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Infrared Reflectance as a Tool to Reveal Preferential Molecular Orientation of Polymers Adsorbed onto Flat Substrates

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SUMMARY: FTIR-Reflectance experiments have been made on thin ethylene-vinyl acetate (EVA) copolymer layers deposited on aluminum mirrors in order to determine orientation of polymer functional groups at the interface. This was accomplished by using various reflection angles under p polarization state of the incident IR beam. Film thicknesses were estimated by ellipsometric experiments. Kramers-Kronig analysis is first applied to the external infrared reflection spectrum from a single copolymer surface measured near the normal incidence angle. Absorption spectra, k(ν), are then deduced and used to calculate specular reflectance intensities of the functional groups of interest as a function of incidence angle, polarization state and film thickness. The calculated values are compared to those observed. A layer model is developed, which allows the molecular orientation of both EVA carbonyl groups and the main chain axis at the interface to be determined. Only carbonyl groups involved in specific electron donor-electron acceptor interactions at the interface appear to be subject to specific orientation. A persistence thickness of the preferential orientation in the film is determined, also from which it is concluded that even in nanofilms, preferential molecular orientation induced by an hydroxylated substrate does not persist throughout the film thickness. It is localized at a near interfacial region, the thickness of which depends on the ability of the comonomer to undergo conformational changes.

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INTRODUCTION

The formation, structure and properties of organic macromolecular thin films are subjects of interest. Certain important parameters relating to their structure, such as molecular orientation and conformational changes due to macromolecular adsorption at the polymer/metal interface are of fundamental interest. While a number of surface analysis tools are available, only a few are suited to the analysis of the subtle features associated with chemical structures of complicated macromolecular thin films adsorbed onto metallic substrates. Surface techniques using ions or electrons as probes[1] are excluded because of the damage they cause to organic molecules. We have chosen therefore to use FTIR reflectance spectroscopy[2-4], since with this technique photon probes are used for the determination. Orientation of polymer functional groups at the interface of molecular structure of poly(ethylene-co-vinylacetate) adsorbed onto aluminum mirrors was studied by performing experiments at various reflection angles with p-polarization of the incident IR beam. Film thickness was estimated by ellipsometry. Specular reflectance intensities of the functional groups of interest, as a function of reflection angle, polarization state and film thickness, were calculated and compared to those observed. A novel layer model has been developed to allow the molecular orientation of EVA carbonyl groups at the interface to be determined. The studies suggested also that in the near-interface region functional groups may be oriented. This orientation extends to a certain depth, which we propose to call the "orientation persistence length". The layer thickness remaining beyond this region is assumed to be isotropic, and no orientation persists. It would appear that only those carbonyl groups involved in specific electron donor-electron acceptor interactions at the interface are subject to this specific orientation.

THEORETICAL BACKGROUND

Band intensity calculations. The theory that relates the macroscopic experimental variables to the propagating incident and reflected electric fields for reflectance spectroscopy in a multilayered medium have been described in the literature[5]. For specular reflectance under p-polarization the equations following are used to simulate the optical behaviour of a multi phase system. Fresnel complex reflectivity between two media i and j, of indices $\hat{n}_i(\nu) = n_i(\nu) - i.k_i(\nu)$ and $\hat{n}_j(\nu) = n_j(\nu) - i.k_j(\nu)$, may be expressed as follows:

$$\hat{r}_{ij}^{P} = \frac{(n_j^2(\nu) - k_j^2(\nu) - i.2n_j(\nu)k_j(\nu))\hat{n}_i(\nu)\cos(\theta_i) - (n_i^2(\nu) - k_i^2(\nu) - i.2n_i(\nu)k_i(\nu))\hat{n}_j(\nu)\cos(\theta_j)}{(n_j^2(\nu) - k_j^2(\nu) - i.2n_j(\nu)k_j(\nu))\hat{n}_i(\nu)\cos(\theta_i) + (n_i^2(\nu) - k_i^2(\nu) - i.2n_i(\nu)k_i(\nu))\hat{n}_j(\nu)\cos(\theta_j)} \tag{1}$$

