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ROTATIONAL MOLDING OF ACRYLONITRILE-
BUTADIENE-STYRENE POLYMERS
AND BLENDS

by

Mark Grant Spencer

A thesis submitted to the faculty of

Brigham Young University

in partial fulfillment of the requirements for the degree of

Master of Science

Department of Chemical Engineering

Brigham Young University

December 2003

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BRIGHAM YOUNG UNIVERSITY

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As chair of the candidate's graduate committee, I have read the thesis of Mark Grant Spencer in its final form and have found that (1) its format, citations, and bibliographical style are consistent and acceptable and fulfill university requirements; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the graduate committee and is ready for submission to the university library.

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ABSTRACT

ROTATIONAL MOLDING OF ACRYLONITRILE- BUTADIENE-STYRENE POLYMERS AND BLENDS

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Department of Chemical Engineering

Master of Science

The development of acrylonitrile-butadiene-styrene (ABS) resins for use in rotational molding would provide a medium performance material, thus opening doors to new markets for the rotational molding industry. Unfortunately, ABS resins have shown serious problems during the rotational molding process, namely discoloration, bridging, and poor impact strength. It is believed that these effects are due to degradation of the carbon-carbon double bond in the butadiene, through attack by either oxygen or heat. Previous efforts have shown some success in addressing these issues. However, additional improvements are necessary to make ABS resins commercially viable to rotational molders.

This study, fourth in a series of similar projects conducted though Brigham Young University, was focused on remediation of the ABS difficulties via two different

approaches. First, a survey of several additives was performed with the intent of investigating four different strategies: increased protection from oxygen, decreased butadiene concentration, increased butadiene concentration, and promotion of flow. The best formulation was achieved when 15 wt % of a benzoate ester (XP-2280 available through ChemPoint) was blended into MAGNUM 342 EZ, an ABS resin (The Dow Chemical Company). This formulation showed the best balance between increased impact strength and improvement of cosmetic properties.

Second, optimization of several rotational molding processing parameters was executed. These included particle size distribution of the resin, drying of the resin, internal mold atmosphere, and oven temperature. It was found that using coarse particle sizes (ground at 20-mesh rather than the industry standard of 35-mesh) increased the impact strength by about 19%. None of the other parameters proved to have a significant effect upon the system, except for the use of a nitrogen atmosphere, which lowered the impact strength.

Final properties testing of this best formulation at the optimal processing conditions showed increased impact strength from 2 ft-lbs (the previous best value) to 8 ft-lbs. There was also a marginal decrease in surface hardness (95 to 78 on the Rockwell R scale) and yield tensile strength (3,900 psi to 3,300 psi). Larger differences were observed in flexural modulus (200,000 psi to 110,000 psi) and heat distortion temperature (95°C to 61°C). Therefore, these formulation and processing changes show a trade-off where stiffness and thermal stability (i.e. flexural modulus and heat distortion temperature) can be sacrificed for an increase in toughness and aesthetics, made manifest by increased impact strength, elimination of bridging, and eradication of discoloration.

ACKNOWLEDGEMENTS

Funding for this research was provided by The Association of Rotational Molders (ARM). In addition, ARM also provided excellent guidance and leadership to help define the scope, provide learning experiences, and offer suggestions on how to proceed. Critical to this effort was the support of the ARM Special Materials Committee which directly supervised the proceedings of this research.

Corporate sponsorship of this research was quite significant. Akro-Plastics and Chroma Color Corporation offered internship opportunities, so that I could quickly come up to speed on the rotomolding process. These companies also offered the use of equipment and expertise.

Materials and services were supplied with charge from: ChemPoint Corporation, Ciba Specialty Chemicals, The Dow Chemical Company, DuPont Coating and Release Systems, GE Plastics, Ingenia Polymers Corporation, Poly Processing Company, Velsicol Chemical Company, and WEDCO/ICO Polymers. Without the support of these sponsors the project could not have moved forward.

Three individuals facilitated much of the research through extra-mile efforts. I would like to offer thanks: to Robert Swain (Chroma Color Corporation) for his insights, creativity, and drive; to Bruce Muller (Plastics Consulting) for his salesmanship, sacrifice, and dedication; and to Darrell Laney (Akro-Plastics) for his persistence,

mentoring, and ability to bring all the right people together. The efforts of these three men were critical to the success of this project.

On the academic side, I wish to thank Dr. William Pitt who has offered patient support throughout the project, walked me through much of the science, and encouraged my writing. Thanks are also due for Jeremy Sudweeks, Jonathan Gatlin, Rebecca Nichols, and Dr. John Lawson who aided in the design and analysis of challenging statistical models.

I would especially like to thank Dr. Brent Strong. It was Dr. Strong who offered me a research position and sparked my interest in plastics. Our conversations have been long and frequent. Often they needed to be repeated. His polymer knowledge and hands-on experience were absolutely essential to the achievements of this research.

On a personal note, I would like to acknowledge the constant efforts of my wife Andrea who has been a pillar strength and support for me throughout many early mornings and sleepless nights. She has given me purpose and has made it all worthwhile. Thank you!

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GLOSSARY OF TERMS AS USED IN THIS DOCUMENT

Polymer - A collection of monomer units reacted together to form a single chain. When all the monomer is of the same type, the polymer is called a homopolymer. When more than one type of monomer is incorporated into the chain, the polymer is called a co-polymer. In this document, ABS is referred to as a terpolymer, a sub-class of co-polymer made up of three ingredients: acrylonitrile, butadiene, and styrene.

Resin - A polymeric-based, raw material. While the repeat units of the polymer may be identical, other subtle structural differences may be present between different resin grades. These may include molecular weight, crystallinity, branching, and the degree of cross-linking. Typically, resins contain a small fraction of additives, non-polymeric materials added to modify the properties and performance of the material. Examples of additives include antioxidants, UV stabilizers, pigments, processing aids, etc. For the purposes of this document, a resin is a commercially sold product consisting principally of polymeric materials, possibly containing a small amount of non-polymeric chemicals.

Blend - A combination of a resin with some other material(s). Examples included a resin with another resin, a resin with an additive, two resins with an additive, etc. Blends are not available from original raw material manufacturers. The blend may be made on-site by the finished parts manufacturer or by a third party, often referred to as a compounder.

Plastic - One type of polymeric material found as the material of construction of a finished good. A single finished good may contain several different plastics, each originating from a different raw material (a resin or a blend). The key difference between plastics and raw materials is that plastics have undergone at least one processing step.

CHAPTER 1

INTRODUCTION

Rotational molding (or rotomolding) is a manufacturing process which provides hollow, plastic parts with relatively low cost. Although the process itself is quite simple, only a few resins have proven successful in the manufacture of commercial quality parts. In an effort to increase the number of “rotationally-moldable” resins, the use of acrylonitrile-butadiene-styrene (ABS) polymers has been investigated. This chapter is intended to provide overviews of both rotational molding and ABS resins, to convey a general understanding of the industrial climate, and to present the objectives of this research.

Introduction to Rotational Molding

Rotational molding is a process for forming large, hollow, plastic parts. The process begins as a hollow mold is partially filled (charged) with resin, closed, and then rotated in an oven. As the temperature of the inner mold wall rises, the resin becomes tacky and, upon contact with the mold wall, begins to adhere. While in the oven, the mold is rotated in such a way so that the resin is evenly coated onto the inner wall. After a sufficient heating cycle, the mold is removed from the oven and moved into a cooling chamber where it is subjected to a combination of forced air and sprayed water. Rotation

continues in the cooling chamber. Once the part has cooled, it is removed. The mold may then be charged again and the cycle may repeat. Figure 1 shows the basic rotational molding cycle.

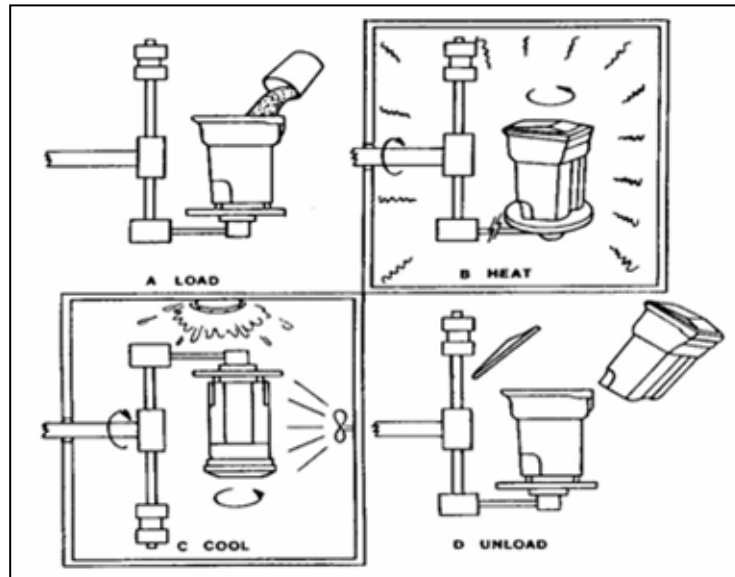


Figure 1 - Steps of the rotational molding process. A) Load the resin into the mold. B) Heat the mold; begin rotation. C) Cool the mold; solidify resin. D) Unload the formed part. Image provided courtesy of Glenn L. Beall.¹

Advantages

Rotational molding offers several key advantages. First, rotomolded parts are hollow. In some applications this offers a lower overall product weight (toys, structures). In other applications the hollow is critical to functionality (duct work, storage containers). Often, a molded unit will be cut into two or more other parts (panels and lids).

Second, rotomolded parts have strong corners and edges. The other two major manufacturing processes used to form hollow parts are blow molding and twin-sheet thermoforming. Both of these processes stretch molten masses of resin by a blowing process and by a drawing process, respectively. Stretching the material tends to produce parts with thinned walls, seen most notably in large parts and in areas with high draw

ratios, such as corners. For small parts, blow molding and thermoforming design engineers have been successful in keeping the edges and corners thick with process design solutions. Rather than stretching molten resins, the rotomolding process causes a build-up of material in the corners and edges. While thermoformers and blow molders must make special design considerations to strengthen their parts, rotomolders find that their parts are inherently strong. The thickness of the corners is a feature desirable in toys, storage containers, and other products subject to dropping or impact.

A third advantage of rotomolding is the ability to make large parts. Other processes are limited by their abilities to stretch molten resin. When blow molders or thermoformers find demand for a large part, considerable design work must occur in order to produce that part successfully.^{1,2} Rotomolding is limited only by the size of the oven. When rotomolders find a demand for a larger part than they can currently handle, they simply build a bigger oven. For example, 15,000 gallon agricultural tanks (height of 16 feet, outer diameter of 14 feet) are frequently rotationally molded.

One final advantage to consider is that of relatively inexpensive tooling. Many manufacturing processes for plastics require high pressures to form parts. High pressure increases tooling cost because the molds typically: 1) are made from higher integrity materials, 2) are machined such as to include both venting systems and cooling systems within the mold, 3) include complex ejector mechanisms for removal of formed parts.²

Twin-sheet thermoforming is also a low pressure process, but the design and machining of hundreds of small vacuum holes into the mold causes a marginal increase in the cost. While tooling cost gives rotomolding only a slight advantage over twin-sheet thermoforming, it becomes a tremendous advantage over blow molding. In blow

molding, once the above-mentioned costs of materials, venting, cooling and removal are combined with the probable costs of mold-specific blow pins and extruder dies, blow molding tooling costs become roughly an order of magnitude greater than rotomolding tooling costs for the same part. This important advantage makes rotomolding the most preferred process for the custom (i.e. low volume) manufacture of large, hollow parts. This advantage may hold even for smaller parts, but more often some of rotomolding's disadvantages make the custom manufacture of smaller parts economically prohibitive.

Disadvantages

There are also some very serious disadvantages to the rotomolding process. First, the time required to form a single rotomolded part is typically much longer than most other manufacturing processes for plastics. Single part cycle times (the time from loading the mold with powder to unloading the molded part) in rotomolding often approach a full hour. Thermoforming cycle times might be as long as a few minutes, but often are much quicker. Blow molding cycle times are most often on the order of tens of seconds. Long cycle times affect not only the production rate of the plant, but also increases the degradation of polymer chains, weakening the polymer.

To help improve cycle times, industrial rotational molding machines are typically capable of handling many molds at one time. The most popular design is the carousel system depicted in Figure 2. In this design, six molds are mounted on three arms, two on each arm. One arm is positioned in a heating chamber, one in a cooling chamber, and one accessible to operators to remove formed parts and charge molds. Such a design is able to produce approximately 6 large parts per hour per machine.

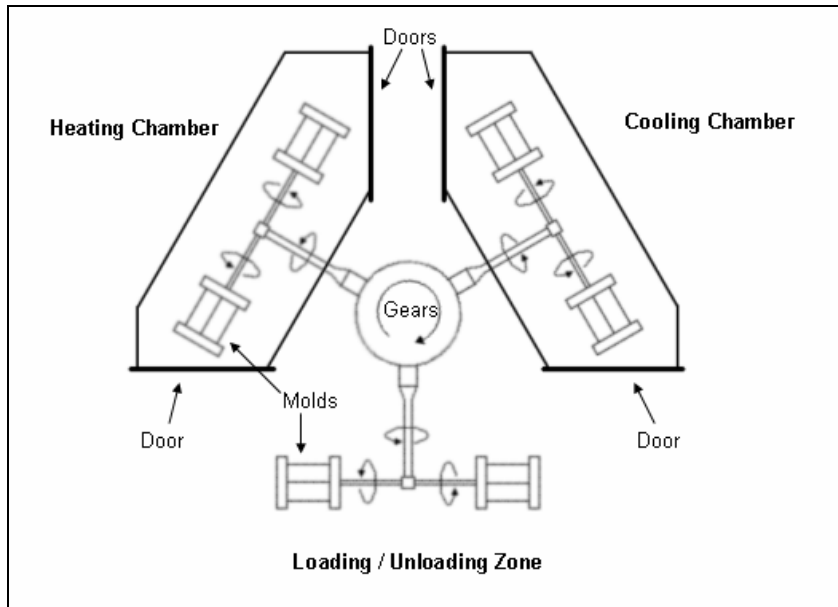


Figure 2 - Typical rotational molding machine.

One final disadvantage is the cost of rotomolding. For small parts, cycle times and the need to employ operators to load and unload the machines makes rotomolding the more expensive process. However, as the size of the part increases, cycle times in blow molding and thermoforming begin to rise. As parts reach the size of a 5-gallon drum, economic considerations favor rotomolding. Figure 3 shows this comparison.

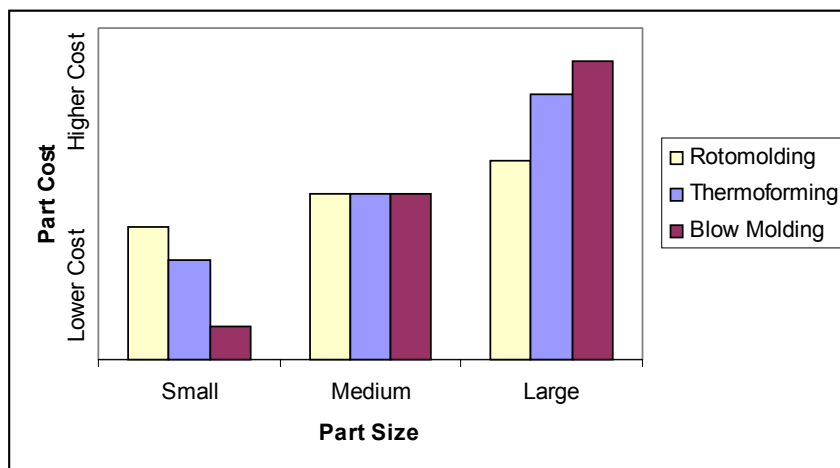


Figure 3 – Dependence of part size on part cost for the three major hollow part production processes. Intended for illustrative purposes only.

Introduction to ABS Resins

ABS is an acronym for the engineering polymer acrylonitrile-butadiene-styrene. Contrary to what the name suggests, ABS is rarely made by simply reacting acrylonitrile, butadiene, and styrene; intermediate stages are usually necessary. Nor is the polymer structure homogenous; multiple phases are usually present. In 1970, there were hundreds of patents to make ABS, 89 of which described a different series of chemical reactions.³ Today, it is estimated that there are over 2300 grades of ABS resins available commercially.⁴ Almost all of these are produced by unique processes.

End products made from ABS have properties passed on from each of the three components. Acrylonitrile makes the plastic hard, heat resistant and chemical resistant. Styrene adds rigidity, strength, and processibility. Butadiene makes the plastic more elastic, increasing the impact performance and toughness of the plastic.⁵

The mechanical properties of ABS are comparable to resins that cost far more. It is easy to process in standard injection molding, extrusion, thermoforming, and blow molding machines,⁶ which make up the majority of the plastic processing sales volume. It has high gloss, can be easily colored, has minimal shrinkage during molding, and is scratch-resistant making it aesthetically pleasing both after processing and through the life of the part.^{3,5,6} It is considered to be one of the most versatile engineering thermoplastic resins.⁷ Common ABS products are telephones and computer housings, appliance housings, helmets, automotive panels, and pipe.

With all the benefits of ABS come a few drawbacks. First, ABS degrades when exposed to heat, light, and oxygen. Without any modifications, this excludes ABS resins from use in outdoor or other harsh environments. With the addition of stabilizers,

pigments, or protective coatings, this problem can be partially overcome.⁸ However, added steps and materials increase processing time and cost of manufacturing. For this reason, the primary uses of ABS are found indoors or in UV protected environments.

Another disadvantage of ABS is that nearly all grades are opaque. This problem has been partially overcome by newer grades of ABS that graft methyl methacrylate onto a special styrene-butadiene substrate, which makes the polymer transparent. One such example is the TERLUX^{®*} line of “MABS” resins (methyl methacrylate-butadiene-styrene) produced by BASF Corporation.⁹ This special modification makes these polymers more expensive than standard ABS. It has found limited use in medical applications.

Another major disadvantage of ABS is its susceptibility to degradation during processing. When many thermoplastics are exposed to heat (near melting temperature), they may bend or stretch, but they suffer little chemical degradation. Polyethylene is an example of such a plastic. ABS, on the other hand, will slowly degrade over time.¹⁰ Its mechanical properties are reduced as it is exposed to high temperatures, as in processing. ABS has a strong thermal history, meaning that there is a limit to the number of times it can be reprocessed without significant loss of mechanical properties.³ Because of the short cycle times in injection molding, extruding, and blow molding, this only becomes a factor in regrind or recycling. However, in rotational molding, with inherently long heating cycles, this disadvantage is important.

* TERLUX is a Registered Trademark of BASF Corporation.

Industrial Perspective

ABS is one of the most important man-made polymers in today's market. Nearly every person in the modern world owns something that is made of ABS, whether it is a telephone, computer housing, or a small appliance. This level of popularity proves the value of the resin and its importance in the world of polymers. Because ABS is so well known, it has certain appeal to some customers.

The nature of the rotational molding process requires the raw polymer to withstand long heat exposures with minimal loss in mechanical properties. This requirement has made the choices of resin supply in the rotational molding industry somewhat unique. Over 90% of the products manufactured via rotational molding employ polyolefin resins (polyethylenes and polypropylenes).¹¹ Polyvinyl chloride resins have also become popular recently.¹² These resins are relatively inexpensive, but, because of their poor physical properties, they are limited to uses such as toys, agricultural tanks, and small storage containers. Other applications frequently demand physical performance beyond what polyolefin and polyvinyl chloride resins can offer.

Several "high performance" resins, such as polyamides and polycarbonates, are also available to rotomolders.¹³ These resins have physical properties which greatly exceed those of polyolefins and polyvinyl chlorides. However, the cost of these resins is generally three to four times the cost of polyolefins, making them prohibitive for use in many molding operations. Resin supply in the rotational molding industry is considered to be unbalanced. The resin choices are limited to low cost, low performance materials and high cost, high performance materials. There is not a medium performance resin available at a moderate cost.

Acrylonitrile-butadiene-styrene resins have been suggested as a candidate material which may add balance to the rotational molding industry, offering physical properties and costs somewhere between polyolefins and “high performance” polymers. Rotational molders agree that there is a strong market potential for rotomolded ABS parts. The development of an ABS resin would allow them to manufacture parts of medium performance. An ABS resin would allow rotomolders to create new markets and to increase their ability to compete with thermoforming and blow molding, thereby bringing growth to the rotational molding industry.

Project Overview

Previous research has demonstrated that at least two ABS resins can be rotationally molded.¹⁴⁻¹⁸ However, the performance of these resins is still not of the quality required by consumers. The chief concerns of ABS resins to molders are the poor flow characteristics and the low impact strength. Other performance criteria are satisfactory.

This research project investigated the improvement of physical properties, especially impact strength, through the blending of modifiers (additives which enhance performance) into two ABS resins: MAGNUM 342 EZ^{®*} (Dow Chemical Company) and CYCOLAC BDT 6500^{®**} (General Electric Plastics).

After identifying blend formulations which yield satisfactory parts, testing was done to determine the ideal size distribution of the resin particles, optimum molding cycle

* MAGNUM is a Registered Trademark of The Dow Chemical Company

** CYCOLAC is a Registered Trademark of General Electric Plastics

parameters, and resulting mechanical properties. This work was performed in both laboratory and industrial settings to yield ABS resins more compatible with this industry.

CHAPTER 2

LITERATURE REVIEW

The compatibility of ABS resins to the rotational molding process has been investigated by both industry and academia. The only known commercially available grade of ABS available to rotational molders was produced by Daicel Limited of Japan, over 20 years ago. Unfortunately, the plant which produced the resin was destroyed by an accidental fire. The product was not viewed to be profitable enough to justify rebuilding a production line, so this product was forgotten.

Only one document about this resin is currently available.¹⁴ It gives few clues about the formulation of the resin. It does state that the resin was suspension polymerized. However, recent work has shown that suspension and emulsion ABS resins show similar physical properties¹⁸, so the significance of the polymerization method is uncertain. Rotomolders and resin supply companies within the Association of Rotational Molders (ARM) have attempted to mold parts with ABS. Over the past several years, ARM has supported academic research aimed at unraveling the mystery of ABS for rotomolding.¹⁵⁻¹⁸ These later efforts have found two commercially available grades of ABS which show improved physical properties over previous attempts, namely CYCOLAC BDT 6500 and MAGNUM 342 EZ. In terms of mechanical properties, these resins have met and exceeded the target values (defined by the ARM Special Materials Committee) for

everything except impact strength (See Table 1). However, several additional problems remain that prevent ABS resins from being used in commercial rotomolding applications, including voids, bridging, and degradation, the latter being manifest as embrittlement and yellowing. Each of these problems has its own set of causes, but the issue of particles size distribution plays into all three. So, the following topics will be discussed in this section: particle size distribution (PSD), voids, bridging, and degradation.

Table 1 – Comparisons of mechanical properties of the best performing ABS material from previous research (labeled as Previous Best) to targets specified by the ARM Special Materials Committee (labeled as ARM Target).¹⁸

Property	ARM Target	Previous Best
Surface Hardness (Rockwell R)	85	95
Yield Tensile Strength	2,500 psi	3,900 psi
Flexural Modulus	60,000 psi	200,000 psi
ARM Impact Strength (-40°C)	20 ft-lbs	2 ft-lbs
Heat Distortion Temperature	40°C	95°C

Particle Size Distribution

The size distribution of the particles in a powder is one of the more important considerations in rotational molding. As will be discussed below, the wrong PSD can cause a multiplicity of problems. Choosing the right PSD is not always a simple task often requiring a balance between two sets of properties. For example, one molder may find that smaller particles give shorter cycle times and stronger parts, but that larger particles provide a smoother inner wall and reduce raw material costs. The trade-offs may be based on part design, application, and resin.

