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Mechanical properties and resistance to oxidation tests of cable polyethylene modified with plasma carbon black

Summary — The new kind of cable polyethylene was produced by modification with plasma carbon black, which can be use as an antioxidant and pigment. The paper presents mechanical and oxidation induction time tests of cable polyethylene modified with changeable content of plasma carbon black from 0.1 % to 1.0 wt. %. The mechanical tests enclose Brinell-Vickers hardness number, melt flow rate and static tensile strength. The results showed the increased oxidation induction time, 57 min, for 0.5 wt. % of plasma carbon black in the composition. The results were compared with those concerning commercial cable polyethylene modified by furnace carbon black.

Key words: cable polyethylene, plasma carbon black, mechanical properties, oxidation induction time.

An increase in applications and using of plastics products in various branches of industry all over the world creates the needs of finding the new additives, like plasma carbon black, what could guarantee economical and profitable production of ecologically safe products showing better properties and stabilities. That is why there is necessity to elaborate the highly efficient, economically friendly process of carbon black production and its use for modification of special use plastics, like cover plastics [1]. The goal of the investigation was to work out and develop the composition of cable polyethylene with plasma carbon black as pigment and antioxidant agent.

EXPERIMENTAL

Materials

The amount of plasma carbon black used for cable polyethylene modification was 0.1—1.0 wt. %. The application of gliding discharge for the preparation of carbon black from properly selected hydrocarbon gases, like methane, ethane, ethylene or acetylene as source gases, allowed to produce the material of stable and regular structure [2].

The composition contained polyethylene (PE-LD, Malen E produced by Polish Oil Company ORLEN [3]), ethylene-vinyl acetate copolymers (EVAC, EVATENE 2803 produced by EXXON CHEMICAL BELGIUM Company [4]), thermal stabilizer (Irganox 1010 produced by Ciba-Geigy Company [1]) and plasma carbon black concentrate with EVAC prepared on the basis of carbon black concentrate (produced by Cabot Plastics Company [5]).

Method of samples preparation

The composition of cable polyethylene were prepared by mechanical mixing of the components: PE-LD (87 wt. %), thermal stabilizer Irganox 1010 (0.12 wt. %) and plasma carbon black concentrate contained EVAC. The amount of plasma carbon black concentrate changed dependently on the planned concentration of plasma carbon black in the total composition.

Methods of carbon black and samples characterization

Scanning electron microscopy

The surface structure of plasma carbon black was studied in Centre of High Pressure Researches "Unipress" of Polish Academy of Science in Warsaw.

The tests were carried out using LEO 1530 scanning electron microscope produced by Oxford Company, which is a type of electron microscope, where the electron beam, focused on the sample's surface to the speck

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with diameter to 0.1 nm, sweeps the chosen rectangular field by scanning motion, line by line. The electron beam is accelerated in the electromagnetic field of potential 0.1—30 kV and focused by the electromagnetic lens and the deflection coil gives to it the scanning motion. The electrons penetrate into and come back from the sample, what is called backscattering. The SEM image is the simple ratio of the figurative monitor screen size and the scanning field size.

Adsorption measurements

The adsorption of prepared plasma carbon black was measured in respect to nitrogen (BET method) based on PN-ISO 9277:2000 Standard, iodine (IA) based on BN-79/6048-02.07 one and dibutyl phthalate (DBP) according to BN-79/6048-02.09 Standard.

Bulk density test

The measurements of the bulk density of produced plasma carbon black were based on BN-79/6048-02.06 Standard.

Particles size measurement

The size of particles of prepared plasma carbon black products were measured using ALPHAPHOT 2 Microscope, Japan. JCC-8201 CCD Color Camera with enlargement 415x and nonpolarized light was used.

Brinell-Vickers hardness number

The measurements were based on the PN-EN ISO 2039-1:2000 (U) Standard and made with using Brinell-Vickers WPO-250 apparatus (Germany). The samples (15×25×4 mm) were prepared by pouring out the granulate to the forms and pressing using hydraulic press. The samples were tested by 153.2 N load of the ball with diameter of 5 mm.

Melt flow rate and density

The method based on PN-EN ISO 1133:2002 (U) (PN-EN ISO 1872-1:2000) Standard. Measurements were made at temperature 190 °C and load of 2.16 kg using "CEAST" Melt Flow Tester apparatus (Italy). The mass melt flow rate (MFR) and density at temperature 190 °C were measured.

Static tensile strength

The tests were done according to PN-EN ISO 527-2:1998 Standard using ZMGi-500 testing machine (Germany) and dumbbell samples with the measure part of 25 mm. The unit elongation, yield point and breaking stress were determined.

Oxidation induction time test

The method of oxidation induction time (*OIT*) determination is based on ASTM D 3895-94 Standard for polyolefines and PN-EN 728 Standard.

RESULTS AND DISCUSSION

Plasma carbon black investigation

The high adsorption capacity (Table 1) indicated a good absorbability, allowing molecules of various substances, for example stabilizers, easily drive into and settle on carbon black surface. As can be seen from Table 1, the kind of a source gas in plasma carbon black production had no essential influence on the properties of plasma carbon black.

Table 1. Results of adsorption measurements of plasma carbon black samples used as a modifier of plastics

Source gas	Specific surface — nitrogen adsorption (BET method), m^2/g	Iodine adsorption (IA) mg/g	Dibutyl phthalate adsorption (DBP) $cm^3/100$ g
CH_4	183	156	125
C_2H_2	166	94	126
C_2H_4	187	94	125
C_2H_6	235	155	126

The examples of the structures of plasma carbon black are shown in Fig. 1. The structure is atypical for carbon black and the particles look like fuzzy flakes connected very closely together what is complete different and original in comparison with traditional furnace carbon black structure, which shows the traditional round particles.

