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Adhesion tension force between mould and pattern wax in investment castings

Kevin Lee *, Stuart Blackburn, Stewart T Welch

Abstract

5   The adhesion tension of commercial filled and unfilled waxes in contact with a representative ceramic shell system used in investment casting was determined by the Wilhelmy plate method. The average adhesion tension force of four filled waxes reduced at a rate of approximately 6.0×10^{-8} Nmm^{-1}°C^{-1} and the unfilled wax at a rate of 3.4×10^{-8} Nmm^{-1}°C^{-1}. Adhesion tension measured by Wilhelmy plate method was compared to the surface tension of wax measured by the Du-Nuoy ring method. It is suggested that Du-Nuoy ring method is

10   the simplest practical experiment to obtain the characteristics of wax-shell interaction for modelling applications.

       Keywords: Wilhelmy plate method, adhesion tension, surface tension, pattern wax, investment casting shell, de-waxing

15   **Introduction**

       A key step in the investment casting process is the removal of the wax from the mould. During the de-waxing process, the heating rate is rapid; so that bulk expansion of the wax does not occur before a proportion of the wax melts and flows from the mould or penetrates the shell. This is due to the wax having a lower thermal conductivity but a greater thermal

20   expansion coefficient than the shell. This difference of thermal expansion would otherwise cause the shell to crack. Peter Wang (2012) has described the way stresses can be relieved, by:

- propagating an existing crack or defect (fracture toughness)
- absorbing the force exerted by wax on the shell (strength)

25 - allowing the wax to flow through the shell (permeability)
- removal of wax before critical stress values are reached

       It is believed that permeability and strength of the ceramic shell are the two most critical properties to prevent shell cracking. Surface tension (γ) is an important parameter that influences the penetration of wax into the porous shell and the flow of molten wax out of the

30   mould. It is however, not understood if the interaction of the investment casting ceramic's surface energy with the wax in terms of contact angle is significant. Gebelin *et al.* (2004) used computer modelling to understand the wax penetration into shell and made the assumption that the contact angle of wax and ceramic was zero.

In this paper, the adhesion tension, $\gamma \cos(\theta)$ where θ is the contact angle is determined using the Wilhelmy method and compared to surface tension measured by Du-Nuoy ring to establish an estimate of ceramic-wax interaction.

The flow of liquid (wax) into porous materials is governed by the Washburn equation (Washburn, 1921).

$$\frac{dl}{dt} = \frac{r}{\mu} \frac{\gamma}{4l} \cos\theta \qquad\qquad 1$$

where r is radius of pores (m), μ is the viscosity of permeate (Pa.s) and l is the depth of penetration (m)

The equation is derived from the Poiseuille's law where volumetric flow rate is replaced with length of fluid flow over time. Hagen-Poiseuille equation is used to describe flow of liquids passing through tubes (horizontal capillaries) and neglecting the effect of gravity (figure 1). The length of penetration L_{lf} can be simply found by integrating the Washburn equation,

$$L_{lf} = \sqrt{\frac{\gamma D_e \cos(\theta)}{4\mu} t} \qquad\qquad 2$$

where D_e is diffusivity (m^2.s^{-1}), μ is viscosity (kg.m^{-1} s^{-1}), t is time (s)
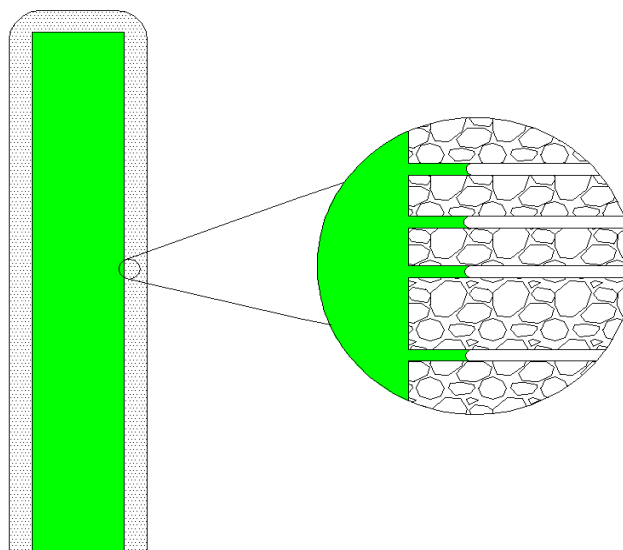
Figure-1 Schematic representation of the initial de-waxes process where wax is forced into the porous ceramic shell. In the models where Poiseuille is assumed, the pores are represented as horizontal tubes

