TESTS FOR DETERMINING VISCOELASTIC PROPERTIES OF INVESTMENT CASTING WAXES

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Abstract

The Investment Casting Institute developed standard tests for the investment casting industry. For waxes, most of these tests are concerned with engineering properties, such as flow, softening point, strength, and sink. The available tests provide the information for handling and processing wax patterns. The volumetric expansion is the only test that can be used to estimate wax shrinkage allowances neglecting all other mechanical properties of the wax. The wax deformation and ensuing shrinkage allowances during processing can be estimated based on their thermo-mechanical properties.

In this study, tests used to determine mechanical properties of investment casting waxes are reviewed. As waxes are viscoelastic materials, their mechanical properties can be determined using dynamical mechanical analysis (DMA) measurements. The DMA measurements can be also be used to determine the filler effects on the mechanical properties. There are several ASTM standards for conducting DMA measurements and other industries have their own standards. Recommendations for mechanical testing of waxes are made based on testing one unfilled wax and one filled wax. The recommendations made could be used to establish new testing guidelines for waxes in the investment casting industry.

1.0 Introduction

Wax pattern deformation has a large effect on tooling allowances. Rosenthal (1979) and Okhuysen et al. (1998) indicated that the shrinkage of the wax is one of the largest components of the overall dimensional change between the pattern tooling and its corresponding cast part. The Investment Casting Institute published the "Standard Test Procedures for Pattern Materials" handbook in which standard specifications for use in investment castings are recommended. The tests considered are ash content; flow test; determination of softening point; determination of consistency; determination of filler content; determination of percentage of acid insolubles in soluble wax; specific gravity of waxes and plastics; sink test; and dimensional stability. These current tests are used for quality control and provide the information for handling and processing wax patterns. The volumetric expansion provides information on how much a wax system is prone to distortion or deformation. To date, wax shrinkage allowances are estimated using only the volumetric expansion data, since other mechanical properties of waxes are not available.

The lack of data on mechanical properties of waxes hindered the progress in die tooling for many years. Die dimensions are reworked by trial-and-error procedures until casting dimensions are produced within acceptable dimensional tolerances, increasing the lead time and costs (Okhuysen et al., 1998). With the worldwide increase demand in reducing production cycle times, the dimensioning practices in the investment casting process must be advanced. One way to advance the dimensioning practices is to estimate the shrinkage allowances based on material properties and process parameters. Thus, the mechanical properties of investment casting waxes must be measured. The availability of mechanical property data for waxes will provide a strong basis for estimating the shrinkage factors, allowing the investment casters to take full advantage of unique properties of each class of waxes in the process design.

As waxes are viscoelastic materials, their thermomechanical and thermophysical properties can be determined using measurements techniques that were developed for polymers. The measurement of viscoelastic properties of waxes is not a trivial task since the investment casting waxes are complex blend of polymers that exhibit a wide range of behaviors. Monks (1993) presented the first attempt to quantify the rheological behavior of investment casting waxes. Monks (1993) used an oscillatory shear rheometer to characterize overall elastic and viscous behavior of liquid waxes above the congealing point. It is indicated that for levels of resin content greater than 8%, experimental measurements could not be conducted.

Recently, Sabau and Viswanathan (2000 and 2001) worked on the measurement of thermophysical and thermomechanical properties of Cerita™ 29-51, a commercial, semi-crystalline, unfilled wax. In the second Section, techniques for measuring the thermo-mechanical properties of waxes are discussed. Recommendations are presented in the third Section for wax testing. Example results for unfilled and filled waxes are provided in the fourth Section.

2.0 Measurement techniques used for investment casting waxes

Dynamical mechanical analysis (DMA) is a proven testing technique for viscoelastic materials (Menard, 1999). In (DMA) tests, an oscillatory strain is applied to the material and the resulting stress is separated into elastic and viscous components. Elastic stress is the component of the stress in phase with the applied strain while the viscous stress is in phase with the strain rate. There are several ASTM standards for conducting DMA measurements and other industries have their own standards (Table 1).

Table 1. ASTM Standard for the DMA.

