

Increased Dielectric Breakdown Strength of Polyolefin Nanocomposites via Nanofiller Alignment

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ABSTRACT

The high field electric breakdown of polyethylene/montmorillonite nanocomposites was studied in detail, and compared to the unfilled respective films. The electric breakdown strength (E_{BD}) of ‘aligned’ composite films (i.e., films with fillers oriented parallel to the film surface) is much higher than the E_{BD} of the respective ‘isotropic’ composites (i.e., films with fillers of random orientation) and of the unfilled polymer films. This behavior suggests a barrier mechanism as the origin of electric strength improvement, a supposition that was investigated in detail here and is supported by: (a) E_{BD} is not related to filler-induced or strain-induced polymer crystallinity changes; (b) E_{BD} decreases with modulus, but improves with toughness for these films; (c) there is no change in the polymer E_{BD} for a small temperature jump (ΔT from 25 °C to 70 °C), but there is a definitive change in the composite E_{BD} for the same ΔT . All these, support the postulation that the electrical breakdown of these systems is predominately through thermal degradation mechanisms, which can be affected by the existence of oriented inorganic nanofillers (and of oriented polymer crystallites). Thus, the controlled orientation of nanofillers is shown to be an effective approach to substantially improve the electric breakdown strength of PE dielectric/insulating films.

INTRODUCTION

It has long been demonstrated that the addition of a small amount of montmorillonite (MMT), a two dimensional nano platelet with a large aspect ratio can concurrently improve many properties of commodity grade polyolefins (e.g., thermomechanical properties, barrier properties, flame resistance), without sacrificing other good properties that these polymers inherently possess (e.g., transparency, low weight, easy processing). More recently, it was found that the same clay-based polymer nanocomposites also demonstrated desirable dielectric behaviors. The resistance to partial discharges is strongly increased, and the space charge accumulation is greatly mitigated in these nanocomposites, which are responsible for the enhanced breakdown strength (E_{BD}), as compared with the respective unfilled polymers [1-5]. The improvement in the electrical-insulating properties are in concert with increased path tortuosity for e-treering propagation [6], but the same improved high field performance can also be assigned to interfacial properties [4-9], e.g., filler interfaces can trap space charges, even reduce charge accumulation, if interfaces with enhanced local conductivity overlap.

Most studies to date have been done on “isotropic” composites with randomly dispersed MMT [7, 10-12], leaving largely untapped opportunities from composites with prescribed/controlled morphologies or predefined hierarchical structures. In previous work [6], it was found that ‘oriented’ nanocomposites with aligned MMT nanoplatelets had substantially better electrical properties, compared to their ‘isotropic’ counterparts. For instance, in PE/MMT nanocomposites, alignment of MMT nanoplatelets can enhance E_{BD} from 290 MV/m (in random-filler nanocomposite, or unfilled polymers) to 370 MV/m (in oriented-filler nanocomposite),

with also substantial improvement in reliability (markedly eliminating low-field failures) [6]. That work strongly suggested a barrier mechanism to charge treeing as responsible for the high improvement in performance.

Here, we revisit those materials aiming to: (1) in this first paper, provide additional evidence that tests the hypothesis of the above barrier mechanism, and determines whether failure is predominately through thermal or electromechanical mechanisms. Also, in a second paper, (2) we systematically tailored the morphology of these polymers and polymer composites, with the emphasis on the orientation of polymer crystals and of inorganic fillers, to delineate contributions of these two structural alignments on the electrical breakdown properties for these composites.

EXPERIMENTAL DETAILS

Materials. PE/MMT composite films were produced at a commercial blown film line at Pliant Corp. as before [6,13]. The matrix was a Dow Integral polyethylene [a nucleated 80/20 LLDPE/LDPE blend] reinforced by nanofillers that were commercially available layered-silicate organo-montmorillonites (o-MMT, Nanomer grade, by Nanocor), with cation exchange capacity about 1.0 meq/g, organically modified at capacity by dimethyl-dioctadecyl-ammonium surfactants. A masterbatch (25 wt% inorganic concentrate) was produced first in a maleic anhydride functionalized PE (0.26 wt% MAH-graft-LLDPE, $\bar{M}_w=67000$ g/mol and $\bar{M}_w/\bar{M}_n=6.1$) by extrusion and was subsequently diluted by the PE matrix (in the commercial blown film line, to obtain 6 wt% and 9 wt% MMT composite films).

