6-30-1974

The effect of dry-blending high density polyethylene on final product properties

Charles H. Klestadt
New Jersey Institute of Technology

Recommended Citation

Klestadt, Charles H., "The effect of dry-blending high density polyethylene on final product properties" (1974). *Theses*. 2177.
https://digitalcommons.njit.edu/theses/2177

THE EFFECT OF DRY-BLENDING HIGH DENSITY POLYETHYLENE ON FINAL PRODUCT PROPERTIES

BY

CHARLES H. KLESTADT

A THESIS
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE WITH A MAJOR IN POLYMER ENGINEERING
AT
NEWARK COLLEGE OF ENGINEERING

NEWARK, NEW JERSEY

1974

ABSTRACT

The Effect of Dry-Blending Polyethylene on Final Product Properties

The incentives for Dry-Blending Polyethylenes of varying property type may be economic gain, improved product quality, or both. The manufacturers' latest mode of operation involves seeking to meet their customers' needs with a product line made by using one catalyst system and operating at maximum capacity, while varying the fewest possible control parameters. Off-spec materials and on-spec materials not fitting customers' requirements are two prime targets for additional profits with proper dry blending techniques. The approach used in solving the problem involved starting with an existing product line and converting these products into a number of experimental blends. The blends were to be fully tested for both rheological and physical properties after injection molding test specimens. Each final product property could then be correlated with the original properties of the materials used for each blend, yielding a statistically significant regression equation for that property. This could be used for predicting levels of that property for future blends. With these equations in hand, the manufacturer could dry-blend to meet with customer specs or for depletion of off-specification materials as he chooses.

APPROVAL OF THESIS

THE EFFECT OF DRY-BLENDING HIGH DENSITY POLYETHYLENE ON FINAL PRODUCT PROPERTIES

BY

CHARLES H. KLESTADT

FOR

DEPARTMENT OF CHEMISTRY
AND CHEMICAL ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

JUNE, 1974

ACKNOWLEDGMENT

The author is thankful to Messrs. L. A. Kaiser and J. P. Porter for their technical assistance in experimentation and testing; to Mr. G. L. Champagne for his analytical support; to Mr. C. W. Sandford, Director of HDPE R & D and Dr. W. T. Zagar, Manager of Product Development, both of Allied Chemical Corporation, Baton Rouge, Louisiana, for their interest and guidance; to Dr. Wenisch for his long distance constructive support; to Mrs. K. Jenkins for her aid in publication preparation; and to Allied Chemical Corporation for permission to report on this work.

TABLE OF CONTENTS

CHAPTER PAGE

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

CHAPTER I

THE PROBLEM AND DEFINITION OF TERMS USED

Recent resin shortages have given material suppliers in the Plastics industry an abnormal sense of security of market, since every pound produced has been sold at a high price. Past history indicates this trend will come to a halt at which time, once again, the marketable materials will be those of consistent and good quality. The high density polyethylene (HDPE) market has shifted from that of a highly competitive supply business to a highly competitive demand business. In recent months, many smaller users literally have been forced out of business.

The obvious promise of increased future capacity of HDPE will return some sanity to the supply business whereby the resin suppliers will be prompted to increase both their stream factor and their material quality in order to maintain present levels of business share.

Although there has been an increasing knowledge of the hows and whys of producing HDPE since it was first introduced circa 1956, and although advanced computer control systems are running many of the production units of the major suppliers, production of off-specification material has always been a by-product of the polymerization process. Fear of inhomogeneity and incompatible flow behavior have limited the blending of off-specification materials whereby widely amiss materials are not blended but sold at depressed prices. This practice is safe, but is it smart?

I. THE PROBLEM

Statement of the problem. It was the purpose of the study presented herein (1) to compare the performance of blends of HDPE versus those of the pure component materials used in making the blends; (2) to develop statistically significant regression equations relating final molded part properties to the rheological properties of the virgin resins; and (3) to propose the use of these regression equations to optimize blend performance and perhaps to reach even higher property levels than with pure resins.

Importance of the study. The impact of the study on resin producers is obvious. If yields of on-specification material are increased appreciably by raising stream factors from 90% to 98% as a result of dry blending, net profit of a 300MM lb/yr plant would increase $720,000/year on the basis of a $.03/lb differential for on-spec versus off-spec material. Justification of blending equipment becomes quite reasonable at these profit levels. If the burden of availability of widely varying material types can be taken off the polymerization end of a plant and perhaps placed on a highly sophisticated computer controlled blending system, both resin suppliers and users would benefit. The development of test methods that mean something to the industry as opposed to rheological measurements that mean something to the research scientists has aided the study of overall cause and effect of HDPE material behavior.

II. DEFINITIONS OF TERMS USED

Disc Mold. A large portion of the data was developed via testing of specimens cut from discs made by injection molding HDPE in a 7" diameter, center sprued disc mold.

Environmental Stress Crack Test (ESCR). A special test was developed for the measurement of the environmental stress crack resistance of injection molding type materials, since ASTM procedures prove too rigorous to obtain any variance in failure times. The test conditions used for this work specify running a nominal .045" thickness specimen, unnotched, at room temperature, with a 100% Igepal solution as the stress cracking agent.

Transverse and Radial Specimens. Since orientation effects are often critical to material performance evaluations, data were obtained, where possible, on specimens cut in two varying machine directions. Figure 1 illustrates specimens cut in both the transverse and radial directions. These terms refer to across the flow path of the material during molding and along the flow path of the material during molding, respectively.

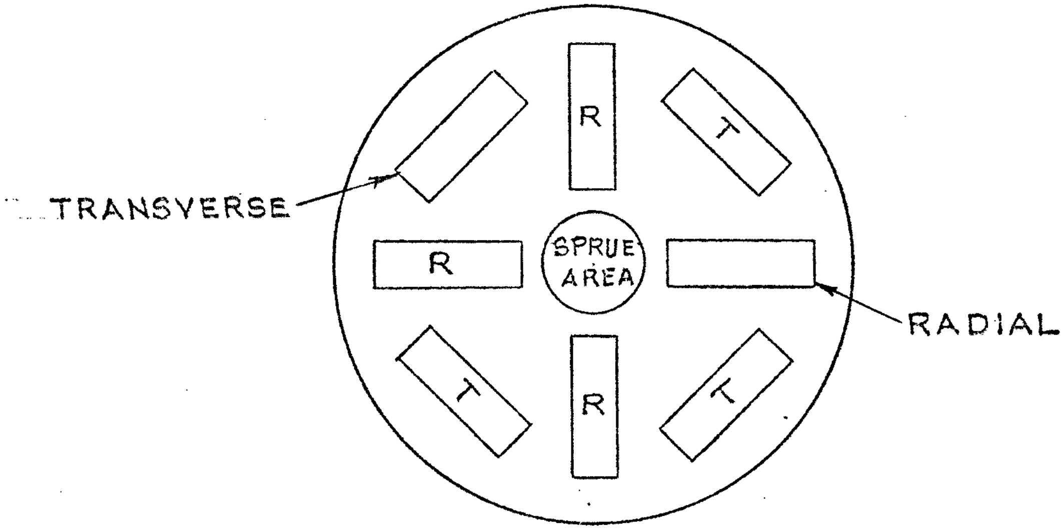
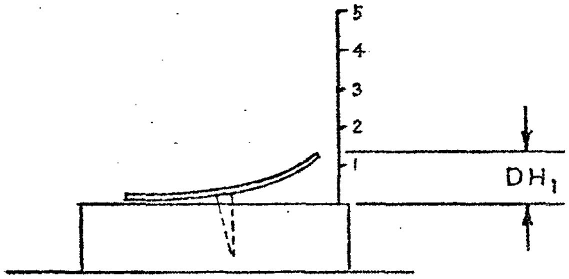


FIGURE 1

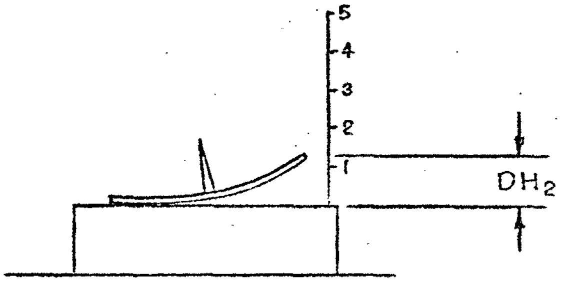
DEFINITION OF RADIAL AND TRANSVERSE SPECIMENS

<u>Dart Impact Strength Test (DI)</u>. A test was developed in an attempt to measure material impact strength via simulation of impact by using a dart drop with a prescribed number of specimen discs. Using the apparatus designed for free falling dart impact test described in ASTM-D170 for testing film specimens and stair-stepping weights of dart rather than height of dart drop yielded impact strength measurements noted in ft.lbs. The numbers obtained are not absolute, but may be used for comparative purposes.

Warpage Test (WP). A simple method for measuring warpage of the disc was devised by measuring a height deviation from a central plane. The height deviation was measured both above and below the central plane and the sum of the two heights in inches is used as a warpage factor (see Figure 2).



SPRUE DOWN



SPRUE UP

FIGURE 2

WARPAGE FACTOR MEASUREMENT

Tensile Impact Strength (TI). Tensile impact data is normally expressed in ft.lb. per in^2; however, since this study was of a comparative nature with data being used for statistical analyses only, raw impact numbers were used and should be treated as tensile impact factors only.

Spiral Flow Test (SP Flow). This test measures length of flow of a material in a .030" x 3/8" spiral channel mold under standard injection molding conditions. The resulting flow length in inches gives the investigator a good estimate of actual molding flow behavior as opposed to standard rheological flow behavior measurements (i.e., melt index).

CHAPTER II

REVIEW OF THE LITERATURE

An enormous quantity of work has been published regarding the use of HDPE as a modifier in blends with other thermoplastics, especially LDPE. However, very little has been reported regarding the dry-blending of similar HDPE type materials. Moreover, the work done in this area has been limited to predicting final rheological properties only, with no mention of physical properties of final products that would be of prime interest to the fabricators of these resins.

Sabia[1] developed a relationship predicting melt index of blends as a function of weight percent composition:

$$\text{LOG MI}_{\text{Blend}} = W_1 \text{LOG MI}_1 + W_2 \text{LOG MI}_2$$

where: W_1 = Wt. % of Component No. 1

W_2 = Wt. % of Component No. 2

On this basis, he concluded that blend rheological properties may be predicted with low error. This conclusion has definitely been supported by the data presented in future chapters herein. It has been shown that rheological parameters such as melt index, molecular weight distribution and spiral flow measurements are directly correlatable to the original component properties and their respective weight percents with a very high degree of statistical reliability. The equation developed in this work is shown below:

$$MI_{AM} = -1.9933 + .14637M_1 + .82228W_2M_2\rho_2 + .71763W_1M_1$$

The correlation coefficient is high at R = .97 and the F-ratio significance level is much greater than 99.9%.

H. P. Schreiber[2] claimed that blends of greater than or equal to two linear high density polyethylenes may be prepared yielding a predictable viscosity based on the $\overline{Mn}$ and $\overline{Mw}$ of the components. The following equation states the theory:

$$\begin{aligned} LOG(\eta'd/\eta''d) = {} & 1.5[LOG(Mw/4x10^4) - .62] \\ & -1.23[LOG(Mw/Mn) - .301] \end{aligned}$$

where $\eta'd$ = upper critical melt viscosity

$\eta''d$ = lower critical melt viscosity

Mw = wt. avg. molecular weight of blend

Mn = number avg. molecular weight of blend

The logarithmic relationship noted here is similar to that described by Sabia. However, Schreiber chose to work with molecular weight as opposed to melt index.

Both of the above investigators failed to relate the predicted rheological behavior of these blends to physical properties of an end use part. Hillmer[3], however, prepared powder blends of HDPE in an attempt to improve stress crack resistance behavior of these homopolymers. Stress crack data were compared to previous results and showed improvement to some degree.

As noted above, the trend of these investigators had been directed toward research tools such as melt viscosity and other rheological parameters. There is an obvious need for the prediction of physical properties that can be employed in the marketplace rather than in the laboratory.

In dealing with pure materials, many investigators have found any number of good quality control tools by sampling finished parts for properties of interest. Sharp[4] stated that for quality control procedures to be truly effective, they ought to be based on the testing of molded parts by methods related to the end use performance requirements. He noted the importance of multi-axial impact testing (falling ball and/or dart) as well as the measurement of stress crack resistance.

It should be obvious that each particular end use application carries its own set of critical final part properties. More recent investigations have been performed using molded part physical parameters as control criteria. Prose and Johnson[5] discuss the use of tensile impact data as a means of determining the effects of various molding conditions on performance of molded parts. They concluded that higher melt index materials exhibit low anisotropy as indicated by only slight variation in the tensile impact test due to orientation.

Paschke[6], in an attempt to more efficiently characterize a number of HDPE materials for a particular application, used a shrinkage test on a molded part and concluded that a definite relationship existed between molecular parameters and specific injection molding parameters. Warp and shrinkage are relatable final product properties. The study presented in future chapters using warpage as a quality control test procedure supports Paschke's conclusion. These related parameters are highly predictable based on material rheological properties and, as Paschke noted, should aid the injection molder and the raw material manufacturer reach a better understanding.

Allen and Van Putte[7] described a method for determining process control conditions in the injection molding process by measuring molded part parameters such as stiffness, drop impact strength, shrinkage, and tensile impact strength. Their work with polystyrene may be related to other polymer systems in that molding techniques are made much more obvious by measuring part properties than they are by only measuring material rheologicals.

It would appear then that material selection by the end user should be based on his particular application. If a material supplier can predict final part performance based on rheological measurements and relay to the injection molder those parameters that mean something to him (stiffness, impact strength), then the industry could tolerate the sale of resin "code name" to any of a number of varying markets.

CHAPTER III

EXPERIMENTAL APPROACH

The experimental technique was so designed as to have statistical significance whereby direct correlations could be derived for the dependent variables based on the varying levels of the independent variables.

All the data used in the study were developed from this work and the data array was unique in that there were no spurious values. The development of the data involved analytical testing of molded preblends for a number of physical parameters considered important to the process industry.

The data as accumulated were handled via stepwise regression analyses yielding sets of equations allowing the investigator to (1) draw conclusions about the data itself; (2) recommend blend ratios for future materials; and (3) predict the final product properties of these new blends.

