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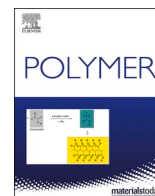
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Electrically and thermally healable nanocomposites via one-step Diels-Alder reaction on carbon nanotubes

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ABSTRACT

Carbon nanotubes (CNTs) were directly employed as reactive fillers in furan-pendant polyketones via the Diels-Alder (DA) reaction. CNTs and furan groups function as dienophile and diene, respectively, forming a reversible crosslinking network. Here, pristine CNTs not only serve as crosslinking agents, but also improve the thermal and electrical conductivity. The DA covalent linkage was confirmed by IR, TGA, DSC, elemental analysis and dispersion tests. This one-step approach offers a facile route to synthesize reversibly crosslinked thermoset polymer nanocomposites. The rigidity of the nanocomposites could be controlled through the number of furan groups in order to achieve distinct properties. The nanocomposites demonstrated dynamic temperature-dependent behavior due to the retro Diels-Alder reaction. Cyclic tests via rheology showed good reversibility below 120 °C. However, an irreversible increase of modulus was observed at higher temperatures, which is possibly attributed to a side reaction. At filler loadings above 5%, both electrical and thermal self-healing tests showed good results. The Diels-Alder reaction between CNTs and furan-pendant polymers opens up a new possibility of directly employing fillers in the polymer matrix without any prior modifications. It is also possible to use other fillers with diene/dienophile properties in future reversible polymer nanocomposites.

1. Introduction

Self-healable polymer nanocomposites are a class of materials that have been widely researched in recent years due to the reversibility [1–6]. The reversible interactions between the polymer matrix and the fillers typically include covalent bonding [7,8] and/or supramolecular chemistry [9–11]. The Diels-Alder (DA) reaction between furan and maleimide, one of the famous reversible chemical reactions, has been extensively studied due to the high strength of the newly formed covalent bond and facile reversibility at modest temperatures [12–22]. The DA reaction takes place between a conjugated diene and a dienophile (substituted alkene) at low temperatures, producing a cyclohexene moiety. The retro Diels-Alder (rDA) reaction reverses the cycloaddition at high temperatures. Typically, the temperature for DA is 25–120 °C and the temperature for rDA reactions is higher than 120 °C [23,24]. To complete the healing process, one usually needs to heat the materials so that they could undergo rDA reactions and break the linkages inside. When the temperature decreases again, DA reactions take place and the linkages are restored. The temperature can be controlled by direct heating [25,26], resistive heating (also known as Joule effect) [27] and

photothermal effects [28,29].

In a previous work from our group, Zhang et al. [18] studied the DA crosslinking polymer with furan-pendant polyketones and bis-maleimide. The synthesized thermosets showed highly efficient reversible processes and achieved near 100% recyclability after 3 cycles without any loss in mechanical properties. The reversible polymer networks could be recycled up to 7 times in dynamic mechanical analysis and those with low crosslinking density also possessed shape memory effects [21]. Due to the requirement of heat during the healing process, carbon nanotubes (CNTs) were added as the conductive filler to attain resistive heating [20]. Surprisingly, the current redistributed the filler inside the nanocomposites and formed a more effective percolative network at 5 wt% loading. Other researchers followed the same route of furan/maleimide system with CNTs to investigate the electroactive self-healing and shape memory effects [13,19]. Although a lower filler loading of 1.5 wt% was sufficient enough to make the nanocomposites conductive, only a loading higher than 5 wt% allowed reaching the temperature for the rDA reaction. The conductivity increased with the furan intake on the polymer backbone, from which was estimated that the reaction between fillers and furan groups led to better dispersion of

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CNTs. The furan intake also had a positive impact on the shape memory effects as replacement of the furan groups by alkyl groups resulted in a slower recovery rate. This behavior did not change upon replacement of the furan groups by hydroxyl groups. These findings only use CNTs as non-reactive fillers in the furan/maleimide reversible network.

Meanwhile, several researchers reported that CNTs could undergo DA cycloaddition with dienes. Lu [30] predicted the viability of DA reaction of quinodimethane onto the side walls of single-walled carbon nanotubes (SWCNTs) via computational chemistry. This functionalization was later experimentally confirmed by microwave irradiation [31]. Other dienes such as anthracene [32], 2,3-dimethoxy-1,3-butadiene [33], and benzocyclobutene [34] were used to perform controlled functionalization. It was reasoned that the side walls of CNTs consist of a huge number of sp^2 carbons, which is one of the vital requirements for DA reaction. Later, other compounds with simpler diene/dienophile structures were shown to functionalize the filler similarly. Chang [35, 36] reported DA reaction with CNT by dienes (furfuryl derivatives) and dienophiles (maleimide). It is worth mentioning that the reaction was set at mild conditions of 50 °C without any catalyst. Polymer chains with dienophile groups were used to synthesize nanohybrid materials, which opens a new way to employ CNTs as crosslinkers in the nanocomposites directly. Munirasu [37] did a thorough study on the CNT modification using various furfuryl derivatives with different functional groups based on the ability of electron-donating/withdrawing. All of them showed considerable reactivity of more than 0.3 mmol/g grafted content with carbonaceous materials while electron-donating hydroxyl and amine groups showed higher reactivity as compared to electron-withdrawing carboxyl groups. This suggests that various functional groups could be introduced onto the nanotubes by furan derivatives and maleic anhydride derivatives.

Following the revelation of DA reactivity of CNTs, the interest has shifted to investigate the relationship between filler and furan-pendant polymers. The intrinsic crosslinking network resulting from this strategy makes it a competitive approach compared to physical blending. There are usually two ways to connect polymer chains with carbon materials: “grafting from” and “grafting to” [38]. The ‘from’ indicates that the polymer chain will grow from the surface of the filler and form the nanocomposites afterward. This can be achieved by chemically modifying CNTs for subsequent crosslinking. Zhang [39] reported a novel CNTs/polymer network by amide linkages with polyamines, where CNTs were oxidized with HNO_3 and suspended in thionyl chloride to get acyl chloride functionalization. Furfuryl-2-bromoisobutyrate was anchored on CNTs via DA reaction to synthesize atom transfer radical polymerization (ATRP) initiator [37,40]. The surface-initiated polymerization then took place and created a core-shell structure. The thickness of the coatings could be adjusted by varying the grafted content to control the permittivity and dielectric loss. Furfuryl-functionalized CNTs could also be formulated by amide functionalization [41] and ATRP with bromide functionalized CNT initiator [42].

