

Medical device processing development based on rheology and thermal analysis

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Abstract

A case history for the process development of an injection molded polyester alloy medical device was presented. It was determined that traditional molecular weight determinations was difficult and not easily correlated with performance. However, a rheological parameter, the steady shear viscosity was found to control the failure rate with good predictive power. In the course of the investigation, it was also found that moisture level much lower than what was called for was required to insure good molecular weight retention and prevent failures. A modified ASTM melt flow procedure was developed that facilitated date comparison between multiple sites along the production path for 'defect free' production. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymer alloys with superior engineering properties are being introduced for many demanding applications. In the medical device field, the molded product may be subjected to one or more post molding assembly steps, solvent bonded with other components, packaged and subjected to terminal sterilization by, most frequently, that of the ionizing radiation from gamma or electron beam sources. Upon arriving at the user's location, after shelf-life and transportation through demanding conditions, these devices must perform under intended and sometimes unintended stress and chemical conditions.

There is a well established requirement in the plastics industry that all condensation polymers be thoroughly dried before melt processing. This is due to the reversibility of the polymerization reaction. For every molecule of water that remained, potentially one main-chain bond could be hydrolyzed, thus leading to serious molecular weight reduction and property

losses. However, the rigor with which the drying process must be carried out is frequently ill defined.

In this paper, the process development for a polyester polycarbonate alloy device will be presented. It was found that due to the complex alloy nature traditional molecular weight determination were extremely difficult and yielded imprecise data. Yet rheological techniques were found to be highly quantitative and efficient. The rheology techniques was used to trace the entire path of manufacturing from alloy blending to resin drying, to injection molding to final components to pinpoint areas of concern and rectify procedures.

Finally, the rheological parameters were correlated with actual product performance to establish a master 'failure envelop' for acceptance criteria. And a modified ASTM melt flow test was developed which allowed multiple sites along the product flow to monitor process conditions to allow true 'zero defect' performance in final device.

2. Experimental

A TA instruments thermal analyzer 2100 with differential scanning calorimeter cell 2910 and a liquid

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nitrogen cooling accessory calibrated with indium standards was used to monitor the thermal behavior of the resin and molded parts. Heating rates of 20°C/min and cooling rates of 10°C/min were used throughout the study. DSC thermogram indicated that the glass transition is located at about 155°C, approximately halfway between the parent polycarbonate and the polyester polymers. The existence of a single T_g is a strong evidence that the alloy is thermodynamically miscible.

A Rheometrics RFR fluid rheometer was used to characterize the melt in the parallel plate configuration using 2.50 cm plates from 0.1 to 300 rad/s with the dynamic mode at 260°C. In order to minimize sample degradation, a very rapid heating program that brings the sample to an equilibrium test temperature under 2 min was adopted. From the dynamic viscosity versus frequency plot, a Newtonian viscosity was calculated by graphical averaging the low shear data points and extrapolating to zero shear rate. To insure temperature reproducibility, the sample temperature thermocouple was calibrated periodically using the indium standard. The sample drying procedure was found to be critical for the condensation polymers in this study, and a special protocol was developed which is described later in this article.

A Mitsubishi model CA-06 micro Karl Fisher moisture analyzer was used for accurate moisture determinations.

A Thermodyne melt indexer (ASTM-1238) was modified for a 260°C operation with special consideration of accurate temperature of the melt and the placement of the thermocouple thermometers to allow accurate determinations.

For failure surface characterization, scanning electron microscopy was conducted on either a JEOL 35CF or a JEOL FE-6300 field emission instrument, with surface preparations of palladium sputter coatings for conductivity.

