Adhesion of Photocurable Acrylates to Solid Polymer Substrates

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Synopsis

The adhesion of a hydrophilic (surface tension $\gamma \approx 40$ mJ/m^2) and a hydrophobic ($\gamma \approx 30$ mJ/m^2) photopolymerized acrylate lacquer to low-density polyethylene, polystyrene, polycarbonate, polyamide-6-6, polyvinylchloride, polyethyleneterephthalate, poly-(1,1)-difluoroethylène, and polymethylmetacrylate has been investigated. A primary condition to obtain sufficient adhesion, as probed by the Scotch tape test, is that the surface tension of the lacquer has to be lower than the critical surface tension of the lacquer. There is no obvious correlation with possible donor/acceptor interactions between lacquer and substrate. Even when spreading occurs, other factors may cause insufficient adhesion. On polyamide, residual moisture on the surface is very detrimental to adhesion. Extending the lag-time between application and curing reduced adhesion, in particular to polymers containing aromatic groups. This appears to be due to inhibition of the polymerization reactions by radiation-adsorbing aromatic groups in the swollen interphase. The effect can be avoided by proper choice of initiator and radiation source. Curing of the lacquers in a nitrogen atmosphere generally results in poor adhesion because the rate of polymerization/curing becomes very high compared with rates of relaxation of stresses in the lacquer.

INTRODUCTION

Radiation-curable coatings are now used in several applications. Some of its advantages over solvent-based coatings are reduction of solvent emission, decrease in energy consumption, ease of processing, improved surface properties, and reduction of overall cost. In particular, ultraviolet (UV)-cured coatings are used increasingly in varnishing of paper, wood, and polymers; printing inks, primers, optical fiber coatings, photoresists; and protective coatings on printed circuits, boards, and adhesives.

The main components of a UV-curable coating are mono- and polyfunctional acrylic monomers, prepolymerized resins, pigments, extenders, inhibitors, stabilizers, and photoinitiators. Radicals can essentially be formed by two mechanisms: photofragmentation or excitation of a photosensitizer followed by hydrogen abstraction. Both mechanisms have been thoroughly discussed in the literature.

The curing rate and the overall performance of the film are critically dependent on (i) the functionality of the monomers, the miscibility of the components, and the viscosity, which depends on the prepolymerized resin; (ii) the overlap between the emission spectrum of the UV radiation source and the UV absorption spectrum of the photoinitiator, the binders, and the pigments.

Once the initiator radical has been formed, terminating reactions with oxygen will easily predominate over propagation reactions with acrylic double bonds due to the biradical nature of oxygen in its ground state. Thus, in the outermost layer of a coating, peroxyradicals which react much more slowly than the alkyl or alkoxy radicals will be formed. Consequently, the surface curing is retarded, resulting in extensive surface tack.

Another disadvantage of radiation curing, particularly in electron beam curing, is that the rate of molecular relaxation is much slower than the rate of polymerization. This may result in considerable shrinkage and cracking of the film. It is also known that UV-cured coatings often do not adhere very well, particularly to polymeric substrates.

We believe that some of these problems may be overcome through a better understanding at a molecular level of the adhesion mechanisms of UV lacquers to different polymers. The aim of this study is to achieve some such understanding by investigating the adhesion mechanisms of two model UV-curable lacquers with different surface energy to six commonly used polymers. Both lacquers consist of simple, well-characterized monomers. The surfaces were characterized by ESCA, as well as contact angle and surface tension measurements, and adhesion was measured by the Scotch tape test; in addition, qualitative evaluations of solubility parameters were made.

EXPERIMENTAL

Materials

The following pigment- and additive-free substrate films were used as substrates:

Transparent low-density polyethylene (LDPE) from NOAX, Sweden

Polystyrene (PS) from BASF Ag, West Germany

Polycarbonate (PC), Makrolon, from Bayer Ag, West Germany

Polyvinyl chloride (PVC) from KemaNord Ab, Sweden, containing < 0.5% of either plasticizer or organic tin stabilizer

Polyethyleneterephathalate (PET), Mylar from DuPont, Inc, USA

1,1-Difluoroethylene (PVF), from DuPont Inc., USA

Polymethylmethacrylate (PMMA), Plexiglas from Röhm, GMBH, West Germany

All substrate films were sonificated in a 70/30 solution of ethanol and water and then thoroughly rinsed in distilled water (purified by passing through a Millipore RO-system).

Chemicals

2-Hydroxyethylacrylate (HEA) (Dow Chemicals Europe), 2-hexylacrylate (EHA) and ethyldiglycolacrylate (EDGA) (BASF), vinylpyrrolidone (NVP) (GAF Europe, UK), and diacrylated etoxilated bisphenol A (AEB) (Diamond Shamrock, England), were all of technical grade. The photoinitiator 2-propiophenone (Merck Ag), was also of technical quality.

Methods and Instrumentation

Irradiation for photocuring was provided by two microwave-excited standard mercury bulbs (Fusion System, USA), giving a total output of 100 W/cm^2. The polymer substrates were coated with 10 μm lacquer films using a laboratory spiral rod applicator.

The DIN cross-cut knife Scotch tape test was used to test lacquer adhesion. The adhesion is expressed as the percentage of the film squares, created by the cross-cut knife, remaining after removal of the Scotch tape.

Surface tensions were measured with a duNoüy ring tensiometer. A Ramé-Hart goniometer was used for contact angle measurements.

