

6-2014

# Influence of Nanofiller Morphology on the Viscoelastic Properties of CNF/Epoxy Resins

Liberata Guadagno  
*University of Salerno*

Marialuigia Raimondo  
*University of Salerno*

Khalid Lafdi  
*University of Dayton, klafdi1@udayton.edu*

Annalisa Fierro  
*University of Salerno*

Salvatore Rosolia  
*University of Salerno*

*See next page for additional authors*

Follow this and additional works at: [https://ecommons.udayton.edu/cme\\_fac\\_pub](https://ecommons.udayton.edu/cme_fac_pub)

 Part of the [Other Chemical Engineering Commons](#), [Other Materials Science and Engineering Commons](#), and the [Polymer and Organic Materials Commons](#)

---

## eCommons Citation

Guadagno, Liberata; Raimondo, Marialuigia; Lafdi, Khalid; Fierro, Annalisa; Rosolia, Salvatore; and Nobile, Maria Rossella, "Influence of Nanofiller Morphology on the Viscoelastic Properties of CNF/Epoxy Resins" (2014). *Chemical and Materials Engineering Faculty Publications*. 9.

[https://ecommons.udayton.edu/cme\\_fac\\_pub/9](https://ecommons.udayton.edu/cme_fac_pub/9)

This Article is brought to you for free and open access by the Department of Chemical and Materials Engineering at eCommons. It has been accepted for inclusion in Chemical and Materials Engineering Faculty Publications by an authorized administrator of eCommons. For more information, please contact [frice1@udayton.edu](mailto:frice1@udayton.edu), [mschlangen1@udayton.edu](mailto:mschlangen1@udayton.edu).

---

**Author(s)**

Liberata Guadagno, Marialuigia Raimondo, Khalid Lafdi, Annalisa Fierro, Salvatore Rosolia, and Maria Rossella Nobile

# Influence of Nanofiller Morphology on the Viscoelastic Properties of CNF/Epoxy Resins

Liberata Guadagno<sup>a</sup>, Marialuigia Raimondo<sup>a\*</sup>, Khalid Lafdi<sup>b</sup>, Annalisa Fierro<sup>a</sup>,  
Salvatore Rosolia<sup>a</sup>, Maria Rossella Nobile<sup>a</sup>

<sup>a</sup>*Department of Industrial Engineering – DIIn - Università di Salerno  
Via GiovanniPaolo II ,132 - 84084 Fisciano (SA), Italy (UE)*

<sup>b</sup>*University of Dayton, 300 College Park, Dayton, OH 45440, USA*

**\*Corresponding author: e-mail: mraimond@unisa.it**

**Abstract.** In this paper we discuss the viscoelastic properties of CNF/Epoxy-Amine Resins for structural applications. The use of reactive diluent inside the unfilled and nanofilled epoxy mixture as proven to be of benefit to strongly decrease the viscosity.

**Keywords:** Epoxy resins; Viscoelasticity in rheology; Scanning electron microscopy; Composite materials rheology; Nanotechnology nanoscale materials and structure

**PACS:** 83.80.-k; 83.60.Bc; 83.60.Df; 68.37.Hk; 83.80.Ab; 81.07.-b

## INTRODUCTION

Resins filled with conductive nanofillers were proposed in literature to overcome drawbacks related to insulating properties of the epoxy resins used to manufacture carbon fiber reinforced composites (CFRCs) [1-5].

Nanofilled resins made of conductive nanostructured forms of carbon show significant increases in their electrical conductivity even at low nanofiller concentrations. Among mono-dimensional shaped forms of carbon, carbon nanofibers (CNFs) offer very promising results. The values of electrical conductivity of nanofilled epoxy resins are similar to those found for epoxy matrices filled with CNTs. However, it has to be considered that CNFs/epoxy resins are obtained by an easier production process mainly in the step of nanofiller dispersion inside the epoxy liquid mixture, which is a very difficult step before the curing process. Further criticalities are related to the processing methods employed to manufacture CFRCs. Economic and efficient means of producing high performance fibre-reinforced composites, containing nanofiller embedded in the resin which impregnates CFs, are critically limited by the initial viscosity of epoxy precursors. Generally, the physical properties of epoxy resins strongly depend on the functionality of the epoxy precursor; a tetrafunctional precursor for example assures good properties of the cured resin due to the high level of crosslinking density. Unfortunately, this advantage also causes inconveniences resulting from the high viscosity of the tetrafunctional precursor, the brittleness and poor resistance to crack propagation. In this paper we show the first results on the rheological properties of an aeronautic formulation [6-7] obtained by blending the epoxy precursor with a reactive modifier that performs a double function, as flexibilizer and regulator of viscosity for a best dispersion of nanoparticles.

