Determination of Cosmetic Ingredients Causing Extrusion-coated and Adhesive Joint Multilayer Packaging Delamination

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In order to study the effect of several compounds on packaging stability, different cosmetic ingredients at two concentration levels were added to a NeoPCL® (Acofarma, Terrassa, Spain) water emulsion, and the preparations packed in sachets and stored at 40°C during 3 months. After that, the packaging was subjected to a T-peel test and headspace solid-phase microextraction gas chromatography mass spectrometry (HS-SPME-GC-MS) analysis. The HS-SPME-GC-MS analyses were performed using a 75 μm carboxen polydimethylsiloxane fibre to check for the presence of the studied analytes in the inner layers. The study revealed that the presence of a phenyl and a hydroxyl group in the compound structure lead to an important loss of adhesion between packaging layers joined by an adhesive. The interaction between the cosmetic ingredient and the adhesive was proposed as the main cause of the loss of adhesion. However, extrusion-coating packaging was more susceptible to delamination, particularly with the volatile compounds. Copyright © 2009 John Wiley & Sons, Ltd.

INTRODUCTION

The large number and wide variety of new products in development, and the huge volume of capital invested in this field, are two important characteristics of the cosmetic industry. Shampoos, gels, soaps, exfoliating creams, nourishing creams, cleansers, etc. are just some examples of the large number of cosmetic products available on the market.

Flexible multilayer packaging materials obtained by adhesion processes are widely used to promote cosmetic products. In this respect, the most common format for promoting these new products is the four-side sealed sachet. This format consists in two layers of laminated material thermally sealed at the edges. Additionally, the multilayer comprises of several layers fixed together by extrusion with a polyethylene (PE) film or by an appropriate adhesive; the materials normally used in this packaging are polymers (PE, polyester, polyamide, etc.) joined to an aluminium foil used to provide a hermetic barrier.

Despite the huge number of advantages (impermeability, flexibility, price, etc.), the main disadvantage of these materials is interaction with the product. Interaction between packaging and product has been widely studied,[1,2] as the transfer of additives,[3,4] monomers,[5] adhesive compounds,[6]

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etc. to products is a matter of great concern, especially when food products are packed. The other problem with packaging materials is the opposite phenomenon, the absorption of product compounds, causing the loss of essential product characteristics.[7,8] Moreover, the presence of these compounds (mainly flavours and aromas) in the interface between layers leads to adhesion loss, known as delamination. This phenomenon implies the use of more expensive materials instead of the common sachet format. As a result, numerous research studies have focused on developing an adhesive more resistant to degradation[9] or studying the delamination process[10–12] and the compounds responsible for this phenomenon.[13–15]

Certain formulations of cosmetic products contain compounds that can damage packaging. They have the capacity to migrate through the polymer layer in contact with the product and can then interrupt the cohesive forces between layers, reducing adhesion strength and producing delamination. Several studies have revealed the presence of different compounds in the interface of the multilayer packaging such as menthol, phenylethyl alcohol, phenoxyethanol, benzyl alcohol, dihydromyrcenol, p-propenylanisole, etc.;[13,14] hence, they are suspected of causing delamination.

The characteristics of the compounds suspected of causing delamination (low molecular weight and volatile compounds) make solid-phase microextraction (SPME) a useful tool for researchers' analysis.[16] This technique was first introduced by Arthur and Pawliszyn[17] and is a simple, rapid, solventless sample pre-treatment technique that can automatically perform sampling, clean-up, concentration, derivatization and introduction to the chromatograph.[18] It is based on the partition of an analyte between the sample matrix and the coating on a fused-silica fibre.[19] The fibre can be immersed in the sample or placed in the headspace (HS) above the sample where the target analytes are extracted. After partitioning, the fibre is retrieved from the sample and introduced into the gas or the liquid chromatograph where the analytes are desorbed from the fibre coating.

The main advantages of this technique are that extraction and concentration are performed in a single step, it allows on-line chromatographic analysis and it is a solventless technique. Therefore, it avoids previous extraction steps with ultra-

sonic bath,[7] by microwave-assisted extraction[20] or pressurized liquid extraction.[21] Moreover, supercritical fluid extraction[8] coupled to gas chromatography (GC; implying on-line analysis and avoiding the use of organic solvents) is not as good an alternative because it is more expensive. SPME-GC has also been used to analyse a large number of analytes in a wide variety of matrices and has been successfully applied to the analysis of packaging materials.[22–24]

In this study, the effect of different formulations, prepared using an autoemulsionable base cream, on multilayer packaging was tested. Thus, formulations at two concentration levels of each compound were introduced in sachets and stored at 40°C over a certain period of time. Then, adhesion strength was measured to check the effect on the laminated material. Moreover, an analysis of the inner layers was carried out by HS-SPME coupled to GC-mass spectrometry (GC-MS) in order to detect the presence of the cosmetic ingredient in the interface of the foils.

The objective of this study was to determine which of the cosmetic ingredients detected between inner layers were responsible for delamination of the packaging. This information can be used for selecting the appropriate material for the promotion of new cosmetic products.

EXPERIMENTAL

Materials and reagents

2-Phenoxyethanol, phenylethanol, menthol, benzyl alcohol, trans-anethole (p-propenylanisole), dihydromyrcenol, (R)-(+)-limonene, α-terpinene, methyl 4-hydroxybenzoate (methylparaben), ethyl 4-hydroxybenzoate (ethylparaben), propyl 4-hydroxybenzoate (propylparaben), (R)-(+)-carvone, α-terpineol, α-pinene, 3,7-dimethyl-3-octanol were purchased from Sigma-Aldrich (St. Louis, MO, USA). Standard solutions of each analyte were prepared in a base cream containing 20% NeoPCL® Autoemulsionable O/W (oil in water) from Acofarma (Terrassa, Spain) and 80% water.

