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A convenient route for the dispersion of carbon nanotubes in polymers: Application to the preparation of electromagnetic interference (EMI) absorbers

Jean-Michel Thomassin [a], Daniela Vuluga [a], Michaël Alexandre [a], Christine Jérôme [a], Isabel Molenberg [b], Isabelle Huynen [b], Christophe Detrembleur [a,*]

[a] Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium
[b] Microwave Laboratory, Université Catholique de Louvain, B-1348 Louvain-la-neuve, Belgium

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ABSTRACT

A new dispersion technique has been implemented which consists in the polymerization of a monomer in the presence of CNTs in a bad solvent of the polymer. During its formation, the polymer precipitates and entraps all the CNTs. Thanks to the establishment of a suitable CNTs dispersion, this method promotes much higher electrical conductivity in the resulting nanocomposite than more conventional techniques, i.e. melt-mixing and co-precipitation. Moreover, the quantity of solvent required is much lower than in the co-precipitation method that makes this process industrially viable. One potential application of these nanocomposites has been demonstrated by the preparation of foams using the supercritical CO_2 technology that present very high electromagnetic interference (EMI) absorbing properties since more than 90% of the incoming power being absorbed in the foam.

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1. Introduction

Carbon nanofillers/polymer nanocomposites foams have received steadily increased attention during the last few years due to their potential applications in biomedical [1], acoustic absorption [2,3], electromagnetic interferences (EMI) shielding [4,5] and protection against electrostatic discharge (ESD) [6]. The lightness, low thermal conductivity, low dielectric constant and good sound isolation inherent to foams combined with the electrical conductivity and mechanical reinforcement properties of carbon nanofillers make them excellent candidates for absorbing electromagnetic radiations in a broad frequency range without any reflection. In order to suppress the electromagnetic pollution by absorption, the EMI absorber must indeed combine a high electrical conductivity to dissipate the electromagnetic radiation by conductive dissipation with a low dielectric constant to keep the reflectivity at the material interface low [4]. Carbon nanotubes (CNTs) offer substantial advantages over conventional carbon fillers due to their ability to simultaneously enhance the electrical conductivity and reinforce the mechanical performances of the filled polymers at very low contents (<5 wt %) as result of their high aspect ratio (>1000) and their nanoscopic dimensions. The first critical step for designing efficient EMI absorbers lies in the appropriate dispersion of CNTs within the polymer matrix to establish a conducting CNTs network. Therefore, attention must be paid to not completely isolate the CNTs because this dispersion would prevent any contact between them at reasonable CNTs loadings (few wt%). Additionally, the dispersion method must not be too aggressive in order to avoid extensive breaking up of the CNTs that would be detrimental to the electrical conductivity [7]. Melt-mixing method has been the most studied dispersion technique due to its transferability to an industrial scale [7–10]. While the dispersion of CNTs is good in several matrices (poly(butylene terephthalate) [8], polyamide [9], polycarbonate [10], polycaprolactone [7]…) without the need of any CNTs functionalization, the conductivity at low CNTs content (few wt%) is not often as high as expected as the result of the low length of the cut CNTs that limits the contacts between too perfectly dispersed CNTs. Several studies have shown that the conductivity of these nanocomposites could be significantly enhanced by annealing them at a suitable temperature that allow them to gently percolate to each other and therefore favor their contacts [11,12]. Other dispersion methods have been implemented such as *in situ* polymerization [13–15] and co-precipitation [7,16,17]. These techniques have demonstrated very high efficiency due to their limited impact on the CNTs length (less aggressive dispersion methods). However, most of them are hardly transferable to an industrial scale due to the large amount of solvent used for polymerization and for the precipitation of the final product.

* Corresponding author.
E-mail address: christophe.detrembleur@ulg.ac.be (C. Detrembleur).

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In this paper, we propose a new dispersing method that combines the advantages of the two previously mentioned techniques while scaling-up is no more a limitation. This method consists in the polymerization of a monomer in the presence of CNTs in a bad solvent of the polymer. During its formation, the polymer precipitates and entraps all the CNTs as it is the case in the co-precipitation process. The amount of solvent to be used is strongly decreased compared to the co-precipitation technique that needs to first dissolve the polymer in the presence of CNTs in a good solvent of the polymer before precipitation in a huge amount of bad solvent of the polymer (about 10 times the volume of the initial polymer solution). The electrical properties of the samples prepared by this new method have been measured and compared with the one obtained with more conventional techniques. In order to design EMI absorbers, the nanocomposites were then foamed using the supercritical carbon dioxide technology (pressure-induced batch-foaming method). The EMI shielding properties were finally evaluated.

2. Experimental part

2.1. Materials

Methyl methacrylate (>99%, Aldrich), α,α′-azoisobutyronitrile (AIBN) (Fluka), methanol (Aldrich) and dimethylformamide were used as received. Purified Multi-Walled Carbon Nanotubes (purified CNTs, FutureCarbon) were produced by Chemical Vapor Deposition (CVD). Poly(methyl methacrylate) (PMMA) (Diakon®) was provided by ICI.

