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The thermo-oxidative durability of polyethylene reinforced with wood-based fibres

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ABSTRACT

Aiming at better understanding the ageing behaviour of cellulose composites, the accelerated thermo-oxidative ageing of polyethylene reinforced with two types of wood-based cellulose fibres was studied. Materials were prepared by extrusion mixing of either un-stabilized or stabilized polyethylene reinforced with 5 and 20 vol % cellulose content. The materials were extruded into strips and then aged at 90°C in circulating air. The effect of accelerated ageing up to 31 days was assessed by oxidation induction time and mechanical properties in tension. The results indicated that the added cellulose fibres did not increase the degradation of the composites during this ageing. Reinforcement with 20 % cellulose fibre having a 28 % lignin content together with 0.005 % Irganox 1010 antioxidant resulted in a remarkable improvement in the resistance against accelerated thermo-oxidation, compared to the pure polyethylene with added antioxidant. The findings of increased lifetime of LDPE by addition of wood-based reinforcement is of great interest, since the durability aspect is crucial to understand and predict before usage in commercial applications and especially as structural composites.

1. Introduction

Substantial research efforts have been devoted to the reinforcement of thermoplastics with cellulosic fibres, such as with wood-based fibres. The interest in using cellulosic reinforcement has been mainly based on expectations of improved mechanical performance with a renewable reinforcement at a favourable cost [1,2]. A rather broad span of potential or intended applications can be found in the literature for such composite materials, ranging from relatively short-term packaging applications to longer term applications in automotive and building [3-5]. Currently, substantial volumes of cellulose composites (mainly wood powder composites) are used for outdoor building applications, such as roofing and decking [6,7], and for automotive interior parts [6-9]. Polyethylene and polypropylenes are greatly in favour as matrices, mainly due to their relatively low melting ranges and their low cost [5,6,10]. It can be noted that the low melting temperature and the flow properties of low-density polyethylene (LDPE) are very interesting for such composites [11].

Some of the well-studied scientific problems associated with these composites are connected to the water absorption of cellulose, the incompatibility between the cellulose surface and the polymer matrix, the difficulty in dispersing cellulosics for melt processing and the low thermal stability of cellulosics at normal melt-processing temperatures [1,2,5,9,12]. However, considering the rather long-term applications often aimed at, the durability of cellulose composites has not been well [10,13]. Concerns in current applications are generally related to their degradation in both outdoor and indoor applications, as a result of exposure to UV radiation, temperature variations, atmosphere oxygen and moisture. It is understood that the long-term durability (or the degradation) of products made of cellulose composites is mainly governed by thermo-oxidation [14,15].

The thermo-oxidative degradation of wood-based composites can be significantly influenced by the porosity of the composite, the physical and chemical structure of the polymer matrix, the type and amount of cellulosic fibre, the presence of moisture and metal catalysts and the amount and type of antioxidants present, all of which are activated by temperature and/or oxygen [13,15]. Whereas both LDPE and cellulosic fibres exhibit their own oxidative degradation processes, they have been reported in combination as a composite to possibly accelerate degradation since the degradation products may promote further degradation [16-20].

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The thermo-oxidative degradation processes of both LDPE and cellulose generally result in peroxides, carbonyls, chain branches and unsaturated structures. The degradation of polyethylene is known to involve both chain scission and cross-linking, depending on the conditions such as the availability of oxygen and the temperature [17]. The thermo-oxidation mainly propagates via highly reactive peroxy radical intermediates and this to the formation of hydroperoxide species and free radical chain reactions [17]. The main thermo-oxidative degradation products of LDPE are said to be hydroperoxides, hydroxyl groups and carbonyl groups such as carboxylic acids, esters, ketones, aldehydes, and lactones [21-24]. Similarly, the thermo-oxidative degradation of cellulose is based on free-radical initiators and thermal auto-oxidative reactions in which propagation occurs mainly by the production of hydroperoxides [20]. The main degradation products of cellulose contain carbonyl and carboxyl groups [20]. Beside cellulose, a lignocellulosic material also contains hemicellulose and lignin which may contribute to the degradation process. The thermo-oxidative degradation of hemicellulose has not been studied to the same extent as that of cellulose and there are several types of hemicelluloses where the main chemical units depend on the origin of the biomass [25]. However, because of its highly branched structure, hemicellulose is thermally less stable than both cellulose and lignin [26]. Werner et al. [25] has shown that, regardless of the type of hemicellulose, the main degradation products are carbonyl groups and hydroxyl groups such as carboxylic acids, esters, ethers and alcohols. Lignin exhibits a complex degradation process, caused by its highly branched three-dimensional structure, with various oxygen functional groups having different thermal stabilities, which leads to a wide range of scission temperatures from 200 to 500°C [27]. The thermal degradation of lignin is expected to occur more slowly and over a wider temperature range than cellulose and hemicelluloses. The main decomposition process is expected to occur at ca 400°C, with the formation of aromatic hydrocarbons, phenolics or guaiacyl-/syringyl-type compounds as the main degradation products. In general, low heating rates increase the formation of oxygen-containing compounds [27], but aryl-ether bonds in the structure may be cleaved at lower temperatures, already below 310°C, resulting in the formation of free radicals [27].

Against the above background, the accelerated thermo-oxidation of LDPE reinforced with commercial cellulose fibres or with thermomechanical pulp was studied. The general interest was to better understand the influence of thermo-oxidation on the mechanical performance, aiming at estimating the durability of composites in common applications. A special part of the study was devoted to the antioxidation effect of the cellulosic (lignin) components [28-30].

2. Experimental

2.1. Materials

Low-density polyethylene, in the form of pellets, from Borealis AG (FT6230) was used as the matrix material. This is a medical grade having no additives, with a density of 0.913 g/cm^3 and a melt flow rate of 2 g/10 min (190°C/2.16 kg, ISO 1133).

A two-layered tissue made of chemical pulp was used as the source of cellulose fibres, denoted as CT. The pulp consisted of 75 % short fibres (eucalyptus) and 25 % long fibres (pine) and the tissue had a grammage of 34 g/m^2. The carbohydrate content of the tissue was determined using the method of Jedvert et al. [31] which, in turn, is based on the work of Theander and Westerlund [32] with a total acid hydrolysis of the carbohydrate portion of wood to identify the insoluble lignin (Klason lignin) supported by an estimation of the acid-soluble lignin (ASL) using UV analysis. The residual carbohydrate content was measured using high-performance anion-exchange chromatography (HPAEC) giving the approximate composition of the CT to be 78 % cellulose, 14 % hemicelluloses and 1 % lignin (7 % non-detected).

