PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

edited by
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FOREWORD

In recent years, polymers and polymeric composites have found ever increasing acceptance as engineering materials of choice. Polymers and polymeric composites offer a combination of properties not available among the materials they replace, and often promise reduction in part weight and manufacturing cost without sacrificing performance.

The pace of development and introduction to market of new polymeric materials and processing methods has been breathtaking. In some applications, for example, automotive body panels, the average time between introduction and acceptance of revolutionary new technologies and materials is only about five years, a remarkably short time considering that it takes three years to design an automobile from scratch.

It is now well recognized that the processing method is the bottleneck in maintaining the rate of innovation in polymeric engineering materials, and intensified research in improving existing processes and introducing new processes is urgently called for in the areas of preparation of fiber/fabric reinforcements and preforms, process modeling and control, and understanding of the interactions between performance properties and processing parameters.

The papers presented in this Symposium represent a wide spectrum of research activities on polymer and polymeric composite materials. In the area of polymer processing, Nelson and Nicholson applied a finite element method to study the sheet sealing process. Soh, and Tseng, Kaplan, and Arinze studied the injection molding process with the goal to improve the operation and mold design.

In preparation of preforms, Du, Popper, and Chou modeled the circular braiding process; Byun, Leach, Stroud and Chou present a theoretical method of predicting the porosity of 3-D preforms. Kumar, Weller, and Hoffer studied the bubble nucleation and growth. In the related area of fiber treatment, Hamade and Pickwick investigated the electrostatic processing.

Processing of continuous fiber reinforced thermoplastics has been studied by Soh and Jeszke and by Tsahalis, Pantelakis and Schulze. While the former studied the material behavior under the thermostamping process, the latter used a diaphragm forming process. Dimensional tolerances of processed composites are modeled by Githuku and Giacomin for extruded pipe wall thickness distribution and by Oswald for warping of compression molded SMC sheet. Friedrichs, Guceri, Subbiah, and Altan investigated the mold filling process.

In the area of thermoset processing, Hamade and Wharfield present a case study of automotive body panel manufacturing process development using an SRIM process and Chiou and Letton studied empirical identification of the curing kinetics of thermosets. Arefmanesh and Advani report a computer modeling of bubble growth in convected Maxwell fluid.

In summary, the new developments in processing of polymer and polymeric composites are well illustrated in this symposium volume. It is hoped that this symposium will be of particular interest to scientists and engineers engaged in the area of polymers and polymeric composites processing at a time when the importance of material processing is being recognized as vital to the nation's economy and welfare.

This symposium is sponsored by the ASME Materials Division; the editors acknowledge their support and the help of the ASME staff. The editors would also like to take this opportunity to thank the authors for the quality of the work submitted to the symposium and reviewers for their efforts during the preparation of this volume.

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CONTENTS

A THREE DIMENSIONAL REPRESENTATION OF SLUMP IN PLASTIC PIPE EXTRUSION

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ABSTRACT

Extruded plastic pipe leaving an annular die is solidified in a long cooling tank by spraying the outer surface with cold water. The inside surface can take a long time to solidify as the solidification progresses radially inward. This results in flow of molten polymer down the inside of the pipe. This gravity flow of molten extrudate is called slumping, and it can cause serious non-uniformity in pipe wall thickness particularly in large diameter, thick walled pipes. It can also lead to another phenomenon known as "knuckle" formation where melt accumulates at specific locations. A simple numerical scheme to model this flow has been developed and has been ran on a VAX mainframe computer. Three dimensional graphical illustrations of the slumping phenomenon based on this simulation are presented in this paper.

NOMENCLATURE

E	=	Eccentricity of extrudate exiting die, m
R_i	=	Inner radius at die, m
R_m	=	Radius at melt front, m
R_o	=	Outer radius, m
T	=	Temperature, deg C
t_f	=	Total solidification time, s
$\langle V_z \rangle$	=	Mean velocity
Δt	=	Time step, s
$\Delta\Theta$	=	Angular step size, radians
δ	=	Melt thickness, m
μ	=	Viscosity, Pa.s
ρ_m	=	Density of melt, Kg/cm^3
ρ_s	=	Density of solid pipe, Kg/cm^3

INTRODUCTION:

Plastic pipe is normally produced by extruding molten polymer through an annular die. After leaving the die, the pipe passes through a sizing sleeve and into a cooling tank for solidification. The circular shape of the outer surface is obtained when the pipe presses firmly against the calibration sleeve. For large diameter, thick walled pipes, the firm contact is achieved by applying pressure (eg compressed air) on the inside of the pipe after the end has been sealed by a rubber plug. The pipe is then solidified by spraying the outer surface with cold water.

