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CHARACTERISATION OF THE COMONOMER COMPOSITION AND DISTRIBUTION OF COPOLYMERS USING CHEMOMETRIC TECHNIQUES

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Abstract

Chemometric techniques have been applied to FTIR and DSC data to correlate polymer composition. Since structural differences in the polymers with only hydrocarbon structure, often cause subtle changes in spectra, the ability of chemometric techniques is required to discern these differences. FTIR spectra and thermal fractionation using DSC were measured for 28 types of polyethylenes (PE) varying in chain branching type, content and distribution. Unsupervised clustering methods such as principal component analysis (PCA) and supervised discriminant analysis were used to classify the PEs according to their structural class. The DSC data was the more successful in both classifying PEs according to their class.

Keywords: chemometrics, DSC, discriminant analysis, polyethylenes, thermal fractionation

Introduction

Commercial polyethylenes are marketed in three general grades; high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE). HDPE is a linear polyethylene with no branching. LDPE is a polyethylene with both short-and long-chain branching. LLDPE is a copolymer of ethylene and 1-olefins, with short-chain branching. The densities for LLDPEs are normally about 0.920 g cm^{-3}.

Many new polyethylenes have been prepared using typically metallocene catalysts, and they are now commercially available. They provide a combination of more evenly spaced branches, increased branch content, narrow branch distribution, narrow molar mass distribution and in some cases long chain branching. Polyethylenes, with densities between 0.89–0.91 g cm^{-3} are called very low-density polyethylene (VLDPE) and those with densities less than 0.89 g cm^{-3} are called ultra low-density polyethylene (ULDPE).

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The various grades of polyethylene differ in the degree of short-and long-chain branching, as well as the branching distribution. These variations affect the crystallinity, thermal and mechanical properties of the polymer [1, 2]. Infrared (IR) spectroscopy has been used extensively to characterise polymers. The IR spectra of linear low-density polyethylenes were found to have significant differences in the 1300–1400 cm^{-1} region [3]. The ratio of absorptions at 1368 and 1376 cm^{-1} showed an almost linear relationship between the ratio and length of branching in the comonomer. Physico-mechanical properties of polypropylene copolymers have been determined by chemometric analysis of the infrared spectra [4]. Near infrared (NIR) and Raman spectroscopy have been combined with Multi-Variate Analysis (MVA) for the prediction of ethylene content in propylene copolymers [5, 6]. Principal Component Analysis (PCA) and Principal Component Regression (PCR) were used and NIR and Raman data compared and the spectra bands providing higher significance were identified. Chemometric analysis using Partial Least Squares (PLS) has been used to predict the densities of LLDPE samples from NIR [7] and Raman [8] data. IR, Raman, IR and NIR data have been used with MVA to quantify mixtures of LLDPE, LDPE and HDPE [9]. Ethylene-vinyl acetate [10, 11], styrene-butadiene [12], ethylene-styrene [13] and styrene-sodium methacrylate [14] copolymers have been studied using vibrational spectroscopy techniques combined with PCA and PLS.

One technique that has been found to be useful to study the degree of branching in polyethylenes is differential scanning calorimetry (DSC) using thermal fractionation [15, 16]. The technique is based on the analysis of the melting behaviour after a suitable thermal treatment, such as stepwise annealing during cooling from the melt. After thermal fractionation, crystals within the sample separate according to the short chain branching distribution (SCBD) distribution, which determines the lamellar thickness and hence melting temperature. The distribution of lamellar thickness depends on the amount and distribution of the α-olefin units in the macromolecular chains, provided that the crystallisation conditions allow the lamellae to approach equilibrium. Lamella thickness is also related to crystallisation conditions. As equilibrium lamellae are approached, their melting temperatures approach the copolymer melting temperature defined by Flory [17]. Thermal fractionation has been used to characterise the various types of polyethylenes [16, 18]. It can be used quantitatively to determine branching distribution or methylene sequence length distribution. It was expected to provide discriminant results for identification of polyethylene types using chemometric techniques, as has been performed with IR, NIR and Raman spectroscopy.

Chemometric techniques have not been applied as widely in the thermal analysis of polymers. For example, pyrolysis products of ethylene-methyl methacrylate copolymers have been analysed to determine copolymer composition [19] and PCA used to extract information from thermal decomposition of Kraton 1107 copolymer [20].

