

Modification of low-molecular-weight polyethylene through grafted copolymerization with methyl acrylate

Valentin O. Kudyshkin^{*,1}, Nurad I. Bozorov¹, Ruslan K. Madiev², Bakhtiyor K. Ruziev², Nurbek S. Ashurov¹, and Sayora S. Rashidova¹

¹Institute of Polymer Chemistry and Physics, Academy of Sciences of the Republic of Uzbekistan, 100128 Tashkent, Uzbekistan

²JSC “Shurtan Gas Chemical Complex”, 131300, Kashkadarya viloyat, Shurtan stl., Uzbekistan

*Corresponding author E-mail: persival2015@yandex.ru; polymer@academy.uz

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ABSTRACT

Copolymers of methyl acrylate were grafted onto low-molecular-weight polyethylene in the presence of benzoyl peroxide in *o*-xylene. The formation of these copolymers was confirmed by functional analysis of the ether groups and Fourier-transform infrared spectroscopy. Various synthesis patterns were demonstrated, which furnished grafted copolymers with a wide range of compositions. X-ray diffraction analysis showed that grafting led to changes in the crystalline structure of low-molecular-weight polyethylene. The grafting sequences of the methyl acrylate units may disrupt the order of the crystalline planes in polyethylene, and with an increase in their content, the crystalline phase in polyethylene becomes less prominent. These copolymers can be used as compatibilizers for CB-filled polyethylene (CB: carbon black). The effect of the grafted copolymers on the properties of high-density polyethylene composites containing CB was evaluated. The composites of polyethylene and the grafted copolymers exhibited enhanced thermal stability, plausibly associated with a decrease in the average size of the CB particles.

Keywords: Grafted copolymerization; polyethylene; methylacrylate; carbon black; structure.

INTRODUCTION

Various polyethylene composites materials can be fabricated for a wide range of applications. Different substances can be used as fillers in the polymer matrix, enabling the production of materials with various properties based on the same polymer. To enhance the compatibility between the fillers and the polymer, compatibilizers containing functional groups that interact with other components of the mixture can be added to polyethylene [1]. Grafted and block copolymers have been successfully used as compatibilizing agents to create composites from incompatible polymer mixtures [2, 3]. Linear or grafted multiblock copolymers, which consist of blocks of different monomers, can also be used as compatibilizers [4]. Localization of these modifiers at the interface prevents coalescence of the particles and helps stabilize the morphology of the polymer mixture.

Recently, several grafted copolymers that can be used as compatible materials in polyethylene composites have been synthesized. A series of novel functional poly(ethylene-co-vinyl alcohol) copolymers with controlled molecular characteristics was synthesized. These grafted copolymers are effective compatibilizers for blends of low-density polyethylene and polystyrene [5].

Maleic anhydride was grafted onto low-density polyethylene using dicumyl peroxide as the initiator and xylene as the solvent. The initiator concentration had a significant impact on the degree of grafting, whereas the reaction temperature had a minimal effect. Under the optimal conditions, a copolymer with a high degree of grafting (up to 4%) was obtained [6].

Grafted copolymers of polyethylene and acrylic acid have also been developed. Low-density polyethylene was subjected to reactive melt blending with a low-molecular-weight polymer of acrylic acid in the presence of a free radical initiator such as benzoyl peroxide [7]. Acrylic acid was subjected to photoinduced grafted polymerization on the surface of a polyethylene film using water-insoluble benzophenone as the photoinitiator [8]. An ethylene-octene random copolymer was modified by grafting with acrylic acid both in solution and in the melt to increase the polarity and adhesion to cellulose-based substrates. Graft copolymerization was initiated using an oxygen-ozone mixture [9].

Limited information is available on the grafting of acrylic or methacrylic acid esters onto polyolefins. To improve the phase compatibility between the thermoplastic vulcanized methyl vinyl silicone rubber and polypropylene, a special double-reactive compatibilizer was developed. This compatibilizer consists of a terpolymer of ethylene, methyl acrylate, glycidyl methacrylate, and polypropylene grafted with maleic anhydride. These compatibilizers are designed to ensure compatibility between immiscible materials that do not contain reactive groups in either component [10].

Carbon-containing materials play a significant role in the development of polyethylene-based composites. Composites of polyethylene (PE) with carbon black are commonly used in the production of pressure-pipes and fittings. Carbon black (CB), also known as soot, improves the resistance of these materials to ultraviolet (UV) radiation and enhances their thermal stability. This effect largely depends on the size and distribution of the soot particles in the polyethylene matrix [11, 12, 13]. The conductivity of high-density polyethylene composites with CB differs depending on the amount and size of CB particles in the composition [14].

