Study of Post-Consumer Recycled (PCR) Content Integrity in Plastic Aerosol Containers

Conducted by the Plastic Aerosol Research Group, LLC, published by the HCPA Aerosol Products Division, 10 October 2023

Abstract

The Plastic Aerosol Research Group, LLC (PARG), now incorporated into the Household & Commercial Products Association (HCPA), pursued the understanding of the impact and effect of adding various amounts of Solid-State Polymerization (SSP) Post-Consumer Recycled (PCR) content to virgin Polyethylene Terephthalate (PET) used to produce plastic aerosol containers. The intent was to improve sustainability to meet Consumer Product Goods corporate strategies and to comply with some U.S. State's and European Union mandates for plastic containers sold in consumer markets.

Background

At the time of the study, there was no public or industry literature available regarding the effect(s) of adding SSP PCR, specifically related to integrity of PET resin, used in aerosol containers. Under the PARG industry membership, the Packaging Technical Committee aimed to determine the effect(s) of adding PCR to a pressurized PET aerosol container. PARG, as a Limited Liability Company (LLC) was dissolved in December, 2022; however this project was still in progress and offered value to industry members, so it was motioned and approved to continue under HCPA's Aerosol Products Division as a task force under the Scientific Committee.

This study was designed to analyze the impact of integrity when adding various levels of PCR, specifically SSP PET, using both analytical and physical property test measurements to assure equivalent safety and quality in the manufacture, storage, distribution and use of aerosol products compared with current technologies. Currently, within the United States, aerosols in plastic containers fall under Federal transportation regulations that pre-empt State demands, excluding PCR requirement for Department of Transportation (DOT) DOT-2S containers[1]. Incorporating PCR content is believed to improve the sustainability and is a viable means to satisfy the demand of corporation goals and environmental influences by regulatory bodies to increase the use of PCR in consumer plastic containers.

This study was not intended to:

1. Evaluate or claim the recyclability of the plastic aerosol containers in municipal recycling facilities (MRF) or PET reclaimers.
2. Design or develop a bottle that would pass all the PARG protocols, but rather to use a control 1000 ml which is the maximum allowable volume permitted by the Pipeline and Hazardous Materials Safety Administration (PHMSA), as an industry standard bottle for comparison.
3. Test any specific product formula.

Industry Methodology and Set-Up

The addition of PCR brings with it the possibility of changes to the resin properties, which could potentially have a negative effect on the integrity of a container under conditions of high pressure, design differences and various product (chemical) interactions. Therefore, to understand this potential, the industry took a two step approach.

Step one was analytical testing to ensure the consistency of material. The goal was to conduct material characterization studies to evaluate the extent of physical, flow, and visual property changes of PCR material blends vs. virgin resin. Based on the material analysis data, the team determined it was appropriate to proceed with the second step of testing. This involved conducting the physical testing on the 1000 ml overflow volume (OFV) containers using a previously validated PARG test methodology for developing plastic aerosol containers to understand the effects of adding solid-stated PCR to virgin resin to meet current U.S. DOT regulatory tests across PCR variables. The 1000 ml aerosol bottle was used because it is the largest aerosol container permitted in the marketplace. Testing sample containers and validation was done across three industry member labs. The three lab approach was used previously to validate all of the PARG methodology and allowed PARG to validate the statistical consistency of the results. Each lab executed the PARG testing methodology on the various PCR variable bottles. This set of scientific data could then be used to gauge the potential impact on DOT-2S containers. The intent of this testing was to fully understand and verify the integrity of the container prior to applying for any code changes for the industry.

[1] US DOT 49CFR, Subtitle B, Chapter I, Subchapter C, Part 178.33b-5 and 178.33b-6.

