Supporting Information for

Electricity on rubber surfaces: a new energy conversion effect

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Supporting Text

Tribo- and piezoelectricity are effects of mechanical action on materials, whose structural features determine the amount of electrical energy obtained. The two effects account for the electrostatic potentials detected in most anthropic and natural environments, often reaching many-thousand volts. Elastomers acquire charge when they are handled and this is loosely assigned to tribo- and/or piezoelectricity, but it has not yet been studied in sufficient detail to understand charge build-up and dissipation in elastomers.

In this paper, well-controlled experiments show that when rubber tubing is subjected to cyclic stretching and relaxation, a Kelvin probe measures a periodic potential variation. The experiments were performed using the experimental setup shown in Figure 9 and electricity was successfully generated and collected with the apparatus shown in Figure S3. Also, the Kelvin probe dimensions are given below:

*Dimensions: 11.2 mm diameter 65.7 mm L*
*Body Shape: Round / Aperture Location: End-viewing / Aperture Size: 1.32 mm diameter*

**Simulation Methods**

Evaluation of surface charge density on the samples follows the procedure described in previous papers. Each pixel on the surface map is a square with 5 mm sides and this is further subdivided in a 500 x 500 pixel matrix, where virtual charges are placed. The electrostatic potential ($V_T$) measured 2 mm away from the matrix plane is generated by all charges ($q_i$) weighted by the distance $r$ from the charge to the measuring point, and can be calculated, using a C++ code for equation of superposition principle defined as follows:

$$V_T = \sum_{i=1}^{n} \frac{q_i}{4\pi\varepsilon_0 r_i}$$

The number of excess charges per pixel is adjusted by trial and error, until the calculated and measured potentials match, within experimental error.

Using the Superposition Principle as it was done in previous works, we have calculated the surface charge density of natural and silicone rubber in the range of 100 to 250 units of charge/µm² or 0.01 to 0.025 units of charge/µm³ (considering rubber tubing volume). For the area covered by the copper cylinders, we estimate 28 nC/cycle for silicone rubber and 11 nC/cycle for natural rubber.

Using this estimate of surface charge concentration and assuming that each excess charge is located on some atom, we can calculate charged atom % concentration in the charged rubber surface as follows:

1) each cubic micron contains 0.01 to 0.025 charged atoms;
2) the total number of atoms in one cubic micron of silicone rubber is calculated as follows:

- typical composition of silicone rubber is SiO(CH₃)₂. The average atom number is thus (28+16+24+6)/10 = 7.4
- density of silicone rubber is within 1.1 and 2.1. Taking the 1.6 average, one cubic micron of silicone rubber weighs 1.6x10⁻¹² g. This, it contains (1.6x10⁻¹² x 6x10²³)/7 = 1.3x10¹¹ atoms.

- the atom % concentration of charged atoms in silicone rubber is thus 0.025/1.3x10¹¹ or 2x10⁻¹¹ atom %. This is nine orders of magnitude lower than the sensitivity of XPS equipment currently used for the analysis of contaminants in rubbers.
Another calculation procedure:
1) 1 cubic centimeter of silicone rubber weights 1.6 g;
2) given the 7.4 average atom number, 1 cubic centimeter of silicone rubber contains
   \(1.6/7.4 = 0.22\) times the Avogadro number of atoms, or \(0.22 \times 6 \times 10^{23} = 1.3 \times 10^{23}\) atoms.
3) 1 cubic micron = \(10^{-12}\) cubic centimeters. Thus, it contains \(1.3 \times 10^{11}\) atoms.
4) the ratio between the number of charges and number of atoms in this rubber is
   thus \(0.025/1.3 \times 10^{11} = 2 \times 10^{-13}\) or \(2 \times 10^{-11}\) atom %, the same as found above.

Specific experimental conditions and setups
A few experiments were conducted in a dark room, where the rubber surface was
monitored with a Canon EOS Rebel T1i camera with Shutter Speed adjusted to 30s,
Aperture F20 and ISO 3200, as in previous work.\(^3\) No triboluminescent phenomena was
observed during these experiments under conditions employed in this work.

