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Classification of polyethylene cling films by attenuated total reflectance-Fourier transform infrared spectroscopy and chemometrics†‡

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Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was utilised to analyse nine differently branded cling films. Principal component analysis (PCA) was used to assess the intra-sample variability, *i.e.* the variation within individual cling film rolls; as well as the inter-sample variability, which explores the variability between different rolls of cling film. Linear discriminant analysis (LDA) was then employed to develop a predictive classification model which gave 100% correct differentiation between three brand groupings of cling film, and accurately classified all of the validation samples obtained from different rolls from the same manufacturers.

Introduction

Cling film, also known as cling wrap, is a food-grade thin film commonly used for wrapping food items in order to keep them fresh in storage. Traditionally, cling film has been manufactured from polyvinyl chloride (PVC) spiked with plasticisers such as di-(ethylhexyl)adipate (DEHA),[1] dibutyl phthalate (DBP)[2] and di(2-ethylhexyl)phthalate (DEHP).[3] However, health concerns regarding the contamination of food with these plasticisers[4] and environmental issues stemming from halogenated polymers[5] has seen manufacturers migrating towards the use of low-density polyethylene (LDPE). The manufacturing process of such cling films utilises a blown film extrusion process, whereby a large bubble of molten LDPE is produced and then pressed between rollers.[6,7]

Although PVC films remain popular in the food services industry due to their superior performing stretch and adherence attributes, LDPE films are much more commonly available to average consumers shopping at their local supermarket. Unfortunately, pure LDPE films are not as adherent as alternatives manufactured from PVC. Consequently, additives are utilised during manufacture to increase the adhesiveness of the film, making them more suitable to use as a food wrap. The most common additives are small molecular weight polymers[8,9] such as polyisobutene (PIB) and poly[ethylene-vinyl acetate] (EVA) copolymers, as these compounds help to provide a greater degree of adherence. Other compounds that may be added include antimicrobial agents[10] and hindered amine UV stabilisers.[11,12]

Cling film is of interest in a forensic setting as it is commonly used as a wrapping for illicit drugs,[13–15] due primarily to its nature, availability and cost. Typically, the forensic analysis of cling film has involved both physical and chemical examinations. Although physical analysis of edge markings can prove challenging due to the stretching and distortion that takes place when the serrated cutter is used to tear a section from the roll, the blown film extrusion manufacturing method can invariably result in the formation of distinctive striation marks, caused by inconsistencies when the rollers are pressed onto the film. These striation marks can be matched between two samples of cling film to show evidence of their common origin.[14] Other forms of physical analysis such as birefringence using polarised light microscopy can only be employed to discriminate between, rather than link, samples.[16]

Chemical differences between films exist as a result of variations in the manufacturing method, such as differing ratios of additives and contaminants, or differing degrees of LDPE polymerisation caused by environmental factors such as reaction temperature.[7] Chemical analysis of cling film samples has been utilised to characterise the chemical profile of a film by establishing the constituents of the sample. Fourier transform infrared (FTIR) has been used extensively to determine different polymers within the film,[17] as has pyrolysis gas

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‡ Electronic supplementary information (ESI) available: Typical cling film spectrum and scores plot for PCA carried out over the full 4000–400 cm^{-1} spectral region. See DOI: 10.1039/c6ay02960d

§ Deceased.

chromatography-mass spectrometry (Py-GC-MS),[18] with FTIR being the preferred method due to the non-destructive nature of the process.[17] Discrimination between polyethylene films has been successfully achieved using thermal methodologies such as thermal desorption capillary gas chromatography,[19] differential scanning calorimetry (DSC),[20,21] and thermogravimetric analysis (TGA).[22]

Previous work by Holman, Emmett and Cole suggested that when analysed using ATR-FTIR, the chemical variation between samples of food-grade LDPE cling film from within a roll was not significantly different to samples obtained from different manufacturers.[23] However, their study employed only three brands of cling film, and the lack of discrimination may thus be a consequence of the samples selected (as acknowledged by Holman *et al.* in their conclusions). Additional factors, such sampling strategy and spectral acquisition, may have also contributed to that study's outcomes.

