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EFFECT OF LOW MOLECULAR WEIGHT POLYETHYLENE ON STRUCTURE AND PROPERTIES OF CARBON-FILLED POLYETHYLENE COMPOSITIONS

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ABSTRACT

Polymer composites based on high-density polyethylene, carbon black and low-molecular-weight polyethylene were obtained. The addition of low molecular weight polyeth-ylene increases the melt flow index and helps to reduce the particle size of the dispersed phase in the composition. XRD analysis showed changes in the structure of both carbon black and high-density polyethylene in the presence of low molecular weight polyethylene in the compo-sition. At the same time, the tensile strength at yield, elongation at break and thermal stability of the composition meet the requirements for raw materials for the production of pipes based on polyethylene.

Introduction

Carbon black (CB) is widely used as a filler in compositions with polyethylene. CB increase in its resistance to UV irradiation, oxidation induction time and tensile properties of polyethylene compounds. The size of CB particles and their distribution in the polyethylene matrix significantly affect the properties of the compositions [1-3].

It was found that high-density polyethylene composites filled with carbon black presented different conductive percolation behaviors depending on the content and size of carbon black particles in the compositions [4].

An important task is the dispersion of CB in polyethylene compounds. To improve the dispersion of CB in polyethylene, the latter is modified by grafting chains of poly(ethylene glycol) [5]. Graft copolymers of low-molecular-weight polyethylene (LMP) and acrylic acid were used in the composition of carbon black-filled high-density polyethylene to decrease the particle size of the dispersed phase and increase the thermal stability of the composites [6].

Special additives, lubricants, are used in the processing of polyethylene compositions for reducing the viscosity of the molten polymer and as a homogeneous melt [7].

Polyethylene waxes (PE wax) are used in the processing of polyethylene as an external lubricant, dispersant and plasticizer in masterbatches and polymer compositions [8]. The addition of PE wax enables melt processing of ultrahigh molecular weight polyethylene and improves solid-state drawability, providing opportunities in recycling waste [9].

According to the technologies of "Mitsui" (Japan) and "LOTTE Chemical Corporation" (Korea), LMP is released as a coproduct of the synthesis of high-density polyethylene (HDPE).

LMP is a valuable product that can be applied in various technological processes. In particular, it is used as a lubricant in the production of carbon-filled master batches [10].

The aim of this work is to establish the influence of LMP on the melt index, structure, thermal stability and physico-mechanical properties of high-density polyethylene/carbon black compositions.

Materials and Methods

Materials

HDPE [P-Y346 grade, melt flow index 0.30-0.36 g/10 min (at 2.16 kgf), density 0.94 g/cm^3] produced at the Shurtan gas chemical complex in Uzbekistan using SCLAIRTECH technology under licence from NOVA (North America).

LMP (highest grade) was produced at JV Uz-Kor Gas Chemical LLC (Uzbekistan) according to the technologies "Mitsui" (Japan) and "LOTTE Chemical Corporation" (Korea). LMP has a melting point of 110 °C, whiteness of 90%, and ash content of 0.028%.

CB (OMCARB P72 grade, LLC Omsktehuglerod), oil absorption of 100.2 cm^3/100 g, iodine adsorption of 87.8 mg/g, and ash content of 0.08%.

Methods

The compositions were obtained on a mixer model 815602 (Brabender), T = 140°C for 10 min.

Structural studies were carried out by atomic force microscopy (semicontact method) on an Agilent 5500 scanning probe microscope. The experimental procedure is described in detail in [6].

XRD analysis was conducted on a Miniflex 600 (Rigaku, Japan) with monochromatized CuKα radiation and an isolated nickel filter, with a wavelength of λ = 1.5418 Å at 40 kV and a current of 15 mA. The results were processed using SmartLab Studio II.

The melt flow index (MI) of the compositions was determined on an MP993A extrusion plastometer (Tinius Olsen) at T = 190°C, loading 2.16 kgf (ASTM D 1238-10 "Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer").

The composites were tested for thermal stability on a DSC 200 F3 analyser (NETZSCH-Gerätebau GmbH). The experimental procedure is described in detail in ASTM D3895-2014. "Standard test method for oxidative-induction time of polyolefi ns by differential scanning calorimetry".

The yield strength and elongation at break were measured by the ASTM D 638-14. "Standard test method for tensile properties of plastics" on an AG-X plus tensile tester (Shimadzu Corporation).