However, in the “grafting to” approach, no necessary pretreatments will be applied on CNTs. The polymer matrix itself contains functional groups, such as furan groups and other dienophile groups, to undergo one-step crosslinking with CNTs directly. Furfuryl-pendant polystyrene was covalently attached to the pristine nanotubes [43]. The styrene-based polymers contain extra labeled fluorescent groups which were used to visualize the grafting effect by optical microscopy. Another polymer with cyclopentadiene terminal was used to graft SWCNTs at mild conditions [44]. The polymer grafting content of 0.064 mmol/g is much lower than the furan derivatives mentioned earlier [36,37]. This could be attributed to the difficulty of grafting a long polymer chain and the only diene group was on the terminal end of the polymer. Temperature also has a huge effect on both DA and rDA reactions [45]. It was found that 80 °C resulted in a higher grafting content of furan-pendant polymers than the room temperature and the retro reaction was more thorough at 160 °C than at 120 °C. Bai and Shi [46] utilized the DA crosslinking in a self-healing system between furan-modified

thermoplastic copolymers and CNTs. Moreover, laser irradiation successfully induced the self-healing effect and the shape memory ability via the photothermal effect. The healing performance was efficient with almost full recovery in 10 s. The chemistry between CNTs and furan-pendant polymers has been thoroughly reported. However, applications of the DA reaction on CNTs still need to be investigated. No studies on the direct reaction of polyketones and CNTs, including their thermo-rheological behaviors, have been reported to the best of our knowledge.

In this paper, the thermally responsive nanocomposites were prepared by the Diels-Alder reaction. Unlike previous studies [18–22] where the crosslinking agent was bismaleimide and the conductive filler was CNTs, pristine CNTs were directly grafted with furan-pendant polyketones without any modifications. Therefore, the synthesis route is much more simplified in this case. The grafting results were assessed through elemental analysis, IR spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. Afterward, nanocomposites consisted of furan-pendant polymers and CNTs were synthesized, where CNTs served dual roles, the physical reinforcing filler and the crosslinking agent. The mechanical properties and recyclability of different compositions of nanocomposites were evaluated by rheology. The self-healing ability of the nanocomposites was studied both thermally and electrically.

2. Experiment

2.1. Materials

Multiwalled carbon nanotubes (MWCNTs, O.D. \times L = 6–13 nm \times 2.5–20 μ m, >98% carbon basis) were purchased from Sigma Aldrich, the Netherlands. The polymer matrix used was polyketones (PK) obtained from Shell [47,48], which are copolymers of carbon monoxide and unsaturated hydrocarbon monomers (30% ethylene and 70% propylene) with a molecular weight of 5362 Da. Furfurylamine (FA), butylamine (BA), N-methyl-2-pyrrolidone (NMP), chloroform ($CHCl_3$) and tetrahydrofuran (THF) were bought from Sigma Aldrich as well. All chemicals were used as received.

2.2. Nanocomposites

2.2.1. Diels-Alder reaction on MWCNTs

The feasibility of the Diels-Alder reaction on MWCNTs was first tested by furfurylamine. The synthesis route is depicted in Figure S1. According to Refs. [36,37,40], MWCNTs of 50 mg were dispersed in 10 mL NMP inside a 50 mL round-bottom flask and sonicated for 30 min, followed by purging argon for 20 min and addition of 1 mL FA. Although Zhang [40] reported that higher concentration of CNTs would bring more grafted functional groups, it could also lead to uneven dispersion of CNTs and produce unreproducible results. Therefore, the volume of solvents was chosen to be 10 mL. The reaction lasted 24 h at 80 °C with 500 rpm. The mixture was filtered by a 0.45 μ m membrane and washed by THF repeatedly to remove the unreacted amines. The modified MWCNTs-FA (MF) was dried for further use. The grafted content (mmol/g) of diene groups on the CNT surface was calculated from the nitrogen content of the elemental analysis, as shown below:

$$\text{grafted content} = \frac{w_N}{M_N} \times 1000 \quad (1)$$

where w_N is the weight percentage of nitrogen, %; and M_N is the molar mass of nitrogen, 14.00 g/mol.

2.2.2. Furan-pendant polyketones

In order to prepare a polymer matrix with furan pendant groups, polyketones were functionalized by the Paal-Knorr reaction to attach furan groups on the backbone. The Paal-Knorr reaction takes place

between 1,4-diketones and amines, where in this case, FA was applied to get diene groups and BA was used as the contrast alkyl groups (Figure S2). In a typical Paal-Knorr reaction with the amine/carbonyl (NH_2/CO) ratio of 80%, PK of 40.00 g was added in a 500 mL three-neck round bottom flask, soaking in an oil bath at 100 °C. Then, FA of 23.80 g was added dropwise to the flask in the first 20 min. The reaction was set at 500 rpm with a Teflon stirrer for 4 h under reflux in open atmosphere. No solvents were added during the reaction due to the properties of the polyketones employed, which are in a liquid state at room temperature and possess low viscosity at higher temperatures. The product, furan-pendant polyketones (FPK), was dissolved by 70 mL CHCl_3 at room temperature, followed by 3-times extraction with Milli-Q water to remove the unreacted amines. The organic phase (CHCl_3) first evaporated inside a Teflon plate in the fume-hood and then dried in the vacuum oven at 50 °C. The sample was frozen by liquid nitrogen and ground into powders. The detailed calculation of the conversions of PK and FA is included in the Supporting Information.

2.2.3. CNT nanocomposites

The nanocomposites were synthesized through the DA reaction between pristine MWCNTs and FPK (Fig. 1). Typically, MWCNTs of 20 mg were dispersed in 10 mL CHCl_3 and sonicated for 30 min. Then 0.98 g FPK with an initial NH_2/CO ratio of 80% was added as the polymer matrix to get the 2 wt% nanocomposites, MWCNTs-FPK, MPF. (The compositions remain the same unless otherwise stated) The reaction was performed at 50 °C with 500 rpm under argon atmosphere for 24 h. The nanocomposites were dried in a Teflon plate under vacuum and ground into powders. All samples mentioned above were stored at 6 °C for further use.

2.3. Characterizations

Fourier transform infrared spectroscopy (FT-IR) was carried out on a Shimadzu IRTracer-100. The samples were prepared into KBR pellets beforehand. The spectra were recorded from 500 to 4000 cm^{-1} with a resolution of 2 for 64 scans. Thermogravimetric analysis (TGA) was performed from 40 to 800 °C with 10 K/min under nitrogen using a Perkin Elmer TGA 4000. Differential scanning calorimetry (DSC) was carried out using a TA-Q1000 V9.8 Build 296 under nitrogen atmosphere (50 mL/min). The sample was weighed (5–10 mg) in an aluminum pan. The temperature program was set as follows: first heating cycle from 0 °C to 180 °C with 10 K/min, followed by cooling to

0 °C and then again ramped up to 180 °C. Gel permeation chromatography (GPC) measurements were performed with a Mixed-E column. The samples were dissolved in THF at a concentration of 1 mg/mL. ^1H NMR was recorded on a Varian Mercury Plus 400 MHz spectrometer using $\text{DMSO}-d_6$ as a solvent.

