Sorption of Fatty Acids into Low-Density Polyethylene and Its Effect on Adhesion with Aluminum Foil in Laminated Packaging Material

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Unsaturated fatty acids dispersed in water/SLS/ethanol (87/3/10) were stored in laminated packaging material at room temperature for 4 weeks (study A). Monounsaturated fatty acids were sorbed 2–4 times better than polyunsaturated ones and resulted in LDPE/Al foil delamination already within 2 days. Polyunsaturated acids were less uniformly sorbed but caused a severe decrease in interlayer adhesion, followed by an increase up to 50–60% of initial adhesion. In a second study (study B) the effect of chain length was investigated by dissolving fatty acids in 95% ethanol. The sorption rate of this fatty acid series increased with increasing chain length. The interlayer adhesion decreased to about half of the initial adhesion in 1 week and stayed at that level throughout the study. It appeared that the rate of delamination was not directly proportional to the amount of sorbed fatty acid.

INTRODUCTION

Interactions between food and plastic packaging materials are a well-known phenomenon with practical consequences. Three main types of interaction are defined: (i) permeation of organic and inorganic compounds through the packaging material; (ii) migration of substances from the packaging material into the packed food; and (iii) sorption of compounds from the food into the plastic. Much attention has been focused on the migration of substances from the packaging material into the food products for example monomers, plastisizers, and other additives from the polymer processing (Gilbert, 1976; Gilbert et al., 1980; Figge, 1980; Miltz et al., 1984).

Research on the sorption of lipid-soluble food components into packaging materials has mainly been focused on flavor scalping, i.e. the sorption of aroma substances such as citrus oils, particularly D-limonene (Kwapong and Hotchkiss, 1987; Hirose et al., 1987; Mannheim et al., 1987; Charara et al., 1992; Nielsen et al., 1992). Koch and Figge (1976, 1978) and Bieber et al. (1980) studied the effect of fat absorption on the migration of polymer additives into fatty foods and reported that sorption of fat into packaging material, especially polyolefins, caused a swelling of the polymer which in turn increased migration. The transport of compounds from food products into packaging material can cause problems in the adhesion in laminated material and in the worst case a total delamination between different layers (Schroeder et al., 1990). When this happens the packaging material is not able to fulfill its purpose to sustain the shelf life and quality of the packed product.

In two previous studies, organic acids (acetic acid, propionic acid, citric acid, and lactic acid) were inves-

tigated with regard to the effects on adhesion in laminated packaging material (Olafsson et al., 1993a,b). These studies indicated that aliphatic monocarboxylic acids such as acetic acid and propionic acid caused a rapid delamination between low-density polyethylene (LDPE) and Al foil. The results encouraged us to extend the studies to fatty acids. The objective was to study the sorption and transportation of free fatty acids of different chain lengths, both saturated and unsaturated, into LDPE and the effect of this absorption on the adhesion between LDPE and Al foil in laminated packaging material, commonly used for aseptic packaging of milk.

Many food products are emulsions of fat and water, such as milk and milk products, mayonnaise, sauces, dressings, and gravies. Some of these products contain substantial amounts of fat, the major part of which is present as triglycerides (>99%). The concentration of free fatty acids in fresh products is low, but tends to increase with storage time owing to hydrolysis. The concentration of free fatty acids in oils and fats vary widely, from ~0.02–0.05% for refined oils such as rapeseed oil and up to 0.5–1% for virgin olive oil (Karlshamns Oils & Fat AB, personal communication, 1994). Fresh milk (4% fat) and butter (80% fat) contain ~0.002% and 0.16% free fatty acid, respectively, according to the Swedish Dairy Association. Aseptically packed products have a shelf life of 6–12 months. It is therefore possible that the concentration of free fatty acids may increase and cause a decrease in interlayer adhesion in laminated packaging material.

MATERIALS AND METHODS

Fatty Acid Solutions. *Study A.* Test solutions (0.2% w/w) of palmitoleic acid ($C_{16:1}$), oleic acid ($C_{18:1}$), linoleic acid ($C_{18:2}$), or linolenic acid ($C_{18:3}$) (Sigma Chemical Co., St. Louis, MO) were prepared by dissolving the free fatty acids in ethanol 95% (Kemetyl, Stockholm, Sweden). The ethanol solution was dispersed in water containing 3% (w/w) sodium lauryl sulfate (SLS) (Sigma Chemical Co., St. Louis, MO) as emulsifier, to a

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final composition of 90% (w/w) water and 10% (w/w) ethanol. *tert*-Butylhydroquinone (TBHQ) (Janssen Chimica, Geel, Belgium) (400 ppm of the fatty acid content) was added as an antioxidant. The water (SLS)/ethanol mixture with TBHQ (without the fatty acid) was used as a control solution in the experiment. All chemicals were of analytical grade and water was Millipore purified.

Study B. Test solutions (1% w/w) of capric acid ($C_{10:0}$), lauric acid ($C_{12:0}$), myristic acid ($C_{14:0}$), palmitic acid ($C_{16:0}$), stearic acid ($C_{18:0}$), oleic acid ($C_{18:1}$), and linoleic acid ($C_{18:2}$) (Sigma Chemical Co, St. Louis, MO) were dissolved in 95% ethanol containing TBHQ (400 ppm of the fatty acid content) as antioxidant. Ethanol with TBHQ (400 ppm of the fatty acid content) was used as a control solution in the experiment. All chemicals were of analytical grade.