Results and discussion

HDPE compositions containing 2% CB [11] and various LMP contents were obtained. The HDPE:CB compound in the absence of LMP includes CB agglomerates of irregular shape and micron size (Fig. 1a). The addition of 0.5 – 1 wt% LMP to the composition leads to some elongation of the agglomerates and a decrease in their width (Fig. 1 b, c). In the composition HDPE:CB:LMP = 95:2:3 wt% (Fig. 1 d.), particles of the dispersed phase of an elongated shape with a length of 1 – 1.5 microns and a width of 100 – 300 nm with a uniform distribution over the entire study area are observed. Round-shaped particles with a size of 100 – 200 nm are also visible. Most likely, the decrease in the particle size of CB (Fig. 1 d) is associated with a change in the rheological properties of mixtures of compositions containing LMP.

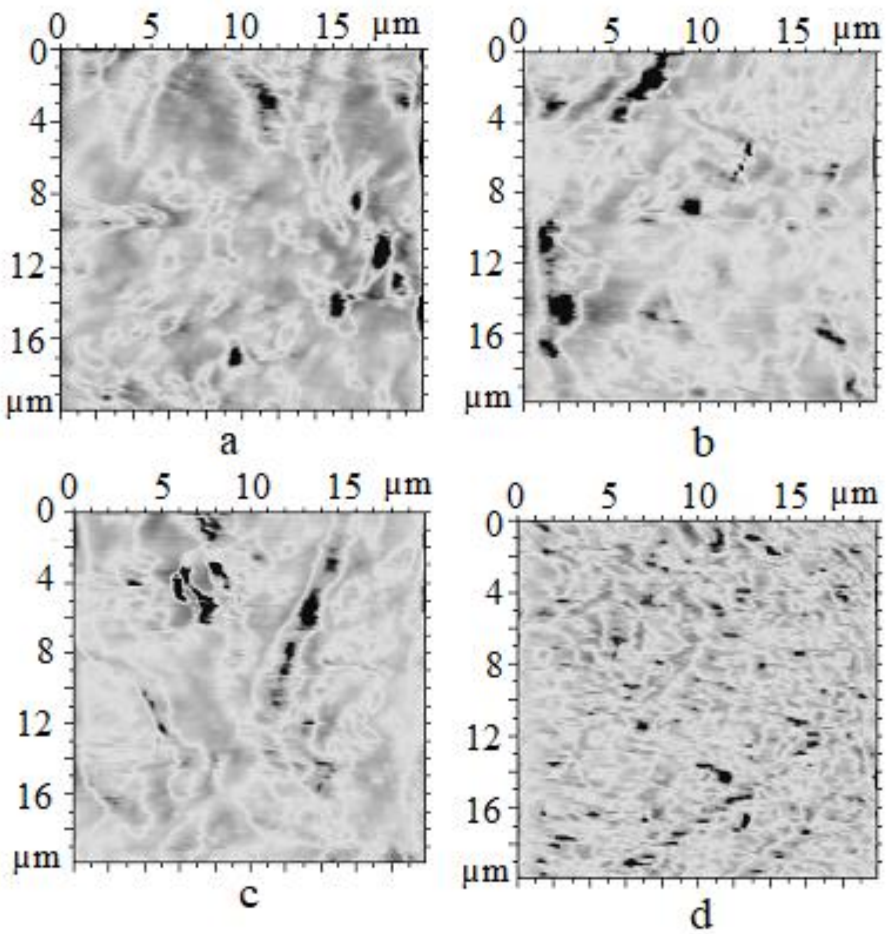

Figure 1 AFM images of surface samples of high-density polyethylene composites containing HDPE:CB:LMP: 98:2:0 wt% (a); 97.5:2:0.5 wt% (b); 97:2:1 wt% (c); 95:2:3 wt% (d)

The X-ray diffraction analysis of the compositions is shown in Fig. 2 and Tables 1 and 2.

