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IDENTIFICATION OF POLYETHYLENE BY DIFFERENTIAL SCANNING CALORIMETRY

Application to forensic science

T. Tsukame[1], *M. Kutsuzawa*[1], *H. Sekine*[1], *H. Saitoh*[2] *and Y. Shibasaki*[2]

[1]Criminal Investigation Laboratory, Saitama Prefecture Police H. Q., 3-15-1, Takasago
Urawa, Saitama 336-8533
[2]Department of Chemistry, Faculty of Science, Saitama University, 255, Shimo-okubo
Urawa, Saitama 338-8570, Japan

Abstract

A forensic sample consisting of melt-recrystallized polymers that was recovered from the scene of a fire in a factory was identified by differential scanning calorimetry. The factory commonly used two kinds of film sheets, A and B, made by different manufacturers. It was necessary to decide whether the forensic sample related to material A or B. The forensic sample and reference samples of materials A and B were subjected to infrared spectroscopy and pyrolysis gas chromatograph mass spectrometry measurements, which revealed their polyethylene nature. The thermal behaviour of the samples was examined by differential scanning calorimetry (DSC) and they were found to be blends of two kinds of polyethylenes, low-density polyethylene and linear low-density polyethylene. The samples could be identified and distinguished from each other via the DSC measurements.

Keywords: DSC, linear low-density polyethylene (LLDPE), low density polyethylene (LDPE), polymer blend, thermal properties

Introduction

Thermal analysis techniques, such as thermogravimetry and differential scanning calorimetry (DSC), are used to characterize the thermal properties of many kinds of materials [1]. However, these methods are applied only rarely to unknown polymer materials. In this paper, an application of thermal analysis involving the use of DSC to identify an unknown forensic sample collected from the scene of a fire is reported.

The melted polymer was discovered at the scene of a factory fire. The polymer was attached to a heater in a manufacturing process. In this factory, two kinds of polymer sheets, A and B, were used in the process. In order to reveal the cause of the fire, were requested by an investigator to decide whether the forensic sample was identical with either A or B.

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Experimental

The apparatus and the analytical conditions used in this work were as follows: FT-IR analysis was performed with a Nicolet Corp. FT-IR model 560 spectrometer with an attached Nic-Plan IR microscope. The measurement method was transmittance mode IR microscopy. GC/MS analysis was performed with a Hewlett Packard Inc. model HP-5890 series 2 gas chromatograph combined with an HP-5972 mass selective detector. The GC was temperature-programmed from 50 to 300°C at a rate of 10°C min^{-1}, with an initial and final hold of 5 min; the injection temperature was 250°C. Pyrolysis was performed with a Japan Analytical Industry Co. Ltd. model JHP-3 Curie point pyrolyzer, combined with the GC injection. The pyrolysis temperature and time were 590°C and 4 s, respectively. Thermal analysis was performed with a MAC Science Co. Ltd. model 3110 differential scanning calorimeter. Heating and cooling rates of 10°C min^{-1} were used in the ranges 50 to 200°C, and 200 to 50°C (twice repeated for heating and cooling). The atmosphere of the measurement was N_2 with a flow rate of 50 ml min^{-1}.

The forensic sample was used without a carbonized part and the reference samples were used without pretreatment.

Results and discussion

The forensic sample and the reference samples were first examined by means of FT-IR and Py-GC/MS. Figure 1 shows IR spectra of the samples. All peaks in the spectra relate to the absorption of C–H; they indicate a typical polyethylene [2, 3]. There was no obvious difference between the forensic sample and the reference. Figure 2 depicts pyrograms of the samples, containing a series of sets of three peaks.

