Journal of
Nanoscience and Nanotechnology
Vol. 9, 6064–6071, 2009

Surface Modification of Multiwalled Carbon Nanotubes via Esterification Using a Biodegradable Polyol

B. Fernandez d'Arlas[1], S. Goyanes[2], G. H. Rubiolo[2,3],
I. Mondragon[1], M. A. Corcuera[1], and A. Eceiza[1,*]

[1] *'Materials+ Technologies' Group, Department of Chemical and Environmental Engineering, Eskola Politeknikoa, Euskal Herriko Unibertsitatea, Pza Europa 1, 20018, Donostia-San Sebastián, Spain*
[2] *Laboratorio de Polímeros y Materiales Compuestos, FCEyN, Univ. Nac. De Buenos Aires, Pabellón 1, Ciudad Universitaria, CONICET, Buenos Aires, 1428, Argentina*
[3] *Unidad de Actividad Materiales, CNEA, Av. Gral. Paz 1499, (1650) San Martín, Buenos Aires, Argentina*

Multiwalled carbon nanotubes (MWCNT) were surface modified firstly oxidizing them with a H_2SO_4/HNO_3 mixture to obtain more reactive carboxylic groups on their surface and then higher functionality. Secondly the oxidized nanotubes (MWCNT-COOH) were dispersed in tetrahydrofuran (THF) and made react via esterification with a poly(hexamethylene carbonate-co-caprolactone)diol, a potentially biodegradable polyol with hydroxyl groups at its ends. Modification process steps were characterized using Fourier transform infrared spectroscopy, FT-IR, ultraviolet spectroscopy, UV, solubility in different solvents, thermo-gravimetric analysis, TGA, as well as atomic force microscopy, AFM. Results suggest that surface carboxylic groups are reactive enough to graft polymer chains onto their surface.

Keywords: Multiwalled Carbon Nanotubes, Esterification, Biodegradable Polyol.

1. INTRODUCTION

Since discovered by Iijima[1] in 1991, carbon nanotubes (CNT) have been claimed to be promising components of smart composites,[2] gas-detectors,[3] flow sensors[4] or as additives in high performance composite materials for applications ranging from civil engineering, robotics, aeronautics or biomedicine.[5] Chemical control of carbon nanotubes functionalization has resulted in being an essential step when designing such class of advanced materials. Mattson et al.[6] demonstrated the use of multiwalled carbon nanotubes (MWCNT) non-covalently coated with 4-hydroxynonenal as substrates for growing embryonic rat brain cells. In this way Webster et al.[7] demonstrated the potential of carbon nanofiber-reinforced polyurethane in neural implants. Khang et al.[8] demonstrated patterned growth of osteoblasts on micro-aligned patterns of carbon nanotubes on polycarbonate urethane. Lovat et al.[9] described an increase in electrical signal transmission in a network of hippocampal neurons grown on purified multiwalled carbon nanotubes. Meng et al.[10] improved polyurethane composite anticoagulant properties by using MWCNT as polymer fillers.

The control of nanotubes surface chemistry could allow to design new kind of nanotubes-based sensors or to create newly high performance light composites with improved thermal, electrical and mechanical properties.[5] Much work has been done in understanding the way CNT could be turn into a reactive element by creating reactive carboxylic groups over carbon nanotubes surface treating them with strong oxidizing-acid solutions.[11] After the acid treatment of carbon nanotubes some authors have managed to graft polyurethane macromolecular precursors onto MWCNT surface by different procedures. Kuan et al.[12] grafted a macrodiisocyanate prepolymer onto diamine-pre-functionalized MWCNT. Xiong et al.[13] prepared single wall carbon natotubes (SWCNT) surface modified with polypropylene glycol (PPG), as polyurethane macromolecular precursor. Xia et al.[14] also managed to graft polyurethane precursors onto MWCNT surface, by the reaction of a PPG-toluene diisocyanate (TDI) prepolymer with nanotubes hydroxyl groups.

This work presents a simple grafting-to procedure to obtain poly(ester-co-caprolactone)diol grafted MWCNT and the grafting analysis results. The effect of grafting

---

*Author to whom correspondence should be addressed.

1533-4880/2009/9/6064/008
doi:10.1166/jnn.2009.1560

molecule has been studied comparing the polyol grafting results with those for a short diol like 1,4-butanediol (BD). Functionalization analysis has been carried out by Fourier transform infrared spectroscopy, FT-IR, ultraviolet spectroscopy, UV, solubility in several solvents, thermo-gravimetric analysis, TGA, as well as atomic force microscopy, AFM.

