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Bilayer solvent and vapor-triggered actuators made of cross-linked polymer architectures *via* Diels–Alder pathways†

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A simple and straightforward approach to produce solvent and vapor-based actuating materials is developed in this work. These actuators are based on rigidity gradients created in bilayer architectures made of reversibly cross-linked poly(ε-caprolactone) (PCL) networks into which functional nanofillers, *i.e.* multi-walled carbon nanotubes (MWCNTs), are incorporated using simple processing techniques. A key element of the bilayer functionality lies in, by taking advantage of thermo-reversible Diels–Alder reactions (between furfuryl and maleimide moieties), ensuring good adhesion between the layers. Thereby, the produced material instantaneously swells in an anisotropic way due to the rigidity gradient, resulting in reproducible bending actuations. Besides, it is shown that the percolating network of electrically conductive MWCNTs offers the possibility of implementing these bilayers as solvent detector sensors. This opens the door to the development of multi-responsive devices with tunable actuating behaviors and potential application in the robotics field as self-deployable structures in different environments (water, organic solvents, *etc.*).

1. Introduction

Programmable stimuli-responsive shape changing polymers are a topic of high importance for fundamental research and are on the leading front of innovation. More specifically, in materials science, there has been ongoing interest in the straightforward fabrication of multi-responsive polymer materials described as complex deployable structures with a great range of functionalities. A new trend in this field is the conception of functional devices described as polymer actuators. Generally, they represent materials capable of reversibly changing their shape and size in response to various stimuli, affecting directly their mechanical properties. Among potential applications of such actuators, one can mention sensors, artificial muscles, controlled encapsulation/delivery systems or biomimetic actuating systems as well as soft robotics.[1] Attractive classes of polymers for actuator production are shape-memory polymers (SMPs). Their major advantages are relatively low cost and weight, high flexibility and ability to recover their permanent shape under different stimuli (heat, solvent, vapor, irradiation, electro-magnetic field and others). Moreover, the ease of conferring desired stimuli-responsive functionalities on them by the incorporation of different nanostructured fillers (carbon nanotubes, cellulose nanocrystals, metal oxide nanoparticles and others) makes them ideal candidates for actuator applications.[2]

Recently, in addition to their heat-responsiveness, it was demonstrated that SMPs are capable of recovering their initial shape by simple immersion in appropriate solvent. As a follow-up, several solvent-triggered SMP systems including hyperbranched polyurethane,[3] polystyrene sensitive to dimethylformamide[4] and toluene[5] or self-healed ethyl acetate-responsive poly(vinyl butyral) networks were reported.[6] Several water-responsive materials based on cross-linked poly(vinyl alcohol) (PVA),[7] PVA/graphene oxide composites,[8] or polyurethane elastomer containing cellulose nanocrystals[9] were also developed. It is worth mentioning that solvent vapor-responsive materials were obtained with natural rubber[10] or porous actuator membranes with responsiveness to solvent vapor[11] or humidity degrees.[12] However, most of these studies demonstrated that complex multi-step procedures were necessary to achieve solvent-responsiveness and shape-memory effects and, most often, the systems presented only one-way

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(temporary to permanent) shape recovery due to a lack of anisotropy within the materials.

The concept of polymer actuators and their reversible motions are centered around an anisotropic deformation within the material (*e.g.* expansion or contraction).[13] A simple and efficient way to produce responsive materials can be achieved with bilayer-type structures. Such structures exhibit self-bending, originating from the dissimilar properties of each layer: thermal expansion coefficients, swelling abilities, layer thickness and size. Several bilayers have already been studied based on thermo-reversible cross-linked crystalline polymers with different melting temperatures,[14] conductivity (incorporation of carbon nanotubes into one of the layers),[15,16] fluorescence[17] or water affinity between the layers,[18–20] but the complexity of the systems and specific conditions for the actuation (*e.g.* CNT alignment) limit their applications.

In the present work, we purposely simplified the production of solvent-based polymeric actuators *via* a one-step synthesis process of bilayer structures made of reversibly cross-linked PCL. These networks were obtained by Diels–Alder reactions between furan- and maleimide-modified PCL oligomers of variable degrees of end-functionalization (2 or 4), making these reactions proceed *via* simple processing techniques (extrusion and compression) and, very importantly, ensuring good adhesion between both layers during processing. In order to create an anisotropic effect in the bilayer architecture and, therefore, the solvent-based actuating polymer, one of the layers was filled with electrically conductive MWCNTs. Taking advantage of the network's thermo-reversibility, it was again possible to produce bilayer nanocomposites with good adhesion ensured by the presence of Diels–Alder moieties and solvent-responsive actuation. The thermo-mechanical, swelling and actuating (upon direct immersion or solvent vapor exposure) properties of the resulting systems were evaluated. Finally, a sensing approach in the presence of vapor was attempted taking advantage of the electrical conductivity of the MWCNTs present in one of the layers.

