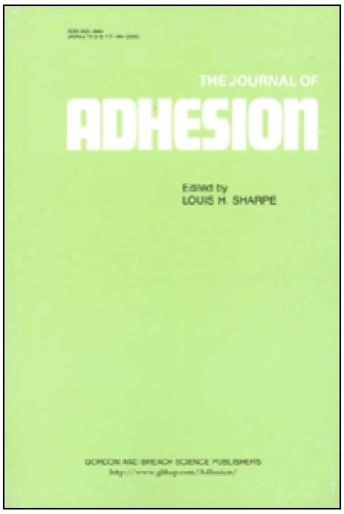

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The Characterisation of Newly Developed and Promising Hydrolyzed Ethylene Vinyl Acetate Copolymers

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The Characterisation of Newly Developed and Promising Hydrolyzed Ethylene Vinyl Acetate Copolymers

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The modification of ethylene vinyl acetate copolymers by hydrolysis yields a broad range of new ter-and copolymers with entirely improved chemical and physical properties, especially important for adhesion applications. An infra-red spectroscopic method was developed in order to achieve a fast and accurate identification of their basic parameter, the mol % vinyl-alcohol, which allows characterisation of the new polymers.

INTRODUCTION

The starting products for the preparation of hydrolyzed ethylene vinyl acetate copolymers were the random ethylene vinyl acetate (EVA) copolymers. These copolymers, often used as a component in hot melts for upgrading the final properties such as flexibility, were a synthesis of ethylene and vinyl acetate (Figure 1) by means of the bulk copolymerisation process.

A basic practical parameter of EVA copolymers is the percentage vinyl acetate (VA) incorporation. An accurate knowledge of this VA content, expressed in percentage by weight (% wt.) or mol percentage (mol %) is essential to distinguish different EVA copolymer types, all having dissimilar physical and chemical properties. To determine the percentage incorporation of VA several methods are available: chemical decomposition[1]; N.M.R.[1];

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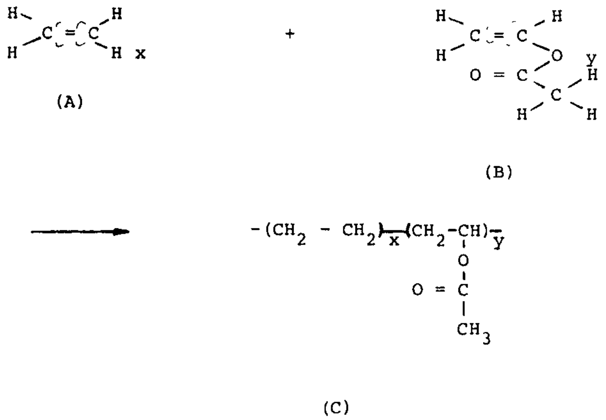

FIGURE 1 The chemical structure of ethylene (A) and vinyl acetate (B). These are the raw materials for EVA copolymer (C) synthesis.

pyrolysis[2] and infrared (I.R.) spectroscopy[3]. Of all methods, I.R. spectroscopy is by far the most convenient industrially applicable determination, according to Van der Linden[3]. I.R. spectroscopy gives fast, accurate and reproducible results, when a calibration curve is developed. Furthermore, apart from the quantitative information, qualitative knowledge is gained without decomposing the small sample required.

Based on this I.R. method developed for EVA copolymers with a mol % from 0 up to 20, by Van der Linden[4] and Vansant[5], a similar procedure was followed here to determine the percentage incorporation of vinyl alcohol (VOH) in partially and totally hydrolyzed EVA copolymers, which considerably increase the range of important polymers for coating applications.

Before any quantitative I.R. analysis is possible, a calibration curve has to be constructed. Therefore, several samples of hydrolyzed EVA copolymers (HEVA) having different VOH incorporation were prepared. The partially hydrolyzed EVA copolymers had three different structural units: ethylene (E), vinyl acetate (VA) and vinyl alcohol (VOH) (these units were not as such, chemically, present in the macromolecules, but these names were used for easy understanding of calculation procedure) and were considered as terpolymers. Accordingly, the total hydrolyzed products were copolymers (Figure 2) when more than 90 % of the ester groups were converted into hydroxy groups. Furthermore the residual VA content was determined by pyrolysis as will be described further in this paper. Finally, an I.R. spectrum was recorded of each sample prepared, and absorption values were combined with pyrolysis results, giving a calibration line for the I.R. determination of VOH percentages.

