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INVESTIGATING THE BEHAVIOR OF CASTING WAX DURING THE AUTOCLAVE PROCESS.

USE OF CONTROLLED STRESS RHEOMETRY AND FTIR

AUTHOR:
Dr. Grant Bradley (REMET UK)

REMETUK.COM

REMET UK LTD
44 Riverside II, Sir Thomas Longley Road
Rochester, Kent, ME2 4DP, UK
Registered No. 4780567 England

T: +44 (0) 1634 226 240
F: +44 (0) 1634 226 241
E: CustomerService@remetuk.com

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ABSTRACT.

Previously we have reported on the use of controlled stress rheometry (alongside DMA and DSC) as a method for investigating the behavior of casting waxes during the injection and subsequent cooling processes.

This paper reports the use of temperature ramped controlled stress rheometry (yield measurement) and temperature controlled FTIR to investigate the behavior of wax during the autoclave process. Drawing on results obtained from Birmingham (UK) University's FOCAST (Fundamentals Of investment CASTing) programme, experiments have been carried out to investigate factors affecting the flow and absorption characteristics of wax at the shell/wax interface during the early stages of the autoclave process. Results are reported focusing on the variation in time and temperature response of various waxes, and the potential effects upon the dewax process.

1. Introduction – Past investigations into the autoclave process and current questions.

1.1 Anecdotal Understanding

It is well known within the foundry trade that there are certain processes that go on within the dark confines of the autoclave. Unfortunately, steam at 170-180°C is not conducive to large viewports and monitoring systems wired through the pressure vessel, so much of the empirical knowledge about these processes is based upon before and after examination of the autoclaved shell.

Amidst this anecdotal knowledge is a certainty that if the melting point of the pattern wax is too low compared to that of the runner wax, then you will have cracking.

A similar certainty is that if your autoclave is not reaching the correct temperature and pressure, and is a bit slow to heat the shells, this also leads to cracking.

Another observation is that some of the wax is absorbed into the shell and is burned off when the shell is fired.

From these and other hard-won nuggets of information gleaned from lifetimes of process experience, the foundrymen of today optimise their autoclaves to give fast and efficient wax removal with the minimum of cracking possible!

There are also those who advocate flash firing as a preferable alternative to autoclaving, though the substantial number of autoclaves still used in foundries suggest that flash firing is not the panacea some would hope.

1.2 Literature Understanding

There have been a number of papers relating to the autoclave process presented at ICI conferences, and indeed in other forums. Authors have compared the autoclave process with flash firing (Marion 2009), have investigated Thermal Profiles and moisture effects on shells (Jones et al 2002), and have even attempted to model the dewaxing process (Gebelin and Jolly 2002).

Some of the results have been decidedly counter-intuitive with one paper even noting an increase in cracking on moving from a low expansion wax to a higher expansion formulation (Bond and Nishikawa 2002).

Despite the many papers there is no clear, detailed understanding of the relationship between wax and shell during autoclaving.

The assumption has always appeared to be that as soon as the wax is liquid it will flow into available pores in the primary layer, driven by the pressure of the expanding wax.

Measurements taken using a specially adapted autoclave as part of the FOCAST program revealed some interesting data.

Experiments with thermocouples at various points supplied data about heat flow into the shell (Pickard 2010).

The FOCAST autoclave was capable of achieving a chamber temperature of 170°C in 4 seconds. There was found to be adequate heat transfer to achieve a near instant temperature rise to 170°C on the outer surface of the shell.

For the heat to transfer into the shell took a little longer. A thermocouple at the interface between the wax and the shell took 24 seconds to reach a temperature of 75°C, and was observed to take up to 6 minutes to reach peak temperature.

The speed of heating for a solid block of wax in such an autoclave is limited by the thermal conductivity of the wax which is generally very low.

As a result, a standard test cylinder of wax (61mm diameter by about 100mm long) with a standardized shell on it (see Jones et al 2001) was found to remain partially solid during a test autoclave cycle with a 6 minute dwell cycle.

Jones (et al 2002) also report that wetting out of their primary shell surface with unfilled wax (observed by contact angle and spot size) progresses from wax melting point all the way to 180°C.

Ironically the temperature sensors fitted to their test cylinder also revealed that by 120°C , convection currents in the outer layer of molten wax were adequate to stop further temperature rise at the interface between wax and shell.

1.3 Work presented here.

In this paper, two main questions are asked. The first is: "Does the drop melt point of a wax adequately represent the temperature at which wax begins to flow?" The second is: "How does the process of wax absorption into shell vary with temperature."

Drop melting point measurements are made by recording the temperature at which a drop of wax falls from a little cup of material heated from solid through its melting point.

Figure 1.1 Drop Melt cups.

The drop melt technique relies on the force of gravity acting on the mass of the wax to force a drop through the hole. This is fine for Newtonian fluids, but materials which go through a non-Newtonian pseudoplastic phase during heating might not produce a drop until after the point where they can actually flow under pressure!

Waxes of known drop point have been examined using the rheology experiment described below to determine whether the measured drop point is representative of autoclave behaviour.

Wax absorption, whilst known and observed is potentially quite difficult to quantify. Reported here is an adapted FTIR technique that it is hoped will shed some light onto rate and quantity of wax absorbed.

2. Analytical Methods-Further experiments in making lab measurements reflect what happens in the foundry.

2.1 Controlled stress rheometry- Measurements of yield temperature.

2.1.1 The Technique

We have previously reported in this forum on the use of parallel plate controlled stress rheometry for investigation of wax behaviour on cooling (Bradley 2012). In that paper we reported the advantages of using a controlled stress approach to rheometry in limiting the amount of shearing energy applied to a wax as it cools so as to better model the rheological behaviour of a wax flowing into a die.

The applications of controlled stress rheometry do not end there however.

Since the constant shear stress experiment keeps a constant force applied to the rotating plate, varying the speed of rotation as the test sample changes in viscosity, then the rheometer can come to a complete halt whilst still being within experimental parameters!.

Equally, as the instrument can slow to a stop, then when the wax begins to flow the rheometer can start to move again. The amount of shear applied to the stationary wax can be varied, and the temperature at which the wax begins to move can be monitored at various levels of applied force

Wax at its melting point is loaded with crystals and is at it's most non-Newtonian at that point. Thus, even when the wax has melted enough to (in theory) flow, there may be a yield stress associated with that flow.

2.1.2 The Instrument and the Experiment.

The work presented here was carried out using a Brookfied R/S-Plus instrument which offers a robust, functional, and reliable measuring system. It is fitted with a Peltier effect thermostatting system which allows for heating and cooling at up to 0.5°C/s. This is the same instrument as cited in previous papers.

Figure 2.1 The Brookfield controlled stress rheometer.

The experiment carried out involves loading the sample in a fully molten state, cooling the sample with shearing down to 25°C, and then subsequently ramping the temperature back up until the wax is molten whilst applying a controlled torque to the movable plate.

