# Binary polyamide hybrid multifunctional composites containing carbon allotropes and metal particles prepared via reactive microencapsulation

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**Abstract**

Novel binary thermoplastic multifunctional composite materials are synthesized by a reactive microencapsulation method and thoroughly characterized. The composites are based on polyamide 6 (PA6) matrix comprising two types of fillers: (i) microsized Al, Cu, Mg, and Fe powders –allowing to tailor electro and/or magnetic properties- and (ii)

nano- or microsized carbon allotropes such as carbon nanotubes (CNT) and carbon black (CB) –allowing to tune electrical and mechanical properties. The composites are prepared in two stages. First, activated anionic ring-opening polymerization (AAROP) of ε-caprolactam (ECL) is performed in suspension, in the presence of the desired amounts of both particle types. This process produces dual core PA6 microcapsules (PAMC) with controlled shape and size containing both metal and carbon particles with a total amount of up to 17 wt. % in respect to the PA6 matrix. Second, the variously loaded PAMC are compression molded to produce binary composite plates. The morphology and the crystalline structure of the different PAMC as well as of the composites thereof are studied by scanning electron microscopy and thermal methods revealing good dispersion of the metal and carbon loads within the PA6 matrices. It is shown that the well-dispersed binary Al/CNT or Al/CB fillers in the PA6 matrix strongly increase its electrical conductivity by 7-9 orders of magnitude. At the same time, up to ca. 60% increase of the Young´s modulus of the binary composites is registered. Data from solid state NMR spectroscopy suggest that the novel binary thermoplastic composites prepared by reactive micro-encapsulation could be potentially useful in electromagnetic interference shielding or radar absorbing materials.

***Key words:*** *activated anionic polymerization of lactams, microencapsulation, electrical conductivity of polymers, polymer composites, mechanical properties, solid state NMR.*

## 1. Introduction

Modern technologies require thermoplastic multifunctional composite materials that are lightweight, with high mechanical strength, stiffness, flexibility and impact resistance. At the same time, they are expected to be low in cost, friendly to automation and recycling.

The intensive research in this area has shown that changing the type, size, shape, volume fraction, interface, and degree of dispersion or aggregation of the different components of the composite materials enables great amount of combinations of properties with high potential for successful commercial development [1].

It is generally accepted that the quality of dispersion of the fillers/reinforcements in the polymeric matrix, besides their intrinsic structures and physical properties, is the most critical factor affecting the properties and performance of the polymer composites. Therefore, finding a scalable and relatively low-cost method for good dispersion of specific organic or inorganic fillers in conventional thermoplastic polymer matrices is an important condition for the preparation of multifunctional composites with tailored electrical conductivity, magnetic and dielectric properties, combined with sufficient mechanical resistance [2].

Unfortunately, the conventional processing techniques based on melt processing of polymer/filler mixtures cannot provide easily the most advantageous state of filler particles dispersion. Its improvement passes through various high-temperature cycles and high processing pressures thus increasing the possibility of matrix polymer degradation [3], [4] resulting unavoidably in inferior mechanical performance. The use of non-conventional polymer processing tools can lead to better particles dispersions within the matrix. This, however, comes on the account of high cost complex machinery limiting the broad application in industry [5].

Other possible pathway toward best particle distribution in composite processing is the chemical modification of the filler to enhance its compatibility with the matrix. In the case of carbon allotropes, their poor dispersion within the polymer matrix affects negatively mechanical and conductive properties of final composite [6]. This limitation can be overcome by surface modification trough covalent or non-covalent

functionalization of the carbon filler. These approach also enhances the adhesion between filler and polymer matrix [7]. It is important to note here that filler functionalization not only can be quite expensive and difficult to scale-up [8], but can also deteriorate or even completely eliminate the useful properties of the functional filler. Excessive covalent functionalization can decrease the conductivity due to defects on the surface of the carbon filler [9], [10]. Moreover, attempts to use conventional melt processing in thermoplastic composites with high loads (typically above 5 wt%) of any filler frequently lead to agglomeration of the latter and inferior mechanical properties [1].