The aim of this study was to provide a comparison of the two techniques, IR spectroscopy and DSC using thermal fractionation, as to their ability to discriminate and assign the class of polyethylene. The ability of the techniques to distinguish the groups of polyethylenes was first investigated using principal component analysis and then discriminant analysis applied to form a model for assigning unknown samples to their structural class.

Experimental

Materials

Commercial grades of polyethylenes were obtained from a range of commercial manufacturers. There were 28 polyethylenes – 2HDPE, 6 LDPE, 10 LLDPE, 5 VLDPE and 5 ULDPE, though all polymers were not used for each method. Details of the polyethylenes are provided in Table 1. Pellets of polyethylene (0.5–1.0 g) were weighed and placed between two Teflon sheets, which were placed between two stainless steel plates. The samples were placed in a pre-heated press. Each sample was melted for about 3 min with no pressure applied and then a load of 2–3 tonne was applied for 1–2 min. The temperature used was about 10°C above the melt temperature of the particular polyethylene. The films were cooled to room temperature and placed in sealed sample bags. Films of about 2–5 mg were cut and sealed in 10 mL aluminium pans for DSC analysis.

Thermal fractionation method

Thermal analysis and thermal fractionation were carried out using the Perkin-Elmer Pyris 1 DSC with Pyris software version 3.81. The DSC was operated at ambient temperature mode with a cold finger cooled to 1–5°C with ice-water. Dry nitrogen gas with a flow rate of 20 mL min^{-1} was purged through sample. The instrument was calibrated with indium and zinc standards. The samples were melted at 180°C and held for 5 min. This procedure was carried out in order to remove previous thermal history. Each sample was then cooled to 122°C at a rate of 200°C min^{-1} and maintained at this temperature for 50 min. The sample was again cooled by 4°C at a rate of 200°C min^{-1} and kept at each temperature for 50 min. This procedure was repeated at 4°C intervals to room temperature. For samples with low melting temperatures the isothermal cooling was commenced at lower temperatures: 106°C for LDPE samples and 98°C for ULDPE samples because preliminary results have shown that no crystallization occurs at temperatures higher than these. The average cooling rate used was 0.08°C min^{-1}. The samples were analysed by heating from 30 to 150°C at 10°C min^{-1}. A baseline was recorded with empty pans, using identical conditions to the heating scan.

Infrared spectroscopy

FTIR spectroscopy of the polymer films was measured using a Perkin-Elmer 1750 FTIR spectrometer in the range 13000–400 cm^{-1}. 32 scans were used for spectral averaging, at a resolution of 16 cm^{-1}. Each film was measured three times at different parts of the film and the spectra were averaged. The spectra were converted to absorbance units for data manipulation and analysis. To allow for differences in film thickness and opacity the spectra were transformed using the Multiplicative Scatter Correction [21].

Table 1 Structure, properties and designation of the polyethylenes

Code	Comonomer	Catalyst type	MFI/ g 10 min^{-1}	Density/ g cm^{-3}	T_m/şC	T_c/şC
HDPE1		ZN	0.3	0.953	130	117
HDPE2		ZN	0.85	0.960	132	117
C4-LLDPE1	butene	ZN	1.0	0.918	122	108.66
C6-LLDPE3	hexene	ZN	0.78	0.935	124	110
C6-LLDPE4	hexene	ZN	0.8	0.920	124	111
C6-LLDPE5	hexene	ZN	0.8	0.920	124	107
C6-LLDPE6	hexene	ZN			123	92
C6-LLDPE7	hexene	ZN			124	111
C6-LLDPE8	hexene	ZN			126	113
C8-LLDPE2	octene	ZN	1.0	0.912	123	104
C8-LLDPE4	octene	ZN	0.94	0.920	120	106
C4-VLDPE1	butene	S,M	1.2	0.910	109	95
C4-VLDPE2	butene	S,M	27.0	0.901	91	72
C8-VLDPE3	octene	S,CGCT	1.0	0.915	111	97
C8-LLDPE5	octene	S,CGCT	1.0	0.908	107	91
VLDPE	butene	S,M	1.2	0.910	103	87
VLDPE	butene	S,M	33	0.912	123	103
LDPE1		P	0.7	0.919	105	93
LDPE2		P	0.7	0.922	93	98
LDPE3		P	22.0	0.98	104	87
LDPE4		P	0.45		110	99
LDPE5		P			109	92
C4-ULDPE	butene	S,M	0.5	0.870	60	47
C4-ULDPE	butene	S,M	100	0.865		
C4-ULDPE	butene	S,M	30	0.882		56
C8-ULDPE	octene	S,M	5	0.868		44
C8-ULDPE	octene	S,M	50	0.870		45

