

# Aging of Modified Glass-Reinforced Polypropylene in Air and in Antifreeze

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**ABSTRACT:** The thermal stability and the mechanical properties of modified and unmodified glass-reinforced polypropylene during aging in air (135°C) and antifreeze (115°C) with exposure up to 80 days was investigated in this study. Aging leads to progressive phase separation. On the contrary, the original modified composite is characterized by a dense structure; aging leads to the structure compacting and pore size decreases. Unmodified composite displays a drastic failure of the mechanical properties after 10 days of heating. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 807–813, 2000

**Key words:** thermostabilizers; chemical modifier; phenolic antioxidant; hindered phosphite; polypropylene; glass fiber

## INTRODUCTION

A great advance in the area of polyolefin composites has been made in the last decades. Chemical modification of polyolefins, for example, chemical binding of a polymer and a filler, may endow composites with a complex of unique properties. Modification of the polymers (polypropylene in particular) by grafting of reactive functionalities at synthesis or compounding is a necessary condition for the creation of high-strength polyolefin composites, containing glass fiber or other reinforcers.<sup>1</sup> The conception of the said modification consists of the creation of chemical adhesion on a

polymer/filler interface.<sup>2</sup> Unfortunately, chemical modification, such as the generation of carboxylic or imide groups in macromolecules, results in a noticeable decrease of the polypropylene thermostability: Oxidation of the polymer proceeds practically without an induction period. Thermostabilization of modified polyolefin composites is complicated by possible interaction between an antioxidant and grafted reactive groups of the macromolecules. This interaction diminishes the polymer–filler chemical adhesion.

The comparative behavior of modified and unmodified glass-reinforced polypropylene during aging in air (135°C) and in antifreeze (115°C) with exposure up to 80 days was investigated in this study. An approach to thermostabilization of the composites is proposed. Mechanical properties (tensile strength, flexural strength, impact

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strength) and melt flow were measured for the original and aged samples. According to Hg-porosimetry data, an unmodified composite has a loose macroporous structure. Aging leads to progressive phase separation. On the contrary, the original modified composite is characterized by a dense structure; aging leads to the structure compacting and pore size decreases. Unmodified composite displays a drastic failure of the mechanical properties after 10 days of heating. Modified thermostabilized glass-filled polypropylene holds its thermooxidative stability during aging in air as in antifreeze, and its molecular weight characteristics remain practically constant.

## EXPERIMENTAL

### Materials

The materials used were the following: isotactic polypropylene (trade name Lipol, Ukraine) with a melt flow of 6.0 g/10 min,  $M_w = 271,000$ ,  $M_n = 72,000$ ,  $M_z = 697,000$ , and  $M_w/M_n = 3.8$ ; glass roving with  $\gamma$ -aminopropyltriethoxysilane as a size; a maleimide derivative (MI) (bismaleimide diphenylmethane, product of laboratory synthesis) as a chemical modifier; and tetrakis[methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)]-methane (Irganox 1010, Ciba-Geigy, Switzerland) (AO); bis(2,4-di-*tert*-butylphenyl)pentaerythrityl-diphosphite (Ultranox 626, Borg Warner, England) (PS-I) and tris(2,4-di-*tert*-butylphenyl)phosphite (Irgafos 168, Ciba-Geigy) (PS-II) as thermostabilizers.

### $^1\text{H}$ -, $^{13}\text{C}$ -, and $^{31}\text{P}$ -NMR Spectroscopy

The solutions of compounds and their mixtures in DMSO- $d_6$  before and after exposure were investigated. The spectra were recorded on an NMR spectrometer Gemini-300 (Varian).

### IR Spectroscopy

Compounds and mixtures before and after exposure were studied. IR spectra of the samples as pellets in KBr were recorded on Specord M80 spectrometer (Karl Zeiss).

### Hg Porosimetry<sup>3</sup>

The structure of the samples was measured using an Porosimeter Autoscan-3. The cell volume was 5 cm<sup>3</sup>. The instrument enables one to measure

both the total volume and the surface of the pores and their size distribution. Hg intrusion of the pores of the sample at different pressures was done. At pressures from 20 to 3000 psi, the pores with an equivalent radius from 350 to 0.003 Å were fixed.

