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Graphite nanoplatelets and carbon nanotubes based polyethylene composites: electrical conductivity and morphology

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Abstract

Graphite nanoplatelets (GNPs) and/or multiwalled-carbon nanotubes (MWCNTs) /low density polyethylene (LDPE) composites have been obtained either via melt-mixing or solvent assisted methods. Electrical properties of samples obtained through the above mentioned methods are compared and the conductance values as function of filler fraction are discussed. The corresponding percolation thresholds are evaluated. Conductivity maps images are acquired under low-potentials scanning electron microscopy (0.3 KV) and the relationship between the obtained conductivity images and electric properties is highlighted. The synergistic role of CNTs (1D) and GNPs (2D) in improving the conductive properties of the polymer composites has been shown.

1. Introduction

Nanocomposite materials, where at least one dimension of the filler is less than 100 nm (due to increased contact area), have attracted great attention due to their superior properties (i.e., electrical, optical, mechanical, thermal resistance, etc.) compared to composites filled with conventional fillers [1-3].

Carbon-based nanofillers such as carbon-black (CB), expanded graphite (EG) or carbon nanotubes (CNTs) have been used to increase conductivity [4-6], the filler dispersion being the key point in determining the conductivity performance. In particular, as far as CNTs are concerned, the attention is focused on the best ways of disentangling the bundles and dispersing the nanotubes, either by increasing the solubility by sonication, or by functionalization, via acid modification and radical addition [7-10]. However, disentangling the bundles to achieve optimal dispersion in polymer is not an easy task also because the sonication, which is the most popular method, often shortens the tubes and can increase their defectivities [11]. A further disadvantage of CNTs as fillers is their production cost, a fact which could be overcome by using graphene (GRs) or graphite nanoplatelets (GNPs) as fillers. Also in this case, the achievement of optimal filler exfoliation and dispersion are representing the main problems, due to restacking phenomena. Moreover, beside the quality of the fillers dispersion, also the volume fraction, the size and the shape of particles are largely contributing to the electrical properties.

Various theoretical approaches have been applied to describe the electrical conductivity of composites [12, 13]. In the classical percolation theory, the conductivity of a composite has been expressed as:

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

where φ is the volume fraction of the filler, φ_c is the volume fraction of the filler at the percolation threshold, σ_0 is the conductivity of the filler, and the critical exponent (t) reflects the dimensionality of the system, being t values comprised between 1-1.3 and 1.6-2 for two dimensional and three dimensional networks, respectively.

New applications on these materials come from the possibility to generate localized enhancements of the conductivity to be used in sensing devices or in electric circuits. Conductive networks have been recently obtained along segregated paths [14, 15], in bulk polymer composites or on their surface by the laser-stimulated percolation of CNTs [16]. Remarkable advantages come also from the combination of different type of fillers (i.e. 1D, 2D and 3D), which, for example, can help in reducing the overall electric percolation threshold with a reasonable use of cheaper fillers [17, 18]. The aim of this study is to investigate the role of the synergistic effect between different type of fillers (CNTs and GNPs) on the electrical properties of polymer composites.

More in details, GNPs/CNTs/LDPE composites have been prepared via melt mixing and solvent assisted methods. The fabricated composites were characterized by electrical measurements, XRD analysis, SEM (with conventional and at low potentials), optical microscopies, to correlate conductivity with the particle morphology and the filler dispersion.

2. Experimental Procedure.

2.1 Materials

Graphite nanoplatelet powders (xGNP) of M Grade (5 μm in size) supplied by XG Sciences, were used as-received. MWCNTs were supplied by Mitsui Chemicals (50-100 nm in diameter and 10-15 microns in length) [19]. Two types of low density polyethylene (LDPE) polymer matrices were used, in form of pellet (LDPE_{pellet}, Riblene F11-50, supplied by Versalis) and of powder (LDPE_{powder}, 1070, 200 μm in size, supplied by Abifor Total Petrochemicals). From thermal analyses, melting points of LDPE_{pellet} (140°C) and of LDPE_{powder} (110°C) were obtained.

2.2 Fabrication and characterization of the nanocomposites

Two fabrication methods (melt mixing and solvent assisted) were employed to obtain xGNP/LDPE nanocomposites (with and without addition of CNTs):

Please, insert here Scheme 1

i. Following the melt mixing method (see Scheme 1), LDPE pellets and xGNP powders were first mixed mechanically at room temperature. Then they were injected into a micro blender device (HAAKE minilab II Microcompounder) with horizontal, co-rotating twin screw extruder. The following processing conditions were selected: $T = 140^\circ\text{C}$, mixing time = 5 minutes at 40 rpm. The extruded composite was then hot pressed at the same temperature, to get a flat surface. Also the

simultaneous effect of the CNT addition (in the 1 ÷ 4 wt % range or 0.48 ÷ 1.90 vol %) to the LDPE matrix has been investigated.

ii. Following the solvent assisted method (see Scheme 1), the sonicated xGNP powder in liquid phase (thus exfoliated to some extent) was mixed with LDPE micro powder to provide a better dispersion [20]. More in detail, xGNP powders, either alone (in the 2 ÷ 8 wt % range or 0.95 ÷ 3.8 vol %) or mixed with 2wt% (0.95 vol %) CNTs, were dispersed in isopropanol alcohol and sonicated by a probe type sonicator for 1h at room temperature. Then LDPE_{powder} was added to the dispersion, and the dispersion was further sonicated in ultrasonic bath for 5 min to ensure homogeneity. Finally the solvent was evaporated under stirring with formation of a homogeneous mixture of xGNP/LDPE_{powder} or xGNP/CNTs/LDPE_{powder}. The dried powder was compressed at 15 MPa for 5 min at room temperature, and then hot-pressed at 120°C to obtain a self supporting polymer composite.

