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Thermo-Reversible Reactions for the Preparation of Smart Materials: Recyclable Covalently-Crosslinked Shape Memory Polymers

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Summary: [4+2] thermoreversible Diels-Alder cycloaddition has been used to crosslink star-shaped poly(ε-caprolactone) in order to produce networks based on strong carbon-carbon covalent bondings. Depending on the nature of the Diels-Alder reactants, these bonds can be thermoreversibly broken, allowing re-processing of the polymer matrix.

Keywords: crosslinking; Diels-Alder polymers; recycling; shape-memory polymers; thermoreversible networks

Introduction

Shape memory materials (SMMs) are smart materials that can be fixed in a temporary shape (fixity) and can recover their permanent shape (recovery) by exposure to an appropriate stimulus such as heat or light. Because of this interesting property, SMMs raised a lot of interest, especially for biomedical applications. This kind of smart materials offer the ability to promote minimally invasive surgeries in the placement of biomedical devices such as vascular stents. Vascular stents are tubular scaffolds used to maintain the structure of a blood vessel and to prevent vasospasm and restenosis after angioplasty. The shape memory effect allows the insertion of small stents that can expand upon a trigger such as local heating after placement in a blood vessel. The first stent, made of stainless steel, has been placed by Sigwart et al. in 1986 and was designed to enable the elastic recoil and remodelling of blood vessels caused by angioplasty.[1] Stenting became rapidly a widely used surgery. In 2006, more than one million of percutaneous interventions were performed in the US alone among which 80% involved stents.[2]

Most stents are currently made of stainless steel, shape memory alloys (SMAs), and other metal alloys. However, this kind of stents presents several drawbacks. First, metallic stents are too stiff to navigate highly tortuous vessels such as those of neurovasculature. Second, they present limited recoverable strains less than 8% and compliance mismatch due to the stiffness of metallic stents which can contribute to restenosis. Finally, their costs are more expensive than alternative materials such as shape memory polymers (SMPs).

One of the most recent breakthroughs in stents technology is drug eluting stents (DESs). This kind of stents is made of a metal stent coated by a thin polymer layer designed to increase biocompatibility and to elute immunosuppressive agents such as paclitaxel and sirolimus (rapamycin) to prevent restenosis.[3] This discovery led researchers to design pure polymer stents. The increased flexibility, ductility and compliance of SMPs could overcome the problems encountered with current metallic vascular stents. Moreover, SMPs can be designed to deploy at human body tem-

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perature. In 2003, Wache et al. were the first to report on the development of an SMP stent based on thermoplastic polyurethane (PU) able to release drugs.[4] The recovery temperature of this smart material was set to be close to body temperature. Baer et al. studied the shape memory properties of a thermoplastic PU, triggered by laser heating.[5] An hybrid thermoplastic polyurethane system containing an organic, biodegradable poly(D,L-lactide) soft block with a hard block bearing an inorganic polyhedral oligosilsesquioxane (POSS) moiety has been developed by Knight et al.[6] They demonstrated that the releasing of drugs from the biodegradable stent coatings can be tailored by the composition of the soft segment and predicted by statistical models.[7]

In the last few years, biodegradable SMPs have been widely studied. This type of SMPs were first introduced by Lendlein et al.[8,9] They present many advantages. First, the complete dissolution of this implant prevents hyperplasia by avoiding reaction due to prolonged exposition of a foreign body in blood vessels. Second, biodegradable SMPs can release antiproliferative drugs during degradation.

There are several polymeric biodegradable stents in development but just a couple drew the attention at this stage on the basis of clinical data. One of the earliest devices in this field was the Igaki-Tamai stent (Kyoto Medical Planning Co.) based on poly-L-lactide (PLLA). The authors demonstrated the efficacy of this pure polymer stent, which has been implanted into fifteen patients and monitored over six months without observation of any cardiac disorder.[10] Another biodegradable stent, the BVS stent developed by Abbott Laboratories, is also made of poly-L-lactide (PLLA) and results from an initial clinical trial have been recently reported.[11] These SMP stents are based on the glass transition temperature of the PLLA to trigger the shape recovery.

