Pergamon

Cement and Concrete Research, Vol. 28, No. 1, pp. 75–81, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(97)00220-2

EVALUATION OF THE STABILITY OF POLYPROPYLENE FIBERS IN ENVIRONMENTS AGGRESSIVE TO CEMENT-BASED MATERIALS

N. Segre, E. Tonella, and I. Joekes[1]
Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154 CEP
13083–970, Campinas - SP, Brazil

(Received April 16, 1997; in final form October 16, 1997)

ABSTRACT

Isotactic polypropylene (PPi) fibers were left in NaOH, H_2SO_4, synthetic seawater, and cement-with-water solutions at different temperatures and exposure times. Infrared microspectroscopy was used to follow the formation of degradation products. Cement-with-water was the most aggressive bath for the fibers, causing marked oxidation after 100 days exposure; also, the molecular weight of PPi increased as determined by viscosimetry. Mortar test specimens containing PPi fibers and exposed to CO_2, synthetic seawater, and $MgSO_4$ 0.25M showed a decrease in compressive strength after 260 days. The compressive strength of mortar test specimens containing 0.75 kg m^{-3} of PPi fibers irradiated with ultraviolet radiation was roughly 10% lower than that of the control specimen, after only 60 days in water. *© 1998 Elsevier Science Ltd*

Introduction

The use of isotactic polypropylene (PPi) fibers in cement-based materials has increased in recent years as a substitute for mineral and metallic fibers and as an alternative way to improve the mechanical properties of this materials (1–4).

Polypropylene is fairly resistant to chemical agents such as acids, alkalis, and salts (5,6). However, all natural and synthetic polymers are subjected to deterioration upon exposure to the environment, as a result of irreversible changes in the composition and structure of polymer molecules (7,8).

The mechanism of polypropylene degradation has been extensively studied (7–14). This polymer has a low resistance to thermooxidative and photooxidative degradation (Fig. 1) (9,12). The most frequently occurring photo-induced chemical degradation of polymers are chain scission and cross-linking, with concomitant formation of oxygen-containing functional groups such as carbonyl, carboxyl, hydroxyl, and peroxides, which can be assessed easily by IR spectroscopy; the rate or extent of degradation of polymers has been measured by monitoring the buildup of oxidation products (7,10,13,14).

In the case of cross-linking, the molecular weight of the polymer increases with increasing

---

[1] To whom correspondence should be addressed.

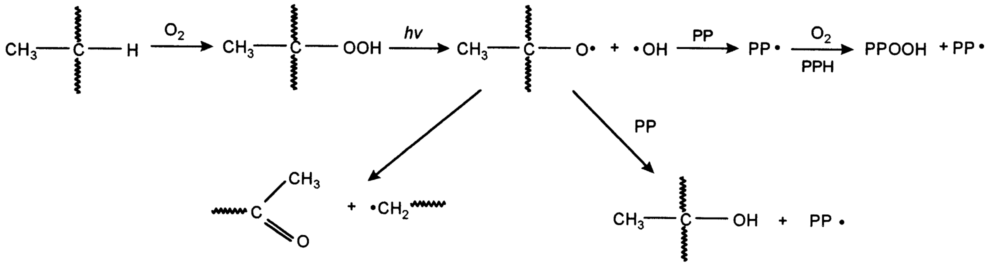

FIG. 1.
Polypropylene photooxidation scheme.

dose until a three-dimensional network is formed. When scission predominates in an irradiated polymer, the molecular weight decreases as dose increases. In some cases, a solid polymer may be transformed into a low molecular fluid (13).

Photooxidative degradation of PPi fibers in cement matrices is not to be expected. However, in the presence of aggressive environments and long exposure times, thermooxidative processes may have significant rate even at room temperature. The aim of this work is to study the longterm response of PPi fibers exposed to environments aggressive to cement-based materials.

Experimental

Portland cement type CP II-E32, PPi fibers 20 mm in length from Vulkan do Brasil, and analytical grade reagents were used.

Aggressive media, consisting of baths containing cement-with-water, sulfuric acid 10 M, 1 M, and 0.1 M, NaOH 0.1 M, synthetic seawater, and water (control) were used. The cement-with-water bath was obtained mixing water and enough CP II-E32 cement to saturate the solution and stirring at room temperature for 48 h; the final pH was 12.7. The NaOH solution was used as a comparative bath to cement-with-water. A saturated solution of NaCl and $MgSO_4$ was used as simulated seawater.

