THE INFLUENCE OF THERMOMECHANICAL PREHISTORY ON LIGHT RESISTANCE OF POLYETHYLENE

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Abstract: *the changes of light stability of polyethylene films from which passed various technological phases of treatment were studied by the mechanical and x-ray methods.*
Three series of samples are studied: initial unannealed (series 1), annealed in free (series 2) and fixed states (series 3). It's shown that in samples of a series 3 the deceleration of photodestruction that is connected with change on supramolecular structure of polymer at annealing is observed. It Is Installed that by annealings of the polyethylene in fixed condition without introduction of some chemical additives will possible raise light resistance of the polymer.
Keywords: *polymer, polyethylene, the temperature, submicrocrack, photooxidizing, stabilization.*

ВЛИЯНИЕ РЕЖИМА ТЕРМОМЕХАНИЧЕСКОЙ ОБРАБОТКИ НА СВЕТОСТОЙКОСТЬ ПОЛИЭТИЛЕНА

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Аннотация: *в работе изучалось влияние предварительной термомеханической обработки на изменения светостойкости пленок полиэтилена. Исследовались три серии образцов: исходные неотожженные (серия 1), отожженные в свободном (серия 2) и в фиксированном состояниях (серия 3). Показано, что в образцах серии 3 наблюдается замедление фотодеструкции, связанное с изменением надмолекулярной структуры полимера при отжиге. Установлено, что путем термической обработки полиэтилена в фиксированном состоянии без введения каких-либо химических добавок можно повысить светостойкость полимера.*
Ключевые слова: *полимер, полиэтилен, температура, субмикротрещина, фотооксиление, светостабилизация.*

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Under influence of ultra-violet radiation in polymers various chemical reactions develop which leads to change of structure and operational characteristics of polymers [1-4]. Aiming to increase the light stability of polymeric materials, the absorbing and disseminating ultra-violet radiation substances are usually in traduced, which deactivate molecules in the excited status, interacting with free radicals and interrupting processes of destruction of polymer chains [l].

In distinction from traditional chemical way of light stabilization in [4-5] a physical way of increase of light stability of polyethylene by change of its physical structure without introduction into a sample of any chemical components was offered. So, the purpose of this work was study the influence of thermomechanical prehistory on mechanical characteristics and light stability of polyethylene.

In this work the similar investigations are carried out on polyethylene.

The oriented samples from polyethylene (PE) in the beginning were subject to heat treatment in fixed and free slabies, and then their light stability was studied. The annealing of samples was carried out in the thermal chamber, in the air environment at 60, 70, and 80°C, the time of annealing varied in an interval of 0-5 hours. The light stability of samples was estimated by results of measurement of hardness, radiation longevity and kinetics of formation of sub micro cracks.

Hardness of samples was determined by deformation curves obtained at speed of expansion of 12 mm/min. The study of radiation longevity at λ=254nm was carried out according to the method described in [4].

The investigation of kinetics of derivation of submicrocrack (SMC) flaws was conducted by SAXS method in meridional and equatorial directions by use of Cu K_{α} - radiation filtered by nickel on KRM-1apparatus. By the distribution of intensity of discrete and diffuse scattering on SAXS the values of major periods, sizes and concentrations of submicrocrack flaws were estimated [6].

Thus samples, annealed at the temperature of 70°C within 1 hour in the fixed state have the greatest the explosive strength (fig. l, curve 6).

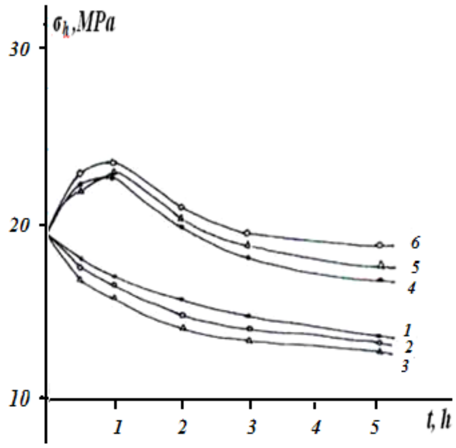

Fig. l. Dependence of explosive hardness of polyethylene films duration of annealing at different temperatures. 1 - 3 samples in a free state; 4-6 in the fixed state. T=60^{0}C (1, 4), 70^0 C (2, 6) and 80°C (3, 5)

For detection of influence of prehistory of samples on development of photodestruction, the stady was carried out on samples of three sorts:

Initial unannealed (series 1), annealed at 70°C during 1 hour in free (series 2) and fixed (series 3) states.

The results of carried out researche of influence of the annealing regime on longevity of polyethylene in conditions of photomechanical destruction are shown in a fig. 2.

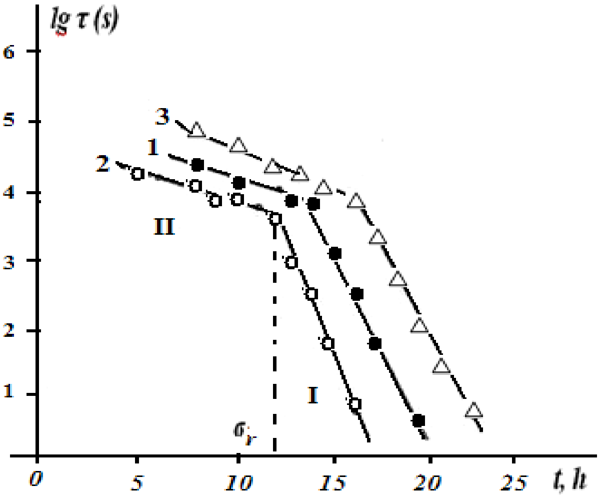

Fig. 2. The effects of annealing regime on radiation longevity of samples from polyethylene at k=254nm for the initial sample (1) the free (2) and fixed states

As one can see that dependence of $lg.\tau = f(\sigma)$ consists of two intervals. On the first interval (I-in the area $\sigma > \sigma_r$) the values of radiation longevity τ_j for samples in the case of radiation and its absence coincide.