2. EXPERIMENTAL DETAILS

2.1. Materials

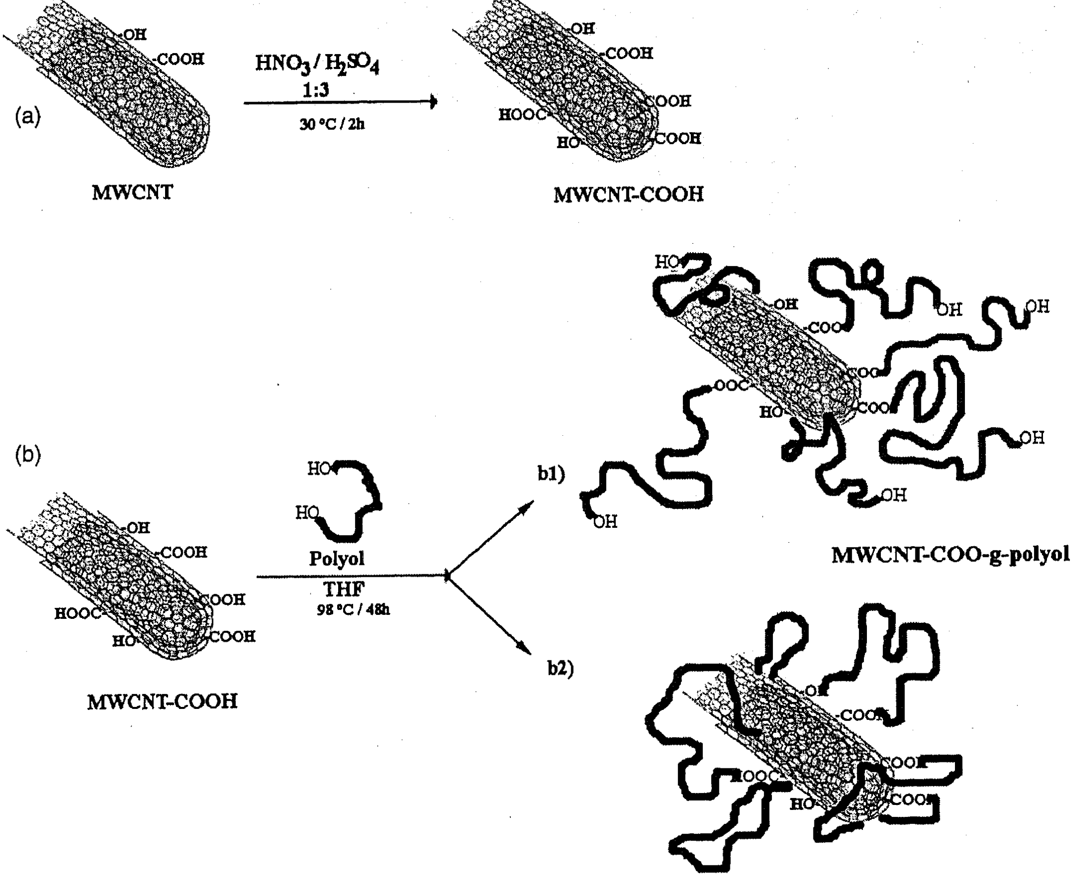
Poly(hexamethylene carbonate-co-caprolactone)diol (PHC-co-PCL) was kindly supplied by Polimeri Europa, from Ravenna, Italy. Molecular weight was evaluated following ASTM-D 4274-88 standard for measuring the hydroxyl number resulted to be 2020 g/mol. The block copolymer is formed by 45 wt% polycarbonate and 55 wt% polycaprolactone. It was dried under vacuum before use. 1,4-butanediol was provided by Aldrich and used as received.

MWCNT were supplied by Nanocyl, Belgium, under the commercial name of Nanocyl-3100. Their purity is of 95%, and they are synthesized by thermal chemical vapor deposition. Though not shown, the weight loss corresponding to nanotubes, obtained by thermo-gravimetrical analysis in nitrogen, was observed between 450 °C and 650 °C without losses at lower temperatures, thus proving their high purity.

Tetrahydrofuran (THF) from Panreac, Barcelona (Spain) was used as received.

2.2. MWCNT Acid Treatment

Pristine MWCNT were acid treated with a mixture of HNO_3/H_2SO_4 with a volume ratio of 1:3 for two hours in an ultrasonic bath at 30 °C, following the procedure previously studied.[11] The resultant dispersion was quenched with deionized water and left to decant the acid treated MWCNT, MWCNT-COOH, for one week. These nanotubes were washed with distilled water until a neutral pH. MWCNT-COOH equivalent weight was measured by a backward potentiometric titration. For that three samples of around well weighed 8 mg MWCNT-COOH were left react overnight with 2.2 mL NaOH 0.02 N in 15 mL of deionized water. Then the reacted nanotubes were filtrated through a 45 μm diameter pore Nylon filter. The filtrated waters were titrated by adding 0.1 mL HCl 0.01 N fractions and measuring the pH until getting



Scheme 1. Modification methodology.

