EVALUATION OF MECHANICAL MIXING IN MULTIWALLED CARBON NANOTUBES (MWNT)/POLYAMIDE NANOCOMPOSITES MANUFACTURED BY SELECTIVE LASER SINTERING

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Nanocomposites of polyamide (PA) and multiwalled carbon nanotubes (MWNT) were prepare through direct mechanical mixing and selective laser sintering, designated by PA/0.5%CNT. The morphology and structure of as-received MWNT were characterized by Raman spectroscopy and scanning electronic microscope. Results indicated a high degree of agglomeration and structure with low defect density. Surface fracture of composites presented more brittle characteristics than pure polymer. Mechanical fracture of composite showed a insufficient dispersion of nanotubes in the matrix, resulting in a small difference on dynamical mechanical analyzes for composite and pure polyamide. Thus, become interesting to try new routes in order to obtain composites with improved dispersion and surface modificated through chemical processes.

1. Introduction

Carbon nanotubes (CNTs) belongs to a special material class. Their unique physical and mechanical properties are specially attractive. These characteristics include their high mechanical strength (elastic modulus ~1 TPa) and unusual electronics properties (Ko, 2004). CNTs can achieve very high aspect ratios because their diameters are in the range of a few nanometers with lengths of several hundred nanometers (Jose, 2007).

Exceptionally strong materials could be synthesized by combination of a soft polymer matrix with nanosized, rigid filler particles (Mulhaupt, 2001). The incorporation of multi-walled carbon nanotubes into polymer matrices can improve mechanical properties with the effective load transfer between matrix and the filler. Formation of nanotube network in the composite matrix promote conducting capacity on insulating materials.

Polyamide (PA) has been regarded as one of the most important engineering polymer due to its good processability, mechanical properties and thermal stability. Nanocomposites of polyamide based on carbon nanotubes are promising to specific applications like aerospace and aeronautic materials, because the intended properties such as low weight, high tensile strength and thermal stability.

Selective Laser Sintering (SLS) is an important and popular technology. SLS can build parts in polymers, ceramics and metals. The process uses a laser that sinters selectively a thin layer of powder spread over a moving platform. This technique is much promise since that become possible

to obtain complex parts directly from CAD data. Combination between specifique material and appropriate manufacturing process have potential future.

In this study we report a direct mechanical mixing in order to obtain nanocomposites of MWNTs and powder polyamide. Dispersion and functionalization techniques are laborious and expensive (Yu, 2006). Mechanical mixing is an alternative method since that both materials used in experiment, MWNTs and PA, presents powder form. The composites were characterized for the morphology and dynamical mechanical properties.

2. Materials and methods

2.1 Materials

Multi-walled carbon nanotubes (MWNTs) proceeding from MER corp., were used in this work. The carbon nanotubes had been gotten by chemical vapour deposition (CVD), and present, according to manufacturer, average diameters of 140 +/- 30nm, lenght of 7 +/- 2µm and purity level higher than 90%.

The polyamide (PA) used as polymeric matrix was, PA Duraform – from 3D SYSTEMS. According to material data sheet (Duraform^{TM}), the melting point is 184 ºC with average grain size of 58µm.

2.2 Mechanical mixing

Nanocomposites containing a filler content of 0.5wt% of multi-walled carbon nanotubes were mixed with polyamide powder by mechanical mixing. The homogeneity was obtained by cylindrical blender during 70 minutes at 700rpm.

2.3 Composite preparations

Specimens built by Selective Laser Sintering (SLS) was obtained in order to make a previous analysis of mechanical behavior of composite PA/MWNTs. The qualitative analyse of dispersion and distribution of CNTs using morphological images was possible using the same specimens. Both pure and composite materials were manufactured with same processing parameters in order to obtain comparative results.

The specimens were manufactured using 3.8W of laser power and scan speed of 44,5mm/s. The nominal power of equipment is 10W. Layer thickness and scan spacing of 200µm and 250µm respectively, had consisted the other processing parameters applied.

2.4 Characterization

Samples of as-received MWNTs were investigated by Raman spectroscopy, Renishaw inVia Raman Microscope equipped with a system of argon laser (514nm). The data acquisition was

obtained with 100% of laser power with only one accumulation in each region. The range scanning was from 100 to 3200cm^{-1}.

Scanning electronic microscope (SEM) was used to verify the efficiency of distribution and morphology of nanotubes on the matrix.