Rheology was performed on a Discovery Hybrid Rheometer (TA Instruments) to study the thermomechanical behavior of the nanocomposites. The samples were molded into discs with a diameter of 8 mm and a thickness of 1 mm (molding conditions: 120 °C, and 40 kPa for 1 h). The rheology results are described in storage modulus G' that stands for the elastic behavior and loss modulus G'' which represents the viscous behavior. For all the rheology tests, an amplitude sweep was always performed first to identify the linear viscoelastic (LVE) range where Hooke's law and Newtonian behavior are valid. The 0.1% strain within the LVE range was chosen. The thermal-dependent behavior was studied by a single cycle of temperature sweep from 50 °C to 120 °C with a ramping rate of 2 °C/min. The time-dependent behavior was investigated through the frequency sweep in the range of 0.01–10 rad/s. Cyclic tests were done to test the reversibility of the samples.

The self-healing samples were prepared by placing the nanocomposites on a 2 × 2 mm anodized aluminum sheet and further compressed at 50 °C. Hand scratch (30–50 μm) was performed by a blade. The 3D optical images of scratches both before and after healing were taken by VHX-7000 digital microscope. All nanocomposites with CNT loadings from 1 to 8 wt% were tested both thermally and electrically. For the thermal healing, the samples were put under thermal treatment in an oven at 120 °C for 1 h. For the electroactive healing, they were connected to a closed circuit where copper wires and copper tapes were used to make good contact with the samples (Fig. 12). The Fluke visual infrared camera was used to monitor the temperature on spot.

3. Results and discussion

3.1. CNT nanocomposites via diels-alder reaction

Pristine MWCNTs were grafted by furfurylamine (FA) and furan-pendant polyketones (FPK), respectively. Table 1 lists the grafted content of different compounds containing furan groups calculated via elemental analysis. There was 0.176 mmol/g FA attached to the CNT surface at 80 °C as compared to only 0.004 mmol/g at room temperature, where the DA reaction is significantly slow. The results are comparable with the data of other furan derivatives [37,45]. The reaction

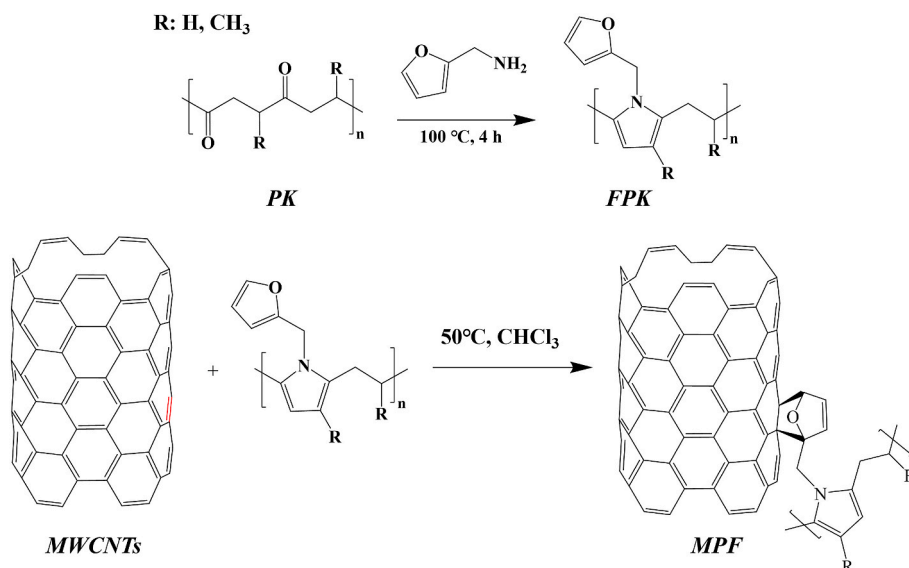


Fig. 1. One-step synthesis of CNT nanocomposites with furan-pendant polyketones (FPK).

Table 1
Grafted content of furan groups on MWCNTs via elemental analysis.

Code	Dienophile	Diene	T/°C	Grafted content/mmol·g ⁻¹
Control	MWCNTs	Furfurylamine	25	0.004
MF	MWCNTs	Furfurylamine	80	0.176
MPF	MWCNTs	FPK ^a	50	0.402
MFPPF	MF	FPK	50	0.362

^a Furan-pendant polyketones.

temperature for MWCNTs-FPK (MPF) was set at 50 °C with CHCl₃ as the solvent. The polymer chains resulted in a higher grafted content of 0.402 mmol/g, which can be explained by the more furan groups they contain. Then the MF was also grafted by FPK to act as a contrast to evaluate the possibility of increasing the grafted content. As shown in Figure S1, MF maintained the dienophile structure and reacted with FPK in the second DA reaction further, namely MF-FPK (MFPPF). It was expected that the pre-modification of MWCNTs could create more dienophile groups on the surface, which would further result in a larger number of furan groups attached. However, no significant difference was seen from the grafted results. MFPPF has a lower grafted content of 0.362 mmol/g. The modification of MWCNTs in the first DA reaction did not increase the number of reactive sites on the surface. The newly formed dienophile (MF) on the CNT surface could also have a steric effect on the follow-up DA reaction with polymers and thus lead to poor grafted results.

Fig. 2(a) illustrates the FT-IR spectra of the pristine and various modified MWCNTs, including MF, MPF, MFPPF. The peak at 3441 cm⁻¹ is present in all three modified fillers, which confirms the addition of the amine groups after the DA reaction. The C=C stretching vibration appeared at 1634 cm⁻¹ [36]. Only MPF and MFPPF showed C-O stretching peaks at 1089 cm⁻¹ and 1055 cm⁻¹, separately. The same IR peaks were also reported by Chang et al. [36] and Zhang et al. [40]. Thermogravimetric analysis results are shown in Fig. 2(b). Pristine MWCNTs did not degrade until 600 °C, whereas all modified fillers

exhibited a perceivable mass drop from 300 °C, which may be due to the decomposition of free FPK in the nanocomposites. The weight loss of MF at 800 °C was around 16 wt.% on average, which is similar to the value of 14 wt.% from reference [36]. It can be seen that MPF and MFPPF showed similar IR spectra and nearly identical TGA curves. Hence, it was concluded that no pre-modifications need to be taken and CNTs can directly react with FPK via DA reaction.

