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Adhesion properties of oxygen plasma-treated polypropylene-based copolymers

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Injection-moulded plates of four polypropylene-based copolymers with ethylene or an unconjugated diene as the comonomer were subjected to oxygen plasma treatments. The main objective was to investigate how the degree of wettability and the adhesion properties were influenced by the type and amount of comonomer and by selected plasma parameters. The change in wettability was monitored by static water contact angle measurements and the adhesion between plasma-treated polypropylene plates and a two-component polyurethane lacquer was evaluated by a 90° peel test. No significant difference in the degree of wettability depending on material composition or treatment conditions could be observed. However, the lacquer adhesion was shown to be a function of both material composition and discharge power, while the influence of gas pressure was less clear. For all processing conditions used, the lacquer adhesion was distinctly improved as the diene content was increased. An increasing extent of crosslinking reactions combined with a reduction in the number of main chain scissions are proposed to account for the observed results. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polypropylene-based materials are increasingly used in a variety of applications, mainly as a result of improved and broadened material properties and their competitive price. Attempts to minimize the number of materials employed in various applications in order to facilitate recycling is another important reason for the interest in these materials, as use is expected to continue to increase in the future. However, for many applications, printing, glueing or lacquering is necessary. This introduces a delicate problem, since polypropylene-based materials, in addition to being highly unreactive, present a low surface energy (*ca.* 30–35 mJ m^{-2}). Consequently, a suitable surface pretreatment must be carried out before satisfactory adhesion properties can be obtained. There are several pretreatment methods available, of which chemical treatment, flame treatment, corona treatment, plasma treatment and u.v. treatment appear to be among the methods most frequently used[1-3].

Numerous papers have reported on the use of plasma treatment as a means to increase the polarity and thereby the wetting properties of polypropylene (PP) surfaces, see for instance refs 3 and 4. Less attention has been paid to the evaluation of adhesion properties however, although exceptions exist[5-7]. We reported earlier on the importance of using optimized plasma conditions in order to obtain successful adhesion between a lacquer and plates of various thermoplastic polyolefins (TPOs)[8]. That study

also showed that the adhesion properties were highly dependent on the material composition. The plasma conditions mainly affect the concentration of active species in the plasma, but they also have an effect on the amount of radicals formed in the substrate. The primary effect of the material composition, on the other hand, is on the outcome of these radicals and, as radical formation in polypropylene-based materials chiefly includes tertiary radicals, chain scission will probably be the dominant reaction[9,10].

If excessive chain scission is the main cause of unsatisfactory adhesion of lacquer to plasma-treated TPO materials, it can be assumed that plasma-treated PP plates will be equally difficult or even more venturesome to lacquer. A way to overcome or at least reduce the detrimental effect that chain scissions involve would be to provide the PP with a functional group that could trigger crosslinking reactions. Such a functional group is an unreacted double bond, which may be introduced through the copolymerization of propylene with an unconjugated diene. However, a necessary condition is that the second double bond remains unreacted after the diene has been incorporated into the main chain via the first double bond. The unreacted double bond can then later (for instance during the plasma treatment) be used to trigger crosslinking reactions.

In this study, four different polypropylene-based copolymers were subjected to oxygen plasma treatment. The primary goal was to investigate the influence of the type and amount of comonomer on the development of satisfactory lacquer adhesion. The effect of processing

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Table 1 Material characteristics

Material	Comonomer[a] (mol %)	MFR[b] (g/10 min)	T_m^c (°C)	Crystallinity[d] (%)	$M_n 10^{-3e}$ (g mol^{-1})	$M_w 10^{-3e}$ (g mol^{-1})
PP-ref	4.4	6.0	143	48	41.1	208
PP-0.6	0.6	6.8	155	59	42.0	237
PP-1.0	1.0	4.5	150	48	37.2	259
PP-1.4	1.4	4.8	148	49	37.4	280

[a] Ethylene (PP-ref) and diene (PP-0.6, PP-1.0, PP-1.4)
[b] Melt flow rate measured at 230°C and 2.16 kg
[c] Melt temperature determined by differential scanning calorimetry (d.s.c.), heating rate 10°C min^{-1}
[d] Calculated from d.s.c. data using 165 J g^{-1} as the heat of fusion for a 100% crystalline isotactic polypropylene
[e] Molecular weights (number and weight averages) determined by size exclusion chromatography (s.e.c.). All molecular weights are given in polypropylene calibration
Note: for further details on the d.s.c. and the s.e.c. analyses, consult ref. 8

conditions (discharge power and gas pressure) on the degree of wettability and the lacquer adhesion was also of great interest.

