

ANALYSIS AND CHARACTERIZATION OF MICROSCOPIC MORPHOLOGY AND ORIENTATION STRUCTURE OF POLYANILINE POLYMERIZED IN A CONSTANT MAGNETIC FIELD*

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Abstract Conductive polyaniline (PAn-M and PAn-O) doped with dodecylbenzene sulfonic acid (DBSA) was synthesized by using emulsion polymerization method in the presence of a constant magnetic field (0.4 T) and the absence of magnetic field, respectively. The effects of magnetic field on the microscopic morphology and orientation structure of PAn were generally analyzed and characterized by using transmission electron microscope (TEM), X-ray diffraction (XRD) and through the conductivity anisotropy of unit resistance of the PAn/PVA(polyvinyl alcohol) composite film. The results showed that, compared with PAn-O, PAn-M had higher crystallinity and more obvious microscopic orientation structure: its particles were arranged orderly and piled into many banded aggregates with a certain length/diameter ratio, after magnetization treatment, it demonstrated a high degree of consistent orientation; PAn-M/PVA composite films showed conductivity anisotropy after magnetization in the film-forming process. The results all fully confirmed that PAn prepared in a magnetic field condition had a high degree of orientation.

Keywords: Polyaniline; Magnetic field; Orientation microstructure; Anisotropic conductivity.

INTRODUCTION

As one of the most promising commercial conductive polymers, polyaniline (PAn) has caused extensive public concerns^[1, 2]. The magnetic field effect has a marked impact on free radical polymerization^[3]; therefore, the introduction of the magnetic field into PAn synthesis has become a hotspot^[4, 5]. According to literature data^[6], PAn prepared in the absence of magnetic field has equal probability in orientation of its molecular chains and grains. Whereas, in the presence of external magnetic field, because of PAn's diamagnetism, PAn has anisotropic diamagnetic susceptibility, which causes its internal structure unit to prefer to grow and arrange along a particular direction, namely to take certain degree of orientation, which makes the molecular chains aligned more orderly forming more regular structure; meanwhile, the material shows anisotropy in physical properties^[7]. Despite of its impact on PAn's micro-structure, such as the conjugated chain length, the regularity of the molecular chains and the aggregation state, *etc.*, the magnetic field affects PAn's macroscopic properties^[6, 8], such as the increase of PAn's conductivity, dissolution/dispersion ratio and pyrolysis temperature^[9, 10].

Current research on the impact of magnetic field on the aniline electrochemical polymerization and solution polymerization, and the product structure and properties, has achieved substantive results^[11, 12], and confirmed that the effects of the magnetic field have a positive correlation with reaction rate of aniline polymerization, the orientation of product molecules, the conductivity, the dissolution/dispersion and other macroscopic properties^[11–13]. But there has been rare report on systematic research of magnetic orientation of aniline emulsion polymerization and its products in the magnetic field. In this paper, based on PAn's synthesis by using

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emulsion method, a 0.4 T constant magnetic field was applied in the polymerization process to systematically explore the impact of magnetic field on PAn's microscopic morphology, orientation structure and properties.

EXPERIMENTAL

Raw Materials

The monomer aniline (reagent grade) was distilled to be colorless under reduced pressure prior to use. Ammonium peroxydisulphate (APS), dodecylbenzene sulfonic acid (DBSA), *m*-cresol, dimethylbenzene and other chemicals were reagent grades and used as-received without further treatment. The polyvinyl alcohol (PVA) had a purity of higher than 90.5%, with the average polymerization degree of about 1799.

Preparation of Doped PAn with DBSA

0.025 mol of aniline monomer and 80 mL of DBSA solution (0.156 mol/L) with a certain mole ratio were measured quantitatively and added to a three-necked flask, which was previously placed in the 0.4 T magnetic field (or no magnetic field) to adjust pH 2–3. 25 mL of xylene was added into the flask with stirring, until the system formed a uniform emulsion. Then, 20 mL of APS solution (1 mol/L) was added to the system slowly. Reaction took place at room temperature for 4 h. After the reaction was complete, polyaniline PAn-M prepared in the presence of magnetic field and polyaniline PAn-O prepared in the absence of magnetic field were obtained through demulsification, filtration, washing, drying and grinding.

