ATR-FTIR: A Simple and Rapid Tool For Coating Fingerprinting

WAY Chiang Poh[1], **TAN** Winie[2*] and **CHAN** Chin Han[2]
[1]PerkinElmer (M) Sdn. Bhd., #2.01, Level 2, Wisma Academy, Lot 4A, Jalan 19/1, 46300, Petaling Jaya, Selangor, Malaysia
Email: Kenneth.way@perkinelmer.com
[2]Universiti Teknologi MARA, Faculty of Applied Sciences, 40450 Shah Alam, Selangor, Malaysia
E-mail: tanwinie@salam.uitm.edu.my and tan_winie@yahoo.com (* corresponding author)
cchan@salam.uitm.edu.my and cchan_25@yahoo.com.sg

Abstract

ATR-FTIR is a simple and rapid tool for coating fingerprinting. Reference FTIR spectra for resin and hardener can be easily generated. The degree of similarity, which is termed as *correlation* (*r*), of a spectrum can be easily generated by comparing the spectra of the samples to that of the reference spectrum. *Correlation* (*r*) = 1 denotes perfect match between the sample and reference spectra. The greater deviation of *correlation* (*r*) value from unity suggests a more significant difference between the sample and reference spectra. FTIR results showed homogeneity of resin and hardener at top, middle and bottom of the mixing tank and good batch-to-batch reproducibility. By referring to the FTIR results, different types of resin and hardener could be deduced.

Introduction

In the oil and gas industry, industry players have invested billions in polymeric coatings in order to protect the steel material used for offshore petroleum transportation. However, the companies in Malaysia are facing a quality issue with polymeric coatings. It was observed that the quality of certified material eroded more rapidly although the certificate of analysis which emphasized only in physical tests complies with the customer required parameters. This can be due to potential problems of reformulated polymeric coatings or adulterations being practiced. The polymeric coatings quality problems have led to enormous monetary losses, which have hit the investors severely. In addition, it has caused serious environmental impact [1].

For paint manufacturers in their quality control processes, it encompasses physical assays for their raw materials (resin & hardener) and finished goods. The test parameters cover solid content, viscosity, specific gravity, adhesive test, pH, color and so on and are practiced routinely. Unique test such as salt-fogging test, chemical resistance test were done upon client request. Until to-date, there is no relevant scientific approach such as FTIR spectroscopic technique being applied. It is because local paint suppliers have concerns of its paint formulation secrets being review [3]. In addition to huge investment and maintenance costs, professionals with strong technical competence in analytical instruments are essential to better quality assurance.

Infrared (IR) spectroscopy is a useful scientific tool in characterizing organic functional groups based on the compound molecular vibrational patterns. Radiation in the IR region resulted in both stretching and bending vibrations of the covalent bonds of the organic compounds. In principle, IR technique can be used to characterize specific polymers by either transmission or reflectance measurements. The resulting spectrum shows the molecular absorption and transmission, creating a molecular fingerprint of the compound especially at the wavenumbers of 1500-400cm^{-1}. In short, each sample has its own distinctive IR spectrum.

ASTM D7588-11 requires the use of attenuated total reflectance (ATR) accessory, coupling with FTIR to rapidly analyse the paint samples without any sample preparation. The FTIR analysis requires minimal operation time and operator skill. The possibility of using the ATR accessory approach appears to be very promising [2].

The objectives of this work are 1) to generate reference FTIR spectra for resin and hardener samples, 2) to check the homogeneity of resins and hardeners at the Top (T), Middle (M) and Bottom (B) of the mixing tanks and batch-to-batch reproducibility by estimation of *correlation* (*r*) using COMPARE algorithm featured by Perkin Elmer at fingerprinting regions, 3) to discriminate different types of resin and hardener.

Experimental

FTIR sample collection

The resins and hardeners were supplied by a local paint manufacturer. 2 batches of resin and hardener collected at interval of 1 day were received for FTIR analysis within a week after sample collection. Each batch consists of 4 types of resin and hardener. Sampling of samples was done from the Top (T), Middle (M) and Bottom (B) of the mixing tanks as shown in Figure 1. Sample coding Resin_*x-yz* and Hardener_*x-yz* denote resin or hardener of *x* type for *y* batch at the location *z* (T, M or B).