The study conducted by Holman *et al.* acquired infrared spectra from randomly selected samples taken from the first 30 cm of each roll, with five measurements recorded on a single side of the film in a single orientation for each sample. Based on the manufacturing methods and processes, it should not be assumed that any given cling film is homogenous, and so sampling should be performed across the width and the length of the whole roll. Due to the nature of the blown film extrusion process used in manufacturing, there is also a distinct possibility that contamination may occur to different degrees on either side of the roll. Analysis should therefore be undertaken on both sides of the film. Furthermore, it has been shown that during the manufacturing process, the LDPE aligns to a degree, causing polarisation.[7] This factor needs to be considered when analysing the sample, as the polarisation of the film will cause variability in the intensity of the spectra acquired.[24,25] Spectra should thus be collected with the sample rotated 90° with respect to the original alignment.

Their 0.5 cm^{-1} high resolution spectra also exhibited modest signal to noise ratios (S/N). The smoothing and deconvolution with Gaussian functions used may have resulted in a loss of spectral detail, contributing to the lack of sample discrimination. Solid state IR peaks often have a mixed Lorentz/Gaussian shape, and fitting these peaks according to a Gaussian function may lead to overfitting.

The data analysis method used by Holman and co-authors involved the selection of ten peaks from three samples for their dataset, processing them using automatic deconvolution and smoothing functions, and then comparing the normalised peak areas on a bivariate plot.[23] For this they used % transmission spectra, which follows a logarithmic rather than a linear scale as a function of concentration. Absorbance would be a more appropriate measure of intensity (and hence concentration). By restricting their investigation to two relatively narrow regions of the spectra, the possibility exists that some observable differences may have been excluded from the analysis, resulting in a lack of discrimination between samples.

A potentially more informative solution would be to employ multivariate data analysis, also known as chemometrics, to analyse the full FTIR spectra obtained from the sample set. Chemometric methods provide statistically valid and objective measurements, rather than a visual comparison of what appears to be an area of interest within the spectra collected. By utilising a chemometric approach to the analysis of the data set, there is also a reduced chance of any conclusions formed from the data being affected by human error or observer bias, as they are based on well-established statistical methods.[26–28]

For the ATR-FTIR analysis of cling film to have any forensic and evidentiary value, it must be shown that the chemical variation between samples within a roll is statistically dissimilar to the variation between samples from rolls from different manufacturers. If there is no discernible difference in chemical variation, it would be impossible to differentiate between samples or attribute a questioned sample to a source.

This paper describes a study of the chemical variability within and between several different brands of LDPE cling film available in Western Australia analysed using ATR-FTIR spectroscopy. This was conducted using a comprehensive sampling methodology in conjunction with multivariate statistical analysis, in order to better evaluate the applicability of ATR-FTIR for the reliable differentiation of cling films.

Experimental

Sample preparation and identification

Nine different rolls of LDPE films from five different brands were purchased from three supermarket chains in Western Australia (Table 1). A scalpel was used to cut a 3 cm wide strip at the beginning of each roll, which was then divided into nine 3 × 3 cm squares. Each of these squares was assigned a unique numeric identifier. This process was repeated every 3 m for the 30 m rolls, 6 m for the 60 m rolls and 1.5 m for the 15 m roll. This resulted in a total of 10 columns (90 samples) per roll. Caution was taken in the handling of samples to ensure that no distortion, physical manipulation or contamination occurred. Samples were stored between two layers of cling film from adjacent areas to the sample. A random number generator was used to select a single sample from each strip for analysis.

Each cling film sample was characterised using the following scheme:

A: samples were analysed with an orientation set with respect to the unfurling of cling film roll, with a background spectrum collected for each sample.

Table 1 LDPE cling films used in this study

Cling film	Roll length (m)
Glad go-between freezer film	15
Woolworths homebrand	30
Woolworths select	60
Coles smart buy	30
Coles cling film	30
Multix	30
OSO	30
Glad	30
IGA black & gold	60

B: samples were analysed with an inverted and orthogonal orientation with respect to the original orientation, with a background spectrum collected for each sample.

