Preparation and Properties of Metal-Containing Polyamide Hybrid Composites via Reactive Microencapsulation

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Abstract

Polyamide 6 microcapsules (PAMC) loaded with 2-8 wt% of Cu, Zn or Fe and up to 30 wt% of Al particles are synthesized *via* activated anionic polymerization (AAP) of ϵ -caprolactam in suspension performed in the presence of the respective micro- or nanosized loads. The high-molecular weight porous PAMC are with typical diameters of 10-90 μm depending on the size of the metal filler particles. The latter are entrapped in the core of PAMC as proven by microscopy methods. The melt processing of the loaded microcapsules produced PA6/metal hybrid thermoplastic composites with homogeneous distribution of the loads without any functionalization. The crystalline structure of all PAMC and molded composites are studied by thermal and microfocus X-ray diffraction methods suggesting polymorph changes during the transition from PAMC to molded plates. Mechanical tests in tension showed that transforming Al-loaded PAMC into composites produces polyamide hybrids with higher modulus and strength at break. Measuring the conductivity and dielectric properties of the composites in linear and cyclic modes showed that 30 wt% of Al can change significantly the permittivity of the hybrid composites without increasing the conductivity of the PA6 matrix.

Key words: Metal-polymer composites, activated anionic polymerization of lactams, microcapsules, dielectric properties, conductivity

Introduction

Due to the notable technological advancement, nowadays the need for novel functional hybrid materials has significantly increased. Systems containing micron- and nanosized metals or metal oxides embedded in polymer matrices exhibit both novel properties and unique property combinations such as magnetic/transparent, conductive/transparent and catalytic/magnetic, among the others [1]. A good control over these properties and their customization for each particular case are highly desirable to obtain reproducible products for practical applications.

A number of studies have shown that addition of finely divided metals or metal oxides to polymers can lead to a significant enhancement of many properties, such as stiffness, strength and hardness [2,3], thermal stability and fire retardancy [4,5], magnetic, optical and electrical properties [6,7]. All these findings make metal polymer containing hybrids potential candidates for a wide variety of engineering applications including catalysis [8], chemical sensing [9], biomedical applications [10], electronics, photonics and for fabrication of electromagnetic [11] and optical [12] devices. Various polymers have been employed as matrices of such hybrids, *e.g.*, the piezoelectric poly(vinylidene fluoride), PVDF for PVDF/Zn systems [13], highly transparent polystyrene, polycarbonate and poly(methyl methacrylate) for embedding of ferromagnetic dispersed phases [14], poly(acrylonitrile) fibers and polyurethane foams for carriers of catalyst complexes bearing Ag [15]. Polypropylene (PP) [16] and various polyethylene types [17] were also tried as matrices for TiO₂-containing systems claiming improvements in the mechanical behavior of the resulting hybrids.

Polyamides are among the best studied matrices for metal-containing hybrids. Thus, Xu et al [18] investigated the properties of Cu/polyamide 6 (PA6) composites prepared by *in-situ* ring-opening hydrolytic polymerization ϵ -caprolactam (ECL) in the presence of Cu nanowires.

The improvement of the tensile strength of the samples containing 0.5 wt% of copper nanowire as compared to the pure PA6 was over 77%, the friction coefficient and wear scar diameter being notably smaller than that of the matrix. Mohamed et al [19] prepared Fe-Ni alloy nanoparticles with average diameters of ca. 80 nm by *ex-situ* reduction of the respective metal (II) chlorides. The alloy nanoparticles were embedded into the PA6 matrix by solvent- or melt-mixing. The resulting hybrids with 3 wt% of alloy displayed up to 35% improvement in the flexural properties as compared to the pure matrix.

Palza [20] reviewed a number of polymer hybrids containing various amounts of Ag or Cu nano- or microparticles suggesting that these systems could be useful as biocide materials for medical applications. Among them, a PA6-based hybrid containing 2 wt% of Ag nanoparticles obtained *in-situ* from silver acetate during the sample melt processing was found to be extremely effective against *Escherichia coli* during a long period of time, while the pure PA6 did not show any antimicrobial efficacy [21]. An original *in-situ* synthesis strategy *via* hydrolytic polymerization of ECL was adopted to prepare PA6/Cu hybrids, in which a CuO precursor was reduced to metallic Cu nanoparticles directly by the amino groups of the matrix polymer [22]. Thus, introducing 0.5 wt% of CuO filler prior to the final melt processing favors the generation of PA6/Cu nanohybrids with improved tensile and wear resistance. In an earlier study [23], Cu particles were deposited upon a polyamide fabric by means of *in-situ* reduction of Cu^{2+} by ascorbic acid in the presence of cetyl trimethyl ammonium bromide as capping agent. Scanning electron microscopy (SEM) images proved that the average diameter of the Cu particles was around 85 nm. The fabrics treated with copper nanoparticles showed higher tensile strength, lower bending length and reasonable antibacterial activities against *Staphylococcus aureus*.

