

# Prediction of Polyethylene Density by Near-Infrared Spectroscopy Combined with Neural Network Analysis

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A rapid and intact method has been developed for predicting polyethylene density by near-infrared spectroscopy combined with neural network analysis. Near-infrared spectra in the region of 1.1–2.2  $\mu\text{m}$  wavelength were measured using pellets or powders of twenty-three kinds of polyethylene (PE) with different densities (0.898–0.962  $\text{g cm}^{-3}$ ). The spectra were used for training a back-propagation neural network after normalized and second-derivative treatments to predict PE density. Although only a small number of spectral data were used for training, a leave-one-out test of neural network analysis has demonstrated good results. In comparison, principal component regression (PCR) analysis and partial least-squares (PLS) regression analysis were applied. The correlation coefficients (R) were calculated to be 1.000, 0.968 and 0.983 for neural network, PCR and PLS analysis, respectively. The root mean square errors of prediction were found to be 0.00026, 0.0043 and 0.0031  $\text{g cm}^{-3}$ , respectively. It is found that near-infrared spectroscopy combined with neural network analysis is useful for the efficient and accurate determination of PE density.

**Keywords:** Neural Networks, Near-Infrared Spectroscopy, Plastics, Polyethylene, Density, Melt Flow Rate

## 1 Introduction

Every year, over 15 million tons of plastics are produced and consumed in Japan. Recycling of plastic waste is steadily gaining importance because of the shortage of disposal sites and the conservation of oil resources. Not only many different kinds of plastics, but also the same plastics of different characteristics or composition, in other words, plastics of different grades are manufactured. In the case of plastic recycling, conservation of

the characteristics of recycled materials is desired. Moreover, plastic wastes have to be sorted according to their types and even more, the same kinds of plastics are to be discriminated according to their grades or density. This diversity is mainly due to economical reasons. The prices of the plastic goods manufactured vary tremendously depending on the grades of recycled plastic materials used. For instance, it has to be noted that recycled high-density polyethylene is more than twice as expensive as low-density polyethylene.

Table 1. Density and MFR of PE samples examined in the present study.

| Sample No. | Grades | Density<br>(g cm <sup>-3</sup> ) | MFR<br>(g 10min <sup>-1</sup> ) | Sample No. | Grades | Density<br>(g cm <sup>-3</sup> ) | MFR<br>(g 10min <sup>-1</sup> ) |
|------------|--------|----------------------------------|---------------------------------|------------|--------|----------------------------------|---------------------------------|
| 1          | LLDPE  | 0.920                            | 2                               | 13         | LDPE   | 0.925                            | 2.8                             |
| 2          | LLDPE  | 0.920                            | 2.1                             | 14         | LDPE   | 0.930                            | 1.5                             |
| 3          | LLDPE  | 0.929                            | 100                             | 15         | HDPE   | 0.944                            | 0.04                            |
| 4          | LLDPE  | 0.930                            | 1.5                             | 16         | HDPE   | 0.946                            | 4                               |
| 5          | LLDPE  | 0.935                            | 5                               | 17         | HDPE   | 0.947                            | 42                              |
| 6          | LLDPE  | 0.935                            | 5.5                             | 18         | HDPE   | 0.950                            | 0.25                            |
| 7          | LDPE   | 0.898                            | 3.5                             | 19         | HDPE   | 0.950                            | 1                               |
| 8          | LDPE   | 0.905                            | 3.5                             | 20         | HDPE   | 0.950                            | 40                              |
| 9          | LDPE   | 0.918                            | 1                               | 21         | HDPE   | 0.952                            | 10.5                            |
| 10         | LDPE   | 0.918                            | 2                               | 22         | HDPE   | 0.960                            | 1                               |
| 11         | LDPE   | 0.918                            | 4                               | 23         | HDPE   | 0.962                            | 36                              |
| 12         | LDPE   | 0.918                            | 7                               |            |        |                                  |                                 |

Polyethylene (PE) is one of the most multipurpose materials in plastics. It has diverse practical fundamental properties (e.g., mechanical properties, chemical stability and so on), and is thereby of diverse capability and moreover, of low cost. It is used for various purposes such as kitchen utensils, toys, general cargoes and so on. However, according to each purpose, different kinds of PE properties are required. As a result, PEs of various densities such as high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) are produced. For advanced plastic recycling, a technique for discriminating various densities of PE is indispensable.

