

Effect of Titanium Dioxide and Silicon Dioxide on the Thermal Stability of Isotactic Polypropylene Deformed via Solvent-Crazing Mechanism

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Abstract—The effect of a finely divided structure created via the mechanism of delocalized crazing on the processes of thermo-oxidative degradation of isotactic polypropylene has been studied. It has been shown that the thermal stability of porous films is reduced at relatively low temperatures (up to 155°C) and they become brittle. In contrast, their degradation rate at temperatures above 400°C is two times below that for the original, nonporous films because of the formation of crosslinked network structures and carbonization. The formation of titania and silica nanoparticles via hydrolytic decomposition of the respective alkoxides directly in the pore space of the polypropylene matrix substantially alters its thermal stability, depending on the precursor concentration, the extent of hydrolysis, and the composite structure. The greatest increases in the mass-loss-onset temperature and the temperature of the maximum mass-loss rate (by 80–100°C) have been observed for the composites with 40 wt % titanium dioxide. It has been assumed that the enhancement of thermal stability is due to the significant concentration of the products of incomplete hydrolysis of titanium alkoxy derivatives. The silica particles, in contrast, exert a significant influence on the thermo-oxidative-degradation processes in polypropylene at their low concentration (up to 5 wt %), a result that is associated with the structural features of such composites.

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The thermal stability of polymers and polymer-matrix composite materials is one of the most important characteristics determining their application. Changes in polymer materials induced by the action of elevated temperature and atmospheric oxygen lead to a sharp decline in the physical and mechanical properties and a release of low-molecular-mass products, which are often toxic and flammable [1]. The thermo-oxidative-degradation properties of a polymer mainly depend on the chemical composition and structure of the polymer chain, the structure (crystallinity and orientation) of the material, and the nature and concentration of the filler.

Polypropylene is considered a flammable material (an oxygen index of 17.4) that is quite easy to oxidize at a temperature above 140°C in air [2, 3]. This property is due to the mobility of the hydrogen atom and the presence of methyl group at the tertiary carbon atom. The oxidation of methyl groups occurs in the first step, resulting in the generation and buildup of hydroperoxides in PP. Their degradation yields free radicals, which initiate the chain reaction of oxidative degradation accompanied by the scission of the polymer main chain. It is noteworthy that the combustion of PP involves the formation of burning droplets owing

to its poor coking ability, a circumstance that facilitates the spread of fire. Therefore, PP is necessarily doped with various stabilizers, antioxidants, and flame retardants. There are two types of appropriate stabilizers [4, 5]: those that interact with primary radicals to inhibit the propagation of the chain reaction of oxidation, e.g. butylhydroxytoluene, and those that induce the degradation of the hydroperoxide groups produced in the first PP oxidation step, such as phosphites and thioesters. Stabilizers of both types are frequently used in combination to obtain a synergistic effect.

To abandon organic stabilizers, the influence of different mineral fillers on the process of PP oxidation and combustion is being intensively investigated now [6]. There are two types of additives of this kind: non-degradable and degradable via heating. The effect of the first type of additives generally consists in that they reduce the concentration of the combustible component (polymer) in the composite and, hence, elevate the lower explosion limit; in addition, there is some heat loss due to heating the fillers to the temperature of the burning surface. The effectiveness of such additives is determined largely by their specific heat capacities; for example, to achieve an oxygen index of 27, the Al₂O₃ content in polyethylene should be higher than

85 wt %. Degradable fillers (metal hydroxides and bicarbonates) reduce the flammability of polyolefins to a greater extent [2, 7]. Water that is released during the decomposition of a flame retardant forms a vapor barrier to oxygen; moreover, part of the heat consumed to maintain combustion is absorbed, and an insulating char layer is formed on the polymer surface. The most active inorganic retardants for polyolefins are ammonium polyphosphate and ammonium fluoroborate combined with Sb_2O_3 .

Data on the influence of silicate particles or titanium dioxide TiO_2 particles on the processes of thermo-oxidative degradation and combustion of PP are controversial. It has been reported [8, 9] that particles of layered silicates enhance the thermal stability of the polymer matrix owing to a decrease in oxygen permeability (the "labyrinth effect"), adsorption of the combustion products on the surfaces of nanoparticles, and deactivation of oxidation sites by metal atoms of the silicates. Other studies have suggested the determining effect of the chemical nature of surface modifiers of nanoparticles [6, 10]. Palza et al. [11] studied the effect of small admixtures of silica and layered silicate nanoparticles (1–5 wt %) synthesized via the sol–gel method on the thermal stability of PP. The composites were prepared via mixing of the nanoparticles and the polymer through a melt with or without an additive that improves the compatibility of the components (a graft copolymer of polypropylene and maleic anhydride). A noticeable effect on the thermo-oxidative properties was not observed until the introduction of 5 wt % spherical SiO_2 particles in the presence of a coupling agent: the mass-loss-onset temperature and the peak degradation temperature increased by 20 and 50°C, respectively. In other cases, the changes were insignificant.

Titanium dioxide is generally used in industry as a nonhazardous white pigment. In addition, TiO_2 is a component of self-destructing polyolefin films [12], which operate on the principle of catalysis of photo-oxidative degradation processes. Nonetheless, a stabilizing effect of titanium dioxide during the thermal oxidation of polypropylene films and fibers has been described in some papers [13–15]. For example, the introduction of 1.5 wt % TiO_2 resulted in the elevation of the mass-loss-onset temperature of PP by 30°C and an increase in the oxygen index to 18 to 19. In addition, the flame-retarding effect may be due to an increase in the coking ability of the polymer. Calculation of the effective activation energy of the thermo-oxidative degradation of PP has shown that it increases by 25% in the presence of titanium dioxide.

Thus, as follows from the published data, it is not fully clear whether titania and silica nanoparticles affect the oxidizability and combustibility of the polypropylene matrix or the observed stabilization effects are associated with the amino- and phosphorus-containing surface modifiers of finely divided fill-

ers. Because traditional blending methods fail to yield PP-matrix nanocomposites with a fairly high amount of the inorganic component (above 5 wt %) without the use of a compatibilizer, crazing in a liquid adsorption-active medium (AAM) was used in this study.