Very few studies exist on the electric or dielectric properties of polyamide hybrids containing metal particles. Lonjon et al [24] report on the preparation and properties of highly

conductive composites of PA11 hybrids containing up to 3.6 vol. % Ag nanowires introduced into the polyamide matrix by a combination of solvent- and melt mixing procedures. The percolation threshold of this hybrid was found around 0.6 vol. % with a level of conductivity above it of *ca.* 10^2 S.m^{-1} .

Summarizing, so far there exist two methods for the preparation of polymer/metal hybrids with micro- or nanosized fillers. In the *in situ* methods the matrix monomer is polymerized in solution, in the presence of selected metal ions introduced before or after polymerization. Then, these ions, already embedded in the polymer matrix, are reduced chemically or thermally. In the *ex situ* processes, the metal particles are chemically synthesized and their surface is functionalized (passivated) by chemical reactions. Next, these functionalized particles are dispersed into a polymer solution or liquid monomer that is then polymerized. Both methods require quite complex chemical transformations and can hardly be used for large scale production. Moreover, they are specifically suited for the preparation of metal nanoparticles that are extremely difficult to handle due to their instability. On the other hand, polymer hybrids containing micron-sized metals are difficult to obtain by conventional melt processing of thermoplastics due to heavy aggregation issues. As communicated by us recently, the said problems can be solved in PA6 hybrid composites by means of a new microencapsulation strategy employing activated anionic polymerization (AAP) of ECL in suspension [25]. The process is carried out in a way to produce microcapsules whose PA6 porous shells entrap the micron- or nanosized filler particles. These loaded PA6 microcapsules (PAMC) can be further subjected to melt-processing to transform them into hybrid PA6/metal composites.

The present work reports a systematic study on the *in-situ* synthesis of PAMC loaded with Cu, Al, Zn and Fe particles by AAP in suspension. The effect of the amount and type of the load on the granulometry, crystalline structure, morphology and thermal properties of the metal-loaded

PAMC is assessed. After transforming PAMC into PA6/metal hybrids by compression molding, the electrical conductivity, dielectric and mechanical properties were evaluated as a function of composition, crystalline structure and preparation conditions.

Experimental

Materials

The ECL monomer with reduced moisture content for AAROP (AP-Nylon® caprolactam) was delivered from Brüggemann Chemical, Germany. Before use, it was kept under vacuum for 1 h at 23°C. As polymerization activator, Brüggolen C20® from Brüggemann Chemical, Germany (C20) was used. According to the manufacturer, it contains 80 wt % of blocked 1,6-hexamethylene diisocyanate in ECL. The initiator sodium dicaprolactamato-bis-(2-methoxyethoxy)-aluminate (Dilactamate®, DL) was purchased from Katchem, Czech Republic, and used without further treatment. The chemical structures of C20 and DL are presented in **Figure 1**. Powdered Cu (>99.5%, grain size <40 µm), Al (>93%, grain size <100 µm) and Zn (>98%, grain size <10 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, xylene, methanol and other solvents are all of *puriss* grade. They were purchased from Sigma Aldrich and used as received.

Sample preparation

The AAROP was carried out in a 250-mL glass flask fitted with thermometer, magnetic stirrer, a Dean-Stark attachment for azeotropic distillation with reflux condenser and inlet for dry nitrogen. In a typical synthesis, about 0.5 mol of ECL and the desired amounts of metal powder (up to 30

wt% in the case of Al, 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 1 hour (from the point of catalytic system addition), the temperature being maintained in the 125-135°C range at a constant stirring of ca. 800 rpm. The metal-loaded PAMC formed as fine powder with the color of the respective metal load and were separated from the reaction mixture by hot vacuum filtration, washed several times with methanol and dried for 30 min at 100°C in a vacuum oven. After 1 hour of polymerization the yields of PA6 in respect to ECL were 49% (empty PA6 microcapsules) and 48-59% for the metal loaded PAMC (**Table 1**).

Compression molding of PAMC to plates was performed in a 25-ton hydraulic hot press (Moore, England) using a rectangular mold with dimensions 85×75×1 mm, pressing for 5-7 min at 230°C and a pressure of 5 MPa.

Characterization techniques

Bright field optical measurements of PAMC sizes, roundness and their distributions were performed in an Olympus BH-2 microscope (Olympus Corp., Japan) equipped with a Leica DFC200 (Leica Microsystems, Germany) digital camera using the Leica Application Suite 4.4 software for image processing. 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 directly 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 average viscometric molecular weight M_v of the neat PA6 was determined by intrinsic viscosity measurements in 97% sulfuric acid at a concentration of 0.2 g/dL with a

suspended level Ubbelohde viscometer thermostatted at 25°C. The Mark-Houwink equation for PA6 was used with $K = 5.066 \cdot 10^{-4}$ and $\alpha = 0.74$ [26]. Flow times are recorded as an average of five runs.

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 samples was calculated according to:

$$X_{DSC} = \frac{\Delta H_m^i}{\Delta H_m^0}, [\%] \quad (\text{Eq.1})$$

wherein ΔH_m^i is the registered melting enthalpy of the current sample and ΔH_m^0 is the melting enthalpy of a 100% crystalline PA6 (190 J/g).

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. For the Zn containing samples the final temperature was 400°C to avoid metal melting. The real load RL of filler in PAMC was calculated according to:

$$RL = R_i - R_{PA6}, \% \quad (\text{Eq.2})$$

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.

