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I am submitting herewith a thesis written by Robin Woracek entitled “Wetting Behavior of Polymer Melts with Refractory Coatings at High Temperature”. I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Engineering Science.

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Wetting Behavior of Polymer Melts with Refractory Coatings at High Temperature

A Thesis
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ABSTRACT

Within the scope of this thesis, an experimental system has been designed, developed and manufactured for the determination of the wetting behavior of liquids and polymer melts with solid surfaces (coated and uncoated) at high temperatures (> 200 ºC). The measurement system incorporates a modified Wilhelmy plate technique, using a precision weighing module, a vertical linear stage, custom developed application software using LabView with suitable hardware and a high temperature furnace with thermocouple feedback control. Experiments have been performed and are reported to evaluate the performance of the testing system, using liquids of known wetting properties. A suitable testing procedure based on dynamic Wilhelmy plate theory is proposed, involving investigation of advancing and receding liquid-probe interactive forces and hysteresis loops.

Interfacial wetting and wicking behavior of polystyrene melt with clay based refractory coatings, as used in the lost-foam casting (LFC) process, are presented a function of temperature using this measurement system. Experiments of particular interest were performed for two different types of refractory coating and for polymer melts at processing temperatures between 220°C and 300°C, where they show pronounced viscoelastic behavior. Different variables, obtained from the hysteresis loops, were utilized as quantitative indicators for comparison, including the area under the loop from contact onwards, the slope of advancing and receding lines in the force-displacement domain, the force hysteresis at zero displacement and Fast Fourier Transform (FFT) analysis of the hysteresis loop.

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List of Abbreviations

LFC	Lost Foam Casting
PS	Polystyrene
EPS	Expanded polystyrene
et al.	Latin: et alii (and others)
CFD	Computational fluid dynamics
GUI	Graphical user interface
RT	Room temperature
Pt	Platinum
e.g.	Latin: exempli gratia (for example)
i.e.	Latin: id est (that means, in other words)
FFT	Fast fourier transform
PC	Personal Computer

List of Symbols

q	Contact angle (general)
q_0	Static contact angle
g	Surface tension
F_{corr}	Corrected force
p	Perimter of probe
F_0	Measured force
r	Density
A_{Probe}	Surface area of probe
h	Immersion depth
g	Gravitational constant
q_a	Advancing contact angle
F_a	Advancing force
q_r	Receding contact angle
F_r	Receding force
t	Thickness of probe
w	Width of probe
v	Probe velocity

Chapter 1: Introduction

Lost foam casting (LFC) is a technology that facilitates fabrication of near-net shape parts by using expanded polystyrene (EPS) patterns coated with refractory slurry, and packed in unbonded sand that is compacted by mechanical vibration. EPS foam used in the LFC process is made from amorphous, linear polystyrene with a molecular weight ranging from 150,000 to 500,000. For a typical Aluminum casting, EPS foam has a density in the range of 0.020–0.030 g/cc and an average cell diameter ranges from 50 – 1500 μm depending on the product [1]. If subjected to heat, EPS bead loses structural rigidity at about 120 °C, becomes viscous at about 220 °C, and almost fully volatilizes at about 430 °C. The average heat of degradation of the EPS foam is ~190cal/g. The heat from the molten metal that is poured into the mold, acts as a source for chemical degradation of the polymeric foam and the metal eventually takes the shape of the pattern. A complex lost foam casting pattern is generally an assembly of smaller sections glued together and dipped into water-based refractory slurry and dried to provide a rigid coating. After the drying operation, the coated foam pattern is placed in a steel casting chamber and packed with unbonded silica sand to fill all the pattern cavities. The sand is compacted by mechanical vibration to provide mechanical structure to the compacted mold. Molten metal is then poured down through the sprue. The foam pattern degrades and permeates into the loose sand as the coating absorbs heat from the molten metal and eventually the target shape is obtained as metal replaces the expendable pattern. The final casting product is obtained by removing the sand and sand blasting off the refractory coating. Refractory coating applied on the polystyrene (PS) foam pattern surface plays a key role in controlling the metal flow and the overall success of the LFC process, as the PS foam is replaced by molten metal when the casting mold is filled.

Early modeling of the LFC process was done by Ohnaka [2] and Sun et al. [3, 4] simulating the effect of backpressure in the LFC process. A finite difference code (FLOW3D), developed by The Flow Science Institute [5] offered a mold filling simulation. Liu et al. [6] developed a simple 1-D mathematical model predicting metal front velocity and backpressure of decomposed gasses for the LFC process. Recently, comprehensive modes of phase changes of expanded polystyrene foam during lost foam casting were considered by Caulk and co-workers [7, 8, 9] to model the complex casting process with good success.

The objective of the current study, reported in this thesis, on wetting and wicking behavior of PS with refractory coatings is to provide constitutive information within the context of using numerical computational fluid dynamics (CFD) type models to realistically represent the interactions of pyrolysis products of expanded polystyrene foam with refractory coatings during metal fill. Such investigation should also contribute largely to the characterization and subsequent evaluation of coatings with different material compositions.

Chapter 2: Experimental Setup

This chapter is a slightly revised version of a paper with the title „Wetting Behavior of Liquids and Polymer Melts at High Temperature: Experimental Setup" which was submitted for the Journal of Materials Research in September 2009 by Robin Woracek, Indraneel Sen, Dayakar Penumadu and Mark Hoover.

My primary contributions to this paper include: (1) development of the problem into a work, (2) identification of the study areas, (3) gathering and reviewing of literature, (4) designing and building building the experiemnetal apparatus, (5) choosing and implementing the instrumentation hardware, (6) writing the software, (7) performing the laboratory experiments, (8) interprestaionb and analysis of the test results and (9) most of the writing.

Abstract

A custom developed experimental setup and measurement protocol is described which can be used to determine the wetting behavior of liquids and polymer melts with solid surfaces (coated and uncoated) at temperatures between room temperature and 800ºC. The measurement system incorporates a modified Wilhelmy plate technique, using a precision weighing module, a vertical linear stage, custom developed application software using LabView with suitable hardware and a high temperature furnace with thermocouple feedback control. Several experimental results are reported using different probe geometries and immersion-emersion conditions to evaluate the performance of the testing system, using liquids of known wetting properties. A suitable testing procedure based on dynamic Wilhelmy plate theory is proposed, involving investigation of advancing and receding liquid-probe interactive forces and hysteresis loops. Wetting and wicking behavior of complex

liquids such as polystyrene melt with clay based refractory coatings are presented in a Chapter 3 as a function of temperature, using this measurement system.

2.1 Introduction

In the existing experimental procedures for the evaluation of such wetting behaviors between liquids and solids, one of the requirements is to know, or obtain, surface tension values for the liquid (in our case PS melt) and subsequently the determination of the advancing and receding contact angles between the liquid and solid surface. The surface tension values for PS of different molecular weights and weight distributions have been reported in literature, for a temperature range of 180°C to 220°C by using the pendant drop technique and the values have been compared with theoretical derivations [10]. The pendant drop method involves analysis of the shape of a liquid drop hanging from a syringe tip [11]. However, the pendant drop technique has serious drawbacks even at a temperature of 220°C, due to substantial polymer degradation and oxidation at long equilibration times (greater than six hours). The industry standard for processing temperature of polystyrene is approximately 230°C, where PS shows appreciable lowering of viscosity for optimized processing. Pendant drop technique at these temperatures would lead to enormous errors [12, 13], and thus it requires the need for a new approach that overcomes the identified drawbacks for temperatures from 220°C to 300°C.

The micro-Wilhelmy technique has been reported to be the most accurate method for the measurement of surface tension for moderate to high molecular weight polymers at elevated temperatures [12, 13] The micro-Wilhelmy technique incorporates the use of a clean glass

fiber (diameter approximately 10μm) as the vertical wetting probe instead of a roughened platinum plate, as used in the Wilhelmy plate method. Fast equilibration time is achieved for the micro-Wilhelmy technique due to the formation of small meniscus dimensions, achieved by the small diameter glass fiber. Other advantages of the micro-Wilhelmy technique are that the sample density is not required and only a very small sample volume is needed. The latter is essential in low thermal conductivity polymers like polystyrene, since a small volume ensures a thin layer of sample, and thus, rapid onset of steady state at target temperature, without appreciable thermal gradient. However, since the current study was essentially to obtain fundamental information about wetting and wicking behavior of refractory coating with molten PS, the micro-Wilhelmy method was not applicable. Since an appreciable mass of refractory coating on the surface of the probe is required for experimental accuracy, the dimensional requirement of the micro fiber probe would be violated.

Wetting of a solid surface by a liquid is characterized by the contact angle that a liquid drop forms with the solid interface. Liquids with a high surface tension will tentatively form a droplet, whereas liquids with low surface tension will spread out over a greater area (bonding to the surface). On the other hand, if a surface has a high surface energy, a drop will tentatively spread or wet the surface. If the surface has a low surface energy, a spherical droplet will form [14]. This phenomenon is a result of the minimization of interfacial energy, described by Young's equation,

$$0 = g_{SV} - g_{SL} - g \cos q \qquad (1)$$

where g_{SV} is the solid-vapor interfacial energy, g_{SL} is the solid-liquid interfacial energy, g is the liquid-vapor energy, e.g. surface tension, and q is the contact angle. It should be noted,

that Young's equation implies an ideal system with a smooth, homogeneous and hydrophobic surface which is chemically and physically inert with respect to the liquid [15]. Therefore in the micro-Wilhelmy technique for example, where a glass fiber with small diameter is utilized as the probe, nearly perfect wetting and a very small contact angle is assumed due to the comparatively high surface energy of glass with respect to molten PS [12, 16].

