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FUNCTIONALIZATION OF LOW-MOLECULAR-WEIGHT POLYETHYLENE BY MELT GRAFTING OF MALEIC ANHYDRIDE FOR USING AS A COMPATIBILIZER

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Abstract. In this study, functionalization of lowmolecular-weight polyethylene by melt grafting of maleic anhydride was investigated. The results reveal that initiator concentration, reaction time and temperature have the greatest influence on the graft degree. Structure of maleic anhydride grafted low-molecularweight polyethylene was proven by FTIR, DTA and XRD methods. The grafted low-molecular-weight polyethylene has a potential application as a compatibilizer for materials based on polyethylene compounds.

Keywords: low-molecular-weight polyethylene, melt grafting, functionalization, grafting degree, compatibilizer.

1. Introduction

Currently, polyolefins (polyethylene, polypropylene, *etc.*) are widely used in different areas of industry and are large-tonnage thermoplastics. Materials based on these polymers are flexible, strong, water-resistant, comfortable to wear, safe and inexpensive. Approximately one-third of the produced capacity of polyolefins is used in the packaging industry, and this quantity will continue to grow.¹⁻³

Polyolefins can be used as a matrix for creating polymer composites, which consist of polymers with inorganic or organic additives. Polymer composites are multi-phase materials in which reinforcing fillers are integrated with the polymer matrix, resulting in synergistic mechanical properties that cannot be achieved from either component alone.⁴ Polymer composite materials based on polyethylene filled with inorganic and organic additives have special properties. The particular characteristics of polymer composites make them very useful in daily life as engineering materials for aerospace, sporting goods, construction, electronics, *etc*.

One of these polymer composites are biodegradable materials based on polyolefins and natural polymers. The need for such polymer systems is increasing due to the deterioration of the environmental ecosystem. It is known, there are biodegradable compositions based on polyolefins and natural polymers such as starch,⁵ cellulose,⁶ chitosan.⁷ Due to good degradability and reasonable mechanical properties, LDPE/starch composites are being widely used as a biodegradable material in a packaging industry.^{3, 8-11}

Fillers for polymers vary in their chemical structures, sizes, shapes and other properties. Most fillers (for instance, mineral fillers) are stiff and are not compatible with the host matrix, thus forming a different disperse phase inside the matrix.¹² Polyethylene (PE) is a nonpolar polymer, which makes it difficult to apply as a matrix for polymer composites because of its low surface energy, poor adhesion, weak dyeing capability and poor compatibility with polar materials.¹³ To improve the performance of polyolefins, they are functionalized by the introduction of different polar groups into their structures. An effective way to develop the application of polyolefins is grafting modification, which endows polyolefins with additional properties besides their original properties.^{14,15} There are several grafting methods, such as solution-, melt-, solid phase-, and radiation-induced methods.

Maleic anhydride (MAH)-modified polyolefins are the most important class of functionalized polyolefins and have been widely used in industrial applications, due to their unique combination of low cost, high activity and good processability.¹⁶ They are used as impact modifiers, anticorrosive coatings for metal pipes and containers, metal-plastic laminates for structural use, in multilayer sheets of paper for chemical and food packaging, *etc.*^{17,18} Grafting polyolefins with maleic anhydride are a technique used for the preparation of copolymers

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that can act efficiently as coupling agents in plastic composites containing metals, inorganic fillers, fibers or any other polar filler or reinforcement.^{19,20} They can also be used in the compatibilization of polar and non-polar immiscible blends.^{21,22} Compatibilization is a method used to improve the properties of immiscible and partially mixable blends; it is a useful approach to set up the interfacial tension between blended components. The compatibilizer can improve the adhesion between the blended components by improving the stress transfer from one phase to another phase. When the stress transfer between blended components is effective, the resulting blends show improved performance.⁴ The application of compatibilizers helps to improve the filler/matrix interface and effectively utilize the interactions between the two counterparts.

