Directed assembly of magnetic nanoparticles in polymers: the formation of anisotropic plastic films containing aligned nanowires.

Despina Fragouli[*], Raffaella Buonsanti[**,***], Giovanni Bertoni[****], Claudio Sangregorio[*****], Francesca Villafiorita[**,***], Carola La Tegola[**], Bruno Torre[****], Roberto Cingolani[*,****], Athanassia Athanassiou[*,**]

[*] Center for Bio-Molecular Nanotechnologies (CBN) of IIT@NNL-UniLe-Lecce, via Barsanti c/o STAMMS, Arnesano 73010 (LE), Italy, despina.fragouli@iit.it, athanassia.athanassiou@iit.it, roberto.cingolani@iit.it

[**] National Nanotechnology Laboratory (NNL) CNR-Istituto di Nanoscienze, via per Arnesano km 5, 73100 Lecce, Italy

[***] Scuola Superiore ISUFI, Università del Salento, Distretto Tecnologico ISUFI, via per Arnesano km 5, 73100 Lecce, Italy, raffaella.buonsanti@unisalento.it

[****] Fondazione Istituto Italiano di Tecnologia (IIT), via Morego 30, I-16163 Genova, Italy, giovanni.bertoni@iit.it, bruno.torre@iit.it

[*****] INSTM Research Unit-Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, 50019 Sesto F.no, Firenze, Italy, claudio.sangregorio@unifi.it

ABSTRACT

We present a facile technique for the preparation of plastic films containing aligned magnetic nanowires with anisotropic behavior. Solutions of magnetic nanoparticles mixed with polymers are drop casted on a substrate under the application of a weak magnetic field, and upon solvent evaporation the nanoparticles are assembled following the field's direction forming thus aligned nanowires into the polymer. The application of the magnetic field in different time intervals reveals the kinetics of the nanowires formation in the film, while microscopy techniques reveal their morphology and their positioning in the film. The resulting nanocomposites exhibit magnetic and mechanical anisotropy. The efficiency and universality of the method is proved by the assembly of the magnetic nanoparticles with diverse polymers, heterostructures and organic molecules resulting in composite materials for a wide range of applications. Finally, the method is successfully applied during the photopolymerization process, allowing the formation of patterns with aligned nanowires.

Keywords:, field directed assembly, magnetic nanoparticles, nanowires, nanocomposites, anisotropic behavior

1 INTRODUCTION

Nanoparticles (NPs) are intensively investigated for their unique properties, and as building blocks for new mesoscopic forms of matter. Assembling NPs in 1D arrays forming nanowires (NWs) is particularly challenging because highly anisotropic objects must be formed starting from essentially isotropic NPs. Magnetic NPs have a large domain of applications, for many of which high density and spatially oriented arrays of polymer embedded magnetic NWs has a critical role, due to their unique properties arising from their anisotropic morphology.

The assembly of magnetic NPs under controllable external magnetic fields (MFs) [1,2,3] during evaporation of a nanocrystal solution is an attractive option for the fabrication of 1D magnetic NWs supported on a film, due to its simplicity, effectiveness, and speed. The nanocomposite films of NWs attract particular attention because of their synergistic and hybrid properties derived from individual components [4]. Specifically, the resulting films demonstrate unique properties, since the physical properties of the polymers are combined with the highly anisotropic properties of the 1D NWs guiding to novel materials with directionally enhanced properties [5,6].The application of MFs for the alignment of fillers in polymers was mainly used in the carbon nanotubes composites, by applying high MFs (>10T) [6]. For the NWs formation in polymers, due to the magnetic orientation of particles, are used mostly micrometer sized particles [7,8], while the use of NPs resulted to formation of oriented supra-aggregates [5]. This work demonstrates that using polymers and MFs, 1D NWs with structural evolution from dots to wires are developed in a controlled manner directly in a polymer matrix. Besides, the nanocomposite films of the NWs may be formed directly upon photopolymerization resulting in patterned structures, while they may be of diverse polymer/NPs combinations. Depending on their individual properties, they exhibit anisotropic behavior of various physical properties, or response to external stimuli, opening thus new perspectives for applications.