Thick-walled HDPE pipes (pipes in the medium and high pressure ranges) have very long cooling times due to the low thermal conductivity of polyethylene. Since the outer surface is cooled first, the solidification starts on the outer surface and progresses slowly radially inward. On the inside of the tube where the pipe has not solidified, the melt flows gently downwards under its own weight. This self-weight flow will govern the final pipe wall thickness distribution (1).

Self weight flow or slump is undesirable since it can give rise to serious non-uniformities in the pipe wall thickness. The processor who is unable to meet pipe thickness specifications mainly as a result of this self weight flow can incur huge losses.

Increasing melt viscosity is one way to diminish self weight flow. Melt viscosity can be increased by chilling the mandrel (2,3) or by injecting a chemically inert liquefied gas eg. liquid nitrogen (4,5). These exotic methods are seldom justified except when for example, material orientation must be preserved.

Self weight flow can also be counteracted by a compensating adjustment of the die eccentricity. Experienced operators can make this adjustment based on thickness distributions on cut sections of non-uniform pipe until the wall thickness distribution is acceptable. Pipe wall thickness distribution has been monitored automatically using capacitive (6), inductive (7) and ultrasonic (8,9) techniques. Automatic adjustment of die eccentricity has been carried out by attaching servo actuators to a specially designed mandrel (10,11,12,13).

Existing solutions for extrudate cooling in the post die region neglect self weight flow; a simple expansion of the die cross section is assumed for pipe wall thickness distribution. Giacomin and Doshi (1) have shown that more accurate predictions for pipe wall thickness distribution are obtained by modeling self weight flow. Based on this work, a three dimensional representation of self weight flow is presented.

METHODOLOGY

For self weight flow inside a solidifying tube, the complete solution to the equations of motion is not practicable. However, this flow is approximated by considering a cascade of interconnected inclined plates. For non-isothermal flow down an inclined plane, the mean velocity of a temperature dependent fluid is:

$$\langle V_z \rangle = \frac{K}{\alpha^2} [(2 - \alpha - 2/\alpha) \exp(\alpha) + 2/\alpha] \qquad (1)$$

where:

$$K = (\rho_m \, g \, \delta^2 \, \cos\beta)/\mu_x \quad \text{and} \quad \alpha = \ln(\mu_x/\mu_m),$$

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ρ_m is the melt density, g is acceleration due to gravity, β is the angle between the plate and the vertical direction, μ_x is the viscosity at the inside temperature and μ_m is the viscosity at the melting point.

An analytical solution is obtained when the temperature dependence of viscosity takes the form:

$$\mu = A \exp (-BT) \tag{2}$$

A and B are constants that can be evaluated given the viscosities at two different temperatures.

Euler's numerical method is used to determine the thickness on a plate i at time $t+\Delta t$ based on the thickness on plate i at the previous time t:

$$\delta_i(t+\Delta t) = \delta_i(t) + \frac{d\delta}{dt}\Delta t \tag{3}$$

From conservation of mass around plate i:

$$\frac{d\delta}{dt} = \frac{\delta}{R_m \Delta\Theta}[\langle V_z\rangle_i - \langle V_z\rangle_{i-1}] \tag{4}$$

where the radius at the melt front, R_m is determined from heat transfer considerations. The melt front is assumed to advance at a constant rate.

To obtain a prediction of wall thickness distribution, one must know the inner and outer extrudate diameters as the extrudate leaves the die, the extrudate eccentricity, the total cooling time, the temperature of the pipe inner surface T_x, the polymer melting point T_m and the liquid and solid densities. Using computer code written in FORTRAN and ran on a VAX mainframe computer, wall thickness predictions are obtained in a few seconds.

