

Material Properties and Test Methods for Molding Analysis

R&D Center

Accurate analysis requires both an accurate model and material property. An improper version of either will absolutely result in an inaccurate analysis. Innumerable factors impact the accuracy of molding analysis. As such, there are the methods of modeling (midplane, fusion, 3D), mesh quality(the size of mesh, aspect ratio, mesh match ratio, reciprocal ratio, etc.), the insertion method of the molding condition, cooling and consideration of fiber orientation, accuracy of material property. Of these, This paper aims to explain material properties, measuring methods for molding analysis, and the effects that each material property impart upon the analysis results.

The main properties of materials for molding analysis appear on the table to the right. The tensile modulus and Poisson ratio are a mechanical property. We will talk about these in detail later at when we discuss the measurement of the structural analysis. In addition, shrinkage will be excepted from this paper as it is a method based on Moldflow's experience.

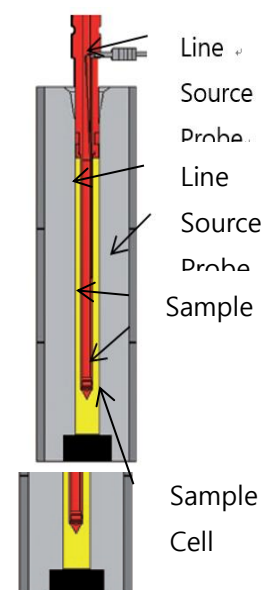
Properties	Method	Test machine
Thermal Conductivity	ASTM D5930	Line-source apparatus
Specific Heat	ASTM E1269 ASTM D3417	DSC with Sapphire
Transition Temp. Ejection Temp.	ASTM D3418	DSC
Shear Viscosity	ASTM D5422	Capillary rheometer
pVT(Pressure-Volume-Temperature)	Direct method Indirect method	Dilatometry
Linear thermal expansion coefficient	ASTM D696	Dilatometer
Tensile modulus Poisson ratio	ASTM D638	UTM with Extensionmeter
Shrinkage	Moldflow method	

Thermal conductivity is the quantity of heat transmitted through a unit thickness of a material in a direction normal to a surface of unit area due to a unit temperature gradient under steady state conditions. It is also an integer number regarding material and changes by temperature and pressure. Thermal conductivity is a property which exhibits the capability of heat conduction. In addition, it is used for predicting mold and product temperatures by calculating transmitted calories from melted materials having the high temperature to low temperature molds and the transferred calories on the direction of thickness in molding analysis. Material which has high thermal conductivity transfers many calories for difference of unit temperatures. So it imparts many calories to the mold. Therefore, it has a great temperature difference and high injection pressure during the filling step. Thermal conductivity can be derived by the following equation, in which we measure the quantity of heat passed through the plastics at the state of the thermal gradient.

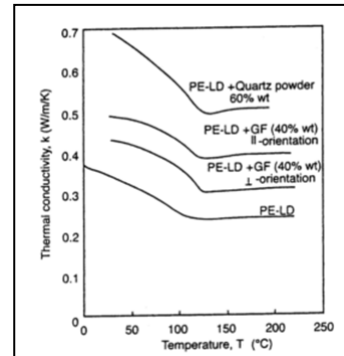
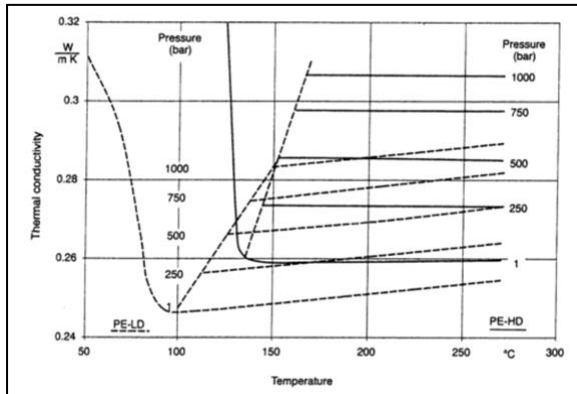
$$\left(\frac{dQ}{dt} \right) = -kA \left(\frac{dT}{dx} \right)$$

There are hot wire method¹⁾, heat flow method, and laser flash method etc. as the measuring the thermal conductivity. Both Moldflow and Moldex3D measure the thermal conductivity as the hot wire method.