The base of the crazing process is the uniaxial deformation of a glassy or semicrystalline polymer in an AAM, a process that results in self-dispersion of a polymer film or fiber into a system of separated fibrils ~10 nm in diameter and nanovoids between them of approximately the same size [16, 17]. Earlier, the crazing process was used to prepare nanocomposite materials based on polyolefins (isotactic PP, HDPE) and titanium(IV) dioxide [18–20] or silicon dioxide [21–23]. A characteristic feature of the preparation of such hybrid materials is that the dispersion of the inorganic component to the nanoscale in a thermodynamically incompatible polymer matrix is easy to accomplish without any additional stabilizer, which can deteriorate not only the mechanical, thermal, and other properties of the composites but also their safety. In addition, it is possible to regulate the structural design of the materials in a controlled way, i.e., to distribute in a definite way the filler phase in the bulk of the polymer: from discrete nanoparticles to a continuous phase in the form of an openwork frame.

Thus, investigation into the behavior at an elevated temperature in an oxidizing (air) atmosphere of polymers and composites having crazing-formed highly dispersed structures and large surface areas has become particularly important. Previously [24, 25], we studied the effect of the parameters of the porous structure formed as a result of uniaxial stretching of HDPE films in isopropanol via delocalized crazing, when the craze generation and growth occur quite uniformly throughout the polymer film, on the thermo-oxidative degradation and combustion processes. It was shown that an increase in the effective bulk porosity lowers the mass-loss-onset temperature of a sample and reduces the oxygen index of the material. The greatest decrements were observed for polymer films with the highest effective bulk porosity, ~40 vol %, being about 50°C for the initial temperature and two units for the oxygen index. In contrast, when the orientation order was increased at a high strain (400%), there was an increase in the temperature of the maximum in the mass-loss rate. Note that the character of combustion of the crazed porous films radically changed relative to that of the bulk material; i.e., suppression of the liquefying and coking processes was observed.

The purpose of this study was to reveal the specific features of the thermo-oxidative degradation of porous isotactic polypropylene films obtained via the mechanism of crazing in liquid absorption-active media and PP– TiO_2 and PP– SiO_2 composites based on these films with the use of differential scanning calorimetry and thermogravimetric analysis.

EXPERIMENTAL

Porous polymeric matrixes and composites were prepared from a commercial isotropic isotactic-PP film ($M_w = 3 \times 10^5$; a thickness of 120–140 μm) produced via melt extrusion. The initial film was annealed in the free-standing state at 140°C for 3 h. After annealing, the polymer had $T_m = 160^\circ\text{C}$ and a degree of crystallinity of 53%.

To obtain porous samples, PP films were deformed in reagent-grade isopropanol (Khimmed) with the use of manual clamps at a strain rate of 25% per minute and room temperature to a certain draw ratio within 10–200%. The craze generation and growth occurred via the delocalized-crazing mechanism [17, 26]. To prevent longitudinal shrinkage, the polymer films after stretching were stabilized via annealing under isometric conditions at 100°C for 1 to 2 h.

Bulk porosity was evaluated according to the change in the geometrical dimensions of PP specimens after deformation in the isopropanol medium and heat treatment. The film thickness was determined with a U3B-2 optical gage, and the linear dimensions were measured with a projector at 8 \times magnification. The effective bulk porosity was calculated through the formula $W = (V_f - V_0)/V_f$, where V_0 and V_f are respectively the initial volume and the final volume of the polymer.

The PP–TiO₂ and PP–SiO₂ composites were prepared via synthesis of the filler phase directly in the pores of the polymer matrix with the use of the principles of the sol–gel method. For this purpose, the liquid precursor compounds titanium tetraisopropoxide Ti(OC₃H₇)₄ (Merck, Germany) and hyperbranched polyethoxysiloxane (HPEOS) ($M_w = 3 \times 10^4$, a density of 1.17 g/cm³, a viscosity of 18.8 cP, and an effective molecular diameter of 2–5 nm, synthesized at the Enikolopov Institute of Synthetic Polymer Materials) were introduced into PP either at the crazing stage, i.e., during its uniaxial deformation, or via impregnation of the as-formed porous matrix for 1–3 h. To vary the inorganic-filler content of the composite, the precursors were introduced either in the pure form or as a 1–60 wt % solution in isopropanol. Next, the precursor-containing samples were fixed along the perimeter in a special frame and either immersed in an aqueous HNO₃ solution (pH 4) in the case of Ti(OC₃H₇)₄ or placed in a desiccator over a 10% HCl aqueous solution for 24 h in the case of hyperbranched HPEOS. Thus, water molecules penetrated into the porous structure of a polymer and reacted with a precursor. As a result of the hydrolytic condensation reaction, the hydrated silicon dioxide or titanium dioxide phase was formed in situ. The obtained composite samples were washed with distilled water, dried at room temperature to constant masses, annealed at 100°C for 1 h, and removed from the frame.

The morphology of the samples was studied via transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM images were obtained with a Leo-912 AB Omega microscope (Carl Zeiss, Germany). For examination, ultrathin sections were prepared via ultramicrotoming with a diamond knife at room temperature (a Reichert-Jung ultramicrotome, Germany). The resulting sections were transferred onto Formvar-coated copper meshes.

The SEM study was performed with Jeol JSM-6390LA and Hitachi S-520 microscopes. Cleaved samples were prepared via freeze fracturing in liquid nitrogen, fixed on a special table, and decorated with gold. Element-distribution maps for the samples were constructed with the use of energy-dispersive X-ray spectroscopy on a Jeol EX-54175JMH detector in Joint Use Center “Nanotechnology and Atmospheric Chemistry” of the Department of Chemistry, Moscow State University.

The thermal properties of porous polymeric matrixes and composites formed on their basis were studied via DSC. Measurements were performed in a DSC-30 cell with the use of a Metler-TA4000 instrument in the temperature range 25–200°C at a heating rate of 10 K/min. The resulting thermograms were processed with the program Metler-TC11.