A recent approach toward polymer composite materials comprising various fillers/reinforcements whose electrical, dielectric and magnetic properties can be appropriately varied is related to the so-called micro- and nanoarchitecture strategy [2]. According to this methodology, each micro- or nanosized filler particle is first covered with selected polymers by grafting-from [11] or grafting-to techniques [12] thus forming core-shell particles. These are transformed into polymer composites by a conventional molding technique. This strategy offers several important advantages over the conventional melt mixing and solution mixing techniques for the preparation of polymer composites. It enables the synthesis of highly loaded composites with homogeneous filler dispersion. Further, the preparation of composites with tailored combinations of functional properties, such as electromagnetic and dielectric properties is made possible, i.e., such with suppressed dielectric loss at high dielectric constant [11], [12]. At the same time a possibility for fundamental insight on the role of the matrix-filler interfaces on the materials properties appears [13].

However, the analysis of the most common micro- and nanoarchitecture strategies reveals some important limitations. First, in most of the cases the chemistries involved to produce the shell-core particles (e.g., click reactions, reversible addition/fragmentation

chain transfer polymerization (RAFT) and atom transfer radical polymerization (ATRP) mechanisms) are relatively complex and hardly suitable for scale-up. Due to the complexity of the catalysts or reagents involved, RAFT and ATRP possess too many reaction variables affecting the characteristics of the final polymer. Moreover, there seems to be still a problem to introduce into the same particle high loads of very different materials.

An attempt to overcome the above limitations and to extend the microencapsulation strategies toward the preparation of high-strength composites based on *n*-polyamides was the use of activated anionic ring opening polymerization (AAROP) of lactams. Thus, reactive microencapsulation of various organic and inorganic loads by AAROP of ε-caprolactam (ECL) in suspension to produce loaded polyamide 6 (PA6) based microcapsules (PAMC) with their subsequent hot compaction to PA6 hybrids was recently communicated [14]. This fabrication concept allowed the synthesis of a number of particulate and laminated PA6 composites comprising various *single* organic or inorganic fillers in wide concentration ranges and with controlled dispersion [15]–[17].

This work studies for the first time the possibility to develop PA6-based hybrid composite materials with tailored electrical conductivity, dielectric and mechanical properties based on PAMC with *binary loads*, i.e., micro- and nanoparticles of both metals and carbon allotropes. The presence of two different finely dispersed fillers in a polyamide matrix can be suitable for the development of novel radar absorbing materials (RAM) or in electromagnetic interference shielding (EMI). Effective RAM and EMI materials can cancel out by selective absorption or reflection both magnetic and electric components of the incident radiation. This effect is usually achieved by the simultaneous incorporation of conductive, magnetic and/or dielectric fillers into a matrix that can be also polymeric [18], [19]. Novel structural RAM or EMI materials is attracted increasing

interest from academia and industry due to their diverse applications in military stealth technologies, in aircraft and ship transports as well as in television for image interference reduction [18]–[25], and in medical diagnostic equipment [26], [27], among others.

In this work, carbon black (CB) and carbon nanotubes (CNT) were used as absorbers that depend on the ohmic loss of energy. Further, they can also provide mechanical reinforcement to the composite. Further, micron-sized powders of Al, Cu, Mg and Fe were employed for also tuning the electrical response of the composite, the latter being also a magnetic absorber. The structure, morphology, electrical conductivity, dielectric and thermal properties and mechanical behavior of the novel composites were investigated as a function of the amount and types of metal/carbon loads. The RAM properties of selected compositions were demonstrated by means of solid-state nuclear magnetic resonance (SS-NMR) spectroscopy.

## 2. Experimental

### 2.1. Materials

The ECL monomer with reduced moisture content for AAROP (AP-Nylon® caprolactam) was delivered from Brüggemann Chemical, Germany. As polymerization activator, Bruggolen C20® from Brüggemann Chemical, Germany (C20) was used. According to the manufacturer, it contains 80 wt% of blocked di-isocyanate in ECL. The initiator sodium dicaprolactamato-bis-(2-methoxyethoxo)-aluminate (Dilactamate®, DL) was purchased from Katchem, Czech Republic, and used without further treatment. The multi-walled CNT were purchased from Sigma Aldrich. The acetylene CB is a product of S.E.A. Tudor, Spain. Powdered Cu (>99.5%, grain size <40 μm), Al (>93 %, grain size <100 μm), and Mg (>99 %, grain size <100 μm) were supplied by Sigma Aldrich. The soft, non-insulated carbonyl Fe powder (>99.5, average grain size 3–5 μm) was kindly donated by BASF Group, Ludwigshafen, Germany. Toluene, methanol, and other

solvents are all of "puriss" grade. They were purchased from Sigma Aldrich and used as received.