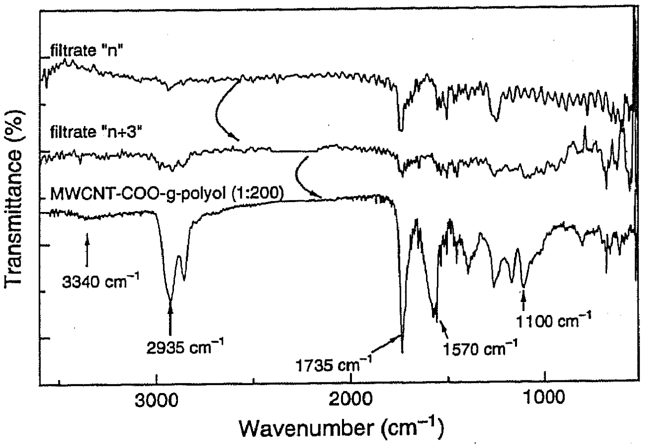


Fig. 1. Spectra of MWCNT-COO-g-polyol, filtrate "*n*" and filtrate "*n*+3" after several rinses of sample.

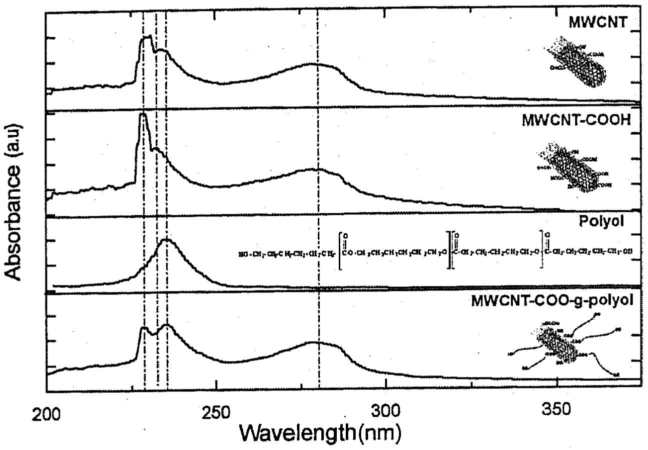


Fig. 3. UV spectra of pristine MWCNT, MWCNT-COOH, polyol, and MWCNT-g-COO-polyol (stoichiometric ratio 1:200).

the employed water pH. Equivalent weight of MWCNT-COOH resulted to be 671 g/eq, what means 1.5 COOH meq/g of nanotubes.

2.3. MWCNT-COO-g-Polyol Synthesis

To analyze the possibility of polyol grafting onto MWCNT-COOH surface, two reactions were performed, one with a small excess of polyol in a stoichiometric ratio of 1:4 equivalents of COOH to OH, and the other with and excess of polyol with a stoichiometric ratio of 1:200. 10 mg MWCNT-COOH were dispersed in 50 mL tetrahydrofuran for one hour in an ultrasonication bath. THF was maintained constant by adding small amounts when solvent was evaporated. The polyol was weighed into a round bottom flask and then the dispersed nanotubes were poured over it and ultrasonicated for another hour. Then the mixture was left under reacting conditions for two days on a plaque provided with magnetic agitation at 98 °C, and THF was left to evaporate. The excess of polyol was washed by pouring different solvents (acetone and THF) over the viscous sample on a 0.25 μm diameter polytetrafluoroethylene filter. At the beginning of the washing the filtration was assisted with a vacuum pump to speed up the procedure. The washing was ended when no polymer was found in the filtration waters. This was checked by adding water to the filtrated solvent and checking the polyol precipitation. When no turbidity was observed, remains of polyol were checked by Fourier transform infrared spectroscopy. MWCNT-COO-g-polyol powders were collected and kept into a desiccator. Nanotubes modification using BD was done following the same reaction conditions than for polyol grafting.

2.4. Characterization

FT-IR characterization of pristine MWCNT, MWCNT-COOH, and MWCNT-COO-g-polyol was performed as follows: 0.5 mg of nanotubes were dispersed in THF. A couple of drops were cast onto KBr plates and solvent

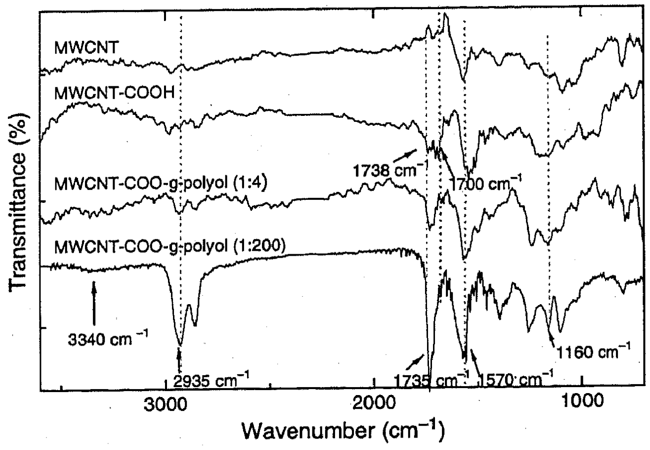


Fig. 2. FT-IR spectra of pristine MWCNT, MWCNT-COOH, and of MWCNT-COO-g-polyol reacted with stoichiometric ratios 1:4 and 1:200.

