CASE STUDIES OF PLASTICS FAILURE RELATED TO MOLECULAR WEIGHT OR CHEMICAL COMPOSITION

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1.0 Abstract

Processability and product performance depend on having the appropriate polymer molecular weight and composition of the formulation. Failures were caused by errors of molecular weight or composition. GPC played a key role in molecular weight cases. IR spectroscopy and GC/MS were used for composition.

2.0 Introduction

Plastics failure and plastics "success" are two sides of the same coin, i.e., the same factors can be the reason for a part or product processing and performing well, or failing to do so. The principal parameters that must be controlled for "success" are material, design, processing and service conditions [1]. Within the broad category of material the main considerations are composition, molecular weight and intermolecular order [2]. In this paper, case studies or examples are given of failure (or "success") due to composition and molecular weight (MW). The latter parameter is fundamental and crucial to the performance of all polymers – processability, strength, environmental resistance, etc. Composition includes polymer chemistry, additives (both intentional and unintentional) and contaminants or foreign substances [3]. Determination of the cause of failure often requires analysis of those two fundamental factors, composition and MW. For composition, two useful methods of analysis are infrared spectroscopy (IR) and thermal desorption gas chromatography/mass spectroscopy (TD/GC/MS). IR provides a "fingerprint" of overall composition [4], (Fig. 8) which often is able to identify the type of polymer, i.e., polyethylene (PE), polystyrene (PS), polyvinylchloride (PVC), etc. For additives or foreign material present at low level, such as ≤1%, IR is usually of limited value because it does not separate components. The spectrum is a composite of the absorbance levels of all materials present. TD/GC/MS, on the other hand, is a separation method which works very well for volatile compounds [5]. These include many additives – antioxidants, stabilizers, plasticizers, lubricants, etc. and foreign material – silicone or hydrocarbon oil, residual solvent or monomers, etc. A chromatogram may consist of many peaks, each corresponding to a particular compound. See Figures 3, 6 and 7. The peak area or height relates to the concentration of the compound. Identification of a peak's composition can be made from its retention time by comparison to the retention time of a known substance. Retention time is the time from injection of the sample until the peak is detected in the chromatogram. An even better method is from its mass spectrum [6], another type of "fingerprint" of a compound. The advantage of GC/MS for identification of composition is that a spectrum of a peak is solely for a separated compound, not for an entire formulation as with IR. Another important aspect of MS is its very high sensitivity. Under appropriate conditions, materials in the low ppm (parts per million) to ppb (parts per billion) range can be detected and quantified. Even if a material's volatility is low, and only a fraction of its weight is detected by GC, a mass spectrum is obtained from which identification may be possible.

For MW, GPC (gel permeation chromatography) [7] is a sensitive method of detecting small subtle differences in MW distribution (MWD). For some polymers a difference of 3-5% in average MW may be great enough to account for differences in processability or product performance. GPC is a much more discriminating measure of MW than the methods of solution viscosity or melt flow index (MFI) [8] because it measures the polymer's whole distribution of MW, not only an average value of MW.

Other methods may also be important in failure analysis such as DSC (differential scanning calorimetry), TGA (thermogravimetric analysis) and SEM-EDX (scanning electron microscopy-energy dispersive x-ray spectroscopy). DSC and TGA are thermal analysis methods; SEM-EDX determines elemental composition, such as inorganic elements.

In this paper the focus is on cases in which IR, GC/MS and GPC were used in the determination of the cause of failure.

3.0 Molecular Weight Distribution by GPC

3.1 Polymer coating application

A polymer that had processed satisfactorily in a coating application experienced difficulty with new lots of the same polymer. GPC was used to determine if differences in MW between good and bad lots were the cause of the problem. The polymer was amorphous and soluble in THF (tetrahydrofuran), a common solvent for GPC. A set of four Jordi high-speed columns (10^5, 10^4, 10^4, 10^3) was used at 2.5 ml/min., with a Polymer Labs evaporative light scattering detector (ELSD). Solution concentration was 0.1% and 100µl samples were injected. Molecular weights calculated were M_n (number average), M_w (weight average), M_z and M_{z+1}. Peak areas were also noted. Table 1 gives the values for a good and a bad lot, regarding processability, for duplicate solutions of each lot.

