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Direct on-line Raman measurement of flying solid samples: Determination of polyethylene pellet density

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ABSTRACT

We demonstrated an on-line Raman measurement of polyethylene (PE) pellet density when it is flying in a sample line. While in flight, pellets are sparsely populated at spectral collection, a spectral collection strategy covering a large spatial volume (larger number of pellets simultaneously) is necessary to acquire reasonable Raman intensity. In addition, the Raman measurement must be less sensitive to pellet position, because position and distribution are uncontrollable in a flying condition. To fulfill these requirements, a wide area illumination (WAI) scheme capable of covering a large sample volume (illumination volume: 0.7 cm^3) was used when the pellets were flying in a 2.5-cm-diameter sample line. In addition, a long focal length (250 mm) was used so that minor changes in pellet position would not significantly affect the resulting Raman spectral feature. Although Raman intensity substantially decreased due to the large void space among flying pellets, a correct spectral feature representing PE was successfully obtained without any significant spectral distortion. Using partial least squares (PLS) regression, the prediction error under flying conditions was 0.0009 $g\,cm^{-3}$, which was comparable to that acquired when the pellets were packed (0.0008 $g\,cm^{-3}$). When a conventional Raman scheme covering a smaller sample volume with a short focal length was used, the PE intensity decreased dramatically, and the resulting signal-to-noise ratio was not proper for quantitative analysis.

1. Introduction

Near-infrared (NIR) as well as Raman spectroscopy has been widely studied for real-time monitoring of powder blending, especially in pharmaceutical fields [1–14]. Since both methods are fast and non-destructive, on-line or in-line analyses of powder blending process are possible. Normally diffuse reflectance and back-scattering modes are employed to collect NIR and Raman spectra of powder sample, respectively. Although both spectroscopic methods are able to monitor the status of powder blending, Raman spectral feature is generally more informative and selective compared to that of NIR. Other than the monitoring of powder blending in which powder samples are densely populated, on-line measurement of flying granule or powder is also in great demand for quality control and assurance. In this situation, samples are transported pneumatically or gravitationally during the course of production. In spite of this need, no studies have demonstrated a spectroscopic method for on-line analysis of flying samples. Under the flying condition, the population of solid samples in a given sampling volume is substantially low and their distribution always varies at measurement. Therefore, development of a proper spectroscopic method to overcome these hurdles is challenging.

In this paper, we present a reliable analytical method based on Raman spectroscopy to directly collect spectra of flying polyethylene (PE) pellet and accurately determine their density in an on-line manner. Since flying particles can be regarded as loosely packed samples, there is a large void volume among samples. Also, laser interaction time with each flying sample is extremely short. In this situation, the resulting Raman intensity would be substantially decreased because the chance of illuminating a laser into the void space, rather than the sample, is high. To achieve reasonable Raman intensity for quantitative analysis, a spectral collection strategy covering a large spatial volume is necessary. In addition, the positions of individual particles vary in flight; therefore, a spectral collection scheme that is less sensitive to sample placement with regard to the focal plane is also desirable.

To cover a large spatial sample volume for spectral collection, a wide area illumination (WAI) Raman scheme [14], capable of illuminating a laser into a 28.3 mm^2 area with a long focal length of 250 mm, was used. Raman spectral features of flying PE pellet were carefully examined to judge whether the quality of collected spectra would be adequate for quantitative analysis, because the resulting Raman intensity collected from flying pellets was expected to decrease significantly due to the large void space among samples and short residence at the laser illumination

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volume. A partial least squares (PLS) [15,16] model was developed using the spectra collected from packed pellets, and the model was used to predict flying pellet densities. The resulting accuracy was assessed to judge the utility of the direct on-line Raman measurement for flying PE pellets. Finally, Raman spectra of flying pellets were also collected using a conventional Raman spectral collection scheme covering a smaller sample volume with a shorter focal length and the resulting spectral features were also examined.

2. Experimental

2.1. Samples and Raman spectral collection

Twenty-five polyethylene (LLDPE: linear low density polyethylene) pellets were used in this study based on a previous publication [17]. The samples were composed of three different grades from different polymerization processes (homopolymerization and copolymerizations by 1-butene and 1-octene). The sample densities ranged from 0.918 to 0.961 g cm^{-3}. In general, the lower density pellets had a more disk-like shape with a larger diameter (∼5 to 6 mm), while the higher density pellets were more spherical with a smaller diameter (∼4 to 5 mm).

