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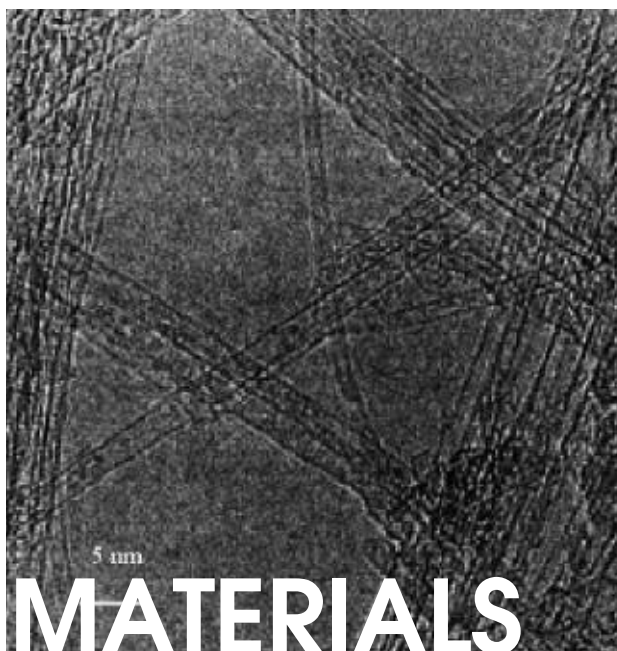


Fig. 1 - TEM image SWNT produced on Co/MgO catalyst. From [12]

CARBON MATERIALS AND CATALYSIS

Part 1: Catalytic Construction

In the last years two catalytic processes have been studied by us to construct useful or destroy harmful carbon materials, respectively. In this Part 1 the catalytic preparation, characterization and example of utilization of carbon nanotubes and amorphous nanocarbons is reviewed.

Despite the very old age (earliest known of charcoal use in the manufacture of bronze and as domestic smokeless fuel by the Egyptians and Sumerians dates back to about 4,000 BC) carbon materials today are still capable to generate a great research interest as novel nanomaterials (Table 1) [1] for various applications. In particular, microporous carbons and carbon nanotubes, respectively for their well-tailored structure and texture and their structural, mechanical and

electronic properties [2], have attracted great attention. However, a parallel interest is addressed to the harmful effects of carbon materials when produced as fine particles in combustion processes. A very well known example is the case of soot particles generated by automotive diesel engines, whose emission is strictly regulated for environmental protection (Table 2). Therefore, there is the necessity of either construct carbon materials such as nanotubes, fibres, diamonds, glassy carbon, either to destruct carbon materials such as soot particulate. In both cases catalysis may have a significant role. In the Part 1 of this paper the work of our group in catalytic construction of carbon materials will be reviewed, while Part 2 will be dedicated to their catalytic destruction.

Devoted to prof. Elio Santacesaria in honour of his 65th birthday and of his constant contribution to innovative new processes development in industrial chemistry.

Catalytic construction of nanocarbons

Multiwall (MWNT) and single wall (SWNT) carbon nanotubes have attracted very great attention due to their structural, mechanical and electronic properties and related potential technological applications. As an example they offer unique mechanical properties unattainable with existing materials: tensile strength about 2,300% greater than steel wire, Young's modulus about 380% greater than steel wire, and strains to failure of approximately 2,000% greater than typical carbon fibre.

First produced in arc-discharge process or by laser ablation, CNTs can be grown by catalytic chemical vapour deposition (CCVD), which allows to achieve defect-free and planned size

materials by controlling the growing process, carried out below 1,000 °C. First CCVD syntheses were carried out by Yacaman [3] and Ivanov [4].

