University of Groningen

Electroactive performance and cost evaluation of carbon nanotubes and carbon black as conductive fillers in self-healing shape memory polymers and other composites

Orozco, Felipe; Salvatore, Alex; Sakulmankongsuk, Anchista; Gomes, Diego Ribas; Pei, Yutao; Araya-Hermosilla, Esteban; Pucci, Andrea; Moreno-Villoslada, Ignacio; Picchioni, Francesco; Bose, Ranjita K.

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

[Link to publication in University of Groningen/UMCG research database](#)

POLYMER

materialstoday

Check for updates

Electroactive performance and cost evaluation of carbon nanotubes and carbon black as conductive fillers in self-healing shape memory polymers and other composites

Felipe Orozco [a], Alex Salvatore [a,b], Anchista Sakulmankongsuk [a], Diego Ribas Gomes [c], Yutao Pei [c], Esteban Araya-Hermosilla [d], Andrea Pucci [b], Ignacio Moreno-Villoslada [e], Francesco Picchioni [a], Ranjita K. Bose [a,*]

[a] *Department of Chemical Engineering, Product Technology, University of Groningen, 9747 AG, Groningen, the Netherlands*
[b] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124, Pisa, Italy*
[c] *Department of Advanced Production Engineering, Engineering and Technology Institute Groningen, Faculty of Science and Engineering, University of Groningen, 9747 AG, Groningen, the Netherlands*
[d] *Center for Materials Interfaces @SSSA, Istituto Italiano di Tecnologia, Viale Rinaldo Piaggio 34, Pontedera, 56025, Pisa, Italy*
[e] *Laboratorio de Polímeros, Instituto de Ciencias Químicas, Facultad de Ciencias, Universidad Austral de Chile, Valdivia, 5090000, Chile*

ARTICLE INFO

ABSTRACT

Multiwalled carbon nanotubes (MWCNT) and carbon black (CB) have been widely used as conductive fillers in electroactive polymer composites. MWCNT-based composites generally have lower resistivity and percolation thresholds, while CB-based ones are considerably cheaper. To balance these pros and cons, ternary composites (TCs) (polymer-MWCNT-CB) can be formulated. Here, we prepared electroactive MWCNT-CB TCs capable of self-healing and with shape memory properties, based on polyketones reversibly-crosslinked via Diels-Alder chemistry. Unexpectedly, the cheaper CB-rich formulations had lower resistivities, thus better electroactive self-healing and shape memory responses. Nonetheless, not all electroactive MWCNT-CB TCs have this clear cost-effectiveness. We evaluated the cost-performance of multiple reported MWCNT-CB TCs systems and found different general trends (positive, negative, and synergistic cost-efficiency relationships). Thus, the cost-effectiveness of these fillers (and their combination) greatly depends on each composite system and what it is intended for. This work includes the first systematic report on cost-performance of MWCNT and CB as conductive fillers.

1. Introduction

Conductive fillers such as carbon nanotubes [1–5], graphene [6,7], metals [8], and carbon black [3] have been widely used for preparing polymer composites. Through this approach, polymer products, characterized by their versatile range of mechanical properties, light weight, and low-cost, are granted with conductive features. As a result, these composites are being used in electronics and as electroactive responsive materials. Additionally, fillers also improve the mechanical properties of polymers, such as mechanical strength and resistance to wear and abrasion [9].

Table 1 shows the key characteristics of two commonly used carbonaceous fillers: multiwalled carbon nanotubes (MWCNT) and

carbon black (CB). Over the last decade, the former has been researched the most for their own remarkable low resistivity and low percolation thresholds. However, MWCNT also have the drawback of being quite expensive. On the other hand, CB is considerably much cheaper since it has been used as filler at industrial scales for over a century by the tire industry. Nowadays, the most conductive kinds of carbon black, known as conductive CB, are produced in hundreds of tons per year at 1 $/kg for preparing conductive polymer composites [9]. However, compared to MWCNT-based composites, CB-based ones are generally less conductive and have higher percolation thresholds [10–12]. Compared to CB, MWCNT also have the drawback of being more environmentally harmful, with greenhouse gas emissions 1–3 orders of magnitude higher than the ones for CB [13,14].

Table 1

Main characteristics of MWCNT and CB.

	Multiwalled carbon nanotubes	Conductive carbon black
Popularity[a]	3 times higher than CB	3 times lower than MWCNT
Resistivity ($\Omega \cdot cm$)	10^{-6}-10^{-2} Ref. [36,37]	10^{-2}-10^{-1} Ref. [9]
Percolation threshold (wt%)	1–5 Ref. [4,10–12]	3–25 Ref. [9–11]
Cost ($/kg) [b]	10^{2}-10^{4}	10^{0}-10^{3}
Greenhouse gas emissions (CO_2 g/g)	10^{1}-10^{3} Ref. [13]	10^{0} Ref. [14]

[a] More details in Section S1, Supporting Information.

[b] More details in Section S2, Supporting Information.

In order to balance the pros and cons of these two carbonaceous fillers, many researchers have combined them in ternary composites (TCs) (polymer matrix + MWCNT + CB) [3,10–12,15–18]. Many of these studies even report synergy between the two fillers, i.e., that some TCs, with a given range of MWCNT-CB ratio, are more electrically conductive than their binary counterparts with the same total filler concentration (TFC) [10–12,15,16]. This synergy is considered to be caused by MWCNT bridging CB aggregates (or vice versa) in a way that improves the percolation network [11,15,16]. Dorigato and coworkers [10] reported a synergistic polybutylene terephthalate TC with 4 wt% MWCNT and 2 wt% CB with a resistivity of approximately 100 Ω cm and capable of reaching 60 °C in a minute through resistive heating (applying 12 V). In another work, Ju et al. [15] prepared a polypropylene-based TC foam for electromagnetic interference shielding applications, and achieved the lowest resistivity (10 Ω cm) with a formulation that used 2.5 wt% of each filler. Also very interesting, Qu and coworkers [11] developed a conductivity model for MWCNT-CB TCs and tested it experimentally with a poly(methyl methacrylate) system. The authors explored a wide range of TFCs and MWCNT/CB ratios. They found regions with sharp synergy in terms of low resistivity, such as formulations with 10 wt% MWCNT and 5 wt% CB with resistivity values of about 10 Ω cm. On the other hand, they also found regions with poor or non-synergy at low and high TFCs.

In a previous work [5], we reported an electroactive self-healing shape memory polymer composite with MWCNT as conductive fillers. The material was based on a polyketone network crosslinked by thermo-reversible tie linkages (furan-maleimide Diels-Alder chemistry, Fig. 1). Thus, through resistive heating, the material was able to self-repair micro-scale scratches, as the damaged surfaces came closer (driven by thermal expansion, shape memory, and increased network mobility) while the broken tie linkages were reformed. On the other hand, in the short term, the reversible tie linkages also behaved as quasi-permanent crosslinks that held the shape memory, as a temporary shape was electroactively being set. The material showed shape recovery ratio and rates similar to the ones reported for other electroactive shape memory polymer composites; i.e., full (or almost full) recovery within minutes by applying tens of volts [6–8,19–21]. They also self-healed efficiently as many of their electroactive counterparts from the literature do [4,6,19,20]. Such dual-responsive materials are quite attractive as self-healing self-deployable structures, and given their rubbery features, also as self-healing actuators in soft robotics [8,22,23].