2.2 Fourier Transform Infra-Red Spectroscopy (FTIR) – Application of a heated single bounce diamond ATR accessory.

2.2.1 The Technique.

Infra-red spectroscopy is one of the most widely used spectroscopic techniques capable of revealing structural information for organic compounds. In the last 20 years the "Fourier Transform" variant, operating as it does with a short pulse of light generated by an interferometer and decoded mathematically has come to dominate the market over the more traditional wavelength dispersive instruments.

One of the intrinsic advantages of FTIR is that an entire spectrum of data can be collected from each short interferogram "burst".

Thus, scanning a sample 10 or even 100 times improves signal to noise ratio and produces clear spectra from even the lowest energy transmitted signals. This enhancement of performance has enabled development of sampling techniques that were impossible with dispersive instruments.

One of the most common varieties of sampling accessory is the ATR attachment. ATR is the acronym for Attenuated Total Reflectance. The interferogram burst of IR light is focused on one end of a piece of IR transparent crystal that behaves as a fibre optic, light being conducted through the crystal by bouncing off the walls of the crystal before emerging at the other end, that phenomenon known as Total Internal Reflection.

In a similar fashion to a fibre optic, the light wave progressing through an ATR attachment generates an evanescent wave travelling on the boundary between the ATR crystal and the air or sample.

It is the attenuation of this evanescent wave and the subsequent reduction of signal intensity for the interferogram burst which gives the signal Attenuation measured through an ATR accessory.

The evanescent wave only extends for a few microns beyond the crystal surface (dependant on the refractive index of the crystal)

Due to the nature of this measurement, ATR accessories measure only the spectra of materials in intimate contact with the crystal. Thus, a piece of shell pressed tightly against the crystal will have a minimum contact area with the plate due to the particulate and slightly textured surface. A puddle of liquid wax on the crystal surface will have a much higher contact area and will be the dominant spectrum. If wax is absorbed into the ceramic, it will disappear from the crystal and the spectral intensity will be reduced.

2.2.2 The Instrument and Experiment.

Figure 2.2 The Pike GladiATR single bounce Diamond ATR

The GladiATR accessory at the Remet UK laboratory is equipped with a computer controlled heater system capable of thermostatting the sample plate from room temperature up to 260°C . Samples of wax were melted onto the plate between 60 and 80°C , and scanned at time intervals over a temperature range. Peaks associated with the wax were assessed as an indication of absorption of wax into the shell. The GladiATR clamp system exerts a 30,000 psi pressure upon the slightly raised diamond of the sample plate.

2.3 Spread tracing.

Samples from the FTIR experiments revealed some capillary action was operating to spread the wax over a broader surface than that in direct contact with the wax. A further simple experiment was devised to investigate the absorption process.

Samples of shell which had absorbed wax were soaked in a 2% aqueous solution of sodium fluorescein. The fluorescein solution is unable to penetrate wax saturated areas and therefore only colours portions of shell where the wax has not penetrated.

2.4 Samples tested.

Testing was carried out on 2 types of samples obtained from one of Remet's customers (an ICI member). The samples were derived from the regular MOR bars sent in by the customer for routine testing.

Sample Type 1 is their regular shell made using a primary dip comprising an enhanced sol and a blend of Zircon and 200 Mesh Fused silica. Sample Type 2 is similar, but with a cobalt aluminate primary. Number and constituents of backup layers were not recorded as they were not believed important given the nature of the experiments.

Thus they were both representative of the standard production process and, more importantly, had been removed from the wax at room temperature thus allowing no opportunity for molten wax to penetrate the shell, or for thermal changes to be caused to the shell material.

Three waxes were used, an unfilled wax, and two filled pattern waxes selected to represent different formulation approaches.

3. Results and Discussion- Have we actually learned anything useful?

3.1 From the rheology experiments.

Figure 3.1 shows an example of the data output from one of the rheology experiments.

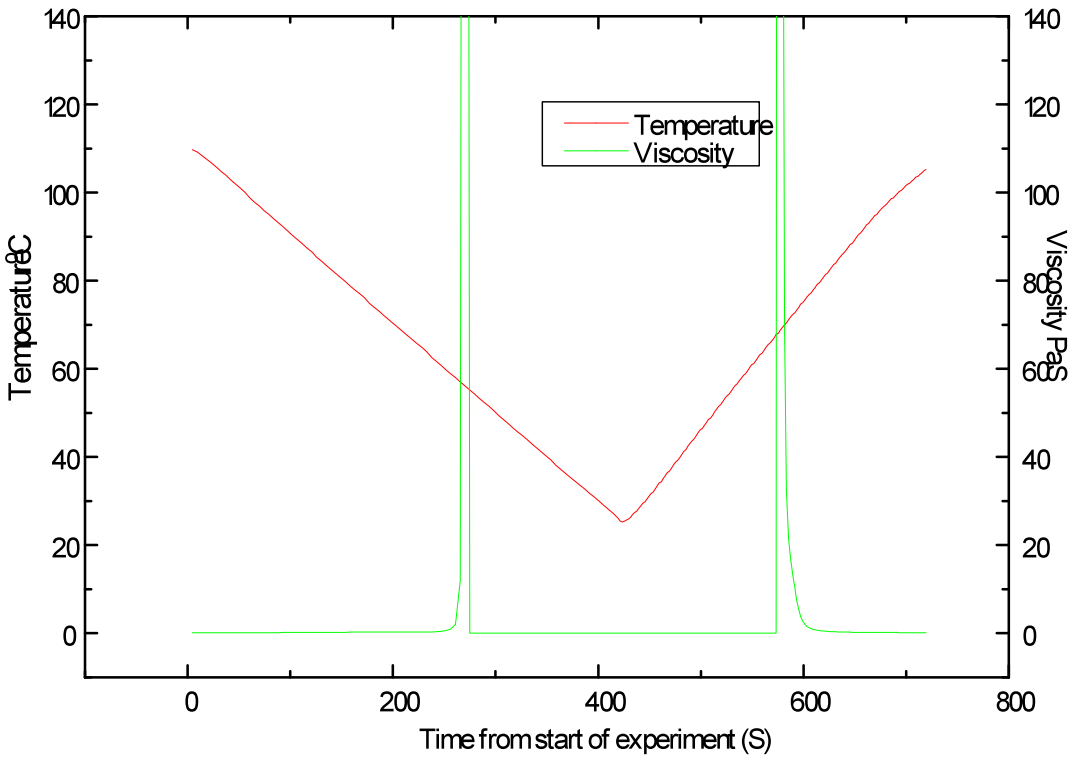

Figure 3.1 Example trace from rheology experiment

Note that as the temperature decreases during the first half of the experiment, there is a sharp rise in recorded viscosity until the wax finally freezes. At this point the instrument software shows a default viscosity of zero, based on the fact that the plate is not turning and the instrument is returning no data to the computer.