For polyethylene, the most popular particle size distribution is referred to as 35-mesh.* Resin pellets are run through a grinding machine and then screened. Those

* Except where otherwise stated, mesh is reported in U.S. standard mesh sizes

particles small enough to fit through a 35-mesh screen (500 microns) are considered to be final products, while most of the particles larger than 35-mesh are circulated back into the grinding mill. A histogram of particle sizes from a typical polyethylene powder (see Figure 4) show a unimodal, left-skewed distribution, centered at 40-mesh (400 microns). Such a PSD is considered typical in the rotomolding industry.¹⁹

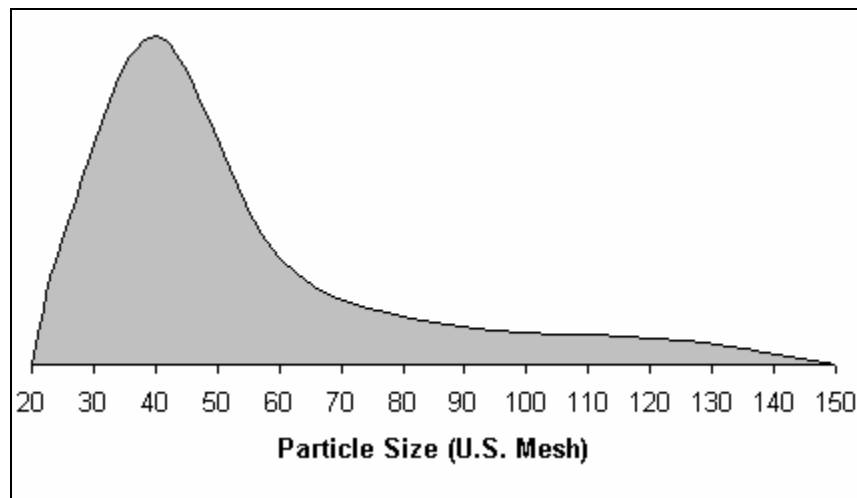


Figure 4 - Representative particle size distribution of a polyethylene powder supplied to the rotational molding industry. Adapted from Throne.²⁰

As polyethylene tends to be the most widely used polymer within the rotational molding industry, the use of 35-mesh powders has become a default mode of operation for many molders, regardless of material. However, as other resins have become available to rotomolders, suppliers have discovered this standard has two problems: 1) that 35-mesh may not be the optimal screen type for all resins, and 2) that more narrowness or broadness in particle size distributions may favor increases in certain properties of molded materials. In other words, both the peak particle size (particle size at the maximum point on the distribution curve) and the breadth of the distribution may be important. Unfortunately, the issue of distribution breadth has not yet been adequately

addressed in rotomolding, even for polyethylene.²⁰ As a result, emphasis has been placed on shifting the position of the peak particle size. This is achieved by changing the mesh size of the grinding screens. Therefore, even though other measures are used, the key measure of PSD in rotomolding is the mesh size of the grinding screens.

Determination of the optimal particle size distribution for ABS is important because it plays into several other areas. The role of PSD will be an important consideration as voids, bridging, and degradation are discussed below. Particle size distribution may also be important for other areas beyond the scope of this research, such as stiffness, optics, weatherability, abrasion resistance, etc.

Voids

When a rotationally molded part has voids, small “pinholes” may be seen on the surface of the part. A clean cut into the wall of an opaque part will reveal many small pockets of air which were trapped in the part wall during the molding phase. If the part is transparent, these bubbles can be seen readily from the outer part wall.

The origin of the voids has been attributed to the air present between the solid resin particles prior to heating.²¹ It may be possible to completely eliminate voids if liquid raw materials were used rather than solid resins. The use of liquids is not uncommon in rotomolding.²² However, for a liquid resin to form a solid part, a chemical reaction must occur during the rotomolding cycle (i.e. cross-linking, polymerization, volatilization of solvent, etc.), meaning that the mold would need to act as a reaction vessel. Liquid resins also tend to be more expensive and less convenient to store and handle.²² As a result of the difficulties liquid resins present, solid resins dominate the rotomolding industry.

Although solid resins are used quite frequently in the manufacture of plastics, the problem of voids is somewhat unique to rotomolding. Other processes employ shear forces, elevated pressures, and/or high temperatures to facilitate coalescence and mixing of the polymer particles. Such conditions promote the migration of air from the molten polymer. Venting of the equipment is sufficient to allow the air to escape, rarely being present in a finished part.

In rotomolding, however, there are no shear forces present, elevated pressures are used only occasionally, and temperatures are low relative to other processes. This is because the resin particles undergo a unique process, which has been compared to the sintering of metal and densification of glass.^{23,24} During rotation, polymer particles come in contact with the inner mold wall, which is being heated. At some temperature above the polymer's glass transition temperature (T_g), but not yet exceeding its melting temperature (T_m),²⁵ these particles will begin to soften and deform, allowing them to adhere to the surface of the mold.²⁶ Then, as heat is transferred through the adhered particles, other particles will begin to stick to these particles, and other particles will stick to these. This process continues until all the particles from the bulk have adhered and coated the inner mold wall.

Soon after contact, the particles will become fused or "sintered" together, meaning that the individual polymer molecules in the two particles begin to intermingle by means of molecular translations, rotations, and vibrations. Fusion of two particles occurs as molecules intermingle, thereby dispersing the particle's surface energy at these points of contact.^{19,25,27} At this stage, the particles will have formed a web of interconnected particles, fused together at the points of contact. The overall density of the web is almost

unchanged from the density of the bulk material because the volume of air between the particles has not changed significantly.²⁷

The next step in the process is termed densification and involves the removal of air from the polymer web by simple percolation. The reduction of surface energy is the chief driving force for this phenomenon.²⁵ A state of lower total energy can be achieved as the surface to volume ratio is minimized. The effect of capillary action comes into play as polymer is drawn into the void spaces and air is displaced.²⁷ Capillary action is largely driven by surface tension, but viscosity, adhesive and cohesive forces are also important. It is strongest when the viscosity of the polymer is low²⁸ and the size of the void is small.¹⁹

However, not all of the air can escape via percolation. Some of the air becomes trapped in the molten polymer, forming bubbles in the bulk material and pinholes at the polymer/mold interface. For this air to be released into the mold cavity, the molecules must either migrate toward the polymer/cavity interface or be dissolved into the polymer. When migration and dissolution do not occur fast enough to expel all of the air from the part wall, these bubbles and pinholes can be seen in the finished part. More recent experimentation shows that, given sufficient time, the densification of the bulk polymer becomes complete, meaning that all voids are removed from the part wall.^{29,30} However, longer cycle times means decreased throughput and increased part oxidation of the polymer. The latter is critical in the case of ABS resins, as will be discussed below.

Much work has been done to decrease the occurrence of voids by changing the internal mold pressure. While the use of negative pressures (predicted to increase the rates of percolation and migration) has shown some merit in decreasing void content,³¹⁻³²

the use of positive pressures (demonstrated to increase the rate of dissolution) has become more popular.³²⁻³⁴ The chief difference is that negative pressures will decrease the number of voids while positive pressures will decrease their size.

The presence of water has also been recognized as a possible cause of voids.³⁵⁻³⁶ As ABS is considered a hygroscopic material, suppliers recommend drying the resins prior to use. This is typically done by exposing the resin to a moderate temperature, usually around 180°F to 200°F for ABS, thereby increasing the vapor pressure of water. Forced air and desiccant ovens are the commonly used to assist in this process as they quicken the drying by maintaining a high water concentration difference. While for polyethylene attempts to remove moisture prior to the heating cycle have shown no effect on the void content,³² such procedures may prove to be effective in decreasing the void content in rotationally molded ABS parts.

Particle size distribution also plays a role in the volume of air initially present. If morphology and distribution were to remain constant while average particle size increased, the size of the particle would have no effect upon the volume of air initially present, as shown in Figure 5. However, the surface to volume ratio of the bulk material will increase as particle size decreases, thereby increasing the available free surface energy (and therefore the rate of percolation). Unfortunately, increasing the surface area will increase degradation (discussed below), suggesting that there may be an optimal particle size for a given set of properties.

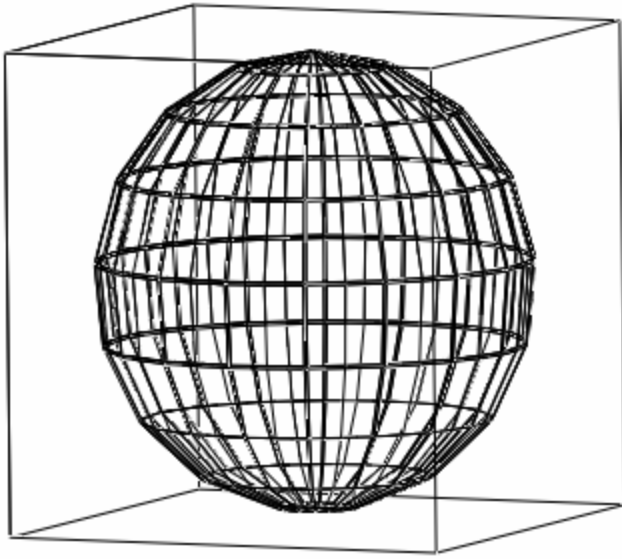


Figure 5 – A sphere inside a cube. The diameter of the sphere matches the length, width, and depth of the cube. Regardless of the size of the sphere, the ratio of spherical volume to cubic volume remains the same, in the case of a perfect sphere and a perfect cube this ratio is 0.524. In other words, the percentage of free space remains fixed at 52.4%. Similarly, 1, 2, 10, or 1,000,000 of these systems taken together would likewise have 52.4% free space. Therefore, when only the average size of the particles is changing, the number of the particles required to fill a given volume will change, but the amount of free space between the particles will be fixed.

Thus, in order to reduce the void content, the fusion/sintering process of the polymer must undergo a more complete densification in the molten state. The chief mechanisms for densification are percolation, migration, and dissolution. At least five strategies could assist in the reduction of void content of rotomolded ABS parts: lengthening the cycle time, decreasing the melt viscosity, pressurizing the mold, drying of the resin, and altering the particle size.

Bridging

“Bridging” is a manufacturing phenomenon where there is a non-uniform distribution of resin in a rotomolded part. During processing, material begins to build-up in the corners and edges of the mold. Rather than forming a flat, smooth inner wall, the inner wall is wavy and is often rough. In the inner corners and edges voids are seen, as are small resin bridges, connecting one wall to another. Typically, the bridges run from

one wall to an adjacent wall, but in severe cases, as seen in Figure 6, the bridges can connect even non-adjacent walls.

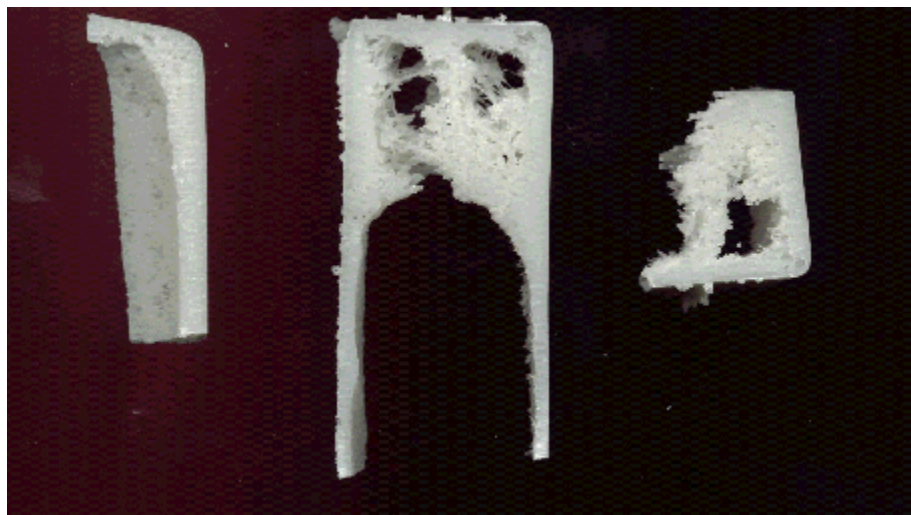


Figure 6 -Bridging in rotomolded ABS samples, fabricated by David Bedell at Brigham Young University.¹⁸

Several of the causes of bridging come from factors not directly related to the resin such as: incorrect mold design, inappropriate mold rotation, uneven mold heating, and improper particle size distribution.³⁷ However, bridging may also be caused by the resin, especially when the resin cannot be ground into a powder that will flow like a liquid.¹ This may be due to at least two causes. First, some physical properties of resins may cause the ground particles to have non-typical sizes and/or shapes which are resistant to flow.³⁸ For example, resins with high stiffness will tend to shatter during grinding giving the particles jagged surfaces. This morphology, in turn, inhibits the flow of the powder. In some cases, this problem may be overcome by remediation strategies such as cryogenic grinding and particle polishing.

A second cause would be related to the bulk behavior of the particles. Just as a soccer ball bounces differently than a basketball, the fluidity of one powdered resin will likely be different than the fluidity on another powdered resin. The physical properties

which may impede fluidity of the powder include density, hardness, elasticity, adhesion, hygroscopicity³⁸, and electrostatic discharge.³⁹ Therefore, to avoid bridging, rotomolding materials must be capable of being adequately ground and the resultant powder must flow similar to a liquid.

Embrittlement and Yellowing

Embrittlement and yellowing can both be attributed polymeric degradation. While only a minor issue for most resins used in rotational molding, in ABS resins degradation has become quite important. Heightened exposure to heat, light, and oxygen, can significantly shorten the service lifetime of ABS parts. In most cases, the addition of stabilizers has proven satisfactory in lengthening service lifetime. However, rotational molding cycle times may be as much as two to three orders of magnitude longer than many of the other processes used to form parts from ABS resins.

On a chemical level, ABS resins have two bonds vulnerable to attack: the unsaturated bond in the acrylonitrile side group and the unsaturated bond in the backbone of the butadiene units. In the first case, the degradation is thermo-oxidative and results in the formation of imide chromophores. These chromophores are believed to be responsible for the yellowing of ABS over time.⁷ In the case of butadiene, the degradation can be thermal,⁴⁰⁻⁴² thermo-oxidative,⁴²⁻⁴⁵ or photo-oxidative.⁷⁻⁸ The main mechanisms of degradation are chain scission and crosslinking, both of which lead to embrittlement.⁸

While the presence of butadiene makes the processing of ABS more challenging, the presence of this elastomeric moiety is the source of increased impact resistance and

flexibility in ABS resins and is often added to other polymers (rubber toughening) to increase these properties.¹⁰ Without butadiene, the polymer would be styrene-acrylonitrile copolymer, or SAN, an important engineering thermoplastic which had been considered as a medium performance material, but which does not have the impact strength required by the rotational molding industry.¹⁷

It is not known what concentration of butadiene in ABS would be optimal for rotomolding. Butadiene content can be either concentrated or diluted by blending the ABS resin with another resin with a respectively higher or lower butadiene concentration. To ensure miscibility, the two resins should be fairly similar. Dilution could be performed quite easily with SAN. “High rubber” ABS concentrates are also readily available and would work to increase the butadiene concentration. Either of these materials could be added without much concern with compatibility issues, providing a means to determine the optimal butadiene concentration of an ABS resin.

In order to limit the effects of degradation, it becomes necessary to minimize the effects of oxygen and excessive heat. Two methods are common in the rotomolding industry to limit oxidation. First, anti-oxidants may be blended into the resin to inhibit the oxidation reaction(s). In practice, rotomolding resins typically contain significantly higher loadings of antioxidant than resins used for other manufacturing processes. Second, inert gases (usually nitrogen) may be used to displace air inside the mold. Typically, the mold is purged only once, just prior to oven entry. However, a flow of nitrogen can be maintained throughout the cycle with entry through the turret arms and exit through a ventilation hole in the mold wall.

To control any excessive amount of heat, rotomolders will typically adjust the temperature of the oven during the molding cycle. Most often, the oven will be programmed to gradually increase, and then gradually decrease the temperature of the oven during the heating cycle. This practice of temperature ramping has proven to be a successful means of quality control for rotomolding resins typically used commercially, providing the more heat during the sintering/densification process and the less heat during oven entry and oven exit.

CHAPTER 3

OBJECTIVES

The central goal of this research project was to identify and document, to the extent possible, new ABS-like resins which could expand markets for rotational molded products. Utilizing past research, resins and additives to test were identified, compounding and pulverizing were coordinated, and molding of candidate resins took place at both laboratory and industrial facilities.

Guidelines from the Association of Rotational Molders suggested that the improvement of impact strength was of primary concern. Strategies aimed at decreasing the presence of bridging, voids, and degradation were expected to improve impact strength, as suggested in the previous chapter. This research was divided into two phases: additive evaluation and processing optimization.

The goals of the additive evaluation phase of this research were to evaluate the performance of different additives in two ABS resins: MAGNUM 342 EZ and GE CYCOLAC 6500 BDT. The following additives strategies were to be tested:

1. Increase protection from oxygen.
2. Decrease butadiene concentration.
3. Increase butadiene concentration.
4. Promote flow.

Upon completion of the additive evaluation phase, the processing optimization phase was initiated. This phase had the following goals:

1. Determine the effects of varying heating and cooling cycle parameters.
2. Determine the effects of varying particle size distribution.
3. Determine the effects of inert gas use.
4. Determine the effects of resin drying prior to molding.
5. Determine the effects of preheating the mold.

Upon determination of the optimal resin formulation and processing conditions, it was necessary to:

1. Perform mechanical testing. Specifically, this was to include a determination of: surface hardness, tensile strength at yield, flexural modulus, impact strength, and thermal stability.
2. Perform molding trials of blends at industrial sites.

CHAPTER 4

EXPERIMENTAL APPROACH

The work to be performed was divided into two phases. The first phase, the additive evaluation phase, was intended to be a screening of the impact strength improvement strategies which related to changes in the formulation of the resin. The second phase, the processing optimization phase, was intended to further investigate the best performing candidate formulation(s) from the first phase by screening other strategies which did not involve re-formulation of the resin. This was done to minimize the compounding and grinding work which would require the use of industrial facilities.

Upon completion of these two phases, the best resin formulation was processed under the best processing conditions. These parts were tested for an understanding of the physical properties and also sent to production-scale rotomolding facilities to validate the commercial use of this material.

Part I - Additive Evaluation Phase

Formulations

The objective of the additive evaluation phase was to examine the performance of eight additives in two ABS resins. Based upon these findings, it would be possible to formulate the best candidate materials to be promoted to the processing optimization

phase. The focus of this phase was to understand the effect of strategies aimed at the improvement of impact strength.

Several strategies had been determined by members of the ARM Special Materials Committee to have a potential benefit to the properties of rotomolded ABS parts. They are presented below in four categories along with the additive(s) selected to either prove or disprove each strategy.

1. Increase protection from oxygen
 - IRGANOX^{®*} B-900 (antioxidant, Ciba Specialty Chemicals)
2. Decrease butadiene concentration
 - LUSTRAN^{®**} 31-1000 (SAN, Bayer AG)
 - SAN 330 (SAN with flow modifiers, Network Polymers)
3. Increase butadiene concentration
 - BLENDEX^{®***} 200 (high butadiene ABS, GE Plastics)
4. Promote of flow
 - Mineral oil
 - XP-2280 (benzoate ester, Velsicol Chemical Company)
 - PREVAIL^{®****} 3050 (thermoplastic urethane, The Dow Chemical Company)
 - PREVAIL 3150 (thermoplastic urethane, The Dow Chemical Company)
 - SAN 330 (SAN with flow modifiers, Network Polymers)

* IRGANOX is a Registered Trademark of Ciba Specialty Chemicals.

** LUSTRAN is a Registered Trademark of Bayer AG.

*** BLENDEX is a Registered Trademark of General Electric Plastics.

**** PREVAIL is a Registered Trademark of The Dow Chemical Company.

To evaluate the performance of these eight additives (note that SAN 330 appears twice) in both MAGNUM 342 EZ and CYCOLAC BDT 6500, 42 blend formulations were established (See Table 2). Initially, a generous amount of CYCOLAC 6500 BDT was available, but there was only a limited amount of MAGNUM 342 EZ. Therefore, all desired additives types and additive levels were formulated using CYCOLAC 6500 BDT, yielding 29 unique formulations. Of these unique formulations, 9 were selected to be repeated using MAGNUM 342 EZ. As it would be possible to include the PREVAIL materials in their pure forms, 2 more formulations were included. This totals 40 blend formulations which follow the protocol described below. The origin of Formulations 41 and 42 will be discussed in the next chapter.

Table 2 - Blend formulations for the additive evaluation phase. CYCOLAC BDT 6500, MAGNUM 342 EZ, and LUSTRAN 31-1000 are referred to as “CYCOLAC”, “MAGNUM”, and “LUSTRAN,” respectively. A standard or double antioxidant dosing is shown as either 1x or 2x in the AO column.

#	Base Resin	Additive (wt%)	AO
1	CYCOLAC		
2	CYCOLAC		1x
3	CYCOLAC		2x
4	CYCOLAC	LUSTRAN (25%)	
5	CYCOLAC	LUSTRAN (25%)	1x
6	CYCOLAC	LUSTRAN (25%)	2x
7	CYCOLAC	LUSTRAN (10%)	
8	CYCOLAC	LUSTRAN (10%)	1x
9	CYCOLAC	LUSTRAN (10%)	2x
10	CYCOLAC	XP-2280 (10%)	
11	CYCOLAC	XP-2280 (20%)	
12	CYCOLAC	BLENDX 200 (10%)	
13	CYCOLAC	BLENDX 200 (40%)	
14	CYCOLAC	Mineral Oil (1%)	
15	CYCOLAC	Mineral Oil (2%)	
16	CYCOLAC	Mineral Oil (3%)	
17	MAGNUM		
18	MAGNUM		2x
19	MAGNUM	LUSTRAN (25%)	
20	MAGNUM	LUSTRAN (25%)	2x
21	MAGNUM	XP-2280 (15%)	
22	PREVAIL 3050		
23	CYCOLAC	PREVAIL 3050 (50%)	
24	CYCOLAC	PREVAIL 3050 (10%)	
25	PREVAIL 3150		
26	CYCOLAC	PREVAIL 3150 (50%)	
27	CYCOLAC	PREVAIL 3150 (10%)	
28	CYCOLAC	XP-2280 (25%)	
29	CYCOLAC	XP-2280 (35%)	
30	MAGNUM	PREVAIL 3050 (10%)	
31	MAGNUM	PREVAIL 3150 (10%)	
32	CYCOLAC	XP-2280 (15%)	
33	CYCOLAC	SAN 330 (25%)	
34	CYCOLAC	SAN 330 (25%)	1x
35	CYCOLAC	SAN 330 (25%)	2x
36	CYCOLAC	SAN 330 (10%)	
37	CYCOLAC	SAN 330 (10%)	1x
38	CYCOLAC	SAN 330 (10%)	2x
39	MAGNUM	SAN 330 (25%)	
40	MAGNUM	SAN 330 (25%)	2x
41	MAGNUM	PREVAIL 3150 (67%)	
42	MAGNUM	PREVAIL 3150 (33%)	

To mix the materials, each of these blend formulations were first dry-blended and then compounded (courtesy of Chroma Color Corporation). Each blend was then ground to powder (courtesy of Ingenia Polymers). The particle size distribution of these powders was such that no particle was larger than 500 microns (35-mesh).

Rotational molding of these powders was performed at Brigham Young University. First, it was necessary to determine a time-temperature program which would be suitable for all formulations. To do this, CYCOLAC 6500 BDT and MAGNUM 342 EZ resins available from the previous ARM research project were used.¹⁸ (These materials are deemed to be equivalent to formulations 1 and 17, respectively). Through trial and error, it was determined that an oven heating cycle at 400°F for 40 minutes, followed by a open air cooling cycle for 20 minutes would produce a commercial quality part.

Ideally, three parts would have been made from each blend formulation, each part having an initial charge weight of two pounds. However difficulties on compounding and grinding limited the amount of material which was available. Formulations 28 and 29 proved to have insufficient melt strength to be compounded. For the remaining forty formulations, difficulty in grinding resulted in most formulations having a very limited amount of material. For four formulations (10, 20, 22, and 25), there was an insufficient amount of material to form any parts. For only six formulations (1, 11, 31, 32, 41, and 42) was there enough material to form three parts. For eight more formulations (4, 5, 6, 9, 12, 16, 26, and 30), there was enough resin to form two parts. For the remaining twenty-two formulations, there was only enough material to make one part.

Therefore, a total of fifty-six parts were molded and tested in conjunction with the screening portion of additive evaluation phase. These parts were made on the M20 ClamShell™* (FSP/Rotoflow™** Industries) rotational molding machine located in 115 Snell Building. (See Figure 7). Mold ventilation was achieved by a PTFE vent tube (¼ inch inner diameter) loosely packed with steel wool. The cast aluminum “Nevada” mold which was used (manufactured by Viking Pattern and Mold, shown in Figure 8) had been sandblasted, polished and treated with mold release just prior to the screening study. Further treatments of mold release were not applied for the remainder of the additive evaluation phase, nor were they necessary.

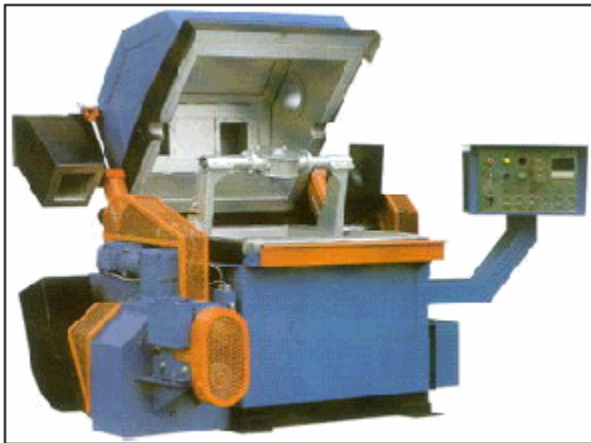


Figure 7 - The FSP/Rotoflow M20 ClamShell. Image courtesy of Ferry Industries, Inc.

