

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 COMPLETE ANALYSIS OF ADDITIVES

Elemental analysis values found the UV stabilisers are given in Table 4.1.

Table 4.1 Elemental analyses: Mass ratios of C:N found for UV stabilisers

UV stabilisers	C:N Experimental	C:N Theoretical
STETA	20.7	23.2
TOTAL	33.5	35.2
TOTA	35.0	33.5
BUTA	44.3	42.0
BUTOL	38.5	43.8
BUMA	37.2	42.9
BUDIOL	19.5	22.7
STEMA	22.7	24.0
STEDIOL	22.6	21.0

The DSC/TGA traces are presented as Appendix C lists DSC data for reagents and products. The DSC curves show that some of the reaction products e.g. BUTOL feature more than one melting endotherm. This implies that the reaction was not complete or that more than one product was formed. The TGA data shows that most additives started to volatilise below 200 °C. This is accompanied by exothermic peaks. It implies that the volatilisation is associated with an oxidative reaction or with the air atmosphere. However, OTMQ was stable up to about 400 °C. This is attributed to its antioxidant activity.

Figure 4.1 shows typical UV spectra for nickel dimethyl glyoxime in PE film (0.5%) and PP film (1%) and for Iron (III) 2,4-pentanedione in PP film (0.5%). Table 4.3 lists the characteristics of UV spectra of these additives. The nickel dimethyl glyoxime additive provides greater UV absorbance

over a broad wavelength range. Actually the UV absorbance of nickel dimethyl glyoxime is superior to other additives.

Table 4.3 Characteristics of UV spectra.

Additives	Peak, nm	Absorbance
Nickel dimethyl glyoxime (0,5%) in PE	560	0.42
	421	0.33
Nickel dimethyl glyoxime (1%) in PP	418	0.50
	538	0.52
Iron (III) 2,4-pentanedione (0.5%) in PP	424	0.49

4.2 OXIDATION INDUCTION TEMPERATURE (OIT)

Measured OIT's for the polypropylene and polyethylene samples are given in Table 4.4 for oxygen. These results suggest that OTMQ, in combination with calcium stearate is an excellent antioxidant combination for polypropylene. OIT measurements are presented as Appendix D.

Table 4.4 Effect of various additives on the OIT of LDPE and PP films.

Measured oxidation induction temperature at a scan of 10°C/min in oxygen flowing at 20ml/min. Additive (0.5% unless stated otherwise)	LDPE (XJF 46/60) OIT, [°C]	PP (1102H) OIT, [°C]
None	217	177
OTMQ (concentration in PE (0.4%))	255	202
Nickel dimethyl glyoxime	230	179
Phenolphthalein	199	-
Aluminium 2,4-pentanedione	189	175
Iron (III) stearate	164	164
Copper 2,4-pentanedione	177	154

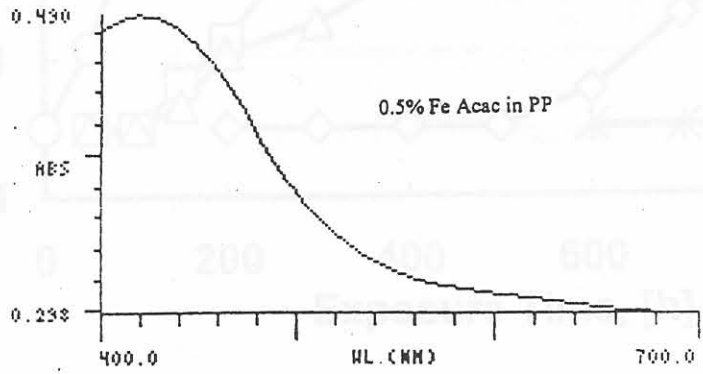
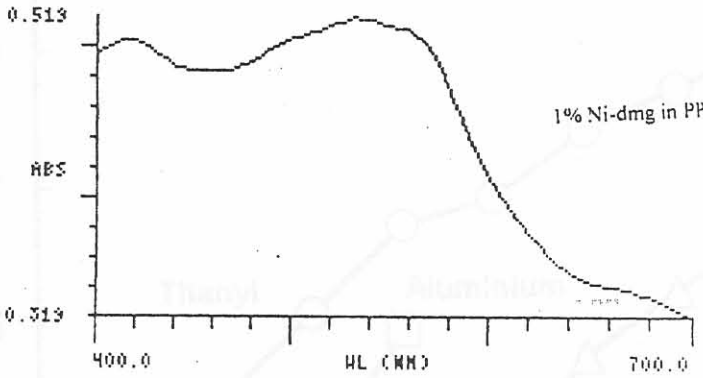
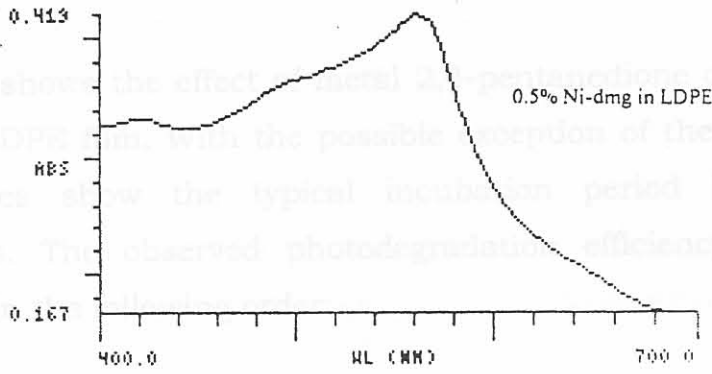


Figure 4.1 UV spectra of Nickel dimethyl glyoxime in PE and PP films and Iron (III) 2,4-pentanedione in PP film.

4.3 ACCELERATED WEATHERING

Figure 4.2 shows the effect of metal 2,4-pentanedione complexes on UV ageing of LDPE film. With the possible exception of the titanyl complex, all additives show the typical incubation period before oxidation commences. The observed photodegradation efficiency of the metals decreased in the following order:

