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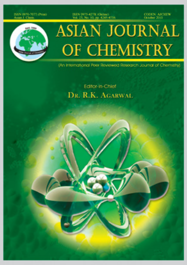

Study on the Preparation and Characterization of Polypyrrole/Montmorillonite Conductive Composites

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Polypyrrole/montmorillonite composite were prepared by the *in situ* polymerization of pyrrole in the presence of montmorillonite. Infrared spectroscopy, thermogravimetric analysis, X-ray diffraction and transmission electron microscopy were used to characterize the composition and structures of composite materials, as well as test the conductivity of composite materials through four-probe technique. The preparation conditions of polypyrrole/montmorillonite conducting composites were optimized, the results showed that when the reaction lasted for 15 h in the ice bath, the amount of montmorillonite, $FeCl_3{\cdot}6H_2O$ and the dopant BSNa was 0.4 g/mL pyrrole, 9.1 g/mL pyrrole and 4.4 g/mL pyrrole, respectively. At the moment, the composite had the larger conductivity up to 56 S/cm. According to FT-IR spectroscopy, it showed that it did exist polypyrrole and montmorillonite in polypyrrole/montmorillonite composite system, which reprented that the montmorillonite certainly exhibited remarkable improvement in materials' properties when compared with virgin polypyrrole composites.

Key Words: Polypyrrole, Montmorillonite, Composite, Dope, Conductivity.

INTRODUCTION

Since the discovery of conducting polymers, a large volume of research work has been performed associated with the physics and chemistry of conducting polymers. Methods of making polypyrrole (PPy) of high conductivity with high yield have been reported in the literature[1-10]. Polypyrrole has been prepared by either electrochemical method in the form of films or chemical method to yield powder. Compared with electrochemical method, chemical oxidation method is in general simpler and more amenable to bulk polypyrrole production. However, a serious problem was encountered in attempting to construct a practical component with high conductivity when using these conducting polymers, because the special chain structure leads to poor processibility which limits their more widespread application. Many studies had made the greatest efforts to prepare a certain of composite materials with mechanical strength and easy processing. In present study, we paid attention to polypyrrole, introduced layered montmorillonite (MMT)[11-20] into organic/inorganic system and prepared polypyrrole/montmorillonite conducting composites by oxidative polymerization. In order to simplify the polymerization techniques, increase the conductivity of composites and lower the consumption, polypyrrole/montmorillonite composites were prepared in water medium. The component structure and properties of the hybrid were characterized by X-ray diffraction FT-IR, TGA and conductivity measurement. Differently from previous study,we also have optimized the preparation conditions of polypyrrole/montmorillonite conducting composites in this experiment. For polypyrrole/montmorillonite composites, the optimized conditions including reaction temperature, reaction time, the amount of montmorillonite, the amount of oxidizer, the amount and kind of dopant *etc*. all have been studied in detail.

EXPERIMENTAL

Pyrrole was vacuum distilled and stored in dark before use. Na^+- montmorillonite (Aldrich) was soated for 24 h prior to use. Ammonium perdisulfate was used as such. All other reagents were of AR grade and used after necessary purification by standard procedures.

Synthesis of polypyrrole and polypyrrole -montmorillonite composites: According to the literature[21], a certain amount of montmorillonite soated for 24 h was transferred in a 250 mL round-bottom flask at 0-5 ºC and stirred vigorously. A certain amount of BSNa and pyrrole was then added to the stirring montmorillonite solution. 50 mL $FeCl_3{\cdot}6H_2O$ aqueous solution was added dropwise to the above mixtures. The most evident point is the mixture immediately turned blue with the formation of a black precipitate. The reaction was kept at 0-5 ºC for 12 h with magnetic stirring and filtered through the vacuum pump, then the cake was washed with methanol and distilled water until the effluent was colourless. Finally, the black polypyrrole powder was dried in the vacuum oven.

Characterization techniques: The products obtained were characterized by FT-IR spectroscopy (JASCO FT-IR-410), XRD pattern of the composites was obtained from a Philips X-ray diffractometer (Cu LFF; 40 kV; 20 mA). Thermogravimetric analysis analysis was operated on TA200-STD29600 of TA-instruments. DC conductivity values were measured by the conventional four-probe method using pressed pellets.

