Dynamical–mechanical and thermal analysis of carbon nanotube–methyl-ethyl methacrylate nanocomposites

C Velasco-Santos[1,2], **A L Martínez-Hernández**[1,2], **F Fisher**[3],
R Ruoff[3] and **V M Castaño**[1,2,4]

[1] Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, A.P. 1-1010, Santiago de Querétaro, Querétaro 76000, México
[2] Universidad Autónoma de Querétaro, Campus Cerro de las Campanas, Santiago de Querétaro, Querétaro 76010, México
[3] Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA

E-mail: castano@fata.unam.mx

Abstract
Composites were prepared by using carbon nanotubes (CNTs) and methyl-ethyl methacrylate copolymer, modified with nonionic surfactant to improve the carbon nanotube dispersion and workability. The thermal results show that the polymer glass transition temperature increases up to 10°C and that only 1wt% CNT content improves the mechanical response by more than 200%, substantially above other reports where large quantities of CNTs were used.

1. Introduction

Carbon nanotubes (CNTs) exhibit amazing mechanical properties, such as extremely high Young's modulus, stiffness and flexibility, as has been demonstrated by experimental studies and theorical modelling [1–4]. Also the CNTs density is very low [5] and its sp^2 carbon–carbon bond in the plane of the graphene lattice is among the strongest of all chemical bonds [6]. However, in order to truly take advantage of their outstanding mechanical properties, they have to be combined to produce engineering composite materials, as it has been proposed in many works [6–11]. The development of CNTs-composites with polymer matrix have been reported in the last years through different approaches, which include load transfer [12–17], distribution [18, 19], orientation [20, 22], conductivity [23–30] , rheological behaviour [31] and optical properties [32, 33] among others. Nevertheless, very different results have been reported in the mechanical behaviour [6, 34–40] of CNTs-composites, showing that the parameters required to optimize the behaviour of these materials depend on many factors such as: the type of CNTs (either single wall CNTs-SWNT—or multiwalled CNTs-MWNT) inasmuch

as it is known that the diameter and chirality are related to elastic properties in the nanotubes [41], the production approach, due to the graphitization degree and pristine depend on the production [42, 43], etc. In addition, polymers play an important role in the important parameters in these composites (load transfer, wetting, etc), and some authors have pointed out that the wetting interaction with CNTs depends in particular on the polymer chain conformation [44, 45], but sometimes the actual experimental results contradict each other. For instance, some authors have mentioned that a linear polymer as Poly(methyl methacrylate) cannot hold the nanotubes [23] and other reports with this polymer suggest possible interaction between these two materials [19], good intercalation of the polymer between the nanotubes and bundles when the sample is not purified [18] and good dispersion [28]. The available results show that the method to produce the composites is also a factor to consider (film casting of suspensions of dissolved polymers [18, 19], polymerization [35] and melt mix [6, 21] in the case of thermoplastics). Research in this field have led to different theories about what is the best reinforcement, either SWNT or MWNT, and recently it has been suggested that the use of SWNT may be more beneficial in composites than MWNT [11], due to the diameter of SWNT respect to MWNT representing higher L/D ratio and higher mechanical

---

[4] Author to whom correspondence should be addressed.

modulus, whereas the Van der Waals forces that link the individual graphene layers together in MWNT [46], could represent a disadvantage. However, recent results agree that one can take advantage of the multiple walls in MWNT and attach functional groups to the end and wall surfaces [16, 35, 47–49], thus increasing the CNTs–polymer interfacial adhesion and chemical bonding [48]. In summary, there is enough evidence to encourage more investigation of nanotubes with different types of polymeric matrix [11], involving all factors that represent good interaction between these materials. Accordingly, in this paper we analyse some of the above factors, through dynamical–mechanical response, thermal behaviour, distribution (using a surfactant and plasticizer) and interface for a system MWNT—methyl-ethyl methacrylate copolymer (MEMA), reaching the conclusion, as it shall be shown in what follows, that MWNTs represent an excellent reinforcement, provided good care is taken in the physico-chemical details of the mixing.