The thermomechanical pulp (TMP) originated from spruce and was supplied by Stora Enso, with an average particle size of 1.7 mm x 20-40 μm. The composition of the TMP was analysed using the same procedures as for CT, giving the approximate composition of the TMP to be 47 % cellulose, 23 % hemicelluloses and 28 % lignin (2 % non-detected).

Irganox 1010 (Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)) which is a hindered phenolic primary antioxidant (radical scavenger) [33] was used as a stabilizer.

2.2. Production of composites

2.2.1. Compounding and mixing

The LDPE was mixed and compounded with cellulose tissue (CT) or thermo mechanical pulp (TMP) using a Werner & Pfleiderer's ZSK 30 M9/2 co-rotating intermeshing twin-screw extruder (TSE). It consists of six heating zones including the die section, the screws being 974 mm in length and 30 mm in diameter.

The TSE screws used, shown in Figure 1, were designed to give a high mixing effect with a configuration from inlet to die: one low pitch screw element, nine high pitch screw elements, two medium pitch screw elements, two low pitch screw elements, one reverse (left-handed) element, five high pitch screw elements, two medium pitch screw elements, one low pitch screw element, four wider 45 ° angled kneading blocks, two narrower 45 ° angled kneading blocks, two medium pitch screw elements and six low pitch screw elements.

The compounding was performed in two twin-screw extrusions followed by one single-screw extrusion for shaping. During the first twin-screw extrusion, LDPE was compounded with TMP or CT by feeding the cellulosic materials into the polymer melt, as shown in Figure 2 which also shows an outline of the twin-screw extruder with the corresponding heating zones. Both TMP and CT were dried at 75°C for at least three days before compounding. Based on a constant feeding rate of the polymer, the feeding of cellulosic material was adjusted to give 5 or 20 % reinforcement which were chosen to represent a low and a high reinforcement level [34].

A second TSE was performed in order to increase the total shear energy and further homogenize the compound. While the second TSE is expected to add to the process-induced degradation, it was found to greatly improve the homogeneity of the composite compounds [35-38]. The extrudates, with a diameter of approximately 3 mm, were pelletized for use in subsequent processing steps. The temperature profile during both twin-screw extrusions for all sample types was: 120, 170, 180, 180, 190, 190°C and the screw speed for the first extrusion was varied between 18 and 50 rpm. Here, the screw speed was selected to result in a material flow rate of 45 and 35 g/min to achieve intended reinforcement ratio of 20 and 5 % respectively, and the screw speed was then adjusted depending on the reinforcement type and amount. The screw speed was 45 rpm for all second TSE compounding. The unfilled LDPE also experienced two twin-screw extrusions to have the same thermal history as the composites.

An amount of 0.005 weight-% antioxidant (AO) type Irganox 1010 was added to the LDPE in the first TSE compounding step and then further homogenized in the second TSE compounding step. The homogenized LDPE+AO was used for compounding cellulose-reinforced composites, as described above.

2.2.2. Shaping

The pelletized compounds were shaped into strips using a Brabender 19/25D single-screw extruder (SSE) with three heating

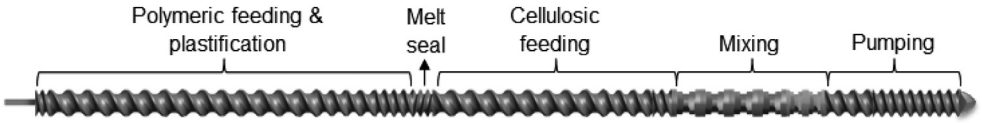

Fig. 1. The screw design showing the different screw elements from inlet (left) to the die (right)

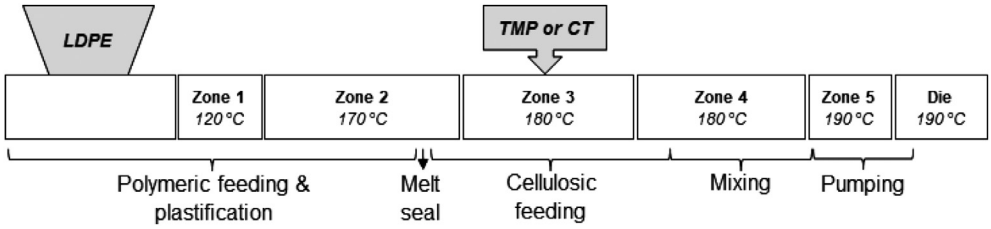

Fig. 2. Scheme of the twin-screw extruder with heating zones, screw properties and feeding zones

Table 1
The material types and corresponding sample codes

Material	Sample code	Material	Sample code
LDPE	LDPE	LDPE-AO	LDPE-AO
LDPE + 20 % TMP	LDPE/20TMP	LDPE-AO + 20 % TMP	LDPE-AO/20TMP
LDPE + 5 % TMP	LDPE/5TMP	LDPE-AO + 5 % TMP	LDPE-AO/5TMP
LDPE + 20 % CT	LDPE/20CT	LDPE-AO + 20 % CT	LDPE-AO/20CT
LDPE + 5 % CT	LDPE/5CT	LDPE-AO + 5 % CT	LDPE-AO/5CT

zones along the screw and one heating zone for the die. A Maillefer barrier type screw with a 2.5:1 compression ratio and a distributive mixing section at the end was used. The screw dimensions were 19 mm in diameter and 475 mm in length. A ribbon die head 50 mm wide and 0.5 mm high was used to give the final shape. A Brabender Univex flat film take-off unit was used to stretch the material and provide flat homogeneous strips.

Throughout the single-screw extrusions, the same screw speed and temperature profile were used for all compounds, 25 rpm and 120, 170, 180, 190°C, respectively. The final thickness of all the samples was 0.55 ± 0.05 mm, achieved by adjusting the Univex take-off speed in the range of 0.5 to 0.8 m/min. Table 1 shows the sample types with their compositions and corresponding sample codes. These ten types of samples were used for the accelerated ageing tests.

2.2.3. Accelerated ageing

Accelerated ageing was performed in a Termaks TS8430 laboratory heat chamber. Eight strips, with a length of 100 cm, were prepared from each type of sample and hung in a well separated arrangement on bars. The samples were conditioned for at least 48 hours in a room at 23 ± 2°C and 50 ± 5% RH, before starting the ageing. Subsequently, a total of 80 strips were placed in the heat chamber that was set to 90°C. Strips were withdrawn at certain time intervals and kept in the conditioning room before further evaluation. During the first 31 days (744 h) of ageing, samples were taken out after 24, 48, 144, 312, 552 and 744 h of ageing and the OIT (oxidation induction time) was determined. The oxidation resistance of the material was considered to be exhausted when the OIT value was below 5 min. For all materials without AO, 744 h was a sufficient ageing time to reduce the OIT below this value. The ageing was continued for the samples containing AO, samples being withdrawn additionally also after 1272, 1560, 2736, 3000 and 3528 h.

