

# Thermo-oxidative aging of high-density polyethylene reinforced with multiwalled carbon nanotubes

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## Abstract

The purpose of this study was to investigate the influence of aging on the properties of high-density polyethylene (HDPE) reinforced with multi-wall carbon nanotubes (MWCNTs). Nanocomposites were prepared with nanotubes at 0, 1, 3, and 5 wt%. The long-term durability of the prepared materials was evaluated by thermo-oxidative aging test. Test bodies were aged at 110°C for up to 10 weeks. The nanocomposites were characterized by differential scanning calorimetry, thermogravimetric analysis (TGA), <sup>13</sup>C-NMR, elongation at break, and transmission electron microscopy. The aging mainly occurred on the surface of the samples and the neat HDPE showed a strong yellowing after the aging. A strong reduction in elongation at break was seen. For neat HDPE, the elongation at break was reduced from roughly 1400–25%. When HDPE was reinforced with the nanotubes, the reduction was less dramatic.

## KEYWORDS

aging, fullerenes, graphene, nanostructured polymers, nanotubes

## 1 | INTRODUCTION

Nanoscale hollow graphite cylinders (carbon nanotubes) are promising fillers in conventional polymers. Carbon nanotubes (CNTs) have high-tensile strength, good electrical conductivity, and a high-aspect ratio.<sup>1–3</sup> This makes them attractive in applications such as anti-static devices, capacitors, sensors, and materials for electromagnetic interference shielding. By adding CNTs to a polymer matrix, characteristics such as electrical and mechanical properties can be improved and this has received a great deal of attention.<sup>4–10</sup>

The effectiveness of the polymer composites depends on the durability in the environments in which they are used. The degradation of the polymers and their composites in outdoor applications reflects in structural and

chemical changes, which result in a significant decrease in the mechanical performance and the service lifetime. The degradation and the durability are therefore an important area in the polymer research. It is well known that CNTs can improve the thermal properties of polymer composites as it increases the oxidative thermal stability of the polymers. The CNTs also decrease the rate of photooxidation of the polymer composites by interacting with oxygen molecules. Several authors have studied thermal properties by thermogravimetric analysis (TGA). For example, Duadagno reinforced syndiotactic polypropylene (PP) with CNTs.<sup>11</sup> The neat PP had a degradation temperature of 340–440°C and when the CNTs were added to the matrix, the degradation temperatures became higher, between 420 and 480°C. Barus et al.

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added MWCNTs to low-density polyethylene and the thermal stability was studied by TGA in atmospheres of both nitrogen or air.<sup>5</sup> In an atmosphere of nitrogen, a relatively modestly increased thermal stability was seen, whereas in air, a very strong stabilizing effect of the CNTs was found. Several other studies have investigated the thermal stability of various polymers reinforced with CNTs using TGA<sup>12–15</sup>. The addition of 0.5 wt% CNTs to polyamide 6 increased the thermal stability of the resulted composites.<sup>16</sup> The changes in crystallization and melting temperatures were also noticed. Similar results have been achieved when CNTs were added to other thermoplastic polymers. Naddeo et al. reinforced PP with MWCNTs and exposed the nanocomposites to accelerated weathering.<sup>17</sup> The MWCNTs had a strong stabilizing photooxidative effect against UV-radiation.

While several tests have been carried out using TGA in order to evaluate the thermal properties, the effect of the addition of CNTs to the polymer matrix on the long-term thermal stability requires further study. The rationale behind the present work was to investigate the thermal stability behavior of the CNT-based polyethylene nanocomposites on aging along with their mechanical, thermal, and morphological properties. Accelerated aging tests are important for determination of how environmental conditions such as temperature, humidity, UV radiation, and other factors will affect the lifespan of the product. In this study, we aged polyethylene reinforced with CNTs up to 5 wt%.

CNT-based polyethylene composites were prepared by melt compounding. Test bodies were aged by thermo-oxidation for 10 weeks at 110°C, and subsequently characterized by thermal, mechanical tests and by <sup>13</sup>C-NMR. We believe that this study lays the foundation for investigation of the thermo-oxidative aging of CNT/PE composites and that subsequent work could reveal the long-term stability of these composites.

## 2 | MATERIALS AND METHODS

### 2.1 | Materials

Neat high-density polyethylene (HDPE) (Purell GA7760) of injection molding grade with a density of 963 kg/m<sup>3</sup> was supplied by LyondellBasell. The supplier recommended processing temperatures between 190°C and 230°C. Multi-wall carbon nanotubes (MWCNTs) were obtained as a master batch. The master batch (PLASTICYL HDPE1501) is based on HDPE with Nanocyl's short tangled MWCNTs (NC7000) at 15 wt%. The polymer had a melt temperature of 135°C and the density was 0.977 g/L. PLASTICYL HDPE1501 was chosen due to its high-melt flow, which makes it suitable for injection molding.

**TABLE 1** Composition of the compounded samples

Sample	wt% Masterbatch	wt% HDPE	wt% CNT
0 wt% CNT	0	100	0
1 wt% CNT	6.67	93.3	1
3 wt% CNT	20	80	3
5 wt% CNT	33.3	66.7	5

Abbreviations: CNTs, carbon nanotubes; HDPE, high-density polyethylene.

