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THE INFLUENCE OF OLEIC ACID AND BENZOYL PEROXIDE AGAINST OLEIC ACID GRAFTED ONTO LLDPE

A.H. Ritonga[1,2], N. Jamarun[1,✉], S. Arief[1], H. Aziz[1], D.A. Tanjung[3] and B. Isfa[1]
[1]Department of Chemistry, Universitas Andalas, Padang-25163, Indonesia
[2]Department of Chemistry, Universitas Sari Mutiara Indonesia, Medan-20123, Indonesia
[3]Department of Agrotechnology, Universitas Medan Area, Medan-20223, Indonesia
✉Corresponding Author: novesarjamarun@sci.unand.ac.id

ABSTRACT

In this study, the graft copolymerization of oleic acid (OA) onto linear low-density polyethylene (LLDPE) was successfully prepared by free radical reaction using benzoyl peroxide (BPO) initiator in the molten state. The study aims to determine the influence of OA monomer and BPO initiator on the grafting degree (GD) percentage of LLDPE-g-OA and its characteristics. LLDPE, OA, and BPO were mixed in an internal mixer, purified using acetone and methanol to separate from the unreacted OA and the OA homopolymer. The results showed that the addition of 12 wt% of OA monomer and 5 wt% of BPO initiator achieved the maximum GD percentage. The presence of a small band at 1707.1 cm-1, which is the OA carbonyl group, indicated that OA had been grafted onto LLDPE. LLDPE-g-OA also displayed better thermal stability than neat LLDPE and has a melting point of 123 °C. There were significant morphological changes and increased mass percentage of elemental carbon after the OA monomer grafting onto LLDPE.

Keywords: LLDPE, Oleic Acid, Benzoyl peroxide, Graft Copolymer, LLDPE-g-OA.

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INTRODUCTION

In recent decades, polymer technology has been of particular interest to researchers and academics for further research and development, especially in polyolefin materials, such as polyethylene. Polyethylene is a non-polar material with low interface adhesion properties and poor compatibility with polar polymers.[1] Functionalization of polyethylene with polar monomers can be a solution to improve the interface adhesion of polyethylene with other materials. Generally, polyethylene functionalization is mostly achieved by the free-radical grafting method. In the grafting reaction, a covalent bond is formed between the monomer surface and the polymer chain, resulting in a copolymer with certain characteristics. The grafting method through the molten state has many advantages, including process simplicity and high reaction rate, low cost, low pollution, and high product yield. The grafting efficiency of a polyethylene material can also be increased by blending, selecting the right co-monomer, and increasing the concentration of radical initiators.[2] The linear low-density polyethylene (LLDPE) has wide commercial applications compared to other synthetic polymeric materials. The hydrophobic surface of LLDPE may limit its application to certain materials, which is overcome by grafting a polar monomer onto the LLDPE without significantly changing its original characteristics.[3,4] The monomers that are often grafted on polyolefin are unsaturated compounds, such as acrylic acid, maleic anhydride,[5–10] and glycidyl methacrylate.[11,12] Oleic acid (OA) can also be used as a monomer because it is a long-chain unsaturated fatty acid. This fatty acid is harmless, inexpensive, abundant, and completely biodegradable.[13,14] The grafting of OA as a monomer onto low-density polyethylene has been previously reported by Liu *et al.*[3] The functionalization of LLDPE with a reactive polar group has been extensively researched and developed. The results have shown an increase in interface adhesion and compatibility between LLDPE and inorganic or organic materials after the polar monomer was grafted onto the polyethylene. The functionalization of LLDPE with OA has never been developed.

Based on the advantages of OA mentioned above, OA also can increase the polarity of LLDPE so that its affinity with other polar materials increases.[3,4] The OA monomers can be grafted onto the LLDPE main

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chain to form an LLDPE-g-OA copolymer. The presence of a side chain of the carboxyl group in the LLDPE-g-OA copolymer can be used as a compatibilizer for polymer blends.[15–17] In the grafting method, the polymer material can be functionalized according to the properties possessed by the covalently bonded monomer without the influence of the basic structure and chemical properties to increase interfacial adhesion. An initiator crucially drives the grafting reaction. Without it, there would be no grafting reaction. Benzoyl peroxide (BPO) is an initiator widely used in the grafting process.[18,19] Polymer blends compatibility is indirectly influenced by the percentage of the grafting degree of a polymer material. Therefore the influence of monomers and initiators on the grafting degree needs to be analyzed. This research aims to determine the influence of OA as a monomer and BPO as an initiator in the grafting process of OA onto LLDPE in the molten phase using an internal mixer.

