Application News

No. AD-0109

IRTracer-100, DTG-60

Determination of Polymer Type and Content in Concrete Materials by FTIR and TGA

❑ Introduction

Modifying cement formulations with polymers provides many important properties that make a variety of niche applications possible. Addition of polymers such as ethylene vinyl acetate copolymer (EVA) or styrene butadiene rubber (SBR) to cement helps to improve the workability, adhesion, curing performance, strength and durability of the cement mortar and concrete. Properties of the polymer modified mortar and concrete are influenced by polymer-cement ratio. Thus, the polymer-cement ratio should be determined to meet the desirable requirements[1].

Fourier Transform Infrared (FTIR) spectroscopy is a useful technique in the identification of the polymer due to its characteristic absorption in the infrared (IR) region. FTIR spectroscopy in combination with chemometrics data analysis method, such as principle component regression (PCR), multi-linear regression (MLR) or partial least squares (PLS) regression, has often been used for quantitative analysis of multicomponent. This combination enables a rapid and simultaneous determination of each component concentration in a mixture without time consuming sample preparation and measurement.

Thermogravimetry (TGA) is an empirical method where the mass of a substance, heated at a controlled rate in an appropriate environment, is recorded as a function of time or temperature. Mass change over specific temperature ranges and in a specific atmosphere provides a compositional analysis of that substances[2]. As mass change can be due to chemical reactions such as vaporization, decomposition and oxidation, TGA can be used for quality control and material screening as a comparison can be made with a known material of the same type.

This paper examines the determination of polymer type and polymer content in construction materials using FTIR and TGA. The use of FTIR with chemometrics as an alternative or supporting method in polymer content determination is also explored.

❑ Experimental

The EVA-Cement-Aggregate mixed composition samples were prepared by Admaterials Technologies Pte Ltd, Singapore.

For FTIR analysis, all samples were measured using Shimadzu FTIR, IRTracer-100. Tetrahydrofuran (THF) was used to extract the polymer in the mixed sample for polymer identification. The raw material polymer and the extracted polymer were measured with Specac Quest Attenuated Total Reflectance (ATR) accessory, with diamond crystal plate. The powder sample was placed and held in contact with the ATR prism for measurement. The extracted polymer in THF solvent was placed dropwise onto the ATR prism, and the residue was measured after the solvent had vaporized. The IR spectra were acquired in the spectra range of $4000cm^{-1}$ to $420cm^{-1}$. The measurement conditions are shown in Table 1.

Table 1: Instrument and Analytical Conditions

Instruments	: IRTracer-100, Quest ATR Diamond
Resolution	: $4cm^{-1}$
Accumulation	: 45
Apodization	: Happ-Genzel
Detector	: DLATGS

For FTIR PLS analysis, Shimadzu Diffuse Reflectance (DRS) accessory was used. A rough mirror (provided together with the accessory) was used for background measurement. The sample was packed into a sample cup and placed onto the sample holder of the DRS accessory for measurement. The IR spectra were acquired in the spectra range of $4000cm^{-1}$ to $400cm^{-1}$. The measurement conditions are shown in Table 2.

Table 2: Instrument and Analytical Conditions

Instruments	: IRTracer-100, DRS
Resolution	: $4cm^{-1}$
Accumulation	: 45
Apodization	: Happ-Genzel
Detector	: DLATGS

For TGA analysis, about 20 to 30mg of sample was placed in an alumina pan and heated inside a Shimadzu simultaneous DTA-TGA model DTG-60, with an empty alumina pan as reference. The samples were heated from room temperature to 600°C with a heating rate of 20°C/minute. Nitrogen gas at a flow rate of 50ml/minute was used as purge gas (Table 3). Each sample was analyzed at least 2 times.

Table 3: Instrument and Analytical Conditions

Instruments	: DTG-60
Heating Rate	: 20°C/minute
Final Temperature	: 600°C
Atmosphere	: Nitrogen
Sample Pan	: Alumina

❑ Results and Discussion

When EVA is heated up in a TGA, loss of acetic acid occurs between 200°C and 400°C and thermal destruction of the residual polymers occurs between 400°C and 600°C[3]. Hence, the weight loss from 200 to 600°C is considered as polymer content. When the raw material EVA 100% was analyzed, the weight loss from 200 to 600°C was 80.7% which indicated the polymer content. This value was then used to calculate the polymer content in Table 4.

