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Foams of polycaprolactone/MWNT nanocomposites for efficient EMI reduction

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Abstract: Nanocomposites of polycaprolactone (PCL) filled with multi-walled carbon nanotubes (MWNTs) were foamed by supercritical CO_2 in order to prepare materials with reduced electromagnetic interference (EMI). Two mixing techniques were used, *i.e.*, melt blending and co-precipitation. Shielding efficiency as high as 60 to 80 dB together with a low reflectivity was observed at a very low vol% of MWNTs (0.25 vol%). The reflectivity of the nanocomposites was advantageously decreased upon foaming. The uniformity of the open-cell structure was assessed by scanning electron microscopy. These foamed PCL/MWNT nanocomposites are very promising EMI shielding materials because their performances result from absorption at low filler content and not from reflection at relatively high filler content as was previously the case.

Introduction

Electromagnetic interferences (EMI) may be defined as electromagnetic radiation emitted by electrical circuits under current operation. These EMI signals are undesirable because they disturb the good working of the electronic appliances and they may cause radiative damage to the human body.[1] Nowadays, electrical circuits are shielded with metal sheets or composites.[2,3] Metal shields have the inconvenience of poor mechanical flexibility, exceedingly high weight, propensity to corrosion, and limited tuning of the shielding effectiveness (SE). In contrast, polymers offer lightness, low cost, easy shaping, *etc.* Nevertheless, most of them cannot prevent electromagnetic waves from propagating because of their electrical insulating properties. The best strategy to overcome this problem consists of dispersing electrically conductive fillers within polymer matrices.[4,5] For instance, polymers have been filled with carbon (*e.g.*, carbon black, carbon fibers and carbon nanotubes) and investigated as EMI shields.[6-9] Carbon nanotubes are however superior to conventional carbon fillers because of their high aspect ratio and low percolation threshold (<5 wt%) that can be reached whenever the dispersion is fine. In this respect, there is a need for very effective dispersion techniques, thus able to disrupt the large van der Waals interactions that stem from the large surface area of the nanotubes. Melt blending and co-precipitation are two dispersion techniques that were compared for the preparation of multi-walled carbon nanotube (MWNT)/polycaprolactone (PCL) nanocomposites.[10] Although good dispersions were observed in both cases, the EMI shielding properties were higher for the samples prepared by co-precipitation, because the length of the carbon nanotubes was less extensively decreased than by melt blending. A major drawback of nanocomposites that contain carbon nanotubes,[11] or other fillers (nickeled carbon fibers, stainless steel fibers,...[12]), is a high propensity to reflect the electromagnetic radiation rather than to absorb it. Although this reflection stops the wave propagation beyond the composite material (shielding effect, P_o, being close to 0 in Fig. 1a), electromagnetic interference prevails in the inner volume as a result of multiple reflections from the walls ($P_r > 0$ in Fig. 1a). These reflections cause damage, *e.g.*, in the case of electronic circuits, because of spurious interferences between the constitutive electronic components: transistors T, resistors R and chips, as illustrated in Fig. lb. For these deleterious effects to be cancelled (P_r close to 0) while preserving the shielding effect (P_o close to 0), the electromagnetic waves must be absorbed by the protecting material and attenuated by conductive dissipation.

For an EMI shielding material to absorb electromagnetic radiation, the dielectric constant must be as close to that of air as possible. 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, and the wave impedance is proportional to the inverse of the dielectric constant of the medium. A straightforward approach to this highly desirable situation may be found in the foaming of carbon nanotube containing polymers. The relative volume of air in an open-cell foam is indeed very high, which is very favorable for the matching of the wave impedances of the expanded material and the ambient atmosphere.

