Fourier-transform infrared analysis of polymeric coatings as benchmark for paint industry

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Abstract

Major oil and gas companies in Malaysia are calling for fingerprint certification for the supply of polymeric coatings from local paint manufacturers as quality assurance requirement of the coatings supplied. This will reduce the possibility of failures of the polymeric coatings, which lead to the corrosion of steel structures. Local paint manufacturers are refraining from certification of polymeric coatings due to trade secret of their paint formulations and lack of knowledge on modern analytical methods. Since materials testing technology, particularly on polymeric materials, have improved significantly over the past decade, it is now possible to fingerprint polymeric coatings by simple FTIR analyses. Single-component systems (the color organic pigment) and multi-component systems (the epoxy paints) were studied. The four yellow color organic pigments as well as the two epoxy paints [consist of two parts for each epoxy paints, i.e. epoxy resin (or base) and hardener (or curing agent)] have similar physical appearance by merely visual inspection. By referring to the fingerprint region of the FTIR spectra, different chemical structures of the four yellow color organic pigments and different paint formulations of the two epoxy paints can be concluded.

Introduction

Each year, oil and gas companies spend billions of dollars on polymeric coatings for steel structures. The existing problem of oil and gas companies faced in Malaysia for on-site jobs of polymeric coatings on steel structures is that the quality of polymeric coatings varies from job to job for the same product brand from the same supplier or paint manufacturer. This can be due to the inherent problem of the reformulation of polymeric coatings or in other words adulterated polymeric coatings are supplied, where the quality of the coatings deviates from the submitted specifications for prequalification and tender purpose. The frequent failures of the polymeric coatings due to poor quality of adulterated polymeric coatings supplied has led to severe inventory loss to the companies and serious threat to the environment and also caused many safety issues to plant personnel and surrounding public [1-2].

As mentioned in ref. [3], the application of analytical techniques for fingerprinting of polymeric coatings [4] from local paint manufacturers is slow to be accepted as standard practice due to the concerns of formula trade secret, high investment costs of the instruments, finding or training suitable personnel to use the instruments since a certain amount of knowledge and expertise are required in order to be able to correctly analyze and interpret the data generated by these instruments [5-6].

The process of paint manufacturing is covered from the raw materials to the finished product including the in-house production quality control tests. Paints or polymeric coatings are essentially made up of the polymer resin, additives (including pigments, extenders, fillers, property-modifying agents etc.) and solvents. The production quality-control tests include viscosity, solids, specific gravity, opacity, finess-of-grind, pigment-volume-concentration, adhesion test, pencil hardness test, color etc. are performed in the in-house laboratory during the paint manufacturing process [7]. Special tests such as the salt-fog test, cathodic disbondment test, chemical resistance tests etc. are carried out upon the request by the customers, and generally are a one-off test carried out by a third-party laboratory. No spectroscopic testing has been carried out on polymeric coatings to-date.

Infrared (IR) spectroscopy has long been a valuable tool for identifying organic functional groups by virtue of their characteristic vibrational frequencies. Radiation in the IR region will cause stretching and bending vibrations of the bonds in most covalent molecules of organic compounds. IR is one of the oldest of the spectroscopic methods used in polymer science for identification of chemical structures. In principle, when IR radiation passes through a sample; some of the IR radiation is absorbed, and the rest is transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. In short, no two unique molecular structures will produce the same IR spectrum.

As mentioned in ref. [3], two related ASTM standards on Fourier-transform infrared (FT-IR) are currently available for quality control of polymeric coatings [8-9]. The first and older standard, ASTM D2621-87 (2011), involves the separation of the different components of paint (solvents, binders, pigments) *via* high-speed centrifuging. The separated components are then analysed individually. The analysis requires the careful and consistent application of a uniform thin film of the separated components onto a NaCl window [3].

The second and relatively recent standard, ASTM D7588-11, does not require the separation of the paint components. However, it requires the availability of attenuated total reflectance (ATR) accessory to be attached to FTIR. The complete paint formulation is analyzed, including the solvent or with complete solvent evaporation. Hence, revelation of product formulation of the paint product by FTIR analysis is technically challenging. Sample preparation is simple and convenient. The FTIR analysis requires minimal operation time and operator skill. This method appears to be similar to one reported much earlier [10]. However, there is lack of guide in ASTM D7588-11 and ASTM D2621-87 for the interpretation of FTIR spectra, i.e. the practical approaches on estimation of the degree of similarity between two FTIR spectra for the same or different polymeric coatings.

