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CIVIL INFRASTRUCTURE

Influence of Healing Agents and Concrete Environment on PLA 3D Printed Mini-vascular Networks for Self-healing Concrete Structures

The aim of this study is to investigate the effect of alkaline environment and healing agents on 3D-printed Poly Lactic Acid (PLA) mini vascular networks (MVNs) for self-healing concrete structures. PLA is an interesting thermoplastic polymer for 3D printing MVNs, due to its good mechanical property and its sustainability. Studies conducted recently on single channel MVNs also known as TETs, and dual channel MVNs, or d-TETs, have indicated that they can effectively store either a single or two-component healing agents to promote the self-healing process in concrete structures. Solubility tests and Differential Scanning Calorimetry (DSC) analysis were conducted in this study to assess the degradation of PLA polymer resulting from various factors, including the printing process, embedment of MVNs in concrete matrices, and prolonged contact with healing agents such as sodium silicate and nanolime solutions.

Keywords:
Self-healing, concrete, 3D-printing, PLA degradation, mini-vascular networks.

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INTRODUCTION

Biomimicry is among the innovative methods being utilized in civil engineering to address the increasing need for construction materials that offer better and longer service-life performance [1-2] This approach enhances the durability of materials by enabling them to detect and respond to damage, thus reducing or eliminating the need for constant repair or replacement of the material.

Recent studies on mini-vascular networks (MVNs) with single channels, also known as TETs, and MVNs with dual channels, or d-TETs, have shown that they can effectively hold one or two-component healing agents to facilitate self-healing in concrete structures [3-4].

TETs and d-TETs, which comprise hollow ligaments that interconnect to form a network with a characteristic dimension, specifically a maximum ligament length that is approximately twice the size of the largest aggregate particle found in the cement composite, are printed from Poly Lactic Acid (PLA) [5].

The broad spectrum of potential applications of PLA, including in building materials, makes it an attractive biopolymer at present [6-8]. Furthermore, the continuous growth of polymers for fuse deposition model (FDM) printing has been reported widely in recent years. [9-10].

PLA is a thermoplastic polymer, completely based on renewable resources and its degradation can be entrusted to microorganisms which would reconvert it to its monomer, lactic acid (LA), and carbon dioxide [11]. The durability of 3D printed parts is largely determined by the conditions in which they are used and operated. As a result, these conditions can impact the mechanical and chemical properties of the parts when subjected to static or dynamic contact [11].

In this study, Solubility tests and Differential Scanning Calorimetry (DSC) analysis were carried out to evaluate the deterioration of PLA polymer caused by different factors, such as the printing process, embedding of MVNs in concrete matrices, and extended exposure to healing agents like sodium silicate (SS) and nanolime (NL) solutions.

MATERIALS AND METHODS

TETs and d-TETs were printed from clear PLA Ultimaker2® printer (Utrecht, The Netherlands) with a 0.25 mm nozzle, as represented in Fig. 1.

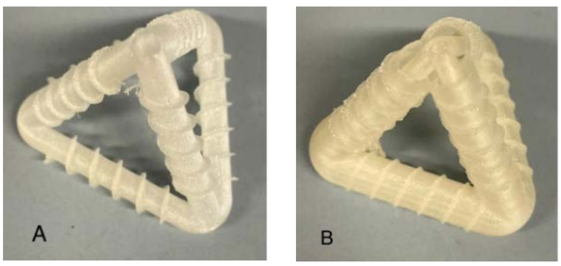

Fig. 1. 3D printed single channel TET (A) and double channel d-TETs (B).

Evaluation of PLA degradation are carried out by Infrared spectroscopy measurement (IR Brucker vector 2), solubility and swelling tests and Differential Scanning Calorimetry (DSC). DSC was performed using a Linseis PTA ST1000 using and amount of polymer of about 40 mg, placed in an open aluminium, under nitrogen flow of 80 ml min^{-1}, with a temperature ramp of 10°C min^{-1} from 30 to 250°C, depending on the type of measurement and polymer.

DSC measurements were carried out on samples collected directly from: i) the filament roll (wire); ii) a single channel TETs ligament after being printing; iii) d-TET ligaments; i.e. internal or external channel, before and after the contact with nanolime (NL)and sodium silicate (SS) (and after the healing period).

The solubility tests of fragments of TETs PLA were conducted using various solvents at room temperature, with a treatment duration of 48 hours.

Some solvents, such as chloroform and styrene used for solubility test are widely recognized as a mutagen and thus potentially carcinogenic, as such its inclusion in the formulations is not recommended, although it has been included here for completeness. Indeed, the solubility tests use solvents both polar and non-polar, in order to take into account a wide range of environments from polar to non-polar.

