Supporting Information

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Repurposing Poly(3-hexylthiophene) as a Conductivity-Reducing Additive for Polyethylene-Based High-Voltage Insulation

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Table S1. Effect of different types of conductivity-reducing additives on the DC conductivity of LDPE expressed in terms of the DC conductivity $\sigma_{DC}$ of the additive-containing resin relative to the DC conductivity of the neat LDPE resin $\sigma_{DC}^{PE}$, and as the efficiency $\eta = (\sigma_{DC}^{PE}/\sigma_{DC})/\phi$, where $\phi$ is the additive content in wt%. We limit our survey to DC conductivity measurements where the electric field was applied for at least 1 h, although values approaching the steady-state are only obtained for much longer measurements.

a The matrix is crosslinked LDPE (XLPE); b Values of the reported charging current in A.

| Type of Additive | $\phi$ (wt%) | $\sigma_{DC}^{PE}$ ($S \cdot m^{-1}$) | $\sigma_{DC}$ ($S \cdot m^{-1}$) | $\sigma_{DC}^{PE}/\sigma_{DC}$ | Efficiency $\eta$ (wt%) | Ref. |
|------------------|--------------|--------------------------------------|----------------------------------|-------------------------------|-------------------------|------|
| Inorganic Nanoparticles | | | | | | |
| ZnO | 3 | $3 \times 10^{-14}$ | $1 \times 10^{-16}$ | 300 | 100 | [1] |
| MgO | 3 | $3 \times 10^{-14}$ | $5.5 \times 10^{-16}$ | 54 | 18 | [2] |
| Al₂O₃ | 3 | $3 \times 10^{-14}$ | $1 \times 10^{-15}$ | 30 | 10 | [3] |
| SiO₂ | 2 | $6.5 \times 10^{-10}$ | $8 \times 10^{-11}$ | 8 | 4 | [4] |
| Polyolefins | | | | | | |
| HDPE⁠ₐ | 1 | $1 \times 10^{-14}$ | $8 \times 10^{-16}$ | 13 | 13 | [5] |
| Hybrid | | | | | | |
| HDPE + Al₂O₃⁠ | 4 + 3 | $1 \times 10^{-14}$ | $3 \times 10^{-17}$ | 333 | 48 | [6] |
| Carbon Allotropes | | | | | | |
| Graphene | 0.1 | $1 \times 10^{-14}$ | $1.1 \times 10^{-15}$ | 9 | 90 | [7] |
| Graphene Oxide | 0.1 | $2.5 \times 10^{-13}$ | $1.2 \times 10^{-13}$ | 2 | 20 | [7] |
| Graphene Oxide | 0.01 | $5.5 \times 10^{-14}$ | $8 \times 10^{-15}$ | 7 | 700 | [8] |
| Voltage Stabilizers | | | | | | |
| Anthracene | 0.5 | $2 \times 10^{-11}$ | $4 \times 10^{-12}$ | 5 | 10 | [9] |
| 3-aminobenzoic acid | 1 | $9 \times 10^{-13}$ | $5 \times 10^{-14}$ | 18 | 18 | [10] |
| 4,4'-dihydroxy benzophenone | 0.5 | $7 \times 10^{-15}$ | $1.5 \times 10^{-15}$ | 5 | 10 | [11] |
| Conjugated Polymers | | | | | | |
| P3HT | 0.0005 | $7 \times 10^{-14}$ | $2.6 \times 10^{-14}$ | 3 | 60'000 | this work |
**Figure S1.** Second heating DSC thermograms of neat LDPE and P3HT.

**Figure S2.** Second heating DSC thermograms of P3HT:LDPE blends.
Figure S3. Visual detection with a Kofler bench of melting of P3HT in a P3HT:LDPE blend

c_{P3HT} = 0.01 \text{ wt\%}; \text{ sample thickness } \sim 0.3 \text{ mm}.
**Figure S4.** Polarized optical micrograph of a P3HT grain placed on top of a 30 µm thick sheet of polyethylene, sandwiched between glass slides and heated for 2 min at 250 ºC.

**Figure S5.** UV-Vis absorbance spectrum of a melt-pressed plaque of a blend with c_P3HT = 0.01 wt%; sample thickness ~ 1 mm.
According to standard Franck-Condon standard progression, the relative intensity of the vibronic replica is given by\textsuperscript{[12]}:

\[ I_{0 \rightarrow m} \propto (\hbar \omega)^3 n_f^3 \frac{s^m e^{-S}}{m!} \]  

(Eqn. 1)

where \( n_f \) is the refractive index at the given photon energy of \( \hbar \omega \) at optical frequency of \( \omega \), \( m \) is the Franck-Condon vibronic index, and \( S \) is the Huang-Rhys factor. PL spectrum can be modeled as a modified Franck-Condon progression with a variable 0–0 amplitude\textsuperscript{[12]}:

\[
I(\omega) \propto (\hbar \omega)^3 n_f^3 e^{-S} \times [(a \Gamma (\hbar \omega - E_0) + \sum_{m=1}^{\infty} \frac{s^m}{m!} (\hbar \omega - (E_0 - mE_P))]
\]

(Eqn. 2)

where \( E_0 \) is the 0–0 transition energy, \( E_P \) is the phonon energy of the C=C symmetric stretch, \( \Gamma \) is the line-shape function (simplified to be purely Gaussian with a constant width), and \( a \) is a constant, known as relative intensity of 0–0 band. In above fitting, the parameters of \( S, E_P \) are kept constant and they are respectively, 1 and 0.18 eV. The fitted \( a \) and \( E_0 \) are obtained respectively, 0.52 ± 0.01 and 1.916 ± 0.002, for the PL spectra of P3HT:LDPE blends with \( c_{P3HT} = 0.1 \) wt%.