Polyethylene wax (PEW) is a low-molecularweight polyethylene produced by the pyrolysis process. It is widely used in polymer composites because of its good mechanical properties, low cost and versatility. PEW has low melting temperatures compared to polyolefins and a significantly reduced melt viscosity. It is a good compatibilizer for composite materials based on polyethylene, polypropylene, polyvinyl acetate, butyl rubber, *etc.*²³⁻²⁵ However, one of its disadvantages is the high hydrophobicity due to the lack of reactive functional groups on the main chain. To improve its properties for the use, PEW is modified with various methods,²⁶ including functionalization with acrylic acid, maleic anhydride and others,^{27,28} and was used to expand the adhesion properties of ultrahigh-molecular-weight polyethylene²⁹ for chemical surface modification of fillers, in particular, calcium carbonate particles.³⁰

Functionalized low-molecular-weight polyolefin (in particular, polyethylene wax) is of interest for use as a compatibilizer. First, the functionalization reaction is easier than other materials due to its low molecular weight, and second, its melting temperature is lower than that of polyolefins, which enables it to spread through the volume of polymers faster and exhibit a compatibilizing effect. The process of functionalization of these materials can be carried out in a typical reactor. Lower melting temperatures also assist processing at temperatures that are considerably lower than those used in the extrusion processing of traditional polyolefins. The free radical mechanism of the reaction can be used to achieve a much higher grafting degree (GD) of functionalization with these materials in a batch process compared to the extrusion processes. The comparatively high degree of grafting and low viscosities of these functionalized lowmolecular-weight polyolefin products provide opportunities for their potential use in applications.³¹

The modified PEW has become one of the most important classes of functional polyolefins in industry.

The grafting of MAH onto PEW can be successfully achieved by using different methods, such as solution. melt, and solid-state routes and the microencapsulation method.³²⁻³⁵ PEW-g-MAH considerably improves the interfacial interaction between the components in polymer blends and polymer composites to improve the physical properties and compatibility with polar polymers. In this case, the GD of MAH groups has a substantial impact on the material and the efficiency of the process. For applications of PEW-g-MAH, it is important to investigate the effects of different factors (the concentration of reagents, temperature, duration, etc.) on the GD and optimize the experimental conditions to increase the GD, meaning that a high GD is required.^{36,37} In previous reports, the authors tried to synthesize PEW-g-MAH with a high GD, and the highest GD was less than 1.5 %.^{38,39} Using ultrasound and co-irradiation can increase the GD of PEW-g-MAH to 1.57 %.⁴⁰

In this study we obtained MAH-grafted lowmolecular-weight polyethylene with a high GD by melting and studied its structure.

2. Experimental

2.1. Chemicals and Reagents

Low-molecular-weight polyethylene (LMPE) with a number-average molecular weight (Mn) of 1000– 2000 was supplied by "Uz-Kor Gas Chemical" Co. Ltd., Uzbekistan (flakes with a melting point of 383 ± 10 K and a density of 0.95 ± 0.02 g/cm³ (298 K)). Benzoyl peroxide (BP, 75 %) as a free radical initiator, maleic anhydride (MA, 98 %) as a monomer, styrene (99 %) as a chain transfer agent, acetone (99.5 %) as a wash solution for products and xylene (90 %) as a solvent for the initiator were purchased from Sigma-Aldrich (USA). Lowdensity polyethylene (LDPE), (MFI 3.2 grade, produced by "Shurtan Gas Chemical Complex" Comp. Ltd., Uzbekistan) was used as a polymer matrix. Corn starch was supplied by Amylco LLC (russia).

2.2. Synthesis

The experiment was performed in a three-neck 250 mL round-bottom flask with a magnetic stirrer, a nitrogen inlet, and a thermometer. In a typical experiment, the reaction flask was heated in an oil bath to melt the LMPE. When the LMPE was melted completely, selected amounts of MAH and styrene were added into the flask. When the system reached homogeneity, the initiator dissolved in xylene was added to the reaction flask. A small nitrogen flow passed through the flask during the whole reaction process.

After reaching the desired time, the reaction was stopped, and the grafted copolymer was precipitated in acetone. The precipitate was washed with acetone and filtered repeatedly to remove unreacted MAH and then dried in a vacuum oven at 333 K to a constant weight.

