Nanocomposites as Advanced Materials for Aerospace Industry

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Abstract: Polymer nanocomposites, consisting of nanoparticles dispersed in polymer matrix, have gained interest due to the attractive properties of nanostructured fillers, as carbon nanotubes and layered silicates. Low volume additions (1- 5%) of nanoparticles provide properties enhancements comparable to those achieved by conventional loadings (15- 40%) of traditional fillers.

Structural nanocomposites represent reinforcement structures based on carbon or glass fibers embedded into polymeric matrix modified with nanofillers.

Structural composites are the most important application of nanaocomposites, in aerospace field, as, laminates and sandwich structures. Also, they can by used as anti-lightning, anti-radar protectors and paints. The paper presents the effects of sonic dispersion of carbon nanotubes and montmorrilonite on the mechanical, electrical, rheological and trybological properties of epoxy polymers and laminated composites, with carbon or glass fiber reinforcement, with nanoadditivated epoxy matrix. One significant observation is that nanoclay contents higher than 2% wt generate an increase of the resin viscosity, from 1500 to 50000- 100000 cP, making the matrix impossible to use in high performance composites.

Also, carbon nanotubes provide the resin important electrical properties, passing from dielectric to semi- conductive class. These effects have also been observed for fiber reinforced composites.

Contrarily to some opinions in literature, the results of carbon nanotubes or nanoclays addition on the mechanical characteristics of glass or carbon fiber composites seem to be rather low.

Key Words: carbon nanotubes, nanoclays, fiber composites, mechanical strength

1. INTRODUCTION

Composites materials consist of a fibrous reinforcements bonded together with a matrix material. Fibers are the reinforcing agents that allow the stiffness and strength of the material to change with direction of loading. Fiber reinforcement properties such as high strength and stiffness and low density combined with the ones of the polymeric matrix such as good shear properties and low density as well result in high performance features for the entire composite. Composites properties depend on the characteristics of the components that form it as well as on the compatibility between the matrix and the reinforcing agents. The components are chosen on the basis of the characteristics required by the application where the composite is used. In any high-tech structural application, where strength, stiffness, durability and light weight are required, epoxy resins are seen as the standard of performance for the matrix of the composite. This is why in aircraft and aerospace applications, as well as

offshore racing boats, epoxies have been the norm for years. [1] The use of composite structures in both commercial and general aviation aircraft has been increasing primarily because of the advantages composites offer over metal (e.g. lower weight, better fatigue performance, corrosion resistance, tailorable mechanical properties, better design flexibility, lower assembly costs) [1]. While most of the Airbus A 380 fuselage is aluminium, composite materials comprise more than 20% of its airframe. [2] Boeing 787 Dreamliner is 80% composite by volume and Each 787 contains approximately 35 short tons of carbon fiber reinforced plastic (CFRP), made with 23 tons of carbon fiber. [3]

The main disadvantage of polymeric composite materials is represented by the nonvisible impact damage, the repairing process being different from the one applied for metal structures. That is why research in this field focuses also on the improvement of the thermomecanical properties of the matrix in order to enhance the efficiency of the composites structural applications. One of the methods used in order to improve the characteristics of the matrix as well as the composite is the incorporation of nanoparticles, such as metallic nanoparticles, nanoclays, carbon nanotubes and carbon nanofibers [4] by impregnating the composite dry performs with the modified nanocomposite matrix.

The possibility to use thermoset nanocomposites for producing structural parts depends on the ability to control the interworking of the composition (resin, curing agent, nanoparticles) and its effect on the polymerization process (density, crosslinking efficiency, cure kinetics). These issues are also dependent upon method of dispersion and cure temperature. The effect of nanofillers in polymeric composites on the kinematic viscosity of the polymer matrix has been studied for different filler-resin composites. In many cases, the amount, the dispersion and the surface state of the nanoparticles have great influence on the rheological behavior and by default on the mechanical properties of the nanocomposites. [5]

The paper presents a study of the process of adding nanofillers to the epoxy resin in order to form nanocomposites and its effects concerning the viscosity and the mechanical properties. Also, there are presented the effects of the addition on the flexural strength and modulus of the carbon fiber reinforced composites having as matrix the modified epoxy resin. It is outlined the importance of having an efficient dispersion of the nanofiller and a proper interfacial bonding, issues that are essential in obtaining nanocomposites with properties improved by the nanofiller presence. The nanofiller agents used for rheological studies are: carbon nanotubes and montmorillonite type nanoclays. The choice of these compounds as nanofillers was made on the basis of their unique characteristics and the features that they provide the composite with.

