

THERMO-OXIDATIVE AGEING OF POLYPROPYLENE GEOSYNTHETICS MONITORED BY THERMAL ANALYSIS AND MECHANICAL TENSILE TEST

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ABSTRACT: The aim of this study is to monitor polypropylene ageing by means of thermal analysis. Thermal results are always compared to mechanical tensile tests so as to get both a chemical characterisation and a macroscopic measurement. Two polypropylene geosynthetics have been chosen, a fibre like one (geotextile) and a thick one (geomembrane). The annealing effects are studied first. Results of macroscopic mechanical loss are compared to chemical rearrangement obtained by DSC. Then, fiber are aged under isothermal oven test and under high oxygen pressure immersion test. A life time criterion is defined, based on the induction temperature (T_{ind}) of the neat resin. DSC has highlighted some secondary effects when fiber are aged high oxygen pressure. When fiber are stabilised with HAS, a mechanism of characterisation is postulated. During geomembrane ageing, a linear decrease of T_{ind} is observed, and an exponential decrease of OIT is obtained. By crossing T_{ind} evolution with OIT behaviour, an activation energy of anti oxidant efficiency in protecting the material is calculated. When phenolic stabiliser are used, E_a remains constant as far as there is still some stabiliser remaining. When HAS are used, a decrease of E_a versus ageing time is observed, explained by a loss of HAS efficiency due to highest oxidation temperature.

1 INTRODUCTION

PP oxidation has been now widely studied. Oxidation mechanism of the neat resin have been characterised thanks to academic works. On an other way, industrial works have focussed on the anti oxidant effects and stabilisers efficiencies in polymer stabilisation. But till now, it is still difficult to predict and to simulate polypropylene life time, because of the relative youth of the products, the constant evolution of the stabilizing packages and also life time expected for more than 100 years. Moreover, polypropylene oxidation is based on an induction time degradation scheme. This means that some of the material properties, such as mechanical tensile properties, remain constant during the induction period. In other words, this turns very difficult the way to monitor the degradation process during this induction period, and then to try to predict this induction period.

It is now admitted that the induction period is strongly linked to anti oxidant depletion time. As a consequence, a quantitative approach of remaining anti oxidants in the material could lead to a remaining life time. But, direct anti oxidant assessment is most of the time difficult and hard to obtain, for instance using chromatographic techniques.

That's why in this study a thermal analysis approach is investigated to try to monitor the degradation process during the induction period. This method is very easy to use, fast and can lead to very good and sometimes surprising results. This technique can be used to characterise the initial state of the material and its behaviour along the degradation. Moreover, some thermally reactive phenomena occurring during degradation process can also be highlighted (secondary effect). The material morphological behaviour can be monitored such as cristallinity and glass transition temperature. The degradation state can be assessed by isothermal (Oxidative Induction Time OIT) or dynamic (Induction Temperature, T_{ind}) measurements.

To go further, two sample shapes are investigated, a thick one, a geomembrane, and a thinner one, fibers from a geotextile.

In each cases, thermal results are always compared to mechanical tensile tests, to be closed to normalisation testing procedures, and also to direct macroscopic characterisation.

2 MATERIAL

The polypropylene fibers have been supplied by Polyflet. This is an isotactic polypropylene. The initial molar mass is 150kg/mol. The As Received fibers are stabilised by a phenolic additive. The stabilising package for the "stabilised fibers" is made of an Hindered Amine, added at 0.75%.

Two other geomembranes are used, commercially called "flexible Polypropylene". They are stabilised against oxidation.

3 EXPERIMENTAL

Mechanical Tests are carried out on a SWICK tensile machine, using a 50 mm/min tensile speed and a 10kN load sensor (for membrane) and 100N (for fibers)

DSC experiments are carried out on a TA DSCQ100 apparatus. Heating rate is fixed at 10K/min, and flow rate at 50 ml/min. Melting is observed under nitrogen gas flow. T_{ind} is measured under oxygen gas flow. Sample mass is fixed at about 10 mg for membranes and 3 mg for fibers. The ASTM D3895-98 is used to perform OIT tests.

Ventilated oven ageing are performed using Memmert ULE 400 oven, with a $\pm 1^\circ\text{C}$ regulation.

Ageing under high oxygen pressure is built as regard to SCHROEDER (2000), SCHROEDER (2002), and prEN ISO 13438:2002.

