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Electromagnetic Shielding Effectiveness of Polyaniline/Modified-Poly(vinyl Alcohol) Film Composite

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Highlights

- This work aims the preparation of an electrically conductive film composite.
- The vinyl methacrylate groups attached -PVA film is coated with the conductive polyaniline.
- The obtained composite film showed satisfactory EMI shielding performance at 30 MHz-3 GHz.

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Keywords

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Abstract

This work reports the preparation of a conductive composite film, from one of the most conductive polymers, polyaniline (PAn), and a methacryloyl group attached-poly(vinyl alcohol) (M-PVA), in a few straightforward process steps. First, the -OH groups of PVA were modified through trans-esterification reaction using glycidyl methacrylate (GMA), in the presence of N, N, N, N-tetramethylethylenediamine (TEMED) as a catalyst at 60 °C. After casting the M-PVA into the film in the organic media, the polymerization of aniline was performed onto this surface using APS as an oxidant in 1.0 M HCl. The effects of conditions, including the concentrations of M-PVA used for film-casting, and aniline, were investigated on PAn content (%) and conductivity. It was observed that the conductivity of the thin and almost transparent composite films (containing 17.5% of PAn) reached to 10^{-4} Scm^{-1}. The characterization of the samples was conducted by ATR-FTIR, contact angle-wetting time measurements, and SEM-EDX techniques. The usability of the conductive composite film in the electromagnetic interference (EMI) shielding was examined within 30 MHz-3 GHz, through the measurement of electromagnetic interference shielding effectiveness (EMSE) and relative shielding efficiency values of absorption (Ab) and reflection (Re). Twice PAn deposited-composite film showed an average 5.6 dB EMSE value that corresponds to 71% of shielding through the Ab mechanism, dominantly.

1. INTRODUCTION

Thanks to possessing attractive properties such as tunable electrical conductivity according to the conditions, rapid responses to the conductivity changes by the color transition from conductive emeraldine salt (green) to none-conductive leucoemeraldine structure (blue), and facile preparation through electrochemical and chemical polymerization methods, PAn has been one of the most preferred conductive polymers by the researchers. With the help of these superior properties, PAn takes part in the broad application fields, including environmental based-sensors such as humidity, gas/volatile organic chemical sensors [1-5], wearable electronics [6], and EMI shielding [7, 8]. However, the processing difficulties, such as limited dissolution in the conventional solvents and low mechanical properties, hinder its direct usage in the applications. Thus, researchers are focused on the preparation of PAn composites through the coating on a relatively rigid, strength materials such as textile fiber/fabrics [9, 10] or film, hydrogel-forming other polymers such as PVA [11, 12], poly(N-vinyl pyrrolidone) [13], and etc. [14]. In this presented study, we preferred the usage of the modified-PVA surface as a main substrate for formation of film.

PVA is one of the most significant polymers among the film-forming materials owing to its desired properties, such as being soluble in the aqueous medium, biocompatible and relatively less hazardous for living things, and having –OH groups that are capable of forming strong seconder interactions (H-bonds). There have been numerous studies reporting the usage of PVA in the film-based conductive composites such as PAn/PVA [11, 12, 15], polypyrrole/PVA [16, 17], and polythiophene/PVA [18] in the literature.

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However, to our knowledge, no report has been published for the employment of modified-PVA for conductive polymer/PVA composite film formation, in the literature. In these studies, most often, PVA has directly used without any pre-modification techniques as a dispersing/capping agent for conductive polymers [19-22], electrochemically [12, 15] or blend [23] film-forming purposes.

In our previous works, we reported the usage of vinyl methacrylate groups attached-PVA prepolymer, in the synthesis and applications of PVA-g-N-vinyl pyrrolidone (PVA-g-NVP) copolymer for different purposes, such as colloidal Ag particles stabilization and surface modification of PET fabric surface [24, 25]. In these studies, we ensured the modification of PVA substituent groups and relatively altered the hydrophilic nature of PVA for the adaptation to the hydrophobic conditions. Differently from our previous studies, in this presented work, we aimed to use the vinyl methacrylate groups attached-M-PVA structure, as a cast film in the preparation of a conductive PAn composite. Thus, we provided a resistive PVA film to the conventional PAn synthesis conditions, such as aqueous acidic media. Subsequently, the obtained composite film was examined in an application field of the conductive polymer composites, EMI shielding, within 30 MHz-3 GHz frequency range, at which radio and microwave radiations are included.

2. MATERIAL METHOD

2.1. Materials

PVA powders with a hydrolysis degree of 87-89% and M_n of 13000-23000 gmol^{-1}, GMA monomer, TEMED catalyst, solvents of DMSO, ethyl alcohol, methyl alcohol, and acetone, aniline.HCl (crystalline) and aniline (for compare), HCl (37%), and APS ($(NH_4)_2S_2O_8$) oxidant were all employed in the study as purchased from Sigma-Aldrich (TURKEY). Aniline monomer supplied from Sigma-Aldrich (TURKEY) was used in the experiments after distillation under reduced pressure (50 °C/7mmHg).

