1984

The effect of embossing process conditions on the surface properties of a plasticized vinyl polymer.

Eileen Wanjek M. Bailey
University of Massachusetts Amherst

Bailey, Eileen Wanjek M., "The effect of embossing process conditions on the surface properties of a plasticized vinyl polymer." (1984). *Masters Theses 1911 - February 2014*. 2173.
Retrieved from https://scholarworks.umass.edu/theses/2173

THE EFFECT OF EMBOSSING PROCESS CONDITIONS ON THE SURFACE PROPERTIES OF A PLASTICIZED VINYL POLYMER

A Thesis Presented

By

Eileen M. Wanjek Bailey

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE

February 1984

Department of Polymer Science and Engineering

THE EFFECTS OF EMBOSSING PROCESS CONDITIONS ON THE SURFACE PROPERTIES OF A PLASTICIZED VINYL POLYMER

A Thesis Presented

By

Eileen M. Wanjek Bailey

H Henning Winter

H. HENNING WINTER, Chairperson

Richard S. Stein

Richard S. Stein

Richard J. Farris

William J. MacKnight, Department Head
Polymer Science and Engineering

ACKNOWLEDGEMENT

The author wishes to thank Dr. H. H. Winter and H. H. Hopfe for their technical support and encouragement through all phases of this study. Special thanks is extended to Mr. Morgan Davis for his assistance in extrusion and sample testing and to Monsanto Chemical Co. for their cooperation and the use of their facilities.

ABSTRACT

The Effect of Embossing Process Conditions on the Surface Properties of Plasticized Vinyl Polymers

Vinyl Polymers

Eileen M. Wanjek Bailey, B.S., Drexel University
M.S., University of Massachusetts
Directed by: Professor H. H. Winter

Experiments were carried out with plasticized polyvinyl butyral (PVB) utilizing a small scale embossing set-up. The main objective of these experiments was to emboss the polymer immediately after extrusion. Past studies have shown that the level of surface roughness permanence obtainable with embossed PVB is well below the necessary 90% needed for deairing in laminate manufacture. Results of the past study indicated that higher surface permanence could be achieved by reducing the travel time between the extrusion die and the embossing nip. Equipment was designed to carry out this objective and the results do show an improvement in surface permanence. The mechanism behind the improved permanence was speculated to be linked to crystallinity. However, the results from this investigation suggest that surface melt viscosity as controlled by shear history is the primary variable.

TABLE OF CONTENTS

ACKNOWLEDGEMENT. iii

CHAPTER

I. INTRODUCTION. 1

Surface Structure 4

Background. 5

II. EXTRUSION APPARATUS AND PROCEDURE 15

Process Equipment 15

III. SURFACE CHARACTERIZATION. 23

IV. POLYMER PROPERTIES. 26

V. RESULTS AND DISCUSSION. 29

VI. CONCLUSIONS 36

REFERENCES 37

APPENDIX 38

LIST OF TABLES

1. Effect of Moisture on Modulus and Viscosity of Plasticized PVB Sheet. 13

LIST OF ILLUSTRATIONS

Figure

1. Flow chart of Laminating Operation. 6
2. Embossing Process 7
3. Embossed Surface as a Function of Travel Time 8
4. Surface Temperature as a Function of Travel 10
5. Surface Moisture Diffusion as a Function of Travel Time 11
6. Experimental Embossing Process. 16
7. Die Lip Designs 18
8. Embossing Roll Surface Pattern. 20
9. Surface Profile 25
10. Viscosity as a Function of Shear Rate for Plasticized PVB. 27
11. Surface Permanence as a Function of Travel Time. 30
12. Surface Permanence as a Function of Travel Time and Viscosity. 32
13. Schematic of Incremental Die Flow Program. 41
14. Schematic of Heat Transfer and Moisture Diffusion Simulator. 50

CHAPTER 1

INTRODUCTION

Millions of square feet of polymer film and sheet are extruded each year with an embossed surface pattern or design. In most cases the purpose is for appearance, i.e., the leather look. But in the case of vinyl acetal polymers used as interlayers in laminate constructions, the surface topography has a purely functional purpose. An example for this is the windshield lamination process in which two glass windows are glued together by a sheet of polyvinyl butyral (PVB). The surface structure on the polymer sheet provides temporary open channels between the glass and the polymer for air escape during lamination. If the polymer surface is too smooth or the structure relaxes too quickly, air pockets can develop resulting in a defective laminate. After deairing, the laminate is usually autoclaved at high temperature and pressure where polymer flow occurs and the surface pattern disappears forming an optically clear windshield.

The surface structure tends to disappear when heating this sheet even without contacting a solid glass surface. The temperature and rate at which a polymer surface pattern disappears in a heat treatment is very important and is characterized by the property of surface permanence. In industry, surface permanence is defined as the amount of surface roughness that remains after exposure to 110°C for 12 minutes divided by the initial roughness. This exposure simulates the thermal conditions of a typical shaping operation during which the sheet is stretched and shaped to the contour of the glass. At least 90% of the surface roughness must be maintained during this step to insure satisfactory deairing. Studies with polyvinyl butyral polymer have shown surface permanence to be dependent on the manufacturing technique used to produce the surface structure. The most popular and versatile technique for surface structuring is embossing. Since an impression of the embossing surface is left on the polymer, the pattern can be easily changed and intricate three dimensional structures can be achieved. For PVB, embossing results in acceptable surface roughness, however, the permanence of the structure is very poor, <50%. The current manufacturing of this material utilizes specially designed sheeting dies to achieve a more permanent structure but pattern design is very limited.

Controlling surface roughness and permanence in order to optimize deairing is very desirable in an industry where laminating operations are diverse. This thesis is an extension of the earlier work in which the two surface forming techniques and resulting properties were studied (review by Fulton, et al., 1979). One highlighted difference between the two processes was that in embossing, the polymer travels some time in the open environment prior to embossing. It was hypothesized that rapid diffusion of moisture from the polymer surface inhibited crystal formation. This would give a lower degree of crystallization at the surface layer and hence a lower permanence since the melting of crystals was assumed to control permanence at elevated temperatures. Even though crystallinity has never been detected in PVB, the co-polymer does contain 15-25% residual vinyl alcohol. It is the alcohol, or the hydroxyl grouping on the PVB chain that is believed to form crystals. The reasoning behind this stems from the fact that polyvinyl alcohol, amorphous and atactic by nature, can be made to crystallize through dehydration of dilute solution and or straining (Packter and Nerurkar, 1975). On the basis of this hypothesis, it was proposed that the embossed surface permanence could be improved by decreasing the travel time, or moisture evaporation time, between sheet extrusion die and embossing roll. The results presented in this investigation support this proposal but whether crystallinity controls permanence has not been proven.

Surface Structure

Properties which define the surface structure are surface roughness, gloss, and surface roughness permanence. Surface roughness is typically 15-25 μm (600-1000 μ in) and random in terms of amplitude variability and spatial frequency. During lamination of the sheet on a glass surface, this roughness provides channels for air escape during the deairing operation. Gloss is a measure of microroughness, <1 μm (39 μ in), which is superimposed onto the surface roughness. Low gloss, or good surface, helps reduce the tendency for sheet sticking together during storage.

Surface permanence is defined as the amount of surface roughness that remains after exposure to 110°C for 12 minutes divided by the initial roughness. This exposure simulates thermal conditions during the deairing step of the lamination process. At least 90% of the surface roughness must be maintained during this step to insure satisfactory deairing. However, it is equally important that the surface roughness disappears during autoclaving in order to produce a defect free, optically clear laminate. A flow chart of the laminating steps and temperatures are shown in Figure 1.

Background

Studies which were carried out with plasticized PVB investigated the surface forming capabilities of various embossing techniques (Fulton et al., 1979, Riek et al., 1971). The best results were obtained with the set up shown in Figure 2. The extruded sheet traveled a minimum distance of 8 inches to the nip of the embossing roll. The sheet was carried around the roll while being cooled to 82^{o}C which was the maximum temperature allowed to insure ease of stripping. Surface roughness and gloss could be controlled satisfactorily if the sheet was embossed at extrusion temperatures between 199-215^{o}C, and subsequently cooled. The surface roughness permanence improved as the embossing roll temperature and pressure increased, but within the limits of the process the maximum value achieved was only 50% (Figure 3).

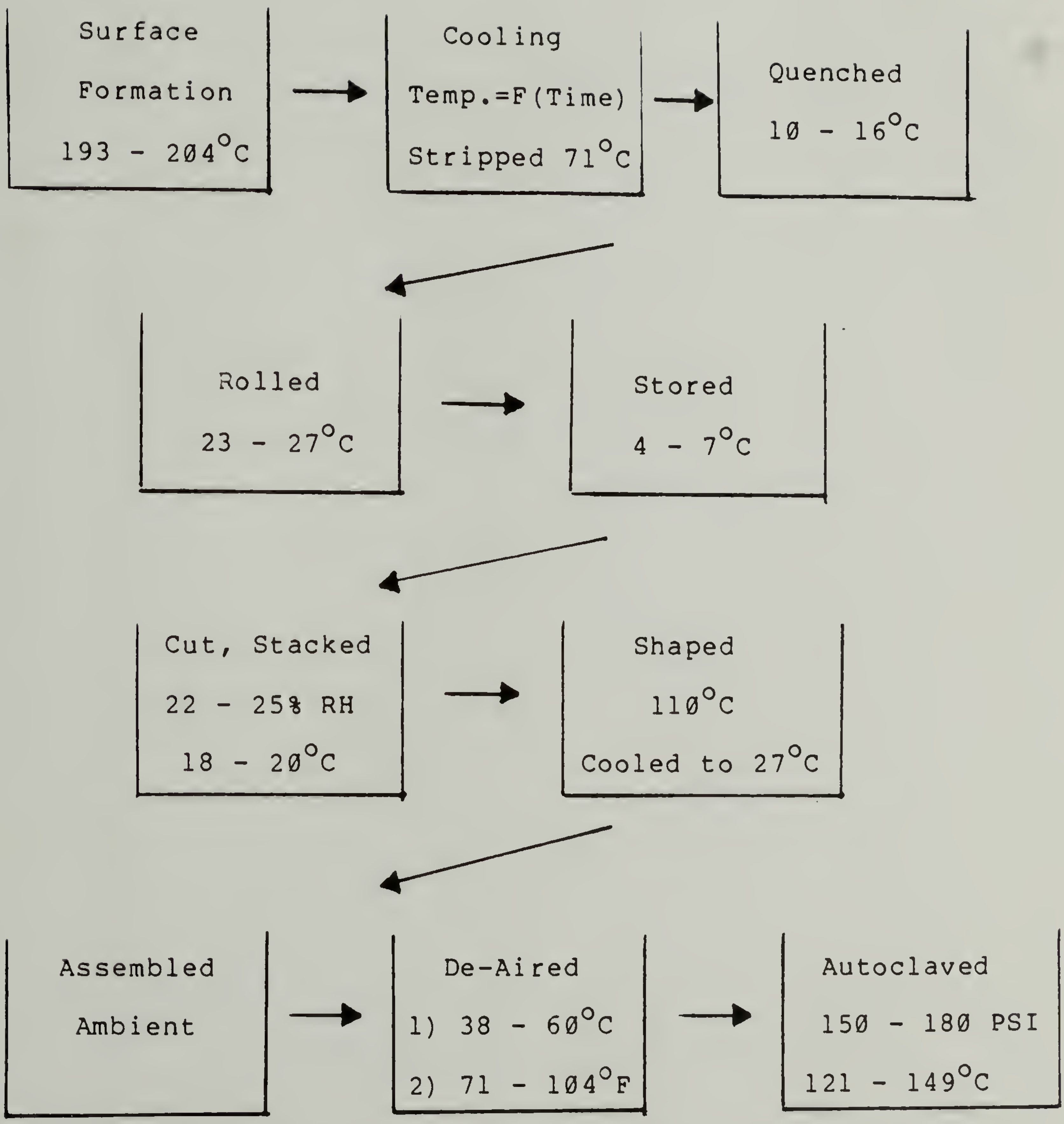


Figure 1. This is a Flow Chart of a typical laminating process which would be used for windshield manufacturing.

