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Interface Bonding Engineering of Transparent Conductive Electrode towards Highly Efficient and Mechanically Flexible ITO-free Organic Solar Cells

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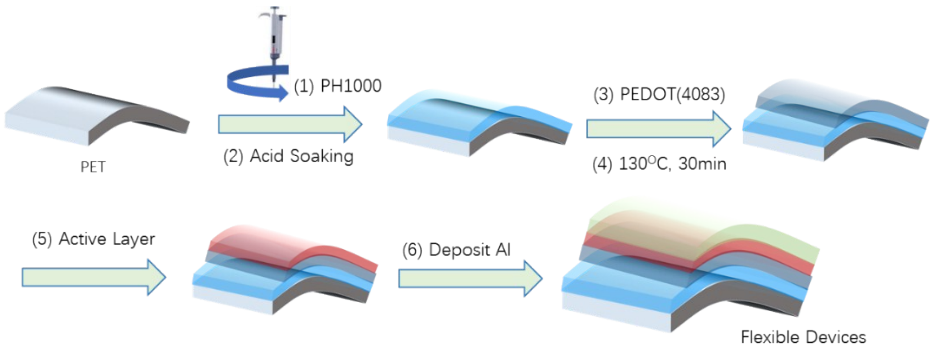
Experimental Section

Materials. PBDB-T-2Cl, IT-4F and PDINO were purchased from Solarmer Materials Inc., and used as received. PEDOT: PSS solution (Clevios PH1000 and Clevios P VP 4083) was obtained from Heraeus Inc., Germany. 1, 8-diiodooctane (DIO), chlorobenzene (CB) and other drying solvent were received from Aldrich Inc. ITO glass (1.1 mm thick, ≤15 Ω/square) were purchased from Wuhu Token Sciences Co., Ltd. PET flexible substrate was obtained from South China Xiangcheng Technology Co., Ltd.

Preparation of PET/PH1000 FTEs. The PET/PH1000 composite electrode doped w/o polyhydroxy compounds were prepared though a facile solution-processed method. First, various polyhydroxy compounds (eg. D-Glucose, D-Sucrose, D-Glucitol, and D-Maltose) with a content of 5.0 wt % was uniformly dispersed in PH1000 aqueous solution, followed by adding 0.3 vol% Zonyl FS300 and stirred for ~2h at room temperature. Then the PH1000 mixture was filtered through a 0.45 μm syringe filter and spin-coated at 2000 rpm on the cleaned PET substrate to form a uniform film, followed by a thermal annealing at 100°C on a hot plate for about 10 min. the dry films were consequently treated by dropwising amount of methyl sulfonic acid to the surface of film for 10 min, then was washed with DI water and ethanol. Then another 15 min thermal drying process at 100°C was applied on these PET/PH1000 films. Finally, PEDOT:PSS (Clevios P VP 4083) solution was spin-coated on the underlying substrate to form a well-distributed PET/PH1000 composite electrodes.

Fabrication of OSCs. The structure of investigated flexible OSCs is PET/PH1000/ PEDOT: PSS / PBDB-T-2Cl: IT-4F /PDINO/Al, the fabrication process of the devices is depicted in **Scheme S1**. Based on the as-prepared PET/PH1000 flexible transparent eletrodes. The PBDB-T-2Cl:IT-4F (1:1, w/w) mixed solution with a total concentration of 20 mg/ml and 0.5 vol% of DIO as additive dissolved in chlorobenzene, was spin-coated onto the PET/PH1000/PEDOT:PSS composite electrode with a thickness of ~100 nm, then annealed at 100℃ for 10 minutes. Subsequently, a perylene diimide functionalized with amino N-oxide (PDINO) dissolved in methanol (1.5 mg/ml) were deposited onto the active layers, Al electrode (~100 nm) was finally evaporated with a vacuity of ~5×10^{-6} mbar, the effective area of prepared devices is 4 mm^2, which is determined by the overlapping region of Al and PET/PH1000 composite electrode.



Scheme S1. The detail fabrication procedure for PH1000/PEDOT: PSS composite electrode and flexible solar cell devices.

