

Quality control of polycarbonate parts ¹

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Abstract

Analytical methods and control charting have been instituted for accessing the integrity of purchased parts molded from General Electric Company's Lexan[®] 503 polycarbonate resin. The glass transition temperature, fiber glass, and loss-on-ignition ash data are used to establish means and control limits. Parts found to be out of control are examined using intrinsic viscosity in conjunction with the routine analyses.

INTRODUCTION

S&C Electric Company manufactures fuses and switches for the distribution of electrical power. We buy molded parts from three different custom molders made out of General Electric Company's (GE) Lexan[®] 503 polycarbonate for assembly into our product. Lexan is a registered trade name of General Electric Company. Lexan[®] 503 is a polycarbonate resin with fiber glass and UV absorber. Only virgin Lexan[®] 503 material is to be used by each custom molder because Lexan has inherent physical properties that are critical to the end use performance of these parts in our assembled products. As a result, these incoming molded parts have been subjected to extensive chemical analysis to verify the presence of only Lexan[®] 503.

The methods used to assess incoming molded part quality are discussed and two examples of outliers are detailed. Our methods are similar to those used at General Electric but they are not identical [1].

EXPERIMENTAL METHODS

The black or gray incoming molded Lexan parts are the actual samples analyzed. Each incoming shipment is sampled by box at random. At least

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one part per box is subjected to an in-house proprietary impact test. This impact test classifies each part as being either ductile or brittle. The fracture surfaces are examined for the presence of voids. After impact testing, the parts are analyzed using chemical testing.

The chemical analyses are designed to monitor the glass transition temperature T_g , the fiber glass content, and the loss-on-ignition (LOI) ash content. These tests verify if the parts are made of Lexan[®] 503 material using the ranges specified by General Electric Company as the guidelines.

The thermal data were obtained using a DuPont Model 1090 programmer and a Model 912 differential scanning calorimetry (DSC) unit. The DSC was calibrated for temperature and enthalpy using indium as a reference standard. The nitrogen purge gas was dried using a molecular sieve trap and an oxygen trap. The molded parts were sampled by clipping approximately 12 ± 3 mg of material from a thin-walled gusset plate. Each sample was crimped into an aluminum sample pan. The DSC was programmed from 25 to 180°C at 10°C min⁻¹. The glass transition temperature T_g was determined as the midpoint of the temperature transition observed between 130 and 165°C as the nominal temperature range.

The LOI ash was determined using a 2 g sample which was first burned using a Meker burner and then ashed at 700°C for 2 h in a muffle furnace. The percentage of ash that remained was calculated. The percentage of ash does not always equal the percentage of glass, owing to the presence of pigment.

The gray part contains titanium oxide, calcium carbonate, and fiber glass. The black parts contain fiber glass, carbon black, and a very small amount of titanium dioxide. The range for fiber glass is $9 \pm 1\%$ without accounting for pigment.

One molded part was sectioned into four pieces. One piece was prepared for X-ray fluorescence analysis (XRF), and the three other pieces were analyzed following ASTM C169 for elemental composition [2]. The fiber glass content was found to be 7.56% and the fiber glass itself consisted of 19.73% CaO, 60.35% SiO₂, 5.89% B₂O₃, and some Al₂O₃. The acid-soluble calcium, which was not bound up in the fiber glass, was calculated as 0.69% and the titanium dioxide was 1.13%. There was no detectable magnesium and the composition of these fibers is consistent with E-glass [3].

One piece of the part analyzed above was made into a secondary standard for analysis of the percentage of glass using the Kevex 0700 X-ray fluorescence spectrometer. The percentage of fiber glass present is calculated using conversion factors on the elemental data for silicon, calcium and titanium. The conversion factors are based on the oxides in the glass composition as determined above. The smallest estimated error in this XRF method can be determined using the titanium dioxide determination. The XRF mean for TiO₂ was $1.118 \pm 0.013\%$ with a relative standard

deviation (RSD) of 1.2% for 13 different determinations. The largest estimated error in this XRF method is the determination of the percentage of fiber glass because it is a combination of the errors for determining both calcium and silicon. Calcium is present in the fiber glass and as calcium carbonate in the molded part. The level of CaO in the fiber glass is constant, but the amount of calcium carbonate varies. The mean percentage of fiber glass was 7.56% and the RSD was 5.38% for 24 determinations.