RESULTS

The following parameters were used for evaluating the model predictions:

R_o=0.4395 m, T_x=204°C, μ(204°C)=1.2*10^6 Pa.s, ρ_m=755 Kg/m^3
R_i=0.3511 m, T_m=129°C, μ(260°C)=2.2*10^5 Pa.s, ρ_s=955 Kg/m^3
t_f=38,400 s, Δt=10 s, $\Delta\Theta$=π/100,

In Figure 1 the extrudate eccentricity is E=0.0118 m. The 3-D plot shows how the thickness of a pipe changes along the cooling line as the pipe solidifies. Initially the pipe is thickest at the top and due to self weight flow it progressively becomes thinner on the upper quadrant and thicker on the lower quadrant. The plot shows a maximum thickness at a point on the lower quadrant. This phenomenon is referred to as knuckle formation and it has been observed on extrusion lines producing large diameter pipes when the die is eccentric. In Figure 2 where initially the extrudate is concentric (E=0), the melt flows down the pipe and eventually the pipe is thinnest at the top and thickest at the bottom. For an initially concentric extrudate, knuckle formation is not predicted. Figures 3 & 4 show the half pipe sections in both cases. It is clear from these plots that the pipe produced with the eccentric die has a more uniform wall thickness distribution even though knuckling occurs.

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CONCLUSION

Self weight flow in annular extrudates can be modeled using a cascade of inclined plates and applying a simple numerical technique to determine the variation of wall thickness distribution with time. The authors plan to incorporate more sophisticated heat transfer equations into the model as well as to compare the model predictions with commercial scale pipe processing data. The model could be very useful in determining optimum die eccentricity prior to start-up thereby reducing start-up costs that are usually incurred from trial and error manual determination of optimum eccentricity. Furthermore, this model could also be used for developing a control strategy for automatic control of die eccentricity.

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PIPE WALL THICKNESS DISTRIBUTION (E=0.0118) ALONG PIPE LENGTH

FIG. I
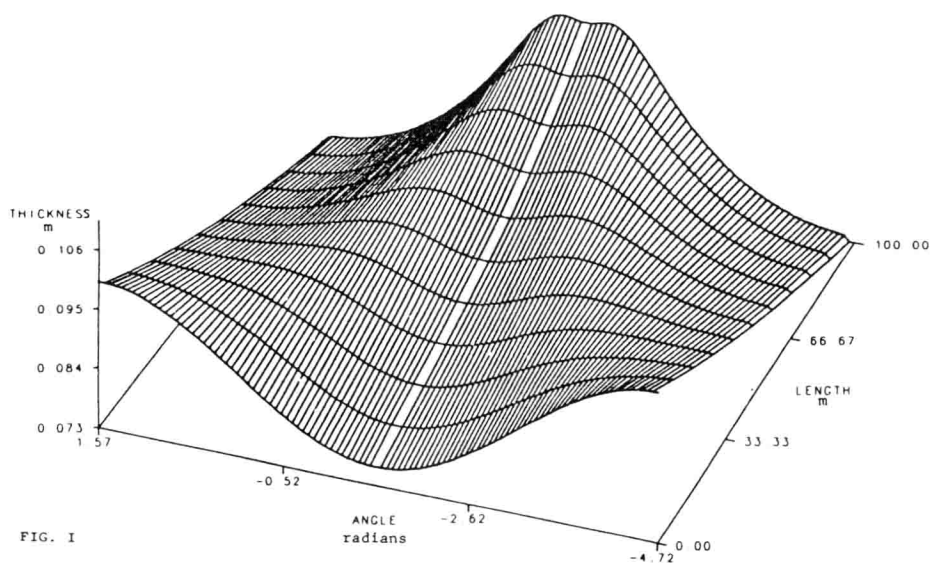
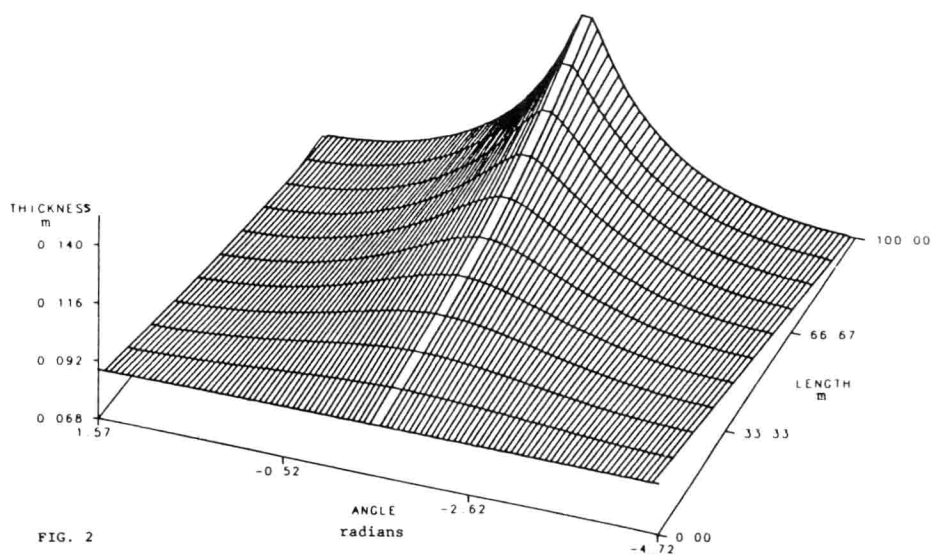## PIPE WALL THICKNESS DISTRIBUTION (E=0) ALONG PIPE LENGTH

