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

Jean-Michel Thomassin[1], Laetitia Urbanczyk[1], Isabelle Huynen[2], Michaël Alexandre[1], Christine Jérôme[1], Christophe Detrembleur[1]
[1]University of Liège, Center for Education and Research on Macromolecules (CERM), Sart-Tilman, B6a, B-4000 Liège, Belgium.
Tel: +32 (0) 43663556 Fax: +32 (0) 43663497 email: christophe.detrembleur@ulg.ac.be
[2] Université Catholique de Louvain, Microwave Laboratory, Maxwell Building, Place du Levant 3, B-1348 Louvain-la Neuve, Belgium.

ABSTRACT

The continuous progress of communication technology has recently raised some questions about the adverse effects of the electromagnetic waves on the human body. Furthermore, 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. This work reports on the preparation of novel nanocomposite foams that are efficient broadband microwave absorbers. These foams are made of polymer/carbon nanotube nanocomposites which are foamed using supercritical carbon dioxide. This very efficient foaming technique leads to regular foams with very small cell size (10-50µm). The effect of nanofiller addition on the cellular structure is first assessed. Then, different foaming conditions (T°, P,...) are tested to prepare nanocomposite foams with a large panel of cell sizes and densities. Finally, the influence of the foam characteristics on the electromagnetic shielding effectiveness is studied in order to evidence the optimal cellular structure for this kind of application.
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INTRODUCTION

With the rapid development of gigahertz electronic systems and telecommunications, electromagnetic pollution has become a serious problem in modern society, which justifies a very active quest for effective electromagnetic interferences (EMI) shielding materials. Electromagnetic interferences may be defined as electromagnetic radiations emitted by electrical circuits under current operation that perturb the operation of surrounding electrical equipments and might cause radiative damage to the human body. Electromagnetic shielding is defined as the prevention of the propagation of electric and magnetic waves from one region to another by using conducting or magnetic materials. The shielding can be achieved by minimizing replied signal or the signal passing through the material using reflective properties and absorptive properties of the material. A large range of applications is concerned from commercial and scientific electronic instruments to antenna systems and military electronic devices [1].
Nowadays, the electrical circuits are shielded with metal sheets with the inconvenience of poor mechanical flexibility, exceedingly high weight, propensity to corrosion, and limited tuning of the shielding effectiveness (SE). During the last two decades, considerable research focuses on the development of shielding materials based on polymers with the advantages of lightness, low cost, easy shaping, etc. Nevertheless, most of the polymer cannot prevent the electromagnetic waves from propagating because of electrical insulating properties. Polymers filled with carbon fillers (e.g., carbon black, carbon fibers and carbon nanotubes) have then been widely investigated for EMI shielding purposes because of unique combination of electrical conductivity and polymer flexibility [2,5]. The use of carbon nanotubes (CNTs) presents several advantages over conventional carbon fillers because, as result of their high aspect ratio, the carbon nanotubes can percolate at very low contents (<5 wt.%). Moreover, they can simultaneously enhance the electrical conductivity and reinforce the mechanical performances of the filled polymers.
However, a major drawback of the nanocomposites that contain carbon nanotubes is a high propensity to reflect the electromagnetic radiations rather than to absorb them. Indeed, the reflection of the signals results from a mismatch between the wave impedances for the signal propagating into air and into the absorbing material, respectively. The introduction of air into these nanocomposites by the formation of an open-cell foam will be favorable to the matching of the wave impedances of the expanded material and the ambient atmosphere. For this purpose, $scCO_2$ has been used to foam carbon

nanotubes nanocomposites based on different polar polymer matrices. The effect of nanofiller filling content, pressure and temperature on the main properties of the foam (density, pore size…) has been widely studied which allowed us to isolate several materials with high shielding efficiency combined with a low reflectivity in a broad frequency range (1-40 GHz) [6-8].

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 of 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.
The foaming of these nanocomposites was performed by supercritical CO_2 in order to decrease the propensity of the materials to reflect the radiation. 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. 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).

a)

b)

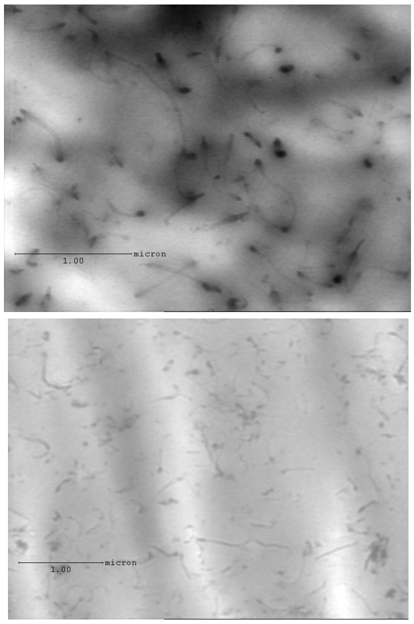
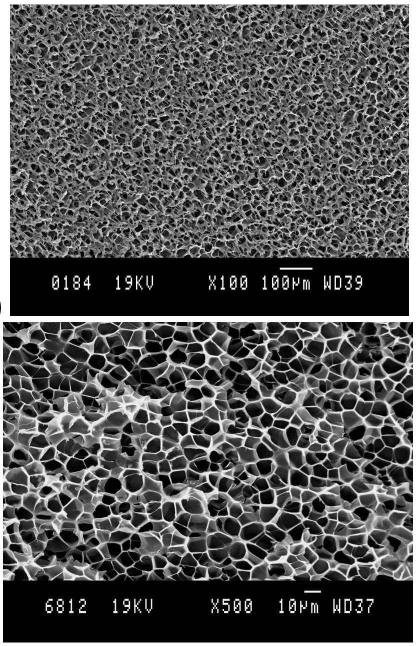