For a three phase system in which the ambient medium is air, the EVA polymer is the second medium ($\hat{n}_2(\nu)$) and the substrate is the third medium ($\hat{n}_3(\nu)$) the complex reflectivity and power reflectivity are respectively :

$$\hat{r}_{123}^{P}(\nu) = \frac{\hat{r}_{12}^{P}(\nu) + \hat{r}_{23}^{P}(\nu)\exp\frac{-i4\pi\hat{n}_2(\nu)d\cos(\theta_2)}{\lambda}}{1 + \hat{r}_{12}^{P}(\nu)\hat{r}_{23}^{P}(\nu)\exp\frac{-i4\pi\hat{n}_2(\nu)d\cos(\theta_2)}{\lambda}} \quad \text{and} \quad R_{123}^{P}(\nu) = \hat{r}_{123}^{P}(\nu).\hat{r}_{123}^{P\,*}(\nu) \tag{2}$$

These mathematical expressions can be used to simulate reflectance experiments, and are capable of handling any number of phases. They give exact solutions within the limits of classical electromagnetic theory and linear optics.

Molecular orientation and molecular orientation persistence length. The orientation of adsorbate molecular groups which have infrared active modes can be calculated from reflection spectra because of the anisotropy of the electric field generated at the polymer/metal interface. For grazing angle of reflection of a p-polarized infrared beam off most metals, the effective contribution to the electric field is normal to the surface

($E^{//} \approx E_Z^{//}$, where the z-direction is normal to the surface). Since the intensity of a given mode is proportional to the square of the scalar product of the electric field $\boldsymbol{E}$ and the transition moment $\boldsymbol{M}$ (or dipole moment derivative) with respect to the normal co-ordinate, then the mode intensity of a functional group i, will vary with its orientation at the surface. Assuming that molecular orientation does not persist through the whole film thickness, we propose determing the molecular *orientation persistence length*, O_{PL}. This method is based on a two-layer model. We consider that the adsorbed film of thickness T, is stratified and consists of an orientated layer, L_1, of thickness $T_1 = O_{PL}$, plus an isotropic layer L_2, of thickness T_2, and $T = T_1 + T_2$. The depth-dependent property of the mean square electric field means that the thickness range for which the proposed model is valid is limited to 1 - 20 nm. To a first approximation the complex refractive index of the polymer may be considered as identical in both layers. To determine O_{PL}, IRAS (Infrared Reflection-Absorption Spectroscopy) measurements must be conducted at various angles of reflection. For p-polarization and for angles that deviate from grazing values, the electric field has two components, $E_X^{//}$ and $E_Z^{//}$, where xz defines the plane of incidence. Surface reflectance is then proportional to the mean square electric field components. Exact values of the electric fields intensities in stratified media have been discussed by Hansen[6]. The mode intensity of a functional group i, will vary with its orientation, φ, at the surface and with the angle of reflection of the plane electric field, θ. The electric field vector has two components, $E_x^{//}$ and $E_Z^{//}$, and the transition moment can also be separated into two contributions. The development of the scalar product of the electric field and transition moment vector is expressed as follows :

$$I_i^{oriented} \propto \left|\boldsymbol{M}_i.\boldsymbol{E}^{//}\right|^2 = \left|(\boldsymbol{M}_{i,X} + \boldsymbol{M}_{i,Z}).(\boldsymbol{E}_X^{//} + \boldsymbol{E}_Z^{//})\right|^2 \qquad (3)$$

where $I^{oriented}$ is the band intensity of the oriented layer.

