

RESEARCH ARTICLE

Specific migration of caprolactam and infrared characteristics of a polyamide/polyethylene composite film for food packaging under conditions of long-term storage before use

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Caprolactam is the monomer typically used for the production of polyamide 6 films. Originating from incomplete polymerization reactions, caprolactam can remain part of the final food packaging and has the potential to migrate from the plastic packaging into the packed good. For film and food producers as well as for end users, it is of great interest that the conformity of a film with migration limits is ensured over its lifetime and that environmental conditions do not affect the migration behavior inadequately. In this work, we have investigated the long-term storage characteristics of a polyamide/polyethylene (PA/PE) film over a storage period of 40.5 months with respect to the specific migration rate of caprolactam. Within statistical indicators, this rate is stable over the complete storage period. Different exposure conditions were applied to the same PA/PE film to accelerate the aging process. Alterations under forced aging conditions (elevated temperature and ultraviolet radiation) were studied by Fourier transform infrared (FTIR) spectroscopy to detect possible chemical changes in the polymer bulk and, by the use of the attenuated total reflection method, on the sample surface. The film was subjected to an extraction study to verify the results obtained using FTIR. Additionally, mechanical tensile tests were carried out. Indication for alterations regarding caprolactam under the different storage conditions were found. The results clearly show that photo-oxidative conditions led to changes in the chemical and mechanical properties of the film. New chemical species occurred caused by degradation of the polymers and their contribution to chemical migration is discussed.

KEYWORDS

caprolactam, food packaging, long-term storage, photo-oxidation, specific migration, UV

1 | INTRODUCTION

The migration of chemical substances from plastic packaging material into foodstuff has been the subject of discussion for years: public interest was gained, for example, by the substances bisphenol A¹ and phthalates,² which can migrate from the packaging into the packed

good and are both classified as hormone-active substances.³ The transfer of substances from packaging into food is regulated by Regulation (EC) no 1935/2004 article 3⁴: materials and articles "intended to come into contact with food must be sufficiently inert to preclude substances from being transferred to food in quantities large enough to endanger human health or to bring about an unacceptable change

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in the composition of the food or a deterioration in its organoleptic properties.” In order to regulate the migration of relevant chemical substances from plastic into food, specific migration limits were set according to EU Regulation 10/2011.⁵ Aside from the overall migration, the regulation governs the specific migration of monomers used for the production of plastic packaging like caprolactam, the monomer used for the production of polyamide 6 (PA 6) films. Besides other nylon resins like polyamide 66 or polyamide 11, PA 6 films manufactured by the polymerization of ϵ -caprolactam are listed, for example, by the U.S. Food and Drug Administration to be safely used to produce articles intended for use in processing, handling, and packaging food.⁶ If the polymerization reaction is incomplete, caprolactam remains as part of the final plastic product^{7,8} and has the potential to migrate from the plastic product into the materials or food in contact with the plastic. Caprolactam is not unobjectionable in terms of consumer protection: according to EU-GHS classification, an acute toxicity (category 4) is established if inhaled or swallowed.⁹ Therefore, a total specific migration limit (SML (T)) was set in the EU Regulation 10/2011⁵ for the monomer caprolactam and caprolactam sodium salt to 15 mg/kg. Plastics manufactured for food contact like packaging films will be tested for legal compliance with the specific migration limit (SML) or SML (T) in general shortly after the manufacturing process. However, two aspects need to be further taken into account: during its lifetime, the film undergoes a natural aging process and the film is in constant contact with environmental conditions, which may accelerate the degradation process.¹⁰ Therefore, it is of strong interest to investigate the chemical and physical properties of a packaging during its entire lifetime. The overall migration behavior under long-term storage was already investigated for a polyamide/polyethylene (PA/PE) film, and it was concluded that the limited migration potential is preserved over the lifetime of the film and even improved with regard to consumer protection because the overall migration rate was decreasing under prolonged time of storage.¹¹ However, the most important monomer of PA 6, caprolactam, is not covered by the overall migration testing procedure.¹² Only a few publications are dealing with the stability of caprolactam under storage conditions. Pramoda et al.¹³ reported a thermal decomposition of PA above 300°C with the evolution of caprolactam followed by other volatiles. Contradictory results on the residual level of caprolactam after γ -irradiation were described by Araújo et al.¹⁴: the examined multilayer PA 6 films showed an increase, reduction, or no modification of the residual caprolactam level after irradiation when compared with nonirradiated films of the same type. The authors concluded that an increased residual caprolactam level occurs due to degradation of the polymer, whereas a reduction could be caused by crosslinking of caprolactam monomers with other compounds. In a previous work, Funk et al.¹¹ reported that the caprolactam migration under simultaneous ultraviolet (UV) and heat treatment appeared to be smaller than for standard testing conditions of 10 days at 40°C but without significant differences. Stoffers et al.¹⁵ monitored the stability of different migrants in polymers over 12 months applying different storage temperatures in the context of material characterization. Stability was observed for caprolactam in a PA 6 polymer, but the findings were not documented

in detail. To the best of our knowledge, migration data of the monomer caprolactam after long-term storage of packaging films are presently not available.

In this work, the migration characteristics of caprolactam are studied for a PA/PE composite film under long-term storage conditions for 1215 days with migration experiments periodically carried out under the inspection conditions of 10 days at 40°C with the different food simulants ethanol 10%, ethanol 50%, distilled water, or 3% aqueous acetic acid. The relevance of the present findings is proven by migration analysis of two independently produced samples of the same type. Additionally, different exposure conditions were applied to the same PA/PE film to accelerate the aging process. The alteration behavior under forced aging conditions was studied by Fourier transform infrared (FTIR) spectroscopy to detect possible chemical changes in the polymer film and on the sample surface. An additional extraction study was performed to detect nonintentionally added substances (NIAS). Mechanical tensile tests were carried out to examine from which point on the degradation starts to affect the mechanical characteristics of the composite films.

2 | MATERIALS AND METHODS

Three rolls of PA/PE composite films (80- μ m PA; 120- μ m PE) encoded RM-WS F 1, RM-WS F 11, and RM CP B F 18 were obtained from a commercial packaging manufacturer. All three films were manufactured according to the same manufacturing process. Details of the production process of the film, its field of application, and homogeneity considerations were published elsewhere.¹¹ All experiments were performed on these commercial composite films in order to provide relevant comparability of the results as opposed to investigations on pure PE and/or PA films, which would, however, be quite instructive for future fundamental assignments.

2.1 | Specific migration testing for caprolactam under long-term storage

For reasons of statistical evidence, the samples were examined by experienced and, to a large extent, accredited laboratories. The examination of the samples for the specific migration of caprolactam was measured in the framework of several proficiency testing (PT) schemes designed according to Eurachem Guide PT type 3.b¹⁶: randomly selected samples that stem from the same homogeneous sample film following the specified storage time and conditions were distributed simultaneously to the participating laboratories for concurrent measurements. At annual intervals, PT schemes were carried out with the sample material under comparable testing conditions to estimate the specific migration behavior of caprolactam.