Food Packaging Material. The packaging material was an experimental laminate supplied by TETRA PAK AB (Lund, Sweden). It consisted, reading from the outside to the inside of the laminate, of LDPE (12 g/m²)/paper (186 g/m²)/LDPE (25 g/m²)/Al foil (6.5 μm)/LDPE (15 g/m²)/LDPE (25 g/m²). All the polymer layers except the innermost layer were extruded at 325 °C. The innermost layer was extruded at 290 °C using ozone treatment (to limit oxidation of the polymer). No tie layers were used. The LDPE (Exxon LD 256) had a density of 0.92 g/cm³ and a melt flow index of 8.2 at 190 °C and a 2.16 kg pressure.

Test Packaging. Pouches of the packaging material (12 × 15 cm) were prepared by means of a thermosealer (temperature 190 °C; pressure 7 bars; dwell time 6 s) and filled with 50 mL of test solution. The pouches were then stored at room temperature. Samples for study A were taken after 1, 2, 3, 4, 7, 10, 14, 21, and 28 days. Samples for study B were taken after 1, 7, 14, 21, 28, and 56 days, except in the sorption measurements where the analysis were made at the same time intervals as in study A, as the sorption process reaches a steady state in 2–4 days. The following measurements were made: (i) the amount of sorbed fatty acid in the inner LDPE layer (the combined 15 and 25 g/m² LDPE layers, as these layers cannot be separated after extrusion), (ii) the adhesion between the inner LDPE layer and the Al foil, (iii) the presence of fatty acid on the inner LDPE film using FTIR, and (iv) the wettability of the Al foil (contact angle measurements). In separate experiments the permeation of fatty acids through the LDPE film was measured using a special permeation cell (Hildingsson and Törnell, 1995). The sorption measurements was made with two replicate extractions and analyses for each sample. In the adhesion measurements, eight replicate analyses were made for each fatty acid and storage time. In the FTIR measurements a single measurement was made for each sample. In the contact angle measurements eight measurements were made for each fatty acid. In the permeation measurements two replicate analyses were made for each fatty acid.

Sorption of Fatty Acids. The pouches were opened and emptied, and the interior LDPE surface that had faced down during storage was rinsed with ethanol and Millipore water. The inner LDPE layer (approximately 1.0 g) was peeled off, weighed, and placed in a 40 mL pear-shaped glass bottle. Petroleum ether (analytical grade, Merck), 30 mL, was added and allowed to stand for 24 h at room temperature. A multiple extraction test revieled that a yield exceeding 95% was achieved in one extraction. After removing the extracted polymer the petroleum ether was removed by vacuum evaporation (Rotavapor R-110, Büchi AB, Switzerland). The fatty acid was redissolved in 10 mL of a 5/4 mixture of diethyl ether and ethanol. The extracts in study A were then derivatized and measured with capillary GC (Tetra Pak, 1993; AOAC, 1984). The free fatty acid concentration in study B was measured by titrating against 0.01 N NaOH in 99.5% ethanol with a phenolphthalein indicator (Karlshamn, 1984).

Adhesion Tests. The adhesive strength of the Al–LDPE interface, on the side that had faced down during storage, was measured as previously described (Olafsson et al., 1993a,b) using a JJ Tensile Testing Machine, Model T30K equipped with a 100 N load cell and a recorder, Model A 128 (JJ Lloyd
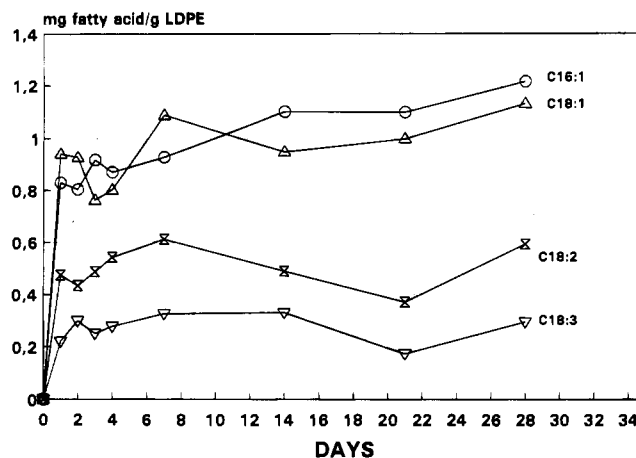
Figure 1. Study A: Amount of unsaturated fatty acids sorbed into LDPE stored in 0.2% (w/w) fatty acid dissolved in an emulsion based on water, SLS, and ethanol (87:3:10) for 4 weeks at 22 °C. Two measurements were made for each fatty acid.