Figure 1 Sampling of samples was done from the Top (T), Middle (M) and Bottom (B) of the mixing tanks

Attenuated total reflection (ATR)-FTIR spectroscopic studies were carried out using a diamond coated ZnSe crystal on a PerkinElmer Frontier FTIR spectrophotometer (USA). FTIR spectra were recorded in the transmittance mode in the frequency range from 600 to 4000 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1}. The obtained FTIR spectra were then analyzed by COMPARE algorithm featured by Perkin Elmer at fingerprinting regions. The fingerprinting regions selected are 1000 – 1300 cm^{-1} (C-O-C) and 700 – 900 cm^{-1} (C-O-C) for resin and 1000 – 1400 cm^{-1} (C-N) for hardener.

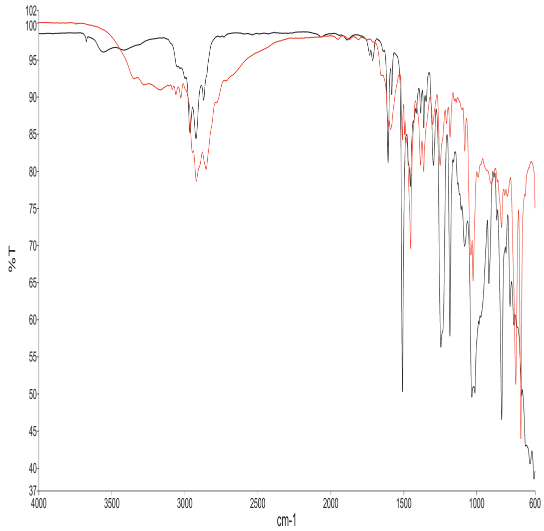

Figure 2 Reference FTIR spectra for resin (Resin_A95-1M) and hardener (Hardener_A96-1M) in the region between 600 and 4000 cm^{-1}

The FTIR spectrum of resin type A95, from batch 1 and obtained from the middle of the mixing tank (sample coding Resin_A95-1M) was selected as the reference spectrum. The reference spectrum for hardener was Hardener_A96-1M (i.e hardener type A96, from batch 1 and middle of the mixing tank) (see Objective 1). Figure 2 presents the reference FTIR spectra for resin and hardener. The degree of similarity, which is termed as *correlation* (*r*), of a spectrum was generated by comparing the spectra of the samples to that of the reference spectrum in the defined fingerprinting regions. *Correlation* (*r*) = 1 denotes perfect match between the sample and reference spectra. The greater deviation of *correlation* (*r*) value from unity suggests a more significant difference between the sample and reference spectra.

Results and discussion

Figure 3 presents the FTIR spectra of Resin_A95-1T, Resin_A95-1M and Resin_A95-1B in the region between 600 and 1800 cm^{-1}. The 1000 – 1300 cm^{-1} (C-O-C) and 700 – 900 cm^{-1} (C-O-C) are the fingerprinting regions for resin. Table 1 presents the *correlation* (*r*) for reference Resin_A95-1M to Resin_A95-1T (or B). *Correlation* (*r*) > 0.90 suggests homogeneity of resins at top, middle and bottom of the mixing tank.

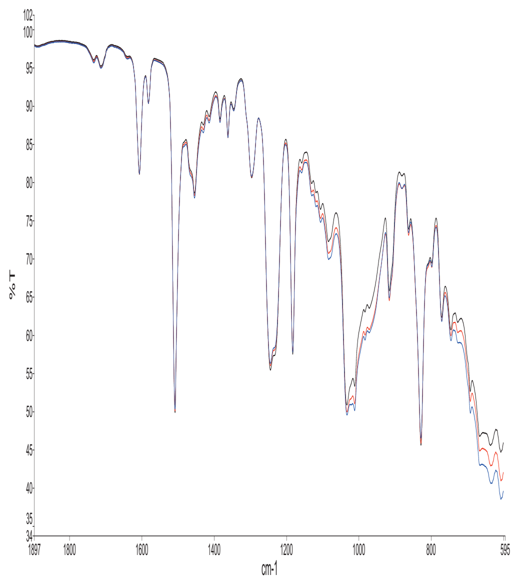

Figure 3 FTIR spectra of Resin_A95-1T, Resin_A95-1M and Resin_A95-1B in the region between 600 and 1800 cm^{-1}.

Figure 4 presents the FTIR spectra of Hardener_A96-1T, Hardener_A96-1M and Hardener_A96-1B in the region between 800 and 1700 cm^{-1}. The fingerprinting region for hardener is 1000 – 1400 cm^{-1} (C-N). Table 2 presents the *correlation* (*r*) for reference Hardener_A96-1M to Hardener_A96-1T (or B). *Correlation* (*r*) > 0.90 suggests homogeneity of hardener at top, middle and bottom of the mixing tank.