EXPERIMENTAL

Material

Linear low-density polyethylene, LLDPE (Asrene UF1810), with a density of 0.918 g/cm^3, was obtained from PT. *Chandra Asri Petrochemical* Tbk, Indonesia. Oleic acid, with a density of 0.895 g/mL, was provided by *Subur Kimia Jaya* Chemical Company, Indonesia. Benzoyl peroxide, xylene, acetone, methanol, acetic acid, potassium hydroxide (KOH), phenolphthalein were all chemical reagents obtained from Merck, Germany.

The Grafting Process of Oleic Acid onto LLDPE

The process of grafting the OA monomer onto LLDPE in the molten state was carried out using an internal mixer (Thermo HAAKE Polydrive) with a maximum capacity of 35 g. The internal mixer was set to a rotating speed of 100 rpm and a heating temperature of 160 °C. The neat LLDPE sample in the form of pellets was put into the mixing chamber of the internal mixer for five minutes until the LLDPE was completely melted. Then, the OA monomer was slowly mixed into the melted LLDPE, followed by the addition of the BPO initiator, with the composition shown in Table-1. The mixing process ran for 10 minutes. The product of the grafting process was removed from the chamber, cooled at room temperature, and cut into small pieces. The result was an unpurified LLDPE-g-AO in the form of granules.[3,20] Unpurified LLDPE-g-OA was weighed and put into a bottom flask containing 200 mL of xylene. Next, a reflux device was connected to a condenser and heated on a hotplate at 180 °C while stirring at 60 rpm until the LLDPE-g-OA dissolved completely. 80 mL of acetone was added to the LLDPE-g-OA solution to separate the OA homopolymer and the unreacted OA. The precipitate formed was filtered and washed with 150 mL of methanol (2 times). After that, LLDPE-g-OA was dried in an oven at 85 °C for 12 hours, stored in a desiccator for 24 hours, resulting in purified LLDPE-g-AO.[3]

Table-1: The Composition of LLDPE, OA, and BPO Various OA Monomers and BPO Initiators

Sample Code	LLDPE	OA	BPO	Sample Code	LLDPE	OA	BPO
	wt%	wt%	wt%		wt%	wt%	wt%
LLDPE	100	0	0	EOP-50	100	15	0
EOP-15	100	3	5	EOP-51	100	15	1
EOP-25	100	6	5	EOP-52	100	15	2
EOP-35	100	9	5	EOP-53	100	15	3
EOP-45	100	12	5	EOP-54	100	15	4
EOP-55	100	15	5	EOP-55	100	15	5

Determination of the Grafting Degree

The determination of the grafting degree (GD) percentage of LLDPE-g- OA was carried out as follows: A 0.4 g the LLDPE-g-AO sample was put into an Erlenmeyer flask containing 60 mL of xylene, heated until it dissolved completely, cooled, 2 mL of acetic acid 0.1 M was added into the xylene. Heating resumed for 2 hours, cooled. Three drops of phenolphthalein indicator were added to the mixture, titrated with KOH 0.1 M in ethanol. The titration was stopped when the indicator color changed. The volume of KOH added was recorded, and the grafting degree was calculated using the following equation[3]:

$$GD\ (wt\ \%) = \frac{V.N.M}{W}\ x\ 100\ \%$$

Where V is the volume of KOH/ethanol, N is the concentration of KOH/ethanol, M is the molecular weight of OA, and W is the weight of LLDPE-g-AO.

Characterization

Samples were analyzed for functional groups using Agilent Cary 630 FTIR spectrophotometer and measured at wavenumber from 650 to 4000 cm^{-1}. Thermal analysis was evaluated using TGA / DTA Hitachi STA 7300 series with a heating rate of 10 °C/min and a temperature from 30 to 600 °C. The morphology of the sample was observed using Scanning Electron Microscope (SEM) ZEISS EVO MA10 equipped with Energy Dispersive X-Ray (EDX) detector.