If the impact test has shown that the parts are brittle, a non-routine test is performed to estimate the molecular weight of polycarbonate using an intrinsic viscosity method. The intrinsic viscosity (IV) was determined in dilute dichloromethane solutions at 25.0°C following the method developed by Campbell [4]. The polycarbonate polymer is separated from the fiber glass and pigment by filtration. The dichloromethane is evaporated leaving behind the clear, unfilled polycarbonate resin. The IV solution is prepared using 0.2000 ± 0.0005 g of polycarbonate in 50.00 ± 0.02 ml of dichloromethane. The solution efflux time t and the blank dichloromethane solvent efflux time t_0 are determined in the same capillary viscometer. The IV is calculated using Campbell's equation:

$$\text{IV} = 2.466 \left[\frac{(t - t_0)}{t_0} \right] - 0.011 \quad (1)$$

The units are deciliter per gram (dl g^{-1}). For GE Lexan® 503, the range for polycarbonate IV values is 0.52–0.46 dl g^{-1} at 25.0°C using a concentration of 0.004 g resin per milliliter of dichloromethane.

The efflux times were measured using the Schott-Gerate Model AVS400 viscosity measuring system with a Model CT 1150/2 temperature bath. The capillary viscometer was selected so that the blank efflux time would exceed 100 s. The solution efflux time was recorded immediately after the blank using the same viscometer. The Ubbelohde viscometer was filled with 20 ml of the sample solution or blank solvent and incubated for a minimum of 10 min in the temperature bath. The efflux times were determined a minimum of six times and the average efflux time was used in Eqn. (1).

These routine quantitative test data were tabulated and entered into SQCPack, a software program obtained from PQ Systems, Dayton, OH. SQCPack is a statistical process-control program designed to provide a control chart format for the data. The statistical calculations used in SQCPack are in agreement with those recommended by ASTM in STP 150 [5].

Control charting is an iterative ongoing process. It is intended to identify trends in the data. The upper and lower control limits are chosen to be narrow so that trends in the data are easily spotted using SQCPack. Each lot varied in the number of parts received. A small lot contained 100 parts

while a large lot contained 4800 parts. Three parts are analyzed from each lot; all three analyses are performed in duplicate. There are 18 individual data points to be plotted in the control charts. The lot is scrutinized for rejection as being out of control if only one data point of the 18 points falls outside the control limits.

The control limits were chosen as the mean plus or minus twice the standard deviation (s.d.) which is defined as

$$\text{s.d.} = \sqrt{\frac{(\bar{x} - x_i)^2}{n - 1}} \quad (2)$$

where x_i is the individual sample value, \bar{x} the arithmetic mean, and n the number of individuals. The range of values between the upper control limit ($\bar{x} + 2$ s.d.) and the lower control limit ($\bar{x} - 2$ s.d.) will contain 95.44% of the values only if the data are normally distributed [6].

RESULTS AND DISCUSSION

The role of incoming quality control is to identify when the molded parts are substantially different from previous shipments. The in-house impact test and the chemical analyses are able to point out the outliers. Once the outliers are identified, the shipment can be rejected. Usually the reason(s) for rejection must be identified and the problem changes from one of incoming quality control to one where additional data must be generated to aid the molder in making “good” parts. In this role, the reason for rejecting incoming shipments of molded parts must be clearly defined through additional qualitative and quantitative data.

The control chart data will be discussed first, then the two examples of outliers will be presented.

The purpose of incoming quality control is to identify when a new shipment of parts is substantially different from the normal shipment. A normal shipment of parts can be described by in-house impact test results and the ranges in GE’s Lexan values until adequate internal laboratory data are generated. The molded parts have been analyzed for over 4 years, and during this time five different analysts have obtained the quantitative chemical data. The sample base includes 29 different incoming shipments from three different custom molders. The parts were molded out of either gray or black pigmented Lexan® 503. The data are summarized in Table 1.

The overall mean data for the individual samples are given in Table 1. The RSD is also calculated. The DSC T_g data have the smallest relative error. The percentage of glass found by XRF analysis has the largest relative error. This is possibly due to inherent error in the measurement and to the secondary analytical standard used for the XRF calibration.

