

SYNTHESIS AND CHARACTERIZATION OF A NOVEL MACROMOLECULAR SURFACE MODIFIER FOR POLYETHYLENE*

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Abstract A new macromolecular surface modifier, a copolymer of lauryl methacrylate (LMA) and poly(ethylene glycol) methyl methacrylate (PEGMA), was synthesized through free radical polymerization. The copolymer was characterized by nuclear magnetic resonance spectrum ($^1\text{H-NMR}$) and thermogravimetric analysis (TGA). The copolymer was used to blend with polyethylene. The binary blends have been characterized by attenuated total reflection/Fourier transform infrared (ATR-FTIR), contact-angle measurements (CDA) and scanning electron microscopy (SEM). The results indicated that poly(ethylene glycol) methyl methacrylate-co-lauryl methacrylate (PEGMA-co-LMA) could diffuse preferably onto the surface of the polyethylene (PE) film, and thus can be used as an efficient surface modifier for PE.

Keywords: Polyethylene; Macromolecular surface modifier; ATR-FTIR.

INTRODUCTION

Polyethylene has become one of the largest polymer materials in use because of its low cost, excellent comprehensive properties and convenient processing. However, because of its low surface energy and low polarity, PE products are difficult to be printed, adhered and dyed^[1–3]. There is a longstanding interest in bringing new surface properties to PE films, while maintaining favorable bulk properties such as transparency, mechanical strength and dimensional stability^[4]. Many technologies, such as flame treatment^[5, 6], chemical treatment^[7, 8], plasma treatment^[9–14] and grafting^[15–18], have been used to increase its surface hydrophilicity. By comparison, blending with a surface modifier is widely recognized as a potential technique to functionalize the surface properties of polymers because of its convenience in processing^[19–21]. The technique relies mainly on using a small amount of small molecular surface modifier to modify the surface properties. It includes blending the surface modifier with an excess of the host polymer and diffusing the modifier to the surface of the products^[19, 22, 23]. Nevertheless, surface modifications with lower-molecular-weight surfactants have many limitations, such as poor thermal stability and weak bonding with the host polymer, which make the modifiers relatively easy to decompose when they are thermal-molded with PE, and easy to be extracted from the surface when the products are subjected to friction or washed with water or organic solvents. Macromolecular surface modifiers can anchor to host polymers by strong intermolecular interaction, and therefore avoid to be detracted from host polymers when the products were frictionized or washed with water or organic solvents, and keep their

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Invited paper dedicated to Professor Fosong Wang on the occasion of his 80th birthday

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lasting effectiveness^[24]. Macromolecular surface modifiers are stable and will not decompose when thermal-molded with PE, which overcome the poor thermo-stability of small surfactants. However, the structure of macromolecular surface modifiers should be designed carefully so as not to hinder the surface modifier to preferred-diffuse onto the surface and lower the efficiency of surface modifiers^[25–27]. Several macromolecular surface modifiers for PP and PE were synthesized and used to improve the surface hydrophilicity of the host polymer in our previous work^[22, 28–34]. It has been shown that the effects of the modifiers on modification can be deduced by studying the surface enrichment of the modifiers with different molecular parameters, such as molecular weight of the functional groups and the length of the side chains. In this work, a novel copolymer, poly(ethylene glycol) methyl methacrylate-*co*-lauryl methacrylate, named PEGMA-*co*-LMA, was designed and synthesized, and used for surface modification of PE. The surface properties of the PE/PEGMA-*co*-LMA films were studied by attenuated total reflection infrared spectroscopy (ATR-FTIR) and static contact angle measurements (CDA).

EXPERIMENTAL

Materials

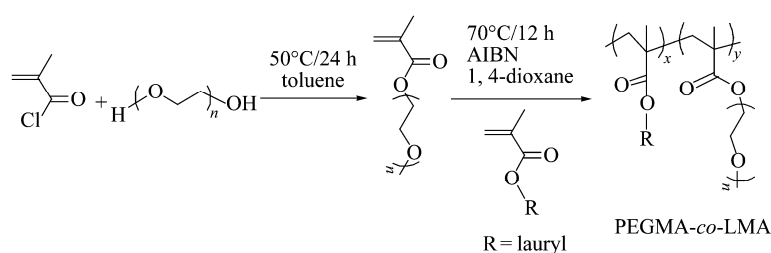
The PE (7042, MI = 2 g/10min) pellet was used in this study, which is a product by Maoming Petrochemical Industrial Co., China. PEG was obtained from Guangzhou Reagent Co., with molecular weights of 2000. Methacryloyl chloride (95%) and lauryl methacrylate (96%) were purchased from Aladdin Co. (Shanghai, China). Reagent grade chemicals such as dichloromethane, 1,4-dioxane, toluene, ether and *n*-hexane were used as received without further purification.