A liquid on a solid surface usually does not follow the behavior predicted by the Young equation. In a non-ideal/real system with rough and/or porous surfaces, a range of contact angles is observed instead of one unique contact angle [17]. Contact angle hysteresis is marked by the locus of the advancing and receding contact angle plots and occurs due to dynamic probing of metastable states as the liquid front advances or recedes over a rough or chemical inhomogeneous probe-surface. This observed hysteresis not only contributes valuable information, but also for the majority of polymer systems the "equilibrium" contact angle state is impossible to attain because of energy barriers between metastable states. A technique, only employing static contact angle measurements can therefore be misleading since an equilibrium state is never reached. For a complete characterization of the system the contact angle hysteresis, e.g. the advancing and receding contact angles, must be measured [18, 19].

Thus, a modified Wilhelmy approach including dynamic testing capabilities has been developed for our experiment. We also designed and assembled the appropriate instrumentation, capable of exploring wetting and wicking properties of other liquids and

melts in various solid/porous materials, especially at high temperatures that cannot be achieved with current commercially available systems.

2.2 Experimental

The static contact angle is given by equation

$$\cos q_0 = \frac{F_{corr}}{g \cdot p} \tag{2}$$

where F_{corr} is the measured force corrected for the weight of the liquid lifted up and p is the perimeter of the probe. Assuming the static contact angle q_0 to be zero, we can calculate the surface tension as:

$$g = \frac{F_{corr}}{p}. \tag{3}$$

If the objective is the determination of contact angle between refractory coating and polymer melt, then for the experimental practice, the surface tension of the melt must be determined first. This can only be achieved using a probe that will have a zero contact angle with the polymeric melt. In the next step, a probe with the same dimensions would need to be coated with the refractory coating, and then the contact angle (or advancing and receding contact angles) can be obtained by using the known surface tension. This will work for liquids with a variety of probe shapes and materials, but for viscoelastic liquids like polymeric melts, it is a) difficult to find a probe to form a zero contact angle and/or b) this probe will not be suitable for the application of refractory coating and vice versa.

Various alternative experimental procedures including static and dynamic equilibrium methods, each utilizing different probe materials and shapes, were explored to acquire information on wetting and wicking behavior of polymeric melt and refractory coating. As will be demonstrated, the modified dynamic Wilhelmy plate technique and the recording of force hysteresis loops were found to be the most suitable procedure.

2.2.1 Experimental Apparatus

The probe is attached via a hook and a rigid stainless steel rod to a precision weigh cell with a resolution of 0.1mg (Sartorius WZ124) and hanging straight down, as shown in Figure 2.1. The weigh cell is positioned on top of a rigid steel frame with a height of 100cm. The specimen, i.e., the liquid or polymeric melt situated in a glass beaker, is placed inside an adiabatic chamber, a compact furnace (Romanoff Jelrus Digi-Melt 8000N) with graphite crucible and ceramic insulator, which is mounted on a vertical linear stage. The furnace, having an inner diameter of 35mm and a depth of 110mm, is thermocouple feedback controlled using a K-type thermocouple and can reach a maximum temperature of 800°C. The custom made furnace lid is made of ceramic and has two narrow holes, one just big enough to feed through the probe attachment and the other one to feed through the thermocouple. The vertically mounted high precision linear stage (100mm travel, 58μm positional accuracy) is driven by a stepper motor. The entire apparatus is controlled by a custom graphical user interface (GUI) using LabView and National Instruments hardware (data acquisition and motor controller). When the system was used for investigation of polymeric melts, it was placed under a fume hood.

To verify the temperature uniformity within the furnace and thermal equilibrium within the liquid/polymer melt, one thermocouple was placed within a polymeric specimen and one inside the furnace, 10mm above the specimen. After choosing the target temperature, the furnace was turned on and as Figure 2.2 shows, the temperature within the polymeric melt follows the ambient temperature with an accuracy of ±2°C.

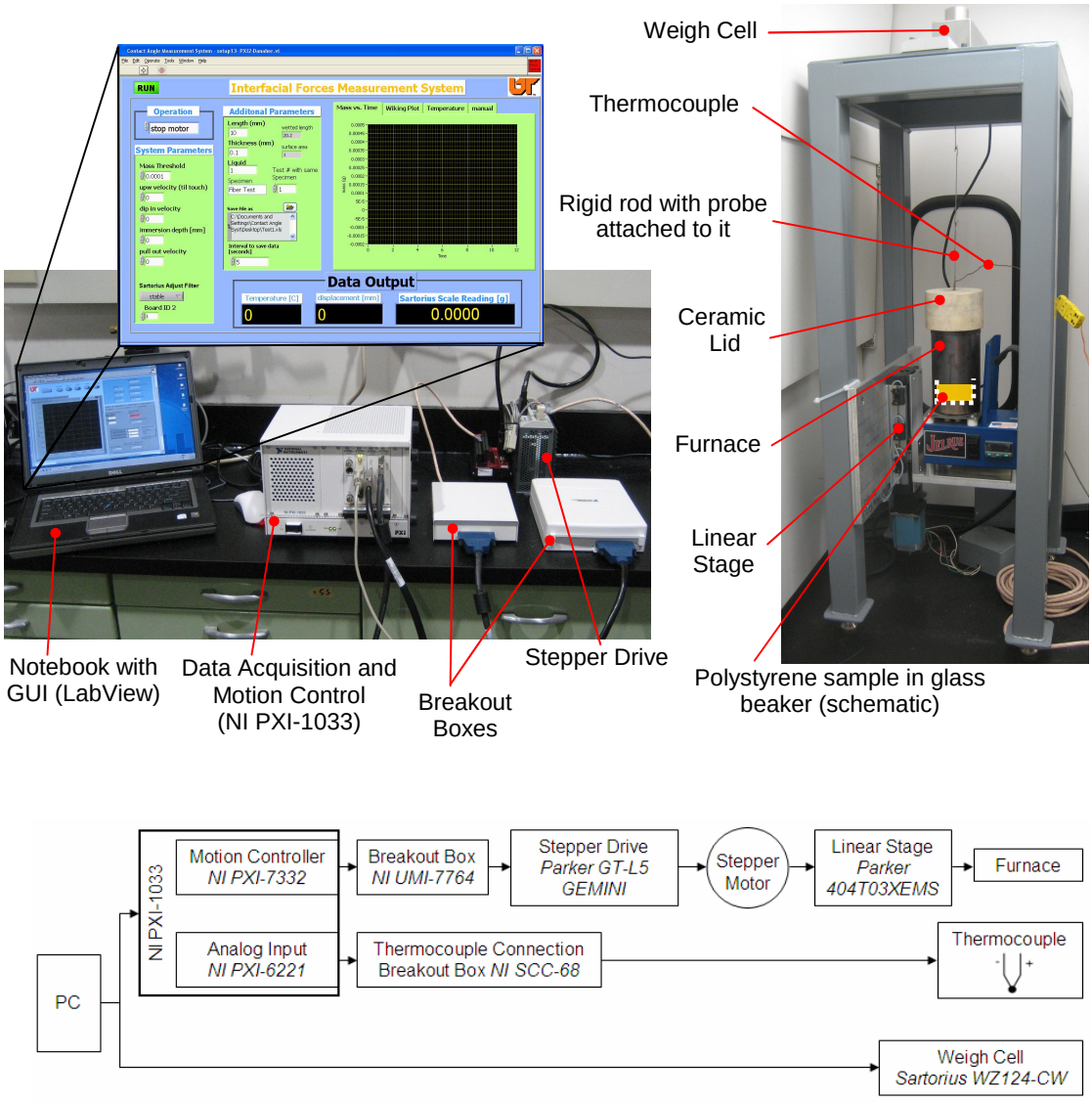


Fig. 2.1 Image (top) and schematic diagram (bottom) for experimental apparatus and instrumentation

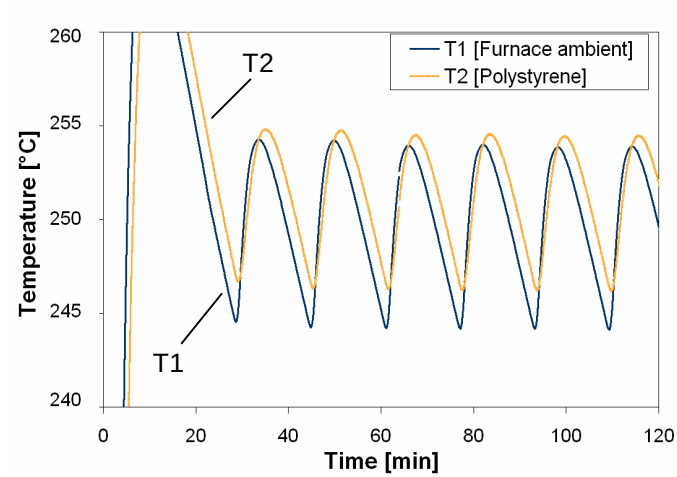


Fig. 2.2 Temperature in polymer and ambient temperature in furnace (Set-point: 250°C)

2.2.2 Experimental Procedure

Initially, a static equilibrium technique has been used and evaluated, and later a dynamic Wilhelmy technique was used and modified for the specific experimental needs. Both of these techniques were performed at different target temperatures.

In the static equilibrium technique [20, 21], the following steps are performed:

i. Probe is positioned above the liquid and the force value is initialized. The liquid surface is then moved towards the probe by using the linear stage at velocity $v_{approach}$.

ii. Liquid/melt surface comes in contact with the probe and records a force. For ideal liquids and for a zero contact angle with the probe, this force represents the surface tension value (Force/wetted length) according to Equation 3.

iii. The approach is stopped and the direction of travel is reversed, so that the probe is moving away from the liquid surface at velocity $v_{reverse}$ until the probe-liquid contact breaks off.

The force vs. time and/or displacement curve is recorded for the entire process.