Methods and Instrumentation. Transmission electron microscopy (TEM, Jeol JEM-2010 with LaB₆ emitter) was performed at an accelerating voltage of 200 kV on samples microtomed by a Leica Ultracut UCT Microtome with cryoattachment. Differential scanning calorimetry (DSC) was carried out in a thermal analysis (TA) Instruments Q100 calorimeter operated at heating and cooling temperature ramps of 10 °C/min under a nitrogen atmosphere. Dielectric breakdown measurements were performed on a TREK P0621P instrument; the specimens has a one-side conducting polypropylene tape (top electrode) and a copper plate (bottom electrode); specimens were tested under a dc voltage ramp of 500 V/s.

RESULTS AND DISCUSSION

In a previous study, it was shown that that o-MMT can substantially improve the electric breakdown of PE, but only when these high-aspect pseudo-2D nanofillers are oriented (aligned parallel to the film surface) [6]. In Figure 1 we compare the electric breakdown data, plotted in Weibull axes, for unfilled PE; ‘isotropic’ PE/o-MMT composites with randomly oriented fillers; and ‘aligned’ PE/MMT composites with fillers parallel to the film surface. It is obvious that (a) there is no marked improvement in the ‘isotropic’ systems (MMT with random orientation), in fact, there is a substantial detrimental effect at lower fields, since definitive, measureable breakdown events start well below the 250 MV/m field, where the unfilled respective PE films are still stable. At the same time, (b) there is a marked improvement upon orienting the fillers (MMT platelets aligned parallel to film surface) with a systematic increase of 50-70 MV/m (20-25% higher E field). This behavior strongly suggests a barrier mechanism, which leads to

E_{BD} improvements through aligned fillers promoting more tortuous pathways for electric treeing, hence, higher E fields for breakdown (more details in [6]).

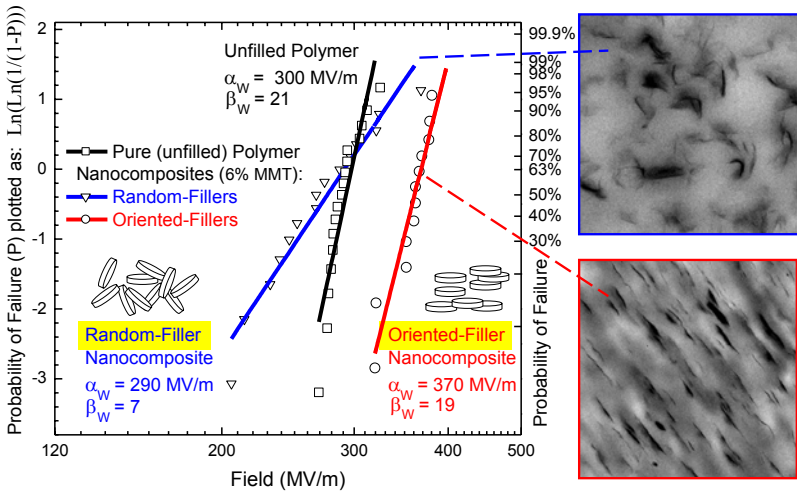


Figure 1. Weibull graph of the (cumulative) probability of failure vs. electric field for unfilled PE, random-filler (isotropic) PE composites and oriented-filler (structured) composite films [6]. The two composite films are identical in physical properties, except for the filler alignment.

Here we explore in more detail the above behavior. First, to further test the validity of the above, we record the covariance of electrical breakdown and mechanical properties, selecting the tensile mechanical properties of the same ‘oriented’ nanocomposites as in Figure 1, so as to obtain additional insights to the electrical breakdown mechanism of these PE/MMT nanocomposites. In Figure 2 we compare the mechanical properties with the electrical breakdown strength for the PE/MMT nanocomposite films. These data show:

