



*Dedicated to the memory of  
Professor Eugen Segal (1933-2013)*

## CONDUCTIVE PROPERTIES OF SOME TERNARY THERMOPLASTIC NANOCOMPOSITES FILLED WITH DISPERSED POWDERS. A COMPARATIVE STUDY

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Nanocomposites with mixed thermoplastic matrices, made of polypropylene (PP) and an aliphatic statistic copolyamide (coPA), and dispersed conductive fillers, namely iron powder (Fe) and carbon nanotubes (CNTs), were comparatively investigated. Their electrical properties were critically assessed in correlation with the nature and amount of filler, and its affinity towards one of the polymers from the matrix blend. Conductivity data, in correlation with the morphology study, revealed the phase inversion phenomenon characteristic to conductive segregated systems. The higher affinity of both fillers towards coPA was also confirmed.



### INTRODUCTION

Conductive composite materials consisting of a polymer matrix and dispersed conductive fillers (such as metal particles, carbon black, graphite, carbon nanotubes or conducting fibers) are a relatively new class of materials with highly interesting properties that make them fit for many applications. Their thermal, electrical and dielectric properties have been the subject of both theoretical and experimental studies over the last decades due to their versatility, especially the possibility to tune some characteristics (*e.g.*, conductivity), in accordance with specific practical requirements, by adjusting the amount of the conductive filler. Moreover, unlike metal fillers,

carbon-based fillers do not have the tendency to oxidize and form an insulating layer on the particles surface.<sup>1,2</sup>

The major advantage of such composites is that electrical characteristics are close to the fillers, whereas their mechanical properties and processing protocols are typical for plastics. These composites have several other advantages over the conventional conductive materials, including processability, flexibility, light weight, ability to absorb mechanical shocks. They can be used as antistatic materials and in applications such as switching devices, medical equipment, cables, transducers and gas sensors, as well as devices for electromagnetic radiation shielding and electrostatic discharge.<sup>1-3</sup>

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At the same time, conductive composites hold a great deal of interest from a fundamental point of view: they can be considered as typical segregated systems, consisting of randomly distributed conductive inclusions within the matrix, a polymer or a polymer blend whether or not conductive. The specific thermal and electric properties of such materials are the result of different factors acting synergistically during their processing. The transfer conditions of the electric charge and heat flow are determined by the properties of the conductive phase formed by dispersed metallic or carbon filler.<sup>4</sup> The influence of the type of polymer matrix and filler on the electrical characteristics of the composite has been studied in many works.<sup>5-9</sup> An important characteristic of these materials is the percolation threshold, defined as the critical concentration of filler that corresponds to the sharp growth of conductivity; it strongly depends on the polymer nature and the processing method. Composites with typical random filler distribution displayed a percolation threshold at different values, depending mainly on the nature of the filler: in the range 10-30wt% for dispersed metals and 5-15wt% for carbon black.<sup>8</sup> Although it was observed that the percolation behavior of conductive composites depend on both filler particle shape and spatial distribution within the matrix, as a rule, the equations and models used do not contain any parameters with reference to the filler particle shape and conductive phase topology.<sup>9-11</sup>

Other particles of great interest to be used as filler in conductive composites formulation are the carbon nanotubes (CNTs), whether single walled (SWCNTs) or multiwalled (MWCNTs). Due to their unique properties (structure, high aspect ratio and high surface area, unparalleled mechanical characteristics, excellent electrical and thermal conductivity, etc.) they are excellent candidates for tailoring electric, thermal and mechanical properties of composites.<sup>12-14</sup> Several reviews summarizing different aspects of the composite investigations displayed a broad spectrum of applications: sensitive electrodes, sensors for chemical vapors, electromagnetic radiation shielding materials, as well as pressure, deformation and temperature sensors and photovoltaic cells.<sup>13,15-21</sup>

In the case of conductive composites filled with dispersed CNTs, it was proven that the percolation threshold strongly depends on the polymer nature and the processing approach, given that CNTs are rather difficult to disperse, due to their long and tangled tubes aspect, which leads to the formation of secondary aggregates.<sup>22</sup> Experimental values of

percolation threshold vary in a wide range of the filler content (0.0025-7.5%),<sup>23</sup> but the low values are more attractive because conductive composites with improved properties may be obtained at very low content of CNTs as a consequence of their high aspect ratio. During processing such segregated systems, it is possible to reach a highly ordered distribution of CNTs, especially in the case of polymer blends, when the filler is localized in one polymer phase or at their interface,<sup>24,25</sup> or in latex-based composites.<sup>26,27</sup>