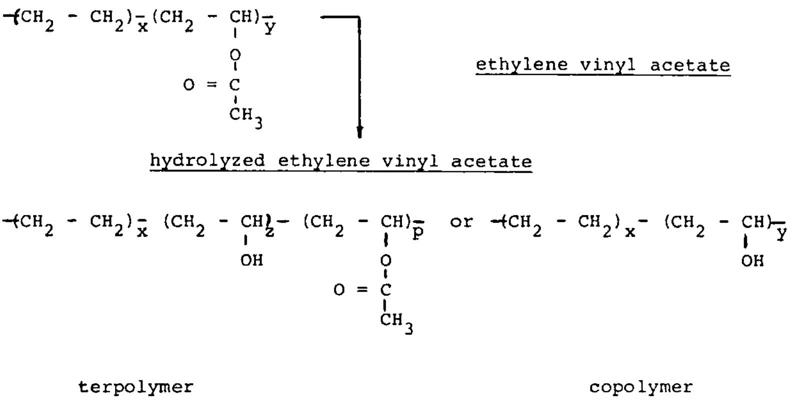

FIGURE 2 The transformation of an EVA copolymer into an HEVA by hydrolysis. The structural units are randomly distributed over the macromolecule. The notations *x*, *y*, *z*, *p* refer to integers not necessarily equal. This figure does not represent the actual structure of EVA or HEVA polymers and is only meant to visualise the chemical transformation.

EXPERIMENTS

a. Hydrolysis

To achieve a broad range of different VOH mol % in hydrolyzed EVA copolymers, the starting products were chosen to contain 18.5, 9.8 and 2.8 mol % VA. These three EVA copolymer types will be respectively referred to as I, II and III in the text. The VA incorporation was determined by pyrolysis before the hydrolysis reaction took place.

According to the method proposed by Hoyt *et al.*[6], very reproducible partial and total hydrolyses were carried out. Approximately 10 g of each EVA copolymer type was hydrolyzed to nearly 20, 40, 60, 80 and 100% of its VA content. The reaction time was 72 hours for each partially hydrolyzed product. For total hydrolysis, times of 0.5, 2, 10, 48, 72 hours were considered. In this way the reaction time to terminate hydrolysis under the conditions used was found to be 0.5 hours. A stoichiometric amount of potassium hydroxide (KOH) was applied according to the desired degree of hydrolysis. An excess of three to four times the stoichiometric amount was used for the 100% hydrolysis. The EVA was added to a boiling mixture (84°C) of 50 ml toluene, 50 ml benzene, 50 ml 2-propanol and dissolved base (all reagent grade) in a single necked 500 ml glass container equipped with a reflux condensor. The reacting mixture was vigorously agitated with a magnetic stirrer to avoid polymer sticking to the wall whilst being heated on a hot-plate. All the HEVA polymers are compared to their VA and VOH content after identical reaction conditions (72 hrs).

After reaching the desired hydrolysis percentage, the reaction mixture temperature was lowered to 64°C, where phase separation occurred after adding 100 ml 2-propanol. The organic solvents were decanted from the powdery, crumb-like HEVA polymer. These products were washed with water to remove remaining salt and base, potassium acetate (KOAc) and KOH respectively. Afterwards the polymers were dried for 24 hours in a constant temperature oven at 60°C. The entire procedure was straightforward, although care had to be taken that no water was introduced before removing the solvents entirely.

b. Pyrolysis

The procedure used in the examination of the HEVA polymers, was identical to the method of Van der Linden and De Winter[2], developed for EVA copolymers. At 395°C, under a nitrogen atmosphere, an EVA copolymer decomposes and produces a gaseous mixture with as the most important component, acetic acid (CH_3COOH). This acid was neutralized in a 50 ml 0.1 N sodium hydroxide (NaOH) solution. The remaining amount of base was titrated with a 0.1 N hydrochloric acid (HCl) solution. In this way it was possible to calculate the VA content, considering that one equivalent HCl equals one equivalent CH_3COOH equals one equivalent VA.