$$\text{Ti} > \text{Al} > \text{Zr} > \text{Va} \gg \text{Cu}$$

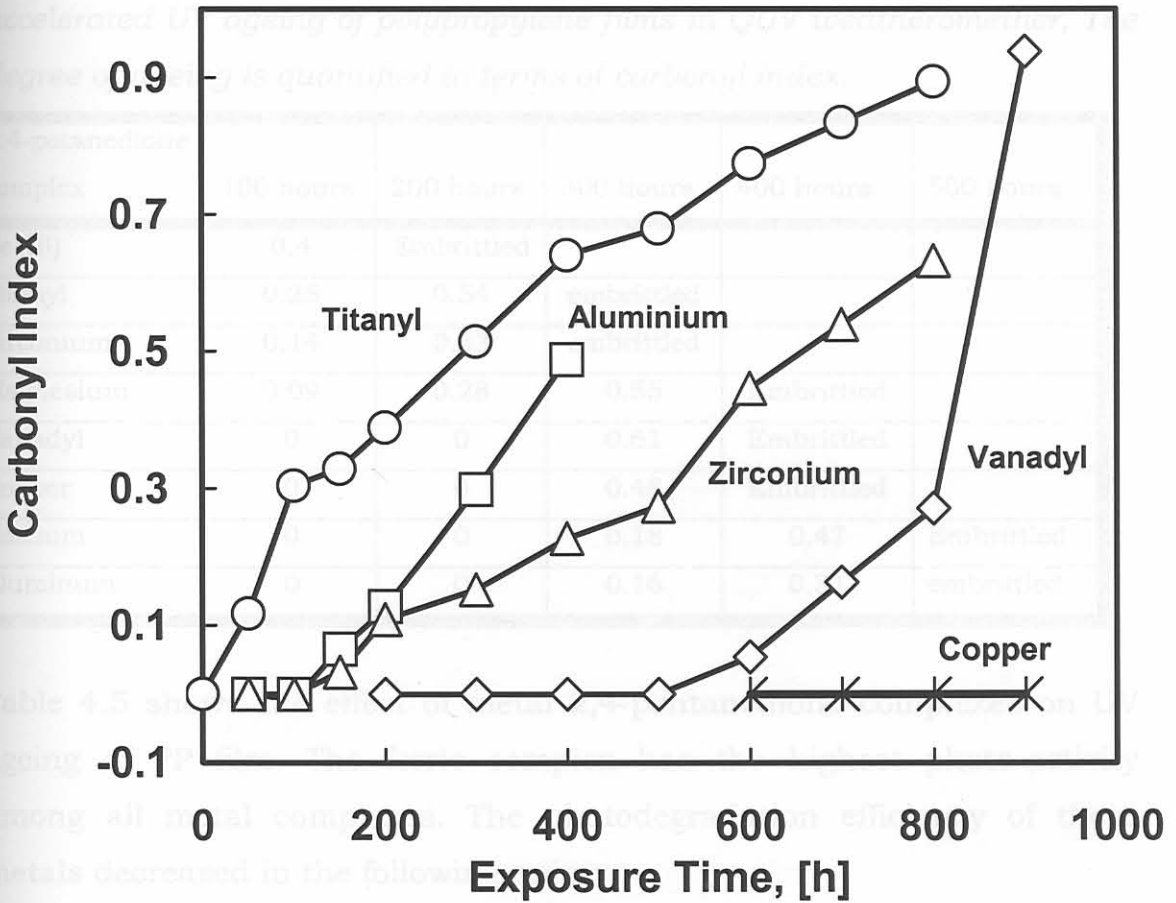


Figure 4.2 Effect of selected metal 2,4-pentanedione complexes on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

The high photo activity of the aluminium complex is encouraging, as it reportedly does not appreciably affect oxidative degradation in polyolefins [11]. Copper, a well-known and potent thermo-oxidation promoter actually acts as an UV stabiliser in polyethylene. Osawa *et al.* [11] previously noted similar behaviour. They studied the effect of metal stearates on the degradation of polyethylene and polypropylene. The photo-stabilising activity of copper stearate was attributed to an UV absorption mechanism [11, 66].

Table 4.5 Effect of metal 2,4-pentanedione complexes (0.5%) on the accelerated UV ageing of polypropylene films in QUV weatherometer. The degree of ageing is quantified in terms of carbonyl index.

2,4-pentanedione complex	100 hours	200 hours	300 hours	400 hours	500 hours
Fe (III)	0.4	Embrittled			
Titanyl	0.25	0.54	embrittled		
Zirconium	0.14	0.33	embrittled		
Magnesium	0.09	0.28	0.55	Embrittled	
Vanadyl	0	0	0.61	Embrittled	
Copper	0	0	0.48	Embrittled	
Calcium	0	0	0.18	0.47	Embrittled
Aluminum	0	0	0.16	0.31	embrittled

Table 4.5 shows the effect of metal 2,4-pentanedione complexes on UV ageing of PP film. The ferric complex has the highest photo-activity among all metal complexes. The photodegradation efficiency of these metals decreased in the following order:



The vanadyl and copper complexes showed a distinct induction time followed by rapid oxidative degradation. Interestingly, even the calcium

and magnesium complexes showed photoactivity. It is suspected that for these complexes it derives from the carbonyl functionality of the organic residue rather than from the activity of the metal.

In Figures 4.3 and 4.4 the photo-activity of molecules with potential anti-oxidant properties are compared with that of ferric stearate in LDPE and polypropylene. While ferric stearate is much more efficient, it is clear that OTMQ does show promising photo-degradation properties. Figure 4.5 shows the effect of dosage level of the anti-oxidant, OTMQ, on the time to reach a Carbonyl Index of 0,2 for polyethylene film. By comparison, films containing ferric stearate reached this level at irradiation times less than 150 hours.

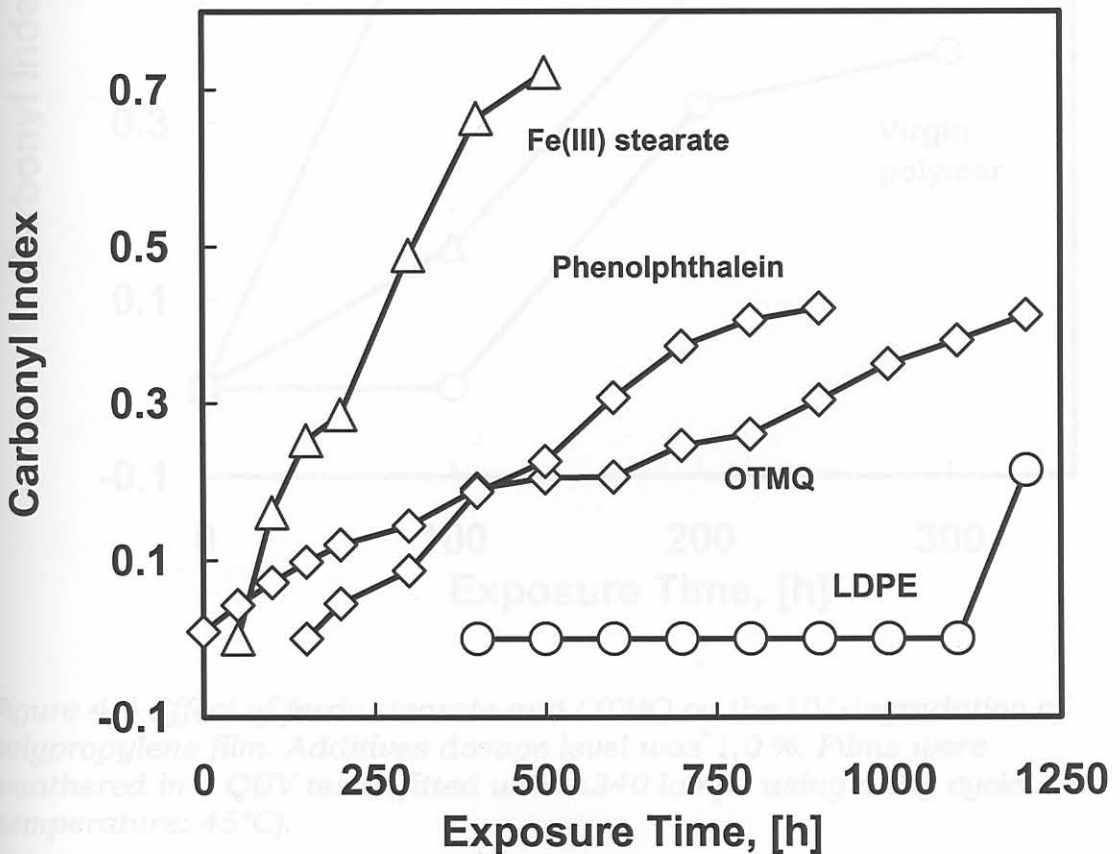


Figure 4.3 Effect of ferric stearate and OTMQ on the UV degradation of polyethylene film. Additives dosage level was 0,5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

The influence of polyester-based UV stabilisers and nickel dimethyl glyoxime on the light stability of polyethylene (LDPE) and polypropylene (PP) films has been examined and compared to the corresponding activity of chimasorb 944 compound.