Then as the temperature rises again, the moment the plate begins to move, the instrument returns a maximum viscosity figure to the computer and the data show a sharp rise from one data point to the next.

For all the samples run, with a variety of scanning rates and applied shear stresses, the temperature at which the first viscosity since the freezing point is returned by the instrument is recorded.

Figures 3.2, 3.3 and 3.4 show the rheology overlays for the three waxes:

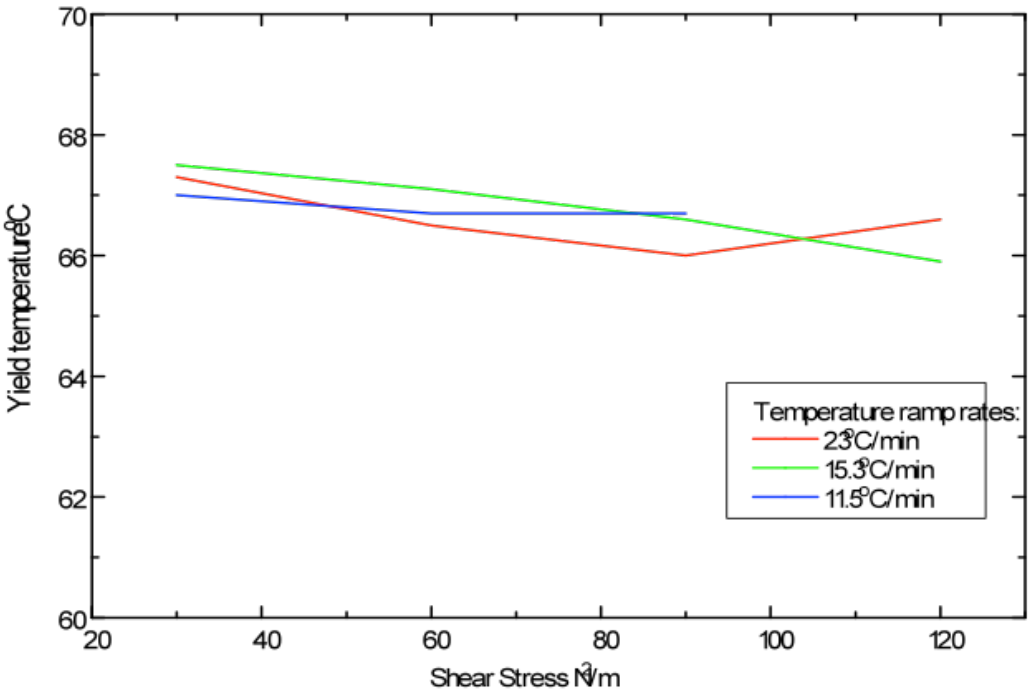

Figure 3.2 Yield temperatures vs shear stresses for unfilled wax heated at various speeds

With the unfilled wax above, variation in the shear stress applied through melting seems to have a relatively limited effect on the yield temperature. Whilst there is a slight downward trend at all ramp rates, when this is compared with the change from the recorded drop melt point (69°C), the trend is small.

This wax might well begin flowing one or two degrees below the recorded drop melt point, but this is unlikely to be significant under autoclave conditions.

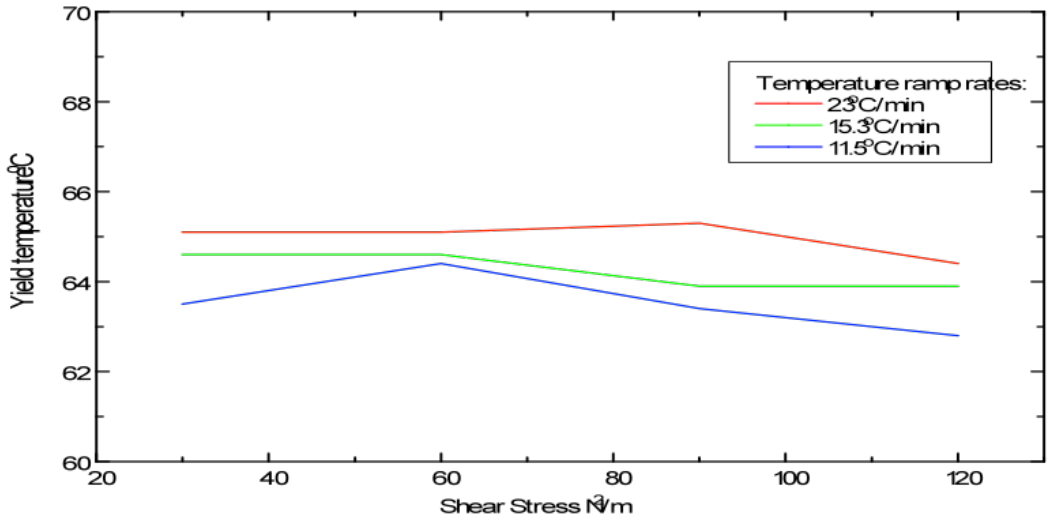

Figure 3.3 Yield temperatures vs shear stresses for filled wax, Class A heated at various speeds

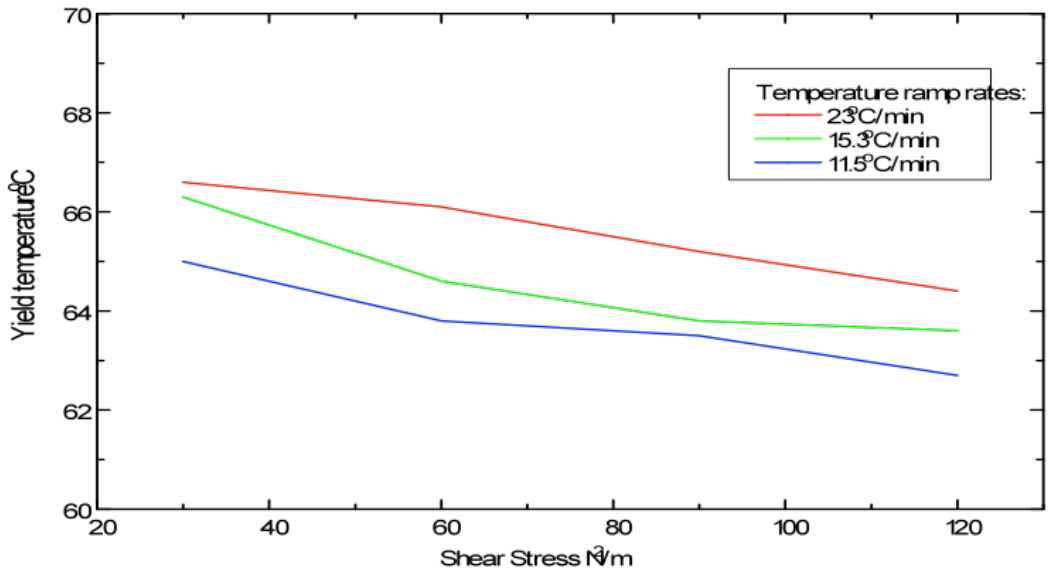

Figure 3.4 Yield temperatures vs shear stresses for filled wax, Class B heated at various speeds

What is interesting is that the "Class A" filled product is closer in behaviour to the unfilled wax than the "Class B" material. The difference between the two classes is linked to the additive packages used to tune the behaviour of the two waxes.

