Electronic Supplementary Information

The role of intermolecular forces in contact electrification on polymer surfaces and triboelectric nanogenerators

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Materials and testing methods

Thermoplastic polymer films used for studies were prepared using hot pressing. This method was used for polymers such as low density polyethylene (LDPE; Exxon Mobil 171BA), high density polyethylene (HDPE; Exxon Mobil HTA108), poly(vinyl acetate) (PVAc, Sigma Aldrich, Mw 500 000), polyvinylidene fluoride (PVDF, Sigma Aldrich, Mw 530 000), polystyrene (PS, recycled), polycarbonate (PC, recycled), poly(methyl methacrylate) (PMMA, Sigma Aldrich), poly(ethylene-co-vinyl acetate) copolymers with two different vinyl acetate contents (EVA; VA content 16 % and 23 %, Sigma Aldrich), two different ethylene-octene copolymers (EO; Engage 8200, Engage 8400, Dow), styrene-ethylene-butylene-styrene copolymer (SEBS; Lifoflex UV 306A 1030), poly(hexamethylene adipamide) (PA 6/6, Sigma Aldrich) and plasticized polyvinyl chloride (PVC pl., recycled). Polymers for hot pressing were obtained as pellets or powders. At first the appropriate amount of polymer was weighed to allow preparation of polymer film with size 70×100 mm. Metal frame of this selected size ensured that all films have uniform thickness – 100 µm. Temperature of hot plates was set according to each polymers melting temperature. After short heating at minimum pressure (1 minute) the polymer was pressed with 4-5 MPa pressure to obtain uniform film. After 3 minutes the sample was removed from hot press and cooled to room temperature.

Some of the polymer films were obtained commercially and used as received. This includes polyethylene terephthalate (PET, Kintec, 0.12 mm), polytetrafluoroethylene (PTFE, Sigma Aldrich, 0.1 mm), polyimide Kapton (PI, Sigma Aldrich, 0.125 mm), polypropylene (PP, SIA “Plastika 1”, 0.1 mm) and cellulose triacetate (Cel. Tr., Sigma Aldrich, 0.125 mm). Polymer films were characterized by atomic force (AFM) surface roughness and nanoindentation hardness measurements.

Polymer films were used to study contact electrification and prepare triboelectric generators (TEG). For TEG polymer films were carefully adhered on Sn doped In_2O_3 (ITO) coated PET (sheet resistance 60 Ω sq^{-1}, Kintec)) by using conductive adhesive carbon tape (Science Services) as depicted in Figure S1.

Polydimethylsiloxane (PDMS, Sylgard 184 kit) films with different cross-linking degree were prepared by mixing base polymer and curing agent in different ratios (1:3, 1:5, 1:10, 1:15, 1:20, 1:25

and 1:30). PDMS films were spin coated directly on ITO/PET substrate. Rotation speed was 3000 rpm. Before spin coating, mixtures were degassed. PDMS films were cured in 100°C for 30 min.

To study the roughness influence on contact electrification smooth and rough EC, PC and PS polymer films were deposited on conductive electrodes by spin-coating. Porous films were obtained by immersing spin-coated polymer in antisolvent. The EC polymer was dissolved in toluene/absolute ethanol (80/20) solution at concentration 10 wt% and hexane was used as antisolvent. The PC or PS polymer was dissolved in chloroform at concentration 15% for smooth sample but for rough sample in dimethylformamide and methanol was used as antisolvent.

The open circuit voltage (V_{OC}) at load resistance $1 \cdot 10^9\ \Omega$ and short circuit current (I_{SC}) was measured for all TEG devices by using a custom-made voltage divider in combination with a Keithley 6514 electrometer connected to a Picoscope 5444B PC oscilloscope to provide high time resolution. The instantaneous power density under resistive load was calculated by Joule's Law (1):

$$P = V^2 R^{-1} \tag{1}$$

where V is voltage and R is load resistance. Energy density was obtained as integral of power over time. The average power density of contact-separation cycle was then calculated accordingly to duration of the voltage peak.

The surface charge was estimated from current measured between TEG electrodes under operation by using equation $Q=\int i dt$ (where i – instantaneous current). The data for all polymers were collected after 5000 contacting-separating cycles after complete stability in measured surface charge was observed. Contacting area (sample size) was 5 cm^2. Pressing force (10 N), frequency (1 Hz), separation speed (10 mm s^{-1}) and gap (5 mm) between sample sides for TEG performance measurements were kept constant by using INSTRON E1000 All-Electric Dynamic Test Instrument. Simultaneously, device is measuring the force needed to separate two films in TEG.

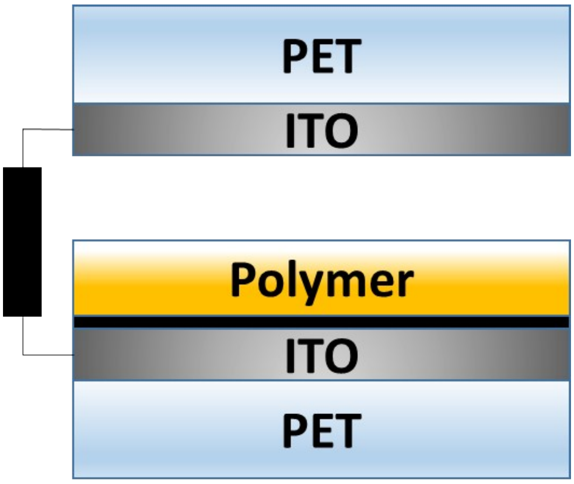

Figure S1. Simplified schematic TEG device. Polymer is attached to ITO layer by conductive carbon black adhesive tape.

Simplified electric circuit for voltage measurement under capacitive load is demonstrated in Figure S2. Voltage was measured by oscilloscope (Picoscope 5444B PC), but to adjust input parameters high input resistance amplifier (electrometer Keithley 6514) was used. Voltage is measured against ground. Capacitance of capacitor in the circuit is variable. Energy was calculated using capacitor stored energy equation: $E=0.5CV^2$, where C is capacitance and V is voltage across capacitor plates.

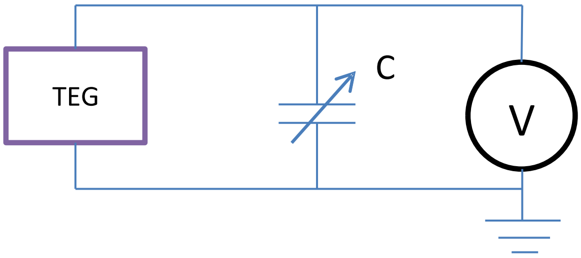

Figure S2. Simplified electric circuit for voltage measurement under capacitive load

To measure hardness and modulus of polymer films we used Agilent Nano G200 nanoindentation unit using Berkovich diamond tip to obtain hardness (H, GPa) of polymer material films, which was crucial to evaluate correlation between hardness and contact electrification of polymer materials. For nanoindentation measurements polymer film samples were rigidly adhered on glass slides. Hardness values for all sample films were measured at indentation depth of 1.5 μm. The roughness measurements were performed with atomic force microscope (Smena, NT-MDT) in semi-contact mode using NSG03 probes (NT-MDT) with tip curvature radius 10 nm and force constant 0.35-6.1 N/m. The roughness values are calculated with Gwyddion software. The X-ray photoelectron spectroscopy (XPS) data was measured using the electron energy hemispherical analyzer Scienta SES100 and a VG Scientific XPS/1 X-ray gun.

To show that upon contacting-separating chemically the same polymer with different physicochemical properties the contact electrification can be observed, we varied physicochemical properties of commercial PP film by changing thermal history by heating at 130°C for 60 min. The changes in physicochemical properties of non-modified and heated PP films were confirmed by Differential Scanning Calorimetry (Mettler Toledo, model DSC3).

The influence of adhesion on contact electrification was studied in two different ways – the adhesion was increased by increasing pressing force and by modifying polymer surfaces. Pressing force was varied for PDMS sample (10:1) where it was contacted for different pressure from 1 N till 50 N. High performance TEG device was prepared by surface modification of SEBS. For surface treatment we immersed SEBS sample film into H_2O_2 solution (Sigma-Aldrich 30%) for 1 hour. After immersion sample was washed with distilled water and dried. The modified SEBS film was adhered on ITO/PET substrate as described above.