All infrared spectra were acquired using a Thermo Scientific Nicolet iS50 FT-IR spectrometer equipped with a single-bounce diamond crystal iS50 ATR sampling accessory. The ATR accessory is equipped with a pressure arm that was used to maintain a consistent pressure of 267 N on the sample. Prior to analysis, the crystal sampling window was thoroughly cleaned using ethanol and lint-free tissue to remove contaminants and particulates. Spectra were collected over a range of 4000 to 400 cm^{-1}, with a resolution of 2 cm^{-1} and 64 co-added scans. Thermo Scientific OMNIC software (version 9.1.24) was used to perform an ATR correction on the entire dataset to correct for the change in absorbance as a function of penetration depth with wavelength.

Data analysis

Spectra acquired from the two different orientations of each sample were averaged prior to analysis. All pre-processing and data analysis was performed using the Unscrambler® X v10.4 software (Camo AS, Oslo, Norway).

The spectra were first truncated, omitting the wavelength ranges 400–700 cm^{-1}, 800–1400 cm^{-1}, and 3000–4000 cm^{-1}, as minimal variation between samples was observed in these regions. Additionally, interference from the diamond sampling crystal was observed from 1800–2600 cm^{-1}, and so this region was also excluded (Fig. S1‡). The truncated spectra were baseline corrected to 0% absorbance, then range normalised (such that the maximum absorbance for each spectrum was scaled to a value of 1) to remove any variability caused by the sample surface texture.

The pre-processed spectra were subjected to principal component analysis (PCA) using the NIPALS algorithm. The samples were plotted against the first two principal components in order to visualise the sample distribution and identify any outliers. A discriminant model was then developed using linear discriminant analysis (LDA) with internal validation. The dataset was arbitrarily split into two distinct sample sets; a calibration or training set (66 spectra) and a test set (24 spectra). The discriminant model was constructed from the training samples using the Mahalanobis distance, employing the first two PCs and classes identified in the PCA. The resultant model was used to predict the classification of the validation spectra, with the predicted and actual classifications compared to determine the efficacy of the model.

Results and discussion

Examination of the infrared spectra (Fig. 1) revealed some variability in absorbances relative to the 2916 cm^{-1} band. In particular, the Glad freezer film has a stronger 2849 cm^{-1} CH_2 stretching band, in addition to stronger absorbances in the 1460 cm^{-1} and 725 cm^{-1} CH_2 deformation regions. The other 8 samples had more subtle absorbance differences in these regions (Table 2). Band assignments are for representative samples from each class are given in Table 3.

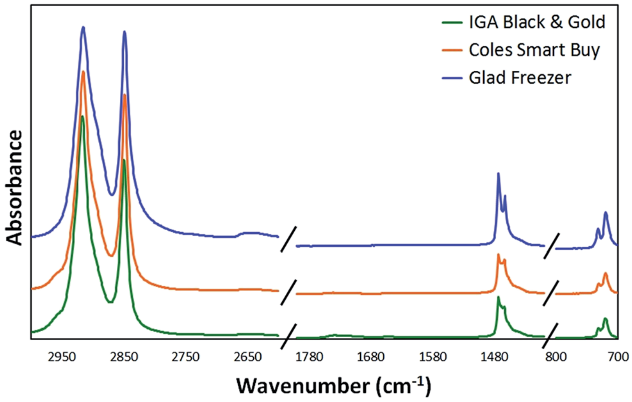

Fig. 1 Infrared spectra obtained from typical cling film samples. Spectra have been offset for visual clarity.

Based on this observation, principal component analysis (PCA) and linear discriminant analysis (LDA) were conducted to determine if the films could be discriminated with confidence, and thus be of forensic use. No bands that might be attributable to additives such as UV-stabilisers or antimicrobials were observed.

