

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### NATURAL AND ACCELERATED WEATHERING OF STABILIZED COPOLYMER ETHYLENE-PROPYLENE (LOW ETHYLENE CONTENT)

Adams Tidjani<sup>a</sup>; Anicet O. Dasilva<sup>a</sup>; Elisabeth Fanton<sup>b</sup>; René Arnaud<sup>b</sup>

<sup>a</sup> Université Cheikh A. Diop de Dakar, Dakar-Fann, Sénégal <sup>b</sup> Université Blaise Pascal de Clermont II, Aubière, Cédex, France

Online publication date: 06 August 1999

**To cite this Article** Tidjani, Adams , Dasilva, Anicet O. , Fanton, Elisabeth and Arnaud, René(1999) 'NATURAL AND ACCELERATED WEATHERING OF STABILIZED COPOLYMER ETHYLENE-PROPYLENE (LOW ETHYLENE CONTENT)', *Journal of Macromolecular Science, Part A*, 36: 4, 633 – 644

**To link to this Article:** DOI: 10.1081/MA-100101553

**URL:** <http://dx.doi.org/10.1081/MA-100101553>

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## NOTE

# NATURAL AND ACCELERATED WEATHERING OF STABILIZED COPOLYMER ETHYLENE-PROPYLENE (LOW ETHYLENE CONTENT)

**ADAMS TIDJANI\* and ANICET O. DASILVA**

Laboratoire des Rayonnements Naturels et Artificiels  
Faculté des Sciences et Techniques  
Université Cheikh A. Diop de Dakar  
Dakar-Fann, Sénégal

**ELISABETH FANTON and RENÉ ARNAUD**

Laboratoire de Photochimie Moléculaire et  
Macromoléculaire  
(U.R.A. C.N.R.S. 433)  
Université Blaise Pascal de Clermont II  
63177, Aubière Cédex, France

Key Words: Stabilized Copolymer Ethylene-propylene, HALS, CaCO<sub>3</sub>, Talc, TiO<sub>2</sub>, Photooxidation, Infrared Spectroscopy, Elongation at Breaks

## ABSTRACT

The photo stability of ethylene-propylene copolymers (low ethylene content) containing different stabilizing systems is investigated. Infrared spectroscopy and elongation at break techniques are used to follow the degradation process under natural and accelerated UV exposure. It is found that the combination of

---

\* Author to whom correspondence should be addressed.

antiacid calcium stearate and phenolic antioxidant acts as a pro-oxidant. The addition of HALS, particularly the one with low molecular weight, remarkably improves its performance by increasing the induction period. Subsequent combinations with inorganic filler prove that it is not beneficial to add  $\text{CaCO}_3$  and Talc to the stabilizing systems tested herein; both drastically reduce the induction period that is opposite to what was observed when  $\text{TiO}_2$  was added. Contrary, these compounds have apparently no effect on retention of mechanical properties that change in a very complex manner.

For practical purposes, natural and accelerated weatherings were compared in the determination of the accelerated factor of the UV exposure device. It varies in a wide range (from 4 to more than 25) depending on the nature of the additive system. Then the prediction of the natural lifetime of polypropylene sample from measurements in accelerated conditions is related to the nature of its stabilization system.

## INTRODUCTION

Under service conditions, polyolefins are subjected to several stresses such as heat, light, and oxygen. These stresses are responsible for both chemical and physical changes occurring in the polymers. This undesirable degradation is a limiting factor to the use of polymers in many applications [1]. In the past several years, great effort has been devoted to the understanding of the degradation mechanism. The knowledge of this mechanism is desirable for the right choice of a stabilization system. Several stabilizer formulations have been reported for polyolefins. An effective stabilization system requires the combination of several different types of stabilizers working together in a synergistic manner. Although considerable advances have been made in the stabilization of polymers against the degradation process, many controversies still exist. These are related to: the chemistry of additives action [2], the real action of each stabilizer included in combinations of stabilizers; the stabilizers that may address several oxidation processes have been demonstrated to be more effective in many cases [3], the loss of stabilizers during the photo degradation process under natural and accelerated conditions [4], and the difficulty of the outdoor lifetime prediction of polymers based only on IR spectrometric laboratory tests [5, 6].