In case of amorphous resins, thermal conductivity increases by increasing temperature until Tg. However, it decreases when over Tg. In general, crystalline resins have high thermal conductivity compared with amorphous resins. And crystalline has higher thermal conductivity compared with a melted state as the crystalline increases density during crystallization. Both crystalline and amorphous resins increase thermal conductivity by increasing pressure.²⁾ In addition, thermal conductivity is



affected by the orientation of polymer chains and a reinforcing agent. In other words, resins having oriented polymer chains have high thermal conductivity and you can make the thermal conductivity increase by the addition of the inorganic fillers which have high thermal conductivity. Finally, there is a dramatic decrease of thermal conductivity at T_m .³⁾



pvT is the property which exhibits the correlation of a specific volume by the temperature and pressure. It is used for calculating thermal expansion and compression of resins in the filling step, and calculation of volume shrinkage in the packing step. It is essential data for calculations of injection pressure, distribution of temperature during filling step, and so on.

The measuring method of pvT can be classified by the type of measuring machine. Those are a piston-die(direct) method and the mercury high pressure dilatometer(indirect) method.⁴⁾ The piston-die method is the method for measuring the specific volume by giving pressure at the one direction of the cylinder axis. The mercury high pressure dilatometer method measures the specific volume by transferring pressure in every direction of the sample using mercury. The mercury high pressure dilatometer method has high accuracy but has many complications because mercury is used. The piston-die method is hard to keep static pressure. It also has the disadvantages of inaccurate data when the friction with a cylinder wall in the solid state and the inflow of bubble. However, it is relatively easy to handle. The difference in accuracy between these two methods is an average of 2.5%, and not over 5% at maximum.

The measured pvT Data is expressed by the Tait Equation and entered into material data.

$$V(T, P) = V_0(T) \left(1 - C \ln \left[1 + \frac{P}{B(T)} \right] \right) + V_1(T, P)$$

$$T < b_5 + b_{6P},$$

$$V_0 = b_{1s} + b_{2s}(T - b_5),$$

$$B(T) = b_{3s} \exp[-b_{4s}(T - b_5)],$$

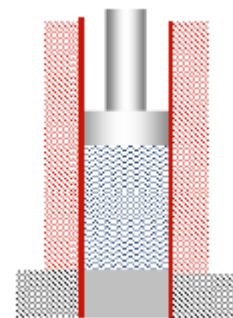
$$V_1 = b_7 \exp[b_8(T - b_5) - b_9P],$$

$$T > b_5 + b_{6P}$$

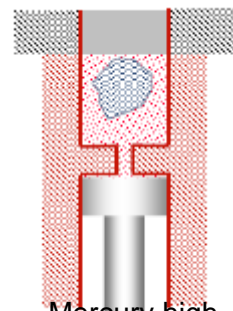
$$V_0 = b_{1m} + b_{2m}(T - b_5)$$

$$B(T) = b_{3m} \exp[-b_{4m}(T - b_5)]$$

$$V_1 = 0$$



Piston-Die method



Mercury high pressure dilatometer method

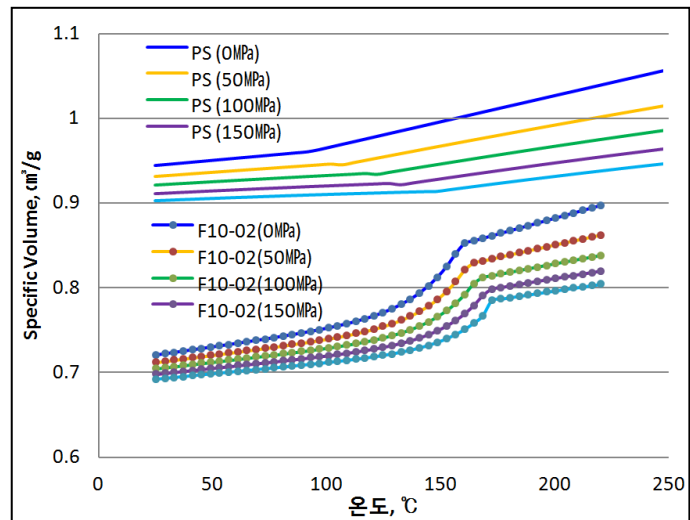
There are the isobaric and isothermal measuring methods on the way to measure. In case of the isothermal method, due to the enough crystallization, the slope of graph is very steep. Therefore, there is a large volume change and the initiation of crystallization early begins.

