

# Characterization of Grafted Polyethylene by Contact-Angle Hysteresis and ESCA Studies

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## SYNOPSIS

Low-density polyethylene (LDPE) has been functionalized in the bulk through dicumyl peroxide (DCP)-initiated grafting of dibutyl maleate (DBM) and vinyltrimethoxysilane (VTMO) in the temperature range from 140 to 200°C. The functionalized surfaces have been characterized through contact angle and contact-angle hysteresis measurements as well as through ESCA studies. The degree of grafting has been determined by infrared spectrophotometry. From the ESCA patterns of the modified polymers, the atomic ratios of oxygen to carbon and silicon to carbon have been calculated. Determination of an empirical relation between contact-angle hysteresis and the oxygen-carbon ratio of the functionalized polymer surfaces has been attempted. It is found that the higher the oxygen-carbon ratio, the lower the contact-angle value for polyethylene. Contact angle-hysteresis increases with increase of the degree of grafting. The total surface energy increases with grafting. The surface energy of the silane-grafted polyethylene (PEgS) is found to be lower than that of dibutyl maleate-grafted polyethylene (PEgDBM). © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Functionalization of polyolefins through graft copolymerization of unsaturated monomers containing polar groups has received considerable attention in recent years. This type of functionalization is generally carried out for modification of some of the properties like adhesion and dyeability. Sometimes, these functionalized materials are further utilized for cross-linking reactions. Graft copolymerization of an unsaturated polar monomer onto a preformed polymer is also widely recognized as a potential practical route to generate a novel class of interaction promoters (compatibilizer) in the case of multicomponent polymer systems. Vinylsilanes are among the most effective classes of such organofunctional monomers; they can be grafted easily onto

the backbone chains of polyolefins through melt processing. The technology of making moisture-curable polyolefins through silane grafting by bulk processing has been developed and is being used commercially.<sup>1,2</sup> The method of making cross-linkable polyolefins through silane grafting has gained attention because of its various advantages, such as easy processing, low cost and capital investment, and favorable properties in the processed materials. To date, there is a lack of broad-based knowledge and expertise in the field of characterization of this polymer and very few reports are in the literature.

Until recently, maleic anhydride has been used mostly for the functionalization of polyolefins due to the high reactivity of the anhydride group toward successive reactions.<sup>3-5</sup> The maleic anhydride, although more reactive and effective than the corresponding ester, is very volatile, toxic, and corrosive. Hence, the ester dibutyl maleate has been used in a few applications. Moreover, dibutyl maleate (DBM) is more compatible with polyolefins than is maleic anhydride.<sup>6</sup>