Aside of the T_g as triggering temperature, the melting transition of semi-crystalline networks can also be used to trigger the shape recovery, which is sharper and faster. Generally, the best fixities are observed when a T_m is used as triggering temperature while the best shape recoveries are observed when the polymer is chemically cross-linked. Poly(ε-caprolactone) (PCL), a semi-crystalline polymer which can be easily chemically cross-linked, is one of the most widely studied polymers for the development of shape memory materials.[8,12] PCL presents several advantages such as a melting transition temperature close to body temperature, high biocompatibility, biodegradability. So, this polymer is highly relevant for biomedical devices such as stents or suture wire.[9] However, a major drawback of cross-linked material is the impossibility of reprocessing after cross-linking, preventing any reuse/recycling of the material. One of the purposes of this work is to find a solution to this limitation, that would then allow, for example, to reshape a stent at will or to recycle trimmings remaining after stent fabrication.

This article aims at describing a new concept for the preparation of well defined reversibly crosslinked shape memory polymer based on the formation of reversible carbon-carbon bonds. Multiarm star shaped PCL have been selectively modified at their chain ends by either a diene (furan, anthracene) or maleimide as a dienophile, then melt processed and cured in order to form well defined semicristalline polymer networks exhibiting excellent shape-memory properties as studied by cyclic tensile thermomechanical analysis. Reversibility of the network formation in case of furan used as dienophile has been assessed by recycling experiment.[13]

Experimental Part

Materials

Toluene, dichloromethane (CH_2Cl_2) and diethyl ether (from Chem-Lab) as well as *N,N*-dimethylformamide (DMF), succinic anhydride, triethylamine (NEt_3), furfuryl alcohol, 9-hydroxymethyl anthracene, 1,1′-(methylenedi-4,1-phenylene)bismaleimide

(BIS-MAL), dicyclohexylcarbodimide (DCC) and 4-dimethylaminopyridine (DMAP) from Aldrich were used as received. 4-(2-hydroxyethyl)-10-oxa-4-aza-tricyclo[5.2.1.0]-dec-8-ene-3,5-dione was synthesized as reported elsewhere.[14] $\alpha,\omega -$ PCL-diol (Mn = 4000; PCL-2OH) and 4-arm star-shaped PCL bearing hydroxyl groups at the end of each arm ($M_n = 8000$ g/mol, PCL-4OH) were kindly provided by Perstorp-caprolactones.

Synthesis of End-Functional PCL (see Figure 1)

Synthesis of 4-Arm Star-Shaped Carboxylic Acid-Bearing PCL (PCL-4COOH)

Typically, 80 g (40 mmol of hydroxyl function) of PCL-4OH were transferred into a previously dried glass reactor. After three azeotropic distillations with toluene, 320 ml of anhydrous DMF were added to the reactor through a rubber septum with a stainless steel capillary. After complete solubilisation, 4.4 g (44 mmol) of succinic anhydride and 6.2 ml (44 mmol) of triethylamine were sequentially added to the DMF solution. The solution was then stirred at 45 °C overnight. PCL-4COOH was recovered by precipitation in diethyl ether, filtered and dried under vacuum.

Synthesis of Telechelic Carboxylic Acid-Bearing Linear PCL (PCL-2COOH)

The same methodology was used to prepare PCL-diacid (PCL-2COOH) from the commercial PCL-2OH. Functionalization was assessed by ^{1}H-NMR characterization.