Raman spectra were collected using a wide area illumination (WAI) scheme (PhAT system, Kaiser Optical Inc., Ann Arbor, MI, USA). An excitation laser (785 nm, diode laser) was magnified to form a circular illumination area with a diameter of 6 mm (area: 28.3 mm^2) to cover a large sample area. A detailed description of the WAI Raman scheme can be found in a previous publication [14]. The resolution of collected spectra was 4 cm^{-1}.

Raman spectra of the PE pellets were collected under three different pellet conditions; packed, flowing, and flying. First, the PE pellets were fully packed in a 2.5 cm diameter glass tube (length: 150 cm) with the bottom closed. The tube packed with pellets was placed at the focal point of WAI scheme for Raman spectral collection. The Raman spectra for flowing pellets were collected, while packed pellets were allowed to flow gravitationally by partial opening of the tube bottom at a flow rate of 18.6 g s^{-1}. Lastly, Raman spectra for flying pellets were collected while the pellets were gravitationally dropped from the top of the tube at a flow rate of 12.5 g s^{-1}.

Fig. 1 shows images of the packed (stagnant) and flying PE pellets (density: 0.918 g cm^{-3}). Circles correspond to the laser illumination area. The image of flying pellet is blurred, as the digital camera shutter speed was not fast enough to catch a clear image of the dropping pellets. The velocity of a dropping pellet at Raman measurement was 4.4 m s^{-1}. In flight, the pellet residence time at the laser illumination was very short, approximately 1.4 ms, and the number of pellets in the laser illumination volume was substantially less than that of the fully packed pellets; therefore, the resulting Raman intensity decreased. In all cases, each Raman spectrum was collected with an exposure time of 10 s at room temperature. All spectral processing, including baseline correction, normalization, and partial least squares (PLS) analysis [15,16] were performed using Matlab Version 7.0 (MathWorks Inc., MA, USA).

3. Results and discussion

3.1. Spectral features of packed and flying PE pellets

Fig. 2 shows Raman spectra of packed (a), flowing (b), and flying (c) PE pellets in the 1504–1054 cm^{-1} range. For all three conditions, eight major PE Raman bands were clearly observed. The 1464, 1443, 1420, and 1372 cm^{-1} bands corresponded to CH_2 rocking, CH_2 bending, CH_2 bending and CH_2 wagging, respectively. The 1298 and 1177 cm^{-1} bands were due to CH_2 twisting and CH_2 rocking, and both the 1138 and 1070 cm^{-1} bands corresponded to C–C backbone stretching. The Raman spectral features of packed and flowing pellets were almost identical in terms of peak shape and corresponding peak intensity.

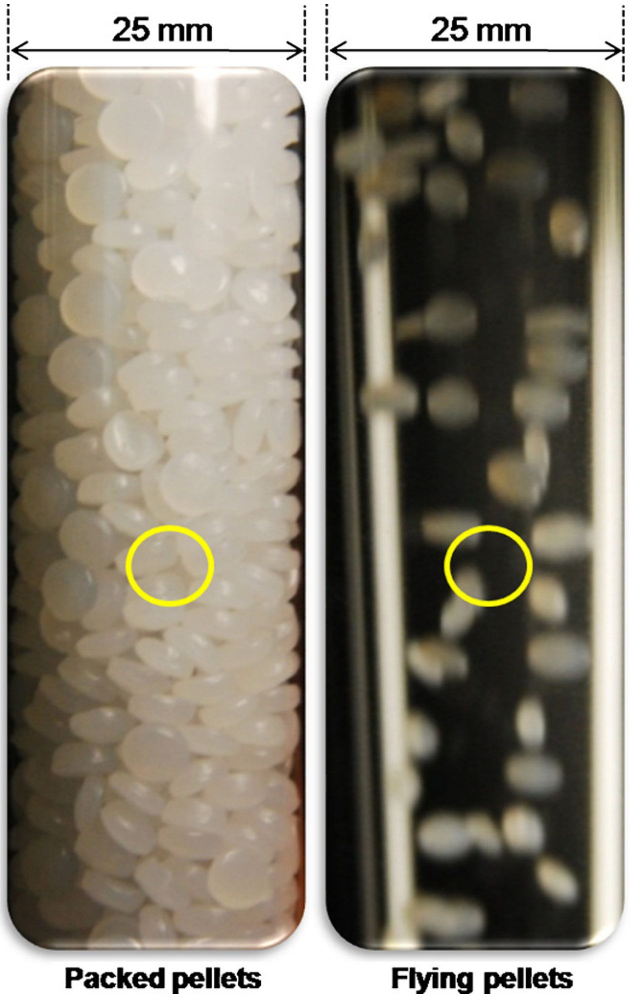

Fig. 1. Pictures of packed and flying PE pellets (density: 0.918 g cm^{-3}) for Raman measurement. Circle corresponds to the laser illumination area.