The two types of laminated packaging studied were supplied by AMCOR-flexibles TOBEPAL (Logroño, La Rioja, Spain). These materials consisted of an aluminium (Al) foil joined with two

layers: a 12 μm thick polyester (PET) layer (outside), and a 70 g/m^2 linear low density polyethylene (LLDPE) layer (inside). The three layers of one of them were joined using an adhesive, while the other was obtained by an extrusion-coating process with PE film between layers. The adhesive used for the first one was a two-component solvent-based polyurethane adhesive. The polyethylene layer extruded used to join the foils of the second one was a 20 g/m^2 PE layer between PET and Al, while an 18 g/m^2 PE layer was extruded between LLDPE and Al.

Preparation of cosmetic ingredients and packaging samples

The cosmetic ingredients were dispersed in NeoPCL® Autoemulsionable O/W at two concentration levels (1% and 10% m/m). The cosmetic formulations were prepared as follows: cream base and water were heated separately in a double boiler (bain-marie) and then mixed (20:80). Then the mixture was left to cool at room temperature and the appropriate amount of each cosmetic ingredient was added in order to obtain the required concentration.

Sachets with dimensions of 10 × 10 cm made up of the laminated materials previously described were filled with 3 g of each formulation. Then, they were kept in an oven at 40°C and were opened at different times (1, 2, 3, 4, 7, 9, 14, 28, 56 and 84 days) and washed with milliQ water.

Adhesion strength measurement and packaging analysis

A 15 mm-wide strips of the sachets were cut with a guillotine, and adhesion strength between the LLDPE and Al foils was measured in quadruplicate at a rate of 100 mm/min using an Instron 4301 universal testing machine (Barcelona, Spain), by the T-peel procedure according to the American Society for Testing and Materials (ASTM) F-904 norm.

For packaging analysis, a Varian 3900 gas chromatograph with a Varian 2100T MS detector (Walnut Creek, CA, USA) was used. SPME injections were carried out in an automated manner using a CombiPal autosampler (CTC Analytics, Zwingen, Switzerland).

The samples were the two different layers obtained from delaminated sachets. For the adhesive joint material, an LLDPE film in contact with the product, and a two-layer material made of Al and PET were used. In the case of the extrusion-coated packaging, LLDPE/PE and Al/PE/PET layers were obtained. For simplification purposes in both cases, these two layers will be referred to as LLDPE and Al layers.

LLDPE and Al packaging layers (28 mm^2 and 8.5 cm^2, respectively) were incubated for 10 min at 80°C in sealed vials and extracted by HS-SPME for 25 min at this temperature using a 75 μm CAR-PDMS fibre (Supelco, Bellefonte, PA). Two millilitre glass vials and steel caps with 3.0 mm thick Teflon/silicone septa were used. Samples were analysed by GC-MS. Desorption was carried out for 8 min at 290°C. Slightly modified conditions from those established in previous studies[13,25] for similar samples were used.

A Varian CP8843 WCOT fused silica column [30m × 0.32 mm i.d., with a 0.25 μm polyethylene glycol phase (CP-WAX 52 CB); Walnut Creek, CA, USA] chromatographic column was used. An initial oven temperature of 50°C for 2 min was used; the temperature was then increased at a rate of 7°C/min to 230°C and finally maintained at this temperature for 10 min. The GC injector was equipped with a 0.8 mm insert and was kept at 290°C with a 1:20 split ratio during an initial time of 0.50 min, followed by a 1:50 split ratio. The carrier gas was helium (99.996%) at 1.0 ml/min.

For MS detection, the electron multiplier was set at 1900 eV and ionization was performed by electronic ionization. The temperatures used were 200°C for the trap, 60°C for the manifold and 280°C for the transfer line. The chromatographic peaks were identified using a GC–MS library (US National Institute of Standards and Technology).

RESULTS AND DISCUSSION

Evolution of adhesion strength for adhesive joint packaging material

A study of the loss of adhesion strength for adhesive joint packaging material was performed for each formulation and concentration level. The results of this study (shown in Figures 1 and 2)