2. Experimental

The polymer was provided by GIRSA (Mexico) in pellets with 96 wt% MMA and 4 wt% EMA. MWNT obtained by the arc discharge approach were employed (purchased from MER corporation grand core material) with $\approx$10–20 nm outer diameter, $\approx$2–6 nm inner diameter and lengths ranging from 1 to 10 μm, as characterized by high resolution transmission electron microscopy (HRTEM), the surfactant was triton X-100 (*t*-octyphenoxypoly-ethoxyethanol) and the Plasticizer trytolyl phosphate, both provided by Aldrich. The composites were produced by solution mixing and then cast in Teflon molds. The preparation of CNTs-composite is as follows: the MEMA copolymer was dissolved in TetraHydrofuren (T.H.) (J.T. Baker) and MWNT were sonicated in T.H. for 5 min (the samples in which we use surfactant or plasticizer were added with CNTs and solvent in this stage) and added to the polymer solution. The whole mix was sonicated at three intervals of 10 min during the first hour in the teflon molds and sonicated by 5 min during the next 5 h in order to have better distribution, then the solvent was evaporated at room temperature; the resulting films have an average thickness of $\cong$0.35 mm. The composites were prepared to 1 wt% CNTs (1), 1 wt% CNTs and 1 wt% surfactant (1S), 1 wt% CNTs and 1 wt% plasticizer (1P). The films were analysed by optical microscopy (in a Nikon Optiphot 2-pol by transmitted light) and the sample that presented apparently better distribution (1S) (as shown in figure 1) was prepared to different concentrations, namely 5 wt% CNTs and surfactant (5S), 7 wt% CNTs and surfactant (7S) and 10 wt% CNTs and surfactant (10S). The following samples were prepared as references: 0 wt% CNTs(0), 0 wt% CNTs and 1 wt% surfactant (0S), 0 wt% CNTs and 1 wt% plasticizer (0P).

All samples were analysed by thermogravimetric analysis (TGA) using a TA instruments 2950 equipment at a rate of 10°C min^{-1} and differential scanning calorimetry (DSC) in a DSC 2910 TA instruments machine heated at a rate of 10°C min^{-1}. For the dynamical–mechanical analysis (DMA) the samples were cut at 5 mm width by 25 mm large and tested in a TA instruments DMA 2980 equipment using a tension clamp, at a frequency of 1 Hz, from room temperature to 120°C.
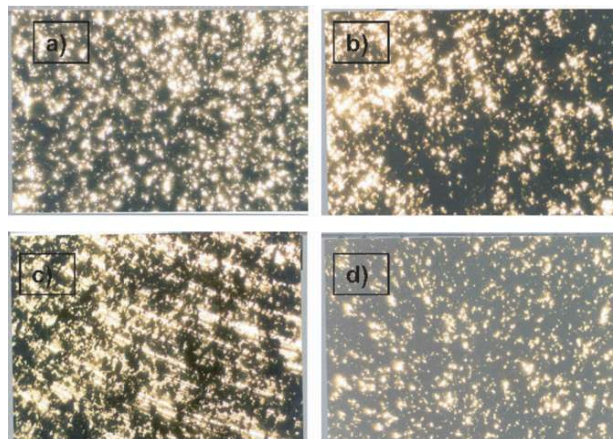

Figure 1. Optical micrograph of CNTs films: (*a*) and (*b*) CNTs composite sample 1 (MEMA—1 wt% of CNTs) different zones; (*c*) CNTs composite sample 1P (MEMA—1 wt% plasticizer–1 wt% CNTs) typical zone; (*d*) CNTs composite sample 1S (MEMA—1 wt% surfactant–1 wt% CNTs) typical zone.

For the scanning electron microscopy (SEM) analysis a LEO 1525 was used with silicon wafers as support.

3. Results and discussion

In figure 2(*a*) we show the results obtained in TGA for the films: 0 (MEMA), 0S (MEMA, 1 wt% surfactant), 0P (MEMA, 1 wt% Plasticizer), 1 (MEMA , 1 wt% CNTs), 1S (MEMA, 1 wt% CNTs, 1 wt% surfactant) and 1P (MEMA, 1 wt% CNTs, 1 wt% plasticizer). We can observe that, in the case of the samples 0P and 0S the degradation temperatures are lower than in the sample 0, which indicates that the additives change the thermal stability. However, once the CNTs (samples 1,1S and 1P) is added, the degradation temperatures are higher than those obtained with the sample 0, showing that the CNTs indeed increase the thermal stability. Here, the curve of the sample 1 is very similar to the curves corresponding to the samples 1P and 1S, indicating that, in spite of the additives improve apparently the dispersion of CNTs in the copolymer, they also decrease the degradation temperature. In figure 2(*b*) the TGA curves for the samples 1S, 5S, 7S and 10S are shown; sample 5S shows the highest degradation temperature, in contrast to the samples 7S and 10S which, despite of having a big quantity of CNTs, also contain a lot of additive and the thermal stability diminishes considerably.