ASTM Standard	Test description
D4440	Measurement of Polymer Melts
D5023	DMA in Three Point Bending
D5024	DMA in Compression
D5026	DMA in Tension
D5279	DMA of Plastics in Tension
D5418	DMA in Dual Cantilever
D6648-01	BBR*: Flexural Creep Stiffness of Asphalt Binder (Standard)
D4 P 245	BBR: Flexural Creep Stiffness of Asphalt Binder (Test)

*BBR Flexural Creep Stiffness of Asphalt Binder

All these standards were developed for other applications than those in investment casting and their applicability to study of wax properties must be assessed. For example, the BBR was developed for materials having flexural-creep stiffness values in the range of 20-1,000 MPa. Although standard recommends the use of the test apparatus within the temperature range [-36:0] ^{o}C, Sabau and Viswanathan (2001) used BBR successfully for an unfilled wax. Some measurement techniques did not work as well as expected (Table 2). We tested the wax material using various fixtures and different instruments with higher sensitivity until appropriate test instruments, procedures, and fixtures were identified (Table 3). In Table 3, few other measurement techniques used in the investment casting community were also included.

Table 2. Inappropriate test procedures and/or instruments

Property/Sample state	*Tests/Test configuration*	*Test instruments*	*Reference*	*Identified problem*
Thermal conductivity	Hot disk technique	Gustafsson (1991)	Sabau and Viswanathan (2000)	Poor contact[1]
Shear modulus (liquid)[2]	Shear oscillatory	RDAII rheometer (RS)[3]	Not published[4]	Low instrument sensitivity
Shear modulus (liquid-paste transition)	Shear oscillatory /concentric cylinder	VOR Bohlin rheometer	Not published[4]	Too much slippage
Shear modulus (liquid-paste transition)	Shear oscillatory/disk	DMTA IV (RS)[3]	Not published[4]	Data is not reproducible during the transition
Shear modulus (paste)	Shear oscillatory/ serated plate	VOR Bohlin rheometer	Not published[4]	Results are not appropriate; could be due to thermal expansion property of wax
Melt flow rate	Extrusion	Kayeness Melt Indexer 4002	Shenoy (2000) ASTM D1238	Cannot be used for high filler content

[1]poor contact between the sensor plate and material results in lower values for thermal conductivity being measured in the solids state than in the liquid state
[2]liquid, temperature above the ring and ball softening point
[3]RS indicates Rheometrics Scientific, Inc.
[4]Work performed by Sabau and Viswanathan (2000).

The tests performed in shear oscillatory, torsion oscillatory, and flexural are part of a larger class of DMA tests. The elastic and viscous stiffness components determined from DMA tests are usually referred to as the loss and storage modulus, respectively. When oscillatory shear measurements are conducted, data on loss and storage modulus are obtained as a function of frequency.

3.0 Recommendations for Wax testing

Based on our experience in measuring the viscoelastic properties of waxes and review of polymer testing, tests and fixtures, which we recommend for wax testing, are highlighted in Table 4. The tests and fixtures depend on material consistency.

Table 3. Tests used for determining wax properties

Property	*Tests/Sample shape*	*ASTM Standard*	*Test instruments*	*Reference*	*IC Industry use*
Density and thermal expansion	Thermomechanical analysis (TMA)	E831	Dupont TMA	Sabau and Viswanathan (2000)	Widely used
Specific heat (latent heat for phase changes)	Differential scanning calorimetry (DSC)	E1269 (ISO 11357)	Netzsch DSC 404C	Sabau and Viswanathan (2001)	Widely used
Thermal conductivity	Transient line-source technique	D 5930-97		Sabau and Viswanathan (2001)	Not used
Bulk modulus	Pressure-specific Volume-Temperature (PVT)		Gnomix PVT	Chakravorty (1999); Sabau and Viswanathan (2000)	Introduced to IC in 1999
Shear modulus (liquid)[1, 3]	Shear oscillatory: melt rheology/parallel plate	D4440-01	RFSII rheometer (RS)[2]	Sabau and Viswanathan (2000)	Widely used in rheometry
Shear modulus (liquid)	melt rheology/cone, concentric cylinder capillary		Rotational viscosimeter and capillary rheometer	Jolly et al. (2002)	Application to wax injection
Shear modulus (paste)[3, 4]	Torsion oscillatory/ rectangular geometry	D5279 (ISO 6721)	Advanced Rheometric Expansion System (ARES) (RS)[2]	Sabau and Viswanathan (2000)	used in rheometry
Shear modulus (paste)[3, 4]	Shear oscillatory/disk	D5279 (ISO 6721)	DMTA IV (RS)[2]	Sabau and Viswanathan (2000)	used in rheometry
Shear modulus (solid)[4]	Flexural/bar	D6648-01 (AASHTO T313-02)	Bending beam rheometer (BBR).	Rowe and Sharrock (2000); Sabau and Viswanathan (2001)	Used for asphaltic binders

