Macromol. Symp. **2003**, *202,* 199—219

UV Stabilising Synergies between Carbon Black and Hindered Light Stabilisers in Linear Low Density Polyethylene Films

A. Richard Horrocks, Mingguang Liu*

Centre for Materials Research and Innovation, Bolton Institute, Bolton, BL1 5AB, UK

Summary: The combined effects of selected carbon black pigments and hindered light stabilisers (HALS) on the UV stabilities of linear low density polyethylene film have been studied under UVA and UVB fluorescent radiation sources. While the presence of HALS do not change the chemistry of film photodegradation, whether they are low or high molecular variants, their presence significantly extends film lifetime relative to the sum of the effects of carbon black and HALS individually. These lifetime extensions may be defined in terms of a synergy factor defined with respect to film time to lose a specific percentage of a tensile property, namely t_{20}, the time to lose 20% of initial elongation-at-break, or the carbonyl index associated with this condition.

It is proposed that possible causes of this synergy are a result of the UV screening effect of the carbon black particles which provide lower concentrations of polymer radicals for the HALS component to interact with and/or an accompanying thermal stabilising effect by the latter as a consequence of the higher polymer local temperature during irradiation of pigmented films.

Keywords: carbon black; HALS; hindered light stabilizer; linear low polyethylene; LLDPE; photodegradation; synergy; UV

1 Introduction

In our previous paper[1] we examined the effect of carbon black variables such as particle size and structure on pigment stabilising efficiency when present in linear low density polyethylene films subjected to artificial weathering. As expected, carbon blacks having the smallest particle size and, in particular those below 20 nm, showed the greatest stabilising capacity in stabilising films to both fluorescent tube (UVA, 340 nm and UVB 310 nm) and xenon arc source radiation. However, there was no consistent influence of aggregate structure but increasing carbon black presence from 1.5 to 3.0 (w/w) % improved the stabilising power of all blacks.

The effect of pigment was not seen to be one of simple UV radiation scattering as previously proposed[2] since for UVA and UVB sources, presence of carbon black, while increasing carbonyl group generation with respect to unit loss in tensile property with respect to unfilled

DOI: 10.1002/masy.200351218

LLDPE, also appeared to suppress Norrish Type II scissions at photochemically generated carbonyl centres in polymer chains.[1] This was especially the case for the smallest (~20nm) particle sizes, thereby suggesting that the photostabilising efficiency of carbon black is based on both physical surface-area-dependent UV absorption and photochemical activity. Under xenon arc exposure, however, this latter appeared to be minimal probably because of its generally low UV content within its overall emission spectrum.

Combinations of carbon black and photo-antioxidants have been used to give higher levels of UV and thermal stability. This is especially important because of the heat absorbing character the pigments which have been reported to produce temperatures as high as 100°C under natural sunlight exposures.[3,4] While both synergistic and antagonistic effects have been reported for polyolefin carbon black-antioxidant ternary systems, adverse effects have been attributed to adsorption and/or decomposition of the antioxidant by carbon black.[5,6] For example, Hawkins reported that phenolic antioxidants are effective in the presence of low concentrations of furnace black but are adversely effected when a channel black with higher concentrations of reactive groups present is used.[7]

The use of hindered light stabilisers during the last 10 years or so has significantly raised the weathering performance of the polyolefins in general.[8] However, the effect of combining them with carbon blacks has not been widely studied although early work demonstrated possible synergy during xenon arc weathering of polypropylene tapes.[9] However, adverse thermal degradative effects were reported if higher black loadings were used because of antioxidant adsorption.[10] Recent work by Allen et al has considered the possible interactions of carbon black and antioxidants[11] and carbon black, antioxidants and HALS.[12] Using carbonyl index as a main indicator of photo-oxidation, this latter work showed that while antagonisms were often the case between primary antioxidants and HALS, small synergies were seen between secondary antioxidants and HALS during photo-oxidation. Furthermore, the presence of HALS and carbon black alone seemed to produce an antagonistic effect which was a balance of antioxidant and adsorptive properties of the former. When HALS, antioxidant and carbon black were together, the overall effect appeared to be one of synergy with the effect of carbon black variables being restricted to variations in degrees of surface oxidation for a standard 22-25 nm particle size. The more oxidised black tended to be present in the more UV stable formulations.

This paper extends our previous work[1] and examines the effects of adding HALS to the UV stability of LLDPE films in which a standard primary/secondary antioxidant is present and which contain carbon blacks having defined particle properties.

2 Experimental

As in our previous study[1] the LLDPE powder used was supplied by Union Carbide (GRSN 7510NT) and is the copolymer of ethylene and hex-1-ene with density of 0.919g/cm^3 and MFI of 0.75 g/10 min at 190°C, 2.16kg. HPLC (carried out at Cabot Plastics (UK) Ltd.,) analysis indicated that the LLDPE powder contained 0.1% (w/w) B-blend of antioxidant system B225 (Irganox 1010 and Irgafos 168a in a 1:1 mass ratio, Ciba Speciality Chemicals) for melt stabilization during manufacture.

In order to fully understand the combined effect of carbon black and HALS stabilizers on photostabilization of the LLDPE films, 5 grades of carbon black (1.5% w/w concentration) with various properties defined in particle size and aggregate structure, and 3 different HALS stabilizers (0.3% w/w concentration) were chosen. The former selection was made in consultation with Cabot Corporation and is based on choosing extreme values of fundamental properties such as particle size, structure and surface area. The matrix of 5 carbon blacks and 3 HALS stabilizers are listed in Table 1 along with 3 unfilled, HALS-containing samples. The detailed properties of the selected carbon blacks (supplied by Cabot Corporation) have been reported elsewhere[1] and former codes are designated in parentheses for the first four blacks in Table 1. The fifth black, C5, was selected because of its lower surface area (as measured by nitrogen adsorption by Cabot Corporation) relative to C3 which has similar size and structure and yet higher surface area. Unfortunately, no data is available regarding the exact chemical characters of the various carbon black surfaces.

Table 1. Matrix of mixtures of carbon black and HALS stabilizers.

