

In-Line Chemical Monitoring for Polymer Processing by Near-Infrared Spectroscopy

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Chapter 1

General Introduction

1.1 Polymer Processing

Polymer products are essential in modern society, used across various fields such as daily life, industry, science and technology. Thermoplastic polymer products are produced through synthesis processes from monomers and processing to shape them into the desired forms.¹ In the processing of thermoplastic polymers, the production follows the steps outlined in **Figure 1.1 (a)**. The first step is heating polymer materials to melt them and impart flowability. Next, a shaping force is applied to form the product shape. The final step is cooling to solidify the molded shape. Types of processing methods are selected and utilized for the required shapes and functionalities of the products. Compression molding, extrusion²⁻⁴, injection molding^{5,6}, and blow molding⁷ are representative processing methods. These processes are utilized for mass production of polymer products. Recently, additive manufacturing has been a promising process due to its flexibility for product shape. Here, injection molding is shown as an example of a processing method. The injection molding process is a molding technique that allows for the rapid mass production of large and complex-shaped products. It is particularly used for producing automotive parts, electronic components, and large containers.⁵ **Figure 1.1 (b)** illustrates an overview of the injection molding process. This process consists of a cylinder section for material melting, mixing, and metering, and a mold section for shaping and cooling the material. The raw polymer supplied from the hopper is melted at high temperatures (plasticization process). When multiple types of materials are supplied, they are mixed and uniformly dispersed during this process. As the screw rotates, the polymer is transported toward the tip of the barrel, while the screw retreats toward the back of the machine. By stopping the screw retreat at a predetermined position, a specific amount of polymer is metered at the tip of the barrel (metering process). After the metering process, the screw advances to inject the polymer into the mold (injection process). Furthermore, pressure is applied to the polymer from the screw for several seconds to completely fill the mold (filling process). Afterward, the injected polymer is cooled in the mold, which fixes its shape (cooling process). Finally, the mold is opened to remove the molded product, and the mold is closed again for the next injection (mold-opening, removal, and mold-closing process). By repeating this molding cycle, continuous production of molded products is achieved. In actual processes, the cooling time typically takes several tens of seconds; therefore, during this time, the mixing and metering processes are conducted simultaneously to reduce the overall molding cycle time.

One of the key roles of modern polymer processing is to impart functionality to polymer materials by compounding them with other materials or by controlling their micro- to nano-scale structures. For instance, the compounding of polymers with other polymers^{8,9}, fiber materials^{10,11}, or fillers¹² is a well-established approach for adding functionality. Polymer composites often exhibit enhanced properties that are unattainable with a single material. Additionally, by controlling crystal structures and molecular orientation, products can exhibit superior mechanical properties.¹³⁻¹⁶ A notable example is the formation of shish-kebab crystals¹⁷ under high-shear conditions during cooling

in extrusion or injection molding processes. This specific crystal structure leads to significantly enhanced mechanical properties compared to crystal structures that form under static conditions. In other cases, creating a porous structure in polymer materials can add properties such as thermal and sound insulation, as well as reduced weight.^{18–21} Various methods for producing polymer foams have been developed, including foam extrusion, foam injection molding, and bead foaming.

However, as greater functionality in polymer products is required, the modeling, controlling, and optimizing of these processing processes become more complex. The reason for such difficulty is the multiscale relationship between processing conditions, phenomena in the process, structure, and properties of the product (P-P-S-P relationship)^{22–34}, which are characteristics unique to polymeric materials. **Figure 1.2** shows the P-P-S-P relationship in polymer processing. Processing conditions contain types of material and its pretreatment methods, and temperature and pressure conditions in the process. The conditions are the only parameters that can be set by the process operator. Phenomena in the process are multiscale phenomena, such as flow, dispersion, phase transition, phase separation, and reaction. Structures of product are also multiscale parameters which are characterized by bulk shape, polymer/polymer phase, polymer/filler phase, crystal, and chemical structure. Properties of the products are evaluated with mechanical, thermal, optical, and electrical properties. Importantly, these multiscale parameters interact with each other. For example, in the foaming process, operators can set the processing conditions such as types of materials, blowing agent delivery conditions, and temperature and pressure during forming. Based on the selected conditions, flow, foaming, and crystallization phenomena change. The phenomena determine the structure of the product, such as expansion ratio, cell diameter, cell density, and crystal structure. Finally, the properties such as thermal and sound insulation properties change according to the structure.^{35–40}

Engineers of polymer processing are required to quickly design such complex processes and ensure the stable production of high-quality products. Now, such process design and quality control depend on the expertise and experience of the engineers. However, due to the increasing diversity of customer needs and demands for shorter R&D lead-time, data-driven process design and quality control are getting more attention. There are some previous research on a data-driven design of polymer processing, such as machine learning method for P-P-S-P relationship^{29,32,34} and digital twin of polymer processing^{41–45}, and quality control using material and process data^{46–49}. To facilitate this data-driven R&D, it is necessary to establish a strict analysis of material and process data. Then, advanced analytical chemistry techniques and operand measurement methods for the process are integrated into research on polymer processing.

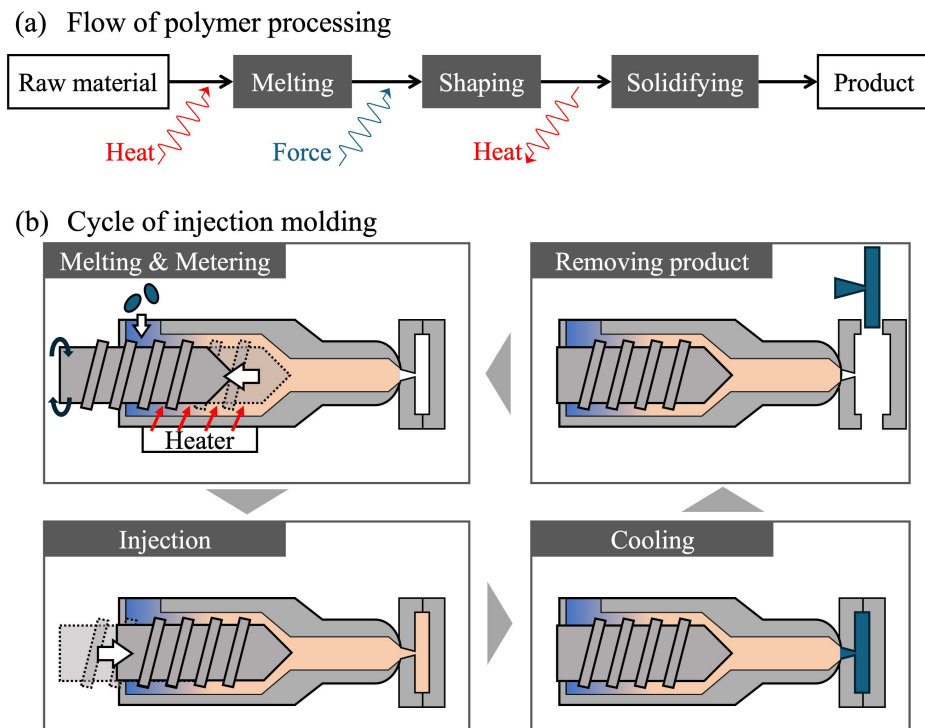


Figure 1.1 (a) Production flow of thermoplastic polymer product through polymer processing. (b) Schematic diagram of molding cycle of injection molding process.

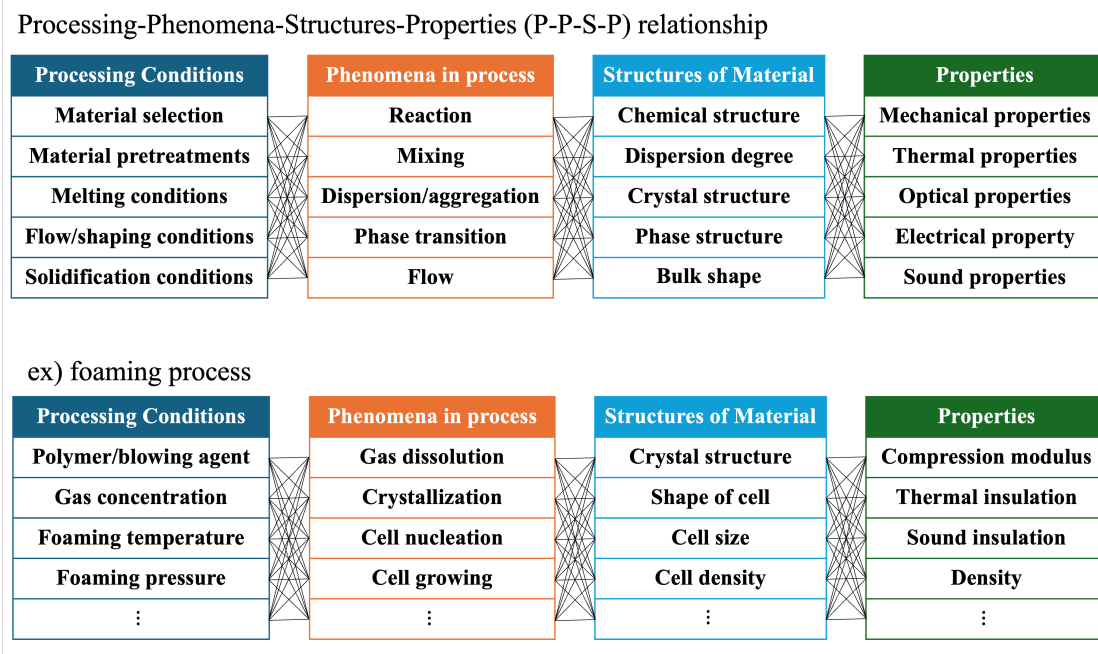


Figure 1.2 Relationship between processing parameters, phenomena, structures and properties(P-P-S-P), and the multiscale component of each factor. The bottom of the figure shows the example of the P-P-S-P relationship during foaming process.

1.2 Analytical Chemistry for Polymer Processing

Analytical chemistry methods used to obtain information on each element of the P-P-S-P relationship described are shown in **Table 1.1**. Properties of raw materials include melting point, glass transition temperature, crystallization rate, viscosity, and PVT data. These data are important for setting process conditions, as well as for process simulation. These properties are measured using thermal analysis instruments^{50,51}, rheometers⁵², and PVT measurement devices^{53–55}. Process data include pressure, temperature, flow, viscosity, phase transitions, dispersion, and chemical structural changes. Depending on the desired information, temperature and pressure sensors, visualization windows^{56–63}, in-line rheometers, ultrasonic sensors^{64–73}, X-ray scattering^{74–84}, and spectroscopic methods^{85–89} are used. To analyze the structure of products, information such as dimensions, phase structure, crystal structure, and chemical structure is needed. Analytical methods include morphological observation using SEM and optical microscopes^{90,91}, crystal structure analysis using X-ray scattering^{92,93} and XRD^{94–96}, and chemical structure analysis using chromatography^{97,98}, NMR^{99–101}, and spectroscopy^{102,103}. Since many of these analyses require sampling a portion of the product, it is generally difficult to perform such structural analysis on all products. Finally, for product quality, mechanical properties, optical properties, thermal properties, and electrical properties are measured. These data are used for process condition optimization and quality control.

Among these data, process data are the most difficult to obtain and have been slow to be utilized in the industry. There are multiple reasons for this. First, polymer processing is high temperature, pressure and shear process, making it challenging to develop measurement devices that can be used in harsh environments.^{104–106} Additionally, measurement devices are expensive, and in simple molding processes, it was easy to control the process and ensure material quality based on the operator's expertise and experience, not based on process data. However, with recent developments in probes that can be used even in harsh environments and the reduction in the cost of measurement devices, in-line measurement has been gaining attention. Additionally, obtaining material information in real time allows for the control and monitoring of material structures and properties. This provides a foundation for incorporating process systems engineering techniques into molding processes.

In-line measurement methods are selected according to the scale of the target information. For example, when observing macroscale phenomena such as flow and material transport, direct imaging using visualization windows^{56–63} or pressure measurements is conducted. When measuring microscale information such as phase or crystal structures, in-line X-ray scattering measurements^{74–84} or ultrasonic sensors^{64–73} are used. Additionally, nanoscale chemical structures and compositions are measured using spectroscopic sensors, such as near-infrared (NIR)⁸⁹, mid-infrared (MIR)⁶⁵, UV-VIS^{107,108}, and Raman spectroscopy^{85–88}. In-line spectroscopic analysis using near-infrared (NIR) and Raman spectroscopy has been applied for monitoring processing in extrusion and injection molding. The advantages of spectroscopic methods include their non-destructive and rapid measurement

capabilities, as well as the ability to obtain chemical information, such as composition and molecular-level structures. Leveraging these characteristics, in-line analysis of composition and reaction progression has been employed in processing. Among these, NIR is the most widely utilized method for in-line analysis. This study focuses on NIR and its application in in-line NIR analysis of the injection molding process. The following sections will discuss the details of NIR and previous research examples.

Table 1.1 Data required in R&D of polymer processing and analytical techniques for each variable.

Category	Variables	Measurement method
Polymer properties	Melting/grass transition temperature	DTA, DSC, ...
	Crystallization rate	DSC, ...
	Viscosity	Rheometer, ...
	PVT data	PVT measurement, ...
In-process data	Pressure and temperature	Pressure and temperature sensor, ...
	Flow	Pressure sensor, Visualization window, ...
	Viscosity	In-line rheometer, ...
	Phase structure	Ultrasound sensor, X-ray scattering, ...
	Chemical structure	In-line spectroscopy, ...
	Chemical composition	In-line spectroscopy, ...
Product structures	Molecular structure	IR, Raman spectroscopy, NMR, GPC, ...
	Crystal structure	TEM, XRD, SAXS, WAXS, DSC, ...
	Phase structure	SEM, SALS, Xray-CT, ...
	Dimensions	Caliper, 3D scanner, ...
Product qualities	Mechanical property	Tensile test, compression test, ...
	Optical property	Haze Measurement, ...
	Thermal property	DSC, TGA, ...
	Electrical property	Dielectric Measurement, ...

1.3 In-Line NIR Monitoring for Polymer Processing

Near-infrared (NIR) spectroscopy is a spectral analysis method that utilizes near-infrared light and is applied across various fields, including chemistry, medicine, pharmaceuticals, and agriculture. NIR light refers to wavelengths between 800 and 2500 nm, which are closer to visible light within the infrared spectrum. This range can be further divided into three regions: Region I (800–1200 nm), Region II (1200–1800 nm), and Region III (1800–2500 nm). Light at shorter wavelengths has higher penetration capability. For instance, light in Region I can penetrate to even deeper layers of the human body and is used in medical applications. For polymeric materials, light in Region II and III is used depending on the thickness of the sample, and absorption of C-H and O-H are observed and analyzed. NIR spectra typically exhibit harmonics and combination bands of fundamental vibrations observed in IR spectra.^{109–111} Because these harmonics and combination bands appear as broad peaks, NIR spectra often show overlapping peaks, making interpretation more challenging compared to IR spectra. As a result, the application of NIR was previously limited. However, since the 1950s, the introduction of chemometrics techniques, such as regression analysis, has significantly enhanced the interpretability and quantitative capabilities of NIR spectra. Chemometrics is a field that applies statistical methods to spectral data containing chemical information, aiming to interpret spectra and perform quantitative analysis.^{112,113} Techniques such as principal component analysis (PCA) are used for spectral decomposition. For quantitative analysis, methods like multiple regression analysis, principal component regression, and partial least squares regression (PLSR)¹¹⁴ are commonly employed. Additionally, for classifying qualitative variables such as variety, clustering techniques like PCA and discriminant analysis methods like PLS-DA are utilized. Recently, more advanced machine learning techniques capable of modeling nonlinear relationships, such as support vector machines^{115–117}, random forests^{118,119}, and neural networks^{120–122}, have also been adopted.

NIR is actively researched as a Process Analytical Technology (PAT) due to its various advantageous features:

- 1) No sample pretreatment required: NIR can analyze samples non-destructively and quickly, making it suitable for time-series analysis of sample changes.
- 2) Remote measurement capability: Using optical fibers and probes, NIR can perform measurements even in harsh environments, such as high temperature and pressure, without placing the measurement device directly in those conditions.
- 3) Ability to analyze thick samples: Unlike mid-infrared methods, which have high absorption coefficients and are limited to micrometer-thick samples, NIR can analyze samples with centimeter-scale thickness due to their relatively low absorption coefficients. This allows for direct probe placement in production lines for spectral measurement.

Applications of NIR as a PAT tool have been reported in various fields, including pharmaceuticals^{123–128}, biotechnology^{129,130}, food science^{131–136}, polymer synthesis processes^{137–143}.

As indicated in Section 1.2, various analytical methods have been proposed for monitoring processing, among which near-infrared (NIR) spectroscopy is one of the most widely used. NIR has been applied for in-line measurements in various processes, including the reaction injection molding of polyurethane^{144–146}, extrusion processes^{147–164}, and the injection molding^{165–167} as shown in **Table 1.2**. The first example of using NIR for monitoring processing was by Fisher *et al.*¹⁴⁸ In this study, the proportion of ethylene-vinyl acetate (EVA) blocks in a polypropylene (PP) and EVA copolymer was quantified in-line. By employing chemometric techniques such as principal component analysis (PCA) and partial least squares regression (PLSR), a statistical model was developed to quantify the proportion of EVA blocks from the spectra, enabling real-time measurements. Other studies have reported in-line evaluations of blend ratios in blended polymers^{154–156}, filler addition amounts^{160–162}, mixing uniformity¹⁶⁸, and the progression of decomposition reactions during the extrusion process¹⁵⁸. Reaction injection molding of polyurethane involves mixing polyols and isocyanates, allowing the curing reaction to occur while filling the mold^{145,146}. Controlling the progression of this curing reaction is crucial for stabilizing the process, leading to research focused on monitoring the reaction progress using NIR. For instance, Benali *et al.*¹⁴⁶ conducted PCA on in-line measured NIR spectra, demonstrating a linear relationship between the first principal component score and the progression of the curing reaction, enabling real-time quantification.

Due to the high temperature and pressure conditions in injection molding, the durability of probes has restricted the implementation of NIR monitoring compared to other processing. In 2005, Dumitrescu *et al.*¹⁶⁵ reported the first instance of in-line monitoring of the injection molding process using NIR. Their study focused on monitoring the addition of colorants during the molding of polypropylene (PP) and demonstrated the capability to monitor moisture content by analyzing the water absorption peak at 5235 cm⁻¹. Additionally, Ghita *et al.*¹⁶⁶ highlighted the potential for quantifying colorant addition rates by focusing on baseline shifts in NIR spectra. They also showed that clustering techniques could classify spectra obtained at different temperatures and injection speeds. Furthermore, McLauchlin *et al.*¹⁶⁷ developed a real-time measurement method for the contamination rate of polylactic acid (PLA) in recycled polyethylene terephthalate (PET) during the injection molding process, addressing issues of molding defects caused by PLA contamination.

1.4 Thesis Objective and Overview

The current in-line NIR has the following challenges:

- 1) Narrow range of process application: Compared to an extrusion process, in-line measurement for injection molding has been delayed. Furthermore, in the injection molding process, the pressure varies dynamically due to the molding cycle. The NIR spectra change according to the condition change, however, there is no general analysis method for such unstable spectra.
- 2) Narrow range of material application: In previous studies of in-line NIR measurements, most were conducted with transparent molten polymers that provide sufficient transmission light intensity. Although some studies analyzed opaque materials using diffuse reflectance, the applicable materials were limited. Therefore, there is a lack of robust measurement methods capable of handling a variety of materials in molding processes involving small-scale production of diverse products.
- 3) Limit of information: Most previous studies have focused on measuring the chemical structures of polymers, blend compositions, and filler concentrations. There is low diversity in the types of information that can be measured.

To address these challenges, this research aims to:

- 1) Develop an in-line NIR measurement probe that can be used continuously under high-temperature and high-pressure conditions of injection molding. The constructed probe will enable stable measurement of NIR spectra during injection molding, and a method for stable material analysis under non-steady-state conditions in the injection molding process will be proposed.
- 2) Establish a measurement system and analysis method that can analyze a wide range of material compositions. Specifically, an analysis method will be developed to quantify broad compositions in blend materials with varying scattering properties depending on the composition.
- 3) Obtain new types of information and chemical data beyond the already established chemical structure analysis and polymer composition information. Specifically, methods will be developed to analyze phenomena such as gas phase separation on the micrometer scale from spectral scattering information and to measure the concentration of infrared-inactive N₂ gas.

Chapter 1 summarizes the overview and current state of molding processes, the importance of in-line measurement in molding processes, and the current state and challenges of in-line NIR measurement.

Chapter 2 presents the results of developing a high-pressure and high-temperature NIR probe applicable to injection molding. The high-durability NIR probe, with its unique structure, is capable of continuous use under high-temperature (270°C) and high-pressure (150 MPa) conditions and is easily maintainable. Using this NIR probe, a system was constructed to simultaneously measure by transmission and diffuse reflection during the injection molding process. This allowed continuous measurement of NIR spectra regardless of whether the target material was transparent or opaque. The

selected material for testing was a biodegradable polymer blend. The results demonstrated that composition analysis is possible over a wide range of applicability for blend polymers with changing scattering properties depending on the blend ratio, utilizing simultaneous measurements by transmission and diffuse reflection. Additionally, the developed measurement method was applied to determine the completion of material replacement in a product changeover process, demonstrating the contribution of in-line NIR measurements to efficient process operation.

