In-situ Characterization of Curing Reaction of GAP and Isocyanates by Near Infrared Spectroscopy

Andreas Imiolek, Wolfgang Becker, Kerstin Sachsenheimer, Volker Weiser

Fraunhofer Institut für Chemische Technologie, Joseph-von-Fraunhofer Str. 7, 76327 Pfinztal, Germany

E-Mail: Andreas.Imiolek@ict.fraunhofer.de

ABSTRACT

Glycidyl azide polymer (GAP) is a suitable binder for future solid propellants with good performance characteristics and no hazardous impact to the environment relating to the burning products. The progress of the curing of GAP and isocyanates to polyurethane is of major importance for the adjustment of process parameters as well as the final product properties. Near infrared spectroscopy is applied in-situ to study the progress of the curing reaction with respect to time. With Multi Component Resolution (MCR), it was possible to get a more comprehensive insight into the reaction. Concentration information of the reagents of this complex reaction could be monitored with this kind of method.

Keywords: In-situ reaction study, GAP, Polyurethane, NIR

1 Introduction

Solid rocket propellants typically consist of a mixture of granules of a solid oxidizer (AP, AN, ADN) placed in a polymeric binder combined with energetic compounds (HMX, RDX), metallic additives (Al, Mg) plasticizers, stabilizers and / or burn rate modifiers (Al) [1].

Today, HTPB (hydroxyl terminated polybutadiene, binder) and AP (ammonium perchlorate, oxidizer are widely used as solid propellants. These propellants are well known for their good performance characteristics, mechanical properties and the wide operating temperature range. But the contamination of the environment by the combustion products of perchlorate is also well known and documented [2]. For this reason the future propellants should keep the performance characteristics and the mechanical properties, but replace the components, which lead through the burning to the hazardous contamination of the environment. One material combination, which has the potential to fulfil the criteria is a propellant based on ADN (oxidizer) and GAP (glycidyl azide polymer). GAP is classified as a high-nitrogen content polymer and due to its availability, good binder properties and low detonation sensitivity it is a suitable polymer for solid propellants [3], [4]. The prepolymer of GAP-diol is a liquid substance with alcoholic functional groups. After adding the curing agent in form of isocyanates, the polyaddition reaction starts and the product is cross-linked polyurethane (PUR, elastomer). It is of major importance for the optimization of the production process to adjust the physical properties of the solid propellant, to keep the original energy content and to minimize the costs [5].

In several publications the polyaddition reaction with PUR as product has been studied [6], [7]. Most of them used infrared spectroscopy to get the information about the reagent and the product concentrations during the curing process. Usually the IR measurements were realized offline. The main disadvantage of this method is the time gap until the results are available and the fact that the curing reaction is not done under constant conditions.

In this work, we explored the curing process of GAP in combination with isocyanates, measuring in-situ the concentrations of the starting materials and the final product with NIR spectroscopy. NIR spectra show bands which can be attributed to the different reagents or the product. Using Multi Component Resolution (MCR), the concentrations of the components were determined and presented in a concentration profile.

2 Experimental Procedure

2.1 Materials

The materials used in the polyaddition reaction included four different reagents. The main component is the prepolymer of the binder with 86,2 w%. GAP 06S12 Polyol is an energetic, hydroxyl-functional liquid polymer from Eurenco which was cured with two different types of isocyanates. Desmodur N100 (12,21 w%) and Desmodur XP 2317 (1,59 w%), both are aliphatic polyisocyanate and were delivered by Covestro AG. The main difference of the two types of isocyanates is the content of NCO groups. Increasing the reaction rate, the catalyst dibutyltin dilaurate (D22) with 0,013 w% was added.

