

MESOPHASE PITCH-BASED CARBON FIBER COMPOSITES FOR ELECTROMAGNETIC SHIELDING AND ELECTROSTATIC DISSIPATION APPLICATIONS

*Sagar Kanhere, Jasmine McTyer, Courtney Owens, Prof. Amod Ogale**
Center for Advanced Engineering Films and Fibers (CAEFF), Department of Chemical and Biomolecular Engineering, Clemson University, Clemson SC 29634

Abstract

Carbon fiber composites are attractive for electric vehicles because they bring twice as much weight savings as those obtained from glass fiber reinforced composites. The major hurdle in the adoption of CF-reinforced composites is their cost. Mesophase pitch-based carbon fibers have a moderate performance but are potentially much cheaper than their high-strength PAN-based counterparts. Due to their highly graphitic structure, mesophase pitch-based carbon fibers are highly conducting compared to other reinforcement fibers. With the increasing digitalization of vehicles, electromagnetic radiations emitted by circuitry create electromagnetic interference, which can lead to the failure of critical components. Hence, the material used for the vehicle body and packaging of the electronic component in the vehicle should be able to protect from catastrophic failures due to electrostatic charge buildup or electromagnetic interference. Therefore, in this study, melt-blown mesophase-based carbon fibers with a tensile strength of 2.1 ± 0.3 GPa and electrical resistivity of 7.0 ± 0.8 $\mu\Omega\cdot\text{m}$ were incorporated into polyethylene. Upon addition of 30 wt% CFs, the electrical resistivity (ASTM D257) of the composite dropped by 6 orders of magnitude to 10^4 $\Omega\cdot\text{m}$ and electrostatic dissipation time (MIL-STD 3010C) reduced to 1.8 s (at 1% cutoff). Electromagnetic shielding effectiveness (ASTM D4935-18) of the composite increased with increasing carbon fiber content; EMI SE increased from 26 dB for 3 wt% CF to 46 dB for 30 wt % CF at 1.5 GHz. At this low CF content, these mesophase pitch-based carbon fiber composites represent some of the best electromagnetically shielded composites.

*Corresponding author: ogale@clemson.edu

Background

Due to their lightweight, design flexibility, and corrosion resistance, polymer composites are being used heavily in the automotive industry. Predominantly glass fiber reinforced plastics are used due to cost considerations, but they are highly insulating and cannot dissipate static charge buildup. With the increasing number of electronics components and sensors in the vehicle, there is susceptibility to failure due to static charge buildup or electromagnetic interference (EMI) due to unwanted electromagnetic waves emitted by electrical circuitry. Thus, it is critical that the electronic components are shielded from static discharge and EMI. Along with electronic considerations, the miniaturized electronic components also emit heat that must be dissipated to protect the component from damage due to overheating of electronic components. Metals are good electrical and thermal conductors and provide excellent shielding from EMI. However, metals are heavy and can corrode. Polymer composites with conductive particulate fillers such as graphite nanoplatelets, metal powders, and carbon nanotubes offer higher conductivity than pure polymer. However, these conductive filler powders need to be added in high volume fractions to achieve the required shielding and yet do not provide high mechanical properties [1,2].

Carbon fibers possess not only high specific strength and modulus but also ultrahigh thermal

and electrical conductivity [3]. Mesophase pitch-based carbon fibers are some of the best conducting carbon fibers due to their highly graphitic structure [4,5]. However, the cost of carbon fibers is a limiting factor for the wider adoption of carbon fiber composites in the automotive industry. Since half of the cost of carbon fibers come from their precursor, using potentially low-cost precursor like petroleum-derived mesophase pitch can provide cheaper carbon fibers. Some estimates suggest that the petroleum-derived mesophase pitch-based carbon fibers can cost as low as \$5/lb [6]. The use of discontinuous fiber reinforcement also makes it cheaper for the fabrication of composite parts. Rather than chopping conventional high-performance PAN-based carbon fibers, melt-blowing of the mesophase pitch can directly produce discontinuous fibers at much faster rate and lower cost. Therefore, this paper reports on the thermal and electrical properties of low-density polyethylene (LDPE) matrix composites containing carbon fibers derived from melt-blown mesophase pitch precursors.