2 EXPERIMENTAL METHODS

2.1 Samples Preparation: Iron oxide colloidal nanocrystal spheres of 10 nm diameter were synthesized by modifying a wet-chemical synthetic approach [9]. $Fe(CO)_5$ was used as the precursor, while oleic acid, oleylamine and hexadecane- 1,2-diol were used as both reactants and capping molecules. Chloroform solutions containing 1%-5%wt of iron oxide and various polymers such as: acrylate copolymer poly(ethylmethacrylate-co-methylacrylate (PEMMA), polystyrene (PS), regioregular poly(3-hexylthiophene) (P3HT), poly (9-vinylcarbazole) (PVK), etc. were drop casted on glass substrates. The system was either subjected or not to a homogeneous MF (~160mT), produced by two permanent magnets, applied parallel to the substrate during the deposition and evaporation process. For the kinetics study the films were exposed to the MF for different time intervals. After the removal of the MF all films were left to dry overnight. The magnetic study has been performed on magnetic films in which NWs are present in the whole volume. For the formation of responsive films 8% wt photochromic molecules, 2H-1-benzopyran-2,2′-(2H)-indole, were dissolved in the chloroform solutions containing PEMMA and 1%wt of NPs. For the photopolymerization process one drop of chloroform solution containing 10%wt of NPs, 0.5%wt of photoinitiator (PI) (Irgacure 1700, Ciba) and 89.5%wt of methylmethacrylate was deposited on glass substrate under magnetic field. After 15min a small area of the drop (0.3 cm^2) was irradiated for 90min at 355nm with fluence F=10.5mJ/cm^2 (Nd:YAG laser, repetition rate=10Hz, Quanta-Ray GCR-190, Spectra Physics). After the photopolymerization, each sample was washed with methanol and then dried in ambient dark condition.

2.2 Samples Characterization: The films were studied at low magnification with an optical microscope (Olympus BX41). Higher magnifications were obtained with a scanning electron microscope, SEM, (JEOL JSM-6490LA) detecting the backscattered electrons (BSE), and a 100kV transmission electron microscope, TEM, (JEOL JEM-1011) in bright field mode (BF), imaging thin film sections with thickness about 500 nm -120 nm, which were cut with a Leica EM UC6 Ultramicrotome. Freestanding films were characterized by holographic microscopy (Lyncèe Tec DHM 1000) in transmission mode. Sample topography and magnetic data are acquired by means of MFP-3D atomic force microscope, AFM, (Asylum Research, Santa Barbara CA) using magnetic force microcopy technique, MFM, in order to resolve magnetic structure with nanometer resolution. Magnetic forces are detected using non-contact cantilevers covered with a thin magnetic film on the tip side, and signal is detected in a modified dynamic-AFM mode.[10] The magnetic properties were studied with a Quantum Design Ltd. SQUID magnetometer. The temperature dependence of zero-field-cooled (ZFC)-field cooled (FC) magnetizations were collected in a static field of 10mT after cooling the samples down to 2 K in a zero magnetic field (ZFC) or in the same probe field of 10mT (FC). The angular dependence of the magnetization was measured at 300 K by rotating the sample by 20° steps, while keeping the 5 mT applied field in the plane of the film. All the measurements were performed applying the field in the plane of the slab, first parallel and then perpendicular to the direction of the aligned NWs in the polymer matrix. All data were corrected for the diamagnetic contributions of the polymer and of the substrate which were separately measured and which were found negligible.

The mechanical properties, and the viscoelastic behavior of the films were studied with the dynamical mechanical analysis, DMA, (Q800 TA Instruments). The stress/strain evaluation was obtained by ramping a controlled force (stress) of 1N/min at constant temperature of 25ºC through breaking.

The irradiation of the films containing photochromic molecules was conducted with a Nd:YAG laser (LDF-80-P, Alphalas) of energy 20μW, repetition rate=10Hz, and irradiation time 260sec at 355nm, and 40μW for 33min at 532nm.