Fe, Co and Ni supported catalysts are very active in the CCVD, while with Cu, Cr, Mn only a negligible amount of CNT is formed. The nanotube growth mechanism in CCVD is still controversial: base- or tip-growth mechanism on catalyst particles have been suggested. The most frequently used hydrocarbons are ethylene, acetylene, benzene, while metal oxides [5] and zeolites [6] are the most usual supports. In the absence of metal, zeolites such as Y, MOR, MFI, L, BEA give different forms of carbon with a controlled microporosity, but nanotubes [7]. MWNTs have been also prepared by CVD of hydrocarbons inside porous alumina membrane with or without addition of transition metal as catalyst [8-9].

Although transmission (TEM) and high resolution transmission (HRTEM) electron microscopy are the decisive way to recognize nanotubes and to distinguish them from other carbon species, many other techniques are employed to their characterization, such as Raman spectroscopy, X-ray diffraction (XRD), scanning electron (SEM), scanning tunnel (STEM) and atomic force microscopy (AFM), thermal analysis (TG-DTG), gas adsorption.

Among various applications [10] the unique CNT properties make them very attractive candidates in polymer composite material formulations [10-11] to improve mechanical properties and performance, to enhance thermal and flammability properties and electrical conductivity. In order to achieve the most effective enhancement of properties, the reinforcement phase must be uniformly dispersed in the matrix.

Tab. 1 - Proposed scheme for classification of carbon materials (from (1))		
Conventional carbon	Graphite	Classic carbons
	Activated carbon	
	Carbon black	
	Natural diamond	
Newly-developed carbons	Carbon fibres	→ Nano-structured
	Highly oriented graphite	
	Porous carbon	
	Glass-like carbons	
	High-density isotropic carbons	
	Intercalation compounds	
	Diamond like carbon	
	Carbynes	
	Fullerenes	→ Nano-sized
	Carbon nanotubes	

Tab. 2 - Proposed EURO 5 for passenger cars and light-duty commercial vehicles							
Valid from	Vehicle class/group		Reference Weight RW (kg)	CO (g/km)	HC (g/km)	NOx (g/km)	Particulate Mass (g/km)
	Class	Group		Petrol Diesel	Petrol Diesel	Petrol Diesel	
1.1.2010	Passenger cars	-	All	1.0	0.050	0.08	0.025
1.1.2010	Light-duty Commercial vehicles	I	RW<1305	1.0	0.08	0.08	0.025
		II	1305<RW<1760	1.0		0.08	0.025
		III	1760<RW	1.25		0.10	0.032

Magnesium oxide supported synthesis of SWNT [12]

MgO supported Co is an effective catalyst to produce SWNTs at 1,000 °C using CH₄/H₂ as feed gas. The diameter of SWNTs, measured by TEM images (Fig. 1) varies between 0.8 and 4 nm. While as produced samples exhibit a BET surface area evaluated by N₂ adsorption-desorption isotherm of 1,170 m²/g, a dramatic increase up to 1,800 m²/g was observed upon purification to remove amorphous carbon formed during the synthesis.

Beta zeolite supported synthesis of MWNT [6]

Co and Fe supported on beta zeolite catalyse the synthesis of CNTs. We found that the yield of deposited carbon, evaluated on the base of catalyst mass, increases with time and temperature. Moreover the selectivity to CNT increases both with time and temperature, reaching 68%, as evaluated by TGA of the as produced materials. In fact, the oxidation profiles of synthesised samples (Fig. 2) show two weight losses: a first one due to amor-

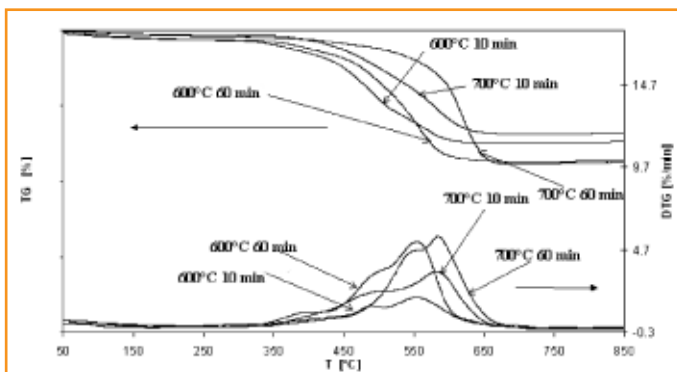


Fig. 2 - TG-DTG profiles for samples synthesis at 600 °C and 700 °C at 10 and 60 min. on Co/beta catalyst. From [6]