Dynamical mechanical analyzes using a DMA Q800 equipment were performed in order to obtain mechanical properties. The stress-strain test was performed using single cantilever clamp, controlled force mode, temperature of 30 ºC and rate of 2N/min. The dynamical test was performed the same clamp and multi-strain mode. The frequency applied was 1 Hz and -50 to 190 ºC for scanning range temperature.

3. Results and discussion

3.1 Characterization of the as-received MWNTs

Fig. 1a show a image of as-received MWNTs with big amount of agglomerated particles. The high degree of agglomeration intend this raw material should be treated in order to improve the dispersability. According to Fig.1b can be seen that the average particles size presents a range of 40µm. Average sizes of particles as this suggest that a great amount of carbon nanotubes are entangled. The enormous surface area can be accepted as one of the main causes of the entanglement, therefore it is related with the raised surface energy characteristic of the nanomaterials.

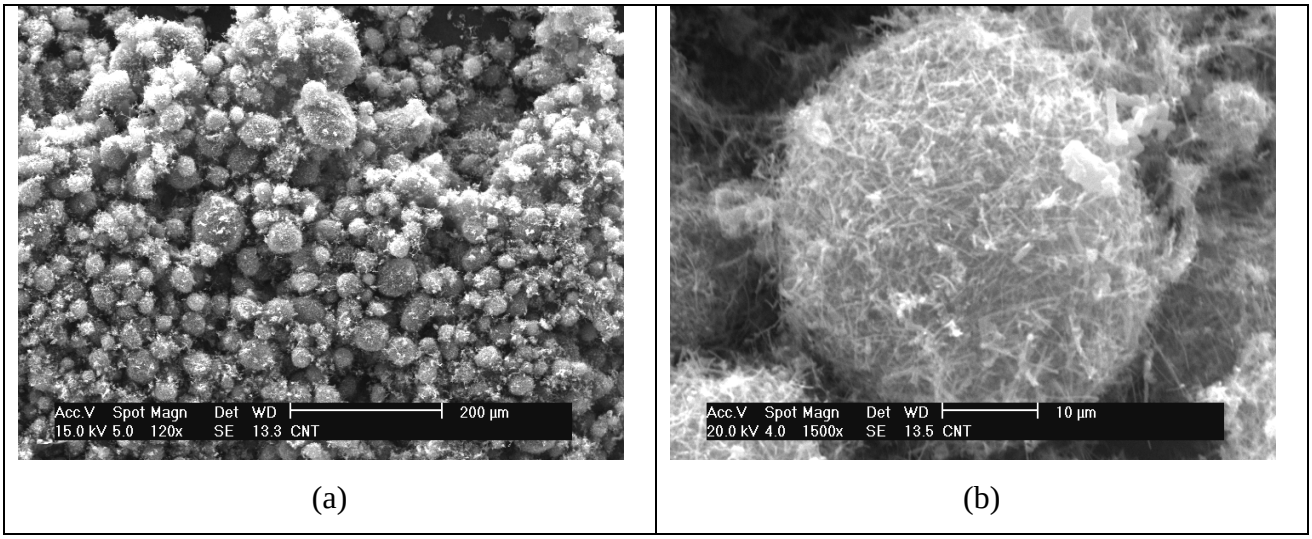

Figure 1 – SEM image of (a) as-received MWNTs, (b) Bundled MWNTs.

Fig. 2 present a Raman spectra recorded at as-received MWNTs. The main features in the first order spectrum are the disorder-induced D band at 1345 cm^{-1}, and the G band corresponding to the crystalline graphitic structure near from 1570cm^{-1}. The intensity ratio of the G and D bands (I_G/I_D) is used to quantify the oxidation process. The second order Raman presents like G1' peak

(~2700cm^{-1}) is characteristic just for carbon nanotubes and appear when an Argon laser is used. Lorentzian fit were obtained in order to evaluate the ratio's area.