Experimental measurement details and supplementary measurement results

Table S1. Hardness and Modulus values measured by nanoindentation

Polymer material	Hardness H, GPa	Modulus, GPa
SEBS	0.0056	0.029
Plasticized PVC	0.0045	0.032
EO copolymer 8400	0.0211	0.054
EO copolymer 8200	0.0010	0.177

EVA copolymer (23 % VA)	0.0223	0.055
EVA copolymer (16 % VA)	0.0156	0.085
LDPE	0.0149	0.516
PTFE	0.0326	0.765
HDPE	0.0445	2.033
PVDF	0.1198	2.815
PP	0.1076	2.820
PC	0.1499	2.861
PET	0.2716	3.375
Cellulose triacetate	0.1743	3.368
PI	0.2210	3.554
PA 6,6	0.1914	3.776
PS	0.2109	4.154
PVAc	0.2136	5.241
PMMA	0.2298	5.478

Table S2. Polymer surface roughness measured by AFM

Polymer	**Roughness, nm**		**Polymer**	**Roughness, nm**
EO copolymer 8200	63.95		PC	69.85
EO copolymer 8400	58.02		PET	36.79
EVA copolymer (16 % VA)	60.34		PVC	60.62
EVA copolymer (23 % VA)	35.29		PP	64.48
SEBS	79.40		PS	52.89
HDPE	54.40		PTFE	67.57

LDPE	57.05		PVAc	55.84
Nylon PA 6,6	122.80		PVDF	77.95
PMMA	61.75		Cellulose triacetate	12.42
PI	44.10			

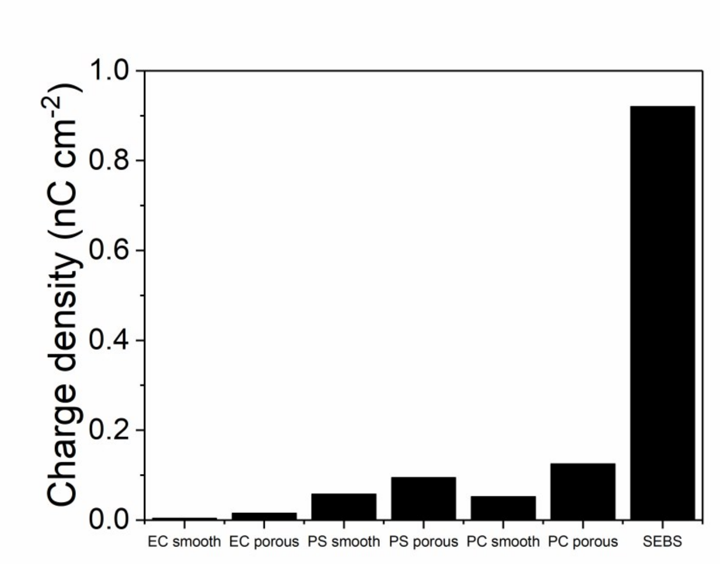

Figure S3. Influence of surface roughness on the contact electrification (charge density). In order to exclude the influence of preparation method, all samples in this case were prepared by spin-coating as described above. Porous film was obtained by immersing spin-coated polymer in antisolvent. Surface charge measured in TEG device presented in Figure S1. Rough polymers exhibit a larger surface charge than their smooth counterparts (exact surface charge and roughness values are presented in Table S3). However, the polymers with small cohesion energy have a larger impact on surface charge.

Table S3. The roughness and surface charge value (contact with ITO) for different rough and smooth polymers in TEG device. In order to exclude the influence of preparation method, all samples in this case were prepared by spin-coating as described above. Porous film was obtained by immersing spin-coated polymer in antisolvent. Rough surfaces show larger surface charge.

Polymer	Surface roughness, nm		Surface charge, $C \cdot cm^{-2}$	
	Smooth	Rough	Smooth	Rough
Cellulose triacetate	13.80	56.70	$3.54 \cdot 10^{-12}$	$1.52 \cdot 10^{-11}$
Polystyrene	52.89	123.00	$5.80 \cdot 10^{-12}$	$9.43 \cdot 10^{-11}$
Polycarbonate	69.85	654.24	$5.20 \cdot 10^{-11}$	$1.25 \cdot 10^{-10}$

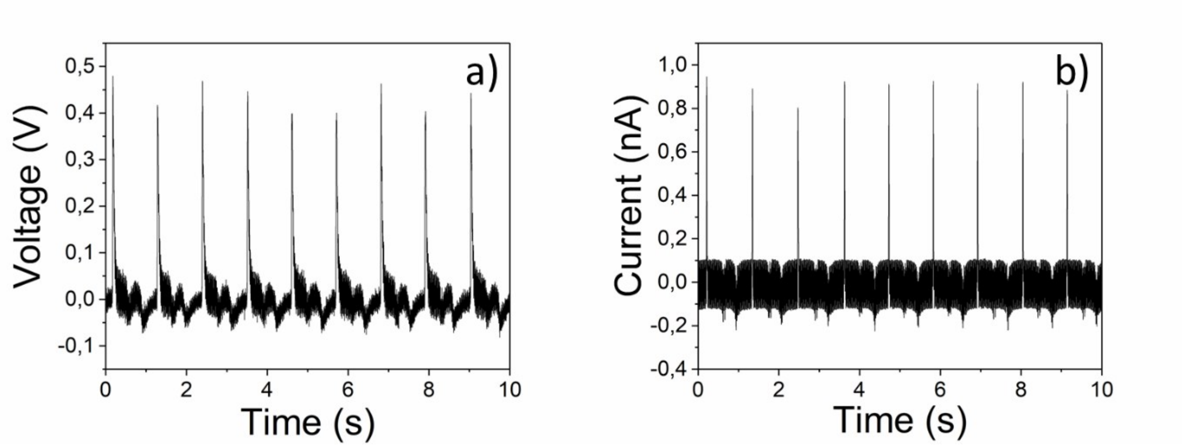

Figure S4. (a) V_{OC} and (b) I_{SC} generated by TEG based on cellulose triacetate and ITO.