Z-N= Ziegler-Natta catalysts, S=Single-site catalysts, CGCT=Constrained geometry catalysts, M=Metallocene catalysts, P=Peroxide, HEX=Hexane extracted

Results and discussion

The infrared spectroscopy data was first examined to determine if the data could be used to classify the polyethylenes into their structural groups. The only usable region of the spectrum for these polymers was found to be in the range 1200–1400 cm^{-1}. It was only in this region that bands exist with moderate absorbance and showing significant differences between samples. There are overlapping bands at 1368 cm^{-1} (due to methylene group C–H deformation) and 1376 cm^{-1} (due to the C–H deformation of methyl groups). The ratio between these two bands represents the degree of branching in the chain [3].

The FTIR spectra of 25 samples were examined using Principal Components Analysis, as a preliminary data treatment to determine if FTIR was able to distinguish the structural classes. The results for the first three principal components are shown

Table 2 Principal component analysis for infrared spectrscopy and DSC data

	Infrared spectroscopy correlation			DSC correlation	
Polyethylene	PcaSco1	PcaSco2	PcaSco3	PcaSco1	PcaSco2
HDPE1	3.66	9.37	0.10	–0.10	0.74
HDPE2	4.49	3.69	2.23	–4.70	–1.90
LDPE1	–7.45	–1.28	0.95	0.04	–0.49
LDPE2	–7.15	3.40	–0.51	0.83	–0.46
LDPE3	–0.82	0.47	0.67	0.05	–0.52
LDPE4	–1.60	–1.45	2.94	0.13	–0.51
LLDPE1	–4.21	1.62	–0.13	–0.72	0.94
LLDPE2	0.45	0.64	–2.91	0.36	0.91
LLDPE3	–0.67	0.97	0.39	–1.11	0.60
LLDPE4	–4.71	2.77	–0.50	–0.96	0.89
LLDPE5	5.15	–2.81	4.47	–0.19	0.98
LLDPE6	3.69	–1.16	–0.05	–0.75	0.78
LLDPE7	3.49	1.02	0.06	–1.19	0.40
LLDPE8	0.06	1.40	0.29	–1.13	0.48
LLDPE9	6.10	–2.67	6.20	–3.00	–0.73
ULDPE1	–7.45	–2.69	–1.51		
ULDPE2	–1.81	–4.30	–3.08		
ULDPE3	2.88	–0.56	–3.25		
ULDPE4	1.03	–2.54	–2.30		
ULDPE5	3.48	–2.67	–4.20		
VLDPE1	–3.31	1.57	–0.10	0.38	–0.10
VLDPE2	–7.34	–2.10	4.51	0.63	–0.26
VLDPE3	4.03	–1.62	–0.50	2.65	–0.72
VLDPE4	1.63	–0.50	–1.00	1.03	–0.05
VLDPE5	6.38	–0.57	–2.80	1.10	–0.22
VLDPE6				1.08	–0.58
VLDPE7				0.90	0.81
VLDPE8				4.67	–0.98

in Table 2. A score plot of the first two principal components (Fig. 1) showed that the HDPE samples could easily be distinguished and the UDPE samples were well separated. However, the other three classes (LLDPE, LDPE and VLDPE) were not well separated in the plot. Other methods of pre-treating the spectra, including using derivative spectra and baseline correction-normalisation, did not improve the separation of these classes. Thus, FTIR spectra did not provide an overall satisfactory method of classifying the polyethylenes.