Dispersing CB in polyethylene composites is an important task. To improve the distribution of CB in polyethylene, poly(ethylene glycol) was grafted onto polyethylene, as a modifier [15]. Special additives and lubricants are used in processing polyethylene compositions to reduce the viscosity of the molten polymer and homogeneous melt [16].

Polyethylene waxes (PE wax) are used in the processing of polyethylene as external lubricants, dispersants, and plasticizers in masterbatches and polymer compositions [17]. The addition of PE wax allows the processing of ultra-high-molecular-weight polyethylene and improves its solid-state drawability, creating opportunities for waste recycling [18]. Low-molecular-weight polyethylene (LMP) can be used in various technological processes, including as a lubricant in the production of CB-filled masterbatches [19]. LMP is produced as a by-product of the synthesis of high-density polyethylene (HDPE) according to the technology of Mitsui (Japan)

and LOTTE Chemical Corporation (Korea).

Grafted and block copolymers have been successfully used as compatibilizers in the fabrication of composite materials based on thermodynamically incompatible components in a polymer mixture [20, 21]. The introduction of a compatibilizer into the composition prevents coalescence and helps stabilize the particle size of the dispersed phase. In previous studies, grafted copolymers of LMP and acrylic acid were synthesized, and the possibility of using the composites as compatibilizers in polyethylene starch systems was demonstrated [22].

There is currently insufficient information on the grafting of acrylic esters onto polyethylene. Grafted copolymers of polyolefins with acrylic acid esters are expected to have good affinity for CB particles owing to the presence of polar carbonyl groups in their composition. The aim of this study is to synthesize a copolymer of methyl acrylate grafted onto LMP and study the structural properties of these copolymers, as well as their potential use in mixtures with CB.

EXPERIMENTAL

Materials

Low-molecular-weight polyethylene (LMP) [highest grade] was produced at JV Uz-Kor Gas Chemical LLC (Uzbekistan) under license from "Mitsui" (Japan) and "LOTTE Chemical Corporation" (Korea). Methyl acrylate (MA) was produced at the JSC "Navoiyazot" in Uzbekistan and was purified by distillation. The initiator, benzoyl peroxide (98%, Tianjin Icason Technology Co.), was purified by recrystallization. As solvents, *o*-xylene (99.0%, Ximreaktivinvest LLC), ethanol (96%), and acetone were purified by distillation. High-density polyethylene (HDPE) [grade P-Y346, melt flow rate: 0.3 g/10 min (at 2.16 kgf), density: 0.94 g/cm³] was produced at the Shurtan Gas-Chemical Complex in Uzbekistan according to the SCLAIRTECH technology, under license from the North American company NOVA Chemicals. Carbon black (OMCARB P72 grade) was supplied by LLC Omsktehuglerod.

Synthesis of grafted copolymers

The grafted copolymers comprising LMP and MA (LMP-*g*-MA) were synthesized in the presence of benzoyl peroxide as an initiator (Table 1), at a temperature of 75 °C, under nitrogen atmosphere. LMP (m_1) was dissolved by stirring in a three-necked flask containing *o*-xylene at 95±0.5 °C. The temperature was then lowered to 75 °C and a calculated amount of MA and initiator was added to the flask. The precipitate, which contained a mixture of the MMA homopolymer and LMP-*g*-MA, was washed three times with ethanol to completely remove the solvent and unreacted MA, and filtered under vacuum. The precipitate was then dried under vacuum to a constant weight (m). To separate polymethylacrylate (PMA) from the copolymer, the polymerization product was repeatedly washed with acetone, filtered under vacuum, and dried to constant weight (m_2). The mass of the acetone-soluble fraction, $m_3 = m - m_2$, was considered as the weight of the PMA homopolymer.

Table 1. Composition of copolymers synthesized with various ratios of low-molecular-weight polyethylene to methyl acrylate. Solvent: *o*-xylene, $T = 75\text{ }^{\circ}\text{C}$, $5 \times 10^{-3}\text{ M}$ benzoyl peroxide initiator.

№	Component concentration, mol %		Ethereal number, mgHCl/g	Copolymer composition, mas %		Copolymer composition, mol %	
	LMP	MA		LMP	MA	LMP	MA
1	70	30	32.77	92.3	7.7	97.36	2.64
2	60	40	69.64	83.64	16.36	94.01	5.99
3	50	50	90.74	78.68	21.32	91.90	8.10
4	40	60	122.95	71.12	28.88	88.32	11.68
5	30	70	149.43	64.9	35.10	85.03	14.97

To determine the composition of the grafted copolymers, the ether group content was analyzed by alkaline hydrolysis of a sample with an alcoholic solution of potassium hydroxide, in accordance with a reported method [23].