Synthesis of PEGMA

PEG (80 g, 40 mmol) was dissolved in 200 mL of toluene and bubbled with argon for 10 min. Methacryloyl chloride (5 g, 48 mmol) was then added under argon atmosphere. The mixture was stirred under 50 °C for 24 h. The product was washed by ether three times and dried in a vacuum oven under 50 °C for 24 h.

Synthesis of PEGMA-*co*-LMA

PEGMA (20 g, 10 mmol), LMA (0.13 g, 0.5 mmol) and AIBN (0.17 g, 1.05 mmol) were dissolved in 1,4-dioxane (200 mL) in a 500 mL three-neck reaction bottle with a magnetic stirrer under argon. The reaction was carried out at 70 °C for 12 h. The polymer was precipitated in *n*-hexane (700 mL) and dried to constant weight under vacuum at 50 °C for 24 h. The reactions are shown in Scheme 1.



Scheme 1 Preparation of PEGMA-*co*-LMA copolymer

Preparation of PE/PEGMA-*co*-LMA Films

PE was melt blended with various ratios of PEGMA-LMA. The binary blend was preheated to 180 °C and then was compressed in a steel mold to form a sheet of film with approximate 70–100 μm in thickness.

Characterization

Nuclear magnetic resonance (¹H-NMR) spectra were measured with a Mercury-Plus 300 (VARIAN, USA) spectrometer for the copolymers dissolved in deuteriochloroform (CDCl₃). The thermogravimetric analysis (TGA) was performed on a TQ 50 thermogravimetric analyzer (TA, USA) at a temperature range of 25–600 °C under air or nitrogen. The experiments were carried out at a flow rate of 40 mL/min and a heating rate of

20 K/min. Fourier transform infrared (FTIR) spectra were obtained by using a Bruker TENSOR 27 Fourier-transform infrared spectrometer. The measurement scope was 600–4000 cm^{-1} , and the results were the sum of 16 individual scans. The surface composition of the blending film was investigated by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy with an attenuated total reflection accessory at an angle of incidence of 45°. The spectra were recorded at 4 cm^{-1} resolution between 4000 and 650 cm^{-1} and were the sum of 16 individual scans. An S4800 scanning electron microscope (Hitachi, Japan) was used to observe the surface morphologies of the films. Contact angles of the film surface were determined by using a DSA100 contact angle goniometer (Kruss, Germany) at 23 °C. All measurements were performed by using the sessile drop method and made with drops of 6 μL of distilled water after about 30 s. The reported values are the average of six measurements at various places on the same film sample. The values of the contact angle measurements (CDAs) varied by $\pm 3^\circ$.

RESULTS AND DISCUSSION

^1H -NMR spectroscopy was used to verify the chemical structure of the copolymer. The ^1H -NMR spectrum of PEGMA-*co*-LMA dissolved in CDCl_3 is shown in Fig. 1. The signal at $\delta = 0.88$ was assigned to the protons of CH_3- in $-\text{O}(\text{C}_{11}\text{H}_{22})\text{CH}_3$, while those at $\delta = 1.25$ –1.75 were assigned to the methylene protons of the copolymer back bone. The $-\text{OCH}_2$ protons of PEG and LMA chains appear at $\delta = 3.65$ –4.35. The results suggest the successful preparation of the PEGMA-*co*-LMA copolymer.