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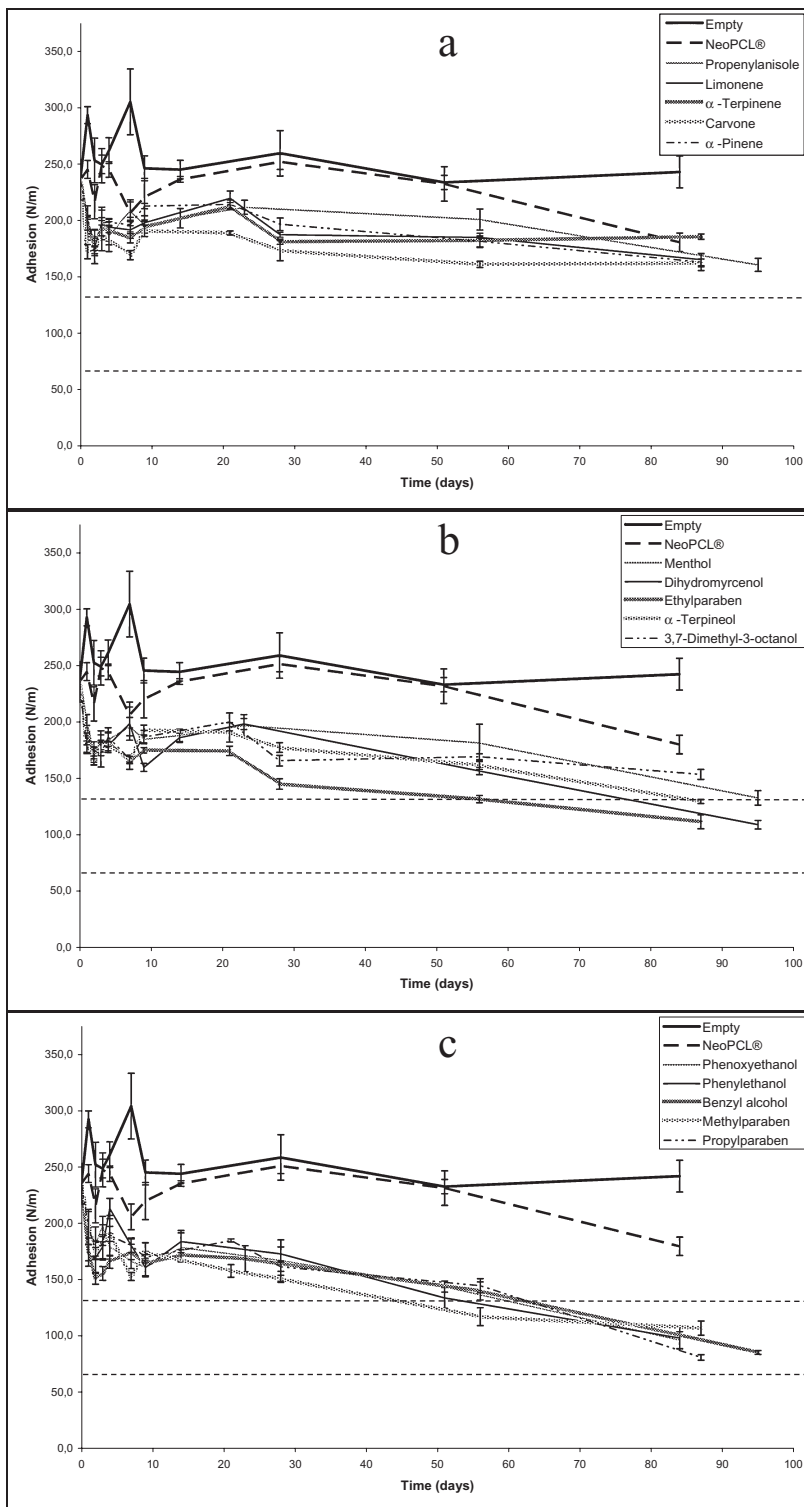**DOI**: 10.1002/pts

Figure 1. Evolution of adhesion strength between LLDPE and Al layers for 1% (m/m) formulations stored in adhesive joint multilayer packaging sachets at 40°C. The dotted lines represent quality (133 N/m) and delamination (67 N/m) levels. Formulations containing (a) propenylanisole, limonene, α-terpinene, carbone and α-pinene; (b) menthol, dihydromyrcenol, ethylparaben, α-terpineol and 3,7-dimethyl-3-octanol; (c) phenoxyethanol, phenylethanol, benzyl alcohol, methylparaben and propylparaben.

were related with the analysis of delaminated packaging samples by HS-SPME-GC-MS.

Figure 1 shows the decrease in adhesion strength between LLDPE and Al foils with time for formulations at 1% (m/m). The adhesion values obtained for empty sachets and those filled with cream base are also represented in these. No significant adhesion losses were observed for p-propenylanisole, (R)-(+)-limonene, α-terpinene, (R)-(+)-carvone and α-pinene (Figure 1a), with values above quality level (133 N/m). For the compounds shown in Figure 1b, adhesion values decreased below the quality level at the end of the study, except for 3,7-dimethyl-3-octanol. Likewise, 2-phenoxyethanol, phenylethanol, benzyl alcohol, methylparaben and propylparaben (represented in Figure 1c) produced an adhesion loss below 133 N/m, but it was above 67 N/m (delamination level) in all cases. Quality and delamination levels were fixed by the manufacturer as internal controls.

The adhesion evolution corresponding to 10% (m/m) formulations is shown in Figure 2. As in the previous figure, adhesion values corresponding to empty sachets and those filled with NeoPCL® are also represented. As can be seen in Figure 2a, 3,7-dimethyl-3-octanol produced an adhesion loss below quality level of 133 N/m at the end of the study, while the other compounds gave adhesion values above this level. Compounds represented in Figure 2b lead to adhesion values higher than 67 N/m except for ethylparaben with adhesion values below delamination level. Finally, all the compounds represented in Figure 2c lead to adhesion values below 67 N/m, with 2-phenoxyethanol, phenylethanol and benzyl alcohol being the most aggressive ones, causing complete delamination of the material in 4 days. These results show that the most aggressive compounds were those

with a phenyl and a hydroxyl group in the molecule (Figure 3) while the other analytes (without those characteristics) yielded adequate adhesion values. Moreover (R)-(+)-limonene, α-terpinene, α-terpineol and α-pinene gave adhesion values above 133 N/m at the higher concentration level (10% m/m).

Evolution of adhesion strength for extrusion-coated packaging material

Adhesion strength that changes over time for the extrusion-coated packaging is presented in Figures 4 and 5 (for 1 and 10% concentration levels, respectively).

As can be seen in Figure 4a, phenoxyethanol, phenylethanol, menthol, benzyl alcohol and propenylanisole produced adhesion values around the quality level for this kind of material (100 N/m), similar to those for the controls (empty sachet and NeoPCL®). Similar behaviour was observed for the compounds represented in Figure 4b [dihydromyrcenol, (R)-(+)-limonene, α-terpinene and methylparaben]. These compounds produced similar adhesion values to those of the controls. Only ethylparaben showed lower adhesion values, but always above the delamination level (50 N/m). Also, (R)-(+)-carvone and 3,7-dimethyl-3-octanol at 1% (m/m) showed adhesion values as controls (Figure 4c) but propylparaben, α-terpineol and α-pinene produced delamination, with adhesion strength values below 50 N/m at the end of the study. Quality and delamination levels were fixed at 100 and 50 N/m by the manufacturer for extrusion-coated multilayer laminates.

