DEVELOPMENT OF NEW CONDUCTIVE AND MICROWAVE-LOSSY MATERIALS INVOLVING CONDUCTING POLYMER COATINGS

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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, who was awarded the Nobel Prize in chemistry in 2000 for co-discovery of CP's. 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.

Dr. Arthur Henn, Pres. of Marktek Inc., has been involved with conductive textiles for 18 years. Prior to founding Marktek Inc. in 1994, he was one of the key team leaders in the technical and commercial development of Flectron® metalized materials at Monsanto Co.

ABSTRACT

Eeonyx Corp. has developed a line of new, conductive polymer coatings that can be applied to fabrics, fibers, felts, foams, films, fillers, and plastic parts over a large range of tunable, controllable resistances (10 ohm/sq, depending on the substrate, to over 10M ohm/sq). Materials of almost any composition, including those of low surface energy, such as polyolefins, can be made conductive by the Eeonyx proprietary process. These uniform polymer coatings possess excellent adhesion and resistance to heat, humidity, UV radiation, and mild laundering. The proprietary technology allows one to combine the desired electrical and radar response of the conductive coatings with, for instance, the mechanically reinforcing properties of glass, quartz, and aramid fabrics or the elastic properties of spandex-containing fabrics. In addition, resistance gradients along a fabric or through the thickness of foam, felt, and other thick structures, such as 3-D woven, antiballistic glass material, are available. Various application and characterization data, including Tx loss and Rx loss of several lossy materials shall be presented. Suitably coated, lightweight, flame-resistant, non-cyanide-emitting felts can serve to replace carbon-loaded polyurethane foams in certain applications.

1. INTRODUCTION

Inherently (or intrinsically), electrically conductive polymers (ICP’s) were discovered about thirty years ago. Their essential characteristic is that they consist of chains of alternating single and double bonds (conjugation). It is only in the past decade that ICP’s have found widespread
use in a variety of applications. In this paper, we discuss the properties and defense- and aerospace-related applications of conducting polymers, predominantly polypyrrole, deposited onto the surfaces of textile substrates. By coating thin layers of conducting polymers onto substrates, such as fabrics, 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, stretchy if needed, fully “processable” conductive material. The thin coatings typically do not change the mechanicals of the base fabrics much, if at all.

The proprietary processing technology that allows us to make such a wide array of products 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, acrylcs, 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 a billion or so 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, nonwoven, and knit fabrics, felts, 3-D woven 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, continuous rolls of fabric or piecewise, to fabricated items. Examples of the latter include electrostatic dissipative (ESD) gloves, hook & loop bands, garments, and 8”x8” wipes, all of which have been prepared by immersing the untreated items in the appropriate baths.

2.A. BASIC PROPERTIES OF CONDUCTIVE FABRICS

Being able to select the starting fabric construction and composition for certain fundamental properties (e.g., strength, porosity, stretch, thickness, flame-resistance, etc.) and subsequently control the end surface resistivity with customized conductive polymer coatings allows one to prepare fabrics that possess a broad range of useful properties. This makes the materials suitable for a variety of applications. As noted, surface resistivities between 10 ohm/sq and a billion ohm/sq are readily achievable, and resistance gradients that cover a large portion of this range have been made along the distance of a fabric or through the thickness of a 3-D material. 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 about 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 appear to be to be fairly constant.

An important, 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, $\varepsilon$, 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, usually by 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 (i.e., isotropic, no orientation effect), PPY-coated, 30-ohm/sq, woven glass fabric.

From Tx and Rx loss data, we can estimate the absorption and reflection contributions to the shielding effectiveness of conductive fabrics. Figs. 3 and 4 show the reflection and transmission loss graphs for EeonTex polyester twill having surface resistivities of 50 and 200 ohm/sq, respectively. These data are used to compute the relative loss mechanisms for the two materials exhibited in the corresponding Figs. 5 and 6. Whereas the relative amounts of incoming radar energy that is dissipated by absorption (plus scattering to a lesser extent) are similar for the two resistances (40 vs. 45%), the 200 ohm/sq version, not surprisingly, allows considerably more power to be transmitted than the 50-ohm version. Maximum relative absorption for these particular fabrics is estimated to occur around 225 ohm/sq. It should be noted that below 100 ohm/sq, reflection of far-field radiation starts to become significant, and the optimal balance of transmission, reflection, and absorption must be considered by the end user.