2.2 Experimental Setup and NIR Parameters

In order to enable in-situ measurements of the curing reaction under real conditions, 50 g of the mixed reagents were filled in a petri dish and stored in oven at 60 °C for 21 hours. The NIR probe was placed 10 mm above the sample and a white reference was installed under the sample. The measurements were performed with the near-infrared spectrometer Matrix F of Bruker. In this work a spectral wavelength range from 4750 cm^{-1} and to 7500 cm^{-1} with a spectral resolution of 8 cm^{-1} was chosen. The spectra were recorded in reflectance by an open system. The measurements were immediately started after the mixing of the components. A total of 253 spectra were collected with a time interval of 5 minutes.

2.3 Multivariate Data Analysis

In Multi Component Resolution (MCR) the spectra are evaluated on the basis of the non-negativity condition of the spectra and concentrations of substances considered. In the present case both conditions are fulfilled therefore the MCR can be employed. Mathematically the MCR disassembles the data matrix of the measured spectra into a score and a factor matrix.

$$X = C'TT^{-1}F^T + E = CS^T + E \qquad (1)$$

Where these conditions are met, the F matrix contains the pure spectra of the substances and the S matrix displays the variation of the specific substances. E contains the unexplained part of the data matrix X. The advantage of this method is that it yields the estimated spectra of the substances of the source material (T-1F, S respectively) and the qualitative course of the concentrations of the related substances (C'T, C respectively). T is a rotating matrix which allows for the incorporation of the conditions valid for the actual measurement. MCR is normally used to describe increasing concentration profiles, fluorescence or reactions. A review of applications of MCR is given in [8], [9].

3 RESULTS AND DISCUSSION

Usually in a last step of a propellant preparation, a curing agent is added to the mixture of the prepolymer, fuel, oxidizer and different additives. GAP as the prepolymer and the two used aliphatic polyisocyanates as the curing agents react with each other to form a polyurethane network that holds the fuel and oxidizer particulates in a composite matrix [10]. The reaction scheme of a polyaddition is shown in Fig. 1.

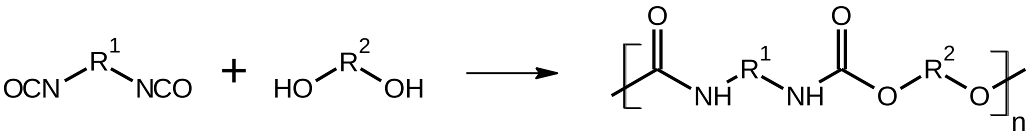
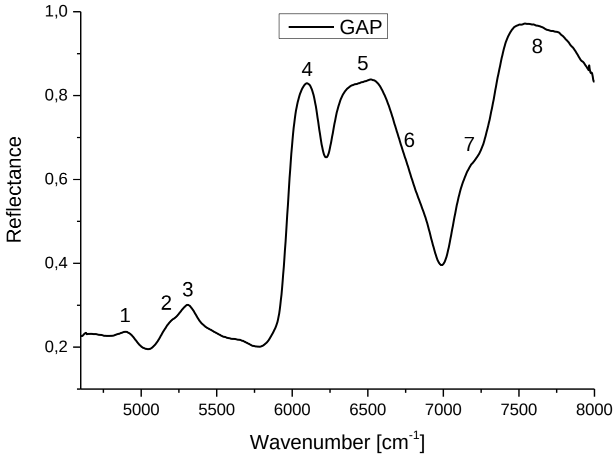


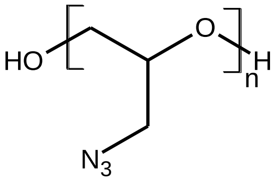
Fig. 1: Reaction scheme of the catalytic polyaddition between GAP and the aliphatic polyisocyanate.

3.1 Characterization of the Pure Components (NIR Spectra)

In a first step, NIR spectra of the initial materials, which are involved in the polyaddition reaction of polyurethane, were taken.

