Thermal Degradation of a Poly(Vinyl Formal)-Containing Adhesive Film on a Polyethylene Rubber Surface. A Photoacoustic Fourier Transform Infrared Spectroscopic Investigation

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Synopsis

Photoacoustic Fourier transform infrared (PAS/FT-IR) spectra of an adhesive film containing poly(vinyl formal) (PVF) coated on a modified polyethylene (PE) rubber surface are reported, and their vibrational assignments proposed. The spectrum of PVF/PE/rubber closely resembled that of the adhesive itself, which was mainly dominated by intense and characteristic bands due to PVF. As found for the PVF compound, the formal group in the PVF polymer of the adhesive was deduced to exist mainly in the form of a six-membered intrachain cyclic structure analogous to the m-dioxane ring. The PVF/PE/rubber system was found to be thermally stable after storage at 20°C for more than 10 months and also unaffected by repeated temperature cyclings (−50 to 60°C). Thermal treatment in air at 60°C for 5 months, however, led to an almost complete loss of the adhesive film on the substrate, as evidenced by the disappearance of bands due to PVF. First-order kinetic parameters were experimentally obtained for the loss of PVF on the rubber surface. The final thermal degradation products were identified as structures containing both carbonyl and olefinic groups. The degradation reactions were primarily a process of oxidation and crosslinking, which led to formation of an embrittled material as evidenced from visual inspection of the degraded film. The behavior of PVF in the adhesive/substrate system was very similar to the thermal degradation behavior of the compound PVF itself.

INTRODUCTION

Nondestructive characterization of thin polymer films on bulk substrates is important for examination of the relationship between the functions of the materials and their chemical structures. Electron spectroscopy has been used for surface characterization; however, it may not be suitable for the analysis of polymer films. For example, irradiation of the electron beam may decompose the film, and ultrahigh vacuum conditions may lead to modification of their chemical structures.

Infrared spectroscopy offers a powerful analytical tool for the structural elucidation of organic materials. However, there exist several types of materials that are difficult to examine by conventional infrared techniques because of problems such as strong absorption of radiation by the sample or undesirable methods of sample preparation.

Photoacoustic Fourier transform infrared spectroscopy (PAS/FT-IR) is a recently developed technique,[1] and appears to be well suited for the measure-

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ment of spectra from solid samples, where conventional methods have failed. The key advantage of PAS/FT-IR is that it requires virtually no sample preparation and is relatively independent of the surface morphology of the sample. Solid samples of different morphologies (e.g., powder, sawed or smoothed surface, pellets, lumps, etc.) can be studied by PAS/FT-IR. This is in contrast with the diffuse reflectance infrared Fourier transform (DRIFT) technique, which also offers nondestructive examination of solid samples, but often requires a highly scattering powder sample diluted in a nonabsorbing alkali halide matrix.

Polyvinyl acetals are thermoplastics that possess a unique combination of properties such as flexibility, tensile strength, impact resistance, elasticity, and high bonding strength not generally available in other polymers.[2,3] Poly(vinyl formal) (PVF) in phenolic resin (PR) matrix is used in a number of industrial applications such as coatings and adhesives where high-temperature conditions are frequently encountered.

In this paper, the photoacoustic spectra of PVF-containing adhesive film on a modified polyethylene (PE) rubber surface are examined, and their full vibrational assignments proposed. Following various thermal treatments, the thermal stability of this adhesive/substrate system was assessed. First-order kinetic parameters were obtained for the loss of PVF on the rubber surface following storage in air at 60°C for 5 months. The final degradation products were identified, and the reaction mechanism is discussed.

EXPERIMENTAL

Materials

The compounded polyethylene rubber (PE/rubber) containing a number of fillers and adhesives was available from a commercial source (Imperial Metal Industries, U.K.). The adhesive sheet, also supplied by the same source, contained off-white PVF granules held in a thermosetting phenolic resin matrix. As described by the supply source, PVF was prepared from a reaction between formaldehyde and poly(vinyl alcohol), the latter being derived from the hydrolysis of poly(vinyl acetate). According to specifications, it contained residual acetate (10–13%) and hydroxyl (40–50%) groups.

The Adhesive / Substrate (PVF / PE / Rubber) System

The preparation of the PVF/PE/rubber system was carried out by the Explosives Factory at Maribyrnong, Victoria, Australia. The surface of the PE rubber sheet (1.5 mm thick) was degreased by wiping with organic solvents. The adhesive sheet was placed on to the degreased PE/rubber surface, and the (PVF/PE/rubber) system was pressurized and subsequently cured in a hot air oven.

