Influence of Diazo Pigment on Polycarbonate Photodegradation

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ABSTRACT: The photostability of polymeric systems can be extensively affected by the presence of dyes and pigments. Achromatic pigments such as carbon black are known as effective stabilizers for polymers, while pigments such as those based on metals oxides may accelerate photodegradation in polymers. Despite innumerous studies addressed to achromatic pigments, the effects and action mechanisms of chromatic pigments on polymer stability are not well established. In this work, an effective photostabilizer action on polycarbonate was verified by the incorporation of a red diazo type condensation pigment. This pigment was incorporated into polycarbonate in an extruder at a concentration of 1 wt %. Injection molded specimens of this material were submitted to photochemical aging following the recommendations of ASTM G-53. The nonaged and aged specimens were characterized by mechanical testing, infrared spectroscopy, UV/visible absorption and fluorescence spectroscopies, and electron spin resonance. The absorption of the UV radiation by the pigment and subsequent quenching by the internal conversion energy process is the probable stabilization mechanism involved in this polymeric system. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1071–1079, 2008

Key words: stabilization; dyes/pigments; polycarbonate

INTRODUCTION

The incorporation of colorants into polymeric systems may affect the stability of the polymeric matrix against photodegradation. Intense acceleration of the polymer degradation process can occur when incompatible colorants are added to the polymer. On the other hand, the presence of colorant can also significantly improve polymer stability. Some achromatic pigments such as carbon black and titanium dioxide (TiO_2) have been extensively studied and they are known as effective blocking agents, decreasing the rate of degradation of the polymer into which they are incorporated.[1–5] However, TiO_2 can also accelerate polymer degradation. The anatase structure of TiO_2 is more chemically active than rutilo structure, being incompatible with several polymer systems. The chemical activity of TiO_2 pigment can be reduced by envelopment of pigment particles with inert compounds such as some silicon-based compounds.[3,4]

Blocking agents can act through two distinct mechanisms: (1) absorbing the luminous radiation responsible for the photodegradation process and converting into other energy forms such as heat (carbon black) and (2) reflecting the luminous radiation incident and avoiding its penetration to internal layers of the material (TiO_2).[6,7]

The photoactivity of the colorants is also determinated by the photochemical features of the colorants, depending on the inherent properties of the colorants and on the polymer-colorant system involved. Thus, the prediction of colorant action in polymer photodegradation is very difficult without experiments.[8–10]

The few studies about the influence of chromatic colorants on polymer photodegradation and the innumerous compounds used as colorants make a complete comprehension about the mechanisms involved in the photodegradation of polymers containing colorants difficult.[8,11]

Azo compounds are frequently used as colorants for polymers. These colorants are classified as compounds containing —N=N— chemical groups or their derivatives in the molecular structure. The action mechanism of azo colorants in polymer degradation is controversial. Normally, azo colorants have a low quantum yield of triplet state formation and present a tautomeric conversion of the azo chemical structure to the hydrazone structure when irradiated with ultraviolet light.[12–15]

In this work, the photoactivity of the diazo condensation colorant Cromophtal BN® was evaluated using polycarbonate as matrix. In polymers, the photodegradation is always started by the formation of highly reactive chemical species in the material, such as free radicals. For polycarbonate, free radical formation can occur by direct scission of chemical bonds in the polymeric chain at short excitation wavelengths ($\approx$254 nm) or excitation of chromophores and oxidation at longer wavelengths ($\approx$365 nm). At short wavelengths, the polycarbonate photodegradation involve the formation of photo-Fries rearrangements, leading to phenylsalicilates and dihydroxybenzophenone products. The photodegradation of polycarbonate at long wavelength in the presence of oxygen process results in oxidation of the lateral groups and the aromatic rings of the polycarbonate.[16,17]

EXPERIMENTAL PART

Polycarbonate (in powder form) was obtained from GE Plastics South America (Hortolândia, Brazil). The diazo condensation colorant (Cromophtal BN), the UV absorber stabilizer (Tinuvin 234®), the free radical probe (Tinuvin 770®), and a secondary processing antioxidant (Irgafos 168®) were obtained from CIBA Specialty Chemicals (São Paulo, Brazil).

The diazo condensation pigment and the Irgafos 168 in the powder form were incorporated into the polycarbonate at 1 and 0.15 wt %, respectively, in a single screw extruder, Wortex® L/D 32 (Campinas, Brazil), with Madock mixer element. Polycarbonate containing 0.30 wt % Irgafos 168 and polycarbonate containing Irgafos 168 and Tinuvin 234 at 0.30 and 1 wt %, respectively, were also prepared. Irgafos 168 was used in every sample to avoid thermal degradation during processing. Specimens for impact resistance testing and stress–strain testing were prepared by the injection molding process in an Arburg Allrouder 221 KS (250-75) equipment (Lossburg, Germany).

Accelerated photochemical aging

Specimens for impact resistance and stress–strain testing of polycarbonate and polycarbonate containing diazo condensation colorant were submitted to different aging times in an equipment manufactured according to suggestions of Standard Practice ASTM G-53 for UVA radiation. UVA radiation (315–400 nm) was produced by a set of Philips CLEO Performance 80W-R lamps (Manaus, Brazil). According to ASTM G-53, rotations and changing operation of the lamps were done to minimize radiation drops during the aging process. Cycles of radiation and water condensation were conducted following the

procedure: 22 h of radiation exposure (25–30°C), followed by 2 h of condensation cycle (around 50°C). Only one face of the specimens was irradiated.