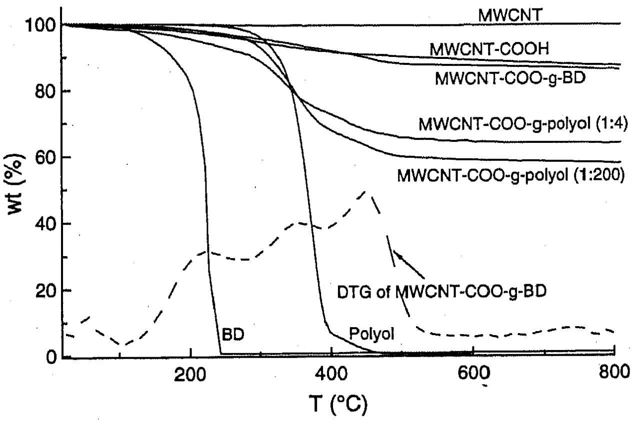


Fig. 4. TGA thermograms of MWCNT, MWCNT-COOH, MWCNT-COO-g-BD, polyol, and MWCNT-COO-g-polyol (stoichiometric ratios 1:200 and 1:4), (dotted line) derivative thermogram of MWCNT-COO-g-BD sample.

was left to evaporate into a heating chamber, heated over 100 °C to avoid water condensation. FT-IR spectra were averaged from 100 scans with 2 cm^{-1} resolution performed per each spectrum in the range from 4000 to 400 cm^{-1}. The equipment used was a Nicolet-Nexus-FT-IR spectrometer provided with a temperature chamber and controller from Specac.

UV samples were prepared by dispersing the different nanotubes in THF keeping a proportion of 0.1 mg of nanotubes in 10 mL THF. The scanning range was from 200 to 400 nm of wavelength. The equipment used was a Spectronic Genesys 5 from Milton Roy.

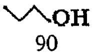
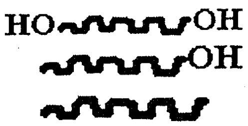
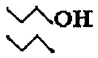
Thermo-gravimetric analysis was performed using a Mettler Toledo TGA/ SDTA851^e equipment performing temperature scans from 25 °C to 1100 °C using N_2 as inert atmosphere.

AFM samples were cast onto silicon wafers from a dispersion of the nanotubes on THF. Silicon wafers were previously washed with dichloromethane and oxidizing mixture consisting in ammonia and hydrogen peroxide solution in water. Cast samples were allowed to dry into a vacuum chamber and temperatures cycles were performed in order to remove the solvent from nanotubes surface.

3. RESULTS AND DISCUSSION

Scheme 1 sketches the synthesis procedure of both MWCNT-COOH and MWCNT-COO-g-polyol. The first

Table I. TGA results and analysis. In bold are written the parts of the molecule considered to be degraded in each situation.

	Nanotube	Δw (%)	meq/g nanotube	Equivalent weight (g/eq)
Experimental	MWCNT-**COOH**	11	2.4 × 10^{-3} (*)	–COOH 45
Predicted from (*)	MWCNT-COO-**g-polyol-g**-OOC-MWCNT (1:1; cross-linking)	71	2.4 × 10^{-3}	 1000
	MWCNT-**COO-g-polyol-g-OOC**-MWCNT (1:1; cross-linking)	72	2.4 × 10^{-3}	 1000
	MWCNT-COO-**g-polyol** (1:2; brushes)	83	2.4 × 10^{-3}	 2000
	MWCNT-**COO-g-polyol** (1:2; brushes)	83	2.4 × 10^{-3}	 2000
	MWCNT-COO-**g-BD** (1:2; brushes)	18	2.4 × 10^{-3}	 90
	MWCNT-**COO-g-BD** (1:2; brushes)	24	2.4 × 10^{-3}	 90
Experimental	MWCNT-**COO-g-polyol**	40	2 × 10^{-4} (mol)	
	MWCNT-**COO-g-BD**	12	1.3 × 10^{-3} (mol)	

step was the pristine MWCNT acid treatment. After washing and characterization by FT-IR, UV, TGA and titration, MWCNT-COOH were dispersed in THF and made react with an excess of polyol. Two possible reactions yields are sketched in Scheme 1. The (b1) represents the extreme case in which the reaction has occurred between each nanotube reactive site with one polyol chain. The (b2) represents the case in which a polymer chain is linked twice into one nanotube by two reactive sites. The (b2) case might also represent nanotubes cross-linking by polyol chains as also considered by other researchers.[15] Figure 1 presents the FT-IR spectra made to two filtrates of the polyol-modified nanotubes washing process, along with the resulted spectra of polyol-modified carbon nanotubes (MWCNT-g-polyol). The spectra called *n* was performed by casting two drops of the waters obtained after several rinses of carbon nanotubes with polyol excess until no turbidity was observed when adding water to them. As can be seen, it presents small bands corresponding to the polydiol. After rinsing it still three more times in around 500 mL THF, spectra $n+3$ was obtained by the same procedure. It is virtually a straight line, thus meaning no polymer was present in this filtrate. The small peaks of around 1740 cm^{-1} present in this spectrum corresponds to an oxidized specie of THF.[16] The spectrum of the modified nanotubes at that point is the one presented as MWCNT-COO-g-polyol. Typical bands of polyol are present, as seen at 3340, 2935, 1735 and 1100 cm^{-1}, as well as the nanotubes backbone characteristic band of 1570 cm^{-1}, indicating that after washing procedure the polyol was incorporated on the nanotubes.

