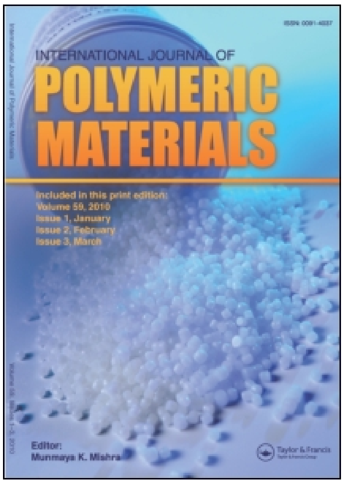

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Critical Surface Tension of Non-crosslinking Linear Low Density Polyethylene-graft-acrylic Acid by the Contact Angle Method

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The contact angles θ of polar liquid on surface of non-crosslinking linear low density polyethylene-graft-acrylic acid (LLDPE-g-AA) were measured. The critical surface tension (γ_c) of LLDPE-g-AA films were evaluated by three different plots, the Zisman plot, the Young-Dupre-Good-Girifalco plot, and the $\log(1+\cos\theta)$ *versus* $\log\gamma_L$ plot. The γ_c of LLDPE-g-AA obtained by the $1+\cos\theta$ *versus* $\gamma_L^{-1/2}$ plot were higher than those obtained by other plots.

Keywords: Linear low polyethylene; graft; non-crosslinking; contact angle; critical surface tension

INTRODUCTION

Functionalization of polyolefins through graft copolymerization of unsaturated monomers containing polar groups has received considerable attention in recent years [1–5]. The increased polarity which can be achieved in this way could improve some properties of the modified polymer, such as adhesion to other materials, and could promote better compatibilizer with other polar polymers.

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Contact angle measurement of a solid/liquid interface is a widely used method for the determination of the surface energy of solid polymers. This technique is an excellent method for characterizing the surface, giving information on the wetting behavior of a liquid on a solid surface.

The surface properties of LLDPE-g-AA are closely related to the surface tension (γ_s). Estimation of γ_s of solid polymer has generally been made by the contact angle method [6–8]. Zisman and Fox [6, 7] measured the contact angle θ of polar liquid on surface of various solid polymers. They found that the relationship between $\cos\theta$ and the surface tension of liquid (γ_L) give rise to a good straight line. The concept of critical surface tension (γ_c) was first proposed by Fox and Zisman. They named the γ_c, which was the value of γ_L at $\cos\theta = 1$ by extrapolating the straight line.

Good and Girifalco [8] defined the interaction parameter Φ_G using the work of adhesion W_a and the work of cohesion W_c:

$$\Phi_G = W_a/(W_{c1}W_{c2}) \tag{1}$$

They presented the following equation:

$$W_a = 2\Phi_G(\gamma_s\gamma_L)^{1/2} \tag{2}$$

Using Eq. (2) and Young-Dupre's Eq. (3), the equation of Young-Dupre-Good-Girifalco was expressed as Eq. (4)

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

$$1 + \cos\theta = 2\Phi_G(\gamma_s/\gamma_L)^{1/2} \tag{4}$$

The $1 + \cos\theta$ *versus* $1/\gamma_L^{1/2}$ plot obtained by the contact angles θ of homogeneous liquids on a solid polymer given a good straight line with the experimental data. However, in many cases the straight line can be expressed as:

$$1 + \cos\theta = \phi + \lambda(1/\gamma_L)^{1/2} \tag{5}$$

Where λ and ϕ are the slop and the intercept of $1 + \cos\theta$ at $1/\gamma_L^{1/2} = 0$ in the $1 + \cos\theta$ *versus* $(1/\gamma_L)^{1/2}$ plot, respectively. These parameters are constant with homogeneous solvents. The critical surface tension γ_c is defined as the value of γ_L at $\theta = 0$. The relationship between λ and ϕ is expressed in the following equation by the use of γ_C:

$$\lambda = (2 - \phi)\gamma_C^{1/2} \tag{6}$$

Using Eqs. (4) and (5), neglecting the spreading pressure π_e, the Good-Girifalco interaction parameter ϕ_G is expressed as:

$$\phi_G = (1/2\gamma_s^{1/2})[(2 - \phi)\gamma_C^{1/2} + \phi\gamma_L^{1/2}] \tag{7}$$

The γ_C was evaluated using the following equation by Kano [9].

$$\log(1 + \cos\theta) = -\psi \log \gamma_L + \log 2\phi^0(1/\gamma_s)^{a-1/2} \tag{8}$$

Good and Girifalco [8] measured the contact angles θ of polar liquids on surface of poly(tetrafluoroethylene). They evaluated Φ_G and γ_s by use of the 1+cos θ *versus* $1/\gamma_L^{1/2}$ plot.

