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# Dielectric behavior of biopolymer based composites containing multi wall carbon nanotubes: Effect of filler content and aspect ratio

Pellegrino Musto [a], Pietro Russo [a,*], Francesca Cimino [b], Domenico Acierno [c], Giovanni Lupò [d], Carlo Petrarca [d]

[a] Institute for Polymers, Composites and Biomaterials, National Council of Research of Italy, Via Campi Flegrei, 34 – 80072 Pozzuoli (NA), Italy
[b] Departments of Chemical, Materials Engineering and Industrial Production, University of Naples Federico II, Piazzale Tecchio, 80 – 80125 Naples, Italy
[c] INSTM – Reference Centre for Processing Technology of Polymers and Composites, University of Naples Federico II, Piazzale Tecchio, 80 – 80125 Naples, Italy
[d] Department of Electrical Engineering and Information Technology, University of Naples Federico II, Piazzale Tecchio, 80 – 80125 Naples, Italy

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ABSTRACT

Multi wall carbon nanotubes (MWCNTs) with different aspect ratios (30, 105 and 667) were included in a commercial fully biodegradable blend using melt mixing. Samples of composite systems prepared by hot molding and containing up to 1.2 vol% of MWCNTs were studied by means of DC electrical resistivity and dielectric spectroscopy in order to enhance effect of filler content and aspect ratio on their dielectric behavior. Raman spectroscopic investigations and morphological observations were also performed in order to correlate dielectric behavior with surface carbon nanotubes features and to check the actual level of dispersion of carbon nanotubes under the applied processing conditions. Results emphasized that the carbon nanotubes aspect ratio and their surface regularity determine the electrical properties of composites because they strongly influence percolation thresholds, dielectric permittivity and dissipation factor of produced materials. A satisfying dispersion of the filler seems to be achieved under the employed processing conditions. These preliminary results demonstrates possible applications of this type of biobased systems in many applications going from stress control to devices for high storage energy.



## 1. Introduction

Recently, the growing awareness about finite petroleum resources and significant environmental impact of plastic items at the end of their useful life have justified a huge amount of research efforts reported in the literature about bio-based materials. The general interest of academic and industrial researchers is to exploit potentialities of the so-called biopolymers, intrinsically biodegradable or derived from renewable resources.

Currently environmentally friendly resins are already applied in various fields as biomedical, food packaging and coating ones. However, limitations essentially in terms of their high cost and inferior physical properties with respect to traditional petroleum based plastics still restrict their potential spectra of industrial applications. In this frame, several researches have been focused on specific methodologies aimed to improve functional properties of commercial available biopolymers as poly(lactic acid) (PLA) [1,2], poly(hydroxy alkanoates) (PHA) [3,4] and polycaprolactones (PCL) [5,6].

Common routes to achieve valuable targets are the inclusion of nanometric fillers or the blending with other

* Corresponding author. Tel.: +39 081 7682268; fax: +39 081 7682404.
*E-mail address:* pietro.russo@unina.it (P. Russo).

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resins, preferably biobased ones, in order to obtain new fully eco-sustainable products. About the first approach, usually the inclusion of rigid nanosized fillers not only improves mechanical properties of the host matrix but also it may enhance specific functional properties of the same. For example, it is well know that carbon nanotubes are promising reinforcing filler for polymers due to their excellent mechanical, electrical and thermal properties.

As far as blending is concerned, appropriate choices in terms of second organic phase, composition, operative conditions and even the inclusion of nanofillers may give rise to co-continuous morphologies, responsible of synergistic interactions between the phases mixed together and products with very interesting performances [7,8]. This is the case of the blend considered in this study, constituted by two semicrystalline co-polymers, poly(hydroxyl butyrate-co-valerate) (PHBV) and poly(butylenes adipate-co-terephthalate) (PBAT), and commercially available as a film grade resin with a weight ratio 30/70, respectively. In fact, although PHBV copolymers are among the most studied PHA resins, their applications are limited by some drawbacks as slow crystallization rate, very high crystallinity, brittleness, relatively difficult processing due to the low melt viscosity and small processing window. PBAT co-polymers, with their high flexibility and processability, are potential candidates to improve properties of PHBV resins and retain biodegradability of products.