Table 4: Sample mixed composition design

No.	Raw Material EVA Content [%]	Calculated Polymer Content from TGA [%]	Cement Content [%]	Aggregate Content [%]
1	0.00	0.00	25.00	75.00
2	1.00	0.81	24.75	74.25
3	3.00	2.42	24.25	72.75
4	5.00	4.04	23.75	71.25
5	7.00	5.65	23.25	69.75
6	10.00	8.07	22.50	67.50
7	15.00	12.10	21.25	63.75
8	20.00	16.14	20.00	60.00
9	0.00	0.00	37.50	62.50
10	1.00	0.81	37.12	61.88
11	3.00	2.42	36.38	60.62
12	5.00	4.04	35.62	59.38
13	7.00	5.65	34.88	58.12
14	10.00	8.07	33.75	56.25
15	15.00	12.10	31.88	53.12
16	20.00	16.14	30.000	50.000

The IR spectra of raw material EVA and extracted polymer from Sample 2 are shown in Figure 1. There are peaks, marked by arrow, in the IR spectrum of the raw material polymer sample which are absent in the IR spectrum of extracted polymer. A comparison of raw material spectrum and extracted polymer spectrum with the IR library spectrum shows that the raw material contains mainly EVA, kaolin and calcium carbonate ($CaCO_3$) as shown in Figures 2 and extracted polymer spectrum is EVA as shown in Figure 3. The polymer, together with other major components, in the raw material could be identified by analysing directly with ATR, and polymer used in mixed composition samples could be identified by extracting the polymer with THF and analysing the extract with ATR after the solvent has evaporated.
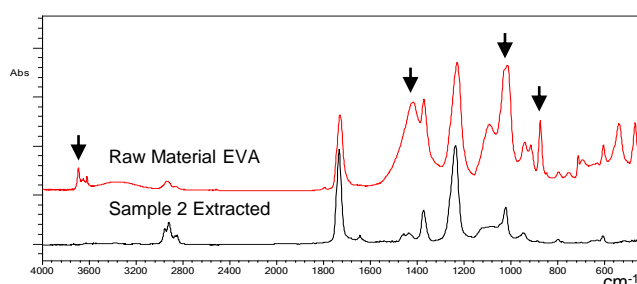

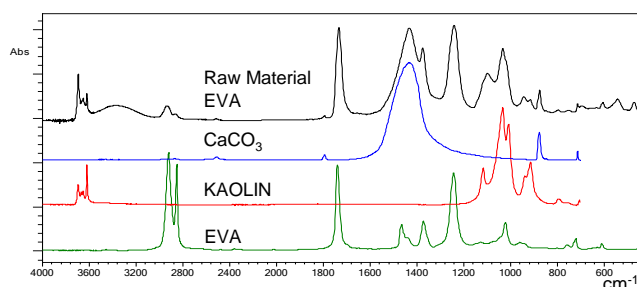Figure 1: IR spectra of raw material polymer and extracted polymer from Sample 2

Figure 2: IR spectra comparison of raw material EVA, $CaCO_3$, KAOLIN and EVA
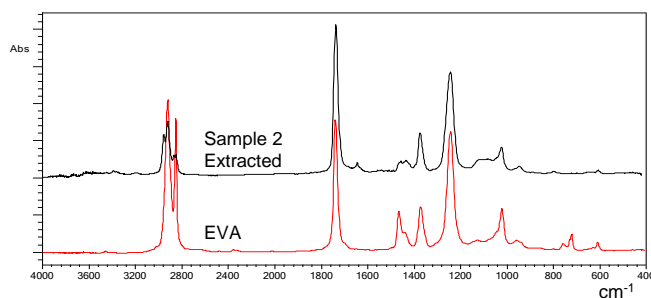

Figure 3: IR spectra comparison of extracted polymer from Sample 2 and EVA

Each sample was measured three times and out of the 16 samples, 14 were used as references to establish a PLS calibration model for polymer, cement and aggregate using Shimadzu LabSolutions IR workstation with Chemometrics PLS function. Sample 3 and Sample 12 were used as samples for quantitative determination.

