

The Position of Solid Carbon Dioxide in the Triboelectric Series*

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The process of releasing liquid carbon dioxide from a fire extinguisher is accompanied by a strong static charging of the plastic material making up the extinguisher discharge horn. Firefighters often report an electric shock when operating CO₂ extinguishers, but the origin of this electrostatic hazard is largely unknown. Here, we begin to investigate this phenomenon, and test the hypothesis of plastic samples being tribocharged on contact with rapidly flowing solid CO₂. Using Faraday pail measurements, we show that non-conductive polymers gain a net static charge when brought in and out of contact with dry ice (solid CO₂). These measurements of charge sign and magnitude give indirect evidence helping to place solid CO₂ for the first time on the triboelectric series. Polydimethylsiloxane (PDMS), polytetrafluoroethylene (PTFE), and polyvinyl chloride (PVC) samples acquire a negative charge when rubbed against dry ice, whereas poly(methyl methacrylate) (PMMA), glass, and nylon surfaces become positively charged. Therefore, we suggest the position of dry ice in the triboelectric series to be close to that of materials with stable cations and unstable anions, possibly locating it between PMMA and PVC.

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Introduction

Contact electrification^[1] is a process in which two materials that are brought in and out of contact acquire a net charge of opposite sign. Although contact electrification is exploited in several important technologies, such as photocopying and laser printing,^[2] electrostatic painting,^[3] industrial separations,^[4] and new forms of alternating current generation,^[5] when uncontrolled it remains a detrimental, or even dangerous, phenomenon.^[6] For examples, in industries such as textiles, manufacturing of explosives, and storage of grains and flour, static electricity is a well-known hazard.^[6b,7] Contact charging is, however, not limited to contact between polymers, as the flow of water or of liquid and gaseous hydrocarbons^[8] is known to generate static charge.^[7a,9] Analogously, when a CO₂ extinguisher is operated, the liquefied gas expands and rapidly moves across the surface of the discharge horn, generating a large amount of electrostatic charge.^[10] Major accidents have been associated with static charging created by the release of CO₂ extinguishers, such as an explosion in Germany in 1966.^[11] Electrification induced by solid CO₂ has been studied by several groups,^[12] and as early as in 1954 Heidelberg and coworkers investigated charge generation during release of CO₂ from a large fire-snuffing installation.^[11] They reported a highly variable rate of charge generation, but to date, how different dielectrics respond to contact with solid CO₂ and how the environment influences CO₂-related tribocharging events are still largely unexplored.

Here, we have begun to quantify the magnitude and sign of static electricity that develops on polydimethylsiloxane (PDMS), polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC), poly(methyl methacrylate) (PMMA), nylon, and glass surfaces that were rubbed against dry ice under either an air or argon atmosphere, and tried for the first time to tentatively place CO₂ in the triboelectric series.

Results and Discussion

We first considered experiments in which solid CO₂ is allowed to slide down an inclined plane made of a sheet of the polymer under test (Fig. 1a). This system is especially convenient in terms of reproducibly controlling the contact force. Solid CO₂ is not found in any available triboelectric series,^[13] and therefore, we performed experiments where dry ice was in contact with different polymers whose position in these charts is known.

Fig. 1a illustrates the experimental set-up in which PDMS, PTFE, PVC, PMMA, nylon, and glass plates were rested on an inclined plane made of a wood surface tilted 30° away from the horizontal plane. Wood was used as to hold the samples because it is known to gain negligible charge after contact with any other polymer. The choices of the polymer materials were motivated as follows: (i) PDMS, PTFE, PVC, and PMMA are known to be close to the bottom (i.e. negative end) of the triboelectric series,^[14] and (ii) glass and nylon are found towards the top (i.e. positive) end of the series. After contact with CO₂,

