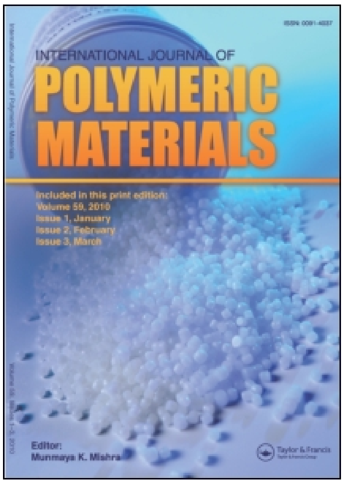

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The Determination of Ethylene-Propylene Copolymer-Grafted-Glycidyl Methacrylate by the Contact Angle Method

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The contact angles θ of some liquids on ethylene-propylene copolymer-grafted-glycidyl methacrylate (EPM-g-GMA) were measured. The critical surface tensions r_c of EPM-g-GMA were evaluated by the Zisman Plot (cos θ versus r_L), Young-Dupre-Good-Girifalco plot (1 + cos θ versus $1/r_L^{0.5}$) and log(1 + cos θ) versus log(r_L) plot. The following results were obtained: the r_c values varied significantly with the estimation methods. The critical surface tension r_c decreased with the increase of the degree of grafting of EPM-g-GMA.

KEY WORDS EPM-g-GMA, Zisman plot, Young-Dupre-Good-Girifalco plot, critical surface tension.

INTRODUCTION

Ethylene-propylene copolymer modification by grafting unsaturated polar groups onto the polymer backbone has been widely investigated.[1-3] The increased polarity which can be achieved in this way can improve some physicomechanical properties of the modified polyolefin such as adhesion to other materials (e.g., metal or glass), and can promote better compatibility with other polymers. The surface properties are closely related to the surface tension r_s. The estimation of r_s of the polymer solid has generally been made by the contact angle θ of organic liquids on polymer solids.[4,5] He found that the relationship between cos θ and the surface tension of liquid r_L gave rise a good straight line. He named the critical surface tension r_c, which was r_L at cos θ = 1 by extrapolating the straight line. Good and Girifalco[6] parameter defined the interaction Φ_G using the work of adhesion W_a and the work of cohesion W_c:

$$\Phi_G = W_A/(W_{c1}W_{c2})^{0.5} \tag{1}$$

They presented the following equation:

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$$W_a = 2\Phi_G(r_s r_L)^{0.5} \tag{2}$$

using Equation (2) and Young-Dupre's equation

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

the equation of Young-Dupre-Good-Girifalco was expressed as:

$$1 + \cos\theta = 2\Phi_G(r_s/r_L)^{0.5} \tag{4}$$

In the present paper, the contact angles θ of EPM-g-GMA were measured. The critical surface tensions r_c of EPM-g-GMA were estimated by the Zisman plot (cos θ versus r_L), the Young-Dupre-Good-Girifalco plot ($1 + \cos\theta$ versus $1/r_L^{0.5}$) and the $\log(1 + \cos\theta)$ versus $\log(r_L)$ plot.

THEORETICAL BACKGROUND

Young-Dupre-Good-Girifalco Plot

The $1 + \cos\theta$ versus $1/r_L^{0.5}$ plot obtained by the contact angles θ of homogeneous liquids on a polymer solid gives rise to a good straight line with the experimental data. However, in many cases the straight line greatly deviated from the origin with the polarity of the liquids.[7] In such cases, the straight line can be expressed as:

$$1 + \cos\theta = \lambda r_L^{-0.5} + \varphi \tag{5}$$

where λ and φ are the slope and the intercept of $1 + \cos\theta$ at $1/r_L^{0.5} = 0$ in the $1 + \cos\theta$ versus $1/r_L^{0.5}$ plot, respectively. These parameters are constant with homogeneous liquids. The critical surface tension r_c is defined as the value of r_L at $\theta \to 0$. The relationship between λ and φ is expressed in the following equation by use of r_c:

$$\begin{gathered} \lambda = (2 - \varphi)r_c^{0.5} \\ \lambda < 0 \quad \varphi < 2 \quad \text{for } d\cos\theta/dr_L < 0 \end{gathered} \tag{6}$$

