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Polymeric Films with Electric and Magnetic Anisotropy Due to Magnetically Assembled Functional Nanofibers

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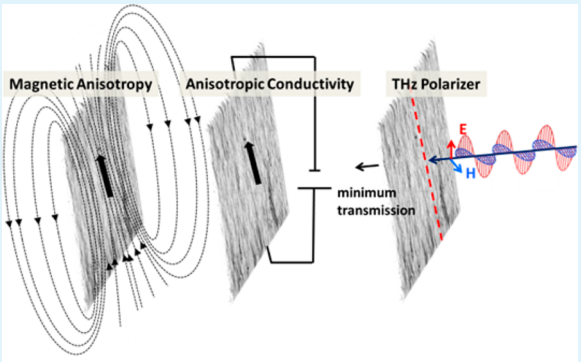
Supporting Information

ABSTRACT: We demonstrate the fabrication of free-standing polymeric nanocomposite films, which present magnetic and electrically conductive anisotropic properties. Magnetically functionalized carbon nanofibers are dispersed in a polymeric solution and, upon casting under a weak external magnetic field, are easily oriented and permanently assembled in a head-to-tail orientation in the polymer film during solvent evaporation. Magnetic and conductive property studies reveal that the resulting films have a high degree of anisotropy in both cases, thus allowing their use in functional complex devices. As a proof of concept, we demonstrate the potential application of these films as flexible THz polarizers. The detailed study shows that very high attenuation values per unit film thickness and fiber mass concentration are achieved, paving thus the way for cost-effective fabrication of substrate-free systems that have advantage over conventional devices realized so far.



KEYWORDS: *magnetophoretic transport, carbon nanofibers, polymer nanocomposites, anisotropy, THz polarizers*

INTRODUCTION

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) can be used as building blocks in nanocomposite materials with engineered physicochemical properties targeting mechanical reinforcement,[1,2] thermal conductivity modification,[3] superhydrophobicity,[4] or even shielding against electromagnetic interference,[4,5] among many possible applications. The high aspect ratio of CNTs and CNFs allows the realization of anisotropic polymeric nanocomposites with enhanced performance in a preferred direction, by controlling and manipulating their orientation. Although CNFs have received less attention as nanofillers compared to CNTs, due to the superior mechanical properties, smaller diameter, and lower density of the latter, CNFs can be an excellent alternative due to their wide availability and lower cost.[6]

The works published on randomly oriented CNFs in polymer matrices[7−9] are more numerous than the respective ones with aligned CNFs. Indeed, CNF alignment in a polymeric matrix is a complicated process and can be partially obtained by methods like mechanical stretching,[10] flow alignment,[2] and compression molding[3] or by application of external electric[11] or magnetic fields,[12] to name a few. Electric fields not only require direct contact of electrodes with the sample but also high-strength fields, which limit broad applicability due to the higher risk for sample damage. On the other hand, magnetic fields offer the possibility of fabricating anisotropic films in a large scale and in a contact-free manner. However, due to the extremely low magnetic susceptibility of CNFs, the dipole moments induced by the magnetic field are insufficient to cause magnetophoretic alignment along the direction of the applied field during the curing of the host polymer. Such alignment has been achieved to date only with extremely high magnetic fields (28T),[12] making this approach impractical. Magnetophoretic alignment can be achieved only partially with lower fields in organic matrices with very low viscosity. Such type of assembly, however, cannot modify the macroscopic electric or magnetic properties of the hybrid system.[13] Therefore, various research groups have tried to functionalize the CNFs with magnetic coatings or nanoparticles[14−17] in order to increase their magnetic susceptibility and facilitate their alignment into polymer matrices under lower field intensities.[14] Such

