

Influence of Maleation of Polypropylene on the Interfacial Properties between Polypropylene and Ethylene–Vinyl Alcohol Copolymer

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ABSTRACT: In order to improve the miscibility between the components of a blend, it is possible to modify the chemical structure by functionalizing one or more of the components. This results in better adhesion at the interface between the components and, consequently, in better mechanical properties. In this work, the influence of maleation of polypropylene on the interface between polypropylene and ethylene–vinyl alcohol copolymer was studied using the measurement of interfacial tension, surface analysis with electron spectroscopy for chemical analysis (ESCA), and morphological observation, using scanning electron microscopy (SEM). The interfacial tension between a 0.1-wt % maleated polypropylene and ethylene–vinyl alcohol copolymer was shown to be 25% lower than the interfacial tension between nonmaleated polypropylene and ethylene–vinyl alcohol copolymer. This resulted in better adhesion between maleated polypropylene and ethylene–vinyl alcohol copolymer. The surface analysis indicates that this decrease of interfacial tension is due to migration of the maleic groups of the maleated polypropylene to the interface between the 2 polymers and that, probably, a chemical interaction occurs at the interface between maleated polypropylene and ethylene–vinyl alcohol copolymer. It is also shown in this work that additives, such as SiO₂, found in commercial polymers, can influence the interfacial tension between 2 polymers. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 75–87, 1998

Key words: blends; compatibilizers; interfaces; polypropylene

INTRODUCTION

Recently, there has been a large increase in the commercial use of blends of polymers that are not normally compatible. These blends combine the properties of different polymers to obtain a material with optimized properties. The polymers that constitute the blend should be at least partially miscible in order to achieve a blend with better

mechanical properties. Such partial miscibility is particularly important in the interfacial region between the components of the blend. It is enhanced when the interfacial tension between the components of the blend is low and when there is good adhesion at the interface. However, even partial miscibility is seldom found in polymer systems. In order to improve the miscibility, it is common to compatibilize the polymers. This can be achieved by using compatibilizers by functionalization of one or more of the polymers, by reactive blending, or still by mechanical locking. These methods have been reviewed already ex-

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Table I Polymers Used in this Study

Material	M_n	M_w/M_n	Chemical Structure	Supplier
Pure polypropylene (PP _{pure})	54,000	5.54	(CH ₂ —CH) _n CH ₃	Polysciences, Inc
Commercial polypropylene (NPP 7200-AF; PP _{com})	75,000	5.44	(CH ₂ —CH) _n CH ₃	Northern Petrochemical Company
Ethylene vinyl alcohol copolymer (EVOH)	35,000	23.12	(CH ₂ —CH ₂) _y —(CH ₂ —CH) _z OH	Usi Chemical
	Maleation Content (wt%)		Maleic Anhydride Acid	
Maleated polypropylene (MAGPP)		0.1		Mitsubishi Petrochemical Company

tensively.¹⁻² Numerous studies have been reported regarding the improvement of the morphological characteristics of polyblends through compatibilization.³⁻⁸ It has been shown that this improvement of the morphological characteristics, from coarse to fine particles, is related to a decrease of the interfacial tension between the components forming the blend, probably due to some sort of interaction at the interface between the components.^{9,10}

Products of polypropylene (PP) and poly(ethylene-vinyl alcohol) (EVOH) are often used in packaging applications. EVOH is useful in packaging because it is resistant to permeation of oxygen and carbon dioxide. Blends of PP and EVOH are immiscible and, unless modified, they exhibit very poor mechanical properties.¹¹ Maleic anhydride can be grafted onto the backbone of PP,

obtaining maleated polypropylene (MagPP). It has been shown that this transformation improves the mechanical and structural properties of PP-EVOH blends.^{7,11-12}

In this article, the effect of maleation on the interface between MAGPP and EVOH is studied using the following 3 different methods: measurement of interfacial tension, surface analysis using electron spectroscopy for chemical analysis (ESCA); and analysis of the interfaces using scanning electron microscopy (SEM).

MATERIALS

Two types of PP were used in this study, a pure resin PP_{pure} without additives and a blow-molding grade PP (NPP 7200-AF), PP_{com}, from Northern Petrochemical Company, Omaha, NE. The EVOH (EP-F101) used in this study had 32% ethylene content. It was supplied by EVAL Company of North America, Lisle, IL. The maleated polypropylene (Modic) was a commercial sample from Mitsubishi Petrochemical Company, New York, NY, with a level of maleation of 0.1 wt %. The content of maleic anhydride grafted on the PP was determined by Fourier transform infrared analysis (FTIR) and titration. Maleated PP is a modified PP obtained by grafting maleic anhydride on the backbone.

The characteristics of the resins used in this study are presented in Table I. The molecular weight of the resins was determined by gel permeation chromatography (GPC). The following procedures were employed in the determination of the molecular weight distributions of the polymer by GPC: the PP samples were dissolved in trichlorobenzene (TCB) at 135°C; the column used was American GPC (10⁶ + linear + 500 Å); the EVOH sample was dissolved in dimethyl for-

Table II Elemental Analysis of the Polymer Surfaces by Electron Spectroscopy for Chemical Analysis

Polymer	C	O	Si	N	S
PP pure	100	—	—	—	—
PP com	93.1	6.4	0.5	—	—
MAGPP	96.2	3.1	2.5	—	0.2
EVOH	74.9	21.1	0.7	1.2	2.1
PP pure-EVOH	92.8	4.8	1.6	—	0.8
PP com-EVOH	90.6	6.3	2.5	—	0.6
MAGPP-EVOH	87	6.5	6.3	—	0.2
EVOH-PP pure	79.3	18	1.7	—	—
EVOH-PP com	73.9	21.3	3.2	—	1.6
EVOH-MAGPP	75.4	18.7	3.7	0.5	1.7

In Table II, the first polymer listed in the first column is the one analyzed. For example, in the EVOH-PP_{com} case, the polymer analyzed is EVOH, which has been in contact with PP_{com}. Two different samples were analyzed for each of the polymers. The results shown above are average of 2 analysis.