The PA part of the plastic film was chosen as the contact side with the food simulant because this side was regarded the primary potential source of caprolactam, the substance of interest. Despite reverse use in food packaging, this test geometry ensured a good

sensitivity of the migration characteristics from the PA part of the films toward the present external variations of the test conditions and, further, ensured compatibility to an earlier study under different environmental conditions.¹¹ Beyond this, direct contact of PA to foodstuffs is relevant in a number of other applications.¹¹

For this purpose, the participating laboratories received the above-mentioned PA/PE films RM-WS F 1, RM-WS F 11, and RM CP B F 18 to perform the specific migration testing of caprolactam. The migration testing had to be examined in one-sided contact to the food simulants ethanol 10%, ethanol 50%, acetic acid 3%, and distilled water under consideration of the testing conditions of 10 days at 40°C. Testing conditions were chosen to simulate a long-term contact according to directives 85/572/EEC¹⁷ and 82/711/EEC¹⁸ rather than EU Regulation 10/2011⁵ for comparison purposes with existing data. According to the current legislation, testing for 10 days at 40°C is still valid and required to test for compliance with the SML or SML (T) in long-term contact under refrigerated or frozen storage conditions. Additionally, EU Regulation 10/2011⁵ allows to use migration conditions of 10 days at 40°C for long-term storage conditions at room temperature “if there is scientific evidence that migration of the respective substance in the polymer has reached equilibration under this test condition.”

As an additional blank experiment, migration was also studied at 60°C with the film RM-WS F 11 for the food simulant distilled water. It was reported earlier that the migration of caprolactam under simultaneous UV and heat treatment (sample heated to 60°C by UV illumination) appeared to be smaller compared with standard testing conditions of 10 days at 40°C for the food simulant distilled water, but without significant differences between both best estimates (coverage factor $k = 1$ for probability $P = 68.3\%$).¹¹ To differentiate between a possible influence of either UV or increased temperature, it was investigated whether moderate heat (60°C) could cause changes in migration within a subsequent PT round. Furthermore, since the EU Regulation 10/2011⁵ became effective, it is now valid legislation that specific migration testing conditions for 10 days at 60°C cover long-term storage at room temperature.

The results of each PT scheme were submitted to the German Reference Office for Proficiency Testing and Reference Materials (DRRR GmbH) where the statistical evaluation was performed. DRRR GmbH is accredited according to DIN EN ISO/IEC 17043:2010¹⁹ for the performance of PT schemes. Details of the present PT schemes can be obtained from DRRR under the following designations: RVEP 0989, RVEP 10159, RVEP 11235, RVEP 12324, RVEP 14555, RVEP 150193, and RVEP 180738. The accreditation of DRRR GmbH covers the competence to do the statistical evaluation of datasets generated within the scope of PT schemes. Details of the applied statistical methods to define the best estimate for the true value for the single datasets have been published elsewhere.¹¹ For reasons of statistical evidence, the standard deviation of the best estimate for the true value was considered together with the best estimate. For the comparison of two datasets, the standard deviation multiplied with the coverage factor $k = 1$ ($P = 68.3\%$) is applied. A significant difference

between two datasets is only stated if the standard deviations of the corresponding mean values do not overlap.

2.2 | IR characterization

Infrared (IR) spectra without contact to a food simulant were recorded in transmission mode by the use of a Perkin Elmer Spectrum BX FT-IR System (for RM WS F 11) using Spectrum v 5.0.1 software or a Perkin Elmer Spectrum Two FT-IR Spectrometer (for RM CP B F 18) using Spectrum 10 software. Spectra were obtained by averaging over eight scans with a resolution of 4 cm^{-1} . Those spectral regions, which were identified to be of interest due to changes as well as the regions which showed complete absorption (0% T), were additionally investigated in the attenuated total reflection (ATR) mode to characterize the PA and PE sides of both films.

Different exposure conditions of either UV with simultaneous heat exposure or solely heat exposure were conducted prior to measurements to accelerate the aging of the composite film: the samples exposed solely to heat were stored at air under 48–50°C, chosen to be above 40°C which was the standard migration temperature in this work but below 60°C chosen to gain comparative migration data. A typical day–night rhythm was established with 10 h of heat exposure per day and nonexposure at ambient temperature for 14 h per day for samples exposed for 1, 2, 4, 7, and 10 days. The samples exposed for 84 days were exposed for 8 h per day on average and under nonexposure for 16 h, respectively. Blank samples (kept in the dark at room temperature) were measured at the beginning (encoded blank sample 1) of the exposure phase and at the end after 84 days (encoded blank sample 2).

The exposure conditions of UV and simultaneous heat exposure were chosen identical to the conditions applied earlier for the global migration experiments¹¹ to examine spectroscopically whether concurrent UV and heat exposure has an impact on caprolactam migration. An ULTRA-VITALUX lamp manufactured by OSRAM was used because of its sun-like radiation spectrum. The sample temperature was adjusted to 60°C during exposure. Further details were published elsewhere.¹¹ The exposure conditions were established under the same day–night rhythm as for the samples stored under 48–50°C. Additionally, one sample exposed to UV for 39 days and stored afterwards in the dark at ambient temperature for 12 days and one exposed to UV for 84 days and stored afterwards for 119 days was measured to differentiate between reversible and irreversible degradation phenomena.

2.3 | Mechanical tests

The mechanical tests were performed using a Zwick Roell Z 0.5 at an elongation speed of 200 mm/min and a 100-N load cell leading to a maximum force of 106 N. According to ISO 527-1,²⁰ RM-WS F 11 specimen 1.5 cm wide and about 15 cm long were cut and fixed between two pressure plates at a distance of 10 cm.