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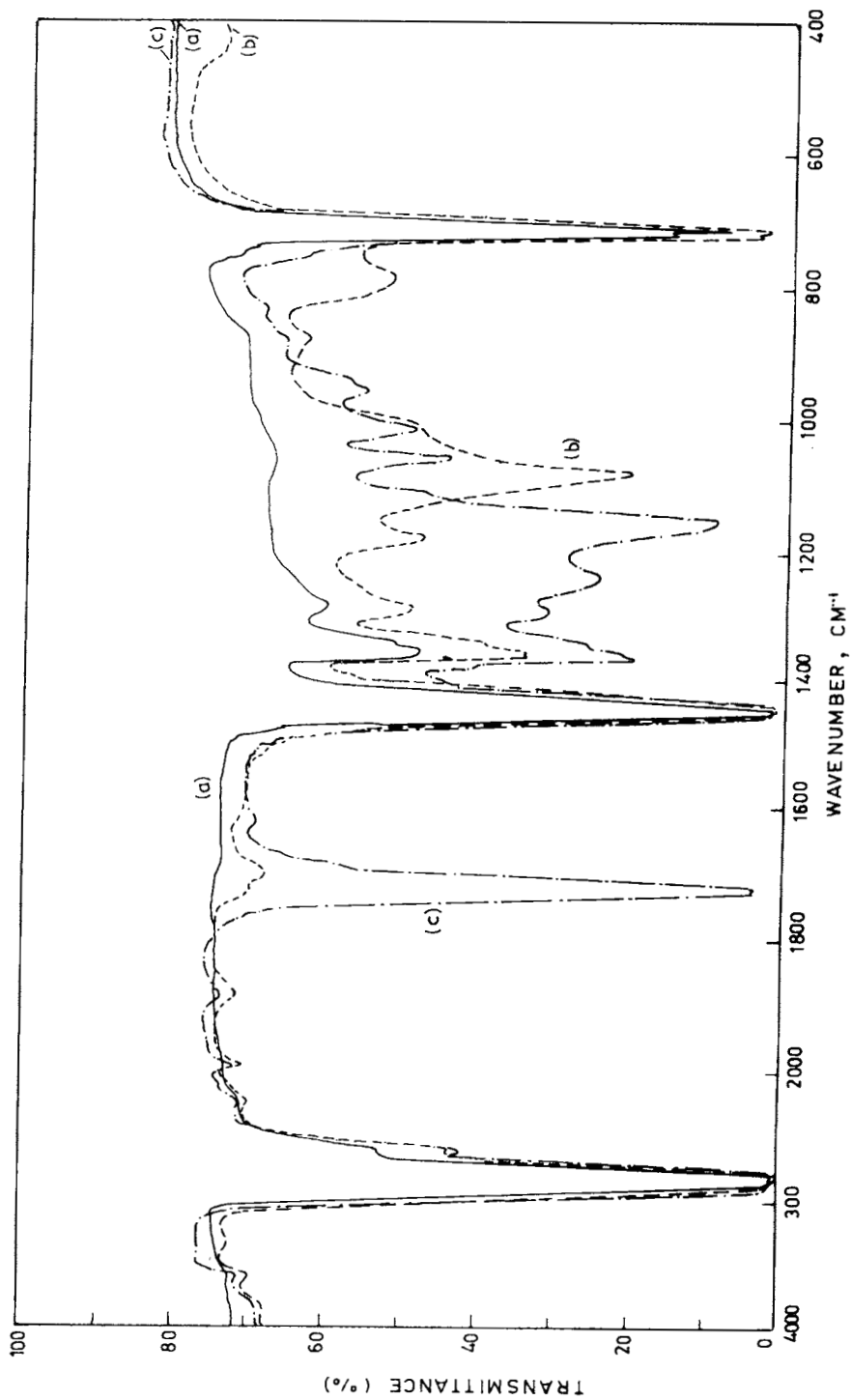


Figure 1 Infrared spectra of (a) LDPE, (b) PEgS, and (c) PEgDRM.

Measurement of the contact angle of a solid/liquid interface is a widely used method for the determination of the surface energy of solid polymers. The contact-angle hysteresis of a polymer/liquid combination that gives further insight into the wetting behavior of a liquid onto a solid is also an excellent method for characterizing the surface. However, it does not appear to have received much attention in the case of hydrocarbon polymers.

If a system of three phases, solid-liquid-vapor, is in thermodynamic equilibrium, an angle  $\theta_e$  is subtended at the triple line by the tangents onto the solid-liquid and liquid-vapor interfaces. In thermodynamic terms, this system parameter  $\theta_e$  depends, via Young's equation, on the interfacial tensions. Instead of the equilibrium angle  $\theta_e$ , two other angles are obtained on real surfaces: the advancing angle  $\theta_a$  after enlarging the drop (wetting) and the receding angle  $\theta_r$  after reducing the contact area of the drop with the solid (dewetting). The difference between the two angles is widely known as hysteresis,  $\Delta\theta = \theta_a - \theta_r$ . Both the advancing and receding angles can be observed with one drop when the substrate is tilted.<sup>7</sup>

