MECHANICAL AND ELECTRICAL BEHAVIOR OF A PEEK / CARBON NANOTUBES COMPOSITE

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Abstract
This study is a part of our on-going research in the frame of the INMAT project managed by AIRBUS Operation (certified by AESE competitiveness pole) and in partnership with some other academic institutions. The main aim of INMAT is to produce carbon fibers/PEEK laminates with enhanced electrical properties by integrating MWCNT without using any compatibilizers. Thus, industrial MultiWalled Carbon Nanotubes (MWCNT) were dispersed into a PEEK matrix to manufacture first granulates owing to a twin screw extruder (IPREM University of Pau). The MWCNT weight contents were 1, 3 and 5%wt. Tests specimens and films were then manufactured in order to carry out mechanical and electrical characterizations, using DDS, DMA, nanoindentation equipments.

1. Introduction

Nanocomposites with carbon nanotubes have been extensively studied for several years now. Among the various publications dealing with nanocomposites, numerous authors have focused their research work on the improvement of electrical conductivity thermoplastics polymers particularly by integrating MWCNT into the matrix. Ref. [1] gives a good overview of the different studies carried out on thermoplastics reinforced with MWCNT. References [8-10] are giving the more recent developments and results concerning thermoplastic matrix nanocomposites. When focusing onto high performances thermoplastic matrix nanocomposites such as PEEK, the number of public published papers becomes lower [4,5,6,10,11]. As said in the abstract, the aim of this study is to obtain a new generation of composite materials by integrating MWCNT into the PEEK matrix of carbon fibers/PEEK composites. Reaching this end requires several steps as: i) filling the PEEK matrix with MWCNT, ii) impregnating the carbon fibers with the PEEK/MWCNT matrix, iii) manufacturing composite carbon/PEEK/MWCNT parts. This paper only deals with the study of some physical properties and the mechanical behaviour of PEEK/MWCNT nanocomposites. Nevertheless our results concerning carbon fibers / PEEK / MWCNT laminated plates are given in [16]. Two kinds of PEEK/MWCNT nanocomposites have been treated here, one is PEEK/MWCNT films and the other one is PEEK/MWCNT tensile test specimens injected. It is important to notice that MWCNT are blending with PEEK matrix without added any compatibilizers. Indeed, it is important to understand that MWCNT are used to obtain electrical isotropic properties and not to improve mechanical properties.

2. Materials and experimental details

The material used in this study is a thermoplastic polymer PEEK supplied by Evonik. During this research program, two grades of PEEK powder were used: 2000P and 1000P. These two grades exhibit different viscosities at PEEK melting temperature. PEEK 1000P has a lower viscosity (150 Pa.s at 380°C) than 2000P (270 Pa.s at 380°C) and consequently its processing is easier. Both PEEK grades exhibit a glass transition temperature of 149°C (determined by MDSC) or 158°C (i.e. temperature of main mechanical relaxation determined by DMA at 10Hz). The MWCNT used in this work were supplied by Arkema: Graphistrength C100. Their main characteristics can be obtained from http://www.graphistrength.fr/. These MWCNT exhibit a length ranging from 0.1 up to 10 µm, outer diameters laying between10 and 15 nm and have between 5 and 15 walls.

After a premixing stage, PEEK powder and C100 multiwalled carbon nanotubes were fed into the hopper of a twin-screw co-rotating extruder. The full dispersion of MWCNT into the PEEK matrix was obtained at 380°C. A single configuration of screw was used, but an analysis of the influence of the extrusion conditions (T°, Torque, Screw rotation speed) upon the electrical conductivity depending on the MWCNT Wt% has been made. This work was carried out by IPREM-CANBIO (iprem.univ-pau.fr/). In this paper are given the results for only one of the PEEK/MWCNT mixing conditions: 400 rpm-with a torque applied of 11 N.m and a hopper feeding of 1 $kg.h^{-1}$.

