DEVELOPMENT AND APPLICATIONS OF NANO- AND MICROSCALE LAYERS OF CONDUCTIVE POLYMERS APPLIED ONTO VARIOUS SURFACES

Dr. Jamshid Avloni[1], Dr. Arthur Henn[2] & Ryan Lau[1]
[1]Eeonyx Corp., Pinole, CA 94564, USA
Tel: 1-510-741-3632, Fax: 1-510-741-3657, Email: javloni@eeonyx.com, Website: www.eeonyx.com
[2]Marktek Inc., Chesterfield, MO 63017, USA
Tel: 1-314-878-9190, Fax: 1-314-878.9558, Email: arhenn@marktek-inc.com

BIOGRAPHICAL NOTE

Dr. Jamshid Avloni, President, COO, has more than 27 years of experience involving the chemistry of traditional polymers and 21 years in developing electrically conductive polymer (CP) materials. He leads development, production and applications of conductive fabrics at Eeonyx Corporation. Prior to joining Eeonyx Corporation in 1995, he was a Scientist at the Department of Chemistry of The University of Pennsylvania in the group of Professor Alan G. MacDiarmid (awarded the Nobel prize in chemistry in 2000 for co-discovery of CPs). There, Dr. Avloni worked (1991-1995) on synthesis, characterization, blending and processing of CP materials. He was the first to demonstrate the effect of CP molecular conformation on their electrical conductivity.

ABSTRACT

Eeonyx Corp. has developed a line of conductive polymer coatings that can be applied to fabrics, felts, foams, films, powders, and plastic parts over a large range of tunable resistances. Materials of almost any composition, including silicones, polyolefins, and fluoropolymers, can be made conductive by the Eeonyx proprietary process. EeonTex(TM) fabrics are lightly colored, totally uniformly conductive fabrics that possess excellent resistance to heat, humidity, UV radiation, sloughing, and cleanroom/ordinary laundering. The use of EeonTex fabrics in biomedical instruments, sensors, antennas, resistive heaters, static control, cleanrooms, automobiles, and military-related applications will be discussed. Coating conductive polymers onto powdered carbonaceous substrates leads to conductive additives, called Eeonomers(R), that possess excellent thermal stability, advanced electrical properties, and superior blending characteristics. Applications of Eeonomers in electronics packaging will be highlighted. New EeonFoam(TM) lossy foams are open-cell polyurethane foams coated with conductive polymer coatings. Such foams are expected to be used for absorbing radar, damping cavity resonances, EMI suppression, and static dissipation.

---

1. INTRODUCTION

Inherently (or intrinsically), electrically conductive polymers (ICP's) were discovered about thirty years ago, but it is only in the past decade that they have found widespread use in a variety of applications. In this paper, we discuss the properties and applications of conducting polymers, predominantly polypyrrole, deposited onto the surfaces of various substrates. By coating thin layers of conducting polymers onto substrates, such as textiles, one overcomes many of the processing problems associated with pure conducting polymers. For instance, if one coats a fabric with a conducting polymer, one now has a strong, flexible, sometimes stretchy, fully “fabricatable” conductive material. The thin coatings do not change the mechanicals of the base fabrics.

Eeonyx's proprietary processing technology that allows us to make all the products discussed below involves immersion of the base substrates in aqueous solutions. One of the main advantages of the present technology is that the conductive polymer coatings can be applied onto almost any surface in almost any form. The most common materials that have been coated with conducting polymers are textiles of polyester, nylon, glass, and polyurethanes. In addition, quartz, aramids, acrylics, and polyimides are readily coated. With a surface pretreatment, even low-surface energy materials, such as polyolefins, fluoropolymers [1], and silicones, can be made conductive on the surface with good coating adhesion. Another major advantage of this coating technology is that it results in uniform, coherent, nonparticulate coatings that afford a very wide range of surface resistivities. Depending on the particular substrate, surface resistivities from about 10 ohm/sq up to 10 billion ohm/sq can be obtained. A good overview describing the basic technology of in situ deposition of conducting polymers onto fabrics is given by Kuhn and Child, in chapter 35 of the “Handbook of Conducting Polymers, 2nd edition [2].

2. EEONTEX™ CONDUCTIVE TEXTILES - TEXTILES COATED WITH CONDUCTING POLYMERS

Conducting polymers, such as polypyrrole (PPY), polyaniline (PAni), and polyethylenedioxythiophene (PEDOT) have been deposited onto various textiles in the forms of woven fabrics, knit fabrics, felts, other nonwoven structures, and fibers. For a given amount of coating add-on, it has been found that, of the three ICP's mentioned, PPY tends to produce the most conductive end materials. The coatings usually are applied to full-width, long rolls of fabric or to fabricated items. For instance, electro-static dissipative (ESD) gloves, hook & loop bands, and 8"x8" wipes have been prepared by immersing the untreated items in the appropriate baths.