Experimental

Material and processing

Petroleum-derived mesophase pitch-based fibers were spun using custom-designed melt-blowing apparatus, and subsequently oxidatively stabilized and carbonized. The resulting carbon fiber mats were placed between low-density polyethylene (LDPE) film and hot-pressed using a hydraulic press (Carver®, Wabash IN) at 150°C and 3 MPa compaction pressure.

Characterization

Thermal conductivity

Through-thickness thermal diffusivity of the films was measured using laser flash analysis technique using LFA 447 Nanoflash (Netzsch, Germany) instrument following ASTM E1461-13 standard. Films were sputter coated with silver and painted with graphite before the diffusivity measurements. Estimated density and heat capacity values of the films were used to calculate the thermal conductivity.

Electrical measurements

Electrical resistivity of individual carbon fibers was estimated using resistance measured across a single filament mounted between two terminals separated by 10 mm and fiber cross-sectional area estimated by measuring diameters. The surface and volume resistivity of the composite specimen was measured with Keithley 6517B Electrometer using Model 8009 resistivity test fixture by following ASTM D257 standard. The electrostatic decay time of the composite specimen was measured following MIL-STD-3010C test method 4046 using Static Decay Meter Model 406D manufactured by Electro-Tech Systems, Inc. (Glenside, PA). The decay time readout has a resolution of 0.01 s. Relative humidity was maintained at less than 12% during measurements, and specimens were conditioned for 24 hrs at 25°C. RoHS compliant ESD shielding electronic packaging film was used as control, and its decay time was measured to be 0.01 s at a 1% cutoff when charged to 5 kV.

Electromagnetic shielding effectiveness

Following ASTM standard D4935-18, electromagnetic shielding effectiveness of the composites was measured using Electro-Metrics EM-2107A split coaxial line fixture and vector network analyzer Agilent HP8753ES. Gold Mylar Assay (Model: X-K711 load and X-K710 reference) with premeasured EMI SE from Electro-Metrics was used as standard to establish the accuracy of EMI shielding effectiveness.

Results and Discussion

Carbon fibers

Figure 1 shows the SEM micrograph of melt-blown carbon fibers. It is evident that the fibers were mostly aligned in one direction, and their cross-sectional microstructure was circular. There is no evidence of major defects like holes in the cross-section or on the lateral surface of the fiber. The tensile strength of the carbon fibers was measured to be 2.0 ± 0.3 GPa, whereas the apparent tensile modulus of the carbon fibers was measured to be 260 ± 31 GPa. The electrical resistivity of the carbon fibers was measured to be at 7.0 ± 0.8 $\mu\Omega\cdot\text{m}$. Issi-Lavin correlation was used to estimate the thermal conductivity of these carbon fibers at 166 ± 44 W/m.K [7]. In comparison, commercial PAN-based CFs like T300 have an electrical resistivity of 17 $\mu\Omega\cdot\text{m}$ and thermal conductivity of about 10.5 W/m.K [8].