RESULTS AND DISCUSSION

Fig. 1 showed the characteristic FT-IR spectrum of Na^+-montmorillonite (MMT) and polypyrrole/montmorillonites (PPy/MMT) sample obtained of which (a) and (b) respectively standed for montmorillonite and polypyrrole/montmorillonite.

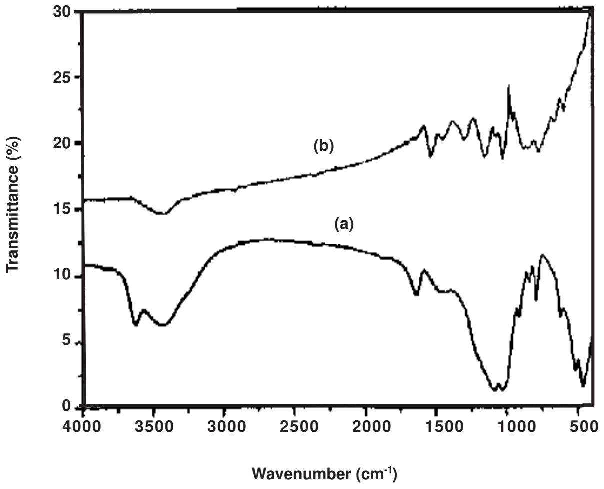

Fig. 1. FT-IR of (a) montmorillonite and (b) polypyrrole/montmorillonite composite

The characteristic absorption peaks of montmorillonite (1040, 590 and 480 cm^{-1}) and polypyrrole (1530, 1470, 1290, 1140 and 890 cm^{-1}) in FT-IR spectrum of polypyrrole/montmorillonite had all embodied. Because the functional groups of composite materials were easily affected by many factors, which might cause a slight movement of peak, but the FT-IR spectra was sufficient to demonstrate that the complexes contained polypyrrole and montmorillonite.

Fig. 2 showed the thermogravimetric analysis curves of montmorillonite and polypyrrole/montmorillonite prepared under different conditions, in which (a) standed for TGA curves of montmorillonite, (b), (c), (d) respectively for TGA curves of polypyrrole/montmorillonite prepared at 0, 20 and 45 ºC, (e) was the TGA curves of pure polypyrrole prepared at 0 ºC. As shown in Fig. 2, the results indicated that the loss of the quality of montmorillonite at 150 ºC is 2.3 % at 800 ºC was 7.4 %, the lessness of quality of compound was less before 300 ºC and its quality had basically constant at 650 ºC and now polypyrrole had completely decomposed, the remnants was white montmorillonite. The content of polypyrrole in complex prepared under 0, 20 and 45 ºC respectively was 69.46, 72.68 and 73.12 %. It could be seen that the content of polypyrrole in the polypyrrole/montmorillonite complexes obtained at different temperatures had not much difference. It clearly showed that the reaction temperature had little effect on the content of polypyrrole in conductive polymers. But in the three cases, the conductivity of composite materials had a huge of difference. The lower temperature of preparation, the higher conductivity of material.

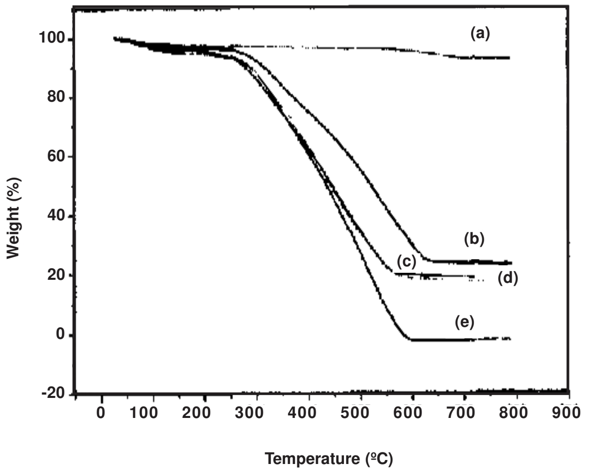

Fig. 2. Thermograms of montmorillonite and polypyrrole/montmorillonite composites prepared at different temperature

Fig. 2 also showed that the mass loss of samples in the same decomposition temperature were followed increasing, heat resistance were reduced. And the ultimate decomposition temperature (Td) of sample was not the same (Table-1). the Td of sample b was 605 ºC and c was 550 ºC. That was to say that the synthesis of composite materials under low-temperature had the better of heat tolerance. Associated with the high conductivity of composite materials under low temperature system, we speculated the product had a higher degree of polymerization under low temperature, So it had a good thermal tolerance.