TABLE I

Experimental and calculated results for the EVA copolymers and their hydrolyzed forms. Indicated are data obtained by (1) pyrolysis; (2) I.R. 3460 cm^{-1} (reference material); (3) I.R. 610 cm^{-1}. (4) calculation based on pyrolysis values and actual base concentration in reaction mixture.

Approximate % hydrolysis		0	20	40	60	80	100
I mol % VA	(1)	18.5	14.2	10.7	7.4	4.3	0.3
	(2)	19.0	—	—	—	—	—
	(3)	—	—	10.1	6.8	4.6	—
	(4)	—	13.9	10.0	6.2	3.3	—
mol % VOH (cfr. eq 1–5)		0	4.2	7.8	11.0	14.2	18.2
II mol % VA	(1)	9.8	7.6	5.3	4.9	3.5	0.4
	(2)	10.5	—	—	—	—	—
	(3)	9.8	6.2	5.5	4.1	2.5	—
	(4)	—	7.3	5.2	3.3	1.5	—
mol % VOH (cfr. eq 1–5)		0	2.3	4.5	5.0	6.3	9.7
III mol % VA	(1)	2.8	2.6	2.8	2.6	2.3	0.2
	(2)	2.5	—	—	—	—	—
	(3)	2.4	2.3	1.9	1.7	1.5	—
	(4)	—	2.2	2.1	1.3	0.9	—
mol % VOH (cfr. eq 1–5)		0	0.3	0.1	0.3	0.6	2.7

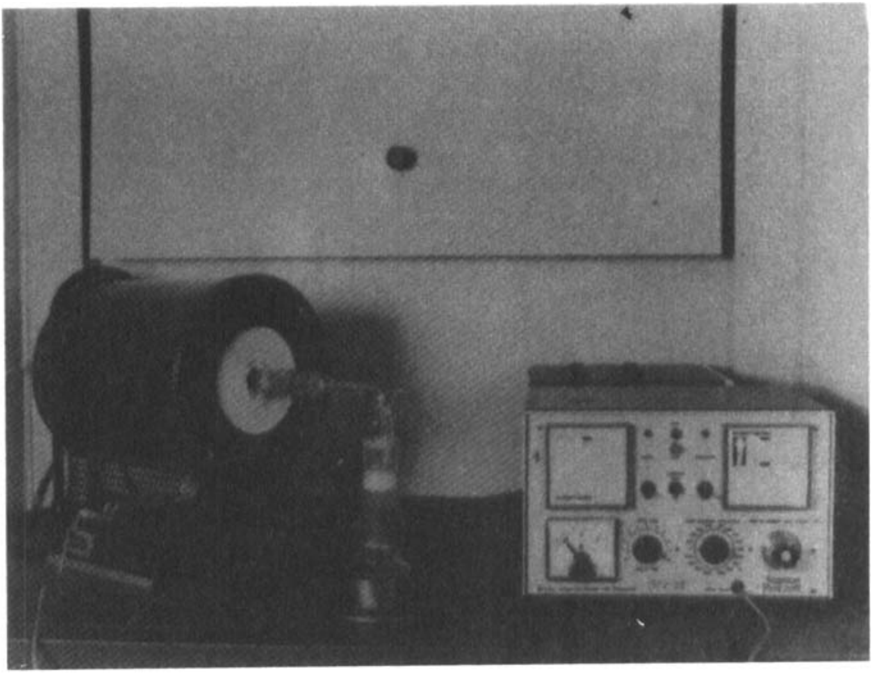

FIGURE 3 A Stanton Redcroft Eurotherm Thyristor pyrolysis device.

Based on gas chromatographic experiments[7] and our own experiments the same conditions were applicable to HEVA (Table I).

A 1 g sample of HEVA, which remained for 20 min. in the pyrolysis oven at 395°C was sufficient for this experiment. The apparatus was a Stanton Redcroft Thyristor Eurotherm (Figure 3). The nitrogen could be made water and oxygen free by sulfuric acid and pyrogallol solution respectively. The inert gas had a flow rate through the system of 250 ml/min. The experimental set-up and flow of the gasses is represented in Figure 4.