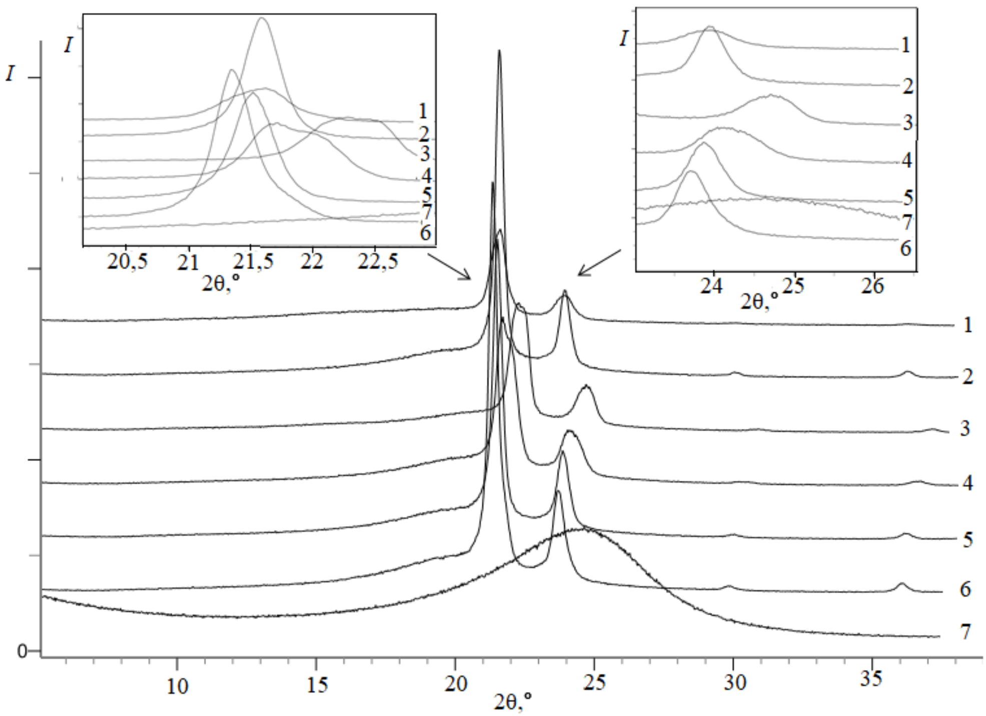

Figure 2 XRD curves of compositions HDPE:CB:LMP: 93:2:5 wt% (1) 95:2:3 wt% (2); 97:2:1 wt% (3); 97.5:2:0.5 wt% (4); 98:2:0 wt% (5); HDPE (6); CB (7)

The data on Bragg angles and peak diffraction for HDPE and CB in composition are given in the Supplementary Information. The main peak at 21.34°– 22.35° corresponds to the (110) crystallographic reflection of HDPE. The peak at 2θ=23.68° –24.72° corresponding to the (200) plane exhibits a low intensity. The HDPE compositions have orthorhombic crystal syngony, in which the lattice parameters vary depending on the LMP content (Table 1,2). The addition of LMP to the composition up to 3% leads to a decrease in the interplane distance (110) and (200), which leads to a change in intensity and a shift of peaks towards large diffraction angles. However, with an increase in the LMP content in the composite to 5%, the reverse process is observed.

Table 1.

Crystal structure parameters of HDPE in the composition of HDPE:CB:LMP

Crystal structure parameters	Compositions HDPE:Carbon:LMP, wt% 93:2:5	95:2:3	97:2:1	97.5:2:0.5	98:2:0	HDPE
HDPE, $\alpha = \beta = \gamma = 90.00^{o}$						
a, Å	7.457	7.456	7.246	7.411	7.467	7.503
b, Å	4.962	4.961	4.814	4.930	4.972	4.992
c, Å	2.547	2.552	2.512	2.535	2.556	2.563

Table 2.

Crystal structure parameters of CB in the HDPE:CB:LMP composition

Crystal structure parameters	Compositions HDPE:Carbon:LMP, wt% 93:2:5	95:2:3	97:2:1	97.5:2:0.5	98:2:0	CB M $\alpha = \gamma = 90.00^{o}$, $\beta = 92.20^{o}$	H $\alpha = \beta = 90.00^{o}$, $\gamma = 120.00^{o}$
CB, $\alpha = \beta = 90.00^{o}$, $\gamma = 120.00^{o}$							
a, Å	8.91	1.68	11.67	11.08	9.01	8.91	1.68
b, Å	1.89	1.68	11.67	11.08	9.01	1.89	1.68
c, Å	7.94	20.0	15.38	13.90	14.11	7.94	20.0

Phase analysis of CB shows that 86% of it has monoclinic syngony (M) and 14% hexagonal syngony (H). In composition, CB crystallites are in the form of a hexagonal syngony and the parameters of the crystal lattice also depend on the LMP content in the composition. Parameters *a* and *b* of the crystal lattice are equal to each other and increase with an increase in the LMP content in the composition from 0 to 1 wt%. With an LMP content of 3 wt% in the composite, there is a significant decrease in the size of the crystallite in directions *a* and *b*. At the same time, the parameter *c* of the crystal lattice, which characterizes the distance between the layers of the crystal, reaches its maximum. Similar conclusions can be drawn based on the analysis of the diffraction peaks of the corresponding planes of the CB crystallites given in the Supplemental Information. The LMP 3wt% content corresponds to a composite containing the smallest particles of the dispersed phase (Fig. 1d), which may be associated with an increase in the interlayer distance in CB crystallites.

