Physicochemical Changes in UV- Exposed Low- Density Polyethylene Films

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Abstract: Unstabilized low-density polyethylene (LDPE) films and films formulated with hindered amine light stabilizer (HALS) were exposed to UV-radiation; and the physicochemical changes during photooxidation processes have been investigated using tensile, FTIR spectro-photometric and thermal analytical (DSC) techniques. The dependence of tensile properties (elongation- and stress-at-break) , carbonyl index and heat of fusion on UV-irradiation time have been discussed. The use of HALS is found to be effective in maintaining the UV- mechanical properties of the LDPE films. The experimental results showed that there exists no correlation between mechanical properties and carbonyl index, whereas crystallinity correlates well with carbonyl index in unstabilized and stabilized films for irradiation times greater than 100 h. The rate of formation of carbonyl groups is found to be dependent on UV exposure time. Crystallinity of the film samples is strongly influenced by both exposure time and presence of HALS.

Keywords: polyethylene, mechanical properties, carbonyl index, thermal properties.

Introduction

A wide variety of polymeric materials absorb solar UV-radiation and undergo photolytic, photo-oxidative and thermo-oxidative reactions that result in the degradation of the materials.[1,2] Data on wave-length sensitivity of polyethylene films exposed to different UV sources showed that radiation with wavelengths of about 400 nm affects drastically the mechanical properties of these films.[3] However, radiation with shorter wave lengths less than 280 nm can initiate the formation of free radicals.[4] It has been also indicated that visible radiation (400-700 nm) accelerates polymer degradation by heating and enhances excitation of chromophores; and that infrared radiation (700-2500 nm) accelerates thermal oxidation.[5] Many works of research literature on polymers deal with the issue of controlling photo-degradation to ensure reliable lifetimes of such materials under outdoor exposure conditions.[6,7] Long term light and thermal stability of polyethylene agricultural films was found to be dependent upon many parameters which include the ambient temperature, the dose-response characteristics of the material and the efficiency of the available light stabilizers.[8]

Effective light absorbers such as benzotriazoles, benzophenones and phenyl esters, as well as hindered amine light stabilizers (HALS) are presently used in polymer formulations intended for outdoor use.

Reported results for weathering experiments suggest that HALS can control photo-degradation in many polymeric materials.[9,10] However, the potential of the conventional photo-stabilizers to breakdown under exposure to enhanced UV-radiation, possibly decreasing their effectiveness and some commercial HALS compounds are reported to be photolyzed by UV-radiation.[11]

Chemical pathways by which common polymers photo-degrade are fairly well known, but various aspects of the mechanisms involved remain unclear. Compounding additives such as pigments, light absorbers and light stabilizers affect strongly the degradation mechanisms in polymers.[12]

Low-density polyethylene (LDPE) is used extensively in agricultural mulch and green house films. Thus, investigations of the loss of tensile properties of these films on exposure to UV-radiation is of particular interest. LDPE films were found to lose their extensibility and strength as well as their average molecular weight when exposed to UV-radiation.[13,14] The general features of the mechanism of photo-degradation in polyethylene may be one of thermo-oxidative or photo-oxidative degradation rather than of direct photolysis.[2] The free radical pathways that lead to hydroproxidation and consequent chain scission are also possible.[7] However, in LDPE films mechanical properties do not change at the same rate as chemical transformation occurring in these materials during photo-degradation.[15] The susceptibility of polyethylene to degrade was found to be dependent on the semicrystalline

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structure in which the polymer chains pass through thin lamellar crystalline and amorphous regions.[15] The effect of morphology on the photo-oxidation of polyethylene have been examined and found to be significant by many workers.[16,17] Winslow et al.[17] reported that the increase in crystallinity of LDPE films is due to oxidative crystallization and scission of constrained chains in the amorphous regions, which allows the resulting segments to crystallize. More recently, Tanaka et al.[18] investigated the effect of the morphology on the photo-degradation of LDPE films and reported that chain scission lowers the molecular weight, whereas crosslinking reaction causes an increase in the higher molecular weight fraction. Also, thermal oxidative processes in LDPE films and their degree of crystallinity were examined using differential scanning calorimetric (DSC) analysis.[19]

The present work aims to study the correlation between changes in mechanical and physicochemical properties of unstabilized and stabilized LDPE films during photo-degradation processes when exposed to UV-radiation. The experimental results are gained by using tensile tensometric, FTIR spectrophotometric and thermal analytical (DSC) techniques.