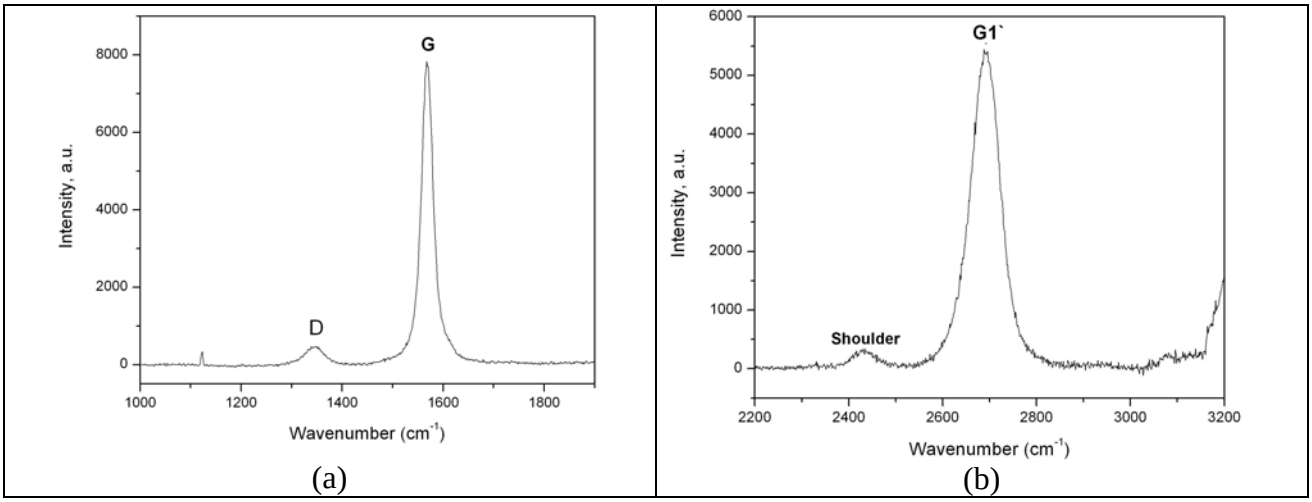

Figure 2 – First order (a) and second order (b) Raman spectra of the as-received MWNTs.

The (I_G/I_D ~ 7.75) for as-received MWNTs represents samples with low degree of defects, since that, the larger number of defects, higher the D band intensity. The linewidth of bands can evaluate qualitatively the defects distibution. The small linewidth indicate a narrower distibution of defects, the other hand, broader linewidth suggest a broad distribution. The linewidth of D and G band were aproximatelly 40 and 25cm^{-1} respectively. According to Antunes et al (2006), relatively low values of linewidth (20-40cm^{-1}) indicate a high degree of graphitization of material.

Analysing the second order raman spectra of MWNTs with 514,5nm excitation shows a shoulder at around 2450cm^{-1}. Shimada et al. Reported that the 2450cm^{-1} band did not show any dispersion and should be characterized as the overtone mode of a LO phonon near the K point. This fact agree with the experimental wavenumber obtained (2440cm^{-1}). The G1' band (2695cm^{-1}) was observed for the analyzed samples. The ($I_{G1'}/I_G$) ratio also represents an indicative of defects density. The results vary according to incidence of laser beam, since that sidewalls and tips of MWNTs can present different amounts of defects. The ($I_{G1'}/I_G$ ~ 2,20) ratio was also obtained by lorentzian fit. CNTs with low density of long tubes with little defect density along their axis studied by Antunes et al (2006), presented ratio of 3.75. Theses results confirm the previous affirmation that the MWNTs analized in this experiment present low density of defects.

3.2 Mechanical mixing

Fig. (3a) and (3b) show polyamide powder and MWNTs after mechanical mixing. It was observed that bundles and big agglomerates were partially destroyed. The distribution of nanotubes among polyamide particles was kind of deficient, because is visible places with bigger

concentration. The average size of agglomerates changes, approximately, from 40 to 10µm. This result is very interesting considering the easiness of applied method.