Prior to use, the fibers were washed with water and then with sugar cane ethanol. The fibers were introduced in 600-mL beakers containing the test solutions and kept at 4 ± 2°C, 25 ± 5°C, and 50 ± 2°C for 230 days.

In a separate experiment, PPi fibers were irradiated with ultraviolet (UV) radiation for 24, 48, and 72 h using a mercury lamp without external jacket to obtain maximum degradation values in this experimental conditions. A Perkin Elmer 16PC FT-IR spectrometer with an optical microscope was used to collect all the infrared spectra by transmission. The band areas were calculated using the software IRDM (Infrared Data Manager).

For the viscosimetric analysis, ASTM D2857–70 was followed. Solutions of fibers in *p*-xylene were prepared in different concentrations through stirring and heating at approximately 120°C. Flow times were obtained using a Cannon-Fenske viscometer. A thermostatized oil bath at 100 ± 1°C was used.

Mortar test specimens were casted following Brazilian Standard (ABNT CDU666942: water/cement ratio 0.48 and graded sand/cement ratio 3.0) using 0.75 kg m^{-3} of fibers. For the test specimens, synthetic seawater, $MgSO_4$ 0.25M, carbon dioxide, and water (control)

TABLE 1
Relative concentrations of degradation products in PPi fibers after UV irradiation as a function of time of exposure, obtained from infrared analysis by band area integration using the 840 cm^{-1} band area as reference. Results of triplicates.

Exposure time (h)	Relative band area		
	1712 cm^{-1}	1672-1540 cm^{-1}	3570-3088 cm^{-1}
0	0.22	0.22	0.57
24	0.57	0.80	2.22
48	0.79	0.88	2.74
72	0.88	0.96	3.06

were used as aggressive environments. Compressive strength measurements (ABNT CDU666942) were made at four different ages up to 260 days. Also, test specimens were made using fibers irradiated with UV radiation for 12 h; the test specimens were left in water for 60 days. A reference test specimen (without fibers) and a control test specimen (with untreated fibers) were used.

Results and Discussion

The formation of degradation products in the PPi fibers after UV irradiation was followed through infrared microspectroscopy (15,16). The values of the areas for the bands at 1712 cm^{-1}, 1672–1540 cm^{-1}, and 3570–3088 cm^{-1} were calculated. These bands can be attributed as follows: at 1712 cm^{-1}, a narrow band appears that is characteristic of carbonyl groups; between 1672 and 1540 cm^{-1}, a broad band appears that should include the absorption of carboxylate ions, as well as double bonds and even aldehides; in the 3570 to 3088 cm^{-1} band, the absorption of hydroxyl groups is expected. In order to correct for variations in sample thickness, it is usual to measure the areas of the bands relative to a reference band whose intensity does not vary with oxidation (17). The band at 840 cm^{-1} was used as reference. Table 1 shows the overall data obtained.

The same measurements were performed with the fibers left in the aggressive baths. The areas of the bands at 1746 cm^{-1} and 1718–1524 cm^{-1} were used. The observed band shift is expected, because the relative concentration of the various carbonyl-type groups is altered with respect to UV degradation. In this case, the formation of hydroxyl products was not followed due to the possibility of residual humidity in the samples. Figure 2 shows the results for fibers left in cement-with-water bath.

The presence of carbonyl groups was observed at 4°C and room temperature, even at early times of exposure. A different mechanism of degradation is found at 50°C, because a decrease in the formation of carbonyl groups happens simultaneously with an increase in the formation of other degradation products, probably by conversion (for instance, from carbonyl to carboxyl groups). The results obtained for the other baths are shown in Table 2.

The degradation extent in the fibers left in the cement-with-water bath is unexpectedly higher than for the other baths. The same degradation behavior as in the cement-with-water