Received: January 16, 2014
Accepted: February 27, 2014
Published: March 13, 2014

   dx.doi.org/10.1021/am500335u | ACS Appl. Mater. Interfaces 2014, 6, 4535−4541

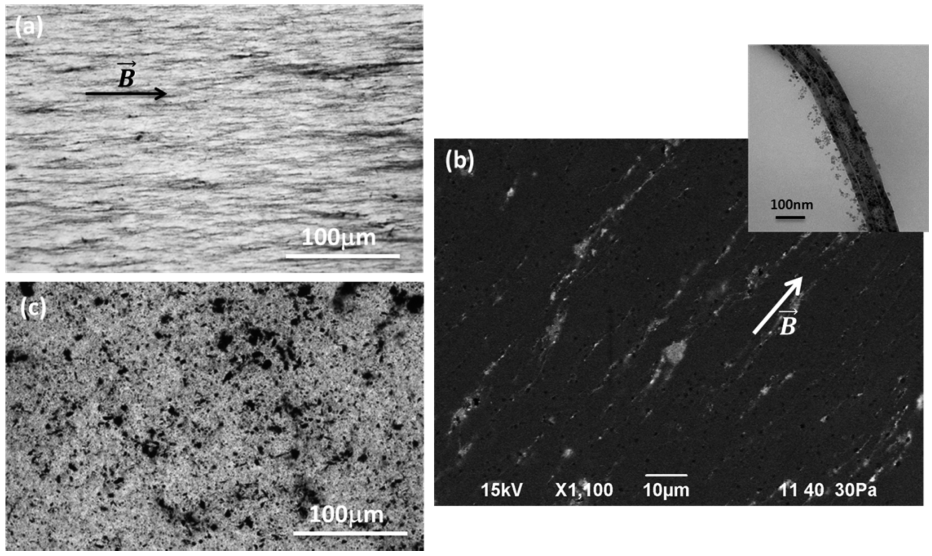


Figure 1. Optical microscope (a) and SEM (b) images of a MCNF/PMMA film formed under a magnetic field of 150 mT. The bright areas in (b) represent the nanoparticle filled MCNFs. The inset in (b) depicts TEM image detail taken from a thin cross sectional slice of the same film. The nanoparticles shown outside of the fiber were drawn out by the mechanical shear stresses during the sample microtoming process. (c) Optical microscope image of a MCNF/PMMA film formed without a magnetic field.

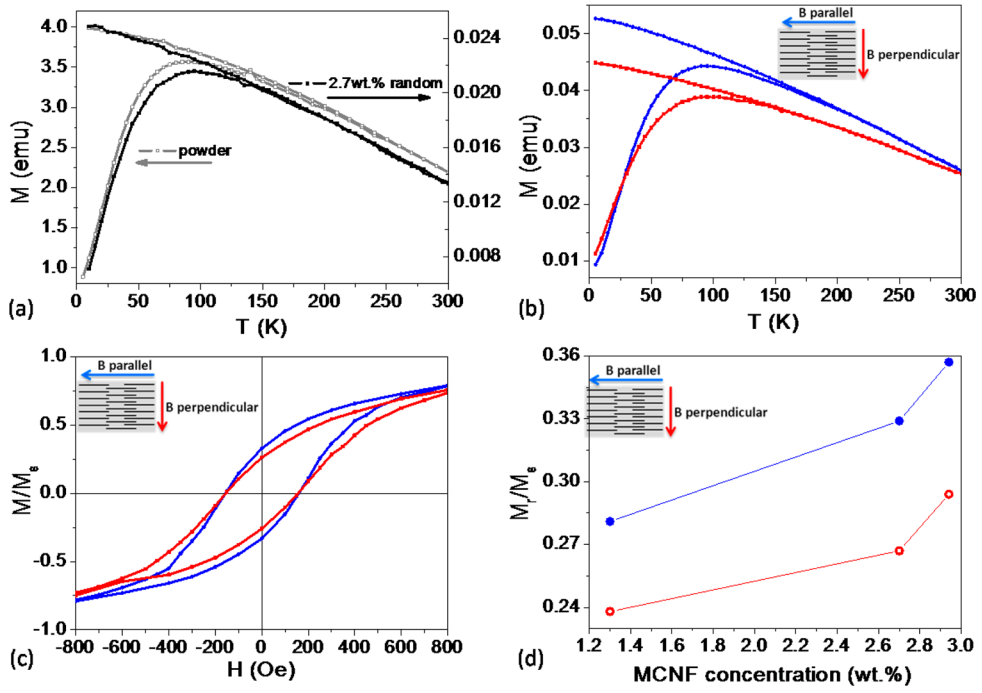


Figure 2. ZFC/FC magnetization curves for (a) MCNFs in powder form and a film consisting of 2.7 wt.% MCNFs randomly oriented in PMMA; (b) 2.7 wt.% MCNFs/PMMA film containing aligned MCNF wires. The direction of the external magnetic field applied during the measurement is parallel or perpendicular to the wires, as indicated in the schematic. (c) Low temperature (2.5 K) hysteresis loops of the same film, at the two orientations. Magnetization values were normalized to the saturation magnetization (M_s) in each case. (d) Reduced remanent magnetization (M_r/M_s) for the two orientations at various concentrations of the aligned MCNFs in PMMA films.

approaches simplify the fabrication process of anisotropic nanocomposites, but the magnetic fields used so far have still been very high, limiting the broad application of such systems.

Herein, we report the use of low magnetic field to fabricate free-standing thin films of magnetic nanocomposites with anisotropic electromagnetic properties. Magnetic CNFs (MCNFs) fabricated with a simple nonchemical technique[18] have been introduced as fillers in the polymer matrix. In particular, we show that it is possible to form plastic films that are a few tens of micrometers thick, with highly anisotropic magnetic and conductive properties, by applying just ~150 mT magnetic field, to efficiently align the MCNFs into the drying polymer matrix. The advanced properties of such polymeric films allow their use as fundamental components in diverse devices, and as a proof of concept we explore their functionality in electromagnetic wave systems. Indeed we demonstrate that the developed films exhibit THz polarizer characteristics. This is an innovative aspect for a cost-effective, environmentally