Instruments, Southampton, England). The peel force was recorded and expressed in units of N/cm (180° peel test).
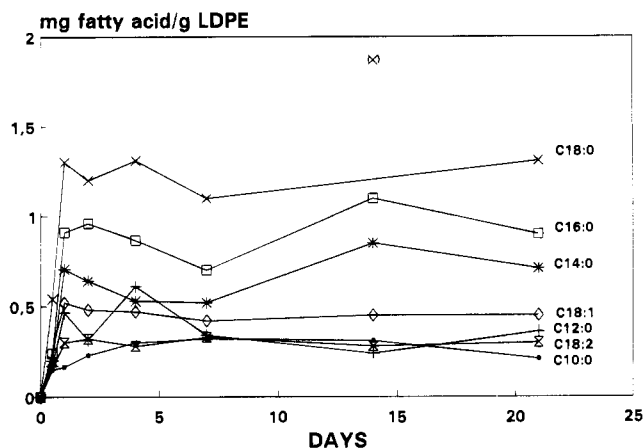
IR Measurements of LDPE. FTIR measurements were made to search for remains of carboxylic acids on on the LDPE laminate. An attenuated total reflection measurement (ATR) was made using a Fourier transform infrared (FT-IR) spectrometer of type Bruker IFS48 (Bruker Analytische Messtechnik Gmbh, Germany) equipped with a nitrogen-cooled MCT detector, as earlier described (Olafsson et al., 1993a,b). The crystal used was a thallium iodide bromide KRS-5 with an 45° angle of incident. The samples were prepared as for the adhesion test, except that they were not kept moist. The LDPE side facing the Al foil was scanned 200 times to give a sufficiently high-resolution spectrum, purging with dry air to remove water vapor. The absorbance of the peak was compared to that of a reference peak at 2660 cm⁻¹ with a baseline at 2420 cm⁻¹, derived from the C–H vibration.

Contact Angle Measurement of Al Foil. Contact angle measurements were made to detect surface changes in the Al foil. This was performed using a motor-driven microsyringe, a video camera, a video monitor, and a video printer (Kober and Wesslén, 1992). A 15 mm strip of the material was cut out and the LDPE layer peeled off. The sample, with the Al facing up, was attached to a glass plate with a double-sided adhesive tape. By means of the microsyringe a water droplet (35–100 μL) was placed on the Al foil, and the advancing contact angle was registered. The syringe motor was then reversed and the water drawn up into the syringe until the edges of the water droplet moved, when the receding contact angle was registered. The angles were evaluated from the video printings taken.

Permeation Measurements. The rate of permeation of different fatty acids through LDPE film was measured using a permeation cell. The cell consisted of two 60 mL glass compartments, with continuous stirring, separated by an LDPE film (43 μm) with a permeation area of 19.6 cm². The permeation experiment was carried out as follows: one chamber was filled with 60 mL of the test solution, containing the fatty acid dissolved in 95% ethanol, and the other chamber was filled with 95% ethanol. The permeation rate was evaluated by measuring the concentration of fatty acid in the pure ethanol solution at different time intervals with capillary GC (see above). The permeability coefficient was calculated according to eq 1:

$$P = \frac{\text{(quantity of permeant)(film thickness)}}{\text{(film area)(time)}} \quad (1)$$

Statistics. Statistical evaluation of the experimental results was made with Minitab Statistical Software (Minitab Inc., NY).

Figure 2. Study B: Sorption of fatty acids of various chain lengths into LDPE stored in 1% (w/w) fatty acid in 95% ethanol for 4 weeks at 22 °C. Two measurements were made for each fatty acid.

RESULTS

Sorption. As can be seen in Figure 1, the major part (70–80%) of the sorption in study A occurred during the first 2 days. Thereafter the content of fatty acids in the LDPE increased only slightly. There was a considerable difference in sorption between the different fatty acids: $C_{16:1}$ and $C_{18:1}$ were sorbed in 2–3 times higher amounts than $C_{18:2}$ and $C_{18:3}$, around 1 mg/g LDPE for the former two and around 0.4 mg/g LDPE for the latter two.

The results of the fatty acid measurements in study B (Figure 2) showed that the sorption of saturated fatty acids increased with increasing chain length, for saturated fatty acids, and decreased with increasing degree of unsaturation, for the unsaturated acids. The major part of the sorption occurred during the first 2 days. The sorption increased in the following order: $C_{10:0}$ < $C_{18:2}$ < $C_{12:0}$ < $C_{18:1}$ < $C_{14:0}$ < $C_{16:0}$ < $C_{18:0}$, ranging from 0.25 mg/g LDPE for $C_{10:0}$ to 1.25 mg/g LDPE for $C_{18:0}$.

Partition Studies. The equilibrium partition coefficients for the fatty acids in study A and study B was calculated according to

$$K_c = [C_p]_{eq}/[C_s]_{eq} \qquad (2)$$

where $[C_s]_{eq}$ is the equilibrium concentration of fatty acids in the solution. $[C_p]_{eq}$ is the concentration of fatty acid absorbed by the polymer after equilibrium was reached. The results of the calculated equilibrium partition coefficients are shown in Table 1. The partition coefficients in study A (0.141–0.545) were much higher than in study B (0.027–0.124).

