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RESUME OF Ph.D. RESEARCH

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Title: A novel approach to fabricate bioinspired programmable composite materials: the 3D Printing way

Three-Dimensional (3D) Printing allows the production of complex structures and the rapid prototyping of objects. The recent advances made in additive manufacturing technology are introducing year after year new 3D printers and new strategies, enlarging the palette of processable materials. Several industrial applications of 3D printers are already reported, ranging from automotive to fashion, and new ones are just around the corner. Recently, new research trends of 3D printing are arousing, and they are predicted to enhance the development of several technological topics. In particular, 4D printing consists of the fabrication of 3D printed objects undergoing controlled temporal modification of their shape and properties upon the application of external stimuli (time is the fourth added dimension). Several stimuli (such as light, moisture, electrical field) can be exploited to induce controlled transformations in the printed materials. Among them, magnetic fields show peculiar characteristics. Indeed, they can be easily applied by the use of permanent magnets and solenoids, they are body-harmless, and they can be actuated remotely, i.e. without direct contact between the source and the material.

The easiest way to produce magneto-responsive polymers consists of incorporating magnetic fillers within the polymeric matrix. To further enhance the magneto-driven control on the fabricated composite materials, the microstructural arrangement of the embedded particles can be used to tune the macroscopic magnetic properties of the material. This can be achieved by exploiting the self-assembly processes of magnetic particles. Indeed, when magnetic fillers are dispersed in a liquid medium and exposed to a uniform magnetic field, they spontaneously assemble into chain-like structures oriented along the field lines.

In this work, we proposed an innovative 3D printing methodology to exploit the self-assembly mechanisms of magnetic particles and control the microstructures and the properties of the produced objects. This strategy allows us to produce magneto-driven devices undergoing complex actuation mechanisms. Moreover, we demonstrated that the designed objects work in closed wet/dry environments, and they can be remotely controlled by the application of magnetic fields. The fabricated objects have applications in several fields ranging from soft robotics to sensing, from drug delivery to biomedicine.

For this Ph.D. work, Digital Light Processing (DLP) was selected as the printing technology as it allows processing the materials in their liquid state. This allows to easily disperse the fillers in the materials and to exploit the self-assembly process of magnetic particles to control the microstructure of the printed objects. DLP 3D printers are based on the photopolymerization process, which is a polymerization reaction initiated by light. In particular, in a liquid mixture of monomers and

oligomers, an organic molecule called photoinitiator is added. When the photoinitiator is irradiated by light, it undergoes photobleaching generating reactive species (radicals, cations, or anions depending on the type of photoinitiator), which can initiate the curing process. In DLP technology, photopolymerization is used to rapidly cure the slices of the objects by projecting the light pattern of the layer to print on the photocurable resin. The step by step addition of several photocured layers leads to the fabrication of the object. However, the load of fillers in the photocurable resin may limit the light absorption of the photoinitiator due to a competitive absorption/scattering of light, leading to a decrease of the polymerization rate or even preventing the printing process.

In the first part of the Ph.D. work, we investigated the development of magneto-responsive polymers with randomly dispersed magnetic particles, employing a DLP 3D printer to fabricate objects. Fe₃O₄ magnetic nanoparticles (NPs) were added to a mixture of a commercial urethane acrylated resin (Ebecryl 8232) and a reactive diluent (Butyl acrylate). The addition of the reactive diluent in the system accelerated the polymerization process of the photocurable formulation counterbalancing the reactivity inhibition due to the light absorption of magnetic particles. Moreover, by increasing the amount of butyl acrylate (BA) added in the formulation we were able to decrease the glass-transition temperature and the elastic modulus of the printed material, producing softer polymers. The load of magnetic nanoparticles did not significantly alter the mechanical response of the object, while the magnetization of the composites increases linearly with the NPs concentration. The prepared formulations showed a good printability up to 6 wt.% of fillers, and the printed objects showed resolution down to 400 μm. The mechanical response of the objects was tailored by varying the Ebecryl 8232 and BA ratio in the formulations. This approach allowed us to investigate different types of motion. With the rigid polymer (i.e. 75Eb25BA) we 3D printed magnetic wheels undergoing rolling and objects undergoing translation motion in confined environments. With the softer polymeric matrix (i.e. 50Eb50BA) we exploited bending motion mimicking the opening and closing of flowers. By the combination of rigid and soft parts in the same object, we were also able to program the bending points in the printed nanocomposites proving folding and unfolding processes activated by magnetic fields.