The electrical conductivity at room T° and the percolation threshold in PEEK matrix as a function of MWCNT weight content has been studied by CIRIMAT (www.cirimat.cnrs.fr/) on films made of grade 2000P PEEK filled with Graphistrength C100 MWCNT. PEEK/MWCNT granulates obtained using a twin-screw co-rotating extruder at 380°C, were hot-pressed (parallel plates press) at 380°C for 2 minutes in order to get thin films (200 µm average thickness). Fig. 1 shows that electrical percolation threshold is reached for a MWCNT weight content of 2.5%wt. At room temperature and with direct current (DC) neat PEEK exhibits an electrical conductivity of 10^{-14} S/cm. When filled with 3%wt of MWCNT in the matrix the electrical conductivity goes up to 1.10^{-4} S/cm. From this MWCNT weight content (i.e. 3%wt), when increasing the weight content the electrical conductivity slightly goes up to reach a maximum of 1.10^{-3} S/cm.

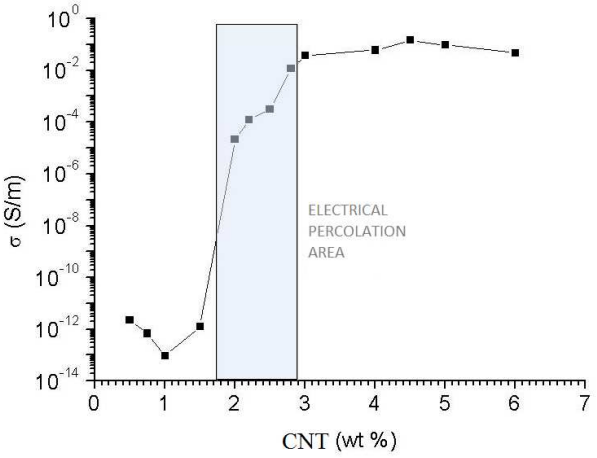

Figure 1. Electrical conductivity σ (S/cm) measurements of PEEK as a function of weight content of MWCNT. Measurements performed by Dynamical Dielectric Spectroscopy (DDS) at 0.01 Hz

After this previous study, it seems logical to work with some blends of PEEK filled by MWCNT around the percolation threshold. Thus, several MWCNT weight content were chosen: 1, 3 and 5%wt MWCNT. The PEEK/MWCNT granulates supplied by IPREM were

poured in an injection molding press to obtain normalized tensile test specimens (bone-like test specimen) with a thickness of 4 mm and a width of 10 mm (EN2561). These tensile test specimens will be used to characterize mechanically PEEK/MWCNT nanocomposites.

3. Results and discussion

3.1 Electrical characterization of PEEK/MWCNT nanocomposites

Electrical characterization has been performed using Dynamic Dielectric Spectroscopy measurements (DDS) made owing a Solartron 1260 on the various PEEK/MWCNT films. This technique uses a wide range of temperatures (-150 to 300°C) and frequencies (10^{-2} to 10^{6} Hz) in order to measure materials impedances from 10 to 10^{14} Ω [17]. Tests were practiced on PEEK/MWCNT films at 1, 3 and 5%wt of MWCNT. Fig.2 shows the results about electrical conductivity. They highlight that samples with 3 and 5 %wt of MWCNT have pretty much the same electrical conductivity (3.10^{-5} and 6.10^{-5} S/cm) which is coherent with previous results about the percolation threshold. Indeed both samples are above the electrical percolation threshold (2%wt of MWCNT). Moreover both of these samples have a conductive behaviour due to their constant electrical conductivity at any frequencies. On the contrary, sample with 1%wt of MWCNT shows an electrical conductivity weaker than others: 5.10^{-7} S/cm. Until 10000 Hz all curves of Fig. 2 show that the materials conductivity remains independent of frequency (i.e. this is typical of a purely conductive material - a metal).

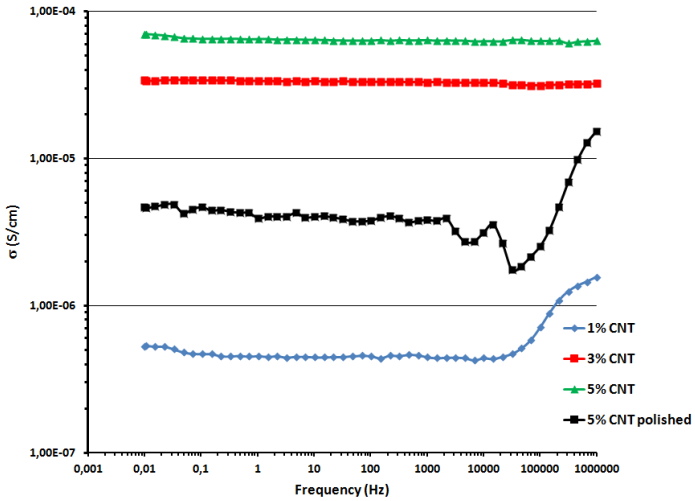

Figure 2. Electrical conductivity (σ) as a function of frequencies at room temperature for different wieght content of PEEK/MWCNT film