### 2.2. Sample preparation

The loaded PAMC were produced by solution-precipitation AAROP of ECL performed as described in detail previously [14]–[17]. In a typical polymerization process about 0.5 mol of ECL and the desired amount of carbon allotrope and metal powder (altogether up to 10 wt% in respect to ECL) were added to 100 mL of 1:1 toluene/xylene mixture while stirring, under nitrogen atmosphere, refluxing the reaction mixture for 10-15 min. Subsequently, 3 mol% of DL and 1.5 mol% of C20 were added at once. The reaction time was always 2 hours from the point of catalytic system addition, maintaining the temperature in the 125–135°C range at a constant stirring of ca. 800 rpm. The metal/carbon-loaded PAMC formed as fine dark powder with metallic luster typical of the respective metal load were separated from the reaction mixture by hot vacuum filtration, washed several times with methanol and dried for 30 min at 80°C in a vacuum oven. The yields of empty PA6 microcapsules were 56% (in respect to ECL) and 50-63% for the loaded PAMC (**Table 1**).

Compression molding of PAMC to composite plates was performed in a Moore hydraulic hot press (UK), using a rectangular mold with dimensions 85×75×1 mm, pressing for 5-7 min at 230°C and a pressure of 5 MPa.

### 2.3. Sample characterization

The scanning electron microscopy (SEM) studies were performed in a NanoSEM-200 apparatus of FEI Nova (USA) using mixed secondary electron/back-scattered electron in-lens detection. The microcapsule samples were observed after sputter-coating with Au/Pd

alloy in a 208 HR equipment of Cressington Scientific Instruments (UK) with high-resolution thickness control. The molded samples were observed after cryofracture. The differential scanning calorimetry (DSC) measurements were carried out in a 200 F3 equipment of Netzsch (Germany) at a heating rate of 10 °C/min under nitrogen purge. The typical sample weights were in the 10-15 mg range. The crystallinity index $X_{DSC}$ of the PA6 matrix was calculated according to Equation (1):

$$X_{DSC} = \frac{\Delta H_m^i}{w \cdot \Delta H_m^0}[\%] \quad (1)$$

where $\Delta H_m^i$ is the registered melting enthalpy of the current sample, $w$ is the weight fraction of the polymer present in the sample and $\Delta H_m^0$ is the melting enthalpy of a 100 % crystalline PA6 (190 J/g)[28]. The effective inorganic load in PAMC was established by means of thermogravimetric analysis (TGA) in a Q500 gravimetric balance (TA Instruments, (USA) heating the samples to 600°C at 10°C/min in nitrogen atmosphere. The real load $R_L$ of filler in PAMC was calculated according to Equation (2):

$$R_L = R_f - R_{PA6}, [\%] \quad (2)$$

where $R_{PA6}$ is the carbonized residue at 600 °C of empty PAMC and $R_i$ – that of the respective loaded PAMC measured by TGA.

Tensile tests were performed on an Instron 5969 testing machine (USA) at 23±2ºC with a standard load cell of 50 kN at a constant crosshead speed of 50 mm/min. From the different composite plates prepared by compression molding of PAMC, standard specimens were cut out according to DIN 53504-S3A. At least five specimens of each sample were studied to calculate the average values and their standard deviation. The engineering stress σ was determined as the ratio of the tensile force to the initial cross-section of the sample. The engineering strain ε was determined as the ratio of the sample gauge length at any time during drawing to that before drawing. The Young´s

modulus *E* values were obtained from the initial slope of the strain–stress curves (until 1% strain). In all cases, conditioned samples stored for ca. 30 days at 23 °C and 65% relative humidity were tested. The improvement factor *IF* for *E* and $\sigma_{br}$ values were calculated according to Equation (3):

$$IF = \frac{P_i - P_{PA6}}{P_{PA6}}.100[\%] \tag{3}$$

where $P_i$ is the respective parameter of the composite material and $P_{PA6}$ – the same parameter of the neat PA6 matrix.