We define the transition moment and electric field vectors as :

$$\boldsymbol{M}_i = M_i\langle\sin(\varphi)\rangle.\boldsymbol{x} + M_i\langle\cos(\varphi)\rangle.\boldsymbol{z} \quad \text{and} \quad \boldsymbol{E}^{//} = E^{//}\cos(\theta).\boldsymbol{x} + E^{//}\sin(\theta).\boldsymbol{z} \qquad (4)$$

and obtain :

$$I_i^{oriented} \propto M_i^2.E^{//2}.\left|\sin(\theta + \langle\varphi\rangle)\right|^2 \qquad (5)$$

Then, assuming that polymer optical constants remain unchanged in both oriented and isotropic layers, the intensity of the bi-layer is the sum of the intensities of both oriented and isotropic layers. For an isotropic layer, the measured intensity is reduced to :

$$I_i^{isotropic} \propto M_i^2.E^{//2}\left|\sqrt{\frac{2}{3}}\cos(\theta) + \sqrt{\frac{1}{3}}.\sin(\theta)\right|^2 \qquad (6)$$

In the case of a stratified medium of thickness T the intensity is expressed as :

$$\frac{I_i^{stratified}}{I_i^{isotropic}} = \frac{T_2}{T} + \frac{O_{PL}}{T}.\left|3\frac{\sin^2(\theta + \langle\varphi\rangle)}{\left|\sqrt{2}.\cos(\theta) + \sin(\theta)\right|^2}\right| \qquad (7)$$

If T is determined by ellipsometry, then only two unknown values, O_{PL} and $\langle\varphi\rangle$, persist in the system, which can be resolved easily using minimization algorithms.

EXPERIMENTAL SECTION

Sample Preparation. The sample studied in this work is an ethylene-vinylacetate (EVA) copolymer having a molar vinyl acetate content of 18.9% mol/mol. Weight average molar mass and polydispersity index are equal to 45 000 g/mol and 2.9 respectively. Transition and phase morphology have been described fully elsewhere[7]. The EVA was spin-coated from an EVA solution in chromatographic grade Chloroform onto a flat polished aluminum mirror. Samples were then annealed for 1 h at 80°C, in order to relax adsorbed macromolecular chains and remove solvent. Nanofilm thickness was estimated using a Sopra ES4M spectroscopic ellipsometer. The value obtained was equal to 120 Å.

IR Reflectance measurements. Reflection FTIR spectra were measured on a Bruker IFS 66 FTIR spectrometer, fitted with a liquid nitrogen cooled MCT detector. 500 averaged scans at 2 cm^{-1} resolution gave experimental spectra with good signal-to-noise ratio. Spectra were recorded at angles of reflection raging from 20 to 85° using p-polarized light. IR band intensity simulation and molecular orientation persistence length were calculated using programs developed with MATHEMATICA® software.

RESULTS

Determination of optical constants

Kramers-Kronig analysis is first used to determine the complex refractive index of the poly(ethylene-co-vinylacetate) polymer from external reflection measurements near the normal angle of reflection (angles ranging from 5 to 8°), see figure I.

