폴리아닐린의 형태학

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Morphology of Polyaniline

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요 약 : 전기화학적으로 합성한 폴리아닐린의 형태학을 전자현미경으로 연구하였다. 폴리아닐린 필름의 용액쪽 표면은 굵기가 약 0.1-0.2μm인 섬유소와 그 표면을 덮고 있는 무정형의 올리고머로 구성되어 있다는 것이 관찰되었다. 한편, 전극에 접한 면은 굵기가 약 0.3-0.5μm인 섬유소로 구성되어 있었다. 아세톤이나 DMF에 대한 이러한 여러가지 형태의 폴리아닐린의 용해도는 다음의 순서로 감소하였다. : 무정형>가는섬유소>굵은 섬유소. 분자량은 이와 반대의 순서로 감소하는 것으로 믿어진다. 폴리아닐린의 분해반응은 개시반응 및 중합반응과 경쟁적으로 일어나므로, 걸어준 전위가 0.9V(SCE 기준) 보다 높고 단위체의 농도가 충분히 높지 않으면 분해반응이 지배적으로 일어났다. 그러나 단위체의 농도가 충분히 높으면, 중합 및 개시반응이 더 잘 일어났다. 이것이 순환 전위 하에서 합성한 폴리아닐린 필름이 일정 전위하에서 합성한 것보다 더 좋은 물성을 갖는 이유이다. 걸어준 전위가 0.75V보다 낮은 경우에는 분해반응이나 중합반응 모두가 잘 일어나지 않았다.

Abstract : The morphology of polyaniline film synthesized electrochemically was studied by means of scanning electron microscopy. It was observed that the solution side of the polyaniline film was composed of fibrils of approximately 0.1-0.2μm thick and amorphous oligomers coated on the fibrils. On the other hand, the electrode side of the polyaniline film was composed of fibrils of approximately 0.3-0.5μm thick. The solubility of these various types of polyaniline in acetone or DMF decreased in the following order : amorphous phase> thin fibrils>thick fibrils. It is believed that the molecular weight decreases in the opposite order. The degradation reaction of polyaniline occurred competitively with the initiation and polymerization reactions . Thus, when the applied potential was higher than 0.9V(vs. SCE) and the concentration of the monomer was not high enough, the degradation reaction was predominant. However, when the monomer concentration was high enough, polymerization and initiation occurred preferentially. This is the reason why polyaniline film of better quality is obtained under a cyclic potential than under a constant potential. When the

applied potential was lower than 0.75V, neither the degradation nor the polymerization was significant.

INTRODUCTION

It is generally understood that the morphology of conductive polymers is closely related to the electrical conductivity of potymers.[1] It has been known that polyacetylene film synthesized by Shirakawa method[2] is composed of fibrils of approximately 0.02μm thick.[1,3] On the other hand, polypyrrole film synthesized electrochemically does not show such a fibrillar structure[4] and polythiophene is known to have globular morphology.[5] It has also been known that electrochemically synthesized polyaniline has fibrillar structure.[6] According to Paul, Rizzo, and Wrighton,[7] the morphology of |electrochemically synthesized polyaniline changes with the thickness of the film. Some researchers[8~10] have reported that polyaniline synthesized under a cyclic potential gives film of better material-properties than that synthesized under a constant potential, namely at 0.9V(vs. SCE). Polyaniline is subject to degradation in aqueous solution. Park and Stilwell[11,12] have studied the degradation reaction electrochemicaly as well as spectroscopically. Still, it is not fully understood how the degradation reaction of polyaniline affects the morphology of the film. The purpose of this work is to investigate how the fibrillar structure of polyaniline changes with the conditions of polymerization and to relate such morphological properties to the other physical properties of polyaniline.

EXPERIMENTAL

In the electrochemical synthesis of polyaniline, commercially available aniline was used after vacuum distillation. N, N-dimethyl formamide (DMF) was used after purification according to Perrin et al.[13]. Reagent grade acetone was used without further purification.

Electrochemical synthesis of polyaniline was performed in a three-electrode cell. A saturated calomel electrode(SCE) was used as the reference electrode, platinum wire as the counter electrode, and platinum plate as the working electrode. Electrochemical experiments were carried out with a potentiostat(AMEL Model 553) and a cyclic voltammetric system(BAS CV-IB). Polyaniline film was prepared by electrolysis of a monomer solution under a cyclic potential between -0.20 to 1.0V (vs. SCE). The monomer solution contained 0.1M of aniline hydrochloride and 1 M of hydrochloric acid. Dark green color of polyaniline film was coated on the platinum plate-electrode. Then the polyaniline film on the Pt electrode was washed with water and kept at a desired constant potential in an electrolyte solution without any monomer until the current dropped almost to zero level, which took about 15 minutes. The pH of the electrolyte solution was controlled with hydrochloric acid.