Classification of the spectral datasets by principal component analysis

PCA was utilised as a data reduction technique; transforming the original variable set into a lesser number of orthogonal variables known as principal components (PCs). These PCs can be used to re-visualise the dataset, potentially revealing trends or patterns between samples that would not be readily evident from the raw spectra. In this instance, the Scree plot (Fig. 2) showed that 98.2% of total variation in the dataset was accounted for within the first two PCs alone. Spectra from the nine cling film rolls were therefore plotted using the first two PCs as a new coordinate system, resulting in a 2-dimensional scores plot as shown in Fig. 3. PC3 (accounting for 0.8% of total variation) was found not to give any further discrimination between the groups, and was therefore omitted from subsequent chemometric analysis. Three main clusters of data were identified, representing classes of cling films sharing similar chemical characteristics. The Glad freezer film was found to be

Table 2 Selected CH stretching and deformation absorbance ratios

Absorbance ratios	Glad freezer	Coles smart buy	Black and gold
A_{2849}/A_{2916}	0.978	0.896	0.803
A_{1473}/A_{2916}	0.344	0.181	0.188
A_{1464}/A_{2916}	0.242	0.157	0.145
A_{732}/A_{2916}	0.096	0.050	0.048
A_{720}/A_{2916}	0.170	0.095	0.092
A_{1473}/A_{1464}	1.421	1.155	1.298
A_{720}/A_{732}	1.766	1.913	1.920

Table 3 LDPE cling film infrared spectra assignment and relative intensities[29,30]

Band (cm^{-1})	Assignment	Glad freezer	Coles smart buy	Black and gold
2960	CH_3 antisymmetric stretch	—	sh[a]	sh
2916	CH_2 antisymmetric stretch	1	1	1
2890	CH_3 symmetric stretch	sh	sh	sh
2849	CH_2 symmetric stretch	0.98	0.90	0.80
2645	Not assigned	0.07	0.02	0.02
1736	C=O stretch	—	0.003	0.005
1473	CH_2 bending	0.34	0.18	0.19
1464	CH_2 bending	0.24	0.16	0.15
1456	CH_2 bending	sh	sh	sh
1440	CH_2 bending	sh	sh	sh
1378	CH_3 symmetric bending	sh	0.015	0.012
1368	CH_2 wagging	0.01	0.012	0.01
1353	CH_2 wagging	sh	sh	sh
1305	CH_2 twisting	0.004	0.004	0.004
732	CH_2 rocking	0.10	0.05	0.05
720	CH_2 rocking	0.17	0.10	0.09

[a] sh = shoulder.

uniquely characterised (Class 1), whereas Classes 2 and 3 each consisted of multiple films (Table 4).

It should be noted that carrying out the PCA with the full spectral range of 4000–400 cm^{-1} resulted in the same clusters, with a greater level of intra-class variation (Fig. S2‡).

The factor loadings for the first two PCs (Fig. 4) can be used to identify the wavelength regions contributing to separation between the samples. PC1 was found to exhibit significant positive loadings at 2910–2885 cm^{-1} and 2848 cm^{-1}, corresponding to the antisymmetric CH_2, symmetric CH_3 and CH_2 stretching regions. Additionally positive loadings were observed for the 1470 cm^{-1} CH_2 bending and 1370 cm^{-1} CH_2 wagging regions. This accounts for the positive score on PC1 for Class 1 samples, whose spectra show the highest relative absorbances in these regions (Fig. 1).

Classes 2 and 3 were primarily separated along PC2, where a significant positive loading was observed at 2923 cm^{-1} and strong negative loadings at 2911 and 2852 cm^{-1}, reflecting the 1–2 cm^{-1} shifts and band width differences observed in the CH stretching region. There is also a smaller positive loading by one of the CH_2 bending mode doublet bands (1472 cm^{-1}). The even smaller positive carbonyl stretch (1736 cm^{-1}) loading and CH_2 rocking mode doublet (730 cm^{-1}) loadings also contribute to the separation.

The differentiation observed is likely due to differences in the density, crystallinity and short chain branching of the polyethylene. The splitting of the 1460 cm^{-1} and 730 cm^{-1} bands indicates that the LDPE in all three classes is crystalline and these bands become more intense and resolved with increasing crystallinity.[31,32] It is thus clear that the freezer film (Class 1) is discriminated on the basis of its significantly higher crystallinity. This film is further differentiated by the very weak bands of the CH_3 and CH_2 deformations in the 1370 cm^{-1} triplet.

The freezer film has its strongest band of the triplet at 1368 cm^{-1} whilst for Classes 2 and 3 it occurs at 1378 cm^{-1} (Table 3). According to Usami and Takayama[33] this would suggest that Classes 2 and 3 have of the order of 20 branches per 1000 carbon atoms and Class 1 less than this.