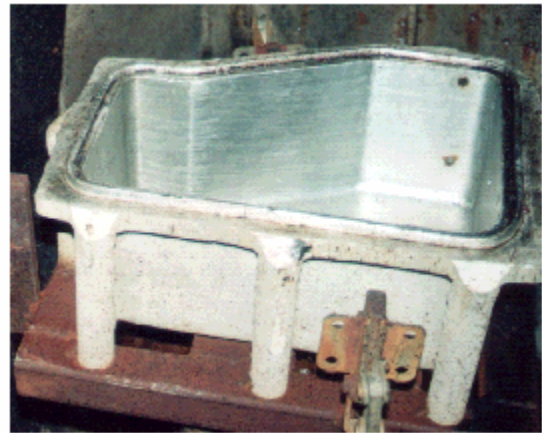


Figure 8 – “Nevada” Mold. Manufactured by Viking Pattern and Mold

Parts were difficult to remove because the mold had not been designed for use with ABS. During the cooling phase of the rotomolding process, polyethylene parts will tend to shrink as their temperatures are decreased to room temperature. Part shrinkage was not observed with any of the ABS parts formed during any of the three phases of this

* ClamShell is a Registered Trademark of Ferry Industries, Inc

** FSP/Rotoflow is a Registered Trademark of Ferry Industries, Inc.

project. A small scissor jack had to be used to open the “Nevada” mold nearly every time a well-formed part was made. Small holes then needed to be punched into the sides of these parts so that they could be pried out of the mold. Lack of shrinkage should be taken into account as new molds are designed for rotomolded ABS parts and as existing polyethylene molds are be considered for manufacture of ABS parts.

Screening Impact Testing

Rotomolders are most concerned with the bridging, voids, and degradation of ABS parts. Indirect measurement of these three phenomena can be done through impact strength. As a bridged part will have very non-uniform wall thickness, the range of values for impact strength should be more broad than a comparable non-bridged part. As voids give no structural support to the polymer, a part with voids should have less impact strength than a similar part without voids (same material, same wall thickness).⁴⁶ Likewise, a part with degradation should have a decreased ability to dissipate energy and should therefore manifest a lower value for impact strength than a part without degradation.

The Instrumented Dart Impact test (ASTM D 3763-95a)⁴⁷ was selected to measure impact strength for screening because of its high precision and sensitivity relative to other available tests⁴⁸ Unfortunately, impact strength values are highly dependant upon the test used, therefore values from this test cannot be directly compared to values obtained from other tests. As the rotomolders have the most experience using the ARM Low Temperature Impact Test (discussed below) additional impact testing, following the ARM method, was necessary to make comparisons to historical data.

The Dynatup XJ-2000, located in 150 CTB, was used to perform all impact testing related to screening. In this test, disk shaped test specimens (3.5 inch diameter) are cut from a flat sheet. One specimen is secured in a clamp while a falling weight, of known mass, is dropped from a known height. Attached to weight is a plunger, consisting of a 12.7 ± 0.025 mm diameter cylinder with a hemispherical end of the same diameter. An accelerometer is used to measure acceleration as a function of time. As the plunger penetrates the specimen (the test is only valid when the specimen fails) an optical sensor (located at a known distance from the specimen) records velocity of the falling assembly just prior to impact.

Total energy can be calculated in the following way. Acceleration of the tup as a function of time is multiplied by the mass of the falling weight, giving force over time. Displacement as a function of time can be determined by integrating the acceleration curve twice with respect to time. The location of the sensor and the velocity of the tup at that location serve as the boundary conditions needed to evaluate the two constants of integration. It is, therefore, possible to calculate force as a function of displacement. Integration of this curve over the test interval gives total energy absorbed by the specimen during the break. This calculation was performed quickly by a microprocessor after each drop.

Unfortunately, there is no testing protocol among the ASTM or ISO standards designed to account for variation in wall thickness. This is mostly due to the great variation of impact strength with respect to wall thickness. All standards require not only that the mean thickness of each specimen be within a given tolerance, they also prescribe a tolerance for the variation in thickness within each specimen. As the variation in wall

thickness was anticipated to be far outside the tolerance ranges, unique departures from the Instrumented Dart Impact test procedure were implemented.

One such departure was to allow for all specimens to be tested regardless of thickness. For the additive evaluation phase, eight specimens were cut from a single part. For the processing optimization phase, due to the use of a larger mold, ten specimens were to be cut from a single part. The specimens were loaded into the testing apparatus unclamped. The falling weight (30.26 lbs.) was dropped from a distance 3.0 feet above the specimen. The total energy absorbed was recorded and the mean and standard deviation were calculated.

In order to reduce sources of extraneous variability in the measurement, three additional controls were set in place. First, the same mold was used to form all parts within the same phase. Second, the charge weight of each part was the same, 2.25 pounds. Third, the locations of the eight or ten specimens relative to the mold were always in the same place. Care was taken to select locations which were free from parting lines, vent holes, and edge/corner effects.

Both room temperature and reduced temperature impact testing were of interest to the Association of Rotational Molders. The reduced temperature data was deemed to be of interest, but not the parameter of optimization as the end-use temperature is more likely to be ambient than subambient. Therefore, reduced temperature impact testing was done during both the additive evaluation phase and the final properties testing.

For reduced temperature testing, four specimens from each part placed in a cooling chamber, set at -40°C , for a period of 16 hours. During reduced temperature testing, each part's four specimens were removed from the freezer in a group and

immediately tested one at a time. The testing for each reduced temperature group was performed within a period of 25 seconds.

For room temperature testing related to the additive evaluation phase, four specimens from each part were tested without thermal conditioning. For room temperature testing during the processing optimization phase, all ten specimens were tested without thermal conditioning.

Selection of Best Performing Formulations

The factors of impact strength, bridging, cosmetics, and blend cost were factored together to select one or more candidate blend formulations which were then tested in the processing optimization phase. As the driving factor under consideration was impact strength, the formulations were ranked according to their impact performance. As shown previously (See Table 1) previous research showed an impact strength of 2 ft-lbs, but the ARM impact strength target was 20 ft-lbs, as measured by the ARM Low Temperature Impact Test. To meet the target, a ten-fold increase in impact strength will be necessary. Those formulations which were not able to deliver this magnitude of change were disqualified. Likewise, significantly increased bridging or unsatisfactory cosmetic properties resulted in disqualification unless the defect could be remedied by some other process modification.

At least one blend formulation with a relatively low blend cost was intended to be included in the processing optimization stage. Six blends formulations were identified as high cost due to the high content PREVAIL resins (PREVAIL costs approx \$4.00 per lb.): 22, 23, 25, 26, 41, and 42. Other blends not included in the original list of 42

formulation, but which may be suggested as candidate materials (i.e. MAGNUM 342 EZ formulations with high loadings of PREVAIL), were also considered to be high cost formulations. This action was taken to ensure that a low cost alternative be explored in the event that high cost alternatives dominated the selection process.

It was anticipated that there would be obvious choices among the different blends. In the event that the selection of candidate blend formulations is not obvious, a Kepner-Tregoe (K-T) Decision Analysis matrix⁴⁹ would have been constructed.

Part II - Processing Optimization Phase

Although many blends showed improvement in cosmetic properties and impact strength, Formulation 21 proved to be significantly superior to all the other formulations (discussed in Chapter 5). Therefore, the primary objective of this phase was to determine those processing parameters best suited for increasing the impact strength of the Formulation 21. Upon completion of this phase, one set of processing parameters was designated as the optimum conditions for Formulation 21. The final properties of the optimized part were then evaluated, as described below.

Several other secondary objectives were also included in this phase. One of these was to quantify the difference of each of the processing changes. This would help rotomolders adapt the optimum set of conditions to their current practices. For example, the need to dry a resin can be a considerable handling cost, requiring either that the plastic be shipped in hermetically sealed containers or that the shop dry the resin prior to use (typically requiring the purchase of drying equipment). If it were found that drying the resin significantly increased the impact strength of the final part, a rotomolding shop

which desired to use ABS, but was unfamiliar with drying resins, would need to consider how they will go about adding this step into their process. However, if drying the resin was deemed to have either an insignificant effect or a detrimental effect on the impact strength, that shop would not need to change their drying procedure. A similar case could be made for each processing parameter. In order to facilitate adaptation, decrease in impact strength would be quantified for all changes from the optimized processing conditions.

To limit the number of parts which needed to be molded, a statistical experiment was designed. Before the optimum conditions could be determined, it was first necessary to understand the effect of the following processing changes on the impact strength of the rotomolded parts: heating and cooling cycle parameters, particle size distribution, use of inert gas, pre-drying of resin, and preheating of the mold. As interactions between factors are anticipated, a designed experiment was initiated to completely examine the candidate material. Pairing of two factors facilitated the design and analysis of the experiments, resulting in a total of four factors. These four factors and the statistical design are discussed below.

Atmosphere

In order to understand the effect of oxygen on the system, changes in the atmosphere of the mold were necessary. The two levels of the atmosphere factor were: ambient and nitrogen. For both gases, ventilation of the mold was achieved by copper tubing run from the mold, through the rotating arms, to the outside of the oven.

When nitrogen was to be used, the tubing was connected to a nitrogen cylinder. When transitioning from air to nitrogen, nitrogen was allowed to flow into an open and uncharged mold for one minute. Upon charging the mold for a nitrogen part, nitrogen was allowed to flow (at 15 SCFM) for one minute in order to displace the air inside the mold cavity. Upon closure of the mold, the nitrogen inside the mold and gas line was sealed from the atmosphere, preventing free ventilation of the system. However, as the volume of the gas line was significant (roughly equivalent to the volume of the mold) the increase in internal mold pressure during heating was anticipated to be 2-3 psi. There were no problems with part warpage or blow holes on the parting line during these experiments.

When air was to be used, the copper tubing was left unconnected. This allowed the mold to fully vent the atmosphere. In transitioning from nitrogen to air, an air hose was used to blow nitrogen out of the line. No additional special precautions were taken in the charging or ventilation of parts formed in an ambient environment.

Drying

A pairing of parameters was made by coupling pre-drying of resin and preheating of the mold together. The purpose of preheating the mold was to increase the temperature of the resin more quickly. This effect could be simulated by removing the resin from an oven immediately before charging the mold. Therefore, the levels of the drying factor became: no drying, dry/store, and dry/use. Dry/store refers to drying (under the same conditions) and then storing the resin in a watertight container for at six hours, allowing the resin to cool. Dry/use refers to drying the resin in a convection oven

(for 2 hours at 190°F) and then transferring it immediately to the mold and commencing manufacture.

Particle Size Distribution

It was necessary to determine what the optimal particle size distribution would be for ABS. In most cases, 35-mesh (see Table 3) is used for polyethylene. However, the optimal mesh size for ABS might not be 35-mesh. The following four levels were included in this factor: 1) 20-mesh and finer, 2) 40-mesh and finer, 3) 20-mesh to 40-mesh, and 4) 40-mesh to 60-mesh. All of the resin was first ground at 20-mesh and then screened to achieve the desired mesh range. Screening the resin produced distributions of non-typical shapes (See Figure 9).

Table 3- U.S. mesh to micron conversion chart

U. S. Mesh	20	35	40	60	80	100	140	200
Microns	841	500	400	250	177	149	105	75

Oven Temperature

Of all the effects included within the heating and cooling cycle parameters, oven temperature is of most concern. Unfortunately, the oven of the M-20 ClamShell molding machine is not large enough to monitor the internal temperature using equipment made available. Therefore, once a temperature was selected, finding the optimal heating time and cooling time was a matter of trial and error.

Due to a great dependence upon oven architecture, tooling, and other factors, oven temperatures are highly variable across the industry. The normal range of temperatures is considered to be between 400°F and 850°F.⁵⁰ While using the same resin, some ovens may approach 700°F while others may not exceed 450°F. In such an

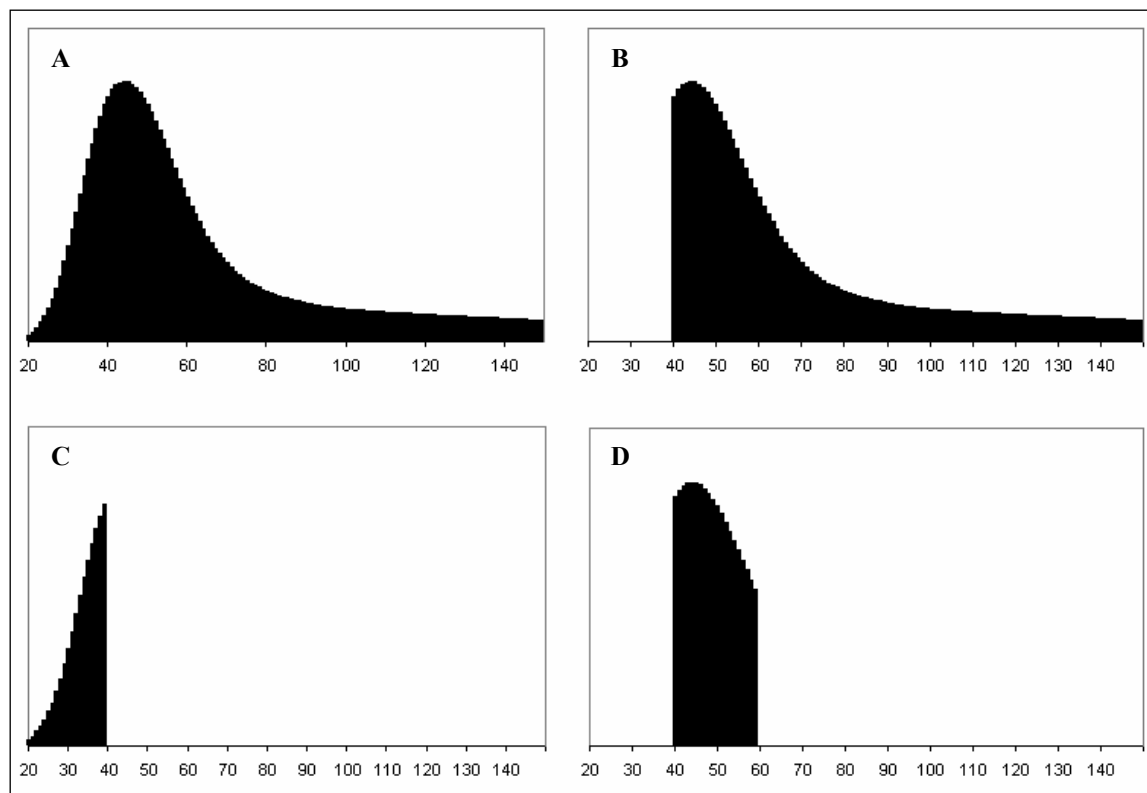


Figure 9 – Particle size distributions. All units in U.S. mesh. A. 20-mesh and finer. B. 40-mesh and finer, C. 20-mesh to 40-mesh, and D. 40-mesh to 60-mesh. The distributions shown in Panes B, C, and D are cut from the distribution in Pane A. These fictional distributions are drawn for illustrative purposes and do not represent measurements.

environment, pinpointing an optimal oven temperature becomes insignificant. A more meaningful evaluation of temperature would be 1) to evaluate the difference in impact strength of the high and low ends of the temperature range for commercially viable parts, and 2) to evaluate the effect of temperature on the other factors. In terms of experimental design, these criteria could be met with only two levels: one of higher temperature and one of lower temperature.

After some trial-and-error molding runs with Formulation 21, it was determined that a commercial quality part could not be manufactured at temperatures lower than 350 °F, as the powder would not sinter, even after long cycle times. Nor could the temperatures above 500 °F be used, as the exterior of the part would be severely yellowed

and the interior of the part would be poorly sintered. Because the minimum and maximum temperature were likely to shift as different processing conditions were applied, use of these extreme temperatures was likely to be a source of experimental error. Instead, 400 °F and 450 °F were used as the two levels for this factor.

Design of Experiments

Conclusions about the importance of each of the factors were determined by means of a statistical design of experiments (DOE). The design included one four-level factor (particle size distribution), one three-level factor (drying), and two two-level factors (atmosphere and oven temperature). The presence of mixed levels causes some difficulty in designing a fractional factorial experiment. In the design, the three-level factor was treated as a four-level factor. Once the standard order was established, this factor was then “collapsed” into a three-level factor. To do this, the “no drying” level was treated as if it were two levels, thereby occurring in eight of the runs, while the other levels occur only four times. (See Table 4, further details in Appendix C).

Table 4 – Run conditions for processing optimization phase designed experiment

Standard Order	Run Order	Particle Size Distribution	Drying	Atmosphere	Oven Temperature
1	5	20-mesh to 40-mesh	Dry/Use	Ambient	400 °F
2	6	40-mesh to 60-mesh	No Dry	Ambient	450 °F
3	12	40-mesh and finer	No Dry	Nitrogen	450 °F
4	10	20-mesh and finer	Dry/Store	Nitrogen	400 °F
5	13	20-mesh to 40-mesh	No Dry	Nitrogen	400 °F
6	14	40-mesh to 60-mesh	Dry/Use	Nitrogen	450 °F
7	7	40-mesh and finer	Dry/Store	Ambient	450 °F
8	1	20-mesh and finer	No Dry	Ambient	400 °F
9	2	20-mesh to 40-mesh	No Dry	Ambient	450 °F
10	8	40-mesh to 60-mesh	Dry/Store	Ambient	400 °F
11	15	40-mesh and finer	Dry/Use	Nitrogen	400 °F
12	16	20-mesh and finer	No Dry	Nitrogen	450 °F
13	9	20-mesh to 40-mesh	Dry/Store	Nitrogen	450 °F
14	11	40-mesh to 60-mesh	No Dry	Nitrogen	400 °F
15	3	40-mesh and finer	No Dry	Ambient	400 °F
16	4	20-mesh and finer	Dry/Use	Ambient	450 °F

The result was a 1/4 fraction factorial experiment, calling for 16 runs rather than 64. This constitutes a resolution III design, meaning there is no confounding among the main effects, but there is confounding among some of the two-way interactions.⁵¹ Three-way and four-way interactions were also confounded and, therefore, unresolvable. In this design, only seven of the seventeen two-way interactions could be resolved.

Care was taken in selecting which two-way interactions would be chosen. From each factor, one level was tested against at least one level from each of the other three factors. (See Table 5). This represents six two-way interactions. One of the remaining two interactions was used to test a second level of the particle size distribution against temperature; the other was used to test particle size distribution against atmosphere.

Table 5 - Description of interaction terms designed to be tested in the Processing Optimization Phase. PSD refers to particle size distribution. These levels are in contrast to the base case (Atmosphere = Nitrogen, Temperature = 400°F, Drying = No Drying, and PSD = 20-mesh and finer).

	Factor	Level	Notation
Main Effects	PSD	40-mesh and finer	P1
	PSD	20-mesh to 40-mesh	P2
	PSD	40-mesh to 60-mesh	P3
	Drying	Dry/Store	D1
	Drying	Dry/Use	D2
	Atmosphere	Ambient	A
	Temperature	450°F	T
Interactions	PSD × Atmosphere	40-mesh and finer × Ambient	P1*A
	PSD × Temperature	20-mesh to 40-mesh × 450°F	P2*T
	PSD × Drying	20-mesh to 40-mesh × Dry/Use	P2*D2
	PSD × Atmosphere	40-mesh to 60-mesh × Ambient	P3*A
	Drying × Temperature	Dry/Store × 450°F	D1*T
	Drying × Atmosphere	Dry/Use × Ambient	D2*A
	Atmosphere × Temperature	Nitrogen × 450°F	A*T

Part III - Final Properties Testing

Upon completion of the Additive Evaluation Phase and the Processing Optimization Phase, parts were made at the optimal conditions. Test specimens were cut

from the flat-walled section of the parts with a targeted thickness of 0.1875 inches. Then, the following key properties were measured: surface hardness, yield tensile strength, flexural modulus, impact strength, and thermal stability. The descriptive information about the execution of each test is given below.

Surface Hardness

One of the most common methods for measuring surface hardness is durometer Hardness, also known as Shore Hardness (ASTM D 2240-02b).⁵² The durometer measures resistance to needle penetration. Both Type A and Type D hardness were measured courtesy of The Dow Chemical Company. (Date: September, 2002. Location: The Dow Chemical Company, B-3833, Freeport, TX).

Another method for determination of surface hardness is the Rockwell method, procedure A (ASTM D-785-93)⁵³. The Rockwell apparatus measures resistance to ball indentation. The R scale has been suggested by the ARM Special Materials Committee. For the R scale, the ball used has diameter of 0.5 inches. (Date: September, 2002. Location: Brigham Young University, 110 CTB, Provo, UT).

Yield Tensile Strength

Following ASTM D 638-96,⁵⁴ Type 1 specimens were cut from the part walls using a pre-programmed mill. Crosshead speed was 10 in/min. (Date: September, 2002. Location: Brigham Young University, 150 CTB, Provo, UT).

Flexural Modulus

Following ASTM D 790-96a, Test Method I, Procedure A,⁵⁵ specimens were milled to 0.5 inches wide and 4 inches long. Support span was 3 inches, support span-to-

depth ratio was 16 to 1, radius of supports was 0.063 inches, radius of nose was 0.156 inches, and crosshead speed was 0.08 in /min. (Date: September, 2002. Location: Brigham Young University, 150 CTB, Provo, UT).

Impact Strength

Although impact strength had previously been measured following a modified Instrumented Dart Drop Test, for comparative purposes, it was necessary to test impact strength in this stage by means of the ARM Low Temperature Impact Test⁵⁶ in order to make comparisons to historical industry data. This was measured by means of the BYU impact tester, built to comply with the test standard. The test weight was 10 lbs. (Date: September, 2002. Location: Brigham Young University, 150 CTB, Provo, UT).

In addition to the low temperature testing, room testing was also performed, leaving all other conditions the same. The reason for the temperature change is the sharp drop in impact strength observed in ABS resins around 0°C.⁵⁷ This is due to a ductile-brittle transition of the butadiene.⁵⁸ As the ARM Low Temperature Impact Test is run at -40°C, the butadiene is expected to be brittle. However, at room temperature, the butadiene phase expected to be ductile. Running the test at both temperatures allows investigation of the impact properties of the resin in both phases. (Date: September, 2002. Location: Brigham Young University, 150 CTB, Provo, UT).

Thermal Stability

This is determined by the Heat Deflection Temperature, measured in accordance with ASTM D 648-96,⁵⁹ and courtesy of The Dow Chemical Company. (Date: September, 2002. Location: The Dow Chemical Company, B-3833, Freeport, TX).

CHAPTER 5

RESULTS AND DISCUSSION

Part I - Additive Evaluation Phase

The performance of each additive has been grouped with the appropriate strategies below, namely: increase protection from oxygen, decrease butadiene concentration, increase butadiene concentration, and promote of flow. Again, the primary objectives of this phase are to evaluate each of these strategies by measuring impact strength and observing any changes in cosmetic properties. In order meet the ARM target for impact strength, an increase of approximately ten-fold is necessary. It is also necessary to minimize bubbles, pinholes, bridging and yellowing to yield satisfactory cosmetic properties.

Test results presented within these four sections are primarily based upon results gathered from CYCOLAC BDT 6500 formulations. Information from Magnum 342 EZ formulations will be presented where relevant. Raw data are found in Appendix A, and statistical calculations are found in Appendix B.

Increase protection from oxygen

The impact testing results for formulations related to the IRGANOX B-900 evaluation can be found in Table 6. Because the data need to be grouped into

Table 6 – Test data for formulations containing IRGANOX B-900. Tested by the modified Instrumented Dart Impact test. CYCOLAC and LUSTRAN refer to CYCOLAC BDT 6500 and LUSTRAN 31-1000, respectively.

Formulation Family	No Antioxidant			Standard Antioxidant			Double Antioxidant		
	Antioxidant Family Formulation Number	Impact Energy (ft-lbs)	90% Confidence Interval (ft-lbs)	Formulation Number	Impact Energy (ft-lbs)	90% Confidence Interval (ft-lbs)	Formulation Number	Impact Energy (ft-lbs)	90% Confidence Interval (ft-lbs)
CYCOLAC w/o additives	1	18.24	12.77	2	10.78	7.09	3	17.38	4.11
CYCOLAC w/ 10% LUSTRAN	7	47.63	29.79	8	34.98	156.96	9	29.48	37.26
CYCOLAC w/ 25% LUSTRAN	4	28.49	20.15	5	43.67	39.82	6	45.93	18.31
CYCOLAC w/ 10% SAN 330	36	26.11	14.64	37	74.51	69.36	38	16.83	11.00
CYCOLAC w/ 25% SAN 330	33	69.96	43.44	34	49.83	37.25	35	77.15	5.57

formulation families to study the effects of each additive, compounded uncertainty of making multiple comparisons is a concern. As a safeguard, the Tukey-Kramer procedure⁶⁰ was performed. This procedure uses a methodology very similar to the Student’s t-test, but it protects against the compounded uncertainty of making multiple comparisons. Here, the Studentized Range Distribution⁶¹ is used instead of the Student’s t-distribution. By using the Tukey-Kramer procedure, all possible pairings of the data can be considered without compromising the statistical validity of the data due to compounded uncertainty.