4 MECHANICAL RESULTS

Whatever ageing conditions, mechanical results always follow the same scheme (figure 1).

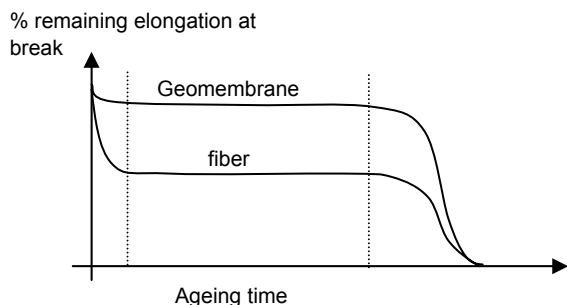


Figure 1 : schematic representation of the remaining elongation at break versus ageing time for geomembrane and fibers

This curve is divided into 3 parts.

- The first one may be very short, and even shorter when ageing temperature increases. The height of the step depends on the way the material is manufactured, thick (geomembrane) or thin (geotextile). This phenomenon is attributed to an annealing effect of the material and will be discussed in this paper.
- The second phase is a plateau. The duration of this plateau corresponds to the time the stabilizing package is protecting the material. This doesn't mean that the material doesn't degrade but this means that reactions that occur at the microscopic scale aren't damaging enough to induce mechanical loss. At this time, it can be remembered that several studies have highlighted that mechanical tensile tests is one of the most sensitive technique linked to chain breaking in polypropylene degradation FAYOLLE (2000). Elongation at break is the most reliable parameter. It is more sensitive than commonly used FTIR, since the ductile brittle transition is observed before carbonyl detection by FTIR. This ductile brittle transition have been linked to some molar mass measurements, and a critical molar mass have been postulated FAYOLLE (2003).
- The last part corresponds to the end of anti oxidant efficiency and the beginning of strong degradation of the polypropylene resin. Microscopic degradation and chain breaking are large enough to make a strong decrease of the macroscopic properties.

The aim of this paper is to investigate the first two stages, annealing and anti oxidant depletion time, versus material shape and exposure conditions, by means of the thermal analysis approach.

5 ANNEALING

Depending on the chemical nature of the polymer, the way the products are manufactured and the products shape, some annealing effects may often occur during material ageing. It is explained as a slow evolution of the material to a thermodynamic state of lower energy. At the microscopic scale, annealing of semicrystalline polymers is not yet solved. It can be attributed to a slow recrystallisation of the crystallites, or a rearrangement of the crystallites. This annealing time is sometimes qualified as a physical ageing of the material. Kinetics of evolution are relatively slow at room temperature but may noticeably rise with temperature. Accelerated ageing temperatures are high, and consequently, annealing time can be very short, and shorter than oxidation process, as shown on figure 1.

Two different behaviours have been observed:

In the case of the geomembrane, tensile samples have been taken along the manufactured axis (X) and perpen-

dicular to the manufactured axis (Y). A small difference of the tensile curves occurs in the reference sample, between the X and Y direction. Elongation at break is slightly shorter for the Y sample, but stress at break is the same. Making the same tests from a poorly aged sample, tensile curves obtained from the X or Y direction are the same and closed to the Y tensile curve of the reference sample.

As a matter of fact, the initial material may appear slightly oriented in the X direction, and this orientation quickly disappeared when the membrane is exposed to temperature. This phenomenon is more pronounced when running a DSC test (figure 2).

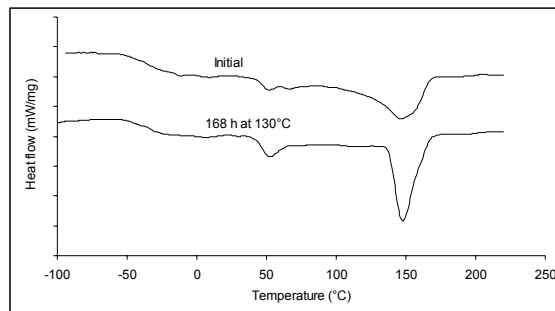


Figure 2: thermograms of a geomembrane in its initial state and aged 168 hours at 130°C

A large melting endothermic peak is observed on the initial material. This is the consequence of a large distribution of crystallite nature in the material. An imperfect crystallisation of the polymer is caused by a slight orientation in the X direction during manufacture. When the membrane is poorly aged, this large endothermic peak is quickly turned into a thinner endothermic peak. The large crystallite distribution due to partial orientation becomes thinner when the material is heated. In this case, it can be assumed that the crystallites homogeneity is increased. By heating the material, even under its melting temperature, molecular motion is increased and high enough to turn the crystallites into rearrangement and to a more stable crystalline state.

