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Electroactive Self-Healing Shape Memory Polymer Composites Based on Diels–Alder Chemistry

Felipe Orozco,[⊥] Mahsa Kaveh,[⊥] Dian S. Santosa, Guilherme Macedo R. Lima, Diego Ribas Gomes, Yutao Pei, Rodrigo Araya-Hermosilla, Ignacio Moreno-Villoslada, Francesco Picchioni, and Ranjita K. Bose*

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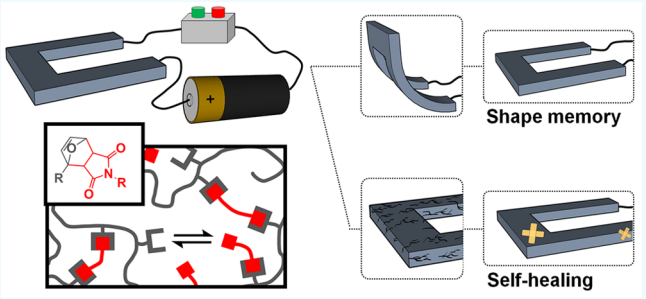
ABSTRACT: Both shape memory and self-healing polymers have received significant attention from the materials science community. The former, for their application as actuators, self-deployable structures, and medical devices; and the latter, for extending the lifetime of polymeric products. Both effects can be stimulated by heat, which makes resistive heating a practical approach to trigger these effects. Here we show a conductive polyketone polymer and carbon nanotube composite with cross-links based on the thermo-reversible furan/maleimide Diels–Alder chemistry. This approach resulted in products with efficient electroactive shape memory effect, shape reprogrammability, and self-healing. They exhibit electroactive shape memory behavior with recovery ratios of about 0.9; requiring less than a minute for shape recovery; electroactive self-healing behavior able to repair microcracks and almost fully recover their mechanical properties; requiring a voltage in the order of tens of volts for both shape memory and self-healing effects. To the best of our knowledge, this is the first report of electroactive self-healing shape memory polymer composites that use covalent reversible Diels–Alder linkages, which yield robust solvent-resistant polymer networks without jeopardizing their reprocessability. These responsive polymers may be ideal for soft robotics and actuators. They are also a step toward sustainable materials by allowing an increased lifetime of use and reprocessability.



KEYWORDS: *self-healing polymers, Diels–Alder, shape memory, electroactive polymer, polymer composites*

1. INTRODUCTION

Some polymers can be deformed and fixed into a temporary shape that can later be returned to the original when subjected to a suitable stimulus. Polymers with this shape memory effect (SME) have potential applications in fields such as biomedicine,[1−5] soft-robotics,[3,5,6] and aerospace engineering.[1] They have been explored as self-expandable stents,[1,5] self-tightening wound sutures,[1,2,5] drug delivery systems,[1,2] deployable devices,[1,3,5] heat-shrinkable packaging films,[4] smart fabrics,[4,5] actuators,[3,6,7] and other products. Figure 1a shows a schematic mechanism of SME triggered by heat for an amorphous polymer based on temperatures around the glass transition (T_g). For crystalline polymers the temperatures are around the crystallization transition.[1] The polymer is heated to above its T_g and deformed into a given shape by applying stress. This temporary shape is then fixed by decreasing the temperature until the polymer network is frozen. Lastly, shape recovery is stimulated by increasing the temperature above the T_g, so that the polymer chains have enough energy to move and rearrange according to their maximum conformational entropy.[1,5] Here, a crucial role is played by the tie linkages in the polymer network. They prevent chain slippage as the system is being deformed, which is required for achieving the SME. These tie linkages do not necessarily need to be of permanent nature such as irreversible covalent bonds. Efficient SME can also be achieved by using reversible bonds as long as they remain stable during the shape programming step.[1] For instance, the aromatic hard segments of shape memory polyurethanes are used as noncovalent tie linkages since they can stack via aromatic interactions.[1,4]

Shape memory polymers (SMPs) with reversible tie linkages present some additional interesting features. For instance, the permanent shape of a thermo-reversibly cross-linked system is reprogrammable. In order to do so, the new shape must be held at temperatures that allow bond exchange and be kept there long enough for the system to rearrange (Figure 1b).[1,8]