The equivalent pore radius was determined from the ratio  $R = 2Q \cos G/P$ , where  $R$  is the equivalent pore radius;  $Q$ , the Hg surface tension;  $G$ , the contact angle ( $\sim 140^\circ$ ), and  $P$ , the pressure (psi). The sample volume was 2–5 cm<sup>3</sup>; the resolution,  $5 \times 10^{-4}$  cm<sup>3</sup>; and the pressure measurements' error, +0.5%. The following parameters were calculated from the data obtained: total interior pore volume (the volume of mercury forced into the pores at  $P = 228$  MPa); total pore surface; pore surface distribution; and average, maximal, and minimal radii of the pores and the volume, corresponding to each type of pores.

### Gel Permeation Chromatography (GPC)

A Waters 150C high-temperature liquid chromatograph was used. The detector used was a refractometer with autosampling, which is a system of chromatographic columns packed with Ultrastraygel (500, 10<sup>4</sup>, 10<sup>5</sup> Å). The eluent was *o*-dichlorobenzene, and the working temperature, 140°C. A Data Module Waters 745 was used for data recording and processing.

### Oxygen Uptake

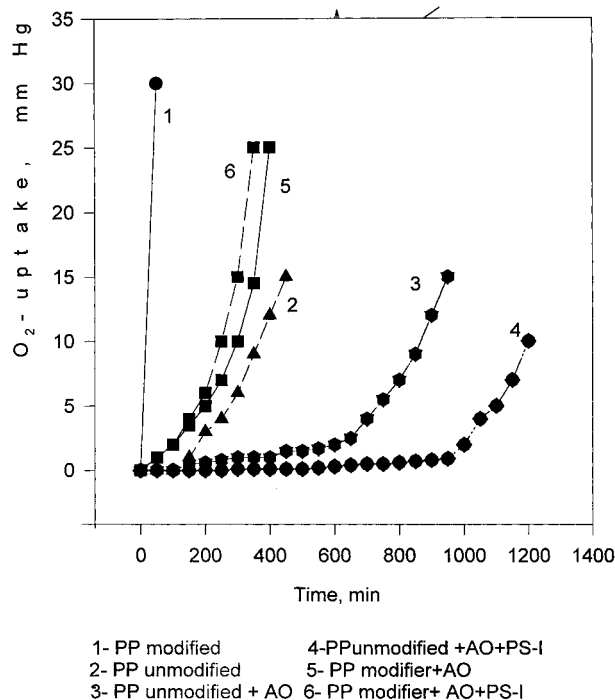
Oxygen uptake was monitored at 160°C using a special glass vacuum assembly.<sup>4</sup> The initial O<sub>2</sub> pressure was 300 torr; the test portion, 100 mg; and the temperature, 160°C.

### Mechanical Tests

Mechanical tests were carried out according to ISO standards. The tensile and flexural strength were measured using an Instron 1195 according to ISO527/2 (Test for Tensile Properties of Plastics) and ISO178, 179 (Test for Flexural Properties of Plastics). The Charpy impact strength for unnotched samples was evaluated in accordance with NF T 51-035 (Charpy Impact Test for Plastics).

### Heat Aging

Heat aging was realized at  $135 \pm 5^\circ\text{C}$  in an oven with air circulation. Chemical aging of the sam-



**Figure 1** Kinetics of  $O_2$  uptake for PP:  $T = 160^\circ\text{C}$ ;  $P(O_2) = 300 \text{ mmHg}$ ; sample = 100 mg.

ples in antifreeze was conducted in tight cameras at  $115 \pm 5^\circ\text{C}$ .