During chemical modification, the surface groups also change. ESCA is a powerful method in identifying the groups formed and in determining concentration. Clark et al. demonstrated the use of ESCA for characterizing the polymer surface.<sup>8</sup> We have also quantified oxidation of polyolefins using ESCA.<sup>9</sup>

In the present work, the surface of the DBM- and silane-grafted polyethylenes have been characterized by contact angle and contact-angle hysteresis measurements. At the same time, the ESCA patterns of the modified polymers have been obtained, from which the atomic ratio of oxygen to carbon has been calculated. Determination of an empirical relation between contact-angle hysteresis and the oxygen-carbon ratio of the modified polymer surfaces has been attempted.

## EXPERIMENTAL

### Materials

Low-density polyethylene (LDPE) (NESTE polyethylene DFDS 4445, Neste Polyeten AB, Sweden) with a density of 0.915 g/cm<sup>3</sup> and an MFI of 2.0 g/10 min (ASTM-D 1238), dibutyl maleate (DBM) of standard reagent grade, dicumyl peroxide (DCP) (99%) (Dicup R, Hercules Inc.), and vinyltrimethoxysilane (VTMO) (Dynamit Nobel, Germany) were used. Deionized water was distilled from permanganate solution in an all-Pyrex apparatus. The water used had a surface tension of 72.8 mN/m. Formamide was of analar grade obtained from the British Drug House Ltd. and had a surface tension of 58.2 mN/m.

### Graft Copolymerization Reaction

PE was fed into the cam-type mixing head of a Brabender Plasticorder (PLE-330) at a temperature of 110 ± 2°C. After stabilization of the temperature, the requisite amounts of DBM/VTMO and DCP were added in the form of solution and continuously mixed for 5 min at a rotor speed of 40 rpm. After the premixing step, the temperature of the Brabender mixing chamber was rapidly raised to the selected temperature (180°C) for grafting within a period of 3–5 min. The rotor speed was raised to 50 rpm and kept constant throughout the reaction.

The evaluation of the amount of grafted groups of dibutyl maleate-grafted polyethylene (PEgDBM) and silane-grafted polyethylene (PEgS) was performed with the help of infrared spectra obtained with a Shimadzu IR-420 using molded thin films of the grafted polymers (Fig. 1). The absorbance of the  $\text{>C=O}$  stretching of the grafted maleate at 1738 cm<sup>-1</sup> was used to determine the degree of grafting, which was generally expressed as amount of

**Table I** Contact Angle and Contact-angle Hysteresis of Modified Polyethylene

Polymer	Degree of Grafting	$\theta_a$ (H <sub>2</sub> O)	$\theta_r$ (H <sub>2</sub> O)	$\Delta\theta$ (H <sub>2</sub> O)	$\theta_a$ (HCONH <sub>2</sub> )	$\theta_r$ (HCONH <sub>2</sub> )	$\Delta\theta$ (HCONH <sub>2</sub> )
	(mmol/100 g Product)						
LDPE	—	83	73	10	75	69	6
PEgS <sub>1</sub>	20	80	68	12	73	65	8
PEgS <sub>2</sub>	25	78	65	13	70	58	12
PEgDBM <sub>1</sub>	13	67	55	12	61	53	8
PEgDBM <sub>2</sub>	17	64	49	15	55	44	11
PEgDBM <sub>3</sub>	20	57	40	17	50	36	14

**Table II Surface Energy of Modified Polyethylene**

Polymer	Degree of Grafting (mmol/100 g Product)	$\gamma_s^d$ (mJ/m <sup>2</sup> )	$\gamma_s^p$ (mJ/m <sup>2</sup> )	Total Surface Energy (mJ/m <sup>2</sup> )
LDPE	—	12.18	10.02	22.20
PEgS <sub>1</sub>	20	12.69	10.89	23.58
PEgS <sub>2</sub>	25	13.35	12.29	25.64
PEgDBM <sub>1</sub>	13	13.63	19.59	33.22
PEgDBM <sub>2</sub>	17	15.36	21.23	36.59
PEgDBM <sub>3</sub>	20	15.46	25.76	41.22

grafted DBM (mmol) per 100 g of product.<sup>10</sup> The absorbance of the —Si—O—C group stretching of the grafted silane at 1090 cm<sup>-1</sup> was used for quantitative estimation of the degree of grafting of silane.<sup>11</sup>