Figure 1 : TEM Micrographs of a) PCL and b) PMMA filled with 1 wt% of MWNT.



a)

b)

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

The beneficial effect of the foaming of PCL/MWNT nanocomposites has been analyzed on the basis of the electromagnetic properties of foamed and unfoamed nanocomposites (Figure 3 and 4). Clearly, high EMI shielding effectiveness (SE) (> 20 dB), defined as the Pr/Pi ratio of the output to the incident power, can be achieved with the PCL/MWNT nanocomposites but at a lower MWNT content for the foamed samples (0.107 vol % vs 0.48 vol%) (Figure 3). Moreover, the reflectivity measured for the foamed nanocomposite is much lower than for the corresponding solid sample.

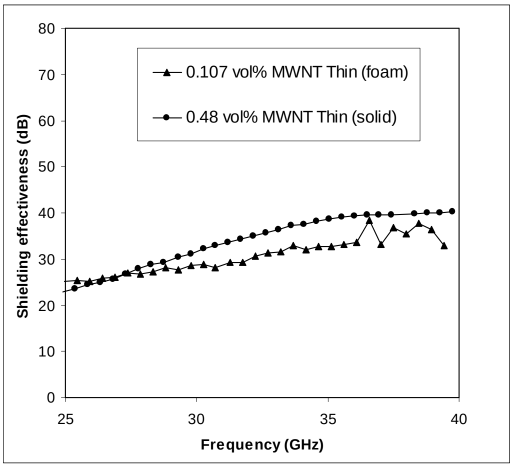


Figure 3 : Sielding effectiveness (SE) of foamed and unfoamed PCL/MWNT nanocomposites.

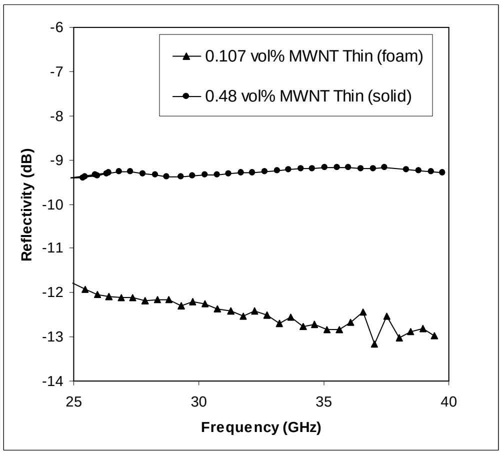


Figure 4 : Reflectivity of foamed and unfoamed PCL/MWNT nanocomposites.

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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REFERENCES

1. A. N. Yusoff, M. H. Abdullah, S. H. Ahmad, S. F. Jusoh, A. A. Mansor, S. A. A. Hamid, *J. Appl. Phys.*, **2002,** 92,(2), 876-882
2. N. C. Das, D. Khastgir, T. K. Chaki, A. Chakraborty *Composites Part A*, **2000**, 31(10), 1069-1081.

3. H. M. Kim, K. Kim, C. Y. Lee, J. Joo, S. J. Cho, D. A. Pejakovic, J. W. Yoo, A. J. Epstein, *Appl. Physics Letters*, **2004**, 84(4), 589.
4. Y. Yang, M.C. Gupta, K.L. Dudley, R.W. Lawrence, *J. Nanosci. Nanotechnol.*, **2005**, 5(6), 927-931.
5. W.S. Kim, H.S. Song, B.O. Lee, K.H. Kwon, Y.S. Lim, M.S. Kim, *Macromol. Res.* **2002**, 10(5), 253-258
6. Thomassin, J. M.; Lou, X.; Pagnoulle, C.; Saib, A.; Bednarz, L.; Jérôme, R.; Detrembleur, C. *J.Phys.Chem.C* **2007**, *111*, 11186-11192.
7. Thomassin, J. M.; Pagnoulle, C.; Bednarz, L.; Huynen, I.; Jérôme, R.; Detrembleur, C. *J.Mater.Chem.* **2008**, *18*, 792-796.
8. Jérôme, R.; Pagnoulle, C.; Detrembleur, C.; Thomassin, J-M.; Huynen, I. ; Bailly, C. ; Lukasz, B. ; Daussin, R.; Aimad, S. patent EP1930364.
9. Di Maio, E.; Iannace, S.; Di, Y.; Del Giacomo, E.; Nicolais, L. *Plastics, Rubber and Composites* **2003**, *32*, 313-317.