EXPERIMENTAL

Materials

Four polypropylene-based copolymers, kindly supplied by Borealis, Finland, were used in this study. Pertinent material data are summarized in *Table 1*. The first is an ethylene-modified polypropylene (ethylene content 4.4 mol%) and the other three are diene-modified polypropylenes (diene content 0.6, 1.0 and 1.4 mol%, respectively). The diene comonomer (the same in all three diene copolymers) is an aliphatic, non-conjugated diene with allylic hydrogens. The ethylene-modified polypropylene was used as a reference material, and the degree of modification was chosen so as to give material properties comparable with those obtained for the diene copolymers. All materials contained a minimum amount of processing aid and standard amounts (*ca.* 0.15% by weight) of antioxidants. Throughout this paper, the materials will be referred to as PP-ref (reference material), PP-0.6, PP-1.0 and PP-1.4 (diene materials). The materials were received as injection-moulded plates of size 100 × 100 mm and thickness 4 mm.

Plasma equipment and plasma treatments

Plasma treatments were performed using a lab-scale reactor built at the Institute for Surface Chemistry. It consists of a glass vessel (inner diameter 15 cm, length 65 cm) connected to a double-stage rotary vacuum pump (Leybold–Heraeus D 65 B). Two externally wrapped, capacitively coupled copper electrode bands (3 cm wide, 10 cm apart) were powered by a 13.56 MHz radio-frequency power generator (ENI, model ACG-3). The discharge power was balanced by an automatic impedance matching network (ENI, model MW-5D) which was controlled by a remote generator controller (ENI, model RFC-5MW). The gas flow rate was controlled by a mass flow controller (HITEC, Bronkhurst). The substrates were mounted on a glass Petri dish and placed on top of a steel sample holder. The sample holder was kept at a floating potential at constant temperature (20°C) and was always positioned just below the most intense plasma zone. Prior to treatments, the chamber was pumped down to a base pressure of approximately 5 mTorr. The discharge gas (oxygen) was introduced at

the top of the reactor and the flow rate was kept at 20 standard cubic centimetres per minute (sccm). The pressure during the plasma treatments was varied between 90 and 500 mTorr by adjusting the exhaust valve. The treatment time was always 30 s, and the applied discharge power was varied between 10 and 50 W.

Contact angle measurements (goniometry)

The effect of plasma treatments was followed by static contact angle measurements using water as the wetting liquid. Both advancing and receding contact angles were measured. Droplets of deionized water were placed at different locations on the plates using a micro-syringe. The droplet volume was 4 µl, and the measurements were carried out using a Ramé–Hart goniometer, model 100. A minimum of eight readings was taken for each plate in order to determine average values. Contact angles were measured immediately after the plates were removed from the plasma reactor and directly before lacquering. Typical standard deviations were 2–3°.

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

X.p.s. analyses were performed on a PHI 5500 ESCA system from Perkin–Elmer equipped with a Mg K_α (1253.6 eV) source used at 250 W and 11.0 kV. The pressure in the analysis chamber was < 10^{-9} Torr during data acquisition and the analysed area was 0.8 mm in diameter. The take-off angle was 45° with respect to the sample surface, which corresponds to an effective sampling depth of ~7 mm[11]. The sensitivity factors used were according to the Perkin–Elmer manual.

Lacquering and adhesion test

The lacquer used in this study was a two-component polyurethane (PUR) lacquer based on a hexamethylene-diisocyanate prepolymer (Beckryflex TV-130) and a hydroxyl-terminated polyester (Beckryflex TH-130 2601) delivered by Beckers, Sweden. Lacquering was carried out one day after the plasma treatments. Specimens for the adhesion test were prepared as follows: a thin layer of the lacquer was manually applied onto the samples with a paint brush. A plasma-treated polyester cloth (Monodur PES 71N, mesh width 71 mm) was used as a reinforcement and was placed in the lacquer followed by another layer of lacquer to ensure that the polyester cloth was completely soaked. The total thickness of the lacquer layer including the reinforcing

cloth was ~130 μm. The lacquered samples were cured at 90°C for 40 min before being stored under atmospheric conditions (room temperature, normal humidity) for one week to complete the curing reaction. The lacquered specimens were finally cut into 15 mm wide strips.

