

# Thermooxidative Degradation of Porous Solvent-Crazed Polyethylene<sup>1</sup>

E. S. Trofimchuk<sup>\*2</sup>, M. Yu. Yablokova<sup>\*\*</sup>, N. I. Nikonorova<sup>\*3</sup>,  
A. V. Antonov<sup>\*\*</sup>, A. L. Volynskii<sup>\*</sup>, and N. F. Bakeev<sup>\*\*</sup>

<sup>\*</sup> Department of Chemistry, Moscow State University,  
Vorob'evy gory, Moscow, 119899 Russia

<sup>\*\*</sup> Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences,  
ul. Profsoyuznaya 70, Moscow, 117393 Russia

Received June 21, 2000;

Revised Manuscript Received December 6, 2000

**Abstract**—The effect of the parameters of porous structure of HDPE prepared by the method of delocalized solvent crazing on the processes of thermooxidative degradation and combustion was studied. According to TGA, with increasing the effective porosity, the weight loss of the polymer commences at lower temperatures; as orientational order is increased, temperature corresponding to the maximum weight loss rate increases by ~50°C as compared with that of the initial undeformed PE. In this case, one may observe a dramatic change in the character of combustion of porous matrices compared to the bulk samples: dripping processes are suppressed, and char formation takes place.

## INTRODUCTION

The phenomenon of the transition of glassy and semicrystalline polymers to a highly disperse oriented state occurring under uniaxial deformation in the presence of adsorptionally active media (the so-called crazing [1]) was described in [1, 2]. Upon crazing, a system of interpenetrating nanometric pores is developed in a polymer, and the walls of pores are bridged by polymer fibrils. This porous system is characterized by a high specific free surface energy [2]. Presently, the effect of various factors (the nature of a polymer and adsorptionally active medium, the strain rate, and the thickness of a polymer film) on the parameters of the porous structure was studied in detail [3].

In this work, we studied the effect of the parameters of the porous structure of polymer matrices based on HDPE prepared by the method of delocalized crazing [4] on the processes of thermal oxidative degradation and combustion of HDPE.

## EXPERIMENTAL

To prepare porous polymer films, we used commercial films of isotropic HDPE ( $M_w = 2 \times 10^5$ ) with a thickness of 75  $\mu\text{m}$ . Using hand-operating clamps, the films of semicrystalline HDPE were deformed in iso-

propanol to a given tensile strain (50–400%) at ambient temperature.

The as-prepared deformed polymer films were dried at 120°C for 3 h in a stressed state. During the thermal treatment, the crazed structure is stabilized, shrinkage is prevented, and the processes of side contraction take place.

Porous polymer matrices were characterized by the values of effective volume porosity  $W$  [4].

Characteristics of porous polymer matrices based on HDPE are presented in the table.

The structure of porous films was studied by the method of scanning electron microscopy (SEM). The samples were prepared by the technique of brittle fracture in liquid nitrogen and decorated with platinum–palladium alloy. SEM studies were performed on a Hitachi S-520 scanning electron microscope. The structure of char obtained from the initial and porous PE

Characteristics of the test PE samples

$\epsilon$ , %	$W$ , %	OI*
0	0	19.3
50	15	18.8
100	28	17.8
200	38	17.1
300	32	17.3
400	22	19.1

\* Oxygen index.

<sup>1</sup> This work was supported by the Russian Foundation for Basic Research, project nos. 98-03-33446a and 99-03-33459.

<sup>2</sup> E-mail: elena\_trofimchuk@mail.ru

<sup>3</sup> E-mail: nni@genebee.msu.ru

films was also examined by scanning electron microscopy.

