Physico-chemical Structure Change of $FeCl_3$ by Heat Treatment of PAN-$FeCl_3$ Hybrid Nanocomposite Film

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PAN-$FeCl_3$ 하이브리드 나노복합필름의 열처리에 의한 $FeCl_3$의 물리화학적 구조변화연구

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1. Introduction

Polyacrylonitrile (PAN)-metal (or metallic salt) hybrid composite system has received considerable attention due to the possibilities as electronic materials[1] and precursors of new carbon materials[2].

Some results have been suggested for the stabilized structure of PAN-$CoCl_2$, PAN-$NiCl_2$ and PAN-CuX_2 complexes[2,3], but the detailed stabilization mechanism has neither been studied, nor was the role of metals (or metallic salts) in the development of hyperstructure of PAN-$CoCl_2$, PAN-$NiCl_2$ and PAN-CuX_2 complexes during carbonization.

In our previous work[4], we have reported that, by the foramtion of PAN/$FeCl_3$ hybrid nanocomposite, the crystal system of $FeCl_3$ changes from hexagonal to triclinic due to the pre-coordination of DMF molecules via which PAN molecule and metallic salt interact electrostatically. By this way, PAN molecules locate at the center of the triclinic unit cell so that the dipole-dipole interaction between nitrile groups of the inserted PAN chain is controlled by the coordinated DMF molecules. It was suggested that PAN with this kind of rather controlled hyperstructure may possibly exhibit different physico-chemical behavior, for example, in thermal stabilization process during the manufacture of carbon fibers (see Scheme 1).

On the basis of the foregoing results, this study aims at examining the physico-chemical structure change of $FeCl_3$ by heat treatment with a view to elucidating the role of $FeCl_3$ in the evolution of the hyperstructure of PAN-$FeCl_3$ hybrid nanocomposite during carbonization process.

2. Experimental

PAN powder that has been widely used for the commercial manufacture of acrylic fibers was supplied by Hanil Synthetic Fibers (Korea) and used without any further treatment. PAN consisted of acrylonitrile (AN) of 90.7 wt%, methylacrylate (MA) of 8.8 wt% and sodium methallylmethylsulfonate (SMMS) of 0.5 wt%. Ferric chloride (97%, Fluka, USA) and dimethylformamide (DMF, 99%, Daejong, Korea) were used without purification.

To make a hybrid nanocomposite film, ferric chloride of 0.283 g was completely dissolved in dimethylformamide (DMF) of 1.8 g and then was added PAN powder of 0.2 g. After thorough dissolution, the solution was cast to a film on a glass plate and vacuum-dried at 55 °C for 48 h in order to expel solvent molecules as completely as possible. The finally obtained hybrid nanocomposite film (coded PAN-h-$FeCl_3$) was of the thickness of 50-70m. For the purpose of comparison, the control samples of virgin PAN and ferric chloride were also prepared by dissolving them in DMF and drying in a vacuum (coded control PAN and cd-$FeCl_3$). Since ferric chloride is very hygroscopic, the film was prepared just prior to the structural characterization and kept the moisture content as low as possible throughout the whole experiments.

PAN-h-$FeCl_3$ and cd-$FeCl_3$ were heat treated at a specified temperature ranging from 500°C to 1000°C. X-ray diffractograms were recorded using Ni-filtered CuKα radiation with the scan rate of 5°/min on MXP18X-MF22-SRA diffractometer (Mac/Science, Japan) operating at 50kV and 100mA. Morphology was examined by FE-SEM (JSM 6330F, JEOL, Japan) operating at 10kV and 12μA.

3. Results and Discussion

The typical X-ray diffractogram of virgin $FeCl_3$ (hexagonal) was shown in Fig. 1(a). When $FeCl_3$ was recystallzed from DMF solution, it showed a completely different diffractogram as shown in Fig. 1(b), which may be attributed to the formation of $FeCl_3 \cdot$ 3DMF complexes[5,6]. This complex structure remained intact up to 300℃ meanwhile PAN underwent the reactions of cyclization and dehydrogenation and DMF molecules decomposed gradually with increasing temperature.

However, $FeCl_3 \cdot$ 3DMF complexes decomposed completely to form iron(III) oxide (Fe_2O_3) in the matrix of carbonized PAN at 500℃. At even higher temperature of 1000℃, Fe_2O_3 was changed to iron carbide (Fe_3C-cementite) as shown in Fig. 2(a), which may possibly be due to the reaction between Fe_2O_3 and the carbonized PAN matrix. It is believed that the iron carbide may catalyze the graphitization of the carbonized PAN matrix of non-graphitic character. Indeed, the transformation of iron carbide to graphite (graphitization) has been observed during isothermal annealing in the temperature range of 560～680℃ for 20～500h[7].

PAN is an intrinsic hard carbon, i.e. carbon that is difficult to be graphitized. However, Fig. 2(b) shows a sharp and strong peak at 2θ=26.5° due to the reflection of (002) planes and some more peaks at 41.9° , 43.8° , and 53.8° by the reflection of (100), (101), and (004) planes, respectively. From the foregoing results, it may be possible to draw a tentative conclusion that the ferric chroride coordinated with DMF molecules oxidizes with heat treatment to form Fe_2O_3 and at higher temperature reacts with the carbonized PAN to form Fe_3C which facilitated graphitization as shown in Scheme 2.