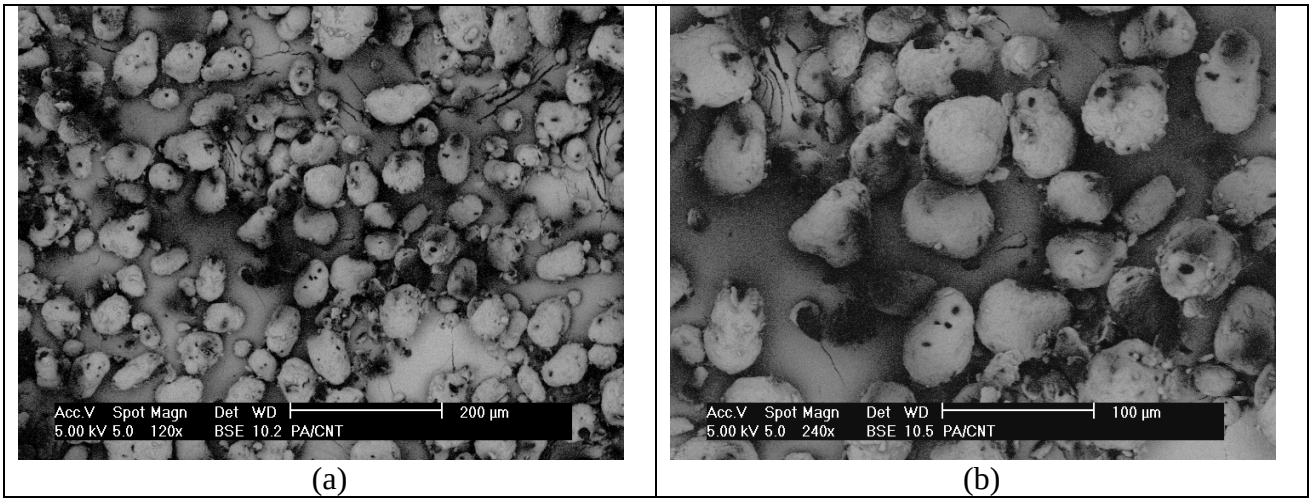

Figure 3 – Micrographs of PA/0.5%CNT after mechanical mixing.

3.3 Morphology

Specimens of nanocomposites based on carbon nanotubes manufactured by selective laser sintering were fractured cryogenically. Fig. 3 show the fracture surface of PA/0.5%CNT, (a), and pure polyamide, (b). The pore density on composite is lower than pure polymeric material and the surface aspect is more brittle. On the top of fig. (3a) it is visible the beginning of the fracture, the radial lines indicate this place, where probably a critical crack start the phenomena.

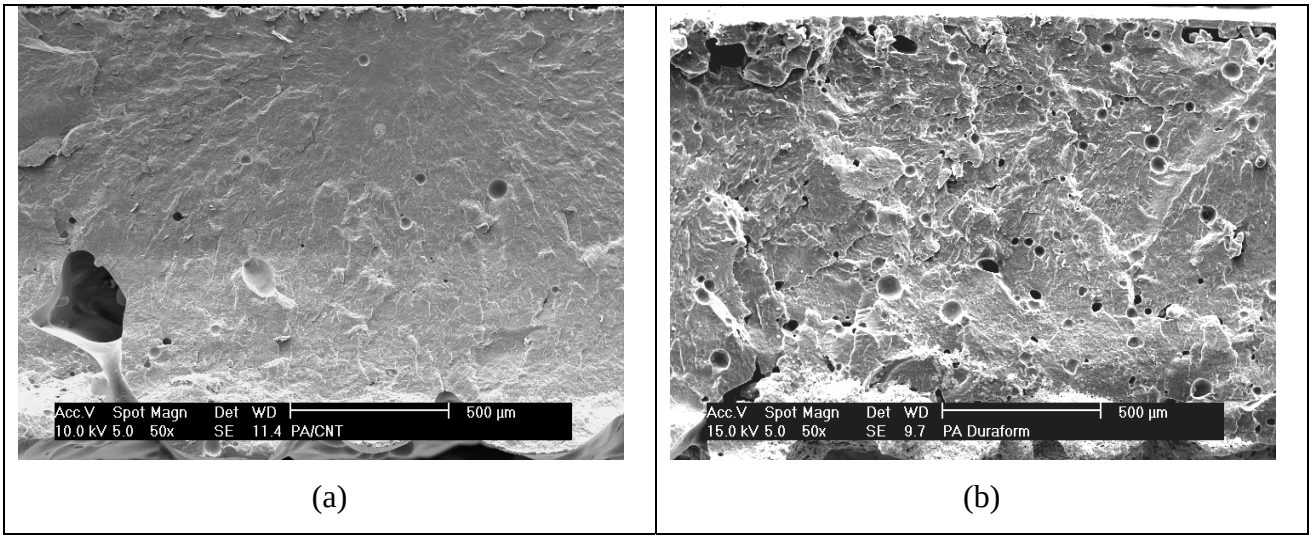

Figure 4 – Cryogenic fracture surface of PA/0.5%CNT (a), and PA (b).

