Plasma treatment of polyolefins: Influence of material composition: 2. Lacquer adhesion and locus of failure

Anna Nihlstrand and Thomas Hjertberg*
Department of Polymer Technology, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

and Kenth Johansson
Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden
(Received 19 August 1996)

The adhesion properties achieved after oxygen plasma treatments of ten polypropylene (PP) and thermoplastic polyolefin (TPO) materials of different compositions were studied. It is shown that the adhesion between a polyurethane (PUR) lacquer and plasma-treated materials was strongly influenced by the plasma treatment conditions and the chemical composition of the materials. Generally, a low power-to-gas pressure (P/G) ratio during the plasma treatment and a high ethylene content, preferably in the form of blocks, and/or the presence of double bonds in the matrix, are favourable for adhesion properties. Moreover, the TPOs were less sensitive towards the plasma treatment conditions than the corresponding PPs. The properties and the type of rubber may also be important for the adhesion properties. Furthermore, it was shown by X-ray photoelectron spectroscopy (X.p.s.) and Fourier transform infrared (*FT*i.r.) spectroscopy (using the attenuated total reflectance (ATR) technique) that all failures—even the apparently interfacial failures—were located in the substrate, *below* the oxidized surface layer, the only difference being the depth of failure. The fracture surfaces of samples showing low peel forces generally had a more PP-like composition than fracture surfaces that were clearly cohesive in the substrate. This observation offers evidence that the lacquer adhesion is determined by the extent to which chain scission reactions occur in the near-surface region of the substrate during the plasma treatment. © 1997 Elsevier Science Ltd.

(Keywords: oxygen plasma treatment; lacquer adhesion; locus of failure)

INTRODUCTION

Thermoplastic polyolefins (TPOs) are widely used in the automotive industry for the manufacturing of bumpers. For aesthetic and protective reasons, it is often necessary to lacquer the bumpers. There are difficulties in lacquering polyolefin-based materials such as TPOs, however, as they are inert and have a low surface energy. To achieve satisfactory adhesion properties, a pretreatment which can promote bondability is therefore needed. In recent years, much attention has been directed towards the use of low-temperature plasmas as a means of altering the surface properties of polyolefins, see for example refs 1–6. Less attention has been focused on the effect of plasma treatments for improving adhesion properties, although exceptions exist[7–10]. Plasma treatments can be performed using a wide range of processing conditions and, as many plasma parameters, e.g. discharge frequency, discharge power, gas pressure, etc. influence the concentration of active species in the plasma—and hence the amount of radicals formed in the substrate—the adhesion properties are also affected.

Another factor of major importance for the adhesion properties of TPOs following plasma treatments is the chemical and morphological composition. In a previous study, it was shown that four commercial TPOs (the chemical composition of these materials was not known) exhibited completely different lacquer adhesion after plasma treatment using the same processing conditions[11]. It was proposed that the lacquer adhesion was determined by the cohesive strength of a 'near-surface' region located *below* the oxidized surface layer, which in turn is determined by the extent to which crosslinking and chain scission reactions occur. Such crosslinking and chain scission reactions were proposed to be induced by the energetic vacuum-ultraviolet (v.u.v.) radiation created during the plasma treatment[12], which leads to the formation of radicals. As tertiary radicals (formed in polypropylene) normally react via β-scission, whereas secondary radicals (formed in polyethylene) more often decay via combination[13,14], the differences were proposed to be associated with the variation in material composition (i.e. ethylene content, etc.).

If a weakening of a region below the oxidized surface layer is the cause of unsatisfactory adhesion properties, it can be assumed that materials containing double bonds would be easier to plasma-treat, as double bonds may prevent or compensate for chain scission reactions. Indeed, such an advantageous effect of double bonds was detected in a study concerning plasma treatment of

---

* To whom correspondence should be addressed

diene-modified PP copolymers[15]. The chemical composition is evidently of major importance for the adhesion properties, but it is still unknown which particular factors (degree of ethylene modification, type and amount of rubber, etc.) are important and, in the case they are important, to what extent. It should not be forgotten that other factors such as the morphology and the degree of surface crystallinity may also influence the adhesion properties observed after plasma treatments.

The objective of the present study, which is the second part of two, was to investigate how selected material parameters influence the lacquer adhesion and the locus of failure after various oxygen plasma treatments. This was achieved by using well-characterized materials (see part one[16]) with known chemical compositions. To investigate whether the mould temperature during production of the plates has any effect on the subsequent adhesion properties was also of interest, as this parameter influences the degree of surface crystallinity.

EXPERIMENTAL

Materials

Ten PP and TPO materials of different compositions, supplied by Borealis, Norway, were used in this work. The materials, specifically designed for the purpose of

this work, are described in *Table 1*. The materials were carefully characterized in a closely related paper[16], and no further details on the materials will be given here. Materials A1–A4 are chemically modified 'PPs', while materials B1–B6 are rubber-modified polypropylenes, i.e. TPOs. In order to more easily see and compare the effects of certain material parameters, the materials are divided into four groups (1–4), see *Table 2*. As a consequence, some TPOs are present in more than one group. The materials were received as injection-moulded plates (150 mm × 70 mm × 3 mm). The same processing parameters (mould temperature 40°C; melt temperature 230°C) were used for all materials except for B6, which was injection-moulded into plates using mould temperatures of 30°C and 70°C. The materials contain standard amounts of stabilizers, and all materials except for A1 contain a small amount of carbon black.

