

Polyethylene Grafted Maleic Anhydride to Improve Wettability of Liquid on Polyethylene Films

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ABSTRACT: Blends of linear low density polyethylene (LLDPE) and LLDPE grafted maleic anhydride (LLDPE-*g*-MA) were prepared by melt mixing. The surface of cast films with different contents and types of maleated PE were characterized through contact angle and wetting tension measurements, as well as attenuated total reflection IR spectroscopy. The tensile properties and light transmission of extruded films, as well as the performance of these films compared with commercial “antifog” films, for greenhouses were determined. The carbonyl polar groups on the surface of LLDPE/LLDPE-*g*-MA blends increased, and the equilibrium contact angles of water and dimethylformamide decreased when the content of maleated PE increased. Films made with these blends showed a noticeable reduction in water drop formation as the MA content was increased and when using LLDPE-*g*-MA of lower molecular weight. The light transmission through these films under condensation was improved when using increased contents of MA, which promotes better wetting of the water on the surface. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1802–1808, 2001

Key words: polyethylene grafted maleic anhydride; wettability; antifog films; greenhouses

INTRODUCTION

Polyethylene (PE), as well as many other polyolefins, are widely used for their low cost and versatile properties; but their poor reactivity, dyeability, and hygroscopicity limit their potential. Chemical modification has been demonstrated to give additional properties by means of grafting unsaturated polar groups onto the backbone of these polymers.^{1–3} Maleic anhydride (MA) has been widely used as a grafting monomer to functionalize polyolefins because of the higher reactivity of the anhydride group.^{4–6} Functionalization

of polyolefins is generally carried out for modification of some of the properties like adhesion and dyeability. They are commonly used as *in situ* compatibilizers of polymer alloys or multilayer structures involving incompatible polymers such as polyolefins/polyamides, polyesters, and so forth.^{7–9}

The wettability of a solid surface by a liquid is typified by a three-phase system, solid–liquid–vapor, that is in thermodynamic equilibrium. An angle (θ) is related as the triple line by the tangents onto the solid–liquid and liquid–vapor interphases. According to Young’s equation, in thermodynamic terms this parameter θ depends on the interfacial tensions. The equilibrium angle (θ) and advancing and receding angles are commonly used for surface characterization and give infor-

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mation on the wetting behavior of a liquid onto a solid surface.^{10,11} For a given solid, different liquids can be categorized in accordance with the θ angle. Liquids are said to be wettable if $\theta < 90^\circ$ and nonwetable if $\theta > 90^\circ$. Conversely, the notion of wettability can be used to distinguish between different solids in relation to a given liquid.¹² Solids that display the best degree of wettability with respect to water are, for example, those whose angle θ is as small as possible. These solids present the lowest solid–liquid surface tension with respect to water.

The so-called antifog formulations for greenhouse coverings represents a notable improvement in agricultural applications. By adding tensioactive additives into the formulation, these films offer better light transmission and avoid droplet formation on the surface. The antifog effect involves a lower solid–liquid surface tension that, when condensation occurs, spreads the droplets evenly over the surface of the solid instead of forming fine droplets.¹³ The ability of PE films to retain inks, coatings, or adhesives or spread a liquid evenly over the surface is primarily dependent upon the character of the surface. It can be improved by several surface treatment techniques or by adding internal tensioactive agents that migrate to the surface to modify the surface tension. This work analyzed the effect of using linear low density PE grafted with MA (LLDPE-*g*-MA) on the surface tension of PE films in order to obtain films with antifog characteristics.