Masoodi & Pillai (2010) showed how Darcy's law can be integrated with the continuity equation (volume-averaged liquid velocity in all directions is equal to zero) to give equation 4

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in which the surface tension effect is taken into account. Darcy (1856) had showed flowrate of permeates can be described as,

$$Q = \frac{-kA}{\mu}\frac{(P_b - P_a)}{l}$$ 3

where Q is the flowrate of permeate (m^3s^{-1}), A is the surface area pores (m^2) and (P_b-P_a) is the pressure difference across the porous media (Pa)

5   The integration gives equation 4 which has similar form as equation 1. It can be seen that both equations require surface tension, contact angle, viscosity and either permeability or diffusivity.

$$L_{lf} = \sqrt{\frac{2Kp_c}{\varepsilon_f \mu}t^2}$$ 4

where K is permeability (m^2), ε_f is porosity, $P_c = 2\,\gamma\cos(\theta)\,/r$ and r is the radius of capillary

The permeability of wax into the shell has been previously measured by Cendrowicz (2004).
10 He forced molten low viscosity gate wax through the shell and measured the flow rate. A permeability of 1100 ± 400 nm^2 was obtained for a standard ceramic shell used to cast steel. In some cases, permeability is measured using gas instead of wax. However, Hendricks *et al.* (2002) state that permeability measurement using gas is less indicative of the de-wax process. They found that this is due to the possibility of inherent variability in the permeability test
15 where the gas flux takes into account the resistance time of gas flow through the shell. Ideally, the test should simulate the actual condition of the de-wax autoclave to obtain a similar pressure difference across the shell where the pressure of steam is pushing in the opposite direction to the wax flux. Henderson *et al.* (2005) and Civan (2001) predicted the permeability of porous media as a function of porosity. Henderson *et al.* (2005) claimed that the equations
20 being used are suitable for heterogeneous porous media. Researchers have demonstrated the use of the Kozeny-Carman equation, which yields permeability as a function of porosity (Latief & Fauzi, 2012), (Xu & Yu 2008). However, Civan (2001) realised the Kozeny-Carman equation does not incorporate a gate effect term, which relates to the pores morphology on the shell surface, for porous media and showed that if this were incorporated the
25 permeability could be accurately predicted. Civan (2001) has validated his model using gypsum and quartz. This model could be applied to shell materials if the porosity was sufficiently well defined. The methods discussed above give a good approximation to obtain the permeability of shell to be substituted into equation 2 or 4.

Obtaining the depth of wax penetration into the shell using equation 2 or 4 and with a known
30 shell surface area would allow the prediction of total volume of wax that penetrates the shell pores. This penetration potentially reduces the hoop stress in the shell. Two of the most common methods to measure surface tension are the Du-Nuoy ring and the Wilhelmy plate. Torres (2003) is one of the few researchers who have used the Du-Nuoy ring method to

determine the surface tension, γ of wax. He found the surface tension of wax varies between 2 to 3 x 10^{-5} N.mm^{-1} depending on temperature and wax type. In this paper, the Wilhelmy method which measures the adhesion tension, $\gamma \cos(\theta)$ was compared to the Du-Nuoy ring method to determine if the contact angle between the wax with the ceramic is an important factor. Most Du-Nuoy rings are made of platinum where the contact angle of most liquids on the surface of platinum can be assumed to be zero as platinum has high surface energy. If this method is used, it would not adequately represent the interaction between wax and ceramic. Adhesion tension is suggested as a complimentary measure to surface tension because other solids may have surface energies significantly different to platinum. If the Du-Nuoy ring method is used then the contact angle would have to be measured separately and at an elevated temperature this becomes an issue due to light diffraction and reflection and therefore, errors can be significant. Comparing adhesion and surface tension allows the contribution of contact angle to be established. The general equation to obtain the surface tension, γ using the Wilhelmy method is:

$$\gamma = \frac{W_g}{l \cos \theta} \qquad\qquad 5$$

where W_g is the force observed (N), l is the perimeter of the rectangular plate (m) used in this test and θ is the contact angle of liquid with plate.