Compared to metalized fabrics, the absorption component of a conducting polymer fabric represents a higher contribution to the overall shielding; metal-coated fabrics shield predominantly by reflection. In many situations, it is much preferred to attenuate electromagnetic radiation by absorption as opposed to simply reflecting it uncontrollably. This is something to keep in mind for specific shielding or radar barrier applications. For instance, a PPY-coated woven fabric is used to make artificial horizon, radar barriers for military aerospace purposes because a significant portion of its shielding is due to absorption, not reflection. One such barrier is pictured in Fig. 7.

Clearly, then, an important performance characteristic of conductive fabrics for the defense and aerospace industries is their ability to reduce the reflection of radar signals in various configurations. Figures 8-10 exhibit the X-band reflection (Rx) losses of, respectively, a pockled, 90 ohm/sq nonwoven, a 2.54 cm-thick gradient (500-135 ohm/sq) polyester felt, and 2.54 cm-thick, 3-D woven, antiballistic glass material. We envision the last being used in lightweight, radar-stealthy, military land vehicles. Figure 11 shows the deep reflection minimum possible using a thin, ~300 ohm/sq EeonTex fabric in a typical Salisbury screen configuration targeted for 10 GHz. Figure 12 is Rx loss in the X-band for a ~5-mm thick epoxy laminate consisting of 5 different resistive layers of EeonTex glass fabric (S2 glass, 8-H satin) and 15 nonconductive spacer layers of the same glass fabric.

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 13 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 in mechanical
properties is observed. Fig. 14 shows the stability of an EeonTex quartz-epoxy laminate subjected to accelerated aging. Within experimental uncertainty, there is little change in the impedance.

2.B. SOME RELEVANT 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. Of particular interest to defense and aerospace companies are:

1. Camouflage netting
2. Low RCS antennas
3. Radar-absorbing materials (RAM), in general
4. Edge cards for military land vehicles, ships, and aircraft
5. Non-radar-reflective, static dissipative skin for high speed aircraft and spacecraft
6. Deicing of aircraft wings by resistive heating.

Fig. 15 is a picture of a prototype, multispectral camouflage cover, while Fig 16 exhibits the Tx loss and weatherability of the PPY-coated polyester net on which the camouflage is based. Fig. 17 shows a low RCS antenna, composed of a multi-ply EeonTex glass-epoxy composite, currently in use for the US Navy. As illustrated in Fig. 18, EeonTex fabric, acting as a resistive heating element, offers very uniform warming characteristics. It is thus ideal for lower temperature, flexible applications, such as personnel warming blankets and garments, for which metal wires and foils often fail due to lack of uniformity or flexibility.

Because conducting polymer-coated fabrics, especially thicker ones, can absorb a high degree of electromagnetic radiation, they can be used to suppress EMI, adjust antenna side lobes, mitigate unwanted (ground plane) reflections and signals between antennas, and reduce electronic circuit crosstalk. Figure 19 shows the reduction in crosstalk when either a 6 mm-thick piece of PPY-coated felt or similarly thick foam is placed inside an electronic enclosure suffering from crosstalk. The ability to reduce circuit crosstalk here actually results from damping cavity resonances (standing waves) inside the shielded enclosure.

3. EEONFOAMS - FOAMS COATED WITH CONDUCTING POLYMERS

Just as conductive polymers can be deposited onto fabrics, so too can they be applied to common polyurethane foams, which provide thickness and 3-D character. As noted in the introduction, other foam compositions can be coated, and 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. Not all of these foams are readily available in open-cell form, which, besides cost, is why most of our work has centered on open-cell polyurethane foams. Such foams, in varying thicknesses, have been coated to possess transmission losses ranging from 1 or less dB/in (dB/2.54 cm) up to over 30 dB/in in the GHz range. Figure 20 shows the Tx loss, or shielding effectiveness, of 1” (2.54 cm)-thick foams having through resistances of 200 and 800 ohm and made with two different conductive coating formulations. SD designates a newly developed, more thermally stable coating. Only very slight differences in performance relative to the original PPY coating can be observed.

