ULTRAPRECISION MACHINING OF NANOCOMPOSITE

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Resumo: *The machinability of a nanocomposite is studied using monocrystalline diamond tools with different rake angles (neutral and highly negative). Micro-turning experiments were carried out under different cutting conditions. The workpiece material is an epoxy polymer (RTM6) sample impregnated with different concentrations of multiwalled carbon nanotubes and amphiphilic molecule ($C_{16}H_{33}NH_2$) concentration, used as dispersant agent. The surface integrity was evaluated in terms of surface roughness as well as the surface damage generated by tool material interaction using an optical profilometry and Scanning Electron Microscope (SEM). The assessment of chip morphology versus material removal mechanism influenced by different concentrations of multiwalled carbon nanotubes HAD (Hexadecyclamine (Sigma-Aldrich)) was carried out by means of SEM. The results revealed that feedmarks may or may not be evident on the machined surface depending on the cutting condition, carbon nanotubes concentration and tool geometry. The results showed that the amount (%wt) of CNT in the sample improves the surface finish. There was a slight influence of the depth of cut upon the roughness of the sample. It was observed that under submicrometer values the surface responded to machining presenting smaller roughness values. Optical profilometry results showed that the amount of CNT in the sample was responsible for improving the material removal mechanism. Presence of microcracks within the cutting grooves was probed: always perpendicular to the cutting direction in the sample with HAD and CNT. The opposite trend is probed when cut with submicrometer depth of cut and no %wt HAD.*

Palavras-chave: *Nanocomposites, Micromachining, Surface Integrity, Diamond tool, Carbon Nanotubes*

1. INTRODUCTION

The demand for high strength-to-weight and modulus-to-weight ratios materials have been attended by nanocomposites such as polymers reinforced with carbon nanotubes (*from now on referred in the text as* CNT) (Du et al., 2004, Gojny et al. 2004, Gorga and Cohen, 2004, Mamalis et al. 2004). Properties improvement have been reported in polymer nanocomposites, including: improved mechanical properties like Young's modulus (Young modulus ≈ 1 TPa), thermal stability (Samuel et al 2006; Du et al 2003) and thermal conductivity (1750 - 5850 $Wm^{-1}K^{-1}$,), flame resistance (Du et al 2003), electrical conductivity (Du et al 2003; Stewart 2004; Kymakis etal 2001Thostenson et al 2001), and; reduced permeability to gases and water (Du et al 2003). These properties make CNTs an ideal reinforcement phase for polymer composites that can uniquely meet some of the requirements of miniaturization.

Results reporting the application of machining operations to nanocomposites of CNT are mainly in thermoplastic (TP) matrix by means of micro endmilling operation (Dikshit et al. 2008a, 2008b, 2008c), which are considerably easier to cut as well as to mix higher concentrations of CNT. The investigation on the effect of CNT loading upon thermomechanical properties and machinability was reported by Samuel et al. (2008). According to these authors the increase in CNT loading results in thermal conductivity increase which results in reduced number of adiabatic shear bands formed on the chips as well as the reduction in the effect of thermal softening induced at high cutting velocities.

Literature on the machining of nanocomposites of TP base polymer impregnated with CNT report samples with 15% in weight of CNT (Jin et al. 2001, Samuel eta l. 2006), whereas epoxy resin percolation is in the range of 2% max (Jasinevicius et al., 2009). In the later study, the authors observed that he amount of CNT on the epoxy matrix may have a direct influence on the mechanical properties of these materials when applied in field. Different method of material removal have been tried in CNT epoxy nanocomposite such laser to produce small holes (Bassil et al. 2006). The authors investigated the surface integrity of nanocoposites showing modifications induced by laser machining upon machined surfaces.

This paper deals with the investigation on machinability of a nanocomposite is studied using monocrystalline diamond tools with different rake angles (neutral and highly negative). Micro-turning experiments were carried out under different cutting conditions and the surface finish as chip removed assessed by means of optical profilometry and scanning electron microscopy (SEM).

2. EXPERIMENTAL DETAILS

The nanotubes were mainly double walled (DW). A dispersion of CNTs in water was first kept in an ultrasonic bath for 1h and stirred. No surfactants were used. CNT composites using RTM6 (Epoxy Resin matrix - Hexcel Density uncured: 1.11 g/cm^3 and cured 1.14 g/cm^3; viscosity is 175 and 33 mPa at 25 ºC and 80 ºC, respectively) (were prepared by dispersion of weight amount of CNTs ranging from 0.02 to 0.7 wt % (see Table 1). The liquid epoxy resin was added to the dilute suspension of nanotubes and water was evaporated at 100 º C. The mixture was then mechanically stirred for 1 h at 2 000 rpm. The hardener was added and the whole mixture was mechanically stirred for 15 min and then cast into a teflon mould and degassed for 20 min under vacuum. The nanocomposite was cured at 120 ºC for 20 min and at 145 ºC for another 8 h. In order to enhance CNTs dispersion in epoxy matrix, *HDA:hexadecyclamine (Sigma-Aldrich) amphiphilic molecule* $C_{16}H_{33}NH_2$*)* was used as dispersant and was added before hardener addition. The percolation threshold is associated to a 10 power change in the conductivity value (Lau et al. 2005).

