

## Study of microwave absorption based Copper/polypyrrole nanocomposite

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**Abstract:** The composites of Cu/polypyrrole (PPy) were synthesized via different methods by in-situ polymerization on the surface of nanoparticles (NPs) with core-shell structure. This paper describes a method for polyacrylic acid (PAA) coating of NPs in aqueous solution. Then PPy coating was performed by template polymerization on NPs-PAA. The enhancement mechanism is thought due to suitable interaction and better electromagnetic match between these materials. Morphology, magnetic and conductivity properties were observed via scanning electron microscopy (SEM). The microwave characterization of nanocomposite was evaluated through arch test based on a network analyzer. The PPy nanocomposites possessed the excellent microwave X-band absorbers properties in 8-12 GHz. The best microwave absorption were obtained in 9.5 GHz for PPy, 9 and 12 GHz for Cu-PPy with minimum reflection loss (RL) in -17.5 and -18 dB at the thickness of 1 mm, respectively. It was also found that nanocomposites with 50% w/w and light weight exhibit good microwave absorbing properties.

**Keywords:** Cu, Nanocomposites, Microwave, Polyacrylic acid, Polypyrrole

### Introduction

In the last decade, various microwave (MW) absorption materials have been widely investigated for electromagnetic interference to protect human health and electronic equipments from electromagnetic pollution which is caused by the wide applications of high-power electronic devices and communication technology [1,2]. Nanosize manganese ferrite reinforced conductive polypyrrole composites reveal a core-shell structure by in situ polymerization, in the presence of dodecyl benzene sulfonic acid as the surfactant and dopant. The structure and magnetic properties nanofillers were measured, by using X-ray diffraction and vibrating sample magnetometer [3].

The microstructure and microwave absorption of carbon-coated Cu nanocapsules have been investigated [4]. The conductive and magnetic nanocomposites with core-shell and different nanostructures were used for electromagnetic absorption application [5,6,7,8,9]. Synthesis of Multi Core-Shell Nanocomposite Based Polypyrrole and Investigation Radar Absorbing Properties [10]. In the work, we attempted to add Cu nanoparticles composite to synthesize a new nanocomposite was applied to prepare by in-situ polymerization on the surface of all components after were coated by PAA. This paper is a revised and expanded microwave absorption properties in the frequency of 8-12 GHz.

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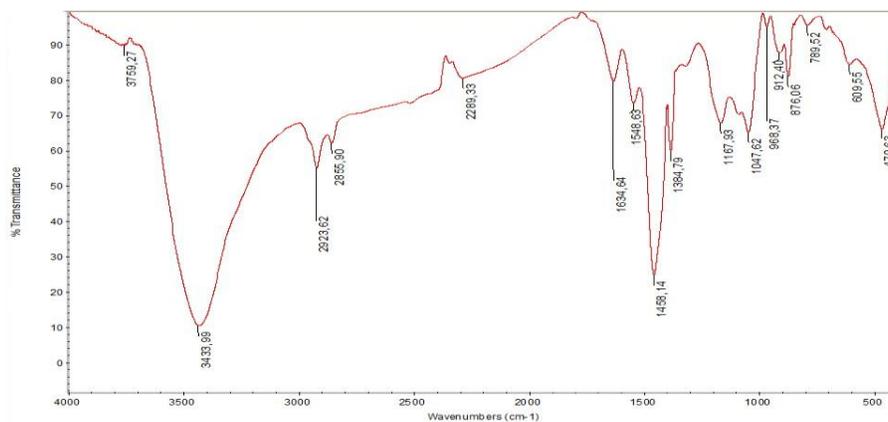
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## Results and discussion

### FTIR study

Figure 1 shows FTIR spectrum of Cu-PAA-PPy vibrations of PPy, The peak at 2923 and 2855  $\text{cm}^{-1}$  are attributed to C-H st. vibrations of PAA DBSA. The peaks at 2289  $\text{cm}^{-1}$  and 1634  $\text{cm}^{-1}$  are related to C=O st. The specific peaks around 1548 and 1458  $\text{cm}^{-1}$  are attributed with vibrational modes of quinonic and aromatic type ring for PPy. The peaks at 1167 and

1047  $\text{cm}^{-1}$  are attributed to C-N and C-C st. vibration mode for PPy. The polypyrrole composite surface, due to space congestion. Reducing their space congestion and also decreasing its peak intensity by coating with PAA, makes it possible to have C = O fineness weak peaks in 1700  $\text{cm}^{-1}$  and in these areas. As seen in the figure. The tensile vibrations of the 609, 789, 876  $\text{cm}^{-1}$  region of the Cu-O bond are nanoscale particles of copper. The 470  $\text{cm}^{-1}$  region of the Cu.