Adhesion. *Study A.* The adhesion was greatly affected by the different fatty acids (Figure 3). The monounsaturated fatty acids $C_{16:1}$ and $C_{18:1}$ were espe-

cially effective as delaminators. After 1 day of storage, the adhesion of the material exposed to $C_{16:1}$ and $C_{18:1}$ was almost zero and after another day the material was totally delaminated and did not recover during the rest of the observation period. In the laminates exposed to $C_{18:2}$ and $C_{18:3}$, the adhesion between the LDPE layer and the Al foil, within the same sample was nonuniform, varying from a total lack of adhesion to almost the same adhesion as in untreated material. This is illustrated in Figure 3 by the inserted bars indicating the standard deviation. A clear trend, though, was seen for laminate exposed to $C_{18:2}$ and $C_{18:3}$. The adhesion decreased at first and then a significant increase ($P < 0.05$) occurred. This was particularly evident for $C_{18:3}$.

Study B. A substantial decrease in the interlayer adhesion, amounting to about half the initial value was observed (Figure 4). The reduction in adhesion was similar for all the fatty acids with no clear relationship to chain length, except that $C_{18:1}$ seemed to affect the adhesion slightly more than the other acids. As in study A the adhesion decreased abruptly during the first 2 days and then gradually during the remaining 4 weeks, but no delamination occurred.

FT-IR Analysis of LDPE. In the LDPE layer, the intensity of two peaks was examined, namely, at 1720 and 1587 cm^{-1}. The carbonyl group ($R_2C=O$) in the aldehydes, ketones, and carboxylic acids absorb strongly in the region around 1700 cm^{-1} (Rugg et al., 1954; Cooper and Prober, 1960; Colthup et al., 1964). Carboxylate anion (COO^-) absorbs strongly in the region round 1600 cm^{-1} (Colthup et al., 1964). In addition, a broad peak at about 3400 cm^{-1} and another at 1050 cm^{-1} were observed, deriving from hydroxide (Colthup et al., 1964; Silverstein et al., 1981). The results are presented in Table 2.

Study A. Carbonyl Carbon (1720 cm^{-1}). The carbonyl content of the LDPE exposed to all the fatty acids was considerably higher than that of the LDPE material exposed to the blank (Table 2a). From day 1 to day 14 the carbonyl carbon concentration seemed to be constant and increased somewhat from day 14 to day 21.

Carboxyl Carbon (1587 cm^{-1}). The results of the FT-IR measurements showed a steady increase in carboxylate concentration for all the acids from day 1 to day 21 (Table 2a). LDPE from the material exposed to $C_{16:1}$ and $C_{18:1}$ showed higher values than LDPE from the material exposed to $C_{18:2}$ and $C_{18:3}$. LDPE when exposed to $C_{18:3}$ acid had a considerably lower carboxyl content than when exposed to the other acids. This is consistent with the results of the sorption measurements.

Study B. Carbonyl Carbon (1720 cm^{-1}). The carbonyl concentration on the surface of the material exposed to all the fatty acids except $C_{16:0}$ and $C_{18:0}$ seemed to be

Table 1. Partition Coefficients (K_c) and Permeation Coefficients (P) for Free Fatty Acids of Various Chain Lengths and Degree of Saturation Dissolved in a Water/SLS/Ethanol (87:3:10) Emulsion (Study A) or in 95% Ethanol (Study B) in Equilibrium with LDPE[a]

	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{16:1}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
				Study A					
K_c	na	na	na	na	na	0.545	0.522	0.285	0.141
				Study B					
K_c	0.027	0.037	0.060	0.090	0.124	na	0.045	0.031	na
P (10^{-3}) (g mm/m^2 day)	0.688	0.654	0.913	1.030	1.030	na	1.090	0.610	na

[a] Duplicate measurements were made for each sample; na, not analyzed.