Mechanical testing

Impact resistance tests were performed in an EMIC AIC1 apparatus (São José dos Pinhais, Brazil), according to Standard Practice ASTM D256, IZOD method. The specimens were notched before the aging process. Stress–strain testing was performed on an EMIC LA2000 universal machine (São José dos Pinhais, Brazil) at strain rate of 6 mm/min. Before testing, the specimens were kept at 25°C and 50% humidity for 48 h. At least six specimens were tested.

Infrared spectroscopy

Infrared spectroscopy (FTIR) analyses were performed on the aged surface specimens by specular reflectance in Nicolet 520 equipment (Waltham, MA), at 178 scans and 4 cm^{-1} of resolution. Mathematics operations of dispersion, automatic baseline correction, and normalization by total area of the spectrum were done after spectra acquisition. The oxidation degree on the surface was evaluated by the carbonyl index defined as the ratio between intensity of absorption bands centered at 1730 and 1195 cm^{-1}.

Colorimetry

Color changes of the aged specimens were monitored by ΔE parameters, which is calculated by the square root of the square coordinates L^*, a^*, b^* (color parameters), according to the CIELAB color system, following procedures of the standard practice ISO 7724. The analyses were conducted using a Macbeth Color-eye spectrometer (Research Triangle Park, NC) in the reflection mode and illuminant D.

UV/visible absorption and fluorescence spectroscopy

UV/visible absorption spectra of polycarbonate and the diazo condensation pigment were obtained in CHCl$_3$ solution, using a Hewlett Packard 8456 A spectrometer (Waldbroon, Germany). Fluorescence spectra of diazo pigment and polycarbonate were obtained in CHCl$_3$ solution, containing the surfactant monolaurate polyethylene-oxide sorbitan (Tween 20), in a PTI® CS-100™ spectrofluorometer (Birmingham, NJ). The excitation wavelength was 270 nm.

Electron spin resonance

Electron spin resonance (ESR) measurements were carried out with a Bruker ER 200D SRC X-band
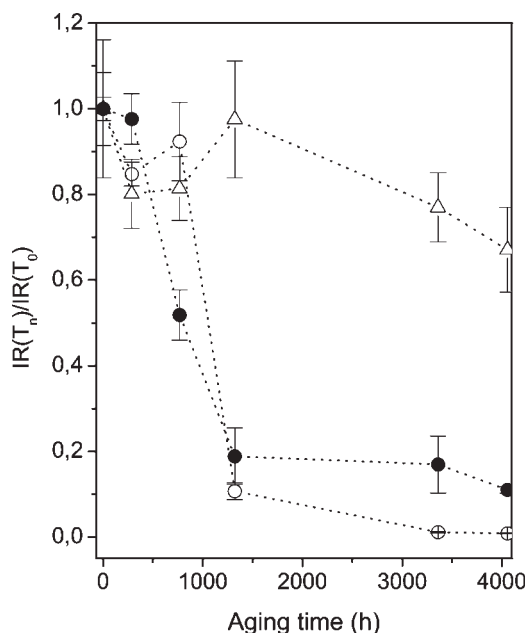
Figure 1 Impact resistance retention $[IR(t_n)/IR(t_o)]$ as a function of the aging time: polycarbonate (○), polycarbonate containing Tinuvin 234 (●), and polycarbonate containing diazo pigment (Δ).

spectrometer (Rheinstetten, Germany), (microwave frequency about 9.5 GHz) equipped with a Bruker ER035M NMR gauss-meter (Rheinstetten, Germany). The phase revelation of the signal is done by modulating the magnetic field to improve the signal to noise ratio. Because of the amplitude modulation of the magnetic field, ESR line-shapes are obtained in their first derivative form. Quartz tubes were used to hold the samples in the cavity of the spectrometer.

Diazo pigment and polycarbonate were analyzed in the powder forms. To characterize possible interactions between diazo pigment and polycarbonate, a solution of diazo pigment (2 wt %) and polycarbonate (1 wt %) in CHCl₃ was also analyzed.

The ability of diazo condensation pigment and polycarbonate under UVA radiation to form free radicals was tested using the following procedure: the probe bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 770) was added to the diazo pigment and polycarbonate solutions in CHCl₃. Then the solutions were bubbled with atmospheric air for 20 min and irradiated (0–6 h) with same lamp used in the photochemical aging experiments. Finally, the solutions were submitted to ESR measurements.

RESULTS AND DISCUSSION

The diazo condensation colorant used in this work is a red pigment insoluble in polycarbonate. Thus, the

samples of polycarbonate containing 1 wt % of this pigment are opaque.

Mechanical testing

The impact resistance (IZOD) for polycarbonate without additives and containing diazo colorant and Tinuvin 234 is shown in Figure 1 as the ratio between impact resistance at the aging time t_n ($IR(t_n)$) and the initial impact resistance, before the aging process ($IR(t_o)$).

Photochemical aging results in a significant decrease in the impact resistance of the polycarbonate as the aging time increases. After 4000 h of aging, the impact resistance retention became practically null. However, some stabilization effects are observed for polycarbonate containing the UV stabilizer Tinuvin 234, for which the impact resistance retention is about 20% after 1000 h of aging. The highest impact resistance retention was observed for the polycarbonate containing the red diazo condensation pigment, for which only a slight decrease of impact resistance during the aging process is verified. These results suggest that the diazo pigment is an effective stabilizer against polycarbonate photodegradation.