ESCA spectra were recorded with a Leybold-Heraeus spectrometer equipped with an Al K^α radiation source ($h\nu$ = 1486.6 eV) operating at 13 kV and 17 mA with the electron emission angle set to 70° with respect to the normal of the sample surface. Details of Cls peaks were recorded at 10^{-9} torr. The cross-sections $\sigma(C(1s)) = 1.00$, $\sigma(O(1s)) = 2.93$, $\sigma(Cl(2p)) = 2.29$ were used.[1] The binding energy scale was fixed by assigning $E_B = 285.0$ eV to the $-CH_2-$ carbon in Cls. The following chemical shifts for carbons attached to different oxygen-containing groups were used:

$-CH_2-O-$ (hydroxyl, hydroperoxide, ether, sulfate ester), $\Delta E_b = 1.5\,eV,$[2]

$>C=O$ (carbonyl or amide), $\Delta E_B = 3.0$ eV,[2]

$-COO-$ (carboxyl or carboxylate), $\Delta E_B = 4.2$ eV,[2]

$-CH_2-Cl$, $\Delta E_B = 1.5,$[3]

$-CF_2-$, $\Delta E_B = 7.8$ eV.[4]

RESULTS

Lacquers

Two model lacquers were formulated, one (A) with more hydrophobic properties than the other (B). The recipes for these lacquers are given in Table I, together with the surface tensions and the solubility parameters of their components. In both recipes the prepolymer is a diacrylated adduct of ethoxylated Bisphenol A (AEB) and 2-hydroxy-2-propiophenone is used as initiator. The surface tensions of these lacquers at 25°C were 30 mJ/m^2 (lacquer A) and 39 mJ/m^2 (lacquer B).

Substrate Surfaces

The different substrates are listed in Table II, with the measured contact angles of water as well as surface tensions (γ_s) and solubility parameters taken from literature. Generally, the contact angles are slightly lower than those reported in the literature.[8] The reason is probably that the substrates were thoroughly cleaned and that *receding* contact angles were measured. Generally, low contact angles are obtained for surfaces for which high surface tensions are reported in the literature. Polycarbonate is an exception; a probable reason is the presence of residual hydrophobic contaminations from mould release agents.

The Cls spectra of the different polymer surfaces are shown in Figure 1. The peaks were deconvoluted graphically and the relative intensities with

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TABLE I
Recipes for Lacquer (A) ("Hydrophobic") and Lacquer (B) ("Hydrophilic")

Component	γ^1 (mJ/m^2)	δ (cal/cm^3)$^{1/2}$	Amount (wt %) A	Amount (wt %) B
N—vinyl—2—pyrrolidone CH_2=CH—N (ring) O	39.3	11.0	—	10
Ethyldiglycolacrylate O‖ $CH_3CH_2(OC_2H_4)_2OCCH$=CH_2	30.4	≈ 9.0	—	10
2-ethylhexylacrylate O‖ $CH_3CH(CH_2)_4OC$—CH=CH_2 | CH_2CH_3	26.1	7.7	24	—
2-hydroxyethylacrylate O‖ $HO(CH_2)_2OCCH$=CH_2	38.3	≈ 10.0	24	19
Acrylated adduct of ethoxylated Bisphenol A CH_2=$CHCO(OCH_2CH_2)_2OC_6H_6CC_6H_6O(OCH_2CH_2)_2OCCH$=$CH_2$ (O‖, CH$_3$, O‖, CH$_3$)	42.5		48	57
2-hydroxy-2-propiophenone O‖ CH$_3$| C_6H_6C—C—OH | CH_3			4	4

respect to the CH_2 peak were estimated (see Table III). The PE surface gives a pure aliphatic C(1s) peak. In addition to the aliphatic hydrocarbon, PS shows a characteristic shake-up satellite at E_B = 6.8 eV, due to the π-electrons of the aromatic rings. On the PMMA surface, the polar groups are slightly enriched, as indicated from the comparison with intensities expected for bulk polystyrene shown in the last column of Table III. The ester groups of the PET surface, the amido groups of the PA surface and the carbonate groups of the PC show the same tendency. Apparently the hydrophobic contaminations on the PC surface that are indicated by the contact angle measurements form a very thin or incomplete film. Essentially, one expects the contact angle measurements to be sensitive to the outermost atomic layers while the information depth of ESCA on polymer surfaces typically is about 5 nm.

The Air / Lacquer Interface

The contact angle of the cured lacquer A ("hydrophobic") is slightly lower than for lacquer B ("hydrophobic"), 55° ± 2 and 61° ± 3, respectively. The

TABLE II
Properties of Different Polymers

Polymer	Contact angle	γ_c[a] mJ/m^2	δ[b] (cal/cm^3)$^{1/2}$
Polyethylene (PE)	87	31	8.1
Polystyrene (PS)	81	33	9.1
Polymethylmethacrylate (PMMA)	62	39	9.3
Polyethyleneterephthalate (PET)	60	43	10.7
Polyvinylchloride (PVC)	60	39	8.9
Polyamide 6,6 (PA)	32	46	13.6
Polycarbonate (PC)	88	42	10.2
Polyvinylidene fluoride (PVF)	90	25	12.2

[a] From Refs. 5 and 6.
[b] From Ref. 7.

differences in surface composition are also reflected in the relative amounts of polar groups indicated by the C(1s) peaks in the ESCA spectra (sample spectra for films on PMMA are shown in Fig. 2 and intensities for these films are given in Table IV).

Note that the amounts of both hydroxyl (or ether) and carbonyl groups are lower for lacquer A, which contains the more hydrophobic and hence more surface-active monomer EHA in its formulation. The results in Table IV also show that the concentration of polar groups in the surface is higher than expected from bulk stoichiometry. This, as will be discussed below, is certainly an effect of surface oxidation during the curing reaction.[9]

Substrate / Lacquer Adhesion for Lacquers Cured in Air

The well-known empirical rule formulated by Zisman and co-workers[10] states that a liquid should spread on a solid surface provided its surface tension is lower than a critical surface tension γ_c for that surface; γ_c is determined from measurements of the contact angles for homologous series of liquids. The critical surface tensions given in Table II show that this condition is fulfilled by lacquer B on PC, PET, and PA while for lacquer A it is valid also for PVC, PMMA, and perhaps also for PS. In many cases, correlation is found between good adhesion and spread on the surface.[8,11] The results from the Scotch tape adhesion tests (Table V) show this to be the case, with the exception of PA (see below).

When adhesion between the lacquer film and the substrate was poor the film could be stripped off. The lacquer failure surfaces were then analyzed by means of ESCA and the contact angles on the surfaces were measured.