Figure 2 compares the spectra of different treated carbon nanotubes obtained by casting the dispersed samples, from above downwards, pristine MWCNT, MWCNT-COOH, polyol grafted MWCNT obtained by reacting MWCNT-COOH and polyol with a stoichiometric ratio between

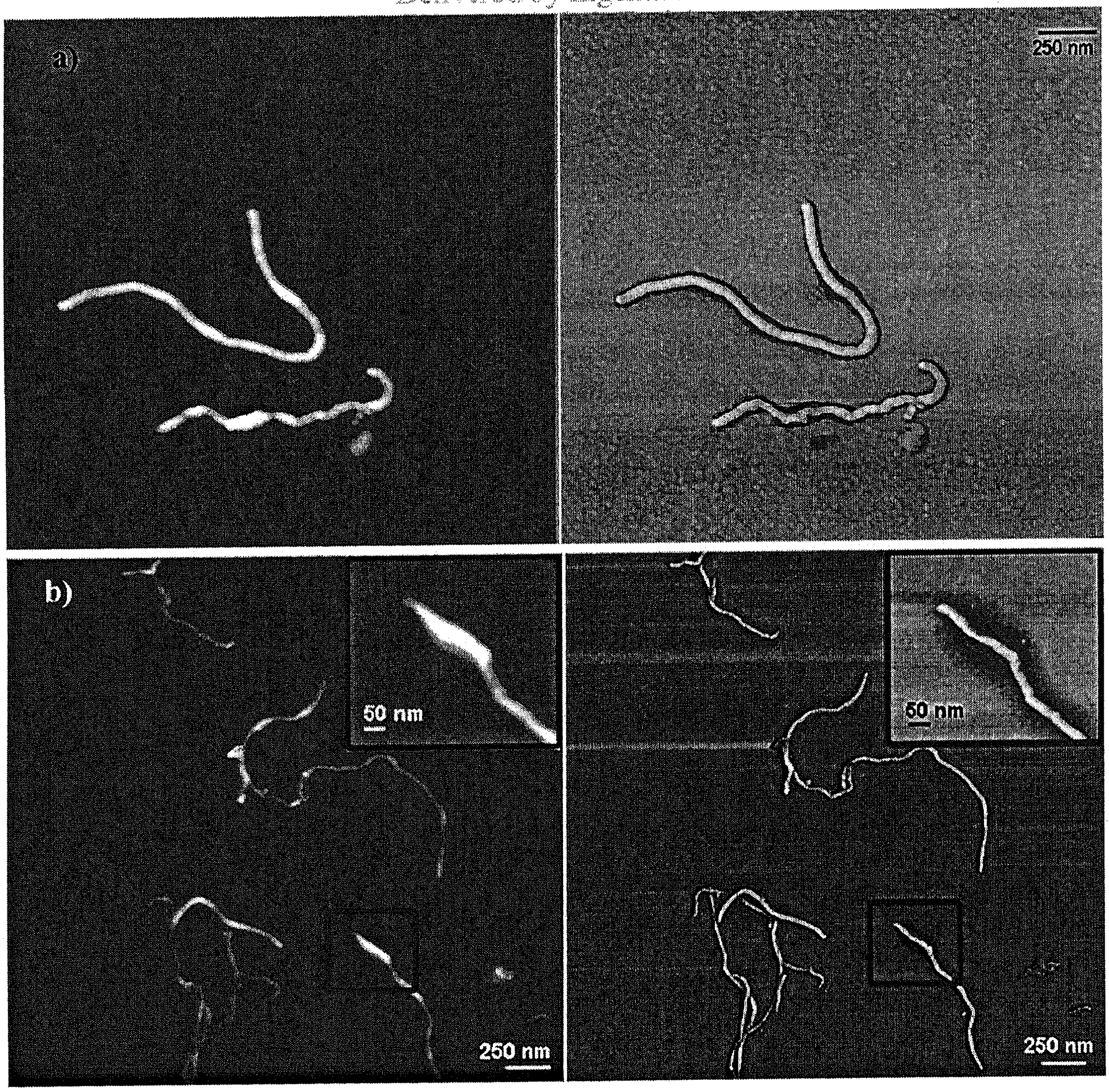


Fig. 5. AFM height (left) and phase (right) images of: (a) MWCNT-COOH nanotubes and (b) MWCNT-COO-g-polyol, indicating polyol presence on nanotubes surface.

nanotubes carboxylic groups and hydroxyl groups of 1:4, and polyol grafted obtained by reacting MWCNT-COOH and polyol with a stoichiometric ratio of 1:200. From this last reaction, it resulted in a higher functionalization of nanotubes probably by the known fact that increasing the hydroxyl amount in an esterification reaction the ester formation is favoured.[17] The acid treatment was seen to increase the amount of acid carbonyl groups, as seen in the region of 1700 cm^{-1}, but also the amount of ester carbonyl groups, as seen in the region of 1735 cm^{-1}, owing to the formation of some other functional groups containing carbonyl groups as ketones, aldehides, anhydrides or esters.[18] After reacting these nanotubes with the polyol, typical bands from it appeared in the spectrum but there was no an increase of acid carbonyl group intensity. Bands in the range of 1150–1300 cm^{-1}, corresponding to C–O groups stretching vibrations, also increased through functionalization. As mentioned above, the polyol functionalization degree increased as the OH/COOH stoichometric ratio increased.