Chapter 3 presents the results of applying in-line NIR measurements to foam injection molding. A method for measuring the concentration of CO₂ in the polymer during the process using CO₂ as the foaming agent was developed. A method to address measurement instability under the unique process conditions of injection molding, which involve large pressure fluctuations during the molding cycle, is proposed. Furthermore, a detection method of phase separation of the foaming agent inside the barrel was developed. This phase separation phenomenon is a major cause of molding defects that result in large voids in the foam. Detecting this phenomenon helps predict molding defects and contributes to stabilizing product quality in the process.

Chapter 4 presents the results of measuring the concentration of N₂ as a foaming agent in foam injection molding. Since N₂ is an infrared-inactive molecule, its absorption peak cannot be observed by infrared spectroscopy, making conventional concentration measurement impossible. In this study, it was demonstrated that the apparent density change of the polymer due to N₂ dissolution could be quantified indirectly from the NIR spectrum, making it possible to quantify N₂ concentration. This method combines a multivariate analysis model for quantifying polymer density from NIR spectra with an equation of state for estimating N₂ concentration, resulting in an integrated model for quantification. The measurement method was shown to quantify the dynamic characteristics of N₂ concentration in response to N₂ supply conditions, and it demonstrated that control could be introduced based on information obtained from in-line NIR measurements.

Finally, Chapter 5 summarizes the overall findings and discusses the future outlook for this research field.

Table 1.2 Target process, information, and material of previous research on in-line near-infrared spectroscopy for thermoplastic polymer processing.

Target process	Target information	Target material
Reaction Injection molding (Pressure) < 30 MPa	Curing degree	Polyurethane
Extrusion (Pressure) < 30 MPa	Density Molecular structure Composition Reaction	Polypropylene Block ratio of copolymer PP/PE, PP/EOV, CO ₂ , Filler Degradation, Ester exchange
Injection molding (Pressure) > 100 MPa	Composition	Colorant, Water, PLA contamination in PET

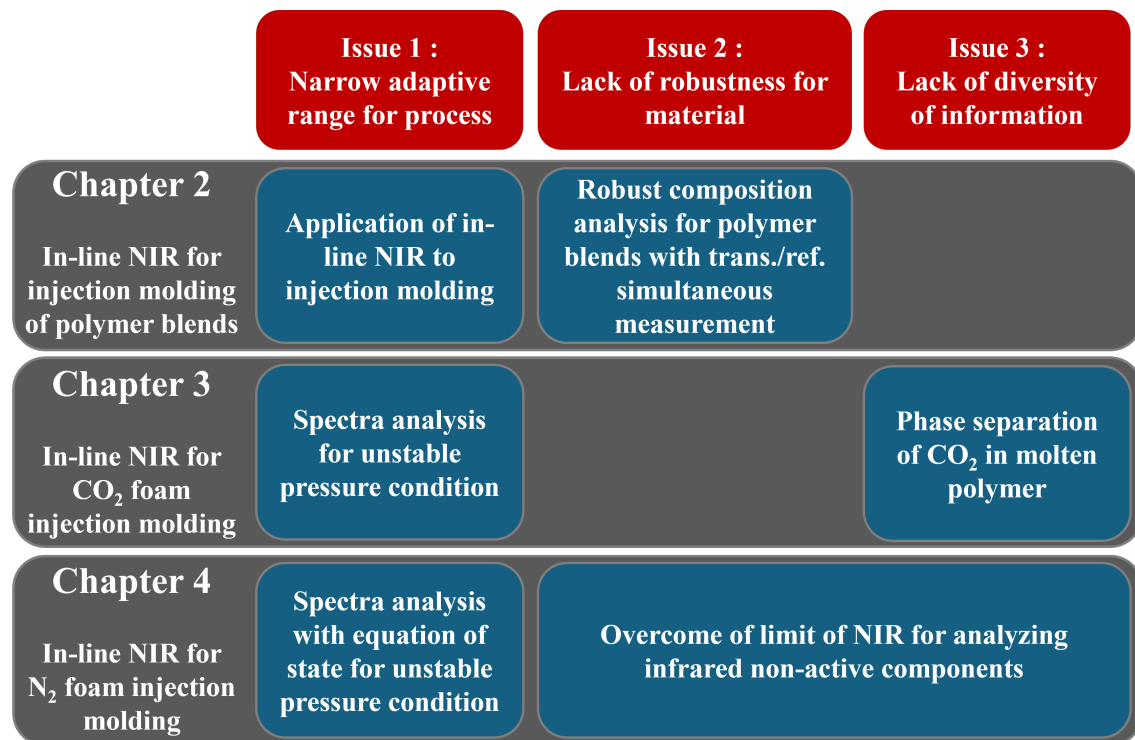


Figure 1.3 Issues of in-line NIR and objectives of each chapter in this thesis

Chapter 2

In-Line Chemical Composition Monitoring for the Injection Molding Process of Biodegradable Polymer Blends Using Simultaneous Measurement of Near-Infrared Diffuse Reflectance and Transmission Spectra

2.1 Introduction

The challenging processability and inherently low physical properties of biodegradable polymers hinder their successful use. For instance, while poly(lactic acid) (PLA) is synthesized from a well-established biomass-derived method and is compostable, it has a glass transition temperature of approximately 60 °C, slow crystallization, and high brittleness.^{169,170} Researchers have focused on blending with other biodegradable polymers or combining biodegradable fillers to solve these issues.^{171–179} Flexible polybutylene succinate (PBS)^{171–173} and polybutylene succinate adipate (PBSA)^{174–176} have garnered significant attention. Ojijo *et al.*¹⁷⁴ researched PLA/PBSA blends to improve the brittleness of PLA. The authors found the optimal composition of the blend to maximize the flexibility. Precise control of the polymer blend composition is crucial for improving biodegradable plastic properties.

In the processing of polymer blends and composites, in-line monitoring techniques for the composition and composite uniformity are essential for rapid process development and stringent quality control. NIR^{168,180–187}, Raman spectroscopy^{188,189}, and ultrasonic sensors^{190,191} have been reported for in-line compositional analysis in extrusion processes for the stable continuous production of sheets and films. In particular, NIR spectroscopy, which provides information on the functional groups of polymers and allows analysis of optical path lengths on the order of millimeters, has been used in numerous applications. NIR probes designed for continuous use in the extrusion process have been developed and utilized for monitoring the compositions of polymer blends, such as PP/PE polymer blends and PP/POE polymer blends.^{168,192} He *et al.*¹⁶⁸ reported the use of NIR for monitoring blend ratios in the extrusion process of PP/POE polymer blends, successfully evaluating the blend ratio of a PP/POE blend polymer extrusion process from the diffuse reflectance spectra of the polymer using NIR probes at five locations on the extruder. They also demonstrated the possibility of assessing the dispersion evolution of polymer blends through screw kneading in-line by estimating dispersion uniformity from spectral variation.

However, in the injection molding process, the study of the composition monitoring of polymer blends has been delayed. When analyzing composites using NIR, the scattering of NIR light at the interface of different materials poses a challenge for accurate analysis. Specifically, the transmission method of NIR measurements, previously used for in-line injection molding process monitoring, is unsuitable for analyzing opaque materials. To address this issue, we developed a new diffuse-reflectance NIR probe that can be adapted to the injection molding process. The objective of this study was to establish a robust in-line composition measurement method using this probe, enabling simultaneous in-line measurements of diffuse reflectance and transmission spectra and facilitating the quantification of material composition across a wide range of regions.

Furthermore, in extrusion and injection molding processes, a single machine often manufactures multiple types of products. Consequently, a polymer changeover process occurs when

different product types are transformed. Traditionally, skilled operators visually judge the completion of polymer replacement in a processing machine by checking the purity of the materials. However, this qualitative judgment results in excessive purged material and time loss due to overpurging. Therefore, we investigated the ability of composition monitoring to track blend ratio changes during the polymer changeover process.

2.2 Methods

2.2.1 In-line NIR Analysis

The probes in this study must bear the high temperature, high pressure, and high viscosity of the molten polymers. The pressure cycling and drastic flow rate change in the injection molding operation create harsh conditions for the sensor probe. The probe has to transfer NIR light efficiently and stably to the spectrometer under harsh and nonsteady-state operations. The probe shown in **Figure 2.1** is newly designed to satisfy the requirements. It consists of a tapered sapphire window, an O-ring, an optical quartz rod, and a stainless steel sleeve. The optics are embedded in the sleeves. The geometry shape of the probe sleeve is the same as that of a typical pressure transducer so that the probe can be easily housed in the pressure transducer's holes. The sapphire window is attached to the tip of the probe by a screw-type lid with a hole. The sealing between the sapphire window and the sleeve was made mechanically by screwing the lid. No welding was used for sealing. If the sapphire is accidentally broken or the molten polymer flows into the sleeve's inside and contaminates the window, then the probe can be easily cleaned by disassembling and reconstructing the parts after cleaning or exchanging. A standard optical fiber SMA connector is on the tip's other side of the probe. The quartz rod can transfer NIR light from the optical fiber to the sapphire window or vice versa.

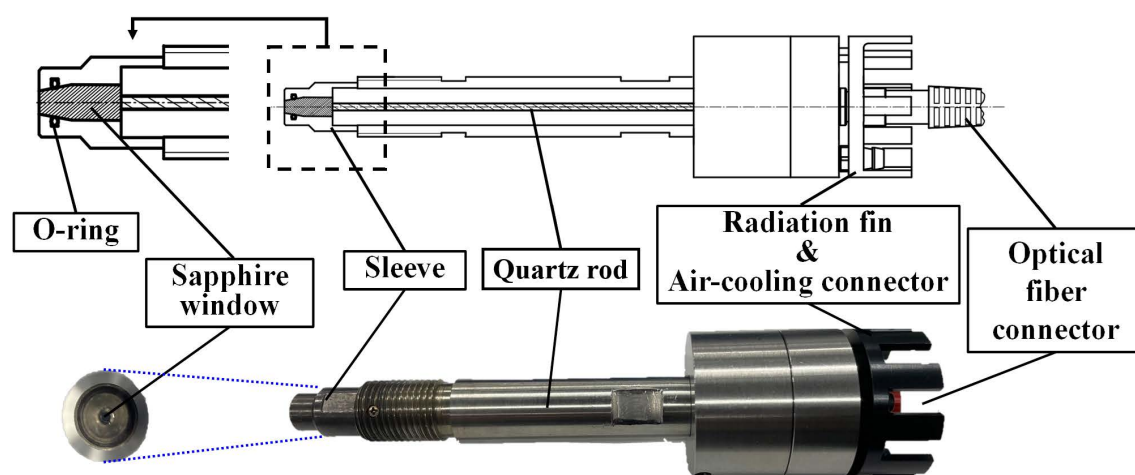


Figure 2.1 A schematic diagram and a digital camera image of the fiber optic probe. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

We developed two types of heat- and pressure-resistant NIR probes: one for diffuse reflectance measurements and the other for transmission measurements. **Figure 2.2** shows a schematic of the injection molding machine and the installed in-line NIR probes. Both types of probes faced

opposite each other and were installed after the screw was cut but before the shut-off nozzle of the injection molding machine (J35ELIII-F, JSW, Japan).

The diffuse reflectance probe comprises a quartz window and a heat-resistant bundle of optical fibers housed in a cylindrical SUS tube. An end of the bundle fiber was attached to the quartz window installed at the tip of the SUS tube. The other end of the fiber was split into two lines: one was connected to a halogen light source (HL-2000-HP, Ocean Insight, USA), and the other was connected to a spectrometer (NIRONE S1.7, Spectral Engines, Finland). This configuration enables near-infrared light to be emitted from the probe tip and diffuse reflective light to be received through the optical fiber for spectral analysis. The transmission measurement probe is composed of a quartz rod and a quartz window housed in a cylindrical SUS tube, which enables the near-infrared light to be received at the tip and transmitted through the quartz rod to the other rod's end. The transmitted light travels through the optical fiber to a near-infrared spectrometer (NIRONE S2.2, Spectral Engines, Finland).

Table 2.1 shows the measurement conditions for the NIR spectrum. The spectra were measured at approximately 0.3 s intervals. Before conducting the in-line measurements, the background spectrum was acquired at room temperature for transmission measurements. The background spectrum of diffuse reflectance measurements was acquired by facing the diffuse reflectance probe tip to a white reflectance standard plate.

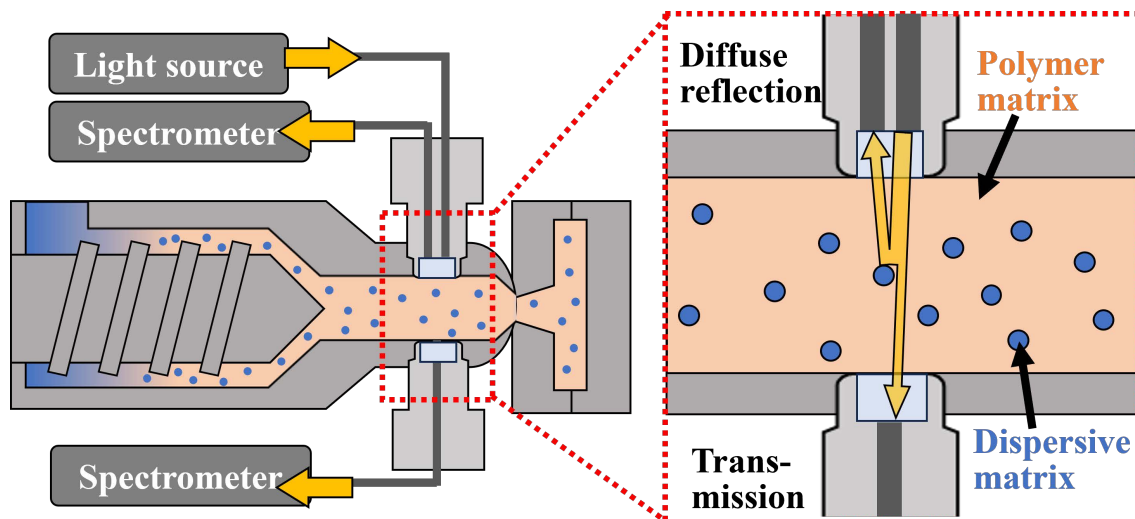


Figure 2.2 Schematic diagram of an in-line NIR monitoring system for the injection molding process. Reprinted with permission from Yoshikawa et al., *Applied Spectroscopy*, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

Table 2.1 Measurement conditions for the FT-NIR spectrometer. Reprinted with permission from Yoshikawa et al., *Applied Spectroscopy*, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

Parameters.	NIRONE S1.7 (Diffuse reflectance measurement).	NIRONE S2.2 (Transmission measurement).
Wavelength region [nm]	1350~1750	1850~2250
Resolution [nm]	4	4
Accumulation number [-]	100	100
Light path length [mm]	-	8
Measurement interval [s]	0.3	0.3

2.2.2 Material

Experiments were conducted using PBSA (FD92PB, PTT MCC Biochem, Thailand) and PLA (TP4000, UNITIKA, Japan). The pellets were predried at 60 °C for 14 hours. Eleven samples were prepared by simple dry blending of two polymer pellets with different blend ratios varying from 0 to 100 wt.% PLA in 10 wt.% increments.

2.2.3 Data Acquisition for Developing a Blend Ratio-Spectra Calibration Model

Development of a calibration model is essential for estimating blend ratios in real time from in-line measured NIR spectra. Spectral measurements were performed to acquire the calibration data by processing the eleven samples with an injection molding machine under the conditions listed in **Table 2.2**. The acquired spectra were used to create a calibration model.

Table 2.2 Molding conditions for the PLA/PBSA blends. Reprinted with permission from Yoshikawa et al., *Applied Spectroscopy*, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

Parameters.	Value
Polymer temperature [°C]	(Tip)205/205/200/205/190/160/120/60(hopper)
Maximum injection pressure [MPa]	130
Injection speed [mm s ⁻¹]	50
Screw rotation speed [/min]	100
Screw back pressure [MPa]	15
Cycle time [s]	60

2.2.4 Monitoring of Material Changeover Processes

The blend ratio-spectra calibration model was used to identify the change in the polymer composition during the injection molding process. The molding machine was initially filled with a polymer blend sample with a PLA weight fraction of 70 wt.%. While the polymer blend sample was still present in the barrel of the molding machine, another polymer sample with a 30 wt.% PLA weight fraction was introduced from the hopper to the injection molding machine. While 30 molding shots were executed, the NIR spectrum was measured in-line with the sensor setup described in the previous section.

2.2.5 Determination of Blend Ratios by DSC Measurements

Differential scanning calorimetry (DSC) (DSC 8500, Parkin Elmer, USA) was conducted for all injection-molded samples and used to develop the blend ratio-spectral calibration model with higher model precision. The ratios of PLA to PBSA were calculated from the DSC thermal curves, considering that PLA and PBSA are both crystalline polymers with distinct melting points (approximately 180 °C and 90 °C, respectively). PLA and PBSA are incompatible¹⁷⁶, and it is assumed that the composition of blended PLA/PBSA and the ratio of heat of fusion have a linear relationship. The molded samples were cut to 5 mg pieces and packed in an aluminum pan. To maximize the degree of crystallization of PLA, all DSC samples were annealed at 110 °C for 20 min before the measurement. Subsequently, the samples were left at room temperature for at least one day to facilitate the progression of PBSA crystallization. DSC measurements of the prepared samples were then conducted by increasing the temperature from 30 to 190 °C at a rate of 20 °C/min, and a heating curve was obtained.

2.3 Results and Discussion

2.3.1 Comparison of PLA and PBSA Spectra

In the injection molding process, polymer injection, pressure holding, polymer metering, and in-mold polymer cooling were sequentially conducted as one injection molding cycle. The whole injection molding process for one shot lasts less than one minute. During the polymer injection step, a designated amount of molten polymer was injected into the mold cavity by moving the screw forward. At this step, the polymer pressure increases rapidly to more than 100 MPa and drops to the holding pressure when the screw movement stops. The injection time was less than one second. Subsequently, at the pressure holding step, the polymer pressure in the mold cavity was maintained at a constant level (holding pressure) by pushing the screw forward to completely fill the mold cavity with the molten polymer. Finally, the polymer was cooled and solidified in the mold cavity. At this cooling step, the molten polymer was metered for the next shot.

The variation in the polymer pressure during the molding cycle was recorded. The highest pressure recorded during the injection step was 130 MPa. The polymer pressure reached approximately 15 MPa at the holding temperature and 10 MPa during the metering and cooling steps. All the spectra obtained during one cycle were averaged and used as the spectrum corresponding to one molded shot.

Figures 2.3 (a) and (b) show the average reflectance and transmittance spectra, respectively, obtained during a shot of eleven polymer blend samples. The spectral data demonstrated the stable measurement capability even in the presence of significant pressure variation in a short time.

In the diffuse reflectance and transmission spectra, bands at 1385 nm and 1410 nm are assigned to a combination of second overtones of CH stretching and CH deformation of PLA's CH₃ and PBSA's CH₂, respectively. In the transmission spectrum, bands at 1820 nm, 1919 nm, and 1942 nm are attributed to the first overtone of the CH stretching vibration of PLA, the second overtone of the C=O stretching vibration of PLA, and the second overtone of the C=O stretching vibration of PBSA, respectively.^{193,194} The reflectance and transmittance spectra exhibited significant changes with the change in the blend ratio. The average values of the reflectance spectra obtained in the range of 1350~1650 nm and that of the transmittance spectra averaged in the range of 1750~2150 nm are plotted against the PLA weight fraction of the eleven blend samples in **Figure 2.3 (c)**. A minimum point existed in both the reflectance and transmittance spectra against the PLA fraction. The minimum point can be attributed to the presence of the scattering interface. PLA and PBSA are incompatible, therefore, the interfacial area between PLA and PBSA increased as PLA and PBSA were blended, altering the intensity of light scattering. Light is reflected from the opposite barrel wall, and a diffuse reflectance probe observes it. For the samples with PLA fractions of 0 and 100 wt.%, there was no scattering interface, but light reflectance from the wall existed, as shown in the left-hand side of the cartoon in **Figure 2.3 (d)**. A higher reflectance was subsequently recorded for the 0 and 100 wt.% polymer blend samples. With an increase in the polymer interface area, some light is scattered out of

the optical path, as shown in the right-hand side of the cartoon in **Figure 2.3 (d)**, and the baseline transmittance and diffuse reflectance light are reduced. An increase in the interfacial area between the two polymers also reduced the amount of transmitted light, causing minimum transmittance.