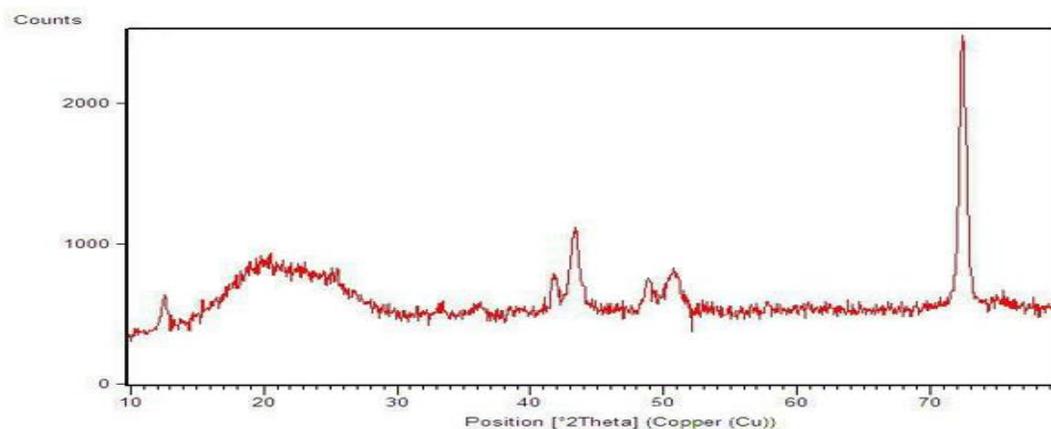


**Figure 1:** FT IR spectrum of Cu-PAA-PPy

### XRD patterns study

Figure 2 shows XRD pattern for Cu-PAA-PPy respectively. The results show the diffraction peaks of NPs structures were not destroyed after the chemical polymerization of PPy as shell. According to Figure 2 characteristic peaks at  $2\theta=17.25, 42, 44, 48, 50, 72.38$  with base peaks at  $2\theta=22.33, 72.38$  and  $24.83$  were observed for the Cu-PAA-PPy that correspond to JCPDS files no. 1646-002-98 respectively. These results indicated that the nanocomposite containing NPs-PAA-PPy are semi-crystalline and amorf. We can make sure of their's existence of NPs form XRD peaks

The average crystallite size can be calculated by the Debye-scherrer formula:  $D = 0.89 \lambda / \beta \cos \theta$  where  $\lambda$  is the wavelength of Cu  $K_{\alpha}$  radiation and the value of K depends on several factors, including the Miller index of reflection plane and the shape of the crystal. If the shape is unknown, K is often assigned as a value of 0.89, D is average crystallite size,  $\theta$  is the Bragg's angle, and  $\beta$  is the full width at half-maximum of the diffraction peaks, From the obtained peak width of XRD patterns, the average crystallite sizes of Cu are calculated to 20.3, respectively.



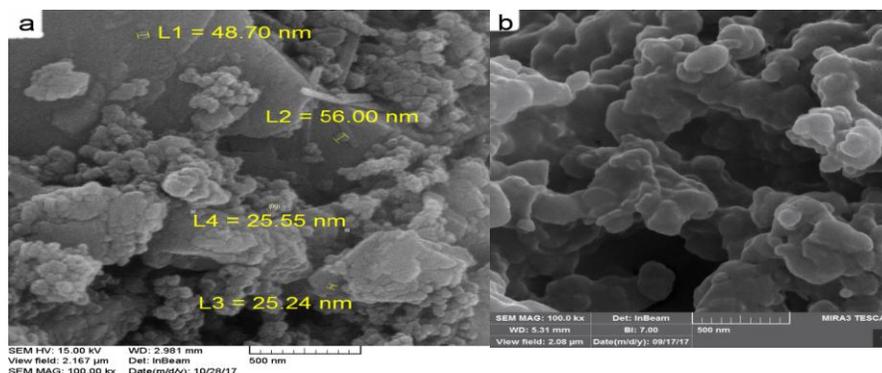
**Figure 2:** XRD pattern for Cu-PAA-PPy

### SEM images study

Figure 3 (a-b) shows FESEM images of Cu NPs and Cu-PAA-PPy nano composites. The diameters of sample are about 30 and 40 nm, respectively. All NPs are completely coated by PPy. The thickness of PPy as shell in all nanocomposites are about 10-20 nm. The surface of SEM images of nanocomposites were shown uniformity with some hollow and sponge structures.

### Electrical conductivity study

Electrically conductivity of NPs and their nanocomposites were measured by four probe method and were summarized in Table 1. The conductivity of PPy after polymerization by Fe(III) as initiator and DBSA as dopant is 0.044 S/cm. The conductivity of Cu that prepared by chemical method is higher than green method. When mass content of Cu as core and PPy as shell were incorporated in composites, conductivities are increased.



**Figure 3.** FESEM images of a) Cu b) Cu-PAA-PPy nano composite

**Table 1.** The electrical conductivity of samples

sample	Conductivity (S/cm)
PPy (doped)	0.044
PPy (undoped)	$1.4 \times 10^{-6}$
Cu (chemical)	245
Cu-PAA-PPy	130

### Microwave absorbing study

The microwave absorbing properties of nanocomposites with the coating thickness of 1 mm investigated by using vector network analyzers in the frequency range of 8-12 GHz, that this range is contained X band. The results for PPy, Cu-PAA-PPy,

The best microwave absorption were obtained in 9.5 GHz for PPy, 9 GHz for Cu-PAA-PPy with minimum reflection loss in -17.5, -17 and -18 dB, respectively the absorption band with under -10 dB are 8.5, 9 and 9.5 GHz ranging from 8 to 12 GHz for PPy, Cu-PAA-PPy.