The tensile tests were performed in an Instron 4505 testing machine (USA) at $23 \pm 2^\circ\text{C}$ 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-S3. 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 modulus E was calculated from the stress–strain curves as the tangent at 1% strain. In all cases conditioned composite samples stored for ca. 30 days at 23°C and 65% relative humidity were tested. The improvement factor IF for E and σ_{max} values were calculated according to:

$$IF = \frac{P_i - P_{PA6}}{P_{PA6}} \cdot 100, \% \quad (\text{Eq.3})$$

wherein P_i is the respective parameter of the composite material and P_{PA6} - the same parameter of the neat PA6 matrix.

Synchrotron wide-angle X-ray scattering measurements were performed in the P03 MINAXS microfocus beamline at PETRA III, the German Synchrotron Source DESY in Hamburg, Germany beam size being set to 5×5 μm. A Pilatus 300 two-dimensional detector (DECTRIS, Switzerland) was used, the sample-to-detector distance being 115 mm, and $\lambda = 0.969$ Å. Linear XRD profiles were obtained by radial integration of the 2D XRD images by means of the Fit2D software.

Electrical current/voltage (I-V) measurements were performed in a Keithley 487 pico-ammeter/voltage source (Keithley Instruments, USA), between –10V and +10V, in linear increasing or decreasing modes, during one or ten cycles. The voltage increase was set at 1V/s. To rule out interferences due to external electric field, all measurements were performed in a Faraday cage. The dielectric permittivity ε' was obtained from the geometry of the samples in the shape of a parallel plate capacitor (circular electrodes of 5 mm diameter and typical thickness of 600 μm) and the measurement of the capacity and the loss factor $\tan \delta$ with a QuadTech model

1920 precision LCR meter at room temperature and pressure, at frequencies between 20 Hz and 1 MHz. The permittivity ϵ' of the samples was thus determined according to the equation

$$C = \epsilon' \cdot \epsilon_0 \cdot \frac{A}{d} \quad (\text{Eq. 4})$$

where A is the area of the capacitor plates and d – the sample thickness. The electrical DC conductivity σ_{dc} , the real ϵ' and imaginary parts ϵ'' ($\tan \delta = \epsilon''/\epsilon'$) of the dielectric function were obtained for all composites produced from compression molded PAMC. A standard procedure was followed in which the I-V dependences for all materials were determined and analyzed. From the slope of the graphs (straight lines for Ohmic materials) the resistance R [Ω] was determined, from which the resistivity ρ [$\Omega \cdot \text{m}$] and conductivity σ [S/m] were calculated according to the following equation:

$$\sigma = \frac{1}{\rho} = \frac{1}{R} \frac{d}{A} \quad (\text{Eq. 5})$$

wherein 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.

Results and Discussion

Synthesis of the loaded PAMC

Figure 1 present schematically the AAP reaction is suspension leading to the formation of PAMC. The metal payloads were used without any physical pretreatment of chemical functionalization and were completely insoluble in the reaction medium. As known from detailed earlier studies [27], the initiation and propagation of lactam AAP require an anionic initiator and an activator comprising imide links $\text{C}(\text{O})\text{-N-C}(\text{O})\text{-}$. It is important that this catalyst system should remain active in the presence of metal payloads and the solvent employed. These requirements

determine the selection of the initiator DL and the commercial activator C20. As indicated in a series of previous studies on AAP of neat lactams, without any payload, in solution [28,29], the growing PA6 chains form initially viscous, low molecular weight particles that upon additional propagation, coalescence and crystallization produce the final empty PAMC. It can be hypothesized that the metal particles dispersed in the constantly stirred reaction medium will be entrapped into the viscous particles and can possibly nucleate their crystallization thus forming the loaded PAMC. The present study shows that the transformation of the viscous particles into loaded microcapsules without formation of lumps requires an optimized stirring rate (600-800 rpm), maintaining the molar ratio $DL/C20 = 2$ and keeping the temperature of AAP below 135°C.

Table 1 shows the designations of the loaded PAMC samples, the respective polymerization yields, the theoretical metal filler contents and the real ones being determined in three different ways. Due to the polymerization yields that were in the range of 50% in respect to ECL, the expected metal load in PAMC (column 4) was almost twice as high as in the starting reaction mixture (column 2). Column 5 displays the real metal loads calculated from TGA data according to Eq. 2. Deviations between the real and expected loads of about 2% were observed only for the higher loads, while for the rest of the samples the two values are almost identical. From this point on the rounded real metal loads are used in the sample designation.

The viscometric average molecular weight M_v of empty PAMC and molded plates obtained from these PAMC were 37000 g/mol and 38000 g/mol, respectively being comparable to the M_v of commercial granulated hydrolytic PA6 with $M_v = 37200$ g/mol. Attempts to measure M_v of loaded PAMC or molded plates thereof led to chemical reaction between the sulfuric acid solvent and the metal load producing insoluble particles that obstructed the viscometer capillary. Since the conditions of all AAP reactions were the same, it was hypothesized that the M_v of the loaded PAMC should be comparable to that of the empty microcapsules, *i.e.*, lower than 40000

g/mol. This is significantly lower than the anionic PA6 ($M_v = 88500$ g/mol) produced with the same initiator/activator system in the bulk at 165°C [30]. The higher M_v in the latter case is because the bulk AAP takes place at higher temperature, in the polar molten ECL and in strongly basic medium. These conditions favor complex side reactions leading to partially cross-linked PA6 characterized by increased molecular inhomogeneity [27].