In general, the elongation at break is the mechanical property most affected by aging. Figure 2 shows a large decrease of elongation at break for polycarbonate without additives during photochemical aging, while a decreasing less accentuated is verified for polycarbonate containing Tinuvin 234 or the
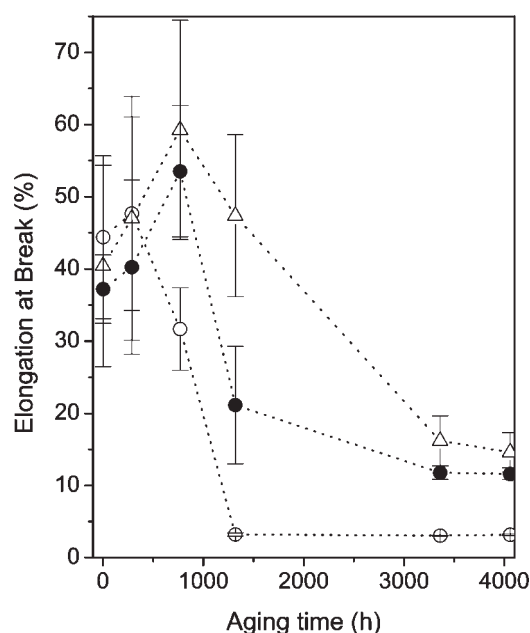

Figure 2 Elongation at break as a function of the aging time: polycarbonate (○), polycarbonate containing Tinuvin 234 (●), and polycarbonate containing diazo pigment (Δ).
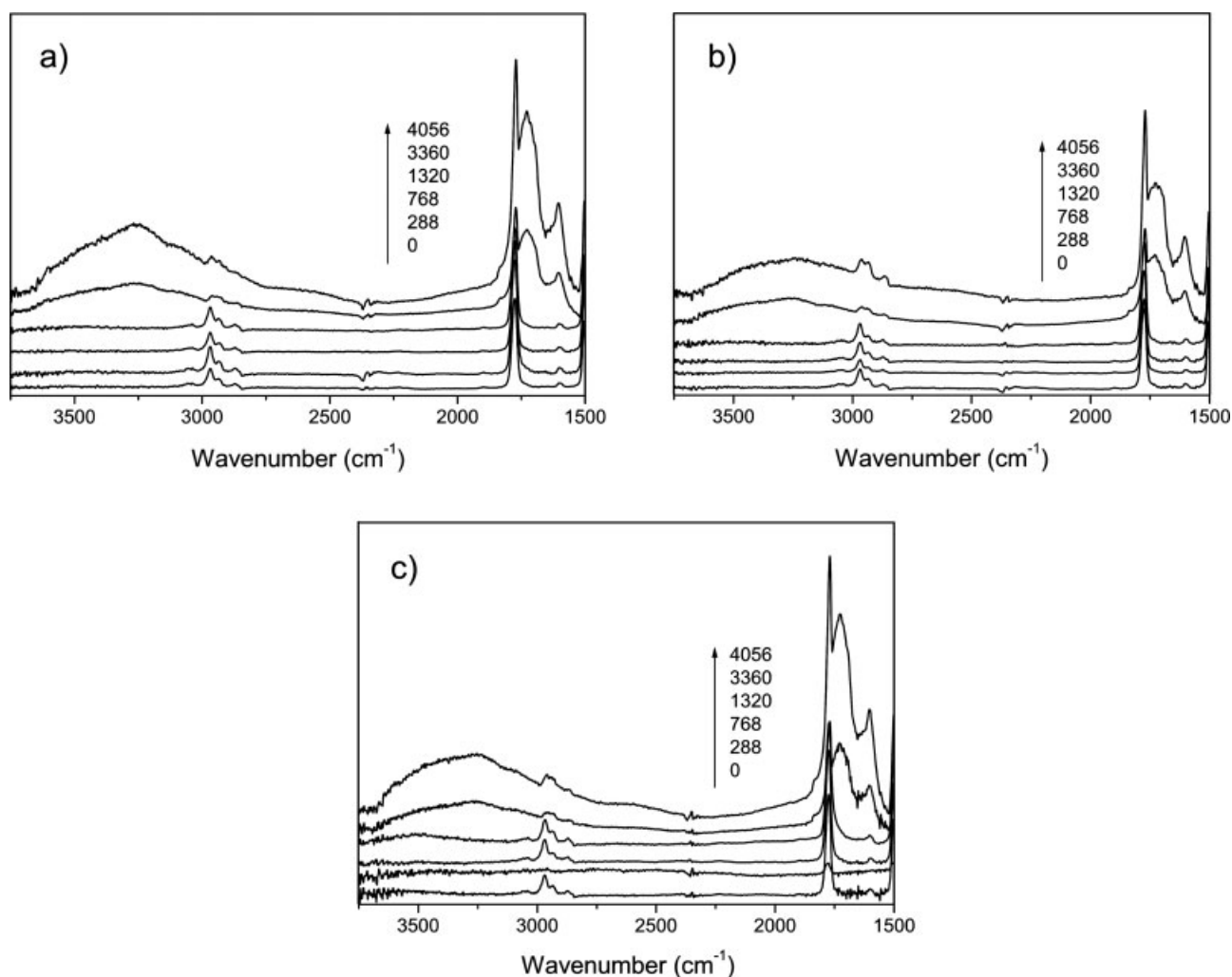
Figure 3 Infrared spectra for different aging times: (a) polycarbonate, (b) polycarbonate containing diazo pigment, and (c) polycarbonate containing Tinuvin 234.

diazo condensation pigment. In fact, the polycarbonate containing the diazo pigment showed a higher retention of elongation at break, reinforcing the hypothesis of the photostabilizing action of the red pigment on the polycarbonate.

Infrared spectroscopy

Figure 3 shows the spectral evolution of polycarbonate without additives and containing Tinuvin 234 and the diazo pigment during the aging.

FTIR spectra of the samples after 3360 h of photochemical aging show absorption bands around 1700 and 3200 cm^{-1}. These absorption bands are attributed to carbonyl and hydroxyl chemical groups and they are related to oxidation on the sample surfaces. It should be noted that FTIR detects degradation only after 3360 h of aging, while mechanical tests indicate degradation already at 768 h of aging.

