Electrical and Microwave Absorbing Properties of Polypyrrole Synthesized by Optimum Strategy

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ABSTRACT: The polypyrrole (PPy) was prepared by *in situ* solution polymerization. The structure and morphology were characterized by X-ray diffractometry, scanning electron microscope (SEM), and transmission electron microscope, respectively. The electrical and dielectric properties of the PPy were measured by four-point technique and impedance/materials analyzer. The results revealed that reaction time, reaction temperature, the types of doping agent, and the molar ratio of initiator to pyrrole monomer (n_{APs}/n_{Py}) had an important effect on electrical and dielectric properties of the PPy. It showed that the PPy doped with phosphoric acid and with $n_{APs}/n_{Py} = 1$ at 10°C for 12 h had better performance of electrical conductivity and dielectric loss. The PPy sample with 2 mm thickness had a minimum reflection loss value of -19.68 dB at approximately 16 GHz and an available bandwidth of 6.2 GHz in the range of 8–18 GHz. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

In recent years, conducting polymers have attracted more and more scientists' attention since the polyacetylene was first synthesized by Shirakawa et al. in 1977.[1] After that, many new conducting polymers, such as polyaniline (PANI), polypyrrole (PPy), and polythiophene, etc., were discovered.[2] Among those polymers, PPy has been extensively studied owing to its high electrical conductivity, good environment stability, relatively easy synthesis, and redox reversibility.[3] Therefore, it has been obtained extensive applications in the fields of rechargeable batteries,[4,5] biosensor,[6,7] gas sensors,[8,9] printing circuit board,[10] antistatic material,[11] stealth material,[12] solid electrolytic capacitor,[13] electrochromic material,[14] and so on.

As the conductivity of conducting polymer was strongly dependent on the polymerization environment, the PPy prepared under different conditions would show different electrical and dielectric properties. Migahed et al.[15] had studied dielectric properties and electrical conductivity of some PPy composite films in the temperature range of 180–300 K and in the frequency range of $20–10^5$ Hz, and found that the conductivity relaxation energy as well as the alternating current (AC) conductivity activation energy decreased as the PPy content increased. Ding et al.[16] had synthesized PPy nanotubule arrays

by electrochemical AC method, and researched the shift of absorbing peaks by means of Fourier transform infrared spectroscopy (FTIR) spectra compared to conventional PPy. Hung et al.[17] had employed fractional factorial design (FFD) and response surface methodology coupled with central composite design to optimize the electrical conductivity of PPy synthesized through an electrochemical route and constant current electrolysis, and selected current density of polymerization, monomer concentration, electrolyte (lithium perchlorate) concentration, and temperature as variables to study the effect on electronic conductivity of PPy through FFD. Carrasco group[18] had carried out a combination of techniques such as WAXS, CCP/MASNMR, and FTIR to monitor the changes in the structure as a function of conductivity for chemical PPy of low (<75 S/cm), medium (75–200 S/cm), and high (>200 S/cm) conductivity, and analyzed dependence of conductivity on conjugation length in the regime of long or short conjugation lengths. However, it has been reported little as yet that the dielectric loss and its microwave absorption properties of PPy depend on prepared conditions.

In this article, PPy was prepared successfully by *in situ* solution polymerization. The influence of reaction time, reaction temperature, the types of doping agent, and the molar ratio of initiator

to pyrrole (Py) monomer on the electrical and dielectric properties of PPy was investigated detailedly. The microwave absorption properties (reflection loss) of as-prepared PPy under optimum conditions were researched preliminarily.

EXPERIMENTAL

Reagents

Py was distilled under reduced pressure and stored below 0°C. Ammonium peroxydisulfate $((NH_4)_2S_2O_8$, APS), phosphoric acid (H_3PO_4), n-pentanol $(n-C_5H_{11}OH)$, alcohol (C_2H_5OH), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and dodecyl-benzenesulfonic acid (DBSA) $(C_{12}H_{25}-C_6H_4-SO_3H)$ were all of analytical purity and used without further purification.