The Photoacoustic Method

The PAS/FT-IR technique has been developed recently and will be briefly described. The sample under study is placed in a small sealed cell which also contains an inert gas and a sensitive microphone. If the sample absorbs a

suitably modulated infrared radiation at a particular wavelength, the absorbed radiation is converted to heat by nonradiative processes, and the heat is transferred to the surrounding gas by thermal diffusion. The boundary layer of the gas next to the solid surface is conductively heated, and expands and contracts at the modulation frequency, resulting in a pressure wave within the sealed cell. This pressure wave is detected by the microphone, and the signal from the microphone will become the output of the photoacoustic detector.

The signal thus produced is usually a complex function of the incident light energy, the absorption coefficient of the sample at a given wavelength, and the thermal properties of the sample. Rosencwaig and Gersho[4] have developed a detailed theory of the photoacoustic effect as applied to solid samples. The PAS/FT-IR technique has recently been reviewed.[1,5,6]

A major feature that makes PAS/FT-IR a valuable surface technique to study solid samples is that only the energy absorbed near the sample surface is effective in heating the surface rapidly enough to contribute to the photoacoustic signal. Thus an optically thick, totally absorbing sample will still give a meaningful photoacoustic spectrum provided that the sample is not completely absorbing at the effective thermal diffusion depth (or sample penetration depth). This depth is determined by the thermal conductivity and heat capacity of the sample and by the modulation frequency of the radiation. The penetration depth will increase as the modulation wavelength increases (i.e., decreasing wavenumbers[7]).

Infrared Measurements

Infrared (IR) spectra were recorded on a Digilab FTS 15/90 Fourier transform infrared spectrometer. The instrument and its accessories were previously described.[8] A Digilab photoacoustic detector accessory was used. The PAS cell had a KBr window and a cylindrical cavity which was 9-mm deep and 9-mm in diameter. A round piece of the sample sheet was cut so that it would fit nicely into the PAS cell on top of a small amount of $Mg(ClO_4)_2$, which was used as a drying agent to remove water vapour in the cell. A piece of aluminum foil separated the sample from the drying agent. The cell was evacuated and filled with dry nitrogen. The sample chamber of the instrument was constantly flushed with dry nitrogen.

The moving mirror velocity of the Michelson interferometer used was 0.3 cm/s. This led to modulation frequencies in the range from 240 to 2400 Hz for the infrared spectral region 4000–400 cm^{-1}.

Spectra were obtained at 4 cm^{-1} resolution and from at least 100 co-added scans. They were ratioed against the reference spectrum of charcoal powder.

RESULTS

Polyethylene (PE) Rubber

The photoacoustic spectrum of PE/rubber is shown in Figure 1(a). The most intense profile at 1120 cm^{-1} was broad and asymmetrical, and assigned to overlapping absorptions from silica filler and doubly bonded S=O groups[9] in the modified crosslinked PE structure.[10]
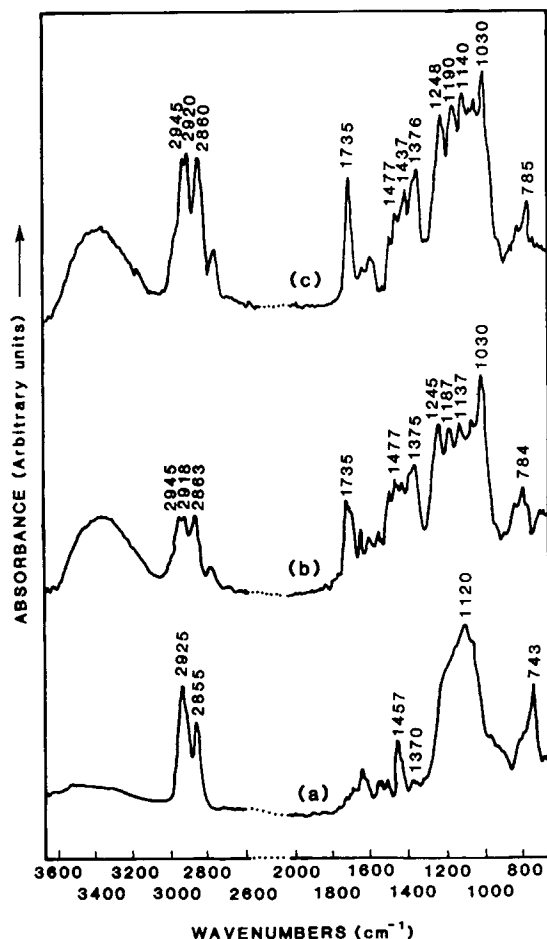
Fig. 1. PAS/FT-IR spectra of (a) PE/rubber, (b) PVF adhesive sheet, and (c) PVF adhesive film on (PE/rubber) substrate.