The samples, obtained from both fabrication methods, were cut into 2x2 cm square plates, each ~0.7 mm thick, and a silver paste was deposited along 1 cm bands on both ends, to have a shape suitable for electrical characterization (Supplementary Data, Figure S1). Electrical measurements were performed by means of a multimeter, able to detect a resistance up to 20 MΩ, and confirmed by HP 4156A Precision Semiconductor Parameter Analyzer, via the two probe method. This allows to measure the current passing through the sample as function of the potential difference. Resistance values were measured along the sample lengths and the electrical conductivity (1/ρ) values can be calculated using the following equation:

$$\rho = R (A/l), \quad (2)$$

where R is resistance, A is the cross section of the sample and l is the distance between the silver paste bands.

Conductivity mapping was obtained on sample cross-sections by secondary electron (SE) phase contrast imaging, using a SE detector of a Zeiss Evo50 SEM operating at low potential of acceleration (0.3-0.5KeV). To reduce the secondary-electrons edge effects, “flat” sections of the material were specifically prepared for conductivity imaging. More in details, sample cross sections were obtained by means of the ultramicrotome technique (the sample was embedded in epoxy resin to fill voids and to constitute a block, which was then cross sectioned). Microtome slices 0.1-1 μm in thickness representing the cross-section area of the samples, obtained from the block material, were then investigated by low potential SEM [16, 21].

Besides, the morphology of the samples was also investigated by means of the same microscope, operating at 30KeV potential of acceleration and by means of the optical microscope (Leica DM 2500M, Meyer Instruments) (the last data shown in Supplementary data Figures S3,S4).

X-ray diffractograms, obtained by Panalytical X’pert Pro PW3040/60, using Bragg- Brentano geometry, were used to identify the phases within composite and to determine the average crystallite size of xGNPs. In fact by applying the Scherrer equation to X-ray patterns:

$$B(2\theta) = \frac{K\lambda}{L \cos\theta} \quad (3)$$

where B = full width at half maximum (FWHM) of the related peak, $K \sim 0.9$ (constant), $\lambda = 1.54 \text{ \AA}$ (Cu $K\alpha$) and L = average crystallite size, a correlation between the peak broadening and the crystallite size can be obtained. In particular, by taking into account the (002) diffraction peak, information about the thickness of the graphite platelets could be obtained.

3. Results and Discussion.

3.1 X-ray Diffraction

X-ray diffraction patterns of the polymer matrices (LDPE_{pellet} and LDPE_{powder}), and of the composite samples have been shown in Figure 1.

Please, insert here Figure 1.

In Figure 1a the LDPE_{pellet} and LDPE_{powder} matrices are compared. On the basis of the observed peaks at $2\theta=21.4^\circ$ and $2\theta=23.54^\circ$ assigned to the (110) and (200) crystalline planes, respectively, and of the broad band covering the $2\theta=15^\circ$ - 25° range, due to the amorphous phase [22], both matrices exhibit basically the same orthorhombic structure, being this one the more stable under ambient conditions [23]. From the XRD pattern, it comes that, depending on the ratio of area under the crystalline features to the total area, which is related to the “degree of crystallinity”, their structure is mainly crystalline in nature.

On the other hand the simultaneous presence of amorphous and crystalline phases in the polymer matrix, as shown from XRD results, is supported by the model discussed in [20], where the polymer nanotube interaction has been described by wrapping effects due to polymer amorphous regions.

XRD patterns of the two composites, coming from the different methods but with equal percentage of filler (3.64 vol.% or 8 wt%) are compared in Figure 1b. Beside the two peaks at $2\theta=21.4^\circ$ and $2\theta=23.5^\circ$ assigned to orthorhombic phase of LDPE_{pellet} and LDPE_{powder} matrices, as previously discussed, the main peak due to graphite is observed at $2\theta\cong 26.6^\circ$. From Sherrer’s analysis of X-ray diffraction patterns a thickness of 31 nm can be estimated, which, taking an average interplanar distance of 0.335 nm, corresponds to about 90 layers. Otherwise for pure xGNPs, 20 nm in thickness, about 60 layers have been estimated (patterns not shown for sake of brevity). This means that restacking phenomena among the nanoplateles dispersed into the polymer matrix are occurring. The stacked structures, made by interlocking of layers, can be explained with compression effects during the processing conditions [24, 25].

3.2 Electrical properties and morphology

The electrical conductance values for samples obtained following the above mentioned methods are compared in Figure 2. It can be observed that the conductance increases with the xGNP filler percentage moving from 2 vol.% to 7 vol.%, regardless of the method used for fabrication and of the shape of precursor matrix (powder or pellet) (Figure 2a-b). In addition, the conductance values of composites obtained from solvent assisted method (using powder LDPE) are superior (about $10^2 \div 10^3$) with respect to those obtained from melt mixing method (using pellet LDPE) along the whole range of filler concentration (Figure 2a-b).

