PROPERTIES OF MASTICS USING DIFFERENT FILLERS WITH BOTH UNMODIFIED AND EVA-MODIFIED BINDERS

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ABSTRACT

The properties of mastics are fundamental to the performance of many types of hot mix in current use. Whilst some fillers appear chemically inert in mastics, others are considered as chemically active. The way these different types of filler affect mastics and mixes was investigated.

Limestone and hydrated lime fillers were incorporated into two binders - 100 penetration paving grade and an EVA polymer modified binder based on the same bitumen. The resultant mastics were assessed using several test procedures, on the bitumen, on the mastics and some on hot mix samples. The tests included rheology, Cantabro and net adsorption. The effect of short-term ageing of the binder was also investigated.

The results showed the greatest effect was due to filler volume concentration whilst the short-term ageing caused substantially less change. With the materials studied, there was no evidence of significant hardening due to a chemical reaction between the active filler and the polymer modified binder.

Keywords: mastic; fillers; modified binder; bitumen; rheology;

1. INTRODUCTION

Traditional road construction with dense asphalts, to satisfy the demands of normal traffic, mainly use paving grade bitumens which comply with CEN standard EN12591 or similar. However, there is a whole industry based on supplying additives to enhance the properties of the bitumen mastic or its adhesion to aggregate. Most materials used are organic polymers, fibrous additives, adhesion promoting agents, or inorganic fillers. Apart from adhesion agents, additives when used individually normally have a physical, stiffening effect on the mastic. However, if two or more of the additives are used together, there could conceivably also be chemical interactions which give unexpected properties to the mastic and consequently to the mixtures.

The fundamental role of filler (mineral aggregate generally finer than 75micron) and the stiffening effects on bitumen mastics has been studied extensively since the 1930's with traditional methods of viscosity and stiffness measurements; Lee and Rigden, 1945 [1]; Rigden, 1947 [2]; Heukelom, 1965; [3]. This work has resulted in recognition that the volumetric packing effects are of key importance in understanding the effect on physical properties. However, certain types of "active" filler such as hydrated lime, which is sometimes used to improve adhesion, could possibly have both physical and chemical effects on the resulting mastic properties, especially if used in conjunction with modified bitumens. The volume effect of the filler can be assessed via methods developed by Rigden [2] who demonstrated that the viscosity increase could be interpreted from the compacted state. It would be postulated that effects to stiffness and viscosity not accounted for via a volumetric assessment would be associated with a chemical interaction. In order to investigate whether there might be an interaction between an active filler and ethylene vinyl acetate (EVA)- a polymer widely used in polymer modified bitumens - the properties of various mastics were measured and critically assessed. Comparison was made between the effects of different fillers in mastics under different ageing conditions to determine

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whether the active aspect caused any greater effect than might otherwise be expected. Filler types used consisted of a conventional limestone (LS), gritstone (GS) and hydrated lime (HL).

2. EXPERIMENTAL

2.1 Materials

Mastic blends were manufactured from the modified binder using 33 and 50% filler by weight. In addition, tests were also conducted on the un-filled modified binder. Three "ageing" conditions were evaluated, initial (1 to 2 minutes mixing), 2 hours (stored in an oven at a constant 150°C) and Rolling Thin Film Oven Test (RTFOT). The 2-hour condition and RTFOT simulate materials in storage for a limited time period and mixed materials, respectively. The combination of materials evaluated and ageing conditions were as follows:

Table 1: Test matrix

Material	Ageing condition		
	Initial	2-hour	RTFOT
100 Pen	×		×
100 Pen+50%LS	×	×	
100 Pen+50%HL	×	×	
PMB	×	×	×
PMB+33%LS		×	
PMB+33%HL		×	
PMB+50%LS	×	×	×
PMB+50%HL	×	×	×
PMB+25%HL+25%GS			×

Binders were evaluated using standard binder test procedures (e.g. penetration and softening point) and rheological methods (bending beam rheometer, dynamic shear rheometer and direct tension test). In addition, net adsorption and Cantabro tests were carried out on mixed materials which included gritstone of different gradings as appropriate. This was done to confirm (or otherwise) that the mixed materials reflected the results found with the binders and mastics.