In spite of all these difficulties, manufacturers and scientists keep trying combinations of different stabilizers to find the most effective one. Because they



are time consuming, most of these experiments are carried out in accelerated testing chambers. The lack of information under natural exposure challenges the validity of many studies in which the efficiency of a stabilizer system is established from accelerated data. This encourages us to conduct, under aggressive natural conditions, an investigation of the photo stability of different systems incorporated in copolymer ethylene-propylene. Infrared spectroscopy and elongation at break changes were used to monitor the photodegradation process.

## EXPERIMENTAL

### Materials

The ethylene-propylene copolymers PPR 1042, consisting of blends of isotactic PP as major constituent and low content of ethylene (15%), were obtained from Hoechst. They were in the form of films around 100  $\mu\text{m}$  thick. The film thickness was measured using a micrometer with  $\pm 1 \mu\text{m}$  accuracy. All of them contained 1000 ppm of antiacid calcium stearate and 1000 ppm of antioxidant (AO) B 215 (Ciba Geigy). Different stabilizer systems, combining several additives from Ciba-Geigy (anti-UV: Tinuvin 326, HALS 1: Tinuvin 770 and HALS 2: Chimisorb 944) were incorporated in the films by the manufacturer (Table 1). Some of the samples in addition contained 20% of  $\text{CaCO}_3$  millicarb OMYA, 2% of  $\text{TiO}_2$  C1 220 CHRONOS or 20% of talc 20 MOOS LUZENAC.

### UV Exposure

The accelerated exposure device used in the experiments was a SEPAP 12-24, which has been described fully earlier [7]. It allows a "medium-accelerated" photo aging. The operating temperature was set at 60°C.

Natural exposures were carried out at Dakar, Senegal as described in a previous paper [6]. In such a tropical climate, one can expect to collect significant information in a matter of weeks.

### Analytical Measurement

The rate of photooxidation of UV degraded samples was followed by measuring the build-up in non-volatile carbonyl oxidation products that have an IR absorption around 1715  $\text{cm}^{-1}$ . IR measurements were carried out with a NICOLET 510 Fourier Transform IR spectrometer.



TABLE 1. Films Used and their Stabilizing Additives (AO: APntioxidant B 215, HALS 1: Tinuvin 770, HALS 2: Chimasorb 944, Anti-UV: Tinuvin 326)

<b>ADDITIONAL SAMPLES</b>	<b>CALCIUM STEARATE</b>	<b>AO</b>	<b>HALS 1</b>	<b>HALS 2</b>	<b>ANTIUV</b>	<b>CaCO3</b>	<b>TITANIUM DIOXIDE</b>	<b>TALC</b>
<b>PP 1C</b>	1000 ppm	1000 ppm	-	-	-	-	-	-
<b>PP 2C</b>	1000 ppm	1000 ppm	1000 ppm	-	-	-	-	-
<b>PP 3C</b>	1000 ppm	1000 ppm	-	1000 ppm	-	-	-	-
<b>PP 4C</b>	1000 ppm	1000 ppm	1000 ppm	-	3000 ppm	-	-	-
<b>PP 5C</b>	1000 ppm	1000 ppm	1000 ppm	-	-	20%	-	-
<b>PP 6C</b>	1000 ppm	1000 ppm	-	-	-	-	-	20%
<b>PP 7C</b>	1000 ppm	1000 ppm	1000 ppm	-	-	-	-	20%
<b>PP 8C</b>	1000 ppm	1000 ppm	-	-	-	-	2%	-
<b>PP 9C</b>	1000 ppm	1000 ppm	1000 ppm	-	-	-	2%	-