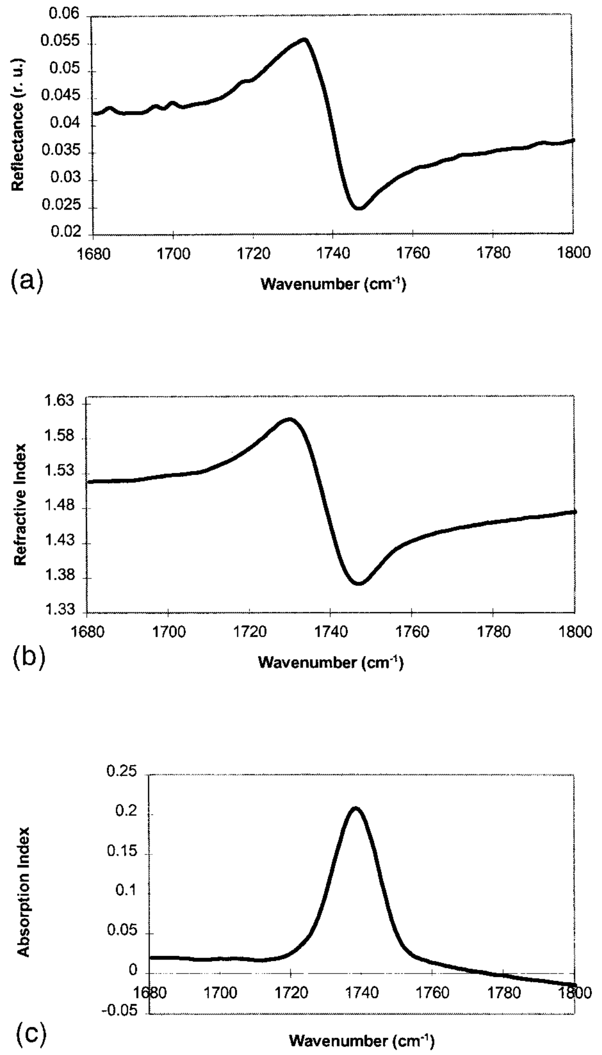

Figure 1a, b and c : Reflectance, refraction index and absorption index of EVA

The frequency dependence of the real, **n**, and imaginary parts, **k**, of the complex refractive index, $\hat{n}(\nu) = n(\nu) - i.k(\nu)$, of an optically thick sample are shown on figure 1b and 1c, respectively.

Values taken for optical constant at 1738 cm^{-1} are $\hat{n}_2 = 1.47 - i0.22$ for EVA and $\hat{n}_3 = 3.7 - i94$ for the aluminum mirror. The complex refractive index of the aluminum mirror does not depend on frequency in the 1680 - 1800 cm^{-1} region. The same procedure is adopted for determinig of the complex refractive index of the CH_2 symnetrical and anti-symnetrical (2849 and 2916 cm^{-1}) transition moments. Values of 1.53 - i 0.072 and 1.54 - i 0.028 are found respectively.

Polarized reflectance spectra analysis. Reflectance measurements were performed using reflection angles ranging from 20 to 85°, under p-polarization. Figure 2 represents the simulated power reflectivity spectra in the 1710 - 1770 cm^{-1} absorption zone of a 120 Å EVA nanofilm adsorbed onto a smooth aluminum mirror for different angles of reflection.