The steps followed for the dynamic testing technique [22] are (Figure 2.3):

i. Same as in static equilibrium method

ii. Same as in static equilibrium method

iii. Probe is immersed into the sample at velocity $v_{immerse}$ for a specified distance and experiences a reduction of recorded force due to combined buoyancy and dynamic viscous drag effects.

iv. Probe travel direction is reversed by moving the linear stage in the opposite direction at velocity v_{emerse} (where v_{emerse} equaled $v_{immerse}$ in all cases).

v. Probe is moved completely out of the melt surface until fully detached from the liquid/molten polymer.

The advancing and receding force can be plotted with respect to probe displacement to generate the force hysteresis and contact angle hysteresis graphs as shown in Figure 2.3.

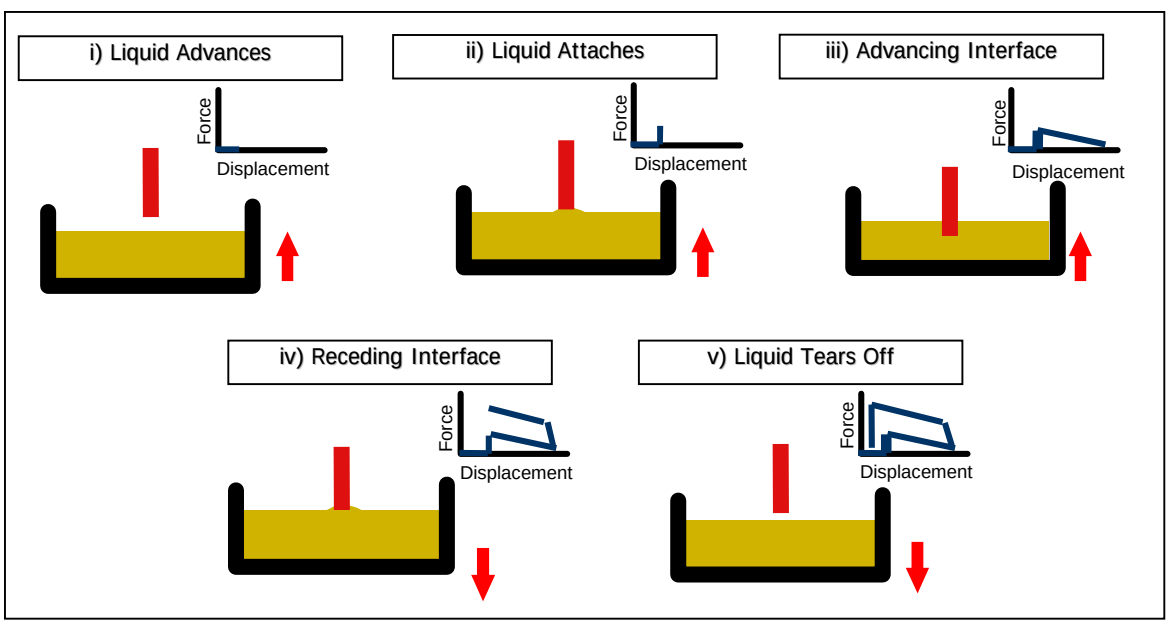


Fig. 2.3 Dynamic measurement technique

The measured force on the probe must be corrected for buoyancy effect, and is given by the equation:

$$F(h) = F_0 - r_{\text{liquid}} \cdot A_{\text{Probe}} \cdot h \cdot g \qquad (4)$$

where F(h) is the corrected force, F_0 is the measured force, r_{liquid} the density of the liquid/polymer melt, A_{Probe} represents the surface area of the probe, h stands for the immersion depth (assuming h=0 signifies the surface level of the liquid/melt) and g is the gravitational constant. A known error in this experiment is that the value of "h" is set to zero as soon as the probe makes contact with the liquid and a force change is measured. This occurs above the liquid surface in most cases as the liquid jumps up and attaches itself to the probe surface due to adhesive surface force effects.

If the advancing and receding force-displacement plots are collinear, the advancing and receding contact angle is zero. Otherwise it is non-zero, and advancing and receding contact angles can experimentally be determined, using equations and neglecting viscous effects:

$$\cos q_a = \frac{F_a}{g \cdot p} \qquad (5)$$

$$\cos q_r = \frac{F_r}{g \cdot p} \qquad (6)$$

Where q_a and q_r are the advancing and receding contact angles, F_a and F_r the advancing and receding force, respectively, g is the surface tension and p the perimeter of the probe. The buoyancy corrected force is used to calculate the surface tension, unless otherwise noted.

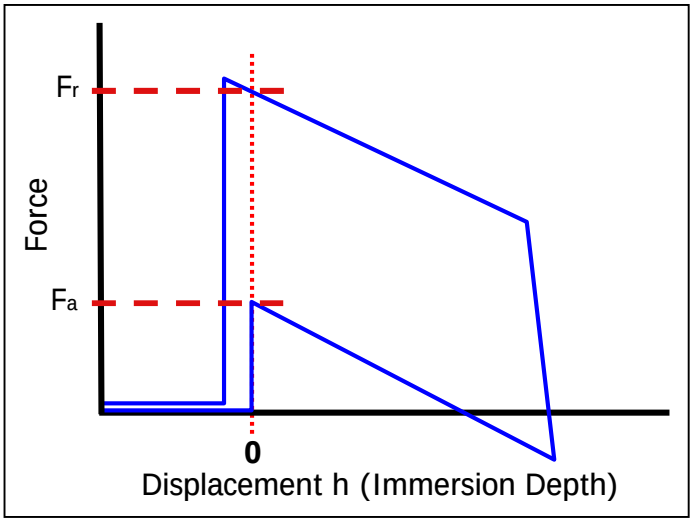


Fig. 2.4 Advancing and receding lines.

2.2.3 Probes, Coating Procedure and Preparation of Polymer Samples

Different probes were explored and used for preliminary tests, including etched and smooth glass rods (2mm diameter) in an attempt to emulate the micro-Wilhelmy technique. The probe diameter was selected keeping in mind accommodation of an appreciable mass of refractory coating on it. Since the results were not satisfactory, as will be shown, a standard platinum plate (length: 19.9mm; thickness: 0.1mm) as used in commercially available contact angle measurements systems from Kruess GmbH was used as a probe. Based on this design a probe was designed for the following experiments. These aspects were considered in designing an appropriate probe for dynamic measurements:

i. Suitable shape and dimensions to allow application of the refractory coating in a reproducible manner and also result in a pronounced interfacial force when interacting with the polymer melt.

ii. Convenience for changing the probe easily for a series of experiments.

iii. Selecting appropriate weight of the probe so that it would recede into the approaching polymer melt under gravity when hanging freely. In other words, the sum of buoyant and viscous forces should never exceed force due to gravity. This problem was encountered using glass rods.

Based on previous experiments, it was decided to use thin stainless steel plates (thickness: 0.05mm; width: 10mm; height: 20mm) and attach them to a custom made probe holder (weight of holder: 25g) as shown in Figure 2.5.

A paint draw down bar was used to apply the refractory coating slurry to the probes to obtain a target thickness value of the dried coating. The probes were positioned on transparent plastic sheets spread on a flat surface. In the first step, a target viscosity (1000cp) of the coating slurry was obtained by adding distilled water and stirring. Then, the coating slurry was applied on one side of the probe and dried at 70°C overnight in a vacuum oven. The probes were pealed off and the edges were cut with a sharp knife. After checking for uniformity in coating thickness on one side, the probes were placed on a new plastic sheet and the entire process was repeated to obtain uniformly coated refractory coating on both sides of the probe, as shown in Figure 2.6.

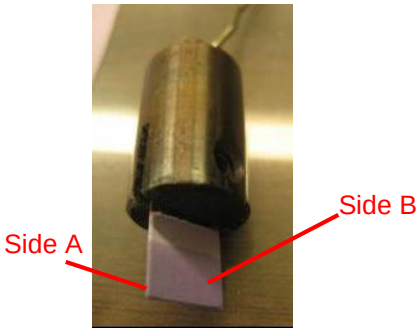


Fig. 2.5 Probe holder with coated probe

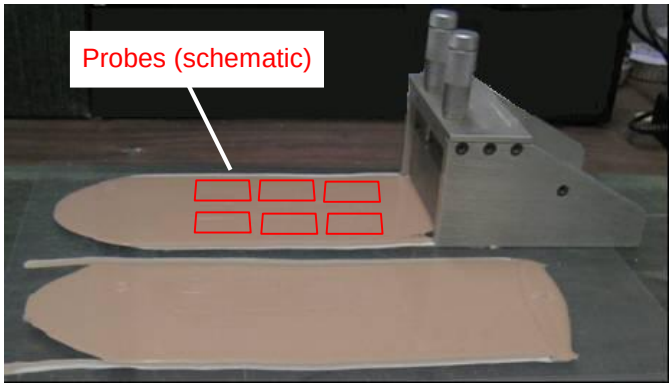


Fig. 2.6 Paint drawdown bar, used to apply coating at a certain target wet film thickness

To prepare the polymer samples, 4.5g of polystyrene beads were taken into glass beakers (inner diameter: 31.5mm) and melted at 130°C in a vacuum oven to obtain a homogenous clear mass of polystyrene. Care was taken to drive out all air bubbles. The glass beakers were modified to snugly fit inside the furnace.

2.3 Results and Discussion

2.3.1 Static Equilibrium technique

Using calibration liquids with known surface tension (such as Silwick and Galwick; see Table 2.1), surface tension at room temperature was confirmed using the experimental system developed in this study with an accuracy of $\pm 3\%$. Data shown in Figure 2.7 represent two examples using platinum plate and glass rod, respectively, as probes and following the static equilibrium technique. Data is shown as Force per wetted length, which corresponds to surface tension.

