Comparison of T_v values and that in fig. 4 indicates the advantage of HRC with one protective layer in comparison with that with two layers. It is evident that application of one protective layer is possible if silver does not diffuse into dielectric and protective layers.

It should be noted that use of SnO_2 in HRC production is conditioned by the fact that its spraying index (cooling rate correspondingly) is several times higher than that of TiO_2 [14]. In our opinion, modification in construction of magnetron spraying devices on the purpose of increasing spraying index of target materials will contribute to introduction of HRC on the basis of TiO_2 into the production [15].

The author is grateful to Dr. of phys.-math. Sciences, Professor V.P. Krivobokov for discussion of the work and useful remarks.

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Arrived on 15.09.2006

UDC 541.16:182

INCREASING CRACKING RESISTANCE OF HIGH-PRESSURE POLYETHYLENE MODIFIED BY ULTRAFINE POWDERS

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The affect of small additions (≤1 wt. %) of ultrafine fillers AlN и Al_2O_3 on cracking resistance of high-pressure polyethylene has been investigated. The most increase of cracking resistance is obtained for polyethylene samples produced at low cooling rate filled with AlN (0,075 wt %).

Introduction

One of the reasons for rapid destruction of polyethylene products and constructions of high pressure (PEHP) is their cracking under the action of external mechanic stress. At the same time polyethylene is widely used in everyday life, in industry, as well as in high-voltage electrophysical devices operating under the condition of high voltage field, stresses, high temperature, different climatic factors. To increase cracking resistance is possible introducing powder mineral substances, for example, aerosol, chalk, talc into the polymer, but the effect is achieved at additives significant in content [1]. A wide application of the given method is inhibited by the absence of efficient modifiers which would increase cracking resistance sufficiently even in low content and would not impair other polymer characteristics. From the viewpoint of economical and technological utility of new polymer modifiers the problem is to produce composite materials by means of the equipment and methods applied in manufacturing goods at present [2].

Previously [3] it has been shown that modified by electroblasting ultrafine powders (UFP), Al_2O_3, AlN and Al the PEHP samples possess high cracking resistance. It should be noted that significant increase in cracking resistance is achieved at relatively high degrees of filling (3 wt. %), at which some impairment of physical-mechanical properties takes place.

The purpose of the given paper is to study the cracking resistance of PEHP when modified with small additives (≤1 wt. %) of ultrafine powders of aluminium nitride and aluminium oxide.

Experimental methods

Technique of filling high pressure polyethylene with ultrafine aluminium nitride and oxide. In the work the mixtures of PEHP+AlN and PEHP+Al_2O_3 have been prepared with filler content: 0,025; 0,05; 0,075; 0,1; 0,25; 0,5; 0,75; 1,0 wt. %. Nanopowders were produced at experimental-industrial installation UDP-4G FGNU of «High Voltage Research Institute», the main elements of which are high voltage power supply, capacitor storage, reaction chamber, gas-supply system, controlled spark discharger [4]. Before the experiment reaction chamber has been vacuumized and filled with working gas: to obtain UFP of aluminium nitride – by nitrogen, that of aluminium oxide – by argon adding oxygen (10 wt. %). Introduction of working gas in the chamber amounted 1,5 atm. Electric conductor blast was performed in «rapid blast» mode with continuous current pause. Electric blast of aluminum conductor of 0,25 mm diameter was carried out at the value of introduced energy $1,8e_c$ (e_c is the energy of conductor material sublimation). UFP particles of AlN and Al_2O_3 had the values of average-surface diameter of 0,12 and 0,01 mkm, respectively.

In the experiments high pressure polyethylene of 10803-020 State Standard 16337-77 was used. To improve adhesion of polyethylene macromolecules to the surface of powder particles they were sized by stearic acid. For this purpose a portion of stearic acid equal to 3 % from the mass of treated powder was taken and dissolved in decane, then the powder was poured over with the resultant solution, the suspension was treated by ultrasound to destroy the agglomerates and increase the suspension stability. The treated suspension was dried in air at the room temperature. Polyethylene was mixed with powders at a twin-screw tuber with the temperatures per zones – 160, – 170, – 180 °C.

To define the influence of mechanical and thermal-oxidative polyethylene degradation during the mixture polyethylene without filler was also subjected to treatment.

Methods of sample production for tests. To determine cracking resistance and density of the filled polyethylene the following methods were used: block method (melting and slow cooling) and hot pressing.

Block method. The model blocks were prepared in press mould by melting granulated polyethylene in vacuum. This method has been developed in the High Voltage Research Institute for manufacturing large-sized defectless polyethylene production. The samples were cut out of the obtained pieces.

Technological process of block production consisted of the following operations: preparation of press-mould (assembling, cleaning, lining) and filling it in with granulated polyethylene, heating press-mould with polyethylene up to specified temperature in the vacuum furnace and soaking during the definite period of time at the specified temperature and residual pressure 5...10 Pa, cooling press mould with the specified rate and letting-to-air in it, pressing-out press mould.

Melting in vacuum was performed to prevent from oxidizing at high temperatures and decrease in gas impurities of the samples. Melting temperature mode is presented in the table.

Table. *Melting temperature mode*

Time from the beginning of melting, h	0	24	32	40	46	50	56	60
T, °C	140	120	110	100	90	80	70	Switch. off

From the block obtained a stripe of 0,05 m width and of nearly 0,001 m thickness was cut. Then the test samples were cut out of this stripe.

Hot pressing. By hot pressing the pieces were made by means of melting granulated polyethylene in vacuum under pressure. The test samples were cut out of the produced pieces.

