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Effects of different organic acids on the adhesion between polyethylene film and aluminium foil

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The effect of organic acids on the adhesion between the polyethylene layer and the aluminium foil in laminated food packaging material was studied after test packaging. A 3% (wt/wt) solution of acetic acid and equivalent solutions of propionic acid, citric acid and lactic acid were packed in envelopes consisting of: LDPE/paper/LDPE/Al foil/LDPE and stored at room temperature for 4 weeks. As previously reported, acetic acid caused a total delamination within a few days followed by a recovery back to 50% of the initial value after 2 weeks. The material stored in propionic acid showed a total delamination of LDPE and aluminium after 8 days of storage and remained at this level during the rest of the observing period. FR-IR scans and ESCA analysis showed a formation of a salt for both acetic acid and propionic acid. The package material in contact with citric acid, lactic acid and water did not show any marked change in adhesion or salt layer formation during the storage time.

INTRODUCTION

Interactions between food components and plastic packaging material include permeation through packaging material from the environment into foods and from foods to the environment. Also included are migration of components from the packaging material into foods and absorption of food components into the packaging material (Gilbert, 1985; Hotchkiss, 1988). The permeation through polymers has been studied thoroughly and the phenomenon and the factors of importance are described by many investigators (Barrer, 1941; Pace & Datner, 1979; Landois-Garza & Hotchkiss, 1987). Migration from the packaging material into the food has also been widely studied and most countries have regulations on indirect food additives (FDA, 1976; Gilbert *et al.*, 1980).

More recently, investigations have started to focus on the absorption of food components into the packaging material (Kwapong & Hotchkiss, 1987; Mannheim *et al.*, 1987). Such absorption might affect the properties of the polymer film, e.g. by the absorption of non-volatile food components, which has been related to migration problems (Bieber, 1985). Also other organic compounds can affect the properties of the packaging material. The effect of acetic acid on the adhesion between LDPE and aluminium foil in laminated packaging material has been studied (Olafsson *et al.*, 1992). A 3% aqueous acetic acid solution was shown to totally delaminate the packaging material after 3 days storage at room temperature. Acetic acid in this concentration is generally accepted as an acidic food simulant.

Chemically acetic acid is a monocarboxylic organic acid and similar acids occur naturally in many foods and are also added as preservatives. The most common ones are probably the fruit acids, e.g. citric acid, malic acid, tartaric acid and succinic acid. Organic acids (e.g. short-chain fatty acids) are produced during the fermentation of milk and vegetables, e.g. acetic acid and lactic acid (Sherz & Kloos, 1981).

The purpose of this work was to study the effect of some common organic acids on the adhesion between LDPE and aluminium foil in laminated packaging material and to compare that with our previous study

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on acetic acid. The organic acids selected for this study were propionic acid, citric acid and lactic acid. Chemically, they differ from acetic acid [CH_3COOH] both in chain length (propionic acid: [CH_3CH_2COOH]) and in containing an extra hydroxyl group (lactic acid: [$CH_3CH(OH)COOH$], citric acid: [$CH_2COOHC(OH).COOHCH_2COOH$]) or extra carboxylic groups (citric acid).

Since organic acids constitute a large, but heterogeneous group of acids present in many food items, it is important to study to which extent their chemical structure and properties contribute to the delaminating effects. The adhesion between plastics and aluminium foil in high-barrier packaging material is vital in order to sustain the nutritional and sensoric quality of sensitive food products, e.g. fruit juices.

MATERIALS AND METHODS

Organic acids

Four organic acids were used: a 3% (wt/wt) solution of acetic acid (Merck, Darmstadt, Germany), pH 2·4 and equivalent solutions of propionic acid (Merck), pH 2·5; citric acid (Merck), pH 2·2 and lactic acid (BDH Chemicals, Poole, UK), pH 2·2. All acids were of analytical grade. Water of HPLC grade (Millipore) was used as a control in the experiment.