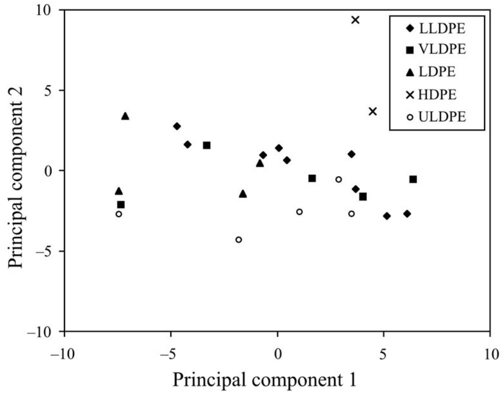

Fig. 1 Score plot of the first two principal components for the FTIR spectra of 25 polyethylenes (1200–1400 cm^{-1})

The use of DSC with Thermal Fractionation was then examined as an alternative method for classification. Fractionation was based on the melting behaviour of the polyethylenes after stepwise crystallisation [15, 16]. This produces a series of melting peaks separated according to branch density. After thermal fractionation, the crystals within the sample are separated into groups of distinct lamellar thickness, which is related to short-chain branching. The apparent specific heat curves of some of the samples are shown in Fig. 2.

Examination of these curves for the polyethylenes showed immediately that the HDPE samples could readily be distinguished. As HDPE has essentially no branching, it exhibits one large melting endotherm with no fractionation. The UDPE samples could also be readily distinguished as they have the most extensive branching and do not have a clearly defined initial melting endotherm. No clear pattern could be observed amongst the other three classes to enable them to be classified by inspection. In order to quantify the DSC specific heat curves and obtain data for further treatment the following parameters were determined (as shown in Fig. 3): (*i*) Peak temperature; the maximum peak temperature of the specific heat curve (°C), (*ii*) Peak height; the specific heat capacity at the peak temperature (J(g °C^{-1}) (*iii*) ΔH; enthalpy change associated with the highest peak temperature (J g^{-1}) and (*iv*) Onset temperature; the beginning temperature of any transition that is distinguished by a significant change from the baseline (°C).

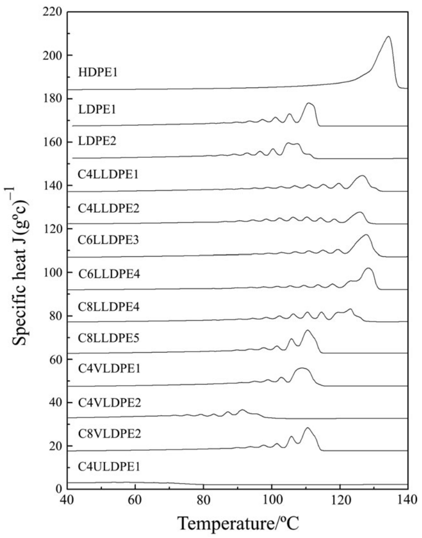

Fig. 2 DSC specific heat curves of polyethylene after thermal fractionation: The curves are separated by adding 10 units to each successive data set

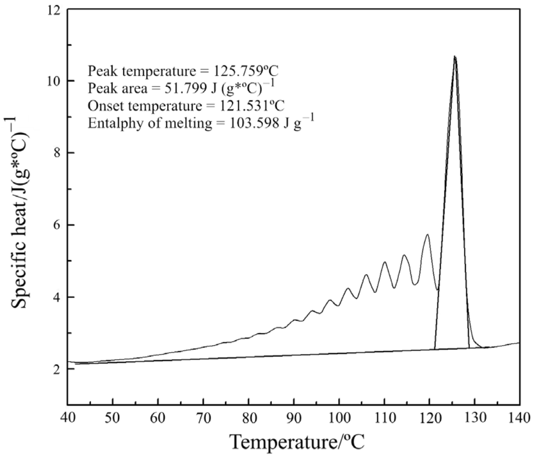

Fig. 3 DSC specific heat curve, after thermal fractionation

Using these four parameters and applying PCA an improved classification was obtained (Fig. 4). For this analysis the UDPE samples were excluded, as they do not have well-defined melting peaks. To further test the ability of DSC to discriminate between the LLDPE, LDPE and VLDPE classes the DSC data for these classes was subjected to discriminant analysis. The samples were divided into a training set of 15 samples and a test set of 8 samples. From the original set of 29 samples, 2 HDPE and