Plasma treatments

The plates were oxygen plasma-treated according to the processing conditions given in *Table 3*. A detailed description of the treatment conditions and the plasma reactor is given elsewhere[16]. The results of the plasma treatments in terms of water contact angles and X.p.s. are reported in the first paper[16] and will not be discussed here. It can be mentioned, however, that one of the most interesting results was that the plates plasma-treated at

Table 1 Description and chemical composition of materials

Designation	Material	Description	C2 content[a] (mol%)	Diene content (mol%)
A1	'PP'	Randomly C2-modified PP	9	–
A2	'PP'	Block C2-modified PP	9	–
A3	'PP'	Block C2-modified PP	20	–
A4	'PP'	Block C2-modified PP	33	–
B1	TPO	Randomly C2-modified PP (same as A1)	9	–
		+ 25 wt% EPR	64	–
B2	TPO	Block C2-modified PP (same as A3)	20	–
		+ 25 wt% EPR	64	–
B3	TPO	Randomly diene-modified PP	–	1.4
		+ 25 wt% EPR	64	–
B4	TPO	Block C2-modified PP (same as A3)	20	–
		+ 25 wt% EPDM	63	1.3
B5	TPO	Randomly diene-modified PP	–	1.4
		+ 25 wt% EPDM	63	1.3
B6[b]	TPO	Block C2-modified PP (same as A3)	20	–
		+ 25 wt% EPR[c]	64	–

[a] C2 is the ethylene content
[b] Plates were produced using two different mould temperatures; 30°C (B6[1]) and 70°C (B6[2])
[c] The EPR in B6 has a higher molecular weight than the EPR in materials B1–B3

Table 2 Group division and parameters studied

Group	Material	Parameter studied
(1)	A1–A4	Amorphous vs block ethylene modification (A1 and A2)
		Degree of ethylene modification (A2, A3 and A4)
(2)	B1–B3	Influence of PP matrix (B1, B2 and B3)
(3)	B2–B5	Influence of rubber type (two cases: B2–B4; B3–B5)
(4)	B2, B6	Influence of EPR molecular weights (B2 and B6[1])
		Influence of mould temperatures (B6[1] and B6[2])

Table 3 Power-to-gas pressure (P/G) ratios resolved into powers and gas pressures. The oxygen plasma treatment time was always 30 s, and the discharge frequency 35 kHz. The flow rate was not measured

P/G (W mTorr^{-1})	Power (W)	Gas pressure (mTorr)	Materials treated
0.25	200	800	A1–A4 and B1–B6
1.0	800	800	A1–A4
2.5	2000	800	A1–A4 and B1–B6
8.0	800	100	A1–A4
10	2000	200	B1–B6
20	2000	100	B1–B6

higher power-to-gas pressure (P/G) ratios were more oxidized than the ones treated at low P/G ratios.

Lacquering and adhesion test

The plasma-treated plates were lacquered in order to evaluate the adhesion properties. The lacquer, a two-component polyurethane (PUR) lacquer delivered by Beckers, Sweden, was composed of a hydroxyl-terminated polyester (Beckryflex TH-130 2601) and a hexamethylene-diisocyanate (HDI) prepolymer (Beckryflex TV-130). Lacquering was always carried out one day after the plasma treatments. A textile cloth (Monodur PES 71N, mesh width 71 μm) was placed in the lacquer as reinforcement and, to avoid failure between the lacquer and the textile cloth, the cloth was also plasma-treated prior to usage. The total thickness of the lacquer layer (including the reinforcing cloth) was ~130 μm. The lacquer was cured at 90°C for 40 min and then stored at atmospheric conditions (room temperature, normal humidity) for one week to complete curing. The lacquered plates were finally cut into 15-mm wide strips.

Lacquer adhesion was evaluated by a 90° peel test. The peel tests were performed using the TCT-5 model from Alwetron, which was equipped with a special fixture. The fixture includes a movable slide which enables the peel force to be measured at a constant angle of 90°. The crosshead speed during the peel test was 600 mm min^{-1}. Three strips from each plate were peeled over a distance of 100 mm or more, and the reported peel forces are average values of at least four plates. The peel forces were registered as N/15 mm.

Static contact angle measurements

Static water contact angle measurements were carried out on fracture surfaces after peeling in order to gain evidence of the locus of failure. Droplets (4 μl in volume) were positioned at different locations on both the lacquer and the substrate side, and at least six readings were taken for each sample in order to determine average values. Both the advancing and the receding contact angles were measured. Typical standard deviations were 2–3°.

X-ray photoelectron spectroscopy (X.p.s.)

X.p.s. was used to determine the atomic composition of the fracture surfaces obtained after peeling. The analyses were carried out at 11 kV and 250 W using a Mg K_α X-ray source (1253.6 eV). The pressure during acquisition was < 1 × 10^{-9} Torr and the take-off angle (the angle between the analyser and the sample surface), ϕ, was varied between 20° and 75°, corresponding to an 'effective' sampling depth of 3.5–10 nm[17]. The analysed area was 0.8 mm in diameter. The analyses were

performed on a PHI 5500 ESCA system from Perkin–Elmer, and the sensitivity factors used were according to the Perkin–Elmer manual.

Fourier-transform infrared spectroscopy (FTi.r.)

Attenuated total reflectance (ATR) was used for analysis of the fracture surfaces obtained after peeling. The penetration depth (d_p) depends on wavelength (λ), angle of incidence (θ), refractive index of the crystal (n_c) and the refractive index of the sample (n_s)[18]. To achieve a high surface sensitivity, the germanium crystal ($n_c = 4.0$) was used at an incident angle of 48.7° (crystal endface angle 45°; optics angle 60°)[19]. If n_s is taken as 1.5 (the refractive index of a PP homopolymer[19]), these conditions correspond to a d_p of 0.06 λ. The sample chamber was purged with dry air in order to obtain high quality spectra. The spectra were recorded at a resolution of 4 cm^{-1}, and 20 scans were co-added for all samples. The analyses were performed on a Perkin–Elmer FTIR 2000 system equipped with a triglycine sulfate (TGS) detector.

