To the Graduate Council:

I am submitting herewith a thesis written by James C. Weaver entitled "Orientation Behavior of Poly(ethylene terephthalate)/ Ethylene-Vinyl Alcohol (EVAL) Copolymer Laminates." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.

Robert W. Seymour

Robert W. Seymour, Major Professor

We have read this thesis and recommend its acceptance:

J. L. Waltz

J. E. Spruiell

Accepted for the Council:

L. Evans Beck

Vice Chancellor
Graduate Studies and Research

# ORIENTATION BEHAVIOR OF POLY(ETHYLENE TEREPHTHALATE)/ ETHYLENE-VINYL ALCOHOL (EVAL) COPOLYMER LAMINATES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

James C. Weaver

December 1981

## DEDICATION

This thesis is dedicated to my wife, Susan, without whose love, confidence, and encouragement I would have never started this program. Also, without her understanding and patience about all those weekends spent studying, I could not have completed the requirements.

Also, it is dedicated to Christopher who tried very hard to keep quiet and could not always understand why he couldn't come into daddy's study. And while the door was closed he grew into a four year old boy.

Finally, it is dedicated to Todd who missed most of the excitement but still managed to make me realize that babysitting isn't all that bad.

ACKNOWLEDGMENTS

I wish to express my appreciation to Tennessee Eastman Company for the financial support of this work through the Tuition Refund Plan. I am also grateful to Dr. W. C. Wooten and other members of the Research Laboratories management for their approval of a company related project used as my thesis, and especially to Dr. R. W. Seymour who served as my thesis advisor at Tennessee Eastman Company.

I am especially grateful to my fellow classmate and laboratory crony Mr. Ron Light for his help and assurance that we could make it through the program.

Appreciation is also expressed to Mr. Alfred Penley, Mr. Jim Sparks, Dr. Jon Moore, and Dr. Henry Gonzalez for their assistance and helpful comments regarding the data.

I am also grateful to Dr. James L. White for his valuable help throughout the program.

## ABSTRACT

The purpose of the project was to determine how the orientation behavior and properties of PET/EVAL copolymer laminates were related to the characteristics of the individual layers. Control films were extruded from poly(ethylene terephthalate) (PET) and ethylene-vinyl alcohol (EVAL) copolymer. Laminates of PET/EVAL/PET were coextruded having various levels of adhesion. Mechanical properties were obtained on the films as-extruded and after biaxial orientation, before and after heatsetting, in the machine and transverse directions. In addition, stretching properties were obtained on the films during orientation. The degree of orientation was estimated from birefringence measurements.

The equations of Schrenk and Alfrey, and Guillotte were used to predict the properties of the laminates from the properties of the substrate films. In the absence of a tie-layer, i.e. representing poor adhesion, most properties of the laminates were found to be additive; otherwise, prediction of properties depended upon the properties and volume percent of the tie-layer and the degree of adhesion existing. In the presence of good adhesion, the properties of the laminate could not be predicted by the methods used.

The orientability of the laminates was found to be controlled by the EVAL component and the degree of adhesion existing between the PET substrate and EVAL. EVAL was found to be crystalline, sensitive to moisture and processing conditions, and difficult to orient.

It was concluded that a tie-layer is not needed for films which will be oriented and can be detrimental to mechanical properties. Also, only the minimum amount of EVAL needed to impart good barrier properties should be used in PET/EVAL laminates.

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# CHAPTER I

## INTRODUCTION

The use of plastics in the packaging industry has become one of the biggest and fastest growing markets in recent years. Numerous types of plastics are used in an assortment of applications from shrink-wrap film to blister packaging to beverage bottles. The latter application has just begun to come into its own in the last three years and indirectly has opened up new markets in the food industry for other types of packaging. Until 1977, the leading contender in the U.S. for use in food applications was acrylonitrile, both in meat packaging and beverage containers, because of its excellent barrier properties. However, in 1977 the Food and Drug Administration outlawed acrylonitrile for beverage container use (1) and suppliers scurried to fill the newly created market.

The introduction of acrylonitrile beverage bottles and its subsequent removal from the market followed by the hesitance of many packagers to use it as a meat wrap, created an industry-wide awareness of one particular packaging property, namely barrier properties. In order to replace acrylonitrile, its mechanical and physical properties, including barrier resistance, must be duplicated or approached. Not many neat plastics possess high barrier properties, especially as good as acrylonitrile.

Schrenk (2) says that it is impractical to synthesize a polymer which has all the properties required for a certain sophisticated end

use, consequently, plastics engineers have used composite laminates to achieve a combination of properties not obtained economically by any single polymer. Laminates are used in packaging foods, drugs, chemicals and textile products, in addition to applications in the photographic, construction, and automotive industries (3).

Further, Schrenk and Alfrey (4) state that laminates can be structured to obtain the desirable physical properties of each component without sacrificing other important properties. For example, befitting the current interest in barrier properties, Schrenk and Alfrey state that Saran is an excellent barrier to oxygen and moisture vapor transmission, but has a very limited heat-sealing range. Polyethylene has excellent heat sealability but only fair barrier properties. By making a laminate of the two films, heat sealability and barrier resistance are obtained. Oswin (5) states that if two or more plastic films are put together some of the deficiencies of one will be overcome by the excellences of the other. There will always be a gain in rigidity due to the increase in total thickness.

In addition to mechanical and physical property advantages of multilayer structures, there are the possibilities of creating unique structures which for economic or processing reasons could not otherwise exist. For example, a heavy layer of an inexpensive polymer could be used to carry a thin layer of a more expensive polymer which has superior properties (6). Composite can structures have recently been made incorporating materials like aluminum foil and polyester. The almost total gas barrier levels obtainable with foil-based liners have

led to applications for products sensitive to oxygen or water vapor (7). However, the increased costs of foil-based liners have created an interest in less expensive products. An example of this interest can be seen from a recent patent issued to American Can Company (8).

Owing to the 1977 FDA action mentioned earlier (1) banning the use of acrylonitrile as a beverage container, poly(ethylene terephthalate) (PET) was introduced as a bottle material and is being used by most soft drink bottlers to package their two-liter products. Smaller containers are being developed. Poly(ethylene terephthalate) has good barrier properties but they are not sufficiently high to allow it to be used for packaging most foods. It does possess high strength characteristics and can be oriented and heatset to obtain high temperature resistance. Since it has FDA approval for food-contact use and is inexpensive relative to polymers such as nylon, PET holds a considerable amount of potential as a packaging product. Laminating PET with other polymers such as those possessing better barrier characteristics would offer a huge market potential.

In addition to acrylonitrile, Saran and aluminum foil, a product which can offer excellent gas barrier properties is ethylene-vinyl alcohol copolymer (EVAL). EVAL is a moisture-permeable copolymer which is patented by Monsanto Company (9) but has been produced commercially only in Japan. It reportedly has limited use in packaging applications unless buried as the central ply between two moisture barriers (10). Three-ply laminates or coextruded films have found a market in Japan. Blow-molded containers of high density or low density polyethylene

outer layers and EVAL core layer have been produced (11). The containers are claimed to have a very low, long term permeability to oxygen, nitrogen, and carbon dioxide. Recently a patent issued to American Can Company illustrates the interest being generated in this country in the use of EVAL (12).

Since EVAL film is presently only marketed in Japan and EVAL pellets have only recently been made available in the United States, very little open technical literature is available on investigations of its use. EVAL is a semicrystalline polymer and little has been reported about its morphology. Numerous patents have been assigned to foreign companies, mostly Japanese, covering products employing EVAL. Two patents of special interest are those assigned to W. R. Grace and Company (13) and UCB, Societe Anonyme (14) which employ ethylene-vinyl alcohol copolymer as an oxygen barrier layer in laminates with poly(ethylene terephthalate). The laminate claimed in the former patent is said to be useful for packaging food while the latter patent applies to the production of a can for pressurized carbonated beverages. Numerous other examples with PET showing similar utility can be cited (15-20). In addition, packaging laminates of EVAL with polyolefins and other plastics have been patented in the U.S. by Japanese companies (21-24). Crown Zellerbach claims that barrier films and barrier resins such as nylon, EVAL, and other vinyl alcohol copolymers will be added to CZ's Crown Zeelon line of performance coextrusions during 1981 and 1982 (25).

# A. THE PROBLEM

## Statement of the Problem

Because of the potential overall high properties exhibited in PET/EVAL laminates, there is a need to understand the type of properties that can be obtained and to relate the properties of the laminate to those of the individual layers. Although the utility of PET/EVAL laminates has been clearly demonstrated for particular applications, a fundamental study has not been undertaken which might allow one to predict the utility of the laminates in other applications such as beverage bottles or cans where complicated orientation factors arise. The purpose of the project was to determine how the orientation behavior and properties of PET/EVAL copolymer laminates were related to the characteristics of the individual layers.

## Importance of the Study

Although vinyl alcohol copolymers (EVAL) were commercially developed in Japan and are currently only available from Kuraray Company and Nippon Gosei Kagaku Company, Osaka, two American companies, DuPont and Allied Chemical, are reported to be considering facilities for domestic production (25). Thus, even though their present prices which range from $2.35 to $2.85/lb. are relatively high, domestic production should make this material more competitive and increase interest in its use.

Combining EVAL with PET, which already has an attractive cost structure of about 29¢ per 1000 sq. in. at 10 mils according to Griesbach (26), should thus yield a packaging material possessing

economic and property advantages. PET has an excellent toxicological history and in addition to its favorable properties mentioned earlier, Griesbach's paper (26) adds that it is tough, has good transparency, good color, and sparkle. This study is important in that it investigates a potentially valuable new packaging material from a basic viewpoint so that maximum utility can be made of the characteristics of the individual components.

## B. SOURCES OF DATA AND METHODS OF STUDY

Neat (unmodified) films of PET and EVAL were extruded on a 12 in. wide flat film line. Coextruded films were made on a 30 in. wide flat film line. The equipment will be discussed more fully in Chapter III. The films were tested according to ASTM procedures as extruded, after heatsetting, and after stretching on a T.M. Long film stretcher.

The procedures used in gathering and treating the data will be discussed in detail in Chapter III.

General properties of PET and EVAL are shown in Appendix A and B.