EXPERIMENTAL

Materials

The materials used in this work were LLDPE (Mobil MJA) with a melt index (MI) of 1.4 g/10 min and weight- and number-average molecular weights (M_w and M_n) of 162,173 and 66,509 g/mol, respectively. Two different grades of LLDPE-*g*-MA were used: one designated as LLDPE-*g*-MA (Dupont Bynel CXA) with an MI = 2.2 g/10 min, $M_w = 139,219$ g/mol, and $M_n = 66,623$ g/mol; and another grade of lower molecular weight designated as LLDPE-*g*-MA(L) with $M_w = 15,340$ g/mol and $M_n = 7000$ g/mol. The MA content was 0.25 wt % for LLDPE-*g*-MA and 3.45 wt % for LLDPE-*g*-MA(L) as determined by acid–basic titration. Deionized water and analytical grade dimethylformamide (DMF, Aldrich Chemical) with surface tensions of 72.2 and 37.3 mN/m,

respectively, were used for the contact angle measurements.

Preparation of Films

Blends with different contents of MA were prepared by melt mixing of LLDPE with each modified PE [LLDPE-*g*-MA and LLDPE-*g*-MA(L)] using a W&P twin screw mixer (ZSK 30) operating at 220°C and 60 rpm. Cast and extruded films were prepared from the blends. The cast films were obtained using xylene at 120°C and casting them on a glass plate and evaporating the solvent in a vacuum oven at 120°C for 8 h. The air-facing side was used for characterization. Extruded 175 ± 2 μm thick flat films were prepared using a Killion single screw extruder ($L/D = 24$) connected to a flat die operating at 260°C on the die. The melt was then cooled directly by contacting it with a chill roll. A commercial 175 μm thick PE antifog film, with propoxylated acid ester as the antifog additive, for covering greenhouses was used as a reference.

Characterization of Films

Tensile tests of the films were carried out in an Instron 1122 tensile tester at room temperature and a crosshead speed of 50 mm/min.

The chemical composition of the film surface was investigated by FTIR attenuated total reflection spectroscopy (FTIR-ATR) using a Nicolet 710 spectrometer and an ATR accessory element with a 45° entrance face.

The contact angles of the distilled water and DMF on the unmixed homopolymers and blend films were measured. Liquid droplets were placed on samples of each film using a Pasteur micropipette, and a photograph of the droplet was obtained through low magnification (ca. 100 \times) optical microscopy. Each contact angle was the average of at least eight measurements. The height (h) and the base of the droplet (w) were measured from the photograph, and the contact angle was obtained from geometric considerations using a microscope with image analysis.

Wetting tension measurements were made following ASTM D 2578. This test method covers the measurement of wetting tension of PE and polypropylene film surfaces in contact with drops of specific test solutions in the presence of air.

In order to estimate the condensation behavior on the film surface, samples of extruded films were mounted on test frames with a roof slope

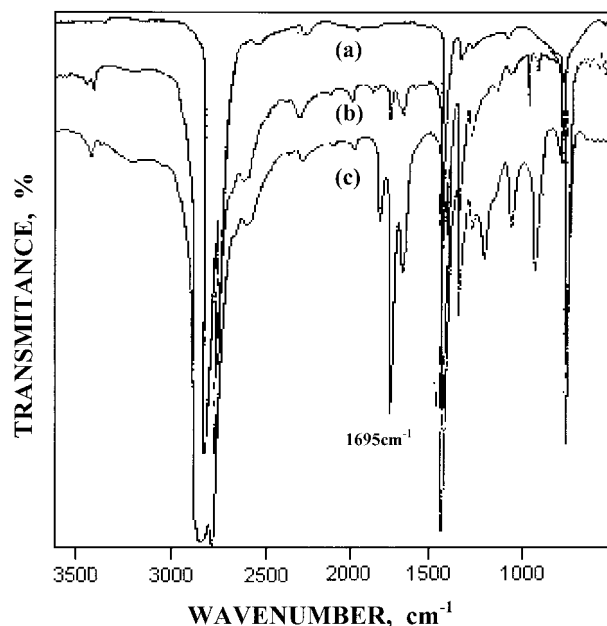


Figure 1 FTIR spectra of LLDPE (spectrum a), LLDPE-g-MA (spectrum b), and LLDPE-g-MA(L) (spectrum c).

angle of 65° and then exposed to condensation cycles for 4 h using a QUV test chamber with controlled UV and condensation cycles.