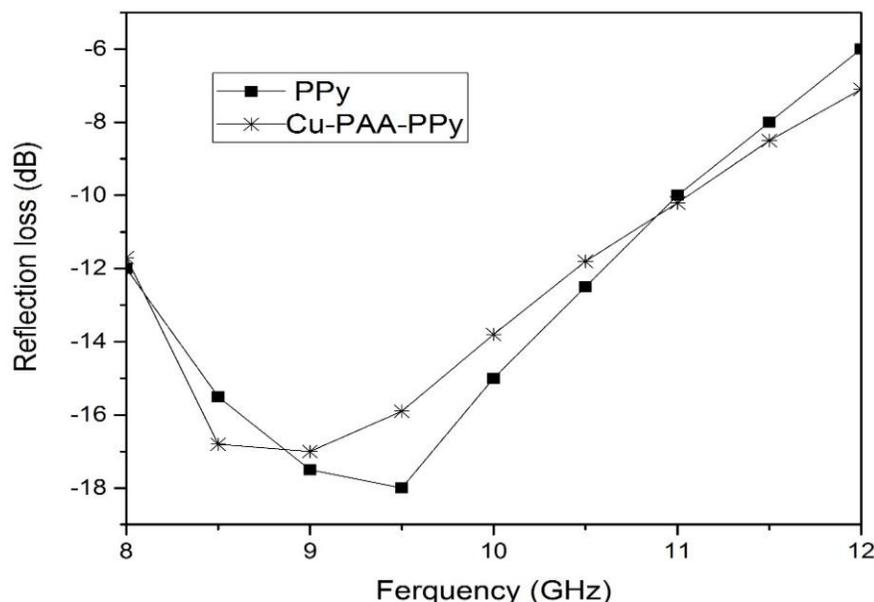


Figure 4: Microwave absorbing The results for PPy, Cu-PAA-PPy

### Conclusion

We have synthesized copper powder described a method for PAA coating on these. Then PPy coating was performed on template polymerization via in-situ method. Finally, we prepared their nanocomposites either separately or complex with core-shell structure. In continue, their microwave absorption properties in range of 8-12 GHz, X band were investigated. The results shows that the optimum absorption are 9, 9.5 GHz with RL of -18 and -17.5 dB and thickness of 1 mm, respectively the microwave absorption of samples were increased by increasing core and PPy weight ratio and electrical conductivity. These samples can be used to microwave absorption as most X-band absorber for civil and military applications.

### Experimental

#### Materials and Method

Pyrrole monomer (analytical grade, Merck) distilled twice under reduced pressure and stored below 0°C. Dodecylbenzene sulfonic acid (DBSA, 90%) and polyacrylic acid were purchased from the Aldrich. Other materials from the Merck.

#### Preparation of Cu nanoparticles

A solution of 0.25 g (0.01) molar  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 19.7 g (0.11) molar ascorbic acid in 100 ml of distilled water are prepared. This solution is slowly stirred by a magnetic partner. Blue was obtained. 0.8 grams of CTAB (cationic surfactant) was added to the solution and the solution was well stirred at room temperature. A relatively dilute solution was prepared from NaOH and slowly injected into a high solution, and its pH was stabilized in the range of 6.5 the solution was then raised to 85 °C, and the pH of the controlled solution remained constant within the same range. The resulting green color gradually turns red. After the red solution appears. It was interrupted for another 15 minutes. The solution was then washed with distilled water and ethanol.

#### Coating of NPs with PAA (NPs-PAA)

0.5 g NPs and 50 ml PAA (5% w/v) were added into 250 mL flask and the mixture was ultrasonicated for 15 min. the mixture was stirred vigorously at 25 °C for 24 h. The mixture was filtered and then washed with acetic acid (2% v/v) and acetone. After vacuum drying the filtrate, NPs-PAA were achieved.

### Characterization

The ultrasonic experiment was carried out by an ultrasonic disperser (Hielsche, UP4005, Germany). The FTIR analyzer performed Thermo U.S of AVATAR model. Field emission scanning electron microscopy (FESEM) were performed by TESCAN MIRA to observe surface morphologies of samples. The XRD patterns of the samples were collected on a Philips-PW 1800 with Cu K $\alpha$  radiation ( $\lambda=1.54184 \text{ \AA}$ ) in the  $2\theta= 4-90^\circ$  with steps of  $0.02^\circ$ , scanning operated at 40 kV and 30 mA (Netherlands). The electrical conductivities of compressed pellets of samples and nanocomposites were calculated using a standard four-probe set-up connected to a Keithly system comprising a voltmeter and constant high-current source, made in IRAN. Microwave absorption properties of nanocomposites were measured using microwave vector network analyzer (Agilent technologies Inc. 8722-USA) in the 8-12 GHz range at room temperature.

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