[1]liquid, temperature above the ring and ball softening point
[2]RS indicates Rheometrics Scientific.
[3]For the wax tested, at temperatures of 60, 65, and 70^{o}C, reproducible data could not be obtained using either the Rheometrics Scientific ARES or melt rheometers.
[4]Bending beam rheometer may provide better data than the ARES system in the solid state.

Waxes used in the investment casting industry are a blend of semi-crystalline polymers, additives and fillers. For waxes tested, the glassy region occurs at temperatures below 20 ^{o}C. As temperature increases, waxes soften gradually. We observed that waxes exhibit a transition from a soft paste to that of a viscous liquid with less elasticity at a certain temperature which is less

than the melting point. For the sake of simplicity we refer to that temperature as the softening point temperature, T_{SP}. T_{SP} is given by the temperature at which the thermal expansion curve and DSC curve attain their peaks. T_{SP} can be associated with either an α transition for the crystalline component of the wax or a transition in the amorphous component of the wax. The former is due to the slippage of the crystallites past each other while the latter is related to the movement of coordinated segments reducing the viscosity (Menard, 1999).

Table 4. Tests and fixtures recommended for investment casting waxes.

Stiffness/ material form	Test	Instrument	Fixture	Temperature range [^{o}C]
Hard/solid	Flexural (3-pt. Bending)	BBR	Rectangular bar	RT< T < 40
Hard/hard paste or Soft/paste	Torsion oscillatory	DMA	Rectangular bar	RT< T < T_{SP}-5
Soft and Gooey/Paste	Shear oscillatory	DMA	Disk	T_{SP}-10< T < T_{SP}
Liquid	Shear oscillatory	Melt rheometer	Disk	T_{SP}+5< T <T_{SP}+20

The test domain is indicated in Table 5. At temperatures close to T_{SP} is it very difficult to obtain reproducible data. Around this temperature, waxes exhibit a sharp change in its stiffness. For example, Cerita^{TM} 29-51 wax is very soft above 60^{o}C, both the loss and storage moduli exhibiting values at 75^{o}C approximately five orders of magnitude lower than their values measured below 55^{o}C. If liquid state effects must be included in the analysis, appropriate methodologies for dealing with the sharp change in stiffness must be developed. For billet injection, the testing in the paste domain needs to be performed in order to obtain shear modulus at larger times.

Table 5. Testing domain for investment casting waxes.

Wax injection	Solid	Paste	Liquid
Billet	●	●	
Paste	●	●	
Liquid*	●	●	●

*As a first approximation, liquid effects could be neglected.

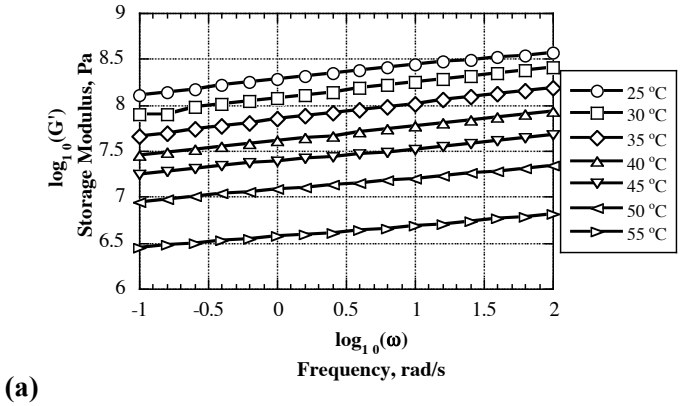
4.0 Results for Waxes

The DMA techniques were used for testing two waxes, one unfilled and the other one filled (Table 6). Figure 1 shows data on loss and storage modulus for Cerita^{TM} 29-51, an unfilled wax, semi-crystalline, which is used in the investment casting industry. This wax was kindly provided by M. Argueso & Co, Inc. Many commercial waxes contain aditives and fillers that are blended with a base polymer to improve properties and to reduce costs.