In this case, it is important to note that even if mechanical properties are poorly affected by the annealing effect, strong morphological and crystalline behaviour can be observed by DSC.

When studying polypropylene fiber ageing by mechanical tests, a drop of more than 40% of the initial properties is observed during annealing. As regard to standard, a material is considered not acceptable when its mechanical properties are divided by 2. In other words, when about 50% of the material initial property is lost. In the case of the fibers, the annealing phenomenon seems important enough to disqualify the material as regard to durability.

This annealing process stands with the same mechanical amplitude at 130°C, 110°C and even 80°C. But, DSC is blind as regard to this annealing process, even if mechanical effects are high. Thermograms of the reference and annealed samples are nearly the same. To go further, it could be interesting to really quantify this annealing phenomenon, when using textiles and not fibers.

Moreover, ageing the material under some nitrogen atmosphere at different temperature could give some important information on the kinetic of annealing and its weight as regard to chemical oxidation process.

6 DEGRADATION

Even if it is a very sensitive technique, mechanical test is blind during the induction period. The aim of using the thermal analysis approach is to investigate this induction

period (after annealing), and to try to quantify the phenomena that occurs during this time. The cases of the fibers and geomembranes will be treated successively since they correspond to two different ways of ageing.

6.1 Polypropylene fibers

6.1.1 Lifetime criterion

OIT measurement of the fibers is zero in the case of the AR fibres as well as the stabilised fibers. This test is inappropriate to monitor the material ageing in this standard configuration. The High Pressure OIT could certainly give some more informations THOMAS (1992) but this technique is less common than classical DSC. That's why, a different DSC approach has been used in this case in order to assess the material evolution during the mechanical induction period. It is based only on the evolution of the Tind. Tind is analysed to be the Temperature at which the neat resin is oxidised, that is the temperature at which anti oxidant are totally consumed or depleted.

According to the normalisation project for oxidative resistance of geotextile, ageing polypropylene at 80°C, in an aqueous medium and under high oxygen pressure has been investigated and compared to results obtained in ventilated oven at 110, 130 and 140°C.

In order to define a life time criterion for oxidation, it has been considered that the oxidation process follows a binary scheme, with two different stages. The first one consists in the antioxidant depletion time: the polypropylene resin remains nearly undamaged, while anti oxidant are depleted. At the end of this period, and just before the second one, the material is a neat resin, without any stabiliser but not yet damaged. The second stage corresponds to the degradation of the neat resin. The time when the material goes from the first stage to the second one is considered as the induction period of the material.

For this assessment, The induction temperature of the neat resin, undamaged and without any stabiliser had to be measured. Stabilisers have been extracted from the AR fibers using a hexane-methanol-chloroform (4:1:1) mixture at 50°C for 40 hours. Those fibers have been characterised by DSC and Tind = 175 °C. This induction Temperature will be called TindEX till the end on the paper. This temperature corresponds to the induction temperature of the neat resin without any stabiliser.

6.1.2 Oven ageing

Figure 3 shows the evolution of the Tind versus ageing time at various temperature. A linear decrease is observed. The induction time is taken at the intersection of the linear Tind versus time and TindEX.

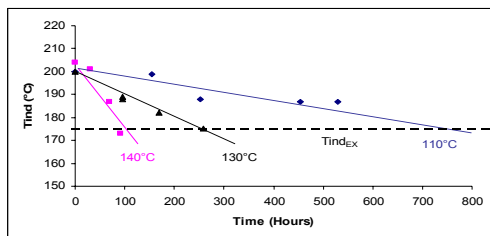


Figure 3: Evolution of Tind versus ageing time at 105, 110 and 130°C

Induction times measured by this thermal approach are summarised on table 1 by comparison to the mechanical tensile tests induction periods. A good trend is observed, but induction measured by mechanical tensile tests is always shorter than the thermal one. This fully agree with the fact that the mechanic approach is one of the more sensitive technique.