The Preparation of PPy

The PPy was prepared by an *in situ* solution polymerization method.[19] The details of the procedure were described as follows: 0.5 mL of Py and 50 mL of 0.1 mol/L HCl were added into a 250-mL three-neck flask and stirred continuously. In brief, 1.65 g $(NH_4)_2S_2O_8$ (APS) was dissolved in 15 mL of 0.1 mol/L HCl and added dropwise to the previous Py solution. Subsequently, the mixed solution was stirred continuously at 10°C for 12 h. The final product was collected by filtering and washed with deionized water and ethanol, then dried for 24 h under vacuum at 60°C. At the same time, for comparison, the PPy was prepared under different conditions, such as reaction time (4, 8, 12, 16, and 24 h), reaction temperature (0, 10, 20, 30, 50, and 60°), types of doping agent $(H_3PO_4$, HCl, H_2SO_4, and $R-C_6H_4-SO_3H$) and the molar ratios of initiator to Py monomer (n_{APs}/n_{Py} = 3/1, 2/1, 1/1, 1/2).

Characterization

The X-ray diffractometry (XRD) patterns of the samples were operated on a Philps-PW3040/60 diffractometer with Cu Ka radiation ($k = 0.15418$ nm). SEM and transmission electron microscope (TEM) images were observed by a scanning electron microscope (SEM, Hitachi S-4800) and a TEM (JEOL JEM2010), respectively. The conductivity was measured on a SDY-4 four-probe instrument at room temperature. The dielectric loss properties of PPy were measured by a 4991A impendence/materials analyzer in the range of 1 MHz–3 GHz. PPy powders were, respectively, mixed with wax in the mass ratio of 1 : 2 to prepare rectangular coating layers with the different thicknesses on square (18 × 18 × 0.6 mm) aluminum plates. Their complex permeability, complex permittivity, and microwave absorbing properties were measured by a vector network analyzer (Agilent N5230) in the range of 2–18 GHz at room temperature.

RESULTS AND DISCUSSION

XRD Analysis

The XRD patterns of PPy samples are shown in Figure 1. Unless stated otherwise, the reaction conditions are as follows: doped with hydrochloric acid, $n_{APs}/n_{Py} = 1$, 10°C and 12 h. The samples shown in Figure 1(a, b) are prepared in 0 and 20°C, respectively; the sample is selected and phosphoric acid is selected as doping agent in Figure 1(c); and the sample is obtained by $n_{APs}/n_{Py} = 2/1$ in Figure 1(d). It can be observed that all sam-
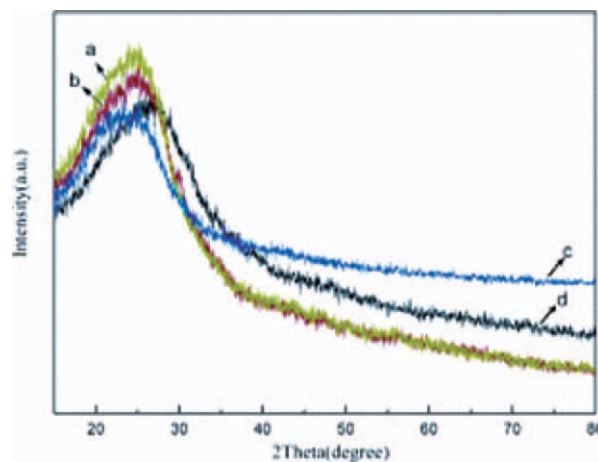

Figure 1. XRD patterns of PPy prepared under different reaction conditions. (a) $T = 0°C$; (b) $T = 20°C$; (c) doped with H_3PO_4; (d) $n_{APS}/n_{Py} = 2/1$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ples of PPy show a broad diffraction peak with an amorphous structure at about $2\theta = 25°$, and it is in good agreement with the literature.[20] The influence of reaction condition on the diffraction peaks of PPy is very small, whereas the diffraction peak in Figure 1(d) shifts to the direction of increasing 2θ, which may be owing to the structural difference of PPy chains caused by doping of different proton acids.

Electrical Properties

It is well known that the polymerization conditions have an important effect on electrical property (conductivity and dielectric loss) of PPy. The influence of reaction time and temperature, the types of doping agent, and the molar ratio of initiator to Py monomer on the electrical of PPy have been investigated detailedly.

