Polyethylene/ poly(3-hydroxybutyrate-co-3-hydroxyvalerate /Carbon Nanotube Composites for eco-friendly electronic applications

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ABSTRACT

The development of new conducting composites, for electric and electronic applications, with lower environmental impact is an increasingly relevant issue. Blending poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), a bio-based and biodegradable polymer, with conventional high-density polyethylene (HDPE), one of the most common polymers in the polymer industry and a conductive filler, such as multiwalled carbon nanotubes (CNTs), represents a suitable strategy for improving sustainability of conducting polymer composites, while maintaining procesability and functional performance. In this work conducting polymer composites based on 50/50 HDPE/PHBV matrix, an immiscible blend that can favours a segregated structure, with CNT as a conductive filler (3, 5 and 7,5%) was performed. In addition, a grafted PE was included with the aim of improving the dispersion of nanotubes within the composites. The study focuses on thermal, mechanical, morphological rheological and electrical properties. The effectiveness of the new composites for EMI shielding applications was also evaluated. Composites show a continuous structure in which CNTs remain in HDPE matrix. From rheological tests, a percolated structure for all composites is observed that is related to the fact that all composites show a certain level of conductivity. Without compatibilizer, only the composite with 7,5% of CNTs achieves a conductivity value suitable for reaching 20 dB of electromagnetic shielding. In composites with PE grafted with maleic anhydride (0.5%) the electrical conductivity

substantially increased, achieving a suitable EMI shielding level with small proportion of nanotubes (5 wt%) probably related with an improvement in the interfacial adhesion between polymer phases and CNT dispersion. Summarizing, composites with reduced environmental impact have been obtained suitable for EMI applications with a reasonable amount of CNTs.

Keywords:
PHBV, polymer composites, carbon nanotubes, electrical conductivity, rheology, EMI

1. Introduction

The dispersion of conductive fillers such as carbon nanofibers (Mondal 2016, Anju 2019), carbon nanotubes (Verma 2015, Lee 2019, Al-Saleh 2013, Vovchenko 2018, Wu 2018), graphene (Kim 2014, Joseph 2020), carbon black (Das 2000, Khastgir 2011) and others, in a polymer matrix can result in electrical conductive polymer composites (CPCs) that are frequently used to manufacture products with electrical properties for designing sensors, electronic devices and for EMI shielding applications. In the latter, CPCs are needed that combine ease of processability and moulding, low cost, light weight and resistance to environmental conditions. in addition to high level of shielding. Amongst different possible fillers, single-walled or multiwalled carbon nanotubes (CNTs) show exceptional electrical properties and high aspect ratio and they are frequently used in electrical and EMI shielding applications (Kato 2017, Liu 2007, Mondal 2018, Zeng 2016, Chikyu 2020, Jia 2015, Al-Saleh 2016).

CPCs can be obtained by means of filler dispersion in a polymer matrix or in a blend. The use of immiscible polymer blends as a matrix can lead to the formation of a segregated structure that has demonstrated to be effective for achieving high electrical properties (conductivity, EMI shielding) using a lower amount of filler than in the case of a single polymer matrix (Pardo 2013).

On the other hand, environmental problem caused by plastic waste is leading the development of materials with a lower environmental impact that can replace current plastics. For this reason, the application of biopolymers is increasing in all fields of sciences and technology (Larissa 2019, Matthew 2019, DOI: 10.32604/jrm.2019.00036). As an example, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), a bio-based, biodegradable and biocompatible polymer

produced naturally by bacteria, is being used as alternative for many non-biodegradable synthetic polymers. Blending PHBV with conventional polymers represents a good strategy for developing more sustainable composites and extend the properties range of pristine polymers (Chan 2019, Larissa 2019, Matthew 2019). PE/PHBV blends with different compositions have been reported with good mechanical, chemical and thermal properties or even with improved barrier properties for packaging applications (Rani-Borges 2016, Norrrahim, 2013, Passos 2015). Although the combination of renewable resources polymers with synthetic polymers may have influence on the biodegradation of polymeric materials (Costa, 2014), the obtained blend continues being biodegradable. Besides, the addition of conductive filler in PHBV not compromises the biodegradability of PHBV matrix, although the biodegradation rate decreases (da Silva 2019, Qazi 2020, Shan 2011).

