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ARTICLE

## Healing by Joule effect of electrically-conductive poly(ester-urethane)/carbon nanotubes nanocomposites†

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Recent demands for polymers with autonomous self-healing properties are being constantly raised due to the need of high-performance and reliable materials. So far, the advances in this field are limited to the production of self-healing materials requiring a high energy input. Therefore there is an urgent need to develop self-healing polymer systems, in which healing can be easily and specifically induced by external stimuli for economical and viable applications. In the current work we demonstrate, for the first time to our knowledge, the possibility to heal locally macroscopic damages by a confined temperature increase arising from Joule effect. The damage healing is promoted by the resistance to an electrical current at the crack tip. This new concept is studied on thermo-reversible and electrically conductive poly(ester-urethane)/carbon nanotube nanocomposites derived from thermo-reversible Diels-Alder reactions between furfuryl- and maleimide-functionalized poly( $\epsilon$ -caprolactone) (PCL)-based precursors. Electrically conductive materials are then obtained after incorporating multi-walled carbon nanotubes into the thermo-reversible networks using reactive extrusion. Under mild electrical conditions, temperature in the range of the retro-Diels-Alder reaction can be obtained near the damaged site. The obtained results reveal the potential of this new approach for healing materials locally while maintaining the overall material properties.

### Introduction

Inspired by the human skin, self-healing polymers have been widely developed since the 1980s to overcome some major limitations of common engineering polymers on failure.<sup>1</sup> During their lifetime, conventional polymers undergo many mechanical and photo/thermal aggressions leading to microcracks and with time to major fractures of the material affecting its efficiency, sustainability and safety. Therefore, many efforts have been made during these last decades to heal microcracks and restore the initial mechanical properties of a given material.

Intrinsic self-healing polymers thereby represent a promising way to heal microcracks due to their autonomous healing properties. This intrinsic healing process is based on reversible bonding allowing to heal a material in a repetitive way after a sufficient energy input.<sup>2</sup> Such reversibility can be triggered by light illumination, supramolecular interaction or thermal activation.<sup>3</sup> In 2002, Chen et al. reported for the first time on self-healing polymers based on [4+2] Diels-Alder reactions by designing a thermo-remendable and cross-

linked epoxy resin.<sup>4</sup> These self-healing resins were obtained by thermo-reversible Diels-Alder reactions between tetrafulan (diene) and trimaleimide (dienophile) monomers. It was shown that when a crack occurs at the material surface, by simply heating the material up to 90-120°C (retro-Diels-Alder favored) and by subsequently cooling it down to 50°C (Diels-Alder favored to restore the covalent bonds) self-healing of the material was possible. Although many self-healing polymers of different architectures designed following reversible bonding such as furan-maleimide Diels-Alder chemistry have been developed since this pioneering work,<sup>3, 5-7</sup> the self-healing process however requires external heating across the overall materials and cannot be specifically localized to the damaged regions to be repaired. Therefore there is a need to develop new alternatives to locally and specifically repair any (micro)cracks, and more preferably in the bulk of materials.

Among the approaches investigated to overcome these limitations, the concept of externally-activated heating via the incorporation of magnetic, photo-thermal and electrical nanoparticles into self-healing polymeric matrices has recently been developed but it remains scarcely addressed to few examples such as temperature-based self-healing of networks filled with magnetic chromium oxide particles, gold nanoparticles, carbon fibers or graphite.<sup>8-15</sup> In the present study, we propose for the first time to the best of our knowledge the design of thermo-reversible and electrically conductive poly(ester-urethane) nanocomposites containing multi-

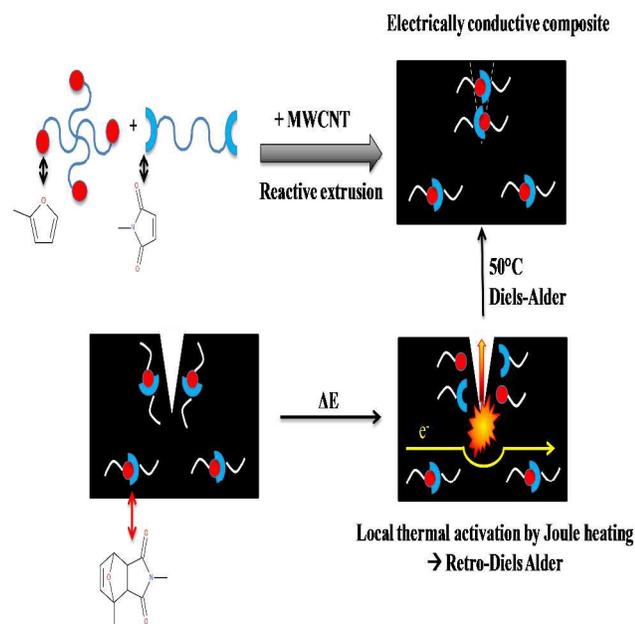
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walled carbon nanotubes (MWCNTs) that are able to be locally healed using Joule effect (Fig. 1). Due to their unique mechanical, electrical and thermal properties,<sup>16</sup> carbon nanotubes are widely used as nanofillers for the mechanical reinforcement of polymeric materials<sup>17</sup> and for the synthesis of composites electrically conductive at low MWCNTs amount (less than 1-2% wt.).<sup>18</sup>