It is likely that the observed difference between the two classes of filled waxes might be attributed to the quantity, size and shape of the crystals in each wax, coupled with the filler present.

3.2 From the FTIR experiments

Figure 3.5 shows the overlaid FTIR spectra of the two shells employed, along with a sample of unfilled wax underneath the regular shell. Note the absence of visible peaks attributable to organic molecules in the shell traces and the presence of a broad absorption band associated with some inorganic materials, weakly visible in those spectra.

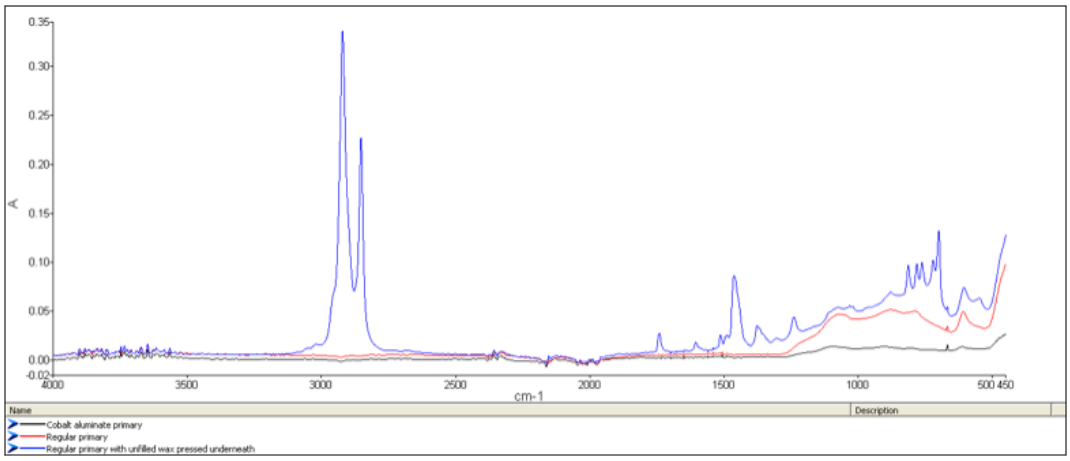

Figure 3.5 Overlaid FTIR spectra showing difference between organic and inorganic materials and demonstrating co-visibility of peaks from wax pressed by shell.

Note also the intense bands visible from the wax, and that the sample with wax pressed onto the diamond by a piece of shell shows both the broad band from the shell and the functional group bands from the wax.

We can thus be certain that there is a thin layer of wax pressed into intimate contact with the shell. Attempts to use an elastic containment to pressurize the wax in contact with the shell proved fruitless, as even 20 microns of rubber gasket removed the surface of the shell too far from the surface of the diamond.

With a wax sample pressed with a piece of shell, the combined system could be heated to look at whether the wax absorbs into the ceramic.

Figure 3.6 shows an example of the changes in the C-H stretch peaks with temperature for a wax and shell combination:

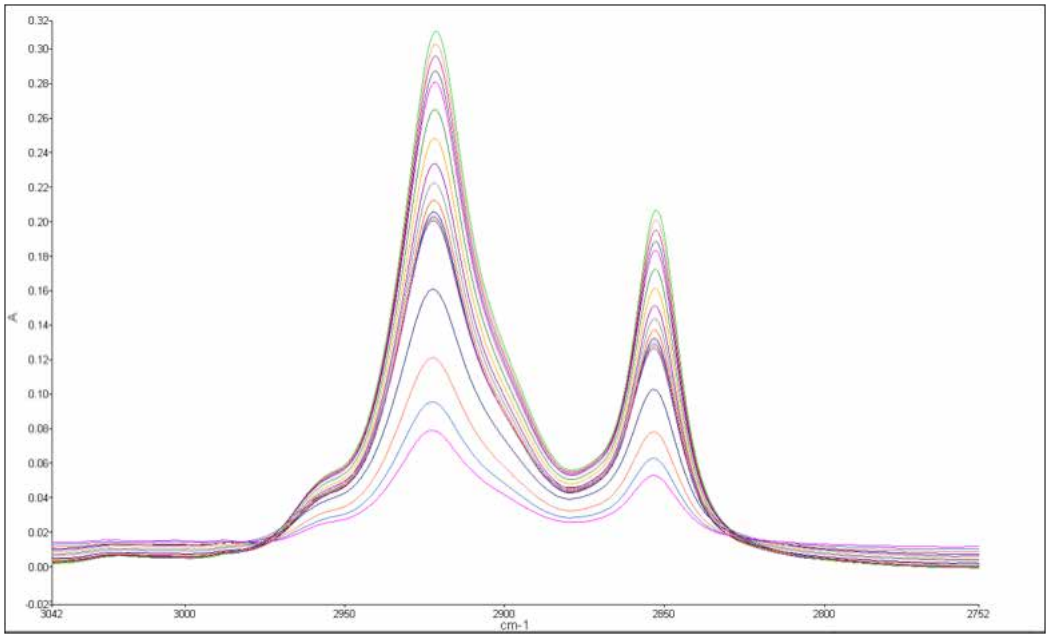

Figure 3.6 Overlaid FTIR spectra showing absorption of wax into shell at different temperatures.

The initial experiment involved the unfilled wax in contact with the regular shell. The plot of temperature against wax visible on plate is shown below. Note the sigmoidal best fit curve to the data points. (Figure 3.7)

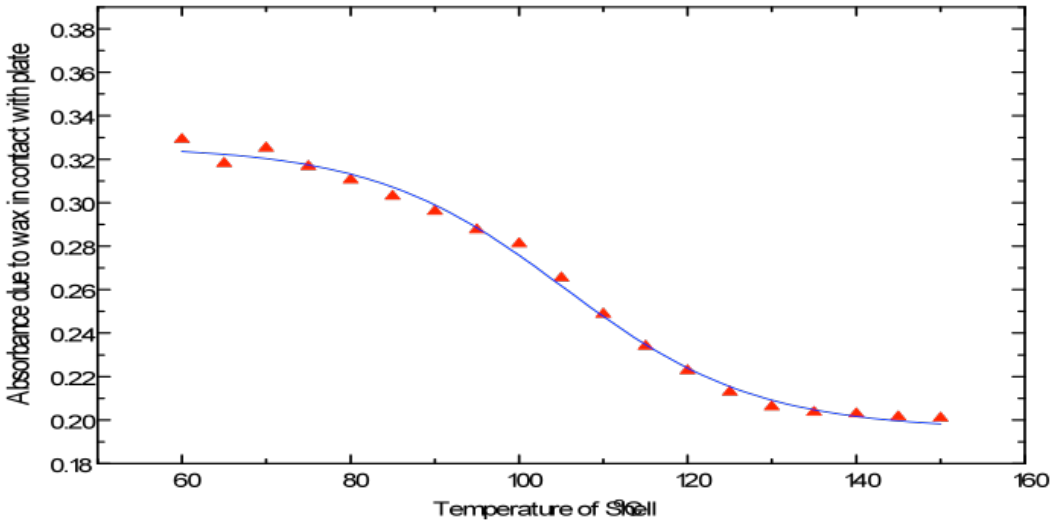

Figure 3.7 Absorption of unfilled wax into regular shell with temperature

The same experiment was carried out with the two filled waxes (Figures 3.8 and 3.9)