The objective of this study is to reveal the simplicity of sample analysis by FTIR and interpretation of results with the assistance of FTIR software for raw material of the polymeric coatings (or paints) (i.e. the color organic pigment in this case) as well as the epoxy paints. Although numerous FTIR tests were carried out on various epoxy coating samples and color pigment samples, this paper highlights the results of the FTIR tests on selected samples.

Experimental

FTIR sample collection

The color organic pigments were supplied by local Paint Manufacturer 1 and the epoxy paints were kindly provided by local Paint Manufacturer 2. These samples were analyzed as received.

FTIR analysis

FTIR analysis was carried out on the as received samples by using the Attenuated Total Reflection method (ATR) on Nicolet iS5 (Madison, USA). FTIR spectra were recorded in the transmittance mode over the range of 600 - 4000 cm^{-1} by averaging 32 scans at a maximum resolution of 4 cm^{-1}. The material of ATR crystal was Diamond coated with ZnSe germanium. The spectra of FTIR were analyzed by OMNIC Software Suite (Madison, USA).

Quality control of the samples

Absorbance spectra were baseline corrected. FTIR spectrum of one of the samples within one set of experiment was adopted as the reference spectrum. The degree of similarity, which is termed as *correlation* (r), of a spectrum was generated by comparing the spectra of the sample to that of the reference using the QC Compare function of the FTIR software. Quantities r (from 0 to 1) were estimated firstly for spectrum with wavenumbers from **i)** 650 - 4000 cm^{-1}, and subsequently from **ii)** 650 – 1700 cm^{-1}. Degree of similarity is directly proportional to quantities of r, i.e. $r = 1$ represents complete matching of the sample spectrum to that of the reference spectrum.

Results and discussion

Color organic pigment of polymeric coatings

Color pigments are one of the common raw materials for coatings industry. Organic pigments, which can be fingerprinted by FTIR, are commonly used. Four yellow color organic pigments were supplied, which were labeled as Yellow Pigments 1 to 4. All the four yellow pigments display high similarity (see Figure 1) in term of color and it is hard to be differentiated by merely visual inspection.

FTIR spectrometer measures the frequencies at which the sample absorbs the IR radiation and the intensities of the absorptions. Determination of these frequencies allows the identification of the possible chemical structures of a sample. This is due to the chemical functional groups are known to absorb IR radiation at specific frequencies. Figure 2a depicts the four FTIR spectra for all the four yellow pigments (whole FTIR region). The characteristic vibrational modes exhibit by Yellow Pigments 1 to 4 are obviously found to be different, especially for the wavenumber in the range of 650 to 1700 cm^{-1} (the fingerprint region, refer to Figure 2b). The differences can be unequivocally described by absorption band shapes, band intensities and in other band properties. In short, all the 4 yellow pigments possess different chemical structures but all display similar yellow color.

Yellow Pigment 1 was randomly selected as the reference FTIR spectrum in this study. The degree of similarity (r) (in term of chemical structure), of Yellow Pigment 2 to 4 were generated by comparing the spectra of the sample to that of the reference spectrum using the QC Compare function of the FTIR software. Quantities r were estimated firstly for spectrum with wavenumbers from **i)** 650 - 4000 cm^{-1} (the whole spectrum), and subsequently from **ii)** 650 – 1700 cm^{-1} (the fingerprint region); and are tabulated in Table 1. For the whole FTIR region and fingerprinting region, quantities $r \leq 0.22$ are noted for Yellow Pigments 2 to 4 as compared to Yellow Pigment 1 (the reference). In other words, the chemical structures of Yellow Pigments 2 to 4 are essentially different from Yellow Pigment 1, which can be revealed easily by simple FTIR analyses and estimation of quantities r using the QC Compare function. In principle, QC Compare function is available for all FTIR spectrometers from different manufacturers.