Composites based on polymer blends are of interest because they combine properties of all components. Thus, co-continuous structure of polymer blends can simultaneously give the maximum contribution of the mechanical modulus from each component.<sup>28</sup> A good example in this case are the polyamide/polypropylene (PA/PP) polymer blends used as matrix for conductive composites due to the PA mechanical properties and enhanced PP processability. On the other hand, heterogeneous systems with immiscible components (such as PA/PP) have overall reduced mechanical characteristics due to their low adhesion at the interface. Incorporation of CNTs into such polymer blends can significantly improve their mechanical properties. Literature data<sup>29</sup> have shown that in PA6/PP/MWCNT composites, nanotubes were preferentially located in the PA6 phase and a small amount of them was located at the interface between polymers. MWCNT localized at interface bridged the two phases. This is an important issue in terms of load transfer through the matrix and it also produces increased values for some specific properties, such as the complex viscosity, storage modulus and loss modulus of the blends.<sup>30</sup> Similar effects were reported for PC/CNT/PE polymer blends, where MWNT bridges the PC and PE phases.<sup>31</sup> Other polymer blends used as matrices for conductive composites were studied, as well: PP/PA,<sup>32,33</sup> PP/PE,<sup>34</sup> EVA/PE,<sup>35</sup> HIPS/LLDPE,<sup>36</sup> PET/PE,<sup>37</sup> PE/POM.<sup>38,39</sup>

Many factors influence the distribution of the conducting filler in matrices made of immiscible polymers. In particular, the components viscosity, processing parameters (temperature, blending time and rotor speed, order of introduction of the blend components), the filler wettability, etc. Thus, by adjusting one or more factors it is possible to control the formation of the conductive phase within the polymer matrix and design composites with tailored properties.

This paper is a comparative study on some conductive composites with mixed matrices, namely PP and PA, with focus on the PA component represented by an aliphatic statistic copolyamide coPA, and different dispersed fillers (iron and carbon nanotubes) as conductive components. Their properties were critically assessed in correlation with the polymers compatibility, nature and amount of filler, and its affinity towards one of the polymers from the matrix blend.

## RESULTS AND DISCUSSION

### Composites with dispersed iron

Experimental results reported on other segregated systems<sup>38</sup> showed that filling of polymer composites with conductive fillers led to a percolation-type dependence of conductivity  $\sigma$  on the filler volume content  $\varphi$ . When the critical content of filler  $\varphi_c$  is reached, a percolation threshold is registered and the value of  $\sigma$  increased rapidly over several orders of magnitude. Below the percolation threshold, the conductivity gradient is negligible and the composite conductivity is equal to polymer conductivity or slightly higher. This behavior might be explained by the formation of an infinite conductive cluster, made of filler particles in contact with each other, when the volume filler fraction  $\varphi$  reaches the critical value  $\varphi_c$ . At this point, the composite becomes conductive.

In the case of Fe-filled composites, evolution of electrical properties reflected changes that occurred in the composites structure along with composition variation. The conductivity of PP/coPA-Fe composites *versus* filler content is presented in Fig. 1.

The ternary composites showed percolation behavior and the value of their percolation threshold are much lower (4 vol.%) than for PP-Fe and coPA-Fe composites, where the values of percolation thresholds correspond to the filler content of 20-23 vol. %. These results are consistent with literature data.<sup>40</sup> Below the percolation threshold, PP/coPA-Fe composites are still resistive.

The distinctive feature of conductivity curves is the presence of a plateau, characteristic to each series of composites, used to define the two-step percolation behavior of these materials.<sup>38,41</sup> Three regions may be identified:

- region 1 (0-4 vol.% Fe) corresponds to the nonconductive state of composites;

- region 2 (4-10 vol.% Fe), the region of co-continuous phases, where the conductive phase is created and the conductivity jump is recorded at the percolation threshold, followed by the corresponding plateau;

- region 3 (>10 vol.% Fe), where conductivity further increases due to the phase change, namely the filled polymer phase (coPA-Fe) became the matrix with separate inclusions of nonconductive polymer (PP) phase.