Yang *et al.* previously reported on the foaming of carbon fiber[12] and carbon nanotube[11] containing polymers for applications in EMI shielding. However, these foams were quite heterogeneous, with a relatively high density, so

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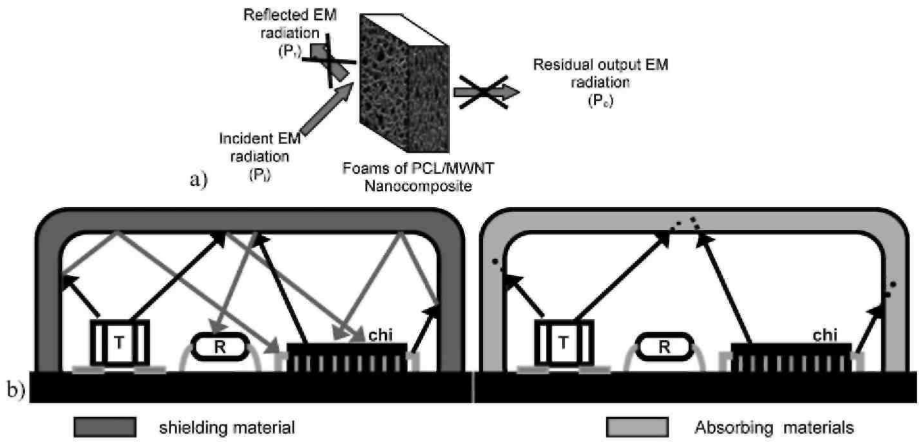
accounting for good EMI shielding effectiveness (20 dB) only at high nanotube content (7 wt% of MWNT). Moreover, these foams were "more reflective and less absorptive to electromagnetic radiation, *i. e.*, the dominant EMI shielding mechanism was reflection rather than absorption", as stated by the authors.[11] The reflectivity, *R*, was indeed 0.81, thus -1.83 dB, which is high compared to absorbers in the marketplace *(R* < -10dB), while the ratio of dissipated to incident power was low, P_{diss}/P_i = 0.1021. Clearly, the shielding effect resulted from a quasi-total reflection of the signal at the input interface *(R*, P_r/P_i close to 1) rather than from penetration within the composite and internal attenuation by conductive dissipation.

Fig. 1: *a) Behavior of PCL/MWNT nanocomposite foams under EMI radiation, b) differences between an EMI shielding material and an EMI absorber in an electronic device.*



In this work, MWNT/PCL nanocomposites were foamed by supercritical CO_2. Foams with a high cell density were accordingly prepared, and their EMI reduction was studied in relation to the MWNT content. Special attention was paid to the adsorption/reflection ratio, the purpose being to preserve the shielding (P_o/P_i low) and to minimize the interference by reflection (P_r/P_i low).

Experimental

Materials

Commercially available thin MWNTs (average outer diameter: 10 nm, purity higher than 95 wt%) produced by Catalytic Carbon Vapour Deposition (CCVD) were supplied by "Nanocyl S.A.", Belgium. Poly(ε-caprolactone) (PCL) was a gift from Solvay Interox (Capa® 6500, M_n = 50 000 g mol^{-1}).

Preparation and foaming of PCL nanocomposites

The MWNT/PCL nanocomposites were prepared by two techniques. According to the first technique, the polymer was melt blended with the required amount of MWNT at 80 °C in a 5 cm^3 DSM microextruder under nitrogen at 200 rpm for 10 min. In the second method (co-precipitation), PCL was first dissolved in THF (2 wt%) followed by the addition of the required amount of MWNT. After 30 min of ultrasonication, the solution was precipitated in heptane.

In a 316 stainless steel high pressure cell (100 ml) from Parr Instruments, a sample (35 x 25 x 8 mm) of PCL nanocomposite was pressurized with CO_2 to 45 bar with an ISCO 260D high pressure syringe pump. The cell was then heated to 60 °C, and compressed CO_2 was finally added to a final pressure of 200 bar. This saturation pressure was maintained for 3h before being released within a few seconds. The cell was then opened, and the expanded nanocomposite was recovered.

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Characterization

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

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

Electrical properties of MWNT/polymer composites were measured with a Wiltron 360B Vector Network Analyzer (VNA) in a wideband frequency range from 40 MHz to 40 GHz. The line-line method[13] 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 the reflectivity and shielding efficiency. The same line-line method was applied to foamed nanocomposites, except that the microstrip lines were replaced by waveguide lines containing the foamed samples, according to the method reported for liquids.[13] The reference thickness for all the samples (foamed and unfoamed) was 2 cm.