Characterizations. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were measured on a multifunctional photoelectron spectrometer (Kratos ULTRADLD UPS/XPS system). Elemental mapping and surface morphologies were analyzed by means of scanning electron microscope (FEI Quanta FEG 250) at 4.0 kV. The film thickness was measured on a surface profiler (Dektak150). Transmittance spectrums were acquired by a spectrophotometer (Perkin-Elmer Lambda 950). The current-voltage (*J-V*) and electrical conductivity test were performed on Keithley 2440 sourcemeter under AM 1.5 G irradiation or dark, respectively, from a solar simulator (Newport-Oriel® Sol3A 450W) without encapsulation in a nitrogen-filled glove box, a standard Si solar cells was used to calibrated the intensity of the simulated solar light. External quantum efficiency (EQE) spectrums were obtained from a solar cell QE tester (QE-R, Enli Technology Co., Ltd) with a 75W xenon lamp source calibrated by a standard probe.

Elemental analysis (XPS)

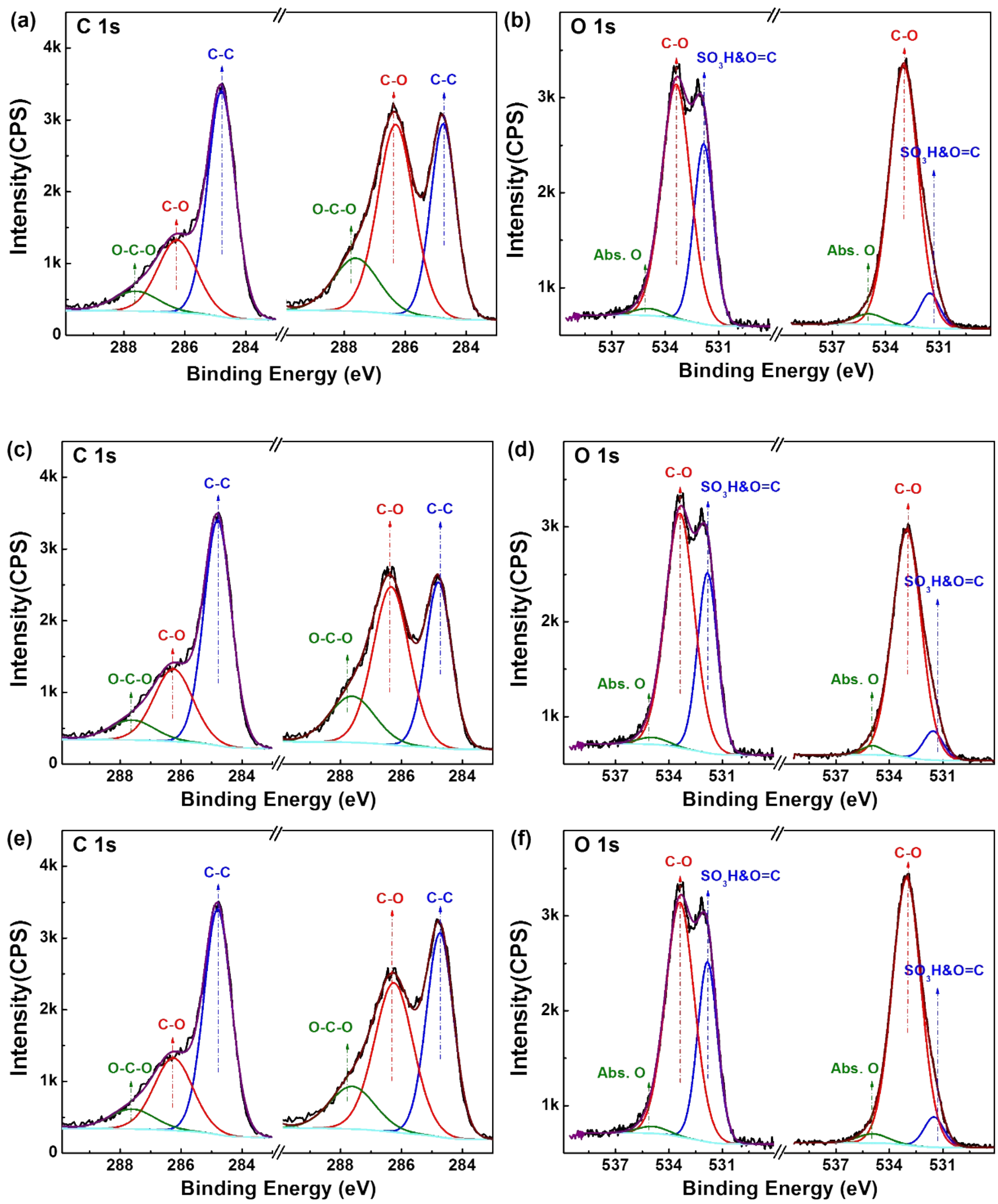


Fig. S2 (a) Contrast XPS spectra of pristine PH1000 electrode (left) and various of water/ alcohol soluble polyhydroxyl compounds doped PH1000 composite electrode, C 1s (a) and O 1s (b) for D-Sucrose, C 1s (c) and O 1s (d) for D-Glucose, and C 1s (e) and O 1s (f) for D-Glucitol, respectively.

Energy banding analysis (UPS)

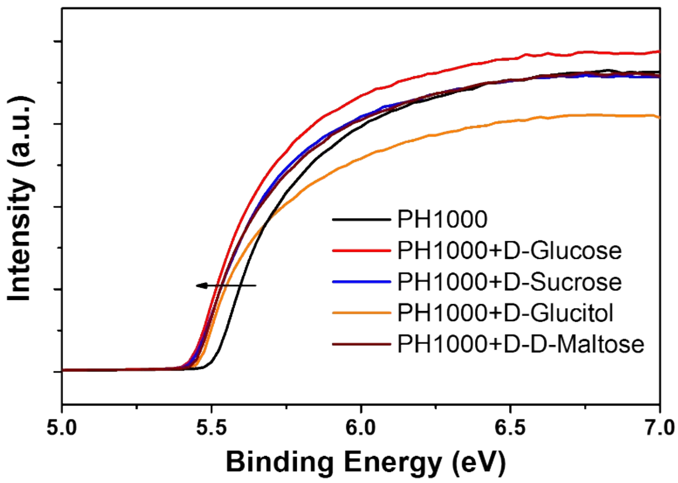


Fig. S3 Ultraviolet photoelectron spectroscopy (UPS) of pristine PH1000 and PH1000 films doped with D-Glucose, D-Sucrose, D-Glucitol, and D-Maltose, respectively.

J-V and light intensity dependence characterization of flexible OSCs based on D-Maltose doped PET/PH1000 electrodes

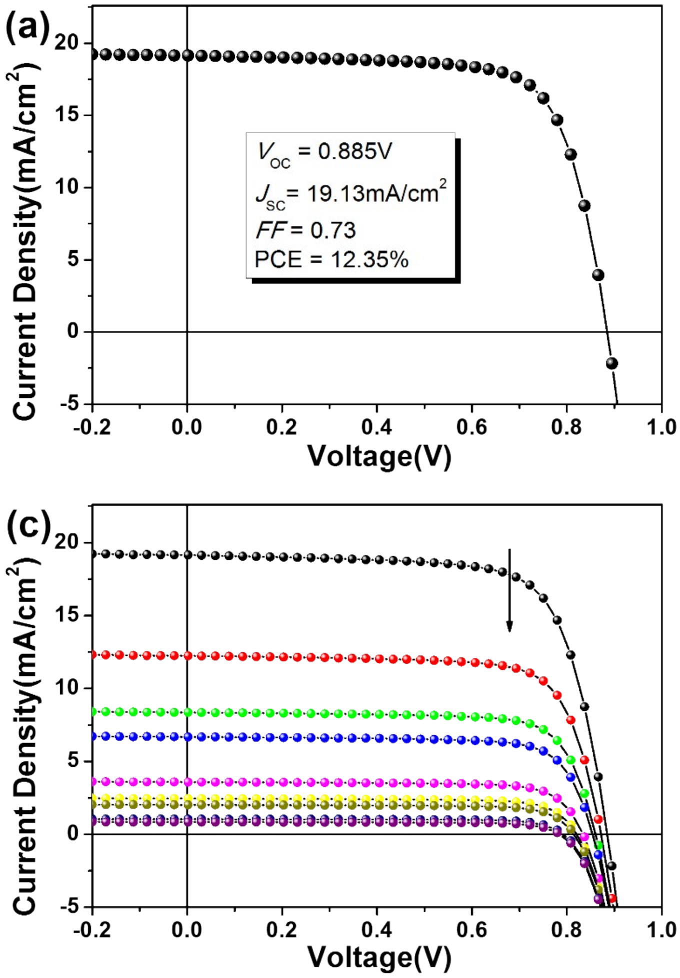


Fig. S4 (a) The highest PCE characterizations of flexible OSCs based on D-Maltose doped PET/ PH1000 electrodes, (b) The light intensity dependence of the *J-V* performance.