The carbonyl indices showed in Figure 4, calculated from the data of the FTIR spectra (Fig. 3),

present a significant increase after 1320 h of aging for all samples. However, polycarbonate containing diazo pigment presents the lowest carbonyl index indicating the stabilizer effect of the diazo pigment. These data are in agreement with those of mechanical testing.

Colorimetry

Colorimetry was used to evaluate the yellowness in polycarbonate caused by the formation of quinone groups in the polymeric chains and pigment degradation during the aging process. The behavior of the color variation parameter ΔE for these polycarbonates during aging is shown in Figure 5.

In polycarbonate and polycarbonate containing Tinuvin 234 the changes in color variation parameter (ΔE) during aging are due to the increase in the chromatic parameter b^*, while in polycarbonate containing diazo pigment the parameter ΔE increases as
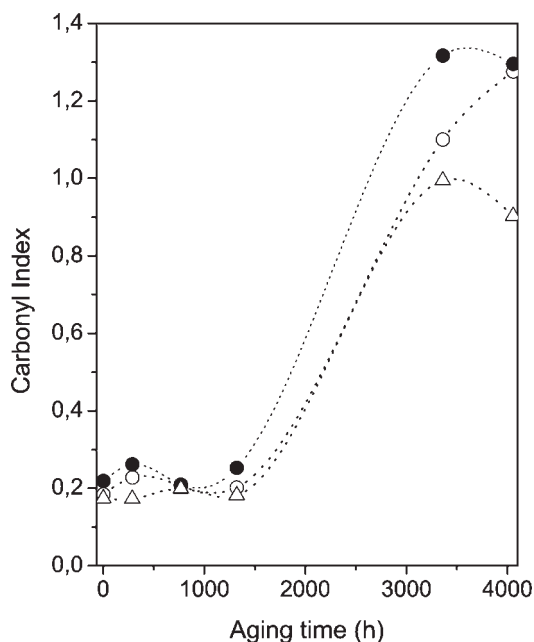
Figure 4 Carbonyl index as a function of the aging time: polycarbonate (○), polycarbonate containing Tinuvin 234 (●), and polycarbonate containing diazo pigment (Δ).
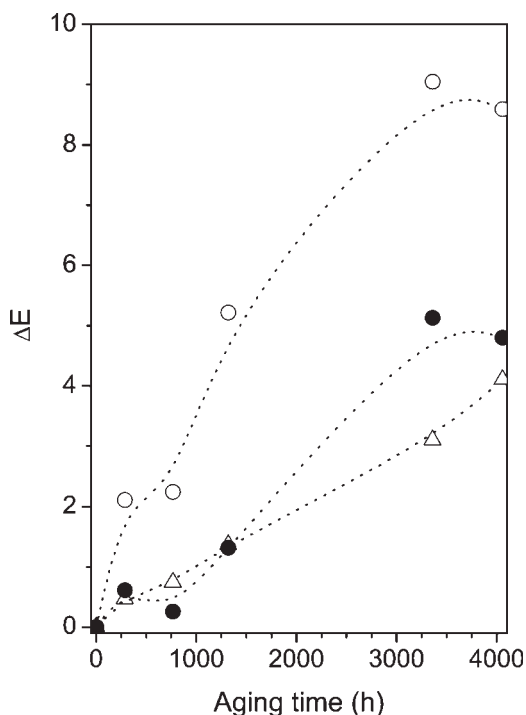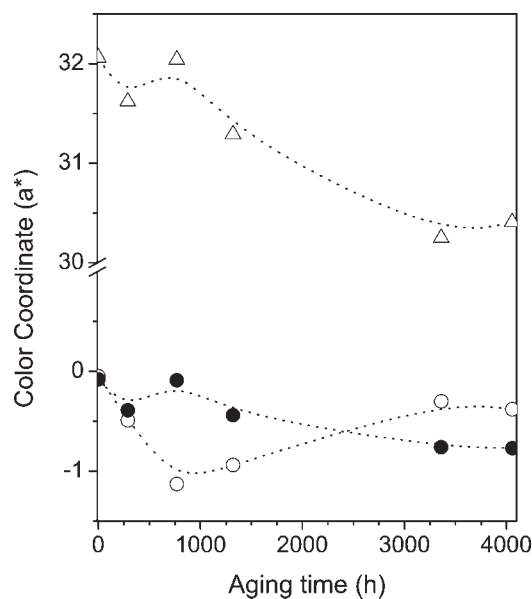

Figure 6 Chromatic parameter a^* as function of aging time for: polycarbonate (○), polycarbonate containing Tinuvin 234 (●), and polycarbonate containing diazo pigment (Δ).

a function of the variation of both the a^* and b^* chromatic parameters (Figs. 6 and 7).

The color change of polycarbonate during the aging process is caused by formation of quinone groups in the aromatic rings of the polymeric chains, which absorb light in the visible portion of the electromagnetic spectrum.[16,17] The color change in polycarbonate is related to a yellowness of the material because of the increase of the chromatic coordinate b^* during the aging process. According to the CIE-LAB system,[18,19] coordinate b^* represents an increase of the yellow hue at the long positive axis and of the