Using Equation (5), Young-Dupre's Equation (3) and Good-Girifalco's Equation (2), and neglecting the spreading pressure π_e, the Good-Girifalco interaction parameter Φ_G is expressed as:

$$\Phi_G = (1/2r_s^{0.5})[(2 - \varphi)r_c^{0.5} + \varphi r_L^{0.5}] \tag{7}$$

where r_s is the surface tension of solid. The parameter Φ_G^0, defined as Φ_G at $\theta \to 0$, is expressed as follows:

TABLE I

Characterization of the investigated copolymer

Code	Composition of the reaction miture (EPM/GMA/DCP by wt)	Grafting degree of GMA (%wt)
A	100/1/0.1	0.26
B	100/2/0.1	0.33
C	100/3/0.1	0.54

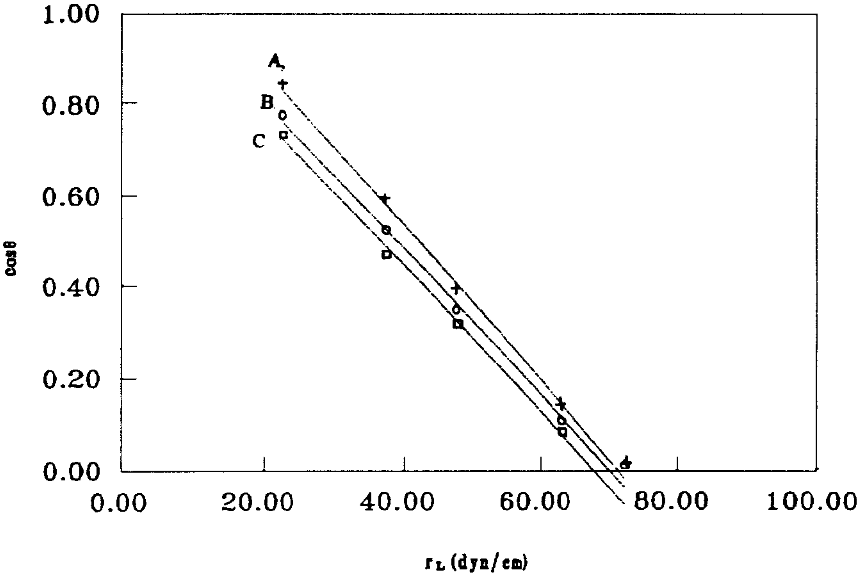

FIGURE 1 Zisman plots for A, B, and C.

$$\Phi_G^0 = (r_c/r_s)^{1/2} \tag{8}$$

The log(1 + cos θ) versus log(r_L) Plot

As the interaction between liquid and solid is approximated by use of the geometric mean law, Φ_0 is defined as the indication of polarity in Φ_G. Furthermore, we also took account of an adjustable parameter (X_{LS}) within Φ_G as a departure from the interaction estimated by the geometric law.[7] Thus Φ_G is expressed as:

$$\Phi_G = (X_L^d X_s^d)^{0.5} + (X_L^p X_s^p)^{0.5} + X_{LS} = \Phi_0 + X_{LS} \tag{9}$$

where X_j^d and X_j^p are the dispersion and the polarity of the j component.