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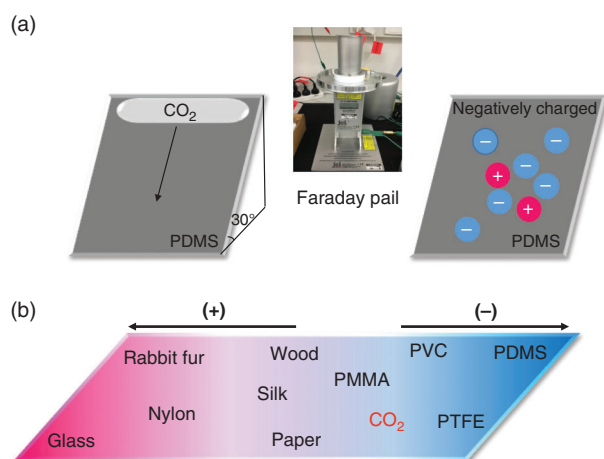


Fig. 1. (a) Illustration of the experimental setup in which dry ice samples are rubbed against (slid down) a polymer surface. The amount and sign of the net charge gained by the plastic sample are measured by inserting it into a Faraday pail connected to a high-precision electrometer. (b) Relative position of various dielectric materials in a triboelectric series: materials located towards the right (–) tend to acquire a net negative charge on contact with materials located to their left (+). The tentative position of CO₂ in the series (red ink in (b)) is based on the Faraday pail data presented in Figs 2 and 3.

glass, PMMA, and nylon gain a positive charge, whereas PDMS, PTFE, and PVC become negatively charged. Our Faraday pail data therefore suggest that solid CO₂ should be placed in a triboelectric series between PMMA and PVC (Fig. 1b). Furthermore, the magnitude of charging is strongly atmosphere-dependent: data comparing tribocharging in air and argon are shown in Fig. 2a and Fig. 2b, respectively. In 2018, Grzybowski and coworkers observed the magnitude of the charges developed on polymers by contact-electrification to be dependent not only on the material, but also on the nature of the atmosphere surrounding the polymer.^[15] The dielectric strength of air (3 kV mm⁻¹)^[16] is six times than that of argon (0.5 kV mm⁻¹),^[17] and our data are consistent with an atmosphere of high dielectric strength favouring tribocharging. For the tribocharging mechanism, guided by our recent work demonstrating that charge carriers are polymer fragments,^[18] we suggest that triboelectrification between solid CO₂ and polymers can be ascribed to material transferred from the polymer to CO₂, and this may be of relevance to gas–solid fluidized reactors.^[19]

Our Faraday pail data show that for PDMS, PTFE, and PVC samples handled in argon, ~34, 52, and 90 % (respectively) of the tribocharge has dissipated 20 s after their separation from a CO₂ surface (Fig. 3b). For these polymers, a faster decay is observed in air, where ~85, 91, and 96 % of the negative charges are lost over the same period of time (Fig. 3a). Charge dissipation, in both air and argon, is faster for PVC than for PTFE or PDMS (Fig. 3c), which is probably linked to the lower work function of the former.^[18] We hypothesized that the differences in charge magnitude observed under argon or in the presence of atmospheric water could be due to the different abilities of these media to stabilize tribocharges.^[20] Under ambient conditions, polymers are known to harbour surface water layers, and charges can potentially dissipate ‘laterally’ through surface conductance. Under a dry and inert atmosphere this mechanism of charge dissipation is likely to be inoperative or less efficient.