2.2 Empirical Tests

Empirical data (penetration and softening point) were obtained from samples of binder, mastic and binder recovered from the mastic (see Table 2). These data suggest that the hydrated lime filler produces the stiffest mastics, whereas the recovered properties indicate that the conventional binder had more significant hardening with limestone filler as indicated by the higher softening point and lower penetration values. A similar effect is observed with the PMB materials. The two-hour data produced values similar to the initial results.

Table 2: Empirical test data for bitumen and binder filler blends

Material	Ageing condition	Before recovery		Recovered binder	
		Pen @ 25°C, mm/10	Ring and Ball Softening Point, °C	Pen @ 25°C, mm/10	Ring and Ball Softening Point, °C
100 pen	Initial	92	43.4		
	RTFOT	57	50.0		
100 pen+50%HL	Initial	12	>95.0	82	50.0
	2-hour	13	>95.0	72	51.0
100 pen +50%LS	Initial	23	64.0	46	57.4
	2-hour	30	58.2	54	56.2
PMB +50%HL	Initial	23	87.2	92	44.6
	2-hour	25	80.6	95	43.6
PMB +50%LS	Initial	42	54.0	66	47.4
	2-hour	41	54.6	68	47.4

2.3 Superpave testing

Three test procedures were used to evaluate the rheological and ultimate properties of the materials, as follows:

Bending Beam Rheometer (BBR) - was introduced as a test method for bituminous binders during the Strategic Highway Research Program (SHRP). The BBR was specifically developed to overcome testing problems that can occur with other methods when testing stiff binders at cold temperatures. This method of testing has been adopted in the AASHTO provisional specification to determine binder stiffness after the test has been running for 60 seconds and the slope of the stiffness curve - log time versus log stiffness - the m-value, to grade bitumen binders. However, recent work has led to an alternate specification parameter being calculated, with data from the BBR being used to generate thermal stress in the pavement structure (AASHTO MP1A method).

Direct Tension Test (DTT) - for bituminous binders was developed during the Strategic Highway Research Project in the early 1990's; Anderson et al., 1994 [4]. Initially, the test was used in the SHRP specifications (implemented as Superpave™ AASHTO M320 (old MP1) specification). The direct tension test measures the low temperature ultimate tensile stress and strain of a bitumen binder. The test is performed at relatively low temperatures, typically ranging from 0°C to -36°C. Initially an optional test parameter of 1% strain was used in the specifications as it was suggested that this represented a transition from ductile to brittle failure. However, due to inability of the M320 specification to capture the increased performance of modified binders, a development of the specification resulted in the AASHTO MP1A specification. This revision uses the bending beam rheometer data to compute the thermal stresses that are then compared to the values of tensile stress/strength measured in the DTT and used to determine critical cracking temperatures (CCT).

Dynamic Shear Rheometer (DSR) - has been used for testing rheology of binders for over thirty years. However, significant development of the device and testing procedures for bituminous binders occurred during the Strategic Highway Research Program that took place in the early 1990's. This resulted in the routine use of the test device in the US Superpave™ specification (AASHTO M320) for parameters related to fatigue and permanent deformation. Subsequently, in the late 1990's the DSR was used in the Highways Authorities Product Approval Scheme (HAPAS) with a temperature sweep required to define the complex modulus (G*) and phase angle (δ) between 5°C and 60°C. More recently, the Institute of Petroleum (IP) has developed a procedure (IP CM/02), for the definition of a master curve for a bituminous binder. This method was used to determine a master curve of behaviour for the materials evaluated and subsequently used to interpolate properties at various conditions.

2.4 Tests on Mixed Materials

Net adsorption was determined using a method based on the SHRP method for adsorption using crushed gritstone to the grading shown in Table 3. The mass of aggregate shows the quantity required to make up 50g, which is required for each test. The binder used included the polymer modified binder, and also the hydrated lime at 2% of the filler content.

Table 3: Aggregate test grading used in Net Adsorption test

BS 410 sieve size (mm)	% retained	Mass of aggregate (g)
5	8.3	4.15
2.36	25.0	12.50
1.18	16.7	8.35
0.6	23.9	11.95
0.3	13.3	6.65
0.15	6.1	3.05
0.075	6.7	3.35

Stock solutions of 1g bitumen/1 litre HPLC toluene were prepared. A sample of 4ml was removed from each solution, diluted to 25 ml with HPLC toluene and a spectrophotometer reading at 410nm taken. Test samples consisting of 140ml of stock solution and 50g of aggregate were shaken for an equilibrium period of six hours at a rate of 200 rotations/minute. They were left to settle before 4ml of solution was sampled. This was diluted to 25ml with HPLC toluene and filtered to remove any fine aggregate particles present. An absorbance reading was taken from which the initial amount of bitumen adsorbed by the aggregate was calculated. This gave the adsorption value.