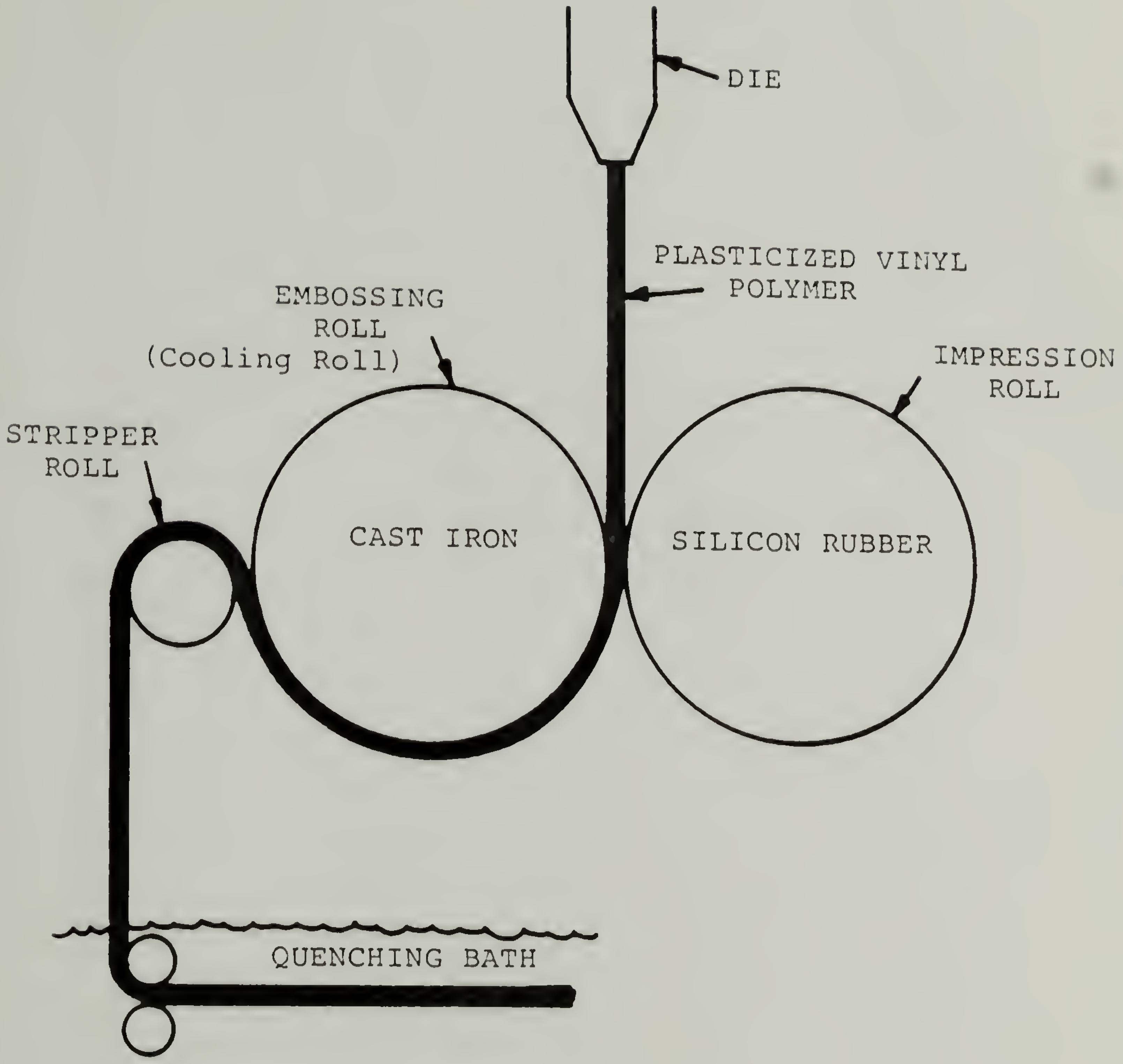


FIGURE 2. Embossing Process Utilized in Previous Work, Fulton et al., 1979.

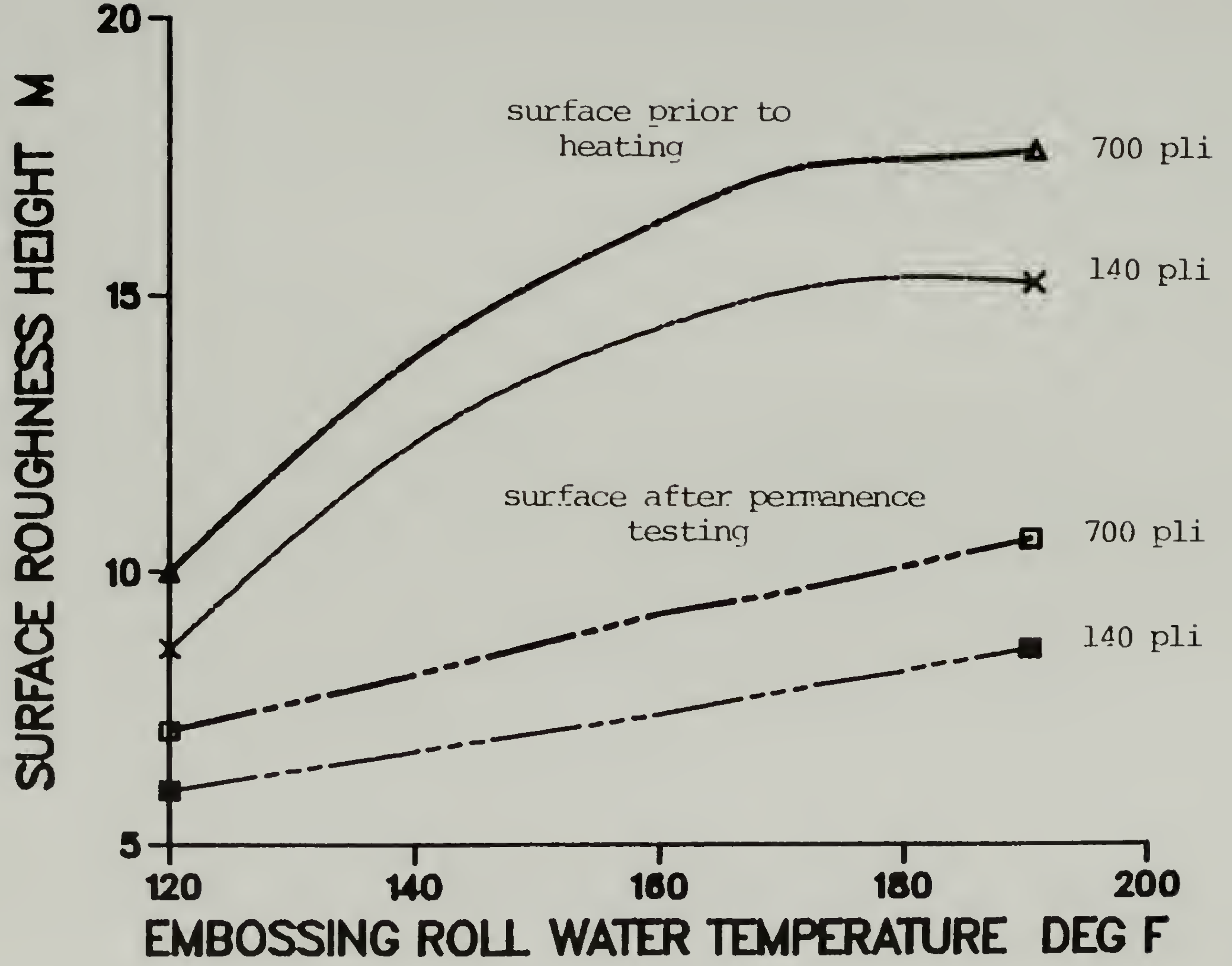


Figure 3. Embossed Surface Results obtained by Fulton et. al., 1979

This permanence was lower than the level achieved in a second process. When the PVB sheet surface was structured by flow through a specially designed sheeting die and cooled under the same conditions as the embossed sheet, surface permanence was greater than 90%. Details of this process are propriatary, but one of the main differences between the embossing process and surface formation at the sheeting die is the transport time between sheet extrusion and surface formation. This increased exposure to the atmosphere for the sheet surface results in:

> cooling of surface,
> moisture diffusion out of surface layer, and
> relaxation of shear history.

Numerical modelling of the process led to the conclusion that the maximum drop in surface temperature between die exit and embossing roll was only 10K (Figure 4). The effect of this temperature change on viscosity is 15% at a shear rate of 100 s^{-1}. While this is not a major factor, it would support modelling assignments which are based on increased surface viscosity.

A study of moisture diffusion and evaporation was also carried out and the results showed that the loss of moisture at elevated extrusion temperatures was extremely rapid (Figure 5). A simulation of the embossing experiment