In this work the contact angles θ of polar liquids on surface of LLDPE-g-AA (content of AA 0.57 1.46 2.57 wt%) were measured. The γ_c of LLDPE-g-AA were estimated by the Zisman plot, the Young-Dupre-Good-Girifalco plot, and $\log(1 + \cos\theta)$ *versus* $\log \gamma_L$ plot.

EXPERIMENTAL

Materials

Non-crosslinking LLDPE-g-AA was prepared by reaction extruding in our laboratory. The content of AA in LLDPE-g-AA used in this work are reported in Table II.

TABLE I Surface tensions of polar liquids

Species liquids	$\gamma_L(mN/m)$
Alcohol	22.27
Formic acid	37.6
Ethylene glycol	47.7
Glycerol	63
Water	72.75

TABLE II Critical surface tension (γ_C) of LLDPE-g-AA and the constants determined from various plots

Constants	*Degree of grafting of AA* (*wt*%)		
	0.57	1.46	2.57
γ_C(mN/m): by $\cos\theta$ *versus* γ_L plot	12.71	18.66	20.73
γ_C(mN/m): by $1+\cos\theta$ *versus* ${\gamma_L}^{-1/2}$ plot	21.21	22.13	22.96
γ_C(mN/m): by $\log(1+\cos\theta)$ *versus* $\log\gamma_L$ plot	20.47	21.37	22.67
ϕ: intercept of $1+\cos\theta$ *versus* ${\gamma_L}^{-1/2}$ plot	0.8741	0.9263	0.9485
$-\psi$: slope of $\log(1+\cos\theta)$ *versus* $\log\gamma_L$ plot	−0.2481	−0.2398	−0.2332

Preparation of Films

Cast film of the LLDPE-g-AA were obtained using xylene at 120°C and cast them on a glass plate. All the 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-g-AA films. The contact angles of polar liquids 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. The surface tension γ_L of polar liquids are listed in Table I.

RESULTS AND DISCUSSION

The contact angle is very sensitive to the chemical and structural changes that occur on a polymer surface, since the liquid makes contact with the outmost molecular layer of the surface. The contact angles of polar liquids on the cast films of LLDPE-g-AA are listed in Table III. It is observed that with an increasing the degree of grafting, contact angles of water on films of LLDPE-g-AA decreased monotonically. Similar results are observed for other solvent on films of

TABLE III Contact angles of polar liquids for the films of LLDPE-g-AA

Degree of grafting AA (wt%)	*Contact angle (deg)*				
	Alcohol	*Formic acid*	*Ethylene glycol*	*Glycerol*	*Water*
0.57	20	42	51	59	63
1.46	16	40	46	58	61
2.57	12	38	44	56	59

LLDPE-g-AA. This result suggests that the surface polarity of grafted copolymer is augmented by an increase of the content of AA in LLDPE-g-AA samples.

The Zisman plots for LLDPE-g-AA with the polar liquids are reported in Figure 1. The critical surface tension γ_C of LLDPE-g-AA films evaluated by Zisman's linear approximation have *versus* values with different the degree of grafting of AA. The critical surface tension γ_C of LLDPE-g-AA films increase with increasing the degree of grafting of AA in LLDPE-g-AA. Using Eq. (4), the relationship between $1 + \cos\theta$ and $1/\gamma_L^{1/2}$ are shown in Figure 2. The γ_C values of LLDPE-g-AA films evaluated with $1 + \cos\theta$ *versus* $1/\gamma_L^{1/2}$ plot also have various values with different the degree of grafting of AA. The magnitudes of γ_C also increase in the order: AA(wt%) = 2.57 > AA(wt%) = 1.46 > AA(wt%) = 0.57. The $\log(1 + \cos\theta)$ *versus* $\log\gamma_L$ plots are shown in Figure 3. The order of magnitudes of γ_C evaluated with this plot was similar to those on the other plots.