All three antioxidant families were considered with the CYCOLAC formulations: “No Antioxidant”, “Standard Antioxidant”, and “Double Antioxidant”. The Tukey-Kramer procedure was used to determine significance of all three possible data pairs (see Table 7). As this was a screening design, any value for probability of difference above

Table 7 – Probabilities of difference calculated by means of the Tukey-Kramer paired comparison for antioxidant loading levels.

Pairings of Formulation Families		Probability
No Antioxidant	Standard Antioxidant	0.1987
No Antioxidant	Double Antioxidant	0.0100
Standard Antioxidant	Double Antioxidant	0.2690

0.8000 was considered a possible difference. Any value above 0.9000 was considered a probable difference. As none of these probabilities were above 0.8000, no statistical difference can be identified among the different levels of antioxidant.

It should be noted that the polymeric materials considered in this research all contain some small loading of antioxidant added by the resin manufacturer. The “standard antioxidant” and “double antioxidant” levels refer to loadings of antioxidant beyond this primary loading. The “standard” loading was recommended by the antioxidant supplier (Ciba Specialty Chemicals) for additional protection of ABS during the rotational molding process. No change in cosmetic properties was observed. The conclusion to be made, based upon the observations above, is that there is no evidence that blending in additional antioxidant to formulations containing CYCOLAC BDT 6500 resin is of any advantage with respect to increasing impact strength.

Decrease Butadiene Concentration

Graphical comparisons of the LUSTRAN 31-1000 and SAN 330 materials can be found in Figures 10 and 11, respectively. As the confidence intervals overlap each other, but do not overlap the means, there may be evidence to suggest some difference between these families.⁶⁰ Again applying the Tukey-Kramer procedure to the LUSTRAN 31-1000 family and then to the SAN 330 family, the probability of statistical difference can be

determined. (See Table 8). These data show that there is no statistical difference between 10% and 25% LUSTRAN 31-1000, but that all other comparisons are statistically significant.

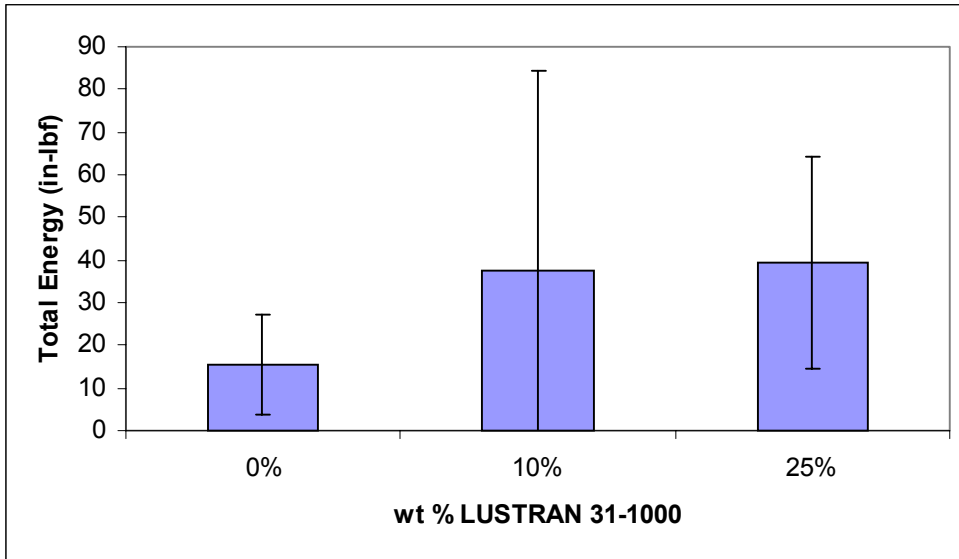


Figure 10 - Impact performance of formulations containing LUSTRAN 31-1000 in CYCOLAC BDT 6500. Tested by the modified Instrumented Dart Impact test. Error bars represent the 90% confidence interval.

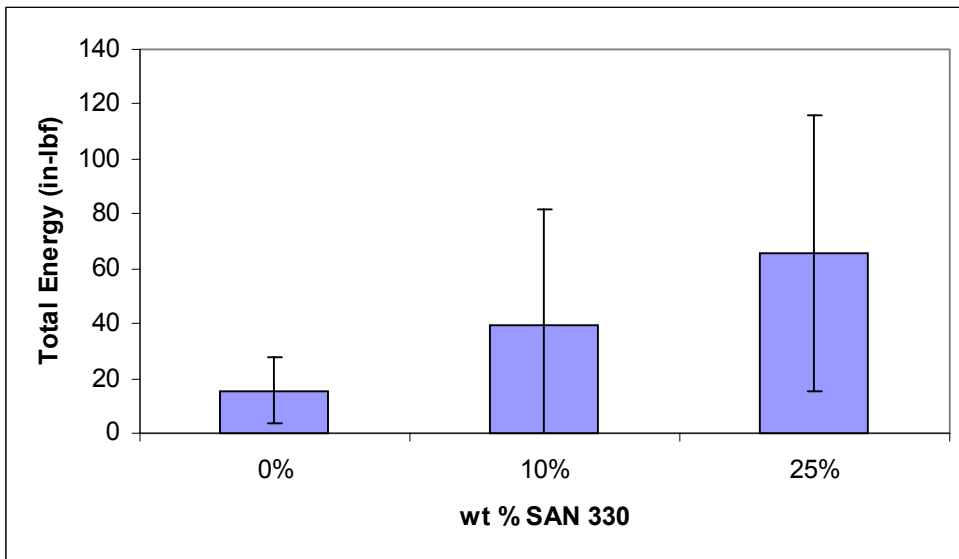


Figure 11 - Impact performance of formulations containing SAN 330 in CYCOLAC BDT 6500. Tested by the modified Instrumented Dart Impact test. Error bars represent the 90% confidence interval.

Table 8 – Probabilities of difference calculated by means of the Tukey-Kramer paired comparison of formulations containing additives which lower butadiene content. CYCOLAC refers to CYCOLAC BDT 6500. LUSTRAN refers to LUSTRAN 31-1000

Pairings of Formulation Families		Probability
LUSTRAN		
CYCOLAC w/o additives	CYCOLAC w/ 10% LUSTRAN	0.9788
CYCOLAC w/o additives	CYCOLAC w/ 25% LUSTRAN	0.9991
CYCOLAC w/ 10% LUSTRAN	CYCOLAC w/ 25% LUSTRAN	0.0303
SAN 330		
CYCOLAC w/o additives	CYCOLAC w/ 10% SAN 330	0.9948
CYCOLAC w/o additives	CYCOLAC w/ 25% SAN 330	0.9998
CYCOLAC w/ 10% SAN 330	CYCOLAC w/ 25% SAN 330	0.8969

Although a formulation proves to be statistically significant, it may not be practically significant. A ten-fold increase in impact strength is required to meet the ARM target. The LUSTRAN 31-1000 formulations, at best, tripled the impact strength of CYCOLAC BDT 6500. The SAN 330 formulations, at best, quadrupled the impact strength of CYCOLAC BDT 6500.

Also, with respect to cosmetic performance, both LUSTRAN 31-1000 and SAN 330 (both colorless) showed poor miscibility with both the CYCOLAC BDT 6500 and MAGNUM 342 EZ resins. Small aggregates of colorless polymer were seen on the surface of the parts and through the part wall. As no such aggregation was apparent in the pre-processed powder form of these formulations, it is assumed that the onset of aggregation occurs during the rotomolding process. As the presence of these aggregates is readily visible to the human eye, they are considered a serious defect to the appearance of the final parts. As such a defect makes these formulations non-viable in a commercial material, they were disqualified from further analysis.

Increase Butadiene Concentration

Impact testing of resins which contained BLENDEx 200 can be seen in Figure 12. As confidence intervals are overlapping means, there is no evidence of differences between the means.⁶⁰ This conclusion is confirmed by the Tukey-Kramer procedure. (See Table 9). As all probabilities are well below 0.8000, no advantage can be attributed to adding BLENDEx 200 into the CYCOLAC BDT 6500 resin.

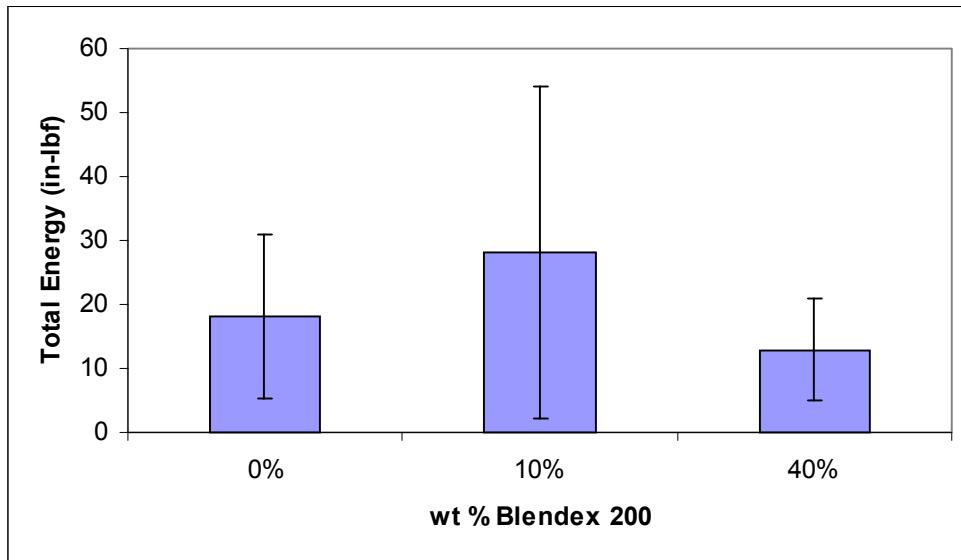


Figure 12 – Impact performance of formulations containing BLENDEx 200 in CYCOLAC BDT 6500. Tested by the modified Instrumented Dart Impact test. Error bars represent the 90% confidence interval.

Table 9 – Probability values from the Tukey-Kramer comparison of formulations containing BLENDEx 200

Formulation Pairs		Probability
Formulation 1 – 0% BLENDEx	Formulation 12 – 10% BLENDEx 200	0.4053
Formulation 1 – 0% BLENDEx	Formulation 13 – 40% BLENDEx 200	0.1902
Formulation 12 – 10% BLENDEx	Formulation 13 – 40% BLENDEx 200	0.5963

Furthermore, the magnitude of increase in impact strength is not likely to be practically significant. The mean impact strength of the best performing BLENDEx 200

blend (Formulation 12) only shows an increase over CYCOLAC BDT 6500 of 34%, far short of the 900% increase (ten times) predicted to be necessary to meet the ARM target.

In addition to an inconclusive effect on impact strength, parts made from formulations containing BLENDEX 200 showed poor cosmetic quality. The formulations were the only formulations to show unacceptable discoloration (yellowness). Also, these parts also contained a higher degree of voids both at the part surface and in the part wall. These observations, combined with no evidence of any effect on impact strength, show a disadvantage to adding BLENDEX 200 to CYCOLAC BDT 6500 formulations.

Promote Flow

Mineral Oil

Graphical comparisons of the mineral oil formulations can be seen in Figure 13.

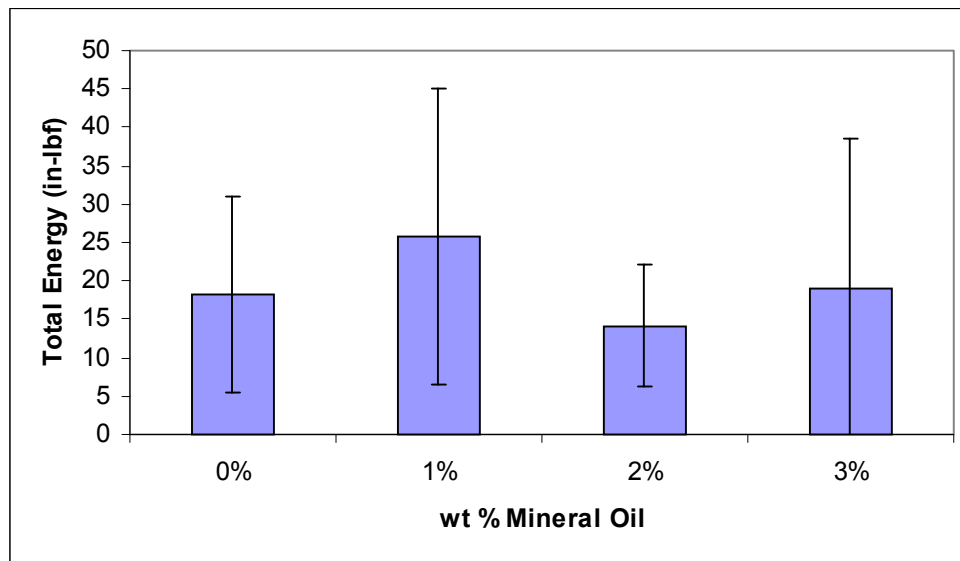


Figure 13 – Impact performance of formulations containing mineral oil in CYCOLAC BDT 6500. Tested by the modified Instrumented Dart Impact test. Error bars represent the 90% confidence interval.

With exception of one case, all of the error bars are overlapping all of the means. (The 2% mineral oil error bars do not overlap the mean of the 1% mineral oil formulation). This signifies that there is little or no difference between these formulations. This can be confirmed by the probabilities calculated by the Tukey-Kramer procedure, (see Table 10) where none of the six possible data pairs shows a probability above 0.8000. No differences in cosmetic properties were observed.

Table 10 – Probabilities of difference as calculated by means of the Tukey-Kramer comparison for formulations containing mineral oil.

Formulation Pairs		Probability
Formulation 1 – 0% Mineral Oil	Formulation 14 – 1% Mineral Oil	0.2483
Formulation 1 – 0% Mineral Oil	Formulation 15 – 2% Mineral Oil	0.0964
Formulation 1 – 0% Mineral Oil	Formulation 16 – 3% Mineral Oil	0.0006
Formulation 14 – 1% Mineral Oil	Formulation 15 – 2% Mineral Oil	0.6033
Formulation 14 – 1% Mineral Oil	Formulation 16 – 3% Mineral Oil	0.1175
Formulation 15 – 2% Mineral Oil	Formulation 16 – 3% Mineral Oil	0.0808

Even if statistical significance could be established, the marginal increase of mean impact strength is not likely to be practically significant. With the best performing mineral oil blend (Formulation 14) the mean impact strength increases by 34%. This is well below the ARM target for impact strength. Therefore, no appreciable advantage to impact strength can be attributed to adding mineral oil.

XP-2280

Figure 14 shows a graphical representation of the formulations containing the XP-2280 additive. As the grinding of Formulation 10 proved to be problematic (cause unknown), the 10% XP-2280 level was not tested. The 15% level appears to give significant increase in the impact performance of the resin. Cosmetically, no voids could be found on the surface of the part, or in cross sections of the part wall. This holds true

for the 20% level as well. However, the 20% level does not appear to have the same effect on the impact performance. Table 11 confirms that the 15% level is distinct from the other two levels.

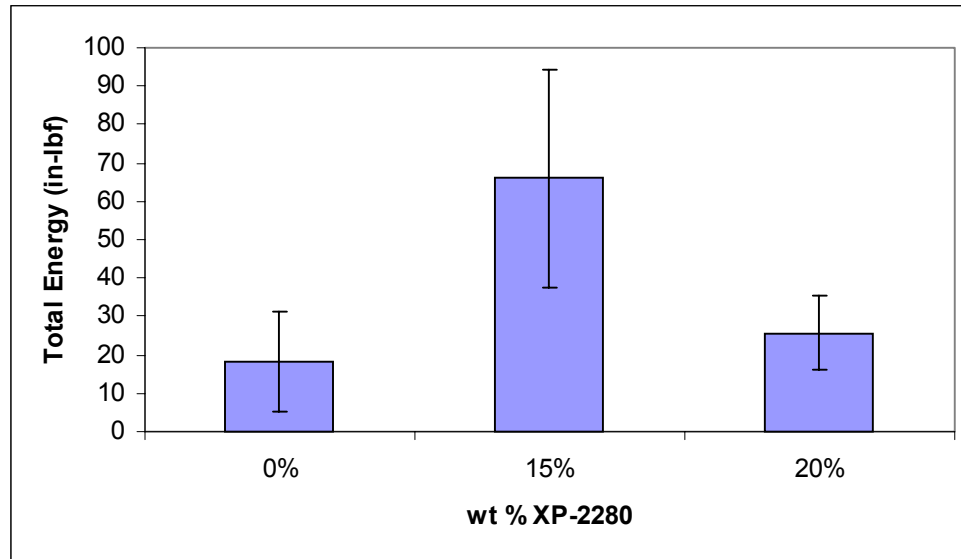


Figure 14 – Impact performance of formulations containing XP-2280 in CYCOLAC BDT 6500. Tested by the modified Instrumented Dart Impact test. Error bars represent the 90% confidence interval.

Table 11 – Probability values from the Tukey-Kramer comparison of formulations containing XP-2280

Formulation Pairs		Probability
Formulation 1 – 0% XP-2280	Formulation 32 – 15% XP-2280	0.9846
Formulation 1 – 0% XP-2280	Formulation 11 – 20% XP-2280	0.5753
Formulation 32 – 15% XP-2280	Formulation 11 – 20% XP-2280	0.9901

There appears to be a balance of properties in play for this additive. At low loadings, XP-2280 is able to promote the flow of the resin. The decreased occurrence of voids is expected to result in higher impact strength. At high XP-2280 loadings it appears that the decreased polymeric content of the material has resulted in a decrease of the impact strength. Therefore, for this system, there exists an optimum level of XP-2280 loading.

PREVAIL 3050 AND PREVAIL 3150

Significant improvements in impact strength can be seen by adding either PREVAIL 3050 or PREVAIL 3150. (See Figures 15 and 16). At only a 10% loading, a significant difference is seen in both materials. At a 50% loading, a significant effect is observed for PREVAIL 3050. (See Table 12).

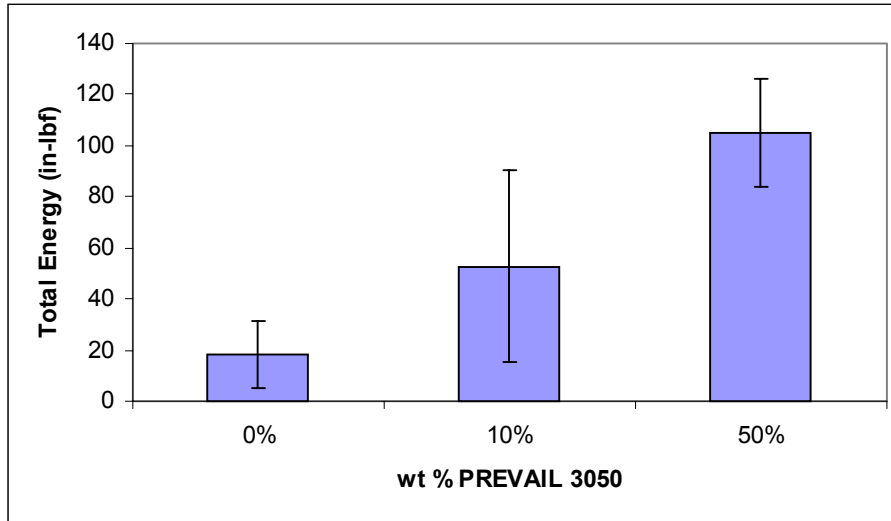


Figure 15 - Impact performance of formulations containing PREVAIL 3050 in CYCOLAC BDT 6500. Tested by the modified Instrumented Dart Impact test. Error bars represent the 90% confidence interval.

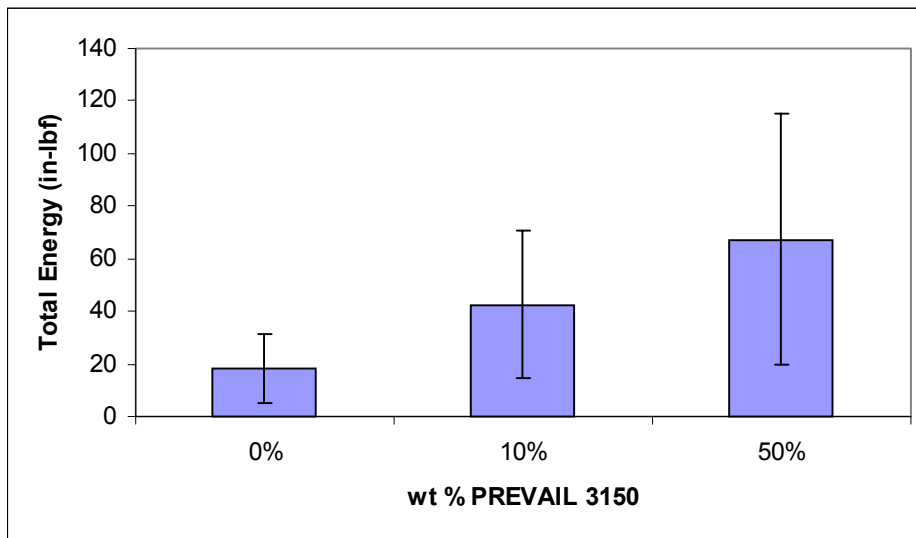


Figure 16 - Impact performance of formulations containing PREVAIL 3150 in CYCOLAC BDT 6500. Tested by the modified Instrumented Dart Impact test. Error bars represent the 90% confidence interval.

Table 12 – Probabilities of difference for formulations containing PREVAIL resins. Calculated by way of the Tukey-Kramer comparison. #1, #23, etc. refers to formulations from Table 2.

Formulation Pairs		Probability
PREVAIL 3050		
#1 – 0% PREVAIL 3050	#24 – 10% PREVAIL 3050	0.9896
#1 – 0% PREVAIL 3050	#23 – 50% PREVAIL 3050	0.9998
#24 – 10% PREVAIL 3050	#23 – 50% PREVAIL 3050	0.9235
PREVAIL 3150		
#1 – 0% PREVAIL 3150	#27 – 10% PREVAIL 3150	0.9396
#1 – 0% PREVAIL 3150	#26 – 50% PREVAIL 3150	0.9866
#27 – 10% PREVAIL 3150	#26 – 50% PREVAIL 3150	0.5436

The cosmetic performance of the PREVAIL formulations were puzzling. An inability to properly sinter the particle together caused extremely high void content (manifest as pinholes and bubbles) in parts made with all formulations containing PREVAIL resins. In spite of this high void content, the PREVAIL formulations had some of the highest values of impact strength. Further research regarding PREVAIL materials will be considered below.

Comparison of Base Resins

Nine of the formulations made during the additive evaluation phase were made with MAGNUM 342 EZ. These nine formulations and their CYCOLAC BDT 6500 equivalents can be paired together and analyzed to determine if there is a difference between the impact performance of the base resins. As one of these formulations (Formulation 20) failed to grind successfully (cause unknown), the remaining eight formulations were compared. (See Figure 17). In all cases, MAGNUM 342 EZ showed either higher impact strength than CYCOLAC BDT 6500 or an inconclusive result due to

high error. From a student's paired t-test, the probability of difference was 0.99999996. With this high probability, it is expected that MAGNUM 342 EZ formulations will result in a higher impact strength than CYCOLAC BDT 6500 formulations 99.999996% of the time. Based on this conclusion, MAGNUM 342 EZ was used as the base resin to be moved to the processing optimization phase.

