
Structural and Chemical Features of Secondary Polyethylene

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Abstract: This article provides information on the properties, use and application of secondary polyethylene materials. There are also data on mechanical properties.

Keywords: polyethylene, PET, secondary polymer, HDPE, polyolefin, PE film, LDPE, SLDPE.

Introduction

The choice of technological parameters for processing polyolefin (PO) waste and the areas of use of the products obtained from them is due to their physico-chemical, mechanical and technological properties, which differ significantly from the same characteristics of the primary polymer. The main features of secondary high-density polyethylene (HDPE), which determine the specifics of its processing, include: low bulk density;

Features of the rheological behavior of the melt due to the high gel content; increased chemical activity due to structural changes occurring during the processing of the primary polymer and the operation of the products obtained from it.

Material and Materials

During processing and operation, the material is subjected to mechanochemical influences, thermal, thermal and photo-oxidative degradation, which leads to the appearance of active groups that, during subsequent processing, are able to initiate oxidation reactions. The change in the chemical structure begins already in the process of primary processing (PO), in particular during extrusion, when the polymer is subjected to significant thermal oxidative and mechanochemical effects. Photochemical processes make the greatest contribution to the changes occurring during operation.

These changes are irreversible, while the physical and mechanical properties, for example, of a polyethylene film that has served one or two seasons to shelter greenhouses, are almost completely restored after repressing and extrusion.

The formation of a significant number of carbonyl groups during operation in a PE film leads to an increased ability of HDPE to absorb oxygen, which results in the formation of vinyl and vinylidene groups in secondary raw materials, which significantly reduce the thermal oxidative stability of the polymer during subsequent processing, initiate the process of photoaging of such materials and products from them, reduce their service life.

Results

The presence of carbonyl groups does not determine either the mechanical properties (the

introduction of up to 9% of them into the initial macromolecule does not significantly affect the mechanical properties of the material), nor the transmission of sunlight by the film (light absorption by carbonyl groups lies in the wavelength range of less than 280 nm, and light of this composition is practically not contained in the solar spectrum). However, it is the presence of carbonyl groups in PE that determines its very important property – resistance to light.

The initiator of photo aging of PE is hydro peroxides formed during the processing of primary material in the process of mechanochemical destruction. Their initiating action is especially effective in the early stages of aging, while carbonyl groups have a significant effect in the later stages.

Discussion

As is known, during aging, competing reactions of destruction and structuring occur. The consequence of the first is the formation of low molecular weight products, the second is an insoluble gel fraction. The rate of formation of low molecular weight products is maximal at the beginning of aging. This period is characterized by a low gel content and a decrease in physical and mechanical parameters.

In the future, the rate of formation of low molecular weight products decreases, there is a sharp increase in the gel content and a decrease in elongation, which indicates the course of the structuring process. Then (after reaching the maximum), the gel content in the VP decreases during its photoaging, which coincides with the complete consumption of vinylidene groups in the polymer and the achievement of the maximum permissible values of elongation. This effect is explained by the involvement of the formed spatial structures in the process of destruction, as well as cracking along the border of morphological formations, which leads to a decrease in physical and mechanical characteristics and deterioration of optical properties.

The rate of change of the physical and mechanical characteristics of the VPE practically does not depend on the content of the gel fraction in it. However, the gel content must always be taken into account as a structural factor when choosing a method of recycling, modification and when determining the areas of use of the polymer.

Table 1. Characteristics of the properties of LDPE before and after aging.

Specifications	LDPE		SLDPE
	Source	After operation	Extrusion
Content of groups C-O, mol	0,1	1,6	1,6
Content of low molecular weight products, %	0,1	6,2	6,2
Gel Content, %	0	20	20
Destructive tensile stress, MPa	15,5	11,4	10
Elongation at break, %	490	17	125
Resistance to cracking, h	8	-	1
Light resistance, day	90	-	50

The characteristics of the properties of LDPE before and after aging for three months and HDPE obtained by extrusion from an aged film are given in Table 1.

The nature of the change in physical and mechanical characteristics for LDPE and HDPE is not the same: the primary polymer has a monotonous decrease in strength and elongation,

which are 30 and 70%, respectively, after aging for 5 months. For secondary HDPE, the nature of the change in these indicators is somewhat different: the destructive voltage practically does not change, and the elongation decreases by 90%. The reason for this may be the presence of a gel fraction in the HDPE, which performs the function of an active filler of the polymer matrix. The presence of such a "filler" is the reason for the appearance of significant stresses, resulting in an increase in the fragility of the material, a sharp decrease in elongation (up to 10% of the values for primary PE), resistance to cracking, tensile strength (10 ... 15 MPa), elasticity, increased stiffness.

In PE, during aging, there is not only an accumulation of oxygen-containing groups, including ketone and low-molecular products, but also a significant decrease in physical and mechanical characteristics that do not recover after recycling of the aged polyolefin film. Structural and chemical transformations in VPENP occur in mostly in the amorphous phase. This leads to a weakening of the interfacial boundary in the polymer, as a result of which the material loses strength, becomes brittle, brittle and subject to further aging both during recycling into products and during operation of such products, which are characterized by low physical and mechanical characteristics and service life.

Its rheological characteristics are of great importance for assessing the optimal processing modes of recycled polyethylene raw materials. Low fluidity at low shear stresses is characteristic of VPE, which increases with increasing stress, and the increase in fluidity for VPE is greater than for primary. The reason for this is the presence of a gel in the HDPE, which significantly increases the activation energy of the viscous flow of the polymer. The fluidity can be adjusted by also changing the temperature during processing – with increasing temperature, the fluidity of the melt increases. So, the material is recycled, the background of which has a very significant impact on its physical, mechanical and technological properties. In the process of recycling, the polymer is subjected to additional mechanochemical and thermo-oxidative effects, and the change in its properties depends on the multiplicity of processing.

When studying the effect of the multiplicity of processing on the properties of the resulting products, it is shown that 3 – 5-fold processing has a negligible effect (much less than the primary one). A noticeable decrease in strength begins with 5-10-fold processing.

Conclusion

In the process of repeated reworking of VPENP, it is recommended to increase the casting temperature by 3 ... 5% or the number of screw rotations during extrusion by 4 ... 6% to destroy the resulting gel. It should be noted, that in the process of repeated reworking, especially when exposed to oxygen in the air, there is a decrease in the molecular weight of polyolefins, which leads to a sharp increase in the fragility of the material. Repeated processing of another polymer from the class polyolefin – PP usually leads to an increase in the melt flow rate (PTR), although the strength characteristics of the material do not undergo significant changes. Therefore, the waste generated during the manufacture of PP parts, as well as the parts themselves, at the end of their service life, can be reused in a mixture with the starting material to obtain new parts.

From all of the above, it follows that secondary raw materials should be modified in order to improve the quality and increase the service life of products made from it.

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