# CHAPTER II

# LITERATURE SURVEY

## A. PROCESSES FOR MAKING LAMINATES

W. R. R. Park defines a laminate as any combination of distinctly different plastic film materials or plastic plus nonplastic materials wherein each major ply is thicker than 1/4 mil, regardless of the method of manufacture (27). Laminates can be made in a number of different ways (28). It was not the purpose of this project to concentrate on the process. The process for making laminates depends heavily on the substrates and whether an adhesive layer is needed.

A simple method for preparing lab-scale quantities is to extrude separate films and then bond them together under pressure as described for making processed meat-packaging tubes (29). Probably the most widely used process industrially in recent years has been coextrusion. During coextrusion, two or more individual polymers are extruded simultaneously through a single die (2). The advantage of coextrusion is the elimination of multiple processing operations and the use of solvents (30). One difficulty which may arise, and thus be a disadvantage for the process, is the need for an adhesive which must also be coextruded. If an adhesive is required, it must be sufficiently thermally stable to adhere to the hot substrates during coextrusion and to the substrates during the subsequent quenching and cooling steps. This places extra demands on the adhesive.

Biaxially oriented blown film laminates have been made in a similar process. A three-ply laminate has been made by coextruding and blowing a laminate of ethylene-vinyl acetate copolymer and high density polyethylene (HDPE) and blowing a HDPE inner bubble inside the coextruded laminate (31).

A process called "co-extru-lamination" has been reported by Frayer of the University of Southern Mississippi (32). The process is essentially coextrusion, except a corona discharge treatment is used in place of an adhesive or copolymer interlayer.

## B. RELATIONSHIP OF LAMINATE PROPERTIES TO THE PROPERTIES OF THE INDIVIDUAL LAYERS

A considerable amount of study has been carried out on laminates in order to relate the final properties to the structure. Most of the work appears to have been done by Schrenk and Alfrey and their coworkers at the Dow Chemical Company. Most of the studies have also been carried out on coextruded laminates which permit a close control of the processing variables, including adhesion.

In 1969, Schrenk and Alfrey published the results of an investigation of Mylar-aluminum-Mylar laminates and polystyrene-polyolefin laminates (4). This work showed that mutual reinforcement could result in a laminate consisting of layers of a high modulus, low elongation material and a high elongation material. The mutual reinforcement was highly dependent upon the adhesion between the layers and the molecular orientation in the brittle polymer layers. Biaxially oriented samples did not exhibit mutual reinforcement in

either direction. Tensile strength in some films was found to be predictable from the volume fractions of the components in accordance with the law of mixtures:

$$S_c = \sigma_1 V_1 + \sigma_2 V_2 \qquad \text{(II-1)}$$

where $S_c$ is stress in the composite; $\sigma_1$, $\sigma_2$ are stresses in layers of phases 1 and 2; and $V_1$, $V_2$ are volume fractions of phases 1 and 2. The permeance of the films was found to be predictable and could be calculated by treating the laminate as a series of resistances, with each ply contributing to the barrier:

$$\frac{1}{\overline{P}_L} = \frac{d_1}{\overline{P}_1} + \frac{d_2}{\overline{P}_2} + \text{-----} \frac{d_n}{\overline{P}_n} \qquad \text{(II-2)}$$

where $P_L$ is the permeance of the film, $d_1$, $d_2$, $d_n$ is the thickness of each ply and $\overline{P}_1$, $\overline{P}_2$, $\overline{P}_n$ is the permeability coefficient of each ply.

In 1974, Schrenk (2) reported that mutual reinforcement in laminates of high elongation polymers and brittle polymers does not always exist. Often, a "mutual interlayer destruction" was observed, i.e., the brittle polymer failed at its characteristic low elongation and caused a premature failure of the high elongation layers. Schrenk stated that mutual reinforcement had been found to be dependent on molecular orientation in the layers, the toughness of the high elongation polymer, and the degree of interfacial adhesion between the high and low elongation polymer layers.

Because of interlayer interactions in multilayer films with alternating "hard" and "soft" layers, which can result in interlayer

reinforcement or interlayer destruction, Alfrey reported in 1975 (33) that not all properties can be predicted from additive contributions from the individual layers. Instead the multilayer film may exhibit properties completely different from a simple "sum of all its parts."

This has been most recently investigated and reported by Bhateja and Alfrey (34) who studied five-layer laminates with Mylar film skin layers and aluminum foil core layers held together with ethylene-acrylic acid copolymer adhesive. By varying the thicknesses of the aluminum foil, the adhesive layer, and the Mylar film and controlling the degree of adhesion, Bhateja and Alfrey found that ductile extension to a high elongation resulted with good adhesion and thick Mylar layers. Good interfacial adhesion with thin Mylar layers resulted in fracture of the entire composite at a low elongation. Poor adhesion resulted in extensive delamination.

Guillotte reported that some physical properties of coextruded films are additive provided the laminar layers have good adhesion (35). By studying laminates which had good adhesion, Guillotte showed linear relationships existed between physical property and percent of one component in the laminate for a number of physical properties. For laminates of polypropylene (PP) and medium density polyethylene (MDPE) made by Elliott and Erb (36), film stiffness (tensile modulus) was found to be predicted by the equation:

$$S = S_1 + f_2(S_2 - S_1) \qquad \text{(II-3)}$$

where S is stiffness of the composite; $S_1$ is stiffness of resin #1 (lower stiffness); $S_2$ is stiffness of resin #2 (higher stiffness); and $f_2$ is fractional thickness of stiffer resin.

The yield strength of a composite ionomer/nylon 66 film was found to obey the linear relationship:

$$Y = Y_1 + f_2(Y_2 - Y_1) \ . \qquad \text{(II-4)}$$

Using Elliott and Erb's ultimate tensile strength data on a PP/MDPE/PP film, Guillotte noted that a linear relationship for tensile strength, T, existed as follows:

$$T = T_1 + f_2(T_2 - T_1) \ . \qquad \text{(II-5)}$$

However, the ultimate tensile strength of ionomer/nylon 66 composites was not initially linear but could be made so by applying a factor of 0.8 to the equation:

$$T = 0.8T_1 + f_2(T_2 - 0.8T_1) \ . \qquad \text{(II-6)}$$

According to Guillotte, barrier properties did not follow a linear relationship but were related to the thicknesses of the individual layers as found earlier by Schrenk and Alfrey (4). Moisture vapor and oxygen permeability (P) of polyethylene/ionomer coextruded films was found to follow the formula:

$$\frac{1}{P} = \frac{f_1}{P_1} + \frac{f_2}{P_2} \qquad \text{(II-7)}$$

where $P_1$ and $P_2$ represents permeability and $f_1$ and $f_2$ are the thickness fraction of each resin.

Dynamic mechanical properties have been studied by Kalfoglou of the University of Patras (37) on a number of two- and three-ply coextruded films. The films studied were combinations of Kapton polyimide and fluorinated ethylene-propylene copolymer and combinations of polyethylene with some of its modified forms. They were chosen for their good adhesion. Mechanical relaxations were examined and correlated with the tensile and ultimate properties of the composites. Ductile reinforcement as reported by Guillotte (35) and Schrenk and Alfrey (4), indicating good adhesion, was noted. Depending upon the laminate being investigated, the $\alpha$ and $\beta$ peaks were found to decrease or shift to lower temperatures as the concentration of one of the components in the laminate decreased. Kalfoglou reported that "the simple additivity rule could satisfactorily predict the temperature variation" of the storage modulus E', and the loss modulus, E''. He concluded that dynamic mechanical properties can indicate the degree of interaction in composite films provided the layers are chemically related. Ultimate physical properties can be related to low-temperature relaxations.

## C. THEORY REGARDING THE BEHAVIOR OF PET/EVAL COPOLYMER LAMINATES

Poly(ethylene terephthalate) is a strong, tough, high modulus thermoplastic (38). Its tensile strength can be increased from 8000 psi to over 30,000 psi by orientation. Elongations at break are moderate, being in the range of 12 to 130%. Numerous studies of unmodified PET have been carried out including those on the oriented polymer (39).

Ethylene-vinyl alcohol copolymer also has high mechanical properties. Its flexural modulus is higher than that of PET and a higher elongation to break of 279% is cited (40) for injection molded samples. Kobayashi lists the elongation of film as being 150% in the machine direction and 200% in the transverse direction (41). EVAL has excellent gas barrier properties and it is this feature which makes it most useful in the packaging of foods. The effects of annealing on the orientation and shrinkage of EVAL films have been studied in Japan (42). Also, saponified ethylene-vinyl acetate copolymers have been prepared and stretched to improve strength. Best stretching conditions are claimed to be at a temperature below 140°C, and the stretched film is heatset at a temperature of 70° to 140°C while in the stretched condition (43).

Based on the studies of laminates described previously, it was expected that mutual reinforcement of properties would result from PET/EVAL laminates provided good adhesion was obtained. However, since both substrates have high moduli and elongations, it was doubtful that the simple equations developed by Guillotte would predict the properties of the PET/EVAL laminates. The increase in properties of the individual components upon stretching indicated that it would be even more difficult to predict the properties of the laminate which had been stretched and heatset. Due to the four-fold increase in properties which appeared feasible by stretching and the fact that many packaging procedures induce orientation into the product, it was imperative that this effect be investigated and the results related to those of the unstretched structures and individual layers.

# CHAPTER III

# PROCEDURE

## A. PRODUCTION OF SAMPLES

### Scope of the Study

The purpose of this research project was to obtain knowledge related to the fundamental characteristics of poly(ethylene terephthalate) film, prior to and after laminating with ethylene-vinyl alcohol copolymer film. This knowledge was used to determine how the orientation behavior and properties of a PET/EVAL copolymer laminate were related to the characteristics of the individual layers. Mechanical properties of PET and EVAL films were determined before and after heatsetting. Three-ply laminates of PET/EVAL/PET of various film thicknesses were made with and without a tie-layer to impart adhesion between the plies. Mechanical properties of the laminates before and after heatsetting were determined. The neat films and the laminates were biaxially stretched and the stress-elongation behavior during stretching recorded. Mechanical properties on the biaxially stretched films as stretched and after heatsetting were also determined.

## B. MATERIALS

### Control Films

Poly(ethylene terephthalate) film was extruded from TENITE PET 6857, Eastman Chemical Products, Inc., Kingsport, Tennessee (Appendix A).