FIG. 2

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FIGURE 3 : SELF WEIGHT FLOW (E=0.0118)

LEGEND
MANDREL POSITION
FINAL INNER RADIUS
OUTER RADIUS

FIGURE 4 : SELF WEIGHT FLOW (E=0)

LEGEND
MANDREL POSITION
FINAL INNER RADIUS
OUTER RADIUS
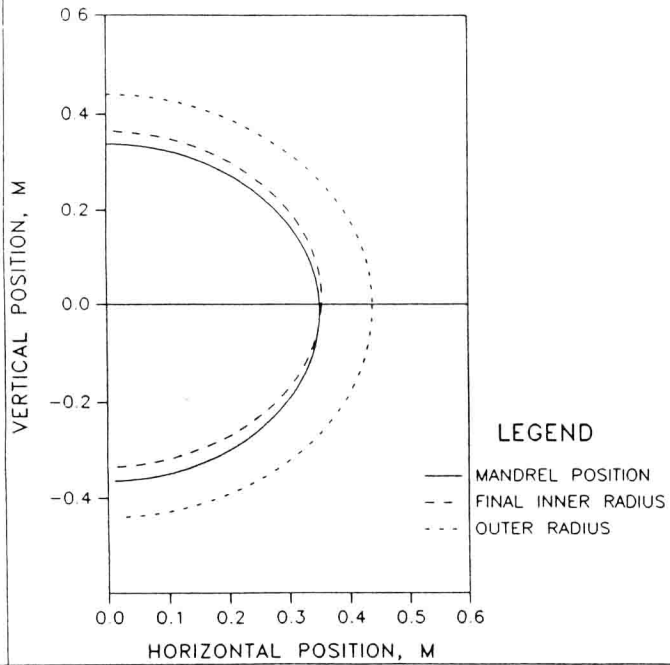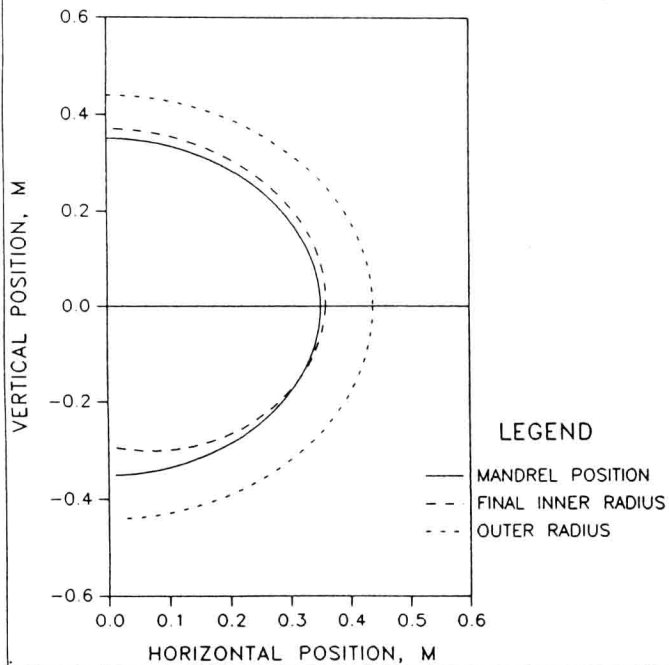
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AUTOMOTIVE EXTERIOR BODY PANELS WITH POLYUREA AND THE REACTION INJECTION MOLDING (R.I.M.) PROCESS