Table 3 presents the *correlation* (*r*) for reference Resin_A95-1M to Resin_A95-2M (T or B) while Table 4 presents the *correlation* (*r*) for reference Hardener_A96-1M to Hardener_A96-2M (T or B). Results from Tables 3 and 4 show *correlation* (*r*) > 0.90 suggests batch-to-batch reproducibility.

Table 1 *Correlation* (*r*) for reference Resin_A95-1M to Resin_A95-1T (or B)

Sample Code	*r* 600 – 4000 cm^{-1}	*r* 1000 – 1300 cm^{-1} (C-O-C)	*r* 700 – 900 cm^{-1} (C-O-C)	Reference Spectrum
Resin_A95-1T	0.9992	0.9992	0.9992	Resin_A9 - 1M
Resin_A95-1B	0.9998	0.9998	0.9999	

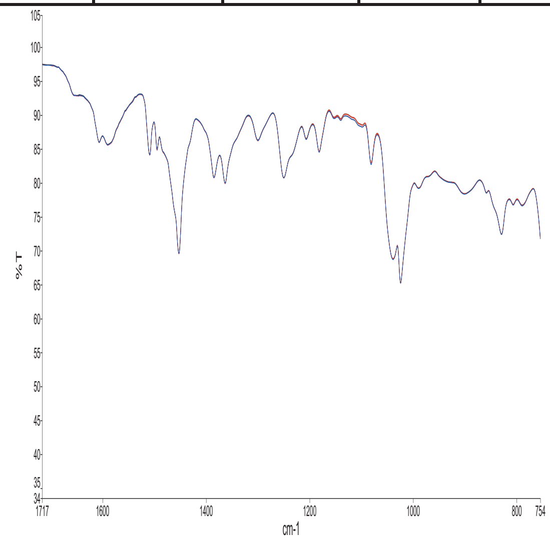

Figure 4 FTIR spectra of Hardener_A96-1T, Hardener_A96-1M and Hardener_A96-1B in

Table 2 *Correlation* (*r*) for reference Hardener_A96-1M to Hardener_A96-1T (or B)

Sample Code	*r* 600 – 4000 cm^{-1}	*r* 1000 – 1400 cm^{-1} (C-N)	Reference Spectrum
Hardener_A96-1T	0.9999	0.9999	Hardener_A96-1M
Hardener_A96-1B	0.9999	0.9999	

Table 3 *Correlation* (*r*) for reference Resin_A95-1M to Resin_A95-2M (T or B)

Sample Code	*r* 600 – 4000 cm^{-1}	*r* 1000 – 1300 cm^{-1} (C-O-C)	*r* 700 – 900 cm^{-1} (C-O-C)	Reference Spectrum
Resin_A95 -2T	0.9974	0.9967	0.9967	Resin_A95 -1M
Resin_A95 -2M	0.9995	0.9995	0.9995	
Resin_A95 -2B	0.9996	0.9996	0.9996	

Table 4 *Correlation* (*r*) for reference Hardener_A96-1M to Hardener_A96-2M (T or B)

Sample Code	*r* 600 – 4000 cm^{-1}	*r* 1000 – 1400 cm^{-1} (C-N)	Reference Spectrum
Hardener_A96-2T	0.9997	0.9997	Hardener_A96-1M
Hardener_A96-2M	0.9996	0.9998	
Hardener_A96-2B	0.9996	0.9997	

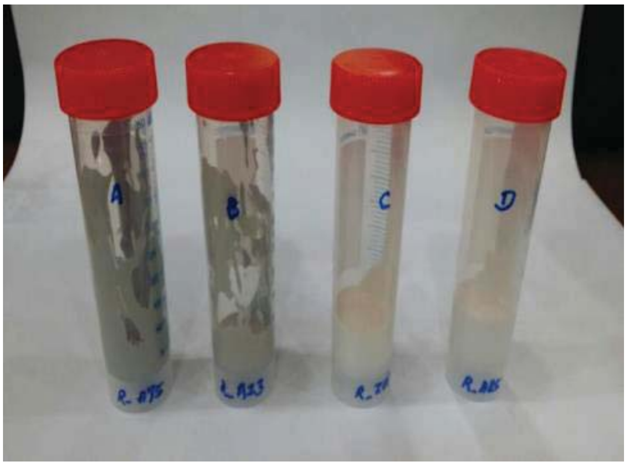

Figure 5 Physical appearances of A) Resin_A95, B) Resin_A23, C) Resin_Z00 and D) Resin_A85

