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INVESTIGATION OF SHIELDING PROPERTIES OF CONDUCTIVE COTTON COMPOSITE FABRIC MATERIALS AGAINST ELECTROMAGNETIC WAVES

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ABSTRACT. Electromagnetic waves are energy carriers formed by combining electric and magnetic fields. Today, shielding methods have been developed to protect against these electromagnetic fields created by the growing technology causing Electromagnetic interference (EMI). In this study, one of the most widely used plant-based fibers, cotton fabric, was chosen to prepare a conductive and magnetic natural composite material to shield against EMI. For this purpose, cotton fabrics were chemically and physically modified in two consecutive steps. In the first step, the conductive PAn/Cu/cotton composites were prepared by in situ oxidative polymerization of aniline in aqueous acidic media using ammonium persulfate (APS) oxidant and Cu(I) ions in the presence of cotton fabrics, resulting in the coating of both conductive polyaniline (PAn) and reduced Cu particles on the surfaces. In the second step, the physical deposition of individually synthesized magnetic Fe_3O_4 particles on PAn/Cu/Cotton composites was also achieved. The imparted electrical, structural, wettability, and morphological properties were investigated by surface resistivity measurement and SEM techniques, respectively. Finally, the prepared composites' electromagnetic wave shielding properties (EMSE) were examined in the range of 15 MHz-3 GHz, and it was observed that the composite with the highest conductivity provided 60% absorption-based protection.

Keywords. Electromagnetic shielding effectiveness, magnetic ferrite particles, polyaniline, copper particles.

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1. INTRODUCTION

With the development of technology, the use of electronic devices in our daily lives is tremendously increasing, and every device that works with electric current leaves living things nearby under the influence of electromagnetic waves. Electromagnetic waves are rays that appear at the intersection of electric and magnetic power stations and move in waves (Figure 1).

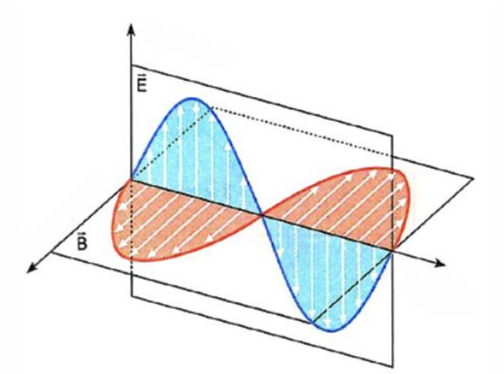

Figure 1. Schematic representation of electric field and magnetic field components.

It has been stated that the electromagnetic field causes side effects such as depression, stress disorder, headache, and insomnia in people and that when it is under the influence for a long time, diseases such as heart diseases, brain tumors, leukemia, etc.[1]. To be protected from these electromagnetic waves, electromagnetic shielding materials are designed and researched to extend the lifespan of living things and the useful life of devices by reducing their interference. The materials for electromagnetic shielding are expected to be flexible, lightweight, low-cost, environmentally friendly, and sustainable [2]. Materials that will provide electromagnetic shielding are expected to have high electrical conductivity and magnetic properties. For this purpose, various electrically conductive materials, such as metals, carbon nanotubes, or conductive polymers, and magnetic ferrite particles, such as hard or soft ferrites, have frequently been preferred by researchers when EMI shielding is considered [3-6]. Shielding is achieved by reflecting the electric field at low frequencies, absorbing it at high frequencies, and absorbing the magnetic field at low frequencies [7-8]. Consequently, these shielding phenomena are provided thanks to the contribution of these conductive or magnetic components. Among the conductive elements, conductive polymers, such as PAn, polypyrrole, polythiophene, and their derivatives, are found promising in providing high and tunable electrical conductivity properties to the composite without a tendency to corrosion. With this help, it has been reported that absorption-based shielding can be imparted to the samples in the literature [4-5]. The other components, magnetic particles, also have remarkable contributions to the absorption-based-EMI shielding, especially when the subjected EMI frequency stands to the high microwave regions. Therefore, combining these two conductive and magnetic particles on a solid substrate may serve as a helpful shielding composite material at a wide frequency range.

Starting from this idea, in this study, we aimed to combine these two crucial materials on a composite surface to reach a satisfactory EMI shielding.

Materials prepared by contributing natural fibers as a reinforcing agent to composite materials are preferred because of their biodegradable and recyclable properties that can significantly solve environmental pollution. Cotton, which contains 90% cellulose, is one of the most preferred plant-based fibers and attracts researchers and industry due to its high tensile strength, moisture adsorption, and sustainability.