Table 2.1 Properties of Silwick and Galwick (used for calibration purpose)

	Silwick	**Galwick**
Manufacturer	Porous Materials Inc.	Porous Materials Inc.
Density at 25°C [g/cm^3]	0.937	1.820
Surface Tension at 25°C [mN/m]	20.1	15.9
Viscosity at 25°C [cSt]	9.5	4.4

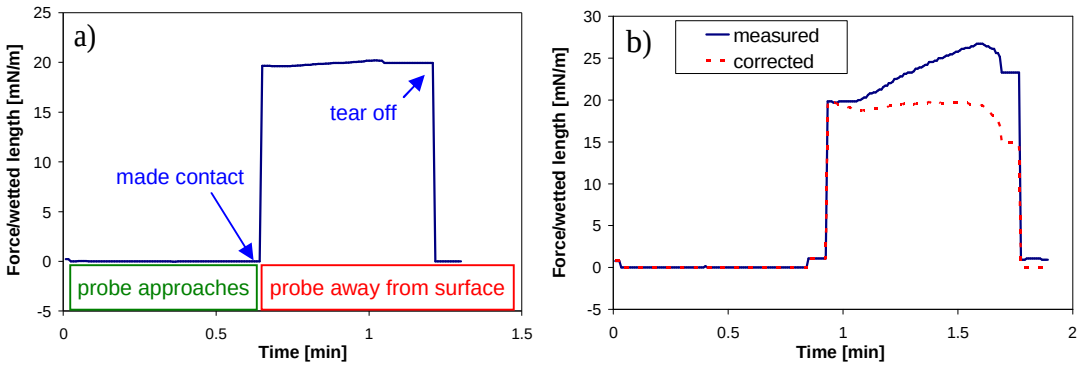


Fig. 2.7 Surface Tension results at RT for Silwick with a) Pt plate (showing measured force per wetted length) and b) glass rod (showing measured and corrected force per wetted length); using equilibrium method (probe velocity: 2.5mm/min)

Using the initial force after contact, the calculated surface tension matches the literature value of 20.1mN/m and 15.9mN/m for Silwick and for Galwick, respectively. For the platinum plate, the measured force and therefore the calculated surface tension stay nearly constant when the probe moves away from the liquid surface until it tears off. Since the plate is relatively thin (0.1mm), the mass of liquid lifted up is negligible. In the case of the glass rod, due to its larger contact area, the force considerably increases before the liquid mass tears off. Therefore, the force must be corrected for the weight of the amount of liquid lifted up (see dotted line Figure 2.7b).

The behavior of polymer melt is fundamentally different from ideal liquids. Due to its viscoelastic nature, polymer melts undergo very fast stress relaxation during the Wilhelmy-test, thus making it almost impossible to reach an equilibrium state [23]. For polymer melts, it was found that the variance in experimental results using the equilibrium method is around 30%, thus making evaluations highly unreliable. Besides viscoelastic effects, the other problem faced with polymer melts in the equilibrium method, was non-uniform contact of the melt with the probe perimeter. Figure 2.8 shows the force on the probe per wetted length for the duration of the test. As we observe, the force increases up to about 6mN/m after first contact. The approach is stopped shortly to allow the system to equilibrate. On further movement of the probe, the force increases due to effects from polymer chain entanglements until the melt starts necking and finally tears off from the probe. In order to overcome the experimental difficulties encountered during the initial attempt to determine the surface tension value g for PS melt using the equilibrium method, the previously described dynamic testing procedure was utilized to determine wetting and wicking behavior of PS.

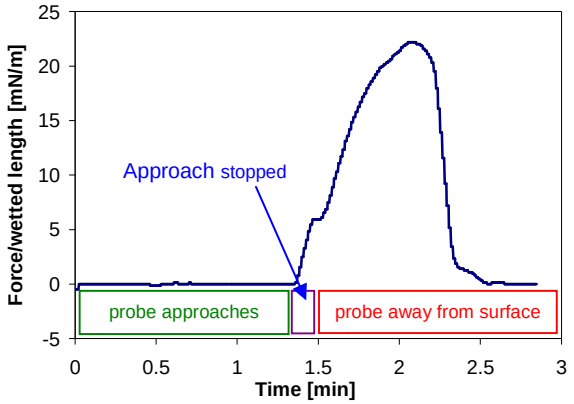


Fig. 2.8 Polystyrene at 250°C: Surface Tension in Equilibrium method not reliable (probe velocity: 2.5mm/min; showing measured force per wetted length)

2.3.2 Dynamic technique

Also for the dynamic testing procedure using the described experimental system, the surface tension of Silwick and Galwick was confirmed as presented in Figure 2.9. If a roughened platinum plate with a perimeter of 40mm (length: 19.9mm; thickness: 0.1mm) is used as a probe, the advancing and receding lines are perfectly collinear and the test is repeatable with an accuracy of less than $\pm 1\%$. This probe is rate independent, since the immersion/emersion velocity is not very critical; results are nearly the same for immersion/emersion velocities between 0.1mm/min and 2.5mm/min. If a 2mm glass rod is used, the velocity has a stronger influence on the experimental result; the difference between advancing and receding lines was found to be smallest at lower speed (an ideal velocity was found as 0.1mm/min) with highest repeatability. However, the contact angle between glass and Silwick is not perfectly zero, and a slip-stick effect on the surface can be concluded from examining the resulting force-displacement graph.

Similar results were obtained for Galwick, which has a surface tension value of 15.9mN/m. As a reference material with known surface tension at elevated temperatures, as presented in Table 2.2, Ethylene Carbonate was examined at different temperatures between 75°C and 180°C. Figure 2.10 presents experimental results using a 2mm diameter glass rod with roughened surface and a 40mm perimeter platinum plate as a probe. It was found that all probes had a non-zero contact angle with the liquid Ethylene Carbonate melt. Therefore, a determination of the surface tension was not possible with this method, but the repeatability of the experimental results was successfully demonstrated. A distinct difference in the hysteresis loops was obtained at different equilibrium temperatures.

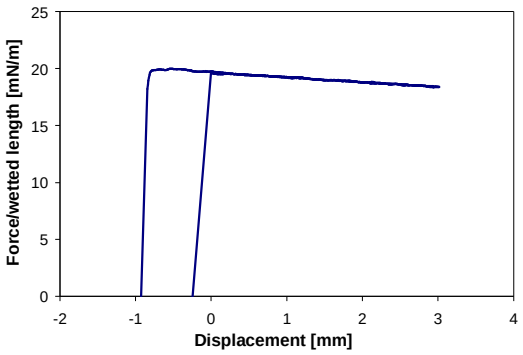


Fig. 2.9a *Contact Angle Hysteresis for Silwick using platinum plate (probe velocity: 2.5mm/min)*

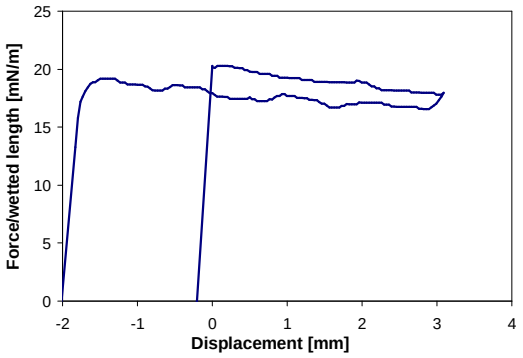


Fig. 2.9b *Contact Angle Hysteresis for Silwick using glass rod (probe velocity: 2.5mm/min*)

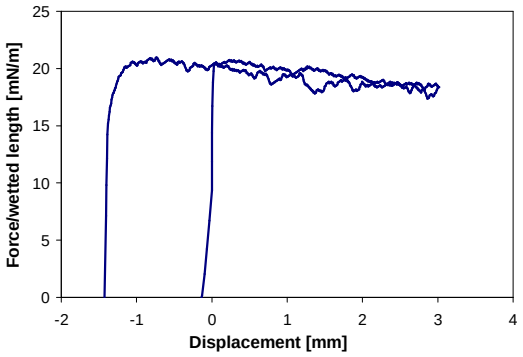


Fig. 2.9c *Contact Angle Hysteresis for Silwick using glass rod (probe velocity: 0.1mm/min*)

Fig. 2.9 Example Experimental results for Silwick with dynamic testing procedure using different probes (Force is corrected for buoyancy)

Table 2.2 Reported Surface Tension of Ethylene Carbonate (used for calibration purpose) [24]

Temperature °C	Surface Tension [mN/m]
40	53.74
60	51.92
80	50.32
100	48.84
120	47.5
140	46.27
160	45.14
180	44.11
200	43.16

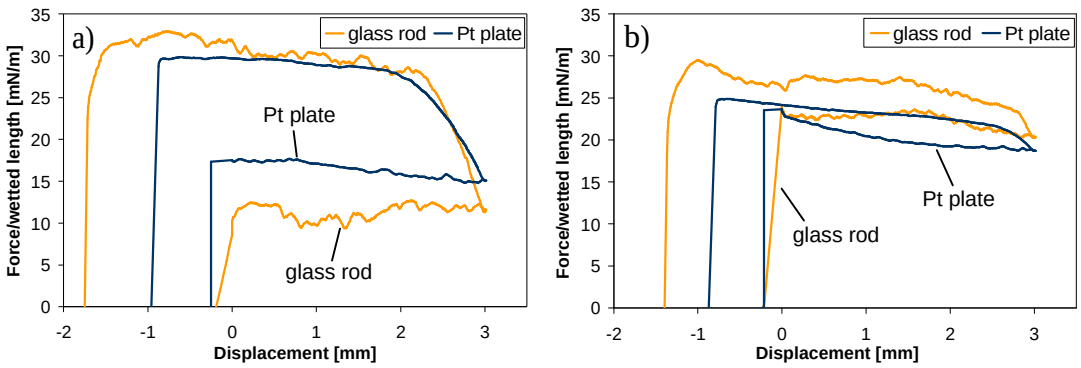


Fig. 2.10 Experimental results for ethylene carbonate at 75°C (a) and 155°C (b) with dynamic testing procedure (probe velocity 0.1mm/min) using two different probes. (Force is corrected for buoyancy)

For Ethylene Carbonate, at higher temperatures the advancing and receding lines are closer together and therefore advancing and receding contact angles are closer, indicating that the liquid wets the probe better. This further indicates that it is not necessary to find the exact value for surface tension and contact angle to examine qualitatively the wetting behavior of the material of interest (in our case PS melt and refractory coating) at different temperatures. Especially since difficulties were encountered in reliably determining the surface tension of PS at elevated temperatures (above 300°C), it was decided to record high temperature force hysteresis loops and use those only as qualitative and comparative data.