TABLE 1

Overall means for incoming molded parts made from Lexan[®] 503

Chemical analysis	$\bar{x} \pm 1$ s.d.	RSD ^a (%)	No. of data points	No. of molded part shipments
DSC, T_g	147.4 \pm 1.0°C	0.7	240	34 ^b
LOI percentage ash	10.09 \pm 0.64%	6.3	174	29
Percentage glass	9.36 \pm 1.38%	14.7	174	29
GE Lexan [®] 503	Manufacturer's range			
DSC, T_g	145-149°C			
Percentage glass	9 \pm 1%			
IV	0.46-0.52 dl g ⁻¹			

^a RSD is the relative standard deviation calculated as $RSD = (s.d. \times 100\%) / \bar{x}$.^b The thermal data were repeated on five shipments.

There may also be year-to-year variations in the elemental composition of the chopped fiber glass.

The RSD (%) for LOI data is 4.1% and these data will be discussed using the SQCPack plots. The individual data for the percentage of ash by LOI are plotted in Fig. 1 as a frequency distribution histogram. This histogram plots the number of observations on the y axis. The range in

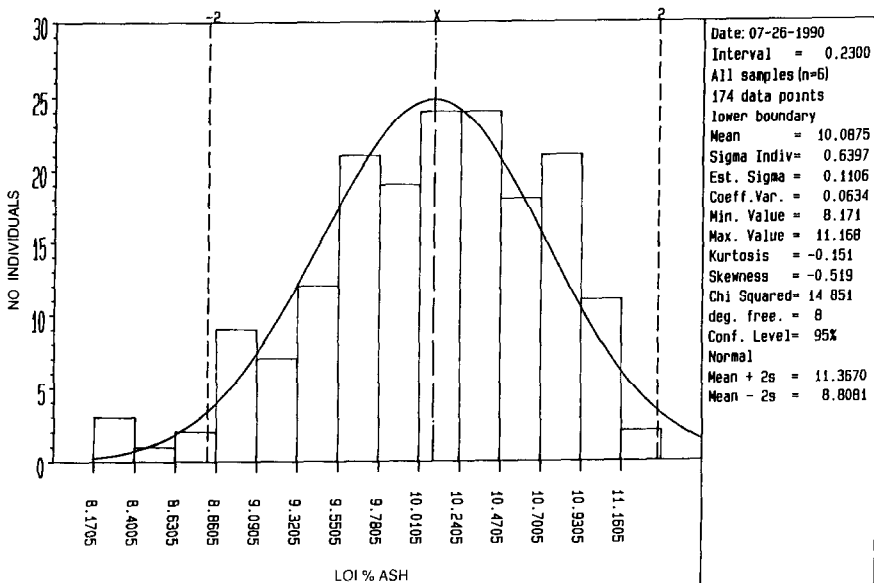


Fig. 1. LOI ash (%) for molded parts.

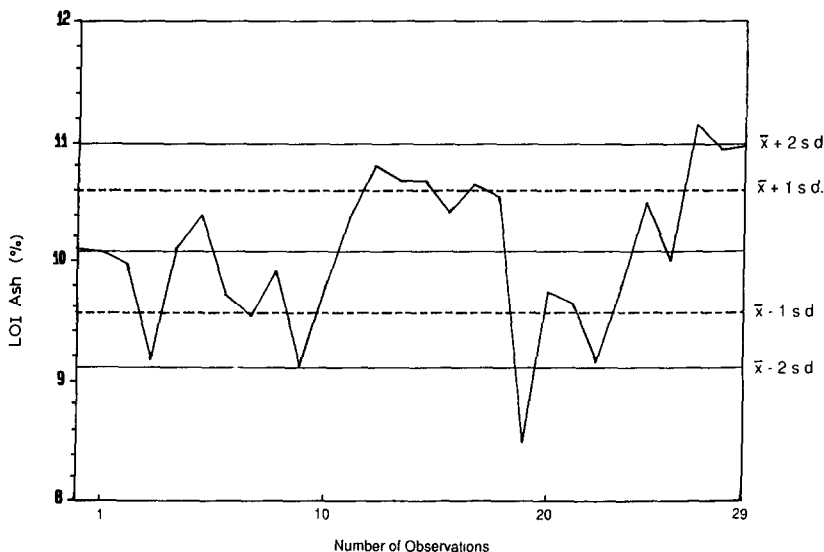


Fig. 2. LOI ash (%) for molded parts; \bar{x} -bar chart.

percentage of ash is plotted on the x axis. There are 174 data points represented in this histogram with an overall mean represented at 10.09%. These data are normally distributed about the mean; therefore the appropriate statistical tables have been used to compare the means.