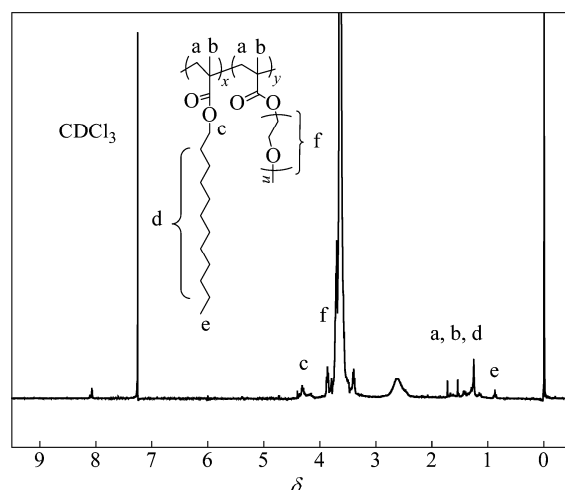


Fig. 1 ^1H -NMR spectrum of PEGMA-*co*-LMA in CDCl_3

Thermal stability is an important issue for polymer processing. To study whether the copolymer was suitable as the surface modifiers of PE in processing, the thermal degradation behavior of PEGMA-*co*-LMA was investigated by TGA. The results are shown in Fig. 2. The thermal degradation temperature of the copolymer was much higher than the thermo-oxidative degradation temperature (over 100 K). In addition, the thermal degradation temperature at 1% weight loss for the copolymer exceeded 200 °C, which was higher than the processing temperature of PE. The results indicated that the copolymer would be suitable for the surface modification of PE in terms of the thermal stability.

Attenuated total reflectance infrared spectroscopy has long been used for qualitative analysis of polymer surface composition. The major problem faced in quantitative analysis of this technology is the necessity of achieving good contact between the polymer film and the internal reflection element. This is an essential factor in obtaining reproducible results^[35]. In order to minimize the impact of this intrinsic problem in measurements of absolute absorbance, the technique of “band rationing” was developed and has been testified that the error of the peak area ratios of interest can be reduced by 5% or below^[24]. To evaluate the surface enrichment, transmission

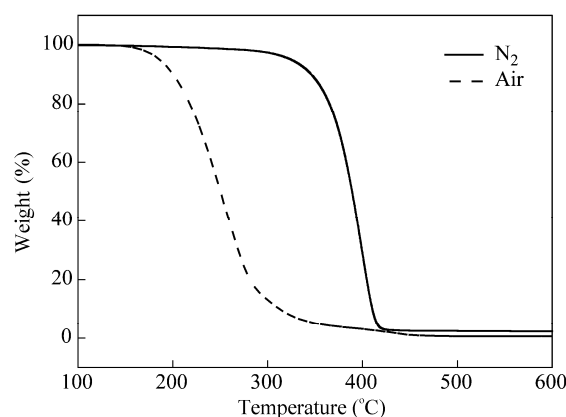


Fig. 2 TGA thermograms of PEGMA-*co*-LMA under N₂ and air

FTIR and ATR-FTIR were used to determine the concentration of PEGMA-*co*-LMA in the bulk and on the surface, respectively. From the FTIR and ATR-FTIR spectra, the band of PE and PEG chain of the copolymer at about 1118 cm⁻¹ was assigned to C—C groups in PE and C—O groups in PEG chain of the copolymer. Infrared peak area ratios at 1118 cm⁻¹ for PEG chain of the copolymer and 1118 cm⁻¹ for PE were therefore used to determine the PE surface composition of the blends. Since the characteristic absorbance bands of PEG chain of the copolymer and PE were overlapping, the ATR-FTIR absorbance spectrum for pure PE was first obtained. Thus the ratio of the band areas at 1118 and 965 cm⁻¹ for PE could be calculated as:

$$A_{1118}^{\text{PE}} = 8.225 \times A_{965}^{\text{PE}} \quad (1)$$

Therefore, the band area ratio of PEG chain of the copolymer and PE at about 1118 cm⁻¹ could be expressed as follows:

$$R = \frac{A_{1118}^{\text{blend}}}{A_{1118}^{\text{blend}}} = 8.225 \times \frac{A_{965}^{\text{blend}}}{A_{1118}^{\text{blend}}} \quad (2)$$

The results are shown in Fig. 3 and Fig. 4. The concentration of PEGMA-*co*-LMA on the PE film's surface was higher than that in the bulk. With increasing the additive of PEGMA-*co*-LMA, the value of *R* increased.