Considering the above, PHBV could be used in the design of new green composites. Heterogeneous polymer blends formed with PHBV and a conventional polymer (as polyethylene), with a segregated structure (which allows an appropriate distribution of filler inside), could improve electrical properties with low filler amounts while improving the sustainability of the composites. On the whole, the addition of CNT in HDPE/PHBV blends with a segregated morphology, constituted a promising approach towards more sustainable conductive polymer composites. Although the literature presents some few works related with polymers blends loaded with CNT, to the best of our knowledge, this work is the first study on feasibility of HDPE/PHBV blends filled with CNTs to obtain conductive polymer composites for EMI shielding applications.

In spite of the intrinsic conductivity of CNTs and their high aspect ratio, low percolation threshold in polymer blends prepared by melting process is not easily achieved due to the tendency of CNT to agglomerate because attractive van der Waals forces. To overcome this drawback, it is important to select the appropriate processing conditions, but also to perform a surface treatment of the CNTs which optimizes their dispersion into the polymer matrix and/or to use an appropriate compatibilizer, to improve the interfacial adhesion between polymer and fillers. As the compatibility increases, other properties like mechanical strength and electrical conductivity are also improved. The employment of maleic anhydride grafting polymers is a common strategy to compatibilize polymeric blends, but the use of ionic liquids is a more novel alternative, which has proven to be successful in PP/PLA blends filled with CNT. In these

composites, the use of an ionic liquid allowed to improve considerably electrical conductivity and electromagnetic interference shielding effectiveness (Soares, 2019).

The main goal in this work is the development of new conducting polymer composites based on 50/50 HDPE/PHBV matrix using CNT as conductive filler. To achieve improved electrical performance, the composites were designed with a segregated morphology, which maximises the properties with lower filler amounts. In order to improve the dispersion of the CNTs, an ethylene and anhydride maleic copolymer was used as compatibilizer. The study was focused on thermal, mechanical and electrical properties of composites, as well as on the effectiveness of the new composites in EMI shielding applications.

In this manuscript PE/PHBV/MWCNT composites were processed by extrusion. A ratio of 50/50 PE/PHBV was used to acheive green composites and different CNT amount were incorporated. A grafted PE was also used to increase the compatibility of the composites. In short, this work reports on the influence of the variables described above on the e thermal, mechanical, rheological and morphological behaviour of PE/PHBV/CNT green composites.

2. Experimental

2.1 *Materials*

A poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV NaturePlast PHI 002 supplied by Natureplast) (density: 1.23 g/cm^3 and Melt flow rate:5-10 g /min (190 ºC, 2.16 kg)) and a high density polyethylene (HDPE 25055E supplied by Down Chemical Iberica, S.L.) (density: 0.955 g/cm^3 and Melt flow index:25 g /min (190 ºC, 2.16 kg)) were used as polymeric matrix. The nanotubes were incorporated into the polymeric matrix from a masterbatch based on high density polyethylene loaded with 15 wt.% of MWCNT (Plasticyl HDPE1501 supplied by Nanocyl S.A**,** Sambrevile, Belgium). MWCNTs (characterized according to the supplier) present an average diameter of 9.5 nm, a length of 1.5 μm, a carbon purity of 90% and a surface area of 250-300 m^2.g^{-1}. A random ethylene copolymer incorporating a monomer which is classified as being a maleic anhydride (MAPE) (FUSABOND M603 by Down Chemical) was used as a compatibilizer. It shows a density of 0.94 g/cm^3 and a Melt Flow Rate of 25 g/10 min (190ºC, 2.16 kg).

2.2 *Preparation of the composites*

Table 1 shows the composite formulations with 50/50 HDPE/PHBV ratio and different contents of MWCNT. The CNT masterbatch was diluted with the same HDPE. The 50/50 proportion of HDPE/PHBV was selected in order to obtain a more sustainable and affordable material for the industry. On the other hand, in this proportion, HDPE/PHBV blend is immiscible, which will help to obtain a segregated morphology in the composite.