In order to analyse the dispersion state of MWCNT into PEEK matrix a superficial polishing above the two sides was made on a PEEK/5% wt MWCNT film (new thickness ≈ 150µm). In that case, and for sample with 1%wt of MWCNT, it is interesting to note that the electrical conductivity changes as a function of frequency for frequencies higher than 10 kHz. Effectively when increasing current frequency, the electrical conductivity also increases. This kind of behaviour is typical of insulating materials. For sample with 1%wt MWCNT, this is not a surprising result. This is due to its too low weight fraction of MWCNT which is under the percolation threshold. Concerning sample with 5%wt MWCNT polished, this behaviour could mean that MWCNT are mainly concentrated on the surface of films and badly dispersed in the thickness. Moreover electrical conductivity varies from 6.10^{-5} S/cm to 4.10^{-6} S/cm whatever the frequency employed. Thus PEEK/MWCNT film process was modified in order to obtain a better dispersion in all the film thickness.

3.2 Crystallization and melting studies of PEEK doped by MWCNT

In order to define the influence of MWCNT weight fraction on the crystallinity of the PEEK matrix, DSC measurements were carried out on PEEK/MWCNT films at different weight content of MWCNT: 2, 4, 6, and 8%wt. Changes in the degree of crystallinity can affect the physical and mechanical properties of a semi-crystalline thermoplastic matrix. For example, as the crystallinity increases the modulus increases, but the toughness decreases [15]. So it is important to know the influence of MWCNT (Graphistrength C100) on PEEK crystallinity. Fig.3 shows DSC thermograms of melting peaks (a) and crystallization peaks (b) of the different nanocomposites tested. As shown in Fig. 3a and Tab.1 there is no influence of MWCNT weight content on PEEK melting temperature which remains at 343°C. However, the melting enthalpy (area of the melting peak) decreases slightly when increasing MWCNT content but it could be considered insignificant due to standard deviation of measures (Tab. 1). However, (Fig. 3b) crystallization has been influenced by the incorporation of MWCNT. From 2%wt MWCNT, crystallization peaks exhibits a shift toward higher temperatures. Neat PEEK has a crystallization temperature of around 302°C whereas nanocomposites PEEK/MWCNT exhibit a crystallization temperature close to 310°C. Considering standard deviation of measurement (± 2 J/g), the crystallization enthalpy slightly decreases when increasing MWCNT weight content. Final degrees of crystallinity (Eq. 1 [7]) shown in Tab. 1 are independent from weight fractions of MWCNT within the range studied here.

$$X_{mc} = \frac{\Delta H}{(1 - X_{mr}) \cdot H_f} \qquad (1)$$

where X_{mc} is crystallinity weight fraction; X_{mr} is MWCNT crystallinity weight fraction; H_f is melting enthalpy of PEEK at 100% of crystallinity (130 J/g) and ΔH is melting enthalpy of PEEK and PEEK/MWCNT samples measured.

