Polyaniline-Carbon Nanotube Composites: From Wrapping and Self-Alignment to Solubility and Enhancement Effects

R. Sainz[1], A.M. Benito[1], M.T. Martínez[1], J.F. Galindo[1], J. Sotres[1], A.M. Baró[1], B. Corraze[2], O. Chauvet[2], J.N Coleman[3], K. Ryan[3], W. J. Blau[3], W.K. Maser[1]

[1]Instituto de Carboquímica (C.S.I.C.), C/Miguel Luesma Castán 4, 50018 Zaragoza, Spain
[2]LPC, IMN, Univ. Nantes, rue de la Houssinière, F-44322 Nantes, France
[3]Physics Department, Trinity College, Dublin 2, Ireland

wmaser@carbon.icb.csic.es

Intrinsically conducting polymers [1] combine many advantages of plastics, e.g. flexibility and processing from solution, with the additional advantage of conductivity either in the metallic or semiconducting regimes. Easily processable into transparent films, this class of materials is of great interest for the development of thin film plastic opto-electronic devices [2]. On the other hand, carbon nanotubes (CNTs) have unique structural, mechanical, electronic and thermal properties [3] and are attractive building blocks for the development of novel polymer-nanocomposite materials with enhanced functionality, especially if it comes to enhanced conductivity, thermal stability, and reinforcement properties [4-6].
Starting conducting polymer as matrix material for our work is polyaniline (PANI) for the following reasons: the monomer is inexpensive, the polymerization is straightforward and it can be processed into films. Its electric and optical properties are reversibly controllable by both charge-transfer doping and protonation, and, additionally, it is environmentally stable [1,2]. First PANI-CNT composites with interesting enhancement characteristics have been fabricated in the last few years [7,8,9], however, solubility and processing, key points for device applications were not achieved yet.

Here, we report the formation of a soluble self-aligned PANI-CNT composite consisting of multi-wall carbon nanotubes (MWNTs) and the non-conducting but soluble emeraldine base (EB) form of PANI. Further processing of the composite into free-standing colored thin films was achieved. The characteristics of the composite in solution, in powder form and as film will be presented. The results provide evidence that polymerization in the presence of carbon nanotubes leads to a more planar conformation of PANI along MWNTs.

This is stabilized by strong π-π interactions between both components and accompanied by simultaneous self-alignment of MWNTs. A processable EB-MWNT composite with enhanced properties (increase of room-temperature electrical conductivity by 9 orders of magnitude and increase of thermal stability by 200ºC) has been obtained, thus opening many new possibilities for further technological applications. This work will be published soon in [10].

Figure 1: Polymerization of polyaniline in the presence of carbon nanotubes (left) results in a soluble carbon nanotube/polyaniline composite (middle). Polyaniline in the proximity of nanotubes grows in a more planar conformation due to strong π-π interactions simultaneously stabilized by self-organization of the nanotubes, thus forming aligned bundles of micrometer lengths (right).

References

[1] A.G. MacDiarmid, *Synth. Met.* 125, 11 (2002)
[2] A.J. Heeger, *Synth. Met.* 125, 23 (2002)
[3] M.S. Dresselhaus, G. Dresselhaus and P. Avouris (eds*), Carbon Nanotubes: Synthesis, Structure, Properties and Applications* vol 80, Berlin: Springer (2001).
[4] S.A. Curran, P.M. Ajayan, W.J. Blau, D.L. Carroll, J.N. Coleman, A.B. Dalton, A.P. Davey, A. Drury, B. McCarthy, S. Maier, A. Strevens, *Adv. Mater.* 10, 1091 (1998)
[5] H.S. Woo, R. Czerw, S. Webster, D.L. Carroll, J.W. Park and J.H. Lee, *Synth. Met*. 116, 369 (2001)
[6] A.B. Dalton, S. Collins, E. Muñoz, J.M. Razal, V.H. Ebron, J.P. Ferraris, J.N. Coleman, B.G. Kim and R.H. Baughman, *Nature* 423, 703 (2003)
[7] M. Cochet, W.K .Maser, A.M. Benito, M.A. Callejas, M.T. Martínez, J-M. Benoit, J. Schreiber, and O. Chauvet, Chem. Comm. 1450 (2001)
[8] H. Zengin, w. Zhou, J. Jin, R. Czerw, D.W. Smith Jr, L. Echegoyen, D.L. Carroll, S.H. Foulger, and J. Ballato, Adv. Mater, 14, 1480 (2002)
[9] N. Ferrer-Anglada, M. Kaempgen, V. Skákalová, U. Dettlaf-Weglikowska, and S. Roth*, Diamond Relat. Mater*. 13, 256 (2004)
[10] R. Sainz, A.M. Benito, M.T. Martínez, J.F. Galindo, J. Sotres, A.M. Baró, B. Corraze, O. Chauvet and W.K. Maser, Adv. Mater: DOI: 10.1002/adma200400921 (in press).

Acknowledgements: We thank J.M. Andrés and M. T. Bona (Inst. Carboquímica) as well as J. L. Serrano and L. Oriol (ICMA-Univ. Zaragoza) for research support and fruitful discussions. Work was financed by MCYT project NANOSIN (MAT 2002-04540-C05-04). Support through GDRE -"Science and Applications of Nanotubes – NANO-E" is acknowledged.