Here, electroactive MWCNT-CB TCs capable of self-healing and with shape memory properties were developed following the aforementioned polyketone-Diels-Alder approach. Formulations with fixed TFC but different MWCNT/CB ratio were prepared and their electroactive responses were studied; i.e., resistive heating, shape memory, and self-healing. Then, simple cost estimations of these composites were made in order to evaluate the balance between their cost and electroactive performance. Besides studying the prepared composites, this work aims to broadly evaluate the cost-effectiveness of MWCNT and CB as conductive fillers in electroactive polymer composites in general. Therefore, multiple electroactive MWCNT-CB TCs reported in the literature were incorporated to the cost-performance evaluation and discussion. To the best of our knowledge, this is the first systematic report on cost-effectiveness of these two carbonaceous fillers used in conductive polymers.

2. Experimental section

2.1. Materials

The polyketone was prepared by Shell as described by Drent and coworkers [24] with Mw 2690 Da, and an ethylene-propylene ratio of 3/7. Furfurylamine was distilled before use (Sigma Aldrich, 99%). Chloroform (Sigma Aldrich, 99.5%), 1,1-(methylenedi-4,1-phenylene) bis-maleimide (Sigma Aldrich, 95%), MWCNT (Sigma Aldrich, O.D. 6–9 nm with average length of 5 μm), and CB (Ketjenblack EC-600JD, Nouryon, 3 mm pellets, 30–50 nm carbon particles) were used as received.

2.2. Synthesis and characterization

The polyketone system was used since it has shown to be easy and safe to work with, particularly, the grafting process through the Paal-Knorr reaction is quite straightforward and ecofriendly, i.e., carried at relatively low temperatures and without any solvent nor catalyst (Fig. 2) [25]. The amount of furan groups was aimed at 1.4 mmol/g and the polymers were crosslinked with bismaleimide at a molar ratio of 2/1 (furan/maleimide). Therefore, the final products were crosslinked enough to have a modulus over 1 MPa, but had enough network mobility to reduce brittleness and enhance the thermo-reversibility (and thus the self-healing effect) [26]. The total concentration of the carbonaceous
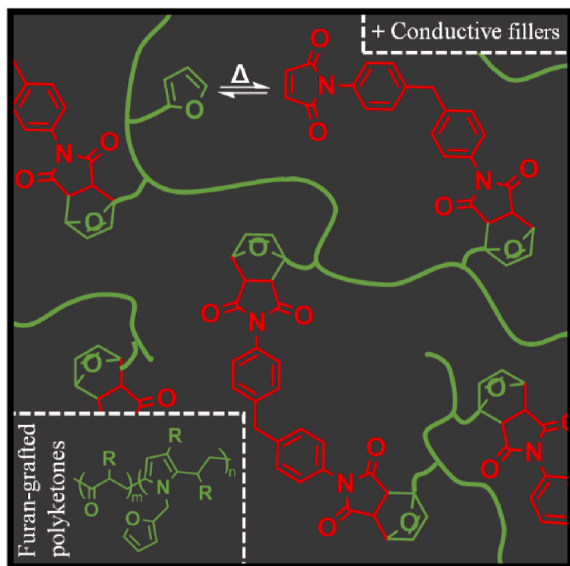
Fig. 1. Thermo-reversibly crosslinked polyketone-Diels-Alder system. Figure inset: randomly furan-grafted polyketone linear backbone.
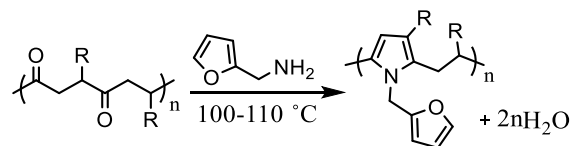
Fig. 2. Polyketone grafting with furan groups through the Paal-Knorr reaction. R stands for –H and –CH₃ groups.

fillers within the TCs was aimed at 8 wt%. This percentage was used since it has shown good percolation in bulky samples [5]; nonetheless, this percentage can be reduced further when working with smaller samples [4].

The grafting procedure was based on the one described by Zhang and coworkers [25]. The polyketone (50 g) was set in a flask at 100–110 °C and vigorously mixed with a mechanical propeller at 600 rpm. The furfurylamine (7 g) was then slowly added dropwise. The reaction system was left to react for 3 h at such temperature and mixing conditions. Then, the mixture was dissolved in chloroform (150 mL) and the unreacted amine was extracted with deionized water (0.5 L). The product was left to dry openly and subsequently dried in a vacuum oven until constant mass was observed. The grafted product was characterized by ^{1}H NMR (Varian Mercury Plus system, 400 MHz).

The composites were prepared based on the report by Araya-Hermosilla [27]. Mixtures of the carbonaceous fillers (0.7 g) were dispersed by sonication in chloroform (10 m/v%) for 30 min. Each of these dispersions was then mixed with a solution of the grafted polyketone (7 g) in chloroform (10 m/v%). Each mixture was set in a round-bottom flask with a reflux condenser and magnetically stirred set at 600 rpm and heated up to 50 °C in an oil bath. After 2 h at these conditions, the bismaleimide was added (0.9 g) and left to react overnight. The final products were left to gel and dry in a Teflon dish, and later dried in a vacuum oven until no further mass loss was observed. Five composites were prepared with 8 wt% TFC but with different MWCNT/CB ratios (8/0, 6/2, 4/4, 2/6, and 0/8). They were named after their respective filler wt%; e.g., CNT(X)_CB(Y), where X is the wt% of the MWCNT and Y the one for CB. The final products were characterized by FTIR (Shimadzu IRTracer_100) and SEM (Philips XL-30 ESEM).

The final products were grinded and molded in a hot press (TP400 Fontune Holland) at 130 °C and 4 bar for 30 min. Two shapes of samples were prepared: the disc-shaped samples for the rheology experiments (8 mm diameter – 1 mm thickness), and U-shaped samples for the conductivity, shape memory and self-healing tests (dimensions shown in Fig. S1, Supporting Information).

The thermo-mechanical profiles of all the samples were investigated using a Discovery HR-2 Rheometer (TA Instruments). The disc-shape samples were prepared and their rheological properties measured using an 8 mm diameter parallel plates in oscillation mode (frequency 1 Hz) and applying a constant axial force of 7 N. Amplitude sweeps between 0.001 and 10% strain were carried to check the viscoelastic linear regime at 50 and 120 °C. Temperature sweeps were performed using 0.05% strain between 50 and 120 °C. The measurements started from 120 °C to erase the thermal history of the material and to ensure a better contact between the plates and the samples. Two cooling and heating cycles were performed.