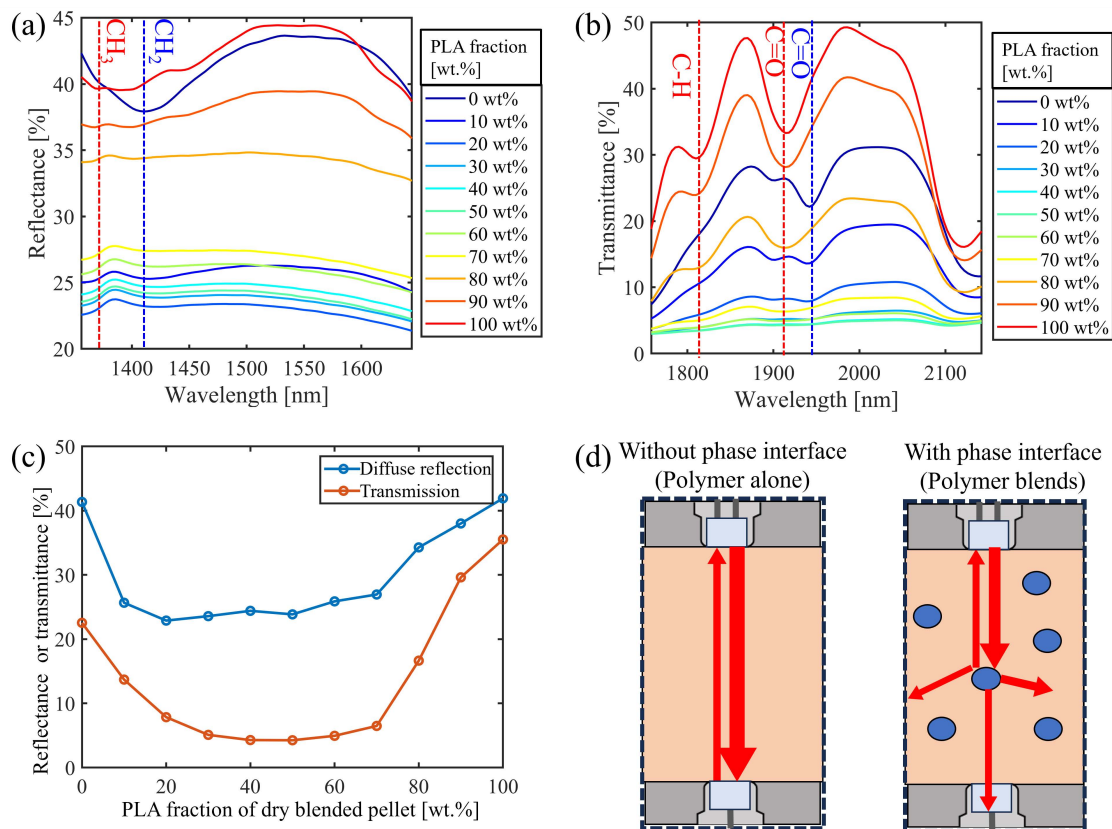


Figure 2.3 Changes in the reflectance and transmittance spectra as the blend ratio changes: (a) whole reflectance spectra measured by the diffuse reflectance probe, (b) whole transmittance spectra measured by the transmission probe, (c) relationship between the PLA weight fraction and the average reflectance and transmittance, and (d) light paths of the NIR with and without the polymer interface. Reprinted with permission from Yoshikawa et al., *Applied Spectroscopy*, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

Absorbance spectra were calculated to analyze the changes in the reflectance and transmittance spectra. **Figure 2.4** shows the variation in the second derivative spectra of the eleven polymer blends, calculated using the Savitzky–Golay filter¹⁹⁵ (3rd order, 11 points). In the second derivative spectra, variations in the baseline were corrected, and the overlapping peaks of PLA and PBSA were separated. As a result, changes in peaks associated with changes in blend ratios were emphasized. Each band exhibited a monotonic increase or decrease in response to changes in the blend ratio. The treated data suggest the feasibility of quantifying the blend ratio from the in-line measured NIR spectra.

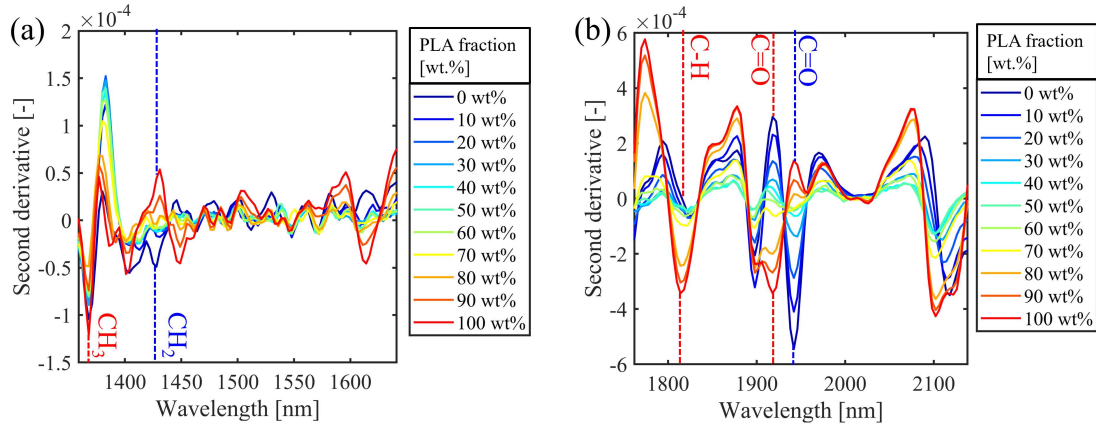


Figure 2.4 The 2nd derivative spectra of the absorbance spectra measured by diffuse reflectance measurement and (b)transmission measurement. Reprinted with permission from Yoshikawa et al., Applied Spectroscopy, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

2.3.2 Quantitative Analysis of Blend Ratios by DSC.

Figure 2.5 (a) shows the first heating curve of the molded polymer blends, where the peak at approximately 85 °C corresponds to the melting peak of the PBSA crystals, and the peak at approximately 167 °C represents the melting peak of the PLA crystals. The peak intensity at approximately 85 °C decreased and that at approximately 167 °C increased monotonically with increasing PLA fraction.

The blend ratio was quantified from the DSC curves in the following way. First, the areas of the PBSA and PLA melting peaks, $\Delta H_{\text{PBSA}}[\text{J g}^{-1}]$ and $\Delta H_{\text{PLA}}[\text{J g}^{-1}]$, respectively, were calculated. The peak areas of neat PBSA and PLA alone, i.e., $\Delta H_{\text{PBSA, pure}}$ and $\Delta H_{\text{PLA, pure}}$, were determined by averaging the DSC data of 10 samples, and the normalized enthalpy of fusion, i.e., $\Delta H_{\text{PBSA, Nor}}$ and $\Delta H_{\text{PLA, Nor}}$, was calculated by dividing ΔH_{PBSA} and ΔH_{PLA} of the eleven polymer blends by $\Delta H_{\text{PBSA, pure}}$ and $\Delta H_{\text{PLA, pure}}$, as given by Eqs. (2.1) and (2.2), respectively.

$$\Delta H_{\text{PBSA, Nor}} = \frac{\Delta H_{\text{PBSA}}}{\Delta H_{\text{PBSA, pure}}} \quad (2.1)$$

$$\Delta H_{\text{PLA, Nor}} = \frac{\Delta H_{\text{PLA}}}{\Delta H_{\text{PLA, pure}}} \quad (2.2)$$

Finally, the PLA fraction was calculated by Eq. (2.3).

$$(\text{PLA fraction}) = \frac{\Delta H_{\text{PLA, Nor}}}{\Delta H_{\text{PBSA, Nor}} + \Delta H_{\text{PLA, Nor}}} \quad (2.3)$$

Figure 2.5 (b) shows the relation between the PLA weight fractions calculated from DSC curves and the ratios of the dry-blended pellet samples. The PLA weight fraction obtained from DSC

measurements agreed well with the blend ratio of the dry-blended pellet samples at lower PLA concentrations. However, when the PLA fraction was increased to 80 wt.% and 90 wt.%, there were discrepancies between the two values. Specifically, the blend ratio of the molded polymer blend did not align with the blend ratio of the pellets, especially when the PLA pellet ratio was high. Therefore, for the subsequent discussions, the blend ratio quantified by DSC was used as the proper blend ratio and was related to the NIR spectra. **Figure 2.5 (c)** shows the change in the DSC-measured blend ratio of the polymer blends molded during the polymer changeover operation. From the 15th shot, the blend ratio gradually decreased and eventually stabilized at approximately 30 wt.%.

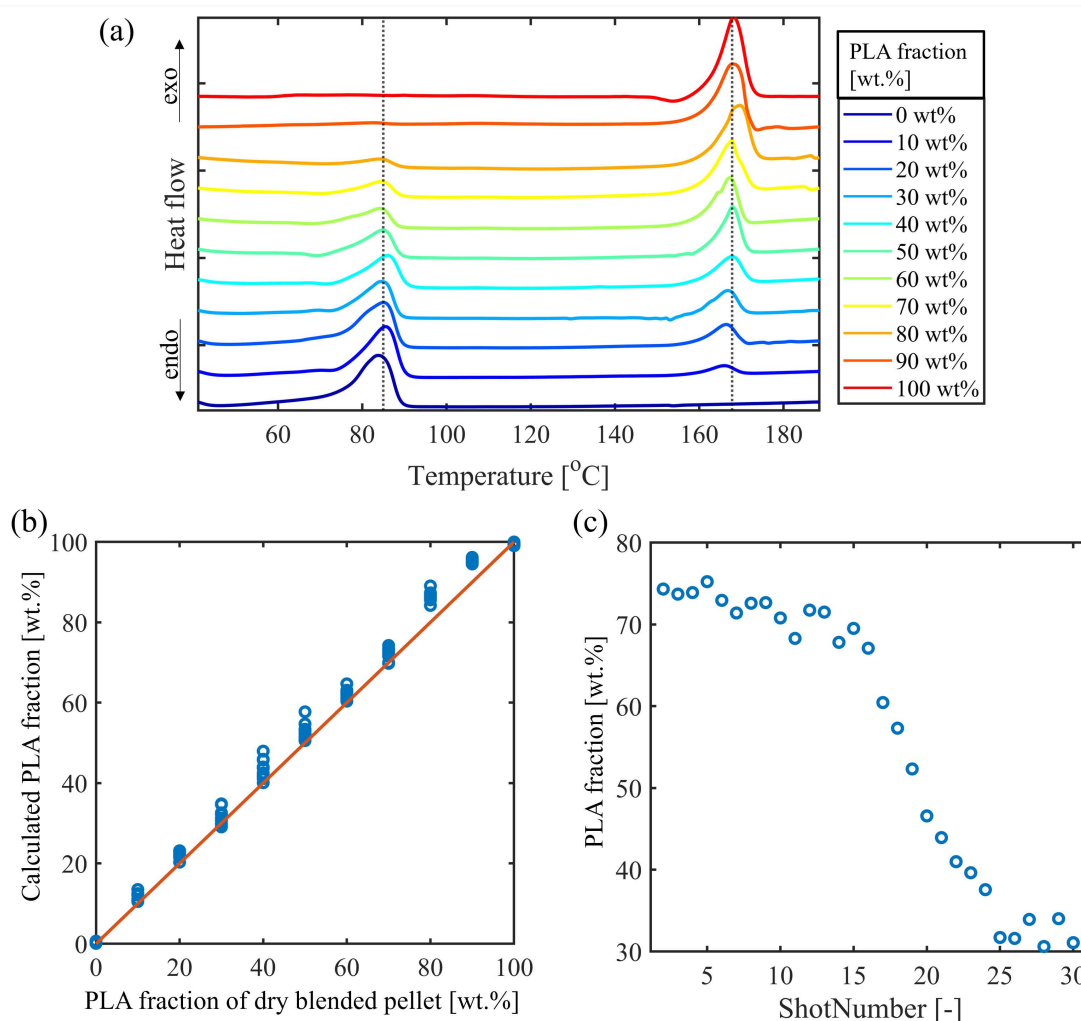


Figure 2.5 (a) DSC curves of each molded sample. (b) Relation between the PLA weight fractions calculated from DSC curves and those of the dry-blended pellet samples. (c) The PLA weight fraction calculated from the DSC curves of the molded samples produced during a changeover operation. Reprinted with permission from Yoshikawa et al., Applied Spectroscopy, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

2.3.3 Partial Least Squares (PLSR) Model for Predicting Blend Ratios

A calibration model was developed by the partial least squares regression (PLSR) method¹¹⁴ using the DSC-measured blend ratios and NIR spectra. PLSR is a type of multivariate analysis method which is frequently used for calibration models of NIR. PLSR can separate meaningful absorption peaks and meaningless noise in spectra by statistic processing. By leveraging covariance between the explanatory and objective variables (X and Y), PLSR identifies latent variables that maximize the explained variance in both explanatory and objective variables. Eq. (4.4) shows the core model of PLSR to decompose X and Y :

$$X = TP + E, Y = Tq + e \quad (4.4)$$

Here, T is the matrix of latent variables. P and q are the matrices of loadings for X and Y . E and e are the residual matrices for X and Y . The latent variables T are constructed to maximize the covariance between X and Y , which ensures that these variables exhibit a strong correlation and separate meaningless variance E and e .

The PLS model was created with NIPALS algorithm¹⁹⁶ with MATLAB® R2023a. The DSC-measured blend ratio was used as the objective variable, and the pretreated spectra were used as explanatory variables. Spectral pretreatment of these variables was performed by conducting second-order differentiation, the standard normal variate method (SNV)¹⁹⁷, and data centering. Additionally, moving window PLS (MWPLS)¹⁹⁸ was applied to determine the wavelength range for model construction. To determine the wavelength range for building the PLS model, informative regions were identified using MWPLS. The window width was set to 21 points (about 80 nm), and the root mean square error (RMSE) was calculated within each window width as explanatory variables. The number of latent variables used ranged from 1 to 10, and the results were plotted against wavelength. **Figure 2.6** depicts the result of the MWPLS. The diffuse reflectance spectrum showed small RMSE values in the 1370-1490 nm region, and the transmission spectrum in the 1850-2000 nm region, which were considered informative. Based on these results, these informative regions were used as explanatory variables in the model construction. After wavelength selection, SNV transformation was performed. One hundred ten datasets were obtained from eleven polymer blend samples with ten shots of each polymer blend sample and used for model development. Eighty percent of the dataset was used for model training, and 20% was used for model validation. The optimal number of latent variables was determined through leave-group-out cross validation to minimize the root mean square error (RMSE). In leave-group-out cross validation, training data set was divided to eleven groups based on blend ratio of dry blended pellet (0, 10, ..., 100wt%). Three different calibration models were built: Model 1 used only diffuse reflectance spectra, Model 2 used only transmission spectra, and Model 3 used both as explanatory variables. These models were subsequently validated against the validation data, and the estimation accuracy of the models was evaluated with the RMSE and coefficient of determination (R^2) and ratio of performance to deviation (RPD) which is the ratio of a standard deviation of a response

variable in a data set to a standard error of estimation. **Table 2.3** indicates the optimal number of latent variables N_{LV} and the estimation accuracy of training data set and validation data set. Among the three models, Model 3 exhibits the highest estimation accuracy. Model 1 and 2 exhibited high estimation accuracy on the training data, however, the accuracy on the validation data decreased, indicating overfitting. Model 3 maintained high estimation accuracy on both of training and validation data set. The superiority of Model 3 was further confirmed by dividing the PLA fraction into three regions: region 1, 0-20 wt%; region 2, 30-70 wt%; and region 3, 80-100 wt.%. **Figure 2.7** shows the RMSEs of the three models in each region. Comparing the RMSE of Model 1 with that of Model 2, which used either diffuse reflectance or transmission spectra alone as explanatory variables, Model 2 showed higher estimation accuracy in Regions 1 and 3, while the accuracy of Model 2 was worse in Region 2. This can be attributed to the increase in the polymer interface area in region 2, which causes a significant reduction in the transmitted light intensity and increased noise in the spectra. In contrast, the diffuse reflectance spectra maintained a relatively high light intensity. Thus, Model 3 maintains high estimation accuracy in all three regions, indicating that the simultaneous use of diffuse reflectance and transmission spectra provides highly accurate estimations regardless of the blend ratio.

Table 2.3 Comparison of the estimation accuracy of Models 1, 2 and 3. Reprinted with permission from Yoshikawa et al., Applied Spectroscopy, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

	N_{LV}	Training			Validation		
		RMSE	R^2	RPD	RMSE	R^2	RPD
Model 1	14	3.93	0.985	8.17	8.30	0.936	4.05
Model 2	14	1.75	0.997	18.4	7.10	0.953	4.74
Model 3	6	2.04	0.996	15.7	3.18	0.991	10.6

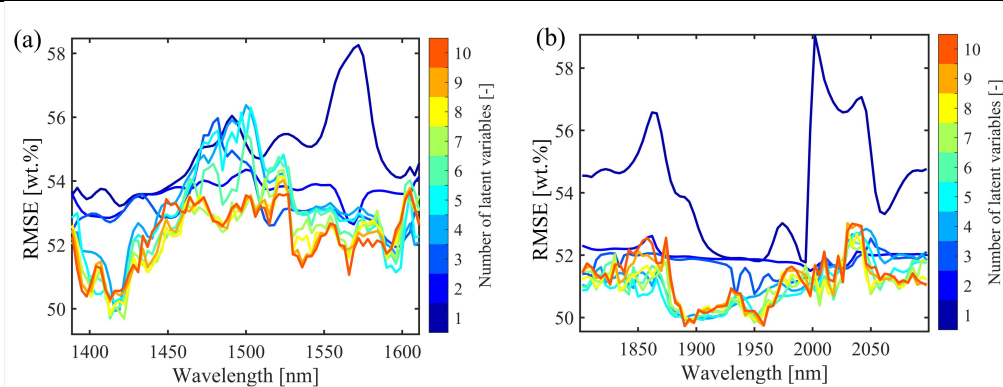


Figure 2.6 Result of MWPLS of (a) diffuse reflection spectra and (b) transmission spectra. Reprinted with permission from Yoshikawa et al., Applied Spectroscopy, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

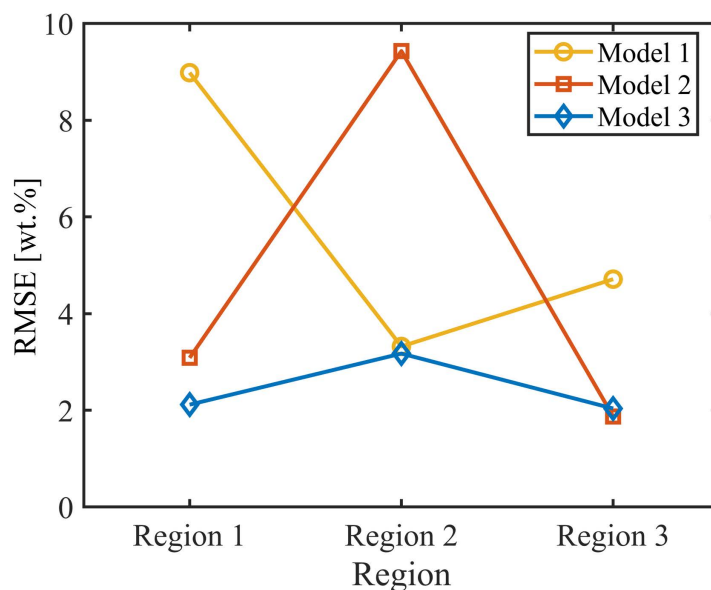


Figure 2.7 RMSE of the PLA fraction estimated by three different PLSR models in three regions: Region 1 (PLA fraction of 0-20 wt.%), Region 2 (PLA fraction of 30-70 wt.%) and Region 3 (PLA fraction of 80-100 wt.%). Reprinted with permission from Yoshikawa et al., *Applied Spectroscopy*, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

2.3.4 Monitoring of Changes in Blend Ratios during Polymer Changeover Operation

Figure 2.8 shows the estimation of temporal changes in the polymer blend ratio during the operation of the polymer changeover. The estimation was conducted using the calibration model (Model 3) and compared with the DSC-measured blend ratio of all the samples molded during the changeover operation. The measured and estimated PLA fractions showed good agreement. The estimated PLA fraction remained stable at approximately 70 wt.% up to the 11th shot. Then, the concentration gradually decreased to approximately 30 wt.%. These results demonstrated that the PLSR model effectively estimated the blend ratio.

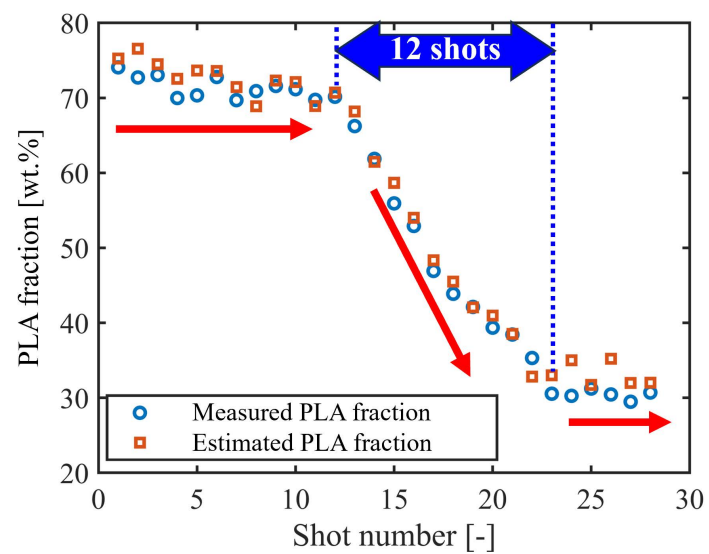


Figure 2.8 Results of estimation of the PLA fraction during the changeover process. Reprinted with permission from Yoshikawa et al., Applied Spectroscopy, 2024. DOI: 10.1177/00037028241247823. Copyright ©2024. SAGE Publications.