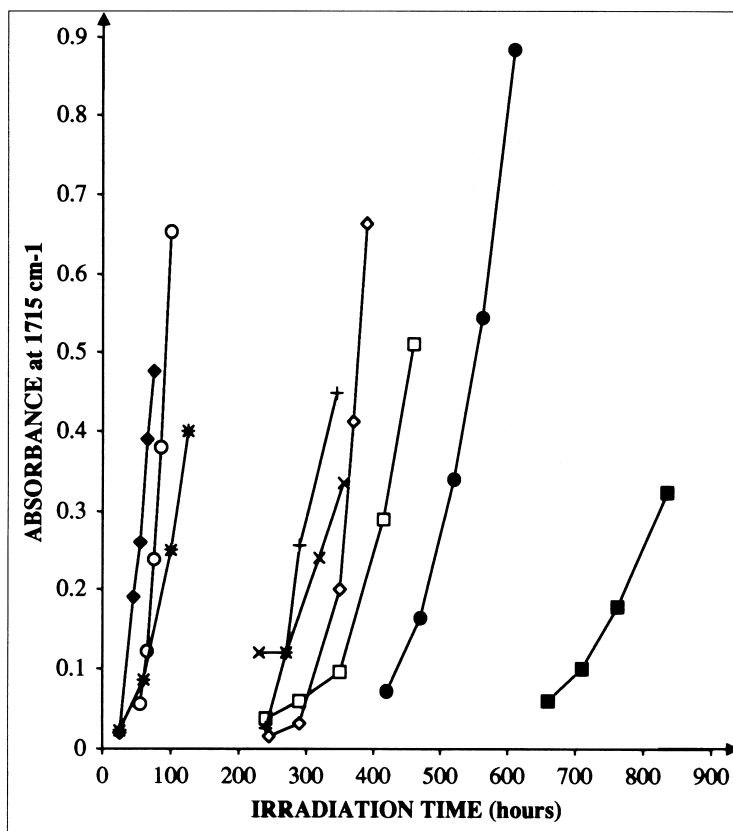
The direct consequence of the chemical structural modifications on mechanical properties during natural weathering was investigated by measuring the elongation at break. The tests were done at ambient temperature ( $25.0 \pm 0.2$ )°C using an Adamel Lhomargy DY 22 testing machine. The elongational velocity was 100 mm/min. The results given here represent an average of at least 5 measurements.

## RESULTS AND DISCUSSION

The UV irradiation of stabilized films in the SEPAP 12-24 unit leads to changes of the IR spectra in carbonyl ( $1900\text{-}1500\text{ cm}^{-1}$ ) and hydroxyl region ( $3800\text{-}3200\text{ cm}^{-1}$ ). We focused our attention on the band at  $1715\text{ cm}^{-1}$  corresponding to the formation of carbonyl species (mainly ketones and carboxylic acids). Figure 1 illustrates the changes of the absorption at  $1715\text{ cm}^{-1}$  with the aging time. In all cases, carbonyl formation is auto catalytic irrespective of the stabilizer system. Except for samples PP1C and PP6C, the formation of carbonyl groups is delayed comparatively to the control sample. This time, which corresponds to the induction period, is highly dependent on the stabilizer system incorporated in the film. It is quite short for PP6C and PP1C (25 and 55 hours, respectively); both are protected with the anti-oxidant. One can note that the addition of talc (20% in PP6C) drastically reduces the induction period as compared to PP1C. On the other hand, the addition of  $\text{TiO}_2$  brings a better effectiveness evidenced by the result obtained for PP8C with an induction period jumping to 200 hours in Table 2.

Incorporation of HALS also greatly improves the performance of the stabilizer system as shown by the increase of the induction period of PP3C, PP7C, PP5C, PP2C and PP9C (200, 230, 250, 400 and 1400 hours of induction times, respectively). HALS 2 seems to be less efficient than HALS 1 with regard to the induction period of PP3C and PP2C. When comparing the induction period of PP9C and PP2C, we also note here, that  $\text{TiO}_2$  contributes greatly to the photo stability already conferred by HALS 1. By adding an anti UV to the stabilizing system containing the HALS 1, we observe a remarkable delay of the induction period (from 400 hours for PP2C to 630 hours for PP4C). On the other hand, the addition of  $\text{CaCO}_3$  or talc leads to a noticeable decrease of the induction period (the induction times of PP5C and PP7C are inferior to the one of PP2C). This confirms the degrading effect of talc observed previously.