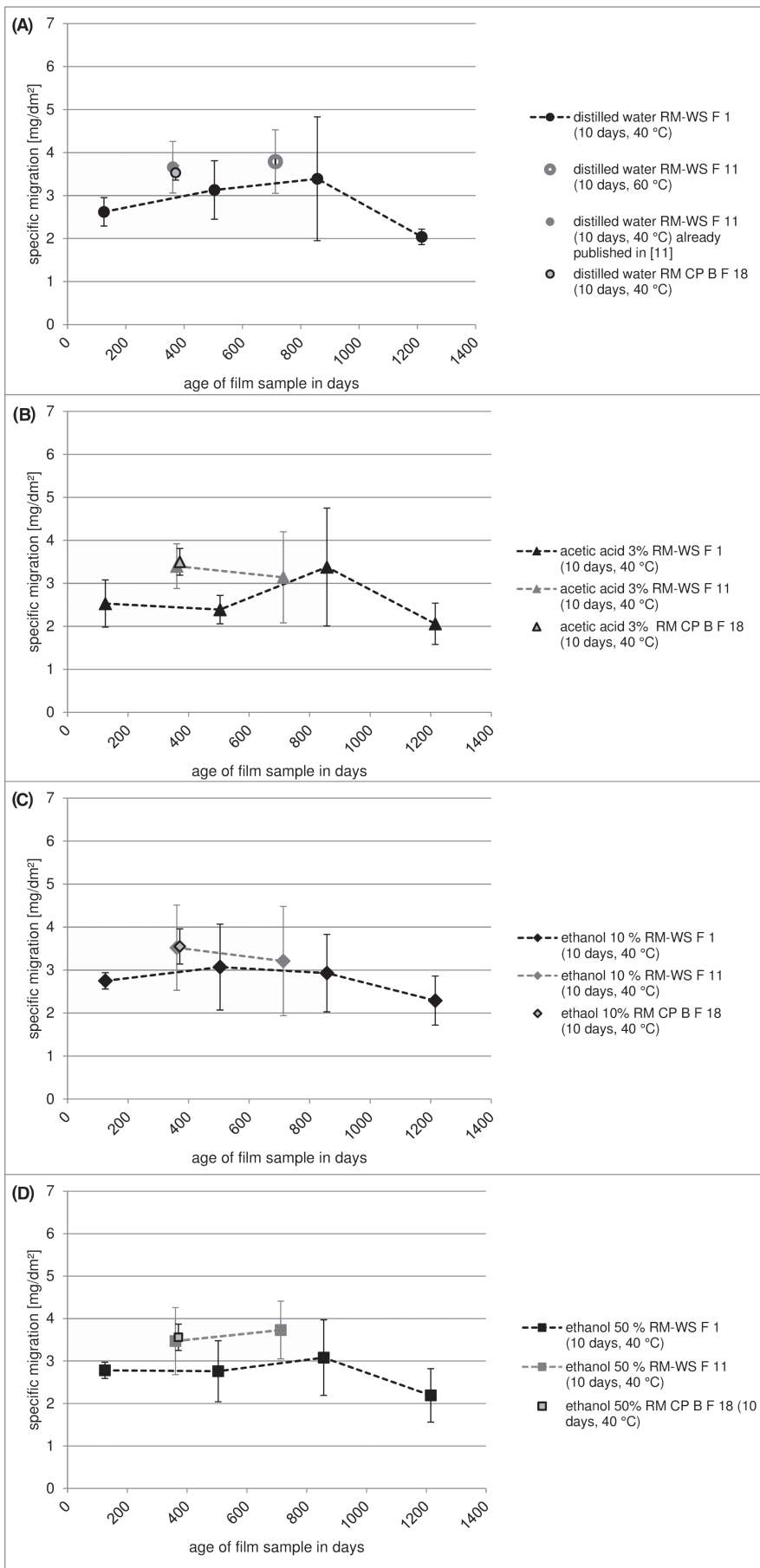


FIGURE 1 Best estimates for the true value of the specific migration of caprolactam (with the corresponding standard deviation) from polyamide/polyethylene films into different food simulants after storage of the packaging film over different periods of time up to 40.5 months prior to testing

TABLE 1 Summary of the statistical data for the specific migration measurements for caprolactam obtained from the long-term monitoring after storage of the PA/PE films RM-WS F 1, RM-WS F 11, and RM CP B F 18 in the dark at room temperature

Food simulating matrix (year of testing, sample material)	Best estimate for the true value (<i>mbest</i>) (mg/dm ²)	Standard deviation of the best estimate for the true value (<i>sbest</i>) (mg/dm ²)	Uncertainty of the best estimate for the true value (95.5%) (mg/dm ²)	Number of values (<i>n</i>)	Applied statistics	Corresponding χ^2 value
Distilled water (2010, RM-WS F 1)	2.62	0.33	0.53	4	Robust	1.24
Distilled water (2011, RM-WS F 1)	3.13	0.68	0.48	10	Robust	1.90
Distilled water (2012, RM-WS F 1)	3.39	1.44	2.29	4	Sensible statistics, all values	1.24
Distilled water (2013, RM-WS F 1)	2.04	0.18	0.17	7	Robust	1.69
Distilled water (2015, RM-WS F 11) already published in Funk et al. ¹¹	3.66	0.60	0.50	8	Sensible statistics with outlier elimination	0.90
Distilled water (2016, RM-WS F 11) conditions: 10 days, 60°C	3.79	0.74	0.62	8	Sensible statistics with outlier elimination	0.90
Distilled water (2019, RM CP B F 18)	3.53	0.17	0.15	8	Sensible statistics with outlier elimination	0.17
Acetic acid 3% (2010, RM-WS F 1)	2.53	0.55	0.88	4	Robust	1.24
Acetic acid 3% (2011, RM-WS F 1)	2.39	0.33	0.24	10	Sensible statistics with outlier elimination	0.48
Acetic acid 3% (2012, RM-WS F 1)	3.38	1.37	2.17	4	Sensible statistics with outlier elimination	1.24
Acetic acid 3% (2013, RM-WS F 1)	2.06	0.48	0.50	6	Robust	0.01
Acetic acid 3% (2015, RM-WS F 11)	3.40	0.52	0.37	10	Sensible statistics with outlier elimination	1.22
Acetic acid 3% (2016, RM-WS F 11)	3.14	1.06	0.71	11	Sensible statistics with outlier elimination	2.52
Acetic acid 3% (2019, RM CP B F 18)	3.50	0.31	0.14	21	Robust	1.04
Ethanol 10% (2010, RM-WS F 1)	2.75	0.19	0.29	4	Robust (median; MAD)	-
Ethanol 10% (2011, RM-WS F 1)	3.07	1.00	0.72	10	Sensible statistics, all values	1.65

(Continues)

TABLE 1 (Continued)

Food simulating matrix (year of testing, sample material)	Best estimate for the true value (<i>m_{best}</i>) (mg/dm ²)	Standard deviation of the best estimate for the true value (<i>s_{best}</i>) (mg/dm ²)	Uncertainty of the best estimate for the true value (95.5%) (mg/dm ²)	Number of values (<i>n</i>)	Applied statistics	Corresponding χ^2 value
Ethanol 10% (2012, RM-WS F 1)	2.93	0.90	1.42	4	Sensible statistics, all values	1.24
Ethanol 10% (2013, RM-WS F 1)	2.29	0.57	0.60	6	Robust	1.4
Ethanol 10% (2015, RM-WS F 11)	3.52	0.99	0.67	11	Sensible statistics with outlier elimination	3.37
Ethanol 10% (2016, RM-WS F 11)	3.21	1.27	0.91	10	Sensible statistics with outlier elimination	1.65
Ethanol 10% (2019, RM CP B F 18)	3.55	0.40	0.29	10	Robust	2.98
Ethanol 50% (2010, RM-WS F 1)	2.78	0.19	0.29	4	Robust (median; MAD)	-
Ethanol 50% (2011, RM-WS F 1)	2.76	0.72	0.51	10	Sensible statistics, all values	0.32
Ethanol 50% (2012, RM-WS F 1)	3.08	0.89	1.41	4	Sensible statistics, all values	1.86
Ethanol 50% (2013, RM-WS F 1)	2.19	0.63	0.53	8	Sensible statistics, all values	0.17
Ethanol 50% (2015, RM-WS F 11)	3.47	0.79	0.57	10	Sensible statistics with outlier elimination	0.48
Ethanol 50% (2016, RM-WS F 11)	3.73	0.68	0.39	14	Robust	2.94
Ethanol 50% (2019, RM CP B F 18)	3.56	0.31	0.22	10	Sensible statistics with outlier elimination	1.22

2.4 | Extraction study to determine NIAS

A screening of the PA/PE film for NIAS was performed at an external accredited laboratory. The sample of RM CP B F 18 exposed to UV for 39 days and a blank sample of the same film were examined. The samples were extracted with acetonitrile for 2 h at 60°C in an ultrasonic bath. The extract was analyzed by LC-QTOF-MS using a generic method (water/acetonitrile gradient, modified C18 column), by a GC-QTOF-MS/FID screening method (PTV injection, DB-5 column, and electron impact ionization), and by headspace GC-MS screening (weighing the samples directly into a headspace vial, heating to 100°C for 60 min; after which, 1 ml of the resulting gas phase was injected into the gas chromatograph).