The density of plastics is determined by infrared spectroscopic analysis, differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) spectroscopic analysis. Rapid and non-destructive analysis of the density is needed for plastic recycling. With those techniques, the density cannot be analyzed quickly and non-destructively. Williams and Everall, and Shimoyama et. al. have reported that PE density was determined by near-infrared (NIR) or Raman spectroscopy combined with chemometrics [1–4]. Only NIR spectra measurement is applicable for plastic recycling, because it can be done quickly and non-destructively.

The combined technique of NIR spectroscopy and chemometrics analysis has been investigated for more than two decades [1–14]. In plastic recycling though, it is also important to analyze more precisely. The amount of information provided by NIR spectra is difficult to detect, but it is an essential and key technique.

The neural network technique has substantial advantages for spectral discrimination. Using this technique, the little difference in information obtained from NIR spectra becomes discriminable. In our previous study, we have already succeeded in developing techniques to discriminate more than 50 different kinds of plastic patterns [15] and to separate PE grades [16]. In the present paper,

we propose a calibration model which predicts precise PE density using this approach.

## 2 Experimental

### 2.1 Samples

Twenty-three kinds of PE samples used in this study were obtained from commercial companies. The densities were in the range of 0.898–0.962 g cm<sup>-3</sup>, as listed in Table 1.

### 2.2 Instrument

The NIR spectra in the region of 1.1–2.2  $\mu\text{m}$  were measured using pellets or powders with a PlaScan-SH (Opt Research Inc., Japan). The number of data points for each NIR spectrum of the above region was 1200. A scan for an NIR spectrum using this device is carried out within less than 1 second.

### 2.3 Data Analysis

NIR spectra were measured five times for each sample with different orientations. The total number of recorded spectra was 115. NIR spectra in the region of 1.1–2.2  $\mu\text{m}$  were subjected to the following pretreatments before training a neural network; (1) the maximum and minimum absorbances in each spectrum are normalized to 1.0 and 0.0, respectively, (2) the data of 1200 points are averaged at every 10 points (reduced to 120 points in total), (3) second-derivative spectra were calculated, and (4) the maximum absolute value was normalized to 1.0 again. Figure 1(a)–(d) illustrate averaged and normalized spectra of 2 different samples i.e. samples of maximum and minimum densities, before and after second-derivative treatment, respectively. Spectra obtained from five directions for each sample showed little difference.