RESULTS AND DISCUSSION

Influence of the Oleic Acid Monomer on the Grafting Degree Percentage

Increasing OA monomer concentrations significantly increased the GD percentage of unpurified and purified LLDPE-g-OA, as shown in Fig.-1a. The increase occurred because the radicals from the initiator have many opportunities to attack OA monomers to form OA radicals. The increased number of OA radicals formed made it easier for OA radicals to graft onto the LLDPE. In the EOP-55 sample, there was a decrease in GD percentage, suggesting that excess OA monomers could disrupt the grafting process since the excess OA may hinder the radicals in attacking the LLDPE. There was also a tendency for OA radicals to interact with themselves, forming an OA homopolymer. Liu *et al.*,[3] have reported that increasing the amount of monomer will increase the GD percentage, but excess OA monomer could inhibit the grafting.

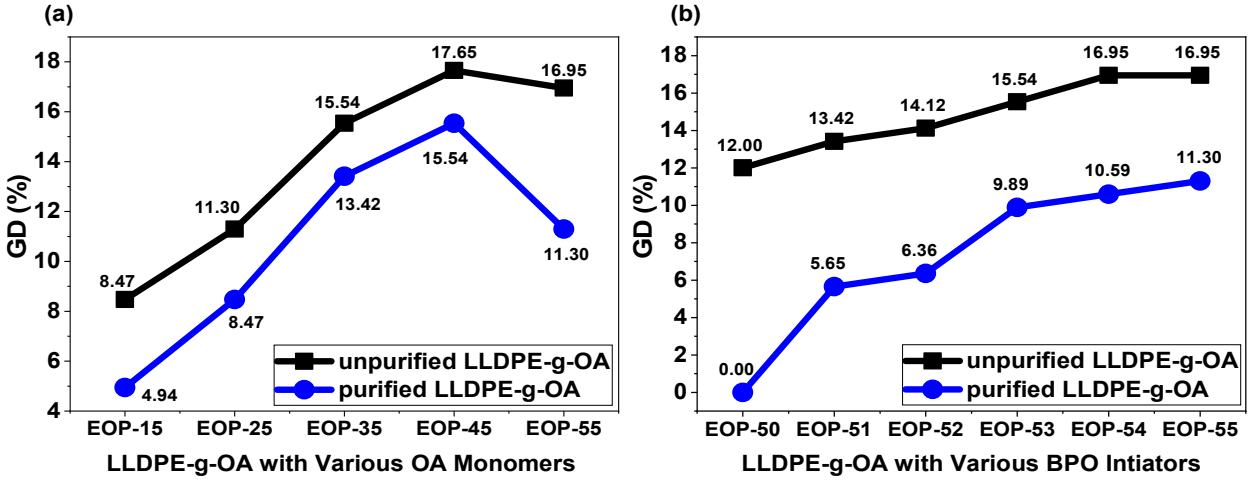

Fig.-1: The Grafting Degree of LLDPE-g-OA with various (a) OA Monomers, (b) BPO Initiators

Influence of the Benzoyl Peroxide Initiator on the Grafting Degree Percentage

Based on Fig.-1b, increasing BPO initiator concentration could increase GD percentage in the grafting process of OA onto LLDPE main chain. When the concentration of the BPO initiator was increased, the free radicals would also increase, making it easier for radicals to attack the OA monomers and LLDPE. However, if the BPO initiator were further added, there would be a macromolecular cross-linking reaction among the LLDPE radicals or the OA homopolymer. Liu *et al.*,[3] have reported that the rate of increase in the GD percentage was reduced due to the cross-linking between the polymer radicals and the homopolymer of OA, which formed due to the high concentration of initiators in the grafting process.

Fourier-transform Infra-red (FTIR) Analysis

The FTIR spectrum of neat OA, neat LLDPE, and LLDPE-g-OA with various concentrations of OA monomers can be observed in Fig.-2a. All spectra of the LLDPE-g-OA sample with various concentrations of OA monomers have similarities with the neat LLDPE spectrum. In the neat LLDPE spectrum, several sharp bands dominate at 2914.7-2847.6 cm^{-1}, 1461.1 cm^{-1}, 1371.7 cm^{-1}, and 723.1 cm^{-1}.