To determine the net adsorption, 2 ml of water was added to each flask and shaken overnight. After being allowed to settle the same procedure of removing 4ml of solution was followed and the absorbance reading after the introduction of water to the system recorded. This gave the net adsorption value.

For the Cantabro test, samples were made using gritstone to the grading in table 4, (including 2% hydrated lime in the filler), and the modified binder. Samples used 5% binder and were compacted using the Marshall hammer and mould. Dimensions were 150mm diameter and 100mm high. Testing was performed in accordance with CEN TC 227/WG1 Testing Bituminous Materials, Particle Loss from Porous Asphalt TG2 Ref. No.1.15 TC227 Work Item 227123 Nov.1995. It involves the samples being placed in a large drum (Los Angeles abrasion drum) at a test temperature of 20^0C and subjecting them to 300 revolutions. The loss of weight or wear after 300 rotations is expressed as a percentage of the original.

Table 4: Aggregate grading used for Cantabro test samples

BS 410 sieve size (mm)	% retained
20	1.8
14	34.1
6.3	39.3
3.35	14.5
0.075	5.8

3. RESULTS

3.1 Cold temperature single-event thermal cracking temperature

The impact of the stiffness variation upon the expected low single-event thermal fracture temperature has been assessed by computation of the CCT; Bouldin et al., 2000[5]. The data obtained are presented in Table 5 along with the root mean square error associated with the fit of the master curve to the BBR data.

Table 5: Critical cracking temperature for single event low temperature cracking based on procedures developed for AASHTO MP1A binder grading and associated error parameter

Material	Ageing condition	Critical Cracking Temp., °C	rms error for master curve fit
PMB	2-hour	-35.5	0.84
PMB	RTFOT	-32.1	1.17
PMB+33%LS	2-hour	-30.1	0.70
PMB+33%HL	2-hour	-28.1	1.64
PMB+25%HL+25%GS	RTFOT	-22.9	3.90

The results indicate that the CCT varies by about 10°C depending upon the formulation. The CCT as evaluated, applies to binder systems without aggregate volume. However, since three of the materials contain mineral matter, an adjustment is required to the value of the "Pavement Constant (PC)" used in the calculation in order to correctly account for this aspect.

The pavement constant is used to account for the difference in stress computed in the binder versus a mixture that is used in real pavements. The value initially proposed was 24; Bouldin et al., 2000[5], which was subsequently changed to 18 as the specification AASHTO MP1A was published.

The effect of volume of binder and ageing type on critical cracking temperature is illustrated in Figure 1. This figure shows the data with the standard pavement constant of 18 and also a variable value that was obtained with consideration of the volume fraction of filler as computed from the density of the various materials. The volume fraction adjustment applied does not appear to account for all the change in behaviour, which is understandable due to the complex nature of this parameter. However, it would appear that a trend is evident with the ageing type used and the binder volume – although the data is limited.

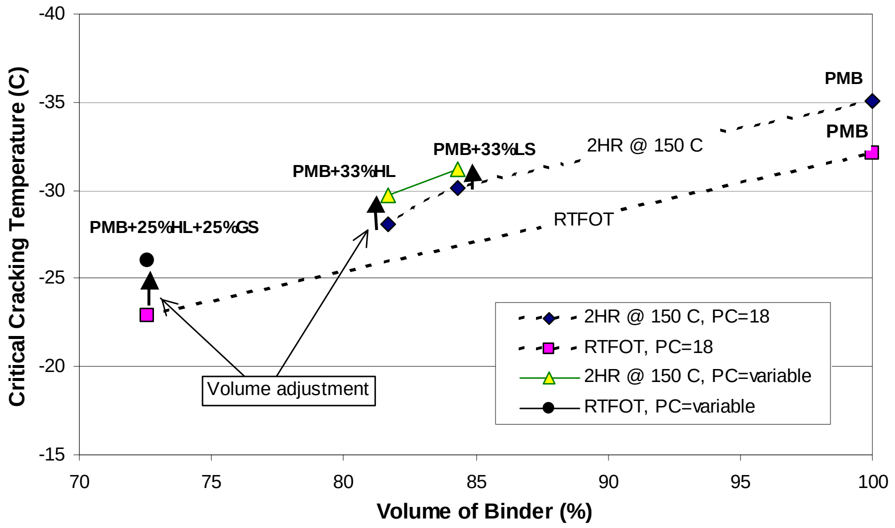


Figure 1: Effect of volume of binder and ageing type on critical cracking temperature