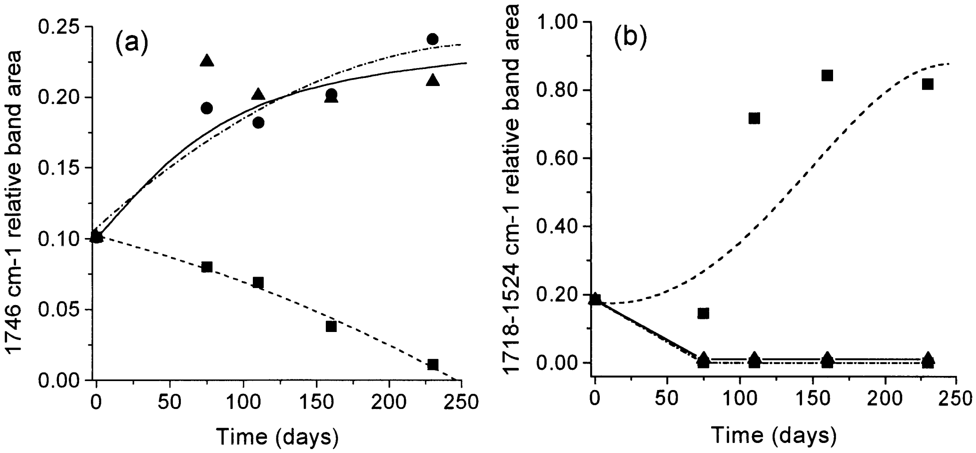

FIG. 2.

Relative concentrations of degradation products in PPi fibers left in cement-with-water bath as a function of time of exposure at 4 ± 2°C (–▲–), 25 ± 5°C (-·-·●·-·-), and 50 ± 2°C (- -■- -). Data from FT-IR measurements at (*a*) 1746 cm^{-1} and (*b*) 1718–1524 cm^{-1}, using the 840 cm^{-1} band area as reference. Average of two experiments.

bath was observed for the fibers left in the other aggressive baths, except for H_2SO_4 10 M, where the formation of carbonyl groups is observed also at 50 °C. As expected, the concentration of degradation products for the fibers left in all the aggressive baths is lower than the maximum values obtained for irradiated fibers.

Another degradation parameter studied was the molecular weight variation. Table 3 shows the results obtained for PPi fibers exposed to UV radiation and to cement-with-water bath.

A different mechanism of degradation is again apparent for fibers left in the cement-with-water bath, because an increase in the molecular weight was observed. The formation of cross-linking in the polymer structure is probably the reason.

Mortar test specimens containing PPi fibers were also studied. Compressive strength measurements of the 28- and 60-days aged test specimens with fibers exposed to UV radiation for 12 h were performed. These test specimens are intended to simulate aged ordinary specimens containing PPi fibers, because it was shown that the fibers will be degraded inside the cement matrix. Results are shown in Table 4.

Compressive strength measurements for the specimens left in the aggressive environments were performed. The values of compressive strength for test specimens without fibers in each exposure time were used as reference. The ratio between compressive strength values and reference was calculated and named variation coefficient. Results are shown in Figure 3.

The compressive strength of the mortar test specimens containing irradiated PPi fibers showed a significant reduction even at so short a time as 60 days. Besides, the behavior of the compressive strength in other aggressive media shows a tendency to increase in short-time aged specimens but decreases even after only 250 days.

TABLE 2
Relative concentratons of degradation products in PPi fibers left in water (control), H_2SO_4 10 M, 1 M, and 0.1 M, NaOH 0.1 M, and synthetic seawater for 230 days at different temperatures, obtained from infrared analysis by band area integration using the 840 cm^{-1} band area as reference. Results of triplicates.

Aggressive bath	Temperature (°C)	Relative band area	
		1746 cm^{-1}	1718-1524 cm^{-1}
water (control)	4 ± 2	0.09	0.05
	25 ± 5	0.07	0.10
	50 ± 2	0.05	0
NaOh 0.1 M	4 ± 2	0.13	0.11
	25 ± 5	0.19	0
	50 ± 2	0.04	0.14
synthetic sea water	4 ± 2	0.13	0.01
	25 ± 5	0.13	0.06
	50 ± 2	0.08	0.27
H_2SO_4 10 M	4 ± 2	0.20	0
	25 ± 5	0.19	0
	50 ± 2	0.19	0
H_2SO_4 1 M	4 ± 2	0.20	0
	25 ± 5	0.22	0
	50 ± 2	0.05	0.51
H_2SO_4 0.1 M	4 ± 2	0.20	0.04
	25 ± 5	0.17	0
	50 ± 2	0.03	0.90

Conclusions

As expected, long-term exposure of PPi fibers to aggressive environments caused polymer degradation. However, the extent of the degradation observed in the cement-with-water bath

TABLE 3
Molecular weight of fibers to UV radiation and to cement-with-water bath at 4°C as a function of aggressive environment. Average of three experiments.