These bands are also present in all LLDPE-g-OA samples. In the neat OA spectrum, there is a band at 3600-2400 cm^{-1} which indicates the presence of a carboxylate group (–COOH). The OH band of the carboxylate group is distinct from the OH band of alcohol because the presence of dimers in carboxylic acid is based on their hydrogen bonds. The –OH band of the carboxylate group slants into the band of CH-aliphatic (the –OH band of the carboxylate group overlaps with the band of –CH aliphatic).[20] It is reinforced by the presence of a band at 1707.1 cm^{-1}, indicating the presence of a carbonyl (C = O) group from OA, and a small band at 1282.2 cm^{-1} indicates a stretching vibration C-O from the carboxylate group. The bands at 2914.7–2855.1 cm^{-1} show the stretching vibrations of aliphatic hydrocarbons (-CH), supported by bands at 1461.1 cm^{-1}, which indicates scissoring vibrations of methylene ($-CH_2$), and the band at 723.1 cm^{-1} indicates CH rocking vibrations. The presence of the carbonyl group from OA on LLDPE-g-OA has confirmed that OA has been grafted on to LLDPE.

This result contradicted Liu *et al.*,[3] who stated that the hydroxyl and carbonyl groups were visible when OA grafted onto polyethylene. It is known that the OA compound does not have a hydroxyl group with a broad and strong band. The band indicating the presence of hydroxyl groups on OA already overlaps with the aliphatic hydrocarbons. However, it does not mean that the LLDPE-g-OA compound does not have a hydroxyl group. Rather, it overlaps with aliphatic hydrocarbons.

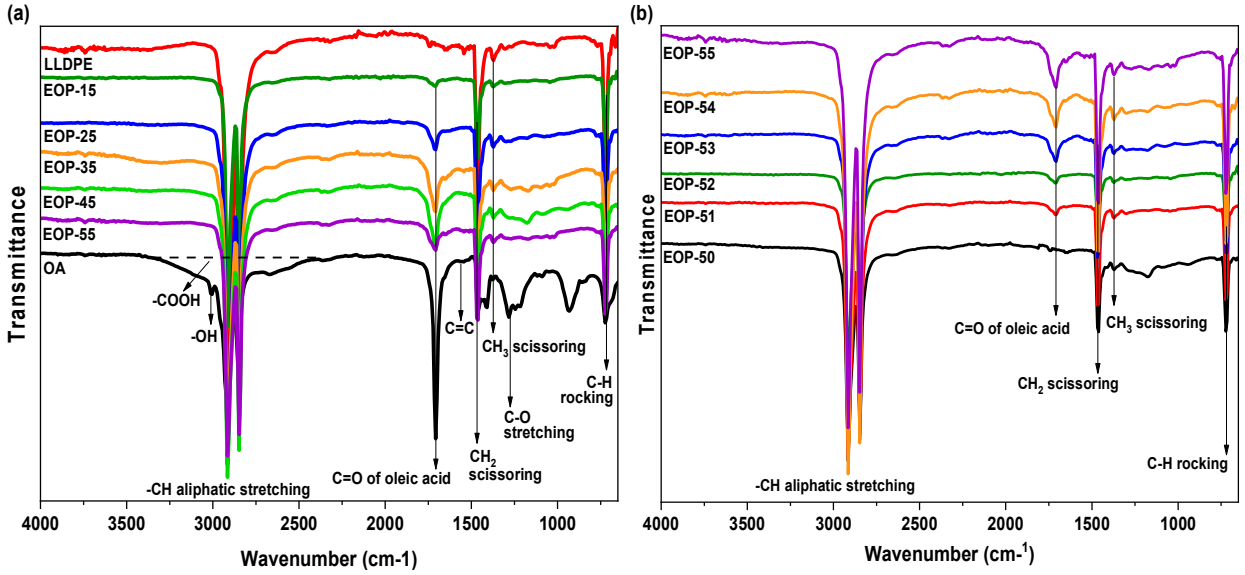

Fig.-2: FTIR Spectra of LLDPE-g-OA with various (a) OA Monomers (b) BPO Initiators

All samples of LLDPE-g-OA with various BPO initiators have similarities in the spectrum. A difference in the absorption band occurred at 1707.1 cm^{-1}, indicating a carbonyl group (C = O) from the OA grafting onto the LLDPE main chain. The EOP-50 sample does not have a small band at 1707.1 cm^{-1}. It showed that the EOP-50 sample had no OA grafted onto LLDPE because the BPO initiator was not added.

