



Beneficial effect of multi-wall carbon nanotubes on the graphitization of polyacrylonitrile (PAN) coating[#]

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Abstract

Polyacrylonitrile (PAN) solutions were deposited on quartz plates by spin coating to yield 2–3 μm thick PAN films. The films were decomposed at 1000°C in N_2 atmosphere into electrically conducting carbonaceous coatings. When the precursor solution contained cobalt (0.2 g Co-acetate per 1 g PAN) and/or multi-wall carbon nanotubes (MWCNTs, 2 mg MWCNT per 1 g PAN) the specific electrical resistance of the product film dropped from the original 492 $\Omega\cdot\text{cm}^{-1}$ value down to 46 $\Omega\cdot\text{cm}^{-1}$. By excluding all other possibilities we came to the conclusion that the beneficial effect of carbon nanotubes is related to their catalytic action in the final graphitization of condensed nitrogen-containing rings into graphitic nanocrystallites.

Keywords: PAN, carbon film, carbon nanotube, electrical conductivity

I. Introduction

Thin carbonaceous coatings have been studied intensively recently because they find important practical applications in two fields: (i) hard and tough diamond-like carbon tool coatings [1] and (ii) electrically conductive coatings applicable in e.g. electromagnetic shielding, or flat panel display technology [2]. Conductive carbonaceous coatings can be prepared by the high temperature carbonization of polymer precursor films like polyimide and its derivatives [3], phenol formaldehyde [4], poly(furfuryl alcohol) [5], poly(vinyl alcohol) [6] and polyacrylonitrile (PAN) and its derivatives [7,8].

The challenge in converting polymer layers into conductive coatings is to maximize graphitization without damaging the integrity of the film. It has been shown that transition metals improve the graphitization of polymer coatings in general [9] and that the final structural order in decomposed PAN films is particularly sensitive to the use of a suitable metal catalyst [10].

We demonstrated earlier that the electrical conductivity of a PAN film annealed at 1000°C in N_2 flow is proportional to the cobalt contents of the precursor PAN solution [11]. However, the viscosity of the polymer solution can also increase with the metal concentration [12]. Since increasing viscosity affects the applicability of the solution in spin coating adversely, there exists an upper limit for the electrical conductivity improvement achievable by metal addition only. In this contribution we investigate if it is possible to push this limit any further by mixing a small amount of multi-wall carbon nanotubes (MWCNTs) into the precursor.

II. Experimental

Commercial polyacrylonitrile fiber (ZOLTEK) and N,N-dimethyl-formamide (DMF, Scharlau Chemie S.A.) were used to prepare the PAN solutions. 1 g PAN was dissolved in 20 ml DMF and mixed with 0.2 g cobalt acetate (Reanal) and/or 2 mg multi-wall carbon nanotubes using an ultrasonic bath. The MWCNTs were prepared in house by catalytic chemical vapor deposition as described earlier [13]. 25×25 mm quartz substrate plates were cleaned with acetone and distilled

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water prior to spin coating them at 80 rps by PAN films to approx. 2–3 μm final thickness using a total amount of 30 droplets (approximately 50 mg) of the polymer solution. Spin-coating was followed by drying at 70°C for 120 minutes in air and then by heating to the final carbonization temperature (1000°C) in N_2 flow at 4°C/min. The decomposition reaction was run for 2 hours then the products were allowed cool to room temperature in N_2 flow.

The thickness of the carbon layers was measured by scanning electron microscopy (Hitachi S-4700 Type II cold field emission SEM instrument). The thermal decomposition was carried out in a Netzsch equipment, model STA 409, by heating from 30 to 1000°C in helium atmosphere at a heating rate of 10°C/min. The evolved gases were analysed by a Pfeiffer QMS 200 quadrupole mass spectrometer. The conductivity of the samples was measured by a purpose-built two-probe apparatus utilizing a PicoScope ADC-216 oscilloscope with 16 bit A/D resolution and a Metex MS9150 power supply.