Although the implementation of MWCNTs in the field of electro-active shape memory polymers was already reported,<sup>19</sup> no studies deal with self-healing of polymers based on Joule effect using MWCNTs. As far as self-healing is concerned, we have herein considered thermo-reversible poly(ester-urethane) networks obtained by reactive extrusion, a solvent-free process, involving linear and branched poly( $\epsilon$ -caprolactone) (PCL) terminated with furfuryl moieties, noted PCL(FUR)<sub>2</sub> and PCL(FUR)<sub>4</sub> respectively, and a PCL-based dimaleimide coupling agent, noted PCL(MAL)<sub>2</sub>.<sup>20, 21</sup> The main advantages of using PCL, an aliphatic polyester, lies on its good chain mobility at ambient temperature ( $T_g = -60^\circ\text{C}$ ), low melting temperature ( $T_m = 60^\circ\text{C}$  - below the Diels-Alder activation temperature) and a good processability. To obtain the electro-conductive networks, MWCNTs were directly dispersed into the polymeric matrix using extrusion method. The thermo-reversibility of the networks in presence or not of MWCNTs, important for the healing process, was attested after five heating/cooling cycles using a rheometer coupled with FTIR spectrometer. Finally, the local healing of the resulting nanocomposites was demonstrated under electrical current and monitored by an IR-camera on scratched films.



**Fig. 1.** Development of thermo-responsive and electrically conductive networks based on Diels-Alder moieties by reactive extrusion and thermal activation at crack tip by Joule effect

## Experimental

### Materials

$\alpha,\omega$ -Dihydroxyl poly( $\epsilon$ -caprolactone) (PCL-diol) (CAPA2402,  $M_n = 4000 \text{ g.mol}^{-1}$ ; PDI = 1.48) and  $\alpha,\alpha',\omega,\omega'$ -tetrahydroxyl poly( $\epsilon$ -caprolactone) (PCL-tetraol) (CAPA4801,  $M_n = 8000 \text{ g.mol}^{-1}$ ; PDI = 1.48) were kindly supplied by Perstorp and used as received. 1-(3-hydroxypropyl)-1H-pyrrole-2,5-dione (MAL(OH)) was prepared from 3-aminopropan-1-ol (Acros, used as received), exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (Sigma Aldrich, used as received) and ethanol 96%vol (VWR) (Supporting Information 1). Furfuryl isocyanate (Sigma Aldrich), methylene diphenyl diisocyanate (Sigma Aldrich), dichloromethane (Alfa Aesar), chloroform (VWR), methanol (VWR) and multi-walled carbon nanotubes NC7000 (Nanocyl, 1.5  $\mu\text{m}$  average length and 9.5 nm diameter) were used as received.

### Synthesis of PCL end-functionalized with furfuryl moieties (PCL(FUR)<sub>2</sub> and PCL(FUR)<sub>4</sub>)

Reactions were carried out in bulk, under inert atmosphere, in a 250 ml previously conditioned flasks. PCL-diol and PCL-tetraol were end-functionalized in presence of an excess of furfuryl isocyanate (1.5 eq.) overnight at  $110^\circ\text{C}$ . Oligomers were dissolved in  $\text{CH}_2\text{Cl}_2$  and poured in an excess of methanol in order to remove out the excess of furfuryl isocyanate. Chemical characterizations were performed using  $^1\text{H}$  NMR spectroscopy (500 MHz,  $\text{CDCl}_3$ ). Yield 99% (Supporting Information 2).

### Synthesis of PCL end-functionalized with maleimide moieties (PCL(MAL)<sub>2</sub>)

Typically, PCL-diol (1eq.), 1-(3-hydroxypropyl)-1H-pyrrole-2,5-dione (2eq.) and methylene diphenyl diisocyanate (2.1eq.) were introduced into a 15  $\text{cm}^3$  twin-screw DSM micro-compounder at  $55^\circ\text{C}$ , 30 rpm and under nitrogen flow. Then both temperature and speed were raised to  $140^\circ\text{C}$  and 70 rpm respectively. The reaction was considered to be complete when the torque was constant (generally after 40 min). The protected maleimide end-groups were deprotected by placing the obtained polymer in an oven under vacuum at  $110^\circ\text{C}$  overnight. Chemical characterizations were performed using  $^1\text{H}$  NMR spectroscopy (500 MHz,  $\text{CDCl}_3$ ) (Supporting Information 3).

### Synthesis of thermo-mendable nanocomposite networks

The desire amount of MWCNTs (between 0.1 and 5% wt.) was added to a solution of PCL(FUR)<sub>x</sub> (where  $x = 2$  or 4) in  $\text{CH}_2\text{Cl}_2$ . The dichloromethane was evaporated overnight under a fumed hood and one hour under vacuum at room temperature to get a master-batch of PCL(FUR)<sub>x</sub>/MWCNTs with a perfect control of MWCNTs amount. This premix was then introduced in a micro-compounder (Supporting Information 4) in presence of

PCL(MAL)<sub>2</sub> (stoichiometric ratio between furfuryl and maleimide functions) at 55°C, 30 rpm and under nitrogen flow. Then both temperature and speed were increased up to 80°C and 70 rpm respectively. After a mixing of 30 min, the obtained nanocomposites were placed in an oven at 65°C to ensure the completion of Diels-Alder coupling reactions.

### Films preparations

0.4-mm thick films for rheological measurement, evaluation of Joule heating and volume conductivity measurements were obtained by compression molding. Typically, 7 g of the samples were placed in circular molds and compressed at 80°C, for 5 min in contact, 3 min at 10 bar and then 2 min during cooling.