The relative amounts of polar components (as before, determined from graphical deconvolution of the C(1s) peak in the ESCA spectrum) in the failure surfaces of the more hydrophilic lacquer B are given in Table IV. It is quite obvious that on all polymer substrates, except for PE and PET, polar groups are enriched at the lacquer/polymer interface compared with the bulk composition of lacquer B. Sample C(1s) peaks for the lacquer failure surfaces are given in Figure 3. The ESCA spectrum of the lacquer side of the failure surface on PE resembles the spectrum of pure PE. This indicates cohesive
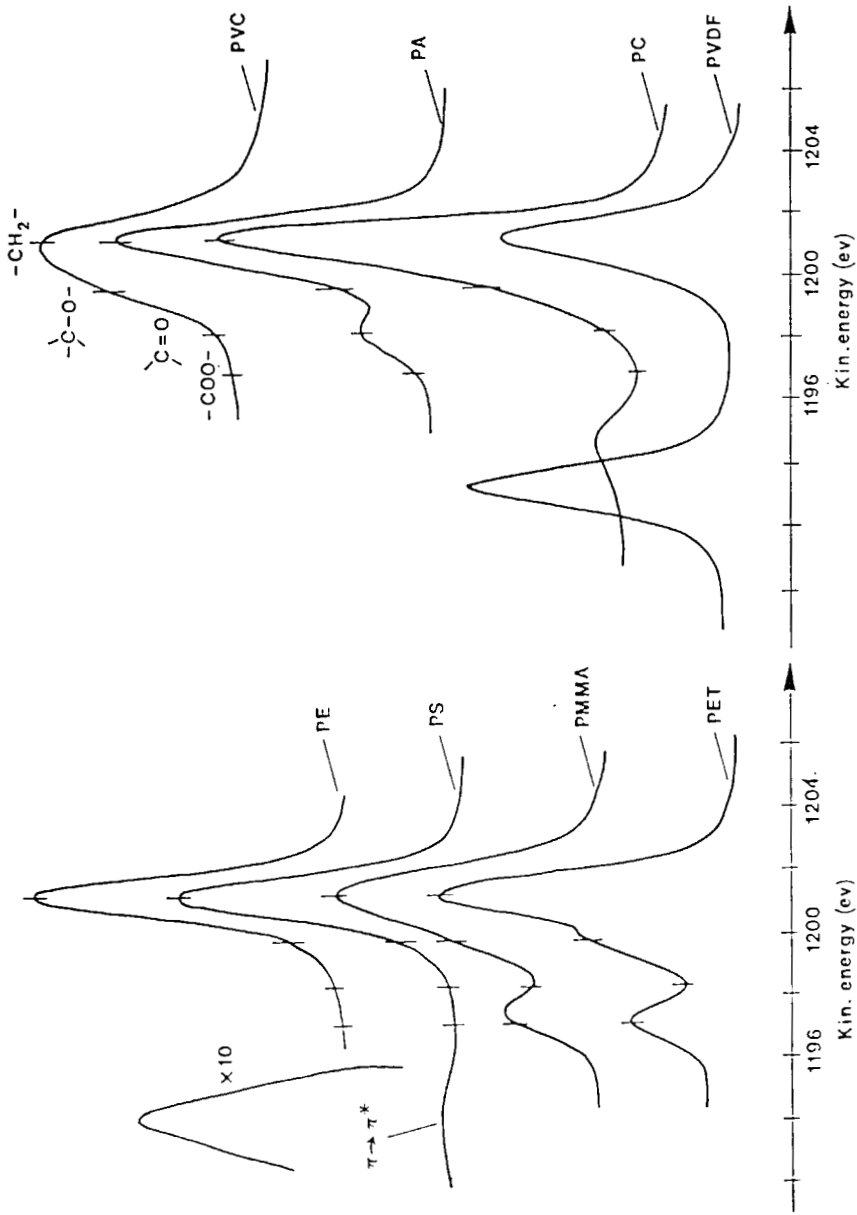
Fig. 1.　C(1s) peaks in the ESCA spectra from the bare polymer substrates.

TABLE III
Relative Surface Concentrations (Intensity of — CH$_2$— Set to 1) of Different
Functional Groups, Determined from the C1s Peak in the ESCA Spectrum

Polymer	—CH$_2$—O— or —CH$_2$—Cl	$>$C=O	$-\overset{\overset{\displaystyle}{\|}}{\underset{\displaystyle O}{C}}$—O—	1) —CH$_2$—CF$_2$— 2) $\pi \to \pi$ satellite 3) —C—N—	$\dfrac{-CX(exp)}{-CX(bulk)}$
LDPE	—	—	—	—	1.0(C—O/CH$_2$)
PS	—	—	—	0.045[2]	1.0(C—O/CH$_2$)
PMMA	0.38	0.01	0.34	—	1.09(C—O/CH$_2$)
PET	0.27	0.02	0.29	—	1.12(COO/CH$_2$)
PVC	0.92	—	—	—	0.92(C—Cl/CH$_2$)
PA	—	0.23	—	0.22[3]	1.12(C=O/CH$_2$)
PC	0.18	—	0.10	—	1.12(O$-\overset{\overset{\displaystyle O}{\|}}{C}$—O/CH$_2$)
PVF	—	—	—	1.0[1]	1.0(CF$_2$/CH$_2$)

failure in a weak boundary layer (WBL),[8,11] as is often formed by low-molecular-weight components in the surface region of polyolefins during processing of the polymer.

Although lacquer B adheres strongly to PET, the film could be peeled off. The C(1s) spectrum of the lacquer side of the failure agrees with pure PET (cf., Figs. 1 and 3). This may indicate a cohesive failure in the polymer (see Discussion). For PVC, a small Cl(2p) peak is observed on the lacquer side of the failure surface, indicating strong interaction between the substrate and the lacquer.
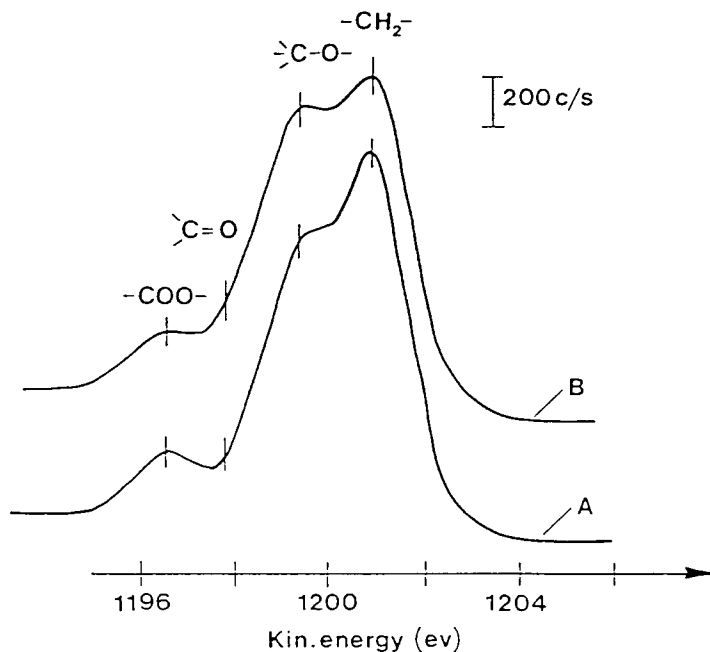