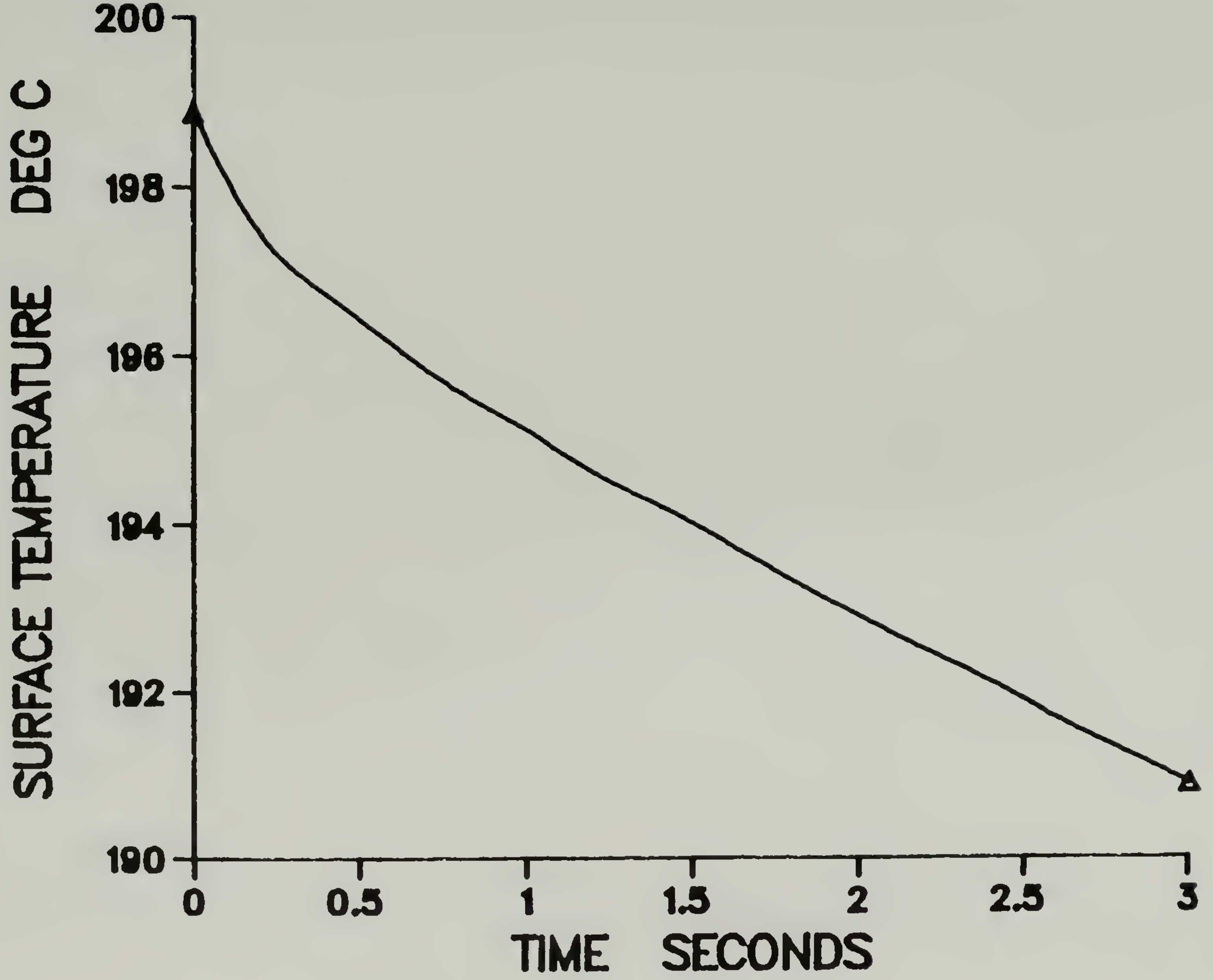
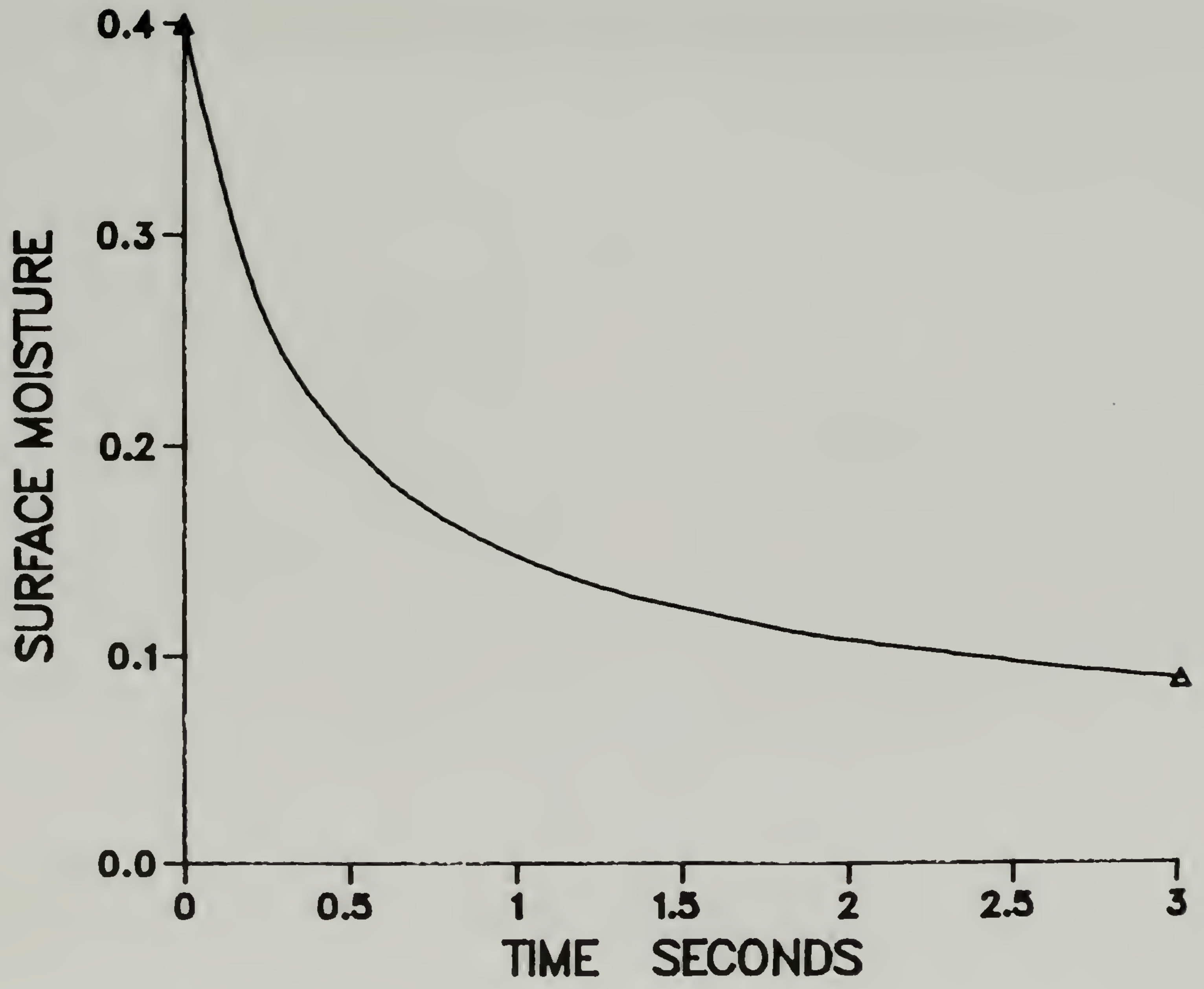


Figure 4. Surface Temperature Change During Sheet Travel to Embossing Nip



<u>Figure 5</u>. Surface Moisture Diffusion During Sheet Travel to Embossing Nip

showed that within 1 s of travel time from the die to the nip the surface moisture dropped from 0.4% to 0.147%. Moisture, however, acts as an additional plasticizer for PVB. The effect of moisture on modulus is noted in Table 1 (Tetreault, 1978). Again, the effect of low moisture on surface rheology would be to stiffen the polymer thus making crystal nucleation or stress relaxation more difficult with decreased chain mobility.

The influence of reduced surface viscosity resulting from high shear at the polymer die interface was not previously addressed but was found through this investigation to have some effect on surface permanence properties. The result of shearing is a reduction in elasticity and viscosity of the polymer fluid. This non-newtonian behavior is attributed to the reduction of physical entanglements of polymer chains due to slipping under stress (Rudin and Schreiber, 1983). Since the most probable state of a given molecule is one in which it is entangled, the polymer will return to this state once sufficient molecular mobility is achieved. Dealy and Tsang, 1981, showed that the response of a polymer to high shearing can be altered by the previous shear history. Based on their results, the stress overshoot and the maximum stress achieved was dependent on rest time between shear applications. Based on these

TABLE 1

EFFECT OF MOISTURE ON MODULUS & VISCOSITY OF PLASTICIZED PVB SHEET

Moisture (%)	TG ($^{\circ}$C)	Modulus X 10^7 (dynes/cm^2)			η * X 10^6 (poises)		
		20	30	110°C	54	100	140°C *
0.17	26	8.1	1.02	0.158	4.00	2.10	0.925
0.40	25	6.2	0.85	0.141	3.75	1.95	0.816
0.67	23	3.65	0.57	0.139	3.60	1.89	0.744

interrupted shear tests, the characteristic reentanglement time for polyethylene molecules was shown to be 385 seconds compared to 3.6 seconds for stress relaxation from a given shear history.

In summary, the phenomena which appear to influence surface viscosity and possibly surface permanence are dependent on polymer travel time from the die to the embossing nip. It was the objective of this thesis to investigate the effect of travel time on embossed surface permanence.

CHAPTER II

EXTRUSION APPARATUS AND PROCEDURE

A small scale embossing set-up was designed and is shown in Figure 6. Die position was varied to obtain die to exit nip distances of 0.5, 0.88 and 3.0 inches (as measured from the nip center). Extrusion rate varied between 15 and 200 grams per min. The combination of extrusion rate and die distance yielded the travel time.

Process Equipment

The polymer was extruded from a 2.5 in, single screw extruder, through a static mixer into a center fed sheeting die. The purpose of the static mixer was to break up the melt stream thus promoting a more uniform temperature profile. Upon exiting the die the sheet transferred to the embossing nip where pressure was applied and surface replication achieved. After surface formation the sheet traveled 5/8 of the circumference around the embossing roll while being cooled. The sheet was then stripped from the roll,

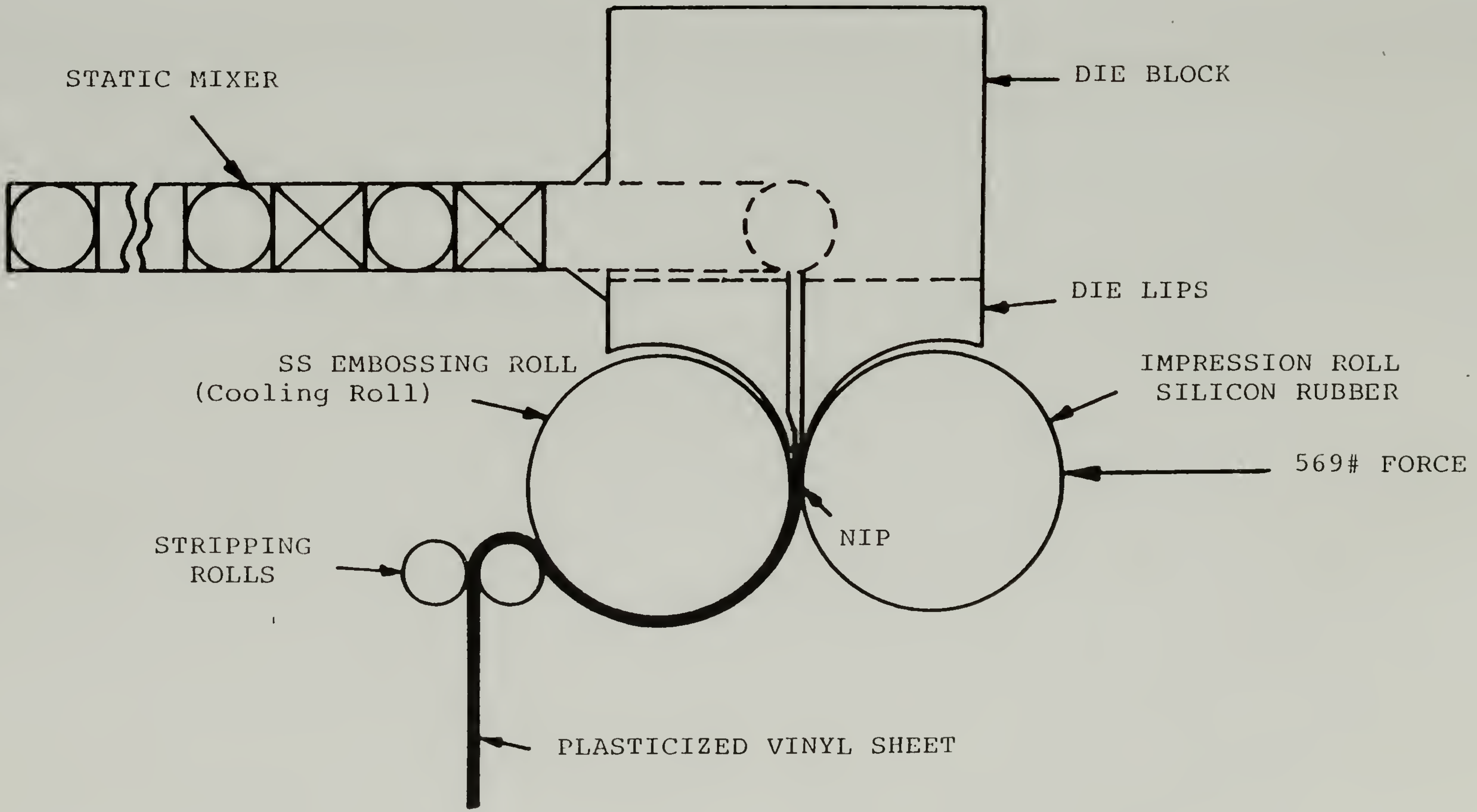
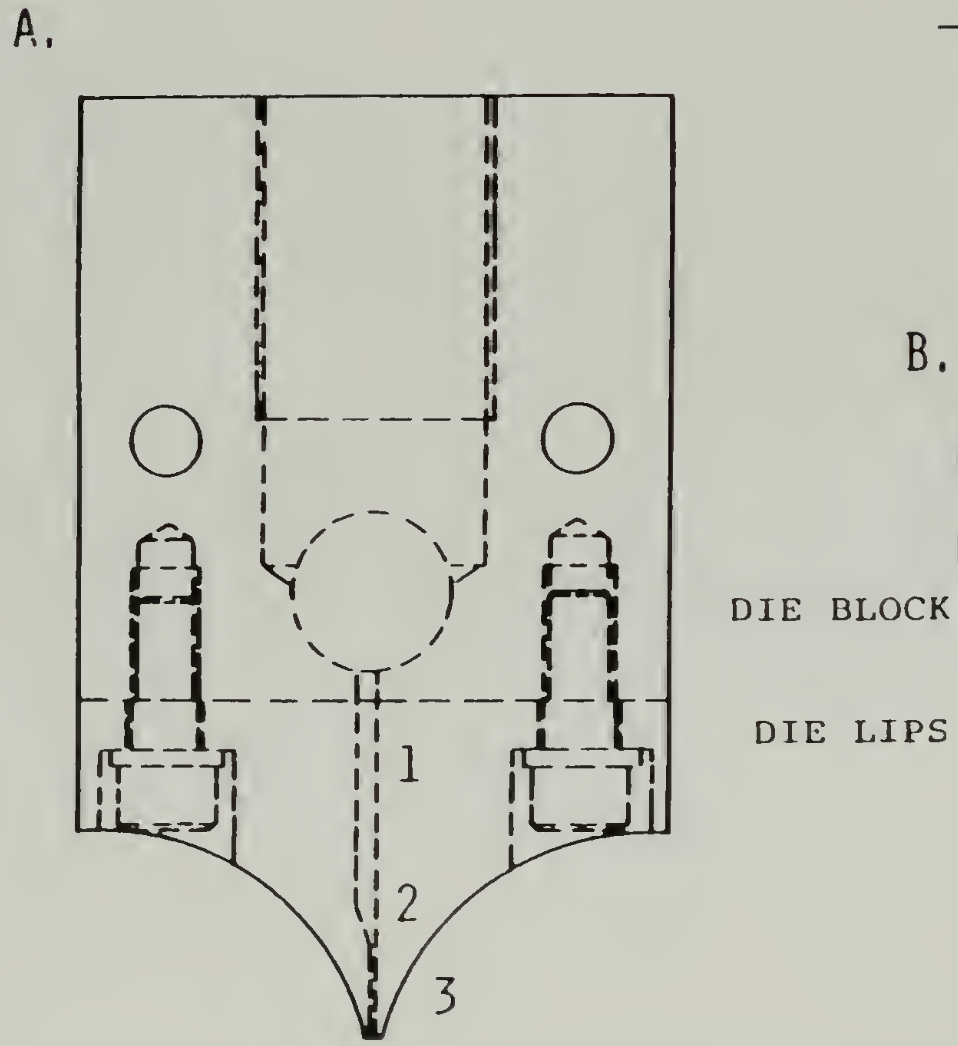


