Conductivity of microfibrillar polymer-polymer composites with CNT-loaded microfibrils or compatibilizer: A comparative study

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Abstract. Conductive polymer composites have wide ranging applications, but when they are produced by conventional melt blending, high conductive filler loadings are normally required, hindering their processability and reducing mechanical properties. In this study, two types of polymer-polymer composites were studied: i) microfibrillar composites (MFC) of polypropylene (PP) and 5 wt% carbon nanotube (CNT) loaded poly(butylene terephthalate) (PBT) as reinforcement, and ii) maleic anhydride-grafted polypropylene (PP-g-MA) compatibilizer, loaded with 5 wt% CNTs introduced into an MFC of PP and poly(ethylene terephthalate) (PET) in concentrations of 5 and 10 wt%. For the compatibilized composite type, PP and PET were melt-blended, cold-drawn and pelletized, followed by dry-mixing with PP-g-MA/CNT, re-extrusion at 200°C, and cold-drawing. The drawn blends produced were compression moulded to produce sheets with MFC structure. Using scanning electron microscopy, CNTs coated with PP-g-MA could be observed at the interface between PP matrix and PET microfibrils in the compatibilized blends. The volume resistivities tested by four-point test method were: $2.87 \cdot 10^8$ and $9.93 \cdot 10^7$ $\Omega \cdot$cm for the 66.5/28.5/5 and 63/27/10 (by wt%) PP/PET/(PP-g-MA/CNT) blends, corresponding to total CNT loadings (in the composites) of 0.07 vol% (0.24 wt%) and 0.14 vol% (0.46 wt%), respectively. For the non-compatibilized MFC types based on PP/(PBT/CNT) with higher and lower melt flow grades of PP, the resistivities of 70/(95/5) blends were $1.9 \cdot 10^6$ and $1.5 \cdot 10^7$ $\Omega \cdot$cm, respectively, corresponding to a total filler loading (in the composite) of 0.44 vol% (1.5 wt%) in both MFCs.

Keywords: *polymer composites, electroconductivity, compatibilizer, polymer-polymer composites, carbon nanotubes*

1. Introduction

An increasing amount of research over the last decade has been dedicated to studying and improving the properties of conducting polymer composites (CPCs). CPCs possess an interesting combination of properties including low weight, non-linear voltage-current behaviour, and environmental-sensitive resistivity, properties which could lead to applications in antistatic, electrostatic dissipative and electromagnetic shielding, as well as in sensors and related devices [1–4]. Anisotropic CPCs could even have applications in the semiconductor industry [5–7].

Conductive fillers have been dispersed in polymers using a variety of techniques, including melt mixing, *in-situ* polymerization, solution mixing, and applying the latex approach [8–10]. However, as far as commercial application is concerned, melt mixing is the most attractive technique. Early attempts for producing CPCs involved mixing conductive

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filler with a bulk polymer, and above a certain filler loading, called *percolation threshold*, the composite begins conducting. This approach, however, depending on the aspect ratio of the conducting filler, usually requires relatively high filler content to achieve conductivity, which is undesirable as far as processability, surface finish and cost are concerned [11]. Therefore, a selective localization of conductive fillers in one component or at the interface of two-component blends is a suitable method to reduce the filler amount needed for electrical percolation. This was shown especially for blends with co-continuous structure, where the conductive filler is localized in one of the components and depending on the component composition the percolation can occur at lower than the half amount of fillers as compared with the bulk filling [12]. For carbon black as filler even the case of interfacial localization was reported [13].

The creation of fibrillar polymer-polymer composites as a special case of polymer blends offers the opportunity to load only the blend matrix or the minor reinforcing component, or even only the interface layer between the matrix and the reinforcing fibrils. The described four cases of loading a polymer or a polymer blend having the structure of a fibrillar polymer-polymer composite with conductive fillers are schematically illustrated in Figure 1. Samples corresponding to case b) of Figure 1. (matrix loading) were not prepared in this study, instead, bulk-loaded samples (Figure 1a) were used as a model system because they are free from any interaction with the reinforcing fibrils.

With reduction of filler content in mind, it should be pointed out that the choice of conductive filler by itself can make a significant difference in the percolation threshold of a filled polymer or blend. Carbon black (CB) had been the conductive filler of choice [14–19] for many years, until the recent surge in application of carbon nanotubes (CNTs) [20–24], which, due to their high aspect ratio, achieve percolation at much lower contents than CB.

With lower filler content as the aim, CPCs based on polymer blends have been observed to achieve percolation at lower filler loadings than those based on a single polymer [12, 25–27]. This can be attributed to a mechanism called double-percolation [28–35] i.e., the filler is selectively localized in one of the blend components forming a conductive network. However, in most of these cases the two polymers

have weak interfacial adhesion, resulting in poor mechanical properties of the blend. This can be improved to a certain extent by applying the concept of microfibrillar composites (MFCs) [36–39]. Microfibrillar composites are prepared from immiscible polymer blends, where the reinforcement is provided by fibrils of the minor component [37, 38]. Requirements to be met in the choice of blend components [39] include: i) both polymers should be amenable to a sufficient amount of drawing to produce microfibrils with high molecular orientation, ii) melting temperature of the minor component should be at least 40 K above that of the matrix polymer, in order to prevent melting of fibrils during consolidation, iii) both polymers should be processable at a single temperature without degrading, iv) blend composition should be selected in that way that the minor component forms a dispersed phase in the matrix. Once suitable blend partners are selected, the process sequence for MFC manufacture can be described simply as follows: i) melt-blending of the polymers above melting of higher melting component, ii) cold-drawing (for fibrillation) of the blend above the glass transition temperature of the minor reinforcing component, iii) isotropization of the blend by processing above melt temperature of matrix, but below that of the reinforcing fibrils.

The MFC concept has been applied to polypropylene (PP) melt blended with nylon-6,6 (PA66) loaded with multiwalled carbon nanotubes (MWCNTs) and cold-drawn, followed by isotropization to form MFCs [40]. Observation under the scanning electron microscope (SEM) revealed good dispersion of MWCNTs in the PA66 microfibrils. The PA66 fibrils themselves were found to reinforce the matrix, while the MWCNTs seemed to have a detrimental effect on the mechanical properties. The experience gained from this study was helpful in selecting the material ratios and processing parameters used in the current study.