Therefore, the plateau of the conductivity curves is a consequence of the phase inversion phenomenon that takes place along with the increase of the filler content. Highly branched networks of conductive phase formed in the region of phase inversion determined the low values of the percolation thresholds. As consequence, compared to PP-Fe and coPA-Fe samples, PP/coPA-Fe composites displayed a lower percolation threshold and a higher conductivity on the plateau, which is in concordance with data previously reported.<sup>29,32,33</sup>

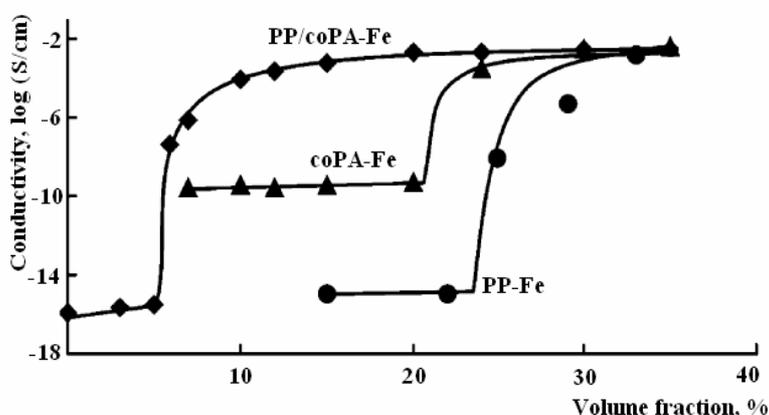


Fig. 1 – The conductivity dependence of PP/coPA-Fe composites on filler content.

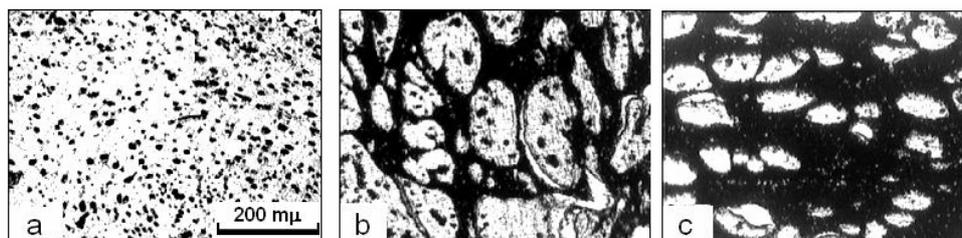


Fig. 2 – Morphology of PP/coPA-Fe composites.

Similar two-step percolation behaviour with very extensive plateau (0.6-1.6% filler) was reported for composites based on polycarbonate filled with 2% multiwalled carbon nanotubes (master batch) and diluted by pure HDPE.<sup>31</sup>

All these data are supported by information obtained through morphological observations by the means of scanning electron microscopy (SEM) and some micrographs are presented in Fig. 2.

The composite morphology, as known, depends on processing parameters, properties and compatibility of components.<sup>36</sup> By controlling these factors, it is possible to modulate the electrical or thermal properties of the material, given that these characteristics does not depend on the filler content only, but on its spatial distribution, too, because it contributes significantly to the conditions of the charge transfer. In segregated systems where the filler is located preponderantly in one polymer component, the local concentration of filler is higher than the overall concentration relative to the entire material. In this case, the conductivity occurs if conditions of double percolation are simultaneously fulfilled: (1) the filler is forming a continuous network inside the host polymer and (2) the filler-containing phase is continuous inside the composite bulk.<sup>42</sup>

As it can be seen in Fig. 2, Fe is localized in one of two polymer phases, namely in coPA (black areas), which was subsequently diluted by PP. This processing approach led to changes in the filler content and composite formulation, simultaneously. Therefore, the conductive phase is the filled polymer, while the pure polymer is the insulating phase. Consequently, a higher amount of filler in the composite is accompanied by an increase of the filled polymer volume (coPA-Fe) and decrease of the diluting polymer (PP). These conditions define the characteristics of the phase morphology.

