

Polymer/inorganic nanocomposites with tailored hierarchical structure as advanced dielectric materials

Evangelos Manias^{1,3,*}, Clive A. Randall^{2,3}, Vivek Tomer^{3,4} and Georgios Polizos^{1,5}

¹ Polymer Nanostructures Lab – CSPS, Penn State Univ, University Park, PA 16802, USA

² Center of Dielectric Studies – MRI, Penn State Univ, University Park, PA 16802, USA

³ Materials Science & Engineering Dept, Penn State Univ, University Park, PA 16802, USA

⁴ Current Address: The Dow Chemical Co., Corporate R&D, Midland, MI 48674, USA

⁵ Current Address: Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ABSTRACT

Most advances and commercial successes of polymer/inorganic nanocomposites rely only on the dispersion of nanoparticles in a polymer matrix. Such approaches leave untapped opportunities where performance can be improved by controlling the larger length-scale structures. Here, we review selected examples where the hierarchical structure (from millimeter to nanometer) is tailored to control the transport properties of the materials, giving rise to marked property enhancements, relevant to dielectric materials for power capacitors. These examples address composite structures that are self-assembled, both at the nm and the micron scales, and, thus, can be produced using standard industrial practices. Specifically, polyethylene (PE) blends or poly(vinylidene fluoride) (PVDF) copolymers are reinforced with nanofillers; these composites are designed with high filler orientation, which yielded marked improvements in electric-field breakdown strength and, consequently, large improvements in their recoverable energy densities.

INTRODUCTION

Inclusion of additives and fillers into polymers is ubiquitous in applications, because of processing considerations and performance requirements. The use of nanofillers as additives is also commonplace, because they can provide high surface-area at low filler levels. Where fine, nm-scale, dispersion is achieved, composite design can capitalize on the filler properties to enhance performances, especially when the filler surface introduces desirable materials properties, *cf.* “nanofilled polymers” [1,2]. In a more creative approach, ‘genuine’ nanocomposites or “polymer/inorganic hybrids” further capitalize on changes in the polymer behaviors at the nm-lengthscales, which introduce new or novel properties and responses [3], effectively changing the nature of the original polymer [1,2]. However, despite the very high R&D effort in the field of polymer/inorganic nanocomposites and the numerous advances in the performance of these materials over the last decade, still opportunities where performance can be improved by controlling the larger length-scale structures, beyond filler dispersion, remain largely untapped.

The principle of hierarchical structure control relates, in a first approach, on the appreciation that controlled-assemblies of nanoscale objects can give rise to new or emergent properties and functions –*i.e.* collective properties beyond those displayed by individual nanoparticle or bulk composites– as in the cases of molecular crystals and supramolecular polymers. The opportunities for polymer/inorganic nanocomposites with well-defined and

* Author to whom correspondence should be addressed (manias@psu.edu).

predesigned hierarchical structures are very exciting [4], but the examples of such materials remain limited [e.g. 4,5,6,7,8]. Here, we review two selected examples of polymer/platelet-inorganic (nano)composites with given nanometer-scale filler dispersion, and where the hierarchical structure (micro- and meso- scale distribution of fillers) is the simplest-possible uniaxial alignment. More specifically, we review the dielectric properties at high electric fields for **(a)** polyethylene (PE) nanocomposites with well-dispersed intercalated montmorillonite (mmt) nanofillers, with and without uniaxial alignment [9], and **(b)** poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) composites with rather poorly-dispersed but uniaxially aligned kaolinite nanofiller clusters [10].

EXPERIMENTAL

PE/montmorillonite Nanocomposites. Materials, nanocomposite/sample preparations, as well as instrumentation are described in detail elsewhere [9,11,12]. Briefly, commercial grade organo-montmorillonite (Nanocor, nominal CEC of 1.0 meq/g, modified by dimethyldioctadecyl-ammonium) was first dispersed at 25 wt.% inorganic in LLDPE-*graft*-MAH (0.26 wt.% MAH, $M_w \sim 67000$ g/mol and $M_w/M_n \sim 6.1$) with a twin-screw extruder; this masterbatch was subsequently let-down with PE matrix (a Dow Integral blend of 80/20 LLDPE/LDPE) to the final mmt concentration (e.g. 6 and 9 wt.% organo-mmt). Films were extruded at thicknesses of around 60 μm at a commercial blown-film line (Pliant). Extrusion film-blowing naturally induces filler orientation [Fig.1,oriented]; control films with “random” filler orientation were obtained by hot pressing a stack of four blown-films, stacked after sequentially rotated by 22.5° relative, to a final thickness of 60 μm [Fig.1,random].