Table 1: Induction times measured by DSC and tensile tests

Temperature	Induction DSC	Induction mecha
110°C	640 h	400 h
130°C	190 h	150 h
140°C	120 h	

DSC appears then as a good tool to study the material evolution during the induction period. The linear behaviour of Tind versus time is also a good tool for induction period prevision. At least 3 or 4 measurement points are needed at the beginning of the ageing procedure to ensure a reliable linear fit and then a induction period prevision in those conditions.

6.1.3 Stabiliser dissolution

Fibers have been aged under high oxygen pressure in a liquid medium as regard to the normalisation project. When fibers are immersed, stabilisers depletion may be leaded by a novel parameter. In the case of oven tests, stabilisers depletion is made of consumption by the oxidation reaction, degradation due to ageing and loss by evaporation. In the case of immersion tests, stabilisers depletion is made of consumption by the oxidation reaction, degradation due to ageing and loss by dissolution in the liquid. On the one hand it is reported that evaporation is most of the time very slow (neglected in accelerated ageing tests), but on the other hand, dissolution of stabiliser can be a major phenomenon.

The aim of this part is to investigate thermal analysis to follow stabilisers depletion and to try to decorrelate the consumption rate of stabilisers from the dissolution rate.

The test consist in immersing the fibers in a liquid media (pH=10) at 80°C, and applying a nitrogen pressure (5MPa) instead of an oxygen pressure to prevent from any oxidation process. The evolution of Tind versus time^{1/2} is represented on figure 4.

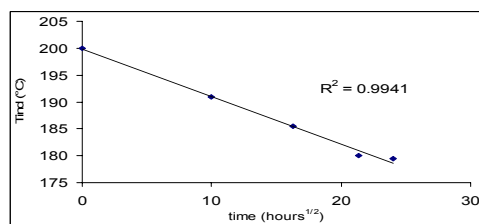


Figure 4 : Evolution of Tind in an aqueous liquid under nitrogen atmosphere

A linear decrease is observed. Tind is monitored by a time square root behaviour that is characteristic of a diffusion controlled process. Then, the time needed to reach TindEX stands for the time needed to obtain a neat resin without any stabiliser. So this time correspond to the time needed to extract and dissolve the stabilisers from the core of the fiber. Since this is a diffusion controlled process, it can be assumed that dissolution is faster than migration of stabiliser from the core of the fiber to the surface.

The same test have been performed by applying a nitrogen pressure of 0.1MPa, instead of 5 MPa. The evolution of Tind is strictly the same as the previous one. This means that the pressure applied has no effect on the kinetic of stabiliser dissolution into the liquid media. As a conclusion at least about 580 hours are needed to extract all the stabiliser from the core of the fibers.

6.1.4 High oxygen pressure ageing

In order to assess the effect of the parameter "liquid" on the ageing behaviour, 3 tests have been carried out.

- The first one stands for the experimental conditions as reported by the normalisation project,

80°C, 5MPa oxygen pressure and pH=10. This test will be called HPalk, for high pressure alkaline medium.

- The second test is the same as the previous one but the alkaline liquid has been substituted by pure water at pH=7. This procedure will be called HPwat, for High Pressure in a water liquid.
- The third test is performed at 80°C under 5MPa oxygen pressure but without any water. The fibers are aged in a dry environment. This test will be called HPdry, for High Pressure in a dry medium.

Evolution of Tind versus ageing time and ageing conditions are reported on figure 5.

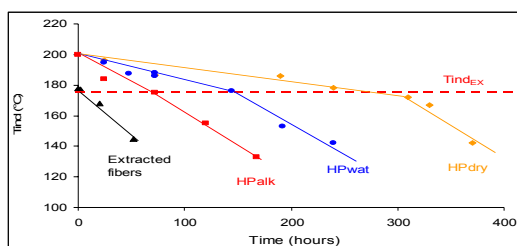


Figure 5 : Evolution of Tind under high oxygen pressure

This evolution is divided into 2 linear parts, when Tind is above or under TindEx. The time needed to reach TindEx stands for the induction period of the material. As previously mentioned, this is the time needed for the whole anti oxidant depletion.