RESULTS AND DISCUSSION

Lacquer adhesion—90° peel test

The peel test results obtained after plasma treatment and lacquering of materials A1 to A4, i.e. group (1), are shown in *Figure 1*. It is clear from the figure that all materials show a strong dependence on the P/G ratio (note the logarithmic scale). All materials show a decrease as the P/G ratio increases. Apart from that, the most striking observation is the difference in peel forces between A1 and A2. Although both materials contain the same amount of ethylene, the randomly modified PP (A1) shows far lower peel forces than the block-modified PP (A2). This is probably because chain scissions caused by radical formation in PP regions can more easily be compensated for by crosslinking reactions taking place in ethylene-rich regions. Such ethylene-rich regions are not present in a randomly modified PP, and the likelihood of crosslinking reactions is therefore reduced. It should be pointed out, however, that A1 does not contain carbon black as the other materials do. As carbon black is an effective u.v. absorber, this may affect the formation of radicals, and hence the degree of oxidation. No difference in the degree of oxidation
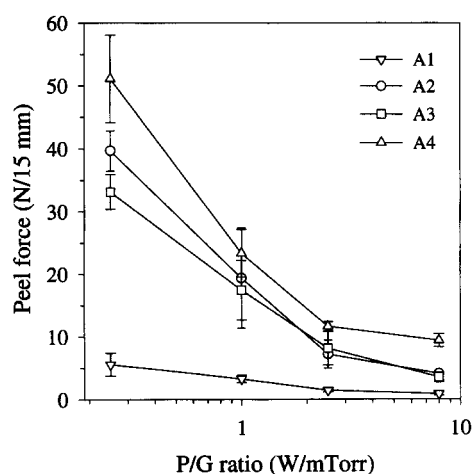

Figure 1 Peel forces vs power-to-gas pressure (P/G) ratios for four differently modified PPs. Group (1)

among the materials was observed, however[16]. Furthermore, we earlier reported that extremely low peel forces ($\sim$1 N/15 mm) were obtained after plasma treatment of a TPO material when treated at certain plasma conditions, although it contained carbon black[11]. We thus strongly doubt that the absence of carbon black in A1 is the primary cause of the huge difference in adhesion properties observed between A1 and A2.

Comparing the block-modified PPs, it is evident that the material with the highest ethylene content (A4) gives the highest peel forces, independent of P/G ratio, while A2 and A3 give peel forces intermediate to the ones observed for A1 and A4. Considering the *FT*i.r.–ATR spectra for the untreated materials[16], the explanation as to why A4 shows the highest peel forces is probably that this material has ethylene in the form of blocks in the first $\sim$ 200 nm (peak at 2850 cm^{-1}), which is not evident for either A2 or A3, or at least not to the same extent. Moreover, it can be seen that A2 and A3 show similar peel forces at high P/G ratios but, at low P/G ratios, somewhat lower peel forces are obtained for A3 than for A2. This is unexpected, considering that the peel forces should increase with increasing ethylene content if the lacquer adhesion is determined by the extent to which chain scission and crosslinking reactions occur. The reason for this is not clear, but could possibly be related to the molecular weights of the materials, as this factor may affect properties such as the degree of surface crystallinity. Although no pronounced difference could be found, A3 was shown to have a somewhat higher molecular weight than the other PPs[16]. It can also be mentioned that the valence-band X.p.s. spectra of untreated materials revealed that the spectrum obtained for A3 was slightly more similar to the characteristic PP spectrum than was the A2 spectrum, which indicates that A3 may be more sensitive to chain scissions than A2. As regards the locus of failure for these samples, what appears to be an interfacial failure is obtained independent of treatment conditions for A1 and A3. Apparently interfacial failures are also obtained for A2 and A4 treated at a P/G ratio of 1.0 or higher while A4, when treated at a P/G ratio of 0.25, shows a clearly cohesive failure, as does A2. In the latter case, however, a much thinner—although observable—layer of polymer is present on the lacquer side.

Figure 2 shows the peel forces obtained for group (2), i.e. materials that contain the same EPR rubber but which are based on three differently modified PP matrices. It can be seen that TPOs are much less sensitive to the treatment conditions than the PPs. (Again, note the logarithmic scale.) Although much tougher treatment conditions are used for the TPOs than for the PPs, B1 and B3 reveal no sign of deterioration in adhesion properties even after treatment at P/G = 20. (The highest P/G ratio used for the PPs was 8.0.) B2, on the other hand, gives the highest absolute peel force but shows a drop and a change-over from a clearly cohesive failure in the substrate to an apparently interfacial failure when treated at P/G = 20. Clearly cohesive failures in the substrates are always observed for B1 and B3. As the peel force cannot be higher than the intrinsic strength of the bulk material, the absolute value of the peel force is not really important when a clearly cohesive failure in the substrate is obtained. Hence, it can be concluded that, even though the diene content of the matrix used in B3 is considerably lower than the ethylene content of the
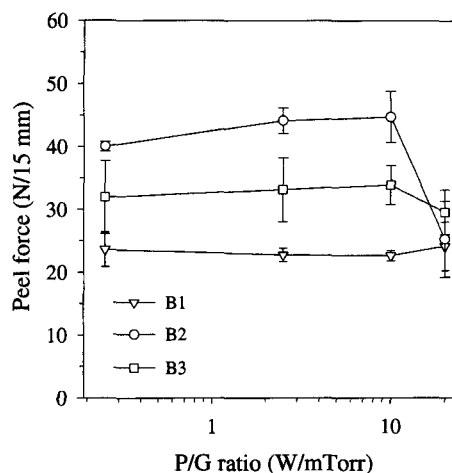

Figure 2 Peel forces vs power-to-gas pressure (P/G) ratios for materials containing the same rubber phase but are based on different matrices. Group (2)

matrix used in B2, the material based on the diene-modified PP seems more durable with respect to the plasma treatment conditions in spite of the fact that the material itself has a lower cohesive strength. Obviously, the presence of double bonds in the matrix yields a more resistant material than a matrix with a high ethylene content.