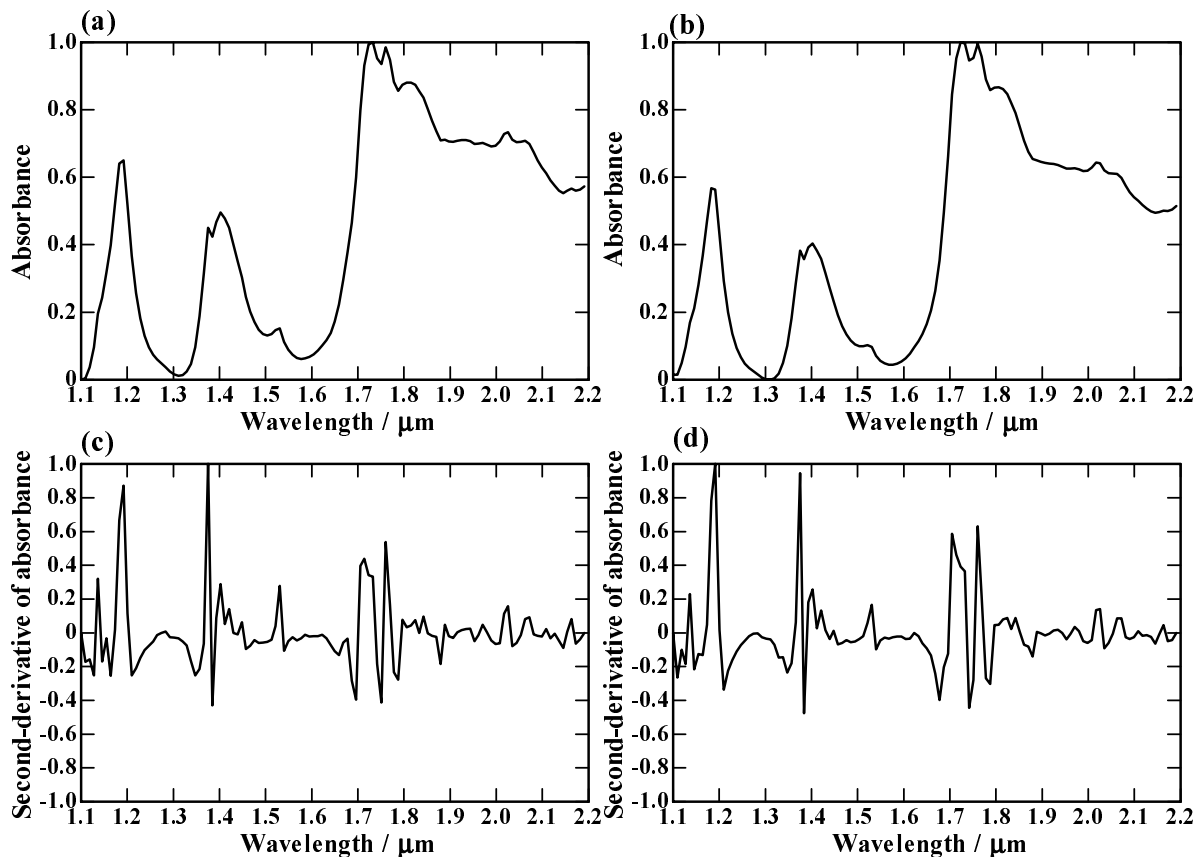


Figure 1. Normalized spectra from sample of maximum density (a), it's second-derivative spectra (c), normalized spectra from sample of minimum density (b) and it's second-derivative spectra (d).

The NEUROSIM/L (version 3.2) software program (Fujitsu Ltd., Japan) was employed for training of a neural network. In comparison, principal component regression (PCR) and partial least squares (PLS) regression were attempted for making a calibration model that predicts the density. The Pirouette (version 3.0) software program (InfoMetrix Inc., USA) was applied for PCR and PLS regression. In the neural network, PCR and PLS regression analysis, a leave-one-out cross-validation was performed. That is, the test was performed using one sample (five spectra) after training using twenty-two of twenty-three samples (110 of 115 spectra).

## 2.4 Architecture of the Neural Network

The neural network was of a three-layered model. The input, intermediate (hidden), and output layers were composed of 120, 5, and 1 unit(s) (neuron(s)), respectively. The trainings of the networks were carried out by using the error back-propagation method in this study. Maximum and minimum densities were normalized to 0.8 and -0.8, respectively, as supervised signals. Training was ended when the maximum error converged to less than 0.01.

## 3 Results and discussion

### 3.1 Principal component analysis

Figure 2 shows a score plot of factor 1 and factor 2 of principal component analysis (PCA). PCA was carried out using one of the five spectra of each sample. The 23 spectra could be roughly divided into three groups, namely LLDPE, LDPE and HDPE. Loadings plots of factor 1 and factor 2 for the score plot shown in Figure 2 are illustrated in Figure 3(a) and (b), respectively. The plot in Figure 3(a) shows one upward peak at 1.72  $\mu\text{m}$  and two downward peaks at 1.70 and 1.75  $\mu\text{m}$ . All peaks can be assigned to methylene groups [2]. The plot in Figure 3(b) shows one upward peak at 1.68  $\mu\text{m}$  and two downward peaks at 1.70 and 1.75  $\mu\text{m}$ . One upward peak can be assigned to methyl groups [2], while two downward peaks can be assigned to methylene groups [2]. Peaks at 1.19 and 1.37  $\mu\text{m}$  correspond to methyl groups [2]. Other peaks at 1.16, 1.39 and 1.53  $\mu\text{m}$  correspond to methylene groups [2]. These peaks do not appear in the raw spectra. They can clearly be detected by PCA after second-derivative treatment though.

