

GIANT ELECTROSTRICTION OF SOFT NANOCOMPOSITES FOR MECHANICAL ENERGY HARVESTING

Jinkai Yuan, Wilfrid Neri, Cécile Zakri, Annie Colin, Philippe Poulin

Centre de Recherche Paul Pascal, CNRS, Université de Bordeaux, 115 Avenue Schweitzer,
33600 Pessac, France.

yuan@crpp-bordeaux.cnrs.fr (J. Yuan)

Keywords: Energy harvesting, Electrostrictive composites, Graphene, Dielectric constant, Permittivity

ABSTRACT

High electromechanical coupling is critical to perform effective conversion between mechanical and electrical energy for various applications of electrostrictive polymers. Herein, a giant electrostriction effect is reported in liquid crystalline graphene doped dielectric elastomers. The materials are formulated by an original phase transfer method which allows the solubilization of graphenic monolayers in non-polar solvents. Dielectric spectroscopy is combined with tensile test devices to measure the true electrostriction coefficients with differentiating the Maxwell stress effect. Because of their unique liquid crystal structure, the resultant composites show a giant permittivity and ultralarge electrostriction coefficient. This work offers a promising pathway to design novel high performance electrostrictive polymer composites as well as to provide insights into mechanisms of true electrostriction in electrically heterogeneous systems.

FULL TEXT

Harvesting mechanical energy of ambient or biomechanical vibrations could provide sufficient energy to power various devices. Nevertheless, in spite of extensive research in the field, examples have been limited to only a few demonstration prototypes. Actual applications don't emerge because of still poor energy conversion efficiency. Typical mechanical energy harvesters can be realized with piezoelectric materials which exhibit natural electromechanical coupling.[1] But the piezoelectric materials have to be polarized at high temperature under a high voltage.[2] This intervention makes their use difficult in autonomous and miniaturized systems. Electrostrictive polymers are alternative candidates and they can be used to realize variable capacitors to harvest mechanical energy by changing capacitance upon deformation. However, most of the electrostrictive polymers suffer from low electromechanical coupling coefficient, i.e., limited permittivity variation in response to the applied strain.[3] Such a response is generally characterized by the so-called electrostrictive coefficient. Thus, the key to develop high-efficiency energy harvester is to largely improve the electrostrictive coefficient of polymers, while retaining their other excellent physical properties.

As indicated previously, the permittivity of a composite loaded with conducting particles is expected to diverge at the percolation threshold. The materials at this point become critically sensitive, which opens up the possibility for large permittivity variations with mechanical deformation. In order to explore this new route, we prepared electrostrictive nanocomposites composed of reduced graphene oxide (rGO) in soft polydimethylsiloxane (PDMS) matrix. The advantage of using graphene is based on the essential feature of their large surface area, which is critical to achieve large polarization in composites. Here, a diblock copolymer aminopropylmethylsiloxane- b-dimethylsiloxane (PAPMS-*b*-PDMS) was chosen to adsorb onto graphene oxide (GO) nanosheets and stabilize their dispersion in composite precursor solutions (**Fig. 1b**). Such interaction is based on the electrostatic attraction between negative charges of GO nanosheets and positive ones of the copolymer (**Fig. 1a**). As such, the

GO nanosheets were continuously transferred from the water phase into the diethyl ether phase as this interaction at water/oil interface proceeded.

The obtained GO suspension is well suited to prepare PDMS matrix composites (**Fig. 1c**), without showing any reaggregation of GO nanosheets during the process. Moreover, with increasing concentration of such GO suspension, a nematic liquid crystal phase can form even with a low GO content, which is, to our knowledge, the first report of GO liquid crystal in a nonpolar organic solvent. More importantly, this observation allows for studying a fundamental physical problem which is currently highly debated. That is the competition of percolation transition and liquid crystal transition for platelike particles.

