EuroGeo4 Paper number 180 **THERMO-OXIDATION OF POLYPROPYLENE GEOTEXTILES**

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Abstract: Geotextiles are polymeric materials widely applied in civil engineering structures, where various agents (such as, oxygen, high temperatures, chemical species or weathering) may affect their durability and, consequently, their useful lifetime. Oxidation is one of the main causes of the degradation of polyolefin's and occurs following a complex chain reaction mechanism. This mechanism is started by free-radicals, which can be either produced by heat (thermo-oxidation) or by ultraviolet radiation (photo-oxidation). However, in the absence of ultraviolet radiation this oxidative degradation process is usually very slow at room temperature. So, in order to achieve a sufficiently short exposure time needed for a thermo-oxidation screening test, it is necessary to accelerate the oxidative degradation conditions (either by raising the temperature or by increasing the concentration of oxygen).

This paper studies the durability of nonwoven geotextiles (manufactured from polypropylene fibres stabilised with different amounts of the additive Chimassorb 944: 0%, 0.2% and 0.4%) under thermo-oxidative conditions. An oven without forced air circulation was used to expose the geotextiles to elevated temperatures in a normal oxygen atmosphere (21% O_2) during different periods of time. Oven-ageing tests were also performed for geotextile specimens previously immersed, during a long period of time, in several chemical solutions like acids, alkalis and solutions of heavy metals (cadmium, copper and iron).

The tensile strength of the exposed geotextiles was determined according to the European standard EN ISO 10319 and the obtained results were compared with those obtained for unexposed materials. Based on these results, conclusions will be taken about the importance of the additive Chimassorb 944 in the protection of the polypropylene fibres against the damaging effects of thermo-oxidation. The occurrence of synergetic effects on the degradation suffered by the geotextiles previously immersed in chemical solutions will be also discussed.

Keywords: geotextile; polypropylene; durability; thermo-oxidation; lifetime prediction; chemical ageing

INTRODUCTION

The degradation that geotextiles (GTXs) will suffer during their service lifetime must be taken into account for the right application of these materials in civil engineering structures. There are many agents (such as: oxygen, high temperatures, ultraviolet radiation and other weathering agents, acids, alkalis and microorganisms) that may induce the occurrence of several degenerative processes on the polymeric structure of the GTXs, shortening their useful lifetime. As GTXs must maintain certain required properties during a long period of time, it is very important to evaluate their resistance against all those agents.

Oxidation is one of the main causes for the premature failure of many polymeric materials. The effects of oxidation are many and may include colour changes, rupture of polymeric chains and reduction of the mechanical strength of the GTXs. The oxidation process of the GTXs occurs following a complex chain reaction mechanism that is started by the formation of free-radicals, either produced by heat (thermo-oxidation) or by ultraviolet radiation (photo-oxidation). The oxidation of polypropylene (PP) materials (the most used polymer for the production of GTXs) is usually very slow at ambient temperatures (providing that the materials are not exposed to direct sunlight). However, this degradation may not be negligible when considering civil engineering materials, which are often expected to last for a very long period of time.

The European standard EN ISO 13438 (2004) describes two methods for evaluating the resistance of GTXs to oxidation: the oven-ageing test and a test working with elevated oxygen pressures. In the oven-ageing test, the GTXs are placed inside an oven and exposed to elevated temperatures (100 °C for polyethylene materials and 110 °C for PP materials) in a normal oxygen atmosphere. In the other test, the GTXs are immersed in a liquid medium (an aqueous solution of NaHCO₃) at 80 °C and subjected to a 50 bar oxygen pressure. In these tests, the oxidative degradation conditions are accelerated by raising the temperature or by increasing the concentration of oxygen.

The degradation promoted by thermo-oxidation is usually inhibited or at least retarded by the incorporation of chemical additives, such as antioxidants, on the GTXs composition. These compounds can cause a significant decrease on the oxidation rate of many polymeric materials, extending their useful lifetime.

EXPERIMENTAL DESCRIPTION

Geotextiles

PP fibres (8 denier, 75 mm long) with different amounts of the additive Chimassorb 944 (C944), 0.2% and 0.4% (w/w), were specially manufactured to produce needle punched nonwoven GTXs (mass per unit area of 280 g.m⁻²). A non-stabilised GTX was produced from PP fibres without any C944.