3 RESULTS AND DISCUSSION

3.1 Formation Details: The starting material is a polymer/NPs solution casted on a substrate, which upon application of a weak MF during solvent evaporation results to nanocomposite films, incorporating aligned NW arrays. In particular the magnetic NPs of the casted solution, follow the direction of the magnetic lines of the field during the evaporation of the solvent, resulting to their assembly and to the subsequent formation of the magnetic NWs in the polymer (figure 1a,c). On the contrary, casted solutions without the MF application result in a nanocomposite film containing amorphous aggregates (figure 1b).

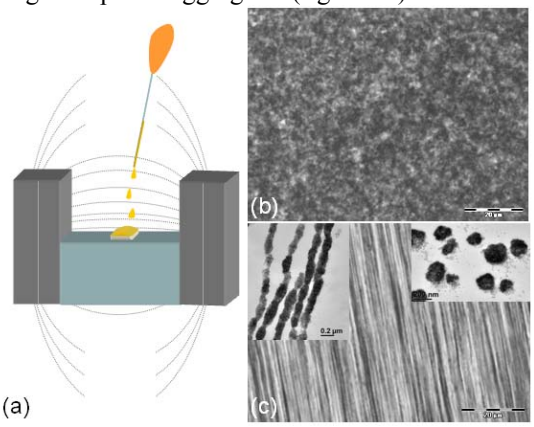

Figure 1: (a) Sketch of the films preparation upon MF. Microscope images of a 1%wt iron oxide/PEMMA film formed (b) without MF; and (c) upon application of a MF; insets: TEM images of film slices cut parallel (left) and perpendicular (right) to the NWs direction.

As shown at the TEM images of figure 1, the aligned structures are composed by the assembled NPs. The combined topographic and magnetic study with the MFM, showed that the NPs maintain their magnetic properties proving thus the formation of magnetic NWs (figure 2).

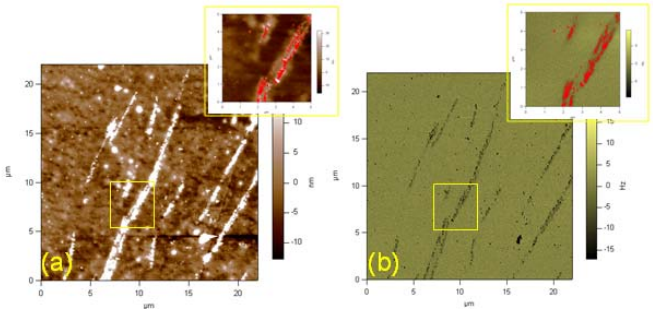

Figure 2: (a) Topography; and (b) magnetic image of a film slice, with thickness 200nm. The insets correspond to the area indicated with the yellow rectangular.[10]

The control of the NWs dimensions (max length 15μm, diameter ca. 80nm) and of their localization across the polymer is achieved by varying the NPs concentration, and the duration of the applied MF. Concerning the former, NPs concentration lower than 0.7%wt results in short elongated structures randomly aligned, whereas concentrations above 5%wt permit the formation of aligned NWs(figure 3).

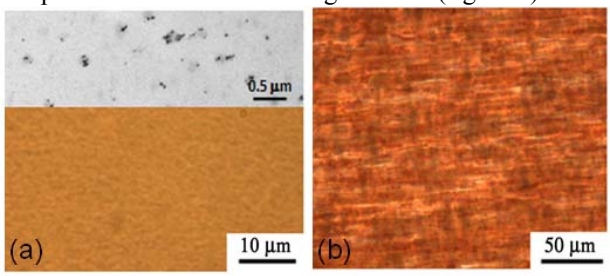

Figure 3: (a) Microscope and TEM image of a 0.5%wt NPs/PEMMA film. (b) Image of a 5%wt NPs/PEMMA film

Concerning the latter, microscopy studies show that the NWs start forming on the liquid/air interface while the increase of MF application time gives longer NWs deeper in the volume of the films (figure 4), phenomenon attributed to the viscosity gradient change during evaporation [9]. (figure 4).