2. Experimental part

Materials

All used materials in the present study are described in the ESI.† The synthesis of chain end functionalized PCL and the production of the thermo-reversible PCL-based networks were carried out using a previously reported procedure (ESI†).[21]

Production of PCL-based films

From the as obtained PCL-based networks, monolayers described as PCL (for PCL(MAL)$_2$–PCL(FUR)$_4$ composition) and PCL–MWCNT (for PCL(MAL)$_2$–PCL(FUR)$_4$/MWCNT composition) and a bilayer PCL/PCL–MWCNT film (composed of PCL and PCL–MWCNT monolayer) with a thickness of 0.8 mm were prepared by compression molding (manual Carver hydraulic press). Circular molds with a diameter of 100 mm and a thickness of 0.8 mm were used. After the compression step of the corresponding polymer (80 °C for 5 min), the monolayer was kept for 3 min at 10 bar and transferred for 2 min under 1 bar during the overnight cooling step (progressive cooling of modes to ambient temperature). The bilayer PCL/PCL–MWCNT film was produced from monolayers preheated at 100 °C in order to favor the retro Diels–Alder reactions. Then the two layers were brought into contact (one above the other) and hot-pressed at 1 bar for 5 min. This step was followed by hot-pressing of the resultant bilayer for 1 min during degassing cycles at 4 bar. Finally, the bilayer structure was conserved between the hot modes at 1 bar for the overnight cooling procedure.

Characterization

The thermo-mechanical properties of the films were determined using a DMTA apparatus (DMTA Q800; TA Instrument, USA) in multi-strain mode evaluating the storage and loss modulus as well as the tan delta. Each specimen was cut into a rectangular shape (30 × 5 × 0.8 mm) and analyzed in the temperature range from −80 °C to 65 °C. For tests concerning the influence of the (de)swelling degree on the thermo-mechanical properties of the materials, the films were previously immersed in $CHCl_3$ for 1 or 3 min, or for 3 min in $CHCl_3$ and 30 min in ethanol (EtOH), respectively. For each specimen the onset T_g was also determined on the basis of the DMA results.

Swelling tests were performed by immersing films with a known weight in 30 ml $CHCl_3$ for 24 h at room temperature. After that the weight of the swelled samples were noted and the degree of swelling was determined using eqn (S1) (ESI†). For solvent actuation experiments, the degree of (de)swelling was evaluated after immersing the films for different periods of time first in $CHCl_3$, for the swelling tests, and after that in EtOH, for the deswelling tests [eqn (S2), ESI†]. The curvature upon swelling, the degree of deformation and the degree of recovery during swelling and deswelling were calculated using eqn (S3)–(S5) (ESI†). The length of the curve of the bent bilayer was calculated using eqn (S6) (ESI†). All used equations are presented in the ESI.†

Experiments with vapor stimulus actuation were realized by placing the bilayer structure 1 cm above the $CHCl_3$ surface for 90 min, after which the bending movement was quantified. Solvent shape recovery was realized by deforming the PCL film in spiral form and immerging it in 30 ml of $CHCl_3$ for 10 min. Once the film achieved a straight swelled shape, it was immersed in EtOH for 90 min in order to deswell and to achieve full shape recovery.

Electrical stimulation tests were performed on a PCL/PCL–MWCNT film deformed to 80% of strain *via* a two-step DMA procedure [heating to 50 °C (3 °C min^{-1}) and cooling to 0 °C (3 °C min^{-1})] by applying a direct current of 2 mA (Keithley BAG1, SourceMeter-2400 apparatus) without or upon exposure to solvent vapors. On both extremities of the film, conductive Cu adhesive tape was used in order to connect the Cu filament to the apparatus electrodes.

3. Results and discussion

In the last few years, Diels–Alder chemistry has allowed the production of new generation polymer materials with remarkable dynamic properties: shape-memory,[21] self-healing[22] or reconfigurable, biodegradable and recyclable polymer materials.[23] In this study, for the first time the advantage of those thermoreversible reactions was explored for the manufacture of actuating systems. Three different kinds of films were prepared: two monolayers, PCL and PCL–MWCNT, and a bilayer made of PCL/PCL–MWCNT, using furan and maleimide moieties as diene and dienophile, respectively. In the case of the bilayer a key element for the functionality of the materials was ensuring the good adherence between the monolayers persisting during several actuation cycles. We achieved this by reversible covalent bonding *via* Diels–Alder reactions between both layers through a simple production procedure (Fig. 1). The efficiency of this approach was proven after rigorous mechanical testing where the bilayer preserved its structural integrity (ESI†). More information on the influence of the layer composition, in terms of the content of furan and maleimide moieties, on the bilayer production capacity can be found in the ESI† (Fig. S2).