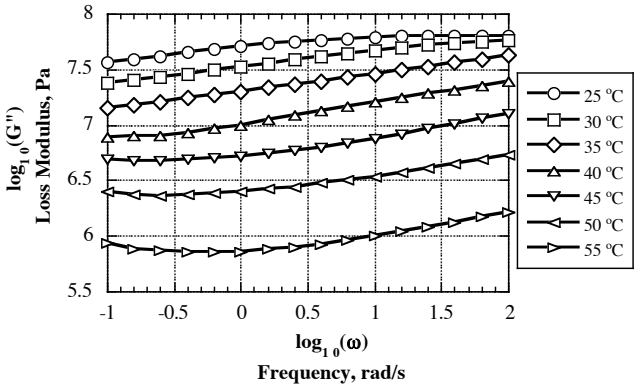
Table 6. Waxes tested for this study.

Wax name	Filler	Filler Weight [%]	Filler Volume [%]	Notes
Cerita™ 29-51	-	0	0	semi-crystalline
Cerita™ F20-6	Terepthalic acid	42	31.6	semi-crystalline

The DMA measurements can be also be used to determine the filler effects on the mechanical properties. Figure 2 shows data on loss and storage modulus for Cerita™ F20-6, a filled wax, which was kindly provided by Precision Castings of Tennessee, Inc and M. Argueso & Co, Inc. The base wax for Cerita™ F20-6 is different than Cerita™ 29-51 and the two data sets cannot be compared to assess the filler effect. However, DMA testing can be used to determine the filler effects on the strength of the wax, which are sometimes seen as changes in the storage modulus curve.



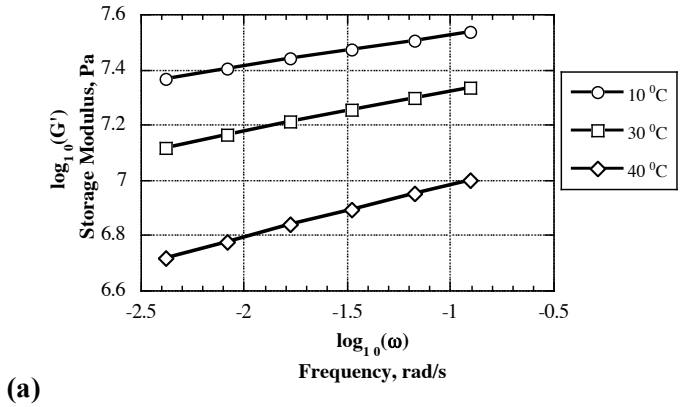
(a)



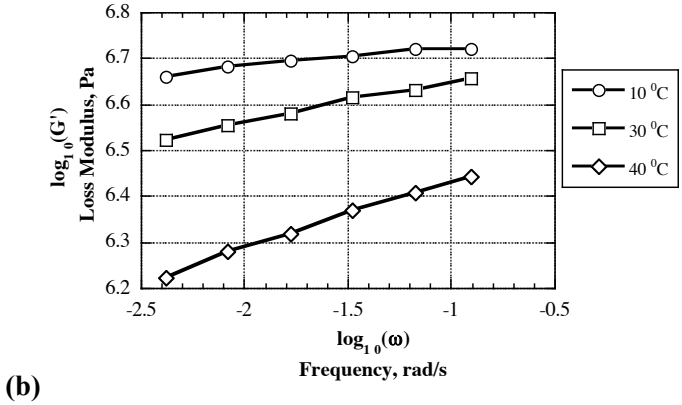
(b)

Figure 1. ARES experimental results for the (a) storage shear modulus, and (b) the loss shear modulus as a function of frequency (Cerita™ 29-51 wax).