In regards to crystalline resins, the specific volume decreases sharply at T_c because of crystallization and T_c increases when pressure increases like in the figure. The change of specific volume of the amorphous resins is smaller than crystalline resins and this explains the shrinkage difference between two resins.

The setting of pressure is important for equal distribution on the every part of the cavity because materials which have a large gap between curves by pressure have a significant volume change by the scale of pressure.

The viscosity is the proportional coefficient between the shear stress and shear velocity. It refers to the loss of energy when the fluid flows. Thus, it can be understood as a resistance toward flow.

In the case of solids, the proportional coefficient of shear stress and strain rate is the modulus of elasticity by Hooke's Law. As for fluids, the proportional coefficient between shear stress and strain rate (shear velocity) is the viscosity. The viscosity data is needed to calculate the flow property by the transition of temperature and velocity in the molding analysis.

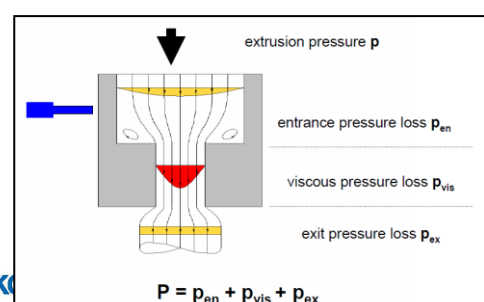


The viscosity of Newtonian fluid is a changeable constant by temperature. However, non-Newtonian fluid changes by not only temperature but also shear velocity. Thus, it isn't related to shear velocity in low shear rates. However, in the high shear rate, the disentanglement velocity of the polymer chain is faster than the entangling velocity, so the shear thinning effect (when the shear velocity increases, the viscosity decreases) generates and the flow resistance decreases.

As the temperature increase, so the polymer chain moves more actively and the intermolecular forces are weaker, so the intermolecular distance gets farther and free space is expanded. Therefore the flow resistance gets lower and the viscosity gets lower, too.

The material that has a big change of slope in graph showing the shear velocity and viscosity has a large shift of viscosity by changing the injection velocity. Beyond that, the material that has a small change of viscosity by temperature can't be expected the increasing effect of fluidity by increasing temperature.

There two methods to measure the shear viscosity. One method is setting the pressure transducer and thermocouple to the injection machine. The other one is combining the shear viscosities getting from capillary rheometer (the shear area over 1,000pa-s) and rotational rheometer(the shear area below 1,000pa-s).



The shear viscosity from the capillary rheometer is the apparent viscosity. The reasons for this are the non-parabolic velocity profile different from Newtonian fluid, slip on the wall, and the loss of pressure at the entrance and exit. So the correction for the reasons is needed to measure the real viscosity. There are Bagley Correction⁵⁾ for the correction of pressure loss, Mooney Correction for the correction of slip, Weissenberg-Rabinowitsch Correction⁶⁾ for the correction of non-parabolic velocity profile.

