

Dynamic Robotic Fibers: Liquid Crystal Fibers for Wearable and Haptic Applications

Early Stage Insights

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1. Introduction

At a time where more and more parts of the body and bodily functions can be mimicked, the skin is a topic of great interest. Its behavior when exposed to internal signals, through for example the nerves, and external signals, like wind or temperature, is very unique and can mainly be visualized through the hairs. These hairs cover the majority of the body and serve as protection for the skin, increase sensory functions and help to regulate body temperature. The importance of these hairs makes them fascinating to study and challenging when trying to mimic their behavior [1]. Actuated fibers made from liquid crystals have the potential to serve as artificial hairs. Liquid crystals combine crystalline alignment with liquid mobility, which means that the material can be forced and locked through crosslinks in a desired shape. If the liquid crystal fibers (LCFs) are shaped correctly, they will have the ability to be reversibly actuated through heat, light or magnetism [2]. To implement the use of LCFs, a compatible substrate is of high relevance. Hydrogels are a good candidate as they have good elasticity, have tunable mechanical properties and, most importantly, they are biocompatible [3]. The fibers can be incorporated into the hydrogel through UV curing. This result could potentially be used in the field of wearables or plasters on (damaged) skin. It is therefore important to try and mimic different variables of the skin, like the pH value. The pH of skin is not constant and changes with different levels of, for example, sweat and skin moisture [4]. In earlier studies, it was found that the fabricated hydrogel responds to a change in the pH; in a basic environment the hydrogel should swell more than in an acidic environment, as a result of the deprotonation and protonation of the -COOH group of the incorporated acrylic acid [5]. The hydrogel also responds to heat – it will curve when heat is applied due to the gradient in crosslinks. This could be helpful for a good fit to the skin, especially when the hydrogel responds to body temperature. This study will show the initial steps taken into developing a new fabrication method of liquid crystal fiber arrays on flexible substrates for haptic wearables applications. Opportunities and challenges with the fabrication method will be identified and explained.

2. Results and Discussion

2.1. Design Concept

The goal of this project is to design a wearable or artificial skin that can be used for injured/damaged skin (burn injuries). The design relies on the use of LCFs and a flexible substrate (hydrogel). The wearable has ‘smart’ responses as the substrate is biocompatible, flexible and able to adhere to the skin, and the LCFs also provide haptic and aesthetic elements. Moreover, the LCFs are also stimuli responsive and can potentially be tuned to respond to light, heat, and/or humidity. An upstanding curled LCF is attached to a responsive hydrogel base. When heated from below the hydrogel base will bend downwards, clamping around an object like a heated rod or eventually a limb. The LCF will respond to temperature (see Figure 1); high temperature will make it bend towards the heat source reversibly (i.e. removing the heat source causes the LCF to return to its original state).

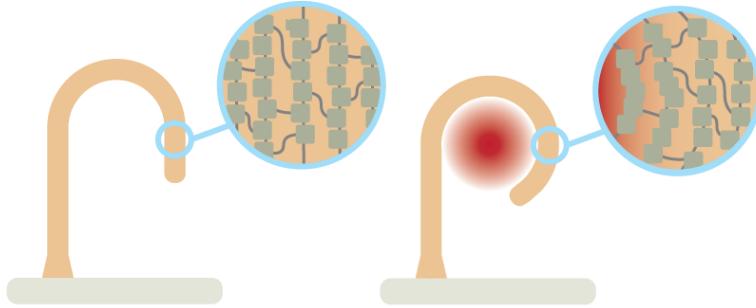


Figure 1. Left shows the LCF in non-actuated state. Right shows the LCF in an actuated state through heat radiation.

2.2 Experiments

2.2.1. Materials

The materials used for photopolymerization of the liquid crystal oligomer are shown in Figure 2. RM82 **1** commercial liquid crystal solution is used. DODT (2,2'-(Ethylenedioxy)diethanethiol) **2** is used as a chain extension agent and DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) **3** as a catalyst. Dichloromethane (DCM) is used as a solvent. Finally, Irgacure-819 **4** is used as a photoinitiator.

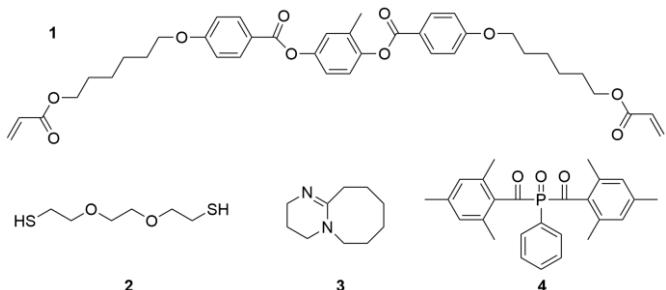


Figure 2. The materials used for oligomer fabrication. (1) RM82 which is a commercial liquid crystal solution, (2) 2,2'-(Ethylenedioxy)diethanethiol, (3) 1,8-Diazabicyclo[5.4.0]undec-7-ene, and (4) Irgacure-819.