The performance of B1 is more surprising. With the knowledge that A1 results in considerably lower peel forces after plasma treatments than does A3, B1 would be expected to be less durable than B2. This is not the case. We believe that, in this case, it is not only the chemical composition of the PP matrix that is important, but also the surface morphology, i.e. the distribution of rubber in the surface region. It was shown by *FT*i.r.–ATR in the first paper[16] that the materials had a gradient in the material composition. Generally, the outermost surface (down to $\sim$200 nm) was more rich in PP and less rich in rubber and/or ethylene-modified material than the first $\sim$ 800 nm, with the exception of one material, B1. Instead, in this case, slightly more PP was found at $\sim$ 800 nm than at $\sim$ 200 nm. Thus, it appears as though the outermost surface of B1 is enriched in EPR while more PP is found at some distance below. It is probably in this PP-rich region that the failure occurs during peeling, resulting in a clear cohesive failure in the near-surface region of the substrate.

Figure 3 shows and compares the peel forces obtained for materials that are based on the same matrix but contain different rubbers (EPR and EPDM). Two sets of materials are shown, one set based on a diene-modified PP and another based on a block ethylene-modified PP. Comparing the materials based on the diene-modified PP (B3 and B5), no difference can be observed as a result of the rubber type. Moreover, all failures are clearly cohesive in the substrate, and no dependence on P/G ratio is present. Thus, from these results, it would be concluded that the rubber type is of no or minor importance. However, if instead the materials based on the block ethylene-modified PP are compared (B2 and B4), a dependence on both rubber type and P/G ratio can be seen. Both B2 and B4 show a drop in peel force with increasing P/G ratio, but the drop starts earlier and is more pronounced for B4. This is surprising, as a material with EPDM is expected to be less sensitive to plasma
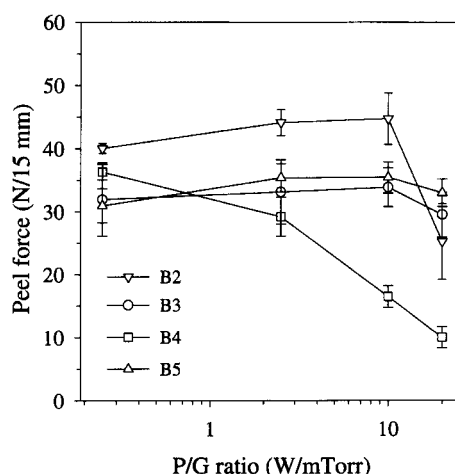
Figure 3 Peel forces vs power-to-gas pressure (P/G) ratios for materials containing EPR (B2, B3) and EPDM (B4, B5) rubber. Group (3)

Figure 4 Peel forces vs power-to-gas pressure (P/G) ratios for materials containing EPR rubber of different molecular weights. Group (4)

treatments owing to its double bonds than a corresponding EPR-containing material. The rubbers should, according to the supplier, be comparable with respect to molecular weights, ethylene contents, etc. but the d.s.c. melting curves and the *FT*i.r. transmission spectra obtained for thin films indicated one difference—the ethylene in the EPR seems to have a more pronounced block character than the ethylene in the EPDM[16]. Furthermore, it is evident from the *FT*i.r.–ATR spectra of the untreated materials that the surfaces of both B2 and B3 (containing EPR) have much more ethylene in the form of blocks (greater peaks at $2850\,\mathrm{cm^{-1}}$) than do B4 and B5 (containing EPDM). The difference is present at both depths, but is particularly pronounced at Ge depth[16]. We therefore suggest that the expected positive effect of double bonds in the EPDM is overshadowed by the greater extent of ethylene in the form of blocks in the case of EPR. Thus, a block structure of ethylene is preferable not only in the PP matrix but in the rubber phase as well. Moreover, with reference to the depth of oxidations of the samples[16], it is interesting to recall that B4, after treatment at P/G = 20, revealed an oxidized layer considerably thinner than what was obtained for the other materials in group (3). Thus, it seems as though the adhesion properties are in some way *indirectly* related to the depth of oxidation. (As will be shown below, the oxidized layer in itself will not be the determining factor for the achievement of good lacquer adhesion.) To conclude the results obtained for this group: if a 'good' PP matrix (diene-modified) is chosen as the base of a TPO material, the rubber type has little or no influence for the outcome of plasma treatments, whereas the rubber type may be of significant importance if a less resistant PP matrix is chosen.