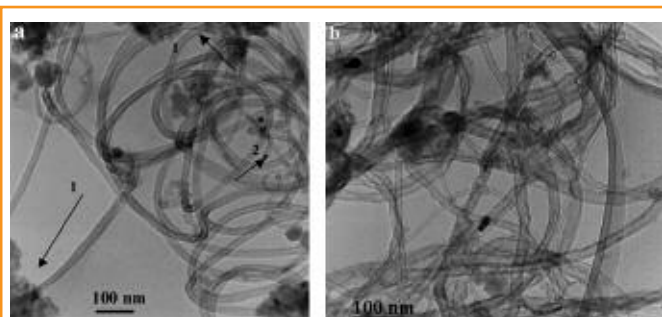


Fig. 3 - TEM images of sample synthesised at 600 °C in 60 min. (a) and its residue of TGA, stopped at an intermediate temperature between the two DTG peaks (b), on Co/beta catalyst. (1) Amorphous carbon; (2) metal particle. From [6]

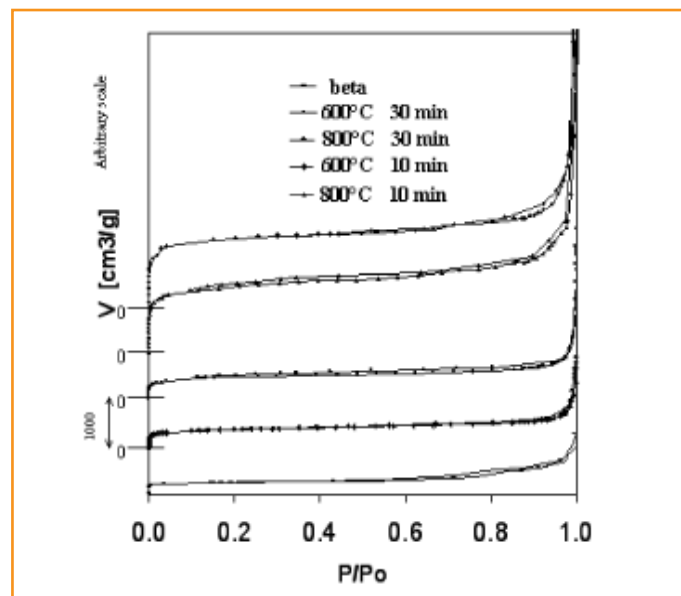


Fig. 4 - N₂ Adsorption-desorption isotherms [13] of beta and microporous carbon synthesised into the pores of beta zeolite

phous carbon burning at lower temperature (in TEM image of sample after intermediate temperature treatment, Fig. 3b, amorphous carbon is absent) and a second one where carbon nanotubes burn in air.

Beta zeolite supported synthesis of nanocarbons [13]

A nanocarbon with extremely high surface area was obtained within the pores of beta zeolite. The BET surface area evaluated by N₂ adsorption-desorption isotherms (Fig. 4) increases with time and temperature to values higher than 2,000 m²/g. Carbon samples show very high microporosity until 90% of the total volume. The measured mesoporosity is likely due to two facts: (i) some part of unfilled zeolite that after zeolite removal becomes mesopores, (ii) weak linkages between carbon clusters in the zeolite channels giving breakage during acidic washing generate mesopores.