Harkins & Harkins (1929) show that the surface tension force from the Du-Nuoy ring method can be calculated using:

$$\gamma = \frac{W_g}{4 \pi R} \times F \qquad\qquad 6$$

where γ is the surface tension (Nm^{-1}), and R is the radius of the ring (m). F is correction factor.

Materials and Methods

Primary slurry used for steel casting was slip cast into 20 x 80 mm rectangular bars. The formulation of primary slurry is shown in Table 1. These bars were then dried and sintered at 1650°C for 2 hours, with a ramp rate of 10°C·min^{-1}. X-ray Diffraction (XRD) was carried out after the sintering process to confirm no dissociation of zircon had occurred (figure 2). Pavlik Jr. & Holland (2001) have shown that zircon converts to zirconia and silica at 1676°C. The high sintering temperature was selected to allow full densification of the zircon, preventing wax absorption as the sample bars were dipped into the wax. The authors are aware that there could be an induced error compared to evaluating the un-sintered sample due to changes in the state of the silica binder and other minerals present and it will be discussed later how the accuracy of the method would be lost if the un-sintered samples were used. The initial bars were then cut into approximately 20 x 10 mm rectangular bars. The bars were polished using

P400, P1200 and P2500 polishing papers consecutively with water for lubrication. This was performed on the Buehler Metaserv 2000 grinder polisher at 200 r.p.m.

Initial formulation	Mass (%wt)
Filler (zircon flour)	79.83
Binder (silica)	17.00
Polymer	1.20
Wetting Agent	0.06
Antifoam	0.10
Deionised water	1.81

Table 1 Standard steel primary slurry composition
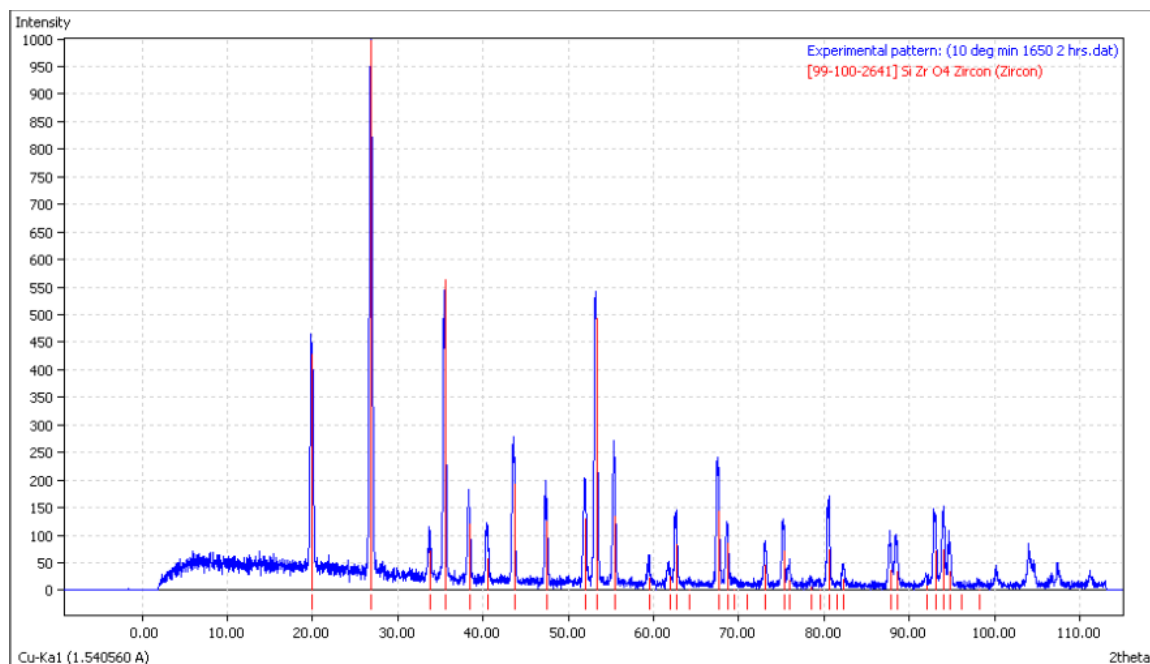
Figure -2 XRD data showing the ceramic made of primary slurry remain as zircon and did not be dissociate during the sintering process

