

8. Results and discussion

8.1 The bottom edge ignition test

The untreated unsized polyester fabric burned out completely within 30 seconds. The vertical burn test results are presented in Appendix 12.2. The results show that excellent self-extinction times can however be achieved at relatively low add-on levels with the oxygenated hydrocarbon flame retardants. For example, dipentaerythritol requires an add-on of just above two percent to be effective as a flame retardant with a self-extinguishing time of approximately three seconds. Similar results were obtained when the fabric was treated with benzophenone and solid epoxy resin Epikote 1001 (oligomers of the diglycidyl ether of bisphenol A) from Shell Chemicals. The average self-extinguishing time for the latter was about one second, and for the former about three seconds. Interestingly, the add-on vs. self-extinction time curve for pentaerythritol starts to rise again above an add-on of about 20 percent, as shown in Figure 8.

These results imply that some of the oxygenated hydrocarbon flame retardants may be effective in an intermediate concentration range only. Such behaviour was previously also observed with hindered N-alkoxy amines (NOR-Hals) as flame retardants in polypropylene fabrics (Srinivasan *et al*, 1998).

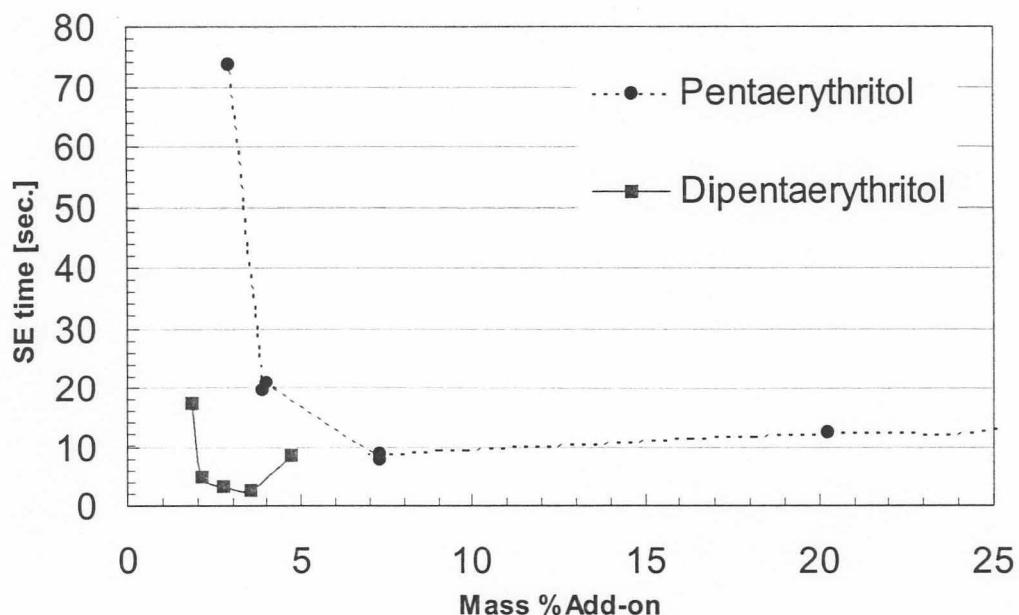


Figure 8: Self-extinguishing times versus add-on of Pentaerythritol and dipentaerythritol treated polyester fabric.

The same behaviour was also observed with phosphorous flame retardants and with phosphorous mineral filler synergism (Weil, 1992). Using vertical burn tests (NFPA 701), polypropylene fibre and films passed the test with the addition of 1% NOR-Hals, but when the concentration was raised to 10% the test was failed.

Figure 9 shows the self-extinguishing time and the mass percentage add-on for polyester fabric treated with Phloroglucinol and Inositol. The line represents the average values of the samples. The Phloroglucinol had an average self-extinguishing time of 1 second and the Inositol an average self-extinguishing time of 4 seconds.

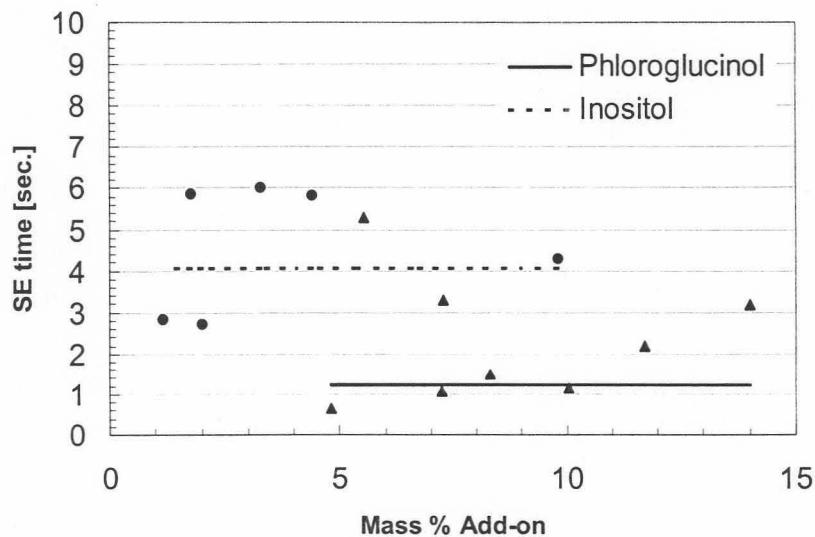


Figure 9: Self extinguishing times versus add-on of Phloroglucinol and Inositol treated polyester fabric.

