Investigation of the Rheological Properties of Rotomolding Resins

Alvin Spence, Centro Incorporated

Abstract

There are many influential factors and processing variables that can impact the mechanical and aesthetic properties of a rotomolded part. One of the main variables is the resin being processed and its associated rheological properties. The manner by which the polymer powder sinters and fuses together needs to be understood to ensure the correct processing cycle is used to obtain an optimum cured part. The influence of bubbles that form during the sintering phase and the melt index of the material, contribute to the quality of the part being produced.

Introduction

During the rotational molding process the mold is rotated at relatively low speeds. Unlike other polymer processing techniques this causes little or no shear force between the molten polymer and the mold wall. The effect of a low shear force on the viscosity of a polymer is not well known. Typically the material's melt index is used as a parameter by which a molder will determine the materials ability to flow and reproduce the surface of the mold. The general rule of thumb being, the higher the melt index, the better the material will flow. However, during the melt index test, the shear force exhibited on the polymer is significantly higher than during the rotomolding process.

The removal of bubbles from a polymer melt has been associated with the rheological properties of that melt. For plastisols in which bubbles are a problem, viscosity depressants are recommended as a possible cure[1]. For polyolefins that mold with bubbles, possible solutions include using a resin with higher melt index or molding the resin at a higher oven temperature[2]. It can be seen that a number of solutions for problems with bubbles in rotationally molded products are connected with the polymers rheological properties. Therefore, it is important to understand what factors influence polymer viscosity.

Polymer Rheology

The work detailed in this paper investigates the differences in rheological properties for a range of rotomolding resins. Other authors[3,4] have shown that polymer viscosity is influenced by four main factors : shear rate, temperature, molecular weight and pressure. Pressure is not present in the rotomolding process and therefore was omitted from this investigation.

Shear Rate

Most polymer melts exhibit non-Newtonian behavior, that is, apparent viscosity decreases as the rate of shear increases. The viscosity of polymers at high shear rates may be several orders of magnitude smaller than the viscosity at low shear rates. During rotational molding it can be assumed that polymer viscosity is Newtonian as the shear rates experienced are low [4].

Temperature

The viscosity of most polymers change with temperature. The temperature dependence of viscosity for Newtonian fluids and for most polymer fluids above the glass-transition temperature, follows the Arrhenius equation to a good approximation:

$$\eta = Ae^{B/T} \qquad (1)$$

where: η is the viscosity of the polymer
T is the absolute temperature
A and B are constants of the liquid.

In general, for Newtonian liquids, the greater the viscosity, the stronger the temperature dependence.

Molecular Weight

The molecular weight of a polymer is the most important factor influencing rheology. Polymer viscosity is approximately proportional to the average molecular weight M_W below its critical molecular weight M_C. This relationship is expressed as follows:

$$\eta = K_1 M_w \quad \text{for } M_w < M_c \qquad (2)$$

However, as M_W increases past M_C then the viscosity is proportional to a power equal to 3.5, therefore:

$$\eta = K_1 M_w^{3.5} \quad \text{for } M_w > M_c \qquad (3)$$

It should be noted that the molecular weight of a polymer also determines its melt index. A polymer with a high molecular weight will yield a low melt index[5].

Experimental Equipment & Materials

Two methods were used to determine the rheological properties of a range of polyethylene materials:

1. Extrusion Plastometer

The melt index of a rotational molding resin is determined by ASTM D 1238, entitled, "Flow Rates of Thermoplastics by Extrusion Plastomer". The extrusion plastometer was used to determine the apparent viscosity of a polymer. Using normal test procedures, the polymer was forced through a die, radius R, length L, at a constant flow rate Q. From this the shear rate γ was calculated:

$$\gamma = 4Q / \pi R^3 \qquad (4)$$

It is recognized that a polymer melt does not strictly obey the laws of Newtonian flow. However, for low shear rates this expression was used as a good approximation to determine the apparent shear rate. By measuring the pressure drop "P" across the die, the shear stress τ was calculated from:

$$\tau = PR / 2L \qquad (5)$$

From these expressions, the apparent viscosity was calculated as the ratio of shear stress to shear rate:

$$\eta = \pi PR^4 / 8LQ \qquad (6)$$

2. Parallel Plate Rheometer

Viscosity was also measured using a Carri-med CSL 100 controlled stress rheometer. This system had a drive/displacement measuring combination comprising of a microprocessor controlled induction motor drive, a minimum friction low inertia air bearing and a high resolution digital optical displacement encoder.