Electrical current/voltage measurements were performed in a Keithley 487 pico-ampermeter/voltage source (Keithley Instruments Inc., USA) between –10 and +10 V using increasing and/or decreasing modes. To rule out interferences due to external electric field, all measurements were performed in a Faraday cage. From the slope of the graphs (straight lines for Ohmic materials) the resistance $R[\Omega]$ was determined, from which the resistivity $\rho[\Omega \cdot m]$ and conductivity $\sigma[S/m]$ were calculated according to Equation (5):

$$\sigma = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{d}{A} \tag{4}$$

where *A* is the area and *d* the thickness of the gold electrodes (5 mm in diameter) deposited by sputtering on both free surfaces of each sample. Four measurements in different parts of each molded samples were performed taking the arithmetical mean as a final value of conductivity.

The dielectric permittivity $\varepsilon'$ was obtained from the geometry of the samples in the shape of a parallel plate capacitor (circular electrodes of 5 mm diameter and sample average thickness of 600 μm). The measurement of the capacity and the loss factor tan % with a QuadTech model 1920 precision LCR meter at room temperature and pressure, at

frequencies between 100 Hz and 1 MHz. The permittivity $\varepsilon'$ of the samples was thus determined according to Equation (5):

$$C = \varepsilon' \cdot \varepsilon_0 \cdot \frac{A}{d} \tag{5}$$

where $A$ is the area of the capacitor plates and *d* the sample thickness. The electrical d.c. conductivity $\sigma$, the real part of permittivity $\varepsilon'$, and the dielectric loss $\tan\delta = \varepsilon''/\varepsilon'$ ($\varepsilon''$ being the imaginary part of permittivity) were obtained for all composites produced from compression molded PAMC.

Solid state nuclear magnetic resonance experiments (ssNMR) were performed on a Tecmag Redstone/Bruker 300 WB spectrometer operating at 75.49 MHz for the observation of $^{13}C$ resonances. Zirconia rotors o.d. 7 mm were used to pack the powdered samples (about 200 mg). The standard cross polarization magic angle spinning (CP MAS) RF sequence was used for the spectrum acquisition. A two-channel spectrometer is necessary to run this CP sequence: the observation channel, tuned at 75.49 MHz, and the $^{1}H$ channel, tuned at 300 MHz, which is used during the contact and decoupling periods. The following parameters were selected: 3.3 kHz spinning rate, 2 ms contact time, 10 s recycling delay and a number of scans between 100 and 400. The chemical shifts were obtained using the glycine carbonyl signal as external reference, which was set at 176.03 ppm. The experiments were carried out at room temperature.

## 3. Results and discussion

### 3.1. Synthesis of the loaded PAMC

The finely divided metal and carbon payloads are used without functionalization and are insoluble in either ECL or toluene/xylene mixed solvent. Initially, the weighed amounts of metal and carbon payloads are added to 100 ml of the solvent and sonicated for 30 min at room temperature. The suspension thus obtained is refluxed for 10 min at 120 ºC under appropriate stirring. Then, the initiator and the activator amounts were added whereby the polymerization of ECL to PA6 around each filler particle started at once. The chemistry of the process is described in detail in previous works [14]–[17], [29]. According to these studies it can be hypothesized that the mixed metal/carbon are entrapped into viscous oligomer droplets formed by growing PA6 polymer molecules. After reaching some critical molecular mass and various acts of coalescence, the latter crystallize transforming the droplets into porous PA6 shell that embeds the mixed payload particles. The payloads can possibly nucleate the PA6 crystallization thus forming the loaded PAMC. The present study showed that the transformation of the viscous particles into loaded microcapsules without formation of lumps requires an optimized stirring rate of ca. 800 rpm, maintaining the molar ratio DL/C20 = 2 and keeping the temperature of AAROP below 135°C.

**Table 1** shows the designations of the loaded PAMC samples prepared, the respective polymerization yields and the theoretical metal-carbon filler contents. For all samples, the real filler concentration (column 4) was determined by TGA according to Eq. (2). Deviations between the real and theoretical loads up to 4-7% are observed for all samples except for the Fe/CNT sample where it was around 2%. The said deviation depends on the polymerization yields that were in the range of 52-63%, whereby the lower the yield, the higher the percentage of the filler.

