

NIR spectroscopy for simultaneous monitoring of residual water content and reactive species in polyurethane systems

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Polyurethane (PU) materials play a critical role in various industrial applications. Continuous production processes, such as reactive extrusion, are widely used in PU manufacturing and demand stringent monitoring techniques to ensure consistent material quality and process stability.

A primary challenge is controlling the amount of residual water in polyols, which can significantly alter the architecture and performance of PUs by inducing side reactions. Moreover, verifying accuracy in stoichiometry between polyols and isocyanates, as well as determining their conversion is essential for complete process control.

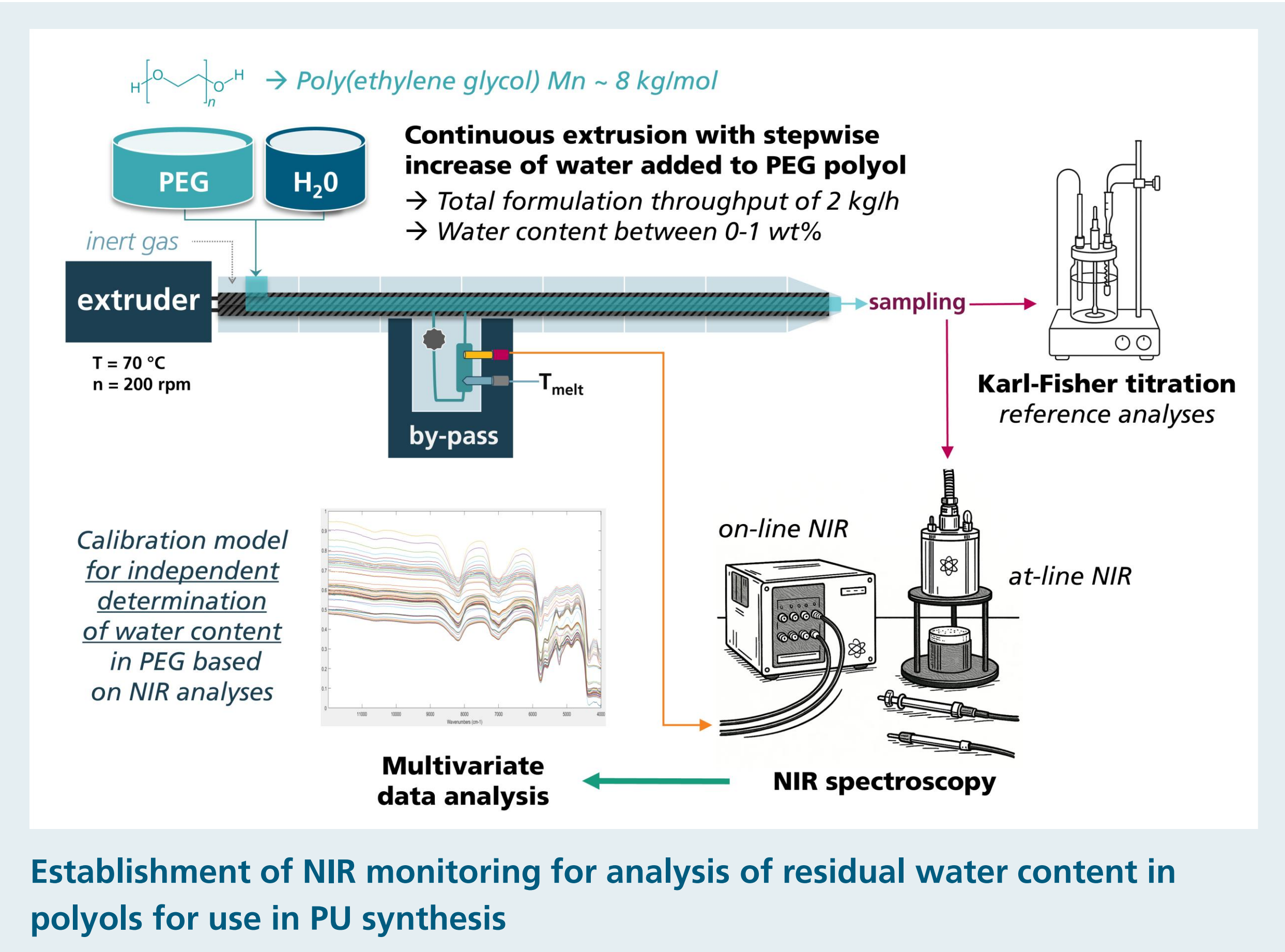
Within this study, we propose a strategy for process monitoring in PU production based on Near-Infrared (NIR) spectroscopy. Using in-situ NIR analysis, we aimed at:

- Quantification of water in Poly(ethylene glycol) (PEG) polyol,
- Distinction of water and isocyanates used in PU production.