Set-up:

- 1000 ml PET Cylindrical bottle (Plastipak Packaging, Inc.) (Appendix 1).
- Outside 1" aluminum valve (Summit Packaging Systems)
- Crimped and pressure filled Through-The-Valve (TTV)
- Fill weight was 600.0 grams of deionized water[2] and approximately 5 grams of nitrogen (60 percent/40 percent volume ratio)
- 11.1 bar (160 psig) at 21.1°C (70°F) conditioning pressure

Analytical Analysis

The industry used both analytical measurements and physical property tests to ensure the results were equivalent. Analytical testing is conducted on plastic raw materials. This serves many purposes: for example the results from the analytical tests can be used to characterize material properties. These test results can be used to compare different materials and help select the right material for the right application. The results of lab-scale analytical testing can be used to correlate the properties of plastic raw materials to the physical property tests of the containers that are made from these raw materials, which can be used to predict performance in the field.

The analytical tests consisted of Intrinsic Viscosity (IV) and Differential Scanning Calorimetry (DSC). These parameters are indicators of the strength, thermal stability and integrity of the material. Both IV and DSC tests are capable of predicting anomalies and degradation in the polymer material.

IV is directly related to the molecular weight and chain length of the polymer material. A higher IV indicates higher mechanical strength of the polymer, which ensures good material properties and containers that are more robust.

The DSC is a test in which the polymer material is subjected to a controlled heating process to indicate the thermal stability of the plastic. The thermal transitions and melting behaviors are examined by measuring the temperatures for various thermal transitions, such as the Glass Transition Temperature (Tg) and the Crystalline Melting Point (Tm). The plastic transforms from a rigid, glassy state to a softer, rubbery at the Tg. It then transforms to a viscous liquid at the Tm.

The IV and DSC studies looked at the base resins as well the preforms made with resin variables of 100 percent virgin (0 percent PCR), 25 percent PCR, 50 percent PCR, 75 percent PCR, and 100 percent PCR (0 percent virgin).

The IV results (Appendix 2) and DSC results (Appendix 3) showed that the virgin and PCR resin blends are very similar.

Moreover, there were no significant differences between the IV or DSC data for the resin and the preforms, indicating no significant material degradation during the molding process.

Physical Analysis

To ensure safe and effective products in manufacture, storage or distribution, the aerosol industry has established voluntary methods and/or standards for aerosol products. In addition, U.S. Federal and State and international agencies have established testing requirements for aerosol products. These physical properties include requirements for burst strength, drop impact and resistance to temperature conditions. Evaluation of the data utilizing the maximum container size 1000 ml used showed acceptable results.

Burst testing (per PARG 10.0) is utilized to understand how the container manages conditions unexpectedly during manufacture, storage, or distribution. Requirements dictate that 1.5 times the intended pressure be tested. In all resin variables, the 1000 ml plastic bottle performed above requirements during testing (Appendix 4).

Upon completion of the burst test, additional sample bottles were then filled with the appropriate media (DI Water), sealed, pressurized and set within a designated temperature chamber for the specified amount of time for drop testing. Each unit was filled to 60 percent volume (DI water) and pressurized to the DOT-2S maximum pressure test condition of 11.1 bar (160 psig) using nitrogen gas. The control temperatures and times for the drop testing (per regulatory, following PARG 11.0) performed were 38°C (100°F) for 26 weeks, 50°C (122°F) for 100 hours, and 55°C (131°F) for 18 hours. Review of the data from the two testing laboratories statistically determined no differences between levels of PCR. Although the 75 percent and 100 percent drop test data did find minor differences between the PCR/temperature/time variables, the statistical analysis showed not significant results (Appendix 5).

Additional samples, which were filled the same way as the drop test samples, were used to conduct an environmental stress crack resistance (ESCR) test, per PARG 8.0, and the 'Material Resistance to Induced Heat Conditions' test, per PARG 15.0. All samples passed the minimum time specification for ESCR; however, there was no consistent pattern between results of virgin and various PCR percentages for the 'Induced Heat' test. All samples were valve disengaging from the rolled finish, which is deemed design related (Appendix 6).

This data demonstrates that adding solid-state PCR to virgin PET can produce a container that is of equal quality to a virgin PET container. Even so, each marketer must still perform testing to assure stability and performance of the container once the formulation has been added.

[2] Deionized water (DI water, DIW or de-ionized water), is water that has had almost all of its mineral ions removed, such as cations like sodium, calcium, iron, and copper, and anions such as chloride and sulfate.