2.2. Synthesis of Modified M-PVA and Film-Casting

The modified M-PVA polymer used for film-casting was prepared according to a study published in the literature [26]. Briefly, 7.08 mL of GMA monomer (0.75/1 w/w, based on PVA) was injected to 10% 100 mL (w/V) of PVA solution prepared in the DMSO solvent at 60 °C. After stirring the mixture for a while, the reaction was started by the introduction of 0.34 mL TEMED, whose amount was adjusted according to the literature [26], and then the reaction was continued for 6 h. At the end of the required time, yellowish-orange colored M-PVA was removed from the mixture through the precipitation with excess distilled water addition. The precipitated gel-like M-PVA polymer was further purified by first dissolving in the acetone/ethyl alcohol solvent mixture (1/1, V/V) at the boiling temperature (~68°C) and then re-precipitation with distilled water.

After the synthesis step, M-PVA cast films (0.040 ± 0.005 g) were obtained through the deposition of specific concentrations of M-PVA solutions (3g/100 mL or 6g/100 mL in acetone/ethyl alcohol solvent mixture), onto 2cm x 2cm PE film surfaces, and subsequent removal of the volatile solvents at ambient temperature.

2.3. Preparation of PAn/M-PVA Composite Film

Specific concentrations of crystalline aniline.HCl or liquid aniline solutions in 1 mL 1.0 M HCl was dropwise added onto the M-PVA films present on the PE wells, and the reaction medium was cooled down to 0-5 °C with an ice bath. Then, equivalent concentrations of APS solutions, prepared in the 1 mL 1.0 M HCl solutions were added onto the monomer enriched-film surfaces to initiate the polymerization. After preceding the polymerization for 4 h, the composite films were separated from the medium and thoroughly washed with distilled water and methyl alcohol to remove the unreacted residues, respectively. Then, the composite films were dried at 50 °C under vacuum until constant weight. The PAn (%) content of the composites was determined gravimetrically, by dividing the weight increase of the films to the initial film weight.

2.4. Characterization

The conductivity of the composite films was calculated from the surface resistivity values measured by two probe method using digital multimeters, including Thurlby 1503 and Uni-T UT70A, according to the measurement up-limit of the devices, such as 3.2×10^7 Ω/cm^2, and 2×10^9 Ω/cm^2, respectively. After recording the resistivity values from 10 different regions on the film surfaces, the average value was accepted as the result, and used in the conductivity calculation. The structural changes of the samples were evaluated by ATR-FTIR spectra, recorded with Perkin Elmer Spectra 100 FTIR spectrometer. The surface morphology of the film samples was revealed with the SEM micrographs, taken by the Quanta 400F Field Emission SEM instrument, after coating with 3 nm Au-Pd. The hydrophilicity/wetting character of the samples was monitored from the contact angle-wetting time measurements, by the Attension Theta Lite Optic Contact Angle instrument using the sessile drop method.

2.5. EMSE Measurements

The EMSE measurements were conducted with a test fixture (Electro-Metrics EM-2107A) that is connected to a Network Analyzer (Agilent E5061B Vector) Instrument within the 30 MHz to 3 GHz frequency range. The EMSE results of the composite films were calculated by the instrument in the decibel unit (dB), according to Equation (1) [27]

$$EMSE = 10\log\frac{P_I}{P_T} \tag{1}$$

where P_I and P_T correspond to the power strengths of the incident and transmitted electromagnetic waves, respectively. While the attenuation (shielding) failure of the composite was indicated by the Transmittance (T), the attenuation through the reflections of electromagnetic waves from the composite surface was given with the Reflection (R_e). These values were calculated according to Equation (2) considering the S parameters of the instrument:

$$T = \left|\frac{Et}{Ei}\right|^2 = \left|S_{21} or S_{12}\right|^2 \quad R_e = \left|\frac{Er}{Ei}\right|^2 = \left|S_{11} or S_{22}\right|^2 \; . \tag{2}$$

Here, the E_t, E_i, and E_r values show the transmitted, incident, and reflected electrical fields strengths, respectively. The S parameter values, including S_{12} (or S_{21}), and S_{11} (or S_{22}), correlate with theattenuation on transmittance and the reflection measurements, respectively. To eliminate the negative (-) signs of the S parameters, the absolute $IS_{12}I$ (or $IS_{21}I$) values were preferred in the expression of the EMSE result.

Then, the attenuation arising from the absorption of electromagnetic waves was given with the Absorption value (A_b), which can be calculated according to Equation (3):

$$A_b = 1 - T - R_e \; . \tag{3}$$

3. RESULTS AND DISCUSSION

It has been known that PVA is one of the most hydrophilic film-forming polymers that can be dissolved in the aqueous media. Thus, the employment of PVA in the conventional PAn synthesis under strongly acidic conditions may result in the formation of highly dispersed colloidal PAn particles [20] instead of film structure. To impart resistance against the dissolution of PVA in the water during the polymerization of aniline, and consequently, decrease the hydrophilicity of PVA to a specific degree, certain appendages of vinyl methacrylate groups were attached to the PVA chains, through the trans-esterification reaction with the GMA monomer [26]. After the conduction of the appropriate reaction conditions, according to the literature, a water-insoluble but moderately hydrophilic M-PVA structure was formed (Figure 1). As seen from the figure, the M-PVA structure had a gel-like texture with a yellow color that was quite different from the powdered structure of pure PVA. It was also noticed that the pre-modification of PVA enhanced its film-forming property, thanks to the facile dissolution of M-PVA polymer in the volatile solvents/solvent mixtures at relatively mild temperatures. Accordingly, to obtain homogenous and transparent film structure with a nonporous texture, specific concentrations of M-PVA solutions, including 3% and 6% (w/V), were prepared, and these solutions were further used in the film-casting at the ambient conditions.