CHAPTER IV

EXPERIMENTAL DESIGN AND PHYSICAL TESTING

An experimental design was set up to handle all possible combinations of 2-component blends of five materials used for injection molding applications. The materials supplied by Allied Chemical Corporation were all produced via the Phillips solution form process. For simplicity, the materials were labeled I, II, III, IV and V. Five varying blend ratios were used for each of the fifteen possible blends, yielding a total of seventy-five experiments. It should be noted that for five of these combinations like materials are treated as unlike materials, giving the investigator a measure of error as to blending capabilities. This may be seen in Table I for blend types 1, 6, 10, 13 and 15.

The blends were all made in a twenty-five pound tumbler blender by physically mixing the component ratios for fifteen minutes. After mixing, the blends were placed in sample bags and treated as homogeneous mixes thereafter. Each sample was then molded under strictly controlled conditions yielding both a disc specimen and a spiral flow specimen (two different molds were used).

The seven-inch disc specimens were used to test the following: (1) as molded melt index; (2) as molded

TABLE I

75 BLEND ARRANGEMENT

Blend Type	Blend No.	Component A	Component B	% Component A
1	1	I	I	.1
1	2	I	I	.3
1	3	I	I	.5
1	4	I	I	.7
1	5	I	I	.9
2	6	I	II	.1
2	7	I	II	.3
2	8	I	II	.5
2	9	I	II	.7
2	10	I	II	.9
3	11	I	III	.1
3	12	I	III	.3
3	13	I	III	.5
3	14	I	III	.7
3	15	I	III	.9
4	16	I	IV	.1
4	17	I	IV	.3
4	18	I	IV	.5
4	19	I	IV	.7
4	20	I	IV	.9
5	21	I	V	.1
5	22	I	V	.3
5	23	I	V	.5
5	24	I	V	.7
5	25	I	V	.9
6	26	II	II	.1
6	27	II	II	.3
6	28	II	II	.5
6	29	II	II	.7
6	30	II	II	.9
7	31	II	III	.1
7	32	II	III	.3
7	33	II	III	.5
7	34	II	III	.7
7	35	II	III	.9
8	36	II	IV	.1
8	37	II	IV	.3
8	38	II	IV	.5
8	39	II	IV	.7
8	40	II	IV	.9
9	41	II	V	.1
9	42	II	V	.3
9	43	II	V	.5

TABLE I (continued)

Blend Type	Blend No.	Component A	Component B	% Component A
9	44	II	V	.7
9	45	II	V	.9
10	46	III	III	.1
10	47	III	III	.3
10	48	III	III	.5
10	49	III	III	.7
10	50	III	III	.9
11	51	III	IV	.1
11	52	III	IV	.3
11	53	III	IV	.5
11	54	III	IV	.7
11	55	III	IV	.9
12	56	III	V	.1
12	57	III	V	.3
12	58	III	V	.5
12	59	III	V	.7
12	60	III	V	.9
13	61	IV	IV	.1
13	62	IV	IV	.3
13	63	IV	IV	.5
13	64	IV	IV	.7
13	65	IV	IV	.9
14	66	IV	V	.1
14	67	IV	V	.3
14	68	IV	V	.5
14	69	IV	V	.7
14	70	IV	V	.9
15	71	V	V	.1
15	72	V	V	.3
15	73	V	V	.5
15	74	V	V	.7
15	75	V	V	.9

density; (3) environmental stress crack resistance; (4) stiffness; (5) tensile impact; (6) dart impact; and (7) warpage. A detailed report covering the measurement of these parameters may be found in Appendix A. Each of these tests has a significance in any of a number of applications designated as injection molding functions.

When as molded melt index (MI_{AM}) is measured as a parameter, it is usually done for the purpose of establishing a resin's processability. Therefore, the true interest in the test is not the MI_{AM}, but whether the processing of the resin from raw material to finished product has greatly lowered the melt index. If the melt index drop is relatively large (greater than 15-20%), then it is likely that processing was difficult and that an abnormal quantity of molded-in stresses had been incorporated in the finished product. This is not a favorable situation and may also effect other measurable final product parameters.

The as molded density (DEN_{AM} or d_{AM}) may be used to determine the degree of shrinkage which can be expected from a particular resin type. A test has not yet been adequately defined to measure shrinkage on small laboratory equipment; however, it is generally believed that shrinkage is a density function and, therefore, by measuring a change in density from pellet to product, a shrinkage factor may be obtained.

Until very recently, environmental stress crack resistance (ESCR) had been used almost exclusively as a quality control test for blow molded containers. A large increase in injection molded 5-gallon pail production has necessitated the use of the ESCR test for injection molded materials. The test itself is designed to predict the shelf life (F_{50} value - 1/2 failed) time of a finished product for its resistance to cracking caused by forces other than impact, specifically constant stress cracking. The test used is designed to compare resins rather than to predict absolute time for failure. The importance of this test is obvious.

A material's stiffness is very often a prime criterion for its selection over other resins, for example, finished products that must be shipped empty for future filling must be rigid to avoid crushing during shipment. The test performed for stiffness in flexure does not yield a true modulus of elasticity since the two forces involved (elastic and plastic) are not separable. The resulting stiffness value is an apparent stiffness, but may be used to determine a materials' relative rigidity.

The tensile impact (TI) test has been shown to yield values of energy loss much more accurately than did the older, more widely used notch impact test. The importance of the test is obvious in that the producer or fabricator hopes that his finished product can withstand certain impact forces even under tension.

The dart impact (DI) test is another form of measuring a material's resistance to impact. This test, however, is used to simulate an actual occurrence in the field wherein a bucket filled with a chemical may be dropped accidentally from a loading dock, etc. Can the resin withstand the impact and/or hydraulic shock? The test itself is very new, in fact, similar data is nowhere to be found. The use of both room temperature (RT) and Zero °F (0°F) testing covers the varying applications that are common to the industry.

The warp (WP) test is also new and is intended to measure a material's relative resistance to warping. The property can be correlated with flow behavior but is more easily measured than shrinkage (definitely a sister property). The obvious importance of this parameter rests with the capability of producing an acceptable finished product. Most manufacturable parts cannot tolerate any degree of warp, especially multi-component products that must be fitted together.

The spiral flow (SP Flow) test is designed to indicate a material's relative degree of flow in a proto-type injection molding machine under likely field conditions as opposed to the ASTM test for melt index which yields flow characteristics of the material at a shear rate of up to one hundred times as small as under actual conditions. Ease of flow in a production unit may govern a material's applicability in a particular process whereby it would be difficult for a fabricator to use the same material for both housewares (thin wall) and 5-gallon pails (thick wall) with equal economic success.

Several of the above test parameters have been measured in both the machine (radial) and transverse directions. This was done in order to use these data in future work describing the importance of material orientation effects as related to final product properties. The discussion of differences noted during measurement of these parameters is beyond the scope of this paper.

Table II lists all the data obtained for the 75 blend design, including initial resin properties of the blends. The Kd number used is a measure of molecular weight distribution as described by Sabia[8]. It is not an absolute value but indicates a material's relative distribution in that a 7.0 Kd material exhibits a broader distribution than does a 4.0 Kd resin. It should be noted that the first blend has been eliminated from the summary data sheet cutting the data base to 74 blends (results for this blend indicated mis-sampling).

TABLE II

SUMMARY DATA SHEET

Comp. A- Comp. B	x_a	Ma-Mb	Ka-Kb	d_a	d_b	Mam	d_{am}	ESCR	Stiff (T)	Stiff (R)	TI (T)	TI (R)	DI (RT)	DI (0°F)	Warp	SF
I- I	.3	4.6- 4.6	4.94-4.94	.9507	.9507	2.27	.9434	150	111.1	95.3	4.41	6.61	4.13	2.60	3.39	7.26
I- I	.5	4.6- 4.6	4.94-4.94	.9507	.9507	2.25	.9434	270	110.0	97.6	4.37	7.03	4.37	2.12	3.30	7.30
I- I	.7	4.6- 4.6	4.94-4.94	.9507	.9507	2.31	.9434	47	108.9	96.4	4.53	7.72	4.95	2.48	3.42	7.33
I- I	.9	4.6- 4.6	4.94-4.94	.9507	.9507	2.86	.9434	75	101.5	96.4	4.41	7.87	5.06	2.17	3.40	7.32
I- II	.1	4.6-10.8	4.94-7.18	.9507	.9509	7.3	.9445	160	90.8	84.4	3.38	4.62	1.56	1.42	2.13	9.47
I- II	.3	4.6-10.8	4.94-7.18	.9507	.9509	5.8	.9441	400	92.9	84.4	3.75	4.72	2.24	1.54	2.34	9.31
I- II	.5	4.6-10.8	4.94-7.18	.9507	.9509	5.2	.9441	560	93.9	72.8	3.75	5.36	3.02	1.57	2.52	8.67
I- II	.7	4.6-10.8	4.94-7.18	.9507	.9509	4.6	.9438	200	102.4	77.1	4.06	5.40	3.17	2.08	2.81	8.37
I- II	.9	4.6-10.8	4.94-7.18	.9507	.9509	4.1	.9441	700	97.1	84.4	4.37	5.72	2.11	1.92	3.10	7.69
I-III	.1	4.6- 9.8	4.94-3.76	.9507	.9520	6.5	.9424	28	111.2	99.0	4.12	6.18	4.07	2.65	2.47	8.12
I-III	.3	4.6- 9.8	4.94-3.76	.9507	.9520	5.7	.9428	27	113.7	85.6	4.03	5.61	3.25	2.34	2.83	8.11
I-III	.5	4.6- 9.8	4.94-3.76	.9507	.9520	4.7	.9428	35	114.9	95.3	4.12	6.27	1.98	2.92	2.83	8.12
I-III	.7	4.6- 9.8	4.94-3.76	.9507	.9520	4.1	.9428	29	101.4	89.2	3.98	6.04	4.00	3.37	3.01	7.83
I-III	.9	4.6- 9.8	4.94-3.76	.9507	.9520	3.5	.9428	27	99.0	86.8	4.27	6.02	4.63	3.33	2.85	7.78
I- IV	.1	4.6-19.9	4.94-2.85	.9507	.9535	11.9	.9440	19	95.3	77.0	3.63	6.11	3.44	2.96	2.58	8.71
I- IV	.3	4.6-19.9	4.94-2.85	.9507	.9535	10.1	.9420	24	102.7	88.0	4.47	5.98	3.09	1.62	1.98	8.74
I- IV	.5	4.6-19.9	4.94-2.85	.9507	.9535	6.4	.9436	25	106.3	92.8	3.85	6.44	2.61	2.34	2.51	8.34
I- IV	.7	4.6-19.9	4.94-2.85	.9507	.9535	5.1	.9440	26	108.8	82.8	4.22	5.74	2.97	3.29	2.83	8.09
I- IV	.9	4.6-19.9	4.94-2.85	.9507	.9535	3.2	.9436	31	102.7	88.0	4.14	5.70	3.61	2.58	3.21	7.57
I- V	.1	4.6-25.5	4.94-3.52	.9507	.9536	20.0	.9445	62	73.9	82.3	3.68	5.48	1.88	1.09	1.16	9.51
I- V	.3	4.6-25.5	4.94-3.52	.9507	.9536	12.2	.9442	15	85.5	70.0	3.84	5.52	2.15	1.45	1.97	9.22
I- V	.5	4.6-25.5	4.94-3.52	.9507	.9536	7.9	.9438	16	105.6	85.5	3.39	6.55	1.56	1.20	2.51	8.75
I- V	.7	4.6-25.5	4.94-3.52	.9507	.9536	5.4	.9438	700	109.8	84.4	3.83	5.78	1.92	1.33	2.56	8.28
I- V	.9	4.6-25.5	4.94-3.52	.9507	.9536	3.9	.9438	800	101.3	78.1	4.11	6.30	2.78	2.08	2.78	8.10
II- II	.1	10.8-10.8	7.18-7.18	.9509	.9509	8.7	.9434	16	100.4	84.0	3.41	5.11	3.60	1.95	2.17	9.21
II- II	.3	10.8-10.8	7.18-7.18	.9509	.9509	8.8	.9430	183	106.0	94.2	3.88	5.45	3.10	1.81	2.17	9.25
II- II	.5	10.8-10.8	7.18-7.18	.9509	.9509	7.8	.9427	20	107.7	86.9	3.35	5.66	3.59	1.73	2.18	9.30
II- II	.7	10.8-10.8	7.18-7.18	.9509	.9509	7.0	.9427	19	108.9	97.6	3.62	4.59	2.58	1.73	2.14	9.26
II- II	.9	10.8-10.8	7.18-7.18	.9509	.9509	7.8	.9427	23	112.2	90.2	3.31	6.32	3.58	1.98	2.22	9.27
II-III	.1	10.8- 9.8	7.18-3.76	.9509	.9520	7.3	.9434	560	93.9	68.6	3.72	6.53	2.37	1.44	2.39	8.40
II-III	.3	10.8- 9.8	7.18-3.76	.9509	.9520	7.6	.9441	300	103.4	91.8	4.10	5.40	1.67	1.22	2.43	8.50
II-III	.5	10.8- 9.8	7.18-3.76	.9509	.9520	7.6	.9448	18	120.3	88.7	4.02	5.66	1.86	1.24	2.37	9.03
II-III	.7	10.8- 9.8	7.18-3.76	.9509	.9520	8.0	.9446	15	119.3	88.7	3.77	5.12	2.23	1.17	2.20	9.20
II-III	.9	10.8- 9.8	7.18-3.76	.9509	.9520	8.7	.9450	7	120.3	91.8	2.76	4.66	2.72	1.49	2.27	9.46
II- IV	.1	10.8-19.9	7.18-2.85	.9509	.9535	13.5	.9450	27	95.0	86.6	4.42	6.16	2.49	1.67	1.68	8.73
II- IV	.3	10.8-19.9	7.18-2.85	.9509	.9535	12.4	.9446	20	87.6	70.7	3.43	5.40	2.67	2.25	1.93	8.80
II- IV	.5	10.8-19.9	7.18-2.85	.9509	.9535	10.7	.9446	22	95.0	86.6	3.39	4.46	1.92	1.26	1.40	9.11
II- IV	.7	10.8-19.9	7.18-2.85	.9509	.9535	9.7	.9450	21	92.9	85.5	3.31	4.73	4.37	1.34	1.62	9.47