The processes of thermal oxidative degradation for the initial and porous HDPE films were studied by TGA on a Mettler TG-50 thermal analyzer under a dynamic regime (the heating rate was 20–50 K/min) at 25–600°C and under an isothermic regime [5]. All samples were tested under similar conditions in an open porcelain crucible with a fixed geometry. To this end, the test samples with identical dimensions and geometry were cut from films with a knife. The accuracy of temperature measurements was  $\pm 1.5^\circ\text{C}$ . For the measurements under the isothermic regime, the testing temperature was selected as temperature corresponding to 50% weight loss of the initial HDPE under dynamic regime; in this work, this temperature is equal to 400°C.

Upon heating from 25 to 360°C at a heating rate of 10 K/min, changes in the appearance of polymer surface were studied by the method of optical microscopy on an Opton microscope (Germany) with a Plan 2.5/0.08 Pol eyepiece equipped with a Mettler FP-82 hot stage with a Mettler FP-80 processor.

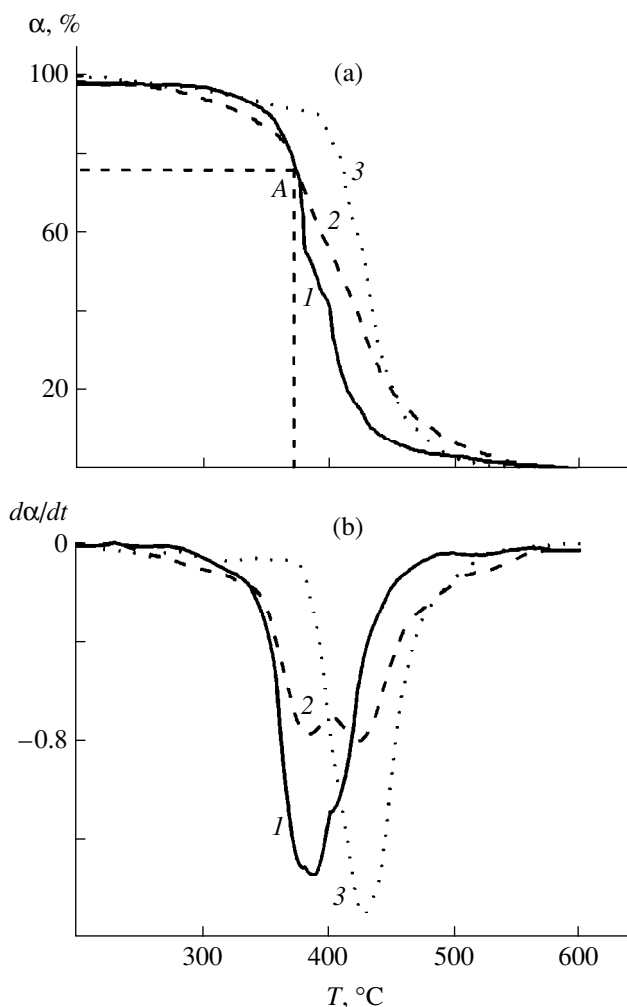
The combustibility of porous PE films was assessed by the method of OI according to GOST (Russian State Standard) 12.1.044-89.

## RESULTS AND DISCUSSION

The processes of thermal oxidation in polymers are known to be initiated at the surface active sites and lead either to gasification or to the development of crosslinked structures. As the porosity of material is increased, the number of sites accessible to oxygen molecules at initial stages of thermal oxidative degradation increases.

The data presented in Fig. 1 show that, for the samples with the different values of volume porosity, the corresponding weight loss curves appear to be different. In the case of the initial PE, weight loss takes place at 300–450°C, and the corresponding weight loss curve shows one maximum of weight loss rate and a weakly pronounced shoulder. For PE deformed to a tensile strain of 400%, oxidation proceeds at high rates in a narrow temperature region of 400–500°C (a single peak is seen). The films deformed to 200% are characterized by a very wide double peak at 350–550°C, and the rate of weight loss is rather low in the whole temperature range. The reasons explaining changes in the profiles of the differential curves of PE films with different values of porosity are still unclear. Even though the temperature of thermal oxidative degradation (350–550°C) is much higher than melting temperature of HDPE (130°C), one may assume that the above changes are related to the physicochemical modification of HDPE upon its deformation in adsorptionally active media and subsequent thermal treatment.