Figure 10 shows the self-extinguishing time and the mass percentage add-on for polyester fabric treated with 2-Furoic acid, Epikote 1001 and Benzophenone.

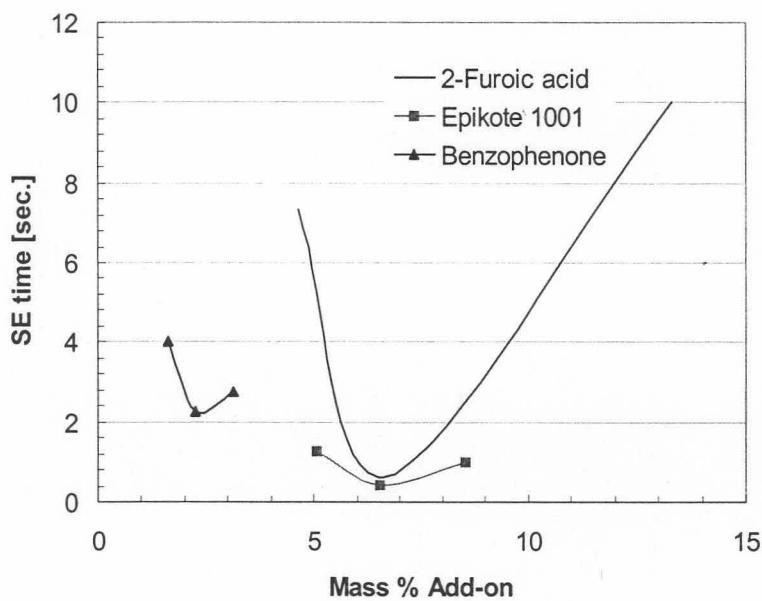


Figure 10: Self extinguishing times versus add-on of 2-Furoic acid, Epikote 1001 and Benzophenone treated polyester fabric.

From Figure 10 it is evident that some of the oxygenated hydrocarbon flame retardants exhibit the same behaviour, in that there is a parabolic relationship between the self extinguishing time and the mass percentage add-on. Benzophenone has an optimum mass percentage add-on at about 2 %, with a self-extinguishing time of 2 seconds. 2-Furoic acid and the Bisphenol A based resin Epikote 1001 both display almost the same self extinguishing time of less than one second at an mass percentage add-on level of 7.5 %. Figure 11 shows the results obtained with Benzyl phenyl ketone, Maltol and Benzoic acid. These oxygenated hydrocarbon compounds exhibit similar parabolic behaviour as Figure 12 show for Benzoyl benzoate and Diethylphthalate.

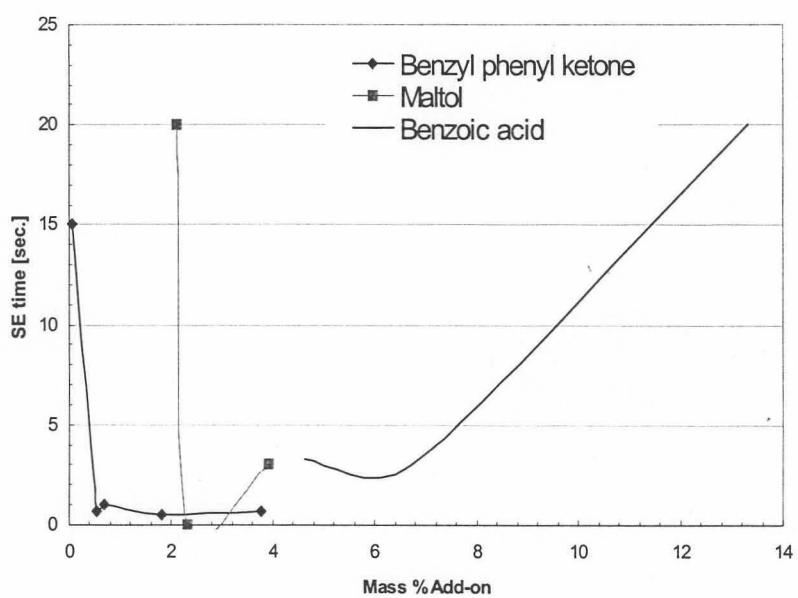


Figure 11: Self extinguishing times versus add-on of Benzyl phenyl ketone, Maltol and Benzoic acid treated polyester fabric.