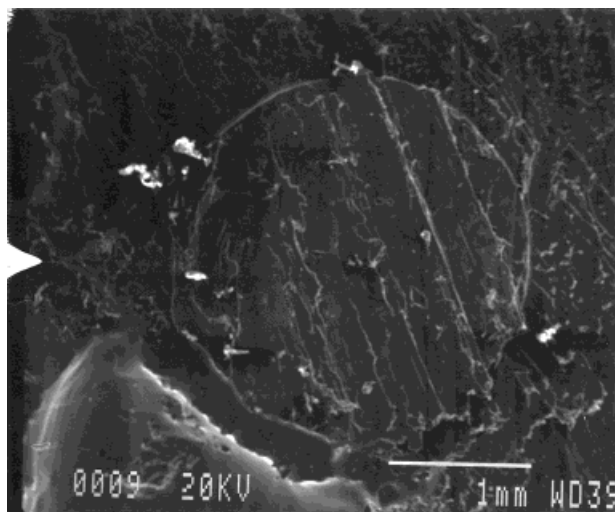


Figure 1 SEM Image of a drop of ethylene-vinyl alcohol in commercial PP.

mamide (DMF) at 50°C; and the column was American GPC (Linear + 500 Å).

EXPERIMENTAL

Measurement of Interfacial Tension

The interfacial tension between PP and EVOH and MAgPP and EVOH was determined using an apparatus based on the pendant drop method. The pendant drop method involves the determination of the geometrical profile of a drop of 1 liquid suspended in another liquid at mechanical equilibrium. The interfacial tension

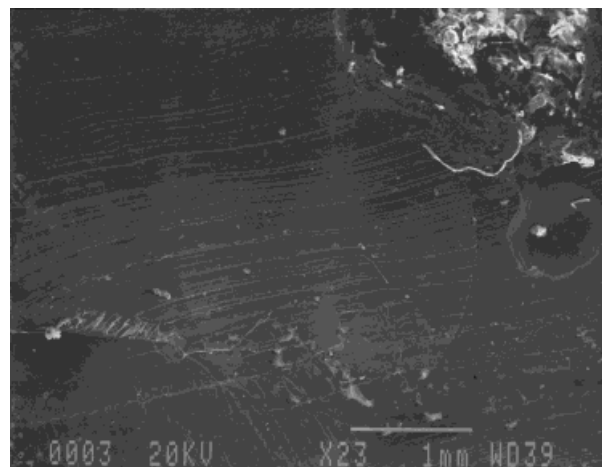


Figure 2 SEM image of a drop of ethylene-vinyl alcohol in MAgPP.

between the 2 liquids can be inferred by solving a differential equation that relates the geometrical coordinates of the drop to the interfacial tension and the difference of density between the 2 liquids.

The pendant drop apparatus used in this research consisted of a heated sample holder where the pendant drop was formed, an optical system to capture the image of the drop, and a data acquisition system with a PC computer equipped with an Intel 80486 processor to compute the interfacial tension from the drop profile. The equipment has been described in more detail elsewhere.¹³⁻¹⁴

Pendant drops of EVOH were formed in a matrix of PP or MAgPP at a temperature of 218°C.



Figure 3 SEM image of the interface between ethylene-vinyl alcohol and commercial PP.

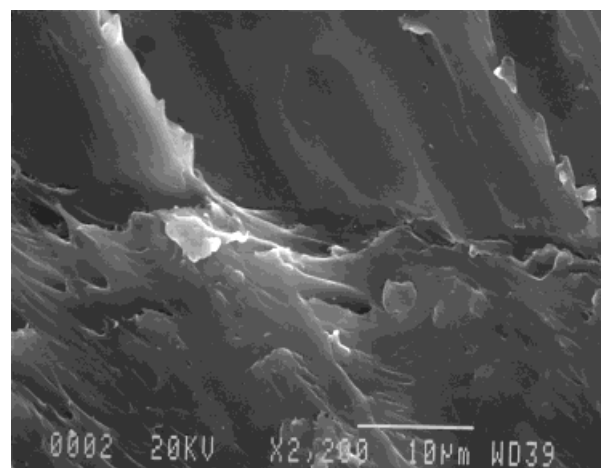


Figure 4 SEM image of the interface between ethylene-vinyl alcohol and MAgPP.