Fig. 2. C(1s) peaks in the ESCA spectra at the lacquer/air interface of lacquers A and B.

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TABLE IV
Contact Angles and Relative Surface Concentrations (from C(1s) ESCA Spectra)
of Different Functional Groups in the Lacquer/Air and Lacquer/Substrate
Interfaces for Lacquers A and B—the Bulk Concentrations of the Lacquers
are Shown within Brackets

No. Interface	Analyzed surface	Contact angle	Surface concentrations		
			$C-O$	$C=O$	COO
1. A/air	A on PMMA	61	0.71	0.05	0.19
			(0.44)	(0.01)	(0.16)
2. B/air	B on PMMA	55	0.87	0.17	0.19
3. B/PE	B	90	0.34	0.02	0.08
4. B/PS	B	63	0.80	0.15	0.19
5. B/PMMA	B	64	0.84	0.07	0.21
6. B/PET	B	—	0.49	0.06	0.26
7. B/PVC	B	75	0.89	0.12	0.20
8. B/PA	B	68	0.84	0.19	0.21
9. B/PVF	B	87	0.88	0.08	0.20
10. B/PC	B	No adhesive failure			
11. A/PE	A	—	0.40	0.02	0.15
12. A/PS	A	—	0.42	0.05	0.17
13. A/PMMA	A	No adhesive failure			
14. A/PET	A	No adhesive failure			
15. A/PVC	A	No adhesive failure			
16. A/PA	A	—	0.57	0.05	0.14
17. A/PVF	A	—	—	0.04	0.14
18. A/PC	A	No adhesive failure			
19. A/PS 5 min	A	—	0.47	0.06	0.17
20. A/PET 5 min	A	—	0.60	0.07	0.27
21. A/PC 5 min	A	—	0.64	0.04	0.18
22. A/PC 5 min	PC	—	0.27	0.02	0.10^a
23. A/PE 5 min	A	—	0.41	0.04	0.18
24. A/N_2^b	A	—	0.54	0.03	0.19
25. A/PMMA in N_2	A	—	0.55	0.03	0.19
26. A/PE in N_2	A	—	0.23	0.06	0.11
27. A/PS in N_2	A	—	0.39	0.04	0.14

[a] Carbonate.
[b] Film spread on PMMA.

Lacquer A contains the rather hydrophobic component EHA, which due to its amphiphilic character is expected to migrate to the surface and to orient close to interfaces. Accordingly, lacquer A has a lower surface tension than lacquer B; the orientation may also contribute to improved adhesion of lacquer A.

Lacquer A does not adhere satisfactorily to PE, PVF, or PA. The ESCA analysis of the corresponding lacquer failure surfaces is reported in Table IV. Although lacquer A spreads on PE ($\gamma_{c,PE} = 31$ mJ/m^2, $\gamma_A = 30$ mJ/m^2), the lacquer did not adhere. The C(1s) spectrum of the failure surface of the lacquer (Fig. 4) resembles pure PE, indicating that a WBL is present. Although the failure surface is enriched in aliphatic carbon residues, the relative amounts of COO and $C-O$ are higher than for lacquer B, indicating that EHA may have migrated into the "greasy" WBL layer.

The failure surface of lacquer A on PA is enriched in polar components (Fig. 4, Table IV). Although the spreading condition is fulfilled for both lacquer A

TABLE V
Scotch Tape Adhesion Tests for UV-Cured Lacquers on Polymer Substrates
(Surface Tension of Lacquer A: 30 mJ/m^2, of Lacquer B: 39 mJ/m^2)

Polymer	γ (mJ/m^2)	On B	Adhesion		
			On A[a]		
			1-min lag time	5-min lag time	Cured with doped lamp and H-abstr. initiator
Pe	31	0	0	0	0
PS	33	0	60–80	0–5	100
PMMA	38	0	100	100	100
PET	43	80–100	100	0–5	100
PVC	39	0	100	100	100
PA	46	0	0	0	(100)[b]
		(100)[b]	(100)[b]		
PVF	25	0	0	0	0
PC	42	100	100	0–10	100

[a]Adhesion of A if cured in nitrogen was 0 in all cases.
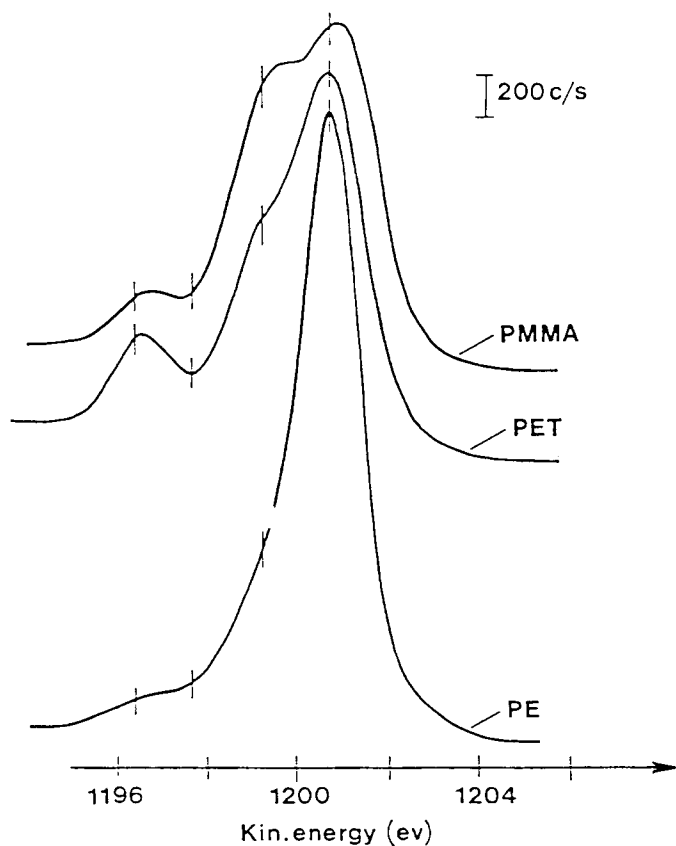[b]On PA dried in a vacuum desiccator.