The grafting degree ($GD, \%$) and grafting efficiency ($GE, \%$) of MA on LMP were calculated using the following equations:

$$GD = \frac{m_2 - m_1}{m_1} \times 100 \quad (1)$$

$$GE = \frac{m_2 - m_1}{m_2 - m_1 + m_3} \times 100 \quad (2)$$

where m_1 is the weight of LMP used for synthesis, m_2 is the weight of the grafted copolymer, and m_3 is the weight of the MA homopolymer.

Infrared (IR) spectroscopic analysis was performed using an IRTracer-100 IR Fourier spectrometer (Shimadzu Corp.) [22].

X-ray studies were carried out on a Miniflex 600 device (Rigaku, Japan) with monochromatized Cu $K\alpha$ radiation at 40 kV and a current of 15 mA, using an isolated nickel filter with a wavelength (λ) of 1.5418 Å. The samples were subsequently studied as films. The analysis was carried out in the 2θ range of 2–70°. The results were processed using SmartLab Studio II software.

Morphological studies of the surfaces of the CB samples and blends of CB:LMP-*g*-MA were performed using a JSM-IT 210 scanning electron microscope (Jeol, Japan). During the measurement, an accelerating voltage (extra-high tension, EHT) of 5.00 kV was used, and the working distance (WD) was 10.9 mm. Images at different scales were obtained using InTouch Scope software.

Different compositions of HDPE, carbon black, and LMP-g-MA were prepared as follows. HDPE was ground in a RETSCH ZM 200 mill to a size of less than 0.5 mm. The crushed HDPE was mixed with the calculated amount of CB and LMP-g-MA. The compositions were prepared by homogenization in a mixer (model 815602 (Brabender)) at $T = 140\text{ }^{\circ}\text{C}$ for 10 min., screw rotation speed 50 rpm, sample weight 40 g.

The compositions were prepared under the conditions specified by the LTP PE 342S/QPE - 352 B procedure "Additive Analysis using FTIR" developed by NOVA Chemical Limited (Canada).

The structure of the compositions was investigated by atomic force microscopy (AFM) in semi-contact mode using an Agilent 5500 scanning probe microscope at room temperature. Silicon cantilevers with a stiffness of 9.5 N m^{-1} and a frequency of 192 kHz were used for the measurements.

The melt flow rate (MFR) was determined on a standard plastometer (MP993A extrusion plastometer, Tinius Olsen), according to ASTM D 1238 "Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer" at $190\text{ }^{\circ}\text{C}$ with a load of 2.16 kgf.

The thermal stability of the composites was tested using a DSC 200 F3 analyzer (NETZSCH-Gerätebau GmbH). The experimental procedure is described in detail in ASTM D 3895-2014. "Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry." The induction period for material oxidation was determined using differential scanning calorimetry (DSC). The samples were heated under a flow of an inert gas (nitrogen) at a constant rate. When the preset temperature ($200\text{ }^{\circ}\text{C}$) was reached, the nitrogen supply to the device chamber was switched to an oxygen supply. The sample was maintained at a constant temperature until an exothermic effect appeared in the thermogram, indicating thermal oxidation of the material. The time from the start of the oxygen supply to the onset of the exothermic effect was measured, which was the oxidation induction period (indicator of the thermal stability).

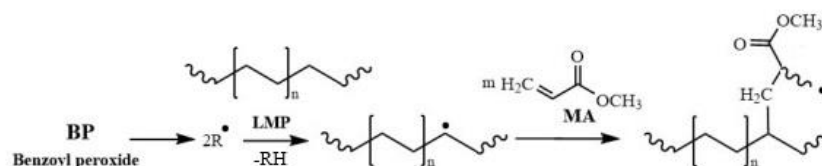
Physical and mechanical studies were performed using an AG-X Plus tensile testing machine (Shimadzu). The measurements were performed according to the ASTM D 638-14 "Standard Test Method for Tensile Properties of Plastics." To determine the modulus of elasticity, stretching was performed at a rate of 1 mm/min up to a strain value of 0.3% and then at a rate of 20 mm/min.

RESULTS AND DISCUSSION

The synthesized copolymers were white, powdery substances that were insoluble in water or organic solvents. The compositions of the copolymers, *GD* and *GE*, depended on the ratio of LMP to MA in the reaction mixture (Tables 1 and 2).