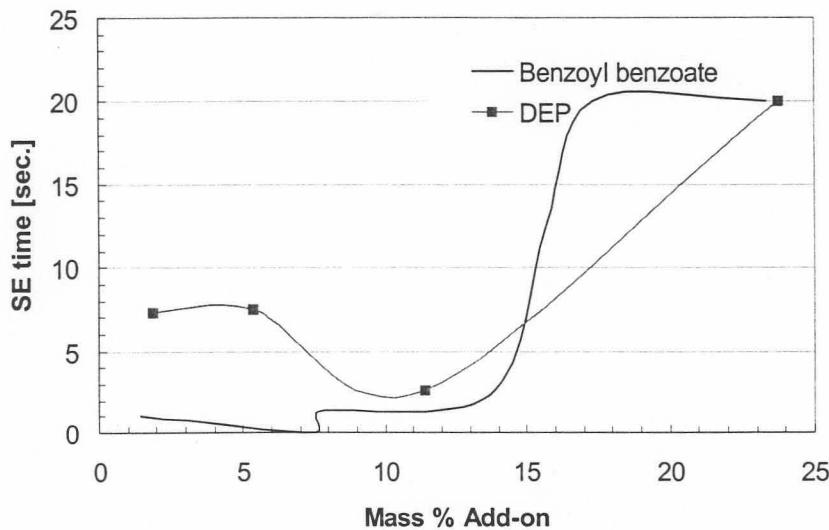


Figure 12: Self extinguishing times versus add-on of Benzoyl benzoate and Diethylphthalate treated polyester fabric.

8.2 The Puddle flame retardancy test

The purpose of this test was to determine whether the fabric ignited and burned in a situation where melt dripping was prevented. Unfortunately none of the treated samples tested, ignited. However, the untreated fabric burned for approximately 3 seconds. Puddle test results are compiled in Table 12. These reported values represent average values measured for the samples tested.

Table 12 : Results obtained from the Puddle Test

| Additive | Add-on [%] | Percentage Mass loss |
|-------------------|------------|----------------------|
| Pure PES | - | 11.5 |
| Pentaerythritol | 1.1 | 13.1 |
| Dipentaerythritol | 0.8 | 19.5 |
| Phloroglucinol | 3.2 | 13.7 |
| Isophthalic acid | 1.9 | 13.3 |

Surprisingly, as shown in Table 12, the pure polyester fabric showed a lower mass loss than the treated fabrics. The highest mass loss was observed with Dipentaerythritol as additive. During the vertical burn test the dipentaerythritol treated samples displayed fast melt dripping. These results suggest that the additive enhances the polymer solid to gas conversion.

8.3 The Face ignition flammability test

Table 13 shows the results obtained with the Face Ignition test on untreated fabric. The average values for the treated fabrics are shown in Table 14. Figure 13 to 17 show the fabric samples after the Face Ignition test.

Table 13 : Results of the Face Ignition Test for Pure Polyester fabric.

| Sample | Percentage mass Loss* | Area of Hole (mm ²) |
|--------|-----------------------|---------------------------------|
| A | 1.8 | 8931 |
| B | 1.3 | 5379 |
| C | 1.4 | Consumed completely |
| D | 3.4 | 3183 |

* Corresponds to the dripped mass collected below the sample. Mass consumed by combustion was assumed negligible.

It is observed during this test that the stretched fabric first contracts at the point where the flame impinges before melting starts. Then a hole starts to form that is surrounded by a ridge of molten polymer. The hole expands owing to an apparent outward pulling force. This force might arise from

build in stress caused by the oriented polymer chains in the fibres. An alternative explanation involves the surface tension forces in the molten polymer bead.

Table 14: Average results from the Face Ignition Tests.

| Additive | Percentage Mass add-on | Percentage mass loss | Hole Area [mm ²] |
|-------------------|------------------------|----------------------|------------------------------|
| Pure PES | - | 2.0 | >5800 |
| Pentaerythritol | 1.1 | 0.5 | 3000 |
| Dipentaerythritol | 0.8 | 0.6 | 6500 |
| Phloroglucinol | 3.2 | 0.4 | 5700 |
| Isophthalic acid | 1.9 | 1.5 | 6900 |

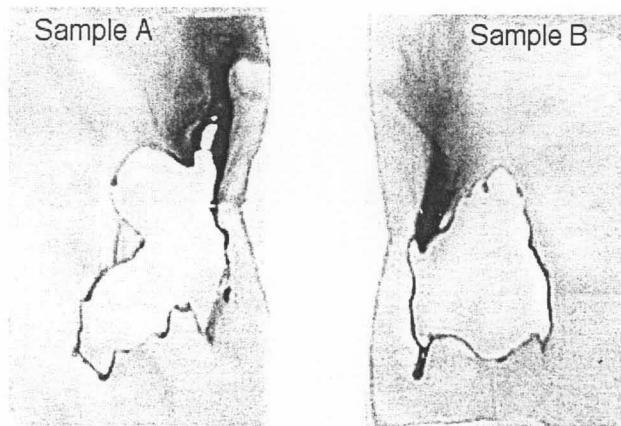


Figure 13: Untreated Polyester fabric samples after the Face Ignition test was applied.