In Table 1 the average peak area of the bad lot is 28% lower than for the good lot. Peak area is proportional to concentration of the polymer in solution. Even though both lots had the same dissolving time with shaking, filtered readily through a 0.45µ filter and appeared to be completely in solution, the bad lot evidently had some insoluble polymer or gel that is revealed as lower peak area. This finding by GPC is a crucial factor as to the processing differences between the lots, which may not have been detected readily otherwise. Also, the molecular weight values indicate higher M_{z+1} and lower M_n for the bad lot.

Figure 1 shows the chromatograms for the two polymers. The broader distribution of the bad lot is readily seen. From Table 1 MWD of the good lot is 1.98 and 2.56 for the bad lot. The figure does not reflect the difference in peak area noted above because the curves were normalized to the same peak height.

3.2 Polycarbonate Injection Molded Part Fracture

The part measured approximately 4" x 6", was secured to metal with screws at the four corners. In service, which included exposure to the outdoors and to detergent washing, parts fractured under the stress of the metal screws. There was direct contact of PC and metal screws, i.e., there was no plastic or rubber to moderate the stress on the plastic from the tightened screws. GPC was done on fractured parts and pellets from which parts were molded. Table 2 gives the M_w values (weight average) and the % drop in M_w for parts relative to the pellets from which they were molded. Failed part #1 dropped 2.9% in M_w from its PC pellets. Part #2 lost 5.8% from its PC pellets. These values may seem too low to be the cause of failure, i.e., within experimental error for GPC. However, it has been known for a long time that for PC, as well as other relatively low molecular weight condensation polymers, a drop in molecular weight of 5% for injection molded parts can cause as many as 50% failures, and 10% can lead to 100% failures. This was given by GE Plastics for solution viscosity and approximately the same effects would be expected for molecular weight by GPC.

The resistance to fracture is determined by the molecular weight of the starting resin and the extent to which molecular weight drops in processing. The responsibility for failure of the parts may be due in large measure to the molecular weight of the starting resin. It is tempting to use the lowest molecular weight polymer for ease of molding. However, that may make the molded part too low in molecular weight. Properties such as strength and environmental stress crack resistance change rapidly as a function of molecular weight at low MW, then tend to level off at higher MW [9]. The effect of molecular weight is very great at the low molecular weight end of the curve, about where PC falls. Thus a small change in molecular weight can cause a relatively large change in properties. Complicating the picture is the fact that PC is very sensitive to water in processing. As little as 0.01% can cause hydrolysis of the PC chain to lower molecular weight at the high processing temperature required for PC (approx. 260°C and higher).

Figure 2 is an overlay of the GPC of the pellets of part #2 and failed part #2. While the differences may not look great enough to cause failure, they are consistent with the known effect of molecular weight on properties referred to above.

In addition to GPC, failed parts and starting pellets were analyzed by thermal desorption GC/MS. Figure 3 is the chromatogram for pellets and for the failed part made from the pellets. The main compounds identified in the pellets, using a thermal desorption temperature of 250°C and 2 minutes, are chlorobenzene, triphenylphosphine (TPP) antioxidant, and a benzotriazole-alkyl substituted phenol, which is probably a stabilizer. In Figure 3 the failed part contains triphenylphosphine oxide and little or no triphenylphosphine. Evidently processing exhausted the TPP antioxidant with formation of the corresponding oxide. New parts that were not in service also showed practically complete elimination of TPP and formation of the oxide. The GC results relate to the GPC molecular weight results in that depletion of antioxidant TPP indicates possible degradation to lower MW. Chlorobenzene is a characteristic component at a low level of the manufacturer's PC.

It seems clear that the PC parts failed due to too low MW and the stress of metal screws tightened directly in contact with the part. With high MW the part may have resisted the stress from the screws. TPP may have been present at too low a level since it was all depleted in processing.

4.0 Infrared Spectroscopy

Extruded medical grade polyurethane tubing contained incompletely dispersed white particles at a low, but unacceptable, frequency. Microinfrared spectroscopy (IR) gave a spectrum of the particles that identified them as barium sulfate, which is present in the formulation (Fig. 4). Often IR is not able to identify inorganic compounds. In this case barium sulfate has a distinctive spectrum. The problem was that the compounding of the sulfate into polymer was incomplete and extrusion did not provide sufficient additional mixing to thoroughly incorporate all the sulfate into the polymer.