Morphological studies by microscopy

Light Microscopy

Figure 2 exemplifies the estimation of the granulometry by means of light microscopy in selected loaded PAMC and in the respective metal powders, including the histograms of size distribution of equivalent diameters d_{eq} and roundness (*i.e.*, the relation d_{max}/d_{min} of the microcapsules). Table 1 summarizes these two values for all PAMC in this study. Thus, 80% of the Al neat particles have d_{eq} in the 30-130 μm range, whereby in the respective PA6/Al 6% sample a relatively broad distribution between 10-80 μm is maintained (Figure 2, line 1). The maximum roundness values of the latter sample fall between 1.1-1.4 *i.e.*, the distribution is slightly narrower than in the starting Al particles where it reaches 1.9 (line 3). This suggests some Al particle fragmentation during AAP. As seen from the magnified light micrograph (the inset of the roundness distribution of the PA6/Al 6% sample in Fig. 2), most of these PAMC include only one Al particle coated with the shell polyamide. Similar morphology was observed in the PA6/Cu 6% samples, wherein most of the neat Cu particles have d_{eq} in the 20-40 μm range and the PAMC sizes are between 10-40 μm .

According to light microscopy data in Figure 2, lines 2 and 4, the sizes of most Fe particles are in the 1-4 μm , with maximum roundness values of 1.1-1.2. The Zn particles are very similar but slightly bigger and less circular with $d_{eq} = 4-8$ μm and $d_{max}/d_{min} = 1.2-1.4$. The

respective PA6/Fe 5% and PA6/Zn 6% PAMC display similar d_{eq} values between 10-40 μm and d_{max}/d_{min} of 1.1-1.3, *i.e.*, the same as of the empty PAMC (Table 1). This means that each Fe and Zn-loaded PAMC will probably contain several metal particles embedded in the polyamide shell. As a whole, with the notable exception of the Al-loaded PAMC, the rest of the microcapsule systems in Table 1 display typical PAMC sizes between 10-40 μm with roundness values of 1.1-1.3. Increasing the load broadens slightly both distributions. The data in Figure 2 and Table 1 allow the conclusion that the sizes and the shapes of the loaded PAMC and their distributions depend closely on the granulometry of the metal particles used, if the parameters of AAP are fixed.

Scanning electron microscopy

A deeper insight on the morphology of PAMC samples can be obtained by SEM (**Figure 3**). Micrographs **3a-3d** visualize the neat metal particles of Cu, Al, Fe and Zn loads and completely confirm the conclusions about their granulometry obtained by light microscopy. It can be observed directly that while Zn and Fe present circular particles of 1-5 μm , Al load is in the form of platelets with sizes in one direction of >100 μm , and Cu particles have complex shape and very broad size distribution. All metal loaded PAMC micrographs (Figure 3, **e-h**), as well as the empty PAMC (image **3i**) show porosity, the pore sizes being typically in the 250-500 nm range, as it can be seen from the magnification in Fig. **3j**. Each microcapsule seems to be formed by the coalescence of several PA6 spheres. This finding is in good agreement with the supposed coalescence-crystallization-precipitation mechanism of AAP in the presence of the load particles whereby the latter are entrapped into the PAMC. Comparing images **3b** with **3f**, **3c** with **3g** and **3d** with **3h** confirms that during AAP the Al platelets are coated by polyamide shell, while the Zn and most of the Fe-loaded PAMC seem to be formed by coalescence of several PA6 spheres,

each one containing several metal particles. As to the PAMC-Cu 6% (Figure 3e), they are most probably a result of a combination of coating and coalescence mechanisms. A small fraction of the PA6/Fe microcapsules display extended morphology with aspect ratio of >4 (image 3g). This can be explained with the magnetization of the Fe particles in the magnetically stirred AAP reaction mixture and their columnar auto assembly, followed by coating with the forming PA6 shell.

The morphological changes of metal loaded PAMC after their compression molding into PA6 hybrid composites are shown in **Figure 4**. As seen from Fig. 4 **b-e**, even at the high load of 5-6 wt%, the metal filler particles are quite homogeneously dispersed within the PA6 matrix. These observations confirm the utility of the transformation of metal-loaded PAMC into hybrid composites, proving that this new concept does not require some kind of treatment of the metal fillers or a complex processing of the PAMC to avoid filler agglomeration. Image 4d shows evidence for auto assembly of the magnetized Fe particles into layers, which can be a reason to study the production of PAMC-Fe and their compression molding in the presence of magnetic fields.