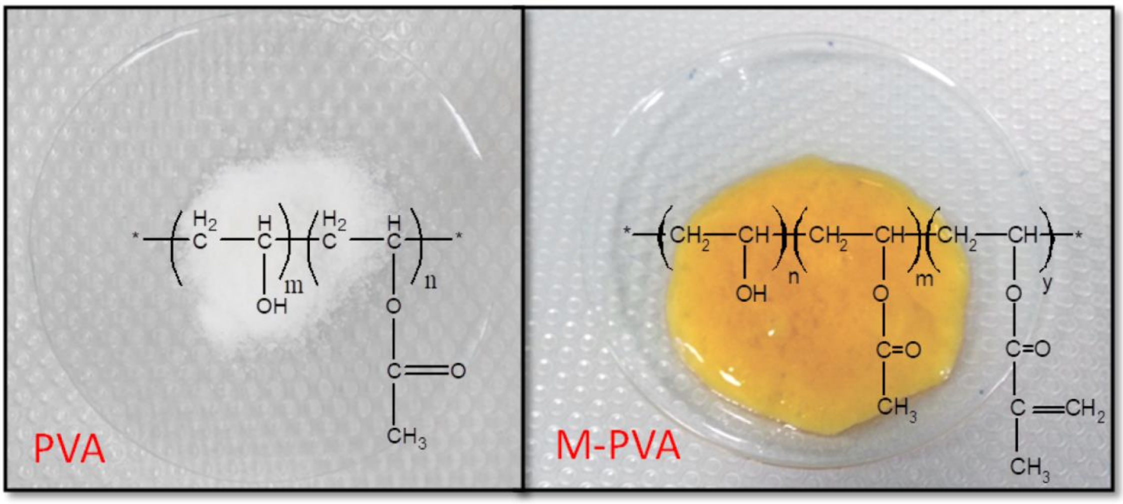

Figure 1. *Optical images of PVA and M-PVA structures*

After the formation of films using different concentrations of M-PVA solutions, the PAn coating process was carried out onto these film surfaces using either 0.33 M aniline (liquid form) or aniline.HCl (solid) as the monomer in 1.0 M HCl medium, in which the highly conductive PAn synthesis was frequently performed [28]. When aniline monomer was used in the polymerization, the surface of the M-PVA film was covered with the PAn layer at the individual regions. With the employment of the aniline.HCl as the monomer; it was observed that the monomer solution quickly diffused onto the surface resulting in the homogenous PAn deposition onto the film surface. Consequently, the PAn coating experiments further continued with the aniline.HCl (Figure 2).

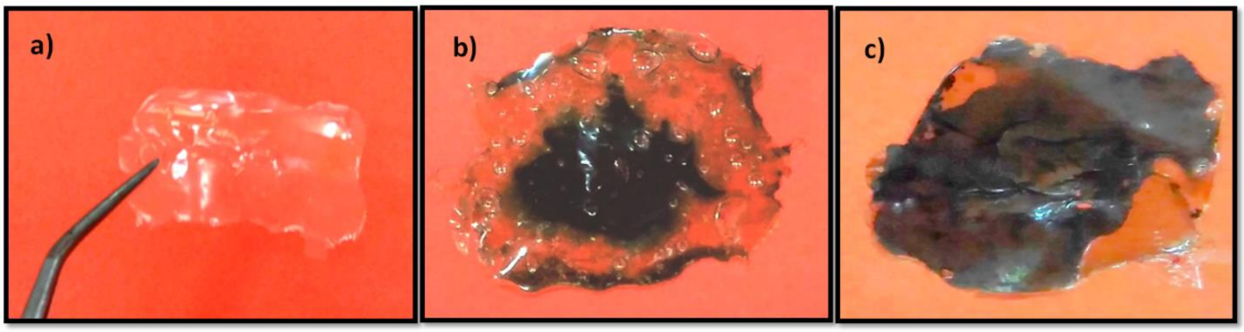

Figure 2. *The optical images of a) M-PVA film (prepared from 3% of solution), b) PAn/M-PVA prepared using 0.33 M aniline, and c) PAn/M-PVA prepared using 0.33 M of aniline.HCl*

After the selection of the monomer, the changes in the conductivity, observational appearance, and PAn content (%) of the composite films were monitored by changing the aniline.HCl concentration between 0.08 - 0.67 M. For that purpose, two different M-PVA films were prepared using 3% and 6% (w/V), and the polymerization reactions were carried out onto these film surfaces, simultaneously. The results are summarized in Table 1. When the polymerization was performed using 0.08 M and 0.16 M aniline.HCl, it was observed that the deposition of PAn on the film surfaces became either non-homogenous or partial (individual). Additively, no measurable increase was obtained in the film weights, as a possible result of insufficient percolation of the monomer molecules onto the film surfaces. When the monomer concentration increased to 0.33 M, it was observed that the surfaces of the M-PVA films were homogenously and densely covered with the PAn layers. This case can also be supported by the relatively high PAn content (%) of the composites. It was also noticed that the PAn content (%) of the composites prepared using 3% M-PVA solution took relatively lower values when compared to those of 6%, suggesting that the M-PVA films prepared using concentrated solution might be more resistive to the applied washing procedure after PAn coating. The other explanation may be the presence of more numbers of PVA chains in a unit area, leading to the adsorption of more monomer molecules by the M-PVA chains. These findings can also be evidenced by the relatively more free-standing behavior of the composite film prepared with 6% of the M-PVA solution.