SEM-EDX (scanning electron microscopy/energy dispersive x-ray spectroscopy) confirmed that the undispersed particles contained mainly barium and sulfur (Fig. 5). Titanium dioxide was also present in the formulation as a pigment and there was a question if the particles also contained titanium dioxide and to what extent. The dioxide does not have a distinctive IR spectrum so IR could not tell if it is present in addition to barium sulfate. Unfortunately the EDX spectrum of titanium and of barium overlap so that EDX was also not specific for barium vs. titanium. However, the sulfur peak is unique for sulfur and provided the basis for concluding that the particles were primarily from barium sulfate with little or no titanium dioxide.

5.0 GC/MS of Liquid Samples by Direct Injection

5.1 Printed Ink Smear

In this case direct injection of liquid samples into a GC was performed. In other cases below (6.0) solid samples were analyzed by thermal desorption. Printing on a plastic product smeared at some locations and not others. Different pad printers were used at different locations in an automated product line. A top coating was applied over the print. The print was black and the same ink was used at locations that did not smear. GC/MS was used to determine the cause of smearing. The hypothesis was that it was due to incompletely removed solvent or other material before the top coating was applied, effectively trapping the solvent or other material inside the coating. The analysis did not turn up a significant difference between inks or thinners at good and at bad (smearing) locations.

Further examination of smeared prints revealed that smearing locations had inconsistent thickness that was high where smearing occurred. Smearing was due to inadequate removal of solvent at thick locations. The problem was traced to certain pads that deposited higher than normal print thickness. More rigorous cleaning and replacement of pads eliminated the problem. The role of chemical analysis was to show that the composition of inks was not the cause of the problem. Optical microscopy showed that the edge of a printed black letter was much darker than the rest of the letter, due to high thickness, which in turn caused solvent to be removed incompletely and to smear.

6.0 Thermal Desorption GC/MS

6.1 Cause of Clogging of Extruder Screen

Metal screens are routinely used in extruders to remove particles larger than the screen spacings. Location is before the extruder die so that the extrudate is uniform and free of large particles. When the compound being extruded contains a higher than normal content of large particles, the screen becomes clogged more often than normal and the extruder has to be taken out of service to replace the screen. In such a case of a filled polymer the frequency of clogging was unusually high for a formulation that usually processed well with limited screen clogging. Analysis by TD/GC/MS was done on particles caught on the screen (Fig. 6). Unsaturated hydrocarbons do-, tetra- and hexadecene isomers were found on the filter particles caught on the screen. Similar looking material on a screen that did not clog as much as the first one did not contain the unsaturated hydrocarbons, which may be a contaminant on the filler. Possibly the hydrocarbons affected the reaction of filler with silane used to effect a bond between filler and polymer. In any case, they apparently contributed to agglomeration of the filler into larger particles than otherwise, causing screen clogging.

6.2 Matching a Polymer of Uncertain Origin to its Source

A black extruded polyethylene (PE) cable insulation could not be traced from records or otherwise to its source. This presented a problem of accountability in an application that called for strict knowledge of all materials as to manufacturer, etc. Five candidate PEs were analyzed along with the one in question to locate its source. DSC (differential scanning calorimetry) gave melting points and heats of fusion. Two of the five were eliminated in this way. The other three were similar by DSC to the one to be identified. TGA (thermogravimetric analysis) was done to compare carbon black content and ash content. All were within experimental error. TD/GC/MS was done on the possibility that trace compounds would provide the identification. Figure 7 is the chromatogram of the unknown PE. Only one of the three candidates contained the same compounds as in Figure 7. Recall that GC/MS identifies in two ways – by GC retention time and mass spectra of each GC peak. In Figure 7 a mixture of hydrocarbons is present, as well as an antioxidant (#1) and a second one (#2). The other large peaks are low MW PE oligomers. GC/MS provided unambiguous identification of the source of the unknown PE.

