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AFASES 2015  
Brasov, 28-30 May 2015

## CONDUCTIVE THERMOPLASTIC POLYMER NANOCOMPOSITES WITH ULTRALOW PERCOLATION THRESHOLD

Fulga Tanasa\*, Madalina Zanoaga\*, Yevgen Mamunya\*\*

\*"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania, \*\*Institute of Macromolecular Chemistry, Kiev, Ukraine

**Abstract:** *The polymer composites with conductive properties are a subject of great interest due to their remarkable characteristics. Depending on their formulation, different morphologies can be achieved, yielding in composites with superior conductivity ranging from electrostatic dissipative to highly conductive. Conductive fillers able to give highly ordered distributions lead to composites with segregated morphology where the critical volume fraction of filler is ultralow, while the electrical resistivity reaches values of  $10^{-4}$   $\Omega$ -cm. This article aims to highlight a few advantages of segregated conductive composites versus random conductive composites, based on the value of their corresponding percolation threshold. Factors that can influence the critical volume fraction of filler and its distribution in the matrix, such as nature of filler and matrix, processing approach and specific parameters, etc., are also reviewed, as well as the range of applications.*

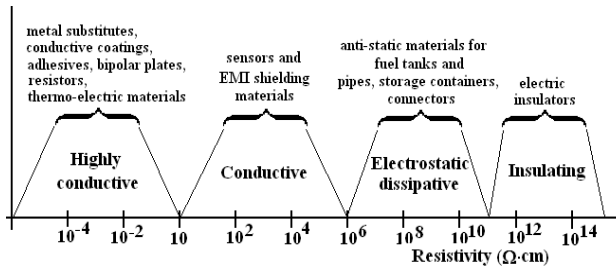
**Keywords:** *segregated conductive polymer composites, ultralow percolation threshold, applications*

### 1. INTRODUCTION

Conductive polymer composites are a relatively new class of materials with highly interesting properties which recommend them for various applications. They 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 (electric conductivity) according to specific requirements by only adjusting the amount of the conductive filler and its distribution. Conductive carbon-based fillers (as carbon black, carbon nanotubes or nanowires, graphene, graphene oxide, etc.) are preferable because, unlike metal fillers, they do not get oxidized and subsequently covered

with an insulating layer on the particles surface [1,2].

The major advantage of the conductive composites is that electrical properties are close to the fillers, while their mechanical characteristics and processing 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, low production costs. 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 [1-7], as summarized in Fig. 1.



**Figure 1.** Classification and applications of conductive polymeric composites

As conductive composites can consist of randomly distributed conductive fillers (powders, nanoparticles, -wires, -sheets, -tubes, etc.) within the matrix, which can be a polymer or a polymer blend, either conductive or not, they hold a great deal of interest from a fundamental point of view when the filler content is ultralow and they can be considered as typical segregated systems. The specific thermal and electric properties are determined by the morphology and properties of the conductive phase and are the result of different factors acting synergistically during their processing. The influence of the matrix type and nature of filler on the electrical characteristics of the composite has been studied in many works [8-12].

The aim of this article is to highlight a few advantages of segregated conductive composites *versus* random conductive composites, based on the value of their corresponding percolation threshold. Factors that can influence the critical volume fraction of filler and its distribution in the matrix are also reviewed, as well as some applications.

## 2. NANOCOMPOSITES WITH ULTRALOW PERCOLATION THRESHOLD

**2.1 The percolation threshold and the critical volume fraction of the filler.** It is known that most of the common industrial polymers are basically insulating from electrical point of view. Therefore, they can be transformed into conductive media only by incorporating a conductive phase, conductive fillers, respectively. Basically, the electric conductivity of a segregated system can be empirically described using the equation 1,

$$\sigma = \sigma_0 (\varphi - \varphi_c)^t \quad (1)$$

where  $\sigma$  and  $\sigma_0$  are conductivity values,  $\varphi$  and  $\varphi_c$  are the filler volume fractions and  $t$  is a critical exponent (for 2D networks,  $t=1.3$ ; for 3D networks,  $t=2$ ). When the volume filler fraction  $\varphi$  reaches a critical value  $\varphi_c$  (also called the percolation threshold), an infinite conductive cluster (IC) is formed and the composite becomes conductive [13]. In general,  $\varphi_c$  depends on several factors, such as the shape of filler particles, the interaction between filler and host polymer and the spatial filler distribution. The more the shape of particles diverges from the spherical one; the lower is the percolation threshold. The interaction between the polymer matrix and filler influence on  $\varphi_c$  through the capability of the polymer melt to wet the filler particles: the stronger this interaction, the better the wettability, the higher  $\varphi_c$ . As for the spatial distribution of the filler, it depends on the polymer-filler interaction, as well as on viscosity of polymer melt and the processing method: the polymer with the higher shear viscosity will generate the larger shear stress and enables a different particle size distribution [11].