3 | RESULTS AND DISCUSSION

3.1 | Long-term migration studies

Because caprolactam can be considered the most important migrant from PA 6 films, its specific migration behavior is of particular interest. The long-term migration behavior of caprolactam was investigated after storage of the packaging film in the dark for a period of up to 1215 days (40.5 months) (Figure 1). Despite apparent changes in the best estimate of the true value, a significant difference between the best estimates of caprolactam migration from RM-WS F 1 over time cannot be stated in view of the corresponding standard deviations ($k = 1$, $P = 68.3\%$). Results for the films RM-WS F 11 and RM CP B F

18 are also included, showing the results for the caprolactam migration that were determined in three independent PTs under comparable testing conditions. A value determined for the simulant distilled water after storage for 10 days at 60°C is also included.

Caprolactam migration to all food simulants is slightly higher for the films RM-WS F 11 and RM CP B F 18 than the estimated result at the same age for the film RM-WS F 1. Taking into account the standard deviations ($k = 1$, $P = 68.3\%$) of the best estimates for the true values (Table 1), however, the results are not significantly different. All three films revealed quite similar migration characteristics and reproducible stability of the film properties under storage pointing at the reproducibility of film preparation, storage, sample preparation, and PT reliability.

The results clearly show no significant difference in efficiency of the chosen food simulating matrices under the storage conditions of 10 days at 40°C. The absolute amount of migration and the time-related development of migration are similar between the different food simulants in the context of their corresponding standard deviations ($k = 1$, $P = 68.3\%$). According to Heimrich et al.,²¹ aqueous/ethanolic simulants are worst-case simulants for caprolactam due to their polar character. For the food simulant distilled water, it was proposed earlier that it is likely that almost the total amount of caprolactam is migrating under the inspection conditions of 10 days at 40°C.¹¹ The results of the migration experiment shown here support the assumption that also for the other examined simulants, it is likely that almost the total amount of the monomer caprolactam is migrating under the inspection conditions of 10 days at 40°C.

To discuss the influence of an increased temperature during the migration tests of caprolactam, an additional round of migration experiments was conducted at 60°C with the film RM-WS F 11 for the simulant distilled water (Figure 1). Under standard testing conditions of 10 days at 40°C, a best estimate for the true value of 3.66 mg/dm² for RM-WS F 11 had already been determined for the food simulant distilled water.¹¹ In a subsequent PT under testing conditions of 10 days at 60°C, RM-WS F 11 showed a migration of 3.79 mg/dm², apparently slightly higher but still within the standard deviation ($k = 1$, $P = 68.3\%$). Thus, it is concluded that a temperature difference of 20°C during testing does not lead to a change in the specific migration of caprolactam after 10 days. This observation clearly confirms the assumption that the total available amount of caprolactam already migrates under the conditions of 10 days at 40°C. Furthermore, a decomposition of caprolactam was not observed by heat at moderate temperature.

To further clarify the kinetics of caprolactam migration at 40°C, additional migration experiments with shorter contact times would be needed. According to the literature, the absolute proportion of caprolactam migration slightly decreased from distilled water (migration conditions of 2 h at 100°C) to 50% ethanol to 95% ethanol (both with migration conditions of 3.5 h at 60°C).²¹ A full extraction of the initial amount of caprolactam into the simulant distilled water was observed for migration conditions of 2 h at 100°C. Although it is likely that the migration rate at 40°C differs for the single simulants when shorter contact times are applied, saturation is reached after the present

longer contact times of 10 days, as also required by the EU Regulation 10/2011⁵ to simulate long-term contact. Because none of the tested simulants was more effective than others over 10 days at 40°C, costs for compliance testing regarding caprolactam can be decreased by the use of just one simulant (food simulant A, B, or D1) within the framework of existing regulations.

After being repeatedly observed in all time series, the best estimates for the true values for the specific migration of caprolactam obtained after 40.5 months of film storage for all food simulants seem to be lower than those after shorter storage. Under the present experimental conditions (from the PA side of the film), the specific migration of caprolactam was repeatedly higher than its SML (T) of 2.5 mg/dm² (calculated by the conventional conversion factor from SML (T) = 15 mg/kg), but all best estimates for the true values after 40.5 months of storage are lower than the SML (T). Despite hard statistical evidence missing, it is indicated that caprolactam migration is slightly decreasing upon prolonged storage of the film. This would go in line with the reported decrease of the overall migration observed earlier over a storage period of 40 months.¹¹ Despite the lack of hard evidence, we suggest a slow postcrystallization of PA as possible origin: when exposed to humid air, PA is known to absorb water, which lowers the glass transition temperature (T_g).²² Because a decreasing T_g increases molecular motion, ongoing crystallization appears reasonable even at room temperature under the present conditions. A decreased migration of caprolactam as indicated in our study could then result from such increased crystallinity.

3.2 | IR spectroscopy

Further characterization of the films was done by means of IR spectroscopy. The bulk polymer and the PA surface as the contact side for the migration testing and source of caprolactam migration were investigated. IR spectra of the films RM-WS F 11 and RM CP B F 18 showed several spectral regions in which the transmission characteristics of the samples differed following photo-oxidative conditions compared with unexposed samples and to samples under thermo-oxidative conditions (Figure 2).

The FTIR spectra of the films are a result of the superposition of the transmission behavior of PA and PE. Caused by the total thickness of the film of 200 μm (80- μm PA; 120- μm PE), the transmittance partially dropped to zero. Those regions were not considered for the discussion of changes for the bulk films (e.g., spectral region between 2975 and 3300 cm^{-1} and between 1201 and 1679 cm^{-1}) but were separately investigated by ATR from the surfaces of the film (see below).

Four relevant regions were identified in Figure 2 for which spectral changes occurred during exposure of the films to either heat or UV/heat: region (a) around 3360–3700 cm^{-1} , region (b) around 1741–2830 cm^{-1} , region (c) around 1680–1740 cm^{-1} , and region (d) around 800–1200 cm^{-1} .