Figure 5 Color variation parameter (ΔE) as a function of aging time for: polycarbonate (○), polycarbonate containing Tinuvin 234 (●), and polycarbonate containing diazo pigment (Δ).
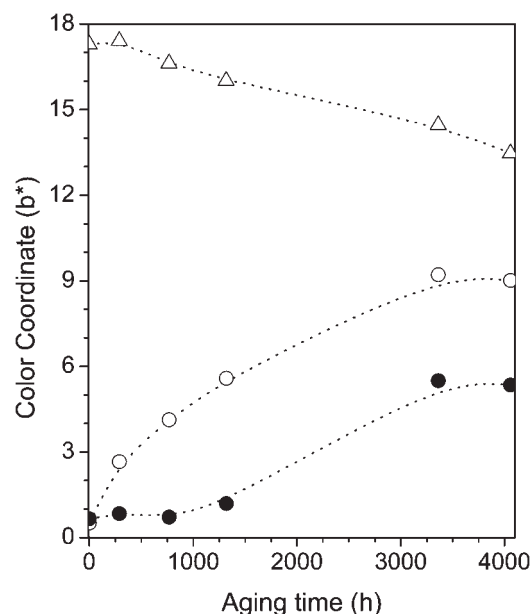

Figure 7 Chromatic parameter b^* as a function of aging time for: polycarbonate (○), polycarbonate containing Tinuvin 234 (●), and polycarbonate containing diazo pigment (Δ).
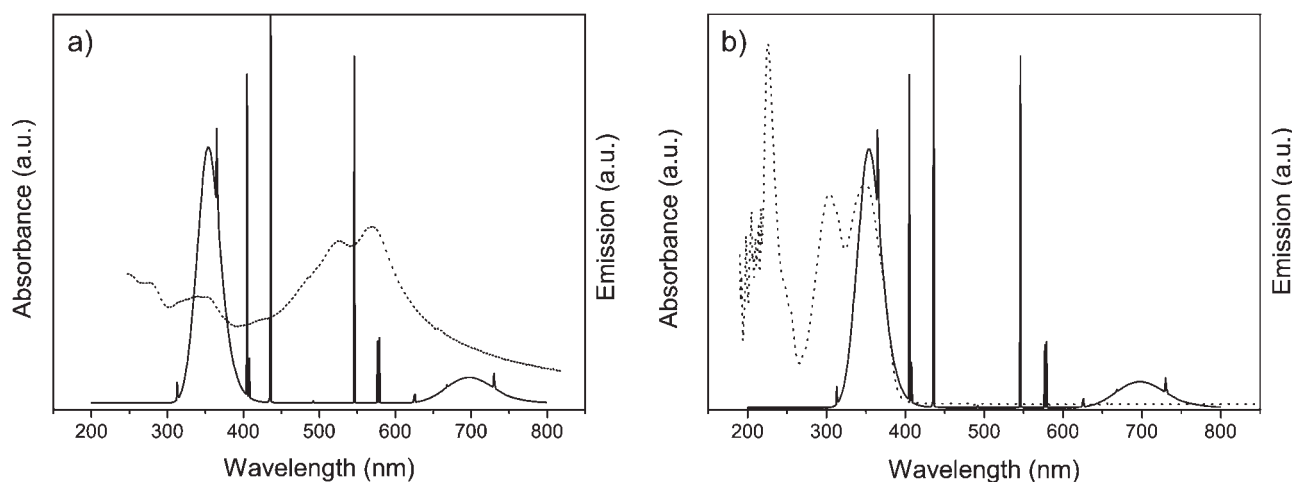
Figure 8 (a) Absorption spectrum of diazo pigment (dashed line), (b) Absorption spectrum of Tinuvin 234 (dashed line). Emission spectra of lamp used in the photochemical aging (solid line).

blue hue at the long negative axis. ΔE practically does not change for polycarbonate containing Tinuvin 234, at least until 1320 h of aging, showing the stabilizing action of Tinuvin 234 in the initial step of the photodegradative process.

The color change of the polycarbonate containing diazo pigment results from decreases of both a^* and b^* chromatic coordinate values during the aging process. The coordinate a^* represents an increasing of red hue at the long positive axis and of green hue at the long negative axis. The higher values of a^* and b^* parameters for polycarbonate containing diazo pigment before the aging process is a consequence of material coloration produced by incorporation of diazo pigment. The approach of both a^* and b^* to the zero value in the chromaticity axis means a loss of material coloration, which may occur when the pigment has its chemical structure altered. Therefore the decrease of a^* and b^* during the aging process may be caused by a progressive degradation of the pigment.

UV/visible absorption and fluorescence spectroscopy

Figure 8 shows the absorption spectra of diazo pigment in $CHCl_3$, Tinuvin 234 in hexane, and the emission spectrum of the lamp used as radiation source in the photochemical aging.

The diazo pigment presents absorption bands in the visible region of the electromagnetic spectrum (400–700 nm), which are responsible for the red color of the pigment, and a less intense absorption band in the ultraviolet region, in the same wavelength range as the main emission band of the UV lamp [Fig. 8(a)]. This coincidence of emission and absorption bands make possible the excitation of pigment by absorption of UV radiation.

Tinuvin 234 [Fig. 8(b)] accomplishes all requirements of a typical UV absorber stabilizer, which should have high light absorption in UV region and low or no absorption in the visible region. The UV absorber stabilizers should also have a high efficiency of internal energy conversion. The stabilization mechanism of an UV absorber such as Tinuvin 234 in polymers is due to a tautomeric of the hydroxyphenyl structure to a unstable quinone structure through UV absorption. The inverse tautomeric conversion should be accompanied by energy liberation.
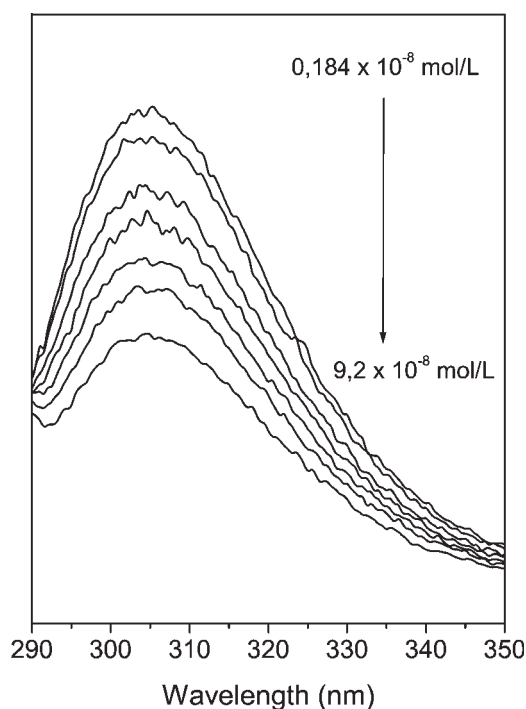