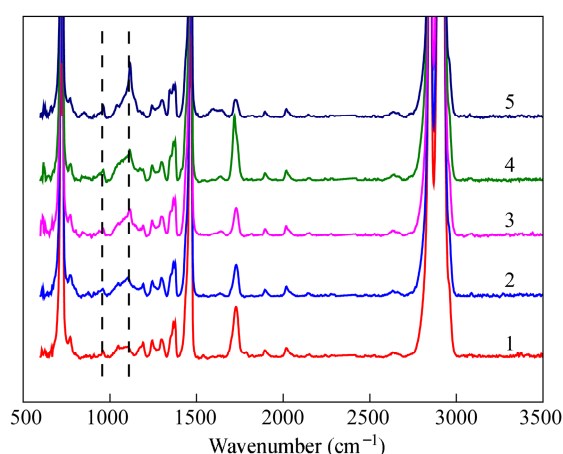


Fig. 3 The ATR-FTIR spectra of PE/PEGMA-*co*-LMA blend films: (1) PE/1% PEGMA-*co*-LMA, (2) PE/2% PEGMA-*co*-LMA, (3) PE/3% PEGMA-*co*-LMA, (4) PE/4% PEGMA-*co*-LMA and (5) PE/5% PEGMA-*co*-LMA

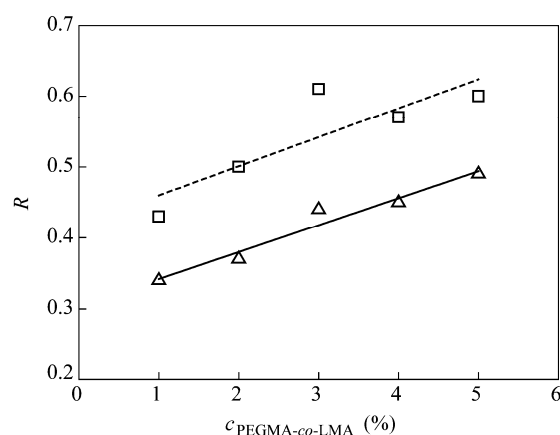


Fig. 4 The peak area ratio of PE blends films at different contents of PEGMA-*co*-LMA (□ surface, △ bulk)

This is because the PEGMA-*co*-LMA is an amphiphilic copolymer. The LMA segments were hydrophobic and compatible with PE, while the PEGMA segments were hydrophilic and incompatible with PE which can be separated from the PE phases. Furthermore, PE was a semi-crystalline polymer, during the crystallization process, part or all the PEGMA-*co*-LMA segments should be ejected from the crystalline region, which is benefit for the surface enrichment of the modifier. The result indicated that PEGMA-*co*-LMA copolymer could preferably diffuse to the surface of the PE film and thus could be used as a surface modifier.

The PEGMA-*co*-LMA component is not compatible with PE, phase separation can occur together with the surface enrichment and diffusion of PEGMA-*co*-LMA during blend processing. In order to understand the modification of the surface properties, the SEM micrographs of PE/PEGMA-*co*-LMA blend films with different PEGMA-*co*-LMA contents were obtained. The results are shown in Fig. 5. The surface of the pure PE film was very smooth, while those of the blend films showed different. Some white parts spread randomly can be observed, and the surface enrichment increased with increasing the content of PEGMA-*co*-LMA. It indicated that parts of the PEGMA-*co*-LMA copolymer could diffuse to the surface of the PE film.

