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Magnetic metal nanoparticles coated polyacrylonitrile textiles as microwave absorber

O. Akman [a,b], H. Kavas [c], A. Baykal [d,*], M.S. Toprak [e,f], Ali Çoruh [b], B. Aktaş [a,**]

[a] Physics Department, Gebze Institute of Technology (GYTE), 41400 Gebze-Kocaeli, Turkey
[b] Department of Physics, Sakarya University, 54100, Sakarya, Turkey
[c] Department of Physics Engineering, Faculty of Sciences, Istanbul Medeniyet University, 34720 Istanbul, Turkey
[d] Department of Chemistry, Fatih University, 34500, B. Çekmece-Istanbul, Turkey
[e] Functional Materials Division, KTH Royal Institute of Technology, SE-16440 Stockholm, Sweden
[f] Yildirim Beyazit University, Department of Materials Science and Engineering, Ulus-Ankara, Turkey

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ABSTRACT

Polyacrylonitrile (PAN) textiles with 2 mm thickness are coated with magnetic nanoparticles in coating baths with Ni, Co and their alloys via an electroless metal deposition method. The crystal structure, morphology and magnetic nature of composites are investigated by X-ray Powder diffraction, Scanning Electron Microscopy, and dc magnetization measurement techniques. The frequency dependent microwave absorption measurements have been carried out in the frequency range of 12.4–18 GHz (X and P bands). Diamagnetic and ferromagnetic properties are also investigated. Finally, the microwave absorption of composites is found strongly dependent on the coating time. One absorption peak is observed between 14.3 and 15.8 GHz with an efficient absorption bandwidth of 3.3–4.1 GHz (under −20 dB reflection loss limit). The Reflection loss (RL) can be achieved between −30 and −50 dB. It was found that the RL is decreasing and absorption bandwidth is decreasing with increasing coating time. While absorption peak moves to lower frequencies in Ni coated PAN textile, it goes higher frequencies in Co coated ones. The Ni–Co alloy coated composites have fluctuating curve of absorption frequency with respect to coating time. These results encourage further development of magnetic nanoparticle coated textile absorbers for broadband applications.

1. Introduction

The radar absorbing and shielding technology has attracted a growing interest due to the recent developments in telecommunication, industry, defense, security and military systems. All these developments lead researches to the microwave absorbing materials with proper thickness, cost, efficiency, weight, hardness/flexibility, stability and electromagnetic and physical compatibility. The requirements are different for different applications such as; radar absorber, shielding material, navigation, aircraft technology, radio-electronic devices, wireless systems. The intensive usage of Electromagnetic wave in such areas causes electromagnetic interference (EMI) and electromagnetic compatibility (EMC) problems [1]. To overcome these problems metallic shields [1,2], ferrite absorbers [3–11], ferroelectric materials [12–14], composite materials [15,16], and conductive polymers [17–23] are used. Metal nanoparticles on polymer structure is not forming a metallic infinite layer, reflecting all EM, and the damping of it via interparticle reflections on the surface makes nano-metals as proper candidate material for shielding and absorbing. Also the polymer structure has a role of impedance matching between media where EM incident and transiting. Moreover both nano metal and polymer gives mechanical advantages. First, the nano metal allows constructing homogenous composite on whole fibers surface. The polymer with its flexible nature and simple fabrication in all shapes let it to be used as a host material. This mechanical properties of polymers also makes it part of absorber or shielding composite with different physical structures. Not all the polymers have the advantage of matching medium, just the conductive polymers can be considered with this property. They prevent the matching problems between nano-metals and polymer fiber medium [24,25]. Chemical properties and adjustable electrical conductivity of Polyacrylonitrile (PAN) make it more a much more appropriate candidate than other conductive polymers [26,27].

There are many ways to coat the polymer surface with target metals such as vacuum deposition, sputtering [28,29] or electroless plating [1]. Among all these techniques, the electroless

* Corresponding author. Tel.: +90 212 8663 300 2060; fax: +90 222 8663 402.
** Corresponding author. Tel.: +90 262 605 10 00x1301; fax: +90 262 653 84 90.
E-mail addresses: hbaykal@fatih.edu.tr (A. Baykal), aktas@gyte.edu.tr (B. Aktaş).

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plating is quite different in which the metals seeds grow on polymer surface with random crystal and electronic structures. Metal islands possess randomly aligned magnetic anisotropy. Additionally, the metallic structures on polymer are grown in a wide range of sizes, from nano- to micrometer, which gives an advantage of different electronic and magnetic interactions. Such interactions contribute to the EM absorption or shielding characteristics of the material within a wide frequency band. The electroless coating method was chosen based on these advantages.

Ni, Co and various ratio of these metals are deposited by reduction of polymer [1,30–34] and also using polymer-metal chalets with an aqueous solution of $NaBH_4$ into the polymer phase to establish the basis for the use of the polymer-mediated extraction as a pre-concentration method of metal ions [35,36].

Here the PAN textiles with 20 μm fiber diameter were coated with Ni, Co and $Ni_{0.5}Co_{0.5}$ particles via electroless deposition technique for various durations. The crystal structure, morphology, magnetic property and microwave absorption behavior (in 8.2–18 GHz band) were investigated and discussed in detail.