DSC heating experiment was conducted to study the DA reaction between CNT and FPK. Fig. 2(c) and (d) show the thermal behavior of FPK and 2 wt.% CNT nanocomposites within a heat-cool-heat cycle treatment between 0 and 180 °C. The endothermic peak centered at 42.7 °C in FPK and 47.8 °C in the nanocomposites can be attributed to enthalpic relaxation since the samples were initially maintained at 0 °C (much below their T_g of 33 °C) [22]. The relaxation enthalpy corresponds to the release upon heating of degrees of freedom after the material had been aged below its T_g [49]. In the 2 wt.% CNT nanocomposites, there is a broad exothermic peak at 62.6 °C related to the DA reaction. Another endothermic peak was found at 85.8 °C, which corresponds to the rDA reaction. In the cooling step, DA reaction can be seen at the exothermic peak at 52.2 °C. The second heating step did not show any endothermic peaks normally associated with the rDA reaction. This is because the time interval between steps is too short to complete the forward reaction, which has very slow kinetics, and rebuild the crosslinking network. At 171.1 °C, the nanocomposites show one clear exothermic peak which is suspected to be a side reaction. The high temperature also caused irreversibility in the cyclic tests (section 3.4). These findings confirmed the DA reaction between CNT and FPK in the nanocomposites.

The rheological behavior of FPK and nanocomposites between 50 and 75 °C is shown in Fig. 3. The FPK has a glass transition temperature of 33 °C [22]. Above 50 °C, the modulus decreased quickly and FPK became flowable, which indicates it cannot be processed at high temperatures. On the other hand, the modulus in the nanocomposites increased by three orders of magnitude at 75 °C, presenting certain

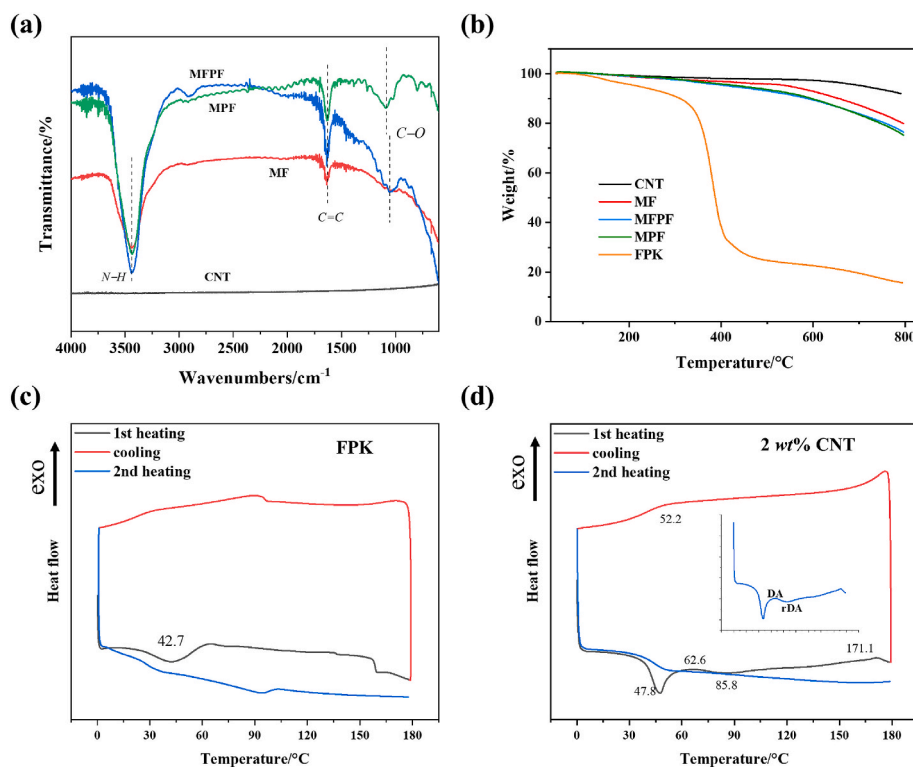


Fig. 2. (a) FT-IR spectra of various MWCNTs; (b) TGA curves MF: MWCNTs-FA; MPF: MWCNTs-FPK; MFPPF: MF-FPK; (c) DSC curves of FPK from 0 to 180 °C; (d) DSC curves of 2 wt% CNT from 0 to 180 °C.

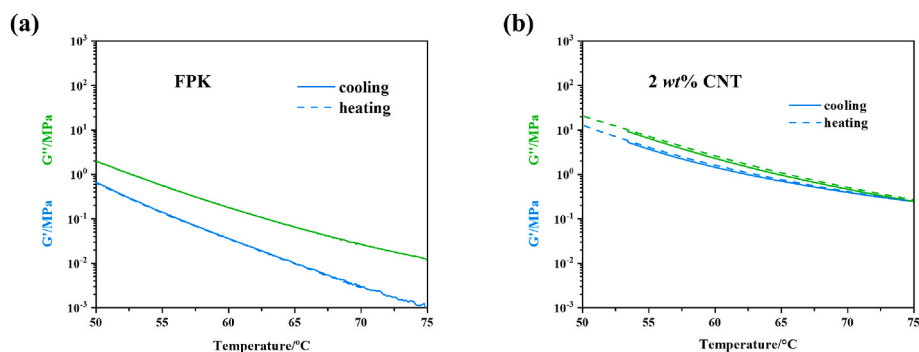


Fig. 3. Modulus comparison of FPK and 2 wt% nanocomposites from 50 to 75 °C.

processability at high temperatures. It is suspected that this influence came from the chemical crosslinking. The thermal-dependent behavior will be studied in the following sections.

The dispersion of various MWCNTs in THF is shown in Fig. 4. All samples were sonicated for 30 min and stored at room temperature for one week before the image was taken. It was found that pristine MWCNTs were well-dispersed in THF after one week, as well as the physically mixed MWCNTs and FPK. As for the crosslinked 2 wt% nanocomposites, obvious precipitation was observed. It can be explained by the fact that MWCNTs have covalent DA linkages with FPK, which caused poor dispersion as time went by. All of the evidence pointed towards that the DA reaction had taken place between CNTs and FPK in the nanocomposites.

3.2. Rheological study of nanocomposites with different functional groups on polymers

3.2.1. Different functional groups

In order to further study the DA interaction between furan groups and CNTs, polyketones were functionalized with two kinds of amines, furfurylamine and butylamine, to compare the effect of different functional groups (Figure S2). Other than FPK and butyl-pendant polyketones (BPK, modified by butylamine) with an 80% NH_2/CO ratio, there was a random co-polymer synthesized that had both groups with a number ratio of $\text{BPK:FPK} = 1:3$. The GPC data can be found in Table S2. The chemical structures of functionalized polyketones were characterized and confirmed by ^1H NMR spectra and FT-IR spectra (Figure S3). Fig. 5 lays out the temperature sweep results of the nanocomposites with different functional groups. The G' curve of BPK was less temperature-dependent compared to the rest. The absolute value of the gradient increased accordingly as the portion of FPK rose. In other words,

nanocomposites with more furan groups were more easily affected by temperature. For FPK, the DA reaction at 50 °C led to a rigid crosslinking network with a high modulus. It is worth mentioning that there is another crossover point of G' and G'' at temperatures lower than 50 °C, which is not shown in the graph. When G'' dominates over G' around 50 °C, the nanocomposites exhibit viscous flow behavior. As the temperature increases, the rDA reaction takes over and the polymer becomes free to flow due to disassociated covalent bonds. The modulus at 50 °C (G' and G'') increased two orders of magnitude from BPK to FPK, indicating that the nanocomposites with BPK are more viscous and softer than that of FPK, which is consistent with the higher T_g of FPK than BPK from the previous study [22]. Similar temperature-dependent behaviors were also found in the furan/maleimide system [50]. Therefore, it is possible to tune the rigidity of the nanocomposites with the crosslinking density through the types of functional groups on the polymer backbone.