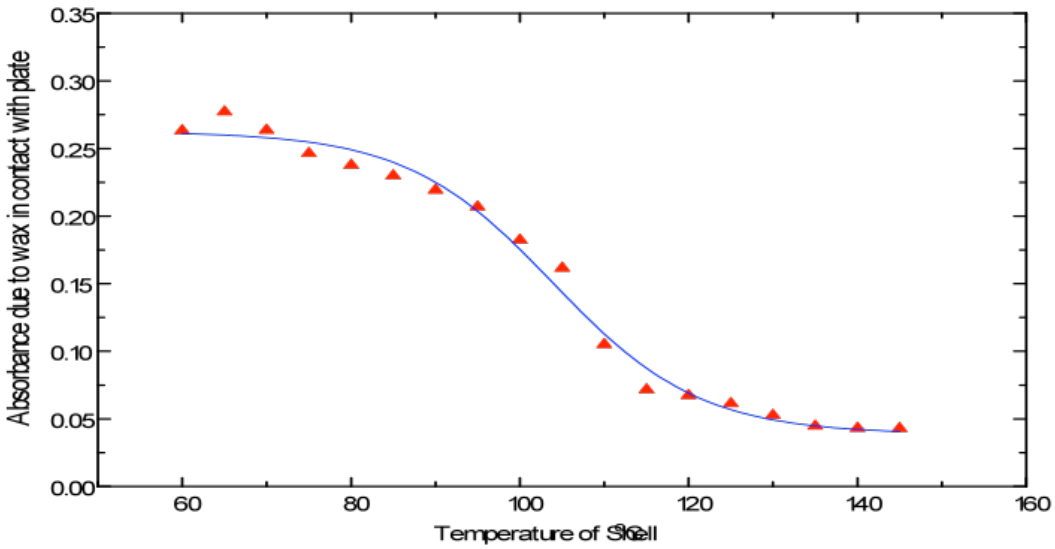

Figure 3.8 Absorption of filled wax A into regular shell with temperature

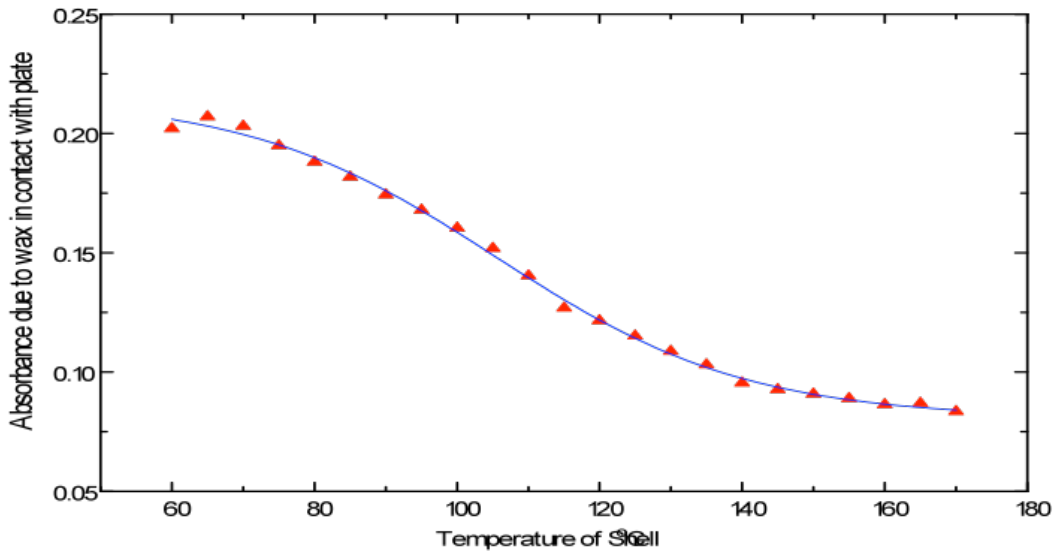

Figure 3.9 Absorption of unfilled wax into regular shell with temperature

In all three cases there was a sigmoid fit to the absorption data. This is not quite what might have been expected, and the question had therefore to be asked as to whether the sigmoid curve was due to a change in absorption kinetics or a varying equilibrium.

The early part of the sigmoid curve is what one might expect, with what appears to be an initial slow absorption accelerating with time and temperature. Likewise, the end of the curve, where a small residuum of wax is left on the plate is equally expected. The slowdown in absorption rate whilst there is still wax on the plate which might be absorbed is odd.

There was not enough wax present to saturate the entire shell, so slowdown should not be expected from any saturation effect, nor can the kinetics be effected by any "dilution" effects. Isothermal studies were carried out at 80°C and 120°C to ascertain whether there was a slow absorption below the midpoint of the sigmoid curves and a faster one above. Figures 3.10-3.12 contain overlays of the 80 and 120°C time/absorbance plots.

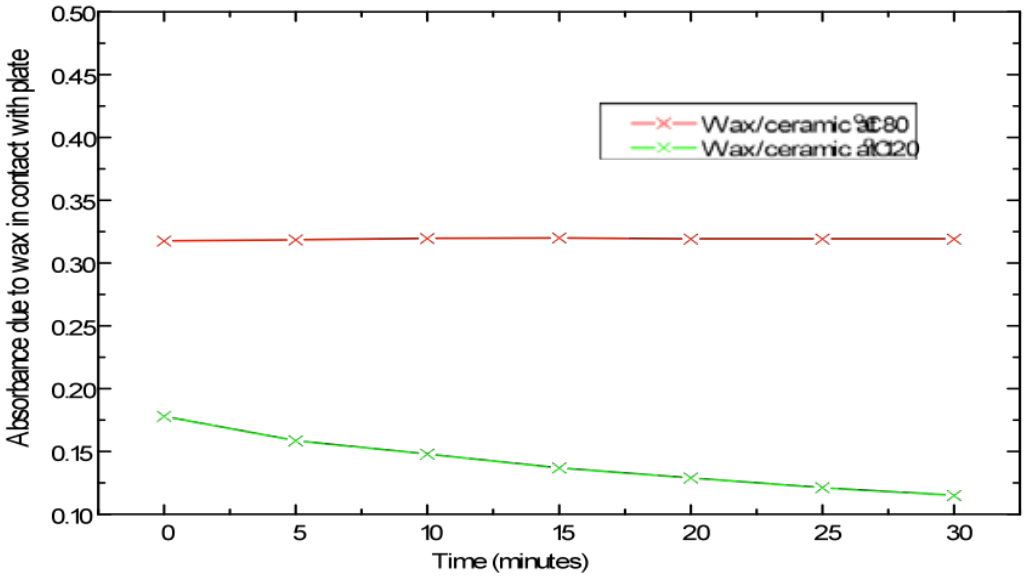

Figure 3.10 Absorption of unfilled wax into regular shell at two temperatures.