Samples were rinsed with ethanol to remove any organic material prior to testing. The washed sample was crocodile clipped to a wire of 0.2 mm diameter attached to a microbalance, the wire passing the through the top of the oven. This arrangement supported the sample just above the wax surface. The ceramic and wax were slowly heated to the required temperature and left for a further 10 minutes to equilibrate. Approximately 10 g of solid wax was melted in a glass container for each test.
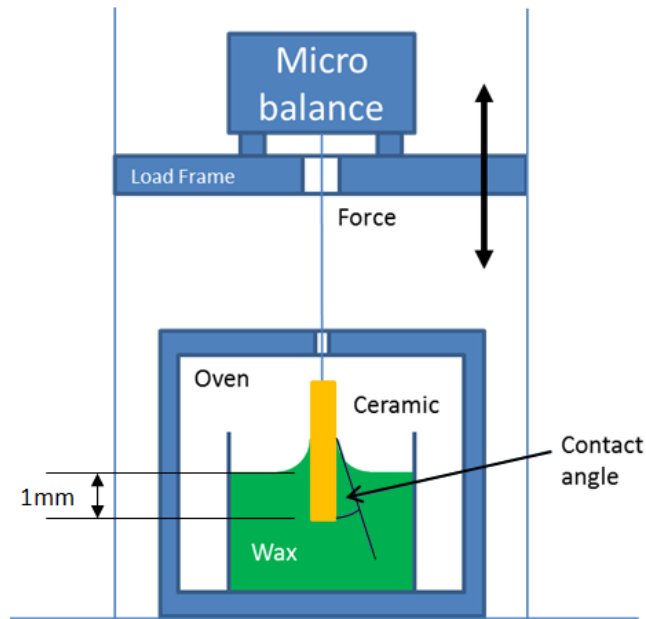
Figure -3 Wilhelmy plate method setup in an oven using a load frame to submerge the ceramic into the molten wax and then emerge it from the same wax. The maximum submersion depth was 1 mm

Dynamic Wilhelmy plate method was used to evaluate the adhesion tension force. The
5   bottom surface of the ceramic sample was immersed into the molten wax to a depth of 1 mm
from the surface of wax at constant velocity of 1 mm·min^{-1} and removed at the same rate
without a hold period (figure 3). The removal continued until a constant weight was recorded.
A typical submersion-retraction curve was shown in figure 4. There was an instantaneous
increase of weight as the plate touched the liquid followed by a period of weight reduction as
10   the plate penetrated the liquid, displacing more liquid by submersion (line α to β, figure 4).
After submerging for 1 mm into the liquid, the sample was retracted. During this stage, the
adhesion force continued to increase (line β to χ, figure 4). The force measured represents
the adsorption of liquid to the surface of the ceramic. The higher the adsorption energy, the
higher the adhesion force and the smaller the contact angle will be. When the plate was pull
15   away from the surface of the liquid, a constant weight which was the weight of liquid wax
that remained on the surface of the plate was recorded (line δ to ε, figure 4). The advancing
and receding forces were averaged to obtain the adhesion tension value (figure 4). It is
important to note that the maximum receding force effectively contains an offset equivalent
to the residual wax weight left on the test bar and this is subtracted before calculating the
20   mean mass. The calculated mass is converted to force. The system of measurement was
calibrated using borosilicate microscope glass slide and water at varying temperatures from
room temperature to 68°C. The measured surface tension of water agreed with the literature
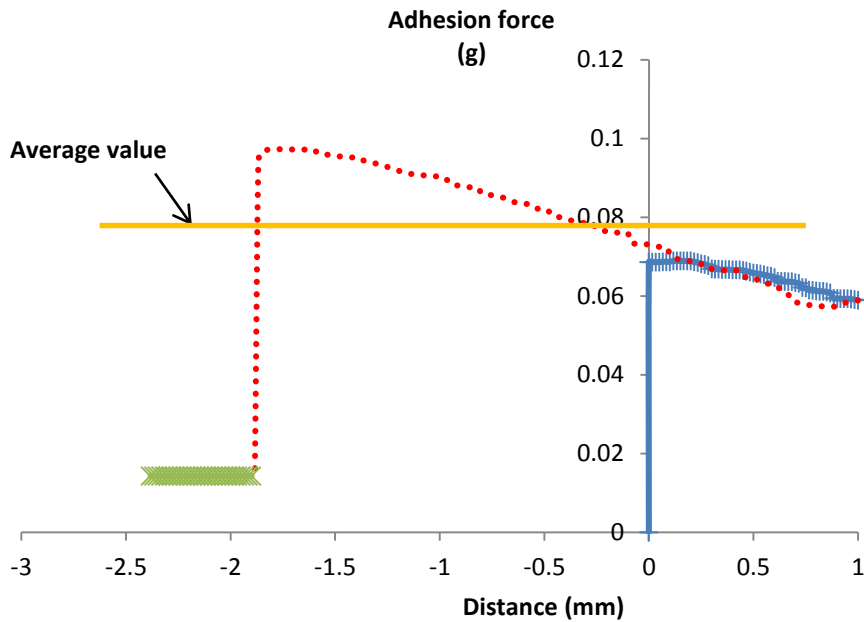(Kawanishi, et al., 1970) (Vargaftik, et al., 1983).

