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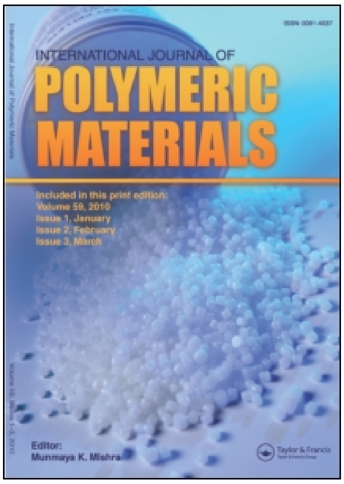

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The Aging of Modified Glass Fiber-Reinforced Polypropylene in Air and in Antifreeze

T. N. Novotortzeva[a]; O. B. Kulachinsckaya[a]; M. B. Andreeva[a]; E. V. Kalugina[a]; I. L. Aizinson[a]; A. S. Lunin[a]; V. A. Tochin[a]; Ya. G. Urman[b]; I. G. Kalinina[c]; K. Z. Gumargalieva[c]; G. E. Zaikov[d]
[a] Research and Production Company "Polyplastic", [b] Research Institute for Plastics, [c] Institute of Chemical Physics RAS, [d] Institute of Biochemical Physics RAS,

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The Aging of Modified Glass Fiber-Reinforced Polypropylene in Air and in Antifreeze

T. N. NOVOTORTZEVA [a], O. B. KULACHINSCKAYA [a], M. B. ANDREEVA [a], E. V. KALUGINA [a], I. L. AIZINSON [a], A. S. LUNIN [a], V. A. TOCHIN [a], YA. G. URMAN [b], I. G. KALININA [c], K. Z. GUMARGALIEVA [c] and G. E. ZAIKOV [d,*]

[a] *Research and Production Company "Polyplastic";*
[b] *Research Institute for Plastics;* [c] *Institute of Chemical Physics RAS;*
[d] *Institute of Biochemical Physics RAS*

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Comparative behavior of modified and unmodified glass-reinforced polypropylene during aging in air (135°C) and in antifreeze (115°C) with the exposure up to 80 days was investigated. Mechanical properties (tensile strength, flexural strength, impact strength) and melt flow were measured for original and aged samples. According to Hg-porosimetry data, unmodified composite has a loose macroporous structure. Aging leads to progressive phase separation. On the contrary, original modified composite is characterized by a dense structure; aging leads to the structure compacting, pore size decreases. Unmodified composite displays a drastic decrease of mechanical properties after 10 days of heating. Modified thermostabilized glass-filled polypropylene holds its thermooxidative stability during aging in air and in antifreeze, its molecular weight characteristics remain practically constant.

Keywords: Thermostabilizers; chemical modifier; phenolic antioxidant; hindered phosphite; polypropylene; glassfiber

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*Corresponding author.

RESULTS AND DISCUSSION

Materials:

Isotactic polypropylene, melt flow 6.0 g/10 min;
Glass roving with γ-aminopropyltrietoxysilane as a size;
Chemical modifier – maleimide derivative;
Thermostabilizers – Tetrakis[methylene (3,5-di-tert.-butyl-4-hydroxyhydrocinnamate)] methane (Irganox 1010, Ciba-Geigy) (AO); Bis(2,4-di-tert.-butylphenyl) pentaerythrityldiphosphite (Ultranox 626, Borg Worner) (PS-I), Tris(2,4-di-tert.butylphenyl) phosphite (Irgafos 168, Ciba-Geigy) (PS-II).

^{1}H, ^{13}C and ^{31}P NMR – spectroscopy – the solutions of compounds and their mixtures in DMSO-d_6 before and after an exposure were investigated. The spectra were recorded on NMR-spectrometer Gemini-300 (Varian).

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

Hg-porosimetry – Microporosity of the samples was investigated with porosimeter Autoscan (Autochrom). The volume of mercury forced into the pores at the pressure increase was automatically recorded. 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;
- average, maximal, minimal radius of the pores and the volume, corresponding to each type of pores.

Gel permeation chromatography Waters 150°C high-temperature liquid chromatograph was used. Detector – refractometer, autosampling, a system of chromatographic columns packed with Ultrastyrogel (500, 10^4, 10^5 Å). Eluent – *o*-dichlorobenzene. Working temperature – 140°C. Data Module Waters 745 was used for data recording and processing.