2.4 Conclusions

High heat and pressure resistance NIR probes were developed, by which the chemical composition can be monitored in-line with the injection molding processes in a high temperature and pressure environment. The probe was stable under 130 MPa pressure and 270 °C molten polymer temperature conditions. The heat and pressure resistances were increased by selecting the O-ring of the probe.

In-line NIR measurements with diffuse reflectance and transmission probes were used to successfully monitor the blend ratio during injection molding. The analysis of the NIR spectra revealed that the average reflectance and transmittance spectra alone exhibited a certain degree of variation associated with the blend ratio. The variation was attributed to changes in the interracial area between PLA and PBSA, causing alterations in the scattering intensity. The analysis of the second derivative spectra also revealed the spectral bands corresponding to PLA and PBSA, and the peak heights of the spectra changed in proportion to the blend ratio.

The blend ratio was calculated offline by DSC measurements and used as the objective variable for developing three blend ratio-spectra calibration models. A comparison of the three different models revealed that the simultaneous use of diffuse reflectance and transmission spectra as explanatory variables yielded the highest estimation accuracy in the entire region of the blend ratio. The polymer changeover operation was monitored, the change in the blend ratio, i.e., the PLA concentration, in the molded product was estimated using the highest accuracy model, and the blend ratio was successfully estimated.

The proposed NIR sensor system with the developed probes can improve the production, research, and development efficiency of polymer composites and blends, and it has the potential to provide a data-based judgment of the completion of the changeover operation on any polymer processing process, leading to substantial reductions in polymer waste and changeover time. In addition, further analysis of the variations in the diffuse reflectance and transmission spectra of the polymer blend in the NIR region will provide information on the polymer blend morphology and phase inversion under these processing conditions.

Chapter 3

In-Line Monitoring of the Physical Blowing Agent Concentration by Transmission Near-Infrared Spectroscopy with High-Pressure Resistance Fiber Optic Probes for Foam Injection Molding Processes

3.1 Introduction

Lightweight and strong polymeric foams are highly applicable in mitigating the global energy crisis and plastic consumption because they reduce material and energy consumption and decrease resource requirements. Polymeric foam has a structure of bubbles dispersed in a solid polymer. Owing to the presence of a gas phase in the polymer, these foams exhibit excellent heat insulation and sound absorption properties. Two types of foaming methods, physical and chemical, are used to produce polymeric foam. In the physical foaming method, a physical blowing agent (PBA) is dissolved into the polymer under high pressure, bubble nucleation occurs in the polymer by reducing pressure, and the polymer phase fixes the cellular structure. Alternatively, in the chemical foaming method, chemical species that generate blowing agents by chemical reactions are dispersed in the polymer, and heating induces gas generation from the blowing agent and makes the polymer foam. Compared to the chemical foaming method, the physical foaming method is suitable for material recycling because reaction residues do not remain in the molding body. In the past, low molecular weight hydrocarbons with high solubility in polymers were used as PBA, but in recent years, carbon dioxide (CO₂) or nitrogen (N₂) have been used in terms of safety and environmental compatibility.¹⁹⁹

The injection molding process is a typical molding method for thermoplastic polymers. Foam injection molding (FIM) is a process that continuously produces molded foam of thermoplastics; that is, a PBA is added to the base polymer in FIM. With the blowing agent, the polymer is injected into the mold to facilitate foaming. The advantage of this process is that it can mass-produce polymeric foams with various shapes, depending on the shape of the mold. The MuCell® FIM process is a well-known FIM process using environmentally benign blowing agents^{200,201}. Recently, new FIM processes, such as Optifoam®, ErgoCell®, ProFoam®, IQ-Foam®, RIC-FOAM, and SOFIT®, have been developed to reduce the process costs and stabilize operations^{199,202–205}. In any FIM process, the concentration of PBA in the base polymer affects foaming in the mold and is an important parameter that determines the structure of cells, such as shape, size, and density²⁰⁶. Control of the PBA concentration in molten polymers is a critical factor in achieving stable production of polymer foam, but to date, even a method for measuring blowing agent concentration has not been established. Additionally, phase separation of PBA in the barrel of the molding machine is a representative cause of non-uniform cell structure of molded foam. However, the in-line monitoring method for the anomaly phenomenon has not been developed.

In this study, a fiber optic probe for transmission NIR measurements with high-pressure and high-temperature resistances was developed. It was applied to two FIM processes, namely, MuCell®²⁻⁴⁾ and SOFIT®⁶⁻⁸⁾, to monitor the concentration of CO₂, and to detect the phase separation of CO₂ from the molten polymer.

3.2 Methods

3.2.1 Materials and Equipment

The polymer used was polypropylene (PP) (J105, Prime Polymer, Japan), with an average molecular weight of 150,000. The PBA was carbon dioxide (CO₂), 99.9% in purity (Izumi Sangyo, Japan). The NIR spectroscopic system with the developed probes was applied to two types of 35-tonnage clamping force FIM machines: one is a high-pressure FIM machine, MuCell® (J35ELIII-F, JSW Japan), and the other is a low-pressure FIM machine, SOFIT® (J35AD-30H, JSW, Japan). **Figure 3.1** shows the schematic of the low-pressure FIM^{204,205} with the NIR probes. The inner tube diameter was 8 mm. The probes were connected with the NIR spectrometer (FT-NIR: FIR100L, Yokogawa Electric, Japan) via optical fibers with SMA connectors. Unlike the conventional microcellular high-pressure FIM process, there was no supercritical fluid pumping unit. The injector valve for PBA delivery was directly connected to a gas cylinder, which enabled the PBA to be dosed into the molten polymer without a pumping or compressing device. A gas delivery hole with a pressure vessel is in the middle of the injection molding machine. PBA is directly provided from a gas cylinder and introduced into the molten polymer via the delivery hole in the pressure vessel. The concentration of PBA dissolved in the molten polymers can be adjusted by regulating the pressure in the vessel. The pressure of the vessel is adjusted by manipulating a reducing valve on the gas cylinder. By configuring a deeper space in the screw, a polymer starvation zone was intentionally created to contact PBA continuously with the molten polymer, as illustrated in **Figure 3.1**. In the following zones, the molten polymer with dissolved gas is again compressed to produce a single-phase PBA/polymer solution in preparation for foaming. Since no pumping or compressing device is installed between the gas cylinder and the injection molding machine, the amount of PBA delivered into the molten polymer is measured by logging the weight change of the CO₂ cylinder.

The configuration of the high-pressure FIM, MuCell®, machine consists of a screw and a metering system for the supercritical fluid (SCF). The PBA supplied from a cylinder was pressurized using the specialized SCF pumping/gas compression system. Then, the SCF was intermittently delivered into a molten polymer through an exclusive injector valve to form a single-phase polymer/gas solution before injection. The amount of SCF delivery is controlled by manipulating the valve opening time and the SCF pressure level (delivery pressure).

The details of the operation conditions of both FIMs are listed in **Table 3.1**. Only the PBA delivery pressure to the molding machine and the method of PBA delivery were different, and the other operating parameters were the same. The NIR spectroscopic system with the fiber optic probes was first applied to the low-pressure FIM process. NIR spectra were acquired during the molding of PP without and with CO₂. When operating with the CO₂ supply, the CO₂ delivery pressure was changed every 1 MPa stepwise from 3 to 5 MPa. The screw back pressure was set to 1 or 2 MPa higher than the gas delivery pressure to prevent the molten polymer from phase separating CO₂ from the

molten polymer in the injection molding machine. The longer the cooling time, the more likely the phase separation occurs due to the long waiting time under low pressure. Therefore, the back pressure for a 40 s cooling time had to be higher than that for 20/30 s cooling times. For each level of delivery pressure, injection molding was conducted more than 50 times (shots).

When the NIR spectroscopic system with the fiber optic probes was applied to the MuCell® process, the NIR spectra were acquired by changing the injector valve opening period every 0.2 s stepwise from 0 to 0.6 s, corresponding to the concentration range of 0 to 2.8×10^{-3} g-gas/g-polymer.

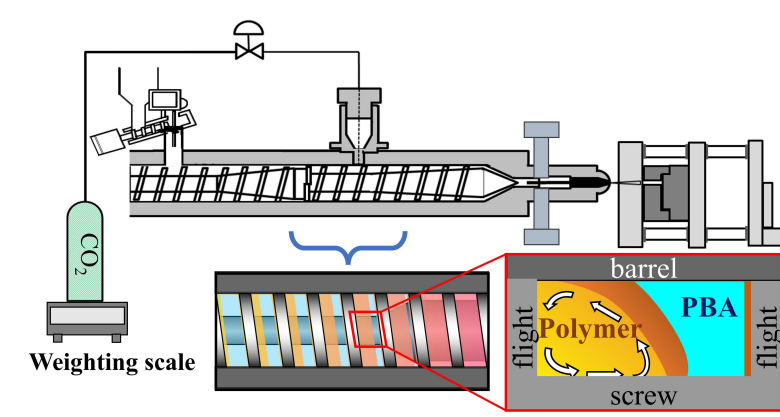


Figure 3.1 A schematic diagram of the low-pressure foam injection molding machine and its polymer starvation zone. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

Table 3.1 Operating Condition of FIM. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

Operating Parameters	SOFIT®	MuCell®
Polymer	PP (J105G)	PP (J105G)
Polymer (melting) temp. [°C]	200	200
Max injection pressure [MPa]	100	100
Cooling time [s]	20/30/40	20
Injection speed [mm/s] (IV)	40	40
Holding pressure [MPa]	30	30
Screw rotation speed [rpm]	100	100
Valve opening period [s]	--	0.2, 0.4, 0.6
Gas delivery pressure [MPa]	0, 3, 4, 5	24
Screw Back pressure [MPa]	Gas deli. press. +1 MPa (at cooling time 20/30 s) Gas deli. press. +2 MPa (at cooling time 40 s)	15
PBA delivery type	Continuous	Intermittent

3.2.2 In-Line Measurement Procedure

The measurement conditions of transmission NIR spectra are listed in **Table 3.2**. The background spectrum was measured by facing the two probes with an 8 mm path length without polymer at room temperature. After the probes were installed into the FIM machines, the spectra were recorded continuously during injection molding. In the experiment with low-pressure FIM, the time variation in injection pressure and pressure at the polymer starving zone were recorded through a data logger (mini LOGGER GL 24, Graphtec Corporation, Japan). Taking advantage of the no-pumping system on the gas delivery line, the CO₂ consumption rate was measured from the weight change in the gas cylinder by a weighing scale (BW32KH W/AC, SHIMADZU, Japan), and a calibration curve between NIR absorbance and CO₂ concentration in PP was derived from the weight change data.

Table 3.2 FT-NIR spectrometer measurement conditions. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

	SOFIT®	MuCell®
Measurement interval [s]	19~20	19-20
Spectral resolution [cm ⁻¹]	8	16
Number of accumulations	32	64
Light path length [mm]	8	8
Max/min wavenumber [cm ⁻¹]	10000/4000	10000/4000

3.2.3 Measurement of Solubility of PBA in Polypropylene

A magnetic suspension balance (MSB) (Rubotherm, MicrotracBEL, Japan) was used to measure the solubility of CO₂ in PP. When CO₂ dissolves in a polymer, the weight of the polymer increases owing to the weight of the dissolved gas. Thus, weighing the polymer in pressurized gas can allow us to calculate the solubility of the gas. The MSB makes it possible to weigh samples under high pressure and temperature environments without placing any balance in high pressure and temperature environments. The balance is placed outside the high-pressure chamber under ambient atmospheric conditions, as shown in **Figure 3.2**. A disk-shaped polymer sample 20 mm in diameter and 3 mm in thickness is put in a stainless basket, and the basket is hooked up to a suspension magnet. It consists of a permanent magnet and a position sensor and can couple and decouple the measurement load. An electromagnet outside the chamber keeps the suspension magnet in a freely suspended state. The balance is also located outside of the chamber, and attached to the electromagnet. The magnetic force of the electromagnet with the electronic control unit controls the position of the basket. When the gas dissolution increases the weight of the polymer sample, the position of the suspension magnet is

lowered unless the magnetic force is increased. Keeping the suspension magnet at the same position by manipulating the electromagnet force, the weight of the sample in the high-pressure chamber is measured by the balance without direct contact. A more detailed description can be found in the literature^{207–210}

The buoyancy effect makes this measurement complicated. When gas dissolves in the polymer, it swells the polymer. The amount of dissolved gas changes the degree of swelling in the polymer, and the buoyancy caused by the swelling will affect the weight of the sample in the chamber. The weight of dissolved gas has to be measured by considering the buoyancy effect to perform accurate measurements. The MSB used in this study can directly measure the density of pressurized gas. The swollen polymer's volume and buoyancy were calculated using the Sanchez–Lacombe (SL) equation of state with a mixing rule. The polymer sample's pressure-volume-temperature (PVT) relationship is needed to establish the SL equation of state. The PVT curve of PP (J105G) was obtained using a PVT measuring instrument (P-V-T TEST System, Toyo Seiki Co., Ltd.). **Figure 3.3** shows the resulting PVT curves, and the characteristic parameters (T^* , P^* , ρ^*) of the SL equation of state calculated from the PVT curve are listed in **Table 3.3**. The solubility of CO₂ was measured at 198°C.

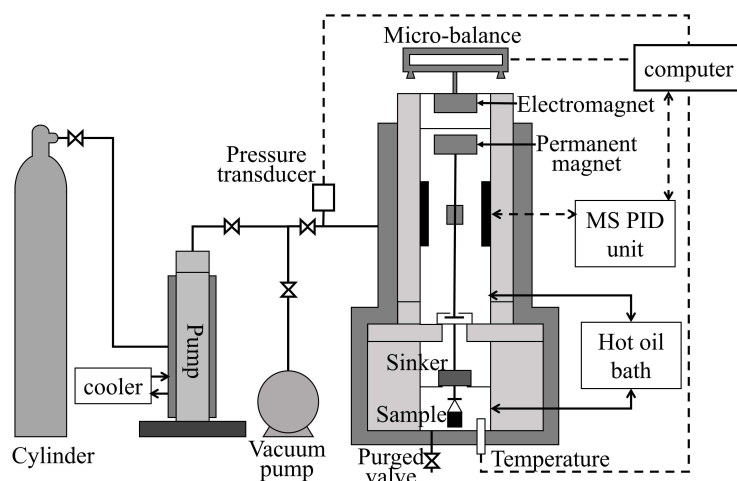


Figure 3.2 Schematic diagram of magnetic suspension balance. Reprinted with permission from Yoshikawa et al., *Industrial & Engineering Chemistry Research*, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

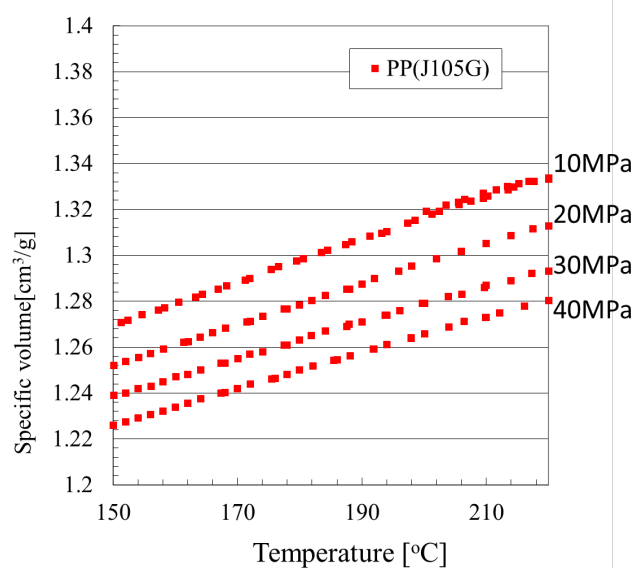


Figure 3.3 Pressure-Temperature-Volume Relationship of PP(J105G) . Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

Table 3.3 Parameters for Sanchez-Lacombe equation of state. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

Parameter	Unit	PP(J105G)	CO ₂
T^*	[K]	645.2	341.2
P^*	[Pa]	2.84×10^8	3.69×10^8
ρ^*	[kg/m ³]	896.8	1253
Weight averaged molecular weight	[g/mol]	3.30×10^5	44
Interaction parameter of SL (k12)	-	-	0.116410(198°C)

3.3 Results & Discussion

3.3.1 Calculation of CO₂ Concentration Using Cylinder Weight Data

Figure 3.4 (a) shows a pressure profile during a molding cycle, observed during both high- and low-pressure FIM processes. The pressure was increased dramatically to inject the molten polymer into the mold at the injection gate. Then, the pressure was held at a constant level (holding pressure) to pack the injected polymer in the mold. The pressure was maintained at a screw-back pressure during metering and cooling. The NIR probe has to bear these pressure changes every injection molding cycle. **Figure 3.4 (b)** shows an example of the temporal change in the CO₂ gas cylinder weight (orange line) and movement of the injection pressure (blue line) during the foam injection molding operation, where the CO₂ delivery pressure was set at 3 MPa and the cooling time was 30 s during low-pressure FIM. During one injection molding cycle, the polymer pressure initially increased to approximately 100 MPa; the pressure was maintained at 30 MPa during the holding period and leveled out at the screw-back pressure during the metering of the polymer. This pressure profile was repeated during every molding cycle. Because CO₂ was consumed during the foaming process, the gas cylinder weight decreased as the molding cycles were repeated. The weight change in the CO₂ gas cylinder was measured by placing the gas cylinder on an electronic weighing scale, and this change was recorded by a computer. Eq. (3.1) gives the average CO₂ concentration in the molten polymer from the weight change in the CO₂ cylinder and the total weight of polymer foams using the weight of CO₂.

$$C_{CO_2} = \frac{ST}{W} \quad (3.1)$$

where S [g/s] is the weight reduction rate of the CO₂ gas cylinder. T [s] is the operating time to produce 20 injection shots of foam products. W [g] is the total weight of the 20 injection shots of polymer foam products.

Figure 3.5 shows the relationship between the CO₂ delivery pressure and C_{CO_2} estimated by the weighing scale during foam injection molding operations with three different delivery pressures while keeping other operating parameters at the same values listed in **Table 3.1**. The solubility of CO₂ in PP (J105G) at 198 °C was measured by the magnetic suspension balance (MSB) method with the Sanchez-Lacombe equation of state (SL EoS), represented by the dashed line²¹⁰²¹⁰¹⁷⁶¹⁷⁴¹⁵¹¹²³¹⁰².

C_{CO_2} increased proportionately with increasing gas delivery pressure, but it did not reach an equilibrium state in the FIM machine. Furthermore, the C_{CO_2} value measured in the foam injection molding operation with a 30 s cooling time was higher than that in the operation with a 20 s cooling time, which was attributed to the contact time between the polymer and CO₂ in the polymer starving zone. The longer the cooling and one-cycle time is, the longer the contact time of CO₂ with the molten polymer. When the 40 s cooling time experiments were conducted by setting the screw back pressures 2MPa higher than the gas delivery pressure, the 40 s cooling time experiments showed lower C_{CO_2} values than those of the 30 s cooling time. This is because of the change in the volume ratio of

polymer to gas in the starving zone. In the SOFIT process, the polymer starving zone is intentionally induced beneath the physical blowing agent (PBA) supply vent, where the PBA and molten polymer come into gas-liquid contact. The PBA diffuses and dissolves in the polymer through the interface with the molten resin. However, as shown in **Figure 3.5**, the concentration of the PBA in the polymer didn't reach saturation and the concentration varies depending on the process conditions. In this study, the concentration of CO₂ decreased when the back pressure was set to a higher value. Naito et al.^{211,212} reported the gas dissolution phenomenon in this process, revealing that increasing back pressure leads to a polymer filling rate in the starvation zone in SOFIT. As depicted in **Figure 3.6**, the length of the starvation zone decreases as back pressure is increased. This reduction in length results in a decrease in the gas-liquid interfacial area and the amount of PBA dissolved. Therefore, in this paper, the concentration of CO₂ decreased with increasing back pressure for the reasons mentioned above. It is likely that the CO₂ concentration changes with the delivery pressure and the screw back pressure, and other operating parameters, such as temperature, screw rotation speed, and holding time.