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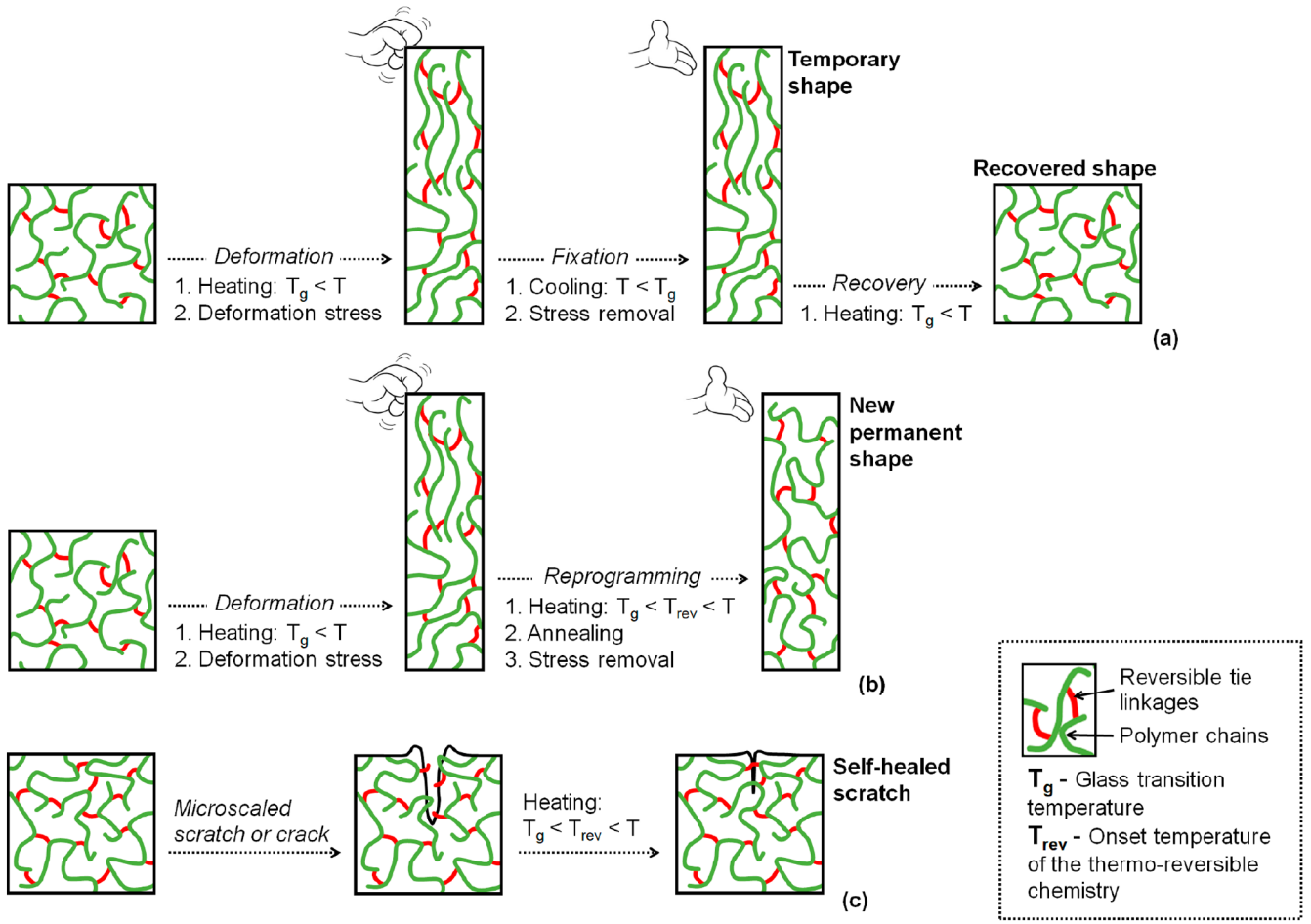

Figure 1. Mechanism schemes of (a) shape memory, (b) shape reprogrammability, and (c) self-healing effect.

Such bond interchangeability implies that these cross-linked polymers have thermoplastic behavior and therefore can be reprocessed, a sustainable feature hardly seen in conventional irreversibly cross-linked thermosets and elastomers.[1,9,10] Additionally, these materials may also exhibit self-healing effect (SHE), i.e., repair of microcracks within the polymer matrix through reformation of the local broken reversible bonds (Figure 1c).[5,11] These latter two characteristics, reprocessability and SHE, greatly contribute to the sustainability of polymer products, for they allow recycling and extending the lifetime of the materials, respectively.

The thermo-reversible Diels–Alder (DA) reaction between furan and maleimide groups has been extensively used in developing these reprocessable and self-healing polymers, since the reaction has fast kinetics and undergoes reversible changes within a moderate and practical temperature range (60–110 °C, with the lower temperatures favoring the formation of the adduct and the higher ones favoring the cleavage of it).[10,12−16] Different authors have described these furan/maleimide based cross-linked polymers capable of both SHE and SME.[8,17−20] Zhang and co-workers[8] reported an epoxy-based self-healing SMP with furan pendant groups and reversibly cross-linked with bismaleimide, showing great recyclability and shape reprogramming. In another report, Zheng et al.[18] described a biobased polyurethane using soy oil and furan-maleimide dynamic chemistry, which showed efficient SME, SHE, and reprocessability.

A practical strategy to induce both SME and SHE is preparing the polymers as composites with conductive fillers such as carbon nanotubes,[7,21−23] graphene,[23−25] or metals.[23,26] Then, as an electric current is applied, the system is heated due to its resistivity (known as the Joule effect). This approach allows reaching the required temperatures in a controlled and uniform way without the need of external heaters.[3,27] Moreover, electroactive SMPs are quite attractive as soft robotic actuators.[6,26,28]

SME is closely linked to SHE, since the former is believed to aid closing the fractures so that the polymer can heal.[5,29] However, surprisingly, to our knowledge, there are not many reports of electroactive polymer composites studying both effects.[29−31] Some of these reports use reversible tie linkages that are noncovalent, and the SHE is caused by the rearrangement of the thermoplastic polymers in the material.[30,31] This approach has good performance; however, the lack of covalent tie linkages (such as DA adducts) make these materials nonresistant to solvents and may limit their thermoset and elastomeric characteristics.[9] Using a different approach, Fan et al. reported an elegant and complex polyurethane/styrene–butadiene–styrene block copolymer system with reversible tie linkages of covalent nature.[29] They used the synchronous fission/radical recombination of alkoxyamine bonds that take place around 100 °C. This material showed interesting and efficient electroactive two-way SME. However, its mechanical performance greatly changed after the first healing cycle. The authors attributed this to radical

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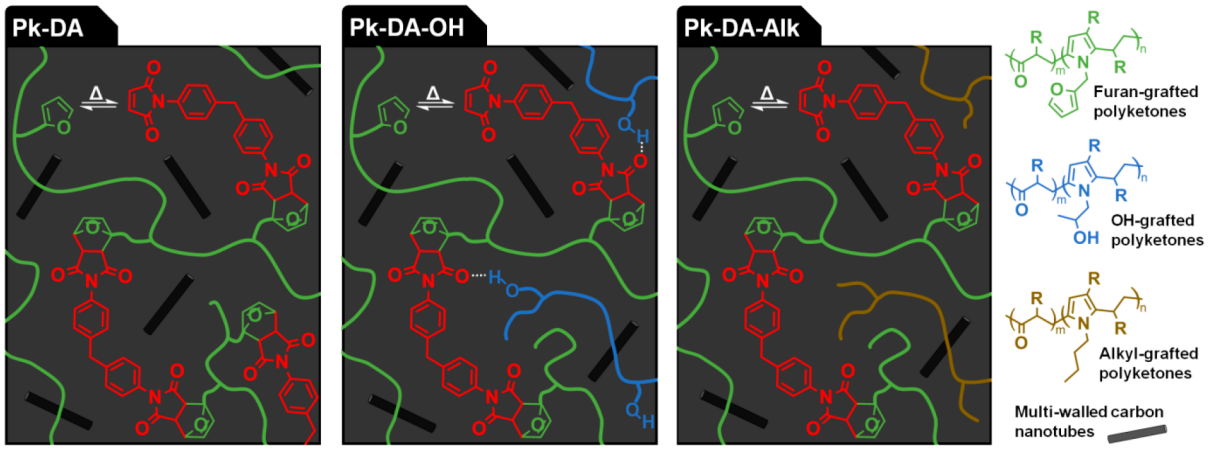