Moreover, by considering the electrical behavior of composites obtained from the two methods, but using the same type of polymer matrix, it comes that the solvent assisted method allows to achieve the highest conductance (e.g., compare red square in Figure 2a with green square in Figure 2c both corresponding to 3.3 vol % $xGNPs/LDPE_{powder}$).

Please, insert here Figure 2.

From this figure, it is inferred that the percolation thresholds (ϕ_c) for nanocomposites prepared by solvent assisted and melt mixing-based approaches are about 2.3vol.% (5 wt%) and 3.2 vol. % (7 wt%), respectively.

According to the solvent assisted method, first proposed by L. T. Drzal et al. [20, 26], exfoliated xGNP particles, upon removal of solvent, are assumed to form a layer on $LDPE_{powder}$ particles, thus leading to conductive regions. It is reported that, the use of smaller GNPs can be more effective in coating the individual LDPE powder particles because of the increased contact area. This allows the formation of a continuous network even at lower loadings [20], thus enabling to achieve higher conductance with lower filler material, and to decrease the percolation threshold.

Notice, however, that the percolation threshold obtained with melt mixing is significantly lower than that obtained by Drzal's group, who reported a value between 12-15 wt% (5.5-6.8 vol.%) [26]. This gives new evidence that different types of LDPE matrices, with different structure and crystallinity, as well geometric features, have a role in determining the orientation and spacing of the filler, so affecting the molding procedure and actually the conductivity and the percolation threshold of the composite [26].

Nevertheless, although the conductivity data obtained with the solution based approach represent an improvement with respect to melt mixing, due to a better exfoliation and then an enhanced dispersion of xGNP powders, they are not as low as expected, when compared to other composites produced with the same procedure [14]. Also in this case the different shapes, aspect ratio and dispersion of particles or matrix crystallinity could play a role.

In Figure 2a (blue spheres), the effect of CNTs addition (0.95 vol. % or 2 wt%) to the samples coming from solvent assisted method (containing 2.4 vol % or 5 wt %, 2.9 vol % or 6 wt % and 3.8 vol % or 8 wt % GNPs) is shown. Analogous data for CNTs addition (0.95 vol. % or 2 wt%) to samples coming from melt mixing method are reported in Figure 2c (red spheres). From both samples, the main changes in conductance values, due to the addition of CNTs, are observed at low GNP percentages, even if for samples obtained from solvent assisted method a minor increment with respect to samples obtained by melt mixing method can be highlighted. This means a lower synergistic role of CNTs in composites prepared by solvent assisted method.

The effect of the addition of a variable amount of CNTs (0.48 vol % or 1wt %, 0.95 vol. % or 2 wt%, 1.43 vol % or 3 wt %, 1.90 vol % or 4 wt %) to the samples coming from melt mixing method (containing a well defined amount of GNPs, 3.8 vol % or 8 wt%), is also shown in Figure 2c (colored dots).

The morphology of samples containing increased amounts of CNTs (0.95 vol. % or 2 wt% and 1.90 vol % or 4 wt %) together with 3.8 vol % or 8 wt% GNPs is SEM imaged (Supplementary Data, Figure S2). For a same amount of GNPs, higher percentages of CNTs, within LDPE matrices, cause higher conductivities (in the order of more than 10^3), whereas samples containing CNTs alone up to 1.42 vol. % (or 3 wt%) are not conductive (*data not reported for sake of brevity*).

As for the optimized CNT/GNP ratio to make synergy, a suitable way to solve such question could be to evaluate the change of the conductance, by moving from GNPs/LDPE to CNTs/GNPs/LDPE composites. According to this, the higher variations have been observed by addition of 0.95 vol. % (2 wt%) CNTs to samples containing 2.3 vol % (5 wt %) GNPs (solvent assisted method) and to samples containing 2.3–2.9 vol % (5–6 wt %) of GNPs, (melt mixing method) (Figure 2a-c), which are quite close to the observed percolation thresholds values. On the contrary at higher GNPs concentration, a further addition of CNTs does not improve in remarkable way the electrical properties (Figure 2c). This is supported by high resolution SEM images (Figure 3), which give evidence that the addition of CNTs to GNPs polymer composites promotes the formation of new conductive paths, mainly by connecting graphite platelets, as highlighted by arrows in Figure 3b,d. In particular, the addition of CNTs to composites containing low amounts of graphite nanoplatelets, causes a significant growth of connections among both fillers (Figure 3a,b). Besides, a dense network made by closely interconnected platelets is already formed in samples containing high amounts of GNPs (Figure 3c) without a further addition of nanotubes (Figure 3d).

Please insert here Figure 3.

In conclusion, we can state that the optimized ratio for synergy could be found in the composition range quite close to percolation thresholds values, where a significant improvement of the electrical properties of composites is occurring [14, 18, 27].

According to this model, the introduction of one-dimensional filler (MWCNTs), which can bridge adjacent two-dimensional graphite platelets, is resulting in a hierarchical MWCNTs/xGNPs architecture with formation of GNPs stacking [18].

3.3 Secondary electron conductive mapping

SEM images have been obtained at much lower voltages (0.3 -0.5 kV) than usually applied for SEM morphology acquisitions (typically \approx 5-30 kV, depending on samples). Upon these low acceleration potentials the electrical properties of the material can be obtained, being the image contrast related to the local conductivity [28]. More in detail, under the adopted acquisition parameters (300V, 100 pA) bright and dark regions indicate conductive and non-conductive regions, respectively [21, 29]. Once the value of \approx 1 kV was exceeded, the contrast begins to be reversed: this means that bright and dark regions appear respectively non conductive and conductive for this kind of materials [21]. The principles of the brightness inversion due to acceleration potentials in SEM are discussed elsewhere by some authors [30]. Briefly, they are associated to influx of electrons from the polymer matrix to the filler in the 0.3–0.6 kV interval, where the polymer matrix is positively charged. These electrons lower the potential of the filler and enhance the local SE emission, a fact which makes the conductive areas bright.