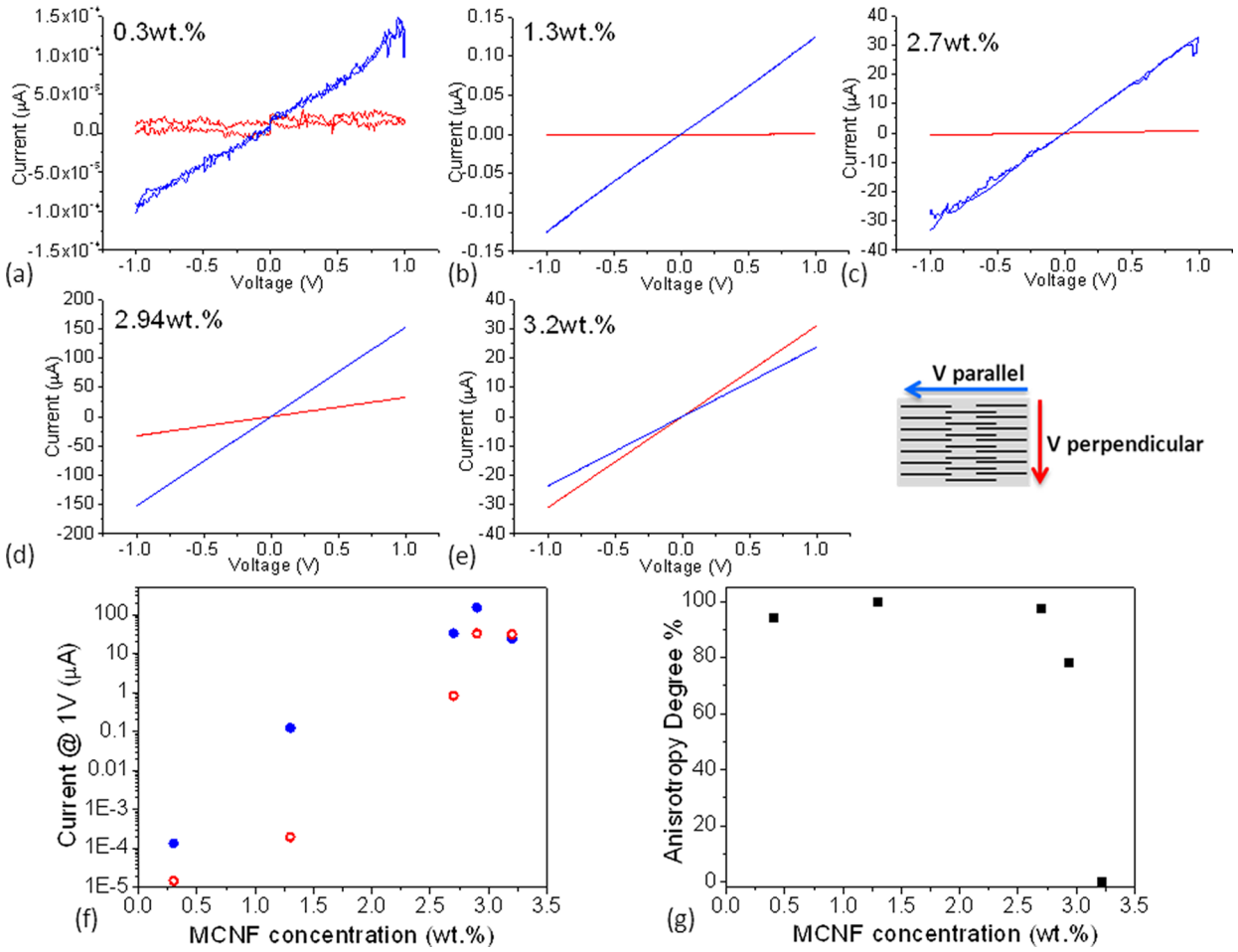


Figure 3. (a-e) I–V curves of MCNF/PMMA films with MCNFs aligned parallel and perpendicular to the applied DC voltage, as indicated in the inset schematic, for different MCNF concentrations. (f) Current recorded after application of 1 V in parallel and perpendicular direction with respect to the MCNF wires in nanocomposite films with different MCNF concentrations. (g) Anisotropy degree of the film electroconductive properties for each concentration.

friendly, scalable fabrication of substrate-free THz polarizers when compared to conventional devices realized so far[19−23] with expensive, heavy, fragile, or bulky components, complex and time consuming fabrication techniques, or aggressive chemicals, all of which are important limiting factors. Furthermore, as previously demonstrated,[24] starting from a monomer-MCNF solution and thermally or photopolymerizing during the magnetic alignment of the MCNFs offers the possibility to easily incorporate such type of systems in integrated devices as partial components, by their in situ formation in specific areas.

RESULTS AND DISCUSSION

As previous studies have shown, magnetic wires of controlled shape and spatial distribution can be formed into polymer matrices by the magnetophoretic transport and assembly of colloidal magnetic nanoparticles induced by external magnetic fields during the polymer curing/drying step.[25,26] The efficiency of these films as magnetic detectors[24] or in radiofrequency applications[27] has been successfully demonstrated. Using the same approach, small amounts (<3.5 wt.%) of MCNFs are mixed with poly(methyl methacrylate) (PMMA) in a common solvent, and after drop casting and solvent evaporation under an external magnetic field of ca. 150 mT, nanocomposite films with morphology similar to that shown in Figure 1a are formed. The formation of such structures is attributed to the magnetic properties of the MCNFs (Supporting Information Figure S1) provided by the presence of iron oxide nanoparticles intercalated in the open ended CNFs (Supporting Information Figure S2). This is accomplished following a nonchemical technique that involves ultrasonication of CNFs and nanoparticles in suspension and subsequent self-sustained concentration gradient driven filling.[18] The magnetic moment of the nanoparticles filling the MCNFs, as induced by the external magnetic field, causes the magnetophoretic transport and assembly of the MCNFs parallel to the field's direction in a head-to-tail orientation, resulting in elongated wirelike structures immobilized and distributed throughout the film. This is further supported by SEM analysis (Figure 1b) where it is clearly demonstrated that the magnetic nanoparticles embedded in the MCNFs are assembled parallel to the external field direction. When films are dried in the absence of the field, the MCNF arrangement is completely different, as shown shown in Figure 1c, where aggregated structures of nondefined shape and size are distributed randomly in the polymer.