A Dupont 910 differential scanning calorimeter was used to determine melting and crystallization temperatures. Heating and cooling rates were $10^\circ\text{C}/\text{min}$. The weight of the specimens was about 10 mg.

Light transmission determinations were carried out in an optical Hazegard XL-211 system. The values obtained are averages of at least eight determinations.

RESULTS AND DISCUSSION

FTIR spectra of the plain LLDPE, LLDPE-g-MA, and LLDPE-g-MA(L) are shown in Figure 1. It is clearly seen that a new absorption band at 1695 cm^{-1} , which is attributed to the carbonyl groups of the MA, appears for the LLDPE-g-MA and LLDPE-g-MA(L) samples. Note also that the intensity of this band is much stronger for the LLDPE-g-MA(L) sample, indicating a higher grafting level.

Table I shows the tensile strength and elongation at break for the extruded films. It can be seen that the blends' properties are between those of each component. The reference commercial film

Table I Tensile Strength and Elongation at Break for LLDPE/LLDPE-g-MA Blends

Material	Tensile Strength (kg/cm ²)		Elongation at Break (%)	
	MD	TD	MD	TD
LLDPE/LLDPE-g-MA				
100/0	280	290	690	710
75/25	270	285	705	725
50/50	265	270	745	780
25/75	250	260	770	790
0/100	245	250	790	805
Antifog film	280	285	690	700

MD, Machine direction; TD, transverse direction.

shows tensile strength and elongation at break values similar to the homopolymer (LLDPE).

From FTIR-ATR spectra of the film surface, a carbonyl index (CI) was obtained as the ratio between the peak at 1695 cm^{-1} , which is related to the C=O stretching, and a constant reference peak height at 1461 cm^{-1} . The CI as a function of the MA content is shown in Figure 2. This index is almost insignificant for the LLDPE film and increases with the MA content in the blend. This increase in the CI implies that the film surface contains increased amounts of C=O polar groups as the content of the modified polymer in the blend is also increased. It can also be observed that for a similar MA content, higher carbonyl indexes were obtained when using LLDPE-g-MA(L) of lower molecular weight.

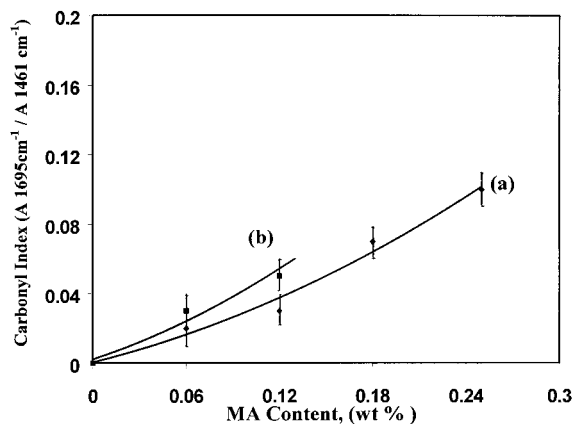


Figure 2 The carbonyl index as a function of the MA content in blends of LLDPE with (a) LLDPE-g-MA and (b) LLDPE-g-MA(L).

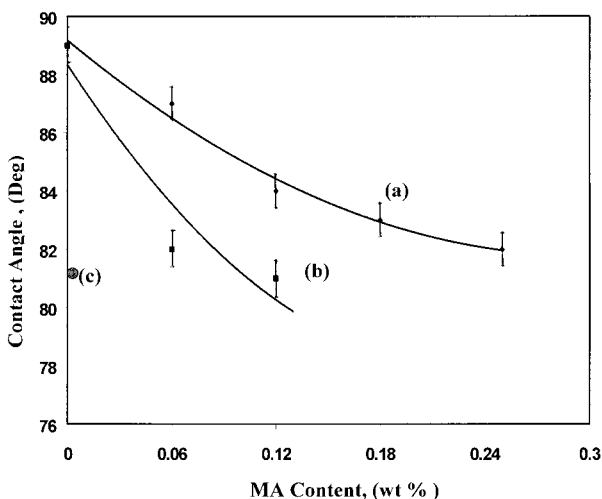


Figure 3 The contact angles (θ) of water on air-facing surfaces of cast films as a function of MA content in blends of LLDPE with (a) LLDPE-g-MA and (b) LLDPE-g-MA(L); (c) the reference antifog film.

