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Multiwalled Carbon Nanotube/Poly(ϵ -caprolactone) Nanocomposites with Exceptional Electromagnetic Interference Shielding Properties

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Multiwalled carbon nanotubes (MWNTs) with two different diameters were dispersed within poly(ϵ -caprolactone) (PCL) by melt-blending and coprecipitation, respectively, with the purpose to impart good electromagnetic interference shielding properties to the polyester. Transmission electron microscopy showed that the MWNTs were uniformly dispersed as single nanotubes within the matrix. Because the nanotubes were broken down during melt-blending, the percolation threshold was observed at a lower filler content in the case of coprecipitation. Substitution of poly(ethylene-*co*-octene), poly(vinyl chloride), polypropylene, and polystyrene for PCL resulted in a much lower shielding efficiency. Finally, polycarbonate and poly(methyl methacrylate) appeared as promising substitutes for PCL, suggesting that π - π interactions between the nanotubes and constitutive carbonyl units of the polymers would be beneficial to the dispersion and ultimately to the electrical properties of the nanocomposites.

Introduction

The very fast development of gigahertz electronic systems and telecommunications is responsible for the steadily increasing electromagnetic pollution, which justifies a very active quest for effective electromagnetic interference (EMI) shielding materials. A large range of applications is concerned from commercial and scientific electronic instruments to antenna systems and military electronic devices.¹ Polymers filled with carbon fillers (e.g., carbon black, carbon fibers, and carbon nanotubes) have been extensively investigated for EMI shielding purposes because of the unique combination of electrical conductivity and polymer flexibility.^{2–5} The use of carbon nanotubes (CNTs) offers substantial advantages over that of conventional carbon fillers because they can simultaneously enhance the electrical conductivity and reinforce the mechanical performances of the filled polymers. Moreover, the nanotubes can percolate at very low contents (<5 wt %) as result of their high aspect ratio.

However, the large surface area of the CNTs increases the impact of the van der Waals intermolecular interactions, which accounts for a strong tendency to aggregate when dispersed within polymers. This aggregation is, of course, detrimental to the intended percolation, and this heterogeneous dispersion frequently hurts the properties that are meant to be enhanced. Different strategies have been proposed and tested to improve the CNT dispersion within polymer matrixes. For example, CNTs were dispersed within polypropylene (PP)^{6–8} and polyethylene⁹ by melt-mixing. Du et al. prepared good dispersions of nanotubes within poly(methyl methacrylate) (PMMA) by

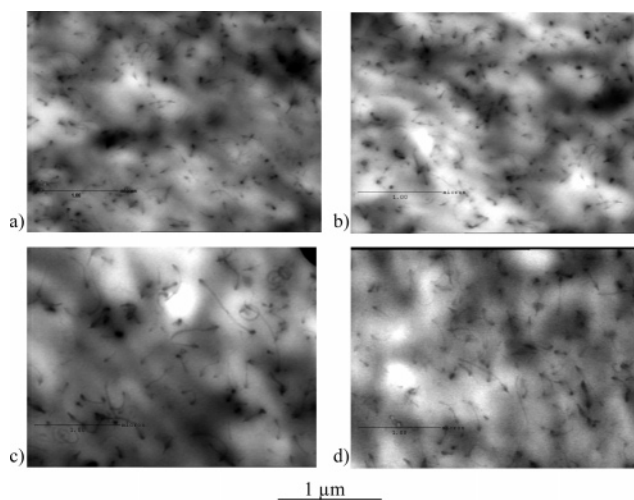


Figure 1. TEM micrographs of PCL filled with (a) thin MWNTs by melt-blending, (b) thick MWNTs by melt-blending, (c) thin MWNTs by coprecipitation, and (d) thick MWNTs by coprecipitation.

a coprecipitation method.^{10,11} In situ polymerization was also carried out in the case of dispersion within polyimide,¹² polystyrene (PS),¹³ and polylactide.¹⁴

In this paper we aim at reporting on dispersions of multiwalled carbon nanotubes (MWNTs) within poly(ϵ -caprolactone) (PCL) with the purpose to prepare materials with high electromagnetic wave shielding performances. Two types of MWNTs have been used that differ in the number of carbon walls and in the amount of easily oxidized structural defects, i.e., the “thin” nanotubes (outer diameter 10 nm, oxygen content <1%) and the “thick” nanotubes (outer diameter 25 nm, oxygen content 7%). Both the melt-mixing and the coprecipitation techniques have been implemented and compared. The MWNT dispersions have been observed by transmission electron microscopy (TEM),