The NIR spectrum of GAP displays in total 8 peaks (Fig. 2). Three of them are O-H specific. The shoulder at 5192 cm^{-1} is assigned to O-H stretching and HOH deformation combination from alcohol groups. The typical O-H stretching band of polyols at 6746 cm^{-1} is hidden under the wide peak between 6357 and 6580 cm^{-1}, which is corresponding to the combined stretching and deformation vibration of polymers with alcohols as functional groups. The overtone of the O-H band is at 6094 cm^{-1}. The wide signal from 7428 cm^{-1} to 7922 cm^{-1} is induced by stretching vibration of C-H. The C-N stretching is responsible for the band at 4899 cm^{-1} [11].

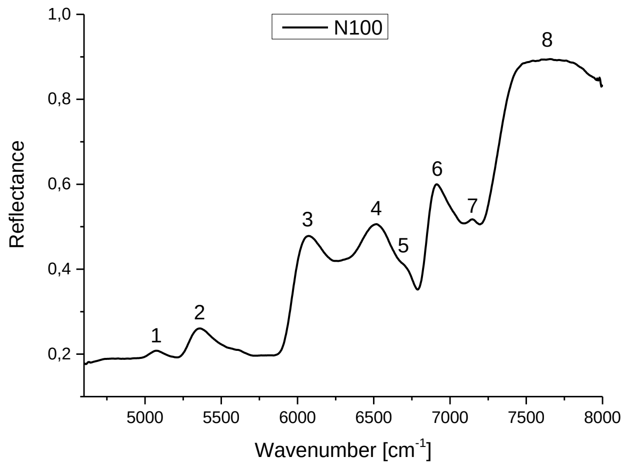


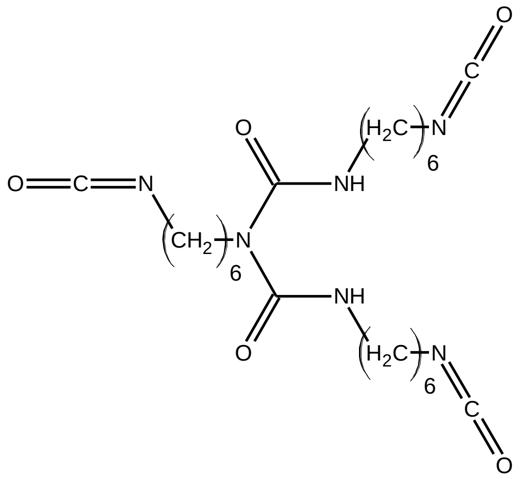


Numbering	Wavenumbers [cm^{-1}]	Assignment
1	4899	C-N stretching
2	5192	O-H stretching
3	5311	C-O
4	6094	C-H overtone
5	6357-6580	O-H combination
6	6757	O-H stretching
7	7212	O-H
8	7428-7922	C-H aliphatic

Fig. 2: NIR spectrum of the pure component and the structural formula of GAP. The peak assignment is shown in the table.

The spectra of the two used aliphatic polyisocyanates are almost equivalent. For that reason the focus is on the Isocyanate Desmodur N100, which is involved in the reaction with 12,21 w%. In Fig. 3, the structural formula of the molecule, the spectra of the curing agent and the corresponding peak assignment are shown.