The formation of the copolymer was evidenced by its ethereal number, which increased with an increase in the proportion of MA in the reaction mixture (Table 1). The weight of the grafted copolymer (m_2) in all experiments exceeded the weight of the LMP used for synthesis (m_1) (Table 2). Grafted copolymers with various compositions and *GD*s were synthesized by varying the ratio of LMP to MA in the reaction mixture. The *GE* reached a maximum when the reaction mixture had an initial LMP:MA ratio of 50:50 ($GE = 53.3\%$). These

results indicate the essential role of the MA homopolymerization reaction. The proposed sequence for grafting the MA units onto LMP is shown in Scheme 1.



Scheme 1. The proposed sequence for grafting the MA units onto LMP.

Chain growth can be restricted by the recombination or disproportionation of radicals, or by chain transfer. The *GE* data (Table 2) also indicate the essential role of the MA homopolymerization reaction.

The IR spectrum of LMP (Figure 1) shows absorption bands at 720 and 1462 cm^{-1} , which correspond to the pendulum and bending vibrations of the $-\text{CH}_2$ groups. A pair of strong absorption bands, characteristic of the symmetric and asymmetric stretching vibrations of the $-\text{CH}_2$ groups, was observed at 2920 and 2850 cm^{-1} . A weak absorption band appeared at 1377–1338 cm^{-1} , which suggests symmetrical deformation of the C-H bonds in the methylene groups.

Table 2. Dependence of grafting degree (*GD*, %) and grafting efficiency (*GE*, %) of methyl acrylate to low-molecular-weight polyethylene ratio, solvent: *o*-xylene, $T = 75\text{ }^\circ\text{C}$, $5 \times 10^{-3}\text{M}$ benzoyl peroxide initiator

№	Component concentration, mol %		m_2 g	m_1 g	m_3 g	<i>GD</i> , %	<i>GE</i> , %
	LMP	MA					
1	70	30	3.24	2.94	0.49	10.2	38.0
2	60	40	3.09	2.52	0.55	22.6	50.9
3	50	50	2.82	2.10	0.63	34.2	53.3
4	40	60	2.43	1.68	0.94	44.0	44.0
5	30	70	2.03	1.26	1.31	61.1	37.0

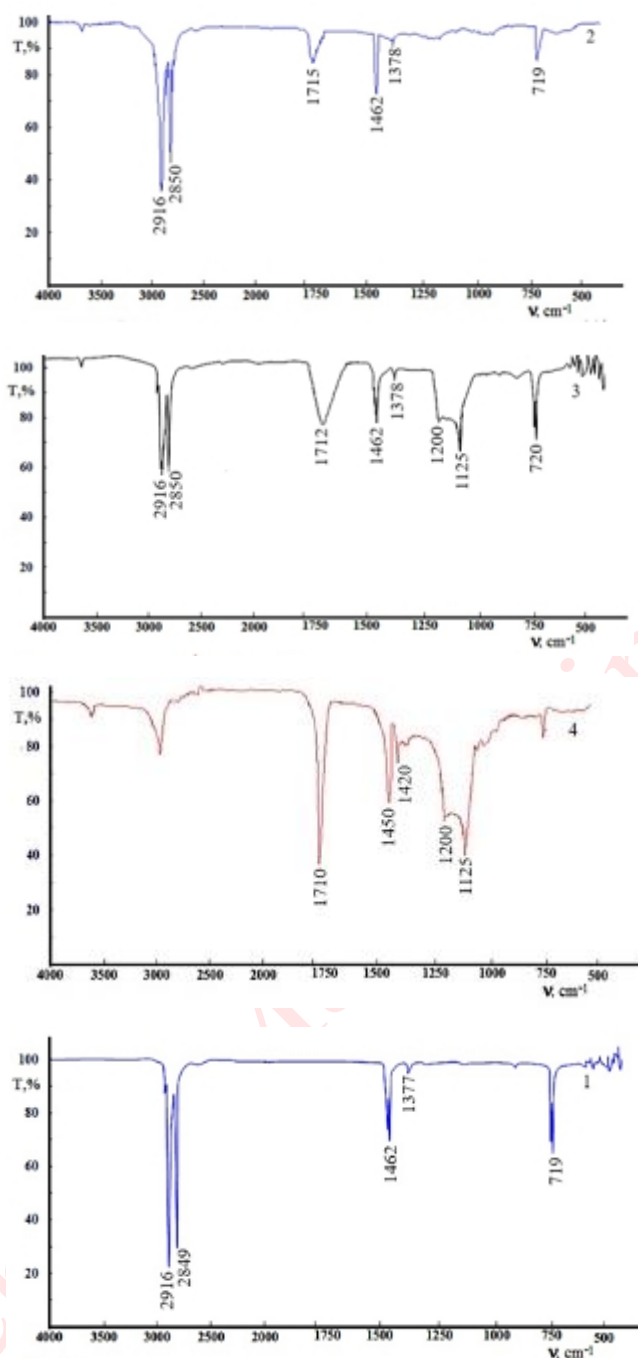


Figure 1. FT-IR spectra of (1) low-molecular-weight polyethylene, (2) grafted copolymers synthesized with molar ratios of low-molecular-weight polyethylene to methyl acrylate of 70:30, (3) 30:70, and (4) polymethyl acrylate.