Nanocomposite samples (15mm x 30mm, and 1.5mm thick) as shown in Fig. 1 a) were face turned on a Rank Pneumo ASG 2500 diamond turning lathe (Fig. 1 b). No cutting fluid was used during cutting tests. Table 2 presents diamond tool geometries and the cutting conditions. The topography and surface finish were evaluated by means of an Optical Profiler (WYKO NT1100 made by VEECO™). Four measurements were taken at the same neighbor in both samples at every 90º quadrant and average and standard deviation values were calculated. Scanning electron microscope LEO model 440 was used to assess chips formed. The cutting tests results that will be presented here were selected in order to show an overview on the influence of cutting conditions upon nanocomposite different compositions. It is important to mention that the material removal behavior under machining conditions will be treated.

Table 1. Composite description.

Sample #	CNT content (wt%)	HDA* content (wt%)
7	0	0
4	0.2	0.2
5	0.4	0.4
6	0.7	0.7
8	0.4	0
11	0	0.7

Table 2. Tools geometries and cutting conditions used in the face turning operation

Tool Geometry			***Feedrate (µm/rev)***	***Depth of Cut (µm)***
Tool nose radius (mm)	Rake Angle γ (º):	Clearance Angle α (º)	2.5	0.5
0.635	-25	12	5	1
0.75	0	12	10	3
1.5	0	12	15	5

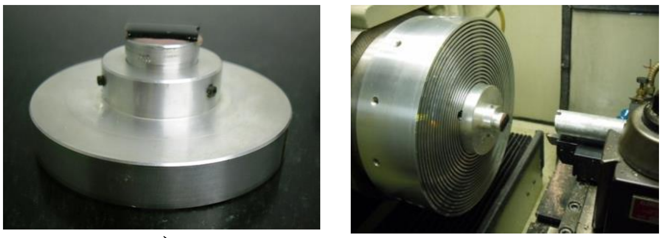

a) b)

Figure 1. Sample preparation for micromachining tests, a) composite sample is glued to a aluminum stub which is mounted in a special fixture device; b) fixture device is fixed on a vacuum chuck to be diamond turned.

3. Results and Discussion

Figure 2 shows a graph with the values of root mean square roughness Rq as a function of the feed rate. The results show that there is an expected trend of the surface roughness to increase with the increase of federate. However, surface roughness the sample of RTM6 with with 0.7%wt of CNT and HDA added presented the smallest value of Rq roughness for the whole range of feed rate. The samples of epoxy resin RTM6 and the RTM6 with very small amounts of CNT (0.02 and 0.1%wt) and HDA(0.02 and 0.1%wt) presented unexpected increase of Rq values for the range from 10 up to 15 µm/rev. The sample of pure RTM6 showed a slightly smaller value of surface finish when compared to the sample with highest amount of CNT and HDA for the whole range of feedrate. This difference in surface roughness may be attributed to the material removal mode.

Different compositions of the nanocomposite were teste for comparison, to know: pure RTM6, RTM 6 plus 0.7%wt in HDA and RTM6 with 0.7wt% of both HAD and Carbon Nonotubes (CNT).Three-dimensional images of a surface diamond turned in the ductile mode are shown in Fig. 3 a-c). In all surfaces, the cut grooves are regularly spaced and running parallel with the cutting direction, which confirms the absence of chatter vibration. The surface roughness measured is 58.15 nm Rq for the sample with CNT and HDA.

It seems that there is no correlation between the type of chip removed from the nanocomposite samples and the surface formed. Fig 4 a) and 4 b) present images from scanning electron microscope (SEM) of chips removed from the nanocomposite with 0.02%wt and 0.1%wt of CNT and HDA. Both images show a continuous ribbon-like chip removed. Figure 4 a) shows the chip laid down on the machined surface cut with federate of 2.5 µm/rev. The amount of carbon nanotubes is very small and is not easy to spot them in the chips. In Fig.4 b) is possible to observe that the surface is formed by a series of microcracks running parallel and formed perpendicular to the cutting direction. This may be use to explain the increase in surface roughness obtained for both samples when higher value of feed rate were used.