III. Results and discussion

In Fig. 1 scanning electron microscopic images of a fresh and a decomposed PAN film are presented. Both coatings appear homogeneous and crack-free. The thickness of the coating decreased from $\sim 2.7 \mu\text{m}$ to $\sim 0.97 \mu\text{m}$ during the thermal treatment. These values are typical in our experiments as film shrinkage is the combined result of (i) completed drying, (ii) material loss in the chemical reactions (cyclization, dehydrogenation, aromatization) taking place during heating and (iii) structural rearrangement within the remaining carbonaceous layer.

Let us now consider Fig. 2 in order to understand the chemistry of PAN decomposition in the presence of a transition metal catalyst [14]. The first reaction is cobalt catalyzed homopolymer PAN cyclization commencing in our system at $\sim 260^\circ\text{C}$. The lone pair electrons of the $\text{C}\equiv\text{N}$ nitrogen coordinate to Co^{2+} and consequently, the bond energy of the triple bonds in the PAN nitrile groups decreases and therefore, the cyclization reaction takes place at a lower temperature than that of the PAN without metal compounds ($\sim 285^\circ\text{C}$ [15]). In the second reaction phase (300–800°C) the decomposition of the cyclic intermediate takes place accompanied by the evolution of HCN , NH_3 and at higher temperatures, H_2 . Decomposition is concluded at high temperature (above 800°C) in the final aromatization step when N_2 is released and the structure relaxes into graphitic domains. This mechanism was confirmed earlier by Xue et al. [16] and also agrees well with our own mass spectrometry data collected *in situ* during the controlled heating of PAN films (Fig. 3).

It can be seen in Table 1. that without any additives the final product of the 1000°C PAN conversion reac-

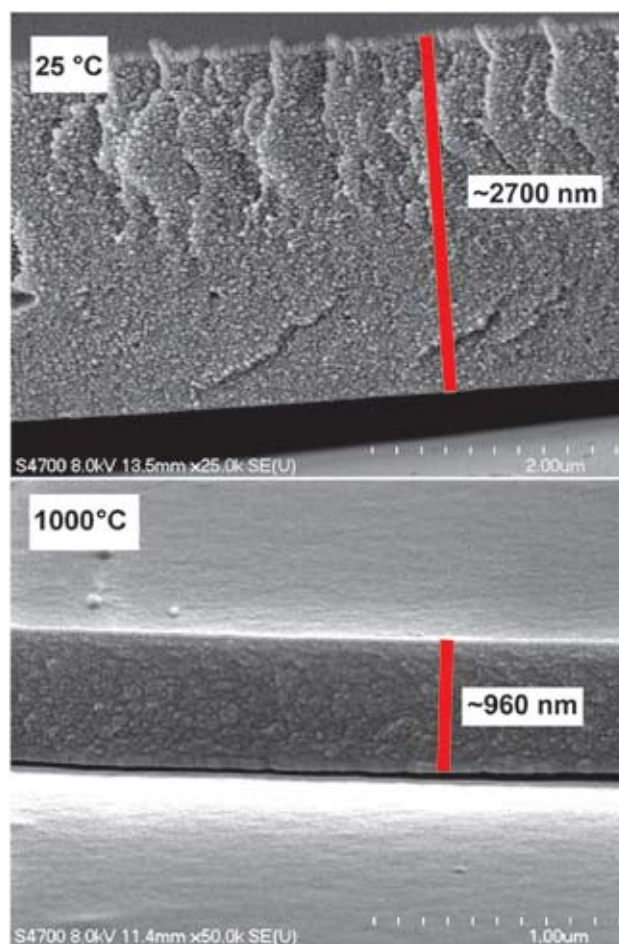


Figure 1. SEM images of PAN films before heat treatment (top) and after carbonization at 1000°C for 2 hours in N_2 atmosphere (bottom)