The spectrum of polymethyl acrylate exhibits absorption bands at 1120–1125 cm^{-1} , which indicate the presence of C-O-C groups. The absorption band of methyl bound to oxygen was observed at 1420 cm^{-1} . The presence of the carbonyl group of the ester bond was indicated by the absorption band at 1710 cm^{-1} .

A doublet of strong absorption bands was observed in the region between 2920 and 2850 cm^{-1} in the spectrum of LMP-*g*-MA. This characterizes the symmetric and asymmetric stretching vibrations of the $-\text{CH}_2$ groups. A new band appeared with a maximum in the region of 1710–1715 cm^{-1} , characteristic of the C=O groups of the MA ester bond. Absorption bands of the stretching and bending vibrations of the C-O-C groups

appeared in the regions of 1200 and 1125 cm^{-1} . The intensity of these absorption bands increased as the content of MA units in the grafted copolymer increased. Thus, the FTIR results confirmed the formation of the grafted copolymer.

The X-ray diffraction pattern of LMP showed reflections at $2\theta = 21.69^\circ$ and 23.97° , corresponding to the (110) and (200) crystal planes, respectively (Figure 2). The X-ray diffractograms of LMP-g-MA (Figure 2) show reflections corresponding to the (110) and (200) crystal planes in the region $2\theta = 21^\circ$ and 24° , respectively. The intensity of the reflections decreased with increasing MA content in the grafted copolymer. At an angle of $2\theta = 36^\circ$, a reflection of the (020) crystal plane was observed, which decreased and narrowed with increasing MA content. The grafting sequences of the MA units may disrupt the order of the crystalline planes in polyethylene, and with an increase in their content, the crystalline phase in polyethylene becomes less prominent.

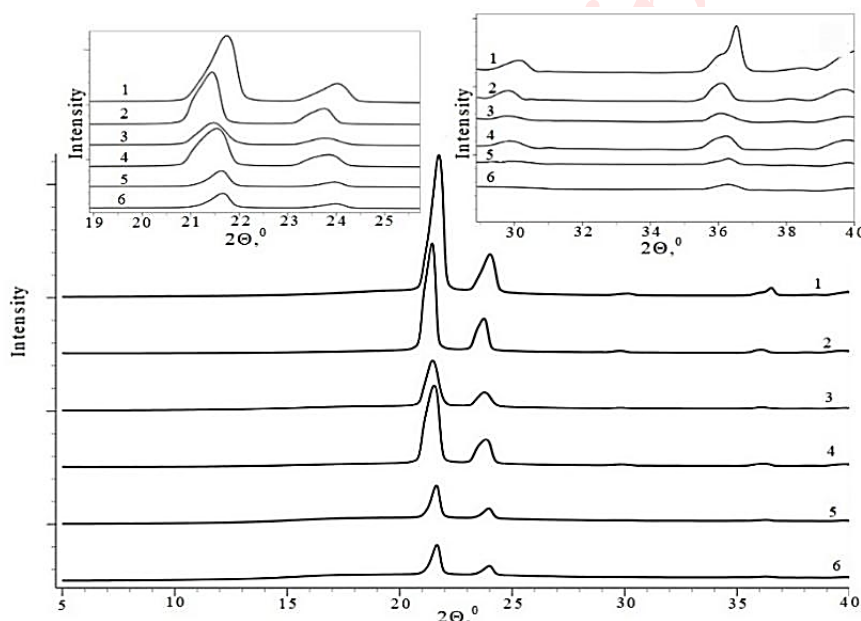


Figure 2. X-ray diffraction patterns of the initial low-molecular weight polyethylene (1); grafted copolymers synthesized with molar ratios of low-molecular-weight polyethylene to methyl acrylate of 70:30 (2), 60:40 (3) 50:50, (4) 40:60 (5), and 30:70 (6).