Experimental

The low-density polyethylene (LDPE) films are commercially synthesized by Shouman Plastic Co.(New Domiette, Egypt) and were used as received from the supplier. The film samples were produced by extrusion blowing technique with thickness of approximately $100 \mu m$. The hindered amine light stabilizer (HALS) was provided by Ciba-Geigy (as Tinuvin 783). It was grinned and added to polyethylene in concentration of 0.6% (w/w) and a homogenous mixture was achieved before manufacturing the stabilized films. The unstabilized films were produced at the same conditions but without addition of stabilizers. HALS type additives are used for long-term stabilization of agricultural films because of their high efficiency in retarding photo- and thermal-degradation. Their principal action mode in the degradation processes have been studied and found to act as free-radicals scavenger and hydroperoxide deactivator.[20,21]

The film samples were placed in an accelerated aging UV-chamber consisting of four UV fluorescent tubes with emission between 280 and 320 nm. All the samples were exposed to UV radiation at same conditions of humidity and at temperature of 40 °C.

Tensile properties were carried out using a testing machine (type LRX, Lloyl Instr.) with a speed of 50 mm/min, gauge length 25 mm, load cell 2500 N and at ambient temperature. Retained elongation and retained stress at-break were computed from stress-strain graphs, each of which is an average of four tests per sample. Plots of retained elongation at-break, E_o/E_t and retained stress at-break, S_o/S_t against UV exposure time, t were used to compare the changes in the

stabilized and unstabilized LDPE films. E_o and E_t are the initial elongation at-break and after an exposure time, t for a given sample; S_o and S_t are also defined in the same manner.

The infrared measurements were carried out in an FTIR-spectro-photometer (Jasco 5300) using KBr disc method. The carbonyl index (CI) was calculated from the transmission spectra by taking the ratio of absorbances at $1710 \ cm^{-1}$ (carbonyl group) and $1380 \ cm^{-1}$ (reference) bands.[22]

Differential scanning calorimetric (DSC) was used to determine the thermal characteristics of the LDPE films. The thermogramms were obtained by using a Shimadzu 50 DSC. Each sample of about 1.5 mg was heated at 25 deg/min from ambient up to 200 °C in a nitrogen atmosphere. The endotherm area from a DSC curve was integrated by the computer analyzer to measure the heat of fusion (ΔH_f), which measures the degree of crystallinity of the sample.

Results and Discussion

Tensile Properties. The results for mechanical properties of LDPE films are presented in Table I. Retained elongation-at-break, E_o/E_t shows a significant dependence on exposure time, t; a faster decrease in E_t of unstabilized films begins at $t = 120$ h and exhibits a minimum value at $t = 150$ h before it increases again as shown in Figure 1. This may be attributed to the surface oxidation, which occurs rapidly in unstabilized films, and thus tensile properties may achieve a critical dimensions after exposure time of about 150 h to promote failure. In this case elongation-at-break, E_t loses about its half initial value. However, E_o/E_t shows fluctuations over the whole studied period of irradiation, which may be due to the cyclic effect of the photo-induced reactions of crosslinking/chain scission and their influence on the mechanical properties of the LDPE films. In contrast stabilized films show nearly constant E_o/E_t for $t > 50$ h which reflects the effi-

Table I. Values of Retained Elongation-at-break (E_o/E_t) and Retained Stress-at-break (S_o/S_t) of Stabilized and Unstabilized LDPE Films at Different UV-exposure Times

Exposure Time, t(h)	Retained Elongation-at-break (E_o/E_t)		Retained Stress-at-break (S_o/S_t)	
	Unstabilized	Stabilized	Unstabilized	Stabilized
0	1.0	1.0	1.0	1.0
25	1.02	1.09	1.11	1.0
50	1.0	1.32	1.07	1.14
75	0.94	1.25	1.14	1.12
100	1.20	1.23	1.44	1.03
125	0.95	1.26	1.16	1.07
150	1.73	1.28	1.63	1.20
175	1.05	1.31	1.38	1.24
200	1.35	1.23	1.56	1.14

