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POLYAMIDE 6 COMPOSITES: A SOLID-STATE NMR STUDY

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MOTIVATION: The search for new thermoplastic materials with electromagnetic interference (EMI) properties led to the preparation of PA6 micron-sized particles carrying 10-20 wt.% of metal payloads. To assess their applicability in various applications, e.g., in magnetic resonance imaging, systematic analysis by means of solid state NMR are necessary. The main idea of this work is to study the influence of well-dispersed metal fillers (Al, Cu, and Mg) on the semi-crystalline structure and molecular dynamics of PA6 microparticles obtained by anionic polymerization in suspension. The response of the amorphous and crystalline PA6 phases are recorded using conventional ^{13}C MAS and CP-MAS RF pulse sequences, respectively. NMR relaxation studies were performed to determine the motions in the kHz and MHz frequency scales, characterized by the relaxation times $T_{1\rho}$ (ms) and T_1 (s) of the C1-C6 carbons of the PA6 matrix. Finally, metal loaded PAMC are tested as EMI shielding materials by means of ^{15}N solid state NMR at 30 MHz.

## SYNTHESIS and MORFHOLOGY of POLYAMIDE 6 MICROCAPSULES (PAMC)

PAMC are produced by anionic ring-opening polymerization of ε-caprolactam (ECL) in suspension. The reaction is carried out at 130ºC in the presence of the metal particles (10 wt.% in respect to ECL of **Al**, **Cu** or **Mg)**, in a hydrocarbon solvent, in which the ECL monomer is soluble. The conversion of ECL to PA6 for empty PAMC was 56% and 45-49% for the metal-loaded PAMC.
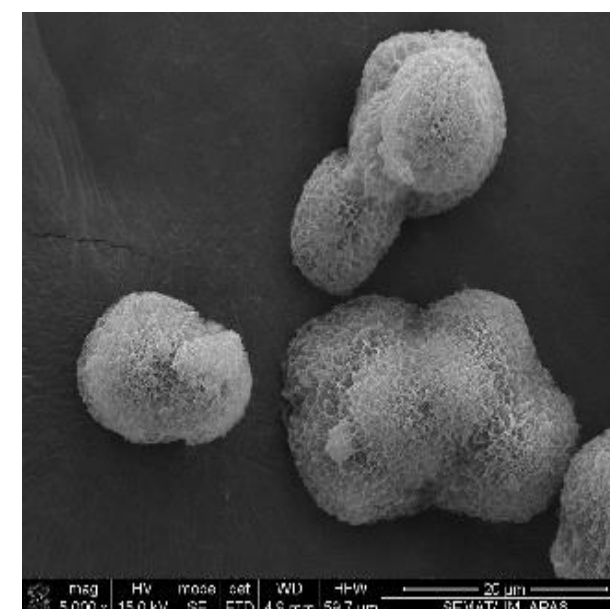
Visual aspect of the PAMC