Figure -4 A typical submersion – retraction curve for wax A, α to β ▬ showing submerging of samples into wax, β to χ
• • • • • is emerging and δ to ε ✕ plateau of weight after lifting. It shows the advancing and receding force of wax A in
this case did not have any obvious hysteresis behaviour. The horizontal orange line shows the averaged adhesion tension
value

Du-Nuoy Ring method requires correction because in the ring method it has an additional
volume of liquid which is lifted during the detachment of ring from the interface where the
three phase contact line is twice the circumference of the ring (inside and outside of the ring).
Adamson (1964) suggested that the Wilhelmy method gives reliable results without any need
for correction. Kawanishi *et al.* (1970) however suggested a correction equation for adhesion
tension measured using Wilhelmy method, equation 7.

$$\sigma_{corrected} = \sigma \frac{[1 - (s - S)]}{\left[1 + (\frac{l_o}{L})\right]} \qquad 7$$

where σ is the adhesion tension force observed, S is the surface area of vessel containing
liquid, s and L is cross sectional area and peripheral length respectively of the sample. The
value of l_o for plate geometry used ranges from -0.08 to -0.1 mm. Kawanishi *et al.* (1970)
found that the l_o being used is independent of material and purely dependant on geometry.
In this case, a value of -0.09 was used.

The correction factor combines the meniscus correction and the peripheral correction.
Meniscus correction is to compensate for the slight lowering of the liquid surface as certain
amount of liquid is required to form the meniscus around the plate. The peripheral correction
is to include the correction term, l_o into the geometrical peripheral length, L to obtain the
effective peripheral length of the plate which is expressed as L+l_o.

In Du-Nuoy ring tests, a platinum ring was used to replace the ceramic plates (Figure -5). The setup of the system remained the same but for the substitution of the ring. In this case, the correction factor for surface tension in Du-Nuoy rings ranges from 0.87 to 0.86 for a temperature range of 90 to 170°C respectively. The correction factor changes as the surface tension force of ring reduces with temperature.
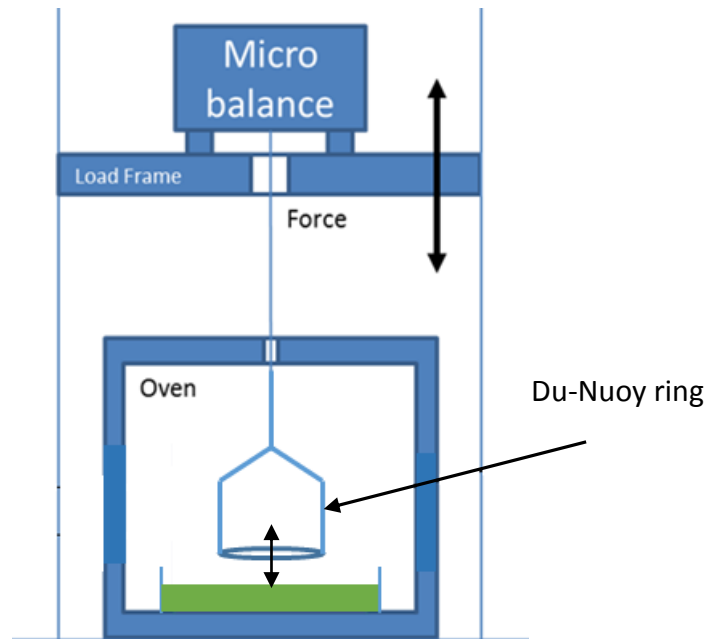

Figure -5: Schematic diagram with Platinum ring for Du-Nuoy ring test setup to replace the flat plate in Wilhelmy method

On a wax pattern tree, it is common to use unfilled wax for the sprue system and filled wax for the pattern of the part. Unfilled wax usually has a lower melting point and viscosity to increase the flowrate during dewaxing. Filled wax has better mechanical strength and reduced shrinkage for greater dimensional accuracy. Both are considered.