The conductivity (σ) is used to characterize the capability of conducting electrons for substance. According to semiconductor theory, $\sigma = ne\mu$, where σ is proportional to the carrier density (n), the electronic charge (e), and the mobility of the carrier (μ).

Tangent value of the dielectric loss ($\tan\delta$) is used to characterize the loss of conductive polymers on electromagnetic waves and is defined as follows: $\tan\delta_e = \varepsilon''/\varepsilon'$, where ε' and ε'' are the real and imaginary parts of the complex permittivity, respectively. The real part ε', representing storage energy or charge capacity, is the same with relative dielectric constant in electrostatic field, and the imaginary part ε'' is dielectric loss factor representing the energy loss, just like paralleling equivalent resistor. It can be seen that the larger $\tan\delta$ value of material is, the greater its dielectric loss is, and the better its absorbability on electromagnetic wave is.

The Effect of Reaction Time on Electrical Properties of PPy. Figures 2 and 3 show the conductivity (σ) and dielectric loss ($\tan\delta_e$) of PPy with the different reaction times, respectively. It can be seen that the conductivity and dielectric loss of sample with 12 h achieve the maximum. The possible reasons
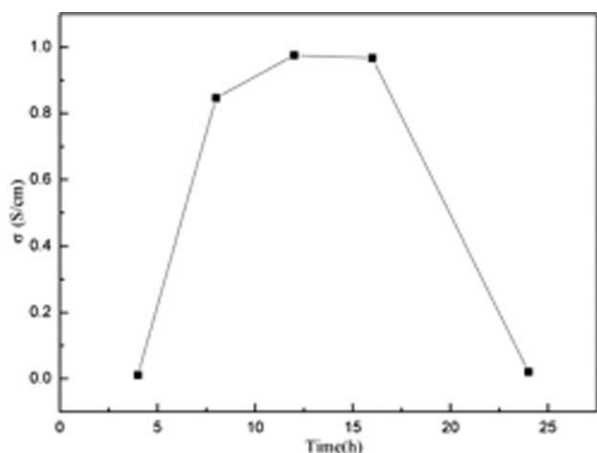
Figure 2. Conductivity of PPy with the different reaction times.

Figure 4. Conductivity of PPy with the different reaction temperatures.

are as follows: as the polymerization time is increased, the length of conjugated chain increases and the arrangement of the chain grows up to integrity in a given length of time. When the time is up to 12 h, the Py monomer is consumed up on the whole, here the length and the arrangement of PPy-conjugated chain reach their optimal form and have the least defects, largest electronic fluidity, and carrier mobility in the big π conjugate system and hence the conductivity reaches the maximum. When the time continuously increases, some side reactions, such as chain transfer and the peroxidation of Py rings also increase, and the regularity and conjugated degree of PPy chains decrease; therefore, the conductivities of system decline. Meanwhile, the conductivities have an important effect on dielectric loss for samples. The dielectric loss of samples is largely owing to PANI chains with the bound/localized charges and the dipolar reorientation processes, whereas the dipolar reorientation processes are proportional to the conductivity.[21] Hence, it is not difficult to understand that the dielectric loss has the same tendency with the conductivity.

The Effect of Reaction Temperature on Electrical Properties of PPy. Figure 4 is the conductivity pattern of PPy with the different reaction temperatures. It can reveal that the conductivities decrease with the increase of the temperature. This phenomenon can be explained as follows: On the one hand, the arrangement of PPy chains is disordered in the higher temperature, the regularity, and conjugated degree of chains decrease, and far away from its optimal form, and hence conductivities of polymer decrease. On the other hand, according to $\sigma = ne\mu$, the mobilities (μ) vary with the temperature, whereas the carrier densities (n) maintain basically constant in a certain temperature range. Thus, the effect of temperature on conductivity depends mainly on the mobility of the carrier. The lower reactive temperature is, the more ordered the arrangement of polymer chains is, the fewer the structural defects on chains are, the higher the mobilities of carrier are, and the better the conductivities of polymer are.