Ethylene-vinyl alcohol copolymer film was extruded from EVAL EP, Type F, Kuraray International Corporation, New York, New York (Appendix B).

Adhesive Tie-Layers for Coextruded Films

Initial coextruded films consisting of PET/EVAL/PET layers also contained about 0.5 mil of CXA 3095 resin, an ethylene-vinyl acetate copolymer with other functional groups, DuPont Company, Wilmington, Delaware, between each layer. Finally, a 50 wt. % pellet-pellet blend of EVAL EP-F and Elvax 260 ethylene-vinyl acetate copolymer, also a product of DuPont Company, was used as a tie-layer in one coextruded film.

Coextruded Films

All PET/EVAL/PET coextruded films were coextruded from the same polymers used to extrude the control films.

## C. EQUIPMENT AND CONDITIONS

Control Films

PET films, 10, 15, and 20 mils, were extruded on a 3.5 in., 24:1 Prodex extruder. A 36 in. wide Johnson die having a 1 in. land length was used to produce 30 in. wide film. The PET was dried 4 hours at 300°F (149°C) and film was extruded at a melt temperature of 475-510°F (246-266°C), chill roll temperature of 160°F (71°C)(roll No. 1), 155°F (68°C)(roll No. 2), and 90°F (32°C)(roll No. 3).

EVAL EP-F films, 5, 10, 20 mils, were extruded on a 1.75 in., 24:1 Prodex extruder. A 12 in. wide Johnson die having a 1 in. land length

was used to produce 9.5 in. wide film. The EVAL was dried 4 hours at 212°F (100°C) and the film was extruded at a melt temperature of 430°F (221°C), chill roll temperatures of 160°F (74°C) (roll No. 1) and 160°F (71°C) (roll No. 2).

Coextruded Films

The multi-layer coextruded films were produced on a sheet extrusion line fed by three extruders. The two outer layers of PET 6857 were extruded from a 3.5 in., 24:1 Prodex extruder. The PET was dried 4 hours at 300°F (149°C) and extruded at a melt temperature of 550°F (288°C).

The EVAL EP-F middle layer was extruded from a 1.5 in., 20:1 Davis Standard extruder. The resin was dried 4 hours at 212°F (100°C) and extruded at a melt temperature of 430°F (221°C).

When used, the adhesive tie-layers were extruded from a 1.75 in., 24:1 Prodex extruder. For the coextruded films containing CXA 3095 as the tie-layer, the resin was extruded without prior drying at a melt temperature of 420°F (215°C). For the coextruded film containing a 50/50 wt. % Elvax 260/EVAL blend as the tie-layer, a pellet/pellet blend of undried Elvax 260 and EVAL, dried 4 hours at 212°F (100°C), was tumble mixed and extruded at a melt temperature of 420°F (215°C).

A multi-chamber extrusion feedblock die was employed. It had a 30 in. length and a 1 in. land length. A Goulding 3-roll stack take-off with 8.5 in. diameter, 46 in. wide chrome rolls was also used. Roll temperatures were maintained at 125°F (51°C) and 145°F (63°C).

After equilibrating the extrusion run for about 15 minutes, 100 feet of each coextruded film was collected.

## D. FILM STRETCHING

Films (4 in. × 4 in.) were stretched biaxially at a stretch ratio of 300%, at 90°C (194°F), and at a rate of 2 in./sec. on a T. M. Long machine. This machine has the capability of varying temperature of stretch, strain rate, and stretch ratios. In addition, the machine is equipped with force transducers which enabled the measurement of force as a function of elongation upon stretching, from which stress-elongation curves were generated. Such a curve is illustrated in Figure 1 for 20 mil PET.

Several pieces of information can be obtained from the curve and from the properties of the film generaged while it is being stretched, as shown in Table I. Information of most interest is the secant modulus (measured at a constant strain if the strain rate is constant), the yield point, the strain-hardening point, and the natural draw ratio (NDR). Strain-hardening occurs in PET during stretching owing to its tendency to crystallize rapidly when stretched above $T_g$. Strain-hardening allows PET to be oriented into a uniform article. If a test piece of nonuniform cross-section is uniaxially stretched, the tensile stress at any point will be higher the smaller the local cross-section. As a result, strain will initially increase much more rapidly in the small part until the "natural draw ratio" is reached; from then on further elongation of the smaller part at the expense of deformation in the wider part of the specimen will become less favorable and therefore strain will become uniformly distributed in the whole specimen in spite of the initial nonuniformity (44).

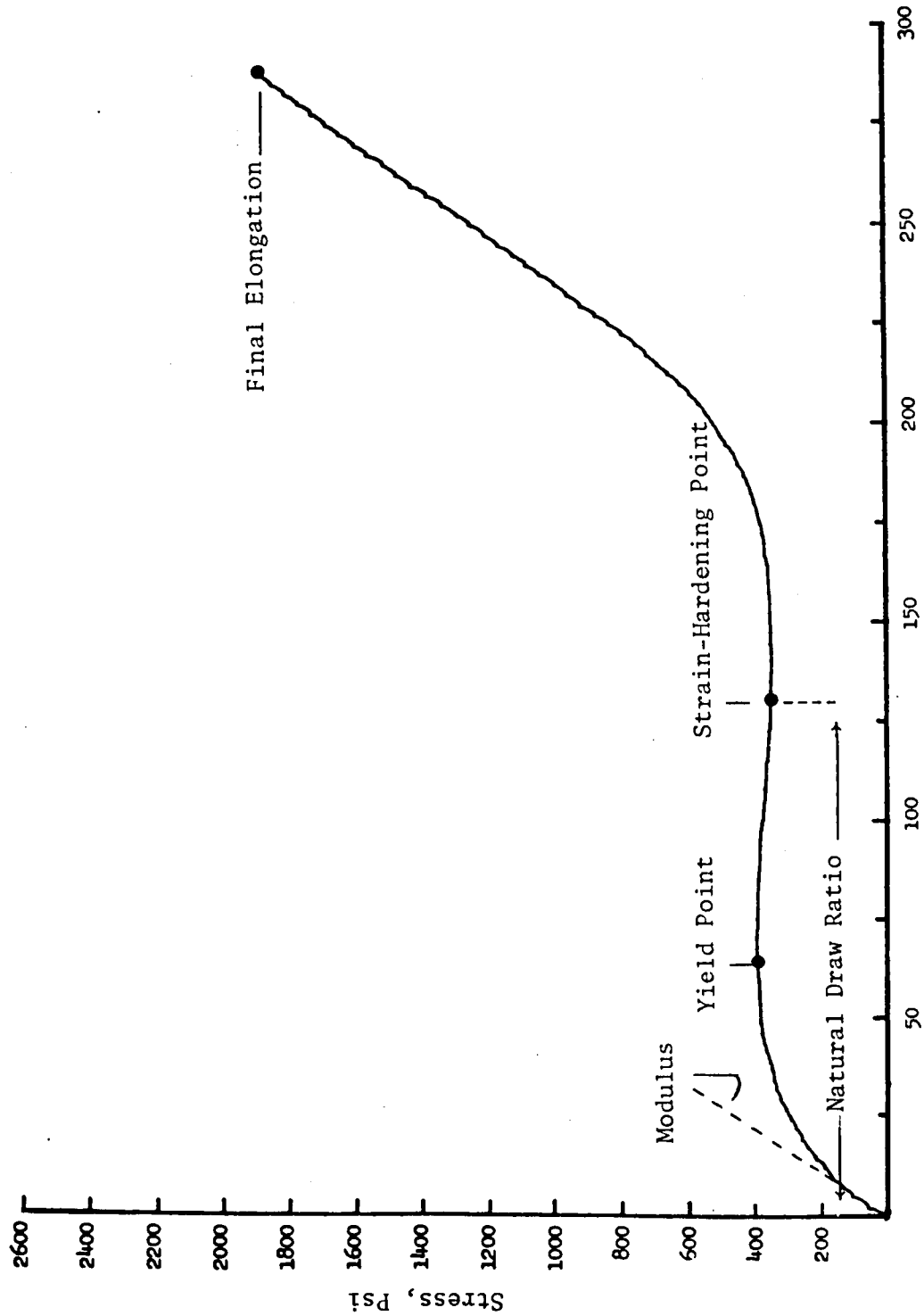


Figure 1. Typical Stress-Elongation Curve Produced During Biaxial Stretching of Poly(Ethylene Terephthalate).

TABLE I

Typical Properties of Poly(Ethylene Terephthalate)
Film Generated upon Biaxial Stretching

| | |
|---|---|
| C--MATERIAL | PET-6857 |
| E--TESTING REF | |
| F--PROJECT NO | |
| G--PEL NO | |
| H--THICKNESS, IN | .02000 |
| I--TEMP, C | 90 |
| J--EXT DIR | X |
| K--X-STR | 4.00000 |
| L--Y-STR | 4.00000 |
| M--X DIAL SETTING | 1.00000 |
| N--X RANGE | 6.00000 |
| O--Y DIAL SETTING | 1.00000 |
| P--Y RANGE | 6.00000 |
| ---TIME SCALE | 5909.79* |

** SAMPLE 1. ***** DISK_REF_# **********

"X" DIRECTION

TYPE A BEHAVIOR

| | |
|---|---|
| VELOCITY, IN/SEC | 2.09 |
| TOTAL STRETCH, IN | 11.53 |
| % STRETCH | 288.48 |
| ACTUAL STRETCH RATIO | 3.88 |
| MODULUS, PSI | 1406.66 |
| HARDEN COF | 5.60 |
| YIELD COF | 1.13 |
| YIELD ELONG, % | 64.08 |
| HARD ELONG, % | 130.84 |
| FINAL ELONG, % | 288.48 |
| YIELD STRESS, PSI | 388.29 |
| HARD STRESS, PSI | 341.97 |
| FINAL STRESS, PSI | 1916.96 |
| 1000 PSI ELONG, % | 234.15 |

For the sample illustrated, a modulus of 1406 psi was calculated, it yielded at 64% or at a stress of 388 psi, and strain-hardening occurred at 131% or at a stress of 342 psi.

## E. TESTING

Mechanical properties were determined on neat and coextruded films before and after stretching, both before and after heatsetting in a forced-air oven. Heatsetting was accomplished by heating the films for 5 minutes at 160°C using frames to hold the films in a fixed position. All films were tested both in the machine and transverse directions.