Fig. 2a presents the morphology of composites wherein the matrix is the pure polymer PP with

small and discrete inclusions of filled coPA-Fe. It corresponds to the region 1 (0-4 vol. % Fe) in the conductivity diagram (Fig. 1), where the composite is non-conductive. Along with increase of the filler content, due to the increase of the master batch amount, the inclusions of filled polymer merge in continuous chains and the specific structure, consisting of two co-continuous phases, filled and unfilled, is formed (Fig 2b). This morphology can be assigned to the region 2 (4-10 vol. % Fe), the region of co-continuous phases. Further increase of filler in the composite destroys the continuous structure of PP and the filled phase (coPA-Fe) becomes the matrix with separate inclusions of PP (Fig. 2c). It is correlated with region 3 (>10 vol. % Fe) in the conductivity chart.

Other studies confirmed the same behavior in composites with dispersed fillers and different mixed matrices. In the case of carbon black (CB) filled composites based on PP-PA,<sup>33</sup> where PA component is a random statistic copolyamide 6/6.9, high values of conductivity were confirmed, associated with a double percolation threshold, effects that occurred due to the specific distribution of CB particles in the PA phase (in bulk) or in PA at the PA/PP interface, due to the higher affinity of filler towards PA. For PE/POM-Fe (polyethylene-polymethylene oxide) segregated systems<sup>38,39</sup> were obtained results that confirmed the correlation between composites electric properties and the affinity of the dispersed filler towards one polymer, in this case POM. The two distinct phases (the conductive one POM-Fe and the insulating pure PE) create an interpenetrating network, where the local Fe concentration in POM is higher than that in the material bulk. So, the percolation threshold is determined by the continuity of the POM-Fe conductive network within the PE/POM blend.

Correlating data from all these studies, it can be concluded that intervals of the phase inversion are different in PP/coPA-Fe and PE/POM-Fe composites. The structure of the conductive phase in PP/coPA-Fe is more finely dispersed and highly branched than that in PE/POM-Fe.

### Composites containing carbon nanotubes

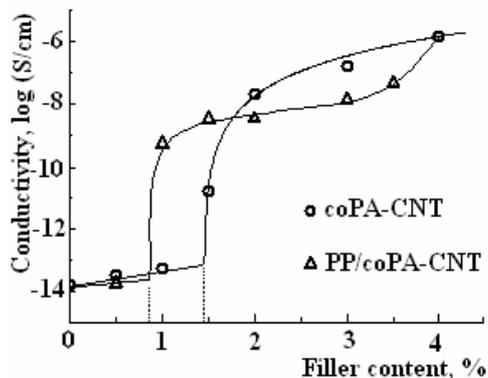
Carbon nanotubes (CNTs) owe their exceptional electric properties to their particular chirality<sup>44</sup> that can induce metal or semiconductor character. Due to the synthesis conditions, most of CNTs are yielding in a mixture of nanotubes with different properties: 1/3 has metallic character and 2/3 display semiconductor behavior. All carbon atoms are part of an extended conjugated aromatic system and display a  $sp^2$ -hybridization geometry wherein the delocalized  $\pi$  electrons are weakly bonded to their corresponding atoms. Therefore, they are involved in the charge transport and conduction occurs along the nanotubes, which makes them functional quantum wires. When CNTs are used in polymer composites, they impart their electric properties to the polymer matrix. These composites are characterized by high

conductivity (although lower than that of pure CNTs) and low percolation threshold (due to the high aspect ratio of CNTs which may reaches values in the range 100÷1000).

Conductivity curves obtained for both series of composites with PP-coPA mixed matrices are presented in Fig. 3.

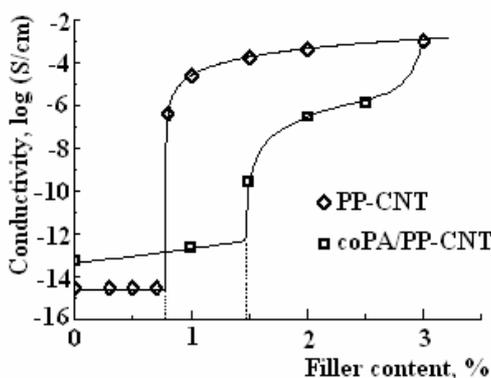
Notable differences were recorded in the conductivity of composite series A and B. In the first case, the master batch coPA-CNT was diluted with PP and the corresponding value of the percolation threshold decreased from 1.4 to 0.8% CNT. For series B, the percolation threshold of the master batch PP-CNT was at 0.7% CNT; after dilution with coPA, the percolation threshold was at 1.48% CNT. Three distinct regions corresponding to different morphology phases may be observed on the curves plotted for ternary composites:

**SERIES A**  
 < 0.8% CNT non conductive phase (PP)  
 0.8-3% CNT plateau  
 >3% CNT highly conductive phase



**SERIES A**

**SERIES B**  
 <1.48% CNT non conductive phase  
 1.48-2.8% CNT plateau  
 >2.8% CNT conductive phase



**SERIES B**

Fig. 3 – The conductivity dependence of composites on the CNT content.