Figure 2. Polyketone-based composite formulations prepared in this work. The depicted polymer chains and cylinders are the grafted polyketones and MWCNT, respectively, as shown on the right. The formulations Pk-DA-OH and Pk-DA-Alk have a mass ratio between furan-grafted and nonfuran-grafted polyketones of 8:2. R stands for −H and $-CH_3$ groups.

deactivation-derived irreversible C−ON bonds or misalignment of the reconnecting surfaces. In contrast, very simple furan/maleimide DA-based reversibly cross-linked polymers can be found in the literature with almost no changes to their mechanical performance after many healing cycles.[5,16−19,32]

Here we present the first systematic study of electroactive self-healing SMP composites based on the widely studied furan/maleimide DA thermo-reversible cross-linking chemistry. To do so, we prepared furan-grafted polyketone polymers with dispersed multiwalled carbon nanotubes (MWCNT) that are cross-linked with bismaleimide (Figure 2). OH-grafted and alkyl-grafted polyketones were also incorporated into the formulations to tune the mechanical properties of the products. Polyketones were used due to their versatility and straightforward chemical modification with amine-substituted compounds by the Paal-Knorr reaction which is safe and eco-friendly to work with.[10,22,32−37] Through this approach, we obtained polymer composites that show efficient SHE and SME induced by electricity as well as shape reprogrammability, reprocessability, and tunable properties.

2. RESULTS AND DISCUSSION

2.1. Formulation Design, Synthesis, And Characterization. As depicted in Figure 2, three formulations were prepared in this work. The base formulation consists of furan-grafted polyketone, bismaleimide, and MWCNT and was named Pk-DA (details in section 4.1). The other two, with additional OH-grafted and alkyl-grafted polyketones, were named Pk-DA-OH and Pk-DA-Alk, respectively. The non-furan-grafted polyketones were added in small amounts (16% m/m) to modulate the mechanical properties of the products. These additives are expected to behave as plasticizers and reduce the complex modulus (G^*) and softening temperature of the composite. In addition, the OH-grafted polyketones interact via H-bonding with the many O and N atoms present in the matrix,[22,37,38] which may aid in retaining the reversible tie linkages, albeit via weaker linkages, when programming temporary shapes in SMP.[1] This strategy allows the formation of a set of different formulations just by mixing ready to use polymers. The fact that these three polymers are based on polyketones enhances compatibility among the different components.

MWCNT were incorporated into the matrix since they have been extensively studied and used as conductive fillers.[7,21,22,39] They have even been used in polyketone-based electroactive self-healing polymers previously reported by the authors.[22] This kind of polyketone system also helps to exfoliate and disperse the MWCNT throughout the composite due to the interactions between the graphitic surface of the nanotubes and the pyrrole rings along the polyketone backbones (pyrrole rings are formed in the grafting process−Paal-Knorr reaction).[38,40]

The synthesis and characterization of these products have been described in detail in previous reports.[22,39] The chemical composition of the grafted-polyketones and the final cross-linked products were confirmed by ^{1}H NMR (Figure S1 of the Supporting Information, SI) and FTIR (SI Figure S2), respectively.

2.2. Mechanical and Electrical Properties. Figure 3 shows the thermo-mechanical profiles of the prepared

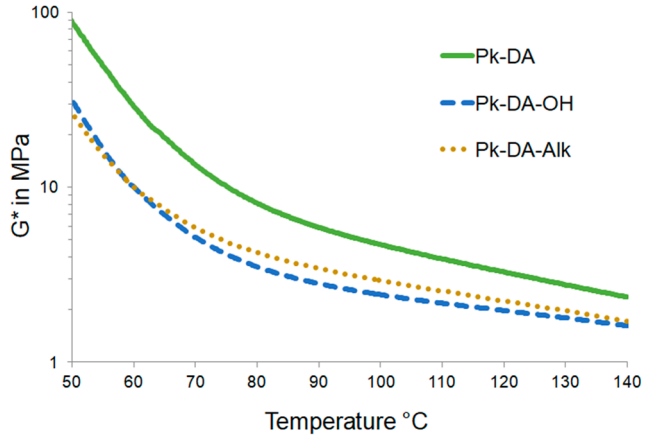

Figure 3. Thermo-mechanical profiles of the prepared composites.

polymers obtained by rheology. Only data points above 50 °C are shown as the samples tend to slip between the parallel plates of the rheometer (thus giving inadequate measurements) at lower temperatures. As expected from previous reports,[10] G^* is lower at higher temperatures due the increased mobility of the linear segments of the polymer and the DA

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equilibrium shifting toward breaking the adducts. Thus, the composite, that is rigid at room-temperature, becomes a soft rubber when heated above 50−60 °C. Pk-DA shows a thermo-mechanical profile with higher G^* than the other two formulations. This was expected since Pk-DA does not have any hydroxyl or alkyl-grafted polyketones (plasticizers) in its formulation, thus it has a higher density of covalent tie linkages which makes the material more difficult to deform.[10,41]