Fig. 3. C(1s) peaks in the ESCA spectra from the lacquer side of the failure surface at the lacquer B/polymer interface on PMMA, PE, and PET.
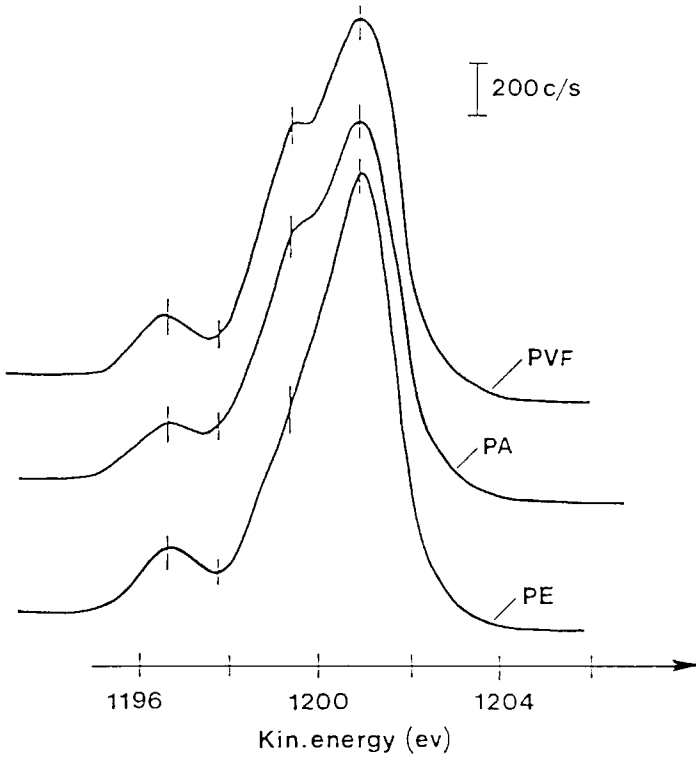
Fig. 4. C(1s) peaks in the ESCA spectra from the lacquer side of the failure surface at the lacquer A/polymer interface on PE, PA, and PVF.
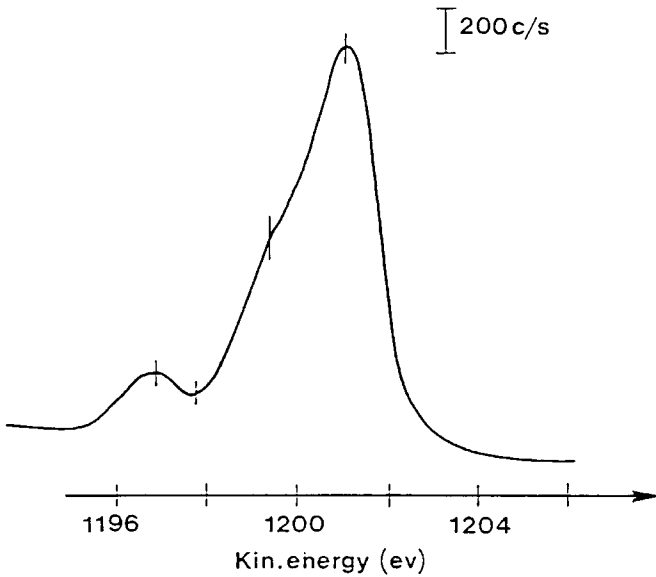

Fig. 5. C(1s) peaks in the ESCA spectra from the lacquer side of the failure surface between lacquer A and PS.

and B on PA, both failed to adhere. It is well known that PA is hygroscopic and hence may develop a water-swollen layer in a humid atmosphere which may act as a WBL. That this indeed appears to be the case is indicated by the results given in Table V, which show excellent adhesion of lacquers A and B to PA that has been dried overnight in a vacuum desiccator.

The failure surface of lacquer A on PVF is also enriched in polar components (Fig. 4, Table IV), which are expected to have good affinity to the PVF surface. However, due to incomplete wetting, adhesion is poor.

The film formed by lacquer A on PS could also be stripped off. The failure surface contained more aliphatic hydrocarbon than the bulk lacquer (Fig. 5, Table IV). Most likely, the failure is not completely adhesive, but occurs in a WBL appearing on the PS side due to swelling of the surface by the lacquer (see Discussion).

Influence of Lag Time Before Curing

In all the experiments described above, the lag-period between application of the lacquer and UV curing was 1 minute. However, it was recognized at an
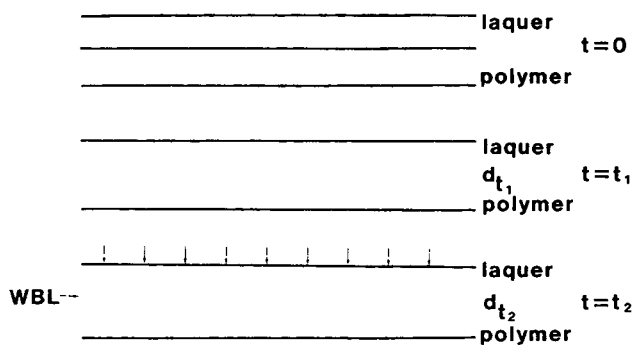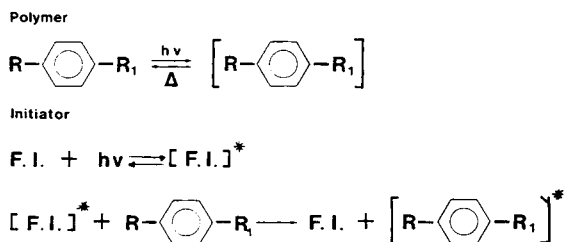

Fig. 6. Schematic illustration of the swelling of polymers by acrylic monomers. In the swollen WBL, extensive quenching occurs, in particular in the presence of aromatic groups. $0 < t_1 < 1$ min, $5 < t_2 < 10$ min.

early stage that this lag period strongly influenced the ultimate adhesion of the film. The adhesion of lacquer A after a lag-period of 5 minutes is shown in Table V. Adhesion is now poor on PS, PET, and PC.