Figure 13 shows some results after untreated samples have undergone the Face Ignition test. The black residue is char residue and/or soot from the combustion process. It deposited on the colder surfaces of the fabric during the burning process. It is evident that the shape of the burn hole is

neither uniform nor symmetric in shape. The damage to the fabric is inclined towards one side of the mounted sample. Molten polymer drops can be clearly seen on the sides of the hole, as well as a downward flow of polymer melt. The area of the hole in the untreated polyester fabric is also variable ranging from the smallest to the largest of all the samples tested.

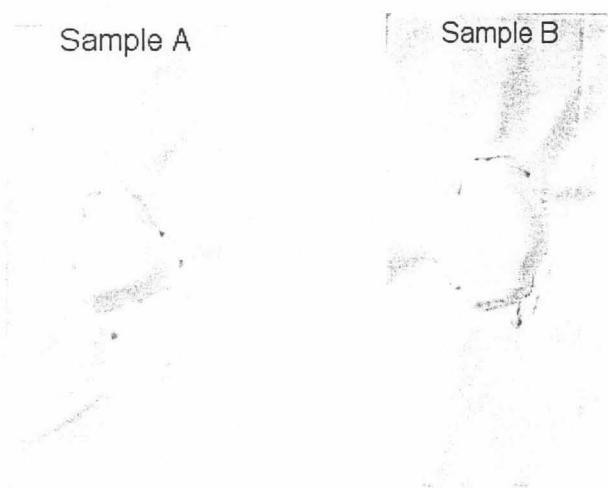


Figure 14: Polyester samples treated with Pentaerythritol.

In the case of the treated samples, there is less evidence of charring and the holes burned into the fabric have a more rounded shape. In addition, most of the samples did not ignite at all. The Pentaerythritol treated polyester samples from Figure 14 shows no black carbon residue whatsoever. Thus there was no discernable combustion of molten polymer during the test. In this case the hole in the fabric formed quickly and the molten polymer flowed away rapidly. On the fabric samples treated with Dipentaerythritol shown in Figure 15 there is almost no evidence of burning of the molten polymer melt. The Dipentaerythritol samples melted and burned slightly slower than the Pentaerythritol treated samples. Dripping of the molten polymer occurred at a fast rate.

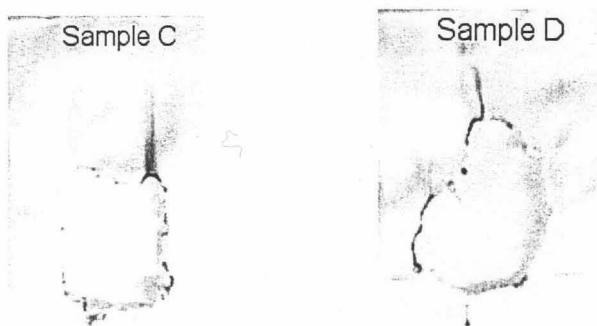


Figure 15: Polyester samples treated with Dipentaerythritol
On the fabric samples treated with Phloroglucinol shown in Figure 16 there is slight evidence of burning of the molten polymer melt. The Phloroglucinol samples melted and burned slightly faster than the Pentaerythritol treated samples. Dripping of the molten polymer occurred at a very fast rate as can be seen by the streaks of drops on the solid fabric.

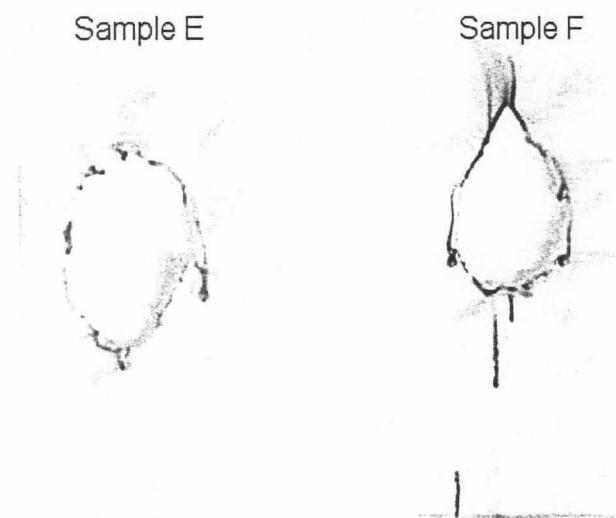


Figure 16: Polyester samples treated with Phloroglucinol.