For flying pellets (Fig. 2(c)), Raman intensities of the bands decreased approximately by a factor of 10, as expected. Noise was more dominant in the flying pellet spectrum due to low intensity, and the underlying glass background (dash line spectrum) was more featured. The glass background should have also been present in the spectra of packed and flowing pellets; however, it was hardly recognizable due to overlap with the higher intensity PE bands. For quantitative analysis of flying pellets, a selective elimination of the glass background would be important, and a degraded signal-to-noise ratio would adversely affect the accuracy of density determination.

The glass background showed a non-linear pattern with broad Raman scattering around 1350 cm^{-1}. To subtract the glass background, the baselines of both a sample and glass Raman spectra were linearly offset to zero intensity at 1054 cm^{-1}. Then, the glass spectrum was linearly scaled to the same intensity of a sample at 1400 cm^{-1}, and the scaled glass spectrum was subtracted from the corresponding sample spectrum. The procedure of glass background subtraction was performed to all of the spectra collected. As performed in a previous study, after the background subtraction, the resulting baselines were linearly corrected at 5 different wavenumbers (1504, 1402, 1196, 1114 and 1054 cm^{-1}), and the

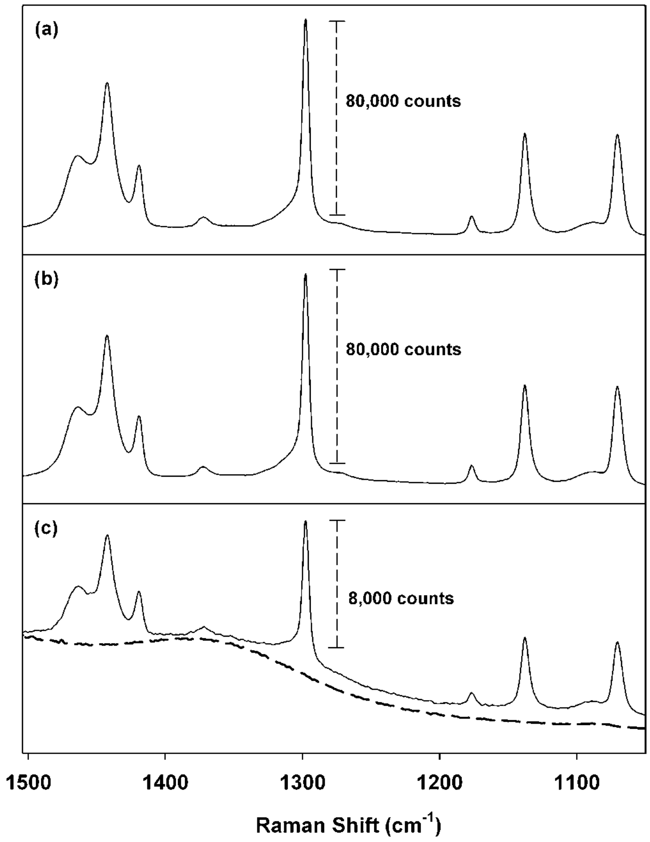

Fig. 2. Raman spectra (1504–1054 cm^{-1} range) of packed (a), flowing (b), and flying (c) PE pellets (density: 0.918 $g\,cm^{-3}$). Raman spectrum corresponding to a glass tube (dashed line) is also shown (c).

peak area under the 1504–1054 cm^{-1} range was calculated; each baseline-corrected spectrum was divided by the corresponding peak area [17].