These polymers all contain aromatic groups, which leads us to suggest the possible mechanism for the reduced adhesion shown schematically in Figure 6. When allowed sufficient time, the surface region of the polymer may swell with the lacquer, leading to a surface phase containing carbonyl-substituted aromatic species that adsorb strongly in the 240–400 nm range, that is in the most intensive emission range of the UV curing source. This overlap between the UV emission and the polymer adsorption spectra may lead to a reduced degree of polymerization or incomplete curing in the boundary phase and to the formation of a WBL.

The ESCA C(1s) spectra of the failure surfaces shown in Figure 7 with the relative concentrations given in Table IV sample numbers 19–23 support this mechanism. The relatively large amount of COO on the lacquer side of the failure surface on PE indicates enrichment of EHA after the prolonged lag-time. Similar increases are noted for the PS, PET, and PC surfaces, where
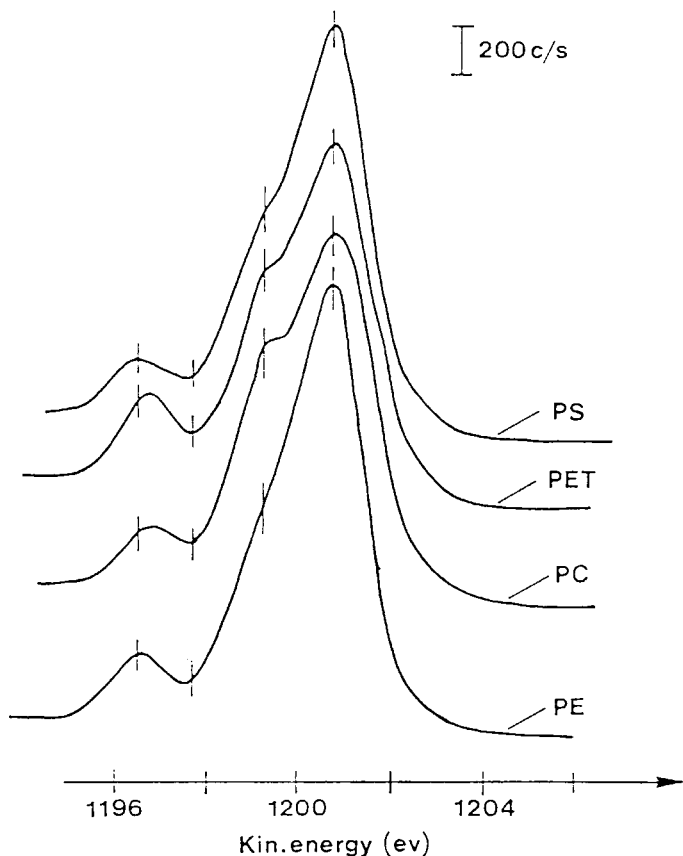

Fig. 7. C(1s) signal in the ESCA spectrum of the lacquer side of the failure surface between lacquer A and PE, PC, PET, or PS. 5 min lag time before curing. Cf. Fig. 4.
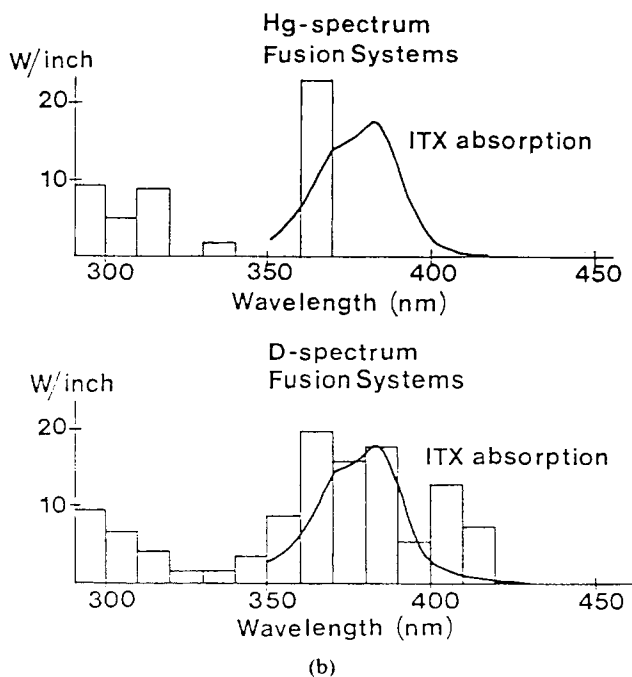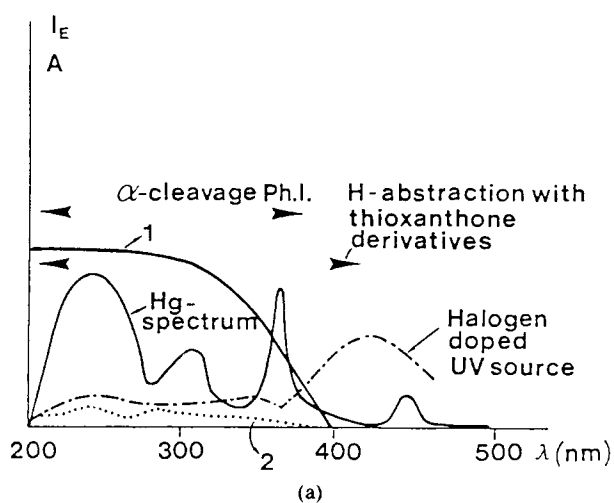
Fig. 8. Possibilities to cure by irradiation outside the adsorption range of aromatic groups in the solid polymer. (a) 1. absorbance spectrum for solid polymers containing aromatic groups. 2. absorbance spectrum for "nonadsorbing" solid polymer. The arrows indicate the adsorption ranges for the two photoinitiators used. (b) Emission spectra for the Hg and the halogen doped lamps compared to the adsorption spectrum of the H-abstraction type photoinitiator (isopropylthioxanthone).

both C—O and COO groups increase. In these cases, the solubility parameters of the polymer and the EHA monomer agree well (see Table II) so that considerable swelling can be expected.