On the fabric samples treated with Isophthalic acid shown in Figure 17 there is no evidence of burning of the molten polymer melt. The Isophthalic acid samples melted and burned slightly slower than the Pentaerythritol treated samples. Dripping of the molten polymer occurred at a moderately fast rate.

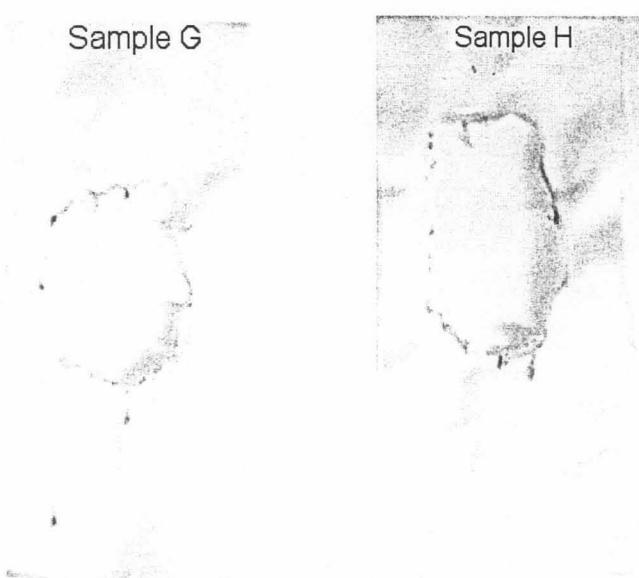


Figure 17: Polyester samples treated with Isophthalic acid

8.4 Polymer dripping test

Figure 18 depicts the results from a typical drip test. The average values obtained for the polymer drip test are shown in Table 15. Except for isophthalic acid, the presence of additives led to an increased tendency to drip. Pentaerythritol treated samples dripped at the fastest rate, almost 70 % faster than the observed rate for the untreated sample.

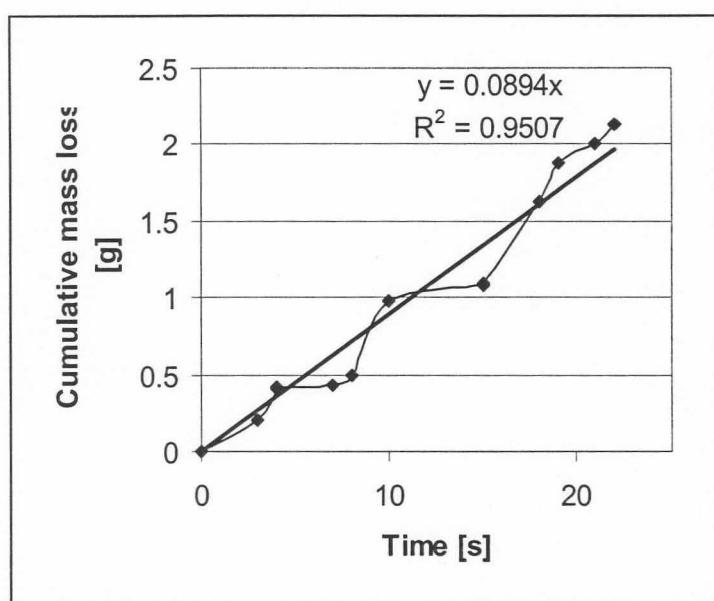


Figure 18: Typical drip test result for Pentaerythritol.

Table 15 : Results obtained from the polymer dripping tests.

| Additive | Correlation coefficient, R | Rate of dripping [g/s] |
|-------------------|----------------------------|------------------------|
| Untreated | 0.9289 | 0.077 |
| Pentaerythritol | 0.9433 | 0.130 |
| Dipentaerythritol | 0.9044 | 0.086 |
| Phloroglucinol | 0.8939 | 0.081 |
| Isophthalic acid | 0.8787 | 0.070 |

8.5 Differential Scanning Calorimetry and Differential Thermal Analysis

The results obtained for Differential Scanning Calorimetry are shown in Figure 19 for the untreated and the treated polyester fabrics. It is clear that the additives affect the shape and position of the melting endotherm peak for the flame retarded polymer. Interestingly, the additives shift the peak temperature to higher values. The observed heat of melting was approximately 52 kJ/g for all the samples.