For the copolymers, the X-ray scattering angle (2θ) depended on the MA content (Table 3). Sequential grafting of MA units led to a shift in the value of 2θ towards smaller angles compared to that of LMP. This applies to the (110), (200), and (020) planes. Moreover, the greatest shift was observed for LMP-g-MA synthesized with MA contents of 30–40 mol% in the reaction mixture. A further increase in the MA content led to an increase in 2θ , which, nevertheless, remained lower than the corresponding value for unmodified LMP.

These results suggest that methylacrylate grafting leads to the deformation and amorphization of the crystalline phase, with the most significant changes occurring at specific component ratios.

Table 3. Crystal structure parameters for grafted copolymers synthesized with various ratios of low-molecular-weight polyethylene to methyl acrylate. Solvent: *o*-xylene, $T = 75\text{ }^{\circ}\text{C}$, $5 \times 10^{-3}\text{ M}$ benzoyl peroxide initiator.

(Co)polymer	Peak diffraction	Bragg angle 2θ , $^{\circ}$	Interplanar distance d , \AA	Peak half height β , $^{\circ}$	Crystallite size L_{hkl} , \AA
LMP	(110)	21.79	4.08	0.61	138.7
	(200)	24.05	3.70	0.66	128.1
	(020)	36.52	2.46	0.33	265.0
LMP-g-MA 30:70	(110)	21.68	4.10	0.45	186.9
	(200)	24.01	3.70	0.51	166.6
	(020)	36.37	2.47	0.77	114.0
LMP-g-MA 40:60	(110)	21.65	4.10	0.45	186.8
	(200)	23.98	3.71	0.49	171.7
	(020)	36.35	2.47	0.64	136.0
LMP-g-MA 50:50	(110)	21.53	4.12	0.61	137.9
	(200)	23.82	3.73	0.65	129.7
	(020)	36.18	2.48	0.74	119.0
LMP-g-MA 60:40	(110)	21.45	4.14	0.61	138.4
	(200)	23.75	3.74	0.65	129.9
	(020)	36.05	2.49	0.72	122.0
LMP-g-MA 70:30	(110)	21.46	4.14	0.31	269.0
	(200)	23.76	3.74	0.37	231.0
	(020)	36.05	2.49	0.60	145.6

The interplanar distance also depended on the MA content. The presence of grafted sequences of MA units in the copolymers led to an increase in the d value compared to that of LMP. This applies to the (110), (200), and (020) planes. The maximum d was observed for LMP-g-MA synthesized with an MA content of 30–40 mol% in the reaction mixture. A further increase in the MA content led to a decrease in the interplanar distance. Nevertheless, the interplanar distance remained higher than the corresponding value for unmodified LMP.

Grafting MA onto LMP altered its crystal structure, resulting in an increase in the interplanar distance within the crystal lattice. At all ratios, the grafted copolymer had a more amorphous structure than LMP.

The dependence of the crystallite size on the MA content was complex for the (110) and (200) planes. For the LMP-g-MA (70:30) copolymer, the value of L_{hkl} was higher than that of unmodified LMP. The LMP-g-MA 60:40 and LMP-g-MA 50:50 copolymers had crystallite sizes close to that of unmodified LMP. The crystallite sizes of LMP-g-MA (40:60) and LMP-g-MA (30:70) were larger than that of unmodified LMP but smaller than that of LMP-g-MA (70:30). A different pattern was observed for the (020) plane. The crystallite size decreased with increasing MA content in the copolymer.

Thus, the formation of grafted copolymers of LMP and MA led to changes in the supramolecular structure of LMP. Apparently, owing to the large number of grafted MA units, the copolymer molecules have difficulty in forming ordered structures.

Grafted copolymers can be used as modifiers in composite materials to improve the thermal stability [24, 25]. The effects of LMP-g-MA on the properties of high-density polyethylene (HDPE) composites containing CB were studied. The grafted copolymers synthesized with LMP:MA molar ratios of 70:30 (LMP-g-MA 70:30) and 50:50 (LMP-g-MA 50:50) were used as additives. The mass fraction of CB was constant for all compositions and amounted to 2% by weight, which met the requirements of ISO 4427-1 “Plastic Piping Systems—Polyethylene (PE) Pipes and Fittings for Water Supply—Part 1: General”. For comparison, compositions similar to those of unmodified LMP were also obtained. Table 4 lists the MFR and thermal stability parameters of the composites.