2A. BASIC PROPERTIES OF CONDUCTIVE FABRICS

Being able to choose the starting fabric construction for certain properties (e.g., strength, porosity, stretch, thickness, etc.) and subsequently control the end surface resistivity with customized conductive polymer coatings allows one to prepare fabrics that possess a broad range of properties. This makes them suitable for a variety of applications. As noted, surface resistivities between 10 ohm/sq and 10 billion ohm/sq are readily achievable, and resistance gradients that cover a large portion of this range have been made.

A reasonable estimate of the bulk resistivity, R_b, of a thin, conductive fabric that is coated through and through is to multiply the dc surface resistivity, R_s by the fabric thickness, t. Since typical fabric thicknesses range from 0.1 mm to a few mm or so (beyond that thickness, the simple relationship starts to breakdown), the approximate bulk resistivities of our fabrics vary over even a wider range than cited for surface resistivity. For reference purposes, the dc bulk conductivity of the deposited polypyrrole coating itself is usually 170 – 180 S/cm [3]. It is important to note that the conductivity will vary with frequency, although, at high (GHz and above) and low (kHz and below) frequencies, the conductivities are expected to be fairly constant.

An important, potentially useful property of any conductive fabric is its ability to shield against electromagnetic radiation. Figure 1 shows the insertion loss (IL) of several, PPY-coated, ~0.635 mm-thick, microfiber nonwovens of increasing surface resistivities. The data were obtained from dual-TEM cell measurements up to 900 MHz [4]. As expected, the (IL) loss, which is equivalent to shielding effectiveness (SE) and transmission (Tx) loss, increases with decreasing electrical resistance. The very low resistance (below 10 ohm/sq) samples were specially prepared by multiple dips. For ordinary, low-level shielding applications, a PPY-coated fabric will do the job.

From Tx loss measurements, one can extract permittivities, ε, and impedances, Z, of the materials at the measured frequencies. It is observed that the impedances at the higher frequencies are always lower than the dc surface resistivities by usually 10-20%. This is due, we believe, to a small capacitance (reactive) contribution to the complex impedance that arises from a slight degree of granularity of the coating and the irregular structure of the base fabrics [4;5]. Conductive coatings containing discrete carbonaceous particulates, in contrast, show a much higher capacitance contribution and greater variation in transmission loss at high frequencies. Likewise, the phase angle of carbon black coatings is higher relative to conducting polymer-coated fabrics. Figure 2 is the transmission loss and phase angle graph for a balanced (no orientation effect), PPY-coated, 30-ohm/sq, woven glass fabric.

From the insertion loss data above and using the appropriate equations, we can estimate the absorption and reflection contributions to the shielding effectiveness of PPY-coated fabrics. Compared to metallized fabrics, the absorption component of a conducting polymer fabric represents a higher contribution to the overall shielding. Metal-coated fabrics, on the other hand, shield predominantly by reflection. In many situations, it is preferable to attenuate electromagnetic radiation by absorption as opposed to simply reflecting it uncontrollably. This is something to keep in mind for specific shielding applications. For instance, PPY-coated woven polyester twill fabric is used to make artificial horizon, radar barriers for the military aerospace industry because a significant portion of its shielding is due to absorption.

Because conducting polymer-coated fabrics, especially thicker ones, can absorb a high degree of electromagnetic radiation, they can be used in EMI suppression and crosstalk reduction applications. Figure 3 shows the reduction in crosstalk when either a 6 mm-thick piece of PPY-coated felt or ¼"-thick foam is placed inside an electronic enclosure suffering from crosstalk.

Another important performance characteristic of conductive fabrics, also related to microwave absorption, is their ability to reduce reflection of radar signals in various configurations. Figure 4 exhibits the reflection (Rx) loss of a 6 mm-thick plush fabric coated with PPY to 110 ohm/sq. Note the deep minimum, at 15 GHz, of the material by itself and the obvious orientation dependence. Below 100 ohm/sq, while absorption increases, reflections start to become more significant as well.

Important to any laminate composite application are the fabric porosity and fabric-to-resin adhesion. PPY-coated fabrics offer good adhesion to common thermoset resins such as epoxies and polyesters. The conductive glass fabrics, in particular, possess the desired electrical or radar response properties while providing mechanical strength for reinforcement. Figure 6 compares some mechanical properties of a thermoset polyester laminate composite made with ordinary, untreated glass to that made with PPY-coated glass fabric. Little difference is observed.

2B. SPECIFIC APPLICATIONS OF CONDUCTIVE POLYMER-COATED FABRICS

Based on their tailored properties and characteristics, conductive polymer-coated fabrics have found use in several, specific, commercial and development applications. The following figures, Figs. 7 – 13, illustrate the diversity of these applications.