ASTM procedures were followed for measuring density (D1505), and heat deflection temperature (D1637), and for obtaining tensile modulus, strength, and elongation (D882) using an Instron tensile tester.

Refractive index measurements of oriented films of PET were measured with an Abbé refractometer using the method described by Samuels (45). The three principal refractive indices, the birefringences calculated from them, and the densities determined on PET biaxially oriented 100%, 200%, and 300% are shown in Table II. The refractive indices for 100% amorphous and 100% crystalline PET were determined by extrapolation using the experimental average refractive indices and the densities (45).

Using the intrinsic birefringences for PET ($\Delta_C^\circ = 0.220$, $\Delta_{AM}^\circ = 0.275$) determined by Dumbleton (46) as described by Samuels (47), the reference state birefringence, $(N_{\parallel}^\circ - N_{\perp}^\circ)$, and function $f(N_i) = \frac{N_i - N_{\perp}^\circ}{N_{\parallel}^\circ - N_{\perp}^\circ}$, related

TABLE II

Indices of Refraction of Biaxially Oriented PET

| Biaxial Orientation % | Thickness Direction $N_t$ | Machine Direction $N_M$ | Transverse Direction $N_T$ | Average in All Directions | Average in Plane of Film, $N_{I-P}$ | Birefringence $\Delta N = N_{I-P} - N_t$ | $\Delta N = N_m - m_t$ | Density g/cc |
|---|---|---|---|---|---|---|---|---|
| 100 | 1.550 | 1.588 | 1.595 | 1.577 | 1.592 | 0.042 | -0.007 | 1.342 |
| 200 | 1.520 | 1.624 | 1.618 | 1.587 | 1.621 | 0.101 | 0.006 | 1.356 |
| 300 | 1.510 | 1.632 | 1.632 | 1.591 | 1.632 | 0.122 | 0.000 | 1.357 |

to orientation were calculated as shown in Table III. A plot of $f(N_M)$ and $f(N_T)$ versus % biaxial elongation for PET was made and is shown in Figure 2.

TABLE III

Reference State Refractive Indices and $f(N_i)$ Values Calculated for Biaxially Oriented PET

| Functions Calculated | Percent Biaxial Elongation 100 | 200 | 300 |
|---|---|---|---|
| $X_c$ [1] | .08 | .17 | .17 |
| $N_{\parallel}^{\bullet}$ [2] | 1.754 | 1.760 | 1.760 |
| $N_{\perp}^{\bullet}$ [3] | 1.483 | 1.495 | 1.495 |
| $f(N_M)$ | .39 | .49 | .52 |
| $f(N_T)$ | .41 | .46 | .52 |
| $f(N_t)$ | .25 | .09 | .06 |

[1]Volume fraction of crystalline PET.

[2]Ideal axial refractive index.

[3]Ideal transverse refractive index.

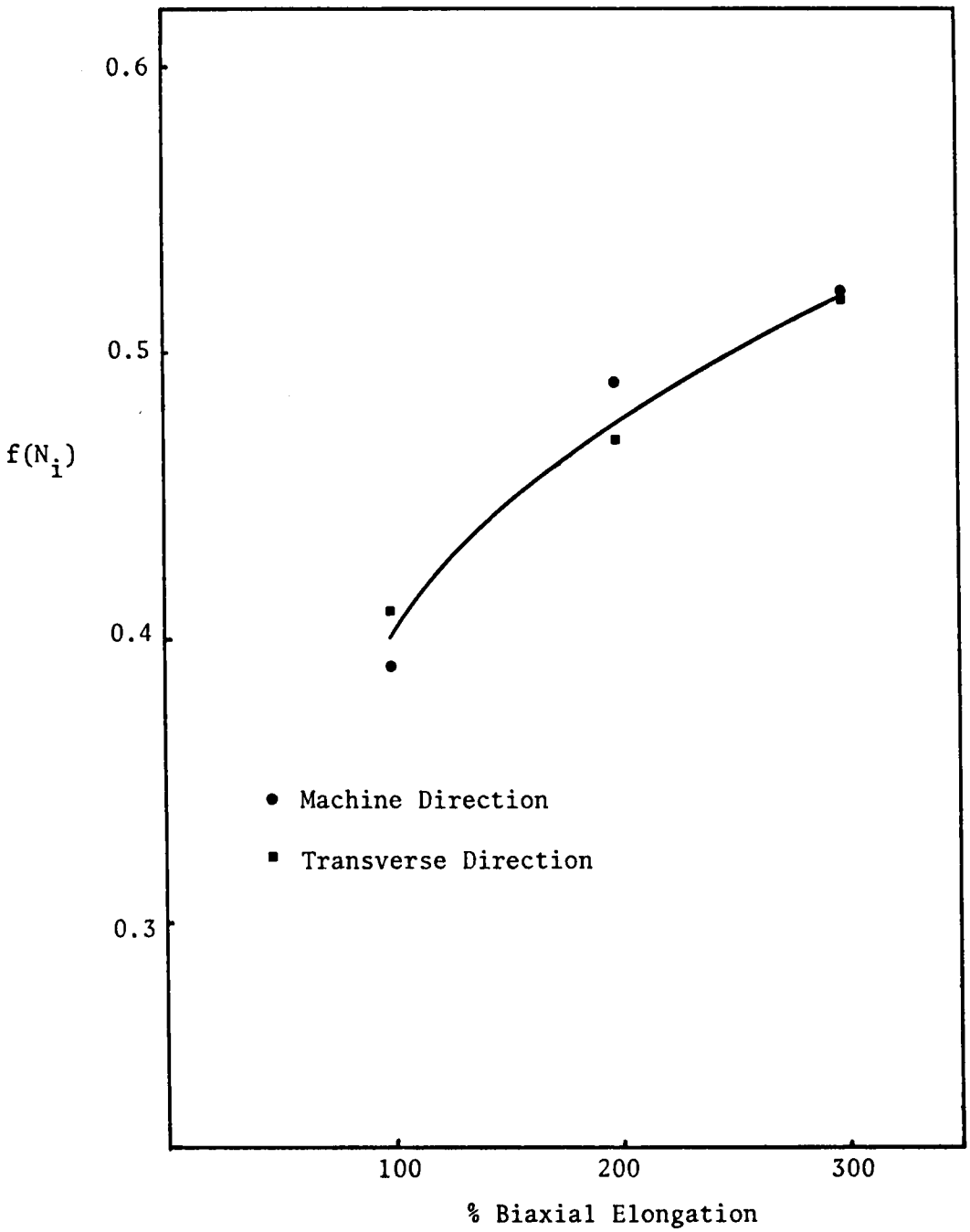


Figure 2. $f(N_i)$ versus Elongation for Oriented PET.

# CHAPTER IV

# DISCUSSION OF RESULTS

## A. EFFECT OF INDIVIDUAL COMPONENTS ON MECHANICAL PROPERTIES OF FINAL LAMINATE

### Unoriented Film

The effect of the PET and EVAL components on the mechanical properties of the coextruded films before orientation are shown in Tables IV - VIII. In order to determine properties of PET and EVAL, the individual layers of the coextruded films were separated prior to testing. Slight difference in properties of the neat films resulted due to minor differences in extrusion conditions from run to run and the presence of tie-layer which remained on the film after being separated. Although EVAL is always a semicrystalline material, its density varied from 1.04-1.21 under similar processing conditions when coextruded with PET. The reason for this discrepancy is not known.

For PET, EVAL, and the PET-EVAL-PET coextruded films, the mechanical properties measured in the machine direction (MD) were generally within experimental error of those measured in the transverse direction (TD). This was also true for properties measured on films which had been heatset (HS) 5 minutes at 160°C.

Films were heatset in order to fully crystallize them and a temperature was selected common both to PET and EVAL. For PET (Table IV), heatsetting caused an increase in tensile modulus, tensile yield, break, and ultimate strength while causing a decrease in elongation. An

TABLE IV

Properties of 11.5 Mil PET-EVAL-PET Coextruded Films Containing No Tie-Layers

| Property | PET As Ext[1] M.D.[2] | PET As Ext T.D.[3] | EVAL As Ext M.D. | EVAL As Ext T.D. | PET-EVAL-PET As Ext M.D. Obt'ed[4] | Pred[5] | PET-EVAL-PET As Ext T.D. Obt'ed | Pred | PET H.S.[6] M.D. | PET H.S. T.D. | EVAL H.S. M.D. | EVAL H.S. T.D. | PET-EVAL-PET H.S. M.D. Obt'ed | Pred | PET-EVAL-PET H.S. T.D. Obt'ed | Pred |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tensile Modulus, $10^5$ Psi | 3.04 | 2.71 | 3.22 | 3.33 | 3.19 | 3.07 | 2.95 | 2.79 | 3.54 | 3.81 | 3.38 | 3.47 | 3.76 | 3.52 | 3.95 | 3.77 |
| Tensile Yield, $10^3$ Psi | 7.7 | 7.4 | 6.9 | 7.4 | 7.6 | 7.6 | 7.2 | 7.4 | 9.1 | 9.6 | 7.7 | 7.9 | 9.3 | 8.9 | 9.3 | 9.4 |
| Tensile Break, $10^3$ Psi | 6.2 | 6.7 | 8.1 | 8.7 | 5.3 | 6.5 | 5.5 | 6.9 | 7.4 | 7.5 | 8.7 | 8.3 | 6.5 | 7.5 | 6.4 | 7.6 |
| Elongation at Break, % | 413 | 264 | 260 | 245 | 426 | 394 | 463 | 262 | 88 | 67 | 200 | 258 | 101 | 101 | 116 | 89 |
| Tensile Strength, $10^3$ Psi | 7.7 | 7.4 | 8.1 | 8.7 | 7.6 | 7.8 | 7.2 | 7.5 | 9.1 | 9.6 | 8.7 | 8.4 | 9.3 | 9.0 | 9.3 | 9.5 |
| Heat Deflection Temperature, 50 Psi, °C | 83° | 84° | 161° | 175° | 82° | 83° | 86° | 84° | 140° | 150° | 159° | 167° | 156° | 140° | 144° | 150° |
| Density, G/CC | 1.33 | 1.33 | 1.07 | 1.07 | 1.32 | 1.29 | 1.32 | 1.29 | 1.38 | 1.38 | 1.07 | 1.07 | 1.35 | 1.34 | 1.35 | 1.35 |
| Thickness, Mils | 4.9 | 5.1 | 1.5 | 1.3 | 11.3 | 11.3 | 11.8 | 11.5 | 5.2 | 5.3 | 1.4 | 1.4 | 11.9 | 11.8 | 11.1 | 12.0 |