Preparation and Magnetization of PAn/PVA Composite Film

0.2 g of PAn-M and 0.2 g of PAn-O were measured and fully mixed with 1.2 mL of 5% PVA hydrosol respectively in equal volume. 1 g of dispersion liquid was used to cast two parallel film plates respectively on the slides, with the same specification. One plate of each slide was placed in the 0.4 T constant magnetic field whose direction was parallel to the casting liquid surface (see Fig. 1); the other film plate was placed in non-magnetic environment; both were solidified at room temperature. All the resulted films' width, length and thickness were 25 mm, 75 mm and 0.5 mm, respectively.

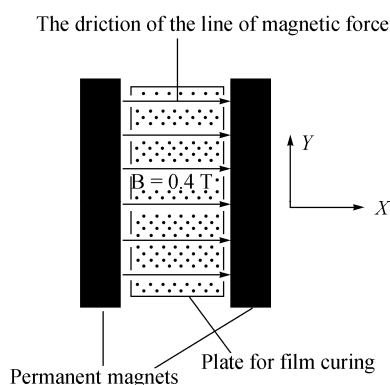


Fig. 1 The curing process of the PAn/PVA composite film in magnetic field

Determination of the Anisotropic Conductivity of PAn/PVA Composite Film

The resistance of the PAn/PVA composite film on its surface was measured by multimeter along a line parallel to the direction of magnetic field (*X* direction) and a line perpendicular to the direction of magnetic field (*Y* direction), respectively, with a pole distance of 1 cm.

Sample Preparation for TEM

Embedding: PAn-M and PAn-O was mixed respectively with epoxy resin uniformly, either sample was injected into two moulds.

Magnetization: During the solidification process, one mould was placed in the 0.4 T magnetic field for magnetization, while the other underwent the solidification without magnetization. The embedded samples were kept on standby.

Measurement by XRD

XRD 6000 using CuK α radiation of wavelength 0.154 nm and continuous scan speed of 0.045 ($^{\circ}$) min $^{-1}$.

RESULTS AND DISCUSSION

Effects of Magnetic Field on the Microscopic Morphology and Orientation Structure of PAN

Figure 2 shows the TEM maps of PAN-M and PAN-O after embedding treatment in the presence and absence of magnetic field. From Fig. 2 we can see that, there is great distinction in microscopic morphology and structure of PAN-M and PAN-O. For PAN-M (Figs. 2a, 2b), its particles are arranged in an orderly manner, becoming banded aggregates with a certain length / diameter ratio, suggesting that PAN-M has obtained an obvious microscopic orientation. Because the polymerization in the magnetic field had greatly enhanced the anisotropic diamagnetic susceptibility of PAN-M particles^[6, 14], leading to an obvious differentiation in the characteristics of response to magnetic field in different directions (there was an internal net magnetic moment which has a certain direction)^[15], and thus greatly enhancing the orientation when particles aggregate. By comparing (a) and (b) in Fig. 2, we can see that the banded aggregates of PAN-M embedded without magnetization (Fig. 2b) lack consistency in the extension direction, while those of PAN-M embedded with magnetization (Fig. 2a) show a high degree of orientation consistency. Because the particles with strong anisotropic diamagnetic susceptibility and the banded aggregate units in PAN-M have undergone a consistent rotation or rearrangement under the impact of magnetic field in the embedding process^[6, 14]. In addition, in the process of aniline polymerization, the stretch and orientation effects of magnetic field^[16, 17] caused prior arrangement and growth of molecular chains, chain segments, crystal and micro-fiber in a certain direction, and extended conformation of molecules, *etc.*, which were the internal factors leading to orientation consistency.