Oxygen uptake was monitored at 160°C using a special glass vacuum assembly [3]. Initial O_2 pressure 300 torr, test portion – 100 mg, temperature 160°C.

Mechanical tests were carried out according to Russian Standards. Tensile and flexural strength were measured with the help of Instron 1195 according to GOST 4648-71 (Test for tensile properties of plastics) and GOST 4648-71 (Test for flexural properties of plastics). Charpy impact strength for unnotched samples was evaluated in accordance with GOST 4647-80 (Charpy impact test for plastics).

Heat aging was realizes at 135 ± 5°C in an oven with air circulation. Chemical aging of the samples in antifreeze was conducted in tight cameras at 115 ± 5°C.

High-strength polyolefin composites, containing glass fiber or other reinforcer, may be obtained by grafting of reactive functionalities to the polymer [1]. The concept of this modification is based on improvement of chemical adhesion at polymer/filler interface [2].

Chemical modification – the generation of active groups in polymer chains (carboxylic or imide groups, for example) – results in a noticeable decrease of polypropylene thermostability. Figure 1 displays the kinetics of oxygen uptake for unmodified polypropylene and for the polymer modified with maleimide derivative (MI). We can see that modified PP oxidizes without noticeable induction period. This shows how important is to maintain thermostability of a basic polymer at the development of high-strength composites. Even high initial mechanical characteristics do not provide a mean for a long-term service life of the final material. Preliminary study of the thermostabilization of unfilled modified polypropylene has revealed an optimal thermostabilizing formulation – a mixture of primary and secondary antioxidant – phenolic antioxidant (AO) and hindered phosphite (PS-1) (see Fig. 1). This formulation permits as to increase the induction period of thermooxidation by a factor of 100.

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

The possibility of interaction between maleic anhydride derivatives (modifier) and γ-aminopropyltriethyoxysilane (size) was reported in [4]. To investigate the reactions taking place on the modified polymer/glass fiber interface in the presence of PS, we carried out some model experiments with aminopropyltriethoxysilane, maleimide derivative (MI),

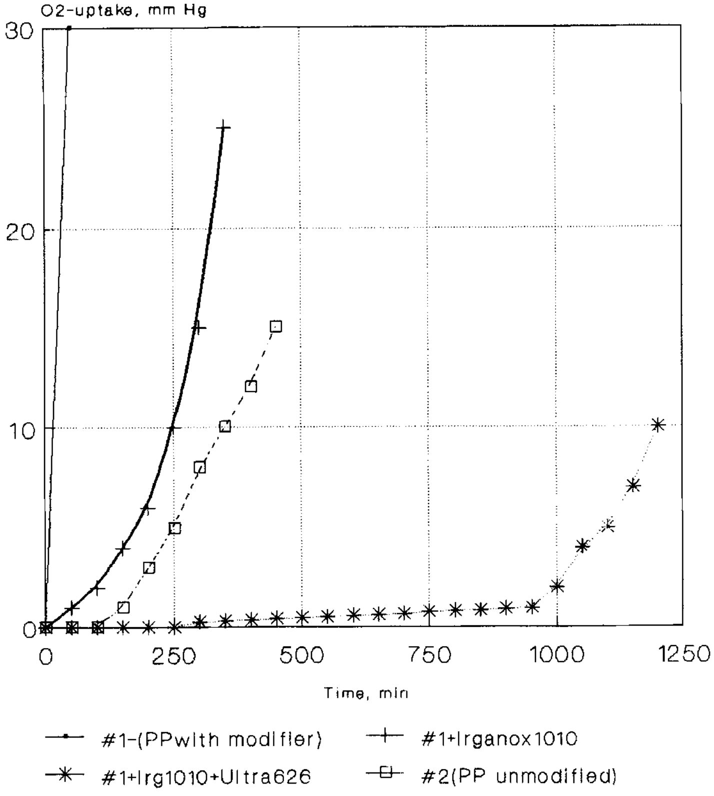


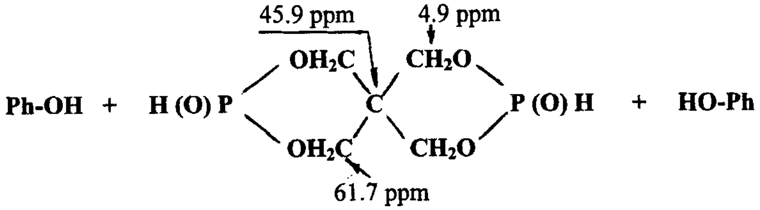
FIGURE 1 The kinetic of O_2-uptake for PP $T = 160°C$, $P(O_2) = 300$ mm Hg, sample = 100 mg.