Comparison of this work with reported results

Table S1. Comparison of PCE parameters between this work and reported results in flexible organic solar cells with various FTEs.

FTE categories	Active layer	Ave. PCE (%)	Refer.
PET/PEDOT:PSS	P3HT:PCBM	4.1	[1]
PET/PEDOT:PSS	P3HT:PCBM	3.56	[2]
PET/PEDOT:PSS	PTB7:$PC_{71}BM$	6.6	[3]
PET/PEDOT:PSS	PBDB-T:IT-M	10.12	[4]
PET/PEDOT:PSS	PBDB-T-2Cl, IT-4F	12.35	This work
PET/PEDOT:PSS	PffBT4T-2OD:$PC_{61}BM$:$PC_{71}BM$	6.6	[5]
PET/Silver NWs	PTB7-Th:$PC_{71}BM$	8.75	[6]
PET/Ag grid	PTB7-Th:$PC_{71}BM$	6.51	[7]
PET/Ag NPs	P3HT:PCBM	3.26	[8]
PET/Ag-mesh/ PEDOT:PSS	PBDB-T:PTB7-Th:IHIC	8.76	[9]
PET/Ag grid/PH1000	PTB7:$PC_{71}BM$	9.5	[10]
PET/ ultrathin Ag/PEIE	PBDTT-F-TT:$PC_{71}BM$	10.4	[11]
Parylene/ITO/ZnO	PNTz4T: $PC_{71}BM$	7.9	[12]
PEN/ITO/PEIE	PCE-10:IEICO-4F	12.5	[13]
WO_3/Ag/WO_3	PTB7:$PC_{71}BM$	5.71	[14]
PET/ITO/ZnO/PEIE	PTB7:$PC_{71}BM$	8.12	[15]
PET/AgNWgraphene	PTB7:$PC_{71}BM$	6.47	[16]
PEN/Graphene/ PEDOT:PSS	PTB7:$PC_{71}BM$	7.1	[17]
PEN/ITO	PSBTBT:$PC_{71}BM$/P3HT:ICBA	8.7	[18]

Bending test of flexible OSCs

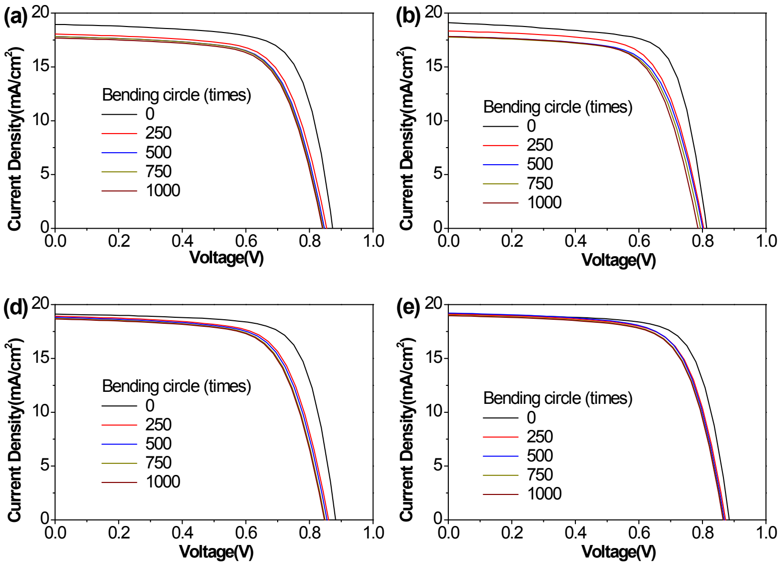


Fig. S5 *J-V* results of bending test for flexible organic solar cells based on: (a) pure PH1000/PET; (b) PH1000+D-Glucose/PET; (c) PH1000+D-Sucrose/PET; (d) PH1000+D-Glucitol/PET, and (e) PH1000+D-Maltose electrode, respectively. The bending test was carried out by subjecting the devices to a cylinder with a radius of r =4 mm.