	Particle Size, nm	Structure (as DBPA, cm^3/100g)*	Surface area via nitrogen adsorption, m^2/g	HALS1 Chimassorb 944	HALS2 Tinuvin 770	HALS3 Tinuvin 765
LLDPE	-	-	-	X	X	X
C1(C1)**	60	65	30	X	X	
C2(C11)	45	121	42	X	X	
C3(C3)	18	117	200	X	X	
C4(C7)	17	68	210	X	X	
C5	19	114	140		X	X

Notes: * denotes use of dibutyl phthalate to determine surface area of carbon black aggregates;[13] ** figures in brackets denote former carbon black codes in reference 1; X denotes film samples collected before and after exposures for full characterization.

The three HALS stabilizers (supplied by Ciba) were selected based on molecular size with regard to the relatively small Tinuvin 770 (bis-2,2,6,6-tetramethyl-4-piperidyl sebacate) (HALS2) and the polymeric Chimassorb 944 (poly {[6-[(1,1,3,3-tetramethylbutyl)-imino]-1,3,5-triazine-2,4-diyl][2-(2,2,6,6-tetramethylpiperidyl)-amino]-hexamethylene-[4-(2,2,6,6-tetramethylpiperidyl)-imino]} (HALS1). The potential effect of alkylation of the secondary amine hydrogen was examined by including Tinuvin 765 (bis-1,2,2,6,6-pentamethyl-4-piperidyl sebacate) (HALS3) in the study. The matrix in Table 1 thus provides carbon black particle size/structure combinations of Large/Low (C1), Large/High (C2), Small/High (C3 & C5) and Small/Low (C4) each in the presence of two of the three HALS selected.

Masterbatches at a nominal 5% loading in LLDPE for each HALS stabiliser were prepared on a BR Brabender mixer in Cabot Corporation laboratories, USA and then diluted to a concentration of 0.3% (w/w) by mixing with LLDPE pellets or carbon black (1.5 %(w/w))-LLDPE pellets prior to film production. The concentration of carbon black in each black-HALS-LLDPE ternary becomes 1.41% (w/w) during the compounding and subsequent extrusion into 75μm films described previously.[1]

The HALS stabilizer-containing films with and without carbon blacks were exposed in the Q-Panel, QUV/se source under UVA and UVB conditions at 1.25 and 0.63 Wm^{-2} respectively and at 60°C followed by characterization using the same techniques as described previously.[1]

3 Results

3.1 Unexposed Film Properties

A summary of mechanical and physico-chemical properties of carbon black-containing LLDPE films with and without HALS stabilizers is shown in Table 2.

After addition of the HALS stabilizers, the elongation-at-break values (with an error of about ±5%) increase for all the films except C3 film which shows decreases with respect to HALS-free analogues. Furthermore, a general decrease in fusion endotherm maximum temperatures occur suggesting that HALS have encouraged growth of a population of smaller polycrystallites. This is probably because these stabilizers have polar structures[14] which modify the intermolecular force and fine structural characteristics. However, all the stabilizer-containing films filled with carbon blacks show lower retained elongation-at-breaks than those for respectively HALS-stabilized films without carbon black due to the reinforcing effect of the pigment.

Table 2. Mechanical and morphological properties of carbon black-containing LLDPE films in the absence and presence of HALS stabilizers.

Code	ε, %	BL, N	T_m, °C	H_f, J/g	T_{on},°C
LL	773	12.2	115	67.4	234
HALS1-LL	809	12.9	114	72.7	223
HALS2-LL	796	12.4	110	97.0	241
HALS3-LL	808	12.8	-	-	-
C1	717	12.1	113	75.3	234
HALS1-C1	782	11.5	115	73.3	227
HALS2-C1	801	12.5	111	84.3	241
C2	754	12.9	114	76.6	237
HALS1-C2	776	11.9	-	-	-
HALS2-C2	781	11.9	-	-	-
C3	773	12.9	115	66.5	238
HALS1-C3	729	11.0	-	-	-
HALS2-C3	743	11.1	-	-	-
C4	724	11.4	113	73.3	237
HALS1-C7	738	11.0	110	76.2	232
HALS2-C7	749	11.0	109	84.0	239
C5	771	13.2	114	60.4	235
HALS2-C5	770	11.3	-	-	-
HALS3-C5	789	11.9	-	-	-

Key : ε - Elongation-at-break.
BL - Breaking load.
T_m - Melting temperature obtained from DSC melting peak.
H_f - Heat of fusion calculated from DSC melting endothermic area.
T_{on} - Onset temperature of post-fusion oxidation.

The addition of HALS2 stabilizer results in an increase in the DSC-derived crystallinity (as heat of fusion, H_f) for the pure, C1 and C4 films while the HALS1-filled films show comparable results to the HALS-free films. The results in Table 2 indicate, therefore, that apart from a possible nucleating effect by HALS, to a first approximation, all films have very similar tensile and morphological properties.

3.2 Films Exposed to UVB (310nm) Radiation

3.2.1 Tensile Properties

The tensile properties in terms of retained elongation as a function of exposure time for the LL films containing HALS1, HALS2 and HALS3 stabilizers only are plotted in Fig.1. It can be seen that the use of HALS in LLDPE films leads to pronounced improvement in UVB stability, as expected. However, it was observed that little if any difference of photostabilizing efficiency between the low (HALS2 and HALS3) and high molecular mass HALS (HALS1) exists in these films. It has been suggested[15,16] that diffusion of low molecular mass stabilizers to the outer film surfaces subjected to photo-oxidation may lead to an enhancement of UV stability. The comparable performances of low molecular mass NH-HALS, HALS2 and the corresponding N-methyl HALS, HALS3 have been attributed to very rapid transformation of the N-methyl group into the formic acid salt of NH-HALS during initial photo-oxidation[8] and the photostabilization of films results from subsequent reaction of the NH form.[15]