In this work, specific interest is dedicated to the improvement of the dielectric behavior of this blend in order to extend its potential use [9,10], focusing the attention on the effect of filler content and aspect ratio [$\eta$]: geometrical parameter affecting, as well established, percolation thresholds and, consequently, physical properties of final products [11,12].

Electrical resistivity (conductivity) of polymer composites containing carbon nanotubes of different type (single, double, multi wall), synthesis method, treatment, manufacturer and aspect ratio have been extensively studied [13]; a wide range of resistivity values has been reported but a comparison among different data can be still very difficult. Fewer results are available on biodegradable composites, as for instance on polyvinyl alcohol PVA [14] or poly(L-lactide) PLLA [15], which are becoming of increasing interest for many electrical and electronic devices.

At this purpose, systems containing low amounts of multiwalled carbon nanotubes were prepared by melt compounding and analyzed in terms of dielectric and morphological issues. Raman spectroscopy was used to investigate nanotubes surface with the aim to correlate dielectric behavior with interface features. Main results obtained so far allow to foresee interesting perspectives of investigated systems in electric/electronic and storage energy fields.

## 2. Experimental

### 2.1. Materials

A commercial PHBV/PBAT blend (named E-PHBV) was purchased in pellet form from Ningbo Tianan Biologic Material Co. Ltd. (Tianan-ENMAT) (China) under the trade name 6010P. The weight ratio between PHBV and PBAT is 30:70.

Multi wall carbon nanotubes (MWCNTs) used as fillers differ essentially in terms of their aspect ratio parameter as clearly highlighted by Table 1 reporting some features of the same.

Prior to melt mixing, the matrix and the fillers were vacuum dried at 70 °C for 12 h.

### 2.2. Composite and sample preparation

All formulations containing multi wall carbon nanotubes contents up to 1.5 vol% were prepared using a HAAKE Polylab mixer at 175 °C, with a screw speed of 60 rpm and a residence time of 7 min. Systematic thermogravimetric measurements, not shown here, confirmed a good agreement between nominal and actual filler contents.

Samples for DC electrical volume resistivity ($\rho_v$) measurements were obtained by applying a hydraulic pressure of about 2 MPa at 180 °C for two minutes with a compression molding machine (LabTech Engineering, LP20-B). They have a circular shape, with a diameter of about 40 mm and a thickness approximately equal to 1.0 mm.

### 2.3. DC volume electrical conductivity

Measurements were performed at room temperature by a standard volt-amperometric method by holding each specimen in a shielded cell with guarded ring electrodes. The volume electrical conductivity $\sigma_v$ was estimated on the basis of the quasi-steady state value of the current $I_{DC}$ taken after 180 s from the application of a step voltage $V_{DC}$:

$$\sigma_v = \frac{I_{DC}}{V_{DC}} \frac{S}{d}$$

where $d$ and $S$ are the thickness and area of the sample, respectively.

In order to reduce the thermal effects, fields ranging between 0.5 and 1 kV/m were applied to the samples. With the aim of verifying the reproducibility of the measurement, a rigid procedure was also adopted. Prior the electrical measurements, the specimen were conditioned by keeping them in an oven at the controlled temperature of 40 °C for 48 h. Each sample was then measured four times

**Table 1**
Information about considered carbon nanotubes.

| Trade code | Supplier | Mean outer diameter (nm) | Length (μm) | Aspect ratio [$\eta$] | True density (g/cc) | Purity (%) |
|---|---|---|---|---|---|---|
| 4060 | Shenzen Nanotechnologies | 50 | 1.5 | 30 | 2.16 | >97 |
| 3150 | Nanocyl | 9.5 | 1 | 105 | 1.94 | >95 |
| 724769 | Sigma Aldrich | 7.5 | 5 | 667 | 2.1 | >95 |