3. EEONOMERS - ICP-COATED POWDERS

Carbon blacks coated with ICP's, such as PPY or PAni, have several advantages over ordinary, untreated carbon blacks. The main advantages are 1) reduced surface area, allowing higher loadings into resins with reduced viscosity, 2) enhanced resin compatibility, which results in better dispersion, greater adhesion to resins, and minimal sloughing, and 3) more flat resistance vs. loading behavior, leading to more control of resistances in the ESD region. Figure 14 illustrates the flatter resistance vs. loading behavior of certain ICP-coated carbon blacks vs. ordinary carbon black. The percolation range is broadened in the presence of the ICP.

ICP's, in particular PPY, have been deposited onto a variety of particles, including graphite fibers and inorganic powders. The presence of the ICP on carbon fibers, for instance, improves the adhesion of the fibers to the resin matrices. Interestingly, a side benefit of having a carbon substrate is that the ICP seems to gain significant thermal stability relative to that of ICP on non-carbonaceous surfaces [6;6a].

The major applications for ICP-coated carbon blacks are conductive adhesives, ESD laminates and flooring, and in xerography. It has been found that the addition of a small amount (0.75 wt.%) of these composite powders to cyanate ester- and epoxy-based, die-attach adhesives loaded with ~75% silver flake resulted in electrical conductivity increases of well over 100-fold or more. Likewise, the thermal conductivity of conductively filled systems increased upon the small addition of the ICP-coated carbon blacks [7,8].

The conductive polymer-coated carbon blacks, when loaded into plastics, possess high permittivities and good loss characteristics that can be exploited for shielding or microwave absorption applications. Figure 15 shows complex permittivity and shielding effectiveness data for nylon 12 loaded with a few levels of ICP-coated carbon blacks. Note that the 35 wt% composite has a shielding effectiveness of close to 40 dB and a complex permittivity of 2000. The loss tangent is 2. It is very unlikely that any structured carbon black could be loaded into nylon 12 at this high a level.

4. EEONFOAMS - FOAMS COATED WITH CONDUCTING POLYMERS

Just as conductive polymers can be deposited onto fabrics, so can they be applied to ordinary polyurethane foams which provide greater thickness and 3-D character. As noted in the introduction, other chemical compositions can be coated, so some work has been done on polyethylene, silicone, and polyimide foams. However, open-cell foams are preferred in order to allow complete penetration of the coating solution. Besides cost, this is why most work has centered on open-cell polyurethane foams. Such foams, in varying thicknesses, have been coated to have transmission losses ranging from 1 or less dB/in (dB/2.54 cm) up to over 30 dB/in in the GHz range. Figure 16 shows the Tx loss or shielding effectiveness of 1"(2.54 cm)-thick foams having a couple resistances and made with two different coating formulations. SD designates a new, more thermally stable coating. There are slight differences in performance. Figure 17 shows the calculated propagation constant, γ, which consists of the attenuation and phase constants, as a function of frequency for the 80 and 400 ohm versions of the 1" foams.

These conductively coated foams are finding use in EMI suppression, especially against high intensity fields, cavity resonance damping, crosstalk reduction, radar absorption, vibration dampening, and static dissipation. Because the straight polymer coatings do not contain particulates, they are superior to carbon-coated foams in terms of sloughing and smoother, high frequency response. We should mention that coated, thick felts are currently being investigated as replacements for polyurethane foams due to lower cost, lighter weight, greater flexibility, ease of making gradients, and better burn characteristics. Figure 18 is a picture of a special, tool control case in which its black and yellow polyethylene foam has been made static dissipative with a translucent, conducting polymer coating.

5. CONCLUSIONS

Applying conducting polymer coatings is an excellent way to impart electrical conductivity to nonconductive materials or to improve the properties of already conductive materials. Conducting polymer coatings are now commercially applied to a large variety of substrates, especially textiles, to create new classes of tailored, conductive products. These products possess interesting, useful properties and are being employed in an ever-increasing array of specialty applications.

6. REFERENCES

1. "Patterned Polymer Multilayer Fabrication by Controlled Adhesion of Polyelectrolytes to Plasma-Modified Fluoropolymer Surfaces" T. G. Vargo, J. M. Calvert, K. J. Vynne, J. K. Avloni, A. G. MacDiarmid and M. F. Rubner, Supramolecular Science, 2, 3-4, 169-174 (1995).

2. H. Kuhn and D. Child, in *Handbook of Conducting Polymers*, 2nd edition, T. A. Skotheim, R.L. Elsenbaumer, and J.R. Reynolds, eds., chap. 35, pp. 993-1013, Marcel Dekker, New York (1997).

3. A. R. Henn, *Interference Technology Engineering Master (ITEM) Update*, 66-72 (1996).

4. J. Avloni, L. Florio, A.R. Henn, R. Lau, M. Ouyang, and A. Sparavigna, “Electromagnetic Shielding with Polypyrrole-coated Fabrics”, presented at the EMC Europe Conference, Barcelona, Sept. 2006.