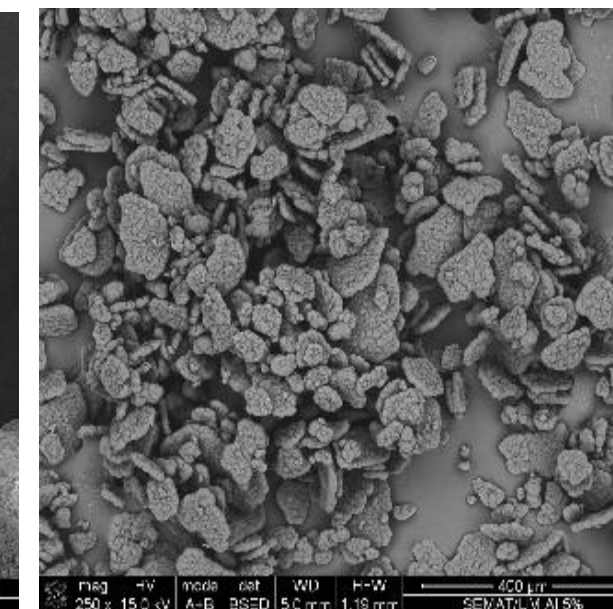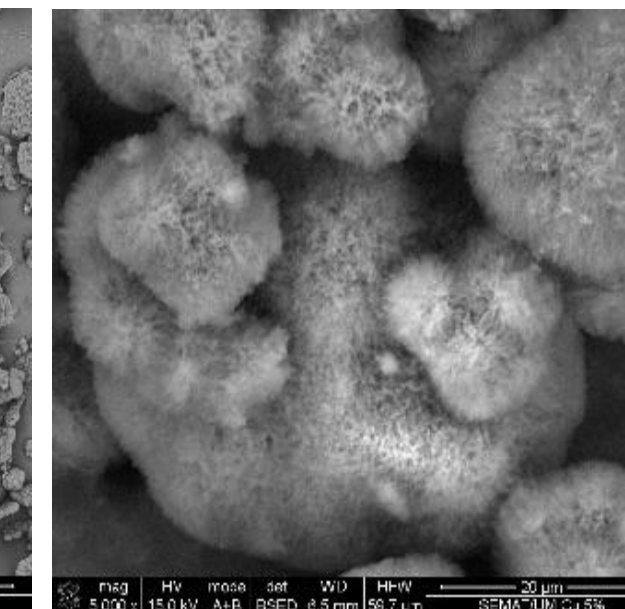Selected SEM micrographs of the materials
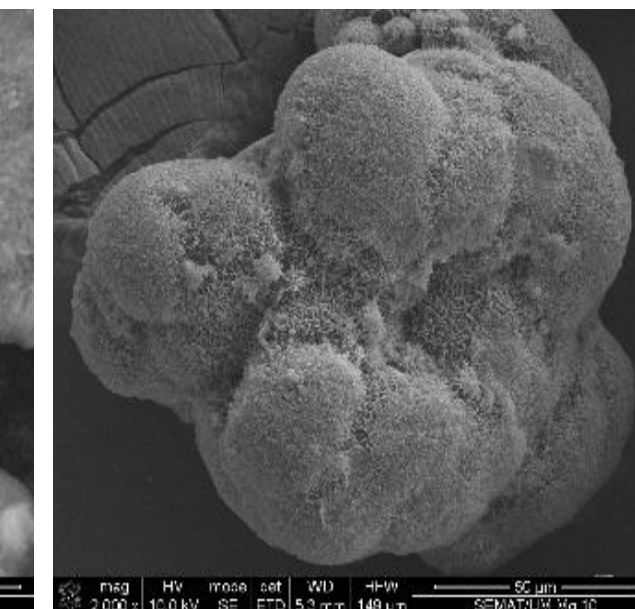
Pure metals