The amplitude sweeps in Figure 4 also show the interesting thermo-mechanical characteristics of these systems. They show the sharp changes in the storage and loss modulus (G' and G'') caused by the polymer networks partially breaking under strain.[42] At lower temperatures, the networks break at lower strains since the materials are more rigid. Interestingly, at higher temperatures (125 °C), the drop of G' comes along with an increase in G''. This implies that when the strained networks partially break, the systems have enough mobility to accentuate viscous-like behavior. Regarding individual formulations, the more rigid Pk-DA, with no plasticizers and higher density of covalent cross-links, breaks at lower strain. Similarly, Pk-DA-OH, is more cross-linked than Pk-DA-Alk, given that the hydroxyl moieties of the plasticizer also contributes to the cross-linking network through H-bonding, thus the former breaks at lower strains at low temperature (50−75 °C). However, at high temperature, Pk-DA-OH can withstand higher strain than Pk-DA-Alk. This is likely because the dynamic H-bonds at this temperature are not strong enough to contribute to the cross-linked network so that the material is easy to deform, but they provide enough cohesiveness so that the network can withstand these higher strains. Interestingly, for all formulations and temperatures, this partial breakdown of the polymer network is immediately repaired as the deformation strain is withdrawn. This is observed in Figure 5, where cycles of low and high strain (the latter being high enough to cause the partial break down) are shown at different temperatures. This attests to how dynamic these cross-linked networks are due to their reversible tie linkages. This dynamic feature is essential for the intrinsic SHE and the reprocessability of these materials. For a deeper insight regarding the mechanical performance of these thermoreversibly cross-linked polyketone systems the reader is referred to previous works.[10,22,32,37]

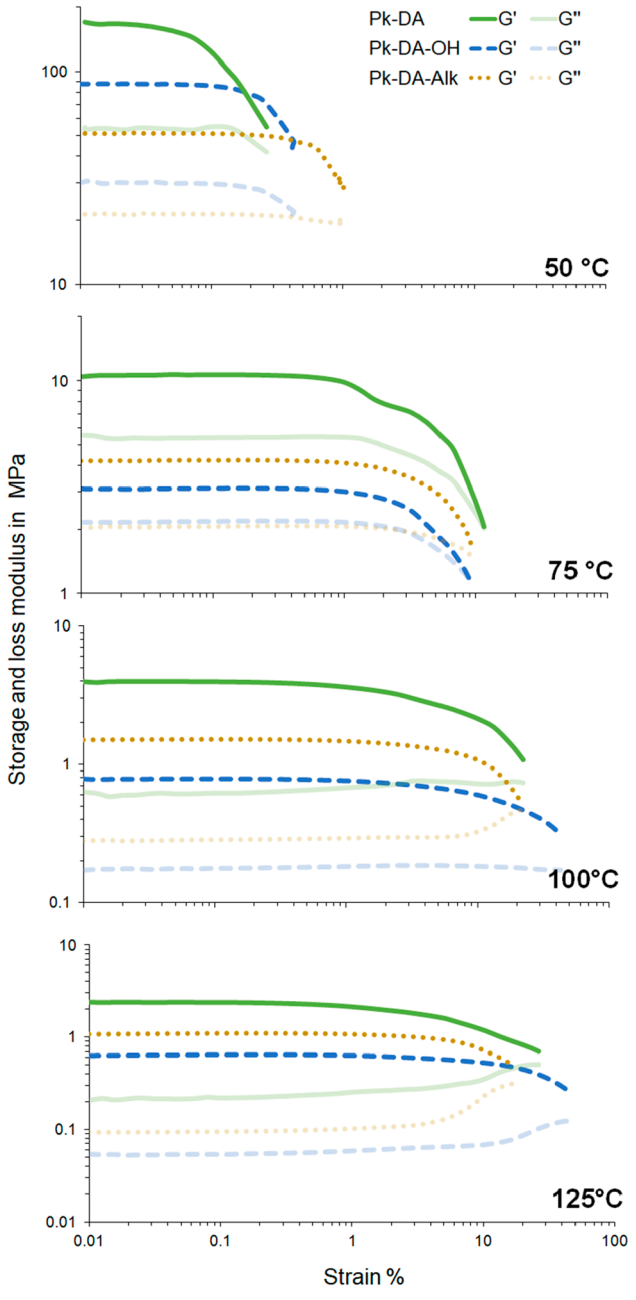

Figure 4. Amplitude sweeps of the prepared formulations at different temperatures.

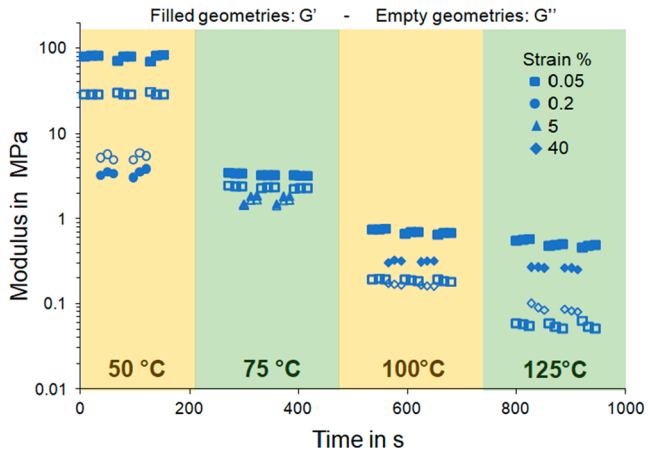

Figure 5. Low to high strain cycles at different temperatures. For simplicity only the results from Pk-DA-OH (the rest of experiments are shown in SI Figure S3).

Since sufficient conductive fillers (MWCNT) were incorporated into the polymer matrix, all composites are conductive and can be resistively heated. Figure 6a−c shows the current, resistance, and temperature reached when applying voltages between 20 and 50 V. Higher voltages come along with higher currents and more resistive heating. According to the Joules-Lenz law, the heating power is proportional to the resistance times the square of the current.[43] Figure 4d shows the estimated values of the heating power following a trend very similar to the one observed for the experimental temperature values reached by resistive heating. For all samples, a voltage of 40 V is sufficient to reach temperatures high enough for reducing their mechanical properties by 1 order of magnitude