**Figure 1.** Variation in the absorbance values at 1715 cm<sup>-1</sup>, corrected for 100 mm, during the accelerated photoaging: Control (\*), PP1C (○), PP2C (●), PP3C (□), PP4C (■), PP5C (◇), PP6C (◆), PP7C (+) and PP8C (X). Note that PP9C is not displayed because of its out-of-scale induction time (1389 hours).

Under natural exposure, the development of the IR spectrum in the carbonyl and hydroxyl regions was quite similar to that observed under accelerated UV irradiation. Figure 2 compares the oxidation rates of the stabilized systems with that of the control under natural photoaging. Additional data is available in Table 2 for an easy comparison of the effectiveness of the stabilizer systems tested. Taking the induction time as the comparative extent in Table 2, the order in terms of ability to stabilize the polymer under natural conditions is PP5C > PP9C > PP2C > PP4C > PP3C > PP7C > PP8C > control > PP1C > PP6C. Few differences are noticeable with the order obtained under accelerated conditions ( PP9C > PP4C > PP2C > PP5C > PP7C > PP3C = PP8C > control > PP1C > PP6C).

TABLE 2. Parameters Measured During UV Exposure: (a) Absorbance Values at  $1715\text{ cm}^{-1}$  Correspond to the Loss of 50% of the Elongation at Break Under Natural Photooxidation; (b) T<sub>50</sub> is the Time Corresponding to 50% Loss of the Elongation at Break; (c) Time of the First Sampling. The Acceleration Factor F is the Ratio Between the Induction Period Under Natural Conditions (in hours) to the One Under Accelerated Conditions (in hours)

SAMPLES	Initial Elongation at Break (%)	A <sub>50</sub> (a)	T <sub>50</sub> (days) (b)	Induction time under		Acceleration factor F
				natural conditions (days)	accelerated conditions (hours)	
PP 1C	374±52	0.3	60 (c)	18	55	8
PP 2C	403±22	0.15	230	150	400	9
PP 3C	384±36	0.08	220	100	200	12.0
PP 4C	368±56	0.03	210	130	630	5
PP 5C	340±35	0	210	>269	250	>26
PP 6C	322±40	0.35	60 (c)	10	25	10
PP 7C	312±11	0.01	100	120	230	9
PP 8C	365±16	0.20	130	45	200	5
PP 9C	385±15	0.02	250	230	1400	4.0
CONTROL	-	-	-	25	60	10

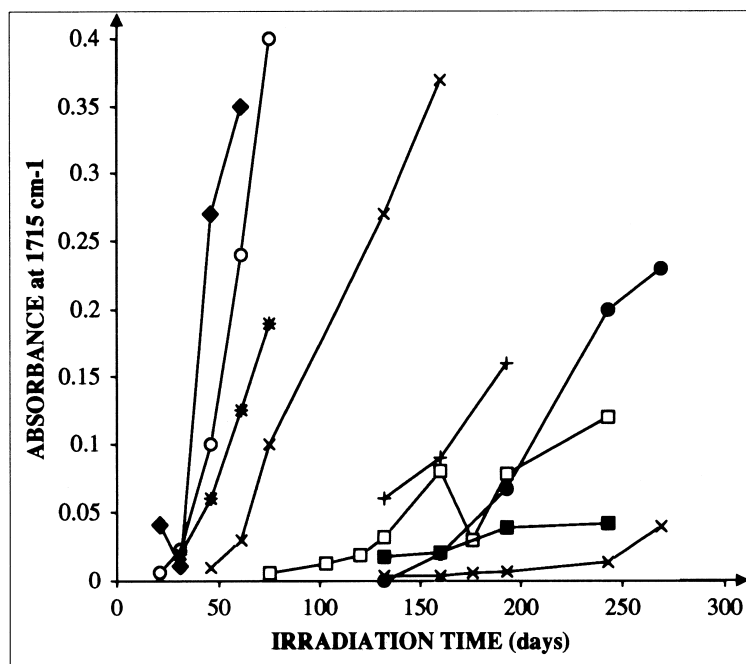
The photooxidation of stabilized or unstabilized polymers results in numerous chain scissions. This leads to physical deterioration of the polymers. Elongation at break is one of the most sensitive methods for measuring the physical modification that occurs. Figure 3 shows an overview of the concomitant variations of the elongation at break and the absorbance at  $1715\text{ cm}^{-1}$  during the natural weathering for two film samples. All other films displayed identical curves. These curves are conventional. Usually the loss in the elongation at