The unreasonably high amount of COO groups on the film failure surface from PET indicates that polymer fragments adhere to the film. On the other hand, very high amounts of C—O groups are found on the PC polymer failure surface, evidently due to lacquer residues.

Further support for the suggested mechanism of formation of a WBL was obtained by exchanging the mercury lamp for a halogen-doped lamp with efficient emission also outside the adsorption range of the aromatic species in the polymer [see Fig. 8(a)]. Furthermore, an initiator, isopropylthioxantone (IXT), with an adsorption spectrum that overlaps more with the lamp emission spectrum was chosen [Fig. 8(b)]. The photoinduced generation of free radicals in this system is based on H-abstraction rather than on α-cleavage, as is the case for 2-propiophenone.

Results from adhesion tests of lacquer films formed by this new system are shown in Table V. Excellent adhesion, even after prolonged contact time before curing, is found for PS, PET, PA (vacuum dried), and PC. Improved, although not fully satisfactory adhesion is obtained for PE and PVF.

Curing in a Nitrogen Atmosphere

Essentially oxygen-free films of lacquer A were prepared by saturating the lacquer with nitrogen before application. The films were then cured in a nitrogen atmosphere. This decreased adhesion to zero (see Table V).
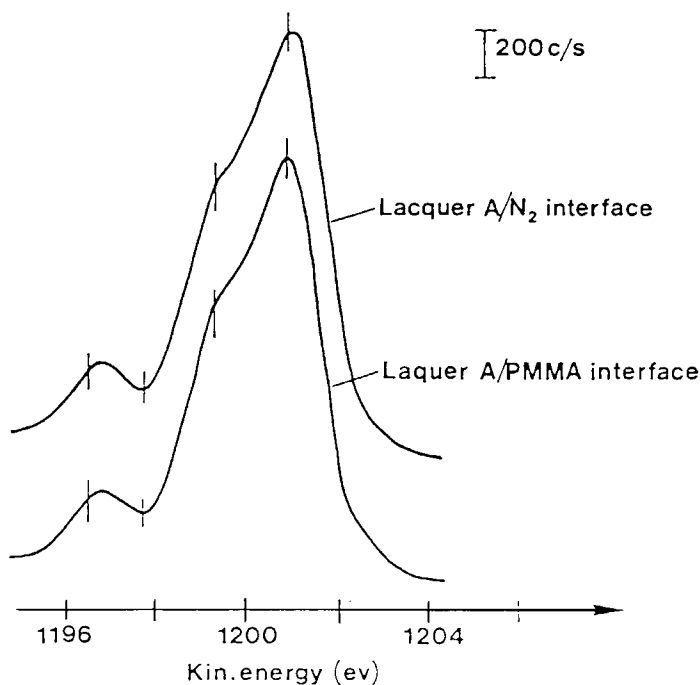

Fig. 9.   C(1s) signals in the ESCA spectra of lacquer A at the lacquer/N_2 and lacquer/PMMA interfaces after UV curing in nitrogen atmosphere.

The C(1s) spectrum of the side of the failure surface of lacquer A on PMMA facing the N_2 atmosphere is shown in Figure 9 and the relative concentrations of different groups in Table IV (number 24). The concentration of CO residues has decreased compared to in air, but some residues with which oxygen is associated remain in the lacquer since there is a slight enrichment of C—O functional groups in the surface compared to in the bulk.

The C(1s) spectrum of the side of the failing lacquer surface facing PMMA is shown in Figure 9 and for other polymers in Table IV (numbers 25–27). The C(1s) spectra of the lacquer surfaces in nitrogen and the failure surfaces of the lacquer facing the polymers all agree, which indicates that no reorientation has taken place in the interface and that the failure is truly adhesive.

The high concentrations of aliphatic carbon on the failure surfaces from PE and PS (Table IV, numbers 25–27) indicate that adhesion failure still occurs in the WBL of these polymers (for PS due to swelling).

The obvious reason for the complete loss of adhesion after curing in a nitrogen atmosphere is that a too-high concentration of free radicals in the system leads to the rapid formation of a cross-linked network before relaxation of stresses has occurred. The ratio photoinitiator/monomer used in the recipes is based on the assumption that O_2 quenching of photoinitiator fragments does occur. Normally, the ratio to be used for curing in nitrogen atmosphere should be much lower.

DISCUSSION

An important conclusion to be drawn from the results is that a primary condition to obtain good UV-lacquer/polymer adhesion is complete spreading of the lacquer. Donor/acceptor (acid/base) interactions[13] seem to be of less importance. Thus, the acrylate lacquers, considered to be electron acceptors (bases) show no difference between their adhesion to PMMA (a basic polymer) and PVC (an acid polymer).

It is somewhat surprising that the lacquer composition at the polymer interface varies so much between different polymers (Figs. 2–5, 7, 9). As the polymers were all thoroughly cleaned by sonication in ethanol before application of the lacquer, these differences cannot be explained by contaminations on the substrate surfaces. Rather, they must be ascribed to migration and reorientation at the surface.

The only component in the lacquer that can be expected to be reasonably surface active is EHA. The results, however, indicate that swelling is an important mechanism. In such a case, solubility parameter matching between the lacquer components and the polymer should be of importance. The solubility parameters for the acrylate monomers and the polymer substrates are given in Tables I and II. Using Hansen's solubility parameter radius[6,7] as a criterion, one finds that the solubility parameters of the more polar lacquer constituents (HEA, EDGA) fall within the solubility spheres for all polymers except for PVF and PE. In particular, one expects PS to expand extensively swelled by the polar monomers, which explains the observed increase in the relative amount of polar components on the polymer failure surface of PS. Similarly, EHA falls well within the solubility sphere of PE, which explains the appearance of this acrylate in the WBL on PE when the lag-time before curing is extended (see Fig. 7). The 5-min lag-time used in some experiments

corresponds to a diffusion length of ≈ 1 μm in true solution. On the other hand, the oligomeric AEB is probably too large to diffuse into the polymers in such a short time.