Synthesis of 4-Arm Star-Shaped Furan-Bearing PCL (PCL-4FUR)

40 g (20 mmol of carboxylic acid functions) of PCL-4COOH were transferred into a previously dried glass reactor. 150 ml of anhydrous CH_2Cl_2 were transferred to the reactor through a rubber septum using a stainless steel capillary. After the solubilisation of the PCL, 2.4 ml (22 mmol) of furfuryl alcohol, 4.5 g (22 mmol) of DCC and 0.27 g (2.2 mmol) of DMAP were transferred inside the reactor. After one night of reaction at room temperature and filtration of the formed dicyclohexylurea

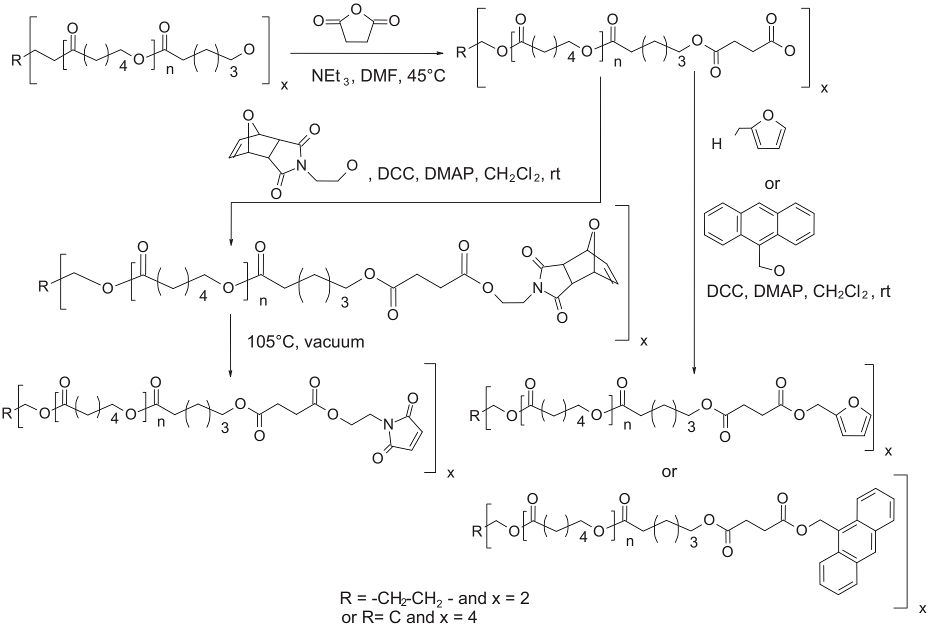

Figure 1.
Synthetic pathways for the preparation of PCL network precursors.

(DCU), PCL-4FUR was recovered by precipitation in diethyl ether, filtered and dried under vacuum. Functionalization was assessed by ^{1}H-NMR characterization.

Synthesis of Telechelic Furan-Bearing Linear PCL (PCL-2FUR)

The same experimental procedure than the one followed to prepare PCL-4FUR was used to prepare telechelic furan-bearing linear PCL (PCL-2FUR), using PCL-2COOH.

Synthesis of 4-Arm Star-Shaped Anthracene-Bearing PCL (PCL-4ANTHR)

The same experimental procedure than the one followed to prepare PCL-4FUR was used to prepare 4-arm star-shaped anthracene-bearing PCL (PCL-4ANTHR), using 9-hydroxymethyl anthracene instead of furfuryl alcohol.

Synthesis of 4-Arm Star-Shaped Maleimide-Bearing PCL (PCL-4MAL)

40 g (20 mmol of carboxylic acid functions) of PCL-4COOH were transferred into a previously dried glass reactor. 150 ml of anhydrous CH_2Cl_2 were transferred to the reactor through a rubber septum using a stainless steel capillary. After the solubilisation of the PCL, 2.2 g (22 mmol) of 4-(2-hydroxyethyl)-10-oxa-4-aza-tricyclo[5.2.1.0]dec-8-ene-3,5-dione, 2.2 g (21 mmol) of DCC and 0.26 g (2.1 mmol) of DMAP were transferred inside the reactor. After one night of reaction at room temperature and filtration of the formed DCU, the protected PCL-4MAL was recovered by precipitation in diethyl ether, filtered and dried under vacuum. The polymer was then transferred into a glass reactor before to be heated at 105 °C under vacuum for 10 hours to eliminate furan and regenerate the maleimide functions. PCL-4MAL was kept at room temperature. Functionalization was assessed by ^{1}H-NMR characterization.