Region (a) is dominated by hydroxyl bands. Changes were determined from transmission between 3360 and 3700 cm^{-1} . The

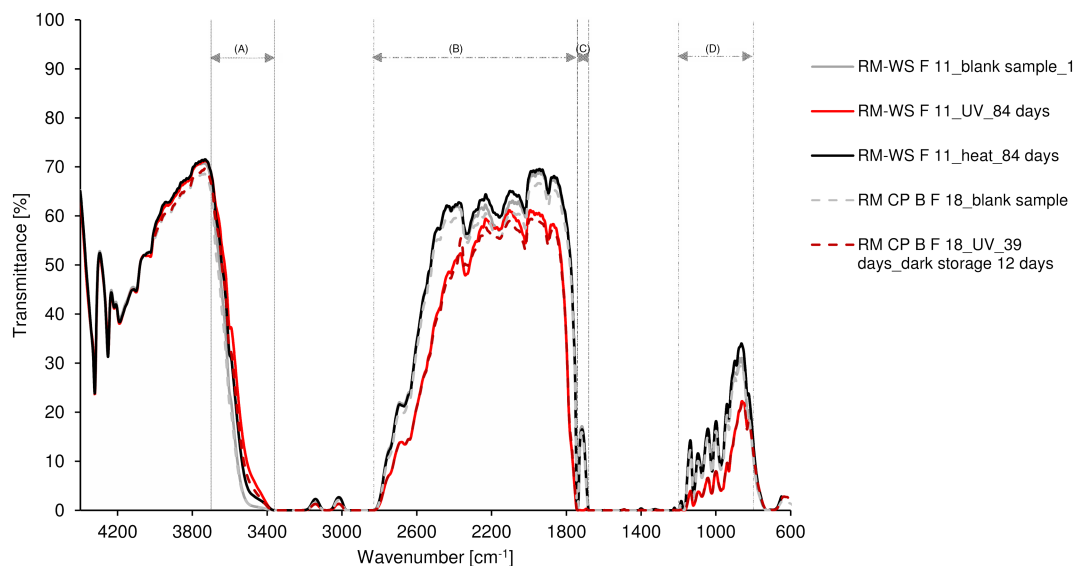


FIGURE 2 Fourier transform infrared spectra of the bulk under different exposure conditions. Spectral changes are indicated by dashed lines. Four regions (a), (b), (c), and (d) are identified whose origin is discussed in the text. Blank sample 2 was measured identical to blank sample 1

transmission increased upon exposure to UV (and heat) but recovered upon storage of samples at ambient air, which indicates that different amounts of absorbed water cause these changes. Because the humidity in air was not explicitly controlled, a discussion of these bands is omitted here (detailed results are included in Figure S1).

Region (b) shows a decrease in the transmission for the sample exposed to UV, however, without any characteristic spectral signature. In this spectral range, neither for PE nor for PA typical bands occurred in the ATR mode (see below). The observed decrease in transmission of the bulk films must, therefore, be caused by morphological alterations, which change the scattering characteristics. In view of the brittleness, which becomes obvious for samples exposed to UV

for 84 days (see below), the assumption of such morphologic change appears reasonable.

Region (c) around $1680\text{--}1740\text{ cm}^{-1}$ is characteristic for carbonyl stretch vibrations. A clear signal that arose after 7 days of UV exposure indicated changes in the transmission characteristics for the bulk: a new absorption (transmission minimum) at $\sim 1715\text{ cm}^{-1}$ occurred, indicating ketone groups as typical oxidation products of PA and PE (Figure 3). It is known that carbonyl compounds like ketones and aldehydes indicate the oxidation of PA and PE.^{23,24} Consistently, a characteristic odor was detected (but not professionally assessed) for films following UV treatment. With increasing exposure time, a continuous oxidation of the composite films took place: for the longest exposure

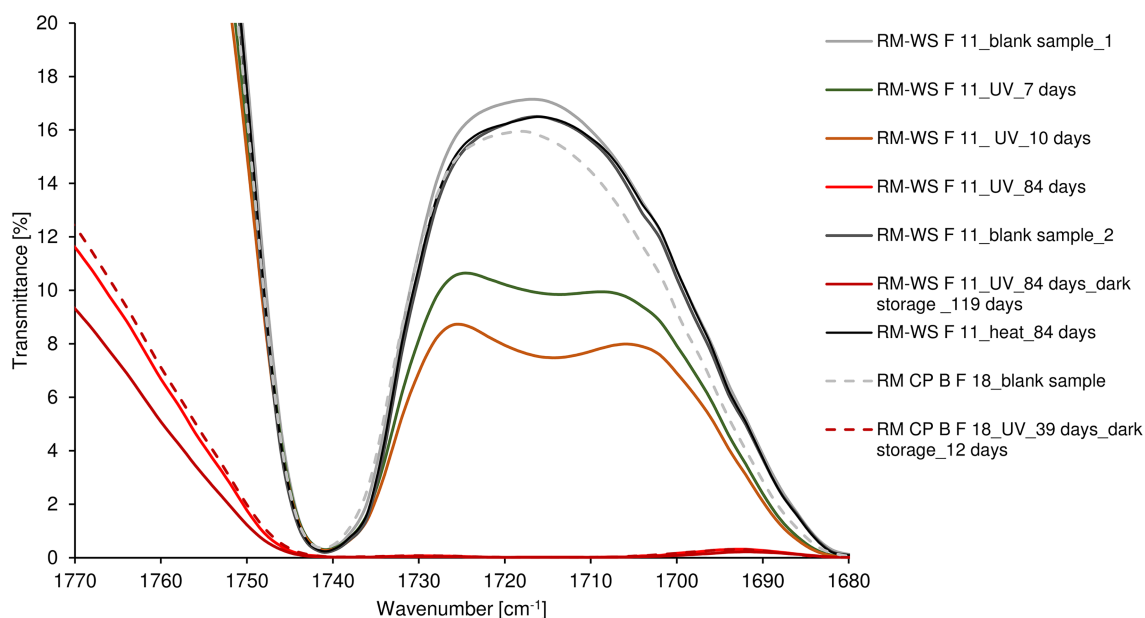


FIGURE 3 Fourier transform infrared spectra for the carbonyl region of samples following different exposure

times to UV of 39 and 84 days, the transmission dropped to almost zero, regardless of whether the samples were measured immediately after exposure or whether exposure was followed by storage for several days or even several weeks before the samples were measured. Changes in the carbonyl region of the films were found to occur irreversibly; permanent damage of the polymer was observed.

Thermo-oxidized samples do not show such change in the carbonyl region. Independent of the chosen exposure time, the samples showed similar transmission as the blank samples. Spectra for the sample exposed to heat for 84 days are exemplarily presented in Figure 3 (black line). The results indicate that a temperature of 48–50°C did not lead to significant thermo-oxidation.

Region (d) shows a decrease in the transmission for the UV-exposed sample. Within this spectral range, one can assume a superposition of bands of the PE and the PA part of the film, for example, absorption of unsaturated moieties in the range between ~ 850 and 1050 cm^{-1} .²⁵

Changes of the IR characteristics on the PA side of the films were investigated in the ATR mode for the carbonyl region. The same decreasing transmission at $\sim 1715\text{ cm}^{-1}$, which was found for the bulk of the polymer, was found on the PA side (Figure 4), in particular in the spectra acquired after 39 and 84 days of simultaneous UV and

heat exposure, confirming the formation of ketones.²³ It is worth to notice that at room temperature, the newly formed components seem to be stable because they are still detected even after storage for 119 days subsequent to the UV and heat exposure. In the case of the thermo-oxidized samples, no such change in the transmission characteristic was observed for the PA surface of RM-WS F 11 (Figure 4), indicating that under the present conditions, no thermo-oxidation of the PA part of the film occurred.

