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MEASUREMENT OF HYDROXYL VALUE OF PALM-BASED POLYOL BY ATTENUATED TOTAL REFLECTANCE/FOURIER TRANSFORM INFRA-RED SPECTROSCOPY

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ABSTRACT

A rapid method for the quantitative determination of the hydroxyl value (OHV) of palm-based polyols by Attenuated Total Reflectant-Fourier Transform Infra-red Spectroscopy (ATR-FTIR) with partial least square regression (PLS) was developed. Calibration standards were based on 25 palm-based polyols, synthesised in the Advanced Oleochemical Technology Division (AOTD), Malaysian Palm Oil Board (MPOB) covering OHV values ranging from 59 to 229 mg KOH g^{-1} *of sample. The OHV values were also determined using AOCS Cd 13-60 standard method. The FTIR-generated calibration plot had a correlation coefficient* (R^2) *of 0.9925 and a standard error of calibration (SEC) of 5.58, while the validation plots had* R^2 *of 0.9884 and standard error of prediction (SEP) of 5.35.*

Keywords: oleochemicals, chemometrics, polymer, palm-based polyols, hydroxyl values, Attenuated Total Reflectant-Fourier Transform Infra-red Spectroscopy, partial least square regression.

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INTRODUCTION

The hydroxyl value (OHV) is a quality control parameter measured routinely by polyol manufacturers. The OHV is used as the criteria by polyol manufacturers to indicate the completeness of polymerisation reactions. In the case of polyurethane preparation, the final OHV of the polyols plays an important role. Currently, MPOB's Advanced Oleochemical Technology Division (AOTD) is producing palm-based polyols and is working towards commercialisation of such polyurethane products. The current method used for OHV analyses of palm-based polyols is via the wet titration method such as the American Oil Chemists Society method for OHV determination (AOCS, 2007a). However, this method suffers from disadvantages in that it is time-consuming, labour intensive, accuracy dependent on the skill of the analyst and can be hazardous to the analyst due to the use of acetic anhydride. Acetic anhydride is also a controlled chemical in Malaysia, registered under the Malaysian Ministry of Health. The use of Fourier Transform Infra-red (FTIR) method for the determination of OHV in soyabean based polyols has been reported by Godoy *et al.* (2007). Near Infra-red (NIR) Spectroscopy has also been shown to be able to quantify OHV in palm-based polyols (Bonnie *et al.*, 2011). In this study, an Attenuated Total Reflectance (ATR)-FTIR method was developed for measurement of OHV in palm-based polyols.

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MATERIALS AND METHODS

Determination of Acid Number and Hydroxyl Value by the AOCS Titration Method

The acid number (AN) and OHV of the calibration standards and validation samples were determined by AOCS standard methods (Cd 3d – 63 and Cd 13-60, respectively)(AOCS, 2007b).

Polyol Treatment

The various palm-based polyol samples were first homogenised in an oven at about 50°C for 20 min for samples with lower viscosity (< 1000 mPa.s at 25°C) and at 65°C for 60 min for more viscous samples (> 1000 mPa.s at 25°C) before FTIR analyses.

Calibration Standards

Palm-based polyols were used as calibration standards and also for the validation of the calibration models. POP pioneer polyol (100% palm olein as feedstock), 100% palm kernel oil (PKO)-based polyol, POP primer polyol (blends of different ratios of POo with PKO as feedstock), POP premier polyols (blends of PKO with a high unsaturated vegetable oil as feedstock) and palm oleic acid-based polyol (PolyMO) were all produced by the Polymer and Composite Group in AOTD. These polyols were produced from different types of feedstock and have different OHV.