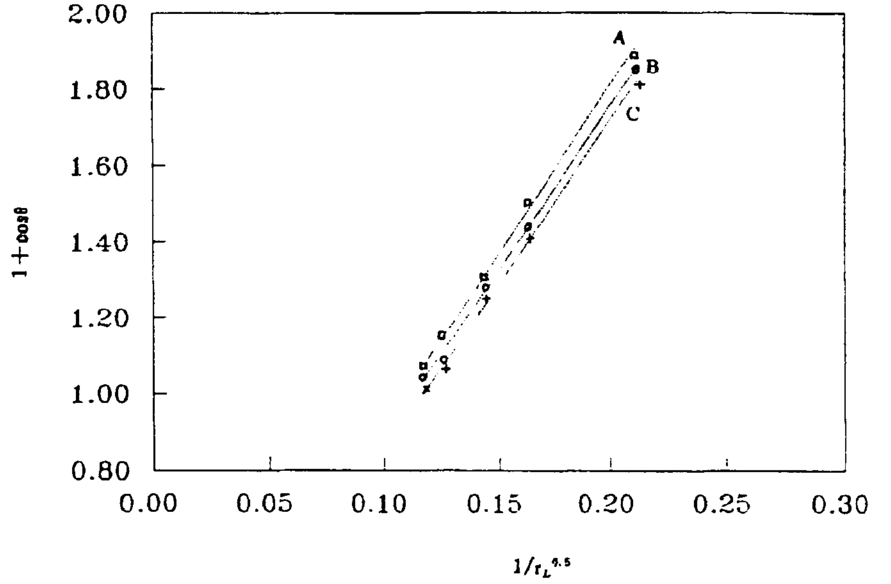

FIGURE 2 Young-Dupre-Good-Girifalco plots for A, B, and C.

Wu[8] reported that the polarity X_j^p was estimated with the solubility parameter δ and the polarity component of solubility parameter δ^p by the following equation:

$$X_s^p = (\delta^p/\delta)^2 \tag{10}$$

Also, the parameter a, determined with the polarity and X_{LS}, is introduced into Φ_G as follows:

$$\Phi_G = \Phi_0(r_L/r_s)^a$$

$$\alpha = \left[\log\left(\frac{\Phi_0 + X_{LS}}{\Phi_0}\right)\right] \Big/ \log(r_L/r_s) \tag{11}$$

$$a < 0.5 \quad \text{for } d\cos\theta/dr_L < 0$$

The Φ_0 is equal to the bonding efficiency parameter of Kaelble and Uy.[9] Therefore, Φ_G^0 is expressed by:

$$\Phi_G^0 = [(X_c^d X_s^d)^{0.5} + (X_c^p X_s^p)^{0.5}](r_c/r_s)^a \tag{12}$$

where X_c^d is the ratio of r_c obtained with D liquids and r_c obtained with P or H liquids.[7] The surface tension r_s is obtained from Equations (8) and (12) as follows:

$$r_s = r_c[(X_c^d X_s^d)^{0.5} + (X_c^p X_s^p)^{0.5}]^{2(2a-1)} \tag{13}$$

Also, the reversible work of adhesion W_a is expressed by:

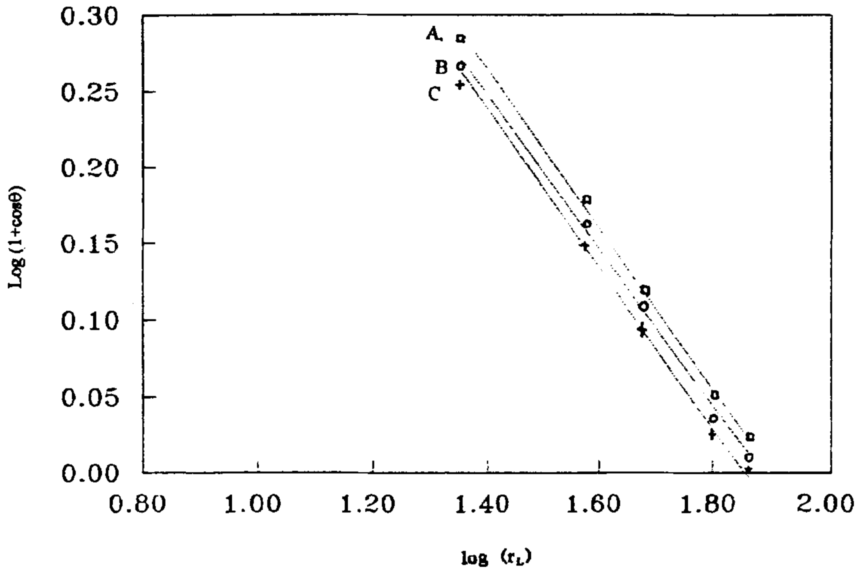

FIGURE 3 Log(1 + cos θ) versus log(r_L) plots for A, B, and C.