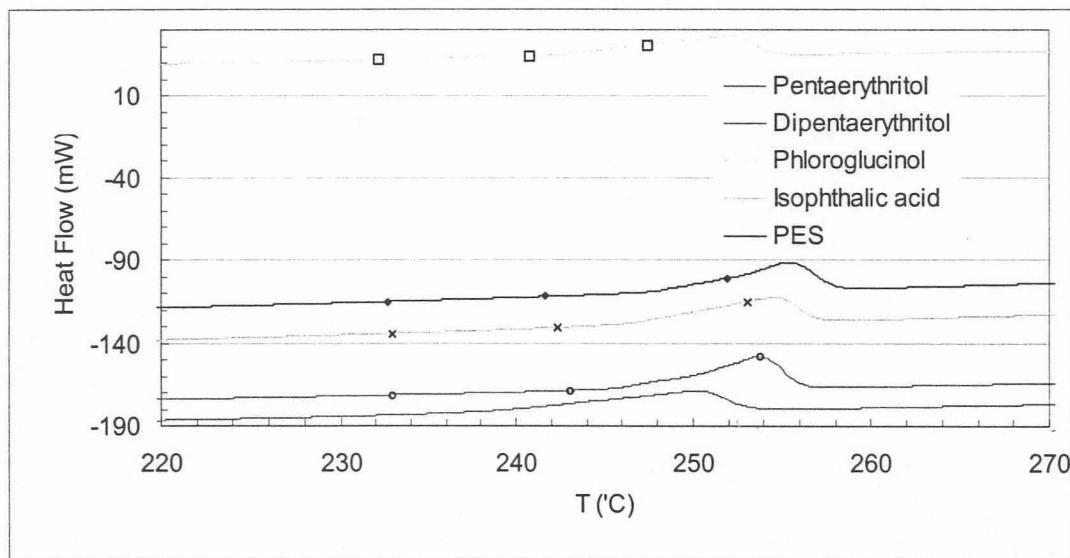


Figure 19: DSC curve of PES and treated PES samples.
Endothermic up, scan-rate of 10°C/min in oxygen atmosphere.

The results for the Differential Thermal Analysis (see Figure 20) confirm the results obtained with DSC. The melting onset-temperatures observed in the DTA were higher for treated samples than for the pure PES. The reasons for these observations are not currently understood.

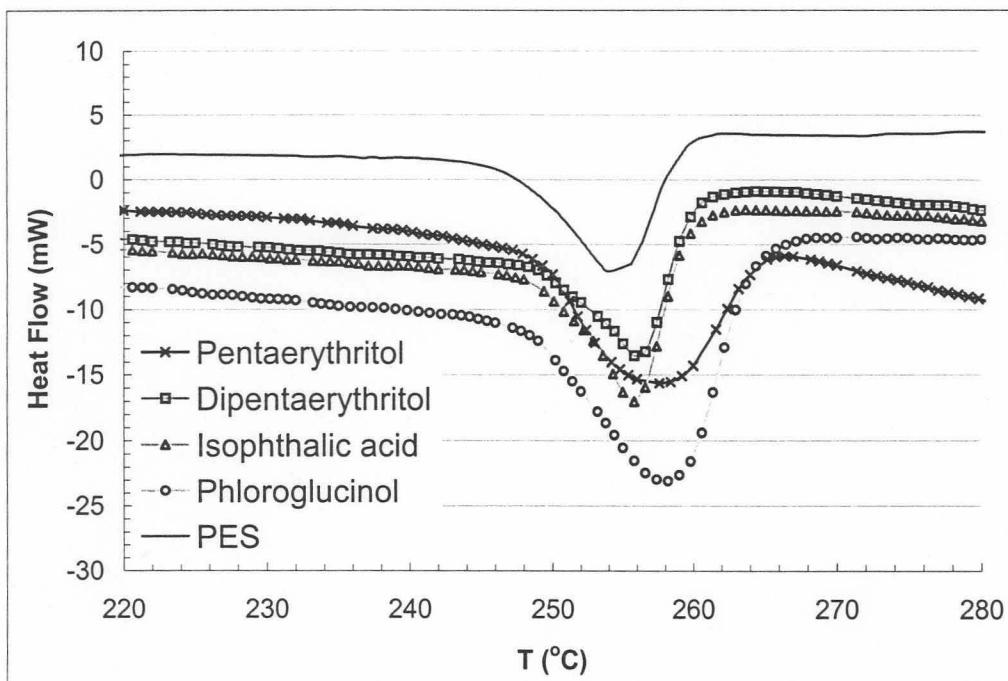


Figure 20: DTA curve of PES and treated PES samples.
Endothermic down, scan-rate of 10°C/min in nitrogen atmosphere.

8.6 Thermogravimetric Analysis

The results obtained with Thermogravimetric Analysis are shown in Figure 21. All samples show similar rapid volatilisation, with a mass loss of ca. 80% between 400°C and 420°C. Further mass loss occurs at a slower rate up to about 580°C and is complete for the untreated polyester fabric. The additives appear to affect this second degradation step. The presence of the additives also appear to reduce the rate of mass loss, and also results in higher levels of char residue. For example, the Isophthalic acid treated sample provided the best performance with respect to char formation, and Phloroglucinol treated samples degraded almost completely.