Oven-ageing tests

Oven-ageing tests at 110 °C

Oven-ageing tests were carried out at 110 °C (normal oxygen atmosphere, without forced air circulation) during different periods of time. The GTXs with 0.2% and 0.4% of C944 were exposed during 14, 28, 42 and 56 days, while the GTX without C944 was only exposed during 4, 7, 9 and 11 days.

Effect of the oven temperature on the degradation rate of the geotextiles

Oven-ageing tests were carried out at lower temperatures (80 °C, 90 °C and 100 °C) for the GTX without C944, in order to study the effect of the temperature on the degradation suffered by this material. These tests were carried out till complete degradation of the exposed specimens.

Influence of chemical solutions on the oxidative resistance of the geotextiles

Oven-ageing tests were also performed for specimens of the GTX with 0.2% of C944 previously contaminated with different chemical solutions. This study intended to evaluate the effect of some chemical species on the oxidative resistance of this material.

Specimens of the GTX with 0.2% of C944 were immersed in acids (sulphuric acid and nitric acid), alkalis (sodium hydroxide), solutions of heavy metal salts (cadmium, copper and iron) and water during a long period of time. The pH of the solutions of the heavy metals was adjusted to pH 2 by the addition of nitric acid. The immersion conditions are summarized in Table 1.

Degradation agent	Test conditions
$H_2SO_4 (0.1 \text{ mol.L}^{-1})$ (pH \approx 1)	20 °C, 150 days
NaOH (0.1 mol.L ⁻¹) (pH \approx 13)	20 °C, 150 days
$\begin{array}{c} H_2O\\ (pH\approx7) \end{array}$	20 °C, 150 days
$HNO_3 (0.01 \text{ mol.L}^{-1})$ $(pH \approx 2)$	20 °C, 100 days
Cd(NO ₃) ₂ .3H ₂ O (5 g.L ⁻¹) (pH \approx 2) *	20 °C, 100 days
Cu (NO ₃) ₂ .3H ₂ O (5 g.L ⁻¹) (pH \approx 2) *	20 °C, 100 days
Fe(NO ₃) ₃ .9H ₂ O (5 g.L ⁻¹) (pH \approx 2) *	20 °C, 100 days

Table 1. Experimental conditions of the immersion tests

*pH adjusted to pH 2 by the addition of nitric acid

After immersion, the specimens were dried at least for 7 days in a dark place (specimens not washed) and then oven-ageing tests were carried out at 110 °C, during 14, 28, 42 and 56 days. Control specimens (contaminated with the chemical solutions, but not exposed to the oven-ageing tests) were also considered; this was necessary to evaluate if the specimens suffered any degradation during immersion.

Tensile tests

The tensile strength of the GTXs was determined (in the machine direction of production) according to EN ISO 10319 (1996) (Table 2).

Table 2. Experimental conditions used on the tensile tests					
Specimen width	Specimen width Specimen length *		Test velocity		
200 mm	100 mm	5	20 mm.min ⁻¹		

Table 2. Experimental conditions used on the tensile tests

*between grips

The degradation suffered by the GTXs during the thermo-oxidation tests was evaluated by comparing the tensile results obtained for exposed specimens with those obtained for reference specimens (without any degradation). The results are expressed in terms of percentage of retained tensile strength (obtained by dividing the tensile strength of the exposed specimens by the tensile strength of the reference specimens).

RESULTS AND DISCUSSION

Oven-ageing tests at 110 °C

The GTX without C944 did not resist to the oven-ageing test, being easily reduced into small pieces or powder (Figure 1). After 11 days of thermo-oxidation, the unstabilised GTX was yellowish (originally it was white) and the degradation of its PP fibres was easily perceptible due to the liberation of volatile compounds. The degradation process was accompanied by a loss of mass (loss of 11% after 11 test-days) and by a reduction on the dimensions of the GTXs (shrinkage of 12% after 11 test-days).



Figure 1. Small pieces (a) and powder (b) of the GTX without C944 after 11 days of oven-ageing at 110 °C

The unstabilised PP fibres depolymerised completely during the oven-ageing test and the tensile strength of the GTX without C944 was reduced to zero just after 9 test-days. The GTXs stabilised with 0.2% and 0.4% of C944 were not destructed during the oven-ageing tests. This readily shows the importance of C944 on the protection of the PP fibres against the damaging effects of thermo-oxidation. The stabilised GTXs maintained their original colour and mass during the 56 days of oven-ageing; a slight decrease on the dimensions of these materials was observed (shrinkage of about 2% to 3% in all specimens). Figure 2 shows the evolution of the retained tensile strength of the GTXs during the oven-ageing tests.