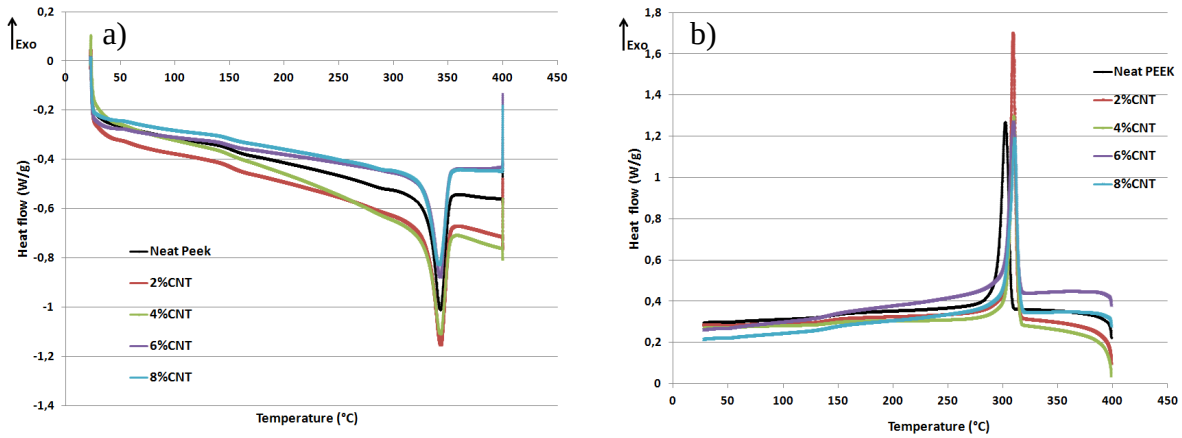

Figure 3. DSC thermograms of melting peaks and crystallization peaks of neat PEEK and PEEK/MWCNT. Three samples were measured per MWCNT rate.

	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	X_c (%)	Tg (°C)
Neat PEEK	342,9 ± 0,2	39,3 ± 1,3	302,2 ± 0,2	49,7 ± 2,3	30 ± 1	149,4 ± 0,3
2%wt MWCNT	343 ± 0,2	39,2 ± 1,9	309,3 ± 0,1	48,5 ± 2,5	31 ± 1	150,9 ± 0,9
4%wt MWCNT	342,8 ± 0,1	36,5 ± 5	309,1 ± 1,5	46,7 ± 1,4	29 ± 4	148,9 ± 1,3
6%wt MWCNT	343 ± 0,2	33,9 ± 1,1	309,3 ± 0,6	43 ± 2	28 ± 1	147,2 ± 2,9
8%wt MWCNT	342,5 ± 0,4	34,2 ± 4,8	310,5 ± 0,5	42,7 ± 3,1	29 ± 4	150 ± 0,3

Table 1. Summarize of DSC results on neat PEEK and PEEK/MWCNT. (Glass transition temperature T_g not shown on Fig. 3)

3.3 Mechanical characterization

3.3.1 Static study

Tensile tests were done with an INSTRON 8501 testing machine. They were carried out on tensile test specimen for with appropriate dimensions according to AIRBUS standard. For each nanocomposite five samples were stressed with strain gages or an extensometer (with a tensile speed of 2 mm/min). Fig. 4 shows the results and it appears that the introduction of MWCNT into PEEK matrix modifies drastically the mechanical behaviour of PEEK thermoplastic. Indeed this effect is well known for PEEK composites doped by short fibres (glass or carbon), or PEEK with important weight fraction of MWCNT (> 9% wt) [11]. Pictures of samples and curves stress/strain of Fig. 4 exhibit very well this modification. In fact, PEEK composite changes from ductile behaviour (neat PEEK) to brittle behaviour (PEEK/MWCNT). Moreover breakage strain is divided by 10 for PEEK/MWCNT compared with neat PEEK. Tab. 2 highlights mechanical results for neat PEEK and PEEK/MWCNT. Concerning elastic modulus there is no important variation except for 5%wt of MWCNT where a significant increase can be noticed (+ 12%). The others mechanical properties like ultimate tensile stress or yield stress ($Re_{0.2\%}$), exhibit no important changes between neat PEEK and PEEK/MWCNT (Tab.2).