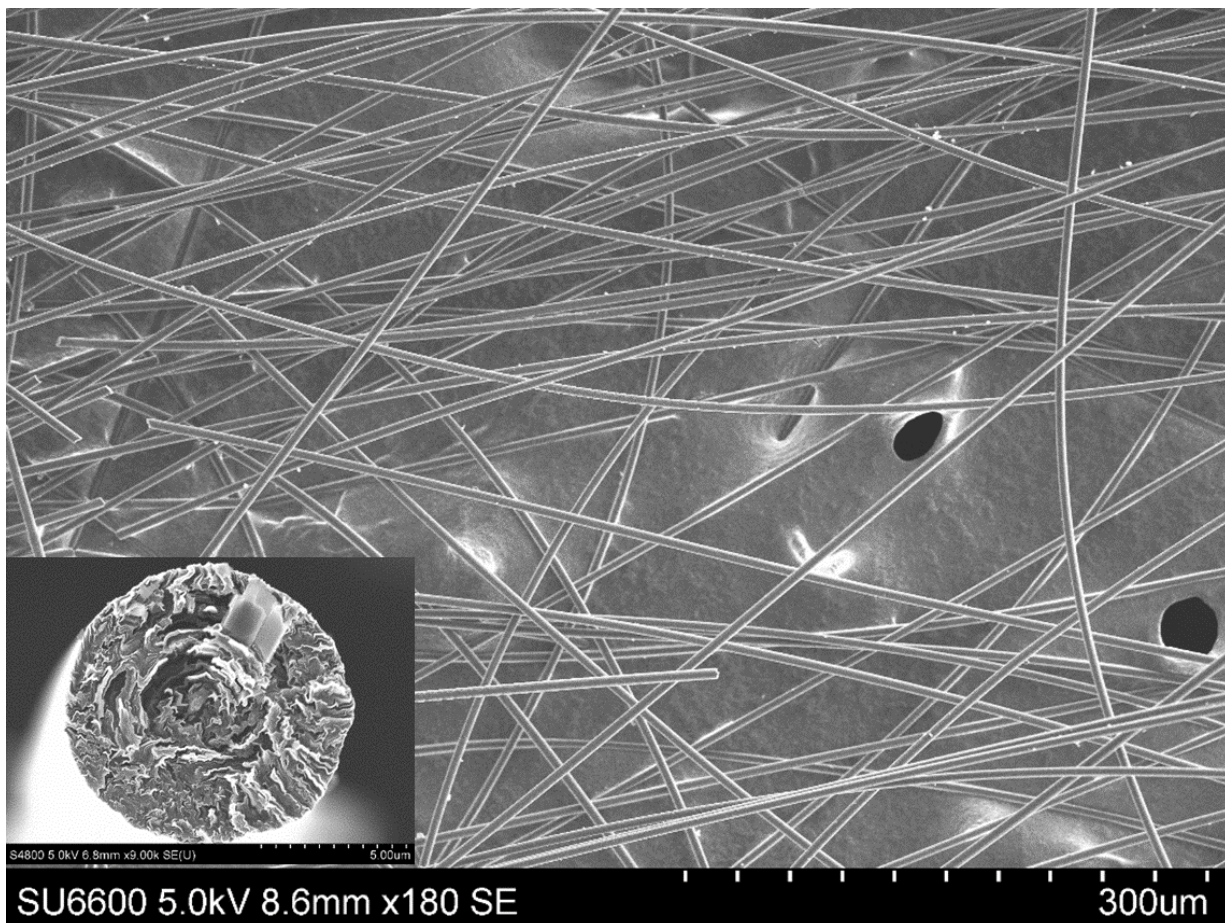


Figure 1: Scanning electron micrograph of melt-blown fibers. Inset : Cross-sectional microstructure of CFs

Composite Characteristics

Thermal conductivity

Figure 2 presents the measured through-thickness thermal conductivity of composites containing various concentrations of carbon fibers. Pure LDPE polymer (matrix) displayed a low thermal conductivity of 0.20 ± 0.02 W/m.K, consistent with that reported in the literature [9]. With

the addition of conducting CFs, thermal conductivity gradually increased over 300% to 0.76 ± 0.13 W/m.K when carbon fiber content was 50 wt%, which is almost three times as much as that of pure LDPE polymer thermal conductivity. This is consistent with the rise in thermal conductivity of short discontinuous carbon fiber-filled polyethylene composites reported at about 0.8 W/m.K for 60 wt% CF content [10].