## Materials

CNFs in the form of powders 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. The morphological parameters are shown in Table 1. Sample PR25XTPS1100 was heat treated to 2500 °C to provide the best combination of mechanical and electrical

properties, giving the sample the name PR25XTPS2500.

The epoxy matrix was prepared by mixing an epoxy precursor, tetraglycidylmethylene dianiline (TGMDA) (epoxy equivalent weight 117–133 g/eq), with an epoxy reactive monomer 1-4 butanediol diglycidyl ether (BDE) that acts as a reactive diluent. The curing agent investigated for this study is 4,4-diaminodiphenyl sulfone (DDS). The epoxy mixture was obtained by mixing TGMDA with BDE monomer at a concentration of 80%:20% (by wt) epoxide to flexibilizer. The hardener agent was added at a stoichiometric concentration with respect to all the epoxy rings (TGMDA and BDE), this mixture will be named TBD in the following. Epoxy blend and DDS were mixed at 120 °C and the CNFs (samples PR25XTPS1100 and PR25XTPS2500) were added and incorporated into the matrix by using an ultrasonication for 20 min. An ultrasonic device, Hielscher model UP200S (200 W, 24 kHz) was used. Our experiments show that nanofilled resins with loads beyond 1.3% by weight have difficulty in establishing a homogeneous mixture.

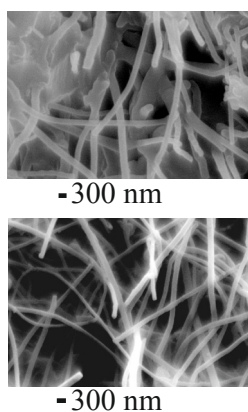
**TABLE 1.** Morphological parameters of PR25XTPS1100 CNFs.

Average Bulk Density of Product, (lb/ft <sup>3</sup> )	1.2-3.0
Nanofiber Wall Density, (g/cm <sup>3</sup> )	2.0-2.1
Nanofiber Density (including hollow core), (g/cm <sup>3</sup> )	1.4-1.6
Average Catalyst (Iron) Content, (ppm)	<14,000
Average Outer Diameter, (nm)	125-150
Average Inner Diameter, (nm)	50-70
Average Specific Surface Area, m <sup>2</sup> /g	65-75
Total pore volume (cm <sup>3</sup> /g)	0.140
Average Pore Diameter (angstroms Å)	82.02

Micrographs of nanofilled epoxy composites were obtained using a Field Emission Scanning Electron Microscope (FESEM, mod. LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany). Nanofilled sample sections were cut from solid samples by a sledge microtome. These slices were etched before the observation by FESEM. The nanofilled sample sections were placed on a carbon tab previously stuck to an aluminum stub (Agar Scientific, Stansted, UK). The samples were covered with a 250-Å-thick gold film using a sputter coater (Agar mod. 108 A). The rheological measurements were carried out in a Physica MCR 301 (Anton Paar) rotational rheometer equipped with a parallel plate geometry (50 mm diameter, 1mm gap) on the pure TGMDA epoxy precursor, on the binary TGMDA-BDE system (named TB blend), on the ternary TGMDA-BDE-DDS system (named TBD in the following) and on the CNFs-TBD nanocomposites with 0.5 wt % nanofiber content. Nanocomposites with PR25XTPS1100 nanofibers as well as nanocomposites with PR25XTPS2500 nanofibers have been tested. Strain sweep tests, at the frequency of 1 rad/s and T=75°C, were previously performed to determine the linear viscoelastic region. Small amplitude oscillatory shear measurements at 1% strain, within the linear viscoelasticity regime, were, then, performed in the frequency range comprised between 10<sup>-2</sup> and 10<sup>2</sup> rad/s, at the temperature of 75 °C.

### Morphological analysis

Figure 1 shows FESEM images of nanofilled epoxy composites at loading concentration of 1.0 per cent by weight of CNFs. The as-received CNFs filled composites are on the top and those with heat-treated CNFs are on the bottom.

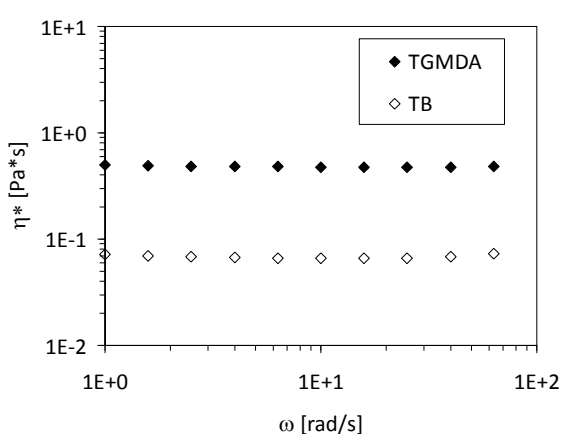


**FIGURE 1.** Fracture surface FESEM images (enlargement) of the nanofilled epoxy resins at loading concentration of 1.0 per cent by weight: as received CNFs filled resin is on the top, heat-treated CNFs filled resin is on the bottom.