### Measurement of Contact Angle and Contact-angle Hysteresis

The contact angles were determined using a contact-angle meter (Kernco, Model GII). The method was based on the measurement of contact angles by the sessile drop method with water and formamide. Each contact angle quoted was the mean of at least five measurements with a maximum error in  $\theta$  of  $\pm 2^\circ$ . All investigations were carried out using a polymer plate with dimensions 10 × 10 × 1 mm<sup>3</sup> in vapor-saturated air at 20 ± 2°C in the closed sample box. Further, the polymer plate with a sessile liquid drop was tilted by an angle 35° while the drop diameter was more than 4 mm. All the data for hysteresis reported here are the means of at least five measurements.

### X-ray Photoelectron Spectroscopy (XPS)

XPS data were obtained using an ESCALAB MK II spectrometer employing exciting radiation of 1487 eV (AlK $\alpha$ ). Samples examined were in the form of

rectangles (20 × 8 mm<sup>2</sup>) cut from a thin sheet and mounted with double-sided adhesive tape onto the probe tip. The working pressure in the spectrometer was 4.8 × 10<sup>-9</sup> Torr. All spectra were referenced to the C1s peak for neutral carbon, which was assigned a value of 285.0 eV. All spectra were drawn at an electron takeoff angle of 90° with respect to the polymer surface. Peak areas were corrected for different photoemission crosssections of the core electrons to obtain atomic ratios.