Figure 4 shows the effect of using an EPR with a higher molecular weight (B2 and B6[1]), as well as the effect of a higher mould temperature during production of the plates (B6[1] and B6[2]). Comparing the materials containing EPR of different molecular weights, it can be seen that B6[1] (higher EPR molecular weight) is far more sensitive to the plasma treatment conditions than B2. For B6[1], the peel force drops considerably at a P/G ratio of 2.5 (as usual, the drop is accompanied with a changeover from a clearly cohesive failure to an apparently interfacial failure), while B2 is resistant up to P/G = 10.
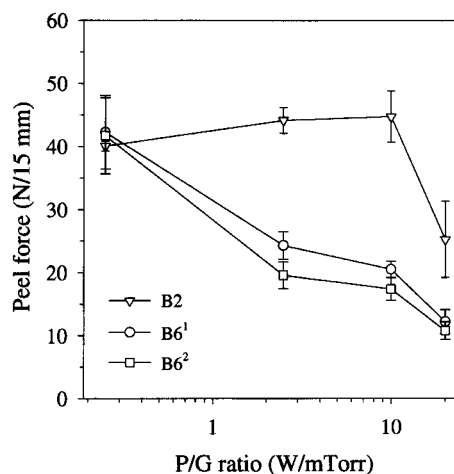
This shows the significance of not only the rubber type but also of the molecular weight of the rubber phase. Why the molecular weight of the EPR would influence the adhesion properties is less clear, but it can be assumed that there is an effect on the distribution of rubber in the surface region. With reference to the first paper[16], B2 and B6[1] show a similar material composition down to a depth of ~200 nm, while an indication of somewhat more EPR at ~800 nm is evident in the case of B2. Obviously, the molecular weight affects the distribution of rubber in the surface region, but it is not certain that the surface morphology alone causes the difference in adhesion properties. In fact, the distribution of ethylene in the rubber can again be an important factor, as both the *FT*i.r. transmission spectra and d.s.c. melting curves obtained for the bulk materials indicated that the EPR in B6 had fewer signs of ethylene in blocks than the 'normal' EPR in B2 (both materials are based on the same matrix)[16]. Comparing B6[1] and B6[2], only minor differences are found. Both samples show a drop in peel force with increasing P/G ratio, but it appears that B6[2] is slightly more sensitive to the treatment conditions despite the fact that this sample shows a significantly higher degree of surface crystallinity[16]. The mould temperature used during the production of these plates seems therefore to be of minor importance for the adhesion properties, although it does influence the degree of surface crystallinity. Furthermore, it is interesting to once again recall the depths of oxidation as, apart from B4, that has the shallowest oxidized layer, both B6[1] and B6[2] showed a dependence on the X.p.s. take-off angle. Thus, a thin oxidized layer is again observed for samples that are highly sensitive to the plasma treatment conditions.

Location and depth of failure
X.p.s. Thus far, we have discussed the locus of failure only in terms of a failure that is apparently interfacial and a clearly cohesive failure in the substrate. There is no guarantee that the failures that appear to be interfacial actually are interfacial. However, to test this and ascertain the locus of failure, X.p.s. analysis was carried out on selected fracture surfaces after peeling. The analyses were performed using a take-off angle of 45° on samples showing low peel forces, i.e. samples plasma-treated at P/G = 8.0 (A1–A4) or P/G = 20 (B1–B6). The

Table 4 Atomic composition of failure sides as measured by X.p.s. The reported values are obtained at $\phi = 45°$. No nitrogen was detected for any of the samples

Material	P/G ratio	Lacquer side		Polymer side	
		At% C	At% O	At% C	At% O
A1	8.0	98.6	1.4	98.3	1.7
A2	8.0	99.1	0.9	_^{a}	_^{a}
A3	8.0	99.0	1.0	_^{a}	_^{a}
A4	8.0	98.1	1.9	_^{a}	_^{a}
B1	20	99.0	1.0	98.6	1.4
B2	20	97.5	2.5	97.7	2.3
B3	20	98.7	1.3	98.9	1.1
B4	20	99.5	0.5	99.0	1.0
B5	20	_^{b}	_^{b}	_^{b}	_^{b}
B6^1	20	99.8	0.2	98.0	2.0
B6^2	20	99.5	0.5	98.2	1.8

^{a} Not measured. Water contact angle measurements indicated cohesive failure in the substrate (advancing angles > 109°; receding angles > 89°)

^{b} Not measured. All failures were clearly cohesive in the substrate
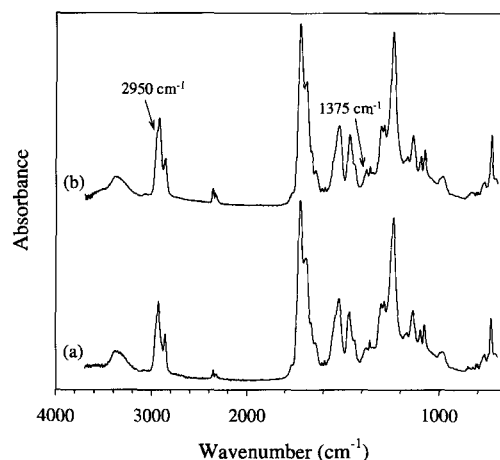

Figure 5 FTi.r.-ATR spectra of (a) a clean lacquer surface and (b) a typical fracture surface (lacquer side) of a sample that appeared to have an interfacial failure

lacquer side and the polymer side were analysed, the results of which are summarized in *Table 4*. The chemical composition of both fracture surfaces are similar to those of untreated materials. Thus, these failures must also be cohesive in the substrates in a region significantly below the oxidized surface layer. To obtain additional information on the depth of failure, X.p.s. analyses were also carried out on selected samples at take-off angles of 20° and 75°. The oxygen content on the polymer side did not vary to any great extent with take-off angle, however, which substantiates the conclusion that the failure must indeed have occurred below the oxidized layer. The oxygen content on the lacquer side was, for some samples, slightly higher at $\phi = 75°$, however, demonstrating the proximity to the underlying oxidized layer. It can be concluded from these results that the depth of failure must be at least some 10 nm *below* the oxidized layer, which in turn is significantly thicker than 10 nm[16]. As discussed elsewhere[12], the weakening of this 'near-surface' region is probably induced by the v.u.v. radiation created during the plasma treatment, which is known to be able to penetrate deeper into the polymer substrate than other reactive species in the plasma[20].

FTi.r.–ATR. As no significant oxygen content could be detected on the lacquer side by X.p.s., *FT*i.r.–ATR analyses of selected fracture surfaces (lacquer sides only) were carried out. To maximize the contribution of the polymer layer remaining on the lacquer side, the Ge crystal was used at an incident angle of 48.7°. These conditions probe the topmost ~200–900 nm (calculated for 3000–700 cm^{-1}), i.e. a layer considerably thicker than the layer covered by variable-angle X.p.s.