3.2.2. Different concentrations of furan moieties

The effect of the number of furan groups on the crosslinking density of the nanocomposites was also investigated. Different amount of furan groups on the polymer chains were synthesized by choosing a series of NH_2/CO ratios (40%, 60%, 80%) in the Paal-Knorr reaction. The conversion rates of amine and carbonyl groups were calculated according to the nitrogen content from elemental analysis, which are in the same range as the previously reported data [13,22]. FPK with 100% NH_2/CO ratio was not included since the conversion of carbonyl groups is the same as the one with 80% ratio. (Table S1). The GPC data can also be found in Table S2. Temperature sweep rheology experiments were employed to study the thermal dependence (Fig. 6). Nanocomposites with 40% NH_2/CO ratio had relatively low modulus at 50 °C and similar temperature-independent behavior like BPK in section 3.2.1. The sample was soft and even sticky under room temperature, indicating a low DA crosslinking density. When NH_2/CO ratio increased to 60% and 80%, the stiffness of the nanocomposites increased significantly at 50 °C. The modulus change of nanocomposites at low temperatures is in agreement with the reference that more furan moieties result in higher T_g [22]. As the rDA reaction reaches maximum at 120 °C, the modulus dramatically reduced with the cleavages of crosslinking [51]. The intersection point of G' and G'' also shifted from 70 °C to 75 °C as NH_2/CO ratio increases from 60% to 80%, which suggests that more thermal energy was required to cleave the DA linkages. As a result, the crosslinking density rose with the number of furan groups. To ensure a high crosslinking density in the nanocomposites, FPK with 80% NH_2/CO ratio was used in the following study.

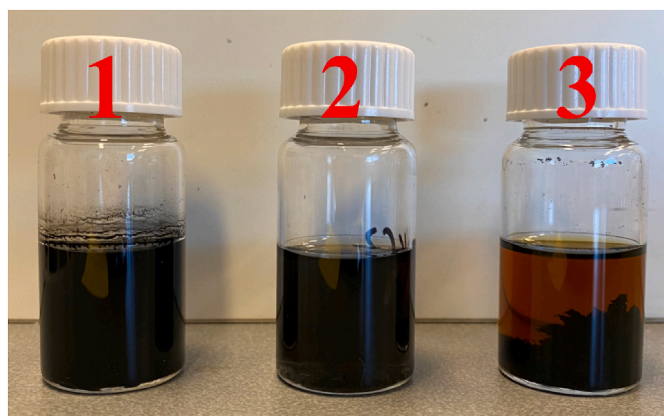


Fig. 4. Dispersion of various MWCNTs in THF, 0.1 mg/mL. (1, pristine MWCNTs; 2, pristine MWCNTs and FPK, physically mixed; 3, 2 wt% CNT nanocomposites).

3.3. Thermal behavior of the CNT nanocomposites

Nanocomposites with different CNT loadings (1, 2, 5, and 8 wt%) were prepared to evaluate the influence of CNTs crosslinking with polymers. Temperature sweep rheology results from 50 °C to 120 °C are shown in Fig. 7. In general, all samples showed noticeable temperature-

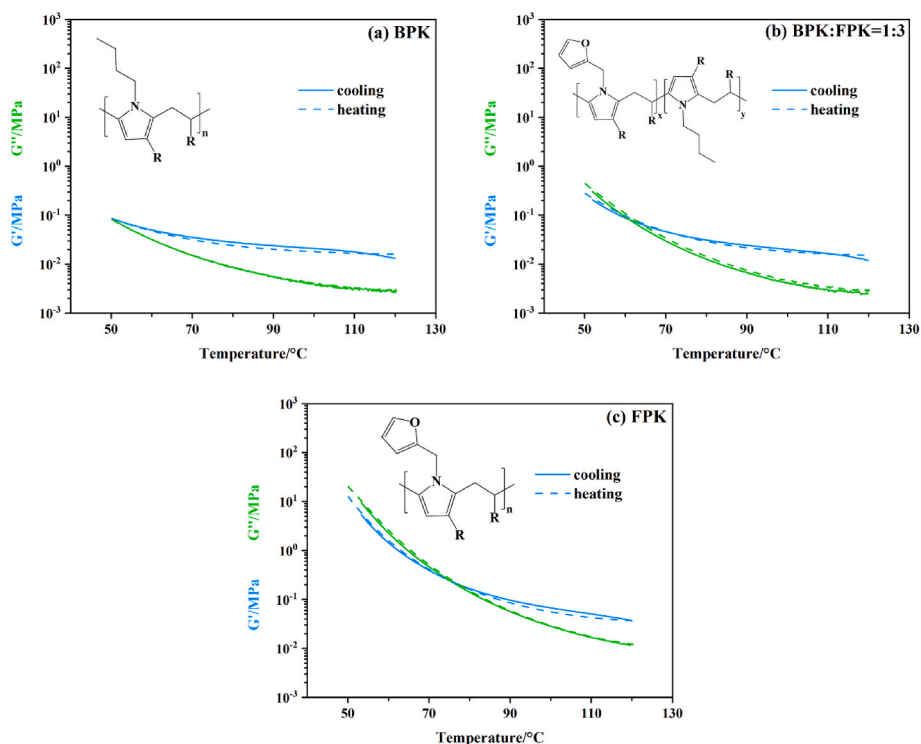


Fig. 5. Thermal behavior of nanocomposites with different functional groups. (a) BPK; (b) BPK:FPK = 1:3; (c) FPK.