The IR spectra of Sample 1 to Sample 16 measured by DRS method (Figure 4) show that the spectra are broad. This is mainly due to strong absorption and reflection peaks from high percentage of cement and aggregate. Mixing the samples with diluting substances may cause the concentration to change and lower percentage of polymer may not be detected. Since the main purpose is multicomponent quantitative analysis of polymer, cement and aggregate in the mixed composition samples and not identification, these spectra could be used for PLS analysis.
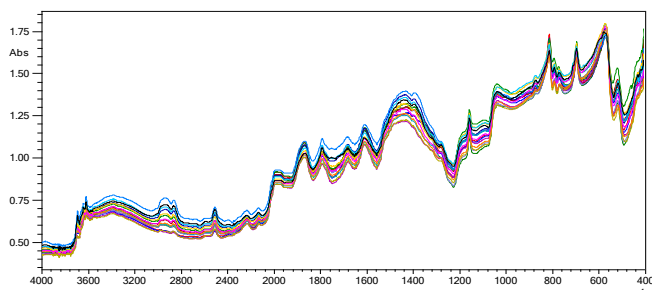

Figure 4: Overlapped IR spectra of Sample 1 to Sample 16 measured by FTIR-DRS

Second derivative spectra were actually used in data analysis for better resolution of overlapping and shoulder peaks, as well as removal of baseline fluctuation. Table 5 shows the PLS calibration parameter and results. From the repeated measurements of Sample 3 and Sample 12, the percentage variation from mean is less than 10%. The measured values were very closed to the expected values (Table 6).

Table 5: PLS calibration parameters and results

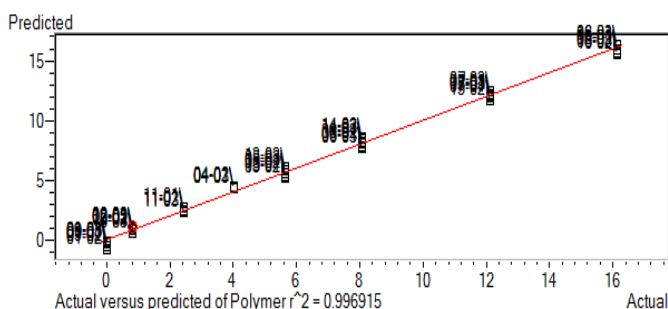| Number of references	42 (three measurements per sample)		
Range [cm^{-1}]	400 – 4000		
Pre-process	Derivative, Order=2, Points=7		
Scale	Autoscale		
Component	Polymer	Cement	Aggregate
Number of factors	5	5	5
Square of Correlation coefficient	0.9969	0.9952	0.9962
MSEP	0.0030	0.0047	0.0037
SEP	0.0549	0.0683	0.0611

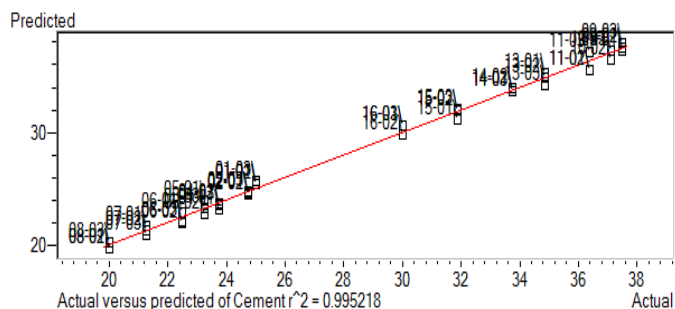Figure 5: PLS calibration for polymer predicted versus actual values

Figure 6: PLS calibration for cement predicted versus actual values
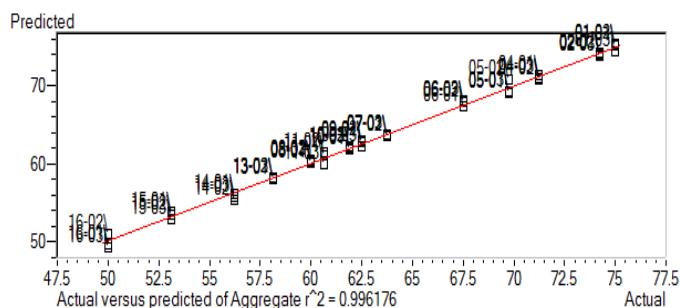

Figure 7: PLS calibration for aggregate predicted versus actual values

Table 6: Predicted values of polymer, cement and aggregate in Sample 3 and Sample 12

Sample	Predicted Value [%]				Expected [%]
	03-1	03-2	03-3	Mean	
Polymer	2.535	2.619	2.230	2.46	2.42
Cement	25.380	24.524	25.640	25.18	24.25
Aggregate	71.480	72.231	71.596	71.77	72.75
Sample	12-1	12-2	12-3	Mean	Expected [%]
Polymer	3.906	4.062	4.376	4.11	4.04
Cement	35.205	34.556	35.365	35.04	35.62
Aggregate	59.955	60.411	59.212	59.86	59.38

The polymer content in samples were obtained by measuring the weight loss from 200 to 600°C with a TGA. Figure 8 shows that the TGA thermal curves have similar weight loss profiles even though the samples have different raw material EVA content.