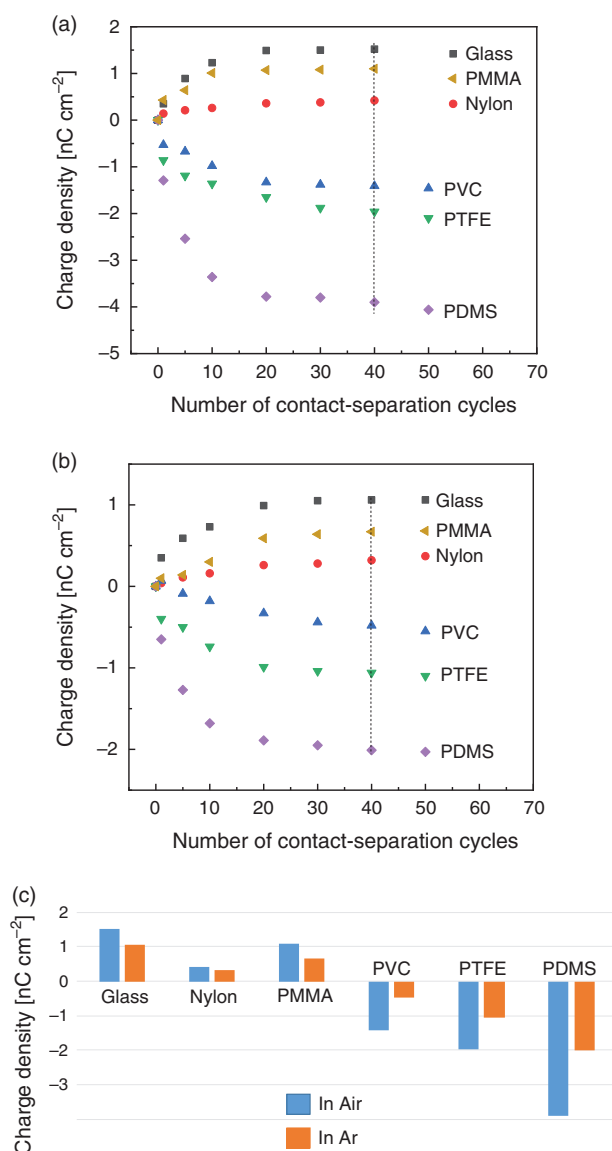


Fig. 2. Tribocharging of polymer samples against dry ice. (a) Faraday pail data for samples charged by cyclically sliding solid CO₂ across an inclined surface. Data were acquired under ambient air: glass, nylon, and PMMA samples gained a net positive charge, whereas PVC, PTFE, and PDMS became negatively charged. (b) Tribocharging data for experiments performed under argon; all the polymers’ net charge is smaller in argon than in air. (c) Difference in the tribocharging – air versus argon – for samples that were subject to 40 contact–separation cycles.

Conclusion

The conclusions of the present work are two-fold. First, solid CO₂ can be tentatively placed between PMMA and PVC in a triboelectric series. This is important because it can guide the engineering and design of materials such as to either maximize or minimize their static charging on contact with solid CO₂. For example, the Australian Standard concerning the manufacturing of CO₂ extinguishers (AS/NZS 1841.6:2007) states that ‘a discharge horn shall be constructed of electronically non-conductive material’. CO₂ extinguishers are primarily used on electrical fires, or on fires involving electrical equipment, hence the need of an insulating horn, but here we have shown that not all insulators have the same tendency to build up static electricity after contact with dry ice. Second, we have shown that