UV Analysis

Based on prior studies conducted by PARG and industry learnings, this study did not conduct an ultraviolet (UV) light methodology on various PCR percentages, per PARG 20.0. A research study was previously conducted by PARG to determine how UV impacts the integrity of PET. The results showed no significant effect, analytically or physically, to the PET container. It was concluded that there was no significant effect both analytically and physically to the PET container[3]. Working with the carbonated bottle and consumer cleaning industries, it was also determined that bottles made with virgin PET had no significant difference in field performance compared to bottles made with recycled PET that were adequately cleaned and solid-stated to intrinsic viscosity levels equivalent to those of virgin material. Information from PET resin vendors confirmed that UV exposure is not expected to cause significant difference in the performance properties of virgin and recycled PET with similar intrinsic viscosities.

It should be noted that UV can be a detriment to a product inside a clear bottle. Therefore, evaluating formula/product using PARG 21.0 would be recommended, but the resin itself is not impacted.

Conclusion

Comparing the analysis results of the material properties, there was no material degradation or significant analytical property value differences due to processing the various levels of SSP PCR (25, 50, 75 and 100 percent). Additionally, there was no significant difference in the physical integrity of the virgin or various level of SSP PCR 1000 ml container at the DOT-2S maximum pressure condition. This included meeting all the regulatory integrity requirements for plastic aerosol commercialization:

- Material—Complies with 49CFR, §178.33b-5(b)
- Drop Testing – Complies with 49CFR, §178.33b-7
- Hydraulic Burst Testing – Complies with 49CFR, §178.33b-8

Recommendation

Using solid-stated polymerization PCR content PET is a viable means to include or incorporate a virgin PET resin to produce a plastic aerosol container. Thus, industry is recommending to PHMSA to modify Title 49, Part 178, Subpart B, Section §178.33b-6, as such:

§ 178.33b-6 Manufacture.

(a) Each container must be manufactured by thermoplastic processes that will assure uniformity of the completed container. No material other than production residues or regrind from the same manufacturing process or solid-stated polymerization PCR content may be used. The packaging must be adequately resistant to aging and to degradation caused by either the contained substance or ultraviolet radiation.

This will allow the industry to develop and improve sustainability measures, as applicable, while remaining compliant with regulatory entities, such as the International Carriage of Dangerous Goods by Road (ADR) under the United Nations Economic Commission for Europe (UNECE) and U.S. state requirements.

Definitions

Intrinsic Viscosity (IV)—related to the molecular weight of the polymer through the Mark–Houwink relationship. The technique used to perform IV measurements is described in ASTM D4603.

Solid-State Polymerization (SSP)—process during the manufacture of PET resin in which the molecular weight and chain length of the PET resin are increased through the action of heat and time usually under an inert nitrogen atmosphere. This process increases the IV of the PET resin, while removing moisture and volatiles from the PET resin.

Solution Intrinsic Viscosity (SIV) using ASTM D4603—Method of measuring the IV of PET in a solution of 60 percent phenol / 40 percent tetrachloroethane. The PET is at a concentration of 0.50 percent at a temperature of 30 °C.

Differential Scanning Calorimetry (DSC)—Test in which the polymer material is subjected to a controlled heating process (related to Tg).

References

1. ASTM D638-Standard Test Method for Tensile Properties of Plastics, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA.
2. ASTM D4603-Standard Test Method for Determining Inherent Viscosity of Poly(Ethylene Terephthalate) (PET) by Glass Capillary Viscometer, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA.

3. PARG 8.0–Environmental Stress Crack (PET) for Aerosol Products in Plastic Containers.

PARG 10.0–Burst Performance for Aerosol Products in Plastic Containers.

4. PARG 11.0–Drop Impact for Aerosol Products in Plastic Containers.
5. PARG 15.0–Material Resistance to Induced Heat Conditions for Aerosol Products in Plastic Containers.
6. PARG 20.0–UV Exposure using Xenon Arc Light Apparatus for Aerosol Products in Plastic Containers.
7. PARG 21.0–UV Exposure of Product Formula using Xenon Arc Light Apparatus for Aerosol Products in Plastic Containers.