3.2 High temperature performance

High temperature performance has recently relied upon the computation of G*/sinδ and determining the temperature when this reaches 1.0kPa and 2.2kPa for initial, 2-hour and RTFOT aged materials respectively. Using the master curve data and the interpolation tools within the RHEA software; Rowe, et al 1999 [6], the temperature has been determined corresponding to both the 1.0 and 2.2 kPa conditions for the materials evaluated. These data are presented in table 6.

Table 6: High temperature performance criteria, AASHTO M320

Material	Ageing condition	$T_{G^*/\sin\delta\square = 2.2\text{kPa}}$, °C	$T_{G^*/\sin\delta\square = 1.0\text{kPa}}$, °C
PMB	2-hour	81.7	76.0
PMB	RTFOT	88.3	82.3
PMB+33%LS	2-hour	85.3	79.6
PMB+33%HL	2-hour	87.9	82.4
PMB+25%HL+25%GS	RTFOT	98.2	92.3

The effect of the filler on the magnitude of G*/sinδ is evident from table 6, with the filled materials having higher stiffnesses under similar ageing conditions.

3.3 Mixed materials

The practical tests on the mixed materials were used to confirm that the results, when compared with those from the more theoretical assessments, were as expected when both the polymer and the "active filler" were incorporated. The testing and hence the results are limited.

Table 7: Summary of Adsorption test data

Average Initial Adsorption (%)	Average Net Adsorption (%)
70.2	54.9 (15.3%diff)

Table 8: Summary of Cantabro test data

Mould Ref	Cantabro loss @ 300 rotations
1	23
2	5.7
3	10
4	10.6
Average Value	12.3

4. DISCUSSION

The quality of the binder can be expressed as the performance range that it will span. This can be obtained by subtracting the cold-grade temperature from high-grade temperature to produce the *performance range*. However, an alternate approach that is used in the industry is to place a double emphasis on the cold temperature performance in the computation of a *quality index*. This information, derived using both the 1.0 and 2.2 kPa limits for G*/sinδ, is presented in Figure 2 from which it can be observed that *performance range* is similar for all materials (110°C to 121°C). This figure indicates a slight improvement in performance range as filler is added but a small reduction is obtained in the *quality index*. As apparent performance is lost at the cold temperature end, a gain in performance is achieved at the high temperature end of the specification. However, when comparing the blends of different fillers there is no significant difference between the materials.