ciency of HALS in increasing the durability of the films. Also, plots of retained-stress-at-break, S_o/S_t against (t), Figure 2 indicates that unstabilized films suffer strong variations compared with stabilized ones, particularly for $t > 72$ h.
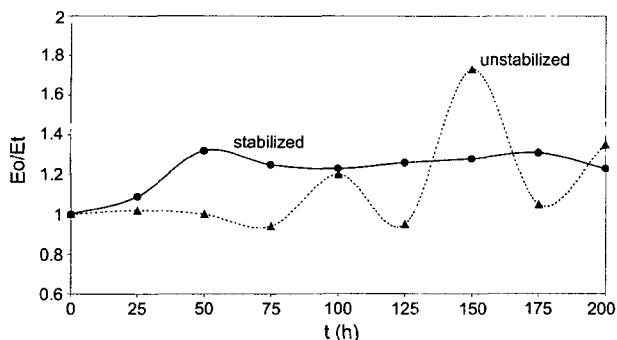
Chemical Changes. FTIR spectra of stabilized and unstabilized LDPE films for different exposure times are illustrated in Figure 3. The calculated values of the carbonyl index (CI) are quoted in Table II and plotted as a function of the time of irradiation, t, Figure 4. It can be observed that up

Figure 1. Effect of exposure time, t on retained elongation-at-break, E_o/E_t for unstabilized and stabilized LDPE films.
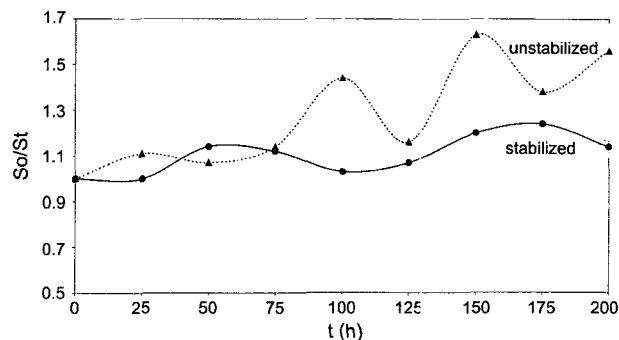
Figure 2. Effect of exposure time, t on retained stress-at-break, S_o/S_t for unstabilized and stabilized LDPE films.
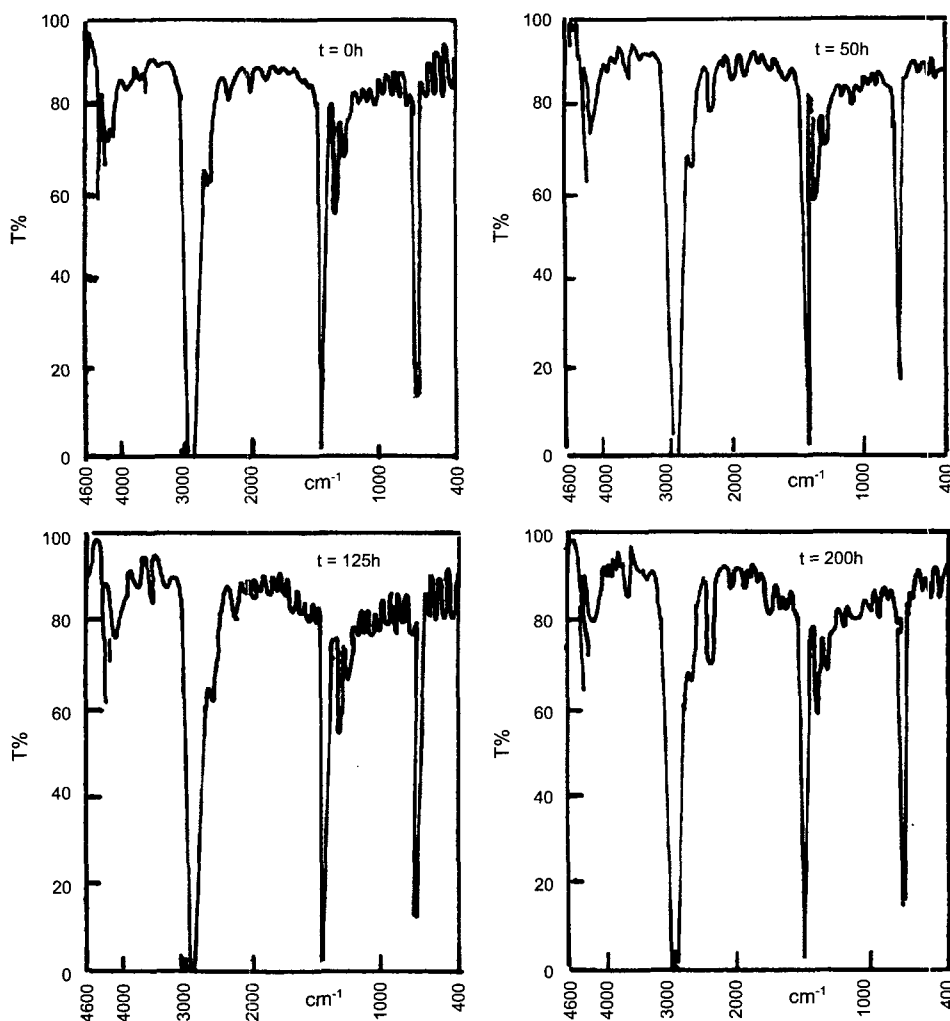