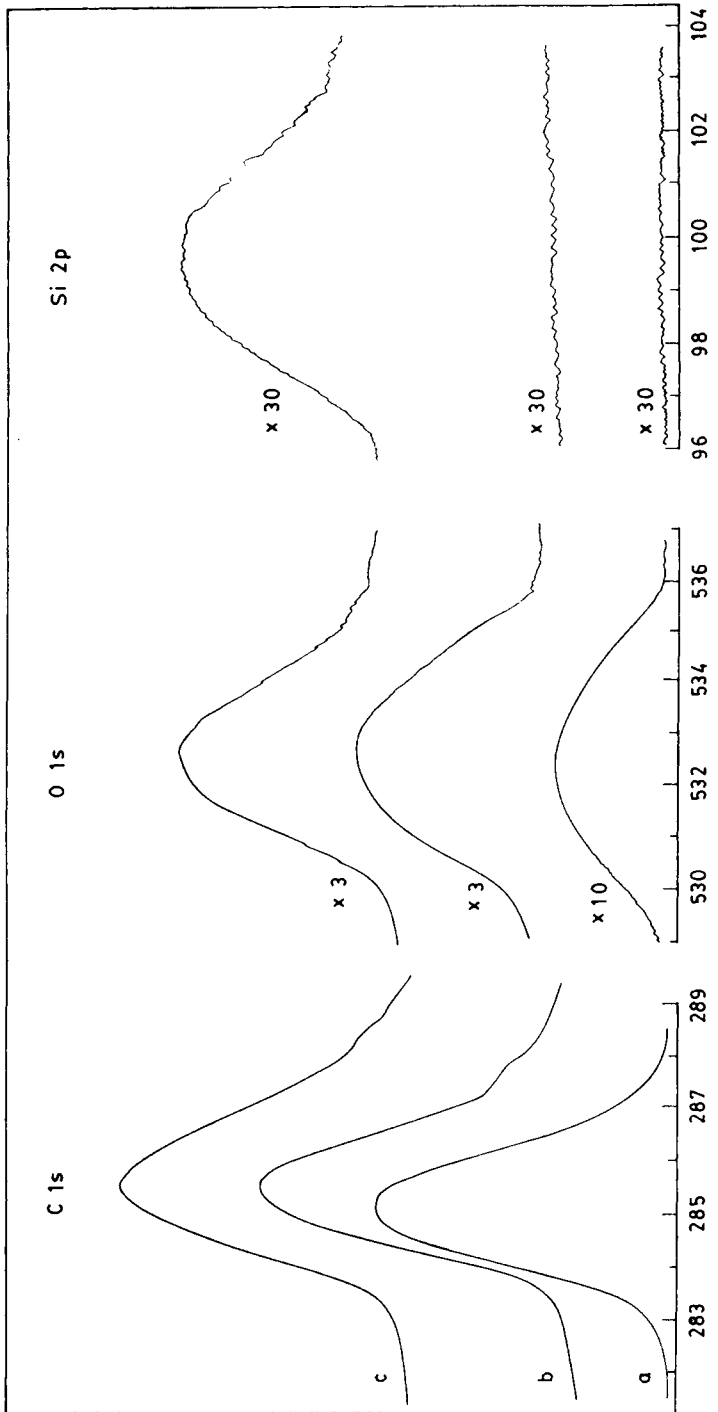
## RESULTS

### Contact Angle and Contact-angle Hysteresis

The advancing and receding contact angles of water and formamide on PEgS and PEgDBM are tabulated in Table I. The corresponding values of contact-angle hysteresis are also presented in that table. The advancing as well as receding angles for all the grafted PEs decrease when compared with the values of the control PE. PEgDBM shows lower  $\theta_a$  and  $\theta_r$  than those of the silane system. These differences are more marked when the plane of PE is tilted at 35°. The change in  $\theta_{H_2O}$  value is 12° for DBM-grafted PE<sub>1</sub> as compared to PE. The contact-angle hysteresis value for grafted PEs increases with increase of the degree of grafting.

**Table III Work of Adhesion for Modified Polyethylene**

Polymer	Degree of Grafting (mmol/100 g Product)	$\theta_c$ (H <sub>2</sub> O) (Degree)	$W_A$ (H <sub>2</sub> O) (mJ/m <sup>2</sup> )	$\theta_c$ (HCONH <sub>2</sub> ) (Degree)	$W_A$ (HCONH <sub>2</sub> ) (mJ/m <sup>2</sup> )
LDPE	—	86	77.88	77	71.29
PEgS <sub>1</sub>	20	84	80.41	75	73.26
PEgS <sub>2</sub>	25	81	84.19	72	76.18
PEgDBM <sub>1</sub>	13	70	97.70	67	84.62
PEgDBM <sub>2</sub>	17	66	102.41	58	89.04
PEgDBM <sub>3</sub>	20	60	109.20	53	93.23



**Figure 2** Binding energies (in eV) of C1s, O1s and Si2p peaks from surfaces of (a) LDPE, (b) PEGDBM, and (c) PEGS.

Since a liquid makes contact with the outermost molecular layer of a surface, the contact angle is very sensitive to the chemical and structural changes that occur on that surface. The polar and dispersion components of the surface free energy have been obtained from the following equations:

$$W_A = \gamma_1(1 + \cos \theta) \quad (1)$$

$$W_A = 2(\gamma_s^p \gamma_l^p)^{1/2} + 2(\gamma_s^d \gamma_l^d)^{1/2} \quad (2)$$

where the superscripts *d* and *p* denote dispersion and polar force contributions, respectively. These quantities are included in Table II. To calculate  $\gamma_s^p$  and  $\gamma_s^d$ , the following values for  $\gamma_l^p$  and  $\gamma_l^d$  were taken:

Water:  $\gamma_l = 72.8$ , mN/m;  $\gamma_l^d = 21.8$ , mN/m;  
 $\gamma_l^p = 51.0$  mN/m.