As indicated in the Results section, some modifications of the photochemical methods can be used to overcome the problems with the weakly bonding "boundary solution phase." Using a photofragmentation type of initiation (PhI) and a 250–400 nm UV source the following three photochemical reactions will be of importance:

$$PhI \xrightarrow{h\nu} PhI^* \longrightarrow A\cdot + B\cdot \tag{1}$$
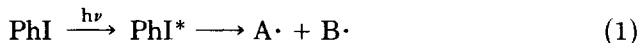
where A· and B· are free radicals formed in the photocleavage reaction. This is the process which normally initiates free radical polymerization.

$$R_1-Z-\hexagon-Z-R_2 \xrightarrow{h\nu} (R_1-Z-\hexagon-Z-R_2)^* \tag{2}$$
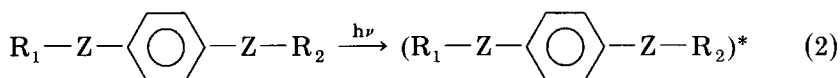
where R_1 and R_2 are backbone residues having no photochemical activity and Z is, for instance, a substituent containing a carbonyl group. In most cases the excited states of the aromatic system (S_1, T_1) of the aromatic system do not contribute to the formation of polymerization-initiating radicals. Rather, the excited state is deactivated by radiationless conversion to heat or in some specific cases by fluorescence or phosphorescence.

$$(PhI)^* + R_1-Z-\hexagon-Z-R_2, \longrightarrow (R_1-Z-\hexagon-Z-R_2)^* \tag{3}$$
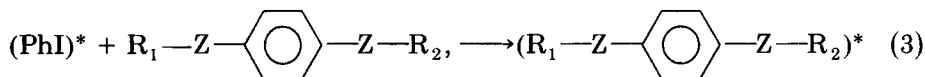
i.e., quenching of the excited photoinitiator by energy transfer to a polymer molecule.

These three reactions occur simultaneously since the aromatic polymer adsorbs strongly in this range of wavelengths. As explained schematically in Figure 8, the photoinitiator has its highest adsorption coefficient in the range where a Hg radiation source emits most of its energy.

Some methods to avoid reactions 2 and 3 are:

1. Use of halogen-doped radiation sources which emit efficient amounts of radiation outside the adsorption range of the substrate polymer.

2. Matching the emission spectra with an initiator that has a high adsorption coefficient outside the range in which the substrate polymer adsorbs light. Useful initiators for excitation around 400 nm are the thioxanthones. In this case photoinitiation is based on H-abstraction, which, as illustrated in Figure 10, may also lead to improved adhesion by direct H-abstraction from the substrate followed by grafting reactions.

As described in the Results section, strongly improved adhesion of lacquer A even after prolonged lag-time before curing could be obtained by employing these two methods (using isopropylthioxanthone as initiator).

Initiation by H-abstr.

H-abstr. from oligomer or substratepolymer

grafting ⟹ improved adhesion

Fig. 10. Upper reaction: conventional initiation mechanism for an H-abstraction photoinitia-tor. Lower reactions: alternative reactions that may contribute to improved adhesion by H-abstraction from the polymeric substrate.

3. It is also possible to decrease problems with incomplete overlapping of photoinitiator adsorption and radiation source emission spectra by using fluorescing compounds with high adsorption coefficients and high quantum yields (e.g., some oxopyrrazoles).

The influence of oxygen on the curing of type B lacquers has been thoroughly investigated by Göthe[12] and others. The presence of oxygen leads to an induction period before polymerization takes place[13] because the oxygen radical ($\cdot O - O \cdot$) reacts very rapidly with photo-generated free radicals.

Some of the more important reactions involving O_2 are:

$$R\cdot + O_2 \longrightarrow ROO\cdot \tag{4}$$

$$R-OO\cdot + R\cdot \longrightarrow R-OO-R \tag{5}$$

$$R-OO-R \longrightarrow RO\cdot + RO\cdot \tag{6}$$

$$S_{T_1} + O_{2_{T_1}} \longrightarrow S_{S_0} + O_{2_{S_1}} \tag{7}$$
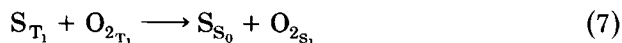
where S is a sensitizing molecule,

$$R-OO\cdot + RH \longrightarrow R-OOH + R_1\cdot \tag{8}$$

$$R-OOH \longrightarrow RO\cdot + OH\cdot \tag{9}$$

$$R-O\cdot + PH \longrightarrow ROH + P\cdot \tag{10}$$

$$HO\cdot + PH \longrightarrow H_2O + P\cdot \tag{11}$$

$$P\cdot + O_2 \longrightarrow P-OO\cdot \tag{12}$$

$$P-OO\cdot + RH \longrightarrow R\cdot + ROOH \tag{13}$$
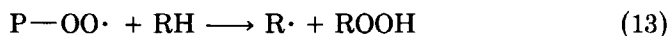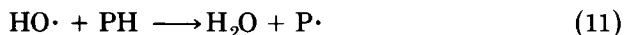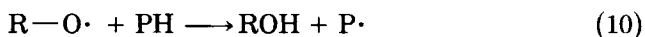
The induction period allows for relaxation of stresses during the curing reactions. As shown by our results, films cured in a N_2 atmosphere do not adhere well because there is no mechanism allowing for such relaxation.

Another important feature is that the polymerization rate, once the reaction has started, is larger in O_2 than in air than in N_2. This is due to the sudden cleavage of a large amount of peroxy groups built up during the induction period in an oxygen-containing atmosphere (cf., reactions 5, 6, 8, 9). These reactions may possibly also increase adhesion between the cured lacquer and the substrate polymer. The alkoxyradicals formed cannot be deactivated by O_2, so that during the curing reactions there are always oligomeric alkoxy radicals present which easily form ether bonds with polymer radicals:

$$R_nO\cdot + P\cdot \rightarrow R_nO-P \tag{14}$$

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