UV obtained spectra are gathered in Figure 3. Pristine MWCNT showed three remarkable peaks, one around 280 nm associated with nanotubes π to π transitions arising from their graphitic structure, another close to 240 nm related with carbonyl groups associated with esters or ketones, and another close to 230 nm, related with carbonyl groups associated with more polar groups such as acid groups. The MWCNT-COOH spectrum presented an increase of this band respect to the others, and a slightly decrease in the band of 280 nm, probably due to the disruption of nanotubes backbone. The spectra of the polyol showed a wide peak centered at 240 nm and related to carbonate and ester carbonyl groups. This peak was also present in the spectra of MWCNT-COO-g-polyol, in which also a decrease of the band close to 230 related to acid carbonyl groups is seen. This fact matched to the formation of ester carbonyl groups instead.

As shown in Figure 4, TGA analysis also indicated organic modification of nanotubes after the acid treatment, and butanodiol and polyol grafting with different polyol contents. The acid treatment increased the amount of defects and oxygen based functional groups which are more prone to degrade than primarily graphene pristine structure.[18] MWCNT-COO-g-BD sample presented a small decrease close to BD boiling point which could mean there was small amount of BD physisorbed besides that chemisorbed or grafted. These different weight loss transitions are better seen in the derivate thermogram (DTG), also shown in Figure 4. The MWCNT-COO-g-polyol thermogram shows a similar shape to that of the polyol, as seen by the main degradation peak and the shoulder at higher temperatures, but with less proportional mass loss due to the presence of nanotubes in the sample, which did not degrade within the studied interval. Table I gathers TGA results and degree of functionalization analysis of the different modified nanotubes. MWCNT-COOH presented

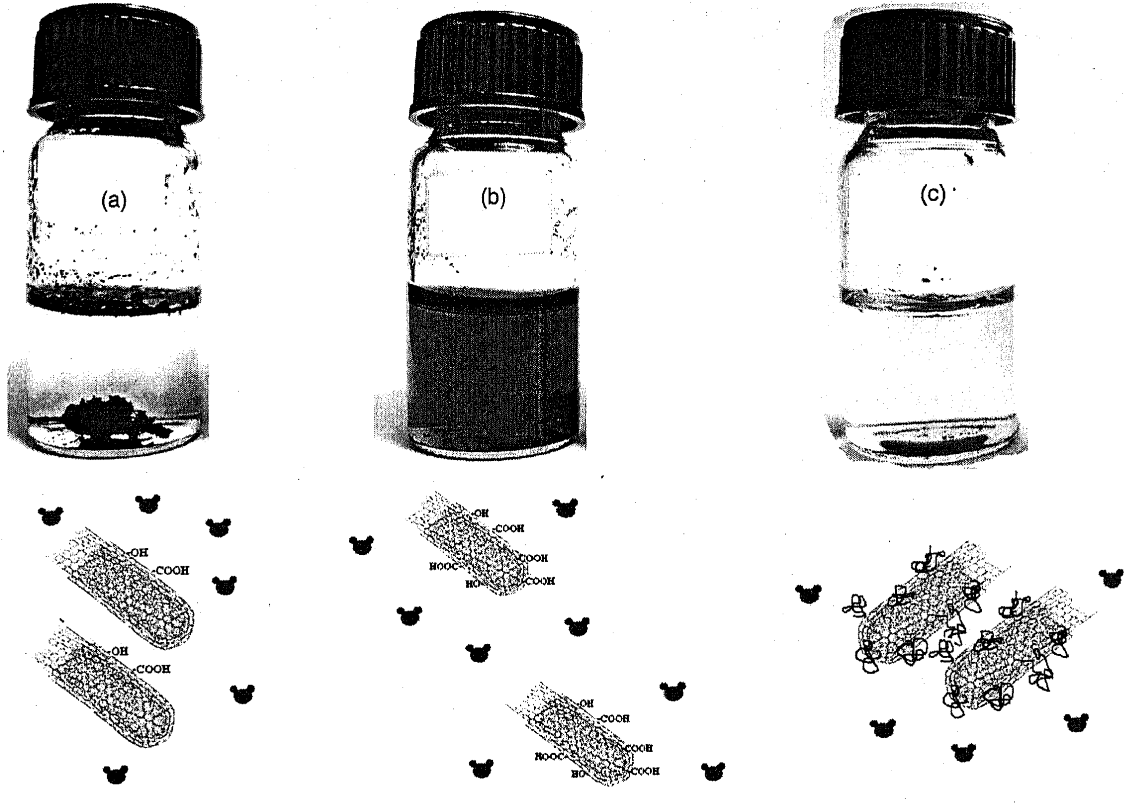


Fig. 6. Vials containing (a) MWCNT, (b) MWCNT-COOH, and (c) MWCNT-COO-g-polyol (stoichiometric ratio 1:200) in water, and the schematics for physico-chemical situation in each case.