2.3. Electroactive tests

The U-shaped samples were set in a circuit that includes a multimeter (Metra Hit 18S) and a power source (Velleman DC lab switching power supply). The power source was set at 60 V for all the conductivity, shape memory, and self-healing tests. The current was monitored with the multimeter and the temperature with an infrared thermometer (Fluke VT02 Visual IR Thermometer). The heating power of the samples was determined by the Joules-Lenz law, which states that the heating power is directly proportional to the resistance (R) times the square of the current (I) (Eq. (1)) [28]. The resistivity (ρ) was determined as shown in Eq. (2), where A and l are the cross-sectional area and length of the sample.

$$Heating\ power \propto R \cdot I^2 \tag{1}$$

$$\rho = R \cdot A / l \tag{2}$$

The shape memory tests were carried by placing the U-shaped

samples against a protractor ruler and connecting it to the power source. A voltage of 60 V was applied to the samples in order to surpass the glass transition temperature (T_g) of the polymer matrix, subsequently, the samples were deformed 90° and the voltage set back to zero. The samples were held in this temporary shape until they cooled down to approximately room temperature. Finally, the voltage was set once more to 60 V and the recovered angle and recovery time were recorded. The shape recovery ratio and rate were determined as shown in Eq. (3) and Eq. (4), respectively.

$$Shape\ recovey\ ratio = \frac{angle_{fixed} - angle_{recovered}}{angle_{fixed}} \tag{Eq.3}$$

$$Shape\ recovey\ rate = \frac{angle_{fixed} - angle_{recovered}}{time_{recovery}} \tag{Eq.4}$$

The self-healing tests were based on the procedure reported by Vega and coworkers [29]. The samples were first polished using a SiC abrasive paper with grit size 4000. Then a CSM Revetest scratch-tester was used in constant load mode of 1.0, 2.5, and 4.0 N to make three scratches on each sample with a Rockwell tip with a radius of 10 μm. The scratches were monitored using an optical microscope (VHX-7000, Keyence) as they were self-healed by applying 60 V (followed ex situ for 18 min or until healed).

2.4. Cost evaluation

The cost analysis used in this work is based on the approximate cost of the raw materials that the composites are made of, i.e., the MWCNT, CB, and the polymer matrix. The price of the latter consists of the polymer back bone, which is considered an overall cost of conventional commercial polymers, and the price of the furfuryl derivative and bismaleimide crosslinker used in this work. The estimations were done using prices at both industrial and lab scale. The formulations of other MWCNT-CB TCs from the literature were also considered in the analysis. More details regarding the costs are shown in Section S2 (Supporting Information).

3. Results and discussion

3.1. Synthesis and characterization

The preparation and chemical characterization of the used polyketone-Diels-Alder system have been described in detail in previous works [4,25–27,30]. Here, we corroborated the grafting of the furan moieties into the polyketone by ^{1}H NMR. A functionalization degree of 1.3 mmol/g was obtained (aimed at 1.4 mmol/g – i.e., 90% reaction efficiency) (Fig. S2, Supporting Information). The final crosslinked composites were chemically characterized by FTIR (Fig. S3, Supporting Information).

The distribution of the carbonaceous fillers within the polymer matrices was determined using SEM. Fig. 3 shows micrographs of the studied formulations, which all show good dispersion of both CB aggregates and MWCNT, although the latter seem to be less well dispersed than the former, as best seen in the micrographs of the CNT(8)_CB(0) and CNT(0)_CB(8) binary systems. From the micrographs of the TCs, it seems that loose MWCNT bridge CB aggregates better than CB aggregates bridge MWCNT agglomerates (best seen in the micrographs of CNT (4)_CB(4) and CNT(6)_CB2, respectively). Notably, MWCNT and CB fillers have been reported to aggregate strongly with each other given their mutual affinity (both being carbonaceous structures with aromatic domains [9]) and having very large surface areas [16]. However, the polyketone-Diels-Alder system used here shows strong competing interactions that minimize aggregation between MWCNT and CB. Indeed, the aromatic surface of MWCNT is known to interact with the pyrrole moieties from the polyketone backbone (product of the Paal-Knorr reaction during grafting process) through π– π stacking [31], and with the
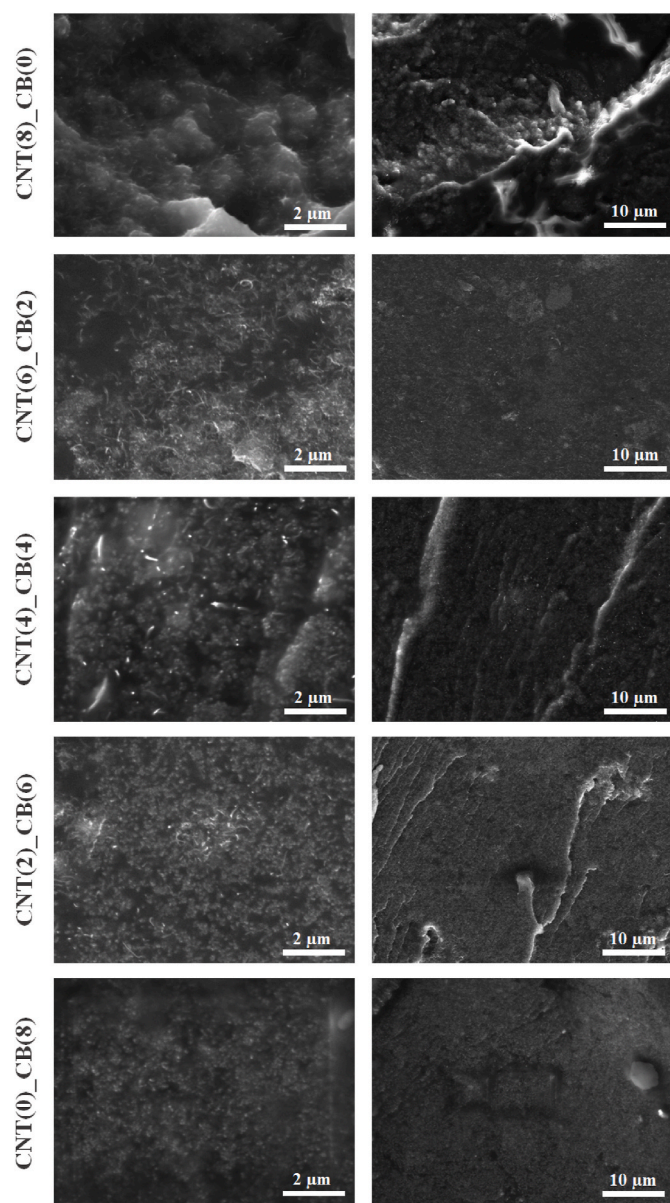
Fig. 3. SEM micrographs of the binary composites and CNT(4)_CB(4).

Fig. 4. Thermo-mechanical profiles of the prepared composites (more replicates and cooling-heating cycles shown in Fig. S4, Supporting Information).