When the composites are evaluated in terms of conductivity changes, one can see that the front sides of the films are relatively more conductive than that of the backsides (around ~10^3 times), owing to the surface polymerization of aniline.HCl. In a similar manner to the PAn contents, the conductivity values also gradually increased with the increase in the monomer concentration, and the composites prepared with 0.67 M aniline.HCl and both M-PVA concentrations took almost the same conductivity value as 1*10^{-4} S.cm^{-1}. To conclude, the PAn/M-PVA film composite with the desired PAn content (%) and conductivity could be prepared when 0.67 M aniline.HCl and 6% of M-PVA solutions were selected.

Table 1. *Changes in PAn content (%) and conductivity of the PAn/PVA composite films with M-PVA and Ani.HCl concentrations*

3% M-PVA films	**[Aniline.HCl] (M)**			
	0.08 M	**0.16 M**	**0.33 M**	**0.67 M**
PAn (%):	nd	nd	4.3	17.5
Front side conductivity (S.cm^{-1})	1.2x10^{-7}	7.7x10^{-6}	5.9x10^{-5}	***1.0x10^{-4}***
Backside conductivity (S.cm^{-1})	2.0x10^{-10}	2.1x10^{-9}	5.6x10^{-8}	7.1*10^{-7}
Appearance (observational)	a	b	c	c

6% M-PVA films	**[Aniline.HCl] (M)**			
	0.08 M	**0.16 M**	**0.33 M**	**0.67 M**
PAn (%):	nd	nd	9.9	23.7
Front side conductivity (S.cm^{-1})	2.0x10^{-7}	3.3*10^{-6}	2.9*10^{-5}	***1.1*10^{-4}***
Backside conductivity (S.cm^{-1})	1.9*10^{-10}	1.5*10^{-9}	5.0*10^{-8}	2.1*10^{-7}
Appearence (observational)	a	b	c	c

nd: not detected.
a:non-homogenous PAn coating; b: individual PAn coating; c: homogenous and dense PAn coating.

3.1. ATR-FTIR

The structural changes that occurred after the formation of the composite are comparatively given with the ATR-FTIR spectra in Figure 3. As seen from the spectrum of the M-PVA film, the bands arose at 3350 cm^{-1}, 2920 cm^{-1}, 1710 cm^{-1}, 1630 cm^{-1}, 1170 cm^{-1}, and 940 cm^{-1} correspond to the stretching vibrations of O-H and C-C, bending vibrations of C=O (ester), C=C (vinyl), stretching vibration of C-O-C (ester), and out of plane bending vibration of R$_2$C=CH$_2$ groups, present on the M-PVA chains, respectively [26]. The absence of the characteristics epoxide bands of the GMA, including 1255 cm^{-1} (breathing), 908 cm^{-1} (antisymmetric), and 845 cm^{-1} (symmetric) deformation was also reported to evidence the formation of M-PVA structure, with the removal of epoxide group, through transesterification reaction, as compatible with the literature [26].

In the first view of the spectrum of PAn/M-PVA composite, it was observed that the intensity values of the bands decreased, and the bands expanded. Some of the bands of ground M-PVA structure could not be detected due to the low intensity. The position of the C=O band was also shifted to 1680 cm^{-1}, which was explained by the H-bonds formation between PVA and PAn structure in the literature [29]. Similar band shifts were also reported to be observed in the PAN spectra after the formation of an organogel between PAn and PVA in the literature [30]. The characteristic C-H bending modes of quinoid and benzenoid rings of PAn chains were obtained at 1551 cm^{-1} and 1416 cm^{-1}, respectively [31, 32]. The band placed ca~1230 cm^{-1} was assigned to the C-N antisymmetric stretching mode of the quinoid ring in the literature [31]. Finally, the band at 796 cm^{-1} was attributed to the out of plane deformation of 1,4-disubstituted benzenoid rings of PAn [33, 34]. Accordingly, the possible interaction between M-PVA and PAn backbone was illustrated in Figure 4.

