Improved Maleic Anhydride Grafting to Linear Low Density Polyethylene by Microencapsulation Method

Iman Rahayu[1,*], Achmad Zainuddin[1], and Sunit Hendrana[2]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jl. Raya Bandung-Sumedang km. 21, Jatinangor, Sumedang 45363, West Java, Indonesia*

[2]*Laboratory of Applied Physics, Indonesian Institute of Sciences, Jl. Sangkuriang, Kompleks LIPI, Bandung 40135, West Java, Indonesia*

Abstract: *A common graft copolymerization method usually results in a low degree of grafting due to its poor inter-component interactions. A monomer microencapsulation method should be useful to enhance the current graft copolymerization technique. The maleic anhydride (MAH) grafted with linear low-density polyethylene (LLDPE) was successfully synthesized by monomer microencapsulation without using a direct method in order to find a high degree of grafting. The results showed that the degree of grafting of the LLDPE synthesized by microencapsulation (5.9%) was higher than that achieved with the direct method (5.0%).*

Keywords: *grafting; LLDPE; maleic anhydride; microencapsulation*

■ INTRODUCTION

The functionalization of polyolefin can increase its chemical and physical properties, leading to its wider application. Several methods that are widely used for functionalization are blending [1], surface treatment [2], and grafting [3-6]. There are several known types of the latter method, namely grafting in the aqueous phase [7], ultrasonic initiation [8], solid phase, photoionization [9], and free radical in the melting phase [10]. Among those methods, grafting by free radical in the melting phase using a polar monomer is one of the most frequently applied techniques due to its potential and wide applications [10-12].

To best of our knowledge, the functionalization of polyolefin through the free radical copolymerization by maleic anhydride (MAH) as the polar monomer is very popular in commercial applications due to its high activity [10, 13-14]. The use of MAH in the grafting process is preferable since it produces small oligomers, and no homopolymerization occurs [15-16]. Polyethylene-graft-maleic anhydride (PE-g-MAH) has been commercially used as fiberglass, anti-corrosive coating for metal pipes, paper for food containers, adhesives, and is compatible as PE for polar polymers such as polyamide and polyester [13,17-19].

The functionalization of MAH to polyolefin is conducted to homogenize the graft reactions of MAH-polyolefin with a high degree of grafting. This method is used to avoid the non-favorable side-product resulting from crosslink and chain-breaking reactions [10]. Rosales et al. investigated the graft of LLDPE with diethyl maleate (DEM) in different extrusion conditions, which resulted in a maximum degree of grafting at 0.5 moles [14]. Moreover, the grafting degree (GD) of LLDPE-g-MAH by ultrasonic initiator was 0.54% [8]. So far, the grafting process using MAH remains unsatisfactory, as indicated by the low grafting degree and heterogeneous functionalization of the chemical group. To overcome this problem, several techniques have been developed through the modification of the monomer, initiator, and synthesis method or graft copolymerization. The graft copolymerization of MAH to the LDDPE using the monomer microencapsulation method is a relatively new approach. Theoretically, it is based on the directed-diffusion of the termination step where monomer molecules are trapped inside the pore

of the polymer. Thus, the closer segmental-diffusion would improve the interaction between the polymer and the monomer.

In the present study, the graft copolymerization of MAH to LLDPE using the monomer microencapsulation method was developed and compared to the direct method. The grafting degree in the process of graft copolymerization of MAH to the polyolefin was also investigated. This study was aimed to synthesize the maleic anhydride (MAH) grafted with low-density polyethylene (LLDPE) using the monomer microencapsulation method and to determine its degree of grafting and crosslink.

■ **EXPERIMENTAL SECTION**

Materials

The materials used in this study included LLDPE (melt flow rate (MFR) 1 g.10 min^{-1} and ρ = 0.920 g.cm^{-3}) from Bassel, Inc., Indonesia, dicumyl peroxide/DCP (Aldrich), acetone (Merck), chloroform (Merk), maleic anhydride (Merk, p.a grade), and xylene (Merk, p.a grade).

Instrumentation

The instruments employed in this experiment involved Oven 6PHP-200 (Tabai), Haake Reomix 600p Roller Rotors R600, analytical balance, vacuum oven DP 33 (Yamato), soxhlet extraction apparatus, hot and pressure (Gonno), MFR (Dynisco Polymer Test), FT-IR spectrophotometer (Perkin Elmer), Nuclear Magnetic Resonance (Bruker Avance III 300 MHz), Differential Scanning Calorimetry (Mettler Toledo 1 Star), and Thermal Gravimetric Analysis (Mettler Toledo 1 Star).