PAMC

Anionic polymerization mechanism of ECL – C20 is the activator and DL is the initiator
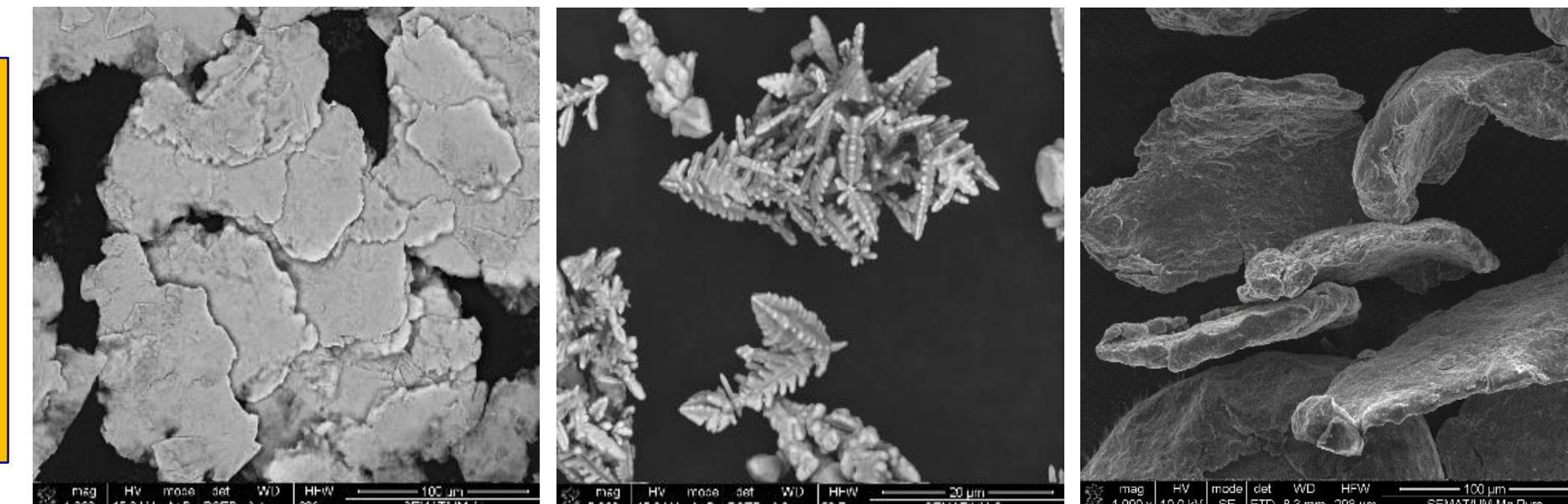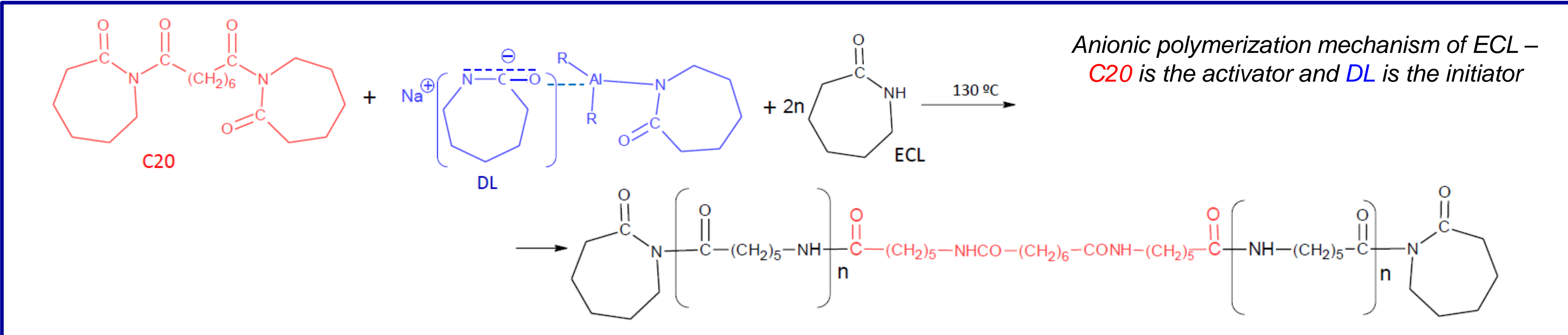
C20 + DL + 2n ECL → 130 ºC

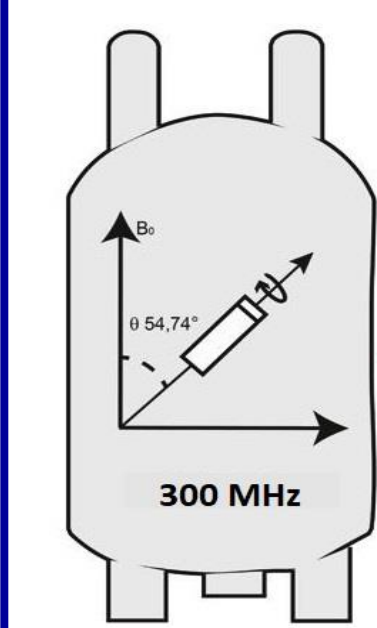Empty PAMC | Al | Cu | Mg

## SOLID STATE NMR ANALYSIS

ssNMR Methods

ssNMR spectra were acquired using a Tecmag Redstone/ Bruker 300 WB spectrometer. Powdered samples (~200 mg) were packed into 7 mm o.d. zirconia rotors, equipped with Kel-F caps. ^{13}C spectra were acquired at 75.49 MHz using two different RF sequences:
- One pulse (Bloch decay) with 1s relaxation delay;
- Cross polarization/MAS (CP/MAS) spectra with a relaxation delay of 10 s, a contact time of 2 ms and a frequency field of 62.5 kHz for the spin-lock field B_1.