The frequency dependence of dielectric loss ($\tan\delta_e$) for PPy prepared in different temperatures is shown in Figure 5. It indicates
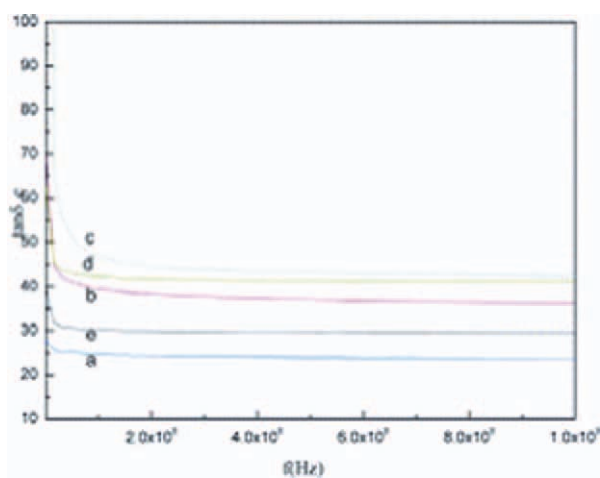

Figure 3. Frequency dependence of dielectric loss ($\tan\delta_e$) for PPy prepared in different times. (a) 4 h; (b) 8 h; (c) 12 h; (d) 16 h; (e) 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
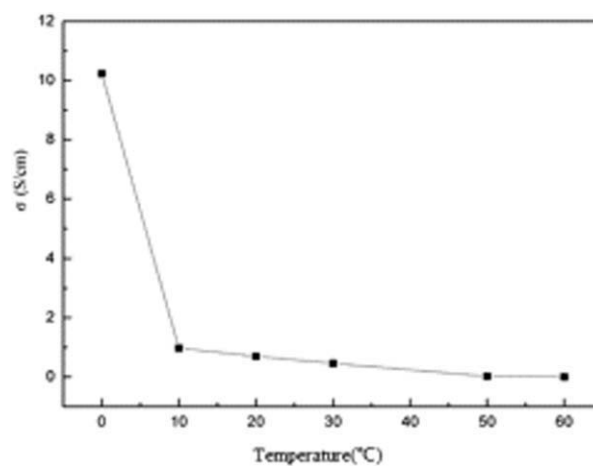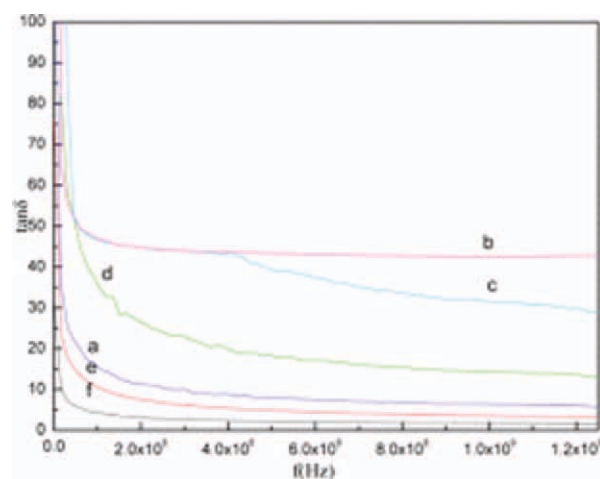

Figure 5. Frequency dependence of dielectric loss ($\tan\delta_e$) for PPy prepared in different temperatures. (a) 0°C; (b)10°C; (c) 20°C; (d) 30°C; (e) 50°C; (f) 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
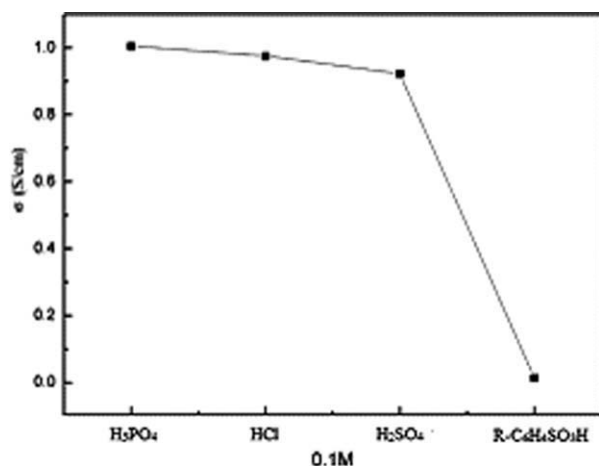
Figure 6. Conductivity of PPy doped with the different protic acids (0.1M).