Downloaded At: 13:27 24 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.





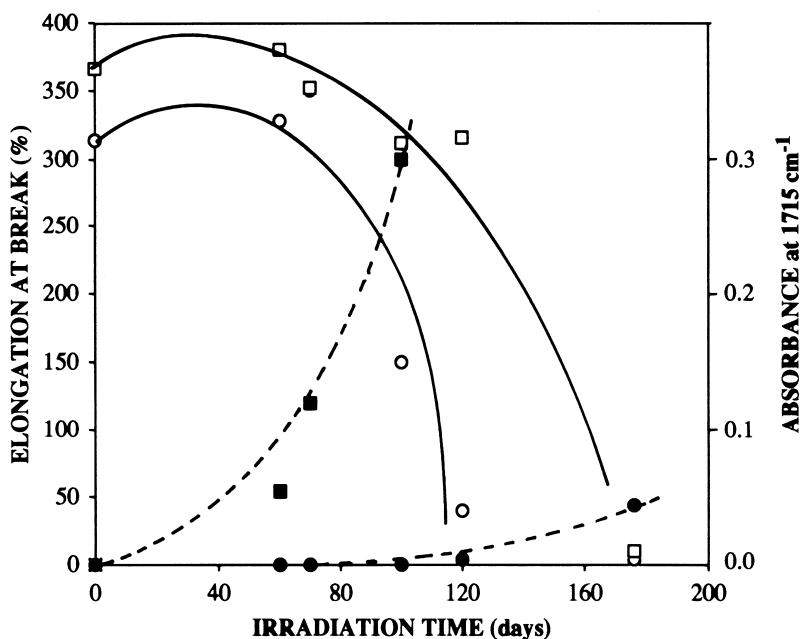


**Figure 2.** Variation in the absorbance values at 1715 cm<sup>-1</sup>, corrected for 100 mm, during the natural photoaging: Control (\*), PP1C (○), PP2C (●), PP3C (□),

break is characterized by the so-called “half-time”  $T_{50}$  at which a 50% reduction of the elongation is observed. This time corresponds to the value  $A_{50}$  of the absorbance at 1715 cm<sup>-1</sup>. The  $T_{50}$  and  $A_{50}$  values are listed in Table 2; the latter calls for a major observation: there is no correlation between the level of oxidation and the loss of elongation at break. Some samples lose their mechanical property at a relatively high level of oxidation, others at a low one and even at zero level (PP5C and PP7C).

The classification established from the exposure days  $T_{50}$  corresponding to the half of the elongation at break gives the following order: PP9C > PP2C > PP3C > PP5C = PP4C > PP8C > PP7C > PP1C = PP6C. Here too, we note that this order is not different from the ones obtained previously from the induction time.

Ethylene-propylene copolymers containing the antiacid calcium stearate (1000 ppm) and the antioxidant (1000 ppm) show very poor stability against photooxidation. Compared to the control, we can even say that this stabilization system is a prooxidant as indicated by a reduction of the induction period. A marked improvement of UV stability is achieved by adding an HALS; we



**Figure 3.** Variations of the elongation at break (open symbols) and the absorbance at  $1715\text{ cm}^{-1}$  (closed symbols) of two ethylene-propylene copolymers: PP7C (○) and PP8C (□).