A significant amount of work related to MFC-based CPCs has been carried out previously [11, 17, 41–43]. Early studies dealt with MFCs of polyethylene (PE)/poly(ethylene terephthalate) (PET) with CB as a filler. Filler loadings as high as 5.9 vol% were required to achieve percolation. These authors were later successful in finding out that the CB particles are selectively located in higher concentration near the PE/PET interface (without any special target-
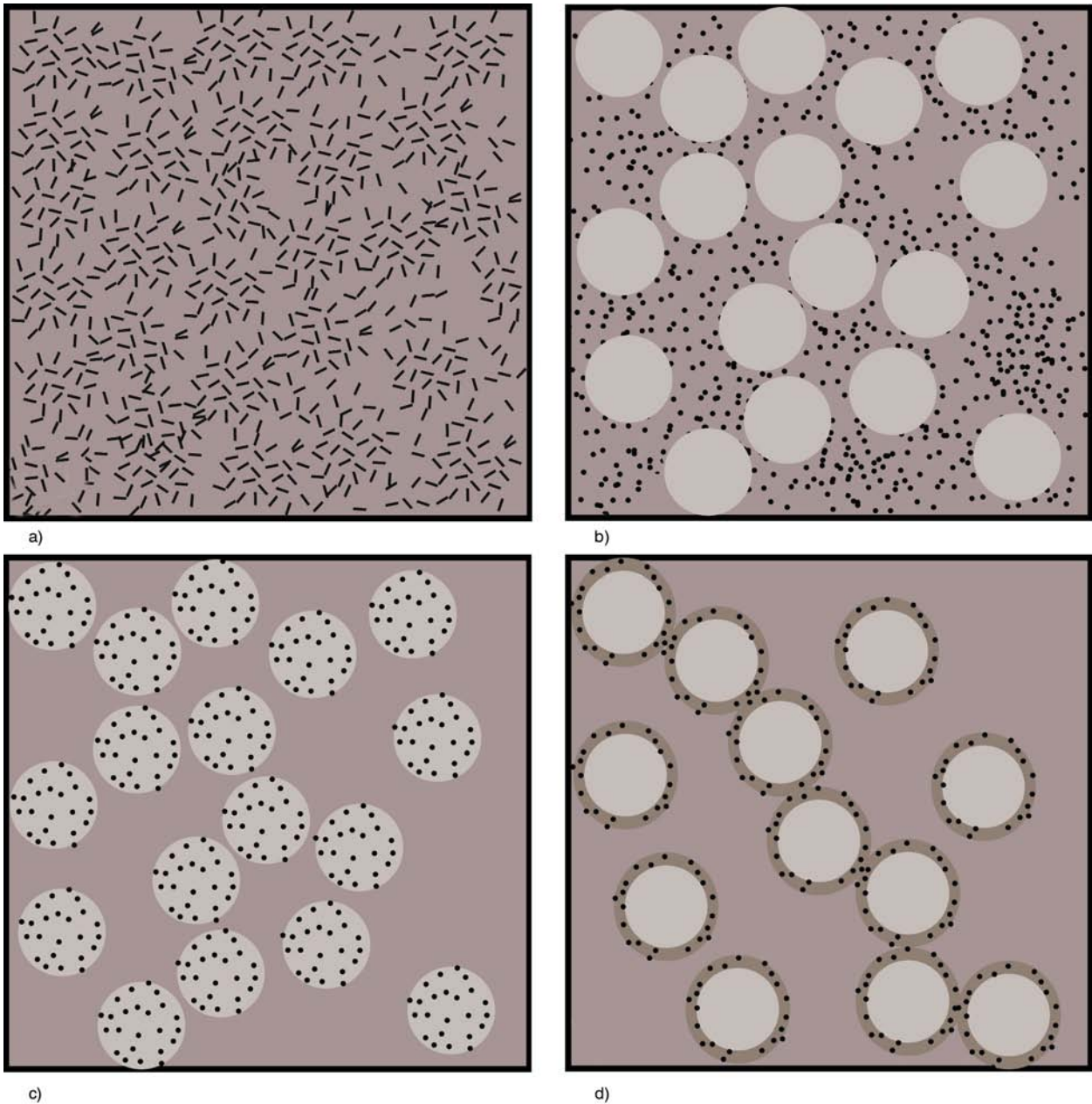
Figure 1. Schematic of different types of loading with conductive fillers: a) bulk loading, b) fibrillar polymer-polymer composite in which only the matrix is loaded (matrix loading), c) as b), but only the reinforcing fibrils are loaded (microfibrils loading), and d) as b) but only the compatibilizer is loaded (interfacial loading); the views are perpendicular to the extrusion direction

ing), which lowered the percolation threshold [19]. In this way it was demonstrated that for the blend PE/PET and conductive filler CB the threshold percolation is 11 vol% when both, the PE and PET are loaded [44], 5.2 vol% CB when only PET microfibrils are loaded [11], and only 3.5 vol% when CB particles are selectively distributed around the microfibril surface [45].

The main goal of this study is to compare the electrical conductivity for three different cases of loading with conductive filler the basic elements of a poly-

mer-polymer composite, namely the matrix only, the microfibrils only, and the compatibilizer only, i.e. to realize the three cases of bulk loading, microfibrils loading and interfacial loading (Figure 1).

It should be noted that the conducting filler in the current study are CNTs of multi walled type. Further on, in contrast to the studies of Li and coworkers [11, 44, 45], who found increased concentrations of CB on the interface, in the present study a 'special carrier' for delivering of CNTs to the same location, the interface between matrix and reinforc-

ing microfibrils, will be used – a suitable compatibilizer loaded with CNTs.

An additional task of the study is to find an appropriate technique for introducing the compatibilizer into the blend, thus avoiding the known negative effect of compatibilizers on the microfibrils formation.

2. Experimental
2.1. Materials

The materials used include PP, conductive grade poly(butylene terephthalate) (PBT) loaded with CNTs, PET and neat PP-g-MA and CNT-loaded PP-g-MA. The details of the materials are as follows.

Two grades of PP were used, both supplied by Lyondell Basell of Corio, Australia: HP555G grade (melt flow index (MFI) of 1.3 g/10 min, ultimate tensile strength (UTS) of 35 MPa) denoted further as high viscous PP (PPhv) and the lower viscous HP548S grade (MFI 35 g/10 min, UTS 33 MPa) denoted as PPlv.