Fig. 3 shows normalized spectra (1504–1054 cm^{-1} range) of three PE samples with different densities (0.918 (a), 0.931 (b), 0.959 $g\,cm^{-3}$ (c)), collected under the three different conditions (packed, flowing, and flying). For a more detailed comparison, the 1443, 1298 and 1070 cm^{-1} bands are individually enlarged in each figure. After glass background subtraction and normalization, the overall spectral features of the same sample from the three different measurements were generally similar to each other, although the Raman intensity of flying pellets was significantly lower before normalization. The spectral features of packed and flowing pellets are almost identical. However, subtle differences were observed in the enlarged bands of the flying pellets (dash line spectra), especially with slightly larger variation in the 1443 cm^{-1} band. Because the 1443 cm^{-1} band was present on the top of the broad glass feature, as shown in Fig. 2(c), it could be influenced during the course of background subtraction. In practicality, selective elimination of the pure glass background was not easy because of overlap with the sample spectrum. In addition, the signal-to-noise ratio of the flying pellet spectrum was lower due to decreased Raman intensity; as such, more uncertainty was associated during the area calculation for normalization.

Nevertheless, the overall spectral features of flying pellets were similar to those of packed and flying pellets. This demonstrates the possibility for the on-line determination of PE pellet density. However, the degraded signal-to-noise ratio of the spectrum acquired from flying pellets would negatively impact the accuracy of the measurement.

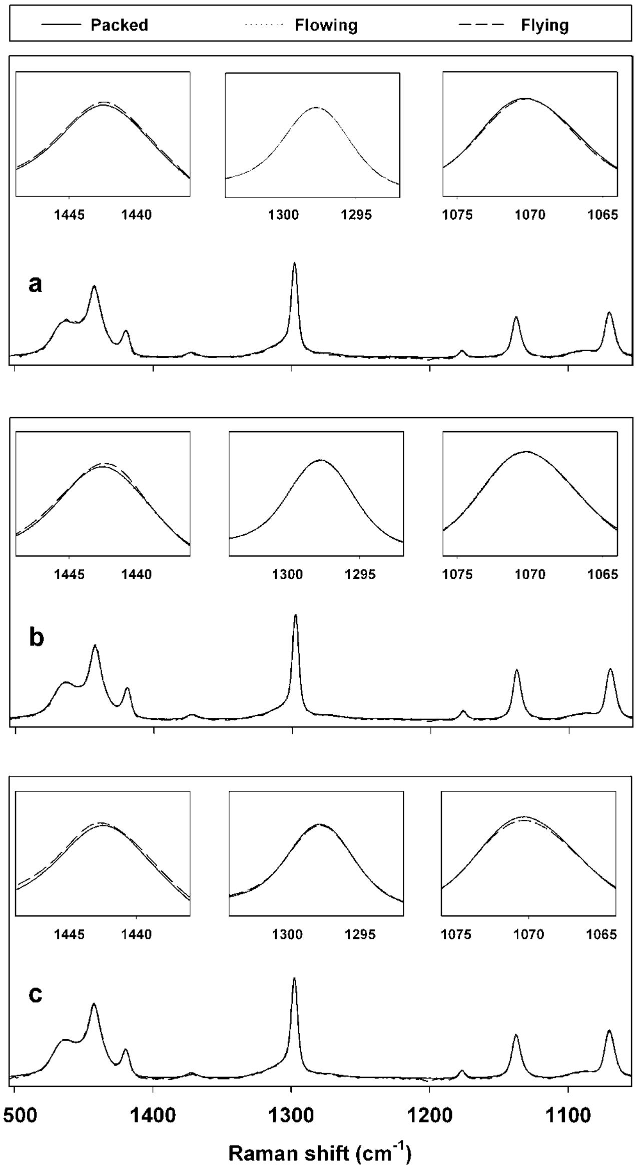

Fig. 3. Normalized spectra (1504–1054 cm^{-1} range) of three pellets with different densities (0.918 (a), 0.931 (b), 0.959 $g\,cm^{-3}$ (c)) collected when packed, flowing, and flying, respectively. The 1443, 1298, and 1070 cm^{-1} bands are individually enlarged in each figure.