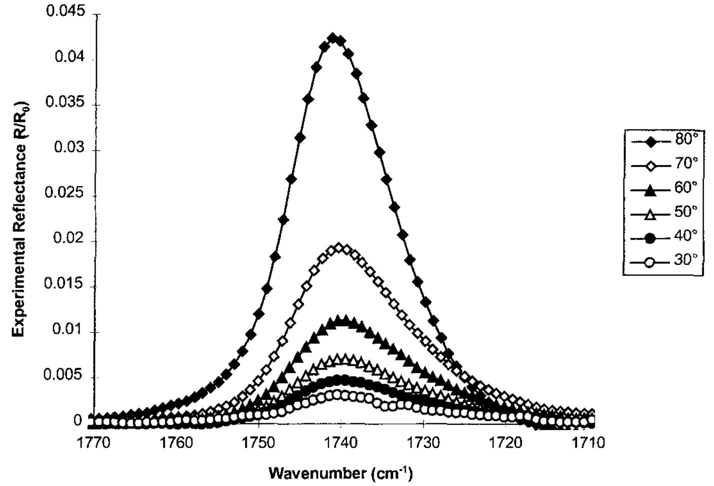

Figure 2 : Simulated reflectance C=O absorption band vs. angle of reflection

As expected, the reflectivity decreases as the angle of reflection decreases as predicted from classical electromagnetic theory. To compare experimental reflectivity to simulated reflectivity two important points must be discussed. First, it is known that reflectance spectra clearly show large changes in both peak position and shape compared to transmission spectra. These differences reflect spectroscopic artefacts[8] and not simply structural differences magnified by the non-equivalent thickness analyzed from one experiment (reflectance) compared to the other (transmission). Secondly, we have demonstrated[9] recently that the adsorption of EVA onto aluminum mirror leads to the development of specific interactions at the interface. Indeed, electron acceptor-electron donor interactions (i.e. acid-base interactions in the Lewis sense[10]) are favored between the C=O of the acetate group and surface aluminol (Al-OH). C=O groups act as a Lewis base. A molecular orbital (MO) overlap exists between the LUMO (Lowest Unoccupied MO) and HOMO (Highest occupied MO) of both functional entities. This overlap affects strongly the C=O stretching frequency, leading to a splitting of the C=O absorption band. The two contributions are a free C=O, which remains unchanged in wavenumber position and an acid-base C=O, which corresponds to vibrators involved in acid-base interactions at the interface. The magnitude of the frequency shift of this mode is related directly to the enthalpy of adduct formation[11]. Calculated profiles, in the free isotropic state, as represented on Figure 2 are used to perform spectral deconvolution of the experimental band as shown in Fig. 3.

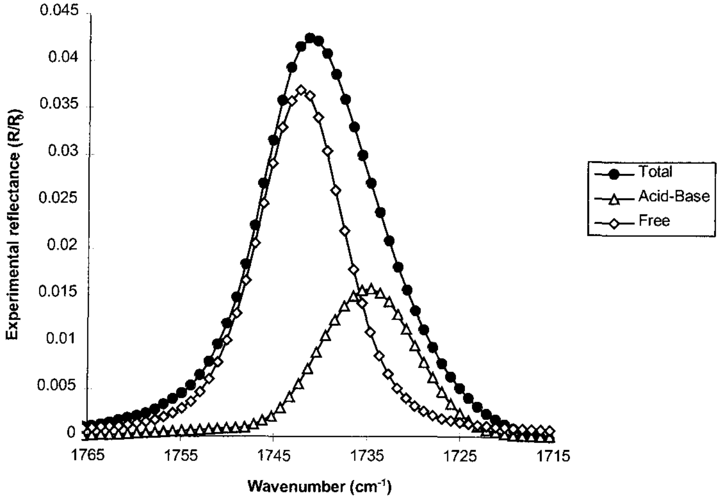

Figure 3 : Calculated power reflectivity versus angle of reflection (C=O band)

Values of band intensities of the free and acid-base bonded C=O bands as a function of angle of reflection are given in Table 1. The free component is located at 1742 cm^{-1}, whereas the acid-base component absorbs at 1735 cm^{-1}.

Band intensity simulations and molecular orientation persistence length. In Figure 4 we show the difference as a function of the IR beam angle of reflection between the experimental and calculated reflectance values of the 120 Å EVA/aluminum system. Significant differences are observed at high angles of reflection. These differences may be due to either, preferential molecular orientation in the adsorbed nanofilms or to systematic errors in the calculation routine. This latter point can be clarified easily by performing well conducted experiments. Therefore, we have both measured the power reflectivity of an EVA nanofilm adsorbed on a gold mirror and predicted the power reflectivity. The results are consistent and the differences do not exceed 0.4%. Therefore interpretation of the differences on Figure 4, requires that both orientation and bonding differences between isotropic bulk EVA and EVA macromolecular chains adsorbed on aluminum mirror are considered. Of course, both effects are linked. One must consider whether the interfacial acid-base force field acts as a driving force to orient the interacting C=O groups at the interface and, if it does, what is the molecular orientation persistence length within the adsorbed nanofilm ?