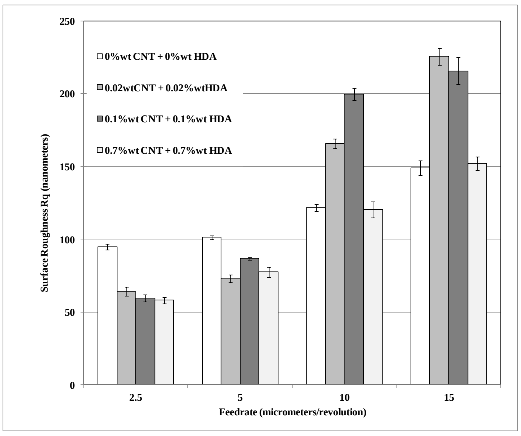
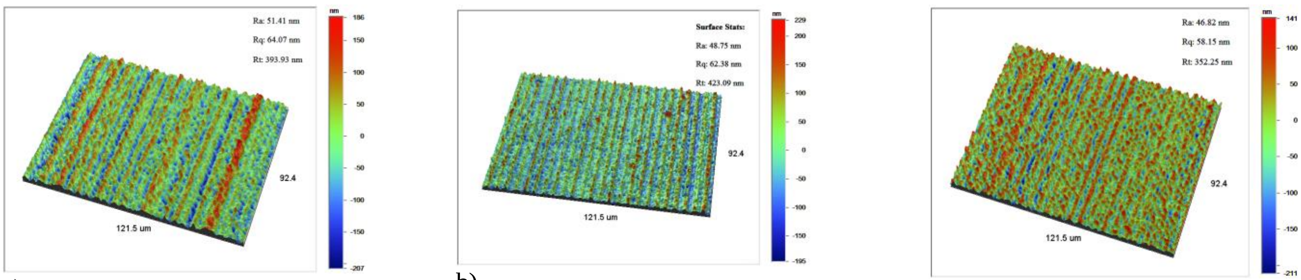
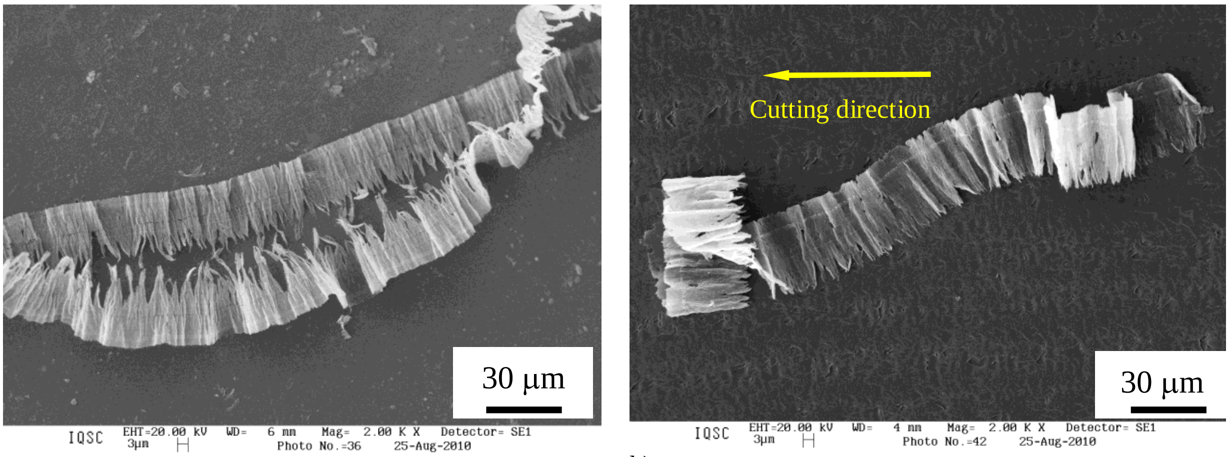


Figure 2. Graph showing the values of root mean square roughness Rq as a function of the feed rate at a constant depth of cut (ap =1 µm). Diamond tool has a nose radius of 0.76 mm and neutral rake angle (γ= 0º)



a) b) c)

Figure 3. Three dimensional image of the surface finish *of the machined samples with different concetrations of* CNT+HDA. Cutting conditions and tool geometry were, respectively: f = 2.5 µm/rev, ap =1 µm; Rp = 0.75 mm and γ = 0º. a) RTM6 +0.02%wt CNT + 0.02%wt HDA; b) RTM6 +0.1%wt CNT + 0.1%wt HDA; c) RTM6 +0.7%wt CNT + 0.7%wt HDA.



a) b)

Figure 4. Scanning electron microscopy photomicrograph of continuous chip removed from the nanocomposite samples; a) general view of the chip removed with federate of 2.5 µm/rev RTM6 +0.02%wt CNT + 0.02%wt HDA; and; b) general view of the chip removed with federate of 15 µm/rev RTM6 +0.1%wt CNT + 0.1%wt HDA.

Micro defects such as microcracks were probed on the machined surface when using neutral rake angle (Fig. 4b), a very negative rake angle tool was used in order to investigate if it would have a converse effect, i.e., hindering microcracks to form during cutting. Figure 5 present a graph showing different nanocomposite machined under the same feed rate used in the former tests using a negative rake angle tool (γ= -25º). It was interesting noticing that for the federate range of 2.5 up to 5 µm/rev the roughness Rq results were much lower than the former results including pure RTM6 used as reference for comparison in both tests. The results are almost half as those for pure epoxy resin. The values of surface finish for the sample with higher concentration of CNT and HDA presented similar range of values of roughness for the higher range of federate, being almost the same values.