The \bar{x} -bar control chart plot of the data, grouped by shipment, is shown in Fig. 2. There are 29 shipments represented in this plot. Each point on the x axis is the arithmetic average of six separate LOI determinations; all points are connected by straight lines. The solid horizontal line is the mean (\bar{x}), and the upper control limit (UCL) and lower control limit (LCL) are represented. These limits are $\bar{x} \pm 2$ s.d. The control limits of these LOI data will be used to discuss outliers in Example 1 below.

Individual DSC T_g data points, along with the \bar{x} -bar chart and associated control limits, are shown in Fig. 3. There are 204 data points plotted and only nine points fall as outliers outside the 2 s.d. control limits. This ± 2 s.d. window is narrower than that for ± 3 s.d. because the lot size varied from 100 to 4800 parts while the sample size remained at 3 parts per lot.

The DSC heating curves for two parts are shown in Fig. 4. The ductile part gave a DSC curve typical of normal or properly molded Lexan[®] 503 parts. The brittle part gave a DSC curve with a glass transition temperature at 140.5°C which is out of control when compared to the overall individual mean of 147.4°C. This T_g value is an outlier using Dixon's Q test and the lower control limits. The data for this shipment of parts will be discussed in more detail in Example 2 below. The third DSC curve shown contains two glass transitions and those data will also be discussed in Example 2.

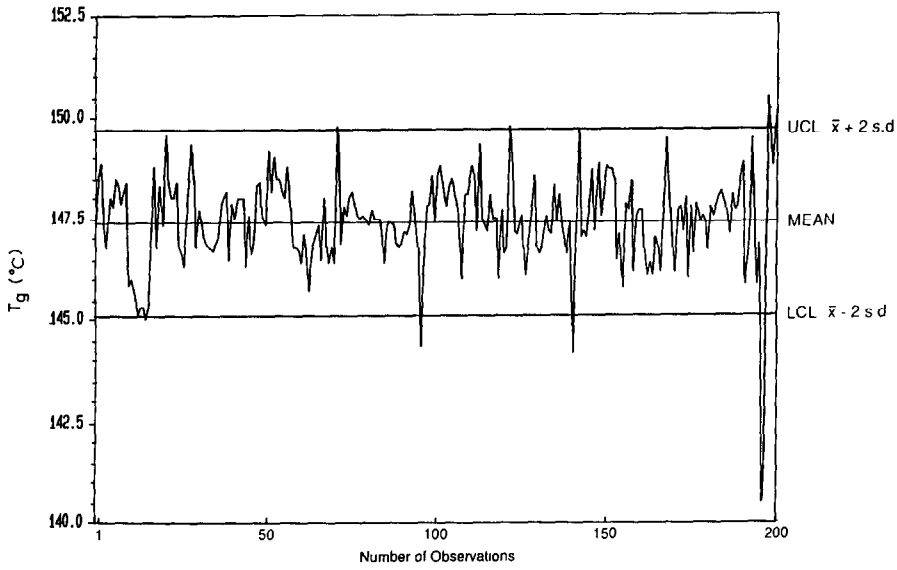


Fig. 3. T_g by DSC for incoming parts; individuals.