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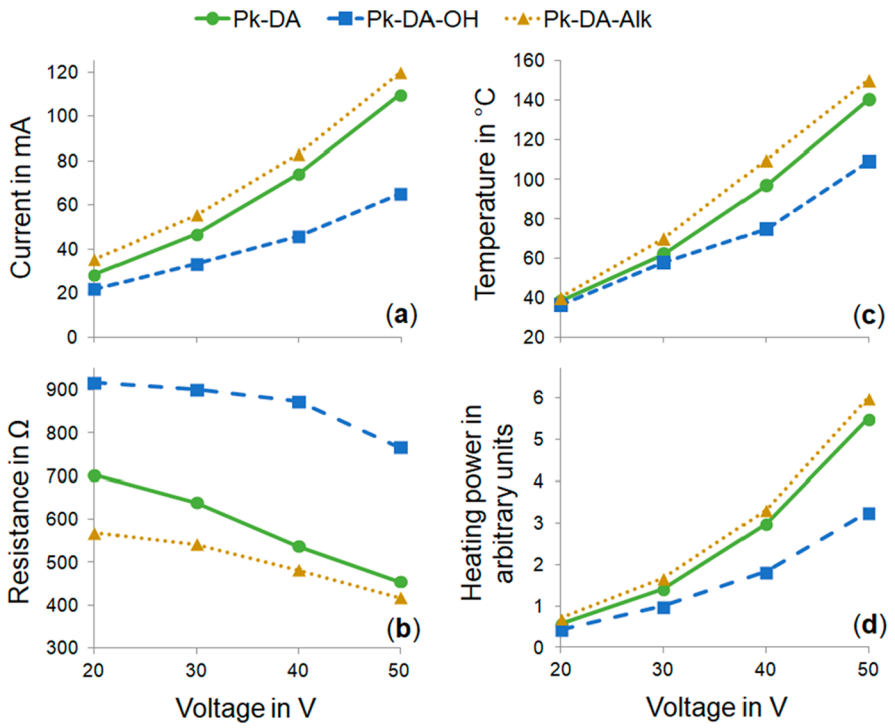

Figure 6. Resistive heating features of the prepared composites: voltage plotted against (a) current, (b) resistance, (c) temperature, and (d) heating power (plotted as $R{\cdot}I^2$).

(Figure 3), which is important for inducing the electroactive SME and SHE.

Several other observations can be made from Figure 6. Pk-DA-OH is notably less conductive than the other formulations. This may be due to the hydroxyl functionalities dissipating the electric energy.[44,45] This effect can be seen in a previous report by Lima et al. where conductive polymer composites with more hydroxyl groups required more voltage to reach a given temperature.[22] This dissipation (dielectric dissipation factor) has also been reported to increase with temperature,[44] which fits the observed increased difference between the conductivity of Pk-DA-OH and the other formulations as higher temperatures are reached through resistive heating. Also, interestingly, the resistance of all three formulations decreased when higher temperatures were reached. This is most likely caused by the higher mobility of the polymer network at higher temperatures that allows a better connection of the MWCNT conductive pathways.[46,47]

2.3. Shape Memory. Electroactive shape memory tests were set up as shown in Figure 7. 40 V was applied for both deformation and recovery steps. The formulations show a high extent of recovery, visually approximated to a shape recovery ratio around 0.9, and shape recovery rates in a range of 30 to 80 mrad/s (Figure 8, caption equations). This is in agreement with previous reports on electroactive SMP showing full (or almost full) shape recovery ratios triggered by tens of volts within a minute.[24−26,30,31,48] The three formulations exhibit similar shape recovery ratios; however, they differ in the time taken by each formulation to recover each initial shape. Pk-DA-OH shows the slowest shape recovery rate. This is most likely because this formulation is less conductive and reaches lower temperatures when the 40 V is applied (Figure 6) (75 °C rather than above 100 °C). Therefore, the DA equilibrium is shifted more toward the formation of adducts and the material is less flexible, which translates in slower actuation.

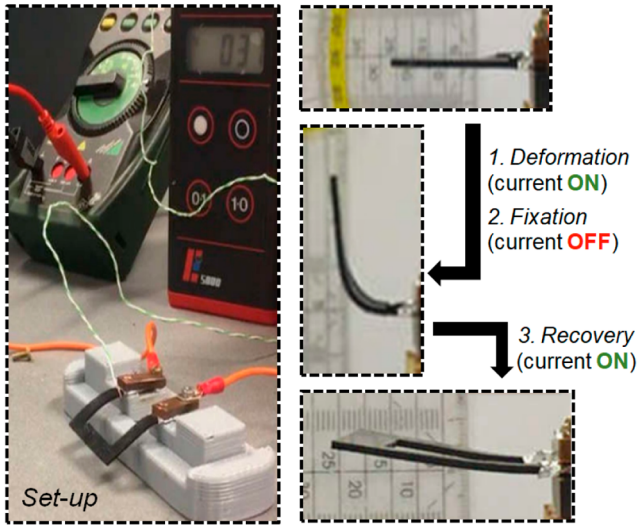

Figure 7. Electroactive shape memory tests setup.

Thermally induced shape memory tests were also performed using a rheometer to ensure equal testing conditions (Figure 9). All formulations were exposed to the same temperature in the deformation and recovery steps (140 °C). Shape recovery ratios in the range of 0.6−0.9 were obtained and shape recovery rates of 10—15 μrad/s. In these experiments, Pk-DA-OH shows the highest shape recovery ratio and has the fastest recovery rate (Figure 8). This best performance among the three formulations might be due to the presence of the OH-grafted polyketones within the polymer matrix. This helps by granting more mobility to the system (relative to Pk-DA) while forming tie linkages via H-bonds.[38] In contrast, the alkyl-grafted polyketones within Pk-DA-Alk also enhance the network mobility but do not form tie linkages with the