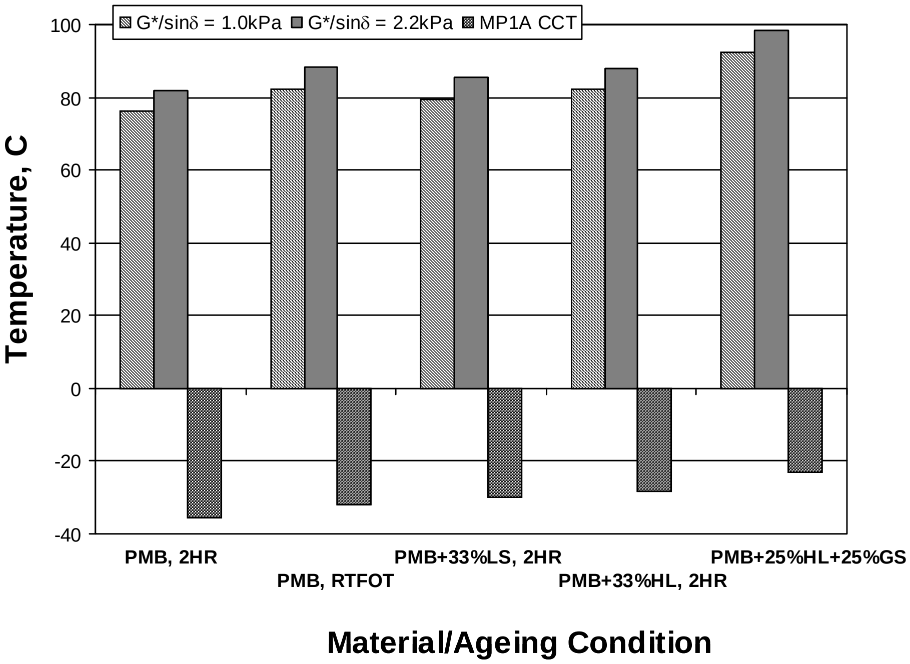


Figure 2: Effective temperature range for PMB and PMB filler binder

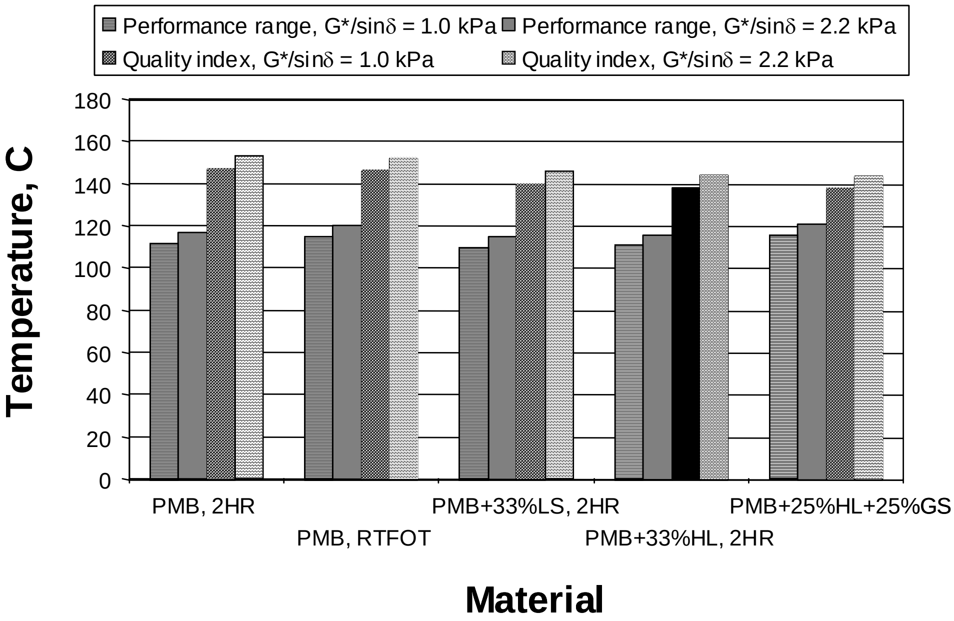


Figure 3: Performance range and quality index for PMB and PMB filler binder

From the measurements conducted, it is clear that the fillers have an effect on the stiffness properties. This effect on stiffness has been understood for a considerable period of time; Einstein 1906 [7], 1911 [8]. For volume concentrations up to 50% the stiffness ratio for a filled liquid (assuming the filler is infinitely stiff compared to the liquid) is as follows:

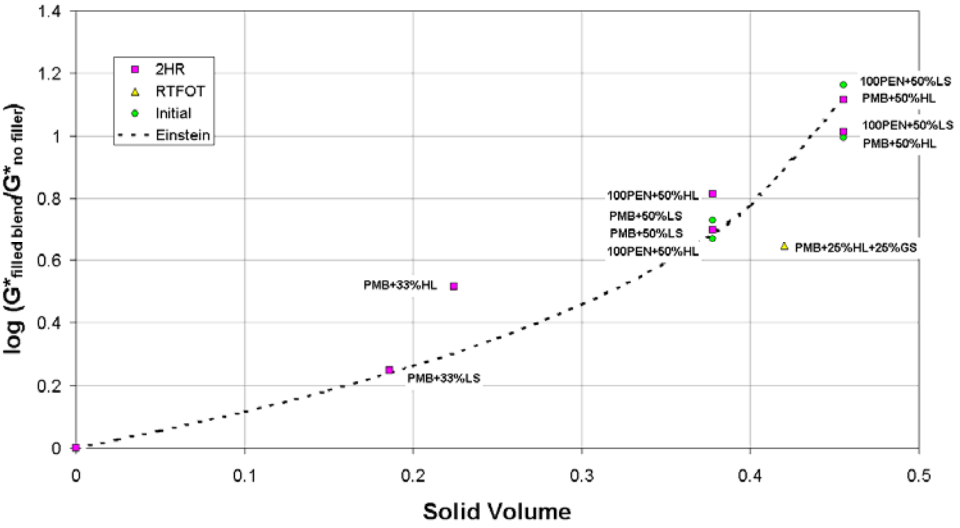
$$\frac{S_{filled}}{S_{liquid}} = \left[\frac{1 + \frac{C}{2}}{1 - 2C} \right]$$