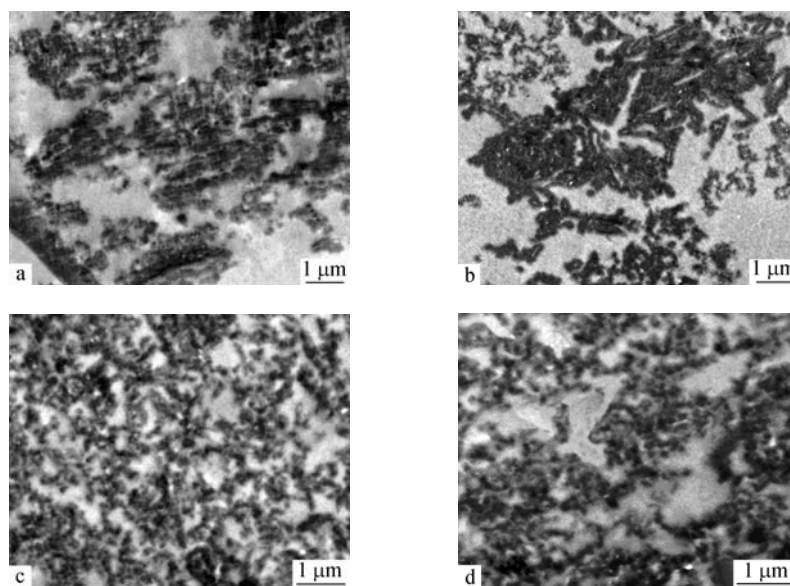


Fig. 2 TEM images of PAN-M and PAN-O
a) PAN-M embedding with magnetization; b) PAN-M embedding without magnetization;
c) PAN-O embedding with magnetization; d) PAN-O embedding without magnetization

For PAN-O (Figs. 2c, 2d), its particles disorderly piled with each other. It has no obvious micro-orientation, and its anisotropic diamagnetic susceptibility is weak. Therefore, no matter it underwent the embedding processing with magnetization or not, its particles show a discrete and disorderly arrangement and distribution.

Anisotropic Conductivity of PAn/PVA Composite Films

Figure 3 shows the test results of unit resistance of different PAn/PVA composite films formed with and without magnetization.