In view of the apparent changes due to accelerated aging conditions, it was examined whether other effects on the PA-part of the composite film can also be found as a consequence of forced aging. For reasons of clarity, only the results of the sample that was exposed for 39 days and the corresponding blank sample are shown. The spectrum from the PA part (Figure 5) shows more IR absorptions typical of caprolactam^{26,27}: a weak signal at 3470 cm^{-1} that indicates NH groups, CH_2 groups at 2935 and 2865 cm^{-1} , the typical amide bands at 1435 cm^{-1} , and the fingerprint pattern in the region 1372 – 1120 cm^{-1} . The signals at 2935 and 2865 cm^{-1} do not undergo any change caused by exposure. Spectral changes can be detected for the signals at 3470 cm^{-1} , 1435 cm^{-1} , and in the fingerprint area. Transmission at 3470 and 1435 cm^{-1} increased with exposure. In the fingerprint area, the transmission for the observed signals is slightly

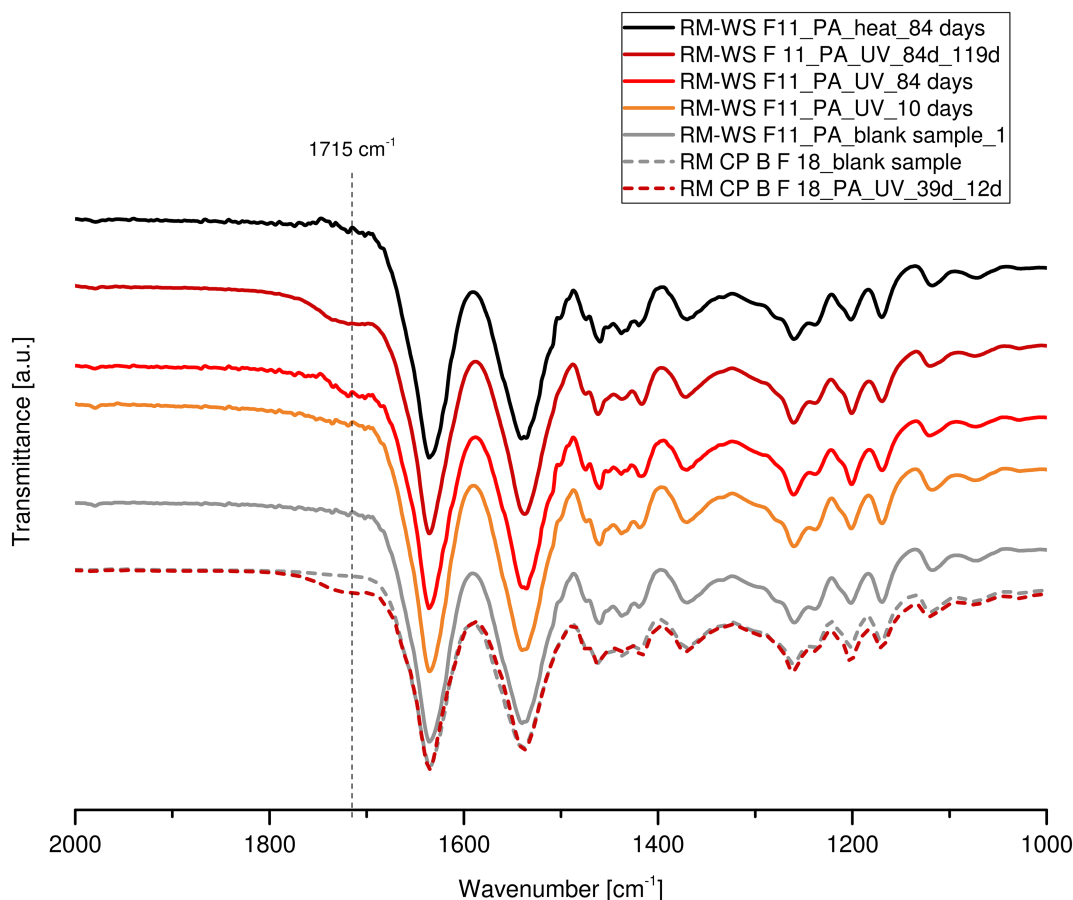


FIGURE 4 Fourier transform infrared-attenuated total reflection spectra of the polyamide (PA) side. The position of the carbonyl stretch vibration assigned to ketones is marked by the dashed line. An offset in arbitrary units (a.u.) is added for detailed comparison aside from the last line

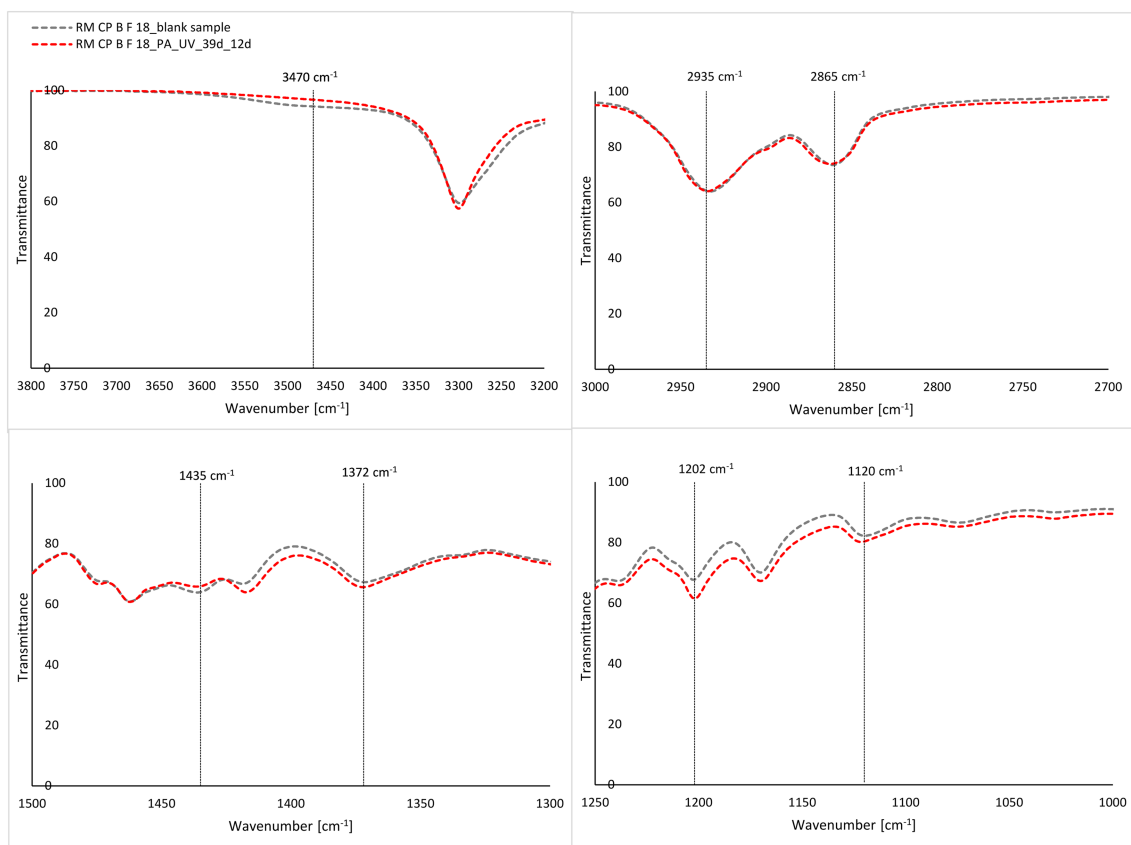


FIGURE 5 Details of the Fourier transform infrared–attenuated total reflection spectra of the polyamide (PA) side for RM CP B F 18 with bands characteristic for caprolactam marked by dashed lines

weaker for the UV-exposed samples compared with the nonexposed samples. The observed changes of individual signals characteristic of caprolactam indicate that the concentration of caprolactam has decreased upon exposure. Extraction of caprolactam from the films before and after exposure was, therefore, explicitly investigated (see below).