A magnetic study of the MCNF/PMMA films reveals that the nanocomposites maintain the magnetic behavior of the pristine MCNF powder, as shown by the Zero-Field-Cooled/Field-Cooled (ZFC/FC) magnetization curves reported in Figure 2a. Indeed, the value of the mean blocking temperature

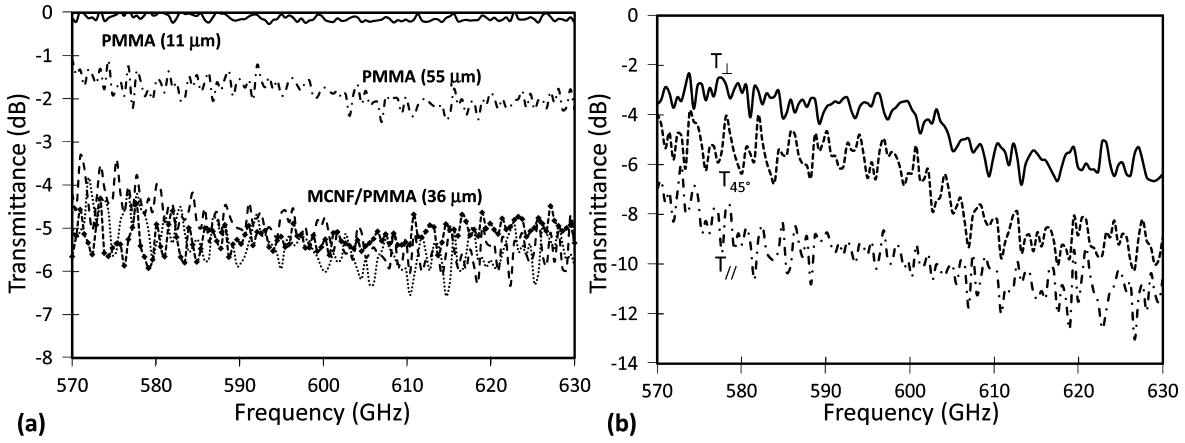


Figure 4. THz transmittance measurements for (a) pure PMMA and unaligned (isotropic) 2.2 wt.% MCNF-PMMA composite films, and (b) for anisotropic MCNF/PMMA films (2.2 wt.%, average thickness ~44 ± 2.2 μm) placed at different orientations with respect to the waveform direction.

(T_B) estimated by the maximum of the ZFC curve is ca. T_B = 90 K for both MCNF powder and MCNF/PMMA film, indicating that the polymeric system is superparamagnetic at room temperature. As already discussed, when an external magnetic field is applied during the film formation, the MCNFs assemble and preferentially orient parallel to the field, forming long wirelike structures. The resulting MCNF/PMMA films present anisotropic magnetic properties for all concentrations studied, as shown in Figure 2b,c,d (see also Figures S3, S4 of the Supporting Information). In particular, the temperature dependent magnetizations of the structured films show a strong directional dependence on the orientation of the applied field with respect to the MCNF alignment, with maximum difference between parallel and perpendicular directions located around T_B. The higher magnetization observed for the parallel orientation is consistent with previous studies[24] and with the different roles of internal fields expected for the two orientations.[28] Moreover, the hysteresis loops measured in the blocked state (2.5 K $\ll$ T_B) show a clear directional dependence, as seen in Figure 2c (see also Supporting Information Figure S4). In particular, while the coercive field is not much affected by the applied field orientation, the remanent magnetization (M_r) measured in the parallel direction is higher than in the perpendicular direction, with the relative difference between the two varying from 15% to 19% in the range of the MCNF concentration studied (1.3 wt.% to 2.94 wt. %) (Figure 2d). The performance of the system could be further improved by enhancing the magnetic character of the CNFs, for example by functionalizing the nanofibers with ferromagnetic nanoparticles[36] or by increasing the concentration of the nanoparticles in the MCNFs.

Additionally to the magnetic properties, the MCNFs are also electroconductive and thus are expected to modify the electrical properties of the insulating PMMA matrix. In fact, as the MCNF loading in PMMA increases, the DC current recorded at a fixed applied voltage becomes higher due to the formation of new conductive paths into the polymer matrix (Supporting Information, Figure S5). Most importantly, the change of the spatial distribution of the MCNFs by applying the external magnetic field during film formation, results in highly anisotropic conductive films, in agreement with other studies on aligned CNFs or CNTs in polymer films.[29−32] Indeed, as DC current−voltage (I−V) curves demonstrate, all films exhibit a stable linear Ohmic I−V behavior, becoming conductive from very low MCNF concentrations when the DC voltage is applied in a parallel direction to the MCNF orientation (Figure 3a-e). On the other hand, when voltage is applied in the perpendicular direction, the current recorded is very low proving that the spatial arrangement of the MCNFs facilitates percolation only in a specific direction into the matrix. However, as the overall MCNF concentration increases, this directional dependence becomes less evident,[32] since conductive paths are now formed also laterally between the assembled wires that are distributed much closer to one another as compared to films with lower concentrations (Figure 3f). Indeed, for concentrations lower than 2.94 wt.%, the anisotropy degree, defined in the experimental part, is higher than 95%, while at higher concentrations the anisotropic property disappears (Figure 3g).