Figure 2. Retained tensile strength of the GTXs during the oven-ageing tests at 110 °C

The GTXs stabilised with 0.2% and 0.4% of C944 presented a good resistance against oxidation. Indeed, the tensile strength of these materials remained practically unchanged during the 56 days of the oven-aging test. The degradation of the PP fibres was retarded or inhibited by the incorporation of C944 on their composition; a low quantity of C944 (0.2%) was enough to provide a good protection against thermo-oxidation.

Effect of the oven temperature on the degradation rate of the geotextile without Chimassorb 944

The degradation of the PP fibres without C944 occurred very fast at 110 °C (after 9 test-days the GTX was already destructed, with no tensile strength). Figure 3 illustrates the evolution of the retained tensile strength of the GTX without C944 during the exposition to lower temperatures (80 °C, 90 °C and 100 °C) in the oven ageing test.



Figure 3. Effect of the oven temperature on the degradation rate of the GTX without C944

The degradation rate of the GTX without C944 was highly dependent on temperature; as the oven temperature decreased more time was needed for the complete depolymerisation of the unstabilised PP fibres. At 80 °C, 71 days were needed for the complete destruction of the GTX without C944, about twice the time needed at 90 °C (36 days) and nearly 8-times more than the time needed at 110 °C (9 days).

The degradation profile of the GTX without C944 illustrated in Figure 3 shows that thermo-oxidation begins with a period (induction period) where the tensile strength of the materials remains practically unchanged (about 57 days at 80 °C or 21 days at 90 °C). After that period, the degradation occurs relatively fast. The time passed from the moment that the GTX without C944 had 50% of its original tensile strength till its complete degradation was very low (7 days at 80 °C, 5 days at 90 °C, 3 days at 100 °C and only 1 day at 110 °C).

Lifetime prediction using an Arrhenius-type modelling

The lifetime of the GTX without C944 at ambient temperatures was estimated by using an Arrhenius-type modelling. In this model, the experimental results obtained in the accelerated degradation tests performed at elevated temperatures can be used to estimate the lifetime of the materials at lower temperatures. The well known Arrhenius equation is as follows:

$\ln K = \ln A - E_a/RT$

Where *K* is the reaction rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant and T is the temperature in Kelvin.

In many chemical reactions, the plot of $\ln K$ against 1/T gives a straight line. So, if we have experimental values of a degradation rate (such as the time required to 50% tensile strength loss or the time required to the complete destruction of the GTXs) obtained at different temperatures, we can determine, at least theoretically, the degradation rate at any temperature of interest. A minimum of two experimental values of a degradation rate are needed for performing this kind of predictions. However, the accuracy of the extrapolations usually increases considerably when more experimental results are available.

An Arrhenius-type modelling was applied to the results obtained in the oven-ageing tests of the GTX without C944 at four different temperatures (80 °C, 90°C, 100°C, 110 °C). The natural logarithm of the inverse time to 50% tensile strength loss was plotted against the inverse temperature (Figure 4). Table 3 summarizes the parameters used in the Arrhenius plot.

Т (°С)	T (K)*	10 ³ (1 / T) (K ⁻¹)	t50% TSL** (days)	ln (1 / t50% TSL)
80	353.15	2.83	64	- 4.16
90	363.15	2.75	31	- 3.43
100	373.15	2.68	16	- 2.77
110	383.15	2.61	8	- 2.08

Table 3. Parameters used in the Arrhenius plot

 $* T (K) = T (^{\circ}C) + 273.15$

** Time required to 50% tensile strength loss



Figure 4. Arrhenius plot used for predicting the degradation rate of the GTX without C944 at low temperatures

The plot of ln (1/t50% tensile strength loss) against 1/T gave a straight line ($r^2 = 0.9997$). Based on experimental data obtained at elevated temperatures, the Arrhenius plot was used to estimate the degradation rate of the GTX without C944 at low temperatures (Table 4).

Т	Т	$10^{3} (1 / T)$	ln	t50% TSL	t50% TSL
(°C)	(K)	(K ⁻¹)	(1 / t50% TSL)	(days)	(years)
0	273.15	3.66	- 11.9	146654	402
10	283.15	3.53	- 10.7	43576	119
20	293.15	3.41	- 9.56	14215	39
30	303.15	3.30	- 8.54	5091	14
40	313.15	3.19	- 7.56	1823	5

Table 4. Prediction of the time needed for 50% tensile strength loss of the GTX without C944 at low temperatures

Using the Arrhenius model, it was possible to estimate that at average room temperature (about 20 °C) about 39 years will be needed for a 50% tensile strength loss of an unstabilised PP GTX. At 10 °C, about 119 years will be needed for a 50% tensile strength loss, about 3-times more than the time needed at 20 °C and almost 9-times more than the time needed at 30 °C (14 years).