A controlled stress was applied to the sample placed between the measuring plates. The resulting strain was measured by the optical encoder and fed to a microcomputer. The software then calculated the values of viscosity from the stress-strain data.

The materials used during the course of this work[6] are listed in Table 1.

Results & Discussion

Effect of Shear Rate on Rheological Properties

The melt index of a rotomolding resin is the key parameter by which the molder will gauge how a material will flow and reproduce the inner surface of the mold. However, the shear rates that are used during the melt index test greatly exceed the shear forces that the resin will be subjected to during the rotomolding process.

Using the Extrusion Plastomer a series of experiments were carried out to investigate the relationship between shear rate and apparent viscosity for three typical rotomolding resins (see Figure 1). From the graph it can be seen that the viscosity of the higher melt flow resin increases linearly as the shear rate decreases. This is not true for the lower melt index resins, which exhibit more exponential growth as the shear rate tends towards zero.

These results confirm that there is a significant difference in apparent viscosity for a high melt index (8 g/10mins) resin, compared to a low melt index (3.2 g/10mins) resin. However, more importantly, the results show that reducing the rate at which the polymer is being sheared magnifies the differences in viscosity that exist.

Correlating the results to the rotomolding process would suggest that low melt index materials are more difficult to mold. This is because the low shear rates experienced during the molding process have a greater influence on the viscosity of low melt index resins.

Effect of Temperature on Rheological Properties

Temperature also has a significant influence on the rheological properties of a resin. Rotomolding is a dynamic process in which the temperature of the resin continually changes - unlike the melt index test, which is performed at 190 C.

Using the parallel plate rheometer, a series of experiments were performed using a fixed shear rate of 0.1 s^{-1}. The viscosity characteristics of a number of resins were investigated with increasing temperatures (see Figure 2). These results show a similar trend to the effects of reducing the shear rate. High melt index resins increase in viscosity linearly with decreasing temperature. However, lower melt index materials display more rapid exponential growth with decreasing temperature.

These results help to confirm why rotational molders have to vary their heating cycle depending on the resin they are molding. Low melt index resins need to be heated to higher levels to achieve comparable viscosity or flow properties.

Effect of Molecular Weight on Viscosity

As previously stated, the molecular weight of a resin has the greatest influence on its rheological properties. The molecular weight of each resin used in the research program is listed in Table 1. It can be seen that as the melt index increases, the average molecular weight decreases. This can be explained by the fact that the molecular chain length is decreasing.

From the molecular weight data listed in Table 1, it can also be seen that the inclusion of black pigment does influence the molecular weight value of the resin by a marginal amount. Rheological testing showed that differences in viscosity also existed (see Figure 3) when carbon black pigment was present.

The inclusion of black pigment was shown to increase the viscosity of the resin. This result correlates to findings by others[7], who suggested that it was more difficult to produce rotomolded part without surface pores when the resin contained black pigment.

Effect of Additives on Rheological Properties

Additives are used by other plastics industries to aid the flow of material during the molding process. These additives tend to be more effective when subjected to high shear forces. This work investigated one such additive called "Stearamide".

Increasing percentage levels of Stearamide up to 5%, were added to a resin (A–1) and dry-blended. The rheological properties were then investigated using the parallel plate rheometer. In addition, the resin was rotomolded to determine the effect of the additive on impact strength and surface porosity. The tests showed that the additive was capable of reducing surface porosity and viscosity. It was encouraging to observe that the material's impact properties were not sacrificed.

Relationship between Melt Index & Viscosity

Using materials with a range of different melt indexes, the apparent viscosity was determined using the standard melt index test setting i.e. weight = 2.16kg and extrusion temperature = 190 C. These results are plotted in Figure 4. The graph illustrates that the relationship between the material's melt index and its viscosity is reasonably linear between the 3.2 and 8 g/10 mins melt index range. As the melt index of the material increases up to 25 g/10 mins the reduction in viscosity is less pronounced.