The measured data of viscosity is also not used as the raw data directly. Fit the raw data to the model forecasting viscosity and insert it to material DB as the factor form and then use. There are the Newtonian Model, Second Order Model, Power Law Model과 Cross-WLF Model in the viscosity Model. The Cross-WLF Model in which viscosity is expressed by the function of shear velocity, temperature and pressure is mainly used.

$$\eta(\dot{\gamma}, T, P) = \frac{\eta_0(T, P)}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*} \right)^{1-n}}$$

$$\eta_0(T, P) = D_1 \exp \left[- \frac{A_1 (T - T^*)}{A_2 + (T - T^*)} \right] \quad T > T^*$$

$$T^*(P) = D_2 + D_3 P$$

$$A_2 = A_3 + D_3 P$$

$$\eta_0(T, P) = \infty \quad T < T^*$$

The viscosity is influenced by molecular weight, distribution of molecular weight, and existence of chain branches. Long chain branches make viscosity decrease at low molecular weights (the decrease of entanglement). On the other hand, it makes increase at high molecular weights (increase of entanglement).

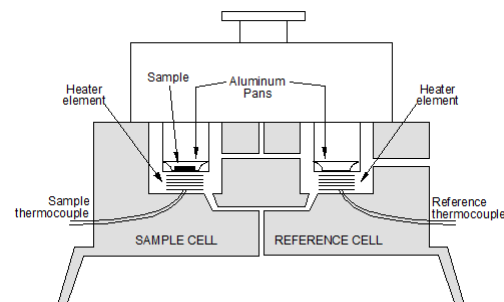
In addition, when the molecular distribution is narrow, there are Newtonian properties in the low shear rate. When the molecular distribution is wide, molecules relatively have low molecular weight. And, the number of entanglements decrease and the molecules having low molecular weight take on the role of a lubricant. With these principles, when the shear velocity gets higher, materials having the wide distribution of molecular weight have lower viscosity than the materials with the narrow thing.

Mean Heat Capacity, \bar{C} defined as the calorie's ratio, depends on temperature variation. It is the calorie needed to make the object's temperature increase 1°C. Specific heat capacity is defined as the heat capacity per unit mass of material.

$$\bar{C} = \frac{\Delta Q}{\Delta T}$$

The unit of specific heat capacity is J/(kg · K). The specific heat capacity is measured on constant volume or constant pressure and is expressed by C_v , C_p . It is normal to use the C_p as there is too much shear stress in the vessel when the sample is heated on the specific part. It is hard to measure the change of heat capacity by the temperature variation on the constant volume or constant pressure conditions. As such, measure the change of heat capacity by the temperature with a standard sample that already has the specific heat capacity defined. Next, calculate the specific heat capacity of the unknown sample. The standard material is usually Sapphire or Sb_2O_3 and the method is DSC.⁷⁾

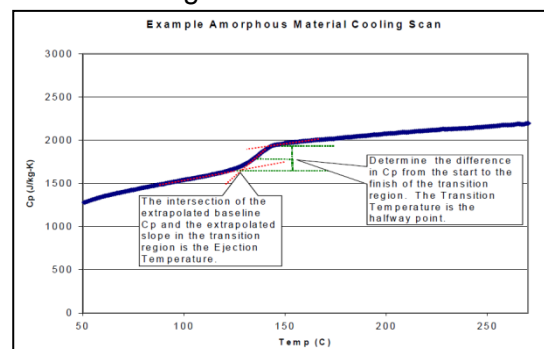
The specific heat capacity is different whether



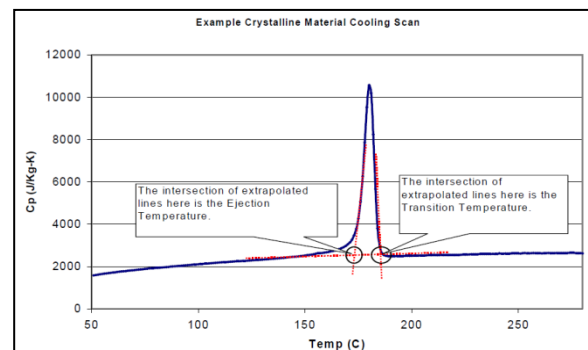
it is heating or cooling. The specific heat capacity also depends on the velocity of heating and cooling. The data of specific heat capacity for molding analysis is measured by the process of cooling with 20°C/min. It is for measuring at the similar state with real cooling process at the mold.