Figure 9 Quenching of polycarbonate fluorescence by the diazo pigment (λ exc. = 270 nm).
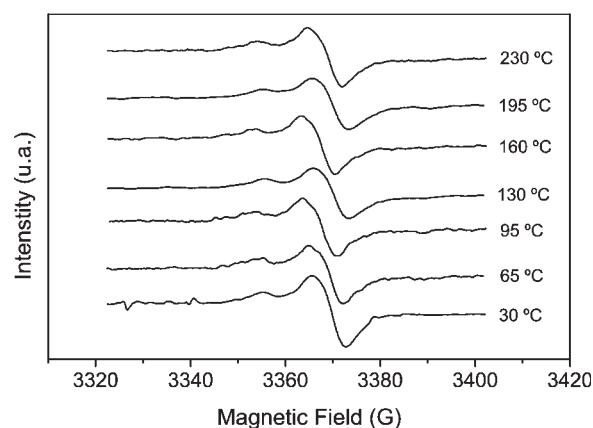
Figure 10 ESR signal for diazo pigment.

Fluorescence spectroscopic analysis showed that the diazo pigment is not fluorescent specie. Therefore, other pathways of excited state energy dissipation such as internal energy conversion or reactive species formation may be predominant in the diazo pigment.

In Figure 9 the fluorescence spectra of polycarbonate in the presence of diazo pigment at different concentrations are shown. The increase of the pigment concentration produces a progressive quenching of polycarbonate fluorescence. Comparative analysis with others colorants, such as Cu-phthalocyanine dye,[11] bismuth vanadate pigment and anthraquinone dye,[20] showed a more pronounced decrease in fluorescence quantum yield for polycarbonate in presence of red diazo pigment. This result suggests that the red diazo pigment acts as an internal filter. Thus, absorption of a part of incident UV radiation by the diazo pigment and its consequent deactivation by an internal conversion energy mechanism or chemical reactions in pigment may be considered.

Tautomeric conversion of the azo to hydrazone structures in the diazo pigment is an effective way of energy dissipation and a possible mechanism of stabilization of PC against photodegradation.

Electron spin resonance

ESR is sensitive to chemical species with unpaired electrons such as free radicals, paramagnetic compounds, and ionic metals. Because of this ESR is a powerful technique to detail the photochemical mechanism in polymer degradation. Figure 10 shows the ESR spectra of diazo pigment at different temperatures.

The ESR signal of the diazo pigment does not change with the temperature, showing that the signal does not originate from radicalar species or structural conformations that can be affected by temperature, being characteristic of chemical structure of the pigment.

Free radicals cannot be easily detected because they are normally unstable, presenting short lifetimes. However, the ability of the diazo pigment to produce radicalar species under ultraviolet irradiation can be evaluated by using the probe bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 770). Tinuvin 770 is used as a photostabilizer for polycarbonate, belonging to the photostabilizer group of the hindered amine light stabilizers (HALS).[21] Tinuvin 770 is sensitive to the oxidative attack of the oxygen singlet, producing radicalar species structure B in Figure 11 that presents a typical ESR signal.[22,23]

The intensity of piperidoxyl ESR signal is a function of the concentration of unstable free radicals or of oxidative chemical species able to convert the Tinuvin 770 form A to form B.[22,23]

Figure 12 shows a time sequence of ESR spectra of a Tinuvin 770 solution in $CHCl_3$ containing or not polycarbonate and diazo pigment obtained immediately after exposure to UV radiation produced by the same lamp used in the photochemical aging experiments.

The ESR spectra of the solution containing only Tinuvin 770 [Fig. 12(a)] do not show any significant change during 6 h of exposure to UV radiation, indicating that form A of Tinuvin 770 is not significantly converted to form B during this time. However, when the experiment is conducted in solutions containing diazo pigment and Tinuvin 770 solution [Fig. 12(b)] a triplet signal appears after 2.5 h of UV irradiation. This signal is attributed to the conversion of the form A to B of the Tinuvin 770 and indicates the formation of reactive forms of the diazo pigment, such as free radicals or singlet oxygen ($^1O_2$) in solution after UV irradiation. Intense signals of piperidoxyl free radicals are also verified when Tinuvin 770 solutions are irradiated in the presence of polycarbonate [Fig. 12(c)]. In this system, the formation of piperidoxyl free radicals is possibly due to the reaction of Tinuvin 770 with free radicals generated in polycarbonate chains after UV irradiation.
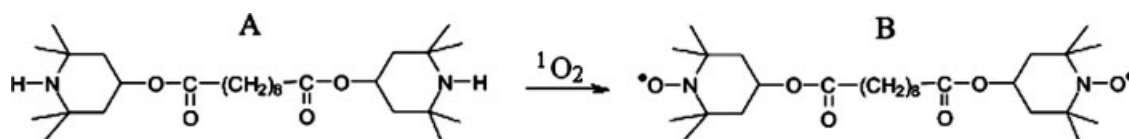