As the polymer layer is invisible to the naked eye, it is not surprising to find that the ATR spectrum of a lacquer side, after an apparently interfacial failure, is similar to that of a clean lacquer surface, see *Figure 5*. At first glance, the spectra appear identical but it becomes evident at a closer look that spectrum (b) shows weak signs of polymer remainings in the form of a shoulder to the asymmetric methylene stretching peak at ~2925 cm^{-1} (this peak also shows a higher intensity) and a peak at 1375 cm^{-1}. These peaks again confirm the cohesive nature of the failures, but no further information can be
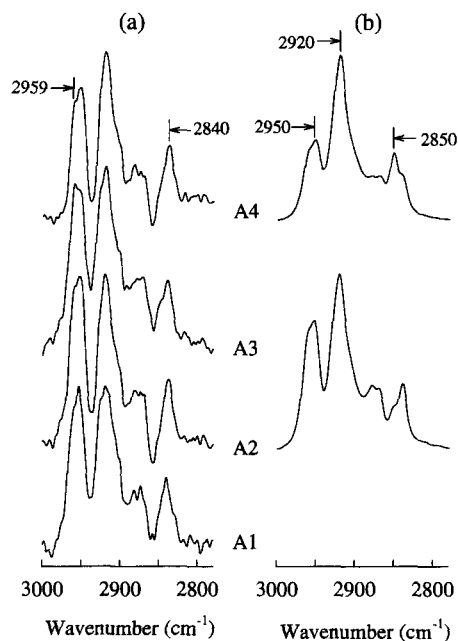

Figure 6 FTi.r.–ATR spectra (in absorbance) of samples showing (a) apparently interfacial failures and (b) clearly cohesive failures. Group (1)

gained from this type of spectra. Instead, difference spectra were calculated using the spectrum of the clean lacquer surface as the reference. As the signal from the polymer is small and the signal-to-noise ratio consequently quite low, the difference spectra below 2700 cm^{-1} are not of much use. However, the region between 3000 and 2800 cm^{-1} (the methyl and methylene stretching region) proved to be extremely useful.

Figure 6 shows such difference spectra of failures that were apparently interfacial (a) and clearly cohesive failures (b) obtained for the materials in group (1). As no clearly cohesive failure was obtained for either A1 or A3 at any treatment conditions, no spectra for these samples are shown in (b). Starting with the spectra shown in (a), the most interesting observation is that no obvious sign of ethylene-modified material can be seen for any of the materials (absence of a peak at 2850 cm^{-1}). This is also supported by the strong intensity of the

$-CH_3$ asymmetric (as) stretching peak at 2950 cm^{-1} in relation to the $-CH_2-$ regions, particularly in the cases of A1, A2 and A3. Since the ATR spectra obtained for the untreated materials indicated a gradient in material composition—an increase in PP towards the outermost surface—(for further details see ref. 16) it can be concluded that the failure must occur significantly less than ~200 nm from the surface. Another interesting observation, valid for A3, is the appearance of the peak at 2950 cm^{-1}. This sample shows evidence of a highly disordered PP surface, as a separate peak appears at 2959 cm^{-1} [21,22]. For the other samples and for untreated materials, this peak is observed only as a shoulder to the peak at 2950 cm^{-1}. Thus, for A3, the failure occurs in a region enriched in amorphous PP, and this certainly explains why A3 gives lower peel forces than A2 under certain circumstances. If a comparison is made between the spectra shown in (a) and corresponding spectra shown in (b), it is evident that the clearly cohesive failures are deficient in PP and richer in ethylene-modified material (presence of peak at 2850 cm^{-1}) than the apparently interfacial failures. A comparison of the spectra in (b) with the spectra for untreated materials[16] also reveals that the cohesive failures show a greater resemblance to the spectra obtained using the KRS-5 crystal than those obtained using the Ge crystal. This indicates that a clearly cohesive failure occurs at a depth near or greater than ~800 nm.

Figure 7 shows the difference spectra obtained after peeling of the materials in group (2). As discussed above, B1 and B3 normally showed clear cohesive failures independent of treatment conditions but, in both cases, there was a lacquer side of a peeled strip that had a small area with an apparently interfacial failure. The spectra shown for B1 and B3 in (a) are taken from these areas. Starting with a comparison of the spectra obtained for B3 with the spectra of the untreated material[16], it can be seen that a clearly cohesive failure occurs at a depth similar to the penetration depth of the Ge crystal, i.e. ~200 nm. It can also be concluded that, in the case that an apparently interfacial failure occurs at all, it is definitely located in a region highly enriched in PP, as
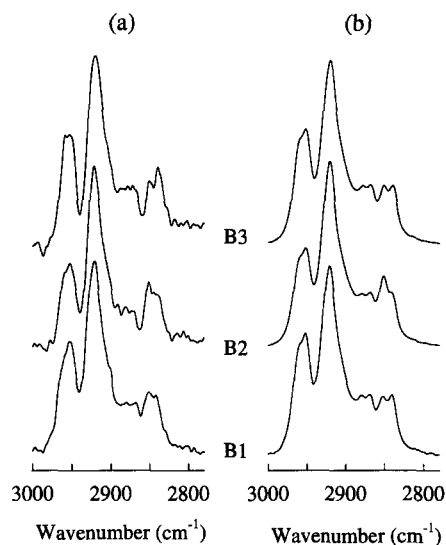

Figure 7 *FT* i.r.–ATR spectra (in absorbance) of samples showing (a) apparently interfacial failures and (b) clearly cohesive failures. Group (2)

the 2840 cm^{-1} peak is much more intense than that observed for the untreated material. Taking into account the gradient in material composition, this indicates a depth of failure significantly more shallow than 200 nm. It should also be noted that this region is not only rich in PP, but also in amorphous PP (see the peak at 2959 cm^{-1}). However, as pointed out earlier, apparently interfacial failures are normally not observed for this material after any treatment condition. Studying the spectra obtained for B2, no great difference can be found between (a) and (b). Both spectra reveal evidence of rubber (2850 cm^{-1}), and a comparison with spectra obtained for untreated material[16] shows that the spectrum shown in (b) shows a greater similarity to the spectra obtained with the KRS-5 crystal, while the spectrum shown in (a) shows a greater similarity to the spectrum obtained using the Ge crystal.