The polyaniline film was washed with water, acetone, or with DMF followed by drying in a vacuum oven for several hours at 50℃. Then the polyaniline film was carefully peeled off with a razor blade. Scanning electron micrographs were taken with a scanning electron microscope (International Scientific Instruments, SX-32).

RESULTS AND DISCUSSION

Scanning electron micrographs (SEM) of polyaniline film synthesized electochemically in 1M HCl under a cyclic potential between -0. 20 and 1.0V(vs. SCE) are shown in Fig. 1. The solution side and the electrode side of the polyaniline film which has been washed with water after the electrochemical synthesis are shown in Fig. 1(a) and (b), respectively. It can be clearly seen that the solution side of the film is composed of fibrils which are coated with oligomeric material. The diameters of the fibrils are approximately
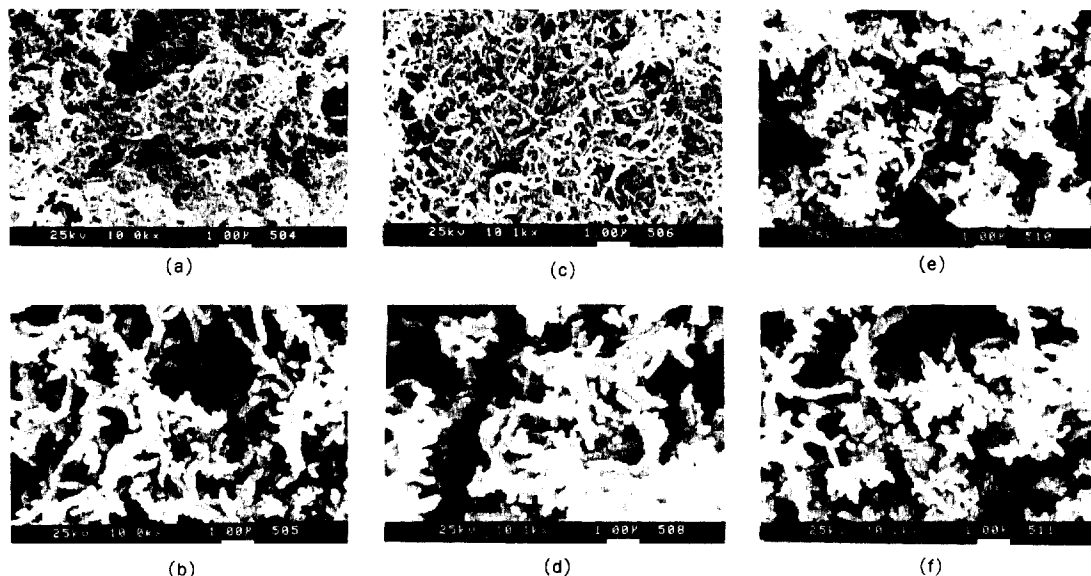
Won-Suk Nam, Myung-Ki Baek, Jung-Il Jin, and Hoosung Lee

Fig. 1. Scanning electron micrograph of polyaniline film synthesized electrochemically in 1M HCl under a cyclic potential between -0.2 and 1.0 V(vs. SCE). (a) the solution side, washed with water : (b) the electrode side, washed with water : (c) the solution side, washed with acetone : (d) the electrode side, washed with acetone : (e) the solution side, washed with DMF : (f) the electrode side, washed with DMF.

0.1μm. On the other hand the electrode side of the film is composed of fibrils of approximately 0.3μm thick.

The solution side and the electrode side of polyaniline film which has been washed with acetone after the electrochemical synthesis are shown in Fig. 1(c) and (d), respectively. No significant difference can be found between the SEM's of the film washed with water and washed with acetone. However, it appears that, by washing with acetone, part of the oligomeric material has been removed revealing more of the fibrillar structure. In fact, when washing with acetone, it was visible that some species composing the film are soluble. The solution side and the electrode side of polyaniline film which has been washed with DMF after the electrochemical synthesis are shown in Fig. 1(e) and (f), respectively. It can be clearly seen that, by washing with DMF, almost all the oligomeric material has disappeared. The SEM photographs of both sides

show alomst the same structure with fibrils of almost the same thickness. Actually, it was observed that more material is soluble in DMF than in acetone. This indicates that DMF is a better solvent of polyaniline than acetone. It has been also found that the oligomeric substance is more soluble than the fibrils and the thinner fibrils are more soluble than the thicker fibrils. Therefore, it is reasonable to conclude that the molecular weight increases in the following order : oligomer 〈thin fibril〈thick fibril.