2. Exprimental methods and characterization techniques

The industrial polyacrylonitrile (PAN) fibers, without any protection or coloring dye, were tightly knitted as a flat surface in dimensions of $1 \times 15\ m^2$. The knitted textiles were cut to the size of $10 \times 10\ cm^2$ to coat with nanoparticles in different baths. The textiles coating process consists of 5 stages. Two of these stages cover pre and post coating operations, while the remaining three main stages involve coating operations. Each stage requires a special bathing process of certain duration, pH and temperature. These are summarized below for each treatment, respectively. Pre-treatment stage; firstly, all samples were cleaned with non-ionic detergent (pH 7) and then held 10 min in an ultrasonic bath of ethanol, and finally washed with de-ionized water abundantly and dried in oven at 40 °C. Sensitization stage; all textiles were subjected to surface sensitizer of $SnCl_2$ and HCl (37% v/v) with slow agitation for 10 min at room temperature. During this process, some chemical bonds on the surface of PAN are broken and ready for a new chemical bonding. Then, the textiles were rinsed with de-ionized water. At the Activation stage; $PdCl_2$ was used in order to provide metal nucleation. This bath composed of certain amount of $PdCl_2$, HCl and H_3BO_3 to obtain required conditions (pH=2) of surface activation. The activated fabrics were finally rinsed with de-ionized water. Deposition stage (electroless metal deposition) is the most important section of coating process. The metal plating solution containing total metal salts (25%) in order to coat the activated PAN surfaces in different times. Last-treatment stage is coating of electrolessly metal deposited PAN with liquid polymer with low molecular weight to protect the composite from oxidation and corrosion. The coated samples codes and corresponding deposition times are listed in Table. In the rest of the manuscript the samples coated for the shortest time (OA2 for Ni bath, OA24 for Co bath and OA54 for Ni–Co bath) and the longest time (OA5 for Ni bath, OA27 for Co bath and OA57 for Ni–Co bath) were chosen for detailed characterization.

The crystalline structure of resultant composites was determined with X-ray diffraction measurements (XRD) using Rigaku D/Max—IIIC with Cu Kα radiation in the 2θ range of 20°–80°. The surface morphology of the composites was analyzed with Philips XL30 SPEG Scanning Electron Microscopy (SEM). Magnetic properties under magnetic field were determined by VSM SQUID (Quantum Design PPMS 9 T) magnetometer between −2 T and 2 T at room temperature. Finally the coated textiles with 2 mm thickness were cut at dimensions of $9.5 \times 18.5\ mm^2$ for Transmission/Reflection measurement with rectangular waveguide system. Before, the microwave measurements the True-Reflected-Line (TRL) calibration standards were set. The complex Transmission (S21) and Reflection (S11) coefficients were measured with ATM technology waveguide system and HP PNA E8364B Vector network analyzer in the frequency range of 8.2–18 GHz The obtained coefficients were used in the NRW algorithm to calculate the effective relative permittivity and the permeability of each composite with thickness of 2 mm. Finally, the Reflection Loss (RL) were calculated by the following equations [37,38]:

$$RL = 20\mathrm{Log}\left|\frac{Z_1 - Z_0}{Z_1 + Z_0}\right| \quad (1)$$

where the impedance of medium is

$$Z_1 = Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[\left(-j\frac{2\pi}{c}\right)fd\sqrt{\mu_r\varepsilon_r}\right] \quad (2)$$

Here μ_r and ε_r are the measured relative complex permeability and permittivity, respectively, c is the speed of light, f is the frequency of microwave and d is the thickness of the absorber. The results were discussed in the following section with the relevant preparation parameters.

3. Result and discussion

The PAN fibers were coated in Ni, Co and Ni–Co mixed salt baths. The obtained composites were analyzed by SEM and XRD.

3.1. Morphology and crystal structure characterization

Sample descriptions are given in Table 1. SEM micrographs of PAN alone and PAN samples coated with Ni, Co and Ni–Co are presented in Fig. 1a–g. Fibers with diameters around 20 μm were observed for the pure PAN as shown in Fig. 1a. Each row in Fig. 1 represents the shortest and longest coating durations for samples Ni (Fig. 1b and c), Co (Fig. 1d and e) and Ni–Co (Fig. 1f and g), respectively. As the coating duration is increased, the roughness on the surface of these nanofibers has been observed to increase due to the formation of nanoparticles. This is an important assessment for the success of the coating process.

The XRD measurements are carried out between 20° and 80° for the Ni, Co and Ni–Co coated fibers at shortest and longest coating durations. The amorphous structure of PAN gives a broadening at small angles. For lower coating times (sample OA2, OA24, OA54) the metal crystallinity is not clear and also residual SnO structure is observed, originating from the sensitization bath. The coated composite at longest times in Ni, Co and the Ni–Co baths show more intense peaks due to the formed nanoparticles, as expected. The peak positions and the most intense peaks are consistent with the reference XRD patterns. Crystal structures were indexed with respect to the following XRD reference patterns: SnO (JCPDS 99-100-8876), NiO (JCPDS 99-101-0286), Ni-1 (JCPDS 99-101-3040), Ni-2 (99-101-0883),

Table 1
Sample codes and corresponding coating times.

Ni		Co		Ni–Co	
Coating time (min)	Sample code	Coating time (min)	Sample code	Coating time (min)	Sample code
0.5	OA2	2	OA24	1.5	OA54
1	OA3	2.5	OA25	2.5	OA55
1.5	OA4	3	OA26	3.5	OA56
2	OA5	3.5	OA27	4.5	OA57