The thermo-oxidative degradation of the samples was studied via thermogravimetry with a Metler-TG50 instrument in the dynamic mode at a heating rate of 20 K/min in the temperature range 25–600°C. The thermogravimetric study under isothermal conditions was conducted on a setup designed at the Enikolopov Institute of Synthetic Polymer Materials [27]. The temperature of the experiment was chosen to be 300°C, because this is the onset temperature of intense mass loss by undeformed PP.

RESULTS AND DISCUSSION

Thermo-Oxidative Properties of Porous PP Films Prepared via the Crazing Mechanism

The kinetics of radical reactions in polymers has several features that distinguish it from the characteristics of the reactions in their low-molecular-mass counterparts [28, 29]. These features are due, on one hand, to the physical state and phase state of a polymer as a structurally microheterogeneous solid with limited molecular mobility and, on the other hand, to the long-chain nature of a polymer and its inherent conformational diversity and neighbor effects. Therefore, the kinetics of any process in a polymer is affected by not only the nature and chemical structure of the polymer but also its supermolecular structure.

In the present study, the influence of the fine porous structure formed in the PP matrix via delocalized crazing on the thermo-oxidative-degradation processes was investigated. Figure 1 shows integral and differential TGA curves for the initial PP samples and

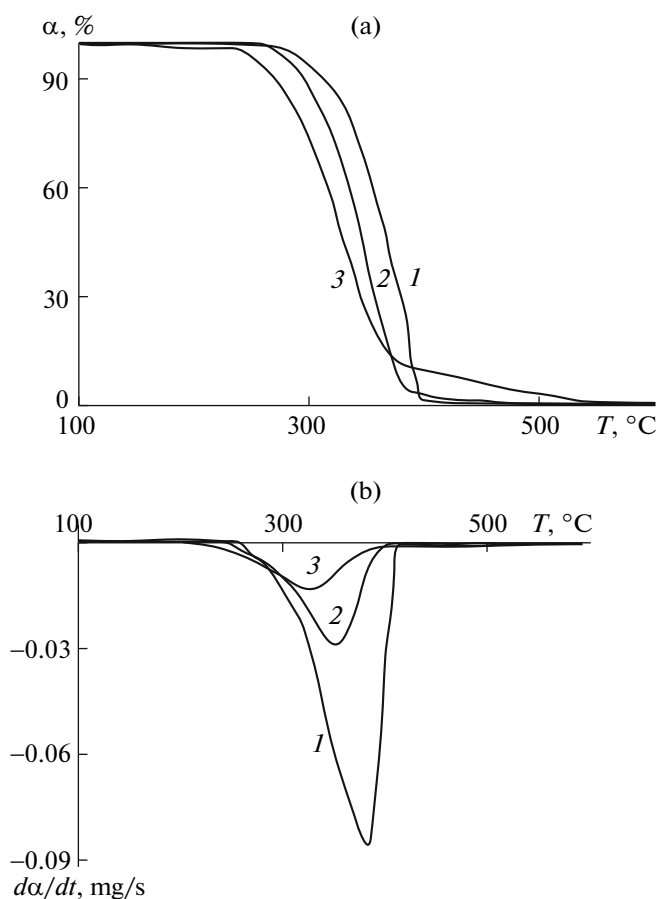


Fig. 1. (a) Integral and (b) differential TGA curves for (1) a commercial PP sample, (2) a PP film annealed at 140°C for 3 h, and (3) a porous PP film deformed in isopropanol by 200%. Heating rate, 20 K/min.

the porous film produced through the crazing technique. Note that curve 1 in Fig. 1 was obtained for the commercial product, which contains various additives, such as a stabilizer, a dye, and a flame retardant. The porous sample (200% strain, 37 vol % porosity) starts losing mass at as early as 210°C, and the peak of the mass-loss rate shifts by 25°C to lower temperatures. However, the complete degradation of the crazed film occurs at a higher temperature (540°C) than that of the bulk sample (480°C).

To understand these results, thermal analysis under isothermal conditions—a more informative method—was used to reveal the characteristics of thermo-oxidative degradation of porous samples, because it is free of the drawbacks of dynamic TGA, such as nonequilibrium conditions, temperature control, and sensitivity to the presence of low-molecular-mass impurities. Figure 2 shows curves for the mass loss of porous samples with time at a temperature of 300°C. The porous samples with strains of 100 and 200% (bulk porosities of 30 and 37 vol %, respectively) lose mass somewhat more slowly than the initial film. The mass loss after 30 min by sample 3, which is char-

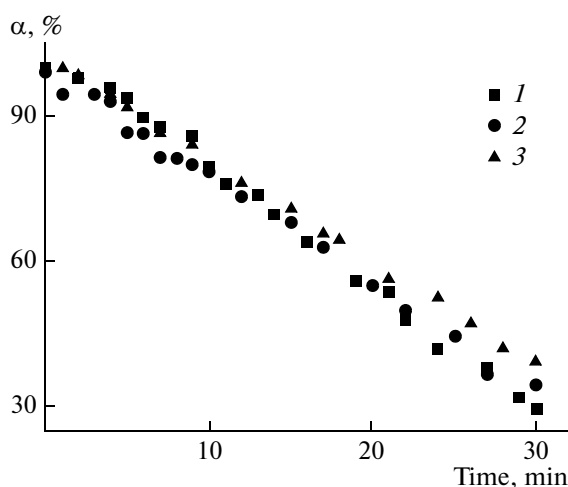


Fig. 2. Isotherms of (1) the initial PP film and (2, 3) porous PP films deformed by (2) 100 and (3) 200%.

acterized by the highest value of porosity, is as low as 60%, whereas this loss for the original film is 70%. These data indicate that the formation of the fine structure via crazing does affect the thermo-oxidative degradation of PP, although all of the specimens are in the molten state at the start of mass loss.