In this study, we also preferred cotton fabrics as the main component of the composite to prepare a conductive and magnetic material. Cotton was physically and chemically modified in two consecutive steps. In the first modification step, the surface of cotton fabrics was coated by in-situ oxidative polymerization of aniline in the presence of CuCl aqueous solution to ensure the simultaneous decoration of conductive polyaniline (PAn) and metallic copper particles (Cu). In the second step, the individually synthesized magnetic ferrite particles (Fe_3O_4) were physically deposited on the conductive PAn/Cu/Cotton fabric surface by dropwise introduction of ferrite dispersion onto the composite. The obtained composite materials were further characterized using different techniques. Finally, the EMSE investigations were conducted to monitor the usability of the developed composites against EMI waves between 15 MHz- 3GHz.

2. MATERIALS AND METHODS

2.1 Materials

The chemicals used in the study, such as aniline and aniline.HCl monomers, APS used as an oxidant, HCl (37%), CuCl, Na_2CO_3, and ethyl alcohol were all received from Sigma-Aldrich (Türkiye) and employed in the study without further purification technique.
The cotton fabrics were washed in 0.02 M Na_2CO_3 solution in an oil bath at 95 °C for half an hour before being used in the experiments. At the end of the washing, the fabrics taken from the alkaline environment were rinsed three times with distilled water and dried in the oven. Then, cotton fabric was cut in 1.25 x 2.5 cm dimensions for the experiments.

2.2 Methods

2.2.1 Preparation of PAn/Cu/Cotton Composite Fabrics

Cotton fabrics (1.25 x 2.5 cm sizes) were impregnated in particular concentrations (0.156-1.25 M range) of 0.1 mL aniline or aniline.HCl solutions prepared in 1.0 M HCl solution. Then, 0.1 M of CuCl solution prepared in 1.0 M HCl was introduced onto the fabrics dropwise. The polymerization was initiated by adding specific concentrations (0.156 M) of APS solution prepared in 1.0 M HCl and continued for one h. At the end of the determined polymerization duration, the composite samples were removed from the reaction medium and rinsed well with distilled water to remove oxidant and monomer residues. Afterward, the synthesized samples were doped in 1.0 M HCl solution and dried at 50°C under vacuum. The as-prepared samples were described as PAn/Cu/Cotton. The PAn/Cotton fabric composite was also prepared similarly, except using CuCl during the polymerization. PAn or PAn/Cu contents (%) of the composites were determined gravimetrically, considering the mass values of the cotton fabrics before and after the composite preparation.

2.2.2 Deposition of Fe_3O_4 onto the PAn/Cu/Cotton Composite Fabrics

Before preparing the ferrite particles deposited in composite fabrics, the ferrite particles were synthesized according to a report published in the literature [3]. Accordingly, 10 mL of 0.3 M $FeCl_3.6H_2O$ and 0.15 M of $FeCl_2.4H_2O$ aqueous solutions were mixed in a flask under N_2 atm at 50^0C. Then, the Fe_3O_4 particles were precipitated by introducing a concentrated NH_4OH solution until pH=11. The ferrite particles were isolated from the solution using a magnet and further washed with distilled water using centrifuging at 8000 rpm. Finally, 1 mL of aqueous ferrite dispersions was dropwise added onto PAn/Cu/Cotton composites (1.25 cm x 2.5 cm in size). The samples were dried under vacuum at 50 °C, and the ferrite content (%) was calculated gravimetrically. The schematic illustration of the synthesis route is provided in Figure 2.