Results obtained (at 0.3 kV) on a group of samples are shown in Figure 4 and in Figure 5.

Please, insert here Figure 4.

From the images reported in Figure 4, for samples coming from solvent assisted method, it can be inferred that the contrast difference increases with the filler concentration, while non-conducting samples have no contrast difference with respect to the hosting polymer. In particular from Figure

4, it comes out that 8 wt% xGNP/LDPE_{powder} sample shows extended and uniform conductive regions (bright areas). This means that, at this filler percentage, networks of conductive material are formed within LDPE_{powder} matrix, as testified by conductance results. Moreover, the cross section of LDPE composites obtained by melt-mixing method, shows bright regions (associated to conductive areas) at percentages higher than those of samples coming from solvent method (Figure 5). This means that a higher amount of filler is required to form conductive network structures and then to achieve the same conductivity level of LDPE_{powder} matrix. This result is in agreement with conductivity data.

By adding 2wt% CNTs to (8%wt) xGNP/LDPE_{pellet}, obtained by melt mixing, quite similar values of conductivity are observed, which are quite similar to those of (8%wt) xGNP/LDPE_{powder}, obtained by solvent method (Figure 4b, 5c). These results are in agreement with electrical measurements (Figure 1a,c). From these results, the synergistic effect between CNTs and xGNPs is confirmed, because the conductivity increases by improving the electrical contacts among platelets through MWCNTs, as previously discussed [18]. Notice, however, that the synergistic effect is vanishing for higher xGNP content (Figure 5d,e).

Please, insert here Figure 5.

The conductivity maps based on SEM acquisitions agrees with conductivity data obtained from multimeter measurements and can also give information on the presence of segregated regions of the conductive network within the polymer matrix.

4. Conclusions.

xGNP composites with two types of LDPE polymer matrices have been fabricated following two procedures, namely melt mixing and solvent assisted methods. The resulting composites have been investigated to correlate morphology, level of dispersion and conductivity properties. The relationship between graphite nanoplatelets dispersion within matrix and conductivity behavior has been discussed. It is shown that the solvent assisted method, also thank to the exfoliation of the GNPs obtained in the sonication step, allows to obtain lower percolation threshold values, as compared to melt mixing method at the same filler percentage. The synergistic role of CNTs in improving the conductive properties of xGNP polymer composites, prepared by melt mixing method, has been highlighted. It is also shown that the effect is vanishing for CNT/xGNP/polymer composites containing a high percentage of xGNP.

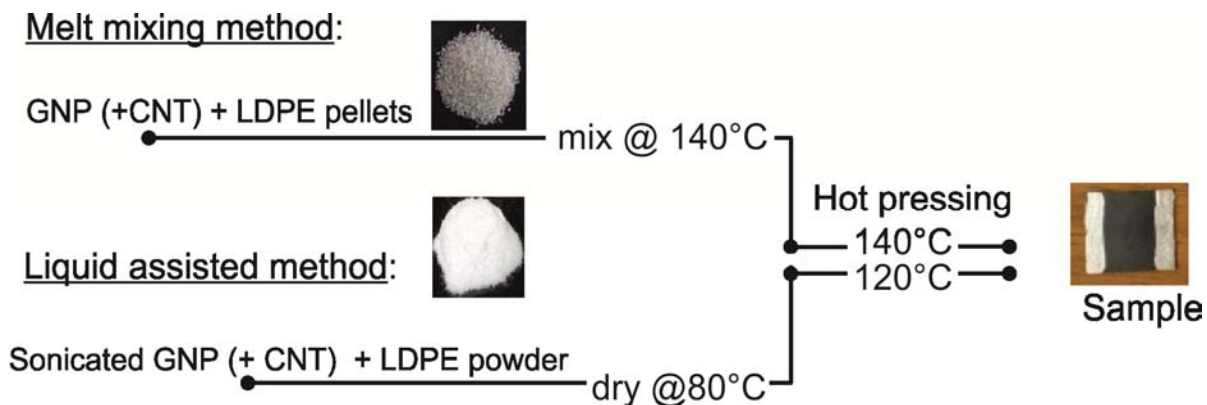
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Scheme 1. (no caption)



Figures and Figure Captions.