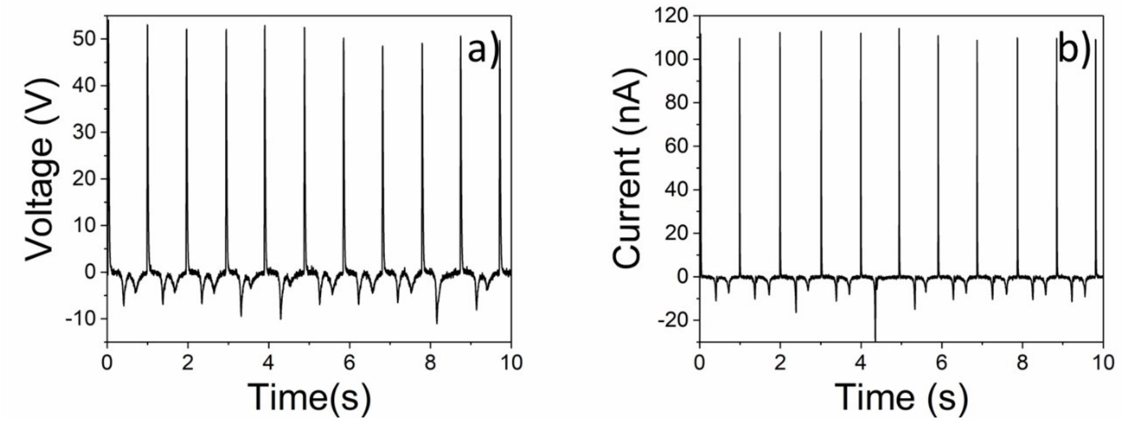

Figure S5. V_{OC} and (b) I_{SC} generated by TEG based on EO 8200 and ITO

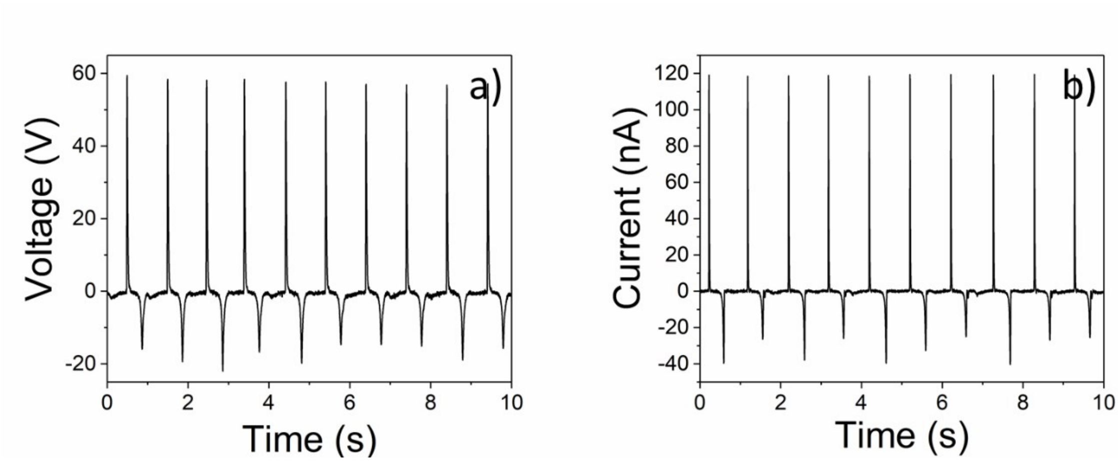

Figure S6. V_{OC} and (b) I_{SC} generated by TEG based on EO 8400 and ITO

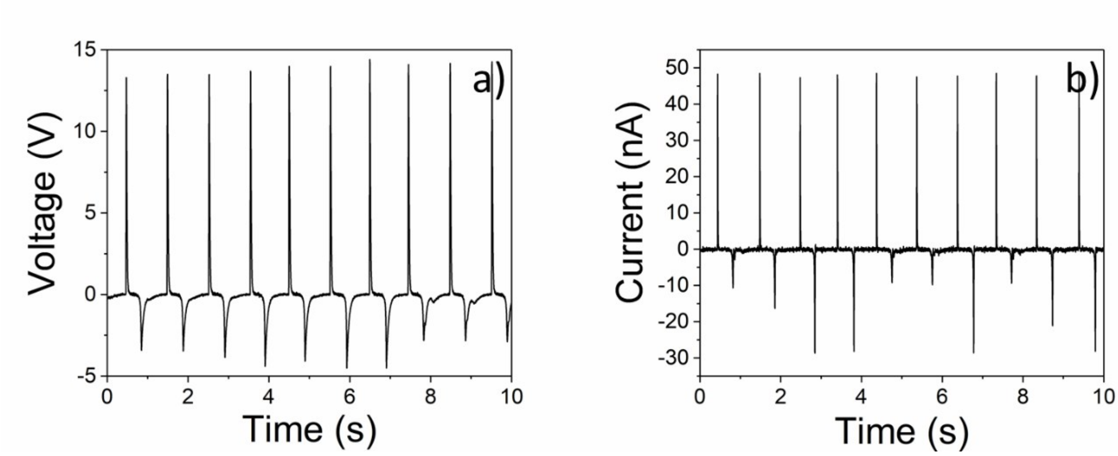

Figure S7. V_{OC} and (b) I_{SC} generated by TEG based on EVA; VA content 16% and ITO

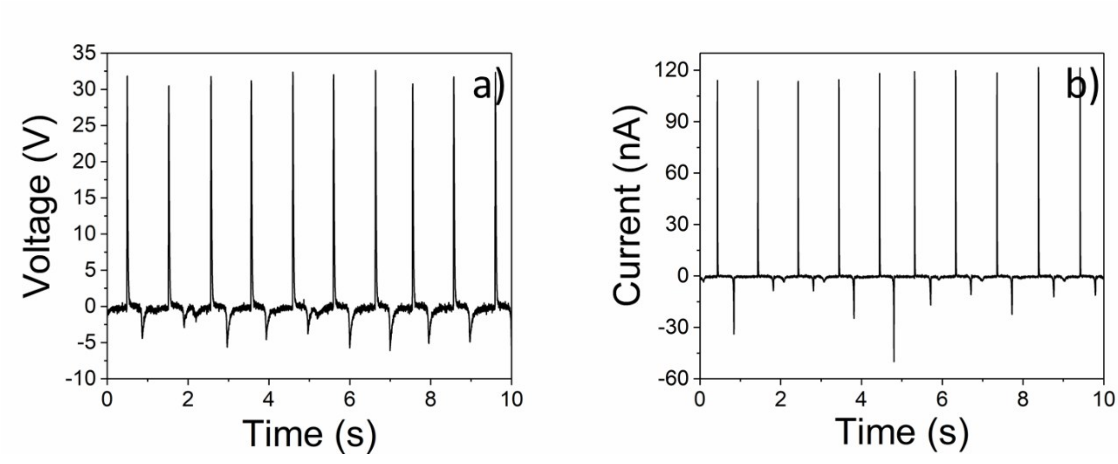

Figure S8. V_{OC} and (b) I_{SC} generated by TEG based on EVA; VA content 23% and ITO

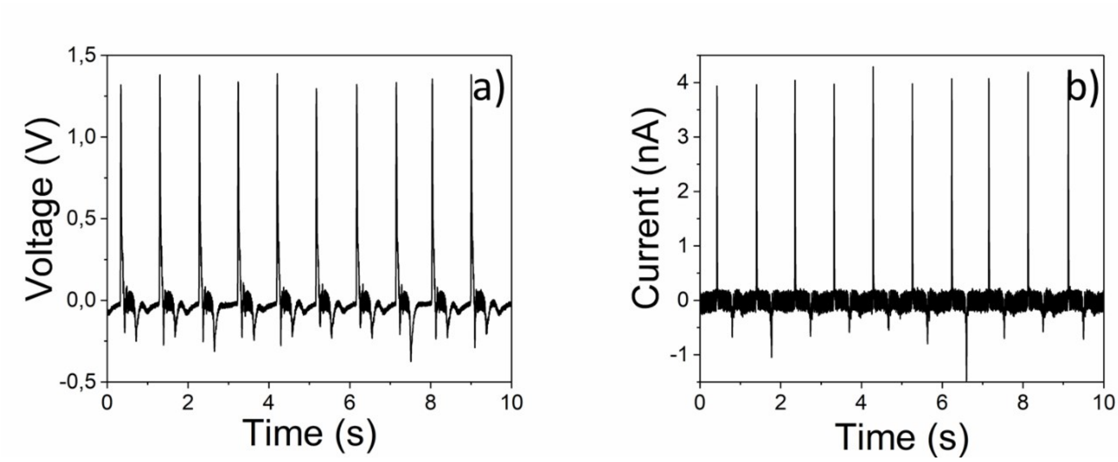

Figure S9. V_{OC} and (b) I_{SC} generated by TEG based on PS and ITO

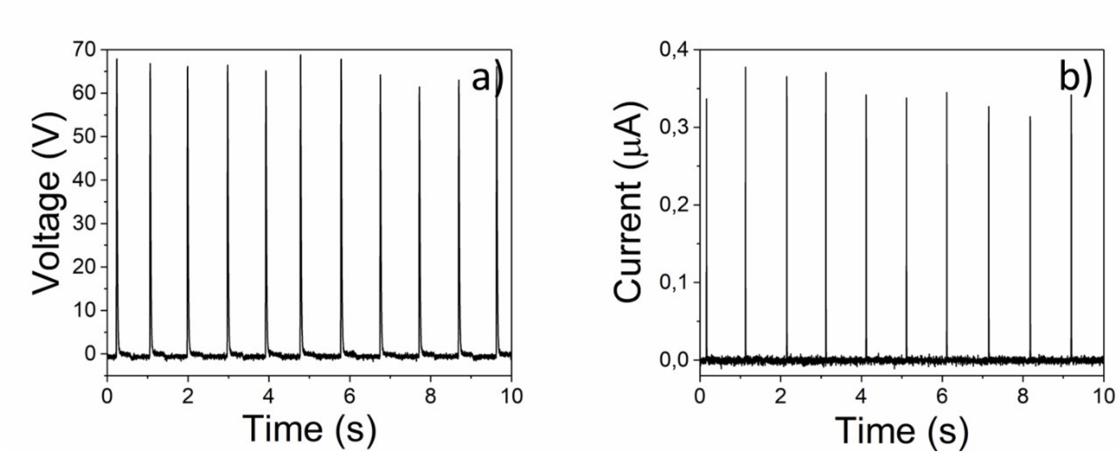

Figure S10. V_{OC} and (b) I_{SC} generated by TEG based on plasticized PVC and ITO