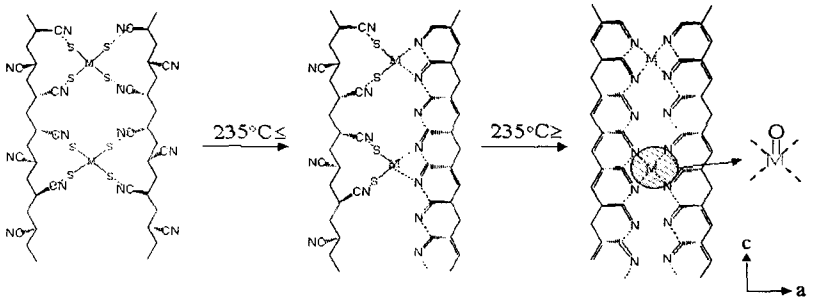
Fig 3 shows that, with the heat treatment of PAN-h-$FeCl_3$, iron carbide crystal tends to be formed at the film-surface, indicating that the iron oxide migrates from inside to the film-surface meanwhile some graphitization occurs at the interphase between iron carbide and the carbonized PAN matrix.

4. Conclusions

From this work, it was found that $FeCl_3$ plays very important roles in the development of hyperstructures of both the precursor and the carbonized PAN-h-$FeCl_3$ nanocomposite film. That is, in the precursor film, it is a kind of structure controlling angent and in the carbonized film, it is a kind of mediated catalyst to facilitate the graphitization of non-graphitic PAN.

5. Reference

1) C. Calber, M. Mertens, N. Baute, R. Jerome, V. Carlier, M. Sclavons, R. Legras, *J. Polym. Sci., Part B: Polym. Phys.* ***36***, 543(1998).
2) C. R. Wu, Liedberg, B. *Syn. Met.* ***26***, 21(1988).
3) Schurz, J. *J. Polym. Sci.* ***28***, 438(1958).
4) Y. J. Kim, C. R. Park, *Polymer Preprints*, ***41***, 452(2000).
5) J. Y. Johnson, G. W.J ohnson, British Patent 774,956(1957).
6) W. E.Bull, S. K. Madan, J. E. Willis, ***1***, 374(1962).
7) Z. Haiyan, C. Jun, H. Yanyang, X. Xinmin, P. Shaoqi, *Mater. Chem. Phys.* ***55***, 167(1998).



Scheme 1. Schematic stablized mechanism of PAN-h-$FeCl_3$.

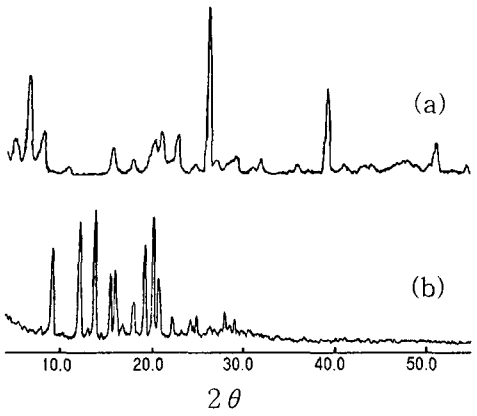


Figure 1. X-ray diffractograms of (a) $FeCl_3$ and (b) PAN-h-$FeCl_3$.

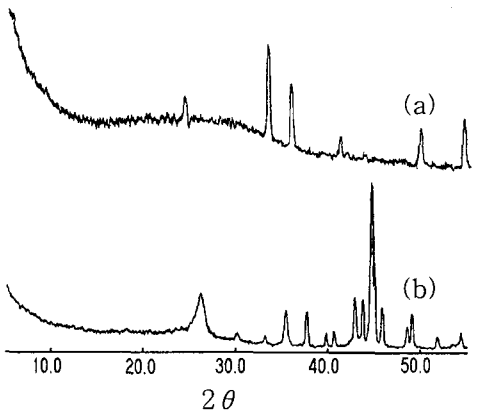


Figure 2. X-ray diffractograms of PAN-h-$FeCl_3$ (a) at 500℃ and (b) at 1000℃.

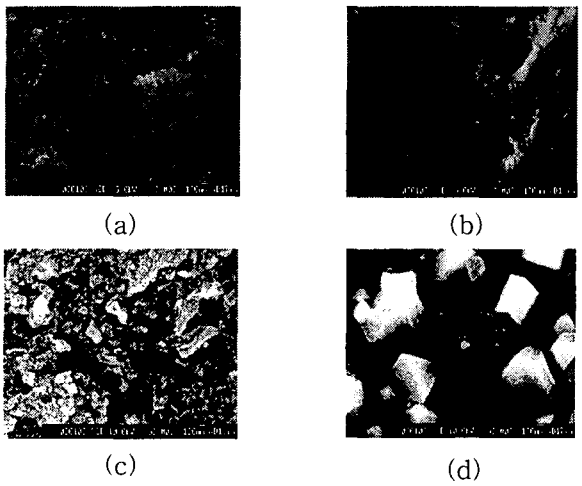
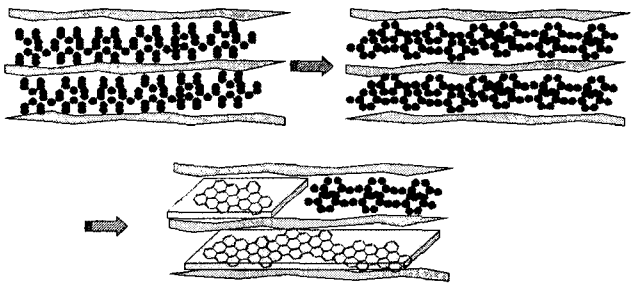


Figure 3. Scanning micrograms of (a) PAN(cross) (b) PAN(surface) (c) PAN-h-$FeCl_3$. at 1000℃(cross) and (d) PAN-h-$FeCl_3$ at 1000℃(surface).



Scheme 2. Schematic carbonization mechanism of PAN-h-$FeCl_3$.