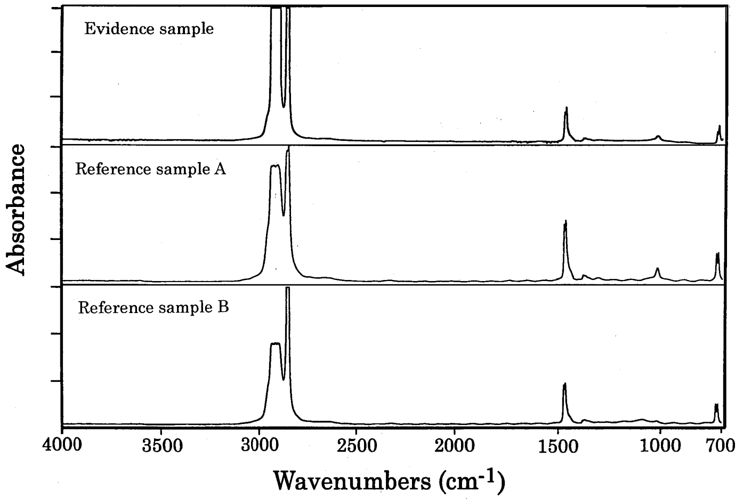

Fig. 1 IR spectra of forensic sample and reference samples (upper – forensic sample; middle – reference sample A; lower – reference sample B)

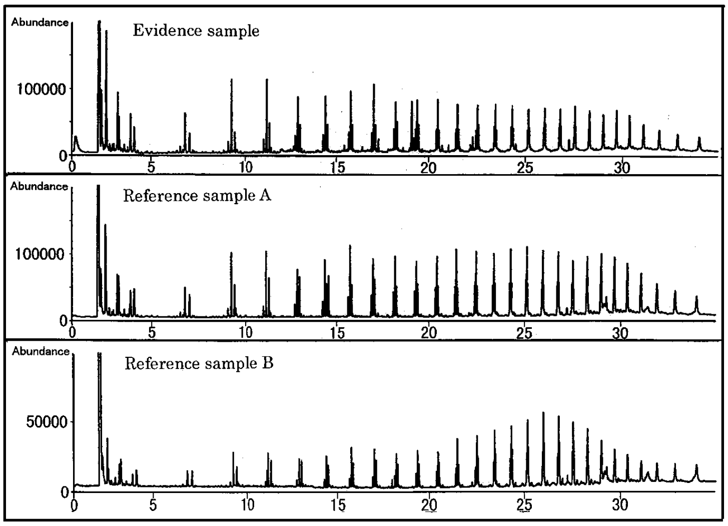

Fig. 2 Pyrograms (total ion chromatograms) of forensic sample and reference samples (upper – forensic sample; middle – reference sample A; lower – reference sample B)

These peaks were assigned to hydrocarbons on the basis of the mass spectra. A typical enlarged chromatogram of a set of three peaks in the range 15–20 min, and the mass spectrum of peak 3 are depicted in Fig. 3. Peak 1 is due to di-hexadecene, peak 2 to hexadecene, and peak 3 to hexadecane. This thermal degradation pattern indicates typical random scission of a polymer chain, and the samples were easily identified as polyethylene [4]. There is no peak of any additional compound in any of the programs, and we could not discriminate between the forensic sample and the reference samples on the basis of these pyrograms.