Figure 3(*a*) shows the storage modulus (E') obtained by DMA (which is indicative of the elastic behaviour of the material) for the samples 0, 0S, 0P, 1, 1S and 1P. The sample with 1 wt% of surfactant (0S) has a little increase in the modulus, however, the CNTs increase the modulus at 40°C in $\cong$180%, when surfactant was used and $\cong$95% when plasticizer was used, this latter due to the plasticization that decreases the elastic modulus [50], however the most outstanding modulus is obtained with only 1 wt% CNTs without additives (sample 1), increasing the modulus by more than 200% at 40°C. This modulus represents a higher increase with respect to the matrix used at the same temperature than those obtained in CNTs composites with 26 wt% of reinforce on poly methyl methacrylate (PMMA) [6] by melt
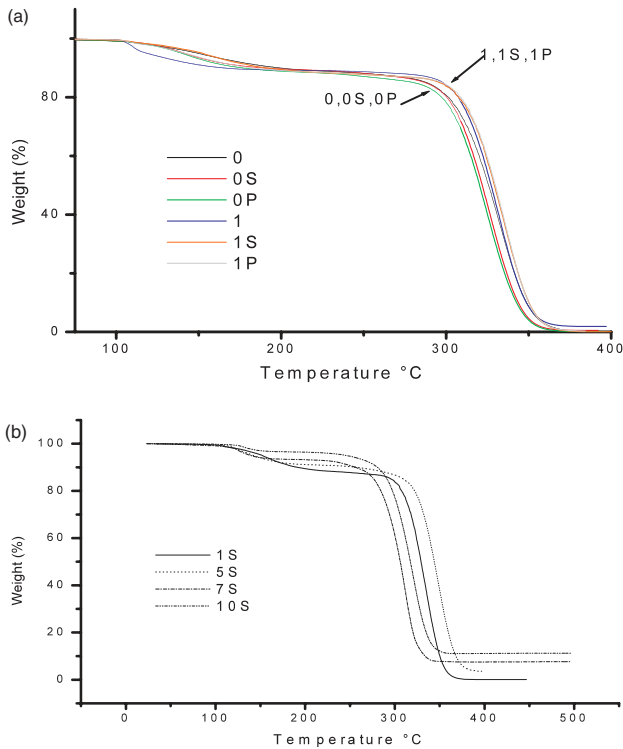
Figure 2. TGA of CNT films: (*a*) samples: 0 (MEMA), 0S (MEMA—1 wt% surfactant), 0P (MEMA—1 wt% plasticizer), 1 (MEMA–1 wt% CNTs), 1S (MEMA—1 wt% surfactant–1 wt% CNTs), 1P (MEMA—1 wt% plasticizer–1 wt% CNTs); (*b*) samples: 1S (MEMA—1 wt% surfactant–1 wt% CNTs), 5S (MEMA—5 wt% surfactant–5 wt% CNTs), 7S (MEMA—7 wt% surfactant–7 wt% CNTs), 10S (MEMA—10 wt% surfactant–10 wt% CNTs).

Figure 3 a-b

Figure 3. Storage modulus of CNTs films: (*a*) samples: 0 (MEMA), 0S (MEMA—1 wt% surfactant), 0P (MEMA—1 wt% plasticizer), 1 (MEMA—1 wt% CNTs), 1S (MEMA—1 wt% surfactant–1 wt% CNTs), 1P (MEMA—1 wt% plasticizer–1 wt% CNTs); (*b*) samples: 0S (MEMA—1 wt% surfactant), 1S (MEMA—1 wt% surfactant–1 wt% CNTs), 5S (MEMA—5 wt% surfactant–5 wt% CNTs), 7S (MEMA—7 wt% surfactant–7 wt% CNTs), 10S (MEMA—10 wt% surfactant–10 wt% CNTs).