TABLE II (continued)

Comp. A- Comp. B	x_a	Ma-Mb	Ka-Kb	d_a	d_b.	Mam	d_{am}	ESCR	Stiff (T)	Stiff (R)	TI (T)	TI (R)	DI (RT)	DI (0°F)	Warp	SF
II- IV	.9	10.8-19.9	7.18-2.85	.9509	.9535	9.5	.9452	11	93.9	82.3	1.45	4.61	1.97	1.25	1.88	9.70
II- V	.1	10.8-25.5	7.18-3.52	.9509	.9536	20.6	.9490	32	101.4	102.7	4.29	5.80	4.58	4.60	1.05	9.75
II- V	.3	10.8-25.5	7.18-3.52	.9509	.9536	17.5	.9490	47	105.1	83.1	4.05	5.77	2.59	3.03	1.25	9.73
II- V	.5	10.8-25.5	7.18-3.52	.9509	.9536	14.4	.9490	50	108.8	99.0	4.22	5.84	3.89	3.76	2.02	9.70
II- V	.7	10.8-25.5	7.18-3.52	.9509	.9536	11.6	.9490	55	108.8	95.3	4.39	5.81	3.66	3.60	1.42	9.66
II- V	.9	10.8-25.5	7.18-3.52	.9509	.9536	9.2	.9433	87	117.3	99.0	4.05	6.00	2.29	2.79	1.82	9.66
III-III	.1	9.8- 9.8	3.76-3.76	.9520	.9520	6.8	.9419	237	101.5	90.2	4.23	7.48	4.83	2.37	2.60	7.52
III-III	.3	9.8- 9.8	3.76-3.76	.9520	.9520	6.4	.9419	66	117.3	82.9	4.07	6.69	5.05	2.84	2.54	7.53
III-III	.5	9.8- 9.8	3.76-3.76	.9520	.9520	6.5	.9415	274	110.0	85.7	3.99	6.53	4.30	2.75	2.39	7.56
III-III	.7	9.8- 9.8	3.76-3.76	.9520	.9520	6.5	.9415	161	105.5	81.8	3.60	7.04	5.50	2.53	2.41	7.55
III-III	.9	9.8- 9.8	3.76-3.76	.9520	.9520	6.6	.9419	146	111.1	96.4	3.83	6.72	5.64	3.27	2.40	7.53
III- IV	.1	9.8-19.9	3.76-2.85	.9520	.9535	12.7	.9433	89	100.2	91.7	4.69	6.46	3.51	2.89	2.30	8.76
III- IV	.3	9.8-19.9	3.76-2.85	.9520	.9535	10.8	.9428	131	103.9	83.1	4.99	7.01	3.62	4.05	2.38	8.70
III- IV	.5	9.8-19.9	3.76-2.85	.9520	.9535	9.3	.9428	130	99.0	90.4	4.60	7.02	4.31	3.53	1.79	8.50
III- IV	.7	9.8-19.9	3.76-2.85	.9520	.9535	8.3	.9428	340	106.3	85.6	4.76	6.71	4.83	4.28	2.00	8.43
III- IV	.9	9.8-19.9	3.76-2.85	.9520	.9535	7.3	.9428	203	108.8	91.7	5.01	6.31	5.15	3.25	2.43	8.11
III- V	.1	9.8-25.5	3.76-3.52	.9520	.9536	19.5	.9462	13	92.9	78.1	3.36	5.25	2.46	1.18	1.29	9.72
III- V	.3	9.8-25.5	3.76-3.52	.9520	.9536	15.3	.9450	25	87.6	80.2	3.45	4.74	1.13	1.34	1.62	9.46
III- V	.5	9.8-25.5	3.76-3.52	.9520	.9536	11.9	.9446	27	86.6	86.6	4.00	5.41	2.94	1.92	1.80	8.75
III- V	.7	9.8-25.5	3.76-3.52	.9520	.9536	9.4	.9444	45	78.1	76.0	3.67	4.03	3.23	2.98	1.82	8.77
III- V	.9	9.8-25.5	3.76-3.52	.9520	.9536	7.0	.9450	24	86.6	83.4	3.45	7.07	1.97	1.12	2.19	8.30
IV- IV	.1	19.9-19.9	2.85-2.85	.9535	.9535	12.8	.9426	103	103.8	91.4	4.00	5.79	5.81	1.76	2.34	8.13
IV- IV	.3	19.9-19.9	2.85-2.85	.9535	.9535	12.8	.9426	64	101.5	89.1	4.27	6.38	5.80	2.74	2.05	8.18
IV- IV	.5	19.9-19.9	2.85-2.85	.9535	.9535	12.6	.9422	117	103.8	96.4	4.10	6.22	5.05	2.79	2.25	8.10
IV- IV	.7	19.9-19.9	2.85-2.85	.9535	.9535	13.7	.9426	82	112.2	101.5	4.71	7.28	5.95	2.22	2.19	8.25
IV- IV	.9	19.9-19.9	2.85-2.85	.9535	.9535	13.8	.9434	57	111.1	99.3	4.66	6.75	5.56	2.18	2.73	8.24
IV- V	.1	19.9-25.5	2.85-3.52	.9535	.9536	22.3	.9450	12	85.2	80.2	3.20	4.60	1.13	1.45	2.42	9.70
IV- V	.3	19.9-25.5	2.85-3.52	.9535	.9536	19.4	.9450	13	86.6	79.2	3.22	4.96	1.87	1.32	.99	9.64
IV- V	.5	19.9-25.5	2.85-3.52	.9535	.9536	17.6	.9446	19	90.8	88.7	3.79	5.11	2.07	1.94	1.57	9.26
IV- V	.7	19.9-25.5	2.85-3.52	.9535	.9536	16.0	.9446	17	87.6	88.7	3.39	4.88	2.25	1.80	1.14	8.99
IV- V	.9	19.9-25.5	2.85-3.52	.9535	.9536	14.6	.9444	28	82.3	80.2	3.69	5.27	2.75	2.18	1.23	8.36
V- V	.1	25.5-25.5	3.52-3.52	.9536	.9536	23.3	.9437	37	99.3	99.3	3.58	5.21	3.80	2.70	1.31	9.51
V- V	.3	25.5-25.5	3.52-3.52	.9536	.9536	23.1	.9435	43	103.8	99.3	3.33	4.95	3.99	1.84	1.20	9.50
V- V	.5	25.5-25.5	3.52-3.52	.9536	.9536	22.9	.9435	65	100.4	104.9	3.56	5.21	4.62	2.33	1.18	9.50
V- V	.7	25.5-25.5	3.52-3.52	.9536	.9536	22.3	.9435	34	104.9	96.4	3.49	5.43	3.40	2.00	1.41	9.50
V- V	.9	25.5-25.5	3.52-3.52	.9536	.9536	22.2	.9435	37	96.4	91.4	3.51	4.71	3.50	1.85	1.03	9.64

CHAPTER V

ANALYSES OF DATA

The data base, being as large as is indicated in Table II, lent itself to any of a number of possible analyses. It was obvious that the ideal way of both handling the data and using the information derived from the analyses would be to discount material nomenclature and handle the data as results obtained from seventy-four (74) combinations of two-material blends, each of which had rheological parameters X_1, X_2, X_3, etc.

Each measurable physical parameter, for example, warp would be defined as a dependent variable to be related to the independent variables as stated above with the inclusion of a weight percent factor as an additional independent variable. This data could then be handled by least squares regression technique which would yield an equation for that particular dependent parameter of the form shown below:

$$\begin{aligned} Y_{warp} = {} & A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_5X_1X_2 + \\ & A_6X_1X_3 + A_7X_1X_4 + A_8X_2X_3 + A_8X_2X_4 + A_9X_3X_4 + \\ & A_{10}X_1X_2X_3 + A_{11}X_1X_3X_4 + A_{12}X_1X_2X_4 + A_{13}X_2X_3X_4 \end{aligned}$$

It should be noted that any number of the coefficients A_0 through A_{13} may be zero, dependent upon the number of steps that the least squares analyses uses as the procedure calls for adding one variable at a time dependent upon statistical significance.

As an example of this technique, let the dependent variable, spiral flow, be selected and traced as to the predictability of the developed regression equations. Data input to the computer for least squares regression includes columns 1-7 plus column 18 shown in Table II, pages 19 and 20. Several transformations on columns 1-7 were made allowing for likely interaction terms yielding a final data array as indicated by Table III for Blend #2 only.

With this transformation completed, the regression analysis produced the following equation:

$$(1)\quad \text{Sp. Flow} = 6.7765 + .0393(x_B)(M_B)(K_B) + .040882(x_A)(M_A)(K_A) - .03474(M_A)$$

The correlation coefficient was .96 which is excellent as was the F-ratio statistic being much greater than 99.9%. This example illustrated one of the best of the eleven physical parameters tested. In an attempt to correlate physical parameters other than flow oriented parameters (warp and as molded MI also worked quite well), the final results are far from idealistic. The following indicate the regression equations developed for all physical parameters tested and treated in this same manner.

$$(2)\quad \text{Dart Impact } (0°\text{F}) = 2.8133 - .1455(K_B)$$

$$R = .24;\ F = 96.5$$

$$(3)\quad \text{Stiffness (Radial)} \ (\times 10^{-3}\text{psi}) = 87.607 + .5807(M_A) - .3291(M_B)$$

$$R = .40;\ F > 99.9$$

TABLE III

TRANSFORMED VARIABLE MATRIX FOR BLEND #2

Column #	Variable
1	x_A
2	M_A
3	M_B
4	K_A
5	K_B
6	d_A
7	d_B
8	Spiral Flow
9	x_B
10	$x_A M_A$
11	$x_A K_A$
12	$x_A d_A$
13	$x_B M_B$
14	$x_B K_B$
15	$x_A M_A K_A$
16	$x_A M_A d_A$
17	$x_B M_B K_B$
18	$x_B M_B d_B$
19	$(x_A)^2 M_A$
20	$(x_A)^2 K_A$
21	$(x_B)^2 M_B$
22	$(x_B)^2 K_B$
23	$(x_A)^2 d_A$
24	$(x_B)^2 d_B$
25	$x_B d_B$

(4) $\text{Log (ESCR)} = 134.98 - 139.15(d_B) - .10081(K_A)$
$- .016037(M_A)$
$R = .38;\ F = 99.7$

(5) $\text{Stiffness (Trans)} = 122.54 - .9445(M_B) + .16467$
$(\text{x}10^{-3}\text{psi})$ $(x_A)(M_A)(K_A) - 2.1526(K_B)$
$R = .59;\ F > 99.9$

(6) $\text{Tensile Impact Factor (Trans)} = 5.0739 - .011798$
$(x_A)(M_A)(K_A) - .013051(x_A)(M_A)(d_A) -$
$.1582(x_A)^2(K_A) - .10671(x_B)(K_B)$
$R = .56;\ F > 99.9$

(7) $d_{AM} = .93877 + .00013257(M_B) + .00056358(K_A)$
$R = .69;\ F > 99.9$

(8) $\text{TI (Radial)} = 7.2951 - .041347(x_B)(M_B)(K_B) -$
$.022487(x_A)(M_A)(K_A) + .073173(x_B)^2(M_B)$
$R = .64;\ F > 99.9$

(9) $\text{MI} = -1.9933 + .14637(M_A) + .82228(x_B)(M_B)(d_B)$
$+ .71763(x_A)(M_A)$
$R = .973;\ F \ggg 99.9$

(10) $\text{Dart Impact (Room Temp)} = -1122.0 - .089154(K_A)$
$- .18344(M_B) + 742.65(d_B) + 442.93(d_A)$
$R = .56;\ F > 99.9$

(11) $\text{Warp} = 4.2092 - .027934(M_B) - .0073505(M_A)$
$- .10581(K_A) - .016947(x_B)(M_B)(K_B)$
$- .07422(x_A)(M_A)$
$R = .87;\ F \gg 99.9$

It must be noted that, although the scatter predicted by some low R values (multiple correlation coefficients) would hinder the reliability of predicted results, the high F-ratios indicate that the selection of the appropriate independent variables was quite successful. The question arises, then, if the basic premise is good, how may the producer better handle the available data to insure acceptable product to the resin user?

It should also be noted here that not all the error implied by the small R values is due to error in blending technique. As mentioned earlier, included in the study were twenty-four fictional blends since some blends are blends in nomenclature only. Table IV illustrates some of the variance noted for these "blends" by means of indicating an average and a standard deviation. The physical parameters directly related to flow behavior here also exhibit variance generally lower than the other physical parameters. Of particular note are the higher errors for ESCR and tensile impact.

A second technique for establishing relationships between final product properties and blend rheologicals was developed by first measuring these dependent parameters for the pure resins to be blended and then using these values as independent parameters when regressing the data against the blend final product properties. To do this, the 74 blends were first classified into five (5) groups wherein Group 1 included those blends containing Type I resin, Group 2 included those blends containing Material II, etc. All groups arranged in this manner include 20 blends.

Each group's data was then handled as an experiment in itself whereby, if the producer had off-grade Material I,

TABLE IV

ERROR INDICATED BY VARIANCE OF DATA FOR PURE BLEND PHYSICAL PROPERTIES

MATERIAL TYPE	I		II		III		IV		V	
	Avg.	(S.D.)	Avg.	(S.D.)	Avg.	(S.D.)	Avg.	(S.D.)	Avg.	(S.D.)
MI_{AM}	2.42	(.29)	8.0	(.70)	6.6	(.16)	13.1	(.57)	22.8	(.49)
d_{AM}	.9434	(.000)	.9429	(.0003)	.9417	(.0004)	.9427	(.0004)	.9435	(.0001)
ESCR	135.5	(100)	52	(73)	177	(88)	85	(25)	43	(12)
ST (T)	107.9	(4.3)	107.0	(2.8)	109.1	(6)	106.5	(4.8)	101.0	(3.9)
ST (R)	96.4	(.9)	90.6	(5.5)	87.4	(6)	95.5	(5.2)	98.3	(4.9)
TI (T)	4.43	(.07)	3.51	(.24)	3.94	(.24)	4.35	(.32)	3.49	(.10)
TI (R)	7.31	(.60)	5.43	(.64)	6.89	(.38)	6.48	(.58)	5.10	(.29)
DI (RT)	4.63	(.45)	3.29	(.45)	5.06	(.54)	5.63	(.36)	3.86	(.48)
DI (0°F)	2.34	(.23)	1.49	(.12)	2.75	(.34)	2.34	(.43)	2.14	(.37)
WARP	3.38	(.05)	2.18	(.03)	2.47	(.10)	2.31	(.26)	1.23	(.14)
SP. FLOW	7.30	(.03)	9.26	(.03)	7.54	(.06)	8.18	(.07)	9.53	(.06)

for example, and wished to blend it with off-grade Material II, he would check the results obtained through regression for either Group 1 or Group 2 in order to predict the necessary blend ratio.

