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Discrimination of thermally treated low density polyethylenes using DSC and principal component analysis

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Abstract The potential for differential scanning calorimetry (DSC) as a tool for the discrimination of forensic polymer specimens is investigated for a series of commercial low density polyethylene (LDPE) samples. Variation in the melting temperatures of 'as received' samples was found to be too small for its use in sample discrimination. The melting behaviour of thermally treated samples, quenched from the melt in liquid nitrogen followed by annealing at temperatures below the melting temperature, showed promise in discrimination potential. The application of principal component analysis to aid discrimination demonstrated the necessity in using a controlled thermal history to aid the discrimination process. The clustering of the LDPEs based on the factors selected demonstrated the potential of DSC for the discrimination of forensic LDPE samples.

Keywords DSC · Principal component analysis (PCA) · LDPE · Forensic

Introduction

The discrimination of specimens of plastics is important in a forensic context as plastic materials are found in a variety of evidence types, such as drug packaging or material remaining at a fire scene [1, 2]. There are established analytical techniques, such as infrared spectroscopy, used by forensic practitioners for the identification of plastics as evidence and this largely enables the constituent polymer classes to be identified [3]. Less work has been carried out on developing methods that enable the differentiation of the more subtle structural properties of polymers that could potentially link specimens of plastics as evidence to a particular source.

Polyethylene (PE), the most abundant commercial plastic, exists in a number of forms depending on the method of manufacture. Specimens of PE vary as a function of the degree, length and distribution of chain branching. The variations in branch length and distribution affect, most notably, the density of the polymer resulting in typical commercial grades including low density (LDPE), linear low density (LLDPE) and high density (HDPE). The temperature at which a specific PE melts is also significantly affected; LDPEs melt at approximately 110 °C, LLDPEs at approximately 125 °C and HDPEs at approximately 130 °C. Some simple physical tests can, therefore, discriminate between these classes of polyethylene.

The variations in branch length and distribution also have a subtle influence on the morphology of a specimen. For example, LDPE, LLDPE and, to a lesser extent, HDPE are known to exhibit a 'memory' effect in their thermal histories. Stepwise isothermal crystallisation of specimens of PE has been demonstrated to institute a form of crystallisation fractionation of domains of crystallites that are fractionated according to the temperature at which crystallisation has occurred [4]. The fractions are related to the branching density, resulting in a range of crystallite orders that melt at temperatures corresponding to the crystallisation temperature. As fractionation is dependent on the distribution of branching, this process may yield a route to discrimination of specimens within a class of polyethylene.

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Several investigations of the thermal characterisation of polyethylenes using differential scanning calorimetry (DSC) in a forensic context have been reported. The identification of the plastic materials in these studies has been required to link evidence to a perpetrator of a crime [1–3, 5]. In general, DSC has been applied to the discrimination between samples where significant differences have been observed, e.g. samples are from a different grade of polyethylene [2], and hence, visual inspection of the data and measurement of melting points yields the required discrimination. For the more subtle differences between specimens within a polymer grade or class, the application of DSC as a discriminating analytical technique requires the use of multivariate analysis software to aid differentiation of specimens.

Multivariate analysis identifies uncorrelated factors (differences) within sets of data aiding subtle differentiation between specimens, thus providing greater value to trace evidence by increasing the uniqueness of discriminating potential. This type of analysis has been applied to DSC data for a range of PEs, where specimens from separate classes, LLDPE, very low density PE and LDPE were differentiated [6]. The discrimination of the relatively subtle differences in polymers from the same class, however, has yet to be achieved using these techniques. The present study investigates the potential of DSC for the discrimination of commercial LDPEs by imparting controlled, but extreme thermal histories to the polymers and by comparing their melting behaviour using the exploratory multivariate analysis method of principal component analysis.

Experimental

Commercial pelletised samples of LDPE (denoted LDPE 1 to 6) were supplied by Qenos Pty Ltd. Thin slivers of the LDPEs were cut from the pellets and encapsulated in aluminium pans and run ‘as received’ on a TA Instruments 2920 DSC at a heating rate of 10 °C min^{-1} under a flowing nitrogen purge (50 mL min^{-1}) to 180 °C. The specimens were then removed from the DSC furnace and immediately quenched in liquid nitrogen. The specimens were then warmed to room temperature before being subjected to annealing at temperatures between 50 and 100 °C for 1 h before cooling to room temperature. Samples were then heated at a rate of 10 °C min^{-1} to 180 °C.

Principal component analysis (PCA) was carried out using Infometrix Pirouette Multivariate Data Analysis software version 4.0. The first derivative of the DSC data in the range 50–150 °C at 0.2 °C intervals was prepared and the data was range-scaled and vector normalised before performing PCA analysis. Both 2-dimensional and 3-dimensional plots were obtained and the most discriminating factors were selected.

Results and discussion

The DSC curves for the ‘as received’ specimens of LDPE are shown in Fig. 1 and the peak melting temperatures are listed in Table 1. From these data, LDPE-6 can be easily differentiated from LDPEs 1–5 based on the melting temperature. Further inspection of the data in Fig. 1 suggests that LDPE-5 may be differentiated from the other samples; however, analysis of a multiple of DSC melting curves shows a large standard deviation in the measured peak melt temperature indicating that this differentiation is premature.