Fig. 3a show mechanical fracture of nanocomposite. The aspect represents both ductile and brittle behavior, since that, it was possible to verify a small yielding in a big amount of surface, on the other hand, places of brittle fracture were observed too. On the fig. 3b was located an enormous agglomerated of carbon nanotubes. The insufficient dispersion can generate a local of stress

concentration, where probably the failure started. Voids presents on the images are causing by detaching of unsintered particles, trapped gas or closed porous.

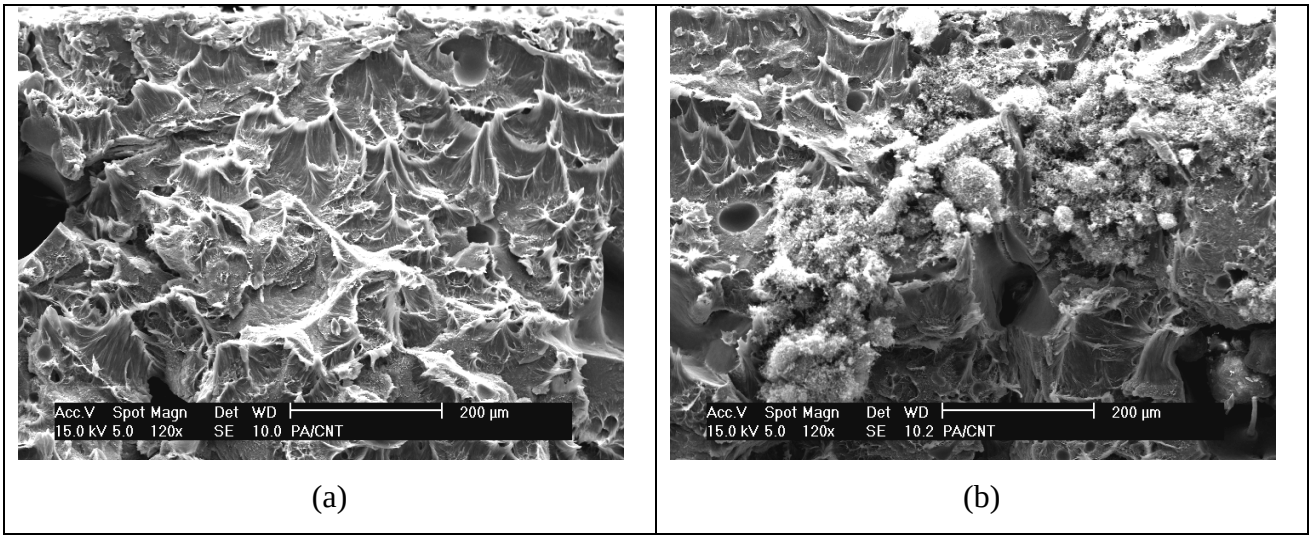

Figure 5 – Mechanical fracture surface of PA/0.5%CNT (a), agglomerate at surface (b).

Fig. 5 compare surface of nanocomposite (a), with pure material (b). Roughly surface was observed on the nanocomposite. The main cause for the worse surface finish relate the tendency of agglomeration and consequently, difficult to spread the composite powder. The bigger infrared absorbing of MWNTs may cause high degree of sintering among particles. A pronounced shrinkage can cause balling and warping on the surface of specimens.