The obtained values of residual VA allowed the calculation of the VOH mol % assuming that the E mol % in EVA and the corresponding HEVA were equal, by means of five equations:

$$\text{VA \% wt.} + \text{E \% wt.} + \text{VOH \% wt.} = 100\ \text{\% wt.} \tag{1}$$

$$\text{VA mol \%} = \text{VA \% wt. } 100/86.09/X \tag{2}$$

$$\text{E mol \%} = \text{E \% wt. } 100/28.05/X \tag{3}$$

$$\text{VOH mol \%} = \text{VOH \% wt. } 100/44.05/X \tag{4}$$

$$X = \text{VA \% wt.}/86.09 + \text{E\% wt.}/28.05 + \text{VOH \% wt.}/44.05 \tag{5}$$

86.09, 44.05 and 28.05 are the molecular weights of vinyl acetate, vinyl alcohol and ethylene respectively.

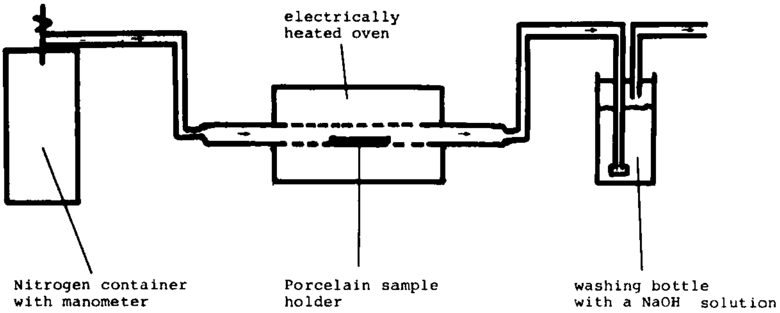

FIGURE 4 The set-up for the pyrolysis device with the gas flow indicated. The five wash bottles needed to make the nitrogen water- and oxygen-free are omitted.

c. Infra-red spectroscopy

The next step was to record an I.R. spectrum of each sample prepared and to find suitable absorption bands, usable for quantitative purposes. Therefore the HEVA powder was transformed into a transparent film by means of a hydraulic Pasadena Press with heated pressure plates. The powder was put between two Mylar films covered with smooth surfaced steel plates. This was held at 150°C and a pressure of 27.6×10^7 Pa was exerted during 1.5 to 2 min. This time was considered suitable in order to avoid oxidation effects and to produce a homogeneous film. No thinner films could be prepared with the Pasadena Press than those used. After cooling, a film sample of about 0.015×0.04 m was put into the I.R. beam. By rotating and rerunning the IR spectrum the sample homogeneity was experimentally checked. A spectrum from 4000–400 cm^{-1} was recorded with a Beckman 4240 I.R. spectrometer (Table II).

TABLE II

Operating conditions for the Beckman 4240 I.R. spectrometer.

—ordinate scale	100%
—chart format	I.R. 9, 12
—sensitivity	0
—chart expansion	1 x
—period	2 sec.
—balance	0
—scan speed	300 cm^{-1}/min
—gain set	without sample and at a wave number of 3000 cm^{-1} —slit; 0.3 mm —pen: 100% DB —pen: 100% SB
—automatical slit program	
—before recording the spectra, the sample films were placed in the I.R. beam for 2 minutes	
—scan: 4000–400 cm^{-1}	

RESULTS AND DISCUSSION

The hydrolysis process itself, which was carried out in an essentially apolar medium to speed up the conversion of acetoxy into hydroxy groups and to dissolve the EVA, was straightforward. The reagent was the OH^- ion of KOH. The EVA pellets had to be entirely dissolved otherwise hydrolysis would only have taken place at their surface resulting in a mixture of polymers, EVA and both kinds of HEVA, ter and copolymers. The separation of newly formed polymer and solvents was the most difficult aspect especially with partially hydrolyzed EVA copolymers. These had a tendency to remain in solution producing a glue-like solution. Therefore 1l 2-propanol was added after cooling to room temperature and pouring the solution into a big enough vessel. Thus 2-propanol was used as a solvent to dissolve the reacting base and as a means of achieving phase separation.