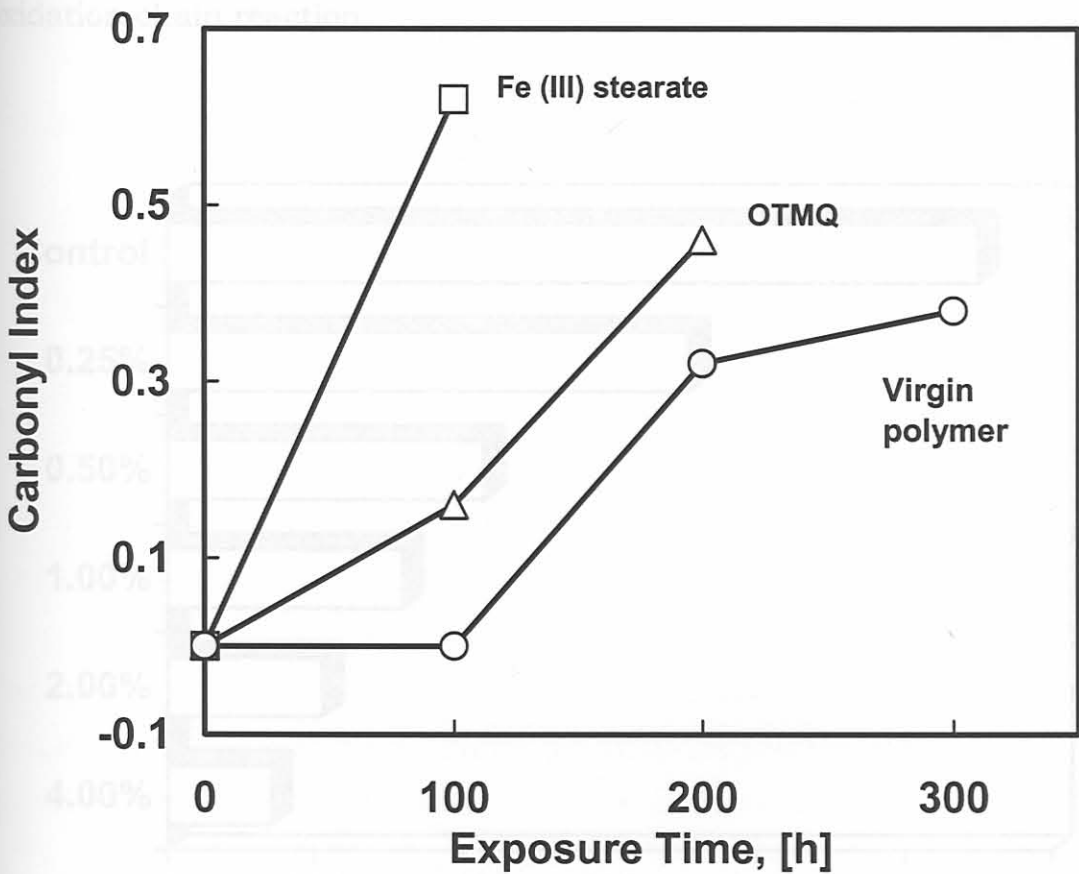


Figure 4.4 Effect of ferric stearate and OTMQ on the UV degradation of polypropylene film. Additives dosage level was 1,0 %. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

The oxidation rates have been determined by measuring the rate of carbonyl growth in the films through FT-IR analysis and the respective absorption peak maxima. Embrittlement values for the films are normally taken at 0.1 carbonyl units as a comparison of stabilities. The weathering of polyethylene (LDPE) and polypropylene (PP) leads to the production of several oxidation products. Most of these can be truly characterised and quantified with FT-IR. Several mechanisms have been proposed to explain chemical changes during UV exposure of polyethylene (LDPE) and polypropylene (PP) in which hydroperoxy radicals play a major role in the oxidation chain reaction.

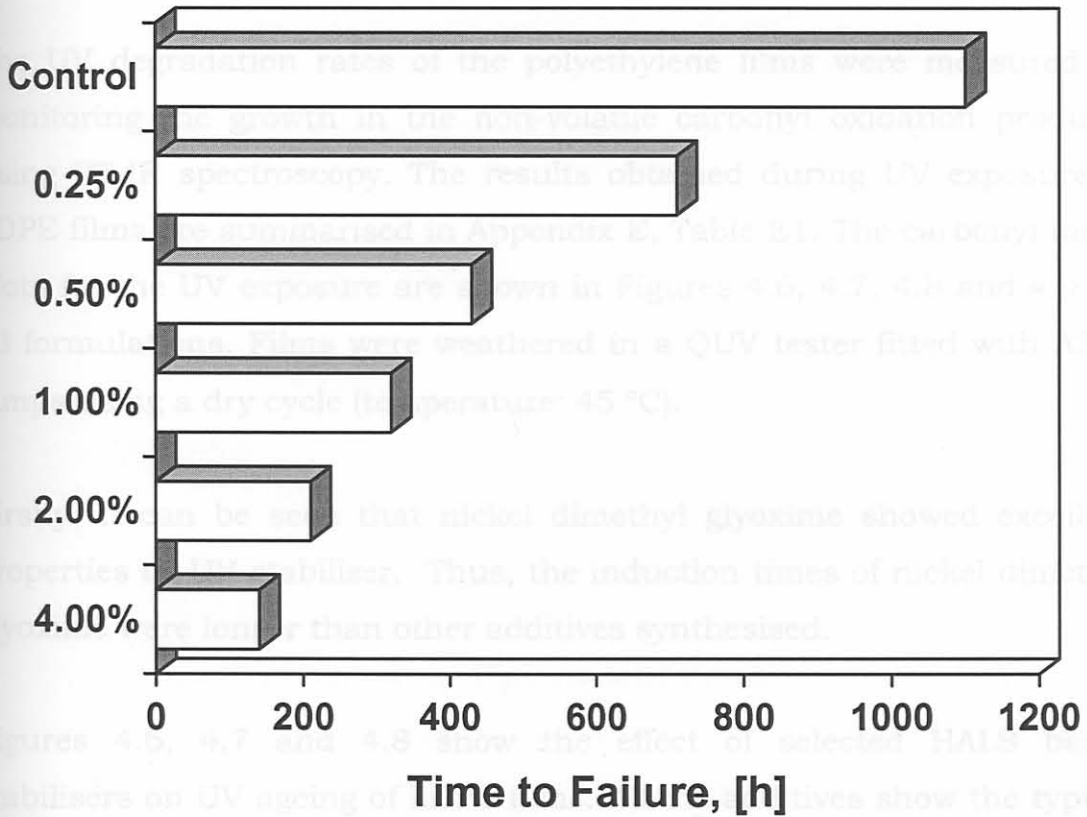


Figure 4.5 QUV photo degradation of LDPE film: Effect of the OTMQ dosage level on the time to reach a Carbonyl Index of 0,2 in polyethylene film.

STEMA > BUMA > BUTA > STEDIOL > BUTOL > STEIN > TOTOL > TOTA

It is generally accepted that hydroperoxides are the key compounds in the mechanism of photo-oxidation of polyethylene (LDPE) and polypropylene (PP). Their production is generally followed by their photochemical decomposition. Under UV exposure, the quantum yield of hydroperoxide decomposition may lead to several photo-products such as carboxylic acid, alcohol, ketone, etc...[22].

The oxidation rates of the polyethylene (LDPE) and polypropylene (PP) were measured by monitoring the growth in the non-volatile carbonyl oxidation products using FT-IR spectroscopy.

POLYETHYLENE

The UV degradation rates of the polyethylene films were measured by monitoring the growth in the non-volatile carbonyl oxidation products using FT-IR spectroscopy. The results obtained during UV exposure of LDPE films are summarised in Appendix E, Table E1. The carbonyl index plots for the UV exposure are shown in Figures 4.6, 4.7, 4.8 and 4.9 for all formulations. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45 °C).

Firstly, it can be seen that nickel dimethyl glyoxime showed excellent properties as UV stabilizer. Thus, the induction times of nickel dimethyl glyoxime were longer than other additives synthesised.