The γ_C values of LLDPE-g-AA films obtained by all the plots, the intercept ϕ of $1 + \cos\theta$ at $1/\gamma_L^{1/2} = 0$, in the $1 + \cos\theta$ *versus* $1/\gamma_L^{1/2}$ plot and the slope $-\psi$ on the $\log(1 + \cos\theta)$ *versus* $\log\gamma_L$ plot are listed in Table II. The γ_C values of LLDPE-g-AA films estimated by $\log(1 + \cos\theta)$ *versus* $\log\gamma_L$ and $1 + \cos\theta$ *versus* $1/\gamma_L^{1/2}$ plot were very near, but they were higher than those estimated by the Zisman plot. The ϕ increased with increasing the degree of grafting of AA in LLDPE-g-AA.

Using Eqs. (4) and (7), the relationship between $\cos\theta$ and γ_L could be defined with ϕ by the following equations.

$$\cos\theta = (2 - \phi)(\gamma_C/\gamma_L)^{1/2} + (\phi - 1) \tag{9}$$

Therefore, the relationship between $\cos\theta$ and γ_C obtained by using Eq. (9) (for $\phi < 2$) illustrated a downwardly convex cure. The γ_C

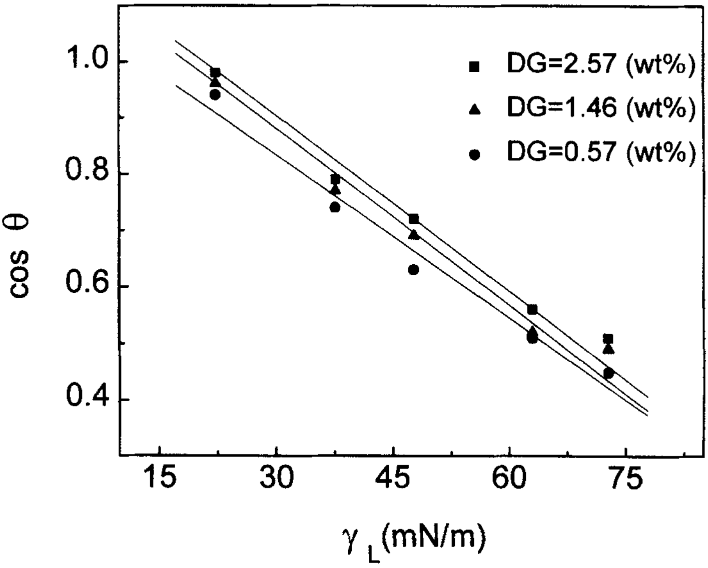

FIGURE 1 Zisman plots for LLDPE-g-AA.

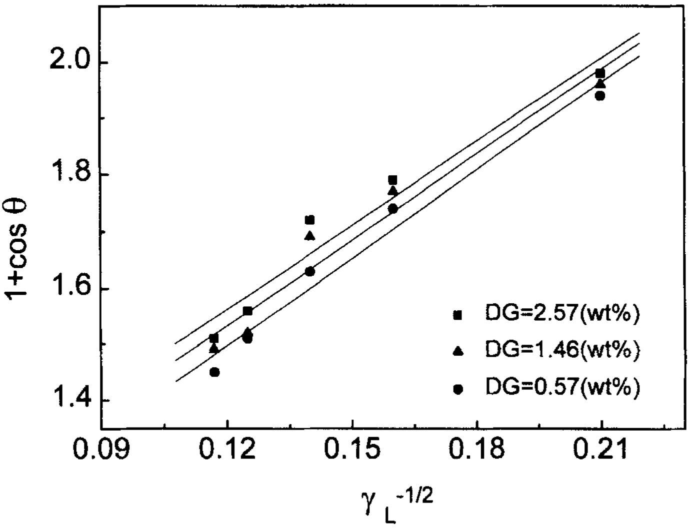

FIGURE 2 Young-Dupre-Good-Girifalco plots for LLDPE-g-AA.