2.2.4. Migration of AO

The migration of AO was studied on samples of LDPE containing 0.05 % AO, placed between sheets of either TMP pressed into the form of a rough TMP tissue or the CT. The thickness of the LDPE-AO film was 0.50 ± 0.01 mm, and the thicknesses of the TMP and CT were 1.35 ± 0.18 mm and 0.14 ± 0.01 mm, respectively. The samples were conditioned for at least 48 hours at 23 ± 2°C and 50 ± 5 % RH, before starting the migration test. They were then cut to 99 × 36 mm and stacked between metal plates and clamped together. The stacks were further protected by aluminium folio wrapped around the edges. These stacks were made in duplicate and put in a Termaks TS8000 heat chamber at 70°C for 360 and 1320 h respectively. Both the LDPE-AO and the TMP or CT were analysed after the thermal program using DSC and FTIR to study the possible migration of antioxidants between the materials. The aged samples were stored at 23 ± 2°C and 50 ± 5% RH for at least 288 h before the DSC measurements and stored under the same conditions for 48 h before the FTIR measurements.

2.3. Characterization methods

2.3.1. Environmental scanning electron microscopy (ESEM)

The morphological characteristics were determined using a XL-30 ESEM (Philips, Netherlands). Prior to the examination, the samples were fractured after being submerged in liquid nitrogen and the brittle fracture surface was mounted onto aluminium stubs using carbon glue and sputter-coated with gold (S150B Edwards Sputter Coater, UK) for one minute under vacuum. Samples of neat LDPE(AO) and composites with 20 % TMP and 20 % CT were studied before and after ageing at 90°C.

2.3.2. Differential scanning calorimetry (DSC)

A Mettler-Toledo DSC 2 was employed to evaluate the oxidation induction time (OIT) and the thermal transitions of the composite materials. The methods used for characterizations are based on ISO 11357-6 [39] and ISO11357-1 [40]. Because of the limitations of the DSC equipment, the sample weight varied between 1.4 - 2.5 mg and the samples were disc-shaped with a diameter of 2 mm. The OIT was evaluated for all sample types to study the effect of the cellulose reinforcement on the thermal characteristics. Samples without reinforcement and samples with 20 % reinforcement were examined for thermal transitions and crystallinity assessment. The degree of crystallinity (X_c) was assessed using the heat of fusion

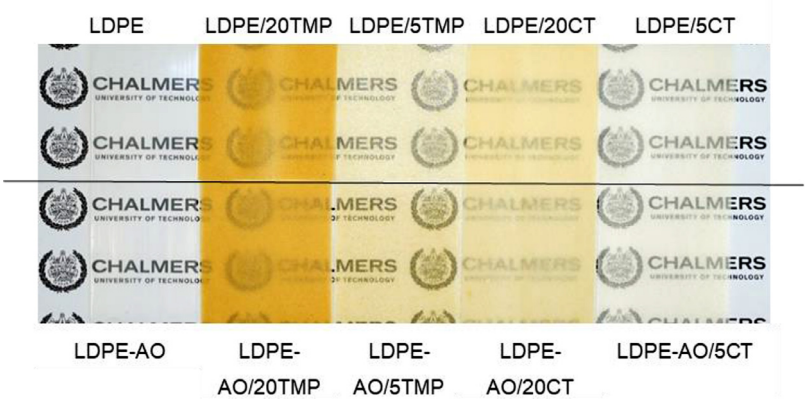

Fig. 3. The apparent transparency of the samples produced, upper five without antioxidant and the lower five with antioxidant added

of the composite (ΔH_c) acquired from the first heating, using the equation: $X_c = \Delta H_c / w_{LDPE} \Delta H_0$; where w_{LDPE} is the weight fraction of LDPE and ΔH_0 is the heat of fusion for 100 % crystalline polyethylene (PE) taken as 277.1 J/g [12]. The materials used in the migration test were also evaluated by OIT measurements.

2.3.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was performed with a Thermo Fisher Scientific Nicolet iS50 FT-IR in the attenuated total reflection (ATR) mode, to examine the functional groups present on the surface of the samples. Here, 32 scans were run between 4000-400 cm^{-1} with a resolution of 4 cm^{-1} for each sample. Samples without reinforcement and samples with 20 % reinforcement were analysed and the FTIR spectra of each material were presented as the average of three spectra collected from three different locations on the same sample. The materials in the migration test were analysed in the same way using FTIR.

2.3.4. Mechanical properties

The tensile tests were carried out at 23 ± 2°C and 50 ± 5 % RH using an Instron 5984 tensile tester equipped with a video extensometer and a load cell of 500 N. The specimens were prepared from conditioned strips (at least 48 hours) using a cutting die corresponding to specimen type 5A in ISO 527-2 [41]. The specimens were 0.55 ± 0.05 mm thick. The gauge length was 20 ± 0.5 mm and the method consisted of four ramps. The material was first extended 0.3 % (strain), then compressed back to zero extension and again extended 0.5 % at a strain rate of 0.8×10^{-3} s^{-1}. Finally, the samples were extended from 0.5 % up to fracture at a strain rate of 0.08 s^{-1}. The pre-strain (0 - 0.3 %) was applied to reduce the influence of residual stresses in the material. Young's modulus (E) was evaluated in the strain range between 0.15 and 0.30 % at a strain rate of 0.8×10^{-3} s^{-1}. The ultimate tensile strength and elongation at break were also recorded. The mean values and standard deviations are based on five independent measurements.

2.3.5. Dynamic-mechanical analysis (DMA)

A Rheometrics RSA II instrument was used to measure the tensile dynamic-mechanical properties at room temperature (21°C) at a frequency of 1 Hz. A pre-strain of 0.1 % (in tension) was applied to the specimens and kept constant during the test. A strain sweep was applied to the specimens with a strain amplitude from 0.02 to 0.12 %.

3. Results and discussion

3.1. Visual and morphological characterization

Figure 3 shows the apparent transparency of the extruded strips from of 10 different samples with the codes indicated in table 1.