The lacquer adhesion was evaluated by a 90° peel tester. The peel test were performed using a tensile tester (model TCT-5 from Alwetron) 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} and the reported peel forces are average values for four strips peeled over a distance of 70 mm or more. The peel forces were registered as N/15 mm and are accurate to within ±15%. A detailed description of both sample preparation and peel test has been given elsewhere[8].

RESULTS

Oxygen plasma treatments using various gas pressures

The effect of oxygen gas pressure on wettability is shown in *Tables 2* and *3*, which include the advancing contact angles obtained immediately after the plasma treatments and the advancing and receding contact

Table 2 Influence of gas pressure on water contact angles (Θ_A, advancing and Θ_R, receding) obtained after oxygen plasma treatment of polypropylene-based copolymers. Plasma conditions: 10 W, 20 sccm and 30 s

Substrate	Pressure (mTorr)	$\theta_A(°)^a$	$\theta_A(°)^b$	$\theta_R(°)^b$
PP-ref	90	63	74	24
	250	60	69	26
	500	67	75	21
PP-0.6	90	72	75	19
	250	60	73	23
	500	74	77	17
PP-1.0	90	69	75	11
	250	69	68	18
	500	57	74	18
PP-1.4	90	72	75	5
	250	58	72	16
	500	69	74	22

^{a} Measured immediately after plasma treatment
^{b} Measured directly before lacquering

Table 3 Influence of gas pressure on water contact angles (Θ_A, advancing and Θ_R, receding) obtained after oxygen plasma treatment of polypropylene-based copolymers. Plasma conditions: 30 W, 20 sccm and 30 s

Substrate	Pressure (mTorr)	$\theta_A(°)^a$	$\theta_A(°)^b$	$\theta_R(°)^b$
PP-ref	90	67	72	22
	250	53	63	5
	500	61	72	10
PP-0.6	90	70	75	18
	250	65	74	13
	500	70	73	16
PP-1.0	90	67	75	8
	250	62	69	10
	500	61	72	12
PP-1.4	90	69	74	6
	250	62	72	14
	500	59	72	16

^{a} Measured immediately after plasma treatment
^{b} Measured directly before lacquering

angles obtained directly before lacquering. Contact angles of untreated control plates are 99–101° for the advancing and 96–98° for the receding. The results clearly show that all plasma treatments are effective in improving the wetting properties. Immediately after oxygen plasma treatment at 10 W (*Table 2*), the advancing contact angles are reduced to between 57 and 74°, whereas the contact angles are in the range of 68–77° (advancing) and 5–26° (receding) directly before lacquering. This implies that a restructuring of the surfaces takes place within the first 24 h after the treatments and leads to an average increase in the advancing contact angles of about 8°. A closer look at *Table 2* reveals that no particular trend can be distinguished, although there is some variation in the advancing contact angles. On the other hand, the receding contact angles show a weak trend towards lower values as the diene content increases. The variation is most pronounced at 90 mTorr and decreases thereafter with increasing gas pressure. At 500 mTorr, nearly the same receding contact angles are obtained for all materials. The contact angles obtained after plasma treatment at 30 W (*Table 3*) are similar to those obtained after plasma treatment at 10 W (*Table 2*), with the distinction that no particular trend in receding contact angles can be observed. One can conclude that the wettability is little influenced by changes in gas pressure and type of material.

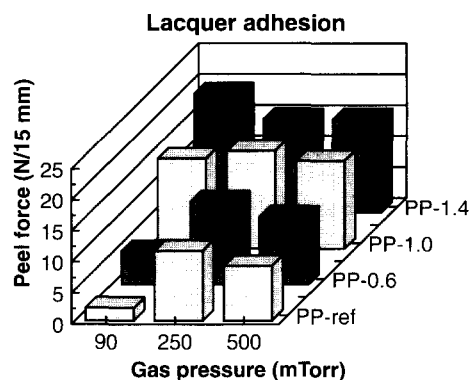If wettability is the determining factor for good lacquer adhesion, one would not assume the peel forces