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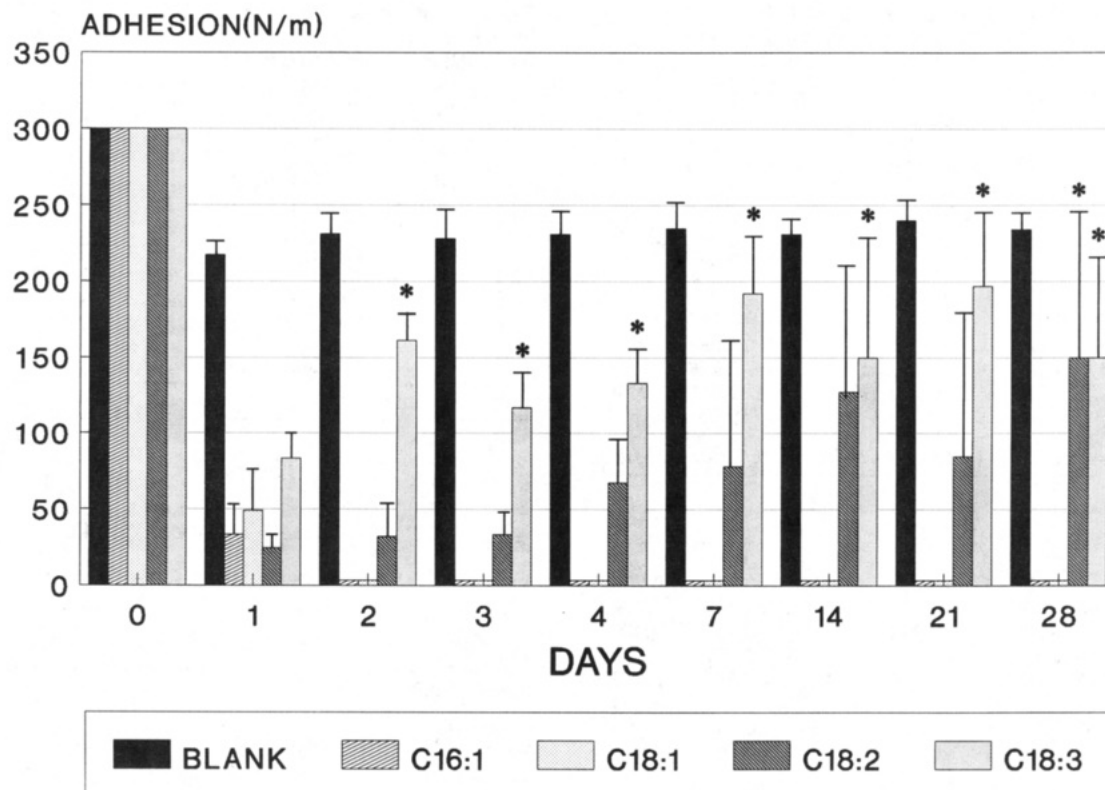
Figure 3. Study A: Strength of adhesion between LDPE and Al foil layers of laminates stored in solutions containing 0.2% free unsaturated fatty acids in a water, SDS, and ethanol (87:3:10) emulsion for 4 weeks at 22 °C. Error bars represent the positive standard deviation of eight replicates. The significance was tested against the value for day 1 (*, $P < 0.05$).
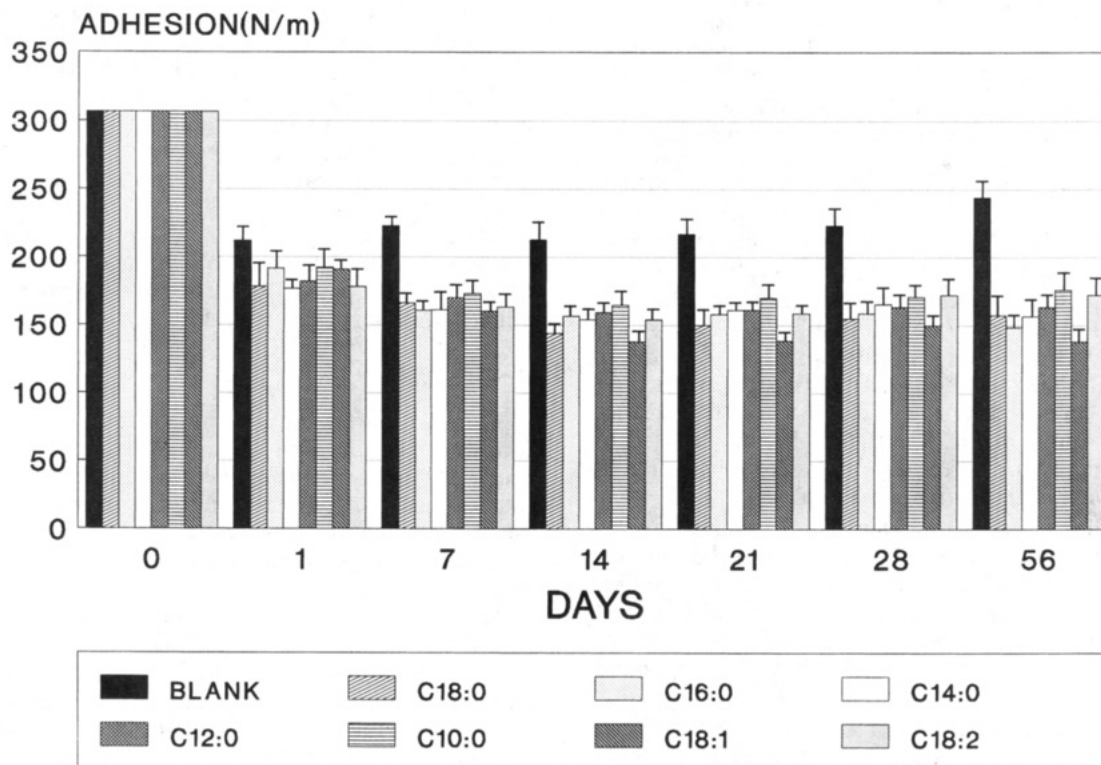
Figure 4. Study B: Strength of adhesion between LDPE and Al foil layers of laminates stored in solutions containing 1% (w/w) fatty acids of various chain lengths in 95% ethanol for 4 weeks at 22 °C. Error bars represent the positive standard deviation of eight replicates.

more or less constant during the observation period of 8 weeks and only slightly higher than the blank value (Table 2b).

Carboxyl Carbon (1587 cm⁻¹). The carboxylate concentration did not change at all throughout the experi-

mental period and the concentration on day 56 was not higher than for the material exposed to the blank solution for any of the samples tested (Table 2b).