3. Result and discussion

3.1. Molecular weight characterization and correlations

Since the alloy contained a crystallizable component, dissolution of samples for gel permeations chro-

matography (GPC) molecular weight determinations was found to be difficult with conventional solvents at room temperature. Further, correlation with product performance (rate of failures) with GPC molecular weight of components was found to be very poor. This may be in part due to the difficult procedure and lack of long-term reproducibility of data. However, for rheology, the following relationship

$$\eta_0 = KM_w^{3.4} \quad (1)$$

where η_0 is the steady shear (Newtonian) viscosity, M_w the average molecular weight has been found to be universally obeyed for linear polymers from both theoretical and experimental considerations [1–3]. Due to the high exponent, the steady shear viscosity is a very sensitive measure of molecular weight. Even for the case of the two component alloy, the viscosity was found to be a sensitive indicator of the relative molecular weight degradations at each step of the process. Since most GPC determinations use polystyrene as standards, the absolute molecular weight can only be obtained through extensive calibration. As a comparison, a 5% long-term accuracy is considered excellent for GPC while from Eq. (1), more than 15% variation in viscosities would result in an easily achievable accuracy. For example, in Fig. 1, the melt viscosity of the device was characterized along the manufacturing path. It can be clearly seen that drying led to slight increase in viscosity, but as soon as the material entered the mold, significant reductions occurred. Hence, the challenge becomes that of mana-

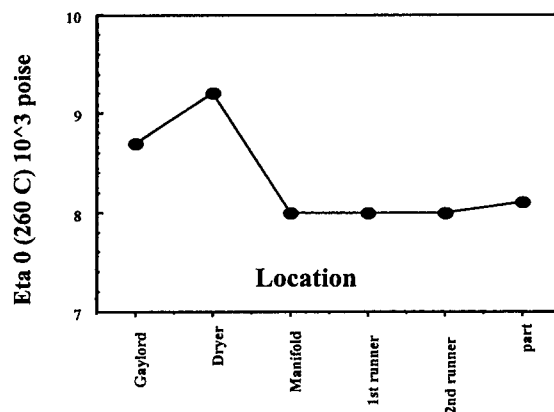


Fig. 1. Viscosities along manufacturing path.

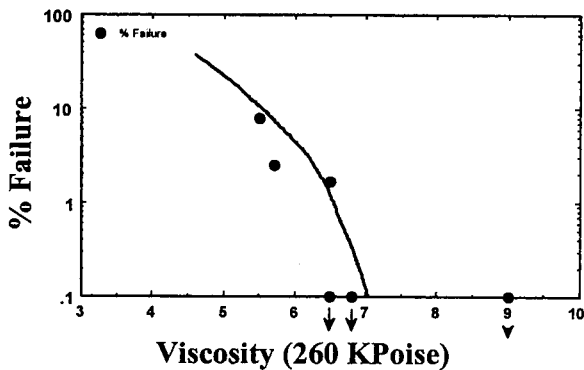


Fig. 2. Failure envelop.

ging the resin manufacture to maximize the incoming viscosity and optimizing the molding process to retain the highest viscosity, or molecular weight.

3.2. Failure envelop determination

From a large number of samples from very different material lots and process histories, η_0 was determined and using an established criteria for failure determination, the incidence of failure for these sample groups were also determined. When the failure rate was plotted against η_0 (Fig. 2) a distinct boundary between the samples that are prone to failure and those that are failure resistant emerged. The boundary defines what is called the ‘failure envelop’ which establishes the performance dependence on the parameter of interest. In other words, the existence of the envelop indicates the linkage of functional performance to a molecular weight based parameter that one can monitor and control. The failure rate is a statistical quantity whose determination frequently requires examination of hundreds or even thousands of fully assembled products. On the other hand, accurate determination of η_0 only requires the preparation of a handful of pellets or a single molded product along the production path. When more data become available, the failure envelop can be further refined for greater statistical significance and predication accuracy.

3.3. Sample drying procedure

To estimate the effect of water on potential molecular weight reductions, the number of water molecules per polymer was plotted as a function of water

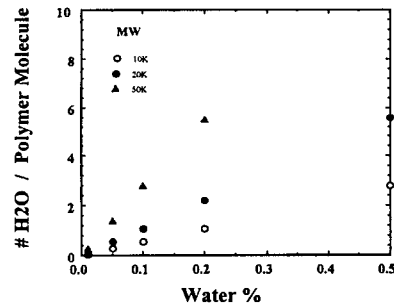


Fig. 3. Water/polymer ratios.

content for molecular weights (M_n) of 10, 20 and 50 kD in Fig. 3. It is seen that the traditionally accepted 0.1% moisture content [4] can lead to between 0.5 to almost three water molecules per polymer. This high ratio is clearly not acceptable for good property retention. A more reasonable target should be set at about 0.01%. Since trace quantity of moisture can have drastic influence on the product molecular weight via the reverse condensation reaction, prior to any melt processing, moisture must be rigorously eliminated. A vacuum oven was used to study the conditions needed for rheology determination and processing.