PVDF/kaolinite Composites. Materials, preparations, and instrumentation are described in detail elsewhere [10]: Briefly, poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)] a random copolymer with 10% HFP co-monomer, was a commercial Solvay-Solexis polymer (Solef 11010/1001). The inorganic kaolinite fillers (Burgess KEVR, Burgess Pigment USA, nominal particle size 1.5 μm , fully calcined clays) were surface treated with (3-mercaptopropyl)trimethoxysilane (Gelest). Composites were made by the co-precipitation method, from a 5 wt. % PVDF-HFP solution in DMF mixed with the appropriate amount of DMF suspension of organically-modified kaolinite, and films were cast (ca. 50 μm) on glass plates. Prior to measurements the films were peeled off the glass substrate, dried under vacuum at 80 °C and then at 115 °C, hot-pressed at 200 °C/55 MPa, and then allowed to crystallize at room temperature. The resultant films were uniaxially stretched by a zone drawing process at 100 °C to five times their original length (draw ratio 5x; stretch ratios: $\lambda_x=5$, $\lambda_y \approx 1$, $\lambda_z \approx 0.2$), and annealed 120 °C/6 h prior to electrical measurements [10]. Filler alignment was achieved by means of the uniaxial stretching step.

RESULTS and DISCUSSION

This paper reviews polymer/nanoscale platelet-inorganic composites with fillers having controlled nanometer-scale dispersion *and* uniaxial alignment of fillers at larger scales, *cf.* controlled hierarchical structure [Fig.1]. Uniaxial filler alignment can be achieved through various routes, such as by application of electric or magnetic fields, by uniaxial or biaxial stretching, or through flow-induced alignment [13]. For the composites reported here, the alignment of fillers was done either by flow in the PE/mmt during the processing step, *i.e.*, during the extrusion film-blowing [9,11], or by post processing uniaxial film-stretching at

elevated temperatures for the PVDF-HFP/kaolinite composites [10]. In the case of PE/mmt two sets of nanocomposites were made with the same filler dispersion at the nanoscale, as quantified by XRD [Fig.1a] and by TEM [Fig.1c], whereas at the meso-scale the fillers and the filler-tactoids were oriented parallel to the film surface in one set of samples [Fig.1b,oriented] and, in a second set of samples, were random/non-oriented [Fig.1b,random]. The rest of the composite characteristics were identical, within measurement accuracy, between the two set of films [9]: Namely, both types of composites had the same crystalline fraction and melting point, measured by DSC, and the same low electric-field properties. Thus, the two composites in Fig.1 provide a consistent platform to compare the high electric-field behavior of these nanocomposites as a function only of their hierarchical structure, *cf.* only of the macroscopic filler orientation [9].

For the PE/mmt, when comparing the oriented-filler versus the random-filler composites, the two set of films had the same low electric field response, but markedly different high electric field properties [Fig.2]: Specifically, at low fields all measured dielectric properties were the same for aligned *vs.* non-oriented fillers: same permittivity, $\epsilon'(\omega)$ and $\epsilon''(\omega)$, same conductivity, $\sigma_{ac}(\omega)$, and same space-charge dynamics (Maxwell-Wagner) [9]. However, at high electric fields