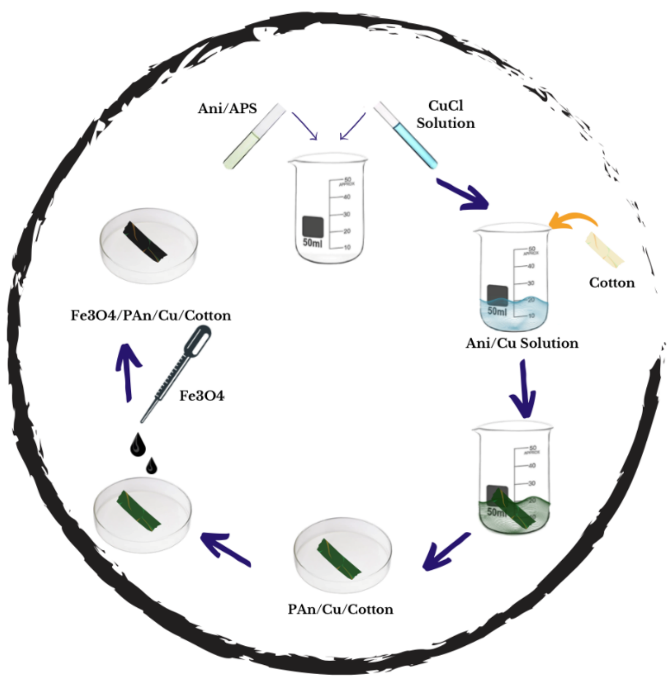

Figure 2. Schematic illustration for preparing the Fe_3O_4/PAn/Cu/Cotton composites.

2.3.Characterization

The surface resistivity measurements were performed using a Thurlby 1503 digital multimeter. The surface resistivity values were taken using the average resistivity values read from 10 different regions of the composite surface. The surface morphology of the composite samples was investigated using a Quanta 400 F SEM device after coating the pieces with Au/Pd.

2.4. The EMI Shielding Investigation

The EMI shielding performance of the conductive and magnetic samples was performed using an Agilent Network Analyzer equipped with Electro-Metrics 2107 A as a test fixture, according to a method published in the literature [9]. Accordingly, the EMSE (in dB) value of a composite was calculated according to Eq. (2.1):

$$EMSE = 20\log(\frac{E_i}{E_t}) \tag{2.1}$$

E_i and E_t values are the electric field strengths of the incident and transmitted electromagnetic waves, respectively. The shielding failure of the composite was expressed with the Transmittance (T) value, and the shielding through the reflections of electromagnetic waves from the sample was defined by the Reflection (Re) value. The T and Re magnitudes were calculated considering the Network Analyzer's S parameters (S_{11}, S_{22} or S_{12}, S_{21}), using the E_t, E_i, and E_r (electric field strength of reflected waves) values. The shielding provided by the absorption (Ab) was also determined considering the total Re and T values of the composite in the following equations (2.2-2.4):

$$Re = \left|\frac{E_r}{E_i}\right|^2 = |S_{11}|^2 \ or \ |S_{22}|^2 \tag{2.2}$$

$$T = \left|\frac{E_t}{E_i}\right|^2 = |S_{12}|^2 \ or \ |S_{21}|^2 \tag{2.3}$$

$$1 = Ab + Re + T \tag{2.4}$$

3. RESULT AND DISCUSSION

3.1. Effect of Aniline Monomer and Concentration

During the synthesis of PAn and metallic Cu particle precipitation, the reaction is schematized in Figure 3. In this study, we aimed to prepare conductive and magnetic composites, and the effect of the monomer concentration used during the first step of obtaining conductive polymer is presented in Figures 4-6.

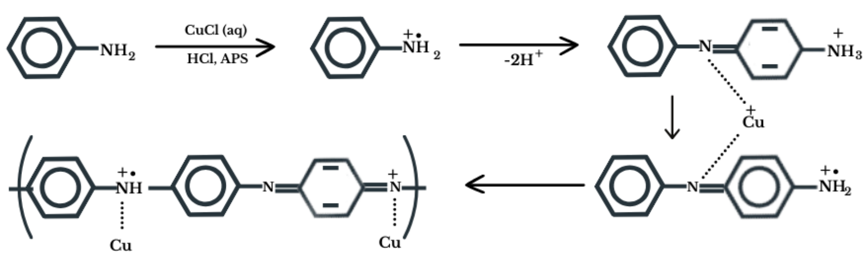

Figure 3. Polymerization mechanism of aniline using APS as an oxidant in the presence of CuCl solution.

In the chemical oxidative polymerization of aniline, ammonium persulfate (APS), frequently preferred in the synthesis studies of PAn, was also employed as the oxidant in this study. We also aimed to deposit Cu particles onto the fabric samples during the polymerization. For this purpose, a solution of CuCl salt was added to the medium during the polymerization of aniline. Along with APS, Cu(I) ions also participated in the redox reaction in the environment, allowing Cu particles to precipitate on the fabric together with the conductive polymer structure. Polymerizations were completed at room temperature and in 2 hours concerning literature studies [10-13].