The antisymmetric CH_3 stretch (2960 cm^{-1}) observed for Classes 2 and 3 was not observed in the freezer film spectra, nor was the carbonyl band at 1736 cm^{-1}, the latter indicating that it

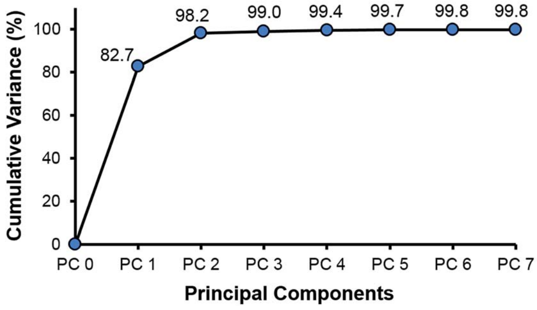

Fig. 2 Scree plot depicting the cumulative variance in the cling film infrared spectral dataset retained by each PC.

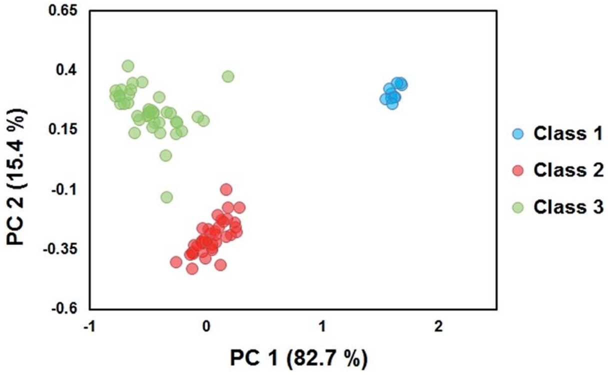

Fig. 3 Two-dimensional PCA scores plot showing distribution of cling film samples into three distinct classes based on their infrared spectral properties.

Table 4 PCA classification of cling film samples

Class	Cling film samples
1	Glad go-between freezer film
2	Woolworths homebrand, Woolworths select, Coles smart buy, Coles cling film
3	Multix, OSO, Glad, IGA black & gold

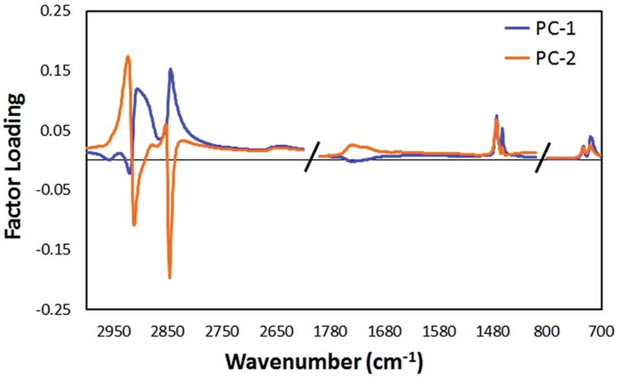

Fig. 4 Factor loadings plot of the first two PCs for PCA of entire spectral dataset.

is less oxidised than the other two classes of film.[34] Whilst the freezer film could be distinguished from the other two classes by inspection of the spectra, the differences between Classes 2 and 3 are much more subtle and were only extracted with confidence by PCA of the data. The negative score of Class 3 on PC2 in the scores plot (Fig. 3) is due to a small shift (~2 cm^{-1}) to higher frequencies of its antisymmetric and symmetric CH_2 stretches, a small change in its crystallinity shown by the change in relative intensity of the 1473 cm^{-1} and 1464 cm^{-1} peaks (Table 2), and a higher degree of oxidation as shown by the carbonyl band (1736 cm^{-1}).

The films thus appear to be discriminated on the basis of function and manufacturer, but not retail brand. The freezer film, which is designed as a separation film rather than a food wrap film is distinctly different, whereas the food wrap films could possibly come from two manufacturers. The Coles and Woolworth films could not be separated, suggesting that these retail chains source their films from the same manufacturer. The IGA black & gold, Multix, Glad and OSO food wrap films also appear to be from a common, but different, source. Restricting the PCA to just Classes 2 and 3 did not lead to further brand discrimination.