7.0 Infrared Spectroscopy (IR) and TD/GC/MS Together

7.1 Leaking of Conductor Filler of an Electrical Cable

In some applications electrical cables require that water will not leak into the central stranded conductor via an exposed junction or terminal or other way. The cable may be pressure filled with a water impermeable sealant to fill the spaces between twisted conductor strands. This is a requirement, for example, in some military applications.

In one such case, leakage was found in a test in which cable is held vertically and sealant that drips out is noted. The same cable had performed perfectly in this test previously. To determine why the cable was failing the test, sealant of earlier and of current material was analyzed by IR and GPC. The two materials were clearly different in composition and molecular weight. Figure 8 gives IR spectra of the two sealants. The supplier of the sealant had made an unauthorized change; the new sealant was more fluid and leaked out of the conductor strands.

TD/GC/MS identified the plasticizers and other compounds of the two sealants. Leakage was related to lower compatibility of plasticizer with the polymer of the sealant. Pressure is present at various locations of the stranded conductor depending on the twisting and how tightly the conductor is held against the insulation. A sealant with plasticizer of lower compatibility in polymer than before is more likely to respond to pressure by exuding and flowing.

As part of the investigation, a diamond cell for transmission IR was used to obtain spectra. Pressure is exerted inside the cell to compact samples and to control thickness. It was noted that in some cases liquid separated from sealant samples under the pressure inside the cell. With leaking sealants, liquid could be seen in a few minutes, and the distance of flow noted for five minutes. The IR diamond cell in effect became a rapid test for compatibility and leaking of sealant samples. In this way chemical composition, molecular weight, etc. could be directly related to how the sealant would perform as a non-flowing conductor strand sealant.

Figure 9 is a photo of a sealant in an IR diamond cell showing the flow front.

8.0 Summary and Conclusions

The solution to the cause of plastics failure or composition uncertainty often requires analysis of chemical composition and/or molecular weight, as well as other properties. This paper has highlighted the role of GPC for molecular weight distribution and the methods of infrared spectroscopy (IR) and TD/GC/MS for chemical composition. GPC can be informative about insoluble gel content from peak area as well as molecular weight. IR is limited in sensitivity to components at low level but is effective for identifying major components. TD/GC/MS is extraordinarily sensitive for identification of volatile compounds because it is a separation method and provides mass spectra of separated peaks.

9.0 References

1. Ezrin, M., Plastics Failure Guide – Cause and Prevention, Hanser, 4 (1996).
2. Ref. 1, p. 12.
3. Ref. 1, p. 21-35.
4. Ezrin, M., Plastics Analysis – The Engineer's Resource for Troubleshooting Product and Process Problems and for Competitive Analysis, *Plastics Engineering*, **58** (2), 41 (2002).
5. Ref. 4, p. 48.
6. Ref. 4, p. 48, Fig. 12.
7. Ref. 1, p. 37, Fig. 2-17.
8. Ref. 1, p. 37, ASTM D1238.
9. Ref. 1, p. 38.

Key Words

Plastics analysis, plastics failure, molecular weight, plastics composition.

Table 1. GPC of Good and Bad Lots of Polymer Processing in a Coating Application

Sample	M_{z+1}	M_n	M_w	Peak area
Good	335,000	64,500	127,500	5,030,000
Bad	449,000	49,800	127,500	3,610,000
Good/Bad ratio	0.746	1.295	1.00	1.393

Table 2. Polycarbonate Pellets and Molded Parts M_w GPC

	M_w*	% Drop of parts from pellets
New part not in service	44,200	0.90**
Failed part #1	43,300	2.91**
Failed part #2	43,600	5.83***
Pellets of part #1	44,600	
Pellets of part #2	46,300	

*M_w based on calibration with polystyrene standards; UV detector at 254nm.
**Relative to pellets of part #1.
***Relative to pellets of part #2.

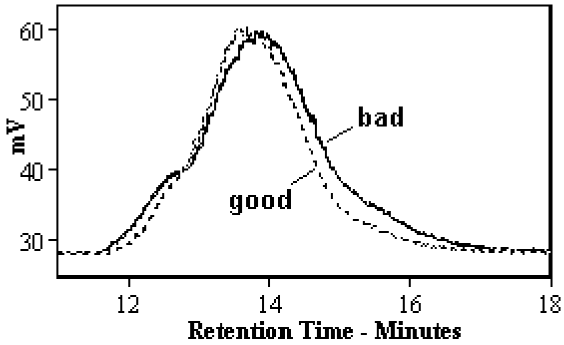

Figure 1. GPC of good and bad lots of polymer regarding processing for a coating application.