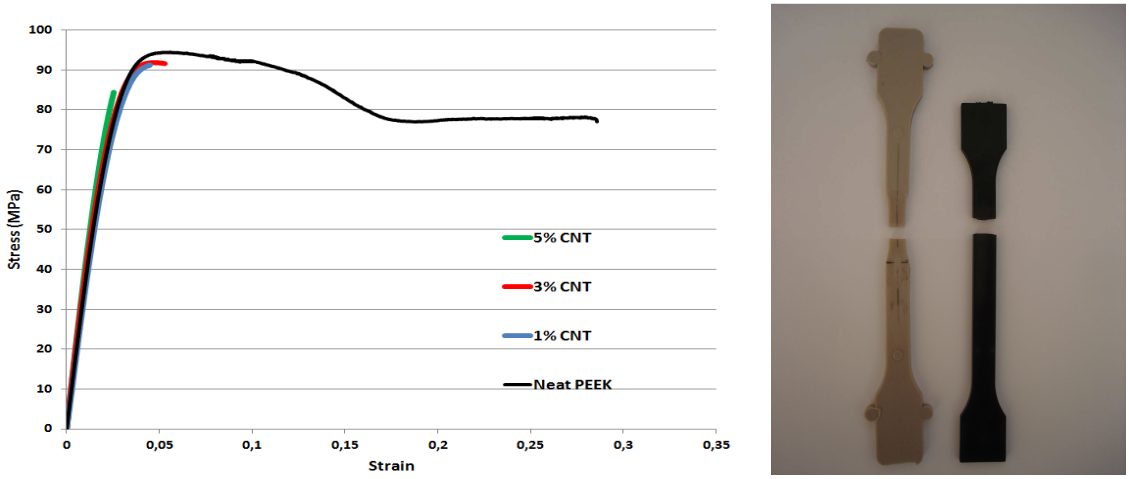

Figure 4. Stress / strain curves of neat PEEK and PEEK/MWCNT at different weight fractions. Pictures of tensile test specimen of neat PEEK and PEEK/5%wt of MWCNT after breakage.

Material	*Neat PEEK*	*1%wt MWCNT*	*3%wt MWCNT*	*5%wt MWCNT*
Young Modulus (MPa)	3678.6 ± 71.3	3703.3 ± 82.9	3774.5 ± 125.1	4145.3
σ_{rmax} (MPa)	91.8 ± 4.9	83 ± 9.1	80.5 ± 10.8	84.4
ε_{rmax} (%)	28.6	3.3 ± 1	5 ± 1	2.5
σ at ε_x= 0.2% (MPa)	62.2 ± 0.1	60.6 ± 5	60.6 ± 4.6	66

Table 2. Summary table of the different experimental mechanical results for neat PEEK and PEEK/MWCNT

3.3.2 Dynamic mechanical characterization

In order to complete mechanical characterization, some other tests were done using a Dynamic Mechanical Analyzers (DMA) Metravib +100. Samples, sizes 20 x 10x 4 mm^3, were exposed to tensile test (ε_{max} 0.3%) at a frequency of 10 Hz from room temperature to 320°C. The heating rate is 5°C/min. Fig.5a) shows storage modulus of neat PEEK and

PEEK/MWCNT whereas Fig. 5b) exhibits the loss angle tangent (Tan δ) as a function of temperature. The introduction of MWCNT at low rate (max 5% wt) does not improve the storage modulus of PEEK thermoplastic in agreement with previous tensile results (3.3.1). Moreover, on the rubber-like state (T > 220°C), the storage modulus E' is constant whatever the MWCNT weight fractions. Fig. 5b) shows that whatever the MWCNT weight content, the mechanical manifestation of glass transition occurs always at the same temperature. Effectively, α peak, which is the main mechanical relaxation, exhibits a temperature T_α = 168°C for all tested samples and this independently of the MWCNT weight content. This result is in good agreement with those reported in references [4, 11] regarding PEEK thermoplastic matrix with CNT, but do not meet the conclusions given in reference [1] which deals with MWCNT in a thermosetting matrix. In this latter case, introduction of MWCNT generates an increase in T_α or T_g (depending on experimental method used). For the thermosetting matrix [1], this increase in T_g is usually due to covalent bond between MWCNT and matrix three-dimensional crosslinked network. However, peak temperature is not the single information that can be obtained from DMA experiments. The shape (i.e. magnitude and half-height width) of α peak gives also some information about the material. As it can be seen in Fig. 5b) the α peak magnitude changes as a function of MWCNT weight content. PEEK samples containing 1 and 3% MWCNT exhibit higher Tan δ peak magnitudes than neat PEEK. Nevertheless, Tan δ peak magnitudes becomes lower than the one of neat PEEK when the MWCNT weight content reaches 5%. Thus, the significant presence of MWCNT decreases chains mobility of polymer macromolecules in the amorphous phase of PEEK matrix. Finally, it should be pointed out that whatever the MWCNT weight fraction, there is no changes of the half-height width of α peaks.