The effect of the influence of annealing on the value of τ_j, appears only on the second interval (II at $\sigma < \sigma_r$). It's appeared that in conditions of a photomechanical destruction the longevity of samples annealed in the fixed state is more than in initial ones, and samples annealed in a free state. At the same time the longevity of samples annealed in the free state is less than initial ones.

That is, if the preliminary annealing in the fixed state decelerates the process of a photomechanical destruction, the annealing in the free state on the contrary accelerates this process. These results show that preliminary annealing in the fixed state brings to increase of light stability of polyethylene in conditions of photomechanical destruction.

The discovered effect also was confirmed by experimented result on investigations of influence of the heat treatment regime on the kinetics of derivation of submicroscopic flaws on conditions of photomechanical destruction of polyethylene. These tests were carried out at loads of σ =0,4 σ_b, when the effects of break on curve longevity are brightly shown $l_{g.}\tau(\sigma)$. In. fig.3 the typical SAXS of series 3 are shown.

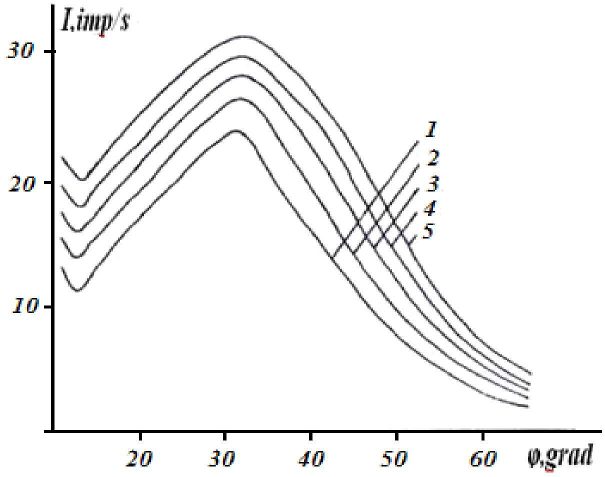

Fig. 3. Small angular dispersion of gen rays in the meridianal direction under simultaneous operation of load and Ultra-violet lights for samples of polyethylene l-t=0; 2-t=5 hours; 3-t=10 hours; 4-t=15 hours; 5-t=20hours

It is visible that at simultaneous effect of ultra-violet radiation and load with growth of irradiation time the increase of intensity of diffuse and discrete dispersion on SAXS tare place.

Let's mark that the similar changes are typical for other series of samples.

The processing of the obtained SAXS as per works [5-6] showed that sizes of submicroscopic flaws (longitudinal Hu and transversal Hi) for the series of samples are the following: accordingly 25 and 3 lnm for initial, 27 and 31 nm for annealed in a free state, 28 and 30 nm for samples annealed in a fixed state. The sizes of submicrocrack flaws do not depend neither from a prehistory of samples, nor from duration of irritation.

The dependence of concentration of submicroscopic flaws from the time of ultra-violet radiation and mechanical load σ=5MПa is shown in fig.4. It's visible that concentration of submicrocrack flaws by increasing of validity time of radiation and load increases. However, concentrations of submicrocrack flaws in initial and the thermos treated samples in the free state are much more than in samples annealed in the fixed state. The preliminary annealing in the fixed state decelerates the process of derivation of submicrocrack flaws in conditions of photomechanical destruction.

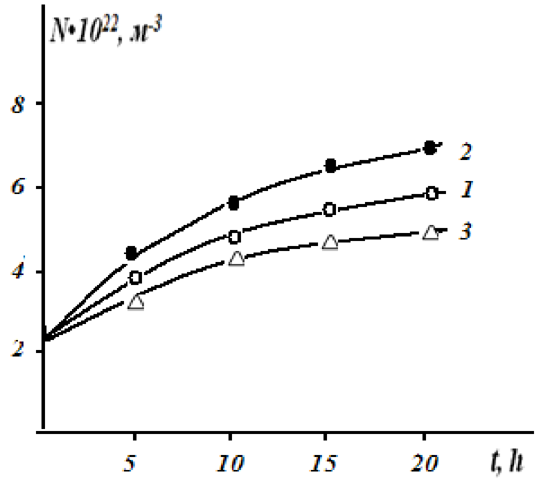

Fig.4. The changes of concentration of submicrocrack flaws in the samples from polyethylene depending on the time of power operation and ultra-violet light for the initial sample (1) and samples annealed in the free and fixed states

According to paper [5] the annealing of samples in the fixed state is accompanied by increase of packing density of structural elements, improvement of orientation that causes increase of hardness of the system. These processes in turn can decelerate the development of photooxidizing processes, destructions of chain molecules and cause deceleration of the process of derivation of submicrocrack flaws. This results show that by way of heat treatment of samples in the fixed state, it is possible to increase the light stability of polyethylene in conditions of photo destruction. The offered way of rise of light stability without usage of light stabilizers is ecologically clean and can be recommended in the practical technology.

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