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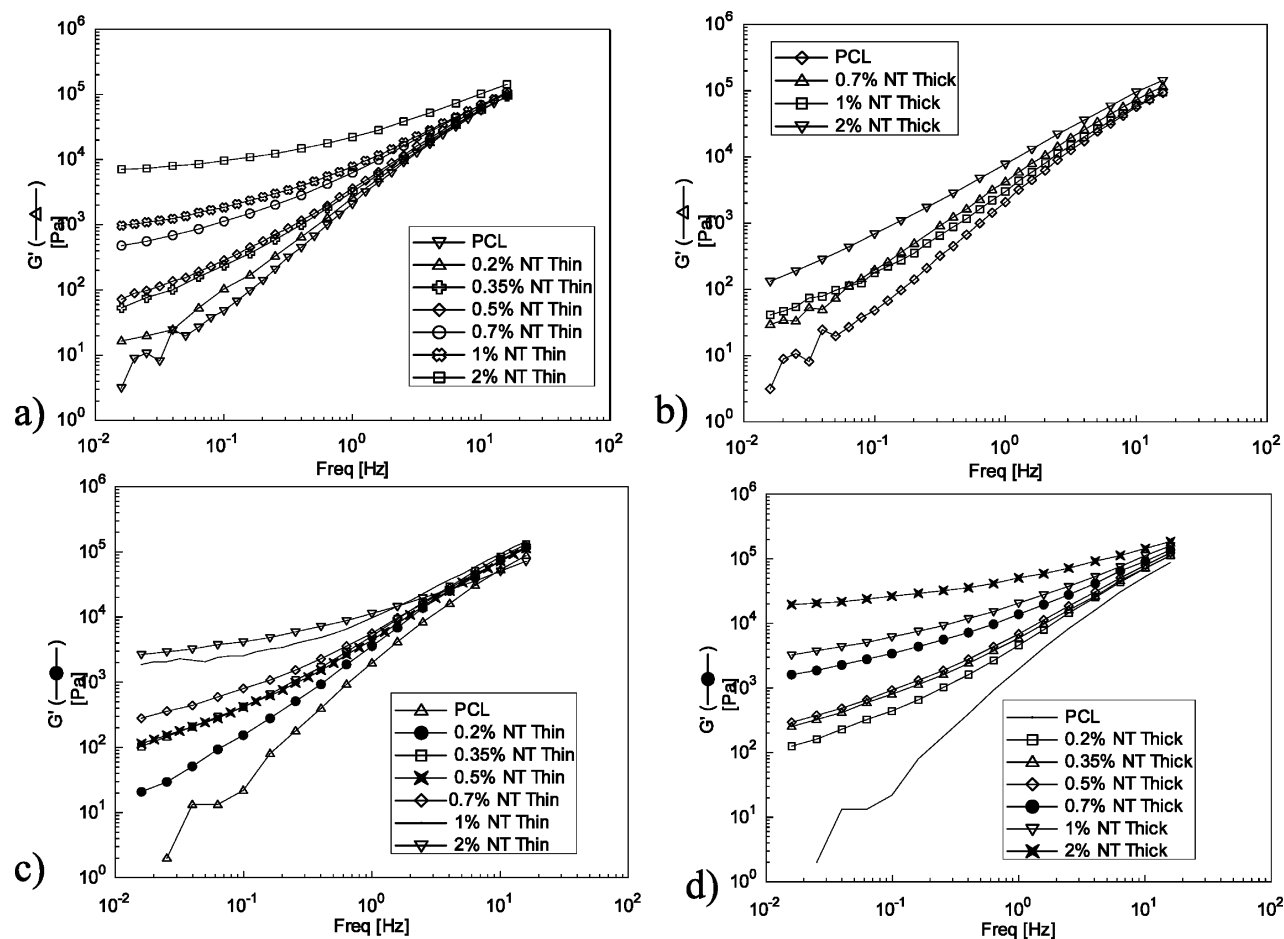


Figure 2. Storage modulus as a function of frequency for different MWNT contents: (a) thin MWNTs dispersed by melt-blending, (b) thick MWNTs dispersed by melt-blending, (c) thin MWNTs dispersed by coprecipitation, (d) thick MWNTs dispersed by coprecipitation.

whereas the rheological and tensile properties of the MWNT/PCL nanocomposites have been measured. The EMI shielding properties have been quantified by the technique of microstrip transmission lines that allows both the permittivity and the conductivity to be determined over a wide frequency range (40 MHz to 40 GHz in this study).^{15,16} The conductivity measurement is the most interesting for EMI performances, because it characterizes the intrinsic ability of the material to absorb electromagnetic waves and is a parameter independent of the geometry of the sample. A good electromagnetic absorber must typically exhibit high conduction properties ($> 1 \text{ S/m}$).¹⁷

Experimental Section

Materials. Commercially available thick MWNTs (average outer diameter 25 nm, purity higher than 95 wt %, oxygen content $< 1\%$) and thin MWNTs (average outer diameter 10 nm, purity higher than 95 wt %, oxygen content 7%) were supplied by Nanocyl S.A., Belgium, and produced by catalytic carbon vapor deposition (CCVD). PCL was received as a gift from Solvay Interlox (Capa 6500, $M_n = 50\,000 \text{ g/mol}$).

Preparation of the Composites. The MWNT/PCL nanocomposites were prepared by two techniques. The first technique consisted in melt-mixing the polymer with the required amount of MWNTs at 80°C in a 5 cm^3 DSM microextruder under nitrogen at 200 rpm for 10 min. In the coprecipitation technique, PCL was dissolved in THF (2.5 wt % PCL in THF) and the required amount of MWNT was added to the solution. After 30 min of an ultrasonic treatment, the solution was precipitated in a nonsolvent of PCL, i.e., heptane.

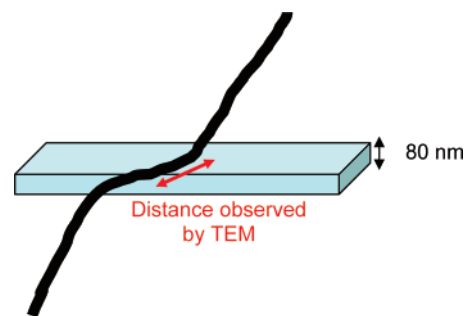


Figure 3. Schematic view of the length of carbon nanotubes really observed by TEM.

