Role of The Carbon Nanofiber Defects On The Electrical Properties of CNF-Based Resins

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University of Salerno

UNIVERSITY of DAYTON

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The IASS Project is funded by the Seventh Framework Programme.

Outline

- Preliminary Remarks
- Aim of the work
- Materials (nanofiller and Polymeric Matrix)

- Results and Discussion
- Conclusions

Preliminary Remarks

The introduction of composite materials to the aeronautic industry was driven by performance gains (better fatigue performance, no corrosion, better design flexibility, etc) and weight reduction. However, composites possess some properties which reduce their advantage with respect to traditional metal alloys. One inherent shortcoming is the reduced electrical conductivity of composites.

Preliminary Remarks

This fact has raised concern over the performance of the composite structure during a lightning event due to the remarkable risk that a puncture of the structural part would cause a catastrophic failure of the aircraft.

Aircraft struck by lightning

Reduced Electrical Conductivity

Airplanes get struck by lightning frequently.

Fortunately, they're built to handle it.

Current Technology

Some modern aircraft are made of advanced composites which they are significantly less conductive than aluminum. Then, the composites are reinforced with conductive metal fibers or metal screens in order to dissipate lightning currents. **But many of these solutions add additional weight and reduce composite advantage.**

However, in the last decade, the availability of different nanofiller or nanostructured conductive materials has sensibly contributed to the continuous improvement of the engineering properties or abilities of the composites for aeronautic or automotive industries.

RESEARCH STRATEGY

1. Use of conductive nanofiller into polymeric matrix to enhance electrical properties and mechanical properties.

2. The choice of the nanofiller is critical and should meet the requirements.

By choosing the appropriate control of the matter structure as well as the specific fillers, researchers with appropriate expertise can work to overcome this critical point.

AIM OF THE WORK AND RESEARCH STRATEGY

The aim of this work is situated in this contest.

We have tried to increase the electrical conductivity of nanofilled epoxy resins by dispersing conductive nanofillers inside an epoxy mixture.

As conductive nanofillers, we have chosen CNFs.

AIM OF THE WORK

Study of the potential use of CNFs as filler to produce new nanofilled epoxy resins for improving electrical conductivity and other properties of aeronautic resins.

Analysis of the changes in structural ordering of the CNF during graphitization processes and how these changes influence the physical properties of the final material as a function of filler concentration.

Materials - Carbon nanofibers

Nanofillers

Vapor-grown carbon nanofibers used in this study were produced at Applied Sciences Inc. and were from the Pyrograf III family.

The pristine CNFs used in this study are labeled as PR25XTPS1100 where XT indicates the debulked form of the PR25 family, PS indicates the grade produced by pyrolytically stripping the as-produced fiber to remove polyaromatic hydrocarbons from the fiber surface and 1100 is the temperature in the process production.

Materials - Carbon nanofibers

Nanofillers

Morphological parameters of Carbon Nanofibers

The carbon nanofibers have average diameters ranging from 125 to 150 nm and lengths ranging from 50 to 100 µm

Average Bulk Density of Product (lb/ft^3)	1.2 – 3.0
Nanofiber Density (including hollow core) (g/cm^3)	1.4 - 1.6
Nanofiber Wall Density (g/cm^3)	2.0 - 2.1
Average Catalyst (Iron) Content (ppm)	< 14,000
Average Outer Diameter, (nm)	125 - 150
Average Inner Diameter, (nm)	50-70
Average Specific Surface Area, m^2/g	65 - 75
Total pore volume (cm^3/g)	0.140
Average Pore Diameter(angstroms Å)	82.06

NANOFILLER

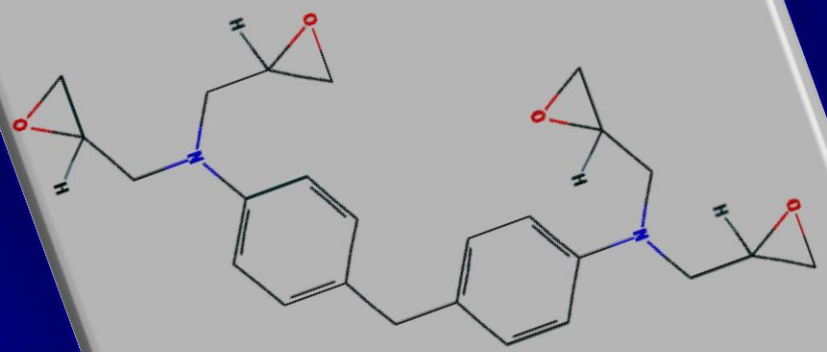
The nanofibers were heat treated in an atmosphere controlled batch furnace. Approximately 300 g of nanofibers were placed in a ceramic crucible for the heat-treatment. The furnace was purged with nitrogen gas for one hour prior to heating. The heating rate was 100◦C per hour, and the furnace was held at the target temperature for one hour prior to cooling.

The target temperature was 2500◦C.

Materials - Epoxy Matrix

The epoxy matrix was prepared by mixing an epoxy precursor (TGMDA) with an epoxy reactive monomer (BDE).

Epoxy precursor



(4,4′-Methylenebis(N,N-diglycidylaniline) - Acronym TGMDA

(Epoxy equivalent weight 117-133 g/eq)

1 - 4 Butandioldiglycidylether

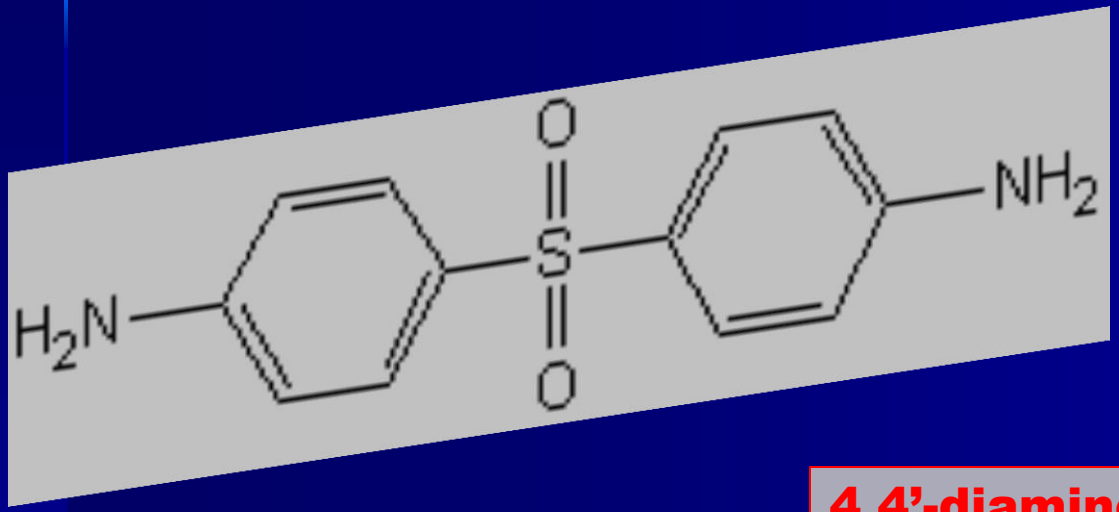
reactive diluent

The epoxy matrix was obtained by mixing TGMDA with BDE monomer at a concentration of 80%: 20% (by wt) epoxide to flexibilizer.

Chemical structures of the compounds used for the epoxy matrix

Materials – Epoxy Matrix

The curing agent investigated for this study is 4,4'-diaminodiphenyl sulfone (DDS).



DDS was added at a stoichiometric concentration with respect to the epoxy rings

4,4'-diaminodiphenyl sulfone (DDS). (hardener agent)

Chemical structures of the compounds used for the epoxy matrix

Epoxy specimens manufacture (Composition)