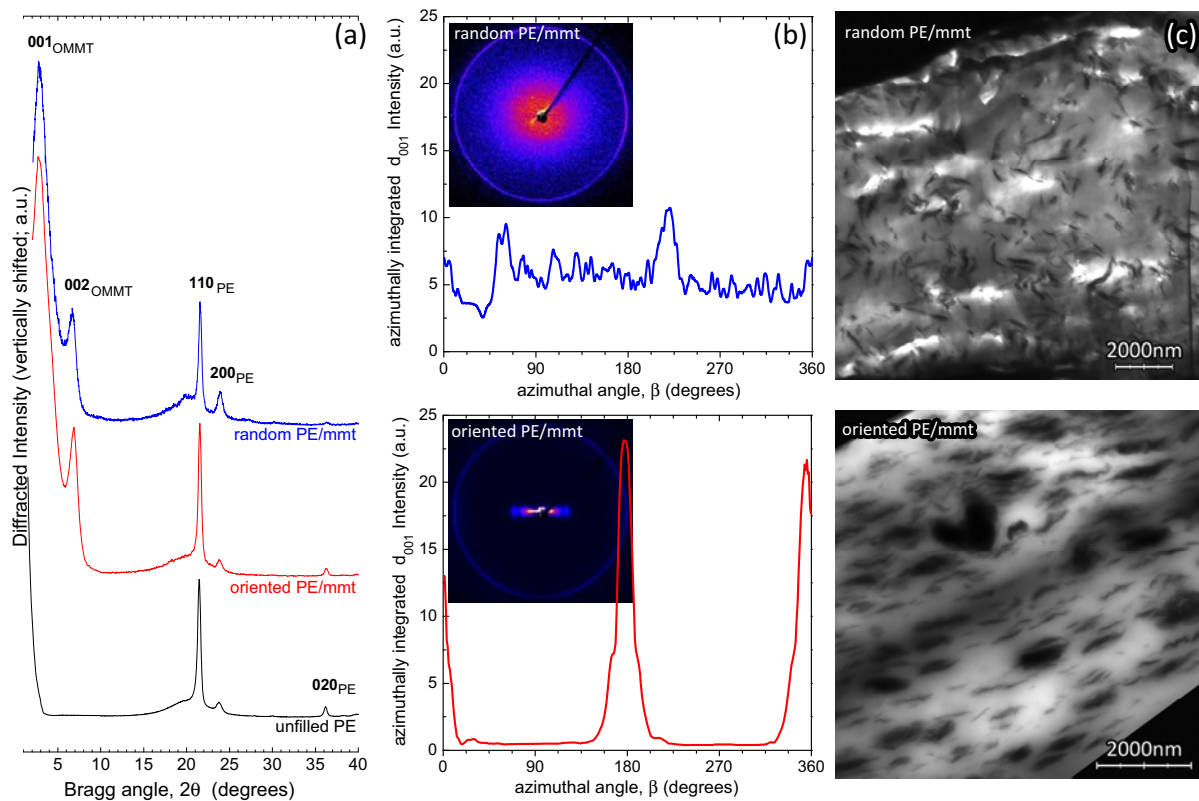


Figure 1 Polyethylene-blend/montmorillonite nanocomposites: **(a)** X-Ray diffraction traces for unfilled PE, a 80:20 blend of LDPE:LLDPE (black, bottom) compared with nanocomposites made by let-down of a LLDPE-g-MAH/mmt masterbatch by the same blend, with two different filler structures: flow-aligned oriented fillers (red, middle) and isotropic randomly-oriented fillers (blue, top); the nanometer-scale filler dispersion is similar, as evidenced by the 001 and 002 diffraction peaks. **(b)** Two-dimensional XRD patterns and azimuthally-integrated intensities of the 001 peaks for the two type of nanocomposites, showing a marked difference between nanocomposites with aligned and random fillers. **(c)** Bright-field TEM (transmission electron microscopy) images of the two composites, at low enough magnification to visualize the complete film thickness. Figure elements and data reproduced after permission [9].