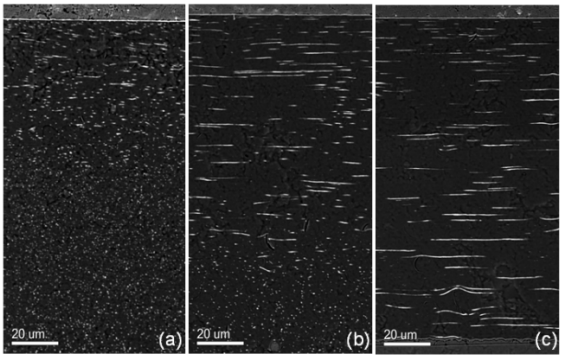

Figure 4: SEM images of cross sections of 1%wt iron oxide/PEMMA films formed after the MF application of 1min (a); 5min (b); and 15min (c) during solvent evaporation.

3.2 Anisotropic Properties: A magnetic study of the films demonstrates that the NWs embedded in the polymer maintain the room temperature superparamagnetic behavior of the pristine NPs, since it is observed thermal reversibility above ca. 140 K in the magnetization recorded as a function of temperature after ZFC and FC procedures. Moreover, the magnetizations of the temperature dependence of the structured films after application of a static MF parallel and perpendicular to the NW alignment direction shows a strong directional dependence with the temperature, with the magnetization higher in the parallel orientation. The anisotropy is better evidenced by measuring the angular dependence of the magnetic moment, which shows an increase of ca. 90% upon rotating the film from the perpendicular to the parallel orientation (figure 5). [9]

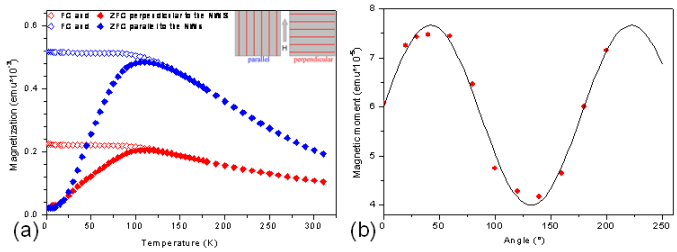

Figure 5: a) ZFC and FC magnetization curves measured with the direction of the external MF parallel and perpendicular to the aligned NWs as indicated in the inset. b) Angular dependence of the magnetic moment measured at 5 mT and 300 K. The film used is a 1%wt iron oxide/PEMMA.

Additionally the films also exhibit mechanical anisotropy. In particular, by studying the stress/strain behavior of films, applying a stretching force parallel and perpendicular to the NWs, it is shown that the films have different behavior. In detail, when the stress force is applied parallel to the aligned NWs, the strain of the film is much lower than in the case that the stress is perpendicular to the NWs alignment. These results demonstrate that the films in the direction of the alignment of the NWs are much more resistant.(figure 6)

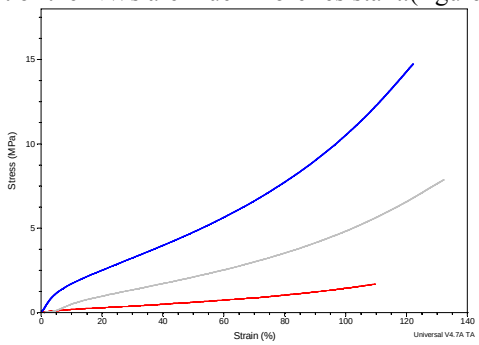

Figure 6: Stress strain curves of 1%wt iron oxide/PEMMA films without NWs (grey line), with NWs aligned parallel to the applied force (blue line) and with NWs aligned perpendicular to the force (red line).

3.3 Further Applications: The method followed for the NWs formation in the polymer matrix may be applied to various NP/polymer combinations. NW plastic films are obtained by mixing iron oxide NPs with diverse polymers e.g. acrylates, conductive polymers etc., while the use of bigger iron oxide NPs (diameter 18nm), or colloidal heterostructures such as iron oxide/titanium dioxide, or iron oxide/gold spheres, form NWs in the polymer matrices (figure 7).

