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4D printed thermally activated self-healing and shape memory polycaprolactone-based polymers

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ABSTRACT

The ability to change the shape of 3D printed objects as a function of time is known as 4D printing. Shape memory polymers with their shape-changing behavior are emerging as attractive materials to produce actuators for soft robotics. They can be transformed from one shape to another by a thermo-mechanical programming process. Self-repairing capabilities are also desirable for soft actuators to enhance their durability and mimic natural tissues. The possibility to produce 4D printed polymers with shape memory effect has proven but self-healing behavior was not attained so far in 4D printed shape memory objects. The focus of the present work is to demonstrate the capability of a newly developed material and of a customized low-cost 3D printer to produce 4D printed self-repairing objects. A 4D printed shape memory polymer with thermally induced healing abilities is first presented in this work and achieved by digital light projection (DLP) technology. Shape memory and self-healing functionalities are thermally triggered and obtained respectively using polycaprolactone (PCL) chains and 2-ureido-4[1*H*]-pyrimidinone (UPy) units co-crosslinked in this newly prepared material. Printed PCL/UPy-based objects show a stiffness similar to PCL-based ones, a higher elongation at break and a shape memory effect better than other printed PCL samples found in literature. The printability of shape memory objects is demonstrated with the printing of an opposing thumb, capable of being moved forward to the tip of a forefinger and then backward. Shape memory functionalities are still preserved after healing, making these printed actuators suitable for the production of components for human-machine interactions and soft robotics.

1. Introduction

Over the past few years, the potential of additive manufacturing, also called 3D printing [1], as a versatile technology platform for computer-assisted design (CAD) and rapid manufacturing was explored and demonstrated in a number of clear successes [2]. Several additive manufacturing technologies have been developed for processing pure polymers and polymer nanocomposites [3], such as stereolithography (SL), digital light projection (DLP), direct inkjet and extrusion-based printing as well as liquid deposition modeling (LDM) [4]. They enable less-expensive free-form fabrication of complex, customized and multi-scale 3D geometries for application in a vast range of fields, from tissue engineering scaffolds [5] to strain and skin-like sensors [6,7].

The capability to obtain four dimensional (4D) printed structures with a dynamic behavior as a function of time, where the time is the fourth dimension in the 3D space coordinates, has recently gained considerable interest [8]. 4D printing was firstly introduced by a research group of MIT and defined as the fabrication of 3D printed structures with adaptable and programmable shapes, properties or functionality as a function of time [9]. This time-dependent change in shape, property or functionality can appropriately be triggered by different types of stimuli. Gladman et al., for instance, used water to activate 4D printed water-sensitive biomimetic structures inspired by nature [10]. Other stimuli can also be utilized in 4D printing such as heat [11], pH [12], a combination of heat and water [13] as well as of heat and light [14]. The ability of 4D printed structures to self-assemble and self-repair opens new opportunities of application, such as the fabrication of minimally invasive surgery devices that can be placed in human body through a little surgical incision and then assembled at the required position for surgical operations [15]. In addition to additive manufacturing facility and stimulus, other fundamental elements of 4D printing are stimuli-responsive material, stimulus-triggered programming process and mathematical modeling, as reported by Momeni et al. [16].

One of the most crucial factors of 4D printing is the stimuli-responsive material, which receives, transmits, or processes a stimulus and respond by producing a useful effect, including an actuation mechanism or a signal that the materials are acting upon it. Over the last

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two decades, the development of such smart materials has received great interest due to the potential applications in a wide range of areas, from robotics to tissue engineering and biomedical devices [17–20]. Of the possible smart materials, both self-healing polymers and shape memory polymers (SMPs) have gained ever-increasing interest [21,22].

Self-healing of polymers can be achieved by a few categories of reactions, which include covalent bonding, supramolecular chemistry, H-bonding, ionic interactions, and π–π stacking [23–25]. More recently, self-healing materials have shown great potential for producing soft actuators with enhanced durability, due to their ability to self-repair damage ranging from bulk cracks to surface scratches [26]. Moreover, the use of self-healing hydrogels as "inks" for additive manufacturing was successfully demonstrated [27].

As for SMPs, they are widely studied due to their prospective use in a variety of technological fields, including biomedical engineering [28,29], in vivo tissue regeneration [30], device microfabrication [11,31] and self-actuation [32]. This class of materials has inspired multidisciplinary researchers with the possibility to trigger shape changes in polymer systems upon an external stimulus (*e.g.* temperature, light, magnetic field, pH and moisture) [22,33], combined with biocompatibility [34,35] and ease of processing of SMPs [36]. By exploiting DLP technology, a heat-activated SMP was also 4D printed and structured, using a photocurable polycaprolactone (PCL) [31,37]. Unlike other 4D printed smart materials, SMPs require a thermo-mechanical programming process, also called constrained-thermo-mechanics, to be transformed from a permanent shape to a temporary one and vice versa [38]. The temporary shape is obtained when the material is heated above its transition temperature (T_{trans}) and deformed. The temporary shape is then fixed at $T < T_{trans}$. The permanent shape is, meanwhile, "memorized" by the material and can be recovered by heating at $T > T_{trans}$.