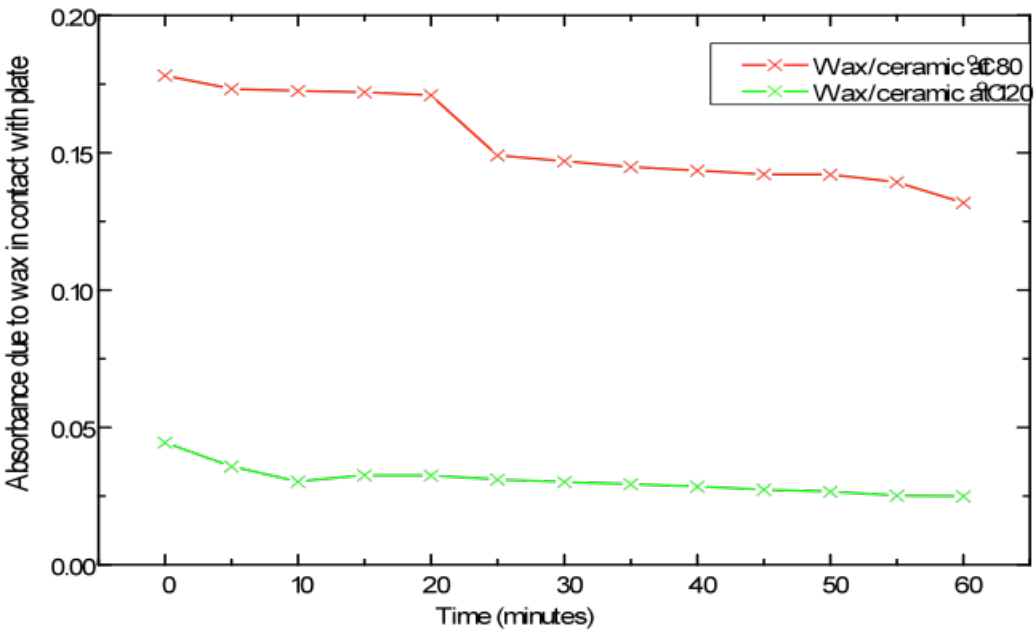

Figure 3.11 Absorption of filled wax A into regular shell at two temperatures

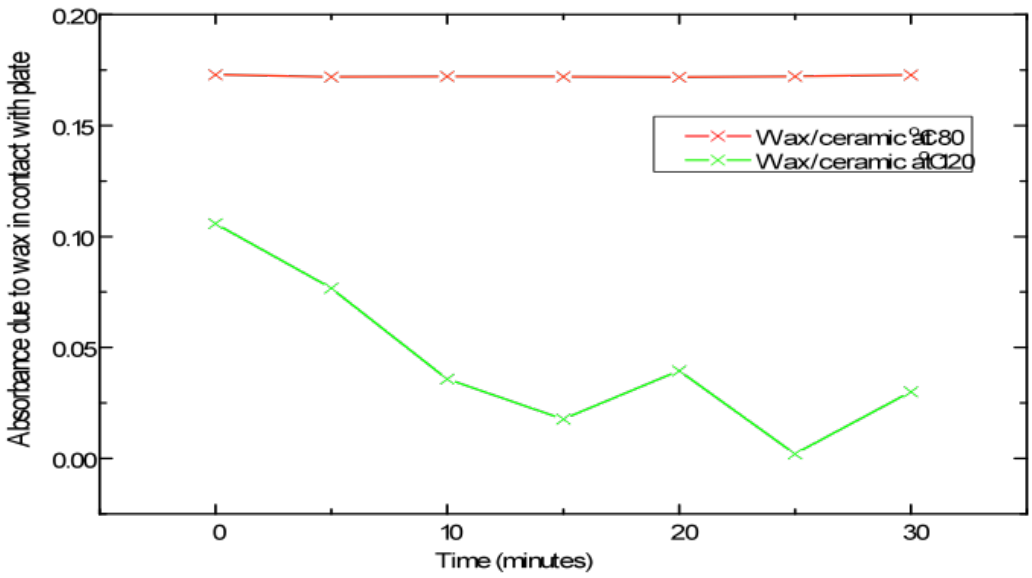

Figure 3.12 Absorption of filled wax B into regular shell at two temperatures

Clearly, there is a situation where the absorption of wax into the test shell at 80°C is on a substantially longer timescale than the absorption at 120°C . At the beginning of each experiment, there was a 5 minute period allowed for the thermal equilibrium of the shell and the heating plate. It would appear that the difference in initial measured absorbance for each temperature, is due to absorption of wax during the heating time.

The lack of ongoing wax absorption at 80°C suggests that little material is lost during up to 80°C , and that the reduction of visible wax at 120°C is due to pre-experiment absorption of wax between 80 and 120°C during equilibration.

A repeat of the original temperature ramp experiment was carried out using the unfilled wax and the cobalt aluminate containing shell. The results are shown in Figure 3.13.