A relationship between these factors was defined (equation 2),

$$\sigma = \sigma_c + (\sigma_m - \sigma_c) [(\varphi - \varphi_c) / (F - \varphi_c)]^t \quad (2)$$

where  $F$  is the packing factor (a structural parameter that depends on the filler particles size and shape) and  $\sigma_m$  is the maximum value of conductivity.

The conductive properties of composites thus obtained can be modulated by controlling the filler spatial distribution and, consequently, the percolation threshold which is a measure of the critical volume fraction of filler  $\varphi_c$ . At this specific point, a jump in conductivity can be recorded. Further addition of filler will yield in a gradually increase in conductivity, due to the formation of supplementary conductive pathways, up to a saturation that results in a plateau where the conductivity reaches the maximum value,  $\sigma_m$ .

The mechanism for the formation of a segregated conductive network relies on the capability of the polymeric matrix to provide exclusion micro-domains where the conductive filler particles are allowed a constrained volume, such as the interface



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between immiscible polymers in a blend. This conditionality substantially increases the density of the ordered conductive pathways at ultralow filler volume fraction.

Conductive composites based on polymer blends bring out more interest because they combine the properties of all components. Thus, the co-continuous phase of polymer blends can simultaneously give the maximum contribution of the mechanical modulus of each component [14]. An illustrative example is the case of polyamide/polypropylene (PA/PP) blends successfully used as matrix for conductive composites due to the mechanical properties of PA and enhanced processability of PP. At the same time, heterogeneous polymeric systems made of immiscible components (such as PA/PP) have overall reduced mechanical characteristics due to their low adhesion at the interface. This is one fundamental factor which leads to segregated composites as the filler preferentially occupies certain areas, thus creating a highly ordered morphology with the minimum amount required. This phenomenon is driven by the following factors: thermodynamic (surface tensions between each polymer and filler, and between polymers), kinetic (the viscosity of the polymeric components at the processing temperature), processing (the method and parameters can influence on the thermodynamic and kinetic factors) and chemical (chemical interactions of the filler with one constituent of the blend) [15,16]. Studies performed on different polymeric blends (PP/PA, PP/PE, EVA/PE, HIPS/LLDPE, PET/PE, PE/POM) and fillers [17-27] revealed that the filler can be localized in one of the two polymer phases and/or at the interface bridging the phases, as schematically represented in Fig. 2.

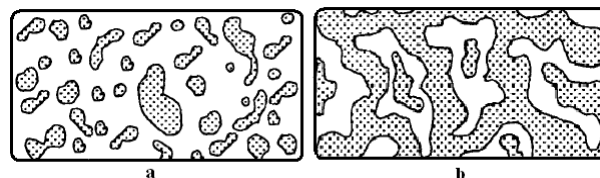


Figure 2. Spatial distribution of the filler in:  
a – random and b – segregated composites

This is an important issue in terms of load transfer through the matrix and it also yields in increased values for some specific properties, such as the complex viscosity, storage modulus and loss modulus of the blends.

**2.2 Processing strategies.** As for the processing, the conventional methods employed to obtain conductive composites are solution processing, melt mixing and *in situ* polymerization [28,29]. The melt mixing approaches (the twin-screw extrusion, internal mixing and injection molding) are the preferred ones since they are compatible with the industrial technologies for polymers and proved their effectiveness in terms of filler dispersion even considering the primary and secondary agglomeration of particles. Such composites generally have a percolation threshold close to the theoretic value calculated by the classical percolation theory [30,31]. Even nanometric fillers, such as carbon nanotubes or graphene nanosheets with high aspect ratio and able to favour highly ordered dispersions, can undergo abnormal aggregation (secondary agglomeration) that results in high value percolation thresholds (10–20 vol%). In the end, these conductive composites have some disadvantages, such as high melt viscosity, low economic affordability and poor mechanical properties (mainly ductility and toughness) [32,33].

