FIRE RESISTANT HIGH PRESSURE POLYETHYLENES FORMED BY USING OLYGOMERIC AND POLYMERIC PHOSPHORUS CONTAINING FIRE RETARDANT SYSTEMS

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Abstract

The method of modification of high pressure polyethylene including secondary polyethylene using phosphorus containing epoxy resin and polyvinyl alcohol is proposed. Conditions of the phosphorylation of epoxy resin and polyvinyl alcohol by anhydrides of methylphosphonic acid and/or by the methylphosphonic acid are determined. Reactive olygomeric and polymeric phosphorus containing components which can form crosslinked structures and/or interact with the functional group of a polymeric matrix, for example, in a secondary polyethylene are obtained. While reproducing a polymeric composition the competitional process of migration of fire retardant phosphorus containing systems (P-FRS) and the processes of the formation of crosslinked structures are observed. The formation of a crosslinked structure is possible into P-FRS as well as at the interaction of the FRS with active functional groups of the secondary polyethylene on the boundary of phases. The complex FRS which contains phosphorylated epoxy resin and red phosphorus is decomposed during reproducing of a modified polyethylene composition. In this case the phosphorylated epoxy resin diffuses with the formation of a crosslinked structure into a warm surface layer, and the red phosphorus is distributed into the polymeric matrix with a sufficient uniformity. During the destruction of phosphorylated polyvinyl alcohol the formation of polyenic structures and condensed polyphosphates or polyphosphoric acid takes place. These processes promote the carbonization and the decreasing of flammability.

Therefore the FRS on the basis of phosphorylated polyvinyl alcohol is more effective than the system based on the phosphorylated epoxy resin. Modified polyethylenes (high pressure and secondary) can be classified as fire resistant materials according to the test results.

Introduction

One of the effective methods of a thermoplastics modification is the introducing of olygomeric or polymeric reactive additives into polymeric compositions [1,2]. The introduction of epoxy resins with a crosslinked agent (polyethylene polyamine) into polyolefines leads to the formation of a crosslinked polymer with passed chains [3].

The application of phosphorylated epoxy resins as well as other phosphorylated olygomeric or polymeric additives for the polyolefine modification which are used to reproduce these polymers by the die casting or extrusion is expedient for obtaining fire resistant materials based on the high pressure polyethylene including the secondary polyethylene.

Objects and investigation methods

The high pressure polyethylene and secondary polyethylene were modified. The secondary polyethylene contains 1% oxygen in hydroxy- or carbonyl groups. Two types of the phosphorus containing fire retardant systems are used: a). the phosphorylated epoxy resin with red phosphorus; b). the phosphorylated polyvinyl alcohol. After the heating of methyl phosphoric acid above its melting point this acid is used for the phosphorylation of epoxy resin or polyvinyl alcohol. As a result of the methyl phosphonic acid melting the anhydride of this acid is formed. Thus the anhydride interacts with hydroxy groups of epoxy resin or polyvinyl alcohol. The process of the interaction of acidic groups P(O)OH with epoxy groups in the resin and also with the remaining acetic groups in the polyvinyl alcohol is possible at 110-130°C during 15 min at a mixing. The P-FRS obtained are powders with the dispersion less than 60 mkm and with the melting point approximately equalled to 120-130°C. These systems are thermostable at the temperature of polyethylene composition reproducing in products. Compositions contain from 10 to 20 mass % of P-FRS. After the pre-mixing of P-FRS powders with granules or with powders of appropriate polyethylenes a futher reproducing of components is carried out by the die casting or the extrusion.

The investigation of a modified polyethylene was carried out using the following methods: a). a chemical analysis of the phosphorus content on the surface and in cuts of samples (an area of a cut equals $10^{4}m^{2}$, an altitude of a sample $2 \cdot 10^{-3}$ m, and a thickness of a cut $2 \cdot 10^{-4}m$); b). a layer by layer studying of a chemical structure in samples by the X-ray photoelectron spectroscopy; c). a functional analysis by the IR spectroscopy; d. the interface interaction of additives with polymeric matrix using the difractometry [4].