Aggressive environment	Exposure time	$\overline{M}_v$ (kg·mol^{-1})
control	0	134 ± 3
UV	24 h	37 ± 1
UV	72 h	b.d.i.*
cement-with-water	150 days	159 ± 1

*below detection limit

TABLE 4
Compressive strength as a function of age for test specimens prepared with fibers irradiated with UV radiation for 12 h, reference test specimens (without fibers) and control test specimens (with untreated fibers).
Average of three experiments.

Specimen	Compressive Strength (MPa)	
	28-days aged	60-days aged
reference	34.0 ± 1	39.6 ± 0.1
control	34.9 ± 0.1	39.0 ± 0.7
with irradiated fibers	35.4 ± 0.3	34.9 ± 0.5

is unexpectedly higher than in the other baths. Moreover, two mechanisms of degradation are apparent: one at 4°C and room temperature and the other at 50°C. Because no correlation can be found with the degradation observed in the alkaline bath, it can be assumed that the metal ions contained in the cement solution acted, in some way, as degradation catalysts for PPi.

This result and the lowering of the compressive strength also observed indicates that the use of PPi fibers may be interesting only if short-time effects are expected.

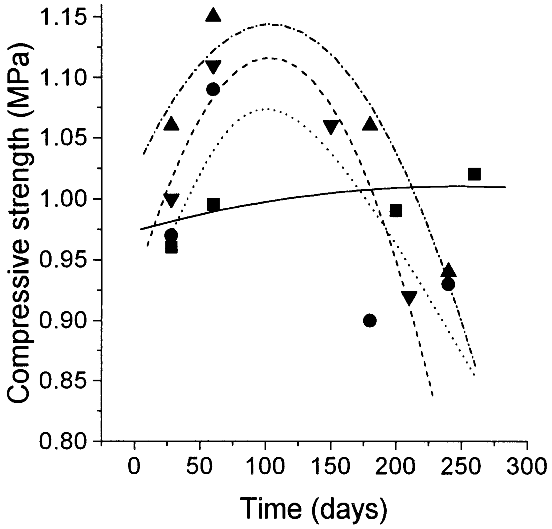

FIG. 3.
Variation coefficients as a function of exposure time for test specimens left in water (control) (—■—), carbon dioxide (–▼–), synthetic seawater (-.-.▲.-.-), and $MgSO_4$ 0.25 M (····●····). Average of three experiments.

Acknowledgments

N.S. and E.T. gratefully acknowledge the fellowships from CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico).

References

1. M. Mashima, D.J. Hannant, and J.G. Keer, ACI Mater. J. 87, 172 (1990).
2. S.P. Shah, ACI Mater. J. 88, 595 (1991).
3. P.K. Metha, Concrete: Structure, Properties and Materials, p. 390, Prentice-Hall, Inc., Englewood Cliffs, 1986.
4. S. Mindess and G. Vondran, Cem. Concr. Res. 18, 109 (1988).
5. Ullmann's Encyclopedia of Industrial Chemistry, Vol. A-10, p. 615, VCH Publishers, New York, 1987.
6. A.J. Al-Tayyib, M.M. Al-Zahrani, Rasheeduzzafar and G.J. Al-Sulaimani, Cem. Concr. Res. 18, 561 (1988).
7. A.J. Chirinos Padron, J. Photochem. Photobiol. A, 49, 1 (1989).
8. S.H. Hamid, M.B. Amin, and A.G. Maadhah, Handbook of Polymer Degradation, p. 19, Marcel Dekker Inc., New York, 1991.
9. Encyclopedia of Polymer Science and Engineering, 12nd ed., Vol. 4, p. 653, John Wiley & Sons, New York, 1988.
10. J.H. Adams, J. Polym. Sci. Part A-1, 8, 1077 (1970).
11. D.J. Carlsson and D.M. Wiles, Macromolecules 2, 587 (1969).
12. A.R. Horrocks, K. Valinejad, and J.S. Crighton, Polym. Degrad. Stab. 43, 81 (1994).
13. D. Feldman, Polimeric Building Materials, cap. 8, Elsevier Applied Science, London, 1989.
14. H.H.G Jellinek, Aspects of Degradation and Stabilization of Polymers, p. 196, Elsevier, New York, 1978.
15. B. Gosse, J.P. Gosse, S. Saïd, A. Gadoum, and M. Nemamcha, J. Appl. Polym. Sci. 46, 1121 (1992).
16. C.Q. Yang and L.K. Martin, J. Appl. Polym. Sci. 51, 389 (1994).
17. N.S. Allen, Degradation and Stabilization of Polyolefins, p. 4, Applied Science Publishers, New York, 1983.