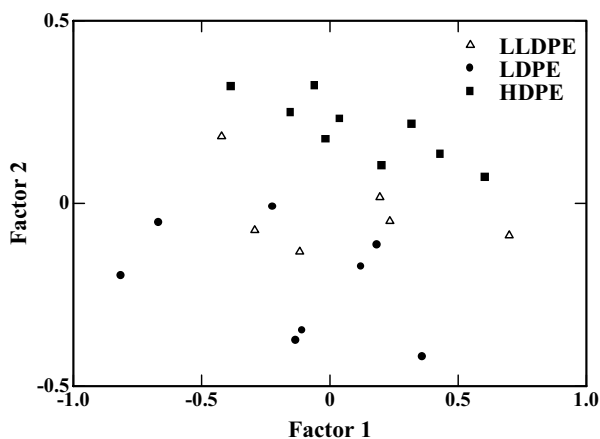


Figure 2. A score plot of principal component analysis of factor 1 and factor 2 from the second-derivative spectra.

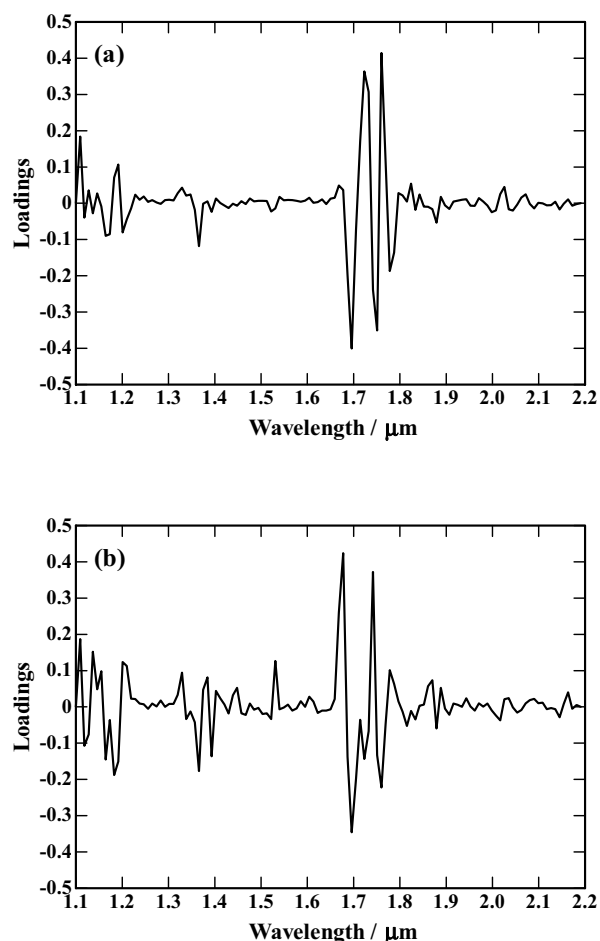


Figure 3. A loadings plot of factor 1 (a) and factor 2 (b) for the model shown in Figure 2.

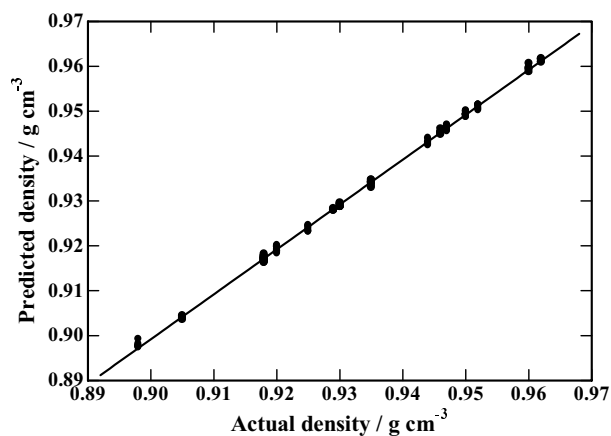


Figure 4. A neural network analysis for predicting the polyethylene density from the second-derivative spectra.

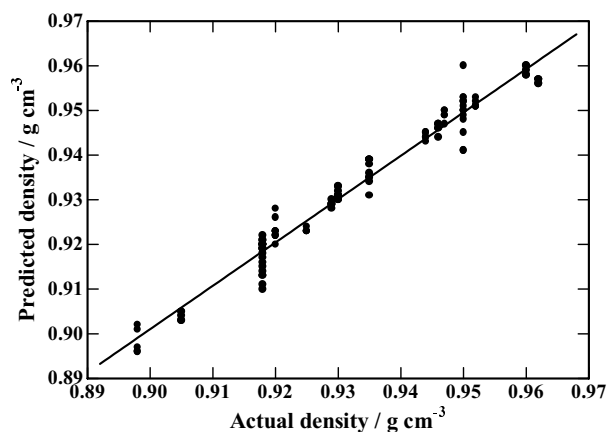


Figure 5. A partial least-squares regression calibration model with four factors for predicting the polyethylene density from the second-derivative spectra.