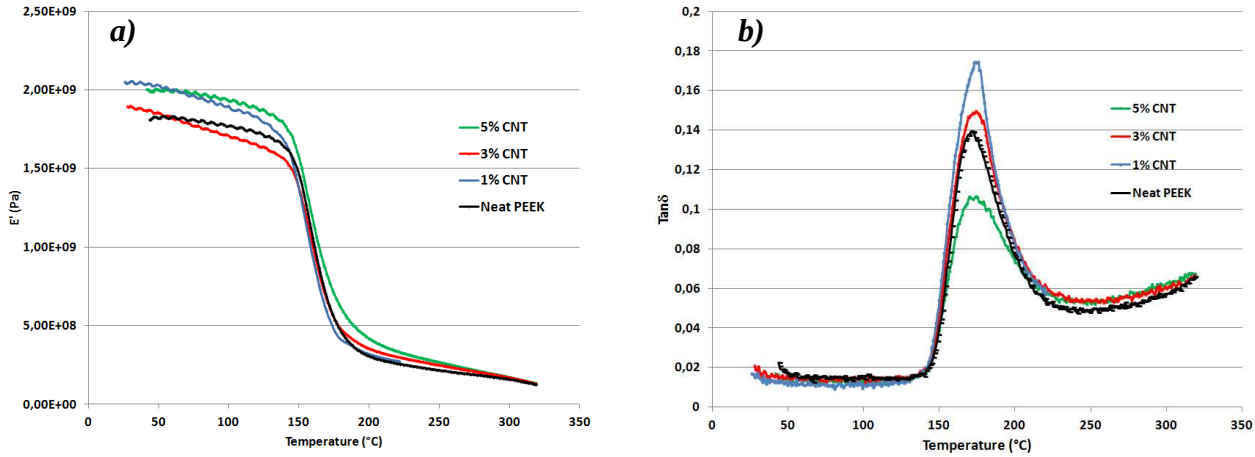

Figure 5. Dynamic Mechanical Analysis of nanocomposites behaviour. a) Storage modulus E' (Pa) and b) Tan δ as a function of temperature for neat PEEK and PEEK filled with 1, 3 and 5 %wt of MWCNT

3.3.3 Nanoindentation study

In order to specify MWCNT dispersion into PEEK matrix all along the surface and in its thickness, a nanoindentation study was performed using a CSM Nano Hardness Tester. Measurements were made on neat PEEK and PEEK/MWCNT tensile test specimens. This nanoindenter used a Berkovitch diamond head which penetrates vertically in the sample surface with a maximal load of 100 mN. This load is kept constant during 10 s and gradually decreased until a total relaxation. Nanoindenter also measures depth penetration into the sample (here 4000 nm). In this way the elastic modulus may be determined due to the relationship between hardness and elastic modulus. Roughness of sample surface is an important parameter [12]. Indeed ISO 14577-4 standard requires a R_a lower than 5% of the maximal depth penetration. Several authors [3, 13, 14] also study roughness influence on

nanoindenter measures. In this study, depth penetration is 4000 nm so R_a has to be lower than 200 nm. Thus, a polishing operation was carried out on sample surface with different SiC papers and diamond powders until 1 µm. The mean R_a obtained for each sample is between 0.04 and 0.2 µm which is in good agreement with ISO 14577-4. Fig.6 shows for each samples surface how 12 indents were made and the shape of nanoindent. After the first sweep of measures on the sample surface, a milling operation is carried out in order to remove 1 mm of thickness. After the milling, it is necessary to polish again due to the high roughness of this process. All this steps are carried out until the core of sample (2 mm thickness).

