Keywords: geotextiles, polypropylene, durability, weathering, photo-oxidation, Chimassorb 944

ABSTRACT: The exposition to solar radiation (mainly due to ultraviolet radiation) can lead to a premature failure of many polymeric materials, including the geotextiles. An extended exposure to ultraviolet radiation may cause damages in the polymeric structure of the geotextiles, shortening their useful lifetime. In this work, a needle-punched nonwoven geotextile (stabilised with 0.4% of Chimassorb 944) was exposed to ultraviolet radiation, both under natural and artificial conditions. The photo-degradation suffered by the exposed samples was evaluated by infrared spectroscopy. Simultaneously, the level of Chimassorb 944 was monitored by high performance liquid chromatography with ultraviolet detection.

1 INTRODUCTION

The geotextiles (GTXs) applied in civil engineering infrastructures can be exposed to several degradation agents, such as: ultraviolet (UV) radiation and other weathering agents, high temperatures, atmospheric oxygen or chemical species like acids or alkalis. An extended exposition to such degradation agents can have a negative impact on the physical, mechanical, hydraulic and chemical properties of these materials. Polypropylene (PP) is the polymer most used for the production of GTXs. PP has a relatively good chemical and microbiological resistance. However, it has a poor resistance against UV radiation, making the outdoor usage of PP products more delicate.

The solar radiation that reaches the earth surface has wavelengths between 295 and 3000 nm. Though, only the UV radiation (between 295 and 400 nm) is sufficiently energetic to cause the degradation of the GTXs. The high-energetic UV radiation can promote the formation of highly reactive free-radicals and, in the presence of oxygen, it is possible the occurrence of photo-degradation of the polymeric chains of the GTXs, according to the following chemical reaction:

\[ n(RH) + O_2 + h\nu \rightarrow R^\bullet + ROO^\bullet + RO^\bullet + OH \]

where RH is the polymeric chain, h\nu is the energy supplied by UV radiation and R^\bullet, ROO^\bullet, RO^\bullet and •OH are free-radicals formed during the degradation process. The degradation induced by UV radiation will continue until all free-radicals are transformed into non-reactive species (for example, by the action of an antioxidant); this process is usually accelerated by high temperatures and by the existence of high moisture contents on the materials.

One way to minimize the degradation suffered by polymeric materials is by adding chemical additives (such as: antioxidants, UV stabilisers or pigments) to their composition. Nowadays, there are in the market many products that can be used to perform all types of stabilisation. Chimassorb 944 (C944) (a hindered amine light stabiliser) is an example of an additive used for the stabilisation of polyolefins against the damaging effects of UV radiation and oxygen. C944 acts by blocking the free-radicals formed during the photo-oxidation process, retarding and/or inhibiting the propagation of that process.

Today, there are several analytical techniques for evaluating the chemical degradation suffered by the polymeric materials. Infrared spectroscopy is one of the most used for studying the degree of oxidation of PP (Philipart et al. 1999, Castejón et al, 2000, Sinturel at al. 2000, Hussain et al. 2002, Ahmadi et al. 2008). Several analytical methods can be found in literature for the determination of many chemical additives often present in polymeric materials.

In this work, a PP GTX (stabilised with 0.4% of C944) was exposed to UV radiation outdoors and in a weatherometer. The photo-degradation suffered by the GTX was evaluated by FTIR (Fourier transform infrared spectroscopy). At the same time, the level of C944 was monitored by high performance liquid chromatography with UV detection (HPLC-UV).
2 EXPERIMENTAL PROCEDURE

2.1 Geotextiles
This work studies a needle-punched nonwoven GTX (G4) (500 g.m⁻²) produced from PP fibres (8 denier, 75 mm long) stabilised with 0.4% of C944 (w/w).

2.2 UV-degradation tests
GTX G4 was exposed to UV radiation, both under natural and artificial conditions.
The laboratorial tests were performed at 60 °C in a weatherometer – the QUV (Q-Panel Lab Products, model QUV/spray). Fluorescent lamps (UVA-340) were used as the UV radiation source (these lamps provide a quite good simulation of the UV radiation emitted by sunlight). The test-samples were exposed to four different total UV radiant energies: 35, 69, 104 and 138 MJ.m⁻² (290-400 nm).
The natural weathering tests were carried out in Portugal (latitude of 41º13’N, longitude of 8º39’W, elevation of 49 m above sea level). The test-samples were mounted outdoors on exposed racks, facing south with an inclination angle of 30º. Samples were collected for characterisation after 6, 12, 18 and 24 months of natural weathering. The air temperature, solar radiation and rainfall were registered during the 24-month outdoor exposition (Table 1).