The shear modulus is next obtained from data on loss and storage modulus. The shear modulus of viscoelastic materials depends on time and temperature.



(a)



(b)

Figure 2. BBR experimental results for the (a) storage shear modulus, and (b) the loss shear modulus as a function frequency (Cerita™ F20-6 wax).

It is very convenient to deal with shear modulus as a function of time and then to adjust the time dependent function for different temperatures. In order to find the modulus at a given temperature, data taken at different temperatures over the same frequency range is shifted horizontally along the frequency axis to overlap the ends of each curve, extending the material characterization at wider frequency ranges, or wider time ranges. This time-temperature superposition principle does not apply across the transition domain when the wax behavior changes from that of a paste to that of a liquid.

The master curves, obtained using all ARES data available at isothermal tests, are shown in Figure 3 for Cerita™ 29-51 wax. For the Cerita™ F20-6 wax, the master curves are shown in Figure 4. The testing for Cerita™ F20-6 wax is incomplete, since the BBR could only be used for temperatures less than 40 ^{o}C. The next step is to perform a nonlinear regression from the master curves for the storage modulus, *G'*, and loss modulus, *G"*, in order to obtain material parameters that can be used viscoelastic models (Sabau and Viswanathan, 2000).

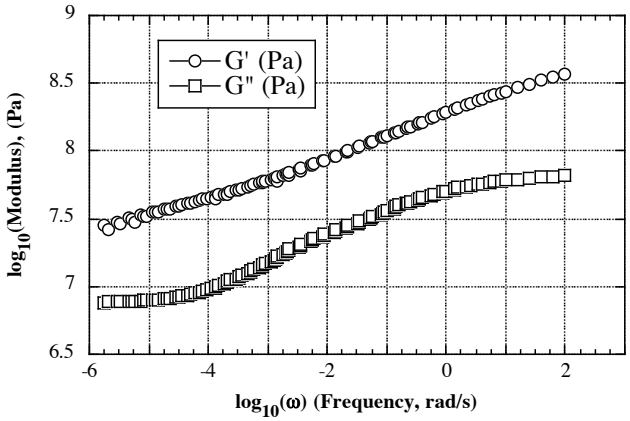


Figure 3. Master curves for the storage (G') and loss moduli (G") obtained from ARES experimental data at the reference temperature of 25°C (Cerita™ 29-51).

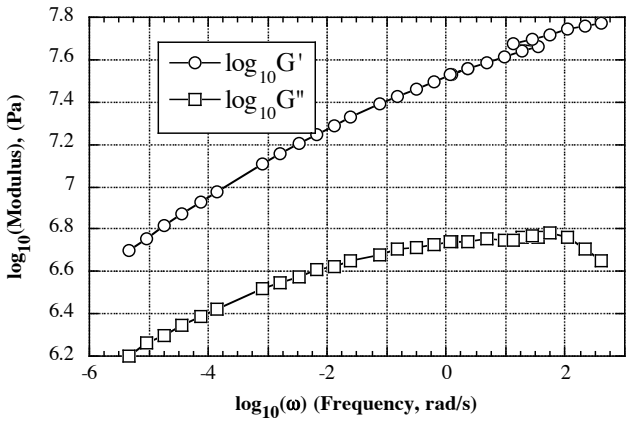


Figure 4. Master curves for the storage (G') and loss moduli (G") obtained from BBR experimental data at the reference temperature of 25°C (Cerita™ F20-6 wax).

Alternatively, we can use Ferry and Ninomiya's method to approximately calculate the equivalent stress relaxation master curve (Boyd, 1985; Schwarzl and Struik, 1967):

$$G(t) = G'(\omega) - 0.4G''(0.4\omega) + 0.014G''(10\omega); \quad \omega = 1/t$$

$$G(t) = G'(\omega) - 0.5303G''(0.5284\omega) - 0.021G''(0.085\omega) + 0.042G''(6.37\omega); \quad \omega = 1.25/t$$