Alumina and aluminium hydroxides supported synthesis of MWNT [14]

Bayerite (α -Al(OH)₃), bohemite (γ -AlO(OH)), gibbsite (γ -Al(OH)₃) and γ -alumina (γ -Al₂O₃) were investigated as support of Co, Fe for the synthesis of CNTs. The influence of time, gas volume/catalyst mass ratio and catalyst preparation on the CNT growth were studied. We have found that either the drying time before

the synthesis and the aging time affect the catalyst activity. Very high carbon yields up to 300% were obtained with gibbsite and bayerite, while γ - Al_2O_3 gives lower yield. By varying the ratio between the gas volume and the catalyst mass, reaction yields up to 78% were obtained. MWNT selectivity, evaluated by TG-DTG analysis is close to 100% with gibbsite and bayerite. Fig. 5 shows a typical SEM image of CNT obtained by using gibbsite as support.

Nanotubes bundles starting from the catalyst are grown in the direction of gas flow. Catalyst particles (support + metals) are absent. Increasing catalyst mass from 100 to 200 mg the bundle length increase up to 100 μm .

SEM images (Fig. 5g and 5h) show that CNT's length increase with reaction time in the range from 10 to 60 min., while after 60 min. only small increase of length is observed (Fig. 5l) together with the formation of few agglomerates of carbon coming from homogeneous decomposition (Fig. 5n). Higher resolution SEM images give evidence of the bundles organisation, consisting in a dense network of tangled carbon nanotubes. The coiled morphology of gibbsite and bayerite bundles ends suggests in these cases a different catalyst deactivation