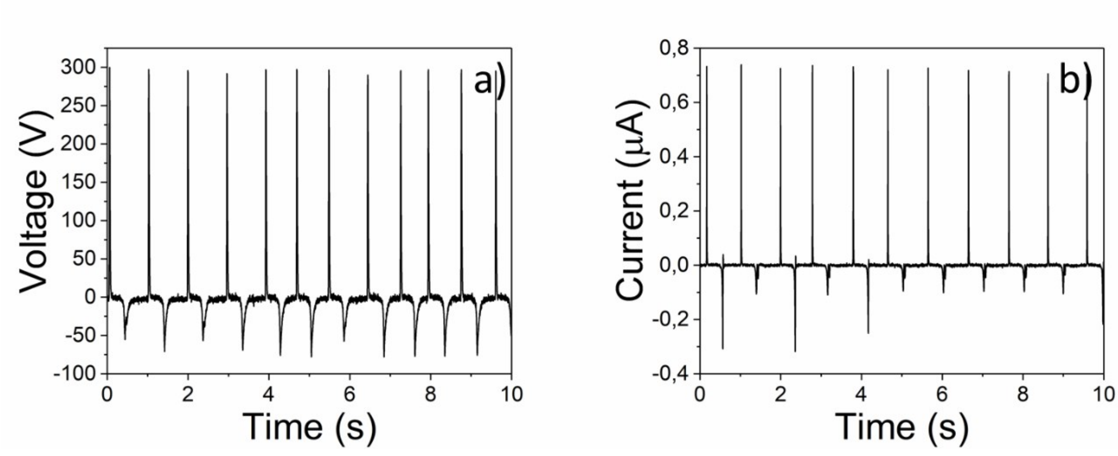

Figure S11. V_{OC} and (b) I_{SC} generated by TEG based on SEBS and ITO

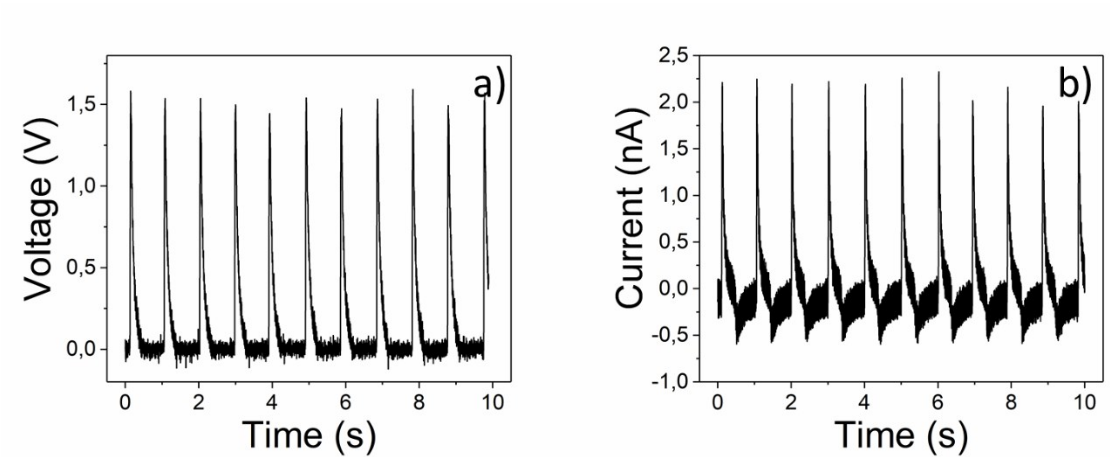

Figure S12. V_{OC} and (b) I_{SC} generated by TEG based on PC and ITO

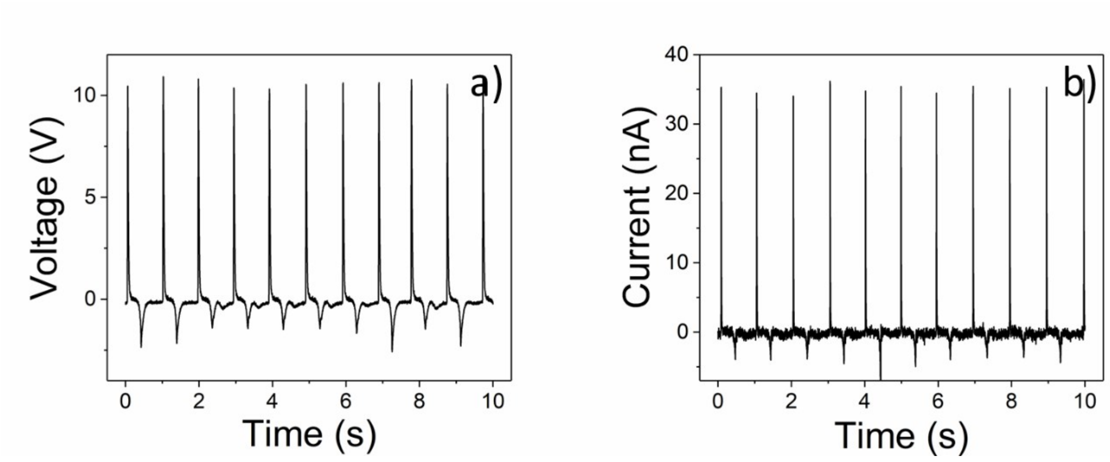

Figure S13. V_{OC} and (b) I_{SC} generated by TEG based on PTFE and ITO

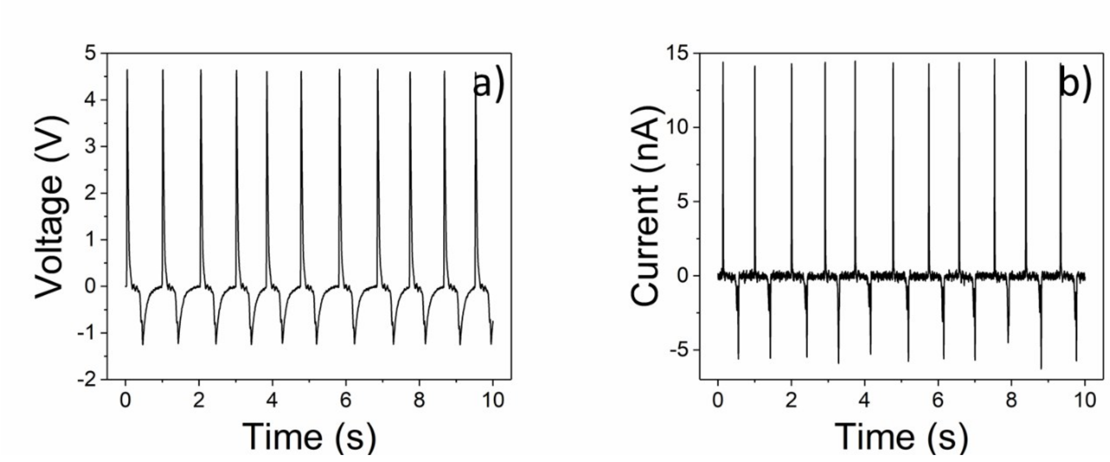

Figure S14. V_{OC} and (b) I_{SC} generated by TEG based on HDPE and ITO

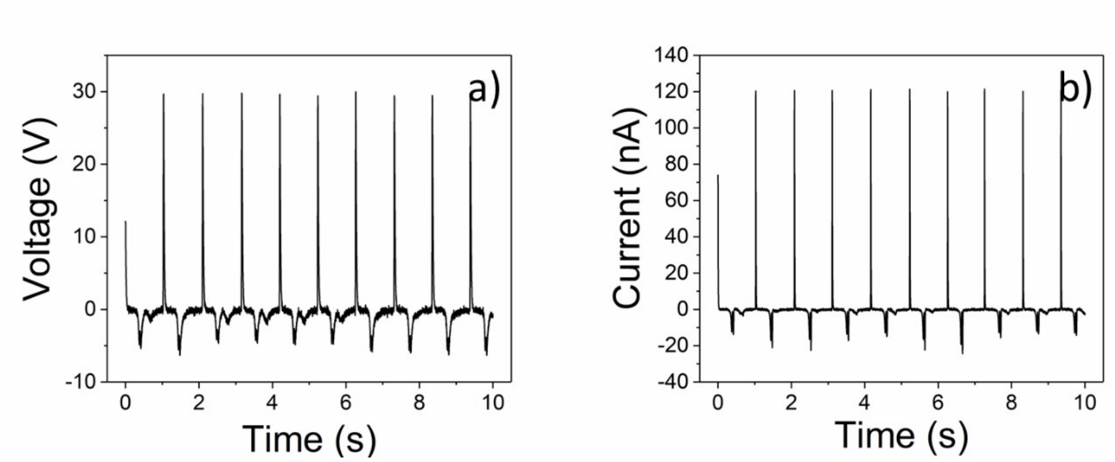

Figure S15. V_{OC} and (b) I_{SC} generated by TEG based on LDPE and ITO

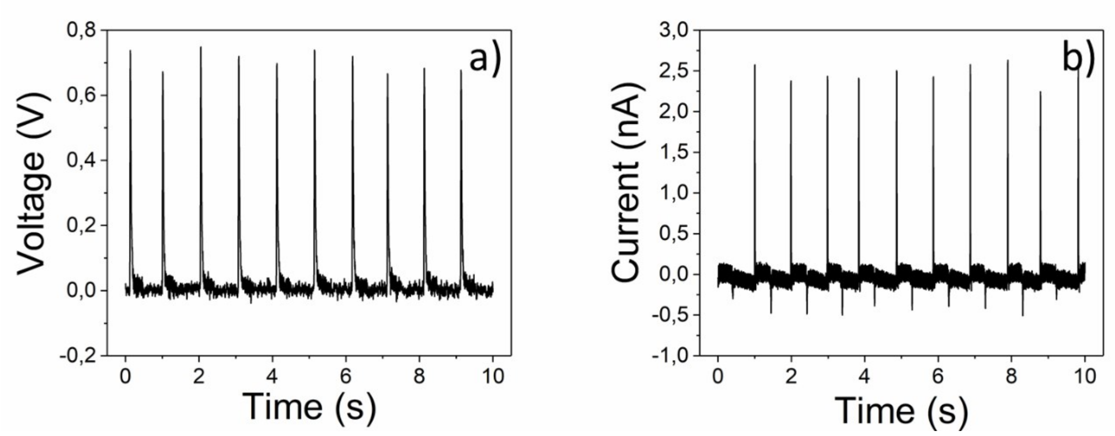

Figure S16. V_{OC} and (b) I_{SC} generated by TEG based on PA 6.6 and ITO