When Tind is above TindEx, the slope of Tind versus ageing time strongly depends on the way the samples are aged. In an alkaline aqueous media, the slope is higher than in water and much higher than in a dry environment. This means that the aqueous medium has a strong influence on anti oxidant depletion time, and more when pH is high. This could be explained by the whole stabiliser dissolution (increased in the alkaline liquid: phenols are easier solubilised) that could increase strongly anti oxidant depletion. But, the induction time measured by DSC (HPalk) is about 1/10th as the time for the whole diffusion/dissolution. So this diffusion/dissolution phenomenon may not be a major effect in fiber damaging. Consumption seems to be the major phenomenon.

When Tind is lower than TindEx, the slope of Tind versus ageing time depends no more on the aqueous liquid. All the lines are parallels and closed to the oxidation of the neat resin. A liquid has no effect on the neat resin oxidation by comparison to a dry medium.

As a first conclusion, when samples are stabilised with phenolic additives, thermal analysis have shown that an aqueous liquid medium has a strong influence on the material ageing process, and a stronger influence in some alkaline environment. After stabiliser depletion, the neat resin oxidation doesn't depend on the medium the fibers are immersed in. Oxidation rate may only depends on Temperature and oxygen pressure

Table 2 summarises the induction period measured by thermal analysis, and mechanical tensile tests.

Table 2: Comparison of induction period obtained by DSC and tensile tests

	HPalk	HPwat	HPdry	Diff/disso
DSC	72 h	140 h	240 h	580 h
Mecha	48 h	90 h	200 h	

A good trend is obtained between the two kinds of results, even if induction periods from tensile tests are smaller than DSC ones.

During characterisation of the fibers under nitrogen gas flow, an exothermic peak has been identified in the same temperature range as the melting endothermic peak. This exothermic peak appears at the end of the induction period and grows till the end of the ageing process. Previous studies have shown that ageing polyolefin under high oxygen pressure could lead to the formation of an excess of hydroperoxyde MUELLER (2003b). In an other side, in order to monitor some hydroperoxyde cured coated systems, MALLEGOL (2001) has shown that a hydroperoxyde quantification was detectable and easy to measure by DSC.

In order to find out that the exothermic peak could be attributed to an excess of hydroperoxyde in the fibers, sample have been treated by SO₂ during 24 hours (SO₂ is a strong peroxide killer). After this treatment, a second characterisation of the fibers has been performed. It doesn't show any longer the presence of the exothermic peak. Figure 6 shows both of the thermograms, the sample before and after treatment.

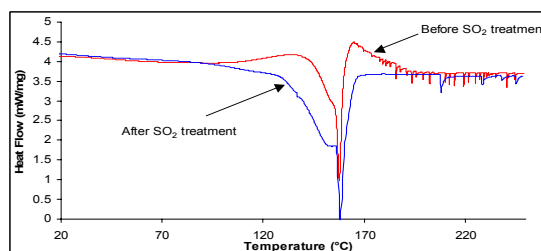


Figure 6: thermograms of high oxygen pressure aged fibers, before and after SO₂ treatment.

As a conclusion, by means of this thermal approach, it can be shown the formation of an excess of hydroperoxyde due to the high oxygen pressure. Moreover, by means of a previous calibration of the area of the exothermic peak, it could be possible to monitor peroxide accumulation during the high oxygen pressure test.

6.1.5 HAS characterisation during ageing

When fibers are stabilised with HAS, the evolution of Tind versus ageing time is reported on figure 7.

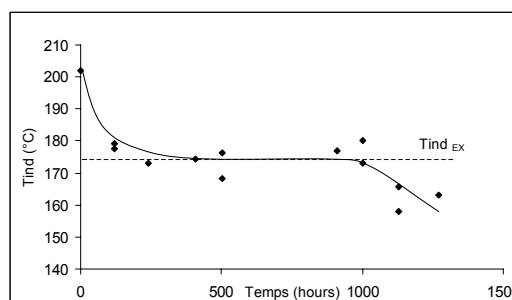


Figure 7: Evolution of Tind for HAS stabilised fibers, in HPalk ageing conditions