[1]As extruded
[2]Machine Direction
[3]Transverse Direction
[4]Obtained
[5]Predicted from Volume Percent Calculations, Equations II-1, II-3, II-4 (pp. 9,10 and 11).
[6]Heatset 5 min. at 160°C

TABLE V

Properties of 11.2 Mil PET-EVAL-PET Coextruded Films Containing CXA 3095 Resin Tie-Layers

| Property | PET As Ext M.D. | PET As Ext T.D. | EVAL As Ext M.D. | EVAL As Ext T.D. | PET-EVAL-PET[1] As Ext M.D. | | PET-EVAL-PET[1] As Ext T.D. | | PET H.S. M.D. | PET H.S. T.D. | EVAL H.S. M.D. | EVAL H.S. T.D. | PET-EVAL-PET[1] H.S. M.D. | | PET-EVAL-PET[1] H.S. T.D. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Obt'ed | Pred | Obt'ed | Pred | | | | | Obt'ed | Pred | Obt'ed | Pred |
| Tensile Modulus, $10^5$ Psi | 2.93 | 2.78 | 1.75 | 1.77 | 2.80 | 2.63 | 2.98 | 2.53 | 3.63 | 3.56 | 1.92 | 2.35 | 3.17 | 3.19 | 3.24 | 3.25 |
| Tensile Yield, $10^3$ Psi | 8.0 | 7.3 | 3.6 | 3.8 | 6.1 | 6.8 | 6.8 | 6.4 | 9.7 | 9.3 | 3.8 | 3.9 | 8.2 | 8.2 | 8.5 | 8.0 |
| Tensile Break, $10^3$ Psi | 10.1 | 10.1 | 5.8 | 5.5 | 5.5 | 9.0 | 5.9 | 8.9 | 7.7 | 7.4 | 5.1 | 5.2 | 5.3 | 7.0 | 6.0 | 6.9 |
| Elongation at Break, % | 617 | 633 | 398 | 362 | 383 | 560 | 404 | 564 | 91 | 114 | 323 | 312 | 105 | 151 | 108 | 166 |
| Tensile Strength, $10^3$ Psi | 10.1 | 10.1 | 5.8 | 5.5 | 6.3 | 9.0 | 6.8 | 8.9 | 9.7 | 9.3 | 5.1 | 5.2 | 8.2 | 8.5 | 8.5 | 8.3 |
| Heat Deflection Temperature, 50 Psi, °C | 85° | 86° | 112° | 126° | 85° | 86° | 92° | 86° | 145° | 151° | 126° | 131° | 149° | 145° | 156° | 151° |
| Density, G/CC | 1.34 | 1.34 | 1.04 | 1.04 | 1.26 | 1.26 | 1.26 | 1.26 | 1.37 | 1.37 | 1.05 | 1.05 | 1.29 | 1.29 | 1.29 | 1.29 |
| Thickness, Mils | 4.2 | 4.3 | 2.9 | 2.9 | 11.3 | 11.3 | 11.0 | 11.5 | 4.3 | 4.4 | 3.0 | 3.0 | 11.3 | 11.6 | 11.0 | 11.8 |

[1]Also contains ~ 0.5 Mil CXA 3095 Resin between each PET-EVAL layer.

TABLE VI

Properties of 26.0 Mil PET-EVAL-PET Coextruded Films Containing CXA 3095 Resin Tie-Layers

| Property | PET As Ext M.D. | PET As Ext T.D. | EVAL As Ext M.D. | EVAL As Ext T.D. | PET-EVAL-PET[1] As Ext M.D. Obt'ed | Pred | PET-EVAL-PET[1] As Ext T.D. Obt'ed | Pred | PET H.S. M.D. | PET H.S. T.D. | EVAL H.S. M.D. | EVAL H.S. T.D. | PET-EVAL-PET[1] H.S. M.D. Obt'ed | Pred | PET-EVAL-PET[1] H.S. T.D. Obt'ed | Pred |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tensile Modulus, $10^5$ Psi | 3.07 | 3.49 | 2.38 | 2.54 | 2.82 | 2.97 | 2.76 | 3.31 | 3.67 | 3.31 | 2.39 | 2.52 | 3.14 | 3.48 | 3.13 | 3.26 |
| Tensile Yield, $10^3$ Psi | 6.8 | 7.7 | 4.3 | 4.4 | 7.0 | 6.4 | 7.0 | 7.2 | 9.4 | 8.3 | 4.7 | 4.7 | 9.0 | 8.7 | 9.2 | 7.8 |
| Tensile Break, $10^3$ Psi | 9.1 | 9.0 | 4.6 | 4.5 | 4.7 | 8.4 | 4.8 | 8.4 | 7.3 | 6.4 | 5.4 | 6.0 | 6.5 | 7.0 | 6.8 | 6.4 |
| Elongation at Break, % | 748 | 678 | 292 | 208 | 254 | 680 | 263 | 613 | 85 | 159 | 228 | 344 | 120 | 106 | 149 | 185 |
| Tensile Strength, $10^3$ Psi | 9.1 | 9.0 | 4.6 | 4.5 | 7.0 | 8.4 | 7.0 | 8.4 | 9.4 | 8.3 | 5.4 | 6.0 | 9.0 | 8.8 | 9.2 | 7.7 |
| Heat Deflection Temperature, 50 Psi,°C | 83° | 84° | 124° | 126° | 81° | 83° | 82° | 84° | 143° | 143° | 132° | 130° | 142° | 143° | 155° | 143° |
| Density, G/CC | 1.34 | 1.34 | 1.07 | 1.07 | 1.30 | 1.30 | 1.30 | 1.31 | 1.37 | 1.37 | 1.07 | 1.07 | 1.33 | 1.32 | 1.33 | 1.36 |
| Thickness, Mils | 11.3 | 11.5 | 3.9 | 3.7 | 25.7 | 26.5 | 26.0 | 26.7 | 10.8 | 11.1 | 3.8 | 3.7 | 26.0 | 25.4 | 26.3 | 25.9 |

[1]Also contains ~ 0.5 Mil CXA 3095 Resin between each PET EVAL-layer.

TABLE VII

Properties of 17.0 Mil PET-EVAL-PET Coextruded Films Containing No Tie-Layers

| Property | PET As Ext M.D. | PET As Ext T.D. | EVAL As Ext M.D. | EVAL As Ext T.D. | PET-EVAL-PET As Ext M.D. Obt'ed | Pred | PET-EVAL-PET As Ext T.D. Obt'ed | Pred | PET H.S. M.D. | PET H.S. T.D. | EVAL H.S. M.D. | EVAL H.S. T.D. | PET-EVAL-PET H.S. M.D. Obt'ed | Pred | PET-EVAL-PET H.S. T.D. Obt'ed | Pred |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tensile Modulus, $10^5$ psi | 2.92 | 3.00 | 4.78 | 5.23 | 3.08 | 3.16 | 3.14 | 3.33 | 3.49 | 3.60 | 5.18 | 5.09 | 3.27 | 3.77 | 3.69 | 3.80 |
| Tensile Yield, $10^3$ Psi | 7.2 | 7.0 | 8.1 | 8.7 | 7.2 | 7.4 | 7.0 | 7.2 | 9.2 | 9.6 | 8.3 | 8.4 | 8.7 | 9.1 | 9.6 | 8.4 |
| Tensile Break, $10^3$ Psi | 7.3 | 9.9 | 9.8 | 10.2 | 6.4 | 7.6 | 6.1 | 9.9 | 6.7 | 8.4 | 8.7 | 9.9 | 5.4 | 6.9 | 6.7 | 8.6 |
| Elongation at Break, % | 500 | 635 | 317 | 284 | 520 | 476 | 443 | 593 | 47 | 28 | 234 | 303 | 56 | 71 | 56 | 64 |
| Tensile Strength, $10^3$ Psi | 8.0 | 9.9 | 9.8 | 10.2 | 7.4 | 8.2 | 7.0 | 9.9 | 9.2 | 9.6 | 8.9 | 9.9 | 8.7 | 9.2 | 9.6 | 8.6 |
| Heat Deflection Temperature, 50 Psi, °C | 87° | 88° | 172° | 180° | 82° | 87° | 84° | 88° | 173° | 152° | 171° | 173° | 145° | 173° | 154° | 152° |
| Density, G/CC | 1.34 | 1.34 | 1.21 | 1.21 | 1.33 | 1.33 | 1.34 | 1.36 | 1.36 | 1.36 | 1.21 | 1.21 | 1.34 | 1.34 | 1.34 | 1.34 |
| Thickness, Mils | 7.4 | 7.7 | 2.2 | 2.1 | 17.0 | 17.0 | 17.0 | 17.5 | 7.5 | 7.3 | 2.3 | 2.2 | 18.0 | 17.3 | 17.0 | 16.8 |