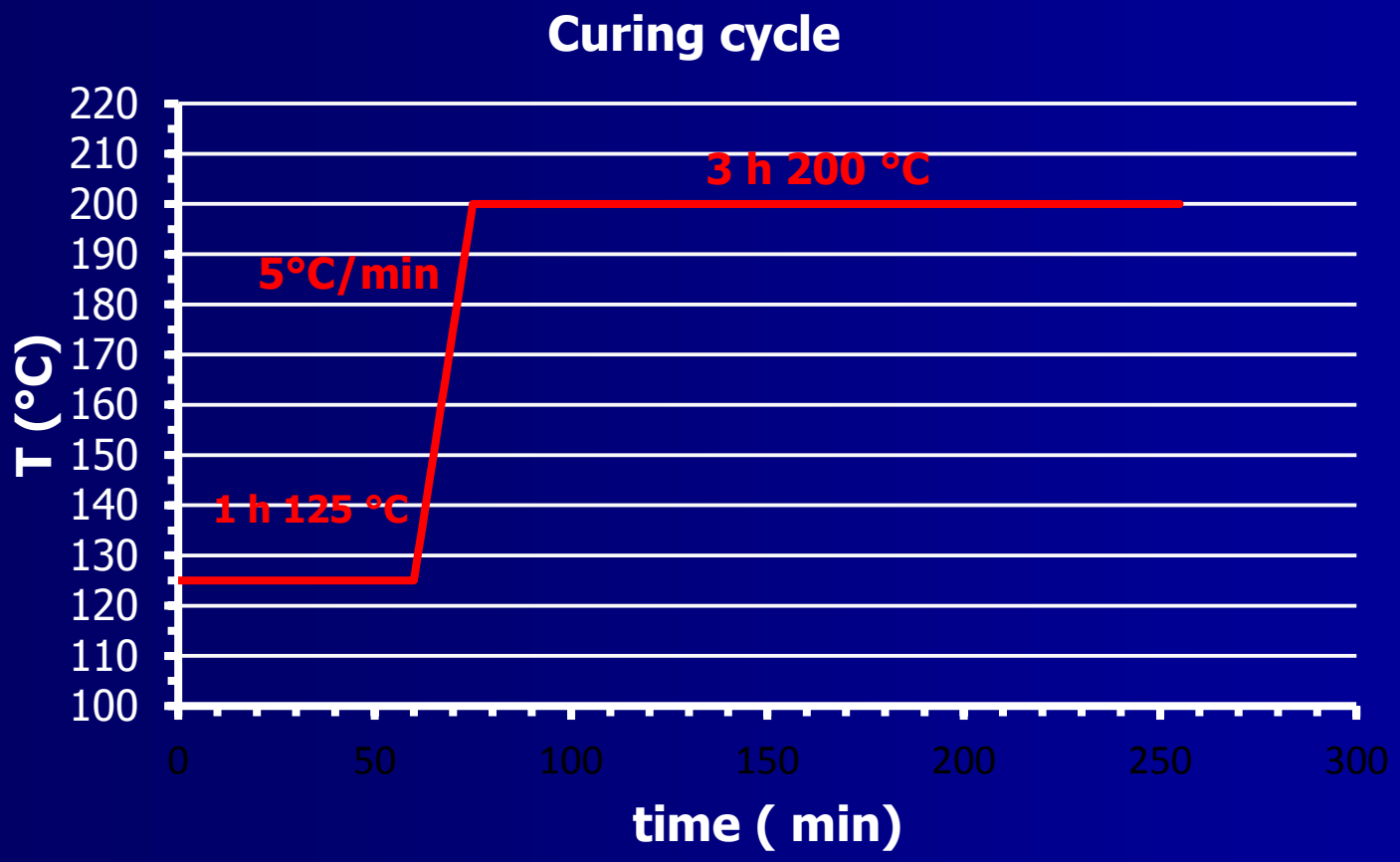
Epoxy blend and DDS were mixed at 120 °C and the CNFs were added and incorporated into the matrix by using an ultrasonication for 20 minutes (Hielscher model UP200S-24KHz high power ultrasonic probe).

The carbon nanofibers were dispersed within the epoxy resin at loading rates of 0.05, 0.32, 0.64, 1.00 and 1.30 per cent by weight.

Epoxy specimens manufacture

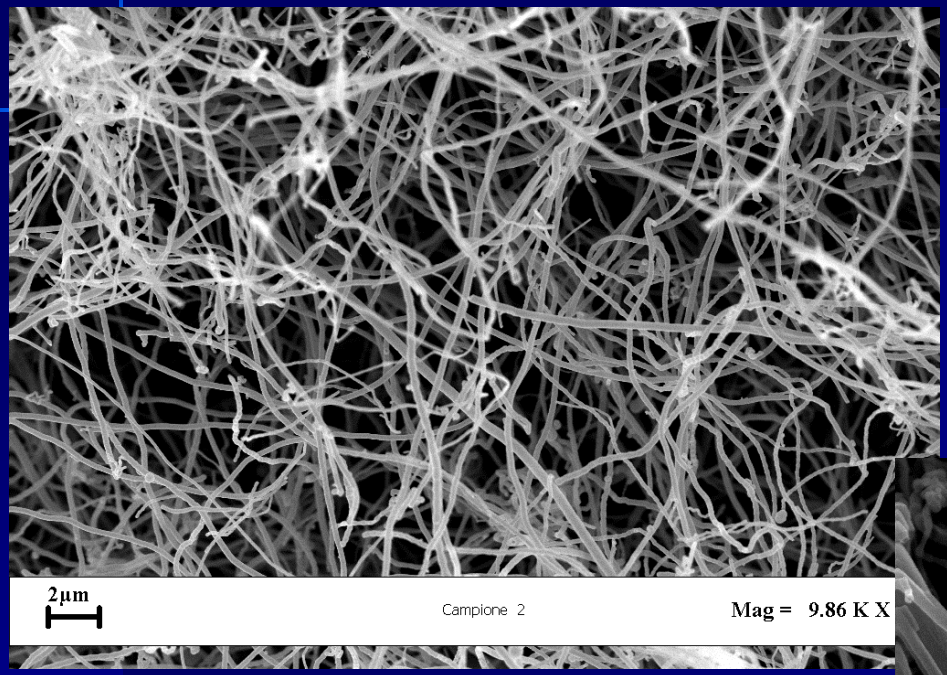
(Curing Cycle)

All the mixtures were cured by a two-stage curing cycles: a first isothermal stage was carried out at the lower temperature of 125 °C for 1 hour and the second isothermal stage at higher temperatures up to 200 °C