Figure 7. Frequency dependence of dielectric loss (tanδ_e) for PPy doped with different protic acids. (a) H_3PO_4; (b) HCl; (c) H_2SO_4; (d) R-C_6H_4-SO_3H. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the tanδ_e of samples presents increasing trend with temperatures (except for 0°C), and decreases quickly in the range of low–middle frequency (<100 MHz) and decline slowly (tend to flat) in the range of high frequency (>100 MHz). When the temperature is up to 10°C, the tanδ_e of sample reaches the maximum. The tanδ_e of PPy is largely owing to the synergistic effect of ε' and ε'', namely the relaxation effect and the polarization interaction caused by the local bound charges (polaron and dipole) of PPy chains. On the one hand, the conductivity (σ) is proportional to the polarization of dipole.[21] As the conductivities (σ) of PPy are in the range of 10^{-3}–100 s/cm, it presents the character of semiconductors with good absorption on electromagnetic waves, whereas when the conductivities (σ) of PPy are higher than 100 s/cm, it exhibits metallic character and reflects the most of microwaves and hence the tanδ_e of PPy decreases instead. On the other hand, the polarization interaction is proportional to the temperature. The higher the temperature is, the larger effective mass of polaron is,[22] the stronger polarization interaction of the dipole is, the larger the dielectric loss of sample is. The comprehensive effects of the abovementioned factors result that the tanδ_e of PPy samples achieves the maximum at 10°C.

The Effect of Protonic Acid on Electrical Properties of PPy. Figure 6 shows the conductivity pattern of PPy doped with different protonic acids. The frequency dependence of the tanδ_e for PPy doped with different protonic acids is shown in Figure 7. It can be seen that the conductivities and dielectric loss have a great difference among the samples, that is, the performance of inorganic protonic acids is better than that of organic protonic acid, and the PPy doped with phosphoric acid is the best of all samples doped with inorganic acids, which may be related to the regularity of polymer chains and balance of opposite charge on the chains. The correlate mechanism will be further researched. The conductivity of PPy doped with DBSA is lower than that of the PPy doped with inorganic protonic acid. The possible reasons are as follows: at first, the H$^+$ ion numbers of inorganic protonic acid are more than that of the DBSA in the same concentration. The more the numbers of H$^+$
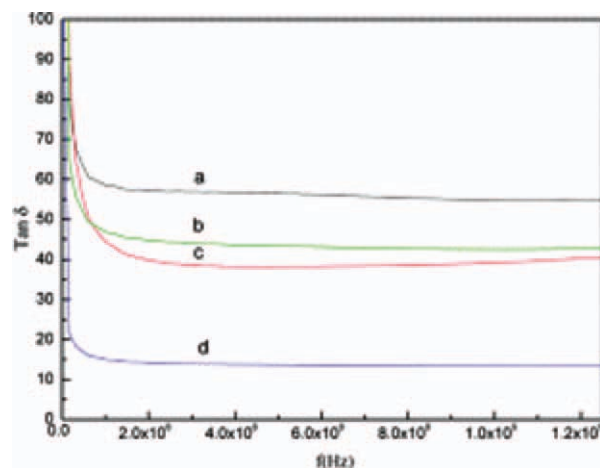
ion are, the more the numbers of dipole on the polymer chains are, and thus the polarons become the main part of carriers. The rapid increase of the carrier concentration could change the Fermi energy, and the energy gap between conduction band and valence band is diminished and hence the carriers are easily transmitted to the empty orbit, and the mobilities of carriers are highly improved. Second, the polymerization reaction could be taken place in the α- and β-site of Py. DBSA with large steric effect hinders the normal growth of PPy chains to some extent, and migration path of carriers on the PPy chains is blocked partly, which would result in the lower conductivity of PPy. The dielectric loss in Figure 7 has the same change as the conductivity in Figure 6, as the polarization of dipole is proportional to the conductivity.[21]