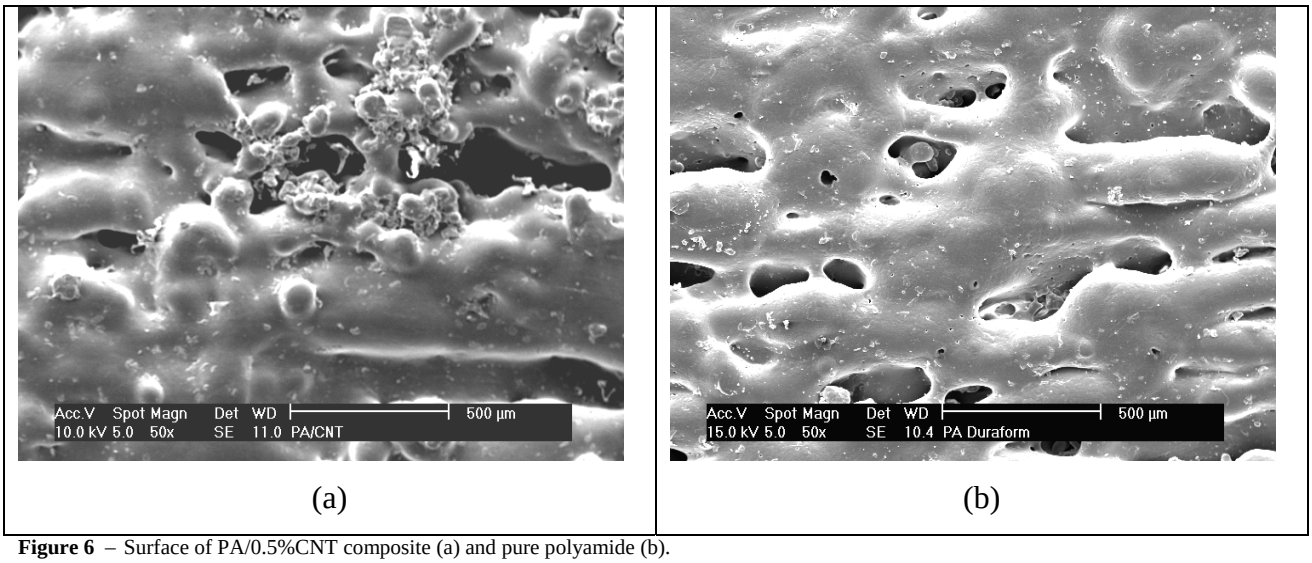

Figure 6 – Surface of PA/0.5%CNT composite (a) and pure polyamide (b).

3.4 Mechanical properties

A stress-strain curve is presented in fig. 6. Nanocomposite and pure polymeric material had presented mechanical behavior similar. Addition of 0.5wt% carbon nanotubes it caused a discrete

increase at tensile strength and reduction of elongation. These results determine an increase of brittle character of nanocomposites.

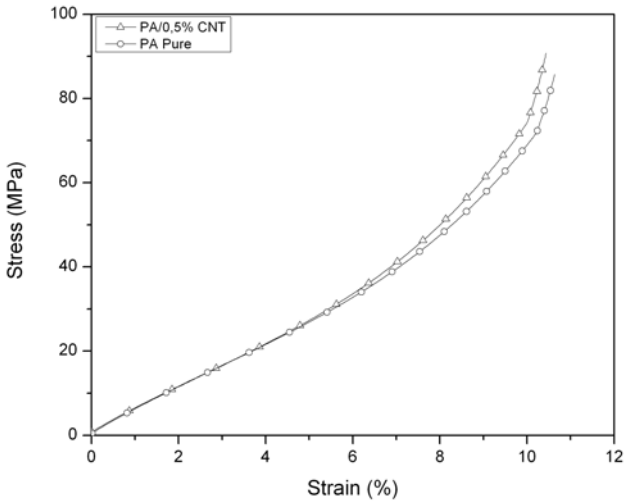

Figure 7 – Stress – strain comparative curve for PA and PA/0.5%CNT composite.

Table 1 show a summary of mechanical properties obtained with stress-strain curve.

Table 1 - Summary of mechanical properties.

	PA Pure	***PA/0.5%CNT***
Tensile strength (MPa)	85.73	90.80
Elastic modulus (MPa)	500.0	521.9
Elongation (%)	10.64	10.44

In order to evaluate the changes in the polymer mobility, DMA analysis was carried out. The variation in the storage modulus (E´) and loss modulus (E´´) with temperature are presented in fig. 7. The storage modulus (E´) of composite presented different value for plateau observed in the glassy region (below the Tg), from -50 to 20 ºC, approximately. According to Satapathy et al (2007), the relative difference in the molecular mobility of the polymer segments in the vicinity of the nanotubes from that of the bulk polymer can cause a significant difference between the viscoelastic responses of the pure material and the MWNT reinforced composite. The average increase was 12% for addition of 0.5% of MWNTs. The glass transition temperature, indicated by behavior change of curve, was not pronounced sharp.