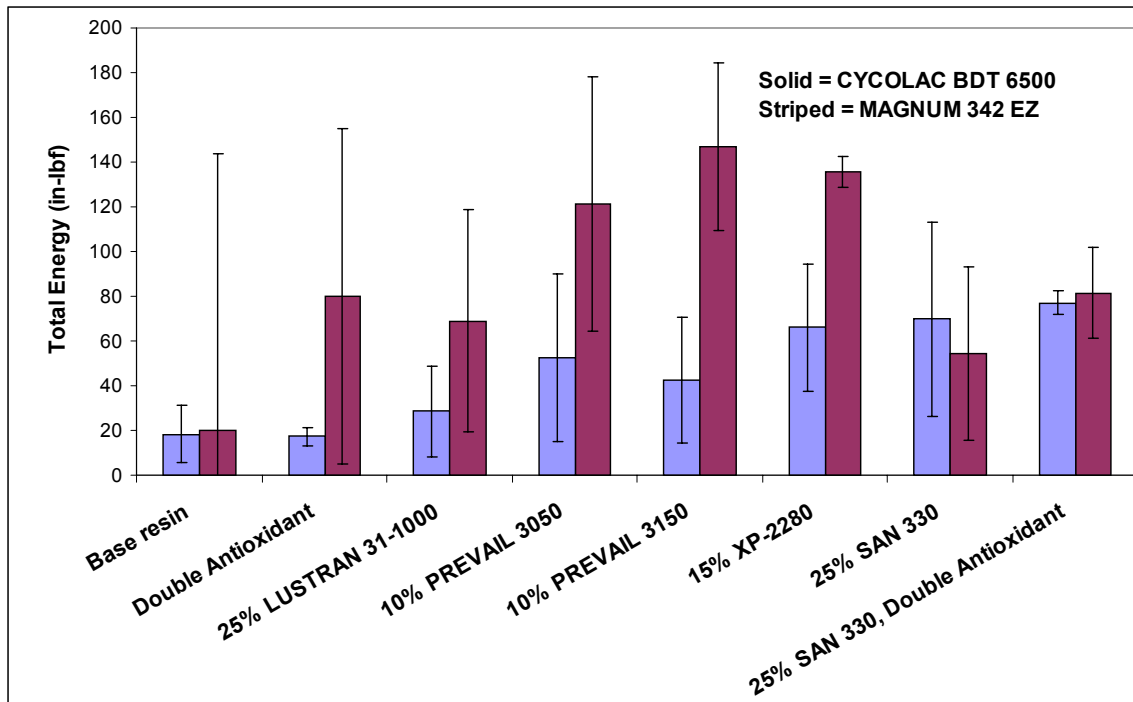


Figure 17 – Base resin comparison of paired formulations containing either CYCOLAC BDT 6500 or MAGNUM 342 EZ. Tested by the modified Instrumented Dart Impact test.

Discussion of Results from Additive Evaluation Phase

As stated previously, the impact strength of the ABS base resins needs to be increased ten-fold to meet the ARM target impact strength. Although several of the strategies proved to give statistically significant improvements in impact strength, only XP-2280, PREVAIL 3050, and PREVAIL 3150 were capable of giving an increase of this magnitude. The best performing formulations of these additives in MAGNUM 342

EZ gave impact values with seven-fold and eight-fold improvement over Formulation 1. (See Table 13). Although the values for impact strength were shy of being ten times the base case, further increases could be gained during the processing optimization phase.

Table 13 – Results of baselines compared to best performing additives. CYCOLAC refers to CYCOLAC BDT 6500. MAGNUM refers to MAGNUM 342 EZ. Impact Strength measures by the modified Instrumented Dart Impact test and reported in in-lb_f.

Description	Impact Strength
Formulation 1 – CYCOLAC	18.24
Formulation 17 - MAGNUM	38.16
Formulation 21 – 15% XP-2280 in MAGNUM	130.59
Formulation 30 – 10% PREVAIL 3050 in MAGNUM	128.90
Formulation 31 – 10% PREVAIL 3150 in MAGNUM	145.00

If impact strength had been the only criteria for moving on to the processing optimization phase, all three additives would have moved on. However, cosmetic performance was also taken into account. The high void content of the PREVAIL materials disqualified them. However, as these additives are polymeric in nature, it is possible that the generalized heating cycle used in this evaluation provided insufficient thermal energy to fully sinter the PREVAIL blends. As it was possible that the PREVAIL blends 1) might be able to increase the impact strength by ten-fold with the optimized processing parameters and 2) might show better cosmetic properties with different heating cycles, their advancement to the processing optimization phase was contingent upon the ability to overcome the high void content by changing the oven temperature and oven time.

Iteration of PREVAIL 3150

Unfortunately, PREVAIL 3050 had been commercially discontinued between the formulation of the original forty formulations and the analysis of the data above. So, proceeding with only PREVAIL 3150, a total of three PREVAIL formulations were

trialed. One was Formulation 25 (100% PREVAIL 3150), which had previously shown difficulty in being extruded. In this study, it was sent to be ground without compounding. Two new formulations were developed: Formulation 41 (33% PREVAIL 3150 in MAGNUM 342 EZ) and Formulation 42 (67% PREVAIL 3150 in MAGNUM 342 EZ). Compounding of Formulations 41 and 42 was performed courtesy of Chroma Color Corporation. Grinding of all three formulations was performed courtesy of ICOWEDCO Polymers Corporation.

Changing the oven temperature and oven time did not improve the cosmetic properties of the PREVAIL 3150 formulations. Oven temperatures from 400 °F to 650 °F were tried in 50°F gradations. Small foil cups were filled with powder from each of the three PREVAIL 3150 formulations. These cups were placed in the oven and removed at 10 minute intervals. The results of this experiment (see Table 14) show that for oven times under one hour, formulations containing PREVAIL 3150 were not able to sinter at any temperature between 400°F to 650°F. Temperatures above 650°F will likely continue the trend of accelerated degradation, manifest by shorter times necessary to reach an

Table 14 – Results of oven temperature experiment for three PREVAIL formulations

Temperature	33% PREVAIL 3150	67% PREVAIL 3150	100% PREVAIL 3150
400 °F	Unacceptable sintering after 1 hour	Unacceptable sintering after 1 hour	Unacceptable sintering after 1 hour
450 °F	Unacceptable sintering after 1 hour	Unacceptable sintering after 1 hour	Unacceptable sintering after 1 hour
500 °F	Unacceptable sintering after 1 hour	Unacceptable sintering and unacceptable discoloration after 60 mins.	Unacceptable sintering and unacceptable discoloration after 50 mins.
550 °F	Unacceptable sintering and unacceptable discoloration after 60 mins.	Unacceptable sintering and unacceptable discoloration after 40 mins.	Unacceptable sintering and unacceptable discoloration after 40 mins.
600 °F	Unacceptable sintering and unacceptable discoloration after 50 mins.	Unacceptable sintering and unacceptable discoloration after 30 mins.	Unacceptable sintering and unacceptable discoloration after 30 mins.
650 °F	Unacceptable sintering and unacceptable discoloration after 30 mins.	Unacceptable sintering and unacceptable discoloration after 20 mins.	Unacceptable sintering and unacceptable discoloration after 20 mins.

unacceptable level of discoloration. Also, oven times in excess of 1 hour are too long for a commercial rotational molding process. As neither higher temperatures nor longer cycles were able to reduce the high void content in the PREVAIL blends, these formulations were disqualified as candidates for the processing optimization phase.

Completion of the Additive Evaluation Phase

Of all the additives tried, only the XP-2280 additive proved to give a significant increase in impact strength with minimal bubbles, pinholes, yellowing, and bridging. The cause of the increase can be explained by a decreased melt viscosity. As XP-2280 has a melting point of 118°C⁶² and the Vicat softening point of MAGNUM 342 EZ is 220°C,⁶³ it is assumed that the viscosity of a XP-2280/MAGNUM 342 EZ blend will be lower in the molten state.

The effect is essentially a plasticization of the ABS with XP-2280. The molecular structure of this benzoate ester includes two large phenyl groups which would be readily compatible with the high hydrocarbon character of the ABS monomers, especially styrene, which also contains a phenyl ring. As the XP-2280 molecules are dispersed among the polymer chains by mixing, a reduced occurrence of chain entanglements should be expected. As entanglements restrict the ability of the polymer chain to move, a reduction in chain entanglements would mean that less shear force would be required at a given shear rate. Therefore the addition of the XP-2280 additive works to lower the melt viscosity of MAGNUM 342 EZ blends.

Lower melt viscosity should increase impact strength through at least two mechanisms. The first is that because the melt phase is less viscous, more air is able to

escape during the densification stage of the sintering process. Fewer air bubbles in the part wall signifies fewer stress risers which can cause premature failure when the part is under load. Therefore, the reduction of air bubbles can be attributed to part of the increase observed in impact strength.

A second effect further increases the impact strength. As the viscosity of the resin is lower, the coalescence of the particles happens at a faster rate. This accelerates the reduction of total particle surface area, thereby restricting thermo-oxidative degradation. This mechanism preserves the integrity of the polymeric chains, as noted by the improved impact performance.

Part II - Processing Optimization Phase

Formulation 21 (15% XP-2280 in MAGNUM 342 EZ) was the only resin to advance to the processing optimization phase. Before continuing through the experimental design of the processing optimization phase it was necessary to determine a pair of oven time and temperature programs which would be best suited for this formulation. As already stated above, 400°F and 450°F were determined to be oven temperatures for this experiment. Based upon trial and error runs and using nominal run conditions (20-mesh and finer particle size, ambient atmosphere, and no drying), it was found that 30 minutes (400°F) and 28 minutes (450°F) of oven time were needed to fabricate a well formed part. Also, discoloration began to be apparent at oven times of 42 minutes (400°F) and 36 minutes (450°F). Using the midpoint of oven times between these two effects, the oven times of 36 minutes (400°F) and 32 minutes (450°F) were

chosen for the experimental design. In both cases, 20 minutes exposure to cooling fans was found to cool the parts sufficiently for removal.

Based upon the experimental design presented previously, sixteen runs were executed in order to ascertain the relative advantages of the proposed processing changes in this formulation. The means and confidence intervals (CI) of the impact testing were calculated. (See Table 15).

Table 15 – Impact strength measurements from the processing optimization experimental design. Tested by the modified Instrumented Dart Impact test. LCL and UCL are the lower and upper bounds of the 90% confidence level.

Experimental Conditions					Impact Strength (ft-lbf)		
Standard Order	Particle Size Distribution	Drying	Atmosphere	Oven Temperature	LCL	Mean	UCL
1	20-mesh to 40-mesh	Dry/Use	Ambient	400 °F	8.03	11.32	14.61
2	40-mesh to 60-mesh	No Dry	Ambient	450 °F	9.43	11.82	14.20
3	40-mesh and finer	No Dry	Nitrogen	450 °F	9.33	12.19	15.06
4	20-mesh and finer	Dry/Store	Nitrogen	400 °F	10.56	12.76	14.97
5	20-mesh to 40-mesh	No Dry	Nitrogen	400 °F	7.50	10.07	12.64
6	40-mesh to 60-mesh	Dry/Use	Nitrogen	450 °F	7.92	9.75	11.58
7	40-mesh and finer	Dry/Store	Ambient	450 °F	12.42	14.41	16.40
8	20-mesh and finer	No Dry	Ambient	400 °F	11.48	14.34	17.19
9	20-mesh to 40-mesh	No Dry	Ambient	450 °F	9.09	11.79	14.49
10	40-mesh to 60-mesh	Dry/Store	Ambient	400 °F	7.76	10.37	12.98
11	40-mesh and finer	Dry/Use	Nitrogen	400 °F	10.57	12.81	15.05
12	20-mesh and finer	No Dry	Nitrogen	450 °F	7.81	9.75	11.68
13	20-mesh to 40-mesh	Dry/Store	Nitrogen	450 °F	8.26	11.27	14.27
14	40-mesh to 60-mesh	No Dry	Nitrogen	400 °F	9.19	11.94	14.69
15	40-mesh and finer	No Dry	Ambient	400 °F	12.43	15.59	18.75
16	20-mesh and finer	Dry/Use	Ambient	450 °F	9.83	12.19	14.54

A regression of these data was performed by use of Equation 1, which includes seven main effect terms and seven interaction terms, as discussed in the previous chapter.

$$\text{Impact Strength} = P1 + P2 + P3 + D1 + D2 + A + T + (P1*A) + (P2*D2) + (P2*T) + (P3*A) + (D1*T) + (D2*A) + (A*T) \quad \text{Equation 1}$$

The regression was then analyzed to determine which effects are most significant. Terms which were not at least 90% probable to be significant were excluded. The details of this regression can be found in Appendix D.

Of the fourteen terms initially included in the regression only two, P3 and A, proved to be statistically significant. (See Figure 18). For the particle size distribution level P3 (20-mesh and finer) there was a 19% (90% CI = $\pm 11\%$) increase in the impact strength. For the atmosphere level A (ambient) there was a 14% (90% CI = $\pm 11\%$) increase in the impact strength.

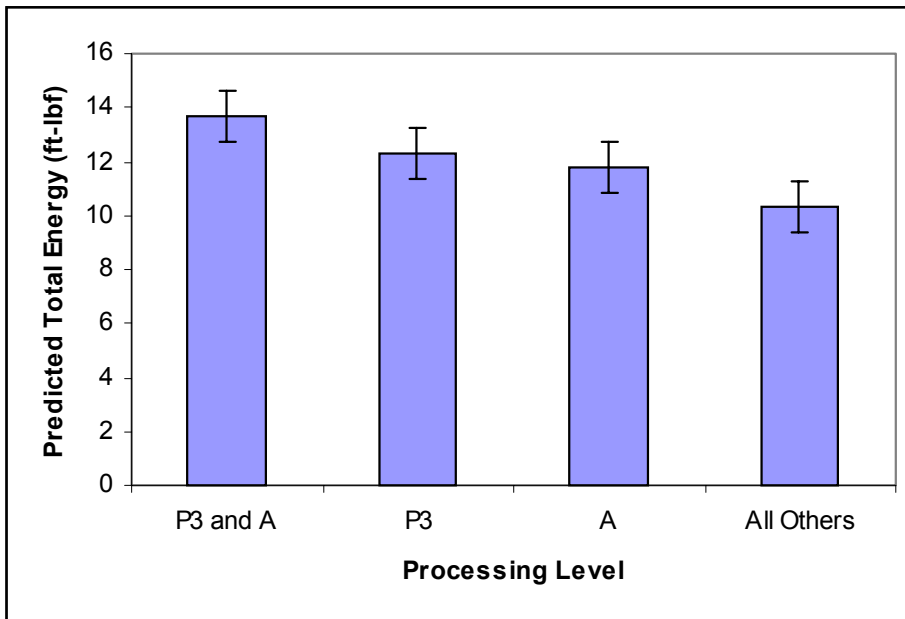


Figure 18 – Predicted impact strengths from the regression model. Error bars represent the 90% confidence interval. Note that the “All Others” mean does not overlap the other confidence intervals, nor does the “All Others” confidence interval overlap the other means.

All other levels proved to be indistinguishable from each other and, therefore, have an insignificant effect on the impact strength. This includes all other main effect terms as well as all the interaction terms, including the P3*A interaction. The lack of significance of the P3*A term demonstrates that while the individual effects of each of these terms are cumulative, they are not synergistic.

Discussion of Effects

Understanding these effects is important as it may lead to further optimization. There are two main characteristics of particle size distribution: breadth of the particle size distribution and mean particle size. Broad distributions allow for more dense packing of the bulk resin particles. This will reduce the interstitial air volume, increasing the impact strength as discussed above. As P1 (40-mesh and finer) was one of the last factors to be eliminated from the regression, it is likely that the effect of distribution is more important than size. However, the mean size of the particle should not be overlooked. Although broad, the P1 level was not significant. It was necessary that the grind be both broad and coarse in order to show significance.

More puzzling is the effect of nitrogen on the system. As the thermodynamic properties of air and nitrogen are roughly equivalent, the heat transfer dynamics of the two systems should be similar. Internal mold pressures in both cases were ambient. Essentially, the same run conditions were implemented for both nitrogen and ambient runs except that the oxygen concentration was minimized at the start of the nitrogen experiments. The explanation of this effect must therefore be that 1) oxygen has some beneficial effect upon Formulation 21 during the rotomolding cycle (meaning that there exists an optimal oxygen concentration) and 2) a detail in the method of nitrogen purging, assumed to be unimportant was, in fact, a driving factor in the success of the experiment.

Selection of Processing Parameters for Final Properties Testing

With this analysis complete, the optimized set of processing conditions can now be determined. For particle size distribution, 20-mesh and finer is the ideal case. For atmosphere, the ambient atmosphere should be selected. As no difference was observed

for the oven temperatures and drying schemes included, any level can be selected without an effect upon the impact strength. So, for faster cycle times, the optimal oven temperature was selected to be 450°F. Likewise, rather than add an insignificant processing step, the “No Drying” level was considered to be optimal.

Part III – Final Properties Testing

Parts were made using the ideal formulation (Formulation 21) and the optimal processing conditions (20-mesh and finer particle size distribution, no drying, ambient atmosphere, and an oven temperature of 450°F). Specimens were cut from these parts and then tested for final physical properties. (See Table 16).

Table 16 – Final properties of Formulation 21 at optimal conditions.

Properties	Value
Surface Hardness Type A (Shore A)	61
Surface Hardness Type D (Shore D)	51
Yield Tensile Strength	3,300 psi
Flexural Modulus	110,000 psi
ARM Impact Strength (Room Temperature)	11 ft-lbs
ARM Impact Strength (-40°C)	8 ft-lbs
Heat Distortion Temperature	61°C

The Association of Rotational Molders Special Materials Committee had set target value for some of the properties which they felt would guide the project. As shown in Table 17, Bedell was able to meet all of these targets except for ARM impact strength. There were trade-offs between impact strength and surface hardness, yield tensile strength, flexural modulus, and heat distortion temperature. Again, losses in these properties were acceptable if they 1) remained above the ARM targets and 2) increased the impact strength.

Table 17 – Comparisons of final properties of Formulation 21 at optimal conditions (“Current”) with “ARM Target” and “Previous Best” from earlier research.¹⁸ * denotes where Rockwell Hardness was estimated from Shore Hardness values. MAGNUM 342 EZ values were not generated at BYU.

Property	ARM Target	Previous Best	Current	MAGNUM 342 EZ (Injection Molded)⁶³
Surface Hardness (Rockwell R)	85	95	86*	n/a
Yield Tensile Strength	2,500 psi	3,900 psi	3,300 psi	6,000 psi
Flexural Modulus	60,000 psi	200,000 psi	110,000 psi	300,000 psi
Heat Distortion Temperature	40°C	95°C	61°C	91°C
ARM Impact Strength (-40°C)	20 ft-lbs	2 ft-lbs	8 ft-lbs	n/a
Instrumented Dart Impact Strength (total energy)	n/a	n/a	205 in-lb (brittle)	380 in-lb (ductile)

Under the optimal processing conditions, Formulation 21 did not perform as well as expected in the ARM Low Temperature Impact Test. The modified instrumented dart impact test showed a ten-fold improvement (20 in-lbs to 205 in-lbs). However, only a four-fold improvement in the ARM impact strength was realized.

The mode of failure is also important. Ductile failure is the failure mode preferred by the customers of the rotational molding industry. However, brittle failure was observed almost exclusively during the course of the experiment. This observation is valid for test performed both at -40°C and at room temperature.

Applications

The applications of this material are somewhat limited. Compensation for the poor impact performance can be made by thickening the part wall. However, this adds to the cost to the part. Considering that most of the customers of the rotomolding industry currently purchase polyolefin parts with superior impact performance at a lower cost,

there is no grounds for recommending this formulation for applications requiring impact strength.

However, other features of this material may find application in the marketplace. When compared with polyolefins, ABS resins have been demonstrated to be more “paintable.” Paint tends to adhere more readily to ABS parts, providing value in both ease of manufacture and long-term aesthetics. The paintability of Formulation 21 has been demonstrated by Chroma Color Corporation.

Also, Formulation 21 showed virtually no shrinkage. Applications which require tight tolerances, especially large parts, are especially problematic when using polyolefin resins. The dimensions of ABS would be more consistent, meaning that tighter tolerances are possible. Although this characteristic caused some problem in part removal from molds designed for polyethylene, mold designs for ABS could be made to account for the lack of shrinkage.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The use of acrylonitrile-butadiene-styrene (ABS) copolymers has not been a popular material choice for rotomolded parts due to high void content, noticeable discoloration, excessive embrittlement, and a higher-than-normal occurrence of bridging. Through the addition of additives and optimization of the processing parameters, these deficiencies have been significantly overcome. These improvements have been manifested both by an increase in the impact strength and by improved aesthetics.

Although many different additives were tested, XP-2280 (a benzoate ester available through ChemPoint) provided a significant increase in impact strength when compounded (at 15 wt.%) with MAGNUM 342 EZ (an ABS resin produced by The Dow Chemical Company). This additive also increased the flow of the resin in the molten state, thereby decreasing the void content in the final part and giving a smooth inner wall surface (no bridging). Discoloration was not apparent with the use of this additive. These improvements were made with minimal decrease in other physical properties.

Further improvements were also made by optimizing the processing parameters. By selecting a 20-mesh screen size (more coarse than is typical for polyethylene) impact strength increased by about 19%. Schemes for drying the resin proved to have no effect.

Likewise, small changes in oven temperature were insignificant. The use of nitrogen proved to be detrimental to the impact strength, making an ambient environment the optimal situation. Further changes in the cosmetic properties were not observed.

Recommendations

This research has validated the concept of adding XP-2280 to MAGNUM 342 EZ resins for general rotomolding use. Other benzoate esters (or even other plasticizing agents) could be added to different ABS resins to yield improved properties. This would be especially true as ABS resins are rotomolded for use in applications with more specific performance requirements.

It was found that a 20-mesh grind yielded better properties than a 35-mesh grind, suggesting that the optimal grind for ABS is certainly more coarse than 35-mesh. As coarser grinds are generally less expensive, molders may want to experiment with various mesh sizes for their applications. Also, these materials were ground cryogenically. Additional cost savings could be achieved by developing a method for ambient grinding.

Coating molds with PTFE is a common practice among rotomolders. It was observed that the ABS materials did not stick to PTFE coated surfaces, forming one large solid ball instead of a hollow part. Perhaps different types of PTFE coatings would produce a different result. However, a light coat of mold release was found to be sufficient to remove parts. The main challenge in part removal was the lack of shrinkage in ABS parts. More generous draft angles are recommended for ABS mold designs.

Use of nitrogen may prove to reduce the amount of degradation. A constant flow of nitrogen through the mold (rather than the initial purging with nitrogen) may decrease

the concentration in the mold cavity and thereby decrease the amount of degradation. Further increases in impact strength may also be possible through the use of other inert gases.

If a constant flow of gas is used to remove oxygen, adjusting the temperature of these gases (either above or below the sintering temperature) may help to balance the amount of degradation and cycle time. Gas temperatures which are warmer than the sintering temperature would help to deliver more heat to the system faster. This should reduce cycle time, but should result in an increased rate of degradation. Likewise, cooler gas temperatures should lengthen cycle time, but should decrease the rate of degradation. The effect of gas temperature on total degradation during the cycle is unknown.

There was a greatly decreased concentration of bubbles within the part wall observed when using XP-2280. In fact no bubbles could be found in the part wall, in any of the parts made from the XP-2280 formulations. It may be possible that this additive will have a similar effect in other resins. If so, there may be some improvement in the physical and/or optical properties of parts made with XP-2280, or similar materials. It may be worthwhile to further investigate XP-2280 (or similar materials) in other resins currently used in the rotomolding industry. For example, XP-2280 (or similar materials) in a clear polycarbonate may prove successful in making a thick walled, optically clear part.

The excellent impact performance of the PREVAIL polymers may be worth a second look. The blends tested proved to have unsatisfactory aesthetics, attributed to poor flow. However, the impact performance was superior to that found in formulations with XP-2280. It may be possible that superior performance can be attained by blending

PREVAIL with XP-2280 and MAGNUM 342 EZ. It may also be possible that XP-2280 may have sufficient ability to improve the performance of PREVAIL materials without the addition of MAGNUM 342 EZ into the system.

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APPENDICIES

Appendix A – Raw Data

Appendix B – Statistical Calculations for Additive Evaluation Phase

Appendix C – Design of Experiments

Appendix D – Model Reduction Process for Processing Optimization Phase

Appendix A – Raw Data

ADDITIVE EVALUATION PHASE

Weight is in grams; Max Load is in lbf; Impact energy, Energy to Max Load, and Total Energy are in ft-lbf.