LMP additives in the composition can significantly influence its physical and mechanical properties. The introduction of LMP leads to an increase in the melt flow index of carbon black-filled HDPE (Fig. 3) [6]. LMP is characterized by significantly lower molecular weights in comparison with industrial polyethylene grade HDPE. Therefore, its introduction into the composition of the blend leads to a decrease in the viscosity of the melt.

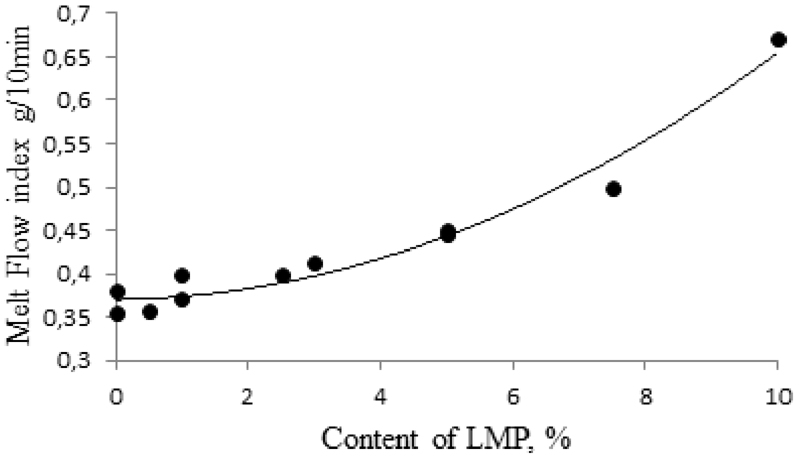

Figure 3. The dependence of MI (2.16 kg, 190°C) on LMP content.

The presence of LMP may adversely affect the strength properties of the compositions. In this regard, the dependence of the strength properties of the compositions on the LMP content is established in Figure 4.

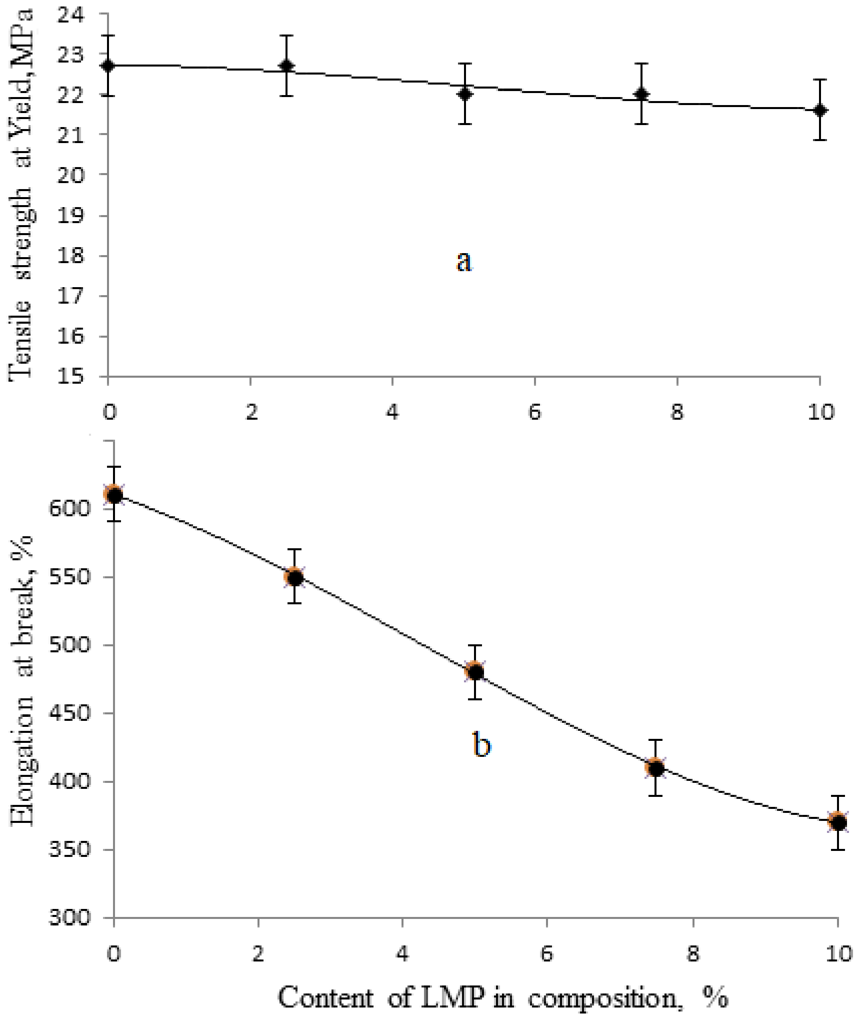

Figure 4. Dependence of tensile strength at yield (a) and elongation at break (b) on LMP content