Before extrusion, PHBV was dried in an oven at 80 ºC for 4 h. Then, the different composites were extruded using a miniextruder equipped with twin conical co-rotating screws and a capacity of 7 cm^3 (Minilab HaakeRheomex CTW5, Thermo Scientific). The extrusion was carried out in two steps: in the first step, the masterbach was diluted with HDPE, in order to obtain the desired amount of CNTs, using a rotation rate of 40 rpm, a temperature of 190ºC and a residence time of 3 min; during a second extrusion step (at 190ºC and 40 rpm for 3 min), PHBV was incorporated into the HDPE/CNT blend. The maleic anhydride grafted polyethylene used as compatibilizer was added in the second step of extrusion. Composite formulations and their nomenclature are displayed in Table 1.

The samples for the different tests were injection molded in circular specimens (diameter of 25 mm and thicknesses of 1.5 mm) and prismatic specimens (2x4x10 mm) using a Haake MiniJet Pro injection molding machine (Thermos Scientific) at 190ºC, applying 800 bar for 10 s.

2.3 *Sample characterization*

The morphology of the composites was evaluated by Scanning Electron Microscopy (SEM). Specimens were broken under cryogenic conditions and then examined using a JEOL JSM-7200F Field Emission Scanning Electron Microscope at an accelerating voltage of 10 kV. Prior to observation, the samples were sputter-coated with a thin palladium/platinum layer (Cressintong 208HR).

The rheological measurements were performed using a controlled strain rheometer (ARES, TA Instruments) with parallel-plate geometry (25 mm diameter, 1 mm gap) at 190ºC. The complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') were measured as a function of frequency (ω). The rheological tests were performed in the linear viscoelastic region (LVE). This linear viscoelastic region was determined previously from a strain sweep test. The frequency sweep measurements were set up in the frequency range $1x10^{-1}$ to 10^2 $rad.s^{-1}$.

Thermal measurements were carried out with a differential scanning calorimeter (DSC 2020, TA Instruments)) under nitrogen atmosphere. The samples (6-10 mg) were heated from 0ºC to 230ºC at a rate of 10 °C.min^{-1} and mantained 5 min. at 230ºC to erase their thermal history. Finally, they were cooled to 0 ºC at a rate of 10 °C.min^{-1}.

Thermogravimetric Analyses (TGA) were performed using a TGA 4000- Perkin-Elmer, set-up under nitrogen atmosphere supplied at a constant flow rate of 50 ml.min^{-1}. The composites were subjected to a heating rate of 10.0 ± 0.1 ºC.min^{-1} in the temperature range between 50 up to 700 ºC.

Uniaxial tensile test were performed in an Instron dynamometer 5566 at 2 mm/min in accordance with ASTM D-638-02 standard recommendations. Stress-strain curves were obtained from these tests. Young´s modulus, tensile strength and elongation at yield and at break were determined from these curves. A minimum of six specimens were tested for each system. The average values of the mechanical parameters and their deviations were calculated.

Shore D hardness values were also determined by using a Durotech MD-202 durometer in accordance with UNE-EN-ISO 7619-1:2011 standard. The measurements were carried out 15 s after the durometer tip had touched the sample. All mechanical tests were performed at room temperature and at least six measurements were performed for each sample.

The electrical conductivity (σ) at room temperature was calculated from the electrical resistance data by the four-probe method (LORESTA-GP, Mitsubishi Chemical, MCP-T610). The electrical conductivities reported for each formulation are the mean values of at least 12 readings determined on three different samples.