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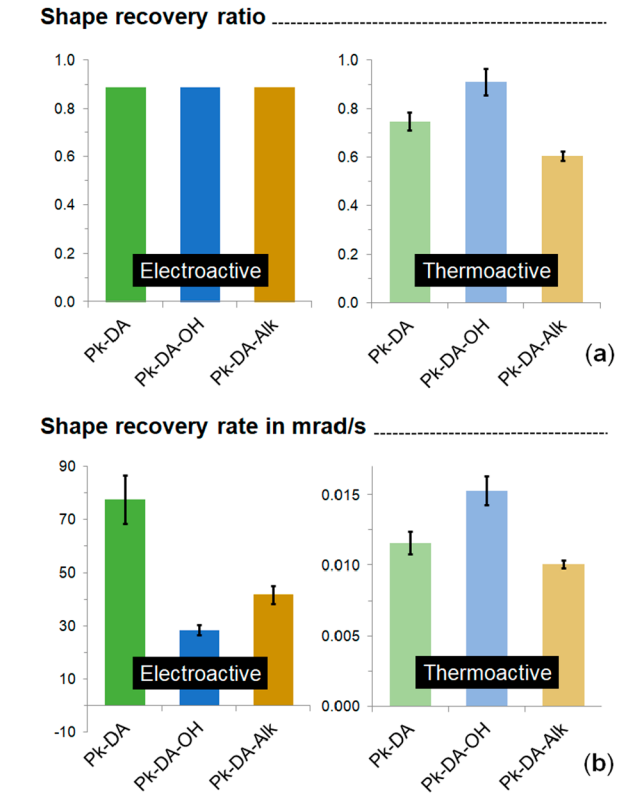

Figure 8. (a) Shape recovery ratio ([$angle_{fixed}$ − $angle_{recovered}$]/$angle_{fixed}$) and (b) shape recovery rate ([$angle_{fixed}$ − $angle_{recovered}$]/$time_{recovery}$) obtained through the shape memory tests induced by electricity and convection heating. (Error bars on the top left graph have a value of zero.).

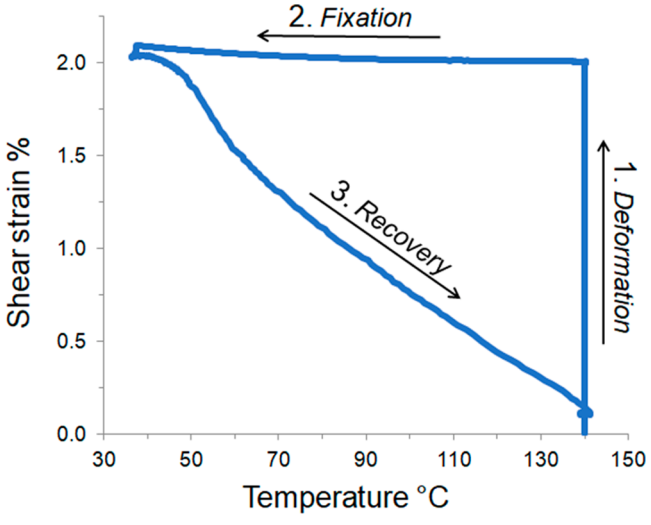

Figure 9. Strain vs temperature plot obtained through thermo-induced shape memory tests. For simplicity only a plot of Pk-DA-OH is shown (all plots shown in SI Figure S4).

polymer network, thus showing lower recovery ratio and rate of the SME. Pk-DA-Alk also shows a much lower recovery ratio compared to the one measured electroactively. This may be mainly due to the different temperatures reached in each test while keeping the voltage constant. In the electroactive test, the sample was programmed and recovered at 110 °C (temperature reached by applying 40 V); in contrast, in the thermoactive one, at 140 °C. This latter temperature is most likely high enough for the Pk-DA-Alk dynamic network to have too much mobility and exchange of the reversible tie linkages so that the material partially loses its memory. The scales of the shape recovery rates are also quite different between the electroactive and thermoactive tests (mrad/s vs μrad/s). This can be due to the sharp difference between the methods used: in the electroactive one, the deformation is along a 34 mm long U-shaped sample (as seen in Figure 7); in the other, the deformation is in shear strain of a small 8 × 1 mm^2 (diameter × thickness) disc. In addition, samples are heated faster by resistive heating (less than a minute) than by the rheometer convection oven (a couple of minutes).

2.4. Shape Memory Reprogrammability. The permanent shape of Pk-DA-OH was reprogrammed as shown in Figure 10a,b, where the U-shape sample was set to 120 °C by

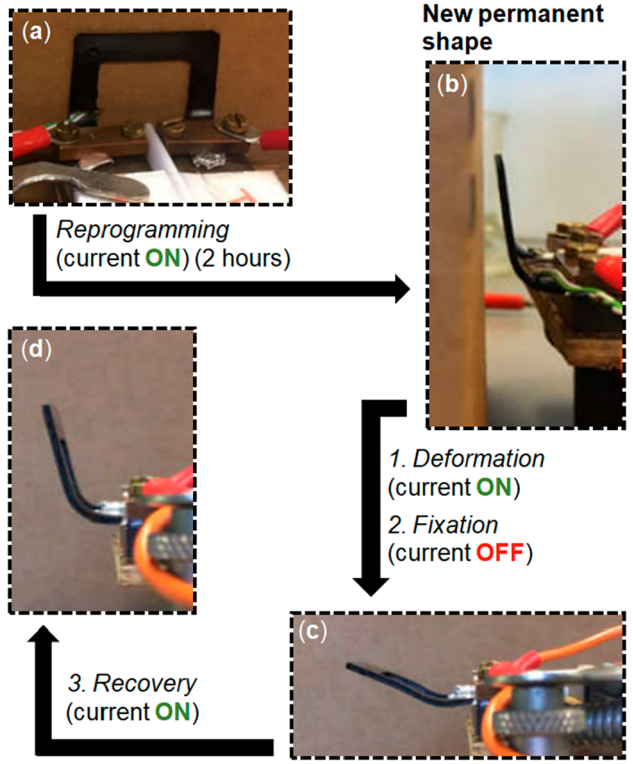

Figure 10. (a) Pk-DA-OH reprogrammed into a 90° shape through prolonged resistive heating. (b) New permanent 90° shape with (c,d) SME.

resistive heating (applying 50−60 V), deformed 90° and kept there for 2 h. After this treatment, the fixed 90° shape did not change when the temperature was increased. In turn, this new permanent shape also showed an evident SME (Figure 10c,d). These observations imply that an efficient network rearrangement takes place through this electrical treatment, i.e., relaxation of the polymer chains allowed by the interchangeability of the reversible tie linkages at temperatures higher than the T_g and the onset temperature of the thermo-reversible chemistry (Figure 1b).