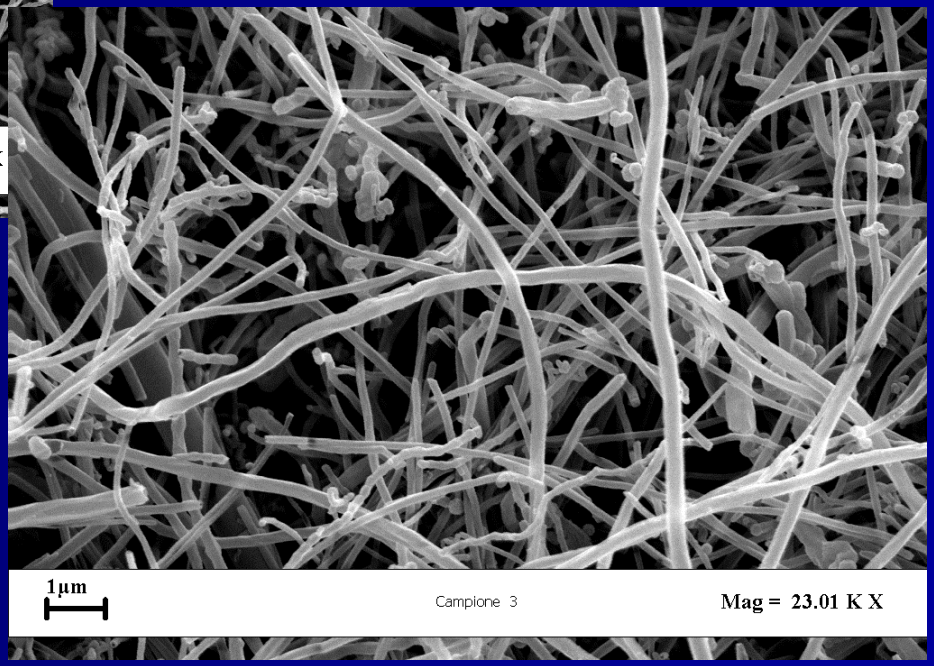
Materials - Carbon nanofibers

Nanofillers



as-received CNFs

PR25XTPS1100



Heat-treated CNFs

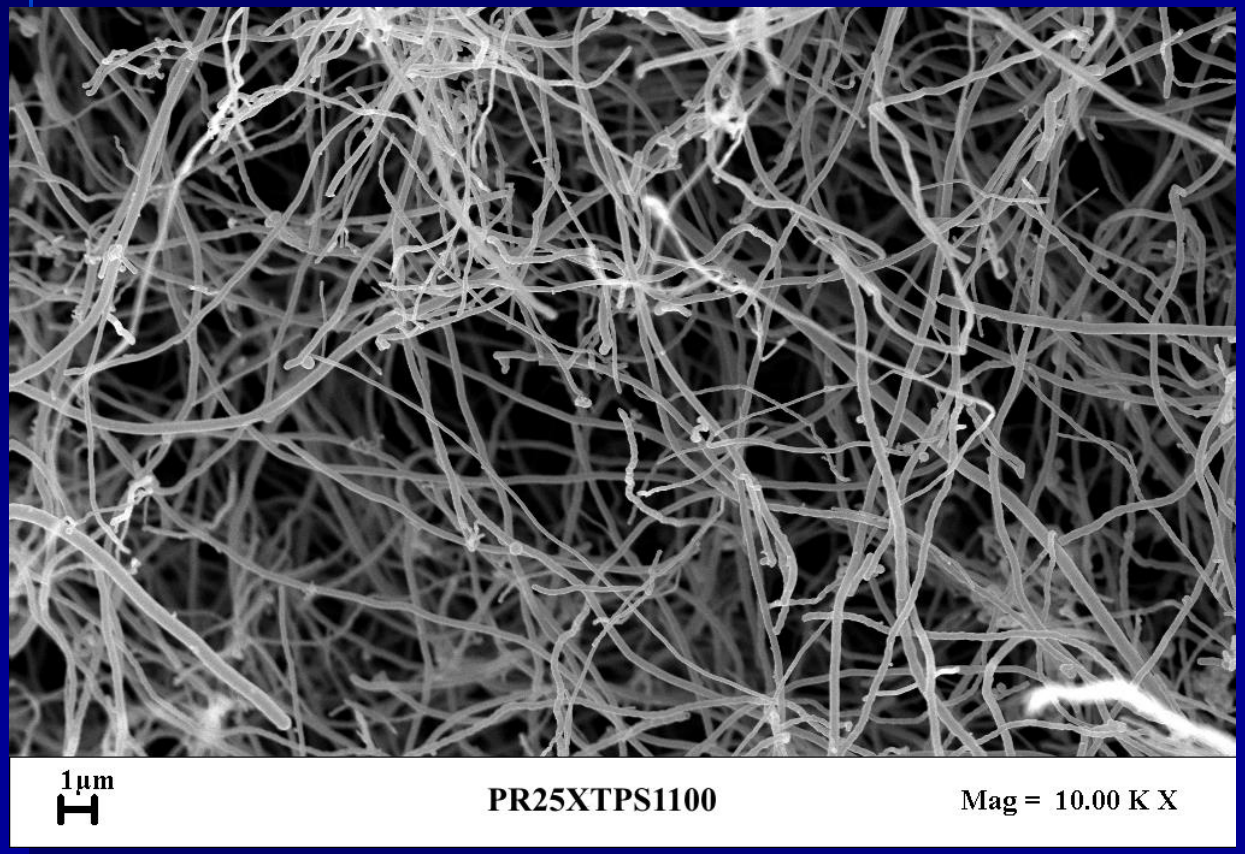
PR25XTPS2500

RESULTS AND DISCUSSION

CARBON FIBER CHARACTERIZATION

SEM INVESTIGATION

FESEM investigation of CNFs was performed to analyze the morphology of the nanofibers before their incorporation into the epoxy precursors. The image shown in this figure indicates that the as-received CNFs are debulked enough to avoid additional treatment.



as-received CNFs

PR25XTPS1100

Carbon fiber characterization

P

SEM IMAGES (before and after heat treatment)

The influence of heat treatment on the nanofiber morphology can be seen in figure where the inserts at higher magnification show that in the as-received CNFs a nested configuration is observed. The heat treatment seems statistically to reduce this effect; in fact heat treated CNFs seem to be characterized by smoother walls where the nested configuration is not clearly visible.

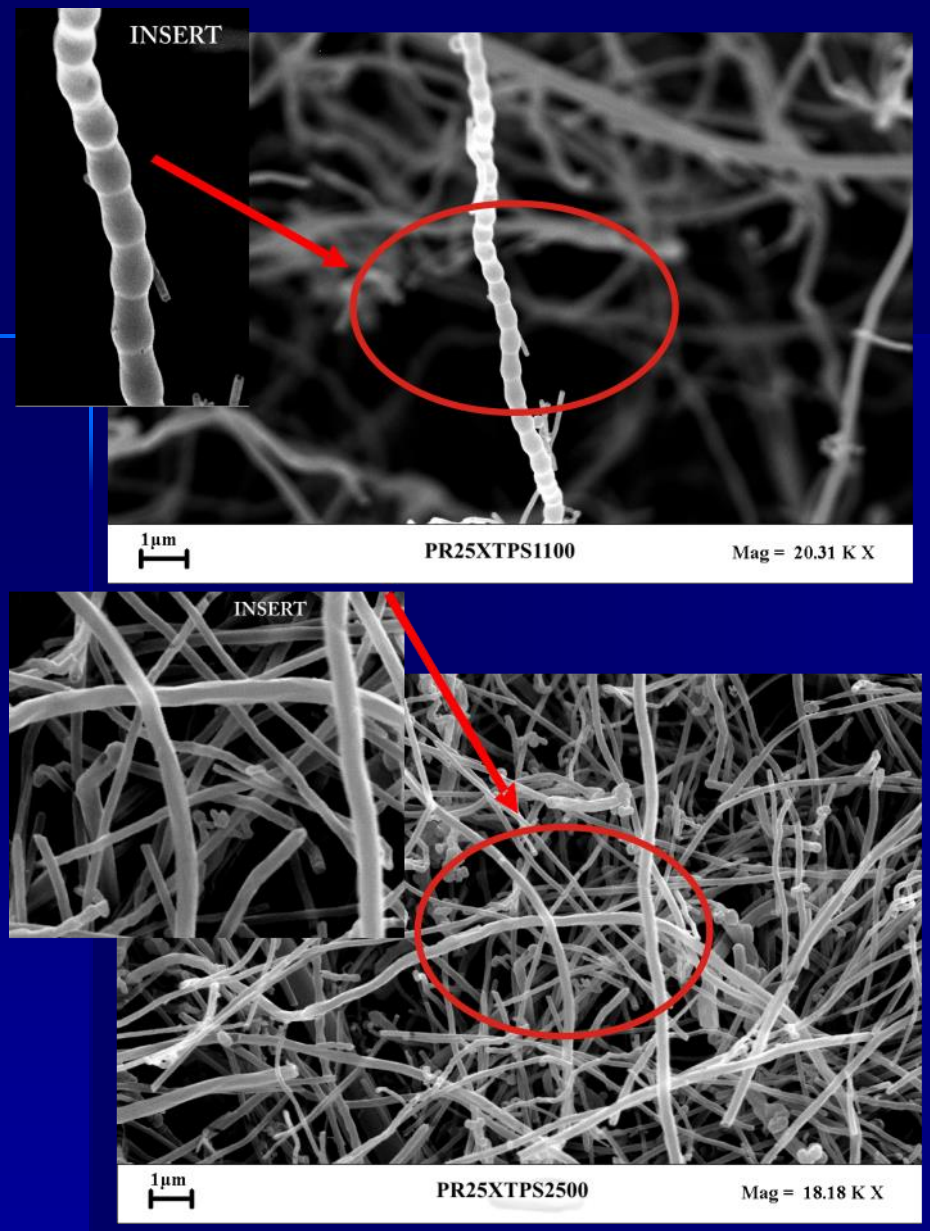
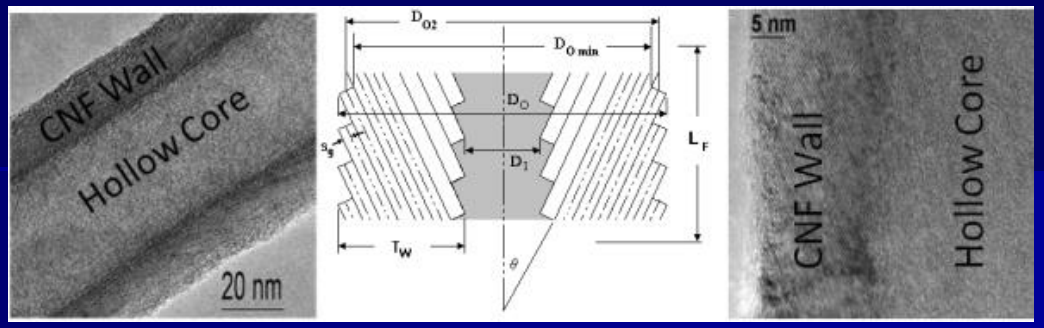
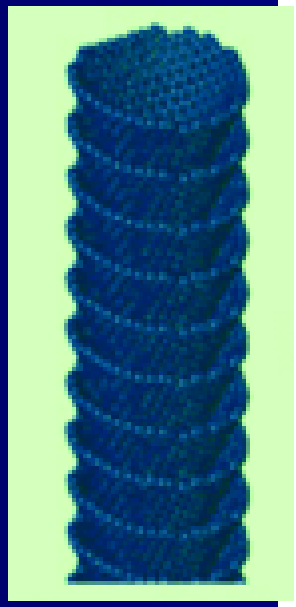


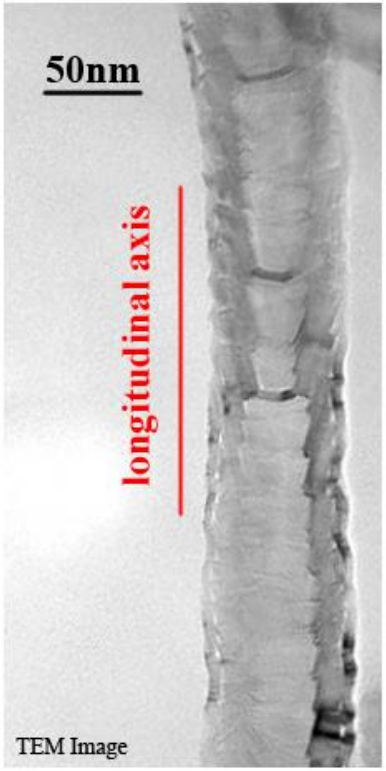
Figure : SEM images of as-received CNFs (PR25XTPS1100) and CNFs heat-treated at 2500 °C (PR25XTPS2500); insert at higher magnifications can be observed for each sample.

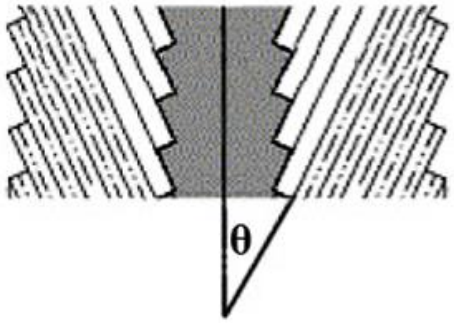
The changes in morphology due to heat-treatment can be better analyzed by means of TEM investigation.