TABLE VIII

Properties of 18.9 Mil PET-EVAL-PET Coextruded Films Containing Elvax 260/EVAL Tie-Layers

| Property | PET As Ext M.D. | PET As Ext T.D. | EVAL As Ext M.D. | EVAL As Ext T.D. | PET-EVAL-PET[1] As Ext M.D. Obt'ed | Pred | PET-EVAL-PET[1] As Ext T.D. Obt'ed | Pred | PET H.S. M.D. | PET H.S. T.D. | EVAL H.S. M.D. | EVAL H.S. T.D. | PET-EVAL-PET[1] H.S. M.D. Obt'ed | Pred | PET-EVAL-PET[1] H.S. T.D. Obt'ed | Pred |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tensile Modulus, $10^5$ Psi | 2.92 | 3.00 | 4.78 | 5.23 | 2.56 | 3.16 | 2.57 | 3.33 | 3.49 | 3.60 | 5.18 | 5.09 | 2.68 | 3.77 | 2.29 | 3.80 |
| Tensile Yield, $10^3$ Psi | 7.2 | 7.0 | 8.1 | 8.7 | 5.9 | 7.4 | 5.2 | 7.2 | 9.2 | 9.6 | 8.3 | 8.4 | 7.6 | 9.1 | 6.8 | 9.2 |
| Tensile Break, $10^3$ Psi | 7.3 | 9.9 | 9.8 | 10.2 | 3.8 | 7.6 | 3.2 | 9.9 | 6.7 | 8.4 | 8.7 | 9.9 | 3.7 | 6.9 | 6.8 | 8.4 |
| Elongation at Break, % | 500 | 635 | 317 | 284 | 143 | 476 | 121 | 593 | 47 | 28 | 234 | 303 | 67 | 71 | 70 | 64 |
| Tensile Strength, $10^3$ Psi | 8.0 | 9.9 | 9.8 | 10.2 | 5.9 | 8.2 | 5.2 | 9.9 | 9.2 | 9.6 | 8.9 | 9.9 | 7.6 | 9.2 | 6.8 | 9.4 |
| Heat Deflection Temperature, 50 Psi, °C | 87° | 88° | 172° | 180° | 85° | 87° | 86° | 88° | 173° | 152° | 171° | 173° | 155° | 173° | 156° | 152° |
| Density, G/CC | 1.34 | 1.34 | 1.21 | 1.21 | 1.26 | 1.33 | 1.26 | 1.36 | 1.36 | 1.36 | 1.21 | 1.21 | 1.28 | 1.34 | 1.28 | 1.34 |
| Thickness, Mils | 7.4 | 7.7 | 2.2 | 2.1 | 19.5 | 17.0 | 18.5 | 17.5 | 7.5 | 7.3 | 2.3 | 2.2 | 18.9 | 17.3 | 10.8 | 16.8 |

[1]Also contains ~ 0.5 Mil 50/50 Elvax 260/EVAL Blend between each PET-EVAL layer.

increase in density and heat deflection temperature were also indicative of further crystallization. However, in the case of EVAL (Table IV), no significant changes in properties occurred upon heatsetting, indicating that the film was crystalline upon coextrusion.

The PET and EVAL films shown in Tables V and VI were taken from laminates which employed CXA 3095 resin as a tie-layer. Although CXA 3095 exhibited poor performance as an adhesive layer, its presence appeared to alter the mechanical properties of the components slightly. One factor which contributes to some error in the calculation of mechanical properties of EVAL when CXA 3095 tie-layer was used is an error in measuring the film thickness of EVAL. Between 1-1.5 mils of CXA 3095 resin was added as a tie-layer. When the laminated films were separated, most of the CXA resin adhered to both sides of the EVAL film, though some of it may have adhered to the two PET films. Since the tie-layer was transparent it was difficult to determine where the CXA resin remained. No compensations were made in the film thickness or property measurements for its presence, which amounted to about 9-13 vol.% for the data in Table V and 4-6 vol.% for the data in Table VI. Since film thickness is used in calculating all the tensile properties, some error exists in the data.

The tensile yield, break, and elongation of PET of Table V were higher than those presented in Table IV, and except for elongation, more closely resembled heatset results. A slightly higher density is indicative of slightly high crystallinity. Conversely, the properties of EVAL were lower than those in Table IV. A slightly lower density

(indicative of lower crystallinity) most likely contributed to the lower properties.

In Table VI, the tensile properties of EVAL were again lower than those of films taken from laminates containing no tie-layer (Table IV, p. 26). Some of this difference may be attributed to the error included in the measuring of the EVAL films in Table VI, as described earlier, due to the presence of 4-6 vol.% CXA resin. Yet a much lower heat deflection temperature for the EVAL films in Table VI relative to those in Table IV (p. 26), indicates a further difference in the films. Since the densities are equal, and one would expect equal crystallinities, perhaps a less ordered crystalline structure exists in the Table VI samples. A good explanation does not exist for these differences.

The same properties for PET and EVAL shown in Table VII were used in Table VIII. Because of the presence of the good tie-layer in the laminates of Table VIII, it was difficult to separate the layers to obtain neat PET and EVAL films for property measurements for Table VIII. The properties of PET and EVAL were generally as expected except for a higher EVAL density indicating the highest level of crystallinity obtained. Generally, it was noted that the mechanical properties of EVAL were not as reproducible as those of PET. This has shown up as large differences in crystallinity and may be due to EVAL's sensitivity to processing variables and moisture as noted by Sogi (48).

PET-EVAL-PET coextruded laminates were made in thicknesses from 11.2 to 26.0 mils containing from 11 to 27 vol.% EVAL. Generally, the mechanical properties of the laminates fell between those of PET and EVAL. A more detailed analysis of the prediction of properties will

follow in Section B. For most laminates, the tensile break value was lower than either that of PET or EVAL. As found for the neat films, properties increased upon heatsetting, with the exception of elongation which decreased due to increased crystallinity of the PET layers.

Although the laminates containing CXA 3095 tie-layer (Tables V and VI, pp. 27 and 28) possessed a very low degree of adhesion as measured on an Instron tensile testing machine (<25 g/in.), its presence did affect the properties of the laminate relative to those containing no tie-layers (Tables IV and VII, pp. 26, 29).

By comparing the properties of the laminate containing 15% EVAL (Table VI, p. 28) to that containing 26% EVAL (Table V, p. 27), a trend of slightly higher heat deflection temperature with increase in EVAL concentration is noted, otherwise, most properties are similar.

Of numerous tie-layers evaluated, only a 50/50 pellet blend of Elvax 260/EVAL imparted adhesion to both the PET and EVAL layers during coextrusion. The T-peel bond strengths of the coextruded laminate was 908 g/in. Although excellent adhesion existed, all mechanical properties (Table VIII) were low relative to other laminates previously discussed. The tie-layer blend did not flow uniformly between the PET and EVAL and a rippled appearance resulted. Although the tie-layer was very thin (1.0 - 1.5 mils total), the rippled nature likely induced stress points throughout the laminate and caused premature failure.

The problem of obtaining tie-layers which adhere to both substrates was very difficult. Many polymers adhere either to EVAL or PET but few adhere well to both. Polyurethanes, polyamides, ethylene-acrylic acid copolymers, and ethylene-vinyl acetate copolymers were evaluated. Most

polymers would not withstand the high temperatures encountered with extrusion of the PET layers (510°F) and thermal degradation occurred.

Based on the mechanical properties of the laminates, it is evident that improvement is still needed in a tie-layer system. Although isotopic properties can be obtained on unoriented film and improvement in these properties can be obtained upon heatsetting, maximum benefit of the EVAL resin as a barrier layer in unoriented film will depend upon the presence of good adhesion between the PET and EVAL and the proper selection of the tie-layer. Because of the crystalline nature of the EVAL layer, its apparent sensitivity to moisture and processability, and the difficulty in obtaining reproducible properties, careful control is needed in the coextrusion of film containing EVAL.

Biaxially Oriented Film

Although all the films discussed in Tables IV - VIII (pp. 26-30) were also biaxially oriented, the discussion of only two coextruded films and their components (Tables IX and X) will be sufficient to illustrate the effects of PET and EVAL on the mechanical properties after orientation. Properties were determined on the PET and EVAL films by separating them from the laminate after orientation. Although no tie-layer was used for the laminates from which the films were obtained to determine the neat PET and EVAL properties, it was very difficult to separate the layers. A limited number of good quality EVAL films were obtained, however, all EVAL films split upon heatsetting, thus no data are available on heatset oriented samples.

TABLE IX

Properties of Biaxially Oriented Coextruded Films Containing No Tie-Layers

| Property | PET B.O.[1] M.D. | PET B.O. T.D. | EVAL B.O. M.D. | EVAL B.O. T.D. | PET-EVAL-PET B.O. M.D. Obt'ed | PET-EVAL-PET B.O. M.D. Pred | PET-EVAL-PET B.O. T.D. Obt'ed | PET-EVAL-PET B.O. T.D. Pred | PET H.S.[2] M.D. | PET H.S. T.D. | EVAL[3] H.S. M.D. | EVAL[3] H.S. T.D. | PET-EVAL-PET H.S. M.D. Obt'ed | PET-EVAL-PET H.S. T.D. Obt'ed | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tensile Modulus, $10^5$ Psi | 6.73 | 6.64 | 3.85 | 3.72 | 6.75 | 6.36 | 6.95 | 6.42 | 7.39 | 7.26 | — | — | 7.16 | 7.34 | |
| Tensile Yield, $10^3$ Psi | 16.90 | 16.02 | 20.60 | 16.07 | 16.14 | 17.4 | 16.42 | 16.02 | 34.36 | 41.58 | — | — | 40.85 | 40.96 | |
| Tensile Break, $10^3$ Psi | 39.09 | 35.54 | 20.60 | 16.07 | 31.17 | 36.7 | 43.82 | 34.11 | 34.36 | 41.58 | — | — | 40.85 | 40.96 | |
| Elongation at Break, % | 70 | 66 | 30 | 23 | 58 | 65 | 81 | 63 | 68 | 97 | — | — | 86 | 87 | |
| Tensile Strength, $10^3$ Psi | 39.09 | 35.54 | 20.60 | 16.07 | 31.17 | 36.7 | 43.82 | 34.11 | 34.36 | 41.58 | — | — | 40.85 | 40.96 | |
| Heat Deflection Temperature, 50 Psi,°C | 83° | 83° | Too Thin | Too Thin | 81° | 85° | 79° | 83° | 125° | 133° | — | — | 119° | 112° | |
| Density, G/CC | 1.36 | 1.36 | 1.21 | 1.20 | 1.34 | 1.35 | 1.34 | 1.35 | 1.37 | 1.37 | — | — | 1.37 | 1.37 | |
| Thickness, Mils | 0.58 | 0.63 | 0.10 | 0.10 | 1.10 | 1.26 | 1.10 | 1.36 | 0.70 | 0.60 | — | — | 1.23 | 1.30 | 1.30 |

[1]Biaxially oriented 300% at 90°C.
[2]Biaxially oriented followed by heatsetting 5 min. at 160°C.
[3]Unable to obtain sample.

