. Yoon, S. D. *J. Agric. Food Chem.* 2014, **62**, 1755.

Morphology of degraded films

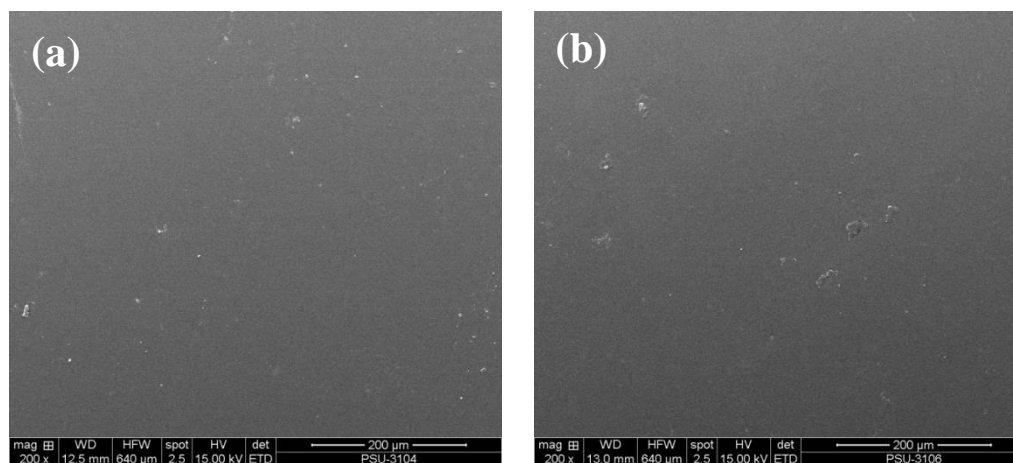


Figure S6. SEM top-view micrographs of PVA/Gly film after burial in soil for (a) 15 and (b) 30 days.