Figures 4.6, 4.7 and 4.8 show the effect of selected HALS based stabilisers on UV ageing of LDPE films. All the additives show the typical induction time before oxidation commences. The observed UV stability efficiency of UV stabilisers synthesised decreased in the following order:

STEMA > BUMA > BUTA > STEDIOL > BUTOL > STETA > TOTOL > TOTA.

It is important to remark at this stage that additives STETA, TOTOL and TOTA show promising UV stabilisers properties. The oxygen scavenging activity of STETA, TOTOL and TOTA is good and this behavior can help to enhance the UV stability of the films by preventing the growth of hydroperoxides. Simultaneously, this would also protect the HALS functionality.

It is very likely that certain intramolecular interactions between the moieties of the molecule can be taking place. Anox 20 is very effective as antioxidant and this behavior combined with the ability of hindered piperidines to react with oxygen and alkyl radicals result in synergism. On the other hand, the phenomenon of synergism was not observed in the mixture of other additives (STEMA, BUMA, BUTA, STEDIOL and BUTOL) and Anox 20. Furthermore, the induction time was decreasing and the carbonyl induction was very high.

Figure 4.9 shows the effect of nickel dimethyl glyoxime on the UV degradation of LDPE films. The result is encouraging and it can be seen that this additive presents excellent properties as UV stabiliser.

POLYPROPYLENE

The results observed when the PP films were subjected to UV exposure are summarised in Appendix E, Table E2. The carbonyl index plots for the UV exposure are shown in Figures 4.10, 4.11, 4.12 and 4.13. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45 °C). It is clear that polypropylene is more susceptible to degradation than polyethylene. As before, all graphs show a typical induction time before oxidation starts.

The UV stability efficiency of the synthesized additives in polypropylene films increased in the following order:

BUDIOL<BUTA<BUMA<STEMA<BUTOL<TOTOL<STEDIOL<TOTA<STETA

STETA showed the highest UV stabilisation activity of the additives synthesised. Chmela and Hrdlovic [18] previously noted similar behavior. Additive TOTA showed only a moderate activity as an ultraviolet stabiliser for PP films.

Figure 4.13 shows the effect of nickel dimethyl glyoxime alone and together with Anox 20 on the UV degradation of PP films. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45 °C).

The result is very encouraging. Addition of Anox 20 marginally improved the performance of the nickel dimethyl glyoxime.

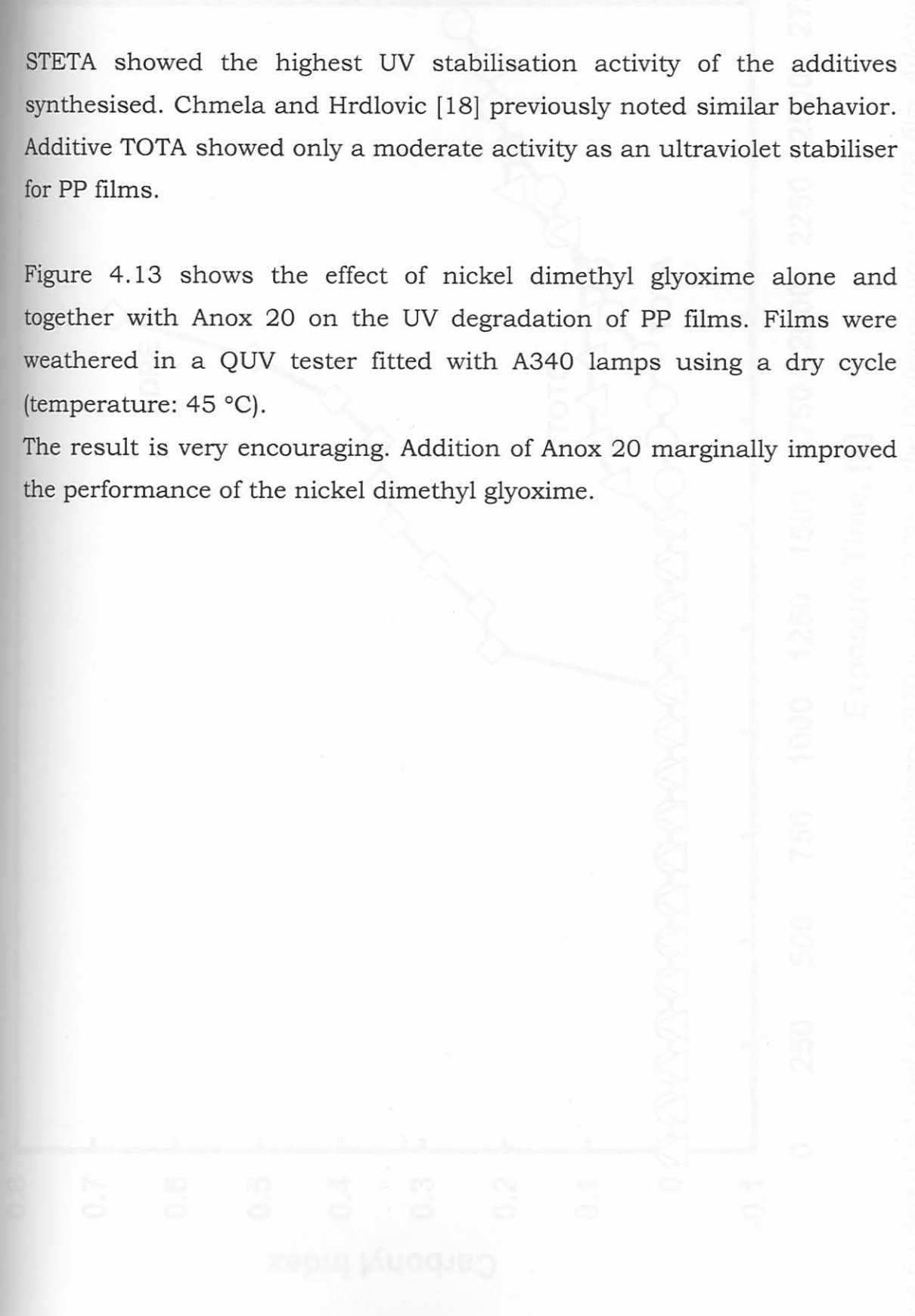


Figure 4.13 Effect of nickel dimethyl glyoxime and UV stabiliser Anox 20 on the UV degradation of PP films. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45 °C).