The swelling tests were conducted at room temperature after solubility tests, comparing the fragment before solubility treatment and observing the volumetric change.

RESULTS

In Figure 2 are reported the thermogram of the PLA samples. Solubility tests results are reported in Table 1.

As can be seen in Table 2, although some solvents did not solubilize the PLA, a certain degree of swelling was observed, except for neat water.

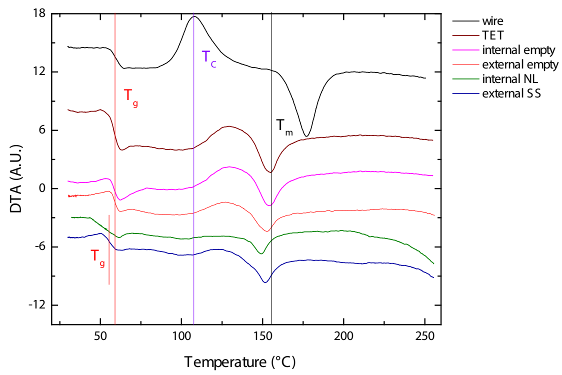

Fig. 2. DSC measurements of various PLA samples obtained from TETS in different conditions. Run conditions: open aluminium crucible, sample 40 mg, ramp 10°C/min to 250°C, nitrogen flow 80mL/min.

Solvents	Polylactide acid (PLA)
Dichloromethane	Y
Chloroform	Y
Diethyl ether	N
Styrene	N
Acrylic Acid	N
Ethyl Acrylate	N
Acetic Acid	N
Trifluoroacetic acid	Y
Aqueous Na(OH)	Y
Aqueous $Ca(OH)_2$	Y
Methyl alcohol	N
Ethyl alcohol	N
Water	N

Table 1. PLA Solubility tests degradation of PLA in organic solvents, water and alkaline condition; Y= soluble, N=insoluble.

Solvents	*Polylactide acid (PLA)*
Diethyl ether	Y
Styrene	Y
Acrylic Acid	Y
Ethyl Acrylate	Y
Acetic Acid	Y
Methyl alcohol	Y
Ethyl alcohol	Y
Water	N

Table 2. Swelling tests of degradation of PLA in organic solvents and water; Y= swelling, N= no swelling.

DISCUSSION

It appears in Fig 2, the pure PLA wire shows the typical thermogram (curve 1) of the polymer suggesting the absence of significant amount of additives and co-polymers, whose presence may interfere with the typical behaviour of the PLA. Thermogram curves (curves 2) obtained from TETs' ligament showed a displacement of the peak of crystallization at higher temperature (from 108°C to 128-130°). Furthermore, the measurements show an even more evident displacement of the melting point from 177°C to 153-154°C for PLA wire and worked ones, respectively. It appears there are practically no effect due to the permanence inside the concrete (compare curve 2 with 3 and 4). Regardless, the enthalpies of both crystallization and melting seem to be reduced once the PLA has been processed by the printer. It should be noted that precise enthalpy values were not measured as they were beyond the scope of this study and no calibration was conducted.

This reduction in enthalpies indicates a modification in the polymer's crystallinity. This behaviour is even more evident when the TETs are filled with sodium silicate, nano- silica and nano- lime (curves 5-6) suggesting the presence of these compounds reduce further the crystallinity of the polymer. No clear variations of the glass transition temperature are evidenced by the thermogram (curves 1-4, Tg=58-59°C), thus suggesting no relevant modification of the polymer structure is occurred. On the contrary, curves 5-6 showed a displacement in range the Tg to 52-55°C suggesting a certain modification of the polymer structure induced by the presence of solvent whose adsorption may modify substantially such a physical property.

According to Table 1, degradation of the material occurred in both an alkaline environment and in the presence of organic substances. To prevent this issue, a future research study will explore a strategy aimed at reducing the degradation of PLA, which will involve investigating both healing materials and PLA surface treatments.

Table 2 shows that the polymer experiences swelling in the presence of all organic solvents except for water, which does not cause significant swelling of the PLA. This is in agreement with the results of DSC where modification of the thermal properties of the PLA are more evident when alkali and solvent are present together.

To assess their compatibility with PLA, we tested all of these solvents since they are potentially used in healing polymer formulations. Our findings indicate that an aqueous solvent with mildly basic or acidic conditions would be the most appropriate choice. In future studies, surface treatments could be incorporated to safeguard the polymer bulk and prevent any internal modifications.

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Conflicts of interest
The authors declare no conflict of interest.

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