Food packaging material

The laminated packing material used had the following composition: LDPE (15 g/m^2) paper (210 g/m^2)/LDPE (25 g/m^2)/Alfoil (7 μm)/LDPE (45 g/m^2). All the polymer layers were extrusion-coated, without any tie layers, at a temperature of 325°C. Corona discharge was not applied. The LDPE had a density of 0·92 g/cm^3. Packaging material was supplied by TETRA PAK AB (Lund, Sweden).

Test packaging

The material was formed into envelopes of an approximate size of 10 × 20 cm and filled with 50 ml of the test solution. The envelopes were stored at 20°C and 55% relative humidity. Samples for peel test were taken after 1, 3, 4, 5, 8, 11, 14, 21 and 28 days. Samples for the FT-IR test were taken after 3, 4, 5, 7, 14, 21 and 28 days. Samples for ESCA were taken after 1, 3, 5, 8, 14 and 28 days for acetic acid and after 14 and 30 days for the other acids.

Adhesion tests

The adhesion was measured using a JJ Tensile Testing Machine, model T30K with recorder, model A 128 (JJ Lloyd Instruments, Southampton, UK). The test was a 180° peel test and performed, as earlier described (Olafsson *et al.*, 1990), with a crosshead speed of 50 mm/min using a 100 N load cell. Eight samples were analysed from each envelope.

IR analysis

An attenuated total reflection measurement (ATR) was made using a Fourier transform infra red (FT-IR) spectrometer of type Bruker IFS48 (Bruker Analytische Messtechnik Gmbh, Germany) equipped with an MCT detector. A thallium iodide–bromide KRS-5 crystal was used. Samples were scanned 100 times purging with dry air, as described earlier (Olafsson *et al.*, 1992). A single measurement was made for each sample. The ATR analysis was made on the side of the LDPE film facing the aluminium foil. The peak was compared to a reference peak at 2660 cm^{-1} with a baseline at 2420 cm^{-1} probably coming from C-H vibration as previously described (Olafsson *et al.*, 1992).

Electron spectroscopy for chemical analysis (ESCA)

A Kratus XFAM 800, with an AlK (1486·6 eV) X-ray source was used. A 15 mm strip of the packaging material was cut out and the LDPE layer peeled off. The sample was placed in a vacuum desiccator for 48 h to eliminate water. An ESCA analysis, one measurement for each sample was then made on the aluminium foil.

RESULTS

Adhesion

The results of the peel-tests are summarized in Fig. 1. The laminate stored in acetic acid behaved as described earlier (Olafsson *et al.*, 1992). The adhesion decreased to almost zero after 3 days and remained at this level for about 4 days. At this stage the LDPE layer could easily be removed, and under the polymer a thin film of liquid was seen, which was assumed to consist of acetic acid and water. During the next 3 days the adhesion increased to about half of the initial value and remained

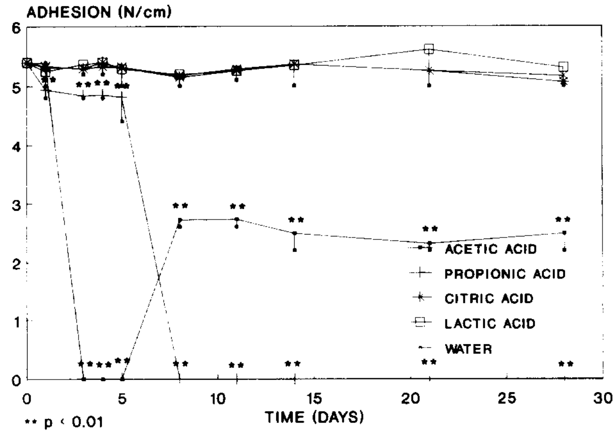


Fig 1. Changes in adhesion of laminates stored in: 3% (wt/wt) acetic acid and equimolar solutions of propionic acid; citric acid lactic acid and water. Measurements were made after 1, 2, 3, 4, 7, 14, 21 and 21 days. The significance of the changes were tested at each time point versus water as control and are indicated in the figure (**: $P < 0{\cdot}01$).