Procedure

Synthesis of LLDPE by monomer microencapsulation

To a container holding 2 kg LLDPE (MFR 1 g/10 min and density 0.920 g.cm^{-3}), 100 mL of 5% MAH in acetone was added. The mixture was mixed thoroughly, and the container tightly closed. It was opened and stirred to evaporate the acetone every day for a week. Furthermore, the process was continued until 6 days in, at which point came the addition of 100 mL of 10% MAH in acetone. The sample was homogenized weekly for six months. Successful microencapsulation is indicated by a cloudy

solution. The microencapsulated polymer was named mLLDPE.

Synthesis of mLLDPE-g-MAH and LLDPE-g-MAH

To a mixing container, 50 g of mLLDPE and DCP, as an initiator with a concentration of 40% mol, was added and blended using Haake Rheomix 600p at 200 °C and a mixing speed of 40, 60, 80, and 100 rpm for 4 min. During the blending, the torsion value was recorded over time. Torsion is defined as the energy of rotation (Nm), which is used throughout the polymer blending process.

Analysis of grafting degree of LLDPE-g-MAH using titration

The sample was refluxed with xylene for 30 min before the temperature was lowered to 80 °C, which was followed by the addition of 0.2 M potassium hydroxide in ethanol. Reflux was carried out for another 15 min. Phenolphthalein was added to the reflux product, followed by the titration using 0.2 M of hydrochloric acid/isopropyl alcohol until the color changed from magenta to colorless. The grafting degree was calculated from the volume of hydrochloric acid/isopropyl employed in titration using Eq. (1) [7].

$$GD(\%mass) = \frac{N(V_o - V) \times 98.06}{2000W} \times 100\% \quad (1)$$

N = concentration of HCl/isopropyl alcohol (mol.L^{-1})
V$_o$ = volume of HCl/isopropyl alcohol used as a blank (mL)
V = volume of HCl/isopropyl alcohol used in titration (mL)
W = mass of sample (g)
98.06 = relative molecular mass of MAH

■ **RESULTS AND DISCUSSION**

Synthesis and Characterization of Grafted LLDPE

The change of torsion during the blending process using 40% of DCP at 80 rpm rotation rate indicated the different interactions of mLLDPE-g-MAH and LLDPE-g-MAH (Fig. 1). An obvious change of torsion between mLLDPE-g-MAH and LLDPE-g-MAH was observed from 0.3 up to 0.4 min, indicated by a sharp change of torsion value. At the beginning of the reaction, the first peak showed that the plasticization of LLDPE had occurred [10].
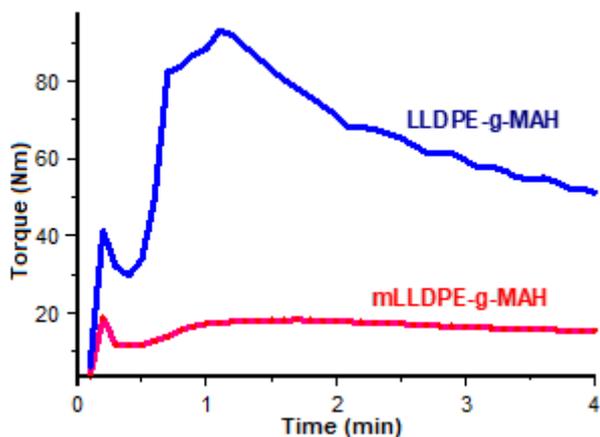
Fig 1. The plot of torsion over time for samples of mLLDPE-g-MAH and LLDPE-g-MAH (fabricated using 40% of DCP at 80 rpm rotation rate)

The second maximum peak or "cure peak" from LLDPE-g-MAH was higher than that of mLLDPE-g-MAH. This peak is known to be related to the viscosity [20]. Therefore, the high peak of LLDPE-g-MAH is indicating the formation of crosslinks within the sample. The results were supported by the torsion data (Fig. 1), where the torsion of mLLDPE-g-MAH was stable under 20 Nm, while that of LLDPE-g-MAH reached 50 Nm. Thus, it is suggested that the monomer encapsulation method could decrease the occurrence of the crosslink. The reason behind this observation is related to the theory of directed-diffusion, in which the polymer-monomer interaction is independent of the reactivity, but affected by the distance or physical interaction between the two. After the diffusion-translation occurred between the two propagated radicals, the diffusion-segmental between radicals of the polymer and monomer took place. Lastly, the chemical interaction between radicals would result in graft copolymerization of the monomer to the polymer.