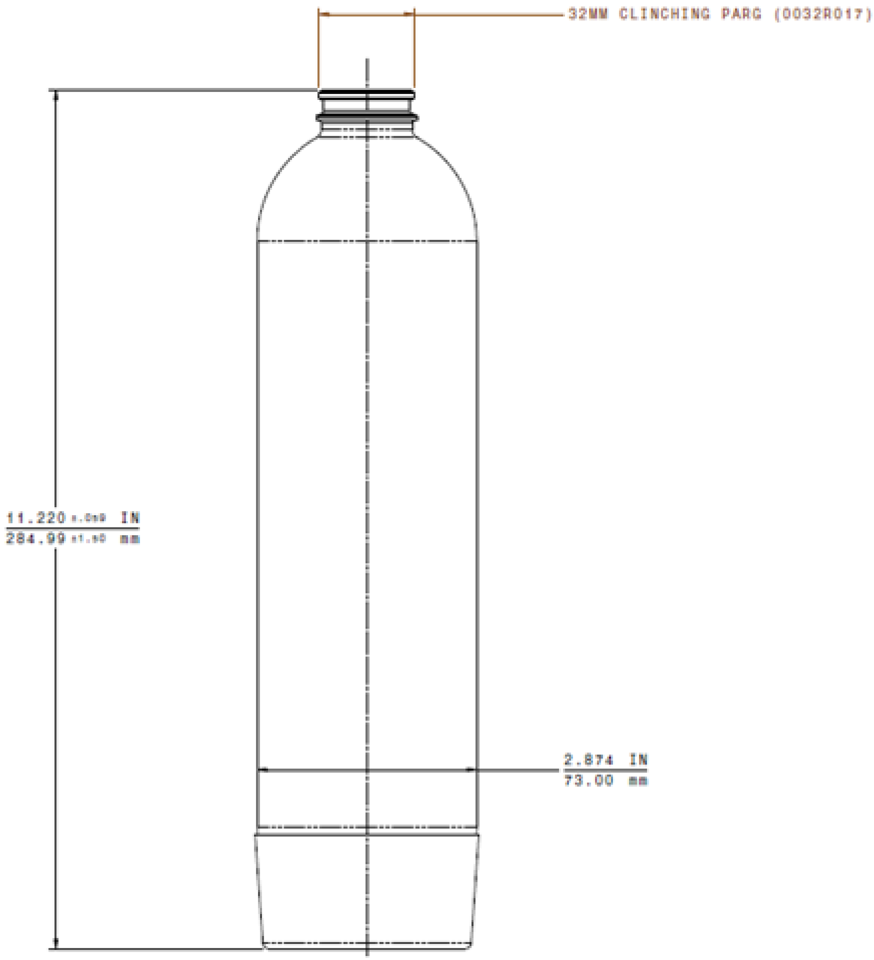
[3] Study of UV Degradation on Plastic (PET) Aerosols, Rochester Institute of Technology (RIT), Journal of Applied Packaging Research (full study available at *scholarworks.rit.edu/japr/vol12/iss1/8/*).

Note: referenced PARG methods can be located and downloaded at www.thehcpa.org under Resources/Publications or https://member.thehcpa.org/products/product/Aerosol-Products-in-Plastic-Containers-Guide.

Disclaimer

* This does not preclude the fact that a bottle manufacturer or consumer product goods company shall not do their due diligence on container design, resin selection and formula interaction against all the physical testing set forth in the 49CFR, 178.33.b and voluntary standards set forth in the PARG 1.0 to 22.0 (HCPA 4.01-4.22) methods and practices.
* The mention of trade names, commercial products, industry references and technical resources does not constitute an endorsement or recommendation for use.
* While every attempt has been made to provide readers with definitions/explanations of the terms used in this study, readers who are unfamiliar with SSP are encouraged to discuss specifics with subject matter experts in the field of plastic resin properties.
* The information in this study is current as of its publication date.