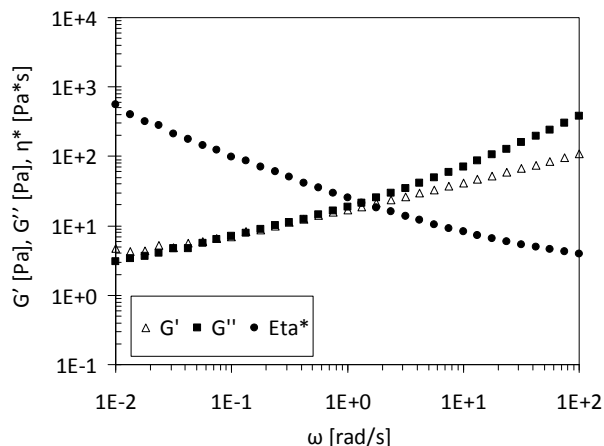
FESEM investigations highlight that heat-treated CNFs seem to be characterized by a more straight structure than un-treated CNFs. This morphological characteristic is most probably due to a more perfect rigid structure which results in a less tendency to bend with respect to untreated CNFs. This straight morphological feature is statistically observed for all the concentrations of heat-treated CNFs. FESEM images also evidence that heat-treated CNFs seems statistically to show a narrowing of the diameter, this effect can be well observed in Figure 1, where the samples filled with untreated and heat-treated CNFs were acquired with the same magnification after a strong etching procedure. In addition, heat-treated CNF seems statistically less bonded to the epoxy matrix; in fact, in the case of untreated CNFs, the majority of the CNFs is tightly tied to the epoxy matrix.

## Rheological analysis

The complex viscosity ( $\eta^*$ ) values versus the frequency ( $\omega$ ) for the TGMDA epoxy precursor and for the binary TGMDA-BDE blend 80%:20% (by wt), named TB, are reported in Figure 2. The results evidence that  $\eta^*$  is constant in the whole frequency range tested, showing a Newtonian behaviour for the pure TGMDA epoxy precursor and for the binary TB blend. The inclusion of the flexibilizer BDE diluent, then, decreases the viscosity of the TGMDA, so that the dispersion of the nanofibers in the high viscosity TGMDA epoxy precursor is improved.



**FIGURE 2.** Complex viscosity ( $\eta^*$ ) vs frequency ( $\omega$ ) for the TGMDA epoxy precursor and for the TGMDA-BDE blend (TB); T= 75°C.



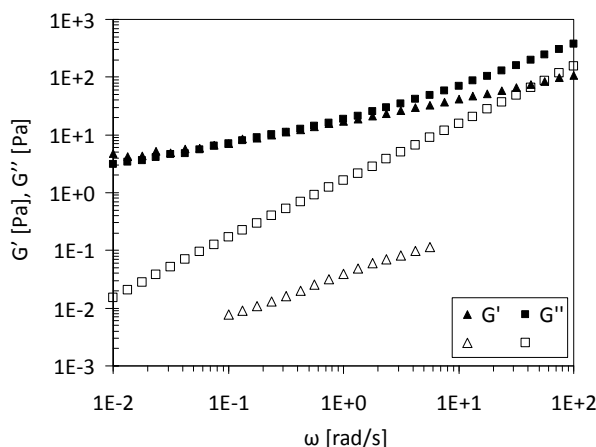
**FIGURE 3.** Complex viscosity ( $\eta^*$ ), storage ( $G'$ ) and loss ( $G''$ ) moduli vs frequency ( $\omega$ ) for the 0.5 wt% PR25XTPS2500-TBD nanocomposite; T = 75°C.

The inclusion of the heat-treated PR25XTPS2500 carbon nanofibers in the formulated TBD epoxy mixture (TGMDA-BDE-DDS) significantly modifies the rheological behaviour of the TBD mixture itself. In fact, at 0.5 wt % PR25XTPS2500 nanofiber content, the complex viscosity clearly shows a shear thinning behaviour with  $\eta^*$  values much higher at the lower frequencies, as shown in Figure 3 for the temperature T = 75°C. On the contrary, the nanocomposite with 0.5 wt % of the as received PR25XTPS1100 carbon nanofibers behaved essentially as a Newtonian fluid with complex viscosity values only slightly higher than those exhibited by TBD epoxy system.