Contact Angle of the Al Foil. Contact angle measurements were made to determine the wettability

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Table 2. FT-IR (ATR) Measurements of LDPE Film[a]

a. Film Exposed to Unsaturated Free Fatty Acids (Study A)[b]

fatty acid	days						
	1	2	3	4	7	14	21
[>C=O]							
blank	0.289	0.221	0.236	0.188	0.299	0.260	0.363
C16:1	0.444	0.390	0.419	$-^c$	0.423	0.428	0.604
C18:1	0.438	0.387	0.393	0.424	0.396	0.455	0.604
C18:2	0.436	0.363	0.401	0.381	0.365	0.440	0.648
C18:3	0.397	0.359	0.408	0.360	0.557	0.496	0.869
[COO⁻]							
blank	0.008	0.005	0.007	0.019	0.030	0.062	0.013
C16:1	0.051	0.110	0.280	$-^c$	0.580	1.083	1.724
C18:1	0.040	0.103	0.166	0.257	0.670	1.126	1.326
C18:2	0.061	0.135	0.217	0.317	0.756	1.056	1.058
C18:3	0.058	0.032	0.047	0.110	0.268	0.351	0.593

b. Film Exposed to Free Fatty Acids of Different Chain Length

fatty acid	days					
	1	7	14	21	28	56
[>C=O]						
blank	0.372	0.241	0.207	0.263	0.249	0.236
C10:0	0.392	0.242	0.249	0.393	0.343	0.359
C12:0	0.363	0.302	0.342	0.368	0.304	0.359
C14:0	0.378	0.362	0.345	0.311	0.287	0.358
C16:0	0.318	0.280	0.284	0.332	0.339	0.492
C18:0	0.402	0.458	0.499	0.712	0.551	0.564
C18:1	0.368	0.216	0.311	0.371	0.341	0.395
C18:2	0.382	0.211	0.264	0.303	0.256	0.332
[COO⁻]						
blank	0.047	0.050	0.056	0.083	0.067	0.080
C10:0	0.032	0.043	0.080	0.104	0.061	0.054
C12:0	0.033	0.062	0.075	0.089	0.059	0.076
C14:0	0.057	0.053	0.069	0.071	0.060	0.061
C16:0	0.041	0.097	0.072	0.077	0.060	0.062
C18:0	0.045	0.055	0.064	0.090	0.045	0.083
C18:1	0.039	0.040	0.075	0.085	0.064	0.064
C18:2	0.049	0.045	0.079	0.077	0.065	0.057

[a] Results are presented for the relative intensity of the carbonyl group [>C=O] and the carboxyl group [COO⁻]. A single measurement was made for each sample. [b] Relative intensity compared to C–H vibration at at 2660 cm⁻¹. [c] –, not measured.

Table 3. Study A: Contact Angles for Al Foil, from a Laminate Exposed to 0.2% Unsaturated Fatty Acids in a Water/SLS/Ethanol (87:3:10)[a]

a. Advancing Contact Angles

days	blank	$C_{16:1}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
0	96 ± 1	96 ± 1	96 ± 1	96 ± 1	96 ± 1
1	96 ± 2	102 ± 3	102 ± 2	102 ± 2	95 ± 2
2	98 ± 3	108 ± 2**	105 ± 3**	100 ± 3	80 ± 4**
3	96 ± 1	105 ± 1**	104 ± 2*	92 ± 2**	74 ± 4**
7	98 ± 1	105 ± 2**	107 ± 1**	97 ± 2**	86 ± 4**
10	97 ± 3	106 ± 3**	106 ± 2**	95 ± 3**	85 ± 7**
14	98 ± 3	108 ± 2**	108 ± 2**	93 ± 3**	90 ± 2**
21	98 ± 3	109 ± 2**	108 ± 2**	96 ± 2**	90 ± 5**

b. Receding Contact Angles

days	blank	$C_{16:1}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
0	71 ± 1	71 ± 1	71 ± 1	71 ± 1	71 ± 1
1	69 ± 1	80 ± 4	79 ± 3	77 ± 4	70 ± 3
2	69 ± 2	80 ± 2	83 ± 3*	73 ± 3*	46 ± 3**
3	63 ± 2**	82 ± 2	81 ± 4	69 ± 4*	48 ± 3**
7	64 ± 2**	84 ± 4*	85 ± 3**	74 ± 9	48 ± 2**
10	65 ± 3**	88 ± 2**	92 ± 2**	71 ± 6*	47 ± 4**
14	65 ± 2**	92 ± 2**	95 ± 2**	60 ± 3**	49 ± 2**
21	64 ± 2**	91 ± 3**	97 ± 3**	62 ± 2**	50 ± 1**

[a] Water was used as a blank solution. Mean ± SD of 8 replicates. The significance was tested against the value on day 1 (*, $P < 0.05$; **, $P < 0.01$).

of the Al surface. The results of the contact angle measurements are presented in Tables 3 and 4.

Study A. The advancing contact angle for the monounsaturated fatty acids, $C_{16:1}$ and $C_{18:1}$, increased significantly after 2 day's storage and stayed more or less constant after that (Table 3a). The polyunsaturated fatty acid $C_{18:2}$ both increased and lowered the advancing contact angle on the Al foil. On the Al exposed to $C_{18:3}$, the contact angle decreased considerably over 2–3 days, thereafter increasing somewhat.