$$W_a = 2\Phi_0(r_s^{0.5-a} r_L^{0.5+a}) \quad (14)$$

Consequently, the combination of Equation (14) and Young-Dupre's Equation (3) leads to:

$$\log(1 + \cos\theta) = -\Psi \log(r_L) + \log(2\Phi_0 r_s^{0.5-a}) \quad (15)$$

Using Equation (15), the parameter a is determined with the slope $\Psi = (0.5 - a)$ in the plot of log(1 + cos θ) versus log(r_L) and r_c is obtained from the value of r_L at log(1 + cos θ) = log 2 by extrapolating the straight line.

EXPERIMENTAL

Materials

The preparation of EPM-g-GMA have been reported.[10] The degree of grafting was calculated by using chemical titration method. A copolymer sample (2 g) was added to 100 ml xylene. After copolymer was dissolved completely, 2 ml of concentrated hydrochloric acid was added. After 15 min of stirring at room temperature, neutral ethanol (40 ml, containing cresol red indicator) was added and the mixture was titrated with 0.05 N methanolic sodium hydroxide solution to the first violet colour of the end-point. The grafting degree of the samples are shown in Table I.

TABLE II

The critical surface tension r_c of EPM-g-GMA and the constant determined from various plots

Constant	A	B	C
r_c: critical surface tension by zisman plot Cosθ versus r_L	12.960	8.031	5.715
r_c: critical surface tension by (1+Cosθ) vresus $1/r_L^{0.5}$ plot	20.348	19.120	18.450
r_c: critical surface tension by log (1+Cosθ) vresus log (r_L) plot	1.332	1.296	1.283
φ: intercept of (1+Cosθ) axis in the plot of (1+Cosθ) versus $1/r_L^{0.5}$	0.038	0.0332	−0.008
(−Ψ) = −(0.5−a): slope (−Ψ) in the plot of log (1+Cosθ) versus log (r_L)	−0.511	−0.526	−0.526

Contact Angle Measurements

The contact angle of EPM-g-GMA films with various liquids were measured in our laboratory. The 1.5 mm diameter drops of liquids were prepared with a microsyringe and they were dropped on the surface of EPM-g-GMA films at 20°C.

RESULTS AND DISCUSSION

The concept of critical surface tension was first proposed by Fox and Zisman.[11] An empirical linear relation was found between cos θ and r_L for a series of testing liquids

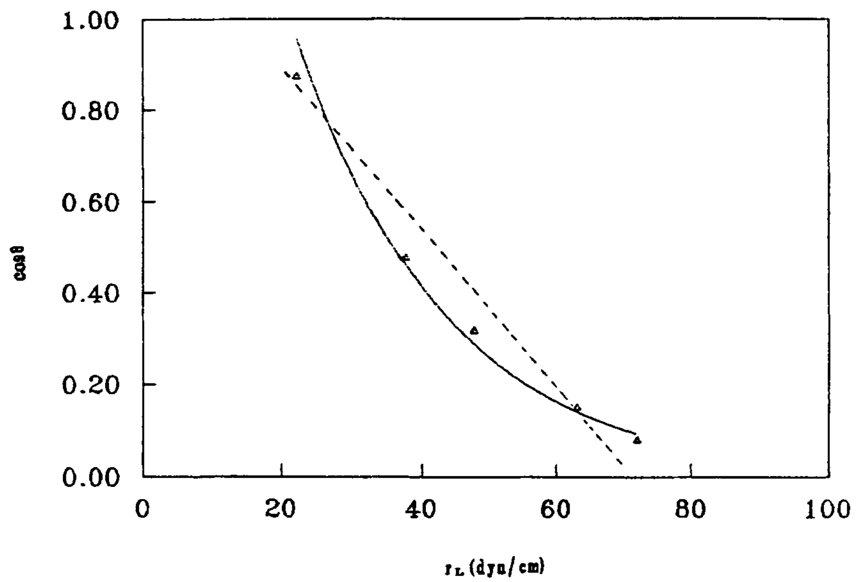

FIGURE 4 Theoretical curves of cos θ versus r_L for sample A on the equation $\cos\theta = (2 - \varphi)(r_c/r_L)^{0.5} + (\varphi - 1)$.