Preparation of the PCL Networks

PCL networks have been prepared by reactive extrusion followed by thermal curing. The amount of material introduced in the mini-extruder has been calculated in order to reach 4.6 to 4.8g and to be mixed in stoichiometric ratio between Diels-Alder reactants. As a typical example, 2.4 g of PCL-4FUR and 2.4g of PCL-4MAL were melt blended at 105 °C in a 6 ccm co-rotating twin screw mini-extruder (Xplore, DSM) for 15 min at 150 rpm. The extruded materials was then placed in a 0.65mm thick metallic frame and placed under a load of 10 kg for 72 h in a ventilated oven at 65 °C. The sample was recovered in form of a flat sheet that was kept min 7 days at room temperature before measurement. For the PCL-2FUR/PCL-4MAL blend, 3.2 g of PCL-2FUR were melt-mixed with 1.6 g of PCL-4MAL; for the PCL-4FUR/BIS-MAL blend; 4.2 g of PCL-4FUR were melt-mixed with 0.38 g of BIS-MAL and for the PCL-4ANTHR/PCL-4MAL blend, 2.4 g of PCL-4ANTHR were melt-mixed with 2.4 g of PCL-4MAL.

Characterization Techniques

Gel permeation chromatography measurements (GPC) were carried out in THF at 45 °C at a flow rate of 1 mL/min with a SFD S5200 auto sampler liquid chromatograph equipped with a SFD refractometer index detector 2000. The PL gel 5 μm (10^5 Å, 10^4 Å, 10^3 Å and 100 Å) columns were calibrated with polystyrene standards. ^{1}H-NMR spectra were recorded on samples dissolved in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN 400 apparatus at 25 °C. Shape memory properties have been measured with a DMA Q800 (TA Instruments) using the tensile film clamp in controlled force mode. The sample (typically 4 mm × 5 mm × 0.65 mm) was first equilibrated at 65 °C for 5 min then experienced a tensile stress ramp (0.06 MPa/min) till 0.6 MPa. Then, the sample was cooled down, under stress at 3 °C/min to 0 °C and maintained at that temperature for 5 min. The stress is then released and the sample is reheated, stress-free at 3 °C/min to 65 °C. The process is cycled 4 times.

Results and Discussion

A telechelic hydroxyl-bearing linear PCL with a molecular weight of 4000 g/mol

(PCL-2OH) and a 4-arm star-shaped PCL with a molecular weight of 8000 g/mol (PCL-4OH) also functionalized by a hydroxyl group at each chain end were selected as precursors to generate the networks. The chain-ends of these different PCLs were selectively converted into diene (furan or anthracene) or dienophile (maleimide) by a two-step process following the synthetic pathway depicted in Figure 1. The characteristics of the polymers are given in Table 1.

PCL-furan and PCL-maleimide were melt-blended into a mini-extruder at 105 °C. This temperature was chosen in order to favor the retro-Diels-Alder reaction during blending and so avoiding any cross-linking into the mixing chamber.[15] As evidence of the absence of significant crosslinking reaction, no torque increase was noted during the process. After extrusion, the mixing was rapidly injected into a mold in order to confer an identical and well-defined shape to each sample. These samples were then cut into five pieces having the same weight before to be placed in a thermostated oven at 65 °C for curing. Indeed, this temperature is reported as ideal in order to favor the Diels-Alder reaction [15] leading to the cross-linking of the material. Crosslinking evolution was followed by measurement of the swelling rate (and the amount of insolubles) of the material in $CHCl_3$, in function of reaction time (up to 7 days), for three systems: PCL-2FUR/PCL-4MAL, PCL-4FUR/BIS-MAL; PCL-4FUR/PCL-4MAL. For the PCL-2FUR/PCL-4MAL, the swelling test leaded to the dissolution of the samples, whatever the curing time. SEC analysis of the obtained material revealed a very large and multimodal molar mass distribution, at masses larger than the precursors, indicating the probable formation of a hyperbranched structure. The two other systems have lead to the formation of a gel when swollen in $CHCl_3$, allowing for the study of the crosslinking reaction. The swelling rate and the fraction of insoluble materials with reaction time are reported in Figure 2.