PBT of grade SR525 loaded with 5 wt% CNTs (manufacturer tested volume resistivity of 6.61 Ω·cm) was supplied by Hyperion Catalysis International, Cambridge, USA. The CNTs were of type FIBRIL™ nanotubes (type MWCNT, diameter ~10 nm, density 1.66 g/cm^3).

PET of grade Shinpet 5015W (density 1.4±0.1 g/cm^3) was supplied by Shinkong Synthetic Fibres Corporation, Taiwan.

PP-g-MA was of grade Orevac 18732 (MFI 8 g/10 min, UTS 20 MPa). PP-g-MA was melt-mixed with 5 wt% CNTs to generate a conductive compatibilizer. The CNTs used were of grade Nanocyl™ NC7000 (type MWCNT, diameter ~10 nm, density 1.75 g/cm^3 [46]), supplied by Nanocyl SA, Sambreville, Belgium.

2.2. Sample preparation

The samples had to be prepared in such a way to allow the conductivity measurements of the three basic types of loading, namely, bulk loading, fibrils loading, and interfacial loading (Figure 1). Please refer to Table 1 for a list of the samples prepared, and the designations used for them in the paper.

2.2.1. Samples with bulk loading

For this type of samples, one polymer melt mixed with CNTs was used, corresponding to Figure 1a. PBT granules containing 5 wt% of MWCNTs, as supplied by the manufacturer, were compression moulded at 180°C and pressure of 7 MPa to produce samples with sizes of 10 mm × 80 mm × 0.3 mm suitable for measuring the electrical conductivity.

2.2.2. Samples with fibrils loading

For this purpose PP was used as matrix and PBT/CNT as reinforcing fibrils. The standard MFC protocol was used [47], namely both grades of PP and PBT were dried at 80 or 110°C, respectively, dry-mixed to a weight ratio of 70/30, followed by melt blending at 265°C in a Brabender DSE20 twin-screw extruder with 25 mm screw, and an *L/D* ratio of 40 and 5 rpm, using a 1.3 mm die. The extrudate was cooled in water bath immediately after its exit from the die. The extruded blend was then subjected to cold drawing at 80°C to ratios between 4.7 and 5, using two winders and a 2 m long heated chamber. Cold drawing was followed by isotropization of the matrix – the drawn blend was wound uniaxially on a plate, followed by compression moulding at 180°C to a sheet with a thickness of about 0.3 mm. Thus, MFC samples with microfibril reinforcement were manufactured. The next series of MFC samples using the second type of PP was prepared in the same way.

A small amount of each PP/(PBT/CNT) blend, after cold-drawing was subjected to removal of PP using hot xylene in a modified Soxhlet apparatus according to a procedure described in [48].

From the PP/(PBT/CNT) MFC sheet, specimens of 10 mm × 80 mm × 0.3 mm (length direction along direction of cold-drawing) were cut to test the electrical conductivity.

2.2.3. Samples with interfacial loading

As mentioned in the introduction, in order to guarantee a more precise localization of CNTs just on the interface boundary, a 'special carrier' has been used, a compatibilizer of the type PP-g-MA, which, due to its peculiar chemical composition, positions itself at interface between the matrix and the microfibrillar reinforcement only.

At the same time, as noted above, the use of compatibilizer during the MFC manufacturing is not recommendable since it has a negative effect on the microfibrils formation via preventing the coalescence of the starting spherical particles during the drawing stage [36]. For this reason it had to be checked firstly the recommendation given in ref. [36], namely, to add the compatibilizer to the blend

Table 1. Blend designations and the constitution of the composites and blends by weight

No.	Blend designation	Components	Component content in the composite/blend [wt %]
1	PBT/CNT	PBT CNT (Hyperion)	95 5
2	PP-g-MA/CNT	PP-g-MA CNT (Nanocyl)	95 5
3	PPhv/(PBT/CNT)	PP, high viscosity PBT/CNT	70 30
4	PPlv/(PBT/CNT)	PP, low viscosity PBT/CNT	70 30
5	PP/(PBT/CNT)	Refers to blends 3 and 4	
6	PPhv/PET	PP, high viscosity PET	70 30
7	PPlv/PET	PP, low viscosity PET	70 30
8	PP/PET	Refers to blends 6 and 7	
9	PPhv/PET/(PP-g-MA/CNT1)	PPhv/PET PP-g-MA/CNT	95 5
10	PPhv/PET/(PP-g-MA/CNT2)	PPhv/PET PP-g-MA/CNT	90 10

only after the drawing stage and subject the new blend to a reprocessing including re-extrusion at lower temperature and redrawing. This reprocessing requires an additional checking regarding the safe existence of the microfibrils created during the first processing. Only thereafter it is meaningful to repeat the same scenario using a compatibilizer loaded with CNTs.

For the samples with interfacial loading the best studied MFC system was used – PP as a matrix and PET as reinforcement. PP-g-MA loaded with CNTs was used as blend compatibilizer. The PP/PET/(PP-g-MA/CNT) blends were prepared in the following way:

The compatibilizer PP-g-MA loaded with 5 wt% CNTs was prepared using melt mixing in a Berstorff ZE25 co-rotating twin-screw extruder with $L = 36D$ at a throughput of 10 kg/h and a rotation speed of 500 rpm. PP granules and CNT powder were added into the hopper as premixtures and the temperatures were set to be between 200 and 180°C (from the hopper to the die). The conductivity of this composite as measured on compression moulded sheets is well in the percolated range (about 10 Ω·cm [49]).

For the preparation of blends of interest, the respective components as PP, PP-g-MA/CNT and PET were dried prior to processing at 80 and 110°C (PET). The PP/PET microfibrillar drawn blend was first prepared using the same method described in section 3.2.2., and pelletized to sections of 3 mm length.

Some of the pelletized material of the drawn PP/PET blend was subjected to a second melting in the extruder at 215°C (below the melting temperature of PET). From the extrudate, a small piece was subjected to cryofracture in liquid nitrogen, and the cross-sections was cut out. A small portion of the PP/PET after the first processing was subjected to removal of PP using hot xylene [46]. These samples were inspected by SEM to confirm the preservation of the fibrils in the re-extruded PP/PET blend.