TABLE I Mechanical properties of glass-reinforced (30%GF) polypropylene before aging

Material	*Impact strength, kJ/m²*	*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

Ultranox 626 (PS-I), Irgafos 168 (PS-II) and investigated the reaction products by IR-and NMR-spectroscopy.

The mixtures MI + PS, γ-aminopropyltriethoxysilane + PS and every component were heated at 250°C in sealed glass ampules, that is under conditions, which simulate polypropylene processing. According to IR- [5, 6] and NMR- [7, 8] results, partial hydrolysis of PS-I may take place even at dry mixing of the components. In IR-spectrum of PS-I after 10 min heating and in the spectrum of MI+PS-1 mixture we have detected new absorption bands. The bands may be assigned to P—H and P=O bonds vibrations (2425 and 1277 cm^{-1} correspondingly). NMR spectra showed complete hydrolysis of PS-1 after 30 min of heating.



SCHEME I

After dry mixing of MI + PS-I the content of monophenol in the mixture was 67 mol.%, unchanged stabilizer – 33 mol.%. At the same time, the signals of pentaerythritol at 59 – 60 ppm [9] were absent. This shows that the hydrolytic resistance of P—O—C bond in pentaerythritol fragment is higher than the bond in monophenol fragment. As a result of heat treatment or dry mixing with MI the hydrolysis of the ester bonds in PS takes place, and P^{-3} transforms into P^{+5}.

Heating of MI leads to the cleavage of unstable [10, 11] C=C bond. The intensity of the band at 3108 cm^{-1} ($C=C_{aliphatic}$) gradually decreases, and after 1 hour the band disappears. Table II shows the ratio of optical densities for model compounds and mixtures before and after heat treatment.

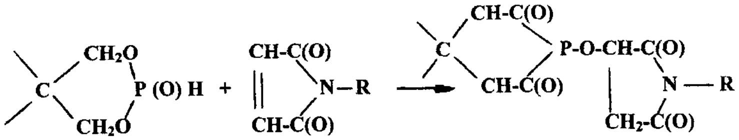
The experimental and calculated data have revealed that:

- after 30 min of heating C=C bond in MI disappears;
- hydrolysis of PS may be noticed even at storage, after 30 min of heating PS-1 is completely hydrolyzed;
- for MI + PS-I mixture C=C bonds of MA and P—H, P=O bonds (2425 and 1277 cm^{-1} disappear already after 10 min heating.

TABLE II Assignments for the main absorbtion bands and optical densities ration

Vibration	*Absorbtion, cm^{-1}*	*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
ν_{Ar}	1514				
PS-1					
$\nu_{P—H}$	2425	$D_{P=H}/D_{C—C}$	Not	0.19	0.51
$\nu_{P=O}$	1277	$D_{P=O}/D_{C—C}$	Not	3.3	3.6
$\nu_{(CP)—OH}$	3408	$D_{(CP)OH}/D_{C—C}$	Not	0.9	4.7
$\nu_{C—C}$	911				
Blend MI/PS-1					
		$D_{=CH}/D_{Ar}$	0.52	Not	Not
		$D_{P=H}/D_{C—C}$	0.65	Not	Not
		$D_{P=O}/D_{C—C}$	1.9	Not	Not
		$D_{(CP)OH}/D_{C—C}$	2.9	Not	Not

Therefore, we propose the following reactions:



SCHEME II

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

Similar experiments with PS-II showed higher thermostability of this additive because of its better hydrolytic resistance (monophenol and acid phosphite were detected only after 30 min of heating).