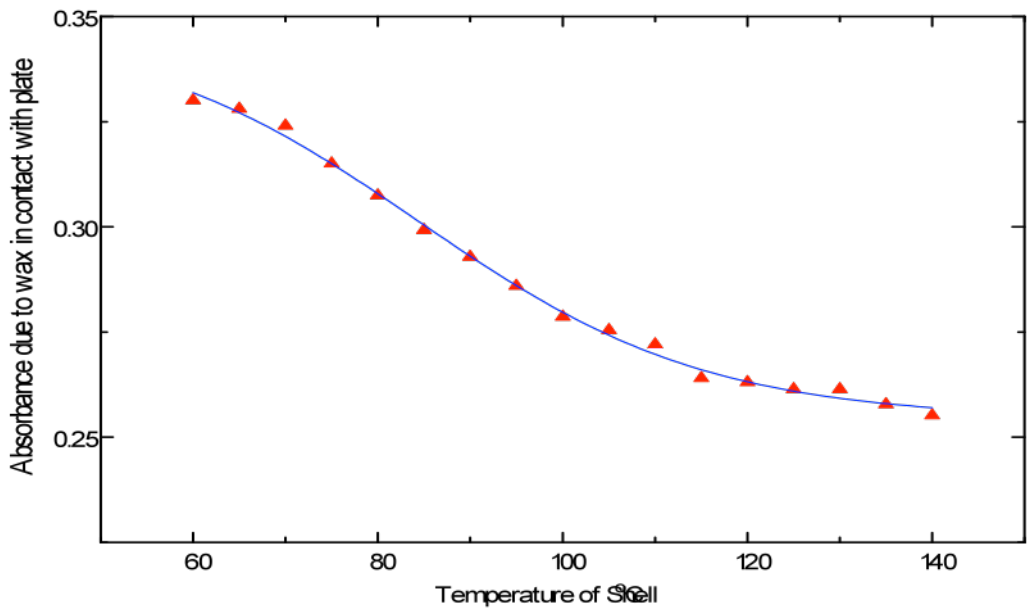

Figure 3.13 Absorption of unfilled wax into cobalt aluminate shell.

The results above demonstrate a similar sigmoid curve, albeit one which is shifted slightly to lower temperature.

Thus the same isothermal experiments were carried out as before using the unfilled wax and the cobalt aluminate shell. (Figure 3.14)

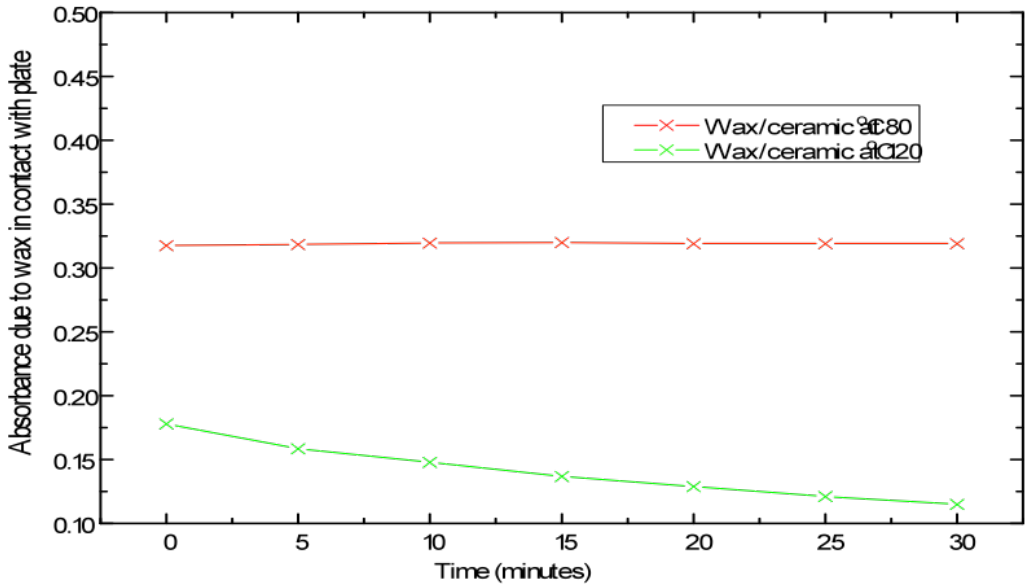

Figure 3.14 Absorption of unfilled wax into cobalt aluminate shell at two temperatures.

The same effect as observed for the regular shell is seen here where there seems to be a fast initial "equilibrium" absorption which is substantially greater for the 120°C experiment, and then at 120°C there is a slower ongoing absorption.

This equilibrium effect might possibly influence wax behavior in the autoclave. Whilst it has not been possible with these experiments to externally pressurize the wax, the contact area between the wax and the ATR accessory has been held at around 30,000 psi.

Thus these result may indicate that wax does not fully migrate into some primary layers after 24 seconds in the autoclave when the wax first melts, but perhaps is only absorbed effectively when the wax reaches 120°C , far later in the autoclave cycle.

If this is indeed the case then the implications are profound in that at least some shell formulations might have to endure a higher internal wax pressure during the autoclave cycle.

There is separate anecdotal evidence that the use of dusty refractory can impede flow of wax into primary layer and can result in a higher probability of shell cracking. This would correlate with the dust further impeding wax absorption into shell.

3.3 Results from minor experiments.

Once it had been ascertained that the wax had migrated sideways through the primary, the question was asked as to whether the migration was as well as the wax penetrating into the backup layers or instead.

Figure 3.15 shows a stained sample of shell which shows that when the wax has been able to migrate sideways through the primary layer, it does not penetrated into the backup layers.

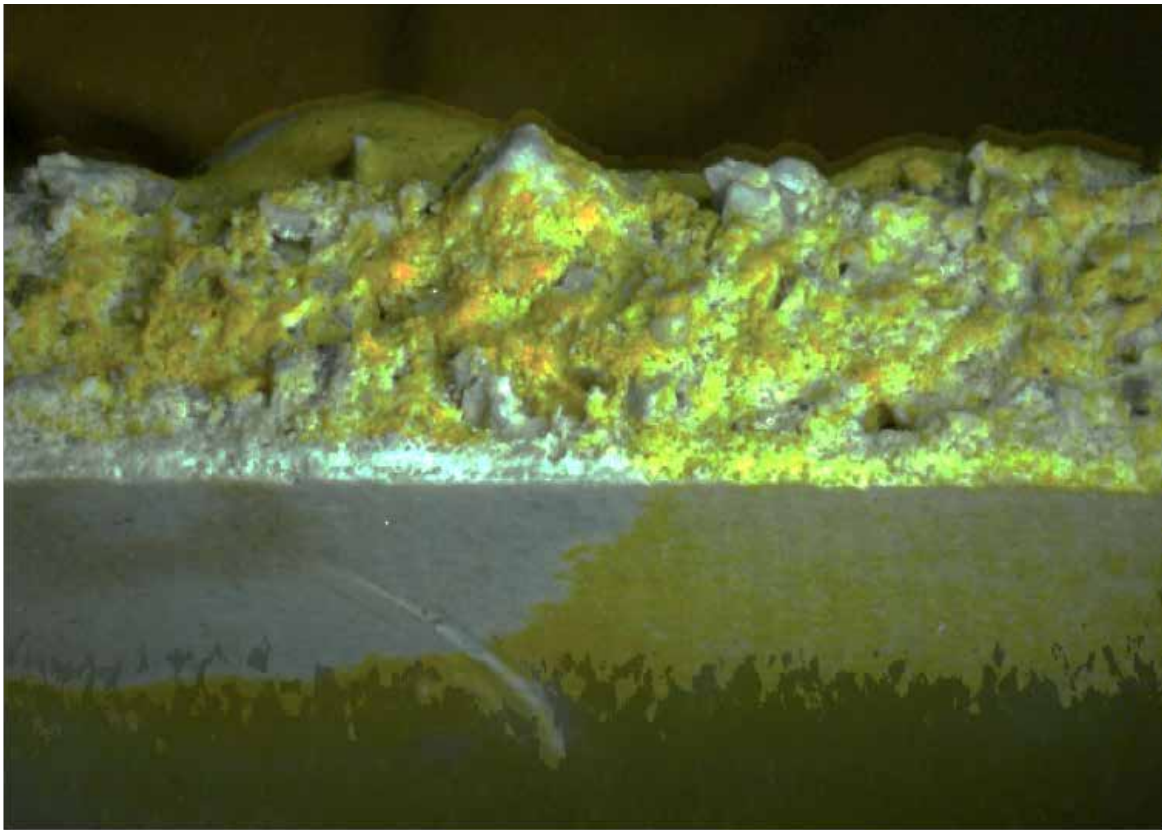

Figure 3.15 Absorption of unfilled wax into shell showing spread and limited penetration into backup layers.