processing, 5 wt% on PS (polystyrene) [37], 7% on PSBA (poly(styrene-co-butyl acrylate)) [38] (in that case the T_g of the polymer is 12°C obtained by DMA) and 50 wt% on poly vinyl alcohol (PVA) [40]; some of these reports have suggested that the amorphous structure of some polymers could play an important role in improving the modulus when CNTs are used as reinforcement, which is in agreement with the results published by Shaffer and Windle [40] and Jin *et al* [6], these latter authors use PMMA as polymer matrix which is an amorphous polymer and obtain more significant effects in the storage modulus than obtained by Shaffer and Windle which used PVA semicrystalline polymer. However, as explained earlier, the increase in the storage modulus obtained in this paper with 1% of CNTs is higher than the one obtained by Jin *et al* [6] with 26% of CNTs using a very similar polymer and the same type of CNTs (arc discharge MWNT used without further purification).

Also, it is important to say that we use the same polymer than them (PMMA) utilizing a polymerization approach in order to obtain the CNTs composite and the same type of CNTs [48] increasing the storage modulus ≅66% with only 1% of CNTs which is very similar to that reported by them with a higher concentration of CNTs (17 wt%, 26 wt%). This shows that other parameters take important part in the behaviour of the properties in CNTs composites, for instance the approach to produce the composites used by Jin *et al* [6] is melt blending and compression, which could cause the CNTs to have some
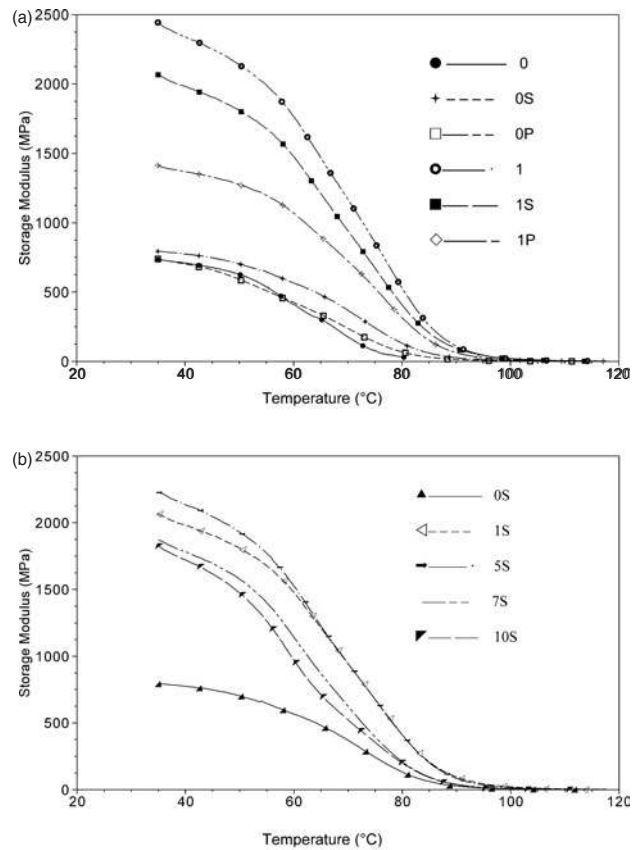
damage and perhaps the viscosity when the sample mixed is not the best to separate the CNTs from the bundle. Other reason could be that the high concentration causes the composite to become brittle as other papers report [35]; however, it is important to say that the CNTs composites produced by Jin *et al* [6] with big quantities of CNTs maintain the modulus at high temperatures. Table 1 presents a review of these results in comparison to that obtained in this paper.

Figure 3(*b*) shows the storage modulus (E') results obtained for the samples when surfactant was used (0S, 1S, 5S, 7S, 10S), E' is increased in the samples with 1 wt% and 5 wt% of CNTs with respect to the sample with only 1 wt% of surfactant, however in the samples with 7 wt% (7S) and 10 wt% (10S), E' decreases with respect to the sample 5S and 1S, this shows the possibility that in the samples 7S and 10S the surfactant affects the modulus, through a chemical mechanism, inasmuch as the surfactant was aggregated in the same quantity of CNTs. Also the surfactant here has a different behaviour in contrast to the results shown by Gong *et al* [36] in a thermoset polymer (epoxy). In their results the surfactant decreases the modulus when only 1 wt% is additionated to

Table 1. Comparative results (E', % increase E') of CNTs composites obtained in different polymer matrices at 40°C 1 Hz of frequency.