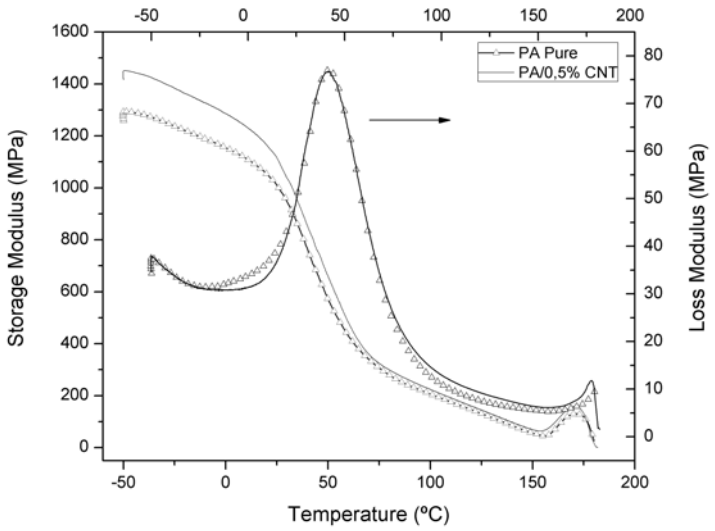

Figure 8 – Storage (E´) and loss (E´) modulus as function of temperature for PA and PA/0.5%CNT composite.

Comparative fatigue behavior was present in fig. 8. The higher initial stress of composite is according to the other mechanical testings. The decrease of stress as function of number of cycles was more effective on pure material, suggesting that the carbon nanotubes were responsible to modify the molecular mobility of polymeric chains. Results show that after, approximately 2500 cycles, the composite maintain the strength.

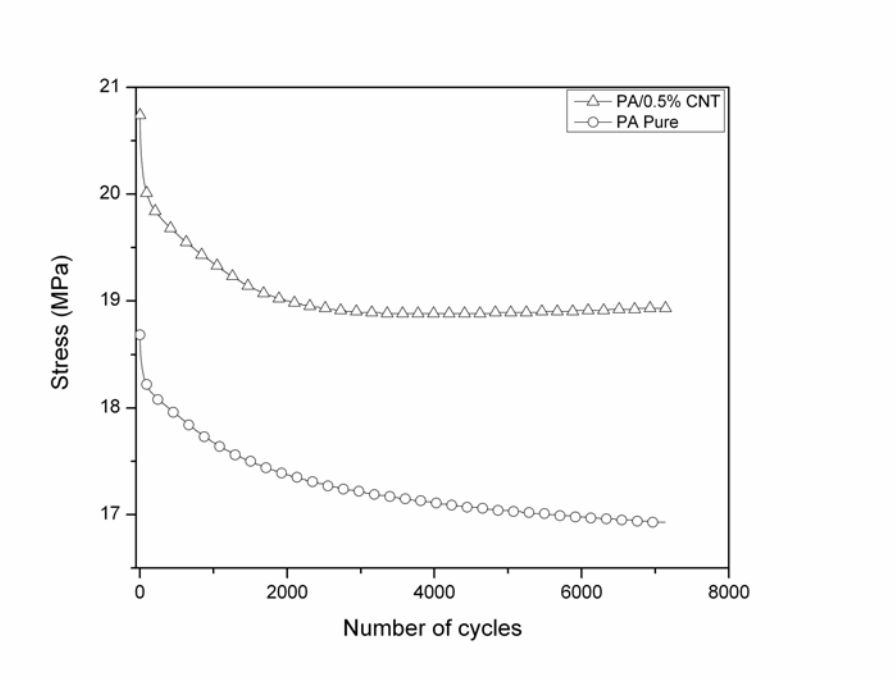

Figure 9 – Fatigue behavior PA and PA/0.5%CNT composite.

4. Conclusions

An alternative and simple mixing method was evaluated in this study. Direct mechanical mixing consist an interesting route to homogeneity powder materials, like polymers and MWNTs, but the obtained results had evidenced poor dispersion of fillers in the matrix. Micrographics of

fracture surface composites presented agglomerates, indicating that these structures can be responsible for propagation of instable cracks that may cause the failure of material.

From the results of dynamical mechanical properties can be concluded that content of MWNT used in this study, although small, cause a change of polymer chain mobility due to polymer-nanotube interactions. Stress-strain curves showed an increase of the brittle character with nanotube addition.

This work had a preliminary intention, since that, with the investigations of more contents of MWNTs, using selective laser sintering to obtain composites, has become interesting to evaluate the behavior and the effects. Chemical treatment can improve the dispersion of MWNTs in the matrix and will have to be investigated. Study about surface functionalization with O-H, C-O and other groups, cause hydrogen or van der Waals bondings between polymer and filler.

5. Acknowledgements

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6. References

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