Once this was confirmed, the remaining pelletized material of PP/PET drawn blend was dry-mixed with PP-g-MA/CNT, to 95/5 and 90/10 weight ratios and re-extruded. The re-extruded blends were redrawn at 80°C to a draw ratio of around 3.5, wound uniaxially on a plate, followed by compression moulding at 180°C and a nominal pressure of 7 MPa in a hydraulic press to obtain sheets with MFC structure.

2.3. Sample characterization

Strips from the various types sample sheets with MFC structure with dimensions of 10 mm × 50 mm × 0.3 mm (length direction along direction of cold-drawing), were cryofractured in liquid nitrogen, and the cross sections were mounted on adhesive stubs. Specimens for the SEM were coated with colloidal platinum for 10 min prior to observation and loaded into a Philips/FEI FEG-XL30S scanning electron microscope. Micrographs were taken at different locations of each specimen at different magnifications.

Electrical conductivity was characterized using a four-point test rig (ASTM D4496). As mentioned earlier, specimens of dimensions 10 mm × 80 mm × 0.3 mm (length direction along direction of cold-drawing) were prepared. Silver paste was spread on the specimens on the lines of contact with the sharp edged contacts of the rig. The rig was connected to a constant current source (Keithley 220, Keithley, Ohio, USA) or a high resistance electrometer (Keithley 6517A, Keithley, Ohio, USA).

3. Results and discussion
3.1. Effect of matrix viscosity and the presence of compatibilizer on microfibril formation: Morphological characterization

PP was removed from both the PPhv/(PBT/CNT) and PPlv/(PBT/CNT) blends for SEM characterization. The remaining microfibrils of PBT loaded with CNT were inspected by means of SEM for getting an idea about their thickness and length. The results are shown in Figure 2. The fibrils prepared from the PPhv/(PBT/CNT) blend (Figure 2a) are rather thin (diameters between 250 and 500 nm) thus approaching the nano-range, while those from the PPlv/(PBT/CNT) blend (Figure 2b) are considerably thicker and have thicknesses between 1 and 5 µm. At the same time, the second type of fibrils seem to be smoother (Figure 2b) and possibly longer than those of the first type (using PPhv), Figure 2a. This difference can be explained by the matrix viscosity of the two PPs, whereby the higher viscous matrix generates due to higher shear stresses acting on the disperse phase smaller particles available for later coalescence. In addition, the PP with higher viscos-

ity offers better conditions for the microfibril formation during cold drawing (around T_g of PBT or PET) as compared to the lower viscous matrix PP in sense of more effective coalescence. The coalescence is the crucial process for the formation of microfibrils – without coalescence the cold drawing results in formation of elliptical particles with aspect ratio of 2–4 (Figure 4b).

It should be mentioned that the microfibrils of Figure 2 are the reinforcing component of the polymer-polymer composites of MFC type, which could be prepared from the drawn blend via compression moulding at temperatures when PP only melts.

The cryofracture surfaces of the manufactured MFCs in the direction perpendicular to the drawing direction for the two types of PP are shown in the SEM micrographs in Figure 3. Comparing the two types of composites, namely applying PPhv (Figure 3a) and PPlv (Figure 3b), a substantial difference in the structure of the cross-section surface can be observed. In the first case (Figure 3a), the fibrils are much thinner, up to ten times as compared to the second type (compare Figure 3a and 3b), which is in agreement with the results of comparison of the extracted fibrils (Figure 2). Furthermore, the cryofracture in the first case occurs with dominating pull out of fibrils from the matrix (Figure 3a), contrasting to that of the second case (Figure 3b) where break of the microfibrils is more evident. And finally, in the second case due the fibril's break one can see the carbon nanotube loading in the PBT microfibrils (Figure 3b, inset). In this way, polymer-polymer composites (PPCs) of MFC type were successfully prepared, in which only the microfibrils are loaded with CNTs
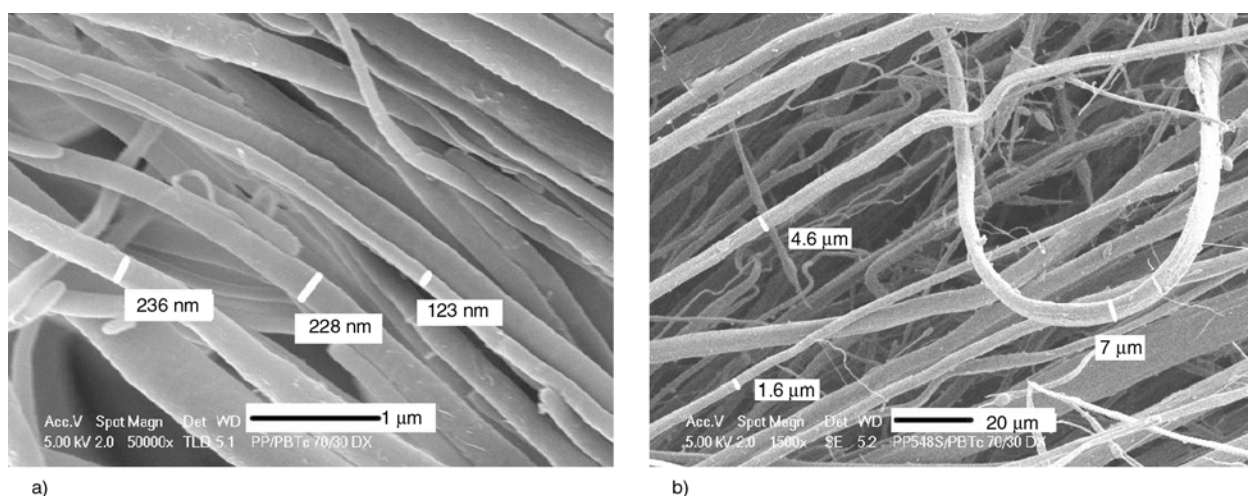

a)

b)