Tind reach quickly TindEx, but it doesn't cross the line TindEx. It can be noticed that the previous linear evolution of Tind is turned into a more curved one. In other words, HAS tends to turn the linear behaviour of Tind to a more curved, and quite exponential like shape. Using an inverse interpretation, the curved shape of Tind versus ageing time can be interpreted as the presence of HAS in the stabilizing package. Till now, it is still difficult to explain such a Tind evolution. Here is one assumption. It can be assumed that HAS are degraded during Tind measurement process. So, they are no detectable by the technique. But, at the ageing temperature, they are still efficient to stabilise the fibers. As a consequence, the Tind measurement shows a

neat resin (since HAS are destroyed during measurement : $T_{ind}=T_{indEX}$). The neat resin is not damaged since it is stabilised at the ageing temperature. So, the induction period must not be taken at the time when T_{ind} reach T_{indEX} by higher values, but at the time when T_{ind} decreases from T_{indEX} to lower values. An induction period about 950 hours is obtained.

6.2 Geomembrane

The first geomembrane has been aged in ventilated oven at 105, 110 and 130°C. In each cases, T_{ind} and OIT have been measured. Figure 8 shows data recorded at 130°C.

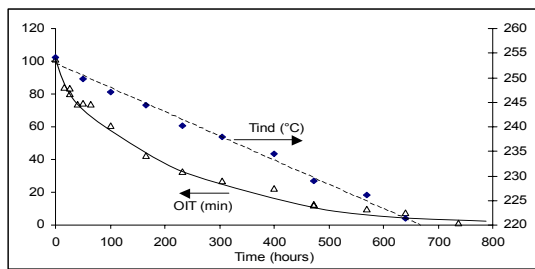


Figure 8: T_{ind} and OIT versus ageing time, aged at 130°C

A linear decrease of T_{ind} is observed versus ageing time, whatever the oxidation temperature. This linear behaviour is very important since it allows the user to explore the material evolution during the induction period.

The slope of each lines has been calculated. As mentioned earlier, this linear behaviour could mean that the material is stabilised by a phenolic package. Results are reported in table 3.

Table 3: Slope of T_{ind} versus ageing time

Temperature	Slope °C/hour	R ²
105	-0.0091	0.958
110	-0.0187	0.917
130	-0.0482	0.992

An activation energy of the process has been calculated, assuming an arrhenian behaviour all over this temperature range, $E_a=82$ kJ/mol $R^2=0.993$. At this time, we are not allowed to make some extrapolation of the data to room temperature for many reasons. First of all, previous studies have shown that activation energy of polypropylene is not constant from room temperature to 130°C A-CHIMSKI (1997). It has been observed a break at 80°C. E_a is constant before 80°C and above 80°C due to a change in hydroperoxyde decomposition. This decrease of E_a versus ageing temperature have even been highlighted with other polyolefins DING (2000), DING (2001).

Nevertheless, we think that this approach is a good way to study remaining anti oxidant and to monitor ageing process, but it may be difficult to use this approach for direct sample characterisation and room temperature extrapolation.

The evolution of OIT data versus ageing time is exponential like. This kind of behaviour have already been observed by MUELLER (2003a) in the case of HDPE geomembranes. The exponential behaviour can be written as $OIT(t)=OIT(t=0).exp(-k_{eff}.t)$. Table 4 summarise the dependence of k_{eff} versus ageing temperature. k_{eff} is measured by taking the slope of $\ln(OIT(t)/OIT(t=0))$ versus time. R^2 is the correlation coefficient for the fitted line.

Table 4: Calculated values of k_{eff}

Temperature	k_{eff} hours-1	R ²
105	0.00088	0.978
110	0.00128	0.992
130	0.00402	0.942

Assuming that k_{eff} follows an arrhenian relationship with temperature, the activation energy has been calculated : $E_a=77$ kJ/mol $R^2=0.998$. Both activation energies obtained from T_{ind} and OIT have the same order of magnitude. This could mean that both measurements are related to the same process.

As a conclusion, this activation energy is related to the anti oxidant depletion in the range of 105-130°C. A large out of range extrapolation may appear very hazardous.