FIGURE 6. Experimental Embossing Equipment

air cooled and tested.

Die. Two die lip designs were used during the program and are shown in Figure 7. The lips were attached to a heated center fed die block. The original lip design, A, evolved from an optimization of metal thickness and embossing nip distance. The exit gap was set at 0.02 in prior to start-up but this opened up by an unknown amount during extrusion due to high melt pressures and bolt stretching. In order to avoid die to roll contact the die had to be adjusted upward. The resulting mid nip to die distance was 0.5 in. Experiments were also run with this design at a distance of 3.0 in. A second set of die lips, B, were used at a distance of 0.88 in from the nip. The larger exit gap, .030 in, and the heavier design reduced "clamshelling" during extrusion. Due to the uncertainty of the actual gap, process conditions were used to estimate the flow channel opening (Appendix B). The shear rate and viscosity at the die - polymer interface were calculated based on estimated gap. The die channel width was 3.0 in and the rate of extrusion varied up to 200 g/min. At a density of 54 lbs/ft^3 and an estimated gap of 0.055 in, this corresponds to an average velocity of 7 ft/min at the die exit. Melt temperature ranged from 196-202°C for most experiments. Die temperature was held at 177°C because

	1 Channel Gap	2 Entrance Angle	3 Land Gap	 Length
A	0.10"	45^{o}	.020"	0.50"
B	0.10"	45^{o}	.030"	0.50"



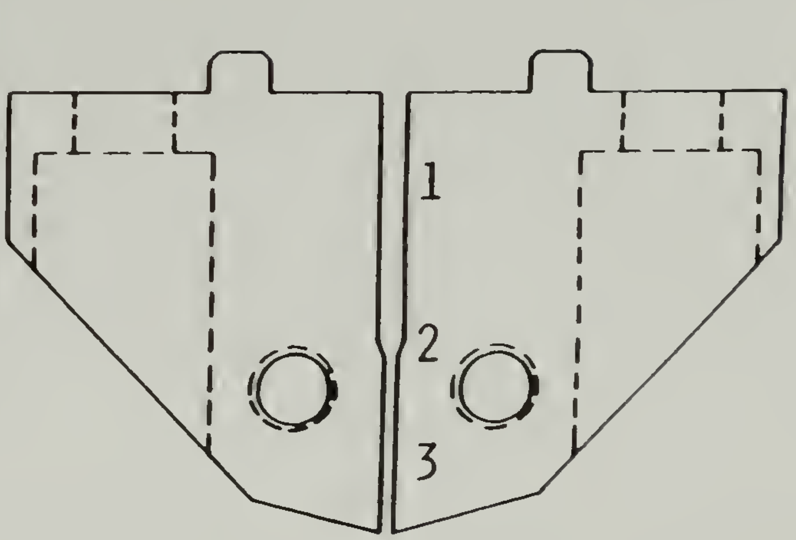


FIGURE 7. Die Lip Designs used for Embossing Study.

higher temperatures resulted in flow defects. Lower die temperatures resulted in increased die pressure.

Embossing Rolls. The metal embossing, cooling roll was 3.0 in in diameter which was the maximum diameter for optimizing nip distance and the minimum for cooling efficiency. The roll was manufactured by Rodney Hunt (see Appendix C) and contained the helix design for water flow. The surface of the embossing roll was originally sand blasted but this proved to be too fine a structure for replication under the process conditions chosen. Therefore, the surface was refinished with an engraved diamond knurl pattern as shown in Figure 8. The cooling water which flowed at a rate of .9 gal/min, was maintained at temperatures between 34 and 39°C. While these conditions were less than optimum for achieving good surface properties, they allowed the broadest range of experimental rates. High water temperatures coupled with high extrusion rates would have given higher permanence but made stripping very difficult and occasionally impossible.

A pressurized air cylinder was used to apply the force to the rubber impression roll. This roll was also 3.0 in in diameter and made of silicon rubber with a shore hardness

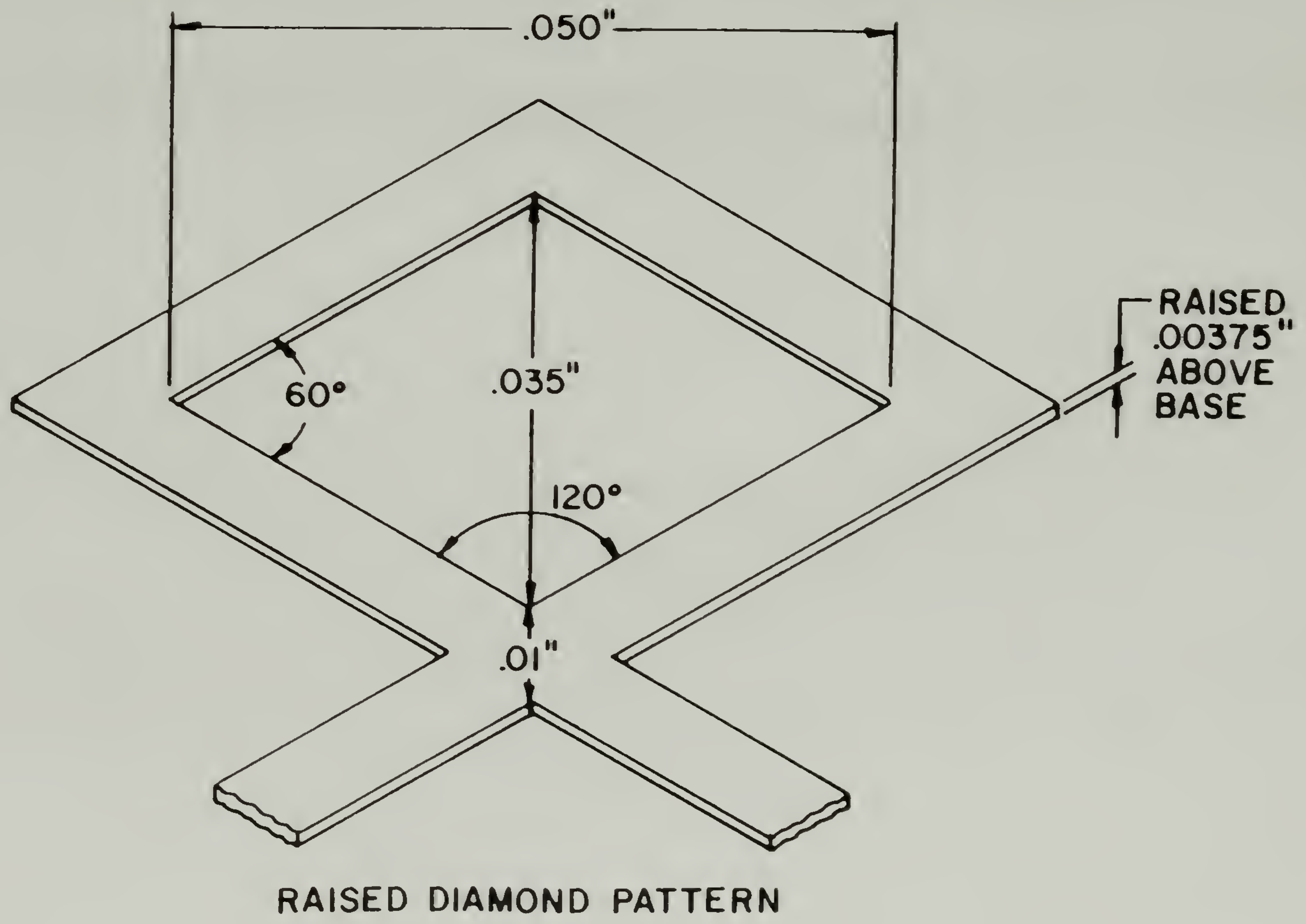


Figure 8. Embossing Roll Surface Pattern

of .075. Since the effect of embossing pressure had been reviewed in earlier work (Fulton et al., 1979), the pressure was maintained at 15 psig on the cylinder. This transforms to an applied sheet force of 569 lbs, or a stress of 883 psi. The nip pressure, 883 psi, was calculated based on nip dimensions 0.23 in width and 2.8 in length. The width was determined by measuring the impression made on carbon backed paper which was squeezed in the nip.

Extrusion rate was varied up to 200 g/min and the line speed up to 15 ft/min. Because the average velocity of the sheet in the die was lower than the average velocity after the die, some machine direction stretch resulted. The degree of this extensional flow can be defined by a stretch ratio,

$$\frac{l_f}{l_d} = \frac{\rho_d}{\rho_f}\frac{h_d}{h_f}\frac{W_d}{W_f}$$

Eventhough this was not constant for all experiments, the machine direction stretch ratio for 87% of the samples was calculated to be between 0.4 and 0.62. A constant density was assumed for this calculation and the die gap was estimated based on flow calculations. Sample width varied between 2.5 and 3.1 in and gauge was usually maintained between 0.027 and 0.035 in. The sheet was stripped by hand

and allowed to air cool prior to surface measurement testing.