2.3. Preparation of the Compositions

The preparation of the compositions was carried out under the action of a high-temperature laboratory rotary mixer by Brabender at 463 ± 2 K. The mixture was grinded for 20 min at 30 rpm. The films from blends were produced in a thermal press (Model CMP 30) at 463 ± 2 K for 10 min at 250 N/cm² pressures.⁸

2.4. Determination of the GD

The GD was determined by a titration method. A small amount of the purified LMPE-g-MAH was dissolved in xylene, and the solution was titrated to a thymol blue end point using potassium hydroxide in ethanol (0.1N). Grafted samples were completely soluble and did not precipitate during the titration. The GD was calculated using the acid number (AN):⁴¹

$$AN = \frac{V_{KOH} \cdot N_{KOH} \cdot 56.1}{W_{elMP}};$$
(1)

$$GD(\%) = \frac{AN \cdot 98}{2 \cdot 561},$$
 (2)

where V_{KOH} and N_{KOH} are the consumed volume (mL) and the equivalent concentration (*N*) of potassium hydroxide in ethanol, respectively.

2.5. Methods of Analysis

Fourier Transform Infrared Spectroscopy (FTIR). The evidence of functionalization as well as its extent was determined by FTIR spectrometer "Inventio-S" (Bruker, Germany). FTIR spectra were recorded from 500 to 4000 cm⁻¹.

Characterization by wide-angle X-Ray Diffraction. The purified neat LMPE and LMPE-g-MAH were ground into powders and then made into thin films with a smooth surface with a thickness of 1 mm. Wide-angle XRD was carried out with an XRD "MiniFlex 600" (Rigaku, Japan) in reflection mode. Cu–K α radiation was employed as a radiation source. The scanning range was 5–40° at a rate of 2°/min. The generator was operated at 40 kV and 15 mA.

Thermal Analysis (DTA). The thermal properties of the melting temperature (T_m) of neat LMPE and LMPE-g-MAH were recorded with STA TG-DTA/DSC "STA PT 1600" (Linseis, Germany) by heating ~5 mg of samples at 10 K/min under an air atmosphere from an ambient temperature to 473 K. The results obtained by DTA are used to calculate the percentage of crystallinity (χ , %) and the activation energy of thermooxidative destruction (E_a , kJ/mol).

Determination of the melt flow index (MFI). The MFI value refers to the amount of polymer that is extruded through a known given orifice (die) and is expressed as a quantity in g/10 min. The MFI of polymer compounds was determined by a DH-MI-BP tester. Polymer compound powders were introduced into a heated barrel, at the bottom of which there is a die with a known bore diameter (2.095 mm). Once the bore was full, a piston was placed in the barrel with a known dead weight on the top of it. The extruded samples were cut and weighed, and the MFI value was calculated.

Mechanical properties of polymer composite films. Measurements of the mechanical properties of the films were performed using a tensile tester "AG-X plus" (Shimadzu, Japan) according to the standard methods at a 50 mm/min crosshead speed. Ribbon-shaped specimens that were 50 mm long and 15 mm wide were used for the measurement of the tensile strength and the percentage of elongation.

Morphology. Morphology of composition films was observed by an optical microscope "BA 210 Digital" (Motic, USA).

Transparency. Transparency of composition films was studied by the UV-spectrophotometer "Specord 210 UV-VIS" (Analytic Jena, Germany)

3. Results and Discussion

A simplified grafting mechanism is shown in Scheme 1.

According to the classic mechanism, the reaction starts thermal decomposition of BPO with the formation of radical (Eq. 3). The radical attacks the polyethylene chain, and the active center appears on the polymer chain (Eq. 4). After the grafting reaction begins (Eqs. 5, 6), the reaction finishes according to Eq. (7).

We investigated the influence of different factors (the BP concentration, MAH concentration, reaction time, reaction temperature) on the GD of LMPE-g-MAH.