The anisotropic MCNF/PMMA films can be used not only as detectors and sensors in various fields like biology (e.g. molecular separation or detection, localized and directional growth), and environmental science, but also as magnetic devices, in data storage, in electromagnetic wave absorption, etc. In particular, in the latter case, various recent studies[5,33] have focused on the fabrication of polymer-based THz polarizers in order to avoid the various limitations of the metal wire or microstrip grids used elsewhere. As demonstrated above, the fabricated polymer composite films show a confined motion of carriers in 1D, a fundamental functionality of THz polarizers, and consequently it is natural to explore their ability to act as such.

Since the film fabrication process involves the mixing of MCNFs into the PMMA matrix, we first characterized the THz transmission property of pure PMMA films in the frequency range of 0.57−0.63 THz using the frequency-domain spectrometer system described elsewhere.[4,34] As shown in Figure 4a, a thin PMMA film is quite transparent to THz signals with a measured shielding effectiveness (SE) less than 0.2 dB over the entire frequency range. When the thickness of the PMMA film increased, the SE increased due to higher losses, arriving to an average value of ~1.8 dB. In the same figure is shown the THz transmittance of three different nanocomposite samples of randomly distributed MCNFs (2.2 wt.%) in the PMMA matrix. The three independent measurements show reasonable agreement with each other, with an SE value roughly between 4−6 dB. At higher frequencies the SE is slightly larger, demonstrating that the THz transmission properties of these films follow the well-known Druid

model.[35] During the above experiment, the orientation of samples was randomly chosen. Therefore, the similar results obtained from the three independent measurements clearly show that the THz transmittance of unaligned MCNF/PMMA films is independent of sample orientation, or, in other words, these films do not show polarization properties in the examined frequency range.

In contrast, when the MCNFs are aligned, the nanocomposite films show unique THz properties. In fact, PMMA samples with 2.2 wt.% aligned MCNFs show anisotropic transmission, as shown in Figure 4b. When the sample was placed at close-to-perpendicular orientation (i.e., 90° between the electrical field of the THz incident wave and the MCNF alignment direction), a maximum transmission ($T_{\perp}$) was measured, while the lowest transmission was measured at the close-to-parallel orientation ($T_{//}$). Theoretically, 90° and 0° orientation (or perpendicular and parallel) should give the highest and the lowest transmission, respectively. However, since it is difficult to define such orientations accurately during these measurements, we took the lowest measured transmission as $T_{//}$ and the highest one as $T_{\perp}$. A 45° degree orientation recorded a transmission level between $T_{\perp}$ and $T_{//}$ as expected, designating clearly that these films behave as THz wave polarizers. The extinction ratio ($T_{\perp}/T_{//}$) corresponds to roughly 4−5 dB, and the degree of polarization (P)[34] was calculated to be nearly 0.5 over the measured frequency range. The polarization performance of the films could be potentially improved by using thicker films, optimized MCNF concentrations into the polymer, or by increasing the magnetic properties of MCNFs by loading them with a higher amount of nanoparticles or with nanoparticles with stronger magnetic properties. Furthermore, the utilization of different magnetic fields during the fabrication of the films can offer the opportunity to tune the dimensions and the periodicity of the wires in the polymer matrix,[25] thus producing optimal conditions for increased polarization performance. Nonetheless, it should be mentioned that the attenuations recorded in the parallel orientation ($T_{//}$) are far superior when normalized with respect to the film thickness and the MCNF filler content of the film. Specifically, this quantity is about 10 dB/μm for the present MCNF/PMMA films (2.2 wt.% MCNF content), compared to 1 dB/μm for the carbon nanowhisker/fluoropolymer coatings (50 wt.% CNW content) analyzed in ref 34.

CONCLUSIONS

We presented the formation of free-standing polymeric nanocomposite films with anisotropic electrical conductivity and magnetic properties. Well-oriented wirelike structures are formed by the magnetophoretic transport and assembly of MCNFs into a PMMA matrix during solvent evaporation of a drop-casted solution under a relatively weak external magnetic field. The resulting films present significantly high anisotropic magnetic and DC conductivity properties and act as wave polarizers in the 0.57−0.63 THz frequency range. Although the degree of polarization (0.5) is relatively small compared to the performance of an ideal polarizer (P = 1) and to other studies,[20,33] the present films present very high attenuation values per unit film thickness and MCNF mass concentration and have multiple anisotropies. Furthermore, the composite films are prepared with a nonchemical room-temperature process using low magnetic fields and are flexible and free-standing. This procedure can be followed for various polymer matrices that can be specifically selected according to the desired application, e.g. resistance to humid environments or to organic solvents for chemical analysis or biological sensing, high elasticity for flexible electronic devices etc., while their multiple anisotropic properties make them attractive for complex devices where more than one functionality is demanded.