Table V shows the breakdown of Table II, pages 19 and 20, into a smaller group of data that may be handled as a miniature experiment. A slightly varied treatment is used for these smaller data bases than was used above in the 74-blend data base. As was noted above, a major difference in these regression analyses is the use of known pure resin final product parameters as if they were independent variables in these shorter experiments.

As with the total blends technique, the data base is modified with transformations converting the summary data for each group into a 25-column data base for each dependent variable. Table VI, page 29, indicates the manner in which this was handled.

The use of Table VI for step-wise regression analyses yielded eleven equations for Group 1 that may be used to predict these final product parameters for the future use of Group 1 resins. The eleven resulting equations are tabulated below (note the better values of R and F here as opposed to those obtained with the 74-blend technique).

$$(12)\quad TI(R)_{1*} = 6.014 - .10824(x_B)(K_B)(Y_B) + .005697(x_B)(Y_B) - .0059413(x_B)(d_B)(Y_B)$$

$$R = .82;\ F > 99.9$$

* indicates Group 1 Type.

TABLE V

SUMMARY DATA FOR BLENDS CONTAINING MATERIAL I

Comp. B	x_a	Ma-Mb	Ka-Kb	d_a	d_b	Mam	d_{am}	ESCR	Stiff (T)	Stiff (R)	TI (T)	TI (R)	DI (RT)	DI (0°F)	Warp	SF
II	.1	4.6-10.8	4.94-7.18	.9507	.9509	7.3	.9445	160	90.8	84.4	3.38	4.62	1.56	1.42	2.13	9.47
II	.3	4.6-10.8	4.94-7.18	.9507	.9509	5.8	.9441	400	92.9	84.4	3.75	4.72	2.24	1.54	2.34	9.31
II	.5	4.6-10.8	4.94-7.18	.9507	.9509	5.2	.9441	560	93.9	72.8	3.75	5.36	3.02	1.57	2.52	8.67
II	.7	4.6-10.8	4.94-7.18	.9507	.9509	4.6	.9438	200	102.4	77.1	4.06	5.40	3.17	2.08	2.81	8.37
II	.9	4.6-10.8	4.94-7.18	.9507	.9509	4.1	.9441	700	97.1	84.4	4.37	5.72	2.11	1.92	3.10	7.69
III	.1	4.6- 9.8	4.94-3.76	.9507	.9520	6.5	.9424	28	111.2	99.0	4.12	6.18	4.07	2.65	2.47	8.12
III	.3	4.6- 9.8	4.94-3.76	.9507	.9520	5.7	.9428	27	113.7	85.6	4.03	5.61	3.25	2.34	2.83	8.11
III	.5	4.6- 9.8	4.94-3.76	.9507	.9520	4.7	.9428	35	114.9	95.3	4.12	6.27	1.98	2.92	2.83	8.12
III	.7	4.6- 9.8	4.94-3.76	.9507	.9520	4.1	.9428	29	101.4	89.2	3.98	6.04	4.00	3.37	3.01	7.83
III	.9	4.6- 9.8	4.94-3.76	.9507	.9520	3.5	.9428	27	99.0	86.8	4.27	6.02	4.63	3.33	2.85	7.78
IV	.1	4.6-19.9	4.94-2.85	.9507	.9535	11.9	.9440	19	95.3	77.0	3.63	6.11	3.44	2.96	2.58	8.71
IV	.3	4.6-19.9	4.94-2.85	.9507	.9535	10.1	.9420	24	102.7	88.0	4.47	5.98	3.09	1.62	1.98	8.74
IV	.5	4.6-19.9	4.94-2.85	.9507	.9535	6.4	.9436	25	106.3	92.8	3.85	6.44	2.61	2.34	2.51	8.34
IV	.7	4.6-19.9	4.94-2.85	.9507	.9535	5.1	.9440	26	108.8	82.8	4.22	5.74	2.97	3.29	2.83	8.09
IV	.9	4.6-19.9	4.94-2.85	.9507	.9535	3.2	.9436	31	102.7	88.0	4.14	5.70	3.61	2.58	3.21	7.57
V	.1	4.6-25.5	4.94-3.52	.9507	.9536	20.0	.9445	62	73.9	82.3	3.68	5.48	1.88	1.09	1.16	9.51
V	.3	4.6-25.5	4.94-3.52	.9507	.9536	12.2	.9442	15	85.5	70.0	3.84	5.52	2.15	1.45	1.97	9.22
V	.5	4.6-25.5	4.94-3.52	.9507	.9536	7.9	.9438	16	105.6	85.5	3.39	6.55	1.56	1.20	2.51	8.75
V	.7	4.6-25.5	4.94-3.52	.9507	.9536	5.4	.9438	700	109.8	84.4	3.83	5.78	1.92	1.33	2.56	8.28
V	.9	4.6-25.5	4.94-3.52	.9507	.9536	3.9	.9438	800	101.3	78.1	4.11	6.30	2.78	2.08	2.78	8.10

TABLE VI

TRANSFORMED VARIABLE MATRIX FOR BLEND #2

Column #	Variable
1	x_A
2	M_A
3	M_B
4	K_A
5	K_B
6	d_A
7	d_B
8	Y
9	x_B
10	Y_A
11	Y_B
12	$x_A Y_A$
13	$x_B Y_B$
14	$x_A M_A Y_A$
15	$x_A K_A Y_A$
16	$x_A d_A Y_A$
17	$x_B M_B Y_B$
18	$x_B K_B Y_B$
19	$x_B d_B Y_B$
20	$x_A M_A K_A Y_A$
21	$x_A M_A d_A Y_A$
22	$x_A K_A d_A Y_A$
23	$x_B M_B K_B Y_B$
24	$x_B M_B d_B Y_B$
25	$x_B K_B d_B Y_B$

$$(13)\quad \mathrm{DI}\ (0^\circ\mathrm{F})_1 = 2.5602 - .020222(x_B)(M_B)(K_B)(Y_B) + .95529(x_B)(d_B)(Y_B)$$

$$R = .74;\ F > 99.9$$

$$(14)\quad \mathrm{Stiff}\ (R)_1 = 106.42 - .003531(x_B)(M_B)(K_B)(Y_B) - .23191(x_A)(Y_A)$$

$$R = .59;\ F = 98.2$$

$$(15)\quad \mathrm{Stiff}\ (T)_1 = 105.79 - .0060465(x_B)(M_B)(K_B)(Y_B) + .290085(x_B)(Y_B)$$

$$R = .80;\ F > 99.9$$

$$(16)\quad \mathrm{LOG}(\mathrm{ESCR}_1) = 2.1795 - .06219(x_B)(M_B)(d_B)(Y_B) + .018228(x_B)(M_B)(K_B)(Y_B) - .54885(x_B)(Y_B)$$

$$R = .64;\ F = 98.3$$

$$(17)\quad d_{am_1} = .94352 + .000049612(x_B)(M_B)(K_B)(Y_B) - .0032734(x_B)(d_B)(Y_B)$$

$$R = .76;\ F > 99.9$$

$$(18)\quad \mathrm{DI}\ (\mathrm{Room})_1 = 3.0775 - .011210(x_B)(M_B)(K_B)(Y_B) + .60076(x_B)(d_B)(Y_B)$$

$$R = .61;\ F = 98.6$$

$$(19)\quad \mathrm{TI}\ (T)_1 = 4.246 - .0041942(M_B)(x_B)(K_B)(Y_B) + .0068515(x_B)(M_B)(Y_B)$$

$$R = .69;\ F = 99.75$$

$$(20)\quad \mathrm{LOG}(\mathrm{MI}_{am_1}) = .51674 + .065785(x_B)(Y_B) - .0003194(M_B)(x_B)(K_B)(Y_B)$$

$$R = .983;\ F >>> 99.9$$

$$(21)\quad \mathrm{Warp}_1 = .047535 + .19823(x_A)(M_A)(Y_A) + .93585(x_B)(Y_B)$$

$$R = .90;\ F >> 99.9$$

$$(22)\quad \mathrm{Sp.\ Flow}_1 = 7.6751 + .0031228(x_B)(M_B)(K_B)(Y_B) - .0020251(x_B)(M_B)(d_B)(Y_B)$$

$$R = .97;\ F >>> 99.9$$

Similar equations have been developed for Groups 2 through 5 and are also listed below as equations 23 through 66:

$$\begin{aligned}(23)\quad \mathrm{Warp}_2 &= 1.9656 + .13087(x_B)(Y_B)(K_B) - .010478\\ &\quad (x_B)(Y_B)(K_B)(M_B)\\ R &= .88;\ F \gg 99.9\end{aligned}$$

$$\begin{aligned}(24)\quad \mathrm{DI}\ (0°\mathrm{F})_2 &= 1.6494 + .034483(x_B)(M_B)(K_B)(Y_B)\\ &\quad -3.8644(x_B)(Y_B)(d_B) + .60261\\ &\quad (x_B)(Y_B)(K_B)\\ R &= .88;\ F \gg 99.9\end{aligned}$$

$$\begin{aligned}(25)\quad \mathrm{Sp.\ Flow}_2 &= 7.2302 + .024951(x_A)(M_A)(Y_A)\\ &\quad + .0029161(x_B)(M_B)(K_B)(Y_B)\\ R &= .98;\ F \ggg 99.9\end{aligned}$$

$$\begin{aligned}(26)\quad \mathrm{DI\ (Room)}_2 &= 2.4327 + .011137(x_B)(M_B)(K_B)(Y_B)\\ &\quad - 1.1692(x_B)(Y_B)(d_B) + .17596\\ &\quad (x_B)(K_B)(Y_B)\\ R &= .54;\ F = 94.0\end{aligned}$$

$$\begin{aligned}(27)\quad \mathrm{TI\ (Radial)}_2 &= 6.0285 - .24784(x_A)(d_A)(Y_A)\\ R &= .63;\ F = 99.7\end{aligned}$$

$$\begin{aligned}(28)\quad \mathrm{TI\ (Trans)}_2 &= 4.41 - 584.79(x_A)(K_A)(Y_A)\\ &\quad + 388.75(x_A)(M_A)(Y_A)\\ R &= .61;\ F = 98.7\end{aligned}$$

$$\begin{aligned}(29)\quad \mathrm{Stiff\ (R)}_2 &= 90.114 + .061638(x_B)(K_B)(Y_B)\\ &\quad + .0047404(x_B)(M_B)(K_B)(Y_B)\\ &\quad - .59073(x_B)(d_B)(Y_B)\\ R &= .58;\ F = 96.3\end{aligned}$$

$$\begin{aligned}(30)\quad \mathrm{Stiff\ (T)}_2 &= 107.37 - .5866(x_B)(d_B)(Y_B)\\ &\quad + .0068523(x_B)(M_B)(K_B)(Y_B)\\ &\quad - 20.64(x_B)(M_B)(d_B)(Y_B)\\ &\quad + 19.678(x_B)(M_B)(Y_B)\\ R &= .43;\ F < 90\ \text{(very poor)}\end{aligned}$$

(31) $$\mathrm{LOG}(\mathrm{ESCR}_2) = -.44787 + .34736(x_B)(K_B)(Y_B) + 1.1575(x_A)(d_A)(Y_A)$$

$$R = .74;\ F > 99.9$$

(32) $$d_{am_2} = .94492 + .00019518(x_B)(M_B)(K_B)(Y_B) - 1.8819(x_B)(d_B)(Y_B) + 1.7831\ (x_B)(Y_B)$$

$$R = .89;\ F >> 99.9$$

(33) $$\mathrm{LOG}(\mathrm{MI}_{am_2}) = .30268 + .0071493(x_B)(M_B)(d_B)(Y_B) + .71914(x_A)(d_A)(Y_A) + .64885\ (x_B)(d_B)(Y_B)$$

$$R = .994;\ F >>>> 99.9$$

(34) $$\mathrm{LOG}(\mathrm{MI}_{am\ 3}) = .2114 + .00077499(x_B)(M_B)(Y_B) + .02054(x_A)(M_A)(K_A)(Y_A) + .80443\ (x_B)(Y_B)$$

$$R = .997;\ F >>>> 99.9$$

(35) $$d_{am\ 3} = -.51649 - .000071477(x_B)(M_B)(K_B)(Y_B) - .35745(x_B)(d_B)(Y_B) + 1.8848\ (x_B)(Y_B) + .41225(x_A)(K_A)(Y_A)$$

$$R = .90;\ F >> 99.9$$

(36) $$\mathrm{LOG}(\mathrm{ESCR}_3) = 2.1294 + 6.1584(x_B)(K_B)(d_B)(Y_B) - 27.558(x_B)(Y_B) - .45108\ (x_B)(M_B)(K_B)(Y_B) + 1.8288(x_B)(M_B)(Y_B)$$

$$R = .68;\ F = 98.6$$

(37) $$\mathrm{Stiff}\ (T)_3 = 100.26 - 1021.9(x_B)(K_B)(Y_B) + 54.815(x_B)(M_B)(Y_B) + 1075.2(x_B)(K_B)(d_B)(Y_B) - 57.985(x_B)(M_B)(d_B)(Y_B)$$

$$R = .70;\ F = 99.0$$

(38) $$\mathrm{Stiff}\ (R)_3 = 96.446 - .0062449(x_B)(M_B)(d_B)(Y_B) - 803.89(x_A)(K_A)(Y_A) + 844.37\ (x_A)(Y_A)(K_A)(d_A)$$