Figures 5 and 6 present the physical appearance of different types of resins and hardeners, respectively. Resins and hardeners may smell and appear physical alike. ATR-FTIR can be used to differentiate different types of resins and hardeners. Table 5 presents the *correlation* (*r*) for reference Resin_A95-1M to Resin_A23-1M, Resin_Z00-1M and Resin_A85-1M. Based on the extremely low value of *correlation* (*r*), Resin_Z00 reviewed its significant variation of chemical composition compared to the other 3 types of resin. An online IR library search showed that sample labeled, as Resin_Z00 was polyurethane resin. On the other hand, library search results showed that Resin_A95, Resin_A23 and Resin_A85 were epoxy-type resin. Different types of hardener could also be detected using ATR-FTIR tool (see Table 6).

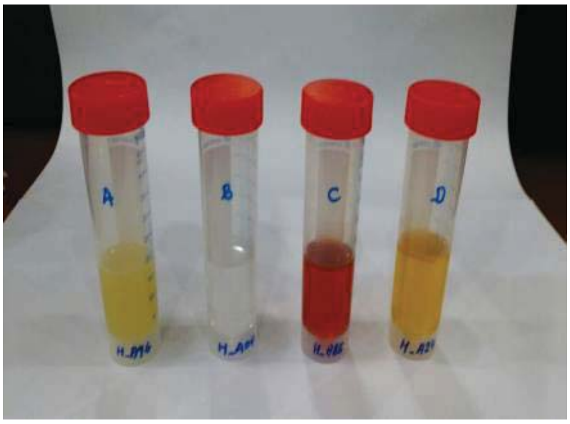

Figure 6 Physical appearances of A) Hardener_A96, B) Hardener_A04, C) Hardener_A85 and D) Hardener_A24

Table 5 *Correlation* (*r*) for reference Resin_A95 to Resin_A23, Resin_Z00 and Resin_A85

Sample Code	*r* 600 – 4000 cm^{-1}	*r* 1000 – 1300 cm^{-1} (C-O-C)	*r* 700 – 900 cm^{-1} (C-O-C)	Reference Spectrum
Resin_A23-1M	0.9770	0.9850	0.8927	Resin_A95-1M
Resin_Z00-1M	0.1573	0.1817	0.0630	
Resin_A85-1M	0.8599	0.9557	0.9090	

Table 6 *Correlation* (*r*) for reference Hardener_A96 to Hardener_A04, Hardener_A85 and Hardener_A24

Sample Code	*r* 600 – 4000 cm^{-1}	*r* 1000 – 1400 cm^{-1} (C-N)	Reference Spectrum
Hardener_A04-1M	0.1237	0.0349	Hardener_A96-1M
Hardener_A85-1M	0.5006	0.3875	
Hardener_A24-1M	0.5145	0.1669	

Conclusion

Reference FTIR spectra for resin and hardener can be easily generated. FTIR results showed homogeneity of resin and hardener at top, middle and bottom of the mixing tank and good batch-to-batch reproducibility. Different types of resin and hardener could be detected by FTIR.

Acknowledgement

IMM Coating Fingerprinting Task Force committees would like to thank the paint manufacturer for supplying the samples. Acknowledgement to application chemists, Mr Lim Bon Tong & Ms Ling Jia Yi from Perkin Elmer (M) Sdn Bhd for the technical support provided. Besides, the authors gratefully acknowledge the research funding by Knowledge Transfer Programme Grants [100-CAN(ICAN/AIC.37/2/14) provided by Ministry of Education for parts of the experimental works.

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Biodata

Kenneth WAY obtained his Bachelor and Master degree of Science from Universiti Putra Malaysia (UPM) in both Biochemistry and Molecular Biology & Genetic Engineering respectively. He worked in Sigma-Aldrich as the sales & application specialist in Research

Biotechnology segment, taking care of molecular biology, cell biology, signaling molecules and diagnostic divisions for 3 years before continued his post-graduate research, which was research project collaboration between Sigma-Aldrich and a prestigious research institute in gene silencing therapy used in cancer treatment. He has published a few technical papers in established journals. Meanwhile, he is also the member for the professional body of Malaysia Society for Biochemistry and Molecular Biology (MSBMB) and MENSA since 2004 & 1994 respectively. Currently, he is the product manager for spectroscopy such as UV-VIS-NIR, Fluorescence, FTIR, Thermal analyzers (TGA, DSC, TMA, DMA) and Hyphenation Techniques (TG-IR, TG-MS, TG-GCMS, TG-IR -GCMS, DSC-UV, DSC-NIR)

TAN Winie is a senior lecturer at School of Physics and Material Science, Universiti Teknologi MARA, Malaysia. Solid State Ionics are her main research areas. She is an Associate Fellow of the Malaysian Scientific Association (2012–present), Council Member of Institute of Materials, Malaysia (2014-2016) and member of Malaysian Solid State Science and Technology Society (2009-present). She is appointed as one of the editors in International Journal of Institute of Materials, Malaysia (IJIMM), Science Letters, Materials Research Innovation (2009) and American Institute of Physics (2009). Her contribution is also in the form of written chapter in books and over 40 International journal publications. Her research outcomes won her several medals and awards in international and national events.