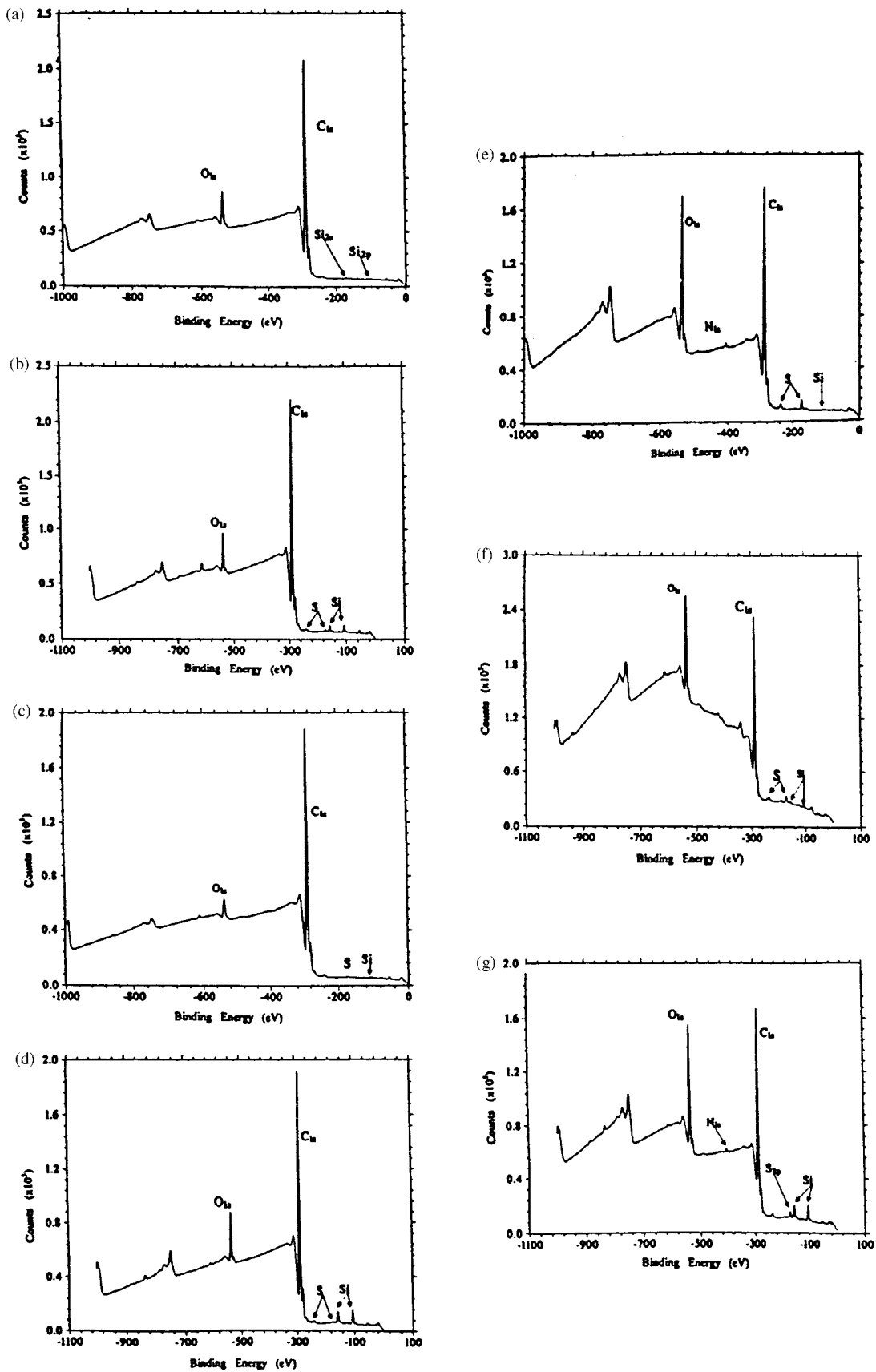


Figure 5 Broad range scan of the polymers used in this work: (a) commercial polypropylene (PP_{com}); (b) PP_{com} after contact with ethylene-vinyl alcohol copolymer (EVOH); (c) maleated polypropylene (MAGPP); (d) MAGPP after contact with EVOH; (e) EVOH; (f) EVOH after contact with PP_{com} ; (g) EVOH after contact with MAGPP.

The evolution of the drop was recorded and values of interfacial tension were inferred from the determination of the profile of the drop at mechanical equilibrium and the knowledge of the density difference between the two polymers. A typical experiment for the determination of interfacial tension lasts about 8 hours in an argon atmosphere.

Electron Spectroscopy for Chemical Analysis

Electron spectroscopy for chemical analysis (ESCA) is one of the best methods to analyze the composition of polymer surfaces. In this type of analysis, the surface to be studied is bombarded with a monoenergetic beam of X-rays. The photons of the X-rays interact with the molecules present at the surface, and electrons are ejected. The electrons are collected on special grids, where their binding energy will be determined. The binding energy is specific to each element and to the chemical bonds present at the surface. The analysis can provide information on the elemental composition of the surfaces and on the chemical state of the elements at a depth of up to a few Angstroms. It is one of the few nondestructive methods for analyzing polymer surfaces.

The 3 different polymer interfaces (PP_{com}-EVOH, PP_{pure}-EVOH, MAgPP-EVOH) used in this work were studied by ESCA. The 4 polymer interfaces were analyzed before and after the experiment, conducted to determine the interfacial tension using the pendant drop method described above. The preparation of the polymers for ESCA analysis is described as follows.

Polymers Before an Interfacial Tension Determination

The polymer surfaces were analyzed by ESCA as received. The PP_{com}, the MAgPP, and the EVOH were in pellet form, and the PP_{pure} was in powder form.

Polymers After an Interfacial Tension Determination

In the experiment for interfacial tension determination, the EVOH was always the drop, which was inserted in a matrix of either PP_{pure}, PP_{com}, or MAgPP. After the interfacial tension experiment, the sample was cooled, and the drop was removed from the matrix, cut, and analyzed, this being possible due to the poor adhesion between

the 2 phases. All the composition results given in this work refer to the interface regions of the different systems.