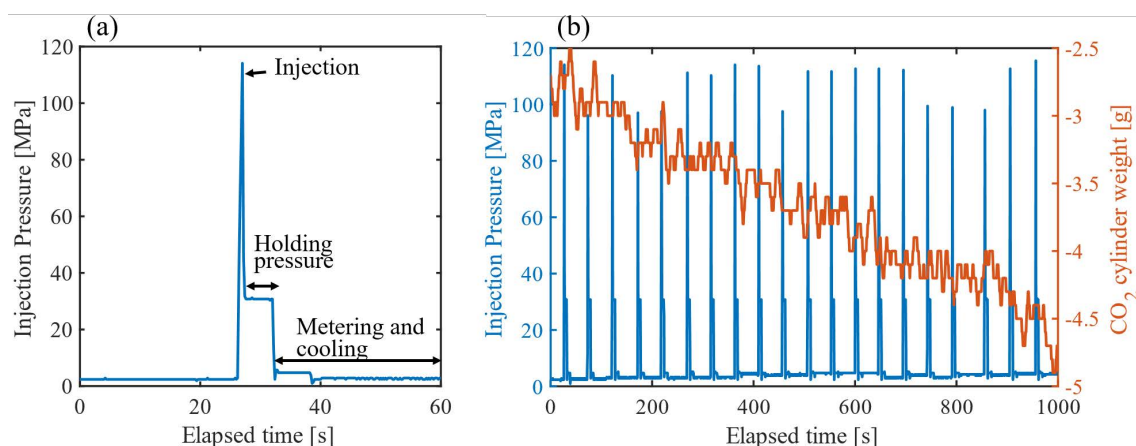


Figure 3.4 (a) A typical pressure profile during one molding cycle (b) Dynamic movement of the injection pressure and the change in the gas cylinder weight during 30~50th shot during low-pressure FIM with 3 MPa CO₂ delivery pressures. Reprinted with permission from Yoshikawa et al., *Industrial & Engineering Chemistry Research*, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

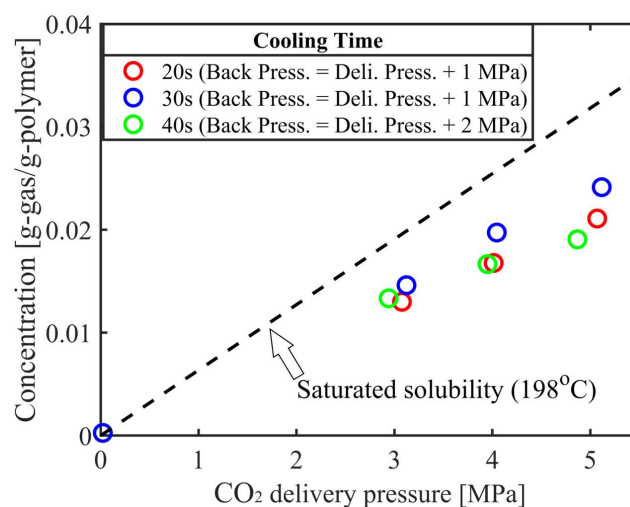


Figure 3.5 Relationship between the CO₂ delivery pressure and C_{CO_2} calculated from the cylinder weight data. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

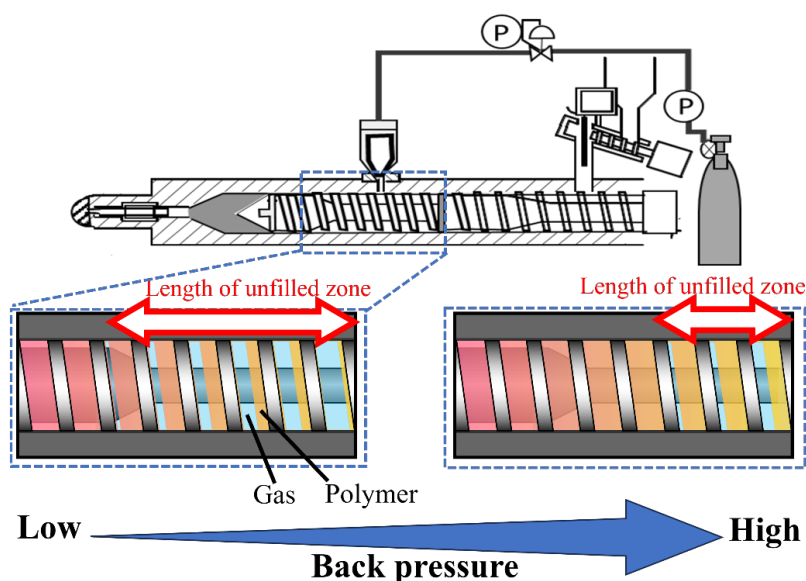


Figure 3. 6 A schematic diagram of the change of polymer starving zone in the SOFIT process as back pressure was changed. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

3.3.2 Raw NIR Spectrum

Figure 3.7 (a) shows the NIR spectrum measured during foam injection molding with 5 MPa CO₂ delivery pressures during low-pressure FIM. The spectrum covers the range of wavenumbers from 4000 to 10000 cm⁻¹. The peaks associated with PP were observed at approximately 5100 cm⁻¹.

Figure 3.7 (b) is an enlarged image of the spectrum in the wavenumber range of 4500 to 5500 cm^{-1} . The spectral peak of CO_2 was also observed at 4952 cm^{-1} , which is attributed to the combination vibration of symmetric stretching, inverse symmetric stretching, and the first harmonic of angular vibration²¹³.

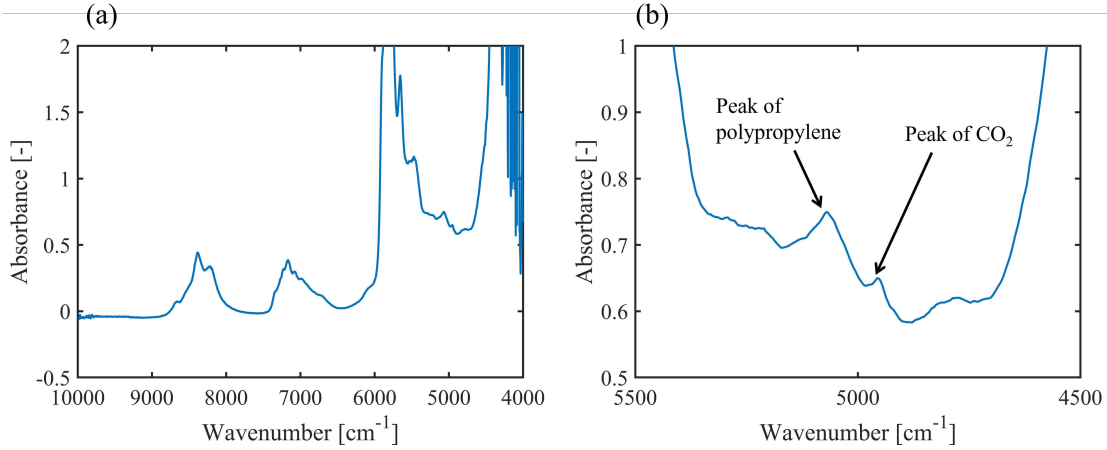


Figure 3.7 (a) NIR spectrum of PP and CO_2 obtained during the FIM operation with 5 MPa CO_2 delivery pressures. (b) An enlarged NIR spectrum around the CO_2 spectral peak at 4952 cm^{-1} . Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

3.3.3 Treatment of the NIR Spectra

The height of the CO_2 absorption peak at 4952 cm^{-1} might be directly used as an indicator of CO_2 concentration. However, as shown in **Figure 3.7 (b)**, the CO_2 absorption peak overlapped with the PP absorption peak at approximately 5100 cm^{-1} . The precise evaluation of the CO_2 concentration from the height of the peak at 4952 cm^{-1} cannot be made unless the effect of the PP absorption spectrum is removed.

The Lambert–Beer’s law can express the NIR spectra at time t , $A(t, \nu)$, by Eq. (3.2), i.e., a linear combination of the polymer, $W_{\text{pol}}(t)$, and CO_2 concentration, $W_{\text{CO}_2}(t)$, with the absorption coefficient $\epsilon_{\text{pol}}(\nu)$ and $\epsilon_{\text{CO}_2}(\nu)$.

$$A(t, \nu) = W_{\text{pol}}(t) \epsilon_{\text{pol}}(\nu)l + W_{\text{CO}_2}(t) \epsilon_{\text{CO}_2}(\nu)l \quad (3.2)$$

where l is the optical path length and ν is a wavenumber. To remove the effect of the PP absorption peak from the overlapped spectra, the spectra were first normalized by dividing $A(t, \nu)$ by $A(t, \nu_{\text{ref}}) := W_{\text{pol}}(t) \epsilon_{\text{pol}}(\nu_{\text{ref}})l$. The resulting normalized spectra are given by

$$A_{\text{nor}}(t, \nu) = \frac{\epsilon_{\text{pol}}(\nu)}{\epsilon_{\text{pol}}(\nu_{\text{ref}})} + \frac{W_{\text{CO}_2}(t)}{W_{\text{pol}}(t)} \frac{\epsilon_{\text{CO}_2}(\nu)}{\epsilon_{\text{pol}}(\nu_{\text{ref}})} \quad (3.3)$$

The reference wavenumber, ν_{ref} , has to be chosen from the wavenumbers where the absorption peak of CO_2 does not exist, but the absorption peak of PP exists. The first term on the right-hand side of Eq.

(3.3) is a function of the spectrum of PP alone. Eq. (3.4) is derived by denoting $\frac{W_{\text{CO}_2}(t)}{W_{\text{pol}}(t)}$ by $C_{\text{CO}_2}(t)$ and $\frac{\epsilon_{\text{pol}}(\nu)}{\epsilon_{\text{pol}}(\nu_{\text{ref}})}$ by $A_{\text{nor}}(t_0, \nu)$. t_0 is the time at which the PP spectrum was obtained from the spectra when CO₂ was not introduced.

$$A_{\text{nor}}(t, \nu) = A_{\text{nor}}(t_0, \nu) + C_{\text{CO}_2}(t) \frac{\epsilon_{\text{CO}_2}(\nu)}{\epsilon_{\text{pol}}(\nu_{\text{ref}})} \quad (3.4)$$

Subtracting $A_{\text{nor}}(t_0, \nu)$ from both sides of Eq. (3.4) gives Eq. (3.5), showing that $A_{\text{CO}_2}(t, \nu) := A_{\text{nor}}(t, \nu) - A_{\text{nor}}(t_0, \nu)$ is proportional to the CO₂ concentration. $A_{\text{CO}_2}(t, \nu)$ can be used as an indicator of the CO₂ concentration dissolved in PP.

$$A_{\text{CO}_2}(t, \nu) := A_{\text{nor}}(t, \nu) - A_{\text{nor}}(t_0, \nu) = C_{\text{CO}_2}(t) \frac{\epsilon_{\text{CO}_2}(\nu)}{\epsilon_{\text{pol}}(\nu_{\text{ref}})} \quad (3.5)$$

3.3.4 CO₂ Concentration Estimated from NIR Spectrum

Choosing the reference wavenumber, ν_{ref} , to be 7166 cm⁻¹ and selecting two base points, 6430 and 7555 cm⁻¹, which cover the reference wavenumber, $A(t, \nu_{\text{ref}})$ was calculated by averaging the spectra in the range from 7158 to 7173 cm⁻¹ after the baseline correction. $A_{\text{nor}}(t_0, \nu)$, was first selected from the spectrum during injection molding without CO₂ delivery (0 MPa). Then, $A_{\text{CO}_2}(\nu)$ was calculated using Eq. (5). **Figure 3.8 (b)** shows the baseline corrected spectra, $A_{\text{CO}_2}(t, \nu)$. The change in the CO₂ peak corresponding to the CO₂ delivery pressure was clearly seen at 4952 cm⁻¹, $A_{\text{CO}_2}(t, 4952)$, which increased with increasing gas delivery pressure. Hereafter, the absorbance of CO₂, $A_{\text{CO}_2}(t, 4952)$, is denoted by A_{CO_2} and is used as the indicator of CO₂ concentration.

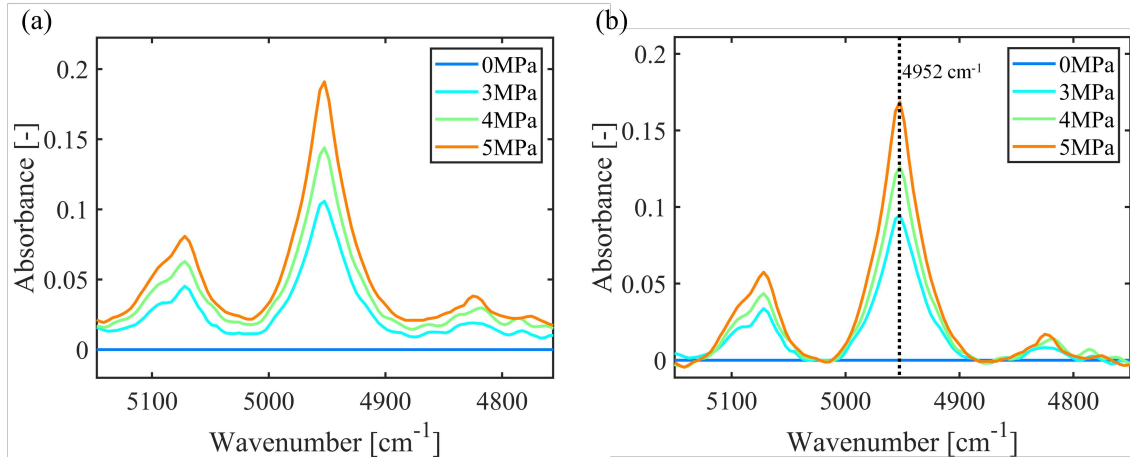


Figure 3.8 (a) NIR spectra around the CO₂ absorption peak after subtracting $A_{\text{nor}}(t_0)$ and (b) the baseline corrected $A_{\text{CO}_2}(\nu)$. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

3.3.5 Calibration of the CO₂ Concentration and A_{CO_2}

Figure 3.9 shows the relationship between A_{CO_2} and C_{CO_2} , which is calculated by Eq. (1) from the weight change in the gas cylinder and NIR spectral change. There is a linear relationship between the CO₂ concentration and A_{CO_2} , regardless of the difference in the cooling and the back pressure conditions. Using this calibration curve and NIR spectra measurement, the CO₂ concentration can be estimated online in real time.

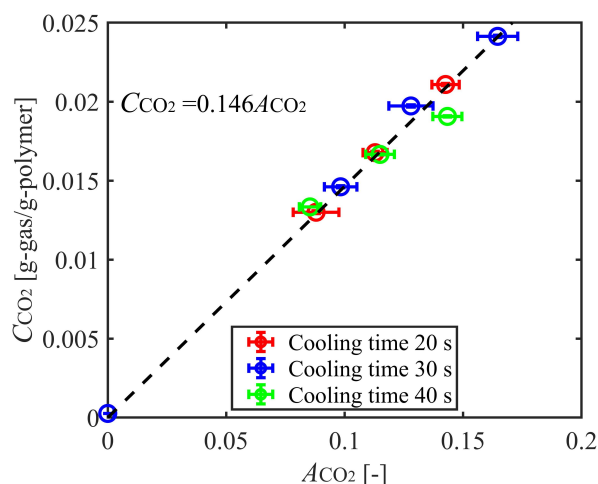


Figure 3.9 The calibration line for measuring the concentration of CO₂. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

3.3.6 Monitoring Dynamic Behaviors of CO₂ Concentration

The CO₂ concentration was successfully estimated from the NIR spectra with the calibration curve. **Figure 3.10** shows the temporal changes in the CO₂ concentration during a series of injection molding operations where the CO₂ delivery pressure was consecutively changed from 0 to 3, 4, and 5 MPa stepwise while the other operating parameters remained the same. As shown in **Figure 3.10**, the NIR-measured CO₂ concentration moved with a time delay against the change in the CO₂ delivery pressure.

Figure 3.11 shows the changes in polymer pressure and CO₂ concentration during the first eight shots of injection molding after changing the CO₂ delivery pressure from 4 to 5 MPa. The dashed line indicates the time the CO₂ delivery pressure was changed. The CO₂ concentration did not change immediately after the change in CO₂ delivery pressure and started increasing after three molding cycles. This time delay was due to a transportation delay of the molten polymer from the gas delivery zone to the NIR probe position.

Figures 3.10 and **3.12** show that the CO₂ concentration fluctuated during six or seven shots

of injection molding after it started increasing. **Figure 3.12** shows the shot-by-shot variation in the metering time and the CO₂ concentration measured by NIR during injection molding with a CO₂ delivery pressure of 5 MPa. It was found that the fluctuation was associated with the metering time, that is, the time to move the screw backward and push the molten polymer to the nozzle zone. The metering time increased at approximately 800 s, reached a maximum at approximately 900 s, decreased, and stabilized. The fluctuation in the metering time can be attributed to the polymer starvation zone. When the gas delivery pressure increased, the gas tended to expand the space of the starvation zone, which increased the contact area between the polymer and gas, and then the CO₂ temporarily increased to a value higher than its steady-state value. However, the constant feeding of the polymer from the plasticization zone to the polymer starvation zone squeezed back the starvation zone and stabilized the zone.

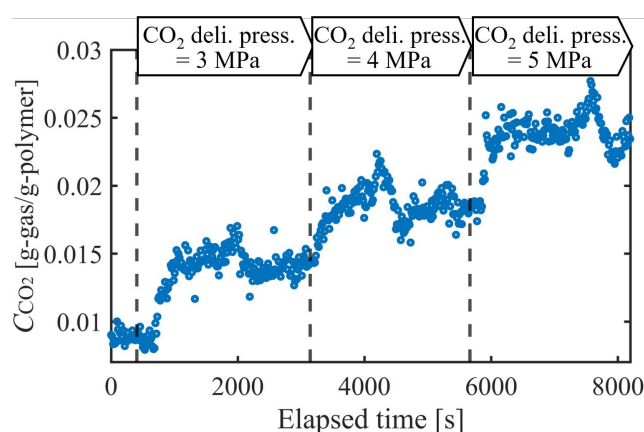


Figure 3.10 Temporal changes in CO₂ concentration with increasing CO₂ delivery pressure during low-pressure FIM. Reprinted with permission from Yoshikawa et al., *Industrial & Engineering Chemistry Research*, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

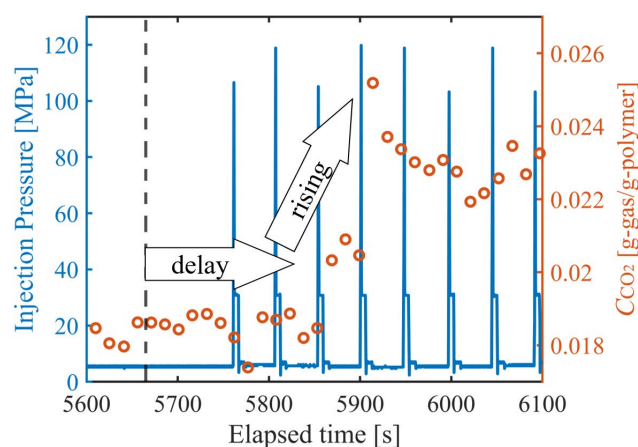


Figure 3.11 Temporal changes in the polymer pressure and CO₂ concentration during low-pressure FIM with a 5 MPa CO₂ delivery pressure. Reprinted with permission from Yoshikawa et al., *Industrial*

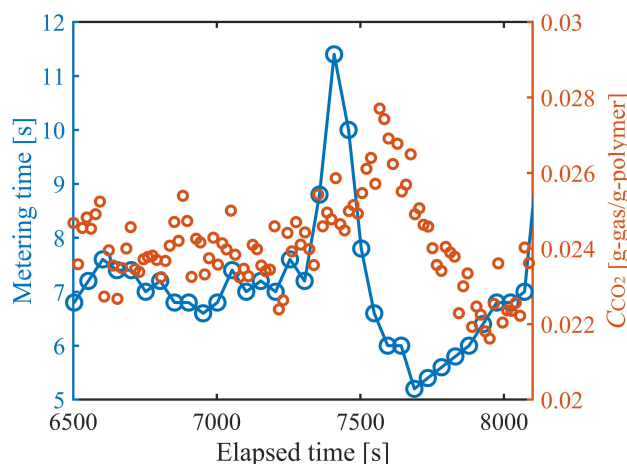


Figure 3.12 Dynamic movement of the CO₂ concentration attributed to the fluctuation in the metering time. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

As shown in the phenomenon mentioned above, the CO₂ concentration could not be stabilized instantaneously after the change in operating conditions, and the developed NIR measurement system enables the detection of the movement of the CO₂ concentration in real time.

3.3.7 Monitoring Dynamic Behaviors of CO₂ Concentration

The developed NIR spectroscopy system with the developed probe was applied to another FIM (MuCell®) technology, where the CO₂ concentration was controlled by manipulating the injector valve opening period. Similar to the low-pressure FIM process, the developed fiber optic probes were installed in the molding machine. The probe head was housed after the barrel section but before the nozzle. The NIR spectra were analyzed using Eqs. (2)~(5). The linear baseline correction was also applied in the same way to obtain A_{CO_2} .

Figure 3.13 shows time-series data of A_{CO_2} during injection molding operations with different injector valve opening periods. The opening period was changed from 0 to 0.2 stepwise. As shown in **Figure 3.13**, A_{CO_2} increased with some delays after changing the valve opening period. This time delay was attributed to the polymer transportation delay from the gas injector valve location to the NIR probe location. A_{CO_2} was stable after some fluctuations.

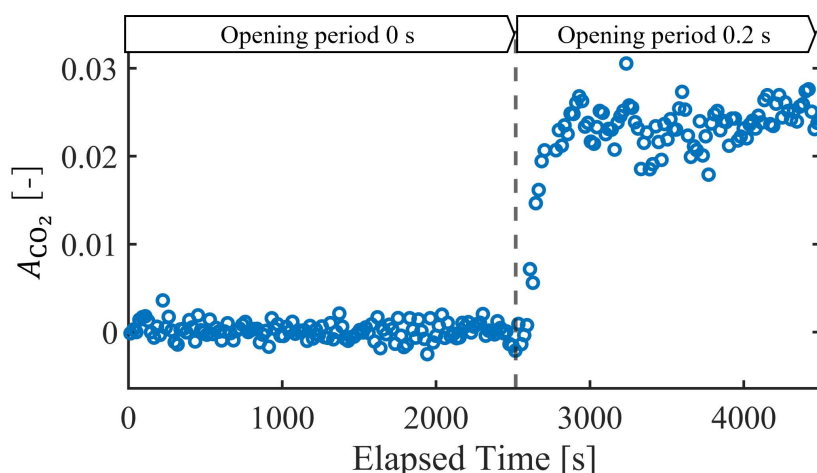


Figure 3.13 The time variation in A_{CO_2} as the opening period of the SCF injector valve increased. Reprinted with permission from Yoshikawa et al., *Industrial & Engineering Chemistry Research*, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

3.3.8 Detection of Polymer-Gas Phase Separation

To achieve stable foam injection molding, the molten polymer and the physical blowing agent should be well mixed to ensure a single-phase solution in the nozzle and metering zones. Once polymer-gas phase separation occurs in these zones, the phase-separated gas is injected into the mold separately from the molten polymer, and large bubbles are formed, which leads to severe defects in the cell structure of the foams. When the gas overdoses, phase separation tends to occur. The developed NIR spectroscopy system can detect phase separation phenomena in real time.