observe an increase of the induction period. Comparing the induction period of PP2C and PP3C under both natural and accelerated weathering conditions, a further interesting effect was noted, HALS 1 was more efficient than HALS 2. It is largely accepted that the activity of HALS is due to the conversion of the amine to the corresponding nitroxyl radicals. These are powerful trapping agents for alkyl and/or peroxy radicals according to the oxidation conditions. We observed a difference in the efficiency of HALS 1 (low molecular weight) and 2 (high molecular weight). This can be attributed to the ability of HALS 1 to diffuse more freely in the matrix of the polymer than HALS 2. As a result, HALS 1 displays a better capacity to do its job. Others physical processes such as volatilization and exudation may also contribute, to a different extent, to loss of the HALS's, according to the molecular weight.

During the induction period, scission reactions responsible for the loss of elongation at break are supposed to be delayed. Some results obtained under natural exposure contradict this hypothesis. A loss of mechanical property at an



apparent zero level of carbonyl species for some samples is evidenced. The photooxidation of ethylene-propylene copolymer with low content of ethylene occurs mainly in the polypropylene phase, and we can consider that photo products come essentially from the PP component [8]. Recently, we have found strong indications that carbonyl species (ester, acid and ketone) were probably issued from scission reactions during the photoaging study of PP under natural and accelerated UV exposure [9]. In the present study, under natural conditions, the loss of mechanical property at an apparent low degree of oxidation can be attributed to the disappearance of these carbonyl species produced by scission reactions. According to Delprat *et al.* [8], the loss of photo products, having an absorption at  $1713\text{ cm}^{-1}$  by migration out of the polymer, can be observed in the case of very long irradiation durations. This is the case for the stabilized samples that require long aging time under natural conditions. Another route for the disappearance of photo products is their transformation into volatile products such as acetic acid, methanol, etc. [10]. Moreover, the presence of HALS as a stabilizer could modify the stoichiometry of the photooxidation, leading to an inhibition of the formation of the carbonyl products at  $1715\text{ cm}^{-1}$ .

From our results, it is found that the photooxidation of stabilized ethylene-propylene copolymer is accelerated by  $\text{CaCO}_3$  and talc (comparison of PP7C and PP2C, and PP6C and PP1C). Two possible hypotheses may explain this effect. First, fillers could adsorb stabilizers from the polymer during processing. This inhibits the capacity of the latter to protect the polymers against harmful UV light. Furthermore, it has been shown that  $\text{CaCO}_3$  may contain impurities such as Mn, Fe, Zn and Al [11]. These metal ions absorb UV-lights and could induce secondary photochemical reactions, therefore favoring the photo-degradation process. On the other hand, the effectiveness of the chosen stabilizing system is considerably increased when the stabilization systems are modified with  $\text{TiO}_2$  (comparison of the induction periods of PP8C and PP1C, and PP9C and PP2C). As described in several papers,  $\text{TiO}_2$  pigment plays a twin role in polymer; by absorbing and/or screening energy light, they can exhibit a protective effect or they may be photo-active and sensitize the photochemical breakdown of the polymer [12, 13]. The results presented here suggest that  $\text{TiO}_2$  plays a stabilizing role in the photoaging of ethylene-propylene copolymer in our experimental conditions. In contrast to the observation for the induction period, the contribution of  $\text{TiO}_2$ ,  $\text{CaCO}_3$  and Talc to the preservation of mechanical properties is insignificant. This means that these compounds do not intervene in the course of mechanical property deterioration.



The classification of stabilizing systems studied were not too different when using the induction period and/or the exposure time  $T_{50}$  corresponding to the half of the elongation at break. This observation is quite remarkable because very often, the results obtained under natural exposure do not match those collected under accelerated conditions. Therefore, the acceleration factor  $F$ , defined as the ratio between the induction time under natural conditions (in hours) and the one under accelerated conditions (in hours), varies in a wide range (from 4 to more than 25). This range of values is much larger than the one obtained for LLDPE stabilized by different systems using an anti UV, a metal chelate and a HALS (from 4 to 9) [5]. These results prove again that the acceleration factor depends on the polymer and the stabilization system incorporated. Therefore, natural weathering is usually too long to be practical; the prediction of the natural lifetime of a polymer sample by means of accelerated laboratory tests is possible only if the  $F$  factor is known from previous studies.