## RESULTS AND DISCUSSION

High-strength polyolefin composites, containing glass fiber or other reinforcers, may be obtained by the grafting of reactive functionalities to the polymer.<sup>1</sup> The conception of the said modification consists of creating chemical adhesion on a polymer/filler interface.<sup>2</sup>

Chemical modification—the generation of active groups in polymer chains (carboxylic or imide groups, e.g.)—results in a noticeable decrease of polypropylene (PP) thermostability. Figure 1 displays the kinetics of oxygen uptake for unmodi-

fied PP and for the polymer modified with the MI. We can see that modified PP oxidizes without a noticeable induction period. This is an example of how important it is to maintain the thermostability of a basic polymer at the development of high-strength composites. Even high initial mechanical characteristics do not provide a means for a long-term service life of the end material. A preliminary study of the thermostabilization of unfilled unmodified PP revealed an optimal thermostabilizing formulation—a mixture of primary and secondary antioxidants—a phenolic antioxidant (AO) and a hindered phosphite (PS-1) (see Fig. 1). This formulation permits one to increase the induction period of thermooxidation by a factor of 100. The additive PS-1 decreases of thermostability of unfilled modified PP.

The effect of different thermostabilizers on the mechanical properties of the original unmodified and modified glass-reinforced PP is presented in Table I. Introduction of the AO provides the best mechanical characteristics for modified PP. Addition of PS-1 leads to the properties' decrease to the point of the modified PP.

Some literature data point to the possibility of interaction between maleic anhydride derivatives (modifier) and  $\gamma$ -aminopropyltriethoxysilane (size).<sup>5</sup> To investigate the reactions taking place on the modified polymer/glass fiber interface in the presence of polystyrene (PS), we carried out some model experiments with aminopropyltriethoxysilane, the MI, Ultrinox 626 (PS-I), and Irgafos 168 (PS-II) and investigated the reaction products by IR and NMR spectroscopy.

The mixtures of MI + PS,  $\gamma$ -aminopropyltriethoxysilane + PS, and every component were heated at  $250^\circ\text{C}$  in sealed glass ampules, that is, under conditions, to some extent, simulating PP processing. According to the IR<sup>6,7</sup> and NMR<sup>8,9</sup> results, partial hydrolysis of PS-I may take place even with dry mixing of the components. In the IR spectrum of PS-I after 10 min heating and in the spectrum of the MI + PS-1 mixture, we detected

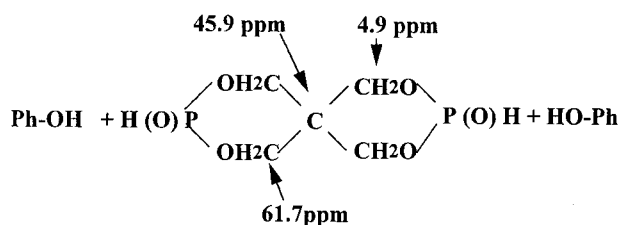
**Table I** Mechanical Properties of Glass-Reinforced (30% GF) PP Before Aging

Material	Impact Strength (kJ/m <sup>2</sup> )	Tensile Strength (MPa)	Flexural Strength (MPa)
Unmodified	18.1	35.0	62.0
Modified, nonstabilized	34.1	95.0	111.5
Modified, stabilized with AO	36.1	96.2	112.5
Modified, stabilized with AO + PS-I	22.1	62.5	60.0