Appendix 1



1000 ml Height: 11.220 in (285 mm)

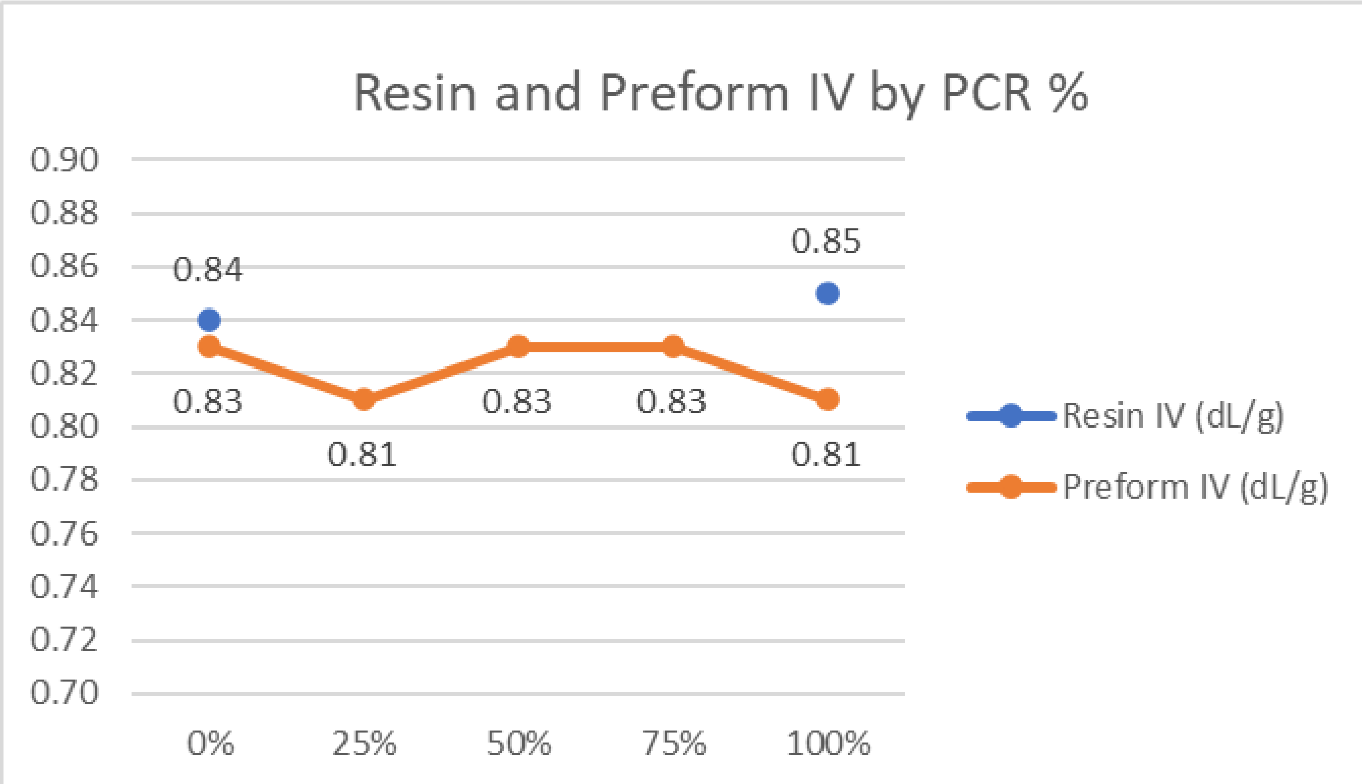
Dia.: 2.874 in (73 mm)