## CONCLUSION

The combination of the antiacid calcium stearate (1000 ppm) and the antioxidant behave as a prooxidant in the accelerated and natural UV photo degradation of ethylene-propylene copolymers. The addition of HALS and anti UV to this stabilizing system greatly improves its performance by increasing the induction period. Low molecular weight HALS 1 has proven to be more efficient to delay the photooxidation process than HALS 2 with higher molecular weight; this is probably due to a difference in their ability to diffuse into the matrix of the polymer.

Under natural exposure, stabilized ethylene-propylene polymer with a low content of ethylene does not display any systematic correlation between the half of elongation at break and the absorbance at  $1715\text{ cm}^{-1}$ . We explain this observation by the probable disappearance of carbonyl species- that absorb at  $1715\text{ cm}^{-1}$  issued from scission reactions.

The addition of fillers  $\text{CaCO}_3$  or does not seem beneficial to the stabilizing systems tested here in. Both drastically reduce the induction period. Fillers could adsorb stabilizers during processing leading to its failure to protect the ethylene-propylene copolymer against photooxidation. For  $\text{CaCO}_3$ , the presence of impurities may also be responsible for the rapid degradation observed. On the other hand, the addition of the pigment  $\text{TiO}_2$  seems to be a benefit with regard to the increase of the induction period. Therefore, the contribution of  $\text{TiO}_2$ ,  $\text{CaCO}_3$  and Talc to the retention of the mechanical properties is practically neglected.



The disparity in the values of the acceleration factors confirms the specificity of the various stabilizing systems and the necessity to determine the dependency of the acceleration factor for a given class of stabilizer.

## REFERENCES

- [1] B. Ranby and J. F. Rabek, *Photodegradation, Photooxidation and Photostabilization of Polymers*, J. Wiley & Sons Ed., 1975.
- [2] A. J. Chirinos Padron, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C30**, 107 (1990).
- [3] F. Gugumus, *Polym. Degrad. Stab.*, **50**, 101 (1995).
- [4] A. P. Mar'in and Y. A. Shlyapnikon, *Polym. Degrad. Stab.*, **31**, 181 (1991).
- [5] A. Tidjani, E. Fanton, and R. Arnaud, *Die Angew. Makromol. Chem.* **212**, 35 (1993).
- [6] A. Tidjani, R. Arnaud, and A. Dasilva, *J. Appl. Polym. Sci.*, **47**, 211 (1993).
- [7] G. Penot, R. Arnaud and J. Lemaire, *Angew. Makromol. Chem.*, **117**, 71 (1983).
- [8] P. Delprat, X. Duteurtre, and J-L. Gardette, *Polym. Degrad. Stab.*, **50**, 1 (1995).
- [9] A. Tidjani, *J. Appl. Polym. Sci.*, **64**, 2497 (1997).
- [10] J-L. Philippart, F. Posada, and J-L. Gardette, *Polym. Degrad. Stab.*, **49**, 285 (1995).
- [11] P. Jiangqing, X. Hongmei, Q. Juying, C. Jinfen, and M. Zhenmin, *Polym. Degrad. Stab.*, **33**, 67 (1991).
- [12] N. S. Allen, H. Khatami, and F. Thompson, *Eur. Polym. J.*, **7**, 817 (1992).
- [13] B. Ohtani, S. Adzuma, S-I. Nishimoto, and T. Kagiya, *Polym. Degrad. Stab.*, **35**, 53 (1992).

Received April 17, 1998

Revision received November 30, 1998



## **Request Permission or Order Reprints Instantly!**

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the [U.S. Copyright Office](#) for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on [Fair Use in the Classroom](#).

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our [Website User Agreement](#) for more details.

**[Order now!](#)**

Reprints of this article can also be ordered at

<http://www.dekker.com/servlet/product/DOI/101081MA100101553>