5. A. Sparavigna, A. R. Henn, and L. Florio, *Rec. Res. Dev. Appl. Phys*., 8, 1-20 (2005).

6. "Thermally Stable Intrinsically Conductive Polymer - Carbon Black Composites" J. K. Avloni, W. L. Wison and K. M. Schwartz, Polymer Preprints 39, 131, (1998).

6a. "Thermally Stable Intrinsically Conductive Polymer-Carbon Black Composites As New Additives For Plastics" J. K. Avlyanov, and S. Dahman, in ACS Symposium Series 735, Semiconductive Polymers, p. 270, 1999, ed. B. Hhieh and Y. Wei.

7. N. Iwamoto, “Composite Adhesive Enhancements for the Microelectronics Packaging Industry Using Conductive Polymers”, Proceedings of the Sixth Annual International Conference on Composites Engineering, June 27 – July 3, 1999, D. Hui, ed., pp. 357-8.

8. "Adhesive Composition for Bonding a Semiconductive Device" N. Iwamoto, J. Pedigo, US Patent 5,774,533

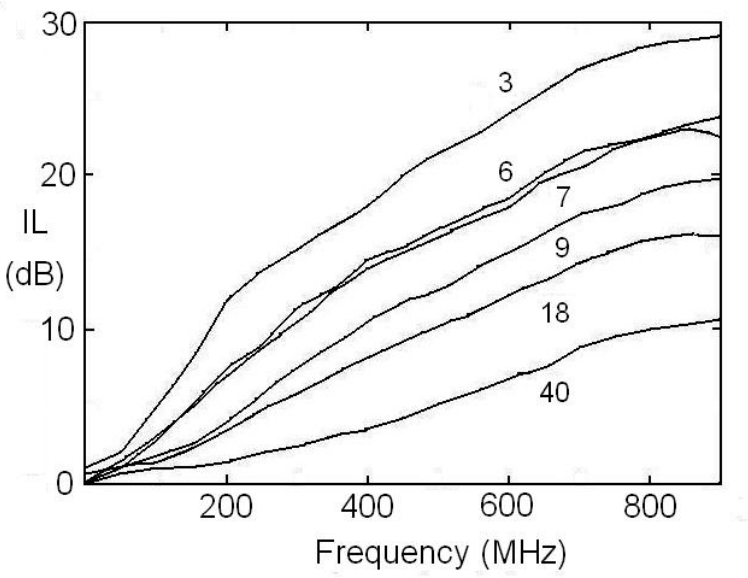


Fig. 1. Insertion loss of PPY-coated microfiber nonwovens of varying electrical resistances. Surface resistivities, in ohm/sq, indicated above each curve.

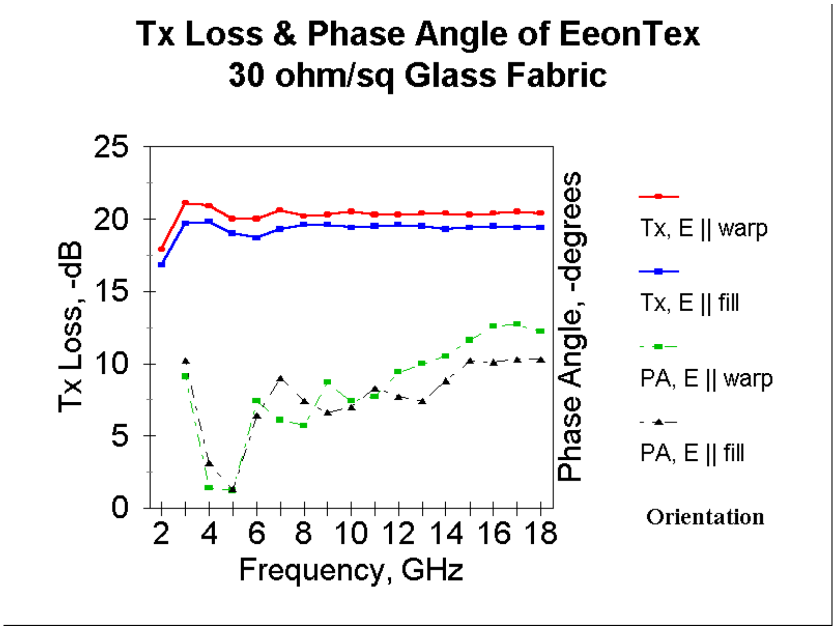
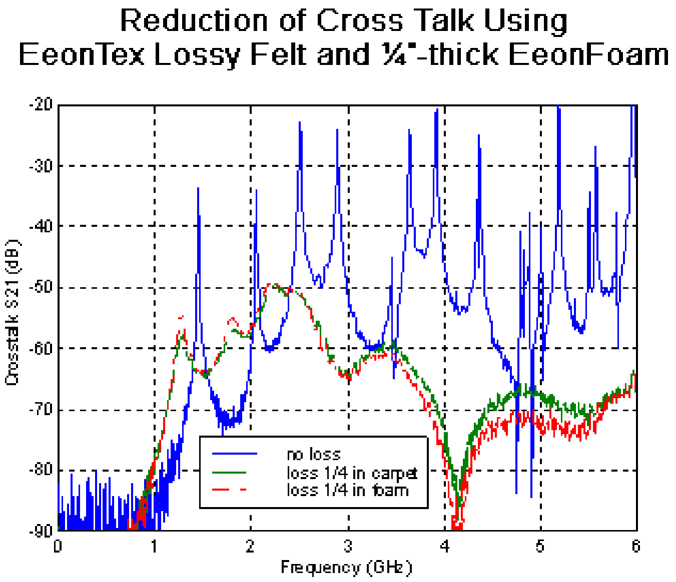