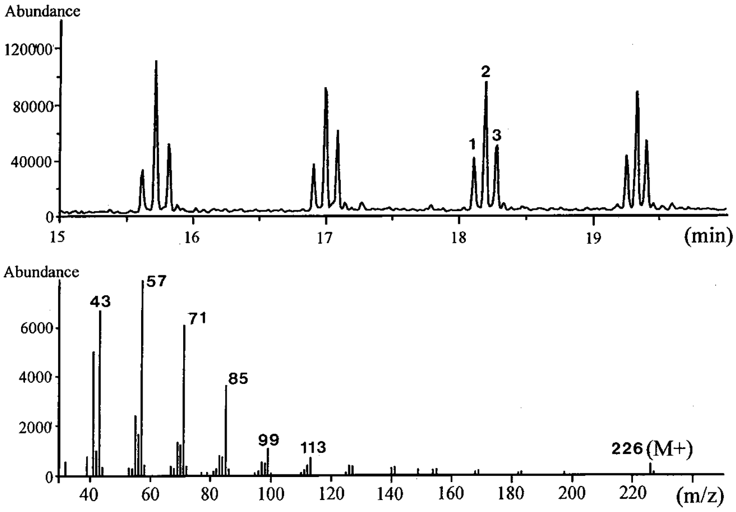

Fig. 3 Enlarged pyrogram of range 15–20 min (upper), and mass spectrum of peak 3

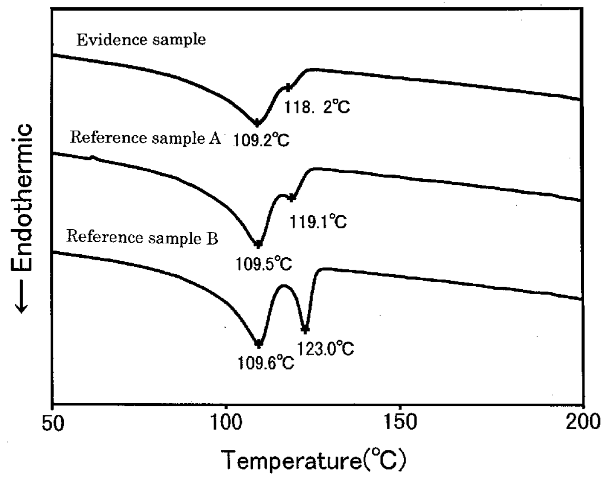

Fig. 4 DSC curves for 2nd heating of forensic sample and reference samples (upper – forensic sample; middle – reference sample A; lower – reference sample B)

Secondly, DSC measurements were performed. Figure 4 shows the DSC curves for the 2nd heating of these samples. As the thermal history of the forensic sample from the fire scene was not available, only 2nd heating curves are shown in Fig. 4. These curves exhibit two endothermic peaks at almost the same temperature. The peak at lower temperature seems to correspond to the melting point of low-density polyethylene (LDPE), and the upper peak to the melting point of linear low-density polyethylene (LLDPE) [5]. Consequently, it can be concluded that these samples are blends of LDPE and LLDPE. It was apparent that the molecules of these polyethylenes were not mixed sufficiently, because the DSC peaks were sharp and well separated from each other.

Figure 5 presents typical well-separated DSC curves of a LDPE and LLDPE blend. This sample was mixed by heating in a DSC pan. The melting points of LDPE

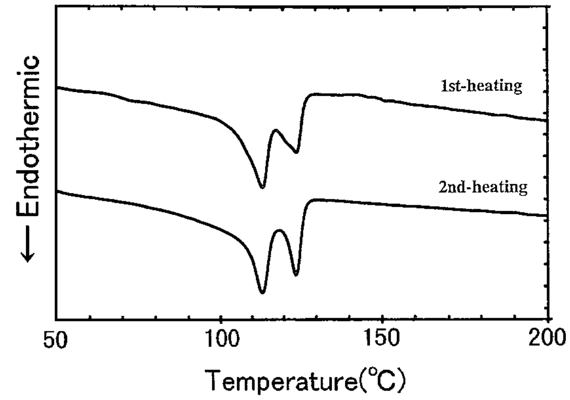

Fig. 5 Typcial well-separated DSC curves of LDPE and LLDPE blend

(lower-temperature peak) and LLDPE (upper-temperature peak) are scarcely changed between the 1st and 2nd heatings. When the two kinds of polyethylenes were well blended, entanglement of the main-chains and also the side-chains of LDPE and LLDPE occur, and these endothermic peaks should broaden [6]. The melting points of well-blended mixtures of LDPE and LLDPE also change with their blend ratio. The results led to the conclusion that the forensic sample was identical with reference sample A.

Conclusions

DSC measurement proved to be a useful method for examination of the thermal properties of polymers. The method is applicable to forensic science. Especially the results of thermal analysis by DSC are useful from the aspect of a decision as to whether a forensic sample is identical or not with a given reference material.

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