The polymeric samples were placed on the holder of the ESCA device with a silver glue in order to avoid contamination by silicon. It has been shown that, very often, the silicon present in the glue used to mount the samples migrates to the surface of the samples.¹⁵ The X-ray source for the analysis had a 12 kV source of MgBE with a current of 20 mA. The pressure of the chamber was 9×10^{-9} Torr.

Scanning Electron Microscopy

The interface regions between PP_{com}-EVOH, PP_{pure}-EVOH, and MAgPP-EVOH were analyzed using a scanning electron microscope. The regions observed were the interfaces between the pendant drop and the matrix obtained as a result of performing an interfacial tension measurement. Pendant drops of 1 polymer in another were formed, the mechanical equilibrium of the drop was reached, and the sample was left to cool until it reached ambient temperature. The polymers were cut in the region of the interface. The samples of polymer to be observed were then mounted on scanning electron microscopy (SEM) sample holders. The samples were then coated with colloid graphite and placed in a sputtering device and coated with an alloy of Pd-Au. This coating was needed in order to avoid charging of the polymer samples since they are nonconductive. The samples were analyzed with 15 to 20 kV electron beam voltage at a working distance of 39 mm.

EXPERIMENTAL RESULTS

Polymer Characterization

In order to determine interfacial tension between 2 polymers using the pendant drop method, it is

Table III C/O Ratio at the Surface of PP_{com} or MAgPP Before and After Contact with EVOH

Polymer	C/O	C/O
	Before Contacting EVOH	After Contacting EVOH
PP _{com}	14.53	14.50
MAgPP	31.03	13.27

necessary to know the density of the polymers used. The different methods used to determine the density of each polymer are presented as follows.

Density of Polypropylene

The density of PP was evaluated using the following equation proposed by Zoller¹⁶:

$$V(P,t) = V(0,T) \left\{ 1 - C(T) \ln \left[1 + \frac{P}{B(T)} \right] \right\} \quad (1)$$

$$C = 0.0894 \quad (1a)$$

$$B(T) = B_o \exp(-B_1 T) \quad (1b)$$

$$B_o = 1520 \text{ kg/cm}^2 = 1471 \text{ atm} \quad (1c)$$

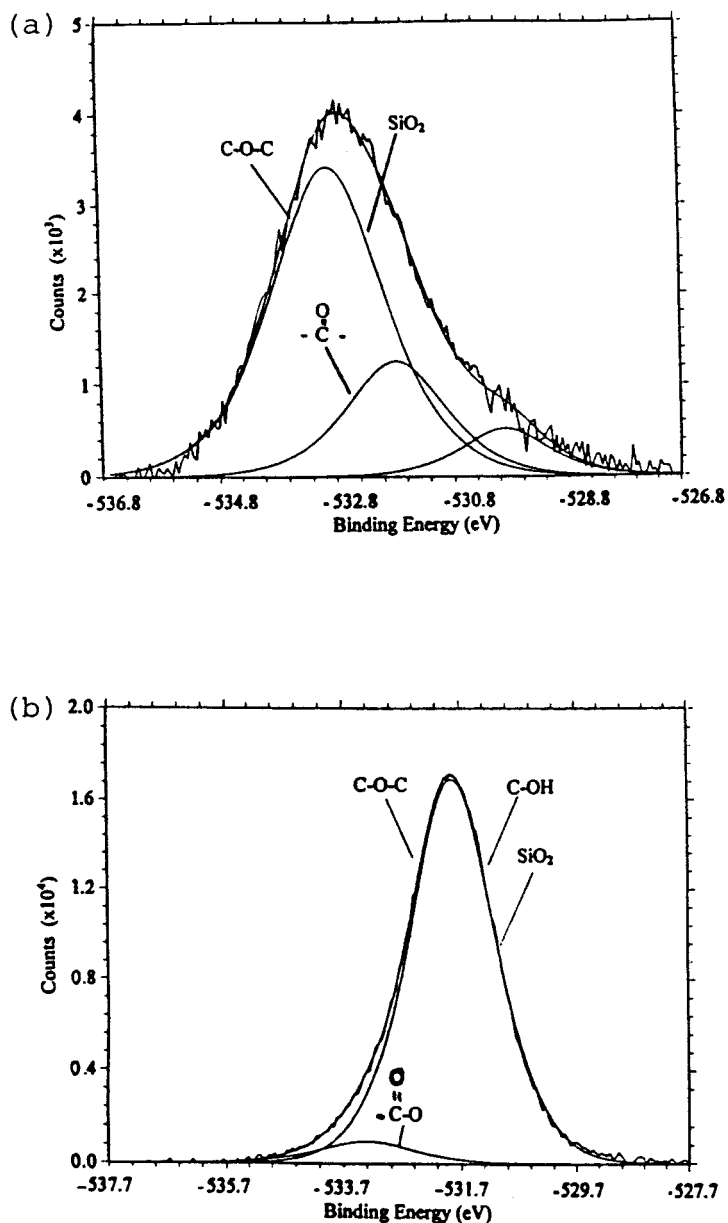


Figure 6 Deconvolution of the O(1s) for MagPP (a) before contact with EVOH and (b) after contact with EVOH.