Thermal properties of PAMC and plates

The results from the DSC measurements with metal loaded PAMC samples and the respective compression molded plates are presented in **Table 2**. **Figure 5** displays the DSC traces of differently loaded PAMC during the first scan (**a**), cooling (**b**) and the second DSC scan (**c**). All metal-containing PAMC showed melting temperatures T_{m1} during the first scan in a narrow range between 207-209°C (Figure 5a) displaying a single melting peak. During the cooling after melting, the loaded PAMC recrystallize at higher temperatures as compared to the empty microcapsules, whereby the difference in the crystallization temperatures ΔT_c reaches 16°C for

the PA6/Fe 5% (Figure 5b, Table 2), changing gradually in the following order: Fe>Zn>Al>Cu>empty PAMC. This effect can be explained with the different nucleation effects of the metal fillers. During the second DSC scan (Figure 5c) the T_{m2} are almost the same as in the first scan, whereby in all PAMC, including the empty microcapsules, a low-temperature shoulder of the nominal melting peak appears that is typical of the γ -PA6 polymorph [31]. Notably, the intensity and resolution of this shoulder depends on the metal type, decreasing from Fe to Cu (Fig. 5c). In general, all PAMC samples display melting temperatures 15-20°C lower than the hydrolytic or bulk anionic PA6 with similar M_v with $T_m = 225^\circ\text{C}$.

Figure 6 and Table 2 display the thermal behavior of the composite plates prepared by compression molding of PAMC at 230°C. As expected, the differences between the T_m values of the samples during the 1st (Fig. 6a) and 2nd (Fig. 6c) DSC scans are negligible and the shape of the curves are similar to that of the 2nd scan of PAMC (Figure 5c). All endothermic peaks show dual melting behavior typical for the co-existence of α - and γ -PA6 polymorphs. Figure 6b evidences the same ordering of T_c values as it was registered in PAMC (Figure 5b).

From Table 2 it can be also seen that, as a rule, the crystallinity index X_{DSC} of PAMC measured during the 1st scan is significantly higher than that of the respective compression molded composite. The difference is in the range of 20-25% and depends on the filler metal. This difference almost equalizes after the 2nd scan in the range of 2-7%. This observation can be explained with the thermal pre-history of the PAMC samples. During AAP, the metal-loaded PAMC samples were synthesized and crystallized at isothermal conditions (135°C for one hour) and then cooled gradually to room temperature *i.e.*, no melting occurred. This explains the high X values of PAMC in the first scan. The respective molded plates were obtained after melting the PAMC at 230°C and cooling down with ca. 20°C/min to room temperature. That is why the second DSC scan of PAMC and the first scan of plates show similar crystallinities.

Another comparison based on the data in Table 2 can be made between the glass-transition temperatures T_g of loaded PAMC and their molded composites. Within the microcapsules sample set, the T_g increases in the order empty PAMC < Cu < Al < Zn < Fe. As expected, the presence of metal particles reduces the segmental mobility of the PA6 molecules, *i.e.*, the amorphous matrix becomes more rigid. A similar but less-expressed trend is observed with the molded composite set.

The purpose of the TGA studies of PAMC was the determination of the real metal content on the basis of the carbonized residue, which was discussed previously. Studying the thermal stability of empty and metal-loaded PAMC as a function of the metal loads type and its amount showed relatively small differences being statistically significant only with Fe and Al fillers. Thus, in empty PAMC the thermal degradation starts at $T_S = 298^\circ\text{C}$ and the maximum degradation rate is reached at $T_{MDR} = 347^\circ\text{C}$, whereas with the best performing PAMC-Al 6% sample these values are 307°C and 362°C , respectively. Similar results of $T_S = 307^\circ\text{C}$ and $T_{MDR} = 357^\circ\text{C}$ displayed the PA6/Fe 5% system. For Cu and Zn loads of 6% the differences were less than 5°C , *i.e.*, within the experimental error of the method.

Structure of PAMC and molded plates by microfocus X-ray scattering

As seen from the microscopy studies, the metal-load PAMC are porous objects with diameters typically in the 20-80 μm range. Conventional SEM (Figure 3) reveals the topology of PAMC but not the distribution of the metal particles inside them. Using SEM with energy dispersive X-ray spectroscopy on as-prepared loaded PAMC did not show any content of Al, Cu, Zn or Fe meaning that the filler particles are embedded deeply within the PA6 shell of the microcapsules. To provide information about the microgradients in the fine structure of the loaded PAMC, *e.g.*, degree of metal particles dispersion in various points of the microcapsule, polymorph content of

the PAMC shell, the degree of crystallinity X_C of the matrix PA6 in both microcapsules and molded plates thereof, microfocused X-ray beam from synchrotron was used applying a previously developed methodology [32]. Summarizing, PAMC samples in the form of monolayers were placed on a sliding stage moving consecutively along the X (horizontal) and Z (vertical) axes and making 11×11 steps of $5 \mu\text{m}$ (*i.e.*, the microbeam size). In such a way, total areas of $3025 \mu\text{m}^2$ were scanned in transmission wide-angle X-ray scattering (WAXS) mode, the irradiation time in each point being 5 s. The 2D WAXS patterns in each of the 121 grid points were stored and analyzed automatically to obtain the intensity maps for four typical PAMC-metal samples (**Figure 7**). The intensity images in the left column characterize the metal load distribution and can provide information about the filler particles' sizes. The phase contrast in those images is due to the intensity changes of a selected metal WAXS reflection while scanning the sample area. The respective peaks are indicated in the linear WAXS profiles in **Figure 8a**, found at the following 2θ values: $27\text{-}28^\circ$ for Cu (111), 25° for Al (111), ca. 28° for Zn (101) and 29° for Fe (110). The images in the right column of Figure 7 are constructed from the intensities of the WAXS reflection found at $2\theta = 13\text{-}14^\circ$ related to the $\alpha(200)$ plane of the PA6 shell material. They show the silhouettes of the microcapsules and will provide information about the packing density in the given area.