Dielectric measurements were carried out at room temperature with a Quadtech 1920 Precision LCR Meter in the 20 Hz-1 MHz frequency range with an applied voltage of 1 V. Five millimeter diameter gold electrodes were sputtered with a ~25 nm thin gold layer, using a Polaron SC502 sputter coater under nitrogen atmosphere. The capacity (C) and dielectric losses (tan δ) were obtained as a function of frequency (ν). The real and imaginary part of the dielectric constant (ε'and ε'') and real part of the conductivity function (σ') were obtained according to:

$$\varepsilon' = \frac{C.d}{\varepsilon_0.A'}$$

$$tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

$\sigma' = \varepsilon_0 \omega \varepsilon''$

where A indicates the plate area, d is the plate distance (samples thickness), ε_0 (8.85×10^{-12} $F.m^{-1}$) is the permittivity of free space, ε' and ε'' are the real and imaginary dielectric constants, respectively, and $\omega = 2\pi f$ is the angular frequency. With the dielectric measurements data of the different composites, the classic electromagnetic theory was used to predict the shielding effectiveness (SE) data.

According to Colaneri and Shacklette for the far-field shielding, the classic the EMI shielding is given by:

$$SE = 10log\left(\frac{\sigma'}{32\pi f \varepsilon_0}\right) + 20\frac{d}{\delta}\log(e)$$

where σ' (S/cm) is the bulk conductivity of the conductor, f (Hz) is the frequency, ε_0 $\varepsilon 0$ (8.85×10^{-14} $F.cm^{-1}$), d (cm) is sample thickness, e = 2.718281828, $\mu_0 = 4.\pi.10^{-9}$ (H/cm) and $\delta = \sqrt{1/\mu_0 \pi f \sigma}$ cm, which is called "skin depth" of conductor. The skin depth is a measure of the depth to which the radiation will penetrate within the material (with a decrease in intensity of 1/e of its original strength).

The first term of Eq. 1 is the contribution to the shielding due to the single reflections to the incident wave by the front and back surfaces of the sample. The second term represents the attenuation by absorption as the wave passes though the sheet. The contribution of the multiple reflections is ignored in this model.

This model was successfully applied previously to measure the EMI shielding effectiveness of blends of PVC/polyaniline (Colaneri 1992) and carbon nanofiber/liquid crystalline polymer composites (Yang 2005) or even carbon nanotube/polycarbonate composites (Pardo 2013).

3. Results and discussion

3.1 *Morphology characterization*

The micrographs obtained by scanning electronic microscopy (SEM) for polymeric blend and composites with different amounts of MWCNTs are shown in Figure 1a. SEM analysis were conducted to explore the location and distribution of the CNT within the HDPE/PHBV blend. From Figure 1a two major observations can be drawn. The first one is the heterogeneous morphology in the case of the 50/50 HDPE/PHBV that seems a sea-island structure. Probably the material is near to the phase inversion that is in fact achieved when CNTs are added to the blend (M1, M2 and M3). The

second observation is the selective location of CNTs in PE phase. The morphology of the phases depends on the blend composition, viscosity ratio between the components, and processing parameters (extrusion parameters in this work). A co-continuous structure would be expected in a 50/50 HDPE/PHBV blend (Norrahim 2013) that in this case is obtained adding the filler. The location of MWCNTs in PE phase is related with a viscosity ratio lower than 0.5 (η_{PHBV}/η_{PE} = 0.46, measured at 190ºC and 100 s^{-1}). PHBV with a lower melting temperature, melts, while the HDPE/CNT masterbatch remains semi-solid. As the mixture moves forward in the extruder PE melts, the co-continuous phase is formed but the larger part of the CNT do have no time to move to the other phase. Finally, it can be observed an acceptable dispersion level of nanotubes in the polyethylene matrix, as CNT content increases. This can be corroborated in Figure 1b where composite M3 is shown with higher magnification.

The lack of adhesion between the PE and PHBV phases, due to the immiscibility of the mixture at these ratios, becomes more pronounced when larger amounts of nanotubes are incorporated. .It is important to note that as the percentage of nanotubes increases (from M3 with a 3% of CNTs to M1 with a 7.5% of CNTs), the surface becomes rougher and the lack of compatibility between PE and PHBV phases is more evident. This fact is probably related to a greater stiffness of the matrix as the amount of filler increases and therefore to a more brittle breakage of the samples.

Figure 2 shows the effect of adding maleic anhydride grafted PE in composites´ morphology. The most significant consequences are that the fracture surface appears much smoother and the fracture was progressively more cohesive. The two phases appear more strongly connected and this indicates an increase in the interfacial adhesion as a result of the compatibilization effect of the maleic anhydride.