This Figure shows the TEM micrograph of the CNFs used in this study. The individual pristine nanofiber has a hollow core that is surrounded by a cylindrical fiber comprised of highly crystalline, graphite basal planes stacked at about 25 degrees from the longitudinal axis of the fiber. This morphology, termed "stacked cup" or "herringbone", generates a fiber with exposed edge planes along the entire interior and exterior surfaces of the nanofiber.



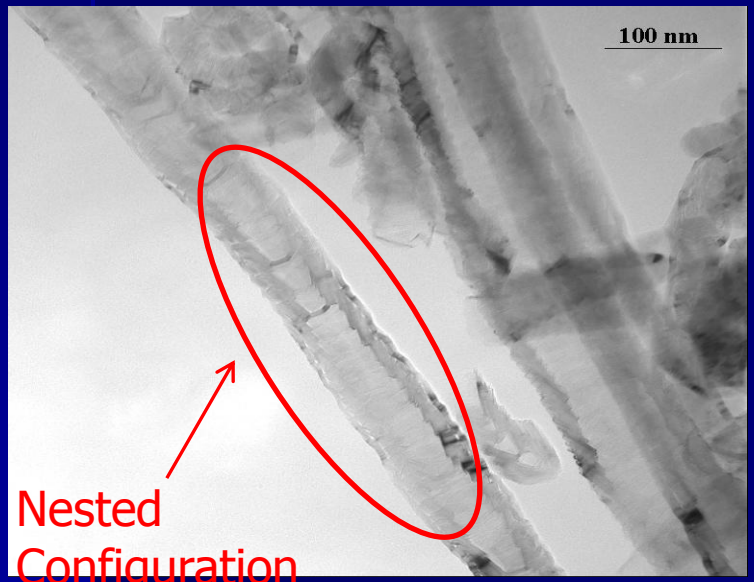


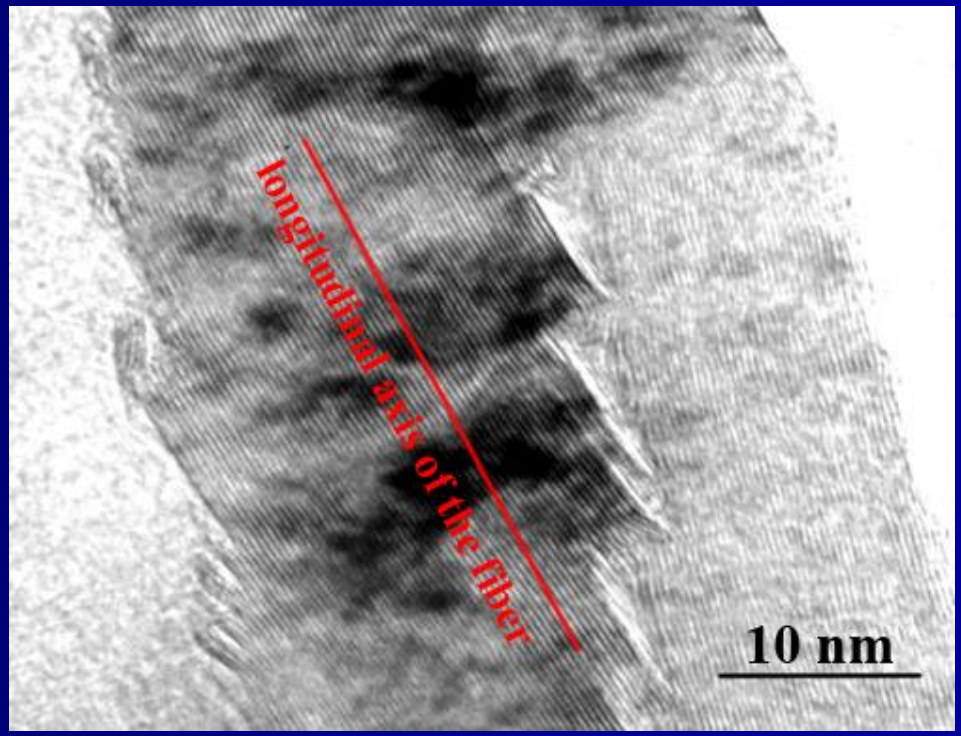


Internal structure
(cross sectional view)
of Stacked-Cup of CNF

Nested carbon nanofibers have an orientation similar to that of a set of stacked Dixie cups with a hollow core. The Dixie caps of the pristine CNFs are also clearly visible in the Figure (red ellipse).

The pristine CNFs exhibit only local molecular ordering. As they are heat treated, an increase in temperature results in the aromatic molecules become stacked in a column structure ; after heat treating the pristine nanofibers to a temperature of 2500 °C, graphene layers became straight, and minimum interlayer spacing was reached for the PR-25-2500C. As shown by a TEM micrograph in the Figure, the layers within the "Dixie Cup" carbon nanofiber have coalesced following heat-treatment.