The WAXS intensity maps for PAMC-Cu (Fig. 7a and 7b) and PAMC-Al micro-capsules (7c and 7d) containing 6% show that the first system seem to contain Cu particles with sizes of $20\text{-}40 \mu\text{m}$ included in slightly bigger PAMC ($25\text{-}60 \mu\text{m}$), *i.e.*, one particle per microcapsule. In the case of PAMC-Al the WAXS mapping indicates similar form and size of metal particle and PAMC, respectively. The Zn and Fe particles (Fig. 7e and 7g) are comparable in size with the beam (*i.e.*, close to $5 \mu\text{m}$), and are quite homogeneously distributed within microcapsules

significantly bigger than them, *e.g.*, 15-40 μm for the PAMC-Fe5% system. The shape of the Zn-containing PAMC in Figure 7f is not clearly distinguishable since the sample packing had to be increased so as to visualize the very homogeneous distribution of small metal particles in image 7e. All these findings are in good agreement with the results of the granulometry studies (Table 1, Figure 2).

The intensity maps in Figure 7 can be used to select the points of interest where the nanostructure of the metal-loaded PAMC needs to be quantified. Figure 8b shows the linear WAXS patterns in selected grid points for microcapsules containing 5-6% of metal. The XZ grid points are selected from the images in Figure 7 in a way that the respective metal concentration is maximal so as to reveal better its influence on the nanostructure of the neighboring PA6 material. The visual inspection of curves 2-5 in Figure 8b display a clear predominance of the monoclinic α -PA6 polymorph in the four metal-loaded PAMC, just like in the empty PAMC reference (curve 1). The two characteristic reflections at 13.2 and 15.6° correspond to the α 200 and α 002/202 crystal planes formed between adjacent chains by van der Waals forces and H-bonds, respectively. It seems that the presence of different metal particles does not change the position of these two reflections, nor their intensity ratio.

The patterns of the compression molded plates (Figure 8c) show the presence of the above two strong reflections of α -PA6 phase in all hybrids (curves 2-5), as well as in the neat PA6 (curve 1). In addition to this, in the gap between the two reflections a shoulder at $2\theta \approx 13^\circ$ appears that corresponds to the γ 001 plane and proves the coexistence of α - and γ -PA6 polymorphs in all compression molded samples.

The curves in Figure 8b and 8c can be deconvoluted by peak fitting [33], which produced quantitative data about the crystallinity index X_c , the polymorph content α/γ , and the unit cell

parameters d_{hkl} for the particular grid point (Table 3). It can be seen that the total crystallinity indices X_c of PAMC and the respective plates are very similar or even coincide, whereby all values are in the 43-51% range. The influence of the metal filler on total X_c seems to be weak. Judging by the α/γ ratio, it can be concluded that the as- prepared empty PAMC are up to 3 times richer in α -PA6 as compared to the neat molded plates produced thereof. The introduction of metal filler in PAMC decreases the α/γ ratio from 5 to 2.9 for Cu and Zn or to 1.6-1.8 for Al and Fe. This means that the metal particles are all promoters of the γ -PA6 formation during the PAMC synthesis, this effect being stronger for Al and Fe than for Zn and Cu.

This finding is in good agreement with the DSC results, 1st scan (Table 2), where only one melting peak was detected in all PAMC/metal samples. The X-ray diffraction results confirmed that the α -PA6 was the preferred polymorph during the PAMC formation. After melt processing of PAMC to composite plates, the polymorph ratio becomes closer to unity (typically 1.4-1.8) (Table 3), which was established in earlier studies on PA6 obtained by AAP in bulk [30]. At the same time, this finding confirms the DSC results in Figures 5c and Figure 6a, presenting dual melting peaks.

The analysis of the d-spacings in Table 3 shows that within the PAMC or molded plates datasets the metal filler does not change the PA6 unit cell dimensions, whereas the transitions from PAMC to molded plates results in an observable increase of the unit cell. Interestingly, the Cu filler seems to be the strongest γ -PA6 promoter after melt processing reaching a $\alpha/\gamma = 1.00$ which revealed the $\gamma(020)$ reflection of the matrix PA6 at $2\theta \approx 8.5^\circ$ (Figure 8c, curve 2).