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ABSTRACT

A process was developed to manufacture automotive exterior body panels from Polyurea composites by using the Reaction Injection Molding (R.I.M.) method. The produced panels have many structural and economical advantages over conventional steel and other composite panels, such as reduced weight, lower cost and improved on-line/off-line assembly. This is done without compromising critical dimensional and physical characteristics. Utilization of Polyurea (R.I.M.) process by carefully controlling filler type and resulting key physical characteristics can produce panels to fulfill and exceed assembly plant processing requirements without forfeiting durability, performance, and appearance. Controlling factors for this process included: the selection of proper material to meet needed physical properties such as distinctness of image (D.O.I.), impact, coefficient of linear thermal expansion (C.L.T.E.), heat distortion, heat sag, shrink and other product relation properties. This involved the development and optimization of material suitability (solvents, fillers, paint), tooling and equipment optimization (after mixer and gate design, injection rate, oven design, paint buck orientation, moldability) and actual processing of material (molding, post curing, painting/prime, part installation, assembly plant painting/color).

Computer models with spreadsheets were developed to aid in the design, evaluation and eventual determination of total manufacturing facility. The spreadsheet models with required input variables define instantaneously plant equipment/tooling for quick investment and total business plan assessment in using polyurea (R.I.M.) for exterior body panel applications.

I. INTRODUCTION

The Polyurethane family of materials has found usefulness in selected automotive applications where design flexibility and styling have dictated polyurethane utilization. Fascias, bumper covers, stone shields, claddings, foam seats, and spats are among the most utilized applications today for polyurethane. The future, however, offers a greater range of applications for the polyurethane family of materials such as exterior vertical and horizontal body panels, interior door and instrument panels, and structural cross members and bumper beams. The focus of this paper presently is to identify with the application of the reaction injection molding (R.I.M.) process to produce exterior body panels made from the polyurethane family of materials polyurea and discuss developmental strategies that can be used to obtain a viable material and product.[1]

Chemistry

Polyurea is based from basic polyurethane chemistry in which a polyol is substituted with an polyamine to produce a urea linkage when reacted with isocyanate. Likewise, polyureas are perfectly suited for reaction injection molding (R.I.M.), as are polyurethanes, due to the fast exothermic reaction resulting from urea formation. The advantages of polyurea over polyurethane are two fold. With polyurea, kinetics can be varied more so than polyurethane without forfeit of critical physical properties such as heat sag and heat distortion; thus allowing for more innovative chemistries to meet specific needs especially of automotive body panels. In addition, heat distortion and sag properties are superior to polyurethanes primarily due to lower water absorption levels which is directly related to the urea vs. urethane linkages. Of greater importance for the manufacture of exterior body panels, lower water absorption corresponds to improved dimensional stability which is a major requirement of body panels in general. The basic polyurethane and polyurea microcellular equations are given below:[1-6]

(EQUATION #1)

(EQUATION #2)