Instrumentation

A Nicolet Magna 550 FTIR series II spectrophotometer using the OMNIC software program was used for spectra collection of palm-based polyols. The spectra were collected at 32 scans in the transmission mode with 1 cm^{-1} resolution against a blank as background. The homogenised palm-based polyol sample was applied over the surface of a pike horizontal attenuated total reflectance (HATR) ZnSe crystal sample-handling accessory. All the samples were scanned in four replicates, with the spectra recorded as absorbance and/or transmittance at each data point. The absorbance spectra can be retrieved from the OMNIC program for chemometric analysis.

Calibration and Prediction

Palm-based polyols were used in the calibration model. The TQ analyst software program allowed the selection of particular regions of the spectrum to be used for analysis. The best Partial Least Square (PLS) calibration model with the highest correlation coefficient was suggested by the software where four different spectral regions, *i.e.* 3743-3018 cm^{-1}, 1674 – 1664 cm^{-1}, 1965 – 1538 cm^{-1} and 2747 – 3018 cm^{-1}, were used. The accuracy of the PLS model was based on both the smallest root mean square error of calibration (SEC) and the highest coefficient of determination (R^2). When the calibration program was developed to produce the required accuracy for the range of concentrations, the prediction program can be run to determine the hydroxyl value of unknown samples.

RESULTS AND DISCUSSION

Figure 1 shows the overlaid spectra of the different types of palm-based polyols samples used in the calibration model. All the representative palm-based polyols, although produced using different feedstock, showed similarity in their respective spectrum. This criterion allowed them to be used as the calibration standards. Twenty-five palm-based polyols with OHV ranging from 59 to 229 mg KOH g^{-1} sample were used as calibration standards.

Figure 2 shows the calibration plot for the calibration model. The correlation coefficient of the calibration plot was 0.9925 at 99% confidence interval. The root mean square of calibration (RMSEC) was 5.58 and root mean square error of cross validation (RMSECV) was 7.07. Another set of external validation samples OHV was predicted by the FTIR calibration model. *Figure 3* shows the plot of actual *vs*. FTIR-predicted values for validation. The correlation coefficient for the validation plot was 0.9884. The RMSEP calculated for the external validation samples was at 5.35.

The RMSECV for this model is slightly higher than the RMSEC (RMSEC/RMSECV:0. 79). Cross validation may not accurately evaluate the calibration model in this case. The quality of the models was further evaluated by comparing RMSEC and RMSEP values. If the ratio of RMSEC/RMSEP is close to 1.0, then the model has a good prediction ability (Ferrao and Davanzo, 2005). The ratio of RMSEC/RMSEP was 1.04 for this model, and the correlation coefficient of the validation plot was high, suggesting that this model will have good predictive ability. *Table 1* shows the values of some external validation standards and the percentage differences from the AOCS method. It can be seen that the difference was less than 10%.

CONCLUSION

The OHV of palm-based polyols can be rapidly determined using HATR-FTIR spectroscopy by establishing a PLS calibration model using palm-based polyol samples. This method is rapid because the sample preparation step is short, and the samples can be analysed directly using the HATR.