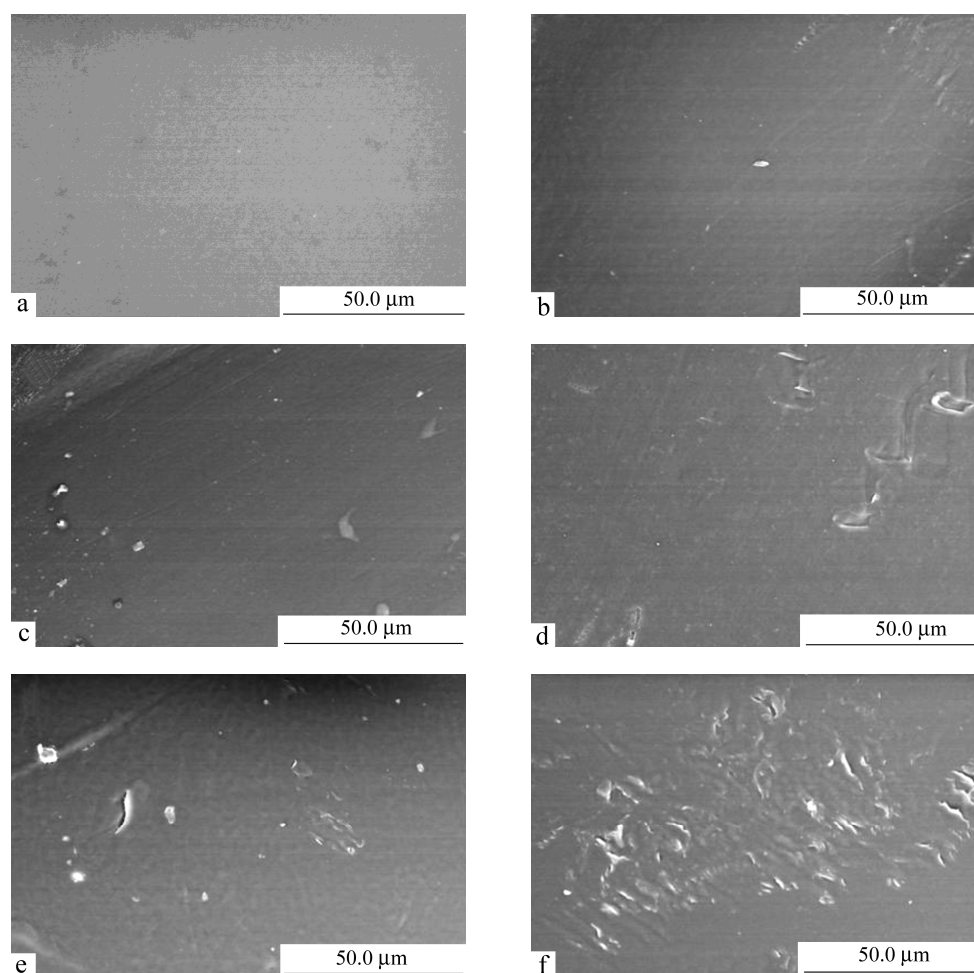


Fig. 5 The SEM micrographs of PE/PEGMA-*co*-LMA blend films: (a) PE, (b) PE/1% PEGMA-*co*-LMA, (c) PE/2% PEGMA-*co*-LMA, (d) PE/3% PEGMA-*co*-LMA, (e) PE/4% PEGMA-*co*-LMA and (f) PE/5% PEGMA-*co*-LMA

Water contact angle measurements were conducted to estimate the hydrophilicity of the materials. To calculate the surface tension of the blend films, another testing liquid, diiodomethane was used to perform

contact angle measurements. The results are listed in Table 1. The water and the diiodomethane contact angles for all the blend films decreased as comparing with the neat PE film. The contact angle was gradually decreased as the increase of PEGMA-*co*-LMA, but do not change much when the weight percentage of PEGMA-*co*-LMA was higher than 3%.

The surface tension data including disperse (r_s^d) and polar (r_s^p) components have been calculated from the values of contact angles of the two testing liquids by analysis software of the contact angle goniometer. The data are also listed in Table 1. The value of surface tension (r_s) for the blend films notably increased as the increase of PEGMA-*co*-LMA. The results showed that the hydrophilicity of the PE surface could be evidently improved by the addition of the PEGMA-*co*-LMA. This was in agreement with the results of ATR-FTIR, although various measuring depths are used for ATR-FTIR and contact angle analysis method. Compared to our prior report^[30], the PEGMA-*co*-LMA copolymer was superior to the comb-like amphiphilic copolymers based on styrene-maleic anhydride copolymer backbone for improving the wettability of PE.

Table 1. Contact angles and surface free energy of PE and its blends

Samples	Contact angle (°)		Surface tension data (mN·m ⁻¹)		
	Water	Diiodomethane	r_s^d	r_s^p	r_s
PE	95.6	58.1	29.67	1.08	31.75
PE/1% PEGMA- <i>co</i> -LMA	91.6	52.6	32.81	1.48	34.28
PE/2% PEGMA- <i>co</i> -LMA	87.3	50.4	34.05	2.32	36.37
PE/3% PEGMA- <i>co</i> -LMA	80.4	49.3	34.66	4.43	38.98
PE/4% PEGMA- <i>co</i> -LMA	79.2	49.9	34.33	4.93	39.26
PE/5% PEGMA- <i>co</i> -LMA	77.7	49.7	34.44	5.50	39.94

CONCLUSIONS

The result of ¹H-NMR confirmed the PEGMA-*co*-LMA was synthesized successfully. The thermal degradation temperatures at 1% weight loss for the copolymer exceeded 200 °C which was higher than the processing temperature of PE. The results of contact angle measurements and ATR-FTIR indicated that the PEGMA-*co*-LMA copolymer could diffuse preferably to the surface of the PE films and would be suitable as an efficient macromolecular surface modifier for PE.

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