The carbon spin-lattice relaxation time ($^CT_1$) and the carbon spin-lattice relaxation time in the rotating frame ($^CT_{1\rho}$) were measured using ^{13}C CP/MAS experiments.
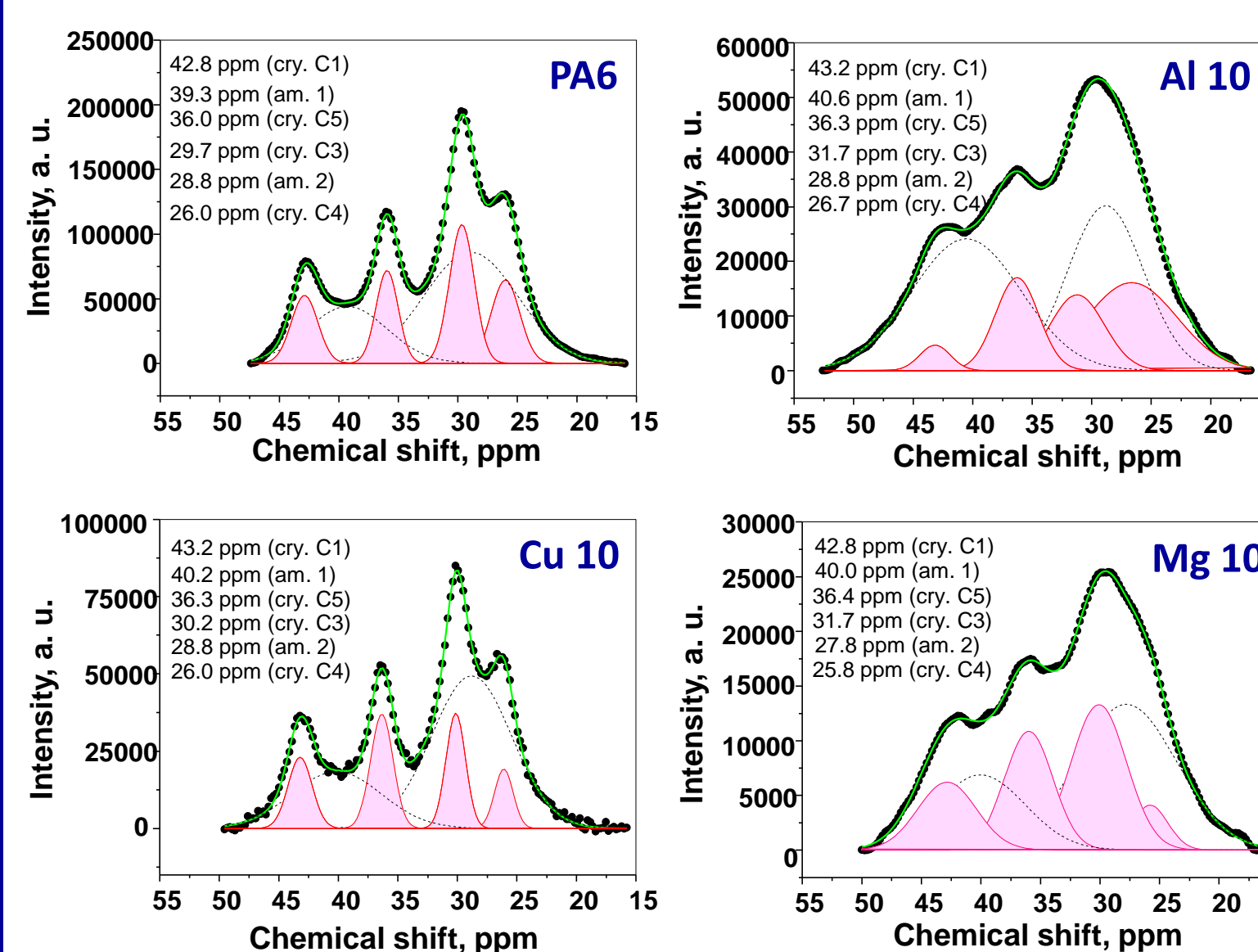
300 MHz