For the purpose of comparison, we also collected Raman spectra of the same flying PE pellets using a conventional Raman spectral collection scheme, with a non-contact Raman probe with a 10-mm focal length, a beam size of approximately 100–200 μm, and a 30 s exposure time (λ_{ex} = 785 nm, Kaiser Optical Inc.). The resulting spectrum is shown in Fig. 4. When compared to the spectral features collected by the WAI scheme, the resulting Raman intensity decreased dramatically by approximately 40 times, and the spectral noise was much more dominant, although the major PE bands were still observable. The band around 1320 cm^{-1} corresponded to the glass tube. When the laser illumination area was small and its focal length was short, there was a higher chance of illuminating the laser into the void space rather than onto the individual flying pellets. In addition, the position of each pellet during flying was always inconsistent, so that the chance that each pellet was located at the exact focal point of the conventional scheme decreased. As a result, the Raman intensity decreased

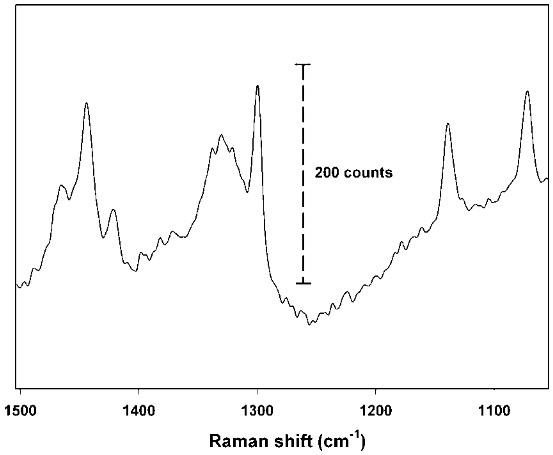

Fig. 4. Raman spectrum of flying PE pellets (0.918 g cm^{-3}) collected using a conventional Raman spectral collection scheme.

greatly. When using the conventional scheme, lengthening the exposure time could increase the corresponding Raman intensity; however, approximately 1200 s (30 s exposure multiplied by 40) would be required for the same level of intensity collected by the WAI scheme. A 1200 s exposure time is too long and not practical for a real-time monitoring of process variation. Consequently, the conventional scheme used in this study would not be adequate for on-line measurement of flying solid samples.

3.2. Determination of PE pellet density using PLS

To determine the density of PE pellets, a PLS model was developed using the dataset collected from packed pellet samples. The PLS model was developed by 5-fold cross-validation using the full spectral range of 1504–1054 cm^{-1}. We divided the total of 25 samples for calibration and validation sets into 20 (80% of the total) and 5 (20% of the total) samples, respectively. This procedure was repeated 200 times by randomly assigning the samples into the calibration and validation set, and then the standard error of cross-validation (SECV) was finally obtained. The resulting SECV was 0.0007 g cm^{-3} with the use of three factors, comparable to that from a previous publication [17].

Using the three-factor PLS model, the spectra of flowing pellets were directly predicted. The resulting standard error of prediction (SEP) was 0.0008 g cm^{-3}, and the acquired accuracy was the same as that of a previous study [17]. The corresponding prediction plot, showing the correction between reference and predicted density values, is shown in Fig. 5(a). The accurate prediction of density for flowing PE pellets was possible because there was no significant spectral difference between the spectra of packed and flowing pellets (Fig. 3).

In general, a faster and more frequent on-line measurement will always be in demand for optimal process control, since variation of the process can be promptly recognized, and necessary process control will follow. However, if a faster measurement requires sacrifice in accuracy due to diverse factors, such as lowered signal-to-noise ratio, then the speed of analysis should be properly balanced with