Further evidence of the occurrence of crosslink in

LLDPE-g-MAH is presented in Table 1. The MFR value of mLLDPE-g-MAH was higher than LLDPE-g-MAH, which was immeasurable. A higher value of MFR reflects low viscosity of the sample, and hence it is diluted and flows easily [20]. In fact, LLDPE-g-MAH did not flow easily, indicating the gel formation due to the crosslink reaction. A high number of crosslinks in LLDPE-g-MAH is shown by the result of Soxhlet extraction (Table 1). The higher quantity of crosslinks in LLDPE-g-MAH was predicted to be formed at the "cure peak" (Fig. 1). This observation is in agreement with the theory of the mechanism of directed-diffusion. In a thick liquid, the reaction between polymer radicals is higher than the reaction between radicals of polymer and MAH, thus increasing the number of crosslinks in the product. Several analyses were performed to provide a better explanation of this phenomenon.

Fig. 2 shows the FT-IR spectra of mLLDPE-g-MAH and LLDPE-g-MAH after the extraction with acetone. The presence of maleic anhydride, which is attached to the LLDPE, is confirmed by the absorbance at wavenumber of 1720 and 1780 cm^{-1} for C=O stretching; at 1260 cm^{-1} for asymmetrical C–O–C stretching, and at 960 cm^{-1} for five-membered ring anhydride stretching [16].

Fig. 3 shows the FTIR spectra of the soluble fractions of mLLDPE-g-MAH and LLDPE-g-MAH. The successful maleation process is confirmed by the peaks at wavenumber between 1700 and 1800 cm^{-1}, i.e., 1720 and 1780 cm^{-1}. These absorptions are higher in mLLDPE-g-MAH than those in LLDPE-g-MAH. It indicates that the formation of succinic anhydride was higher than the maleic anhydride. However, the gel fraction showed a contrast result compared to the soluble fraction (Fig. 4).

Table 1. Values of MFR, monomer conversion, gel fraction, and grafting degree of mLLDPE-g-MAH and LLDPE-g-MAH (at 40% of DCP and 80 rpm rotation rate)