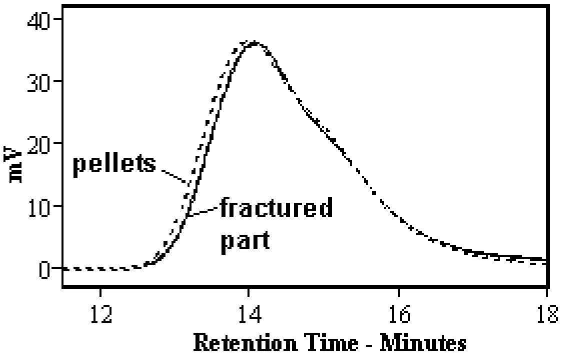

Figure 2. GPC of pellets and fractured PC part.

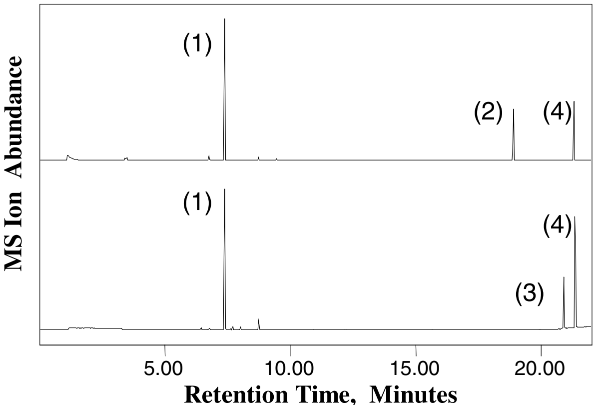

Figure 3. TD/GC/MS of pellets (top) and fractured PC part (bottom). (1) chlorobenzene; (2) triphenylphosphine; (3) triphenylphosphineoxide; (4) benzotriazole alkyl phenol.

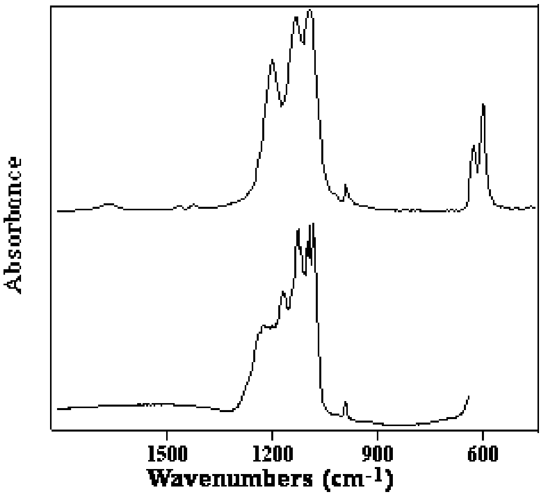

Figure 4. IR spectrum of undispersed particle (bottom) and reference spectrum of barium sulfate (top).

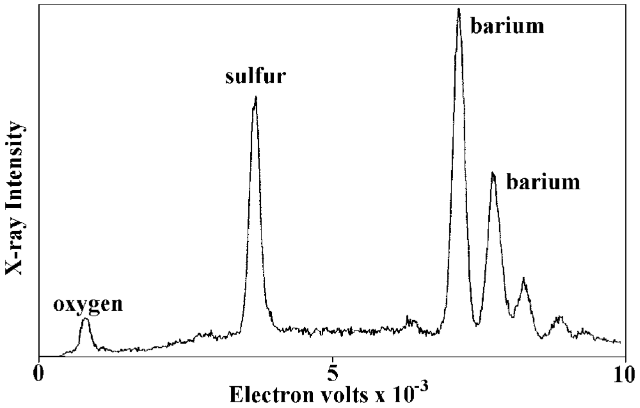

Figure 5. SEM-EDX of undispersed particle.