a weight loss of 11% from where an acid number of groups per gram of nanotube was estimated (*). With this value the grafted polyol and small diol weight loss calculations were made considering an esterification reaction yield between acid treated nanotubes and hydroxyl groups of 100% in each case. The values are presented in the upper rows and named as "Predicted" of Table I. The figures into last column represent the way the functionalizating molecule is supposed to be grafted on nanotubes. The molecules are represented with the number of hydroxyl groups considered to be reactive for each case. The molecules depicted without hydroxyl molecules represent the case in which the molecules were physisorbed onto the nanotubes. Experimental values, shown in bottom rows named "Experimental," are considerably lower indicating that reaction yield is smaller than the theoretical prediction. This was an expected fact since the reaction was not catalyzed.

Apart from situations (b1) and (b2) sketched in Scheme 1, another reasonable situation might be the no covalently bonding of polyol molecules onto nanotubes, preferable over BD molecules for the bigger size of them and for the difficulty of being removed from nanotube surface due to thermodynamic aspects.[19,20] The weight loss observed for MWCNT-COO-g-polyol functionalized with a stoichiometric COOH/OH ratio of 1:4 was lower than for the nanotubes modified with the 1:200 ratio, thus indicating the importance of the hydroxyl abundance in order to have high levels of grafting. This result is in agreement with those of FT-IR. In any case the resulting functionalization type should be intermediate between (b1) and (b2) cases, and with a low reaction yield. This low reaction yield along with the presence of (b2) situation takes also account of the low intensity band of O–H stretching vibration seen by FT-IR.

Surface modification of nanotubes was also monitored by AFM. As Figure 5(a) shows MWCNT-COOH nanotubes surface is smooth. Figure 5(b) shows thinner nanotubes than in Figure 5(a), this fact being consequence of walls disruption due to ultrasonication used to manage a good dispersion when promoting the reaction between MWCNT-COOH with polyol. In the upper right-hand side small square of Figure 5(b) a closer zoom of functionalized nanotube is presented. As can be seen, polymer is present through nanotubes surface forming aggregates of the order of 5 to 20 nm in size. Those aggregates are softer than nanotubes, as phase image shows, thus allowing us to confirm that they are polymer chains irreversibly attached to nanotubes surface. The functionalization is observed also in other bright spots in height image which also correspond to soft material in phase image.

The diverse types of nanotubes studied in this work were dispersed in different solvents to study the effect of the different modifications. In Figure 6 the different nanotubes, MWCNT, MWCNT-COOH and MWCNT-COO-g-polyol, are presented in vials after being dispersed in water. The pristine MWCNT were not dispersed in water and decanted in a few time. After the acid treatment, the oxidation of nanotubes and the incorporation of new polar functional groups favored thermodynamic compatibility of MWCNT-COOH and water and resulted in a very stable dispersion. The functionalization with polyol provided the nanotubes a non-polar character together with a low density, what made the MWCNT-COO-g-polyol to appear as a supernatant after their dispersion. Meanwhile, MWCNT-COO-g-polyol dispersed easily and forms stable dispersion in THF. This last physico-chemical situation is sketched in Figure 7.