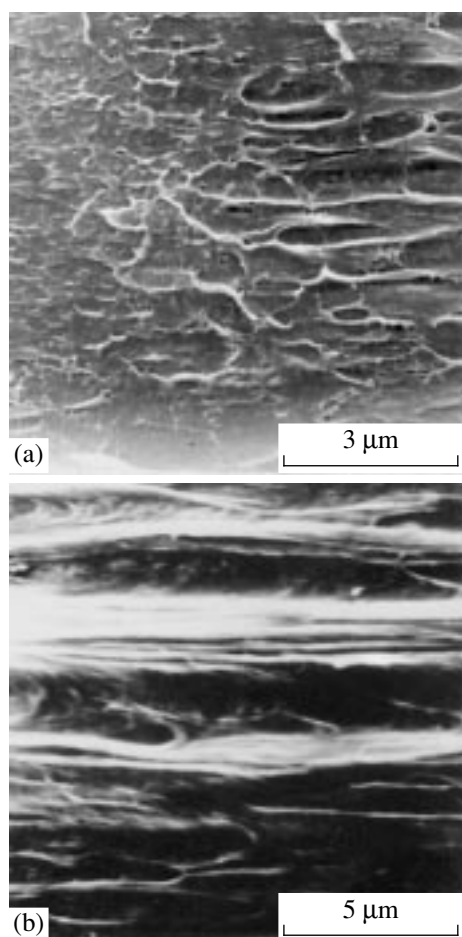
Figure 2 shows the SEM images of porous PE films deformed to 200 and 400%. As is seen, the structure of



**Fig. 1.** (a) Integral and (b) differential TGA curves obtained under integral regime for porous PE matrices with a tensile strain of (1) 0, (2) 200, and (3) 400%.

the polymer matrices studied changes with increasing the tensile strain, and this observation agrees with the literature data [1, 3]. As the tensile strain is increased, the development and the gradual growth of crazes are observed; this process is accompanied by an increase in the number of pores per surface unit. At high tensile strains, the collapse of porous structure takes place; as a result, the fibril diameter increases, and the number of pores drops. The evolution of porous structure was demonstrated for the porous samples with different tensile strains. The sample of PE deformed to 200% is characterized by the maximum volume effective porosity; hence, its structure constitutes a system of interpenetrating pores, and the walls of pores are bridged by fine fibrils. For porous PE samples with high tensile strains (400% and higher), the collapse of porous structure takes place, the number of pores decreases, and the orientation of fibrils along the drawing axis enhances.

The effect of the structure of the initial polymer matrix on the processes of thermal oxidative degrada-



**Fig. 2.** Microphotographs of porous PE with a tensile strain of (a) 200 and (b) 400%.

tion is vividly demonstrated by changes in the appearance of polymer film observed upon heating (Fig. 3). As follows from the optical micrographs shown in Fig. 3, the surface of bulk PE at 310°C is covered with “bumps” and “craters;” at the same temperature, the surface of PE deformed to 200% is smooth. However, at higher temperatures (360°C), the surface of the initial PE also becomes smooth (Fig. 3c) but one may distinguish big-sized craters; this observation suggests the occurrence of intensive processes of thermal oxidative degradation. At these temperatures, the surface of the PE samples deformed to 200% remains smooth and contains no visible defects. Analysis of the TGA data (Fig. 1) shows that, in the temperature range studied (point A in Fig. 1a), the weight loss of PE deformed to 200%, similar to the initial PE, is about 20 wt %; this trend suggests the development of an intensive thermal oxidation which is accompanied by gasification. The absence of any visible defects on the surface of PE deformed to 200% may be only rationalized by small dimensions of the formed craters which escape detection. This assumption is proved by the microscopic examination of the morphology of char obtained from

the same samples at ~390°C (Fig. 4). As follows from the microscopic images, the surface of the char contain craters; however, the dimensions of the above craters in the initial PE are equal to 5–8 μm, whereas, in the case of the char obtained from PE deformed to 200%, this size is 0.2–0.4 μm (these dimensions are actually beyond the detection limit of optical microscope).