Carbon nanotubes properties are remarkable at several levels:

- Single wall carbon nanotubes (SWCNT) possess exceptional mechanical characteristics, their tensile strength being a hundred times greater than steel's,
- All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction" [6] (the transport of electrons in a medium with negligible electrical resistivity due to scattering-ballistic transport is determined by electronic structure of semiconductor [7]), but good insulators laterally to the tube axis
- Thermal conductivity along its axis of about 3500 $W \cdot m^{-1} \cdot K^{-1}$, comparing this value to copper, a metal well known for its good thermal conductivity, which transmits 385 $W \cdot m^{-1} \cdot K^{-1}$ [8]
- Carbon nanotubes can be either metallic or semiconducting depending on their orientation (geometry).

So, their thermal and electric properties are comparable to those of some fiber type reinforcing agents (graphite, Kevlar, SiC, and alumina fibers).

The strength, elastic modulus, and fracture properties of CNT are an order of magnitude higher than most common composites used in civilian and military applications. Moreover, CNT reinforcement was proven to increase the toughness of the polymers and composite to absorb impact energy [9]. Nanoclay additives are valuable for their thixotropic characteristics, when used as fillers they can attenuate the air permeability of tyres and fuel tank, as a replacement for talc powder and for titanium dioxide. [5]

Montmorillonite belongs to the layered silicates nanoclay class, representing nanoparticles with anisotropic, plate-like, high aspect-ratio morphology, morphology that leads to an improved permeation barrier. Using montmorillonite, the matrix is expected to have increased dimensional stability at low reinforcement loading, [10] characteristic that makes it useful in aerospace and automotive industry. One of the main disadvantages of layered silicates is represented by the need of their compatibilization with the resin matrix [11]. Montmorilonitte is a hydrophilic compound, as all nanoclays from its class, a characteristic that makes it incompatible with the polymer. In order to increase its organophily, it can be modified using different methods. [12]

2. EXPERIMENTAL

2.1 Materials

The matrix used to obtain the nanocomposites and structural composites was diglycidyl ether of bisphenol A (Ropoxid P 401), liquid epoxy resin provided by SC Policolor SA Bucharest. The curing agent for this resin was a Triethylenetetramine compound TETA1 (I 3301), also provided by SC Policolor SA Bucharest.

The epoxy/ hardener system has the following characteristics:

- Dynamic Viscosity at 250 C: 1400-2500 mPa * s;
- Epoxy Equivalent: 0.4-0.45 echiv at 100 g;
- Epoxy equivalent weight: 222-250 g / eq;
- Epoxy number: 22.8-25.6%;

The structural composites were reinforced with carbon fibre or glass fibre fabric. Carbon fibre tissue characteristics:

- No of filaments: 3000 (3K)
- Thickness: 250 µm
- Weight: 193 g/m^2

Glass fibre characteristics:

- E-type
- Thickness: 240 μm
- Weight: 280 g/m^2

The carbon nanotubes used as fillers where neat multi- wall carbon nanotubes (MWCNT) and functionalized with carboxylic groups (COOH- MWCNT). They were purchased from Shenzhen Nano-Technologies Port Co –China and had the following characteristics:

- Diameter: 2 nm;
- Length: 5-15 μm;
- Purity > 95%;

- Specific surface : 40-300 m²/g;
- Amorphous carbon content < 3%.

Two types of organically modified montmorillonite modified with different ternary ammonium salts, purchased from Southern Clay Products- USA were used.



The Cloisite 30 B and 93 A silicates characteristics were:

- Organic Modifier: methyl tallow bis-2-hydroxyethyl ammonium chloride (30 B), methyl methyl, dehydrogenated tallow ammonium (93 A)
- The tallow (T) composition: fat acids with ~65% C18; ~30% C16; ~5% C14.
- Moisture Content: <2%
- Modifier Concentration: 95 meq/100g clay
- Density: $1,98 \text{ g/cm}^3$

The silicates were dried 4 hours at 80°C before utilization.

2.2 Nanocomposites and structural composites samples achievement

Nanocomposites synthesis consisted in the dispersion of different concentrations of each nanofiller into the epoxy resin for 30 minutes, using ultra- sonication method in order to ensure a proper dispersion. The equipment used for ultra-sonication was Bandelin Sonopuls instrument, having a 2000 Watt power. During the dispersion procedure, the temperature of the system must be kept below 70°C, because temperatures higher than this could damage the nanostructures. The nanoadditivated epoxy resin is then cured, using the aminic hardner. The curing takes place at room temperature during 24 hours, then the samples are kept at room temperature for 7 days for maturation. It can be mentioned that the curing process of prepared samples is considerable accelerated when using a microwave furnace (2.45 GHz, 130 W).