It is known [29] that the intense accumulation of hydroperoxide groups, which are oxidation sites and yield free radicals via decomposition, occurs at as early as 130–140°C. Therefore, one of the causes of lowering of the mass-loss-onset temperature of the porous samples may be an increase in the concentration of oxidation sites due to a highly developed interface and facilitation of the access of oxygen molecules to the internal volume of the polymer. Furthermore, in addition to washing out of stabilizing additives with ethanol, mechanochemical degradation of macromolecules may occur under mechanical stress during uniaxial deformation in an AAM [30]. It was found that, when a PP film is preliminarily stretched by 100% in ethanol, held in the free-standing state in air at room temperature for one day (its relative shrinkage is more than 90%, and the pore structure almost disappears), and then heated at 155°C for 1 h, the film loses its mechanical strength and disintegrates into small fragments on touch. Figure 3 shows DSC curves before and after thermal treatment for the initial PP film and the film preliminarily deformed by 100% in ethanol and shrunk. It is clearly seen that the strain has little effect on the thermal characteristics: The melting-peak temperature and the crystallinity determined from the peak area with allowance for the baseline and the polymer mass fraction in the sample remain almost the same. The heat treatment of the solvent-crazed polymer dramatically changes the pattern of the DSC curve: namely, the peak narrows and shifts to higher temperatures (165°C). Beginning from a temperature of 130°C, the occurrence of a certain process

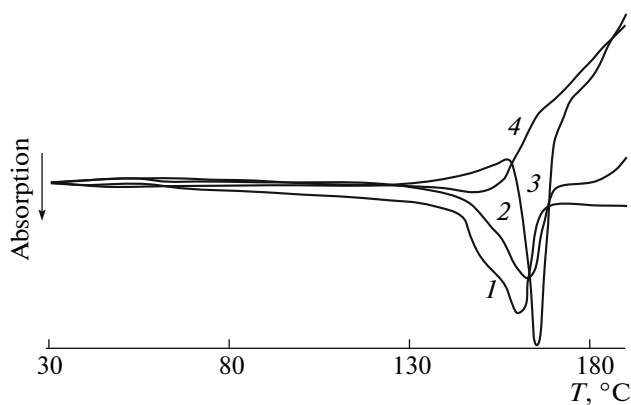


Fig. 3. DSC curves of (1) the PP film annealed at 140°C for 3 h and (2–4) PP films deformed in ethanol by 100% (2) before and (3) after annealing at 155°C and (4) heated again a day later. Heating rate, 10 K/min.

accompanied by heat evolution is seen against the background of the endothermic melting process. In addition, annealing leads to a decrease in the crystallinity from 55 to 44% for the crazed sample.

All these developments may be an indication of the intense process of oxidative degradation (primarily in the amorphous phase at the interface with the crystallites) occurring on very small and imperfect lamellae. Note that the repeated heating of the sample (Fig. 3, curve 4) a day after its storage in the DSC measurement cup at room temperature shows that the oxidation process obviously affects the crystalline phase as well: Curve 4 lacks the melting peak, and intense PP degradation begins from a temperature of 150°C. Similar, the TGA study revealed that the crazed sample after annealing begins to lose mass already at a 140°C, which is 70°C below (Fig. 4, curve 2).

In contrast, the appearance of a large amount of radicals due to the intense oxidation of PP at quite a low temperature increases the probability of their combination to form a crosslinked network structure, a phenomenon that leads to carbonization of the polymer. Indeed, unlike the bulk PP samples, which form burning drops during combustion, the porous films readily undergo coking. Coking most likely slows down the degradation process (the maximum rate of mass loss by the porous sample is two times lower than that of the initial sample), and a significant elevation of the temperature of complete degradation is observed for the solvent-crazed sample (Fig. 1, curve 3).

Now consider whether it is possible to inhibit the intense oxidation and the radical-formation processes at sufficiently low temperatures in the porous films. Crazing is a unique means of delivery and dispersion of small molecules in the polymeric matrix. With the use of this approach, the stabilizer Neozone D (*N*-(2-

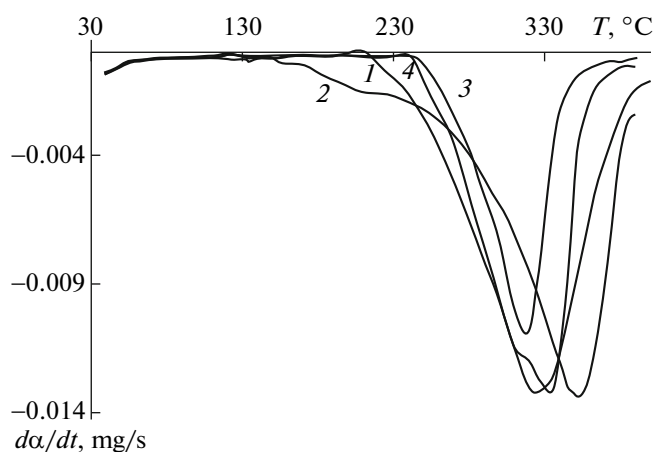


Fig. 4. Differential TGA curves for PP films deformed by 100% in ethanol (1, 2) or an ethanolic solution of Neozone D (3, 4) before (1, 3) and after (2, 4) annealing at 155°C. Heating rate, 20 K/min.

naphthyl)aniline) was introduced into PP. For this purpose, crazing was conducted in an alcoholic solution of the substance with a concentration of 0.016 g/mL. The stabilizer content in the polymer was 0.5 wt %. Analysis of the TGA data for the stabilized sample (Fig. 4, curve 3) showed that its onset degradation temperature increased by 30°C relative to that of the porous sample free of the stabilizer. Therefore, the annealing at 155°C of such an additionally stabilized sample does not increase its brittleness (Fig. 4, curve 4).

Thus, the deformation of the polypropylene film in the AAM via delocalized crazing is accompanied by the formation of a highly dispersed structure throughout the volume and by washing out of the stabilizing additives. This circumstance results, on one hand, in a decline in the thermal stability of the polymer at relatively low temperatures, as manifested in the increase of its fragility, and on the other hand, in a decrease in the rate of degradation at higher temperatures because of the formation of crosslinked network structures and coking. However, with the use of crazing, it is possible to prevent the occurrence of the low-temperature oxidation process if PP is stretched in a solution of the stabilizing additive in an AAM. This possibility makes the crazing process a potential means of controlling the stability of a polymer material, for example, in the manufacture of polyolefin articles that rapidly degrade after use.