Both percolation curves showed a region of phase inversion (plateau) in different ranges, 0.8-3% CNT for series A and 1.48-2.8% CNT for series B. At lower content of CNT, these materials displayed a non-conductive state characterized by small inclusions of CNT-containing polymer dispersed in the matrix. At higher CNT content, composites are in the conductive region where the insulating phase is dispersed in the conductive matrix continuum. The plateau interval is narrower for series B than for series A and this phenomenon might be explained by the breaking of CNT conductive network in PP upon dilution with coPA

and migration of the filler from PP at the PP/coPA interface. Filler migration is favored by the enhanced affinity of CNT towards coPA. Similar behavior was previously reported for other segregated systems based on polyamide blends and CNTs, such as PA6/PVDF (polyvinylidene fluoride),<sup>46</sup> PA6/ABS (acrylonitrile/butadiene/styrene),<sup>47</sup> and PA6/PP.<sup>48,49</sup> At the same time, the low compatibility between CNTs and PP, and PP high viscosity in molten state, which yielded in a poor filler wettability and distribution, must be considered.<sup>45</sup>

## EXPERIMENTAL

### Materials

The polymers used for the mixed matrices were as follows:

- polypropylene (PP, Malen P F401), obtained from Basell-Orlen, as pellets, with the following characteristics: melt flow index 3.2 g/10 min (230°C, 2160 g), density 0.9 g/cm<sup>3</sup>;

- an aliphatic statistic copolyamide (coPA 6/6.6/6.10), supplied by "Petru Poni" Institute of Macromolecular Chemistry Iași, Roumania, having the following characteristics: molecular weight 2600±200, polydispersity index 1.050, melting interval 125-135°C, melt flow index 11.8 g/10 min (230°C, 2160 g), density at (23 °C) 1.11g/cm<sup>2</sup>.

The conductive fillers used for the considered composites were:

- the iron carbonyl (Fe, R-10) for radiotechnical use was supplied by Powder Metallurgy Co. (Brovary, Ukraine) with high purity (96.6–97.7% Fe), according to GOST 13610-79, and an average particle size of 2.0 μm, and particle shape close to spherical;

- the multi-walled carbon nanotubes (CNTs, NC-7000), from Nanocyl Inc. (Belgium) were synthesized by the catalytic chemical vapour deposition (CVD) method. Outer diameter *d* is 9.5 nm and length *l* is about 1.5 μm, purity 90% and specific surface area 250-300 m<sup>2</sup>/g.

All materials were properly dried in a vacuum oven for 12h at 100°C prior to processing.

### Composites preparation

Composites containing dispersed Fe were prepared in a laboratory extruder, having a single screw with diameter 17 mm and a ratio length/diameter of 20, in a two-step procedure. Processing parameters were: temperature 200°C, rotor speed 50 rpm. In a typical procedure, a master batch of coPA with 35 vol.% Fe was first prepared, then, in the second step, the ground master batch was diluted with pure PP up to the needed content of Fe in the composite (0, 3, 5, 6, 7, 10, 12, 15, 20, 30, 35 phr). For comparison, two series of composites of neat coPA-Fe and PP-Fe were prepared by melt blending under the same conditions. Testing samples were obtained by pressing in a mold at 190°C under a pressure of 50 kg/cm<sup>2</sup> in the shape of a disc with a diameter of 30 mm and a thickness of about 1.5 mm.