Example 1

Two lots of black parts were received that were supposedly molded out of Lexan[®] 503. Analysis showed that these parts were brittle and made out of a polycarbonate resin. The question was “are these parts made out of

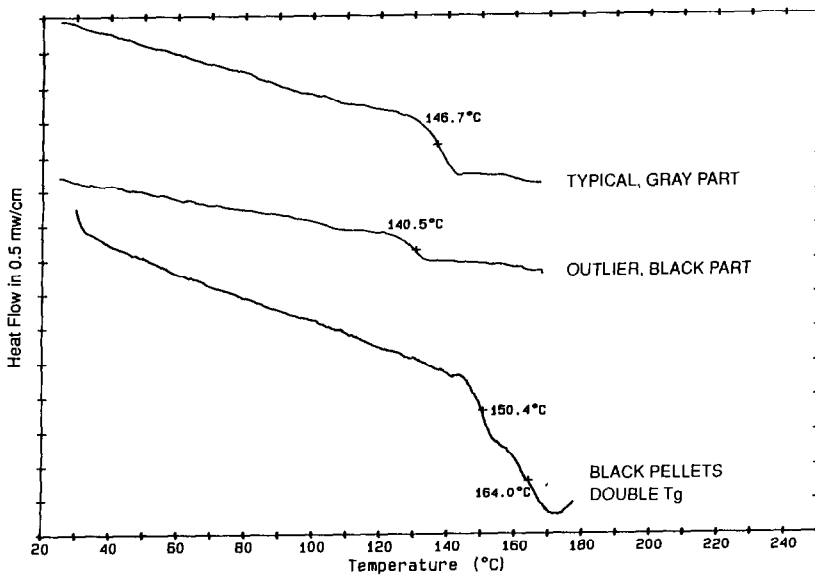


Fig. 4. DSC heating curves.

TABLE 2

Summary of data for black parts in Example 1

	Impact test	DSC T_g (°C)	IV (dl g ⁻¹)	XRF glass (%)	LOI ash (%)
Lot A	Brittle	138.4	0.304	–	–
	Brittle	137.7	0.356	17.24	12.87
	Broken	139.7	0.366	17.21	15.04
	Marginal	143.9	0.426	–	–
Lot B	Ductile	147.6	0.467	None found	0.01
	Ductile	141.7	0.435	None found	0.01

GE Lexan[®] 503 material?”. The data are summarized in Table 2: the T_g and IV data are outliers. The data for the percentage of ash and fiber glass suggest that the parts from lot B were not filled. The lot A parts have too much filler; therefore it is obvious that these parts are not made from Lexan[®] 503 material and can be rejected.

Example 2

In Fig. 3, an outlier is shown, with 140.5°C for the glass transition temperature. This part was black and brittle, so the lot was resampled and five additional parts were analyzed using non-routine methods.

Because the glass transition temperature is sensitive to degradation, low values suggest that a decrease in molecular weight may have occurred. Polycarbonate is a narrow-molecular-weight polymer and its molecular weight can be easily monitored by solution viscosity. The IV method of Campbell was used as in eqn. (1).

The IV data are shown in Table 3 along with the T_g , LOI and percentage of fiber glass data. An example is given of the data typical for good gray parts. The brittle black parts are labeled D–L. Parts D–H were molded in June 1990 from the same lot of pellets as parts I–L. These last four parts were molded in September 1990. Parts D and E gave T_g values which were clearly out of control.

The IV and DSC data were generated on different pieces of the same part. It is assumed that each part is homogeneous with respect to the samples taken to generate these data. For parts D and E, the polycarbonate is degraded with respect to IV and T_g . For parts H–L, this is not easily concluded on the basis of the T_g and IV data. For parts F and G, the percentage reduction in IV is greater than 5% and this reduction in the IV value can be used to reject these two parts. The percentage reduction in IV is calculated as

$$\text{Percentage reduction in IV} = \left(100\% - \frac{\text{IV part}}{\text{IV pellet}} \right) \times 100\% \quad (3)$$

TABLE 3

Summary of data for Example 2

	IV (dl g ⁻¹)	IV reduction ^a (%)	DSC T _g (°C)	LOI ash (%)	XRF fiber glass (%)
Pellets (gray)	0.481	–			
Good part 2	0.478	0.6	147.6	10.26	7.58
Good part 3	0.499	(–3.7)	147.4	10.39	7.95
Good part 4	0.490	(–1.8)	147.5	10.36	8.14
Pellet (black)	0.467	–	148.1	9.80	9.99
Bad part D	0.316	32.3	141.1	9.69	–
Bad part E	0.426	8.8	142.5	10.42	–
Bad part F	0.431	7.7	147.8	10.33	–
Bad part G	0.418	10.5	148.3	9.80	–
Bad part H	0.447	4.3	149.9	10.43	–
Bad part I	0.461	1.3	148.3	10.57	10.66
Bad part J	0.469	(–0.5)	148.4	10.22	10.43
Bad part K	0.471	(–0.8)	148.2	10.56	10.33
Bad part L	0.470	(–0.7)	148.3	10.13	9.99

^a IV reduction is calculated using Eqn. (3).