Table 4. Physical and mechanical properties of carbon black-filled composite with LMP and graft copolymer LMP:MA. Concentration of carbon black = 2 mass%

(Co)polymer	Concentration (mass%)		Oxidation induction period (min)	MFR (g/10 min)	Tensile Stress at Yield (MPa)	Elongation (%)
	(Co)polymer	HDPE				
-	0	98.0	67.0	0.33	26.0	27,5
LMP-g-MA 70:30	0.5	97.5	79.4	0.33	-	-
	1.0	97.0	80.0	0.33	30.7	30.6
	3.0	95.0	95.9	0.36	36.2	28.0
LMP-g-MA 50:50	0.5	97.5	86.9	0.33	-	-
	1.0	97.0	92.2	0.33	35.3	22.3
	3.0	95.0	137.7	0.35	32.2	38,3
LMP	0	98.0	67.2	0.38	-	-
	0.5	97.5	63.3	0.39	-	-
	1.0	97.0	57.6	0.40	-	-
	3.0	95.0	56.8	0.41	-	-
	5.0	93.0	54.9	0.42	-	-

The introduction of grafted copolymers into the CB-filled HDPE composites resulted in a significant increase in the thermal stability. For the blends with 0.5% of the grafted copolymer, the oxidation induction period increased from 67 to 79 min for LMP-g-MA 70:30 and from 67 to 86.9 min for LMP-g-MA 50:50. Similar results were recently obtained for CB-filled HDPE composites in the presence of LMP and acrylic-acid-grafted copolymers [26]. Unlike the grafted copolymers, the presence of unmodified LMP in the CB-filled HDPE composite led to a slight decrease in the thermal stability.

The improvement in the thermal properties of CB-filled HDPE composites with the incorporation of grafted copolymers is possibly related to a decrease in the average size of the CB particles in the blend [26].

The samples of CB and mechanical mixtures of LMP-g-MA:CB obtained at mass ratios of 3:2 and 4:1 were examined using SEM (Figure 3). The CB powder contained agglomerates of particles in a wide range of sizes from 500 nm to 120 μm . In the LMP-g-MA (50:50) blend with a CB mass ratio of 3:2, particles with sizes ranging from 50 to 150 nm were observed. In the LMP-g-MA (50:50) composite with a CB mass ratio of 4:1, CB particles with sizes ranging from 50 to 100 nm were also observed. In the blend of grafted copolymers with CB, the agglomerated CB particles were dispersed and evenly distributed in the mixture. The range of CB particle sizes is significantly narrower in the presence of grafted copolymers. These results suggest that an interaction between the CB and the grafted copolymers may exist, leading to a more uniform distribution of particles in the dispersed phase.

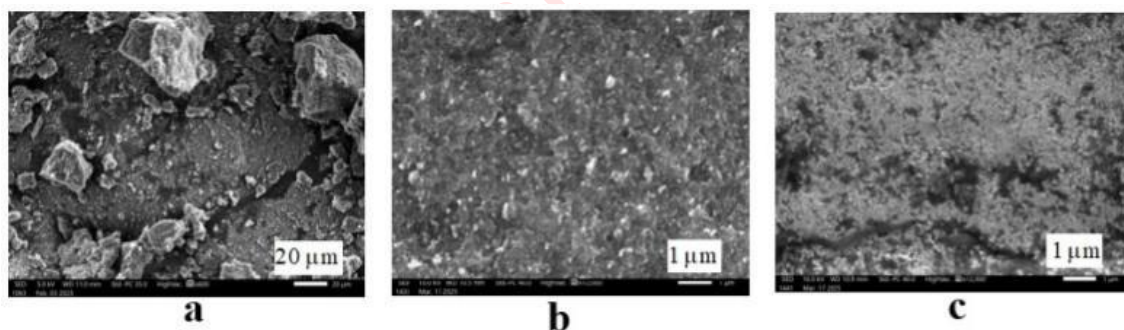


Figure 3. SEM images of (a) CB; (b) blend LMP-g-MA (50:50):CB = 3:2 mass ratio; (c) blend LMP-g-MA (50:50):CB = 4:1 mass ratio.

Atomic force microscopy (AFM) analysis (Figure 4) showed that in the absence of grafted copolymers in the HDPE:CB composite with a mass ratio of 98:2, elongated particles with a thickness of more than 1 μm and a length of up to 10 μm were observed. In the composites containing the grafted copolymers, particles of the dispersed phase with a rounded shape and a size of up to 500 nm were observed, with a more uniform distribution. HDPE:LMP-g-MA (70:30):CB = 95:3:2 mass% also contained agglomerates of elongated particles of up to 1 μm in size. In the presence of grafted copolymers, the particle size distribution is narrower compared to the composition obtained in the absence of grafted copolymers (Figure 5).