Another approach to obtain segregated conductive composites with ultralow percolation threshold is based on compressing a mixture of polymer granules decorated with

conductive fillers via dry or solution mixing [34]. Despite its advantages (process simpleness, great variety of fillers, relatively good dispersion), only polymers with high melt viscosity can be used for this method in order to preserve the segregated morphology and the low critical volume fraction of the filler.

The latex technology can also be considered when such composites are envisaged [34]. It comprises a polymeric emulsion where the filler particles are allowed only in the constrained volume of the interstitial space surrounding the latex particles during the freeze-drying processing. The method provides a good dispersion of the filler, availability to almost any polymer–filler system, low production costs and an environmentally friendly processing when water is used as solvent. The main drawback of this approach is the complex manufacturing.

**2.3 Factors that influence the ultralow percolation behavior.** The challenges of tailoring the morphology of the segregated conductive composites resulted in specific methods to obtain ultralow critical volume fraction of the filler. The type and nature of the matrix, type and nature of filler, as well as processing method and parameters (kinetic and thermodynamic factors) can influence the percolation threshold.

**a. The polymer matrix.** The polymeric matrices influence the percolation behavior by the molecular weight and modulus. It was proven that polymers with high molecular weights and moduli better preserve the segregated morphology. When single polymers are employed, the preferred matrices are usually thermoplastic high melt viscosity polymers (such as UHMWPE [35-37], PS [38,39], natural rubber [40], PA66 [41], etc.), because they can keep the conductive pathways localized in the interfacial regions during processing. The high modulus polymers compel filler particles into the interstitial space, facilitating the segregated network; thus, using a copolymer based on methyl methacrylate (MMA), n-butyl acrylate (BA), methacrylic acid (MAA) and poly(vinyl

alcohol) with a high modulus (~640 MPa),

segregated conductive composites with ultralow percolation threshold (1.5 vol%) were obtained [42].

On the other hand, if the glass transition temperature ( $T_g$ ) of the polymer matrix is lower than the processing temperature, the polymer modulus is too low and cannot promote the formation of the segregated conductive structure [43]. In such cases, the filler is easily mixed with the soft polymer particles, leading to a random conductive network. Therefore, polymers with high modulus and  $T_g$  values are suitable matrices when emulsion methods are employed.

The polymer particle size also affects the segregated conductive composites formation by influencing the density of conductive pathways and the selective location of the conductive filler: the  $\varphi_c$  value decreases along with the increasing particle size ratio polymer: filler [44].

The influence of the thermodynamic factor on the formation of segregated morphology is defined by the polymer surface tension. The high polymer surface tension leads to low polymer-filler interfacial tension and strong affinity between the conductive filler and matrix. Therefore, an insulating polymer layer can occur, that decreases the composite conductivity. For composites obtained by melt compounding, the high polymer-filler interfacial tension thermodynamically favors the aggregation of the conductive particles in the polymer melt, facilitating the formation of the segregated conductive structure [34]. Furthermore, a higher conductivity can be achieved using a semi-crystalline polymer matrix instead an amorphous one, because the conductive particles are expelled from the crystalline segments during crystallization; consequently, the amorphous phase accumulates most of the filler [45].

On the other hand, conductive composites with ultralow percolation threshold can be obtained using polymer blends as matrices. Thus, HIPS/UHMWPE [46], PC/ABS/ABS-g-MA [47], PE/PET [48], PE/PS [49],



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PP/PS/ABS [50], UHMWPE/PMMA [51], PP/PA, PP/PE, EVA/PE, HIPS/LLDPE, PET/PE, PE/POM [17-27] are examples successfully illustrating the wide variety of available convenient combinations. A particular case deserves a special mention, namely the use of thermoplastic copolyamides in the polymer blends used as matrix for conductive composites with ultralow percolation threshold. Studies [52-54] revealed the ternary co-polyamide coPA (PA6/PA66/ PA610) used in composite formulations with PP and CNTs, obtained by melt mixing, favored the formation of the segregated morphology in the corresponding conductive composites and enabled an ultralow percolation threshold (0.8-1.48 vol%) [52].

