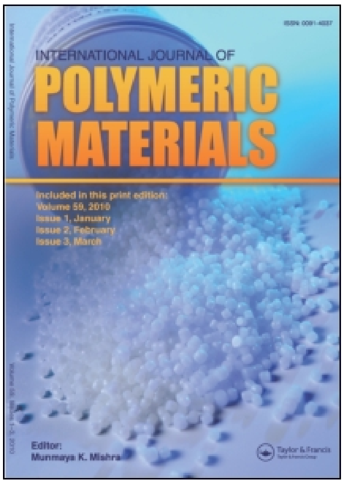

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Zhanhai, Yao , Jinghui, Yang and Jinghua, Yin(2000) 'Characterization of LLDPE/LLDPE-g-AA Blends by Contact Angle and FT-IR Methods', International Journal of Polymeric Materials, 47: 2, 343 — 350
To link to this Article: DOI: 10.1080/00914030008035069
URL: http://dx.doi.org/10.1080/00914030008035069

Intern. J. Polymeric Mater., 2000, Vol. 47, pp. 343–350
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Printed in Malaysia.

Characterization of LLDPE/LLDPE-g-AA Blends by Contact Angle and FT-IR Methods

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(Received 10 May 1999)

Blends of linear low density polyethylene (LLDPE) and linear low density polyethylene-grafted-acrylic acid (LLDPE-g-AA) were prepared by melt mixing. The surface of films with different content LLDPE-g-AA were characterized through contact angle measurements and FT-IR spectroscopy. The contact angles of water and glycerol on films surfaces of LLDPE/LLDPE-g-AA blends decrease with increase of LLDPE-g-AA. From FT-IR spectra of the blends, the carbonyl peak strength on the films surface was calculated. It was found that larger the carbonyl peak strength, the lower the value contact angle for LLDPE/LLDPE-g-AA blends.

Keywords: LLDPE-g-AA; LLDPE; blends; contact angle

INTRODUCTION

In both composite polymer structures and polymer blends the compatibilization of the polymer/polymer interfaces is of critical importance. It is well known that most polymer pairs are immiscible and do not have strong enough interactions [1–3]. However, several compatibilizations strategies have emerged to resolve the poor adhesion between polymer pairs [4–6]. Functionalization of polyolefines through graft copolymerization of unsaturated monomer containing polar groups has received considerable attention in recent years

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[7–9], especially in the modification of some of the properties, like adhesion, dyeability and wettability. Acrylic acid has been used for the functionalization of polyolefins due to the high reactivity of carbonyl group. In a number of studies a graft copolymer is used a compatibilizing agent, where the polymer consists of a polyolefin backbone grafted with functional groups such as maleic anhydride, acrylic acid and glycidyl methacrylate [10–13].

Blends of modified polymer change the polar groups on the surface of polymer. Contact angle measurement of a solid and liquid interface is a widely used method for determination of the surface energy of solid polymer. This technique is an excellent method for characterizing the surface, giving information on the wetting behavior of a liquid on a solid surface. FT-IR is a well-accepted method for identification and quantification of the polar group that are present in a polymer surface.

In this work the surface of blends of linear low density polyethylene (LLDPE) and low linear density polyethylene-grafted-acrylic acid (LLDPE-g-AA) were characterized by contact angle measurements, as well as FT-IR from which the carbonyl peak strength on the polymer surface has been obtained.

EXPERIMENTAL

Materials

The materials used in this work a linear low density polyethylene (LLDPE) and linear low density polyethylene-grafted-acrylic acid (LLDPE-g-AA). The LLDPE was purchased from China Petrol Daqing Petrochemical Co. (China), its trade name is DFDA7042. The LLDPE-g-AA was prepared in our laboratory. The main characteristics of LLDPE and LLDPE-g-AA are reported in Table I. The

TABLE I Main characteristics of the LLDPE and LLDPE-g-AA

Sample	*Melting temperature (°C)*	*Melt index* (g/10 min)*	*Density (g/cm^3)*	*Degree of grafting (wt%)*
LLDPE(DFDA7042)	123	2.0	0.926	0
LLDPE-g-AA	123	1.7	0.926	2.57

* 190°C, 2.16 Kg.

LLDPE-g-AA contains 2.57% acrylic acid (AA) by weight as determined by acid-basic titration. Deionized water with a surface tension of 72.75 mN/m was used for the contact angle measurements. Glycerol of analytical grade was purchased from Beijing Chemical Factory (China). Xylene was used for extraction experiments.