In another preliminary test, using the dynamic technique and Galwick, the refractory coating type B was applied to the custom probe. It was found that the advancing and receding lines were different, as shown in Figure 2.11. Here, this phenomenon is due to the wicking of Galwick into the coating during the emersion/immersion cycle. As one can see the very sharp inflection point at maximum immersion depth, which indicates that there is no, or nearly no, change in advancing and receding contact angle. The reason that the receding line differs from the advancing line is simply due to the increase of weight, caused by wicking of Galwick into the coating. Since liquid is adsorbed throughout the whole immersion-emersion cycle, the measured force constantly increases, until the liquid tears off. Also, the force per wetted length at initial contact is slightly higher, than the surface tension of 15.9mN/m, which is likely due to an immediate absorption of liquid into the coating. At the end of the experiment, the force does not return to zero again due to wicking of the liquid. This was verified by checking that the difference between the maximum measured force and the initial measured force was approximately the same as the weight gained by the probe at the end of the experiment. If no wicking were to occur, the measured force would drop back to zero after the probe detaches from the liquid and advancing-receding lines would be collinear, which would indicate a zero contact angle more clearly. This observation must be kept in mind when evaluating hysteresis loops for PS melt and refractory coating. Using the described, modified dynamic Wilhelmy technique with custom probe and refractory coating, testing molten PS at different temperatures, highly repeatable results were produced as shown in Figure 2.12. A distinct difference in the hysteresis loops is notable for different temperatures. Experimental results for PS and refractory coating are presented and discussed in chapter 3.

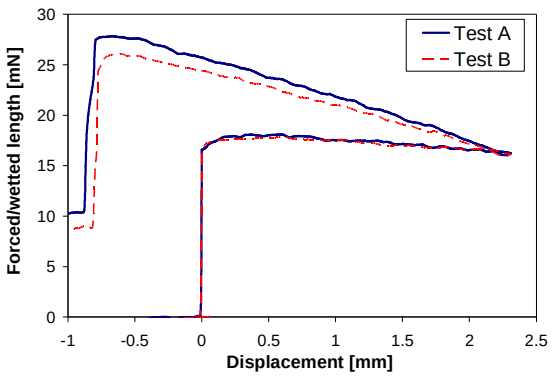


Fig. 2.11 Two experimental results (Test A & B) for Galwick with dynamic testing procedure using coated probes (Force is corrected for buoyancy)

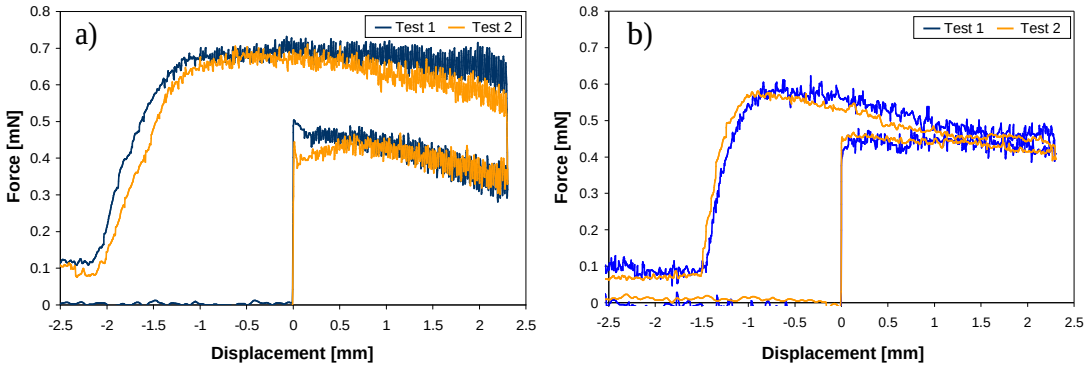


Fig. 2.12 Repeatability of experimental results for PS melt and refractory coating at 225°C (a) and 275°C (b) with dynamic testing procedure (probe velocity 0.1mm/min; measured force is shown)

2.4 Summary and Conclusions

A custom experimental setup was reported in detail, which was developed in order to characterize wetting and wicking behavior of refractory coatings with polymer melts at elevated temperatures. The experimental setup reported in this study can be used to conduct either the equilibrium or the dynamic Wilhelmy type testing to evaluate the wetting behavior of complex liquids at temperatures up to 800°C. Experimental results, conducted with calibration liquids of known surface tension, have demonstrated the accuracy and repeatability of the testing system. An application involving materials used in lost foam casting was studied with the new experimental system. The wetting and wicking behavior of polystyrene with refractory coating samples at varying temperatures was observed and recorded. A modified dynamic Wilhelmy method was established with analysis based on the recorded force hysteresis loops, and such results are presented in a companion paper.

Chapter 3: Wetting Behavior of Polystyrene Melts with Refractory Coatings

This chapter is a slightly revised version of a paper with the same title which was submitted for the Journal of Materials Research in September 2009 by Robin Woracek, Indraneel Sen, Dayakar Penumadu and Mark Hoover.

My primary contributions to this paper include: (1) development of the problem into a work, (2) identification of the study areas, (3) gathering and reviewing of literature, (4) performing the laboratory experiments, (5) interprestaion and analysis of the test results and (6) most of the writing.

Abstract

The following article reports the interfacial wetting and wicking behavior of polystyrene (PS) melts with clay based refractory coating, for research related to lost-foam metal casting (LFC). A custom developed experimental system and testing protocol was used to obtain data as a function of temperature. The experimental system and procedure, based on the dynamic Wilhelmy plate technique, have been reported in detail in a companion paper [24]. The procedure basically involves investigation of the dynamic advancing and receding liquid-probe interactive forces and hysteresis loops. Experiments of particular interest were performed for polymer melts at processing temperatures between 220°C and 300°C, where they show pronounced viscoelastic behavior. Wetting behavior of porous materials with polymers at high temperatures is unavailable in the past literature, and is a new contribution from this study.

Suitable quantitative variables, obtained from the hysteresis loops, were utilized to describe interfacial behavior, including the area under the hysteresis loop from initial contact onwards, the slope of advancing and receding lines in the force-displacement curves, the force magnitude at zero displacement, and Fast Fourier Transform (FFT) analysis of the advancing/receding curves. This paper has important contributions to studying wetting behavior of complex liquids with porous coatings and materials.

3.1 Introduction

A major need in the casting industry is to develop reliable models of complex metal casting techniques such as Lost Foam Casting (LFC) in order to optimize and improve casting properties and process parameters as well as predict metal flow and solidification behavior for new casting designs. The objective of the current study on wetting and wicking behavior of PS with refractory coating is to provide improved constitutive information, associated with the interaction of degrading PS with refractory coatings at processing temperatures, to develop suitable numerical computational fluid dynamics (CFD) models to realistically represent the metal filling and solidification of complex castings. Such investigation should also contribute largely to the characterization and subsequent evaluation of coatings with different material compositions. Refractory coating applied on the foam pattern surface plays a key role in the overall success of the LFC process, which is described in more detail in the companion paper [25]. Defects, such as folds, porosity, carbon defects, melt penetration and misruns that are commonly observed in the LFC process are strongly correlated to the coating properties and degradation aspects of PS foam [26].

To study the interfacial behavior between refractory coating and PS melt, the experimental procedure involves a liquid – solid interface measurement, using techniques such as Wilhelmy plate, micro-Wilhelmy or Sessile drop method. In the Wilhelmy plate and micro-Wilhelmy method, first the surface tension of the melt needs to be determined with a perfectly wetting probe, e.g. having a contact angle of zero with the melt. Subsequently, the coating can be applied onto the probe and the contact angle between coating and melt can be determined. Due to reported experimental difficulties [25, 27], the determination of the surface tension of polystyrene using Wilhelmy plate method is challenging. The micro-Wilhelmy technique [27, 28, 29] has been reported to a viable approach for the measurement of surface tension for moderate to high molecular weight polymers at elevated temperatures. Since an appreciable mass of refractory coating on the surface of the probe is required for experimental accuracy, the dimensional requirement of the micro fiber probe would be violated.

Thus in our study, a modified Wilhelmy approach has been established and appropriate instrumentation has been designed and assembled, with the goal to overcome these difficulties. The functionality of the system has been verified using several calibration liquids with known solids. The key function of the experimental system developed by the authors is the ability to obtain measurements at high temperatures that cannot be achieved with current commercial systems. Qualitative and quantitative comparison of wetting and wicking behavior was based on analysis of the force hysteresis loops, and therefore depend only indirectly on the surface tension and contact angle. Discrepancy between advancing and receding forces as presented in the following sections can be due to a variety of effects [30,

31, 32], including surface roughness, chemical heterogeneity, surface deformation, surface configuration change and adsorption/desorption mechanisms. The observed hysteresis loops contain two major factors: The meniscus change at the transition region [33] and the wettability change of solid surfaces [34]. Both factors are due to interaction forces between the solid surface and the liquid/melt molecules at the solid-liquid/melt interface [35] and enable us to compare different refractory coatings at certain ambient conditions.

3.2 Experimental

In the results presented here, two different commercially available refractory LFC coating types were used, and applied in a uniform thickness on both sides of the probe. The different coating types are referred to as coating A and coating B and details are presented in Table 3.1. The coatings, having a viscosity of 1000 cP before application, were applied onto custom probes, made of stainless steel plates (thickness: 0.05mm; width: 10mm; height: 20mm). The target coating wet film thicknesses, controlled by a paint draw down bar, and resulting dry coating thicknesses for coating A and B are listed in Table 3.2. The probe is attached to a custom probe holder (weight: 25g), as shown in Figure 2.5, allowing easy exchange of the probes and providing enough weight to ensure that the probe recedes into the approaching polymer melt under gravity when hanging freely. The water content of the refractory coatings A and B at a viscosity of 1000 cP is approximately 61%.