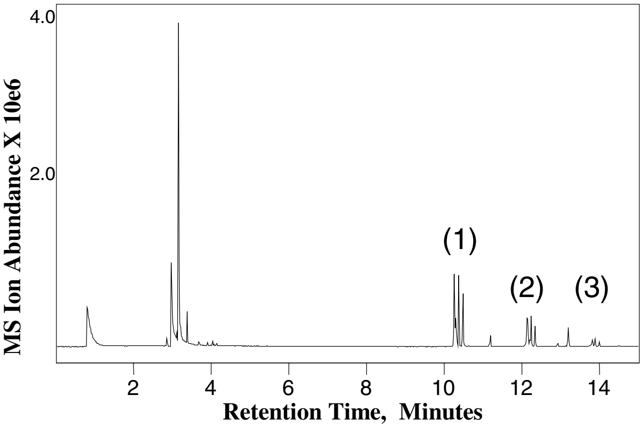

Figure 6. TD/GC/MS of particle caught on extruder screen. (1) dodecene isomers; (2) tetradecene isomers; (3) hexadecene isomers.

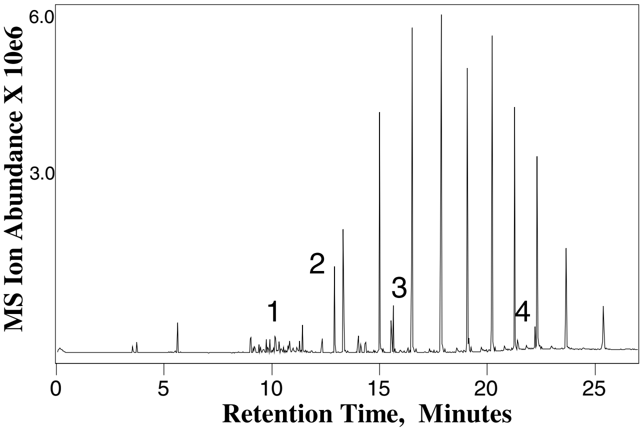

Figure 7. TD/GC/MS of unknown PE and candidate sources. (1) hydrocarbons; (2) antioxidant #1; (3) first peak – cyclic compound MW 196; (4) first peak – antioxidant #2.

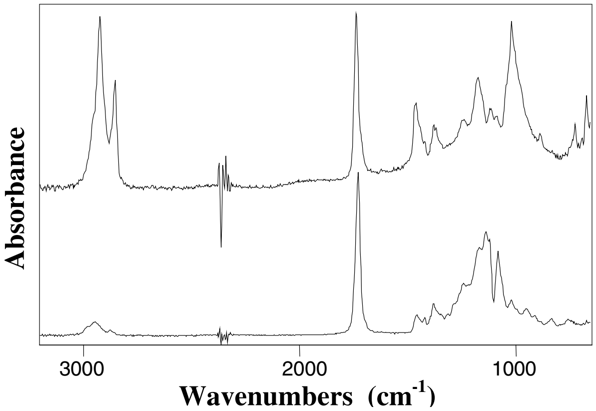

Figure 8. IR spectra of non-leaking (top) and leaking sealants (bottom).

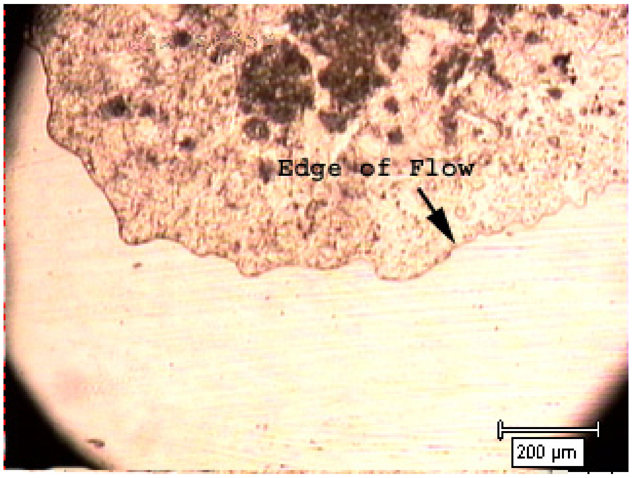

Figure 9. Photo of a sealant in IR diamond cell showing the flow front of liquid in the sealant.