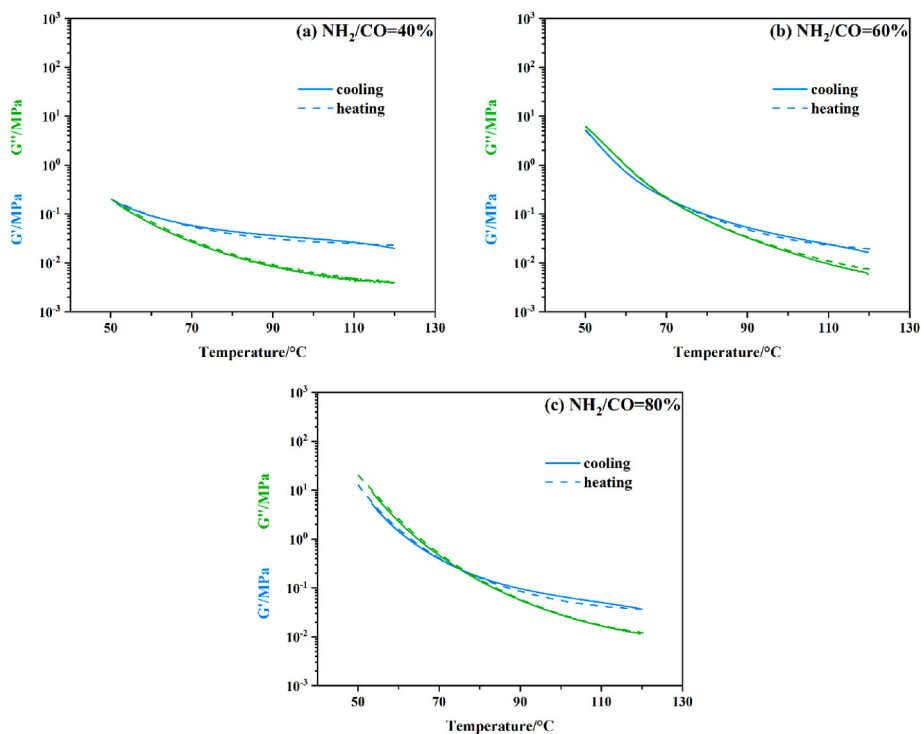


Fig. 6. Thermal behavior of nanocomposites with different furan moieties. (a) NH₂/CO = 40%; (b) NH₂/CO = 60%; (c) NH₂/CO = 80%.

dependent behavior from 50 °C to 120 °C that supports the thermal sensitive DA reactions inside the nanocomposites. As the CNT loadings increase, the overall modulus increased moderately at 50 °C and a lot at 120 °C. The DA linkages at 50 °C resulted in the high modulus and higher CNT loadings brought higher modulus due to the increased crosslinking density. With the covalent bonds breaking at 120 °C, only

the physical stiffening effect remained in the nanocomposites. The modulus values increased by three orders of magnitude from 1 wt% to 8 wt%, which is much higher than at 50 °C. Therefore, CNTs can crosslink with the polymers even at a low loading of 1 wt%. The crosslinking density increases with higher filler loadings. It is also able to tune the filler loadings to achieve different rigidity.

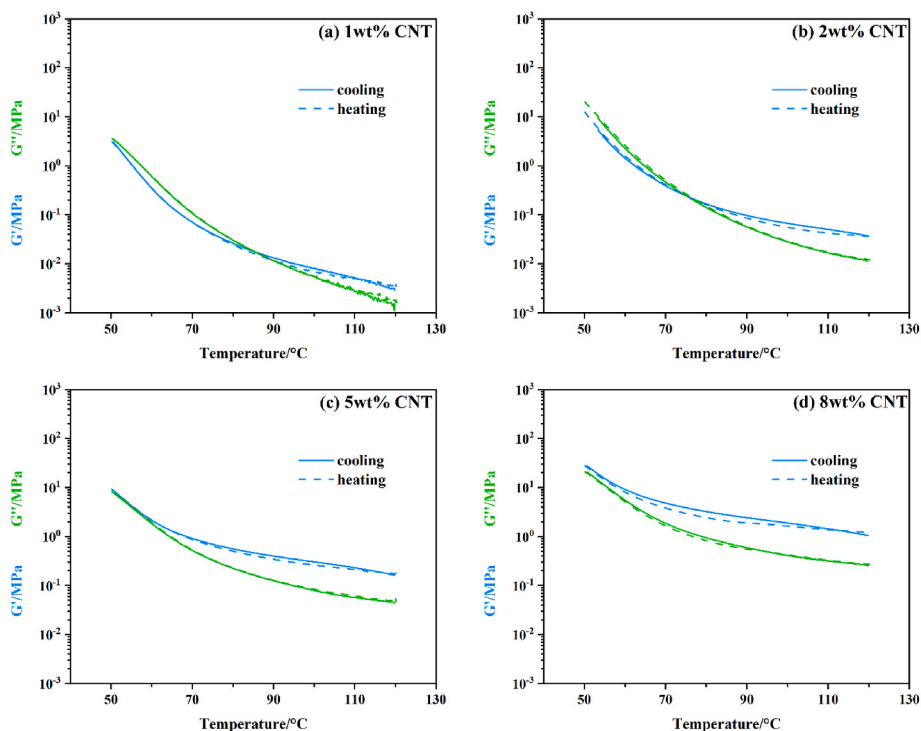


Fig. 7. Thermal behavior of nanocomposites with different CNT loadings. (a) 1 wt%; (b) 2 wt%; (c) 5 wt%; (d) 8 wt%.

Since frequency is the inverse value of time, the time-dependent behavior can be studied at different frequencies, where short-term behavior is simulated at high frequencies and long-term behavior is measured at low frequencies [52]. Fig. 8 illustrates the frequency sweep results of nanocomposites with 2 wt% loading at different temperatures (50, 80, and 120 °C respectively). At 50 °C, the G' and G'' curves practically overlapped with G' slightly higher. The sample also behaved like a solid which is not in favor of flowing and healing over time. When the temperature rose to 80 °C, a cross-over point was found at 1.26 rad/s that showed elastomer behavior at high frequencies but a more rigid network at low frequencies, indicating certain mobility and healing ability at a long time scale. Finally at 120 °C, the DA linkages cleaved and the polymers are completely free in the system. Since the

temperature was way above the T_g of 33 °C, the dominance of G' is attributed to the presence of CNTs. The low modulus value means the sample was still viscous, which can guarantee a flowable network. The healing temperature for the nanocomposites should be at least 80 °C. At higher temperatures, a faster healing process can be expected due to improved mobility.