**b. Effect of the conductive fillers.** The nature of the conductive fillers has a decisive role in the electrical properties of conductive composites with ultralow percolation threshold. Considering a uniform dispersion of the conductive filler particles at the interface of the polymeric domains, the  $\varphi_c$  values decrease along with the increasing aspect ratio of the filler, in concordance with the theory of the excluded volume [55]. On the other hand, it is known the high aspect ratio fillers have superior transport properties and effectiveness in forming segregated conductive morphologies. Thus, depending on the nature of the filler and the corresponding segregated morphology, different percolation thresholds can be reached for the same matrix: in the case of UHMWPE-based composites, it can vary from 0.003 vol% (graphene nanosheets as filler; method: solution mixing) to 0.5 vol% (fillers: carbon black and MWCNTs; method: dry mixing) [34].

Most of the conductive fillers are to be found at the interface of polymer domains,

which requires a highly uniform dispersion, difficult to reach especially at relatively high loadings. This is a typical situation for MWNTs-based conductive composites, where secondary agglomeration is a common drawback [56,57]. Therefore, the high aspect ratio conductive nanofillers are not to be used for conductive composites with segregated structures without employing highly efficient dispersion methods.

Different segregated morphologies can be found in conductive composites due to disparities in the microstructure of the filler, be it nano-bundles, -sheets or -wires. Commonly, the nanosheets are frequently restacking forming a "plane-to-plane" conductive network which can be considered a 2D structure. Therefore, fillers like graphene nanosheets are less susceptible to generate highly branched networks as compared to CNTs [58], and the percolation threshold moves from ultralow to low values.

Besides the geometry, the chemistry of the conductive fillers surface also affects the properties of the segregated conductive composites through the corresponding changes in the inherent electrical conductivity [59].

**c. Processing method and parameters.** The processing approach and process parameters can dramatically influence the morphology of the segregated composites, with direct effect on their percolation behavior. The main approaches are already presented herein. While solution and dry mixing methods are costly and complex, and the results reported are sometimes arguable in terms of dispersion effectiveness and percolation threshold value, the melt mixing and latex approaches seem more appropriate, given that their characteristics favor the diffusive rearrangement of the conductive filler in the polymeric matrices (dynamic

percolation, formation of additional conductive channels and improving their electrical performance). The latex approach leads to composites with relatively high  $\varphi_c$  (0.6 vol% [43,46], 0.9 vol% [41]) due to the difficulties to stabilize the filler particles in the constrained volume between matrix particles, as the molecular weight and modulus of the latex polymer is relatively low [60].

Considering the maximum conductivity  $\sigma_m$  [S/cm] as analysis criterion, it can be noticed that its values depends on the same factors. Thus, the CNTs-containing composites showed higher conductivity than those containing graphene nanosheets due to the better transport properties of CNTs [38,40,60].

During latex processing in the presence of surfactants such as sodium-dodecyl sulfate (SDS), insulating gaps may occur inside the composite, creating high resistivity point along with segregated conductive channels [61]. When melt mixing is considered, the segregated morphology of the conductive filler prevents the diffusion of the macromolecular chains, obstructing the melting at high loadings [62]. Therefore, the filler amount cannot exceed 10% when these composites are prepared through dry compounding and melt blending, but can vary between 0 and 100 wt% if they are obtained by the latex technology, without any limitation due to the melt viscosity [34].

The high temperature processing lowers the melt viscosity of the host polymers yielding in significant mixing between the matrix and conductive filler, and thus prevents the formation of the segregated morphology.

The high pressure treatment can increase the packing factor  $F$ , up to a certain value, generating tightly packed networks [34]. Beyond this value, the network breaks into separate conductive segments.

The mechanical mixing is strongly related to the wettability of the filler particles by the polymer and this is affecting their coating and the composites percolation behavior, respectively. In addition, pre-mixing insulating polymers can generate static electricity that facilitates the absorption of the conductive fillers on the surfaces of the polymer granules [34]. Still, excessive mixing creates additional stress and reduces the conductive network,

similar to high pressure. A critical mixing time must be established in order to optimize the processing/performance ratio.