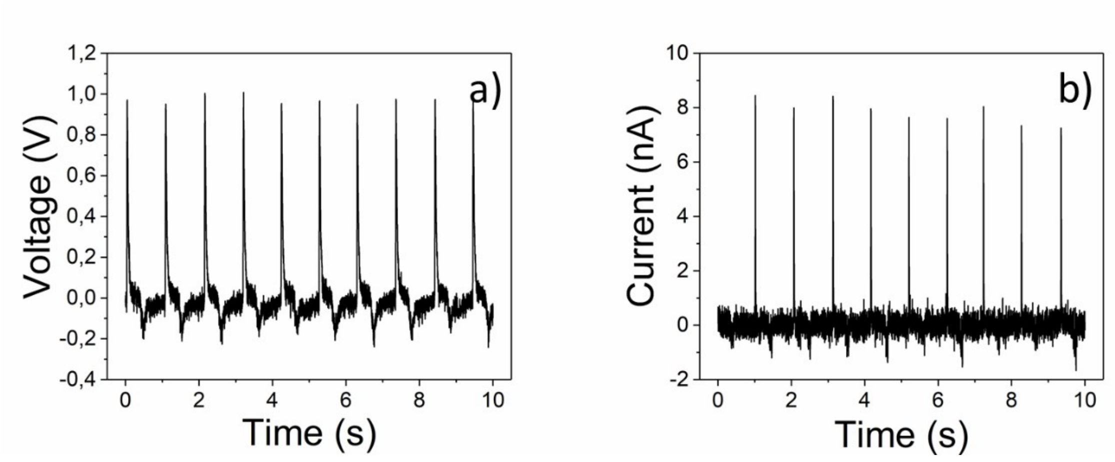

Figure S17. V_{OC} and (b) I_{SC} generated by TEG based on PET and ITO

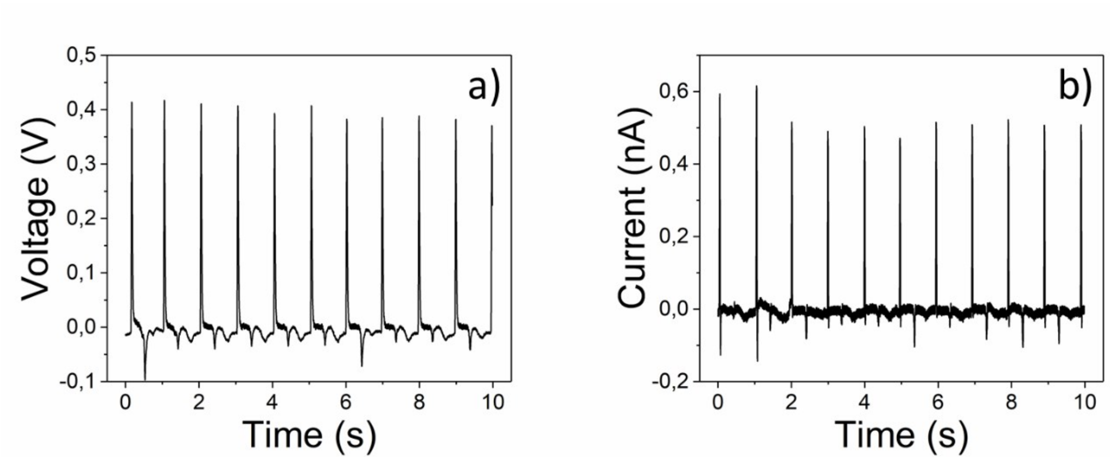

Figure S18. V_{OC} and (b) I_{SC} generated by TEG based on PMMA and ITO

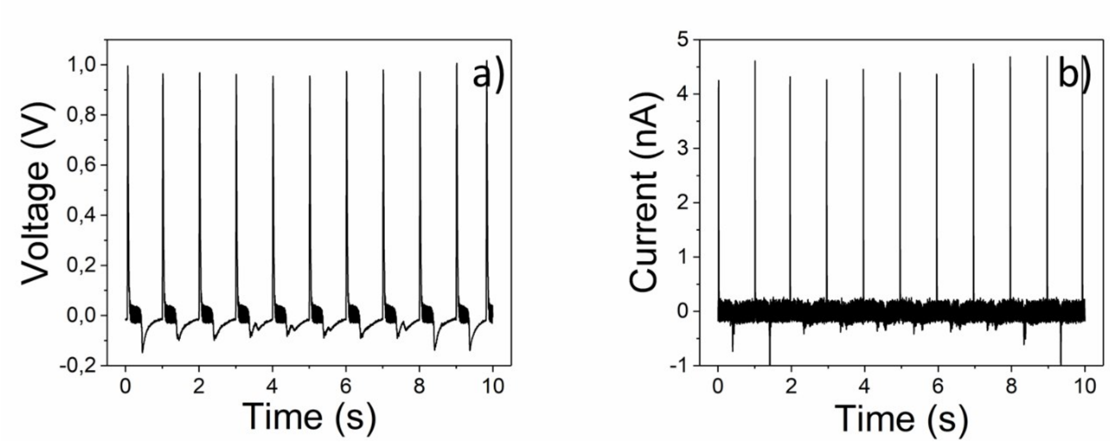

Figure S19. V_{OC} and (b) I_{SC} generated by TEG based on Polyimide and ITO

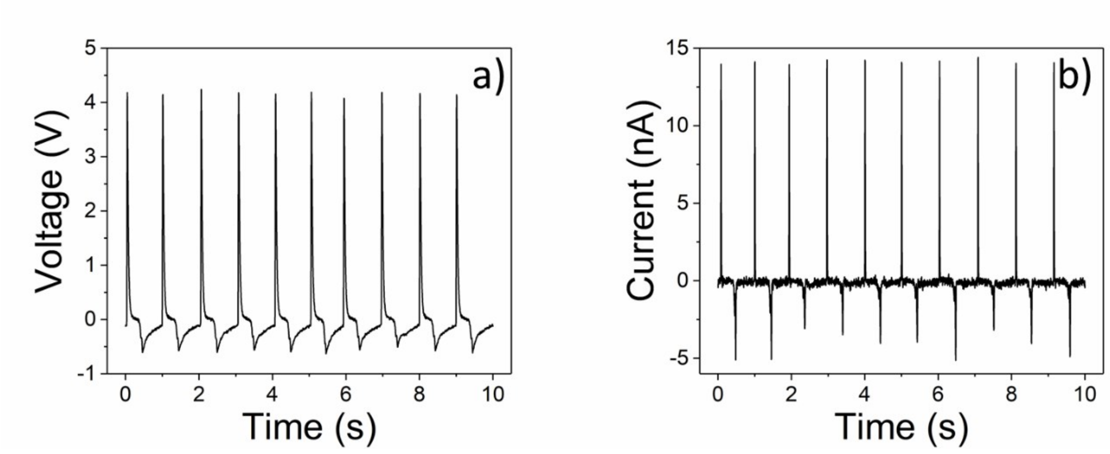

Figure S20. V_{OC} and (b) I_{SC} generated by TEG based on PVDF and ITO

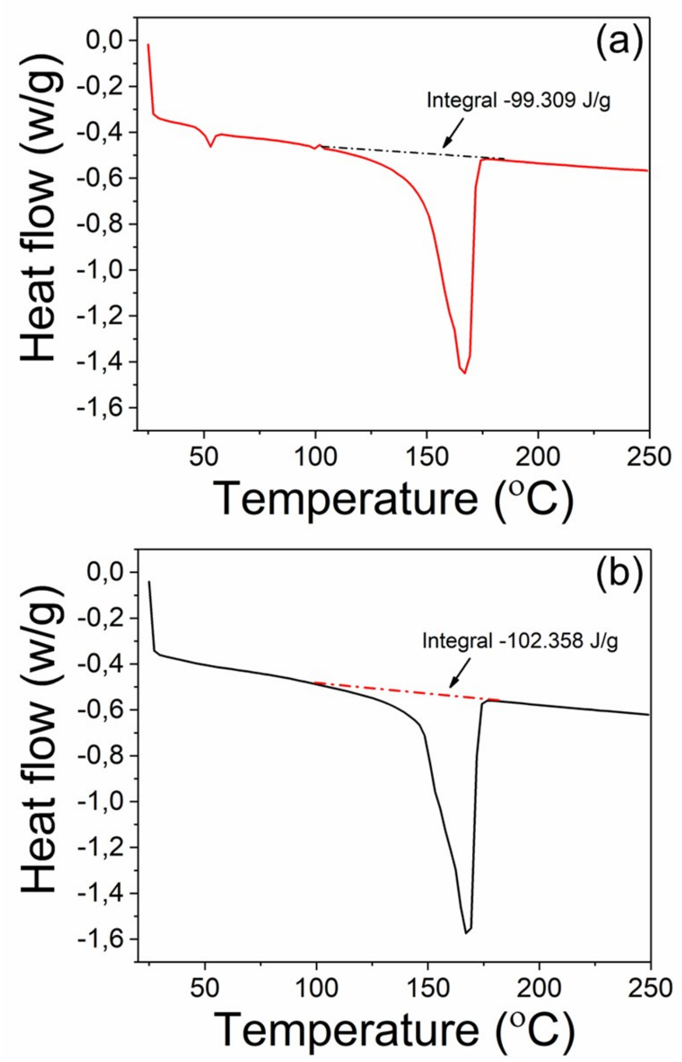

Figure S21. DSC data from (a) non-heated PP and (b) heated PP

We used Shore A hardness (S_A) to calculate modulus (E) of PDMS samples in accordance with equation (2):

$$log_{10}E = 0.0235S_A - 0.6403 \tag{2}$$