**Table II** Assignments for the Main Absorption Bands and Optical Densities Ratio

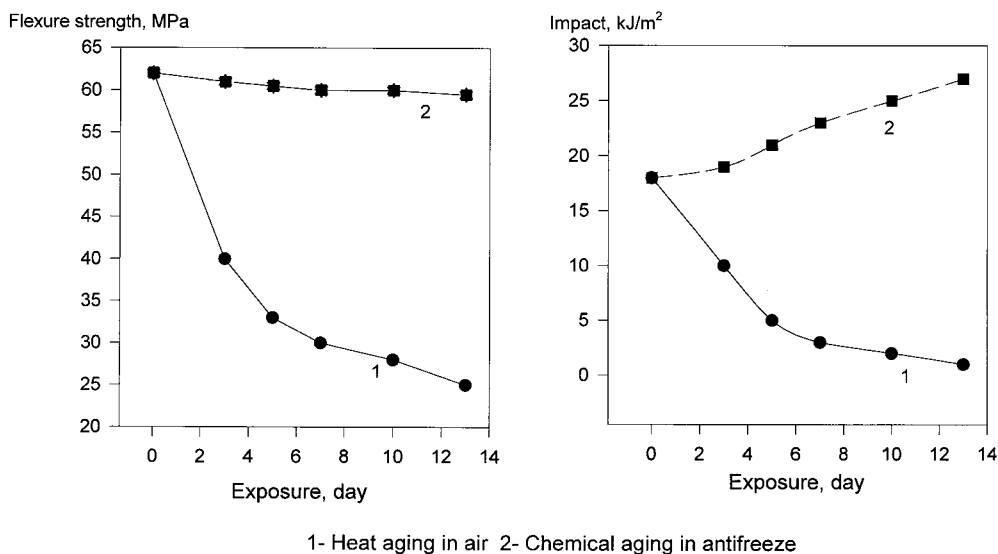
Vibration	Absorption (cm <sup>-1</sup> )	Optical Densities Ratio	Before Heating	After 10 min Heating	After 30 min Heating
MI					
$\nu_{=CH}$	3108	$D_{=CH}/D_{Ar}$	0.38	0.30	0.22
$\nu_{Ar}$	1514				
PS-1					
$\nu_{P-H}$	2425	$D_{P-H}/D_{C-C}$	Notdone	0.19	0.51
$\nu_{P=O}$	1277	$D_{P=O}/D_{C-C}$	Notdone	3.3	3.6
$\nu_{(CP)-OH}$	3408	$D_{(CP)OH}/D_{C-C}$	Notdone	0.9	4.7
$\nu_{C-C}$	911				
Blend MI/PS-1					
		$D_{=CH}/D_{Ar}$	0.52	Notdone	Notdone
		$D_{P-H}/D_{C-C}$	0.65	Notdone	Notdone
		$D_{P=O}/D_{C-C}$	1.9	Notdone	Notdone
		$D_{(CP)OH}/D_{C-C}$	2.9	Notdone	Notdone

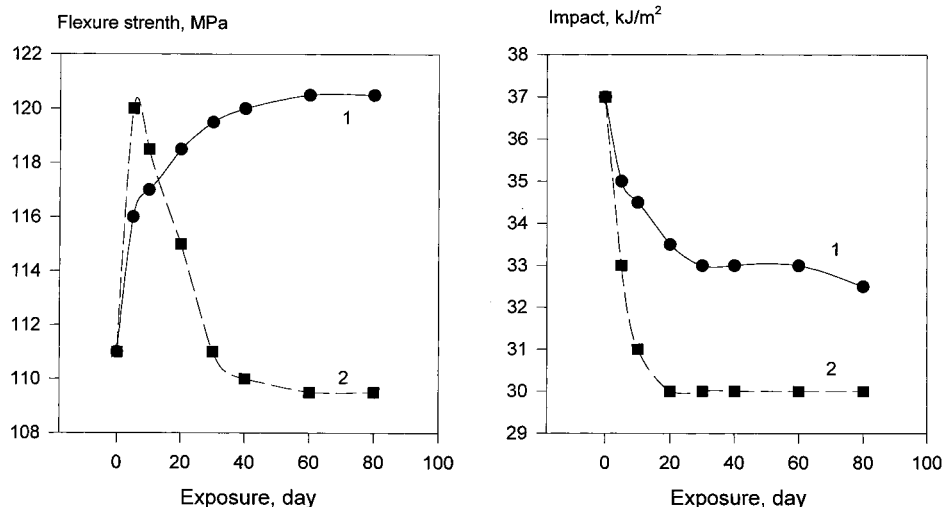
new absorption bands. The bands may be assigned to P—H and P=O bond vibrations (2425 and 1277 cm<sup>-1</sup>, correspondingly). The NMR spectra showed complete hydrolysis of PS-1 after 30 min of heating:



After dry mixing the MI + PS-I, the content of monophenol in the mixture was 67 mol %, and of the unchanged stabilizer, 33 mol %. At the same time, the signals of pentaerythritol at 59–60 ppm (ref. 10) were absent. This result shows that the hydrolytic resistance of the P—O—C bond in the pentaerythritol fragment is higher than is the bond in the monophenol fragment. As a result of the heat treatment or dry mixing with the MI, the hydrolysis of the ester bonds in PS proceeds and P<sup>+3</sup> transforms into P<sup>+5</sup>.