Thin MWNTs were also dispersed within polypropylene, poly(vinyl chloride) (PVC), poly(ethylene-co-octene) (PEtOc), PMMA, polycarbonate (PC), and polystyrene by melt-mixing in a 5 cm^3 DSM microextruder at $180, 160, 100, 210, 255,$ and 180°C , respectively.

Characterizations. MWNT dispersions were observed with a transmission electron microscope, Philips M100, at an accelerating voltage of 100 kV. Thin sections (90 nm) were prepared by ultramicrotomy (ULTRACUT E from Reichert-Jung) at -130°C . The micrographs were analyzed by using the KS 100 (Kontron Imaging System) software.

Stress-strain curves were recorded at room temperature with an Instron tester (model DY24) at a 20 mm/min tensile speed. The tensile modulus was calculated from the slope in the linear regime at 1% deformation.

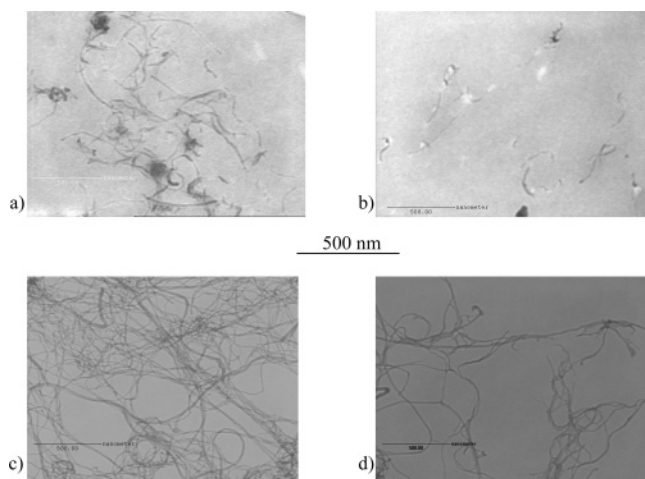


Figure 4. TEM micrographs after dissolution of (a) thin MWNTs dispersed within PCL by melt-blending, (b) thick MWNTs dispersed within PCL by melt-blending, (c) thin MWNTs dispersed within PCL by coprecipitation, and (d) thick MWNTs dispersed within PCL by coprecipitation.

Dynamic rheological measurements were carried out with an “advanced rheometric expansion system” (ARES) from Rheometrics. Samples (diameter 25 mm, thickness 2 mm) were run at 90 °C with a strain of 1%.

The electrical properties of MWNT/polymer composites were measured with a Wilttron 360B vector network analyzer (VNA) in a wide-band frequency range from 40 MHz up to 40 GHz.

The line–line method¹⁶ was used with two microstrip transmission lines deposited on the nanocomposite surface. Conductivity was extracted from the VNA transmission and reflection measurements.

Results and Discussion

MWNT/PCL nanocomposites have been prepared by melt-blending and coprecipitation. Figure 1 compares the extent of dispersion for the two types of MWNTs within poly(ϵ -caprolactone) observed by TEM. Whatever the dispersion technique, the thin and thick MWNTs are uniformly dispersed as single nanotubes, no agglomeration being observed whatever the spot probed on the samples. The effective dispersion of MWNTs in PCL has been confirmed by melt state oscillatory rheology of the nanocomposites. Indeed, the frequency dependence of the storage modulus (G') of the base polymer is sensitive to the percolation of nanofillers in the low-frequency range.^{18–20} Parts a and c of Figure 2 illustrate the dramatic effect that the dispersion of thin MWNTs has on the rheological behavior of PCL even at a loading as low as 0.5 wt %, whatever the dispersion technique. As the loading increases, the storage modulus G' increases rapidly at constant low frequency and becomes essentially independent of ω in the low-frequency range when the nanotube loading is 1 wt % and higher, which is indicative of transition from a liquid-like to a solid-like viscoelastic behavior. This nonterminal low-frequency behavior results from the building up of a nanotube network, which restrains the long-range motion of the PCL chains. In contrast,