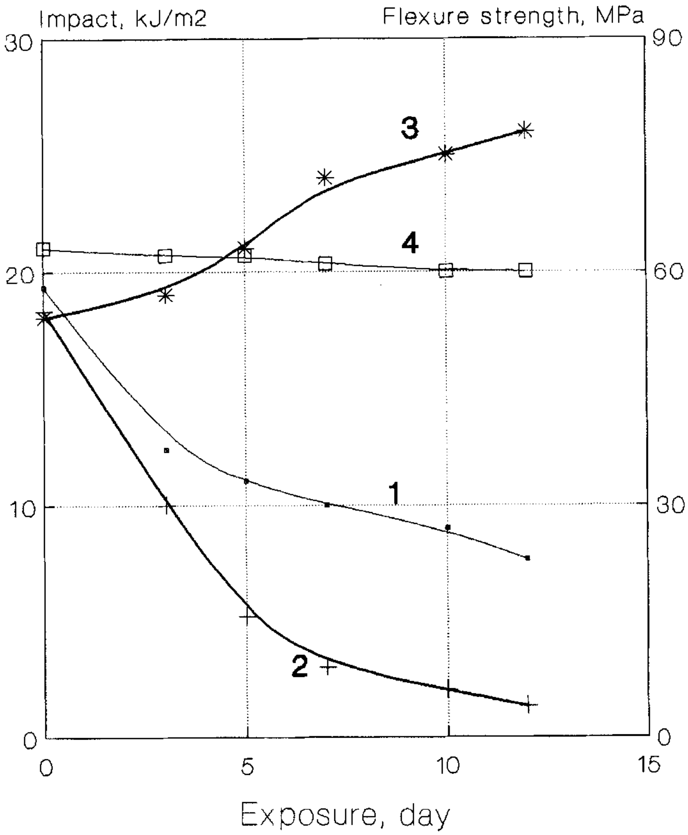
There is no reaction between γ-aminopropyltrietoxysilane and PS-I at the heat treatment. The intensities of absorption bands at 2425 and 1277 cm^{-1} (P—H and P=O bonds) do not change after the exposure of 30 min and even more.

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

The improvement of modified polypropylene stability under prolonged exploitation at elevated temperatures in air and in antifreeze may be achieved by addition of phenolic antioxidant. The results of aging in air and antifreeze for unmodified and modified glass-filled polypropylene are presented in Figures 2, 3.

According to Table I, modified PP has higher initial properties than unmodified polymer. Alteration of mechanical properties for both materials during aging is of interest.

Aging in air leads to significant decreasing of mechanical properties for unmodified material already within 10 days. Visual inspection shows the separation of the polymer from glass fibers and the embrittlement of the samples. Aging in antifreeze does not change the samples appearance. Plasticization by antifreeze produces some increases of; impact strength while flexural strength remains unchanged.

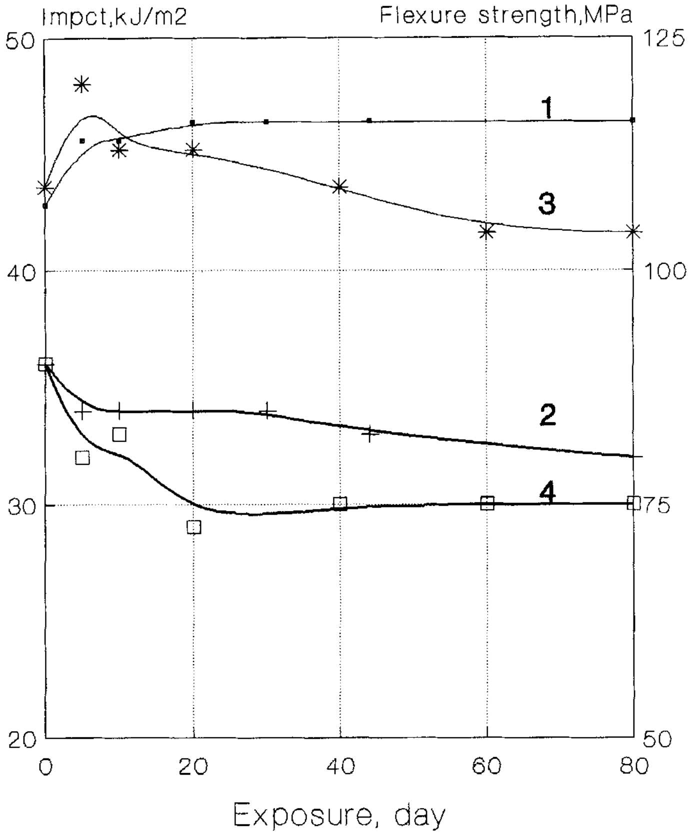


1,2- Heat aging in air, 3,4 Chemical aging in antifreeze.