Preparation of Blends

Blends of LLDPE with overall contents of 0, 20, 40, 60, 80, and 100 wt% of LLDPE-g-AA were prepared by melt mixing in a SHJ-30 co-rotating twin screw extruder (L/D = 44, Φ = 30 mm) at 200°C and 95 rpm.

Preparation of Films

Cast film of the LLDPE/LLDPE-g-AA blends were obtained using xylene at 120°C and cast them on a glass plate. All the LLDPE/LLDPE-g-AA films were dried under a reduced pressure, placed between two leaves of filter paper, and stored in a desiccator kept at 25°C and 60% relative humidity (RH).

Contact Angle Measurements

All measurements were performed in a clean batch maintained at a constant temperature (20°C) and humidity (60–65% RH). The polar liquids droplets ranging from 0.5–1.0 mm in diameter were prepared with a microsyringe, they were placed on the surface of LLDPE/LLDPE-g-AA films. The contact angles of water and glycerol on surface of LLDPE-g-AA films were measured by using a home made apparatus. Each contact angle was the mean of at least eight measurements.

Surface Characterization

FT-IR measurements were made on a FTS-7 Fourier-transform infrared spectrophotometer (Bio Rad Co.) with film samples.

RESULTS AND DISCUSSION

Contact Angle of Measurement

The contact angle of water and glycerol on surface of LLDPE/LLDPE-g-AA films are listed in Table II. As can be seen, the contact angle of the LLDPE/LLDPE-g-AA blends decrease with increase of the LLDPE-g-AA content. The contact angle of water and glycerol show no significant changes when LLDPE-g-AA content lower 20%. On the other hand, for LLDPE-g-AA content higher 40%, the contact angle shows a notable reduction with increase of LLDPE-g-AA. The contact angle is very sensitive to the chemical and structural changes that occur on a polymer surfaces, since the liquid makes contact with the outermost molecular layer of the surface.

It is well known that the contact angle between liquid and solid is expressed by Young's equation

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} - \pi_e \tag{1}$$

where γ_S and γ_L are the surface tension of solid and liquid, respectively and γ_{SL} is the interfacial tension between solid and liquid. The spreading pressure π_e can be neglected because $\pi_e \ll \gamma_L$. Using Eq. (1) and Dupre's equation

$$W_A = \gamma_S + \gamma_L - \gamma_{SL} \tag{2}$$

the equation of Young-Dupre equation is expressed as:

$$W_A = \gamma_L(1 + \cos\theta) \tag{3}$$

TABLE II Contact angles (θ) and work of adhesion (W_A) for films of LLDPE/LLDPE-g-AA blends

LLDPE/LLDPE-g-AA wt/wt	*θ of Water (degree)*	*W_A of Water (mN/m)*	*θ of Glycerol (degree)*	*W_A of Glyceyol (mN/m)*
100/0	89	74.02	72	82.95
80/20	85	79.09	69	86.08
60/40	77	89.12	65	90.15
40/60	69	98.82	60	95.06
20/80	62	106.90	57	97.88
0/100	59	110.22	56	98.81

Combining the harmonic-mean equation [14] with Young-Dupre equation gives

$$W_A = 4[\gamma_S^d\gamma_L^d/(\gamma_S^d + \gamma_L^d) + \gamma_S^p\gamma_L^p/(\gamma_S^p + \gamma_L^p)] \tag{4}$$

whereas combining the geometric-mean equation with Young-Dupre equation gives

$$W_A = 2[(\gamma_S^p\gamma_L^p)^{1/2} + (\gamma_S^d\gamma_L^d)^{1/2}] \tag{5}$$

where W_A is the work of adhesion, θ is the contact angle, γ_S^d and γ_L^d are dispersion components of surface free energy for the solid and liquid, respectively. The γ_S^p and γ_L^p are polar component of surface free energy for the solid and liquid, respectively.

The γ_L^d and γ_L^p for water and glycerol are reported in Table III. The γ_S^d and γ_S^p could be calculated by solving Eqs. (3) and (5) for water and glycerol. The values of γ_S^d and γ_S^p are shown in Table IV. It can be observed that the total surface energy increase with increase of LLDPE-g-AA content. The increased surface energy of the LLDPE/LLDPE-g-AA blend comes mostly from the polar component when the LLDPE-g-AA content increases. This indicates that, due to the presence of polar groups on the surface of LLDPE/LLDPE-g-AA, the surface energies of blends are expected to increase as a function of LLDPE-g-AA content. The results of work of adhesion calculated