Figure 3 shows that there was no significant colour difference between samples without (samples 1-5) and with antioxidant (samples 6-10). The addition of TMP gave the composite a light brown colour whereas the cellulose fibres gave a light-yellow colour. Visual inspection showed that there was no significant filler agglomeration in either the TMP- or the CT-containing samples. All samples were semi-transparent at this thickness. Figure 4 shows ESEM images, using an acceleration voltage of 2-3 kV and the secondary electrons mode, of a brittle fracture surface of the LDPE samples with 20 % TMP or CT, with and without AO, after 0 h and 744 h of ageing.

A closer examination of the fracture surfaces of the composites were more irregular then those of the unfilled polymer and the reinforcing elements could be distinguished. The unfilled LDPE exhibited a smoother and more sharp fracture surface. There were no great differences in fracture appearance of the LDPE with or without AO, between unaged samples and those aged for 744 h, but a slightly smoother surface and possibly more brittle fracture was observed after 744 of ageing in the LDPE without AO. The micrographs indicated a homogeneous distribution of the reinforcing elements in the composites with a rather low porosity and in general a rather good adhesion between LDPE and TMP or CT. There were no significant differences between the fracture surfaces of the unaged and the aged composites, nor between the samples with and without AO. A slight increase in voids or porosity could possibly be observed after ageing. The samples containing AO appeared somewhat more homogeneous than those without AO, but these effects were too vague to permit substantial conclusions to be drawn.

3.2. Thermo-oxidation

Figure 5 presents the oxidation induction time (OIT) of the materials as a function of ageing time.

As shown in Figure 5a, most of the samples without AO exhibited an OIT of ca. 0.5 min after all ageing times, indicating an insignificant resistance to thermo-oxidative degradation. The only exception was the unaged LDPE/20TMP which had an initial OIT of 6.8 ± 3.1 min before ageing. A significant improvement in the thermo-oxidative performance was seen when 20 % TMP was added, while the CT did not show any effect on OIT, possibly because the lignin acted as an antioxidant [15,28,29,42]. After ageing

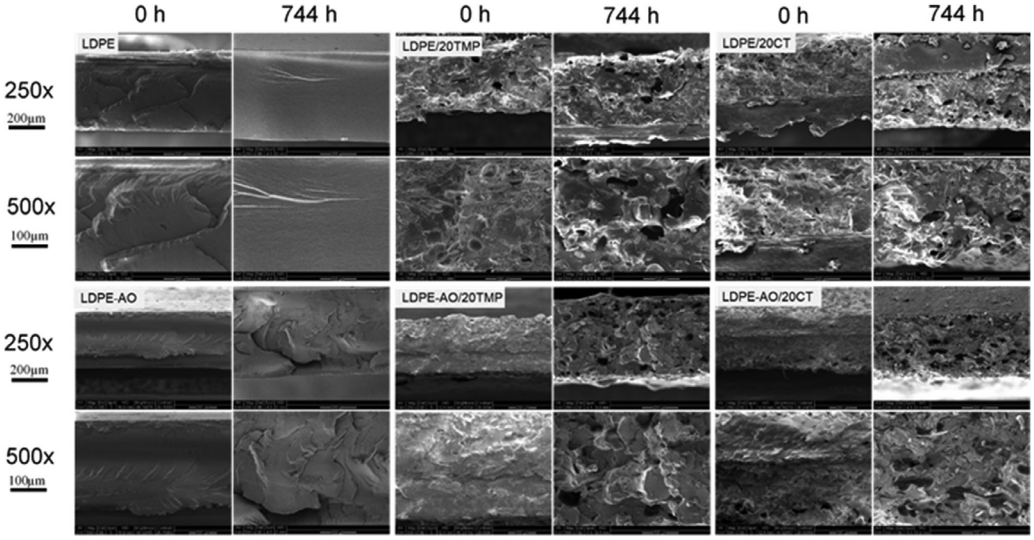

Fig. 4. Environmental scanning electron micrographs of LDPE, LDPE/20TMP, LDPE/20CT, LDPE-AO, LDPE-AO/20TMP and LDPE-AO/20CT after 0 h and 744 h ageing with 250x and 500x magnification

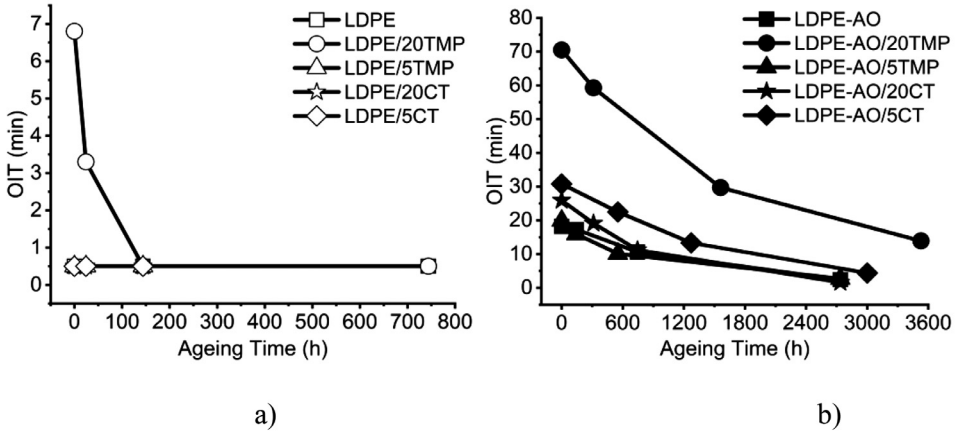

Fig. 5. The oxidation induction time after different ageing time for samples (a) without AO, (b) with AO

Table 2
OIT (min) of all samples prior to ageing and the ageing time giving an OIT below 5min (except for sample LDPE-AO/20TMP which did not reach below this value during the ageing time limit of the project).

Sample	OIT (min)				
	0 h	*24h*	*2736 h*	*3000 h*	*3528 h*
LDPE	0.4 ± 0.05				
LDPE/20TMP	6.8 ± 3.1	3.3 ± 1.3			
LDPE/5TMP	0.5 ± 0.04				
LDPE/20CT	0.5 ± 0.03				
LDPE/5CT	0.5 ± 0.01				
LDPE-AO	18.2 ± 1.7		2.4 ± 1.1		
LDPE-AO/20TMP	70.5 ± 5.0				13.9 ± 1.3
LDPE-AO/5TMP	19.9 ± 2.7		2.7 ± 0.5		
LDPE-AO/20CT	25.9 ± 1.4		1.6 ± 0.2		
LDPE-AO/5CT	30.8 ± 4.6			4.4 ± 1.5	

for 144 h, the OIT of the LDPE/20TMP decreased to 0.5 min, which indicates that the thermal degradation eliminated the stabilizing effect of the added reinforcement.