The spectra obtained for B1 are more interesting. Although they appear similar, a weak, but valuable, difference can be distinguished—slightly more PP (2840 cm^{-1}) and less EPR (2850 cm^{-1}) can be observed in (b) than in (a), which is exactly the opposite of what is observed for all other samples. A comparison with the spectra obtained for untreated material[16] shows that (a) is similar to the spectrum obtained using the Ge crystal and (b) is similar to the spectrum obtained using the KRS-5 crystal. Thus, an apparently interfacial failure occurs in a region enriched in rubber (2850 cm^{-1}), while a clearly cohesive failure occurs in a region enriched in PP (2840 cm^{-1}). A possible scenario to explain this is the following: since the PP matrix (A1) in itself is extremely sensitive to chain scissions, plasma treatment of B1 at tough conditions will lead to excessive chain scissions of the PP matrix (caused by v.u.v.), which is enriched at some distance *below* the EPR-rich top layer. (The EPR phase is assumed to be less weakened by chain scissions than the PP matrix.) This would explain why slightly more PP is found for a clearly cohesive failure than for an apparently interfacial failure. However, if the plasma treatment is extremely mild (low P/G ratio), so that the cohesive strength of the PP matrix is less deteriorated, the lacquer adhesion would instead be determined by the strength of the overlying region enriched in EPR. This is why an apparently interfacial failure shows slightly more evidence of EPR than a clearly cohesive failure. This also explains why the peel force level of a clearly cohesive failure in B1 is as low as ~24 N/15 mm, while is ~32 N/ 15 mm for B3 and ~40 N/15 mm for B2 (see *Figure 2*), as the cohesive strength of the weakest layer in the surface region of B1 must be lower than the cohesive strength of the EPR itself.

Figure 8 shows the difference spectra obtained after peeling materials B2–B5, i.e. group (3). No spectrum of B5 is shown in (a), as under no circumstances was an apparently interfacial failure obtained for this material. Comparing the spectra in (b) with the spectra of untreated materials[16], it is seen that the clearly cohesive failures obtained for B3 and B5 occur at a depth close to 200 nm (Ge depth) while, for B4, the failure occurs somewhere close to or deeper than 800 nm (KRS-5 depth). The depth of failure for B2 appears to be intermediate, i.e. somewhere in the range of 200–800 nm. With respect to the spectrum shown in (a), it is evident that an apparently interfacial failure in B4 occurs in a PP-rich region, as only a weak sign of rubber and/or ethylene-modified material is present (2850 cm^{-1}), while,
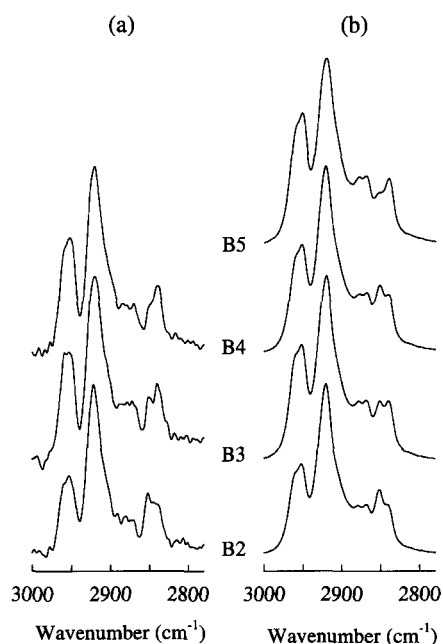
Figure 8 *FT* i.r.–ATR spectra (in absorbance) of samples showing (a) apparently interfacial failures and (b) clearly cohesive failures. Group (3)
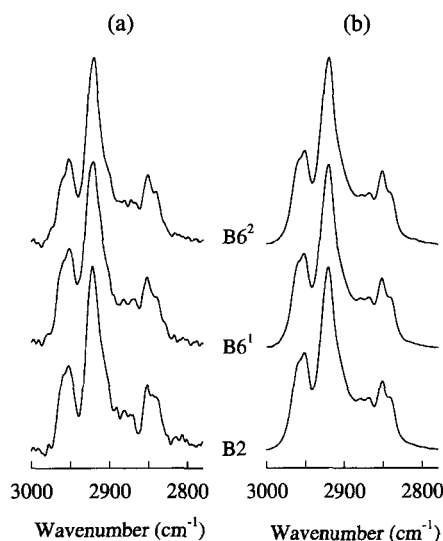

Figure 9 *FT* i.r.–ATR spectra (in absorbance) of samples showing (a) apparently interfacial failures and (b) clearly cohesive failures. Group (4)

for the other materials, this peak is more pronounced. This is again striking, as B4 was the material most sensitive towards plasma treatment conditions. As the spectra of B2 and B3 shown in (a) were discussed above, no further comment will be offered at this point.

Finally, *Figure 9* displays the difference spectra obtained for the samples in group (4). These spectra do not contain a great deal of information. All spectra are similar, regardless of whether the failures are apparently interfacial failures or clearly cohesive failures, a result of the fact that even the untreated samples showed an almost identical composition at both Ge and KRS-5 depths. Consequently, even if the failures occur at different depths, no difference in material composition will be detected.