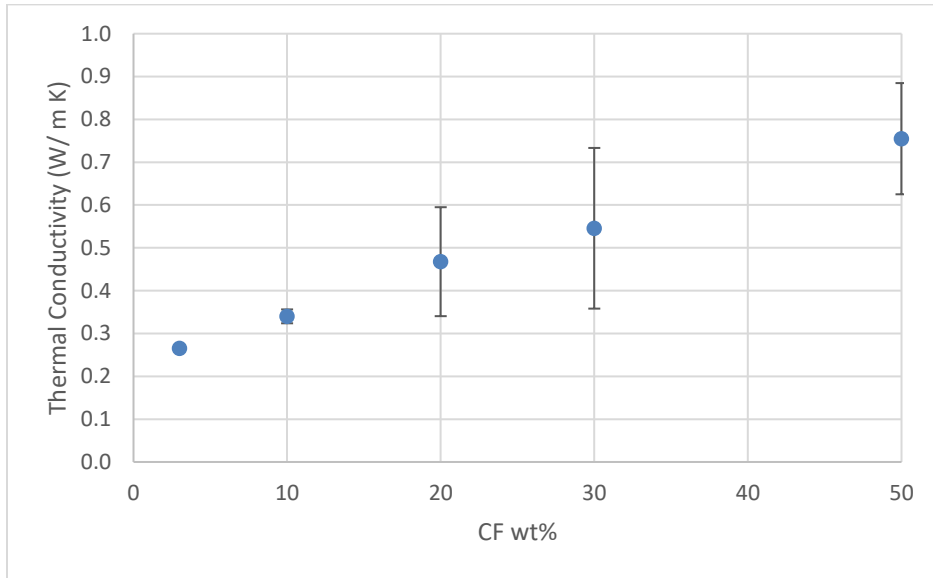


Figure 2: Thermal conductivity of the composite as a function of carbon fiber content (wt%)

Electrical resistivity

Volume resistivity of the neat LDPE polymer was measured at 10^{12} Ω .m, which dropped five orders of magnitude to 10^7 Ω .m upon the incorporation of 3 wt% carbon fibers. As carbon fiber content increased, the volume resistivity of the composite decreased, and it was 10^5 Ω .m for composites containing 50 wt% CFs. The surface resistivity of neat LDPE is 10^{15} Ω per square and upon CF filling, it dropped to 10^9 Ω per square with three wt% CF filling and further four orders of magnitude to 10^5 Ω per square at 50 wt% CF content.

Electrostatic dissipation time

Table 1 displays electrostatic decay (ESD) time at 50%, 10% and 1% cutoff voltage for composites for various CF content. Neat LDPE required more than 500 seconds for static charge dissipation, a highly undesired characteristic. In contrast, the measured decay times for all of the composites were below 2 seconds. Per military standard Mil-B-81705C [11,12], 99% of the surface's static charge buildup (i.e., 1% cutoff) must be dissipated in less than 2 seconds to be considered dissipative material for electronic applications. Thus, all of these melt-blown mesophase pitch-derived CF-LDPE composites can be regarded as electrostatic-dissipative materials.

Table 1: Electrostatic decay time for composites with different CF contents

CF wt%	Cut off %		
	50%	10%	1%
	Time (s)		

3	0.01	0.02	1.00
10	0.01	0.01	1.82
20	0.01	0.01	1.47
30	0.01	0.01	1.20
50	*	0.01	1.83

*Below instrument detection limit

Electromagnetic shielding effectiveness

Figure 3 displays the electromagnetic shielding effectiveness measured between 30 MHz and 2 GHz. It is evident from the results that a composite containing as little as three wt% CF content possesses an EMI shielding effectiveness of about 26 dB. With increasing CF content, EMI-SE increases almost two-fold, close to 50 dB at 50 wt% CF content. These EMI SE values are comparable to those of continuous CF composites and carbon nanotube-modified continuous CF composites [2,13,14].