Figure 1 Influence of gas pressure and material composition on lacquer adhesion (F, given as N/15 mm). Plasma conditions: oxygen, 13.56 MHz, 10 W, 20 sccm and 30 s
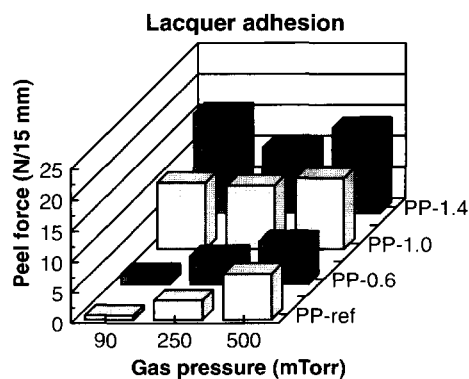

Figure 2 Influence of gas pressure and material composition on lacquer adhesion (F, given as N/15 mm). Plasma conditions: oxygen, 13.56 MHz, 30 W, 20 sccm and 30 s

to vary much with either increasing gas pressure or among the various materials. *Figure 1* (10 W) and *Figure 2* (30 W) reveal that this expectation is not fulfilled. Both figures show noticeable differences among the materials. Independent of gas pressure, the general trend is the higher the diene content, the higher the peel force. The effect of increasing gas pressure is more complex. Depending on the diene content and the discharge power (10 or 30 W), the peel force may increase or decrease as the gas pressure increases, but may also show a more varying dependence on gas pressure, see for instance PP-0.6 at 10 W or PP-1.4 at 30 W.

Oxygen plasma treatments using various discharge powers

The influence of increasing discharge power on wettability is shown in *Table 4* and corresponding values for the lacquer adhesion are shown in *Figure 3*. It is evident from *Table 4* that the advancing contact angles do not change a great deal with either discharge power or material composition. The initial advancing contact angles vary between 63 and 72° while the advancing contact angles obtained directly before lacquering are found to be in the range of 69–75°, an average of 6° higher that the initial values. This indicates again that a restructuring of the surfaces occurs within the first 24 h. Furthermore, if no trends can be found in the advancing contact angles, it is quite clear that, when one specific discharge power is followed, the receding contact angles decrease as the diene content is increased. Moreover, when one specific material is followed, the receding contact angles are seen to decrease with increasing discharge power, although this effect becomes weaker as the diene content increases.

Figure 3 shows the influence of discharge power on peel forces. According to the above discussion, no significant variation in peel forces would be expected with increasing discharge power, as judged from the advancing contact angles, as these do not change significantly with either diene content or increasing discharge power. However, independent of power level used, the receding contact angles suggest that the highest peel forces should be obtained for PP-1.4 (lowest receding contact angles), while the lowest peel forces should be obtained for PP-ref (highest receding contact angles), and this is indeed the case. Accordingly, the best lacquer adhesion is obtained for PP-1.4, followed by PP-1.0 and PP-0.6, and the poorest lacquer adhesion is
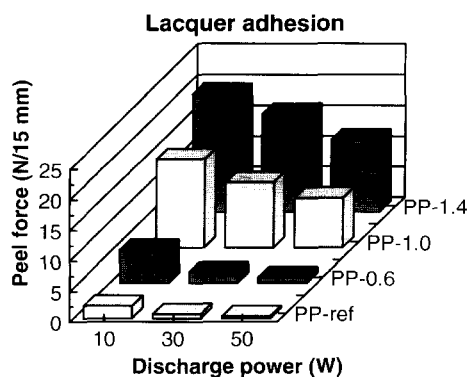
Table 4 Influence of discharge power on water contact angles (Θ_A, advancing and Θ_R, receding) obtained after oxygen plasma treatment of polypropylene-based copolymers. Plasma conditions: 90 mTorr, 20 sccm and 30 s

Substrate	Power (W)	$\theta_A(°)^a$	$\theta_A(°)^b$	$\theta_R(°)^b$
PP-ref	10	63	74	24
	30	67	72	22
	50	64	74	16
PP-0.6	10	72	75	19
	30	70	75	18
	50	69	73	5
PP-1.0	10	69	75	11
	30	67	75	8
	50	60	72	5
PP-1.4	10	72	75	5
	30	69	74	6
	50	64	69	5

^{a} Measured immediately after plasma treatment
^{b} Measured directly before lacquering

obtained for PP-ref. Moreover, a serious deterioration in peel forces is observed for all materials as the discharge power is raised. This is contradictory to the receding contact angles, however, as they indicate the highest lacquer adhesion to be obtained at 50 W (lowest receding contact angles). Thus, neither the advancing contact angles nor the receding contact angles can be used to safely predict the levels of lacquer adhesion.