In order to improve the potential for discrimination of these samples, controlled processing histories were imparted to the LDPE samples; the samples were melted to remove the pelletisation history and then thermally treated by quenching in liquid nitrogen followed by annealing at temperatures below the melting temperature. The aim of the controlled thermal history was to use the known potential of LDPEs to fractionate into a range of different melting temperature crystallites [4]. To achieve

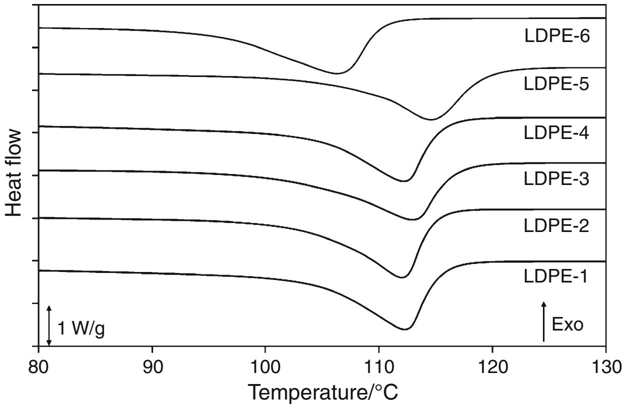

Fig. 1 DSC curves for ‘as received’ LDPE samples

Table 1 Peak melting temperatures for the ‘as received’ specimens

Polymer	T_m/°C	Standard deviation	Melt index[a]	Density[a]/ g cm^{-3}
LDPE-1	112.3	0.2	0.43	0.9220
LDPE-2	112.3	0.3	2.52	0.9221
LDPE-3	112.5	0.5	22.59	0.9192
LDPE-4	112.5	0.3	0.33	0.9221
LDPE-5	113.0	1.2	2.58	0.9203
LDPE-6	106.7	0.5	12.13	0.9185

[a] Data supplied by the manufacturer

equilibrium fractionation, however, long annealing times of the order of 10–12 h are required [7]. As aim of this study was to simply discriminate between different samples of PE, annealing was limited to a shorter 1 h period. The thermal treatment was, therefore, applied to provide a controlled thermal history to the polymers to attempt further separation of the samples based on differences in the molecular structure (i.e. molecular weight and MW distribution and branch density, distribution and length). In order to identify an optimum thermal treatment, sample LDPE-1 was subjected to a number of treatment procedures. For each treatment, specimens were quenched from 180 °C in liquid nitrogen followed by annealing at the assigned temperature. The DSC data are shown in Fig. 2 and Table 2 lists the peak melting temperatures of crystallites because of the annealing (T_a) and the final melting (T_m). An annealing temperature of 80 °C was selected as the standard post-quench annealing temperature based on the relative separation and size of the secondary melting peak and the final melting peak. This procedure was applied to all the LDPEs; the data for which are shown in Fig. 3 and values of T_a and T_m are tabulated in Table 3. Visual inspection of the standard DSC data results in a similar degree of discrimination of the specimens as was observed for the 'as received' sample data shown in Fig. 1. Sample LDPE-6 is clearly separated by its low melting temperature.

In order to determine the potential for discrimination of the LDPEs using the quench and anneal heat treatment procedure, PCA was carried out on the DSC data of at least three specimens of each sample characterised 'as received' or 'quenched in liquid nitrogen and annealed at 80 °C'. The first derivative of the DSC curves was used to remove baseline variations and the data was vector normalised to remove any amplitude effects. The PCA is shown in Fig. 4a and b for discriminating factors 1 and 2 determined by the analysis. It is apparent that separation of the 'as received' samples is limited to LDPE-6. Separation of sample LDPE-6 is expected as its melting temperature is significantly different from the other LDPEs. LDPEs 1–5 are not particularly well separated for the 'as received' samples.

Controlling the history of the specimens yields much greater degree of discrimination between the LDPEs which are separated into 'clusters' (Fig. 4b). LDPE-6 remains separated from LDPEs 1–5 as is expected. LDPEs 2–5,

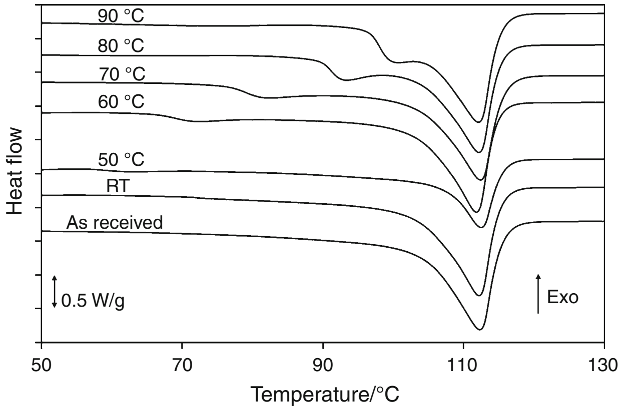

Fig. 2 DSC curves for the LDPE sample LDPE-1 annealed at the temperatures listed after quenching in liquid nitrogen from the melt (180 °C)