$R = .39;\ F < 90.0$ (very poor)

$$(39)\quad \mathrm{TI}\ (\mathrm{Trans})_3 = -10.451 - 87.113(x_B)(K_B)(Y_B) + 2.2434(x_B)(Y_B) + .10104(x_A)(Y_A)(M_A)(K_A) + 91.85(x_B)(d_B)(K_B)(Y_B)$$

$R = .79;\ F = 99.88$

$$(40)\quad \mathrm{TI}\ (\mathrm{Radial})_3 = 6.3239 - .02496(x_B)(M_B)(K_B)(Y_B) + 49.813(x_B)(M_B)(Y_B) - 52.145(x_B)(M_B)(d_B)(Y_B) - .12636(x_B)(d_B)(K_B)(Y_B)$$

$R = .74;\ F = 95.8$

$$(41)\quad \mathrm{DI}\ (\mathrm{Room})_3 = -1.1144 - .0050788(x_B)(M_B)(K_B)(Y_B) + 1.2929(x_B)(d_B)(Y_B) + .023416(x_A)(M_A)(K_A)(Y_A)$$

$R = .55;\ F = 95.0$

$$(42)\quad \mathrm{DI}\ (0°\mathrm{F})_3 = 2.3963 - .077605(x_B)(M_B)(K_B)(Y_B) + 78.645(x_B)(M_B)(Y_B) - 82.208(x_B)(M_B)(d_B)(Y_B)$$

$R = .77;\ F > 99.9$

$$(43)\quad \mathrm{Warp}_3 = .0043847 + .19399(x_B)(K_B)(Y_B) + .25258(x_A)(K_A)(Y_A) - .011706(x_B)(M_B)(K_B)(Y_B) + .054015(x_B)(M_B)(d_B)(Y_B)$$

$R = .91;\ F \gg 99.9$

$$(44)\quad \mathrm{Sp.\ Flow}_3 = 7.3466 + .0030698(x_B)(M_B)(K_B)(Y_B) + .01167(x_A)(Y_A)(M_A)(d_A)$$

$R = .98;\ F \ggg 99.9$

$$(45)\quad \mathrm{Sp.\ Flow}_4 = 7.2761 + .0031716(M_B)(x_B)(K_B)(Y_B) + .00872(x_A)(M_A)(Y_A)$$

$R = .94;\ F \gg 99.9$

$$(46)\quad \mathrm{Warp}_4 = 1.7219 + .65053(x_B)(Y_B) - .008587(x_B)(M_B)(K_B)(Y_B)$$

$R = .72;\ F = 99.85$

$$(47)\quad \mathrm{DI}\ (0°\mathrm{F})_4 = -5.3153 - .0062076(x_B)(M_B)(K_B)(Y_B) + 3.8655(x_B)(d_B)(Y_B) + 3.5013(x_A)(d_A)(Y_A)$$

$R = .82;\ F > 99.9$

(48) $$\mathrm{DI\ (Room)}_4 = -43762 - 30.075(x_B)(K_B)(M_B)(Y_B) + 736.58(x_B)(d_B)(Y_B) + 8152.7(x_A)(d_A)(Y_A) + 1719.5(x_B)(d_B)(Y_B)(K_B) + 311.02(x_B)(d_B)(M_B)(Y_B)$$

$R = .93;\ F > 99.9$

(49) $$\mathrm{TI\ (Radial)}_4 = -49.369 + .043032(x_B)(Y_B)(M_B)(K_B) + 6.9105(x_B)(d_B)(Y_B) + 3.1501(x_A)(K_A)(d_A)(Y_A)$$

$R = .85;\ F > 99.9$

(50) $$\mathrm{TI\ (Trans)}_4 = 4.199 - .031088(x_B)(K_B)(M_B)(Y_B) + 23.536(x_B)(M_B)(Y_B) - 24.581(x_B)(M_B)(d_B)(Y_B)$$

$R = .86;\ F > 99.9$

(51) $$\mathrm{Stiff\ (R)}_4 = 91.038 - .0013334(x_B)(Y_B)(M_B)(K_B) - 23.342(x_A)(Y_A)(M_A)(d_A) + 3729.4(x_A)(Y_A)(d_A) - 54.891(x_A)(M_A)(K_A)(Y_A)$$

$R = .44;\ F < 90$ (very poor)

(52) $$\mathrm{Stiff\ (T)}_4 = 93.522 - .031186(x_B)(M_B)(d_B)(Y_B) + 125.84(x_B)(d_B)(Y_B) - 119.35(x_B)(Y_B)$$

$R = .86;\ F > 99.9$

(53) $$\mathrm{LOG}(\mathrm{ESCR}_4) = -10.306 + .021056(x_B)(M_B)(K_B)(Y_B) + 5.2568(x_B)(d_B)(Y_B) + 30.826(x_A)(M_A)(Y_A)$$

$R = .94;\ F \gg 99.9$

(54) $$d_{am_4} = .25793 + .000049546(x_B)(M_B)(K_B)(Y_B) - .47217(x_B)(Y_B)(d_B) + 1.1743\ (x_B)(Y_B) + .76305(x_A)(d_A)(Y_A)$$

$R = .81;\ F > 99.9$

(55) $$\mathrm{LOG(MI)}_4 = .1901 + .0065186(x_B)(M_B)(d_B)(Y_B) + .85674(x_A)(Y_A) + .64139(x_B)(Y_B) + .01702(x_B)(K_B)(Y_B)$$

$R = .994;\ F >>> 99.9$

(56) $\text{Sp. Flow}_5 = 1.2749 + .94302(x_A)(d_A)(Y_A) + .89359(x_B)(Y_B)$

$R = .972;\ F \ggg 99.9$

(57) $\text{Warp}_5 = 1.4799 + .1356(x_B)(K_B)(Y_B) - .009906993(x_B)(M_B)(K_B)(Y_B)$

$R = .76;\ F > 99.9$

(58) $\text{DI }(0°\text{F})_5 = 1.9618 + .030914(x_B)(Y_B)(M_B)(K_B) - .055804(x_B)(M_B)(Y_B) - .68054(x_B)(Y_B)$

$R = .53;\ F = 93.3$

(59) $\text{DI (Room)}_5 = 2.158 + .0083755(x_B)(Y_B)(M_B)(K_B) - .002328(x_B)(M_B)(Y_B)$

$R = .28;\ F < 90$ (very poor)

(60) $\text{TI (Radial)}_5 = 5.111 + .043571(x_B)(K_B)(Y_B) - .007015(x_B)(M_B)(Y_B)$

$R = .56;\ F = 97.1$

(61) $\text{TI (Trans)}_5 = 3.6153 + .063009(x_B)(K_B)(Y_B) - .22033(x_B)(Y_B)$

$R = .62;\ F = 99.0$

(62) $\text{Stiff (R)}_5 = 83.353 + .0035377(x_B)(M_B)(K_B)(Y_B) - .2875(x_B)(d_B)(Y_B) + .029829(x_B)(K_B)(Y_B)$

$R = .62;\ F = 98.0$

(63) $\text{Stiff (T)}_5 = 88.672 + .091399(x_B)(K_B)(Y_B) - .3437(x_B)(d_B)(Y_B)$

$R = .80;\ F > 99.9$

(64) $\text{LOG}(\text{ESCR}_5) = 1.2007 + .18243(x_B)(K_B)(Y_B) - .0098435(x_B)(Y_B)(M_B)(K_B)$

$R = .75;\ F > 99.9$

(65) $d_{am_5} = .94652 - .0065326(x_B)(d_B)(Y_B) + .000079523(x_B)(Y_B)(M_B)(K_B)$

$R = .54;\ F = 96.6$

$$(66)\quad \mathrm{LOG}(\mathrm{MI})_5 = .24728 + .033739(x_A)(Y_A)(M_A)(d_A) + .015149(x_B)(Y_B)(M_B) + .44999(x_B)(d_B)(Y_B) + .024523(x_B)(Y_B)(d_B)(K_B)$$

$$R = .998;\ F >\!\!>\!\!>\!\!> 99.9$$

Digesting all of the above 66 equations is not an easy task; however, each of the equations does have its own unique importance. Even more important is the combining of two or more of these equations for the purpose of obtaining proper final product blend ratios.

It was noted, as mentioned briefly above, that in general the correlation coefficients (R) were higher when using the breakdown technique than when using the total 74-blend approach. This point is indicated in Table VII.

The table illustrates the obvious point that more accurate equations of regression may be obtained given more knowledge of the situation at hand. Also to be noted are the relative differences in R values dependent upon which group's equations are used. It would appear that blends using Type IV resin yield more homogeneous mixes than those using Type V resins.

TABLE VII

CORRELATION COEFFICIENTS
INDICATE PREFERENCE FOR USING BREAKDOWN TECHNIQUE

	Variable	R74 Blend	R1	R2	R3	R4	R5	R1-5 Avg.
1	LOG MI_{am}	.973	.98	.995	.997	.994	.998	.993
2	d_{am}	.69	.76	.89	.90	.81	.54	.78
3	LOG (ESCR)	.52	.64	.74	.68	.94	.76	.75
4	STIFF (T)	.61	.80	.43	.70	.86	.82	.72
5	STIFF (R)	.45	.59	.58	.39	.47	.62	.53
6	TI (T)	.56	.69	.61	.79	.89	.62	.72
7	TI (R)	.64	.82	.63	.74	.85	.56	.72
8	DI (Room)	.56	.67	.54	.55	.85	.28	.58
9	DI (0°F)	.24	.74	.88	.77	.82	.53	.75
10	Warp	.87	.90	.92	.91	.72	.76	.84
11	Sp. Flow	.96	.97	.98	.98	.94	.972	.97
	Avg. (R)	.64	.78	.75	.76	.83	.63	.76

CHAPTER VI

USE OF THE DEVELOPED REGRESSION EQUATIONS

The regression equations developed in the preceding chapter lay the groundwork for developing the technique which allows a resin manufacturer to increase his stream factor via blending off-grade materials in order to supply the fabricator with an acceptable product.

The procedure involves (1) obtaining fabricator requirements, (2) the determination of all independent parameters for the two off-grade materials to be used, (3) the selection of the appropriate regression equations, (4) the solution of the equations individually for x_B, letting $x_A = 1-x_B$, and (5) the determination of blend range by comparing x_B for each fabricator requirement.

The following two illustrations exemplify the technique in its simplest form:

<u>Illustration 1</u>: <u>Two Off-Grade MI's</u>

Given two materials -- A is off-spec MI-Type I and B is off-spec MI-Type V -- what blend ratio must be used to insure a final product spiral flow ≥ 8.1 and a tensile impact (R) ≥ 5.5?

TABLE OF PROPERTIES

	MI	KD	D	SF	TIR
A	8	5	.951	7.8	7.0
B	23	3.7	.953	9.8	5.2

The above information defines steps 1 and 2 of the technique. Selection of equations (22) and (12) respectively for Sp. Flow and TIR for Group 1 satisfies step 3. Solving the equations (step 4) is shown below:

(A) $SF = 7.6751 + .0031228(M_B)(K_B)(Y_B)(x_B) - .0020251(M_B)(d_B)(Y_B)(x_B)$

$SF = 7.6751 + 2.604353x_B - .435004x_B$

$SF = 7.6751 + 2.169349x_B$

Let $SF = 8.1$

$$x_B = \frac{8.1 - 7.6751}{2.16349}$$

$x_B \geq .20$

(B) $TIR = 6.014 - .10824(x_B)(K_B)(Y_B) + .005697(x_B)(Y_B) - .0059413(x_B)(d_B)(Y_B)$

$TIR = 6.014 - 2.082538x_B + .029624x_B - .029443x_B$

$TIR = 6.014 - 2.082357x_B$

Let $TIR = 5.5$

$$x_B = \frac{-.514}{-2.082357}$$

$x_B \leq .25$

Therefore, the answer for step 5 is x_B or % of material Type V should be between 20 and 25% blended with 80 - 75% material Type I respectively.

Illustration 2: An Off-Grade Density and an Off-Grade Kd

Given two materials -- A is off-spec density Type II and B is off-spec Kd Type IV -- what blend ratio must be employed to insure a final product ESCR ≥ 50 and a spiral flow ≥ 9.0?

TABLE OF PROPERTIES

	M	K	D	ESCR	SF
A	10	3	.948	20	9.3
B	17	4.2	.953	109	8.5

The above information defines step 1 and 2 of the technique. Selection of equations (31) and (25) respectively for ESCR and Sp. Flow satisfy step 3. Solving the two equations (step 4) is shown below:

(A) $$\text{LOG(ESCR)} = -.44787 + .34736(x_B)(K_B)(Y_B) + 1.1575(x_A)(d_A)(Y_A)$$

$$\text{LOG(ESCR)} = -.44787 + 2.977639x_B + 1.4276 - 1.4276x_B$$

$$\text{LOG(ESCR)} = .97973 + 1.550039x_B$$

$$\text{Let(ESCR)} = 50$$

$$1.701 = .97973 + 1.550039x_B$$

$$x_B \geq .47$$

(B) $$SF = 7.2302 + .024951(M_A)(Y_A)(x_A) + .0029161(x_B)(M_B)(K_B)(Y_B)$$

$$SF = 7.2302 + .024951(M_A)(Y_A)(1-x_B) + .0029161(Y_B)(M_B)(x_B)(K_B)$$

$$SF = 7.2302 + 2.320443 - 2.320443x_B + 1.769781x_B$$

$$SF = 9.550643 - .550662x_B$$

Let SF = 9.0

$$x_B = \frac{-.550643}{-.550662}$$

$$x_B \leq 1.00$$

Therefore, the blend range is 47-100% of material Type IV. Since 50/50 mix would eliminate any surplus problem, this ratio would be recommended.

Although both illustrations worked out quite well, it would be a fallacy to assume that there is a unique solution for all cases that may be attempted. What should be noted is that there is a high degree of likelihood that materials normally considered off-grade by the resin manufacturer may be considered high quality resin at any of a number of fabricator's sites.

CHAPTER VII

SUMMARY AND CONCLUSIONS

In order to determine the relative value of dry-blending HDPE to increase on-specification stream factors, seventy-five blends comprised of combinations of five materials were produced and samples tested for various important rheological and physical parameters. The data was tabulated and used in a step-wise least squares regression technique yielding various equations which may be used to both pick desired blend ratios and predict the final product properties of the resulting blends.