An overview of the materials used to fabricate the hydrogel is provided in Figure 3. Acrylic acid **5** was mixed with crosslinker tripropylene glycol diacrylate (TPGDA) **6** and a UV photoinitiator 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure-2959) **7**. This specific mixture is derived from Liu et al. [5].

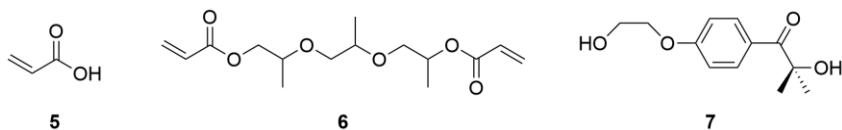


Figure 3. The materials used to fabricate the hydrogel. (5) Acrylic acid, (6) TPGDA, (7) Irgacure-2959.

2.2.2 Fabrication

The liquid crystal oligomer was prepared using a 1.25 ratio of **1** (DODT):**2** (RM82). The mixture was then dissolved in 2 mL DCM followed by the addition of 20 μ L of **3** (DBU) catalyst and 1 wt% of **4** Irgacure-819. The mixture was then heated up to 40 °C on a hot plate for 30

minutes for the reaction to take place. Finally, the solvent in the product was evaporated under vacuum for 3 hours at 40 °C resulting in a LC oligomer.

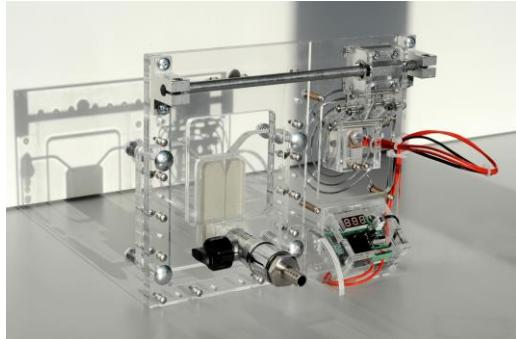


Figure 4. Vacuum extrusion machine. A mold is placed in the middle of the back of the left side. The oligomer is put in the mold after which the heating element, which can be seen on the right side, is put on the front of the left side. This will liquify the oligomer so that by applying a vacuum it can be sucked into the mold and a fiber can be created.

A vacuum extrusion machine (see Figure 4) is used to create the LCFs. Several molds are used with different shapes (curled, straight, and ribbon) and diameters. These molds are created by 3D-printing the negative of the mold, where consequently silicon is poured into.

First the LC mixture is heated up to 85-90 °C where the isotropic phase is achieved. Then they are applied in the funnel of the mold on the machine. Consequently, the heating unit of the machine is set to 100 °C, which causes the temperature of the LCs in the mold to remain at approximately 85-90 °C. After 2-5 minutes, the soft LC oligomer is ideal for extrusion and the vacuum pump is turned on. Due to the vacuum conditions, the oligomer is sucked through the mold and LCs are aligned due to the shear along the contact surface.

The hydrogel is fabricated by photopolymerization of a mixture containing 89wt% acrylic acid **5**, 10wt% TPGDA **6** and 1wt% photoinitiator **7**. Two mixtures were made that differed in the amount of water that was added. The volume of **5** and **6** was calculated using the corresponding densities. To one mixture 25% of the calculated volume was added in water and to the other mixture 50% water was added. The hydrogel formulation was made by gently mixing the compounds in a glass vial. Films were made by polymerizing the monomers in a constructed cell. The cell was made with two glass plates, between which four glass spacer plates with a thickness of 50 µm (one on each corner) were placed. The cell was filled with the mixture through capillary suction. The mixture was UV polymerized using an EXFO lamp under a light intensity of 36 mW cm⁻² for 20 minutes.

2.3 Device Characterization

2.3.1 Fiber actuation

The bending of the fiber has been characterized by the means of measuring the displacement. For evaluating the relation between temperature and displacement, a curled fiber with a diameter of 0.6mm was positioned on a glass plate and consequently heated up. A soldering iron was positioned in the center (see Figure 5) of the curled fiber. The temperature was gradually increased from 100 °C up to 270 °C in steps of 10 °C. Figure 5a shows the relation between the temperature and the displacement at the end of the fiber. When a temperature of 270 °C is reached, measurements are not valid anymore because of the limitations of the test setup, where the fiber touches the soldering iron.