As shown in Fig. 3 the thermal decomposition rate curves of b, c, d, e, from the Fig can be drawn the largest thermal decomposition rate of composite corresponds to the temperature T_{max}. The data was shown in Table-1.

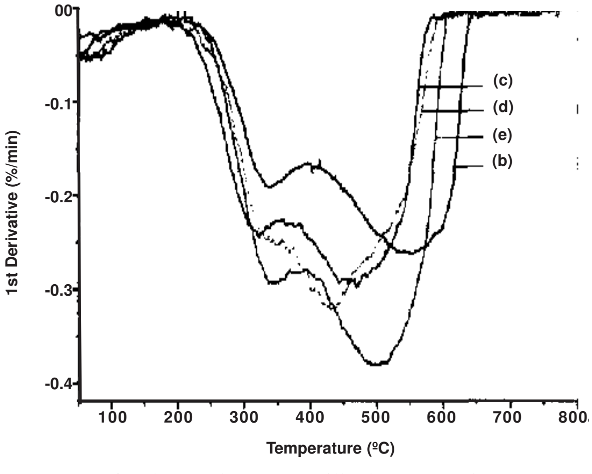

Fig. 3. DTG of polypyrrole/montmorillonite composites prepared at different temperature

TABLE-1
T_{max} AND Td OF POLYPYRROLE/MONTMORILLONITE COMPOSITES AND POLYPYRROLE

Sample (°C)	b	c	d	e
T_{max} 1	310	315	305	320
T_{max} 2	500	450	420	468
Td	605	550	550	570

From Fig. 3 and Table-1, it is found that the polypyrrole and its complexes with montmorillonite both had two T_{max}. This showed that polypyrrole had an uneven composition through this method of synthesis. A low T_{max}, accordingly, resulted that its product had a low molecular weight and the decomposition temperature was usually at the 310 °C. T_{max-2} was truly representative of the thermal decomposition temperature of the long-chain polypyrrole which contributed to the conductivity. The T_{max-2} of pure polypyrrole was higher than that of composite in the higher temperature. However, under low temperature of synthsis, the T_{max-2} of composite had already increased to 500 °C, higher of 32 °C than pure polypyrrole, 50 °C than c and 80 °C than d. The final sample decomposition temperature of a few have the same trend. The reason may be that a larger degree of formation of polymerization products at low temperature had better heat resistance. The addition of montmorillonite re-structured the arrangement of chain in the complex to a certain extent, it had played a similar cross-linking role, thus enhanced the thermal decomposition temperature.

Figs. 4 and 5 respectively showed that XRD map of original montmorillonite and polypyrrole/montmorillonite complexes. According to Bragg equation : $2d \sin \theta = \lambda$, the diffraction angle (2θ) can be calculated from the crystal lattice spacing. When 2θ was less than 10°, the peak was the diffraction peaks of montmorillonite layer, which reflected the size of interplanar spacing montmorillonite. Therefore, from Figs. 4 and 5, it can observed that the interlayer distance of montmorillonite had expanded from 0.918 nm to 1.90 nm. Moreover, the sharp level of peak had dropped noticeably. This showed that the polypyrrole chain had been inserted into the layer of montmorillonite layer and part of the lattice structure of montmorillonite had been damaged.