Table 2. Correlation coefficients (R) and root mean square errors of prediction (RMSEP) of PE densities.

| Algorithm                   | R     | RMSEP (g cm <sup>-3</sup> ) |
|-----------------------------|-------|-----------------------------|
| Neural Network              | 1.000 | 0.00026                     |
| PCR <sup>a</sup>            | 0.968 | 0.0043                      |
| PLS Regression <sup>a</sup> | 0.983 | 0.0031                      |

<sup>a</sup>Four factors

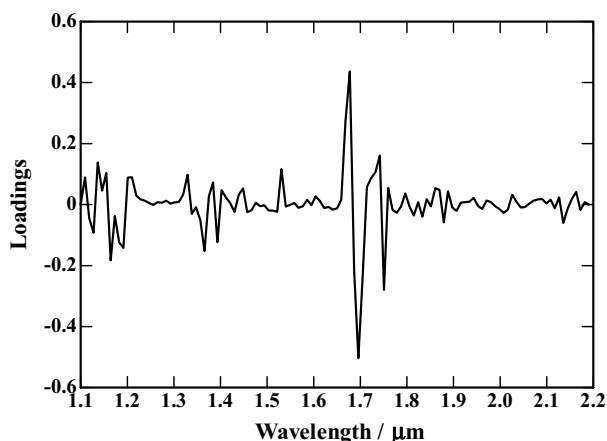


Figure 6. A loadings plot of regression coefficients for the model shown in Figure 5.

### 3.2 Prediction of Density by Neural Network Analysis

Figure 4 presents PE densities predicted for 115 NIR spectra by neural network. A good straight line could be obtained between the actual and predicted densities.

### 3.3 Comparison with PCR and PLS analyses

In comparison, we made a calibration model by PCR and PLS. The PLS model with four factors for predicting PE density is presented in Figure 5. A good straight line could be obtained between actual and predicted densities too. Table 2 summarizes the correlation coefficients ( $R$ ) and the root mean square errors of prediction (RMSEP). The neural network analysis, which is one of the most typical methods of nonlinear analysis, gave better results than either PCR or PLS analysis.

It is known that the PE density is determined by the number and kinds of branches attached to the main chain of PE. The larger the number of branched methyl, ethyl, or butyl groups, the lower the density. A loadings plot of regression coefficients for the model shown in Figure 5 is presented in Figure 6. This plot is similar to the loadings plot factor 2 in Figure 3(b). The plot shows one upward peak at  $1.68 \mu\text{m}$  and two downward peaks at  $1.70$  and  $1.75 \mu\text{m}$ . One upward peak can be assigned to methyl groups [2], while two downward peaks can be assigned to methylene groups [2]. Peaks at  $1.19$  and  $1.37 \mu\text{m}$  correspond to methyl groups [2]. Other peaks at  $1.16$ ,  $1.39$  and  $1.53 \mu\text{m}$  correspond to methylene groups [2]. As can be seen from the above results, the kinds of branches can be detected from the NIR spectra.

Shimoyama et.al [2] reported PLS calibration of NIR data of LLDPE (16 samples) with densities between  $0.911$  and  $0.925 \text{ g cm}^{-3}$ . They obtained the values with  $R$  of  $0.965$  and SEP of  $0.001 \text{ g cm}^{-3}$ . We have shown that similar results can be obtained even within a much

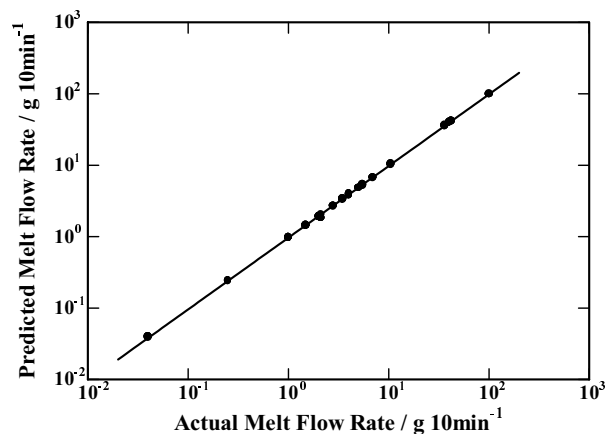


Figure 7. A neural network analysis for predicting the polyethylene MFR from the second-derivative spectra.

wider range of densities ( $0.898$ - $0.962$ ) and more samples (23 samples).