Formamide:  $\gamma_l = 58.2$ , mN/m;  $\gamma_l^d = 39.5$ , mN/m;  
 $\gamma_l^p = 18.7$  mN/m.

It is observed that the total surface energy increases with grafting. The values become almost double for DBM-grafted PE<sub>3</sub>. The increased surface energy of the grafted polymer comes mostly from the polar component ( $\gamma_s^p$ ).  $\gamma_s^p$  changes more than twofold for PEgDBM. Owing to the presence of polar groups on the surface, the surface energies of grafted PEs are expected to increase; the extent of this enhancement will depend on how many polar groups have been incorporated. This has been determined and is explained later. Table III reveals the values of the work of adhesion of control PE, PEgDBM, and PEgS. Since the contact angle decreases, the work of adhesion calculated using eq. (1) increases. This is true for both water and formamide.

### X-ray Photoelectron Spectra

The X-ray photoelectron (XP) spectra of pressed polyethylene indicates a low level of oxygenated

species. The C1s and O1s regions of the XP spectra of PEgDBM are shown in Figure 2. Figure 2 also depicts the C1s, O1s, and Si2p region of the XP spectra of PEgS. The C1s spectrum of polyethylene shows a single peak at 285.2 eV, indicative of the carbon-carbon bonds in PE. The C1s spectra of grafted polyethylene show new peaks at high binding energy (near 288–289 eV), the shift in the C1s peak indicating the presence of carbon-oxygen functionalities. O1s, C1s, and Si2p peak areas have been corrected for different photoemission crosssections of these core electrons to obtain atomic ratios. These data are summarized in Table IV. It is observed that the O : C ratio increases with grafting and, surprisingly, it is more for silane-grafted polymer. There is about a four- to 12-fold increase depending on the level of grafting and DCP contents.

An examination of Table IV also confirms that increasing DCP concentration leads to increased O : C ratio for DBM and PEgS and also increased Si : C ratio for PEgS. The increased O : C ratio for PEgDBM might be due to the presence of DBM groups on the polymer backbone. The appearance of a new peak at higher binding energy region (288–289 eV) of the C1s spectra can be ascribed to the carboxylic ester group.<sup>12</sup> The shift of the O1s peak toward high binding energy further establishes the presence of the ester group.<sup>12</sup>

The higher O : C and Si : C ratios for PEgS can be explained by considering the incorporation of the —Si—O—C group onto the polymer backbone during grafting.

At higher values of the O : C ratio, lowering of the contact angle is expected. Higher O : C ratio means more functional groups are present and, naturally, one can expect an enhanced surface energy of the solid. Lowering of contact angle suggests better wetting and, therefore, enhancement of surface energy. It is, however, interesting to note here that the surface energy of PEgS is lower, although the O : C ratio is higher than that of PEgDBM. It is well known that the silicones are release agents and have

**Table IV XPS Data of Modified Polyethylene**

Polymer	Degree of Grafting (mmol/100 g Product)	% O to total C	% Si to total C
LDPE	—	0.65	—
PEgS <sub>1</sub>	20	6.95	4.2
PEgS <sub>2</sub>	25	7.52	6.5
PEgDBM <sub>1</sub>	13	2.30	—
PEgDBM <sub>2</sub>	17	4.12	—
PEgDBM <sub>3</sub>	20	6.90	—

very low surface energy.<sup>13</sup> Apparently, the expected increase in  $\gamma_s$  due to increased O : C ratio is partially nullified by the presence of silicon atoms.

## CONCLUSIONS

The contact-angle hysteresis of grafted polyethylenes increases with the increase of the degree of grafting. PEGDBM shows a lower contact angle value than that of the silane system. The surface energy of PEGS is lower than that of PEGDBM. Both the oxygen-carbon ratio and silicon-carbon ratio increase with increase of the degree of grafting.

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