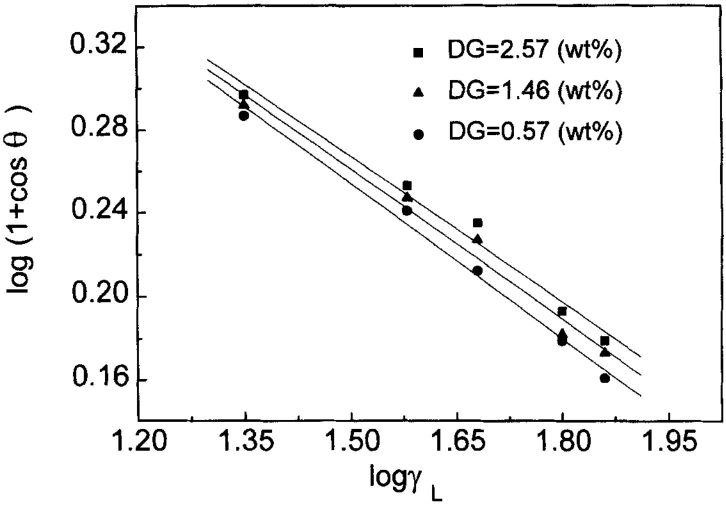

FIGURE 3 Log(1 + cos θ) *versus* log γ_L plots for LLDPE-g-AA.

values estimated by the Zisman plot and Eq. (9) were provided as $\gamma_C{}^E$ and $\gamma_C{}^T$, respectively.

The parameters ϕ of LLDPE-g-AA was given in Table II. The relationship between $\cos\theta$ and γ_L for LLDPE-g-AA with different degree of grafting of AA, evaluated with ϕ and γ_C in Table II, was expressed with Eq. (9) as follows:

AA(wt%) = 0.57: $\cos\theta = 5.20\ \gamma_L{}^{-1/2} - 0.13$
AA(wt%) = 1.46: $\cos\theta = 5.03\ \gamma_L{}^{-1/2} - 0.07$
AA(wt%) = 2.57: $\cos\theta = 4.94\ \gamma_L{}^{-1/2} - 0.05$

Both the relationship between $\cos\theta$ and γ_L obtained from Eq. (9) and Zisman plot for different degree of grafting of AA in LLDPE-g-AA are reported in Figures 4–6. We can observe that $\gamma_C{}^E$ are obviously smaller than $\gamma_C{}^T$ for polar liquids. The relationship between $\cos\theta$ and γ_L (experimental data) was approximately fitted with the theoretical curve calculated by Eq. (9). Therefore, we could presume that the Zisman plot was essentially a downwardly convex curve with the polar liquids having $\gamma_C \ll \gamma_L$. This result was consistent with that of Gutowski [10].

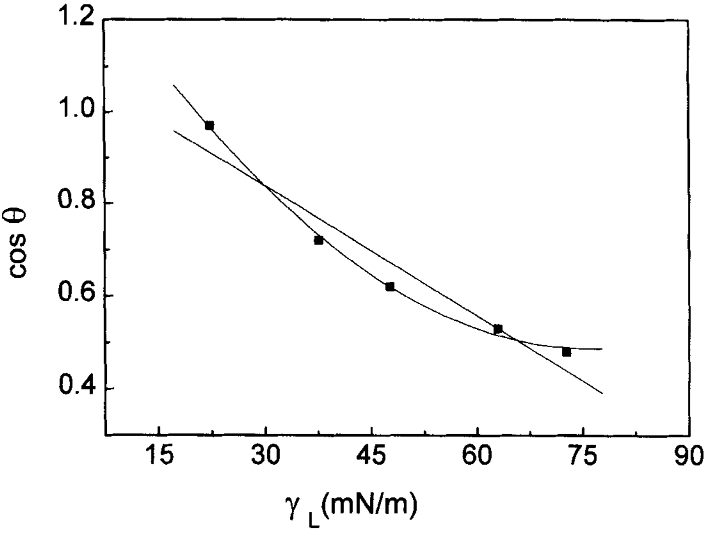

FIGURE 4 Theoretical curve of $\cos\theta$ *versus* γ_L based on the equation $\cos\theta = (2-\phi)(\gamma_C/\gamma_L)^{1/2} + (\phi - 1)$ for LLDPE-g-AA with 0.57 wt% AA content.