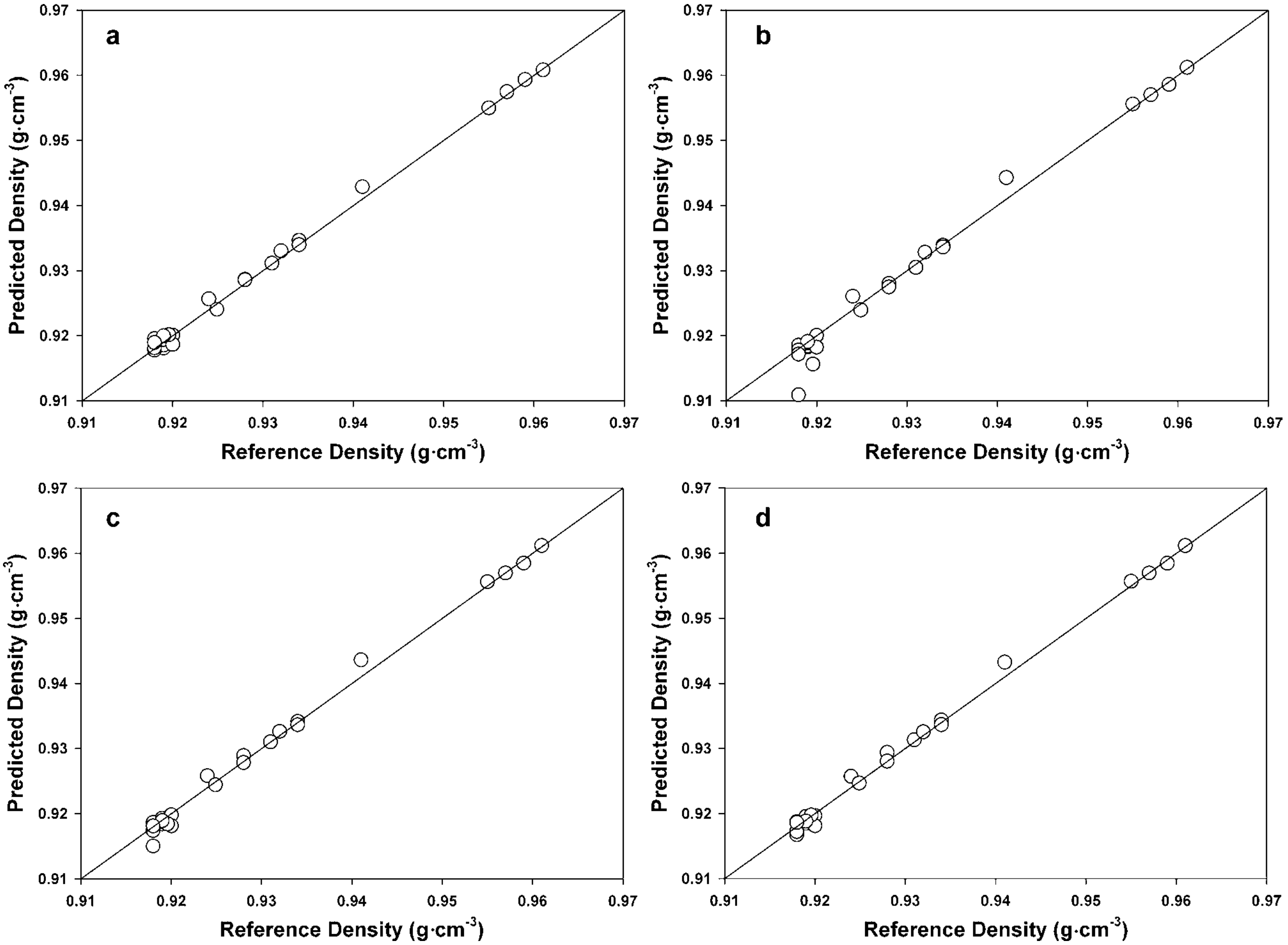

Fig. 5. The prediction plots showing the correlation between reference and predicted density values resulting from the use of spectra collected from packed pellets (a) and flying pellets with the exposure times of 10 (b), 20 (c), and 30 s (d).