Quite different results were obtained for the compounds at 10% (m/m) in the NeoPCL® cream

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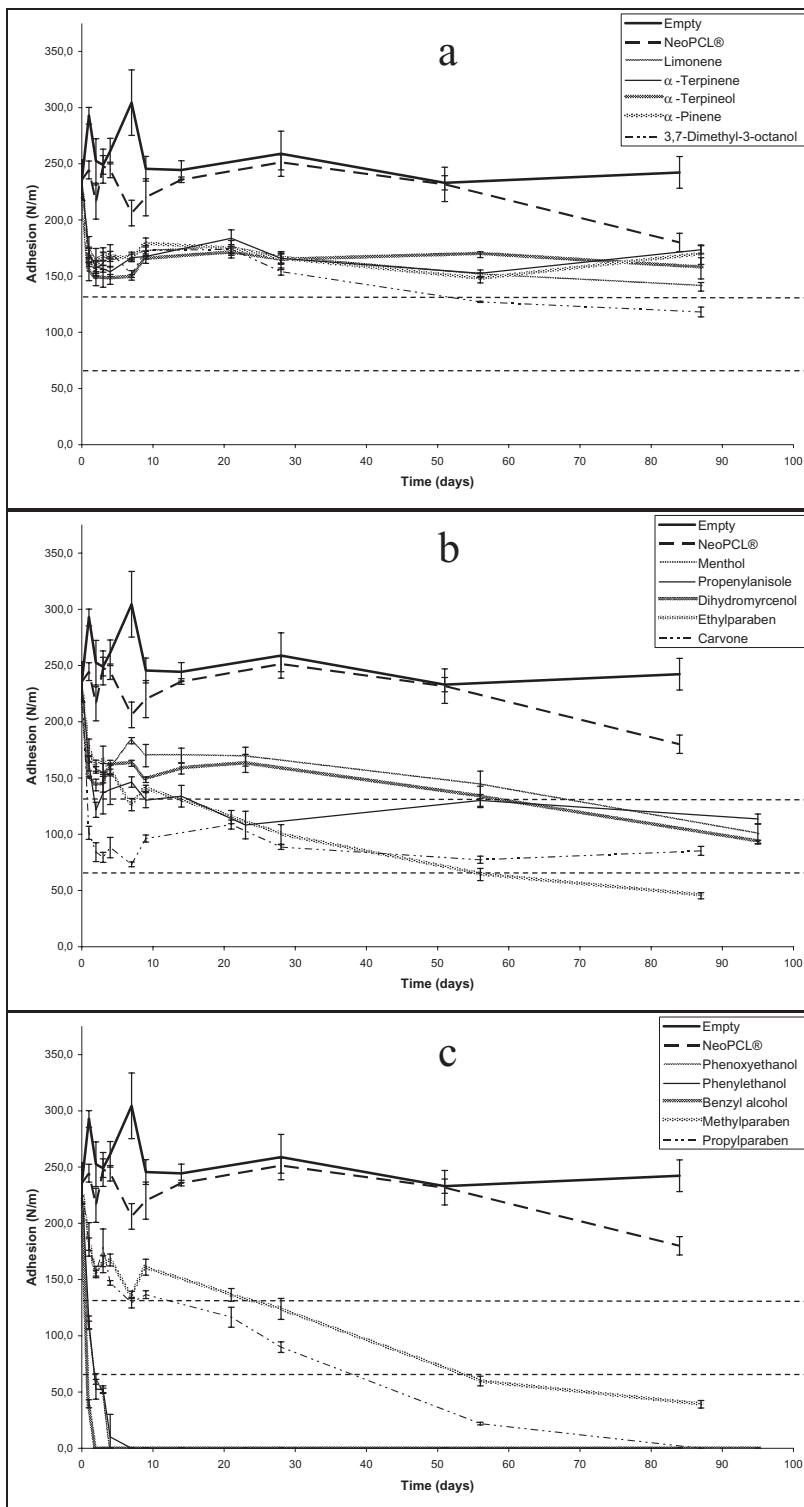**DOI**: 10.1002/pts

Figure 2. Evolution of adhesion strength between LLDPE and Al layers for 10% (m/m) formulations stored in adhesive joint multilayer packaging sachets at 40°C. The dotted lines represent quality (133 N/m) and delamination (67 N/m) levels. Formulations containing (a) limonene, α-terpinene, α-terpineol, α-pinene and 3,7-dimethyl-3-octanol; (b) menthol, propenylanisole, dihydromyrcenol, ethylparaben and carbone; (c) phenoxyethanol, phenylethanol, benzyl alcohol, methylparaben and propylparaben.
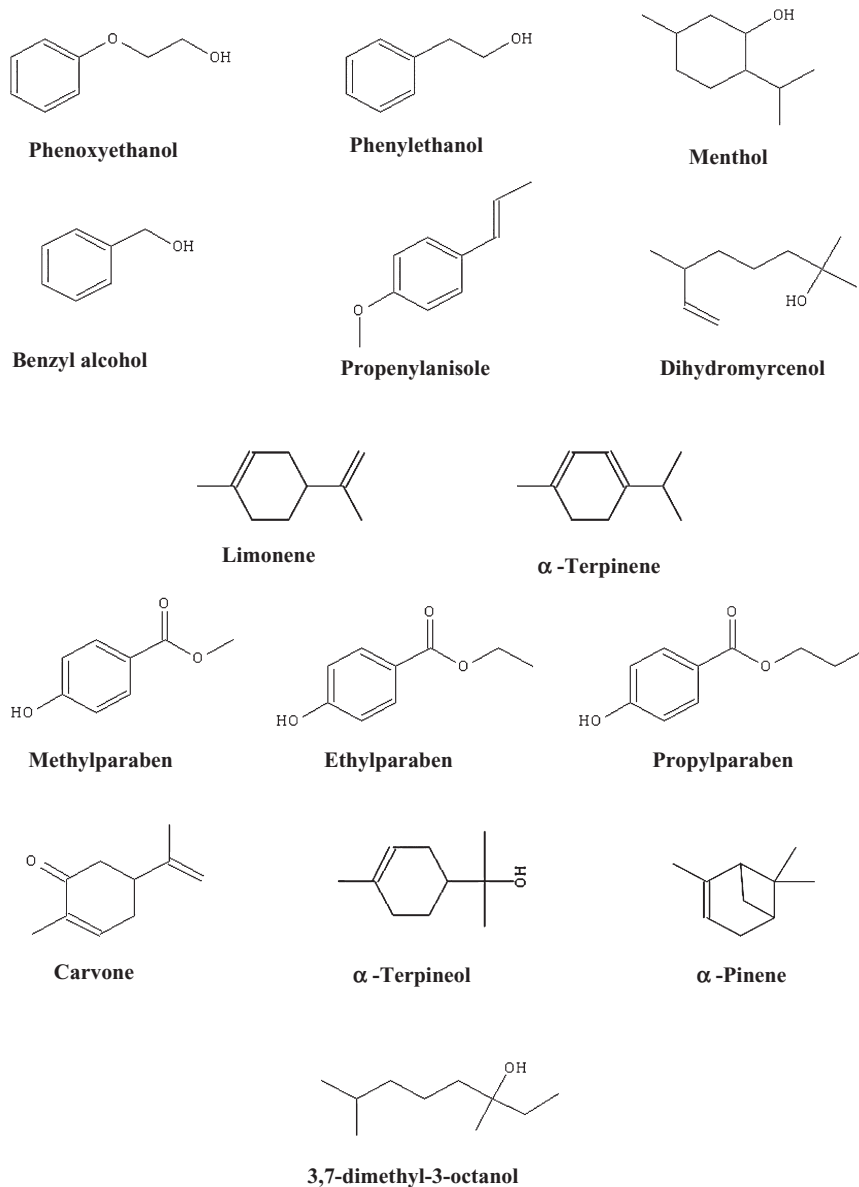
Phenoxyethanol