Results and discussion

As reported in the Experimental, MWNT/PCL nanocomposites were prepared by melt blending and by co-precipitation. The morphology of these nanocomposites was investigated by TEM. An uniform dispersion of individual MWNTs was observed in both cases,[10] and the percolation threshold was determined by rheology (<0.33 vol%) as reported in a previous publication.[10] In contrast to co-precipitation, melt blending was responsible for a decrease in the length of the nanotubes in agreement with inferior EMI shielding properties.

The MWNT/PCL nanocomposites were foamed with supercritical CO_2 as an expanding agent with the prospect of decreasing the material permittivity, and thus the reflectivity, and promoting the percolation of the carbon nanotubes.

Fig. 2: *SEM micrographs of PCL foams filled with a) 0 vol% of thin MWNTs, b) 0.1 vol% thin MWNTs (melt-blending), c) 0.222 vol% thin MWNTs (melt-blending), d) 0.107 vol% thin MWNTs (co-precipitation) and e) 0.249 vol% thin MWNTs (co-precipitation).*

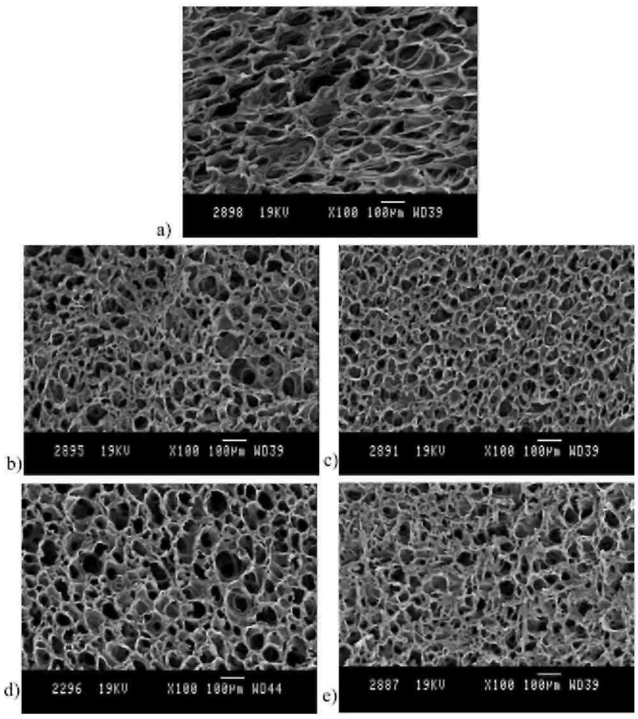

Fig. 2 compares the SEM micrographs for PCL foams containing 0, 0.1 and 0.222 vol% MWNTs prepared by melt blending and PCL foams containing 0, 0.107 and 0.249 vol% MWNTs prepared by co-precipitation. The unloaded PCL foams exhibit a non uniform open-cell structure with pores larger than 100 µm. Upon addition of

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0.222 vol% MWNTs, the porous morphology is better defined with smaller pores and a higher cell density. The MWNTs have more likely a twofold role, *i.e.*, they increase the internal viscosity at 60 °C and they act as nucleating agents, so leading to a larger number of cells growing to a smaller size. This is a general observation whenever the expanded polymer is preloaded with inorganic fillers, such as nanoclays.[14]

The density of the foams and the actual content (vol%) of carbon nanotubes are reported in Table 1. Compared to the PCL density, the average volume expansion of the nanocomposites upon foaming is close to five. The volume content of the MWNTs is decreased within the same ratio, for instance a decrease from 0.5 to 0.1 vol% is noted for the 1 wt% filled PCL prepared by melt blending. The foam density increases with the MWNT content, as result of a lower chain mobility at the foaming temperature. This effect is amplified by the actual length of the nanotubes, which is higher in samples prepared by co-precipitation (see above).