Figure 2. SEM micrographs of fibrils prepared from PP/(PBT/CNT) (70/(95/5) wt%) after extraction of PP: a) from blend containing high viscosity PPhv, and b) from blend containing low viscosity PPlv
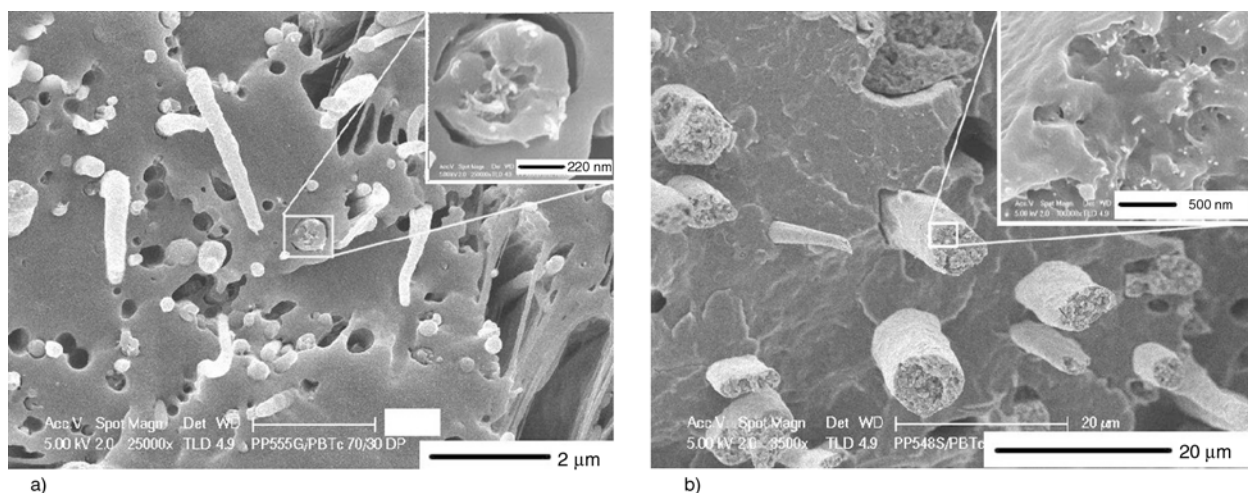
Figure 3. SEM micrographs of cryofractured cross-sections of PP/(PBT/CNT) (70/(95/5) wt%) drawn blend after compression moulding (isotropization step) using two types of PP: a) high viscosity PPhv and b) low viscosity PPlv, with insets at higher maginifications

(Figure 3b), following the previous experience with a blend of PP and CNT-loaded polyamide-6,6 [40]. The difference between the two studies is that the masterbatch of PBT/CNT used in the current study is of conductive type, and the previous one was not. In this way, in addition to samples with bulk loading (Figure 1a), we have the second candidate (Figure 1c) for the comparative study, and only the third type, with interfacial loading of fillers (Figure 1d) is missing.

Many researchers [11, 17, 19, 43] published results of similar studies, where they prepared polymer blends with MFC structure, loading with carbon black either the microfibril forming component (PET) or the matrix (PE) in amounts between 3 and 13 vol%. They found an accumulation of CB at the interfacial layer, so that a higher CB concentration

as compared to that of the microfibrils or the matrix was reached at the interface.

Contrasting these studies [11, 17, 19, 43], our main target was to deliver the conductive filler (CNTs) more precisely – only to the interface between reinforcement and matrix as mentioned above. Towards this target, a compatibilizer was chosen as the carrier of CNTs. Compatibilizers being in nature and action surfactants, have a molecule designed in such a way that one part is 'friendly' with one of the blend components, and another part with the other blend component. It can only fulfill this target by localizing at the interface The driving force for the migration to the interface is the diphilic character of the molecule – the homogeneous one-component medium is not the final localization place. During the migration process, it is quite possible that the
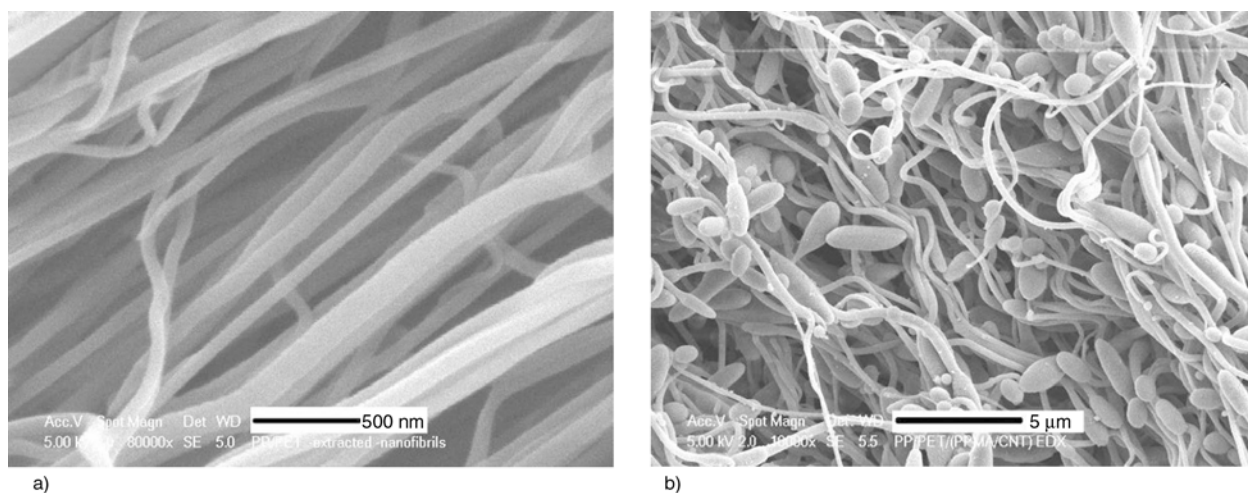

Figure 4. SEM micrographs of PET microfibrils extracted using hot xylene from drawn PPhv/PET blend: a) blend without compatibilizer, and b) blend containing PP-g-MA compatibilizer in the amount of 5 wt% referred to the total blend

compatibilizer loses part of its CNTs, particularly if the concentration gradient is very high. However, interactions between functional groups on the surface of the MWCNTs and the MA groups of the compatibilizer can fix the CNTs within the compatibilizer phase [34]. At the same time, the compatibilizer inhibits the formation of microfibrils [36] as demonstrated also by the results of the current study. In Figure 4 one can see well defined nanofibrils (Figure 4a) if the MFC material is prepared without the use of compatibilizer. In the presence of compatibilizer, mostly elliptical particles can be seen (Figure 4b) instead of smooth 'endless' nanofibrils. These samples were prepared to illustrate the effect of presence of compatibilizer on fibril formation, and do not contain CNTs.