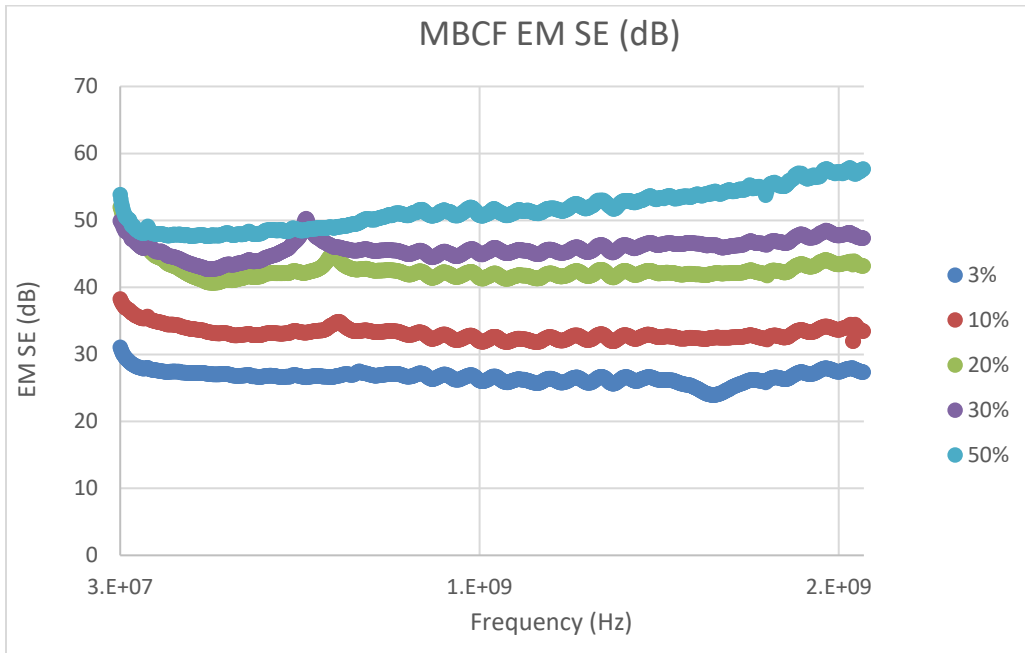


Figure 3: Electromagnetic shielding effectiveness (EM SE) of CF-LDPE composites at different CF contents.

Concluding Remarks

In conclusion, the addition of highly conducting mesophase pitch-based CFs increased thermal conductivity by 300% and reduced the electrical resistivity by over 5 orders of magnitude. Significant reduction in surface resistivity also reflected in electrostatic dissipation time of under 2 seconds for CF content as low as 3 wt%. Significantly, the EMI shielding effectiveness of the composites was about 26 dB at 3 wt% CF content and 50 dB for 50 wt% CF content. Thus, the low-cost, high-volume mesophase melt-blowing process led to highly conducting carbon fibers that could directly be incorporated into LDPE. Due to the highly conducting nature of individual filaments and the network of CFs formed, the composites were not only electrostatically dissipating but also possessed excellent electromagnetic shielding at low CF content.

Acknowledgments

This project made use of Engineering Research Center (ERC) Shared Facilities supported by the National Science Foundation under Award Number EEC-9731680 to the Center for Advanced Engineering Fibers and Films (CAEFF). We also thank Elijah Taylor for his help during fiber spinning and Mark Walsh for his help with tensile testing and electrical resistivity of carbon fibers.