The contact angles of a water and DMF drop on the surfaces of cast film samples of plain LLDPE and LLDPE-g-MA and LLDPE-g-MA(L) blends are reported in Figures 3 and 4, respectively, as a function of MA content. Observe that with an increasing percentage of MA, the equilibrium contact angles of water and DMF decrease monotonically. This result suggests that the surface polarity of these films is augmented by an increase of the content of the functionalized polymer. The contact angle values obtained for DMF were lower than water because of its lower surface tension

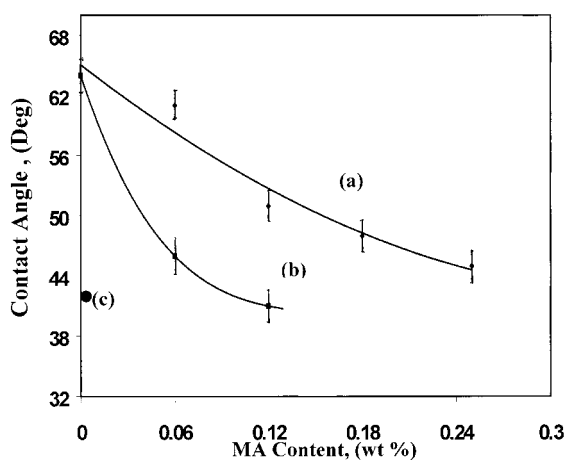


Figure 4 The contact angles (θ) of DMF on air-facing surfaces of cast films as a function of the MA content in blends of LLDPE with (a) LLDPE-g-MA and (b) LLDPE-g-MA(L); (c) the reference antifog film.

Table II Wetting Tension Measurements as Function of MA Content

MA Content (wt %)	Wetting Tension (dynes/cm)
LLDPE-g-MA	
0	30 (0.083)
0.06	30.5 (0.078)
0.125	31 (0.098)
0.187	31 (0.090)
0.25	32 (0.070)
LLDPE-g-MA(L)	
0.06	31.5 (0.055)
0.125	32.5 (0.078)
Reference antifog film	33 (0.081)

The values in parentheses are the standard deviations.

(37.3 mN/m). For a similar MA content, lower contact angle values were obtained when using LLDPE-g-MA(L) of lower molecular weight. This feature can be explained by considering that a lower molecular weight would improve migration

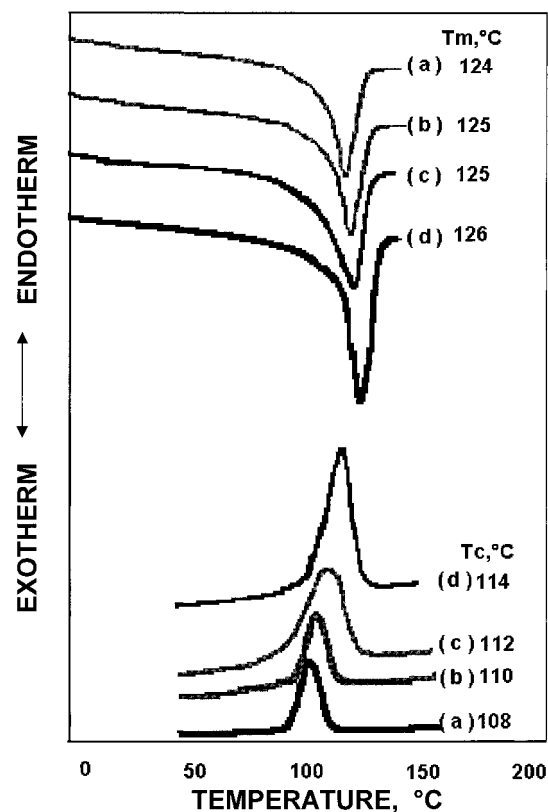


Figure 5 DSC thermograms of LLDPE/LLDPE-g-MA blends: 100/0 (spectrum a), 50/50 (spectrum b), 75/25 (spectrum c), and 0/100 (spectrum d).