Taking into account the mechanism of fibril formation – via stretching and coalescence of the starting spherical or elliptical particles [36], the result displayed in Figure 4b becomes quite clear. The inhibiting effect of the compatibilizer consists of coating the spherical particles with a thin film, which prevents their coalescence even if in contact. This situation is quite normal, if one remembers that the main task of the compatibilizers is to enhance and stabilize the dispersion of two thermodynamically immiscible liquids via prevention of coalescence of droplets. This inhibiting effect of the compatibilizer on fibril formation had to be overcome when dealing with MFCs manufacturing.

3.2. MFCs with interfacial CNT loading: Morphological characterization

The above defined problem regarding the inhibiting effect of the compatibilizer on nanofibril formation was solved following the recommendation given in [36], namely to add the compatibilizer to the blend after fibril formation. In such a case the processing steps will be in the following order: melt blending of the two starting polymers, extrusion, cold drawing, pelletizing, mixing with the compatibilizer, drying, remelting, re-extrusion and redrawing.

Before applying this more complex processing route using a compatibilizer loaded with CNTs, the effect of the repeated treatment on the structure of the MFCs was examined. Due to the properly selected reprocessing temperature (215°C), the previously created PET fibrils were completely preserved (Figure 5). The only change observed is that they exist as twisted bundles after the reprocessing the drawn blend. Having these results, it was possible to perform the same reprocessing using the PP-g-MA compatibilizer loaded with 5 wt% CNTs.

The cryofractured surfaces of the drawn PPhv/PET/ (PP-g-MA/CNT1) blend (Table 1) are shown in Figure 6. The main task of this microscopic inspection of the prepared samples was to find reliable proofs for the proper localization of the CNTs delivered by the compatibilizer – just at the interface between the matrix (PP) and the reinforcing microfibrils (PET). For this purpose, SEM micrographs are taken from various spots using increasing magnifications. The fibrils appear to be coated by the PP matrix in most cases, as in the case of the bundle shown in Figure 6a. The CNTs can be seen only on the surface of the fibrils (Figure 6b) as a random network, coated by the compatibilizer (Figures 6c–6f). This gives an idea that the CNT filler has indeed localized near the interface of PP matrix and PET reinforcement, as desired.
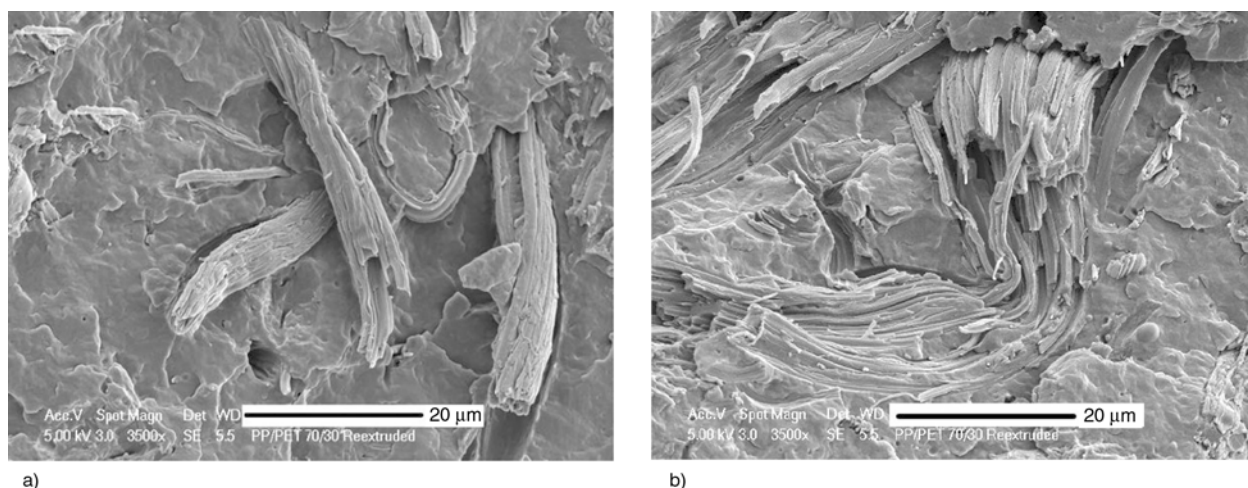

a)   b)