Parameter	mLLDPE-g-MAH	LLDPE-g-MAH
MFR (g/10 min)	0.89	Not detected
Monomer conversion (%)	59.7	53.3
Gel fraction (%)	68.3	79.8
Grafting degree (%)	5.92	4.98
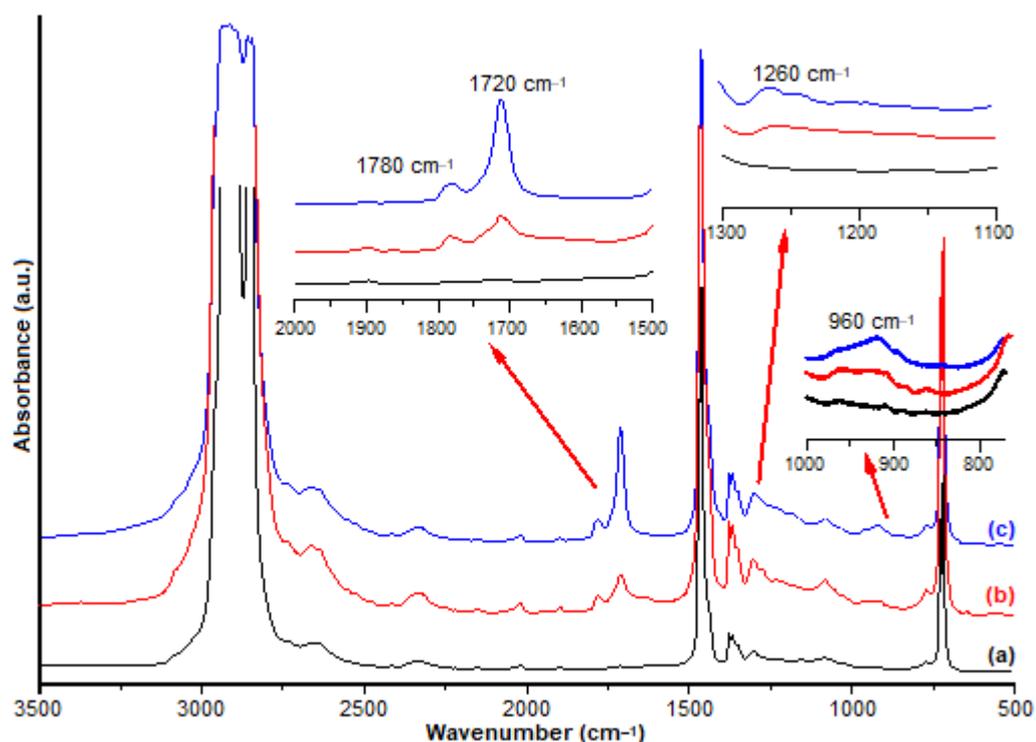
Fig 2. The FTIR spectra of acetone extract of (a) LLDPE, (b) mLLDPE-g-MAH, and (c) LLDPE-g-MAH (fabricated using 40% of DCP at 80 rpm rotation rate)
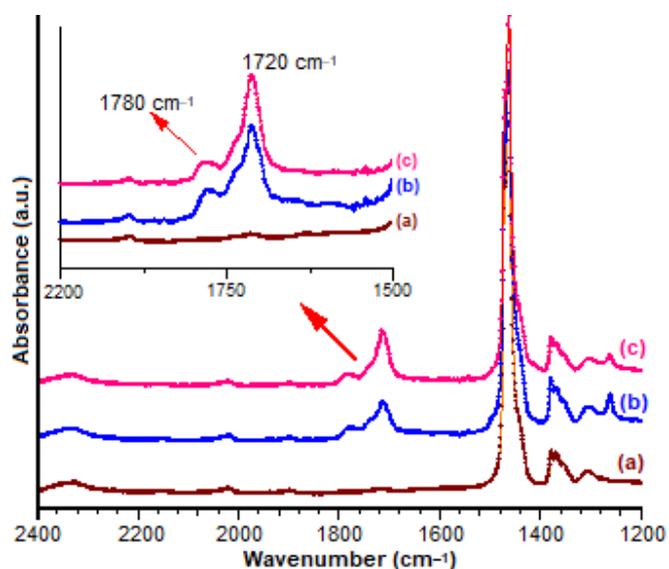
Fig 3. FTIR spectra of xylene soluble fraction extract of (a) LLDPE, (b) mLLDPE-g-MAH, and (c) LLDPE-g-MAH (fabricated using 40% of DCP at 80 rpm rotation rate)
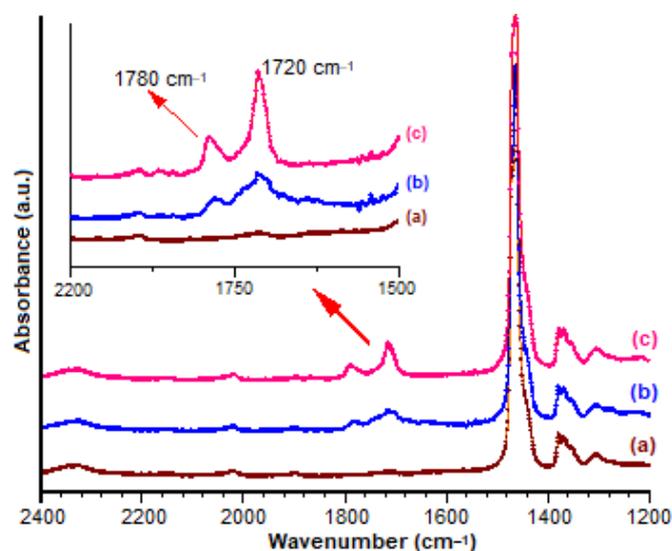
Fig 4. FTIR spectra of xylene extract gel fraction of (a) LLDPE, (b) mLLDPE-g-MAH, and (c) LLDPE-g-MAH (fabricated using 40% of DCP at 80 rpm rotation rate)

Thermal Properties

The DSC thermogram of glass transition temperature (T_g) and melting point (T_m) from both soluble and gel fractions of mLLDPE-g-MAH and LLDPE-g-MAH are shown in Fig. 5. Fig. 5 and Table 2 illustrate that in both fractions, the T_g of mLLDPE-g-MAH is higher than that of

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LLDPE-g-MAH. In the soluble fraction, the Tm of mLLDPE-g-MAH is lower than that of LLDPE-g-MAH, while in the gel fraction mLLDPE-g-MAH has a higher value. The presence of MAH and gel formation in the polymer lead to sturdier material, and lower crystallinity and Tm [21].