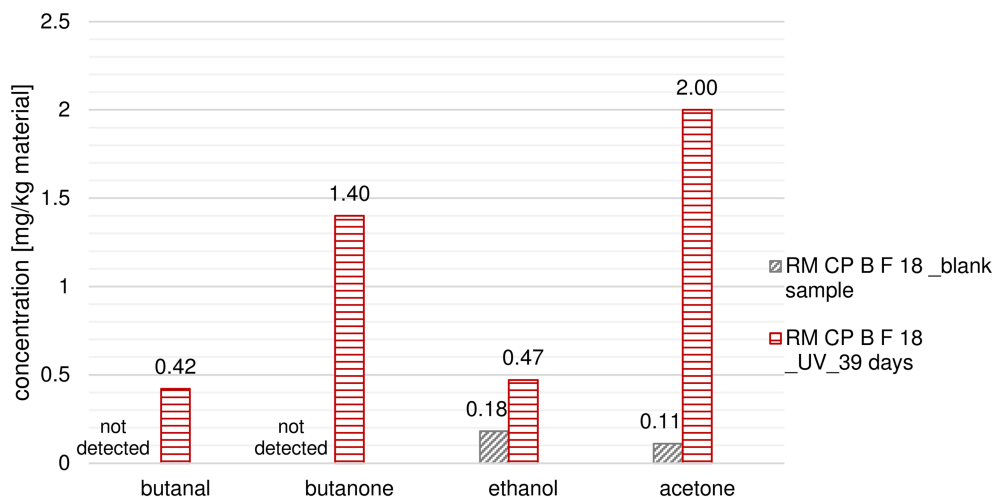
Corresponding measurements in ATR mode on the PE side of the packaging film (Figure S2) showed similar results as those on the PA side: new absorption bands in the carbonyl range occurred on the PE part of the composite film as a consequence of photo-oxidative conditions. The detectable alterations seem to be mainly irreversible. This goes in line with the results reported for the PA surface. It is worth to notice that the newly formed substances in the composite film induced by degradation are defined according to EU Regulation 10/2011⁵ as NIAS. The term NIAS covers reaction by-products, which can be formed during the manufacturing process or during the lifetime of a packaging material.

3.3 | Mass spectrometry on extracts from the differently exposed films to analyze NIAS

An extraction study was performed to verify the results of IR spectroscopy and confirmed that a significant change in the film occurred

under simultaneous UV and simultaneous heat treatment and newly formed substances were extracted from the UV-exposed PA/PE-films (Figures 6 and 7). In the headspace GC-MS analysis, two new substances, namely, butanal (CAS No 123-72-8) and butanone (CAS No 78-93-3) also known as methyl ethyl ketone (MEK), were identified in the extract of the film after 39 days of simultaneous UV and heat exposure, in addition to ethanol and acetone, which were found both in the exposed and in the nonexposed samples. Butanal and MEK correspond well with the findings of the IR investigations, which showed an increase in aldehyde and ketone concentration as typical oxidation products (Figure 6). Fatty acids, a fatty acid ester, and a fatty acid amide were additionally detected in the exposed sample by GC-QTOF-MS/FID (Figure 7). All these compounds are newly formed degradation products that were not detected in the reference sample. Butanal is listed as typical food contact material substance in the EU Regulation 10/2011, but no SML or SML (T) is assigned. MEK on the other hand is a substance that is not listed in EU Regulation 10/2011. Due to its low boiling point around 80°C, MEK is not included in the overall migration investigations, and it is likely that the substance will remain undetected during routine compliance testing. MEK is not unobjectionable in terms of consumer protection: according to EU-GHS classification, a specific target organ toxicity (category 3) and eye irritation (category 2) is established.²⁸ The fatty acids found are non-volatile substances. These substances are, therefore, included in

FIGURE 6 Concentration of substances found in headspace GC-MS screening after extraction of RM CP B F 18 before and after exposure to UV for 39 days



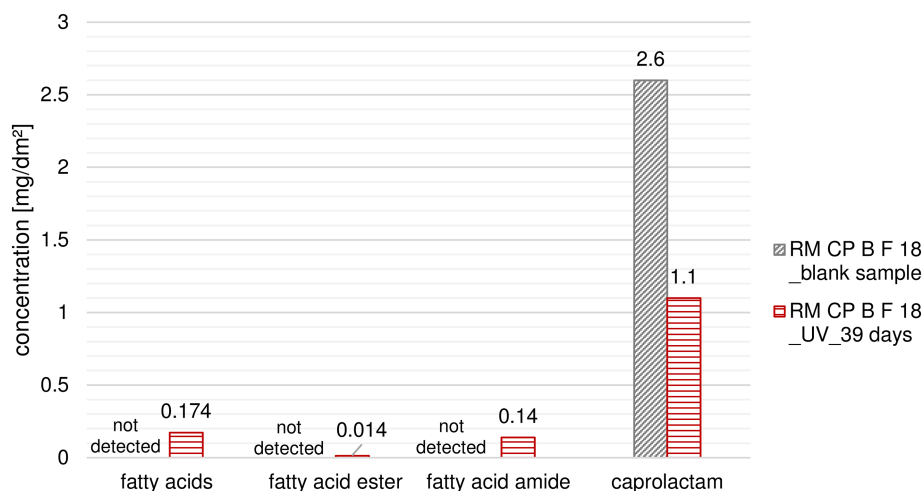
overall migration studies. A limit value of 10 mg/dm² or 60 mg/kg according to EU Regulation 10/2011⁵ applies. An earlier work dealt with such global migration under simultaneous exposure to UV and heat.¹¹ The results showed that the global migration after 10 days of exposure (UV and simultaneous heat treatment) for the PA/PE film increased significantly compared with standardized overall migration conditions but stayed below the limit of 10 mg/dm². No data are currently available on global migration following prolonged exposure.

In the LC-QTOF-MS screening, five unknown substances were detected in the nonexposed comparison sample, as opposed to 13 unknown substances in the exposed sample. These substances also have the potential to migrate to food upon contact. A potential risk cannot be assessed nor excluded because these substances were not chemically identified.