For both wax types, the Wilhelmy method and Du-Nuoy Ring methods have been examined. Five waxes, four were filled and denoted as A, B, C, D and one unfilled denoted E were studied. Figure 6 shows that the filled waxes contained different forms of filler. Waxes A and B appeared to contain a mixture of two filler types while waxes C and D contained only one filler form. However, the density of all wax was assumed to be 1000 kg.m^{-3} at 90°C and not to change with temperature for the purpose of calculation.
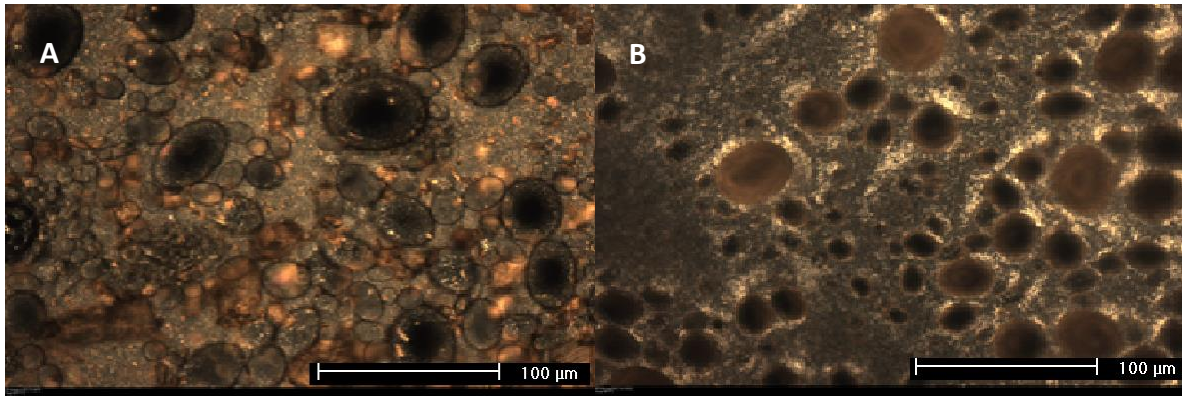
Figure -6 Selected transmitted light micrographs of the waxes (A) material A containing two filler forms and (B) wax C containing one filler form. The filler diameter ranged between 10 and 100 microns in both materials.

Results

For each material there was a linear fall of adhesion tension with temperature. The adhesion tension force of wax A for example reduces with temperature at a rate of 5.8×10^{-8} N·mm$^{-1\circ}$·C^{-1}. The linear relationship allows the data to be extrapolated to the temperature that is representative of the condition commonly used in dewaxing, which is approximately 180°C. The limitation of the equipment prevents the oven reaching 180°C. By extrapolation to 180°C, the adhesion tension force of filled wax was approximately 2.3×10^{-5} N·mm^{-1}. The adhesion force value can be inserted into equation 2 or 4 to calculate the depth of wax penetration into the shell providing that the viscosity and either the permeability or diffusivity are known.