### 2.2 | Preparation of nanocomposites

Composites were produced by blending of Purell GA7760 and PLASTICYL HDPE1501 at known ratios using DSM Xplore Micro 15 cc Twin Screw Compounder. The weight of the nanotubes in the composites varied between 1 and 5 wt% (1, 3, and 5 wt%) and the compounding temperature was 190°C, see Table 1. The blending time in the compounder was 5 min. Neat polyethylene (Purell GA7760) was processed with the same processing parameters for reference.

The blended mixture was then injection molded using an Xplore 10 cc Injection Molding Machine. The composite was injected in a two-cavity mold, producing one dumb-bell shaped specimen for tensile testing and one block structure. The block, the sprue, the runner, and the gate were used to perform other tests mentioned under characterization.

### 2.3 | Accelerated aging

The samples were exposed to thermo-oxidative aging. The dumb-bell shaped test bodies for tensile testing were placed in an oven (Termaks TS 8056) and aged at 110°C for 10 weeks and in an atmosphere of air. Samples were taken from the oven every second week and tested for elongation at break.

### 2.4 | Characterization

The composites were analyzed for mechanical, thermal, chemical, and morphological properties. This section covers the test design, the test apparatus, methods of gathering data, and type of control.

Samples were characterized by Fourier transform infrared spectroscopy (FTIR). The infrared spectrum of absorption of a composite sample was obtained using a Nicolet 6700 FTIR spectrometer from Thermo Fisher Scientific. FTIR spectra were acquired in a range from 4000 to 600 cm<sup>-1</sup> with 64 scans and 4 cm<sup>-1</sup> band resolution.

Samples were also characterized by carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR). For the NMR experiments,

the samples were dissolved at 120–130°C in a 1,2,4-trichlorobenzene/benzene- $d_6$  mixture. The  $^{13}\text{C}$ -NMR spectra were measured at 110°C at 200 MHz using a Bruker AVANCE-III 800 spectrometer with a standard DUAL probe from Bruker. The spectra were acquired with NOE using an excitation pulse of 70° and a 2 s relaxation delay. The number of transients acquired was between 256 and 4096.

Dumb-bell shaped specimens, 75 mm long, were prepared by injection molding according to ISO 527 for tensile testing. The tests were carried out according to the same standard using a Tinius Olsen H10KT universal testing machine and QMat software. The force and the extension were measured using a 5 kN load cell and a mechanical extensometer. The test speed was 10 mm/min and the elongation at break was recorded. Testing was done at room temperature. A minimum of five specimens were tested for each batch and the average was noted.

Differential scanning calorimetry (DSC) analysis was carried out using a Q series DSC instrument (Q2000; TA Instruments, supplied by Waters LLC) to investigate the thermal properties of the composites, such as the degree of crystallinity and heat enthalpy. A sample weighing approximately 10 mg was sealed in an aluminum pan and the pan was heated from 20 to 200°C at a heating rate of 10°C/min. The sample was cooled to 20°C and heated again to 200°C. The analysis was performed in a nitrogen atmosphere. The measurements were performed at least twice for each sample and the transitions were recorded from the second heating.

Oxidation induction time (OIT) tests were conducted by heating an aged sample weighing approximately 10 mg from 30°C to 200°C with a heating rate of 20°C/min. The nitrogen gas was switched to oxygen when the temperature reached 200°C. The measurements were performed at least three times for each sample.

The thermal stability of the samples was investigated using thermogravimetric analysis using a TGA Q500 from TA Instruments (supplied by Waters LLC). A sample weighing approximately 20 mg was heated from 30°C to 600°C in a platinum pan at a heating rate of 10°C/min in an atmosphere of air. The tests were performed at least twice for each sample.

Transmission electron microscopy (TEM) micrographs were prepared by an external company, using a 100 kV transmission electron microscope from Zeiss. Unaged samples at 1, 3, and 5 wt% were characterized.

### 3 | RESULTS

The mechanical and thermal properties of CNT/HDPE nanocomposites have been published from several