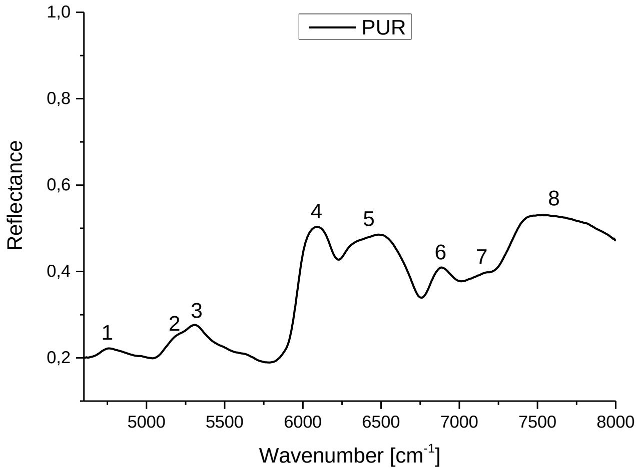


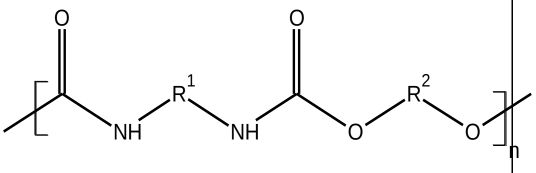
Numbering	Wavenumbers [cm^{-1}]	Assignment
1	5072	N-H asymmetric
2	5357	C=O
3	6075	C-H overtone
4	6511	N-H stretching
5	6684	N-H combination
6	6908	first overtone N-H
7	7147	C-H_2 combination
8	7432-7865	C-H_2 combination

Fig. 3: NIR spectrum of the pure component and the structural formula of Desmodur N100. The peak assignment is shown in the table.

Most of the bands are induced by the N-H groups of the aliphatic polyisocyanate. The sharp peak at 6908 cm^{-1} corresponds to the first overtone of the N-H groups. The reason for the week band at 5072 cm^{-1} is the combination of the N-H in-plane bending and the asymmetric N-H stretching vibration of the amide bonds. The signal at 6511 cm^{-1} and the shoulder at 6684 cm^{-1} correspond to the stretching vibration of secondary amines (R-NH-R) and the combination of symmetric and asymmetric stretching vibration of amines. The peak at 5357 cm^{-1} indicates the presence of a C=O group. The two bands at 7147 cm^{-1} and the wide one between 7432 and 7865 cm^{-1} can be ascribed to the combination of stretching and deformation vibrations of C-H_2 [11].

The spectrum of the formed product of the polyaddition reaction between GAP and Desmodur N 100 and Desmodur XP 2617 is plotted in Fig. 4.





Numbering	Wavenumbers [cm^{-1}]	Assignment
1	4764	C=O,C-O stretching
2	5195	C=O amide (C=ONH)
3	5303	C=O
4	6086	C-H overtone
5	6337-6553	N-H stretching; O-H combination
6	6885	N-H combination (urea)
7	7005	N-H symmetric
8	7413-7829	C-H aliphatic

Fig. 4: NIR spectra and the structural formula of the formed PUR. The peak assignment is shown in the table.

The polyurethane specific signals are at 5195 cm^{-1}, 6885 cm^{-1} and 7005 cm^{-1}. They are corresponding to C=O or to symmetrical stretching vibrations of N-H from the urethane groups. The wide band between 6337 cm^{-1} and 6553 cm^{-1} is induced by a combination of N-H and O-H stretching vibrations. The week signal at 4764 cm^{-1} can be explained by the presence of a combined C=O and C-O stretching vibration [11], [12].

3.2 Analysis of the NIR Spectra during the Reaction

The progress of the catalytic curing reaction between GAP-diol (Fig 2.) and the polyisocyanates Desmodur N100 (Fig 3.) and Desmodur XP 2617 can be followed by the quantitative NIR spectroscopy of the bulk.

In a first overview the spectra of the polyurethane formation are shown in Fig. 5. The reflectance bands at 5211 cm^{-1}, 6757 cm^{-1}, 6893 cm^{-1} and 6997 cm^{-1} are crucial for the polyaddition reaction between GAP and Desmodur N100.

