USE OF THE SUPERCRITICAL FLUID TECHNOLOGY TO PREPARE EFFICIENT NANOCOMPOSITE FOAMS FOR ENVIRONMENTAL PROTECTION PURPOSE

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BIOGRAPHICAL NOTE

Laetitia Urbanczyk has a Master degree in Chemistry at the University of Liège (Belgium) and she is now doing a PhD thesis at the Center for Education and Research on Macromolecules (CERM), in the field of supercritical fluids applied to polymers. Indeed, for several years, the CERM has been developing the promising supercritical fluid technology in diversified areas, such as polymer synthesis, fillers modification, extraction and foaming. The lab is now equipped with a large panel of apparatuses, going from different types of small capacity reactors to a 50L pilot plant, as well as a continuous extruder allowing supercritical fluid injection.

ABSTRACT

This work reports on the preparation of novel nanocomposite foams that are efficient broadband microwave absorbers. Carbon nanotubes are first successfully dispersed into PCL and PMMA by melt blending. Then, foaming is promoted by supercritical CO_2 by depressurization. Regular cellular structures are obtained in both cases with cells size around 10-50µm. The electromagnetic interference (EMI) shielding efficiency of these materials are then evaluated and compared to the non-foamed nanocomposites.

INTRODUCTION

For several decades, polymeric foams have become very popular materials that can be found in diversified applications, thanks to their attractive properties, like lightness, flexibility, shock absorption, insulation or sound dampening properties. For foams prepared through solvent vaporization, their processing usually involves chlorofluorocarbons (CFCs) or other organic solvents, which are environmentally harmful and/or highly flammable[1]. Nowadays, CFCs are progressively banned from industrial foaming processes and must therefore be replaced by more environmentally friendly agents. Among the potential alternatives, a lot of research has been dedicated to supercritical carbon dioxide ($scCO_2$), for its good affinity with a lot of polymers together with its much lower impact on the greenhouse effect, compared to chlorofluorocarbons[2]. Furthermore, the foams prepared with $scCO_2$ are characterized by very regular porosity and smaller cells size compared to classical foaming processes, leading to microcellular foams. This kind of porosity provides higher mechanical resistance to the cellular material, thus enlarging its range of applications[3].
In this work, our supercritical foaming skill has been combined with nanocomposite technology[4] in order to prepare innovative materials for electromagnetic waves absorption[5]. In fact, the steady growth of communication technology has recently raised some questions about the adverse effects of those radiations on the human body. These waves also generate interference problems to medical apparatus and many other electronic instruments. There is thus a growing interest for efficient shielding materials to protect people and those apparatus from the electromagnetic wave pollution[6]. Metallic sheets are most of the time used as protection but they result only in wave reflection without any absorption of the signal[7].
This work reports on the preparation of novel nanocomposite foams that are efficient broadband microwave absorbers. Carbon nanotubes, when well-dispersed throughout the polymer matrix, render the polymer conductive. This kind of nanocomposite can partially absorb and reflect electromagnetic waves of broad frequency range. The novelty brought by the CERM, in collaboration with two other Belgian labs, i. e. EMIC and POLY, consists in introducing many small voids into the nanocomposite, in order to increase the wave absorptive capacity, thus minimizing signal reflection. This improvement has been validated with the promising supercritical fluid foaming process, and has then been accordingly patented[8].

The present paper deals with the preparation of these polymer/carbon nanotube nanocomposite foams, followed by the evaluation of their electromagnetic interference (EMI) shielding efficiency.

MATERIALS AND METHODS

Poly(ε-caprolactone) (PCL), CAPA 650, comes from Solvay Interox and PMMA from Lucite International. Commercially available thin multi-walled carbon nanotubes (MWNT) (average outer diameter : 10nm, purity higher than 95wt%) produced by Catalytic Carbon Vapour Deposition (CCVD) were supplied by Nanocyl S.A Belgium. Nanocomposites were prepared by melt blending the polymer with the filler in a mini-extruder (5g capacity) at 80°C (PCL) or 210°C (PMMA), for 10 minutes at 200rpm. The nanocomposites were then molded into 3mm sheets for 5 minutes at the same temperature. The foaming method consists in placing the sample into a 50ml reactor under 300bar of CO_2 at a temperature higher than the melt or glass transition temperature of the polymer plasticized by CO_2. Foaming is then induced by fast depressurization of the reactor (40°C for PCL and 120°C for PMMA)[9]