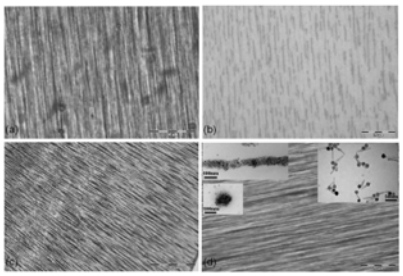

Figure 7: Microscope images of (a) 1%wt iron oxide/PS; (b) 1%wt iron oxide/P3HT; (c) 1% wt iron oxide/PVK; (d) 1%wt iron oxide-titanium dioxide/PEMMA.

Moreover, the mixing of the abovementioned solutions with other responsive molecules guide to the formation of responsive anisotropic magnetic films. Specifically, polymer/iron oxide solution was mixed with the photochromic molecule spiropyran (SP) and dried under MF. The SP is a molecule which upon UV irradiation is proved to photoisomerize to merocyanine (MC). MC reverts back to the SP form photochemically, using visible light irradiation [11], and this transformation between the isomers alters reversibly the macroscopic volume of their host polymer matrices [11]. The nanocomposite film was irradiated with UV and green light, and a holographic microscopy study was conducted after each irradiation. Figure 8a demonstrates 3D phase image of the film, where it is shown that the NWs are responsible for the phase modification, with apparent aligned stripes parallel to each other in the focused area. These stripes contain all the aligned NWs at the focal plane of examination. The line profile analysis of the whole phase image (figure 8b) before and after UV-vis irradiation, and the calculation of the mean width of the observed stripes reveals that they follow a reversible behaviour (figure 8c) attributed to the reversible behaviour of the photochromic molecules.

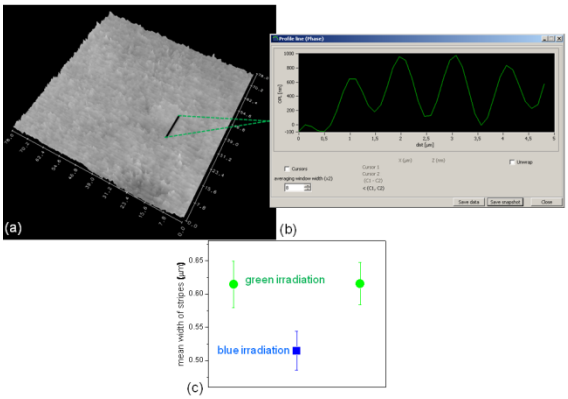

Figure 8: (a) 3D phase image of the film; (b) line profile of a selected area of (a); (c) the mean width of the stripes upon UV and green irradiation.

Finally, we achieved to form patterned nanocomposite films containing aligned NWs upon photopolymerization with pulsed UV irradiation. Figure 8a shows the microscope image of a monomer/PI/NPs film before the photopolymerization process. After irradiation of a small area, is formed a polymer film with embedded aligned NWs. The rest of the film contains amorphous aggregates after washing. (figure 8b)

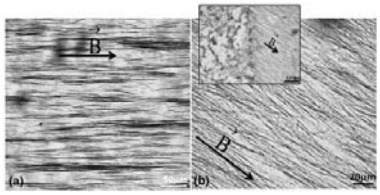

Figure 8: Microscope images of (a) the monomer/NPs film; (b) the photopolymerized film. Inset: an edge of the film showing the photopolymerized area (left) and the non-polymerized area (right).

4 CONCLUSIONS

We present a simple method for the formation and alignment of magnetic NWs in polymer matrices. The resulting plastic films exhibit magnetic and mechanical anisotropy and may be of various polymer/NPs combinations. The NWs can be formed and positioned in the films during the drying process of the NPs/polymer solutions under MF, or during photopolymerization process. They are either free-standing or may have the desired shape, making easier their incorporation to devices. In addition, the analytical results presented may be used as model systems for the reproduction of similar nanocomposite systems, or for the theoretical exploration of the forces and interactions taking place in the formation procedure. Finally, the possibility of having NWs of different lengths, aligned in various layers, can imply different physical behavior in the same film and opens the way for the application of this advanced multilayer structure in various devices.

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