Phenylethanol

Menthol

Benzyl alcohol

Propenylanisole

Dihydromyrcenol

Limonene

α -Terpinene

Methylparaben

Ethylparaben

Propylparaben

Carvone

α -Terpineol

α -Pinene

3,7-dimethyl-3-octanol

Figure 3. Chemical structure of the cosmetic ingredients studied.

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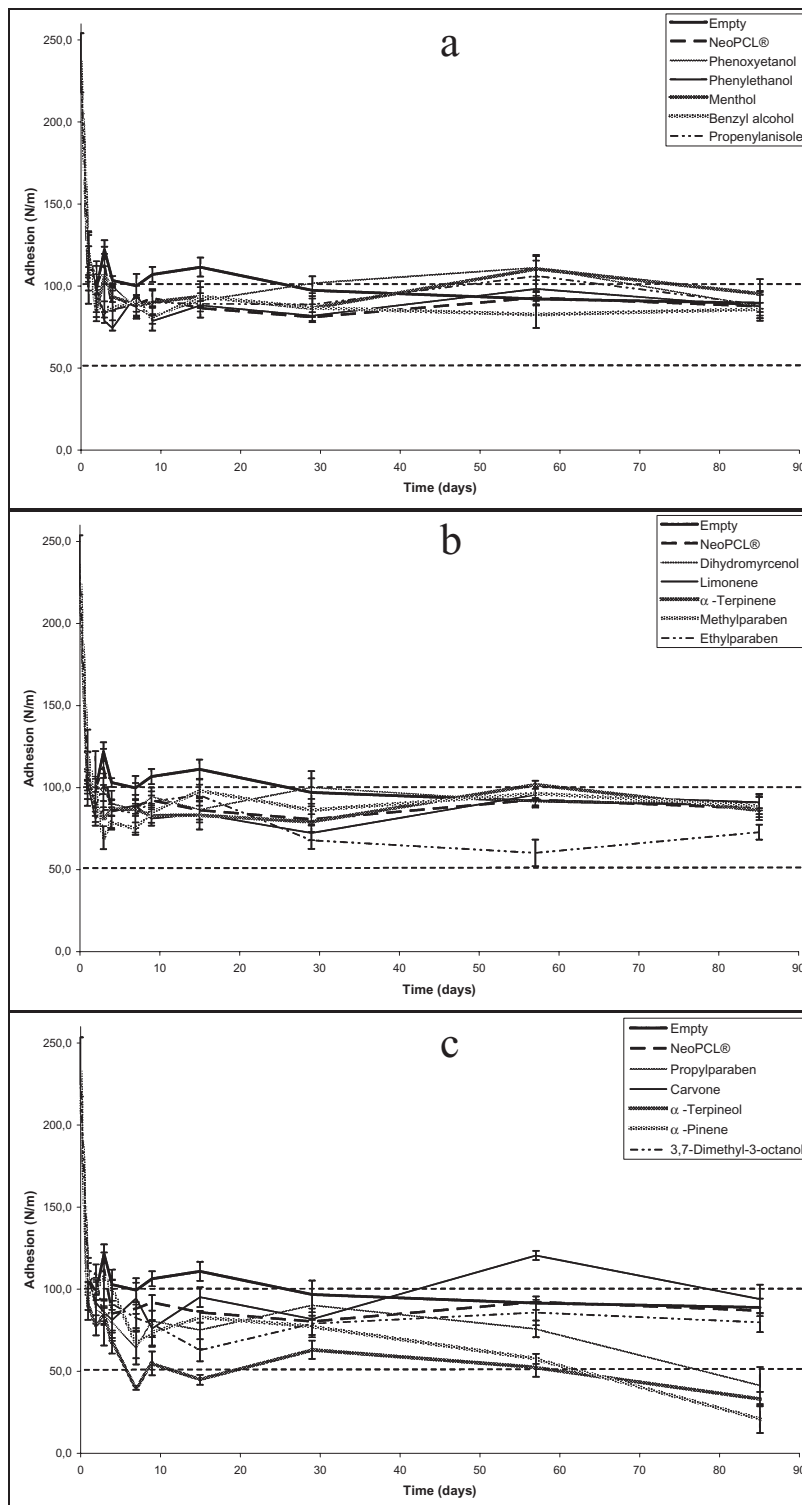**DOI**: 10.1002/pts

Figure 4. Evolution of adhesion strength between LLDPE and Al layers for 1% (m/m) formulations stored in extrusion-coated multilayer packaging sachets at 40°C. The dotted lines represent quality (100 N/m) and delamination (50 N/m) levels. Formulations containing (a) phenoxyethanol, phenylethanol, menthol, benzyl alcohol and propenylanisole; (b) dihydromyrcenol, limonene, α-terpinene, methylparaben and ethylparaben; (c) propylparaben, carbone, α-terpineol, α-pinene and 3,7-dimethyl-3-octanol.