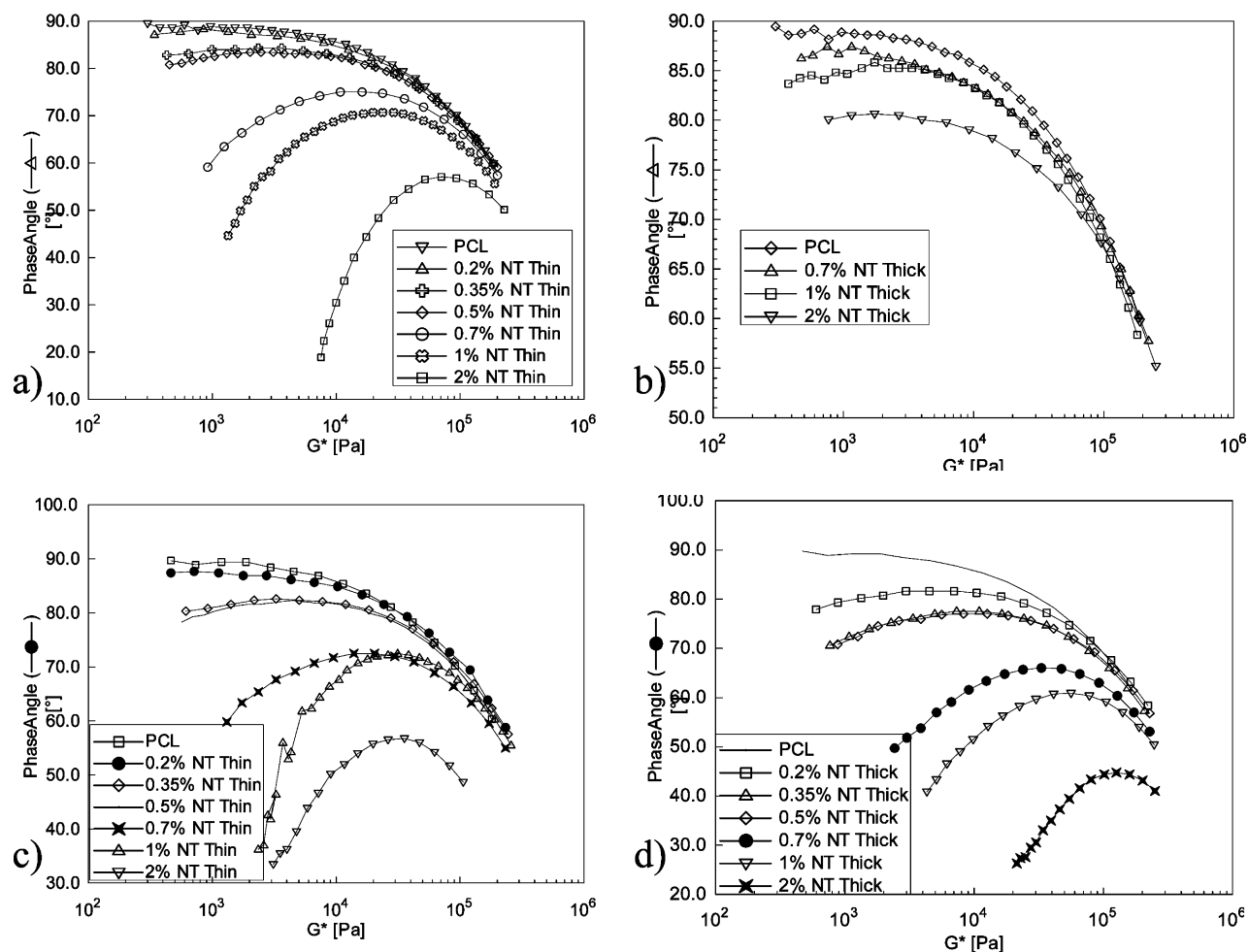


Figure 5. Phase angle versus absolute complex modulus G^* (van Gurp–Palmen plot): (a) thin MWNTs dispersed by melt-blending, (b) thick MWNTs dispersed by melt-blending, (c) thin MWNTs dispersed by coprecipitation, (d) thick MWNTs dispersed by coprecipitation.

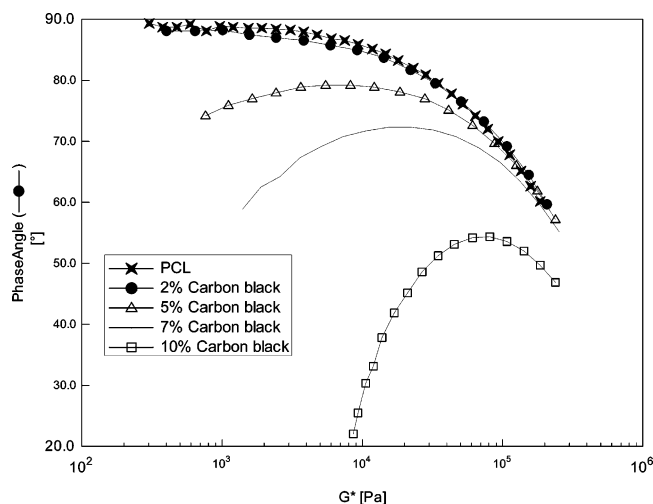


Figure 6. Phase angle versus absolute complex modulus G^* (van Gorp–Palmen plot) for PCL with different contents of carbon black.

thick MWNTs have a comparable impact on the rheological behavior of PCL only in the case of dispersion by coprecipitation. Indeed, these MWNTs have no effect on the G' curve of PCL (Figure 2b) when dispersed by melt-blending, which suggests that they do not percolate under these conditions. Dispersions of the thick MWNTs cannot however be discriminated by TEM on the basis of the dispersion technique. In both the cases, the dispersion looks fine. This apparent discrepancy actually indicates that TEM is not an appropriate technique to estimate the real length of the nanotubes and their percolation merely because only part of the nanotubes lie in the plane of the ultrathin sections (90 nm) observed by TEM (Figure 3). To know whether the length of the nanotubes has been modified by dispersion within PCL, samples of nanocomposites have been dissolved in THF, and the nanotubes have then been collected by filtration and observed by TEM. Figure 4 shows that, in contrast to the coprecipitation technique that does not significantly modify the length of the nanotubes (larger than 1 μm), melt-blending is responsible for an extended breakdown of the nanotubes. This effect is more pronounced for the thick MWNTs (length 0–200 nm) than for the thin MWNTs (length 0–500 nm), which explains why percolation is effective only in the latter case. The higher breakdown extent of the thick MWNTs is consistent with the presence of more structural defects, which greatly weakens the nanotubes.