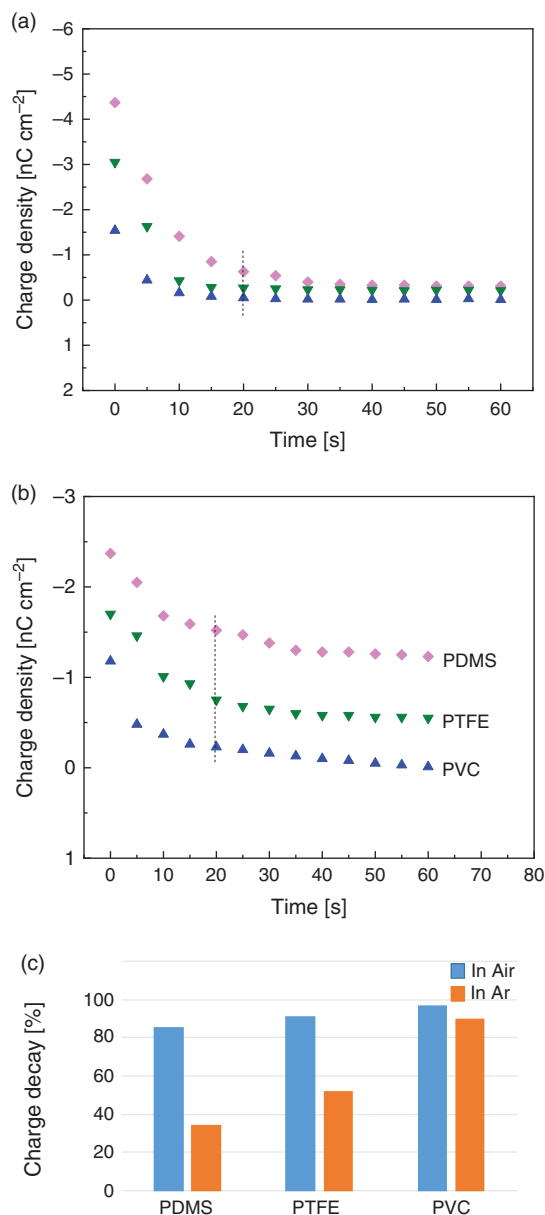


Fig. 3. Decay in (a) air, and (b) argon of the static charge (Faraday pail measurements) of tribocharged PDMS, PTFE, and PVC samples charged against CO₂. In air, ~85, 91, and 96 % of the samples' tribocharge has dissipated after 20 s. For the experiment in argon, the decay of charge is slower and these samples lose ~34, 52, and 90 % of their net charge over the same time. The faster charge decay in air is probably due to reaction with water molecules adsorbed on the polymer surface. For PVC samples, the decay is more rapid than PTFE and PDMS both in air and argon; the faster charge decay in PVC is ascribed to its lower work function and larger electron affinity.^[18]

contact electrification between CO₂ and polymers is not just material-dependent, but also dependent on the environment: in an atmosphere of high dielectric strength, the density of surface charges generated upon contact is maximized. This work extends our growing understanding of static electricity and it may guide the development of experimental platforms for the study of how charged groups can influence chemical bonding and reactivity, an area that is beginning to attract significant interest in chemical catalysis.^[21]

Experimental

Materials

Redistilled solvents and Milli-QTM water (>18 MΩ cm) were used for substrate cleaning. Samples of PTFE (McMaster-Carr, part no. 8545K26), PDMS (McMaster-Carr, part no. 87315K65), PVC (McMaster-Carr, part no. 87545K521), PMMA (McMaster-Carr, part no. 8536K141), nylon (nylon-66, RS Components Australia, part no. 514-607), and glass (microscope slides from Qorpak®) were cut to sheets 2 × 2 cm and were ~0.3 cm thick. Solid CO₂ was purchased from BOC Australia.

Methods

Prior to being tribocharged, polymers were washed with water, methanol, and dichloromethane and then dried under a flow of nitrogen gas. The charge on the polymer was measured using a Faraday cup connected to an electrometer (JCI 140 static monitor and JCI 147 charge measurement units) operating on the 10⁻⁹-C scale. Charging data are reported as charge-to-geometric area ratios. A solid timber wedge was used to hold the plastic (nylon, PMMA, PVC, PTFE, and PDMS) and glass sheets at 30° from the horizontal. A small sample of dry ice (generally 3.5 g, rod-shaped) was rubbed against the inclined plane made by the plastic and glass samples by letting it slide, assisted by gravity, from the top to the bottom of the inclined plane (Fig. 1a). This operation of contacting and then separating the dry ice sample from the dielectric sheet was repeated a number of times. After the last contact-separation cycle, the plastic or glass sample was transferred to the Faraday pail to measure the magnitude and sign of its tribocharging. The number of contact-separation cycles (with one cycle defined as one slide down the tilted plane) was varied between 1 and 50 and the time that elapsed between the last cycle and the charge measurement was generally between 3 and 5 s. Experiments and charge measurements under an argon atmosphere were conducted using a glove box (Innovative Technology, PL-HE-2GB with PL-HE-GP1 inert gas purifier) with water and oxygen levels of less than 1 ppm.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgements

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