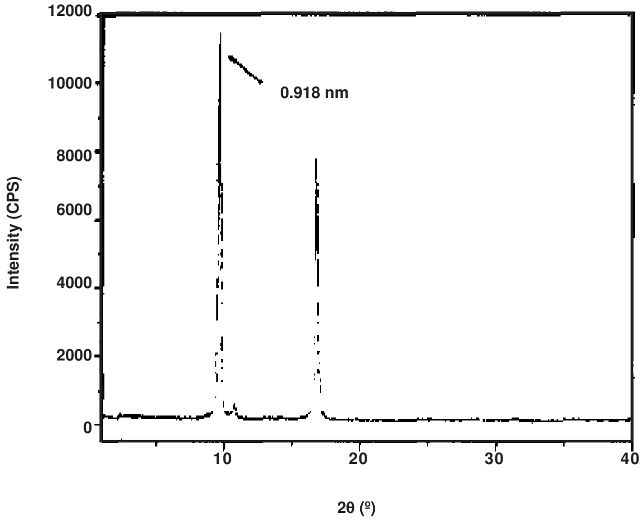

Fig. 4. XRD pattern of montmorillonite

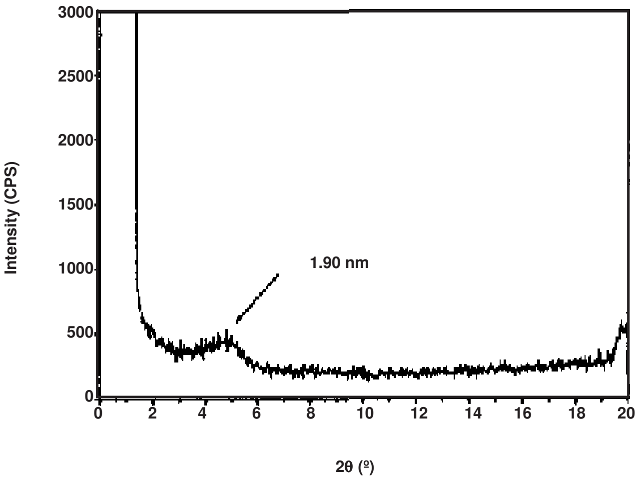

Fig. 5. XRD pattern of polypyrrole/montmorillonite composites

Fig. 6 is the XRD image of polypyrrole/montmorillonite (sample b) prepared at 0°C and Fig. 7 is that of sample d prepared at 45 °C. From the two images, we can see that they both had a wider diffraction peaks when 2θ equaled to 21.92, compared products obtained at 0 °C with at 45 °C, the former was a little narrower and stronger. From the literature, the peak indicated the characterization of the crystalline material. The more sharp and more strong of the peak, the more regularity of the polymer chain. Thus, it may be inferred that the composites prepared under low temperature were arranged in a more structure. Right combination of temperature effects on the conductivity. It is suggested that the chain tacticity of polypyrrole is the main factor effecting on the conductivity. The polypyrrole/montmorillonite prepared under low temperature had the high conductivity, because polypyrrole had a more equal molecular chain under such circumstances.

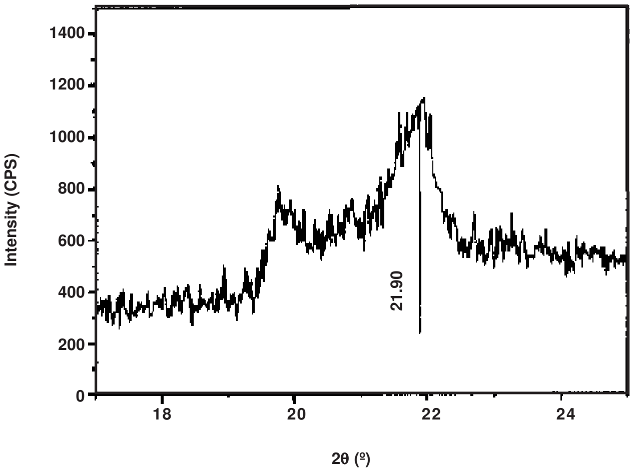

Fig. 6. XRD pattern of polypyrrole/montmorillonite composites prepared at 0 °C

Mechanism of synthsis: According to the the reported literature. When the content of Na^+ - montmorillonite in water was less than 4 %, montmorillonite was dispersed in a fashion of single layer. In this paper, the quality of montmorillonite in the system had accounted 0.2-1 %. Montmorillonite was uniformly dispersed in the water and there was no significant precipitation.