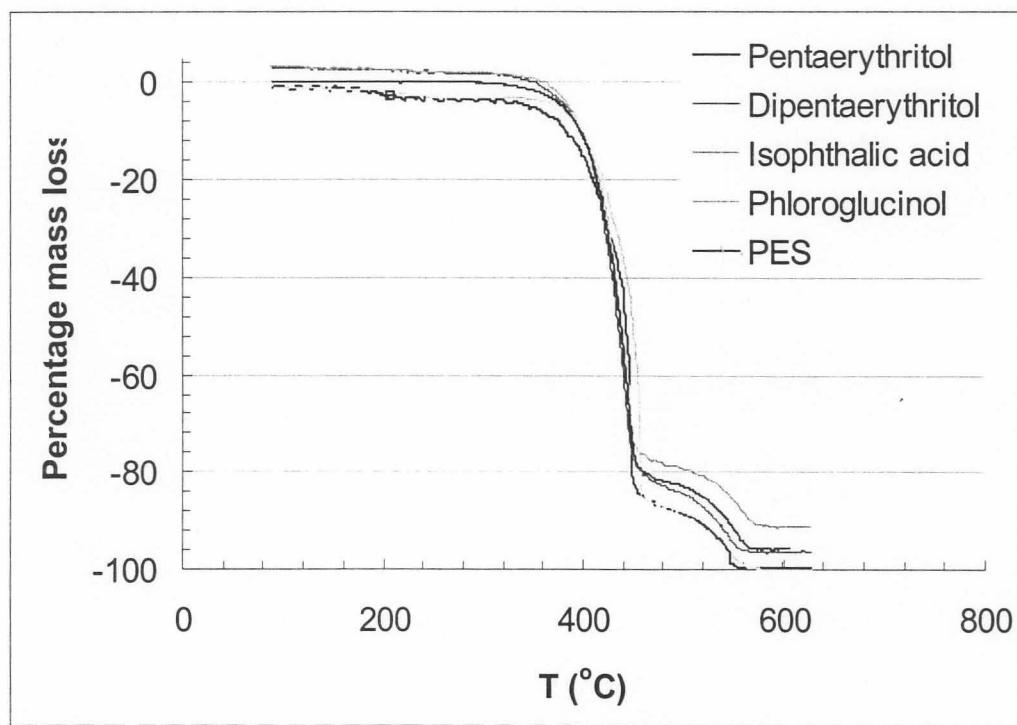


Figure 21: TGA results for PES and treated PES samples.

8.7 Rheometry

The loss modulus for the treated and untreated fabrics is shown in Figure 22.

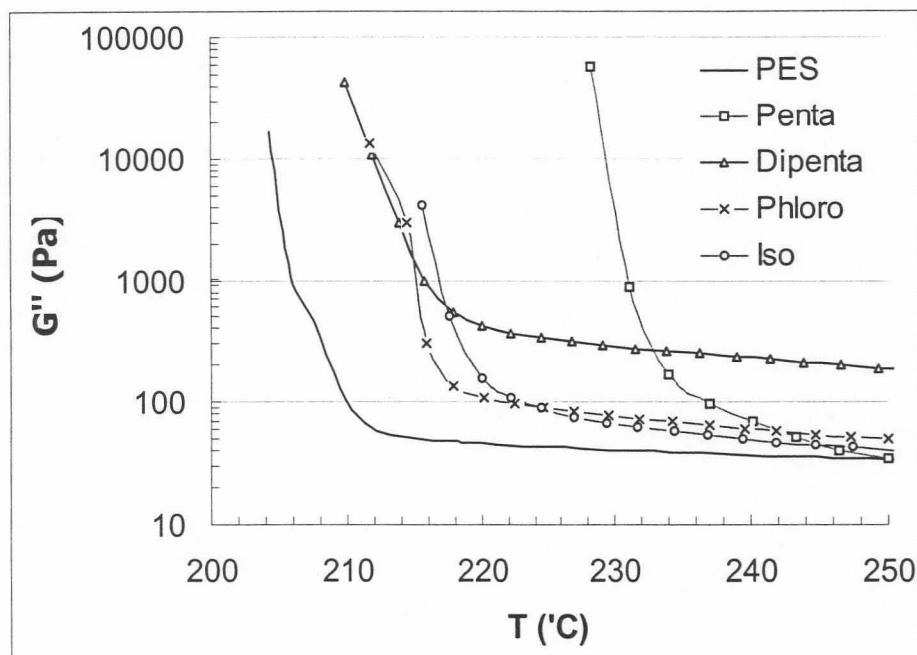


Figure 22: Loss modulus from parallel plate rheometry of PES and PES treated samples.

$G^*(\omega)$ is the frequency dependant complex dynamic modulus consisting of a real and complex part. $G'(\omega)$ is the real part that is in phase with the strain and is called the storage modulus. $G''(\omega)$ is the complex part called the loss modulus, defined as the ratio of the component 90° out of phase with the stress to the stress itself.