### Electrical properties determination

Volume resistivity ( $\rho$ ,  $\Omega\cdot\text{cm}$ ) of the nanocomposites was evaluated with the four-probe method on rectangular samples with length, width and thickness of respectively 6 cm, 1 cm and 2 mm for low resistivity samples ( $1$  to  $10^7 \Omega\cdot\text{cm}$ ) and with the resistivity test chamber Keithley 8009 method on circular films with a diameter of 7 cm and a thickness of 0.4 mm for high resistivity samples ( $> 10^7 \Omega\cdot\text{cm}$ ). The volume conductivity ( $\sigma$  ( $\text{S}\cdot\text{cm}^{-1}$ )) was calculated with  $\sigma = 1/\rho$ .

### Tensile properties determination

Tensile tests were performed based on ASTM D638 using a Zwick universal tensile testing machine (speed = 10  $\text{mm}\cdot\text{min}^{-1}$  and preload = 1 N).

### Thermogravimetric characterization

Thermogravimetric analyses (TGA) of the samples were carried out on a TA Instrument Q500 model, under nitrogen flow, with a heating rate of 20  $^\circ\text{C}\cdot\text{min}^{-1}$  from 25°C to 800°C, in an open platinum pan.

### Scratch recovery evaluation

A Rockwell 100- $\mu\text{m}$ -diameter diamond tip apparatus was used to scratch the samples and for the evaluation of associated recoveries. Superficial surface scratches ( $P_s$ ) were performed at 25°C by applying a load of 0.5 N and post-scans were subsequently carried out to estimate recoveries. For this, post-scans after 5 min and after a heating treatment at 140°C for 20 min were used to quantify respectively the elastic recovery of the polymer ( $P_e$ ) and the residual depth  $R_d$ . Finally in order to quantify the scratch recovery ( $\eta$ ) after the heating treatment and get rid of the elastic recovery ( $P_s - P_e$ ) Equation 1 was used:

$$\eta = (1 - R_d/P_d) * 100 \quad (1)$$

where  $P_d$  is effective penetration depth ( $P_d = P_s - P_e$ ).

For each scratch a hundred of depth recoveries were calculated at different points of the scratch and an average was taken.

Further qualitative scratch recovery after electrical activation was imaged with a field emission gun scanning electron microscope (FEG-SEM Hitachi SU8020).

### Cross-linking density evaluation

Between 50 and 100 mg of the thermo-reversible networks were swollen in chloroform for 24 h at 25°C and polymer volume fractions ( $V_R$ ) were determined using Equation 2.<sup>22</sup>

$$V_R = \frac{m_1 d_s}{m_1(d_s - d_r) + m_2 d_r} \quad (2)$$

Where  $m_1$  and  $m_2$  are the weights before and after swelling tests;  $d_s$  and  $d_r$  are the density of the solvent and the polymer respectively. Then  $V_R$  values were used in the Flory-Rehner equation to obtain cross-linking densities of the networks ( $M_c/2$ ) following Equation 3:

$$M_c = - \frac{\rho V_s (V_R^{1/3} - V_{R/2})}{\ln[(1 - V_R) + V_R + \chi V_R^2]} \quad (3)$$

Where  $M_c$  ( $\text{g}\cdot\text{mol}^{-1}$ ) is the average molecular weight between the crosslinks,  $\rho$  ( $\text{g}\cdot\text{cm}^{-3}$ ) is the density of the polymer,  $\chi$  is the solvent-polymer interaction parameter (0.343 for the PCL/chloroform system),  $V_s$  ( $\text{cm}^3\cdot\text{mol}^{-1}$ ) is the molar volume of the solvent and  $V_R$  is volume fraction of the polymer.

### Thermal reversibility of the PCL-based networks

Thermal reversibility was evaluated by a rheometer coupled with FTIR spectrometer (Haake Mars III, Thermofisher coupled with Nicolet iS10). This device allows the simultaneous measurement of the rheological properties and the related changes in the chemical composition of the sample with temperature.<sup>23</sup> The diamond attenuated total reflectance (ATR) element that collects spectroscopic data simultaneously with rheological data is located at the bottom part of the rheometer. Oscillatory shear mode (at a shear strain of 0.1% and a frequency of 1 Hz) with parallel 20-mm-diameter stainless steel plates was used for all experiments. The sample thickness was fixed at 0.4 mm. In order to follow the reversibility of the Diels-Alder reactions five heating/cooling cycles were performed (20 min at 140°C and 1 h at 50°C per cycle) but only two heating/cooling cycles are presented in the manuscript for a better visualization. The data were recorded every 30 s at 140°C and every minute at 50°C. The consumption of the Diels-Alder moieties was quantified by following the intensity of the furan ring breathing band centered at 1024  $\text{cm}^{-1}$  and the maleimide double band centered at 695  $\text{cm}^{-1}$ .

<sup>1</sup>, normalized with respect to the carbonyl stretching band centered at  $1726\text{ cm}^{-1}$ , which is not affected by the temperature cycles.

### Evaluation of the thermal activation by Joule effect

Copper stickers connected to electrodes connected in turn to a voltage generator (Agilent U8002A, max 30V-5A) were placed on samples (with a distance of 1 cm) to ensure good electrical contact. Temperature increase was monitored by an infrared camera (FLIR A655sc) at one image/30s frequency.