The TGA results have a good reproducibility of less than 3% (Table 7). The measurement accuracy for all samples was also acceptable with 95 to 105% recovery except for the sample where the raw material EVA content was 1%.

The data in Table 7 was then used to plot the calibration curve in Figure 9. The calibration curve show a linear relationship between polymer content measured by TGA and the raw material EVA content. This further showed that polymer content in the raw material can be measured accurately using TGA.
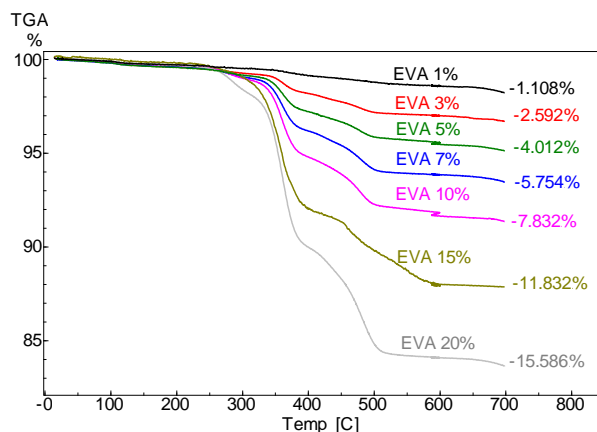
Figure 8: TGA thermal curves

Table 7: TGA results

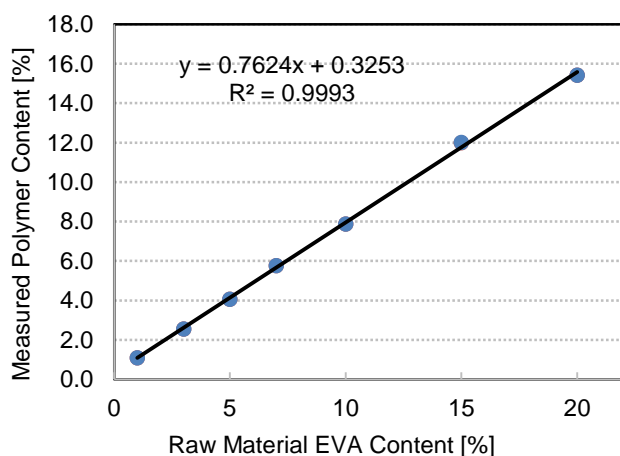| Raw Material EVA Content [%]	Polymer Content [%]			
	Calculated (Table 4)	Measured	RSD [%]	Recovery [%]
1.00	0.81	1.10	1.0	136.3
3.00	2.42	2.56	1.9	105.8
5.00	4.04	4.06	1.8	100.5
7.00	5.65	5.77	0.3	102.2
10.00	8.07	7.87	0.8	97.5
15.00	12.10	12.00	2.0	99.2
20.00	16.14	15.42	1.5	95.6

Figure 9: Calibration curve for polymer content measured with TGA versus raw material EVA content

Conclusions

The FTIR can be used to determine the polymer and other major components that have IR absorption in the raw material by comparing sample spectrum with IR library spectrum. Polymer in the mixed composition samples could also be identified by FTIR analysis with THF extraction. FTIR in combination with PLS data analysis has shown potential as an alternative analytical technique for the determination of polymer content in mixed composition samples. Cement and aggregate content can also be determined. The PLS calibration gives a good calibration model with square of correlation coefficients greater than 0.995 and recovery percentage of verification samples to be within ±10% of the actual values for polymer, cement and aggregate.

Besides FTIR, TGA can also be used to measure polymer content in a mixed composition sample.

For different concrete and polymer composition, further FTIR and TGA analysis would be required.

References

1. Ohama, Y. (1995). Handbook of Polymer-Modified Concrete and Mortars. Page 31-32. Noyes Publications, USA.
2. ASTM E1131 (1997). Vol 14.02. Standard Test Method for Compositional Analysis by TGA.
3. Tokura, T., Lim, J., Chua, A.M., Ohta, M., Naganishi, A. and Takeuchi, S. (2015). Analysis of Gaseous Products by DTA/TGA-FTIR System. Shimadzu Review 71(3-4): 129-133.

This paper has been presented at 15th International Congress on Polymers in Concrete (ICPIC) and published in Advanced Materials Research (2015) 1129: 151-158.

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