Discussion

A linear relationship was found between the adhesion tension force between ceramic and wax with respect to temperature. The adhesion tension force reduced with increase of temperature in a manner similar to most materials (Torres, 2003) (Vargaftik, et al., 1983). The slope for unfilled wax was approximately half that of a filled wax (Figure 7). The adhesion tension of filled wax was greater and fell more rapidly with temperature compared to the unfilled wax. It was observed that the adhesion tension for filled wax at 170°C was similar to the unfilled wax at 90°C. In the filled waxes it appears that in the top 1 mm of the wax sample there is a progressive loss of particulate material until 180°C when the filled and unfilled waxes have similar adhesion tension values. This could be explained if the filled wax exhibit flocculation and/or sedimentation.
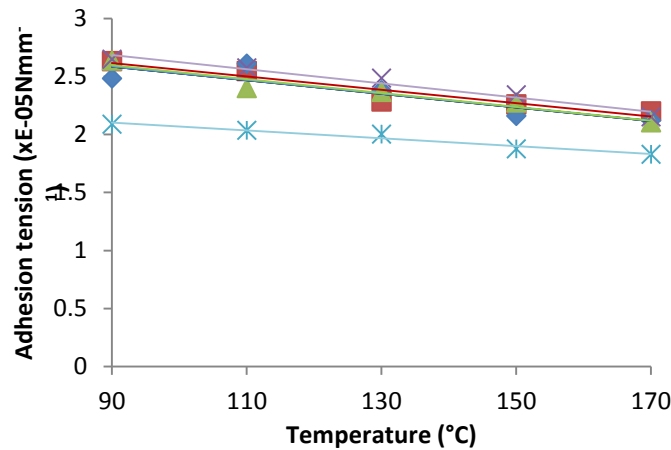
Figure -7 The adhesion tension force of molten wax is averaged and plotted as above ■ A, ◆ B, ▲ C, ✕ D, ✳ E wax. It is observed that unfilled wax has a different gradient to the filled wax when adhesion tension plotted against temperature.

5   The sedimentation rate would increase with temperature because the viscosity of the based wax would reduce with temperature. This is in accordance with Stokes's law which shows that the frictional force between the fluid and particle is proportional to the dynamic viscosity of the fluid. This is also supported by Torres (2003) work, where he observed sedimentation in filled pattern waxes while undertaking rheological studies at elevated temperatures.

10   Furthermore, increased Brownian motion with temperature and greater collision intensity may lead to greater filler flocculation and an increase in sedimentation velocity according to Stokes's law. Barnes *et al.* (2005) stated that flocculation is strongly size-dependent; it is only influential when the particle size is below 1 μm. Even if it is only smaller particles which flocculate by this mechanism, sedimentation may well account for the more rapid fall in

15   surface tension with temperature which is observed in the filled waxes compared to the unfilled. The reduction in adhesion tension of the unfilled wax with temperature was mainly controlled by the entropy of the system as no sedimentation was occurring. Thus, the tension force reduces to a lesser extent than in the filled wax as temperature increases.

The average pores diameter of the shell system fired under the conditions used in casting was

20   131.2 nm measured using the mercury porosimetry and porosity on the inner surface of shell (primary layer) is known to be smaller than the average porosity and structure can therefore act as a filter. Figure 8 shows wax fillers that were 'filtered' onto the inner surface of the mould. Thus, it would be more representative to measure the tension force of the waxes when the particles are sedimented from the carrying wax.
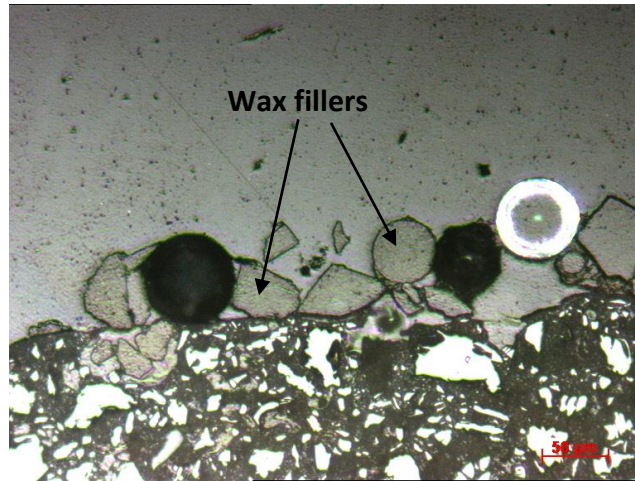
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Figure -8 Morphology of wax on inner surface of shell after de-waxing process with fillers particles remains on the surface