For the preparation of conductive composites, the effects of the aniline monomer type and the concentration of these monomers on the PAn/Cu content of the composites are shown in Figure 4. Accordingly, when the figure is examined, it can be seen that the highest PAn/Cu contents and relatively the most homogenous and dense PAn deposition were ensured when Ani.HCl was employed in the polymerization reactions. Therefore, in further experiments, Ani.HCl was selected as the monomer for producing the conductive composites.

The effect of Ani.HCl concentration on PAn/Cu content and surface resistivity of the composites were investigated, and the results are given in Figure 4. Accordingly, when the aniline concentration effect was examined, it was determined that the PAn/Cu content of the composites increased with increasing concentration in both series. However, it was determined that this increase was more pronounced when the Ani.HCl monomer was selected. In the series using only aniline, it was understood that the PAn/Cu content did not show a significant change after 0.312 M, while in the polymerization set using the Ani. The highest PAn/Cu content was obtained in the series when a 1.25 M monomer was used.

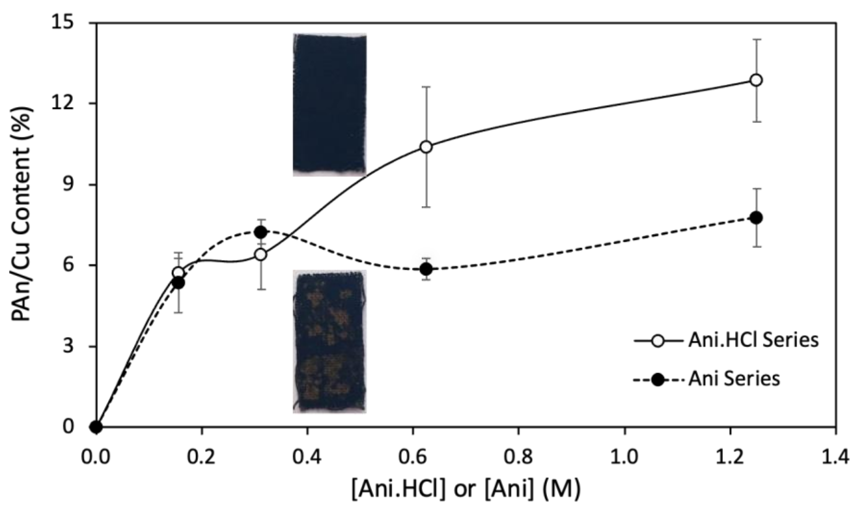

Figure 4. Ani.HCl and aniline concentration and percentage change of the amount of PAn/Cu coated on the cotton fabric surface.

Figure 4 also shows the photographic images of PAn/Cu/Cotton samples obtained in polymerizations using Aniline and Ani.HCl. As seen from the photos, Ani.HCl gave the composite a more homogeneous coating texture.

Figure 5 shows the changes in surface resistivity of the composite samples with aniline or Ani.HCl monomer types and their concentration. It was found that the lowest surface resistivity (highest conductivity) was obtained in the samples using the Ani.HCl series is compatible with the results of the PAn/Cu contents. Accordingly, since the lowest surface resistivity was obtained at 0.625 M, the study continued using this condition (0.625 M) in this series.

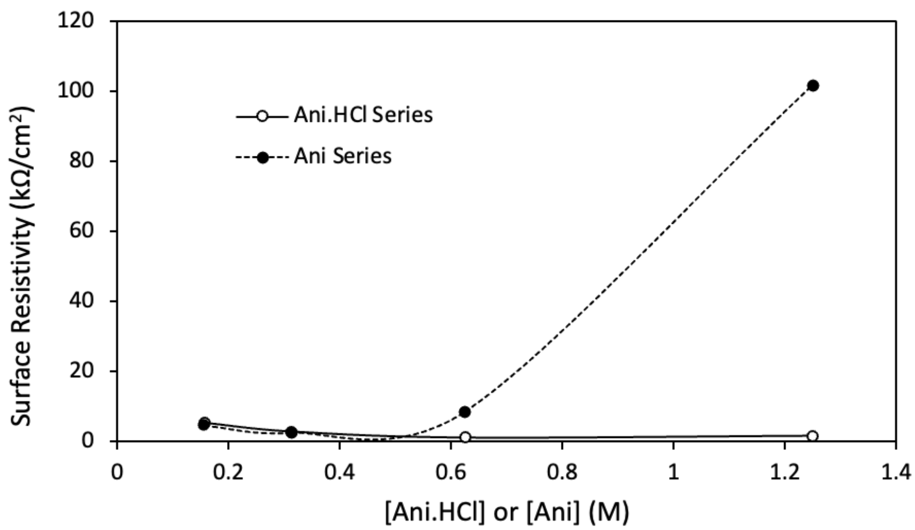

Figure 5. Ani.HCl and aniline concentration the change of the surface resistivity values of the conductive cotton fabric composite.