TABLE X

Properties of Biaxially Oriented Coextruded Films Containing Good Tie-Layers

| Property | PET B.O. M.D. | PET B.O. T.D. | EVAL B.O. M.D. | EVAL B.O. T.D. | PET-EVAL-PET[1] B.O. M.D. Obt'ed | Pred | PET-EVAL-PET B.O. T.D. Obt'ed | Pred | PET H.S. M.D. | PET H.S. T.D. | EVAL[2] H.S. M.D. | EVAL[2] H.S. T.D. | PET-EVAL-PET[1] H.S. M.D. Obt'ed | PET-EVAL-PET[1] H.S. T.D. Obt'ed |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Tensile Modulus, $10^5$ Psi | 6.73 | 6.64 | 3.85 | 3.72 | 4.18 | 6.36 | 3.39 | 6.42 | 7.39 | 7.26 | — | — | 4.16 | 3.99 |
| Tensile Yield, $10^3$ Psi | 16.90 | 16.02 | 20.60 | 16.07 | 12.97 | 17.4 | 15.05 | 16.02 | 34.36 | 41.58 | — | — | 17.59 | 17.41 |
| Tensile Break, $10^3$ Psi | 39.09 | 35.54 | 20.60 | 16.07 | 14.77 | 36.7 | 15.05 | 34.11 | 34.36 | 41.58 | — | — | 17.59 | 17.41 |
| Elongation at Break, % | 70 | 66 | 30 | 23 | 68 | 65 | 65 | 63 | 68 | 97 | — | — | 63 | 77 |
| Tensile Strength, $10^3$ Psi | 39.09 | 35.54 | 20.60 | 16.07 | 14.77 | 36.7 | 15.05 | 34.11 | 34.36 | 41.58 | — | — | 17.59 | 17.41 |
| Heat Deflection Temperature, 50 Psi,°C | 83° | 83° | Too Thin | Too Thin | 78° | 83° | 76° | 83° | 125° | 133° | — | — | 116° | 109° |
| Density, G/CC | 1.36 | 1.36 | 1.21 | 1.21 | 1.26 | 1.35 | 1.26 | 1.35 | 1.37 | 1.37 | — | — | 1.27 | 1.27 |
| Thickness, Mils | 0.58 | 0.63 | 0.10 | 0.10 | 1.60 | 1.26 | 1.90 | 1.36 | 0.70 | 0.60 | — | — | 1.8 | 2.2 |

[1]Also contains 50/50 Elvax 260/EVAL Blend (0.5 Mil before oriented) between each PET-EVAL layer.
[2]Unable to obtain sample.

Comparing Tables IX and VII (p. 29) it can be noted that most mechanical properties of PET and EVAL are considerably increased by biaxial orientation. For both PET and EVAL, elongation decreased upon orientation. The density of EVAL remained unchanged on orientation, supporting the theory that the EVAL film was crystalline as-extruded and little, if any, further crystallization occurred upon orientation. As expected, however, orientation crystallized the amorphous PET. A more detailed analysis of the behavior of the material during stretching will be discussed in Section D; however, the theory of stress-induced orientation and the effects on physical properties are well documented (49).

Heatsetting induced slight additional cyrstallization of the oriented PET which was sufficient to eliminate the tensile yield point. Other properties remained unchanged. Based on the heatsetting effects of unoriented EVAL, it is reasonable to assume that the properties of the oriented EVAL after heatsetting would also remain unchanged.

The mechanical properties of the oriented PET-EVAL-PET laminate without a tie-layer (Table IX) were generally between those of oriented PET and EVAL.

In the case of the laminate possessing good adhesion (Table X), all properties were lower than those of the laminate possessing no tie-layer, both before and after heatsetting. This indicates that good adhesion may impart more of the characteristics of the substrate possessing lower strength properties to the laminate. Since a tie-layer does not appear to be needed to impart adhesion to oriented laminates, it would not be desirable to use one, as the mechanical properties would be lowered.

## B. OVERALL BEHAVIOR OF MECHANICAL PROPERTIES OF LAMINATES AS A FUNCTION OF FILM THICKNESS

### Different Laminate Thicknesses

It has been observed from comparison of the properties of the laminates before orientation (Tables IV-VIII, pp. 26-30), that in the absence of good adhesion tensile modulus, tensile yield, and ultimate tensile strength are generally within experimental error of being independent of laminate thickness. More scatter exists in tensile break strengths. Elongations at break are always high before heatsetting but vary widely between 254-564%. After heatsetting the values are lower but more consistent, ranging from 56-149%.

As stated previously, a tie-layer does not appear to be needed to impart adhesion to oriented laminates, thus thicknesses of the more expensive EVAL above those required for barrier properties should not be used. Additional EVAL will not contribute substantially to the mechanical properties of the laminate, regardless of the degree of adhesion present to the PET substrate.

### Prediction of Properties from Film Thicknesses

In Tables IV-X (pp. 26-30, 35, and 36) predicted properties of the coextruded films were calculated from the measured properties of the layers using the equations of Schrenk and Alfrey (4), Equation II-1 (p. 9), and Guillotte (35), Equations II-3, II-4, and II-5 (pp. 10 and 11). For those laminates in which a tie-layer was not used (Tables IV, VII and IX, pp. 26, 29 and 35), the properties were generally well

represented by a simple additive model, considering the variation in the properties of PET and EVAL discussed earlier. One exception was unoriented tensile break strength which was always lower than the predicted value and lower than either PET or EVAL. PET and EVAL are much more similar in mechanical properties than the materials used by Schrenk and Guillotte; however, in spite of the differences between the PET/EVAL system and the high stiffness/low stiffness systems investigated by Schrenk and Guillotte, the equations seem to work reasonably well.

For those laminates in which CXA resin, a poor tie-layer, was used (Tables V and VI, pp. 27 and 28), there was a larger discrepancy between the measured properties and those calculated from a simple additive model. The greatest disagreement existed in tensile break strength and elongation, which were generally lower than the predicted values. The predicted values were calculated from values of individual layers which, as noted previously, were influenced somewhat by the presence of the tie-layer and the failure to consider its presence when measuring film thicknesses. This introduces error into the measurement of film properties such as break strength and thus into calculation of the predicted values. The effect of the presence of tie-layer will be accounted for in Section C. Although the laminates yielded at the high values predicted, they always tended to break at low stresses typical of EVAL.

The properties of the unoriented laminate having good adhesion (Table VIII, p. 30) were generally not predicted by the simple additive equations. The effect of the properties of the Elvax 260/EVAL tie-layer will also be discussed in Section C.

Prediction of properties of the oriented laminates follows closely to that of the unoriented laminates, that is, good agreement existed in the absence of a tie-layer and poor agreement existed in the presence of a good tie-layer.

## C. EFFECT OF TIE-LAYER PRESENCE ON MECHANICAL PROPERTIES OF LAMINATES

### Adjustment of Predicted Properties for Tie-Layer Presence

It was noted that the values predicted from a simple additive model in Tables V and VI (pp. 27 and 28) disagreed with the actual measurements for tensile break strength and elongation. One error that contributed to this disagreement was the measurement of the film thickness of the EVAL layer and the failure to consider the presence of 1 mil of CXA 3095 ethylene-vinyl acetate copolymer (3.8 vol.% for Table VI [p. 28] and 8.9 vol.% for Table V [p. 27]).

When the layers of the laminate were separated, the CXA 3095 resin tended to stick to the EVAL layer and although the EVAL was measured to be about 3 mils thick, it is known from the extrusion data that it probably contained a minimum of about 0.5 mil of tie-layer on either side; thus the true thickness of EVAL should have been recorded as ~2 mils in the case of Table V (p. 27) and ~2.8 mils in the case of Table VI (p. 28). By making these corrections and compensating for the properties of 1 mil tie-layer, the predicted values would be decreased by alout 1-3% for tensile properties and 11% for tensile modulus. The tensile break and elongation values would remain high.

An even lesser effect would result by making corrections for 1 mil of a 50/50 Elvax 260/EVAL tie-layer used in Table VIII (p. 30). A correction for 2.6 vol.% Elvax 260 would only lower the predicted modulus value by 1.2%.

However, as noted earlier, the discrepancy in predicted versus actual data may arise from the stress points created by the uneven tie-layer rather than the properties of the tie-layer itself. It should be noted that heatsetting the films at 160°C tended to produce properties more in line with the predicted values. This may be due to the fact that Elvax 260 softens at 115°C and the $T_g$ of EVAL is 69°C. Thus, during heatsetting, the softening of the tie-layer may relieve the stress concentrations and produce a more uniform laminate.

## Guillotte's Adjustment of Data to Produce Linear Relationships

As noted in Chapter II, Guillotte (35) found that a simple linear relationship between component and laminate properties often does not exist for certain resin components. When good adhesion exists between resins whose original ultimate elongation values differ widely, the composite film will break at the lower elongation and all tensile properties will be affected. To produce a linear relationship between the composite made from films having elongations of 350% and 450%, he reduced the property of the resin having the higher elongation by a factor of 0.8 (Equation II-6, p. 11). However, this type of adjustment does not apply to the laminates in Table X. Both PET and EVAL possess low elongations and the laminate extends to the higher value before breaking.

## D. BEHAVIOR OF FILM UPON STRETCHING AT 90°C

### Characteristics of Neat Films

PET film (10-20 mils) and EVAL film (5-20 mils) were extruded as described previously. Attempts were made to biaxially stretch all the films on the T. M. Long machine. Conditions were chosen which would be common to both polymers so that the same conditions could be used for stretching the neat films as well as coextruded film made from PET and EVAL.

For PET, the minimum temperature above its $T_g$ of 81°C which permits uniform stretching is about 90°C. This value fell within the range recommended for EVAL (43). This temperature was used for all samples. It was found early in the project that EVAL could only be stretched at a very slow rate, consequently, a stretch rate of 2 in./sec. was used for all samples of PET, EVAL, and the laminates. As shown in Figure 1 (p. 18), PET must be stretched > 100% to assure that strain-hardening occurs. All films were stretched to the maximum limits of the machine, 4x × 4x, or 300%. A comparison of the stress-strain curves for 10 mil PET and 5 mil EVAL are shown in Figure 3. A large difference in moduli of the two films during stretching at 90°C can be seen. PET was found to possess a secant modulus of only 1100 psi while EVAL has a much higher modulus of 19,700 psi.