The results showed that among the tested factors, the initiator concentration has the greatest influence on the GD, and the GD mostly increased with increasing concentrations of BPO (Fig. 1a). It is well known that the grafting reaction depends on the amount of free radicals. GD was the highest when the BP concentration was 3 %. Increasing the concentration of BP to 4 % slightly influenced the GD, and it showed a very little change. When the concentration of initiators is too low, the quantity of free radicals is not enough to initiate the LDPE chain to form macroscale free radicals, which leads to a lower GD.



Fig. 1. Effect of initiator concentration (a), temperature (b) and time (c) on the GD. For (a): the temperature 388 K, reaction time 120 min; for (b): initiator concentration 2.66 %, reaction time 120 min; for (c): initiator concentration 2.66 %, reaction time 120 min

The reaction temperature has also a substantial effect on the GD (Fig. 1b). In the first stages, the GD increases until the temperature reaches 383–388 K and

then decreases. High temperatures increase the reaction speed (Eq. 3); however, most initiators have a certain temperature and time of decomposition, so a higher temperature is not an appropriate way to induce a higher GD. The half-life of benzoyl peroxide depends on the temperature, and it is one hour at 365 K and one minute at 404 K.⁴² When the temperature was low, the GD was reduced because the decomposition rate of BP was very slow. The concentration of initiator free radicals was low, which was not favourable for the grafting reaction. The higher temperature decreased the GD because of the quicker decomposition of BP, which may have led to some unreacted radicals, thus quickly terminating the grafting reaction. The GD was affected by the reaction time, in which the GD increased rapidly in the first 2 h and then increased slightly (Fig. 1c). In the initial stage, the concentration of MAH and the amount of macroscale free radicals was high, so there were more chances for

the monomer MAH and the macroscale chain free radicals to collide, so the GD increased rapidly. However, the concentration of MAH and the amount of macroscale free radicals decreased as the reaction continued, so there were fewer chances for the monomer MAH and the macroscale chain free radicals to collide, and the GD increased only slightly.¹⁵

As mentioned above, the samples were synthesized under different conditions by changing the initiator concentration, reaction temperature and reaction time. The sample abbreviations and reaction conditions are given in Table 1.

IR spectroscopy was used to characterize the grafted products. The IR spectra of LMPE and LMPE-g-MAH are shown in Fig. 2.

Table 1. Sample abbreviations and reaction conditions

Sample abbreviation	Ratio of LMPE:MAH	BP, %	Reaction time, min	Reaction temperature, K	AN	GD, %
LMPE-g-MAH-1	9:1	0.66	120	388	52.7	4.6
LMPE-g-MAH-2	9:1	1.33	120	388	91.6	8.0
LMPE-g-MAH-3	9:1	2.66	120	388	104.0	9.1
LMPE-g-MAH-4	9:1	1.33	240	388	99.6	8.7



Fig. 2. The IR spectra of LMPE and LMPE-g-MAH (from up to down): LMPE; LMPE-g-MAH-1; LMPE-g-MAH-2; LMPE-g-MAH-4; LMPE-g-MAH-3

Compared with the spectrum of LMPE, the spectrum of LMPE-g-MAH had some new peaks, which are the characteristic absorption peaks of the grafted MAH, while these peaks were absent in the neat LMPE. Increasing the initiator concentration and the reaction time leads to the appearance of peaks at 1780 cm⁻¹ due to the symmetrical and unsymmetrical stretching modes of C=O. Similar results were obtained by Youngjun *et al.*,⁴³ who used carboxylic acid (1790–1780 cm⁻¹) to verify the grafting of MA onto PE.

It has been shown that the intensity of peaks increased with increasing reaction time, and the BP content increased from 0.66 to 1.33 %, which led to an increase in the graft percentage. The absorption of carbonyl was shifted to a lower wavenumber with an increasing GD. These results show that MAH was grafted onto the LMPE backbone successfully.

To study the change in the structure of LMPE-g-MAH, X-ray and thermal analyses were carried out and compared.

Possible changes in the crystal structure and crystallinity between LMPE and the grafted LMPE were characterized by a wide-angle XRD. X-ray investigations showed that after the grafting modification, the symmetry and regularity of the molecular structures changed; correspondingly, the crystallization behavior changed (Fig. 3).