2.2. Preparation of the nanocomposites

1. Precipitation polymerization technique. In a typical experiment, 150 mg of CNT have been dispersed in 100 ml of methanol and placed in an ultrasonic bath (35 kHz, 320 W, Sonorex RK 255H) for 30 min. 0.1 g of AIBN and 15 g of MMA are then added and the solution is degassed by nitrogen. The solution is placed again in an ultrasonic bath for 10 min at room temperature. Then, the mixture is heated at 60 °C while stirring with a magnetic stirrer. During its formation, the polymer precipitates entrapping all the CNTs. When the monomer conversion reached 50%, the reaction is stopped and the solid sample is removed from the solution and washed with methanol before being dried under vacuum at 50 °C.
2. Melt-blending technique. The melt-mixing of PMMA with the required amount of CNTs has been performed at 210 °C in a 5 cm^3 DSM microextruder under nitrogen at 200 rpm for 10 min.
3. Co-precipitation technique. 10 g of PMMA are dissolved in 400 ml of DMF and the required amount of CNTs was added to the solution. After 30 min of an ultrasonic treatment, the solution was precipitated in 4 L of a non-solvent of PMMA, i.e., methanol. The sample was then collected by filtration and washed with methanol before being dried under vacuum at 50 °C.

2.3. Foaming of the nanocomposites

21 × 7 × 3 mm samples of the different PMMA/CNTs nanocomposites were prepared by compression molding (200 °C, 80 bars, 2 min) and foamed using supercritical CO_2 in a pressure-induced batch-foaming method. The samples are placed in a 316 stainless steel high pressure cell (100 ml) from Parr Instruments pressurized with CO_2 at 45 bar with an ISCO 260D high pressure syringe pump. The cell was then heated to 120 °C, and compressed CO_2 was finally adjusted to a final pressure of 280 bar. This saturation pressure was maintained for 16 h to fully impregnate the sample before being released within a few seconds to induce foaming.

2.4. Characterizations

MWNTs dispersions were observed with a transmission electron microscope PHILIPS CM100 at an accelerating voltage of 100 kV. Thin sections (90 nm) were prepared by ultramicrotomy (ULTRACUT E from REICHERT-JUNG) at −130 °C. Micrographs were analyzed by using the megaview GII (Olympus) software. Owing to the sufficient contrast of MWNTs in PMMA no staining was necessary.

The foam structure was observed by scanning electron microscopy (SEM; JEOL JSM 840-A) after metallization with Pt (30 nm).

Electrical measurements were performed with a Vector Network Analyzer Model Wiltron 360B operating over the frequency range 40 MHz–40 GHz. Each nanocomposite sample to be characterized for its conductivity consists of a thin plate of same thickness (1 mm) and surface (4 × 4 mm^2) prepared by compression molding (200 °C, 80 bars, 2 min), and is used as a microwave substrate on which a ground plane and a microstrip line are deposited [18]. This ensures broadband guided propagation of the signal inside the nanocomposite substrate. A standard calibration of the VNA is performed before measuring the microstrip configuration, in order to remove any influence of the connecting cables and of their transitions to the sample. Measurements provide the so-called vector S-parameters S_{11} and S_{21}. From those S_{ij} measurements the conductivity of each nanocomposite is also extracted.

For the EMI measurements of solid and foamed samples shown in Fig. 4, the same preliminary coaxial calibration applies. Each sample is then inserted between two coax-to-waveguide transitions acting as launchers for the microwave signal, according to the experimental setup described elsewhere [19]. Two additional calibration measurements are performed in order to remove the effect of the launchers: a “thru” measurement resulting from the connection of the 2 launchers, and an “air” measurement without the sample, i.e. with the 2 launchers separated from a distance equal to the thickness of the specimen. These measurements are sufficient to retrieve the de-embedded S-parameters of the sample, from which the shielding effectiveness SE and reflectivity are defined. Parameter S_{11}, measured when a short-circuit reflective termination is placed at the output of the sample, corresponds to the reflectivity, $R = 20 \log_{10} |S_{11}|$, i.e. the reflected power measured at input interface of the substrate, normalized to input power. Parameter S_{21} corresponds to normalized transmission through nanocomposite. Hence the shielding effectiveness SE is simply equal to $-20 \log_{10} |S_{21}|$. The fraction of incident power which is absorbed through the sample is obtained from the

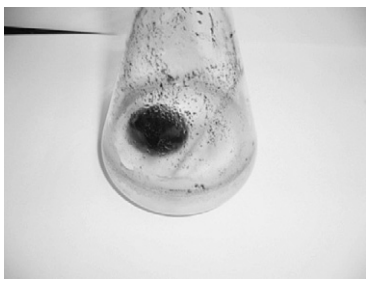

Fig. 1. Picture of a precipitation polymerization process at 50% monomer conversion showing that all the CNTs are entrapped in the precipitated polymer.

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