8
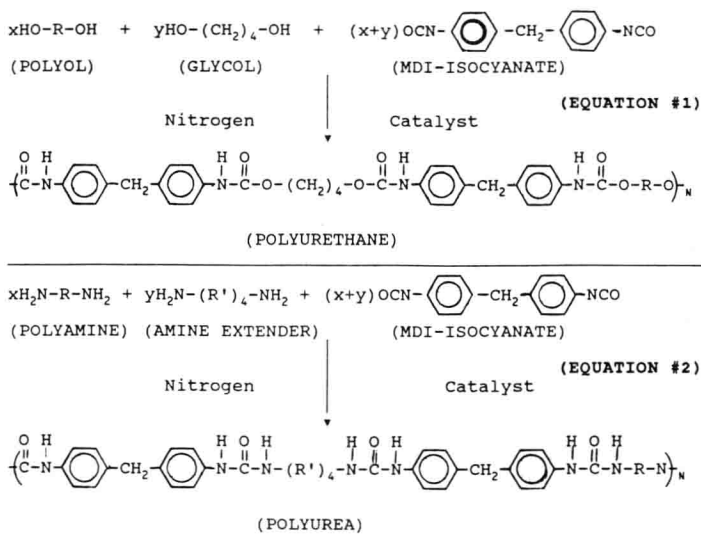
Physical Property Requirements

With the need of rigid materials for replacement of certain automotive exterior parts, the combination of processing advantages, lightweight, adequate impact resistance, superior rigidity, and apparently acceptable thermal properties make R.R.I.M. (Reinforced R.I.M.) an attractive candidate for automobile body panels such as fenders. In the R.R.I.M. process, however, it is important to find a reinforcement that will produce maximum physical properties without causing processing problems. Milled fiber glass has been considered to be the preferred R.I.M. reinforcement due to its compatibility with appropriate R.I.M. machinery and its lower degree of degradation of impact properties when compared to other inorganic fillers. Mica and Wollastonite, however, have become a more important consideration due to the high surface characteristics of distinctness of image (D.O.I). and gloss which are a key requirement of body panels. Glass does not fulfill this critical requirement. It has also been found that there is a considerable degree of fiber orientation along mold flow lines, thus leading to an approximately 2:1 enhancement of properties in that direction with fibrous fillers. Mica, however, contributes isotropic physical properties, particularly coefficient of linear thermal expansion (C.L.T.E.), which are desired in automotive applications where high temperatures are required. [1, 3, 6]

Two systems were studied; A-pure polyurea and B-hybrid polyurea/polyurethane. Flake glass reinforcement fillers were for the two systems used as the basis of physical properties due to flake glasses uniform spherical geometry which would contribute to desired isotropic physical expansion properties. [1, 5]

The physical properties for both A and B systems are shown in Table 1. Other fillers were also considered and their selected properties are shown by Table 2.

The differential in C.L.T.E.'s is essentially the same regardless of the filler type which indicates that another property in combination with C.L.T.E. must be a contributor to surface appearance. [1, 3-5]

TABLE 1: PHYSICAL PROPERTIES
21% Glass Flake

Properties	System A	System B
Specific Gravity	1.19	1.25
Flex Modulus, psi	240,000	200,000
Tensile Strength, psi	4,000	4,575
Tear Strength, P.L.I.	750	625
Elongation (%)	50	43
IZOD Impact - Notched, ft.lb/in	4.0	3.5
Heat Sag, Inches (6 inch overhang) - 1 hour @ 250°F	0.2	0.2
- 1 hour @ 350°F	0.4	0.5
C.L.T.E. $X10^{-6}/°F$ @ 70°F	30.0	33.0
*D.O.I. (Steel and un-filled polyurea = 97)	69	77

Referring to Table 2, Wollastonite and Mica offer several interesting combinations to be considered. Wollastonite offers lower hardness than glass for better compatibility with substrate but lower C.L.T.E.'s than glass which would be less desireable, due to lower surface appearance than glass because of the largest C.L.T.E. differential as compared to glass. ($\triangle$ Wollastonite = $67 \times 10^{-6}/°F$, and $\triangle$ Glass = $65 \times 10^{-6}/°F$). As noted above, however, this differential is negligible comparably so harness would be more contributing.[1, 4, 5, 7]

TABLE 2: SELECTED PROPERTIES OF FILLERS

	WOLLASTONITE	GLASS	MICA	$CaCO_3$
C.L.T.E. ($°F \times 10^{-6}$)	3.2	5	4	5
DENSITY (g/cm^3)	2.90	2.54	2.82	2.71
THERMAL CONDUCTIVITY ($cal/g.s.°C \times 10^3$)	6.0	7.0	6.0	5.6
SPECIFIC HEAT ($cal/g.°C$)	.240	0.190	.206	.205
DIELECTRIC CONSTANT	6.0	4.3	.23	6.14
HARDNESS (MOHS)	5-5.5	6.5-7.0	2.5-3.0	2.5-3.0
YOUNG'S MODULUS ($Kg/cm^3 \times 10^{-6}$)	3.0	3.0	3.0	2.60