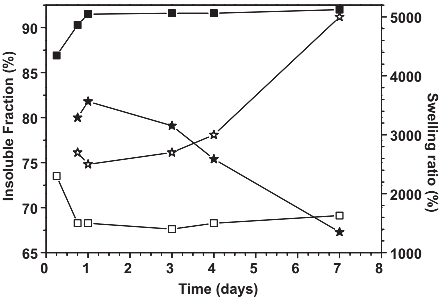

Figure 2.
Evolution of the swelling ratio (open) and the insoluble fraction (plain) for the PCL-4FUR/BIS-MAL (star) and the PCL-4FUR/PCL-4MAL (square) systems with curing time.

On the basis of these results, several observations can be made. First, the rate of crosslinking was larger for the PCL-4FUR/PCL-4MAL system than for the PCL-4FUR/BISMAL as indicated by the larger swelling ratio and the lower insoluble fraction recorded for the latter. Moreover, the PCL-4FUR/BISMAL system showed a continuous decrease in the amount of insolubles and hence in the crosslinking degree after 24 h of curing. These observations can be rationalized by the combina-

Table 1.
Molecular characteristics of the starting and functionalized PCLs.

PCLs	End-function	Mn, SEC a) [g/mol]	Mw/Mn, SEC	% function b) [%]
PCL-2OH	Hydroxyl	7800c)	1.35	100
PCL-4OH	Hydroxyl	14000	1.18	100
PCL-2FUR	Furan	8800c)	1.25	85
PCL-4FURd)	Furan	16800	1.30	87
PCL-4MALd)	Maleimide	16400	1.22	85
PCL-4ANTHR	Anthracene	N.D.	N.D.	83

a)PS standards; b)as calculated from ^{1}H-NMR spectra; c)PCL mass, following Mark Houwink equation: M_n (PCL) = 0.29 $M_n(PS)^{1.703}$; d)discussed in ref [13]; N.D.: not determined tion of three factors: the existence of a dynamic equilibrium between Diels-Alder and retro-Diels-Alder reactions already significant at 65 °C for the furan/maleimide couple; the low functionality (only 2 maleimide moieties) and low molar mass of the BIS-MAL molecule and the poor solubility of BIS-MAL in PCL (observed when trying to mix PCL-4OH and BIS-MAL in a round bottom flask at 90 °C). The dynamic equilibrium coupled to its low functionality statistically favor the easy liberation of BIS-MAL and its low mass and weak affinity for PCL allows for its phase segregation during curing, forming BIS-MAL "reservoirs" in PCL and impeding its reaction with furan moieties borne on PCL.

The PCL-4FUR/PCL-4MAL was characterized by a much higher degree of crosslinking (lower swelling ratio, larger insoluble fraction) with the optimum values obtained after 72 hours. In this case, excellent miscibility of the two partners, coupled with the higher functionality of the maleimide-functionnalized PCL-4MAL favors crosslinking of the material. Therefore, this last couple, crosslinked under these optimized conditions, has been used for the preparation of chemically-crosslinked yet recyclable SMM.