The strong band at 743 cm^{-1} was attributed to the CH_2 rocking mode of the polyethylene backbone. The medium-intensity band at 1457 cm^{-1} with a shoulder near 1435 cm^{-1} was assigned to the CH_2 bending mode of the ($CHCl-CH_2-CH_2$) group.[9] The broad weak band at 1370 cm^{-1} was due to absorption of the sulfonate group, which agrees with early studies about the conversion of sulfonyl chloride groups through hydrolysis.[11,12] The other much weaker bands in the region 1700–1500 cm^{-1} were probably due to unsaturated structures from various additives and fillers. In the CH stretching region, the two strong sharp bands at 2925 and 2855 cm^{-1} were attributed to CH stretching vibrations of the methylene groups of the polymer backbone.

PVF Adhesive

The PAS/FT-IR spectrum of the adhesive containing PVF in a phenolic resin (PR) is shown in Figure 1(b). The full assignments are summarised in Table I.

In general the spectrum of adhesive showed the predominant absorption bands from PVF with several weak and uncharacteristic mixed vibrations from the thermoset resin. The spectrum of PVF was similar to the IR transmission spectrum of PVF films reported in earlier studies.[13, 14]

In the following the CH_2 group in the $O-CH_2-O$ moiety of PVF will be referred to as substituent CH_2 and the CH_2 group of the vinyl chain as chain CH_2, which agrees with Padhye and Iyer's proposal.[13]

In the 3100–2700 cm^{-1} region, the strong doublet at 2945 and 2918 cm^{-1} was assigned to the asymmetric and symmetric modes of the chain CH_2 of PVF. The substituent CH_2 had two stretching bands at 2863 and 2775 cm^{-1}. A shoulder at 2980 cm^{-1} was assigned to the CH stretching mode of the tertiary CH group of the PVF chain.

A strong sharp band at 1735 cm^{-1} with satellites near 1720 and 1700 cm^{-1} was attributed to the residual acetate group in PVF.

The assignments of bands in the region 1700–1300 cm^{-1} were more complex. Substituted ring stretching modes from PR, bending, wagging, and scissoring modes of CH_2 groups in PVF and PR were all expected in the region (see Table I). In agreement with previous studies,[13] the bands at 1477 and 1436 cm^{-1} were assigned to the substantial contributions of the scissoring modes of the substituent and chain CH_2 groups of PVF, respectively. The broad, overlapping features with a maximum at 1375 cm^{-1} probably arose from two mixed vibrations (see Table I), although Padhye and Iyer[13] preferred to assign a band at 1366 cm^{-1} to the bending mode of tertiary CH group in PVF.

A group of five intense absorptions at 1245, 1187, 1137, 1074, and 1030 cm^{-1} appeared very similar to the transmission spectrum previously reported.[13] Based on the analogy with the ring structure vibrations of m-dioxane, Padhye and Iyer[13] have assigned the bands at 1176, 1130, 1068, and 1022 cm^{-1} to substituted ring modes of PVF and the 1241 cm^{-1} band to a mixed mode of chain CH twisting and substituent CH_2 wagging of PVF. The mixed mode at 1245 cm^{-1} observed for the adhesive in the present study could also have contributions from the $C-O$ stretching vibration of the acetate in PVF.

In the region 900–600 cm^{-1}, the more intense band at 785 cm^{-1} was attributed to mixed wagging vibrations of the substituent CH_2 of PVF[13] and of the aromatic CH of PR.[15]

Adhesive / Substrate (PVF / PE / Rubber) System

The PAS/FT-IR spectrum of PVF/PE/rubber is shown in Figure 1(c). In general, this spectrum closely resembled that of the adhesive itself. The observation of a weak shoulder near 1455 cm^{-1}, assigned to $\delta(CH_2)$ in the PE structure (see Table I), revealed the presence of the rubber underneath the adhesive film. This band, together with other bands due to PE, grew remarkably more intense following extended storage of the PVF/PE/rubber system at 60°C, thus contributing evidence for the loss of the adhesive film on the rubber surface (see later).