3.2. Effect of CuCl Concentration

Before investigating the influence of CuCl concentration on the mass increase contribution (PAn/Cu content) and surface resistivity of the composite, attempts have been made to determine the most appropriate Ani.HCl concentration on individual PAn content (%) and resistivity of the samples. Therefore, the experiments were conducted without employing CuCl during the oxidative polymerization of Ani.HCl at different concentrations with the APS, and the results are provided in Figure 7. Accordingly, the Cu-free PAn/Cotton composites, prepared for comparison purposes, had a 6% PAn% content at 0.625M, considered the most appropriate condition due to providing the lowest surface resistivity as 2.63 kΩ/cm^2.

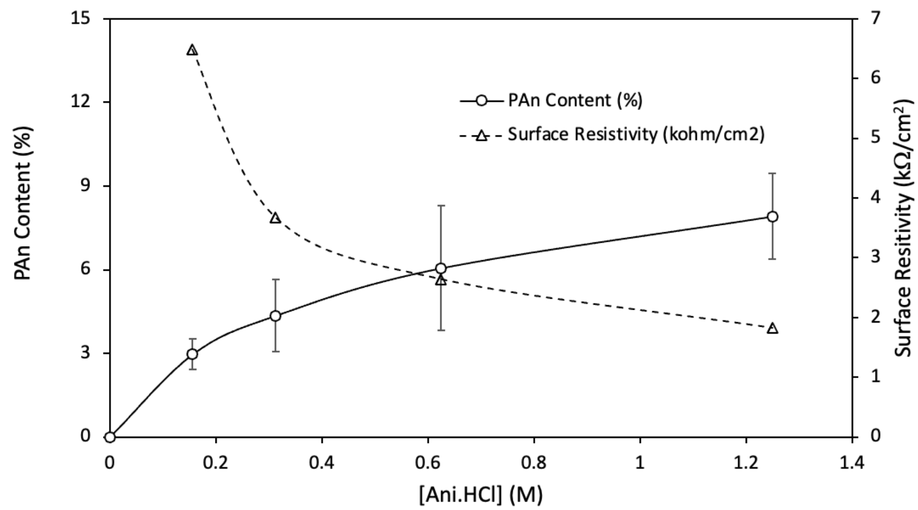

Figure 7. The changes in PA content (%) and surface resistivity of the samples with Ani.HCl concentration, in the absence of CuCl solution.

The investigations were continued by monitoring the effect of CuCl concentration (in the range of 0.025-0.075 M) on the samples' PAn/Cu content (%) and surface resistivity. Accordingly, it was observed that when the CuCl concentration was increased to 0.05 M, the PAn/Cu content showed an increasing trend, and after that point, it decreased. As for surface resistivity, a decrease in surface resistivity was detected with increasing CuCl concentration. However, since there was no significant difference between the surface resistivity values between 0.05 and 0.075 M, the study continued with 0.05 M CuCl concentration, which gave the highest PAn/Cu content. The condition yielded the highest PAn/Cu content (%) (12%); the lowest surface resistivity was 0.05 M.

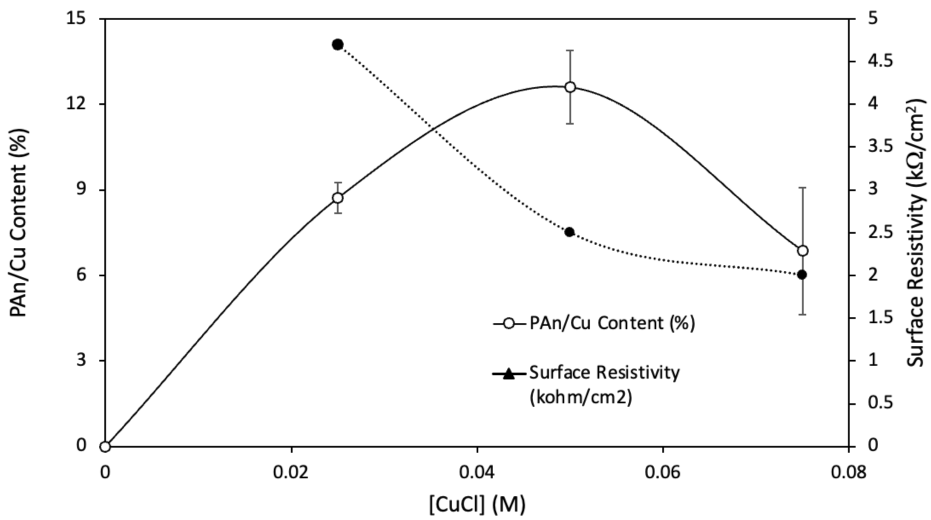

Figure 8. Change of PAn/Cu and surface resistivity values of conductive cotton fabric composite with CuCl concentration.