The receding contact angle for Al foil exposed to $C_{16:1}$ and $C_{18:1}$ increased steadily throughout the observation period (Table 3b). The contact angle on the Al foil exposed to $C_{18:2}$ decreased steadily from day 1 and throughout the study. The receding angle on the Al foil exposed to $C_{18:3}$ acid dropped ~35% from day 1 to day 2 and remained at that level throughout the study.

Study B. The advancing contact angles for the Al foil of the laminates exposed to the saturated fatty acids increased slightly compared to the blank. The advancing contact angle was not significantly affected by $C_{18:1}$ or $C_{18:2}$.

The receding contact angle for the Al foil of the laminate exposed to $C_{10:0}$ decreased significantly from day 1 to day 28. The receding angle for the Al foil exposed to $C_{12:0}$, $C_{18:2}$, and the blank solution remained almost unchanged throughout the study. The receding angle for $C_{18:1}$ increased from day 1 and throughout the

study. The receding angle for the laminates exposed to the fatty acid solutions $C_{18:0}$, $C_{16:0}$, and $C_{14:0}$ increased significantly on day 7, in that order, and remained at that level throughout the study (Table 4b).

Permeation Measurements. Permeation measurements were made for the fatty acids: $C_{10:0}$, $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{18:0}$, $C_{18:1}$, and $C_{18:2}$. A steady state was reached in less than 2 days, as was observed in the sorption studies (i.e. the permeation of fatty acid through the LDPE film was linear with time after 2 days). The results presented in Table 1 showed that the permeation coefficient increased with increasing chain length for the saturated fatty acids. The permeation coefficient decreased as the unsaturation increased. The rate of permeation increased from 0.610 to 1.086 in the following order: $C_{18:2} < C_{10:0} \leq C_{12:0} < C_{14:0} < C_{16:0} \leq C_{18:0} < C_{18:1}$. The low permeation rate of $C_{18:2}$ was consistent with its low sorption in LDPE.

DISCUSSION

A delamination induced by sorption occurred in the laminates exposed to the unsaturated fatty acids in study A, but a certain recovery in adhesion was observed for $C_{18:2}$ and $C_{18:3}$. In the laminates in study B a similar sorption occurred, followed by roughly a 40% reduction in the interlayer adhesion, but no delamination was observed.

The adhesive forces between LDPE and Al are believed to consist mainly of acid–base interactions (including H-bonds) and van der Waals forces between the aluminum oxide (Al_2O_3) and oxidized groups on the polymer surface (aldehydes, ketones, and carboxylic acids), formed when the polymer is extruded at elevated temperatures (Fowkes, 1982; Allen, 1987; Hjertberg et al., 1989). The delamination is believed to have occurred when the fatty acids penetrated through the LDPE layer and accumulated in the polymer–Al interface, creating a weak boundary layer (WBL) by acid–base interactions between the acid and the Al_2O_3 surface layer of the Al foil.

The sorption of fatty acids increased with increasing chain length, as the number of van der Waals bonds

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Table 4. Study B: Contact Angles for Aluminum Foil Exposed to 1% (w/w) Fatty Acids of Various Chain Lengths in 95% Ethanol[a]

a. Advancing Contact Angles

days	blank	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
0	96 ± 1	96 ± 1	96 ± 1	96 ± 1	96 ± 1	96 ± 1	96 ± 1	96 ± 1
1	96 ± 3	98 ± 1	100 ± 1	98 ± 1	101 ± 1	101 ± 2	100 ± 1	99 ± 1
7	100 ± 2**	104 ± 2**	102 ± 2**	104 ± 2**	105 ± 2**	107 ± 1**	100 ± 2	99 ± 2
14	101 ± 2**	102 ± 1**	103 ± 2**	106 ± 2**	107 ± 2**	105 ± 2**	104 ± 3**	100 ± 1
21	102 ± 2**	104 ± 1**	105 ± 2**	104 ± 2**	106 ± 2**	106 ± 2**	101 ± 2*	99 ± 2
28	102 ± 2**	103 ± 2**	105 ± 2**	107 ± 2**	107 ± 3**	108 ± 1**	102 ± 1**	101 ± 2*
56	99 ± 1**	101 ± 1*	97 ± 2*	102 ± 2**	103 ± 3*	106 ± 2**	101 ± 1	102 ± 2**

b. Receding Contact Angles

days	blank	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
0	71 ± 1	71 ± 1	71 ± 1	71 ± 1	71 ± 1	71 ± 1	71 ± 1	71 ± 1
1	69 ± 1	68 ± 1	73 ± 1	77 ± 1	74 ± 2	72 ± 1	74 ± 1	73 ± 1
7	69 ± 2	68 ± 2	71 ± 1*	75 ± 1*	77 ± 1**	78 ± 1**	73 ± 1*	72 ± 1*
14	69 ± 2	59 ± 1**	66 ± 2**	76 ± 1	78 ± 1**	78 ± 2**	76 ± 1*	73 ± 1
21	68 ± 2	64 ± 1**	68 ± 2**	77 ± 1	77 ± 1**	78 ± 1**	74 ± 2	70 ± 2**
28	68 ± 2	63 ± 3**	70 ± 1**	78 ± 1	76 ± 1*	79 ± 1**	78 ± 2**	72 ± 2*
56	70 ± 2	62 ± 2**	69 ± 3**	77 ± 1	77 ± 1**	78 ± 2**	76 ± 2*	70 ± 1**