Room Temperature

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Outlier = *
1-1	1	9.69	Brittle	21.36	44.42	0.33	0.41	
	2	16.57		Test Failure				
	3	11.05	Brittle	21.38	33.60	0.11	0.16	*
	4	10.86	Brittle	21.41	39.95	0.17	0.34	
1-2	1	12.07	Brittle	21.56	49.64	0.26	0.35	
	2	16.08	Brittle	Test Failure				
	3	16.32		Test Failure				
	4	11.77	Brittle	19.63	75.52	1.00	1.15	
1-3	1	12.68	Brittle	21.74	33.58	0.10	0.23	
	2	12.6	Brittle	21.56	29.28	0.14	0.18	
	3	11.95	Brittle	21.72	20.35	0.05	0.16	
	4	13.53	Brittle	21.66	19.71	0.05	0.05	
2-1	1	11.75	Brittle	20.52	50.51	0.35	0.44	
	2	10.66	Brittle	20.44	25.01	0.15	0.20	
	3	11.76	Brittle	20.59	32.18	0.10	0.12	
	4	12.51	Brittle	20.06	34.55	0.12	0.22	
3-1	1	13.48	Brittle	21.15	65.36	0.26	0.38	
	2	12.97	Brittle	21.05	39.08	0.17	0.29	
	3	10.99	Brittle	20.64	50.50	0.17	0.47	
	4	10.55	Brittle	21.00	48.47	0.27	0.44	
4-1	1	12.05	Brittle	21.36	90.91	0.33	0.73	
	2	16.26	Brittle	Test Failure				
	3	10.26	Brittle	21.21	83.81	0.44	0.68	
	4	13.02	Brittle	21.28	65.56	0.17	0.22	*
4-2	1	9.97	Brittle	21.41	80.95	0.47	0.76	
	2	11.61	Brittle	21.40	86.20	0.52	0.74	
	3	10.36	Brittle	21.35	103.37	1.10	1.37	
	4	10.84	Brittle	21.36	63.68	0.40	0.54	
5-1	1	11.06	Brittle	21.36	93.34	0.76	0.84	
	2	10.54	Brittle	21.43	58.17	0.40	0.57	
	3	11.51	Brittle	21.38	86.73	0.55	0.70	
	4	12.81	Brittle	21.38	101.59	0.72	0.88	
5-2	1	9.6	Brittle	21.63	62.96	0.49	0.71	
	2	9.86	Brittle	21.62	127.76	1.75	2.31	
	3	9.86	Brittle	21.76	109.56	1.29	1.66	
	4	15.11	Brittle	21.75	46.26	0.06	0.27	*

Sub-ambient Temperature (-40°C)

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Outlier = *
1-1	5	11.16	Brittle	26.25	101.08	1.13	1.31	
	6	12.21	Brittle	26.42	121.18	0.92	1.30	
	7	14.87	Brittle	26.57	203.16	1.04	1.71	
	8	11.39	Brittle	25.86	111.34	1.10	1.38	
1-2	5	11.95	Brittle	24.51	117.44	0.57	1.08	
	6	9.72	Brittle	25.68	90.09	0.87	1.07	
	7	13.68	Brittle	24.86	142.61	0.83	1.18	
	8	11.53	Brittle	24.62	106.14	1.15	1.34	
1-3	5	12.64	Brittle	26.78	160.43	0.72	0.96	
	6	13.96	Brittle	26.33	155.50	0.86	1.35	
	7	15.65	Brittle	26.22	192.83	0.82	1.58	
	8	15.55	Brittle	26.14	126.58	0.45	1.01	
2-1	5	14.87	Brittle	24.78	202.84	1.48	2.06	
	6	14.11	Brittle	24.75	215.75	1.66	2.51	
	7	13.97	Brittle	25.44	95.43	0.25	0.51	
	8	11.26	Brittle	24.97	131.26	1.34	1.69	
3-1	5	12.08	Brittle	24.92	149.92	0.95	1.38	
	6	9.93	Brittle	24.85	127.04	1.13	1.64	
	7	14.72	Brittle	25.56	238.61	1.97	2.63	
	8	10.65	Brittle	25.50	106.49	1.11	1.43	
4-1	5	11.36	Brittle	26.14	89.96	0.09	0.66	
	6	10.66	Brittle	25.68	72.01	0.46	0.70	
	7	9.85	Brittle	26.39	76.58	0.11	0.66	
	8	10.48	Brittle	25.83	60.49	0.24	0.61	
4-2	5	11.55	Brittle	24.96	102.10	0.66	0.82	
	6	10.01	Brittle	24.12	62.42	0.07	0.49	
	7	12.3	Brittle	24.50	80.79	0.38	0.63	
	8	15.47	Brittle	24.88	100.51	0.44	0.60	
5-1	5	16.13	Brittle	25.57	207.39	0.39	1.14	
	6	11.36	Brittle	25.92	137.33	0.32	0.84	
	7	10.37	Brittle	26.36	93.60	0.92	1.11	
	8	10.59	Brittle	26.09	113.21	0.24	1.03	
5-2	5	12.01	Brittle	27.17	112.03	0.48	0.91	
	6	11.59	Brittle	26.59	115.25	0.80	1.07	
	7	12.57	Brittle	27.05	134.03	0.25	1.08	
	8	10.05	Brittle	27.07	101.14	0.21	0.90	

Room Temperature

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Observations	
6-1	1	11.34	Brittle	21.11	93.10	0.67	1.00		
	2	10.61	Brittle	21.06	100.44	0.92	1.00		
	3	10.44	Brittle	19.12	89.64	1.19	1.47		
	4	10.39	Brittle	21.19	84.06	0.92	1.02		
6-2	1	14.22	Brittle	Test Failure					
	2	12.38	Brittle	Test Failure					
	3	10.32	Brittle	21.81	82.10	0.69	1.11		
	4	10.35	Brittle	21.88	75.04	0.49	0.82		
7-1	1	10.96	Brittle	21.24	104.66	0.89	1.56		
	2	10.48	Brittle	21.11	105.76	0.87	0.98		
	3	12.49	Brittle	21.23	54.40	0.12	0.31 *		
	4	10.55	Brittle	21.26	97.61	1.08	1.48		
8-1	1	14.86	Test Failure						
	2	11.56	Brittle	21.94	47.59	0.13	0.23 *		
	3	11.33	Brittle	20.81	90.00	0.96	1.36		
	4	14.39	Test Failure						
9-1	1	10.7	Brittle	21.00	126.13	1.49	2.05		
	2	13.07	Brittle	21.02	38.46	0.14	0.23 *		
	3	12.56	Brittle	21.03	65.15	0.23	0.55		
	4	10.7	Brittle	21.35	51.55	0.20	0.44		
9-2	1	11.81	Brittle	21.45	67.77	0.72	0.37		
	2	11.13	Brittle	21.40	62.84	0.13	0.40		
	3	11.56	Brittle	21.44	63.94	0.37	0.41		
	4	10.32	Brittle	21.20	87.28	0.77	0.91		
11-1	1	13.14	Brittle	21.68	99.30	0.35	0.51		
	2	15.27	Brittle	21.75	54.75	0.02	0.10 *		
	3	11.11	Brittle	21.63	58.70	0.18	0.42		
	4	11.48	Brittle	21.51	87.69	0.60	0.82		
11-2	1	11.96	Brittle	21.76	40.45	0.18	0.20 *		
	2	10.62	Brittle	21.82	80.79	0.45	0.54		
	3	12.92	Brittle	21.81	94.33	0.77	0.86		
	4	10.22	Brittle	21.83	98.68	0.89	1.06		
11-3	1	13.33	Brittle	21.73	94.15	0.56	0.63		
	2	11.19	Brittle	21.87	67.37	0.51	0.55		
	3	11.28	Brittle	21.84	59.00	0.27	0.59		
	4	13.84	Brittle	21.89	107.20	0.55	0.72		
12-1	1	15.37	Brittle	21.74	15.60	0.01	0.22		
	2	10.77	Brittle	21.58	84.11	1.01	1.12		
	3	11.11	Brittle	21.77	41.61	0.17	0.31		
	4	13.93	Brittle	21.65	70.99	0.25	0.57		
12-2	1	12.81	Brittle	21.84	55.12	0.16	0.30		
	2	10.24	Brittle	21.68	60.32	0.72	0.97		
	3	15.2	Brittle	Test Failure					
	4	10.7	Brittle	21.75	57.33	0.30	0.57		

Sub-ambient Temperature (-40°C)

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Observations
6-1	5	15.37	Brittle	25.65	214.07	0.43	1.04	
	6	13.06	Brittle	25.57	159.46	0.30	1.06	
	7	11.50	Brittle	25.09	174.01	0.46	1.11	
	8	9.32	Brittle	25.44	117.18	0.30	1.23	
6-2	5	11.37	Brittle	26.25	158.31	0.36	0.92	
	6	9.84	Brittle	26.08	106.58	0.28	0.99	
	7	9.65	Brittle	26.55	109.34	0.25	1.10	
	8	14.81	Brittle	26.23	184.03	0.38	1.66	
7-1	5	13.85	Brittle	25.07	113.35	0.38	0.87	
	6	10.92	Brittle	24.52	85.53	0.56	0.84	
	7	11.61	Brittle	25.47	109.98	0.25	1.07	
	8	10.51	Brittle	25.03	78.87	0.39	0.71	
8-1	5	10.77	Brittle	25.17	142.68	0.35	1.31	
	6	9.81	Brittle	25.61	119.06	0.26	1.25	
	7	9.69	Brittle	25.25	113.56	0.26	1.38	
	8	13.82	Brittle	25.11	201.57	0.56	1.65	
9-1	5	10.02	Brittle	24.74	124.07	0.34	0.99	
	6	14.14	Brittle	24.89	190.75	0.40	1.57	
	7	10.93	Brittle	25.06	140.10	0.30	1.25	
	8	11.63	Brittle	25.20	133.43	0.26	1.33	
9-2	5	11.34	Brittle	26.07	116.35	0.30	1.16	
	6	10.94	Brittle	25.85	126.15	0.29	1.13	
	7	14.10	Brittle	26.39	205.37	0.50	1.17	
	8	12.65	Brittle	26.56	168.71	1.50	1.88	
11-1	5	10.58	Brittle	26.84	49.01	0.25	0.37	
	6	10.50	Brittle	27.14	39.99	311.00	0.35	
	7	11.20	Brittle	26.64	47.25	316.00	0.33	
	8	12.58	Brittle	25.88	54.58	319.00	0.38	
11-2	5	12.14	Brittle	26.28	140.31	0.34	0.67	
	6	13.35	Brittle	26.58	87.15	0.37	0.54	
	7	11.14	Brittle	2657.00	68.58	0.41	0.48	
	8	16.07	Brittle	26.53	131.65	0.11	0.96	
11-3	5	13.09	Brittle	25.57	96.22	0.44	0.61	
	6	10.48	Brittle	25.83	60.98	0.08	0.48	
	7	14.93	Brittle	26.03	118.70	0.50	0.69	
	8	10.77	Brittle	26.48	59.01	0.25	0.46	
12-1	5	12.84	Brittle	26.57	143.44	1.17	1.59	
	6	11.63	Brittle	26.37	154.80	1.38	1.58	
	7	9.65	Brittle	26.53	100.80	0.27	1.65	
	8	11.69	Brittle	26.21	146.36	1.05	1.63	
12-2	5	11.62	Brittle	27.41	137.30	0.66	1.39	
	6	11.39	Brittle	26.66	130.71	1.17	1.69	
	7	12.87	Brittle	26.83	150.62	1.43	1.85	
	8	9.78	Brittle	26.99	133.13	1.29	1.57	

Room Temperature

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Observations	
13-1	1	11.31	Brittle	21.28	29.84	0.14	0.18		
	2	10.6	Brittle	21.23	47.55	0.19	0.41		
	3	12.13	Brittle	21.10	28.50	0.10	0.14		
	4	10.62	Brittle	21.14	42.98	0.35	0.44		
14-1	1	11.89	Brittle	Test Failure					
	2	10.64	Brittle	21.14	77.36	0.63	0.84		
	3	12.11	Brittle	21.12	49.61	0.24	0.32		
	4	12.2	Brittle	21.17	68.65	0.41	0.60		
15-1	1	14.14	Brittle	21.12	26.22	0.08	0.10	*	
	2	10.13	Brittle	21.01	42.81	0.38	0.44		
	3	12.24	Brittle	21.08	51.53	0.28	0.35		
	4	11.6	Brittle	21.11	53.35	0.29	0.40		
16-1	1	9.73	Brittle	21.58	62.57	0.62	1.02	*	
	2	12.38	Brittle	21.71	57.82	0.29	0.45		
	3	10.46	Brittle	21.56	35.30	0.30	0.34		
	4	10.64	Brittle	21.60	43.00	0.27	0.37		
16-2	1	13.61	Brittle	21.89	35.20	0.11	0.15		
	2	10.66	Brittle	21.91	36.54	0.11	0.15		
	3	10.68	Brittle	21.80	31.13	0.09	0.17		
	4	9.83	Brittle	21.82	61.54	0.70	0.81	*	
17-1	1	9.7	Brittle	20.87	11.20	0.06	0.90		
	2	9.03	Brittle	20.27	6.21	0.01	0.01	*	
	3	9.99	Brittle	Test Failure					
	4	11.09	Brittle	Test Failure					
18-1	1	14.46	Brittle	Test Failure					
	2	10.95	Brittle	21.48	62.61	0.42	1.08		
	3	9.72	Brittle	21.59	73.95	0.61	1.40		
	4	10.82	Brittle	21.49	141.26	1.61	2.97		
19-1	1	9.99	Brittle	21.51	105.67	1.40	1.88		
	2	13.26	Brittle	21.52	61.29	0.00	0.14	*	
	3	11.17	Brittle	21.50	132.26	1.74	2.04		
	4	10.26	Brittle	21.49	121.23	1.84	2.20		
21-1	1	10.93	Brittle	21.14	130.42	1.17	3.06		
	2	19.81	Test Failure						
	3	14.66	Test Failure						
	4	10.5	Brittle	21.07	122.06	1.51	3.11		
23-1	1	11.27	Brittle	21.15	93.36	1.46	2.11		
	2	11.88	Test Failure						
	3	12.15	Brittle	21.53	91.95	1.53	2.35		
	4	11.26	Brittle	21.55	105.02	1.06	2.68		
24-1	1	13.97	Brittle	21.30	27.61	0.06	0.51		
	2	10.45	Brittle	20.86	91.30	1.08	1.77	*	
	3	10.8	Brittle	21.10	64.65	0.31	1.00		
	4	10.8	Brittle	20.97	67.71	0.45	0.82		

Sub-ambient Temperature (-40°C)

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Observations	
13-1	5	13.38	Brittle	24.76	179.56	1.22	1.89		
	6	13.91	Brittle	24.58	171.79	1.56	1.91		
	7	10.72	Brittle	24.71	107.78	0.24	1.53		
	8	16.42	Brittle	24.80	195.97	0.90	1.24		
14-1	5	18.17	Brittle	25.78					
	6	10.64	Brittle	24.44	118.47	1.20	1.51		
	7	10.38	Brittle	24.86	112.76	1.15	1.51		
	8	11.69	Brittle	25.50	115.45	0.50	1.28		
15-1	5	9.81	Brittle	26.36	91.57	0.41	1.32		
	6	12.81	Brittle	25.57	144.92	0.74	1.52		
	7	12.59	Brittle	25.89	141.94	0.81	1.59		
	8	13.92	Brittle	25.47	221.23	1.91	2.68		
16-1	5	10.31	Brittle	26.63	113.05	1.38	1.70		
	6	11.35	Brittle	25.89	118.24	0.58	1.37		
	7	13.7	Brittle	26.06	176.84	1.48	2.08		
	8	15.38	Brittle	25.98	221.31	0.50	2.25		
16-2	5	9.04	Brittle	27.01	115.16	0.37	2.08		
	6	14.91	Brittle	27.27	137.21	0.50	0.76		
	7	9.05	Brittle	26.84	102.07	1.12	1.44		
	8	12.58	Brittle	26.44	137.74	1.04	1.57		
17-1	5	11.42	Brittle	26.00	165.44	2.43	2.93		
	6	10.16	Brittle	23.54	137.76	2.03	2.60		
	7	17.34	Test Failure						
	8	13.63	Brittle	25.52	211.85	2.28	3.64		
18-1	5	16.03	Brittle	24.69	255.18	0.64	4.94		
	6	9.78	Brittle	25.78	137.04	2.65	3.12		
	7	11.15	Brittle	25.76	142.77	1.89	2.75		
	8	13.31	Brittle	25.25	229.03	3.58	4.20		
19-1	5	15.86	Brittle	24.89	255.34	0.67	2.11		
	6	9.27	Brittle	24.46	118.15	1.04	1.46		
	7	13.61	Brittle	24.31	255.34	0.52	1.58		
	8	10.31	Brittle	23.68	130.42	1.24	1.66		
21-1	5	11.07	Brittle	25.08	110.05	1.18	1.47		
	6	12.25	Brittle	25.23	169.36	0.45	1.61		
	7	13.05	Brittle	25.64	171.96	1.07	1.62		
	8	14.63	Brittle	24.76	209.59	0.44	1.63		
23-1	5	11.01	Brittle	25.01	98.47	0.23	1.33		
	6	10.7	Brittle	24.75	105.97	0.30	0.98		
	7	10.96	Brittle	28.02	100.86	1.01	1.17		
	8	14	Brittle	24.90	120.38	0.23	1.21		
24-1	5	13.66	Brittle	25.10	143.99	0.47	1.36		
	6	11.39	Brittle	24.82	95.58	0.70	1.16		
	7	14.56	Brittle	25.35	153.01	1.16	1.87		
	8	10.7	Brittle	24.98	87.50	0.93	1.32		

Room Temperature

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Observations
26-1	1	14.14	Brittle	21.51	68.53	0.35	1.02	
	2	11.61	Brittle	21.49	96.80	0.65	1.10	
	3	11.1	Test Failure					
	4	10.85	Brittle	21.62	89.92	1.25	1.66	
26-2	1	10.25	Brittle	21.88	103.98	1.38	2.75	
	2	11.14	Brittle	21.96	90.34	1.01	1.72	
	3	13.33	Brittle	21.88	61.75	0.50	0.68 *	
	4	12.1	Brittle	21.85	105.39	1.63	2.05	
27-1	1	17.41	Test Failure					
	2	10.98	Brittle	21.53	57.32	0.47	0.53	
	3	13.44	Brittle	21.58	93.50	0.74	1.14	
	4	12.48	Brittle	21.44	112.40	0.77	1.22	
30-1	1	10.69	Brittle	21.74	149.20	1.22	3.67	
	2	16.71	Test Failure					
	3	10.04	Brittle	21.74	81.08	0.62	1.66 *	
	4	9.41	Brittle	21.73	166.94	0.94	3.10	
30-2	1	11.19	Brittle	21.94	116.86	0.88	2.54	
	2	8.62	Brittle	21.79	106.55	0.99	2.75	
	3	10.84	Test Failure					
	4	10.95	Brittle	21.79	125.31	1.33	2.82	
31-1	1	12.41	Brittle	21.23	145.22	1.16	2.80	
	2	10.89	Brittle	21.01	111.81	0.92	2.34	
	3	10.45	Brittle	21.12	159.46	2.02	3.80	
	4	9.24	Brittle	21.35	126.60	1.13	3.60	
31-2	1	9.95	Brittle	21.30	140.31	1.85	3.66	
	2	12.27	Brittle	21.19	146.31	1.67	3.25	
	3	11.91	Brittle	21.34	161.58	2.03	3.70	
	4	12.84	Brittle	21.54	13.62	0.03	0.14 *	
32-1	1	11.58	Brittle	20.51	104.65	1.02	1.14 *	
	2	11.26	Brittle	20.67	140.41	1.98	2.10	
	3	13.44	Brittle	20.57	95.83	0.60	0.91 *	
	4	9.94	Brittle	20.67	106.45	0.85	1.48	
32-2	1	10.17	Brittle	21.24	150.44	2.57	2.73	
	2	12.45	Brittle	21.45	73.52	0.34	0.49 *	
	3	12.43	Brittle	21.39	146.29	1.11	1.64	
	4	14.35	Brittle	21.43	85.96	0.42	1.05	
32-3	1	12.36	Brittle	21.77	79.31	0.20	0.36 *	
	2	10.69	Brittle	21.74	140.52	1.57	2.01	
	3	11.78	Brittle	21.71	121.10	1.28	1.65	
	4	10.26	Brittle	21.79	141.93	1.54	2.45	
33-1	1	13.29	Brittle	21.14	69.77	0.31	0.38 *	
	2	12.81	Brittle	21.22	162.95	1.91	2.04	
	3	9.94	Brittle	21.15	114.41	1.44	1.69	
	4	9.39	Brittle	20.98	139.72	1.43	2.25	

Sub-ambient Temperature (-40°C)

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Observations
26-1	5	14.22	Brittle	25.08	130.14	0.64	1.36	
	6	10.74	Brittle	24.74	122.18	0.32	1.54	
	7	13.08	Brittle	25.49	143.80	0.96	1.44	
	8	11.3	Brittle	25.88	118.07	1.20	1.31	
26-2	5	12.81	Brittle	26.24	118.06	0.94	1.17	
	6	10.31	Brittle	25.77	92.49	0.65	1.54	
	7	10.13	Brittle	25.95	95.29	1.13	1.36	
	8	10.36	Brittle	25.86	104.67	0.23	1.24	
27-1	5	10.77	Brittle	24.84	101.60	0.16	1.16	
	6	11.11	Brittle	25.19	107.04	0.76	0.93	
	7	10.25	Brittle	25.06	92.48	0.77	1.48	
	8	9.91	Brittle	24.73	125.71	0.87	1.16	
30-1	5	12.32	Brittle	26.70	159.40	1.54	2.59	
	6	10.66	Brittle	26.22	154.57	2.00	2.53	
	7	13.05	Brittle	25.97	183.31	1.95	2.52	
	8	9.82	Brittle	26.23	131.60	0.40	2.04	
30-2	5	14.69	Test Failure					
	6	13.54	Test Failure					
	7	13.77	Brittle	26.54	185.24	1.29	2.50	
	8	10.1	Brittle	26.10	134.95	1.42	2.15	
31-1	5	15.06	Brittle	24.14	255.32	0.73	2.72	
	6	12.31	Brittle	25.13	239.38	0.83	2.89	
	7	9.47	Brittle	25.44	130.61	1.50	2.07	
	8	15.33	Brittle	25.09	255.24	0.61	3.42	
31-2	5	9.57	Brittle	25.27	131.63	2.41	2.80	
	6	8.77	Brittle	25.41	99.65	0.32	1.72	
	7	8.74	Brittle	25.02	133.20	1.83	2.53	
	8	9.55	Brittle	25.38	122.67	1.72	2.19	
32-1	5	11.77	Brittle	25.26	126.03	0.21	0.63	
	6	12.53	Brittle	25.15	123.75	0.21	0.51	
	7	9.68	Brittle	25.29	181.87	0.16	0.44	
	8	13.91	Brittle	25.64	167.99	0.38	0.64	
32-2	5	12.07	Brittle	26.08	82.55	0.20	0.54	
	6	13.35	Brittle	25.58	140.74	0.25	0.62	
	7	11.09	Brittle	25.63	102.25	0.20	0.78	
	8		Not Available					
32-3	5	11.39	Not Tested					
	6	12.94	Not Tested					
	7	13.56	Not Tested					
	8	14.57	Not Tested					
33-1	5	9.34	Brittle	25.30	91.01	0.17	0.72	
	6	11.62	Brittle	25.91	117.00	0.18	0.73	
	7	12.07	Brittle	25.44	161.12	0.39	1.00	
	8	11.05	Brittle	25.54	166.08	0.55	0.68	

Room Temperature

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Observations
34-1	1	10.68	Brittle	21.36	71.11	0.54	0.79	
	2	10.3	Brittle	21.25	94.87	1.07	1.21	
	3	14.99	Brittle	21.46	50.28	0.04	0.43	*
	4	12.38	Brittle	21.35	158.54	1.67	2.10	
35-1	1	13	Brittle	21.49	118.96	1.44	1.71	
	2	12.77	Brittle	21.40	151.79	0.90	1.71	
	3	10.78	Brittle	21.27	132.27	1.68	1.84	
36-1	4	13.9	Brittle	21.44	65.74	0.10	0.38	*
	1	13.93	Brittle	21.54	49.70	0.10	0.46	
	2	15.31	Test Failure					
	3	12.03	Brittle	21.38	79.49	0.68	0.82	
37-1	4	10.38	Brittle	21.31	48.17	0.46	0.50	
	1	15.54	Test Failure					
	2	9.75	Brittle	21.11	131.15	1.25	2.71	*
	3	10.28	Brittle	21.28	62.81	0.52	0.87	
38-1	4	12.48	Brittle	21.25	115.68	1.18	1.50	
	1	13.77	Brittle	21.05	58.97	0.24	0.67	
	2	11.13	Brittle	21.88	47.35	0.21	0.26	
	3	13.12	Brittle	20.89	63.40	0.19	0.41	
39-1	4	11.42	Brittle	20.92	37.71	0.12	0.19	*
	1	11.46	Brittle	21.41	96.12	0.87	1.25	
	2	10.17	Brittle	21.23	142.02	1.78	2.28	
	3	15.43	Brittle	21.42	64.93	0.22	0.78	*
40-1	4	16.71	Brittle	21.53	41.19	0.10	0.62	*
	1	10.72	Brittle	21.45	121.91	1.28	1.57	*
	2	10.03	Brittle	21.53	101.27	1.58	1.86	
	3	17.61	Test Failure					
41-1	4	11.29	Brittle	21.50	127.04	1.85	2.12	
	1	11.54	Brittle	68.16	169.26	2.88	5.80	
	2	12.99	Brittle	69.26	205.62	3.21	7.40	
	3	12.12	Brittle	69.05	170.94	2.35	6.08	
42-1	4	13.25	Brittle	69.46	189.20	2.79	6.45	
	1	13.69	Brittle	70.15	261.10	4.72	7.78	
	2	12.29	Brittle	68.60	175.21	2.80	5.99	
	3	12.1	Brittle	67.86	175.22	1.99	5.38	
43-1	4	13.33	Brittle	68.66	231.52	3.48	7.55	
	1	13.17	Brittle	67.52	231.52	3.73	7.32	
	2	11.63	Brittle	68.39	196.31	2.39	5.79	
	3	12.24	Brittle	69.82	206.82	3.18	5.15	
	4	11.91	Brittle	68.86	183.88	1.97	6.02	

Sub-ambient Temperature (-40°C)

Formulation / Rep #	Specimen #	Weight	Failure Mode	Impact Energy	Max Load	Energy to Max Load	Total Energy	Observations
34-1	5	12.21	Brittle	24.48	99.23	0.80	0.94	
	6	11.58	Brittle	24.79	168.31	0.34	0.70	
	7	10.1	Brittle	25.43	105.74	0.24	0.81	
	8	10.52	Brittle	24.94	65.10	0.37	0.64	
35-1	5	11.26	Brittle	25.43	133.00	0.31	1.07	
	6	10.17	Brittle	25.17	210.09	0.58	0.73	
	7	10.41	Brittle	25.64	103.08	0.22	0.97	
	8	10.05	Brittle	24.42	94.21	0.23	1.05	
36-1	5	10.05	Brittle	24.77	100.76	0.79	1.39	
	6	11.34	Brittle	24.92	102.90	0.18	1.16	
	7	14.54	Brittle	24.94	143.58	0.81	1.36	
	8	11.3	Brittle	25.87	100.21	0.80	1.11	
37-1	5	9.63	Brittle	24.70	101.67	0.26	1.33	
	6	10.271	Brittle	24.93	123.69	0.43	0.88	
	7	11.34	Brittle	25.24	157.08	0.38	1.32	
	8	13.15	Brittle	24.99	202.64	0.47	1.65	
38-1	5	14.48	Brittle	23.86	205.09	0.44	1.73	
	6	10.69	Brittle	24.73	120.79	0.33	1.03	
	7	15.99	Brittle	25.63	254.95	0.57	1.53	
	8	11.5	Brittle	25.85	114.16	0.25	1.17	
39-1	5	9.37	Brittle	24.85	110.91	1.17	1.55	
	6	11.63	Brittle	24.23	145.16	0.37	1.78	
	7	10.39	Brittle	24.89	162.04	0.44	1.43	
	8	10.54	Brittle	24.20	111.86	0.67	1.30	
40-1	5	8.97	Brittle	26.27	113.33	0.34	1.53	
	6	14.37	Brittle	26.06	230.39	0.58	2.22	
	7	11.71	Brittle	26.68	148.75	0.39	1.70	
	8	15.79	Brittle	25.98	254.98	0.47	2.74	

PROCESSING OPTIMIZATION PHASE

All measurements in ft-lbf.