The same experiment was carried out where the spread of wax through the primary layer was constrained by scoring of the primary layer. Where the spread of wax was constrained, wax penetration into the backup layers was observed (figure 3.16). In practice, there would normally be wax over the entirety of the primary layer, and no spread of wax would be possible.

It is however possible to envisage a situation where one part of the wax might melt before an adjacent section, and spread migration could in theory limit absorption of the latter melting section.

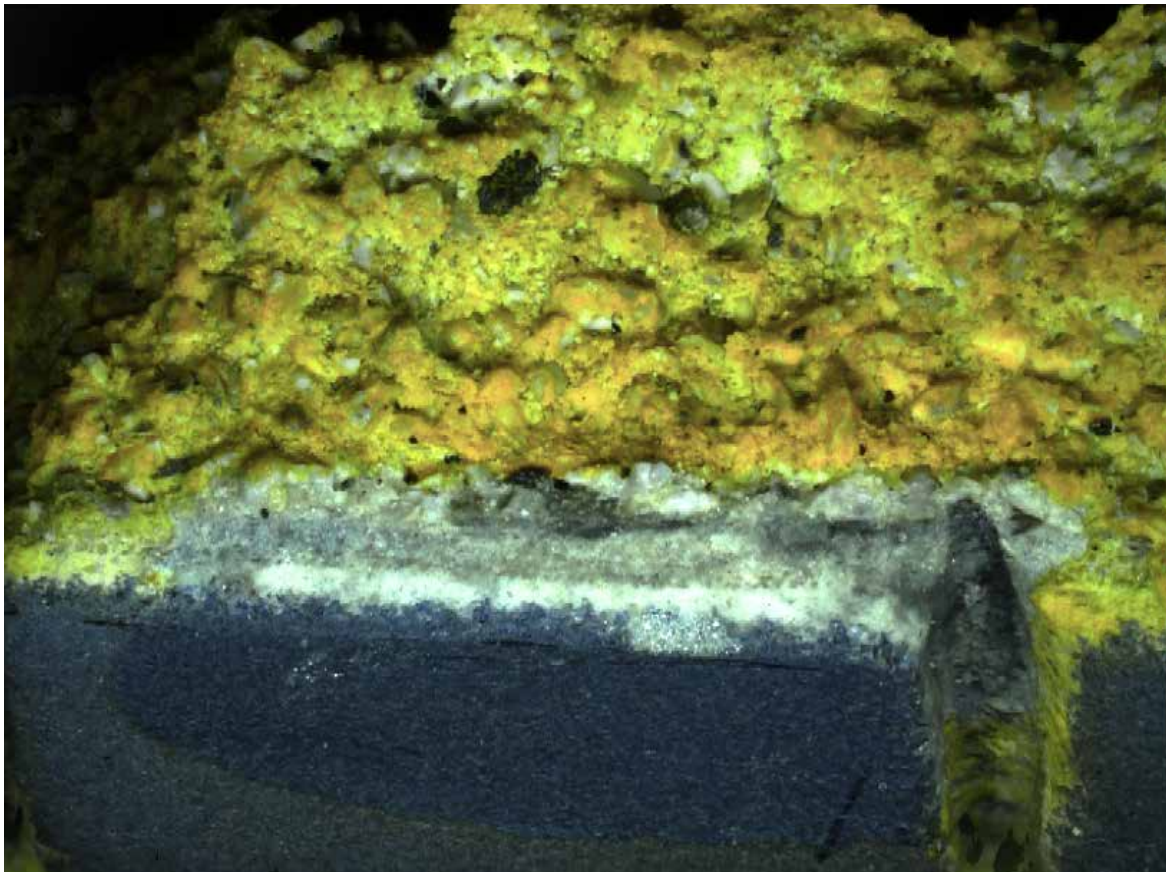

Figure 3.16 Absorption of unfilled wax into a constrained area of primary shell showing penetration of wax into backup layers.

4. Conclusions.

What was intended to be a comparison of how quickly three waxes migrated into a portion of shell has produced results which warrant further investigation.

The second question posed at the beginning of the paper (variation of wax absorption) was based on the assumption that there would be a simple kinetic process where wax would be absorbed faster at higher temperatures.

The possibility that wax absorption might be a temperature moderated equilibrium, and one which was sensitive to shell composition was not an idea that was entertained at the start of the work.

Compared to this shell absorption equilibrium effect the minor variations due to rheological processes are probably inconsequential. By 80 or 120°C , most waxes will probably be fully molten. Thus, whilst the answer to the first question posed is that drop melt point does not precisely predict wax yield temperature, though compared to the equilibrium effect, it is accurate enough.

Whilst it has not been possible to duplicate the pressure conditions which might exist within a foundry shell once the wax has begun to expand, the observed reluctance of shell to absorb wax at close to wax melt temperatures can only contribute to the pressure exerted by the wax on the shell.

The autoclave process would thus appear to be more of a "knife edge" process than one might otherwise expect and relatively minor process changes might therefore have a disproportionate effect.

5. Further Work.

From the results presented here, at the moment it looks like wax melting characteristics are not worth further investigation.

What is far more important to investigate further is the shell absorption effects. FTIR is a good technique for detecting the presence of wax within the ceramic matrix of a shell.

It might yet prove possible to coat a model primary layer directly onto the surface of the diamond. The 30,000 PSI clamp system could then be used to pressurize a wax sample directly onto the shell layer, and record the rate at which the IR absorption attributable to the wax increases, both with time and temperature.

It is also worth investigating whether other techniques might be used to study the absorption of wax into shell, and perhaps could verify whether the effect observed here occurs in real autoclave conditions.

6. Thanks.

Thanks go to my colleagues in the Remet UK laboratory, especially Matthew Everden, our most recent addition to the Remet UK laboratory, for working his way through seeming endless sequences of FTIR spectra.

Thanks also go to the ICI member foundry who provided the samples we used for the testing.

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