The advantage of this simple procedure lies in its feasibility to be adapted for any polymer systems capable of undergoing such reactions. Moreover, the present approach offers the possibility of preparing multilayer structures with desired monolayer compositions by choosing polymers or incorporating nanofillers with diverse properties (photoactive, fluorescent, electroconductive, *etc.*), in order to confer multi-stimuli-responsiveness and functionality on the final material. As a result of the heterogeneous composition of the layers, the bi- or multilayer architectures can undergo sequential motions to form various desired 3D actuated folding shapes with a given extent of bending, contraction, swelling or curvature. In this context, the polymers present a great possibility of creating novel devices for soft actuators owing to their biocompatibility, lightweight, high deformability and multiple degrees of reshaping and the ease of manufacturing and programming mechanical properties through the addition of nanofillers.

In order to investigate the ability to produce a PCL/PCL–MWCNT polymer bilayer actuator based on the layer rigidity differences a detailed study of the thermo-mechanical and swelling properties of the materials was first performed.

The MWCNTs were chosen as functional nanofillers to finely modulate the rigidity and to impart conductive properties to one of the two layers. This hypothesis was firstly validated by studying the thermo-mechanical properties of the films through dynamic-mechanical thermal analysis. As presented in Fig. 2, all films had a clear glass–rubber transition between −60 °C and 20 °C with the tensile storage modulus (E') decreasing, until a plateau was reached at 20 °C. In addition, a second sigmoidal transition region near T_m of the films (ESI†) was registered between 30 °C and 50 °C followed by an extended rubbery plateau. The formation of the latter region was an indication of the successful formation of the resulting networks with E' values typical for cross-linked elastomers. The incorporation of 5 wt% of MWCNTs into the PCL matrix led to the production of films with enhanced thermo-mechanical properties in accordance with the data described in the literature.[24] It is interesting to note that the PCL/PCL–MWCNT system was characterized by a lower rigidity than that of the PCL–MWCNT monolayer (Table 1 and Fig. 2), likely due to the influence of the neat PCL layer.

In relation with solvent-actuation, we investigated the influence of two solvents (with different affinities towards the PCL polymer matrix) on the thermo-mechanical properties of the films. For this purpose, $CHCl_3$ was selected as a good solvent for PCL, and EtOH as a poor one.[25] It was found that E' decreased with an increase in the immersion time of the materials in $CHCl_3$ (Fig. 2). This effect was accompanied by a lower stiffness compared to the networks in the dry state and was more pronounced for the unfilled PCL film, as it has the lowest rigidity (Table 1). The data are in good accordance with the Hildebrand solubility theory since, in our case, a good solvent (*i.e.* $CHCl_3$ due to its compatible polarity with PCL) penetrated easily into the PCL network and, in turn, swelled the polymer network more easily than a poor solvent (*i.e.* EtOH). Subsequently, the macromolecular chain mobility was enhanced, favoring the diffusion of more solvent molecules, leading to an increase in material volume and a decrease in mechanical stability.[26]

The quantity of the absorbed solvent had a direct impact on the glass transition temperature of the materials (T_g, Table 1) since the T_g onset values decreased with the immersion time. This demonstrates the plasticizing/solvating effect of $CHCl_3$ on the PCL matrix. This rubber-like behavior of polymer materials upon immersion in a given solvent, leading to lower E' and T_g

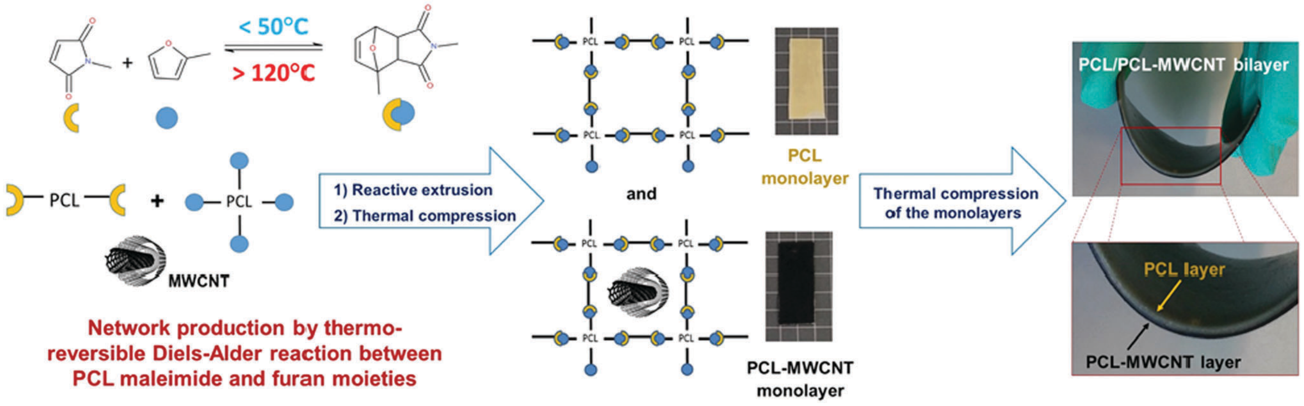


Fig. 1 Mono- and bilayer film production.