## Results and discussion

### Synthesis of electro-conductive network

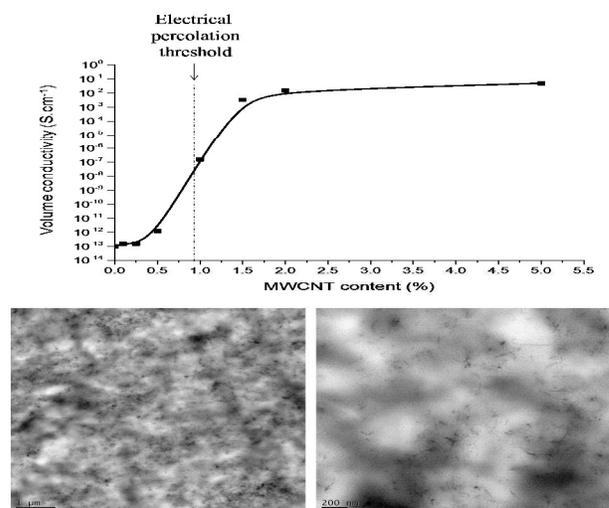
Carbon nanotubes, characterized by  $sp^2$  bonds, can react as diene or dienophile agents in the frame of [4+2] Diels-Alder reactions. It has recently been reported that, in presence of maleimide or furfuryl compounds, MWCNTs can be efficiently surface-functionalized through Diels-Alder reactions.<sup>24, 25</sup> In the present study such competitive reactions can be detrimental to the synthesis of electrically responsive materials and, in the meantime, to the healing process. Preliminary experiments showed that the length of dimaleimide is of great importance to reduce this competitive reaction as much as possible. For instance, when a short dimaleimide coupling agent, *i.e.*, the *N,N'*-(1,3-phenylene)dimaleimide, was initially employed in the preparation of these thermo-mendable PCL(FUR)<sub>2</sub> networks in presence of MWCNTs (from 0.25 to 1% wt.), the extrusion force, remaining constant (between 50 to 70 N) during the process, indicated that the coupling reactions between the PCL(FUR)<sub>2</sub> and the dimaleimide coupling agent were relatively low (*i.e.*, no increase in the molecular weight and the viscosity) and only brittle materials, mainly oligomers, were obtained. However, FTIR performed on the resulting samples showed the disappearance of the maleimide band at  $830$  and  $695\text{ cm}^{-1}$  (See Supporting Information 4), confirming that the maleimide moieties most likely reacted at the MWCNTs side walls as reported elsewhere.<sup>25</sup>

To reduce the coupling reactions between MWCNTs and maleimide moieties as much as possible, PCL oligomers end-functionalized with maleimide groups (PCL(MAL)<sub>2</sub>) were preferred in this work. Interestingly and in contrast to the short maleimide coupling agent investigated, coupling reactions between PCL(FUR)<sub>2</sub> and PCL(MAL)<sub>2</sub> did occur in presence of MWCNTs (from 0.1 to 5% wt.) as attested by an increase of the extrusion force (observed at  $80^\circ\text{C}$ ). Such a behavior could be explained by the steric hindrance of the long PCL(MAL)<sub>2</sub> chains compared to the short *N,N'*-(1,3-phenylene)dimaleimide, being in favor of the reaction towards PCL(FUR)<sub>2</sub>. At this point, even if

some coupling reactions between carbon nanotubes and PCL(MAL)<sub>2</sub> or PCL(FUR)<sub>2</sub> chains are still possible, there are less pronounced as compared to the desirable reactions between PCL(MAL)<sub>2</sub> and PCL(FUR)<sub>2</sub> that enables the synthesis of thermo-mendable Diels-Alder networks.

Besides, in order to obtain an efficient healing of the polymer arising from Joule effect a good electrical conductivity is required. For this end, MWCNTs were incorporated into the matrix and electrical properties of the obtained nanocomposites as function of MWCNTs amount were addressed (Fig. 2).

As expected, the electrical conductivity of the resulting composites derived from PCL(FUR)<sub>2</sub> increases with the MWCNT content, leading to conductive materials after ca. 1.5% wt. of MWCNTs (Fig. 2, top). The electrical percolation threshold, corresponding to the inflection point of the curve, was also estimated at ca. 1% wt. of MWCNTs. To have a good compromise between MWCNTs amount (relatively low) and good electrical properties, an amount of 2% wt. of MWCNTs was selected for the subsequent part of the study. It is worth noting that TEM images performed on this film confirm the good dispersion of MWCNTs within the matrix as shown in Fig. 2 (bottom). Tensile test performed on a nanocomposite filled with 2% wt. of MWCNT and a neat matrix also revealed an increase of the Young modulus with the addition of the fillers ( $425 \pm 5\text{ MPa}$  vs.  $559 \pm 12\text{ MPa}$ ), without clearly compromising the elongation at break of the polymeric matrix ( $745 \pm 43\%$  vs.  $636 \pm 19\%$ ). Moreover the presence of 2% wt. of MWCNTs slightly increased the thermal degradation temperature of the resulting material with a main degradation peak of  $422^\circ\text{C}$  for the neat matrix and  $438^\circ\text{C}$  for the composite (Supporting Information 5).