where: C = volume concentration of aggregate (volume of filler/total volume)

The ratio of stiffness increase has been determined for all binder/filler blends evaluated and all ageing conditions. In the case of this experimental work, all the volume concentrations were below 50% and consequently the data has been compared to that which would have been achieved using Einstein’s approach, see Figure 4. As expected, the data points lie about the line representing Einstein’s relationship, suggesting that the main influence on the stiffness increase can be explained by the solid volume concentration of aggregate (filler) particles that exist in the blended materials.

The empirical data (Pen and Softening Point) presented in Table 1 do show some differences in the recovered properties. In particular the mixtures made with the limestone filler appeared to be stiffer. However, recovery of a binder can be problematic and without additional studies it is difficult to account for these differences. The initial and 2-hour data were not significantly different and consequently we can conclude that little ageing occurs in the 2-hour procedure.

In asphalt mixtures, the filler proportion is specified by a ratio of filler to effective binder (in addition to gradation limits and other tests). For example the Superpave mixture require a “Dust Proportion” (percent passing 75micron/effective binder) to lie within the 0.6 to 1.2. For typical fillers, this will give solid volume concentrations ranging between 20 and 45% and consequently Einstein’s equation could be used to estimate the effectiveness of the filler stiffening the binder film. Differences obtained by testing using this approach would account for effects that cannot be explained via volumetric analysis.



(ratio of G obtained using properties at 25 C and 0.4 Hz)*

Figure 4: Stiffness ratio versus solid volume for all materials considered

The tests carried out on samples of mixed material included both the polymer modified binder and the "active" filler. This was done to establish whether an unexpected reaction occurred in practice that had not been noticed in the tests on the binders and mastics alone. The results from both the net adsorption test and the Cantabro test were as expected for polymer modified binders in association with normal mixes. Because the results were as expected, the binder and mastic results were considered to be valid.

5. CONCLUSIONS

From analysis of the data collected with an EVA polymer modified binder and filler blends we can make the following conclusions:

1. From the three different ageing conditions that were evaluated; initial, 2 hour and RTFOT, the initial and 2-hour data produced very similar results.

2. The addition of filler impacts the "apparent" critical cracking temperature. A change to the pavement constant considering only volumetrics could not account for the change. It is postulated that the complex stress state that occurs in filled systems are affecting the results.

3. The addition of filler increased the stiffness of the materials. However, the apparent *performance range* was marginally greater for the filled materials whereas the *quality index* was marginally lower.

4. The increase in stiffness (expressed as a ratio to the unfilled binder) can be explained by the use of Einstein's equation that considers the stiffness increase that will occur when a fluid has a suspension of solid particles. The approach is considered valid to solid volume concentrations of 0.5.

5. The effect of different filler types could be considered for making use of Einstein's approach since most Hot Mix Asphalt (HMA) is manufactured with solid volume concentrations (binder/filler blend) that are within the range covered by the procedure. Rheology measurements on binder/filler blends could be used to account for differences in behaviour that would not be considered by use of a volumetric adjustment.

6. In order the give added confidence to the work on the binders and mastics, test work was also carried out on mixes incorporating aggregate. These results confirmed that no unexpected phenomena occur when the binder or mastics in the test programme are mixed with stone.

7. When considering the conclusions above, there is no evidence of any chemical reaction between the added components in the binders, whether they are considered to be "active" or not.

The data obtained from this study are limited to relatively small number of binders and fillers. In the continued assessment of this method of analysis it would be recommended that this approach be applied to a much wider selection of materials to increase the confidence in the approach and the analysis method.

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