Effect of Titanium Dioxide on the Thermo-Oxidative Degradation of PP

Analysis of published data on the effect of TiO₂ particles on the thermal stability of PP showed the existence of different, often diametrically opposed, views and experimental results. Researchers usually limit themselves to the introduction of a solid filler in an

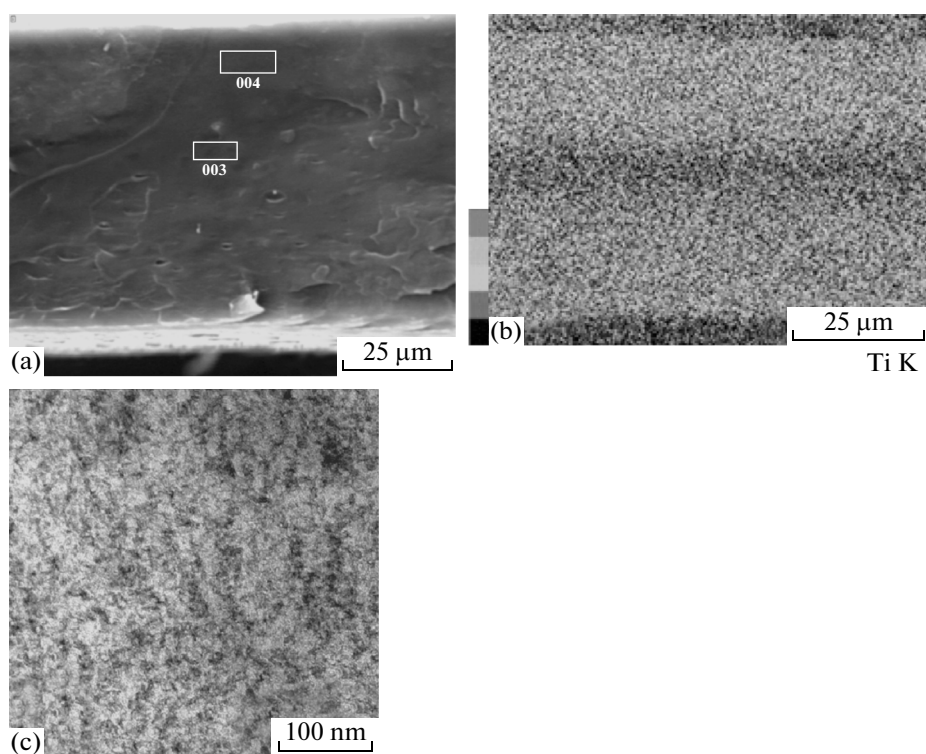


Fig. 5. (a) SEM and (b) TEM images of the PP–TiO₂ composite and (c) the distribution map of Ti atoms in the bulk. Titanium dioxide content, ~40 wt %.

amount of a few weight percent into a polymer matrix because of their poor compatibility; moreover, TiO₂ surface modifiers and compatibilizing agents are used as additives even in this case. In such a complex system, it is difficult to distinguish the effect of TiO₂ on the properties of the polymer matrix and the composite material as a whole.

In this study, composites were prepared through the crazing process, which makes it possible to avoid the difficulties associated with polymer solubility and poor compatibility of the components in the case of introduction and preservation of various inorganic particles in the nanosized state over a wide concentration range (several dozen weight percent) without any additional modifiers. The titanium dioxide phase was prepared in situ in the pores of the PP matrix with the use of the hydrolytic-decomposition reaction of alkoxides as a synthesis method for nanoparticles of high-purity metal oxides with the understanding that this reaction usually proceeds under mild conditions [31]. The titanium dioxide phase was synthesized in the PP matrix according to the specified procedure. The maximum amount of the second component was 40 wt % if pure titanium tetraisopropoxide was used. The TiO₂ content was varied through the use of various concentrations of Ti(OC₃H₇)₄ in its isopropanol solutions. Figure 5 shows micrographs of a freeze-fractured surface and a thin section of the PP–TiO₂ composite obtained via the crazing method and presents the distribution

map of titanium atoms in the PP volume. As was shown previously [20], the filler at a low content is quite uniformly dispersed into nanosized particles 1–2 nm in diameter throughout the polymer matrix and the particles gradually aggregate to form a continuous phase with an increase in their concentration (Fig. 5c).

The introduction of the titania phase via the crazing mechanism slightly affects the melting point and the crystallinity of the PP matrix. The DSC curves (Fig. 6) are almost identical for the initial and filled films. The behavior of the composite slightly differs in that curve 2 exhibits a smeared endothermic peak (starting at 40°C). This peak is apparently due to the elimination of water adsorbed on TiO₂.

Indeed, the TGA examination of composite samples (Fig. 7) revealed the presence of a low-temperature peak in the range 40–150°C at which the mass loss amounted to ~5 wt % (curves 3, 4).

The analysis of the TGA data (Fig. 7) and their comparison with the results for the unfilled porous matrix showed that the thermal stability of the PP–TiO₂ composite is much superior to that of the polymer: Namely, the onset temperature of intense mass loss and the temperature of the maximum in the mass-loss rate (loss peak) for the filled sample are displaced by more than 80°C toward higher temperatures. This phenomenon can be explained in terms of the complex structure of the titanium dioxide phase produced

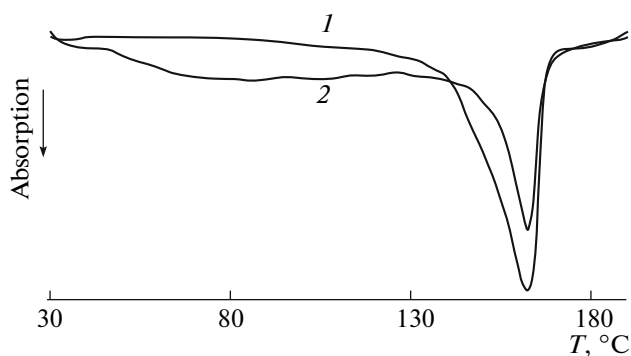


Fig. 6. DSC curves for (1) a porous PP film deformed by 200% in isopropanol and (2) the PP-TiO₂ composite. Heating rate, 10 K/min.