3.2 Rheological characterization

Melt rheological characterization provides information about the structure of blends and composites. Figure 3a shows complex viscosity versus frequency. Raw polymers (HDPE and PHBV) shown a Newtonian behaviour almost in all the frequency range. Binary blend show shear-thinning behaviour, the reason for this is related to the immiscibility of both phases that prevents stress transfer between them and results in interfacial slippage. Composites show shear thinning behaviour too, as previously observed in other filled blends (Pöstchke 2002, Ares 2010, Hashmi 2007, Bera 2012, Paleo 2014, Ares 2014, Arboleda-Clemente 2016). An increase in viscosity is observed

with an increase in filler concentration, this increment being larger in the region of low frequencies. At high frequencies, the polymer chains do have not enough time to recover the original filler particle distribution. In addition, the probability of direct interaction between the filler particles rises as the concentration of filler increases making shear-thinning more noticeable.

Figure 3b shows the frequency dependence of elastic modulus for pure polymers, unfilled HDPE/PHBV blends and composites. The effect of adding CNTs on the storage modulus is an increase in its value due to the interconnected network structure within the matrix, as can be observed in filled blends (Pöstchke 2002, Ares 2010, Hashmi 2007, Bera 2012, Paleo 2014, Ares 2014, Arboleda-Clemente 2016).

At low frequencies, the fully relaxed PE and PHBV chains exhibit the typical Newtonian viscosity plateau with the scaling properties of approximately $G' \alpha \omega^2$, whereas the incorporation of carbon nanotubes in the polymer gradually transforms the liquid-like terminal behaviour to solid-like non terminal behaviour characterized by having G' independent of ω. This non-terminal low frequency behaviour has been attributed to the fact that, though the polymer chain interaction still exists, the introduced nanotube-nanotube and CNT-polymer interactions come to dominate, eventually leading to percolation and the formation of an interconnected structure of CNTs in the matrix.

The crossover point (ω_c, G_c), the point at which curves of G' and G'' against frequency intersect, is also recorded in Table 1. This point is characteristic of the transition from viscous to elastic behaviour (Arboleda 2016, García –Fonte 2018). For pure polymers and binary blend G'' is higher than G' in all frequency range, indicating a liquid-like behaviour. For composites with low percentages of filler (3 and 5%) the behaviour do not change indicating a lack of percolation, while composite with a 7.5 % of CNTs is percolated, showing a crossover point at intermediate frequencies.

The compatibility of immiscible blends was investigated from the variation of rheological properties by adding a compatibilizer and compared with the properties previously obtained. Figure 3a shows that, with the addition of maleic anhydride, higher values of viscosity than the immiscible blends are observed, which reflects the fact that extent of the compatibilization is increasing. This is due to the improvements of interfacial adhesion between PE and PHBV, as can be seen in the morphology (Figure

2) and the probably better CNTs dispersion due to the compatibilization. In the same way higher G' values are observed in Figure 3b.

3.3 *Thermal properties*

Table 2 show thermal properties obtained from DSC thermograms of the samples with similar thermal history (Figure 4). It is shown that the pristine polymers melt in different temperature ranges, showing well-defined melting peaks centred at 130ºC (HDPE) and 175ºC (PHBV), respectively. Regarding to crystallization temperatures (T_c), they have a value around 100ºC for HDPE and 115ºC for PHBV. 50/50 HDPE/PHBV blend shows two separate melting peaks but centred at slightly lower temperatures than the pristine thermoplastics. Besides, there is a shoulder, around 170ºC, ascribed to the heterogeneous crystallisation of PHBV in the presence of HDPE. This fact is related with a lack of thermodynamic miscibility between HDPE and PHBV, as can be observed previously in rheological and morphological results and it is a typical behaviour in immiscible blends. When the CNTs are added, the effect obtained is different in HDPE than in PHBV. The nanotubes acts as a nucleating agent in HDPE matrix, increasing the melting temperature and enthalpy during melting (ΔH_m) as function as CNT amount. No effect is observed in the melting temperature of PHBV, but its melting enthalpy was significantly reduced as CNT increases in the composite. This may be related to the fact that both polymers crystallize in the same temperature range, but the CNTs only act as nucleating agent in the HDPE matrix, hindering, probably, some of PHBV crystallization.