Additionally, it may seem as if the diene comonomer is more effective at mild plasma conditions, as the highest *absolute* peel forces are obtained at 10 W, independent of material. In a comparison of the *relative* peel forces, however, the best effects of the diene comonomer is obtained at 50 W. Consequently, when the peel forces obtained for PP-1.4 are related to the corresponding values obtained for PP-ref, a 9-fold increase is observed at 10 W and a 33-fold increase at 50 W.

DISCUSSION

Cause and result of radical formation

The results obtained clearly reveal the lack of consensus between the water contact angles and the lacquer adhesion. This is in agreement with a previous study[12] in which it was found that the water contact angles could not be correlated with the results obtained after peeling of plasma-treated and lacquered TPO plates. The study revealed instead that the lacquer adhesion was determined by the cohesive strength of the near-surface region of the substrate. For peel forces >25 N/15 mm, the failures were undoubtedly cohesive in the substrate as judged by the naked eye (a thin layer of polymer was observed on the lacquer side), whereas the failures appeared to be interfacial for peel forces <20 N/15 mm. However, analyses of the fracture surfaces of samples showing low peel forces revealed that the failure in these cases was also cohesive in the substrate, although it was located closer to the surface region (but still below the oxidized surface layer). The weakening of the near-surface region of the substrate—which was particularly pronounced when the plasma treatments were performed at high power-to-gas flow ratios—was proposed to be the result of the vacuum-ultraviolet (VUV) radiation that is being formed in the plasma. VUV radiation has enough energy to break chemical bonds and VUV

Lacquer adhesion

Figure 3 Influence of discharge power and material composition on lacquer adhesion (F, given as N/15 mm). Plasma conditions: oxygen. 13.56 MHz, 90 mTorr, 20 sccm and 30 s

radiation of wavelengths <160 nm is strongly absorbed by hydrocarbons such as polypropylene and polyethylene[13,14]. Furthermore, VUV radiation can penetrate more deeply into the substrate than can other species in the plasma, such as atoms or ions, and radicals may therefore be formed not only at the outermost surface but also in the near-surface region of the substrate.

The outcome of radical formation in polymers is dependent on the type of radicals being formed. This is primarily because various types of radicals have different stabilities and thus different reactivities (radical reactivity being inversely proportional to radical stability)[10,15]. For instance, if secondary radicals are formed—such as in polyethylene—combination is likely to occur, whereas tertiary radicals—which normally are formed in polypropylene-rich materials—generally decay via β-scission or disproportionation[9,10]. In this context, it is interesting to compare how the plasma conditions affect the paintability of PP and TPO plates. In our experience, it has always been possible to achieve excellent lacquer adhesion (clear cohesive failure in the substrate) after oxygen plasma treatment of TPO materials in different reactors, provided that optimized processing parameters are used (low discharge power, relatively high gas pressure). Obtaining sufficient lacquer adhesion after oxygen plasma treatment of an unfilled PP is an extremely difficult task, however (see for instance PP-ref in *Figures 1–3*). It appears to be almost impossible to achieve a *clear* cohesive failure in the substrate even when optimized processing parameters are used, although somewhat higher peel forces can be obtained. The main difference between TPOs and PP is that the former contain a rubber phase, usually an ethylene-propylene rubber (EPR), or possibly an ethylene-propylene-diene-monomer (EPDM) rubber. The variation in sensitivity can thus be a consequence of the ethylene units present in the rubber phase, as these will tend to form secondary radicals which predominantly terminate via combination.

The effect of the diene comonomer

The diene copolymers used in this work differ only from the reference PP in that another comonomer is used. The introduction of a comonomer primarily affects the crystallinity and hence the mechanical properties of the material, and an ethylene-modified PP instead of a homopolymer was therefore chosen as the reference material. Furthermore, there is no reason to believe that the variation in molecular weight observed among the materials (see *Table 1*) would lead to any appreciable difference in the cohesive strength of the materials.