The obtained samples had different hydrolysis percentages which could be calculated from the VA mol % pyrolysis results as were mentioned in Table I as well as VA percentage values found with the I.R. spectroscopy values explained later in the text. The most important feature of this table was the comparison between the pyrolysis and the I.R. spectroscopy VA percentages. Because of their small differences, the conditions applied to pyrolysis of EVA were valid for HEVA. Furthermore, it was shown that under the experimental conditions used it was impossible to reach 100% hydrolysis even with 3 to 4 times the stoichiometric amount of base and this was independent of the reaction time. Comparable results were found for the VA percentages after reaction times of 0.5 and 72 hours (Table III).

Also when stoichiometric amounts of base were used for partial hydrolysis, the vinyl alcohol content was less than expected from calculated values of actual base concentration in solution. The differences between calculated and experimental (pyrolysis) determined VA values in HEVA polymers were smaller when the starting EVA copolymer had a higher VA incorporation (18.5 mol %) compared to a low (9.8 mol %) VA content. Furthermore, for one type HEVA polymer *e.g.*, type I (18.5 mol % VA in original EVA copolymer), the differences between calculated and experimental mol % VA

TABLE III

Pyrolysis results of HEVA samples (100% hydrolyzed) in function of time.

Time (hours)	0.5	2	10	24	48	72
I mol % VA	0.5	0.2	0.3	0.2	0.1	0.3
II mol % VA	0.4	0.3	0.1	0.2	0.1	0.1
III mol % VA	0.2	0.3	0.1	0.1	0.1	0.2

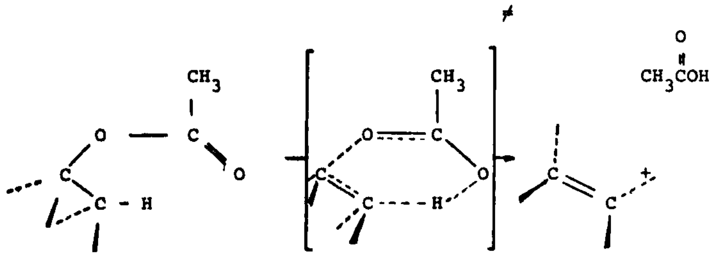

FIGURE 5 The elimination reaction with a six-center transition state of the VA incorporated in EVA/HEVA polymers with consequent production of acetic acid in an inert atmosphere at 395°C.

were larger when more than 50% of the ester groups were transformed. An explanation could be found in the availability of acetoxy groups to OH^-. As the reaction proceeded the amount of KOH and VA were reduced, so when stoichiometric amounts of base were used it became gradually more difficult to find available ester groups in the first place. Additionally, because of the higher polymer concentration in solution it was difficult for the OH^- ions to find all acetoxy groups due to steric hindrance, which explains the lack of 100% hydrolysis. The relative accuracy of pyrolysis was considered to be 2%[2].

As shown in Figure 5 the molecule actually detected was acetic acid, formed out of the VA incorporation, through an elimination reaction with a

TABLE IV

The most significant bands in the I.R. spectra of the EVA copolymer and its hydrolyzed forms with reference to corresponding spectra A, B, C in figure 6

cm^{-1}	functional group	reference
3460	C–O(2 × 1730)	A
3700–3100	O—H	B, C
2980–2850	$CH_3\nu$	A, B, C
2680	CH_2	A, B, C
1742 (split)	C–O	B, C
1730	C–O	A
1470	CH_3 asym δ	A, B, C
1375	CH_3 sym δ	A, B, C
1130	—COOR	B, C
1020	—COOR	A, B, C
730–720	$(CH_2)_n$, $n > 4$ (rocking)	A, B, C
610	—COOR wagging	A, B