Figure 3a. IR transmission spectra of unstabilized films at different exposure times.

to $t = 72$ h, there is no significant difference in CI between stabilized and unstabilized films. However, at $t = 100$ h, CI

Table II. Values of Carbonyl Index (CI) Calculated from FTIR-spectra

Exposure time, t (h)	Carbonyl Index (CI)	
	Unstabilized	Stabilized
0	0.30	0.30
25	0.38	0.38
50	0.29	0.30
75	0.38	0.39
100	0.32	0.40
125	0.38	0.37
150	0.43	0.34
175	0.45	0.33
200	0.50	0.30

increases linearly with t in unstabilized films, whereas it decreases linearly in stabilized ones. It is well established that in photo-oxidation process HALS react with oxygen to sensitize their photo-stabilizing character[23] and the amine derived radicals are oxidized to the persistent nitroxyl radi-
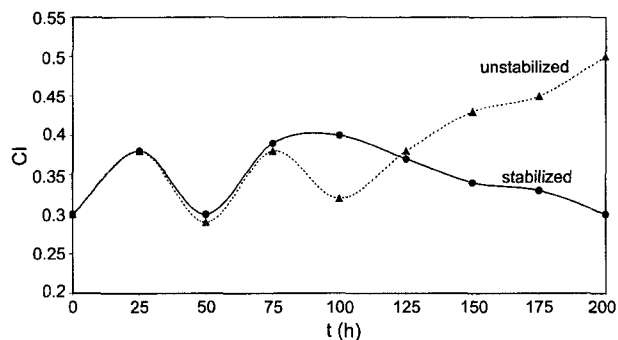
Figure 4. Effect of exposure time, t on carbonyl index, CI for unstabilized and stabilized films.
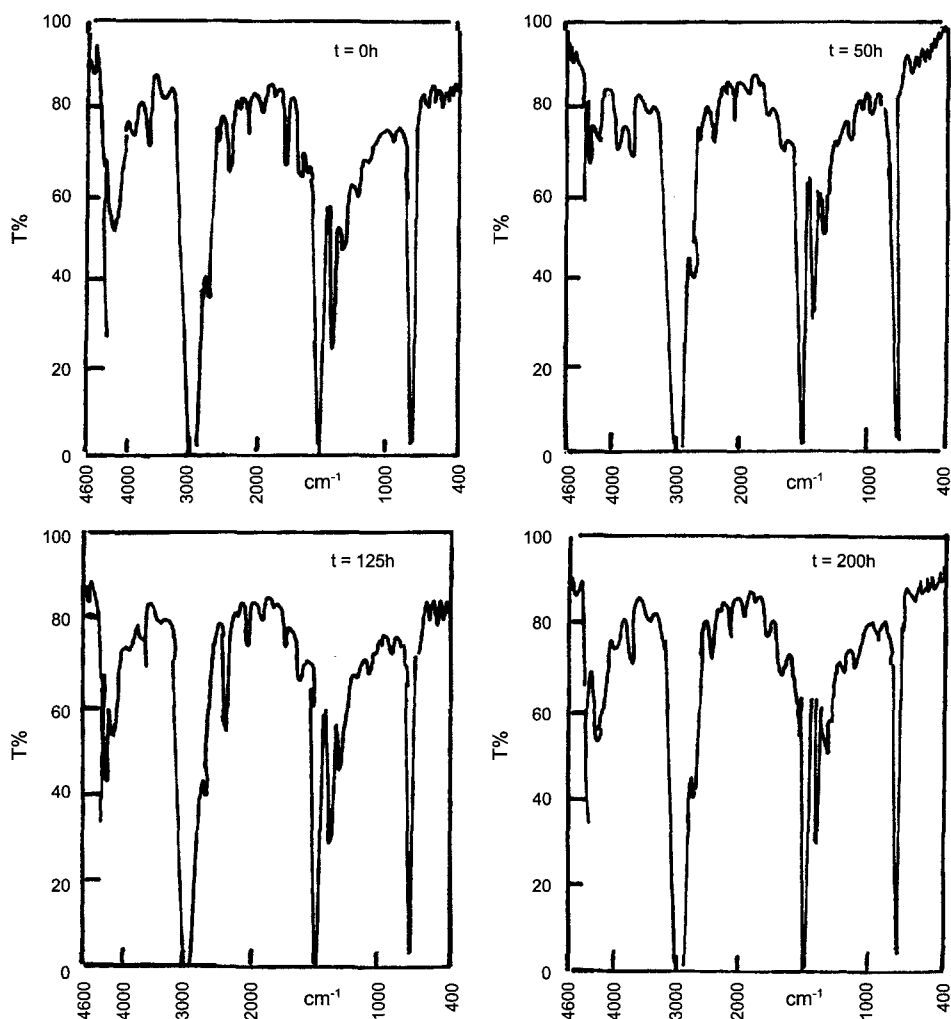
Figure 3b. IR transmission spectra of stabilized films at different exposure times.