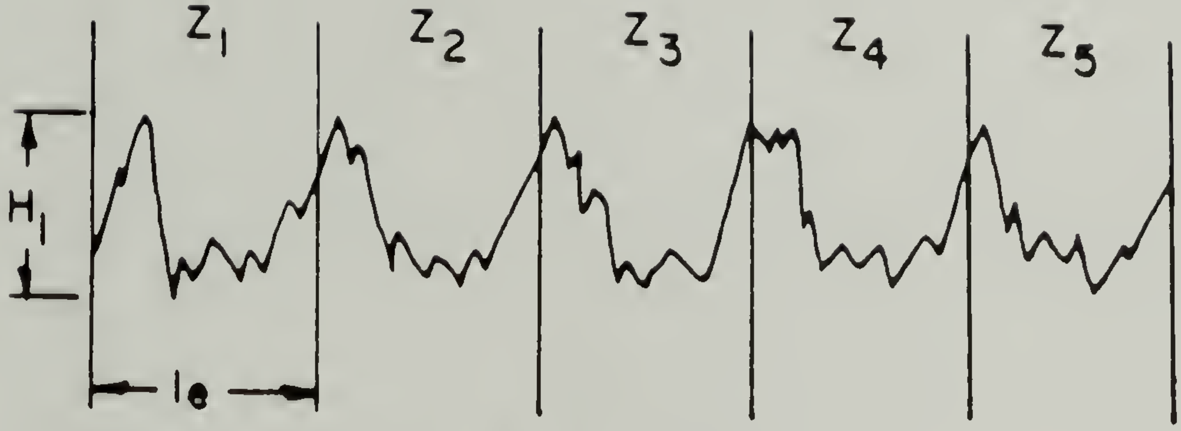
CHAPTER III

SURFACE CHARACTERIZATION

The polymer surface height was measured with a Perthen Perthometer C5D. This instrument uses a mechanical tracer which moves along the surface at constant speed. A movable stylus touches the surface continuously and thus follows all roughness. The movements of the stylus are transferred to an electrical converter, which converts them into measured values depicting the depth of profile. A tracing length of 12 mm was used and 5 traces were averaged per set. Six sets were run on each sample and again averaged to produce the mean roughness height. Each sample was characterized in an area which was embossed in exactly the same location on the roll. This was achieved by transferring a point on the embossing roll onto the sheet sample. A minimum of two sheet samples were taken per test condition. After the surface height was recorded, the sheet was attached securely to a wooden frame and heated at 110°C for 12 min (permanence test). After this heat treatment the samples were cooled to room temperature and remeasured. The percent permanence was calculated as the mean height of the heated surface over the original mean surface height multiplied by 100.

$$\frac{\text{Heated Height}}{\text{Height}} \times 100 = \%\ \text{Permanence}$$

Sample to sample replication for a given process condition is $\pm 8\times10^{-5}$ in. Measured heights and other sample data is contained in Appendix D. A typical tracing profile is shown in Figure 9.



$$l_m = 5 \times l_e = 12\text{mm}$$

$$H_1 = \frac{1}{5}(Z_1 + Z_2 + Z_3 + Z_4 + Z_5)$$

$$H_m = \frac{1}{6}(H_1 + H_2 + H_3 + H_4 + H_5)$$

Figure 9. Surface Profile and Calculated Mean Surface Height as Traced by Perthometer

CHAPTER IV

POLYMER PROPERTIES AND MODELLING CALCULATIONS

Polyvinyl butyral (PVB) is a co-polymer of vinyl alcohol and vinyl acetal with 1.0-2.0% residual vinyl acetate. The formulations used in laminate constructions are usually plasticized with high molecular weight esters to enhance toughness. The formulation used in this study was a PVB resin with a molecular weight average between 160,000 and 180,000, plasticized to a glass transition temperature of 25-28°C. The glass transition temperature was determined using a Rheometrics Mechanical Spectrometer in the temperature scan mode at 1 Hz frequency. Other melt rheology measurements were made using a capillary rheometer with a 30 L/D capillary. The Rabinowitsch corrected viscosity vs. shear rate data is shown in Figure 10.

Moisture acts as additional plasticizer for PVB. At elevated extrusion temperatures the diffusion of moisture and other low molecular weight materials is extremely rapid. A moisture diffusion finite difference computer program was utilized to predict the surface moisture on the sheet surface (Appendix E). The mass diffusivity value, D, was calculated at 199°C to be .003 ft^2/hr. The effect of

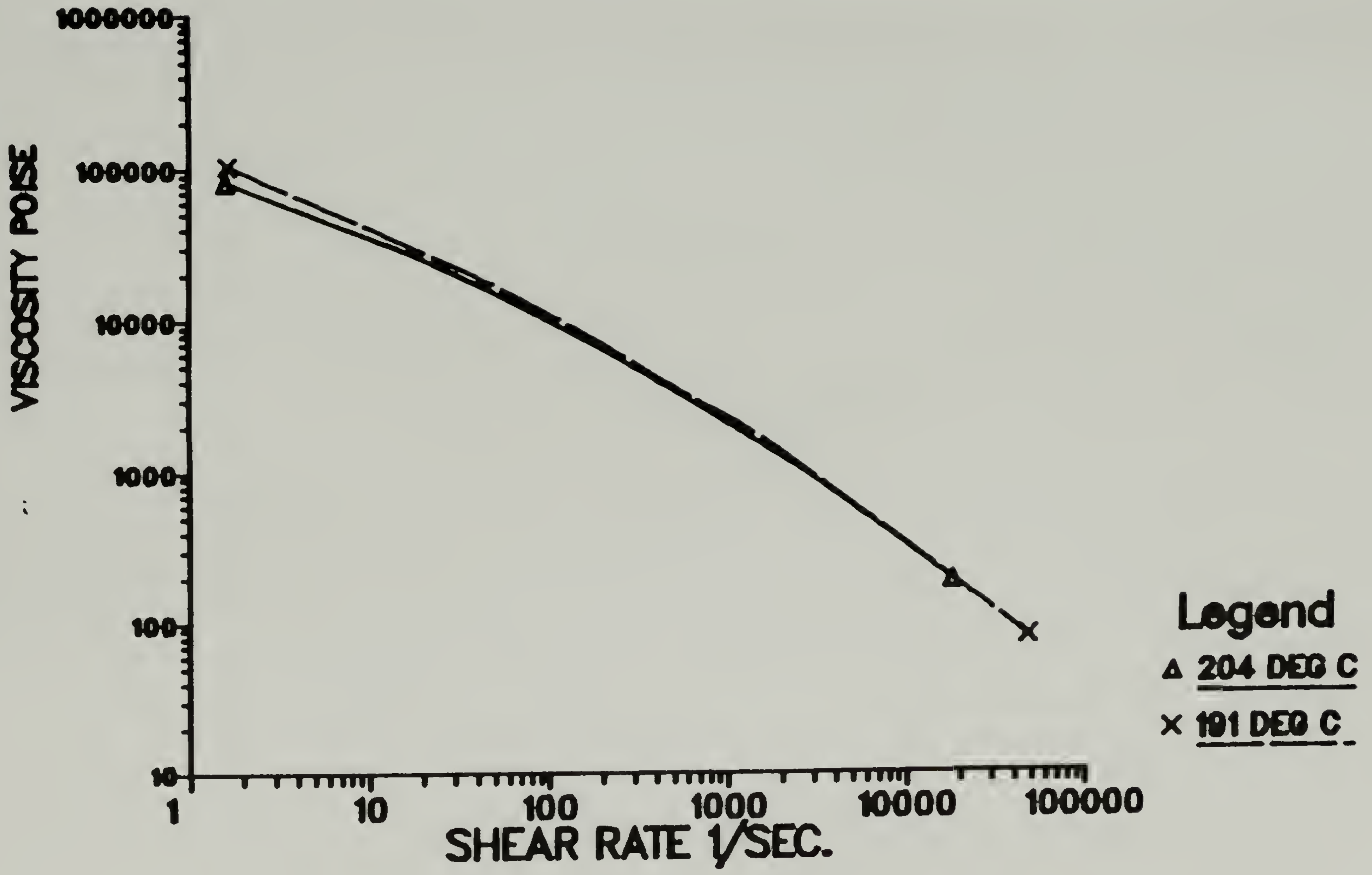


Figure 10. Viscosity as a Function of Shear Rate for Plasticized PVB Sheet.

moisture on dynamic rheology properties is shown in Table 1. The reduction in moisture results in an increase in modulus which could cause higher residual stress levels during embossing. Also, lower mobility would inhibit crystal nucleation.

A similar finite element computer program was also used to predict the surface temperature of the cooled sheet on the embossing roll as well as sheet exposed to the environment. (Appendix E.) The thermal diffusivity value, α , used for PVB was 0.0031 ft^2/hr.

The polymer response time or relaxation time, λ, for PVB was estimated using a Rheometrics Stress Rheometer in the creep recovery mode. Measurements were made at 150°C and time-temperature superposition was used to estimate the elevated temperature response. The corresponding values are listed below.

at 150°C	λ = 160.0 s
at 190°C	λ = 16.0 s
at 195°C	λ = 12.7 s
at 200°C	λ = 10.1 s

The density of the polymer used in rate calculations was 54 lbs/ft^3.

CHAPTER IV

RESULTS AND DISCUSSION

Three die distances coupled with a range of extrusion rates allowed travel time of the material to vary from 3.2 seconds to 0.1 seconds as shown in Figure 11. During this time, surface moisture and heat are lost to the environment. Moisture and temperature changes were estimated using a finite difference computer program written by H. Hopfe. (Appendix E.) The results, shown in Figure 5, indicate that at extrusion temperatures of 199°C, the surface moisture level drops from 0.4% to 0.147% in 1.0 s of travel. This is predicted to cause a 12% increase in viscosity at low shear rates. The change in temperature is shown in Figure 4 to be negligable, T=4K for 1.0 s of travel. If moisture diffusion rate controlled surface permanence properties, travel time should correlate directly. The data indicates an increase in surface permanence as travel time decreases but the level of permanence appears to be dependent on die position. The closer the die for a given travel time, the lower the permanence achieved. This suggests that another variable, dependent on die position, is influencing the surface. When the die is positioned 3 in away from the nip, the polymer needs to travel at a rate of 3 in/s (15 ft/min) to