3.2. Electroactive tests

The resistivity values of the studied composites are shown in Fig. 5a. They range between 10 and 20 Ω cm which are comparable to those reported for other MWCNT-CB TCs [10,11,15]. Contrary to the general trend and our expectations, the TCs with lower MWCNT/CB ratios were more conductive than the ones with higher ratios, with the binary system of only CB having the lowest resistivity. Although unusual, this is not unheard of and has been previously described in the literature [11]. This is likely caused by the CB fillers surpassing the MWCNT at having a better balance between aggregation and dispersion within the polymer matrix, which is essential for good percolation [9,11]. Indeed, in Fig. 3, CNT(0)_CB(8) seems to have the best conductive pathway, made of CB aggregates that are well dispersed and percolated. As also evident from Fig. 5a, this system lacks synergism under the conditions that were explored in this work. This implies that, in none of the prepared TCs, the fillers arranged in such a way that the percolation improved by one filler bridging the other effectively enough. This was not unlikely to be the case, since the MWCNT/CB conductive synergy in TCs is by no means guaranteed, and it is known to strongly depend on factors such as TFC, MWCNT/CB ratio, and polymer matrix [11]. Interestingly, the studied system does show a negative synergic effect, as CNT(6)_CB(2) has the highest resistivity of all the composites. This can be due to the MWCNT being less well dispersed than the CB (as seen in Fig. 3), such that the MWCNT agglomerates are not well interconnected by the scattered CB and CB aggregates.

All composites showed good resistive heating capabilities and reached temperature plateaus between 80 and 130 °C when applying 60 V between both ends of the material. Fig. 5b nicely shows how the composites that are more conductive (less resistivity) have more heating power (Eq. (1)) and therefore reach higher temperatures (Fig. 5c). Reaching a target temperature range, and reaching it fast, is key to a good performance as temperature is the stimulus that triggers the response on many electroactive materials, such as the shape memory and self-healing effects studied in this work. It can be seen in Fig. 5c that the temperature plateau is almost reached in the first 3 min for each sample.

Fig. 6 shows the results of the shape memory tests. All formulations have full shape recovery (ratios of 1) and shape recovery rates between 12 and 16 mrad/s (recovery in 130 and 90 s, respectively). As expected from the conductivity tests, the CB-rich formulations, that have lower resistivities and warmed up faster, recovered their shape more quickly. These results are comparable with the ones reported for other electroactive shape memory composites, i.e. having full or nearly full shape recovery taking nearly a minute by applying tens of volts [6–8,19–21].

furan and maleimide groups through the Diels-Alder reaction [27].

Fig. 4 shows the thermomechanical profiles of the prepared composites. As expected, the complex modulus sharply decreases with increasing temperature due to the increasing mobility of the polymer network associated to thermal effects and to the Diels-Alder equilibrium shifting towards decrosslinking [26]. This interesting dual effect, responsible for the very sharp decrease in the mechanical properties of the composite materials with temperature, is useful for self-healing and shape memory retention and programming. From Fig. 4 it is also worth noting that all the thermomechanical profiles are somewhat overlapping. This contrasts the fact that TCs with higher MWCNT/CB ratios are known to have higher moduli [16], since fillers with high aspect-ratio, such as MWCNT, are more effective in reinforcing than fillers with low aspect-ratio, like CB [9]. Nonetheless, the dispersion of the fillers also impacts the mechanical properties of the composites, and, as seen in Fig. 3, the CB is more evenly dispersed in the polymer matrix than the MWCNT. Therefore, the two contrasting effects result in TCs with very similar thermomechanical properties.
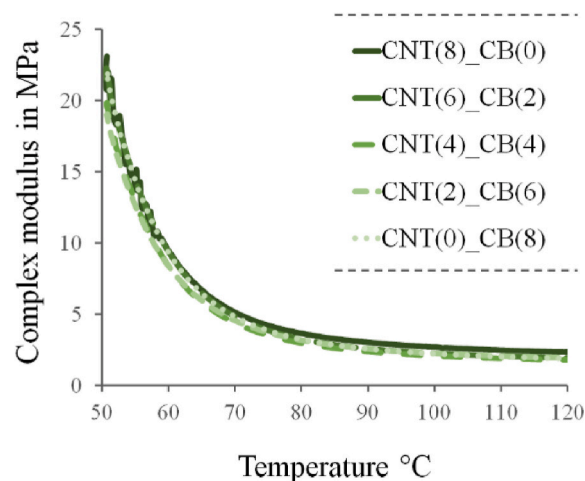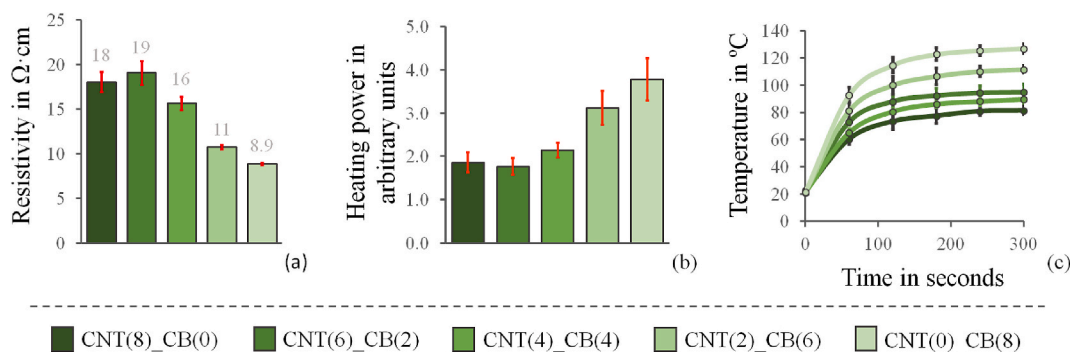
Fig. 5. (a) Resistivity, (b) heating power, and (c) heating profiles of the prepared composites when applying 60 V.
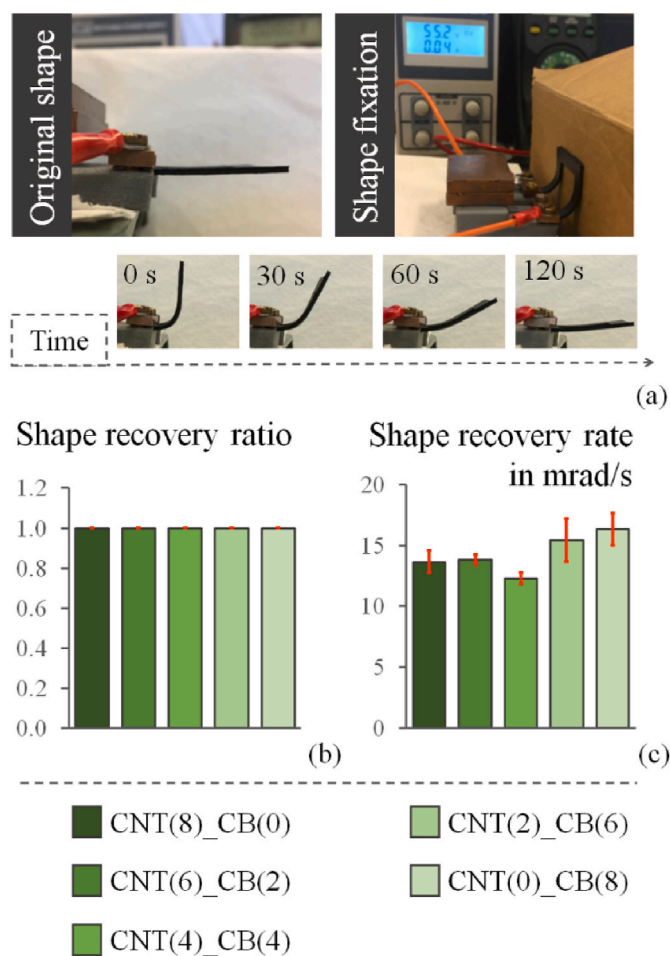

Fig. 6. (a) Shape memory tests set up and an example of actuation (CNT(4)_CB (4) shown as an example). Shape recovery (b) ratio and (c) rate of the prepared composites when applying 60 V.