CHAN Chin Han is an associate professor at Universiti Teknologi MARA, Malaysia. Her research interest is devoted to physical properties of macromolecules. She was appointed as Visiting Scientist at China University of Petroleum, Beijing, China (2011-2012), as Chair Professor on Advances in Hybrid Materials at Mahatma Gandhi University, Kottayam, India (2014), National Representative (Malaysia) of International Union of Pure and Applkied Chemistry (IUPAC) for Polymer Division (2014-2015) etc. She has been one of the editors of Malysian Journal of Chemistry, Berita IKM – Chemistry in Malaysia, Deputy Editor of Materials Mind of Institute of Materials, Malaysia and books published by Royal Society of Chemistry (2013) and Apple Academic Press (2014) (distributed by CRC

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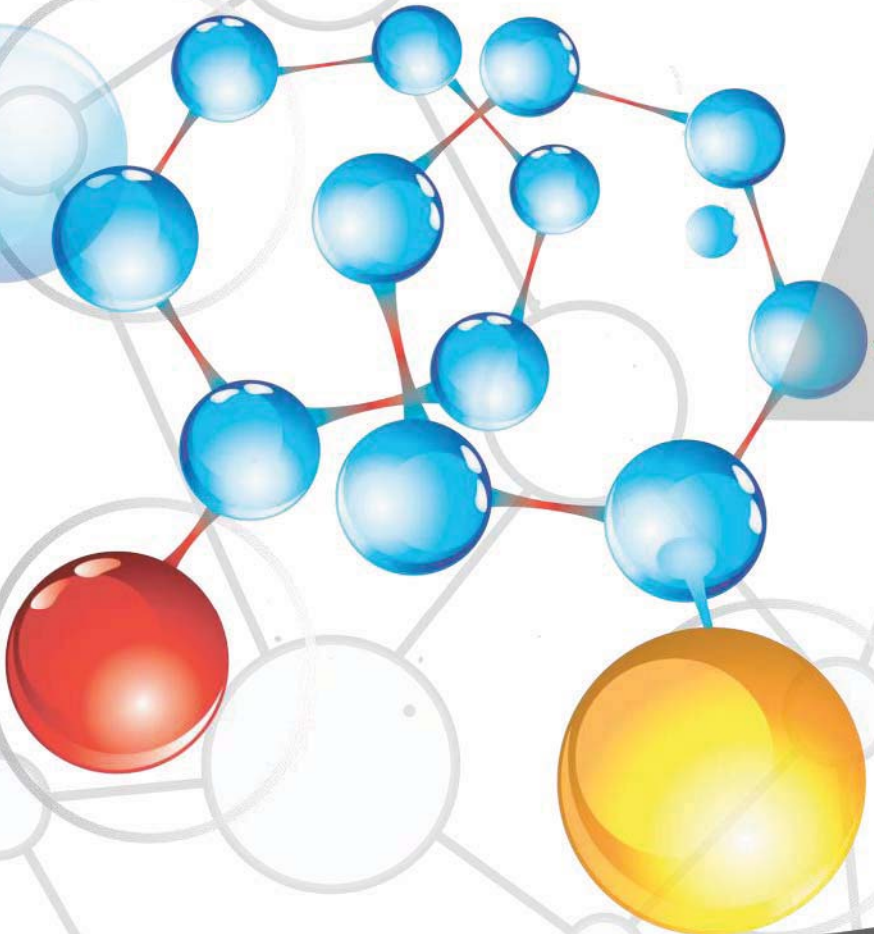

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INSTITUTE OF MATERIALS, MALAYSIA
No 10-1, Jalan Bandar 3,
Pusat Bandar Puchong, 47160 Puchong,
Selangor Darul Ehsan,
MALAYSIA
Tel: +603-5882 3574
Fax: +603-5882 3524
Website : www.iomm.org.my
Email : admin@iomm.org.my