For the preparation of CNTs-filled composites based on PP and coPA as matrix, a Haake MiniLab II Micro Compounder (Thermo Scientific, Germany) was employed. The processing parameters were: temperature 200°C, time 10 min for the master batch and 7 min for ternary blends, screw speed 90 rpm. Two series of composites A and B, where A is PP/coPA-CNT and B is coPA/PP-CNT, were prepared in order to compare their electric properties. A typical two-step procedure was used. In the first case (series A), 4% CNTs were compounded with the polymer having the lower viscosity (coPA) to obtain the master batch, which was then diluted with pure PP. Series B (coPA/PP-CNT) was obtained by diluting the master batch made of PP-3%CNT with pure coPA. For series B, the amount of CNTs was 3 vol.% in the master batch because the highest level of conductivity has been reached at this concentration, whereas for series A the same value was recorded at 4 vol.% CNTs. Both series formulation are summarized in Table 1.

Testing samples were discs with 30 mm in diameter and 1 mm in thickness, obtained from the extruded material by pressing in a steel mould at 180°C.

### Composites characterization

The DC electrical conductivity and temperature dependence of conductivity were measured using a two-contact scheme. The values of DC conductivity  $\sigma_{DC}$  (S/cm) were calculated using the equation:

$$\sigma = h/(R \cdot S) \quad (1)$$

where *R* (Ohm) is the electrical resistance measured experimentally by E6-13 teraohmmeter Radiotechnika (Riga, Latvia), *h* (cm) and *S* (cm<sup>2</sup>) are the thickness and area of the sample, respectively.

The electrical resistivity  $\rho$  (Ω cm) was determined as  $1/\sigma$  (S/cm), when necessary.

Morphological observations (SEM) of the fractured surface of composites were performed using a TESCAN VEGA II SBH scanning electron microscope (Brno, Czech Republic). All samples were cryogenically fractured by immersion in liquid nitrogen for 30-50 minutes. Shortly after fracturing, surfaces were coated with a thin silver layer (of about 50 nm) prior to examination under the electron beam. An operating voltage of 30kV was used.

Table 1

CNTs-filled composites with PP and coPA mixed matrices

Polymer matrix, wt.%		CNT, wt.%
PP	coPA	
Series A (PP/coPA-CNT)		
0	96	4
25.0	72	3
50.0	48	2
62.5	36	1.5
75.0	24	1.0
87.5	12	0.5
100	0	0
Series B (coPA/PP-CNT)		
97.0	0	3
80.8	16.7	2.5
65.0	33.0	2.0
48.5	50.0	1.5
32.0	67.0	1.0
0	100	0

## CONCLUSIONS

This comparative study aimed to critically evaluate the electrical properties of two types of conductive ternary thermoplastic composites. As matrices, two thermoplastic polymers were used: a commercial PP and an aliphatic statistic copolyamide coPA. Two types of conductive fillers were employed: dispersed Fe powder and CNTs. Composites were prepared by melt blending through a typical two-step procedure: a master batch, made of one polymer and the conductive filler, was first prepared and then it was diluted with the other polymer up to preset filler contents.

All composite samples displayed highly conductive properties and the corresponding diagrams revealed percolation thresholds at low values of filler content. It was possible to identify three distinct regions on these diagrams, characterized by different electrical properties, in correlation with the morphology changes occurred in materials. Thus, for filler content up to the percolation threshold, all samples were in non-conductive state that corresponds to a morphology characterized by small inclusions of conductive phase dispersed in a continuous insulating phase. After the conductivity jump, all diagrams recorded a plateau where conductivity increased; in the case of composites filled with Fe, it was possible to evidence, by the means of SEM, the simultaneous existence of the two co-continuous phases, morphology specific to this interval and characteristic to the double percolation behavior. For higher filler content, the conductivity reached maximum values and the phase inversion occurred; in this stage, the insulating phase is dispersed as small islands inside the continuous conductive matrix.

Comparing the values of percolation threshold recorded for Fe- and CNTs-filled composites, it was easy to notice the difference: 4% for PP/coPA-Fe, 0.8% for PP/coPA-CNT (series A) and 1.48% for coPA/PP-CNT (series B). These results were attributed to conductivity and particle size differences between the two fillers. Although both of them displayed an enhanced affinity towards coPA, there are still significant disparities between their electrical properties that entailed the distinct percolation behavior of the corresponding composites.

Further research will be focused on the composites morphology investigation by the means of SEM and TEM, mechanical properties evaluation, as well as the study of factors that influence composites properties. This supplementary information will be subject of a future report.

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