3.3. Effect of Ferrite Deposition on Conductive Cotton Fabric Composite

Figure 9 gives the results of Fe_3O_4/PAn/Cu/Cotton fabric composites obtained by loading different amounts of Fe_3O_4 aqueous dispersion. The quantity of Fe_3O_4 coverage was calculated as a percentage of the weighing differences before and after the experiment.

The components that caused the mass increase of the composite contained in the samples were monitored with the amount of Fe_3O_4, and the surface resistivity was measured. As seen in Figure 9, while there was no remarkable change initially with the increase in the amount of Fe_3O_4, a slight increase and a following fall were obtained in the samples. As for the surface resistivity, where the change in the mass increase was not noticeable, the surface resistivity also didn't alter significantly compared to a non-ferrite loaded sample, while the surface resistivity increased under the condition that the mass increase decreased. It can be interpreted that the Fe_3O_4 particles may have removed the conductive PAn layer from the material surface, causing a decrease in the conductivity.

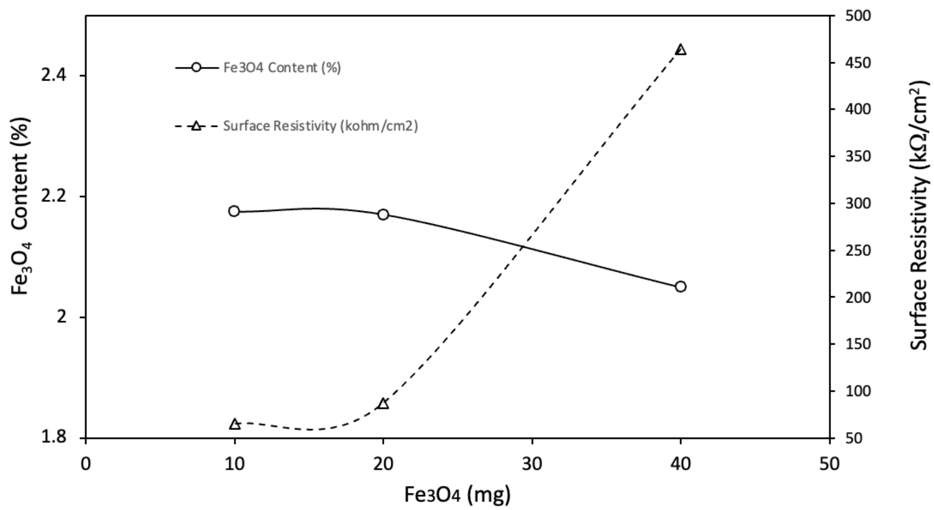

Figure 9. The changes in Fe_3O_4 amount (%) of the PAn/Cu/Cotton composites with changing Fe_3O_4 loading amount.

3.4. SEM Images

In Figure 10, SEM images of untreated cotton fabric are visualized. As can be seen from the figure, the individual cotton fibers preserved their characteristic curly texture even after Na_2CO_3 washing pretreatment, showing that no chemical modification was ensured on the samples. After the deposition of conductive PAn/Cu onto the cotton, a dense and homogeneous PAn/Cu layer can be selected along the fiber surface with heavy PAn/Cu aggregate formation in Figure 11. This micrograph gives the impression that no unoccupied region is left on the cotton surface by staple PAn curly fibrils and globular Cu particles.