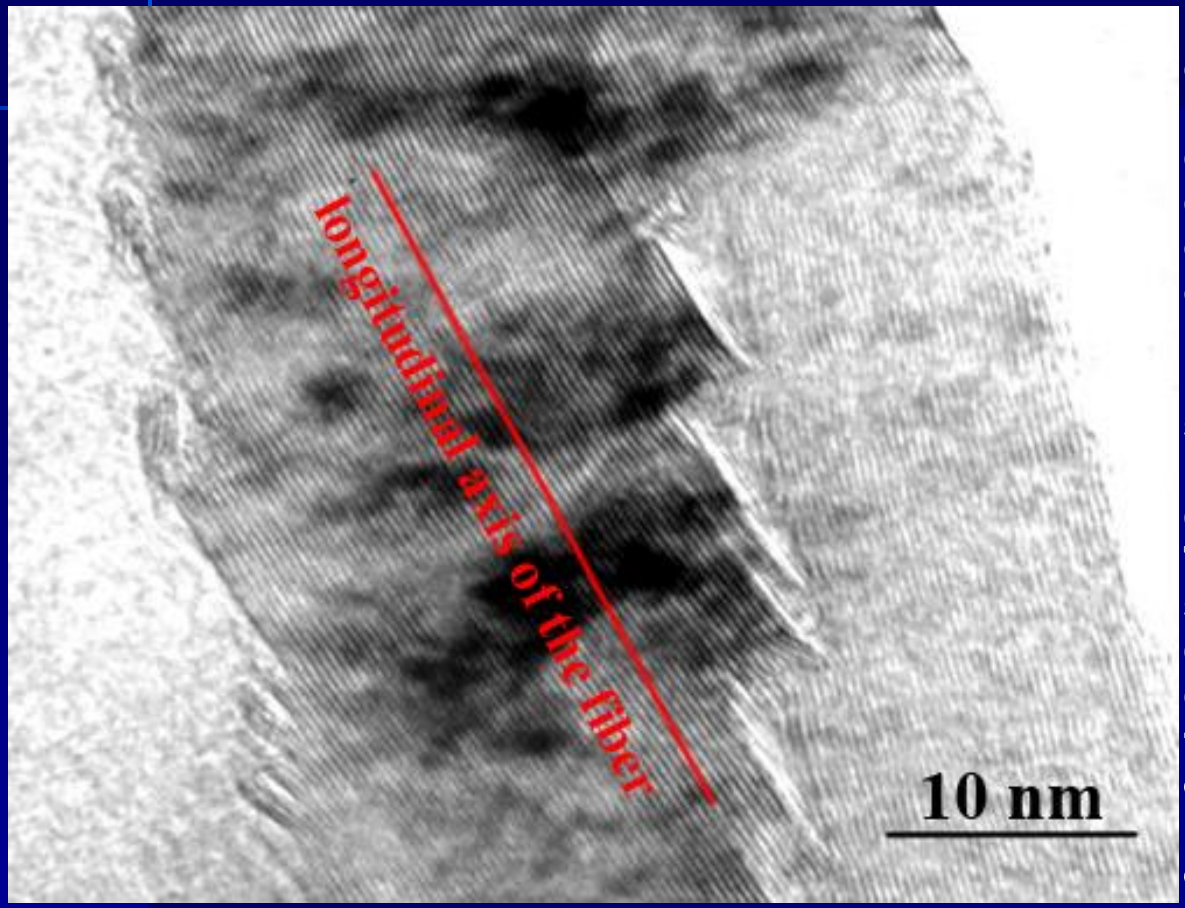




CARBON FIBER CHARACTERIZATION

RESULTS AND DISCUSSION

TEM IMAGE

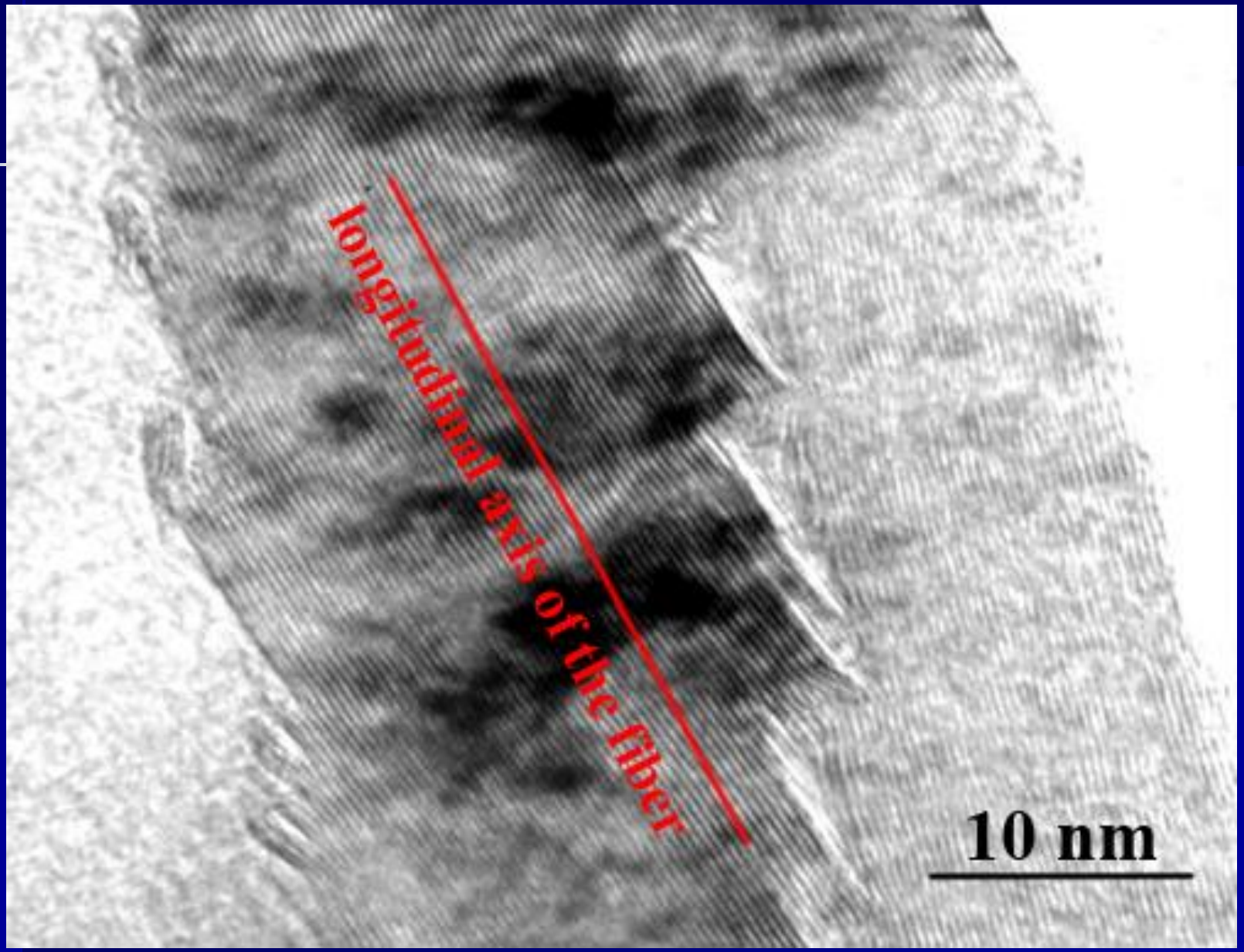


At this magnification the inclination angle of each “cup” is apparent. Within each cup it can be seen that the localized ordering of the graphene planes has been changed due to coalescence resulting in continuous planes. The stacking effect is shown through the use of a grey-scale. The walls of the nanofibers are dark due to their high electronic density. The surrounding regions are starkly lighter with low electronic densities.

The graphene layers appear very straight without any disclination defects. However, there is no change in the inclination angle to the central core axis. The edge of any pair of graphene layers have been rounded encapsulating carbon planes’ exposed edge. This allows the exposed graphene planes to attain a level of maximum structural stability.