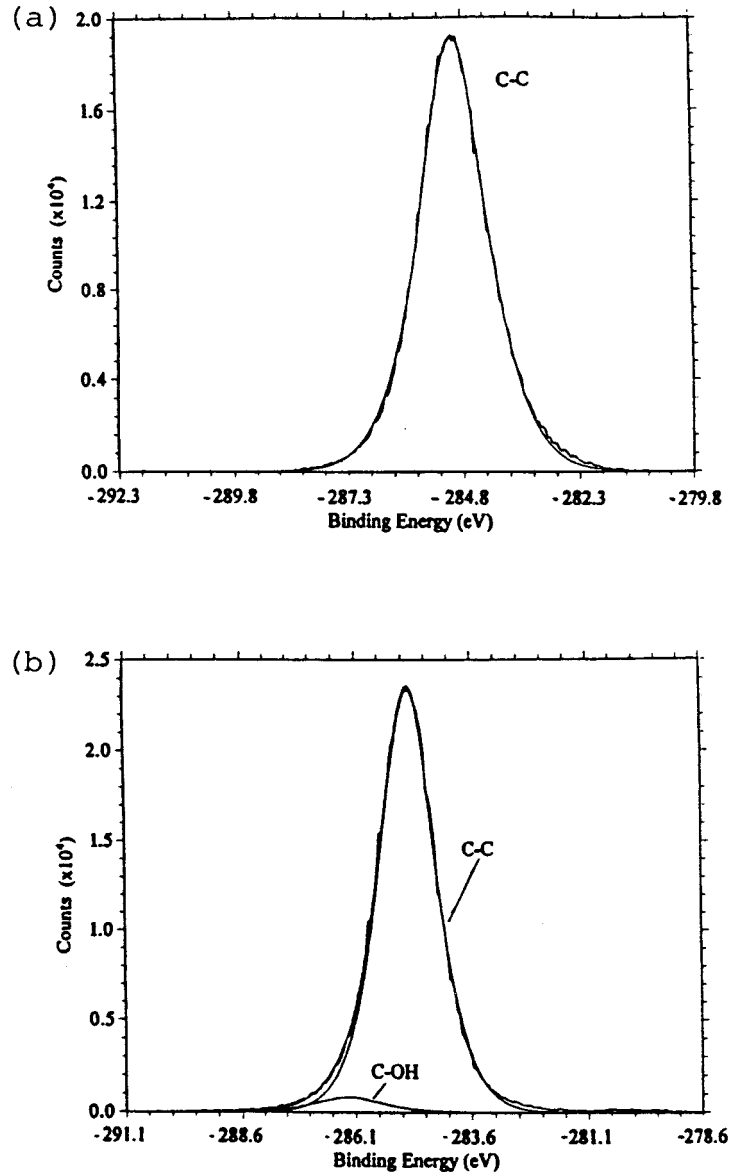


Figure 7 Deconvolution of the C(1s) for MagPP (a) before contact with EVOH and (b) after contact with EVOH.

$$B_1 = 4177 \times 10^{-3} C^{-1} \quad (1d)$$

where P is the pressure, T is the temperature in K , and V is the specific volume. Zoller¹⁶ showed that his experimental data and the equation of state give the same results to within 0.001 g/cm^3 .

Density of Ethylene Vinyl Alcohol

The density of EVOH was measured using a capacitance probe attached to a spinning drop ap-

paratus.¹⁷ The error in the evaluation of the density by this method is less than 2%.

Density of Maleated Polypropylene

The density of the MagPP was assumed to be the same as that of PP, due to the small amount of a maleic anhydride incorporated in the resins.

Interfacial Tension Measurement

The interfacial tension between MAgPP-EVOH is 25% lower than the interfacial tension for PP_{com}

Table IVa Deconvolution Analysis of the O(1s) Peak

Polymer	529,7	531,5	532,5	533,8
		O —C—	C—OH C—O—C SiO ₂	O C—O
MagPP (before contact), $\Sigma = 3,1$	8,6	22,9	68,5	
MagPP (after contact), $\Sigma = 7,1$			94,1	5,9

and EVOH. Also, the interfacial tension for PP_{pure}-EVOH is 34% lower than the interfacial tension between PP_{com} and EVOH. The absolute values of the interfacial tension will be reported elsewhere.

Surface Analysis by ESCA

Table II gives the atomic percentages of the elements contained in the different polymers. The accuracy of the results is within 3%. The results shown in Table II are the averages of data obtained with 2 different samples for each polymer.

The analysis of the polymeric samples studied here showed the presence of the following 3 elemental impurities: N, F, and S. The 2 elements N and F are present in very small quantities, only in 2 samples. The presence of S seems to be due to a contamination of 1 of the 2 batches of samples used for the analysis. The deconvolution of the peaks of the elements C, O, and Si did not show any bonding with N, F, or S. Therefore, these 3 elements (N, F, and S) were considered to be impurities. The analysis of the deconvolution of the silicon peak showed that the silicon was in SiO₂ form for the samples studied here.

It can be observed from the results presented in Table II that, for each resin, Si seems to migrate to the interface. The amount of silicon after

an interfacial tension measurement is higher than before the measurement for all the samples.

Analysis of the Interface by SEM

Figures 1 and 2 show a drop of EVOH in PP commercial and a drop of EVOH in MAgPP, respectively, after the pendant drop measurement. It can be seen from the photographs that the interface of EVOH with MAgPP is less prominent than the interface between EVOH and PP. Figure 3 and 4 show the interface between the same polymers, and it can be seen that there is a gap of approximately 1 μm between the EVOH and the PP, whereas the EVOH and the MAgPP seem to be in very close contact. The same conclusions could be reached at different locations all around the drop.