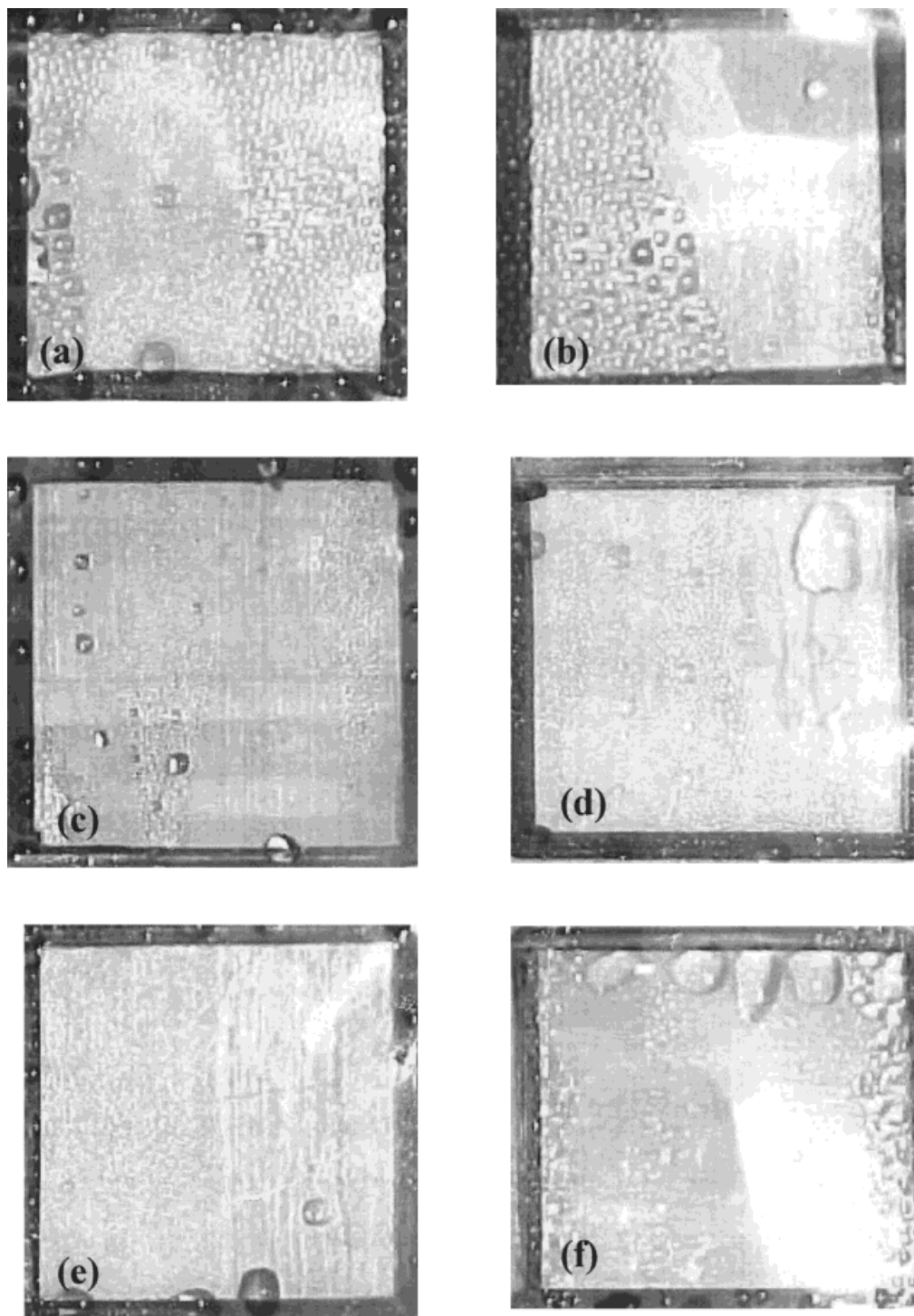


Figure 6 Photographs of films surfaces exposed to condensation cycles. The MA content (wt %) using LLDPE-g-MA in the blends is (a) 0, (b) 0.125, and (c) 0.25 and using LLDPE-g-MA(L) in the blend is (d) 0.06 and (e) 0.125; (f) the reference antifog film.