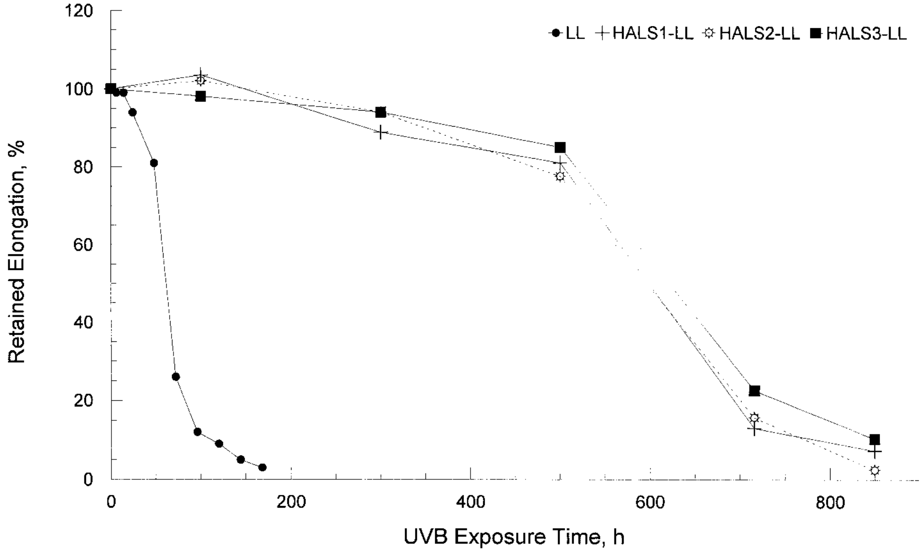
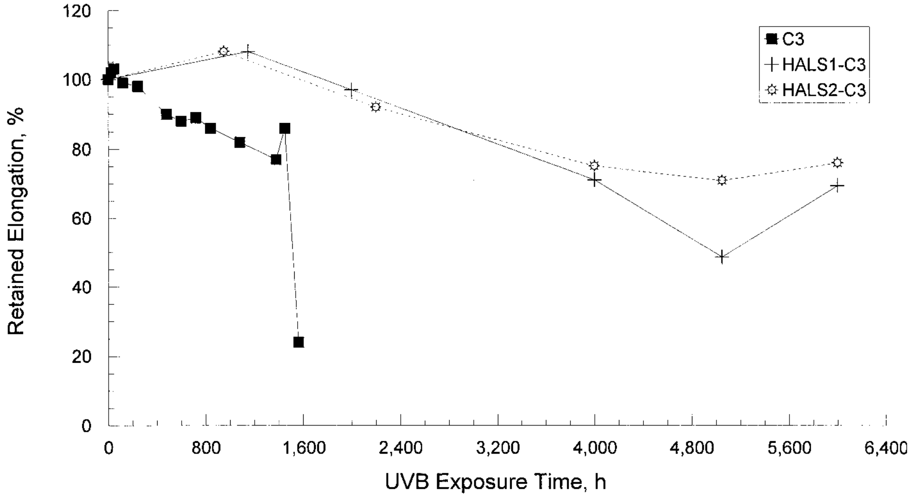


Fig. 1. Effect of UVB exposure and HALS on retained elongation of LLDPE films.

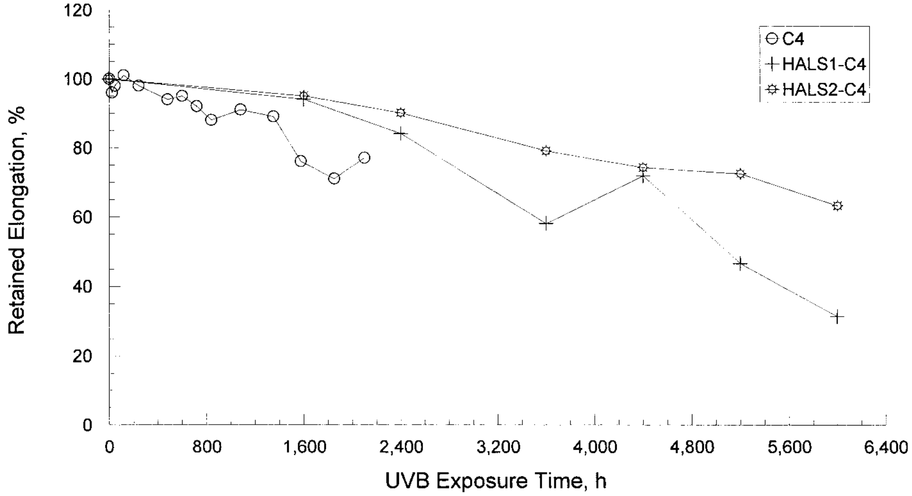
The effects of HALS1, HALS2 and HALS3 stabilizers on retained elongation for the films containing small particle-sized blacks are shown in Figs. 2 (a), (b) and (c) respectively in comparison with the HALS-free films. In all filled films, the addition of HALS stabilizers results in considerable increases in UV stability.

In terms of respective t_{20} values (the time for 20% elongation-at-break to be lost), the HALS1 and HALS2 films containing C1 and C2 blacks with large particle size show different HALS stabilizing effectiveness in contrast to the pure films (see Fig. 1 and Table 3). The HALS1 films containing either C1 or C2 black show better UV stability than respective HALS2 films. It is also noticed that all C2 films give better UV durability than similarly stabilized C1 films. These differences in behaviours may be associated with reduced migration of HALS1 coupled with varying levels of black-HALS interactions.

a)



b)



c)

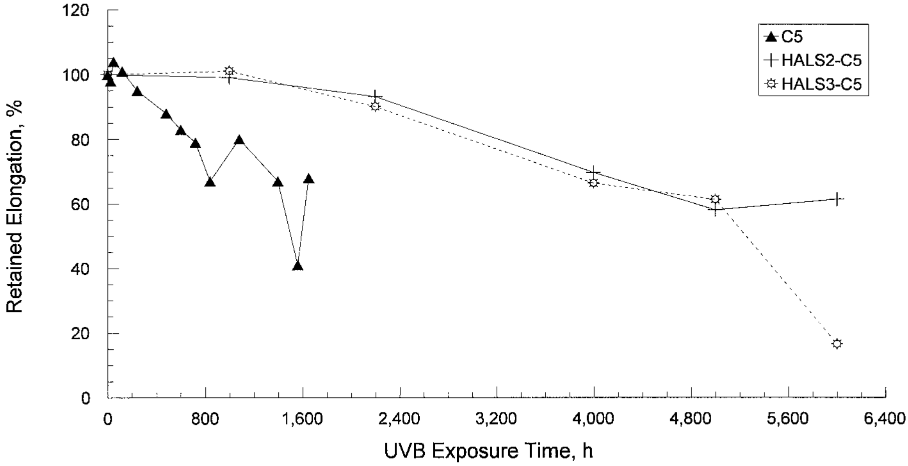


Fig. 2. Effect of UVB exposure and HALS on retained elongation of films filled with small particle-sized carbon black; (a) C3; (b) C4 and (c) C5.

Table 3. Times of 20% and 50% loss of retained elongation for HALS films in comparison with non-HALS films under UVB irradiation.