The melt blending method is highly recommended when two incompatible polymers are used as matrix because segregated conductive structures with tuned properties are difficult to obtain by other approaches. There are two methods to obtain the segregated conductive composites by melt blending. One implies adjusting the thermodynamic parameter (interfacial tension) through the kinetics features (melt viscosity and compounding); thus, the conductive filler is initially dispersed into the polymer thermodynamically unfavorable (the polymer with the lower melt viscosity) and, subsequently, the master-batch is melt blended (“diluted”) with the other polymer (the more favorable polymer having the higher melt viscosity). The thermodynamic driving forces favor the distribution of the conductive filler into the favorable polymer and at the interface [16,52]. The other method consists of the introduction of a third polymer with high affinity for the conductive filler, acting as compatibilizer for a selected pair of incompatible polymers. The percolated filler-compatibilizer phase will be selectively placed in the interfacial region of the polymer blend [34].

A successful example of optimization of all these factors acting synergistically is the system poly(3,4-ethylenedioxy-thiophene): poly(styrene-sulfonate)(PEDOT:PSS), used as the conducting surfactant for the dispersion of CNTs instead of the usual insulating stabilizers [34]; thus,  $\sigma_m$  reached values comparable to pristine CNTs.

**2.4 Applications.** The electrical properties of the conductive composites with ultralow percolation threshold are directly connected with their sensing characteristics, given their capability to alter the conductive network under the action of some external stimuli, such as temperature, mechanical stress, and chemical environment. Therefore, these hi-tech materials are used for sensors and actuators, as well as in electronics as thermoelectric or EMI shielding materials.

The positive (PTC) and negative (NTC) temperature coefficients of these materials





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depend on their resistivity around the melting point of the matrix polymer. Due to their strong interrelation, they are used for extremely high temperature protection devices, self-regulating heaters, micro-switch sensors, etc. [63,64].

The electrical response of the conductive composites toward mechanical stress (the piezo-resistive effect) occurs when the distance between the conductive particles changes to exceed the tunneling distance under the applied load [34]. Despite their interesting strain-resistivity behavior, the use of these bulky sensors is limited by necessity of reaching the high loadings of conductive filler in order to enable pathways for an effective charge transport [65].

The use of conductive polymer composites as materials for chemicals detection relies on their ability to swell when exposed to organic compounds, when vapors or liquids diffuse into the polymer matrix, yielding in increased distances between the conductive particles. This swelling process is often too slow causing a low response rate. Conductive composites with segregated morphologies are ideal for such applications because the conductive phase is located at the interfacial regions and allows the accelerate permeation of chemicals through the capillary effect [66,67].

The conductive polymer composites have been widely used for EMI shielding applications, but the high filler loadings required for adequate shielding properties ( $\geq 20$  dB) negatively affect the production costs and mechanical characteristics due to their secondary aggregation [68,69].

### 3. CONCLUSIONS AND FUTURE DEVELOPMENT

The conductive thermoplastic polymer composites having segregated morphology have an efficient charge transport at very low content of filler, which entails unique advantages: the ultralow percolation threshold, high value maximum conductivity, sensing abilities, thermo-electric properties etc.

Comparing the percolation thresholds of conductive composites obtained by different methods, it can be concluded that segregated composites obtained by emulsion technique and melt blending have higher  $\varphi_c$  values than those prepared *via* dry or solution mixing. The choice in terms of method and process parameters is made, ultimately, based on the nature and properties of the polymer or polymer blend and filler. Given that the lowest

$\varphi_c$  ( $\sim 0.0054$  vol%) was obtained in a system

made of CB/ABS after introducing large

polymeric beads ( $\sim 5$  mm in diameter) as a

scaffold for the segregated conductive morphology [34], one question remains: is low *versus* ultralow percolation threshold a competition toward segregated conductive composites with 0 vol% filler?

Significant efforts have been made in order to develop these materials for various applications. Yet, there are still certain challenges that must be addressed (wise selection of polymers for the mixed matrices, improved dispersion of the filler, avoid the formation of micro-voids, optimization of the processing parameters as a function of specific pairs matrix-filler, use of hybrid fillers instead of classic CNTs which are highly expensive

etc.) in order to make the transition from theory to application and enable the conductive thermoplastic polymer nanocomposites with ultralow percolation threshold multiple functionality.

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