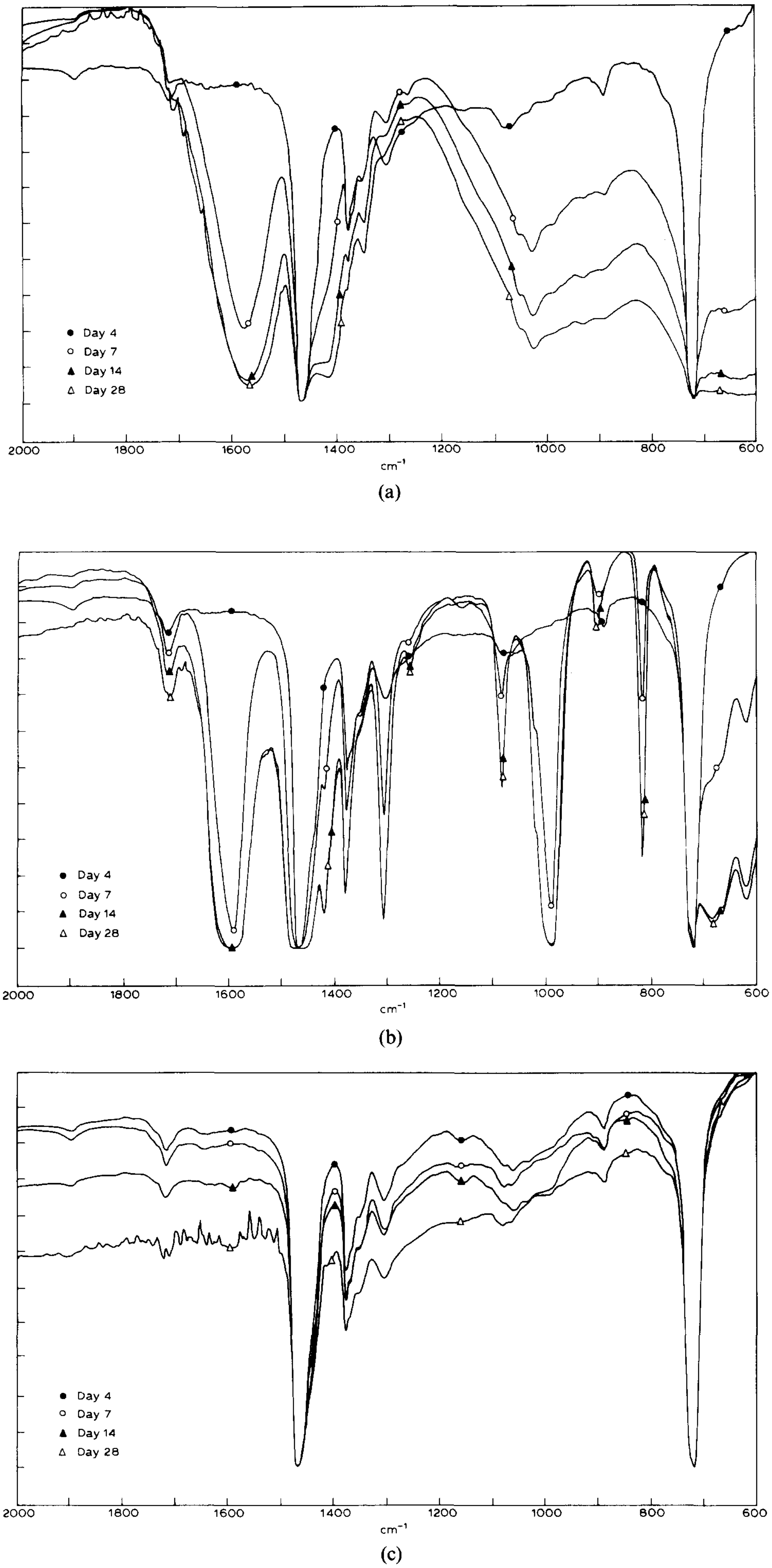
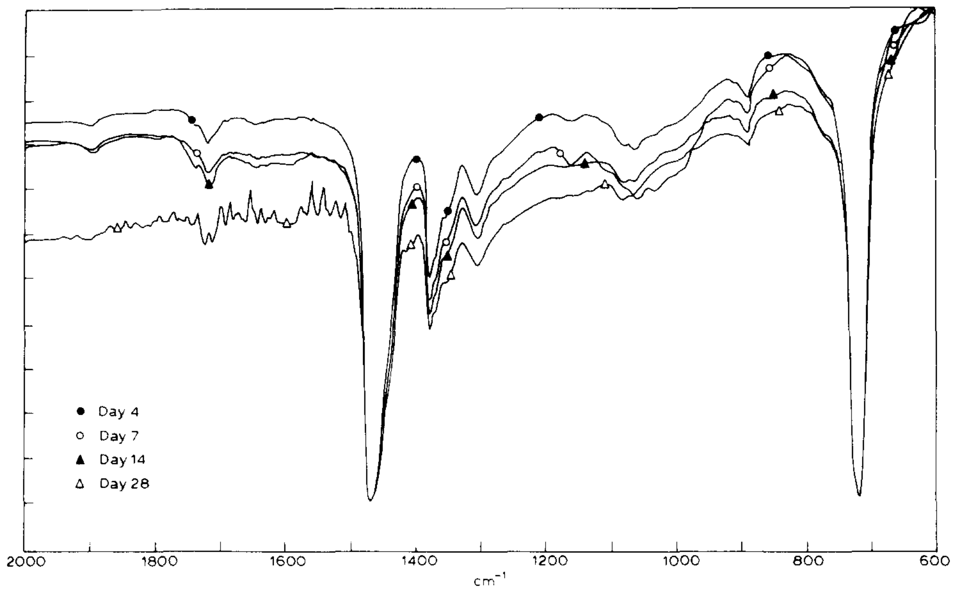