Non-HALS Films			HALS Films				
Code	t_{20}, h	t_{50}, h	Code	t_{20}, h	t_{50}, h	Synergism (%)	
						$S(t_{20})$	$S(t_{50})$
LL	50	60	HALS1-LL	510	600	-	-
			HALS2-LL	480	600	-	-
			HALS3-LL	540	620	-	-
C1	300	540	HALS1-C1	1550	2100	111	100
			HALS2-C1	1300	1650	84	56
C2	350	540	HALS1-C2	2000	3200	157	208
			HALS2-C2	1750	2450	133	134
C3	1050	1550	HALS1-C3	3400	>6000	130	>196
			HALS2-C3	3200	>6000	120	>196
C4	1450	>2200	HALS1-C4	2600	5100	37	-
			HALS2-C4	3600	>6000	94	-
C5	800	1550	HALS2-C5	3300	>6000	175	>193
			HALS3-C5	3000	5400	138	163

In C3 films, the HALS1 and HALS2 stabilizers show comparable results (see Fig. 2a) while in C4 films, the HALS2-containing film seems to be less UV degraded than the HALS1-containing film at each time (see Fig. 2b). In C5 films, both HALS2 and HALS3-containing films show similar gradual decreases in retained elongation with increasing exposure time up to 5000h after which the HALS3 film suddenly loses retained elongation-at-break compared with the HALS2-containing films which remain unchanged (see Fig. 2c).

The relative UV protective effects of the combination of HALS stabilizers and carbon blacks in comparison with the effects of HALS and blacks alone may be simply quantified in terms of changes in t_{20} and t_{50} values, the respective times of exposure required for a given film to lose 20 and 50% of elongation-at-break respectively.[1] These are given in Table 3 and show that in HALS1 films, stabilising performance order is C3>C4>C2>C1>LL and for HALS2, C4>C5>C3>C2>C1. The superior performance of the small particle-sized blacks is clearly evident. According to Al-Malaika *et al*,[17] the synergism between two stabilizers could be determined by using the following equation:

$$\%\ \text{Synergism} = \frac{[E_s - E_c] - [E_1 - E_c] - [E_2 - E_c]}{E_1 - E_c + E_2 - E_c} \times 100\% \qquad (1)$$

where, E_s = Embrittlement time (t_{20}) of synergist

E_c = Embrittlement time (t_{20}) of control

E_1 = Embrittlement time (t_{20}) of stabilizer 1 (carbon black)

E_2 = Embrittlement time (t_{20}) of stabilizer 2 (HALS)

If we replace "Embrittlement time" by $t_{20,}$ then the calculated results based on this equation are shown in Table 3. These indicate that the mixtures of the three HAL stabilizers and any grade of carbon black used give synergistic photostabilizing effects in the LLDPE films during UVB exposure. In large particle-sized black films, the C2 films show higher values of synergism than the C1 films after the addition of HALS1 and HALS2 stabilizers.

3.2.2 FTIR Spectroscopic Studies

The main changes that have occurred in IR spectra for HALS-filled films with and without carbon black are characteristic of those relating to hydroperoxide and carbonyl groups in the absorption regions of 3100-3700cm^{-1} and 1500-1850cm^{-1}. Other IR peaks identified previously,[1] such as the 887 cm^{-1} vinylidene band were also monitored but found to be of low intensity during UV ageing of HALS only films and almost absent in HALS-carbon-containing films (see Figs. 3 and 4).

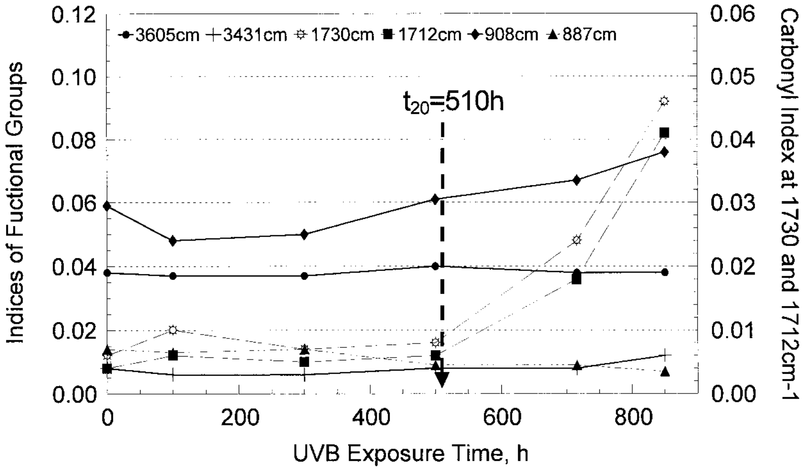


Fig. 3. Changes in absorbance index of functional groups with UVB exposure for LLDPE films containing HALS1.

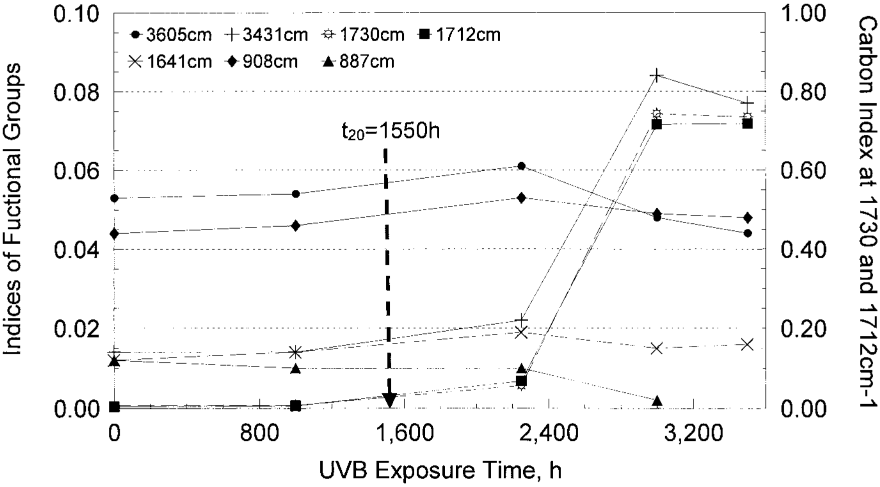


Fig. 4. Changes in absorbance index of functional groups with UVB exposure for C1 films containing HALS1.