The M_C of each composition was calculated using equation (3):

$$M_C = 3\rho RgTE^{-1} \tag{3}$$

where ρ is density of polymer material, R_g the gas constant (8.314 J mol^{-1} K^{-1}) and T absolute temperature (298 K). Density of PDMS was measured with hydrostatic weighing, ρ is 1.03 g cm^{-3}.

Table S4. Hardness and modulus of PDMS samples

Prepolymer : curing agent (weight)	Hardness S_A, Shore A	Modulus E, MPa
3:1	54.0	4.25
5:1	43.5	2.41
10:1	40.0	1.99
15:1	35.3	1.55
20:1	27.3	1.00
25:1	23.5	0.82
30:1	17.0	0.58

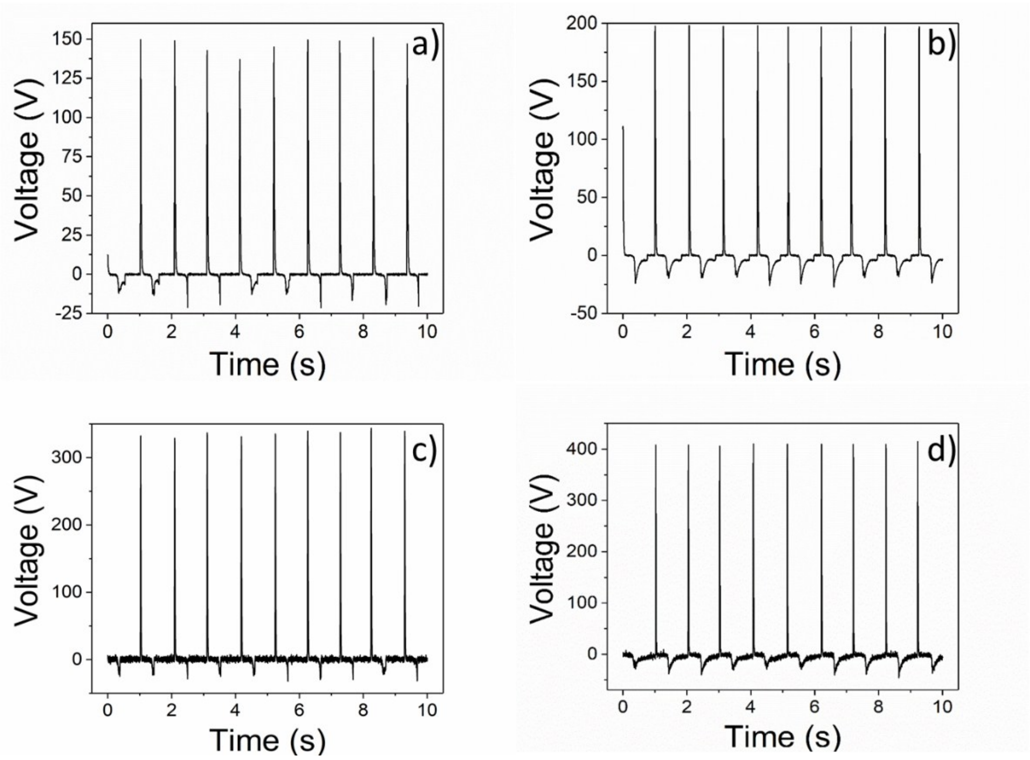

Figure S22. The V_{OC} for TEG device where contacting different crosslinked PDMS vs ITO: a)3:1; b) 10:1; c) 20:1 and d) 30:1