In order to assess its thermal stability, the adhesive/substrate was subject to various thermal treatments. Temperature cycling from −50°C (4 h) to 60°C (4 h) did not seem to have any effect on the system, nor did storage in

TABLE I
Infrared Spectra (cm^{-1}) of PVF Adhesive Film on PE/Rubber before and after the Thermal Treatment

		Adhesive/substrate			Vibrational assignment	
PVF adhesive[a]	PVF[b] compound	Not treated	Thermally treated at 60°C for 5 months	(PE/ rubber) substrate	Adhesive/substrate	(PE/rubber)
3360 (st, vbr)	3470 (m)	3350 (st, vbr)	3400 (st, vbr)	3400 (w, vbr)	$\nu(OH)$ of H-bonded OH	
2980 (sh)	2975 (w)	2985 (sh)			$\nu(CH)$ chain in PVF	
2945 (doublet,	2940 (st)	2945 (doublet,			$\nu_{as}(CH_2)$ chain in PVF	$\nu_{as}(CH_2)$
2918 vst s)	2915 (st)	2920 vst s)	2925 (vst, s)	2925 (vst, s)	$\nu_s(CH_2)$ chain in PVF	$\nu_s(CH_2)$
2863 (st, s)	2852 (st)	2860 (st, s)	2853 (vst, s)	2855 (vst, s)	$\nu_{as}(CH_2)$ in O_2CH_2	
2775 (w, s)	2775 (m)	2778 (w)	2780 (ws)		$\nu_s(CH_2)$ in O_2CH_2	
1735 (st, s)		1735 (st, s)	1735 (w, s)		$\nu(C=O)$ of residual acetate group in PVF	
1720 (sh)		1718 (sh)	1715 (vs)			
1700 (sh)		1705 (sh)	1700 (vw)			
1650 (w)		1650 (w)	1650 (w)	1650 (w)	$\nu(C=O)$ from thermal degradation product	
			1635 (m, s)			
1615 (m)		1615 (w, s)		1615 (w)		
1593 (w)		1595 (w, s)			ν(substituted ring) of phenolic resin (PR)	ν(substituted ring) of additives
1560 (w, s)		1560 (vw)	1560 (w)	1560 (w, s)		
1540 (w, s)		1540 (vw)	1540 (w)	1540 (w, s)		
1510 (st, s)		1510 (m)	1510 (m)	1507 (w)		
1477 (st, s)	1476 (w)	1477 (m)			$\delta(CH_2)$ of PR + $\delta(CH_2)$ chain + $\delta(CH_2)$ in O_2CH_2 of PVF	$\delta(CH_2)$ in $(CHClCH_2CH)$
1460 (sh)	1456 (vw)	1456 (vw)	1458 (st, s)	1457 (m, s)		
1436 (st, s)	1433 (m)	1437 (st, s)	1438 (sh)	1435 (sh)		

					Assignment[c]
1395 (sh)	1404 (st)	1405 (sh)			$w(CH_2)$ chain in PF
1375 (vst, s)	1392 (sh)	1395 (sh)			
	1366 (sh)	1376 (vst, br)	1370 (w, br)	1370 (w, br)	$\nu(SO_3)$
				1320 (vw)	$\delta(CH)$ in PVF + $\delta(OH)$ in-plane in PR
		1320 (vw)			$\nu(C-O)$ of residual acetate group in PVF
1245 (vst, s)	1241 (m)	1248 (vst, s)			$\gamma(CH) + \omega(CH_2)$ of O_2CH_2 in PVF
				1225 (sh)	$\nu(C-O)$ in PR
1187 (vst, s)	1176 (vst)	1190 (vst, s)	1190 (sh)		
1137 (vst, s)	1130 (st)	1140 (vst, s)			
1097 (sh)	1096 (vw)	1098 (w)	1115 (vst, vbr)	1120 (vst, vbr)	$\nu(SiO)$
					$\nu(SO)$
1074 (vst, s)	1068 (st)	1073 (vst, s)			ν(substituted ring) in PVF analogous to m-dioxane ring mode
1030 (vst, s)	1022 (vst)	1030 (vst, s)			
940 (vw, sh)	928 (vw)	940 (sh)			
885 (vs)	858 (w)				
833 (m)	838 (w)	830 (w)		820 (sh)	$r(CH_2)$ of O_2CH_2 in PVF_1
785 (st, s)	800 (w)	785 (m)	790 (sh)	790 (sh)	$r(CH_2)$ of O_2CH_2 in PVF_1 + $\omega(CH)$ in PR
			750 (st, s)	743 (st, s)	$r(CH_2)$

[a] s = strong, vst = very strong, m = medium, w = weak, vw = very weak, s = sharp, br = broad, sh = shoulder.