Figure 5b shows that there was a significant increase in OIT for all samples when AO was added. The LDPE-AO/20TMP exhibited the strongest resistance to thermo-oxidative degradation, having an OIT of 13.9 min after 3528 h accelerated ageing, as shown in Table 2. Samples with an OIT less than 5min were considered to have insignificant resistance to thermo-oxidation.

The stabilizing effect of the combination of TMP and commercial AO has been reported previously [28]. In our study, the composite LDPE-AO/20TMP exhibited the best performance and longest resistance to thermo-oxidation and it performed clearly better than the unfilled LDPE with AO. It seems that the combination of lignin and AO gives a synergic effect on resistance to thermal oxidation degradation. The LDPE-AO/5CT showed the second-best resistance to degradation, but there were no great differences between the other LDPE-AO, LDPE-AO/5TMP

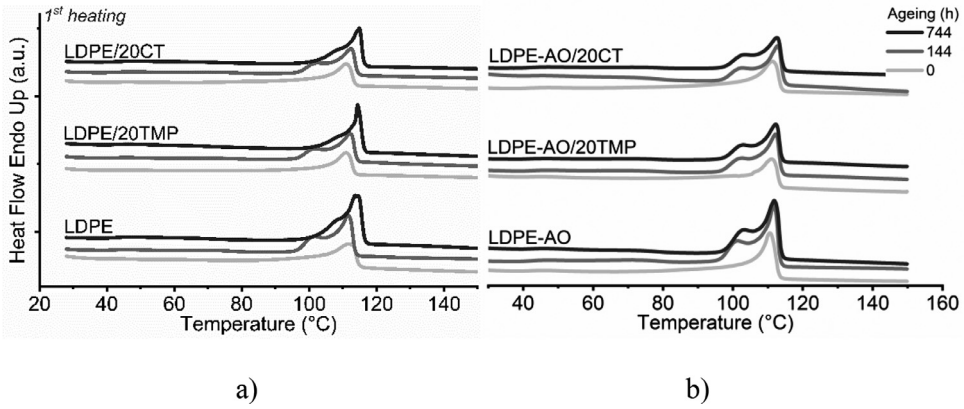

Fig. 6. Overlaid DSC endotherms obtained after different ageing times (0, 144 and 744 h) for (a) pure LDPE and composites with 20% TMP or CT without AO (b) LDPE and composites with 20% TMP or CT with AO

Table 3
The effect of ageing time on the main melting temperature (T_m) and total crystallinity (X_c) of the samples

Sample	T_m (°C)					X_c (%)				
	0 h	*144 h*	*744 h*	*2736 h*	*3528 h*	*0 h*	*144 h*	*744 h*	*2736 h*	*3528 h*
LDPE	113	112	114	-	-	26	31	33	-	-
LDPE/20TMP	111	112	114	-	-	28	32	34	-	-
LDPE/20CT	111	113	115	-	-	35	31	38	-	-
LDPE-AO	111	112	112	112	-	31	33	32	40	-
LDPE-AO/20TMP	111	112	112	-	113	33	33	33	-	39
LDPE-AO/20CT	111	113	113	113	-	36	30	34	41	-

and LDPE-AO/20CT materials, which show similar behaviour in Figure 5b.

The addition of 20 % TMP was much more efficient than 5 %, probably because lignin acted as a stabilizing agent [28,43], but the opposite was observed with CT where 5 % provided a somewhat better resistance to thermo-oxidation than 20 %. The reason for the difference between the behavior of 5 and 20 % CT is at present not clear but one explanation may be that the addition of CT can increase the formation of free radicals and accelerate the degradation [43]. Since 20 % means a higher concentration of cellulose, the radical formation may have been increased.

3.3. Thermal transitions and crystallinity

Figure 6 presents the thermograph for the first heating endotherms of the samples. For each type of sample, endotherms are given for 0 h, after 144 h and 744 h of ageing.

Figure 6 shows only some minor shifts in melting peaks, either between different sample types or due to ageing. For the samples without AO, shoulder peaks appeared after 144 h, but these peaks were not seen after 744 h of ageing. This could be due to changes in molecular structure of LDPE as a result of the degradation and the formation of a more thermally stable crystalline phase after a longer exposure time [13,19,44]. After both 144 and 744 h of ageing, the samples with AO displayed shoulder peaks that possibly indicate an initial molecular degradation. The shoulder peak remained for LDPE-AO and LDPE-AO/20CT after 2736 h, and for LDPE-AO/20TMP after 3528 h. The main melting temperature and total crystallinity of all the samples are given in Table 3.

There were no great changes in T_m, ±1- 4°C, but a slight increase in crystallinity was seen in the unaged (0 h) materials reinforced with TMP or CT, which may be due to the fillers acting as nucleating agents [45]. The crystallinity of the samples without AO showed a slight increase after 744 h of ageing that could be caused by chain scission induced by the degradation, resulting in shorter molecular chains with increased mobility to rearrange into crystals [42,46]. There was no significant change in crystallinity of samples with AO up to 744 h of ageing, in agreement with their increased stability against thermal degradation, but the crystallinity increased significantly to 40, 39, 41 % for LDPE-AO, LDPE-AO/20TMP and LDPE-AO/20CT, respectively after 744 h. These increases in crystallinity and preserved shoulder peaks indicate chain scission reactions caused by thermo-oxidative degradation leading to shorter and more mobile chains [47].

3.4. FTIR-spectroscopy

The formation of carbonyl groups (C=O) is one of the most important indicators of thermo-oxidation. This was observed in the FTIR spectra together with various overlapping bands assigned to acids (1700-1713 cm^{-1}), ketones (1714-1723 cm^{-1}), aldehydes (1728-1733 cm^{-1}), esters (1733-1740 cm^{-1}) and lactones (1780 cm^{-1}) [21,22,48,49]. Figure 7 shows the FTIR-ATR spectra for the LDPE and LDPE-AO samples, after: 0, 144 and 744 h of accelerated thermo-oxidative ageing.

In the case of LDPE without AO, a new peak appeared within the carbonyl formation bands (1680-1800 cm^{-1}) and this was more evident after 744 h of ageing. The spectra of the sample that contained AO showed no significant carbonyl group formation with or without reinforcement. There was no substantial increase in absorbance within the hydroxyl group (-OH) region (3000-3500 cm^{-1}) [48] after the ageing which implies that the degradation caused mainly carbonyl group absorbance. Figure 8 provides a more detailed picture of the carbonyl formation region after several ageing times for the unfilled LDPE and for the composites containing 20 % TMP or CT, with and without AO.