In order to better understand the changes of performance, bending performance of PBDB-T-2Cl: IT-4F based flexible organic solar cells with various polyhydroxyl compounds doped PH1000/PET electrodes are shown in **Fig. S5**, the detailed photovoltaic parameters are summarized in **Table S2**. The test is performed by subjecting the investigated devices to a cylinder (r = 4 mm) in a N_2 atmosphere without encapsulation. In **Fig. S5** (a) for pure PH1000/PET, the original PCE value without bending is 11.85%, with V_{oc} of 0.873 V, J_{sc} of 18.93 mA/cm^2, and *FF* of 71.58%, respectively. After 250 bending cycles, the parameters of V_{oc}, J_{sc}, and *FF* show a significant decline simultaneously, especially for the J_{sc}, and *FF*, resulting in a decreased PCE of 10.42%. Notably, the reduction of latter bending test is not as obvious as that in front, excluding the unavoidable errors exhibit in the testing process, finally resulting in a PCE of 9.84% after 1000 bending cycles, which is ~ 83% to the original values. In addition, For D-Glucose, D-Sucrose and D-Glucitol doping, they still can remain ~87%, ~88%, and ~90% of the original values after 1000 bending cycles, respectively. It can be clearly seen that Maltose doping electrode exhibits a best blending performance, the original PCE value without bending is 12.35%, with V_{oc} of 0.885 V, J_{sc} of 19.13 mA/cm^2, and *FF* of 72.92%, respectively. After 250 bending cycles, it still can maintain ~ 95% of the original value with a decreased V_{oc}, and *FF*, resulting in a PCE of 11.75%. Similar to the previous results, latter bending test show less impact on the devices' performance, finally resulting in an excellent PCE of 11.36% after 1000 bending cycles, which is ~92% to the original values.

Table S2. Bending performance of flexible organic solar cells with various polyhydroxyl compounds doping PH1000 electrode. The bending test was carried out by subjecting the devices to a cylinder with a radius of r =4 mm.

Devices	Bending circle	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	*PCE* [%]
PH1000/PET	0	0.873	18.93	71.58	11.85
	250	0.854	17.87	68.32	10.42
	500	0.847	17.72	67.28	10.10
	750	0.843	17.53	67.21	9.93
	1000	0.843	17.42	67.04	9.84
PH1000+D-Glucose/PET	0	0.814	19.08	71.64	11.12
	250	0.805	18.36	68.96	10.20
	500	0.802	17.86	68.75	9.86
	750	0.796	17.77	68.84	9.74
	1000	0.788	17.84	68.79	9.67
PH1000+D-Sucrose/PET	0	0.839	19.68	70.10	11.58
	250	0.821	19.11	68.06	10.68
	500	0.817	18.67	68.13	10.39
	750	0.815	18.53	67.96	10.27
	1000	0.814	18.44	67.90	10.19
PH1000+D-Glucitol/PET	0	0.870	19.46	70.15	11.82
	250	0.858	18.90	68.21	11.06
	500	0.853	18.79	67.76	10.86
	750	0.847	18.67	67.85	10.73
	1000	0.845	18.61	67.66	10.64
PH1000+D-Maltose/PET	0	0.885	19.13	72.92	12.35
	250	0.873	19.08	70.53	11.75
	500	0.869	19.18	69.48	11.58
	750	0.866	18.99	69.56	11.44
	1000	0.865	18.92	69.41	11.36