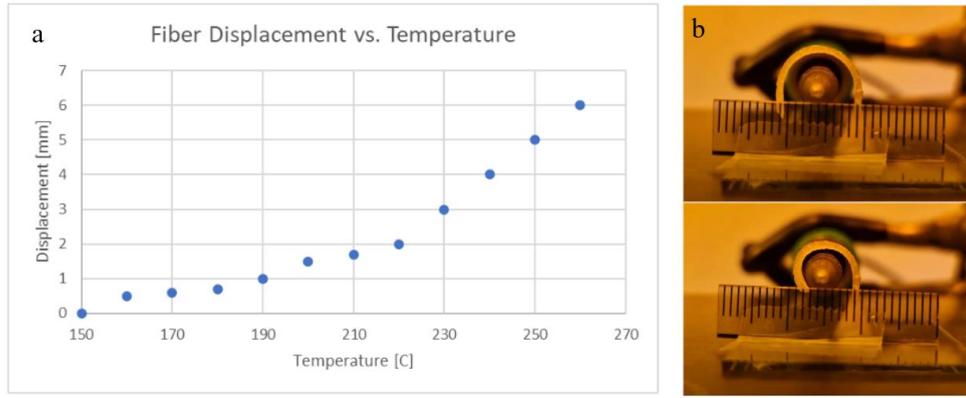


Figure 5. (a) Displacement of the 0.6 mm curled LCF as a function of temperature using a soldering iron. (b) LCF at 100-150 °C (top) and at 260-270 °C when it is touching the iron (bottom).

Before the characterization of the fiber was done, the alignment of the fibers was investigated, by using a light plate with crossed polarizers. No change in transmission of light through the fiber was observed at 0°, 45° and 90° angles with respect to the polarizers. Thus, no alignment was observed in the curled fibers with a diameter of 0.6mm. It can be speculated that the displacement of the curled fiber is caused by the bilayer effect within the fiber. The LCF is potentially too thick for the shear forces to cause alignment in the middle of the fiber. Another speculation is that the combination of conditions (operating temperature and pressure) is not ideal.

To increase shear during extrusion, 0.2 mm diameter molds of the curled fibers were made to test the alignment in the thinner fibers; however, due to bubble formation in the fiber, they were not sufficiently firm and “weak” spots made them prone to breakage. The bubble formation is thought to be caused by the non ideal vacuum conditions.

Finally, molds with different shapes have been created to see if the production method also allows for different shapes of fibers (see Figure 6).

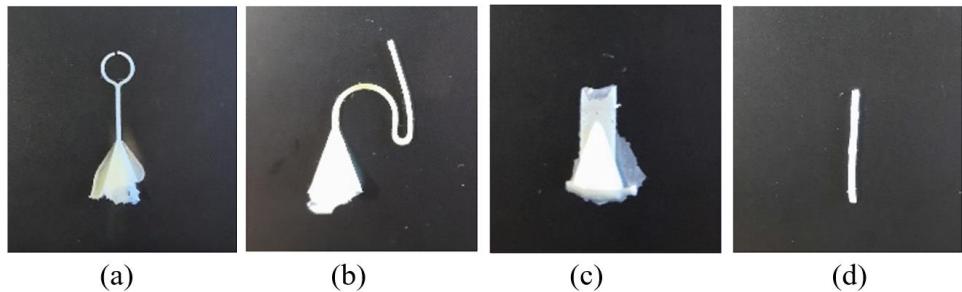


Figure 6. Different fiber shapes: (a) Split fiber, (b) Curled fiber, (c) ribbon and (d) straight fiber (with bottom cut off).

Despite the successful fabrication of fibers with different shapes, no good alignment was achieved. Some alignment was detected in a ribbon shape with a 0.2 mm thickness. Unfortunately, due to the time limit of the project, optimization and characterization of a straight fiber, ribbon shape and 0.2 mm splitted fiber was not possible. However, controlled actuation tests were conducted, using the test set-up from Winters et al. [2], with a straight fiber having a diameter of 0.2 mm and a ribbon shape having a diameter of 0.2 mm and width of 4 mm. The straight fiber showed some displacement when putting the resistors in the highest setting. The ribbon showed no displacement. It could be argued that the latter occurred due to no or limited alignment within the material and improper adhesion to the set-up.

2.3.2 Hydrogel characterization

The swelling ratio was measured for the 25% and 50% water hydrogel mixtures. This was done by using acidic, neutral and basic water, to mimic the varying pH of skin. HCl was used to acidify the water and KOH was used to basify the water. Pieces of 1x1 cm hydrogel were cut using a razor blade. The swelling was measured by a change in weight and in size (only in the x and y direction), of which the measurements can be seen in Table 1.