- the expected increase of E_{BD} with reduced film thickness (since films of varied thickness were produced at the same blown-film line (thinner films require a larger blowing-ratio) thinner films inherently possesses a higher orientation degree for MMT and for the polymer crystals, and should be characterized by higher E_{BD} , per Figure 1).
- there exists a negative covariance between E_{BD} and the film Young’s modulus. This is opposite to the expected trend for electromechanical failure (for which $E_{BD} \propto (Y/\epsilon')^{1/2}$), strongly suggesting thermal degradation mechanisms as the dominant failure modes.
- an E_{BD} improvement with toughness (with tensile strength and with max elongation) is observed, which is consistent with the previously proposed failure mechanism (e treeing-induced thermal degradation being the dominant failure mode [6]). For this failure mode, thermal degradation is defined as the breakdown triggered or exacerbated by the motion of thermally activated charge carriers (ions, space charge, etc.) leading to a partial discharge and subsequent thermal breakdown. This recognition further highlights the role of geometric

barriers, such as those defined by oriented ceramic MMT nanofillers, in the E_{BD} . In this case, processes resulting in increasing such barriers (higher filler concentration, filler alignment cf. E-field orientation, etc) can result in obstructions of the partial discharge propagation, leading to improvements in E_{BD} .

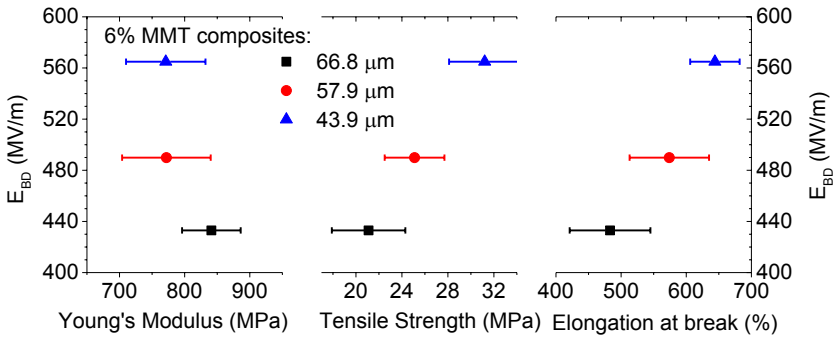


Figure 2. Electrical strength E_{BD} vs. mechanical properties for composite films; demonstrating that E_{BD} is decreasing with modulus (i.e., MMT fillers operate oppositely to the traditional mechanisms of failure associated with semicrystalline polymers), and E_{BD} is increasing with toughness (in concert with what would be expected from a barrier mechanism).

The temperature dependence of E_{BD} is presented in Figure 3 for the unfilled polymer

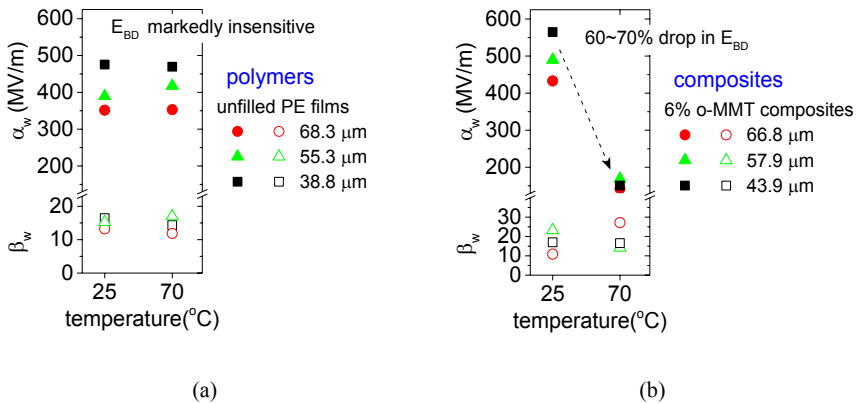


Figure 3. (a) Polymers maintain their E_{BD} at a higher temperature, suggesting again that the polymer does not fail electromechanically. (b) Composites display a notable drop in E_{BD} with temperature, attributing the partial-discharge of space charges (organic cationic surfactants, etc.) as the primary breakdown mechanism.