Polymer	E' (40°C, 1 Hz) (matrix) (MPa)	E' (40°C) CNTs composite (MPa)	CNTs (wt%)	% Increase E'	Reference
PMMA	$\cong$800	$\cong$1600	26	100	[6]
PS	$\cong$2400	$\cong$3500	5	44	[37]
PSBA	$\cong$0.681	$\cong$1.584	7	132	[38]
PVA	$\cong$5000	$\cong$11200	60	124	[40]
MEMA	708	2340	1	230	a

[a] Results presented in this paper.

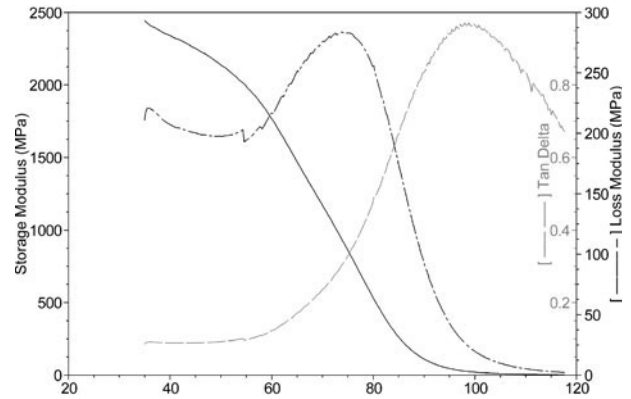**Table 2.** Comparative results of DMA on CNT composites using a surfactant in two different polymers.

Sample	Epoxy (36) E' 40°C (Mpa)	T_g °C (tan δ)	MEMA [a] E' 40°C (Mpa)	T_g °C (tan δ)
Polymer	1390	63	708	92
Polymer + surf	1150	62	774	89
Polymer 1 wt% CNTs	1550	72	2340	99
Polymer 1 wt% CNTs, 1 wt% surf	1750	88	1983	102

[a] Results presented in this paper.

Figure 4. DMA of CNT film (sample 1).

Table 3. Transition temperatures of CNT films obtained in DSC and DMA (tan δ).

Sample	T_g DMA	T_g DSC
0	92	80
0S	89	78
OP	88	74
1	99	89
1S	102	89
1P	96	86
5S	102	89
7S	98	88
10S	97	85

the polymer, however when 1 wt% of CNTs was added with same quantity of surfactant, E' increases at 40°C in $\cong$25% with respect to the epoxy sample and with 1 wt% of CNTs, E' (40°C) only increases $\cong$12% with respect to the same sample, therefore the surfactant there shows useful to improve E' when used with the same quantity of CNTs; however in this paper, the sample with 1 wt% of surfactant (0S) increases E' (40°C) $\cong$8% and, in the sample with 1 wt% of CNTs and surfactant (1S) E' (40°C) increases $\cong$180%, with 5 wt% of CNTs and surfactant E' (40°C) increases $\cong$200%, however the addition of only 1 wt% of CNTs without additive increases $\cong$230% which indicates that in this case the surfactant does not improve the modulus. This is opposite to those results using thermosetting (epoxy) [36], table 2 is a comparison between our results and those obtained using epoxy.

The mechanical results of the sample with 7 wt% and surfactant (7S) are in agreement with the results found in other papers [38], where the same quantity decreases the storage modulus (E'), however the sample 10S decreases also in different way than those found by Dufresne *et al* [38]. In fact, the majority of the results demonstrate that the spatial distribution is an open question and that it is possible that the nonhomogeneity of the samples has a strong influence, as important as the type of used polymer.

Figure 4 shows the dynamical mechanical behaviour for the sample 1; as we mentioned, E' is the storage modulus which is representative of the elastic behaviour and E'' is the loss modulus indicative of the lost energy due to the resistance to flow of the polymer chains, the ratio between E''/E' is known as tan δ, the maximum of this ratio is defined as the polymer glass transition temperature T_g [36, 51], the T_g obtained in DMA is normally higher than that obtained in DSC, the results for T_g obtained for the CNTs-composites in DMA and DSC are shown in table 3, where the T_g obtained by DMA is increased

in the samples 1S and 5S in $\cong$10°C and in DSC $\cong$9°C with respect to the sample with only MEMA (0). The sample 1, which shows the highest E', modifies the T_g in $\cong$7°C in DMA and $\cong$9°C in DSC. All the samples that contain CNTs increase the T_g, the samples 0P and 0S show a clear reduction in the T_g due to the behaviour of the plasticizer and surfactant in the polymer.