In this work, the SME of the used polyketone-DA system was described for the first time. Therefore, we focused further on this effect. However, the self-healing features of many DA-polyketones systems have already been studied in detail in previous works.[10,16,22,32,37,39,41] Therefore, the following

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sections focus in only one of the prepared formulations, Pk-DA-OH. Its best shape memory performance, when testing all samples at the same temperature, was the criteria for the selection. Although this sample has the drawback of having less resistive power than the other two, this can be easily compensated by increasing the voltage (Figure 6).

2.5. Self-Healing. Self-healing tests were performed on Pk-DA-OH using a method similar to that described by Vega and co-workers.[49] Defined scratches of about 100 μm width were made using a scratch tester. After applying an electric current, that allowed the polymer to reach 120−140 °C for about an hour, all scratches were almost fully repaired (80−100% of the scratched area was healed), barely leaving scars between 0 and 40 μm wide (Figures 11 and S5, SI).

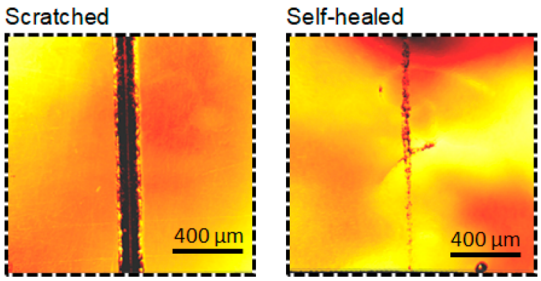

Figure 11. Micrographs of a scratch on Pk-DA-OH before (left) and after (right) electroactive self-healing.

The recovery of the mechanical properties was also evaluated by thermally inducing the SHE in the rheometer. Pk-DA-OH was molded into discs, and their complex modulus was measured before and after cutting through across the radius (Figures 12 and S6, SI). Subsequently, the SHE was induced in situ by heating the samples at 120 °C for 30 min. As a result, the mechanical properties before damage and after self-healing are similar (with 70−100% recovery of G^*).

There are varied strategies to quantify the SHE and, depending on the method used, the recovery efficiency may vary.[50,51] Nonetheless, overall, the results shown here are similar to those reported for self-healing polymers, i.e., repair of microcracks and almost full recovery of the mechanical properties applying a voltage in the range of tens of volts or thermally induced around 120 °C.[22,24,30,31] This efficient SHE displayed by Pk-DA-OH indicates that the polymer network has enough mobility so that the furan and maleimide moieties can move and reform the DA adduct during the healing process (Figure 1c).[10]

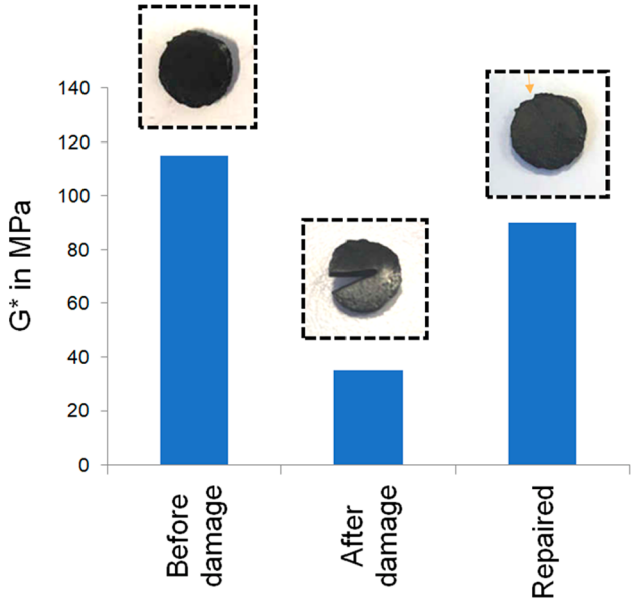

Figure 12. Complex modulus of Pk-DA-OH before damage, after damage, and after self-healing.

2.6. Final Remarks. Here we showed conductive polymer composites with DA cross-linking chemistry that grants them efficient electroactive SME, shape reprogrammability, and SHE. Due to their reversible tie linkages, the materials described here are also reprocessable, as evidenced by the fact that the final products were obtained by pressure molding powder of the already cross-linked materials (Section 4.1). This reprocessability is absent in SMP based on irreversible tie linkages.[9] In a previous report, Zhang et al. showed the reprocessability of this polyketone-DA system in detail and its capability of healing multiple times without important changes in the mechanical properties of the polymer.[32]

In this work, the inclusion of a small quantity of OH-grafted polyketones in the matrix seems to work well in terms of the overall shape memory and self-healing performance. It reduces the stiffness of the material and decreases the softening temperature while still contributing with reversible tie linkages (noncovalent H-bonding). However, in practical terms, this strategy compromises the conductivity of the electroactive composite to some extent, and thus its resistive heating power, which implies that the material is somewhat less energy-efficient. A more convenient approach would be to modulate the properties and performance of the material, not by the addition of plasticizers, but through adjusting the amount of furan groups grafted into the polymer backbone or aiming at different furan/maleimide ratios.

Some of the prepared materials show electroactive responsiveness and properties comparable to other efficient SM and SH systems reported in the literature. Remarkably, this is achieved through a very simple procedure that is based on the well-studied thermo-reversible DA chemistry. Nonetheless, a good performance of both SME and SHE requires a system designed with reversible tie linkages that are optimally tuned. For instance, loosely tied systems would be advantageous for self-healing since there would be more network mobility, however this can jeopardize the shape memory capabilities as the loosely tied network may rearrange while programming a temporary shape.

The fractures that this material is capable to self-heal electroactively are in the micrometric scale (Figure 11). Such microscale damages are not expected to have any significant impact on the electroactive SME of the macroscopic devices that were used in this work. However, this could have an impact when the material is prepared as films.

3. CONCLUSIONS

This work stands as a proof of concept converging four well-known concepts into a responsive material: resistive heating, SME, SHE, and DA thermo-reversible chemistry. The preparation of the materials is quite simple and the products have efficient electroactive shape memory, self-healing, and shape-reprogramming, as well as tunable properties and fine reprocessability. They are a positive contribution toward sustainable materials by allowing an increased lifetime of use

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and reprocessability. This impacts fields such as spatial and automotive engineering where self-deployable self-healing structures are attractive. This kind of material is also quite useful for actuation in soft robotics, given its good performance, rubbery features, and capability of repairing superficial damages caused during shape-memory-driven actuation.