cals which scavenge other radicals very effici-ently.[24] Thus, the behavior of S_o/S_t, Figure 2 and CI, Figure 4 may be due to that in initial UV irradiation the photo-oxidation process is slow and the HALS begin to act efficiently for $t > 72$ h.

Earlier attempts have been made to correlate CI with E_o/E_t in LDPE films.[25] According to the present results, there exists no correlation between tensile properties and carbonyl index values. This means that tensile properties of LDPE films do not change at the same rate as carbonyl groups formation. Such behavior seems to be in a good agreement with the recently concluded by Mingguang *et al.*[15]

Thermal Analysis. Figure 5 shows the DSC thermograms under nitrogen for stabilized and unstabilized films for different UV exposure times. The computed values of heat of fusion, H_f, which measures the degree of crystallinity are given in Table III. The effect of exposure time, t on H_f for studied film samples is shown in Figure 6. Crystallinity of unstabilized films increases at initial irradiation, then decreases up to $t = 125$ h and then increases again. However, crystallinity of stabilized films is seen to increase slightly with exposure time up to $t = 75$ h then decreases again. This behavior supports the idea that HALS begin to act effectively after exposure time of about 75 h and agrees well with the rate of carbonyl groups formation , Figure 4. Thus, crystallinity of LDPE films is strongly influenced by UV exposure time and presence of HALS. On considering Figures 1, 2 and 6 it can be seen that there exists a poor correlation between mechanical properties and crystallinity. However, for $t > 75$ h , H_f and hence the crystallinity increases linearly with carbonyl index (CI), which assumes that crystallinity correlates well with carbonyl groups formation rather than mechanical properties. Therefore, photo-oxidation process in LDPE films is accompanied by increased crystallinity. However, mechanisms govern photo-degradation in these films are complicated and strongly influenced on other factors such as structural inhomogenities, filler and impurities, which catalyze the breaking of polymer chains during UV-irradiation.

Conclusions

The results of UV-mechanical, chemical and thermal properties, measured as retained elongation-, stress-at-break, carbonyl index and heat of fusion, of unstabilized LDPE and films formulated with HALS have enabled the following points to be concluded :

(1) The use of HALS are effective in maintaining the tensile properties of the films when exposed to UV radiation.

(2) For $t > 75$ h, the rate of carbonyl groups formation increases linearly with exposure time in unstabilized films, whereas it decreases linearly in stabilized ones.

(3) There exists no correlation between mechanical properties and Carbonyl index.