Table 1. Weather parameters registered during the 24-month outdoor exposition of the geotextile G4

<table>
<thead>
<tr>
<th>Exposition time (months)</th>
<th>Average air temperature (°C)</th>
<th>Total solar radiation* (MJ.m⁻²)</th>
<th>Total rainfall (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>14.0</td>
<td>2189</td>
<td>318</td>
</tr>
<tr>
<td>12</td>
<td>17.8</td>
<td>5612</td>
<td>574</td>
</tr>
<tr>
<td>18</td>
<td>16.7</td>
<td>6146</td>
<td>1121</td>
</tr>
<tr>
<td>24</td>
<td>17.6</td>
<td>9475</td>
<td>1580</td>
</tr>
</tbody>
</table>

*Solar radiation measured between 300 and 3000 nm

2.3 Infrared spectroscopy analyses
The PP fibres (mass of about 5 mg) were removed from the test-samples and crushed in a mechanical press to form translucent pellets. The FTIR analyses were performed in a spectrometer (Perkin-Elmer, model Spectrum RXI FT-IR system) operating in the transmission mode, with a resolution of 2 cm⁻¹ in the range 450-4400 cm⁻¹.

2.4 Determination of C944 by HPLC-UV
An analytical methodology was developed for the determination of C944 on the PP fibres. First, C944 was extracted from the test-samples (mass of 0.5 g) by ultrasonics at 60 °C during 60 minutes, using 20 mL of chloroform; the extractions were carried out in an ultrasonic bath from Bandelin (model Sonorex TK52, frequency of 35 kHz). After cooling to room temperature and filtration (nylon filter with 0.45 µm pore size), the extracts were analysed by HPLC-UV.
The chromatographic analyses were performed in a HPLC system from Jasco. Separation was carried out in a N衡水 column, using chloroform (flow rate of 1 mL.min⁻¹) as the mobile phase; C944 was detected at 224 nm. In these conditions, C944 had a retention time of about 5 minutes.

3 RESULTS AND DISCUSSION

3.1 Visual inspection
The GTX G4 had no visible signs of degradation after the laboratorial exposition to 35 and 69 MJ.m⁻² of UV radiation. However, the exposition to higher UV radiant energies caused the appearance of visible damages. After an UV-exposure of 138 MJ.m⁻², the GTX G4 was releasing high amounts of damaged fibres (white powder), which indicated the existence of serious damages on its structure.
The 24-month outdoor exposition did not cause any visible damages to the GTX G4. However, the material (originally white) acquired a greyish colour due to the accumulation of small particles (dust and filth) between its fibres. The physical (mass per unit area and thickness) and mechanical (tensile strength, tearing strength and static puncture resistance) characterisation of GTX G4 during the exposition to natural weathering can be found in Carneiro et al. 2008.

It is important to notice that, in the absence of the additive C944, the GTX G4 would be completely destructed after 24 months of natural weathering and after exposition to 35 MJ.m⁻² of UV radiation in the laboratory weatherometer. These results show the importance of C944 in the protection of the PP fibres against the deleterious effects of UV radiation. The weathering resistance of PP GTXs (with different amounts of C944) was evaluated by Carneiro et al. 2006 (under artificial conditions) and by Carneiro et al. 2008 (under natural conditions).

3.2 Infrared spectroscopy
The exposition to UV radiation (in laboratory and outdoors) caused the appearance of a band (centred at 1720 cm⁻¹) on the FTIR spectra of GTX G4 (band inexistent on the spectra of the reference samples) (Figure 1).
The changes occurred on the FTIR spectra of the exposed samples are due to chemical modifications that took place on the PP fibres during the exposition to UV radiation. Many degradation compounds can be formed during the photo-oxidation process of PP materials; the band centred at 1720 cm⁻¹ indicates the presence of carbonyl compounds. The height of
this band can provide useful information about the degree of degradation of PP (higher heights indicate greater degradation) (Table 2).