films and the composite films. As shown in Figure 3(a), the polymer films markedly maintain E_{BD} at a higher temperature (increasing from 25 °C to 70 °C), which (a) is expected in the absence of any T-transitions for PE in this temperature range and (b) offers another strong evidence that the polymer does not fail electromechanically (as temperature increase leads to a Young's modulus reduction, *cf.* 375 MPa at 25 °C vs. 60 MPa at 70 °C, which for electromechanical failure would have led to a reduction of E_{BD} by a factor of 2.5). On the other hand, a notable drop in E_{BD} (by 60%-70%) for the same temperature step is observed for the composite films (Figure 3(b)); given that MMT is not expected to alter the dominant failure mechanism for these films, this E_{BD} drop can be attributed to thermal liberation of trapped charges (ions or surfactants associated with or trapped on the organoclay surfaces) and enable their diffusive movement within the matrix (i.e., a T-triggered population increase of mobile space charge).

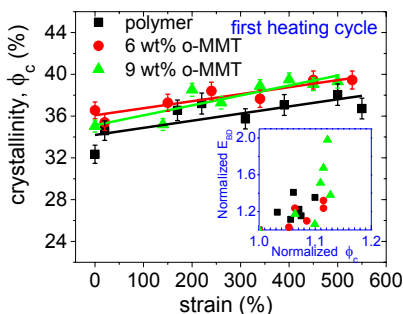


Figure 4. Crystallinity (DSC enthalpy of first melting) as a function of strain for all films, showing the typical strain-induced crystallization (**inset**): E_{BD} is markedly unrelated to crystalline fraction for these systems.

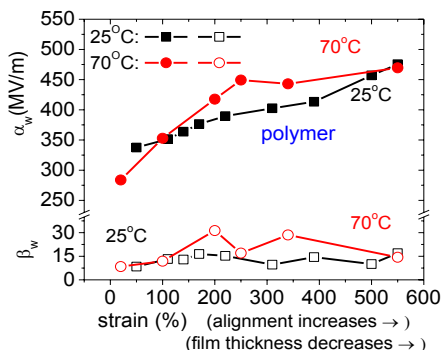


Figure 5. Weibull α_w (E_{BD}) and β_w of unfilled uniaxially-strained films. E_{BD} systematically increases with better crystal orientation parallel to the film surface, supporting the proposed barrier hypothesis (*cf.* Figure 1). In addition, polymers retain their E_{BD} at higher T, suggesting predominant thermal failure mechanism.

It should be pointed out that although the composite films of Figure 3(b) were produced at various thicknesses by varying the blow-molding parameters (varied blowup ratio), the unfilled films of Figure 3(a) were obtained through uniaxial cold-stretching of a 95 μ m blown film. Since uniaxial stretching can result in strain-induced crystallinity changes, we verified that this does not have a substantial effect on E_{BD} , for neither the unfilled films, nor the composites (Figure 4 inset). This is a direct consequence of our choice to use a highly nucleated PE as the matrix, i.e., crystallinity is already high, even in absence of the MMT fillers.

On the other hand, any strain-induced crystallite reorientation, in both the unfilled polymers and in the composites films, would effectively promote oriented barriers in the same manner as discussed in Figure 1 and is expected to lead to increased E_{BD} values for higher strains, i.e., better ordering of polymer crystals and inorganic fillers parallel to the film surface

(Figure 5). This behavior can be studied in detail, to delineate the importance of the polymer crystals and of the MMT inorganic fillers as barriers to e-treeing and, also, quantify these two contributions to the E_{BD} improvement seen in the oriented nanocomposite films; this is the subject topic of the second paper in this series (*vide infra*).

CONCLUSIONS

PE-MMT nanocomposites were studied in detail, and compared to the unfilled respective films, as dielectric/insulating materials. The electric breakdown strength (E_{BD}) of 'isotropic' composites is much worse than the E_{BD} of 'aligned' composites, strongly supporting a barrier mechanism as the origin of electric strength improvement. Further, we quantified that E_{BD} is not related to filler-induced or strain-induced crystallinity changes, and E_{BD} decreases with modulus but improves with toughness for these films. All these, support the postulation that the electrical breakdown of these systems is predominately through thermal degradation mechanisms. This study, reveals the dominant mechanisms of electric breakdown for the PE/MMT nanocomposite films, but leaves as an open question whether this barrier mechanism originates from the polymer crystallites and/or from the inorganic nanofillers; this question is addressed in the following paper in this issue.

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