A similar effect of heating to temperatures above the melting temperature of polymer on its surface structure was found in [6] for isotactic PP.

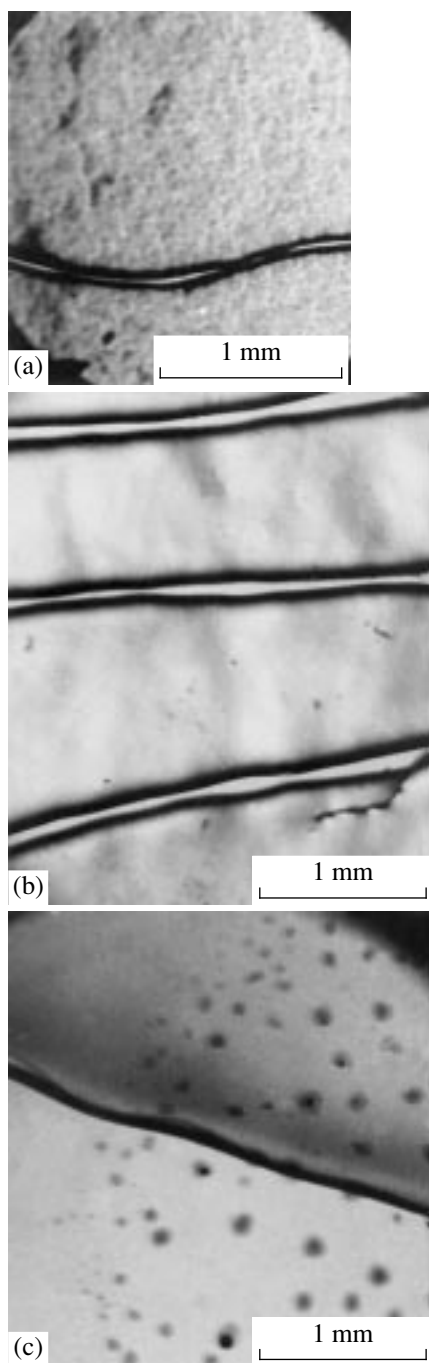
One may assume that the development of the porous structure in PE via crazing not only favors the acceleration of the diffusion of oxygen molecules to polymers upon thermal oxidation but also provides a possible encapsulation of a certain amount of oxygen inside a polymer matrix.

However, let us note that, with increasing the tensile strain, one may observe an increase in the orientational order of crystallites along the deformation direction; hence, at temperatures below the melting temperature, the diffusion of oxygen molecules to polymer is prevented. Therefore, in such a complex system composed of pores and fibrils bridging the pore walls, two concurrent competing processes occur. Depending on the prevalence of this or that factor, the parameters of the degradation of porous samples will change.

These assumptions allow one to explain the experimental data as follows. In the case of the film of the initial PE, slow low-temperature processes related to oxygen diffusion to the surface oxidation sites do not lead to any marked weight loss at the early stages of thermal oxidation because the concentration of such sites is rather low. However, it is this stage when the kinetic oxidation chain is initiated; possibly, this trend is related to the presence of the encapsulated oxygen the content of which increases with increasing the effective porosity and decreases with increasing the orientational order. Once free radicals on active sites are initiated, a rapid stage of polymer gasification via the relay-race mechanism commences, and this stage is accelerated with increasing temperature.