Table 3 reveals the above filler/polyurea system physical property results. In addition to previous values, heat distortion is also included which indicates a temperature where permanent distortion occurs when mechanical stress is placed upon the substrate. Tradeoffs of either substrate are apparent but each substrate has benefits which make them worth considering for body panel material.[1]

TABLE 3: PHYSICAL PROPERTIES

Properties	System A (with Mica)		System B (with Wollastonite)	
Flow Orientation	Para.	Perp.	Para.	Perp.
Specific Gravity	1.20	1.20	1.35	1.35
Flex Modulus, psi	256,000	248,000	260,000	240,000
Tensile Strength, psi	5,215	4,955	4,925	4,880
Tear Strength, P.L.I.	750	725	675	580
Elongation (%)	20	20	14	11
IZOD Impact - Notched, ft.lb/in	2.1	2.1	1.9	1.8
Heat Sag, Inches - 1 hour @ 350°F (6 inch overhang)	0.19	0.18	0.45	0.40
Heat Distortion (°F) @ 66 psi	369	359	350	310
C.L.T.E. $X10^{-6}/°F$ @ 70°F	29.0	30.0	27.0	36.0
*D.O.I. (Steel and un-filled polyurea = 97)	90	90	94	94

Overall, leading indicators reveal that, logistically, polyurea has the material requirements necessary for large heat resistant exterior body panels.[1, 8]

II. DEVELOPMENT
After Mixer Design

After mixer design is a very important consideration when product cost optimization is desired. A model to design a "harp-type" after mixer was developed to aid in optimizing after mixer geometries. There are basically two types of after mixers in industry today, the "harp-type" and the "peanut-type", but because cost optimization is the objective the "harp-type" (see Figures 1 and 2) after-mixer accomplishes mixing by impingement which is more effective than the "peanut-type" after-mixer. This accomplishes mixing by venturi-like velocity changes. Moreover, laminar flow output is required with either design, due to the required uniform flow into mold for material consistency, so it should be quite clear that under the conditions mentioned the "harp-type" after mixer would be and is the most cost efficient mixing strategy because complete mixing occurs earlier which results in less volume of material required.[1, 2, 9-11]

All the dimensional requirements resulted from controlling the Reynolds Number has proved on each of the injection rate scenarios where tools were cut to optimize after-mixer design and minimize scrap. This resulted in lower cost to produce the part. [1, 2, 9-16]

Dimensional Verification

Steel substrates require tight tolerances due to assembly limitations for fit and finish. Typical tolerance for steel body panels is +/- 0.25 mm which is a result of steel body panels capability of being flexed more than +/- .25 mm with out being permanently distorted due to excessive force required to do so. With plastics, as one might expect, flexibility is a characteristic which would ultimately lend itself to wider tolerances as long as surface profiles are maintained. In the foregoing paragraphs, a complete strategy for determining tolerance requirements for polyurea substrates will be presented which will reveal tolerance capability of +/- 1.0 mm and greater can be achieved with no forfeit of assembly and/or geometrical integrity.[1]

From reviewing Figures 3 and 4, most sequential checks reveal a very consistent plot except for the right hand fixture at point #1 which has the highest standard deviation. Excluding this point from the evaluation because of its non-conformity, yields a maximum standard deviation of about 0.2 mm for both right hand and left hand fixtures. From equation (3) above, a minimum total tolerance would be 2.0 mm or +/- 1.00 mm. The fixtures are then only good for tolerances at or above those indicated.[1]

After reviewing capability graphs (C_p & C_{pk}), Figures 5 and 6, a note should be made between the different materials as they are gauged between post cure and prime that Material "B" tends to keep its shape throughout the different heat processes where as Material "A" varies but improves and approaches and exceeds Material "B". Refer to right hand fixtured parts which had better documentation throughout the processing, handling, and measuring activities.[1]