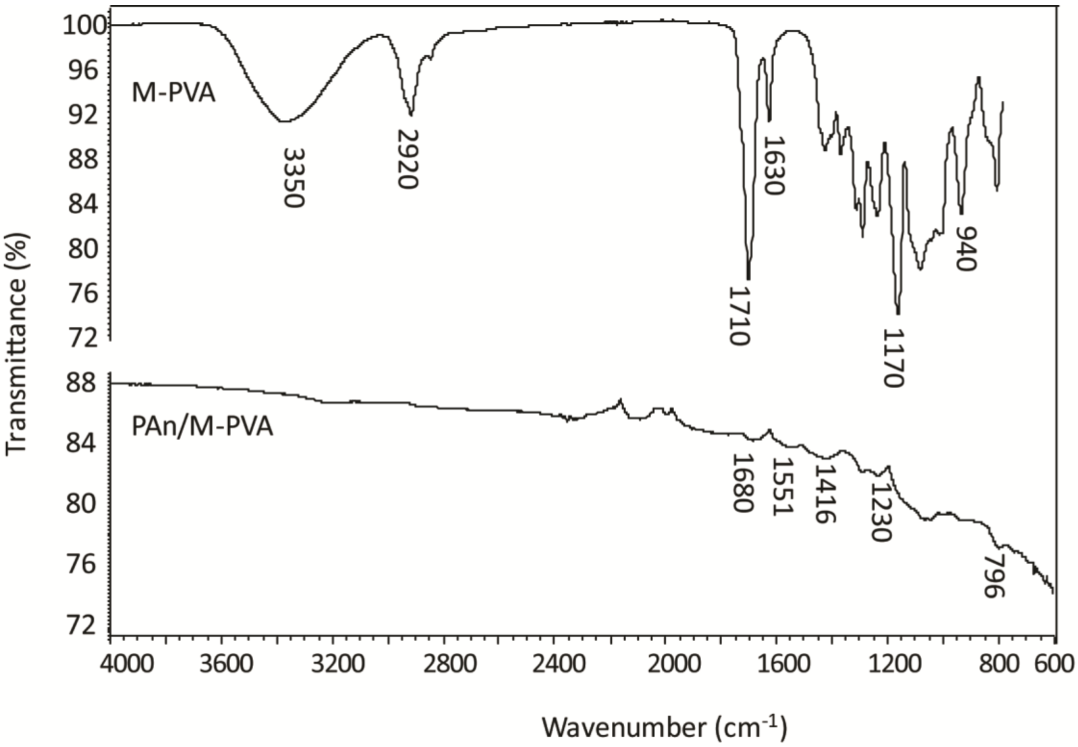

Figure 3. *ATR-FTIR spectra of M-PVA film and PAn/M-PVA composite*

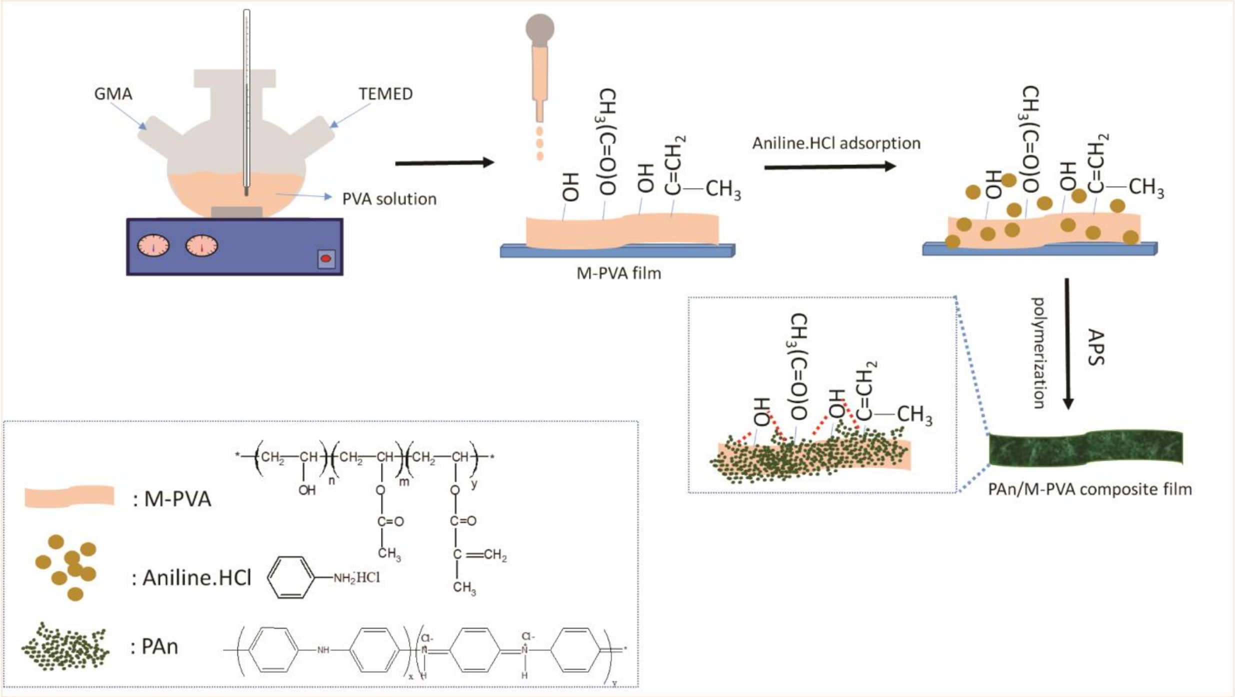

Figure 4. Schematic illustration for the preparation of PAn/M-PVA film composite and possible interactions

3.2. SEM micrographs and EDX spectra

In Figure 5, SEM micrographs of M-PVA film and PAn/M-PVA composite that were taken at different magnifications are presented. It can be apparently seen from the micrographs of the M-PVA that the surface has an entirely smooth texture even at the expanded regions. After the formation of the composite, it can be noticed from the micrographs that the texture of the composite surface remarkably changed and took a wrinkled structure that is uniform throughout the sample. This wrinkled/road-like structure of the composite surface is more prominent in the micrographs taken at higher magnifications (Figure 5d and 5e) compared to those of lower magnifications. The possible reason for the wrinkling of the film surface after PAn coating can be correlated with the shrinkage of the film during drying through the removal/evaporation of solvent molecules.