4. EXPERIMENTAL SECTION

4.1. Preparation of the Self-Healing SMP Composites. The polyketone used was prepared as described by Drent and coworkers[52] and manufactured by Shell (M_w 2687 Da - propylene as 70% of the olefin fraction and 30% of ethylene). Furfurylamine, 3-amino-2-propanol, and butylamine were purchased from Sigma-Aldrich and distilled before use. 1,1-(Methylenedi-4,1-phenylene)bismaleimide, MWCNT (average length of 5 μm, and O.D. of 6−9 nm), chloroform (99.5%), and deuterated chloroform were acquired from Sigma-Aldrich as well and used as received.

The polyketones were first grafted with the respective primary amines through the Paal Knorr reaction. As described in detail in previous reports[32,37,41] this is achieve using low temperatures (100−110 °C) and without solvent nor catalysts. The formulations were set as shown in Table S1 and obtained grafted polyketones with 2−3 $mmol_{functionalities}/g$. ^1H NMR was used to corroborate the grafting of the polyketones and estimate the experimental carbonyl conversion.

In order to prepare the polymer composites, MWCNTs were dispersed in chloroform (0.5 m/v%) through sonication for 30 min. Separately, the furan-grafted (and hydroxyl-grafted or alkyl-grafted, depending on the formulation) was dissolved in chloroform (10 m/v %) in a round-bottom flask with a condenser. The MWCNT dispersion was then added into the polymer solution and set at 50 °C under agitation for 2 h. Subsequently, the bismaleimide was added to the reaction mixture (in a furan/maleimide ratio of approximately 0.5) and the system was kept at 50 °C with stirring for 24 h. The product was then set to dry in a Teflon plate using a vacuum oven. Finally, the polymer was ground into a fine powder and dried. The three prepared formulations had 8 m/m% of MWCNT (which is approximately the percolation threshold of the samples used in this work). As shown in Figure 2, Pk-DA-OH and Pk-DA-Alk have hydroxyl-grafted and alkyl-grafted, respectively. These nonfuran-grafted polyketones were added in a mass ratio of 2:8 relative to the furan counterpart (Table S2). The products were analyzed by FTIR (IRtracer-100, Shimadzu) to corroborate their proper preparation.

The three formulations were molded into two different shapes for further analysis: discs and U-shape. The discs were 8 and 1 mm in diameter and thickness, respectively (shown in Figure 12). The U-shape had the dimensions shown in Figure S6 (SI) (samples seen in Figure 7). A hot press (TP400 Fontune Holland) was used to mold the ground samples at 150 °C and 4 bar for 30 min.

4.2. Mechanical and Conductivity Tests. The thermo-mechanical properties of all the samples were measured with a Hybrid Rheometer Discovery HR-2 (T.A. Instruments) in oscillation mode using an 8 mm parallel plate geometry. The measurements were performed under a constant axial force of 8 N and with an oscillation frequency of 1 Hz. The samples were initially set to 140 °C to erase the thermal history of the polymers, and then the temperature was decreased to 40 °C at 3 K/min. The amplitude sweeps were performed at four different temperatures (50, 75, 100, and 125 °C) from 0.01% strain until the G' sharply dropped. TRIOS software was used to run the experiments and processed the obtained data.

The conductivity tests were performed using the setup shown in Figure 7. U-shape samples were used. A power source was set to four different voltages (20, 30, 40, and 50 V), while the temperature and the current was measured by a thermocouple and a multimeter, respectively.

4.3. Shape Memory Tests. The SME was induced by electricity using the setup shown in Figure 7 against a protractor ruler. 40 V were applied to each sample so that could be deformed 90° (Figure S8, SI). This temporary shape was fixed as the temperature decreased due to opening the electric circuit. Finally, the SME was triggered by closing the circuit.

The SME was also induced solely by changing the temperature in rheometer. The disc-shape samples were set between the 8 mm parallel plates under a constant axial force of 8 N. The samples were deformed at 140 °C with a 2% strain, and fixed at this strain by cooling down the samples until about 30 °C. Shape-recovery was then triggered by increasing the temperature once again. A rather low deformation strain (2%) was used since the disc-shape samples (1 mm thickness) slip at higher strains.

4.4. Shape Memory Reprogrammability. The reprogrammability of the permanent shape was also explored qualitatively for Pk-DA-OH. As shown in Figure 10, the sample was heated by applying an electric current (up to 120 °C), deformed 90°, and was kept with this deformation angle hour 2 h. Subsequently, the SME was tested over this reprogrammed shape.

4.5. Self-Healing Tests. Samples of Pk-DA-OH were first polished using a wet SiC abrasive paper with grit size 4000. Three scratches were performed with a CSM Revetest scratch-tester in constant load mode using 0.5, 1.0, and 1.5 N. A Rockwell tip with 10 μm radius was used for all three. The topographies of the scratches were measured before and after healing using a NanoFocus μSurf white-light confocal microscope. The samples were healed electroactively for an hour at 120 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.1c00999.

Figure S1, ^1H NMR spectra of the polyketone grafted with (a) furfurylamine, (b) amino-2-propanol, and (c) butylamine; Figure S2, FTIR of the prepared composites; Figure S3, low-high strain cycles of all the prepared formulations; Figure S4, strain vs temperature plot obtained through thermo-induced shape memory tests; Figure S5, micrographs of the scratches made on Pk-DA-OH before and after electro-induced self-healing; Figure S6, complex modulus of Pk-DA-OH before damage, after damage, and after self-healing; Figure S7, dimension of the U-shape samples; Figure S8, estimation of the deformation angle using a protractor; Table S1, graphted polyketones; Table S2, formulation of the polymer composites; and raw and processed data available online at https://data.mendeley.com/datasets/nk8p2rtftd/1 (PDF)

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

SME, shape memory effect; SMP, shape memory polymer; SHE, self-healing effect; MWCNT, multiwalled carbon nanotubes; DA, Diels−Alder

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