A cyclic voltammogram (CV) of polyaniline in 1 M HCl without any aniline, the monomer, is shown in Fig. 2. The area enclosed by each cycle is proportional to the amount of charge required to oxidize and reduce the polyaniline film coated on the electrode. Therefore, it should be also proportional to the amount of polyaniline coated on the electrode. The area enclosed by the CV curve in Fig. 2 decreased as the potential cycle was repeated. This is an indication that,
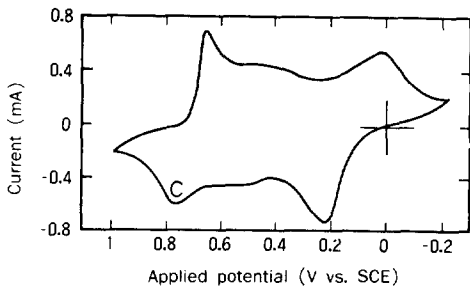
Fig. 2. Cyclic voltammogram of polyaniline in
1M HCl.

when no monomer is available, polyaniline decomposes gradually.

It was observed that, under such circumstances, when the cyclic potential applied on the polyaniline electrode passed beyond 0.75 V(vs. SCE), which is the peak potential of peak C in Fig. 2, degradation of polyaniline became significant. The polyaniline film shown in Fig. 3 has been kept in the electrolytic solution without any monomer under a cyclic potential between -0.2 and 1.0 V. One can readily recognize that the microfibrils in Fig. 3 are severely corroded indicating that degradation reaction has been occurring. However, when the potential was cycled between -0.2 and 0.75V (vs. SCE), no evidence of degradation was visible.

Such phenomena are demonstrated more clearly in Fig. 4 and Fig. 5. The polyaniline films shown in Fig. 4 and Fig. 5 were first electrochemically synthesized under the cyclic potential as described in the experimental section. Then, the electrode was kept in the same solution for about 15 minutes at 0.90V (Fig. 4. and at 0.75V (Fig. 5), respectively.

The solution side (Fig. 4a) shows the fibrils as well as the oligomeric substance. The oligomeric substance is believed to be the lower molecular weight products which just began to polymerize from the monomers. The electrode side(Fig. 4b) shows the fibrils with some degree of deterioration. It is considered that, on the solution side where the supply of monomers was sufficient, polymerizaticn occurred preferentially. On the other hand, on the electrode side where the supply
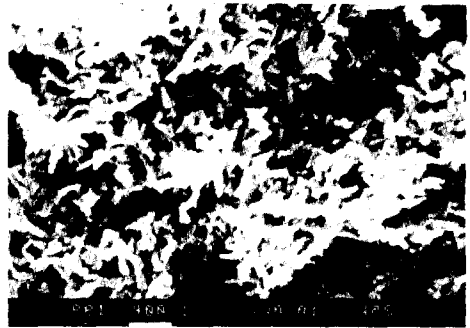

(a)
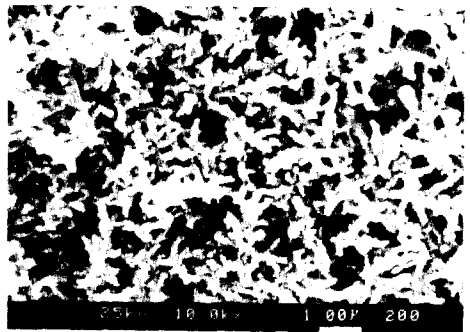
(b)

Fig. 3. Scanning electron micrograph of polyaniline film the potential of which was cycled between -0.2 and 1.0V (vs. SCE) in 1 M HCl without any monomer. (a) the solution side, washed with water : (b) the electrode side, washed with water.

of the monomers was defficient, degradation of polyaniline would have been prefered. This result confirms that the degradation and polymerization reactions occur competitively.[11,12] However, when the polyaniline film was kept at 0.75V instead of 0.9V, neither the degradation nor the polymerization occurred significantly.However, judging from the disappearance of the oligomeric substance, it is believed that, at 0.75V, the oligomers react to form higher molecular weight species. This time the thickness of the fibrils on both sides of the film are thicker than those shown in Fig. 1, i.e. the solution side (Fig. 5a) of the film is mostly composed of thin fibrils of about 0.2μm