Interestingly, in our previous work [5] on this polyketone-Diels-Alder composite system (that used only MWCNT as filler), none of the explored materials had full shape recovery ratio while all the ones prepared here show complete shape recovery. In that report, we showed that the shape memory effect could be enhanced in our system by adding a plasticizer bearing OH groups into the reaction mixture. Thus, the final material would have more network mobility (so that the shape fixation and recovery would be facilitated) but still have enough cohesion to "have memory" (cohesion through H-bonding). In this way, the shape recovery ratio went from 0.7 to 0.9 by including the plasticizer in the formulation. In this work, instead of adding such an

agent, we formulated the polymer matrix with less crosslinking density, i.e., we grafted the polyketones with less furan moieties, and crosslinked it accordingly with less bismaleimide molecules. Through this approach, we obtained the same effect (more network mobility while maintaining cohesion) and obtained much better results and through a much simpler strategy.

Fig. 7a shows the electroactive self-healing process of a scratch on the surface of one of the prepared composites under 60 V. CNT(8)_CB(0) is shown for the example and its scratch is initially about 100–150 μm wide. After the first few minutes, the scratch is mostly unchanged given that the temperature has increased to merely 60–70 °C, which is apparently not high enough for the scratch to fully heal. It is not until over 80 °C, some minutes later, that the surface looks fully repaired (temperatures according to Fig. 5c). Interestingly, this same sample, with a scratch of similar dimensions, easily healed after 2 min in a convection oven at 120 °C, which indicates that the temperature might be the limitation factor for a rapid electroactive self-healing (Fig. S5, Supporting Information). Supporting this hypothesis, is that the CB-rich formulations CNT(2)_CB(6) and CNT(0)_CB(8) reached over 80 °C within a minute of resistive heating and fully self-healed in that time.

The last referred experiments are shown in Fig. 7b. This figure shows a semiquantitative scheme of the electroactive self-healing progress across time of each formulation and for the three different scratch ranges that were inflicted. Fig. 7a exemplify how the states of the healing progress are qualitatively catalogued with color tags referring to: "*Not healed – Partially healed – Almost healed – Completely healed*". The scheme on Fig. 7b was made based on this visual classification. As expected, the formulations with better resistive heating profiles showed the faster self-healing abilities. It is also interesting to see how the larger scratches are more difficult to heal. This is expected because: the thermal expansion that helps closing the scratch is limited to the microscale and its contribution diminishes as the scale increases; and the shape memory effect (caused by the displaced material that was pushed away by the tip of the microscratcher and is retreating as the temperature increases) is jeopardized if the polymer network storing "the memory" is damaged, which is more likely to occur for larger scratches.

Fillers are known to change the thermal expansion of polymer composites, since they commonly have lower thermal expansion co-efficients than polymers [9]. Therefore, as this thermal feature plays a role in the self-healing process, the thermal expansion of the prepared composites was also monitored. This was monitored indirectly during the rheology experiments, where the samples were heated and cooled while being pressed by parallel plates. These plates were programed to maintain a fixed axial force over the samples, so that the gap between them would change accordingly as the sample expands and contracts. Fig. S6 (Supporting Information) shows the percentual gap change of the prepared composites as they were heated from 50 °C to 120 °C. These gap changes ranged between 2.0 and 2.7% without significant differences between the formulations. Therefore, for composites explored in this work, the differences in the electroactive self-healing performance
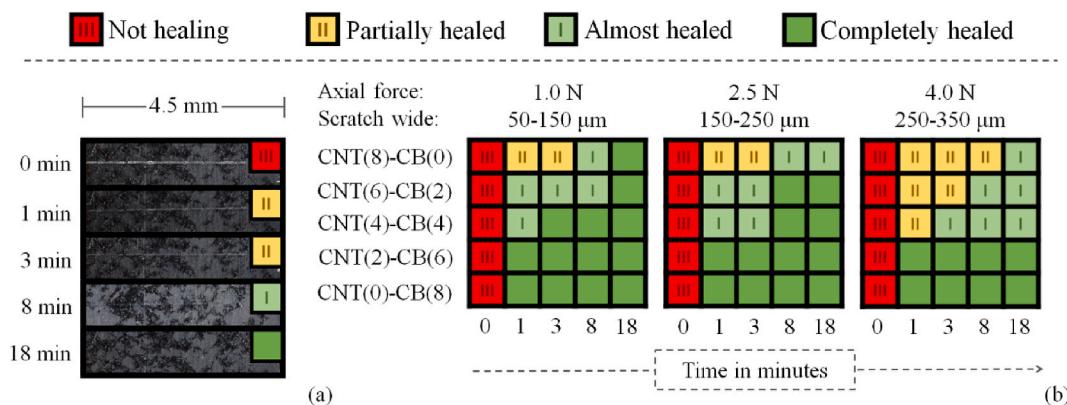
Fig. 7. (a) Compilation of micrographs of a scratch on CNT(8)_CN(0) as it is self-healed through resistive heating (scratch made using a 1 N of axial force) (for simplicity, the remaining compilations of micrographs are shown in Section S3, Supporting Information). (b) Self-healing profiles of different scratch-width ranges of the prepared TCs.

are based on the resistive heating power and not on the thermal expansion.

In the current section, there is a common element for all results: lower resistivity values are accompanied with better resistive heating abilities, shape memory rates and self-healing capabilities. This is in accordance with our expectations since the very heating abilities are the triggers for the other two responses. The plots in Fig. 8 clearly show this relation between resistivity and the electroactive responses. As a result, low resistivity values can be used as indicators of good performance for electroactive materials in general. This allows to compare the performance of the materials prepared in this work with other electroactive MWCNT-CB TCs from the literature (not necessarily with shape memory or self-healing features).