Table 3.1 Properties of refractory coatings used in presented experiments

	Coating Type A (Mica based)	**Coating Type B (Silica based)**
Manufacturer	Ashland Speciality Chemical Co.	Ashland Speciality Chemical Co.
Product name	Ceramcote™ EP9 GM BLK 7	Ceramcote™ EP9 Head 3

Table 3.2 Target and resulting thicknesses of probe after coating with Refractory Coatings

	Coating Type A (1000cp)	**Coating Type B (1000cp)**
Target coating wet film thickness for side A	0.38mm	0.38mm
Resulting dry coating thickness after side A coated	0.15mm – 0.19mm	0.19mm – 0.22mm
Target coating wet film thickness for side B	0.67mm	0.76mm
Resulting dry coating thickness after side B coated	0.40mm – 0.46mm	0.40mm – 0.46mm

To prepare the PS samples, 4.5grams of PS beads were taken into glass beakers (inner diameter: 31.5mm) and melted at 130°C in a vacuum oven to obtain a homogenous clear mass of polystyrene. Care was taken to drive out all air bubbles. The glass beakers were modified to snugly fit inside the furnace.

Dynamic force hysteresis loops were recorded for both coating types at temperatures between 225°C and 300°C. The temperature range was selected based on the processing and degradation temperatures, often associated with polystyrene, of approximately 220°C and 275°C, respectively. The reader should note that thermal degradation of PS is a complex heating rate dependant process. For the timescales associated with the LFC process thermal degradation of PS can be approximated to 275°C [36]. Immersion depth of the probe into the PS sample was selected as 2.3mm and the immersion/emersion speed as 0.5mm/min after trial and error. After positioning the PS sample and the probe into the furnace, approximately ten minutes of equilibration time was allowed to reach a uniform temperature within the furnace and sample prior testing.

3.3 Results and Discussion

Each coating has been evaluated at each testing temperature and miscellaneous experimental indicators are used to obtain state quantitative and qualitative results of wetting behavior. The presented force-displacement hysteresis loops show the true measured force without corrections for buoyancy and the amount of melt lifted up during emersion. It should be noted that the dimensions of the probes are the same for all presented results.

3.3.1 Wetting and Wicking Behavior of Mica based Coating (Type A) at different Temperatures

Figure 3.1 shows Force displacement variations during immersion-emersion process for Coating A at temperatures of 225°C, 250°C, 275°C and 300°C; one experimental result at each temperature is shown.

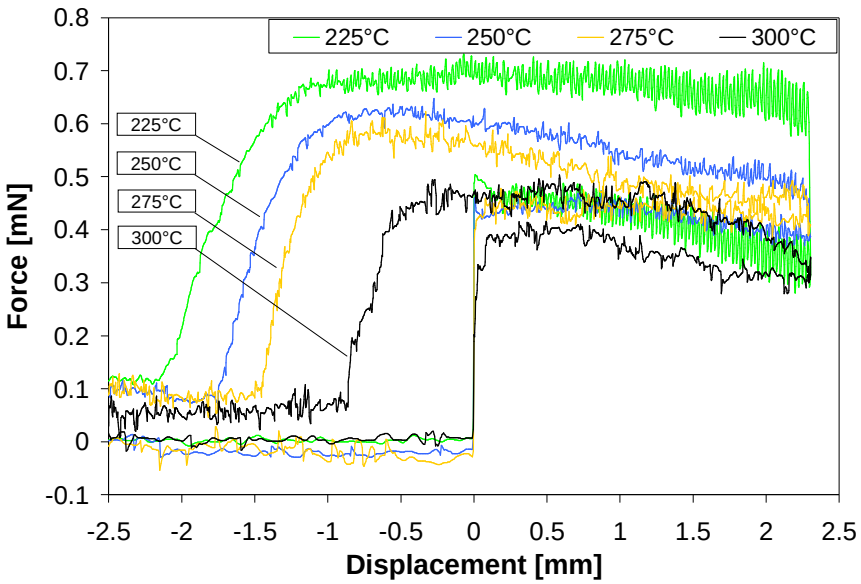


Fig. 3.1 Coating type A at temperature between 225°C and 300°C

Each test was repeated at least three or four times and showed good repeatability. The variation in the order of 0.04mN of measured force when the probe approaches the polystyrene melt surface is due to fluctuation in the measuring load cell (from neg. 2.5mm to 0 mm). For all tests, a substantial force increase is observed when contact is first made between the probe and surface of the melt. This is likely due to the phenomenon that the melt "jumps" onto the probe due to adhesion effects and pulls it down. Often for simple liquids, this force corresponds to surface tension of the liquid. As the probe is further immersed into the melt, the axial force on the coated probe starts decreasing; this decrease is due to buoyancy and also from mobilized interface shear stress and associated viscoelastic effects at the probe-melt interface. The slope would be steeper if no melt would be wicked by the coating during the testing cycle. At maximum emersion depth of 2.3mm, the travel direction of the probe is reversed and an immediate increase of the force is observed. Depending on the temperature, the force further increases as the probe moves out and away from the PS sample until the contact breaks off and the probe is free again.

As shown in Figure 3.1, the measured force does not go back to zero (value before the initial contact) after the melt detaches from the probe which is due to an appreciable mass of liquid polymer wicking into pores of the coating. Figure 3.1 also shows that the force reading seems to have ripples on top of an equivalent value during the immersion and emersion process. These force ripples could be attributed to viscoelasticity and interfacial tension between polymer melt and the refractory coating from the stick-slip failure mode of the polymer chains with porous coating. As the probe travels through a pool of polymer melt, polymer chains constantly entangle and disentangle, creating resistance and stress relaxation

respectively along the probe-melt interface. This effect is most distinct at lower temperatures, since polymer chains degrade at higher temperatures, resulting in shorter chain lengths, and reducing probability of polymer chain entanglements [37]. The observed force ripples were found to be more prominent with increase in immersion depth due to increase in interfacial area. Figure 3.1 further shows that the gap between the advancing and receding force lines vary as a function of temperature and increases with decrease in equilibrium temperatures. At 225°C we see a distinct inflection point for the measured force when the probe changes direction from immersion to emersion. This also indicates that the receding contact angle (slope of emersion force and displacement line) is distinct from the advancing contact angle. One can illustrate this effect, considering a very viscous liquid. The melt meniscus might be even depressed ($q > 90°$) along the vertical wall of the probe during immersion, as illustrated in Figure 3.2.

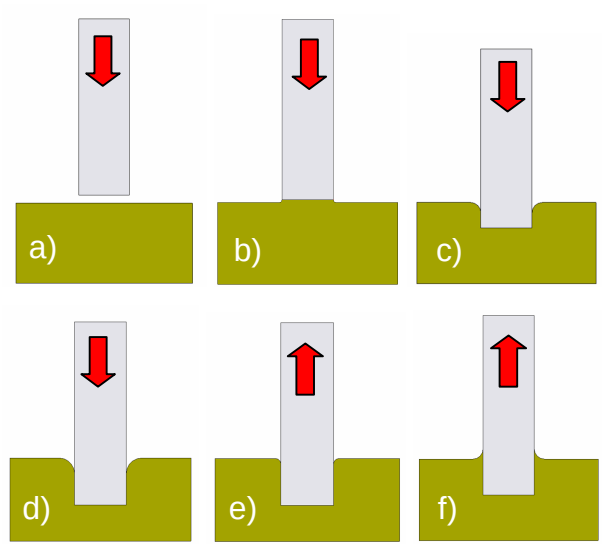


Fig. 3.2 Schematic description of meniscus shape at solid/melt interface during approach (a-b), immersion (c-d) and emersion (e-f); (contact angle is not necessarily >90° during immersion) [35]

When the probe is emerged, the meniscus rises ($q < 90°$). At higher temperatures, as a result of degradation when the polystyrene melt becomes less viscous due to formation of shorter molecular chains, the meniscus change is not that distinct anymore and the advancing/receding contact angles become closer. It was also observed that the hotter the melt is, the sooner it tears off from the probe during emersion, since there is less cohesion within the melt. This can be attributed to lower chain entanglements and higher free volume of the polymer chain at higher temperature as the polymer chain degrades.