With regard to the former, no independent hydroperoxide analysis has been carried out and so the assignment is an assumption and the conclusions drawn could be influenced by this. The control, C1 and C4 black containing films in the presence of HALS1 and HALS2 stabilizers have IR absorption spectral shapes in the region of 3100-3700cm^{-1} that are quite similar to their analogues without HALS where a broad absorption peaking at 3431cm^{-1} from associated hydroperoxide and a sharp peak at 3605cm^{-1} from free hydroperoxide were observed.[1] The former is substantially suppressed in the clear HALS films compared to the clear HALS-free films.

It is interesting that the absorption spectral detail in the region of 1500-1850cm^{-1} for the clear HALS films are quite different from the clear HALS-free films, but the growth of the most typical broad carbonyl band absorbing between 1712-1732cm^{-1} was noticed with increasing UV exposure time for all HALS-containing films. The C=C stretching band at 1641cm^{-1} present in vinyl and vinylidene groups was observed for all films before and after exposures. For the HALS1 films with and without carbon black prior to UV irradiation, two unique peaks were observed at 1531cm^{-1} and 1568cm^{-1} which could be associated with nitroxide derivatives[15] generated in the thermal extrusion process. These two peaks were not present after subsequent exposure. However, in the unexposed HALS3 films with and without carbon black, a sharp peak at 1738cm^{-1} associated with ester from the stabilizer itself was noticed which decreased in intensity with photo-ageing.

To illustrate changes in functional groups with exposure time for control and C1 (large particle size) films containing HALS1, the plots of functional group indices as a function of exposure time are given in Figs. 3 and 4 respectively. Respective t_{20} values are indicated on these curves. For all films with and without carbon black, after a certain induction period, the significant increases in index with exposure time were observed from ketone carbonyl at 1712cm^{-1} and ester at 1730cm^{-1} which were accompanied by increases in associated hydroperoxide at 3431cm^{-1}. However, the gradual growth of vinyl index at 908cm^{-1} observed in the carbon black-free films is not seen in the carbon black-filled films as noted previously.[1] Induction times, t_i, for carbonyl group formation are listed in Table 4.

Comparison of Tables 3 and 4 shows that respective t_{20} and t_i values are similar in the absence of carbon black. However, for C1 $t_i > t_{20}$, for C2 $t_i \sim t_{20}$ and for all small-particle sized black-containing films, $t_i < t_{20}$. It is interesting to note that the growth of carbonyl index stopped after 3000 h for HALS1-C1 (see Fig. 4) and after 4000 h exposure for HALS1-C4 films possibly because of lower diffusional mobility of the reactive centres in the polymeric HALS1 as previously suggested.[15]

Table 4. Induction time and Carbonyl Index at t_{20} and t_{50} under UVB irradiation.

Non-HALS Films			HALS Films			Synergism
Code	CI_{20}	t_i, h	Code	CI_{20}	t_i, h	$S(t_i)$,%
LL	0.047	72	HALS1-LL	0.006	500	-
			HALS2-LL	0.034	720	-
			HALS3-LL	0.012	720	-
C1	0.048	360	HALS1-C1	0.03	2250	204
			HALS2-C1	0.03	3000	213
C2	0.062	360	HALS1-C2	0.028	2000	169
			HALS2-C2	0.050	2000	106
C3	0.13	480	HALS1-C3	0.16	2200	155
			HALS2-C3	0.19	2200	102
C4	0.175	500	HALS1-C4	0.1	1600	79
			HALS2-C4	0.35	2400	116
C5	0.25	500	HALS2-C5	0.30	2200	98
			HALS3-C5	0.14	2200	98

Notes: t_i - Induction time.
CI_{20} - Carbonyl index at the time of 20% loss of retained elongation.

In the large particle-sized black HALS films, the rates of formation of associated hydroperoxide and carbonyl group in terms of index with exposure time for HALS2-C2 film are the fastest. For small particle-sized blacks, changes in these two functional groups with exposure time are very similar, although the rates of formation of these groups in HALS2-C5 film tend to be the fastest. It is further noticed that at longer exposure times, the rates of formation of associated hydroperoxide in the C3 and C5 films containing HALS tend to decrease and the rates of formation of carbonyl group in the C3, C4 and C5 films containing HALS tend to level off.

Using equation (1), percentage synergism factors, $S(t_i)$ may be calculated and these are listed in Table 4. These indicate that for suppression of carbonyl index, the larger carbon blacks are more effective than the smaller blacks unlike the results in Table 3, where no great size dependence was seen for either $S(t_{20})$ or $S(t_{50})$. Table 4 also lists, in addition to the induction times, t_i values, the carbonyl indices at t_{20} , namely CI_{20}. Assuming that surface chemistries are similar and that surface area of carbon black is a significant factor in determining photostabilising efficiency, possible relationships between t_{20}, t_i and CI_{20} values for HALS1 and HALS2 films and increasing carbon black surface area are depicted in Fig. 5. With increasing surface areas of carbon black, the values of t_{20}, t_i and their corresponding carbonyl index increase up to the surface area value of 140m^2/g after which t_{20} seems to remain constant, and CI_{20} tends to decrease, except for the value for HALS2-C4 film.

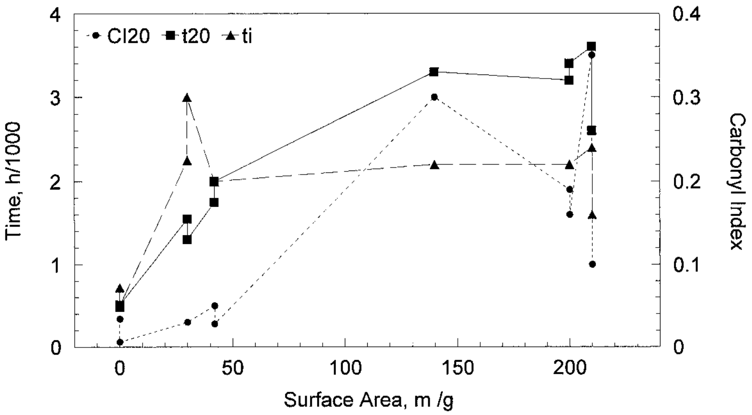


Fig. 5. Relationships of t_{20} , CI_{20} and t_i for HALS1 and HALS2 films versus carbon black surface area under UVB exposure.