Mechanical properties of composite plates produced from PAMC

Figure 9 exemplifies the stress-strain curves of various hybrid composites produced by compression molding of 5-6% metal loaded PAMC (curves 2-5) compared to that of neat PA6

matrix from empty PAMC (curve 1). **Table 4** displays the values of Young's modulus E , tensile strength σ_{max} and strain at break ε_{br} for all hybrid samples studied. At low ε values of up to 7-10%, all curves show quite similar regions of elastic deformation, whereby the PA6/Al hybrids fail right in this deformational region showing brittle behavior. Both E and σ_{max} values of these Al-modified systems display a clear growth as compared to the neat PA6, the maximum improvement factors IF being 28% and 12%, respectively. The Zn and especially the Fe-containing hybrids possess very high ε_{br} values in the range of 190-240%, *i.e.*, very close to that of the neat matrix material. These samples undergo neck formation during tensile test, the stress-strain curves demonstrating clear plateaus for plastic deformation and one or more peaks of strain hardening. Both E and σ_{max} change only slightly as a function of Fe and Zn content, the values remaining close to that of the pure matrix with IF reaching 5 and 12%, respectively. The Cu-modified composites showed intermediate deformations of up to 25% with IF of ca. 5% for E -modulus, the σ_{br} values remaining almost identical or slightly below those of the PA6 matrix. This mechanical behavior is to be related to the sizes and shapes of the metal particles – big platelets in the Al-containing systems, and the small spheres in the Fe and Zn-filled hybrids. It should be mentioned also that the relative density of Al is more than 2.5 times lower than those of Cu, Zn and Fe, which determines a much larger volume fraction of filler in the PA6/Al hybrids. The mechanical data in tension suggest that using the novel microencapsulation approach, the E and σ_{max} values of the resulting hybrids containing up to 8 wt% of Al, Cu, Fe or Zn not only do not deteriorate but depending on the metal content, particles size and shape some perceptible improvements can be achieved.

Electrical properties of molded hybrids

The d.c. electric conductivity σ_{dc} of the molded plates was determined from the slope of the one-cycle I-V curves in linear mode according to Eq. 4. **Figure 10a** shows the respective graph for the PA6/Al 6 composite. These data points can be fitted with a straight line passing through the origin of the I-V graph, the deviation from linearity being in the frames of the experimental error of the measurement. Very similar graphs were produced for all of the PA6/metal plates and the data for σ_{dc} were summarized in **Table 5**. It can be seen that for PA6/metal plates in which the content of Cu, Zn or Fe is 2-8 wt%, the changes of σ_{dc} vary only slightly in the range between 10^{-10} - 10^{-9} S.m⁻¹, *i.e.*, they are comparable to the PA6 not containing metal filler. Somehow higher values were obtained with the Al-containing composites, especially the PA6/Al 8 wt% sample. This should be attributed to the lower density of this metal (2.7 g/cm³) while for Cu, Fe and Zn the densities are between 8.9 and 7.1 g/cm³. It seems that in all samples metal contents of up to 8 wt% are not sufficient to reach the percolation threshold. As regards the dielectric permittivity ϵ' and the loss factor $\tan \delta$ taken at 1 MHz, the PA6/metal hybrid plates display in general higher values than the neat PA6 control sample (Table 5). It is also evident that the σ_{dc} , ϵ' and $\tan \delta$ are not always proportional to the metal content, which can be explained with uneven macroscopic distribution of the metal particles.

The question arises what the σ_{dc} , ϵ' and $\tan \delta$ values would be of samples containing a much larger amount of metal filler. Since the electric and dielectric properties of PA6/Al composites seemed to be the most promising, a new PAMC synthesis was performed with 10 wt% of Al in respect to ϵ CL that resulted in PAMC containing an effective Al load of 29.8 wt% established by TGA according to Eq. 4. In Table 5 this sample was denoted as PA6/Al 30%. As seen from the I-V graph in **Figure 10b**, this sample displays a non-Ohmic behavior. The bigger

slope of the initial part of the I-V dependence (tendency line A) is related to interfacial effects and to the polarization of the composite. Then, most probably due to a loss of mobility of these charge carriers, the slope becomes significantly smaller (tendency line B). This effect can be explained with the retention of a bigger part of the charge carriers at the PA6 matrix/Al particles' interface. Considering only the B part of the line, σ_{dc} value of $3.65 \cdot 10^{-9} \text{ S} \cdot \text{m}^{-1}$ was calculated meaning that even at this high Al content corresponding to 11 vol. % the percolation threshold was not reached. This conductivity is even lower as compared to the system with 8% of Al, *i.e.*, the number of charge carriers in the PA6/Al 30% plate and/or their mobility continues to be reduced. Apparently, in the molded PA6/Al-loaded plates even at very high loads the relatively big Al particles are separated from one another by PA6 interfaces, thus not permitting the formation of conductive paths.

In order to interpret better the non-linear behavior of σ_{dc} in the PA6/Al 30% plate, a ten-cycle linear I-V measurement between -10 and +10 V was performed (**Figure 11**). The graph shows a clear hysteresis loop of the current as a function of the voltage whenever consecutive cycles are applied. This means that in each cycle the way the current varies as a function of voltage depends on this same variation in the previous cycle. Such a behavior can be explained with the significant polarization in the PA6/Al 30% composite in the presence of external electric field, *i.e.*, a certain capacity of energy storage can be suggested for this sample.