Table 1. Summary of the effects of the studied compounds on multilayer packaging adhesion

	Adhesion joint material		Extrusion-coated material	
	1% (m/m)	10% (m/m)	1% (m/m)	10% (m/m)
2-Phenoxyethanol	pass	totally delaminated	pass	delaminated
Phenylethanol	pass	totally delaminated	pass	totally delaminated
Menthol	pass	pass	pass	totally delaminated
Benzyl alcohol	pass	totally delaminated	pass	totally delaminated
p-Propenylanisole	correct	pass	pass	totally delaminated
Dihydromyrcenol	pass	pass	pass	pass
Limonene	correct	correct	pass	totally delaminated
α-Terpinene	correct	correct	pass	totally delaminated
Methylparaben	pass	delaminated	pass	totally delaminated
Ethylparaben	pass	delaminated	pass	pass
Propylparaben	pass	delaminated	delaminated	delaminated
Carvone	correct	pass	pass	delaminated
α-Terpineol	pass	correct	delaminated	totally delaminated
α-Pinene	correct	correct	delaminated	totally delaminated
3,7-dimethyl-3-octanol	correct	pass	pass	pass

Correct: values above quality level; pass: values between quality level and delamination level; delaminated: values below delamination level (after a long period of time); totally delaminated: values below delamination level (after a short period of time).

(see Figure 5). At this concentration level, all the compounds studied except for dihydromyrcenol, ethylparaben and 3,7-dimethyl-3-octanol (Figure 5c) produced complete delamination of the extrusion-coated packaging in a short period of time (adhesion strength below 50 N/m as shown in Figures 5a and b). A complete separation of the layers was observed in a few days for some analytes (menthol, p-propenylanisole, methylparaben and α-pinene).

Table 1 summarizes the effects of all the compounds studied on adhesion for both types of

materials. As can be seen, the most aggressive compounds were phenylethanol and benzyl alcohol, causing the delamination of both materials at a 10% of concentration. The least aggressive compounds were 3,7-dimethyl-3-octanol and dihydromyrcenol with very similar adhesion values to those of the control sachets and both multilayer packaging.

According to these results, extrusion-coated multilayer packaging is prone to delamination (being delaminated by a large number of compounds), while adhesive joint multilayer

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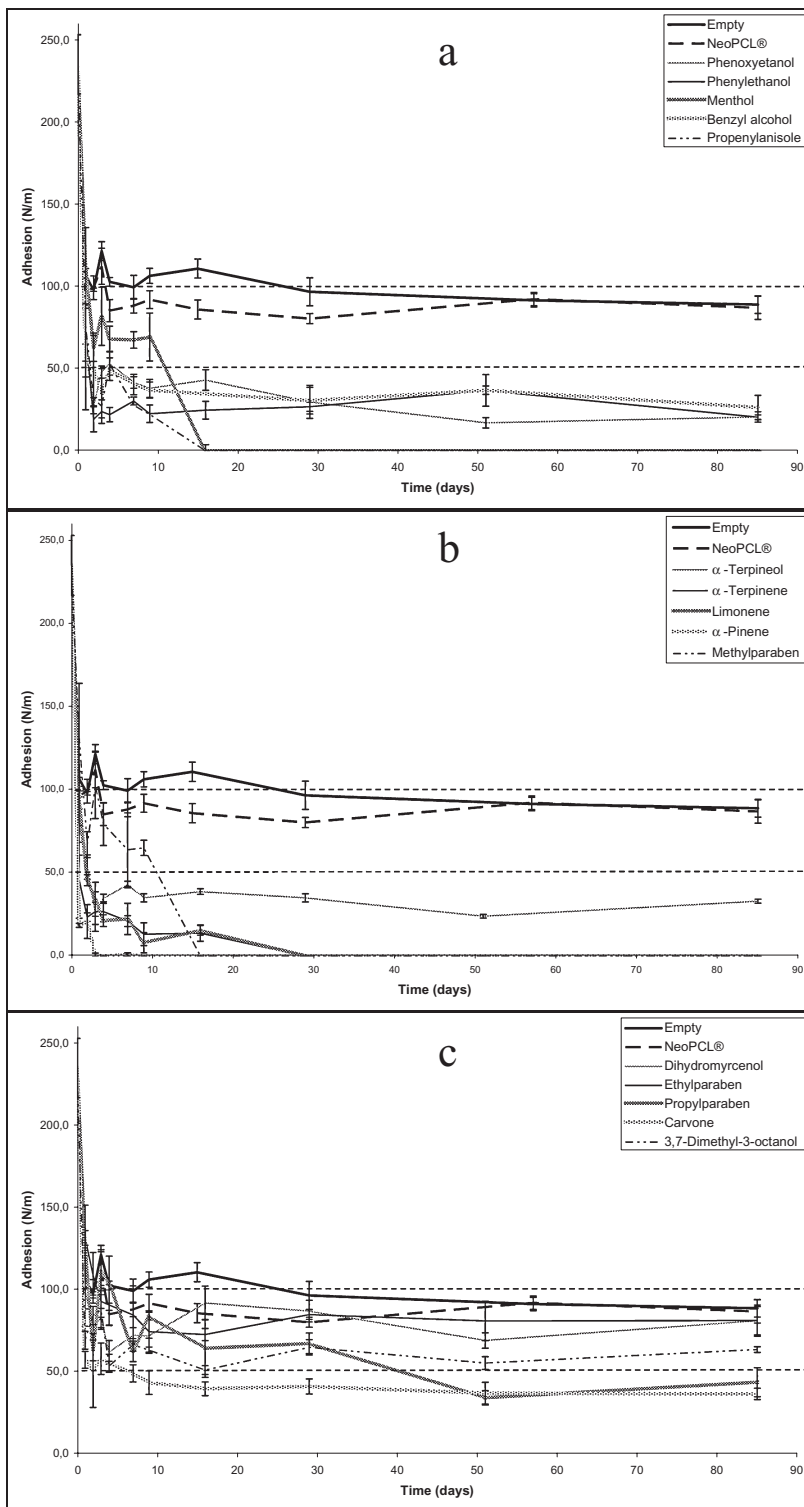**DOI**: 10.1002/pts