Thermal Analysis

Thermal analysis was carried out on neat LLDPE and LLDPE-g-OA samples to determine their thermal stability and degradation characteristics. The EOP-55 sample is LLDPE-g-OA, which is considered to be representative of two variables, namely OA monomer and BPO initiator. The thermal stability and properties of the two samples were investigated using Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA). Based on Fig.-3, the mass degradation temperature of 1% (T1%) was significant in that the LLDPE-g-OA sample degraded earlier than neat LLDPE. At T95%, there was a significant change, where LLDPE-g-OA degraded longer than neat LLDPE. Although the mass degradation temperature did not show significant differences, this confirmed that the LLDPE-g-OA sample had higher thermal stability than neat LLDPE. The DTA results showed an endothermic peak in the neat LLDPE and LLDPE-g-OA, indicating the melting point (Tm). The Tm of the LLDPE-g-OA sample was lower than neat LLDPE. Based on the analysis of thermal properties, it is known that neat LLDPE and LLDPE-g-OA

samples are semi-crystalline, according to Anjos *et al.*,[5] because an endothermic peak has been formed and no other transitions (glass transition, Tg) occurred before the melting point.

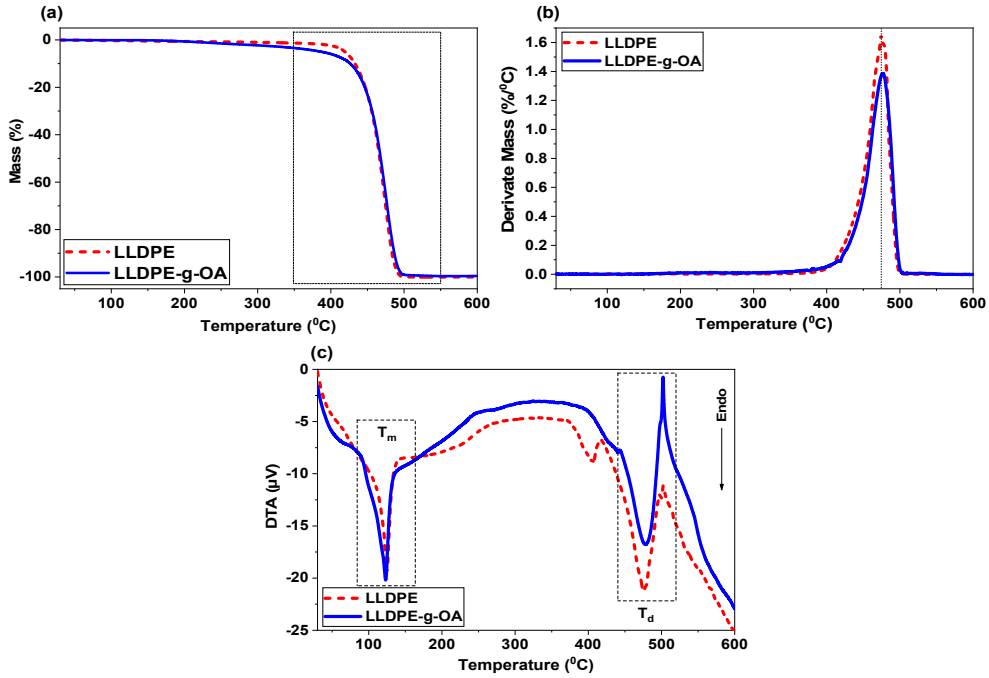

Fig.-3: (a) TGA, (b) DTG, (c) DTA Curves of neat LLDPE and LLDPE-g-OA

Table-2: TGA, DTG, and DTA Data of neat LLDPE and LLDPE-g-OA

Sample	$T_{1\%}$	$T_{5\%}$	$T_{95\%}$	T_{max}		T_m	T_d
	(°C)	(°C)	(°C)	(°C)	(%)	(°C)	(°C)
Neat LLDPE	277	419	487	474	68.4	125	475
LLDPE-g-OA	220	385	491	477	70.1	123	478

Morphological Analysis and Chemical Elements

The surface morphology of neat LLDPE and LLDPE-g-OA samples showed significant differences, as shown in Fig.-4.