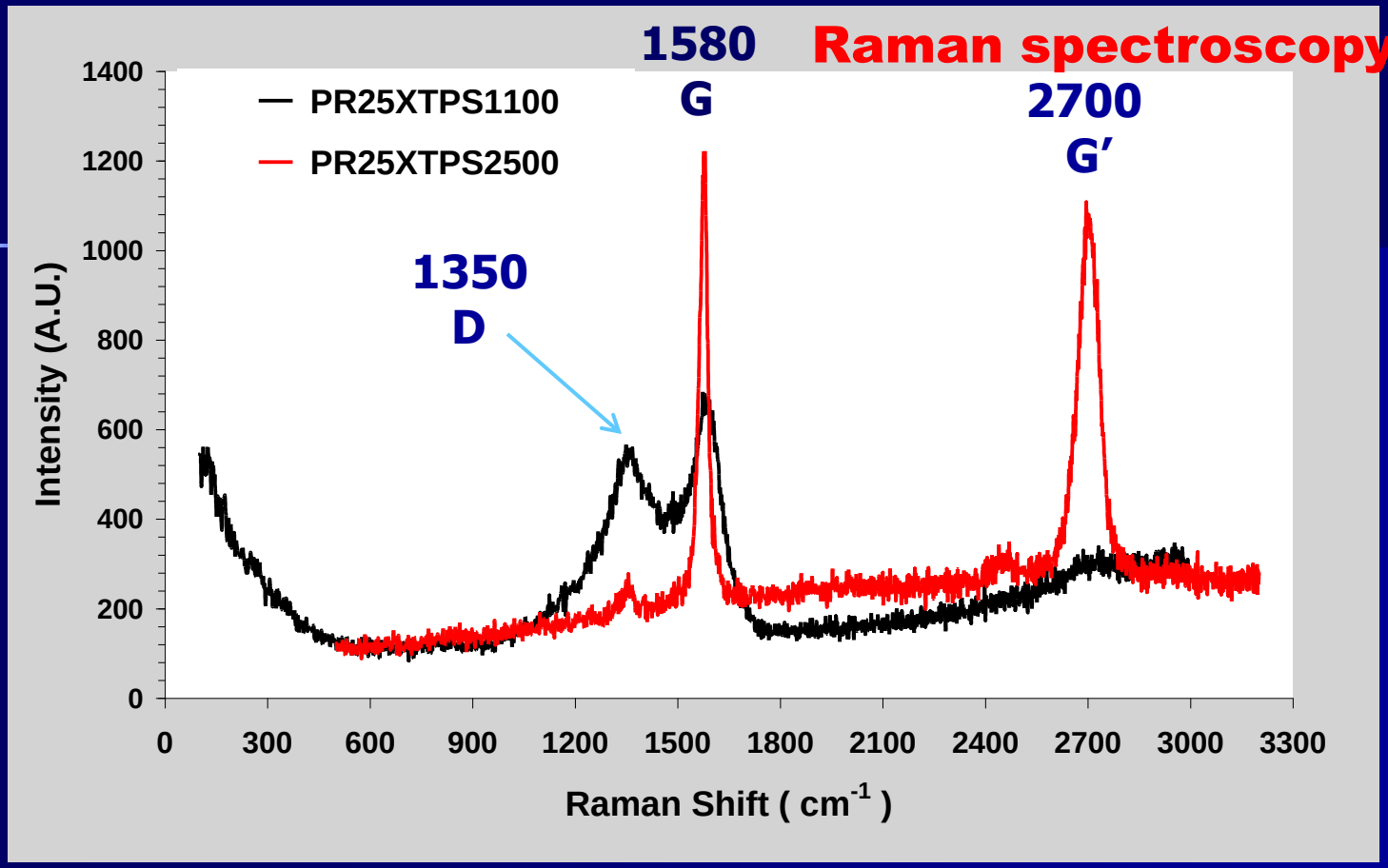
RESULTS AND DISCUSSION

CARBON FIBER CHARACTERIZATION



RESULTS AND DISCUSSION

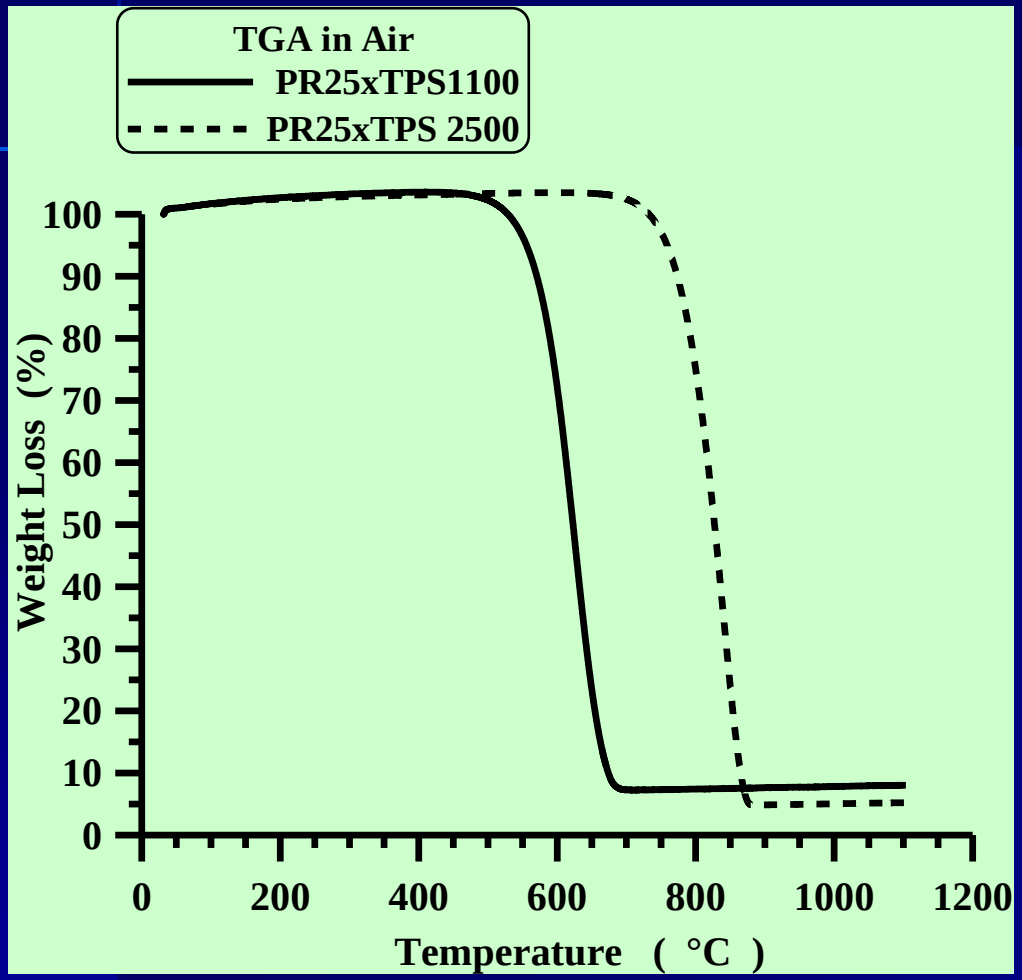
CARBON FIBER CHARACTERIZATION



The I_D/I_G values of the two samples are 0.8 for PR25XTPS1100 and 0.08 for PR25XTPS2500. The red spectrum shows a profile corresponding to Carbon fibers characterized by high level of order with two intense signals (G and G' bands) characteristic of graphitic sp^2 materials. The heat-treatment at higher temperature causes a significant transformation $sp^3 \longrightarrow sp^2$

RESULTS AND DISCUSSION

Thermogravimetric analysis

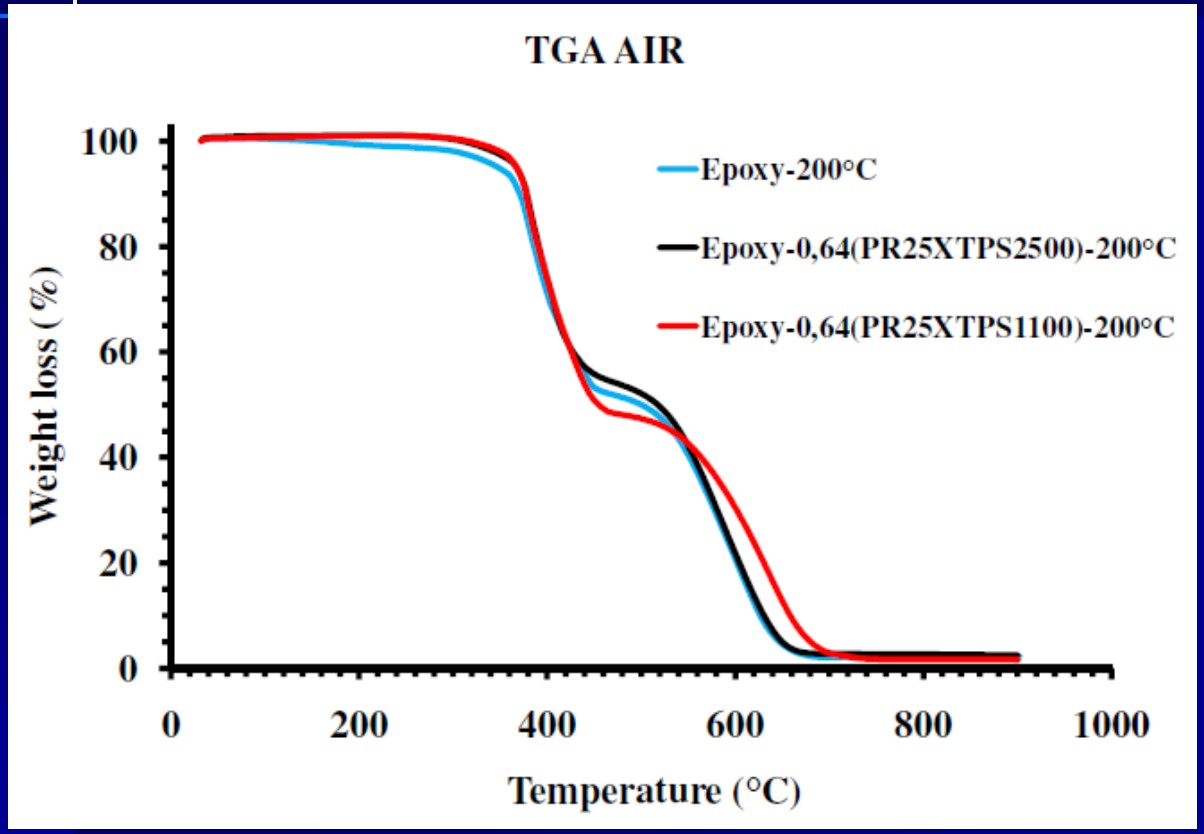


Thermogravimetric analysis (TGA) shows that nanofibers annealed at 2500 °C (PR25XTPS2500) are more air stable than as-received nanofibers (PR25XTPS1100). The oxidative stability enhancement is of about 200 °C.

Fig. 2. TGA of CNF PR25XTPS and CNF PR25XTPS2500 samples.

RESULTS AND DISCUSSION

CNF/EPOXY COMPOSITE CHARACTERIZATION



The first stage of oxidation of both samples substantially occurs in the temperature range of 380–480 °C highlighting that the different thermal treatment of CNFs does not influence the temperature of beginning degradation.

TGA of Epoxy-0,64(PR25XTPS)-200 °C and Epoxy-0,64(PR25XTPS2500)-200 °C samples.

RESULTS AND DISCUSSION

CNF/EPOXY COMPOSITE CHARACTERIZATION

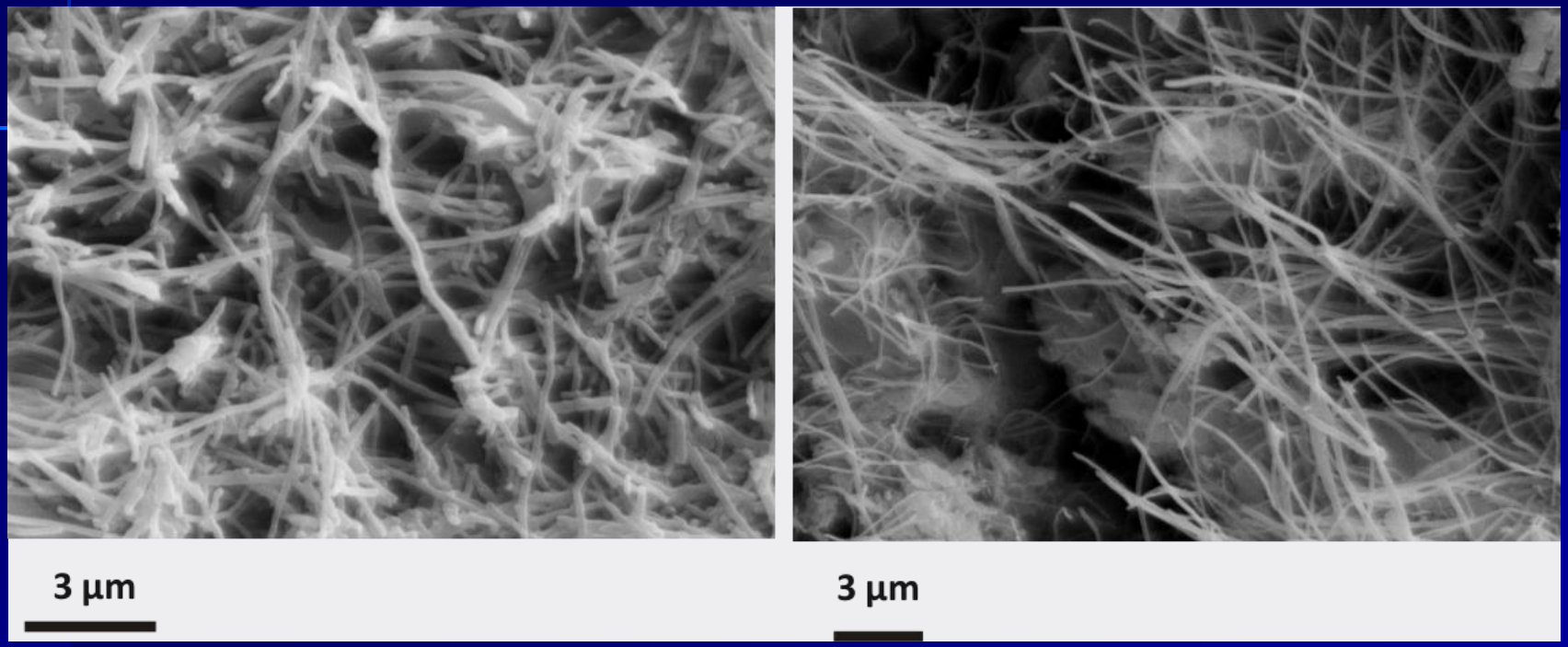
Morphological analysis

In order to analyze the morphological characteristics related to the nanofiller dispersion into the epoxy mixture, the samples with as-received CNFs and heat-treated CNFs were investigated by means of scanning electron microscopy (SEM).