In Figure 3 the storage ( $G'$ ) and loss ( $G''$ ) moduli values vs. frequency for the 0.5 wt% PR25XTPS2500-TBD nanocomposite are also reported. The tendency to a plateau in  $G'$ , clearly detected at the lower frequencies, can be attributed to the formation of an interconnected network between carbon nanofibers. Large scale relaxations in the nanocomposite are, in fact, restrained by the presence of the CNFs indicating that the 0.5 wt % content of the heat-treated PR25XTPS2500 CNFs is higher than the rheological percolation threshold [8-12].

In Figure 4 the  $G'$  and  $G''$  values of the filled epoxy with the untreated and treated CNFs are compared at T = 75°C. The results clearly evidence that the filled epoxy with the heat-treated CNFs show very high elasticity, while the nanocomposite with as received CNFs are essentially characterized by a viscous behaviour. In the case of filled epoxy with as received PR25XTPS1100 CNFs, the rheological percolation threshold is, therefore, higher than 0.5 wt % CNFs. Such a difference in the rheological behaviour can be attributed to the different morphology observed in the filled epoxy with the as received and heat-treated CNFs. Indeed, in both nanocomposites a good dispersion of the CNFs at 0.5 wt % is achieved, but the heat-treated CNFs seem statistically less bonded to the epoxy matrix as well

as more straight compared to the as received CNFs and the interconnected network between PR25XTPS2500 carbon nanofibers is obtained.



**FIGURE 4.** Storage ( $G'$ ) and loss ( $G''$ ) moduli vs frequency ( $\omega$ ) for the 0.5 wt% PR25XTPS2500-TBD nanocomposite (filled symbols) and for the 0.5 wt% PR25XTPS1100-TBD nanocomposite (empty symbols);  $T = 75^\circ\text{C}$ .

## CONCLUSIONS

In this paper it has been shown that the inclusion of the reactive diluent 1,4-butandiol diglycidyl ether in the epoxy resin based on the tetraglycidylmethylenedianiline (TGMDA) precursor reduces the viscosity values of the TGMDA. The viscoelastic properties of the nanofilled epoxy composites at 0.5 wt% content of as received and heat-treated CNFs evidence the formation of an interconnected network between CNFs only in the case of the heat-treated PR25XTPS2500 carbon nanofibers, which seem statistically less bonded to the epoxy matrix than the as received CNFs.

## ACKNOWLEDGMENTS

The research leading to these results has received funding from the European Union Seventh Framework Programme FP7/2007–13 under grant agreement no. 313978.

## REFERENCES

1. L. Guadagno et al., *Carbon* **49**, 1919-1930 (2011).
2. B. De Vivo et al., *Adv. Polym. Technol.* **31**, 205-218 (2012).
3. J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer, A.H. Windle, *Polymer* **44**, 5893-5899 (2003).
4. R. Khare, S. Bose, *Journal of Minerals & Materials Characterization & Engineering* **4**, 31-46 (2005).
5. L. Guadagno et al., *Nanotechnology* **24**, 305704 (2013).
6. S. Russo, G. Iannuzzo et al., Italian Patent "Resina epossidica con basso tenore di umidità" No. TO2013A000926 (15 November 2013)
7. S. Russo, G. Iannuzzo et al., Italian Patent "Resina epossidica multifunzionale con accresciuta resistenza alla fiamma" No. TO2013A001021 (13 December 2013)
8. P. Pötschke, T.D. Fornes and D.R. Paul, *Polymer* **43**, 3247-3255 (2002).
9. M. R. Nobile, G. P. Simon, O. Valentino, M. Morcom, *Macromol. Symp.* **247**, 78-87 (2007).
10. M. R. Nobile, "Rheology of polymer-carbon nanotube composite melts" Chap. 15 in "Polymer-carbon nanotube composites. Preparation, properties and application", edited by Tony McNally and Petra Pötschke P., Woodhead Publishing, Cambridge (UK), Chap. 15, 2011, pp. 428-481
11. M. R. Nobile, "Carbon nanotube polymer composites" in *Wiley Encyclopedia of Composites*, 2nd Edition, editors: L. Nicolais and A. Borzacchiello, Publisher John Wiley & Sons, 2012, pp. 1-20.
12. S. S. Rahatekar, K. K. K. Koziol, S. A. Butler, J. A. Elliot, M. S. P. Shaffer, M. R. Mackley and A. H. Windle, *J Rheol.* **50**, 599-610 (2006).