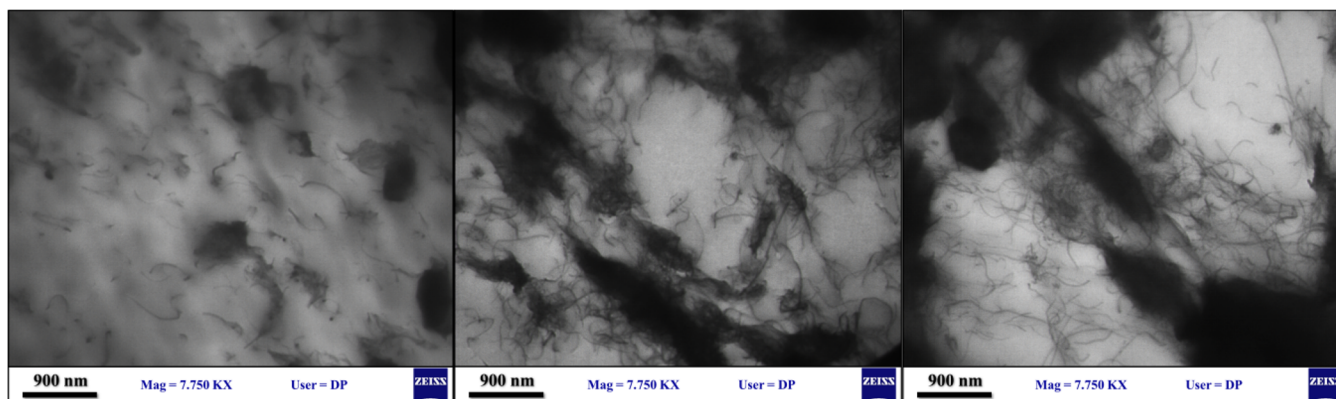
**FIGURE 1** Test body before aging (left) and after 10 weeks of aging (right) [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

previous studies.<sup>18–20</sup> This work deals with the behavior of the composites on thermo-oxidative aging. The change in molecular weight, strain during elongation, oxidation, and thermal stability were studied in order to establish the long-term stability of the composites. The nanocomposites prepared were first characterized by photography's and the result is shown in Figure 1.

The test bodies showed a strong yellowing after 10 weeks of aging. Cracks are visible on the surface. The nanocomposites were also characterized by TEM and the result is shown in Figure 2.

For CNTs at 1 wt%, the nanotubes were relatively well dispersed in the polymer matrix but some agglomerations could also be seen. The nanotubes were randomly oriented and curved nanotubes could be observed. At 3 and 5 wt%, agglomerations could be seen. The lack of sufficient dispersion is a general problem when preparing nanocomposites with CNTs.<sup>21</sup> Good dispersion is a prerequisite for obtaining good mechanical and thermal properties. 3 wt% CNTs is generally considered as a high-filler load to disperse and some agglomerations are expected. It is possible to improve the dispersion of the CNTs by surface modifications.<sup>22</sup>

The thermal stability of the nanocomposites prepared was first determined by TGA of neat polyethylene and HDPE/CNT composites in a nitrogen atmosphere. The results are given in Table 2. It was clear that the thermal decomposition temperatures increased considerably on addition of CNT to PE, which directly indicates improvement in thermal stability. The HDPE decomposition was studied using the onset temperatures ( $T_{10}$  and  $T_{50}$ ) as shown in Table 2. For the unaged samples, a strong increase thermal stability was seen. For example, increasing the CNT loading from 0 to 5 wt% increased  $T_{10}$  with almost 100°C. Also the maximum degradation was strongly affected, and it increased from 362°C (0 wt%) to 471°C (5 wt% CNT). Aging the samples for 10 weeks slightly decreased the thermal stability but the difference was in most cases relatively small. The stabilization effect



**FIGURE 2** TEM micrographs of HDPE with CNTs at 1 wt% (left), 3 wt% (middle), and 5 wt% (right). CNTs, carbon nanotubes; HDPE, high-density polyethylene; TEM, transmission electron microscopy [Color figure can be viewed at wileyonlinelibrary.com]

Sample	T <sub>10</sub> (°C)	T <sub>50</sub> (°C)	Maximum degradation (°C)
0 wt% CNT, unaged	338.17 (16.2)	372.76 (18.6)	362.20 (10.9)
1 wt% CNT, unaged	346.94 (3.7)	438.3 (7.1)	460.43 (0.2)
3 wt% CNT, unaged	420.63 (4.9)	457.05 (3.9)	471.24 (3.2)
5 wt% CNT, unaged	435.06 (3.7)	463.3 (0.7)	470.89 (0.0)
0 wt% CNT, aged	330.52 (1.7)	362.42 (22.5)	349.73 (6.9)
1 wt% CNT, aged	347.66 (2.7)	423.55 (9.5)	431.47 (14.56)
3 wt% CNT, aged	396.00 (3.4)	457.54 (10.0)	470.84 (4.5)
5 wt% CNT, aged	421.31 (1.3)	463.89 (10.1)	469.58 (10.6)

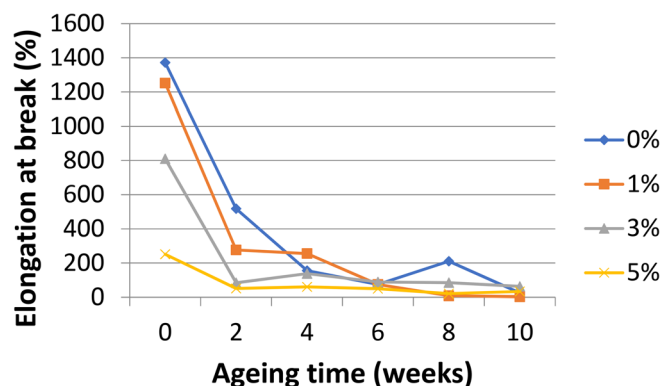
**TABLE 2** Thermal decomposition of HDPE and its composites in an atmosphere of air measured by TGA. The aged samples were aged for 10 weeks. The SD is given within brackets