It appears that the blending of high density polyethylene is definitely a feasible approach to the solving of the problem of moving a greater quantity of quality product to the plastics industry. The blending technique used within the study was very basic and could easily be employed by any resin manufacturer provided he had the available blending capacity.

It has been shown that final product physical properties of the blends are, for the most part, quite predictable according to the relative values of the correlation coefficients of the regression equations developed in the text. The final product parameters related to flow behavior such as warp, spiral flow and as molded melt index were by far the most reliably predictable parameters.

Use of the regression equations, as shown by the two illustrations in the text, is quite simple and real to the industry. This is not to say that the equations may only be used for blending purposes. It is felt that future materials of similar type may be fully characterized by the use of equations (1) through (11) at 100% levels of x_A, for instance.

Future work has been proposed for the use of the data in a study of orientation effects in polymer performance. This topic is not limited to any one field of polymer research but encompasses the entire molding spectrum from blown film to injection-blow molding.

FOOTNOTES

[1] Dr. Raffaele Sabia, "Blending of Solution Polymers-Effect on Processing and Physical Characteristics" (Clifton, New Jersey: unpublished report, Allied Chemical Corporation, November 3, 1961).

[2] Henry P. Schreiber, "Linear HDPE," Canadian Patents Can. 709,459, May 11, 1965.

[3] Arthur G. Hillmer, "Polyethylene Blends," U.S. Patent Gazette, Patent #3,179,720, April 20, 1965.

[4] Warren A. Sharp, "Effect of Material on Quality Control in Injection Molding," SPE Technical Papers, Volume XVI (New York, New York: SPE, 1970), pp. 427-429.

[5] S. P. Prosen and W. T. Johnson, "Injection Molding Control and Its Effect on Performance of the Molded Item," SPE Technical Papers, Volume X (Atlantic City, New Jersey: SPE, 1964), pp. VI-I.

[6] Dr. E. Paschke, "Some New Aspects and Relationships of HDPE for Injection Molding," SPE Technical Papers, Volume XIV (New York, New York: SPE, 1968), pp. 629-633.

[7] Edward O. Allen and Douglas A. Van Putte, "A Method for Determining the Significance of Molding Variables," SPE Technical Papers, Volume XX (San Francisco, California: SPE, 1974), pp. 252-255.

[8] Dr. Raffaele Sabia, "On Characterization of Non-Newtonian Flow," Journal of Polymer Science, Volume 7 (1963), p. 350.

BIBLIOGRAPHY

BIBLIOGRAPHY

A. PRIMARY SOURCES

Allen, Edward O. and Douglas A. Van Putte. "A Method for Determining the Significance of Molding Variables," SPE Technical Papers, Vol. XX. San Francisco, California: SPE, 1974.

Hillmer, Arthur G. "Polyethylene Blends," U.S. Patent Gazette, Pat. #3,179,720, April 20, 1965.

Paschke, Dr. E. "Some New Aspects and Relationships of HDPE for Injection Molding," SPE Technical Papers, Vol. XIV. New York, New York: SPE, 1968.

Prosen, S. P. and W. T. Johnson. "Injection Molding Control and Its Effect on Performance of the Molded Item," SPE Technical Papers, Vol. X. Atlantic City, New Jersey: SPE, 1964.

Sabia, Dr. Raffaele. "Blending of Solution Polymers-Effect on Processing and Physical Characteristics." Clifton, New Jersey: Unpublished report, property of Allied Chemical Corporation, November 3, 1961.

_______. "On Characterization of Non-Newtonian Flow," Journal of Polymer Science, Vol. 7 (1963).

Schreiber, Henry P. "Linear HDPE," Canadian Patents, Can. 709,459, May 11, 1965.

Sharp, Warren A. "Effect of Material on Quality Control in Injection Molding," SPE Technical Papers, Vol. XVI. New York, New York: SPE, 1970.

B. GENERAL REFERENCES

American Society for Testing Materials. Annual Book of ASTM Procedures. Maryland: American Society for Testing Materials, 1972.

Bikales, Norbert M. Characterization of Polymers. New York: John Wiley and Sons, 1971.

Billmeyer, Fred W., Jr. Textbook of Polymer Science. New York: John Wiley and Sons, 1966.

Brindell, Gordon D. "Blends of Polyethylene Having Improved Properties," U.S. Patent Gazette, September 5, 1967.

Byer, William H. Handbook of Tables for Probability and Statistics. Cleveland: The Chemical Rubber Co., 1966.

Campbell, William Giles. Form and Style in Thesis Writing. Boston: Houghton Mifflin Company, 1967.

Clampitt, B. H. "Differential Thermal Analysis of the Co-crystal Peak in Linear-High Pressure Polyethylene Blends," Journal of Polymer Science, February 1965, pp. 671-9.

Davies, Owen L. Design and Analysis of Industrial Experiments. New York: Hafner Publishing Co., 1960.

Eirich, Frederick R. Rheology Theory and Applications. New York: Acadian Press, Inc., 1958.

Fujiwara, Shizuo, Hisatake Narasaki. "Degree of Crystallinity of Blended Polyethylene," Journal of Polymer Science, PT. Bl, No. 3, 139-40 (1963).

Gross, Jean Ferdinand. "Marking Materials Comprising Low-Pressure Polyethylene, High Pressure Polyethylene and Plasticizer," U.S. Patent Gazette, November 5, 1968.

Imoto, M., et al. "Blends of Rubberlike Materials and Thermoplastic Resins," Nippon Gomo Kyo-Kasaki, 39 (3), 161-7 (1966).

Ives, G. C., J. A. Mead and M. M. Riley. Handbook of Plastic Test Methods. Cleveland: Chemical Rubber Co., 1971.

Iwazaki, K., et al. "Polyethylene Compositions," Japan Patents 70 03,215 (Cl.25H31), February 1970.

Klestadt, Charles H. "Characterization Study of HDPE Injection Molding Product Line." Allied Chemical Corporation, Baton Rouge, Louisiana, September, 1973.

Krozer, Szymon and Marck Wajnryb. "Thermomechanical Properties of High Pressure and Low Pressure Polyethylenes," Polimery 7, 367-72 (1962).

Lever, et al. The Properties and Testing of Plastic Materials. Cleveland: The Chemical Rubber Co., 1968.

Mark, Herman F., et al. Encyclopedia of Polymer Science and Technology. New York: John Wiley and Sons, 1964.

McKelvey, James M. Polymer Processing. New York: John Wiley and Sons, 1962.

Misterek, Boguslaw. "Properties of Mixtures of Low-and High-Density Polyethylenes," Tworzywa-Guma-Lakiery 5, 269-72 (1960).

Okamoto, T. and M. Takayanagi. "Application of Two-Phase Mechanical Model to Viscoelastic Properties of Blends of HDPE and LDPE," Journal of Polymer Science, No. 23, 1968, pp. 597-606.

Pieski, E. T., S. H. Jenkins, Jr. and S. P. Foster. "Properties of Intermediate-Density Copolymers of Ethylene," SPE Technical Papers #6, No. 52, 3 pages (1960).

Plochocki, Andrzej and Jerzy Bojarski. "Modification of Polyolefins," Polimery 8 (4), pp. 133-7 (1963).

Reding, F. P. "Polyethylene Modified with Branched Polyethylene Wax," Rapra, 42C11-725 (1968).

Rosato, Dominick V., et al. Environmental Effects on Polymeric Materials. Cleveland: The Chemical Rubber Co., 1968.

Sabia, Raffaele. "On the Characterization of Non-Newton Flow-II," Journal of Polymer Science, Vol. 8, pp. 1053-1061 (1964).

________. "The Relationship of Spiral Flow to Rheological Parameters." Clifton, New Jersey: Unpublished report, property of Allied Chemical Corporation, 1965.

Sato, Tetsuo and Mikio Takahashi. "Study of Polyethylene Blends by Differential Scanning Calorimetry," Journal of Polymer Science, 13 (12), pp. 2665-76, 1969.

Schmitz, John V. Testing of Polymers. New York: Interscience Publishers, 1965.

Snyder, John A. and Harold C. Vakos. "High Shear Strength Blends of High and Low Density Polyethylene," U.S. Patent Gazette, January 25, 1966.

Sobiczewski, Sbigniew. "Polyethylene Mixtures," Macromolecular Chemistry, 63, pp. 100-105 (1963).

Stafford, B. B. "Application of Differential Thermal-Analysis to Polyethylene Blends," Journal of Polymer Science, 9, 2, pp. 729-37 (February 1965).

Wharton, William H. and Barry A. Cooper. "Polyolefin Blend Having Hot Tack Strength," U.S. Patent Gazette, November 11, 1969.

APPENDIX A

TESTING PROCEDURES FOR INJECTION MOLDED SPECIMENS

MACHINE CONDITIONS FOR ANKERWERKE 7" DISC MOLD

I. Introduction

The New Britain Ankerwerke is a relatively small injection molding machine limiting us to a small shot part. We decided to try the .045" x 7" disc as a sample specimen to be used in obtaining final product results as shown in this report. The results proved out quite well.

II. Summary of Method

The method used in setting up the machine is keyed on establishing a constant cycle for any injection molding material using consistent parameters.

The following conditions are set at the start of any run:

A. Set temperature at 450°F for all zones of the extruder.

B. Mold temperature at 80°F (Mokon-unit setting).

C. Hold time at 10 seconds.

D. Cooling time at 30 seconds.

Then the back pressure is adjusted to yield a 20 second charge time (good mixing). At this point, the injection speed is adjusted for a one second mold-fill-time. The injection pressure is not set but may be used as a guide for reproducibility studies. The only injection pressure setting is an initial maximum (we used 960 psi as our maximum) as set (up to 1250 psi hydraulic pressure). Finally, the holding pressure is adjusted to yield a maximum without causing material flashing around the molded part.

ENVIRONMENTAL STRESS CRACK TEST

I. Introduction

This determination defines an injection molding grade PE's resistance to environmental stress cracking in the presence of 100% Igepal solution. Results in hours are to be used only for comparison to other samples.

II. Methods of Testing

Sample specimens are blanked out of our 7" disc as shown in Figure 1, page 52. The sample size is 1.5 inch x .5 inch by 45 mil thick. The samples are bent and placed in channel holders (10/holder) after which they are placed in a test tube and fully submerged in a 100% solution of Igepal and sealed "air tight." The time of test at this point is 0 hours.

III. Recording Data

The number of specimens that have failed for a particular test tube of 10 samples shall be recorded at the following times in hours:

(1) .25
(2) .50
(3) 1
(4) 1.5
(5) 2
(6) 3
(7) 4
(8) 5
(9) 6
(10) 8
(11) 12
(12) 16
(13) 20
(14) 24
(15) 32
(16) 40
(17) 48
(18) 72
(19) 96
(20) 120
(21) 144
(22) 168
(23) 192
(24) 216
(25) 240
(26) 264
(27) Etc. @ ea. 24 hr. interval

As an example, we have shown failures for sample number 2940. (See Table I, page 53)

IV. Reporting Data

The ASTM graphical method will be used to determine the F_{50} or time for 1/2 the samples to fail. This is done by plotting log hours vs. probability (P = # Failed/11) and fitting 10 points to best straight line (we have found eyeball method as good as computer curve-fit or

FIGURE I
ESCR SAMPLES FROM 7" DISC MOLD SPECIMENS OF .045" THICKNESS

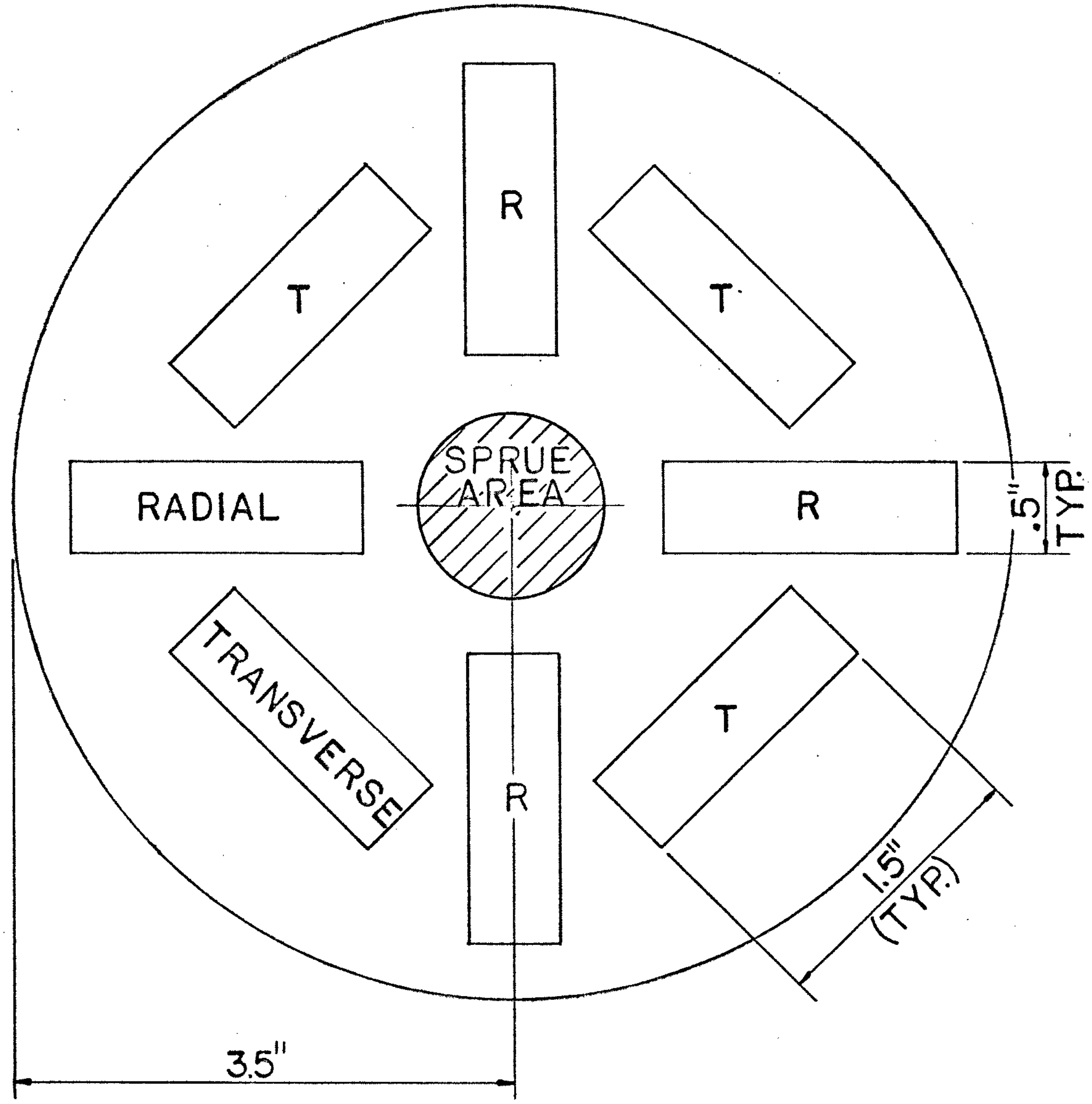


TABLE I

ESCR FOR MATERIAL #2940
IN TRANSVERSE DIRECTION

DATE	TIME	NO. FAILED	HRS. ON TEST
3/15/73	0800	0	0
	0815	0	.25
	0830	0	.50
	0900	0	1.0
	0930	0	1.5
	1000	0	2
	1100	0	3
	1200	0	4
	1300	0	5
	1400	0	6
	1600	0	8
	2000	1	12
	2400	2	16
	0400	3	20
3/16/73	0800	5	24
	1600	8	32
	2400	8	40
3/17/73	0800	8	48
3/18/73	0800	9	72
3/19/73	0800	10	96

log normal distribution curve-fit), and picking off time @ 50% level. See Figure 2, page 55.