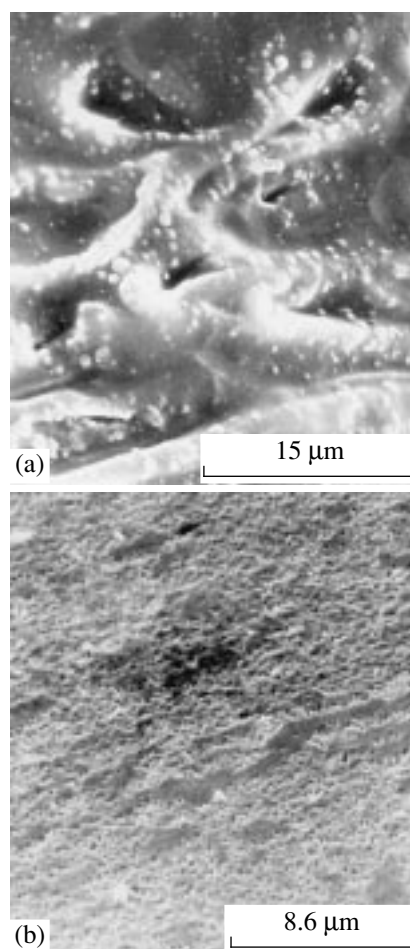
Under dynamic regime, the profiles of weight loss curves as obtained with increasing temperature may be related to the three-stage mechanism of the thermal oxidation of HDPE. At the first slow stage, oxygen molecules diffuse to active sites (to the regions between intercrystallite regions, surface defects, or boundaries of pores) and become encapsulated in the pores of the polymer matrix. At this stage, a key role belongs to structural features such as the degree of crystallinity, defectness, etc. At the temperatures of thermal oxidative degradation, the encapsulated oxygen starts to oxidize polymer and primary oxidation radicals are formed. At this stage, the breakdown of main chains is accompanied by the competing processes of recombination, for example, chemical crosslinking which reduces the total weight loss rate (Fig. 1b).

At the second stage, the oxidation of most macromolecules proceeds via the radical mechanism. At this stage, the principal weight loss of the polymer is observed. At the third stage, oxidation approaches the so-called core, that is, not easily accessible regions in polymers such as, for example, knots of different nature. For all porous HDPE films, at temperatures corresponding to the third stage, experimental weight loss curves are similar and merge into a single curve.

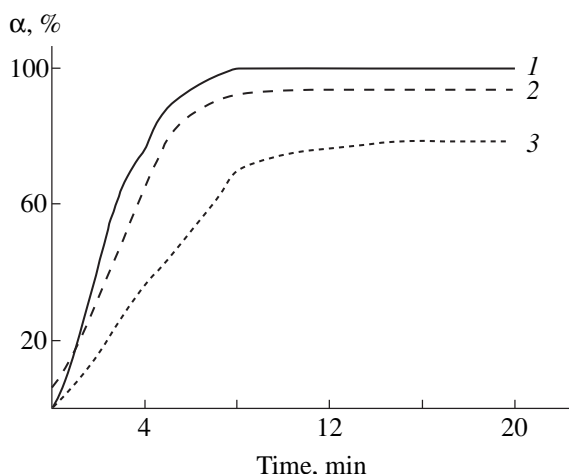


**Fig. 3.** Photographs of the surface of (a, c) the initial PE and (b) PE deformed to 200%.  $T =$  (a, b) 310 and (c) 360°C.

The above assumptions concerning the mechanism of the thermal oxidative degradation of porous PE matrices are proved by the TGA data obtained under isothermic regime (Fig. 5). For the initial PE and PE deformed to 200%, the corresponding isothermic TGA curves almost coincide. The above samples are characterized by high weight loss rates, and this fact suggests a rapid oxidation of macromolecules via the relay-race mechanism. In the case of PE deformed to 400%, oxidation under isothermic conditions proceeds at lower rates (in the integral TGA curves, a temperature of 400°C corresponds to the initial region of weight loss). In the case of PE deformed to 400%, the specific feature of its oxidation at 400°C is a 20% yield of char. This behavior of polymer matrix may be explained if one assumes that chemical modification takes place even at the stage of PE deformation in an adsorptionally active medium, and this trend favors the oxidation-induced formation of the crosslinked structures which, upon combustion, produce char.