3.3.2 Wetting and Wicking Behavior of Silica based Coating (Type B) at different Temperatures

Coating B was also evaluated at 225°C, 250°C, 275°C and 300°C and the results are presented in Figure 3.3. The hysteresis loops for Silica based coatings are fundamentally different from the ones obtained for Mica based coatings (for example Coating A). At all temperatures, the initial contact force is positive, but smaller compared to coating A, meaning the interfacial tension between solid and melt is smaller. For all temperatures, the measured force becomes negative during the immersion process; due to uplift of the probe from buoyancy and due to high shear forces between probe and polymer melt. The buoyancy effect alone, contributes around 0.1mN (see Eq. 7) force change at maximum immersion depth of 2.3mm, which is significantly smaller than the actual uplift force that was recorded as a function of immersion depth.

$$F_B(d) = r \cdot g \cdot t \cdot w \cdot d = 1 \cdot 10^{-3} \frac{g}{mm^3} \cdot 9.81 \frac{m}{s^2} \cdot 0.45mm \cdot 10mm \cdot d \qquad (7)$$
$$F_B(2.3mm) = 0.1015mN$$

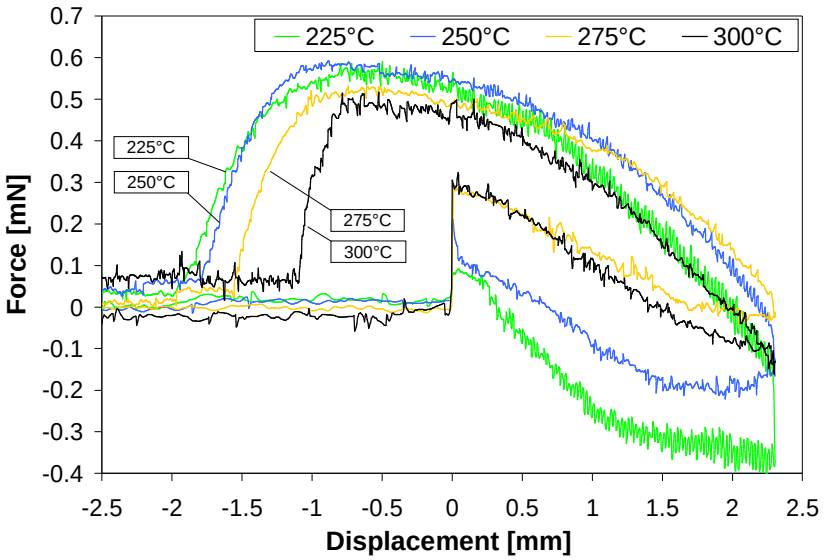


Fig. 3.3 Coating type B at temperature between 225°C and 300°C

At 225°C, the change of force from first contact to maximum immersion is about 0.46mN and at 275°C about 0.32mN. The gap between the advancing and receding forces is most distinct at lower temperatures and ripples of the force reading are also more dominant at decreasing equilibrium temperatures. Again, at the inflection point from immersion to emersion, the force change is most striking for temperatures of 225°C and 250°C. Similar to Coating A, the polymer melt detaches sooner from the probe during retraction with the increase in equilibrium temperature. The tear-off occurs for both coatings at very similar emersion heights. This phenomenon is mostly a characteristic of the PS melt itself, i.e. polymer chain entanglements and drop size, and not so much due to coating properties. Figure 3.4 shows one experimental result for coating Coating A and Coating B each at the target temperatures of 225°C, 250°C, 275°C and 300°C for better comparability.

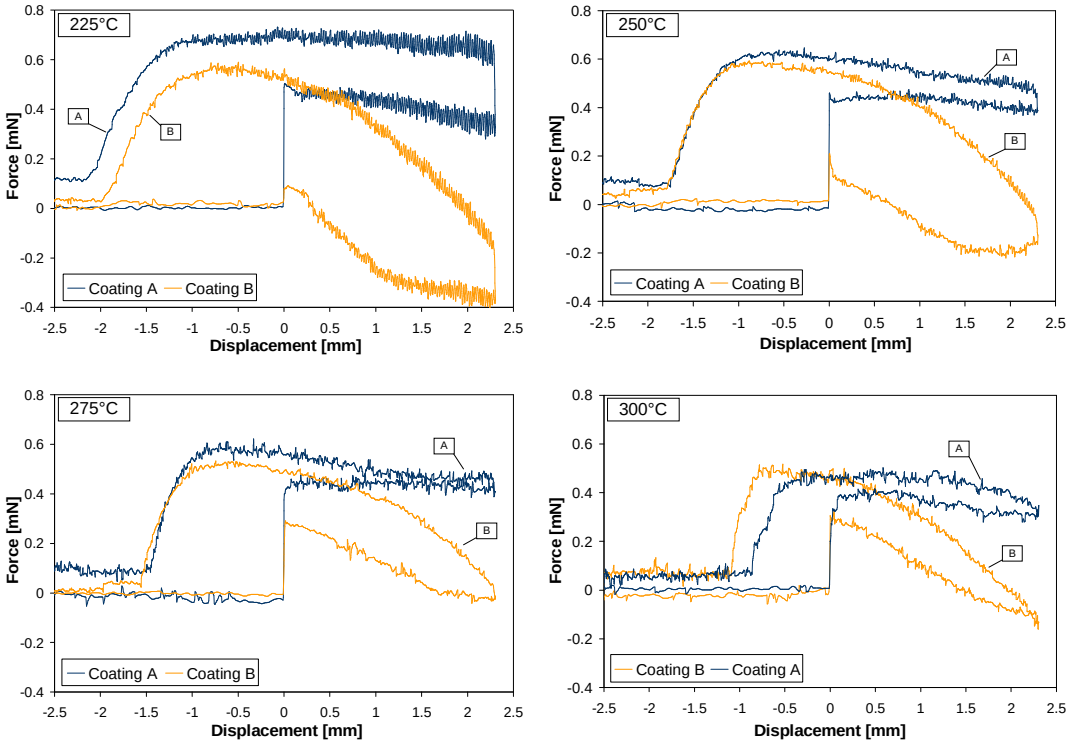


Fig. 3.4 (a-d) Coating type A and B at temperatures of 225°C, 250°C, 275°C and 300°C

3.3.3 Comparisons between the coatings and evaluation factors

For quantification of differences in wetting behavior with temperature and between the two refractory coatings, four variables from the hysteresis plots were used, substantiated with additional quantitative indicators from visual and qualitative data. The four quantitative parameters proposed are:

1. The area under the loop from contact onwards
2. The force hysteresis at zero displacement
3. The slope of advancing and receding lines in the force-displacement domain
4. FFT analysis of the hysteresis loop to describe ripple amplitude and dominant frequency

In addition, a qualitative approach that uses the amount of wicking height visually was also found to be a simple and suitable indicator for wetting and wicking behavior.

Figure 3.5 shows an example of the area under the loop used to calculate the reported values in Figure 3.6. Figure 3.6 shows values for the area under the loop for three experimental results each at temperatures of 225°C, 250°C and 275°C for Coating A and Coating B. The figure also includes results of a cyclic-prewetted test, which will be discussed later. For coating A, the area between the advancing and receding force decreases as the temperature increases. The same tendency is true for coating of type B, but whereas the area values are always higher than for coating A at the same temperature. Figure 3.6 also illustrates the repeatability of experimental results at the same target temperatures, where the median temperature variation was ± 5°C.

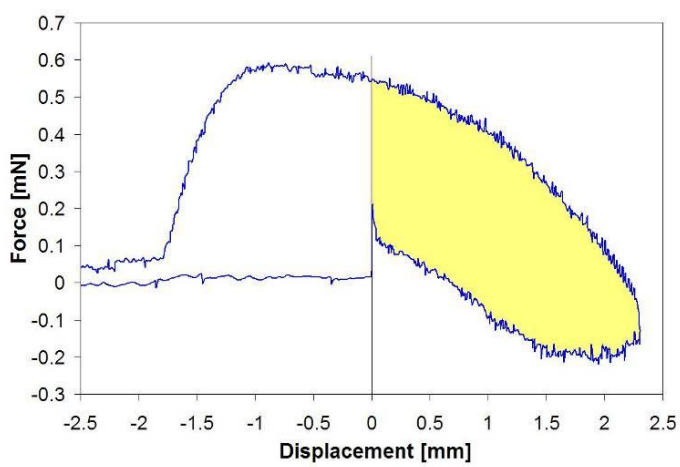


Fig. 3.5 Surface Area in hysteresis loops: quantitative measurement for wetting behavior of coatings

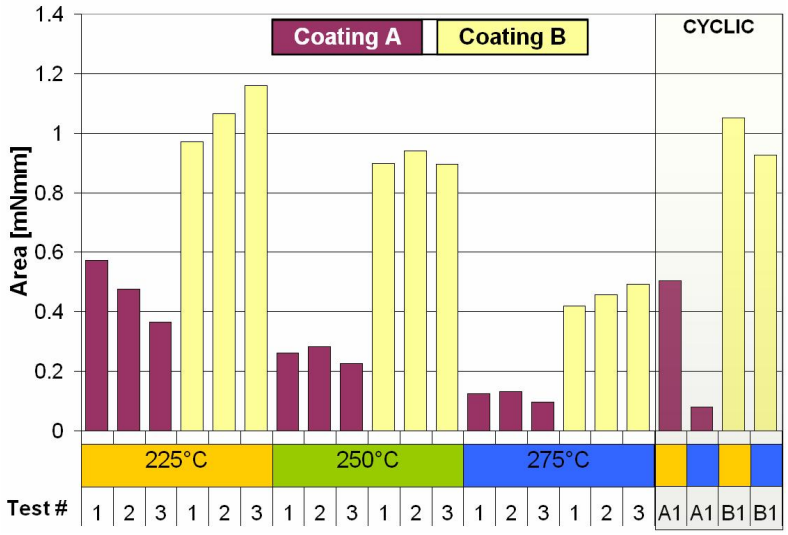


Fig. 3.6 Surface Area in hysteresis loops: experimental results as a function of temperature

The force value at "zero-displacement", at initial contact as well as during emersion, has also been included in the analysis, as presented in Table 3.3. The values represent the gap between advancing and receding force at d=0 and obviously state again that this gap is much smaller for Coating A. The force at initial contact very slightly decreases for Coating A, where for Coating B a distinct increase is notable. The receding force at "zero-displacement" slightly decreases for both coatings as the temperature increases, where the force values for coating B are a little bit lower at each temperature than for coating A.

The slope of receding and advancing force was used for quantitative comparison as well. An approximate line was placed into the force hysteresis loops between d=0mm and d=2.3mm to calculate the slope, and averaged values of three tests are reported in mN/mm in Table 3.4. As discussed previously, the buoyancy force only has limited effect on the slope: theoretically, approximately 0.044mN/mm are due to buoyancy.