from the alkoxide via the hydrolytic-degradation reaction. Previously [20], TiO₂ obtained in the bulk of the porous PP matrix via this method was studied and its structure was proposed. It was established that the hydrolytic reaction did not go to completion, a circumstance that resulted in an amorphous titanium dioxide phase in the form of an assembly of TiO₂ nanoparticles containing titanium oxoalkoxo and oxohydroxo derivatives and linked with one another by different intermolecular bonds. Furthermore, such a system can easily retain adsorbed water. In Fig. 7, curve 2 refers to the amorphous TiO₂ phase obtained through the hydrolysis of Ti(OC₃H₇)₄ in the free volume (in a way similar to that in the PP matrix). The thermal decomposition of the precipitate (hydrated titanium dioxide) proceeds at a high rate in the wide temperature range 30–430°C with mass-loss peaks at 105 and 235°C. Therefore, the action of titanium dioxide containing water and residual isopropoxy groups may be similar to that of aluminum and magnesium hydroxides or hydrogen carbonates [2] for which flame-retardant and stabilizing activities are associated with both the release of water during their thermal degradation and the influence of the produced metal oxides on the coking ability of the polymer. Indeed, the mass fraction of the dry residue relative to pure TiO₂ was as low as 75 wt % after heating of the initial titanium dioxide precipitate (Fig. 7a, curve 2); i.e., the rest was water and CO₂ that had been formed via thermal oxidation of the titanium oxoalkoxo derivatives. Furthermore, the stabilizing effect of the filler in the low-temperature region in which the intense oxidation of the solvent-crazed porous PP matrix starts, as was shown earlier, may be associated with the deactivation of generated radicals on its highly developed surface. Note that the intense mass loss of the sample at a smaller TiO₂ content (23 wt %) begins at a temperature almost 6°C below that for the maximally filled composite (40 wt %). This difference might be due to the lesser amounts of water and the isopropanol derivatives that decompose during heating.

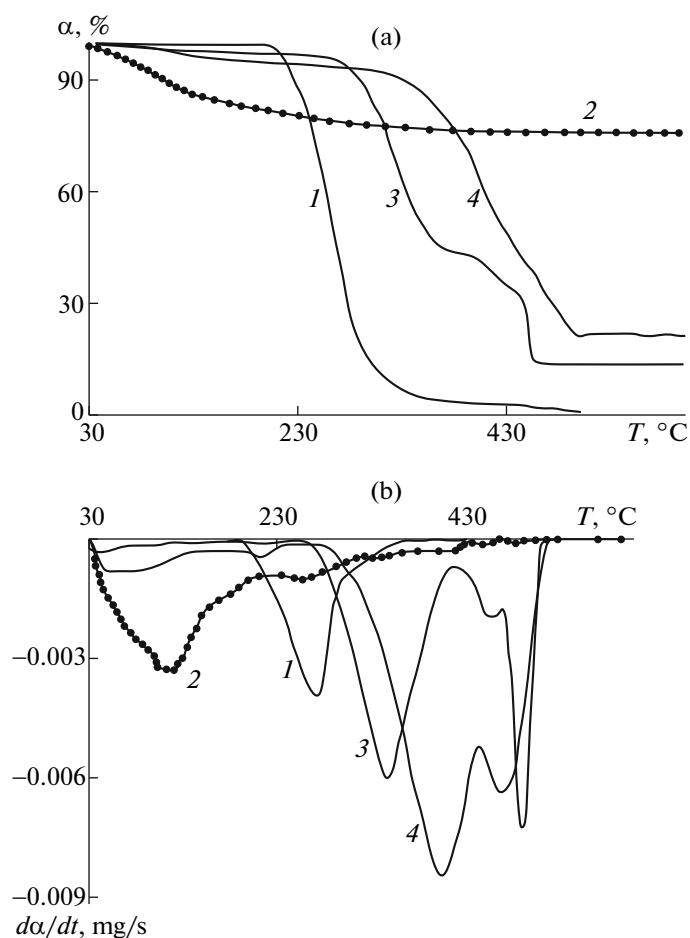


Fig. 7. (a) Integral and (b) differential TGA curves for (1) the porous PP film deformed by 200% in isopropanol, (2) the TiO₂ precipitate, and (3, 4) the PP-TiO₂ composites with titanium dioxide contents of (3) 23 and (4) 40 wt %. Heating rate, 10 K/min.

Note that the degradation of the PP-TiO₂ composites accompanied by mass loss proceeds in two steps. Because the second step starts at about 420°C when the mass loss of the titanium dioxide phase is largely completed, it may be assumed that the degradation of easily accessible sites in the polymer matrix occurs at the first stage and that crosslinked structures and regions poorly accessible to oxygen degrade at the second stage.

Thus, the introduction of the titanium dioxide phase that is stabilized by the products of incomplete hydrolysis of titanium tetraisopropoxide and that has a high surface area significantly increases the thermal stability of the composite in comparison to that of the initial porous matrix prepared via the crazing process.

Effect of Silicon Dioxide on the Thermo-Oxidative Degradation of PP

Next, consider the influence of the SiO₂ phase on the thermal stability of polypropylene. The funda-

mental difference between titania and silica obtained through the hydrolytic-decomposition reaction of the alkoxy derivatives is that this process goes to completion for the SiO_2 precursor and, hence, none of the unreacted ethoxy groups or their derivatives remains [22, 23]. In addition, intense intra- and intermolecular condensation reactions occur simultaneously with the hydrolysis, thereby resulting in either discrete dense SiO_2 nanoparticles or a three-dimensional continuous phase that substantially fills the available pore volume of the polymer matrix, depending on the concentration of hyperbranched HPEOS. Figure 8 shows photomicrographs of sections of the PP– SiO_2 composite with various filler contents. At a low concentration of silica, it is uniformly distributed in the form of spherical nanoparticles 3–10 nm in diameter in the polymer. As the amount of SiO_2 increases, the particles seem to gradually aggregate to ultimately yield a continuous phase and form a composite with the structure of two interpenetrating PP–silica networks. Evidence for the formation of such a structure was given in [21–23].