To determine the percolation threshold of the MWNTs, the phase angle δ has been plotted as a function of the absolute complex modulus G^* (Figure 5). This plot is known as the van Gorp–Palmen plot, which is accepted in the scientific literature as a means to determine the “rheological percolation”.¹⁴ Below the percolation threshold, the phase angle tends to 90° at low G^* , consistent with a behavior dominated by the viscous flow. At and beyond the percolation threshold, the phase angle significantly decreases with the modulus in agreement with an increasing elastic behavior. The percolation threshold of the nanotubes lies between 0.5 and 0.7 wt %, except for the dispersion of the thick MWNTs by melt-blending that shows no percolation threshold at least at and below 2 wt % (Figure 5b). This percolation threshold is approximately 10 times lower than that for dispersion of carbon black in the same matrix, which lies between 5 and 7 wt % (Figure 6).

Figure 7 illustrates the effect of the two types of MWNTs on Young’s modulus of PCL. The reinforcing effect of the MWNTs is very much pronounced, particularly compared to that of carbon black. This effect is however more important for

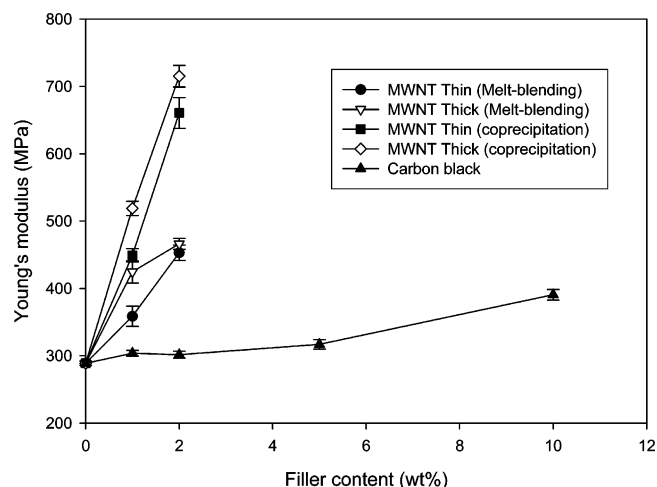


Figure 7. Young’s modulus for PCL filled with MWNTs and carbon black.

dispersions prepared by the coprecipitation technique in direct relation with the length of the nanotubes. The larger effect is reported for the 2 wt % thick MWNTs by coprecipitation, the tensile modulus increasing from 290 GPa for pristine PCL to 715 GPa. It is worth noting that the thick MWNTs have a higher effect on the Young modulus than the thin MWNTs even when the dispersions are prepared by melt-blending.

The EMI shielding properties of the MWNTs containing PCL have been electromagnetically quantified in the microwave frequency range (40 MHz to 40 GHz) using microstrip transmission lines. Results shown in Figure 8 are in qualitative agreement with the rheological behavior of the nanocomposites. Indeed, electrical conductivity higher than 1 S/m (target value for good EMI shielding) can be obtained except for thick MWNTs dispersed within PCL by melt-blending, thus when no percolation occurs. Once again, the higher effectiveness of the coprecipitation method is confirmed. Indeed, the target conductivity of 1 S/m is reached for a thin MWNT content of only 0.7 wt % in nanocomposites prepared by coprecipitation. In contrast, a 1 wt % content is needed to reach the same value by melt-blending. Similarly, at the same MWNT content (1 wt %), the target conductivity is reached at 28 GHz in the case of coprecipitation and above 35 GHz when the samples are processed by melt-blending. The EMI shielding performances of the PCL/MWNT nanocomposites can be emphasized by the comparison of their electrical conductivity with that of nanocomposites obtained with thin MWNTs dispersed within other matrixes. Although MWNTs are well dispersed within PEToc, PVC, PMMA, and PC (Figure 9), the electrical conductivity is lower than that of the PCL nanocomposites at the same 2 wt % content (Figure 10). Needless to say that when the MWNTs are poorly dispersed within PP and PS, the electrical conductivity is also very low. Only PC and PMMA can compete with PCL. A common characteristic feature of these three polymers is a carbonyl group in the constitutive monomer unit. It is therefore proposed that π – π interactions between the aromatic structure of the nanotubes and carbonyl groups in the chains are very beneficial to the morphology of the nanocomposites and their electrical properties. Another way to highlight the excellent performances of the PCL/MWNT nanocomposites is to compare their electrical conductivity to that of carbon black filled poly- ϵ -caprolactone. Figure 11 shows that, even at a carbon black loading as high as 5 wt %, the electrical conductivity of PCL remains much lower than in the case of filling with 0.7 wt % thin MWNTs.