In the second part of this Ph.D. work, we studied how to control the microstructure in the printed materials, to enhance their magneto-responsiveness. Our strategy takes advantage of the self-assembly process of magnetic particles. By applying uniform magnetic fields to the photocurable resin, we promoted the spontaneous assembling of magnetic particles in chain-like structures aligned along the field lines. Once the desired microstructural arrangement is achieved, we irradiated the formulation with light to carry out the photopolymerization process and to “freeze” the magnetic chains in the cured polymeric matrix.

By optical microscopy, we investigated both the self-assembly process of magnetic particles and the rotation of magnetic chains in 2D liquid films. Also, a simplified theoretical model was proposed to describe both the phenomena and numerical simulations were performed to characterize the system. The self-assembly process followed a power-law trend characterized by a fast increase in the length of the aggregates within the first 10 minutes of magnetic field application followed by a plateau region where the dimensions of the chains remain almost unchanged. Next, we varied the self-assembly conditions to evaluate the effect of external parameters in the dimensions of the assembled magnetic chains. Higher magnetic field intensities and higher NPs loads facilitate the self-assembly process leading to longer assembled structures. On the contrary, the use of more viscous resins leads to the formation of shorter aggregates due to the reduction of NPs mobility.

Once the chains were formed, the applied field was rotated by discrete angles to control the orientation (i.e. direction) of the assembled magnetic chains. The evolution of the systems under these conditions was experimentally evaluated by optical microscopy. The existence of a critical rotation angle ($\approx 40^\circ$) and two different rotation regimes was observed. Below the critical angle, the magnetic chains simply rotate with the magnetic field. Above the critical angle, the magnetic chains still rotate solidly with the magnetic field, but also undergo rupture, leading to shorter aggregates. This phenomenon is well predicted by the proposed physical model, and it is ascribable to the trend of the parallel magnetic interactions depending on the angular arrangement between two particles. Above 45° the magnetic interactions become negative and this leads to chains break.

Finally, the self-assembly process and the rotation of the chains were also observed *in situ* and at the nanoscale by Scanning X-Ray Microscopy in SOLEIL synchrotron. By varying the characteristics of the applied magnetic field, several phenomena occurring at the nanoscale were observed such as the rotation of the dispersed aggregates when the field is applied, the assembling of the shorter aggregates to the ends of already formed longer chains, and the rotation of the microstructures.

These investigations allowed us to program the microstructure of polymeric films. The dimension of the chains was tailored by controlling the intensity of the applied magnetic field and by varying the viscosity of the liquid medium and the load of NPs dispersed in the resins. Finally, the direction of magnetic chains was programmed by tilting the direction of the field. In order to control the microstructure of a bulky material in a DLP process, our strategy consisted of replicating the 2D control on magnetic chains in each printed layer of the object. Therefore, the control on the direction and size of magnetic chains in each printed layer would lead to the programming of the microstructure of the 3D printed nanocomposite materials.

To enable the production of controlled magnetic fields during the 3D printing process and to control the magnetic microstructure of objects, we modified a DLP printer. The core of the modification set-up consisted of the addition of a polymeric ball bearing acting as the new resin reservoir of the printer. By adding a couple of permanent magnets outside the ball bearing, it is possible to apply a magnetic field on the photocurable resin to induce the self-assembly processes of magnetic particles. The direction of the assembled chains was tailored by rotating the ball bearing, i.e. the permanent magnets. As a proof of concept, we printed a three-level structure varying the direction of the applied magnetic field in each level during the printing process (0° , 45° , and 90°). Optical microscopy images proved that we controlled the dimension of the embedded magnetic chains by varying the self-assembly conditions. Moreover, the direction of the assembled aggregates was consistent with the direction of the magnetic field applied in each level of the structure. Therefore, we demonstrated that the proposed DLP set-up was effective in programming the microstructure of the 3D printed composites.