Fig. 2. Transmission loss and phase angle of PPY-coated, 30 ohm/sq, 8-H satin woven S2 glass fabric.



Note: ¼ carpet is ~6-mm thick Eeontex Lossy Felt

Fig. 3. Crosstalk reduction inside an electronic enclosure when PPY-coated felt or foam is present.

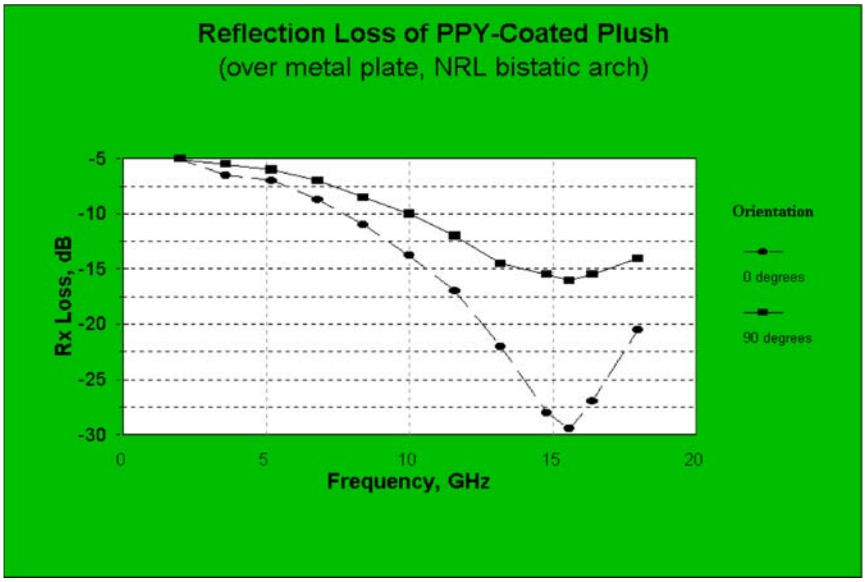


Fig. 4. Reflection loss of a 6 mm-thick, double plush fabric coated with PPY to 110 ohm/sq.

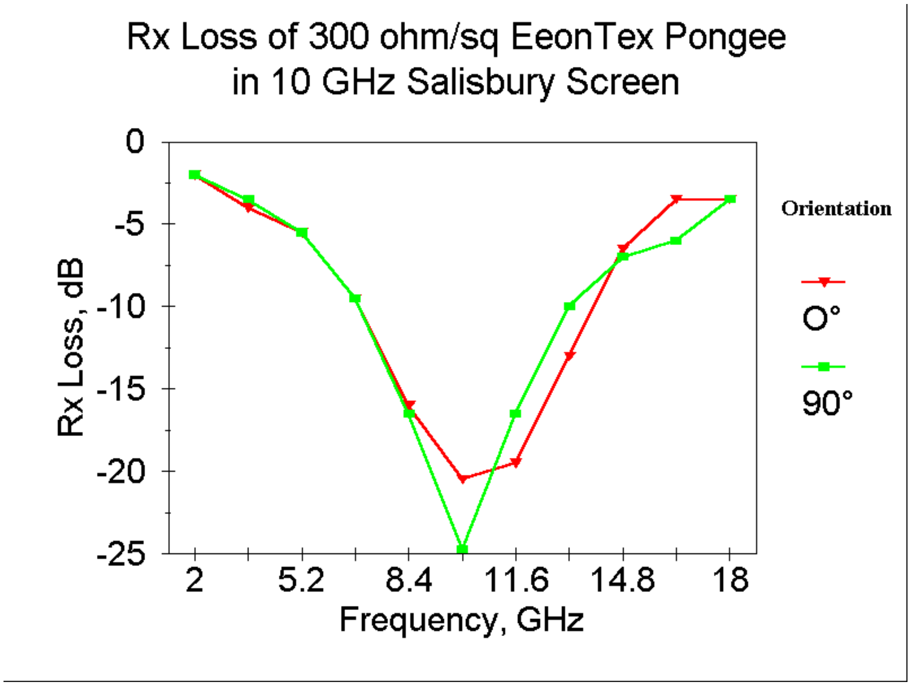


Fig. 5. Reflection loss of a 0.1 mm-thick, 300 ohm/sq fabric in a Salisbury screen configuration with a ¼" dielectric spacer.