DISCUSSION

Influence of Maleation

The interfacial tension results show that the interfacial tension between EVOH and MAgPP is lower than the interfacial tension between EVOH and PP_{com}. This corroborates with the morphological observations (SEM) showing better adhesion between MAgPP and EVOH than between PP and EVOH. The lower value of interfacial tension suggests that the maleate groups act as surfactants. The maleic groups probably migrate towards the

Table IVb Deconvolution Analysis of the C(1s) Peak

Polymer	285,0	286,6
	C—C	C—OH
MAgPP (before contact), $\Sigma = 96,5$	100	
MagPP (after contact), $\Sigma = 87,2$	96	4.00

Σ represents the atomic percentage of O (Table IVa) or C (Table IVb) as presented in table II for 1 of the 2 samples analyzed (in other words, $\Sigma = 3,1$ means that O represents 3.1% of the total components at the surface of the sample)

Table V C/O Ratio at the Surface of EVOH Before and After Contact with PP_{com} or MAgPP

Polymers	C/O
EVOH	3.55
EVOH after contact with PP _{com}	3.48
EVOH after contact with MAgPP	3.90

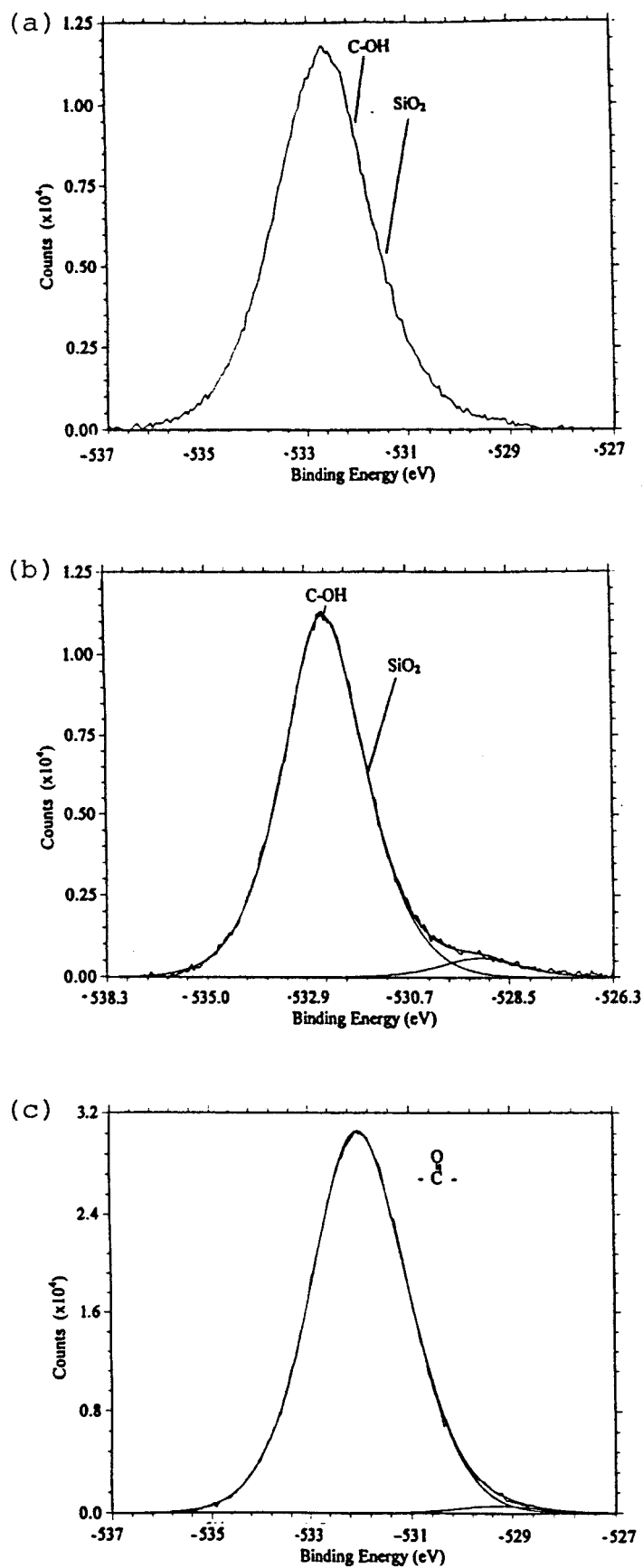


Figure 8 Deconvolution of the O(1s) for EVOH (a) before contact with PP_{com} or MagPP, (b) after contact with PP_{com}, and (c) after contact with MagPP.