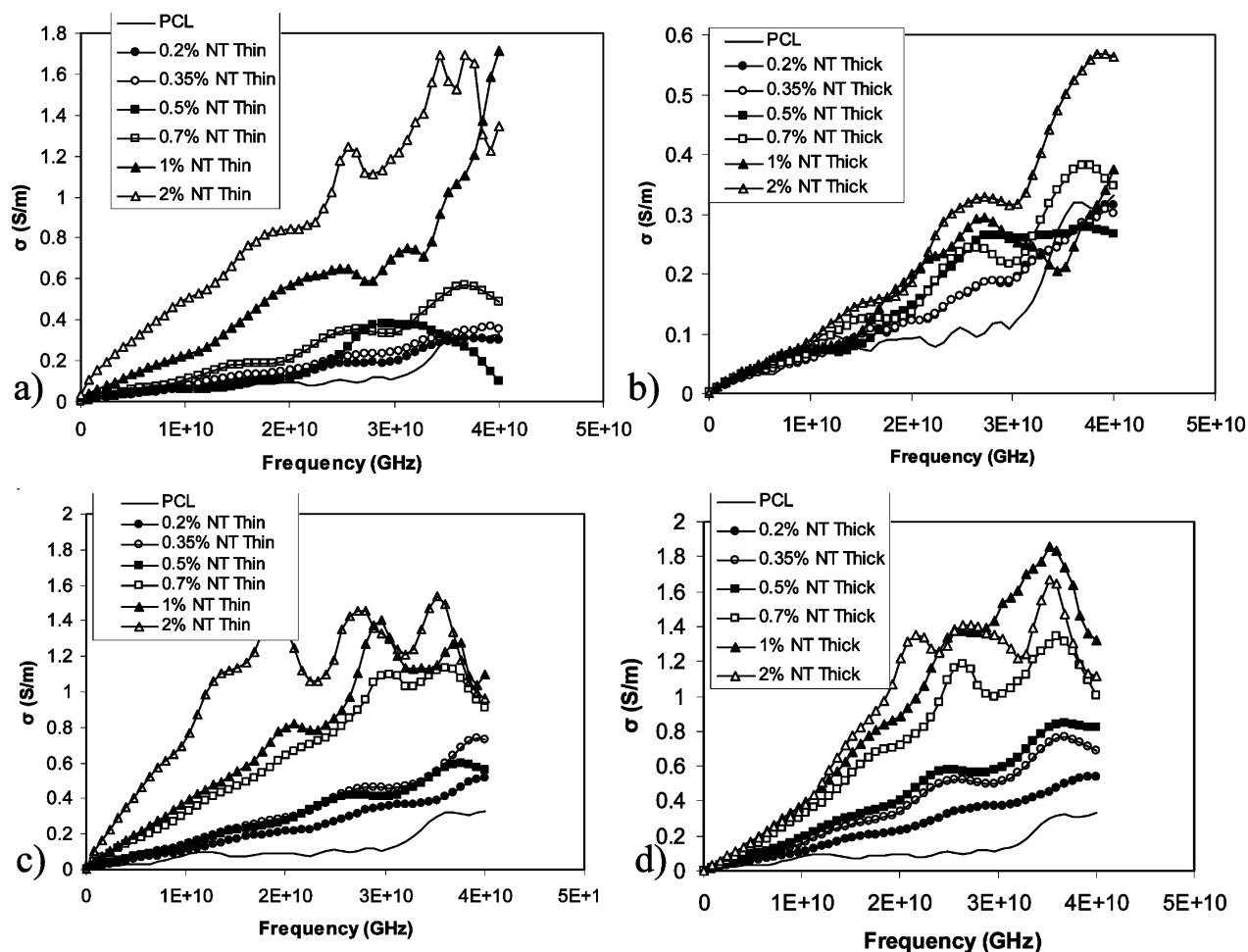


Figure 8. Electrical conductivity as a function of frequency for PCL/MWNT nanocomposites: (a) thin MWNTs dispersed by melt-blending, (b) thick MWNTs dispersed by melt-blending, (c) thin MWNTs dispersed by coprecipitation, (d) thick MWNTs dispersed by coprecipitation.

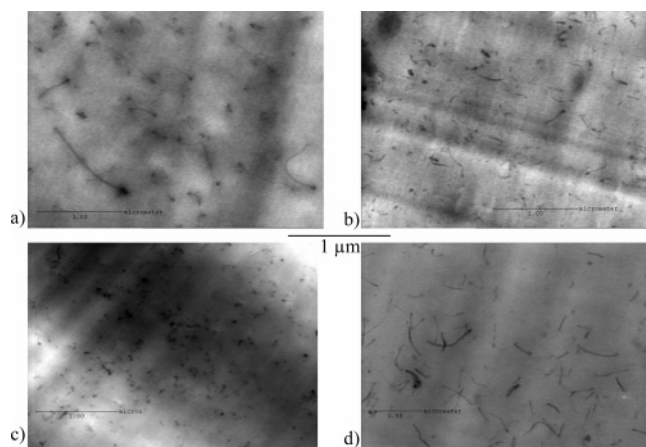


Figure 9. TEM micrographs for (a) PEToc filled with 1% thin MWNTs, (b) PVC filled with 1% thin MWNTs, (c) PC filled with 1% thin MWNTs, and (d) PMMA filled with 1% thin MWNTs.