Resin: Carbonated Soft Drink (CSD) Grade PET

Basecup: PE, glued to PET

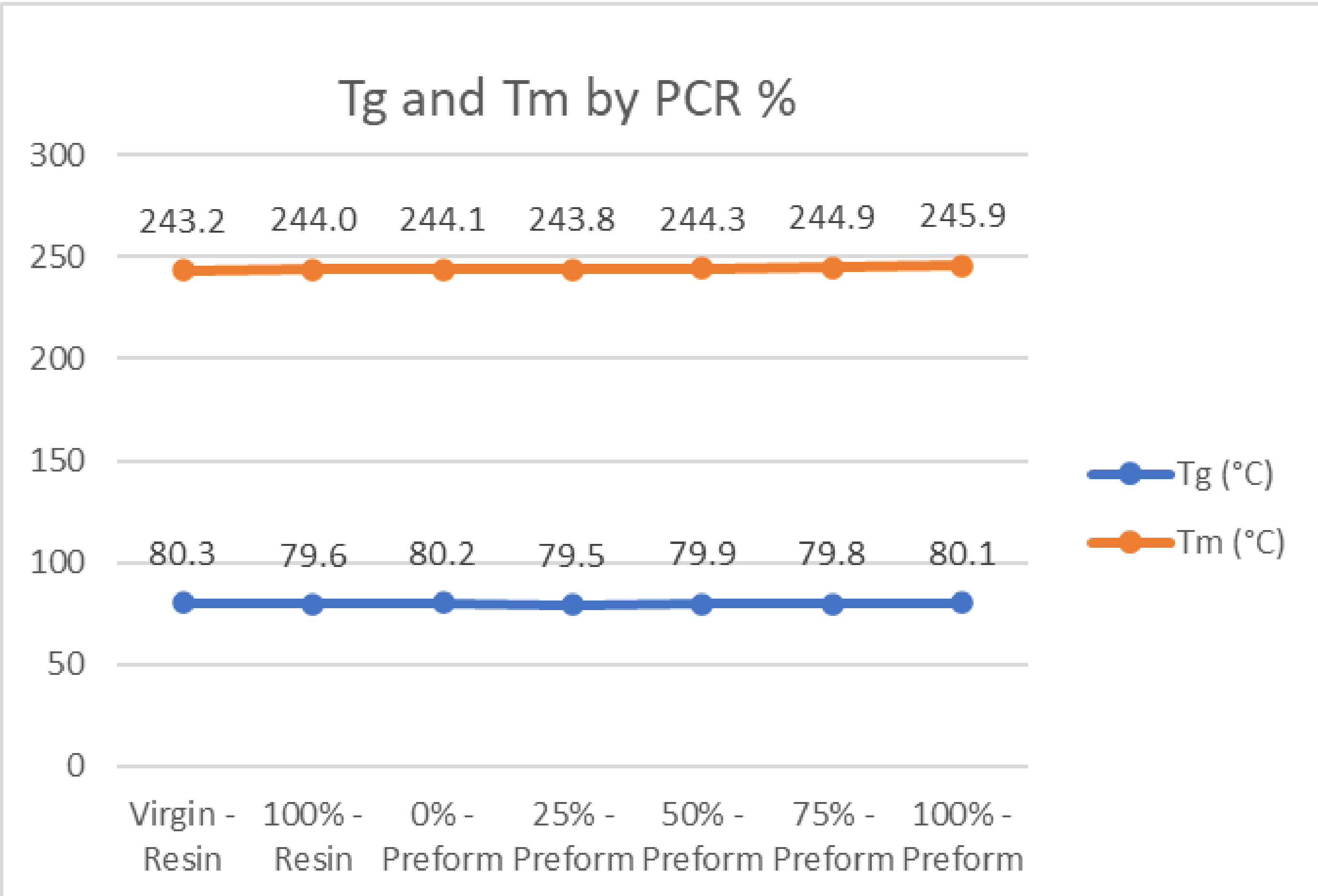
Containers were produced by PARG member company