Increasing the reaction time and initiator concentration decreased the degree of crystallization, and the lateral widths of the crystals in the [110] and [200] directions were reduced. The introduced polar groups increased the surface energy and decreased the regularity of the LDPE structure. The crystal structure parameters of LMPE and LMPE-g-MAH were calculated (Table 2).

The interplanar crystal spacing of LMPE-g-MAH changed only slightly compared with that of LMPE (Table 2), and the degree of crystallization decreased.

DSC analyses showed, that a melting temperature and a crystallization temperature depend on the GD of samples (Figs. 4 and 5), *i.e.*, the higher GD is, the higher the melting temperature and the crystallization temperature, however these figures are lower than that of LMPE.



Fig. 3. X-ray diffraction of LMPE and LMPE-g-MAH: LMPE 91); LMPE-g-MAH-1 (2); LMPE-g-MAH-2 (3); LMPE-g-MAH-4 (4) and LMPE-g-MAH-3 (5)

The results of the calculations of χ obtained by thermal and X-ray structural analyses show that despite some differences in the absolute values of χ obtained by independent methods, there is a general tendency of a gradual decrease of crystallinity with increasing GD, that is directly proportional to BP concentration (Fig. 5).

The χ values obtained by different methods are not identical because these methods are based on the study of different physico-chemical phenomena. The χ of the polymer, determined by XRD, is proportional to the total number of microvolumes of ordered (crystalline) regions of the polymer, contributing to the coherent scattering of X-rays. In the case of determining χ by a thermal analysis, the fraction of polymer macromolecules capable of absorbing energy under thermal action and passing from an ordered to a disordered (molten) state is taken into account.

The energy of activation (E_A) of the thermal oxidative destruction of the synthesized LMPE-g-MAH samples is calculated by using Coats-Redfern method.⁴⁴ It was revealed that the dependence of the E_A of thermooxidative destruction on the initiator concentration has a non-monotonic character (Fig. 6).

At low initiator concentrations, the LMPE is partially functionalized in the presence of cyclic groups, which creates additional steric obstacles to the crystallization process. As a result, χ is decreased to values lower than LMPE. These samples with low degrees of protection correspond to relatively low E_A values.

An increase of initiator concentration leads to an increase the GD of LMPE-g-MAH, which probably contributes to the formation of stronger intermolecular bonds; as a result, higher E_A values are required for their destruction.

To study the possibility of using the synthesized LMPE-g-MAH as a compatibilizer, pilot studies were carried out to obtain composite films based on LDPE and starch.

Samples	Miller indices, hkl	2θ, °	<i>d</i> , Å	β_0 , rad	L_{hkl} , Å	χ, %	
IMDE	110	21.3	4.16	$1.74 \cdot 10^{-3}$	898.94	62.6	
	200	23.6	3.77	1.74·10 ⁻³	902.45		
LMPE-g-MAH-1	110	21.3	4.16	$1.74 \cdot 10^{-3}$	898.94	56.2	
	200	23.7	3.74	$2.61 \cdot 10^{-3}$	601.80	50.5	
LMPE-g-MAH-2	110	21.2	4.17	$2.61 \cdot 10^{-3}$	599.22	53 7	
	200	23.5	3.77	$1.74 \cdot 10^{-3}$	902.37	55.7	
LMPE-g-MAH-3	110	21.2	4.18	$1.04 \cdot 10^{-3}$	1498.00	42.2	
	200	23.6	3.77	$2.09 \cdot 10^{-3}$	752.04	42.2	
LMPE-g-MAH-4	110	21.4	4.15	1.74.10-3	899.01	19.8	
	200	23.7	3.75	$2.09 \cdot 10^{-3}$	792.18	т <i>У</i> .0	

 Table 2. Crystal structural parameters of LMPE and LMPE-g-MAH

Notes: 2θ is two times the diffraction degree; *d* is the interplanar crystal spacing; β_0 is a full width at half maximum; L_{hkl} is the thickness of the crystal; χ is the degree of crystallization