### 3.2. Morphology studies by SEM

To analyze the morphology of the prepared PAMC, SEM studies were performed (Figures 1-3). The scanning electron micrographs in **Figure 1a-f** present information about the size and shape of the Al, Mg, Cu and Fe loads. The Mg and Al particles (images **1e** and **1c**) are shaped as platelets with maximum sizes of 80-100 μm and thicknesses of 10-15 μm. Cu particles display complex dendritic shapes with sizes in the 20-40 μm range [16], and the Fe particles are strictly circular with sizes between 1-5 μm. On the other hand, as seen from images **1d** and **1e** respectively, the CNT filler comprises 10-20 nm thick fibrils and the CB displays particles with spherical morphology with diameters being in the 40-80 nm range.

The shape and size of the loaded PAMC visualized by SEM are presented in **Figure 2**. The empty PA6 microparticles (**Fig. 2a**) are present in the form of aggregates of several, partially fused PA6 spheres with typical diameters of 5-10 μm that form final particles of 20-30 μm. This observation confirms the previously postulated effect of coalescence during the PAMC formation [30]–[32] confirmed by [15], [16]. Larger magnification (image **2i**) shows that the empty PAMC are porous, with scaffold-like morphology, the pores sizes being typically in the 250-500 nm range.

The SEM images of PAMC carrying binary metal/carbon allotrope loads support the coalescence formation mechanism. A dependence between the size of the larger filler particles and that of the final loaded PAMC was found. Thus, the PAMC loaded with CNT/Fe (**Fig. 2b**) and CNT/Cu (**2c**) wherein the metal particles are in the 5-20 μm range are only slightly bigger than the empty PAMC. Notably, the surface texture of both PAMC with binary filler is visibly different as compared to **Fig. 2a**, most probably due to epitaxial crystallization of PA6 in the presence of metal/carbon allotrope binary fillers which is impossible in empty PAMC. At the same time, PAMC that contain Al platelets are either significantly larger and less spherical (e.g., CNT/Al (**2d**)), or embed metal

platelets (sample CB/Al, image **2e**). In CNT/Mg PAMC predominate spherical particles with diameters of 20-30 µm (image **2f**), which could be explained with some fragmentation of the initial Mg platelets during the AAROP due to the energetic stirring. Generally, the metal particles are distributed in the core of PAMC and therefore not directly observable. In some cases, they can be seen on the PAMC surface as in **Fig. 2c** that shows a PA6 covered Cu particle with its specific form (site Z1). Energy dispersive X-ray spectroscopy (EDX) in this site rendered 69% of Cu versus 6.7% in site Z2 where no Cu particle are directly observed. Analogously, the CNT/Al sample (**Fig. 2f)** in sites Z1 (the supposed Al platelet) and Z2 (the PA6 matrix) renders Al contents of 81% and 2.5 % respectively. Similar results were obtained in the CNT/Fe sample (**Fig. 2g)**, in which Fe particles with different coating by PA6 were obtained containing 71% Fe (Z1) and only 5.5% Fe (Z2). In all of the samples in Figure 2 it was not possible to visualize the CNT or CB fillers probably because of their nanometric size and their scattering properties that should be basically the same as of the PA6 matrix.

**Figure 3** shows the SEM images of selected cryofractured molded plates produced from the respective PAMC. The left-hand column with images **3a, 3d** and **3g** reflects the morphology of the PA6-metal hybrid composites, containing 5 wt% of Al, Cu and Fe, respectively. The rest of the SEM images display the surface topography of the molded plates with binary CNT-metal load, 5wt% + 5wt%. As seen from the micrographs in the middle and especially on the right in Figure 3, the CNT appear as bright nanometric dots being very well dispersed, with almost no aggregation, within the PA6 matrix, as well as on the top of the metal particles (Fig. **3c, 3f** and **3i**). The large difference in density between the metal particles and the CNT explains the apparent high concentration of the carbon allotrope in the binary loaded samples. The EDX curves in these last three images confirms the composition of the electron-rich bright metal particles.