The DSC study of the thermal properties of the silica-containing composites did not reveal any specific features; like TiO_2 , SiO_2 does not exert any appreciable influence on the crystallinity or the melting temperature of the PP matrix. Note that the PP– SiO_2 composites do not become more brittle at low temperatures after their heating to 155°C and cooling, a circumstance that indicates the inhibition of the oxidation process in the crazed polymer matrix in the presence of silica particles in the same way as that for the composites with titanium dioxide.

The manner in which the thermo-oxidative degradation of PP– SiO_2 composites occurs at high temperatures is largely determined by the silica concentration and their structuring. Figure 9 shows TGA curves for the PP porous matrix, the PP-matrix composites with various SiO_2 contents, and silicon dioxide synthesized from hyperbranched HPEOS in the free volume.

In the low-temperature region up to 150°C, the composites lose adsorbed water remaining after the synthesis of the silica phase via the hydrolysis reaction (SiO_2 in the free state behaves likewise); therefore, it has no significant influence on the thermal stability of the composites at higher temperatures. Note that the silicon dioxide sample undergoes almost no change in mass during further heating in the range 200–600°C (Fig. 9, curve 2). At 200°C, all of the polymer samples (porous films and composites) begin to lose mass because of PP degradation. However, the position of the peak of mass loss depends on the filler content. For example, the maximum rate of degradation for the sample containing 2.5 wt % silica is observed at 430°C, versus 315°C for the sample with a 23 wt % content, like that for the unfilled porous matrix (320°C), and the peak temperature for the 41% sample decreases to 270°C. Indeed, the dependence of the half-mass loss

temperature on the filler content plotted in Fig. 10 for PP– SiO_2 composite samples on the basis of differential TGA data over a wide range confirms this fact.

There is a significant shift (by 80°C) of the peak to high temperatures for the samples with a silica content of no more than 5 wt %, and the composites with the maximum filler content (~40 wt %) lose 50% of the polymer mass even at 40°C below the half-mass loss temperature of the parent porous PP film. These features suggest that the silicon dioxide itself exhibits neither flame-retardant nor stabilizer properties in the oxidation and combustion of PP and that its presence in the polymeric matrix mainly affects the structure of the composite and, presumably, its barrier characteristics.

The crazing process is known to lead to the formation of a structure with a high surface area in the polymer [16]; however, this structure is highly labile and collapses in the free state (if the sample is removed from the clamps). Filling the porous structure with the solid filler throughout the polymer volume exerts a stabilizing effect on the crazed structure and largely precludes its shrinkage. The change that occurred in the volume of the samples owing to crazing and introduction of the liquid precursor hyperbranched HPEOS was determined along with the change that occurred after the hydrolysis reaction and the subsequent formation of SiO_2 particles in the pores and thermal immobilization. Figure 10 illustrates the change in the bulk porosity for silica-containing samples of various compositions during the formation of the SiO_2 phase. Note that the porosity value for all the samples after crazing was about 50 vol %. In addition, the plot shows that the porosity of the composites gradually decreases with a decrease in the amount of silica. For example, its value decreased by only 6–8 vol % for the composite with a high filler content, while the porosity disappeared completely for the composite with 1–5 wt % SiO_2 , so that its volume became the same as that of the initial PP film. Consequently, a high concentration of the SiO_2 phase preserves the finely divided structure of the polymer matrix and its degradation occurs at lower temperatures. In the case of a small filler content, when the filler is dispersed in the form of individual nanoparticles in PP and does not exert a stabilizing effect on the crazed structure of the matrix, the density of the composite is even somewhat higher than that of the bulk polymer. (The mass of the composite is greater than that of the unfilled film with the same volume.) However, the crazing process is accompanied by the formation of an oriented fibrillar structure of the polymer, and all operations relating to the formation of SiO_2 particles and thermal fixation of the composites are conducted under isometric conditions, a circumstance that preserves the orientation of the polymer matrix. All of the above factors can slow down the diffusion of oxygen and combustion products in the composites with a low filler content and, hence, dis-