Fig. 1 Dispersion of Cloisite 30 B nanoclay into the epoxy resin, folowed by curing reaction with TETA

Structural composites achievement

Fiber reinforced composite samples are obtained by manual impregnation of the fabric. The carbon fiber/ and glass fiber fabrics, respectively are cut into 11 plies and then impregnated with the filled epoxy resin with hardener added, using the manual lay-up method. The curing takes place in a hydraulic Carver press at room temperature during 24 hours. The samples are kept for 7 days at room temperature before subjecting them to mechanical testing.

2.3 Mechanical Testing

The nanoadditivated resin and the carbon fiber and glass fiber reinforced structural composites were tested mechanically using the INSTRON 4301 device. Tensile and flexural strength were evaluated. The tests were performed at room temperature.

2.4 Viscosity Measurement

The epoxy resin modified with different nanofillers was tested using two viscometers: Walter-Ubbelohde (capillary tube) and Brookfield (coaxial cylinder).

3. RESULTS AND DISCUSSION

3.1 Nanocomposites mechanical testing

The preliminary results suggest that there is a close relation between the improved characteristics of the obtained nanocomposites and filler's properties. The properties of a composite are greatly influenced by the size scale of its component phases and the degree of mixing between them. Depending on the nature of the used components (layered silicate, carbon-based nanomaterials, and polymer matrix) and the method of preparation, significant differences in composite properties may be obtained [13].

Given the exceptional mechanical properties and low densities associated with typical nanometric reinforcements, nanocomposites may result in strength and stiffness weight ratios unachievable with traditional composite materials, offering substantial weight savings for weight – critical applications. The mechanical tests refer to the determination of the tensile strength, elasticity modulus and the Shore hardness.

The tensile strength of the epoxy matrix increases with the addition of nanofillers. The strong adhesion between the polymer and filler with uniform dispersion in the polymer matrix is reflected in the increase of the modulus of elasticity.

In Table 1 there are presented the thermo-mechanical results of the prepared samples.

Nanocomposite	Tensile Strength (MPa)	Shore Hardness	Thermal Stability (°C)	Modulus of elasticity x 10^3 (MPa)	
Neat P 401 (+TETA)	95	75	50	2.8	
P401 + 2% 30 B	102.5	83	56	3.1	
P401 + 2% 93 A	92.2	83	56	-	
P401 + 2% MWCNT (Greece)	98	77	55	-	
P401 + 2% MWCNT- COOH (China)	121.8	85	59	3.42	
P401+2% SWCNT	96	77	55	-	

Table 1. Thermo-mechanical tests for the nanoadditivated matrix

The systems epoxy resin – MWCNT-China and epoxy – montmorillonite had better thermo-mechanical properties than the simple matrix, presenting a value of 121.8 MPa, and 102.5 respectively, compared to 95 MPa for the pristine epoxy resin.

Nanocomposite	Flexural Strength, MPa
P401 + 1% MMT	67,67
P401 + 2% MMT	101,9
P401 + 5% MMT	52,18

Table 2. Flexural test results of Montmorillonite (MMT)/Epoxy sample

Table 2 presents the flexural strength of nanocomposites with different amounts of nanoclay. An important observation is the fact that for the sample with the highest amount of nanoclay, the flexural strength decreases dramatically. This can be explained by the increased viscosity of the sample, also noticed during experimental stage. These results were confirmed by the viscosity measurements values that will be presented and explained in the next section of the paper.

3.2 Structural composites mechanical testing

The thermo-mechanical properties of the composite depend on the efficient dispersion of the nanoadditive into the polymeric matrix and on the efficient impregnation of the tissue plies.

The tensile strength of the nanoadditivated composites is lower than the strength of the non-additivated composite. The elasticity modulus increases with the addition of different types of nanofillers.

The thermo-mechanical results of the carbon or glass fiber reinforced composites are presented in Table 3.

Structural	Tensile	Elasticity	Shore	Thermal	Friction
composite	Strength, MPa	Modulus, GPa	Hardness	Stability	coefficient
Neat epoxy resin P401	95	2.8	75	55	0.2
P401/CF	638	25.2	83	130	0.132
P401/GF	416	14.8	83	129	0.25
P401-MWCNT-	490.7	27.1	87	131	0.134
COOH (2%)/CF	490.7	27.1	07		
P401-MWCNT-	301 /	15.8	85	120	0.19
COOH (2%)/GF	571.4	15.0	05	120	
P401-MWCNT	490	26.40	87	136	0.134
(2%)/CF	490	20.49	87	130	
P401-30B	440		۲ ۹	120	0.134
(2%)/CF	440	-	07	150	
P401-30B	366		86	120	0.22
(2%)/GF	500	-			

Table 3 Fiber reinforced composites thermo- mechanical characteristics

As expected, carbon fiber/epoxy resin nanocomposites presented improved mechanical properties compared to the systems that had no fibre reinforcement.