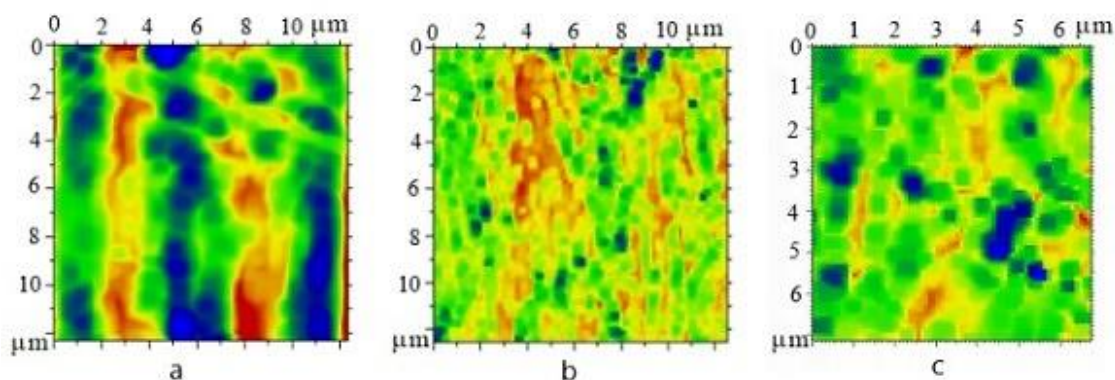


Figure 4. AFM images of surface of HDPE:CB = 98:2 mass% (a), HDPE:LMP-g-MA (70:30):CB = 97:1:2 mass% (b), HDPE:LMP-g-MA (70:30):CB = 95:3:2 mass% (c) composites.

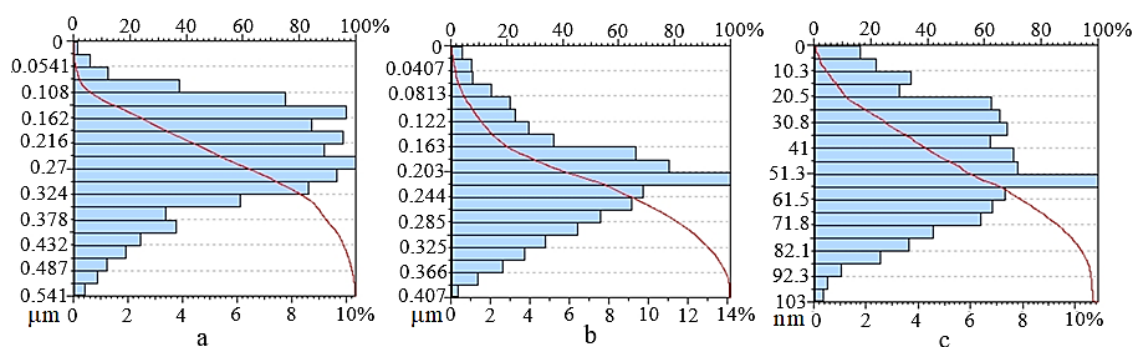


Figure 5. Particle size distribution on the surface of the composition: HDPE:CB = 98:2 mas% (a), HDPE:LMP-g-MA (70:30):CB = 97:1:2 mas% (b), HDPE:LMP-g-MA (70:30):CB = 95:3:2 mas% (c).

Because of its low molecular weight, LMP significantly increased the MFR of the composite; that is, it exhibits the properties of a lubricant. The grafted copolymers also increased the MFR. However, this effect was less pronounced than that of unmodified LMP (Table 4). As shown in Table 4, the presence of grafted LMP-g-MA resulted in an increase in the tensile stress at yield, whereas there is no correlation between elongation at break and the content of grafted copolymers in the composition. The improvement in thermal stability and tensile strength at yield of CB-filled compositions may be due to a decrease in the particle size of the dispersed phase and a narrowing of their distribution, observed in the presence of LMP-g-MA (Fig.3-5).

CONCLUSION

Low-molecular-weight polyethylene can be modified by graft copolymerization with methyl acrylate in solution in the presence of benzoyl peroxide as an initiator. Grafting sequences of MA units led to disruption of the supramolecular structure of LMP. Apparently, owing to the large dimensional volume of the grafted sequences

of the MA units, it is difficult for the copolymer molecules to transition to an ordered state. The synthesized copolymers are prospectively useful compatibilizers in the fabrication of carbon-black-filled high-density polyethylene composites. Grafted copolymers can be introduced into carbon black-filled HDPE blends to increase the thermal stability of the composite materials.

CONFLICT OF INTERESTS

The authors declare that there are no conflicts of interest to disclose.

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