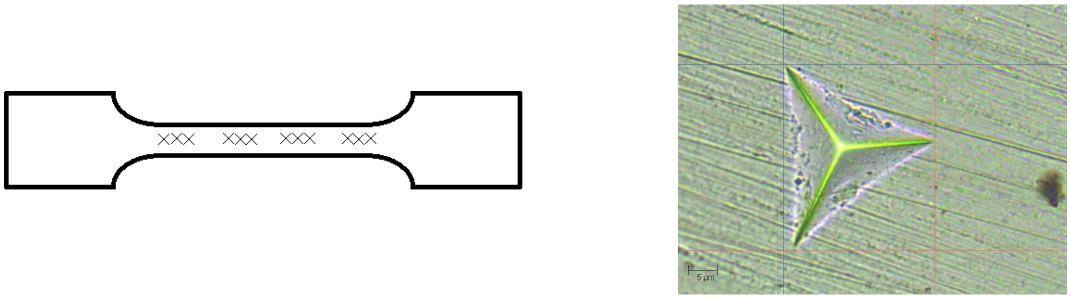

Figure 6. Scheme of 12 indents made on surface samples and picture of one indent

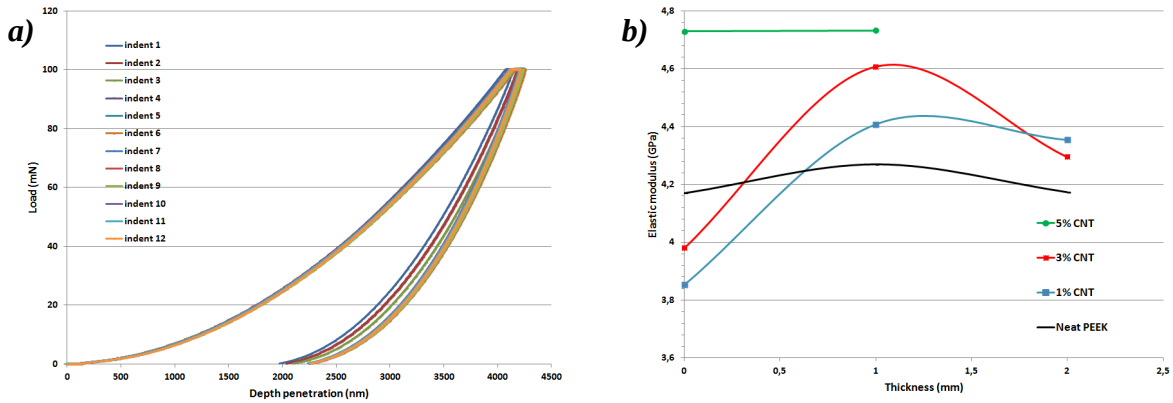

Figure 7.a) Example of load/release curves of nanoindenter as a function of depth penetration and b) Evolution of elastic modulus as a function of sample thickness for neat PEEK and PEEK/MWCNT nanocomposites.

Fig. 7a) exhibits load/release curves of nanoindenter for 12 indents carried out all along the sample surface. There is a very good reproducibility of the results as shown in Fig. 7a). Fig. 7b) shows the changes in elastic modulus as a function of sample thickness. Although neat PEEK reveals an elastic modulus almost constant through all sample's thickness, PEEK/MWCNT nanocomposites display an important increase in elastic modulus from surface to sample core (+16%). This increase suggests that MWCNT are more present in sample core than on surface sample. It should be noted that for 5% wt MWCNT there is only measurements for the surface and 1 mm of thickness because sample was broken during the second milling operation and there is no other sample available at this weight fraction. However, at 5% wt of MWCNT elastic modulus seem to be independent to the thickness. It should be due to the high filler rate and consequently MWCNT are present everywhere in the sample.

4. Conclusion

DDS measurements enabled the minimum MWCNT weight content needed to make the PEEK matrix conductive and reach the electrical percolation threshold to be determined (i.e. 2% wt). Mechanical characterization shows that added filler content into PEEK matrix don't impact its rigidity due to weak weight fraction introduced. However, mechanical behaviour is deeply modified, from ductile for neat PEEK to brittle for PEEK/MWCNT. And this whatever MWCNT weight fractions were. DSC and DMA experiments do not reveal significant changes in the degree of crystallinity and the glass transition temperature T_g between neat PEEK and PEEK/MWCNT. Nevertheless it should be remembered that the introductions of MWCNT in the PEEK matrix induces some non-negligible changes in α peak. This shows that MWCNT modify the chains mobility into PEEK matrix. Obviously a more accurate study of this phenomenon should be performed.
Nanoindentation measurements performed on injected bone-like tensile samples have revealed that the apparent modulus of nanocomposites changes through the thickness of the samples. This shows that the distribution of MWCNT is not constant through the bone-like tensile samples' thickness. The modulus is higher in the samples midplane than in the surfaces. This is certainly due to the flow phenomena occurring during the injection of these samples. In order to complete this analysis upon the distribution of MWCNT through the thickness of injected samples, DSC experiments have just been started on samples cut-out from surfaces and core. Effectively it can be argued that the changes in modulus through thickness could be due to changes in PEEK matrix degree of crystallinity. Consequently DSC experiments will enable to discard or to confirm this assumption.

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