Figure 3 shows the qualitative and the quantitative characteristics of the shape memory properties of the crosslinked PCL-4FUR/PCL-4MAL sample.[13] Above the melting point of PCL, the sample could be manually elongated to about 5x its initial length and kept its temporary shape upon cooling. Then, when immerged in water at 60 °C, it instantaneously (1 to 2 s) recovered its initial (permanent) shape (Figure 3a). Cyclic tensile testing (Figure 3b) allowed better appreciating the behavior of the material. In the loading phase at 65 °C, the sample deformed relatively linearly. Upon cooling under constant stress, the sample first crept until reaching ca. 20 °C then, between 20 °C and 0 °C, the sample experienced a large increase of its deformation, due to the oriented crystallization of the PCL chains. Upon unloading, the sample displayed very high fixing properties (fixity above 99% for each cycle). Then upon heating, the sample recovered its permanent shape when exposed at temperatures above ca. 54 °C (switching temperature). The first cycle is characterized by an incomplete recovery (88%), known as training phenomenon, while the following cycles are characterized by recovery rates above 99%. However, it can be observed on Figure 3b that, when increasing the number of cycles, the ability of the sample to deform increases. This particular phenomenon is explained by the occurrence of retro Diels-Alder reactions at 65 °C. Therefore during loading at 65 °C, some Diels-Alder bonds are broken and the stretched chains can then relax, pulling apart the Diels-Alder reactants that are not able then to reform the adduct during the cycle. At each cycle, the phenomenon occurs, the materials is

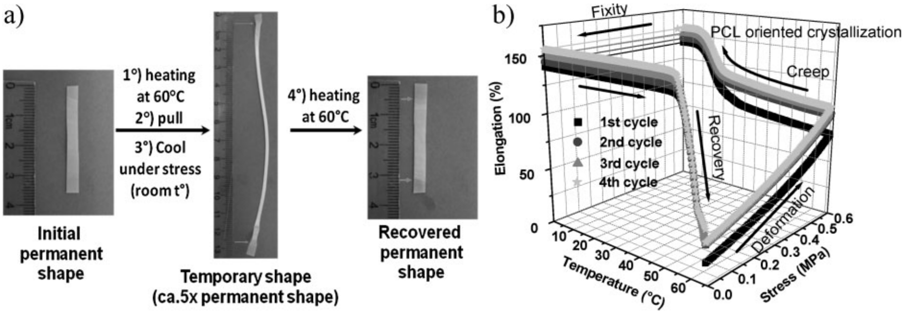

Figure 3.

Shape memory behavior in tensile testing for PCL-4FUR/PCL-4MAL : a. qualitative (manual stress); b. quantitative (DMA analysis)[13].

slightly less crosslinked and therefore more ductile from cycle to cycle.

In order to suppress (and therefore prove) this phenomenon, the use of a Diels-Alder couple characterized by a higher temperature for retro Diels-Alder initiation is needed. This is the case for the anthracene/maleimide couple, for which retro Diels-Alder initiation temperature is well above 180 °C.[16] Thus, PCL-4ANTHR/PCL4-MAL sample has been prepared using adapted conditions, i.e., melt blending was carried out at 60 °C to limit crosslinking during processing. Indeed, during the process, a doubling of the torque value has been observed for this couple, indicating that some Diels-Alder reaction proceed significantly during the 15 min mixing. Then, the resulting material was cured at 65 °C for 72 hours. Figure 4 shows the resulting shape memory cyclic tensile testing of the recovered sample.

The PCL-4ANTHR/PCL-4MAL sample showed also highly efficient shape memory properties with optimal fixity (>99%) and recovery (>99%) for cycle 2, 3 and 4 (cycle 1 has a recovery of 92%) and the switching temperature at 52 °C. Interestingly, due to the much higher temperature for retro Diels-Alder initiation, the sample does not softens with the cycles, proving that by playing with the control of the retro-Diels-Alder parameters, it is possible to stabilize the created SMPs. However, the high temperature needed to induce cycloreversion does not allow recycling, due to the relatively weak thermal stability of the functional PCLs(and especially maleimide groups) at the temperature requested for being in the retro Diels-Alder regime with this couple (above 180 °C).

This is not the case for the PCL-4FUR/PCL-4MAL sample that has been successfully reshaped by melting the chopped shape memory film in the cylinder of a DSM mini-injection device for 20 min at 125 °C, re-injected in form of a barrel, hot pressed and crosslinked again at 65 °C for 72 hours in a film and measured in tensile mode for shape memory properties 2 days and 14 days after processing (Figure 5).