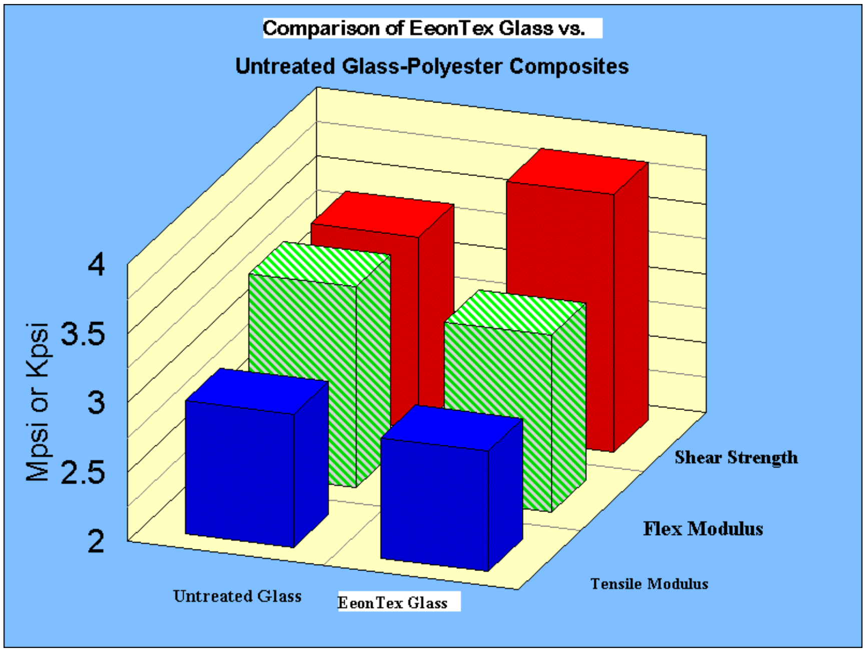


Fig. 6. Comparison of some mechanical properties of conductive polymer-coated glass and untreated glass fabric/thermoset polyester laminate composites.

Fig. 7. A low radar-signature, Navy antenna made from PPY-coated glass fabrics embedded in epoxy.

Fig. 8. A ground-penetrating radar employing conductive fabric to make composite Salisbury screens or Jaumann absorbers designed to eliminate stray radiation.

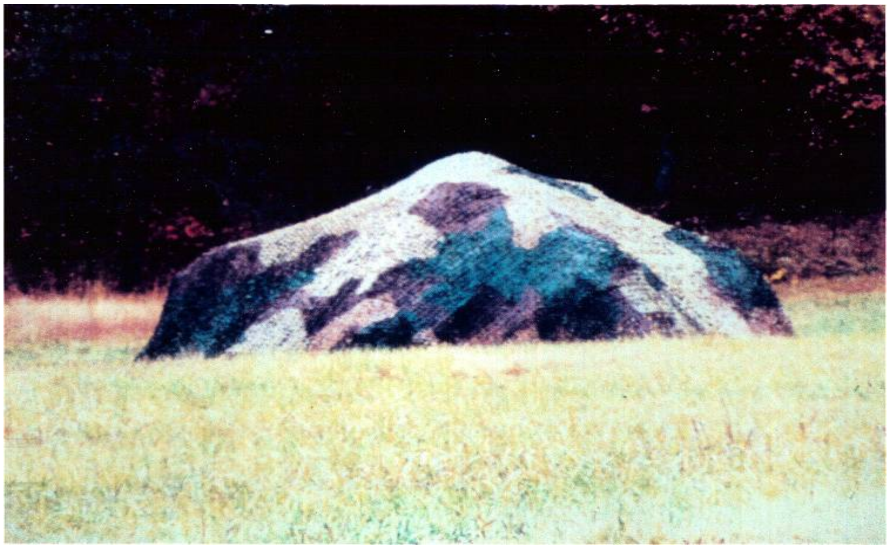


Fig. 9. Multispectral camouflage netting. In addition to providing the radar and IR camouflage, the conductive polymer-coated net functions as the main webbing of the overall camouflage netting.

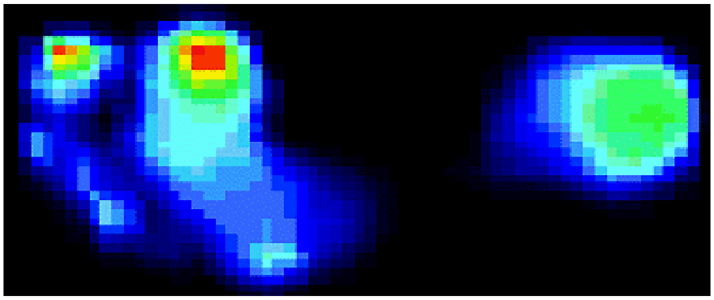


Fig. 10. Illustration of dynamical pressure distribution over the surface of a human foot as sensed by a device employing conductive fabric.