Figure 5. SEM micrographs of cryofractured cross-sections of remelted and re-extruded MFC based on PPhv/PET (70/30 by weight). a) twisted bundles of PET nanofibrils in PP matrix, b) nanofibrils forming the bundles
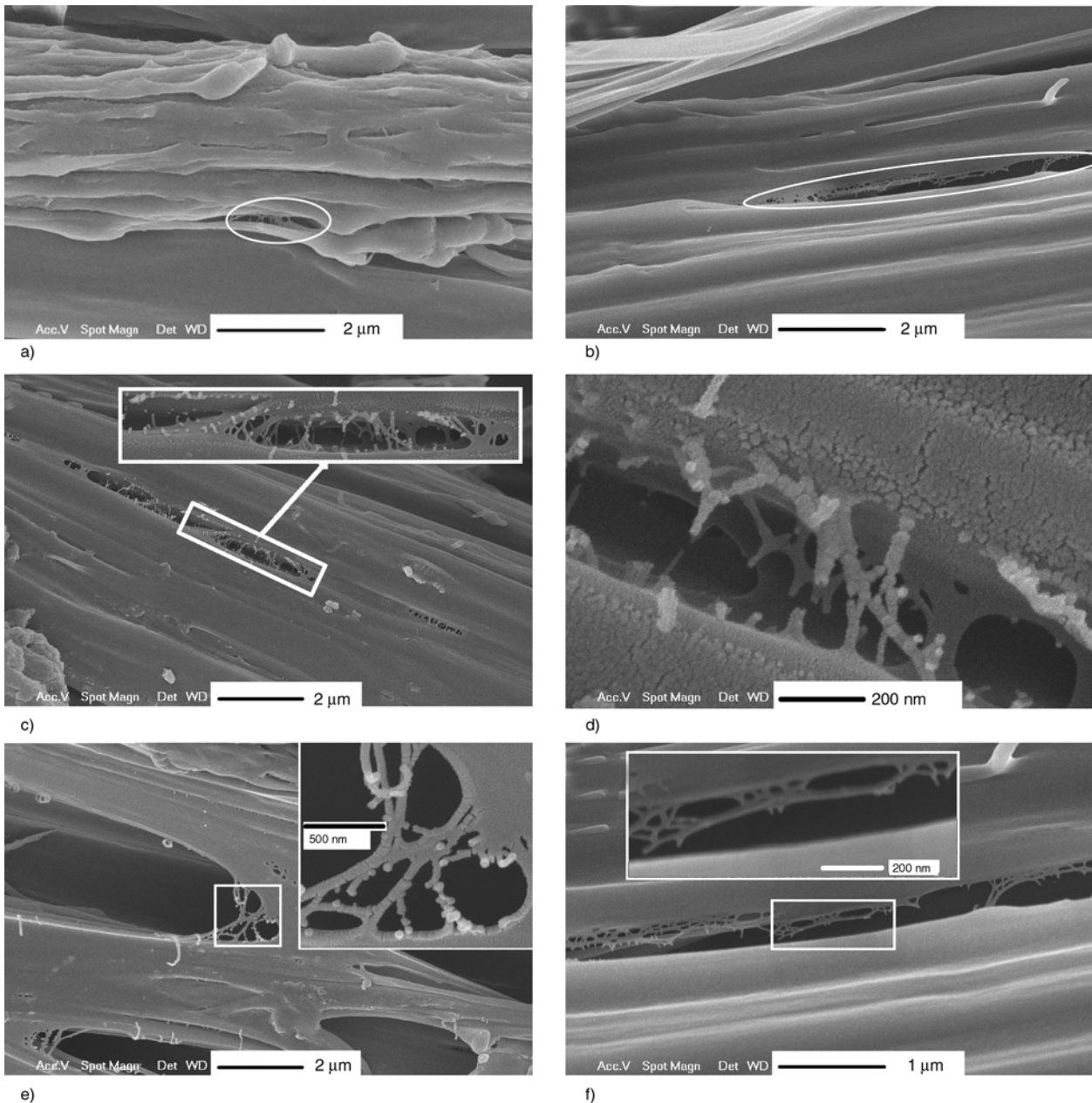
Figure 6. SEM micrographs of cryofractured longitudinal sections of drawn blend based on PPhv/PET/(PP-g-MA/CNT1). The micrographs are taken from different spots of the sample at various magnifications (see the insets)

However, the best proof for the presence of CNTs in this material will be the positive results of the electrical measurements as well as their comparison with the non-compatibilized polymer blend containing CNTs in the fibrils only.

3.3. Electrical properties of the blend PPhv/PET/(PP-g-MA/CNT)

The testing of the electrical properties of the prepared materials was performed on specimens from sheets manufactured by compression molding at such a temperature as to melt PP only, thus forming a polymer-polymer composite of MFC type.

All the materials tested contained MWCNTs but dispersed in different structural elements of the MFCs, namely: i) in the microfibrils alone (microfibril loading, Figure 1c), ii) in the compatibilizer only (interfacial loading, Figure 1d), and (iii) in the matrix polymer only (bulk loading, one polymer blended with CNTs, Figure 1a), using the as supplied PBT/CNT blend. Further on, the microfibrils loaded samples were prepared using the two grades of PP

(PPhv and PPlv). These are denoted as PPhv/(PBT/CNT) and PPlv/(PBT/CNT).

Figure 7 shows the electrical resistivities of the samples produced in this study, which all were made under comparable pressing and measurement conditions. In order to judge the results, these results are plotted together with references from literature, for which the wt% were recalculated in vol% in order to compare materials with matrices of different densities. Of course, the mixing, compression molding and measurement conditions of the composites taken from literature were partially different from those in this study and this comparison has to be taken with care. Also the resistivities of the neat polymers differ. However, this comparison enables to compare the results of this study with electrical percolation results from literature.

The respective values of the volume resistivity for the microfibrils loaded case (Figure 1c) are $1.5 \cdot 10^7$ Ω·cm (for PPhv/(PBT/CNT)) and $1.9 \cdot 10^6$ Ω·cm (for PPlv/(PBT/CNT)). Both values are in the *electrostatic dissipative* range, i.e., between 10^4–10^{12} Ω·cm [50]. The sample comprising the lower viscosity matrix (PPlv) is characterized by a volume resistivity an order of magnitude lower than the sample with the higher viscosity matrix (PPhv). This difference could be due to the difference in microfibril diameters between the two types of MFCs which were 10–

20 times lower in the case of PPhv. Having in mind the fact that the concentration of the CNTs in the two types of fibrils is the same (5 wt%), the preparation of PBT nanofibrils using the PPhv matrix generates in the thinner fibrils higher draw ratios and thus higher orientation of both the macromolecules and CNTs as compared to PPlv. Orientation of CNTs along the fiber axis was found in melt spun fibers to increase the resistivity [51] due to the reduced number of contacts between the individual CNT particles.

What the second basic case of interest, the interfacial loading (Figure 1d) concerns, it should be noted that higher values of resistivity ($2.87 \cdot 10^8$ and $9.93 \cdot 10^7$ Ω·cm) as compared with the case of microfibrillar loading (Figure 1b) are obtained for the two samples prepared with PPhv only and denoted as PPhv/PET/(PP-g-MA/CNT1) and PPhv/PET/(PP-g-MA/CNT2), where 1 and 2 represent 5 and 10 wt% compatibilizer added to PP/PET blends, respectively.