The thermal stability of the nanocomposites was tested via TGA and the results are presented in Fig. 9, where 100 wt% stands for pristine MWCNTs and 0 wt% stands for FPK with 80% NH_2/CO . The remaining weight of pristine MWCNTs declined over 600 °C, which could be attributed to impurities such as metallic and non-nanotube-carbon [53]. Since the polymer matrix accounts for at least 92% of the nanocomposites, the thermal degradation curves are similar to that of FPK. Before 400 °C, the remaining weight decreased with higher CNT

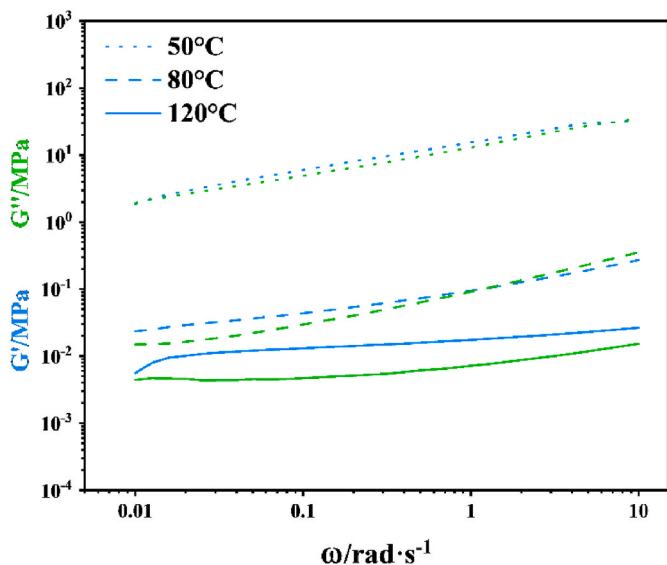


Fig. 8. Time-dependent behavior at different temperatures via frequency sweep.

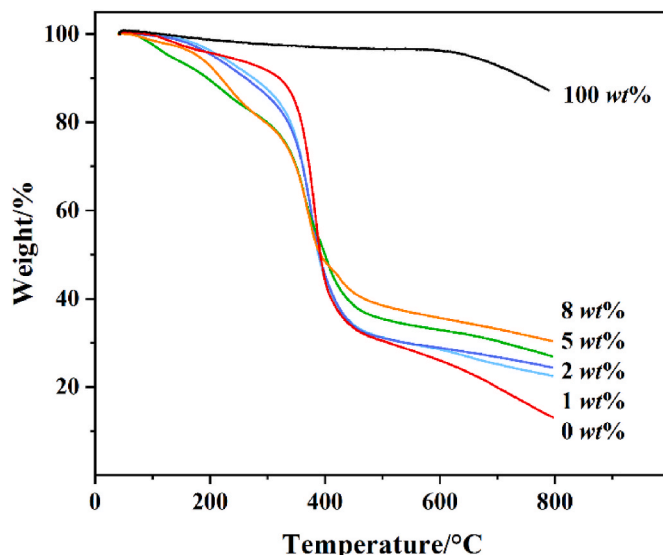


Fig. 9. Thermal stability of nanocomposites with different CNT loadings.

loadings, which can be ascribed to the degradation of polymers grafted. After 400 °C, higher CNT loadings had a larger remaining weight since most of the polymers had already been decomposed. The finding is in alignment with other CNT nanocomposites reported [54].

3.4. Thermal reversibility

In order to test the reversibility of the nanocomposites, three cycles of temperature sweep were performed under different temperature ranges (Fig. 10, only G' is shown for brevity). Three heating-cooling cycles below 120 °C were first carried out to check the reversibility. There was no significant increase in the modulus after three cycles. All the samples showed good reversibility below 120 °C. However, in the cycles up to 200 °C, G' had an abnormal surge around 170 °C. By the time of third cycle, the modulus value had been raised roughly three orders of magnitude at 200 °C. Orozco et al. [55] reported another irreversible modulus increase of the furan/maleimide system at 150 °C, which was attributed to the homopolymerization of maleimide. Other researchers proposed that the DA adduct could undergo aromatization via dehydration at 140 °C, which led to poor reversibility [15,56]. Likewise, it is inferred that an unknown side reaction was happening inside the nanocomposites at temperatures higher than 170 °C.

Besides the temperature sweep, five cycles of frequency sweep were performed to further examine the reversibility at 120 °C and 200 °C separately (Fig. 11, only 3 cycles are shown for brevity and better contrast. Complete results are shown in Figure S4). Frequency sweep can also reveal information about the crosslinking density. Highly cross-linked polymers can only be deformed in a very small range before irreversible changes. So, frequency-independence positively correlates with the crosslinking density [52]. Before every frequency scan, one hour of isothermal treatment was conducted to ensure uniform thermal distribution in the sample. For all the measurements taken, G' dominated across the whole frequency range, indicating an elastic network-like structure and solid-like behavior. At 120 °C, when the CNT loading was 2 wt%, G' had apparent increasing trends along with the frequency. The positive slope means that the nanocomposites had a higher modulus in the short-term behavior and a lower modulus in the long-term behavior. This is a sign that the nanocomposites tend to flow at long time scales and show certain flexibility at rest like elastomers [57]. Two loadings both possess a low degree of crosslinking due to the rDA reaction at 120 °C. However, the 8 wt% loadings showed poor reversibility after 5 cycles. Fig. 11 (c) and (d) exhibit cyclic frequency sweep at 200 °C. The 2 wt% CNT nanocomposites had higher initial modulus compared to 120 °C. It increased by about two orders of magnitude at the end of the fifth cycle. The average modulus was even higher than the value at 120 °C (as opposed to the usually lower modulus at higher temperatures) which strongly indicates that a stiffening process had happened during the test. For the 8 wt% sample, the cyclic tests at 200 °C also showed similar irreversibility and high modulus compared with

120 °C. That being said, the influence of temperature became smaller with higher CNT loadings. It is inferred that when there are more unreacted furan groups, the side reaction is more likely to take place at high temperatures and cause irreversibility. The details on the side reaction mechanism have been reported in another paper from our group lately [58]. Therefore, it is safe to conclude that high temperatures could lead to poor reversibility of the CNT nanocomposites [15,55,56].

3.5. Self-healing performance

The scratched samples were tested both thermally and electrically (Fig. 12). The thermal healing test was carried out first to assess the healing performance. Nanocomposites of 1 wt% and 2 wt% CNT did not show any good healing results. Figure S5 compares the self-healing efficiency for different CNT loadings. The width of the scratches narrowed down to 0–10 μm after heating. The 5 wt% and 8 wt% samples both showed promising healing performance with the highest efficiency of 90% at 8 wt% CNT loadings. The control sample of FPK with no CNT did not show any self-healing ability after the thermal treatment. The electroactive healing test was then performed with an external power supply. The nanocomposites with 1 wt% CNT did not show any conductivity. For the nanocomposites with 2 wt% CNT, even though it was electrically conductive, the sample only reached around 50 °C and the heat produced was not enough to reach the rDA temperature (120 °C). Nanocomposites with CNT loadings equal to or higher than 5 wt% reached between 120 and 140 °C under a current of 0.25 A and a voltage of 14.5 V. After 1 h, the width of the scratches also reduced to 0–10 μm. The self-healing efficiency also reached at least 81%. To make reversible polymer nanocomposites with good self-healing performance, the minimum CNT loadings is 2 wt%. However, to make the system reversible electrically, higher CNT loadings are needed for the rDA reaction to take place.