V. Replicate Sampling

We should use no less than four (4) sets of 10 specimens for characterization purposes. Decisions to eliminate certain replicates should be done via statistical analysis (2σ limits for 95% confidence). We have seen results as strange as 20, 16, 23, 19, and 180 for replicate runs.

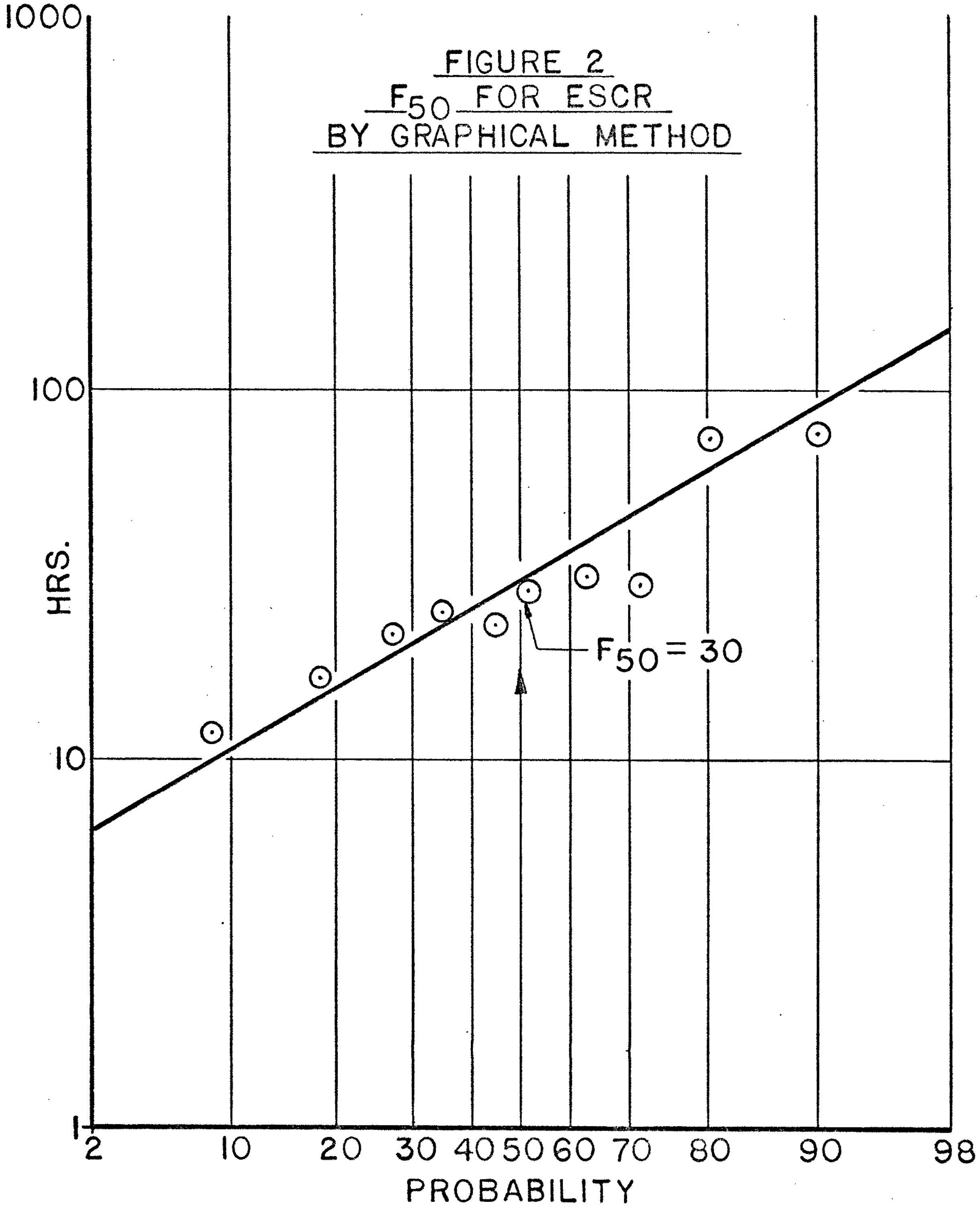


FIGURE 2
F_{50} FOR ESCR
BY GRAPHICAL METHOD

DART IMPACT STRENGTH TEST

I. Introduction

This test method is used to determine the energy needed to cause failure in our 7" disc as molded on the Ankerwerke Machine (45 mil). We are concerned with both room temperature and 0°F impact.

II. Summary of Method

The apparatus used is the same as that described in ASTM D1709 - Free Falling Dart Impact. The machine should be adjusted so that the dart hits the clamped sample center on the center gated sprue (sample will be placed sprue tip down).

Start at approximate F_{50} failure wt. (if unknown, start at 350 gms). Then use stair-step method on 20 samples adding or reducing weight of dart by 30 gms., dependent on passing or failing of specimen. See Figure 3, page 57.

III. Recording Data

The data should be taken as shown in Figure 3, page 57. Certain points should be considered, however:

A. It is best to maintain a constant set of weights in order to serve as an instant check to dart weight.

B. If dart hits off-center, do not repeat with same specimen, just eliminate sample from data and attempt to better level machine or offset sample as necessary.

IV. Reporting Results

The data is used to calculate an F_{50} failure weight and standard deviation. This weight combined with height of drop yields the dart impact in ft. lbs. (Note: 5 ft. height is recommended for room temperature measurements and 3 ft. height is recommended for 0°F measurements).

FIGURE 3

DART IMPACT DATA COLLECTION

SAMPLE #	WT.	PASS	FAIL
1	350	X	
2	380	X	
3	410		X
4	380	X	
5	410	X	
6	440		X
7	410		X
8	380	X	
9	410		X
10	380		X
11	350		X
12	380	X	
13	410		X
14	380		X
15	350		X
16	320	X	
17	350	X	
18	380		X
19	350	X	
20	380		X

One may choose either the pass or failure samples for the F_{50} calculations although it is recommended to use those within the least occurrence (in our example in Figure 3, we would use the 9 passes as opposed to the 11 failures). Table II, page 59, indicates the calculations necessary to define F_{50} and standard deviation.

TABLE II

CALCULATION OF DART IMPACT STRENGTH

WT.	WT_C	N	N WT_C	$N(WT_C)^2$
440	4	0	0	0
410	3	1	3	9
380	2	4	8	16
350	1	3	3	3
320	0	1	0	0
		$\Sigma N = 9$	$\Sigma N\ Wt_c = 14$	$\Sigma N(Wt_c)^2 = 28$

$$F_{50_c} = \frac{\Sigma nWt_c}{\Sigma n} + (1/2)^{**} = \frac{14}{9} + 1/2 = 2.06$$

$$M = \frac{\Sigma n(Wt_c)^2}{\Sigma n} - \left(\frac{\Sigma nWt_c}{\Sigma n}\right)^2 = \frac{28}{9} - \left(\frac{14}{9}\right)^2 = 3.11 - 2.43 = .68$$

Where: Wt = Actual wt. in gms.
Wt_c = Corrected wt. (lowest wt. = 0, etc.)
N = No. of occurrences at each wt.
F_{50_c} = Corrected mean failure wt.
M = Measure of deviation

We may now find the actual F_{50} and standard deviation as follows:

F_{50_c} = 2.06 = 380 gms. + 2 gms. = <u>382</u> gms. on wt. scale

$S_c = f(m)$ as described in Figure 4, page 60, and $S_c = 1.12$

$S = (S_c)$ *30 gms. = 33 gms.

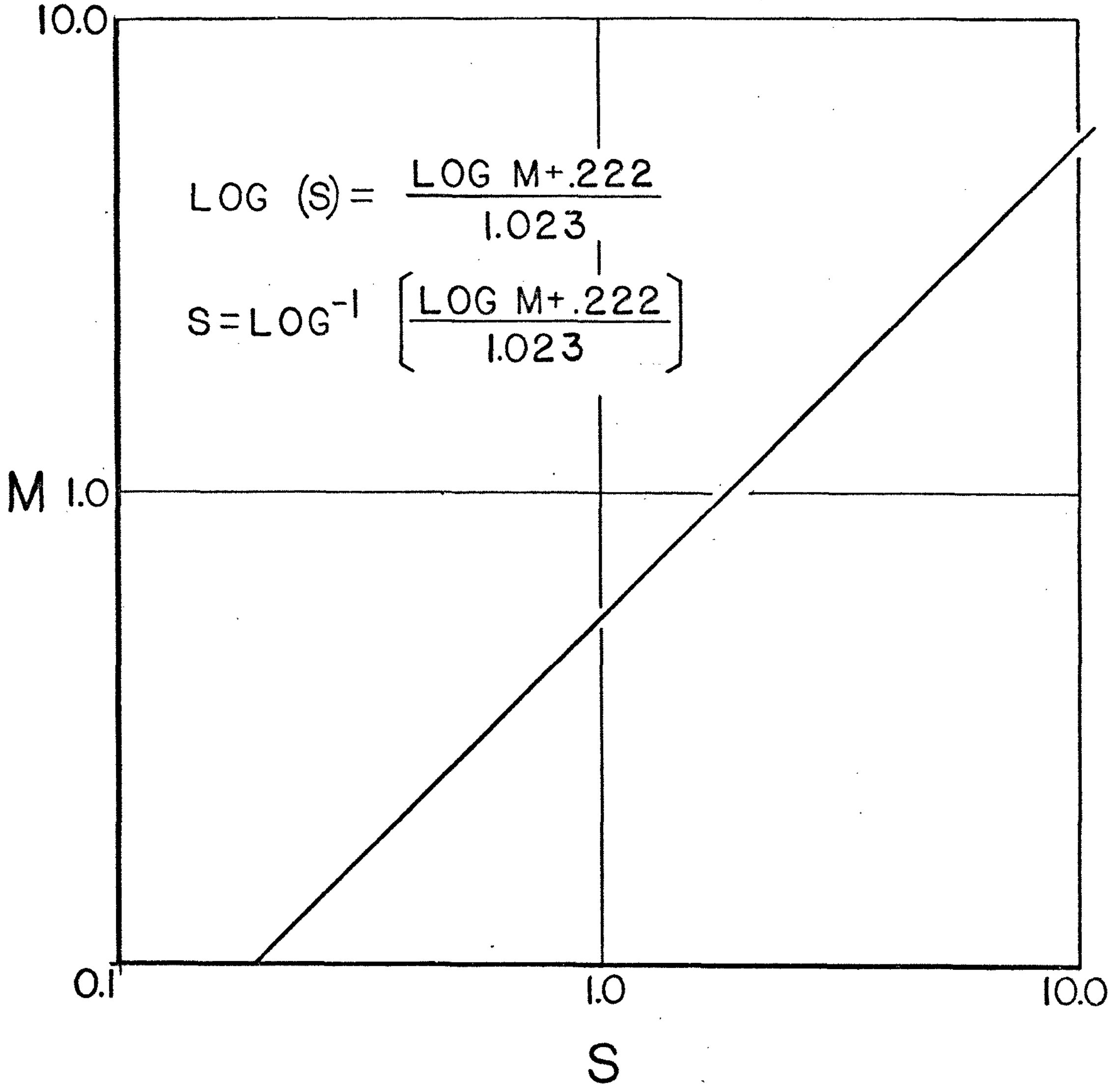
Therefore, Dart Impact = wt. * height

$$\text{Dart Impact} = 5\left(\frac{382}{453.5} \pm \frac{33}{453.5}\right)$$

Dart Impact = 4.17 ± .35 ft.lbs.

**(1/2) is added to $\frac{\Sigma nWt_c}{\Sigma n}$ for passes and subtracted when using failures.

FIGURE 4
DETERMINATION OF
DART IMP. STDD. DEVIATION



TENSILE IMPACT STRENGTH TEST

I. Introduction

This method is used to determine the tensile-impact energy to break and is fully described in ASTM-D1822-68 (Note: We run both radial and transverse specimens as shown in Figure 1, page 52).

II. Method

See ASTM-D-1822.

III. Recording Data

The following information is recorded per specimen:

A. Windage Factor

B. 5 Replicate Test Numbers

IV. Reporting Data

We report an average in. lb. number for the five specimens. The individual values are derived as a function of scale reading (S), wind factor (W) and bounce factor (B):

Then $TI_i = S_i + B_i - W$

Where B_i is derived from Figure 5, page 62.