Run #	Reading #1	Reading #2	Reading #3	Reading #4	Reading #5	Reading #6	Reading #7	Reading #8	Reading #9	Reading #10	Reading #11	Reading #12	Reading #13	Reading #14
1	16.00	9.86	9.53	22.71	8.85	4.57	9.22	23.42	10.18	4.18	5.99			
2	7.29	20.18	7.59	21.57	15.84	12.25	7.30	8.20	10.89	9.62	13.33	7.72		
3	8.51	7.64	18.88	10.79	15.16	25.28	14.60	7.33	9.04	10.16	6.25			
4	10.21	16.20	14.06	11.93	25.08	12.72	8.48	8.06	10.23	25.26	9.60	11.33		
5	6.32	7.00	9.02	6.41	10.84	21.55	5.31	7.66	7.65	10.49	7.94	20.70		
6	12.78	10.05	11.78	9.88	18.63	8.31	6.30	5.11	8.56	8.30	7.51			
7	22.50	10.89	13.69	18.00	16.43	14.07	18.32	9.43	9.33	30.43	31.86	9.28	16.68	14.31
8	18.54	9.70	18.12	6.80	10.42	7.70	10.14	21.28	44.40	13.28	18.74	22.99		
9	22.77	9.79	23.04	11.19	11.88	7.57	9.09	10.11	9.27	9.09	6.91			
10	25.24	10.38	8.57	11.68	6.32	8.33	7.69	6.45	8.77	12.06	8.58			
11	10.37	12.09	8.15	13.94	19.05	14.78	14.91	5.98	16.04					
12	14.54	10.63	9.77	8.42	13.87	20.56	7.93	7.09	6.74	11.30	10.59	5.00	6.00	4.00
13	15.49	12.46	13.45	7.91	21.85	26.13	9.99	6.63	4.98	11.03	3.19	7.18	8.17	
14	8.00	12.77	8.01	4.80	8.31	7.74	20.21	10.97	24.55	22.61	21.21	5.70	8.44	12.83
15	22.10	11.62	8.81	32.16	17.20	17.70	18.40	26.41	16.00	8.60	8.84			
16	10.93	9.94	14.42	20.35	21.62	16.01	19.20	11.72	8.71	6.10	8.76	10.42	4.33	8.08

FINAL PROPERTIES TESTING

Formulation 21 at optimal processing conditions

Physical Property Test	Unit	Reading #1	Reading #2	Reading #3	Reading #4	Reading #5	Average
Surface Hardness (Rockwell R)	----	87	86	89	82	86	86
Surface Hardness Type A (Shore A)	----	65	61	61	59	59	61
Surface Hardness Type D (Shore D)	----	52	52	49	49	52	51
Yield Tensile Strength	psi	3,166	3,429	3,240	3,456	3,226	3,303
Flexural Modulus	psi	108,385	109,683	119,717	111,005	108,924	111,543
Heat Distortion Temperature	°C	61.6	61.1	61.1	-----	-----	61.3

ARM Low Temperature Impact Test results
Formulation 21 at optimal processing conditions

	O	denotes non-failure	Check One: <input checked="" type="checkbox"/>	Method A - 10 lb. (4.536 kg)
	X	denotes failure-ductile		Method B - 15 lb. (6.804 kg)
	*	denotes failure-brittle		Method C - 20 lb. (9.072 kg)

Drop Height	Sample #																														Results			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	n_i	i	i_n	
12																																		
11						*						*													*		*					4	3	12
10					O		*				O		*		*							*			O		O		*			5	2	10
9				O				*			O			O	*						O	*		O						O		3	1	3
8			O						O								*		O				O									1	0	0
7		O																																
6	O																																	
																Total =		13		25														

N = 13	$h_0 = 7$ inches	$h = h_0 + [\Delta h(A/N \pm 0.5)]$	MFE = $h \times w$
A = 25	$\Delta h = 1$ inch	$h = 9$ inches	MFE = 94.23 in-lbs
			MFE = 7.853 ft-lbs

ARM Impact Test results (performed at room temperature)
Formulation 21 at optimal processing conditions

	O	denotes non-failure	Check One: <input checked="" type="checkbox"/>	Method A - 10 lb. (4.536 kg)
	X	denotes failure-ductile		Method B - 15 lb. (6.804 kg)
	*	denotes failure-brittle		Method C - 20 lb. (9.072 kg)

Drop Height	Sample #																														Results			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	n_i	i	i_n	
16																																		
15		*														*												*				3	4	12
14	O	*						*					O	*								*			O		*					4	3	12
13			*				O		*				O		*						*		*		O					O		4	2	8
12				*		O			*		O				*		O	*		O		*		O								4	1	4
11					O						O										O			*								1	0	0
10																																		
																Total =		16		36														

N = 16	$h_0 = 11$ inches	$h = h_0 + [\Delta h(A/N \pm 0.5)]$	MFE = $h \times w$
A = 36	$\Delta h = 1$ inch	$h = 14$ inches	MFE = 137.5 in-lbs
			MFE = 11.46 ft-lbs

Appendix B – Statistical Calculations for Additive Evaluation Phase

Tukey-Kramer paired comparison for "No antioxidant" family compared with "Standard antioxidant" family in CYCOLAC BDT 6500.

groups := 3 N := 5 k := 1..N

$$A := \begin{pmatrix} 18.23555556 & 10.73525863 & 6 \\ 28.49 & 14.6675833 & 6 \\ 47.63 & 25.31784878 & 3 \\ 26.10666667 & 8.681873838 & 2 \\ 69.96 & 36.91981943 & 3 \end{pmatrix} \quad B := \begin{pmatrix} 10.78 & 6.027625292 & 3 \\ 43.67 & 28.98077294 & 6 \\ 34.98 & 35.15734916 & 1 \\ 74.50666667 & 41.14490167 & 2 \\ 49.83 & 31.65631059 & 3 \end{pmatrix} \quad SP := \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}}$$

$$\Delta\text{Mean} := \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} \quad df_A := \sum_{i=1}^N A_{i,3} \quad df_B := \sum_{i=1}^N B_{i,3} \quad DF := df_A + df_B - \text{groups}$$

$$SE := SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} \quad q\text{value} := \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| \quad \begin{array}{l} q\text{value} = 0.9002 \\ DF = 32 \\ \text{groups} = 3 \end{array} \quad \text{Probability} = 0.1987$$

Using the Studentized Range Distribution, Probability can be calculated with the q-value, the degrees of freedom and the number of groups included in the comparison. The calculator used to find the probability values can be found at <http://calculators.stat.ucla.edu/studrange.php>

Tukey-Kramer paired comparison for "No antioxidant" family compared with "Double antioxidant" family in CYCOLAC BDT 6500.

groups := 3 N := 5 k := 1..N

$$A := \begin{pmatrix} 18.23555556 & 10.73525863 & 6 \\ 28.49 & 14.6675833 & 6 \\ 47.63 & 25.31784878 & 3 \\ 26.10666667 & 8.681873838 & 2 \\ 69.96 & 36.91981943 & 3 \end{pmatrix} \quad B := \begin{pmatrix} 17.38 & 3.492391731 & 3 \\ 45.925 & 9.920146168 & 4 \\ 29.48 & 27.11955506 & 6 \\ 16.83 & 9.350215684 & 3 \\ 77.14666667 & 3.30244354 & 2 \end{pmatrix} \quad SP := \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}}$$

$$\Delta\text{Mean} := \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} \quad df_A := \sum_{i=1}^N A_{i,3} \quad df_B := \sum_{i=1}^N B_{i,3} \quad DF := df_A + df_B - \text{groups}$$

$$SE := SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} \quad q\text{value} := \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| \quad \begin{array}{l} q\text{value} = 0.1917 \\ DF = 35 \\ \text{groups} = 3 \end{array} \quad \text{Probability} = 0.0100$$

Tukey-Kramer paired comparison for "Standard antioxidant" family compared with "Double antioxidant" family in CYCOLAC BDT 6500.

$$A := \begin{pmatrix} 10.78 & 6.027625292 & 3 \\ 43.67 & 28.98077294 & 6 \\ 34.98 & 35.15734916 & 1 \\ 74.50666667 & 41.14490167 & 2 \\ 49.83 & 31.65631059 & 3 \end{pmatrix} \quad B := \begin{pmatrix} 17.38 & 3.492391731 & 3 \\ 45.925 & 9.920146168 & 4 \\ 29.48 & 27.11955506 & 6 \\ 16.83 & 9.350215684 & 3 \\ 77.14666667 & 3.30244354 & 2 \end{pmatrix} \quad SP := \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}}$$

$$\Delta\text{Mean} := \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} \quad df_A := \sum_{i=1}^N A_{i,3} \quad df_B := \sum_{i=1}^N B_{i,3} \quad DF := df_A + df_B - \text{groups}$$

$$SE := SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} \quad q\text{value} := \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| \quad \begin{matrix} q\text{value} = 1.0726 \\ DF = 30 \\ \text{groups} = 3 \end{matrix} \quad \text{Probability} = 0.2690$$

Tukey-Kramer paired comparison for "CYCOLAC w/o additives" family compared with "CYCOLAC w/ 10% LUSTRAN 31-1000" family.

groups := 3 N := 3 k := 1.. N

$$A := \begin{pmatrix} 18.23555556 & 10.73525863 & 6 \\ 10.78 & 6.027625292 & 3 \\ 17.38 & 3.492391731 & 3 \end{pmatrix} \quad B := \begin{pmatrix} 47.63 & 25.31784878 & 3 \\ 34.98 & 35.15734916 & 1 \\ 29.48 & 27.11955506 & 6 \end{pmatrix} \quad SP := \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}}$$

$$\Delta\text{Mean} := \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} \quad df_A := \sum_{i=1}^N A_{i,3} \quad df_B := \sum_{i=1}^N B_{i,3} \quad DF := df_A + df_B - \text{groups}$$

$$SE := SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} \quad q\text{value} := \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| \quad \begin{matrix} q\text{value} = 4.1803 \\ DF = 19 \\ \text{groups} = 3 \end{matrix} \quad \text{Probability} = 0.9788$$

Tukey-Kramer paired comparison for "CYCOLAC w/o additives" family compared with "CYCOLAC w/ 25% LUSTRAN 31-1000" family.

groups := 3 N := 3 k := 1.. N

$$A := \begin{pmatrix} 18.23555556 & 10.73525863 & 6 \\ 10.78 & 6.027625292 & 3 \\ 17.38 & 3.492391731 & 3 \end{pmatrix} \quad B := \begin{pmatrix} 28.49 & 14.6675833 & 6 \\ 43.67 & 28.98077294 & 6 \\ 45.925 & 9.920146168 & 4 \end{pmatrix}$$

$$SP := \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}}$$

$$\Delta\text{Mean} := \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} \quad df_A := \sum_{i=1}^N A_{i,3} \quad df_B := \sum_{i=1}^N B_{i,3} \quad DF := df_A + df_B - \text{groups}$$

$$SE := SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} \quad q\text{value} := \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| \quad \begin{array}{l} q\text{value} = 5.9542 \\ DF = 25 \\ \text{groups} = 3 \end{array} \quad \text{Probability} = 0.9991$$

Tukey-Kramer paired comparison for "CYCOLAC w/ 10% Lustran 31-1000" family compared with "CYCOLAC w/ 25% LUSTRAN 31-1000" family.

groups := 3 N := 3 k := 1.. N

$$A := \begin{pmatrix} 47.63 & 25.31784878 & 3 \\ 34.98 & 35.15734916 & 1 \\ 29.48 & 27.11955506 & 6 \end{pmatrix} \quad B := \begin{pmatrix} 28.49 & 14.6675833 & 6 \\ 43.67 & 28.98077294 & 6 \\ 45.925 & 9.920146168 & 4 \end{pmatrix}$$

$$SP := \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}}$$

$$\Delta\text{Mean} := \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} \quad df_A := \sum_{i=1}^N A_{i,3} \quad df_B := \sum_{i=1}^N B_{i,3} \quad DF := df_A + df_B - \text{groups}$$

$$SE := SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} \quad q\text{value} := \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| \quad \begin{array}{l} q\text{value} = 0.3348 \\ DF = 23 \\ \text{groups} = 3 \end{array} \quad \text{Probability} = 0.0303$$

Tukey-Kramer paired comparison for "CYCOLAC w/o additives" family compared with "CYCOLAC w/ 10% SAN 330" family.

groups := 3 N := 3 k := 1.. N

$$\begin{aligned}
 A &:= \begin{pmatrix} 18.23555556 & 10.73525863 & 6 \\ 10.78 & 6.027625292 & 3 \\ 17.38 & 3.492391731 & 3 \end{pmatrix} & B &:= \begin{pmatrix} 26.10666667 & 8.681873838 & 2 \\ 74.50666667 & 41.14490167 & 2 \\ 16.83 & 9.350215684 & 3 \end{pmatrix} & SP &:= \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}} \\
 \Delta\text{Mean} &:= \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} & df_A &:= \sum_{i=1}^N A_{i,3} & df_B &:= \sum_{i=1}^N B_{i,3} & DF &:= df_A + df_B - \text{groups}
 \end{aligned}$$

$$\begin{aligned}
 SE &:= SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} & q\text{value} &:= \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| & q\text{value} &= 5.2521 & \text{Probability} &= 0.9948 \\
 & & & & DF &= 16 & & \\
 & & & & \text{groups} &= 3 & &
 \end{aligned}$$

Tukey-Kramer paired comparison for "CYCOLAC w/o additives" family compared with "CYCOLAC w/ 25% SAN 330" family.

groups := 3 N := 3 k := 1.. N

$$\begin{aligned}
 A &:= \begin{pmatrix} 18.23555556 & 10.73525863 & 6 \\ 10.78 & 6.027625292 & 3 \\ 17.38 & 3.492391731 & 3 \end{pmatrix} & B &:= \begin{pmatrix} 69.96 & 36.91981943 & 3 \\ 49.83 & 31.65631059 & 3 \\ 77.14666667 & 3.30244354 & 2 \end{pmatrix} & SP &:= \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}} \\
 \Delta\text{Mean} &:= \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} & df_A &:= \sum_{i=1}^N A_{i,3} & df_B &:= \sum_{i=1}^N B_{i,3} & DF &:= df_A + df_B - \text{groups}
 \end{aligned}$$

$$\begin{aligned}
 SE &:= SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} & q\text{value} &:= \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| & q\text{value} &= 8.9642 & \text{Probability} &= 0.9998 \\
 & & & & DF &= 17 & & \\
 & & & & \text{groups} &= 3 & &
 \end{aligned}$$

Tukey-Kramer paired comparison for "CYCOLAC w/ 10% SAN 300" family compared with "CYCOLAC w/ 25% SAN 330" family.

groups := 3 N := 3 k := 1.. N

$$A := \begin{pmatrix} 26.10666667 & 8.681873838 & 2 \\ 74.50666667 & 41.14490167 & 2 \\ 16.83 & 9.350215684 & 3 \end{pmatrix} \quad B := \begin{pmatrix} 69.96 & 36.91981943 & 3 \\ 49.83 & 31.65631059 & 3 \\ 77.14666667 & 3.30244354 & 2 \end{pmatrix}$$

$$SP := \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}}$$

$$\Delta\text{Mean} := \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N} \quad df_A := \sum_{i=1}^N A_{i,3} \quad df_B := \sum_{i=1}^N B_{i,3} \quad DF := df_A + df_B - \text{groups}$$

$$SE := SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}} \quad q\text{value} := \left| \frac{\sqrt{2} \cdot \Delta\text{Mean}}{SE} \right| \quad q\text{value} = 3.1792 \quad \text{Probability} = 0.8969$$

DF = 12
groups = 3

Tukey-Kramer comparison for "0% BLENDEX" level compared with "10% BLENDEX" level in CYCOLAC BDT 6500.

A := (18.23555556 10.73525863 6)
B := (28.16 16.93133112 5) groups := 4 df := A_{1,3} + B_{1,3} + 2 - groups

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}}$$

$$SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$q\text{value} := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad q\text{value} = 1.8151 \quad df = 9 \quad \text{groups} = 4 \quad \text{Probability} = 0.4053$$

Tukey-Kramer comparison for "0% BLENDEX" level compared with "40% BLENDEX" level in CYCLOAC BDT 6500.

A := (18.23555556 10.73525863 6)
B := (12.87 6.791553578 3) groups := 4 df := A_{1,3} + B_{1,3} + 2 - groups

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}}$$

$$SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$q\text{value} := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad q\text{value} = 1.2608 \quad df = 7 \quad \text{groups} = 4 \quad \text{Probability} = 0.1902$$

Tukey-Kramer comparison for "10% BLENDIX" level compared with "40% BLENDIX" level in CYCOLAC BDT 6500.

$$A := (28.16 \ 16.93133112 \ 5) \quad \text{groups} := 4 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (12.87 \ 6.791553578 \ 3)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 2.3899 \quad \text{df} = 6 \quad \text{groups} = 4 \quad \text{Probability} = 0.5963$$

Tukey-Kramer comparison for "0% Mineral Oil" level compared with "1% Mineral Oil" level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 4 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (25.81333333 \ 11.45127649 \ 2)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 1.4223 \quad \text{df} = 7 \quad \text{groups} = 4 \quad \text{Probability} = 0.2483$$

Tukey-Kramer comparison for "0% Mineral Oil" level compared with "2% Mineral Oil" level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 4 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (14.19 \ 6.724710651 \ 3)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 0.9522 \quad \text{df} = 7 \quad \text{groups} = 4 \quad \text{Probability} = 0.0964$$

Tukey-Kramer comparison for "0% Mineral Oil" level compared with "3% Mineral Oil" level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 4 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (19.03 \ 14.23157991 \ 6)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 0.1667 \quad \text{df} = 7 \quad \text{groups} = 4 \quad \text{Probability} = 0.0006$$

Tukey-Kramer comparison for "1% Mineral Oil " level compared with "2% Mineral Oil " level in CYCOLAC BDT 6500.

$$A := (25.81333333 \ 11.45127649 \ 2) \quad \text{groups} := 4 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (14.19 \ 6.724710651 \ 3)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 2.4125 \quad \text{df} = 6 \quad \text{groups} = 4 \quad \text{Probability} = 0.6033$$

Tukey-Kramer comparison for "1% Mineral Oil " level compared with "3% Mineral Oil " level in CYCOLAC BDT 6500.

$$A := (25.81333333 \ 11.45127649 \ 2) \quad \text{groups} := 4 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (19.03 \ 14.23157991 \ 6)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 1.0229 \quad \text{df} = 3 \quad \text{groups} = 4 \quad \text{Probability} = 0.1175$$

Tukey-Kramer comparison for "2% Mineral Oil " level compared with "3% Mineral Oil " level in CYCOLAC BDT 6500.

$$A := (14.19 \ 6.724710651 \ 3) \quad \text{groups} := 4 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (19.03 \ 14.23157991 \ 6)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 0.8914 \quad \text{df} = 7 \quad \text{groups} = 4 \quad \text{Probability} = 0.0808$$

Tukey-Kramer comparison for "0% XP-2280 " level compared with "15% XP-2280 " level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (66.03666667 \ 35.88518543 \ 9)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}}$$

$$SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 4.7941 \quad \text{df} = 11 \quad \text{groups} = 3 \quad \text{Probability} = 0.9846$$

Tukey-Kramer comparison for "0% XP-2280 " level compared with "20% XP-2280 " level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (25.66666667 \ 12.31519748 \ 9)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}}$$

$$SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 1.8213 \quad \text{df} = 14 \quad \text{groups} = 3 \quad \text{Probability} = 0.5753$$

Tukey-Kramer comparison for "15% XP-2280 " level compared with "20% XP-2280 " level in CYCOLAC BDT 6500.

$$A := (66.03666667 \ 35.88518543 \ 9) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (25.66666667 \ 12.31519748 \ 9)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}}$$

$$SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 4.7586 \quad \text{df} = 17 \quad \text{groups} = 3 \quad \text{Probability} = 0.9901$$

Tukey-Kramer comparison for "0% PREVAIL 3050 " level compared with "10% PREVAIL 3050 " level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (52.65333333 \ 22.20293074 \ 2)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 4.8712 \quad \text{df} = 14 \quad \text{groups} = 3 \quad \text{Probability} = 0.9896$$

Tukey-Kramer comparison for "0% PREVAIL 3050 " level compared with "50% PREVAIL 3050 " level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (104.72 \ 12.59199746 \ 2)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 15.7852 \quad \text{df} = 7 \quad \text{groups} = 3 \quad \text{Probability} = 0.9998$$

Tukey-Kramer comparison for "10% PREVAIL 3050 " level compared with "50% PREVAIL 3050 " level in CYCOLAC BDT 6500.

$$A := (52.65333333 \ 22.20293074 \ 2) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (104.72 \ 12.59199746 \ 2)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 4.9965 \quad \text{df} = 3 \quad \text{groups} = 3 \quad \text{Probability} = 0.9235$$

Tukey-Kramer comparison for "0% PREVAIL 3150 " level compared with "10% PREVAIL 3150 " level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (42.38666667 \ 16.60575001 \ 2)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 3.9708 \quad \text{df} = 7 \quad \text{groups} = 3 \quad \text{Probability} = 0.9396$$

Tukey-Kramer comparison for "0% PREVAIL 3150 " level compared with "50% PREVAIL 3150 " level in CYCOLAC BDT 6500.

$$A := (18.23555556 \ 10.73525863 \ 6) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (67.32 \ 30.91919792 \ 5)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 5.5944 \quad \text{df} = 7 \quad \text{groups} = 3 \quad \text{Probability} = 0.9866$$

Tukey-Kramer comparison for "10% PREVAIL 3150 " level compared with "50% PREVAIL 3150 " level in CYCOLAC BDT 6500.

$$A := (42.38666667 \ 16.60575001 \ 2) \quad \text{groups} := 3 \quad \text{df} := A_{1,3} + B_{1,3} + 2 - \text{groups}$$

$$B := (67.32 \ 30.91919792 \ 5)$$

$$SP := \sqrt{\frac{(A_{1,3}) \cdot (A_{1,2})^2 + (B_{1,3}) \cdot (B_{1,2})^2}{A_{1,3} + B_{1,3}}} \quad SE := SP \cdot \sqrt{\frac{1}{A_{1,3} + 1} + \frac{1}{B_{1,3} + 1}}$$

$$qvalue := \left| \frac{\sqrt{2} \cdot (A_{1,1} - B_{1,1})}{SE} \right| \quad qvalue = 1.8069 \quad \text{df} = 6 \quad \text{groups} = 3 \quad \text{Probability} = 0.5436$$

Student's paired t-test for CYCOLAC BDT 6500 formulations compared with MAGNUM 342 EZ formulations.