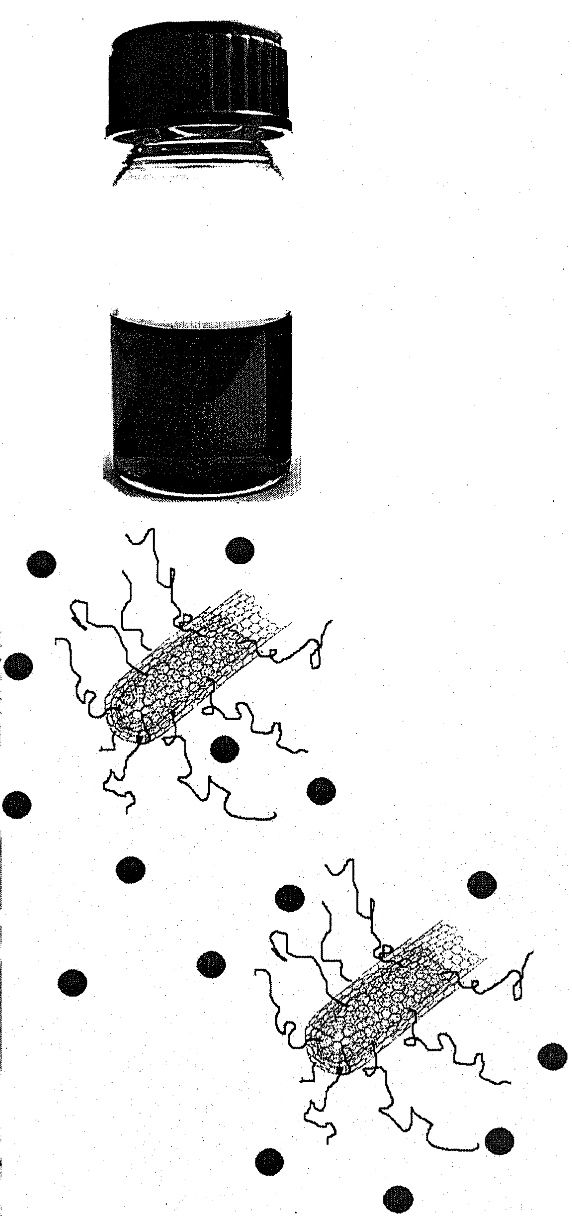


Fig. 7. Vial containing MWCNT-COO-g-polyol (stoichiometric ratio 1:200) in THF, and the schematics for physico-chemical situation.

4. CONCLUSIONS

Acid treated MWCNT resulted in a more reactive surface provided the carboxylic groups presented in the nanotubes surface, whose were analyzed by FT-IR, UV, TGA and AFM. These nanotubes were easily dispersed in water and tetrahydrofuran, contrarily to pristine nanotubes.

Polyol-functionalized nanotubes were obtained by an easy procedure. TGA and FT-IR results indicated that an important amount of polyol was still remaining over the nanotubes after being these thoroughly washed. As shown by AFM images, polyol appeared to be grafted to nanotubes surface. These nanotubes not dispersed in water but were very well dispersed in THF. These nanotubes might be further used for the synthesis of high performance polyurethane nanocomposites.

Acknowledgments: The authors wish to extend their gratitude to Basque Government ('*Etortek 2005/Bioma-GUNE 2005*' (IE05-143), '*Saiotek 2007*' (S-PE07UN02) and 'Grupos de Investigación Consolidados IT-365-07') and also Ministerio de Ciencia y Tecnología (MAT 2005-06530) for financial support.

References and Notes

1. S. Iijima, *Nature* 56, 354 (**1991**).
2. I. Kang, Y. Y. Heung, J. H. Kim, J. W. Lee, R. Gollapudi, S. Subramaniam, S. Narasimhadevara, D. Hurd, G. R. Kirikera, V. Shanov, M. J. Sculz, D. Shi, J. Boerio, S. Mall, and M. Ruggles-Wren, *Composites: Part B* 37, 382 (**2006**).
3. J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, *Science* 287, 622 (**2000**).
4. S. Ghosh, A. K. Sood, and N. Kumar, *Science* 299, 1042 (**2003**).
5. K. Geckeler and E. Rosenberg, Functional Nanomaterials, Am. Sci. Publ. (**2006**), p. 143.
6. M. P. Mattson, R. C. Haddon, and A. M. Rao, *J. Mol. Neurosci.* 6, 175 (**2000**).
7. T. J. Webster, M. C. Waid, J. L. McKenzie, R. L. Price, and J. U. Ejiofor, *Nanotechnology* 15, 48 (**2004**).
8. D. Khang, M. Sato, and T. J. Webster, *Rev. Adv. Mater. Sci.* 10, 205 (**2005**).
9. V. Lovat, D. Pantarotto, L. Lagostena, B. Cacciari, M. Grandolfo, M. Righi, G. Spalluto, M. Prato, and L. Ballerini, *Nano Lett.* 5, 1107 (**2005**).
10. J. Meng, H. Kong, H. Y. Xu, L. Song, C. Y. Wang, and S. S. Xie, *J. Biomed. Mater. Res.* 74A, 208 (**2005**).
11. S. Goyanes, G. R. Rubiolo, A. Salazar, A. Jimeno, M. A. Corcuera, and I. Mondragon, *Diamond Relat. Mater.* 16, 412 (**2007**).
12. H. Kuan, C. Ma, W. Chang, S. Yuen, H. Wu, and T. Lee, *Comp. Sci. Tech.* 65, 1703 (**2005**).
13. J. Xiong, D. Zhou, Z. Zheng, X. Yang, and X. Wang, *Polymer* 47, 1763 (**2006**).
14. H. Xia, M. Song, J. Jin, and L. Chen, *Macromol. Chem. Phys.* 207, 1945 (**2006**).
15. L. Xie, F. Xu, F. Qiu, H. Lu, and Y. Yang, *Macromolecules* 40, 3296 (**2007**).
16. J. Wang, Z. Ma, M. Huang, and Y. Jiang, *Polym. For Adv. Tech.* 7, 88 (**1996**).
17. R. T. Morrison and R. N. Boyd, Organic Chemistry, 5th edn., Prentice Hall (**1987**), p. 826.
18. D. Napal and K. E. Geckeler, Functional Nanomaterials, Functionalization of Carbon Nanotubes, Am. Sci. Publ. (**2006**), p. 57.
19. H. J. A. Zweistra and N. A. M. Besseling, *Phys. Rev. E* 74, 021806 (**2006**).
20. S. Elli, G. Raffaini, F.Ganazzoli, E. G. Timoshenko, and Y. A. Kuznetsov, *Polymer* 49, 1716 (**2008**).

Received: 30 May 2008. Accepted: 31 December 2008.