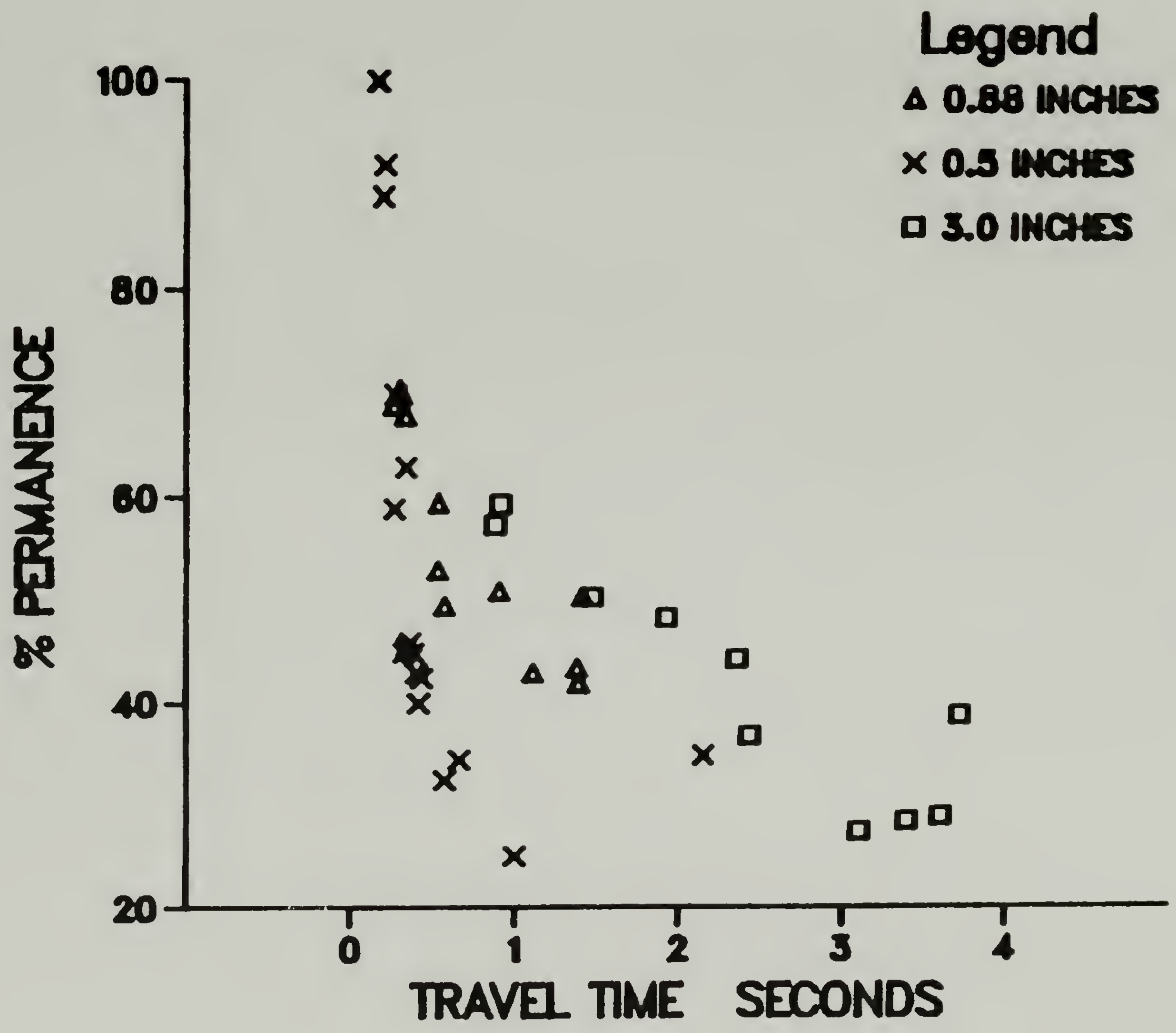


Figure 11. Surface Permanence as a Function of Travel Time and Die to Nip Distance

reach the nip in one second. If the die is positioned only 0.5 in from the nip, the polymer need travel only 0.5 in/s (2.5 ft/min) to reach the nip in the same time. One effect of the higher flow rate is an increase in shear at the polymer/die interface. PVB does exhibit shear thinning behavior at high shear as shown in the viscosity curves in Figure 10. An estimate of the surface viscosity reduction due to shear was carried out using a non-newtonian, non-isothermal computer flow model. (Appendix B) The results show that an increase in flow rate from 40 g/min to 200 g/min produces a shear rate change of 10 to 150/s. This corresponds to a 72% reduction in viscosity. This is quite significant considering the change in complex viscosity due to moisture diffusion is only 12%. Surface permanence plotted as a function of reduced surface viscosity times travel time is shown in Figure 12. The % surface permanence appears to relate better to this combined parameter even though some error was introduced in the estimation of polymer surface viscosity.

As discussed earlier, a shear reduced polymer can take over 5 minutes to recover its elasticity and viscosity (Dealy and Tsang, 1981). If consecutive processing occurs without full recovery from the previous state of shear, then the polymer's response to the second process will be less

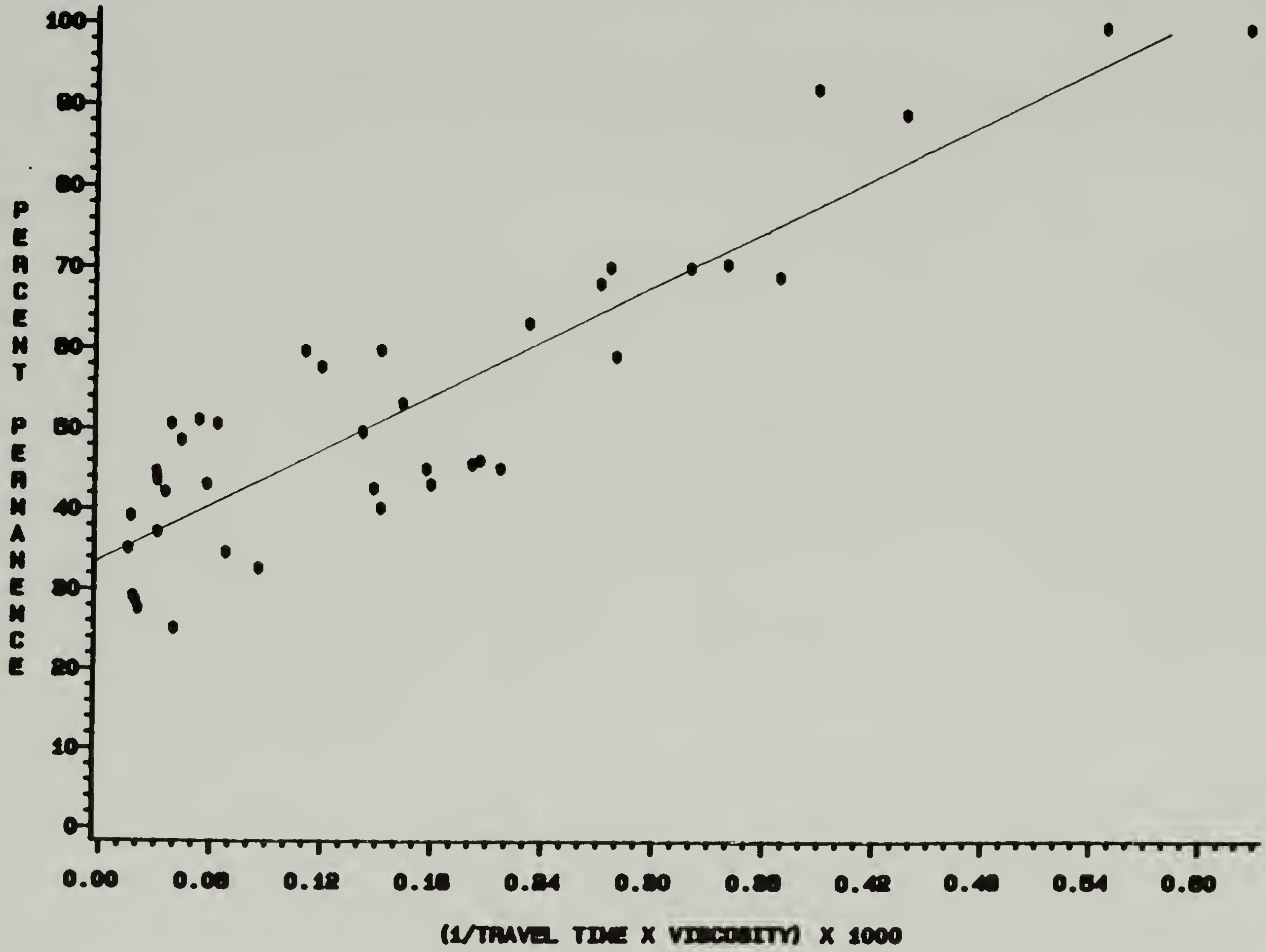


Figure 12. Surface Permanence as a Function of Travel Time and Viscosity

elastic. This phenomenon has been used effectively to reduce "extrusion haze" in polyethylene films, which is caused by the elastic response of the polymer to flow (Stehling et. al., 1981; Huck and Clegg, 1961). In the embossing process the strain history of a material element on the surface of the sheet is complex. In the die, assuming steady shear flow is achieved, the shear strains are large enough to make upstream history unimportant. At high shear rates, shear thinning occurs causing a reduction in viscosity of the polymer at the sheet surface.

As the sheet exits the die, the pressure induced parabolic velocity profile changes to a flat velocity profile across the thickness of the sheet. In order for this to occur, the polymer at the surface undergoes rapid acceleration and extension. During the travel time from the die to the embossing nip, further extension occurs to a small degree and it is uniform throughout. Stress relaxation and reduced viscosity recovery which could conceivably occur at this time is considered to be slight. A characteristic response time, λ, of this material was calculated based on creep data obtained at 150°C. Applying time-temperature superposition theory, the λ at 200°C is approximately ten seconds. The experimental travel times are within this average response or relaxation time. Also, assuming the viscosity recovery time is much longer than the stress relaxation, the sheet embossed in these experiments were processed in a reduced viscosity state. During embossing the polymer is subjected to extension and shear as it is forced into the roll surface cavities. As the polymer is transported around the roll it is cooled and some surface stress introduced during embossing is frozen in.

The role of reduced surface viscosity on PVB surface permanence properties can best be exemplified by considering two cases. Sudden deformation of a polymer melt, such as occurs in an embossing operation, results in a highly elastic response. In all of these experiments the stress level in the nip was sufficiently high to insure rapid deformation. The magnitude of deformation was relatively constant for all cases as evidenced by initial surface height values. After the surface is formed, some relaxation of the stress occurs during cooling. The rate of relaxation depends on polymer viscosity and prior shear history. A lower viscosity material would flow more easily under an applied stress. Also, experimentally it was found that stress relaxes more rapidly as the shear rate, $\dot{\gamma}$, in the preceding steady shear flow is increase (Huppler et al., 1967). In the case of high extrusion rates where shear reduced viscosity occurs, the relaxation is faster than the slightly sheared case. Upon removal from the embossing roll, the sheet sample with the higher relaxation rate is at a lower residual stress level.

When the two samples are reheated to 110°C for 12 minutes, strain recovery occurs and the embossed surface structure vanishes partially. The embossed sheet with the higher residual stress exhibits larger recovery (going back to a smoother surface) and hence less "permanence."

CHAPTER VI

CONCLUSIONS

The results of this investigation show that the surface permanence of embossed PVB sheet can be improved by decreasing the surface viscosity. This was most effectively done by utilizing the phenomena of shear reduced viscosity. Increasing polymer temperature and surface moisture also contribute to lowering viscosity but not to the same extent. Even though the surface cooling rate for these experiments was less than optimum as indicated earlier, the permanence values achieved were much higher. The author chose to relate the surface permanence to residual surface stress and strain recovery rather than crystallinity as proposed earlier. The theory on crystallinity has not been disproven but DSC measurements made on heat treated samples did not yield any supporting evidence of crystals. Certainly if crystals were to exist, reduced surface viscosity and high strain would help nucleation and growth.

REFERENCES

J. M. Dealy and WM. K. Tsang, "Structural Time Dependency in the Rheological Behavior of Molten Polymers," Journal of Applied Polymer Science 26 (1981): 1149-1158.

J. L. Fulton, H. H. Hopfe, R. H. Mosher, K. R. Nickolls, "Sheeting Die/Embossing Process Development, "(Monsanto Proprietary Report): 1979.

H. H. Hopfe,"Unsteady Heat and Mass Transfer in Two Dimensions of a Curved Body," (Monsanto Proprietary Report): 1972.

N. D. Huck and P. L. Clegg, "The Effect of Extrusion Variables on the Fundamental Properties of Tubular Polyethylene Film," SPE Transactions (July, 1961): 121-132.

J. D. Huppler, I. F. MacDonald, E. Ashare, T. W. Spriggs and R. B. Bird, "Rheological Properties of Three Solutions. Part II. Relaxation and Growth of Shear and Normal Stresses," Transactions of the Society of Rheology 11 (1967): 181-204.

A. Packter and M. S. Nururkar, "Crystallization in Films of Polar Vinyl Polymers: Part III," Colloid and Polymer Science 253 (1975): 916-921.