Fig. 5 shows the gel fraction of the LLDPE samples, as indicated by the width of the DSC thermogram. In general, there are no significant differences in Tg, Tm, and Tc values. However, the thermogram of the gel fraction of LLDPE-g-MAH shows a wide endothermic absorption.

Fig. 6 shows the DSC thermogram of the crystallization temperature (Tc) of mLLDPE-g-MAH and LLDPE-g-MAH in both fractions. Tc values are shown in Table 2. The Tc of the soluble fraction of mLLDPE-g-MAH is higher than that of LLDPE-g-MAH, while the Tc values of both samples in the gel fraction are similar. The presence of MAH and gel formation increase the rigidity of polymer, decrease the mobility of the chain, lower the crystallinity, and eventually increase the Tc value.

Fig. 7 shows the TGA thermogram of mLLDPE-g-MAH and LLDPE-g-MAH in both fractions in the range of decomposition temperature from 300 to 550 °C. To observe a clearer change of decomposition percentage, a first derivative of the decomposition thermogram is

drawn and is presented in Fig. 8. It is clear that the gradients of mLLDPE-g-MAH and LLDPE-g-MAH in the soluble fractions changed between 200 and 350 °C, whereas both samples in the gel fractions are not. Interestingly, the decomposition of mLLDPE-g-MAH in the soluble fraction is faster than the decompositions in the other samples. This might be related to the non-carbon decomposition, which probably derived from the maleic anhydride group.

Table 3 shows that between 325 and 425 °C, the percentage decomposition of mLLDPE-g-MAH in both fractions is higher than that of the LLDPE-g-MAH. Meanwhile, at 425 °C, decomposition of the gel fraction of mLLDPE-g-MAH is smaller than that of the LLDPE-g-MAH. We then compared this to the Tc of LLDPE

Table 2. Values of Tg, Tm, and Tc of the gel fractions (g) and solvated fractions (s) of mLLDPE-g-MAH and LLDPE-g-MAH (fabricated using 40% of DCP at 80 rpm rotation rate)