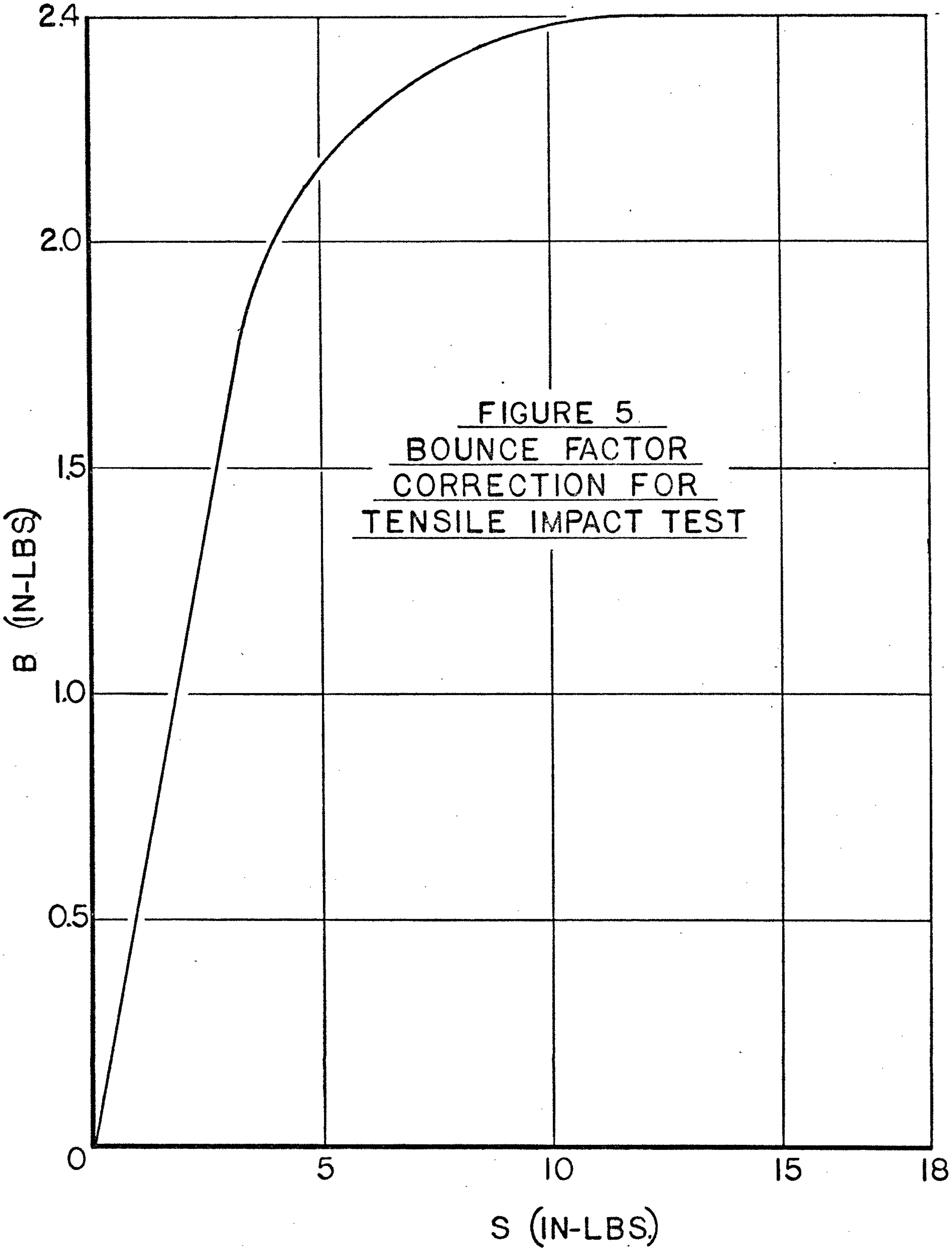


FIGURE 5
BOUNCE FACTOR
CORRECTION FOR
TENSILE IMPACT TEST

STIFFNESS TEST

I. Introduction

This test method determines the stiffness in both radial and transverse directions of our 7" disc by using the cantilever beam ASTM D747 method.

II. Summary of Method

See D747-63.

III. Recording Data

Data is taken for a replicate of five specimens at the 3, 6, 9, 12 and 15° levels. The loads are recorded as the needle sweeps.

IV. Reporting Data

We have found through experience that with HDPE the best straight line is obtained using the 3, 6 and 9 degree values. As a shortcut method of calculation, then, we have eliminated the 12 and 15° points and plotted angle vs. load for 3°, 6° and 9° only. (See Figure 6, page 64).

The formula for stiffness, as written, may be shortened as follows:

$$\text{Stiff} = K \left(\frac{L}{\phi}\right)$$

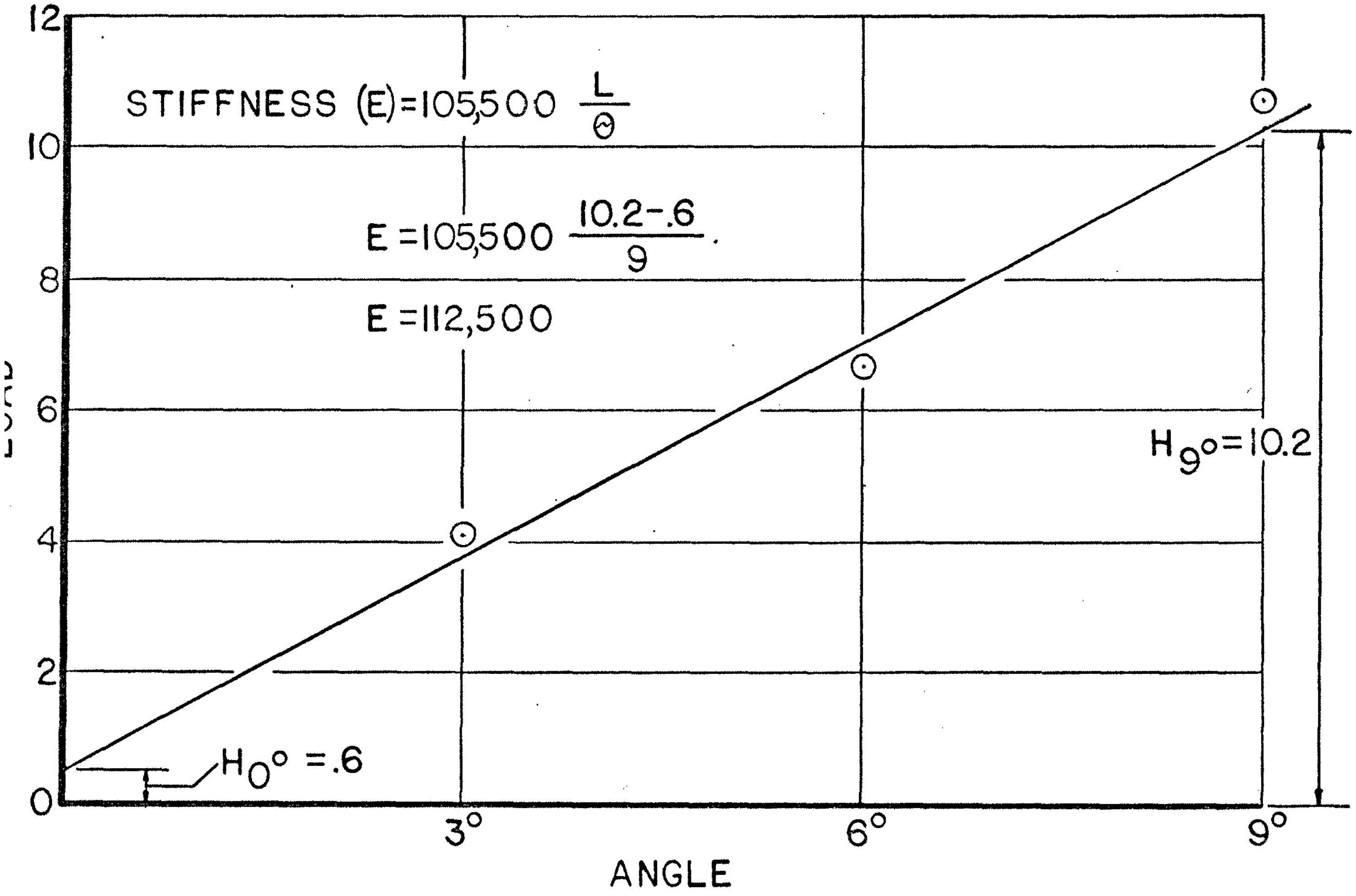
Where $K = \frac{4S(M_t)}{W_d^3(100)(.01745)} = 105{,}500$

L = Load Reading

ϕ = Angle

$$\text{Stiffness} = 105{,}500 \left(\frac{L}{\phi}\right)$$

FIGURE 6
STIFFNESS TEST



Also, rather than translating the line to cross the 0,0 point, one must only note the ordinate height (h_{0°) of the line at 0° and subtract this from (h_{9°) at the 9° angle reading. (See Figure 6, page 64).

We normally plot both directions for a given sample on the same sheet of paper and note both stiffness values:

$$\text{Stiffness} = 105{,}500 \left(\frac{L9^\circ - L0^\circ}{9^\circ}\right)$$

WARPAGE TEST

I. Introduction

Of major concern to the injection molder is the degree of warpage found in a finished part. The less warpage, the less chance for a stress break due to material orientation. We have noted definite differences in degree of warpage for various materials and have developed a means for measuring these differences.

II. Summary of Method

We have devised a simple method for measuring warpage of the 7" disc by using a height from a plane (Δh) which indicates the amount of warpage in a particular direction. Twenty samples are measured (10 tit-down and 10 tit-up) as pictured in Figure 7, page 67. The Δh used for each specimen is the maximum obtainable by rotating the disc 360° (Note: samples should be allowed to warp for at least 48 hours).

IV. Recording Data

Table III below lists an example of data taken on one sample set:

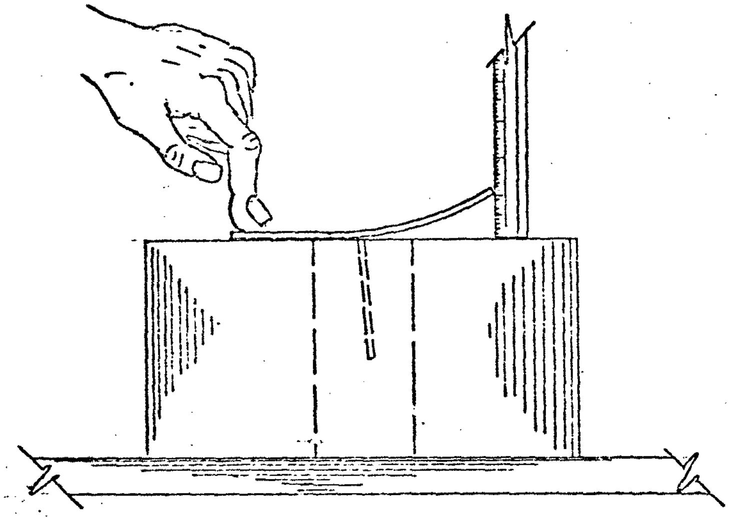
TABLE III

WARPAGE TEST FOR SAMPLE XYZ

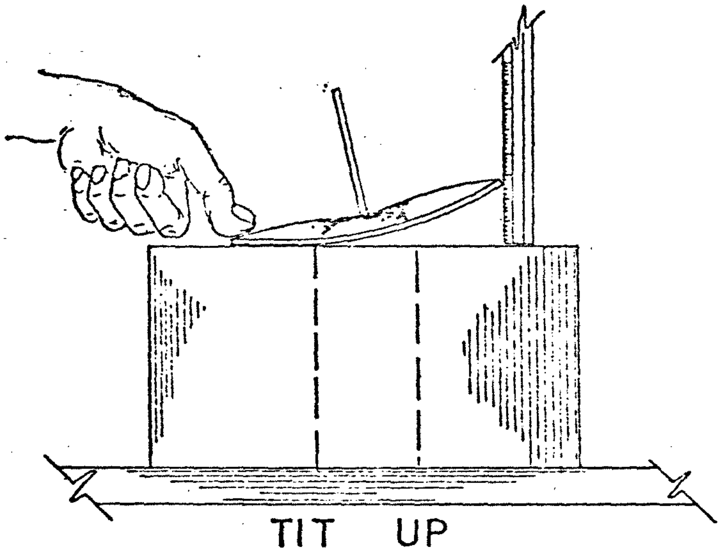
TIT-UP	TIT-DOWN
1.10*	1.30
1.05	1.25
1.10	1.30
1.15	1.35
1.10	1.20
1.05	1.25
1.10	1.35
1.05	1.30
1.15	1.30
1.10	1.25

*Read to nearest .05 inch at center of .045 in. thick disc.

FIGURE 7
WARP MEASURING
PROCESS



TIT DOWN



TIT UP

IV. Reporting Data

The data is averaged in the two positions (tit-up and tit-down) and reported as is the total of the two. In our example for XYZ, we would have:

W (Tit-Up) = 10.95/10 = 1.10 inches

W (Tit-Down) = 12/85/10 = 1.29 inches

W Total = 2.39 inches

AS MOLDED MELT INDEX

I. Introduction

The determination of the melt index of the final product relative to the initial melt index of the resin gives an insight to a material's flow stability.

II. Method of Testing

The 7" disc specimens shall be stranded so that enough material may be allotted to perform a standard melt index run as per ASTM D-1238.

III. Reporting Data

Only the melt index in g/10 min. shall be noted.

AS MOLDED DENSITY

I. Introduction

This determination offers added information when considering moldability of resin, orientation and packing during injection molding.

II. Method of Testing

Samples are cut directly from molded parts as opposed to using compression molded resin specimens. ASTM D-1505 is used.

III. Recording Data

An average of the three specimens is reported as gm/cc.

SPIRAL FLOW TEST

I. Introduction

The determination of this value gives the fabricator a good on-the-job measure of material flow. Rather than working with melt index numbers derived at very low shear rates, the material user can correlate his work with the spiral flow number obtained at field shear rates, $\approx$10,000 sec.$^{-1}$.

II. Method of Testing

The spiral specimens shall be produced by using maximum injection pressure and injection speed with a 5-seconds hold on injection pressure and a 10-second cooling time. All temperature zones are set at 400°F and the mold temperature is set at 105°F.

III. Recording Data

Ten successive spirals are to be measured via the prescribed template and recorded to the nearest .01".

IV. Reporting of Data

An average shall be reported in inches.