on a given solid. When homologous liquids are used as the testing liquids, a straight line is often obtained. The intercept of the line at $\cos\theta = 1$ is the critical surface tension r_c. The Zisman plots for EPM-g-GMA with the organic liquids are shown in Figure 1, it is seen that the critical surface tension r_c decreased with the increase of grafting degree of EPM-g-GMA from 0.26% to 0.54%.

The relationships between $1 + \cos\theta$ and $1/r_L^{0.5}$ are shown in Figure 2. The r_c values of EPM-g-GMA evaluated with the $1 + \cos\theta$ versus $1/r_L^{0.5}$ plot also have various values with varying liquids used. The magnitude of r_c also increases in the order: A > B > C.

The $\log(1 + \cos\theta)$ versus $\log r_L$ plots are shown in Figure 3. The order of magnitude of r_c evaluated with this plot is similar to those on the other plots.

The r_c values of EPM-g-GMA films obtained by all the plots, the intercept φ of $1 + \cos\theta$ at $1/r_L^{0.5} = 0$ in the $1 + \cos\theta$ versus $1/r_L^{0.5}$ plot and slope $-\Psi$ on the $\log(1 + \cos\theta)$ versus $\log(r_L)$ plot are shown in Table II. The values estimated by $\log(1 + \cos\theta)$ versus $\log(r_L)$ plot are smaller than those estimated by other plots. φ decreases with increasing GMA content in EPM-g-GMA. The slope $-\Psi$ decreases with increasing GMA content in EPM-g-GMA.

In this study, the Zisman critical surface tension r_c of EPM-g-GMA are discussed by use of the intercept φ of $1 + \cos\theta$ at $1/r_L^{0.5} = 0$ in the $(1 + \cos\theta)$ versus $1/r_L^{0.5}$ plot and the slope $-\Psi$ in the $\log(1 + \cos\theta)$ versus $\log(r_L)$ plot. The relationship between $\cos\theta$ and r_L can be defined with the φ and by the following equations: from Equation (7) and Equation (4):

$$\cos\theta = (2 - \varphi)(r_c/r_L)^{0.5} + (\varphi - 1) \tag{16}$$

From Equation (11) and Equation (4)

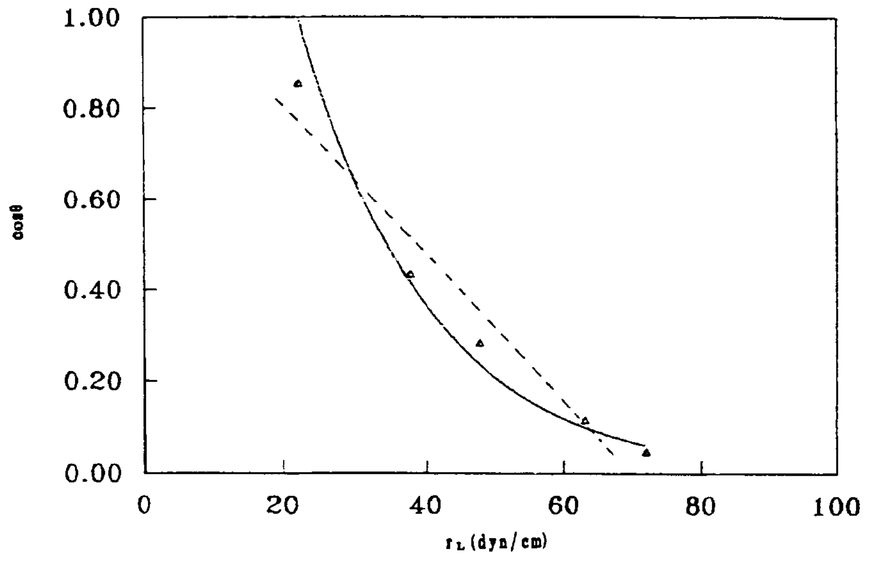

FIGURE 5 Theoretical curves of cos θ versus r_L for sample B on the equation cos θ = $(2 - \varphi)(r_c/r_L)^{0.5} + (\varphi - 1)$.