Experimental setup and evaluation

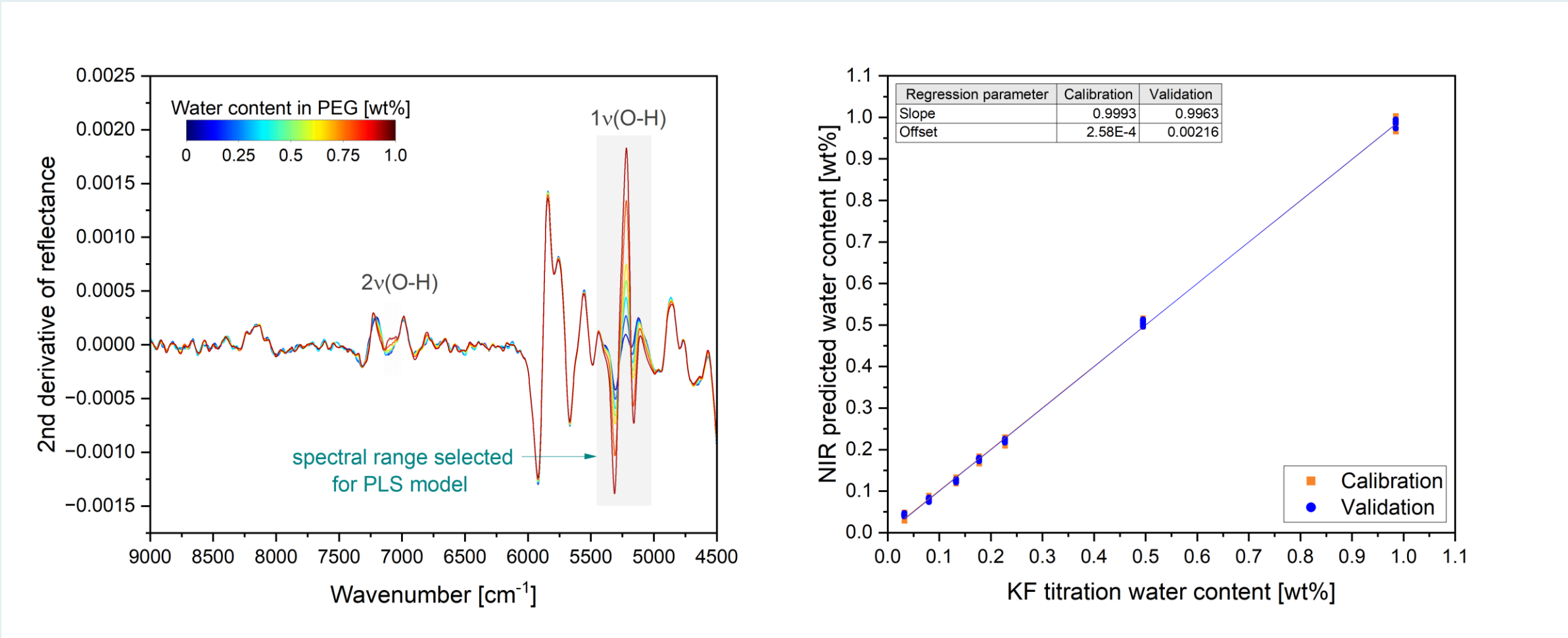
PEG ($M_n \sim 8000$ g/mol) and distilled water were fed continuously into an 18 mm twin screw extruder equipped with a by-pass (0.7 mm capillary). The water content in PEG was varied in a range of 0 to 1.0 wt%. The following analyses were carried out:

- On-line: NIR via transfection probe installed in the by-pass,
- At-line: NIR via diffuse reflection of post-extrusion material,
- Off-line: Karl-Fischer (KF) titration for determination of water, as a reference evaluation of post-extrusion material.



NIR spectra were preprocessed using normalization, smoothing and derivation algorithms. Variation of the water content correlated to changing intensity of the first overtone ($5400\text{--}5050\text{ cm}^{-1}$) and second overtone ($7100\text{--}7000\text{ cm}^{-1}$) of OH groups in water. Partial Least Squares Regression (PLSR) models were generated using the range of the first overtone of water and spectral data were split into calibration and validation data sets. Both models exhibited excellent correlations between NIR data and water content determined with KF titration.

Preprocessed NIR spectra of PEG with varying water content measured on-line (left) and results of PLSR regression comparing NIR and KF measurement