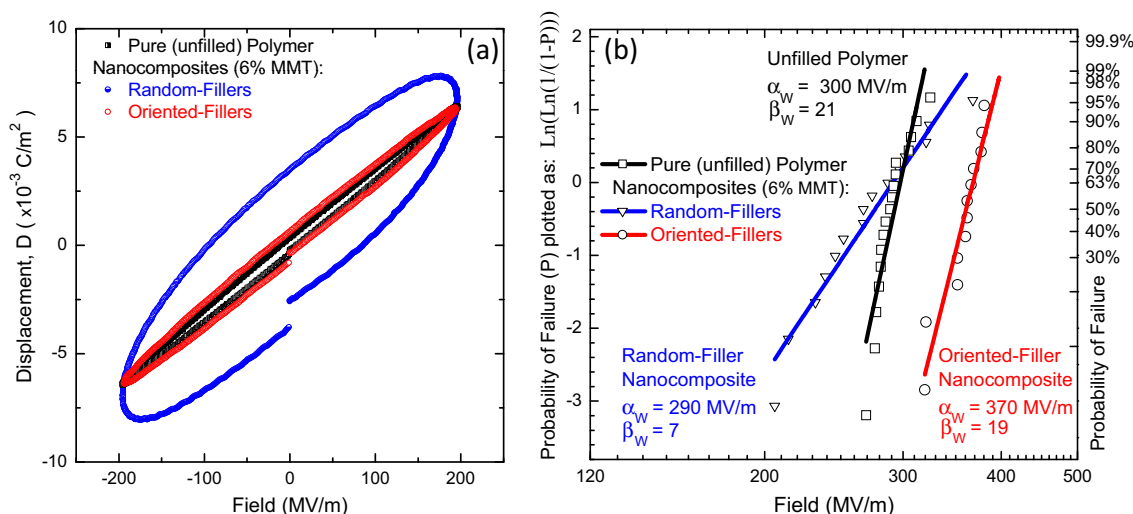


Figure 2 High Electric-field performance of the PE/mmt nanocomposites (Fig.1): **(a)** Displacement-Field loops, showing that the nanocomposites with oriented/aligned fillers have a response very similar to the matrix polymer, whereas the nanocomposites with random fillers exhibit substantially higher losses (markedly widened D-E loops). **(b)** Dielectric breakdown strengths, plotted as a probability of failure versus dc field; the corresponding Weibull fitted lines and the corresponding parameters (α_w , β_w) are also shown for pure PE (unfilled polymer), as well as for nanocomposites with random fillers and with oriented fillers. There is a definitive strong effect of the filler orientation on the breakdown behavior, showing a marked improvement of the breakdown strength for the oriented-filler nanocomposites cf. both the matrix and the random-filler composite. Figures reproduced after permission from [9].

the electric displacement (D) of the oriented-filler composites remained very similar to that of the unfilled PE matrix, whereas the D-E response of the non-oriented filler composites showed substantially larger losses [Fig.2a]. At the same time, at high electric field the electric breakdown strength of the two composites was also markedly different [Fig.2b], with the characteristic breakdown strength α_w showing a strong dependence on the filler orientation, increasing from a value of 290 MV/m for the non-oriented to 370 MV/m for the oriented-filler nanocomposite [Fig.2b]. This impressive difference between the two composites, that are identical except for the meso/macroscopic filler orientation, also extends to shape parameter β_w : for the random-filler nanocomposite β_w was 7 and increased to $\beta_w=19$ for the oriented-filler nanocomposite, indicating that the latter is more homogeneous and exhibits fewer defects, comparable to the behavior of the unfilled polymer matrix ($\beta_w=21$, Fig.2b).

The same trend in electric breakdown strength is also seen for the much higher performance PVDF copolymer, with an impressive increase in α_w from 530 MV/m for the matrix to 780 MV/m for the oriented-filler kaolinite composite [Fig.3a]. At the same time, the PVDF/kaolinite composites exhibit a graceful failure behavior, allowing for voltage cycling through the maximum value more-than-once [Fig.3b]; as well as a markedly improved time-to-failure performance in HALT (Highly Accelerated Lifetime Testing, 500 V at 50 °C) which increases monotonically with filler loading [Fig.3c]. This high electric field breakdown behavior is accompanied by substantial decreases in losses in the D-E polarization response, much like the PE/mmt nanocomposites, albeit in this case permittivity is also decreased (Fig.6 in [10]).

The decrease in electric losses for the oriented-filler composites, in conjunction with their high improvement in breakdown strength, resulted in improvements in the maximum recoverable

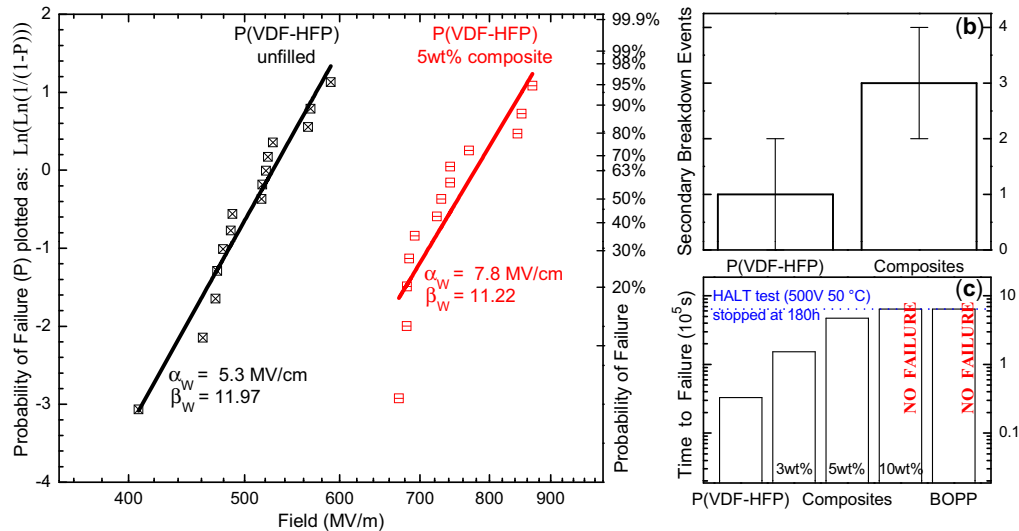


Figure 3 High electric-field performance of P(VDF-HFP)/kaolinite (nano)composites: **(a)** Dielectric breakdown strengths (plotted as a probability of failure versus field, including the corresponding Weibull fitted lines and fit parameters, α_w , β_w). The observed dielectric breakdown strength for stretched films of P(VDF-HFP) and of 5 wt. % composite are strongly reminiscent of the enhancement seen in PE/mmt nanocomposites (Fig.2), despite the differences in systems' chemistry, high-E performance, and lesser nanometer-scale filler dispersion here. **(b)** Number of possible voltage cycles (graceful failure) and **(c)** HALT data (500 V, 50 °C, 180 h max) of P(VDF-HFP) and its kaolinite composites also compared with capacitor-grade BOPP polypropylene films. Figure reproduced after permission from [10].