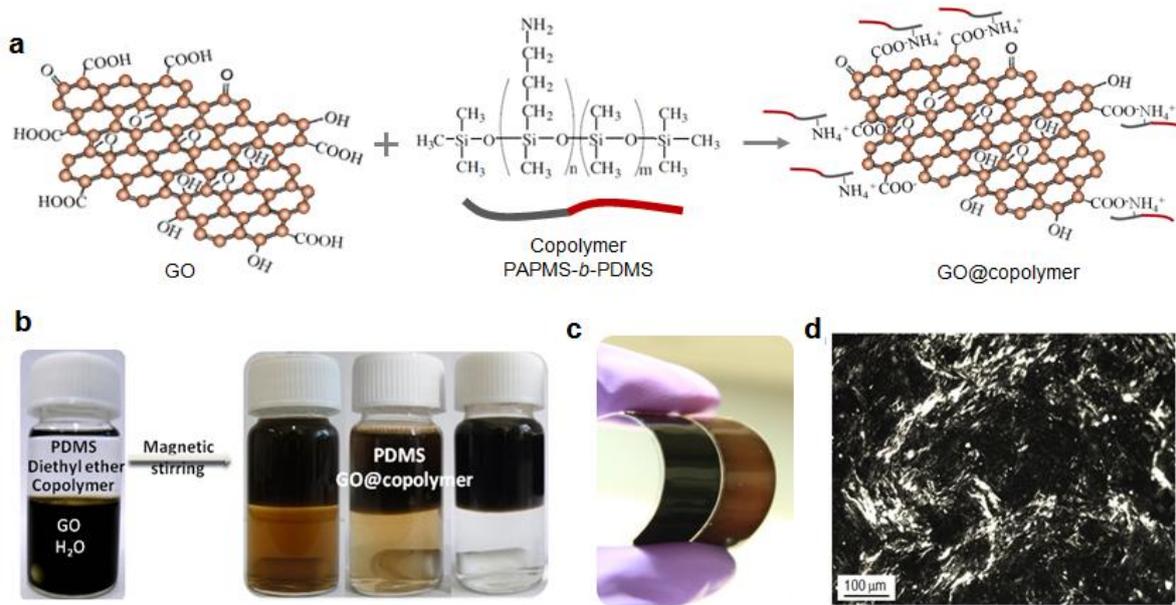


Figure 1 (a) Schematic illustration of the electrostatic attraction between negative charges of GO nanosheets and positive ones of the PAPMS-*b*-PDMS copolymer. (b) Photograph shows the phase transfer of GO flakes from the aqueous to the organic phase. (c) Photograph of soft PDMS composites with GO (brown) and rGO (black) nanosheets at a loading of 1 wt.%. (d) Optical micrographs between crossed polarizers of GO suspensions in PDMS monomer at a concentration of 1 wt.%.

In the case of rods of diameter D and length L as well as platelets of thickness D and diameter L , the percolation threshold, based on excluded volume arguments, is expected to scale as the inverse of the aspect ratio, [5]

$$\phi_p \propto D/L \quad (1)$$

Recent simulations of impenetrable platelets have shown that the percolation threshold does not follow such a scaling.[6] Upon increasing concentration, hard particles (rods as well as platelets) of large aspect ratio preferentially align with respect to each other to maximize packing entropy rather than forming percolated networks of randomly oriented particles. Thus there is a competition between percolation and nematic ordering. For realistic tunneling lengths, the percolation threshold in suspensions of rod-like particles is always below the isotropic-nematic transition. In contrast, in suspensions of platelets, the isotropic-nematic transition can occur at lower concentrations than the percolation transition and thus hinders the formation of a conducting network.[6]

Experimentally, we addressed this issue by assessing the percolation transition in rGO/PDMS composites. As shown in **Fig. 2a**, the margin improvement of conductivity at 1.0 wt.% indicates that this loading is well below the percolation threshold. However, at this rGO-PDMS mass ratio, liquid crystal (LC) transition has already taken place (**Fig. 1d**), indicating that the flakes with large anisotropy indeed tend to self-assemble into nematic LCs (**Fig. 2b**) before they form a percolated path along the direction of the conductivity measurement. Thus we confirmed the theoretical prediction that the liquid crystal transition of platelike particles actually hinders the formation of conductive networks. This phenomenon would fundamentally change our views on the interest of graphene for conductive composites. Such competition can nevertheless be positively exploited to develop dielectric composites. The ordered liquid crystalline graphene structure is expected to promote the formation of effective microcapacitors to afford a very high permittivity (~ 2000 at 0.1 Hz, **Fig. 2d**).