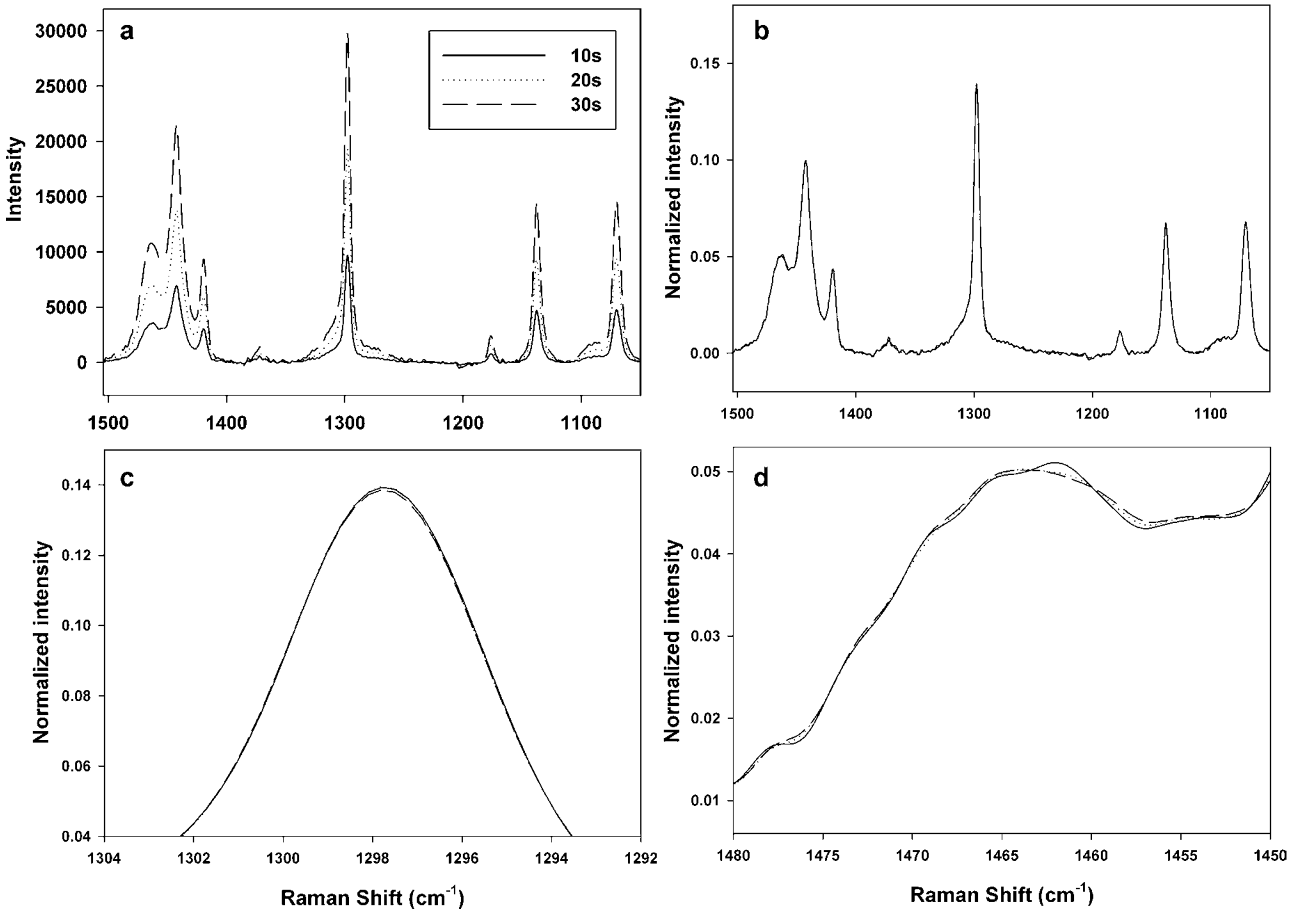

Fig. 6. Raman spectra of flying PE pellets (density: 0.918 g cm^{-3}) collected at three different exposure times (a) and the corresponding normalized spectra (b). For detail, the 1298 (c) and 1465 cm^{-1} bands (d) are enlarged.

the required accuracy of a targeted analysis. As shown in Fig. 2, the signal-to-noise ratio of the Raman spectrum collected for flying pellets over 10 s was relatively lower, as compared to that of packed pellets; therefore higher error was expected in predicting the density of PE pellets. When the signal-to-noise ratio of a collected spectrum was not satisfactory, it could be simply improved by lengthening laser exposure time, thereby increasing the Raman intensity of the bands while maintaining the same noise level. In this case, analysis time would be inevitably longer.

To examine the influence of spectral collection time, or laser exposure time, on prediction accuracy, we predicted the spectra of flying pellets collected with different exposure times. We collected the spectra of flying pellets by increasing exposure time from 10 s to 20 and 30 s (Fig. 6(a)). As expected, Raman intensities of the major PE bands increased with exposure time. The corresponding normalized spectra are shown in Fig. 6(b). The overall spectral features were almost identical after normalization, and the spectral noise was apparent in the regions where Raman bands were not present. For a more detailed examination, the 1298 and 1465 cm^{-1} bands were enlarged in Fig. 6(c) and (d), respectively. There was no significant difference among the 1298 cm^{-1} bands collected from the three different exposure times. Because the 1298 cm^{-1} band is strongest in intensity, the noise was less influential. For the 1465 cm^{-1} band, the influence of noise on the spectral feature was clearly observable. The band shapes of spectra collected at the exposure times of 20 and 30 s were quite similar each other; however, the spectrum collected at the exposure time of 10 s was noisier. Although the shapes were generally similar among the spectra collected at the three different exposure times, the increase of noise in the spectrum collected at the 10-s exposure should adversely affect the accuracy of prediction.