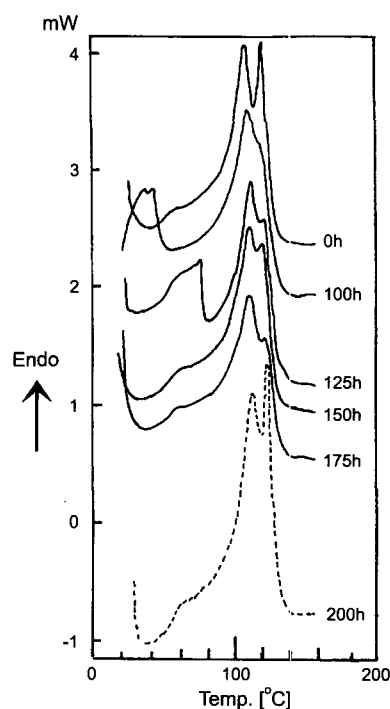(4) Crystallinity of the films is found to be linearly depen-

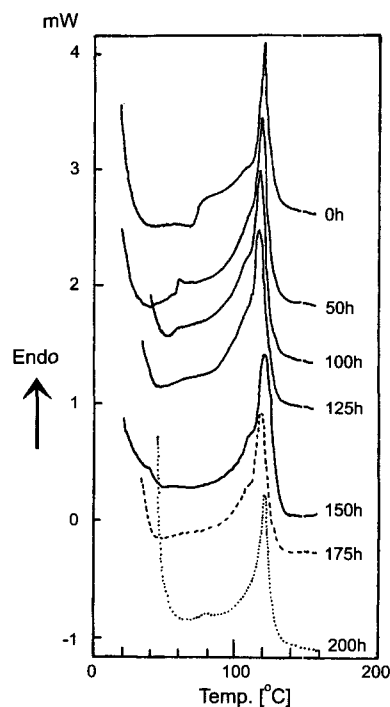**Figure 5a.** DSC curves of unstabilized films at different exposure times.

Figure 5b. DSC curves of stabilized films at different exposure times.

dent on carbonyl index for higher exposure times.

(5) Crystallinity of the films is strongly influenced by UV

exposure time and presence of HALS.

Table III. Values of Heat of Fusion (H_f) Calculated from DSC Graphs

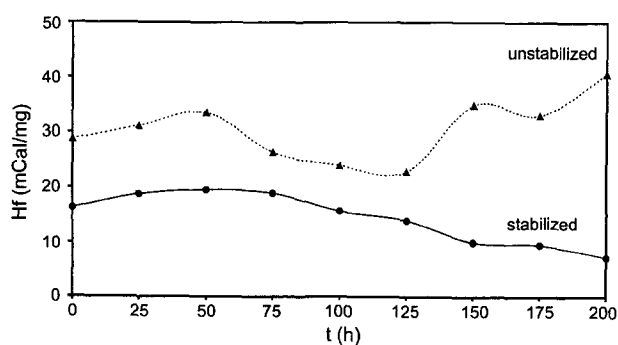| Exposure time, t (h)	Heat of fusion, H_f (mCal/mg)	
	Unstabilized	Stabilized
0	28.71	16.22
25	31.10	18.68
50	33.49	19.47
75	26.32	18.87
100	23.92	15.70
125	22.81	13.90
150	34.86	10.10
175	33.10	9.57
200	40.67	7.18

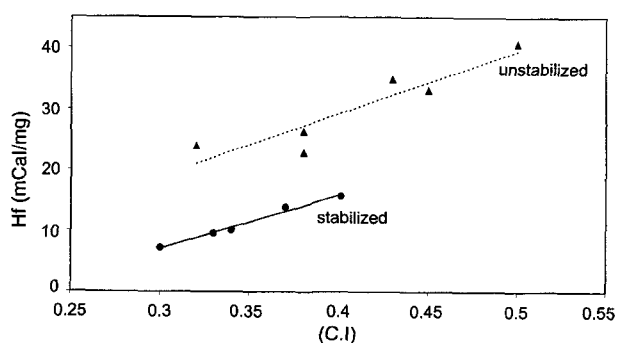**Figure 6.** Dependence of heat of fusion, H_f on exposure time, t for unstabilized and stabilized films.

Figure 7. Relationship between heat of fusion, H_f and carbonyl Index, CI for unstabilized and stabilized films.

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