Heating of the MI leads to the cleavage of an unstable<sup>11,12</sup> C=C bond. The intensity of the

**Figure 2** Mechanical data for unmodified PP30% GF. Aging in air and in antifreeze.



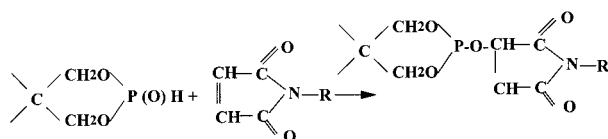
**Figure 3** Mechanical data for PP30% GF with modifier. Aging in air and in antifreeze.

band at  $3108\text{ cm}^{-1}$  ( $\text{C}=\text{C}_{\text{aliphatic}}$ ) gradually decreases, and after 1 h, the band disappears. Table II shows the ratio of optical densities for model compounds and mixtures before and after heat treatment.

The data obtained and calculated revealed that

- After 30 min of heating, the  $\text{C}=\text{C}$  bond in the MI disappears;
- Hydrolysis of PS may be noticed even at storage; after 30 min of heating, PS-1 is completely hydrolyzed; and
- For the MI + PS-I mixture,  $\text{C}=\text{C}$  bonds of MA and  $\text{P}-\text{H}$  and  $\text{P}=\text{O}$  bonds ( $2425$  and  $1277\text{ cm}^{-1}$ ) disappear after 10 min heating.

We suppose the following reactions:



The compound formed is chemically inert and does not react with the glass size.

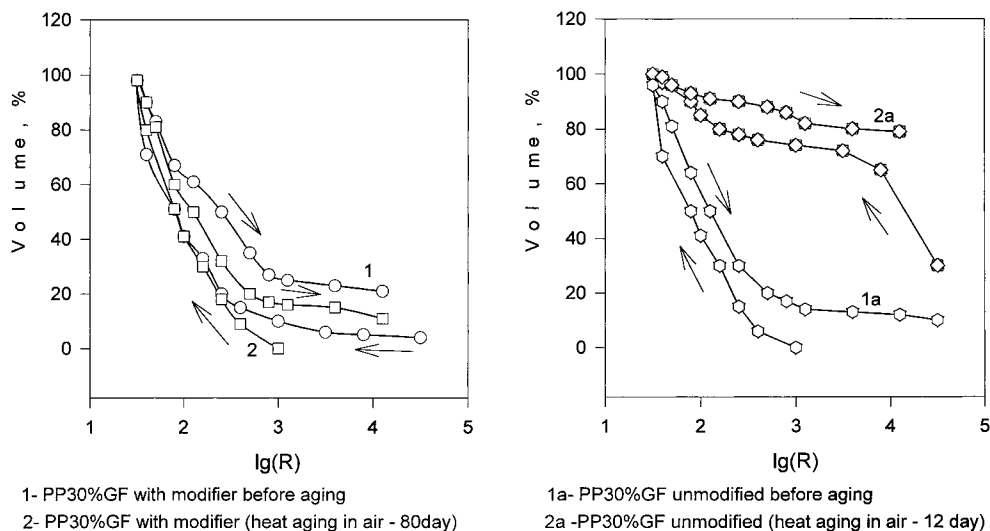
Similar experiments with PS-II showed higher thermostability of this additive because of its better hydrolytic resistance (monophenol < 10 mol % and acid phosphite were detected only after 30 min of heating). There is no reaction between  $\gamma$ -aminopropyltriethoxysilane and PS-I at the heat treatment. The intensities of absorption bands at  $2425$  and  $1277\text{ cm}^{-1}$  ( $\text{P}-\text{H}$  and  $\text{P}=\text{O}$  bonds) do not change after exposure of 30 min and even more.