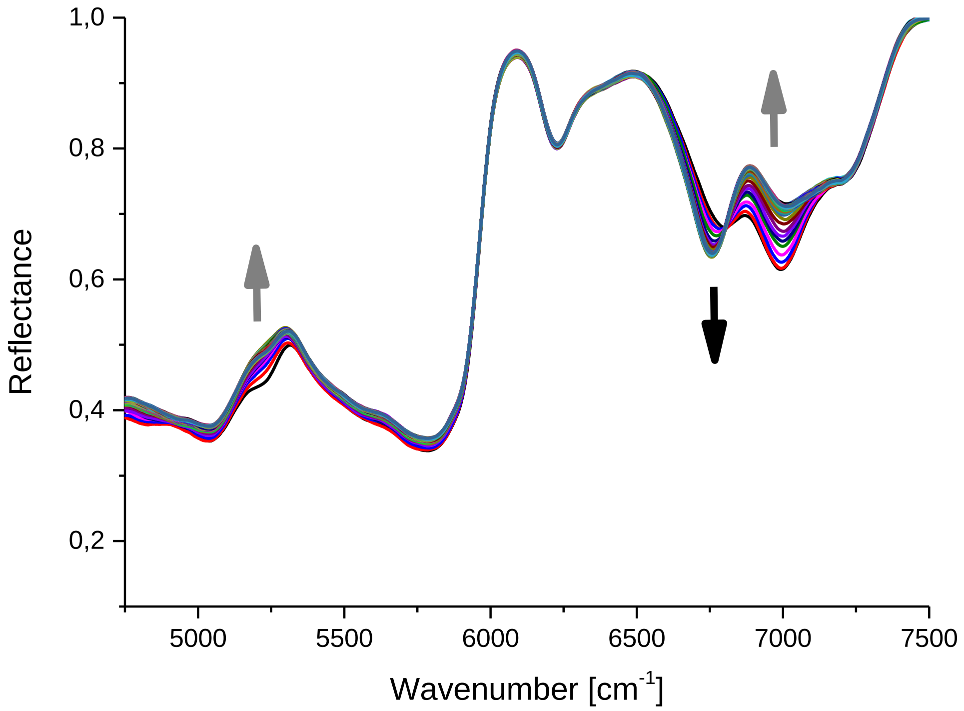


Fig. 5: NIR spectra taken during the formation of polyurethane from GAP and N100 at 60°C.

During the reaction progress, an increase of the signals at 5211 cm^{-1}, 6893 cm^{-1} and 6997 cm^{-1} is monitored. As mentioned in Section 3.1, these changes of the spectra can be explained by the formation of urethane groups. With the formation of the polyurethane, the number of alcohol groups from the reagent GAP-diol is decreasing (6757 cm^{-1}). An isosbestic point (6800 cm^{-1}) at which the total reflectance of the system does not change during the chemical reaction can be reported. In future work, this isosbestic point will be used as a reference point in the study of chemical kinetics (reaction rates) [13].

3.3 Multivariate Analysis of the reaction

The Multi Component Resolution (MCR) was used to study the concentration profile of the main reagents: GAP-diol, Desmodur N100 and the formed Polyurethane. For a better spectral resolution, the second derivative was calculated (Savitzky-Golay) for all in-situ measured spectra [14] Figure 6 shows the same in-situ measured spectra as plotted in Figure 5 using a Savitzky-Golay second derivative.