Abbreviation: CNTs, carbon nanotubes.

of CNT can be explained by the barrier effect of the CNTs and their aggregates, which would temporarily hinder the diffusion of the degradation products from the bulk of the polymer onto the gas phase. An analogous behavior of PP/CNT composites has been reported earlier.<sup>23</sup> It is also known that the barrier can prevent from oxygen action.<sup>7</sup> The barrier effect could also be introduced to increase interfacial interactions between CNTs and PE by functionalizing either CNT or PE, which leads to an increase in the activation energy of degradation.<sup>24,25</sup>

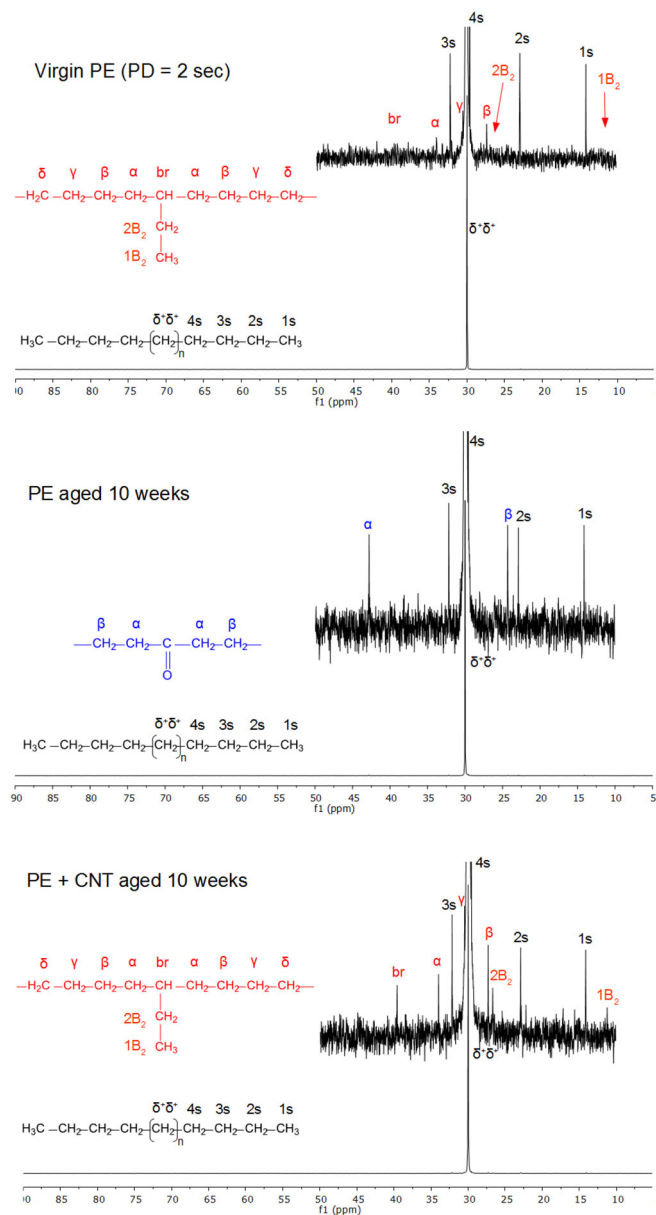
The samples were characterized by elongation at break and the results are shown in Figure 3. The neat HDPE was a ductile material with an elongation of almost 1400%. As neat HDPE ages, the elongation is quickly reduced. After 2 weeks of aging, the elongation had already dropped to almost a third of its original value. After 10 weeks of aging, the elongation at break had decreased to about 25%. The degradation mainly takes place on the surface of the test bodies. This may induce cracks on the surface, which can serve as indication of fracture during tensile testing, explaining the strong reduction in elongation at break.

As HDPE is reinforced by CNTs, the elongation was clearly reduced. At 1 wt% loading, the elongation was still



**FIGURE 3** Elongation as a function of the aging time [Color figure can be viewed at wileyonlinelibrary.com]

relatively high but at 3 wt% it was reduced to almost a third of its initial value. At 5 wt% CNT loading, the elongation was reduced to 250%. When the nanocomposite with 1 wt% CNTs was aged, it had a similar behavior to that of neat HDPE. After 2 weeks of aging, there was already a clear reduction in elongation at break. At higher loadings of the CNTs, the reduction in elongation was not quite so dramatic. At 5 wt% CNTs, the elongation went from 250 to 35%.



**FIGURE 4**  $^{13}\text{C}$ -NMR spectra of neat HDPE (upper frame), HDPE aged for 10 weeks (middle frame) and HDPE + 5 wt% HDPE, aged for 10 weeks (lower frame). CNTs, carbon nanotubes; HDPE, high-density polyethylene [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

In summary, this rather harsh aging procedure clearly affected the elongation at break. The aging period of 10 weeks is estimated to correspond to roughly 100 years of usage at room temperature assuming, that an increase of  $10^\circ\text{C}$  corresponds to a doubling of the reaction rate of the degradation reaction. This model is commonly used and is often referred to as the “10-degree rule.”<sup>26</sup> This should of course only be seen as a rough indication.