### 3.4 Comparison with conventional methods

PE density is measured by infrared, DSC and NMR methods. But these methods cannot be used quickly nor non-destructively, and are unsuitable for plastic recycling.

On the other hand, NIR spectroscopy doesn't have stronger absorption than IR. Overtone and combination bands appear with adequate intensities in NIR spectra. So NIR spectra can be measured quickly and non-destructively without sample preparation. NIR is suited to plastic recycling.

We have shown that a little difference in NIR spectra was detected by neural network analysis. We have developed a rapid and non-destructive technique to predict PE density by combining those methods.

### 3.5 Supplemental experiment

Melt flow rate (MFR) of plastics is also important for plastic recycling. MFR is closely related to the molecular weight. The differences in molecular weights have a big influence on mechanical properties, processability and so on. If MFR is high, the melt viscosity is small and vice versa. We tried to predict the MFR using the above approach. MFR ranges of the test samples are  $0.04$ - $100 \text{ g 10min}^{-1}$  as listed in Table 1. Logarithms of maximum and minimum MFRs were normalized to  $0.8$  and  $-0.8$ , respectively, as supervised signals.

Figure 7 presents PE MFRs predicted for 115 NIR spectra by neural network. A good straight line could be obtained between the actual and predicted MFRs. Values with  $R$  of  $1.000$  and relative RMSEP of  $0.038 \text{ g 10min}^{-1}$  were obtained.

Formerly, it was thought that the difference of MFR does not appear in NIR spectra. Small differences of spectra due to the difference of MFR could be detected by neural network analysis. We have developed a technique to determine MFR quickly and non-destructively.

## 4 Conclusion

In this article, we have demonstrated the useful technique of NIR spectroscopy combined with neural network analysis in the prediction of PE density and MFR.

The neural network analysis has given good results for density prediction with R of 1.000 and RMSEP of 0.00026 g cm<sup>-3</sup>. Using neural network analysis, PE density can be predicted with higher accuracy than PCR or PLS regression analysis. The neural network analysis has also given good results for MFR prediction with R of 1.000 and relative RMSEP of 0.038 g 10min<sup>-1</sup>.

The present result is quite important from the point of view of plastic recycling. Our technique can be applied rapidly and non-destructively. This combined technique using NIR spectroscopy and neural network analysis is helpful in material recycling of plastics. Moreover, the NIR spectroscopic device used in this study is small and is of low price. So this is an applicable in-situ measurement in a plastic waste disposal station. Furthermore, this technique has the possibility to predict densities of plastics other than PE. In this study, the possibility to develop a practical plastic discrimination system using the above approach has been demonstrated.

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# 近赤外分光測定とニューラルネットワーク解析を 組み合わせたポリエチレン密度の予測

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プラスチック廃棄物のリサイクル技術向上のために、近赤外分光測定とニューラルネットワーク解析を組み合わせて、ポリエチレンの密度を迅速に識別する手法を検討した。市販のポリエチレンのペレットもしくは粉末 23 種類（密度範囲：0.898-0.962 g cm<sup>-3</sup>）について、波長 1.1 ~ 2.2 μm 領域の近赤外反射スペクトルを測定した後、二次微分処理を行い、3 層構造のニューラルネットワークでバックプロパゲーション法にて学習を行い、leave-one-out 法による予測テストを行った。その結果、少数の学習データを用いたにもかかわらず、ポリエチレンの密度は平均誤差 0.00026 g cm<sup>-3</sup> 以内で予測可能であることを確認した。比較として主成分回帰分析及び PLS 回帰分析を行ったところ、その平均予測誤差はそれぞれ、0.0043 および 0.0031 g cm<sup>-3</sup> であった。近赤外分光測定とニューラルネットワーク解析を組み合わせるとポリエチレンの密度が正確に予測可能であることが分かった。

キーワード：ニューラルネットワーク, 近赤外分光, プラスチック, ポリエチレン, 密度, メルトフローレート