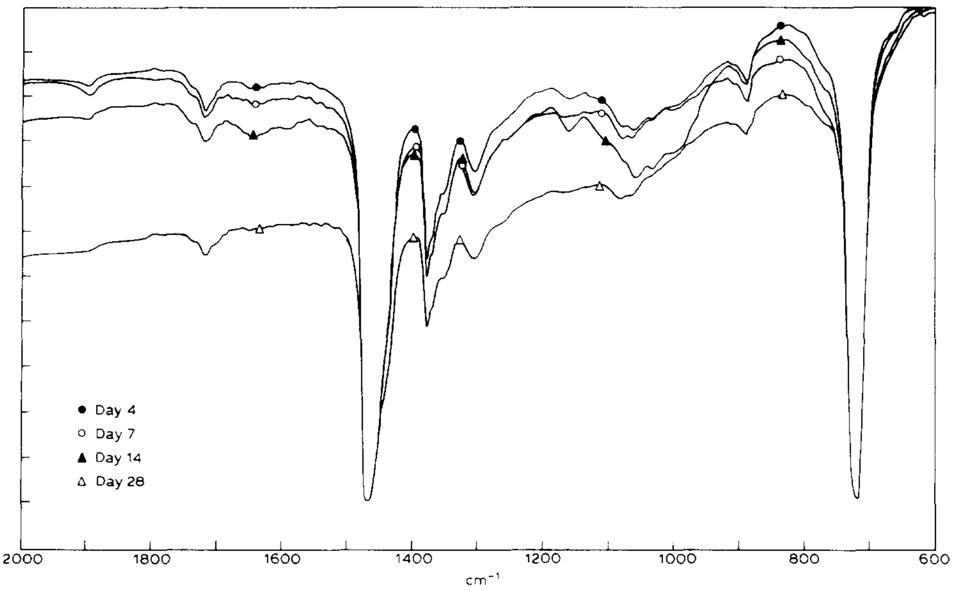