The EMI shielding properties of the nanocomposites were quantified in the microwave frequency range (40 MHz-40 GHz) by using transmission line sections filled with PCL, loaded or not with MWNTs, before and after foaming. The experimental setup is similar to that described elsewhere[13] for the measurement of planar substrates and soil or liquid samples. More attention was however paid to the Kα band [26-40 GHz], because of the increasing need for EMI absorbers in radar and satellites that operate in this frequency range. Electrical conductivity is of the utmost importance for EMI performance, because it expresses the intrinsic ability of the material to absorb electromagnetic waves.[15] As a rule, a good electromagnetic absorber must exhibit a conductivity higher than 1 S m^{-1} and a real part of the effective dielectric constant as close to 1 as possible.[16] Fig. 3 shows that the electrical conductivity of PCL foams filled with MWNTs is high even at very low nanofiller content (<0.25 vol%). This conductivity is systematically higher for nanocomposites prepared by co-precipitation than by melt blending at the same filler content. The same behavior was previously reported for unexpanded samples,[10] more likely because the original length of the nanotubes was better preserved in the case of co-precipitation. Then, the electrical conductivity was higher than 4 S m^{-1}, largely exceeding the target value for good EMI shielding properties (*i.e.*, 1 S m^{-1}).

The beneficial effect of the foaming of PCL/MWNT nanocomposites prepared by co-precipitation (Fig. 3b) has been analyzed on the basis of the electromagnetic properties of foamed and unfoamed nanocomposites of a comparable volume content of carbon nanotubes (Fig. 4). Clearly, foaming improves importantly the electrical conductivity (Fig. 4a), as exemplified by a foam that contains 0.107 vol% of MWNTs and has almost the same conductivity as an unfoamed sample with 0.16 vol% of nanotubes. Similarly, a foam with 0.249 vol% of MWNTs has a two times higher conductivity than an unfoamed sample filled with 0.48 vol% of MWNTs. The EMI shielding effectiveness (SE), defined as the P_r/P_i ratio of the output to the incident power, is directly related to the electrical conductivity, as illustrated in Fig. 4b (to be compared to Fig. 4a). Indeed, foamed and unfoamed samples of comparable conductivity have comparable shielding efficiencies, and the SE of the PCL foam containing 0.249 vol% of MWNTs is in the 60 to 80 dB range, thus three to four times higher than the SE of the unfoamed counterpart. This very high SE also exceeds the 20 dB reported for a foam of polystyrene/MWNT nanocomposite containing 7 wt% MWNTs.[11] The herein reported shielding effectiveness, expressed in dB, is thus directly proportional to the conductivity, which means that SE is increased by a factor of two whenever the conductivity is doubled. Although the conductivity of the PCL/MWNT composites is several orders of magnitude lower than the conductivity of bulk CNTs (approximated to the conductivity of graphite), merely because of a dispersion effect, the reported conductivity of only 1-5 S m^{-1} is enough for the foamed nanocomposites to exhibit excellent EMI shielding. The direct proportionality between shielding effectiveness and conductivity observed in Fig. 4a and b means that the shielding effect actually results from the absorption of the incident signal power entering the composite and its conductive dissipation through the material thickness. This conclusion is also confirmed by the experimental reflectivity (*R*) of the nanocomposites, which is quite an important characteristic feature of EMI shielding and microwave absorbing materials. It depends on the mismatch between the dielectric constants of the material and the surrounding atmosphere (air). In order to minimize the reflectivity, the dielectric constant of the material must be as close to unity as possible. It is however known that dispersion of a conductive additive within an insulating polymer results in a higher dielectric constant proportional to the final conductivity.[17] In this work, the foaming of nanocomposites allows the dielectric constant to be maintained below 4, even at the higher conductivity observed, as illustrated in Fig. 4c by the comparison of the dielectric constants, ϵ_r, of the unfoamed and foamed samples. For the sake of comparison, the dielectric constants of foamed and unfoamed PCL are also reported. Clearly, the dielectric constant of the PCL foam is close to one ($\epsilon_r = 1.2$), nearly two times lower than that of unexpanded PCL ($\epsilon_r = 2.2$). For this reason, the dielectric constant of foamed PCL filled with 0.24 vol% MWNT ($\epsilon_r = 3.5$ at 30 GHz) is comparable to those of unfoamed PCL containing 0.16 and 0.48 vol% of nanotubes ($3 < \epsilon_r < 4$), although the conductivity is roughly 3 to 4 times higher. Moreover foamed PCL with 0.107 vol% MWNT, which exhibits similar shielding effectiveness as the 0.16 vol% MWNT filled unfoamed PCL (28 dB *vs.* 24.2 dB at 30 GHz), exhibits a much lower reflectivity (-12.25 dB *vs.* -10.5 dB at 30 GHz), as result of a lower dielectric constant (ϵ_r = 2.35 *vs.* ϵ_r = 3.3 at 30 GHz). Foaming of PCL nanocomposites is thus an easy and effective way to provide carbon nanotube filled polyesters with a highly desirable combination of shielding efficiency in the 20-80 dB range and reflectivity lying between -15 and -8 dB. These performances are superior to those reported elsewhere[11,12] for foams loaded with 15 wt% carbon fibers, for which the EMI shielding mainly originates from a high reflectivity. Indeed, the 15 wt% loading is responsible for a high dielectric constant (>30) and thus a reflection phenomenon at the input interface. Similarly, PS foams loaded with 7 wt% carbon nanotubes have a SE of 20 dB together with a reflectivity of only -1.83 dB (R = 0.81). Again, reflection is the major contribution to the EMI shielding rather than absorption. In this work, the foaming of the nanocomposites decreases the dielectric constant and thus the reflection at the input interface, whereas the proper dispersion of the CNTs within the polymer provides, even at a low loading (<l vol%), a conductivity high enough for electromagnetic waves to be attenuated by conductive dissipation. The strategy proposed in this work is thus basically different from that previously reported[11,12] because the EMI reduction is the result of absorption at low filler content, and not of reflection at relatively high filler content *via* a higher dielectric constant.