Figures 5(a)–(c) show the distribution in CNTs-composite (with MEMA matrix) of fracture surfaces, as studied by SEM inasmuch as an important argument that many papers report is a very good distribution and interface, in spite of the fact that the mechanical results do not show this effect. It was found that it is difficult that CNTs have very good distribution in the polymeric matrix by using solution mixing and casting, requiring sonication while the solvent is evaporated. This permits to distribute totally the films with the CNTs, however the contact at the interface level could be considered only as regular in some parts of the composite, due to some carbon impurities included in the load transfer. In fact, although we
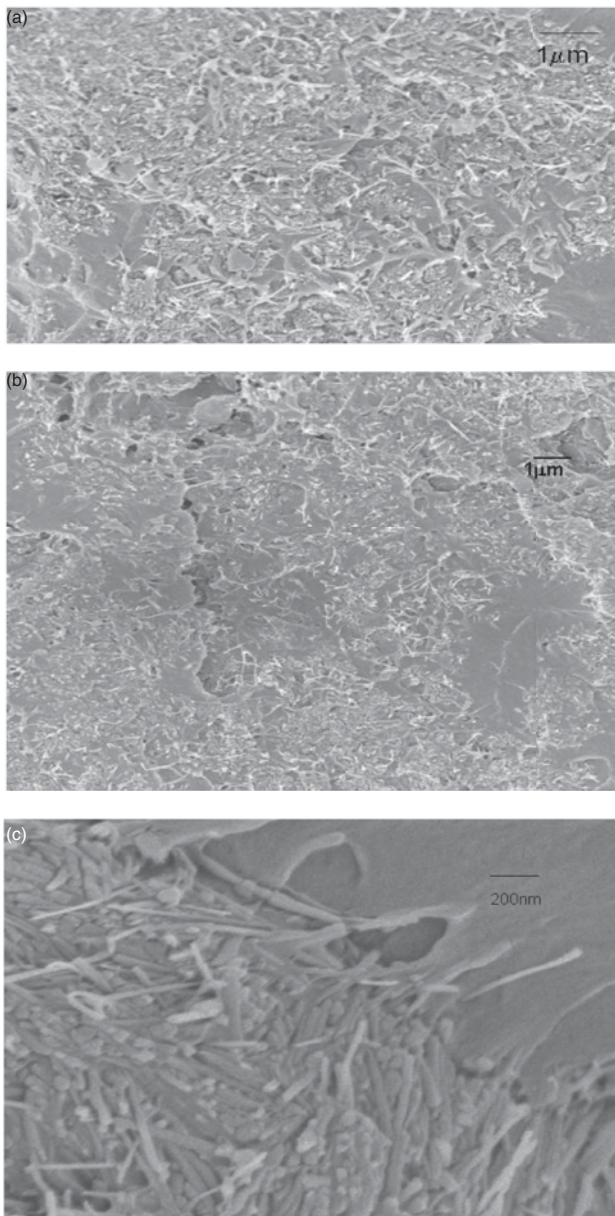
Figure 5. SEM images of CNT composites: (*a*) (sample 1S) dispersion of CNTs in MEMA matrix with surfactant, (*b*) (sample 1) dispersion of CNTs in MEMA matrix without additives (where it is possible see the intercalation of the polymer between the bundles of CNTs), (*c*) (sample 1S) CNTs composite different zone where a clear interface between bundles of CNTs and polymer is formed.

know that the nonionic surfactant utilized is a good dispersant for carbon [52], the wetting could occurs with the impurities found in the CNTs surroundings and thus create an interface only with some part of CNTs without taking full advantage of the CNTs themselves. This would produce interfaces in some parts that are not so convenient, since they form a little barrier that produce different conductivity behaviour on the sides of the film, although these films only have thickness $\cong 0.35$ mm (the conductivity behaviour will be published elsewhere) [53]. Figure 5(*a*) shows the CNTs composite surface (1S) where the CNTs are dispersed and the impurities cover several CNTs with

amorphous carbon which is not separated in the process when the composite was made. In figure 5(*b*) the CNTs composite fracture surface (sample 1) without additives, can be observed. In this figure is noticeable the intercalation of the polymer between CNTs, and the image resembles results by Stephan *et al* [18] where they propose the polymer intercalation by using PMMA between some CNT bundles. Our image shows that several CNTs are covered and wetted by the polymer. Figure 5(*c*) shows the interface found in some parts of the sample 1S, this allows to observe that individual CNTs do not have enough contact with the polymer since, in this case, the polymer seems not be mixed between CNT. It is very difficult to know how many areas like this are possible to find in the composite and this explains the lower storage modulus in CNT composites when surfactant additive was used in comparison to the sample where only CNTs were used, also this could explain the different behaviour in CNTs composites prepared by solution mixing with high concentrations of CNTs in this and other reports.