### 3.3. DSC studies

All samples were subjected to a DSC heating scan at in the 0-250ºC, followed by a cooling to 0ºC and a second heating to 250ºC, all scans being performed at a rate of 10 ºC/min. **Figure 4** displays some typical DSC curves of metal/carbon allotrope composite systems in the form of either microcapsules or molded composite plates. All data extracted from the DSC curves of the PAMC samples and the respective compression molded plates are presented in **Table 2.**

As observed from the 1st scan of the PAMC samples (**Fig. 4a**, left hand group of curves), the metal/carbon allotrope loaded microcapsules display a single melting endotherm at ca. 210 ºC, approximately the same as the empty PAMC. This endotherm should be related to the melting of the predominant α-PA6 polymorph [17]. Apparently, the presence of metal and C-allotrope fillers in the loaded PAMC does not influence significantly the melting behavior in this scan. The broad peak centered at 85ºC in some samples of this series should be explained with evaporation of trace amounts of the solvents used in AAROP and the subsequent PAMC isolation. The samples dried for 1 h at 100ºC and immediately subjected to DSC (CNT-Cu 5/5 and CNT-Mg 5/5 in **Fig. 4a**) do not show such a peak.

The recrystallization study (**Fig. 4a**, the center) shows a double exotherm in the 180-200ºC, while the empty PAMC sample produces a sharp crystallization peak at 150ºC. This can be explained with two effects: (i) the strong heteronucleation effect of the metal/C-allotrope binary fillers that enhances the crystallizability at elevated temperatures and (ii) formation and coexistence in all loaded PAMC of both α and γ-polymorphs. The lower crystallizing γ-phase in PAMC displays a peak with constant intensity, while the one at the higher temperature (typical for the α-PA6) seems to be slightly dependent on the metal particles type. The second DSC scan of the PAMC (the

right-hand side of **Fig. 4a**) results in uniformization of the melting temperature for all samples, however all melting endotherms become broader indicating the presence of more γ-PA6 with lower melting point. The DSC traces (1st, 2nd scan and recrystallization) of the molded composite plates (**Fig. 4b**) are similar to that of the respective PAMC.

**Table 2** shows that the values of the DSC crystallinity index $X_c$ of all PAMC samples obtained during the 1st scan is always higher than those in the 2nd scan. This can be related to the isothermal crystallization of PAMC during the AAROP carried out for 1 h at 120-130ºC that would produce larger and more perfect PA6 crystallites as compared to those obtained during the non-isothermic and much faster crystallization within the DSC equipment during the 2nd scan. This observation confirms the previously established fact that the thermal history of the PA6 sample is of prime importance for its crystallinity index [33], [34].

Comparing the glass transition temperatures $T_g$ of PAMC and molded plates allows the conclusion the $T_g$ of empty PAMC (34.4ºC) is significantly lower than in the neat PA6 sample (46.8ºC). This means that the segmental mobility of the amorphous PA6 chains in PAMC is much higher than in the molded PA6 late which should be related with the pressure applied during the compression molding, leading to more compact and dense microstructures. According to Table 2, introducing the binary metal/C-allotrope filler into the amorphous regions of the matrix, as a rule, increases the $T_g$ of PAMC, meaning lower segmental mobility of chains. Apparently, in the samples containing large metal particles (i.e., in the Al-CNT 7/3 and Al-CB 5/5) the drop of the segmental mobility in both PAMC and molded plates is the highest.

### 3.4. TGA studies

All metal/C-allotrope PAMC and the respective molded composites were studied by TGA in order to establish the thermal stability of the samples as a function of the load type and amount and to determine the real amount of fillers. **Figure 5** displays the TGA traces of selected composites representing the integral curves (left-hand side), and their first derivatives (right hand side). **Table 3** summarizes the numerical data of the thermal degradation of all samples. The determination of the real load content on the basis of the carbonized residue at 600°C is shown in Table 1. This method should account not only for the metal filler content but, as demonstrated in previous work [15], also for that of the C-allotropes.