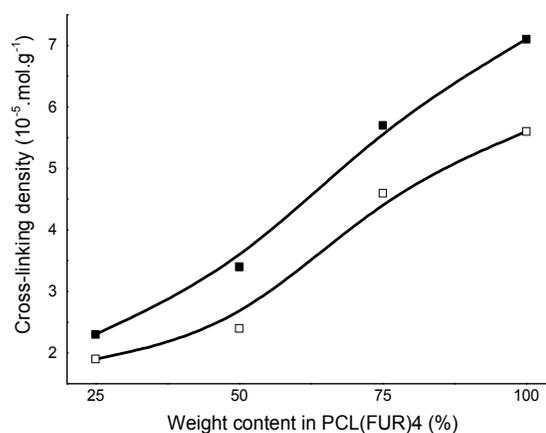


**Fig. 2.** Electrical properties of the linear PCL-functionalized network with MWCNTs amount (top) and TEM micrographs of a sample filled with 2% wt. of MWCNTs (bottom).

### Synthesis of thermo-reversible conductive cross-linked networks

These results, indicating the achievement of a well-defined electro-conductive network by reactive extrusion, allowed us building up the thermo-reversible cross-linked materials in presence of MWCNTs for healing investigations. Since the cross-linking density of a network may be of great importance for the healing processes,<sup>3, 26</sup> the linear PCL(FUR)<sub>2</sub> was partially replaced by a four-arm PCL end-functionalized by furan groups, PCL(FUR)<sub>4</sub>. For this, the network cross-linking density in terms of number of thermo-responsive moieties and availability towards Diels-Alder reactions was investigated through the synthesis of MWCNT-nanofilled networks containing 0/100, 25/75, 50/50, 75/25 and 100/0% wt. of PCL(FUR)<sub>4</sub>/PCL(FUR)<sub>2</sub> and 2% wt. of MWCNTs by reactive extrusion. It is worthwhile to note that independently of the PCL(FUR)<sub>4</sub>/PCL(FUR)<sub>2</sub> ratio, the proportion of end-functionalized furan and maleimide (PCL(FUR)/PCL(MAL)<sub>2</sub>) was maintained at 50/50% (molar) for all the compositions (See Supporting Information 6). For each composition, coupling reactions were monitored by following the extrusion force evolution with time (See Supporting Information 7) and as expected, the force and consequently the viscosity increased with the PCL(FUR)<sub>4</sub> fraction. This indicated that the higher the PCL(FUR)<sub>4</sub> amount in the PCL(FUR)<sub>2</sub>/PCL(FUR)<sub>4</sub> ratio, the higher the cross-linking degree of the network.

To better appraise the cross-linking density of the obtained networks, swelling tests were performed in chloroform and correlated with Flory–Rehner equation for the determination of the cross-linking density of the networks (see Experimental part). Fig. 3 shows cross-linking densities of the PCL networks containing different amount of PCL(FUR)<sub>4</sub> with and without MWCNT. One can notice a continuous increase of cross-linking density with the amount of PCL(FUR)<sub>4</sub>, confirming the qualitative results obtained by the extrusion force monitoring during the material processing. Interestingly, as shown in Fig. 3, the network cross-linking density can be easily tuned by simply adjusting the PCL(FUR)<sub>4</sub> content. It should be mentioned that, except for the linear composition (0% wt. of PCL(FUR)<sub>4</sub>) being fully soluble, the remaining systems were insoluble regardless of the MWCNTs content. This supports our aforementioned statement that the formation of the cross-linked networks through Diels-Alder reactions is not strongly perturbed by the presence of MWCNTs. However, higher cross-linking density values obtained for the systems containing MWCNTs in comparison to the MWCNTs-free systems likely indicating the formation of a joint-network between nanotubes and the polymeric network. This noteworthy effect is especially interesting when considering the fully cross-linked system (100% PCL(FUR)<sub>4</sub>, 2% wt. MWCNTs), which presents a good potential for healing applications due to the



**Fig. 3.** Cross-linking density quantification after swelling test in chloroform for networks containing different amounts of PCL(FUR)<sub>4</sub> with (■) and without (□) MWCNTs (2% wt.).

formation of cross-linked structure related to high amount of Diels-Alder adducts.<sup>26</sup> One should point out that the cross-linking degree does not seem to affect the electrical conductivity of these highly cross-linked composites since, for conversions of more than 99%, volume conductivities of about  $1.10^{-2}$  S.cm<sup>-1</sup> were measured (Supporting Information 8). In addition, good dispersions evaluated by TEM images were obtained for the fully cross-linked nanocomposite (0/100% wt. of PCL(FUR)<sub>2</sub>/PCL(FUR)<sub>4</sub>) (Supporting Information 9).

In the last sections, two systems containing 100/0% and 0/100% of PCL(FUR)<sub>4</sub>/PCL(FUR)<sub>2</sub> (extreme compositions) were selected for the thermo-reversibility study in presence of MWCNT. These systems give rise to different healing behaviors, since the highly cross-linked structure may be at the origin of intense Diels-Alder reactions with restricted chain mobility, whereas the linear system should have less Diels-Alder reactions but higher chain mobility.<sup>27</sup>