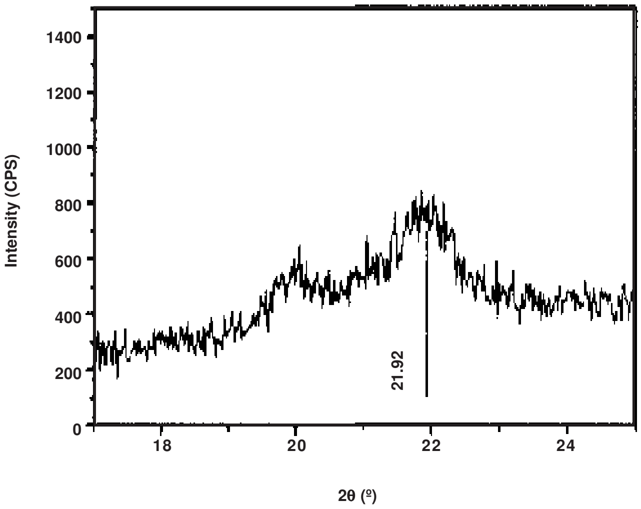

Fig. 7. XRD pattern of polypyrrole/montmorillonite composites prepared at 45 ºC

Fig. 8 showed no diffraction peak when the diffraction angle 2θ was less than 10º, that is to say that we could not see the rules of crystal structure in the layer. It was because of the interlayer cation of montmorillonite was easy to suck up water and occurred cooperation with water led to the montmorillonite swelling. Then montmorillonite layer was in a single form of decentralization in the water.

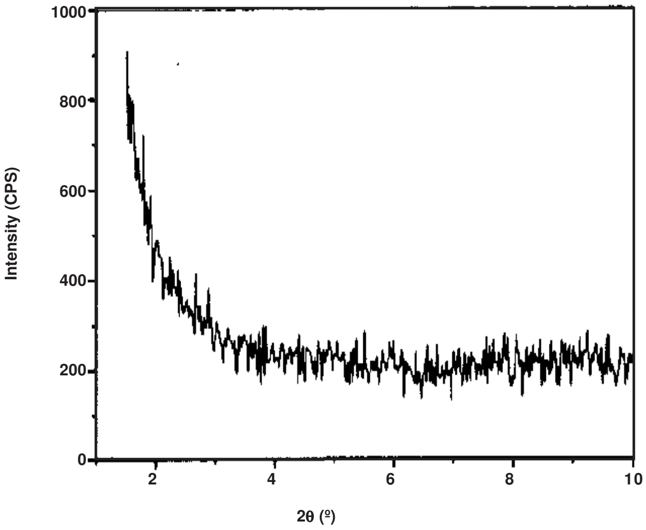

Fig. 8. XRD pattern of montmorillonite suspended system

When added oxidant $FeCl_3{\cdot}6H_2O$ in aqueous suspension of montmorillonite, the system immediately showed yellow floc. It may be inferred that Fe^{3+} has a more positive charge than Na^+. So the electrostatic attraction between Fe^{3+} ions and clay layer with the negative charge showed more strong, which was enough to overcome the siege of the single layer from water molecules and scattered single layer of montmorillonite gathered again. However, the distance of interlayer was much bigger than the original (1 nm) and the rules were not spelled out. After adding the pyrrole, the polymerization reaction would be happened in the place of Fe^{3+} ion. This process was shown in Fig. 9.

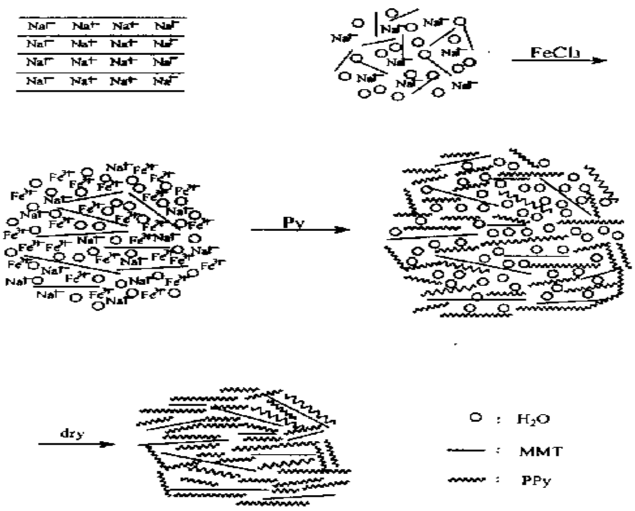

Fig. 9. Model of composites pricess between polypyrrole and montmorillonite

Properties of polypyrrole/montmorillonite and factors which affect on conductivity

Effect of temperature and reaction time on the conductivity of polypyrrole/montmorillonite: As experimental phenomena showed the lower temperature and the slower rate of reaction. Under the low-temperature (0 ºC) conditions, the colour of polymerization system had changed slowly, from yellow to light green, then to dark green, at last to black, this processes had continued for about 15 min.