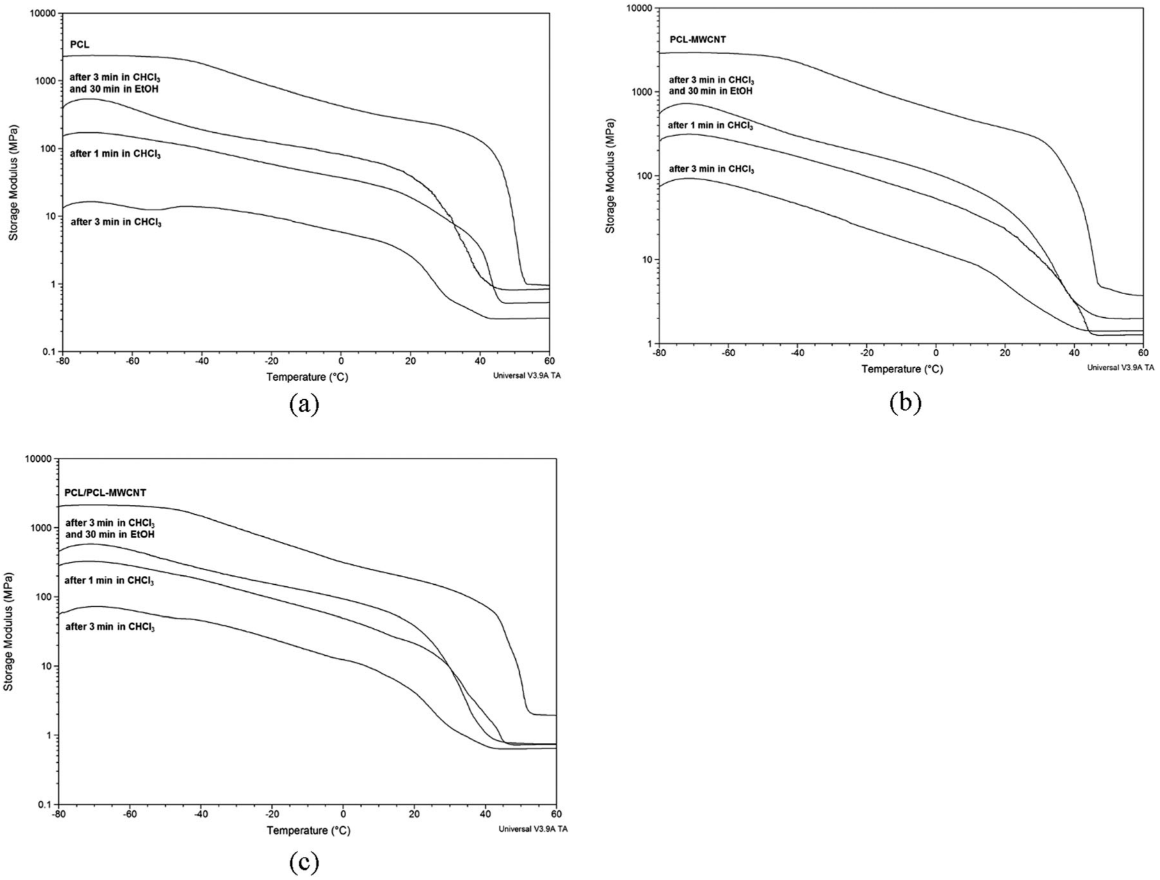


Fig. 2 Storage modulus of PCL (a), PCL–MWCNT (b), and PCL/PCL–MWCNT (c) films before and after immersion in $CHCl_3$ (1 and 3 min) and after immersion for 3 min in $CHCl_3$ and 30 min in EtOH.