[b] From work cited in Ref. 13.

[c] ν = stretching, δ = bending, r = rocking, γ = twisting, ω = wagging, s = symmetric, as = asymmetric.

[d] A very broad absorption profile covering the region 1300–900 cm^{-1} with a maximum near 1120 cm^{-1}.
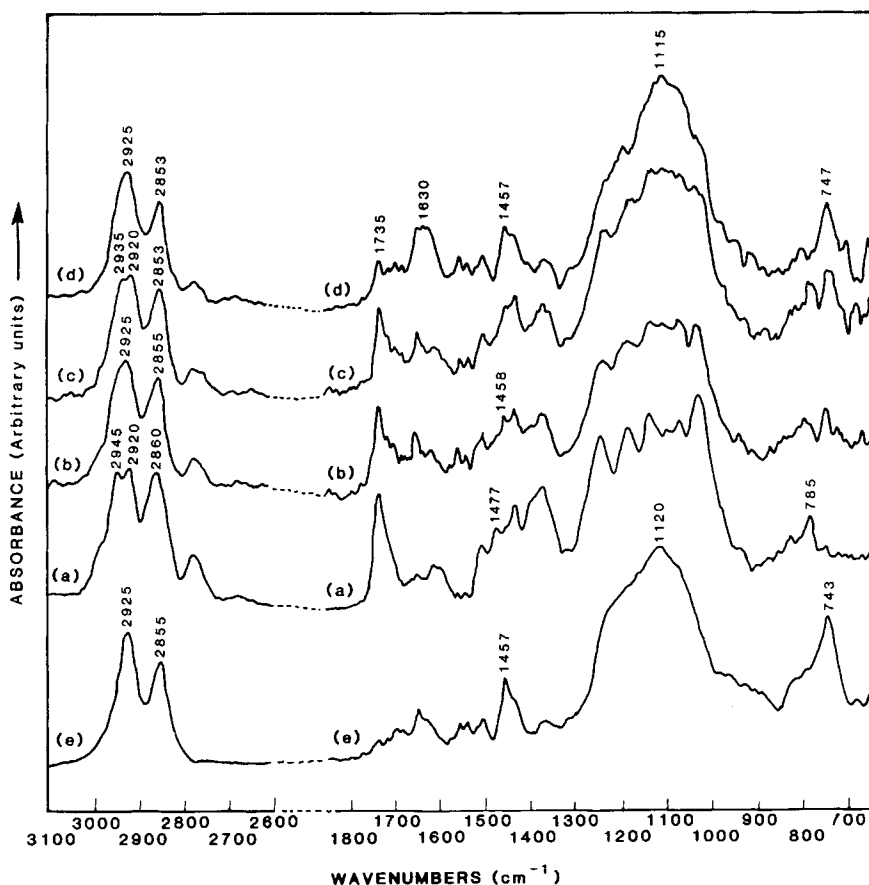
Fig. 2. PAS/FT-IR spectra of PVF/PE/rubber: (a) untreated and after thermal treatment in air at 60°C for (b) 2, (c) 3, and (d) 5 months, compared with (e) spectrum of the (PE/rubber) substrate.

air at 20°C for over 10 months, because the photoacoustic spectrum showed no detectable changes from that observed for the nontreated system.

Thermal aging experiments were performed whereby the samples were heated in air at 60°C in an oven for specified intervals, after which their spectra were examined. Spectra of PVF/PE/rubber samples after thermal treatment at 60°C for 2, 3, and 5 months are shown in Figure 2. The spectrum of the untreated system and that of the PE/rubber itself are also shown for comparison.

Marked spectral changes were observed following the successive thermal treatments. The initial spectrum of the adhesive/substrate [Fig. 2(a)], which closely resembled that of the adhesive, showed marked decrease and disappearance of the bands due to the adhesive to become a spectrum [Fig. 2(d)] similar to that of the substrate itself [Fig. 2(e)].

The group of five most intense bands in the region 1250–1032 cm^{-1} characteristic of PVF almost completely disappeared, and a very broad, structureless profile with a maximum near 1115 cm^{-1} became apparent [Fig.