δ = deformation
ν = stretching

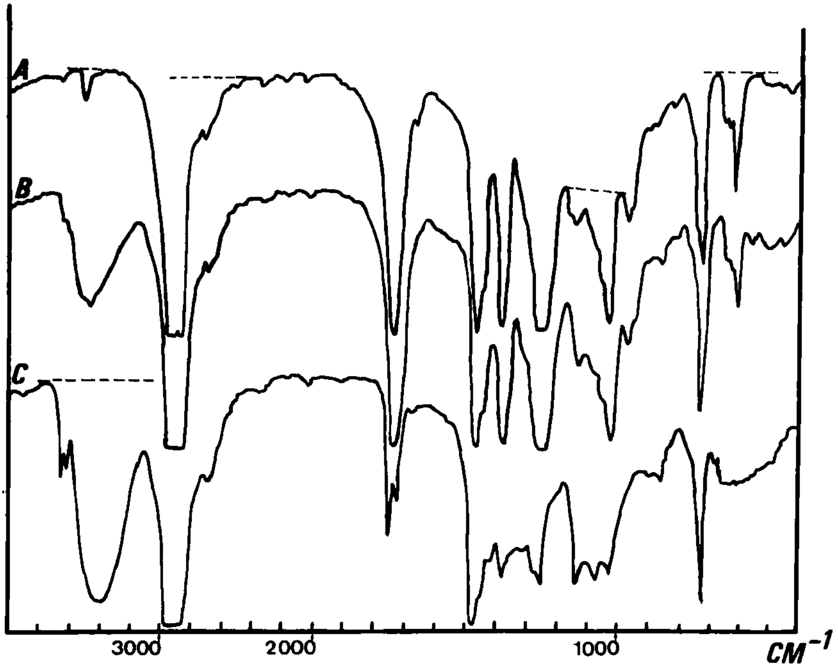

FIGURE 6 Three I.R. spectra of the II (9.8 mol % VA) EVA copolymer type. A represents the unmodified EVA copolymer spectrum, B the approximately 40% hydrolyzed form spectrum and C the 100% hydrolyzed form spectrum. Drawing of baseline is indicated.

six-center transition state, at an elevated temperature above 300°C in an inert atmosphere according to Streitwiesser[8] (Figure 5).

The existence of residual acetoxy groups was proved by I.R. spectroscopy. At 1742 cm^{-1}, the center of a split carbonyl band, although small, remained in totally hydrolyzed EVA copolymers. This could be seen in Figure 6. The most significant bands were reported in Table IV, with references A, B and C to Figure 6.

The origin of the splitting is possibly due to different kinds of interaction between the polar groups, *i.e.*, acetoxy—acetoxy interaction accounts for one part of the band, acetoxy–hydroxy for the other. This is a feature which possibly explains also the three different hydroxy bands. (hydroxy isolated, hydroxy–hydroxy and hydroxy–acetoxy groups interaction).

Among important features were the disappearance of the 3460 cm^{-1} band used for quantitative VA mol % determinations in EVA[4,5], and the unavailability of the 1020 cm^{-1} band due to band overlays. Only the 610 cm^{-1} band remained untouched after partial hydrolysis and could be used to determine the VA mol % in the terpolymers employing the calibration

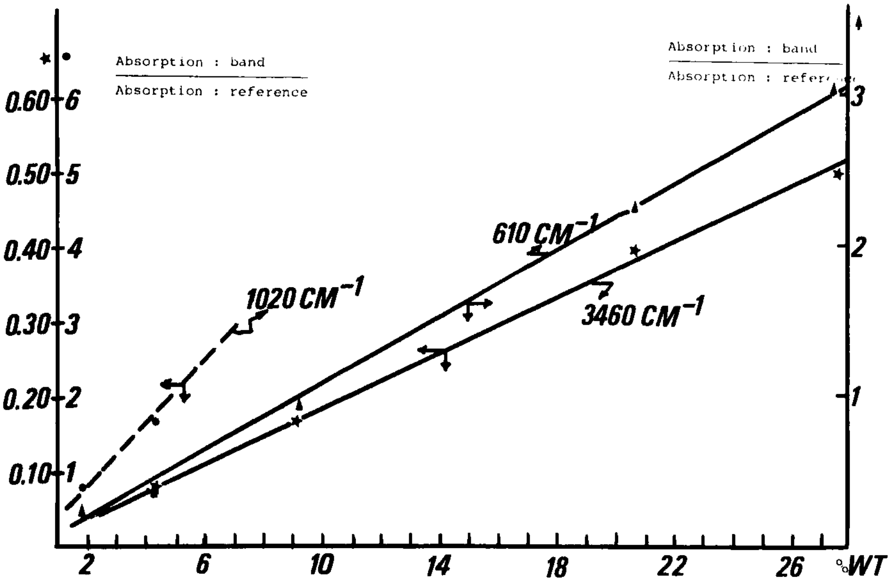

FIGURE 7 The calibration line for quantitative I.R. spectroscopy VA % wt. determination in EVA/HEVA according to Vansant[5] and Van der Linden[4]. Conversion of % wt. into mol % is possible with formulas 1 to 5.