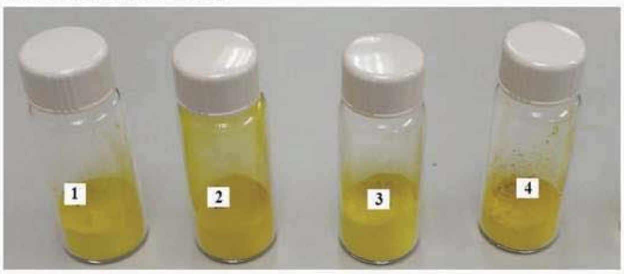

Figure 1 Yellow Pigments 1, 2, 3 and 4 which display high similarity in term of color

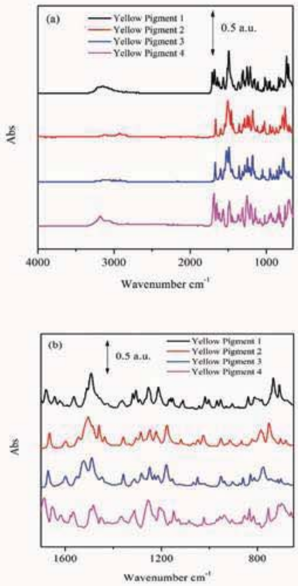

Figure 2 FTIR spectra of Yellow Pigments 1, 2, 3 and 4 for **a)** whole region and **b)** fingerprint region

Table 1 Degree of similarity (r) for Yellow Pigments 1, 2, 3 and 4

Sample	r **650 - 4000 cm^{-1}**	r **650 - 1700 cm^{-1}**
Yellow Pigment 1	reference	reference
Yellow Pigment 2	0.035	0.035
Yellow Pigment 3	0.083	0.083
Yellow Pigment 4	0.22	0.22

Polymeric coatings

After the FTIR fingerprinting on the single-component systems (the color organic pigment), now multi-component systems (the epoxy paints) are discussed in this subsequent section. In general, paints consist of a few basic components (e.g. solvent, resin, filler, pigments, additives), that are mixed homogenously. Epoxy paints, which are always supplied to the job sites in the form of two parts, i.e. epoxy resin (or base) and hardener (or curing agent) were analyzed. Two epoxy resins were labeled as Epoxy 1 and Epoxy 2 and analogue labels for hardeners. Epoxy 1 and Epoxy 2 (as well as Hardener 1 and Hardener 2), which are claimed to provide similar performance as required but with the price differences of roughly 30-60%.

Similarly to the four yellow organic pigments as discussed previously, where by visual inspection, these two epoxies and two hardeners have similar physical appearance. Without the intrusion of the paint formulation, the FTIR spectra of the two hardeners reveal the dissimilarity of the paint formulation for these two hardener samples, but further interpretation of FTIR results is needed for the two epoxies (see Figures 3a, 3b, 4a and 4b).

In this study, Epoxy 1 was randomly selected as the reference FTIR spectrum. Quantities $r \leq 0.83$, as shown in Table 2, for Epoxy 2 are observed for the whole FTIR and fingerprint regions. The quantities r in this study may be correlated to the paint formulation. It is relatively common to set $r \geq 0.95$ as the acceptable tolerance in order to suggest the similarity of different samples. By taking in all the considerations of the random errors derived from the operator performing the analysis, consistency of sample preparation, allowing the paint manufacturers to adjust paint rheology by using solvents etc; quantity $r \geq 0.85$ is proposed as the acceptable tolerance in this case. Epoxy 1 and Epoxy 2 with $r < 0.85$ are suggested to have essential difference in the paint formulation.

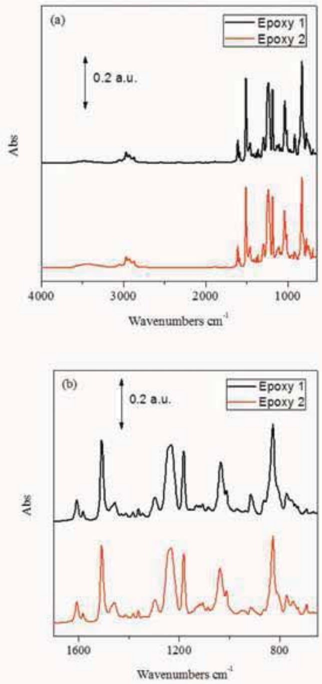

Figure 3 Spectra of two different epoxy resins for **a)** whole region **b)** fingerprint region