Effect of metal particles on the NMR signal
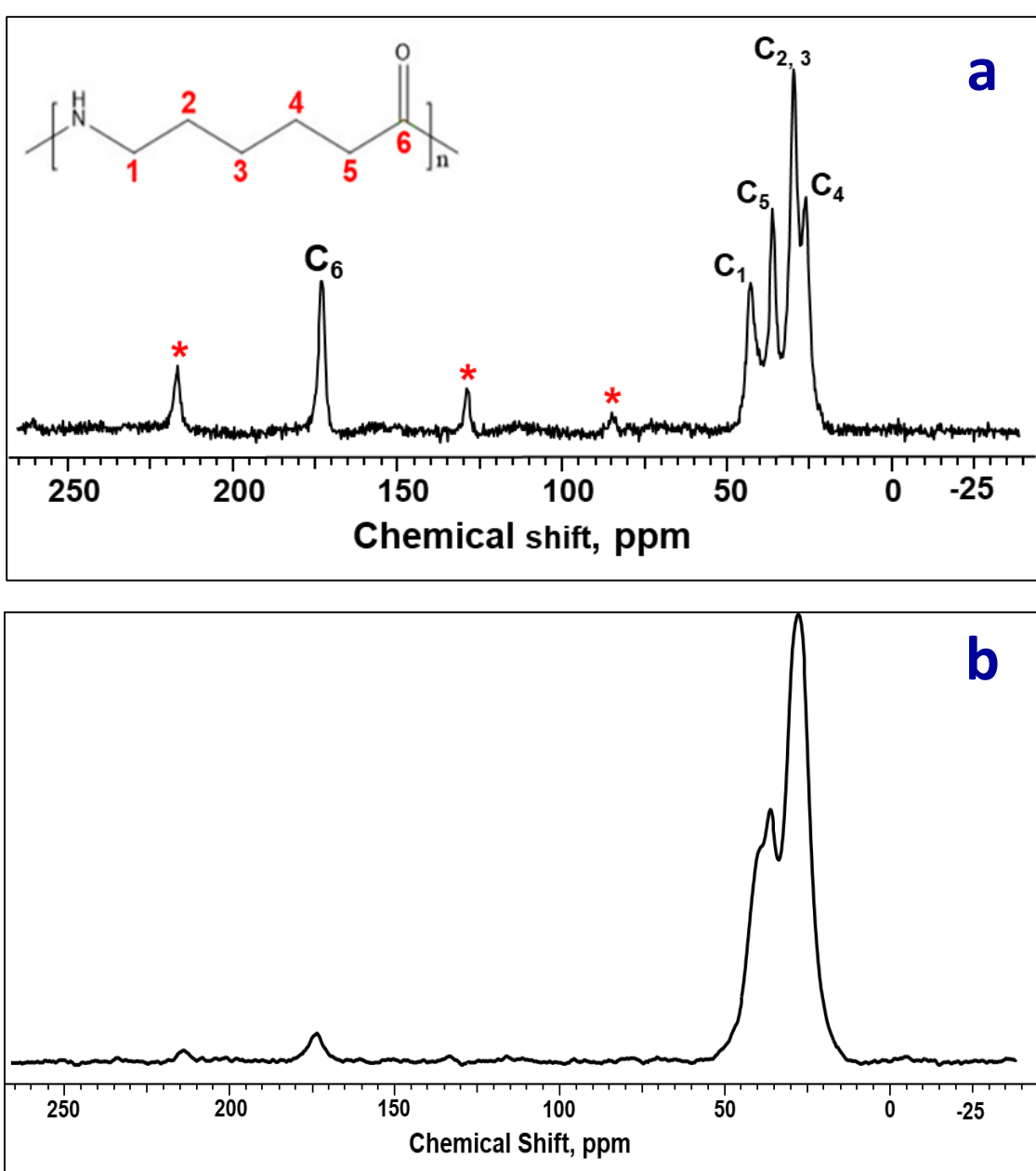
^3C-CP/MAS (a) and ^{13}C-MAS (b) spectra of neat PAMC