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

$G'(\omega)$ therefore measures the amount of energy stored and $G''(\omega)$ the amount of energy dissipated by the material.

It is therefore possible to say that in Figure 22 the sample treated with Pentaerythritol, which shows the highest loss modulus, is altered in such a way that a lot of energy is dissipated and very little recovered. The untreated fabric sample exhibits the lowest loss modulus.

Figure 23 shows the storage modulus of the storage modulus of the treated and untreated fabric samples. It strengthens the results from the loss modulus, as can be expected.

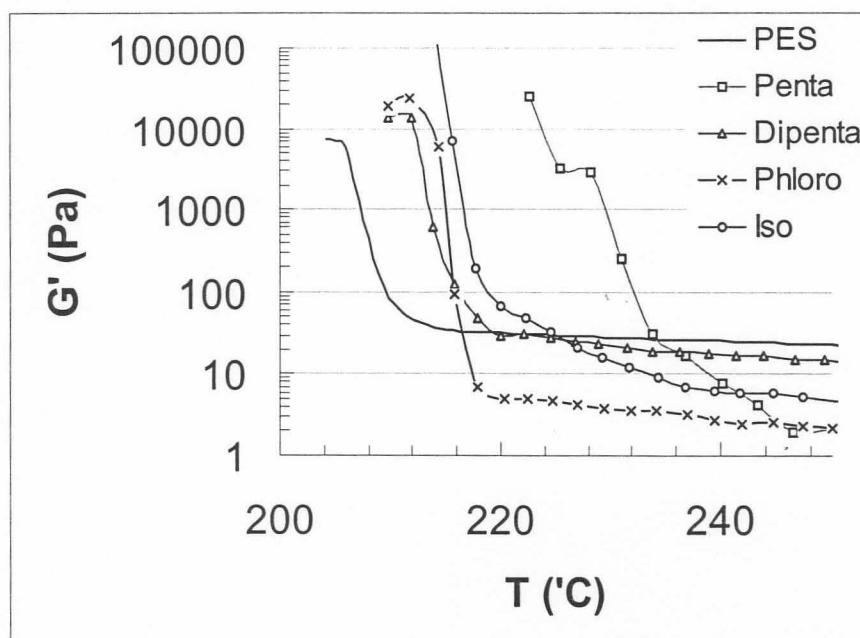


Figure 23: Storage modulus parallel plate rheometry of PES and PES treated samples.

Unfortunately, there was no clear insight into the mechanism of the oxygenated hydrocarbon flame retardants, obtained from the viscosity analysis (see Figure 24). It could however now be said that the viscosity plays not the only role in the mechanism, but is only part of a bigger picture. There was no significant increase in viscosity over the melt temperature range, so the additives did not contribute a temperature dependent viscosity alteration.

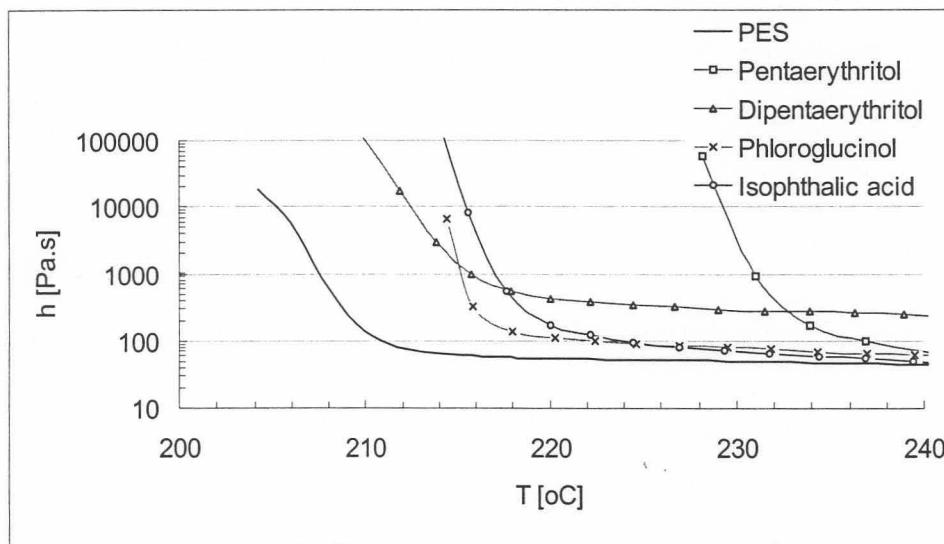


Figure 24: Viscosity response parallel plate rheometry of PES and PES treated samples.

Parallel-plate rheometry produced a surprising result. According to the data of Figure 24, the additives tend to increase melt viscosity in the temperature range of 220°C to 240°C rather than inducing the expected reduction. Unfortunately, it was not possible to measure the viscosity at higher temperatures more relevant to the flame retardancy process e.g. in the region of 400°C.