As seen from Figure 5 and table 3, the empty PAMC and the neat PA6 plate show their 10% weight losses at ca. 300ºC ($T_{10\%}$). The derivatized TGA curves of these samples suggest a single degradation processes with temperatures of maximum degradation rate $T_{MDR}$ of 340ºC and 354ºC, respectively. The samples with compositions Mg-CNT 5/5 and Cu-CNT 5/5 in as either PAMC or molded plate produced $T_{10\%}$ and $T_{MDR}$ being similar or even slightly below those of the respective PA6 counterparts. The microcapsules containing Mg and CNT display a second degradation process with $T_{MDR}$=384ºC not present after obtaining the molded composite. The Al-CNT 5/5 and the Fe-CNT 5/5 samples show significantly higher values for $T_{10\%}$ (with 15-70ºC) and for the first $T_{MDR}$ with up to 25-30ºC. In both samples, a second degradation process appears with $T_{MDR\text{-}II}$ values of up to 465ºC (**Fig. 5b** and **5d**). This means that the binary Al-CNT and Fe-CNT fillers can significantly improve the heat resistance of the PA6 matrix material at low and maximal degradation rate. The Al-CB 5/5 sample (PAMC and plates) show also a high degradation process at $T_{MDR}$ > 400ºC but its $T_{10\%}$ values are even lower than those of the PA6. Summarizing, in terms of heat resistance the Al-CNT composites in either particulate or molded forms containing equal weight amounts of Al and CNT seem to be

with optimal thermal degradation properties, especially in the form of plate. The attempt to change the relation between the metal and C-allotrope (**Table 3**, samples Al-CNT 3/7 and Al-CNT 7/3) has a detrimental effect. Notably, only with Al-CNT 3/7compositions some weight loss below 200ºC was found, most probably due to the presence of oligomer products in the respective PAMC that are then transferred to the molded product (**Figs. 5f, 5h**).

### 3.5. Mechanical properties in tension of molded dual hybrid composites

**Figure 6** shows representative stress-strain curves of the composites produced by compression molding of binary loaded PAMC compared with that of the neat PA6 from empty PAMC. **Table 4** presents the data about Young´s modulus *E*, stress at break $\sigma_{br}$ and deformation at break $\varepsilon_{br}$, extracted from the stress-strain curves, as well as the improvement factors IF for $E$ $\sigma_{br}$. The neat PA6 displays ductile behavior with well-expressed yield point at $\sigma$ = 48 MPa and $\varepsilon$=10-20% strain and hardening region reaching the $\varepsilon_{br}$ value at ca. 220% The Young´s modulus of 1.59 GPa (Table 3) is typical of anionic PA6 [35] and higher than that of hydrolytic non-oriented neat PA6, which was close to 1.0 GPa [36]. The binary metal-CNT molded composites in **Figure 6** display a fragile fracture with $\varepsilon_{br}$ between 4-22%, no yield point and a notable improvement of the *E* values of 18-59% with respect to the matrix PA6. Interestingly, the highest *E*-values are observed whenever the carbon allotrope is CNT (i.e., nanofibrils with high aspect ratio) and at weight ratio metal/CNT of 1:1. At the same time, the decrease of the $\sigma_{br}$ values in these composites is in the 7-20%. It should be noted that for all binary composites in **Fig. 6** the $\sigma_{br}$ values are higher than the yield point stress of neat PA6 which could be of importance for their further applications.

### 3.6. Electrical conductivity and dielectric properties of molded dual hybrid composites

The the d.c. electrical conductivity $\sigma$, real component of the dielectric permittivity $\varepsilon'$, and the loss factor *tan* $\delta$ were determined for all composites produced from compression molded PAMC using Eq. 4 and Eq. 5 and summarized in **Table 5.**

First, the electrical properties of the binary metal-carbon hybrid composites (5/5 wt%) were compared to hybrid composites comprising 10 wt% of either one carbon allotrope or one single metal load (Table 5). As expected, the neat PA6 is insulator with $\sigma$ values of above $10^{-10}$ S/m. In agreement with our previous results [15], the introduction of 10% of CNT and CB led a strong increase of the electrical conductivity in the PA6 hybrids reaching σ values of $10^{-2}$-$10^{-1}$ S/m. The data in **Table 5** confirm the previous findings reported in [16] that metal-modified PA6 hybrids produced by molding of PAMC with loads in the range of 10-20 wt% are still insulators. This effect was explained with a Maxwell–Wagner–Sillars type polarization [16]. The presence of CNT and CB along with the Al, Cu, Fe and Mg content (5/5 wt%) lead to a strong increase of the electrical conductivity $\sigma$ in 7-9 decades, strongly reducing the polarization at the metal/PA6 interface. This facts are related to the very good distribution of metal and especially of the CNT component shown in the SEM images of Figure 3.