At room temperature, the colour of system had changed more obviously and the process of change was in a very short time, it was about three minutes. At 45 ºC, the system would be the colour of black immediately. Figs. 10-12, respectively showed the curve of the relationship between reaction time and the conductivity at different reaction temperature and the conductivity curve. Fig.10 showed that the conductivity of composite materials had even achieved 50.00 S/cm at 0 ºC, when the reaction lasted for 15 h. When using the same reaction time, the maximum value of conductivity was 40 S/cm at room temperature in Fig. 11. In Fig. 12, the reaction time only needed 8 h, when the value of conductivity had achieve maximum at 45 ºC, but its conductivity was only 16.9 S/cm. Obviously the lower the temperature, the longer time achieving maximum conductivity for the polypyrrole/montmorillonite. The reason may be that the low temperature could cause the result of higher average degree of polymerization, the state of molecular chain could help the carrier's transmission which indicated more conducive. Mean while for the gradually polymerization reaction, the molecular increased gradually with the extension of reaction time. But when the reaction time continued, polypyrrole could happen excessive oxidation, the conjugate structure of the molecular were destroyed and the conductivity declined instead.

Effect of montmorillonite's content on the conductivity of composite materials: Although montmorillonite is a kind of insulation material and much resistance. We could make full use of the lamellar structure of montmorillonite to obtain higher conductivity of the composite material though complex between polypyrrole and montmorillonite. Fig. 13 showed the ralationship of amount of montmorillonite and conductivity.

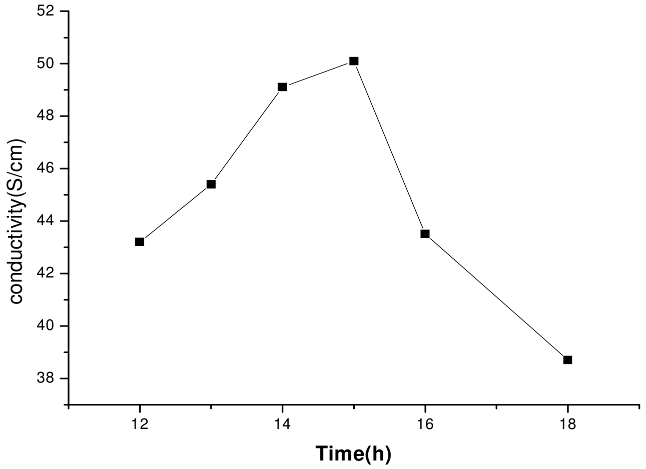

Fig. 10. Influence of reaction time to the conductivity of polypyrrole/montmorillonite prepared at 0 ºC

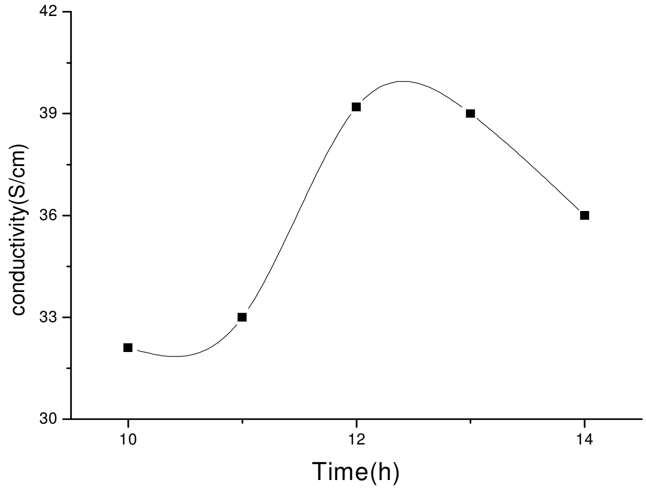

Fig. 11. Influence of reaction time to the conductivity of polypyrrole/montmorillonite prepared at 20 ºC