The temperature on the surface of natural and silicone rubbers subject to
reciprocating motion was monitored with a Horiba i\(^2\) 1024 thermal camera. The
temperature rose 2-4°C above room values during actuation.
**Voltage vs. distance for low frequency actuation**

Electrostatic time series were obtained under low frequency actuation (0.33Hz) for natural rubber and silicone elastomers. The results are shown in Figure S1 (a,c). Natural rubber display a quasi-harmonic behavior while silicone time series is distorted in the ordinate axis. These features are more clearly visualized in the V vs. D plots in Figure S1 (c,d). It is observed that natural rubber charges almost in sync with stretching distance, whilst the potential at silicone surfaces remains near zero for almost half of the actuation cycle. These results parallel those registered in Figure 1 of the main text.
Figure S1.
Stretching-relaxation cycles for (a,b) natural rubber and (c,d) silicone. The stretching amplitude was 6 cm and frequency was 0.33Hz. Figures c,d display the time series and Figures b,d show the corresponding Voltage x Distance profile.
Effect of stretching amplitude
The effect of stretching amplitude was determined for natural rubber, shown in Figure S2. Each train of stretching cycles lasted for ca. 10 seconds followed by 60 second resting periods, during which natural rubber was kept either in a relaxed (a,b) or stretched state (c,d). The figure shows that an increase in cycling amplitude leads to an increase in the potential values observed. Electrostatic oscillations are highly asymmetric at d = 6 cm, when positive potential values predominate. The behavior during the 60-second resting period strongly depends on the rubber final state: if the rubber is kept relaxed during the resting state, the potential quickly decays to zero. However, stretched rubbers show a slow decrease in potential. These results are in line with those presented in Figure 3 of the manuscript, for individual steps. Overall, the results show that charging phenomena is enhanced when the rubber is elongated more vigorously, as expected considering that this effect depends on the rate of rubber surface change during extension and contraction, as discussed in the main text.
Figure S2.

Stretching-relaxation cycles for natural rubber with amplitudes equal to (a,c) 2 cm and (b,d) 6 cm. Initial resting tubing length is 12 cm. During the 60 s resting period, the material is kept either (a,b) relaxed, or (c,d) stretched.
Figure S3.
Device used to collect electricity generated by periodic stretching of rubber tubing. Photograph courtesy of ‘Thiago A. L. Burgo’. Copyright 2017.
**ATR-FTIR spectroscopy**

Attenuated total reflectance (ATR)–Fourier transform infrared (ATR–FTIR) analyses were performed with an Agilent Cary 630 FTIR Spectrometer, equipped with a diamond ATR accessory. Spectra were averaged over 64 scans at a resolution of 4 cm⁻¹. Natural rubber and silicone tubing samples were stored under dry conditions for 24h, previous to the analyses. Three distinct regions in the samples were analyzed: i) exterior surface, ii) inner surface and iii) sub-surface region just below the external surface (200μm).

Figure S4 a,b shows a typical infrared spectrum obtained for silicone rubber. The main peaks assigned to PDMS are observed at 2963, 1258, 1001, 787 cm⁻¹. No significant differences in the spectra of (a) external, and (b) inner surfaces are observed.

Figure S4 c,d shows representative spectra obtained for the (a) inner or sub-surface and (b) external surface of natural rubber tubing. In both cases, typical peaks assigned to isoprene functional groups are observed: 3033, 2961, 2927, 2855, 1664, 1450, 1375, and 837 cm⁻¹. However, there are important differences. The outer surface of the natural rubber tubing contains a much higher hydroxyl content when compared to its internal surface or inner part, as revealed by the signals around 3300 and 1630 cm⁻¹. Note that the material was stored under dry conditions 24h before the measurements, which indicates that water is strongly adsorbed/incorporated at the outer surface. Furthermore the exterior surface also reveals a series of peaks between 1130 and 1010 cm⁻¹, indicating the presence of oxygenated compounds.

Overall, the differences in spectral signature mimic those found for skim and cream fractions of latex dispersions, which are related to the presence of phospholipids and other natural additives.⁴
Figure S4.
Infrared spectra obtained for the (a) subsurface, (b) external surface of silicone tubing and (c) subsurface, (d) external surface of natural rubber tubing.
TGA analysis

Thermogravimetric analysis was conducted under 100 mL/min Ar flow and 20°C/min heating rate, using a TGA 2950 (TA Instruments). The results are presented in Figure S5.
Figure S5.
TGA and DTG profiles for (a) natural rubber and (b) silicone rubber.
**Movie S1**
Mechanical-to-electrical energy conversion by periodic elastomer stretching.

**Movie S2**
Natural rubber at low frequency stretching-relaxing cycle.

**References**

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