Figure 3.14 shows an example of eleven NIR transmittance spectra obtained during 200 s after the valve opening period was changed to 0.4 s. The absorption peaks of PP and CO_2 were observed in the NIR spectra. However, the baseline decreased drastically in the entire wavelength range during the time from 90 to 100 s, as represented by green and water-blue lines. The baseline decrease indicates that the transmitted NIR light decreased due to light scattering. When phase separation occurs, the phase-separated gas scatters the light at the interface between the polymer and gas phases, and the intensity of transmitted light decreases. Therefore, the phase separation can be detected by analyzing the transmittance of the NIR light, i.e., the baseline movement.

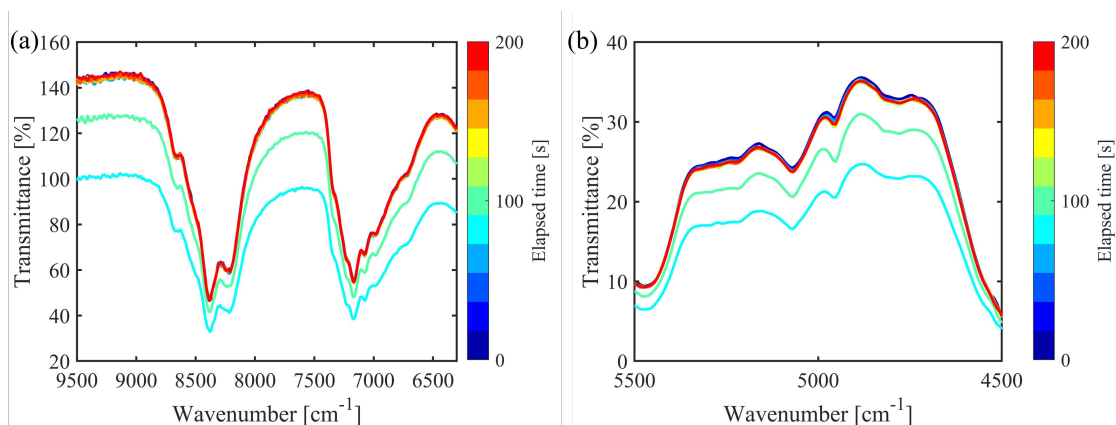


Figure 3.14 NIR transmittance spectra obtained from the MuCell® process: (a) 9500–6300 cm^{-1} and (b) 5500–4500 cm^{-1} . Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

The transmittances were averaged from 7442 to 7768 cm^{-1} and used as an index of the occurrence of phase separation. **Figure 3.15** (a) shows time-series data of the averaged transmittance during the injection molding operation, where the injector valve opening period was consecutively changed from 0 to 0.2, 0.4, and 0.6 s. The dashed lines indicate when the CO_2 injector valve opening period was changed. The transmittance was stable when the valve opening period was 0 and 0.2 s. In contrast, when the opening period was set from 0.2 to 0.4 and 0.6 s, the transmittance fluctuated entirely, indicating the occurrence of phase separation. **Figure 3.15** (b) shows a box-and-whisker diagram of the transmittance during ten shots of injection molding with each valve opening period. The transmittance light fluctuation was increased when injection molding was conducted with valve opening periods of 0.4 and 0.6 s.

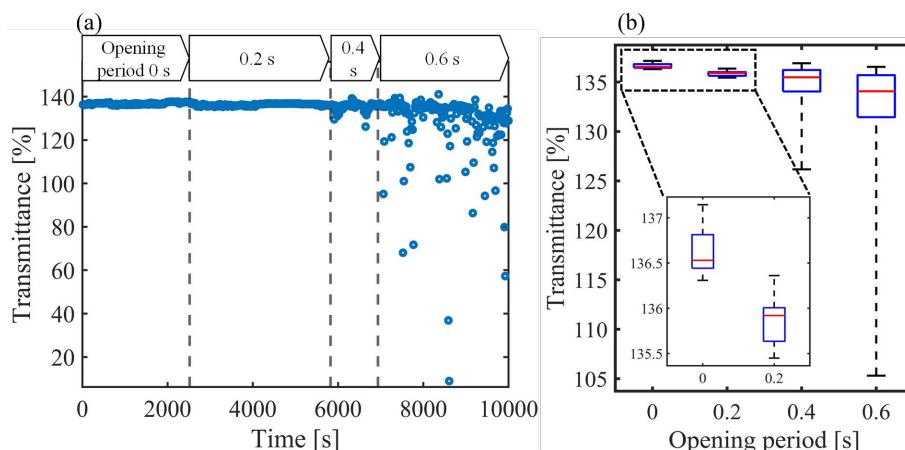


Figure 3.15 (a) Time-series data of the averaged transmittance with the changes in the valve opening period. (b) Box-and-whisker plot of the transmittance of each injection molding operation at each valve's opening period. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

Figure 3.16 (a) shows the change in average transmittance measured during the injection molding operation with a 0.6 s valve opening period, where a large decrease in transmittance was observed. The injection pressure was also monitored and superimposed in **Figure 3.16** (a). The injection pressure increased suddenly, and the polymer containing CO₂ was injected into the mold. **Figure 3.16** (b) shows the camera images of the foams obtained from the numbered shots of injection molding. Between shot numbers (ii) and (iii), the transmittance dropped drastically, indicating that phase separation occurred before the shot number (iii) of the injection process. Correspondingly, a large bubble was observed in the center of the foam produced by shot number (iii) of the injection molding process. These observations show that phase separation can be detected from the baseline movement of the NIR spectra before injection molding is conducted.

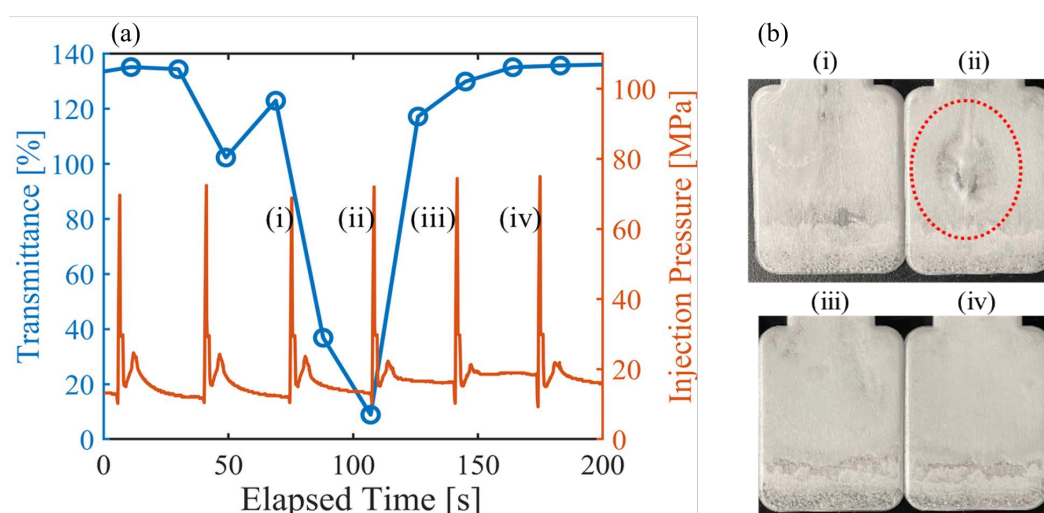


Figure 3.16 (a) Temporal movement of the averaged transmittance during injection molding with a valve opening period of 0.6 s. (b) Digital camera image of the foam injection-molded products obtained during injection molding (i, ii, iii, and iv represent the shot number obtained for each product). Reprinted with permission from Yoshikawa et al., *Industrial & Engineering Chemistry Research*, DOI: 10.1021/acs.iecr.3c00216, Copyright ©2023. American Chemical Society.

3.4 Conclusions

By installing the NIR probes in the nozzle zone of two different types of foam injection molding machines, where CO₂ was used as a physical blowing agent, NIR spectra were acquired in-line. By analyzing these spectra, the following results were obtained. The absorption peak of CO₂ was successfully identified by normalizing with the peak spectrum of the molten polymer and referencing the NIR spectra of the non-CO₂ dosing operation. The CO₂ absorbance peak was proportional to the CO₂ concentration, and a calibration line was obtained. The continuous measurement of the CO₂ concentration was made possible using NIR spectra with the linear calibration line at the injection molding processes. The CO₂ concentration was successfully monitored via two types of injection molding machines, namely, high-pressure and low-pressure delivery FIM machines. The temporal movements of the CO₂ concentration against the change in CO₂ dosage were predicted from the spectral information. The dynamics parameters of the injection molding process, such as the dead time, time constant, and steady-state gain, were identified by analyzing the NIR spectra. Because these dynamics depend strongly on the screw design and molding operation, the information can be used for designing the screw and determining the optimal operations.

From the movement of the baseline, i.e., a decrease in transmittance light, the occurrence of polymer-gas phase separation in the nozzle section can be detected, and the foam's defect could be anticipated.

Chapter 4

In-Line Near-Infrared Spectral Monitoring of Dissolved Nitrogen in Molten Polymers during Foam Injection Molding

4.1 Introduction

In Chapter 3, an innovative pressure-resistant and heat-resistant NIR probe was installed at the barrel tip of a low-pressure FIM machine, enabling real-time measurement of the CO₂ blowing agent concentration in the material just before injection into the mold. The NIR spectrum acquired in-line exhibited the CO₂ absorption peak, and a calibration curve was established to convert the CO₂ absorbance into the foaming agent concentration, thereby achieving real-time monitoring. Furthermore, the probe detected phase separation of the foaming agent, providing insights into potential abnormalities in the bubble structure of the molded product.

This chapter is part of a consecutive study from Chapter 3. While the work in previous chapter was focused on monitoring the concentration of CO₂ dissolved in molten polymers during FIM, monitoring of N₂ concentrations was investigated in this chapter. N₂ is also used as a physical blowing agent for FIM, and real FIM in industry employs N₂ more frequently than CO₂ as PBA due to the foaming ability and low greenhouse effect. However, N₂ lacks infrared activity. Therefore, it cannot be measured with the same scheme applied for CO₂. In this study, in-line pressure, temperature and NIR spectra data were integrated, and an inferential scheme was developed for measuring N₂ concentrations. By quantifying the spectral changes in the absorption peak resulting from N₂ dissolution, the N₂ concentration was determined with an equation of state based on the polymer density using multi-modal in-line data. This innovative method enables real-time monitoring of N₂ concentrations, contributing to improved process control and product quality in FIM.

4.2 Methods

4.2.1 Materials and Experiments

Polypropylene (PP) (J105, Prime Polymer, Japan) with a weight average molecular weight of 260,000 was used. Nitrogen (N_2) with 99.9% purity (Izumi Sangyo, Japan) was used as the PBA.

Figure 4.1 shows a schematic diagram of the experimental setup. Pressure and heat resistant NIR probes for transmission measurements were used for the in-line NIR spectral measurements. The details of the probe configuration are provided elsewhere²¹⁴. A pair of NIR probes was mounted between the shut-off nozzle and the screw head of a low-pressure FIM machine (RIC-FIM II: J35AD-30H, The Japan Steel Works LTD., Japan). The optical path length was 8 mm, and an optical fiber connected the probe to the NIR spectrometer. With this optical setup, the spectrum was acquired continuously. PP pellets were provided from the hopper of the injection molding machine and molded into a plate-like body, as shown in **Figure 4.2**. The main molding conditions are listed in **Table 4.1**.

The molding experiments were conducted by changing the N_2 gas delivery pressure (GDP) and the screw backpressure (BP). The GDP and BP values are listed in **Table 4.2**. The BP value was higher than the GDP to prevent the backflow of N_2 from the resin-starvation zone (gas-delivery zone) to the hopper side during the molding operation. Sixty shots were molded with each GDP and BP condition. The NIR measurements were obtained continuously even during the changeover time to observe the dynamic behavior of the N_2 dissolved in the molten polymer against the changes in the GDP and BP.

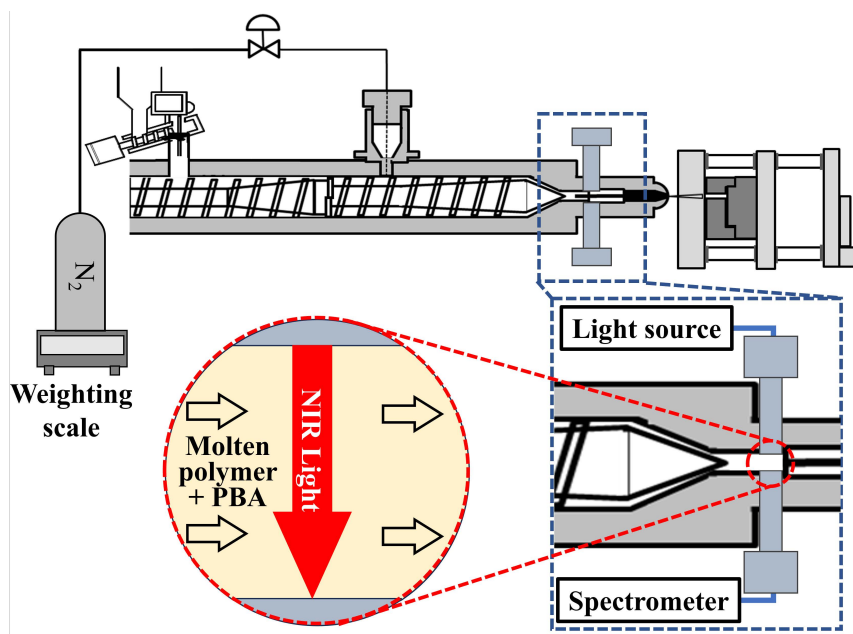


Figure 4.1 NIR measurements made by installing transmission probes at the tip of the nozzle of an FIM machine. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

4.2.2 In-Line Spectroscopic Measurements

A compact near-infrared spectrometer (NIR-Meter, Spectra Co-op., Japan) was used. The measurement conditions for the NIR spectra are listed in **Table 4.3**. The NIR spectra were measured at intervals of about 15 s. The background spectra were air spectra measured at room temperature with two NIR probes placed opposite each other with an optical path length of 8 mm. The temporal changes in the injection pressure, GDP, and N₂ were also recorded with a data logger (mini LOGGER GL 24, Graphtec Corporation, Japan). The N₂ cylinder weight was continuously measured with a weighing scale (BW32KH W/AC, SHIMADZU, Japan) and transferred to the data logger.

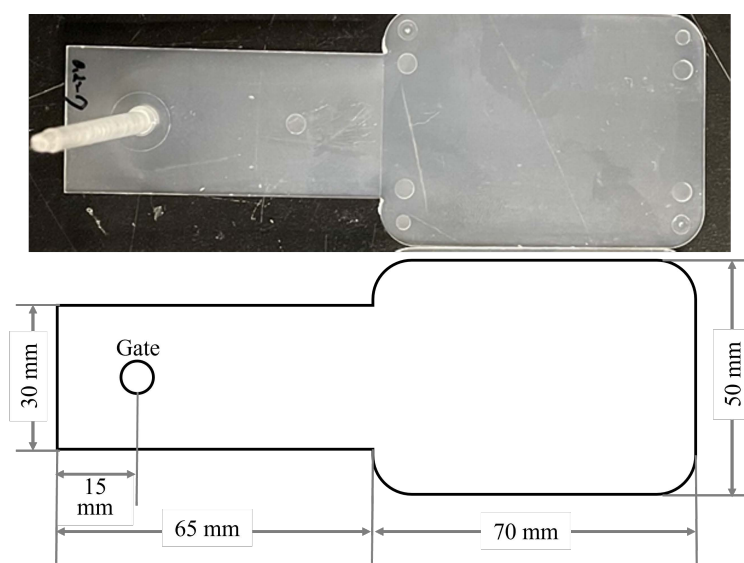


Figure 4.2 Digital optical image of the molded sample. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

Table 4.1 Conditions for injection molding. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

Parameter	Set values
Polymer temperature [°C]	(Tip)200/200/190/200/200/160/120/60(hopper)
Injection pressure [MPa]	120
Injection speed [mm s ⁻¹]	45
Screw rotation speed [/min]	100
Holding pressure [MPa]	30
Cooling time [s]	20
Mold temperature [mm]	40

Table 4.2 N₂ delivery conditions. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

	1	2	3	4
N ₂ delivery pressure [MPa]	0	4	6	8
Screw back pressure [MPa]	2, 6, 8, 10	6, 8	8, 10	10, 12

Table 4.3 Measurement conditions with a compact NIR spectrometer (NIR-Meter). Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

Parameters	Set values
Wavelength resolution [nm]	8
Exposure time [s].	0.635
Gain [-].	4
Accumulation number [-].	75
Light path length [mm]	8
Min/max wavelengths [nm]	900/1700

4.2.3 Measurement of PBA Solubility in Polypropylene

A magnetic suspension balance (MSB) (Rubotherm, MicrotracBEL, Japan) was used to measure the solubility of N₂ in PP as shown in Chapter 2. The characteristic parameters (T^* , P^* , ρ^*) of the SL equation of state calculated from the PVT curve are listed in **Table 4.4**. The measurement temperature was 200 °C

Table 4.4 Parameters for Sanchez-Lacombe equation of state.

Parameter	Unit	N ₂
T^*	[K]	159
P^*	[Pa]	1.04×10^8
ρ^*	[kg/m ³]	803.4
Weight averaged molecular weight	[g/mol]	28
Interaction parameter of SL (k ₁₂)	-	0.302857(200°C)

4.3 Results & Discussion

4.3.1 Calculation of the Average N₂ Concentration

N₂ consumption and the concentration dissolved in the molten polymer were calculated from the weight change of the gas cylinder and the weight of the produced polymer foams in the following way: foam injection molding was conducted to provide 50 shots at a minimum for each molding condition. The time for 30 to 50 shots under a steady state for each molding operation, T [s], the weight reduction rate of the gas cylinder during the steady state molding operation, S [g-gas/s], and the total weight of the polymer foam produced during the operation, W [g-polymer], were measured. Then, the average concentration of N₂, C_{N_2} [g-gas/g-polymer], was calculated with Eq. (4.1).

$$C_{N_2} = \frac{ST}{W} \quad (4.1)$$

Figure 4.3 shows the relationship between C_{N_2} and GDP. The solubility of N₂ in the polypropylene at 200 °C was measured with a magnetic suspension balance^{207–210} and plotted with the dashed line. C_{N_2} was lower than the solubility, indicating that the N₂ concentration did not reach equilibrium in the molding machine. “BP=GDP+2MPa” indicates that the back pressure was set 2 MPa higher than the gas delivery pressure. Comparing the concentration at BP=GDP+2 MPa with that at GDP+4 MPa showed that the N₂ concentration decreased as the back pressure was increased. A similar tendency was observed for CO₂ foaming with a low-pressure foam injection molding machine.^{215,216} This BP effect is attributed to a decrease in the surface area of the polymer-gas phase at the starvation zone as the back pressure increased. When the back pressure was increased, the length of the starvation zone decreased. As a result, the gas–liquid interfacial area in the zone decreased.

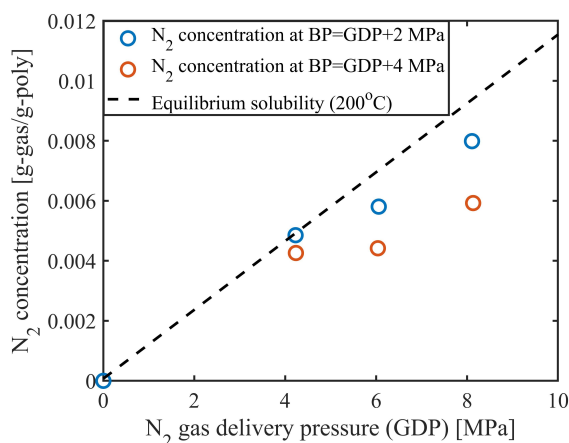


Figure 4.3 Relationship between the N₂ delivery pressure (GDP) and the N₂ concentration for each back pressure (BP). Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

4.3.2 Spectral Changes in Response to Dissolution of N₂ and the Polymer Pressure

Figure 4.4 shows a spectrum measured with the in-line NIR system, which shows an absorption peak originating from the CH bond of PP, but there is no peak for N₂. As shown in **Figure 4.4**, a second overtone of the C-H stretching peak for the CH₃ groups at 1196 nm, a second overtone of the C-H stretching peak for the CH₂ groups at 1214 nm, and a combination of second overtones for C-H stretching and CH₂ deformation gave a peak at 1393 nm¹⁸⁰.