All substances detected here, whether identified or unknown, must also be evaluated in the context of Article 3 of the framework Regulation (EC) no 1935/2004⁴: for compliance of a packaging with existing legislation, it must be ensured that the transfer of substances from packaging to food is neither large enough to endanger human health nor to change the composition or the organoleptic properties of food in an unacceptable manner. Based on what is known about

the substances found under the chosen exposure conditions, this is at least questionable. However, caprolactam was detected and quantified within the extraction study (Figure 7). For the nonexposed reference sample, 2.6 mg/dm² caprolactam were determined. For the sample, which was exposed to UV and heat for 39 days, only 1.1 mg/dm² caprolactam were determined. Following UV/heat exposure, the caprolactam content in the extract decreased significantly. In this context, it is interesting to note that caprolactam migration from RM CP B F 18 is higher for all simulants in the migration test (Figure 1) compared with extraction conditions. The yield of an extraction depends mainly on the film properties, the duration of the extraction and the temperature. The migration studies were performed into different food simulants over a period of 10 days at a temperature of 40°C (in one case at 60°C) as opposed to extraction with acetonitrile over 2 h at 60°C in an ultrasonic bath. The shorter extraction time is the most obvious cause that could lead to the observed decreased uptake of caprolactam. Further, it is known that caprolactam dissolves best in polar solvents like water and ethanol, which corresponds to the simulants used in the migration study. The solubility of caprolactam in acetonitrile used as extracting agent can, therefore, be expected to be lower, caused by the lower polarity of acetonitrile.

FIGURE 7 Concentration of substances found by GC-QTOF-MS/FID or LC-QTOF-MS (in the case of caprolactam) after extraction of RM CP B F 18 before and after exposure to UV for 39 days



Nevertheless, the results of the extraction study clearly consolidate an earlier assumption that the caprolactam migration seemed to decrease under the influence of UV/heat exposure.¹¹ Such lower migration of caprolactam could be caused by postcrystallization of PA and/or by a decomposition of the monomer, both induced by the exposure, as discussed above. To discuss the relevance of either reaction, further studies under different environmental factors would be relevant.

3.4 | Mechanical tests

To test for mechanical consequences of the chemical changes spectroscopically observed during photo-oxidative and thermo-oxidative exposure, all samples have been mechanically tested before and following exposure.

The unexposed samples did not break even under the maximum applied force of 106 N corresponding to a stress of 34.3 N/mm², speaking in favor of the structure of the composite films. This was also observed for samples exposed solely to heat. But already after 2 days of UV exposure, the samples started to delaminate under tensile stress. At a stress of 25–30 N/mm², the PE part of the composite film ruptured and the PA part was stretched significantly at a tension substantially lowered by about 4–6 N/mm². Upon further stretching, the PA part delaminated in regular steps from the remaining PE leaving the transparent contact/delamination areas and the turbid stretched areas on the PA part (Figure 8A). The stress–strain diagram then followed a zig-zag curve with a uniform steep increase and decrease of tension by 2–3 N/mm². Beyond 2 days of illumination, the damage to the composite film has progressed so far that the film lost its original tensile properties. These results showed that, on the one hand, chemical changes occurred on the interface of both polymers decreasing adhesion and, on the other hand, the PE part was changed considerably stronger in its mechanical characteristics leading to rupture and delamination following UV exposure. It is conceivable that substances that formed in the degradation processes affected the interface. Delamination of the two parts of the composite film and

stretching of the PA part under stress can neither be observed for the unexposed samples nor for the samples exposed solely to heat.

A further mechanical consequence of UV exposure was noticed under prolonged exposure. Embrittlement of the composite RM-WS F 11 films was noticed after 84 days of UV exposure even without any stress extended to the samples in the framework of mechanical tests. While cutting a piece of the samples with a knife to carry out FTIR spectroscopy, samples started to spontaneously break in longitudinal direction, parallel to the extrusion direction (Figure 8B).

In summary, the mechanical tests revealed that alterations of the RM-WS F 11 composite film upon UV and simultaneous heat take place already after 2 days of exposure. This supports a conclusion from the spectroscopic findings where changes in the scattering characteristics in the spectral range between 1741 and 2830 cm⁻¹ were traced back to morphological alterations.

4 | CONCLUSIONS

The main consequences of the present results obtained following accelerated aging conditions can be discussed regarding the following:

(a) the knowledge gained on migration characteristics and UV-induced changes in the concentration of caprolactam:

- Over more than 40 months of storage, the migration of caprolactam in the investigated PA/PE film is stable. A specific migration test for caprolactam for a PA/PE film at the beginning of the film's life cycle will be valid for using it throughout its entire lifetime if stored properly.
- Under the inspection conditions of 10 days at 40°C, the available caprolactam is migrating almost completely to the chosen food simulants.
- Decreasing concentrations of caprolactam under photo-oxidative and simultaneous thermo-oxidative conditions were detected by means of IR spectroscopy and MS analysis of solvent extracts from the film, thereby specifying the results of earlier migration tests.¹¹

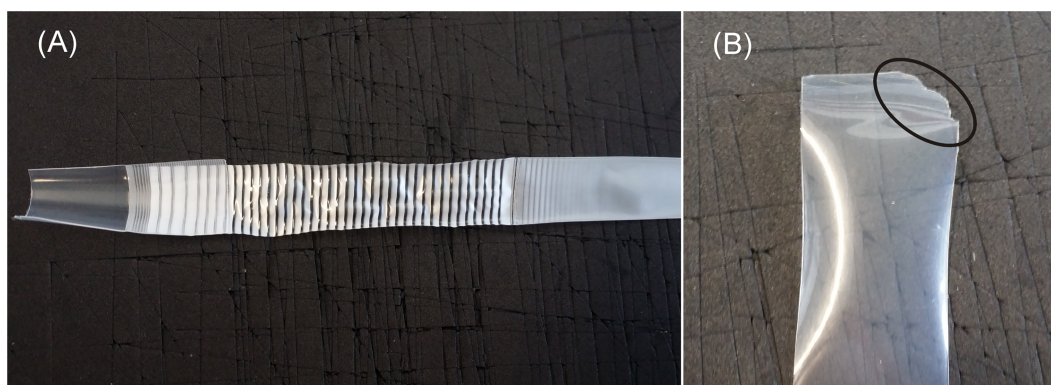


FIGURE 8 A, Delamination of RM-WS F 11 and tearing of polyethylene during tensile test. B, Breaking (marked by black ellipse) of the composite film while cutting test specimen after 84 days under ultraviolet exposure

(b) regarding observations directly relevant for the PA/PE film as packaging material:

- Tensile tests revealed an immediate damage of the PA/PE film under simultaneous UV and heat treatment.
- Newly formed chemical species with characteristic carbonyl groups were detected in the bulk of the polymer as well as on both surfaces due to degradation by means of FTIR spectroscopy.
- The extraction study shows that photo-oxidative alterations led to the formation of butanal, MEK, and fatty acids. Additionally, the amount of extracted unknown substances increased as a result of exposure.
- The formation of degradation products predominantly occurs irreversibly.

Once the degradation process is initiated, the film remains damaged and degradation products become a permanent part of the film. The presented results suggest that packaging exposed to photo-oxidative environmental conditions might negatively affect a packaged food with regard to its composition and organoleptic properties. Migration of NIAS into packed foodstuff appears possible and even likely since such substances were explicitly detected on the polymer surfaces. The present results indicate that such substances need to be taken into account for the risk and conformity assessment to ensure food safety for a specific packaging material.

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SUPPORTING INFORMATION

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