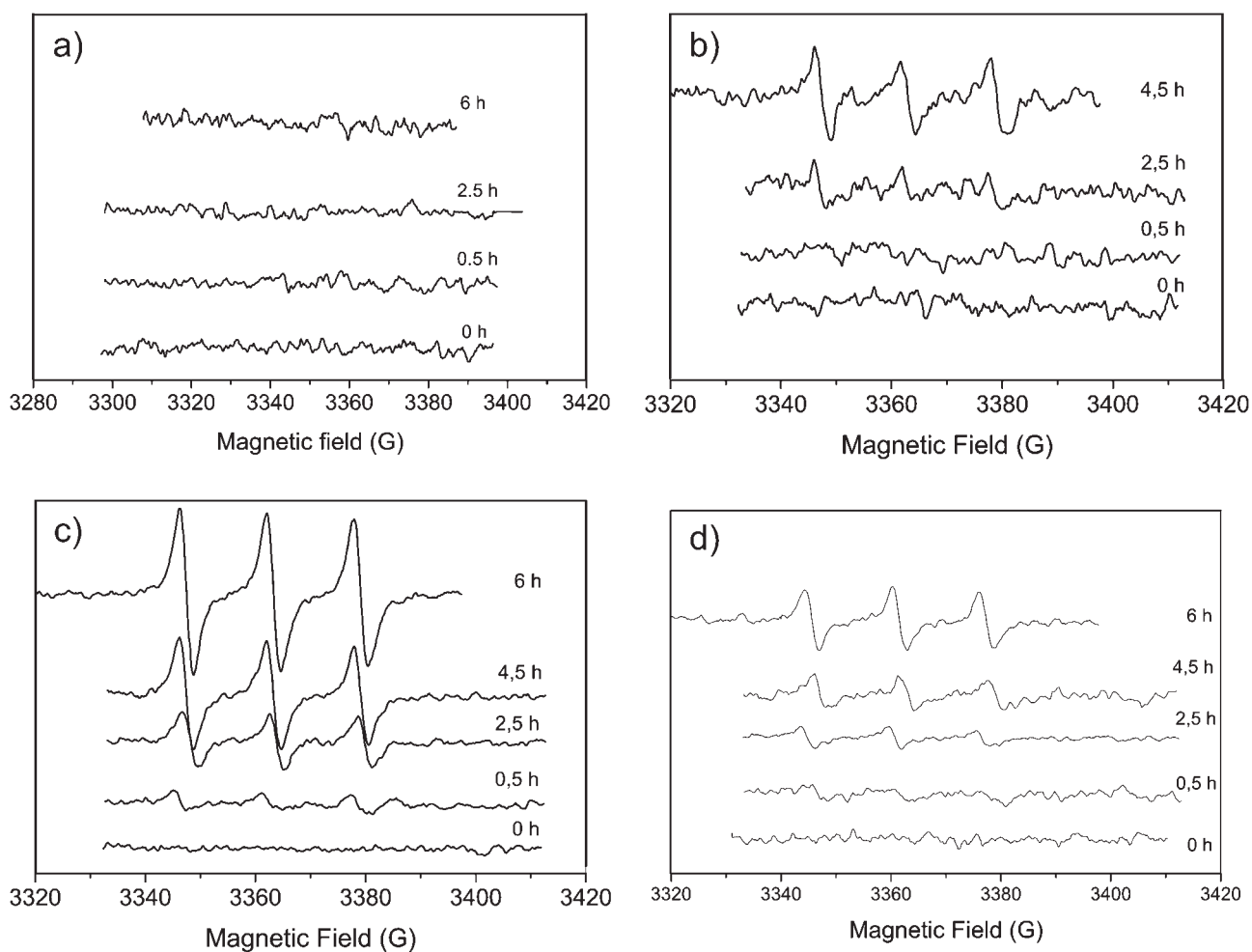**Figure 11** Molecular conversion of Tinuvin 770 to radicalar form.

Figure 12 ESR spectra of Tinuvin 770 solution after UV irradiation: (a) in absence of diazo pigment and polycarbonate; (b) in presence of diazo pigment; (c) in presence of polycarbonate; (d) in presence of diazo pigment and polycarbonate.

When a Tinuvin 770 solution is irradiated in the presence of both diazo pigment and polycarbonate [Fig. 12(d)], the signal of piperidoxyl free radicals has a similar intensity to that found in the system containing only Tinuvin 770 and diazo pigment, suggesting that the photochemical phenomenon occurring in the system containing polycarbonate and diazo pigment may be governed by the pigment.

To verify if this piperidoxyl signal is due to the formation of reactive species in diazo pigment or to the presence of singlet oxygen ($^1O_2$) in solution, similar experiments were conduced in the presence of sodium azide (Fig. 13). Sodium azide is known as a singlet oxygen inhibitor and, therefore, may quench the piperidoxyl signal if this is produced by singlet oxygen.

No quenching of the piperidoxyl signal is noted in the presence of sodium azide leading to the conclusion that singlet oxygen is not responsible for the formation of piperidoxyl radical. Thus the reactive forms of the diazo pigment are formed under UV radiation.