By reducing the mass of the extrusion rod, the extrusion plastometer can also be used to generate apparent viscosity values for low shear rates. The second line on Figure 4 denotes a 0.5 s^{-1} shear rate applied to each of the resins. The reduction in shear rate causes the difference in apparent viscosity to increase significantly between the common rotomolding (e.g. 3.2 to 8 g/10mins) resins. This information is much more relevant to the rotomolder, as it provides a more precise representation of how the material will perform during the rotomolding process.

Effect of Viscosity on Bubble Diffusion

The presence of bubbles is an inherent characteristic of products manufactured by rotational molding. Bubbles form due to the encapsulation of air pockets between powder particles as they melt and fuse together. As the melting process continues, these bubbles remain stationary due to the high viscosity of the molten polymer. The bubbles then slowly diminish in size and may disappear, depending on the heating cycle time, the melt temperature and the viscosity characteristics of the polymer concerned.

Experimental testing has shown that bubbles can be more easily removed from higher melt index materials (see Table 3). Higher melt index (lower viscosity) materials have weaker polymer structures, through which oxygen and nitrogen molecules can pass more freely. The differences in diffusion rates between the 3.2 and 5.0 melt index materials show this to be the case. This confirms why rotomolders would tend to use a high melt index material for a part where surface porosity is undesirable. It was interesting to observe that when the materials had a similar viscosity value, their diffusion rates were also similar.

Conclusions

1. The molecular weight of a polyethylene resin has the greatest influence on its rheological properties and therefore how it will mold during the rotomolding process.

2. The melt index test does not provide a true indication of how a resin will perform during the rotomolding process. This is because of the significantly higher shear rate experienced by the resin during the test, compared to the rotomolding process.

3. The temperature of the polymer resin significantly influences its flow properties. The higher the resin temperature, the better it will flow during processing.

4. Additives such as "Stearamide" can reduce the viscosity of a polyethylene resin. Stearamide was also shown to reduce the surface porosity that on rotomolded parts.

5. The inclusion of carbon black pigment was shown to increase polymer viscosity, resulting in reduced flow properties and makes it more difficult for bubbles to diffuse.

6. The removal of bubbles and surface pores from rotomolded parts can be achieved by either increasing the temperature of the resin during processing or by using a resin with a higher melt index.

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Key Words and Phrases

Rotational Molding, Rheology, Viscosity, Bubbles.

Reference Code	Color	Melt Index (g/10 mins)	Density (kg/m^3)	Molecular Weight
A - 1	Natural	3.2	934	100,300
B - 2	Natural	5	924	89,550
C - 3	Natural	8	935	80,400
D - 4	Natural	12	937	70,000
E - 5	Natural	18	937	64,000
F - 6	Natural	25	937	59,000
G – 7	Black	3.2	934	99,750
H - 8	Black	5	924	92,100
I - 9	Black	8	937	77,750

Table 1 Materials Used During this Research Project

Stearamide (%)	Surface Porosity (%)	Viscosity (Pa.s)	Energy/mm (J/mm)	Mode of Deformation
0	1.88	3065	3.09	Ductile
1	0.64	2986	3.88	Ductile
2	0.35	2920	3.74	Ductile
3	0.27	2818	3.66	Ductile
4	0.22	2730	3.11	Ductile
5	0.19	2620	2.80	Ductile/Brittle

Table 2 Effect of Stearamide on Rheological and Mechanical Properties of Material Ref. # A - 1

Reference Code	Diffusion Rates (mm^2/s x 10^{-3})			Apparent Viscosity (Pa.s)		
	150 C	170 C	190 C	150 C	170 C	190 C
A - 1	0	0	0.089	5,020	3,815	2,745
B - 2	0	0.074	0.685	4,230	2,865	1,925