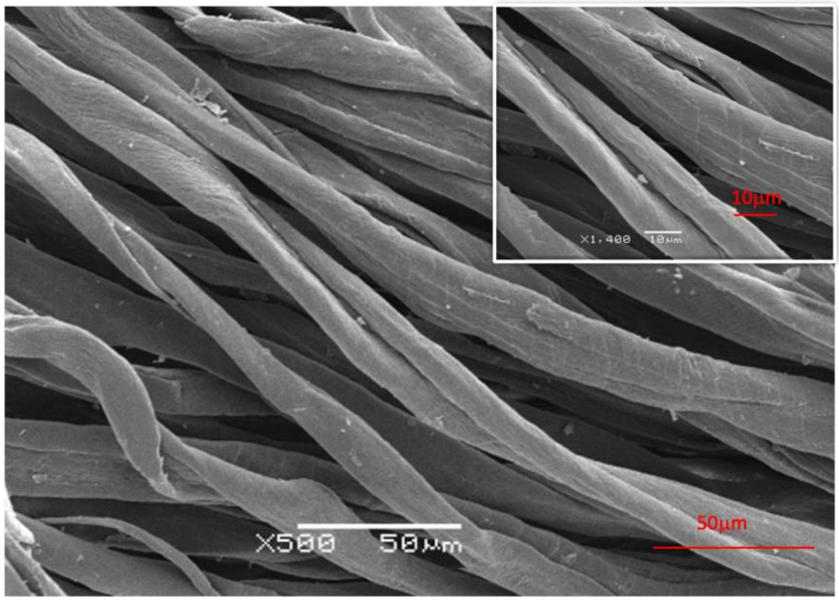

Figure 10. SEM Images of pure cotton woven fabric at different magnifications.

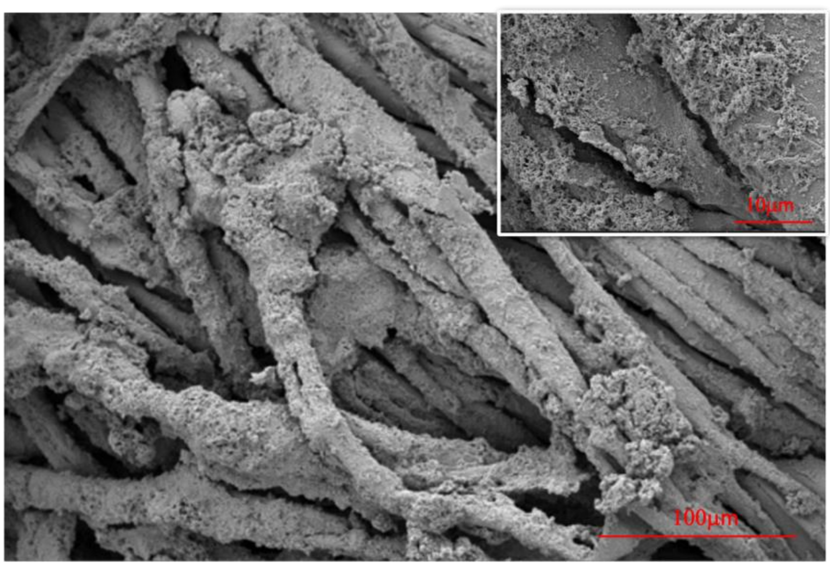

Figure 11. SEM images of 11% PAn/Cu coated cotton woven fabric composite at different magnifications.

3.5. EMSE

The protection against electromagnetic interference of conductive and/or magnetic composites prepared under different conditions was performed with EMSE measurements in the frequency range of 15MHz-3GHz. The results were revealed with the graphs presented in Figures 12-13. When the figure is examined accordingly, it was determined that the pure cotton fabric, which does not have any EMI protection value in the 15MHz-3GHz frequency range, showed the highest protection efficiency around 4.2 dB when its surface was coated with PAn polymer. This value was observed to be 2.9 dB after Fe_3O_4 loading and 4 dB when PAn/Cu was deposited.

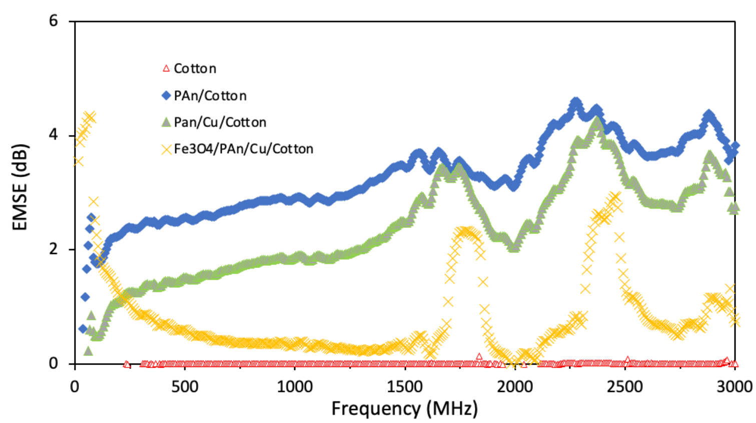

Figure 12. EMSE results of untreated cotton, PAn/Cotton, PAn/Cu/Cotton, and Fe_3O_4/PAn/Cu/Cotton composite fabrics.