The PLS model developed from the dataset acquired from packed pellets was also used to predict the spectra collected from the different exposure times. The prediction plots corresponding to each case are shown in Fig. 5. When the spectra collected with a 10-s exposure were predicted, the SEP was degraded to 0.0014 g cm^{-3} (refer to Fig. 5(b)), and the prediction data were more scattered especially at the low-density range. As stated above, the lowered signal-to-noise ratio could be the major source deteriorating prediction accuracy. When the exposure time was extended to 20 and 30 s, SEPs were improved to 0.0011 and 0.0009 g cm^{-3}, respectively (Fig. 5(c) and (d)). By increasing the exposure time to 30 s for the spectral collection of flying pellets, the spectrum signal-to-noise ratio was further improved, and the resulting accuracy was comparable to that acquired from flowing pellets (0.0008 g cm^{-3}). Typically polymerization is not a fast varying process, so spectral collection every 30 s is frequent enough to follow even minute variations of product quality.

4. Conclusion

With the use of Raman spectroscopy, accurate on-line determination of PE pellet density was feasible, even when the samples were flying during spectral collection. A PLS calibration model for on-line analysis was easily developed with the use of Raman spectra collected from packed pellets, and the developed model was used to accurately predict the spectra collected from flying pellets without any calibration adjustments. This is advantageous because a calibration model can be easily developed using packed samples without the need for cumbersome spectral collection using real flying process samples. Moreover, diverse samples with larger compositional and property variations, which ensure a robust calibration model, can be easily incorporated into the model by collecting spectra of relevant samples under simple laboratory conditions. The overall results presented in this paper clearly demonstrate that the coverage of a large sample volume is essential for quantitative analysis of other flying or highly turbulent solid samples, such as those in pharmaceutical, polymer and feed fields.

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References

[1] A.U. Vanarase, M. Alcalà, J.I. Jerez Rozo, F.J. Muzzio, R.J. Romañach, Chem. Eng. Sci. 65 (2010) 5728.
[2] Z. Shi, R.P. Cogdill, S.M. Short, C.A. Anderson, J. Pharm. Biomed. Anal. 47 (2008) 738.
[3] T.R.M. De Beer, C. Bodson, B. Dejaegher, B. Walczak, P. Vercruysse, A. Burggraeve, A. Lemos, L. Delattre, Y. Vander Heyden, J.P. Remon, C. Vervaet, W.R.G. Baeyens, J. Pharm. Biomed. Anal. 48 (2008) 772.
[4] O. Berntsson, L.G. Danielsson, B. Lagerholm, S. Folestad, Powder Technol. 123 (2002) 185.
[5] J.A. Spencer, J.F. Kauffman, J.C. Reepmeyer, C.M. Gryniewicz, W. Ye, D.Y. Toler, L.F. Buhse, B.J. Westenberger, J. Pharm. Sci. 98 (2009) 3540.
[6] P. Luukkonen, M. Fransson, I.N. Björn, J. Hautala, B. Lagerholm, S. Folestad, J. Pharm. Sci. 97 (2008) 950.
[7] Y. Sulub, B. Wabuyele, P. Gargiulo, J. Pazdan, J. Cheney, J. Berry, A. Gupta, R. Shah, H. Wu, M. Khan, J. Pharm. Biomed. Anal. 49 (2009) 48.
[8] J. Rantanen, H. Wikström, R. Turner, L.S. Taylor, Anal. Chem. 77 (2005) 556.
[9] H. Wikstrom, I.R. Lewis, L.S. Taylor, Appl. Spectrosc. 59 (2005) 934.
[10] R.M. Balabin, R.Z. Safieva, Fuel 87 (2008) 2745.
[11] I.K. De Oliveira, W.F. De Carvalho Rocha, R.J. Poppi, Anal. Chim. Acta 642 (2009) 217.
[12] R.M. Balabin, R.Z. Safieva, Fuel 87 (2008) 1096.
[13] R.M. Balabin, R.Z. Safieva, E.I. Lomakina, Anal. Chim. Acta 671 (2010) 27.
[14] M. Kim, H. Chung, Y. Woo, M. Kemper, Anal. Chim. Acta 579 (2006) 209.
[15] H. Martens, T.M. Næs, Multivariate Calibration, John Wiley and Sons, New York, 1989.
[16] K.R. Beebe, R.J. Pell, M.B. Seasholtz, Chemometrics: A Practical Guide, Wiley-Interscience, New York, 1998.
[17] M. Kim, J. Noh, H. Chung, Anal. Chim. Acta 632 (2009) 122.