3.3. Cost-performance evaluation

The cost estimations shown in Fig. 9 take into account merely the cost of the raw material that the composites are made of. Nonetheless, they give an interesting perspective on how much cheaper it is to formulate CB-rich composites rather than MWCNT-rich ones for the polyketone-Diels-Alder system explored here. In the graph, the shades of green stand for the price contributions from the polymer matrix. The main weight component is by far the polymer backbone, which is also the cheapest component (about 1 $/kg), so that it does not contribute much to the cost. The rest of the contributions from the polymer matrix are the Diels-Alder moieties, which are approximately 10 $/kg each and are key components for the dual shape memory/self-healing response. The cost contribution from the conductive fillers varies greatly depending on the MWCNT/CB ratio. On the CB-rich formulations, as CB is quite cheap (10 $/kg), the contribution is rather small and similar to one from each polymer matrix component. On the other hand, the much more expensive MWCNT (100 $/kg), dominates the cost contributions in formulations rich in this filler. Naturally, these prices depend on the acquisition scale. However, the analysis has similar results by using scales of 1 kg, 1 ton or tens of grams, i.e., the CB-binary composites being 3–4 times cheaper than the MWCNT-binary ones. Similarly, the cost difference between TCs with different MWCNT/CB ratios is affected by the TFC. In this work, our sample dimensions necessitate the use of 8 wt %; however, working with films or much bulkier devices would imply using different TFC. The same estimations can be done for our polyketone-Diels-Alder system hypothesizing other filler content, such as 5 or 15 wt% (filler content examples from reported electroactive MWCNT/CB TCs [11,15]). Nonetheless, the results are rather similar, i. e., the CB-binary composites being 2–4 times cheaper than the MWCNT ones. However, this significant cost superiority of the CB-rich formulations would be somewhat attenuated if the cost estimation were more
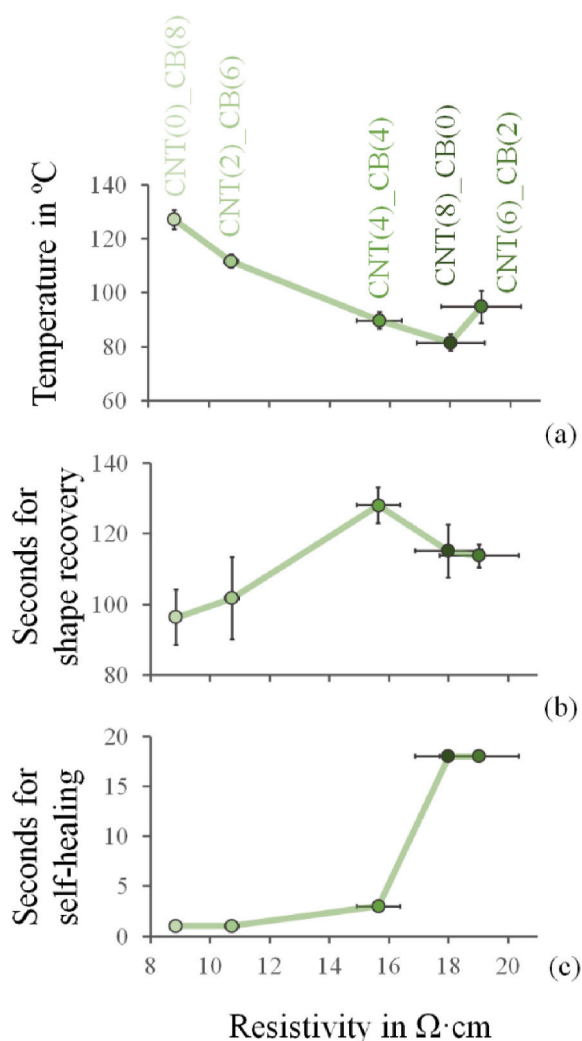
Fig. 8. Resistivity plotted against (a) the temperature reached by applying 60 V, (b) the time taken for fully shape recovery, and (c) the time taken for self-healing the scratches (50–150 μm wide).

complex and included the costs attributed to solvents, energy consumption, waste disposal, and other aspects to take into consideration. (More information in Section S4, Supporting Information).

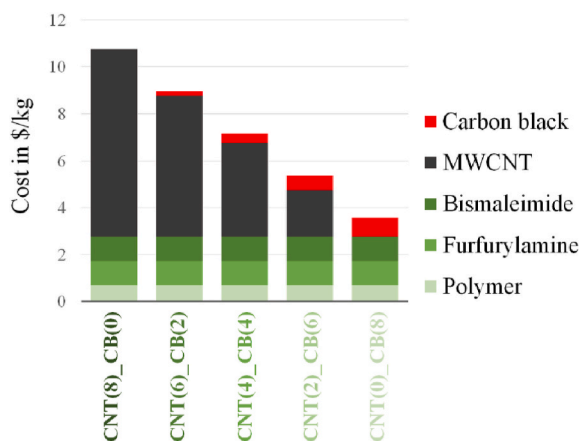Fig. 10 shows a resistivity vs. cost plot that compares the responsive

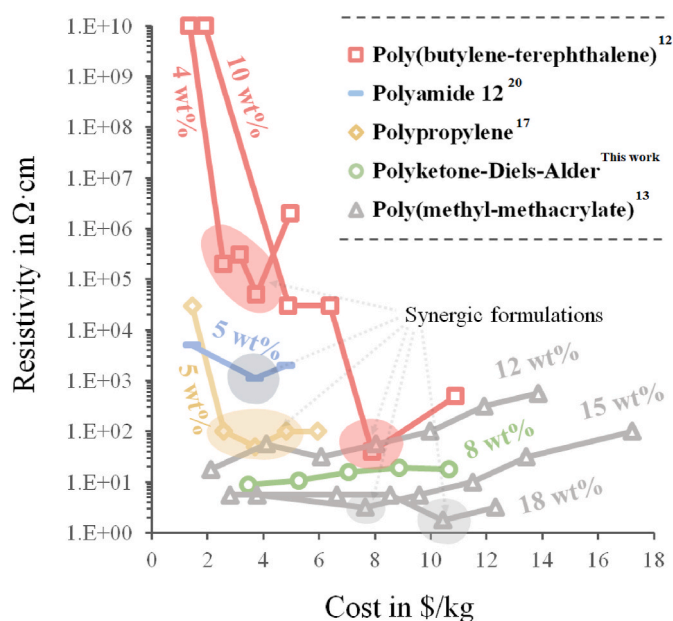**Fig. 9.** Cost estimation of the prepared composites.

Fig. 10. Resistivity vs. cost for different MWCNT-CB TC systems. Each curve represents a TC system with a specific TFC and different MWCNT/CB ratios (the latter increase along with the cost). For each TC system, the formulations that present synergy between the two conductive fillers are pointed out. For clarity and esthetic reasons, a limited number of systems were plotted here. A more complete plot is shown in Fig. S7, Supporting Information.

materials prepared in this work with other electroactive MWCNT/CB TCs reported in the literature. Each curve represents a TC system with a specific TFC and different MWCNT/CB ratios. Naturally, as MWCNT is much more costly than CB, the data points of each curve have a higher MWCNT/CB ratio as they are farther to the right. Additionally, the formulations that present synergism between the two conductive fillers are pointed out (i.e. TC formulations that have lower resistivities than the binary formulations with the same TFC having only MWCNT or CB). Fig. 10 allows to broadly contextualize and evaluate the cost-effectiveness of MWCNT and CB (and combinations of both) as conductive fillers in electroactive polymers in general. For this, low resistivity values are regarded as an indicator of good electroactive performance (as discussed in the previous section – Fig. 8 – correlation between resistivity, temperature, and electroactive responses). Thus, formulations close to the bottom left corner of the plot are the most desirable. From this graph many observations can be pointed out and discussed. Perhaps the most noticeable observation is that the curves

have a negative or a positive slope. The former is the most expected scenario given that TCs with higher MWCNT/CB ratios are more costly and more likely to be less resistive. Nevertheless, TCs systems like the polyketone-Diels-Alder reported here and the poly(methyl methacrylate) reported by Qu and coworkers [11] show positive slopes. As previously discussed, this is observed in systems where the CB surpasses the MWCNT on having a good balance between polymer-filler and filler-filler interactions, thus allowing a good dispersion of the fillers and therefore, an effective percolation network [9,11].