EXPERIMENTAL METHODS

Materials. MCNFs are fabricated with the method reported elsewhere.[18] In brief, commercially available hollow-core, open end CNFs (PR24-XT-LHT, Pyrograf III, Pyrograf Products Inc., USA) of 10−30 μm length, and outer/inner diameter of 100 nm/25−90 nm respectively, were mixed with single-crystal superparamagnetic magnetite (Fe_3O_4) nanoparticles (diameter ∼10 nm) (Ferrotec Inc. USA) in toluene (99.9% ACS Grade, Fisher Scientific), and probe sonicated for several hours in order to imbibe the nanoparticles into the CNF cavities while drying the solvent. The dry MCNFs were washed to rid their outer walls from magnetite particle deposits and then redispersed in toluene for further wet processing.

Poly(methylmethacrylate) (PMMA) (MW 120,000, Sigma Aldrich, USA) in toluene solution (concentration 100 mg/mL) was mixed with different quantities of MCNF/toluene dispersions to attain a desired concentration in PMMA (0.3 wt.%−7 wt.%). The final solutions were drop casted on glass slides and left to dry under ambient conditions forming a solid film. In order to impose the magnetophoretic assembly of the MCNFs, the deposition and evaporation process was done under a homogeneous external magnetic field (∼150 mT), produced by two permanent magnets applied parallel to the substrate. Higher (>400 mT) or lower (<80 mT) magnetic fields led to inhomogeneous distribution or to nonefficient alignment of the MCNFs in the PMMA matrix.

Characterization. Optical microscopy imaging of the nanocomposite films was conducted with a Nikon Eclipse 80i Digital Microscope. Higher magnification imaging on thin film slices, cut with a Leica EM UC6 Ultramicrotome, was performed with scanning electron microscopy (SEM) (JEOL JSM-6490LA) and transmission electron microscopy (TEM) (JEOL JEM-1011).

For the magnetic characterization of the MCNF/PMMA films, a Quantum Design Ltd. SQUID magnetometer was used. The Zero-Field-Cooled (ZFC)/Field-Cooled (FC) magnetization was collected increasing the cryostat temperature from 5 K to 300 K under a static field of 5 mT, after having cooled the samples down to 5 K in a zero magnetic field (ZFC) or in the same probe field of 5 mT (FC). The field dependence was carried out by aligning the magnetometer field in the plane of the polymeric film, first parallel and then perpendicular to the direction of the wires. The magnetization of saturation, M_S, was taken as the magnetization value recorded at 2 Tesla, where the magnetization curves for all measured concentrations had clearly reached saturation.

The film thickness measurements were made on typical films (PMMA-only, nonaligned MCNFs/PMMA, aligned MCNFs/PMMA) that were sliced along two orthogonal directions centered around the point where the THz attenuation measurements were performed. The sliced film sections were separated and viewed by an optical microscope very close to the point where the two cuts intersected. Each section provided three thickness measurements for the corresponding sample. The average thickness of all films measured was between 11 and 55 μm.

For electrical conductivity measurements, a Keithley 2612A sourcemeter and a DL Instruments 1211 current preamplifier were used, both mounted on an ambient probe station from Süss Microtech (Germany). Samples were biased from 0 to −1 V and from 0 to 1 V. Conductive silver paste electrodes were painted on the sample surfaces in order to minimize the contact resistance. The anisotropic degree of the electroconductive properties of the films was calculated by measuring the slopes of the recorded I−V curves in a direction of applied voltage parallel and perpendicular to the alignment of the wires. The anisotropy degree was determined as the ratio ($slope_{//} - slope_{\perp}$)/$slope_{//}$.

The shielding effectiveness (SE) or transmittance (T) of the coatings in the 570−630 GHz frequency range was measured by a frequency domain THz spectroscopy instrument.[4,34] The THz radiation was provided by a VDI (Virginia Diodes, Inc.) frequency extension module (FEM, or multiplier chain), which converted a microwave (10−20 GHz) signal from a synthesizer to THz radiation, in the 0.57 to 0.63 THz range. The average output power in this range was approximately 1 mW. The THz energy was coupled to a zero-bias Schottky diode broadband detector through four off-axis parabolic mirrors. The THz T or SE (in dB) is defined by SE = $-10\log_{10}(P_{tran}/P_{inc})$, where P_{tran} and P_{inc} are transmitted and incident THz powers. The degree of polarization (P) was calculated using $P = (A_{//}-A_{\perp})/(A_{//}+A_{\perp})$ with $A_{//}$ and $A_{\perp}$ the absorbance at parallel and perpendicular directions, respectively, defined as $A = -\log_{10}T$ for each case.

■ ASSOCIATED CONTENT

Supporting Information

Room temperature magnetization curve and low temperature hysteresis loop of the magnetic carbon nanofibers. TEM image of a typical nanofiber. Zero-Field-Cooled and Field-Cooled magnetization curves and low temperature magnetization hysteresis loops of nanocomposite films containing assembled MCNFs at different concentrations. I−V curves of nanocomposite films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Mr. Jared Morrissette (UIC) for performing the film thickness measurements, Ms. Roberta Ruffilli of Istituto Italiano di Tecnologia (IIT) for the SEM and TEM analysis, and Dr. Ilker S. Bayer of IIT for useful discussions.