Fig. 4 shows the moisture content as a function of drying time under 29.5" vacuum at 120°C. A linear dependence on the semi-logarithmic presentation indicates that the elimination of water follows the expected exponential decay function. For true determination of the molecular weight based viscosity, it was found that moisture levels far below the accepted 0.01% level was required. A 0.001% moisture content or 10 ppm was found to be desirable. This level of dryness was achieved by drying at 140°C for 1 h under full vacuum.

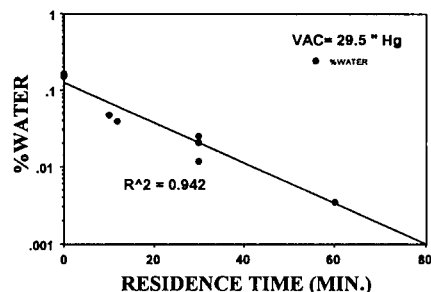


Fig. 4. 140°C vacuum drying.

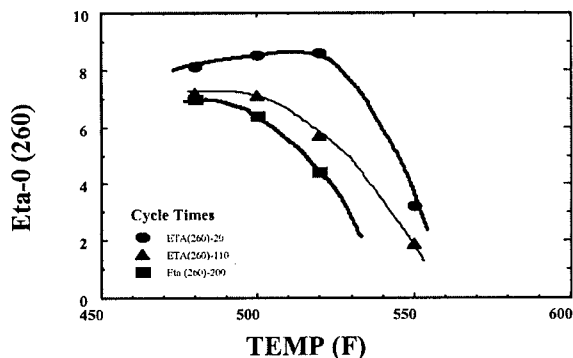


Fig. 5. Component viscosity vs. molding parameters.

3.4. Molding process optimization

A carefully designed experiment was conducted on the commercial scale molding machine to quantify the best molding parameters. The viscosity of the molded components in Fig. 5 showed that short molding cycle times and moderately high melt temperatures of about 510°F (265°C) preserved the highest molecular weight in the resulting components.

3.5. Melt flow rheology correlation

In order to perform the required quality surveillance at various melt processing sites, it is highly desirable that a simple, easily maintained procedure be established. To this end, the ASTM-1238 melt flow method was modified and adapted for our purpose. To overcome the crystallinity which could be created during high temperature drying and yet be sufficiently moderate so as not to degrade the sample during testing, 260°C was chosen as the test temperature. Special care was exercised in insuring temperature constancy over several test sites. Operator training was conducted so that the procedure used was as identical as possible

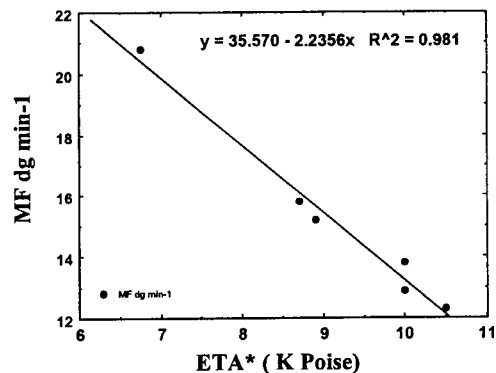


Fig. 6. Viscosity melt flow correlation.

including sample loading, instrument cleaning and capillary maintenance and dimensional checks. As a result, data reproducibility achieved over a round robin testing was about 3%, better than the two-fold improvement over that which can be expected from the standard ASTM procedure.

When the melt flow data was plotted against the steady shear viscosities, an excellent correlation was achieved (Fig. 6). From the melt flow plot, and the failure envelope, acceptance criteria for each melt processing step was established. And with the instituted controls at each step, dramatically improved quality of product was obtained.

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