TABLE III The γ_L^d and γ_L^p for water and glycerol

Liquids	$\gamma_L^d(mJ/m^2)$	$\gamma_L^p(mJ/m^2)$	$\gamma_L(mJ/m^2)$
Water	22.08	50.67	72.75
Glycerol	40.52	22.85	63.37

TABLE IV Surface energy for the films of LLDPE/LLDPE-g-AA blends

LLDPE/LLDPE-g-AA wt/wt	γ_S^d (mJ/m^2)	γ_S^p (mJ/m^2)	*Total surface energy* (mJ/m^2)
100/0	26.81	3.17	29.98
80/20	26.37	4.69	31.06
60/40	22.28	9.88	32.16
40/60	19.98	15.92	35.90
20/80	16.52	23.29	39.81
0/100	14.91	26.96	41.87

according to Eq. (3) are listed in Table II. Because the contact angle decreases with increase of LLDPE-g-AA content, the work of adhesion increases.

FT-IR ANALYSIS

The FT-IR spectras of the pure LLDPE and LLDPE/LLDPE-g-AA are shown in Figure 1. It is clearly seen that for LLDPE/LLDPE-g-AA blends appear absorption peaks at 1712 cm^{-1}, which are attributed to contributions of carbonyl of acrylic acid in LLDPE-g-AA. But spectra of LLDPE film has not absorption peak at 1712 cm^{-1}.

The carbonyl peak strength of LLDPE/LLDPE-g-AA are shown in Table V. Defining carbonyl peak strength as the ratio between the absorption peak at 1712 cm^{-1}and 1378 cm^{-1} height, it was observed that the carbonyl peak strength increased with LLDPE-g-AA content. This increase in carbonyl peak strength indicated that the film surface of LLDPE/LLDPE-g-AA contains more amount carbonyl polar groups. The higher values of carbonyl peak strength, the lowering of the contact angle is. Higher carbonyl peak strength means more

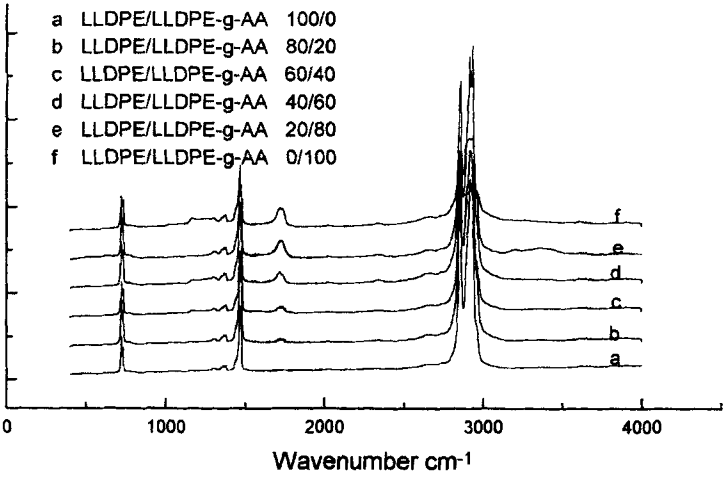

FIGURE 1 FT-IR spectra of film surfaces of LLDPE/LLDPE-g-AA with different LLDPE-g-AA content.

TABLE V Carbonyl peak strength (C_S), peak height (P_h) and contact angle (θ) of films of LLDPE/LLDPE-g-AA with different LLDPE-g-AA content

LLDPE/LLDPE-g-AA (wt/wt)	P_h *of* 1712 cm^{-1}	P_h *of* 1378 cm^{-1}	C_S	θ *of Water (degree)*
100/0	0	0.0976	0	89
80/20	0.561	0.1019	0.57	85
60/40	0.1060	0.0956	1.11	77
40/60	0.1572	0.0946	1.66	69
20/80	0.1991	0.0896	2.21	62
0/100	0.2684	0.0969	2.77	59

carbonyl groups are present on the surface, and the surface energy of LLDPE/LLDPE-g-AA would be improved.

CONCLUSIONS

The contact angle of water and glycerol on surface of LLDPE/LLDPE-g-AA blends decrease with the LLDPE-g-AA content. The total surface energy and work of adhesion of films of LLDPE/LLDPE-g-AA blends increase with increase of LLDPE-g-AA content. Carbonyl polar groups on the surface of LLDPE/LLDPE-g-AA films increase with increase of LLDPE-g-AA content in LLDPE/LLDPE-g-AA blends.

Acknowledgments

The authors would like to acknowledge the financial support of the Technology Foundation Committee of The Ministry of Mechanical Industry of China and The Chinese National Science Foundation Committee.

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