lines constructed by Vansant.[5] Its validity was experimentally checked. (Figure 7). The shoulder at 2680 cm^{-1}, applicable as a reference absorption band could still be used after hydrolysis. The carbonyl band at 1742 cm^{-1} was never used for quantitative purposes due to its very strong absorption into EVA, showing a splitting of the band. This feature is not present using an ultra-thin EVA film cast from CCl_4 solution on a sodium chloride (NaCl) disc. This procedure could not be used for HEVA copolymers because of solubility difficulties. The origin of the band splitting has to be investigated further.

For the quantitative determination of mol % VOH in HEVA the broad

TABLE V

Comparison of mol % VOH values obtained by an independent laboratory and our developed calibration line

			authors
I	mol % VOH	18.2	19.1
II	mol % VOH	10.6	13.2
III	mol % VOH	2.9	2.8

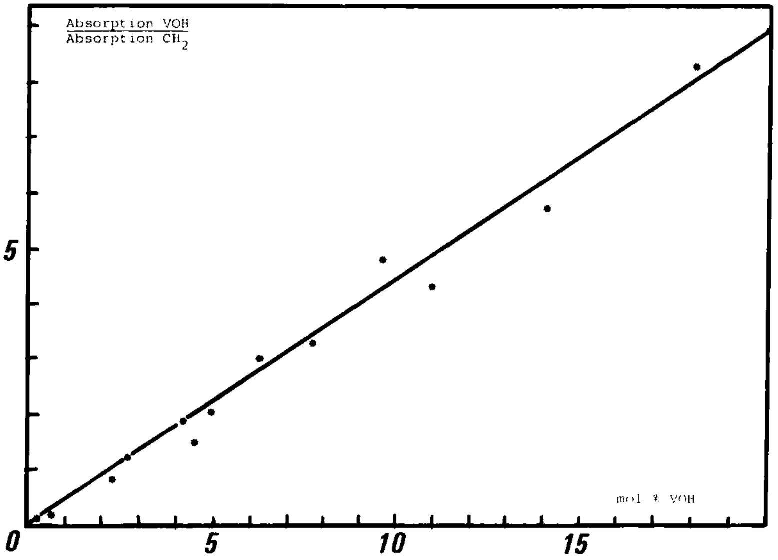

FIGURE 8 The calibration line determined by controlled samples for quantitative I.R. spectroscopy for mol % VOH from 0 up to 20 in HEVA.

OH band in the region 3700–3100 cm^{-1} was used. Together with the pyrolysis data, the absorption ratio of OH band and reference band of the CH_2 shoulder was a measure for the VOH mol %. This resulted in the construction of a calibration line: absorption VOH/absorption CH_2 *versus* mol % VOH. After linear regression a correlation coefficient was found of 0.99 (Figure 8).

The newly constructed calibration line was checked for its validity with three samples of known VOH content. Table V shows that a fairly good agreement was found between mol % VOH obtained through the calibration line and the known values.[9]

CONCLUSION

We may conclude that after hydrolysis of several EVA copolymer types to a desired VOH mol % it was possible to construct a calibration line of absorption VOH/absorption CH_2 *versus* mol % VOH, allowing the determination with I.R. spectroscopy of the VOH incorporation in HEVA polymers. The principle applied was to obtain VOH mol % standard values, by means of pyrolysis, as an absolute method providing more accuracy than I.R. spectroscopy, and to find the corresponding absorption ratio of two representative bands (without overlap or too strong an absorption). Combining these results into a calibration line, I.R. spectroscopy allowed detection of the VOH mol % in HEVA polymers from 0 up to 20.

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