The specific heat capacity decides the required calories when the material melts and the calories removed after molding. In the process of filling and packing, calculate the quantity of heat which is transferred from the melted resins to the mold. It is used for the calculation of temperature, pressure distribution, shrinkage, and strain rate. In addition, it is used for calculating the increasing temperature of melted resins that flows into the cavity by shear heating. Material which has high specific heat capacities has small temperature difference and slow cooling during filling as it should release many calories.

The transition temperature is the point when the material changes from the melted state to the solid state. The transition temperature is the point which the flow stops. This is used for predicting the short shot and calculating the thickness of solidification layer in the direction of thickness. Beyond that, it is used for calculating the shrinkage when reaching the transition temperature in the cooling process.



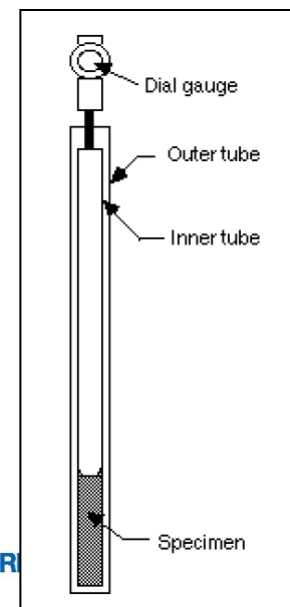
Ejection temperature is used for calculating the stress relaxation in shrinkage analysis and cooling time in flow analysis. Ejection temperature is also measured in the process of DSC cooling process. As for semi-crystalline material, the ejection temperature is predicted as the temperature which the recrystallization occurs. It is the temperature after the temperature of the crystallization peak. In the case of amorphous materials, the ejection temperature is the temperature when the material reaches the glass transition temperature.^{8), 9)}



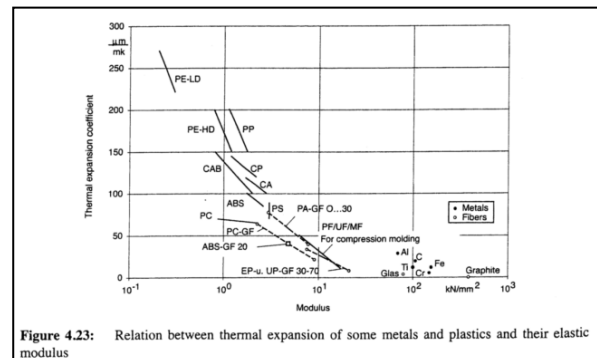
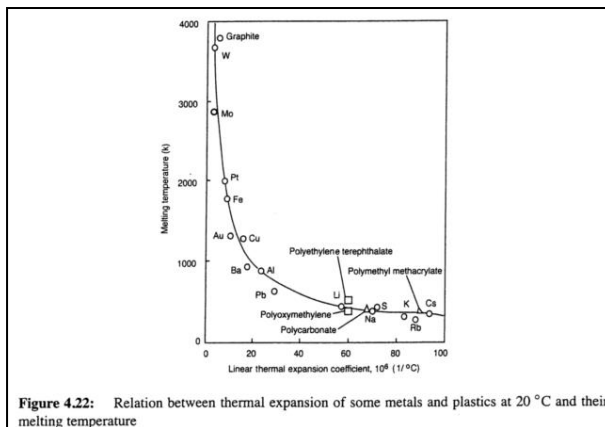
The thermal expansion coefficient(CTE) means the change of the length that becomes longer or shorter by the unit temperature difference. The thermal expansion coefficient is measured by the vitreous silica dilatometer that is the same as the figure to the right.¹⁰⁾

In many materials, the thermal expansion coefficient gets smaller when the melting temperature and elasticity is higher. The thermal expansion rate of the base polymer is easy to be predicted from the melting point and elasticity. However, in case of material reinforced by fiber or filler, it is hard to predict the thermal expansion rate. In addition, the fiber and the other fillers make the thermal expansion decrease highly.

The CTE is the function of temperature. In addition, there is a difference in the CTE data between the direction of flow and perpendicular flow by fiber orientation and it has a strong effect on



deformation. Therefore, the injection molded part shrinks following the line expansion coefficient by cooling from just after finishing the crystallization to mold temperature.¹¹⁾



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