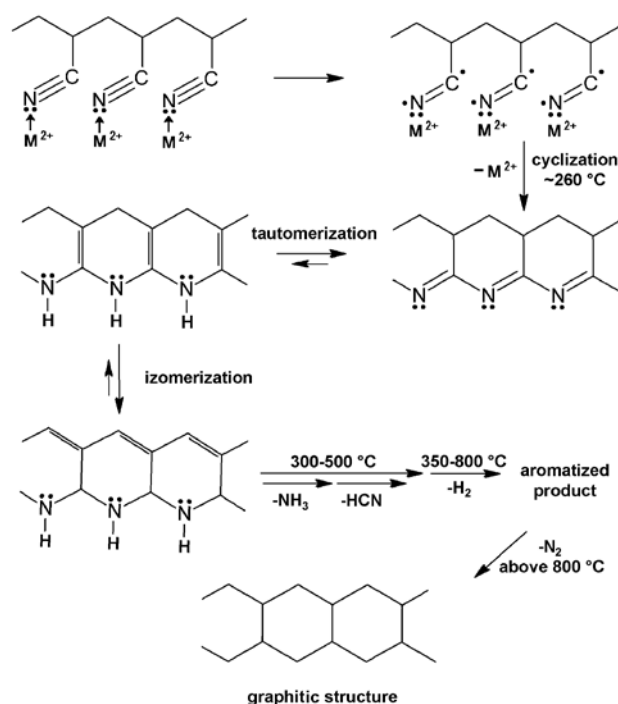


Figure 2. Suggested thermal degradation scheme of PAN

Table 1. Specific electrical resistance ($\Omega \text{ cm}^{-1}$) of PAN films carbonized at 1000°C for 2 hours in N_2 atmosphere

| MWCNT (mg) / PAN (g) | Specific electrical resistance [$\Omega \text{ cm}^{-1}$] | |
|-------------------------|---|-----|
| | Co-acetate (g) / PAN (g) | |
| 0 | 0 | 492 |
| 0 | 0.2 | 86 |
| 2 | 0 | 470 |
| 2 | 0.2 | 46 |

tion exhibits a specific resistance of $492 \Omega \text{ cm}^{-1}$. If a suitable catalyst metal is available as discussed above, the specific resistance can drop to $86 \Omega \text{ cm}^{-1}$. Our earlier experiments have shown that no additional conductivity improvement can be achieved by increasing the cobalt concentration above $0.2 \text{ g Co-acetate} / 1 \text{ g PAN}$ [11]. Moreover, the overall quality of the coating actually deteriorates upon further cobalt addition due to the increasing viscosity of the precursor solution. On the other hand, adding a trace amount of multi-wall carbon nanotubes ($0.2 \text{ mg MWCNT} / 1 \text{ g PAN}$) to the Co-containing precursor solution reduces the specific re-

sistance to $46 \Omega \cdot \text{cm}^{-1}$, a 47 % improvement over the cobalt-only sample.

It is interesting to contemplate on the role of MWCNTs in the graphitization process of the PAN film. For example, nanotubes could form continuous conduction channels in the polymer matrix. Since pure MWCNTs are among the best known electrical conductors, a nanotube chain would certainly decrease the resistance of the film. However, the fact that in the absence of Co^{2+} ions the nanotube induced resistance drop is less than 5 % quickly proves this hypothesis wrong. It should also be noted that the applied $0.2 \text{ mg MWCNT} / \text{PAN}$ loading is well below the typical percolation threshold of MWCNTs in polymers [17,18]. Another possibility is that the nanotubes themselves could decompose into graphite nanocrystallites distributed evenly in the carbonized coating and thus improving its electrical conductivity. Arguments against this explanation are (i) the absence of the beneficial effect in the cobalt-free sample and (ii) the well-known thermal stability of MWCNTs under our experimental conditions. Carbon nanotubes were reported to withstand temperatures up to 3000°C without structural damage in inert atmosphere. In fact, such elevated temperatures are beneficial for the spontaneous healing of nanotube wall defects [19].