Folding test of flexible OSCs

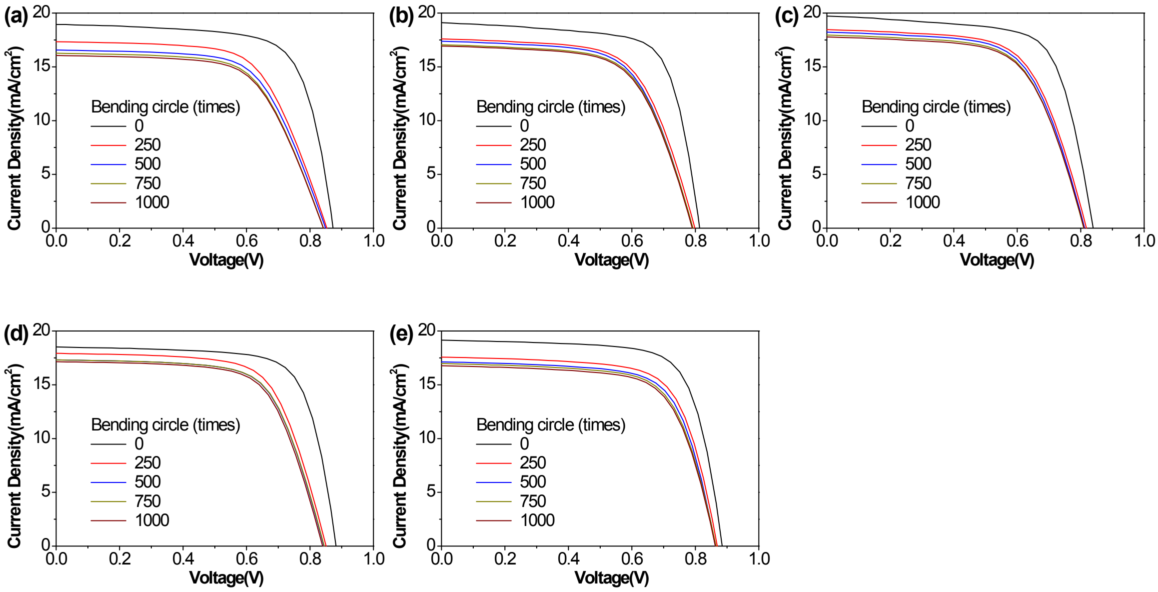


Fig. S6 *J-V* results of folding test for flexible organic solar cells based on: (a) pure PH1000/PET; (b) PH1000+D-Glucose/PET; (c) PH1000+D-Sucrose/PET; (d) PH1000+D-Glucitol/PET, and (e) PH1000+D-Maltose electrode, respectively. The bending test was carried out by subjecting the devices to a cylinder with a radius of r < 1 mm.

As shown in **Fig. S6**, for pure PH1000/PET based devices, the original PCE without folding is 11.85%, after 250 bending cycles, the PCE significantly decreased to 9.43%, which is ~79.6% of the original value. The morphology was damaged by the more-hostile folding test in a certain extent, leads to hugely decreased FF, finally resulting in a PCE of 8.53% after 1000 bending cycles, which is ~ 72% to the original values. For D-Glucose, D-Sucrose and D-Glucitol doping, the results show that they can remain ~76%, ~78%, and ~78% of the original values after 1000 bending cycles, respectively. Maltose doping still presents the best blending performance in **Fig. S6** (d), the original PCE value without bending is 12.35%, after 250 bending cycles, the PCE decreased to 10.61%, finally resulting in a PCE of 9.88% after 1000 bending cycles, which is ~80% to the original values.

Table S3. Folding performance of flexible organic solar cells with various polyhydroxyl compounds doping PH1000 electrode. The folding test was carried out by subjecting the devices to a cylinder with a radius of r < 1 mm.

Devices	Bending circle	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	*PCE* [%]
PH1000/PET	0	0.873	18.93	71.58	11.85
	250	0.853	17.56	62.96	9.43
	500	0.849	16.76	63.11	8.98
	750	0.842	16.47	62.75	8.70
	1000	0.841	16.26	62.36	8.53
PH1000+D-Glucose/PET	0	0.814	19.08	71.64	11.12
	250	0.799	17.62	64.86	9.13
	500	0.792	17.42	63.35	8.74
	750	0.793	17.06	63.19	8.55
	1000	0.791	16.94	63.04	8.45
PH1000+D-Sucrose/PET	0	0.839	19.68	70.10	11.58
	250	0.818	18.46	64.09	9.68
	500	0.813	18.15	62.75	9.26
	750	0.809	17.96	62.93	9.14
	1000	0.810	17.80	62.64	9.03
PH1000+D-Glucitol/PET	0	0.870	19.46	70.15	11.82
	250	0.851	17.86	66.18	10.06
	500	0.844	17.50	65.46	9.67
	750	0.845	17.19	65.71	9.55
	1000	0.840	17.13	65.75	9.46
PH1000+D-Maltose/PET	0	0.885	19.13	72.92	12.35
	250	0.869	17.55	69.56	10.61
	500	0.863	17.11	68.82	10.16
	750	0.865	16.96	68.50	10.05
	1000	0.863	16.74	68.39	9.88

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