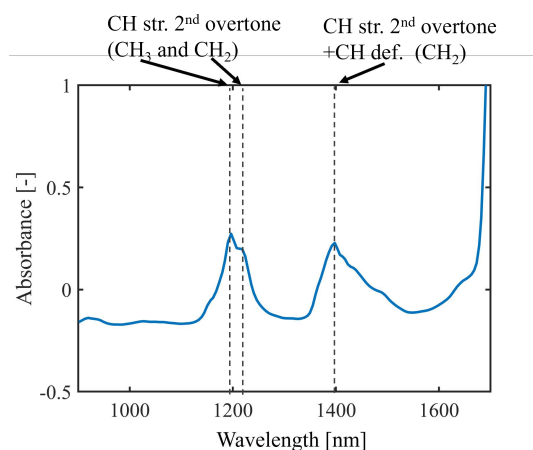


Figure 4.4 Raw spectrum measured in-line during FIM of PP with N₂. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

The peak at 1195 nm was analyzed by calculating the absorbance. Six wavelengths, 1106, 1109, 1112, 1544, 1547, and 1550 nm, were used for linear baseline fitting. Then, the linear baseline correction was performed by subtracting the calculated baseline from the spectrum. The corrected absorbance at 1195 nm was used as the absorbance of PP.

The presence of N₂ in the polymer cannot be detected in the NIR spectrum, but it changed the polymer density, and the change created the possibility of estimating the N₂ concentration from the change in a NIR absorption peak associated with the polymer. **Figure 4.5** shows the relationship between the PP absorbance at 1195 nm and the N₂ concentration calculated from Eq. (1). Since the pressure of the polymer also changed the polymer density, it is necessary to see the effect of the polymer pressure on the spectral band. The pressure of the molten polymer *P* was estimated by averaging the injection pressure during the sampling period of the spectral measurement. The effect of the polymer pressure *P* on the PP-N₂ relationship is shown as a color bar in **Figure 4.5**. A decrease in the absorbance of the PP band was observed with increasing N₂ concentration, indicating that increased N₂ dissolution caused a decrease in the PP density and that the spectrum reflected the change in density. In considering the effect of the polymer pressure on the PP absorption peak, it was confirmed that the peak intensity increased as the polymer pressure increased, regardless of the N₂

concentration. This indicated that the spectrum also captured the density change of PP caused by the pressure change.

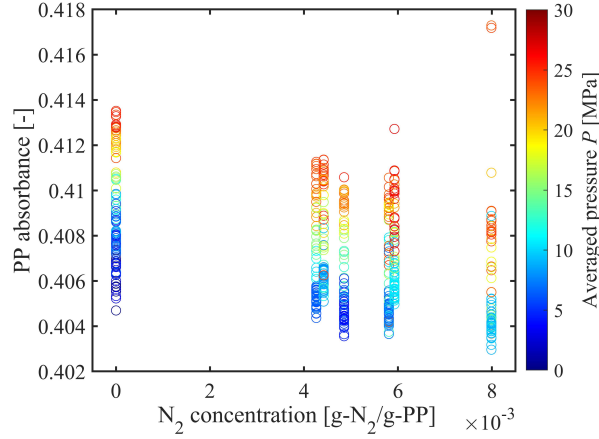


Figure 4.5 Relationship between absorbance of PP and the concentration of N₂ with different polymer pressures. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

4.3.3 Estimation of the Density with the Sanchez-Lacombe Equation of State (S-L EoS)

The NIR spectroscopic results suggested that the absorbance of the PP band at 1195 nm was strongly correlated with the density of the PP. However, the polymer pressure and temperature changed the polymer density, which influenced the absorbance of the PP band. Thus, to estimate the N₂ concentration from the absorbance of the PP band, the effects of the polymer pressure and temperature should be corrected, and the effect of N₂ should be distinguished.

The Sanchez-Lacombe equation of state (S-L EoS)²¹⁷ was used to calculate the polymer density at a given polymer pressure, temperature, and dissolved N₂ concentration. Here, it is acknowledged that the stretching and shear during injection affect polymer density changes. However, given that injection time is less than 1 second while NIR spectra are integrated over 15-second intervals, the influence of flow density changes on the spectrum was assumed to be negligible. The S-L EoS is given by Eq. (4.2).

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right] = 0 \quad (4.2)$$

with $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, $\tilde{\rho} = \rho/\rho^*$, where P , T , and ρ are the pressure [MPa], temperature [K], and density [g/cm³], respectively.

P^* , T^* , and ρ^* are the characteristic parameters. When describing a single-phase mixture of N₂ and polymer, these parameter values were determined with the following mixing law^{207,208}.

$$r = x_{N_2} r_{N_2} + x_{PP} r_{PP} \quad (4.3)$$

$$r_i = \frac{M_{wi}}{\rho_i^* v_i^*} \quad (i = \text{PP or N}_2) \quad (4.4)$$

$$v_i^* = \frac{RT_i^*}{P_i^*} \quad (4.5)$$

$$P^* = \varphi_{\text{N}_2} P_{\text{N}_2}^* + \varphi_{\text{PP}} P_{\text{PP}}^* + \varphi_{\text{N}_2} \varphi_{\text{PP}} \Delta P^* \quad (4.6)$$

$$\Delta P^* = P_{\text{N}_2}^* + P_{\text{PP}}^* - 2 P_{\text{N}_2/\text{PP}}^* \quad (4.7)$$

$$P_{\text{N}_2/\text{PP}}^* = (1 - k_{\text{N}_2/\text{PP}})(P_{\text{N}_2}^* P_{\text{PP}}^*)^{0.5} \quad (4.8)$$

$$T^* = \frac{(T_{\text{N}_2}^* \varphi_{\text{N}_2} + v T_{\text{PP}}^* \varphi_{\text{PP}})}{\varphi_{\text{N}_2} + v \varphi_{\text{PP}}} - \varphi_{\text{N}_2} \varphi_{\text{PP}} X T \quad (4.9)$$

$$X = \frac{\Delta P^* v^*}{RT} \quad (4.10)$$

$$v = \frac{v_{\text{N}_2}^*}{v_{\text{PP}}^*} \quad (4.11)$$

$$v^* = \varphi_{\text{N}_2}^0 v_{\text{N}_2}^* + \varphi_{\text{PP}}^0 v_{\text{PP}}^* \quad (4.12)$$

$$\varphi_{\text{N}_2}^0 = \frac{\varphi_{\text{N}_2}}{\varphi_{\text{N}_2} + v \varphi_{\text{PP}}} = 1 - \varphi_{\text{PP}}^0 \quad (4.13)$$

$$\rho^* = 1 / \left(\frac{m_{\text{N}_2}}{\rho_{\text{N}_2}^*} + \frac{m_{\text{PP}}}{\rho_{\text{PP}}^*} \right) \quad (4.14)$$

Where M_i are the weight average molecular weights of PP and N₂, T_i^* , P_i^* and ρ_i^* are the characteristic parameters for PP and N₂, respectively, and $k_{\text{N}_2/\text{PP}}$ is the interaction parameter for PP and N₂. Additionally, the molar fraction x_{N_2} , weight fraction m_{N_2} and volume fraction φ_{N_2} are calculated by:

$$x_{\text{N}_2} = \left(\frac{W_{\text{N}_2}}{M_{\text{wN}_2}} \right) / \left(\frac{W_{\text{PP}}}{M_{\text{wPP}}} + \frac{W_{\text{N}_2}}{M_{\text{wN}_2}} \right) = 1 - x_{\text{PP}} \quad (4.15)$$

$$m_{\text{N}_2} = \frac{W_{\text{N}_2}}{(W_{\text{N}_2} + W_{\text{PP}})} = 1 - m_{\text{PP}} \quad (4.16)$$

$$\varphi_{\text{N}_2} = \left(\frac{m_{\text{N}_2}}{\rho_{\text{N}_2}^*} \right) / \left(\frac{m_{\text{N}_2}}{\rho_{\text{N}_2}^*} + \frac{m_{\text{PP}}}{\rho_{\text{PP}}^*} \right) = 1 - \varphi_{\text{PP}} \quad (4.17)$$

Where W_i are the weights of PP and N₂. The values of the characteristic parameters used in this study are shown in **Table 4.5**. The parameters were calculated from PVT data for PP and N₂ and the solubility measured with the magnetic suspension balance. The details of the parameter determinations can be found elsewhere^{207–209,218}. The interaction parameter $k_{\text{N}_2/\text{PP}}$ was 0.245²¹⁹.

P was given by the pressure on the polymer measured when acquiring the NIR spectrum. T was also given by the barrel temperature at the location where the probes were installed. The N₂ weight fraction m_{N_2} was determined with Eq. (4.4) from the weight change of the gas cylinder.

$$m_{N_2} = \frac{C_{N_2}}{1 + C_{N_2}} \quad (4.18)$$

The density of the PP/N₂ mixture ρ_{PP+N_2} was calculated by substituting the values of the polymer pressure, temperature, and N₂ weight fraction into the S-L equation of state. Then, the density of PP ρ_{PP} , which is the weight of PP per unit volume in the mixture, was calculated from ρ_{PP+N_2} and the PP weight fraction m_{PP} , as shown in Eq. (4.19).

$$\rho_{PP} = \rho_{PP+N_2} m_{PP} \quad (4.19)$$

Figure 4.6 shows ρ_{PP} calculated by the S-L equation and Eq. (4.19) as a function of C_{N_2} and P . ρ_{PP} decreased as C_{N_2} increased, while ρ_{PP} increased as P increased. The calculation was consistent with the experimental results shown in the previous section.

Figure 4.7 shows the relationship and result of linear regression between the calculated polymer density ρ_{PP} and the measured absorbance at 1195 nm. Here, while the spectrum measurements were taken at 15-second intervals, polymer pressure measurements were taken at 0.1-second intervals. Therefore, the error bars shows the standard error of the variation in ρ_{PP} due to the fluctuations in polymer pressure measured during the 15-second spectrum measurement. Even though some variances exist, a linear relationship between the density and the absorbance was found for the data obtained at the same BP and GDP, indicating that the relationship follows Lambert–Beer’s law, despite the changes in the N₂ dissolution volume and pressure.

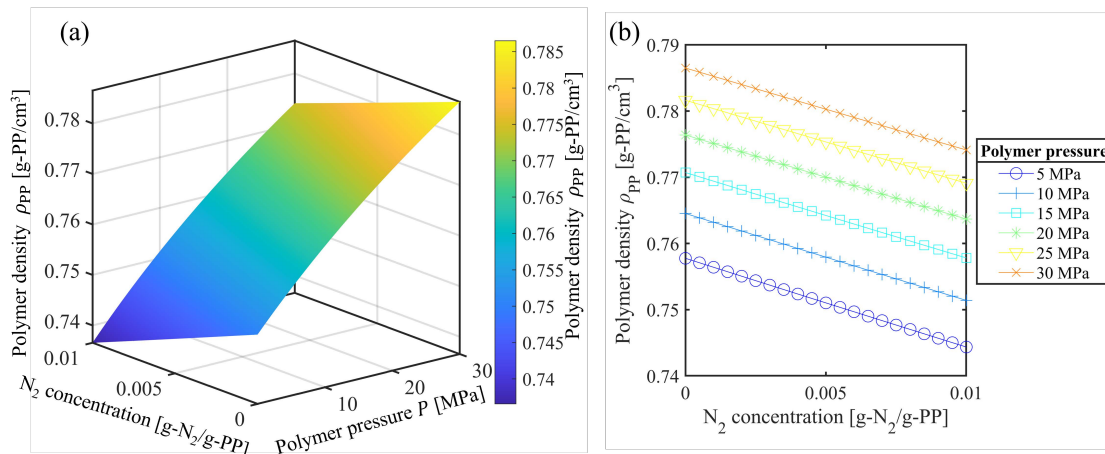


Figure 4.6 Relationships among the polymer pressure, N₂ concentration and polymer density calculated with the S-L EoS; (a) overall view and (b) slice plots. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

Table 4.5 Values of the parameter in the S-L EoS. Reprinted with permission from Yoshikawa et al.,

Parameter	Value	
	Polymer	N ₂
P_i^* [Pa]	2.84×10^8	1.036×10^8
T_i^* [K]	645.2	159
ρ_i^* [kg/m ³]	0.8968	0.8034
M_{wi} [g/mol]	2.6×10^5	28

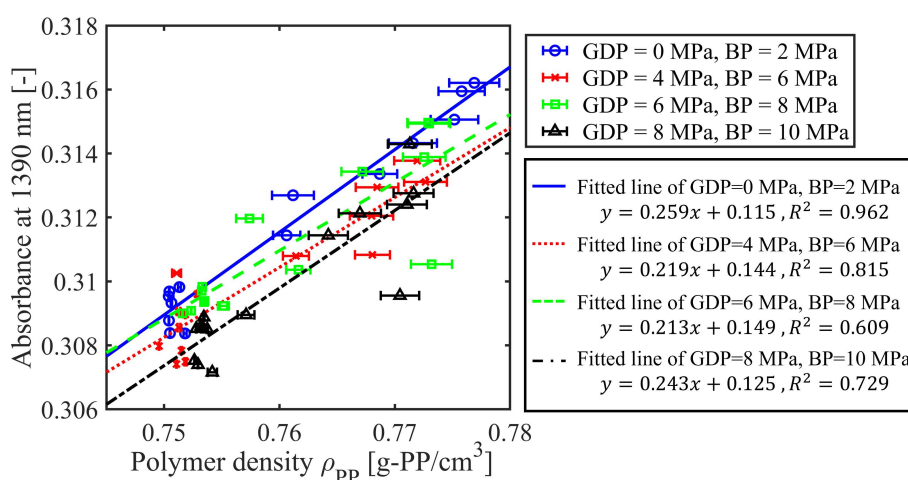


Figure 4.7 Linear relationship between the calculated density and the absorbance at 1195 nm. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

4.3.4 Development of an Inferential Model for the N₂ Concentration

In the previous section, a linear relationship between the polymer density and absorbance was identified for any polymer pressure and N₂ concentration. The polymer density can be estimated from the NIR absorbance in real time using this relationship. Then, assigning the estimated polymer density to the S-L EoS together with online measured polymer pressure and temperature data, the N₂ concentration can be estimated in real time. A dataset consisting of approximately 1000 points measured during the last 30 shots for each condition were used to construct a model for estimating ρ_{PP} from the spectra. Among these data, data measured at GDP=8 MPa and BP=12 MPa were used as test data, and the remaining data were used for model training and validation. 80% of the randomly selected remaining data were used as training data, and the 20% were used as validation data. In the model training process, the model was constructed using the training data and the estimation accuracy

was confirmed using the validation data. Additionally, the robustness of the model was verified by validating the accuracy using test data, which measured under conditions different from the model construction data.

First, a simple linear regression method was employed to estimate the polymer density from the absorbance data. **Figure 4.8 (a)** shows a schematic view of the inferential model. In this model, the polymer density ρ_{PP} was estimated from the polymer absorbance at 1195 nm, which was calculated in Section 3.3.3. Then, the estimated N₂ concentration $C_{N_2,est}$ was calculated by solving Eq. (19) and the S-L EoS with the estimated polymer density, the polymer pressure P and the temperature T . The simple linear regression model was trained with training data and validated with validation data. The root mean squared error (RMSE) and the coefficient of determination, R^2 , were calculated and used as indices for estimating the accuracy. **Figure 4.9 (a)** and **(b)** shows the polymer density and N₂ concentration estimates of the constructed model. The estimation accuracy for the N₂ concentration was not sufficient to monitor the concentration in-line. The noise in the linear relationship between the absorbance and density, as depicted in **Figure 4.7**, was attributed to the low estimation accuracy. Therefore, density estimations utilizing multivariate analyses were employed. Partial least squares regression (PLSR) is a multivariate analysis that enables the use of multiwavelength spectral data as explanatory variables. With multivariate data, a more robust model can be constructed.

Figure 4.8 (b) shows a schematic view of the inferential model used to estimate the N₂ concentration from the NIR spectrum, pressure, and temperature. The polymer density ρ_{PP} in the optical path was estimated from the in-line spectra data, A , and the polymer pressure data, P . The polymer pressure P varied randomly within the molding cycles and contributed to spectral variability. Inclusion of the polymer pressure as an explanatory variable enabled correction of the spectral variations caused by changes in P .

The simple linear regression model was trained with training data $(A, P, T, \rho_{PP}, C_{N_2})$ and validated with validation data. To develop the PLSR model, the optimal number of latent variables was determined with 3-fold cross-validation. The model accuracy was then tested with the validation data. Optimization of the preprocessing method of the PLS model.

The best preprocessing method was searched for choosing the explanatory variables. **Table 4.6** shows the estimation accuracy of the model developed by the different pretreatment methods. No.22 was the optimal pretreatment method. A total of 36 preprocessing methods were applied to the spectra of the training data, which included the three baseline correction methods, the three different wavelength ranges, with and without data centering, and the standard normal variate (SNV) method:

- Baseline correction
 1. no treatment (“1” in the table)
 2. linear baseline correction (“2” in table)
 (Base points: 1106, 1109, 1112, 1544, 1547, 1550 cm⁻¹)

3. second derivative (“3” in the table) (Savitzky-Golay filter, 3rd order, 5 points)

- Spectral Range

1. 1100~1300 cm⁻¹ (“A” in the table)

2. 1300~1500 cm⁻¹ (“B” in the table)

3. 1100~1500 cm⁻¹ (“A+B” in the table)

- Centering

Yes (“o” in the table) or No (“x” in the table)

- SNV method

Yes (“o” in the table) or No (“x” in the table)

The wavenumber region 1100 to 1500 nm was selected for the explanatory variable, and the centering method was applied.

Figure 4.9 (c) and (d) depict the polymer density and N₂ concentration estimates of the constructed model, and they showed high estimation accuracy. The estimation accuracy of the N₂ concentration was lower than that of the polymer density, which was attributed to the fact that the S-L EoS is highly sensitive to density changes, which amplified the noise in the estimations of the polymer density. Finally, using the test data measured at GDP=8 MPa and BP=12 MPa, the estimation accuracy was validated when N₂ concentration was estimated from the data measured under a process condition not included in the training data. Using the model with the spectra and pressure of the test data, the N₂ concentration was estimated, resulting in an RMSE of 8.41×10^{-4} . This value is not significantly different from the RMSE of estimation of the validation data shown in **Figure 4.9** (d). Thus, it was confirmed that this model is a robust model that can be used under a wide range of process conditions.