The results obtained show the possibility of interaction of partially hydrolyzed phosphite with the maleic modifier at the processing temperature. This interaction blocks the modifier action. In spite of the sufficient hydrolytic resistance of PS-II, the phosphite may hydrolyze during the processing (especially if the apparatus is not dry). The partially hydrolyzed stabilizer blocks the modifier action.

Improvement of the modified PP stability under prolonged exploitation at elevated temperatures in

**Table III** GPC Data for Glass-reinforced (30% GF) Heat-Stabilized PP Before and After Aging

Material	$M_w$	$M_n$	$M_z$	$M_w/M_n$
Unmodified (with AO)				
Before aging	271,000	72,000	697,000	3.8
After 12 days aging in air	268,000	69,000	620,000	3.9
After 12 days aging in antifreeze	270,000	72,000	692,000	3.7
Modified (with AO)				
Before aging	272,000	72,000	698,000	3.8
After 10 days aging in air	270,000	72,000	698,000	3.7
After 80 days aging in air	260,000	69,000	62,000	3.8
After 80 days aging in antifreeze	307,000	80,700	786,000	3.8



**Figure 4** Extrusion and entrapment of Hg in/out of the pores compositions.

air and in antifreeze may be achieved by addition of a phenolic antioxidant. The results of aging in air and antifreeze for unmodified and modified glass-filled PP are presented in Figures 2 and 3.

According to Table I, modified PP has higher original properties than those of the unmodified polymer. The alteration of mechanical properties for both materials during aging is of interest.

Aging in air leads to a significant decrease of the mechanical properties for the unmodified material already within 10 days. Visual inspection shows the separation of the polymer from the glass fibers and the embrittlement of the samples. Aging in antifreeze does not change the samples' appearance. Plasticization by an-

tifreeze produces some increasing impact strength; flexural strength remains unchanged.

Degradation reactions, occurring at polymer aging, usually produce changes in its molecular weight distribution (MWD).<sup>4</sup> The MWD for unmodified and modified PP in the course of heat and chemical aging was monitored using GPC. The results are presented in Table III.

The data obtained show no significant changes in molecular weight characteristics of the polymer in the course of aging. Drastic decreasing of the mechanical properties for the unmodified sample is not connected with degradation reactions but, obviously, with significant loosening of the samples' physical structure.

**Table IV** Pore Size and Distribution for Unmodified and Modified PP

Material	Average Radius of Pores (Å)			
	Hg Intrusion		Hg Extrusion	
	Volume	Surface	Volume	Surface
Unmodified (with AO)				
Before aging	335.9	80.41	1101	89.8
After 12 days aging in air	8526	203.6	10210	140.9
After 12 days aging in antifreeze	247.4	88.9	4057	94.9
Modified (with AO)				
Before aging	285.2	80.4	630.5	88.9
After 80 days aging in air	140.2	73.3	281.6	83.3
After 80 days aging in antifreeze	152.1	77.5	678.0	91.6

Changes in the porosity of the materials in the course of heat and chemical aging were investigated using Hg porosimetry. The method permits one to evaluate the density of the composites, pore size, and form. The Hg content in the sample after the pressure release allows one to evaluate pore regularity, namely, an approximation to cylindrical form. Figure 4 shows intrusion and extrusion volumes as a function of the pore radius. Table IV demonstrates the pore size and distribution before and after aging.

The unmodified composite has a loose macroporous structure (maximal pore size 30,010 Å). The modified composite has surface pores with a maximal radius of 710 Å, that is, the material becomes denser after modification. Aging in air and antifreeze of the unmodified samples causes gradual loosening of the polymer structure. On the contrary, modified samples are characterized by gradual compacting of the structure during aging; the pore form remains practically unchanged. The analysis of the data obtained shows that polyolefin composites (PP in this case) with a prolonged service life at elevated temperatures in antifreeze may be obtained using chemical modification and stabilization.

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