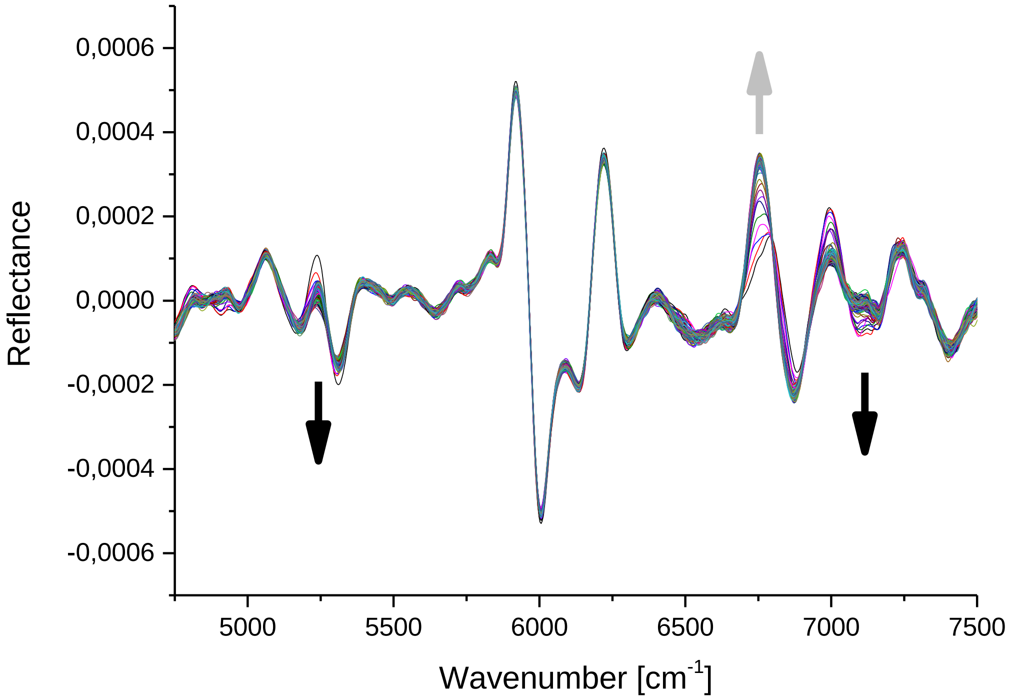


Fig. 6: Overlay of second derivative spectra of the in-situ measurements.

For the calculation of the separate concentration profiles in dependence of time, the three pure component spectra of GAP-diol, Desmodur N100 and Polyurethane were used as the initial guess. The results of the estimated spectra are shown in Fig. 7.

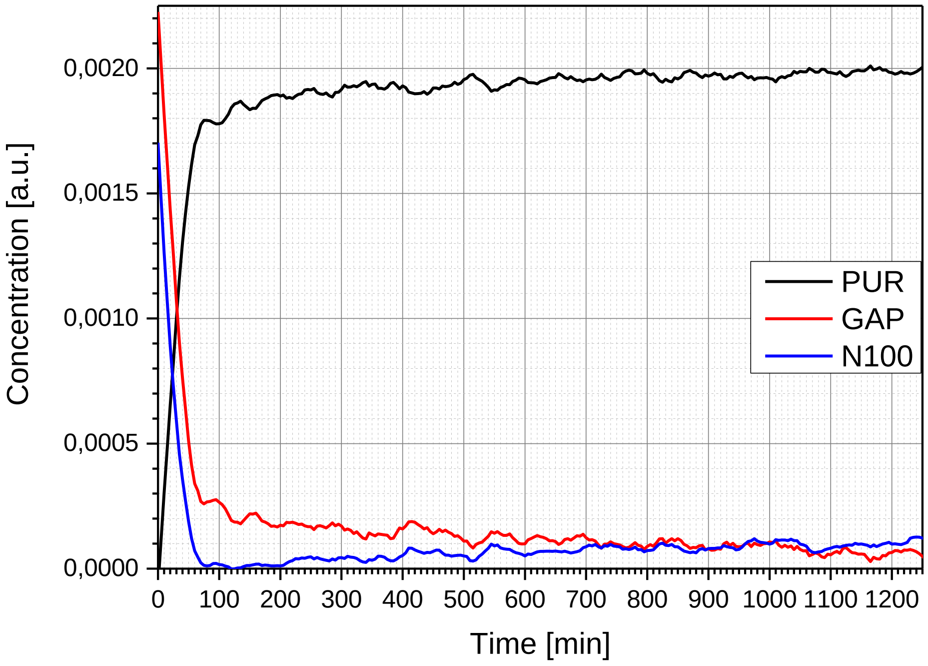


Fig. 7: Estimated concentration profile of the main components during the formation of polyurethane (GAP, Desmodur N100, polyurethane).