Table 2 List of melting temperatures for the annealing peak, T_a, and the final melting peak, T_m, for LDPE-1

Annealing temperature/°C	T_a/°C	T_m/°C
90	100.2	112.2
80	93.1	112.1
70	81.6	112.4
60	71.8	111.9
50	62.0	112.4
RT	–	112.2

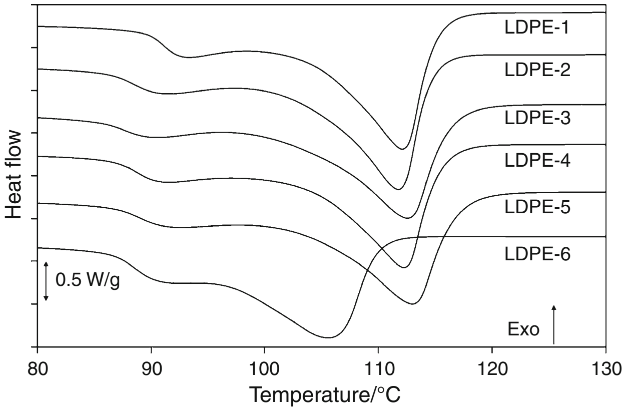

Fig. 3 DSC curves for the LDPE samples annealed at 80 °C after quenching in liquid nitrogen from the melt (180 °C)

Table 3 List of melting temperatures for the annealing peak, T_a, and the final melting peak, T_m for LDPE samples annealed at 80 °C after quenching in liquid nitrogen from the melt (180 °C)

Polymer	T_a/°C	Standard deviation	T_m/°C	Standard deviation
LDPE-1	91.4	1.2	112.0	0.1
LDPE-2	90.9	0.1	112.0	0.2
LDPE-3	91.4	0.2	112.0	0.1
LDPE-4	91.1	0.1	112.5	0.2
LDPE-5	91.1	0.4	112.6	0.6
LDPE-6	90.7	0.3	106.5	0.5

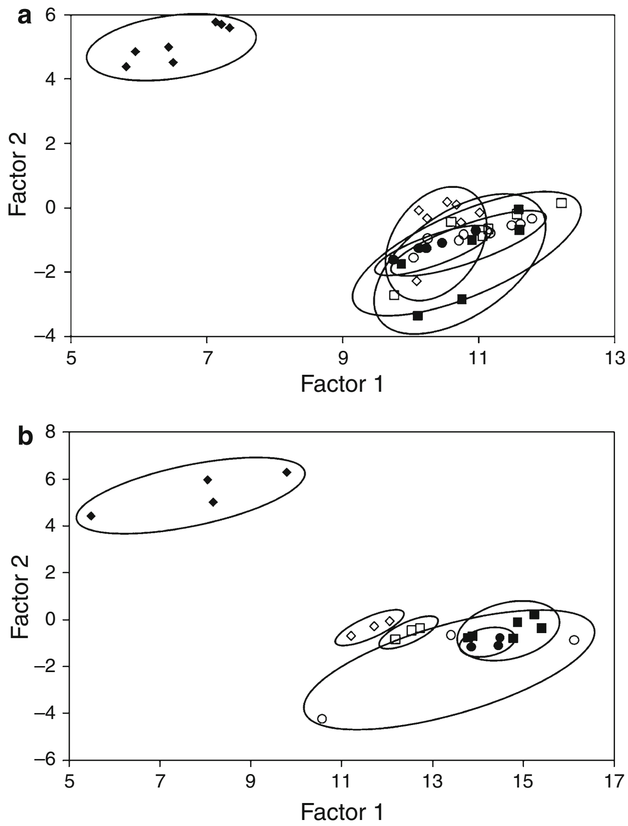

Fig. 4 Factors 1 and 2 derived from the principal component analysis of DSC curves collected for **a** 'as received' and **b** 'quenched in liquid nitrogen and annealed at 80 °C'. LDPE-1 *opened circle*, LDPE-2 *opened square*, LDPE-3 *opened diamond*, LDPE-4 *filled circle*, LDPE-5 *filled square*, LDPE-6 *filled diamond*

however, are now distinguishable by the narrow clusters produced. Although some scatter remains in the data, as evidenced by the scatter and lack of discrimination for LDPE-1, significant steps have been made in the discrimination between the LDPEs and have resulted by controlling the thermal history of the specimens. Further characterisation is, however, required to optimise the sample history to attain optimum discrimination between samples with the ultimate goal of developing a method which can discriminate between different specimens of a single sample of a polyethylene with subtly different processing histories.

Conclusions

A series of samples of LDPE were investigated to identify the potential of DSC for the discrimination of forensic specimens. Heating curves of the 'as received' samples did not provide significant discrimination between samples. Instituting controlled thermal histories into the samples with the aid of principal component analysis, however, resulted in significantly improved results. The improved discrimination between samples suggests that, with further optimisation of the thermal treatment process, DSC has a significant potential for use as a discriminating tool in forensic analysis.

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