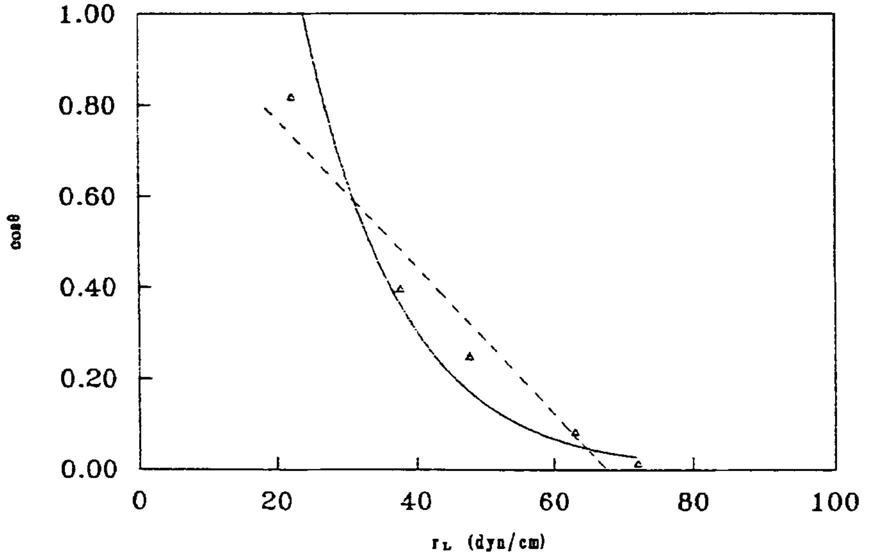

FIGURE 6 Theoretical curves of cos θ versus r_L for sample C on the equation cos θ = $(2 - \varphi)(r_c/r_L)^{0.5} + (\varphi - 1)$.

$$\cos\theta = 2\Phi_G(r_s/r_L)^{\Psi-1} \tag{17}$$

Therefore, the relationship between cos θ and r_L obtained using Equation (16) (for $\varphi < 2$) illustrates a downwardly convex curve. The r_c values estimated by the Zisman plot and Equation (16) are provided as r_c^E and r_c^T, respectively. The relation on the

Zisman plot and the r_c in this study is discussed with Equation (16). The relationship between cos θ and r_L for EPM-g-GMA with different GMA content, evaluated with the φ and r_c in Table II, is expressed with Equation (16) as follows:

$$\text{for A} \quad \cos\theta = 8.848 r_L^{-0.5} - 0.9616$$

$$\text{for B} \quad \cos\theta = 8.601 r_L^{-0.5} - 0.9671$$

$$\text{for C} \quad \cos\theta = 8.625 r_L^{-0.5} - 1.0081$$

Both the relationship between cos θ and r_L obtained from Equation (16) and the straight line on the Zisman plots are shown in Figures 4–6. It is seen that r_c^E for the testing liquids is nearly equal to r_c^T. The relationship between cos θ and r_L (experimental date) is approximately fitted with the theoretical curve calculated by Equation (16).

CONCLUSION

The contact angles of organic liquids on EPM-g-GMA films were measured. The r_c values of EPM-g-GMA films obtained with the log(1 + cos θ) versus log(r_L) plot were smaller than those obtained with either the Zisman plot (cos θ versus r_L) or the 1 + cos θ versus $\cdot/r_L^{0.5}$ plot. It was found that the increase of grafting degree resulted in the increase of the r_c values.

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