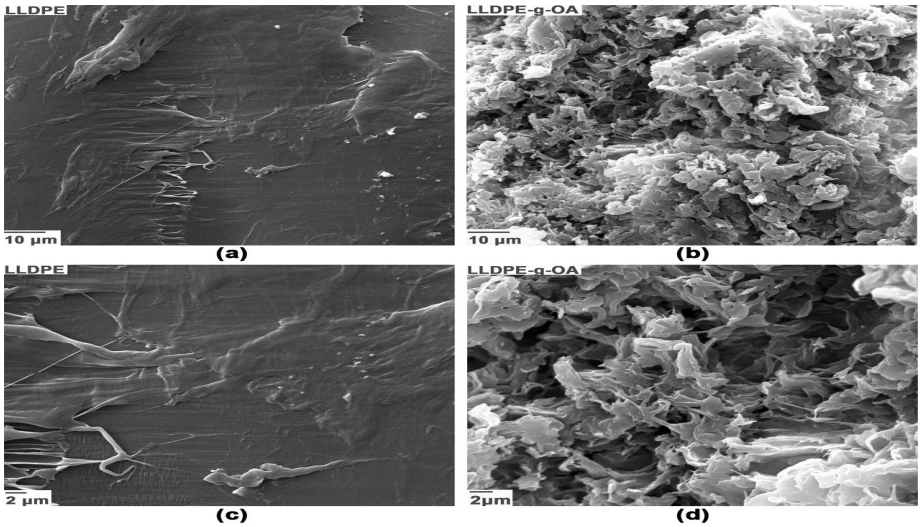

Fig.-4: SEM Micrographs of (a) Neat LLDPE, (b) LLDPE-g-OA at 2000x magnification, (c) neat LLDPE, (d) LLDPE-g-OA at 5000x magnification

Based on the morphology of LLDPE, it appeared that the surface structure was smoother, and the pores were smaller because of the slight branching of the LLDPE chain. The LLDPE-g-OA micrographs

showed that the surface structure was rough, and the pores were large. The grafting degree had a major influence on material morphology.[5,15] The surface structure of LLDPE-g-OA also appeared as hard lumpy shapes because the LLDPE-g-OA radical copolymer was bonded to each other to form LLDPE-g-OA copolymer. Long-chain LLDPE-g-OA copolymers resulted in large overlapping bifurcations. It caused a significant change in the morphology of LLDPE-g-OA. Based on the analysis of chemical elements using SEM-EDX, the mass percentage of the element carbon in neat LLDPE was 85.67%, while the mass percentage of the element carbon in LLDPE-g-OA was 91.28%. There was an increase of 6.55% in the mass percentage of the element carbon, indicating that the neat LLDPE compounds have been grafted with the OA monomer because the OA grafted onto LLDPE also contained many carbon atoms.

CONCLUSION

The graft copolymer of OA onto LLDPE was successfully prepared and characterized by a free-radical grafting process in the molten phase using a BPO initiator. The addition of OA monomer and BPO initiator to LLDPE increased the grafting degree percentage. The FTIR spectrum results showed that OA had been grafted onto LLDPE, as indicated by the appearance of a small band at 1707.1 cm^{-1}, which is associated with the carbonyl group from OA. The higher of grafting degree percentage of LLDPE-g-OA, the intensity of the small band on the carbonyl group increases. The TGA curve showed that the LLDPE-g-OA had better thermal stability than neat LLDPE, with a melting point of 123 °C. SEM micrographs showed significant changes in surface structure, and the EDX results showed an increase in the mass percentage of elemental carbon in LLDPE-g-OA.

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