4. Conclusion

We have demonstrated that pristine CNTs undergo DA reaction with furan-pendant polymers without any pretreatment. The CNTs serve dual roles, both as reinforcing fillers and as reactive components, in nanocomposites. The feasibility of DA on CNTs was successfully confirmed by infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, elemental analysis and dispersion tests. The crosslinking density of the nanocomposites can be controlled with the number of furan groups on polyketones, varying from 40% to 80%. The nanocomposites demonstrated dynamic temperature-dependent behavior, which was reversible below 120 °C, but irreversible above 120 °C with possible side reactions. Furthermore, self-healing was proven to be successful by both thermal treatment and electrical conductivity tests around 120 °C. This one-step Diels-Alder reaction can also be used on fullerene, graphene and other fillers with diene/dienophile properties. It

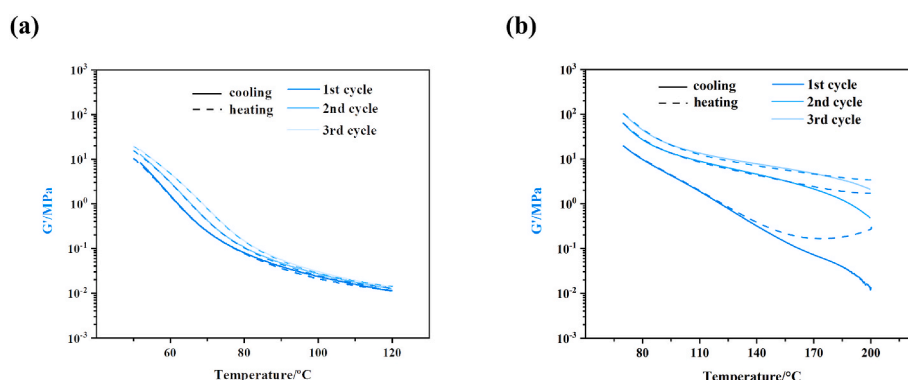


Fig. 10. Rheological behavior of nanocomposites at different temperature ranges (Performed under N_2 atmosphere).

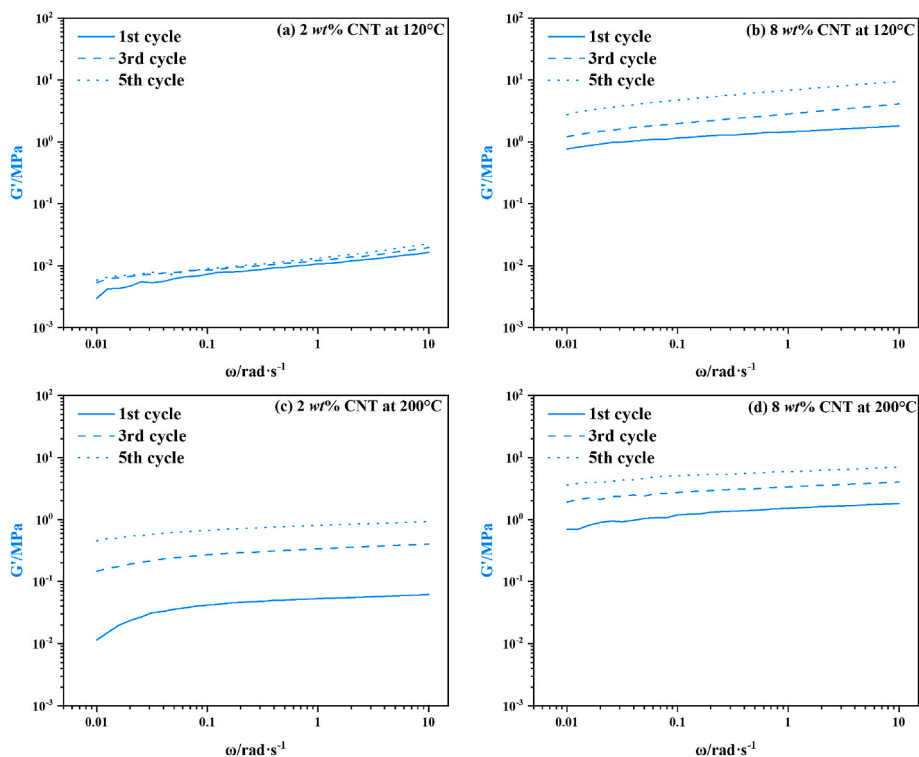


Fig. 11. Reversibility of nanocomposites with different CNT loadings at 120 and 200 °C.

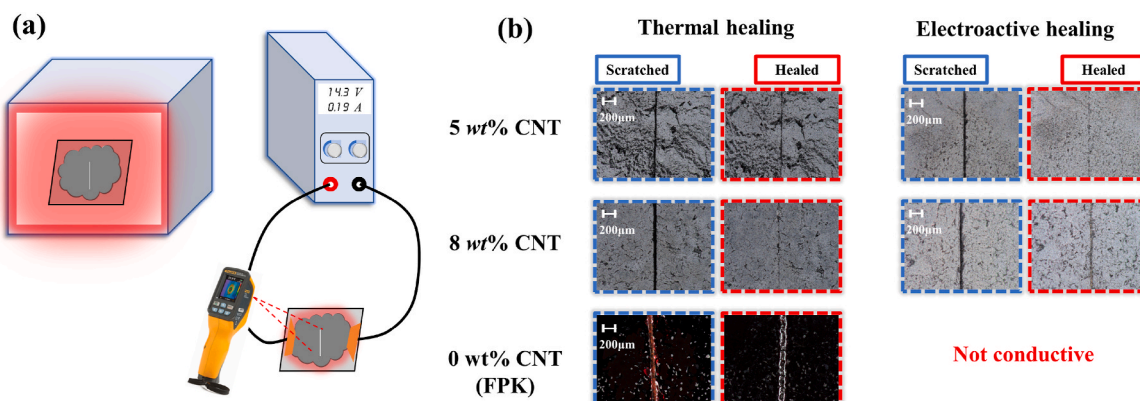


Fig. 12. Self-healing results of nanocomposites with 5, 8 wt% CNT.

should be addressed that the defect sites on carbon materials play an important role in the reaction as more defect sites bring more reactive sites, which may result in a highly crosslinked network. This research provides an easy and unique way to synthesize novel reversible polymer nanocomposites.

CRediT authorship contribution statement

Jie Guo: Writing – original draft, Conceptualization, Methodology, Investigation, Visualization. **Francesco Picchioni:** Supervision, Writing – review & editing. **Ranjita K. Bose:** Writing – review & editing, Conceptualization, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jie Guo reports financial support was provided by China Scholarship

Council.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2023.126260>.

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