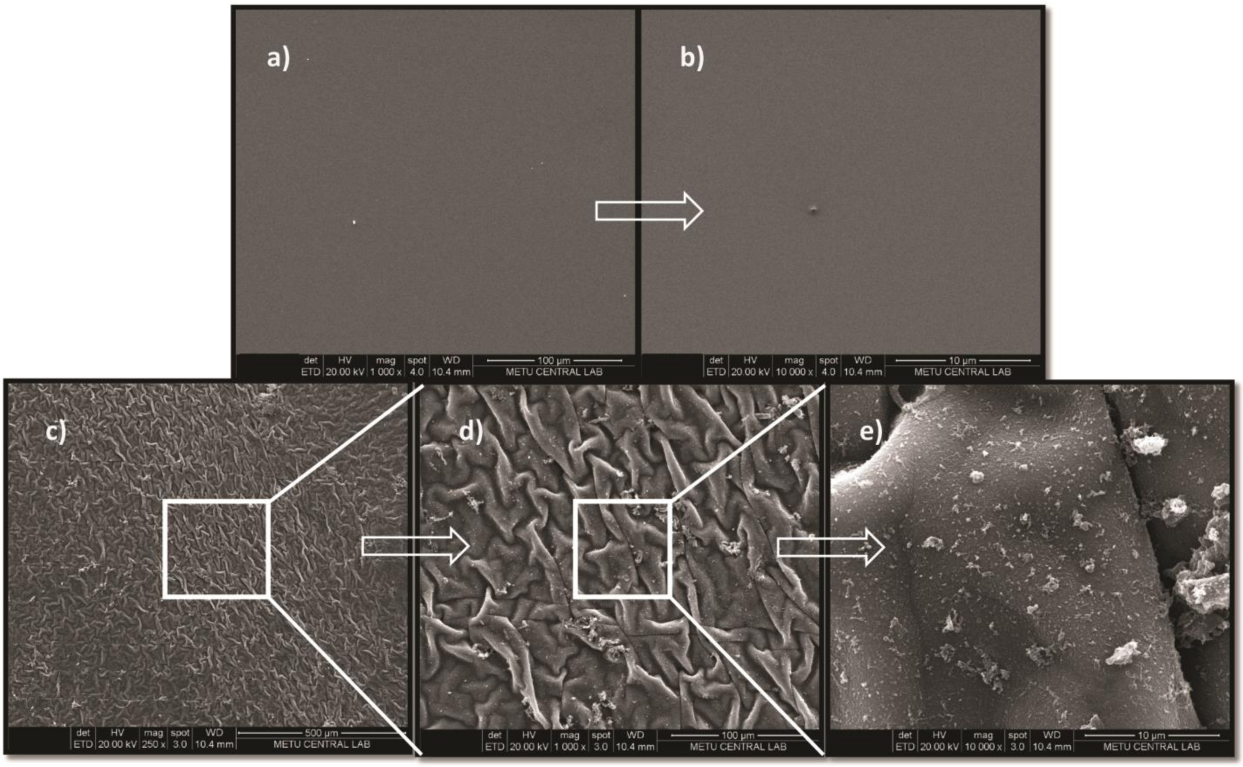

Figure 5. *SEM micrographs of a) and b) M-PVA film (6%); c), d), and e) PAn/M-PVA composite films taken at 250, 1000 and 10000 magnifications, respectively*

In Figure 6, the EDX spectra of the samples were taken from the corresponding-SEM micrographs. Compared to the spectrum of the M-PVA, remarkably high Cl signals were taken from the spectrum of the PAn/M-PVA composite, suggesting that the surface is covered with highly doped PAn. The presence of other N and S atoms also proves the PAn coating with the existence of APS oxidant residue.