Samples were also characterized by  $^{13}\text{C}$ -NMR, and the spectra are shown in Figure 4. The assignments were done using the literature.<sup>27</sup> Carbons adjacent to

**TABLE 3** Assignments of the chemical shifts. For further explanation of the abbreviations, see Figure 3

Chemical shift	Assignment
Shifts for aged HDPE:	
42.8	$\alpha$
24.3	$\beta$
Shifts for HDPE + CNT, 10 weeks of aging:	
39.6	br
34.0	$\alpha$
27.3	$\beta$
26.7	$2B_2$
11.2	$2B_1$

Abbreviations: CNTs, carbon nanotubes; HDPE, high-density polyethylene.

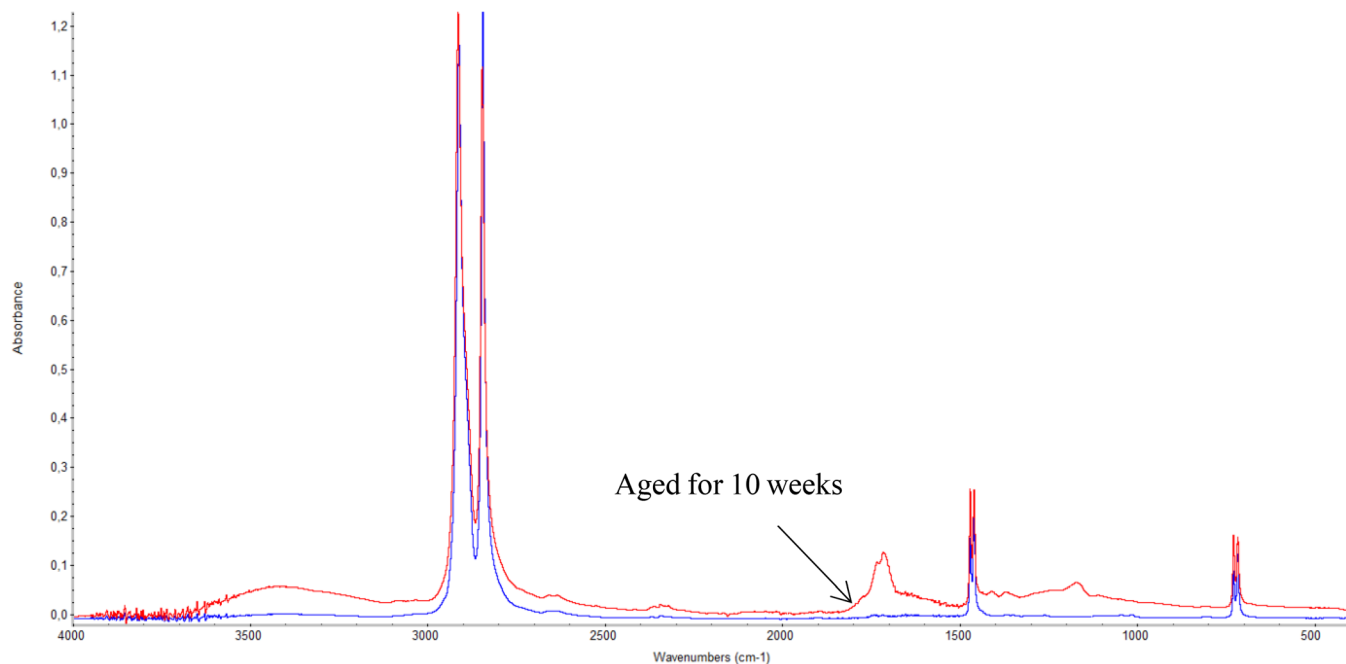
**TABLE 4**  $^{13}\text{C}$ -NMR results showing change in number average molecular weight ( $M_n$ ), ethyl groups per 1,000 carbon atoms (et/1,000 C), and carbonyl groups per 1,000 carbon atoms ( $\text{C}=\text{O}/1,000\text{ C}$ )

Sample	$M_n$	Et/1000 C	$\text{C}=\text{O}/1000\text{ C}$
Virgin HDPE	12,869	0.40	n.d.
HDPE, 10 weeks of aging	12,811	n.d.	2.57
HDPE + 5 wt% CNT, 10 weeks of aging	8600	1.09	n.d.