Table 5 Confusion matrix displaying results of LDA for the samples within the calibration dataset

Actual/predicted	Class 1	Class 2	Class 3	Total	% correct
Class 1	6	0	0	6	100
Class 2	0	30	0	30	100
Class 3	0	0	30	30	100
Total	6	30	30	66	100

Table 6 Confusion matrix showing results of LDA for the samples within the validation dataset

Actual/predicted	Class 1	Class 2	Class 3	Total	% correct
Class 1	4	0	0	4	100
Class 2	0	10	0	10	100
Class 3	0	0	10	10	100
Total	4	10	10	24	100

Table 7 Mean discriminant values and associated standard deviations obtained from the spectra of each class against all three classes, derived from the calibration dataset

	Class 1		Class 2		Class 3	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
Class 1	−1.7	1.2	−1501.7	282.8	−5113.8	1379.3
Class 2	−108.8	5.6	−1.9	2.2	−277.5	114.7
Class 3	−90.5	4.9	−25.2	5.0	−1.9	3.1

Linear discriminant analysis (LDA)

LDA was conducted using the data obtained from the PCA. LDA is a technique used to establish classification rules for known groups of samples, in such a manner that maximum discrimination is achieved between them.[34] The discriminant model can then be employed to classify unknown samples to a corresponding class.[34] The model was constructed using a calibration set of 66 spectra, and tested using an external validation set of the remaining 24 spectra. The effectiveness of the predictive model was evaluated based upon the percentage of spectra assigned to their correct class.

The calibration and validation datasets both produced 100% efficiency, as shown in Tables 5 and 6, suggesting the three classes to be well differentiated. This is supported by inspection of the discriminant values, which act as distance measures between a sample and the centroid of a given class. When performing LDA classification, unknown samples are assigned to the class yielding the smallest magnitude discriminant value, indicative of the 'closest fit'. Table 7 shows the mean discriminant values and associated standard deviations obtained by spectra from each class against all three classes. It is evident that the spectra for any given class exhibit small magnitude discriminant values for their assigned class in comparison to their discriminant values against the other classes, signifying that these classes are well separated.

This result shows that the subtle differences within the spectra of the LDPE films are significant enough to provide effective discrimination. These differences would enable unknown samples to be classified with confidence.

Conclusions

Nine rolls from five different brands of LDPE films were analysed by ATR-FTIR, and the spectra examined using two chemometric techniques; PCA and LDA. PCA resulted in the identification of three main classes. Inspection of the factor loadings showed that the differentiation between these classes could be attributed to variation in the crystallinity, short chain branching and oxidation of the LDPE. The presence of additives and plasticisers added during the manufacturing process was not observed.

LDA based upon the first two PCs produced a highly effective predictive model that yielded 100% classification accuracy of both the training and validation sets. This demonstrates that the variations in spectral features are sufficient to provide reliable discrimination between the samples of each class.

Whilst we did not observe differences arising from sample orientation or different sides of the films, we still recommend that orthogonal spectra be obtained from both sides of a film, at least in the first instance, as such differences may well be found for films in other jurisdictions.

The results presented in this paper show that ATR-FTIR with subsequent chemometric data analysis is in fact an effective means for the characterisation and discrimination of some LDPE food films, in contrast to the earlier findings presented by Holman, Emmett and Cole. This is possibly due to the analysis of a wider range of samples, a more comprehensive sampling method, and the assessment of a wider range of the spectrum using multivariate (chemometric) data analysis techniques.

It would prove very interesting to investigate a population of LDPE films in the rest of Australia and even internationally, especially given the complexity of product strategies and modern supply chains.