FIGURE 2 Mechanical data for PP 30%GF aging in air and in antifreeze.

Degradation reactions, occurring at polymer aging, usually produce changes in its molecular weight distribution (MWD) [3]. MWD for unmodified and modified polypropylene in the course of heat and chemical aging was monitored with the help of gel permeation chromatography. 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. Therefore, drastic decreases of mechanical properties for unmodified samples is not connected with degradation reactions but with some significant loosening of the samples physical structure.



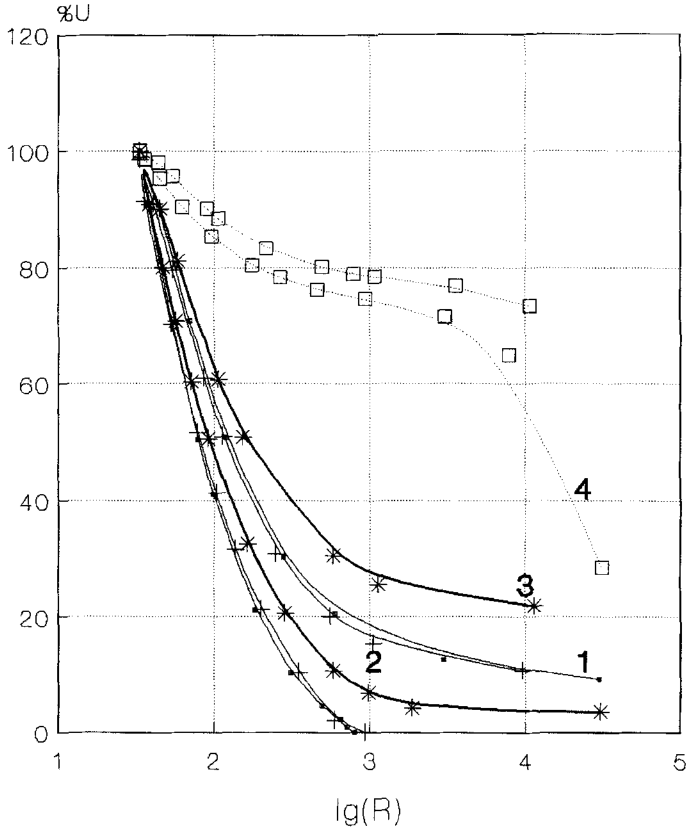
1,2- Heat aging in air, 3,4 Chemical aging in antifreeze.

FIGURE 3 Mechanical data for PP 30%GF with modifier aging in air and in antifreeze.

TABLE III GPC-data for glass-reinforced (30%GF) heat stabilized polypropylene before and after aging

Material	M_w	M_n	M_z	M_w/M_n
Unmodified:				
Before aging	271000	72000	697000	3.8
After 12 days aging in air	268000	69000	620000	3.9
After 12 days aging in antifreeze	270000	72000	692000	3.7
Modified:				
Before aging	272000	72000	698000	3.8
After 10 days aging in air	270000	72000	698000	3.7
After 80 days aging in air	260000	69000	62000	3.8
After 80 days aging in antifreeze	307000	80700	786000	3.8

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



1- PP30%GF unmodified before aging
2- PP30%GF with modifier (heat aging in air – 80 day)
3- PP30%GF with modifier before aging
4- PP30%GF unmodified (heat aging in air – 12 day)

FIGURE 4 Extrusion and entrusion of pores compositions.

TABLE IV Pore size and distribution for unmodified and modified PP

	Average radius of pores, Å			
	Hg intrusion		*Hg extrusion*	
Material	*volume*	*surface*	*volume*	*surface*
Unmodified				
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				
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

Unmodified composite has a loose macroporous structure (maximal pore size of 3×10^4 Å). The modified composite has surface pores with maximal radius of 710 Å, that is the material becomes denser modification. Aging in air and antifreeze of unmodified samples causes gradual loosening of the polymer structure. On the contrary, modified samples are characterized by gradual compacting of the structure during aging; pore form remains practically unchanged.

The analysis of the data obtained shows that polyolefin composites (polypropylene in this case) with prolonged service life at elevated temperatures in antifreeze may be obtained using chemical modification and stabilization.

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