The reduction in elongation at break, despite the nearly unchanged yield strength, can be attributed to the distinct roles played by the crystalline and amorphous phases in HDPE. Elongation at break in polymers is highly sensitive to inhomogeneities within the matrix. These inhomogeneities may include the presence of foreign bodies, variations in the density of tie chains between crystallites, imperfections in lamellar structures within the crystallites, and so on. Such irregularities lead to the development of localized internal stresses. In this case, inhomogeneities caused by minor aggregations of low-molecular-weight polyethylene within the intercrystalline regions act as additional sources of internal stress, promoting the formation of microcracks that eventually propagate into major fracture cracks.

In the investigated concentration range, the increase in LMP leads to a slight decrease in the tensile strength at yield. A more significant decrease was observed for the elongation at break parameter. Increasing the LMPE content in the composition up to 10% elongation at break reduces the elongation at break to 350%. Despite this, both parameters correspond to the requirements for pipe grades of polyethylene [12].

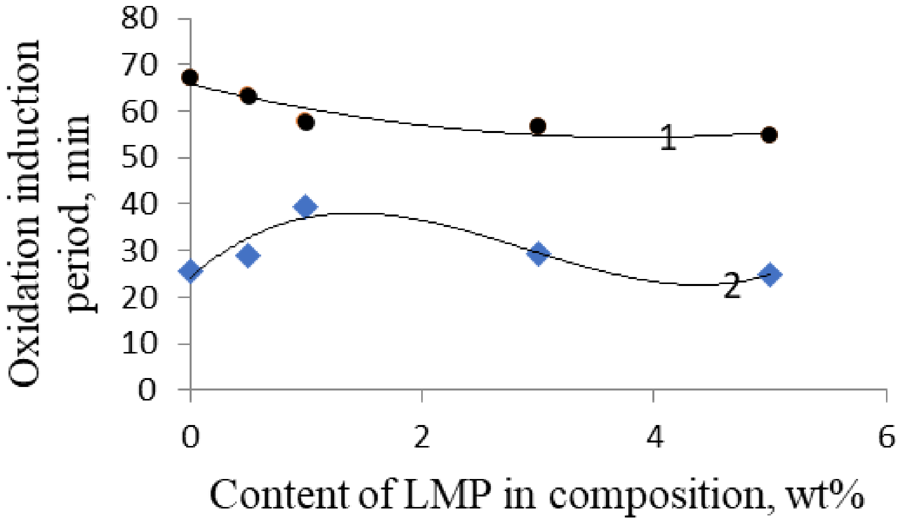

Figure 5. Oxidation induction period of the CB-filled composition of HDPE vs. LMP content. 1,2 - Compositions were obtained on various lots of P-Y 346 with different antioxidant content.

An important technical requirement for compositions for the production of polyethylene pipes is their thermal stability. This parameter should be at least 20 min [12]. Figure 5 shows the effect of the content of NMP in the composition on the induction period of oxidation. When adding up to 1% LMP to the composition, a slight increase in thermal stability is observed. The presence of LMP in the composition gives rise to two mutually compensating effects. It has previously been shown that the addition of LMP to polyethylene, in the absence of carbon black, reduces the thermal stability of the material, as LMP is more susceptible to thermal degradation and promotes the formation of radicals [5]. However, in the presence of carbon black, this effect is significantly diminished due to the antioxidant properties of carbon black, which adsorbs oxygen and radicals. Additionally, LMP can localize at the interface between the polyethylene and carbon black phases, promoting a more uniform distribution of carbon black particles and reducing interfacial tension. This enhances the dispersion of carbon black, increases its stabilizing efficiency, and further contributes to maintaining the thermal stability of the composition. As these two effects counterbalance each other, the overall influence of LMP on the thermal stability of carbon black–filled compositions is minimal. All compositions obtained by us meet the requirements [12].

Conclusions

Low molecular weight polyethylene – a coproduct of the production of high density polyethylene may be used as a lubricant in the production of composition based on carbon black filled polyethylene. The presence of LMP reduces the viscosity of the melt of the composition, which is necessary to increase the manufacturability of material processing. Apparently, this is due to variations in the rheological behavior of the blends in the presence of LMP. Additionally, LMP has an effect on the structure of polyethylene and carbon black in composition. The strength characteristics and thermal stability of the obtained compositions meet the requirements for raw materials for the production of polyethylene pipes.

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