N := 8 k := 1.. N

$$A := \begin{pmatrix} 18.23555556 & 10.73525863 & 6 \\ 17.38 & 3.492391731 & 3 \\ 28.49 & 14.6675833 & 6 \\ 52.65333333 & 22.20293074 & 2 \\ 42.38666667 & 16.60575001 & 2 \\ 66.03666667 & 35.88518543 & 9 \\ 69.96 & 36.91981943 & 3 \\ 77.14666667 & 3.30244354 & 2 \end{pmatrix}$$

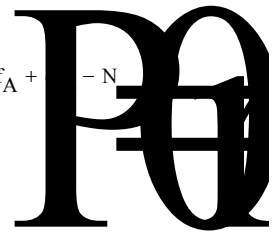
$$B := \begin{pmatrix} 20.02 & 27.69030155 & 1 \\ 79.93333333 & 44.5081985 & 2 \\ 68.86 & 42.19337705 & 3 \\ 121.2933333 & 32.54711457 & 4 \\ 146.7766667 & 24.31386545 & 5 \\ 135.74 & 1.555634919 & 1 \\ 54.23 & 32.90183176 & 3 \\ 81.4 & 12.10599851 & 2 \end{pmatrix}$$

$$SP := \sqrt{\frac{\sum_{k=1}^N [A_{k,3} \cdot (A_{k,2})^2 + B_{k,3} \cdot (B_{k,2})^2]}{\sum_{k=1}^N (A_{k,3} + B_{k,3})}}$$

$$\Delta\text{Mean} := \frac{\sum_{i=1}^N (A_{i,1} - B_{i,1})}{N}$$

$$df_A := \sum_{i=1}^N A_{i,3} \quad df_B := \sum_{i=1}^N B_{i,3}$$

$$DF := df_A +$$



$$SE := SP \cdot \sqrt{\frac{1}{df_A + N} + \frac{1}{df_B + N}}$$

$$tvalue := \left| \frac{\Delta\text{Mean}}{SE} \right|$$

$$\text{Probability} := pt(tvalue, DF)$$

Appendix C – Design of Experiments

Confounding Pattern

Standard Order	1	2	3	4	12	13	14	23	24	34	123	124	134	234	1234
1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	-1	1
2	-1	-1	-1	1	1	1	-1	1	-1	-1	-1	1	1	1	-1
3	-1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	1	-1
4	-1	-1	1	1	1	-1	-1	-1	-1	1	1	1	-1	-1	1
5	-1	1	-1	-1	-1	1	1	-1	-1	1	1	1	-1	1	-1
6	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1
7	-1	1	1	-1	-1	-1	1	1	-1	-1	-1	1	1	-1	1
8	-1	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1	1	-1
9	1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1
10	1	-1	-1	1	-1	-1	1	1	-1	-1	1	-1	-1	1	1
11	1	-1	1	-1	-1	1	-1	-1	1	-1	-1	1	-1	1	1
12	1	-1	1	1	-1	1	1	-1	-1	1	-1	-1	1	-1	-1
13	1	1	-1	-1	1	-1	-1	-1	-1	1	-1	-1	1	1	1
14	1	1	-1	1	1	-1	1	-1	1	-1	-1	1	-1	-1	-1
15	1	1	1	-1	1	1	-1	1	-1	-1	1	-1	-1	-1	-1
16	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Using 3, 4, and 34 to construct a four level factor for PSD

3	4	34	PSD	Levels
-1	-1	1	0	20-mesh to 40-mesh
1	-1	-1	1	40-mesh and finer
-1	1	-1	2	40-mesh to 60-mesh
1	1	1	3	20-mesh and finer
1,3 vs 0,2 2,3 vs 0,1 0,3 vs 1,2				
P3 P1 P2				

Using 13, 24, and 1234 to construct a four level factor for Drying, then collapsing that factor into a three level factor

13	24	1234	Drying	Collapsed	Levels
-1	-1	1	0	0	Dry/Store
1	-1	-1	1	1	No Dry
-1	1	-1	2	1	No Dry
1	1	1	3	2	Dry/Use
2 vs 0		2 vs 0	0,2 vs 1		
		D1	D2		

23 was assigned to Atmosphere (-1 = Nitrogen, 1 = Ambient). 124 was assigned to Temperature (-1 = 400°F, 1 = 450°F). The other assignments can be made to interactions. The assignments can be summarized as follows.

1	2	3	4	12	13	14	23	24	34	123	124	134	234	1234
P3*T	P3*A	P3	P1	P2*D2		D2*A	A	D1	P2	D1*T	A*T	T	P1*A	D2

The experimental design then becomes.

Standard Order	Run Order	Particle Size Distribution	Drying	Atmosphere	Oven Temperature
1	5	20-mesh to 40-mesh	Dry/Use	Ambient	400 °F
2	6	40-mesh to 60-mesh	No Dry	Ambient	450 °F
3	12	40-mesh and finer	No Dry	Nitrogen	450 °F
4	10	20-mesh and finer	Dry/Store	Nitrogen	400 °F
5	13	20-mesh to 40-mesh	No Dry	Nitrogen	400 °F
6	14	40-mesh to 60-mesh	Dry/Use	Nitrogen	450 °F
7	7	40-mesh and finer	Dry/Store	Ambient	450 °F
8	1	20-mesh and finer	No Dry	Ambient	400 °F
9	2	20-mesh to 40-mesh	No Dry	Ambient	450 °F
10	8	40-mesh to 60-mesh	Dry/Store	Ambient	400 °F
11	15	40-mesh and finer	Dry/Use	Nitrogen	400 °F
12	16	20-mesh and finer	No Dry	Nitrogen	450 °F
13	9	20-mesh to 40-mesh	Dry/Store	Nitrogen	450 °F
14	11	40-mesh to 60-mesh	No Dry	Nitrogen	400 °F
15	3	40-mesh and finer	No Dry	Ambient	400 °F
16	4	20-mesh and finer	Dry/Use	Ambient	450 °F

Run order was randomized.

Appendix D - Model Reduction Process for Processing Optimization Phase

Iteration #1 – All terms

Summary of Fit

R-square is the portion of variation attributed to the model, between 0 and 1. Root Mean Squared Error "RMSE" estimates the standard deviation of the residual.

RSquare	0.951385	
RSquare Adj	0.270782	****Low****
Root Mean Square Error	1.446921	
Mean of Response	12.02243	
Observations (or Sum Wgts)	16	

Analysis of Variance

The test that the whole model fits better than a simple mean, i.e. testing that all the parameters are zero except the intercept

<u>Source</u>	<u>DF</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>F Ratio</u>	
Model	14	40.971367	2.92653	1.3979	
Error	1	2.093581	2.09358	<u>Prob > F</u>	
C. Total	15	43.064948		0.5881	****High****

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	11.49812	1.400975	8.21	0.0772
P1[1--1]	-0.819358	0.723461	-1.13	0.4605
P2[1--1]	-0.674213	0.723461	-0.93	0.5224
P3[1--1]	1.9643803	0.723461	2.72	0.2246
D1[1--1]	0.0365497	0.723461	0.05	0.9679
D2[1--1]	-0.326601	0.723461	-0.45	0.7300
A[1--1]	1.4094037	0.723461	1.95	0.3019
T[1--1]	-0.755993	0.723461	-1.04	0.4860
P1*A[1--1]	-0.28126	0.723461	-0.39	0.7639
P2*T[1--1]	-0.120301	0.723461	-0.17	0.8951
P2*D2[1--1]	0.7227523	0.723461	1.00	0.5003
P3*A[1--1]	0.8419189	0.723461	1.16	0.4519
D1*T[1--1]	-0.366543	0.723461	-0.51	0.7015
D2*A[1--1]	-0.985191	0.723461	-1.36	0.4032
A*T[1--1]	0.4030648	0.723461	0.56	0.6764

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F	
P1	1	1	2.685388	1.2827	0.4605	****>0.05****
P2	1	1	1.818250	0.8685	0.5224	****>0.05****
P3	1	1	15.435160	7.3726	0.2246	****>0.05****
D1	1	1	0.005344	0.0026	0.9679	****>0.05**** ****Highest****
D2	1	1	0.426672	0.2038	0.7300	****>0.05****
A	1	1	7.945676	3.7953	0.3019	****>0.05****
T	1	1	2.286101	1.0920	0.4860	****>0.05****
P1*A	1	1	0.316428	0.1511	0.7639	****>0.05****
P2*T	1	1	0.057890	0.0277	0.8951	****>0.05****
P2*D2	1	1	2.089483	0.9980	0.5003	****>0.05****
P3*A	1	1	2.835310	1.3543	0.4519	****>0.05****
D1*T	1	1	0.537416	0.2567	0.7015	****>0.05****
D2*A	1	1	3.882405	1.8544	0.4032	****>0.05****
A*T	1	1	0.649845	0.3104	0.6764	****>0.05****

Summary

Analysis: Although RSquared is good, Adjusted RSquared is poor, suggests a problem. Analysis of Variance shows that a problem exists in that the use of this model fits the data no better than a single mean model.

Conclusion: None of the terms pass have probability <0.05. This should change as insignificant terms are excluded from the model. As D1 has the highest probability of insignificance it should be removed. As D1*T is an interaction including D1, this term should also be removed.

Note: A parallel analysis was performed leaving the D1*T in the regression. It was removed later as terms with high probabilities of insignificance were excluded.

Iteration #2 – Removed D1 and D1*T

Summary of Fit

RSquare	0.938782
RSquare Adj	0.693911
Root Mean Square Error	0.937433
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Model	12	40.428608	3.36905	3.8338	
Error	3	2.636340	0.87878		
C. Total	15	43.064948		0.1478	****High****

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	11.333123	0.84499	13.41	0.0009
P1[1--1]	-0.819358	0.468716	-1.75	0.1788
P2[1--1]	-0.674213	0.468716	-1.44	0.2459
P3[1--1]	1.9643803	0.468716	4.19	0.0248
D2[1--1]	-0.326601	0.468716	-0.70	0.5361
A[1--1]	1.4094037	0.468716	3.01	0.0574
T[1--1]	-0.755993	0.468716	-1.61	0.2052
P1*A[1--1]	-0.28126	0.468716	-0.60	0.5908
P2*T[1--1]	-0.120301	0.468716	-0.26	0.8140
P2*D2[1--1]	0.7227523	0.468716	1.54	0.2207
P3*A[1--1]	0.8419189	0.468716	1.80	0.1703
D2*A[1--1]	-0.985191	0.468716	-2.10	0.1263
A*T[1--1]	0.4030648	0.468716	0.86	0.4531

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F	
P1	1	1	2.685388	3.0558	0.1788	****>0.05****
P2	1	1	1.818250	2.0691	0.2459	****>0.05****
P3	1	1	15.435160	17.5643	0.0248	****>0.05****
D2	1	1	0.426672	0.4855	0.5361	****>0.05****
A	1	1	7.945676	9.0417	0.0574	****>0.05****
T	1	1	2.286101	2.6014	0.2052	****>0.05****
P1*A	1	1	0.316428	0.3601	0.5908	****>0.05****
P2*T	1	1	0.057890	0.0659	0.8140	****>0.05**** ****Highest****
P2*D2	1	1	2.089483	2.3777	0.2207	****>0.05****
P3*A	1	1	2.835310	3.2264	0.1703	****>0.05****
D2*A	1	1	3.882405	4.4179	0.1263	****>0.05****
A*T	1	1	0.649845	0.7395	0.4531	****>0.05****

Summary

Analysis: Analysis of Variance continues to show that this model fit the data no better than a single mean model.

Conclusion: As P2*T has the highest probability of not having an effect on the model it should be removed to establish fit.

Iteration #3 – Removed P2*T

Summary of Fit

RSquare	0.937438
RSquare Adj	0.765392
Root Mean Square Error	0.820705
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	11	40.370718	3.67007	5.4488
Error	4	2.694230	0.67356	Prob > F
C. Total	15	43.064948		0.0579

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	11.272972	0.710752	15.86	<.0001
P1[1--1]	-0.819358	0.410353	-2.00	0.1166
P2[1--1]	-0.674213	0.410353	-1.64	0.1757
P3[1--1]	1.9643803	0.410353	4.79	0.0087
D2[1--1]	-0.326601	0.410353	-0.80	0.4707
A[1--1]	1.4094037	0.410353	3.43	0.0264
T[1--1]	-0.755993	0.410353	-1.84	0.1392
P1*A[1--1]	-0.28126	0.410353	-0.69	0.5307
P2*D2[1--1]	0.7227523	0.410353	1.76	0.1530
P3*A[1--1]	0.8419189	0.410353	2.05	0.1095
D2*A[1--1]	-0.985191	0.410353	-2.40	0.0743
A*T[1--1]	0.4030648	0.410353	0.98	0.3816

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
P1	1	1	2.685388	3.9869	0.1166 ****>0.05****
P2	1	1	1.818250	2.6995	0.1757 ****>0.05****
P3	1	1	15.435160	22.9159	0.0087
D2	1	1	0.426672	0.6335	0.4707 ****>0.05****
A	1	1	7.945676	11.7966	0.0264
T	1	1	2.286101	3.3941	0.1392 ****>0.05****
P1*A	1	1	0.316428	0.4698	0.5307 ****>0.05**** ****Highest****
P2*D2	1	1	2.089483	3.1022	0.1530 ****>0.05****
P3*A	1	1	2.835310	4.2095	0.1095 ****>0.05****
D2*A	1	1	3.882405	5.7640	0.0743 ****>0.05****
A*T	1	1	0.649845	0.9648	0.3816 ****>0.05****

Summary

Analysis: The model now shows capability of fitting the data better than a single mean model (ANOVA Prob>0.1). RSquared and Adjusted RSquared are both good. They begin to drop as more terms are excluded from the model.

Conclusion: Several terms still have prob > 0.05 that they are not significant. As the probabilities change when terms are added or removed, the terms will be removed one at a time, from highest to lowest, until all terms have probabilities of insignificance less than 0.1. As P1*A has the highest probability of insignificance, it will be removed first.

Iteration #4 – Remove P1*A

Summary of Fit

RSquare	0.93009
RSquare Adj	0.790271
Root Mean Square Error	0.775971
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	40.054290	4.00543	6.6521
Error	5	3.010658	0.60213	Prob > F
C. Total	15	43.064948		0.0247

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	11.132342	0.643402	17.30	<.0001
P1[1--1]	-0.819358	0.387986	-2.11	0.0884
P2[1--1]	-0.674213	0.387986	-1.74	0.1428
P3[1--1]	1.9643803	0.387986	5.06	0.0039
D2[1--1]	-0.326601	0.387986	-0.84	0.4383
A[1--1]	1.4094037	0.387986	3.63	0.0150
T[1--1]	-0.755993	0.387986	-1.95	0.1089
P2*D2[1--1]	0.7227523	0.387986	1.86	0.1215
P3*A[1--1]	0.8419189	0.387986	2.17	0.0821
D2*A[1--1]	-0.985191	0.387986	-2.54	0.0519
A*T[1--1]	0.4030648	0.387986	1.04	0.3465

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F	
P1	1	1	2.685388	4.4598	0.0884	****>0.05****
P2	1	1	1.818250	3.0197	0.1428	****>0.05****
P3	1	1	15.435160	25.6342	0.0039	
D2	1	1	0.426672	0.7086	0.4383	****>0.05**** ****Highest****
A	1	1	7.945676	13.1959	0.0150	
T	1	1	2.286101	3.7967	0.1089	****>0.05****
P2*D2	1	1	2.089483	3.4701	0.1215	****>0.05****
P3*A	1	1	2.835310	4.7088	0.0821	
D2*A	1	1	3.882405	6.4478	0.0519	
A*T	1	1	0.649845	1.0792	0.3465	****>0.05****

Summary

Analysis: RSquared lower. Adjusted RSquared higher. They will continue to drop as more terms are removed. Four terms appear to be significant.

Conclusion: Six terms still have prob > 0.05 that they are not significant. Removal of these terms may change the probabilities of the other terms. The term D2 has the high probabilities of insignificance. It will be removed next. Also, the terms P2*D2 and D2*A should also be removed as they contain the term D2.

Note: Although D2*A appears to be significant here, a parallel regression was run and showed that D2*A as well as P2*D2 were removed later as both proved to have high probabilities of insignificance.

Iteration #5 – Remove D2, P2*D2, and D2*A

Summary of Fit

RSquare	0.781511
RSquare Adj	0.590333
Root Mean Square Error	1.084506
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	7	33.655729	4.80796	4.0879
Error	8	9.409219	1.17615	Prob > F
C. Total	15	43.064948		0.0332

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	10.837823	0.766861	14.13	<.0001
P1[1--1]	-0.819358	0.542253	-1.51	0.1692
P2[1--1]	-0.674213	0.542253	-1.24	0.2489
P3[1--1]	1.9643803	0.542253	3.62	0.0068
A[1--1]	1.4094037	0.542253	2.60	0.0317
T[1--1]	-0.755993	0.542253	-1.39	0.2008
P3*A[1--1]	0.8419189	0.542253	1.55	0.1591
A*T[1--1]	0.4030648	0.542253	0.74	0.4785

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
P1	1	1	2.685388	2.2832	0.1692 ****>0.05****
P2	1	1	1.818250	1.5459	0.2489 ****>0.05****
P3	1	1	15.435160	13.1234	0.0068
A	1	1	7.945676	6.7557	0.0317
T	1	1	2.286101	1.9437	0.2008 ****>0.05****
P3*A	1	1	2.835310	2.4107	0.1591 ****>0.05****
A*T	1	1	0.649845	0.5525	0.4785 ****>0.05**** ****Highest****

Summary

Analysis: RSquared and Adjusted RSquared both lower. They will continue to drop as more terms are removed. Two terms appear to be significant.

Conclusion: Five terms still have prob > 0.05 that they are not significant. Removal of these terms may change the probabilities of the other terms. The term A*T has the high probabilities of insignificance. It will be removed next.

Iteration #6 – Remove A*T

Summary of Fit

RSquare	0.766421
RSquare Adj	0.610702
Root Mean Square Error	1.057201
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	33.005884	5.50098	4.9218
Error	9	10.059064	1.11767	Prob > F
C. Total	15	43.064948		0.0169

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	11.039355	0.699273	15.79	<.0001
P1[1--1]	-0.819358	0.5286	-1.55	0.1555
P2[1--1]	-0.674213	0.5286	-1.28	0.2341
P3[1--1]	1.9643803	0.5286	3.72	0.0048
A[1--1]	1.4094037	0.5286	2.67	0.0258
T[1--1]	-0.755993	0.5286	-1.43	0.1865
P3*A[1--1]	0.8419189	0.5286	1.59	0.1457

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F	
P1	1	1	2.685388	2.4027	0.1555	****>0.05****
P2	1	1	1.818250	1.6268	0.2341	****>0.05**** ****Highest****
P3	1	1	15.435160	13.8101	0.0048	
A	1	1	7.945676	7.1091	0.0258	
T	1	1	2.286101	2.0454	0.1865	****>0.05****
P3*A	1	1	2.835310	2.5368	0.1457	****>0.05****

Summary

Analysis: RSquared lower. Adjusted RSquared higher. They will continue to drop as more terms are removed. Two terms appear to be significant.

Conclusion: Four terms still have prob > 0.05 that they are not significant. Removal of these terms may change the probabilities of the other terms. The term P2 has the high probabilities of insignificance. It will be removed next.

Iteration #7 – Remove P2**Summary of Fit**

RSquare	0.7242
RSquare Adj	0.5863
Root Mean Square Error	1.089831
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	31.187634	6.23753	5.2516
Error	10	11.877314	1.18773	Prob > F
C. Total	15	43.064948		0.0127

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	10.702249	0.667382	16.04	<.0001
P1[1--1]	-0.819358	0.544915	-1.50	0.1636
P3[1--1]	1.9643803	0.544915	3.60	0.0048
A[1--1]	1.4094037	0.544915	2.59	0.0271
T[1--1]	-0.755993	0.544915	-1.39	0.1955
P3*A[1--1]	0.8419189	0.544915	1.55	0.1534

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F	
P1	1	1	2.685388	2.2609	0.1636	****>0.05****
P3	1	1	15.435160	12.9955	0.0048	
A	1	1	7.945676	6.6898	0.0271	
T	1	1	2.286101	1.9248	0.1955	****>0.05**** ****Highest****
P3*A	1	1	2.835310	2.3872	0.1534	****>0.05****

Summary

Analysis: RSquared and Adjusted RSquared both lower. They will continue to drop as more terms are removed. Two terms appear to be significant.

Conclusion: Three terms still have prob > 0.05 that they are not significant. Removal of these terms may change the probabilities of the other terms. The term T has the high probabilities of insignificance. It will be removed next.

Iteration #8 – Remove T

Summary of Fit

RSquare	0.671115
RSquare Adj	0.55152
Root Mean Square Error	1.134717
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	28.901533	7.22538	5.6116
Error	11	14.163415	1.28758	Prob > F
C. Total	15	43.064948		0.0104

Lack Of Fit

Using replicated points as the part of residual error that does not depend on the form of the model so that you can test for the adequacy of the form of the model.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	3	2.140022	0.71334	0.4746
Pure Error	8	12.023393	1.50292	Prob > F
Total Error	11	14.163415		0.7085
				Max RSq
				0.7208

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	10.324252	0.634326	16.28	<.0001
P1[1--1]	-0.819358	0.567359	-1.44	0.1766
P3[1--1]	1.9643803	0.567359	3.46	0.0053
A[1--1]	1.4094037	0.567359	2.48	0.0303
P3*A[1--1]	0.8419189	0.567359	1.48	0.1659

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F	
P1	1	1	2.685388	2.0856	0.1766	****>0.05**** ****Highest****
P3	1	1	15.435160	11.9877	0.0053	
A	1	1	7.945676	6.1710	0.0303	
P3*A	1	1	2.835310	2.2020	0.1659	****>0.05****

Summary

Analysis: As Lack of Fit is of concern for this iteration, the Lack of Fit F-test is now included in the analysis. As the value is >0.05, there is no reason to expect a lack of fit. RSquared and Adjusted RSquared both lower. Two terms appear to be significant.

Conclusion: Three terms still have prob > 0.05 that they are not significant. Removal of these terms may change the probabilities of the other terms. The term P1 has the high probabilities of insignificance. It will be removed next.

Iteration #9 – Remove P1

Summary of Fit

RSquare	0.608758
RSquare Adj	0.510948
Root Mean Square Error	1.184933
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	26.216146	8.73872	6.2239
Error	12	16.848802	1.40407	Prob > F
C. Total	15	43.064948		0.0086

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	9.9145735	0.592467	16.73	<.0001
P3[1--1]	1.9643803	0.592467	3.32	0.0062
A[1--1]	1.4094037	0.592467	2.38	0.0348
P3*A[1--1]		0.8419189	0.592467	1.42 0.1808

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
P3	1	1	15.435160	10.9932	0.0062
A	1	1	7.945676	5.6590	0.0348
P3*A	1	1	2.835310	2.0194	0.1808 *****>0.05***** *****Highest*****

Summary

Analysis: RSquared and Adjusted RSquared both lower. Two terms appear to be significant.

Conclusion: One term still has prob > 0.05 that they are not significant. Removal of this term may change the probabilities of the other terms, so P3*A will be removed next.

Iteration #10 – Remove P3*A

Summary of Fit

RSquare	0.54292
RSquare Adj	0.4726
Root Mean Square Error	1.230513
Mean of Response	12.02243
Observations (or Sum Wgts)	16

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	23.380836	11.6904	7.7207
Error	13	19.684112	1.5142	Prob > F
C. Total	15	43.064948		0.0062

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	2.835310	2.83531	2.0194
Pure Error	12	16.848802	1.40407	Prob > F
Total Error	13	19.684112		0.1808
				Max RSq
				0.6088

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	10.335533	0.532828	19.40	<.0001
P3[1--1]	1.9643803	0.615257	3.19	0.0071
A[1--1]	1.4094037	0.615257	2.29	0.0393

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
P3	1	1	15.435160	10.1939	0.0071
A	1	1	7.945676	5.2476	0.0393

Summary

Analysis: No lack of fit. RSquared and Adjusted RSquared both lower. All terms included in the model are significant

Conclusion: The data can be fit by the following model:

$$\text{Impact Strength} = 10.335533 \text{ in-lbf} + 1.9643803 \text{ in-lbf} * [\text{P3}] + 1.4094037 \text{ in-lbf} * [\text{A}]$$

Normalizing the model yields:

$$\text{Impact Strength} = 1.0000 + 0.1900 * [\text{P3}] + 0.1363 * [\text{A}]$$