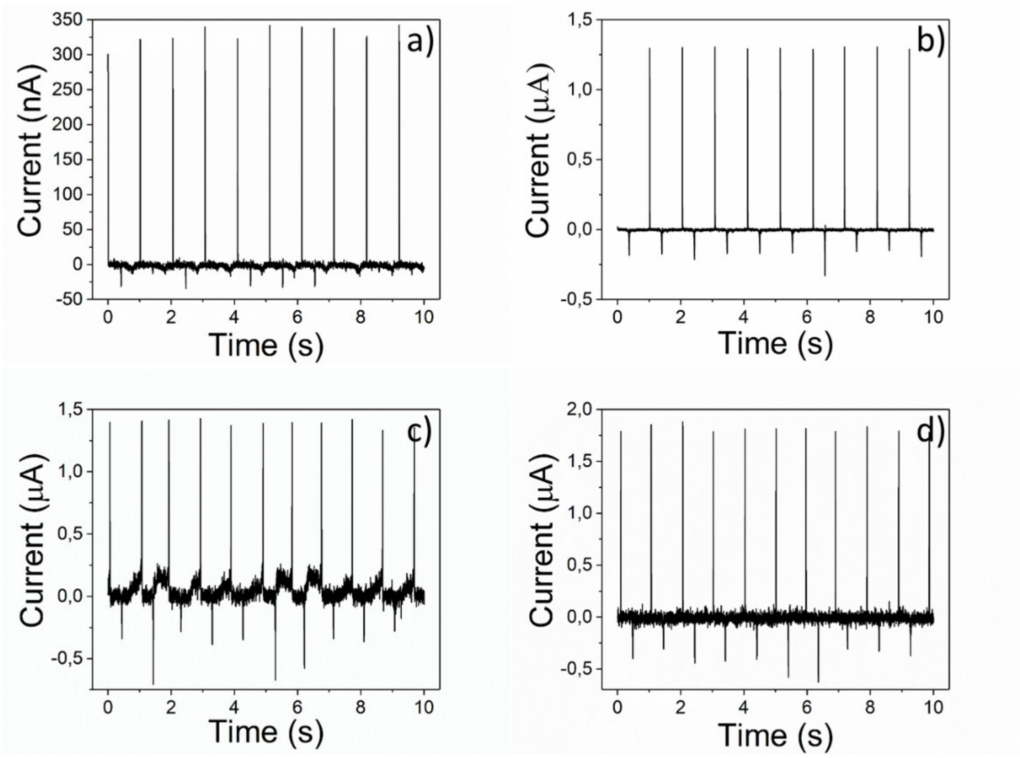

Figure S23. The I_{SC} for TEG device where contacting different crosslinked PDMS vs ITO: a) 3:1; b) 10:1; c) 20:1 and d) 30:1

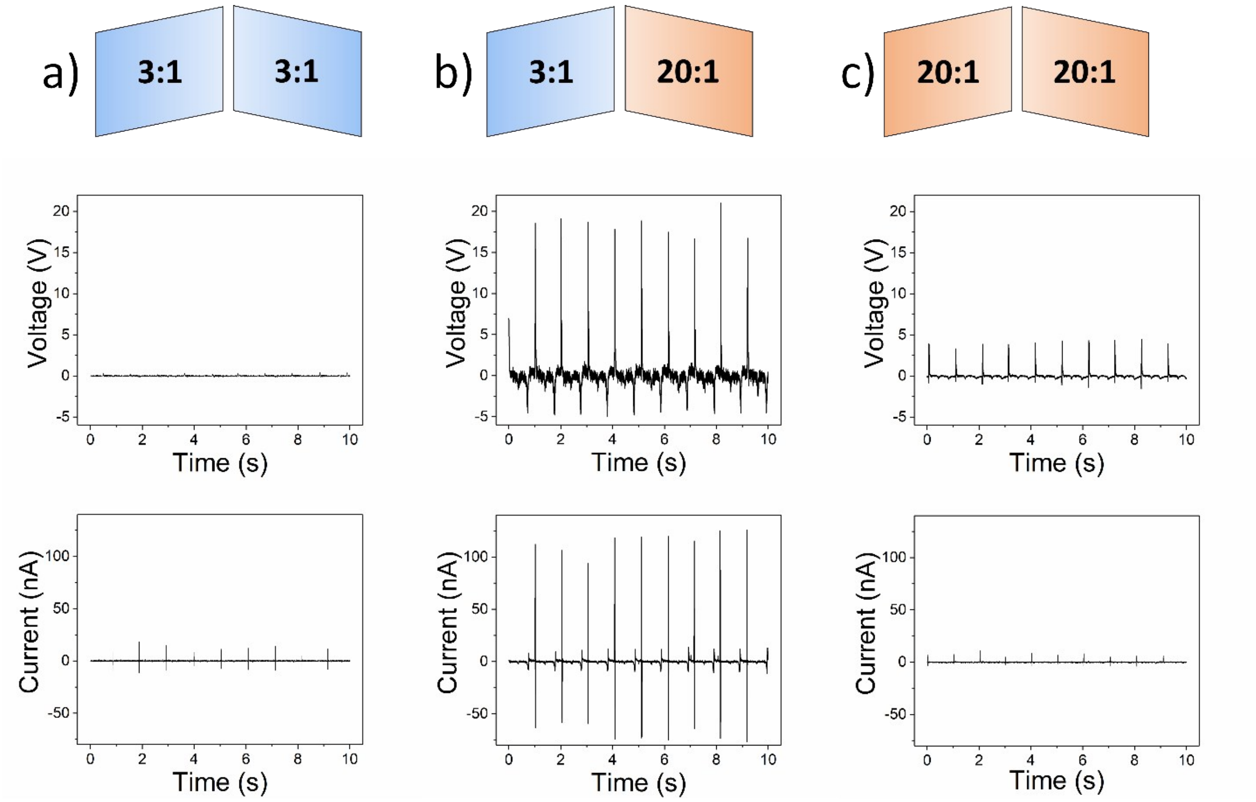

Figure S24. The V_{OC} and I_{SC} for TEG device where crosslinked PDMS films with the same (a and c) or different (b) crosslinking degree are contacted and separated.

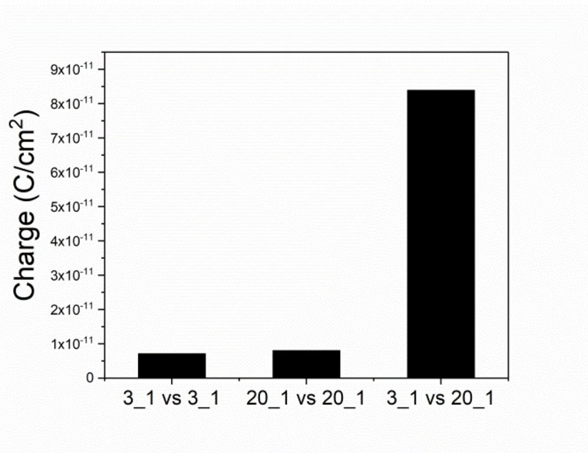

Figure S25. The surface charge for TEG devices based on PDMS contacting layers with the same or different cross-linking degree.

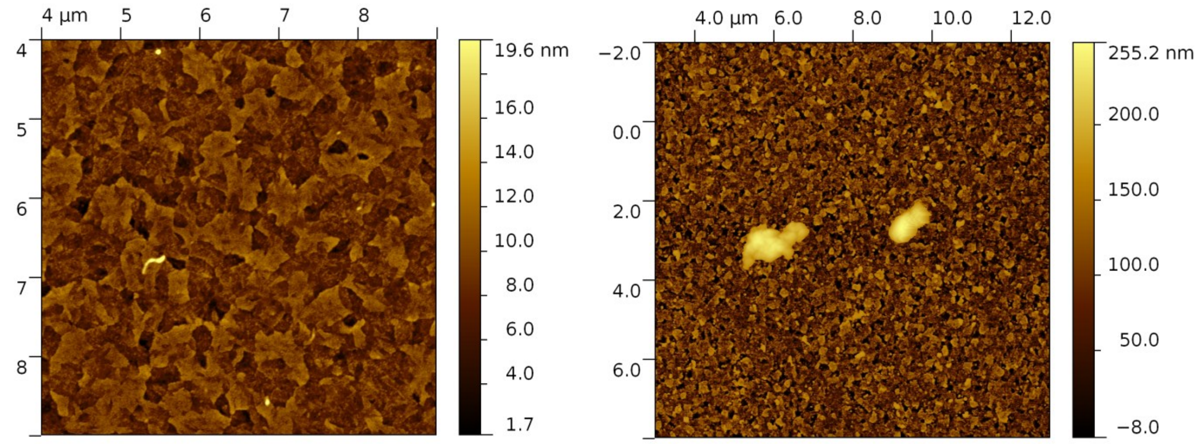

Figure S26. ITO surface before (left) and after (right) contacting with PDMS 10:1 for 10 000 cycles.