The Al-CNT 5/5 sample presents an interesting behavior: together with a good electrical conductivity, it displays also a low loss factor *tan* $\delta$. It is to notice that in most of the other samples the latter increases as the d.c. conductivity also increases. **Table 5** shows that the electric/dielectric properties of the binary composites can be conveniently changed by variation of the metal-carbon allotrope relation, the type of the metal or carbon allotrope and their amount in the composite. Interestingly, the Al-CB 5/5 binary composite also displays $\sigma$ values of ca. $10^{-01}$ S/m, indicating that the expensive CNTs or

a good part of it can be substituted by the much cheaper CB maintaining suitably electrical characterstics for applications.

**Figure 7 a-c** displays the semilogarithmic plots of $\varepsilon'$ as a function of the frequency for the metal-CNT 5/5 composites. At 1 MHz, the composite Fe-CNT 5/5 shows lower $\varepsilon'$ (67.7) than the Al-, Mg- and Cu-CNT 5/5 composites, with $\varepsilon'$ values of ca. 100. Fig. 7c shows that the Al-CNT 5/5 sample keeps almost constant values of the $\varepsilon'$ (500-200) independently of the frequency which could be interesting in some applications. Once again, the use of various metals, C-allotropes in different concentrations or relations in the binary composites leads to tunable conductive and dielectric properties.

### 3.7. NMR studies of selected hybrid composites

Solid state nuclear magnetic resonance (ssNMR) spectroscopy provides structural and molecular dynamic data obtained from interaction between electromagnetic radiation and matter. This non-destructive method was used in the study of electrical and magnetic properties of the prepared materials. A loss of NMR signal was expected with increasing amounts of fillers with paramagnetic or conductive properties, due to a skin effect caused by the conductive properties of fillers limiting the adsorption of radiofrequency [37]. First analyses were performed with PAMC of Al 10, CNT 10, Al-CNT 3/7 and Al-CNT 7/3 for the observation of $^{13}C$ resonances at 75 MHz. **Figure 8** represents the CP-MAS $^{13}C$ NMR full-range spectra of the analyzed materials. In addition, chemical structure of PA6 and the carbon numbering followed in this study is illustrated within **Figure 8**. All spectra contain at least two spinning bands due to the chemical shift anisotropy of the carbonyl groups. **Table 6** displays the $^{13}C$ chemical shifts obtained for the PAMC samples investigated. By comparing PA6 and CNT10 spectra (**Figure 8**), it is noticed that the CNT loaded microcapsules cause a slight increase of peak width in the region of the aliphatic

carbons which results on the following chemical shifts (carbon numbers within parentheses): 42.6 (C1), 30.2 (C2+C3), 27.1 (C4) and 36.5 (C5). On the other hand, when Al is used as filler, the signal resolution strongly decreases and the resonance from C4 nucleus is not resolved. The resolution and the peak intensity decrease further on the binary Al-CNT 7/3 spectrum: the signal to noise ratio is low and, consequently, almost all the aliphatic carbon signals are unresolved. The effect of dispersion of conductive fillers on PA6 is well present on the binary Al-CNT 3/7 due the nearly complete disappearance of the ssNMR peaks. This event suggests that the mixture of metal-carbon fillers has a shielding effect on the RF pulses used to irradiate the polymeric matrix at 75 MHz and 300MHz (see the experimental section for details on the RF sequence). These preliminary results may be correlated to the electrical properties of the composites under study. Hence, they provide an indication about the capability of the binary hybrid composites containing carbon allotropes and metal particles to be applied in RAM. Further studies on potential applications as NMR shielding materials are now in progress.

## 4. Conclusions

The solution/precipitation activated anionic polymerization of ε-caprolactam in the presence of metal and carbon allotrope fillers is a useful route for the preparation of PA6 microcapsules bearing two different payloads at the same time. Compression molding of these loaded microcapsules produces PA6-based hybrid composites with binary reinforcements. By appropriately changing the metal, the carbon allotrope and their relation, composite plates with increased resistance to thermal degradation, high *E*-modulus and tailored electrical properties, with strong increase of both electrical conductivity and dielectric response can be prepared. The best performing composite systems contain Al and CNT or CB. Varying the relation between Al and CNT molded

composites has enabled reducing resonance signals nearly completely at the probed NMR frequencies. This last study exemplifies one of the possible applications of the novel binary metal/C-allotrope PA6 hybrids.

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