Sample (Fitting coef.)	Carbon	Chemical shift, ppm		FWHM, ppm
PA6 (0.9995)	C4	26.00	± 0.02	2.83
	C2, C3, C4	28.92	± 0.14	9.29
	C2 + C3	29.66	± 0.01	2.45
	C5	35.96	± 0.01	2.19
	C1, C5	39.21	± 0.25	7.87
	C1	42.88	± 0.02	2.63
Al10 (0.9996)	C4	27.51	± 0.84	5.73
	C2, C3, C4	28.26	± 5.63	10.56
	C2 + C3	30.77	± 0.26	4.18
	C5	36.30	± 0.83	6.05
	C1, C5	42.33	± 2.71	9.41
	C1	42.75	± 0.22	3.83
Cu10 (0.9980)	C4	26.08	± 0.03	1.84
	C2, C3, C4	28.79	± 0.08	7.92
	C2 + C3	30.12	± 0.02	1.93
	C5	36.34	± 0.01	2.21
	C1, C5	40.07	± 0.39	8.82
	C1	43.21	± 0.03	2.28
Mg10 (0.9993)	C4	25.77	± 0.27	3.49
	C2, C3, C4	27.83	± 4.74	9.94
	C2 + C3	30.08	± 1.05	5.47
	C5	35.97	± 0.43	4.78
	C1, C5	39.97	± 3.42	8.77
	C1	42.81	± 3.76	5.79

Evolution of the C1-C5 signals and shape of the spectra in (a) ^{13}C MAS and (b) ^{13}C CP-MAS experiments

Evolution of the C6 signal in (c) ^{13}C MAS and (d) ^{13}C CP-MAS experiments

Influence of metal particles on the degree of crystallinity, X_c

PA6
42.8 ppm (cry. C1)
39.3 ppm (am. 1)
36.0 ppm (cry. C5)
29.7 ppm (cry. C3)
28.8 ppm (am. 2)
26.0 ppm (cry. C4)

Al 10
43.2 ppm (cry. C1)
40.6 ppm (am. 1)
36.3 ppm (cry. C5)
31.7 ppm (cry. C3)
28.3 ppm (am. 2)
26.7 ppm (cry. C4)

Cu 10
43.2 ppm (cry. C1)
40.2 ppm (am. 1)
36.3 ppm (cry. C5)
30.2 ppm (cry. C3)
28.5 ppm (am. 2)
26.0 ppm (cry. C4)

Mg 10
42.8 ppm (cry. C1)
40.0 ppm (am. 1)
36.4 ppm (cry. C5)
31.7 ppm (cry. C3)
27.8 ppm (am. 2)
25.8 ppm (cry. C4)

There are two groups of aliphatic nuclei (C4, C2+C3) and (C1, C5). Determination of X_c is based on the area of the crystalline and amorphous peaks of the respective groups. A total X_c is also calculated on the basis of the total sum of the area the C peaks.

Carbon	PA6	Al 10	Cu 10	Mg 10
C4				
C2,C3,C4	35.9	46.5	21.6	39.8
C2+C3				
C5				
C1, C5	42.3	54.3	45.9	59.4
C1				
X_c total, %	**39.4**	**49.9**	**30.7**	**47.7**

(X_c partial, %)