θ (°)	$-Log_{10}\left[1-\frac{R_{C=O}^{Free}}{R_0}\right]$	$-Log_{10}\left[1-\frac{R_{C=O}^{Acid-base}}{R_0}\right]$	$-Log_{10}\left[1-\frac{R_{C=O}^{Total}}{R_0}\right]$
30	**0.95 10^{-3}**	**0.27 10^{-3}**	**1.18 10^{-3}**
40	**1.68 10^{-3}**	**0.48 10^{-3}**	**1.97 10^{-3}**
50	**2.71 10^{-3}**	**0.79 10^{-3}**	**3.08 10^{-3}**
60	**4.49 10^{-3}**	**1.35 10^{-3}**	**4.94 10^{-3}**
70	**7.67 10^{-3}**	**2.45 10^{-3}**	**8.47 10^{-3}**
80	**16.33 10^{-3}**	**6.56 10^{-3}**	**18.68 10^{-3}**

Table 1 : Experimental band reflectivities vs. angle of reflection : Free, acid-base and total

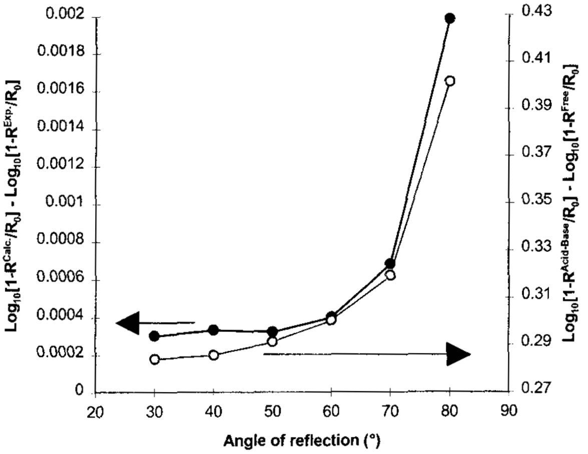

Figure 4 : Calculated - experimental power reflectivity vs. angle of reflection

Acid-base and free reflectivity ratio vs. angle of reflection

When both the experimental and calculated power reflectivities are substituted in eq. (7), agreement between the solutions is verified. The values found for the molecular orientation persistence length O_{PL}, and average orientation angle relative to the surface plane $\langle\varphi\rangle$, are given in Table 2:

Transition Moment	$<\varphi>$	O_{PL}
C=O	74°	29.10^{-10} m
CH_2 Sym.	69°	33.10^{-10} m
CH_2 Anti-Sym	25°	37.10^{-10} m

Table 2 : Molecular orientation data

DISCUSSION

From the IR data presented it here would appear that EVA macromolecular chains are preferentially oriented only in the vicinity of the interface. Previously we have shown that acid-base interactions are developed at the EVA / aluminum oxide interface. These points need to be discussed. Firstly we need to consider the physical meaning of O_{PL} and $\langle\varphi\rangle$ values we have obtained. A molecular orientation persistence length value of 2.9 nm is comparable to the magnitude of the surface roughness, i.e. 2 nm for the aluminum substrate as determined by AFM. This tends to show that only C=O groups of the first "monolayer" are subject to molecular orientation. One may conclude that if O_{PL} reflects surface roughness then only the C=O groups adhering to the surface are oriented. This supports the hypothesis that orbital overlapping between aluminum surface hydroxyls and EVA C=O basic groups promote the orientation of the latter. Such driving force action has been evidenced recently for the case of the adsorption of poly(methyl methacrylate) on an aluminum mirror[12]. If we assume that acid-base interactions promote adsorption and thus chain alignment along the $A\ell$ surface then the angle of 74° for the C=O bound groups have both a minimum conformational energy of EVA i.e. a 180° of the C-O-C=O dihedral angle and 60° value of the CH_3-C-O-C dihedral angle of the acetate group and main chain axis, and a 126.19° angle value between the C=O group and C-O-C link. Indeed, this conformation leads to an angle of 9.91° between the C=O group and the main chain axis, i.e. a value close to 80.09° between the surface plane and the C=O groups in the case of flat adsorption. This kind of transition moment analysis[13] can be useful to understanding experimental results, and here show that the symmetrical CH_2 transition moment is perpendicular to the backbone chain axis. Therefore an average orientation angle value of 69° (i.e a 21° angle between the backbone and the surface plane) supports the postulate that acid-base interactions promote chain alignment. Furthermore, this value is in full agreement with the orientation (25°) of the anti-symmetrical CH_2 transition moment that vibrates along the backbone chain axis.