Due to the high level of conductivity obtained, our samples exhibit competitive performances as microwave absorbers showing good EMI shielding properties. Figure 12 shows the reflectivity for two samples, each having a thickness of 3 cm, using composites of PCL with 0.7 and 1 wt % thin MWNTs (coprecipitated). The reflectivity, noted R , is kept below -9.69 dB ($R < 0.3$) over the whole frequency range, meaning that most of the incident power is entering the composite. This level is improved compared to the reflectivity level reported by Yussouf et al.¹ for thermoplastic rubber composite absorbers

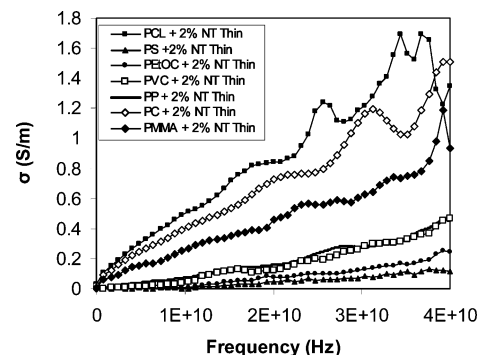


Figure 10. Electrical conductivity as a function of frequency for PCL, PS, PEToc, PVC, PMMA, PC, and PP filled with different contents of thin MWNTs.

loaded with ferrite particles: maxima of reflectivity still higher than -5 dB are observed for the best case (sample thickness of 3 cm). The low reflectivity level of our composites is closely related to high absorbing properties, as shown in Figure 13. The inset of Figure 12 shows the mechanisms involved in shielding/absorbing materials. As already reported by Yussouf et al.,¹ the incident power P_i is divided among the reflected power P_r at the input of the sample, the power P_{abs} absorbed inside the sample by dissipation, and the power P_o remaining at the output of the shielding. The shielding effectiveness, noted SE, is defined as the ratio between the input power P_i and the remaining output power P_o . In our case, SE is higher than 25 dB ($SE > 17.8$), consistent with a negligible power P_o

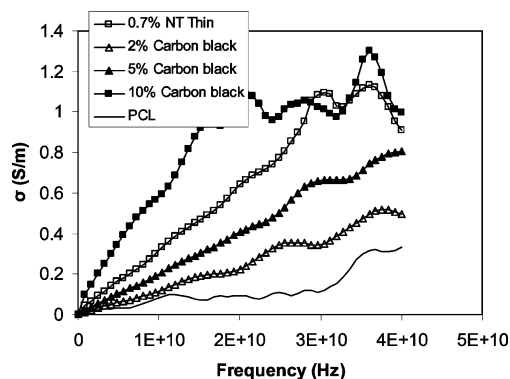


Figure 11. Electrical conductivity as a function of frequency for PCL filled with different contents of carbon black.

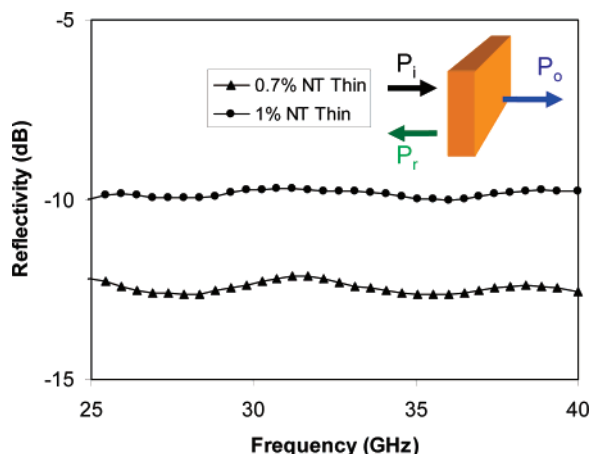


Figure 12. Reflectivity as a function of frequency for PCL filled with MWNTs.

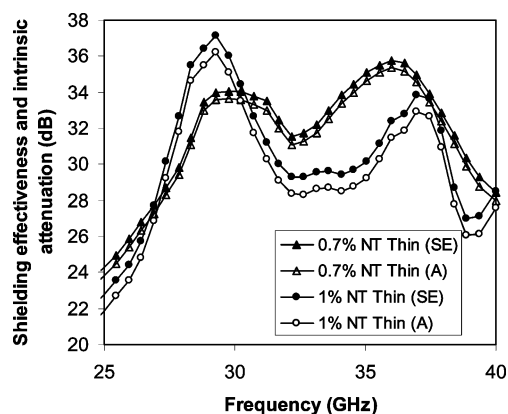


Figure 13. Shielding effectiveness SE and intrinsic absorption A for PCL filled with MWNTs.

beyond the nanocomposite. This high absorbance, combined with a low reflectivity, means that the incident power P_i essentially enters the nanocomposite (very low fraction P_r reflected) and is quasi completely dissipated/absorbed in the conductive sample. The nanocomposite has thus a dual beneficial role. It is a very good absorbent of the radiations, and it is a very effective shield against them. This is confirmed by the fact that very little difference is observed for each sample between SE and the intrinsic attenuation A (also shown as dashed curves in Figure 13, $A > 17.8$): all the incident power is dissipated in the sample, instead of being reflected at its input. The values obtained at 30 GHz for PCL filled with 1 wt % thin MWNTs by coprecipitation ($R = P_r/P_i = 0.1069$, $P_{\text{abs}}/P_i = 0.8928$, and $P_o/P_i = 0.0003$) prove that our composites are good

candidates for microwave absorbers, especially compared to previous work by Yang et al.⁴ where the following values for their composite containing 7 wt % carbon nanotubes were reported ($R = P_r/P_i = 0.8954$, $P_{\text{diss}}/P_i = 0.1021$, and $P_o/P_i = 0.0025$). As they conclude, their “composite is more reflective and less absorptive to electromagnetic radiation, i.e. the dominant EMI shielding mechanism is reflection rather than absorption” ($P_r > P_{\text{abs}}$), while for our composite the absorption due to dissipation of power inside the conductive composite is the dominant effect responsible for EMI shielding ($P_{\text{abs}} > P_r$). The intrinsic absorption per unit length for our composite with 1 wt % MWNTs at 30 GHz is above 1.12 dB/mm, meaning $A = 4$ dB for a 3.5 mm thick sample. This value is superior to those reported by Das et al.² for carbon fiber loaded composites, which also exhibit a much higher reflectivity ($R > -5$ dB in ref 2, Figure 9). It must be noted that the intrinsic absorption A and thus the SE value (dB) are directly proportional to the electrical conductivity, which means that a 2 times higher conductivity results in a 2-fold increase in SE. Any increase in conductivity is thus crucial. In conclusion, the nanocomposites prepared in this work act as typical EMI shielding materials, because the output power is highly attenuated and the shielding performances are due to a remarkable internal absorption associated with power dissipation inside the conductive material rather than to a high reflection of the input power.