TABLE II
Decrease of Peak Intensities of the Band at 1735 cm^{-1}
as a Function of Thermal Treatment Periods

Peak intensity (arbitrary units)	Treatment periods (days)
50	0
38	60
32	90
21	150

2(d)]. In addition, the doublet CH stretching bands at 2945 and 2920 cm^{-1} disappeared, and two strong bands formed at 2925 and 2853 cm^{-1} [Fig. 2(d)]. Furthermore, the band at 1477 cm^{-1}, characteristic of the adhesive, was not observed. Parallel to this loss was a growth in intensity of the bands at 1457 and 1437 cm^{-1} characteristic of the substrate, which finally became very similar to those observed in the spectrum of PE/rubber itself [compare Figs. 2(d) and 2(e)]. Another observation was the disappearance of the band at 785 cm^{-1} due to PVF and the formation of a new band near 747 cm^{-1} attributed to the CH$_2$ rocking mode of the polyethylene backbone of PE. Finally, the

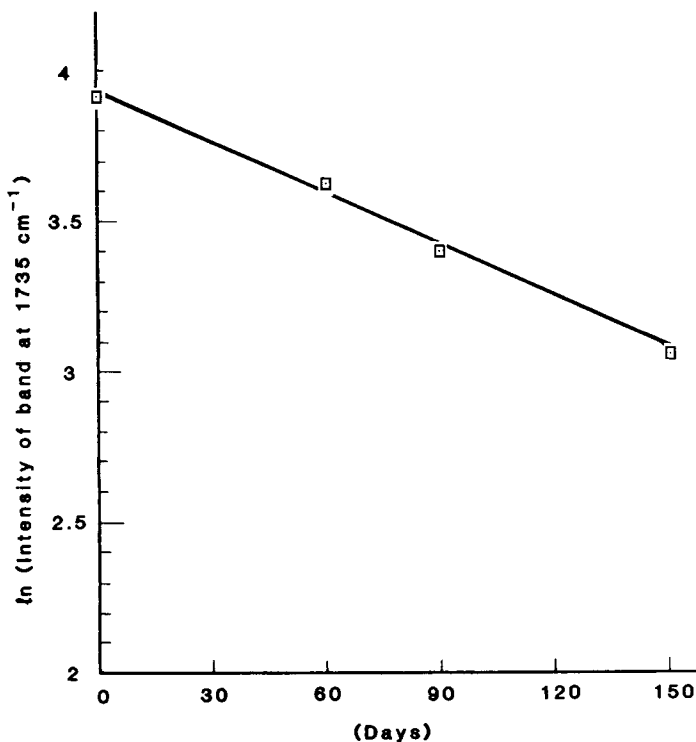

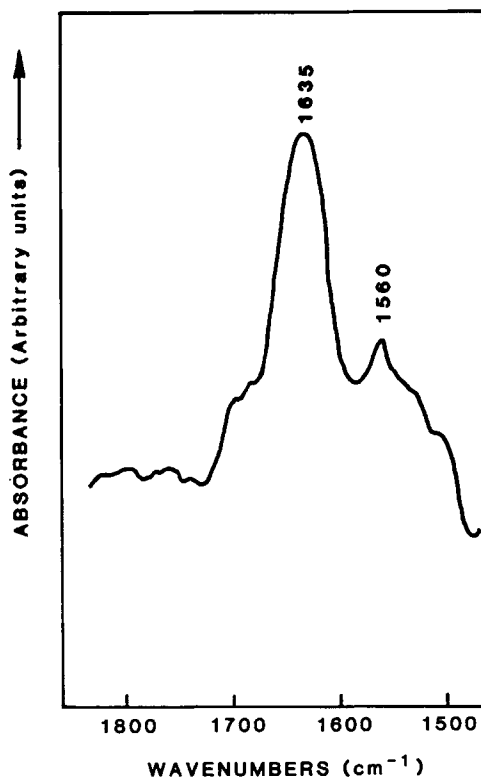Fig. 3.   Plot of the logarithm of the intensities of the band at 1735 cm^{-1} against the treatment periods.

Fig. 4. Spectrum of the thermal degradation product (after spectral subtraction) showing new carbonyl and olefinic bands.

intensity of the band at 1735 cm^{-1} due to acetate in PVF also decreased considerably, indicating that these acetate groups were also not stable under the experimental conditions. All the consistent spectral charges in the foregoing indicated an almost complete loss of the adhesive film from the rubber surface.