In fact, it is important to note that CNTs are mainly dispersed in polyethylene matrix, as can be seen in morphological results.

When polyethylene grafted maleic anhydride is incorporated, the compatibility between the two polymers increases, leading to changes in the thermal properties.

The thermograms show an increase in the melting temperature of HDPE. The melting temperature of the PHBV decreases slightly, but the most remarkable issue is that the shoulder disappears at 170ºC, proving that the crystallisation of the PHBV is becoming more homogeneous. On the other hand, the thermograms show a third peak between the two (around 150ºC), which matches the MAPE melting (see Figure 4a).

Thermogravimetric analysis (TGA) was used to evaluate the thermal degradation of PE, PHBV and composites. From the Figure 5 and Table 2 it is possible to state that PE degrades at 480ºC while PHBV have a degradation temperature around 280ºC. The

TGA thermograms of HDPE/PHBV blend and CNT composites show two steps, a first one corresponding to the degradation temperature of PHBV (around 280ºC) and a second one, at a higher temperature, to HDPE. The incorporation of CNTs increases the thermal stability of the polyethylene, while the degradation temperature of PHBV decreases slightly with respect to the Tdeg in the HDPE/PHBV blend. This may be related to the fact that the nanotubes are more thermally stable and confined in the polyethylene matrix. In the nanocomposites thermograms, the residual mass, measured at 700ºC, agrees with the amount of CNTs incorporated in the matrix, which shows that the samples are homogeneous and that the actual amount of filler matches the nominal one.

3.4 *Mechanical properties*

The modulus, strain and tensile strength at yield p and the same parameters and strain at break are presented in Table 3. While the HDPE shows a ductile behaviour, PHBV, HDPE/PHBV blend and composites are brittle materials, with a break point closer to the elastic limit. The stiffness of the blend shows an intermediate behaviour between the two immiscible polymers (as would be expected due to the lack of compatibility). Nevertheless, this drawback in mechanical properties must be assumed for obtaining a segregated structure. When CNT are incorporated to the blend an enhancement in the modulus regarding to the blend is observed due to the higher rigidity of the filler. This is in agreement with the G' values obtained from the rheological properties. However, not important changes are observed in strain or tensile strength at break point indicating that are not produced changes in the ductility of the samples with CNT addition.

The principal aim of anhydride maleic incorporation into HDPE/PHBV/CNTs composite formulations was to achieve increased toughness and improved morphological (more uniform morphology) and rheological properties of the materials. The target was partially obtained because of the toughness improvement was scarce, respect the nanocomposites without MAPE, although was obtained in the case of morphological and rheological properties.

Hardness of pure polymers, blends and composites is presented in Table 3. Hardness of polymer blend is in the middle of PE and PHBV hardness, being higher in the case of PHBV as it is expected in a more fragile material. A hardness increase with nanotube amount it is observed that it is related with an expected increase of material rigidity with filler. With grafted PE an increase in hardness is observed that can be related with a

higher interaction between PE and PHBV that lead an enhancement in the rigidity of the matrix.

In summary, it is worth noting that the nanocomposites which were partially compatible with MAPE, display a clearly higher toughness than the HDPE/PHBV blend, as well as electrical properties, as was the original goal.

3.5 *Electrical onductivity*

Figure 6 represents the electrical conductivity values of different composites. The addition of CNT n increases the electrical conductivity of HDPE/PHBV blend (clearly electrical insulator) as a function of CNT amount up to a value of $5.29x10^{-2}$ S/cm measured in M1 with 7.5 wt.% CNT. The degree of compatibilization achieved after the incorporation of polyethylene grafted with maleic anhydride in composites M1 and M2, allowed a significant increase in conductivity (near one order of magnitude in M1* and two orders of magnitude in M2* as presented in Table 2).