Fig. 2. Attenuated total reflection (ATR) IR spectra of LDPE stored for 1, 7, 14 and 28 days. Spectrum: (a) acetic acid; (b) propionic acid; (c) citric acid; (d) lactic acid; (e) water.



(d)



(e)

Fig. 2.—*contd.*

at that level to the end of the experimental period. At this stage no liquid was seen on the aluminium foil.

The laminate in propionic acid was totally delaminated after 8 days but in contrast to acetic acid, the adhesion did not recover during the storage period. A similar liquid film was seen here, which evaporated quickly when exposed to air. The laminates stored in citric acid, lactic acid and water were not affected at all during the 4 weeks period with respect to adhesion.

IR analysis

The test is used to demonstrate chemical changes in the surface of the LDPE layer. The results of the ATR analysis are shown in Figs. 2 and 3. In accordance with our previous study on acetic acid (Olafsson *et al.*, 1992) two carbonyl related peaks were detected: at 1720 cm^{-1} and 1570–80 cm^{-1}. The peak at 1720 cm^{-1} was identified as an aldehyde or a ketone originating from the oxidation of the LDPE during extrusion. This peak did not change markedly for any of the acids during the storage time. The peak at 1570–80 cm^{-1} was an acid salt and this peak increased with time for acetic acid and propionic acid. The salt peak for propionic acid was considerably higher than the peak for acetic acid already after 1 week and continued to be so during the next 3 weeks (Fig. 3). The salt formation of the critic acid and lactic acid did not change markedly during the storage time.

Besides these two carbonyl peaks, two other peaks coming from —OH were observed, a broad peak at about 3400 cm^{-1} and one peak at 1050 cm^{-1}. These peaks also increased markedly with time for LDPE in acetic acid and propionic acid, indicating the presence of hydroxyl-containing compounds. The peak

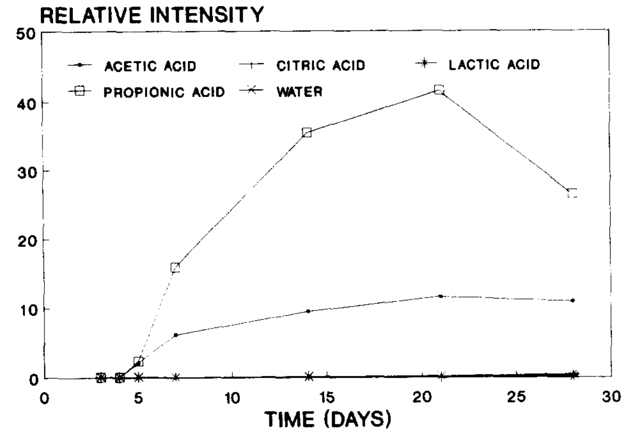


Fig. 3. Changes in infrared spectra of polyethylene in the region 1683–1558 cm^{-1} (salt peak) stored in acetic acid, propionic acid, citric acid, lactic acid and water during 4 weeks. The relative peak height is calculated using a reference peak at 2660 cm^{-1} in the polyethylene spectrum, coming from C-H vibration.

at 1050 cm^{-1} was sharp for the propionic acid but broad for the acetic acid. LDPE stored in citric acid, lactic acid and water did not show any OH peaks.

In accordance with our previous study (Olafsson *et al.*, 1992), adhesion and salt formation seemed to be related for acetic acid. In contrast, propionic acid did not show a similar relationship.

ESCA

ESCA scans were taken from aluminium foil stored in all four acids and water after 14 and 28 days and for the aluminium foil in acetic acid also after 1,3,5 and 8 days. The ESCA test describes changes in the surface of the aluminium foil (it has a sampling depth of ~50 Å). The results are demonstrated in Table 1. The aluminium foil showed three peaks that were identified as aluminium (Al2p), carbon (C1s) and oxygen (O1s). The Al2p peak consisted mostly of Al^{III}, the stable oxidised state of Al, but a small peak from unoxidized Al was also detected. The C1s was divided into two peaks, a large peak from aliphatic carbon at 285 eV and a smaller carboxyl carbon peak at 289 eV. The results are given as ratios, Al/Al^{III} and CO_3^{2-}/CH_2.

Table 1. ESCA analysis on aluminium foil stores in acetic acid, propionic acid, citric acid, lactic acid and water. Results are presented as quotients of Al^{III} versus Al, and of CO_3^{2-} versus CH_2.