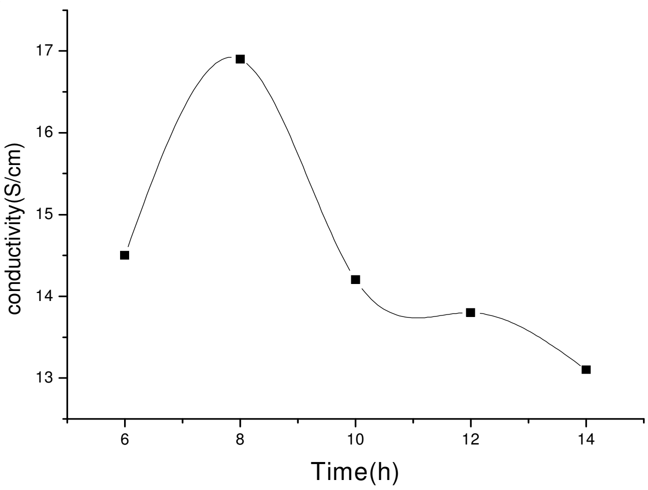

Fig. 12. Influence of reaction time to the conductivity of polypyrrole/montmorillonite prepared at 45 ºC

Fig. 13 showed that the conductivity of complex increased with the increasing of the content of montmorillonite, which had gradually declined when up to the maximum. When the amount of montmorillonite was less than 0.4 g/mL pyrrole. The conductivity of composite increased with the increasing of montmorillonite. With the increase of the content of montmorillonite, the limiting of montmorillonite layer to chain arrangement of polypyrrole had been gradually obvious, which could make the arrangement of polymer chain become more regular and the unimpeded access helped the transmission of carrier. However, when the amount of montmorillonite was more than 0.4 g/mL pyrrole, the composite will showed the performance of insulation and blocked the pathway of conductive polymer, resulting the lower conductivity of composite material.

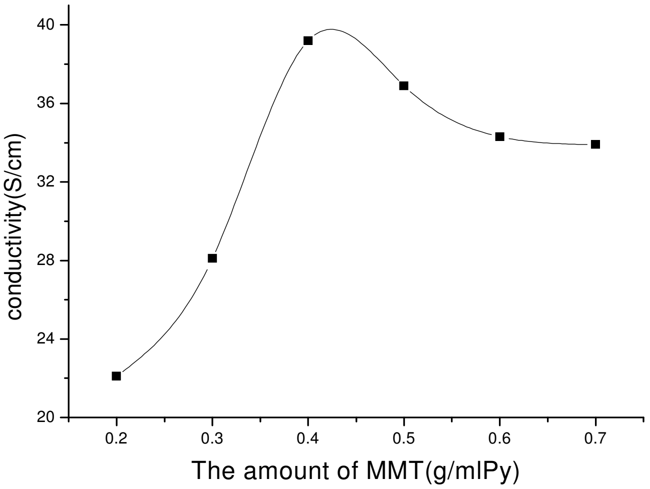

Fig. 13. Influence of the usage of montmorillonite to the conductivity of polypyrrole/montmorillonite

Effect of oxidant contents on the conductivity of composite materials: $FeCl_3 \cdot 6H_2O$ had acted as both oxidant and dopant in the reaction system, the dosage of which had been of a significant impact on the conductivity of composite. Fig. 14 is the ralationship curves of the amount of oxidant and conductivity.

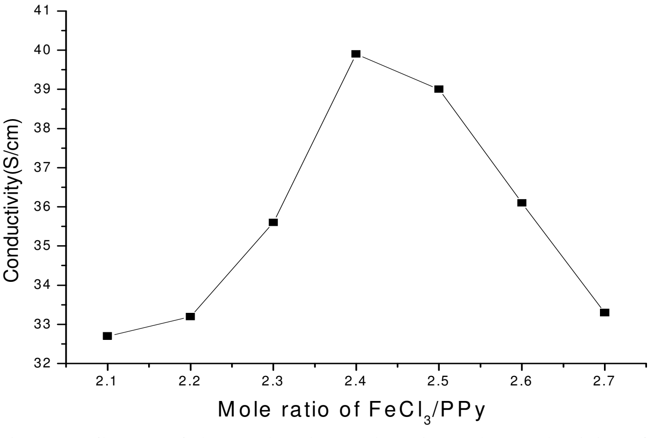

Fig. 14. Influence of the $FeCl_3$/polypyrrole ratio to the conductivity of polypyrrole/montmorillonite

Fig. 14 showed that first of all the conductivity was in the trend of upward and followed in the downward trend with the increasing of the amount of oxidants. When the mole ratio of $FeCl_3$/polypyrrole was 2.4, the amount of ferric chloride was the best and the conductivity of composite could achieve the maximum. When the value was less than 2.4, the role of dopant was more obvious. $FeCl_3$, as a P-type of doping agent in doping/reaction process, had been the electron acceptor, which pulled out of the electronic from the polymer π bonds to formate carrier like radical ions, ion-hole and so on. This would change the energy of π electronic band, so that reduced barriers to facilitate formation of conductive pathway and increased the conductivity. When the ratio of $FeCl_3$/polypyrrole was greater than 2.4, ferric chloride had a relatively high concentration. According to Nernst equation, the high oxidation potential could make polypyrrole deeply oxidate and the conjugate structure of polymers chain was destroyed conductive pathway blocked in the end, the conductivity changed to worse.