To obtain a conductive plastic that can be used to manufacture an electromagnetic shielding (EMI) chassis, the volume resistivity of the material must be 10^4 Ω.cm or lower (same order of magnitude for surface resistivity). Since the electrical volume resistivity is inversely proportional to the electrical conductivity, the minimum conductivity value that guarantees that a certain EMI corresponds to a value of 10^{-4} S/cm. From the values displayed in Figure 6, it can be concluded that M2 and M1 (with and without MAPE) composites are within the EMI shielding range, so the new formulations would be suitable for applications is this field.

Anyway, it must be taken into account that it is established that in order to achieve 99.9% attenuation of EMI radiation, which is considered an adequate level of protection for many applications, a shielding or shielding efficiency greater than 20 dB is needed. According to the bibliography, this target requires, theoretically, an electrical conductivity of 10^{-2} $S.cm^{-1}$ (Li Chuan 2015, Lee 2017, Al-Saleh 2016, Spares 2019, Vovchenko 2018, Wu 2018). Taking into account values in Table 2 it can be observed that for composites M1, M1* and M2* a value of 99.9% attenuation is obtained.

With a 0.5% content of maleic anhydride, the electrical conductivity experiments an increase of two orders of magnitude in M2* composite with respect to M2 composite, and an increase of one order of magnitude in M1* with respect to M1. Therefore, the fact of introducing polyethylene grafted with maleic anhydride represents an appropriate strategy to enhance the electrical conductivity values. With the incorporation of maleic

anhydride appropriate shielding values are obtained with a minor amount of CNTs. In fact, the conductivity value of M2 composite (5% CNT) is similar to the M1 value (7.5 % CNT) without MAPE.

To confirm this results and to ensure that this values are suitable EMI applications, theoretical shielding values were calculated as explained in experimental part. Figure 7 shows the EMI shielding data for nanocomposites in the frequency range between 8 and 12 GHz. All composites display a shielding level constant over the studied frequency range. Again, the material with a better shielding behaviour is the M1*, with values around 80 dB but all of them are over the 20dB value needed to obtain a 99.9% attenuation of EMI radiation adequate for use in electronic housings. The maleic anhydride addition improve shielding values related with the enhancemente in conductivity getting appropiate shielding values with a minor amount of filler (M2*).

Conclusions

Polymer nanocomposites with electromagnetic shielding properties have been designed based on two polymeric immiscible matrices, HDPE and PHBV, in a 50/50 ratio by adding different amounts of CNTs (3, 5 and 7.5%) and their physical properties characterized. The following conclusion can be highlighted:

- The composites show a typical morphology in an immiscible polymeric blend, where the CNTs are placed in HDPE matrix.
- From the rheological analysis, an increase in the viscosity of the compounds and a plateau in moduli that indicates the formation of a percolated structure can be observed.

- The analysis of mechanical properties and hardness display that the nanocomposites have a brittle fracture with low deformation at the break point. However, CNT composites partially compatibilized with MAPE, show higher toughness than the immiscible HDPE/PHBV blend.
- The thermal properties indicate the incompatibility of the matrices due to the appearance of a double peak in the DSC thermogram. The nucleant effect of CNT in HDPE matrix was observed together with an increase in the thermal stability of PE.
- All nanocomposites show a certain level of conductivity but only M1 composite (with 7.5% of CNTs and without compatibilizer), shows a conductivity value suitable for reaching 20 dB of electromagnetic shielding which is an adequate value for many applications.

When 0.5% of PE grafted with maleic anhydride was added to the compounds M1 and M2, their conductivity substantially increased, achieving a suitable EMI shielding level with a small proportion of nanotubes (5 and 7.5 wt%). In addition, the incorporation of MAPE, as compatibilizer improved the interfacial adhesion between the phases and the CNT dispersion and, as a result, the hardness of composites increased.

Therefore, the compounds M1* and M2*, 5% and 7.5% of nanotubes would be suitable for the required applications.

Summarizing, advanced sustainable composite materials have been developed suitable for EMI shielding applications, which constitutes a breakthrough for industrial applications where environmentally friendly polymers are increasingly required with identical performance as conventional polymers.

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