Transmission electron microscopy (TEM, Philips CM100) was used to observe carbon nanotubes distribution throughout the polymers. Ultrathin sections (50-80 nm) were prepared with an Ultramicrotome Ultracut FC4e, Reichert-Jung. Cellular morphology was observed with Scanning Electron Microscopy (SEM, JEOL JSM 840-A) after metallization with Pt. Electromagnetic interference (EMI) shielding efficiency of MWNT/polymer composites foams were measured with a Wiltron 360B Vector Network Analyzer (VNA) in a wideband frequency range from 40 MHz up to 40 GHz. The Line-Line Method was used with two microstrip transmission lines deposited on the nanocomposite surface. Complex dielectric constant and conductivity were extracted from the VNA transmission and reflection measurements, which also yielded reflectivity and shielding efficiency.

RESULTS

Transmission electron microscopy showed that the MWNTs were uniformly dispersed as single nanotubes within both matrices (PCL and PMMA) (Figure 1). As a consequence, these nanocomposites exhibit high conductivity (> 1 S/m) at low filler content (< 2 wt%) which makes them good candidates as EMI shielding materials. However, they are also characterized by a high permittivity which induces a high reflectivity of the radiation at the surface of the materials. The reflection of the signals results indeed from a mismatch between the wave impedances for the signal propagating into air and into the absorbing material, respectively.

a) b)

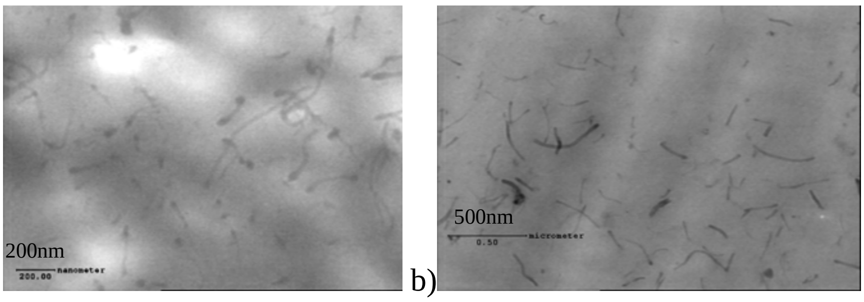

Figure 1 : TEM Micrographs of a) PCL and b) PMMA filled with 1 wt% of MWNT.

Foaming of these nanocomposites has been performed with supercritical CO_2 in order to decrease the propensity of the materials to reflect the radiation. The relative volume of air in an open-cell foam is very high, which is very favorable to the matching of the wave impedances of the expanded material and the ambient atmosphere. Well defined foams were obtained with pore size around 20-50 µm and a volume expansion of 5 in the case of PCL and pore size around 5-10 µm and a volume expansion of 10 for PMMA nanocomposites (Figure 2). Shielding efficiency as high as 60 to 80 dB together with a low reflectivity was observed at very low vol% of MWNTs (0.25 vol%).

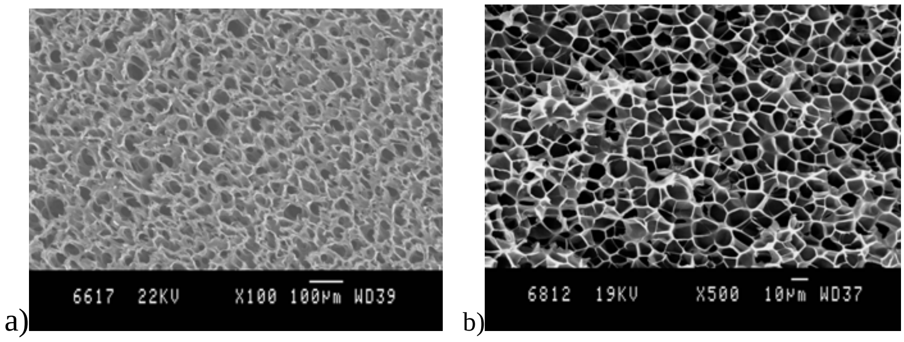

Figure 2 : SEM Micrographs of a) PCL and b) PMMA foams filled with 1 wt% of MWNT.

CONCLUSIONS

New nanocomposite materials with high electromagnetic wave absorptive effectiveness have been successfully prepared with the use of supercritical CO_2 as the foaming agent. It was found that adding small voids into the nanocomposite improved substantially the wave absorptive capacity, thus reducing greatly the signal reflection. The resulting material is also much lighter and more flexible than metallic counterparts currently used, making them very attractive from an industrial point of view.

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