These conductively coated foams are finding use in EMI suppression, especially against high intensity fields, cavity resonance damping, crosstalk reduction (vide supra), radar absorption, static dissipation, and as high surface electrodes. Because the pure polymer coatings do not contain particulates, EeonFoams are superior to carbon-coated foams in terms of sloughing and their smoother, microwave response over a broad frequency range. While the conducting polymer-coated polyurethane foams certainly are viable products and offer advantages over ordinary...
carbon-loaded foams, we believe EeonFelt polyester felts possess several superior characteristics, such as lower cost, lighter weight, greater flexibility, hydrolytic stability, ease of making gradients, and better burn characteristics (viz., no emission of HCN), that should eventually make them the better choice over conductive foams for many applications.

4. CONCLUSIONS

Applying conducting polymer coatings is an excellent way to impart controlled electrical conductivity to nonconductive materials. Conducting polymer coatings are now applied commercially to a large variety of substrates, especially textiles, to create new classes of tailored, conductive products. Among the highly controllable properties that these products possess, their electrical and radar responses can be exploited in an ever-increasing array of specialty defense and aerospace-related applications. Investigations into to improving the conductive and lossy properties of EeonTex products for specific uses are ongoing. Conducting polymer-coated felts are poised to replace ordinary, carbon-loaded foams for many selected applications.

5. ACKNOWLEDGMENTS

We want to thank Dr. Jose Marconcini and his group for making several of the Rx loss measurements exhibited here. Also, the Eeonyx customers who allowed us to show the data and pictures they generated are gratefully acknowledged.

6. REFERENCES


Fig. 1. Insertion loss of EeonTex microfiber nonwovens treated to surface resistivities between 3 and 40 ohm/sq.

Fig. 2. Tx loss and phase angle of a balanced 30 ohm/sq, 8-H satin woven glass fabric.
Fig. 3. Transmission and reflection loss of ~50 ohm/sq, PPY-coated polyester twill

Fig. 4. Rx and Tx loss of ~200 ohm/sq PPY-coated polyester twill
Fig. 5. Loss mechanisms in ~50 ohm/sq PPY-coated polyester twill

Fig. 6. Loss mechanisms in ~200 ohm/sq PPY-coated polyester twill
Fig. 7. Artificial horizon/radar barrier employing PPY-coated fabric

Fig. 8. Reflection loss of a treated thin, pockled, ~90 ohm/sq microfiber nonwoven
Fig. 9. Rx Loss of 2.5 cm thick, gradient felt, 500 – 135 ohm

Fig. 10. Rx loss of treated 3-D woven, 2.54 cm thick, antiballistic glass material (8.2 kg/m²)
Fig. 11. Reflection loss of Salisbury Screen configuration employing a 300 ohm/sq conductive, ~0.1 mm thick, woven fabric and targeted for 10 GHz

Fig. 12. Rx loss of 20-ply (5 conductive, 2350 – 95 ohm/sq) 8H S2 glass-epoxy laminate, ~5 mm total thickness
Fig. 13. Comparison of mechanical properties of untreated and PPY-treated glass fabric/thermoset polyester, laminate composites

Fig. 14. Stability of PPY-coated quartz/epoxy laminate composite under accelerated aging conditions (71°C, 95% RH)
Fig. 15. Prototype, multispectral camouflage cover utilizing a PPY-coated net that provides
the radar portion of the camouflage and to which the IR and visual components are attached.

Fig. 16. Affect of weathering on the transmission loss of the conductive net used in the camouflage material
in Fig. 15.
Fig. 17. New, low RCS antenna for US Navy made of multi-ply, conductive glass-epoxy composite

Fig. 18. Demonstration of the uniform warming generated by a resistive heating element made of PPY-coated fabric
Fig. 19. Reduction of circuit crosstalk within an electronic enclosure using PPY-coated felt and foam.

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

Fig. 20. Shielding effectiveness of 2.5-cm thick foams coated with two, conductive formulations to 200 and 800 ohm through resistances