■ REFERENCES

(1) Chen, J.; Ramasubramaniam, R.; Xue, C.; Liu, H. A versatile, molecular engineering approach to simultaneously enhanced, multifunctional carbon-nanotube−polymer composites. *Adv. Funct. Mater.* **2006**, *16*, 114−119.

(2) Jimenez, G. A.; Jana, S. C. Electrically conductive polymer nanocomposites of polymethylmethacrylate and carbon nanofibers prepared by chaotic mixing. *Composites, Part A* **2007**, *38*, 983−993.

(3) Agarwal, S.; Khan, M. M. K.; Gupta, R. K. Thermal conductivity of polymer nanocomposites made with carbon nanofibers. *Polym. Eng. Sci.* **2008**, *48*, 2474−2481.

(4) Das, A.; Megaridis, C. M.; Liu, L.; Wang, T.; Biswas, A. Design and synthesis of superhydrophobic carbon nanofiber composite coatings for terahertz frequency shielding and attenuation. *Appl. Phys. Lett.* **2011**, *98*, 174101.

(5) Saini, P.; Choudhary, V. Enhanced electromagnetic interference shielding effectiveness of polyaniline functionalized carbon nanotubes filled polystyrene composites. *J. Nanopart. Res.* **2013**, *15*, 1415.

(6) Al-Saleh, M. H.; Sundararaj, U. A review of vapor grown carbon nanofiber/polymer conductive composites. *Carbon* **2009**, *47*, 2−22.

(7) Xu, Y.; Higgins, B.; Brittain, W. J. Bottom-up synthesis of PS−CNF nanocomposites. *Polymer* **2005**, *46*, 799−810.

(8) Prolongo, S. G.; Burón, M.; Gude, M. R.; Chaos-Morán, R.; Campo, M.; Ureña, A. Effects of dispersion techniques of carbon nanofibers on the thermo-physical properties of epoxy nanocomposites. *Compos. Sci. Technol.* **2008**, *68*, 2722−2730.

(9) Powers, D. S.; Vaia, R. A.; Koerner, H.; Serres, J.; Mirau, P. A. NMR characterization of low hard segment thermoplastic polyurethane/carbon nanofiber composites. *Macromolecules* **2008**, *41*, 4290−4295.

(10) Yun, S.; Kim, J. A review of vapor grown carbon nanofiber/polymer conductive composites. *Carbon* **2011**, *49*, 518−527.

(11) Prasse, T. Electric anisotropy of carbon nanofibre/epoxy resin composites due to electric field induced alignment. *Compos. Sci. Technol.* **2003**, *63*, 1835−1841.

(12) Mahfuz, H.; Zainuddin, S.; Parker, M. R.; Al-Saadi, T.; Rangari, V. K.; Jeelani, S. Reinforcement of SC-15 epoxy with CNT/CNF under high magnetic field: an investigation of mechanical and thermal response. *J. Mater. Sci.* **2009**, *44*, 1113−1120.

(13) Takahashi, T.; Murayama, T.; Higuchi, A.; Awano, H.; Yonetake, K. Aligning vapor-grown carbon fibers in polydimethylsiloxane using dc electric or magnetic field. *Carbon* **2006**, *44*, 1180−1188.

(14) Shi, D.; He, P.; Lian, J.; Chaud, X.; Bud'ko, S. L.; Beaugnon, E.; Wang, L. M.; Ewing, R. C.; Tournier, R. Magnetic alignment of carbon nanofibers in polymer composites and anisotropy of mechanical properties. *J. Appl. Phys.* **2005**, *97*, 064312.

(15) Si, Y.; Ren, T.; Ding, B.; Yu, J.; Sun, G. Synthesis of mesoporous magnetic Fe3O4@carbon nanofibers utilizing in situ polymerized polybenzoxazine for water purification. *J. Mater. Chem.* **2012**, *22*, 4619−4622.

(16) Ren, T.; Si, Y.; Yang, J.; Ding, B.; Yang, X.; Hong, F.; Yu, J. Polyacrylonitrile/polybenzoxazine-based Fe3O4@carbon nanofibers: hierarchical porous structure and magnetic adsorption property. *J. Mater. Chem.* **2012**, *22*, 15919−15927.

(17) Gimenez-Lopez, M.; La Torre, A.; Fay, M.; Brown, P.; Khlobystov, A. Assembly and magnetic bistability of Mn3O4 nanoparticles encapsulated in hollow carbon nanofibers. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 2051−2054.

(18) Das, A.; Raffi, M.; Megaridis, C. M.; Fragouli, D.; Innocenti, C.; Athanassiou, A. Magnetite (Fe_3O_4)-filled carbon nanofibers as electroconducting/superparamagnetic nanohybrids and their multifunctional polymer composites. Submitted for publication.

(19) Costley, A. E.; Hursey, K. H.; Neill, G. F.; Ward, J. M. Free-standing fine-wire grids: Their manufacture, performance, and use at millimeter and submillimeter wavelengths. *J. Opt. Soc. Am.* **1977**, *67*, 979−981.