Technological process of sample production consisted in the following operations: preparation of press-mould and filling it in with granulated polyethylene, heating furnace up to 150 °C, placing press-mould with polyethylene into the heated furnace and soaking it in the vacuum furnace to 137 °C during a definite period of time, loading press-mould with gradual cooling and letting-to-air, pressing-out press mould and extraction of the piece.

Melting at the pressure 5...10 Pa was performed in order to prevent from oxidizing during soaking at high temperatures and to decrease gas impurities in the samples.

Polyethylene cracking resistance was studied according to State Standards 13518-68 by the methods described in [3].

Results of experiments and discussion

Dependence of high pressure polyethylene cracking resistance on modifier content (ultrafine powder – AlN) is presented in fig. 1.

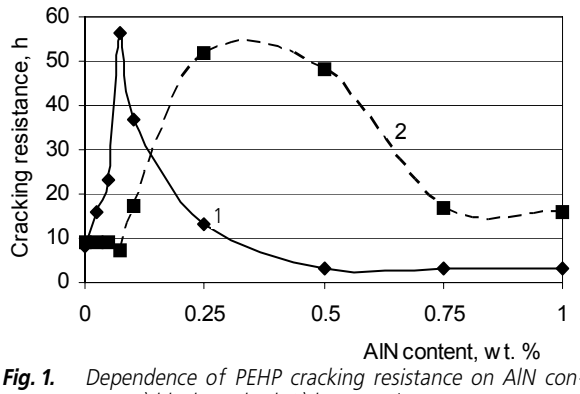

Fig. 1. *Dependence of PEHP cracking resistance on AlN content: 1) block method; 2) hot pressing*

According to the results obtained cracking resistance of PEHP, modified with ultrafine aluminium nitride powder for the samples produced by the method of hot pressing increases sufficiently in the filling range from 0,25 to 0,50 wt. %, and maximal value amounts 52 h. If increased AlN content further, there is a slow decrease in resistance to 17 h, whereas at AlN content of 0,75 wt. % it stabilizes.

For the samples obtained by melting in the block a sharp growth of cracking resistance is observed – up to 8,3 h for PEHP without additives, to 56,3 h for PEHP with 0,075 wt. % AlN content. With further growth of AlN content to 0,5 wt. %. smooth decrease in cracking resistance to 3 h is observed, after which this factor does not change essentially.

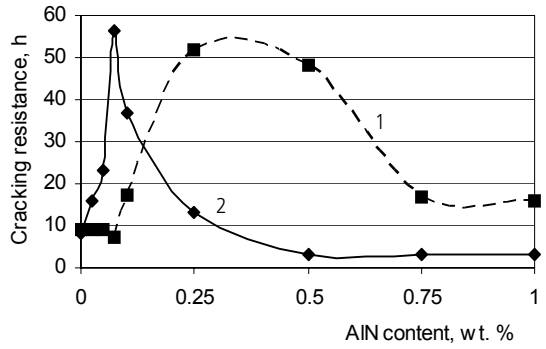

Fig. 2. *Dependence of PEHP cracking resistance on Al_2O_3 content: 1) block method; 2) – hot pressing*

Dependence of PEHP cracking resistance on the content of ultrafine aluminium oxide content has shown that for the samples produced by hot pressing and block method filling resulted in growth of cracking resistance.

In the given case the growth of cracking resistance from 9 h for PEHP without additives to 39 h at Al_2O_3 content 0,5 wt. % was observed for block samples, then decrease in resistance to 7 h at Al_2O_3 – content 1 wt. % followed.

In the case of hot pressing samples within the whole range there was increase in cracking resistance with increasing filler content, it amounted to maximum – 30 h at content of Al_2O_3 1 wt. %.

As a result of dependence analysis of PEHP cracking resistance on UFP it was stated that addition of AlN and Al_2O_3 UDP influenced sufficiently the PEHP cracking resistance, particularly with AlN. Cracking resistance increased to the definite filler content at any method of treatment, after increasing this content resistance decreased. At small concentrations (less than 1 wt. %) UFP particles participated in formation of fine-grained polyethylene structure, being the centres of crystallisation. With increase in the filler content in PEHP the probability of forming agglomerates increased and structure-forming action of the filler decreased. Besides, in forming spherulites the filler particles were displaced in the zone of polyethylene amorphous components and became the defect centres, decreasing cracking resistance.

High activity of AlN as a filler can be explained by difference of bond polarity in AlN and Al_2O_3. Since PEHP is a non-polar material, the better interaction takes place between the polyethylene macromolecules and less polar ones of aluminium nitride. Considering dependence for PEHP filled with Al_2O_3 (pressing), one can notice that in the range of Al_2O_3 contents involved the maximum cracking resistance has not been achieved, but for achievement of maximum higher content of the filler is required.

Conclusions

Introduction of maximal additions of ultrafine powders of:

1. AlN (0,075 wt. %) and Al_2O_3 (0,25...0,5 wt. %) into polyethylene of high pressure increased its cracking resistance several times. The most significant effect of modification was obtained for the material filled with ultrafine AlN powders with average surface diameter of particles 0,12 mkm: cracking resistance became 7 times greater in comparison with polyethylene without additives.
2. The most significant effect in increasing cracking resistance of high pressure polyethylene was observed for the samples with AlN and Al_2O_3 additives produced at low rates of cooling (block method) in comparison with the samples obtained at rapid cooling (hot pressing).

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Arrived on 24.05.2006