6.3 Correlation between OIT and T_{ind}

Some previous study MASON (1998) has assumed that the primary thermally induced oxidation reaction that occurred in DSC was given by : $RH+O_2 \rightarrow R^\bullet+HO_2^\bullet$, where RH is an undamaged polymer chain, R^\bullet is a polymer free radical and HO_2^\bullet is a hydroperoxyde free radical. Even if writing so simply the oxidation reaction may be questionable, the whole discussion around this equation remains reliable. Authors have assumed that this reaction was the same, while carrying out a T_{ind} measurement or an OIT test. Both measurements are made in the melted state, and occur at similar temperatures. As a matter of fact, activation energy of the reaction is the same on both point of view. This activation energy stands for the main parameter of this equation. A high activation energy means that the reaction may be very slow, and then the degradation of the material will take a very long time. At the contrary, a lower activation energy means that the reaction can be faster, and that chemical and/or mechanical failures will occur sooner. This activation energy is strongly linked to the stabilizing package. Consequently, the higher the activation energy, the more efficient the stabilizing package: the material is well protected. More than this, while the material is aged, the material will be protected as far as activation energy remains high. A decrease of this energy during the ageing process could mean that the stabilizing package efficiency is decreasing, and that the material is less and less stabilized against oxidation.

It must be remembered that this efficiency is measured in the melted state. So, the activation energy of the reaction stands for efficiency of the stabilisers at high temperature, and cannot be applied and extrapolated to room temperature conditions. But, if the stabilising package is damaged during ageing, this will appear clearly on the high temperature characterisation. In the same way as OIT and T_{ind} , E_a is an indirect measurement of anti oxidant efficiency, and it is not reliable to used it to extrapolate data.

MASSON (1998) has proposed an equation, that linked OIT, T_{ind} , the heating speed α for DSC run, the isothermal temperature T_{iso} at which OIT is performed and E_a .

$$OIT = \frac{1}{\alpha} \cdot \exp\left(-\frac{E_a}{RT_{iso}}\right) \int_{T_0}^{T_{ind}} \exp\left(-\frac{E_a}{RT}\right) \cdot dT \quad (1)$$

This equation hasn't been used in this paper to link OIT and T_{ind} but it has been used to calculate E_a while samples are under ageing.

The evolution of E_a calculated using equation 1 is reported on figure 9. E_a is nearly constant during the ageing process whatever the ageing temperature, 130, 110 or 105°C. Then E_a drops when ageing time approach the mechanical induction time.

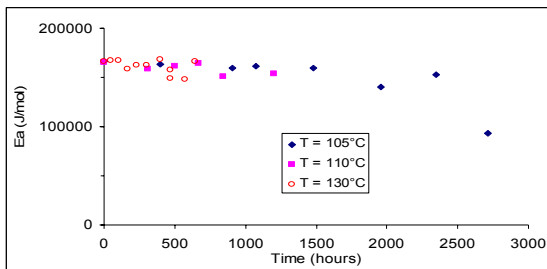


Figure 9: E_a of oxidation reaction calculated from equation 1, in the case of phenolic stabiliser

The fact that E_a is independent of the oxidation temperature means that anti oxidant are as efficient at 105°C than they are at 130°C.

During the ageing procedure, anti oxidant are consumed but E_a is constant. This means that stabiliser efficiency is not linked to the remaining stabiliser concentration.

The correspondence in the drop of E_a and tensile properties means that when anti oxidant aren't efficient any more, the material is immediately and strongly damaged. Moreover, this means that the auto-oxidation period (which correspond to the time to reach the onset of polymer degradation HSUAN (1998)) of the polymer is very short, and nearly reduced to 0 in those ageing conditions.

By comparison, an other membrane have been studied. In this case, an exponential decrease of T_{ind} versus ageing time have been observed. As regard to results obtained from fiber ageing, it can be assumed that this membrane is stabilised by a HAS based package. On figure 10 is reported the calculated activation energy as previously described.

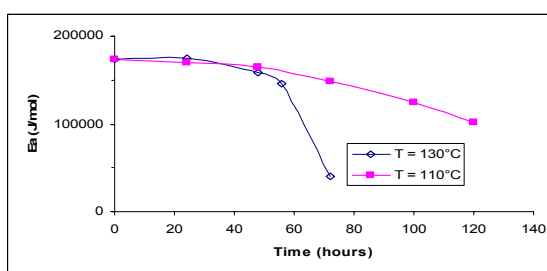


Figure 10: E_a of oxidation reaction calculated from equation 1, in the case of HAS stabiliser

E_a decreases more and more as far as the ageing process occurs. This observation is still true for both of the ageing temperature. It can be assumed that anti oxidant efficiency to protect the material decreases with ageing time. HAS may then be damaged during the ageing procedure, so that they can't stabilise the material enough against oxidation, in this range of ageing temperature (110-130°C). It is now admitted that HAS are efficient at lower temperature but also that their efficiency decreases with increasing ageing temperature. Our experimental results may verify this trend.