(20) Ren, L.; Pint, C.; Booshehri, L.; Rice, W.; Wang, X.; Hilton, D.; Takeya, K.; Kawayama, I.; Tonouchi, M.; Hauge, R.; Kono, J. Carbon nanotube terahertz polarizer. *Nano Lett.* **2009**, *9*, 2610−2613.

(21) Ma, Y.; Khalid, A.; Drysdale, T.; Cumming, D. Direct fabrication of terahertz optical devices on low-absorption polymer substrates. *Opt. Lett.* **2009**, *34*, 1555−1557.

(22) Dong-Bin, T.; Huai-Wu, Z.; Wei-En, L.; Qi-Ye, W.; Yuan-Qiang, S.; Zhi-Guo, W. Double wire-grid terahertz polarizer on low-loss polymer substrates. *Chin. Phys. Lett.* **2010**, *27*, 104210.

(23) Kyoung, J.; Jang, E.; Lima, M.; Park, H.-R.; Robles, R.; Lepró, X.; Kim, Y.; Baughman, R.; Kim, D.-S. A reel-wound carbon nanotube polarizer for terahertz frequencies. *Nano Lett.* **2011**, *11*, 4227−4231.

(24) Fragouli, D.; Torre, B.; Villafiorita-Monteleone, F.; Kostopoulou, A.; Nanni, G.; Falqui, A.; Casu, A.; Lappas, A.; Cingolani, R.; Athanassiou, A. Nanocomposite pattern-mediated magnetic interactions for localized deposition of nanomaterials. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7253−7257.

(25) Fragouli, D.; Buonsanti, R.; Bertoni, G.; Sangregorio, C.; Innocenti, C.; Falqui, A.; Gatteschi, D.; Cozzoli, P. D.; Athanassiou, A.; Cingolani, R. Dynamical formation of spatially localized arrays of aligned nanowires in plastic films with magnetic anisotropy. *ACS Nano* **2010**, *4*, 1873−1878.

(26) Lorenzo, D.; Fragouli, D.; Bertoni, G.; Innocenti, C.; Anyfantis, G. C.; Cozzoli, P. D.; Cingolani, R.; Athanassiou, A. Formation and magnetic manipulation of periodically aligned microchains in thin plastic membranes. *J. Appl. Phys.* **2012**, *112*, 083927.

(27) Pisanello, F.; De Paolis, R.; Lorenzo, D.; Guardia, P.; Nitti, S.; Monti, G.; Fragouli, D.; Athanassiou, A.; Tarricone, L.; Manna, L.; De Vittorio, M.; Martiradonna, L. GHz properties of magnetophoretically aligned iron-oxide nanoparticle doped polymers. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2908−2914.

(28) Sahoo, Y.; Cheon, M.; Wang, S.; Luo, H.; Furlani, E. P.; Prasad, P. N. Field-directed self-assembly of magnetic nanoparticles. *J. Phys. Chem. B* **2004**, *108*, 3380−3383.
(29) Valentini, L.; Bittolo Bon, S.; Kenny, J. M. Anisotropic electrical transport properties of aligned carbon nanotube/PMMA films obtained by electric-field-assisted thermal annealing. *Macromol. Mater. Eng.* **2008**, *293*, 867−871.
(30) Prasse, T.; Cavaillé, J.-Y.; Bauhofer, W. Electric anisotropy of carbon nanofibre/epoxy resin composites due to electric field induced alignment. *Compos. Sci. Technol.* **2003**, *63*, 1835−1841.
(31) Liu, Y.; Kumar, S. Polymer/carbon nanotube nano composite fibers−a review. *ACS Appl. Mater. Interfaces* **2014**, dx.doi.org/10.1021/am405136s.
(32) Lanticse, L. J.; Tanabe, Y.; Matsui, K.; Kaburagi, Y.; Suda, K.; Hoteida, M.; Endo, M.; Yasuda, E. Shear-induced preferential alignment of carbon nanotubes resulted in anisotropic electrical conductivity of polymer composites. *Carbon* **2006**, *44*, 3078−3086.
(33) Polley, D.; Ganguly, A.; Barman, A.; Mitra, R. Polarizing effect of aligned nanoparticles in terahertz frequency region. *Opt. Lett.* **2013**, *38*, 2754−2756.
(34) Das, A.; Schutzius, T. M.; Megaridis, C. M.; Subhechha, S.; Wang, T.; Liu, L. Quasi-optical terahertz polarizers enabled by inkjet printing of carbon nanocomposites. *Appl. Phys. Lett.* **2012**, *101*, 243108.
(35) Lloyd-Hughes, J.; Jeon, T.-I. a review of the terahertz conductivity of bulk and nano-materials. *J. Infrared, Millimeter, Terahertz Waves* **2012**, *33*, 871−925.
(36) Chiolerio, A.; Musso, S.; Sangermano, M.; Giorcelli, M.; Bianco, S.; Coïsson, M.; Priola, A.; Allia, P.; Tagliaferro, A. Preparation of polymer-based composite with magnetic anisotropy by oriented carbon nanotube dispersion. *Diamond Relat. Mater.* **2008**, *17*, 1590−1595.