Appendix 2



IV is the Intrinsic Viscosity

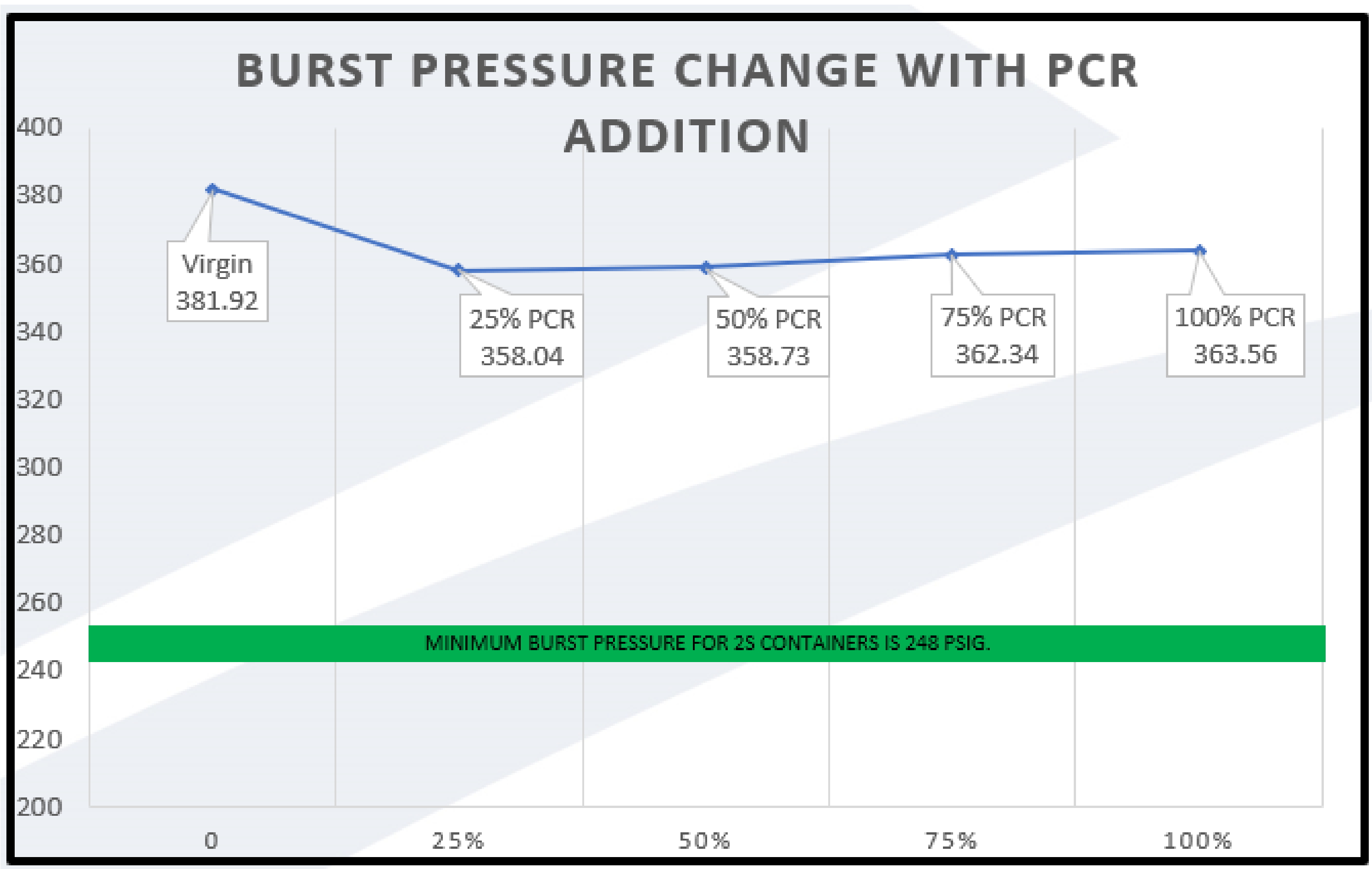
Appendix 3



Tg describes how amorphous plastics or the amorphous portion of semi-crystalline plastics transition from a rigid, glass-like state to a more flexible, rubbery state.

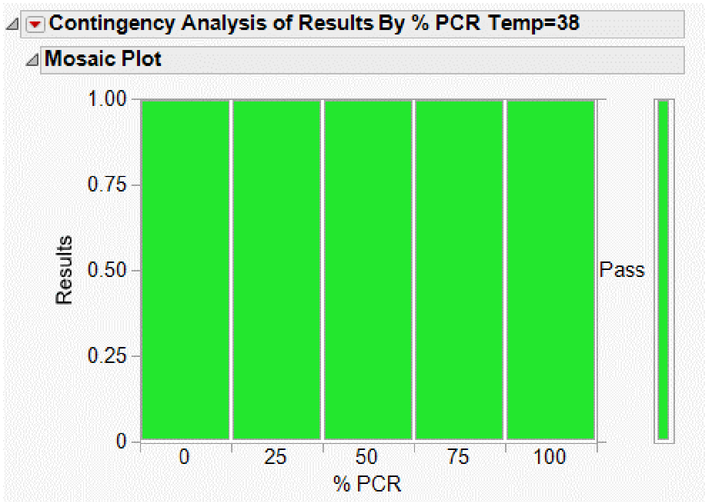
Tm refers to the critical temperature at which the crystalline regions in semi-crystalline plastics flow and transition from a solid to a viscous liquid state.