3.2.3 DSC Studies

The melting temperatures, crystallinity and onset temperatures of post-fusion oxidation were obtained from the DSC tests as shown in Table 5. The melting temperatures for all HALS films tested show little change with increasing exposure time. The crystallinities derived from the DSC measurements with exposure time for both HALS1 or HALS2-containing LL films show continual rises similar to trends seen for all non-HALS-containing films with and without carbon black.[1] However, those containing carbon blacks initially show a similar increasing trend with exposure time as carbon black-free films up to 1000 h but then pass through a maximum. Thus the addition of HALS has no effect on the nucleating effect of carbon black, however, at longer exposure times, the consequences of chemical oxidative chain scissions dominate thus resulting in decreases in crystallinity.[18]

Table 5. DSC morphological properties of HALS filled films with and without carbon black after UVB exposure.

Code	UVB Time, h	T_m, ^{0}C	H_f, mJ/mg	T_{on}, ^{0}C
HALS1-LL	0	114	73	223
	100	110	109	205
	300	107	117	211
	716	111	125	210
	850	111	124	207
HALS2-LL	0	110	97	241
	100	110	107	204
	300	109	112	203
	716	109	124	207
	850	110	128	205
HALS1-C1	0	115	73	227
	1000	110	109	213
	2250	109	119	209
	3000	111	54	201
	3500	112	64	201
HALS2-C1	0	111	84	241
	1000	110	127	210
	2250	111	120	208
	3000	111	96	199
	3500	115	62	187
HALS1-C4	0	110	76	232
	1600	107	104	208
	3600	113	70	202
	4400	112	90	198
	6000	115	70	204
HALS2-C4	0	109	84	239
	1600	107	109	202
	3600	110	88	181
	4400	112	67	184
	6000	114	82	184

Notes: T_m - Melting temperature obtained from melting peak.
H_f - Heat of fusion calculated from melting endothermic area.
T_{on} - Onset temperature of post-fusion oxidation.

Generally, all T_{on} values decrease with time with asymptotic trends being shown by clear HALS films and almost linear behaviour when carbon blacks are present. These trends suggest that thermally reactive species produced as a consequence of UV exposure are significantly reduced in concentration in the presence of HALS and carbon black. Table 5 shows that HALS2-C1 and HALS2-C4 films yield lower temperatures than other films at longer exposure times. While little differences in T_{on} occurred between HALS1 and HALS2 stabilized controls, the latter effect suggests that HALS2 may be a less effective photostabiliser than HALS1. It is interesting to note that this difference between HALS1 and HALS2 is seen in Table 4 where CI_{20} figures are greater for HALS2-containing films.

3.3 Films Exposed to QUV/se, UVA Radiation Only

3.3.1 Tensile Properties

Under the UVA exposure conditions, the use of HALS significantly improves the UV stability of the films and the HALS1 film shows better photostabilizing efficiency than the HALS2 and HALS3 films. The superior photostability of HALS1 may be attributed not only to its stable polymeric structure, but also to the longer wavelength radiation emitted from the UVA source which favours photo-oxidation as opposed to photolysis.

Table 6. Times of 20% and 50% loss of retained elongation for HALS films in comparison with non-HALS films under UVA exposure.

Non-HALS Films			HALS Films			Synergism, %	
Code	t_{20} ,h	t_{50} ,h	Code	t_{20} ,h	t_{50} ,h	$S(t_{20})$	$S(t_{50})$
LL	110	120	HALS1-LL	650	1050	-	-
			HALS2-LL	400	600	-	-
			HALS3-LL	550	650	-	-
C1	450	800	HALS1-C1	1350	2200	41	29
			HALS2-C1	800	1550	10	23
C2	500	900	HALS1-C2	2000	4000	103	134
			HALS2-C2	2000	2800	178	122
C3	2100	2800	HALS1-C3	5400	>6300	109	>71
			HALS2-C3	4400	>6300	88	>96
C4	2200	3200	HALS1-C4	3700	6300	39	54
			HALS2-C4	5000	7200	105	99
C5	1800	2800	HALS2-C5	5200	>6300	157	>75
			HALS3-C5	4700	>6300	115	>99

A pronounced improvement of UVA durability was also seen in the carbon black-filled films after addition of HALS in a manner similar to UVB-exposed films. In the large particle sized-black films, the HALS1 stabilizer provides better protection to photodegradation than the HALS2 stabilizer and the C2 films have better UV durability than the C1 films; this difference was observed as well during UVB exposure. From Table 6, the UV stability of the films containing HALS1 stabilizer can be described as the order of C3>C4>C2>C1>LL and in the presence of HALS2, there is little distinction between the small particle sized-black films giving the durability order of C4 ~ C5>C3>C2>C1>LL films.

By using equation (1), synergism factors between carbon black and HALS during UVA exposure were calculated as shown in Table 6 for t_{20} and t_{50} conditions for HALS films in comparison with HALS-free films for the same UVA exposure. These results again indicate that there exists synergism between carbon black and HALS under UVA exposure conditions as well. Compared to Table 3 for the UVB-exposed films, the values of synergism at t_{20} and t_{50} in Table 6 are generally lower. This may indicate that the addition of HALS results in greater improvement of UV durability during UVB exposure than during UVA exposure.

3.3.2 FTIR Spectroscopic Studies

Overall, the changes in the IR spectra for the selected films during UVA exposures are similar to the same films exposed to the UVB source (see Figs. 3 and 4). Again, the formation of associated hydroperoxide and carbonyl groups in the clear HALS films was significantly suppressed by the presence of HALS. Compared to the HALS-free films, the absorbance indices of the two groups are relatively low even after complete loss of elongations-at-break.

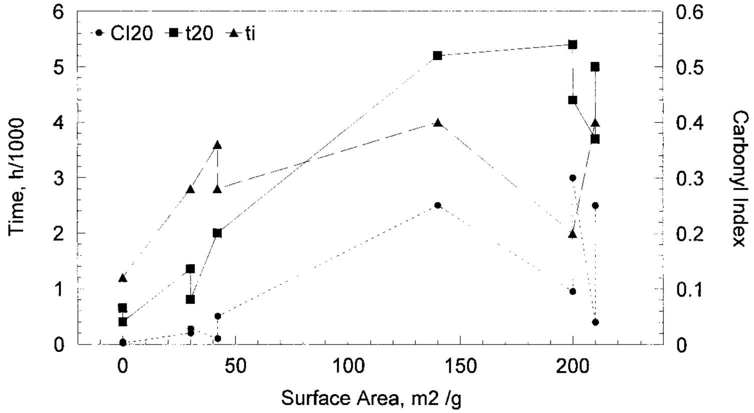


Fig. 6. Relationships of t_{20} , CI_{20} and t_i for HALS1 and HALS2 films versus carbon black surface area under UVA exposure.