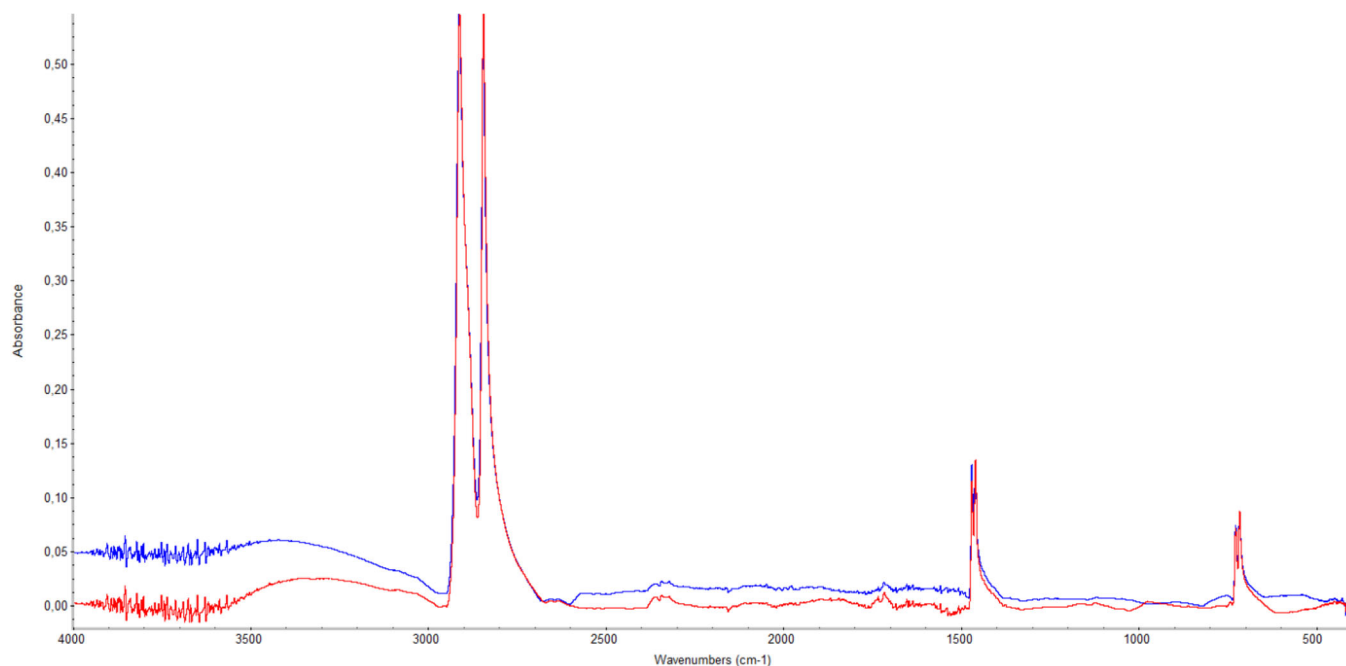
Abbreviations: CNTs, carbon nanotubes; HDPE, high-density polyethylene; n.d., not determined.

the carbonyl group could be seen. Carbons in alpha position relative to the carbonyl group could be seen at 42.8 ppm and carbons in beta position could be seen at 24.3 ppm. Signs of ethyl group branching could also be seen at 39.6 ppm. The results are given in Table 3. The unaged HDPE did not show any signs of oxidation. There was some evidence of ethyl branching, but longer NMR runs would be required to accurately quantify the branching. HDPE aged for 10 weeks did; however, show clear signs of oxidation. The molecular weights of the aged and unaged HDPE did not differ significantly (Table 4). It is interesting to note that the nanocomposite did not show any signs of oxidation. Some polymer degradation probably occurred on the surface of the test bodies, causing the reduction in elongation at break, but this was not seen in the NMR spectra—since it is a bulk method.

Even though the sample with 5 wt% CNTs did not show any signs of oxidation, it had a lower molecular weight. This would have to be confirmed by longer NMR runs; however. It is possible that the CNTs protected the polymer matrix from oxidation and that the



**FIGURE 5** FTIR spectra of neat HDPE samples that were aged for 2 weeks (blue) and for 10 weeks (red). FTIR, Fourier transform infrared spectroscopy; HDPE, high-density polyethylene [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 6** FTIR spectra of CNT-reinforced (5 wt%) HDPE samples that were aged for 2 weeks (red) and for 10 weeks (blue). CNTs, carbon nanotubes; FTIR, Fourier transform infrared spectroscopy; HDPE, high-density polyethylene [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

polymer underwent polymer degradation by some other mechanism.

The samples were also characterized by FTIR. Polyethylene oxidizes to give hydroperoxide, ketone, carboxylic acid groups, and other products which can be seen as

–OH species (with absorption at around  $3400\text{ cm}^{-1}$ ) and carbonyl species (with absorption at  $1780\text{--}1700\text{ cm}^{-1}$ ). It was not possible to establish the exact nature of oxidation and of the contributions from each of these species. However, the contributions of –OH species at  $3400\text{ cm}^{-1}$  and

**TABLE 5** Melting temperatures, fusion enthalpies, crystallization temperatures, and oxidation induction times of aged HDPE/CNT composites