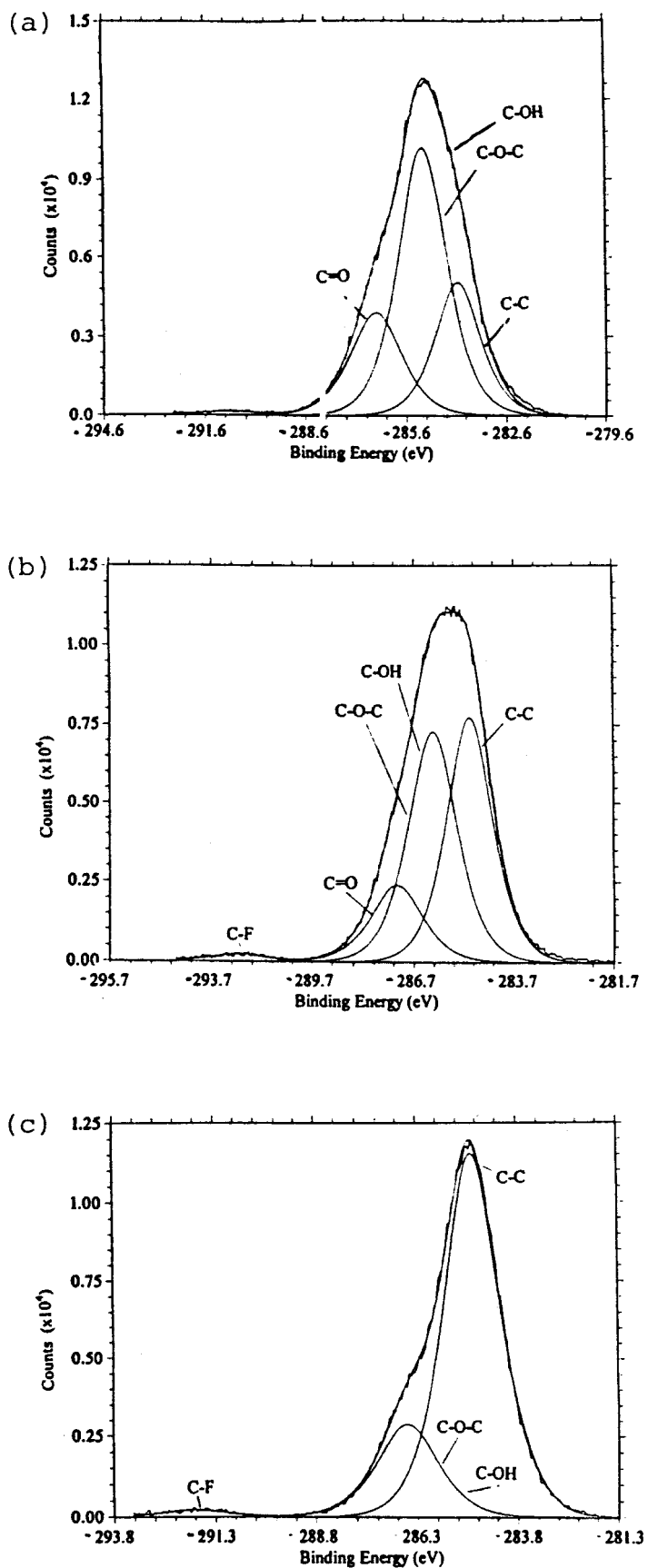


Figure 9 Deconvolution of the C(1s) for EVOH (a) before contact with PP_{com} or MagPP, (b) after contact with PP_{com}, and (c) after contact with MAgPP.

Table VIa Deconvolution Analysis of the O(1s) Peak

Polymer	528,7	531,5 O —C—	532,8 C—OH SiO ₂
EVOH, $\Sigma = 21.1$			100 (533,6)
EVOH/PPcom, $\Sigma = 22.3$	4.7		95.3
EVOH/MAGPP, $\Sigma = 18.6$	1.5 (530,2)	98.5 (532,9)	

polar material (EVOH), a chemical reaction between MAGPP and EVOH could occur at the interface.³

Figure 5 shows the ESCA analysis for the PP, ethylene–vinyl alcohol copolymer and MagPP before and after contacting during the interfacial tension experiment. Table III shows the results of the analysis of C/O ratio for PP_{com} and MagPP before and after contacting EVOH.

It can be seen from the results presented in Table III and in Figures 5(a) and (b) that there is no significant composition difference for the commercial PP before and after contacting the ethylene–vinyl alcohol copolymer, taking into consideration the migration of silicon (in the form of SiO₂). This is an indication that there is no interaction between PP_{com} and EVOH. It can be also seen from Table III that the C/O ratio for MAGPP decreases after contacting EVOH. This is probably due to the migration of SiO₂ and also to a migration of the maleic anhydride groups towards the interface. A comparison between Figures 5(c) and (d) clearly shows that there is more oxygen at the surface of the maleated PP after contacting EVOH than before the contact.

Figures 6 and 7 show the results of the deconvolution of the O(1s) and the C(1s) peaks for MAGPP before and after contacting EVOH. The peaks of the spectra were indentified according to the values reported in the literature.^{15,19–23} The analysis suggests that, after contacting, new

chemical bonds, such as C—OH, are present at the surface of MAGPP. Tables IV(a) and (b) show the quantitative results of the deconvolution of the O(1s) and C(1s) peaks at the surface of the MAGPP. It can be observed that, before contacting, no C—OH was present at the surface of MAGPP and that C—OH was detected after the contacting.

Table V shows the analysis of the C/O ratio for the EVOH before and after contacting PP_{com} and MAGPP. It can be seen that the C/O ratio for EVOH after contacting PP_{com} or MAGPP is the same within experimental error. Figures 8 and 9 show the results of the deconvolution of the O(1s) and the C(1s) peaks for EVOH before and after contacting PP_{com} and MAGPP. Tables VI(a) and (b) indicate that the number of C—OH bonds in EVOH decreases, showing more C=O bonds. Although it is not possible to quantify the results, there is a strong suggestion that indeed an interaction, possibly a chemical reaction, occurs at the interface between MAGPP and EVOH.