The Effect of n_{APs}/n_{Py} on Electrical Properties of PPy. The conductivity and the frequency dependence of the tanδ_e for PPy with different ratios of n_{APs}/n_{Py} are shown in Figures 8 and 9, respectively. It can be seen that the conductivities and the tanδ_e of PPy increase first and then decrease as n_{APs}/n_{Py} decrease, and

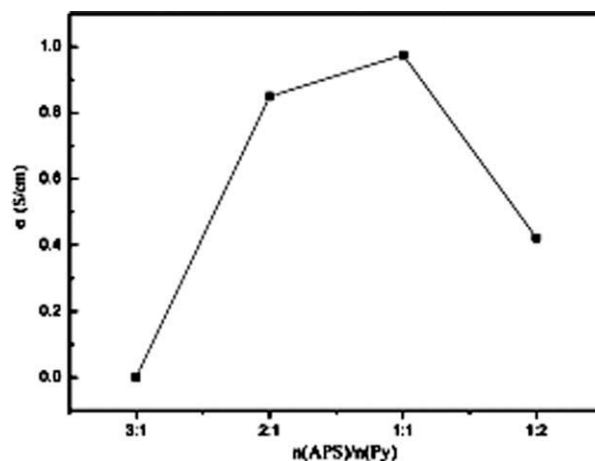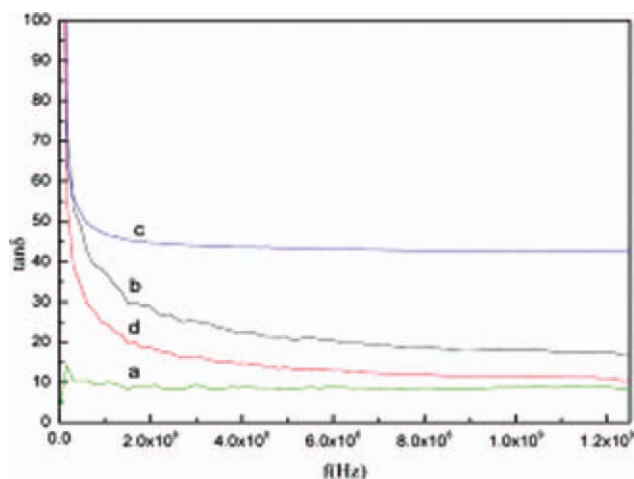**Figure 8.** Conductivity of PPy with different ratios of n_{APs}/n_{Py}.

Figure 9. Frequency dependence of dielectric loss ($\tan\delta_e$) for PPy with different ratios of n_{APs}/n_{Py}. (a) 3/1; (b) 2/1; (c) 1/1; (d) 1/2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the latter decrease quickly in the range of low–middle frequency (<100 MHz) and slowly tend to flat in the range of high frequency (>MHz 100). When $n_{APs}/n_{Py} = 1$, the conductivities and $\tan\delta_e$ of PPy reach to maximum. The possible explanations are as follows: On the one hand, with the contents of Py increase, the Py polymerize into the macromolecules gradually, here the regularity of polymer chain reaches its optimal form and hence the sample presents favorable conductivity. When the contents of Py go on increasing, the conductivities of system decline instead owing to the increase of oligomer content. On the other hand, according to the Nernst equation, with the contents of APS increase, the oxidation potential of system ascends. The excessive potential could lead to the fracture of PPy chains which are oxidized, the migration path of carriers is demolished partly, which would result in the destroying of conjugated structure and the declining of conductivity for PPy. In a word, the PPy doped with phosphoric acid and with $n_{APS}/n_{Py} = 1$ at 10°C

for 12 h has better performance of electrical conductivity and dielectric loss.