Conclusions

Thin and thick MWNTs have been dispersed within PCL by melt-blending and coprecipitation, respectively, with the purpose to prepare materials dedicated to EMI shielding. The thicker MWNTs are more effective in improving Young's modulus and in imparting electrical conductivity to PCL. However, this type of nanotube, which is more fragile than thin MWNTs due to structural defects, is broken down when dispersed within PCL by melt-blending such that percolation occurs at a lower MWNT content when the coprecipitation technique is used. Then the electrical conductivity is higher than 1 S/m in a large frequency range at an MWNT content as low as 0.7 wt %, which is a prerequisite for EMI shielding to be effective. With such a value of conductivity, our composites exhibit a reflectivity lower than -10 dB (good absorbers), with a very good shielding effectiveness (>20 dB) resulting from absorption inside the composite rather than reflection of the input energy.

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References and Notes

- (1) Yusoff, A. N.; M. Abdullah, H.; Ahmad, S. H.; Jusoh, S. F.; Mansor, A. A.; Hamid, S. A. A. *J. Appl. Phys.* **2002**, 92 (2), 876–882.
- (2) Das, N. C.; Khastgir, D.; Chaki, T. K.; Chakraborty A. *Composites, Part A* **2000**, 31 (10), 1069–1081.
- (3) Kim, H. M.; Kim, K.; Lee, C. Y.; Joo, J.; Cho, S. J.; Pejakov, D. A.; Yoo, J. W.; Epstein, A. *J. Appl. Phys. Lett.* **2004**, 84 (4), 589.
- (4) Yang, Y.; Gupta, M. C.; Dudley, K. L.; Lawrence, R. W. *J. Nanosci. Nanotechnol.* **2005**, 5 (6), 927–931.
- (5) Kim, W. S.; Song, H. S.; Lee, B. O.; Kwon, K. H.; Lim, Y. S.; Kim, M. S. *Macromol. Res.* **2002**, 10 (5), 253–258.
- (6) Lopez Manchado, M. A.; Valentini, L.; Biagiotti, J.; Kenny J. M. *Carbon* **2005**, 43, 1499–1505.
- (7) Seo, M. K.; Lee, J. R.; Park, S. J. *Mater. Sci. Eng., A* **2005**, 404, 79–84.

- (8) Seo, M. K.; Park, S. J. *Chem. Phys. Lett.* **2004**, *395*, 44–48.
- (9) McNally, T.; Potschke, P.; Halley, P.; Murphy, M.; Martin, D.; Bell, S. E. J.; Brennan, G. P.; Bein, D.; Lemoine, P.; Quinn, J. P. *Polymer* **2005**, *46*, 8222–8232.
- (10) Du, F.; Fischer, J. E.; Winey, K. I. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 3333.
- (11) Du, F.; Scogna, R. C.; Zhou, W.; Brand, S.; Fischer, J. E.; Winey, K. I. *Macromolecules* **2004**, *37* (24), 9048–9055.
- (12) Jiang, X.; Bin, Y.; Matsuo, M. *Polymer* **2005**, *46*, 7418–7424.
- (13) Zhang, B.; Fu, R. W.; Zhang, M. Q.; Dong, X. M.; Lana, P. L.; Qiu, J. S. *Sens. Actuators, B* **2005**, *109*, 323–328.
- (14) Moon, S. I.; Jin, F.; Lee, C. J.; Tsutsumi, S.; Hyon, S. H. *Macromol. Symp.* **2005**, *224*, 287.
- (15) Saib, A.; Bednarz, L.; Daussin, R.; Bailly, C.; Lou, X.; Thomassin, J. M.; Pagnoulle, C.; Detrembleur, C.; Jerome, R.; Huynen, I. *IEEE Trans. Microwave Theory Tech.* **2006**, *54*, 2745–2754.
- (16) Huynen, I.; Steukers, C.; Duhamel, F. *IEEE Trans. Instrum. Meas.* **2001**, *50*, 1343–1348.
- (17) White, D. R. J. *A handbook on electromagnetic shielding materials and performances*; Library of Congress: Washington, DC, 1975.
- (18) Pötschke, P.; Abdel-Goad, M.; Alig, I.; Dudkin, S.; Lellinger, D. *Polymer* **2004**, *45*, 8863–8870.
- (19) Bhattacharyya, A. R.; Pötschke, P.; Abdel-Goad, M.; Fischer, D. *Chem. Phys. Lett.* **2004**, *392*, 28–33.
- (20) Mitchell, A.; Bahr, J. L.; Arepalli, S.; Tour, J. M.; Krishnamoorti, R. *Macromolecules* **2002**, *35*, 8825–8830.