Fig. 11. LazerSkinz impact/pressure sensor vest made with conductively coated fabric.

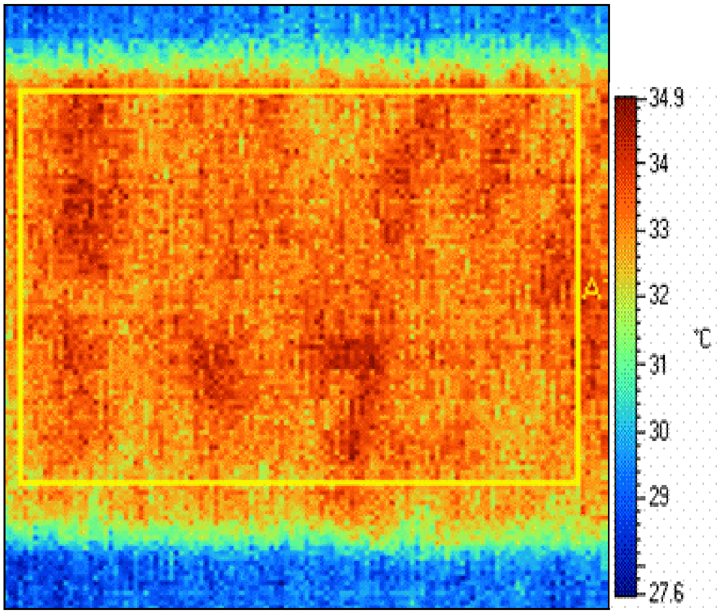


Fig. 12. Demonstration of uniform, resistive heating of a conductively coated fabric in a flexible, surgical warming blanket. IR- temperature image.

Fig. 13. Static dissipative lab coat and gloves coated with light-colored conducting polymer.

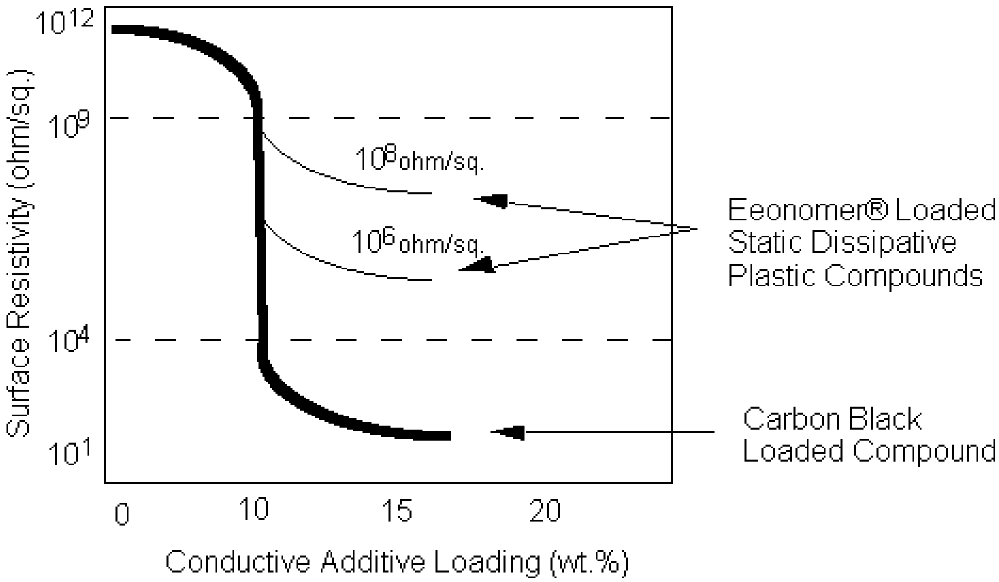


Fig. 14. Flatter loading curves of ICP-coated carbon blacks vs. uncoated carbon black in plastics.

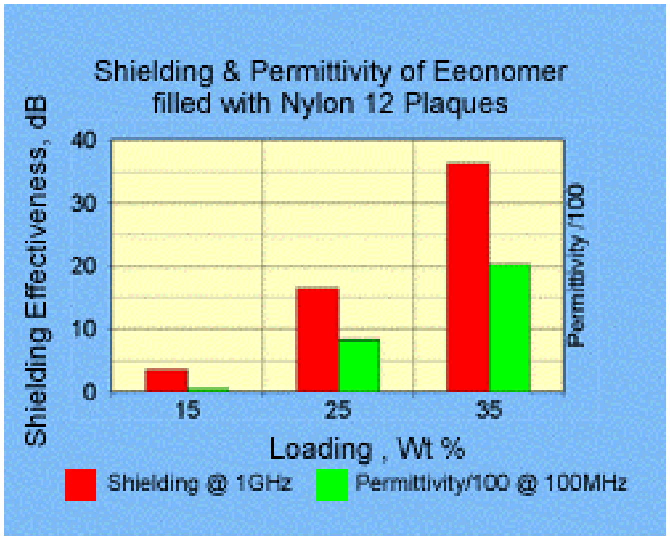


Figure 15. Shielding effectiveness and dielectric constants of nylon 12 filled with three levels of CP-coated carbon black.