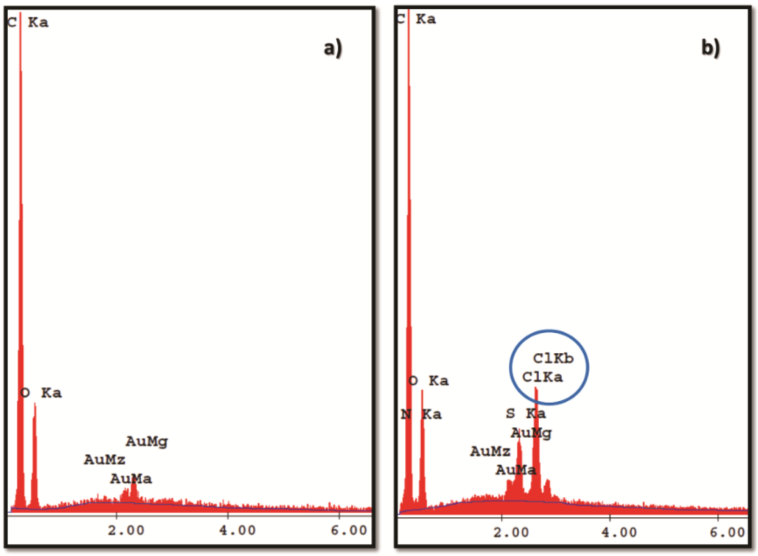

Figure 6. *EDX spectra of a) M-PVA film and b) PAn/M-PVA composite film*

3.3. Contact Angle

The changes in the water contact angle-wetting time of the M-PVA and PAn/M-PVA composite film are comparatively depicted in Figure 7. As seen from the figure, the contact angle values of the M-PVA film showed relatively significant and stable changes with the time (average 81° during 60 s) compared to the untreated PVA films in the literature [35]. This result suggests that the hydrophilicity of PVA was altered to a certain degree with the introduction of vinyl methacrylate groups to the PVA backbone, even the quite smooth texture of the M-PVA film as observed from the SEM micrographs (Figure 5a-b). Because the surface roughness of a material is known to be a very determinative factor in its contact angle value [36]. After coating the M-PVA film with PAn, due to the presence of hydrophilic dopant counter ions (here Cl^-) in the PAn chains, the values of the composite first showed a decrease from 81° to 69° within 3.8s and then stayed almost constant around this value up to 60s. This finding indicates that the surface wetting property of the composite did not remarkably change after PAn coating. Because, in the studies dealing with the surface properties of conductive polymers, it has been observed that a significant hydrophilicity improvement/wetting behavior occurs due to the presence of these polar counter ions [37-39]. However, here, such an observation was not encountered. The observed contact angle stability of the composite film can be explained with the rough texture of PAn coating onto the M-PVA surface, as given in Figure 5. During drying of the films, the removal/evaporation of the solvents, such as water and methyl alcohol, might have led to the formation of road-like texture on the film surfaces. Thus, this porous structure of the composite might have provided a slightly hydrophobic character that is unusual for highly doped-PAn's. The changes in these water droplets on the film surfaces can also be seen in Figure 7b.

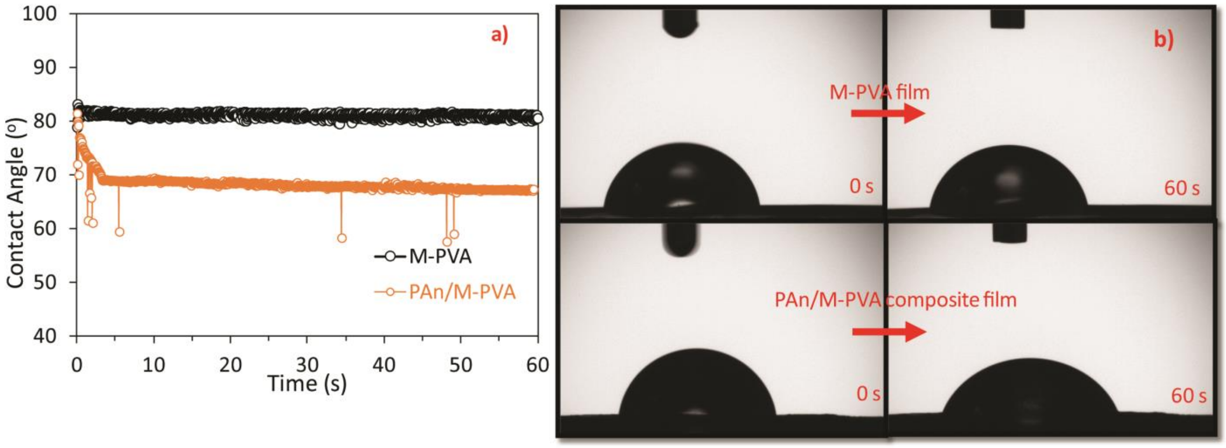

Figure 7. *Changes in water contact angle values of samples*

3.4. EMSE Results

The usability of the composite was examined in the EMI shielding field that is a usual application field for conductive polymers. For that purpose, a PAn/M-PVA composite sample was prepared in 13cm x 13cm diameter, and it was employed measurements within 30 MHz to 3 GHz. The effect of the coating number was monitored by recoating the same sample with PAn, and it was referred to PAn/M-PVA film-double. The results, including EMSE and relative shielding efficiency by Ab and Re, and shielding fault by T, are given in Figure 8. As seen from the figure, the uncoated blank M-PVA film showed an average EMSE value of 0.9 dB, and this value suggests that blank M-PVA film has almost non-suitable for EMI-shielding. After the first PAn coating, the EMSE value of the composite reached 8.3 dB EMSE at the initial 30 MHz, and then this value gradually decreased and became an average 2.8 dB. After the second coating of the composite with PAn, as a result of the increased conductivity and thickness of the shield, the initial EMSE value at 30 MHz increased to 13 dB, and then followed almost the same trend with those of the previous one, and took the average value of 5.6 dB with increasing frequency. Since single coated composite had a relatively low EMSE value, its relative shielding efficiency values were not calculated, and the calculations continued with the double coated composite.