A closer examination of the temperature programmed mass spectrometric data presented in Fig. 3 reveals that the onset of the HCN and H_2 evolution processes is unaffected by the presence of nanotubes. These products both originate from Co^{2+} catalyzed cyclization and dehydrogenation reactions. N_2 formation at high temperature is due to the final graphitization step. Apparently, this process takes place at a significantly lower temperature (825°C vs. 859°C) and thus, must have lower activation energy when carbon nanotubes are also present in the matrix. We suggest that the perfect graphitic structure of the MWCNT walls may serve as a “template” for the graphitization of the N-containing condensed rings via stacking interactions. Although further work is certainly required to rigorously prove this hypothesis, our experiments have clearly demonstrated that there exists a synergetic catalytic effect between Co^{2+} ions and MWCNTs in the thermal conversion of PAN films into electrically conductive carbonaceous coatings.

IV. Conclusions

In this paper we investigated the effect of multi-wall carbon nanotubes (MWCNTs) on the thermal decomposition of polyacrylonitrile (PAN) films into conductive carbonaceous films of submicron thickness. The addition of MWCNTs decreased the specific electrical resistance of the film by 47 % compared to a reference film containing the same amount of Co^{2+} catalyst but no nanotubes. Since the MWCNTs are thermally stable, their loading was below the percolation threshold and low

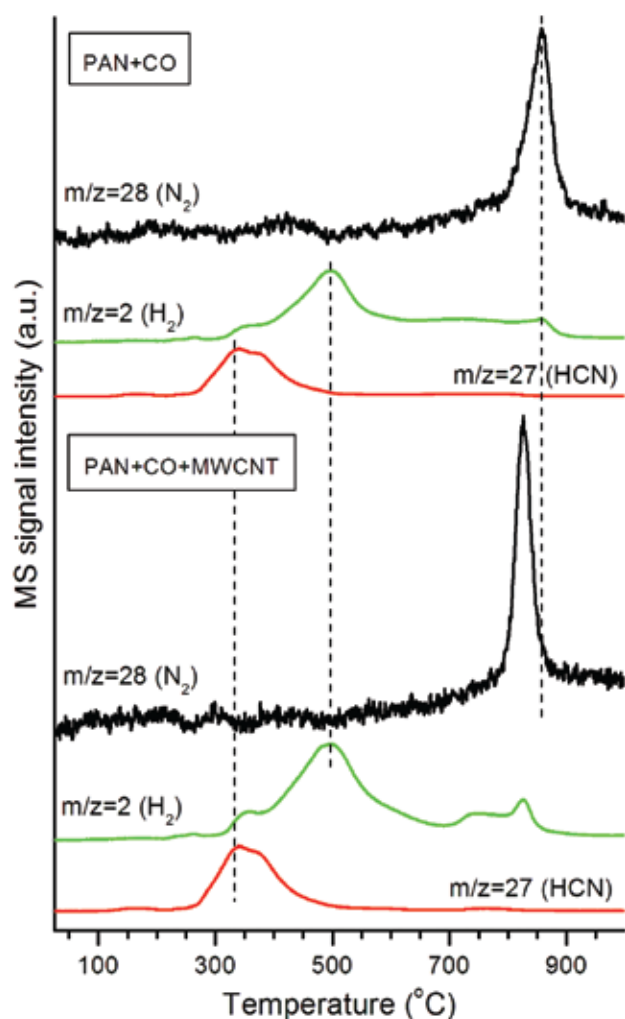


Figure 3. Evolution of HCN, H_2 and N_2 during the thermal decomposition of PAN in the absence (top) and presence (bottom) of multi-wall carbon nanotubes

temperature chemical reactions were unaffected by the presence of the nanotubes, we suggest that MWCNTs may catalyze the final graphitization step of PAN degradation.

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