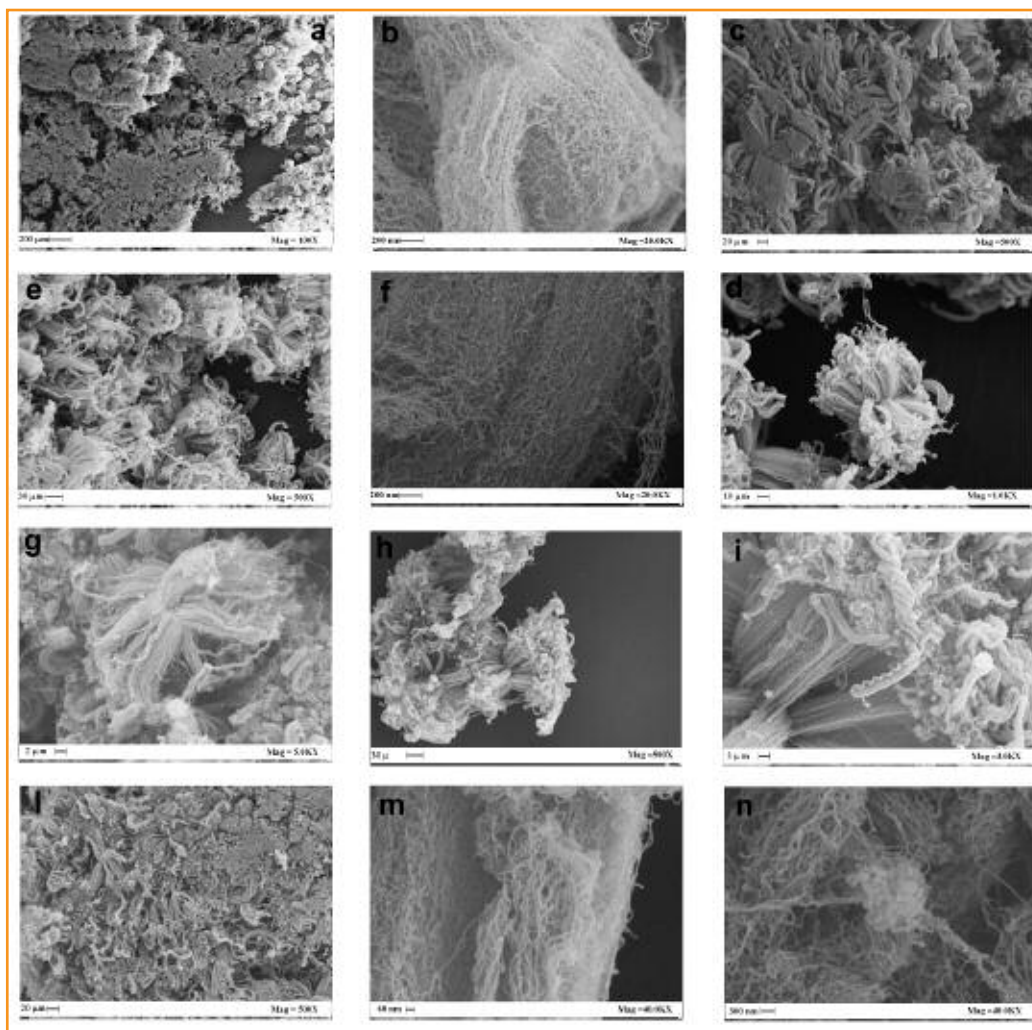


Fig. 5 - SEM images [14] of CNT by gibbsite: 60 min. synthesis time-100 mg catalyst mass (a, b); 60 min. synthesis time-200 mg catalyst mass (c, d); 60 min. synthesis time-300 mg catalyst mass (e, f); 10 min. synthesis time-200 mg catalyst mass (g); 30 min. synthesis time-200 mg catalyst mass (h, i), 120 min. synthesis time-200 mg catalyst mass (l, m, n)

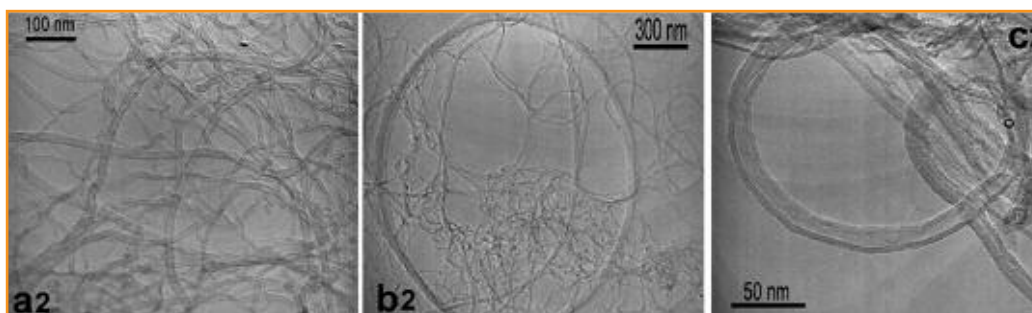


Fig. 6 - TEM images [14] of: 60 min. synthesis time-200 mg catalyst mass (a2); 30 min. synthesis time-200 mg catalyst mass (b2, c2)

mechanism. The tube have an entangled structure (Fig. 6) and a few number of catalytic particles are present in the hallow core of the nanotubes. External CNT diameter after 60 min. of synthesis is in the range 9-22 nm, while internal diameter varies from 5 to 10 nm. Nanotubes synthesised in shorter time show a reduced outer diameter, as previously observed [6], in the range 6-16 nm.

Alumina membrane supported synthesis of MWNT [9]

Carbon nanotubes were synthesised by CVD of ethylene within the pores of a commercial alumina membrane having 200 nm pores diameter and 60 μm thickness. SEM picture (Fig. 7a) shows carbon deposit after 2 h of synthesis consisting of ordered aligned nanotubes having the same length. Further evidence for tubular carbon bundles formation comes from TEM images (Fig. 7b). The external diameter of the tubes is uniform and there is no evidence of any amorphous carbon; bundles of opened parallel tubes, aligned without macroscopic defects are formed. An increase of wall thickness is observed by increasing the synthesis time. X-ray diffraction spectra of samples produced at different synthesis time are shown in Fig. 8. The patterns can be indexed on the basis of the hexagonal close-packed "graphite" unit cell. Our patterns are dominated by two diffraction lines (002) and (100). The (002) reflection peak is broadened, in comparison with that of graphite, and shifted from 26.4° of graphite to around 25.8° , corresponding to an increase of the interlayer distance from 3.35 \AA to 3.44 \AA . The (100) peak (reflection at $\sim 43^\circ$) is similar to that of graphite, even though is much