Table 3 Effect of Polymer Temperature on Diffusion Rates and Apparent Viscosity

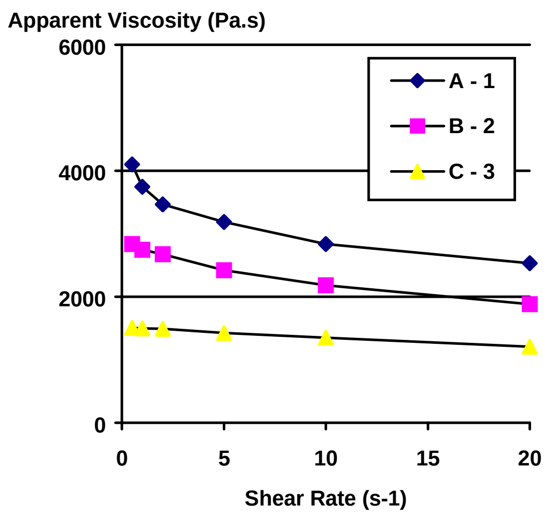

Figure 1 Effect of Shear Rate on Viscosity (at 190 C)

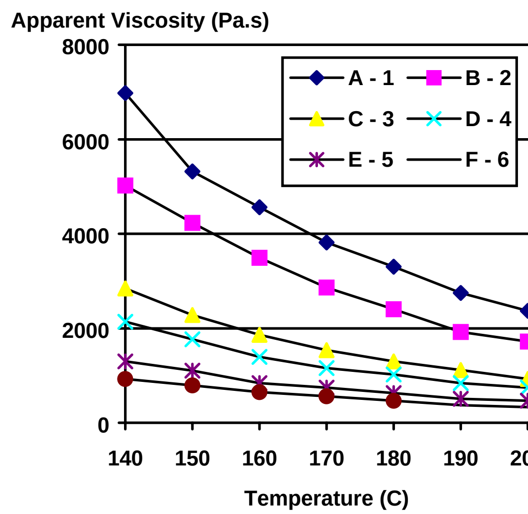

Figure 2 Effect of Temperature on Viscosity (0.1 s^{-1} shear rate)

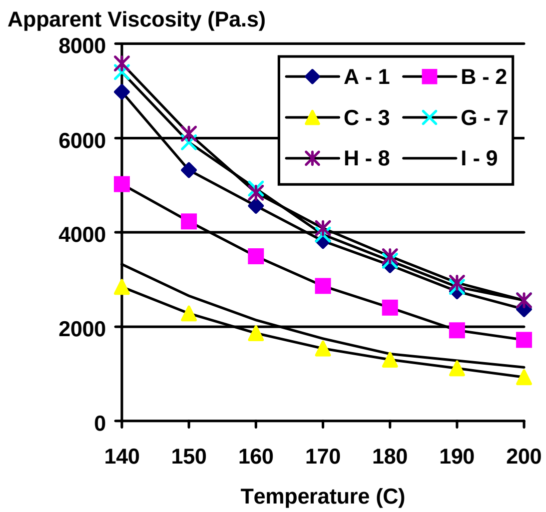

Figure 3 Effect of Carbon Black on Viscosity (0.1 s^{-1} shear)

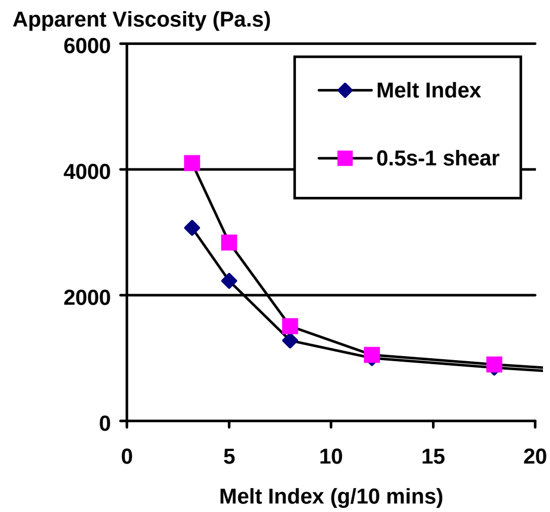

Figure 4 Relationship between Melt Index & Viscosity (at190C)