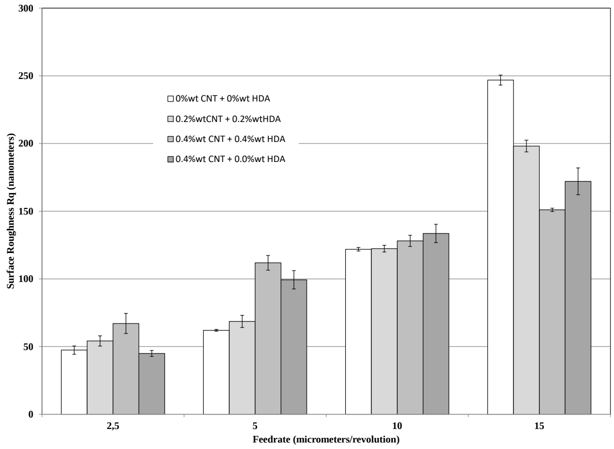


Figure 5. Influence of the %wt of CNT and HAD and the rake angle upon surface finish for different feed rate condition. Graph showing the values of root mean square roughness Rq as a function of the feed rate at a constant depth of cut (ap =1 µm). Diamond tool has a nose radius of 0.76 mm and neutral rake angle (γ= -25º) .

Figure 6 presents the top view image and the chip formed under the smallest cutting condition used with the highly negative rake angle tool. The samples probed were RTM6 + 0.4%wt CNT (Fig. 6 a) and RTM6 + 0.4%wt of CNT +HAD (Fig. 6 b). In both cases, no feed marks are observed on the machined surface Fig. 6 a) and 6 c), respectively. The chip removed present ductile regime and continuous form.

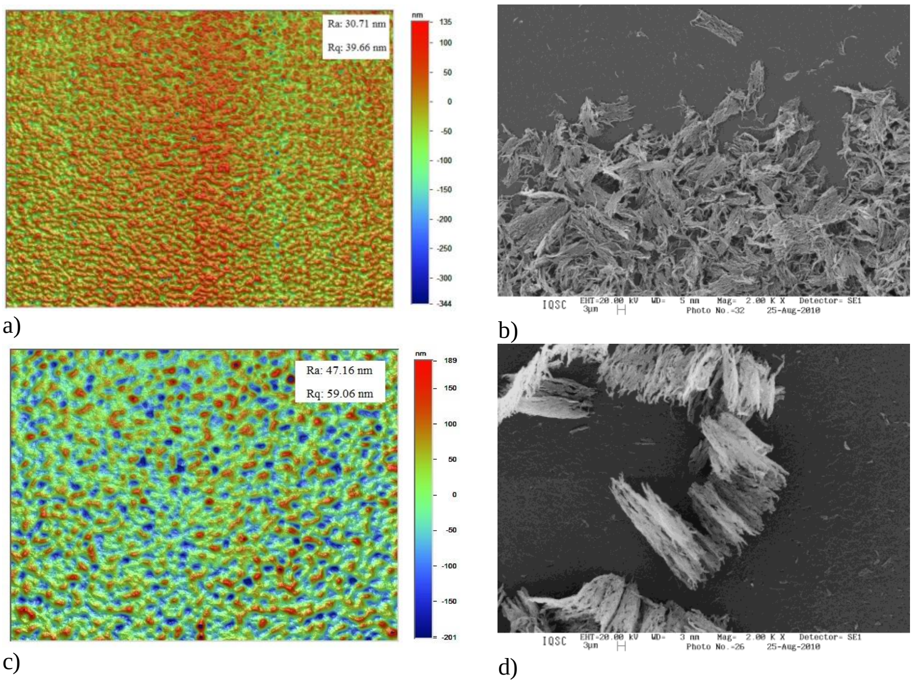


Figure 6. Cutting conditions and tool geometry were, respectively: f = 2.5 µm/rev, ap =1 µm; Rp = 0.76 mm and γ = -25º. a) Top 3D image of the surface finish from RTM6 +0.4wt CNT; b) typical chips found on the machined surface for the RTM6 +0.4%wt CNT sample ; c) Top 3D image of the surface finish from RTM6 +0.4%wt CNT + 0.4%wt HDA, d) typical chips found on the machined surface for the RTM6 +0.4%wt CNT + 0.4%wt HDA sample .

Negative rake angle didn´t avoid microcrack formation and this is demonstrated by the similarity in roughness values shown for higher federate (10 and 15 µm/rev) in all cases, more clearly for pure RTM6 as shown by the three dimensional image shown in Figure 7. According to Carr and Feger (1993), crosslinked materials, as in the case of epoxy resin, above glass transition Temperature (Tg) will always rupture or fracture, producing rough surfaces. The Tg for RTM 6 is 170ºC. The temperature was not measured during machining tests, but it is well known in metal cutting that temperature will rise with the increase in cutting speed. Yashiro and collaborators reported that temperature overcame Tg during end milling of CFRP. When temperature was measured at the tool-work-piece contact point, it reached 180 ºC at 25 m/min of cutting speed, and then exceeded the glass-transition temperature with cutting speed 50 m/min or more. In our case, it is worth mentioning that diamond is good heat conductor, and nanocomposites with CNT present higher thermal conductivity. Conversely, El Sawi et al. (2012) showed that Double Walled Carbon Nanotubes (DWCNTs) have an acceleration effect on the polymerization rate of an epoxy polymer but that no significant effect was noted on the glass transition temperature of the epoxy resin. This study revealed as well that a shear thinning effect of DWCNTs was observed and was more pronounced at increased temperature. More studies would have to be addressed in order to have a more conclusive response on this subject.