Table 1 Storage modulus (E', at −60 °C) and T_g onset values of mono- and bilayer SMP films before and after immersion in $CHCl_3$ (1 and 3 min) and after 3 min and 30 min immersion in $CHCl_3$ and EtOH, respectively

	E' [MPa]				T_g onset [°C]			
Sample	Dry state	1 min $CHCl_3$	3 min in $CHCl_3$	3 min in $CHCl_3$ and 30 min in EtOH	Dry state	1 min $CHCl_3$	3 min in $CHCl_3$	3 min in $CHCl_3$ and 30 min in EtOH
PCL	2324	150	13	395	−50	−77	−80	−67
PCL–MWCNT	2872	270	79	565	−49	−58	−80	−65
PCL/PCL–MWCNT	2085	285	64	480	−48	−59	−79	−63

onset values, is a well-known phenomenon and has already been reported.[8]

Furthermore, it was of interest to determine whether the initial mechanical strength of the films could be restored at the end of the shape-recovery process just after coming into contact with the poor solvent. For this purpose, the films were immersed for 3 min in $CHCl_3$ and then for 30 min in EtOH (30 min was the time necessary for the samples to recover their initial shape). In all cases, the materials demonstrated better mechanical properties after the immersion in EtOH compared to their previously swollen state in $CHCl_3$ as well as an increase in the T_g onset values (Table 1). However, despite the increase in E' and T_g onset values after 30 min in EtOH, the values were still lower than those of the dried samples likely due to the presence of solvent traces within the film (ESI†).

Swelling properties of the films were evaluated by immersing the samples for 24 h in $CHCl_3$ and it was noticed that the degrees of swelling were highly dependent on the composition – values of 1650%, 965% and 1290% were measured for PCL, PCL–MWCNT and PCL/PCL–MWCNT, respectively. It is worth mentioning that good adherence between the layers in the bilayer structure was observed during these different experiments. Interestingly and in line with our final aim to produce a solvent-responsive actuator, the PCL/PCL–MWCNT bilayer film demonstrated self-bending behavior towards the backward direction of the nanofiller-containing layer (Fig. 3a). This phenomenon, not present in the case of monolayer films, results most probably from the rigidity difference between the monolayers and their degree of swelling, in turn generating a swelling gradient. Indeed, in the bilayer, solvent molecules