From Fig. 10 it is also evident that not all MWCNT-CB TCs systems have synergism, as expected from the literature [11]. This effect depends on the nature and interplay of the polymer matrix and both fillers. It also depends on the TFC. E.g., the poly(methyl methacrylate) formulations with TFCs of 15 and 18 wt% show a point of synergy, but the formulations with 12 wt% do not show this effect. The polyketone-Diels-Alder TCs described in this work do not show synergism either. Naturally, formulations with synergy between the MWCNT and CB fillers are good candidates for being the most cost-effective ones within a TC system. Nevertheless, this is not always the case. E.g., in the poly(butylene terephthalate) system reported by Dorigato and coworkers (10 wt% TFC) [10], the synergic formulation is 1000 times less resistive and only 20% more expensive than the next cheaper formulation. On the other hand, in the poly(methyl methacrylate) system (18 wt% TFC) [11], the synergistic formulation is only 3 times less resistive and 300% more expensive than the next cheaper alternative. Thus, in this latter case, the formulation with the maximum synergy is indeed not the best cost-effective option.

Overall, there is no simple answer to which carbonaceous filler (or combinations of them) is more cost-effective. Fig. 10 suggests that it depends on each polymer composite system. Nevertheless, if only the performance is considered (and not the cost), MWCNT are a better filler candidates for ensuring good results (low resistivity). This gives credit to the fact that MWCNT are more popular in research than CB. However, CB and MWCNT-CB combinations (and perhaps other conductive fillers) are definitely worth exploring when optimizing a product, i.e., for it to be as less resistive or as cost-efficient as possible. Naturally, the latter case is quite important when developing commercial industrial products. However, this cost-effectiveness might be also relevant in pedagogy, for instance, when designing lab practicals about electroactive or merely conductive polymer composites [32], since they require relatively large quantities of raw materials, and a suitable cost-effective CB-binary system can be preselected.

Besides cost-effectiveness, environmental factors should also be taken into account upon developing electroactive composites that would be produced in large quantities. Given the current climate crisis due to greenhouse gas emissions [33], the much higher CO_2 emissions of MWNCT (1–3 order of magnitude higher than for CB [13,14]) should be seriously taken into consideration.

3.4. Final remarks

Compared to the other TC systems shown in Fig. 10, the polyketone-Diels-Alder TCs prepared in this work have rather low resistivities. Remarkably, they exhibit these low resistivity values while having relatively low TFCs, suggesting efficient percolation. This supports the existing evidence that grafted-polyketones interact with carbonaceous fillers such as MWCNT (due to aromatic interactions between the pyrrole moieties and the graphene-like surfaces) [31]. Naturally, the relatively low filler loads are responsible for the low costs, given that the conductive fillers are the components with the highest impact on the price (as seen in Fig. 9). As a result, even though the polyketone-Diels-Alder system has additional formulation costs, intrinsic to its dual responsiveness (furan and maleimide components), the system has a competitive cost compared to other reported TCs. This makes the TCs prepared here quite cost-effective. Their best cost-performance formulations are indeed placed near the desirable

bottom left corner of the graph on Fig. 10. The system also shows a curve with positive slope, which makes a good difference between the cost-performance of the binary boundaries, with the CB-binary composite being 2 times less resistive and 3 times cheaper than its MWCNT-binary counterpart. The cost-effectiveness of the prepared composites, along with the ease of grafting polyketones with a wide variety of moieties [4,34,35], makes grafted polyketones an attractive approach to economically and easily explore conductive composites with diverse electroactive functionalities.

It is worth mentioning that this work focuses specifically on the performance of MWCNT and CB fillers in terms of their conductivity and capability to induce an electroactive response in polymer composites. However, other aspects, such as the effect of these fillers in the mechanical properties, are also part of how well the composites perform. In this work, the mechanical properties were briefly explored by rheology while studying the thermomechanical profiles of the prepared composites, and no important difference were found between formulations with different MWCNT/CB ratio (shown and discussed in Section 3.1). However, this might not be case for other kind of mechanical tests such as tensile tests, three point ending, and impact tests which could be considered in future work. This work focused on MWCNT and CB fillers since they both have been widely used in conductive polymer composites due to their attractive features. In short the general trend is: MWCNT produce very conductive composites, but they are expensive; while CB is very cheap, but tends to result in less conductive materials. However, although these two carbonaceous fillers and their TCs are very popular, it is worth noting that they are not the only good options for preparing conductive composites. Other options include metals, graphene, and carbon fibers, and they all have their own ranges of price, conductivity, percolation thresholds, aspect-ratios, and other characteristics that influence the performance or the polymer composites.

4. Conclusions

The polyketone-Diels-Alder MWCNT-CB TCs prepared in this work show good self-healing and shape memory electroactive responses. They also have low resistivity and low cost compared to other conductive MWCNT-CB TC systems reported in the literature. Contrarily to the general trend, the TCs prepared here show lower resistivity for the formulations with lower MWCNT/CB ratios. This implies that in this system, compared to MWCNT, CB fillers have a better balance between the filler-filler and filler-polymer interactions, which results in well dispersed and percolated CB aggregates. Consequently, the CB-rich composites have better resistive heating, self-healing and shape memory capabilities. Evidently, as CB is considerably cheaper than MWCNT, these formulations with the best electroactive performance were also the most economic. However, this clear and straightforward cost-effectiveness is not often the case for other electroactive MWCNT-CB TC systems found in the literature. When a broader picture is taken into account, it is far than clear if one of these carbonaceous fillers (or a ratio between them) grants more cost-effective products. The answer seems to be highly dependent on each specific polymer composite system and its application.

Funding

CRediT authorship contribution statement

Felipe Orozco: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Alex Salvatore:** Conceptualization, Investigation, Writing – review & editing. **Anchista Sakulmankongsuk:** Investigation, Writing – review & editing. **Diego Ribas Gomes:** Methodology, Investigation, Writing – review & editing. **Yutao Pei:** Writing – review & editing. **Esteban Araya-Hermosilla:** Investigation, Writing – review & editing. **Andrea Pucci:** Conceptualization, Writing – review & editing, Supervision. **Ignacio Moreno-Villoslada:** Writing – review & editing. **Francesco Picchioni:** Conceptualization, Writing – review & editing, Supervision. **Ranjita K. Bose:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2022.125365.

References

[1] Q. Peng, H. Wei, Y. Qin, et al., Shape-memory polymer nanocomposites with a 3D conductive network for bidirectional actuation and locomotion application, Nanoscale Royal Society of Chemistry 8 (42) (2016) 18042–18049.

[2] B. Willocq, R.K. Bose, F. Khelifa, et al., Healing by the Joule effect of electrically conductive poly(ester-urethane)/carbon nanotube nanocomposites, J Mater Chem A Royal Society of Chemistry 4 (11) (2016) 4089–4097.

[3] Y. Wei, R. Huang, P. Dong, et al., Preparation of polylactide/poly(ether)urethane blends with excellent electro-actuated shape memory via incorporating carbon black and carbon nanotubes hybrids fillers, Chin. J. Polym. Sci. 36 (10) (2018) 1175–1186.

[4] G.M.R. Lima, F. Orozco, F. Picchioni, et al., Electrically self-healing thermoset MWCNTs composites based on diels-alder and hydrogen bonds, Polymers 11 (2019) 1885.