Sample	Tg (°C)	Tm (°C)	Tc (°C)
LLDPE-g-MAH (**g**)	64	118	107
mLLDPE-g-MAH (**g**)	65	122	107
LLDPE-g-MAH (**s**)	65	122	105
mLLDPE-g-MAH (**s**)	65.5	122	107
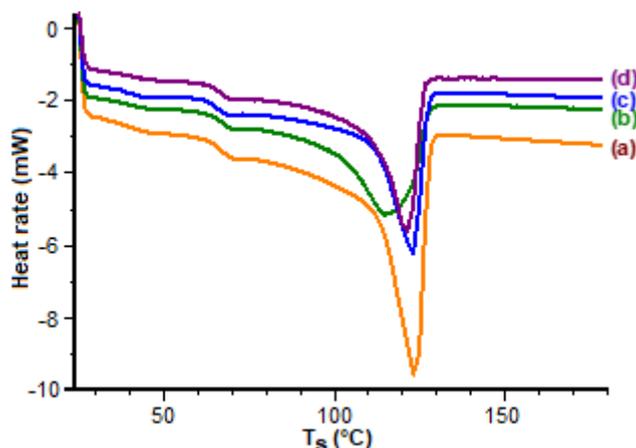
Fig 5. DSC thermogram of (a) mLLDPE-g-MAH gel fraction, (b) LLDPE-g-MAH gel fraction, (c) mLLDPE-g-MAH soluble fraction, and (d) LLDPE-g-MAH soluble fraction (fabricated using 40% of DCP at 80 rpm rotation rate)
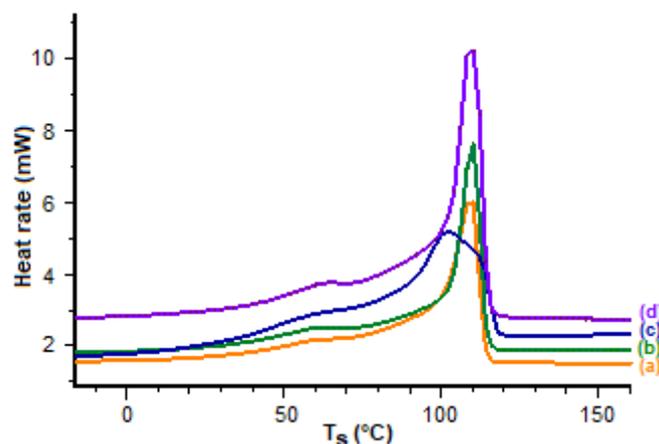
Fig 6. DSC thermogram of Tc of solvated fractions of (a) LLDPE-g-MAH, (b) mLLDPE-g-MAH, and gel fractions of (c) LLDPE-g-MAH, (d) mLLDPE-g-MAH (fabricated using 40% of DCP at 80 rpm rotation rate)
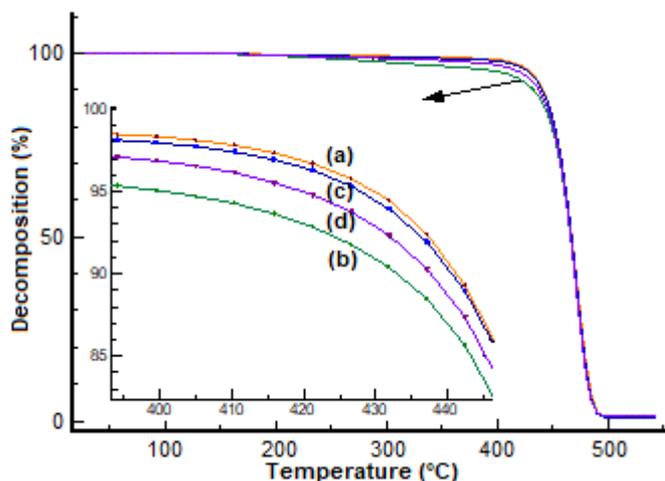
Fig 7. TGA thermogram of the soluble fractions of (a) mLLDPE-g-MAH, (b) LLDPE-g-MAH, and gel fractions of (c) mLLDPE-g-MAH, (d) LLDPE-g-MAH (fabricated using 40% of DCP at 80 rpm rotation rate)
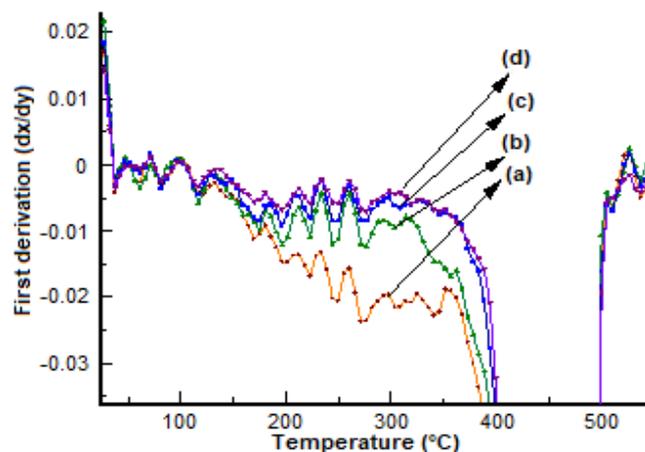
Fig 8. The first derivate of the TGA thermogram of samples decomposition of the soluble fractions: (a) mLLDPE-g-MAH (b) LLDPE-g-MAH, and that of gel fractions: (c) mLLDPE-g-MAH, (d) LLDPE-g-MAH (fabricated using 40% of DCP at 80 rpm rotation rate)
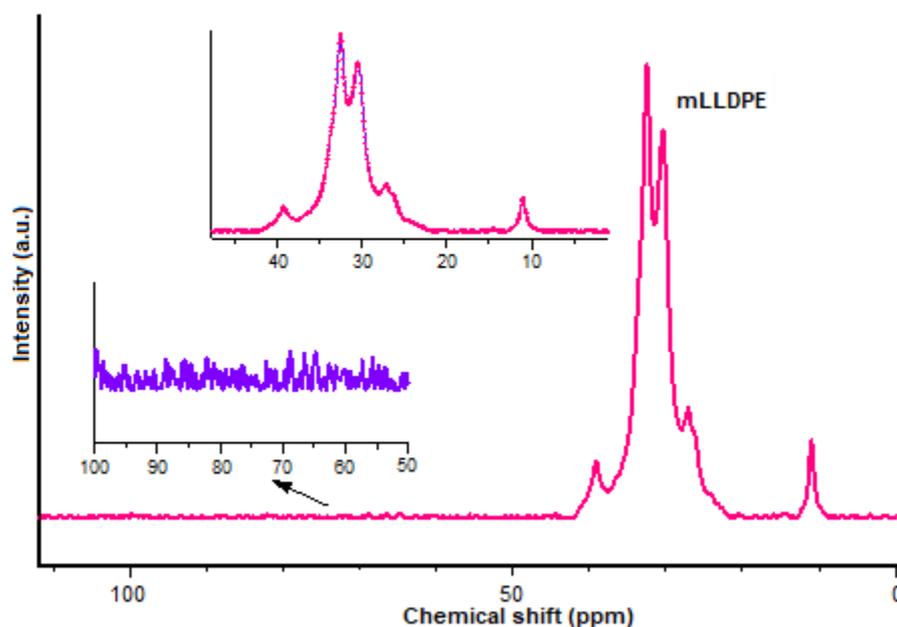
Fig 9. ^{13}C-NMR spectrum of mLLDPE-g-MAH