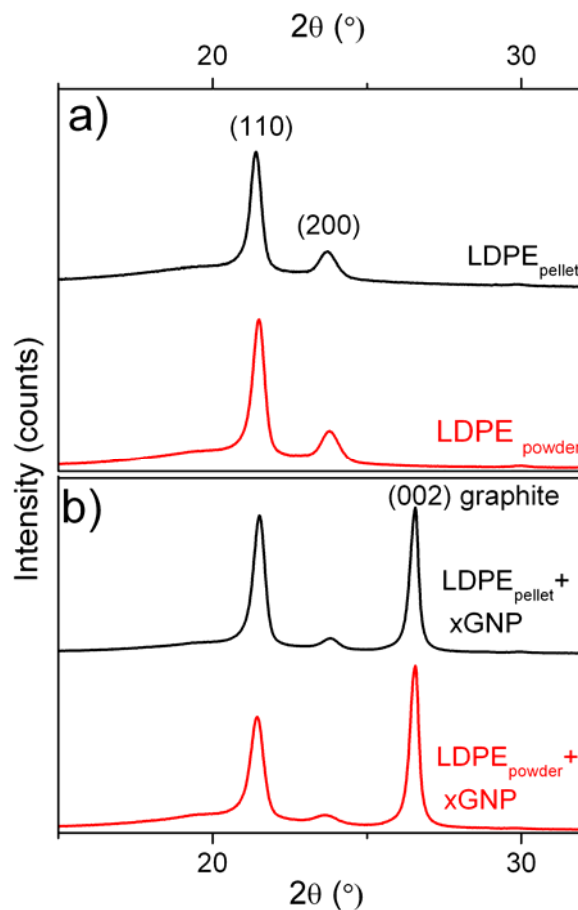


Figure 1. a) XRD patterns of pure precursors, LDPE_{pellet} (black) and LDPE_{powder} (red), b) 3.6 vol.% (8wt%) xGNP / LDPE_{pellet} composite (black) and 3.6 vol.% (8wt%) xGNP / LDPE_{powder} composite (red).

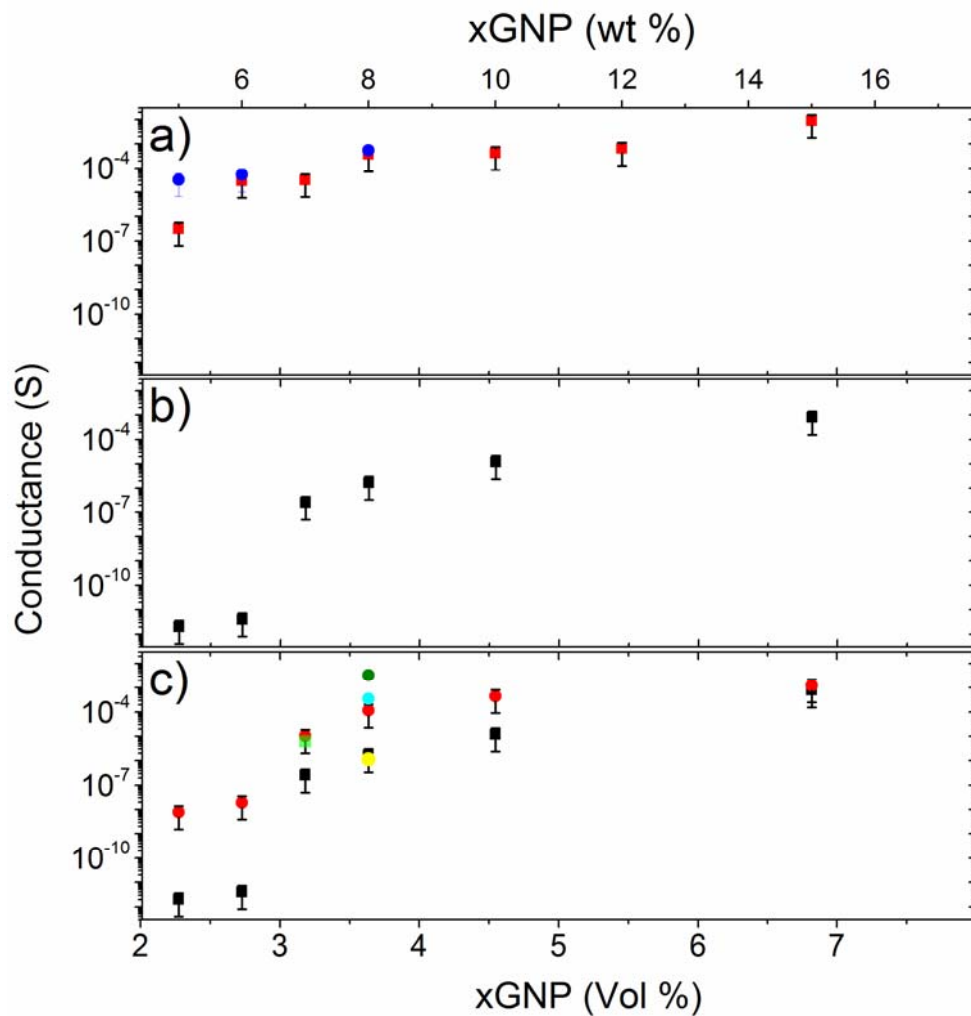


Figure 2. Electrical conductance ($1/R$) properties of xGNP – LDPE composites obtained from different methods: a) red squares indicate composites fabricated by solvent assisted method containing only xGNP /LDPE_{powder}; blu dots indicate samples containing also 0.95 vol % CNTs (2wt%). b) black squares indicate composites fabricated by melt mixing method containing only xGNP /LDPE_{pellet}; c) Effect of CNTs addition on composites obtained by melt mixing method. Black squares and the light green square indicate samples containing xGNP /LDPE_{pellet}, and xGNP /LDPE_{powder} respectively; dots indicate samples containing also CNTs: yellow dots: 0.48 vol % (2wt%); red dots 0.95 vol % CNTs (2wt%); light blue dots 1.43 vol % CNTs (3wt%); green dots 1.90 vol % CNTs (4wt%).