Table 1: *Density and composition (vol%) of nanocomposite PCL foams*

Wt% of MWNT	Method	Density of the foam[a]/kg m^{-3}	Vol% of MWNT before foaming	Vol% of MWNT after foaming
0		180	0	0
1	Melt-blending	225	0.48	0.1
2	Melt-blending	245	0.96	0.222
4	Melt-blending	285	1.92	0.541
0.5	Co-precipitation	230	0.24	0.049
1	Co-precipitation	255	0.48	0.107
2	Co-precipitation	310	0.96	0.249

[a] Density of PCL = 1100 kg m^{-3} and density of thin MWNTs = 2300 kg m^{-3}.

Fig. 3: *Dependence of the electrical conductivity on frequency for expanded MWNT/PCL nanocomposites: a) thin MWNTs previously dispersed by melt blending, b) thin MWNTs previously dispersed by co-precipitation.*

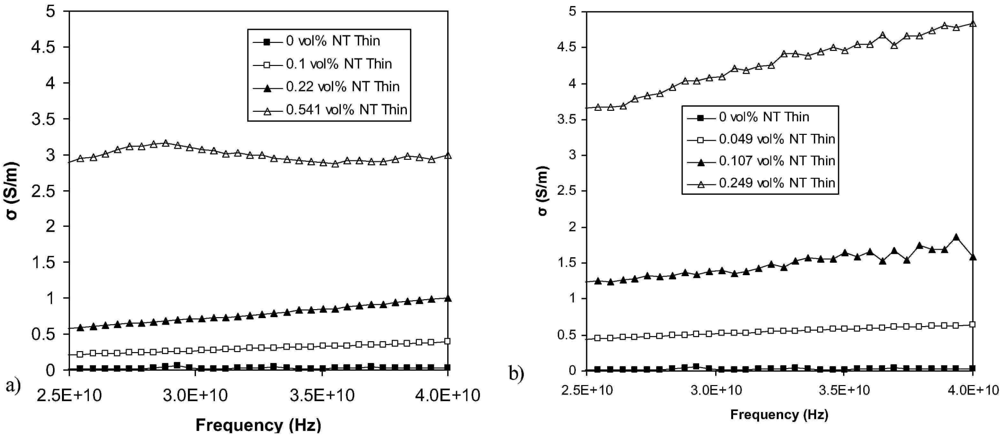
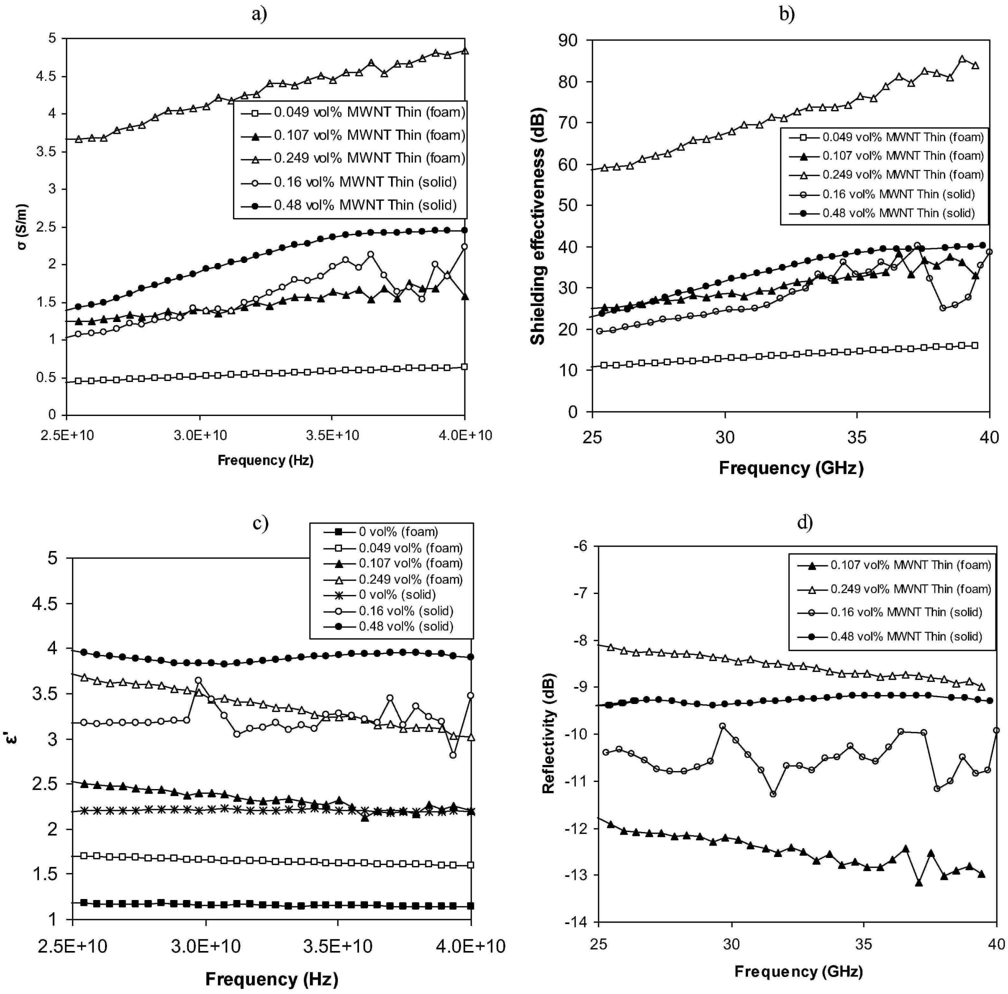


Fig. 4: *Electromagnetic properties of foamed and unfoamed MWNT/PCL nanocomposites prepared by coprecipitation: (a) conductivity, (b) shielding efficiency SE, (c) dielectric constant ϵ_r and (d) reflectivity R.*



Conclusion

New multi-walled carbon nanotube filled PCL foams with an uniform open-cell structure were successfully prepared with supercritical CO_2 with the purpose of preparing EMI shielding materials. Carbon nanotubes were dispersed within PCL by melt-blending and by co-precipitation. Shielding efficiencies as high as 60 to 80 dB together with low reflectivities was observed at very low vol% of MWNTs (0.25 vol%). Compared to unfoamed MWNT/PCL nanocomposites, the expanded nanocomposites prepared in this work have much higher shielding efficiencies and lower reflectivities.

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