Induction time values t_i, for carbonyl group generation are listed in Table 7 along with respective CI_{20} values. Generally when compared with similar results for UVB exposure in Table 4, respective t_i values are longer and CI_{20} values less for UVA-exposed samples. For clear LL HALS-containing films and large particle-sized black-containing films, $t_i > t_{20}$. For small particle-sized blacks, $t_i < t_{20}$ possibly indicating their superior property of reducing Norrish II scissions which would otherwise accelerate carbonyl group formation. Percentage synergism factors, $S(t_i)$, calculated from equation (1) are also listed in Table 7 and apart from C5 films, tend to exhibit respectively lower values than shown in Table 4 for UVB-exposed samples. It is impossible to discern a simple carbon black property relationship here, especially since the C3 films indicate antagonism (with negative $S(t_i)$ values), and the similar small particle-sized, high structured black in C5 films showing very high levels of synergy. Furthermore, they do not match the synergism values based on tensile loss times in Table 6. The plots of t_i, and t_{20}, each as a function of surface area of carbon black are shown for HALS1 and HALS2 films in Fig. 6. In general, t_i and t_{20} values increase with increasing surface area of carbon black up to the value of $140m^2/g$ regardless of the types of HALS, as observed in the same films exposed to UVB exposure conditions (see Fig. 5). Above this, t_{20} tends to gradually increase further before dropping at 200 m^2/g in contrast to the t_i value, which has achieved its maximum. Fig. 6 also shows that, as seen for the HALS films exposed to the UVB source, t_i are greater than respective t_{20} values for the control and C1 ($30m^2/g$) films containing both of HALS1 and HALS2 stabilizers. However, with increasing surface area of carbon black, $t_i < t_{20}$ except for the t_{20} value of HALS1-C4 film.

Table 7. Induction time and carbonyl indices at t_{20} under UVA exposure.

Non-HALS Films Code	CI_{20}	t_i, h	HALS Films Code	CI_{20}	t_i, h	Synergism $S(t_i)$,%
LL	0.04	150	HALS1-LL	0.004	1200	-
			HALS2-LL	0.002	1200	-
			HALS3-LL	0.013	800	-
C1	0.05	700	HALS1-C1	0.02	2800	66
			HALS2-C1	0.028	2800	66
C2	0.10	700	HALS1-C2	0.01	3600	116
			HALS2-C2	0.05	2800	66
C3	0.22	1200	HALS1-C3	0.095	2000	-12
			HALS2C3	0.30	2000	-12
C4	0.22	1200	HALS1-C4	0.04	4000	83
			HALS2-C4	0.25	4000	83
C5	0.22	1200	HALS2-C5	0.25	4000	175
			HALS3-C5	0.23	4000	285

Notes: t_i - Induction time.
CI_{20} - Carbonyl index at the time of 20% loss of retained elongation.

3.3.3 DSC Studies

With exposure, there is little change in the melting temperatures for all the exposed HALS films tested. The DSC-derived crystallinities are very similar to those for UVB-exposed films. In contrast to the control films with HALS that show only an initial increase in crystallinity and then remain constant, those with carbon black and HALS show initial increases to respective maxima with increasing exposure time.

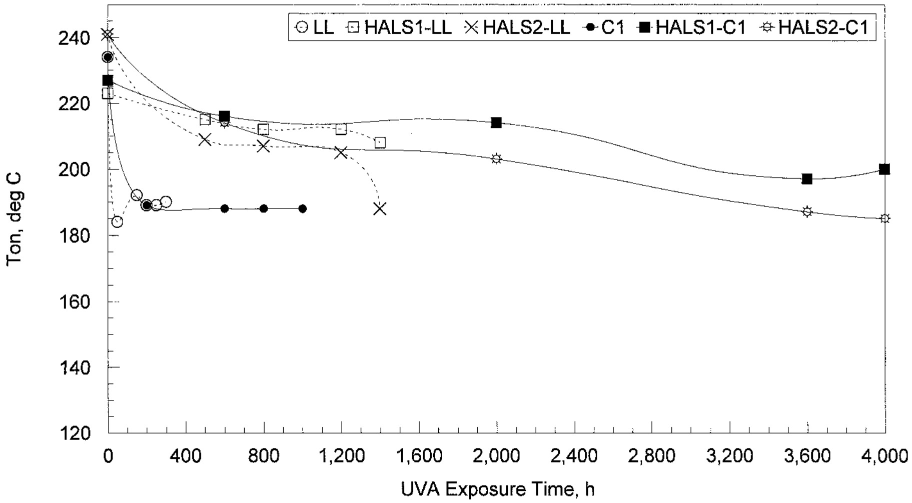


Fig. 7. Effect of HALS on oxidation onset temperatures of the LLDPE, C1 and C4 films after UVA exposure.

T_{on} values as a function of exposure time for the films selected for DSC tests are plotted in Fig. 7. As seen for UVB-exposed films previously (Table 5), under UVA exposure T_{on} versus time trends for HALS films asymptote becoming almost linear when carbon is present (note the HALS-C1 and HALS C2 trends). In the latter, higher T_{on} values may be due to the presence of HALS trapping free radicals thus inhibiting photo-oxidation and the generation of oxidation sensitive groups as mentioned above. T_{on} of the HALS1-filled films have higher values at all exposure times than those of the HALS2-filled films in agreement with the time-dependence of retained elongation results. Thus the relative tensile and physicochemical (by FTIR and DSC) property changes demonstrate consistently the superior photostabilising effect of HALS1 HALS.

4 Possible Mechanism of the Combined Effect of HALS and Carbon Black

The combined photostabilizing effect of carbon black and HALS may be summarized from various points of view:

(i) Elongation-at-break Retention: In terms of retention of elongation-at-break, UV durability of carbon black-HALS-containing films follows the order of small>large particle size of carbon black regardless of types of HALS as seen for the HALS-free films.[1] The HALS1-stabilized films show better UV resistance than the HALS2-stabilized films in large particle-sized black (C1 and C2) films. However, in small particle-sized black (C3 and C4) films, there is superior UV stability of the HALS2-filled compared to the HALS1-filled film containing C4 black in contrast to those containing C3 black. These latter show little if any differences between the HALS1 and HALS2-stabilized films. The percentage synergism values (see Tables 3 and 6) support the above observation.