Without AO, the LDPE, LDPE/20TMP and LDPE/20CT samples exhibited a well-developed peak at 1713 cm^{-1} with two shoulder peaks at 1737 and 1780 cm^{-1} indicating the presence of acid, ester and lactone groups, respectively [21,22,48,49]. In the presence of AO, the formation of carbonyl groups during 744 h of ageing was small, but after ageing for 2736 h, both LDPE-AO and LDPE-

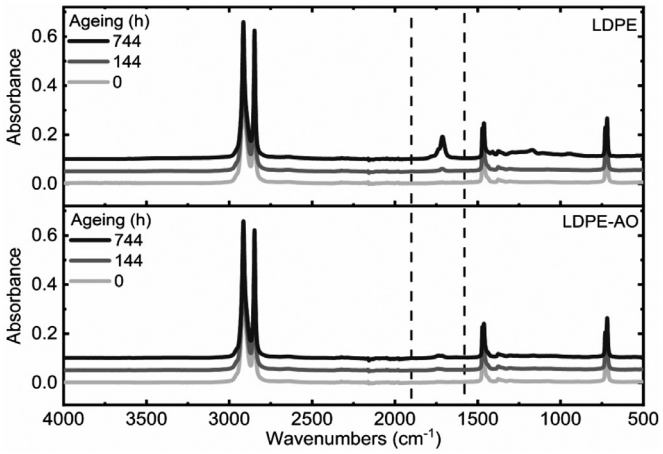

Fig. 7. Full FTIR-ATR spectrum of LDPE and LDPE-AO

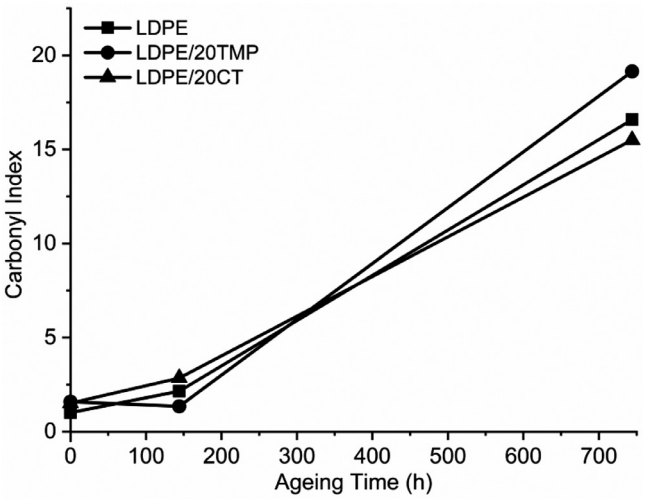

Fig. 9. The formation of carbonyl groups as a function of ageing time of: LDPE; LDPE/20TMP and LDPE/20CT samples. The values shown are averages of 3 measurements with a standard deviation of 0.1-0.3 except for the LDPE aged for 744 h which varied up to 1.7 units

AO/20CT (and also after 3528 h ageing of LDPE-AO/20TMP) showed an increase in peak intensity within the carbonyl region that indicated the formation of degradation products.

Carbonyl indices were calculated for the samples without AO using the equation: *Carbonyl index* $(I) = (I_{1713} / I_{2915})100$; where I_{1713} is the absorbance associated with the degradation products and I_{2915}, the absorbance associated with the alkane CH stretching vibrations of the methylene groups [47]. The peak at 2915 cm^{-1} was chosen as reference because the intensity of this peak was not appreciably affected by 744 h of ageing. Figure 9 shows the changes in carbonyl indices as a function of ageing time for these samples.

Initially, the carbonyl index was slightly higher for the composite LDPE/20TMP and LDPE/20CT samples than for the neat LDPE material. This could be due to increased oxygen in the material due to the addition of TMP or CT [47]. After 144 h of ageing, the carbonyl indexes for LDPE and LDPE/20CT increased. The slight decrease for LDPE/20TMP could be due to an antioxidation effect of lignin in TMP [28,29,42]. During the longest ageing time, 744 h, the carbonyl indices increased markedly, the greatest increase being observed for LDPE/20TMP, followed by LDPE and then LDPE/20CT, but there were no significant differences between the samples.

3.5. Tensile mechanical properties

Table 4 summarizes the effect of ageing on the Young's modulus (E), elongation at break (ε_b) and ultimate tensile strength (σ_b) of the samples. These properties were measured at 0 h and after 744 h for the samples without added AO and also at 1560 h for the LDPE-AO/20TMP and 1272 h for the other samples containing AO.

Increasing amounts of reinforcement to the LDPE whether TMP or CT (with and without AO) increased the Young's modulus and

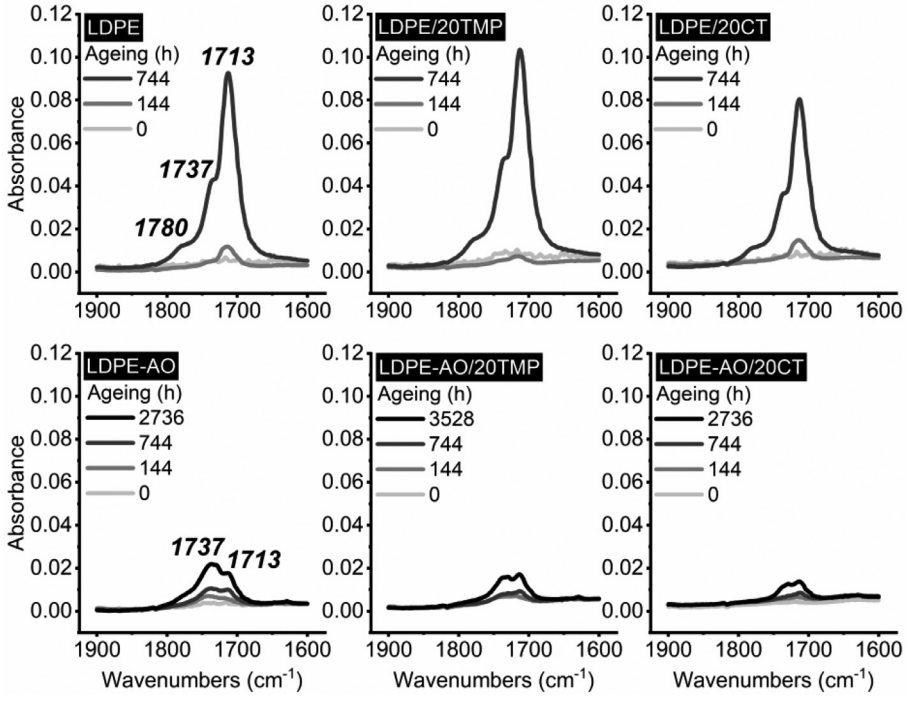

Fig. 8. FTIR-ATR spectra between 1600-1900 cm^{-1}, showing the carbonyl formation bands