At the start of the spectral in-situ measurement, the concentration of PUR is 0. During the first 65 minutes, the concentration is steeply increasing. Between 65 minutes and the end of the measurement, a slight increase of the PUR concentration can be registered. The concentration profiles of both reagents (GAP, Desmodur N100) are similar. Between t=0 and t=70 minutes. The concentration is strongly decreasing. After 70 minutes the concentration of Desmodur N 100 is constant up to t=200 minutes. Then the concentration is slightly increasing until the measurement ends. A possible explanation for this behavior is that the detection limit of the near infrared spectroscopy is reached. In further measurements we will try to elucidate this spectral behavior of the curing agent. The GAP concentration is slightly decreasing after t=70 minutes. Towards the end of the in-situ measurement, the concentrations of the initial substances are similar.

4 **Summary**

The catalytic polyaddition reaction between GAP-diol and the two isocyanates, Desmodur N100 and Desmodur XP2617 was studied in-situ by near infrared spectroscopy at 60 °C. With the use of Multivariate Curve Resolution, a concentration profile of the main components (GAP-diol, Desmodur N100, and Polyurethane) could be calculated. After 75 minutes, the significant part of the reaction is finished, 90% of the final PUR concentration is achieved. Until the end of the measurement after 21 hours, slight concentration changes of the main components can be reported. In a next step, the kinetics of this reaction should be analysed in detail.

REFERENCES

[1] N. Kubota, Propellants and Explosives, *Wiley VCH*, 3. Printing, 2010

[2] T. Hagen, T. Jensen, E. Unneberg, Y. Stenstrom, T. Kristensen, Curing of Glycidyl Azide Polymer (GAP) Diol Using Isocyanate-Free, Synchronous Dual, and Sequential Dual Curing Systems, *Propellants, Explosives, Pyrotechnics*, 2015, 40, 275-284

[3] K. Selim, S. Özkar, L. Yilmaz, Thermal Characterization of Glycidyl azide Polymer (GAP) and GAP-Based Binders for Composite Propellants, *Journal for Applied polymer Science*, 2000, 77, 538-546

[4] A. Larsson, N. Wingborg, Green Propellants Based on Ammonium Dinitramide (ADN), *InTech*, 2011

[5] A. Caraculacu, S. Coseri, Isocyanates in polyaddition processes Structure and reaction mechanism, *Progress in Polymer Science*, 2001, 26, 799-851

[6] F. Burel, A. Feldman, C. Bunel, Hydrogenated hydroxyl-functionalized polyisoprene (H-HTPI) and cyanurate of isophorone diisocyanate (IPDI): reaction kinetics study using FTIR spectroscopy, *Polymer*, 2005, 46, 15-25

[7] K. Hailu, G. Guthausen, W. Becker, A. König, A. Bendfeld, E. Geissler, In-situ characterization of the cure reaction of HTPB and IPDI by simultaneous NMR and IR measurements, *Polymer Testing*, 2010, 29, 513-519

[8] W. Kessler, Multivariate Datenanalyse für die Pharma-,bio- und Prozessanalytik, 1. Auflage, *WILEY-VCH*, 2006

[9] Q. Wang, J. DeJesus, Calibration transfer in near infrared analysis of liquids and solids, *Journal of Near Infrared Spectroscopy*, 6, 1998

[10] T. Heldal Hagen, Energetic Binders for Solid Rocket Propellants, Master Thesis, *Norwegian University of Life Science*, 2014

[11] J. Workman, L. Weyer, Practical Guide to Interpretive Near-Infrared Spectroscopy, *Taylor and Francis Group, LLC*, 2008

[12] D. Burns, E. Ciurczak, Handbook of Near-Infrared Analysis, *Marcel Dekker*, 1992

[13] A. Gow, J. Stamler, Reactions between nitric oxide and haemoglobin under physiological conditions, *Nature*, 391, 1998

[14] P. Williams, K. Norris, Near-Infrared Technology in the Agricultural and Food Industries, 2 Printing, *American Association of Cereal Chemists*, 1990