Calculations were made to determine whether there was absorbance or reflection to reveal the protection mechanism of the EMI shielding effectiveness of the samples, and the results were plotted. The EMSE measurement results of conductive and magnetic composites are given comparatively in Figures 12-13 for cotton coated with pure Cotton, PAn/Cotton, PAn/Cu/Cotton, and Fe_3O_4/PAn/Cu/Cotton fabric composites. It was determined from the figures that the highest absorbance-based protection was achieved as 62% in PAn/Cotton fabric, 60% in PAn/Cu/Cotton, and 43% in Fe_3O_4/PAn/Cu/Cotton. It was observed that the protection in terms of reflection was relatively low in all three samples, and the highest protection efficiency value was obtained in the PAn/Cotton sample, with 62% absorption-based protection.

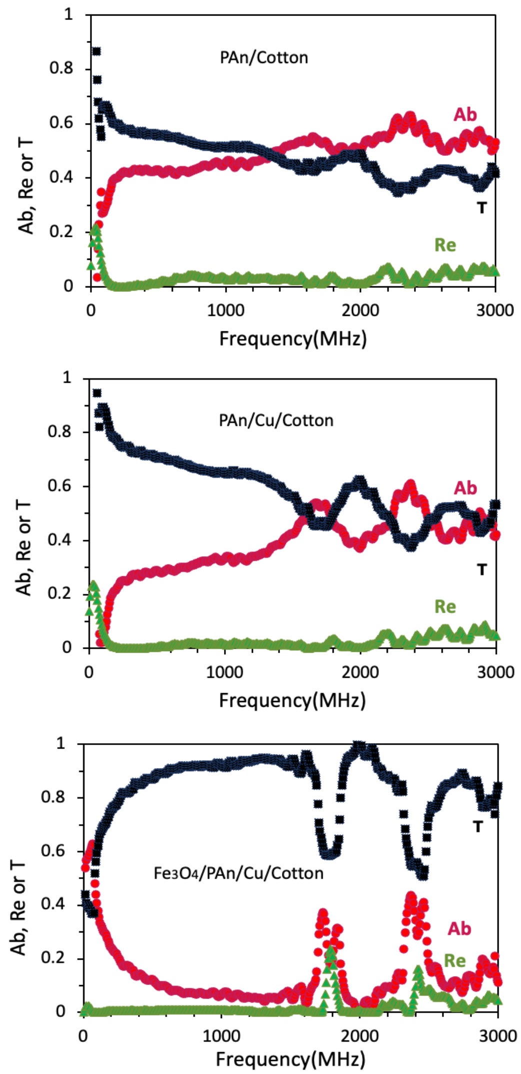

Figure 13. Variation of Ab, Re, or T relative protection efficiency values of cotton, PAn/Cotton, PAn/Cu/Cotton, and Fe_3O_4/PAn/Cu/Cotton composite fabrics.

4. CONCLUSION

In this study, where the results of the study are presented in detail, the study includes the results related to the preparation of composites using the PAn polymer, which is widely used among conductive polymers, has good redox properties in terms of high conductivity and electrochemical behavior, and is therefore highly preferred. At the same time, woven fabrics made of cotton and natural polymers widely chosen for being environmentally friendly, plentiful, and easy to find were used as essential components in preparing conductive composites. According to the results obtained from the fabric composites used, it was observed that the highest amount of PAn/Cu coated on cotton fabrics could reach approximately 15%. The results of the surface resistivity measurement showed that the composite sample with a particular electrical conductivity was achieved after homogeneous PAn/Cu deposition. The cotton's surface morphology changed from a smooth structure to a densely covered, stable fibrous PAn, and Cu bulk formation was revealed using the SEM technique. After the deposition of the magnetic ferrite particles, the EMI shielding performance was examined, and it was obtained that the composite had an absorption-based shielding performance within the selected frequency region that discloses the possible applicability in EMI shield development in a wide frequency range.

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Author Contribution Statement Aleyna Tecer—Performing the experiments, plotting the graphs, analyzing, calculating, and writing the draft. Meral Karakışla—Planning, interpreting, writing, reviewing, and editing the manuscript.

Declaration of Competing Intererest

We declare that there is no conflict of interest between the authors.

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