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References

1 J. H. Petersen, E. Tubæk Naamansen and P. A. Nielsen, *Food Addit. Contam.*, 1995, **12**, 245–253.
2 N. Harrison, *Food Addit. Contam.*, 1988, **5**, 493–499.
3 I. Steiner, L. Scharf, F. Fiala and J. Washüttl, *Food Addit. Contam.*, 1998, **15**, 812–817.
4 D. E. Till, R. C. Reid, P. S. Schwartz, K. R. Sidman, J. R. Valentine and R. H. Whelan, *Food Chem. Toxicol.*, 1982, **20**, 95–104.
5 S. S. Epstein, *Cancer Res.*, 1974, **34**(10), 2425–2435.
6 K. Cantor, *Blown film extrusion*, Hanser Publications, 2011.
7 A. J. Peacock, *Handbook of Polyethylene*, Marcel Dekker, Inc, New York, 2000.
8 A. K. Breck and A. N. Mollison, *Blends of polyethylene and polybutenes*, Du Pont Canada Inc., European Patent EP 0163783 A1, 1987.
9 R. Banerji, *Food wrap film*, Exxon Chemical Patents Inc., US Patent 5 006 398, 1991.
10 Y. Mistry, *Development of LDPE-based antimicrobial films for food packaging*, MSc Thesis, Victoria University, 2006, http://vuir.vu.edu.au/id/eprint/1485.
11 F. Gugumus, *Polym. Degrad. Stab.*, 1995, **50**, 101–116.
12 F. Gugumus, *Polym. Degrad. Stab.*, 1998, **60**, 119–135.
13 C. Roux, S. Bull, J. Goulding and C. Lennard, *J. Forensic Sci.*, 2000, **45**, 99.
14 R. Sugita, K. Sasagawa and S. Suzuki, *J. Forensic Sci.*, 2009, **54**, 1341–1348.
15 F. A. Idoine, J. F. Carter and R. Sleeman, *Rapid Commun. Mass Spectrom.*, 2005, **19**, 3207–3215.
16 D. Castle, B. Gibbins and P. Hamer, *J. Forensic Sci. Soc.*, 1994, **34**, 61.
17 K. W. Chan, G. H. Tan and R. C. S. Wong, *Spectrosc. Lett.*, 2011, **44**, 440–449.
18 T. Tsukame, M. Kutsuzawa, H. Sekine, H. Saitoh and Y. Shibasaki, *J. Therm. Anal. Calorim.*, 1999, **57**, 847–851.
19 J. Gilburt, J. M. Ingram, M. P. Scott and M. Underhill, *J. Forensic Sci. Soc.*, 1991, **31**, 337–347.
20 V. Causin, C. Marega, P. Carresi, S. Schiavone and A. Marigo, *Forensic Sci. Int.*, 2006, **164**, 148–154.
21 L. Yang, P. Thomas and B. Stuart, *J. Therm. Anal. Calorim.*, 2012, **108**, 445–448.
22 E. C. Ihms and D. W. Brinkman, *J. Forensic Sci.*, 2004, **49**, 505–510.
23 S. W. Holman, T. F. Emmett and M. D. Cole, *Anal. Methods*, 2012, **4**, 1667–1673.
24 P. J. Hendra and W. F. Maddams, in *Polymer Spectroscopy*, ed. A. H. Fawcett, John Wiley & Sons Ltd, 1996, ch. 7, pp. 173–202.
25 A. Ajji, X. Zhang and S. Elkoun, *Polym. Eng. Sci.*, 2006, **46**, 1182–1189.
26 M. J. Adams, *Chemometrics in analytical spectroscopy*, Royal Society of Chemistry, 2004.
27 D. L. Massart, B. G. M. Vandeginste and L. Buydens, *Handbook of chemometrics and qualimetrics*, Elsevier Science, 1997.
28 J. N. Miller and J. C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, Pearson Education, Harlow, England, 6th edn, 2010.
29 J. V. Gulmine, P. R. Janissek, H. M. Heise and L. Akcelrud, *Polym. Test.*, 2002, **21**, 557–563.
30 S. Krimm, C. Y. Liang and G. B. B. Sutherland, *J. Chem. Phys.*, 1956, **25**, 549–563.
31 M. J. Cran and S. W. Bigger, *Appl. Spectrosc.*, 2003, **57**, 928–932.
32 M. C. Tobin and M. J. Carrano, *J. Chem. Phys.*, 1956, **25**, 1044–1052.
33 T. Usami and S. Takayama, *Polym. J.*, 1984, **16**, 731–738.
34 T. Ojeda, A. Freitas, K. Birck, E. Dalmolin, R. Jacques, F. Bento and F. Camargo, *Polym. Degrad. Stab.*, 2011, 703–707.