Secondly if one compares the experimental intensities of the "free" C=O stretching band and the calculated values for an isotropic EVA layer of thickness $T - O_{PL}$ adsorbed on aluminum mirror, good agreement between these values is observed. This confirms that the reflectance IR signal of the "free" C=O stretching band is due mainly to isotropic C=O groups, i.e. those that are not oriented and not involved in interfacial acid-base interactions. The reflectivity ratio between acid-base and free components of the C=O absorption groups are strongly dependent on the angle of reflection. Figure 4 shows this ratio increases rapidly for high angles of reflection, proving that C=O groups involved in acid-base mechanisms are preferentially orientated. However, these results do not give information on the fraction of C=O groups of one chain that can be oriented. Therefore we are not able to discriminate between two possible mechanisms.These are (i) that considers that only loops or head and tail parts of the chain are bound to the surface, and (ii) the acid-base driving forces promotes both chain alignmenet and functional group orientation.

CONCLUSION

In this study we have shown that precise orientation information about EVA copolymer nanofilms on aluminum mirror can be extracted from external reflection IR spectroscopy. Average molecular orientation of the C=O groups of the adsorbed copolymer macromolecular chains and a "persistence length" within the film thickness have been determined. This was possible through application of a novel theoretical approach based on measurements at various angles of reflection, using p-polarization. The results presented here support the hypothesis that C=O groups involved in interfacial acid-base interactions are tilted by an average of 16° towards the normal surface. This orientation persists over about 29 Å within the film. Co-operative effects must exist between interfacial orbital overlapping i.e. basic C=O groups and acid O-H aluminum oxide groups, and molecular orientation. In addition, adsorption driving forces induce planar molecular orientation of the main polymer chain axis adjacent to the surface plane of adsorption. Further experiments need be done on EVA copolymers having VA contents ranging from 40 to 70% w/w in order to better elucidate conformational effects on molecular orientation and associated persistence length. Molecular modeling predictions are also being undertaken in order to correlate EVA phi-psi map analysis with preferential adsorption.

REFERENCES

1) Debe M.K., *Prog. Surf. Sci.*, **1987**, 24, 1-4, 1.
2) Greenler R.G., J. Chem. Phys., **1966**, 44, 1, 310.
3) Greenler R.G., J. Chem. Phys., **1969**, 50, 5, 1963.
4) Lekner J., in *Theory of reflection of electromagnetic and particles waves*, Nijhoff Pub., Dordrecht, **1987**.
5) McIntyre J.D.E., Aspnes D.E., *Surf. Sci.*, **1971**, 24, 417.
6) Hansen W.N., *J. Opt. Soc. Am.*, **1968**, *58*, 380.
7) Brogly M., Nardin M., Schultz J., *J. Appl. Polym. Sci.*, **1997**, 64, 1903.
8) Brogly M., Bistac S., Schultz J., *Polym. Int.*, **1997**, 44, 11.
9) Brogly M., Nardin M., Schultz J., *J. Adhesion*, **1997**, 58, 263.
10) Jensen W.B., in *The Lewis acid-base concepts*, Ed. J. Wiley & sons, New-York, **1979**.
11) Fowkes F.M., *J. Polym. Sci., Polym. Chem. Ed.*, **1984**, 22, 547.
12) Brogly M., Grohens Y., Labbe C., Schultz J., *Int. J. Adhesion & Adhesives*, **1997**, 17, 257.
13) Hahn T. D., Hsu S. L., Stidham H. D., *Macromolecules*, **1997**, 30, 87.