Morphology Analysis

The SEM and TEM images of the PPy prepared at optimum conditions (10°C, 12 h, doped with H_3PO_4, $n_{APS}/n_{Py} = 1$) are shown in Figure 10. It is observed from SEM image that the PPy presents a cauliflower grain agglomerated by the spherical particles. As the polymeric probabilities of the α and β carbon on Py[23] are equivalent, the PPy chains grow by three-dimensional in the polymerization and form cauliflower-like microstructures. The TEM picture shows that the PPy is spherical particle with a wider size distribution owing to the difference of polymerization degree and molecular weight of polymer chain.

Microwave Absorption

The reflection loss is calculated as $R(dB) = 20 \lg\left|\frac{Z_{in}-1}{Z_{in}+1}\right|$, where Z_{in} is the normalized input impedance relating to the impedance in free space, $\overline{\mu_r} = \mu' - \mu''$ and $\overline{\varepsilon_r} = \varepsilon' - \varepsilon''$ are the relative complex permeability and permittivity of the absorber medium, d is the thickness of the absorber coating. The impedance matching condition is determined by the combinations of six parameters ε', ε'', μ', μ'', d, and f (the frequency of electromagnetic wave). Additionally, light weight, high strength, thin thickness, wide band of absorption, and high absorbing performances are used to evaluate the absorbers in engineering application. In this article, the available bandwidth is defined as the frequency width in which the reflection loss is <−8 dB.

Figure 11 shows the reflection loss of PPy sample at optimum conditions (10°C, 12 h, doped with H_3PO_4, $n_{APS}/n_{Py} = 1$) with the different thicknesses in the range of 8–18 GHz. As shown in Figure 11, the PPy sample with 2 mm thickness has a minimum reflection loss value of −19.68 dB at approximately 16.05 GHz and a available bandwidth of 6.2 GHz in the range of 8–18 GHz, and the minimum values of reflection loss decrease and shift to high frequency as the thickness of samples increase.

Table lists the minimum R-values and available bandwidths of PPy samples doped by different protic acids with the thickness
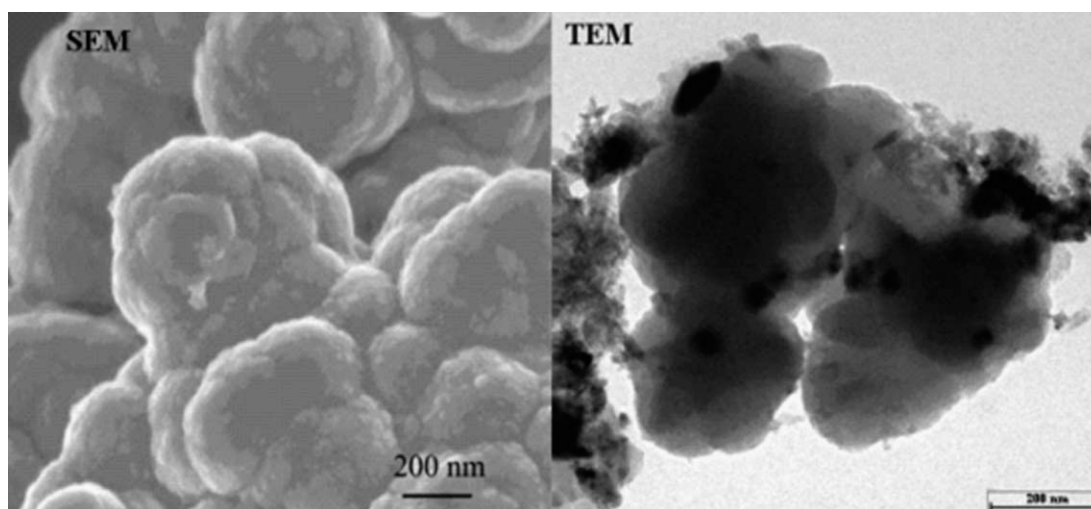

Figure 10. The SEM and TEM images of PPy (10°C, 12 h, doped with H_3PO_4, $n_{APS}/n_{Py} = 1$).