Table 2 Degree of similarity (*r*) for Epoxy 1 and Epoxy 2

Sample	*r* 650 - 4000 cm^{-1}	*r* 650 - 1700 cm^{-1}
Epoxy 1	reference	reference
Epoxy 2	0.83	0.83

Hardener 1 was randomly selected as the reference FTIR spectrum. In Table 3, quantities $r \leq 0.03$ are reported for Hardener 2 for the whole FTIR and fingerprint regions. Without any dispute, Hardener 1 and Hardener 2 have essential difference in the paint formulation.

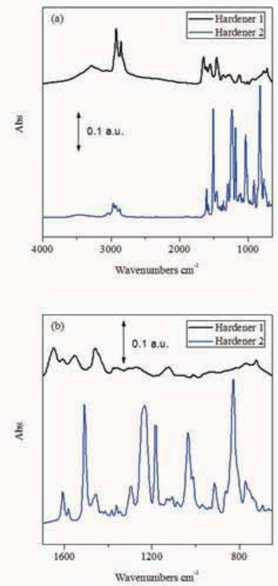

Figure 4 Spectra of two different hardeners for **a)** whole region **b)** fingerprint region

Table 3 Degree of similarity (*r*) for Harderner 1 and Harderner 2

Sample	*r* 650 - 4000 cm^{-1}	*r* 650 - 1700 cm^{-1}
Hardener 1	reference	reference
Hardener 2	0.0004	0.003

Conclusion

Each year, oil & gas companies worldwide spend billions of dollars on polymeric coatings for corrosion protection of steel structures and pipelines for the transportation of crude oil and gas. The frequent failures of the polymeric coatings lead to the corrosion of steel structures and pipelines and thus, leakage of crude oil and gas to the environment. Since mid 90s, oil & gas companies in Malaysia have called for a quality assurance certificate of the supply of polymeric coatings from local paint manufacturers. However, the acceptance of FTIR as one of the tools to fingerprint and to characterize the polymeric coatings is not well received from local paint manufacturers. In this study, FTIR spectrometer was used to analyze single-component systems (the color organic pigment) and multi-component systems (the epoxy paints). The four yellow color organic pigments having similar yellow color as well as the two epoxies and two hardeners having similar physical appearance were fingerprinted by FTIR. Different chemical structures of the four yellow color organic pigments; and different paint formulations of the two epoxies and two hardeners are unveiled. In conclusion, fingerprinting of polymeric coatings using FTIR spectrometer is possible and reliable.

References

1. Mitchell, M., *Selecting protective coatings based on cost/ performance analysis.* Corrosion Management, 1999. **27**: p. 14-20.
2. Byrd, J., *Coatings and cathodic protection for pipeline: An introduction.* Journal of Protective Coatings and Linings, 2002. **19**(3): p. 50-56.
3. Chew, K.C. and C.H. Lim, *FT-IR fingerprinting of organic coatings: Possibilities and practicalities in industry*, in *Materials Mind.* 2013, Institute of Materials, Malaysia: Selangor, Malaysia. p. 19-21, 26.
4. Fletcher, J.F., *Developments in equipment for the quality control of coatings.* Corrosion Management, 2001. **42**: p. 25-28.
5. O'Shea, J.C., *Development in SRET for coating performance evaluation.* Corrosion Management, 2002. **48**: p. 13-17.
6. Hare, C.H., *Infrared spectroscopy for coatings analysis.* Journal of Protective Coatings and Linings, 2002. **19**(1): p. 81-95.
7. Mills, D.J., *Laboratory testing of anti-corrosive paints.* Corrosion Management, 2000. **36**: p. 10-15.
8. ASTM D2621 - 87, *Standard test method for infrared identification of vehicle solids from solvent-reducible paints.* 2011, ASTM International: United States. p. 1-26.
9. ASTM D7588 - 11, *Standard guide for FT-IR fingerprinting of a non-aqueous liquid paint as supplied in the manufacturer's container.* 2011, ASTM International: United States.
10. Hartshorn, J.H. *Compositional assurance testing – A system approach to chemical quality.* in *SPIE 1145, Proceedings of the 7th International Conference on Fourier Transform Spectroscopy.* 1989. Bellingham, WA: The International Society for Optical Engineering.