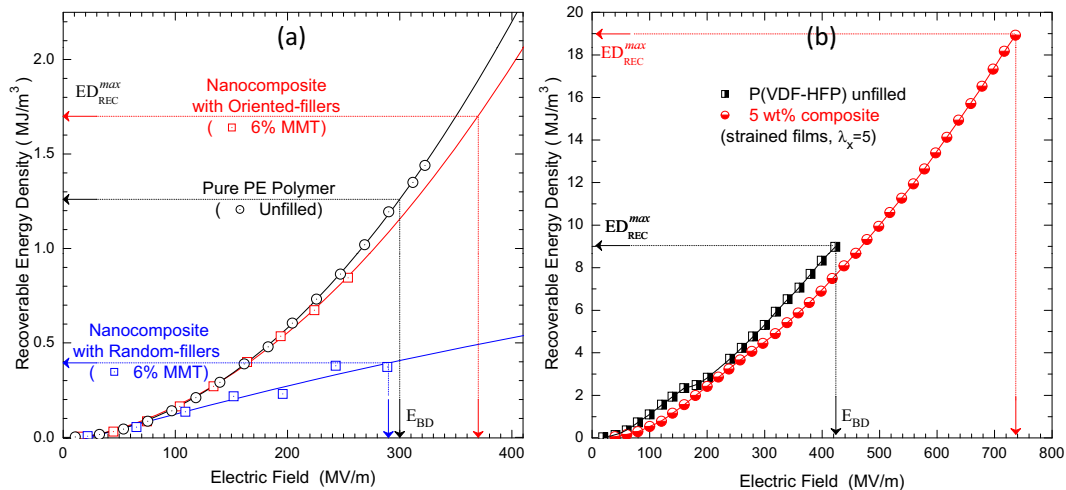


Figure 4 Recoverable energy density (ED) versus ac field, calculated from the D-E loops at discharge, comparing the performance of PE and its 6 wt% mmt nanocomposite films **(a)**, versus the stretched P(VDF-HFP) films and its 5 wt% kaolinite composite **(b)**. In both cases, oriented fillers do not alter the shape of the ED vs. E, but the marked increases in breakdown fields (maximum fields that can be applied) leads to substantial increases in recoverable energy density, the 19 J/cm^3 level measured for PVDF/kaolinite is among the highest values reported for PVDF-based cast films to date. For PE/mmt with no filler orientation (random fillers, blue) there is a deterioration of the ED performance, despite all other materials properties of this composite being identical with the nanocomposite that has oriented fillers (red); here, the increase in losses (Fig.2 loop broadening) can be traced as the underlying reason. Figures reproduced after permission from [9,10].

energy density [Fig.4]. For both the PE/mmt and for the PVDF/kaolinite systems, composites with oriented filler structure exhibit considerable improvements in recoverable energy density, with the enhancements of max ED_{rec} being proportional to the respective improvements in breakdown α_w [10]. Of particular interest is the value of max recoverable energy density for the oriented PVDF/kaolinite composites, at about 19 J/cm^3 , which is the highest value reported for cast PVDF-based films to date [10,14]. These high electric field property enhancements were tentatively attributed to the associated mechanical improvements in the composites, as well as the effects of the oriented filler structure to the initiation and propagation of the electron-tree avalanche across the dielectric film upon electromechanical breakdown [9,10].

CONCLUSIONS

The energy storage capabilities of polymer based dielectrics are reported, and the effects of uniaxial filler orientation (hierarchical composite structure) and of the addition of high aspect ratio nanofillers (nanocomposite) are investigated. Two systems with substantially different dielectric properties are compared: a PE-blend of low crystallinity and low permittivity with a good nanometer-scale dispersion of montmorillonite nanofillers, against a PVDF-copolymer of high permittivity reinforced by kaolinite fillers at inferior nanometer-scale dispersion. Despite differences in the system details and in filler-induced changes, detailed elsewhere [9,10], a clear common trend is seen in the high electric field responses, with marked improvements in the electric breakdown strength and in the recoverable energy density of these composites. Of particular interest here is the fact that marked performance improvements were achieved by design of the simplest possible hierarchical filler structure, that of uniaxially oriented fillers.

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