To summarize the results with reference to the depth of failure, it was found that apparently interfacial failures occur at least 10 nm below the oxidized surface layer, but definitely not deeper than 200 nm from the outermost surface. By using different incident angles during the ATR analysis, calculating the ATR penetration depth for the various conditions used and comparing peak height ratios for a pure lacquer surface with the corresponding peak height ratios obtained for lacquer surfaces with polymer residues, the *shallowest* depth of an apparently interfacial failure was estimated to be in the order of 30–50 nm. (This is only a preliminary result, however, and a detailed presentation is therefore omitted.) Most of the failures that are clearly cohesive in the substrates occur at a depth near or greater than 800 nm.

CONCLUSIONS

(a) The lacquer adhesion showed a strong dependence on plasma processing conditions. The higher P/G ratio, the lower the lacquer adhesion.

(b) The lacquer adhesion is dependent on the chemical composition of the materials, but the distribution of rubber also plays an important role. Generally, a high ethylene content, preferably in the form of blocks, and/or the presence of double bonds in the surface region are favourable for adhesion properties.

(c) The TPOs were less sensitive towards changes in the treatment conditions than the corresponding PPs. The adhesion properties are determined mainly by the PP matrix, but the type and properties of the rubber are also important.

(d) Although a great variation in peel forces was observed (0.1–55 N/15 mm), *all* failures were located in the substrate *below* the oxidized surface layer, the only difference being the depth of failure. Thus, the lacquer adhesion is not directly determined by the degree of surface modification.

(e) Fracture surfaces of apparently interfacial failures (lower peel forces) generally showed a more PP-like composition than fracture surfaces that were clearly cohesive in the substrate (higher peel forces). This observation lends strength to the hypothesis that the lacquer adhesion, i.e. the cohesive strength of the region below the oxidized surface layer, is determined by the extent to which chain scission reactions occur in the near-surface region of the substrate during plasma treatment.

ACKNOWLEDGEMENTS

REFERENCES

1. Occhiello, E., Morra, M., Morini, G., Garbassi, F. and Humphrey, P., *J. Appl. Polym. Sci.*, 1991, **42**, 551.
2. Behnisch, J., Holländer, A. and Zimmermann, H., *J. Appl. Polym. Sci.*, 1993, **49**, 117.
3. Morra, M., Occhiello, E. and Garbassi, F., *J. Adhesion Sci. Technol.*, 1993, **7**, 1051.
4. Shahidzadeh-Ahmadi, N., Arefi-Khonsari, F. and Amouroux, J., *J. Mater. Chem.*, 1995, **5**, 229.
5. Greenwood, O. D., Boyd, R. D., Hopkins, J. and Badyal, J. P. S., *J. Adhesion Sci. Technol.*, 1995, **9**, 311.

6. Shahidzadeh-Ahmadi, N., Chemini, M. M., Arefi-Khonsari, F., Foulon-Belkacemi, N., Amouroux, J. and Delmar, M., *Colloids and Surfaces; Part A*, 1995, **105**, 277.

7. Guezenoc, H., Segui, Y., Thery, S. and Asfardjani, K., *J. Adhesion Sci. Technol.*, 1993, **7**, 953.

8. Wu, D. Y., Gutowski, S. W., Li, S. and Griesser, H. J., *J. Adhesion Sci. Technol.*, 1995, **9**, 510.

9. Friedrich, J. F., Unger, W., Lippitz, A., Gross, T., Rohrer, P., Saur, W., Erdmann, J. and Gorsler, H. V., *J. Adhesion Sci. Technol.*, 1995, **9**, 575.

10. Tatoulian, M., Arefi-Khonsari, F., Mabille-Rouger I., Amouroux, J., Gheorgiu, M. and Bouchier, D., *J. Adhesion Sci. Technol.*, 1995, **9**, 923.

11. Nihlstrand, A., Hjertberg, T. and Johansson, K. S., *J. Adhesion Sci. Technol.—Festschrift in honor of Dr K. L. Mittal*, in press.

12. Nihlstrand, A., Hjertberg, T., Schreiber, H. P. and Klemberg-Sapieha J. E., *J. Adhesion Sci. Technol.*, 1996, **10**, 651.

13. Mark, H. F., Bikales, N. M., Overberger, C. G. and Menges, G. *Encyclopedia of Polymer Science and Engineering*, Vol. 4, 2nd edn. John Wiley & Sons, New York, 1986, pp. 418–436.

14. Lazár, M., Rado, R. and Rychlý, J., *Adv. Polym. Sci.*, 1990, **95**, 149.

15. Nihlstrand, A., Hjertberg, T. and Johansson, K. S., *Polymer*, in press.

16. Nihlstrand, A., Hjertberg, T. and Johansson, K. S., *Polymer*, 1997, **38**, 3581.

17. Andrade, J. D. (ed.), *Surface and Interfacial Aspects of Biomedical Polymers*, Vol. 1, Plenum Press, New York, 1985, pp. 175–184.

18. Griffiths, P. R. and de Haseth, J. A., in *Chemical Analysis*, Vol. 83 (Fourier Transform Infrared Spectrometry), ed. J. R. Elving and J. D. Winefordner. John Wiley & Sons, New York, 1986, pp. 191–194.

19. Knutson, K. and Lyman, D. J. in *Surface and Interfacial Aspects of Biomedical Polymers*, Vol. 1, ed. J. D. Andrade. Plenum Press, New York, 1985, pp. 197–247.

20. Clark, D. T. and Dilks, A., *J. Polym. Sci.; Polym. Chem. Ed.*, 1977, **15**, 2321.

21. Bonnerup, C. and Gatenholm, P., *J. Polymer Sci., Polymer Physics* 1993, **31**, 1487.

22. Pouchert, C. J. *The Aldrich Library of FT i.r. Spectra*, Vol. 1, 1st edn. Aldrich Chemical Company Inc., 1985, pp. 1157–1158.