4. Conclusions

The above results demonstrate that a relatively small quantity of CNTs in a polymer matrix is capable of enhancing the storage modulus significantly and to modify the thermal stability. Interestingly, when larger quantities with additives are incorporated, the storage modulus decreases to values similar to previous reports of CNTs-composites, probably due to the fact that impurities in large concentrations prevent CNTs from achieving a good contact, resulting in a poor polymer–CNTs interfacial interaction, detrimental to the properties of the composite. However, and in spite of the carbon impurities commonly found in CNTs composites, the interaction between CNTs and the polymer can be good enough, provided the polymer is allowed to intercalate between the bundles and to wet the surface of CNTs, which could be, in principle, achieved through repeated sonication, as reported by a number of authors who, nevertheless, did not find this homogenization reflected on the mechanical and thermal properties, indicating that the adequate procedure is more complicated than simple mechanical mixing.

The additives used to distribute CNTs within the polymer composites play different roles, inasmuch as the results found here and in thermosets have different behaviour in terms of the mechanical properties. The CNTs composites analysed in this report, along with the results published by other authors show that the response of these materials depend on many factors where the polymer, the approach to make the composites and the type of CNTs seem to be some of the most important parameters in order to reach a good interface. Therefore, more studies are needed to determine all factors that play an important role in every specific matrix for CNTs composites. In particular, an important parameter could be the purification and functionalization. However, these present results indicate the feasibility to effectively incorporate CNTs as reinforcement in composite materials, since the mechanical response increased in more than 200% with only 1 wt% of CNTs (MWNT), which opens exciting possibilities for nanotubes as truly engineering materials at large scale.

Acknowledgments

References

[1] Treacy M M, Ebbesen T W and Gibson J M 1996 *Nature* **381** 678

[2] Lourie O and Wagner H D 1998 *J. Mater. Res.* **13** 2418

[3] Lourie O, Cox D M and Wagner H D 1998 *Phys. Rev. Lett.* **81** 1638

[4] Yu M-F, Lourie O, Dyer M J, Moloni K, Kelly T F and Ruoff R S 2000 *Science* **287** 637

[5] Iijima S 1991 *Nature* **354** 56

[6] Jin Z, Pramoda K P, Xu G and Goh H 2001 *Chem. Phys. Lett.* **337** 43

[7] Ajayan P M, Stephan O, Coliex C and Trauth D 1994 *Science* **265** 1212

[8] Garg A and Sinnott S B 1998 *Chem. Phys. Lett.* **295** 273

[9] Ajayan P M, Schadler L, Giannaris C and Rubio A 2000 *Adv. Mater.* **12** 750

[10] Ni B and Sinnott S B 2000 *Phys. Rev. B* **61** R16343

[11] Lau K T and Huri D 2002 *Carbon* **40** 1605

[12] Bower C, Rosen R, Jin L, Han J and Zhou O 1999 *Appl. Phys. Lett.* **74** 3317

[13] Lourie O and Wagner H D 1999 *Compos. Sci. Technol.* **59** 975

[14] Qian D, Dickey E C, Andrews R and Rantell T 2000 *Appl. Phys. Lett.* **76** 2868

[15] Ajayan P M, Schadler L S, Giannaris C and Rubio A 2000 *Adv. Mater.* **12** 750

[16] Qian D and Dickey E C 2001 *J. Microsc.* **204** 39

[17] Wagner H D, Lourie O, Feldman Y and Tenne R 1998 *Appl. Phys. Lett.* **72** 188

[18] Stephan C, Nguyen T P, de la Chapelle M L, Lefrant S, Jounet C and Bernier P 2000 *Synth. Met.* **108** 139