Organic acid	Al/Al^{III}	CO_3^{2-}/CH_2
Acetic acid		
Day 1	0·245	0·045
Day 2	0·229	0·110
Day 5	0·179	0·124
Day 8	0·013	0·183
Day 14	0·017	0·186
Day 28	0·074	0·263
Propionic acid		
Day 14	0·189	0·430
Day 28	0·045	0·378
Citric acid		
Day 14	0·242	0·057
Day 28	0·247	0·057
Lactic acid		
Day 14	0·246	0·09
Day 28	0·226	0·104
Water		
Day 14	0·235	0·067
Day 28	0·225	0·056

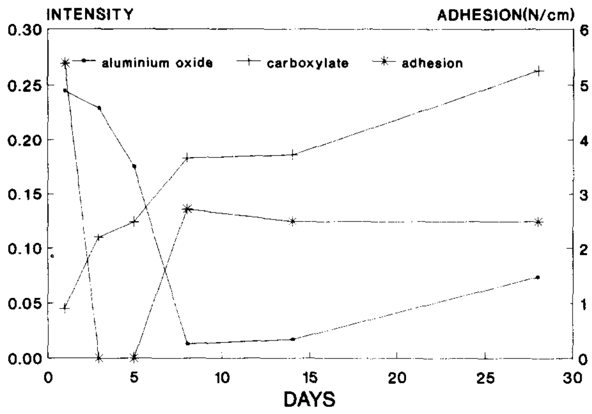


Fig. 4. Changes in adhesion versus formation of Al^{III} and CO_3^{2-}, in laminate stored in 3% acetic acid.

If we look at the Al/Al^{III} ratio for acetic acid, it can be seen that it decreased slowly at first and then sharply from day 5 to day 8. From day 8 to day 14 the ratio was almost constant, and then increased slightly from day 14 to day 28, which might be explained by the fact that the aluminium oxide was not uniformly distributed over the surface. The low Al/Al^{III} ratio indicated a thick layer of oxidized Al on top of the unoxidized Al metal.

The results from the ESCA tests for propionic acid showed the same tendency as for acetic acid, but over a longer time period. The Al/Al^{III} ratio decreased sharply from day 14 to day 28, which showed that the propionic acid was beginning to react with the aluminium layer. However, for citric acid, lactic acid and water, the ratio was high, indicating that the oxidized Al layer in this case was thinner.

The CO_3^{2-}/CH_2 ratio for acetic acid increased markedly from day 1 to day 8 and thereafter more slowly. This indicated that the carboxylic acid penetrated the polymer in accordance with data found by the FT-IR test. In contrast, the CO_3^{2-}/CH_2 ratio for propionic acid decreased slightly from day 14 to day 28, which also was shown by the FT-IR analyses. The CO_3^{2-}/CH_2 ratio for citric acid, lactic acid and water was consistently low, which means that the polymer was not penetrated by these acids. If the CO_3^{2-}/CH_2 ratio for acetic acid is compared to the result from the peel test, the concentration of carboxylic groups seems to be correlated with the polymer–aluminium foil adhesion (Fig. 4).

DISCUSSION

Carboxylic acids, being highly polar substances, should be expected to dissolve only very slightly in LDPE, which is a nonpolar medium. It is well known that carboxylic acids in water exist as dimers due to strong hydrogen bonding (Morrison & Boyd, 1983). We therefore believe that organic acids may diffuse through the polymer phase as dimers, thereby partly neutralizing the effects of the highly polar acid groups. Acetic acid [CH_3COOH] and propionic acid [CH_3CH_2COOH] are linear and should therefore permeate relatively quickly through the polymer. This was confirmed by FT-IR spectroscopy. Propionic acid seemed to penetrate to a greater extent through the polymer film than acetic acid, which is probably due to the fact that propionic acid has a longer aliphatic chain, which makes it more soluble in the nonpolar LDPE. Citric acid [$CH_2(COOH)COH(COOH)CH_2COOH$] and lactic acid [$CH_3CHOHCOOH$], permeate slowly through the polymer, which is to be expected since they each carry one hydroxyl group and citric acid also carries three carboxylic groups. Water, which is highly polar, permeates through LDPE only in small quantities (Brandrup & Immergut, 1989).

In the manufacture of the laminate, which is extruded at 325°C, the surface of the polymer becomes partly oxidized in the process, with the formation of mainly keto groups along with some aldehyde and carboxylic acid groups, as reflected by the ATR-IR at 1720 cm^{-1} (Rugg *et al.*, 1954).