based on the reference, which shows a TG value of 360 °C. The Tc of LLDPE-g-MAH is much higher than the Tc of irradiated and non-irradiated LLDPE, which shows a range value of 380 to 340 °C [21].

The decomposition between 325 and 425 °C indicates the removal of MAH from the LLDPE. The high decomposition percentage corresponded to the high number of MAH that were attached to the LLDPE. After

425 °C, the mass decreased due to the removal of the attached group, which mostly derived from the backbone of LLDPE. As can be seen in the diagram, LLDPE was completely decomposed after 550 °C. It is suggested that the number of MAH that attached to the microencapsulated sample was higher than the LLDPE-g-MAH. To confirm the MAH attached to LLDPE, the NMR analysis was deployed.

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Table 3. Percentage decomposition of mLLDPE-g-MAH and LLDPE-g-MAH in the soluble fraction (s), and gel fraction (g) (fabricated using 40% of DCP at 80 rpm rotation rate)

Sample	Percentage of decomposition (%)	
	325 °C	425 °C
LLDPE-g-MAH (g)	0.88	4.21
mLLDPE-g-MAH (g)	1.14	4.64
LLDPE-g-MAH (s)	1.58	6.22
mLLDPE-g-MAH (s)	2.93	8.21

Table 4. Chemical shift and predicted carbon type/functional group of mLLDPE-g-MAH

Chemical shift (ppm)	Carbon type
173	C (C=O from succinic anhydride)
166	C (C=O from maleic anhydride)
132 and 142	C (C=C from maleic anhydride)
29-35	C (CH₂) from the polymeric chain
28 and 39	C (CH₂) from the ring of succinic anhydride
11	C (CH₃)
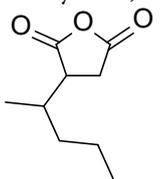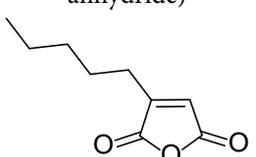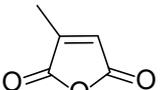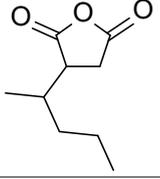
The ^{13}C-NMR was used to determine the structure of MAH that attached to the LLDPE structure (Fig. 9).

Each chemical shift represents the carbon type from a particular functional group. The interpretations of each chemical shift are presented in Table 4 [22].

It is noted that the intensity of the chemical shift at 173 ppm indicates succinic anhydride. This result signifies that the number of MAH attached to the LDDPE is higher in the form of succinic anhydride than MAH. This result is also supported by the presence of a chemical shift at 28.6 ppm, which showed the (CH₂) from succinic anhydride.

■ **CONCLUSION**

The graft copolymerization of MAH to LLDPE using monomer microencapsulation and DCP as initiator increase the grafting degree compared to the direct method. The product of the monomer microencapsulation method, mLLDPE-g-MAH, has a grafting degree of 5.9%, while that of the direct method has a 5.0% degree. The microencapsulation process improves the Tg, Tm, and Tc of mLLDPE-g-MAH compared to the direct method based on DSC analysis. We suggest that the microencapsulation could be a novel method in the polymerization process to attach MAH to LLDPE, which can increase the degree of grafting to enhance the physical properties of LLDPE.

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