Figure 12 presents the changes in the current and tension values in Figure 11 as a function of time (steps of 1 volt per second) for the PA6/Al 30% molded plate. It can be seen that in each of the 10 cycles of the voltage there exists a moment (denoted with B) in which the direction of the current (the red curve) inverts before the inversion of the polarity of the external electric field (the black curve). This is possible if the internal electric field which is a result of the

polarization of the composite at a certain moment becomes larger in absolute values than the external electric field. A schematic presentation of the stages of polarization in the PA6/Al 30 composite in the cyclic I-V experiment is presented in **Figure 13**.

In the beginning of the measurement when -10 V are applied, three types of polarization will co-exist namely: i) electronic, which is practically instant; ii) molecular that results from the orientation of the dipoles existing in the polymer chains; and iii) polarization due to accumulation of charges at the interfaces between the Al particles and the PA6 matrix. The latter is called also Maxwell-Wagner-Sillars polarization (MWS) and is typical for multiphase dielectrics in which the resistivity of the phases is quite different. The total polarization of the composite will create an internal electric field whose direction is opposed to the external field. As the voltage of the external electric field starts changing from -10 V to ca. -3V (Figure 12 A, Figure 13 A), the total polarization of the composite is constant and close to the absolute value of the external electric field. With voltage values of less than -3V , the absolute values of the external electric field become lower than those of the internal one (Fig. 13B) and from this moment on the direction of flux of the charge carriers is inverted (Fig. 12B). As the tension of the external electric field becomes higher than 0V (Figs. 12C, 13C), reorientation of the dipoles of the composite starts, the process being finalized at a tension of $+10\text{V}$ (Figs. 12C, 13C). In the C and D regions, the direction of flux of the charge carriers coincides with the external electric field but the increase of the current is decreasing because the internal electric field grows due to the MWS polarization. This behavior of the internal electric field is repeated in all cycles of Figure 12. Therefore, the hysteresis loop in Figure 11 should be attributed to the lag of the composite's polarization in respect to the variation of the external electric field. Such an effect in the PA6/Al 30% composite

would require quite elevated dielectric constant ϵ' at low oscillation frequencies of the external electric field.

Figure 14a confirms this supposition – the ϵ' value at 200 Hz of this sample is above 140, indicating a strong MWS polarization. As the frequency grows, ϵ' decreases and at 1 MHz where MWS polarization should not be expected the $\epsilon' > 80$, which is about an order of magnitude higher than in the neat PA6 and notably higher than the rest of the PA6/Al composites. It can be therefore concluded that the presence of high Al loads in the PA6 matrix increases also the polarization of the macromolecular chains. **Figure 14b** shows that the PA6/Al 30% plate shows low $\tan \delta$ values that, within the whole frequency range, are closer to the neat PA6 than to the $\tan \delta$ of the other Al-containing composites. It seems that the creation of a larger number of PA6/Al interfaces in the composite with the highest Al load decreases strongly the mobility of the charge carriers retaining them within those interfaces which is the cause of the low $\tan \delta$.

Summary

A one-step *in-situ* process was used for the first time to synthesize porous PAMC loaded with particles of four different metals based on suspension AAP of ECL in a hydrocarbon solvent. The PAMC formation most probably passes through entrapping of the load particles into initially formed viscous aggregates of growing macromolecules followed by coalescence and crystallization. This novel method can introduce up to 30 wt% of metal into PAMC. Transforming these loaded PAMC into composites by conventional compression molding produces good homogenization of the metal filler without the need of its functionalization. The mechanical properties in tension of the Cu, Fe and Zn-containing hybrid composite even at high filler loads of 7-8 wt% are similar to those of the neat PA6 matrix. Al loads cause increase of the

Young's modulus and the stress at break values with 28% and 12% respectively. DSC and microfocus WAXS measurements show a well-expressed transition from α - to γ - PA6 in both PAMC and molded plates due to the presence of the metal load. Nevertheless, in PAMC the α - polymorph remains predominant. The d.c. conductivity for all PA6/metal composites, containing up to 30% of metal were in the range of 10^{-9} – 10^{-8} S. m⁻¹. Even this high concentration seems to be below the percolation threshold, which is contrary to similar existing polymer/metal composites obtained by melt-mixing of polymer and filler. This effect is attributable to the good distribution of the metal particles in either PAMC or molded hybrids revealed by scanning them with microfocused X-ray beam. The X-ray imaging and the numerical data provided from this method may have potential in structural studies of any micron-sized samples. By increasing the metal load, higher values of the dielectric constant were found combined with low loss factor. The polarization phenomena revealed in the PA6/Al 30% sample can be potentially used in energy storage materials.

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Figure legends:

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Figure 2 | Estimation of the size distribution and roundness of selected metal fillers (left column) and metal loaded PAMC (right column) based on their light microscopy images. The data of all samples are presented in Table 1.

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Figure 11 | Ten-cycle I-V linear measurement between –10V and +10V in PA6/Al 30% composite plate.

Figure 12 | Variation of the voltage and current as a function of time during a ten-cycle I-V linear measurement between –10V and +10V in PA6/Al 30% composite plate. For details see the text.

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