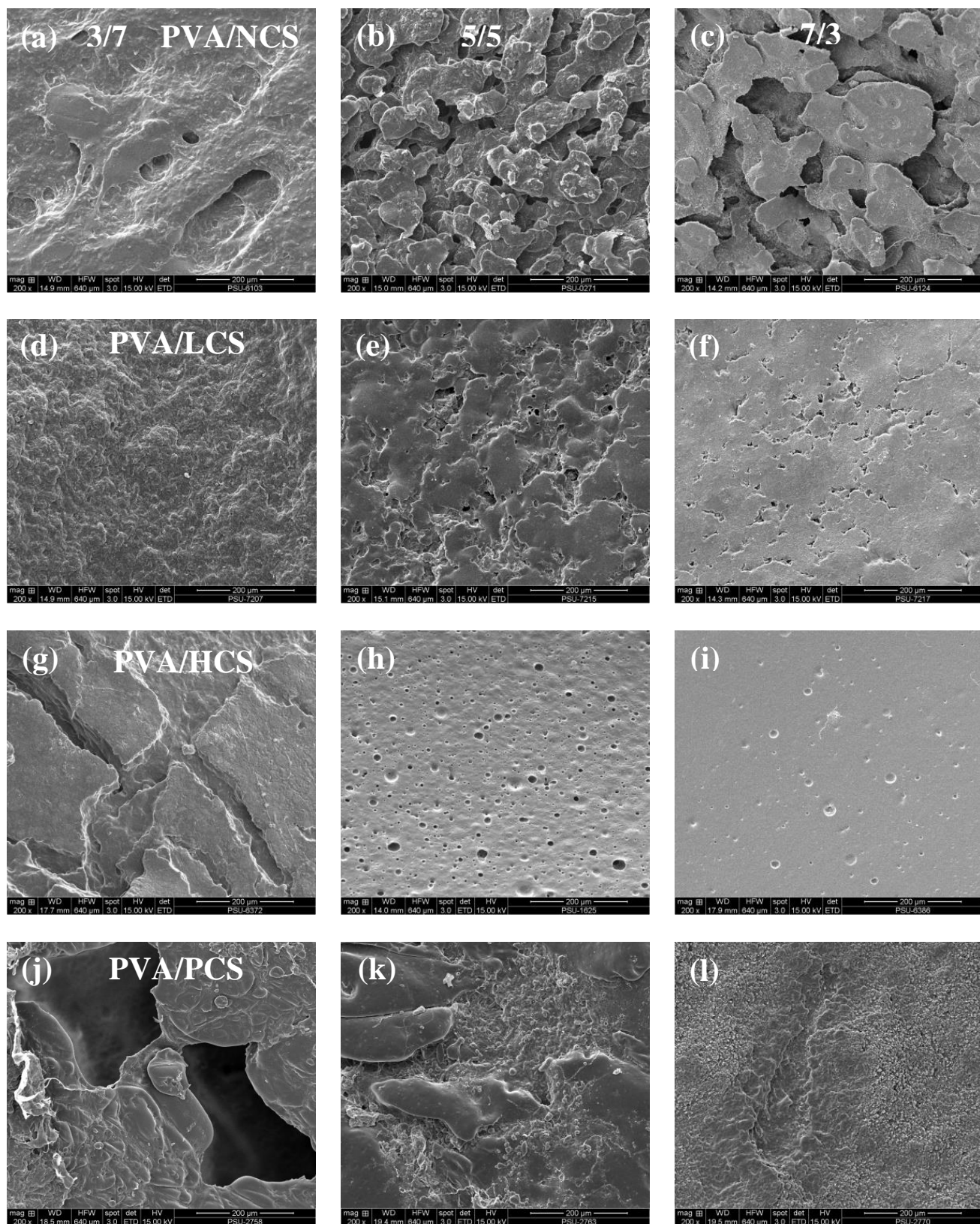


Figure S7. SEM micrographs show top surfaces of (a)-(c) PVA/NCS/Gly, (d)-(f) PVA/LCS/Gly, (g)-(i) PVA/HCS/Gly, and (j)-(l) PVA/PCS/Gly films after burial in soil for 15 days. PVA/starch blend ratios are indicated at the top of each column.

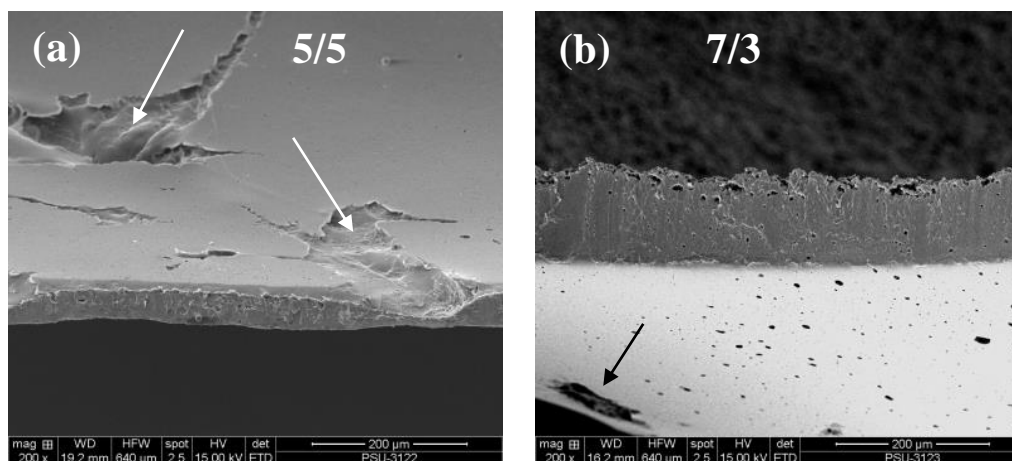


Figure S8. SEM micrographs show (a) 5PVA/5PCS/Gly and (b) 7PVA/3PCS/Gly films after burial in soil for 30 days. The features indicated by arrows are on the film surface that was in contact with the polystyrene tray during casting.