Table 3.3 Force at zero-Displacement

		Force F [mN]							
		Test 1		Test 2		Test 3		Avg.	
		F initial contact	rec. F at d=0	F initial contact	rec. F at d=0	F initial contact	rec. F at d=0	F initial contact	rec. F at d=0
Coating A	225°C	*0.5*	*0.71*	*0.52*	*0.68*	*0.54*	*0.68*	*0.52*	*0.69*
	250°C	*0.46*	*0.6*	*0.43*	*0.58*	*0.48*	*0.58*	*0.46*	*0.59*
	275°C	*0.45*	*0.54*	*0.45*	*0.6*	*0.43*	*0.54*	*0.44*	*0.56*
Coating B	225°C	*0.2*	*0.55*	*0.08*	*0.52*	*0.03*	*0.51*	*0.10*	*0.53*
	250°C	*0.15*	*0.54*	*0.21*	*0.54*	*0.16*	*0.57*	*0.17*	*0.55*
	275°C	*0.28*	*0.49*	*0.3*	*0.52*	*0.29*	*0.49*	*0.29*	*0.50*

Table 3.4 Advancing and receding slope of Force-Displacement hysteresis loops for Coating A and Coating B

		Avg. slope from Tests 1-3	
		advancing slope [(mN / mm)*10^{-3}]	**receding slope [(mN / mm)*10^{-3}]**
Coating A	225°C	74	21.7
	250°C	21.7	43.5
	275°C	17.4	50
Coating B	225°C	264.5	265.2
	250°C	190	252.2
	275°C	143.5	142

Therefore, the slope is mainly an indicator of the interfacial tension, normal and shear stresses between PS melt and coating, all reflecting the complex interfacial behavior in a combined from.

In order to simulate the LFC process more accurately, experiments with pre-wetted coated probes were conducted and results are presented in Figure 3.6 (cyclic). During the metal filling in the LFC process, a volume with a rising temperature gradient is approaching the

polystyrene foam and melting it accordingly. This means, that PS foam is melt at lower temperatures while in touch with the refractory coating, before the temperature increases. For the results presented herein, first one test was performed at 230°C with a “fresh” coated probe and a “fresh” PS sample. Afterwards the same, now “pre-wetted”, probe was used for another test at 275°C using a “fresh” PS sample. The experimental results at 230°C remained the same as reported in the previous section, while a substantial difference for the pre-wetted probes is observed. For coating A, the PS melt is wetting the pre-wetted probe better compared to an un-wetted, “fresh” probe. This is not surprising, since the PS melt is already wicked into the coating, providing easy wetting for the PS melt at the subsequent cycle, resulting in a smaller gap between advancing and receding force. For coating B, the opposite behavior is observed: The gap between advancing and receding force, recorded for a previously pre-wetted probe, is much bigger compared to an un-wetted probe.

There are two qualitative indicators used to quantify the wicking ability of the refractory coatings for PS melt:

1. The recorded force, after a test has been conducted and the PS melt de-attached from the probe, presented in Table 3.5. This represents the amount of PS which has been absorbed or is still attached to the coating. This is only a rough indicator, since it is hard to tell which portion is actually wicked into the material and how much is just attached to the surface.
2. Measuring the visually recognizable wicking height on the probe after the experiment, as shown in Figure 3.7.

Table 3.5 Remaining force reading after PS is detached from probe

		Force [mN]			
	Temperature	**Test 1**	**Test 2**	**Test 3**	**Avg.**
Coating A	**225°C**	0.110	0.109	0.105	0.108
	250°C	0.090	0.070	0.085	0.081
	275°C	0.098	0.116	0.108	0.107
Coating B	**225°C**	0.000	0.020	0.004	0.008
	250°C	0.030	0.040	0.050	0.040
	275°C	0.028	0.076	0.010	0.038

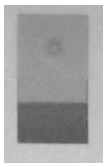
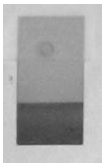
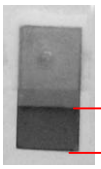
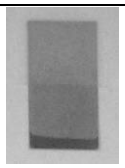
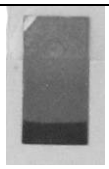
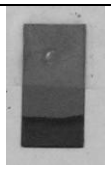
	Temperature	**225°C**	**250°C**	**275°C**
Coating A	**picture of probe after test**			
	Avg. Wicking height [mm]	**5.5**	**6.1**	**6.9**
Coating B	**picture of probe after test**			
	Avg. Wicking height [mm]	**1.6**	**3.6**	**4.6**

Fig. 3.7 Wicking height on coated probes

As observed by visual inspection of the probes after the test, coating of type A absorbs more PS melt than coating of type B. This agrees with the better wicking behavior of coating A compared to coating B, as previously described. The force reading is not very reliable since PS might be still attached to the surface of the coating and not wicked into it. Increasing temperature corresponds to more PS being absorbed by the refractory coating, since smaller polymer chains can easier wick into the coating, which agrees with previous observations of parameters such as the area enclosed in the force-displacement graphs.

Fast Fourier Transform (FFT) analysis of Force-time data shows marked difference in interaction of the two refractory coatings with the polystyrene melt. Figure 3.8 shows a typical data set, which is used to generate the power spectrum presented in Figure 3.9. Results, presented in Table 3.6, show that there is a dominant frequency at 0.34Hz for both coating A and B at temperatures of 225°C and 250°C. At 275°C there is no dominant frequency present. Also, at 225°C the periodic frequency of 0.68Hz is present for both coatings. The dominant frequency is a function of the immersion-emersion velocity, the properties of the PS melt and refractory coating at a certain temperature.

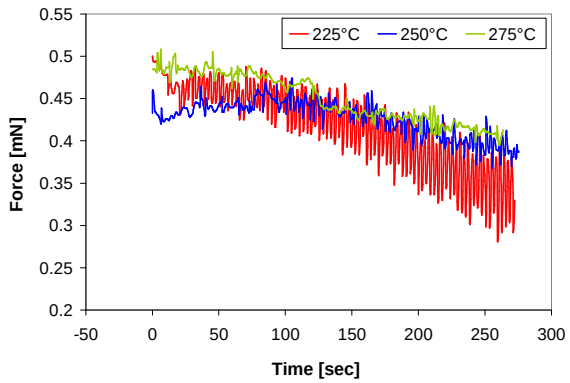


Fig. 3.8 Example data set used for FFT in figures below (advancing lines for coating A)

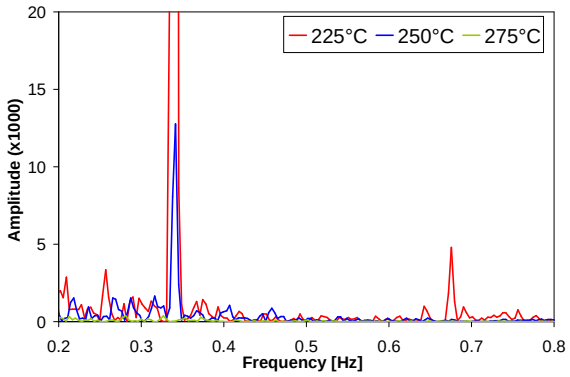


Fig. 3.9 Example FFT results (power spectrum) for advancing lines of coating A (in normal scale)

Table 3.6 Peak amplitude of power spectrum for different temperatures (average values from 3 test)

		Coating A Amplitude (x1000)		**Coating B Amplitude (x1000)**	
Temperature	Frequency [Hz]	Advancing Line	Receding Line	Advancing Line	Receding Line
225°C	0.34	143.7	213.3	292.0	353.7
	0.68	3.3	3.5	5.7	5.5
250°C	0.34	8.2	10.6	6.6	20.3
	0.68	-	-	-	-
275°C	0.34	-	-	-	-
	0.68	-	-	-	-

The more distinct peak amplitude at lower temperatures can be explained since polymer chains constantly entangle and disentangle while the probe travels through the melt, creating resistance and stress relaxation respectively along the probe-melt interface. At higher temperatures, the polymer chains degrade and result in reduced probability of polymer chain entanglements, as mentioned previously.

All the wetting experiments were performed at a translational penetration rate of 8um/sec. The fundamental frequency of 0.34 Hz was observed for all the 3 experimental temperatures with the power spectral density decreasing with an increase of temperature. The 0.34 Hz frequency corresponds to a characteristic length of 24um. The characteristic length may well be a function of the polymer chain length and configuration in the liquid mass. This is a very interesting observation that needs to be carefully investigated with further tests with polymer standards to check if the proposed technique can be used as an indication measure for molecular weight in a polymer melt.

3.4 Summary and Conclusions

This study involved the implementation of a novel experimental system to study wicking and wetting behavior of polystyrene melt with porous refractory coatings at high temperatures. The method involved the use of dynamic Wilhelmy plate technique which obtains a record of force-displacement hysteresis loops of porous coating on a suitable substrate with a liquid polymer melt at target temperature under controlled deformation rate. A procedure has been established which enables a quantitative comparison of different refractory coatings at elevated target temperatures and such measurements are not possible with commercial available experimental systems and demonstrates the contributions from this study. The wetting and wicking behavior of two commercially available refractory coatings with polystyrene melt, as used in Lost Foam metal Casting (LFC) process have been studied at target temperatures of 225°C, 250°C, 275°C and 300°C, which are of relevance to study as related to improving lost foam casting process of aluminum alloys. A Mica based coating (Coating A) has been compared with a Silica based coating (Coating B) and various new experimentally measurable constitutive parameters are proposed which could be obtained from the force hysteresis loops. These results indicate that Coating A has better wetting and wicking properties than Coating B for the temperature range between 225°C and 300°. The difference is most distinct near the processing temperature of 225°C. With an increase of temperature, PS melt wets the coatings better since polymer chains degrade at higher temperatures, resulting in shorter molecular chain lengths and a less viscous mass, thus improving the interface properties. The increase of wetting and wicking ability with increased temperature is more striking for Coating B, and it was observed that at 300°C Coating A has still a better interface properties than Coating B. Results above 300°C are not

reported because of the high polymer degradation which make reliable measurements challenging. The system that has been developed can be used for temperatures as high as 800 degrees centigrade to study complex wetting and interface problems that involve materials such as liquid metals with ceramic coatings and the proposed system is expected to have large impact on a broad class of materials science problems.

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Vita

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