**Figure S6.** PL spectrum of a melt-pressed plaque of a blend with \( c_{P3HT} = 0.1 \) wt% as well as a fit using the modified Franck-Condon model proposed by Spano et al.\textsuperscript{[12-15]} (red solid line); sample thickness ~ 0.1 mm.
**Figure S7.** High-voltage charging current of P3HT:LDPE blends at 70 °C. (a) the applied step-wise electric field and resulting current as a function of time, (b) charging current at the end of each 3 h step as a function of the applied electric field for samples measured with two different setups (with the same arrangements and electrode dimensions) as well as different processing protocols (melt-pressing of precipitated material vs. as-received pellets), (c) quasi-steady-state charging current at the end of each 3 h step as a function of the applied electric field for blends with $c_{P3HT} = 0.0005$-0.1 wt%.
Figure S8. High-voltage DC conductivities of P3HT:LDPE blends at 30 °C.
**Figure S9.** Space charge distribution in melt-pressed plaques of LDPE and P3HT:LDPE blends at 70 °C; PEA space charge distribution of film samples during charging (3 h, applied electric field of 50 kV mm⁻¹) and depolarization (1 h, removal of the electric field). The position of electrodes is shown as (-) and (+) for LDPE.
Figure S10. Space charge distribution of P3HT:LDPE blends with (a) $c_{\text{P3HT}} = 0.001$ wt\% and (b) $c_{\text{P3HT}} = 0.01$ wt\% at 70 °C.
Figure S11. (a) PEA total charge (not net-charge) decay during 1 h discharging, (d) isothermal surface potential decay (ISPD) after charging of 0.1 mm thick melt-pressed plaques at 8 kV.

References:
[1] A. M. Pourrahimi, T. A. Hoang, D. Liu, L. K. Pallon, S. Gubanski, R. T. Olsson, U. W. Gedde, M. S. Hedenqvist, Adv. Mater. 2016, 28, 8651.
[2] L. K. H. Pallon, A. T. Hoang, A. M. Pourrahimi, M. S. Hedenqvist, F. Nilsson, S. Gubanski, U. W. Gedde, R. T. Olsson, J. Mater. Chem. A 2016, 4, 8590.
[3] D. Liu, A. T. Hoang, A. M. Pourrahimi, L. K. H. Pallon, F. Nilsson, S. M. Gubanski, R. T. Olsson, M. S. Hedenqvist, U. W. Gedde, IEEE Trans. Dielectr. Electr. Insul. 2017, 24, 1396.
[4] K. Y. Lau, A. S. Vaughan, G. Chen, I. L. Hosier, A. F. Holt, J. Phys. Conf. Ser. 2013, 472, 012003.
[5] M. G. Andersson, J. Hynynen, M. R. Andersson, V. Englund, P.-O. Hagstrand, T. Gkourmpis, C. Müller, ACS Macro Lett. 2017, 6, 78.
[6] F. Nilsson, M. Karlsson, U. Gedde, R. Kádár, K. Gaska, C. Müller, P.-O. Hagstrand, R. Olsson, M. Hedenqvist, T. Gkourmpis, *Compos. B Eng.* 2021, 204, 108498.

[7] J. S. Park, Y. S. Kim, H.-J. Jung, D. Park, J. Y. Yoo, J. H. Nam, Y. J. Kim, *J. Nanomater.* 2019, 2019, 9035297.

[8] B. X. Du, C. Han, J. Li, Z. Li, *IEEE Trans. Dielectr. Electr. Insul.* 2020, 27, 418.

[9] Y. Yamano, M. Iizuka, *IEEE Trans. Dielectr. Electr. Insul.* 2009, 16, 189.

[10] X. Chen, A. Paramane, H. Liu, J. Tie, Z. Wei, Y. Tanaka, *Polym. Eng. Sci.* 2020, 60, 717.

[11] B. Du, C. Han, Z. Li, J. Li, *IEEE Access* 2019, 7, 66576.

[12] J. Clark, C. Silva, R. H. Friend, F. C. Spano, *Physical Review Letters* 2007, 98, 206406.

[13] F. Paquin, H. Yamagata, N. J. Hestand, M. Sakowicz, N. Bérubé, M. Côté, L. X. Reynolds, S. A. Haque, N. Stingelin, F. C. Spano, C. Silva, *Physical Review B* 2013, 88, 155202.

[14] F. C. Spano, J. Clark, C. Silva, R. H. Friend, *The Journal of Chemical Physics* 2009, 130, 074904.

[15] J. Clark, J.-F. Chang, F. C. Spano, R. H. Friend, C. Silva, *Applied Physics Letters* 2009, 94, 163306.