Effect of dopant's type and amount on the conductivity of the composite: Dopant was the main mean of enhancing the conductivity of polymer, the right anionic of which could balance the distribution of anionic polymer chain so as to enhance their conductive properties. Both the volume and body plot of dopant could directly affect the polarity of polymer chain migration and the aggregation state and affected the conductivity in turn. In this paper, the high potassium chlorate ($KClO_3$), *p*-toluene sulfonate and benzene sulfonate (BSNa) were used as dopant, their results of influence on the conductivity is shown in Table-2.

TABLE-2
INFLUENCE OF DOPING AGENT TO THE CONDUCTIVITY OF POLYPYRROLE/MONTMORILLONITE

Types of dopant	Potassium chlorate	*p*-Toluene sulfonate	Sodium benzene sulfonate
Conductivity (S/cm)	15.62	28.54	30.56

It was clearly that benzene sulfonate as a dopant had the best results. So we chose benzene sulfonate to further research on the relation of its amount and conductivity. Fig. 15 showed that relation of the amount of sodium benzene sulfonate (BSNa) and conductivity of composite. It indicated that composite has the highest conductivity when the amount of sodium benzene sulfonate was 3.4 g. According to the experimental results, it was surmized that dopants as a pair of anions in the composite had not only affected the flow of conductive pathway but also affected a fine structure of polymer chain, which also refered the aggregation of polymer chain.

When the usage of sodium benzene sulfonate was below 4.4 g, benzene sulfonate- as right anionic had a major influence on the electronic arrangement of polymer molecular chain, which constituted a conductive pathway and the macromolecular chains formed between arrays enable the molecular chains of polypyrrole had a better deposition, making up for the defects in the chain of insulation. This indicatived the performance of conductive rate is rising on the macro. When the amount of sodium benzene sulfonate was higher than 4.4 g, the array of benzene sulfonate- had further expanded, electrostatic repulsion and spatial effects may make the molecular chain of polypyrrole mutually separate, then the electronic of molecular chain blocked, following by the more complete conductive pathway destruction, so the conductivity dropped dramatically.

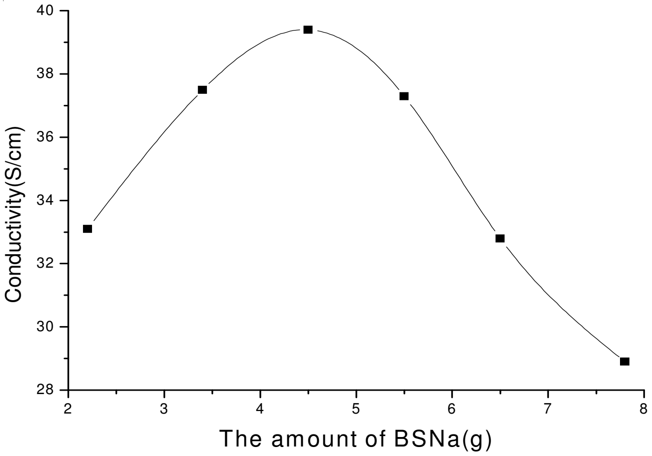

Fig. 15. Influence of the sodium benzene sulfonate (BSNa) on the conductivity

Conclusion

We had successfully prepared polypyrrole/montmorillonite conducting composites by oxidative polymerization in water medium with $FeCl_3·6H_2O$ as dopant. The results showed that when the reaction lasted for 15 h in the ice bath, the amount of montmorillonite was 0.4 g/mL pyrrole, $FeCl_3·6H_2O$ was 9.1 g/mL pyrrole. The dopant sodium benzene sulfonate was 4.4 g/mL pyrrole, the composite had the largest conductivity up to 56 S/cm. According to FT-IR, it showed that it did exist polypyrrole and montmorillonite in polypyrrole/montmorillonite composite system.

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