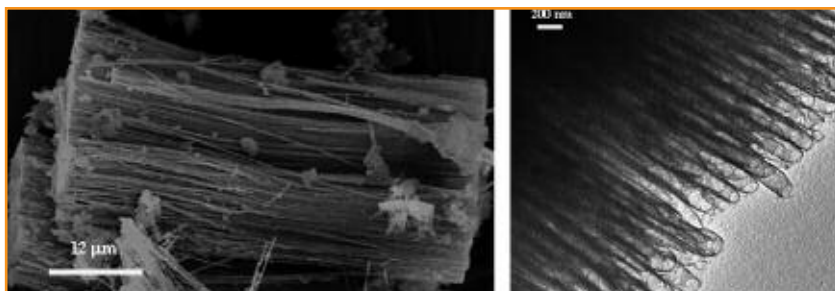


Fig. 7 - SEM picture of synthesised CNT in the channels of alumina membrane: a) TEM picture of synthesised CNT bundle in the channels of alumina membrane; b) From [9]

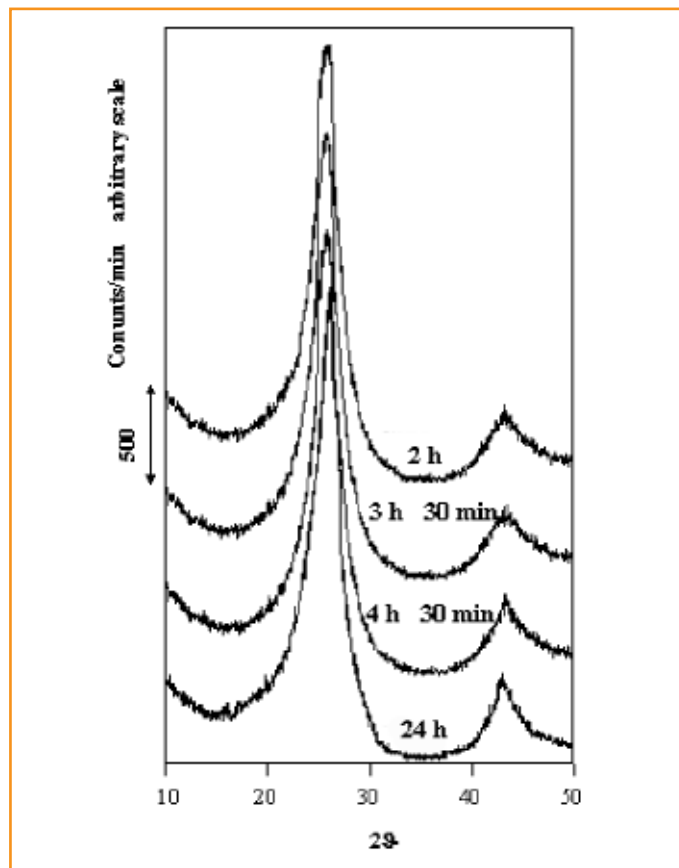


Fig. 8 - XRD patterns of carbon samples synthesised after in 2 h, 3 h and 30 min., 4 h and 30 min. and 24 h, in the channels of alumina membrane. From [9]

weaker and broadened. The peak (101) of graphite at $\sim 45^\circ$ is absent, due to a lack of regularity along the c-axis, as happens in the turbostratic stacking of hexagonal layers of carbon coke.

CNT/polymer composites

Syndiotactic polypropylene (sPP) and CNTs synthesised by zeolite supported Co/Fe were directly blended in the melt [15] to form sPP/CNT composites. The extruded samples were moulded in a hot press at 170°C , forming films rapidly

Materiali carboniosi e catalisi. Parte 1: preparazione catalitica

Negli ultimi anni nei nostri laboratori sono stati studiati due processi catalitici, rispettivamente per la sintesi di materiali carboniosi dotati di promettenti proprietà e per l'abbattimento di particolato carbonioso formato nei processi di combustione e considerato nocivo per la salute. Questa parte del lavoro è dedicata alla preparazione catalitica, alla caratterizzazione e ad esempi di applicazione di nanotubi di carbonio e nanocarboni microporosi.