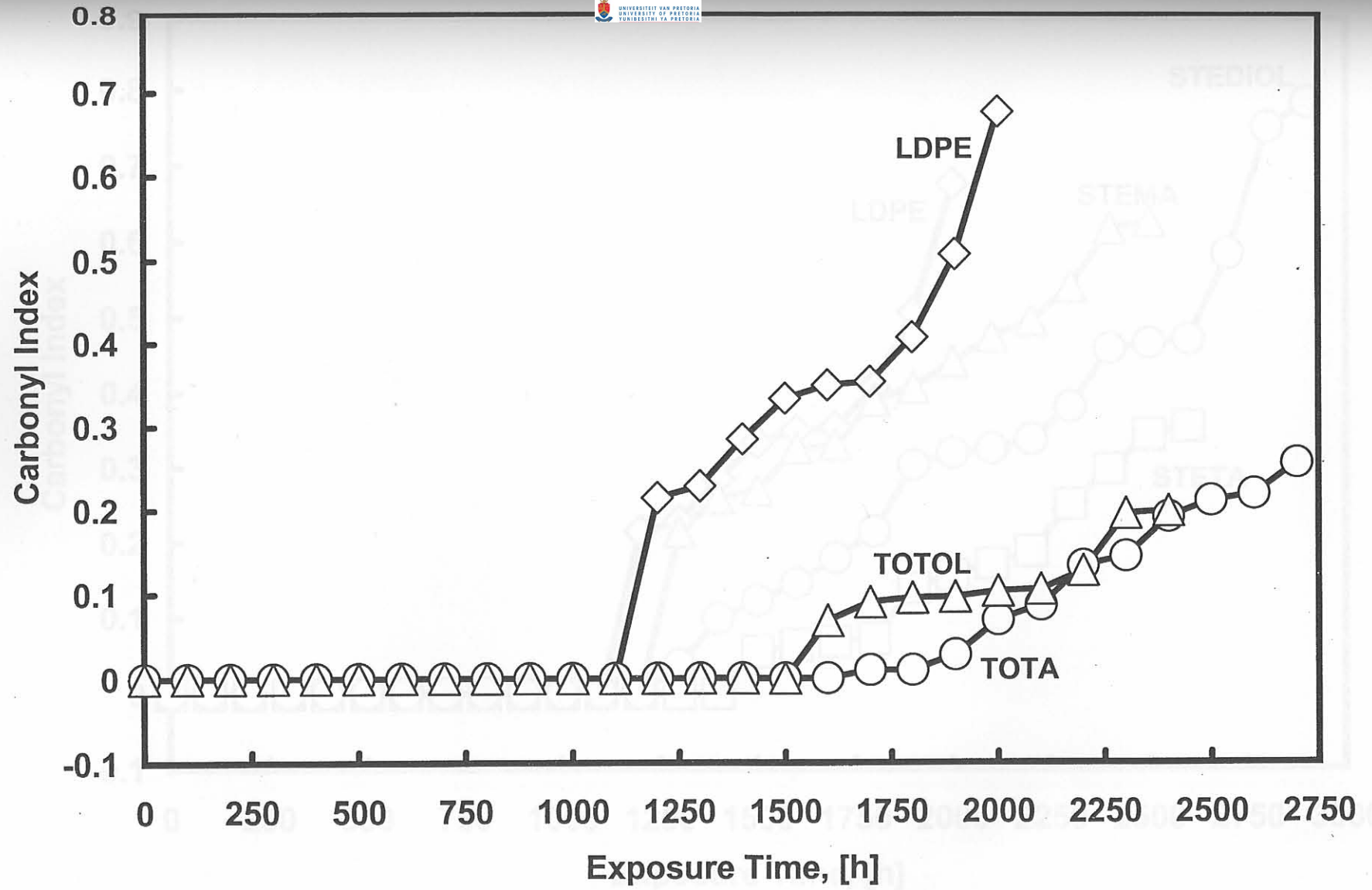


Figure 4.6 Effect of selected synthesised UV stabilisers (TOTAL and TOTA) on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C)

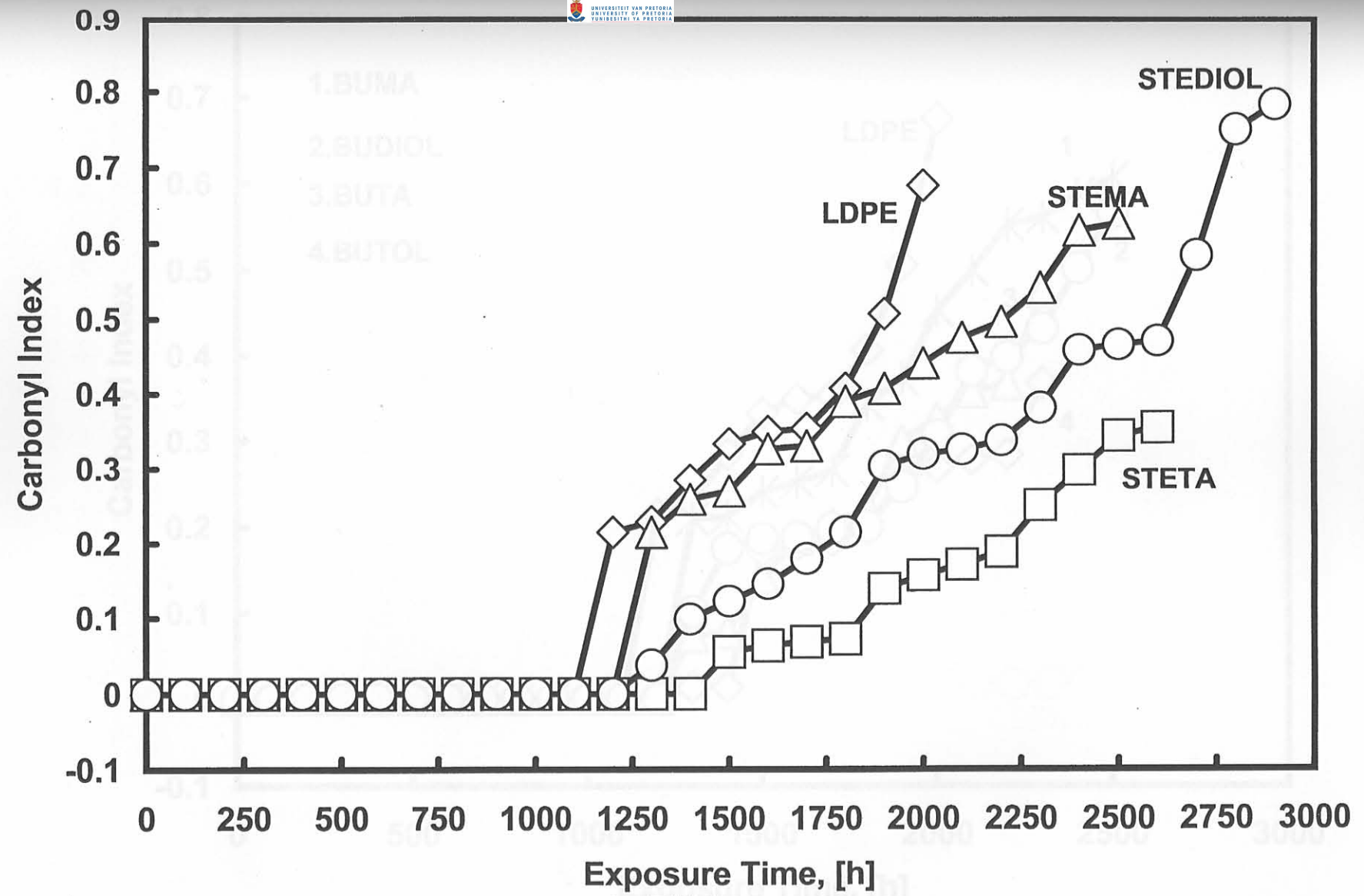


Figure 4.7 Effect of selected synthesised UV stabilisers (STEMA, STEDIOL, STETA) on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C)