When measurements are carried out 2 days after processing, the recycled PCL-4FUR/PCL-4MAL exhibits shape memory properties with excellent fixity (>99%) and recovery (>99%) for cycle 2, 3 and 4 and correct recovery for the first cycle. However, the measured elongations are significantly larger than for the initial material, reaching 310% of deformation at the 1st cycle where the initial material only deformed by 140% upon the same stress. This observation seems to indicate that the recycled material is less crosslinked than the initial material. However, a characteristic difference between the two measures was the time left after processing for shape

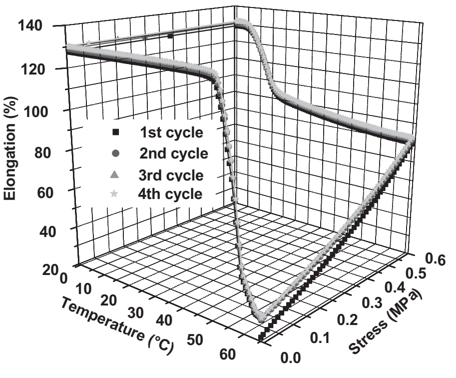

Figure 4.
Shape memory behavior in cyclic tensile testing for PCL-4ANTHR/PCL-4MAL sample.

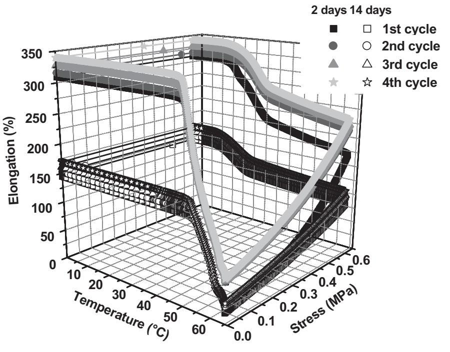

Figure 5.
Shape memory behavior in tensile testing for recycled PCL-4FUR/PCL-4MAL sample, as measured 2 days (plain) and 14 days (open) after the end of curing.

memory properties evaluation. Indeed, the initial SMM was evaluated 2 weeks after processing. Therefore, the recycled SMM sample has been measured once more, 14 days after processing. The shape memory testing is displayed also in Figure 5. After 14 days, the material displays shape memory properties almost identical to the initial material. The explanation for this observation is that Diels-Alder reaction continues to occur in the solid state, within the amorphous fraction of the PCL to reach a comparable degree of crosslinking than the initial SMM within the same period of ageing (14 days). Even if the recycled SMM does not exactly replicate the properties of the initial material, properties are sufficiently close and reproducible to assess excellent recyclability of this innovative SMM upon the conditions used.

Conclusion

Diels-Alder reaction can be used to prepare PCL-based thermoreversible networks exhibiting excellent shape memory properties. Most efficient crosslinking was obtained when mixing 4-arm star shaped PCLs functionalized with complementary maleimide and furan or anthracene moieties. Shape memory properties have been assessed by cyclic tensile thermomechanical measurement and virtually complete fixity and total recovery were recorded in the three cycles following the first one (training effect). An increase in the strain values between successive cycles is observed for the SMM based on the furan/maleimide Diels-Alder couple, due to the occurrence of cycloreversion during deformation at 60 °C that reduces the crosslink density of the SMM. This phenomenon is absent for the anthracene/maleimide couple, since cycloreversion occurs for this adduct at much higher temperature. This high stability impedes the recycling of the crosslinked materials while recyclability is demonstrated for the furan/maleimide sample. Upon ageing for 14 days at room temperature, Diels-Alder reaction between furan and maleimide continues to occur in the solid state, finalizing the crosslinking of the material.

In order to alleviate the encountered problems (inadequate curing temperature and slow Diels-Alder kinetics for the furan maleimide adduct formation), the search for Diels-Alder couples with more adapted cycloreversion initiation temperature and faster kinetics are under current investigation.

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