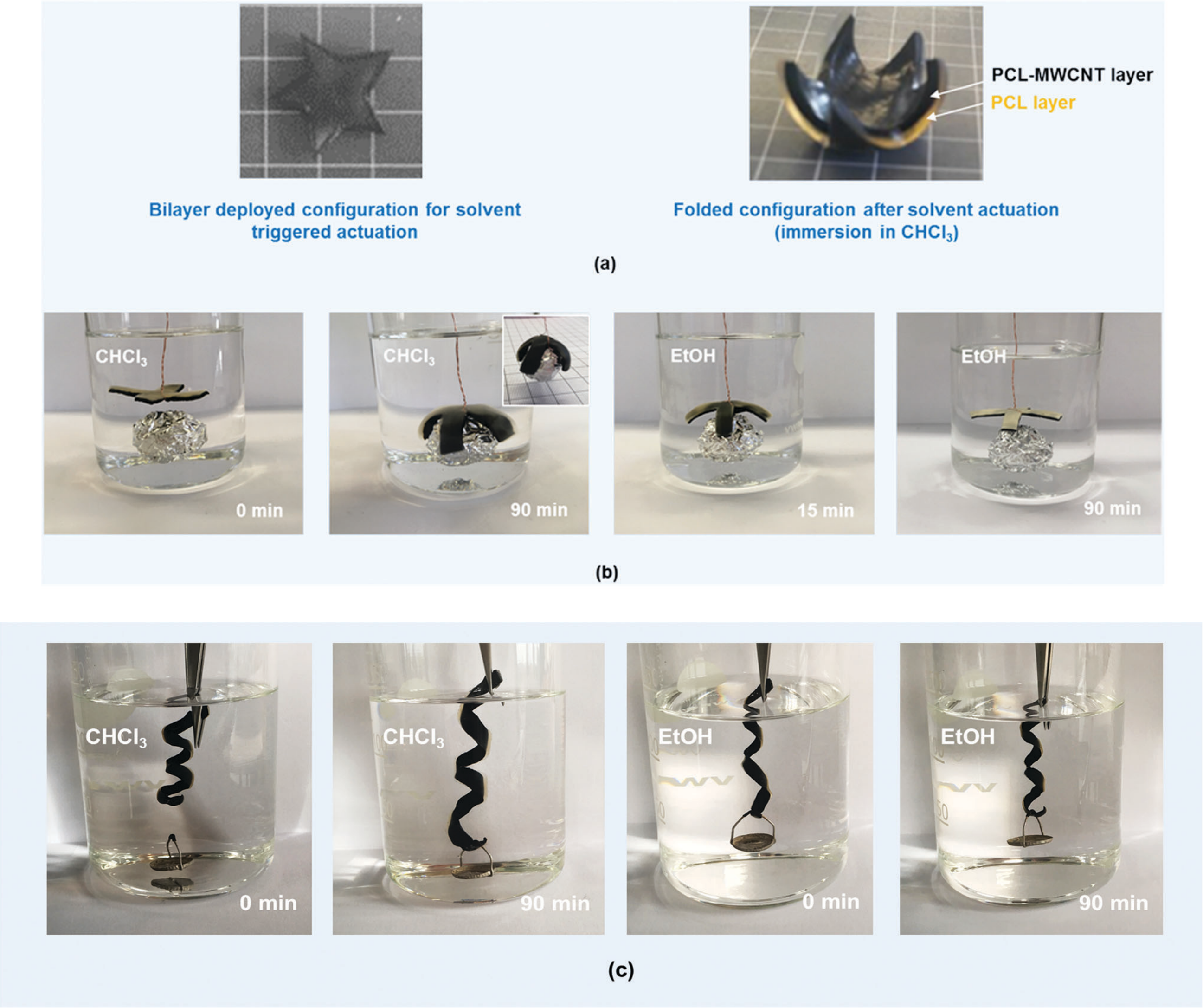
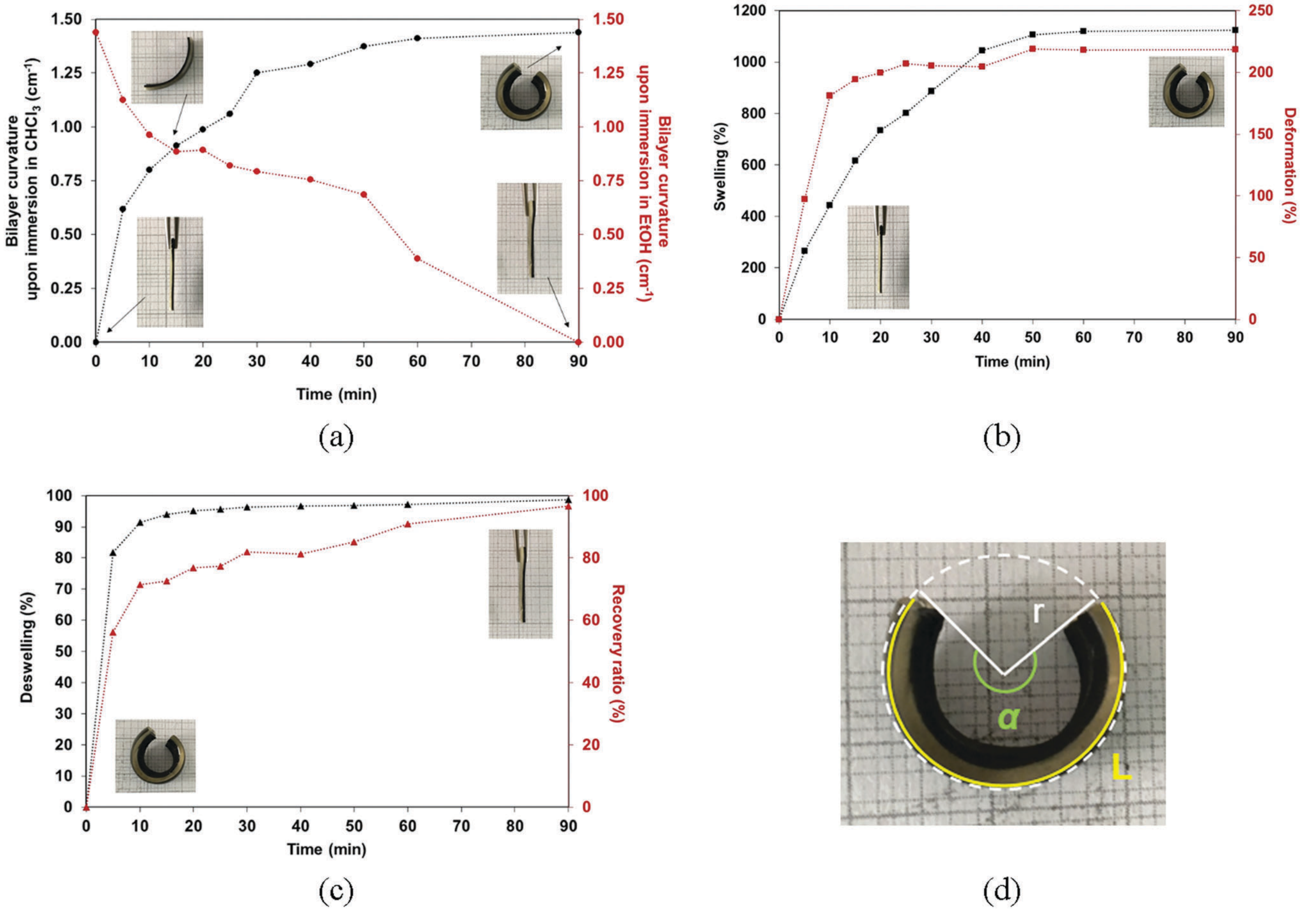