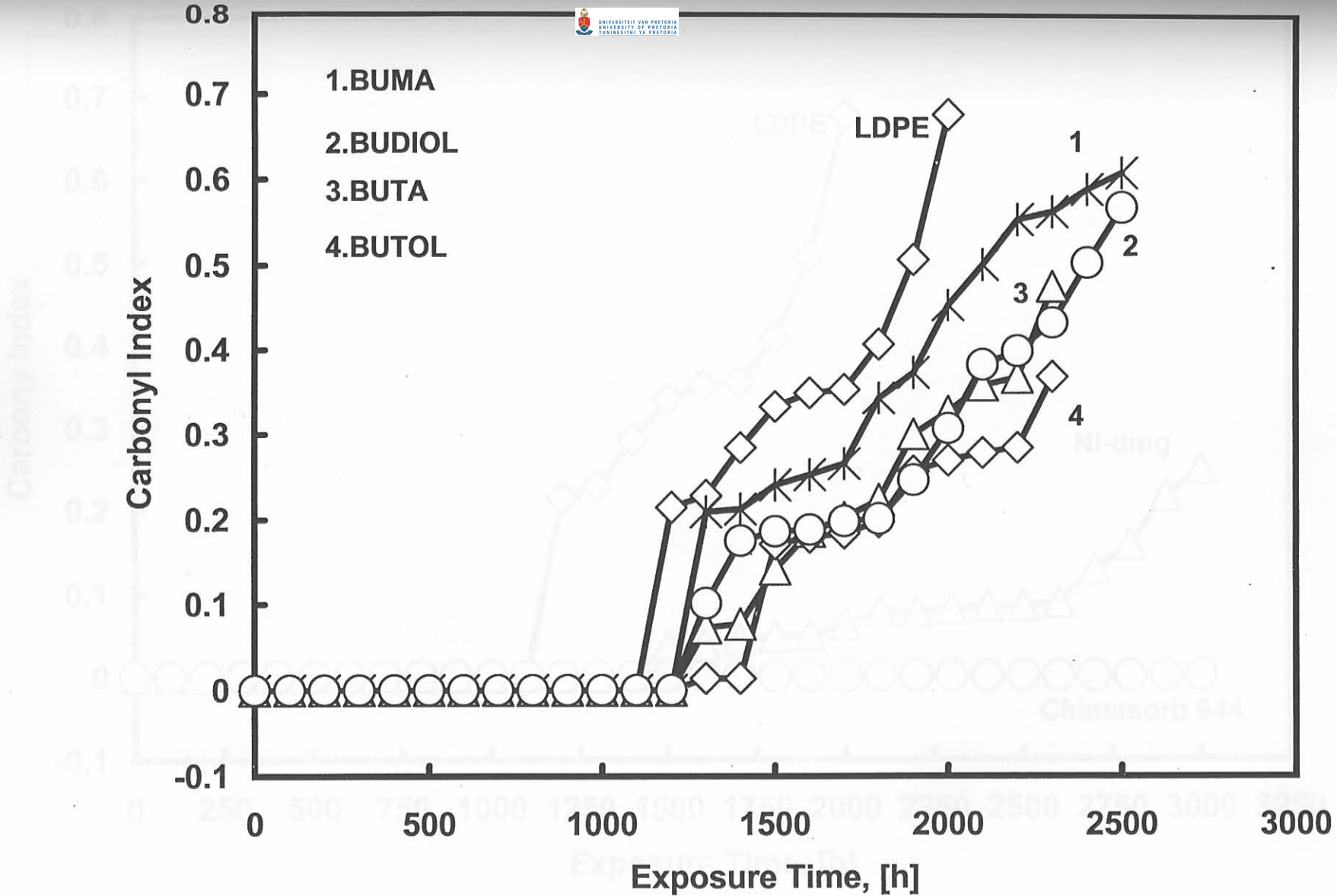


Figure 4.8 Effect of selected synthesised UV stabilisers (BUMA, BUDIOL, BUTA, BUTOL) on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle

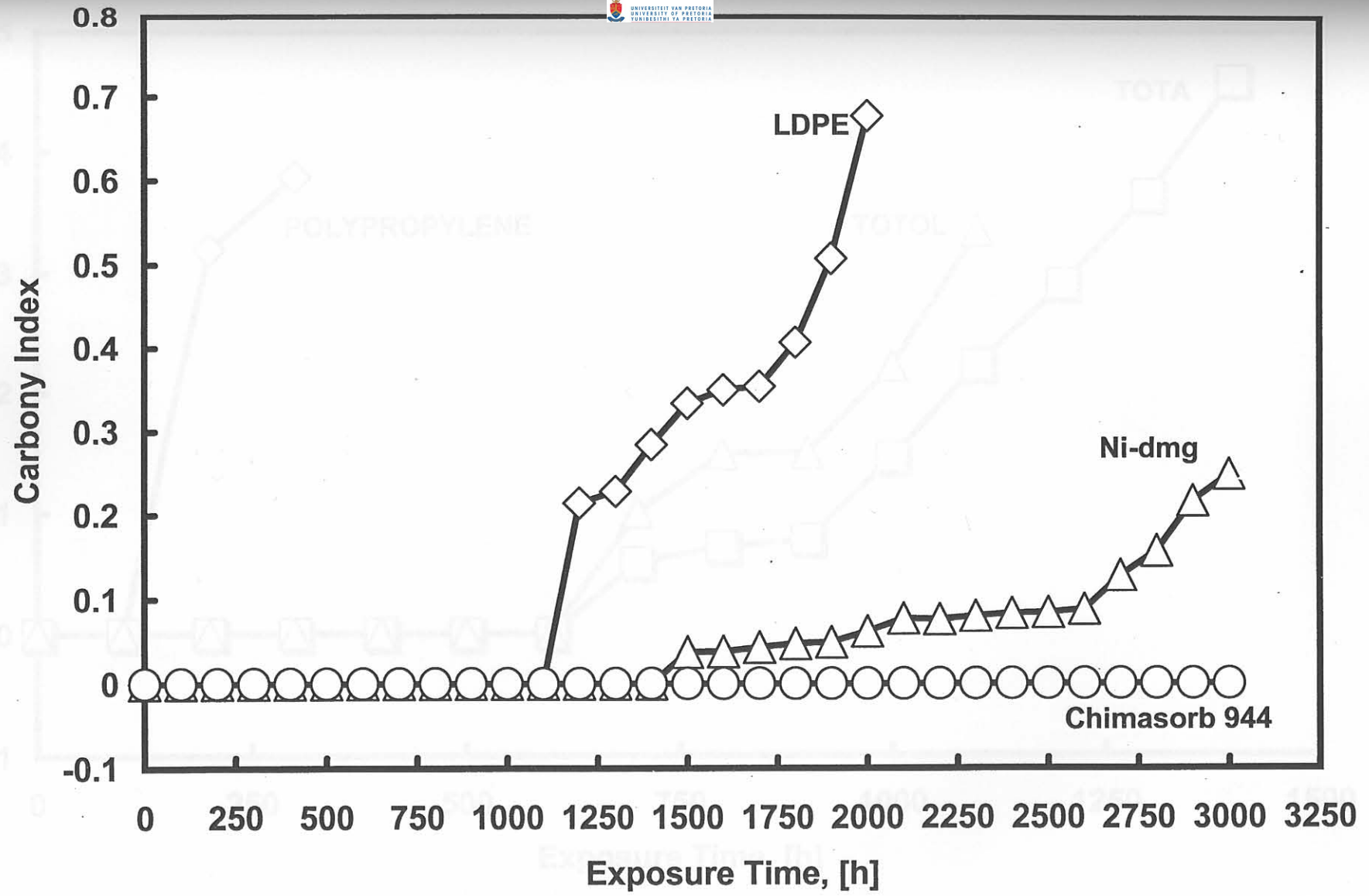


Figure 4.9 Effect of synthesised additive (Ni-dmg) and Chimasorb 944 on the UV degradation of LDPE film. Additives dosage level was 0.5%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C)