of functionalized polymer chains to the surface during film preparation and consequently improve the surface polarity of the films as was

observed by FTIR-ATR. This augmented surface polarity reduces the measured contact angle and increases the wetting of the liquid on the film

surface. This was also observed from the wetting tension measurements (Table II) in which an increase in the MA content increases the wetting tension, and this increase is more notorious when using a modified polymer of lower molecular weight.

DSC thermograms of neat LLDPE, LLDPE-g-MA, and its blends are shown in Figure 5. As can be seen, the melting (T_m) and crystallization (T_c) temperatures of functionalized PE (LLDPE-g-MA) are higher than LLDPE and the blend's temperatures lie between them. It can also be seen that as the content of maleated PE is increased, the T_m changes only slightly (from 124 to 126°C) compared with the T_c (from 108 to 114°C). These results could be explained by considering the grafted MA monomer as acting as a nucleation agent. This might improve the crystallization capability of LLDPE and cause it to crystallize at higher temperatures. This was also observed by other authors^{14–16} who reported a nucleation effect of carbonyl groups on the crystallization of polyolefins.

Figure 6 shows how different film samples react to condensation at a roof slope of 30°. On LLDPE films numerous semicircular drops of different sizes are formed [Fig. 6(a)]. No big drops are formed. The commercial antifog film shows only film condensation and a few big drops that fall from the film [Fig. 6(f)]. Films made of LLDPE/LLDPE-g-MA blends show a noticeable reduction in water drop formation as the MA content is increased. Films using LLDPE-g-MA(L) show lower small drop formation, making water condense as a film when forming big drops that fall from the film, similar to the commercial antifog film. This is attributed to better wetting of water drops on films with improved surface polarity.

The light transmission of the films is reported in Table III as a function of the MA content for neat samples and those exposed to condensation cycles. As can be seen from the neat samples, the light transmission is slightly reduced from 93% for the neat LLDPE film to 89% when using 0.25% of MA in the blend. This reduction in light transmission could be attributed to a difference in crystallinity between LLDPE and LLDPE-g-MA, as was observed from the DSC results. The light transmission of films exposed to condensation cycles shows a notorious reduction compared with neat samples that is due to the reflective action of water droplets on the surface. When using increasing amounts of MA in the film, higher values

Table III Light Transmission through Films With and Without Condensation

MA Content (wt %)	Without Condensation	With Condensation
LLDPE-g-MA		
0	93 (0.040)	77 (0.067)
0.06	93 (0.038)	79 (0.045)
0.125	92 (0.058)	82 (0.070)
0.187	91 (0.044)	83 (0.050)
0.25	89 (0.043)	86 (0.074)
LLDPE-g-MA(L)		
0.06	93 (0.019)	86 (0.087)
0.125	91 (0.040)	89 (0.055)
Reference antifog film	91 (0.048)	89 (0.069)

The values in parentheses are the standard deviations.

of light transmission were obtained and the highest values were obtained when using maleated PE of lower molecular weight. When using LLDPE-g-MA(L), light transmission values similar to the commercial antifog film were obtained. A better wetting of water on polar surfaces involves better light transmission through the film.

CONCLUSIONS

Carbonyl polar groups on the surface of LLDPE/LLDPE-g-MA blends increase and equilibrium contact angles of water and DMF decrease when the content of maleated PE increases. Films made with these blends show a noticeable reduction in water drop formation as the MA content is increased and when using LLDPE-g-MA of lower molecular weight. Light transmission through these films under condensation is improved when using increased contents of MA, which promotes a better wetting of water on the surface.

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