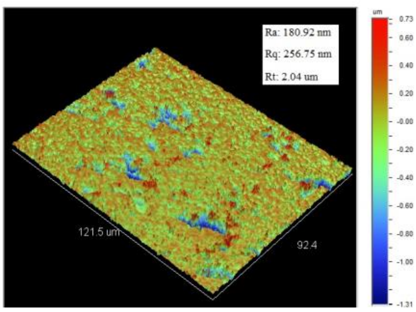


Figure 7. Three dimensional image of pure RTM6 machined with highly negative rake angle tool and federate of 15 µm/rev and ap= 1µm.

It is well known that depth of cut will not have any effect on surface roughness; epoxy resin behaves as a brittle material the volume of material deformed is important to be regarded since micro cracks can be formed. Figure 8 presents the influence of cutting depth on the surface finish of the samples. The results showed that the increase in depth of cut slightly increases the roughness Rq value for the sample filled with CNT and HDA. It was observed that under submicrometer (ap = 0.5 µm) values the surface responded to machining presenting smaller Rq roughness values. It is worth noticing that, when the depth of cut is decreased, and consequently the volume of material removed, the roughness (Rq) decreased around 30% for all composition with the decrease of depth of cut from 3µm down to 0.5 µm. Optical profilometry results showed that the amount of CNT along with HDA in the sample was responsible for improving the surface finish. The presence of defects within the cutting grooves: always perpendicular to the cutting direction was detected in the sample with CNT and HDA and diminishes when cut with sumicrometer depth of cut and no %wt HDA as shown in Figure 9.

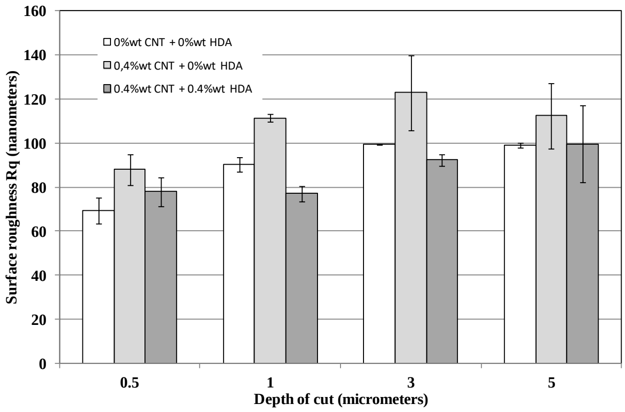


Figure 8. Influence of depth of cut upon three distinct sample: i) Pure RTM6; ii) RTM6 + 0.4%wt CNT and; iii) RTM6 + 0.4%wt CNT and HDA. Cutting conditions f = 15 mm/rev.