The decrease of the intensity of the peak at 1735 cm^{-1} of PVF was monitored during the thermal aging experiment at 60°C. The band at 1735 cm^{-1} was chosen because it was relatively free from interference by other intense bands. The data are summarized in Table II.

Figure 3 shows the linear plot of the logarithm of the peak intensity against the periods of the aging experiment at 60°C. The results indicate a first-order kinetic law for the loss of the adhesive film on the substrate. The first-order rate constant was determined to be 5.47×10^{-3} day^{-1} with a half-life of 126.7 days.

Figure 4 shows the spectrum obtained after spectral subtraction to remove the specimen of residual adhesive and the rubber. A strong band at 1636 cm^{-1} and a weaker feature at 1560 cm^{-1} were observed which were attributed to newly formed carbonyl (C=O) and olefinic (C=C) groups, respectively, in the final product. These attributions were consistent with the earlier infrared results by Beachell et al.[16] and Chanda et al.[17] (see Discussion later).

DISCUSSION

As shown in Table I, the spectrum of PVF on PE/rubber was similar to that of a PVF film alone observed by Padhye and Iyer.[13] This suggested that the PVF coating on PE/rubber had the same molecular structural arrangement as the thin film itself. These workers have proposed that the formal groups in PVF exist mainly in the form of a six-membered cyclic structure (I), based on the analogy with m-dioxane ring vibrations, rather than a 12-membered ring structure containing polyformaldehyde side chain (II).
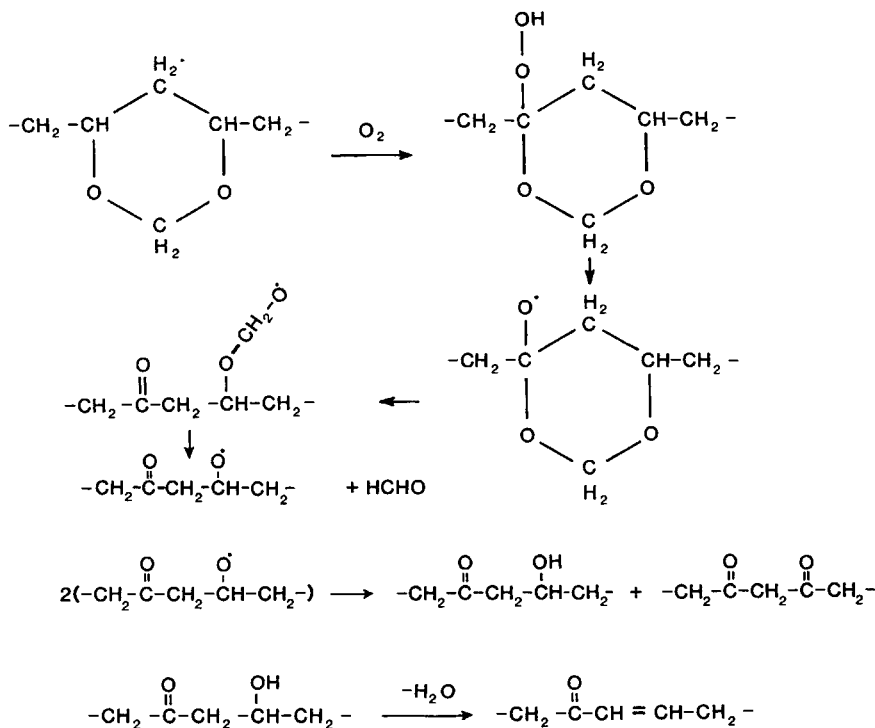

(I)

(II)
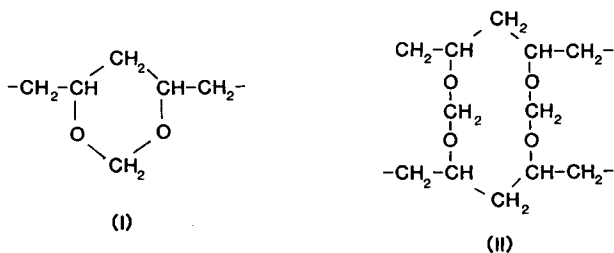
Because of the limited choices on the moving mirror velocities of the Michelson interferometer of the Digilab instrument, no attempt was made to study sample depth profiling by changing the mirror velocity. At a given wavenumber, to change the sampling depth from 10 to 1 μm the mirror velocity may have to be increased[6] by a factor of 100. For typical organic polymers, an average thermal diffusion depth of about 8 μm at 1000 cm^{-1} would be expected.[4] The observation of weak spectral features near 1455 and 1370 cm^{-1} arising from the substrate suggested that the polymer adhesive film probably had a thickness of this order of magnitude.