Table 4
Mechanical properties of the samples before and after ageing, with standard deviations

Sample	E (MPa)			ε_b (%)			σ_b (MPa)		
	0 h	*744 h*	*1272/1560 h*	*0 h*	*744 h*	*1272/1560 h*	*0 h*	*744 h*	*1272/1560 h*
LDPE	269 ± 14	390 ± 35	-	346 ± 81	4 ± 0.4	-	10.6 ± 3.1	10.1 ± 0.7	-
LDPE/20TMP	533 ± 38	680 ± 98	-	7 ± 0.4	2 ± 0.3	-	13.5 ± 0.4	11.4 ± 0.4	-
LDPE/5TMP	298 ± 8	294 ± 41	-	27 ± 4.7	3 ± 0.6	-	9.8 ± 0.3	8.9 ± 0.3	-
LDPE/20CT	480 ± 21	668 ± 47	-	9 ± 1.0	3 ± 0.3	-	15.5 ± 0.5	11.8 ± 1.1	-
LDPE/5CT	308 ± 19	387 ± 64	-	33 ± 7.3	3 ± 0.9	-	10.0 ± 0.4	10.0 ± 1.2	-
LDPE-AO	272 ± 25	304 ± 31	317 ± 14	263 ± 158	428 ± 158	275 ±83	11.6 ± 1.8	10.0 ± 2.9	11.5 ±2.5
LDPE-AO/20TMP	644 ± 10	639 ± 37	678 ± 92	5 ± 0.7	4 ± 0.4	4 ± 0.6	12 ± 0.1	12 ± 0.9	15 ± 0.4
LDPE-AO/5TMP	339 ± 35	379 ± 19	356 ± 32	29 ± 4.9	23 ± 1.5	18 ± 1.3	9 ± 0.4	12 ± 0.4	12 ± 0.5
LDPE-AO/20CT	553 ± 20	539 ± 22	436 ± 44	7 ± 0.9	6 ± 0.7	6 ± 0.7	12 ± 0.6	13 ± 0.5	14 ± 0.8
LDPE-AO/5CT	307 ± 20	356 ± 10	424 ± 25	32 ± 4.8	27 ± 3.4	23 ± 3.4	10 ± 0.2	11 ± 0.5	12 ± 0.3

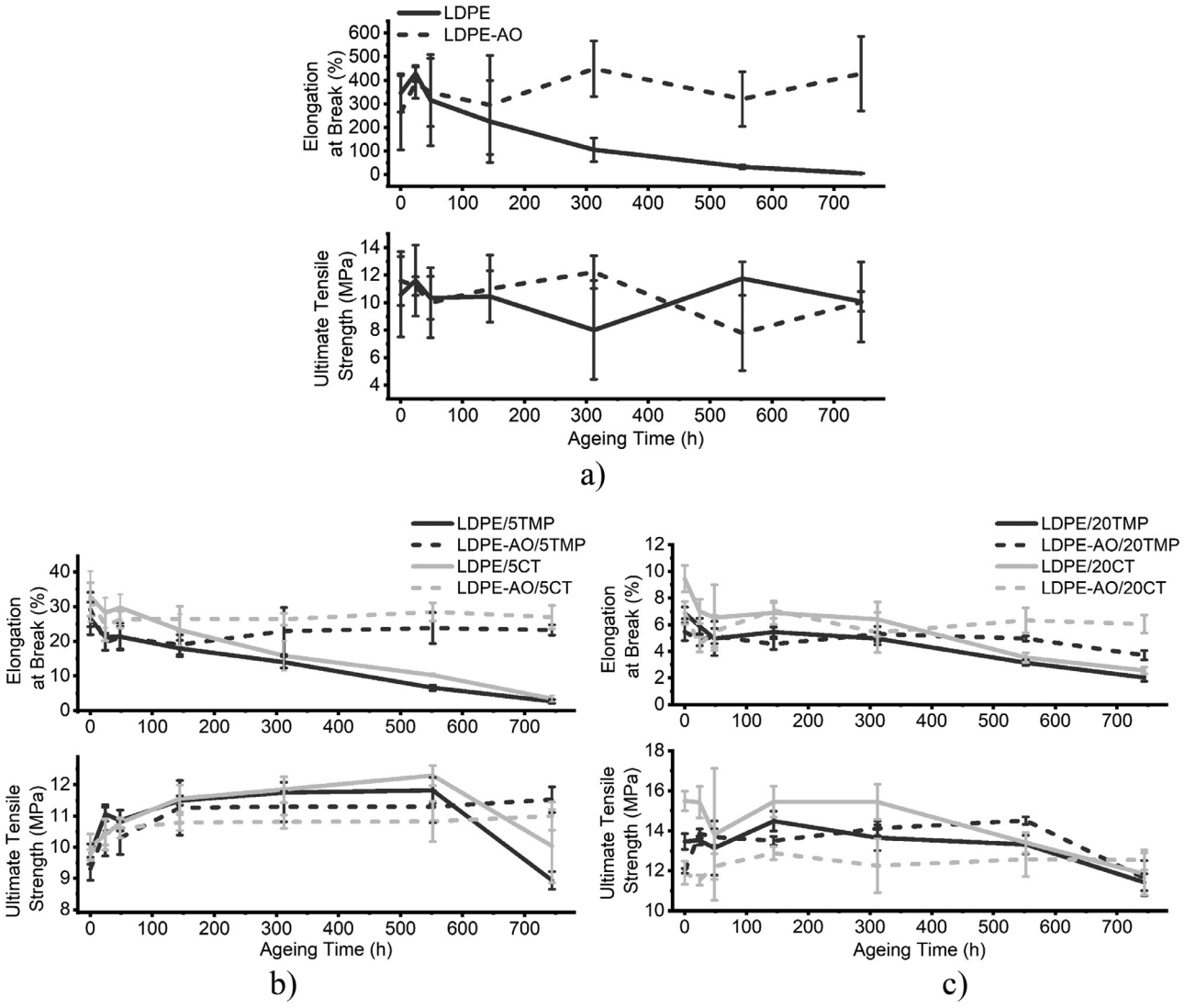

Fig. 10. The effect of ageing time on the tensile failure of (a) the LDPE with and without AO, (b) the composites with and without AO containing 5 % TMP and CT (c) composites with and without AO containing 20% TMP and CT

decreased the ductility, but the ultimate tensile strength remained virtually unaffected. These results showed good agreement with information in the literature concerning the mechanical properties of cellulose-based polymer composites [3,5,35,50].