[a] Ethanol 95% was used as a blank solution. Mean ± SD of eight replicates. The significance was tested against the value on day 1 (*, $P < 0.05$; **, $P < 0.01$).

between the polymer and the fatty acid increased. This was also seen in the FT-IR measurements as the concentration of carbonyl carbon (>C=O), which indicates the presence of carboxylic acid, increased with time and with increasing chain length. Also contact angle measurements showed a decrease in wettability caused by the free fatty acids on the Al surface. The sorption increased with increasing degree of saturation. The solubility in the polymer was also affected by the number of double bonds in the fatty acids. The extra double bonds in $C_{18:2}$ and $C_{18:3}$ give a more rigid molecule that probably diffuses more slowly through the polymer matrix. As a result of this the concentration on, or near, the surface increased, which affected the concentration gradient, that in turn affected the sorption. The results of the FT-IR measurements showed that the concentration of carboxylate (>COO⁻) was much higher for the monounsaturated acids than for the polyunsaturated ones.

The colloid systems in the two studies (A and B) are quite different. In study A, the water and the ethanol formed a continuous phase and the SLS formed micelles (~0.01 μm in diameter). Since the concentration of SLS was much higher (~15 times) than the free fatty acid concentration, it is believed that the free fatty acids and the SLS molecules formed mixed micelles, with the SLS molecules dominating in number. A small amount of fatty acid was probably also dissolved in the water/ethanol phase in equilibrium with that solvated in the micelles. The mixture was quite clear, so it can be considered a one-phase system, or a solution rather than an emulsion. Solution B on the other hand was a true solution, in which the fatty acid molecules were molecularly dissolved and evenly distributed in the solvent.

The concentration of fatty acids was 5 times higher in study B and the rate of sorption should therefore have been higher than in study A, since the driving force for the sorption is the concentration gradient. However, it appeared that the sorption was about the same. The sorption process depends on the solubility of the solute in the solvent as well as in the polymer. A nonpolar solute is adsorbed more strongly from a polar solvent, such as water (study A) to a nonpolar surface than from ethanol, which is less polar (Shaw, 1966). Therefore the amount dissolved in the polymer was relatively low in study B, compared to study A, as is illustrated by the

solubility partition coefficients (K_c, Table 1) which were much higher in study A than in study B. The solubility partition coefficients for $C_{18:1}$, for example, were 0.045 and 0.522 in ethanol and water, respectively. Thus, it appeared that the delamination was not directly proportional to the amount of sorbed fatty acid, since delamination occurred only in study A, despite the amount of sorbed fatty acids in study A and in study B being about the same. In study A, water most likely permeated through the LDPE with the fatty acid and interfered with the adhesive forces between the polyethylene and the Al foil, creating a WBL. The effect of the water can best be seen by comparing the same fatty acids in different solutions. $C_{18:1}$, for instance, caused a delamination, when dispersed in water, but not in ethanol. Ethanol permeates ~3 times faster through LDPE than water (0.28 vs 0.1, g mm/m² day) respectively (Brandrup and Immergut, 1989). However, water forms much stronger hydrogen bonds than the alcohol and therefore interferes more effectively. (The water content in study A was 90%, but only 5% in study B.)

A similar recovery of adhesion in LDPE/Al joints as that observed for the laminate in contact with $C_{18:2}$ and $C_{18:3}$ has been reported previously for laminates exposed to acetic acids, and has been explained by salt (acetate) and hydroxide formation on the surface of the Al foil (Olafsson et al., 1993a,b). The results of the contact angle measurements in study A showed that the wettability of the Al foil exposed to $C_{18:2}$, and in particular $C_{18:3}$, increased while the wettability of the Al foil exposed to $C_{16:1}$ and $C_{18:1}$ decreased. This means that a hydrophilic layer was formed on the Al foil exposed to $C_{18:2}$ and $C_{18:3}$, capable of forming H-bonds and therefore possibly partly replacing the original adhesive forces.

In the permeation studies the same order of permeation was found as in the sorption measurements, namely, according to chain length. Permeability (P) depends on the solubility (S) in and the rate of diffusion (D) through the polymer, $P = DS$ (Barrer, 1941). The solubility increases with increasing chain length while the rate of diffusion decreases with higher molecular weight, but the overall rate increases (Shimoda et al., 1987). It seems, therefore, that the solubility is the dominant factor.

In conclusion, the present study showed that free fatty acids dispersed at low concentrations (0.2% w/w) in water can lead to a rapid delamination between LDPE and Al. The same acids dissolved in less-polar solvents such as ethanol affected the adhesion somewhat, without causing delamination. The salts of the fatty acids do not cause delamination in LDPE/Al joints (unpublished observations) probably because the salts are too polar to be sorbed.

ABBREVIATIONS USED

ATR, attenuated total reflection; FT-IR, Fourier transform infrared spectrometer; KRS-5, thallium iodide bromide crystal; LDPE, low-density polyethylene; MCT detector, mercury cadmium tellurium detector; SLS, sodium lauryl sulfate; WBL, weak boundary layer; Al, aluminum; TBHQ, *tert*-butylhydroquinone.

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