The effect of the magnetic chains on the macroscopic magnetic properties of the sample was investigated by measuring the magnetization cycles along three different directions of the samples (parallel, transversal, and perpendicular). In the samples with randomly dispersed NPs, the three hysteresis loops were perfectly overlapping proving that the nanocomposites were magnetically isotropic that is, the three measured directions were magnetically equivalent. On the contrary, in samples containing oriented magnetic chains, the magnetization curve measured along the chain's direction (parallel) exhibited a higher slope compared to the transversal and perpendicular directions. Since the magnetic cycles were not overlapping, the samples were magnetically anisotropic, and they were characterized by a preferable magnetization direction called easy-magnetic axis coincident with the orientation of the embedded micro-chains. Therefore, by the control of the microstructure, we

were also able to program the magnetic properties of the fabricated materials. The magnitude of the magnetic anisotropy in the objects was tailored by varying the intensity of the printing magnetic field, and the nanoparticles load in the materials. The optimum conditions to enhance magnetic anisotropy consisted of applying a 10mT field during the printing process and increase the NPs concentration up to 6 wt.%.

The produced magneto-responsive polymers with oriented microstructure behaved as magnetic compasses. Therefore, when a uniform magnetic field was applied, the objects underwent rotation to align their easy magnetic, i.e. the major axis of the magnetic chains, along the field lines. Taking advantage of this phenomenon, we produced magneto-driven spur gears undergoing programmed rotation by the remote application of a magnetic field. Two geometrically identical spur gears were 3D printed with different microstructures. Upon the application of a uniform magnetic field (4mT), the spur gear with oriented chains underwent rotation to align its easy magnetic axis to the field. On the contrary, the spur gear with randomly dispersed NPs remained steady as it is magnetically isotropic. Then, we developed a magnetic-driven gear-train, proving that the magnetic “input gear” was effective in transferring the mechanical torque to a non-magnetic driven wheel leading to the rotation of the latter. Finally, we produced more complex mechanics based on several moving parts. In particular, we developed a gripper based on the spur gear – linear rack mechanics. We demonstrated that by the application of remote magnetic fields we were able to control the opening and closing of the gripper arms in closed wet environments.

The control on the microstructure and magnetic properties of the objects was also exploited in producing magnetic hammers-like objects. The rotation of the objects was predicted by programming the microstructure of the materials. Therefore, by the application of a magnetic field, the fabricated devices undergo predictable rotations to align the embedded magnetic chains along the field direction.

In a last set of experiments, the controlled orientation of the magnetic chains was transformed into controlled bending of hammers-like structures. This can be achieved when the magnetic torque overcomes the mechanical resistance of the material. To do so, the objects were produced with the softer polymeric matrix (50Eb50BA). Moreover, taking advantage of the characteristics of 3D printing, the design of the objects was adjusted to concentrate the mechanical stress in a programmed point of the structure. On the other hand, the contribution of the magnetic torque was tuned by varying the intensity of the applied magnetic field. As a result, the produced objects underwent bending, and the amplitude of deformation was directly related to the magnitude of the magnetic field applied.

Throughout the pages of this manuscript, we demonstrated that a designed synthesis of the photocurable formulations, together with physical knowledge on the evolution of magnetic nanoparticles self-assembly mechanism and 3D printing can lead to the fabrication of objects with added values, in which materials characteristics synergistic play with objects design. This leads to achieve different types of motion such as rolling, translating, bending, and folding/unfolding which can be remotely controlled and exploited in closed environments. Ultimately, to fabricate complex devices which use can be envisaged in different fields such as soft-robotics, biomedical devices, and sensors.