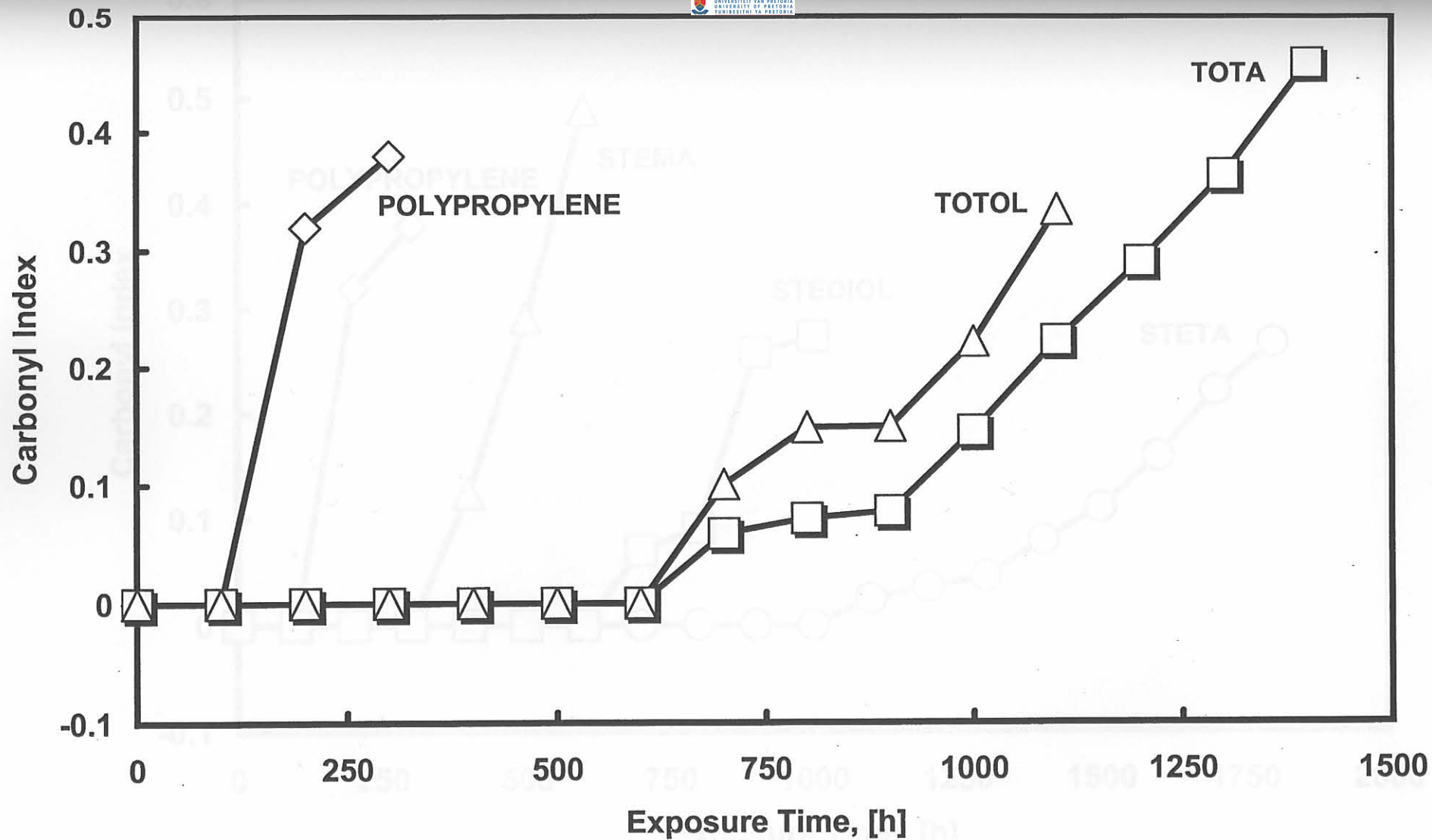


Figure 4.10 Effect of selected synthesised UV stabilisers (TOTOL and TOTA) on the UV degradation of polypropylene film. Additives dosage level was 1%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

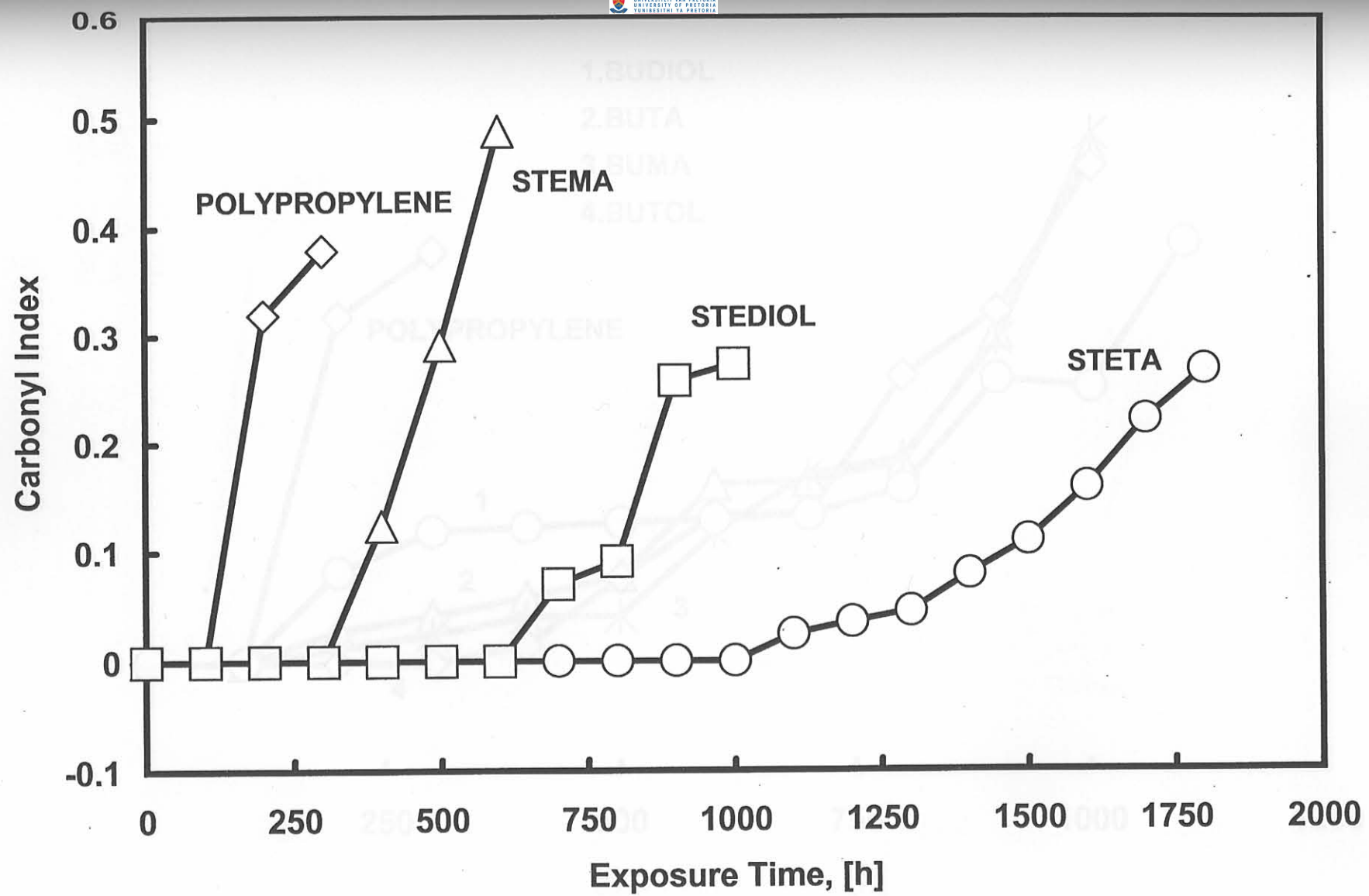


Figure 4.11 Effect of selected synthesised UV stabilisers (STEMA, STEDIOL, STETA) on the UV degradation of polypropylene film. Additives dosage level was 1%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C)