The most notable effects can be observed if evaluating the Shore Hardness and the modulus of elasticity (a boost of $25\% \div 30\%$). But the tensile strengths for the samples with nanoadditivated matrix were inferior to those with non-additivated matrix.



Fig. 2 Flexural Strength of the structural composites with carbon (CF), or glass fiber (GF) reinforcement and 2% carbon nanotubes additions



Fig. 3 Young Modulus of the structural composites with carbon (CF), or glass fiber (GF) reinforcement and 2% carbon nanotubes additions

In the case of structural composites with glass fiber reinforcement and carbon nanotubes modified matrix, there is a clear decrease of the mechanical strength (Fig. 2-b). Regarding the elasticity modulus, an increase by 12- 15% was observed in the case of MWCNT-COOH samples (Fig. 3-b).

In the case of structural composites with carbon fiber reinforcement and carbon nanotubes modified matrix, the mechanical strength decreased by 3-5 % (Fig. 2-a). Concerning the modulus, an increase was observed for all the samples, the best results being obtained for the composites that had the matrix modified with COOH- functionalized carbon nanotubes (Fig. 3-a).

Combining these results with the ones obtained for the nanomodified resin sample, we can conclude that the nanoadditivation using carbon nanotubes (2%) led to the increase of

the mechanical strength of the matrix by 15-17 % and an increase of the elastic modulus by 20-25%, while in the case of composites with additivated matrix and glass fiber or carbon fiber reinforcement, the effects of nanoadditivation were practically negligible.

3.3 Viscosity Measurement

In order to have a better explanation of the mechanical results for the nanocomposites and structural composites, an evaluation of the viscosity characteristics of epoxy matrix modified with nanofillers was made.

In terms of rheological characteristics epoxy resins are included in the class of Newtonian fluids, for which the flow is governed by Newton's equation: $\tau = \eta * dv/dx$, where τ is the shear stress, η is the dynamic viscosity and dv/dx is the shear gradient. The equation is linear, so the viscosity is constant.

Table 4 presents the variation of the Brookfield viscosity of pristine epoxy resin and the samples with different percentages of nanofillers (1, 2, 5%).

Shear		Brookfield viscosity $[cP \equiv mPa^*s] t = 25^{\circ}C$						
Rate γ [1/s]	P 401	1% MWCTN	2% MWCNT	5% MWCTN	1% 30B	2% 30B	Dispersed mechanically 5% 30B	Dispersed via ultrasounds 5% 30B
0,25	1000	1000	1000	6500	2000	8000	3000	140000
0,5	1000	1000	1000	6000	2000	7000	3000	82000
0,625	1000	1200	1000	5600	2000	6800	3100	70000
1	1000	1250	1250	4750	2125	5675	3125	50000
1,25	1200	1200	1300	4400	2250	5400	3100	42000
2,5	1300	1400	1450	3750	2150	4200	3100	27500
5	1350	1450	1500	3175	2075	3575	3125	18000
12,5	1340	1440	1510	2610	1900	2740	3000	11100
25	1340	1450	1500	2355	1770	2400	2940	8150
12,5	1350	1450	1530	2580	1870	2720	2980	10600
5	1350	1450	1550	2975	2075	3450	3050	16650
2,5	1300	1350	1500	3450	2150	4400	3075	24750
1,25	1200	1200	1400	4100	2400	5900	3000	38800
1	1000	1250	1250	4500	2625	6750	3075	24750
0,625	1000	1100	1100	5400	2800	8200	3100	16650
0,5	1000	1000	1000	6000	3000	9250	3000	10600
0,25	1000	1000	1000	8000	3500	13000	3000	8150

Table. 4. Brookfield viscosity of pristine and nanoadditivated epoxy resin

Fig. 4 emphasizes the importance of ultrasonication in the dispersion of nanofillers, there is a remarkable difference between the viscosity of the sample in which the nanoclay was dispersed mechanically as compared to the sonicated sample.



Fig. 4 Brookfield Viscosity Variation for Montmorillonite Cloisite 30 B nanoclay

Fig.5 presents the variation of viscosity as a function of temperature, for different percentages of filler (1%, 2% and 5%) measured with the Walter-Ubbhelode viscometer.