Remembering that the GTXs stabilised with C944 had their tensile strength practically unchanged after 56 days of thermo-oxidation at 110 °C, we can expect that, at ambient temperatures, much more time (hundreds of years) than the estimated for the unstabilised GTX will be needed for a 50% reduction on the tensile strength of these materials.

It is important to note that these predictions are only taking into account the degradation promoted by oxidation induced by heat and are assuming that the mechanism of oxidation is the same for all ranges of temperatures (a change on the mechanism leads to inaccurate extrapolations). In their service lifetime, the GTXs will be exposed to other damaging agents besides thermo-oxidation, which will also contribute for the whole degradation suffered by the materials. This degradation can even be enhanced if synergetic effects occur between the different agents.

Influence of chemical solutions on the oxidative resistance of the geotextile with 0.2% of Chimassorb 944

Influence of acids, alkalis and water

The tensile strength of the GTX with 0.2% of C944 remained unchanged after the immersion of the materials in acids (sulphuric acid and nitric acid), alkalis (sodium hydroxide) and water. The contaminated specimens of this GTX were then exposed to oven-ageing tests at 110 °C. The retained tensile strengths of these specimens after exposition to thermo-oxidation are summarized in Table 5.

Oven-ageing time	Retained tensile strength (%)				
(days)	No immersion	H_2SO_4	HNO ₃	NaOH	H ₂ O
14	100	88	100	94	100
28	105	85	93	96	99
42	102	84	94	93	101
56	97	78	95	94	99

Table 5. Retained tensile strength of the specimens immersed in acids, alkalis and water after the oven-ageing tests

The specimens contaminated with sulphuric acid acquired a brownish colour (originally they were white) just after one day of exposition at 110 °C (Figure 5). The tensile strength of these specimens suffered a reduction during the oven-ageing test. After 56 test-days, the specimens contaminated with sulphuric acid had a retained resistance of 78%. This shows that the contamination of the GTX with 0.2% of C944 with sulphuric acid caused a decrease on the resistance of the material against oxidation induced by heat.



(a)



Contrarily to what happened with the specimens contaminated with sulphuric acid, the specimens contaminated with nitric acid maintained their original colour and suffered only a slight decrease on their tensile resistance during the oven-ageing test. After 56 test-days, these specimens had a retained resistance of 95%. It is important to note that the concentration of sulphuric acid was 10-times higher than the concentration of nitric acid (the immersion time in sulphuric acid was also longer), which may be the reason for the higher degradation suffered by that specimens. The effect of nitric acid (under the studied conditions) on the oxidative resistance of the GTX with 0.2% of C944 was only studied because the pH of the heavy metal solutions was adjusted to pH 2 with this acid. Therefore, it was necessary to evaluate if nitric acid had for itself any effect on the oxidative resistance of the materials.

The specimens contaminated with sodium hydroxide suffered only a slight decrease on their tensile strength during the oven-ageing test. After 56 days of thermo-oxidation, these specimens had a retained resistance of 94%. The effect of an alkaline contamination with sodium hydroxide on the oxidative resistance of the GTX with 0.2% of C944 was not as pronounced as the effect of a contamination with sulphuric acid.

The tensile strength of the specimens immersed in water remained unchanged during the oven-ageing test, showing that water had no effect on the oxidative resistance of the GTX with 0.2% of C944.

A synergetic effect between sulphuric acid and oxidation induced by heat was observed on the degradation suffered by the GTX with 0.2% of C944 (two agents that individually had no effect on the materials, caused together some degradation).

A contamination with chemical solutions may not cause immediate degradation on the GTXs, but may reduce considerably their protection against further degradation agents. For instance, the additives may be lost (extraction by the chemical species) and/or consumed during the immersion tests; some contaminants may also act as catalysts in further degradation processes.

Influence of heavy metals

The tensile strength of the GTX with 0.2% of C944 was not affected by the immersion of the materials in the solutions of heavy metals (cadmium, copper and iron). The colour of the specimens immersed in the iron solution acquired a yellowish colour, while the colour of specimens immersed in the other solutions remained unchanged.