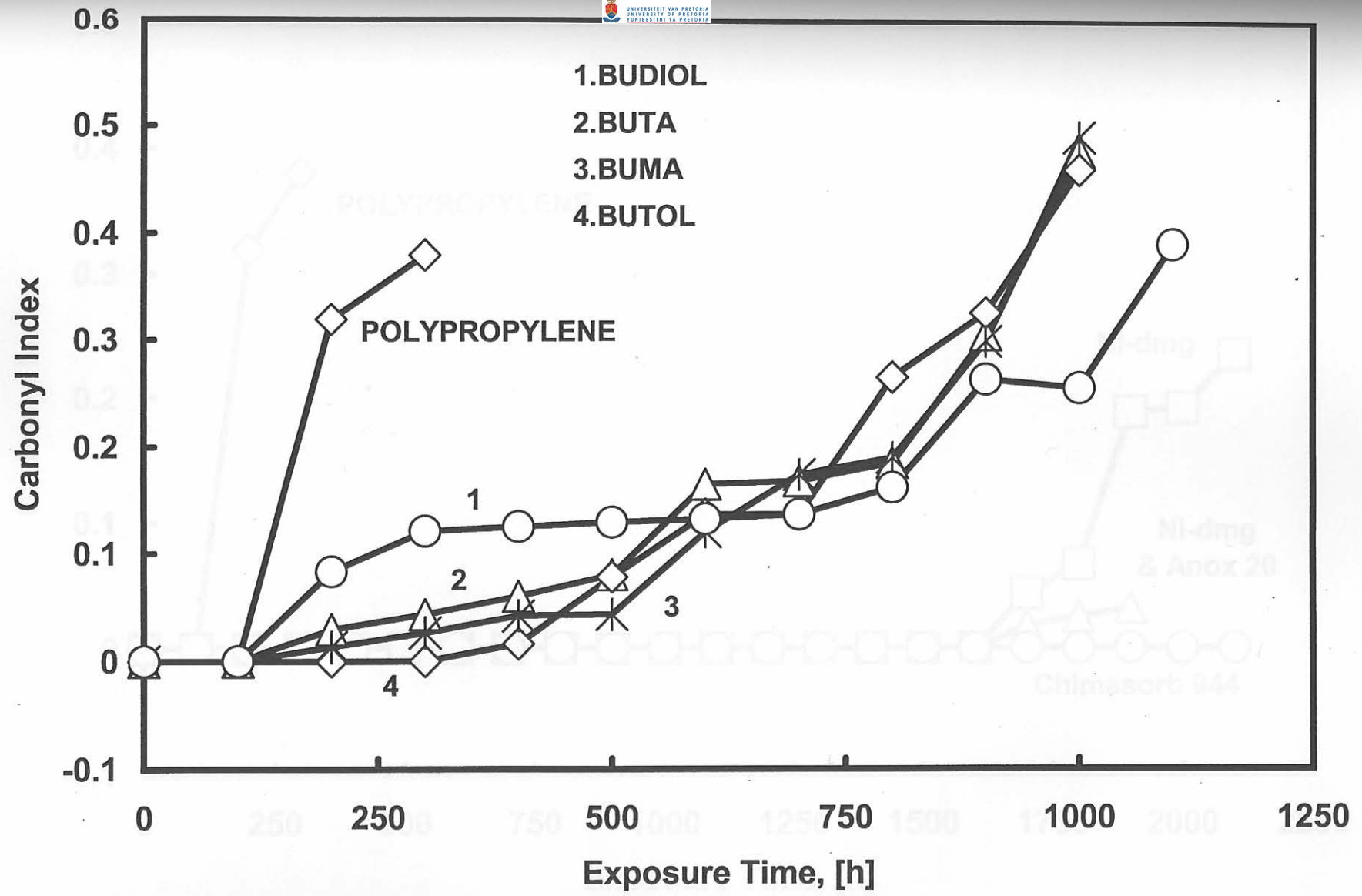


Figure 4.12 Effect of selected synthesised UV stabilisers (BUDIOL, BUTA, BUMA, BUTIOL) on the UV degradation of polypropylene film. Additives dosage level was 1%. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).

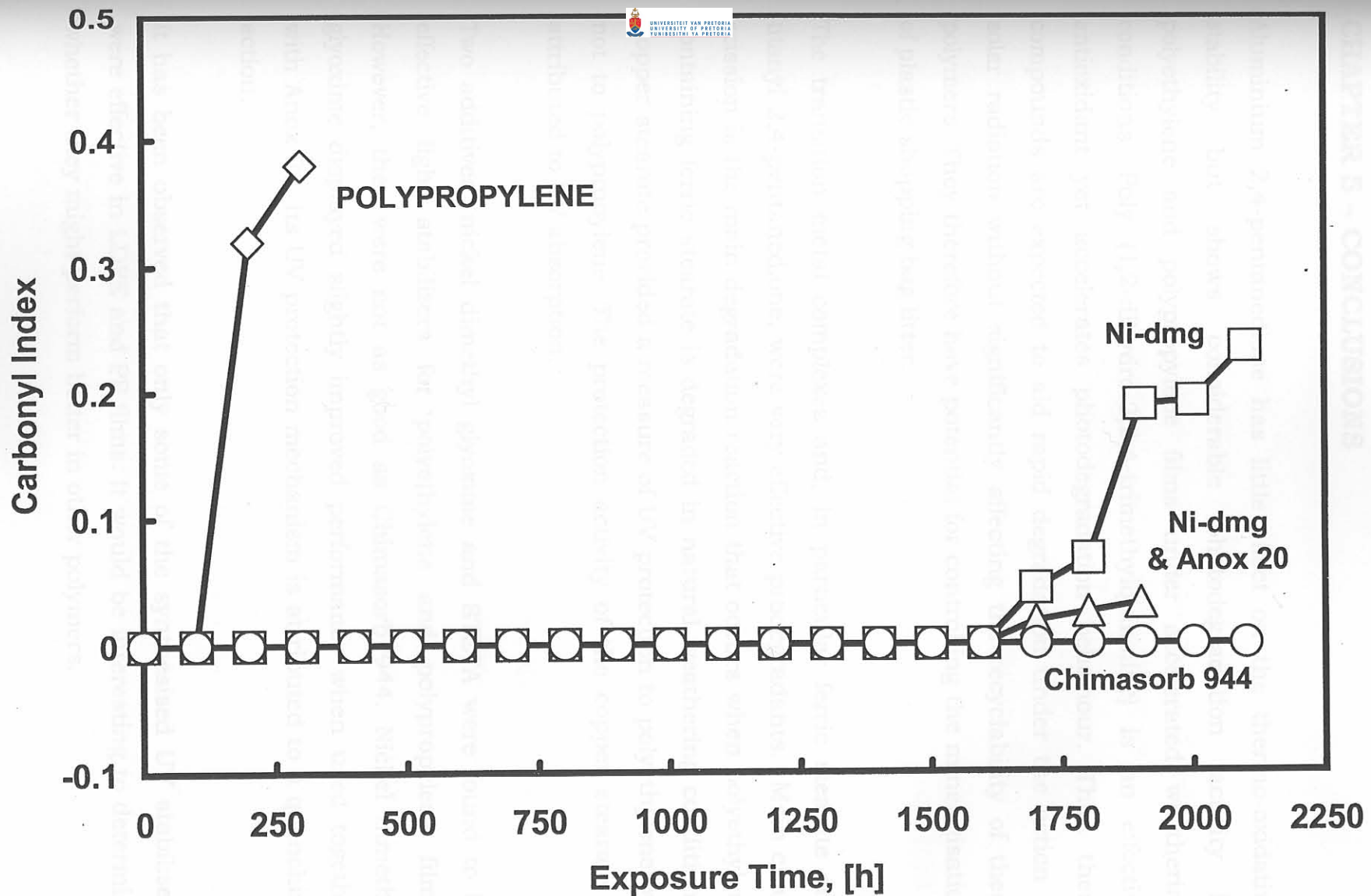


Figure 4.13 Effects of additives Ni-dmg, Ni-dmg mixed with Anox 20 and Chimasorb 944 on the UV degradation of polypropylene film. Additives dosage level were: 1% for Ni-dmg, 1% Ni-dmg mixed with 0.05% of Anox 20, and 0.5% for Chimasorb 944 as reference. Films were weathered in a QUV tester fitted with A340 lamps using a dry cycle (temperature: 45°C).