According to the results obtained, the mechanism shown in Figure 14 is proposed to explain the stabilization effect of the diazo pigment in polycarbonate.
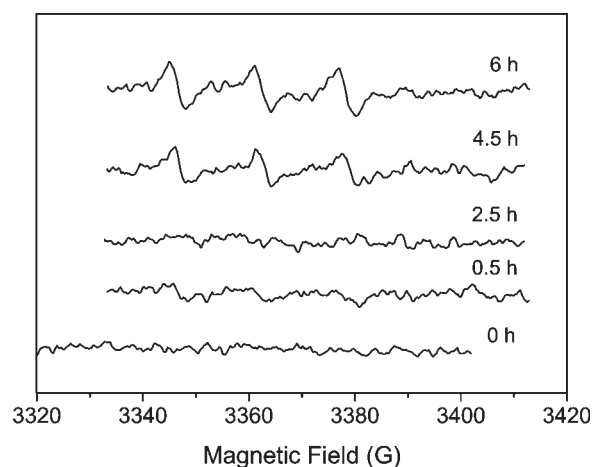

Figure 13 ESR spectra of Tinuvin 770 solution containing diazo pigment and sodium azide after UV irradiation.
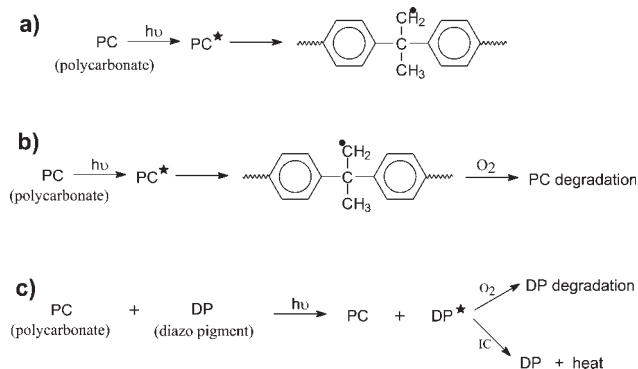
Figure 14 Photochemical process in polycarbonate: (a) free radicals formation with ultraviolet irradiation at wavelengths above 280 nm; (b) photodegradation in presence of oxygen; (c) Mechanism proposed to explain the stabilization effect of the diazo pigment in polycarbonate.

The absorption of UV irradiation by polycarbonate leads to the formation of excited states and free radicals. These free radicals, in the presence of oxygen, result in oxidizing species and consequently in polymer photodegradation. The absorption of UV radiation by polycarbonate containing the diazo pigment results in excited states of the pigment and the polycarbonate is stabilized against photodegradation. The excited state of the pigment can be quenched by an internal conversion energy mechanism or combined with oxygen and further degraded.

CONCLUSIONS

Red diazo pigment Chromoftal BN is an effective stabilizer for polycarbonate against photodegradation. Stabilization effects of the polycarbonate by the diazo pigment are more significant than those of a commercial UV absorber stabilizer, Tinuvin 234, at usual concentration. On the other hand, progressive color changes in the pigment during the photochem-

ical aging process occur as consequence of its degradation. The probable mechanism of stabilization by the diazo pigment is the absorption of UV radiation and energy conversion to non-aggressive energy forms for PC, such as heat.

References

1. Allen, N. S. Polym Degrad Stab 1994, 44, 357.
2. Pospíšil, J.; Nešpurek, S. Prog Polym Sci 2000, 25, 1261.
3. Allen, N. S.; Edge, M.; Corrales, T.; Childs, A.; Liauw, C. M.; Catalina, F.; Peinado, C.; Minihan, A.; Aldcroft, D. Polym Degrad Stab 1998, 61, 183.
4. Vaillant, D.; Lacoste, J.; Lemaire, J. J Appl Polym Sci 1997, 65, 609.
5. Peña, J. M.; Allen, N. S.; Edge, M.; Liauw, C. M.; Valange, B. Polym Degrad Stab 2001, 72, 259.
6. Yang, H. Y.; Zhu, S. K.; Pan, N. J Appl Polym Sci 2004, 95, 3201.
7. Copuroglu, M.; Sen, M. Polym Adv Technol 2005, 16, 61.
8. Saron, C.; Felisberti, M. I. Quim Nova 2006, 29, 124.
9. Kwak, G.; Fujiki, M.; Sakaguchi, T.; Masuda, T. Macromolecules 2006, 39, 319.
10. Zeynalov, E. B.; Allen, N. S. Polym Degrad Stab 2006, 91, 931.
11. Saron, C.; Zulli, F.; Giordano, M.; Felisberti, M. I. Polym Degrad Stab 2006, 91, 3311.
12. Niimi, T.; Umeda, M. J Phys Chem B 2002, 106, 3657.
13. Hihara, T.; Okada, Y.; Morita, Z. Dyes Pigm 2004, 60, 23.
14. Karpicz, R.; Gulbinas, V.; Stanishauskaite, A.; Undzenas, A. Chem Phys 2001, 269, 357.
15. Yang, L.; Wang, G.; Wang, J.; Wang, G.; Xu, Z. Int J Light Electron Opt 2002, 113, 189.
16. Nichols, M. E.; Peters, C. A. Polym Degrad Stab 2002, 75, 439.
17. Rivaton, A.; Mailhot, B.; Soulestin, J.; Varghese, H.; Gardette, J. L. Polym Degrad Stab 2002, 75, 17.
18. Kuehni, R. G. Color: An Introduction to Practice and Principle; Wiley: New York, 1997.
19. Machado, P. P.; Hotza, D.; Peter, C. Ceram Ind 1997, 2, 51.
20. Saron, C.; Zulli; F.; Giordano, M.; Felisberti, M. I. J Braz Chem Soc 2007, 18, 900.
21. Ciba® Tinuvin®. Ciba Speciality Chemicals-Polymer Additives, Technical Report. Ciba® Tinuvin® 770, Nov-99.
22. Chen, Y.; Xu, S.; Li, L.; Zhang, M.; Shen, J.; Shen, T. Dyes Pigm 2001, 51, 63.
23. Rajendran, M.; Ramasamy, S.; Rajamanickam, C.; Gandhidasan, R.; Murugesan, R. Biochim Biophys Acta 2003, 1622, 65.