of 2 mm in the range of 8–18 GHz ($n_{APs}/n_{Py} = 1$, 10°C, 12 h). As summarized in Table I, the sample doped by phosphoric acid has the minimum R-values and the maximum available bandwidth in the measured frequency range. There are significantly positive correlation between the minimum R-values and the conductivities of the samples shown in Figure 6. For conducting polymer with π-electron-conjugated system, their conductivities can be changed in the range of insulators, semiconductors, and metallic state, whereas the absorbing properties of samples are related to their conductivities. The absorbing property of the samples can also be explained according to the Schelkunoff's electromagnetic shielding theory.[24] The shielding efficiency is calculated as follows

$$SE_T = SE_R + SE_A + SE_M \qquad (1)$$

where SE_R is reflection loss, SE_A is absorption loss, and SE_M is multiple reflection loss. SE_R is defined as

$$SE_R = 168 - 10 \lg(\mu_r - \sigma_r) \qquad (2)$$

In which, μ_r is the permeability of material relative to vacuum; σ_r is the conductivity of the material relative to ideal copper.

Reflection loss is the result of the interaction between the charged particles (free electrons and holes) of conductor and the electromagnetic field. By the formula (2), the reflection loss is related to the value of μ_r/σ_r; while the greater the conductivity of polymers is, the greater their reflection loss is in a certain electromagnetic wave frequency and material thickness.

It is known that PPy is an absorbent with dielectric loss, its microwave absorption properties can be explained in terms of electrical conductivity[24] and the presence of bound/localized charges (polarons/bipolarons), leading to strong polarization and relaxation effects,[25,26] and is determined by the combinations of six parameters ε', ε'', μ', μ'', f, and d. Further study on microwave absorption mechanism of PPy sample depends on the dielectric relaxation behavior and is still in progress.

Table I. The Minimum R-Values and Available Bandwidths of PPy Samples Doped by Different Protic Acids

Samples	Minimum R (dB) (corresponding to frequency [GHz])	Available bandwidth (GHz)
Doped with H_3PO_4	−19.68 (16.05)	6.2
Doped with HCl	−19.14 (15.38)	5.6
Doped with H_2SO_4	−18.23 (14.76)	5.2
Doped with R-C_6H_4-SO_3H	−6.35 (14.42)	1.6

The absorbing effect of PPy in this experiment is better than that of the previously published literatures (the minimum R-value of −12.09 dB),[27] (the minimum R-value of −4.8 dB),[28] and (the minimum R-value is <-10 dB).[29] Hence, the present method is of great importance to prepare microwave absorbent with excellent performance.

CONCLUSIONS

The PPy samples with different reaction conditions are successfully synthesized by *in situ* solution polymerization. The experimental results show that the PPy obtained by doping with phosphoric acid and with $n_{APs}/n_{Py} = 1$ at 10°C for 12 h had better performance of electrical conductivity and dielectric loss, and the sample with 2-mm thickness has a minimum reflection loss value of −19.68 dB at approximately 16.05 GHz and a available bandwidth of 6.2 GHz in the range of 8–18 GHz. The electrical and dielectric performance of the PPy can be tuned by controlling of reaction condition, which is of great importance to apply in electromagnetic shield, rechargeable batteries, biosensor, gas sensors, and so on.
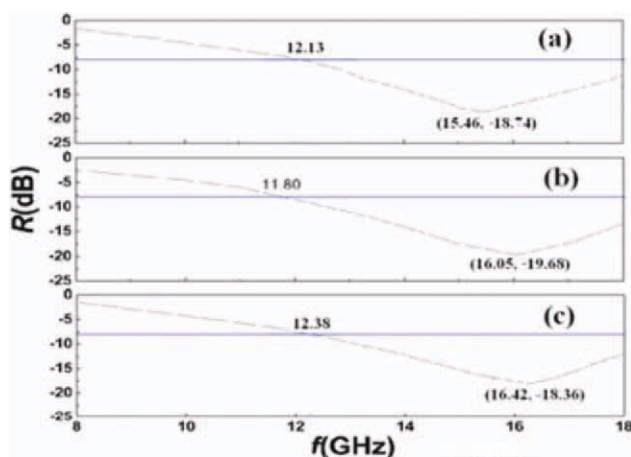
ACKNOWLEDGMENTS

Figure 11. The reflection loss of PPy sample at optimum conditions with thickness of 1 mm (a), 2 mm (b), and 3 mm (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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