The effect of ageing on the mechanical properties was markedly affected by the presence of AO, as illustrated in Figure 10, which shows the mechanical properties as a function of ageing time.

The elongation at break decreased with increasing ageing time for samples that did not contain any AO, however, did not change significantly for the samples with AO. Further, no significant effect of the ageing time on the tensile strength was noted for any of the samples.

In general, the variation in Young's modulus with ageing time followed in general the same trend for all samples. After 744 h of ageing, there was in most cases an increase of the modulus, especially for the samples without AO. The increase in crystallinity due to ageing (Table 3) may explain the minor increase in modulus and possibly also the loss in ductility. There were small changes in the

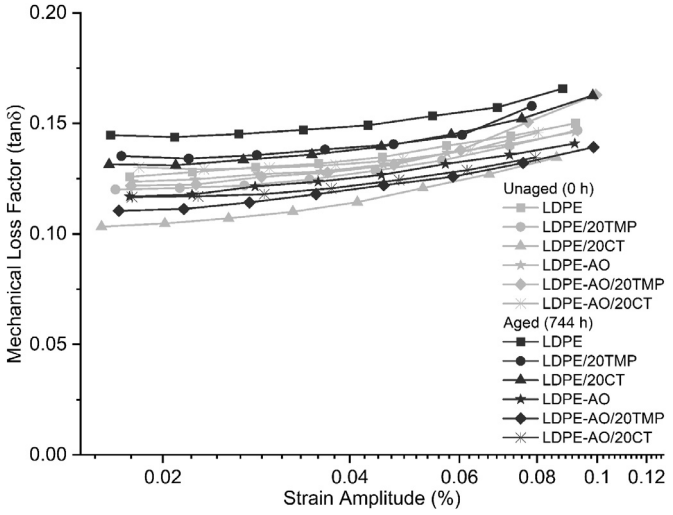

Fig. 11. The mechanical loss factor vs strain amplitude for samples before and after 744 h ageing

Table 5
OIT of the samples before and after migration test, presented as the average value and standard deviation.

Sample	OIT (min)		
	0 h	*360 h*	*1320 h*
LDPE-AO (TMP)	18.2 ± 1.7	18.1 ± 2.4	18.5 ± 0.8
LDPE-AO (CT)	18.2 ± 1.7	19.9 ± 2.3	14.1 ± 2.0
TMP	0.4	0.47	0.35
CT	0.35	0.25	0.23

modulus for samples stabilized with AO, which may indicate that the degradation was not prominent, as indicated by the OIT and FTIR results.

3.6. Dynamic-mechanical properties

Figure 11 shows the loss factor (tanδ) as a function of the strain amplitude for the composites containing 20 % TMP or CT and for the unreinforced LDPE, after 0 h and 744 h of ageing.

The loss factor is known to indirectly illustrates the degree of adhesion between the reinforcement and the polymer matrix [51,52], where a higher tanδ at a given strain amplitude or a discontinuity of tanδ with increasing strain amplitude indicates a weaker bonding or adhesion between the two phases [12,53,54]. The results obtained here shows no differences in mechanical loss factor between composites containing 20 % TMP or CT and the unfilled LDPE. There was thus no indication of any weak interphase region between the fibre and matrix for the composites before ageing, but after ageing, there was a slight increase in the loss factors of samples without AO, indicating a deterioration in the adhesion which could also be observed in ESEM, see Figure 4.

3.7. Migration of AO

Both the LDPE-AO and the TMP or CT used were examined with regard to OIT and FTIR. Table 5 shows no significant changes in OIT with increasing migration time. The TMP and CT showed minimal resistance to oxidation either before or after the migration test. The LDPE-AO film between TMP tissues showed a constant OIT even after 1320 h at 70°C, while the LDPE-AO between CT showed a slight decrease but with a rather large standard deviation.

The FTIR measurements revealed no significant changes in peak intensity, and thus no evidence of migrating AO from the LDPE aged at 70°C for 1320 h, with either CT or TMP. A prolonged migration test was performed for 3984 h, but this did not indicate any migration between the samples either.

4. Conclusions

The OIT measurements showed that without any added AO the addition of 20 % TMP to unreinforced LDPE gave a composite material with improved resistance to thermal oxidation, see Figure 6a. Addition of AO increased the OIT value of all the samples, and the composite with 20% TMP and added AO had an unexpectedly high OIT which indicated high resistance to thermal oxidative degradation. Ageing at 90°C reduced the OIT-values of the materials, but the addition of 20 % TMP resulted in a more stable material regarding to thermo-oxidation than the unfilled LDPE-AO even after prolonged ageing. The FTIR studies supported the OIT measurements and it was concluded that, in the case of samples without AO, the degradation was triggered and propagated mainly by the formation of carbonyl groups.

Accelerated ageing caused a clear decrease in elongation at break for the samples without AO, but for the samples with AO the ductility remained nearly unaffected, even after up to 1560 h of ageing. The ultimate tensile strength and the Young's modulus did not change markedly due to ageing in any of the samples. The dynamic mechanical measurements showed no great disruptions in the mechanical loss factor when the imposed strain amplitude was increased and a rather strong interphase region between the fibre and matrix could thus be indicated. The migration test showed no clear migration of the AO between the LDPE and either the CT or TMP and the antioxidants studied could be considered to be stable in the materials.

The durability aspect of composites and especially cellulosic composites is seldom treated but are of great interest and importance if used in commercial applications. This is certainly crucial if cellulosic fillers are to be used in structural composites or more advanced applications were life-time questions are essential and must be answered before using such composites in real life. The findings of increased lifetime of LDPE by addition of wood-based reinforcements containing lignin could be highly beneficial for future applications.

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Declaration of Competing Interest

The authors declare that they have no conflict of 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.

CRediT authorship contribution statement

Lilian Forsgren: Conceptualization, Writing - original draft, Investigation, Methodology, Validation, Writing - review & editing. **Ezgi Ceren Boz Noyan:** Conceptualization, Writing - original draft, Investigation, Visualization, Methodology, Validation, Writing - review & editing. **Alberto Vega:** Investigation, Methodology, Validation, Writing - review & editing. **Nazdaneh Yarahmadi:** Supervision, Methodology, Writing - review & editing. **Antal Boldizar:** Supervision, Conceptualization, Methodology, Writing - review & editing.

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