7 CONCLUSION

When trying to predict polymer life time under accelerated conditions, the real question must always be : " how reliable are the accelerated ageing conditions as regard to natural ageing?"

The main problem is that we don't know exactly what the natural ageing phenomena are made about. So, we have to be very sensitive and aware about the way we aged samples, and about the way the material is damaging.

In this study, we have highlighted that thermal analysis could be a very good tool so as to monitor polymer ageing, and the different stage in the material degradation. We have put the stress on the annealing effect as well as the induction period. By DSC, it is possible to predict some induction period when sample are stabilised with a phenolic additive, with the assumption that there is a linear decrease of T_{ind} . Then, we have been able to observe some secondary effect of ageing condition such as the excess of hydroperoxyde in polyolefin due to the high oxygen pressure. Anti oxidant efficiency during the ageing process has been monitored and a difference between a phenolic or a HAS package have been observed.

As a conclusion, coupled with a mechanical characterisation of the material, DSC appears to be a very good tool in the monitoring of polymer ageing. Further investigations are needed to extrapolate data to room temperature.

8 REFERENCE

- Achimsky L., Audouin L., Verdu J., Rychly J., Matisova-Rychla L. (1997) On a transition at 80°C in polypropylene oxidation kinetics, *Polymer Degradation and Stability*, 58(3), pp 283-289
- Ding S.Y., Ling M.T.K, Khare A.R, Woo L. (2000) Durability of a reference material over diverse conditions, *Thermochemica acta*, 357-358, pp 147-153
- Ding S.Y., Khare A.R., Ling M.T.K, Standford C., Woo L. (2001) Polymer durability estimates based on apparent activation energies for thermal oxidative degradation. *Thermochemica acta*, 367-368, pp 107-112
- Fayolle B., Audouin L., Verdu J. (2000) Oxidation induced embrittlement in polypropylene -- a tensile testing study *Polymer Degradation and Stability*, 70(3), pp 333-340
- Fayolle B., Astruc A., Audouin L., Bartolomeo P., Verdu J. (2003) Ductile-brittle transition induced by oxidative chain scission in polypropylene, proceedings of MODPOL 2003, Brastislava, pp 41
- Hsuan Y.G., Koerner R.M. (1998) Antioxidant depletion lifetime in HDPE geomembranes, *Journal of geotechnical and geoenvironmental engineering*, 124(6) pp 532-541
- Mallegol J., Gonon L., Commereuc S., Verney V. (2001) Thermal (DSC) and chemical (iodometric titration) methods for peroxides measurements in order to monitor drying extent of alkyd resins, *progress in organic coatings*, 41, pp 171-176
- Masson L.R., Reynolds A.B. (1998) Comparison of Oxidation Induction Time measurements with values derived from Oxidation Induction Temperature measurements for EPDM and XLPE polymers, *Polymer Engineering and science*, 38(7), pp 1149-1153
- Mueller W., Jakob I. (2003a) Oxidative resistance of high density polyethylene geomembranes, *Polymer Degradation and Stability*, 79, pp 161-172
- Mueller W., Buettgenbach B., Jakob I., Mann H. (2003b) Comparison of the oxidative resistance of various polyolefin geotextiles, *Geotextiles and Geomembranes*, 21(5) pp 289-315
- Schroeder H.F., Bahr H., Herrmann P., Kneip G., Lorentz E. Schmuecking I. (2000) Durability of polyolefine geosynthetics under elevated oxygen pressure in aqueous liquids, proceedings of EUROGEO2, Bologna, pp 459-463
- Schroeder H.F., Bahr H., Kneip G., Lorentz E. Schmuecking I., Zeynalov E.B. (2002), Resistance of polyolefin geosynthetics to oxidation: a new accelerated test working at elevated oxygen pressure, *Proceeding of 7th International Conference on Geosynthetics*, Nice, pp1455-1458
- Thomas R.W., Ancelet C.R. (1992) High Pressure OIT for geomembranes, *Geotechnical fabrics report*, pp 12-13