For the specific peel test conditions used in this study, a clear cohesive failure in the PP substrate is associated with peel forces >20 N/15 mm. All other samples appear to have an interfacial failure between the PP substrate and the PUR lacquer. It was not of primary interest in this study to identify where the failure occurred in all the cases where it was not obvious from visual inspection. However, it is reasonable to believe that, in agreement with previous studies, the failure is located in the near-surface region of the substrate provided that the degree of wettability is sufficiently high. In fact, one elucidatory X.p.s. analysis of a lacquered and peeled PP-1.4 strip (treatment conditions: 30 W, 250 mTorr; peel force: 12.5 N/15 mm) supported this assumption. Although the failure seemed to be interfacial, the X.p.s. results revealed a cohesive failure in the substrate with a

chemical composition of the lacquer side similar to that of a pure hydrocarbon surface (oxygen 1.0 at%, carbon 99.0 at%). Contact angle measurements made on the corresponding PP side also indicated a cohesive failure in the substrate, as the advancing and receding contact angles were found to be 98 and 90°, respectively. These results support our theory that the failure occurs below the oxidized surface layer and thus that the adhesion properties are determined by the cohesive strength of the near-surface region of the substrate.

Returning to the peel test results, the most striking observation is that the lacquer adhesion is greatly improved as the diene content in the copolymer is increased. A possible explanation for this could be that the number of main chain scissions had been reduced. However, all copolymers studied consist to the greatest part of propylene units, and chain scissions would therefore be expected to be an important reaction in all materials. Instead, it seems that the diene comonomer accounts for the improved lacquer adhesion as it can potentially trigger crosslinking reactions. The crosslinking capacity of this kind of diene-modified polypropylenes has been tested by both peroxide crosslinking and irradiation crosslinking, the latter giving slightly higher gel contents[16]. It was shown that irradiation crosslinking of a copolymer with a diene content of 1 mol% resulted in gel contents up to 80%, which is a remarkably high value considering the fact that PP is extremely difficult to crosslink[10]. This clearly demonstrates the capacity for the diene comonomer to introduce crosslinks. However, in contrast to peroxide crosslinking of polyethylenes, the diene-modified polypropylene did not reach proper melt strength as measured by a hot set test[17], which implies that main chain scissions still occur simultaneously to the crosslinking reactions.

With respect to the crosslinking mechanism, it is important to note that the diene comonomer can trigger crosslinking reaction in two ways—the crosslink can be introduced directly via the addition of a radical to the double bond, or it can be introduced 'indirectly' through the formation of allylic radicals which, in contrast to tertiary radicals, are known to preferentially terminate via combination[10]. At the first glance, it may seem natural that the crosslinks are formed directly via addition to the double bond since conversion of a double bond into a single bond is energetically favoured. However, as a consequence of the chemical structure of the diene comonomer used in this study, the double bond is sterically hindered and addition reactions may thus be obstructed. This effect was exemplified by Parks and Lorenz[19], who reported the reaction of dicumyl peroxide with 2,6-dimethyloctadiene to result mainly in isometric dimers, whereas the reaction with 1-decene resulted in both dimers and a considerable amount of material of higher molecular weight material. Thus it appears more likely that the crosslinks in our case are formed through the coupling of allylic radicals.

The formation of allylic radicals are energetically favoured over the formation of tertiary radicals[15]. However, the number of allylic radicals that can possibly be formed is limited by the low concentration of the diene comonomer (0.6–1.4 mol%). The number of tertiary hydrogens is consequently considerably higher that the number of allylic hydrogens, and the unselective VUV radiation should therefore statistically lead to an

excess of tertiary radicals. On the other hand, each diene comonomer contributes a number of allylic hydrogens, leading to a concentration of about 10% as compared with the number of tertiary hydrogens. It should also be remembered that, due to its size, the diene comonomer is excluded from the crystalline regions and the diene comonomer will therefore be concentrated in the amorphous phase. Hence, if the crystallinity is about 50%, as in the materials used in this study, the concentration of double bonds and allylic hydrogens will be roughly twice as high in the amorphous phase as in the overall concentration.