Drawing inspiration from multifunctional properties of natural systems such as human skin and double-helix DNA, some emerging pathways have lately combined SMP networks and self-healing materials that can respond to the same external stimulus, *i.e.* heat [39–41]. To provide intrinsic self-repairing properties to polymer materials, various strategies have been developed so far, many of which are based on either covalent bonds [42,43] or non-covalent interactions [24]. Chen et al. prepared polyurethane crosslinked networks, showing both a shape memory effect based on cyclic PCL and self-healing properties based on dynamic covalent bonds arising from a reversible Diels–Alder reaction between furan and maleimide groups [44]. As for self-healing systems based on non-covalent interactions, an example of a self-repairing polymer hydrogel was presented by Phadke et al., who exploited flexible side chains with amide and carboxylic functional groups to create hydrogen bonding across two hydrogel interfaces [45]. Many approaches developed telechelic systems functionalized with self-complementary 2-ureido-4[1*H*]-pyrimidinone (UPy) units, thus introducing multiple hydrogen bonding interactions and reversible intermolecular cross-links to be used as a trigger for a self-healing effect [40,46]. In addition to self-healing properties, UPy moieties can also improve phase component compatibility and mechanical properties of polymer blends [47].

However, in literature there are no examples that explore the potential of 4D printing for creating objects with shape memory and self-healing behavior, concurrently. We believe that this is the first work showing the 4D printing of a self-healing and shape memory polymer. The study presented here is focused on the development of a shape memory polymer that can be 4D printed to produce structures with self-repairing abilities and embedded thermally switching domains. This newly prepared material is photo-crosslinked and printed *via* DLP technology, by combining polycaprolactone dimethacrylate (PCLDMA) macro-monomers with methacrylates bearing 2-ureido-4[1*H*]-pyrimidinone motifs (UPyMA). The incorporation of UPyMA monomers provides self-healing properties to the 4D printed structures. The possibility to print actuators for soft robotics with good mechanical properties and self-healing capabilities is first shown in this work. An example of a shape-changing object, an opposing thumb with a forefinger, is presented here as a proof of concept.

2. Experimental section

All reagents were purchased from Sigma-Aldrich, Milan, except where indicated.

2.1. Methacrylation reaction

After drying PCL at 120 °C under dynamic vacuum for 2 h, the end-capping reaction was carried out by mixing PCLs with 2-isocyanatoethyl methacrylate (2-IEM, Showa Denko) at 60 °C for 2 h. A molar ratio between 2-IEM and PCL (2-IEM/PCL) of 1.9 was used. $Sn(Oct)_2$ was added in a molar ratio of 2:100 with respect to PCL. Both 2-IEM and $Sn(Oct)_2$ were pre-dissolved in the minimum quantity of $CHCl_3$. Chloroform dried under molecular sieves was also added to the system (1 ml per 1.2 g of PCL) to decrease PCL viscosity. The reaction was monitored by means of FT-IR spectroscopy, checking the disappearance of the isocyanate groups at 2275 cm^{-1}. The functionalized PCLDMA macro-monomers were precipitated in cold petroleum ether and dried overnight in a fumehood.

2.2. Ureido-pyrimidinone methacrylate monomer synthesis

6-Methyl isocytosine (MIS) (4 wt% in dimethyl sulfoxide, DMSO) was added to a round bottom flask, which was consequently sealed with a rubber septum and a condenser. After being dehydrating for 56 h under nitrogen atmosphere and in presence of molecular sieves, 50 mL of DMSO were added to the flask by a syringe and heated up to 170 °C. The temperature inside the flask was constantly monitored with a thermometer. Once the temperature of the solution reached 170 °C and the total dissolution of MIS solid powder in the solvent was obtained, the heating system was quickly removed and 2-IEM (5 wt% in DMSO, [2-IEM]:[MIS] = 1.1:1 M ratio) was immediately added to the flask with a syringe, keeping the system under vigorous stirring induced by a magnetic stirrer. Afterwards, the mixture was quickly cooled with an ice bath in order to avoid unwanted side polymerizations. Lastly, the precipitation of UPyMA monomer was induced washing the solution in a large excess of acetone, which enabled the removal of any other traces of unreacted 2-IEM monomer. The liquid suspension was then filtered, and the solid was collected and dried under vacuum at room temperature for 48 h.

2.3. Printable formulation composition and 3D printing set-up

To print self-healing shape memory polymers, we used a mixture of PCLDMA and UPyMA containing 4 wt% of 2,4,6-trimethylbenzoyl-diphenyl-phosphinoxide as photoinitiator (TPO-L, BASF, Germany) and $CHCl_3$ (60 wt% with respect to the weight of PCLDMA and UPyMA) to ensure the best diffusion of UPyMA monomers into PCLDMA. The formulation was kept at 45 °C during the printing process by a custom-made hot plate as reported in Fig. 1. After printing, the specimens underwent a post-curing of 30 min in a UV oven (DWS Systems, Italy). The printing parameters are listed in Table S1 (Supplementary Materials).

2.4. Material characterization

2.4.1. Chemical characterization

FT-IR spectroscopy analysis was carried out by means of a Nicolet 760-FTIR spectrometer in transmission mode at room temperature in air on methacrylated PCL films applied onto NaCl disks. 32 scans with a resolution of 2 cm^{-1} were performed.