Molecular dynamics – Relaxation studies
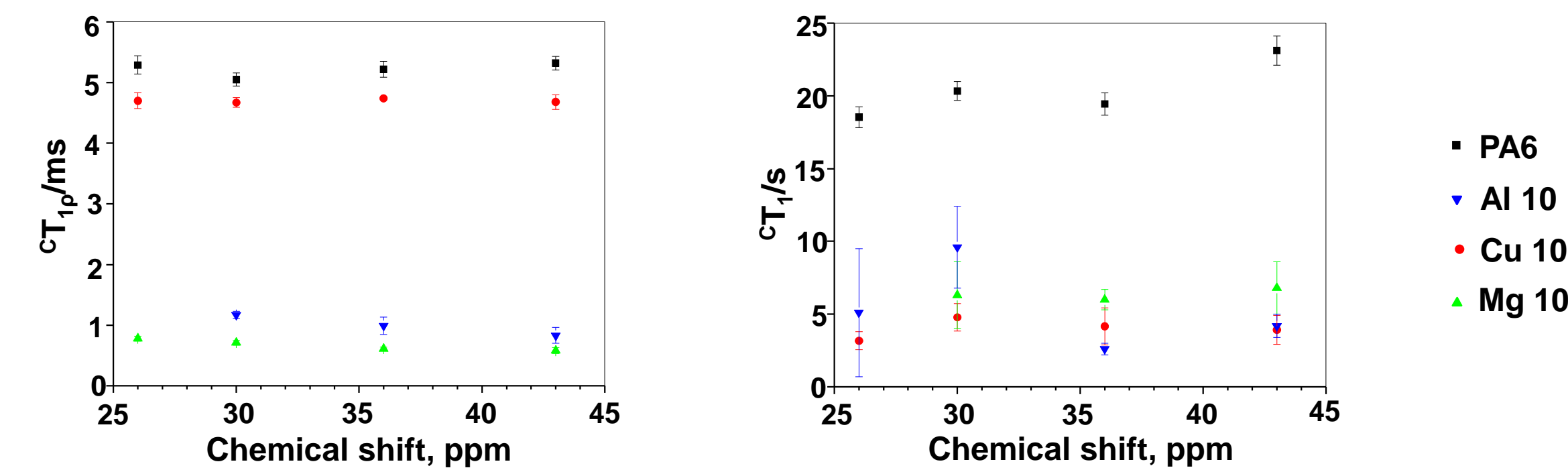
$^CT_{1\rho}$ and $^CT_1$ of the aliphatic carbons in the powdered PAMC

- PA6
- Al 10
- Cu 10
- Mg 10

$^CT_{1\rho}$ decreases in the following order: PA6 > Cu 10 > Al 10 > Mg 10. The presence of metal particles decreases $^CT_1$.

Preliminary EMI shielding tests

^{15}N enriched glycine surrounded by PAMC sample
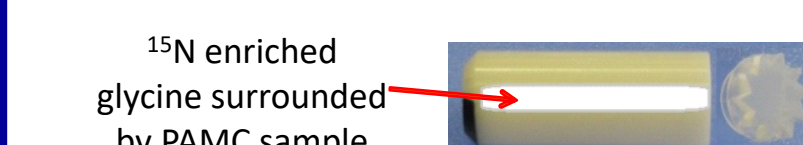
Zirconia cylindrical rotor (Ø 7 mm, L 18 mm)

$$Skin\ depth = \delta_s = \sqrt{\frac{2\rho}{2\pi f \mu_0 \mu_r}}$$

Metal	δ_s, μm
Al	14.86
Cu	11.83
Mg	19.03

Mg 10
Cu 10
Al 10
PA6

^{15}N spectra obtained in static mode at 30 MHz

The importance of filler morphology in RF absorption:
Cu particles exhibit complex dendritic shapes with sizes in the 20-40 μm, which corresponds to values higher than the calculated skin depth in restricted directions. Therefore, the ^{15}N spectrum in the presence of PAMC/Cu should reveal an intensity decrease due to partial absorption of ^{15}N RF throughout Cu particles. The ^{15}N signal was limited to about 1%, which is consistent with the presence of well-dispersed Cu particles within the polymer matrix.
The Mg and Al particles are shaped as platelets with maximum sizes of 80-100 μm and thicknesses of 10-15 μm. Therefore, skin depths determined will induce important ^{15}N signal loss mostly depending on filler aggregation. Since the lowest glycine signal was from PAMC loaded with Mg, it is reasonable to consider higher concentration of aggregated Mg filler particles.

CONCLUSIONS

- The metals affect strongly the shape of the C-signals in the crystalline phase and intensify the overall molecular dynamics;
- The influence of metals varies depending on the diamagnetic (Cu) and paramagnetic (Al and Mg) properties.
- The loss of the ^{15}N glycine signal is related to the skin effect of the paramagnetic Al and Mg.

ACKNOWLEDGEMENTS