### Table 2. Evolution of the absorbance at 1720 cm⁻¹ of the PP fibres exposed to UV radiation

<table>
<thead>
<tr>
<th>Artificial UV exposure</th>
<th>Outdoor exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (MJ m⁻²)</td>
<td>Absorbance at 1720 cm⁻¹</td>
</tr>
<tr>
<td>0</td>
<td>ND</td>
</tr>
<tr>
<td>35</td>
<td>ND</td>
</tr>
<tr>
<td>69</td>
<td>0.005</td>
</tr>
<tr>
<td>104</td>
<td>0.006</td>
</tr>
<tr>
<td>138</td>
<td>0.028</td>
</tr>
</tbody>
</table>

(ND – not detected)

No band at 1720 cm⁻¹ was detected on the infrared spectra of the samples exposed to 35 MJ m⁻² of UV radiation (which showed the inexistence of carbonyl compounds or their existence in low quantities). The increase of the total UV radiant energy caused the appearance of the band centred at 1720 cm⁻¹. Indeed, a small band (with an absorbance of 0.005 at 1720 cm⁻¹) appeared on the infrared spectra of the samples exposed to 69 MJ m⁻² of UV radiation. The amount of carbonyl compounds increased as the UV radiant energy increased (higher degree of photo-oxidation). After an UV-exposure of 138 MJ m⁻², the samples had an absorbance of 0.028 at 1720 cm⁻¹.

The band centred at 1720 cm⁻¹ was also present on the FTIR spectra of the samples exposed to natural weathering (the absorbance of that band increased as the exposition time increased). After 24 months, the samples had an absorbance of 0.034 at 1720 cm⁻¹.

An 18-month outdoor exposure caused an increase of absorbance at 1720 cm⁻¹ similar to the laboratorial exposure to 138 MJ m⁻² of UV radiation. However, the mechanical damages were higher on the samples exposed to artificial UV radiation (data not shown).

Finally, it is important to note that the dirt present in the outdoor exposed samples may have interfered on their infrared spectra (this was not detected).

### 3.3 HPLC-UV

The level of C944 was monitored (by HPLC-UV) on the UV-exposed samples. Figure 2 illustrates the chromatograms obtained for GTX G4, before and after the exposition to natural weathering.

The level of C944 decreased with the increase of the exposition time (in the natural weathering tests) and with the increase of the total UV radiant energy (in the laboratorial tests). Therefore, the additive was consumed and/or lost while protecting the PP fibres against the harmful effects of UV radiation. Figures 3 and 4 illustrate the evolution of the level of C944 during the UV-exposure tests (the FTIR data is also plotted in both figures for comparison purposes).
Figure 4. Consumption loss of C944 versus absorbance at 1720 cm\(^{-1}\) of the test-samples exposed to natural weathering

The comparison of the results obtained by FTIR and by HPLC-UV showed a correlation between the degradation suffered by the samples and the level of C944. The increase of the total UV radiant energy (laboratorial tests) and the increase of the exposition time (natural weathering tests) caused a decrease of the level of C944 (leaving the fibres more vulnerable to suffer photo-oxidation) and, simultaneously, an increase of the absorbance at 1720 cm\(^{-1}\) (indicating the existence of more carbonyl compounds arising from the photo-oxidation process of PP).

4 CONCLUSIONS

The exposition to UV radiation (both under natural and artificial conditions) caused the appearance of a new band (centred at 1720 cm\(^{-1}\)) on the FTIR spectra of a PP GTX stabilised with 0.4% of C944; this band indicates the presence of carbonyl compounds. The height (absorbance) of this infrared band was used to assess the degree of degradation of the UV-exposed samples.

The absorbance of the band centred at 1720 cm\(^{-1}\) increased (higher degree of photo-oxidation) with the increase of the exposition time (in the natural weathering tests) and with the increase of the total UV radiant energy (in the laboratorial tests).

The level of C944 on the PP fibres decreased as the total UV radiant energy increased (laboratorial tests) and as the exposition time increased (natural weathering tests). So, the UV-exposure tests caused a consumption and/or loss of C944. This decrease on the level of C944 was accompanied by an increase on the degree of photo-degradation of the PP fibres.

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REFERENCES