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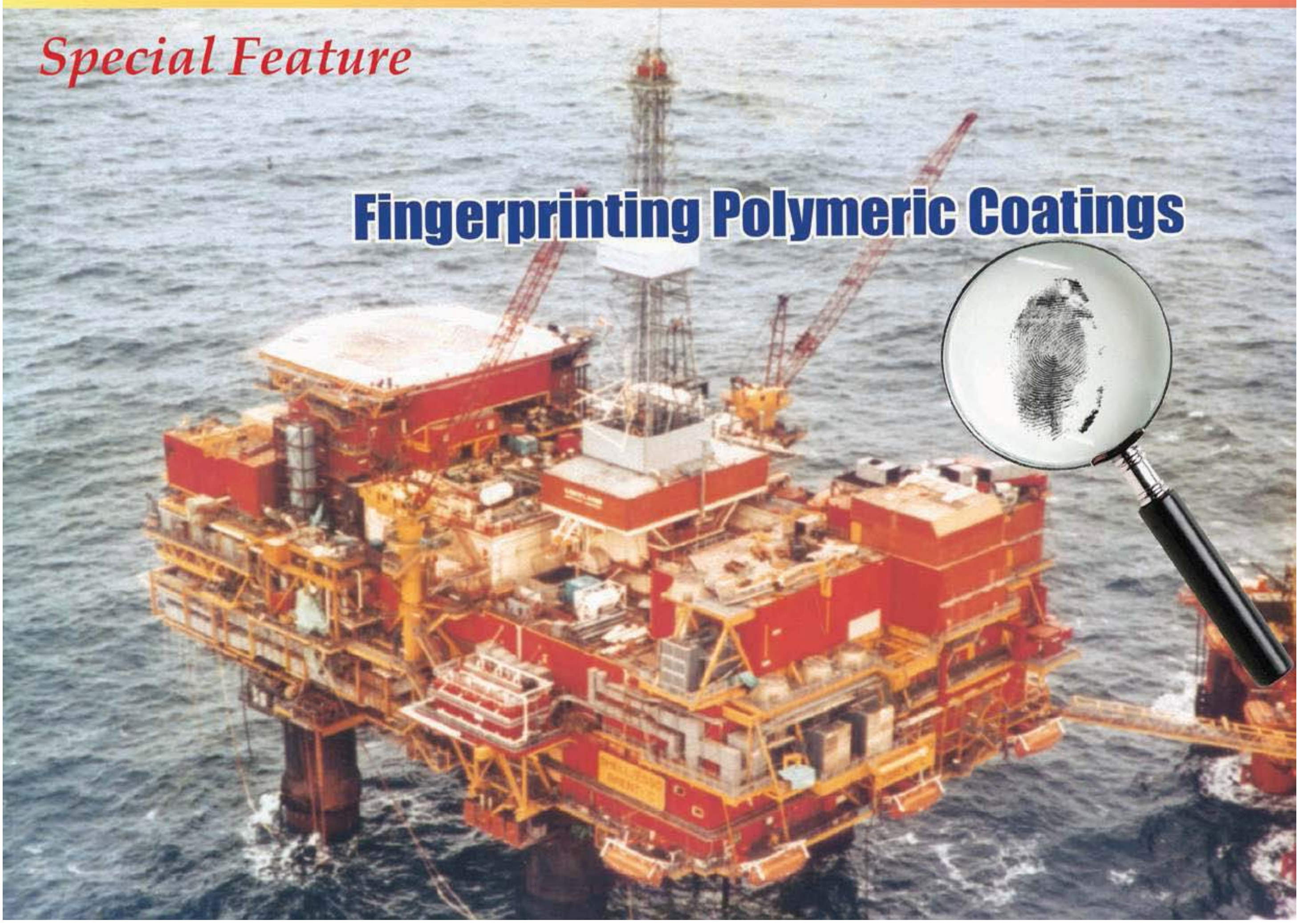

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