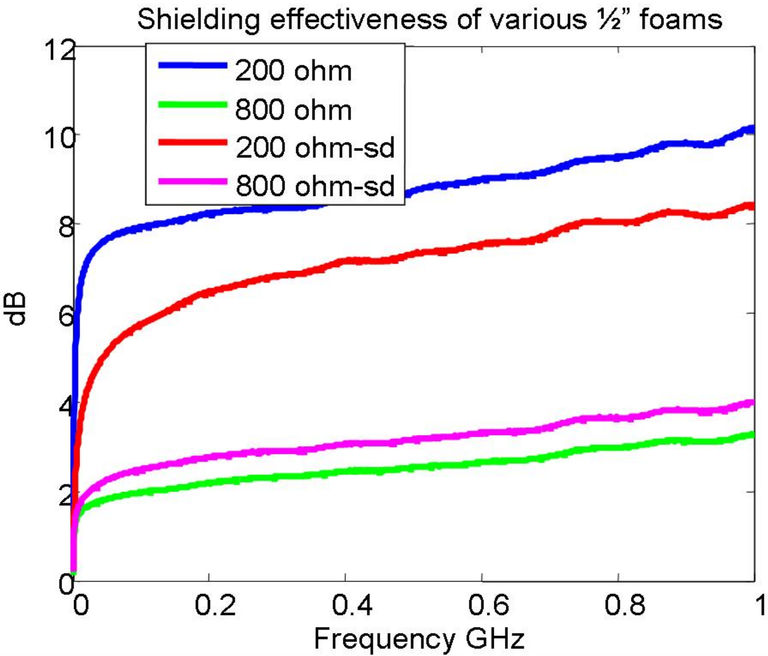


Fig. 16. Shielding effectiveness of 1/2"-thick foams. Legend indicates resistances measured top-to-bottom using point probes, and SD designates a new, thermally stable coating.

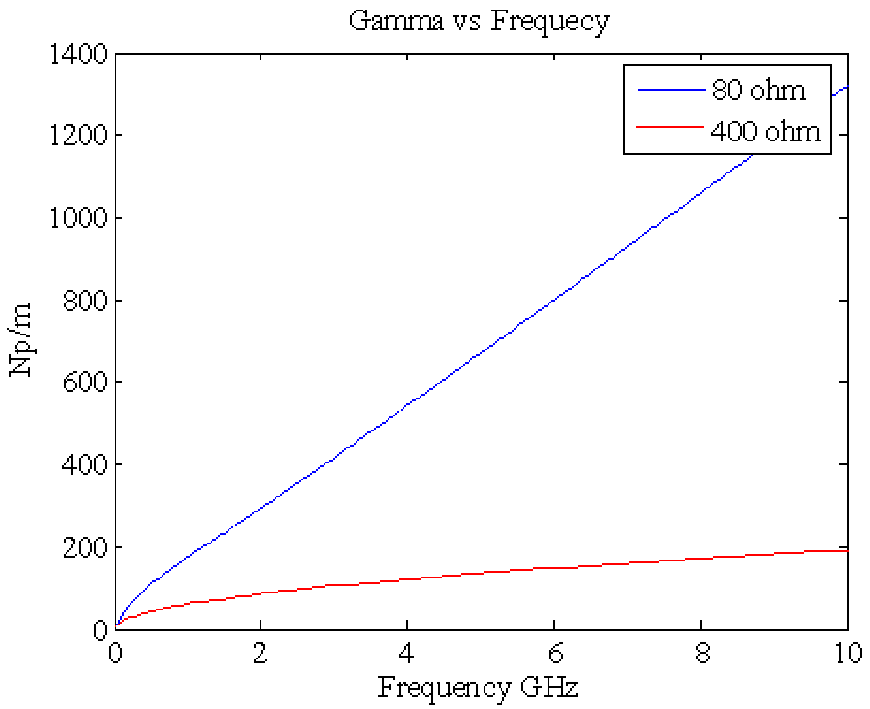


Fig. 17. Propagation constant, γ, as a function of frequency for 80 and 400 ohm, 1” coated foams.

Fig. 18. Static dissipative Tool Control Insert made of yellow/black polyethylene foam coated with translucent conductive polymer layer.