Difference Between PP_{pure} and PP_{com}

It has been indicated earlier that the interfacial tension between commercial PP and EVOH is higher than the interfacial tension between pure PP and EVOH. This difference is too large to be due only to the small differences in the molecular weight or polydispersity of the 2 samples, espe-

Table VIb Deconvolution Analysis of the C(1s) Peak

Polymer	285,0 C—C	286,6 C—OH C—O—C	287,9 C=O	289,3 C—F
EVOH, $\Sigma = 74.9$	25.5	52.9 (286.05)	21.6 (287.5)	
EVOH/PPcom, $\Sigma = 75.1$	42.0	42 (286,11)	14.6 (287.2)	1.4 (291.9 Impu)
EVOH/MAGPP, $\Sigma = 77$	81.2	17.7		2.2 (291.3 Impu)

Σ represents the atomic percentage of O (Table VIa) or C (Table VIb) as presented in table II for 1 of the 2 samples analyzed (in other words, $\Sigma = 21,1$ means that O represents 21.1 % of the total components at the surface of the sample)

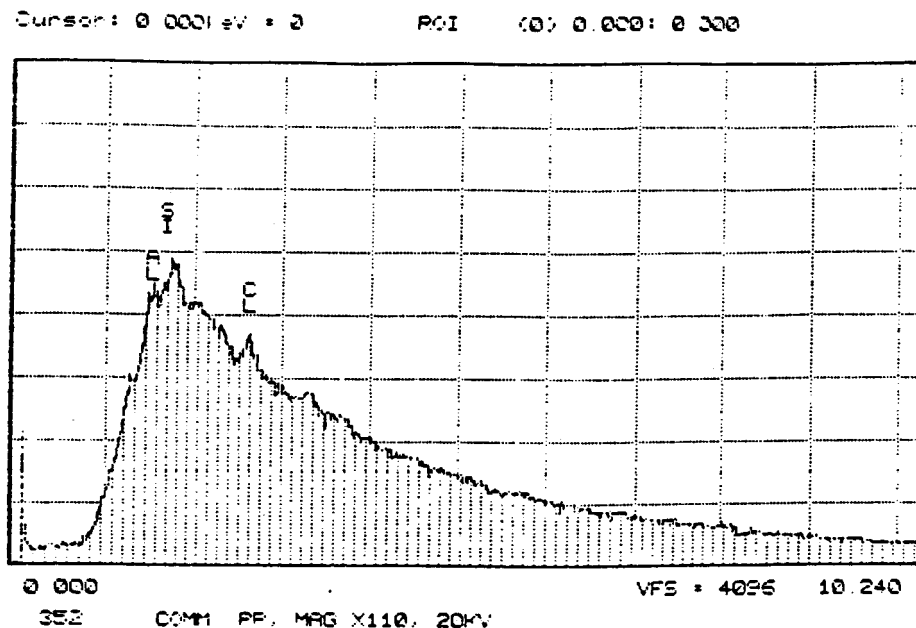


Figure 10 X-Ray spectrum of commercial PP.

cially because the polymers under consideration have a molecular weight higher than the entanglement molecular weight, above which the interfacial tension tends to level off.¹⁸ However, the difference could be attributed to the presence of additives, such as antistatic agents, coupling agents, and other additives in the commercial PP.

Different analytical methods were used to determine composition differences between pure PP and commercial PP. Elemental analyses was performed on both the commercial and pure PP to verify the presence of additives. The method was not accurate enough to detect the differences between the 2 resins. Figure 10 shows the spectrum of the commercial PP obtained with an energy dispersive X-ray detector. It can be seen that besides carbon (and hydrogen, which cannot be detected by this method), the sample contains aluminum, silicon, and chlorine. Both the aluminum and chlorine are contaminants from the sample holder and the glue used to mount the sample. The spectrum of pure PP did not show the presence of silicon.

Table II shows the composition differences between the pure and commercial PP. The pure PP sample contains just carbon and hydrogen, whereas the commercial PP sample also contains oxygen and silicon, which could be added as anti-static or nucleating agents or maybe residues of the catalyst used for polymerization. It can be seen from the results presented in Table II that Si

migrates to the interface. This could explain the difference observed in the interfacial tension values between PP_{com} and EVOH and PP_{pure} and EVOH.

CONCLUSIONS

The influence of maleation of PP on the interface between PP and ethylene-vinyl alcohol copolymer was studied using interfacial tension measurement, analysis of the interface using ESCA, and morphological observations.

The interfacial tension between PP_{com} and EVOH decreased by 25% when 0.1% maleic anhydride was grafted to the backbone of the PP, resulting in better adhesion between the 2 phases.

The results of the interface analysis showed that the composition of the PP_{com} and of EVOH before and after contacting each other did not change. The surface of MAgPP after contacting EVOH was richer in oxygen than before contacting, suggesting either a migration of the maleic anhydride to the interface or a gain of oxygen to MAgPP from EVOH, and most probably a combination of both. Changes were observed in the chemical bonds involving the oxygen and carbon of the MAgPP and EVOH present at the interface. This probably explains the lower value of interfacial tension between EVOH and MAgPP when

compared to EVOH and PP, as obtained experimentally.

It was also shown in this work that the interfacial tension between a pure PP and EVOH was lower than the interfacial tension between a commercial PP and EVOH. X-ray analysis and ESCA results showed that the commercial PP contains silicon in the form of SiO₂. The presence of silicon is likely to be the reason for the increase of the interfacial tension with the commercial samples.

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