R. F. Riek and R. M. Carabetta, "Saflex Sheet via Sheet Die Within Line Embossing," (Monsanto Proprietary Report): 1971.

A. Rudin and H. P. Schreiber, "Shear Modification of Polymers," Polymer Engineering and Science 23 (1983): 422-430.

F. C. Stehling, C. S. Speed, and L. Westerman, "Causes of Haze of Low Density Polyethylene Blown Films 14 (1981): 698-708.

R. J. Tetreault, "Effect of Moisture on PVB Rheology," (Monsanto Proprietary Report): 1978.

C. Woodworth, Memorandum on Calculation of Melt Flow Between Moving Plates, 21 August 1972, (Monsanto Proprietary Document): 1972.

APPENDIX

APPENDIX A

NOMENCLATURE

Symbol	Designation	Units
q	Heat flux	Wm^{-2}
C	Mass concentration of	%
C_p	Specific heat	Dm^3K^{-1}
C	Equilibrium moisture concentration	%
D	Mass diffusivity for water in PVB	m^2/s
K	Thermal conductivity	$Wm^{-1}K^{-1}$
L	change in length	m
P	Change in pressure across L	Pa
P	Vapor pressure of water	Pa
P_{dp}	Vapor pressure of water @ dew point	Pa
P_t	Vapor pressure of water @ temp. "T"	Pa
RH	Relative Humidity	%
T	Temperature of melt at entrance to flow increment	°F
T'	Temperature of melt at exit of flow increment	°F
ΔT	$T' - T$	K
T_a	Air temperature	°C
T_f	Temperature	°F
T_p	Plastic sheet bulk temperature	°C
T_r	Temperature	°R
T_s	Metal shell temperature	°C
T_w	Water temperature	°C
U	Overall heat-transfer coefficient	$Wm^{-2}K^{-1}$
V	Melt velocity	M/S
α	Thermal diffusivity	cm^2/s
$\dot{\gamma}$	Shear rate	1/s
η_0	Viscosity @ zero shear rate	pa s
θ	Residence time	s
λ	Time constant for viscoelastic material	s
ρ	Density	$Kg\ m^{-3}$
τ	Shear stress	Pa
τ_∞	Shear stress as $\dot{\gamma} \to \infty$	Pa

APPENDIX B

Die Flow Model

A non-newtonian, non-isothermal finite difference melt flow program by C. L. Woodworth, 1972, was used to determine the shear rate and melt viscosity at the polymer surface prior to exiting the die. The basic flow equations used in the model were in the form:

$$\tau = y\left(\frac{\partial P}{\partial L}\right) + C$$

$$\dot{\gamma} = \frac{\frac{\tau}{\eta_0}}{\left(1 - \left(\frac{\tau}{\tau_\infty}\right)^k\right)^{1/k}}$$

The velocity profile and shear rate were first calculated using estimated values for $\Delta P/\Delta L$ and C. C is adjusted to give zero velocity at the wall. These values continue to be readjusted until the rate is within 0.1% of the specified rate.

The length and the height of the flow channel are divided into increments as shown in Figure 13. The heat transfer calculations are carried out using the velocity profile and the temperature at the start of a length increment. The basic energy equation is shown below:

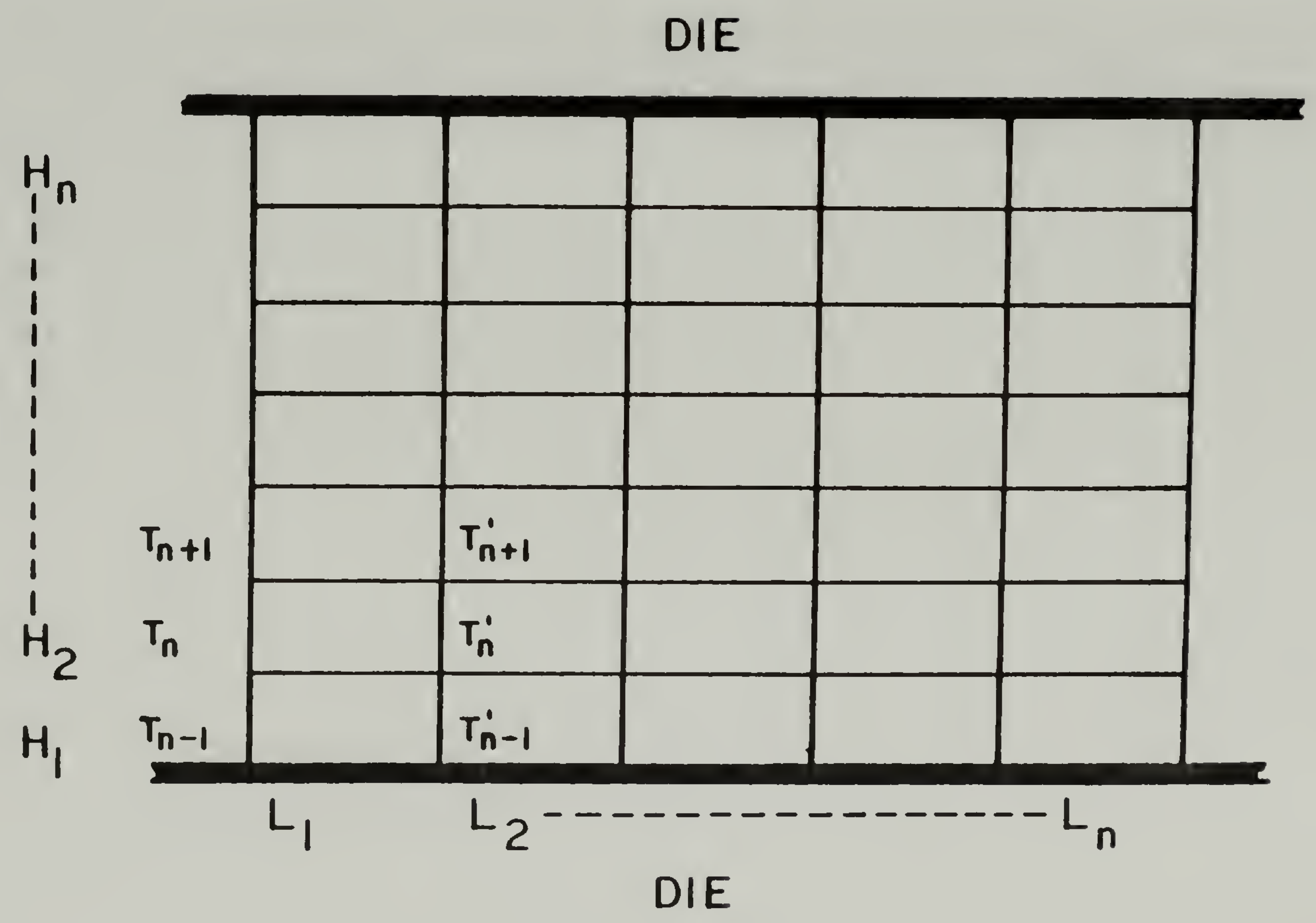


Figure 13. Schematic of Incremental Die Flow Program

$$\rho C_p V_z \frac{\partial T}{\partial z} = \frac{\partial q}{\partial y} + \tau\gamma \; ; \qquad \Delta q = \frac{K\Delta T}{\Delta y} = q_{in} - q_{out}$$

The temperature at the exit of a height increment is influenced by the temperature of the neighboring material. The energy equation in implicit difference form becomes:

$$\frac{\rho C_p V_z}{\Delta z}(T'_n - T_n) = \frac{K}{\Delta y}\left(\frac{T_{n-1} - 2T_n + T_{n+1} + T'_{n-1} - 2T'_n + T'_{n+1}}{2\Delta y}\right) + \tau\gamma \quad ,$$

It can be separated into two parts:

$$T'_{n-1}\left(\frac{-K}{2\Delta y^2}\right) + T'_n\left(\frac{K}{\Delta y^2} + \frac{\rho C_p V_z}{\Delta z}\right) + T'_{n+1}\left(\frac{-K}{2\Delta y^2}\right) = D \quad ,$$

$$D = \frac{K}{2\Delta y^2}(T_{n-1} - 2T_n + T_{n+1}) + \frac{\rho C_p V_z}{\Delta z} T_n + \tau\gamma \quad .$$

where T and T' are the temperatures at the entrance and exit end, respectively, of the length increment for a given increment N. T' is solved for using the Thomas tri diagonal matrix method. The velocity profile, shear heat and rate are recalculated based on the average of input and exit temperatures. The exit temperature is then recalculated and used as the entrance temperature for the next incremental length.

At the wall, the temperature is taken to be the die temperature which typically is below the average temperature of the melt. For this case, the energy equation changes to the form shown below:

$$\frac{\rho C_p V_z}{\Delta z}(T_1' - T_1) = \frac{1}{2dy}((U_w T_w - U_w T_1 - U_m T_1 + U_m T_2) +$$

$$(U_w T_w - U_w T_1' + U_m T_2' - U_m T_1')) + \tau \gamma \quad ,$$

where:

$$U_w = \frac{1}{\frac{\Delta y}{2K_m} + \frac{X_w}{K_w}} \; ; \qquad U_m = \frac{K_m}{\Delta y} \quad \text{(melt)}$$

The geometry, equipment temperatures, flow rate and bulk melt temperatures are independent parameters in the model. Since the actual die gap was unknown, die pressure was used to estimate the gap.

APPENDIX C

Material Specs for Embossing Equipment

Static Mixer:	Kenics (KMOD-20) 316 SS 12 elements
Die:	Center fed - sheet forming 4140 steel 5.19 inches x 3.25 inches gap - 0.1 inches to .020 inches at exit
Embossing Roll: (also cooling roll)	Rodney Hunt helix design (Print #ER-2050) 304 SS 3.0 inch O.D. 5.0 inch face (9.0 inches overall Finish ~ 1000 RMS T.I.R. .0005
Impression Roll:	Rodney Hunt (Print #ER-2051) Silicon rubber - .075 shore 0.25 inch thick Body - 4140 steel 3.0 inch O.D. 5.0 inch face (9.0 inches overall)
Stripper Rolls:	Rodney Hunt (Print #ER-2052) Natural rubber Thickness - .13 inches Body - 4140 steel 0.75 inch O.D. 5.0 inch face

APPENDIX D

	DIE POSITION - 0.5" FROM EMBOSSING NIP								
	TRAVEL TIME (seconds)	VISCOSITY (poise)	H_M (inches x 10^{-5})	H_P		DIE GAP (inches)	DIE PRESSURE (psi)	EXTRUSION RATE (g/min.)	LINE SPEED (ft./min.)
1.	0.43	15820	120	50	42	.062	390	107	5.0
2.	0.43	15820	138	59	43	.062	390	107	5.0
3.	0.397	14143	97	42	43	.060	430	120	6.3
4.	0.397	14143	94	40	43	.060	430	120	6.3
5.	0.357	13723	84	39	46	.061	440	128	6.9
6.	0.357	13723	96	44	46	.061	440	128	6.9
7.	0.329	13233	78	49	63	.062	450	141	7.6
8.	0.409	16209	110	46	42	.062	450	107	6.1
9.	0.409	16209	121	45	37	.062	450	107	6.1
10.	0.32	14530	88	37	42	.062	410	123	7.0
11.	0.32	14530	81	39	48	.062	410	123	7.0
12.	0.650	22663	98	33	34	.061	320	65	3.0
13.	0.650	22663	97	34	35	.061	320	65	3.0
14.	0.336	14899	108	47	44	.060	410	113	7.4
15.	0.336	14899	118	55	47	.060	410	113	7.4
16.	0.336	14899	97	44	45	.060	410	113	7.4
17.	0.20	13074	102	90	88	.065	440	160	12.5
18.	0.20	13074	126	121	96	.065	440	160	12.5
19.	0.20	13074	115	107	93	.065	440	160	12.5
20.	0.15	10839	120	118	98	.069	520	230	16.6
21.	0.15	10839	128	132	103	.069	520	230	16.6
22.	0.26	13918	93	59	62	.065	410	146	9.5
23.	0.26	13918	92	51	55	.065	410	146	9.5
24.	0.19	12239	70	62	89	.067	450	199	13.0
25.	0.19	12239	90	81	89	.067	450	199	13.0
26.	1.0	25300	96	24	25	.036	600	33	2.5
27.	0.57	20699	105	35	33	.033	683	54	4.4
28.	0.57	20699	107	34	32	.033	683	54	4.4
29.	2.14	32674	81	28	35	.040	517	19	1.2
30.	0.30	15021	82	37	45	.045	617	110	6.5
31.	0.164	11358	166	174	105	.051	700	196	15.2
32.	0.164	11358	175	192	110	.051	700	196	15.2
33.	0.263	13959	111	78	70	.065	423	150	9.5