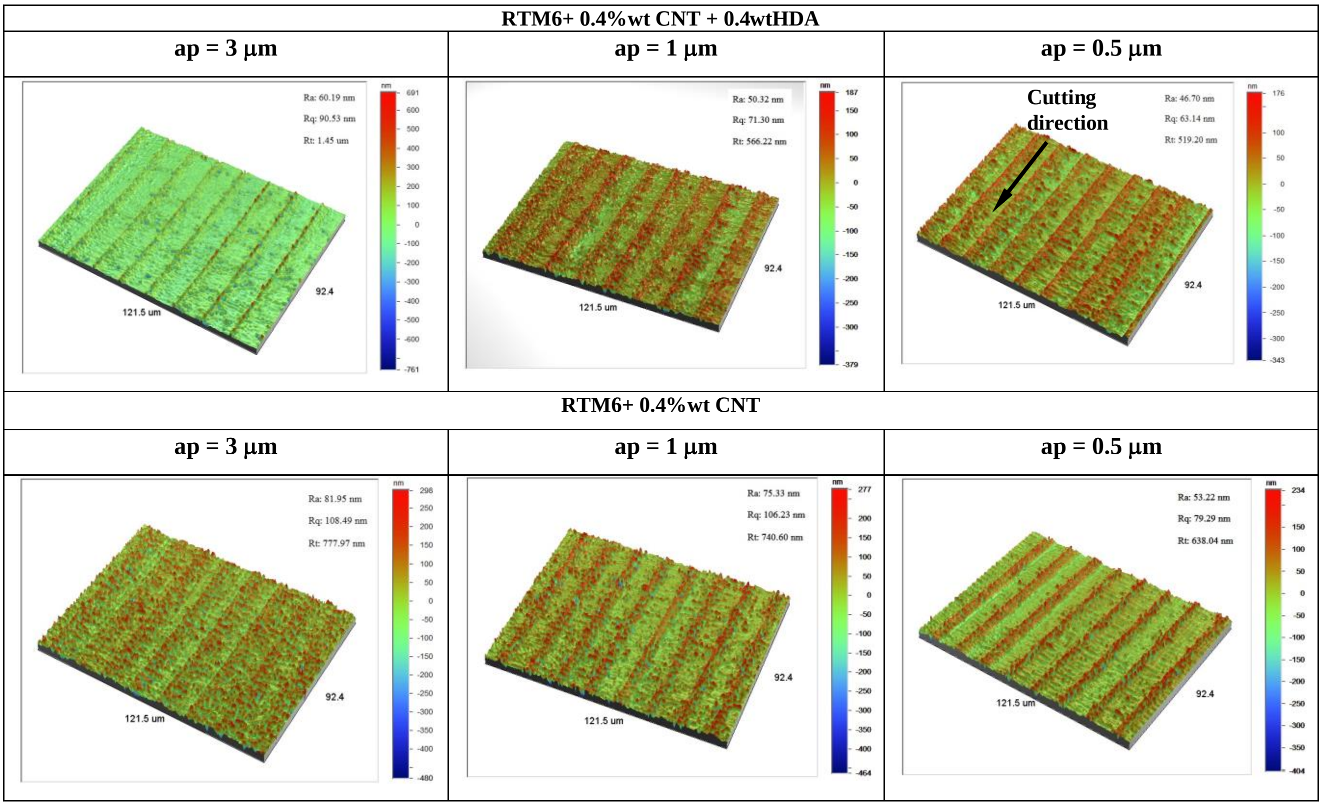


Figure 9 Influence of the depth of cut and %wt HAD (amphiphilic molecule) upon surface finish. Rake angle 0º feedrate 15 µm/rev.

Finally, the effect of positive rake angle was tested. The cutting tool nose radius was 1.5 mm and so it was double the value of that used with neutral rake angle. The sample chosen for the test was the sample 5 (RTM6+ 0.4%wt CNT + 0.4wtHDA). The sample was machined using larger cutting conditions as can be observed in Figure 10 a-d. The surface finish presented by the sample cut under all federate conditions presented the lowest values of surface roughness Rq among all cutting tests made. This result may be partially attributed to two factors: one is the larger tool nose radius and two by the positive rake angle used. According to Carr and Feger (1993), when using positive rake angle tool to cut polymer, the main cutting force vector is oriented upward away from the machined surface and this might contribute for reducing the roughness value. In addition, it is worth noticing that the tool nose radius is larger than the value of that used with neutral rake angle.

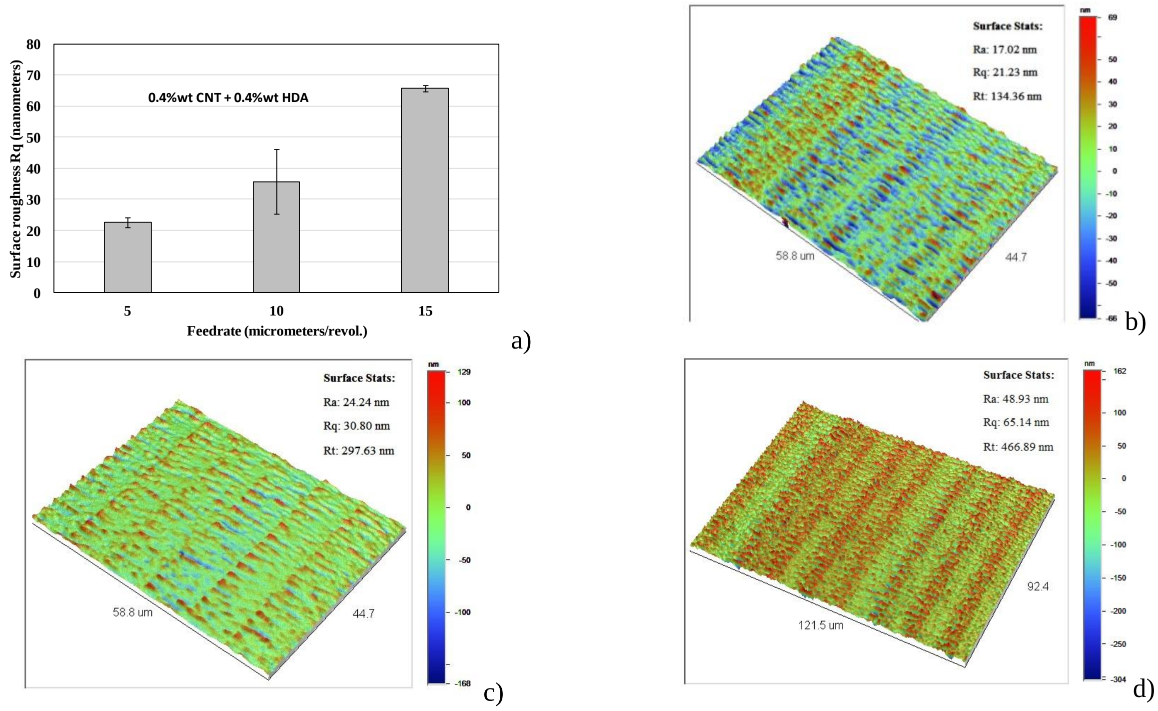


Figure 10. Response of nanocomposite sample cut with different federate and positive rake angle tool (γ = +5º). a) graph showing surface roughness results as function of federate; a) f= 5 μm/rev; b) f= 10 μm/rev ; c) f= 15 μm/rev .