Fig. 5. Dependence of the degree of crystallinity (χ) on the BP concentration according to different methods: XRD (1) and DTA (2)





Scheme 2. Schematic illustration of compatibilizer action

	Table 3.	The MFI	of PE/starch	compounds	and the	mechanical	properties	s of the films
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Composite	LDPE	LDPE/starch	LDPE/LMPE/starch			LDPE/LMPE-g-MA/starch		
Ratio	-	70/30	68/2/30	65/5/30	60/10/30	68/2/30	65/5/30	60/10/30
MFI, g/10 min	3.20	2.00	1.54	2.20	2.54	2.15	2.46	2.97
Tensile strength, MPa	18.0	5.5	6.1	7,8	8.3	12.2	13.5	14.8
Elongation, %	600	85	179	285	347	369	416	512
Transparency, %	99.8	84.0	87.0	88.8	90.0	94.0	96.5	97.0

Islom Turdikulov et al.



Fig. 7. Optical micrographs of composite films: LDPE/starch (a); LDPE/LMPE/starch (b) and LDPE/LMPE-g-MA/starch (c)

As it was mentioned above, the compatibilizer improves compatibility between polar and non-polar immiscible blends (Scheme 2) and has a good efficiency on the morphology and viscoelastic properties of polymer composites.

The MFI of the compounds and the mechanical properties and morphology of the films based on LDPE/ starch compounds were studied. The MFI is a measure of polymer flow characteristics, which are also known as the rheological properties in the molten state under a known applied pressure, and the MFI determines the flow characteristics of polymers.

The results presented in Table 3 and Fig. 7 show that the compounds obtained with the addition of LMPEg-MAH have high MFI values, the films have high mechanical properties and homogeneous distribution morphology compared to the PE/starch and PE/LMPE/starch samples. This is because LMPE-g-MAH plays an important role in increasing the compatibility of nonpolar polyethylene molecules and polar starch molecules.

4. Conclusions

MAH-grafted LMPE blends were obtained by the melting process. The optimal grafting experimental conditions were with a BP concentration of 2.66 %, an MAH concentration of 10 %, a reaction time of 120 min and a reaction temperature of 388 K. The GD reached 9.1 % under optimal conditions. The properties of the functionalized LMPE were characterized by titration, FTIR spectroscopy, contact angle measurements and thermal analysis. It was concluded that the degree of functionalized LMPE depends on the initiator concentration, time and temperature. It was found that the increase in the BP concentration led to the elevation in the GD, and the increase of the temperature elevated the GD, passing through a maximum value. It was determined that the crystallization energy of activation of LDPE-g-MAH was lower than that of LDPE. The degree of crystallinity of LDPE-g-MAH was reduced. It was found that the addition of LMPE-g-MAH to PE/starch composite improves mechanical properties and homogeneous distribution morphology of the film. LDPE-g-MAH has potential applications as the compatibilizer for polymer composite materials.

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ФУНКЦІОНАЛІЗАЦІЯ НИЗЬКОМОЛЕКУЛЯРНОГО ПОЛІЕТИЛЕНУ ПРИЩЕПЛЕННЯМ У РОЗПЛАВІ МАЛЕЇНОВОГО АНГІДРИДУ ДЛЯ ВИКОРИСТАННЯ ЯК КОМПАТИБІЛІЗАТОРА

Анотація. Досліджено функціоналізацію низькомолекулярного поліетилену внаслідок прищеплення розплавом малеїнового ангідриду. Встановлено, що концентрація ініціатора, час реакції та температура найбільше впливають на ступінь прищеплення. Структура низькомолекулярного поліетилену/малеїнового ангідриду була перевірена методами FTIR, DTA та XRD. Показано, що прищеплений низькомолекулярний поліетилен потенційноможна застосовувати як компатибілізатор матеріалів на основі сполук поліетилену.

Ключові слова: низькомолекулярний поліетилен, прищеплення розплавом, функціоналізація, ступінь прищеплення, компатибілізатор.