Fig. 5 Epoxy resin with different percentages of filler viscosity

Evaluating the variation of the viscosity with shear rate and with temperature, respectively, we can remark that the addition of Cloisite 30B in a percentage of 5%, causes excessive increase of viscosity. During the experimental tests, the flow through the capillary tube of this sample was practically impossible. This is a basic disadvantage on several levels,

because high viscosity of the matrix constitutes an impediment in a proper impregnation of the carbon or glass fibres that is the key to obtain structural composites with advanced properties.

So, increasing filler amount added in the matrix leads to an increased difficulty to impregnate the fibers to obtain composite materials. Impregnation difficulties appear when filler exceeds 2 wt. %, generating a poor impregnation of the fibres, an issue that may hurry composite's exfoliation and mechanical flop. Excessive viscosity of the matrix may generate air gaps formation during the process of obtaining composites in a curing autoclave that can also contribute to the mechanical performance decrease of the composite.

4. CONCLUSIONS

The main result of the rheological research consisted in the impressive rheological differentiation of the effects of montmorillonite additives in the case of mechanical dispersion compared to the sonic dispersion. The mentioned results follow the experiments performed using the Walter- Ubbelohde viscometer. The same results were confirmed by the experiments performed with the Brookfield coaxial cylinders viscosimeter, which showed that in the case of concentration values of 5%, the viscosity increases up to 140 000 cP. Montmorillonite additives imprinted a very strong rheological thixotropic character to the resin. Carbon nanotubes additives in 2- 5% concentrations imprinted a rheopectic character to the resin (increasing of the viscosity by approximately 30%).

Conclusions of the results obtained from the experiments performed with the two viscosimeters: Walter- Ubbelohde (capillary tube) and Brookfield (coaxial cylinder) can be summarized as follows:

- The Newtonian behaviour of the P401 resin (constant viscosity or linear variation of friction force with shear rate from 1 to 100 sec⁻¹);
- Thermal behavior of the resin was according to the Walter- Ubbelohde logarithmic law, specific to the mineral oils;
- Carbon nanotubes additives in 2- 5% concentrations imprinted to resin a rheopectic character (increasing of the viscosity by approximately 30%). So, when using a concentration of 1% multiwall carbon nanotubes, the viscosity of the resin increased from 1000 to 1440 cP;
- Montmorillonite clay additives imprinted to resin a very strong thixotropic rheological character;
- The main result of the rheological research consisted in the impressive rheological differentiation of the effects of montmorillonite additives in the case of mechanical dispersion compared to the sonic dispersion. So, in the case of mechanical dispersion of 2% nanoadditive, resin viscosity increased from 1390-1530 cP and in the case of sonic dispersion, viscosity increased from 1390-5500 cP. When adding 5% montmorillonite, fluid viscosity increased from 1390 to 3300 cP in the case of mechanical dispersion. The mentioned results follow the experiments performed using the Walter-Ubbelohde viscometer. The same results were confirmed by the experiments performed with the Brookfield viscometer, which showed that in the case of concentration values of 5%, the viscosity increases up to 140 000 cP;
- It is worth mentioning the similarity of the results obtained with Walter- Ubbelohde viscometer to those obtained with Brookfield viscometer, for low shear rates (1s⁻¹);

• Carbon nanotubes additives in concentration up to 2% do not modify significantly the rheological properties associated with the impregnation of glass fiber or carbon fiber fabrics.

Regarding thermo- mechanical and tribological performance of the nanocomposites, adding up to 2% nanofillers to the matrix, leads to an improvement by 10- 15% for thermomechanical characteristics and notable improvements for tribological properties as well. Adding more than 2% nanoparticles the rheological properties of the polymers are deteriorated: the viscosity increase from 1800 MPa*s until 4000-5000 MPa*s, a disadvantage that is also illustrated in the mechanical characteristics.

Mechanical tests show that COOH functionalized multiwall carbon nanotubes may improve the composite's mechanical characteristics. A maximum of 2% additive is allowed in the epoxy matrix in order to achieve a good impregnation of the fabric.

Nanoparticles are fillers that improve some functional properties of polymers, but they cannot be reinforcement structures like carbon or glass fibre. Contrarily to some expectations and opinions presented in literature, adding carbon nanotubes or nanoclays to the polymeric matrix seems to generate a rather low effect on the mechanical characteristics of glass or carbon fiber composites. The development of threads and tissues made of carbon nanotubes may represent a great evolution in the scientific area.

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