During the manufacture of aluminium foil, the aluminium is cold-rolled to the desired thickness. After the cold-rolling the foil is usually annealed. The purpose of the annealing is first to remove the rolling oil products and secondly to recrystallize the metal. The annealing is normally done in air at 300°C, and produces a layer of about 40 Å of Al_2O_3 (Olefjord & Karlsson, 1986).

Adhesive bonds between LDPE and aluminium are believed to consist mainly of hydrogen bonds, ionic bonds and van der Waals forces between the oxidized polymer and aluminium oxide (Fowkes, 1982; Allen, 1987; Hjertberg *et al.*, 1989). Hydronium ions from carboxylic acids and water, permeating through the polymer to the interface, should have a strong affinity for the keto groups on the polymer surface as well as for the aluminium oxide layer. The polymer–substrate interactions at the interface would be disturbed and consequently the adhesion between the two layers would be destroyed.

The Al_2O_3 is soluble at pH values below 4 (Shatlov, 1952; Alwitt, 1976; Wafers & Misra, 1987). As described previously, the protective aluminium oxide is dissolved by the aqueous acetic acid solution, which then reacts with aluminium with the formation of hydrogen gas and Al^{3+} ions. The oxidized aluminium then forms a basic amorphous acetate, which is insoluble in water or acetic acid (Gmelin, Handbuch der Inorganische Chemie, 1932; Olafsson *et al.*, 1992). The aluminium acetate molecule can bind 2–2·5 molecules of water (Gmelin Handbuch der Inorganische Chemie, 1932), and it is suggested that the recovery of the adhesion might be related to the formation of the hydrated salt.

In the laminate stored in propionic acid, no recovery of adhesion did occur. To improve the adhesion, the salt must be able to form relatively strong adhesive forces with the underlying aluminium as well as with the oxidized LDPE, and must also have a relatively high cohesive strength. The propionate salt formed seemed to adhere quite strongly to the Al although it was possible to scrape it off with a scalpel. Results from the ATR-IR analysis of the polymer showed a large salt peak, which means that the salt also adhered to the polymer. Therefore, a possible explanation is that the propionate layer did not exhibit a sufficiently high cohesive strength to improve the adhesion between the polymer and the aluminium foil.

The level of corrosion of the Al should be controlled by three main factors: first the acidity, second the amount of acid present, and third by the density of the protective aluminium oxide layer. The pK_a values for acetic acid and propionic acid are 4·74 and 4·87, respectively, so there is no major difference between the two acids. Propionic acids seemed to permeate through the polymer in higher amounts than acetic acid, as could be seen by FT-IR. However the density of the oxide layer seems to be different. A white precipitate was formed at the aluminium surface, and formation of aluminium oxide was confirmed by ESCA. However, the gas formation was much less pronounced as compared with acetic acid. The precipitate indicated that corrosion took place, but the modest gas formation seen suggested that it was much less severe than by acetic acid. The interpretation of these results could be that, with propionic acid, a protective layer of aluminium propionate was formed, which slowed down or stopped further corrosion of the metal by the acid.

In conclusion, it was demonstrated that a 3% solution of acetic acid and propionic acid both affected the adhesion between Al and LDPE markedly, resulting in total delamination of the Al/LDPE layers in 1 week. In the case of the acetic acid, the adhesion recovered to half of its initial value after another week. This is believed to be the result of the formation of a layer of aluminium acetate which can form hydrogen bonds with the polymer. No such recovery in adhesion was, however, demonstrated for propionic acid. Citric acid and lactic acid did not affect the adhesion at all, probably due to a very slow permeation rate through LDPE caused by bulky side chains of the acids and a higher degree of polarity. The results clearly show that the linear monobasic carboxylic acids can effect the packaging material. Even in lower concentrations than used here a similar effect might be seen, after prolonged storage periods (Olafsson *et al.*, 1992).

Since acetic acid and propionic acid have such pronounced delaminating effects one should also expect other linear aliphatic monobasic acids to behave in a similar way. Work is therefore in progress to study the effects of free fatty acids. These may be present in many foods naturally or are formed in the hydrolysis of triglycerides that takes place continuously during storage of foods.

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