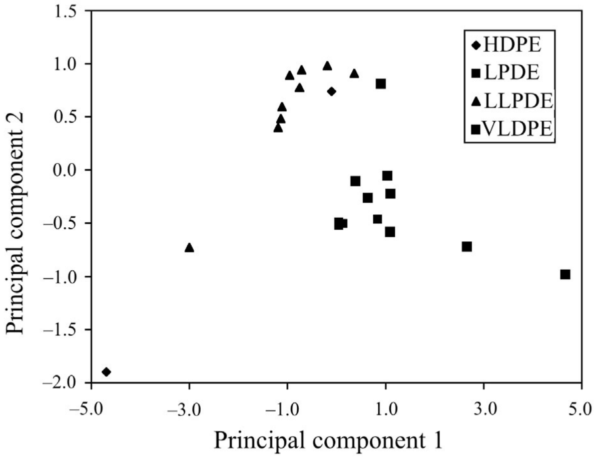

Fig. 4 Score plot of the first two principal components for the DSC data of 23 polyethylenes (excluding the UDLPEs)

4 UDPE were excluded as they could readily be identified by inspection of the DSC curves. The training set consisted of data from 8 LLDPE, 3 LDPE and 4 LVLDPE.

The data was analysed using Regularised Discriminant Analysis (RDA), a technique originally developed by Friedman [22]. When the goal is to find the best predictive model in a grid spanned by the discriminant methods Nearest Means Classifier, Linear Discriminant Analysis (LMC) and Quadratic Means Analysis (QDA) it is sufficient to apply RDA. RDA seeks biased estimates of the class covariance matrices (Sg) in order to reduce their variance. RDA has two biasing schemes. The first converges the class covariance matrix towards a common covariance matrix:

$$Sg(l) = (1-l)\,Sg + lS$$

The second shrinks the class covariance matrix towards a multiple (the average of the eigenvalues) of the identity matrix:

$$Sg(l,g) = (1-g)\,Sg(l) + g\,tr[Sg(l)/p]$$

The first biasing is controlled by the parameter l and the second by the shrinking parameter g. Both range from 0–1. The final values chosen are based on a cross-validated misclassification risk. $l=0$, $g=0$ corresponds to QDA; $l=1$, $g=0$ is LDA and $l=1$, $g=1$ is NMC.

The misclassification plot is a graphical representation of the misclassification matrix. The ‘true class’ of each element is plotted *vs.* the class assigned by the optimal RDA model. If the model is successful, all elements will lie along the diagonal. Figure 5 shows the misclassification plot for the 13 polyethylenes in the training set. RDA assigned all samples to their correct classes. Based on this

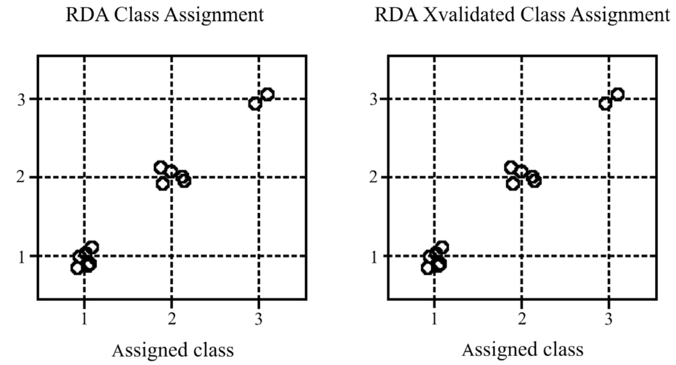

Fig. 5 Misclassification plot for the DSC data of 13 polyethylene samples, Class 1=LLDPE; class 2=VLDPE; class 3=LDPE

procedure, 7 of the 8 test samples were assigned correctly. The optimum values of *l* and *g* were 1.00 and 0.75.

Conclusions

This chemometric analysis shows that differential scanning calorimetry with thermal fractionation can be used to determine the structural classifications of polyethylenes. Inspection of the specific heat DSC curves readily identifies HPDE and ULDPE grades. The other three grades can be identified by applying the RDA discrimination method to parameters determined from the DSC curves. FTIR spectra do give some limited classification of the grades but cannot completely discriminate between all five grades. Although the DSC scanning method used is slow, its improved ability to discriminate the grades makes the use of this technique valuable.

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