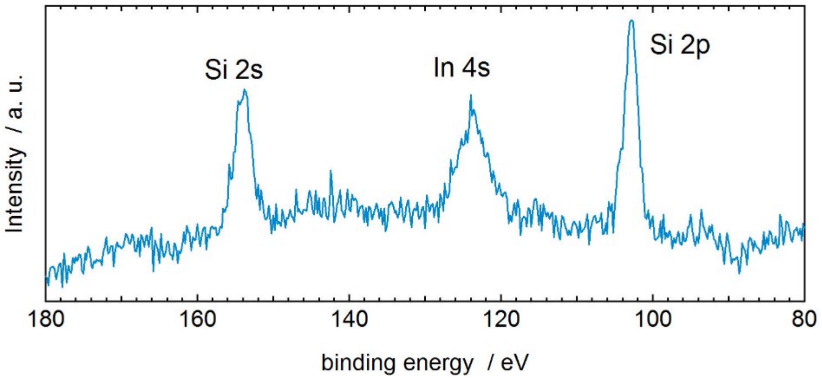

Figure S27. The photoelectron spectrum observed by measuring a signal from ITO surface after contacting with PDMS 10:1 for 10 000 cycles. Signal peaks at 102.7 eV (Si 2p) and 153.8 eV (Si 2s) confirm the transfer of PDMS to the surface of ITO.

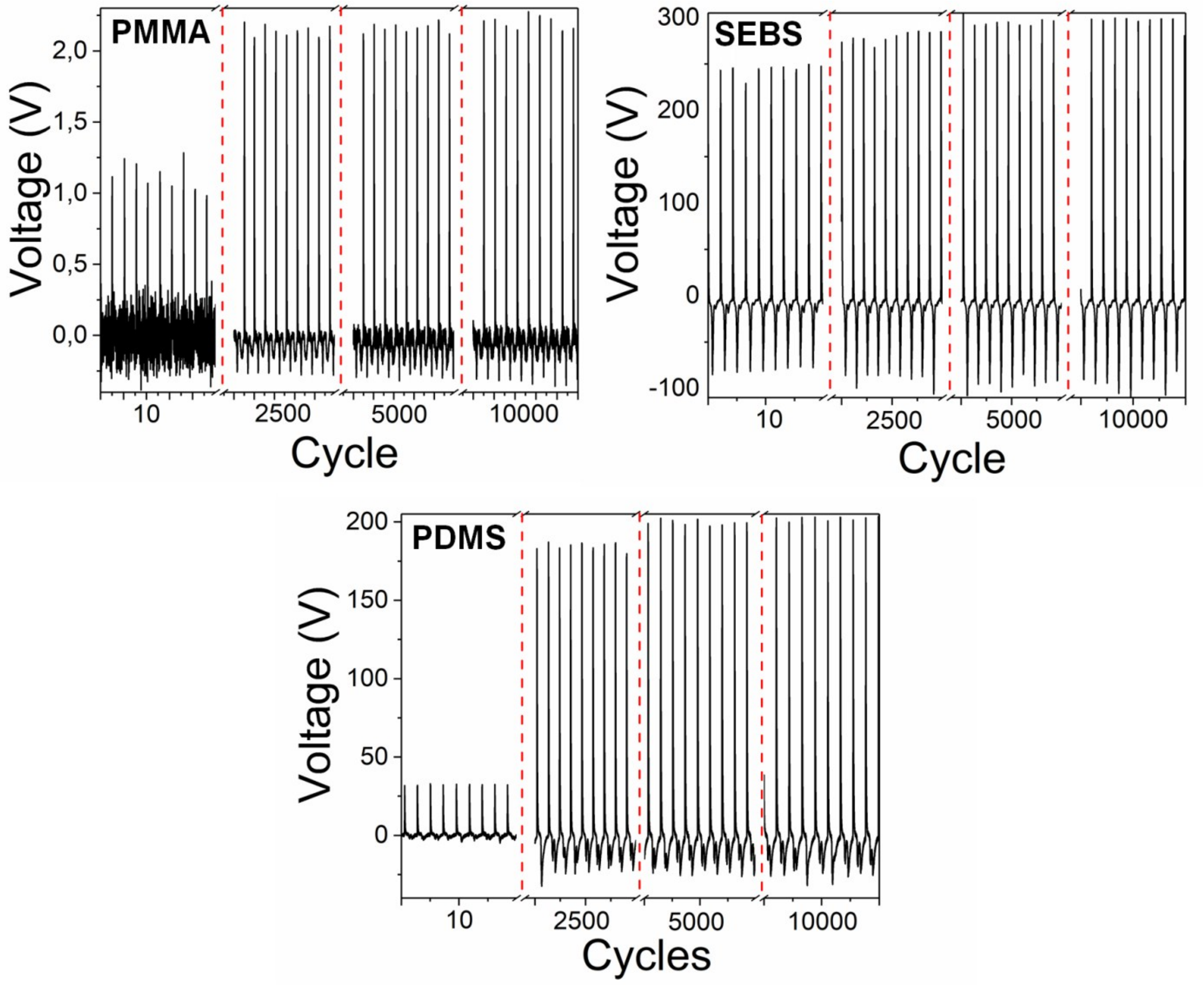

Figure 28. Long term stability for TEG devices from three different polymers: hard (PMMA), soft (SEBS) and soft-crosslinked (PDMS).

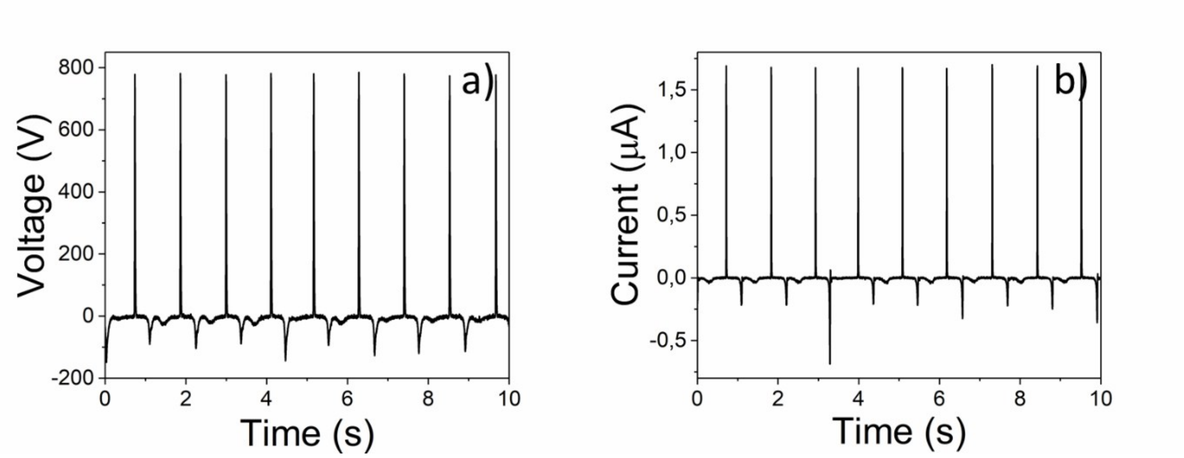

Figure S29. (a) V_{OC} and (b) I_{SC} generated by TEG based on modified SEBS and ITO