The frequency domain in the master curve must be large enough to cover the relevant domain for our process. As we can see from these relationships, if the shear moduls must be obtained over a time domain $[t_1 : t_2]$, the required frequency test domain is $[0.1/t_2 : 10/t_1]$. The time domain over which shear modulus is needed depends on size of the part and thermal diffusivity of waxes. For small patterns of thickness less than one inch, which are injected of unfilled waxes, such as Cerita™ 29-51 wax, the entire wax pattern reaches the room temperature in approximately two

hours. The wax material at the surface of the pattern reaches room temperature much faster, in less than five minutes. For filled waxes, the thermal diffusivity might be higher depending of properties of the filler used, and the solidification/crystallization time may be different. It is known that dimensions of investment casting pattern stabilize after at least one or two days after the patterns were injected. Thus, the time domain over which the shear modulus must be obtained at room temperature is [0:24hours], or [$0.01:10^5$] seconds. This corresponds to a frequency domain of [10^{-6}: 10^3] rad/seconds. Similar considerations may be given to other temperature range at which thicker sections in the wax pattern may stay for hours.

5.0 Summary and Conclusions

Viscoelastic properties of investment casting waxes can be measured using dynamical mechanical analysis (DMA) techniques. Recommendations for mechanical testing of waxes were made based on testing commercial, semi-crystalline, unfilled and filled waxes. The recommendations made could be used to establish new testing guidelines for determining the thermo-mechanical properties of investment casting waxes. The data on viscoelastic properties will be used to estimate the wax deformation and ensuing shrinkage allowances during processing.

6.0 Acknowledgments

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7.0 References

Boyd, R.H., 1985, *Polymer*, Vol. 26, p. 323.

Chakravorty, S., 1999, "Assessment of Properties of Investment Casting Waxes," Paper No. 1, Proceedings of 24th BICTA Conference on Investment Casting.

Gustafsson, S.E., 1991, Rev. Sci. Instrum. 62(3), pp. 797.

Investment Casting Institute "Standard Test Procedures for Pattern Materials," 1999, Investment Casting Institute, 19 pp.

Jolly, M.R., Cox, M., Harding, R.A., Griffiths, W.D., and Campbell J, 2002, "Quiescent Filling Applied to Investment Castings and Its Effect on Their Mechanical Properties" Paper No. 6, Proceedings of the 50th Annual Meeting of the Investment Casting Institute, Chicago, September 29 – October 2.

Menard, K.P., 1999, "Dynamic Mechanical Analysis: A Practical Introduction to Techniques and Applications," CRC Press, Boca Raton, Florida.

Monks, H., 1993, "Flow and Deformation of Casting Waxes in the Solidification Region," Paper No. 3, 8th World Conference on Investment Casting.

Okhuysen V.F., Padmanabhan, K., and Voigt, R.C., 1998, "Tooling Allowance Practices in the Investment Casting Industry," Paper No. 1, 46th Annual Technical Meeting, Investment Casting Institute.

Rosenthal, H.H., 1979, "Shrink Allowance for Pattern Dies in Investment Casting," Paper No. 2, Proceedings of the 27th Annual Meeting of the Investment Casting Institute.

Rowe, G.M., and Sharrock, M.J., 2000, "Development of Standard Techniques for the Calculation of Master Curves for Linear-Visco Elastic Materials," The 1st International Symposium on Binder Rheology and Pavement Performance, The University of Calgary, Alberta, Canada, August 14-15.

Sabau, A.S., and Viswanathan, S., 2000, "Determining Wax Pattern Dimensions in Investment Casting Using Viscoelastic Models," Paper No. 1, 48th Annual Technical Meeting, Investment Casting Institute.

Sabau, A.S., and Viswanathan, S., 2001, "Determining Wax Pattern Dimensions in Investment Casting Using Viscoelastic Models," Paper No. 3, 49th Annual Technical Meeting, Investment Casting Institute, Orlando, Florida, Oct. 7-10.

Schwarzl, F.R. and Struik, L.C.E., 1967, "Analysis of Relaxation Measurements," *Advances in Molecular Relaxation Processes,* Vol. 1, pp. 201–255.

Shenoy, A., 2000, "Material's Volumetric-Flow Rate (MVR) as a Unification Parameter in Asphalt Rheology and Quality Control/Quality Assurance Tool for High Temperature Performance Grading," Applied Rheology, Vol. 10, No. 6, pp. 288-306.