Figure 5. Evolution of adhesion strength between LLDPE and Al layers for 10% (m/m) formulations stored in extrusion-coated multilayer packaging sachets at 40°C. The dotted lines represent quality (100 N/m) and delamination (50 N/m) levels. Formulations containing (a) phenoxyethanol, phenylethanol, menthol, benzyl alcohol and propenylanisole; (b) α-terpineol, α-terpinene, limonene, α-pinene and methylparaben; (c) dihydromyrcenol, ethylparaben, propylparaben, carbone and 3,7-dimethyl-3-octanol.

packaging is only delaminated by analytes with a phenyl and a hydroxide group together on their molecule.

As expected, increasing the amount of the volatile compound present in the formulation increased adhesion loss, with 10% (m/m) formulations being more aggressive than 1% (m/m) formulations for both materials.

Analysis of delaminated Al and LLDPE layers by HS-SPME-GC-MS

A previous study[13,16] showed that certain volatile compounds contained in cosmetic products migrate to inner layers of the laminated material. In order to determine the presence of the compounds studied in the inner layers, an HS-SPME-GC-MS analysis of the two delaminated layers was performed. The LLDPE layer was cleaned thoroughly with hot water prior to analysis in order to remove analytes on the surface.

Target analytes were found in all the samples analysed. Figure 6 shows the HS-SPME-GC-MS chromatograms obtained in the analysis of Al layer (of adhesive joint packaging) for some formulations. The presence of the cosmetic ingredients in this foil showed that the compounds migrated through the PE layer. The interaction of the migrated analytes with the bonds between layers was assumed to be the cause of the delamination process.

CONCLUSIONS

The adhesion strength of two types of packaging filled with cosmetic formulations containing com-

pounds suspected to cause delamination was monitored at 40°C throughout storage at 40°C. The study was performed for each compound individually in order to detect their effects on adhesion strength.

The presence of a phenyl and a hydroxyl group in the compound was shown to induce an important loss of adhesion in adhesive joint multilayer packaging. In contrast, 3,7-dimethyl-3-octanol and dihydromyrcenol did not lead to delamination at the two concentration levels studied.

The extrusion-coated multilayer material was the most prone to delamination by the compounds studied. Future research should evaluate the synergetic effects of cosmetic ingredients on delamination.