Accelerated aging	Reinforcement CNTs (wt%)	Melting temperature, $T_m$ (°C)	Enthalpy from melting curve, $\Delta H_m$ (J/g)	Crystallization temperature, $T_c$ (°C)	Oxidation induction time (OIT; min)
Aged 2 weeks	0	132.08 ± 0.67	212.6 ± 9.7	120.45 ± 0.22	30.29
	1	132.68 ± 0.74	217.1 ± 2.8	122.64 ± 0.07	30.84
	3	132.32 ± 0.30	201.7 ± 2.6	122.71 ± 0.42	29.10
	5	132.25 ± 0.19	193.9 ± 1.9	122.28 ± 0.24	30.30
Aged 4 weeks	0	131.39 ± 0.22	208.6 ± 13.7	119.51 ± 1.99	29.25
	1	132.91 ± 0.21	217.27 ± 0.6	122.48 ± 0.16	28.29
	3	132.28 ± 0.21	207.2 ± 2.0	122.80 ± 0.20	28.39
	5	132.17 ± 0.12	195.8 ± 1.7	122.26 ± 0.16	28.51
Aged 6 weeks	0	132.05 ± 0.25	220.6 ± 3.6	120.58 ± 0.03	28.19
	1	132.36 ± 0.53	215.8 ± 2.2	122.59 ± 0.06	28.43
	3	131.89 ± 0.34	204.6 ± 3.5	122.72 ± 0.17	28.95
	5	132.32 ± 0.10	194.2 ± 0.1	122.09 ± 0.15	29.66
Aged 8 weeks	0	130.89 ± 1.24	192.4 ± 4.9	117.63 ± 0.55	27.19
	1	132.78 ± 0.61	212.4 ± 6.7	121.19 ± 0.65	27.52
	3	132.35 ± 0.03	204.1 ± 2.6	122.52 ± 0.09	28.05
	5	132.52 ± 0.15	189.9 ± 0.0	121.60 ± 0.38	28.48
Aged 10 weeks	0	131.32 ± 0.46	202.7 ± 6.3	117.75 ± 0.92	27.24
	1	131.09 ± 1.51	210.1 ± 11.3	120.50 ± 0.44	27.24
	3	131.98 ± 0.10	202.2 ± 0.6	122.00 ± 0.32	27.71
	5	132.52 ± 0.06	195.7 ± 0.2	121.06 ± 0.48	27.95

Abbreviation: CNTs, carbon nanotubes.

carbonyl species at 1718  $\text{cm}^{-1}$  were evident (Figure 5). The results from the FTIR spectra were in line with those from the  $^{13}\text{C}$ -NMR spectra.

The most interesting results from the FTIR were that the addition of 5 wt% CNTs resulted in disappearance of peaks from -OH and carbonyl species (Figure 6). These results were further confirmed using differential scanning calorimetry.

The melting temperatures, enthalpies, and crystallization temperatures of the aged nanocomposites are given in Table 5. The inclusion of CNTs and the aging of the composites had moderate impact on the enthalpy ( $\Delta H_m$ ), and there was no definite correlation between CNT loading and enthalpy. The enthalpy of the reference, unaged polymer was  $218 \pm 4.2$  J/g and it was reduced up to 4% on inclusion of 3 wt% CNTs. The enthalpy was further reduced to 195 J/g with accelerated aging of the composites. The melting temperature of unaged polyethylene was approximately 133°C, and this was not affected either by the inclusion of CNTs or by the aging of the composites. The tendency was similar with crystallization temperature, as shown in the table. The trend adheres to

previous studies.<sup>24</sup> It is interesting to note that the degree of crystallinity of the polymer ( $74.4 \pm 1.4\%$ ) was considerably affected which is in line with the results from FTIR.

The amount of antioxidant available in the polymer is indirectly apparent from the OIT. Antioxidants hinder the polymer chain scission and inhibit the reduction in molecular weight of the polymer. OIT is summarized in Table 5; the results show that the OIT fell by 10%, from 30 to 27 min. The consumption of antioxidants on accelerated aging was obvious, and the polymer was more prone to oxidation after aging. Furthermore, the addition of CNTs did not affect the OIT significantly. This strong evidence of oxidation supports the results from  $^{13}\text{C}$ -NMR and FTIR.

## 4 | CONCLUSIONS

The incentive of adding CNTs to HDPE could be to improve the mechanical properties as well as to improve the electrical conductivity for electrostatic discharge packaging.<sup>28</sup> It is also known that CNTs can modify the

thermal properties, which have mainly been studied with TGA. Thermo-oxidative aging properties of polymer matrix nanocomposites reinforced with CNTs are presently not well studied. The thermal stability of HDPE reinforced with CNTs was therefore characterized by TGA and by aging tests, followed by thermal and mechanical tests.

1. When studying the thermal stability by TGA in an atmosphere of nitrogen, the CNTs had a relatively strong protective effect. For example, the neat HDPE had a maximum degradation temperature of 500°C while the maximum degradation temperature for 5 wt% nanocomposite was 520°C.

2. The unreinforced HDPE was relatively sensitive to aging, in terms of elongation at break. The aging mainly takes place at the surface, which creates cracks that act as stress raisers. Studies using both NMR and FTIR confirmed that the polymer was oxidized.

3. No signs of oxidation could be detected after 10 weeks of aging of the 5 wt% nanocomposite. However, the reinforced HDPE also showed a reduction in elongation at break. The elongation for the nanocomposite with 5 wt% CNTs was reduced from 250 to 35%.