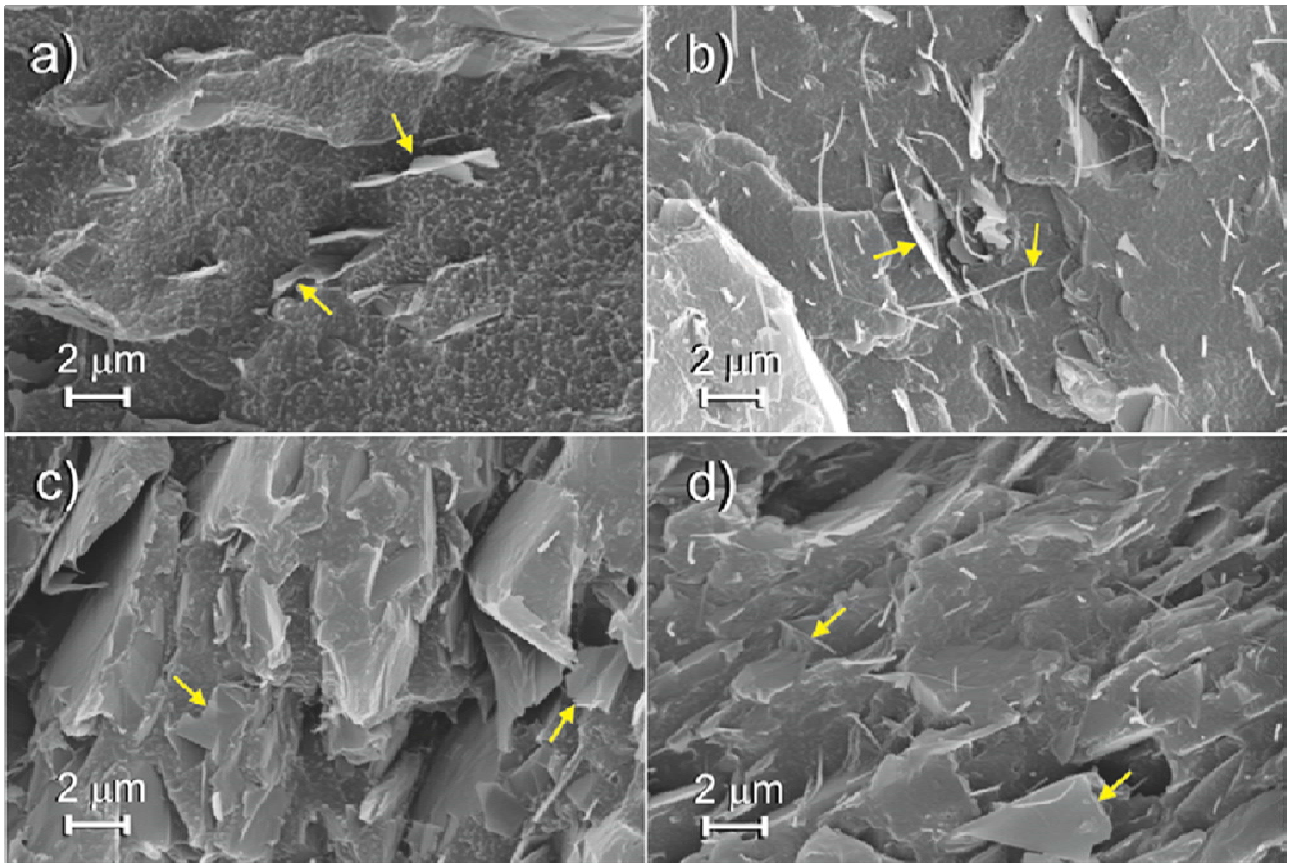


Figure 3. SEM images of composites, obtained by melt mixing method, containing: a) 2.9 vol % (6 wt %) GNPs/LDPE_{pellet}; b) 0.95vol. % (2 wt%) CNTs and 2.9 vol % (6 wt %) GNPs/ LDPE_{pellet}; c) 7 vol % (15 wt %) GNPs /LDPE_{pellet}; d) 0.95vol. % (2 wt%) CNTs and 7 vol % (15 wt %) GNPs /LDPE_{pellet}. A few selected nanoplatforms (a, c) and nanoplatforms together with nanotubes (b,d), respectively, are shown by arrows.

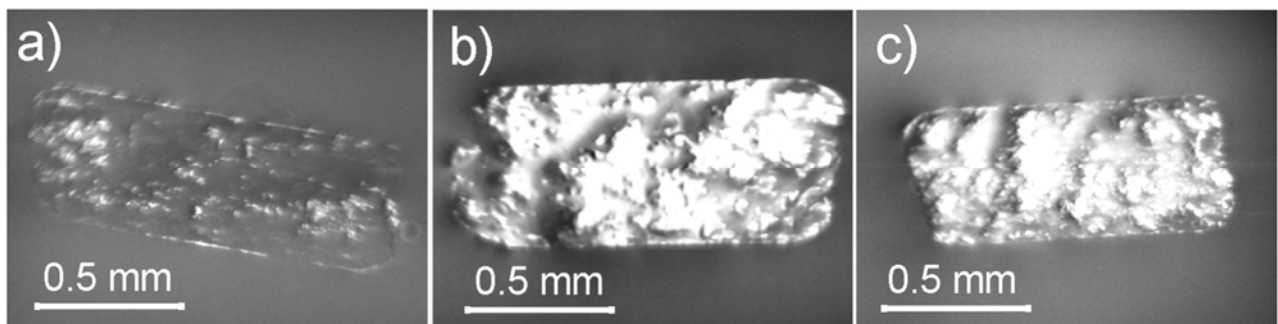


Figure 4. Low-potential (0.3 kV) SEM images of samples fabricated by solvent assisted approach: a) 2.3vol% (5 wt%) xGNP/LDPEpowder, b) 3.6 vol% (8 wt%) xGNP/LDPEpowder, c) 4.6 vol% (10 wt%) xGNP/LDPEpowder. The increase in brightness with increasing filler percent agrees with the electrical conductivity data. The dispersion level of the conductive filler forming a segregated network is clearly visible.