Additionally, the analysis of the inner layers of the composite by HS-SPME-GC-MS allowed us to detect the compounds resulting from the formulation through the LLDPE layer until the Al barrier, and causing delamination of the packaging material.
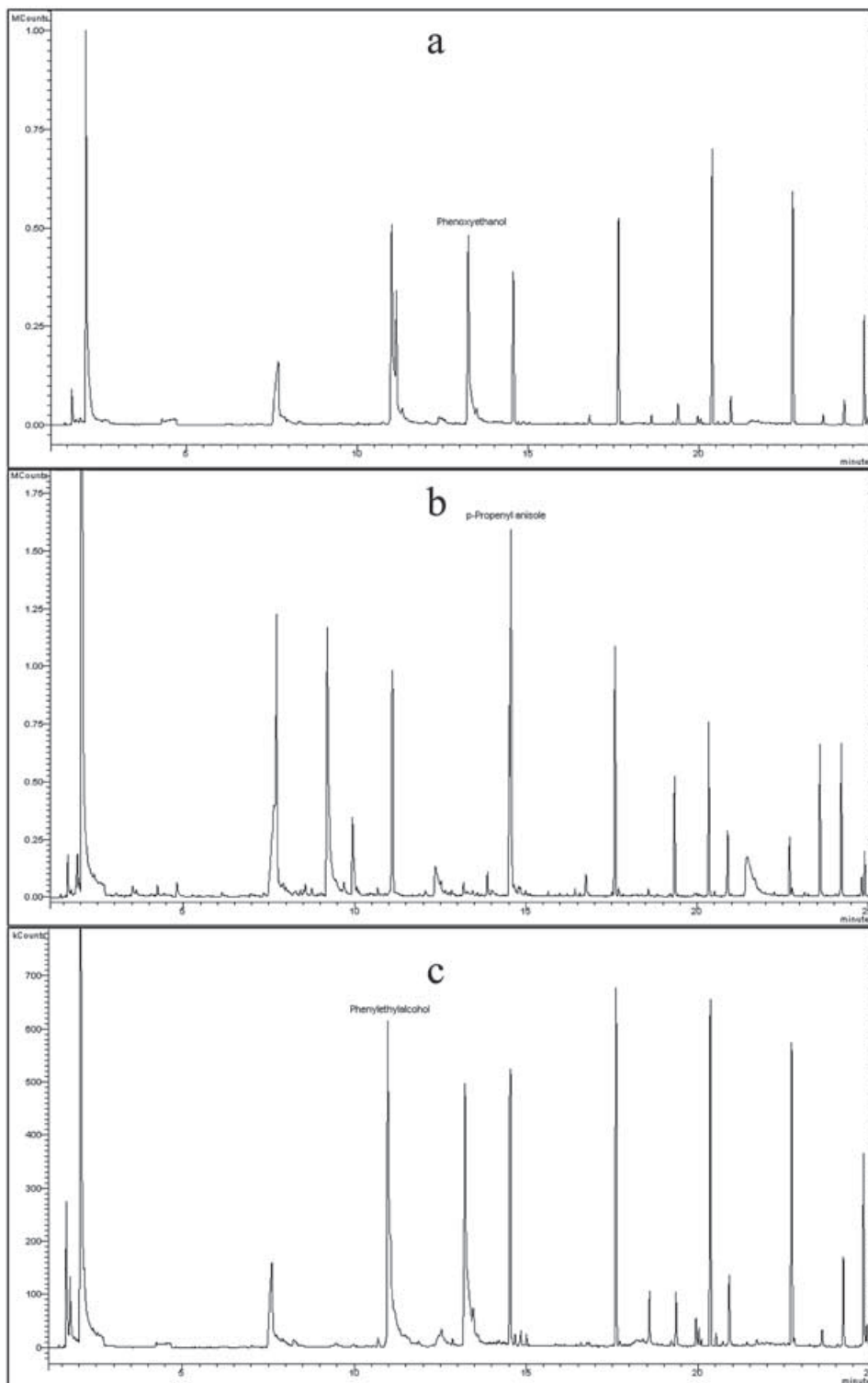
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Figure 6a–c. HS-SPME-GC-MS chromatograms of the Al layer of an adhesive joint multilayer packaging for certain formulations, using a 75 μm CAR-PDMS fibre. For the HS-SPME-GC-MS conditions, see Experimental: (a) 1% m/m phenoxyethanol; (b) 1% m/m p-propenylanisole; (c) 1% m/m phenylethylalcohol.
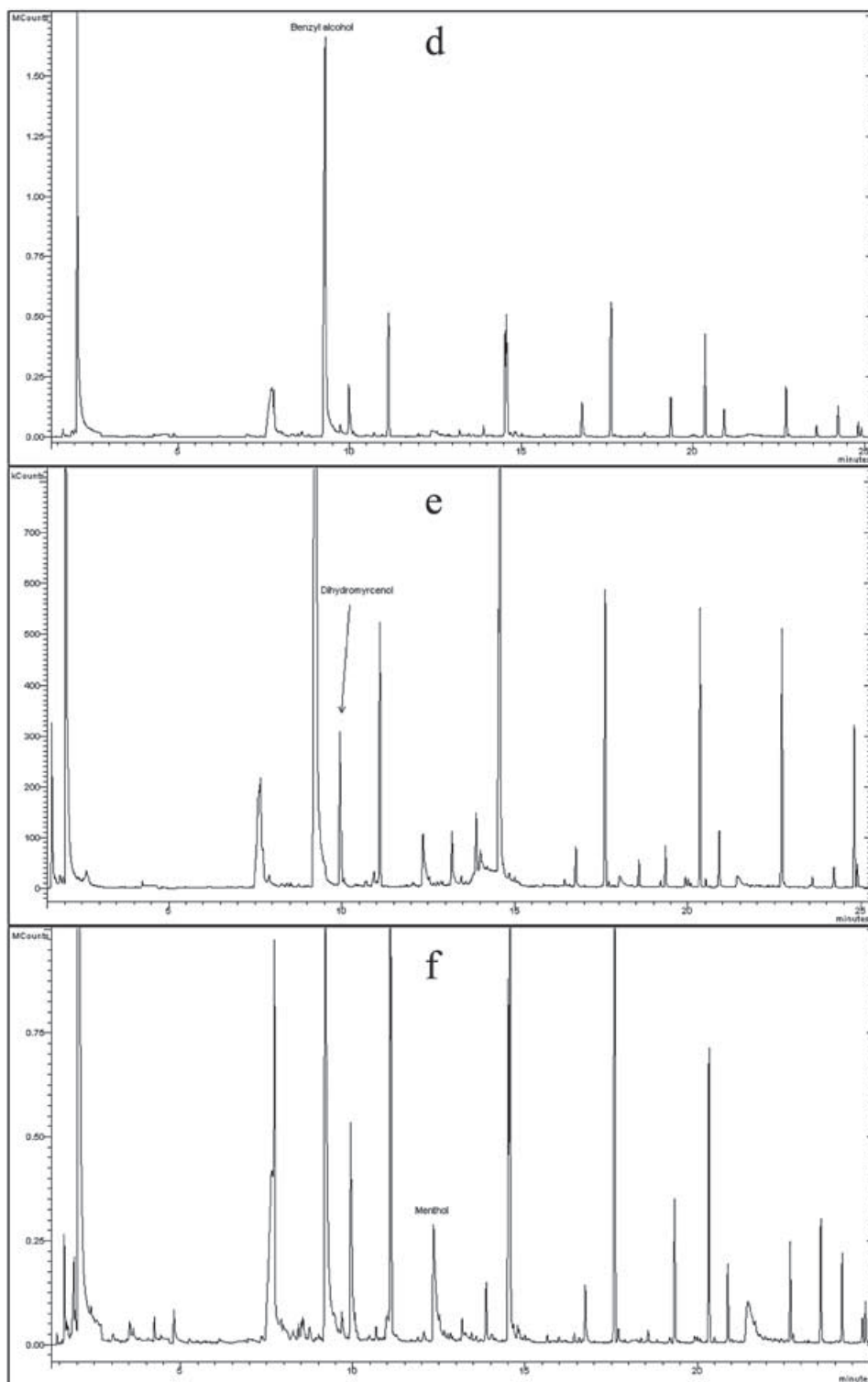
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Figure 6d–f. (d) 1% m/m benzyl alcohol; (e) 1% m/m dihydromyrcenol; and (f) 1% m/m menthol in NeoPCL® cream.

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