Bibliography

- [1] S. Kanhere, O. Guzdemir, C. Owens, E. Taylor, J. McTyer, A. Ogale, GRAPHITE NANOPATELET-FILLED LINEAR LOW-DENSITY POLYETHYLENE: NANOCOMPOSITES FOR ENHANCED HEAT TRANSFER AND ELECTROSTATIC DISSIPATION, in: SAMPE Conference Proceedings, Charlotte, NC, 2022.
- [2] E. Mikinka, M. Siwak, Recent advances in electromagnetic interference shielding properties of carbon-fibre-reinforced polymer composites—a topical review, *J Mater Sci: Mater Electron.* 32 (2021) 24585–24643. <https://doi.org/10.1007/s10854-021-06900-8>.
- [3] V. Bermudez, S. Lukubira, A.A. Ogale, 1.3 Pitch Precursor-Based Carbon Fibers, in: P.W.R. Beaumont, C.H. Zweben (Eds.), *Comprehensive Composite Materials II*, Elsevier, Oxford, 2018: pp. 41–65. <https://doi.org/10.1016/B978-0-12-803581-8.10312-1>.
- [4] S.V. Kanhere, V. Bermudez, A.A. Ogale, Transport properties of carbon fibers derived from petroleum-based mesophase pitch with modified transverse microstructure for enhanced tensile strength, in: *CAMX 2020 - Composites and Advanced Materials Expo: Combined Strength. Unsurpassed Innovation.*, 2020.
- [5] M.G. Huson, *High-performance pitch-based carbon fibers*, Woodhead Publishing, Oxford, 2017. <https://doi.org/10.1016/B978-0-08-100550-7.00003-6>.
- [6] J. Sloan, Coming to carbon fiber: Low-cost mesophase pitch precursor, *Composites World Weekly*. May 10th (2016).
- [7] J.G. Lavin, D.R. Boyington, J. Lahijani, B. Nystem, J.P. Issi, The correlation of thermal conductivity with electrical resistivity in mesophase pitch-based carbon fiber, *Carbon.* 31 (1993) 1001–1002. [https://doi.org/10.1016/0008-6223\(93\)90207-Q](https://doi.org/10.1016/0008-6223(93)90207-Q).
- [8] Inc. Toray Composite Materials America, T300 Standard Modulus Carbon Fiber, 2020 (2018) 2.
- [9] A. Trigui, M. Karkri, I. Krupa, Thermal conductivity and latent heat thermal energy storage properties of LDPE/wax as a shape-stabilized composite phase change material, *Energy Conversion and Management.* 77 (2014) 586–596. <https://doi.org/10.1016/j.enconman.2013.09.034>.
- [10] Y. Agari, A. Ueda, S. Nagai, Thermal conductivity of a polyethylene filled with disoriented short-cut carbon fibers, *Journal of Applied Polymer Science.* 43 (1991) 1117–1124. <https://doi.org/10.1002/app.1991.070430612>.
- [11] R.B. Rosner, Conductive materials for ESD applications: an overview, *IEEE Transactions on Device and Materials Reliability.* 1 (2001) 9–16. <https://doi.org/10.1109/7298.946455>.
- [12] B.S. Villacorta, EFFECT OF GRAPHITIC CARBON NANOMODIFIERS ON THE ELECTROMAGNETIC SHIELDING EFFECTIVENESS OF LINEAR LOW DENSITY POLYETHYLENE NANOCOMPOSITES, PhD, Clemson University, 2013.
- [13] S.İ. Mistik, E. Sancak, S. Ovalı, M. Akalın, Investigation of electromagnetic shielding properties of boron, carbon and boron–carbon fibre hybrid woven fabrics and their polymer composites, *Journal of Electromagnetic Waves and Applications.* 31 (2017) 1289–1303. <https://doi.org/10.1080/09205071.2017.1348257>.
- [14] S. Gong, Z.H. Zhu, M. Arjmand, U. Sundararaj, J.T.W. Yeow, W. Zheng, Effect of carbon nanotubes on electromagnetic interference shielding of carbon fiber reinforced polymer composites, *Polymer Composites.* 39 (2018) E655–E663. <https://doi.org/10.1002/pc.24084>.