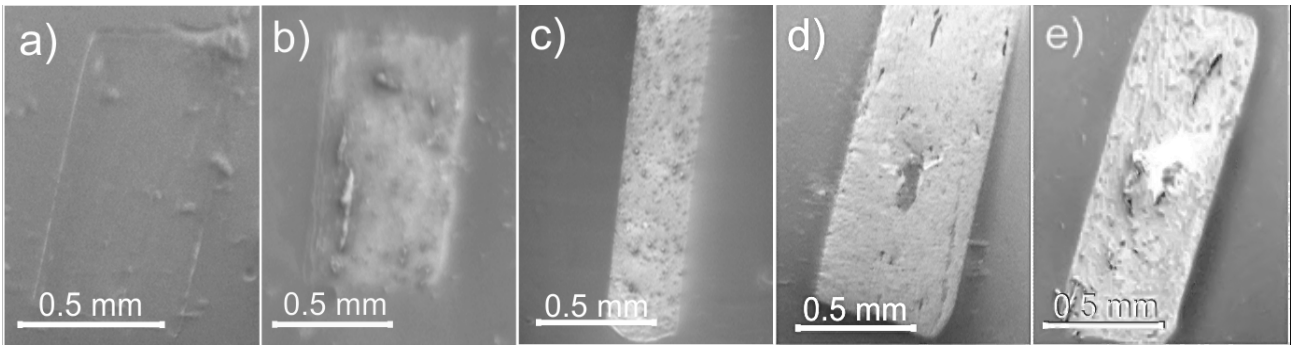


Figure 5. Low-potential (0.3 kV) SEM images of samples fabricated by melt mixing approach: a) 0.95 vol% (2 wt %) CNT/LDPEpellet, b) 3.6 vol% (8 wt%) xGNP/LDPEpellet, c) 3.6 vol% (8 wt %) xGNP/ 0.95 vol% (2 wt%) CNT/LDPEpellet, d) 6.8 vol% (15 wt%) xGNP/LDPEpellet, e) 6.8 vol% (15 wt %) xGNP/0.95 vol% (2 wt%) CNT/LDPEpellet. In a) there is no contrast difference between the composite and the surrounding epoxy resin polymer matrix (non conductive sample); in b,c,d,e) homogeneous and fine filler dispersions are observed within the polymer matrix.

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Supplementary data



Figure S1 2x2 cm² sample for electrical conductivity measurements.

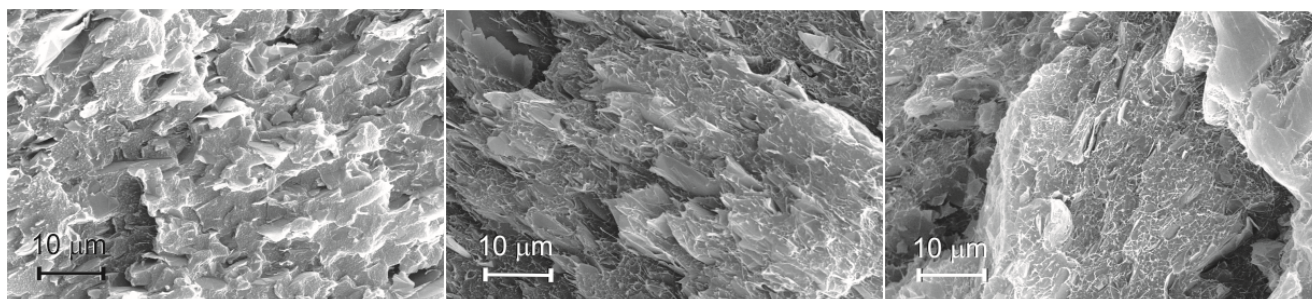


Figure S2. SEM image of 3.8 vol % (or 8 wt%) GNPs/LDPE_{pellet} composites containing increasing amounts of CNTs: without CNTs (on the left side), 0.95 vol. % (or 2 wt%) CNTs (in the middle), 1.90 vol % (or 4 wt %) CNTs (on the right side).