One possibility for further increasing the number of allylic radicals, and thereby enhancing the probability of crosslinking reactions, would be if the system allowed migration of radicals so that tertiary radicals could be converted to allylic radicals through successive hydrogen abstractions. The driving force for such an action would simply be that the allylic site is favoured as a result of its lower energy. This kind of radical migration has been proposed to occur in the peroxide crosslinking of unsaturated ethylene copolymers[19]. Moreover, migration of radicals has been accepted as an important mechanism in the field of stabilization of polyolefins[20]. It should not be forgotten however that plasma treatments are performed at completely different conditions than are used for instance in peroxide crosslinking. In the specific case cited here[19], the peroxide crosslinking was performed at 180°C, which should be compared with a temperature slightly above room temperature in the case of a low-temperature plasma. The radical mobility is thus much lower in our experiments and it may be questioned whether the radicals can migrate at all under such conditions. However, the fact that not only peroxide crosslinking but also irradiation crosslinking of the diene-modified polypropylene led to a high gel content[16] definitely supports the assumption that radicals have a certain mobility even at room temperature. This reasoning is further supported by another study[21] in which it was shown by electron spin resonance (e.s.r.) measurements that the radicals formed after γ-irradiation of PP decayed upon storage at room temperature and vacuum conditions. If it is also taken into account that the glass-transition temperature (the temperature onset for extensive molecular motions) of a PP homopolymer is about $-15°C$, i.e. well below room temperature, the assumption regarding the migration of radicals via successive hydrogen abstractions seems even more credible. To conclude, it appears likely that at least 20% of the total amount of radicals formed in the amorphous regions will be of the allylic type, and if consideration is also taken to the possible effect of radical migration and preferential hydrogen abstraction, the amount can be even higher.

Thus far we have discussed only the advantageous effect that allylic radicals have in the case that they introduce crosslinks. However, it should not be forgotten that the formation of allylic radicals in itself is beneficial, as these are formed at the expense of tertiary radicals which would otherwise have led to undesired main chain scissions. If the allylic radical—after having been formed—combines in addition with another radical leading to a crosslink, the benefit is actually doubled. Thus, the beneficial effect of the diene comonomer can be summarized as being a result of an increasing extent of crosslinking reactions (triggered by the unreacted double

bond) combined with a reduction in the number of main chain scissions. Both actions lead to a near-surface region with a better retained (less deteriorated) cohesive strength which in turn positively influences the adhesion properties.

The effect of storage

Some final comments seem warranted of the effect of storage. The advancing contact angles suggest that some kind of restructuring or 'ageing' of the plasma-treated surfaces takes place during the first 24 h after the plasma treatment. An ageing of polymer surfaces has been observed in many studies[1,4,22,23], and the main cause of this phenomenon is the thermodynamically driven force that strives to minimize the interfacial energy. In the case of a hydrophilic surface in contact with air (a typically hydrophobic environment), the surface will thus try to lower its surface energy (increase its hydrophobicity) in order to more resemble its environment, and the phenomenon is indeed also referred to as hydrophobic recovery. The lowering of the surface energy can be accomplished in many ways, for instance through the reorientation of pendant groups and side chains towards the interior of the material, through adsorption of low energy contaminants from the atmosphere or through the diffusion of oligomers and/or low molecular weight additives towards the surface.

The ageing effect observed in this study is most likely caused by the reorientation of polar groups towards the bulk. Since no lacquering of plates was performed immediately after the plasma treatment, it is not possible to ascertain whether the 24-h storage has any impact on the subsequent lacquer adhesion. However, no clear correlation between contact angles and peel forces can be observed and, since it seems to be the cohesive strength of the near-surface region of the substrate that controls the lacquer adhesion rather that the degree of wettability, it is relatively safe to assume that the increase in the advancing contact angles upon storage is of minor importance for the lacquer adhesion.

CONCLUSIONS

1. All plasma treatments performed are effective in increasing the wettability. The degree of wettability does not change noticeably with gas pressure, discharge power or material composition.
2. The lacquer adhesion is highly dependent on plasma processing parameters. The peel force is seriously deteriorated as the discharge power is raised. The dependence on gas pressure is more complex.
3. It is extremely difficult to achieve satisfactory lacquer adhesion after oxygen plasma treatment of a reference PP. This is probably a consequence of excessive chain scission reactions, which lead to a weakening of the near-surface region of the substrate.
4. The lacquer adhesion is greatly improved as the diene content in the copolymer is increased. An increasing extent of crosslinking reactions (triggered by the unreacted double bond) combined with a reduction in the number of main chain scissions are proposed to account for the observed results.

ACKNOWLEDGEMENTS

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