RIASSUNTO

quenched in either a bath at room temperature or in a bath at 0 °C for ten days, obtaining two different polymorphs. Comparing the X-ray diffraction patterns of the films with that of the pure polymer we have concluded that the presence of CNT enhances crystallization of the sPP helical chains. We have also found that carbon nanotubes improve the thermal stability of either polymorph of sPP in nitrogen as well as in air [15]. CNTs obtained with MgO supported Co/Fe catalyst and -COOH functionalised were incorporated into a polyvinyl alcohol (PVA) matrix [16]. We have found that structural, mechanical and thermal properties of PVA/CNT composite films are markedly enhanced even at very low nanotubes content.

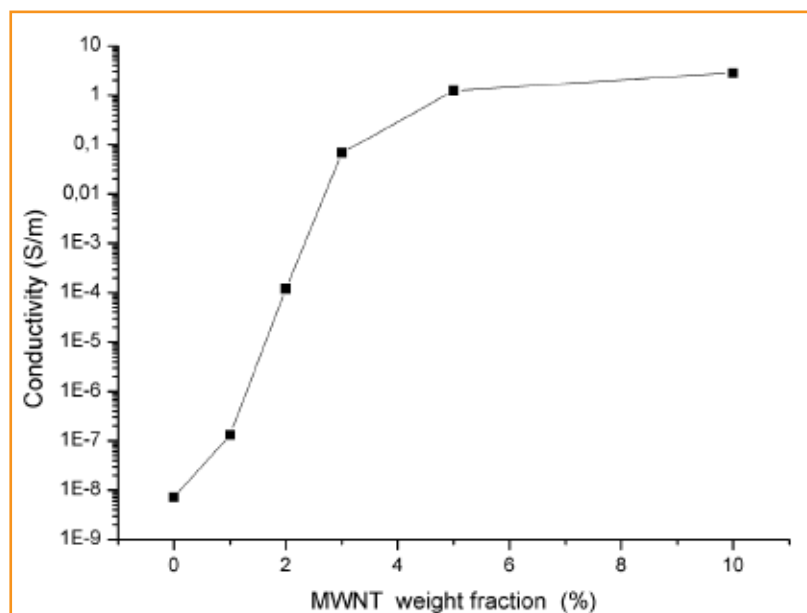


Fig. 9 - Electrical Conductivity of PE/CNT composites as function of MWNT content [17]

CNTs synthesised over gibbsite supported Co/Fe catalyst were incorporated into a polyethylene (PE) matrix by High Energy Ball Milling to form PE/CNT composites [17-18]. This solid-state mixing at near room temperature is an effective unconventional technique for producing PE/CNT nanocomposites avoiding high temperatures, solvents and any physical and/or chemical treatment of CNTs. We have studied their morphology and physical properties (thermal, mechanical, electric) (Fig. 9) finding that the improvement of all these properties is very significant even for low nanotubes content (2-3% wt).

Conclusions

Catalytic chemical vapour deposition (CCVD) of hydrocarbons, using Co and Fe deposited on alumina and aluminium hydroxides, magnesium oxides and zeolites is an effective way to construct carbon materials such as multiwall or singlewall carbon nanotubes and amorphous nanocarbons. MWNTs and SWNTs have been obtained with high yield and selectivity. Aligned, opened carbon nanotubes have been obtained as bundles within alumina porous membrane. Nanoporous carbon with exceptionally high surface area was achieved with beta zeolite. A significant improvement of mechanical and thermal properties, flammability and electrical conductivity performance was obtained by incorporating CNTs in various polymers by solution, melt processing and HEBM method.

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