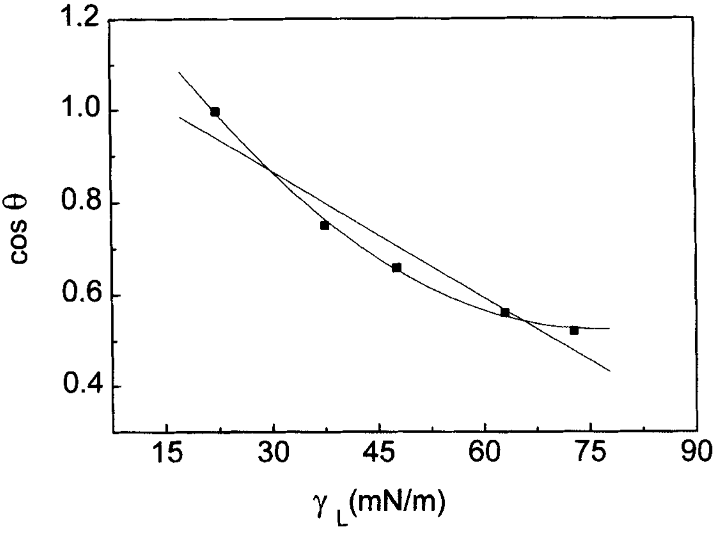

FIGURE 5 Theoretical curve of $\cos\theta$ *versus* γ_L based on the equation $\cos\theta = (2-\phi)(\gamma_C/\gamma_L)^{1/2} + (\phi - 1)$ for LLDPE-g-AA with 1.46 wt% AA content.

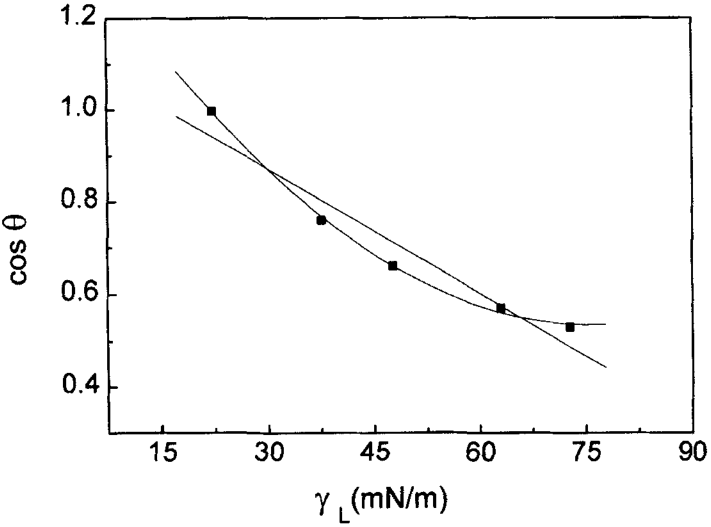

FIGURE 6 Theoretical curve of $\cos\theta$ *versus* γ_L based on the equation $\cos\theta = (2-\phi)(\gamma_C/\gamma_L)^{1/2} + (\phi - 1)$ for LLDPE-g-AA with 2.57 wt% AA content.

It is known that the orientation with polar groups [11, 12] and the rearrangement of the side chain of the polymer occur near the interface when the liquid contacts the solid polymer. In this case, the surface tension γ_S of solid polymer and the theoretical surface tension $\gamma_C{}^T$ were changed with varying polarity of the liquids.

CONCLUSIONS

The contact angles of polar liquids on surface of LLDPE-g-AA films were measured. The γ_C values of LLDPE-g-AA obtained by the $1+\cos\theta$ *versus* $\gamma_L^{-1/2}$plot and the $\log(1+\cos\theta)$ *versus* $\log\gamma_L$ plot were very near, but them were higher than those obtained by the Zisman plot. It was found that the Zisman plot resulted in essentially a downwardly convex curve.

Acknowledgments

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