[5] F. Orozco, M. Kaveh, D.S. Santosa, et al., Electroactive self-healing shape memory polymer composites based on Diels, – Alder Chemistry 3 (2021) 6146–6156.

[6] Y. Du, D. Li, L. Liu, et al., Recent achievements of self-healing graphene/polymer composites, Polymers 10 (2) (2018) 114.

[7] R. Lotfi Mayan Sofla, M. Rezaei, A. Babaie, et al., Preparation of electroactive shape memory polyurethane/graphene nanocomposites and investigation of relationship between rheology, morphology and electrical properties, Composites Part B 175 (2019), 107090.

[8] X. Wang, J. Lan, P. Wu, et al., Liquid metal based electrical driven shape memory polymers, Polymer 212 (2021), 123174.

[9] R. Rothon, Fillers for Polymer Applications, Springer, Cham, 2017.

[10] A. Dorigato, M. Brugnara, A. Pegoretti, Synergistic effects of carbon black and carbon nanotubes on the electrical resistivity of poly(butylene-terephthalate) nanocomposites, Adv. Polym. Technol. 37 (6) (2018) 1744–1754.

[11] M. Qu, F. Nilsson, D.W. Schubert, Novel definition of the synergistic effect between carbon nanotubes and carbon black for electrical conductivity, Nanotechnology 30 (24) (2019), 245703.

[12] P.C. Ma, M.Y. Liu, H. Zhang, et al., Enhanced electrical conductivity of nanocomposites containing hybrid fillers of carbon nanotubes and carbon black, ACS Appl. Mater. Interfaces 1 (5) (2009) 1090–1096.

[13] Y. Abdallas Chikri, W. Wetzels, Decarbonisation Options Fro the Dutch Carbon Black Industry, PBL Netherlands Environmental Assessment Agency, The Hague, 2020.

[14] S. Temizel, S. Fan, A.L. Hicks, Global scale life cycle environmental impacts of single- and multi-walled carbon nanotube synthesis processes, Int. J. Life Cycle Assess. 26 (2021) 656–672.

[15] J. Ju, T. Kuang, X. Ke, et al., Lightweight multifunctional polypropylene/carbon nanotubes/carbon black nanocomposite foams with segregated structure, ultralow percolation threshold and enhanced electromagnetic interference shielding performance, Compos. Sci. Technol. 193 (2020), 108116.

[16] D. Wu, Q. Lv, S. Feng, et al., Polylactide composite foams containing carbon nanotubes and carbon black: synergistic effect of filler on electrical conductivity, Carbon 95 (2015) 380–387.

[17] Y. Nakaramontri, S. Pichaiyut, S. Wisunthorn, et al., Hybrid carbon nanotubes and conductive carbon black in natural rubber composites to enhance electrical conductivity by reducing gaps separating carbon nanotube encapsulates, Eur. Polym. J. 90 (2017) 467–484.

[18] R. Socher, B. Krause, S. Hermasch, et al., Electrical and thermal properties of polyamide 12 composites with hybrid fillers systems of multiwalled carbon nanotubes and carbon black, Compos. Sci. Technol. 71 (8) (2011) 1053–1059.

[19] D. Ren, Y. Chen, S. Yang, et al., Fast and efficient electric-triggered self-healing shape memory of CNTs@rGO enhanced PCLPLA copolymer, Macromol. Chem. Phys. 220 (21) (2019) 2–9.

[20] D. Ren, Y. Chen, H. Li, et al., High-efficiency dual-responsive shape memory assisted self-healing of carbon nanotubes enhanced polycaprolactone/thermoplastic polyurethane composites, Colloids Surfaces A Physicochem Eng 580 (2019), 123731.

[21] M. Sabzi, M. Babaahmadi, N. Samadi, et al., Graphene network enabled high speed electrical actuation of shape memory nanocomposite based on poly(vinyl acetate), Polym. Int. 66 (5) (2017) 665–671.

[22] G. Scalet, Two-way and multiple-way shape memory polymers for soft robotics: an overview, Actuators 9 (2020) 10.

[23] S. Terryn, J. Langenbach, E. Roels, et al., A review on self-healing polymers for soft robotics, Mater. Today 47 (2021) 187–205.

[24] E. Drent, J. Keijsper, Polyketone Polymer Preparation with Tetra Alkyl Bis Phosphine Ligand and Hydrogen, 1993, 5225523.

[25] Y. Zhang, A.A. Broekhuis, F. Picchioni, Thermally self-healing polymeric materials: the next step to recycling thermoset polymers? Macromolecules 42 (2009) 1906–1912.

[26] F. Orozco, J. Li, U. Ezekiel, et al., Diels-Alder-based thermo-reversibly crosslinked polymers: interplay of crosslinking density, network mobility, kinetics and stereoisomerism, Eur Polym J Elsevier 135 (2020), 109882.

[27] R. Araya-hermosilla, A. Pucci, P. Raffa, et al., Electrically-responsive reversible polyketone/MWCNT network through diels-alder chemistry, Polymers 10 (2018) 1076.

[28] S. Olszewski, Electrodynamics of the joule-lenz law applied to the energy emission done by a free electron or harmonically-oscillating microparticle, J. Quant. Inf. Sci. 8 (2018) 121–130.

[29] J.M. Vega, A.M. Grande, S Van Der Zwaag, et al., On the role of free carboxylic groups and cluster conformation on the surface scratch healing behaviour of ionomers, Eur. Polym. J. 57 (2014) 121–126.

[30] F. Orozco, Z. Niyazov, T. Garnier, et al., Maleimide self-reaction in furan/maleimide-based reversibly crosslinked polyketones: processing limitation or potential advantage? Molecules 26 (8) (2021) 2230.

[31] R. Araya-hermosilla, A. Pucci, E. Araya-Hermosilla, et al., An easy synthetic way to exfoliate and stabilize MWCNTs in a thermoplastic pyrrole-containing matrix assisted by hydrogen bonds, RSC Adv. 6 (2016) 85829–85837.

[32] L. Sun, J.Y.O. Reilly, C. Tien, et al., Preparation of electrically conductive polystyrene/carbon nanofiber nanocomposite films, J Chem Educ 85 (8) (2008) 1105–1107.

[33] IPCC, Climate Change 2021: the Physical Sciences Bases, Cambridge University Press, 2021.

[34] Y. Zhang, A.A. Broekhuis, F. Picchioni, Aqueous polymer emulsions by chemical modifications of thermosetting alternating polyketones, J. Appl. Polym. Sci. 106 (5) (2007) 3237–3247.

[35] E. Araya-hermosilla, M. Roscam, J. Catalán-toledo, et al., Synthesis of tuneable amphiphilic-modi fi ed polyketone polymers , their role in the photooxidation of 1,3,5-triphenylformazan con fi ned in polymeric nanoparticles, Polymer 167 (2019) 215–223.

[36] K.K. Kar, J.K. Pandey, S. Rana, Handbook of Polymer Nanocomposites. Processing, Performance and Application, Springer, 2015.

[37] A. Lekawa-Raus, J. Patmore, L. Kurzepa, et al., Electrical properties of carbon nanotube based fibers and their future use in electrical wiring, Adv. Funct. Mater. 24 (24) (2014) 3661–3682.