Starting from the fact that the two values of the volume resistivity obtained for the two concentrations of compatibilizer are rather close to each other, one can conclude that the amount of compatibilizer itself does not affect the electrical properties that strongly. As the compatibilizer itself is conductive (with 5 wt% CNTs well above percolation) and pro-
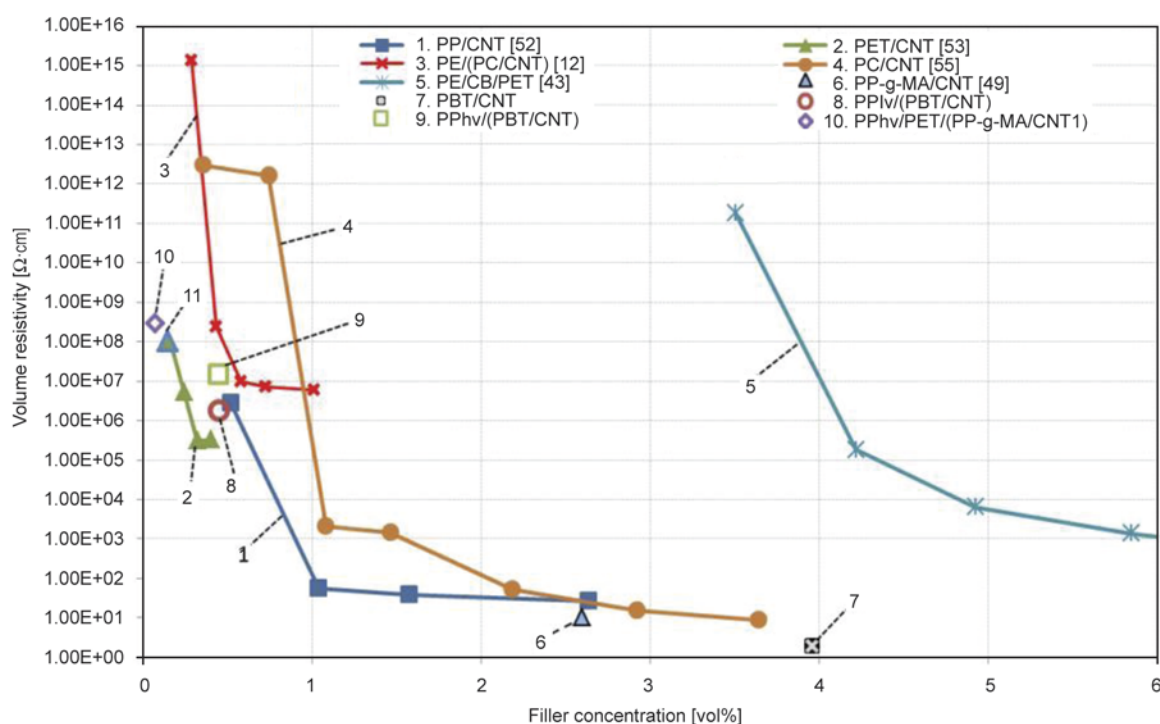

Figure 7. Dependence of volume resistivity on the filler concentration in various polymeric materials loaded with CNTs or CB

vides the conductive path through the sample, the amount of compatibilizer seems to be not so important. This finding also implies indirectly, that the compatibilizer covers the surface of the fibrils in a sufficient way to reach conductivity in the whole sample. At the same time, it is well documented that the compatibilizer, particularly in increased concentrations, has a deteriorating effect on the mechanical performance of polymer-polymer composites. This will mean that a good balance between the electrical and mechanical properties of the same material could be expected via using compatibilizers with higher CNT loading and possibly lower compatibilizer concentrations in the MFC material. An idea of how the values of volume resistivity from samples prepared in this study are related to the typical percolation thresholds of similar systems could be got from Figure 7. Samples 1–6 refer to published data [12, 43, 49, 52–55], whereas sample 6 represents the compatibilizer material used in this study, and samples 7–10 are from the present study. In the majority of cases the conductive filler is dispersed in the polymer bulk (Figure 7, samples 1, 2, 4, 6, 7), in some cases only in the reinforcing microfibrils within MFCs (Figure 7, samples 5, 8, 9) or in one phase of co-continuous blends (Figure 7, sample 3), and only in two cases (present study) in the compatibilizer within MFCs (Figure 7, samples 9 and 10).

One can see that the resistivity values of the blends with MFC structure tested in this study (Figure 7, samples 8–11) are near or lower than the values of the percolation threshold for PE/(PC/CNT) (Figure 7, sample 3), 1–3 orders of magnitude away from the threshold for PET/CNT (Figure 7, sample 2), 3–5 order of magnitude away from the threshold for PP/CNT (Figure 7, sample 1). The curves in Figure 7 demonstrate the extremely strong dependence of the volume resistivity on the concentration of the filler – a change of CNT concentration by 1 vol% can result in a decrease of the resistivity by up to 10 orders of magnitude. This bodes well for MFC blends which will be prepared in a future study, with higher CNT loadings.

Another peculiarity of the polymer conductive materials is their sensitivity to many other factors affecting their electrical conductivity, including also such a 'secondary' factor as pressing conditions.

For this reason a more detailed comparison of the obtained data with the reported ones is hardly justified. Nevertheless, the results obtained in the current study look quite promising because they demonstrate the possibility of obtaining reasonable values for the electrical conductivity when loading conductive filler only in the minor component of the fibrils containing blend or in the interfacial area of such microfibrillar blends. Such an approach also allows avoiding or decreasing drastically the deterioration effect of CNTs on the mechanical properties of the polymer blends. In addition, when working with polymer blends having MFC structure, one is getting considerable improvement of mechanical properties, particularly when the matrix is a polyolefin [37, 39]. In this way, applying the MFC concept to polymer blends, we observe a dual benefit, namely improvement of mechanical performance via fibrils reinforcement and avoiding the detrimental effect of CNTs using microfibrils or compatibilizer loading only for improving the functional properties of the polymer blend.

The further steps of this study will be in the direction of finding the real percolation threshold for these new types of loading via variation of the concentration of CNTs as well as using second conductive filler for improvement of contacts between individual highly oriented carbon nanotubes.

4. Conclusions

The main goal of this study was to investigate the possibility for preparation of conductive two-component polymer blends loaded with conductive filler (CNTs in the present case) only at the interface between the two immiscible polymers. As a reference, blends with MFC structure were used and as carrier for CNTs a compatibilizer was applied. The conductivity of such blends was compared with microfibril loaded MFCs and bulk loaded homopolymers. The dispersion of CNTs in the minor component or in the interface only allows us to avoid significantly the detrimental effect of CNTs on the mechanical properties of polymers and their blends. Exploring the strong dependence of conductivity on filler concentration, experiments with compatibilizer containing higher CNT loadings are in progress with the target to determine the real threshold concentration for this type of loading.

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