The cutting tools used in the cutting tests were evaluated in order to know if the machining tests promote any kind of harm to the tool cutting edge, shown in Figures 11 a) and 11b). As can be observed mainly from Fig. 11 b), no sign of wear was probed on the cutting edge. The reason for the absence of wear may support the following explanations:

a) Polymers and diamond are electrical insulators. However CNT presents electrical conductivity (Thostenson, E. T.et al. 2001)! No problems with static electrification!

b) No wear would be expected once polymers do not contain unpaired d-electrons (Paul et al. 1996);

c) Diamond tool wear with polymer was attributed to thermaly inuced wear (Carr and Feger, 1993) however CNT has high thermal conductivity (1750 - 5850 $Wm^{-1}K^{-1}$).

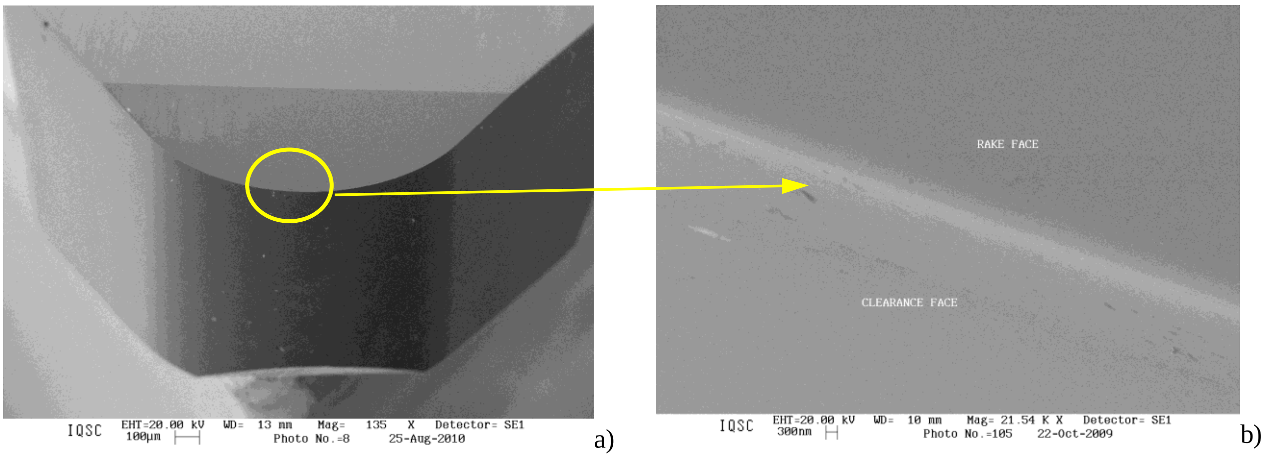


Figure 11. SEM image of diamond tool with 0º rake angle used in the cutting tests; a) general view of the cutting tool; b) detail view of the cutting edge with no detected wear.

4. Final Considerations

In Summary, diamond turning tests were performed for 7 different samples of pure epoxy resin and impregnated with CNT and HDA; under different cutting conditions (depth of cut and feedrate) and tool geometries (neutral and negative rake angle).

The results show that the amount (%wt) of CNT in the sample improves the surface finish. There was a slight influence of the depth of cut upon the roughness of the sample. It was observed that under submicrometer values the surface responded to machining presenting smaller roughness values. Optical profilometry results showed that the amount of CNT in the sample was responsible for improving the material removal mechanism. Presence of microcracks within the cutting grooves: always perpendicular to the cutting direction was detected in the sample with HAD and CNT and diminishes when cut with submicrometer depth of cut and no %wt HAD.

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6. References

Bassil, A., Puech, P., Bacsa, W., Pizani, P. S., Jasinevicius, R. G., Demont, Ph., Barrau, S., Lacabanne, C., Bacsa, R., and Flahaut, E. Laser induced modifications of carbon nanotube composite surfaces. Jap. J. Appl. Phys., 2006, 45(10A), 7776–7779.

Carr, J.W., Feger, C, Ultraprecision machining of polymers, Prec. Engg. Vol. 15(4):221-237, 1993.

Du, F., Fischer, J. E., and Winey, K. I., 2003, "Coagulation Method for PreparingSingle-Walled Carbon Nanotube/Poly _Methyl Methacrylate_ Composites and Their Modulus, Electrical Conductivity, and Thermal Stability," J. Polym. Sci., Part B: Polym. Phys., **41**, pp. 3333–3338.

Dikshit, A., Samuel, J., DeVor, R.E., Kapoor, S.G., 2008a, "Microstructure-Level Machining Simulation of Carbon Nanotube Reinforced Polymer Composites—Part I J. Manufact Sc. and Engg. Trans. ASME, vol. 130.