#### Thermo-reversibility of the selected systems

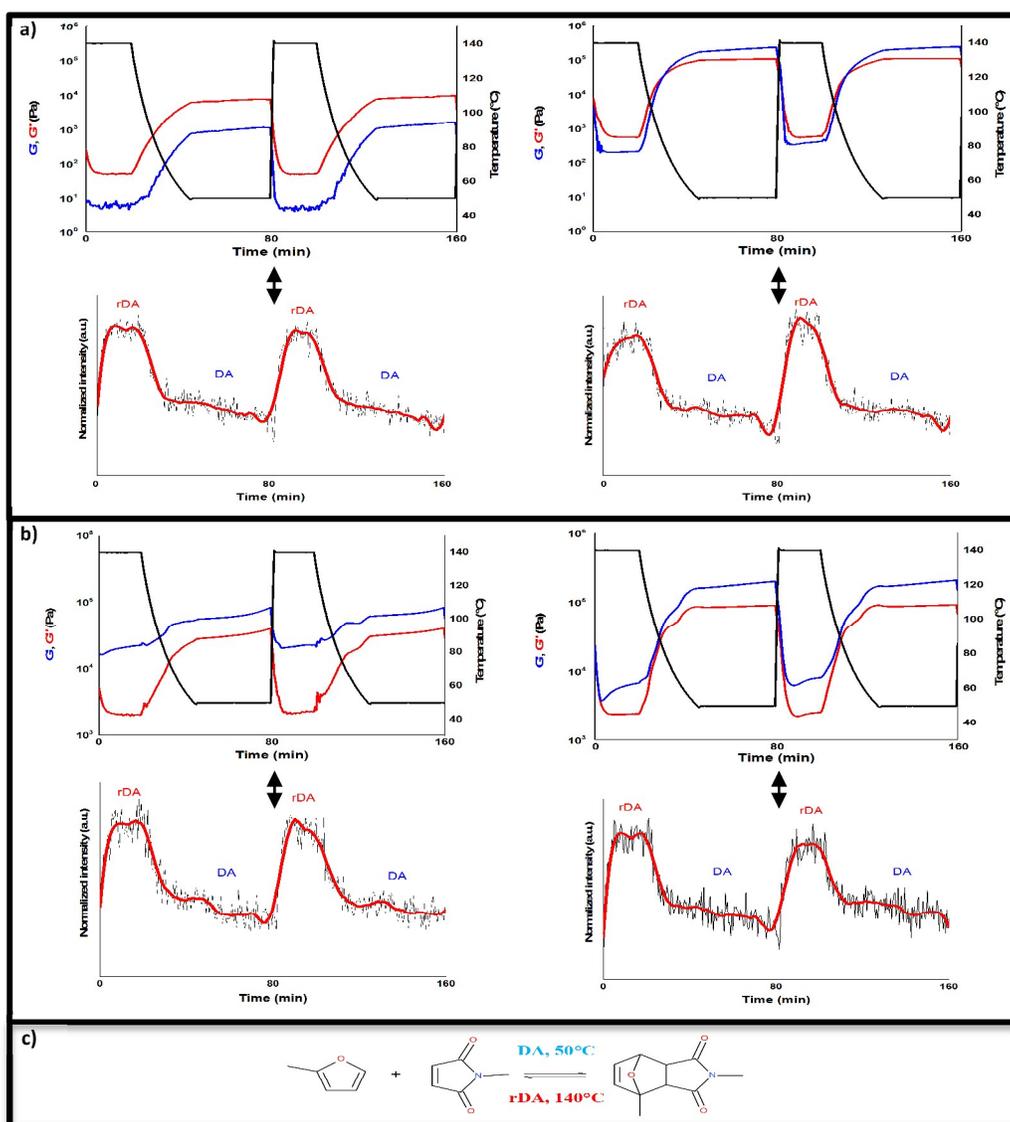
The influence of MWCNTs on the thermo-reversibility of the selected PCL-based networks was monitored by rheological analysis simultaneously recorded with *in situ* FTIR measurements (Fig. 4). Multiple temperature cycles (between 140 to 50°C corresponding to the retro-Diels-Alder and Diels-Alder reactions respectively) were performed and the maleimide band intensity at 695 cm<sup>-1</sup> was more particularly followed during the temperature cycles.

In absence of MWCNTs, storage modulus ( $G'$ ) and loss modulus ( $G''$ ) curves intersect after each heating/cooling cycle showing the reversibility of the cross-linked system. With temperature, the network changes from a cross-linked system at 50°C, where

$G'$  is higher than  $G''$ , to an uncross-linked network at 140°C, where  $G''$  becomes higher than  $G'$  (Fig. 4a top). Even after multiple temperature cycles this behavior remains well defined and perfectly reversible. For the linear system,  $G''$  is always higher than  $G'$  due to the lower viscosity of the linear chains compared to the cross-linked network. For both systems in absence of MWCNTs, *in situ* FTIR spectra of the PCL-based films reveals modifications with temperature and more particularly in the maleimide band region at 695  $\text{cm}^{-1}$ . A closer look at maleimide band intensity shows an increase of the band intensity at higher temperatures and a decrease of the band intensity at 50°C, in accordance to the retro- and Diels-Alder reactions respectively. Those perfectly reversible band modifications

indicate a good response of the networks to temperature cycles (Fig. 4a bottom).

By adding 2% wt. of MWCNTs to the linear and cross-linked systems, surprisingly the intersection of  $G'$  and  $G''$  with temperature is no longer observed, likely due to the formation of a physical MWCNT network incorporated into the cross-linked network, thus limiting the chain mobility. Despite this lack of reversibility evidenced with rheological test, *in situ* FTIR confirmed the occurrence of Diels-Alder and retro-Diels-Alder reactions, as attested by an increase and decrease of maleimide band with temperature, similar to that obtained for the MWCNT-free network (Fig. 4b).



**Fig. 4.** Rheological and maleimide FTIR band intensity results of the linear (left) and cross-linked (right) network (a) without MWCNTs and (b) with 2% wt. of MWCNTs. (c) Diels-Alder reaction between furfuryl and maleimide moieties.