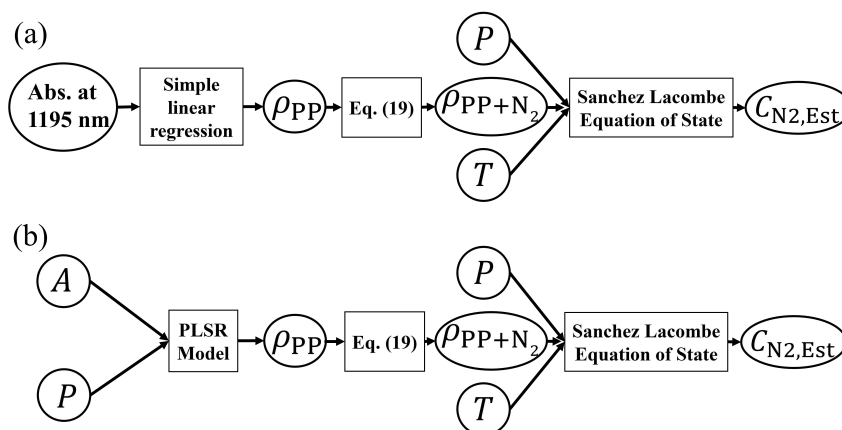


Figure 4.8 Schematic diagram for the models used to estimate N₂ concentrations (a) utilizing simple linear regression and (b) utilizing partial least squares regression for ρ_{PP} estimation. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

Table 4.6 Dependence of estimation accuracy on preprocesses. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

No.	Preprocess method	Wavelength regions	Centering	SNV	The optimal number of LV	RMSE $\times 10^{-3}$ [-]	R ² [-]
1	1	A	○	○	13	1.579	0.962
2	1	A	○	×	8	1.089	0.982
3	1	A	×	○	14	1.578	0.962
4	1	A	×	×	7	1.609	0.961
5	1	B	○	○	20	1.952	0.942
6	1	B	○	×	4	1.464	0.968
7	1	B	×	○	5	2.203	0.927
8	1	B	×	×	8	1.660	0.958
9	1	A+B	○	○	7	1.547	0.964
10	1	A+B	○	×	8	0.855	0.989
11	1	A+B	×	○	8	1.547	0.964
12	1	A+B	×	×	6	1.439	0.969
13	2	A	○	○	9	1.789	0.952
14	2	A	○	×	7	1.105	0.982
15	2	A	×	○	12	1.650	0.959
16	2	A	×	×	8	1.590	0.962
17	2	B	○	○	20	1.881	0.947
18	2	B	○	×	12	1.061	0.983
19	2	B	×	○	12	2.040	0.937
20	2	B	×	×	9	1.751	0.954
21	2	A+B	○	○	14	1.520	0.965
22	2	A+B	○	×	11	0.880	0.988
23	2	A+B	×	○	15	1.519	0.965
24	2	A+B	×	×	9	1.409	0.970
25	3	A	○	○	8	1.774	0.952
26	3	A	○	×	8	1.218	0.978
27	3	A	×	○	9	1.757	0.953
28	3	A	×	×	8	1.907	0.945
29	3	B	○	○	12	2.051	0.936
30	3	B	○	×	12	1.214	0.978
31	3	B	×	○	13	2.035	0.938
32	3	B	×	×	15	1.843	0.949
33	3	A+B	○	○	10	1.593	0.962
34	3	A+B	○	×	12	1.045	0.984
35	3	A+B	×	○	12	1.504	0.966
36	3	A+B	×	×	10	1.716	0.956

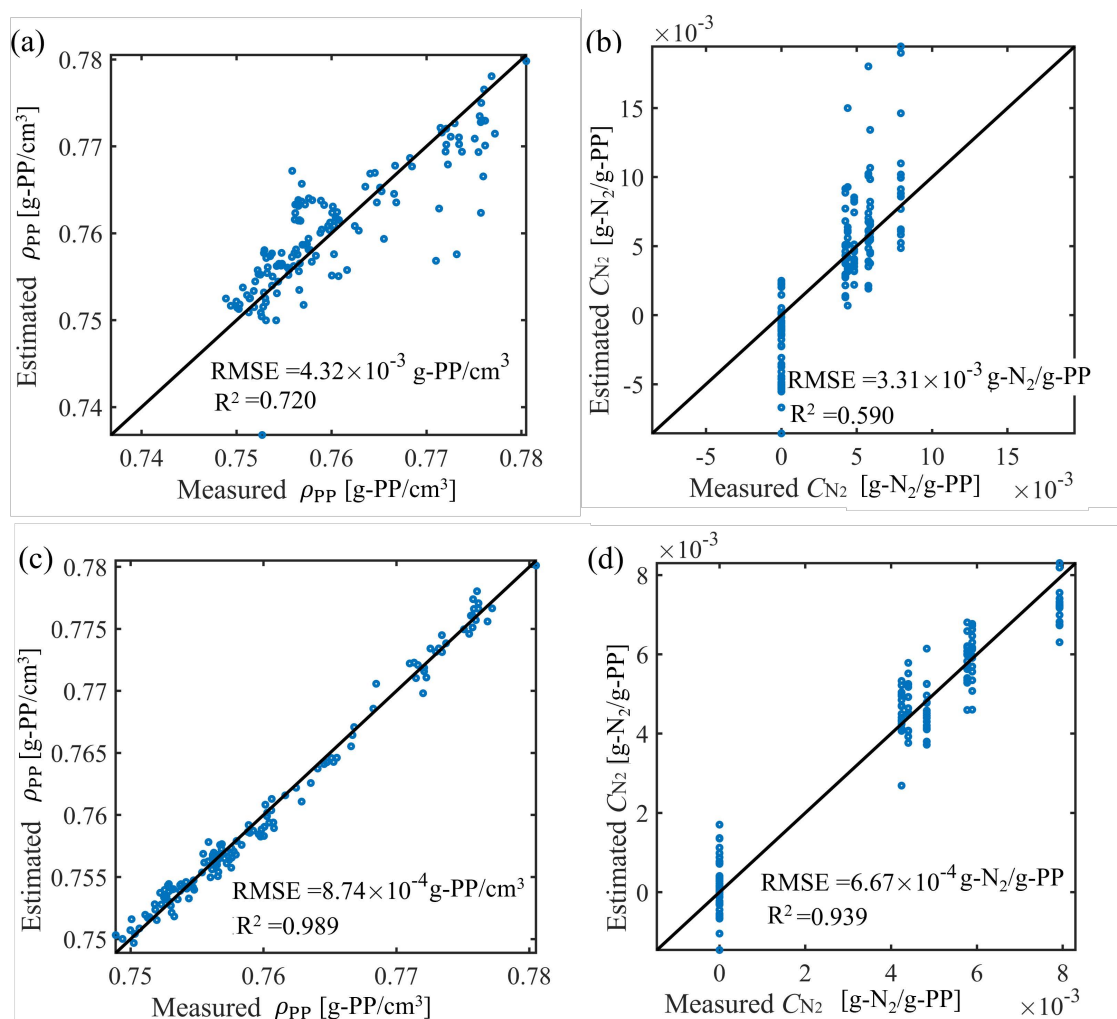


Figure 4.9 Estimation results for (a) the polymer density ρ_{PP} and (b) the N_2 concentration calculated by the model with simple linear regression and estimation results for (c) the polymer density ρ_{PP} and (d) N_2 concentration calculated by the model with PLSR. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

4.3.5 Temporal Changes in the N_2 Concentration During Changeover

The developed inferential model was applied to estimate the temporal changes in the N_2 concentration versus the GDP changes. **Figure 4.10** (a) shows that the estimated N_2 concentration $C_{N_2,est}$ during the N_2 delivery pressure (GDP) was changed, where GDP was changed stepwise from 0 to 4 MPa. The orange solid line represents the temporal change in the estimated N_2 concentration, and the blue line shows the N_2 GDP. The black dotted line represents the average N_2 concentration C_{N_2} , which was calculated from the weight change of N_2 cylinder during the steady state. The estimated N_2

concentration showed good agreement with C_{N_2} .

It was also observed that the estimated N_2 concentration started to increase after the N_2 delivery pressure was increased, and then it stabilized, showing the dynamics of the mixing process against the gas delivery pressure. The dynamic behavior of the N_2 concentration was fitted with the first-order time constant and the delay model defined by Eq. (20).

$$C_{N_2, est} = K \left(1 - \exp \left(-\frac{t-d}{T} \right) \right) + C_{N_2,0} \quad (20)$$

Where, K [g- N_2 /g-PP], d [s], T [s] and $C_{N_2,0}$ [g- N_2 /g-PP] are process gain, dead time, time constant and initial N_2 concentration respectively. The fitting results are shown in **Figure 4.10** (b). The black dotted line represents the fitting results and shows the dynamics of the N_2 concentration against step changes in the GDP. The fitting parameters are shown in **Table 4.7**. As shown in **Figure 4.10**, the developed inferential system for determining N_2 concentrations provides information on the process dynamics, which is helpful for designing the screw configuration of FIM.

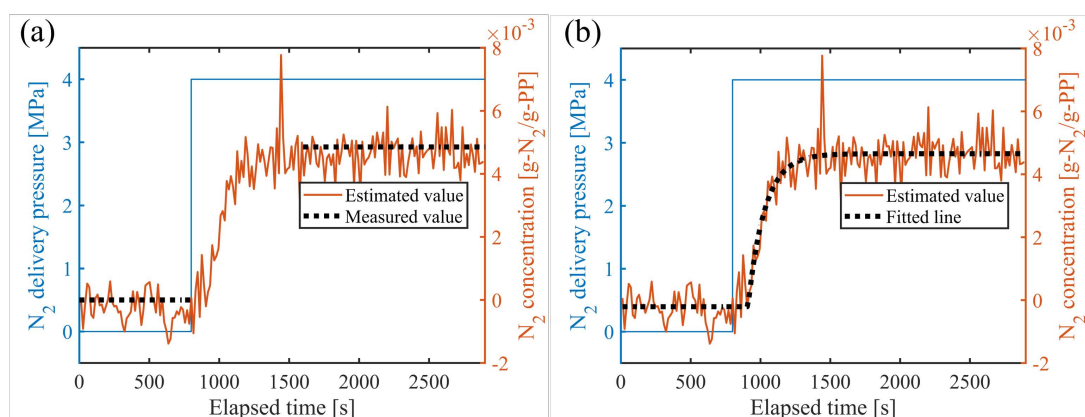


Figure 4.10 (a) Rising estimated N_2 concentration against the set value for the N_2 delivery pressure and (b) result of fitting with the 1st order delay model. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

Table 4.7 Values of the parameters for the 1st order time constant with the delay model. Reprinted with permission from Yoshikawa et al., Industrial & Engineering Chemistry Research, DOI: 10.1021/acs.iecr.3c04324, Copyright ©2024. American Chemical Society.

Parameter	Fitted value
K [g- N_2 /g-PP]	0.00486
T [s]	120
$C_{N_2,0}$ [g- N_2 /g-PP]	-0.000208
d [s]	89

4.4 Conclusions

An in-line NIR monitoring method was developed to estimate N_2 concentrations in foam injection molding. The N_2 absorption peak does not exist in the NIR region, and thus, the N_2 concentration cannot be determined from the NIR spectrum directly. The developed inferential monitoring system consisted of the PLSR model and the polymer equation of state (EoS). The PLSR model correlated the NIR spectrum with the polymer density. The EoS is a nonlinear algebraic equation expressing functional relationships among the polymer pressure, temperature, N_2 concentration, and polymer density. The polymer density was estimated by PLSR from the NIR spectra and pressure generated in-line. By solving the EoS with the estimated polymer density, polymer pressure, and temperature, the concentration of N_2 dissolved in the molten polymer was estimated. It was shown that the N_2 concentration was successfully estimated with high accuracy. The developed monitoring system will be used to design the optimal screw configuration and confirm stable operation of the foam injection molding process.

The developed inferential monitoring (i.e., soft sensor) system can also be applied to high-pressure foam injection molding processes using N_2 as the physical blowing agent. This method is applicable to other infrared active polymer/inactive gas systems when the parameters of S-L EOS are prepared. The fundamental idea of the developed monitoring system can be extended to processes, for which the chemical composition, which cannot be directly detected with the NIR spectrum, can be estimated from the NIR absorbance corresponding to the polymer density or the polymer concentration.

Chapter 5

General Conclusion

5.1 Conclusions of This Thesis

In this study, an in-line NIR-based process monitoring method was developed to meet the demands for advanced and rapid process design and quality control in polymer processing. In Chapter 1, three main issues of previous in-line NIR methods were identified: (1) limited applicability to different processes, (2) limited applicability to different materials, and (3) limited diversity in measurable information. To address these issues, research was conducted as shown in Chapters 2 to 4.

In Chapter 2, an in-line measurement method for blend ratios in the injection molding process of biodegradable polymer blends was developed. To address Issue 1, a high-durability NIR probe capable of continuous use in injection molding processes was developed. The developed probes for transmission and diffuse reflection measurements successfully measured NIR spectra continuously in injection molding processes at polymer temperatures exceeding 200°C and polymer pressures exceeding 100 MPa. Additionally, to address Issue 2, a composition analysis method for polymer blends capable of analyzing a wide range of compositions was developed. In immiscible polymer blends, scattering intensity changes significantly depending on the blend ratio. Conventional composition analysis using either transmission or diffuse reflection information alone could not provide high-precision composition analysis for a wide range of blend ratios. In this study, simultaneous measurement was used to create a calibration model that used both spectra as explanatory variables, enabling stable composition analysis even in systems with significant changes in scattering characteristics. The developed analysis method successfully determined material replacement during the material changeover process.

In Chapter 3, a method for measuring CO₂ concentration and predicting molding defects due to phase separation phenomena in foam injection molding processes was developed. In the foam injection molding process, spectral variations due to pressure fluctuations were modeled and eliminated the effect by a new analysis method. This enabled more stable quantification of CO₂ concentration compared to conventional methods. Furthermore, By focusing on the baseline of the transmission spectrum, the scattering intensity of near-infrared light was evaluated. Temporal increases in scattering intensity from the time-series NIR spectra were detected and the timing of phase separation in the barrel was successfully identified. Additionally, molding defects caused by phase separation of the foaming agent were confirmed, demonstrating the potential for using this method to detect product abnormalities.

In Chapter 4, a calibration model for real-time quantification of N₂ concentration was constructed for foam injection molding using N₂ as the foaming agent. The density of polymer changed by swelling with N₂, and N₂ concentration was estimated from the polymer peak which fluctuated due to swelling. Furthermore, by modeling polymer swelling and density changes due to pressure fluctuations, a high-precision real-time measurement method for N₂ concentration was realized. By incorporating an equation of state into spectral analysis, a stable estimation of N₂ concentration under

non-steady pressure conditions of the injection molding process was achieved. This method succeeded in overcoming the fundamental detection limit of NIR for detecting concentrations of infrared-inactive molecules. Using this in-line measurement of N_2 concentration, the dynamic characteristics of the low-pressure foam injection process were analyzed.

5.2 Future Perspective

Finally, future perspectives and strategies for further accelerating research and development in polymer processing are discussed based on the technologies developed in this research. Figure 5.1 summarizes the benefits that in-line NIR brings to polymer processing research and development, and the technologies that need to be developed. The proposed researches are classified into 4 types, ranging from materials process engineering to process system engineering.

1) Basic Research on Physicochemical Phenomena Under High Temperature, High Pressure, and High Shear Conditions:

Under high temperature, high pressure, and high shear conditions, the phenomena beyond the kinetics of the phenomena under static conditions. For example, shear-induced crystallization^{220–222} is a promoted crystallization phenomenon under shear, and shear-induced phase separation^{223–227} is a promoted bubble nucleation of low-molecular-weight gases under shear. Observing and modeling these phenomena are crucial for understanding the processing processes. However, there are limited experimental methods for analyzing these phenomena, and their kinetic analysis has not been completed. Using the high-durability NIR probe developed in this research, it is possible to directly observe the behavior of polymers under harsh conditions. For example, NIR can be used to observe crystallization processes and quantify orientation using polarized NIR measurements. To realize such research, it is necessary to develop new spectroscopic cells that can control temperature, pressure, and shear. Moreover, further analysis combining kinetic studies using molecular dynamics simulations is also required.

2) Advanced Process Modeling by Modeling PPSP Relationships:

With the advancement of processes, the PPSP relationships of real processes become more complex involving multiscale factors. Developing multiscale simulators that model and predict each of these interactions is highly desirable. NIR is a powerful tool for observing phenomena and analyzing their kinetics, and it can be used to create such process models. In fact, the method proposed in this study successfully measured CO_2 concentrations in SOFIT and modeled the CO_2 dissolution mechanism in starvation zones.^{211,212} Moreover, by utilizing the real-time capabilities of NIR, it is believed that the construction of digital twins that replicate in-process phenomena in real-time can be achieved. To realize such research, hierarchical modeling and simulation for multiscale relationships during polymer processing. Furthermore, the development of multimodal in-line measurements and the establishment of analysis methods are needed. By combining in-line measurements using various

spectroscopic methods, X-ray scattering, and ultrasound, the interactions of phenomena at different scales can be elucidated.

3) Advancing Process Control and Quality Management

In fields where product composition and chemical structure are particularly critical for product quality, such as chemical and pharmaceutical processes, in-line composition analysis and control or quality management based on it have already been implemented. In polymer processing, macroscopic properties such as dimensions have often been managed as quality parameters and chemical information has not been sufficiently emphasized in process control. However, as materials become more complex and require advanced functionalities, monitoring and controlling chemical parameters and final product qualities in polymer processing are expected to become important in the future. The composition analysis using NIR, as proposed in this study, will be a highly useful foundational technology. Additionally, it will become possible to control real-world processes using simulators based on NIR data, such as digital twins. For chemical monitoring, constructing a calibration model is essential. However, most polymer processing processes are small-scale production of diverse products, it is not practical to collect large amounts of data for each material to build calibration models. Therefore, adaptation to small-dataset conditions is necessary. To achieve this, constructing a database of molten polymer spectra, introducing analysis techniques that utilize similar data such as transfer learning, and establishing calibration-free analysis methods are desirable.

4) High-throughput material and process design based on informatics

Research on materials informatics (MI) and process informatics (PI) is being promoted to further accelerate materials and process development. MI constructs machine learning models that predict material properties from compositions and chemical structures.^{228–230} This enables faster property predictions for materials with unknown structures and accelerates high-throughput material exploration. PI models the relationships between process operating conditions and product quality, such as in PPSP relationships using machine learning, to instantly explore optimal conditions for creating materials with target properties.^{32,34} Therefore, using both MI and PI can speed up the entire steps from material development to process development. However, while MI research is actively advancing, PI research is still in its early stages. The reason lies in the lack of process data. In such research and development, building and utilizing big data is extremely important. The 5V (Volume, Variety, Velocity, Veracity, Value) are proposed as requirements for big data.²³¹ However, in process design, the datasets that meet these 5V requirements are rare. In-line NIR can help solve this issue. The techniques proposed in this study contribute to improving Volume and Velocity through real-time measurements. Additionally, measuring various types of information using NIR, which was a theme of this study, contributes to enhancing the Variety of the dataset.

Thus, in-line NIR is a technique that can be widely used, from basic research in materials process engineering to applied research in process systems engineering. Based on in-line NIR

measurements, the construction of new research fields is expected, including the development of new advanced polymer properties, processing processes, and advanced quality management methods.

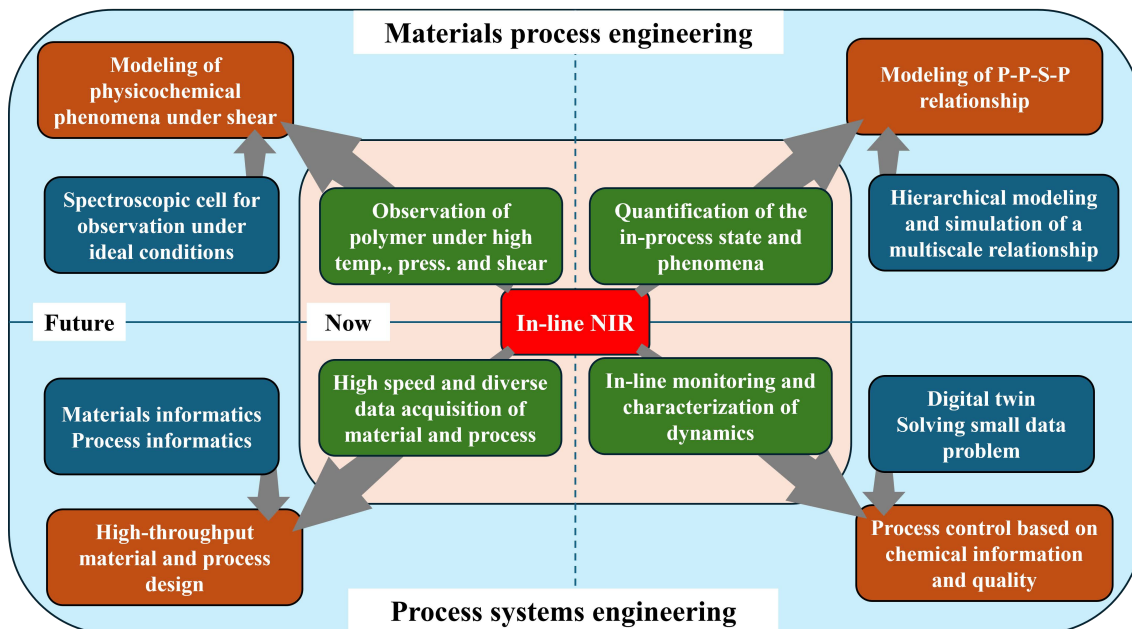


Figure 5.1 Future perspective of research and development of polymer processing based on in-line NIR. The green boxes show the techniques developed in this research. The orange and blue boxes show the expected research to which in-line NIR can contribute, and the required techniques to realize the research.

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- List of Publication

- Peer Reviewed Journals

- [1] **Itsuki Yoshikawa**, Shunsuke Hosoe, Yuta Hikima, Masahiro Watari, Masahiro Ohshima, “In-Line Monitoring of the Physical Blowing Agent Concentration by Transmission Near-Infrared Spectroscopy with High-Pressure Resistance Fiber Optic Probes for Foam Injection Molding Processes”. *Ind. Eng. Chem. Res.* 2023, 62 (15), 6338–6346. Chapter 3
- [2] **Itsuki Yoshikawa**, Yuta Hikima, Masahiro Ohshima, “In-Line Near-Infrared Spectral Monitoring of Nitrogen Concentrations Dissolved in Molten Polymers during Foam Injection Molding Process”, *Ind. Eng. Chem. Res.*, 2024, 63, (9), Chapter 4
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- [4] **Itsuki Yoshikawa**, Omid Aghababaei Tafreshi, Yu-Chen Sun, Naomi Matsuura, Ken-Ichiro Sotowa, Hani E. Naguib, “Data-driven Discovery of Multi-Functional Organic Polymer Aerogel by Machine Learning Assisted Large-Scale Property Screening”, submitted

- Presentations

International Conferences

First author

- [1] **I. Yoshikawa**, Y. Hikima, M. Ohshima, “In-line near-infrared spectroscopic monitoring for injection molding of biodegradable polymer blends”, 12th International Conference on Advanced Vibrational Spectroscopy, Krakow, Poland, (September 2023)
- [2] **I. Yoshikawa**, Akihiro Naito, Shunsuke Hosoe, Y. Hikima, M. Ohshima, “The dissolution mechanism of a blowing agent in the novel foam injection molding process, SOFIT® (RIC-FOAM)”, 38th International Conference of the Polymer Processing Society, St.Gallen, Switzerland, (May 2023)
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Domestic Conferences

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● Awards

- [1] 化学工学会第55回秋季大会 SIS 部会 研究奨励賞 (2024年9月)
- [2] 馬詰研究奨励賞 京都大学 (2023年7月)
- [3] プラスチック成形加工学会第30回秋季大会 優秀ポスター賞 (2022年11月)
- [4] 第38回近赤外フォーラム Student Travel Award (2022年11月)
- [5] プラスチック成形加工学会第33回年次大会 優秀ポスター賞 (2022年6月)
- [6] 化学工学会第87年会 優秀学生賞 (2022年3月)