The observation of the band at 1370 cm^{-1} from the substrate after the loss of the PVF film confirmed that the substrate was thermally stable under the present experimental conditions. This is consistent with the report[12] that thermal degradation of PE/rubber occurred only at temperatures higher than 180°C.

In general, phenolic thermoset resins were found[15,18] to be thermally stable up to 300°C. The storage temperature 60°C was far below from the crosslinking temperature 250°C reported for PR.[15] Therefore, the thermoset resins would be expected to be stable in the present study. However, the spectrum of PR was either rather weak or was not sufficiently characteristic to be distinguishable[15,18] from the complex absorptions of the crosslinked polyethylene structures and of various aromatic additives in the PE substrate (see Table I).

The oxidative degradation of the compound PVF at temperatures of 150°C and above has been found to occur primarily by oxidation and crosslinking.[16] Beachell et al.[16] reported infrared spectra which showed the loss of bands associated with the CH$_2$ and formal groups accompanied by the development of bands from carbonyl (1761 cm^{-1}) and olefinic (1613 cm^{-1}) groups. They postulated a free radical mechanism for the rupture of the six-membered formal ring. This mechanism involved an initial attack of molecular oxygen at the tertiary carbon atom in the ring to lead to subsequent formation of a hydroperoxide and peroxide. Further rearrangements lead to liberation of

formaldehyde and the formation of carbonyl and olefinic groups in the final products. The mechanistic scheme[16] can be summarized as follows:

$$2(-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{\overset{\cdot}{O}}{\overset{|}{CH}}-CH_2-) \longrightarrow -CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2- + -CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-$$

$$-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2- \xrightarrow{-H_2O} -CH_2-\overset{O}{\overset{\|}{C}}-CH=CH-CH_2-$$

This mechanism was later confirmed by Chanda et al.[17] in their kinetic and infrared study of the thermal degradation of poly(vinyl formal)s.

The present results were also consistent with this mechanistic scheme. It is noted, however, that the positions of the carbonyl and olefinic bands, at 1635 and 1560 cm^{-1}, respectively, attributed to the final conjugated product were different from those reported at 1761 and 1613 cm^{-1} by Beachell et al.[16] The 1761 cm^{-1} band seemed to be at too high wavenumbers for a conjugated carbonyl group. It is well known[19] that carbonyl and olefinic bands in conjugated structures would appear at wavenumbers lower, by 40–50 cm^{-1}, than their normally expected positions. Thus the present results were consistent with the conjugated structure proposed. In the complex system under investigation, surface film/substrate interaction may occur, probably through the carbonyl group, which would further lower the wavenumbers of the observed product bands.

The presence of oxygen was necessary to facilitate the initial degradation of PVF. The manifestation of crosslinking in the process was evidenced from visual inspection of an aged PVF/PE/rubber sample which now contained an embrittled material on the rubber surface believed[16] to result from the rigidity of the degraded structures. The degradation of the surface film itself was clearly confirmed by thermomechanical results.[20]

The first-order rate law observed in the present study was in good agreement with the reaction order very close to unity reported by Chanda et al.[17]

Their thermogravimetric study on PVF containing different amounts of formal, hydroxyl, and residual acetate showed that the first-order reaction occurred, and was independent of the composition of the polymer. The activation energy in air was found[17] to increase from 21 to 27 kcal/mol with increasing acetate contents from 6 to 22%. Their results were consistent with an activation energy value of 21 kcal/mol derived[15] from weight loss measurements for a commercial PVF possessing 12% acetate content. The PVF used in the present study had a comparable residual acetate content; therefore, an activation energy close to 21 kcal/mol can be reasonably assumed.

CONCLUSION

The complex PVF/PE/rubber system was studied by PAS/FT-IR. The technique has been shown to be a valuable nondestructive tool to examine surface polymer films. Spectroscopic evidence indicated that thermal treatment in air at 60°C over 5 months led to a loss of the adhesive film on the rubber surface. The degradation occurred primarily via both oxidation and crosslinking processes, and followed a first-order rate law with a half-life of 126.7 days.

The thermal degradation behavior of PVF in this adhesive/substrate system was found to be very similar to that reported earlier for the compound PVF itself.

The whole reactions were consistent with a previously proposed mechanistic scheme leading to a final conjugated product containing carbonyl and olefinic groups.

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