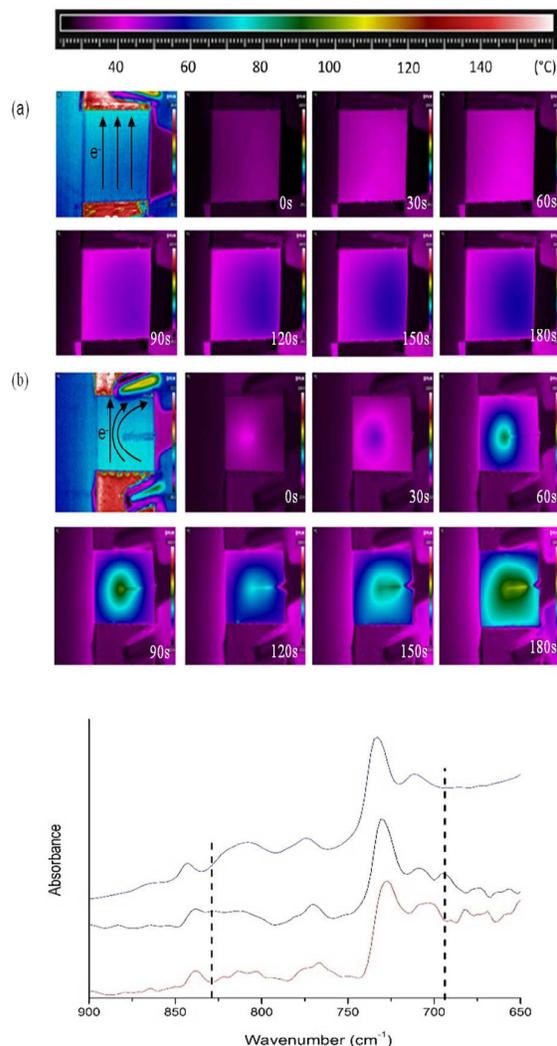
The impact of MWCNTs in the chain-mobility of the films based on PCL(FUR)<sub>x</sub> (X=2 or 4) in terms of scratch recovery efficiency was further investigated by microscratch tests using a Rockwell 100- $\mu$ m-diameter diamond tip (see Experimental part). While the scratch recovery  $\eta$  of the fully cross-linked system was of ca. (77.3 $\pm$ 16.3)% (the high value of the error bar is due to the quite high surface roughness of the cross-linked surface), the recovery of the scratch was complete in the case of the linear system (100.0 $\pm$ 0.4)%.

This can be attributed to the higher mobility of the linear chains as compared to the branched ones in presence of MWCNTs. In their work, AbdollahZadeh et al. already reported a systematic study of the relationship between the cross-linking density, the amount of reversible groups and healing efficiency in a disulfide-based intrinsic self-healing hybrid sol-gel.<sup>27</sup> In their work, the authors introduced a dual network containing permanent crosslinks and disulfide reversible groups and by modifying the cross-linking density, authors showed that, for short healing time (10 min at 70°C), the healing efficiency (500- $\mu$ m wide crack closure) could be doubled for networks containing a lower cross-linking degree. On the other hand, a minimal amount of reactive groups is necessary for a sufficient healing efficiency. Based on these results, the linear composition was selected for the electrically induced healing process by Joule heating.

#### Thermal activation of a scratched film by Joule heating

In order to appraise the thermal activation of a scratched film by Joule effect, a PCL(FUR)<sub>2</sub>/PCL(MAL)<sub>2</sub> with a ratio of 50/50% (molar) film containing 2% wt. of MWCNTs was connected to two electrodes and the heat increase was followed with an IR camera (Fig. 5). In the absence of a crack and with an applied voltage of 25 V, the temperature between the electrodes after 3 min reached ca. 70°C (Fig. 5a). At this temperature, the material is not thermally remendable since the temperature is not high enough to induce retro-Diels-Alder reaction.

After a cut between the two electrodes and by applying the same voltage (25 V) on the scratched sample different temperatures at the film surface are visualized by IR camera (Fig. 5b). After only 90 s a local increase of the temperature up to ca. 110°C nearby to the scratched region is observed. In this case, electrons are not transferred directly from one electrode to the other because of the physical barrier created by the scratch. Instead, electron flow remains concentrated at the crack tip and a local increase of heat is noticed (in the scratched region) even after the polymeric interface recovery. At this point, the temperature reached near the damaged area is high enough to promote retro-Diels-Alder reactions and enables the self-healing of the system through an 'unzipping/zipping effect'. It is worth mentioning that the current value increased slightly (from 10 to 70 mA) during the whole healing process due to a facilitated flow of electrons after the damage repair.



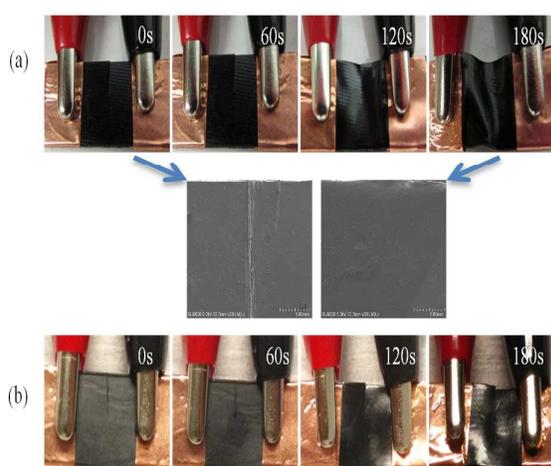
**Fig. 5.** Evaluation of the thermal activation by Joule heating at 25V of non-cut (a) and cut (b) samples. (c) Thermo-reversibility of PCL/MWCNTs nanocomposite at crack tip attested by *ex situ* FTIR measurements before electrical activation (red), after electrical activation (black) and after cooling after electrical activation (blue).