A rule of thumb says that the percentage reduction should not exceed $\pm 5\%$ for normal molding [1]. Values greater than 5% imply that the molded polycarbonate has been degraded when compared to the pellets.

TABLE 4

Intrinsic viscosity: split sample data

Polycarbonate	GE laboratory IV (dl g ⁻¹)	S&C laboratory IV (dl g ⁻¹)
Lexan [®] 143 (3-2-1) ^b	0.497	0.482
Lexan [®] 143 (3-2-3)	0.499	0.481
Lexan [®] 143 (3-7-4)	0.463	0.449
Lexan [®] 143 (3-7-8)	0.456	0.454
Lexan [®] 503, Pellets	0.48	0.467
Lexan [®] 503, Part	0.46	0.470
Lexan [®] 503, 1	0.44	0.458
Lexan [®] 503, 2	0.48	0.478
Lexan [®] 503, 3	0.48	0.467
Lexan [®] 503, 4	0.46	0.470
Not Lexan, PC#2	0.30	0.356
Not Lexan, PC#5	0.31	0.366
Not Lexan, PC#6	0.45	0.467

^a General Electric, Plastics Business Group, Mt. Vernon, IN.^b Lexan[®] 143 is a polycarbonate resin with a UV absorber.

TABLE 5

Variation in IV within sample

	<i>n</i>	\bar{x} (dl g ⁻¹)	s.d.	RSD (%)	Variance (s.d.) ²
Gray Lexan [®] 503 pellets	6	0.481	0.027	5.72	0.00073
Gray part	5	0.490	0.020	4.23	0.00040
Black part	5	0.465	0.006	1.27	0.00004

The intrinsic viscosity method was repeated on split samples to compare the results. The samples were divided and analyzed at S&C and also at GE's Mt. Vernon laboratory. The split sample data are shown in Table 4 for three different formulations of polycarbonate. The replication between laboratories is very good. The variation in IV within one sample is summarized in Table 5.

By evaluating the variation in IV data, the brittle black parts H–L in Table 3 are difficult to reject. A closer examination of the DSC curves may help to substantiate the decision to reject these brittle parts. The third DSC curve plotted in Fig. 4 is due to the black pellets which produced brittle parts. The pellets gave DSC data containing two changes in the heat capacity which is representative of a double T_g [7]. The first T_g is at 150.4°C and the second is at 164°C. Reheating the same sample gave a single T_g at 150°C. Samples obtained from brittle parts contained a double T_g which persisted even after annealing the samples. It is possible that the presence of a double T_g is indicative of a second phase in the crystalline ordering of the chain molecules surrounding the carbon black particles. The carbon black particles are nucleation sites for a localized two-dimensional ordering of the polycarbonate, resulting in the observation of an increase of 14°C in the T_g . This explanation is plausible since the gray parts and pellets exhibited only a single T_g .

The IV data suggest that the black brittle Lexan[®] 503 parts D–H were somewhat degraded from the pellets. Parts I–L were not degraded but contained double T_g s.

CONCLUSIONS

An incoming quality control procedure has been discussed to monitor the receipt of Lexan[®] 503 parts molded by three different suppliers. The control chart format for tracking the data has provided a graphical presentation of the data generated from three different analytical techniques. These data are presented so that it is easy to observe shipments where samples are outliers with respect to the arbitrarily chosen 2 s.d. control limits.

Once an incoming lot of parts is known to be out of control, then a non-routine examination of the parts in the shipment is undertaken to collect data in order to rationalize the reasons that these parts failed incoming tests. These non-routine tests have included the measurement of intrinsic viscosity as documented in this paper. Additional non-routine tests, not reported in this paper, have included observing the results of variations in molding temperature parameters and annealing cycles, as well as studying the effects of changes in impact testing.

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