Dikshit, A., Samuel, J., DeVor, R.E., Kapoor, S.G., 2008b, "Microstructure-Level Machining Simulation of Carbon Nanotube Reinforced Polymer Composites—Part II", J. Manufact Sc. and Engg. Trans. ASME, vol. 130.

Dikshit, A., Samuel, J., DeVor, R.E., Kapoor, S.G., 2008c "A Microstructure-Level Material Model for Simulating the Machining of Carbon Nanotube Reinforced Polymer Composites", J. Manufact Sc. and Engg. Trans. ASME, vol. 130,

El Sawi I, Olivier P, Demont P, Bougherara H. Investigation of the effect of double-walled carbon nanotubes on the curing reaction kinetics and shear flow of an epoxy. J Appl Polym Sci 2012;126:358–66.

Flahaut, E., Casimirius, S., Vieu, Ch., Peigney, A., Laurent, Ch., 2004, "Double-walled Carbon Nanotubes: CCVD Synthesis and filling by 1D-Nanocrystals" *Nanostructured and Advanced Materials for Applications in Sensor, Optoelectronic and Photovoltaic Technology Sozopol.*

Fossa, J.S. Desenvolvimento de um sistema óptico para microperfuração de materiais cerâmicos,metálicos e poliméricos utilizando laser nanopulsado de Nd:YAG. Dissertação de Mestrado, IFSC-USP 2007, 117p.

Gojny, F.H., Wichmann, M.H.G., Köpke, U., Fiedler, B. and Schulte, K. 2004, Carbon Nanotube-reinforced Epoxy-composites: Enhanced Stiffness and Fracture Toughness at Low Nanotube Content, Composites Science and Technology, 64(15): 2363–2371.

Gorga, R.E. and Cohen, R.E., 2004, "Toughness Enhancements in Poly(methyl methacrylate) by Addition of Oriented Multiwall Carbon Nanotube", J. Polym. Sci., Part B: Polym. Phys., 42(14): 2690–2702.

Jasinevicius, R G, Andreeta, M R B Fossa, J S Hernandes, A C Duduch, J G Demont, P and Puech, P, 2009, "Brittle and ductile removal modes observed during diamond turning of carbon nanotube composites", Proc. of the Inst. of Mech. Eng..Part B, J. of Engg. Manuf., v. 223, p. 001-008.

Jin, Z., Pramoda, K.P., Xu, G. and Goh, S.H. 2001, "Dynamic Mechanical Behavior of Meltprocessed Multi-walled Carbon Nanotube/Poly (Methyl Methacrylate) Composites", Chemical Physics Letters, 337(1–3): 43–47.

Kymakis, E., Alexandou, I., and Amaratunga, G. A., 2001, "Single-Walled Carbon Nanotube-Polymer Composites: Electrical, Optical and Structural Investigation," Synth. Met., **127**, pp. 59–62.

Lau, K.T., Lu, M., Lam, C.K., Cheung, H.Y., Sheng, F.L. and Li, H.L. 2005, "Thermal and Mechanical Properties of Single-walled Carbon Nanotube Bundle-reinforced Epoxy Nanocomposites", the Role of Solvent for Nanotube Dispersion, Composites Science and Technology, 65(5): 719–725.

Mamalis, A.G., Vogtländer, L.O.G., Markopoulos, A. 2004 Nanotechnology and nanostructued materials: trends in carbon nanotubes. Precision Engineering, Vol. 28: 16-30.

Martin, C.A., Sandler, J.K.W., Shaffer, M.S.P., Schwarz, M.K., Bauhofer, W. Schulte, K. and Windle, A.H. 2004, "Formation of Percolating Networks in Multi-wall Carbon-nanotube epoxy Composites", Composites Science and Technology, 64(15): 2309–2316.

Paul E, Evans CJ, Mangamelli A, McGlauflin ML, Polvani R.S.,1996, Chemical aspects of tool wear in single point diamond turning. Precis Eng 18(1), pp.4–19.

Samuel, J., DeVor, R.E., Kapoor, S.G., Hsia, K. J., 2006, "Experimental Investigation of the Machinability of Polycarbonate Reinforced With Multiwalled Carbon Nanotubes", J. Manufact Sc. and Engg. Trans. ASME, Vol. 128, pp. 465-473,.

Samuel, J. et al., 2009, "Effect of Carbon Nanotube CNT Loading on the Thermomechanical Properties and the Machinability of CNT-Reinforced Polymer Composites" J. Manufact Sc. and Engg. Trans. ASME, vol. 131, 031008, 9 pages.

Stewart, R., 2004, "Nanocomposites: Microscopic Reinforcements Boost Polymer Performance", Plast. Eng. _N. Y._, **60**, pp. 22–29.

Thostenson, E. T., Zhifeng, R., and Tsu-Wei, C., 2001, "Advances in the Science and Technology of Carbon Nanotubes and Their Composites: A Review," Compos. Sci. Technol., **61**, pp. 1899–1912.

Yashiro, T., Ogawa, T., Sasahara, H.. Temperature measurement of cutting tool and machined surface layer in milling of CFRP, International Journal of Machine Tools & Manufacture 70 (2013) 63–69

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