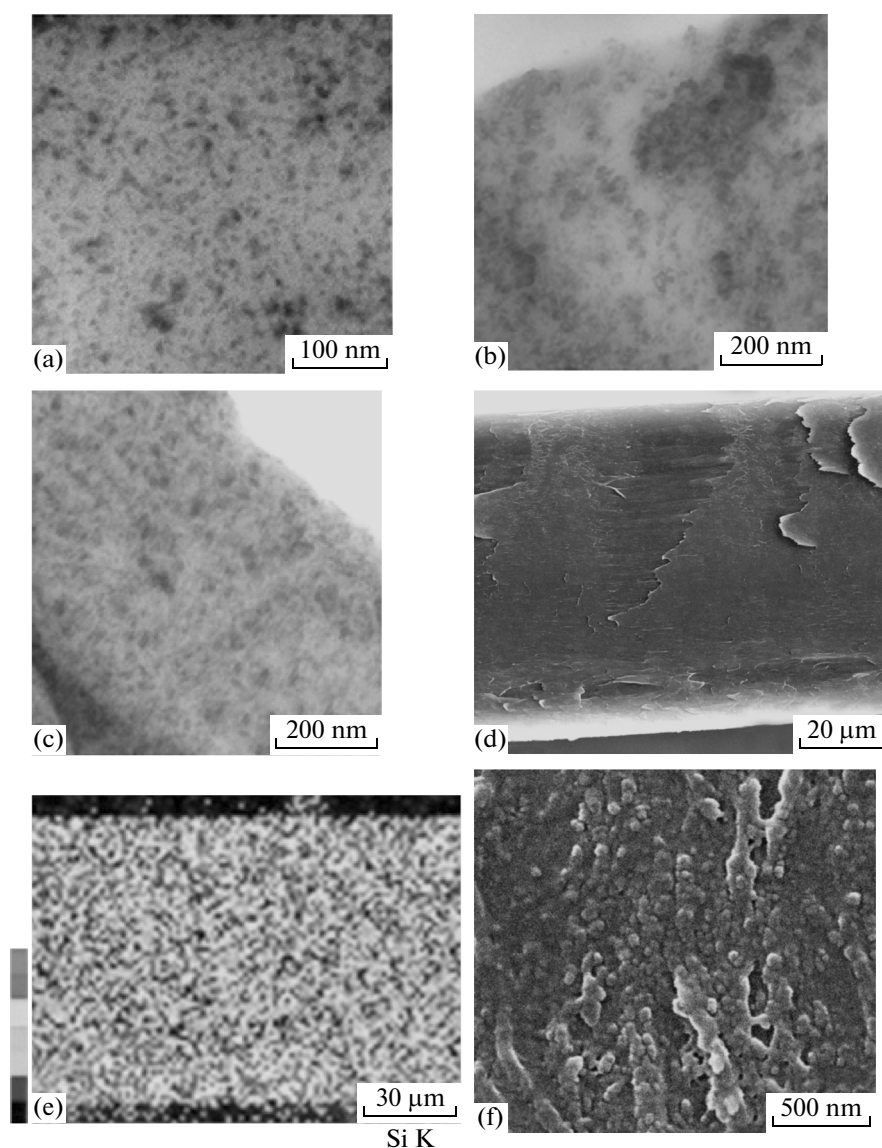


Fig. 8. Micrographs of (a–c) ultrathin sections and (d, f) freeze-fractured surfaces of the PP–SiO₂ composite with silica contents of (a) 8, (b) 23, and (c–e) 36 wt %. Image (e) presents the distribution map of Si atoms in the bulk of the composite with a filler content of 36 wt %.

place the degradation process toward higher temperatures.

Thus, with the use of isotactic polypropylene as an example, it has been shown that crazing in a liquid adsorption-active medium lowers the onset temperature of intense degradation and increases the coking ability of polymers. The introduction of titanium dioxide or silicon dioxide during the use of the crazing mechanism can significantly change the thermal stability of the composite materials, depending on the chemical nature of the precursor alkoxides and on the conditions and the extent of their hydrolysis. For example, the stabilizing effect of TiO₂ nanoparticles on the PP matrix is due to the presence of significant amounts of products of

incomplete hydrolysis of the alkoxy derivatives of titanium, which are the first to decompose during a thermal effect. The effect of silica particles on the thermo-oxidative properties of the polymer is not so significant. The difference may be due to the completeness of the precursor hydrolysis and, hence, the absence of the alkoxy derivatives. However, varying the amount of the SiO₂ phase to thereby affect the composite structure make it possible to alter the temperature of the maximum in the mass-loss rate over a fairly wide range of 270–430°C. The results of this study have led to the conclusion that crazing in an adsorption-active medium can be used as a controllable factor of influence on the thermo-

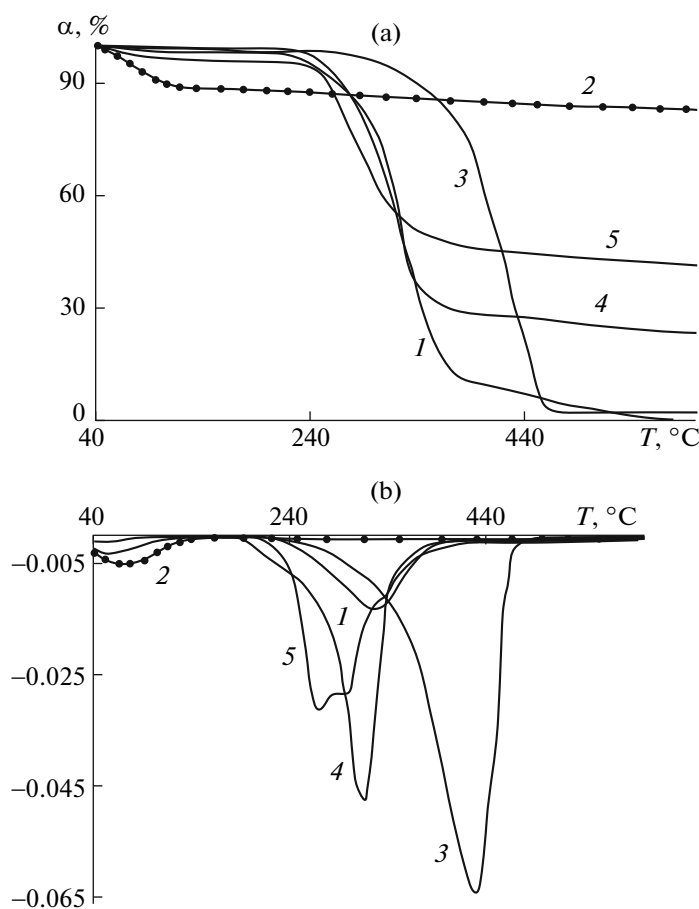


Fig. 9. (a) Integral and (b) differential TGA curves for (1) the porous PP film deformed by 200% in isopropanol; (2) the SiO₂ precipitate; and (3–5) PP–SiO₂ composites with filler contents of (3) 2.5, (4) 23.0, or (5) 41.0 wt %. Heating rate, 20 K/min.

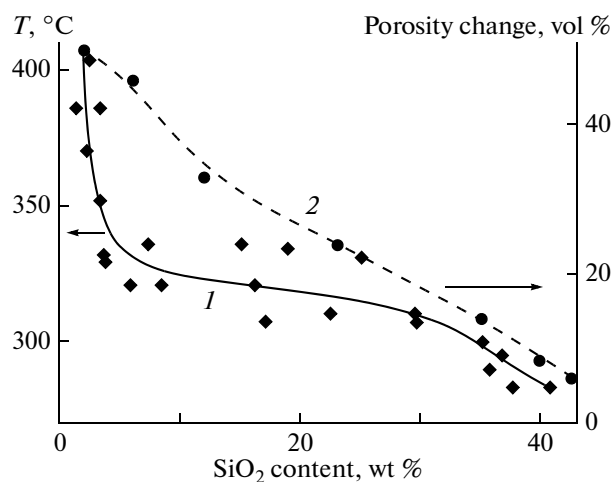


Fig. 10. (1) Temperature at 50% mass loss of PP–SiO₂ samples and (2) change in the effective bulk porosity during composite preparation as functions of the filler content.

oxidative properties and combustion of polymer materials and polymer-matrix composites.

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