	TRAVEL TIME (seconds)	VISCOSITY (poise)	H_η	H_ρ (inches x 10^{-5})		DIE GAP (inches)	DIE PRESSURE (psi)	EXTRUSION RATE (g/min)	LINE SPEED (ft/min)
DIE POSITION - 0.88" FROM EMBOSSING NIP									
34.	1.37	24446	105	45	43	.059	350	54	3.2
35.	1.37	24446	102	45	44	.059	350	54	3.2
36.	1.40	18942	116	56	48	.057	363	56	3.1
37.	1.40	18942	110	58	53	.057	363	56	3.1
38.	0.896	21341	104	53	51	.057	433	91	4.9
39.	0.896	21341	100	51	51	.057	433	91	4.9
40.	0.524	11803	106	52	55	.059	517	154	8.4
41.	0.524	11803	98	50	51	.059	517	154	8.4
42.	0.326	11462	132	85	68	.058	533	159	13.5
43.	0.326	11462	116	78	67	.058	533	159	13.5
44.	0.564	12646	93	46	49	.058	483	136	7.8
45.	0.564	12646	104	52	50	.058	483	136	7.8
46.	0.528	12646	80	52	65	.059	483	138	8.32

continued

	TRAVEL TIME (seconds)	VISCOSITY (poise)	H_m (inches x 10^{-5})	H_p (inches x 10^{-5})	%	DIE GAP (inches)	DIE PRESSURE (psi)	EXTRUSION RATE (g/min)	LINE SPEED (ft/min)
47.	.528	12646	133	74	56	.059	483	138	8.3
48.	.528	12646	106	61	58	.059	483	138	8.3
49.	.290	10283	116	79	68	.062	583	215	15.1
50.	.290	10283	112	82	73	.062	583	215	15.1
51.	.255	10785	115	80	69	.066	535	218	17.2
52.	.301	10539	121	85	70	.061	572	201	14.6
53.	.301	10539	125	85	69	.061	572	201	14.6
54.	1.10	16150	123	53	43	.054	417	66	4.0
55.	1.38	21265	113	48	42	.057	350	50	3.2
DIE POSITION - 3.0" FROM EMBOSSING NIP									
56.	3.10	16219	95	28	29	.053	420	62	1.83
57.	3.10	16219	94	24	26	.053	420	62	4.83
58.	0.9	10178	95	57	60	.054	625	180	15.7
59.	0.9	10178	97	57	59	.054	625	180	15.7
60.	3.39	15955	119	34	29	.052	430	57	4.42
61.	3.39	15955	108	30	28	.052	430	57	4.42
62.	0.87	9747	100	55	55	.054	658	196	17.7
63.	0.87	9747	99	59	60	.054	658	196	17.7
64.	2.42	13722	95	34	36	.052	475	85	6.19
65.	2.42	13722	101	35	35	.052	475	85	6.19
66.	2.42	13722	94	37	39	.052	475	85	6.19
67.	3.6	16356	104	29	28	.052	420	55	4.14
68.	3.6	16356	98	29	30	.052	420	55	4.14
69.	3.7	17097	83	33	40	.053	430	63	4.05
70.	3.7	17097	85	32	38	.053	430	63	4.05
71.	2.3	14514	96	42	44	.050	510	88	6.5
72.	2.3	14514	82	37	45	.050	510	88	6.5
73.	1.9	12177	81	39	48	.052	530	110	7.9
74.	1.9	12177	79	39	49	.052	530	110	7.9
75.	1.46	11024	99	49	49	.054	580	156	10.3
76.	1.46	11024	90	50	52	.054	580	156	10.3

H_m - Height of Surface after Embossing
H_p - Height of Surface after Permanence Test
% - % Permanence
Melt Temperature - 196 to 202°C

Gauge - 0.027 to 0.035 inches
Width - 2.5 to 3.1 inches
Embossing Roll Water Temperature - 34 to 39°C
Nip Pressure - 883 psi

APPENDIX E

Computer Simulators For Heat Transfer and Moisture Diffusion

The heat and mass transfer program written by H. H. Hopfe, 1972, was used to predict the surface conditions during transport from the die to the embossing roll, and surface cooling rate on the roll. The heat transfer model is based on simultaneous unsteady state heat conduction within the embossing roll shell and/or the plastic sheet. The basic differential equation used to describe this is:

$$\frac{\partial T}{\partial \theta} = \nabla \alpha \cdot \nabla T \qquad \alpha = \frac{K}{\rho C_p}$$

In either case, sheet cooled on the roll or sheet exposed to atmosphere, the heat transfer is through the thickness of the sheet and only the one dimensional case is considered. The metal shell and/or sheet are divided into elements which have identical time constants. For a 30 mil sheet of PVB and a 0.25 in thick metal shell, the sheet is divided into 17 elements while the shell contains 9. The interface temperature is the arithematic average of the adjacent element temperatures. Also, the thermophysical properties change as a function of temperature and are adjusted within the program.

Boundary Conditions:

Case 1:	Case 2:
Plastic Sheet on Metal Embossing Roll	Plastic Sheet Exposed to Air
@ $X=0$, $h=800$ BTU/hr ft^2 $^\circ$F	2 BTU/hr ft^2 $^\circ$F
@ $X=\delta$, $h=2$ BTU/hr ft^2 $^\circ$F	2 BTU/hr ft^2 $^\circ$F

Initial Conditions: (See Figure 14.A)

$Tw = 39^\circ C$	@ $X= 0$	$Ta = 27^\circ C$
$T_S \sim Tw$		
$Tp = 199^\circ C$		$Tp = 199^\circ C$
$Ta = 27^\circ C$	@ $X= \delta$	$Ta = 27^\circ C$

In order to obtain repetitive thermal gradients in the metal shell from revolution to revolution, it is necessary to run the simulator through several cycles prior to data acquisition.

The moisture diffusion simulator is similar to the heat

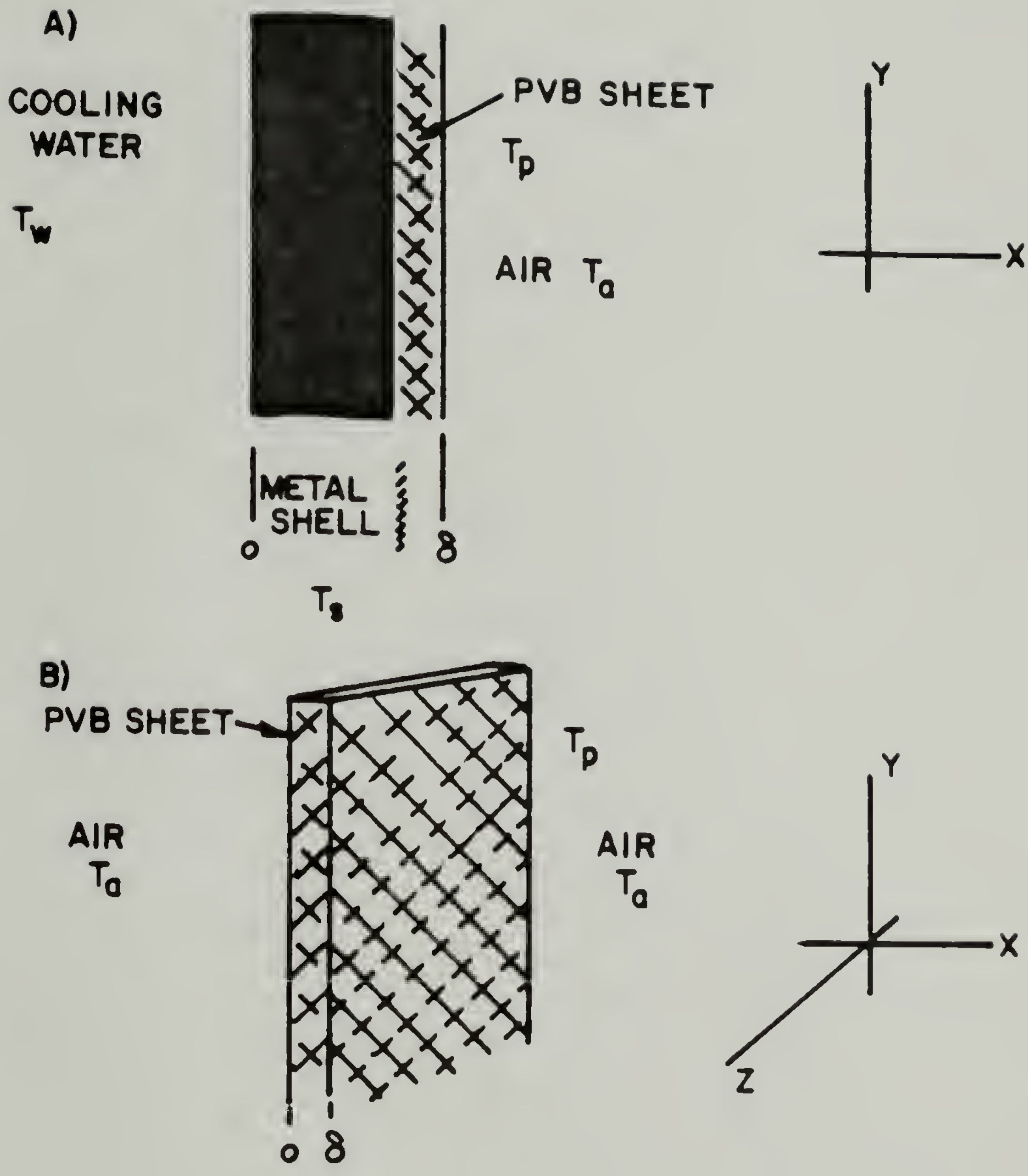


Figure 14. Schematic of Heat Transfer and Moisture Diffusion Simulator

transfer. The evaporation of the moisture from the surface can be described by Fick's second law which constitutes the mass diffusion equation.

$$\frac{\partial C}{\partial \theta} = \nabla D \cdot \nabla C$$

Again, the bulk of the diffusion is in one direction so the problem becomes one dimensional. The mass diffusion is a function of temperature and can be described by

$$D = 10.0^{(0.0122T_F - 7.279)} \text{ ft}^2/\text{hr}.$$

Equilibrium moisture concentration is based on material surface temperature and ambient dew points.

$$P = 10.0^{(19.757 - 4.28 \text{ Log } T_r - 5141.67/T_r)}$$

$$RH = 100.0 \frac{P_{dp}}{P_T}$$

$$C_\infty = .00715 \text{ RH} + .00223 \text{ (RH)}^{1.475}$$

$$\text{for RH} < 80\%$$

Boundary Conditions:

1 at $x = 0$ $C = 0$ contact rolls

$x = \delta$

2 at $x = \delta/2$ $\partial C/\partial x = 0$

Initial Conditions (See Figure 14.B)

$\theta = o$ at die exit $C = C_o \simeq .004$

$T_P = 199^{\circ}C$

$T_A = 27^{\circ}C$