The specimens contaminated with copper were completely destructed during the oven-ageing test. After 14 days of oven-ageing, the specimens were yellowish and could be easily reduced into small pieces and powder (Figure 6); the degradation of these specimens was also accompanied by the liberation of volatile compounds. Liquefied residues of the materials (a yellow viscous liquid) were found at the bottom of the oven; a decrease on the oven temperature (for cleaning purposes) caused the immediate solidification of that liquid.



Figure 6. Specimens contaminated with copper after 14 days of oven-ageing: (a) general aspect of the specimens; (b) pieces and liquefied residues of the specimens at bottom of the oven

It is important to remember that the tensile strength of the GTX with 0.2% of C944 (without any contamination) was practically unaffected after 56 days of oven-ageing at 110 °C, showing a relatively good oxidative resistance. The contamination with copper had such an accelerating effect on the oxidation process that 14 days of oven-ageing were sufficient for causing the complete destruction of the materials.

The specimens contaminated with the other heavy metals were not completely destructed during the oven-ageing test, neither was observed any change in their colour. The retained tensile strengths of these specimens after exposition to the oven-ageing tests are summarized in Table 6.

Oven-ageing time	Retained tensile strength (%)				
(days)	No immersion	Cadmium	Iron	Copper	
14	100	95	94	0	
28	105	92	62	0	
42	102	93	46	0	
56	97	92	32	0	

Table 6. Retained tensile strength of the specimens contaminated with heavy metals after the oven-ageing tests

The specimens contaminated with cadmium suffered only a slight decrease on their tensile strength after exposition to the oven-ageing test, contrarily to what happened to the specimens contaminated with iron. After 56 test-days, the specimens contaminated with cadmium still had a retained resistance of 92%, while the specimens contaminated with iron only had a retained resistance of 32%. A few more days of exposition of the specimens contaminated with iron would probably cause the complete destruction of the materials.

These results show that some heavy metals, such as copper or iron, can act as catalysts and accelerate the oxidation process of the PP fibres. This effect was more pronounced for the specimens contaminated with copper, followed by the specimens contaminated with iron and, finally, by the specimens contaminated with cadmium.

It is worthy to note that, the time necessary for the complete degradation of the specimens contaminated with copper (specimens stabilised with 0.2% of C944) was similar to the time necessary for the complete degradation of unstabilised specimens (complete degradation after 9 days). This shows that C944 was almost unable to retard the copper-catalysed oxidation of the PP fibres.

The lifetime of the PP GTXs exposed to oxidative conditions can be drastically reduced by the presence of some heavy metals. At ambient temperatures, the time needed for a 50% tensile strength loss of GTXs contaminated with these metals is expected to be much less than the time needed for non-contaminated specimens. In the presence of ultraviolet radiation the degradation process of the GTXs will be even faster.

In their applications, the GTXs will probably never be exposed to only one degradation agent. So, it is important to study the joint effect of several degradation agents on the durability of the GTXs. This way, the synergisms between the different agents can be taken into account and the overall degradation suffered by the GTXs can be more reliably estimated.

MAIN CONCLUSIONS

The PP GTX without C944 was completely destructed after 11 days of thermo-oxidation at 110 °C. The degradation rate of this GTX decreased considerably at lower oven temperatures; the time needed for the complete destruction of the GTX more or less duplicated for each 10 °C decrease in temperature.

The lifetime of the GTX without C944 at ambient temperatures was predicted by using an Arrhenius-type modelling. Experimental results obtained at elevated temperatures were used to estimate the degradation rate of this material at low temperatures. At average room temperature (20 °C), about 39 years will be needed for a 50% tensile strength loss of the GTX without C944 (admitting the inexistence of no other degradation processes besides oxidation induced by heat). After reaching a 50% strength loss, the degradation suffered by the materials occurs relatively fast till their complete destruction.

The GTXs stabilised with 0.2% and 0.4% of C944 maintained their original tensile strength during the 56 days of the oven-ageing test at 110 °C, showing a good oxidative resistance. The degradation of the PP fibres was retarded or inhibited by the incorporation of a small quantity of the additive C944. This way, C944 proved to be important in the stabilisation of the PP fibres against the damaging effects of thermo-oxidation.

The oxidative resistance of the GTX with 0.2% of C944 was drastically reduced by the presence of some heavy metals. Copper and iron acted as catalysts and had an accelerating influence on the oxidation process of the PP fibres. A contamination with sulphuric acid also decreased the resistance of the materials against oxidation induced by heat.

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