The analysis was carried out on etched samples to remove the resins surrounding the nanofibers, leaving them bare.

RESULTS AND DISCUSSION

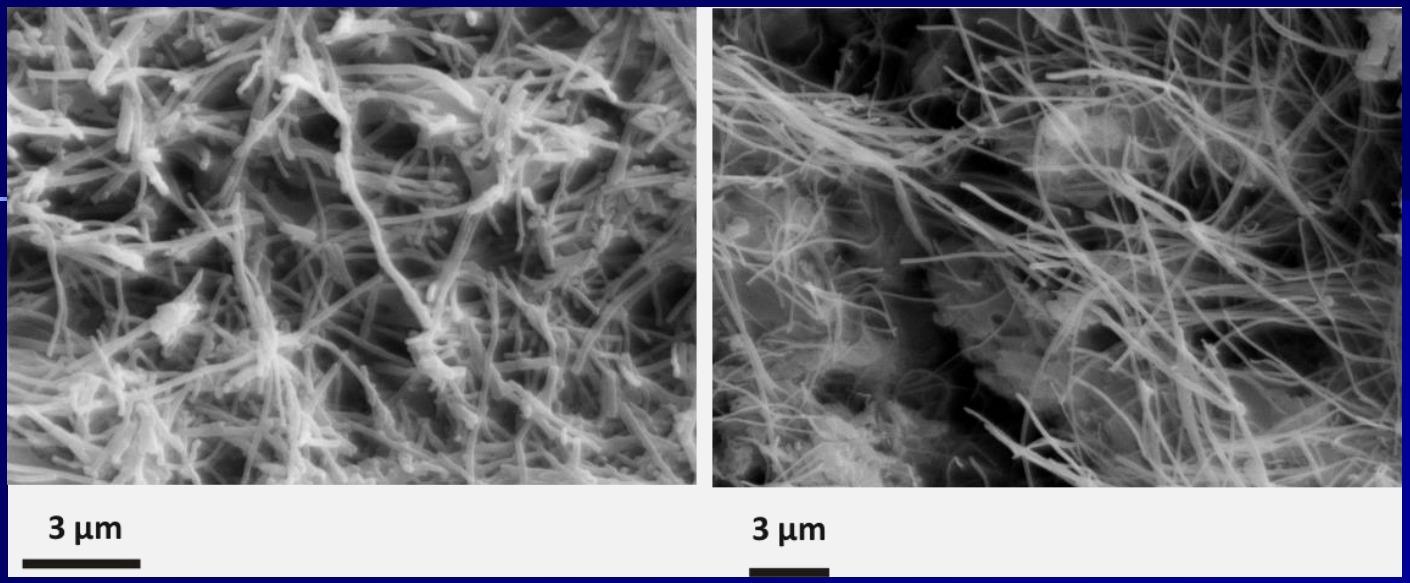
CNF/EPOXY COMPOSITE CHARACTERIZATION



Fracture surface SEM images of the nanofilled epoxy resins at loading rate of 0.64 per cent by weight: as received CNFs filled resin is on the left side, heat-treated CNFs filled resin is on the right side.

RESULTS AND DISCUSSION

CNF/EPOXY COMPOSITE CHARACTERIZATION

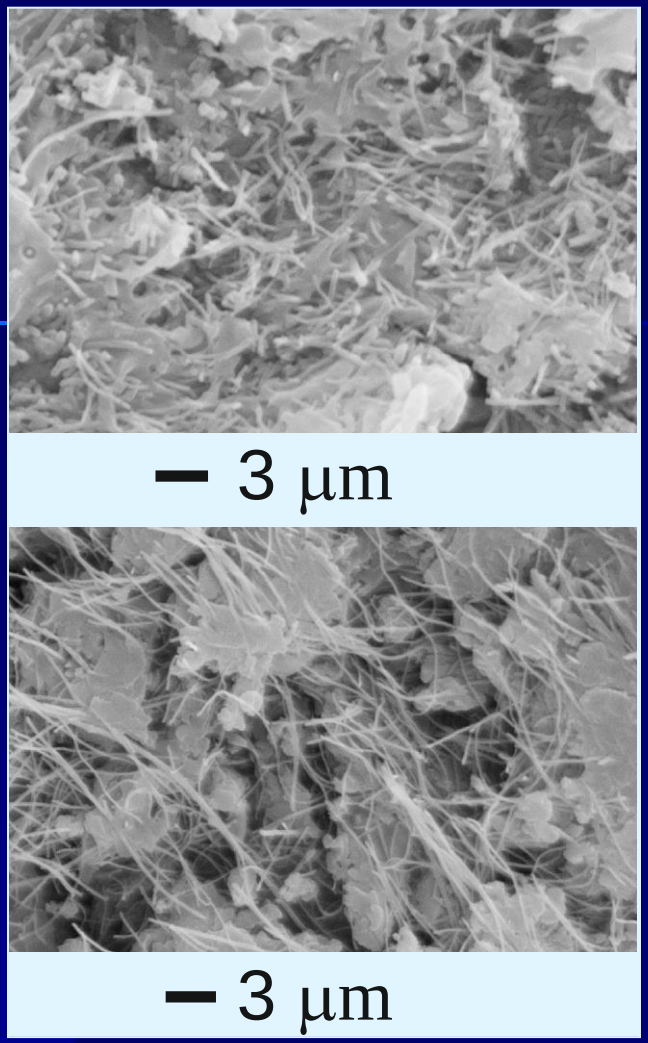


Fracture surface SEM images of the nanofilled epoxy resins at loading rate of 0.64 per cent by weight: as received CNFs filled resins are on the left side, heat-treated CNFs filled resins are on the right side.

- **SEM investigations highlight that CNFs are uniformly distributed inside the epoxy matrix in both the samples-**

- **heat-treated CNFs seem to be characterized by a more straight structure than un-treated CNFs. This morphological characteristic is most probably due to a more perfect rigid structure which results in a less tendency to bend with respect to untreated CNFs.**

CNF/EPOXY COMPOSITE CHARACTERIZATION



The straight morphological feature is statistically observed for all the concentration of heat-treated CNFs, as it can also be observed for samples filled with higher percentage of CNFs.

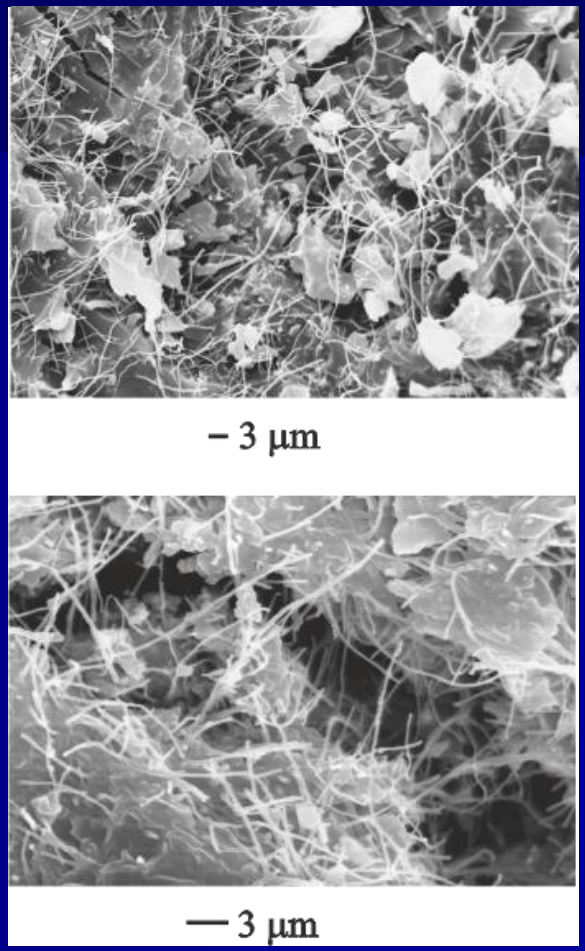
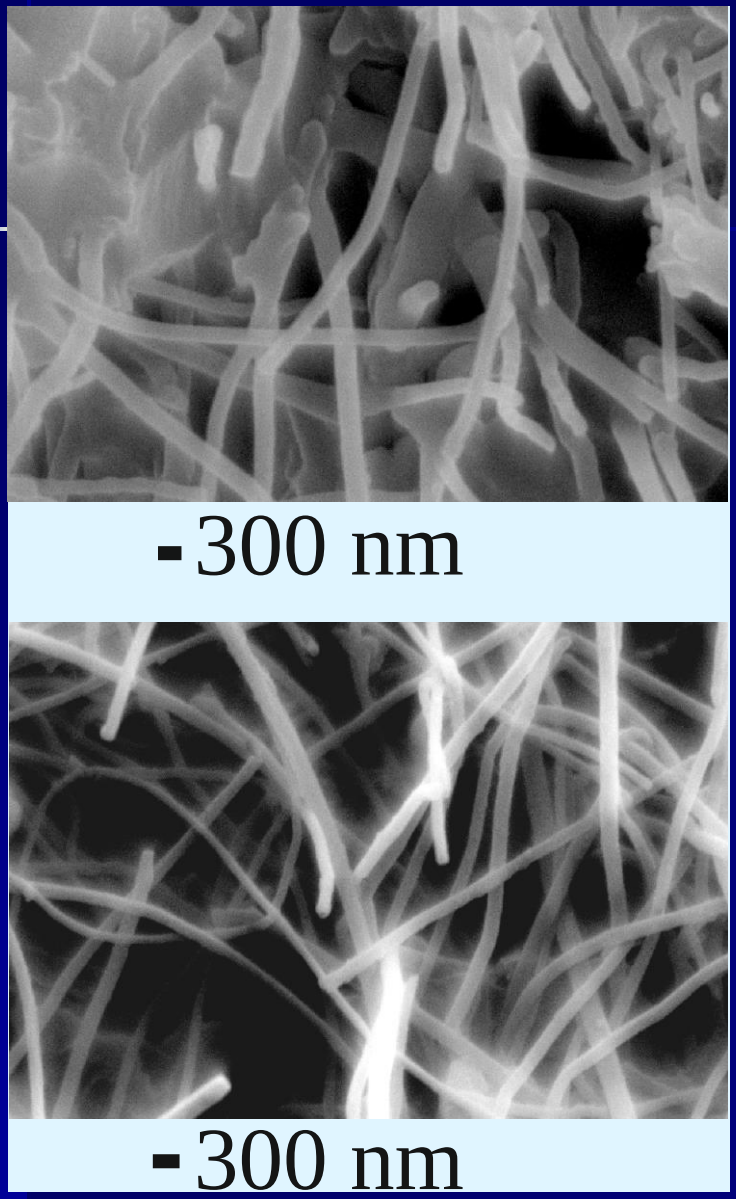