To compare the adhesion tension to the surface tension, the contact angle has to be measured or assume to be zero. For Wilhelmy method, the system is most likely to have zero contact angles if there is no contact angle hysteresis between the advancing and receding curves. Sauer & Nicholas (1991) suggest that hysteresis is only observed when the contact angle is greater than zero. This also means that if hysteresis is not observed, contact angle can be reasonably assumed to be zero. Figure 4 which represent wax A shows a slight contact angle hysteresis which is sufficiently small to be considered negligible. The slight hysteresis could be due to sample surface preparation error or even surface contamination. This was observed for all the tested waxes. Surface tension obtained by assuming the contact angle to be zero provide very similar results compared to the surface tension measured using Du-Nuoy ring method. This shows that the surface energy of a ceramic was similar to platinum. It was suggested that zero contact angle between wax and primary slurry ceramic is a reasonable assumption to be made. Torres (2003) showed that the surface tension of wax decreases with increased temperature and generally there was an increase in surface tension with filler addition. Torres (2003) obtained surface tension values between 2 to 3 x 10^{-5} N.mm^{-1} using the Du-Nuoy Ring method with varying fillers and wax compositions.

Figure 9 shows that there is a small difference in the surface tension value measured using the ring method and those reported by assuming the contact angle to be zero for the results obtained from Wilhelmy method. This difference could be coming from the correction factor value used for ring method. The error could occur because the density of wax is assumed to be 1000 kg·m^{-3} and not change with temperature. Another possible reason could be that the contact angle is not actually zero. The slight hysteresis in figure 4 supports this hypothesis. The difference could also be caused by the material preparation where the surface is not completely smooth and contains pores despite the sintering and polishing process. However, the two experimental comparisons between Wilhelmy method and Du-Nuoy ring method of wax A showed that the interaction between the wax and ceramic is not significant. The contact angle of wax with ceramics is insignificant. For practical experimental work it is suggested Du-Nuoy ring is a simpler method. The corrected and uncorrected adhesion tension

forces are similar as shown in figure 9. Both lines have the same gradient but a slightly different intercept. This also shows that correction factors applied when using the Wilhelmy method are not significant in the case of molten waxes. It is suggested that the correction factors is unnecessary if Wilhelmy method is used.
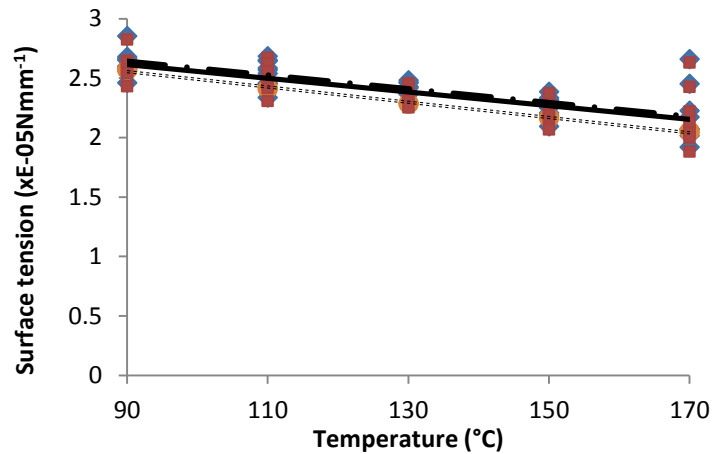

Figure -9 The surface tension force of molten wax is averaged and plotted as above Wax A. ◆ adhesion tension, ● corrected surface tension, ■ corrected adhesion tension, ▬ · ▬ Linear (adhesion tension), ───── Linear (corrected surface tension), ▬▬▬ Linear (corrected adhesion tension)

The assumption made in this paper is that the hydroxyl group on the surface of the sample were not changed during the sintering process where the sample was heated to 1650°C. The material surface would change when the organic compounds and hydroxyl group are burnt off. A test to compare the effect of organic compounds and hydroxyl group on sample surface is not trivial as the un-sintered sample would absorb the wax into the pores and resulting in a non-repeatable result. It is suggested that a larger number of tests would be required to acquire a sufficiently reliable result and would be beyond the requirements of most practicing experimentalists in the field.

Conclusion

- The results show no significant difference between the Wilhelmy and Du-Nuoy methods if the contact angle between ceramic and wax is assumed to be zero. This indicates that the contact angle parameter can be set to zero when modelling the wax behaviour during the dewax process of investment casting.
- It is suggested that the average surface tension value of filled wax should be representative for most filled wax simulation and unfilled wax value is half that of the filled wax.
- Du-Nuoy Ring method has shown to be more practical and provided a more repeatable result.
- If the Wilhelmy method is used, it is suggested that the application of the standard correction factors is unnecessary as the difference in the reported values are not significant within the errors of the test method.

Acknowledgement

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