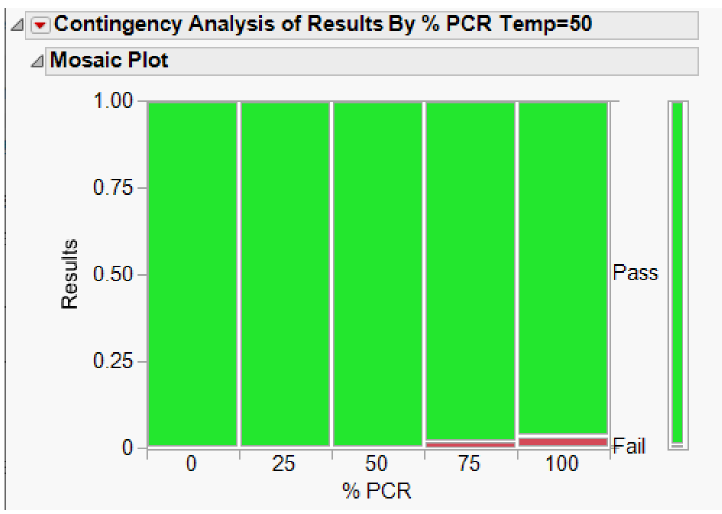
Appendix 4

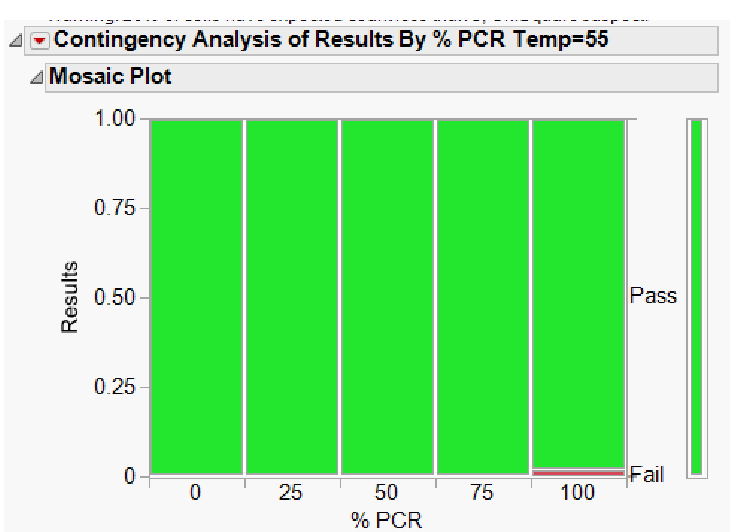


No failures to the container occurred during the PARG 10.0 testing below the minimum for the DOT-2S requirement of 248 psig (17.1bar).

Appendix 5







*The Chi square test used in the Contingency platform requires at least 80% of the cells to have an expected count greater than 5 or else the sum of the cell Chi squares will not have a Chi square distribution and so your test (p-value) will not be valid.

Appendix 6

PARG 15.0 (Ramp Temperature from 50.8°C to 63.6°C) 60% Fill H_2O / 40% N_2 Headspace		
Material Variable	Pass %	Number Failed n=12
All Virgin	92	1
25% PCR	33	8
50% PCR	33	8
75% PCR	42	7
100% PCR	92	1

No failures to the container, such as breakage, occurred during the PARG 15.0 testing. All failures were the result of valves disengaging from the rolled finish due to high temperature, that was approaching the glass transition (Tg), which caused the softening of the PET material.