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## REFERENCES

- [1] D. Vairavapandian, P. Vichchulada, M. D. Lay, *Anal. Chim. Acta* **2008**, 626, 119.
- [2] J. Sun, H. Li, L. Feng, Y. Jia, Q. Song, K. Li, *Appl. Surf. Sci.* **2017**, 403, 95.
- [3] I. Gaztelumendi, M. Chapartegui, R. Seddon, S. Flórez, F. Pons, J. and Cinquin, *Compos., Part B* **2017**, 122, 31.
- [4] S. Y. Kim, K. S. Shin, S. H. Lee, K. W. Kim, J. R. Youn, *Fibers Polym.* **2010**, 11, 1018.
- [5] S. Barus, M. Zanetti, P. Bracco, S. Musso, A. Chiodoni, A. Tagliaferro, *Polym. Degrad. Stab.* **2010**, 95, 756.
- [6] K. Prashantha, J. Soulestin, M. F. Lacrampe, M. Claes, G. Dupin, P. Krawczak, *eXPRESS Polymer Letters*, **2008**, 2, 735.
- [7] B. B. Marosfői, A. Szabó, G. Marosi, D. Tabuani, G. Camino, S. Pagliari, *J. Therm. Anal. Calorim.* **2006**, 86, 669.
- [8] K. Mezghani, M. Farooqui, S. Furquan, M. Atieh, *Mater. Lett.* **2011**, 65, 3633.
- [9] E. Logakis, C. Pandis, V. Peoglos, P. Pissis, C. Stergiou, J. Pionteck, P. Pötschke, M. Mičušík, M. Omastová, *J. Polym. Sci., Part B: Polym. Phys.* **2009**, 47, 764.
- [10] P. Pötschke, T. D. Fornes, D. R. Paul, *Polymer* **2002**, 43, 3247.
- [11] L. Guadagno, C. Naddeo, M. Raimondo, G. Gorrasi, V. Vittoria, *Polym. Degrad. Stab.* **2010**, 95, 1614.
- [12] T. Kashiwagi, E. Grulke, J. Hilding, R. Harris, W. Awad, J. Douglas, *Macromol. Rapid Commun.* **2002**, 23, 761.
- [13] M. Nasir, I. Mohammad, H. Asad, S. Shaukat, K. Ahmad Nawaz, *J. Compos. Mater.* **2013**, 48, 1197.
- [14] E. Y. Choi, J. Y. Kim, C. K. Kim, *Polymer* **2015**, 60, 18.
- [15] M. Chipara, J. Cruz, E. R. Vega, J. Alarcon, T. Mion, D. M. Chipara, E. Ibrahim, S. C. Tidrow, D. Hui, *J. Nanomater.* **2012**, 2012, 6.
- [16] N. Mahmood, M. Islam, A. Hameed, S. Saeed, *Polymer* **2013**, 5, 1380.
- [17] C. Naddeo, L. Vertuccio, G. Barra, L. Guadagno, *Materials* **2017**, 10, 943.
- [18] S. Kanagaraj, F. R. Varanda, T. V. Zhil'tsova, M. S. A. Oliveira, J. A. O. Simões, *Compos. Sci. Technol.* **2007**, 67, 3071.
- [19] M. Trujillo, M. L. Arnal, A. J. Müller, E. Laredo, S. Bredeau, D. Bonduel, P. Dubois, *Macromolecules* **2007**, 40, 6268.
- [20] W. Tang, M. H. Santare, S. G. Advani, *Carbon* **2003**, 41, 2779.
- [21] G. Galtieri, A. Visco, D. Iannazzo, A. Pistone, V. Brancato, *J. Compos. Mater.* **2017**, 51, 1797.
- [22] S. W. Kim, T. Kim, Y. S. Kim, H. S. Choi, H. J. Lim, S. J. Yang, C. R. Park, *Carbon* **2012**, 50, 3.
- [23] X. Wen, Y. Wang, J. Gong, J. Liu, N. Tian, Y. Wang, Z. Jiang, J. Qiu, T. Tang, *Polym. Degrad. Stab.* **2012**, 97, 793.
- [24] D. Bikiaris, A. Vassiliou, K. Chrissafis, K. M. Paraskevopoulos, A. Jannakoudakis, A. Docoslis, *Polym. Degrad. Stab.* **2008**, 93, 952.
- [25] A. A. Kovalchuk, V. G. Shevchenko, A. N. Shchegolikhin, P. M. Nedorezova, A. N. Klyamkina, A. M. Aladyshev, *J. Mater. Sci.* **2008**, 43, 7132.
- [26] ASTM F 1980, Standard Guide for Accelerated Ageing of Sterile Medical Device Packages.
- [27] Randall, J. C., Zoepfl, F. J. and Silverman, J.: A <sup>13</sup>C NMR study of radiation-induced structural changes in polyethylene. In *NMR and Macromolecules*; ACS Symposium Series 247; American Chemical Society, **1984**; Vol. 247; pp 245–267.
- [28] D. Rousseaux, O. Lhost and P. Lodefier, presented at 14th International Conference on Electronic Packaging Technology, Dalian, 11-14 August 2013, p. 386. <https://doi.org/10.1109/ICEPT.2013.6756495>.

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