Figure: Fracture surface SEM images of the nanofilled epoxy resins at loading rate of 1.0 per cent by weight: as received CNFs filled composite is on the top, heat-treated CNFs filled composite is on the bottom.

Fracture surface SEM images of the nanofilled epoxy composites at loading rate of 0.64 per cent by weight: as received CNFs filled composite is on the top, heat-treated CNFs filled composite is on the bottom.

RESULTS AND DISCUSSION

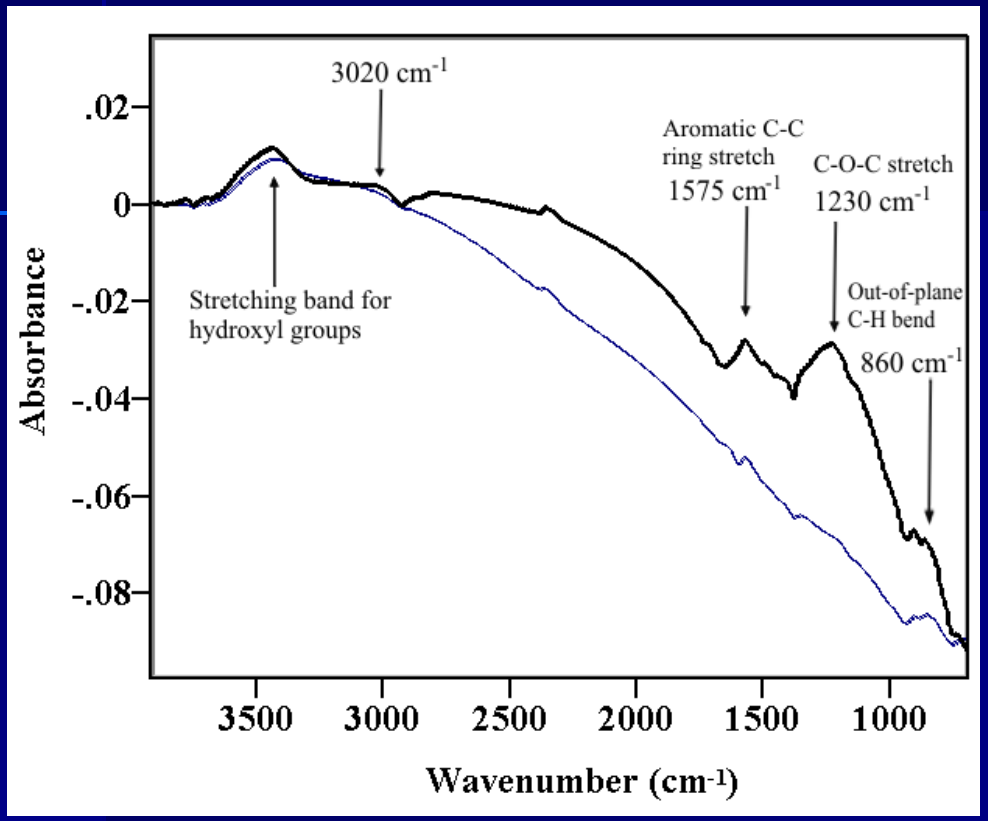
CNF/EPOXY COMPOSITE CHARACTERIZATION



A careful observation of the SEM images seems to highlight the following:

- **heat-treated CNFs seem statistically to show a narrowing of the diameter,**
- **heat-treated CNFs seem statistically less bonded to the epoxy matrix;**

Figure: Fracture surface SEM images (enlargement) of the nanofilled epoxy resins at loading rate of 1.0 per cent by weight: as received CNFs filled composite is on the top, heat-treated CNFs filled composite is on the bottom.



FTIR spectra of the samples PR25XTPS1100 (thick line) and PR25XTPS2500 (thin line).

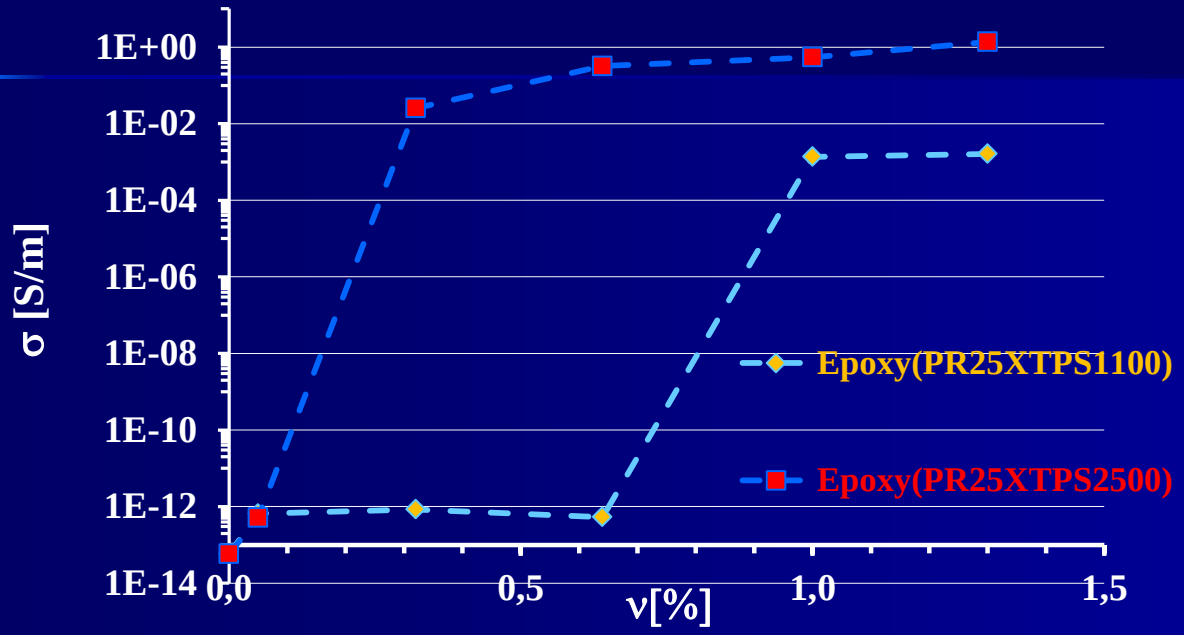
The stronger interaction of un-treated CNFs with the matrix than the heat treated CNFs could be due to a synergic combination of two effects: the carbon planes' exposed edges of the untreated CNFs and the number of functional groups on the walls available for chemical and physical interactions .

Results and discussion

CNF/epoxy composite characterization

Electrical Behavior

The measurements of the dc conductivity are shown in this Figure



The treatment at high temperature causes a strong decrease in the concentration related to the percolation threshold: a less amount of filler is necessary in order to obtain high values in the electrical conductivity.

The obtained value show that the high temperature treatment on the nanofillers leads to an increase in the nanocomposite dc conductivity of about 2 order of magnitude.

Electrical Conductivity of nanofilled resins

The better conduction performance exhibited by the nanofilled systems based on heat-treated CNF is most probably due to their lower tendency to bend due to heat-treatment and to their smoother surface which determines a lower thickness of the insulating layer around the fibers, which in turn controls the value of the resistance associated to the tunneling between conducting clusters forming the percolating paths inside the resin.

Conclusions

Heat-treatment of carbon nanofibers at 2500 °C has proven to be an effective method in removing defects from carbon nanofibers.

Heat-treatment of carbon nanofibers at high temperature also causes an increase in the nanofiller oxidative stability, while leaving substantially unchanged the stability of the reinforced resin.

Conclusions

Enhancement in the fiber structural perfection very positively affects the electrical conductivity of the nanofibers-reinforced resins.

The better electrical conductivity exhibited by the nanofilled systems based on heat-treated CNF may be reasonably ascribed to the changes in the morphological parameters of CNFs due to heat-treatment.

The value in the electrical conductivity of the composite filled with CNFs treated at 2500 °C is very similar to the values already found for epoxy composites filled with CNTs

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Thank You
for Your Attention!