Results and Discussion

During reproducing the polyethylene composition modified by the P-FRS the competitive processes of the FRS migration to the heating side of the equipment surface as well as interactions of the FRS with functional groups in the FRS or in the polymeric matrix take place. The latter process is most probable when the secondary polyethylene is modified. When the complex FRS containing the phosphorylated resin and red phosphorus is used the distribution of the FRS is taken place in the following manner: the phosphorus containing epoxy resin partly diffuses into more heated layers of the composition, and the red phosphorus is distributed in the polymeric matrix proportionally. According to the data of the X-ray photoelectron spectra the increasing of the phosphorylated epoxy resin content is observed under the surface layer:

	Surface	Cut's surface		
P, content, %	2,9	1,2		
		the 1st cut	the 2nd cut	the 3rd cut
P, content, % after 6 month	1,3	4,1	4,4	3,3

The analytical data concerning the phosphorus content from the surface to the middle layer of the sample testifies to the tendency of migration of the P-FRS into the surface layer of the polyethylene composition containing 10% phosphorylated polyvinyl alcohol (Table 1).

According to the data of the IR spectroscopy and difractometry at the modification of the secondary polyethylene by the P-FRS the interaction of functional groups C-OH and C=C of the polymeric matrix with the P-FRS proceeds. The following facts confirm this interaction: a. the increasing of absorption in ranges of 950-1050 cm^{-1} and 1620-1680 cm^{-1} with a simultaneous decreasing of absorption at 1350 cm^{-1} and 1710 cm^{-1} (the formation of P-O-C fragments) are observed in the IR spectra; b. according to difractograms the level of a low angular diffusion is less than the level of diffusion which is received by the addition of curves of secondary polyethylene difractograms and the P-FRS ones. At the same time the intensity decrease of crystallic maximums of polyethylene and the appearance of new maximum of lower intensity are observed at 2Θ=138°. The investigation of the phosphorylated polyvinyl alcohol destruction testifies to the formation of polyenic structures and of the mixture of condensed polyphosphates with polyphosphoric acid. The formation of these structures and substances promotes the

Table 1. The phosphorus content on layers of sample of polyethylene composition modified by phosphorylated polyvinyl alcohol

Numbers of cuts*	Phosphorus content				
	Numbers of cut parts				
	1	2	3	4	5
1	3,11	3,10	3,20	3,15	3,14
2	2,92	2,90	2,93	2,91	2,94
3	2,63	2,61	2,64	2,62	2,60
4	2,38	2,42	2,41	2,43	2,39
5	2,38	2,39	2,42	2,42	2,39

***Cuts are numbered in the order of removal of them from the sample surface**

carbonization in surface layers of the polyethylene composition modified by the above P-FRS.

The comparison of combustion characteristics of polyethylene compositions modified by the P-FRS on the basis of the mixture of red phosphorus and phosphorylated epoxy resin (FRS-1) and modified by the P-FRS on the basis of the phosphorylated polyvinyl alcohol (FRS-2) gives ground to regard that the FRS-2 is more effective fire resistant additive. In Table 2 the results of investigations of the combustion and physico-mechanical characteristics of the secondary polyethylene and its composition containing 85% of this polymer and 15% of FRS-2 are given.

Table 2. The properties of the secondary polyethylene and the composition based.on it and FRS-2

The properties	Secondary polyethylene	Mixed secondary polyethylene
1	2	3
The tensile stress σ_t, MPa	10,2	11,6
The percent elongation ε, %	85	74
The flow index MI, g/10min	0,2	0,16
The ignition time τ_i, s	5	46
The combustion time τ_c, s	60	1-2
The Oxygen Index OI, %	16	28
The Combustion Index (National Standard)	5,6	0,6
The fall drop rate, mg/s	11,8	0,3

The materials obtained are classified as self extinguishing and low flammable materials.

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