When the relative shielding efficiency values of the double-coated composite are evaluated, it can be seen that the Re values are comparatively high at the lower frequency values. For example, at 30 MHz, the Re and Ab values of the composite were 0.92 and 0.050, respectively, indicating that the composite could shield 97% of electromagnetic waves through the dominant reflection mechanism. With increasing frequency, the active roles of Ab and Re changed, and the absorption mechanism became dominant. The average Ab and Re values of the composite were calculated as 0.49 and 0.22, respectively, suggesting that the composite could shield 71% of electromagnetic waves through the dominant absorption mechanism.

The shielding performance of the double PAn coated-composite was compared with the other conductive polymer coating studies published in the literature, and the findings are summarized in Table 2. Accordingly, it could be concluded that the EMSE and relative shielding efficiency values of the double-coated composite can be found close/comparable to the values present in the literature.

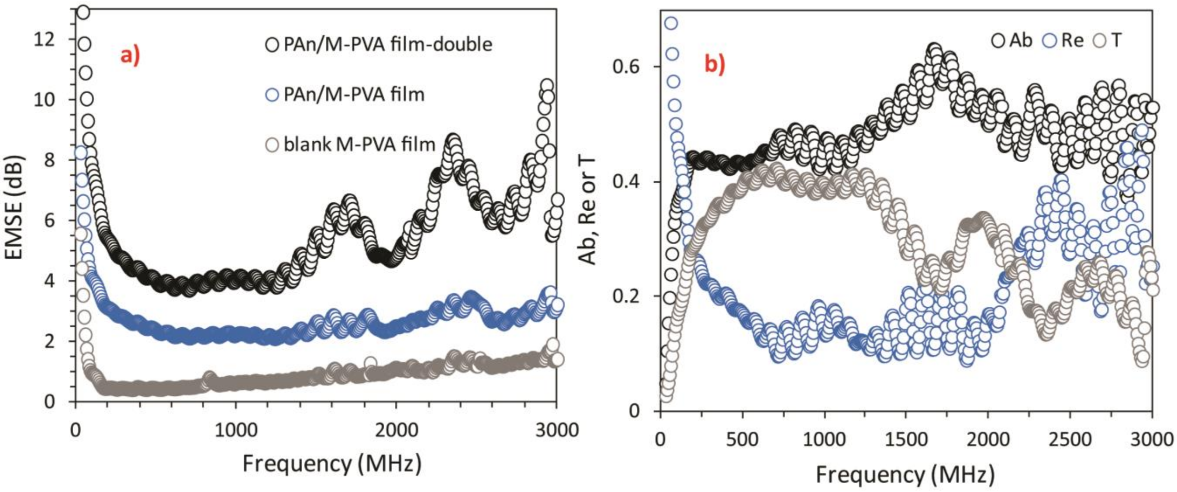

Figure 8. *a) EMSE results, b) relative shielding efficiency by Ab and Re, and shielding fault by T of the double-coated PAn/M-PVA composite within a 30 MHz-3 GHz frequency range*

Table 2. *Comparison of the EMI shielding performance of PAn/M-PVA composite with the other studies published in the literature*

Composite	**EMSE/frequency**	**Ab +Re value/frequency**	**Ref.**
PAni/PTSA/CMC film (0.6 mm coating thickness)	39-45 dB (10 MHz-1 GHz)	-	[40]
PAni/CSA/CMC film (0.6 mm coating thickness)	18-19 dB (10 MHz-1 GHz)	-	[40]
Double coated POA/PET nonwoven composite	33dB (at 15MHz) 6 dB (at 1.5GHz)	0.999 (at 15 MHz) Different values at different frequency	[28]
PAni/DBSA film	12.3 dB (at 750 MHz) and gradually decreasing EMSE values within 30 MHz-3 GHz	94% (750 MHz) Different values at different frequency	[41]
PAni/DBSA film	-	52.67 % (30 MHz- 1.5 GHz) Different values at different thickness	[42]
Double coated PAni/M-PVA film composite	13 dB (at 30MHz) 5.6 dB (30 MHz-3GHz)	0.97 (at 30 MHz) 0.71 (30 MHz-3GHz)	This work

4. CONCLUSIONS

With this work, certain hydrophobicity imparted-M-PVA films were made available in the employment of highly conductive PAn film formation in the aqueous medium. The usage of relatively concentrated M-PVA (6%) enabled the formation of robust film structure compared to a diluted one. The ATR-FTIR spectra demonstrated an interaction was formed between PAn and PVA backbone. SEM micrographs revealed the homogeneous and dense coverage of M-PVA films with the PAn polymer with a wrinkled texture. The EDX spectra evidenced the presence of highly-doped PAn polymer in the composite structure. Although the presence of polar dopant-counterions of PAn coat, the contact angle measurements indicated that the wrinkled texture of the composite slightly increased the contact angle and wetting time values of the composite. One of the most prominent results of this work was the EMI shielding performance of the double-coated composite. The results concluded that the performance of the composite can be evaluated between good (>90%) to fair (<80%) according to the specific requirements of EMI shielding materials (class II: general use), depending on the frequency range of the measurement.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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