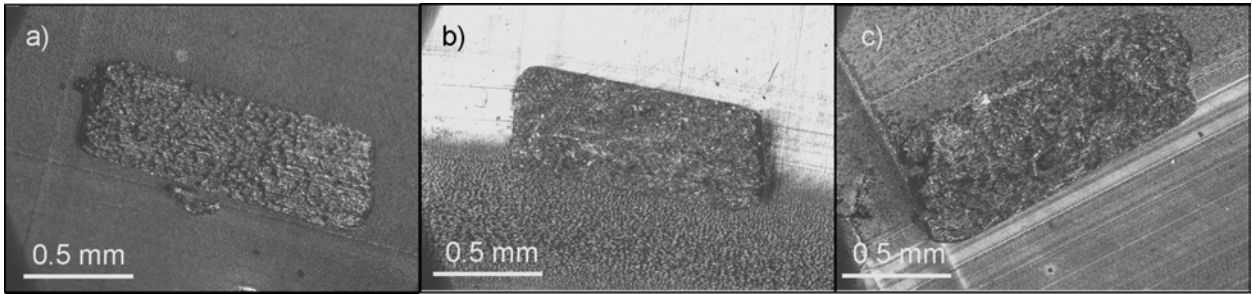


Figure S3 Optical microscopy images of the samples SEM imaged in Fig 4: a) 5% wt.xGNP/LDPEpowder, b) 8 wt.% xGNP/LDPEpowder, c) 10 wt. % xGNP/LDPEpowder.

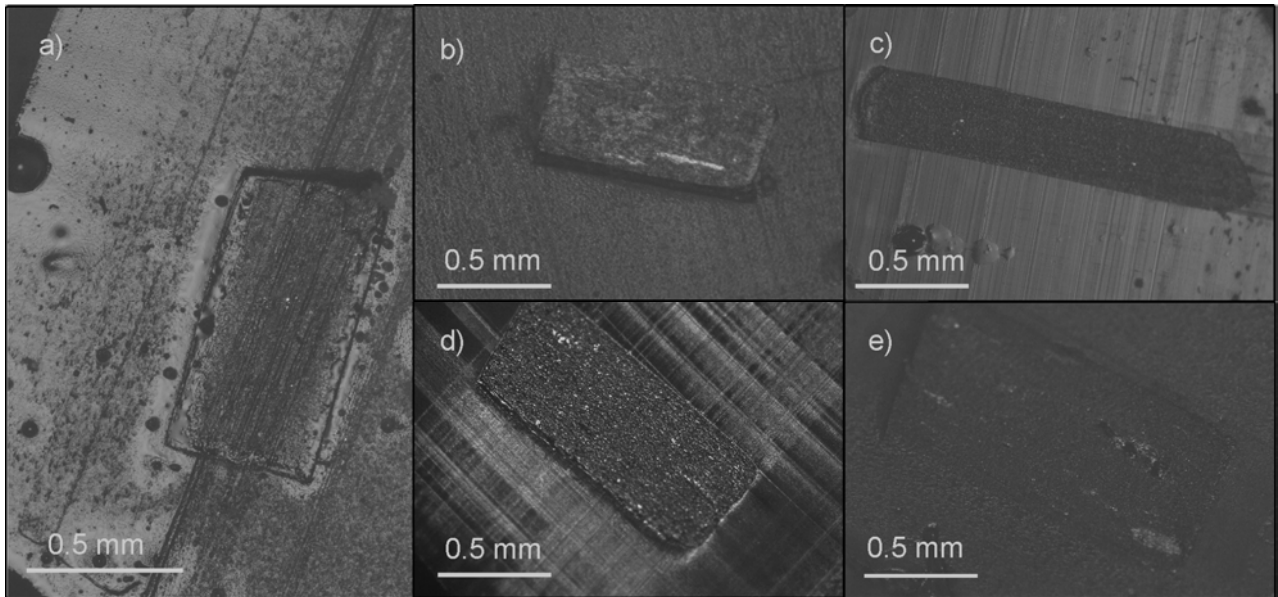


Figure S4 Optical microscopy images of the samples SEM imaged in Fig 5. a) 2 wt. %CNT /LDPE_{pellet}, b) 8 wt. % xGNP / LDPE_{pellet}, c) 8 wt. % xGNP / 2 wt. % CNT /LDPE_{pellet}, d) 15 wt. % xGNP / LDPE_{pellet}, e) 15 wt. % xGNP / 2 wt. % CNT/ LDPE_{pellet}. Remarkable morphology differences between samples coming from solution assisted and melt mixing methods cannot be easily highlighted, but larger aggregates of filler are forming in the melt-mixing method, except the non-conductive sample (a).

For an xGNP – polymer composite, an inter particle distance (IPD) model was proposed by Jing Li et. al., where the electrical percolation threshold (P_c) was determined as follows:

$$P = 27\pi D^2 t / 4(D + IPD)^3 \quad (1)$$

where P is the volume fraction of the filler, t is the thickness, IPD is the interparticle distance between adjacent conductive filler particles and D is diameter of a filler particle, which is assumed circular. For IPD values below 10 nm, a rapid increase in conductivity occurs, via quantum-

mechanical tunneling mechanism, which can be regarded as the percolation threshold (P_c). So, for IPD values of 10 nm and after some simplifications, this expression finally reduces to:

$$P_c = 21.195/\alpha \quad (2)$$

where α is the aspect ratio of xGNP particle. This formula claims that the most important factor in percolation threshold for a given filler volume fraction is the aspect ratio of the particles, and predicts that as the aspect ratio increases, the percolation threshold should decrease. However, this model still does not address several issues: i) irregularities in shapes of nanoplatelet particles, ii) agglomeration or wrinkling and folding of nanoplatelet particles onto themselves, iii) micro-flaws and debonding that may be present between polymer matrix and filler, on the contrary of perfect bonding assumed in model ^[1].

Other references

[1] Jing Li et. al., Percolation threshold of polymer nanocomposites containing graphite nanoplatelets and carbon nanotubes, *16th International Conference on Composite Materials*, **2007**.