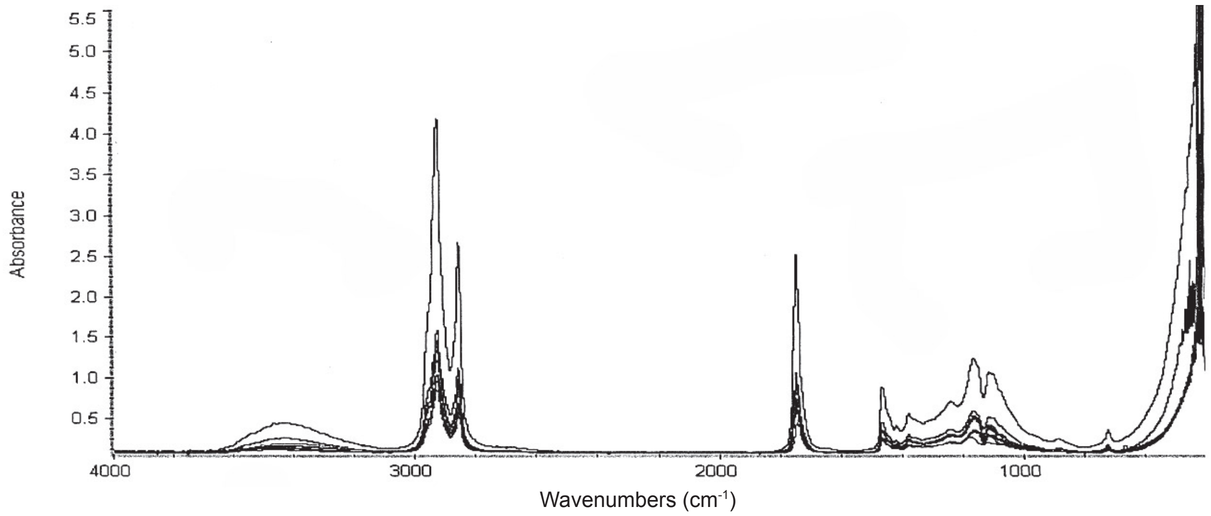

Figure 1. Horizontal Attenuated Total Reflectance/Fourier Transform Infra-red Spectroscopy (HATR/FTIR) overlaid spectra of the representative palm-based polyols samples used in the calibration model.

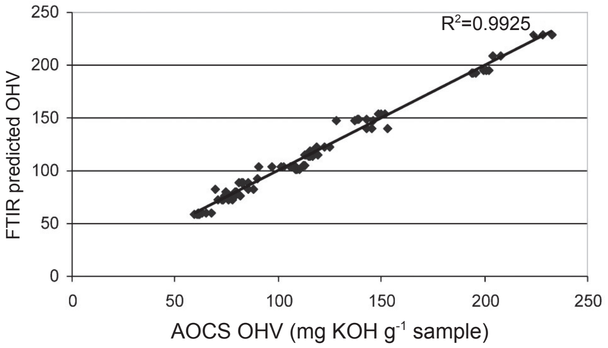

Figure 2. Fourier Transform Infra-red Spectroscopy (FTIR) calibration plot with correlation coefficient of 0.9925.

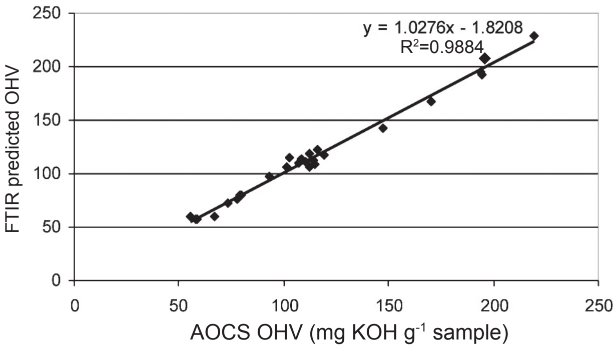

Figure 3. Fourier Transform Infra-red Spectroscopy (FTIR) external validation plot with correlation coefficient of 0.9884.

TABLE 1. PARTIAL LISTING OF VALIDATION SET DATA

Polyol	AOCS OHV (mg KOH g^{-1} of sample)[a]	FTIR predicted values[b] (mg KOH g^{-1} of sample)	% difference to AOCS method
1	194.6	192.9	0.87
2	67.27	60.6	9.92
3	112.49	118.9	5.70
4	73.53	72.2	1.81
5	147.45	142.2	3.56
6	93.31	97.7	4.70
7	115	109.1	5.13
8	55.52	59.55	7.26
9	79.07	79.8	0.92

Note: [a] Mean of four replicates. [b] Mean of four replicates.
FTIR - Fourier Transform Infra-red Spectroscopy.

The time to analyse the samples is cut short to 2 min per sample. This method does not use any chemicals and therefore, greatly reduces the analyst's exposure to hazardous chemicals.

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