**Fig. 4.** Microphotographs of char obtained from the films of (a) the initial PE and (b) PE deformed to 200% by heating from 25 to 390°C at a heating rate of 10 K/min.



**Fig. 5.** Isothermic TGA curves of PE matrices with a tensile strain of (1) 0, (2) 200, and (3) 400%. Temperature is 400°C.

The porous structure of crazed PE also has a certain effect on the process of combustion. Interconnection between the oxygen index and the effective volume porosity is shown in the table. As follows from the table, as the effective porosity of PE is increased, the oxygen index decreases. This behavior may be explained by the fact that, upon the combustion of highly disperse and highly oriented polymer films, the specific features of the combustion of polymer foams and oriented polymers are preserved.

Combustion processes in HDPE are known to be accompanied by dripping. The combustion of porous PE matrices proceeds without dripping but with the formation of an easy-burning char. This character of combustion may either be related to the possible chemical modification of the polymer upon its deformation in isopropanol via the mechanism of mechanochemistry or to structural rearrangements of the polymer upon crazing.

Deformation of polymers may proceed via two principal mechanisms [7]: chain disentanglement and chain scission. Earlier, attempts have been made to assess the number of the induced breakdowns in HDPE by the

spectroscopic method [8]. As was shown, as the tensile strain is increased from 200 to 400%, the number of the induced breakdowns per volume unit increases from  $1 \times 10^{-17}$  to  $2 \times 10^{-17} \text{ cm}^{-3}$ . We assume that the development of porous structure in polymers proceeds via the mixed mechanism, that is, some fraction of polymer chains experiences disentanglement, whereas the other part breaks down. In this case, free radicals are formed, and the probability of breakdowns increases with increasing the tensile strain. The as-formed free radicals may either interact with oxygen molecules (nucleation of oxidative sites) or take part in the reaction of recombination with another macroradical (formation of polymer chains). This process leads to the chemical modification of the polymer studied and manifests itself in the kinetics of the combustion of porous PE films compared to the bulk PE.

Hence, a highly disperse state of polymers produced by the uniaxial deformation of PE in the presence of isopropanol has a marked effect on the thermal oxidation of HDPE.

## REFERENCES

1. Duan, D.-M. and Williams, J.G., *J. Mater. Sci.*, 1998, vol. 33, p. 625.
2. Bakeev, N.F. and Volynskii, A.L., *Solvent Crazing of Polymers*, Amsterdam: Elsevier, 1995.
3. Sinevich, E.A., Prazdnichnyi, A.M., and Bakeev, N.F., *Polymer Science, Ser. A*, 1996, vol. 38, no. 2, p. 159.
4. Volynskii, A.L., Shmatok, E.A., Ukolova, E.M., Arzhakova, O.M., Yarysheva, L.M., Lukovkin, G.M., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A*, 1991, vol. 33, no. 5, p. 1004.
5. Hirata, T., Kawamoto, S., and Okuro, A., *J. Appl. Polym. Sci.*, 1991, vol. 42, p. 3147.
6. Abdouss, M., Sharifi-Sanjani, N., and Bataille, P., *Pure Appl. Chem.*, 1999, vol. 36, no. 10, p. 1521.
7. Han, H.Z.Y., McLeish, T.C.B., Duckett, R.A., Ward, N.J., Johnson, A.F., Donald, A.M., and Butler, M., *Macromolecules*, 1998, vol. 31, no. 6, p. 1348.
8. Marikhin, V.A. and Myasnikova, L.P., *Karbotsepyne polimery* (Carbon-Chain Polymers), Moscow: Nauka, 1977, p. 154.