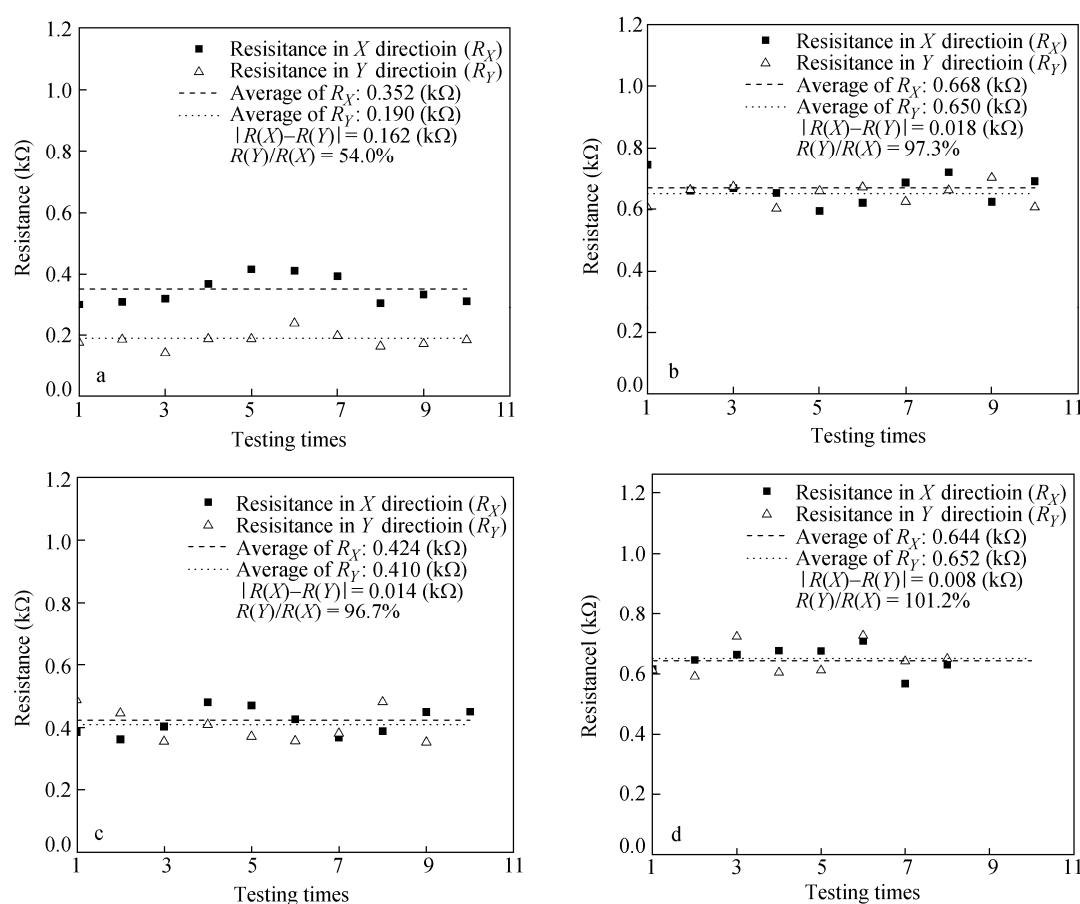


Fig. 3 Effect of forming condition on the unit resistance of the PAn/PVA composite films

- a) PAn-M/PVA film, cured in magnetic field (0.4 T); b) PAn-O/PVA film, cured in magnetic field (0.4 T);
c) PAn-M/PVA film, cured without magnetic field; d) PAn-O/PVA film, cured without magnetic field

From Fig. 3(a) we can see that after film-forming under magnetization, PAn-M/PVA had obvious anisotropy in its unit resistance: the unit resistance in Y direction (0.190 kΩ) was obviously lower than that in X direction (0.352 kΩ). Because PAn-M in the composite film has strong anisotropic diamagnetic susceptibility, it may result in the formation of many banded aggregate units with a large length/diameter ratio. After magnetization, these aggregate units underwent rotation or rearrangement and achieved a high degree of orientation, leading to obvious conductivity anisotropy of PAn-M/PVA composite films formed under magnetization. For the orientation occurred in Y direction^[6, 11], the conductivity in Y-axis direction is higher to that in X-axis direction. For PAn-O/PVA composite film formed under magnetization, and PAn-M/PVA and PAn-O/PVA composite films formed through conventional film-forming process, no significant difference was found in unit resistance along X and Y directions in the same composite film (see Figs. 3b, 3c, 3d), indicating that the conductivity of these films is isotropic (with the same reasons as mentioned in the morphology section).

XRD Analysis

Figure 4 gives the XRD patterns of PAn-M and PAn-O. From the curves, we know that they have similar spectrum, both with an apparent wide diffraction peak at $2\theta = 20^\circ, 25^\circ$, indicating that PAn samples synthesized in the laboratory are all crystalline PAn samples with partial crystallization^[18, 19], similar to the results of MacDiarmid *et al*^[20].

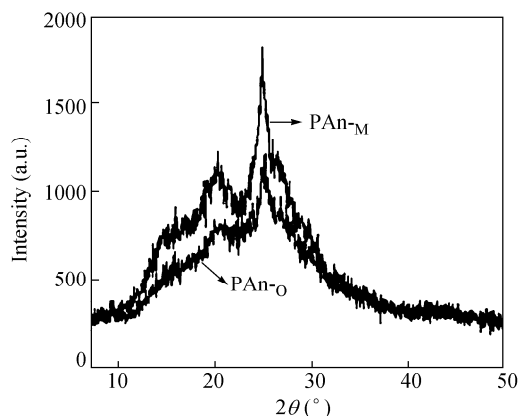


Fig. 4 X-ray diffraction pattern of PAn-M and PAn-O

From Fig. 4, we can see that the peak intensity of PAn-M is significantly higher than that of PAn-O, also with wider width. According to the relationship between the approximate degree of crystallinity and the diffraction peak area in the literature^[21], it can be conferred that the regularity and crystallinity of PAn-M molecular chains are higher than those of PAn-O, because PAn-M has obvious microscopic orientation, and its molecular chain prefers arrangement in a certain direction and extended conformation, leading to the enhancement of the regularity and symmetry of PAn-M samples, and eventually to the improvement in crystalline material performance.

CONCLUSIONS

Because of the anisotropy of diamagnetic susceptibility, the polyaniline polymerized in the magnetic field has obvious microscopic orientation structure, consequently, samples show distinct magneto-orientation during post-treatment process. Meanwhile, due to the existence of microscopic orientation, crystallization is markedly improved.

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