Fig. 3 Digital images of deployed and folded configurations of the PCL/PCL–MWCNT bilayer film before and after immersion in $CHCl_3$, respectively (a), and four arms (b), and spiral shaped (c) bilayer film for object transportation (catching and releasing in different solvents).

penetrate more easily into the PCL layer, subjected to greater deformations and providing good mobility to the macromolecular chains that, in turn, generate compressive stresses against the MWCNT-loaded PCL layer, slightly less swollen by $CHCl_3$ molecules. In addition, the PCL–MWCNT layer due to its greater rigidity and lower degree of swelling exerts a back-force withstanding the pressure of the PCL monolayer. These simultaneous effects are supposed to be the driving force for the observed controlled bending of the PCL/PCL–MWCNT bilayer in $CHCl_3$.

We explored this idea to demonstrate the solvent induced shape-memory of the monolayers after their suitable programming. For this purpose, PCL was deformed into a spiral shape and immersed in $CHCl_3$ (ESI†). The observed recovery process was fast due to the penetration of the solvent molecules into the material volume, with the subsequent swelling of the film and the increased chain flexibility leading to its original stress-free state. Full shape recovery was achieved after 10 min in $CHCl_3$ and 90 min in EtOH. Finally, the solvent-actuation capabilities of the bilayer film were investigated here, *i.e.*, its ability to spontaneously actuate in the presence of good and poor solvents. For this purpose, the PCL/PCL–MWCNT bilayer film was immersed in $CHCl_3$ in order to generate the folded configuration and, subsequently transferred into EtOH for the unfolded state. Several folding/unfolding cycles were performed and, independently of the cycle, the material unbending was characterized with a good degree of recovery (R_r 98%), without loss of weight or detachment of the individual layers. Furthermore, bi-layered structures four arms shaped were produced and their capacity to dynamically self-bend by enwrapping a simple object was evaluated. For this, the four arms designed structure was immerged in a $CHCl_3$ beaker containing a small object of 1.5 cm diameter. After 90 min, the bi-layered system was able to grab the object through cooperative actuation of the arms. Subsequently, the actuating system was transferred to an EtOH beaker and after 15 min the ball was released due to the relaxation of the arms (Fig. 3b). In a similar way, a bilayer with a complex spiral-like structure was obtained after heating the



(a) (b) (c) (d)

Fig. 4 Bilayer solvent-actuation upon immersion in $CHCl_3$ and EtOH (a). The swelling in $CHCl_3$ and the related R_d upon bending as well as the deswelling and the R_r value upon immersion of the bilayer in EtOH are presented in (b) and (c), respectively. Parameters used for the calculation of the curvature on swelling and the degree of deformation were: L – the length of the bilayer before and after swelling, α – the angle upon bending and r – the radius of the imaginary circle drawn around the bent film (d).

material at 100 °C (favoring retro Diels–Alder reactions) and rapidly cooling it at room temperature (favoring Diels–Alder reactions) to fix the new permanent shape of the material. After this procedure, the actuation of the bilayer was preserved (contraction and relaxation of the spiral with reversible transformation of the chemical energy into mechanical one) upon immersion in $CHCl_3$ or EtOH (Fig. 3c). The obtained results demonstrate the potential application of the PCL bilayer as devices for grabbing and transporting objects with complex shapes in a non-conventional environment such as organic solvents. The actuation time of several minutes was in accordance with the one characteristic of the chemically responsive soft actuators.

To get better insight into the bending/unbending process of the films, we have studied their kinetics by plotting the values of the bilayer curvature as a function of immersion time and the solvent nature. The curvature values increased continuously during the immersion time and it was noticed that the major shape changes occurred during the first 30 min of contact with $CHCl_3$ where the resulting bending curvature was around 1.25 cm^{-1}. Maximum bending curvature values of 1.4 cm^{-1} were reached after 90 min (Fig. 4a). In contrast, when immerged in EtOH, a decrease in the bending curvature was obtained reaching a curvature value close to 0 cm^{-1} after 90 min – attesting for a good reversible bending/unbending process within respectively good and poor PCL solvents. During this process, factors including solvent polarity, molar volume and possible interactions with the polymer matrix (*e.g.* hydrogen bonding) play an important role in the actuation process.[27]

In addition, during the swelling phase in $CHCl_3$, a swelling of more than 1000% was reached and a PCL/PCL–MWCNT degree of deformation greater than 200% due to the PCL layer expansion and PCL–MWCNT contraction (Fig. 4b) was measured. During the deswelling phase a good actuation recovery (R_r 98%), obtained after 90 min and corresponding to the complete deswelling time, with no fragmentation and/or cracking of the bilayer was observed even after multiple cycles (Fig. 4c). It is shown that, depending on the curvature value, it was possible to determine the immersion time of the materials in the solvent and consequently to determine the bilayer degree of deformation (R_d) or R_r.