Table 1. The swelling of the hydrogel in acidic, neutral and basic water.

	pH	Dry weight (mg)	Swell weight (mg)	Size (cm)	Swell
25% water	3-4	18.8	29.7	1.3	158.0%
	5-6	18.5	27.3	1.2	147.6%
	8-9	18.4	27.5	1.2	149.5%
50% water	3-4	18.2	27.4	1.3	150.5%
	5-6	17.9	26.9	1.3	150.3%
	8-9	19.9	30.8	1.3	154.8%

As mentioned in the introduction, in earlier studies [4] it was found that the fabricated hydrogel would swell more in a basic environment than in an acidic environment. It is also expected that a hydrogel with a lower crosslink density will swell more, as there is more space available for water molecules. That means that the hydrogel with 50% water should swell more than the hydrogel with 25% water.

In Table 1 it can be seen that the hydrogel with 25% water swells the most in an acidic environment. This is not in line with the theory of deprotonation and protonation of the -COOH group of the incorporated acrylic acid. The hydrogel with 50% water swells the most in a basic environment, which is in line with the mentioned theory. The swelling of the hydrogel with 50% water is slightly higher in acidic and neutral conditions than the swelling of the hydrogel with 25% water, which would support the theory about the crosslink density. It must be mentioned that the weights in Table 1 were acquired from an inaccurate scale, which means they are not reliable. The measured sizes of the pieces of hydrogel were acquired by using a simple ruler with a precision of one millimeter and the judgment of the observer's eye. To obtain more insights in the crosslink alignment, quantitative tests that obtain more accurate swelling measurements should be conducted.

2.3.3 Device product

Despite the unsuccessful alignment in the LCFs, adhesion to the hydrogel was achieved. This was done by creating a cavity in a glass plate by cutting the glass plate through the middle and creating dents along the cut edges followed by gluing. This glass plate is then placed on top of another glass plate with 1 mm spacers glued to the edges. The premade fibers are introduced through the cavity of the top plate. The hydrogel mix is then introduced to fill the cell by capillary suction. After photopolymerization of the hydrogel by exposure to UV-light, the fiber is connected to the hydrogel. Separation of the glass plates is done to release the final product. However, due to forces needed to separate the plates and the relatively thin surface of the glued areas, the top plate split, causing rupture of the hydrogel. Nevertheless, the fiber was still attached to one part of the hydrogel. Figure 7 shows two different attempts of adhering LCFs to the hydrogels with different water content in the mixtures (25% and 50%).

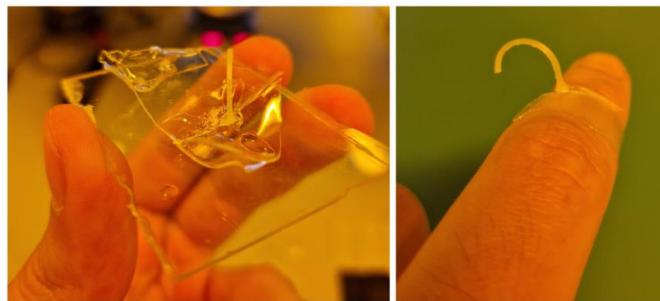


Figure 7 Pictures of 0.6 mm liquid crystals fibers adhered to hydrogels with (left) 50% water content in the hydrogel mix and (right) 25% water content in the hydrogel mix placed on a finger.

3. Conclusion and Outlook

This study shows the initial steps taken into identifying the opportunities and hurdles to overcome when developing a new fabrication method of LCF arrays on flexible substrates for haptic wearables applications. It shows the potential and proof-of-concept of making a variety of fiber shapes and sizes and potential other shapes (e.g. ribbons) on a dynamic flexible substrate using vacuum molding extrusion as a manufacturing method.

The two main issues that were identified regarding the manufacturing method are that insufficient alignment was observed and air bubbles caused “weak” spots which made the LCFs prone to breakage. This hinders the ability to accurately characterize the dynamic effects of the LCFs. By adjusting and identifying relevant parameters to optimize the manufacturing process, such as fiber thickness of the mold, temperature regulation and vacuum conditions, it opens up the opportunity for innovative LCF shapes and sizes to be created that have a wide range of new haptic and dynamic effects.

For the hydrogel substrate, better characterization of the crosslinks and responses to different pH environments needs to be made through quantitative tests. Although other existing substrate materials that are static (e.g. silicone) or with similar dynamic response (e.g. responsive textiles) might be easier to fabricate, the use of hydrogel as a substrate for the LCFs shows an opportunity for a substrate that shows ease in adherence with the fibers and has a combination of flexible, dynamic and biocompatible properties. Having both the LCFs and its substrate be dynamic opens up potential new application possibilities.

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