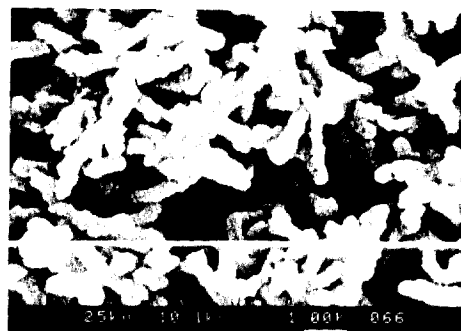Won-Suk Nam, Myung-Ki Baek, Jung-Il Jin, and Hoosung Lee
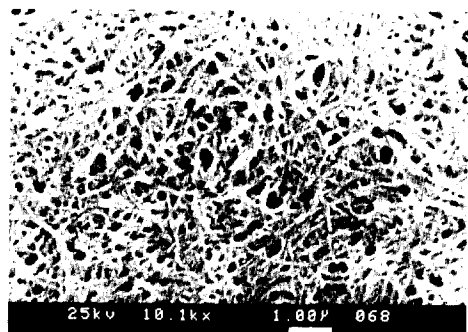
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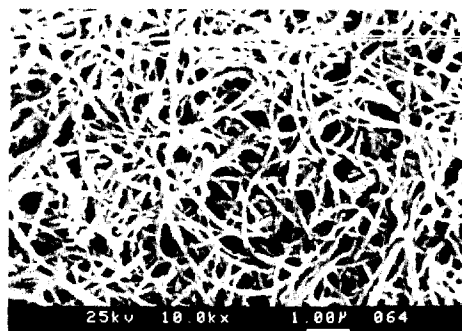
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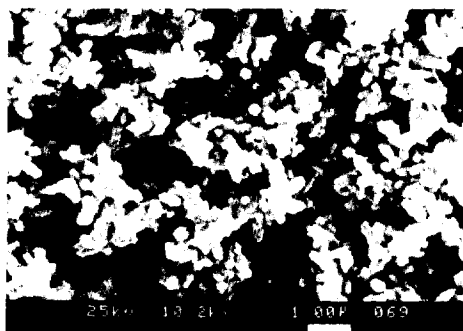
(b)

(b)

Fig. 4. The scanning electron micrograph of polyaniline electrode which was kept at 0.9V (vs. SCE) for about 15 minutes. (a) the solution side, washed with acetone : (b) the electrode side, washed with acetone.

Fig. 5. The scanning electron micrograph of polyaniline electrode which was kept at 0.75V (vs. SCE) for about 15 minutes. (a) the solution side, washed with acetone : (b) the electrode side, washed with acetone.

thick and not much of the oligomeric substance can be seen and the electrode side (Fig. 5b) of the film shows thick fibrils of about 0.5μm in diameter without any evidence for degradation. This is an indication that at 0.75 V newly initiated polymerization did not occur on either side of the film.

These observations may explain the fact that the polyaniline film obtained under the cyclic potential between -0.2 and 1.0V(vs. SCE) has better quality than the film obtained at a constant potential of 1.0 V(vs. SCE). At a high and constant potential, the monomers would have almost no chance to diffuse closer to the elecrode side resuling in depletion of monomer concentration

and leading to degradation of the polymer in that part of the film. However, with the cyclic potential, while the potential stays higher than 0.75V, polymerization as well as initiation of new polymer chain can occur. Before the concentration of the monomers is depleted almost to zero, the potential would return back to a level below which no polymerization can occur. During this period of the cycle, the monomers can diffuse into the inner layer of the polyaniline film. By the time the potential recovered to a high enough level for polymerization, sufficient number of monomer molecules would diffuse into the inner layer of the film raising the concentration of the monomer to a level high enough to prevent

the degradation reaction. Therefore, the polyaniline film obtained under a constant potential around 1.0V would have fibrils with defects due to the degradation reaction. As a result, polyaniline film of better qualitty is obtained under a cyclic potential than under a constant poential.

In conclusion, the solution side of the electrochemically polymersized polyaniline film was composed of fibrils of approximately 0.1-0.2μm thick and amorphous oligomers coated on the fibrils. On the other hand,the electrode side of the polyaniline film is composed of fibrils of approximately 0.3-0.5μm thick. The solubility of these various types of polyaniline decreased in the following order : amorphous phase>thin fibrils>thick fibrils. It is believed that the molecular weight decreases in the opposite order. The degradation reaction of polyanline occurs competitively with the initiation and polymerization reactions. Thus, when the applied potential is higher than 0.9V (vs. SCE) and the concentration of the monomer is not high enough, the decomposition reaction is predominant. However, when the monomer concentration is high enough, polymerization and intiation occurs preferentially. This is the reason why polyaniline film of better quality is obtained under a cyclic potential than under a constant potential. When the applied potential is lower than 0.75V, neither the degradation nor the polymerization was significant.

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