Finally, to assess whether the present material could be used as a vapor-solvent detector, the PCL/PCL–MWCNT responsiveness to $CHCl_3$ vapors was also studied. For this, the sample was placed 1 cm above the solvent surface and after 90 min, the

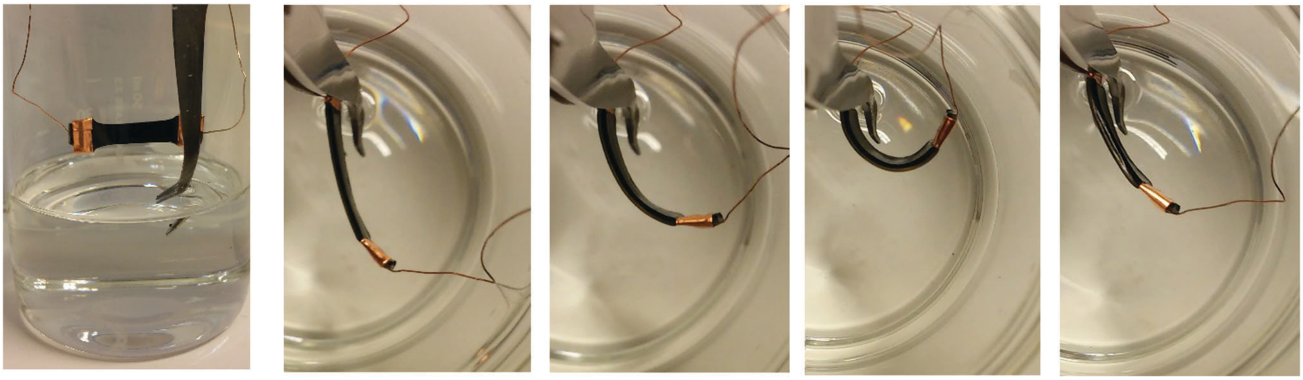


Fig. 5 Digital images of the shape recovering process of PCL/PCL–MWCNT from a temporary (80% of deformation) to the initial shape upon exposure to $CHCl_3$ vapor during electrical stimulation.

material curved in a way positioning the MWCNT containing layer on the inside face (as described in the case of direct immersion). The actuation upon exposure to vapor was slower but the process was fully reversible and reproducible upon several stimuli exposure/drying cycles with excellent R_r (98%) opening a potential way for solvent vapor detection in the sensor field. Herein, the degree of bending was also time-dependent and reached its maximum after 90 min of exposure. Usually such bending/unbending movements can be observed in complex materials with structural porous gradients[11] or specific crystalline phase orientations,[28] thus generating modulus gradients upon exposure to vapors.

The incorporation of MWCNTs into the materials offered the possibility of studying their electrical responsiveness related to the electrical conductivity of MWCNTs. Under electrical stimulation the PCL/PCL–MWCNT (80% of strain deformation) recovered quickly its initial shape through the Joule effect. In the subsequent stage, we studied the ability of the materials to act as sensors for solvent vapor detection. For this purpose, a pre-stretched film (80% of strain deformation) was placed at a distance of 1 cm from the top of the $CHCl_3$ solvent surface. After 1 min of vapor exposure, the material lost its conductive properties, after which the shape was recovered due to film swelling through a bending process as previously discussed. The loss of conductivity is most probably due to a perturbation of the nanofiller percolation network during the film surface swelling process. The greater mobility of the macromolecular chains in the swollen state had an impact on the degree of movements of MWCNTs and caused their dynamic distribution in the material.[20] As a consequence, the connections between the nanotubes were minimized and the conductive capacity of the material was impeded (Fig. 5).

4. Conclusion

In the present contribution, we developed a PCL/PCL–MWCNT bilayer architecture with solvent-based actuator properties. Good adherence between the monolayers was achieved through a simple procedure taking advantage of Diels–Alder reactions. Reproducible and highly reversible bending/unbending actuation was achieved upon immersion in or exposure to $CHCl_3$ and EtOH. In this approach, the bending direction of the bilayer was fully controlled by the rigidity gradient created in the polymer system and its anisotropic swelling behavior. It was found that the degree of bending/unbending was dependent on the solvent nature, the (de)swelling of the materials and the time of immersion. In addition, the actuating properties of the materials allowed shape recovery upon immersion in $CHCl_3$, as a result of the successful thermo-reversible network formation. The obtained materials could find potential application as multi-responsive devices in the soft robotics field with tunable actuating behaviors: grabbing and transportation of objects, solvent vapor sensors, or self-deployable structures. For instance, the production of water responsive devices for biomedical applications can be of consideration in the case where water-soluble polymers are used.

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