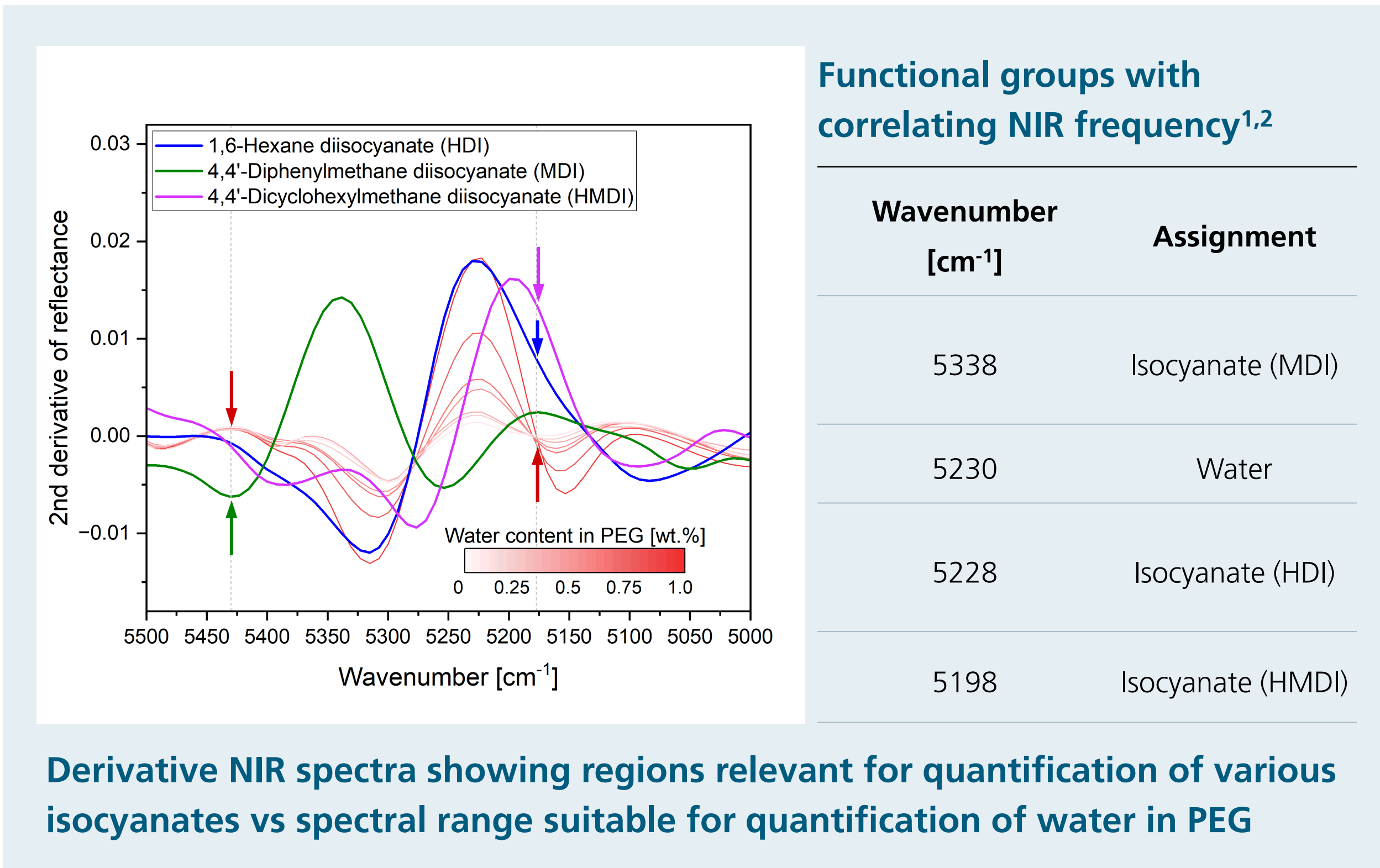


PLSR model parameters

NIR analysis	Number of LVs	R ₂ Cal	R ₂ CV	R ₂ Pred	RMSEC [wt%]	RMSECV [wt%]	RMSEP [wt%]
On-line	2	0.999	0.998	0.998	0.00864	0.0147	0.00819
At-line	3	0.998	0.997	0.998	0.0142	0.0172	0.0122

The characteristic peaks of isocyanates are situated in a similar range as the first overtone of water, whereas significant differences can be observed between aromatic and aliphatic isocyanates. Distinction of isocyanate species and water can be achieved by utilizing selected preprocessing such as derivation, which yields frequencies inert to changes in water concentration. These positions could be used to determine the isocyanate concentration, while effectively avoiding manipulation of prediction results induced by change in residual water content. Isocyanate quantification could be therefore achieved based on:

- Shoulder at 5173 cm^{-1} for aliphatic and cycloaliphatic systems,
- Side peak at 5430 cm^{-1} for aromatic systems.



Conclusion

Based on this work, a process analytical concept could be developed to be used in reactive extrusion approaches to produce PU. Both on-line and at-line monitoring with NIR spectroscopy can be implemented to determine the residual water content. The indicated distinction of water residues and isocyanate reagents presents a basis for further exploitation of the NIR technique to be applicable simultaneously for both components.

1 Cho, Soohwa; Chung, Hoeil; Lee, Youngil (2005): Simple and fast near-infrared spectroscopic analysis of hydroxyl number of polyol using a disposable glass vial. In: *Microchemical Journal* 80 (2), S. 189–193. DOI: 10.1016/j.microc.2004.07.013.
2 Dethomas, F. A.; Hall, J. W.; Monfre, S. L. (1994): Real-time monitoring of polyurethane production using near-infrared spectroscopy. In: *Talanta* 41 (3), S. 425–431. DOI: 10.1016/0039-9140(93)E0055-I.