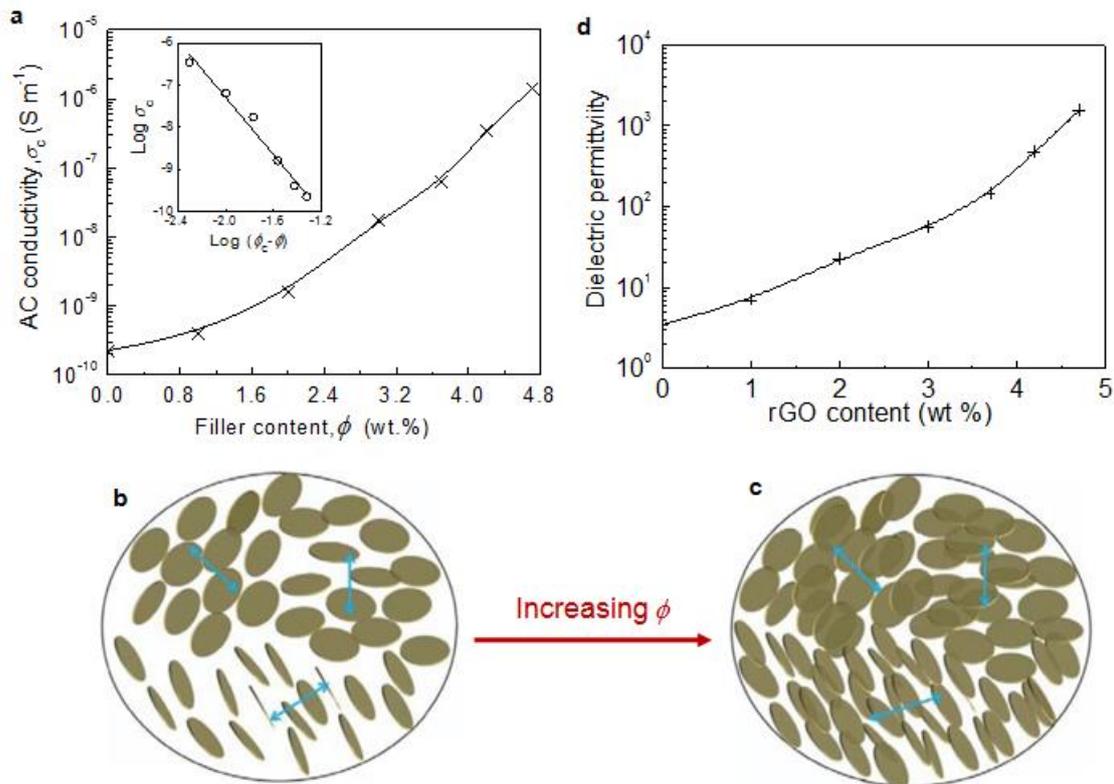


Figure 2 (a) AC conductivity of the rGO/PDMS composites as a function of the filler content, measured at room temperature and 100 Hz. (b) Microstructural representation of PDMS composites, which are composed of randomly oriented monodomains of LCs at low concentration. In each domain, the flakes tend to be aligned but no percolating path is established. (c) Schematic illustration of the microstructure of the composite at high concentration. In this case, the monodomains still remain randomly orientated but flakes inside domains begin to percolate and eventually form an infinity network of connected path through the insulating matrix. (d) Dielectric permittivity as a function of the rGO content, measured at 0.1 Hz.

To investigate electrostriction phenomena, we combined dielectric spectroscopy and tensile test devices to measure permittivity variations of composites near percolation (4.7 wt%) with applied strain. By contrast to most studies in the field, our method allows direct and quantitative measurements of the electrostriction coefficients, without any assumption.[1] The graphene composite exhibits a large permittivity variation within a short strain range. And the variation remains stable after first four loading-unloading cycles, showing a giant electrostrictive coefficient $M = -4 \times 10^{-14} \text{ m}^2/\text{V}^2$ at

0.1 Hz. This giant electrostriction places our materials amongst the best electrostrictive composites.[1] To exploring their potential for energy harvesting applications, the present material (4.7 wt% rGO/PDMS) are currently tested in actual devices with the help of conditioning circuits. Mechanical vibrations provided by a Dynamic Mechanical Analysis (DMA) machine are converted into electrical energy. The levels of forces and frequencies used to deform thin nanocomposite sheets of a few cms in diameter are chosen to mimic ambient vibrations. These ambient vibrations include industrial vibrations (engines, structures, transport vehicles, etc) or bio and natural vibrations (running, wind, rain, etc). Optimization of the testing parameters is currently investigated.

ACKNOWLEDGEMENTS

This work is financially supported by France ANR and Solvay in the frameworks of the project ELENA, and of the Labex AMADEus (ANR-10-LABX-0042-AMADEus).

REFERENCES

- [1] M. Lallart, P.J. Cottinet, D. Guyomar, L. Lebrun, Electrostrictive polymers for mechanical energy harvesting, *Journal of Polymer Science Part B-Polymer Physics*, **50**, 2012, pp.523-535 ([doi: 10.1002/polb.23045](https://doi.org/10.1002/polb.23045))
- [2] A. Toprak, O. Tigli, Piezoelectric energy harvesting: State-of-the-art and challenges, *Applied Physics Reviews*, **1**, 2014, pp.031104 ([doi: http://dx.doi.org/10.1063/1.4896166](http://dx.doi.org/10.1063/1.4896166)).
- [3] Q.M. Zhang, V. Bharti, X. Zhao, Giant electrostriction and relaxor ferroelectric behavior in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer, *Science* **280**, 1998, pp. 2101-2104 ([doi: 10.1126/science.280.5372.2101](https://doi.org/10.1126/science.280.5372.2101))
- [4] J. Yuan, A. Luna, W. Neri, C. Zakri, T. Schilling, A. Colin, P. Poulin, Graphene liquid crystal retarded percolation for new high-k materials, *Nature Communications*, **6**, 2015, pp.8700 ([doi:10.1038/ncomms9700](https://doi.org/10.1038/ncomms9700)).
- [5] E. Charlaix, Percolation threshold of a random array of discs: a numerical simulation, *Journal of Physics a-Mathematical and General* **19**, 1986, pp. L533-L536 ([doi: 10.1088/0305-4470/19/9/013](https://doi.org/10.1088/0305-4470/19/9/013))
- [6] M. Mathew, T. Schilling, M. Oettel, Connectivity percolation in suspensions of hard platelets, *Physical Review E*, **85**, 2012, pp. 061407 ([doi:10.1103/PhysRevE.85.061407](https://doi.org/10.1103/PhysRevE.85.061407))