To further confirm the thermo-reversibility of these electro-conductive thermo-mendable nanocomposites at crack tip under electrical activation *ex situ* FTIR measurements (Fig. 5c) were performed. As expected, before electrical application, FTIR performed on the sample does not show any maleimide bands at 830 and 695  $\text{cm}^{-1}$  due to their complete consumption with furfuryl moieties. After the electrical application, an increase of intensity for the characteristic maleimide bands attests for the occurrence of retro-Diels-Alder reaction. This thermal reversibility leads to lower molecular weight oligomers with higher mobility at the scratched region, and inter-exchange chemical Diels-Alder reactions enabling the healing of the damaged zone. After cooling down the sample to

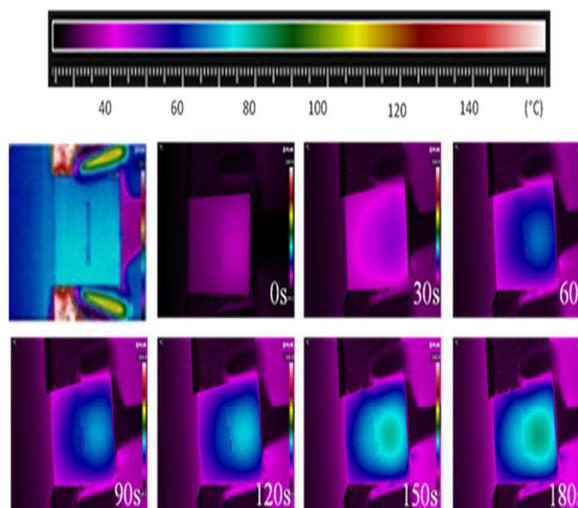
room temperature, the disappearance of maleimide bands at 830 and 695  $\text{cm}^{-1}$  indicates the reformation of Diels-Alder adducts.

A visual evaluation of crack recovery efficiency taken from images during the electrical experiment and the corresponding SEM images before and after scratch reparation also confirmed the good recovery of the material in the scratched region (Fig. 6). For the thermo-mendable film, the disappearance of the crack was observed after 180 s under electrical activation (Fig. 6a). For sake of comparison same experiments performed on a linear non-mendable (i.e. non-functionalized, CAPA FB540  $M_n = 100\,000\text{ g}\cdot\text{mol}^{-1}$ ) commercial PCL filled with 2% wt. of MWCNTs revealed the total absence of material healing after the electrical application. In this particular case, the absence of furfuryl and maleimide moieties precludes any Diels-Alder reactions necessary for an efficient healing of the material. After 180 s at 25 V, only a deformation due to the melting of the PCL could be observed and no recovery was noticed in the scratched region (Fig. 6b).

To further demonstrate the importance of scratch orientation with respect to electrodes, an investigation on this orientation relatively to the electrical current localization was performed. This orientation should affect the Joule resistivity and consequently the response of the scratched material to the thermal fluctuation induced by an electrical current. For this, a sample was scratched vertically to the orientation of the electrodes and electrically activated by applying the aforementioned conditions (i.e. 25 V for 3 min). Interestingly, one can notice from Fig. 7 that, in the present case, the increase of temperature, limited to only 60-80°C, is not located at the scratch position but rather in the whole sample, similarly to what was obtained for the non-scratched sample (Fig. 5a). The absence of any physical obstacle able to limit the electrons diffusion from an electrode to the other prevents from getting temperatures high enough in the scratched area, necessary to induce retro-Diels-Alder reactions for healing the material.



**Fig. 6.** Joule heating experiment on scratched nanocomposites based on thermo-mendable PCL sample and corresponding SEM images (a) and on a commercial PCL sample (b) after 3 min at 25 V.



**Fig. 7.** Influence of the scratch orientation with respect to electrodes on Joule effect

## Conclusions

In this study, we synthesized thermo-mendable and electrically conductive poly(ester-urethane) nanocomposites by reactive extrusion, a solvent-free process. It was shown that the cross-linking density can be easily tuned by simply changing the PCL(FUR)<sub>2</sub>/PCL(FUR)<sub>4</sub> ratio in the presence of the dimaleimide coupling agent PCL(MAL)<sub>2</sub>. Excellent thermo-reversibility, important for the healing process, was confirmed with a rheometer coupled with *in situ* FTIR measurements for the linear system. Incorporation of multi-walled carbon nanotubes (MWCNTs) in the thermo-reversible systems was also achieved by reactive extrusion process. The obtained nanocomposites, with a good MWCNTs dispersion, presented good electrical conductivity at 2% wt. and showed good thermal reversibility. Finally, the activation of the Joule effect at a low voltage (25 V) was followed by infrared camera. In the presence of macroscale damages (i.e. cut), local changes in electrical resistivity at the crack tip led to a local temperature increase, within the range of the retro-Diels-Alder reaction temperatures. Such temperature increase led to sufficient chain mobility to close and seal the cut by an ‘unzipping/zipping effect’ within 3 min. The promising obtained results introduce a new concept for polymer healing using Joule effect and set the bases for the development of self-healing electrically conductive polymers.

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### Table of contents

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