[19] de la Chapelle M L *et al* 1999 *Synth. Met.* **103** 2510

[20] Ajayan P M, Stephan O, Colliex C and Trauth D 1994 *Science* **265** 1212

[21] Haggenmueller R, Gommans H H, Rinzler A G, Fischer J E and Winey K I 2000 *Chem. Phys. Lett.* **330** 219

[22] Jin L, Bower C and Zhou O 1998 *Appl. Phys. Lett.* **73** 1197

[23] Coleman J N, Curran S, Dalton A B, Davey A P, McCarthy B, Blau W and Barklie R C 1998 *Phys. Rev. B* **58** R7492

[24] Coleman J N, Curran S, Dalton A B, Davey A P, Mc Carthy B, Blau W and Barklie C 1999 *Synth. Met.* **102** 1174

[25] Fan J, Wan M, Zhu D, Chang B, Pan Z and Xie S 1999 *Synth. Met.* **102** 1266

[26] Musa I, Baxendale M, Amaratunga G A J and Eccleston W 1999 *Synth. Met.* **102** 1250

[27] Sandler J, Shaffer M S P, Prasse T, Bauhofer W, Schulte K and Windle A H 1999 *Polymer* **40** 5967

[28] Stephan C, Nguyen T P, Lahr B, Blau W, Lefrant S and Chauvet O 2002 *J. Mater. Res.* **17** 396

[29] Kymakis E, Alexandou I and Amaratunga G A J 2002 *Synth. Met.* **127** 59

[30] Benoit J M, Corraze B and Chauvet O 2002 *Phys. Rev. B* **65** 241405

[31] Pötschke P, Fornes T D and Paul D R 2002 *Polymer* **43** 3247

[32] Ago H, Petrisch K, Shaffer M S P, Windle A H and Friend R F 1999 *Adv. Mater.* **11** 1281

[33] Dalton A B, Byrne H J, Coleman J N, Curran S, Davey A P, McCarthy B and Blau W 1999 *Synth. Met.* **102** 1176

[34] Schadler L S, Giannaris S C and Ajayan P M 1998 *Appl. Phys. Lett.* **73** 3842

[35] Jia Z, Wang Z, Xu C, Liang J, Wei B, Wu D and Zhu S 1999 *Mater. Sci. Eng.* A **271** 395

[36] Gong X, Liu J, Baskaran S, Voise R D and Young J S 2000 *Chem. Mater.* **12** 1049

[37] Thostenson E T and Chou T-W 2002 *J. Phys. D: Appl. Phys.* **35** L77

[38] Dufresne A, Paillet M, Putaux J L, Canet R, Carmona F, Delhaes P and Cui S 2002 *J. Mater. Sci. Lett.* **37** 3915

[39] Cooper C A, Ravich D, Lips D, Mayer J and Wagner H D 2002 *Compos. Sci. Technol.* **62** 1105

[40] Shaffer M S P and Windle A H 1999 *Adv. Mater.* **11** 937

[41] Lourie O, Wagner H D, Zhang Y and Iijima S 1999 *Adv Mater.* **11** 931

[42] Ebbesen T W 2000 *Carbon Nanotubes Preparation and Properties* (Boca Raton: CRC Press)

[43] Tanaka K, Yamabe T and Fukui K 1999 *The Science and Technology of Carbon Nanotubes* (Oxford, UK : Elsevier)

[44] McCarthy B *et al* 2002 *J. Phys. Chem. B* **106** 2210

[45] Lordi V and Yao N 2000 *J. Mater. Res.* **15** 2770

[46] Cumings J and Zettl A 2000 *Science* **289** 602

[47] Velasco-Santos C, Martínez-Hernández A L, Lozada-Cassou M, Alvarez A and Castaño V M 2002 *Nanotechnology* **13** 495

[48] Velasco-Santos C, Martínez-Hernández A L, Fisher F, Ruoff R S and Castaño V M 2003 *Chem. Phys. Lett.* submitted

[49] Velasco-Santos C, Martinez Hernandez A L and Castaño V M 2003 *J. Phys. Chem. B* Submitted

[50] Parby R J 1982 *The Technology of Plasticizers* (New York: Wiley-Interscience)

[51] Menard K P 1999 *Dynamic Mechanical Analysis: A Practical Introduction* (Boca Raton: CRC Press)

[52] Rosen M J 1989 *Surfactants and Interfacial Phenomena* (New York: Wiley-Interscience)

[53] Velasco-Santos C, Martínez-Hernández A L and Castaño V M in preparation