(ii) Carbonyl Group Formation: With regard to carbon black variables, the large particle-sized black films show faster rates of formation of carbonyl group compared to those containing small particle-sized blacks. But induction times (t_i) show significant differences only under UVA conditions for small particle-sized blacks where $t_i < t_{20}$ holds for both exposure conditions. As previously observed from the HALS-free films,[1] the carbonyl index values at t_{20} and t_{50} increase with increasing specific surface areas (which relate inversely to particle size) up to a surface area value of 140 m^2/g (equivalent to 19nm particle diameter). This suggests that the presence of HALS may not suppress the formation of carbon black-initiated carbonyl groups from the larger surface area of carbon blacks having particle diameter >19nm while generating high t_{20} and t_{50} values. Furthermore, since it has been proposed[1] that carbon blacks may generate carbonyl groups by reducing Norrish II type chain scissions in UV-exposed HALS-free films, so this effect continues and is little affected in the HALS-containing films.

However, if we consider the stabilizing efficiencies of HALS1 and HALS2 stabilizers in terms of their effects on t_i in filled films, the lower molecular weight HALS2 stabilizer is no less effective than the HALS1 stabilizer (see Tables 4 and 7), in spite of its higher diffusional mobility. In addition, the use of HALS2 stabilizer slightly enhances the formation of carbonyl group in small particle-sized black films.

(iii) DSC-derived T_{on} trends show that after longer exposures, values for the HALS2-stabilized films are lower than those for the HALS1-stabilized films. These results correlate with the higher values of carbonyl index CI_{20} values for the HALS2-stabilized films (see Tables 4 and 8), indicating that the extent of photodegradation may be measured by the magnitude of depression of T_{on}.

In summary, the mechanism of synergism between HALS and carbon black does not seem to involve any new chemical effects. The effect of carbon black may be essentially physical where the screening effect also protects the HALS from photolysis, because the intensity of UV radiation is reduced by its presence. Hence the observed synergistic effects between HALS and carbon black are the greatest for smaller particle sizes with UVA conditions showing greater differences. It is likely that the reduced UV radiation intensity is not intense enough to decompose the light stabilising component and its derivatives giving rise to lower degradation and hence HALS consumption thus extending the induction time for photostabilisation of the carbon black-HALS films. Furthermore, the participation of carbonyl groups generated or present on surfaces of carbon black particles may also be involved in these photostabilizing reactions. This appears to be especially so under UVA conditions where CI_{20} values are generally greater for non-HALS than for HALS-containing black films (see Table 7).

One final consideration, of course, is the possible thermal antioxidant effect of the HALS present which will especially be evident if the local carbon black-polymer surface interface is higher in temperature than is the matrix in clear films. In the present experiments possible resolution of the observed synergistic effects into respective photo- and thermal stabilising effects is not possible. However, it might be assumed in the carbon black only-containing tapes, that increases in t_{20} and t_i values will be sum of a positive photodegradative stabilising effect and a negative enhanced thermal degradative one. Addition of HALS will have a positive effect on both these and so contribute to the S(t) values defined in Tables 3, 4, and 7. That the $S(t_{20})$ and particularly $S(t_i)$ values were greater for UVB than for UVA degraded films may also be partly credited to this thermal stabilising effect, although further work involving local polymer temperature measurement during irradiation would be required to more fully understand its importance.

[1] M. Liu, A. R. Horrocks, *Polym Degrad Stab* **2002**, 75, 485. see also M Liu, PhD Thesis, University of Manchester, UK, 1997.

[2] W. L. Hawkins, M. A. Worthington, F. H. Winslow, *Rubber Age* **1960**, 88: 279.

[3] W. L. Hawkins, F. H. Winslow, in: „*Reinforcement of Elastomers*", G. Kraus, Ed., Interscience Publishers, New York, **1965**, 566.

[4] H. Schneider, in: „Geotextiles, geomembranes and related products" G. Den Hoedt, Ed., Balkema, Rotterdam **1990**, 723.

[5] E. Kovacs, Z. Wolkober, in: „*Degradation and stabilization of polyolefins*", B. Sedlacek, C. G. Overberger, H. F. Mark, T. G. Fox, Eds., J Polym Sci. Polymer Symposia **1976**, 57, 171.

[6] W. L. Hawkins, V. L. Lanza, B. B. Loeffler, W. Matreyek, F. H. Winslow, *J. App Polym Sci* **1959**, 1, 43.

[7] W. L. Hawkins, in: „*Degradation and stabilization of polyolefins*", B. Sedlacek, C. G. Overberger, H. F. Mark, T. G. Fox, Eds., J Polym Sci. Polymer Symposia **1976**, 57, 319.

[8] F. Gugumus. in: „*Oxidation inhibition in organic materials*", .J Pospisil, P. P. Klemchuk, Eds., CRC Press, Florida, **1990**, 29.

[9] R. L. Gray, *Geotechnical Fabric Repor,t* **1990**, (Nov), 22.

[10] E .Stengrevics, P. Horng, *Plast Compd,* **1987**, 10(35), 35.

[11] J. M. Pena, N. S. Allen, M. Edge, C. M. Liauw, B. Valnage, *Polym Degrad Stab,* **2001**, 72, 163.

[12]] J. M. Pena, N. S. Allen, M. Edge, C. M. Liauw, B. Valnage, *Polym Degrad Stab,* **2001**, 72, 259.

[13] W. M. Hess, C. R. Herd, in: „*Carbon Black*", 2nd ed., J. Donnet, R. C. Bansal, M. Wang, eds., Marcel Dekker Inc, New York, **1993**, 116.

[14] Anon. Ciba Geigy Ltd. Publication, No. 28474/e, Sept. **1986**.

[15] D. K. C. Hodgeman, in: „*Developments in polymer degradation*", volume 4, N. Grassie, ed., Applied Science Publishers Ltd, London, **1982**, 189.

[16] F. Gugumus, *J. Polym Degrad Stab,* **1995**, 50, 101.

[17] S. Al-Malaika, G. Scott, in: „*Degradation and stabilization of polyolefins*", N. S. Allen, ed., Applied Science Publishers Ltd, London, **1983**, 283.

[18] M. Liu, A. R. Horrocks, M. Hall, *J Polym Degrad Stab,* **1995**, 49, 151.