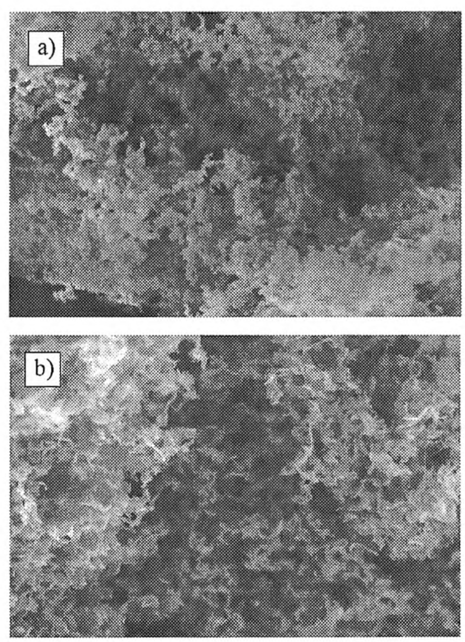

Fig. 1. The surface morphology of plasma carbon black made from: a) acetylene in argon plasma; b) methane in argon plasma (50 000× enlargement)

The miscibility of additives with thermoplastics and rubbers finds the applications *e.g.* in car tires industry, and can guarantee better tire adhesion to the road surface. The average bulk density of our plasma carbon black is about 10 g/dm^3, which is over 10 times lower that the average bulk density of the commercial carbon black. This value makes possible to use few times lower amount of such plasma carbon black in the composition of the cable plastics than in the commercial composition.

Fine-grained carbon black with small particles sizes (0.01—1 mm) could act as strength filler and when used in thermoplastics it could also act as antioxidant [6] and pigment [7]. The size of particles of plasma carbon black obtained, equal to 1.2 mm (Fig. 2) can qualify it to use as a filler for thermoplastics, especially for cable PE. There is a possibility to use this plasma carbon black as an additive for plastics with particles sizes exceeding the limit, because of its atypical structure.

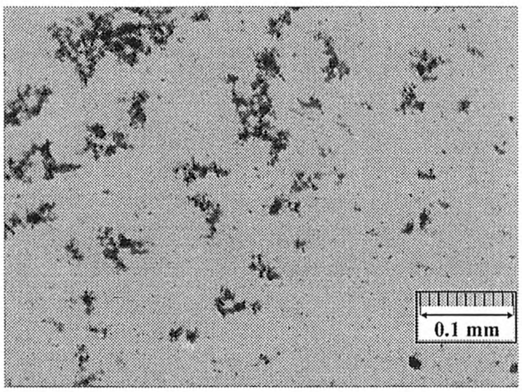

Fig. 2. The image of plasma carbon black (415× enlargement)

Table 2. Mechanical properties and *OIT* values of different compositions of cable polyethylene

Property	Commercial cable PE LE6022	Cable PE + plasma carbon black			
Carbon black content, wt. %	2.6	0.1	0.25	0.5	1.0
Density (at 190 °C), g/cm^3	0.733	0.759	0.756	0.772	0.758
MFR, g/10 min	0.30	0.43	0.42	0.31	0.31
Hardness number, N/mm^2	21.7	17.94	18.43	23.4	20.10
Break stress, MPa	16	13	11	15	13
Ultimate elongation, %	700	437	329	459	391
OIT, min	≥ 22	20	21	57	30

Cable polyethylene investigation

The results of the studies of compositions prepared by us in comparison with commercial cable polyethylene LE6022, produced by BOREALIS Company, are shown in Table 2 [8].

A lot of Standards concerning cable PE require the measurements of the protection against degradation process, like *OIT*. *OIT* depends on the kinds of mediums, like type of polymer stabilized, the method of polymerization and characteristic of the antioxidant. The requirements for polyethylene, modified by carbon black, are specified by ASTM D 4565-9 Standard.

The results of *OIT* studies of cable polyethylene, modified with more than five times lower amount of plasma carbon black as an antioxidant in the composition, showed much better (57 min) properties than those demanded from commercial cable polyethylene (≥ 22 min) without any significant differences in mechanical strength. The detailed data of commercial LE6022 cable polyethylene properties were based on BOREALIS Co. producer's specifications [8]. There was observed, that the ultimate elongation of the compositions of polyethylene modified by plasma carbon black decreased. Breaking stress and hardness number values compared with commercial cable polyethylene properties showed that the addition of plasma carbon black to the polymer did not change the mechanical resistance of composition. Even 26 times lower amount of carbon black in a composition did not cause essential worsening of the properties and let keep resistance to oxidation on the same level. The best properties were observed for the composition of cable polyethylene with 0.5 wt. % of plasma carbon black. It was found that this is the optimum content of plasma carbon black, what can guarantee good ultimate elongation, breaking stress as well as the lowest density and the best result of oxidation induction time of the composition. First two compositions with the amounts 0.1 and 0.25 wt. % of plasma carbon black showed that these contents of plasma carbon black are not enough to achieve the better *OIT* results than for commercial cable PE. The amount 0.5 wt. % of plasma carbon black gives the possibility to obtain the composition of cable PE with the highest *OIT* value. The lower *OIT* value of the cable PE modified with 1.0 wt. % of plasma carbon black was observed, what is unclear. In our opinion more than 0.5 wt. % of plasma carbon black might to be too much to create good miscibility of all additives and to obtain a homogenous composition.

CONCLUSION

The plasma carbon black, obtained from gaseous aliphatic hydrocarbons, can be used as a modifier of thermoplastics, like polyethylene, and can act as an antioxidant and pigment. Useful values of density oxidation induction time and mechanical properties give possibilities to produce cable PE, which is environmentally friendly, and characterized by prolonged time of use.

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