An even larger difference in tensile modulus of PET and EVAL was discovered by testing at 90°C on an Instron machine (Figure 4). Although both materials have $T_g$'s < 90°C (81°C for amorphous PET and

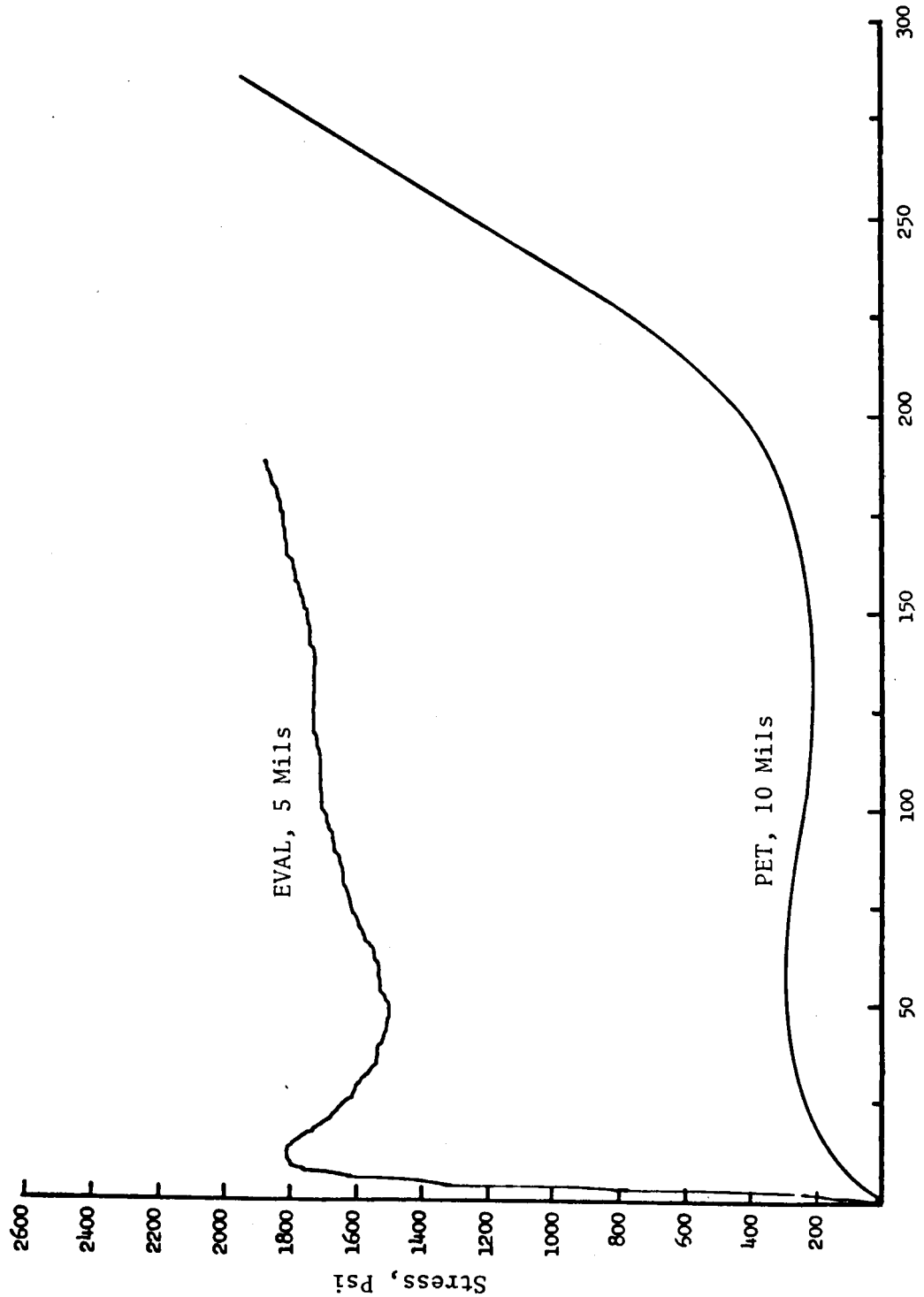


Figure 3. Behavior of Neat Films upon Stretching at 90°C.

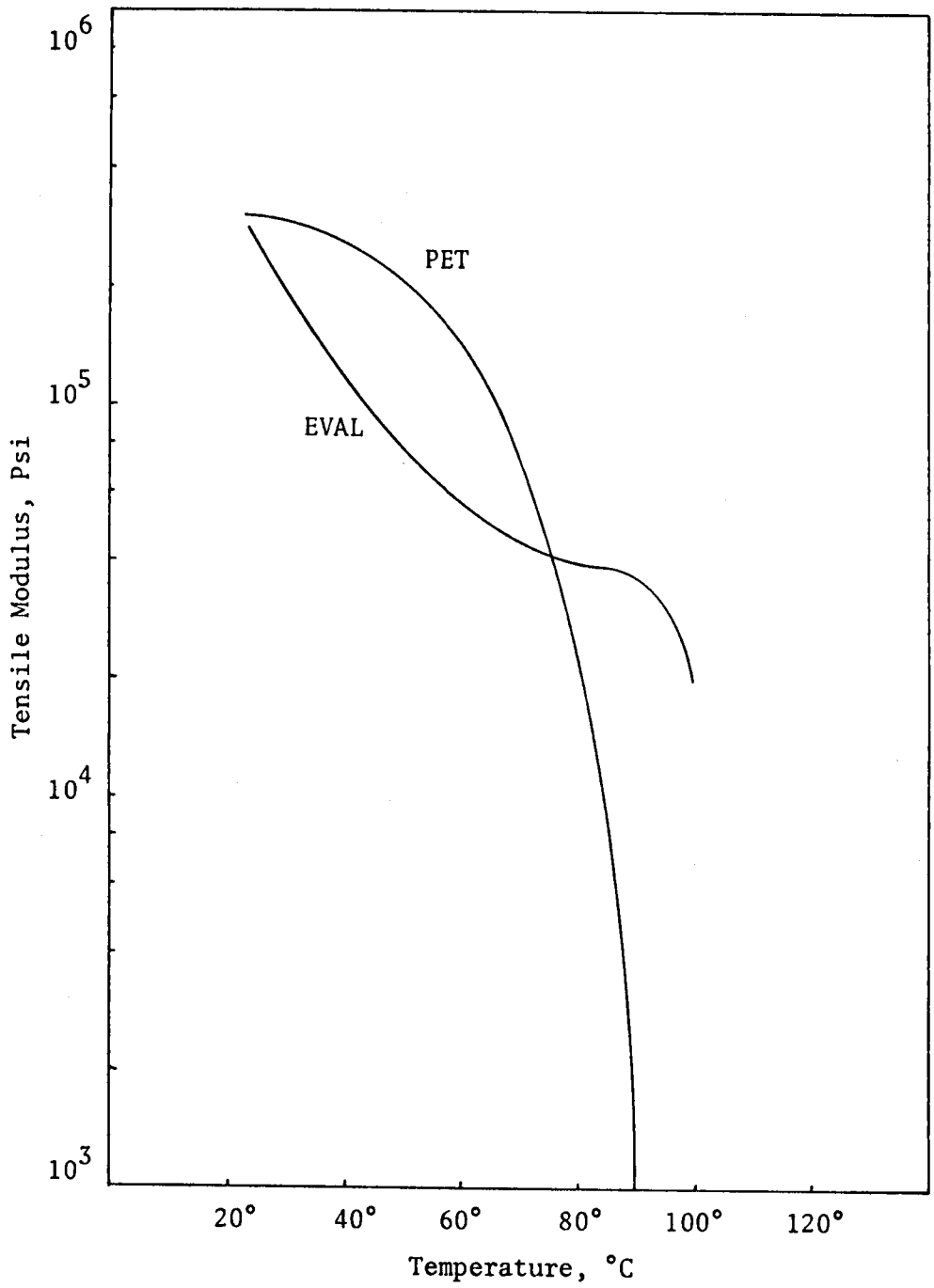


Figure 4. Modulus vs. Temperature of Neat Films Measured on an Instron Machine.

69°C for EVAL), at 90°C, PET has a tensile modulus of 1000 psi while EVAL has a tensile modulus of 40,000 psi, owing to its crystalline character.

Because of the high modulus, numerous problems were encountered in stretching neat EVAL film. Completely uniform stretched films were obtained only from 5 mil EVAL and these were only obtained at 200%. Ten mil films always tore during stretching and this was attributed to the crystalline nature of the films (density = 1.19 g/cc) and the inducement of stress cracking caused by the pressure exerted by the grips. The machine could not begin to stretch the 20 mil films.

The thicker EVAL films (10 mils) were stretched only by sandwiching them between PET support films and holding them together while placing them in the T. M. Long machine by taping the corners together or shearing the edges of the sandwich. By so doing, the stress of the grips was distributed over the two outer, amorphous PET films and uniformly oriented films were obtained for property measurements.

## Effect of Tie-Layer Efficiency upon Stretching of Coextruded Films

In addition to the mere presence of EVAL in the laminated structure and its effect on the final mechanical properties of the film, the degree to which it is bonded to the PET substrate was found to have a marked affect upon the stretching characteristics of the laminate. Considerable information was obtained from observing the stretching behavior and examining the stretching properties.

The effect of adhesion of PET to EVAL and the efficiency of the tie-layer imparting the adhesion on the stretching behavior of the

coextruded films investigated can be observed from Figures 5 and 6. Also, stretching properties which describe these curves are listed in Tables XI and XII.

As compared to neat PET (Figure 5) which has a modulus of only 1418 psi but strain-hardens at 118% (Table XI), it was found that as adhesion is increased between PET and EVAL, the laminate increasingly assumes the high modulus characteristics of EVAL at 90°C. In the absence of a tie-layer, thus minimal adhesion, the laminate possessed a modulus of 2654 psi (87% higher than PET) (Table XI) while strain-hardening still occurred at a high elongation of 125%. However, upon the use of a tie-layer and as the efficiency of the tie-layer increased, it was found that stretching of the laminate became increasingly more difficult. When the strongest adhesion of 908 g/in. existed between layers (Figure 6), the stretching modulus had increased to 3905 psi (Table XII), an increase of 175% over PET. The strain-hardening point had decreased to 71%.

## Further Demonstration of Contribution of EVAL to Modulus

Figure 7 illustrates that the volume percent EVAL present in the film also affects the modulus during stretching. The upper curve of 10-5-10 PET-EVAL-PET resulted by sandwiching 5 mils of extruded EVAL between two 10 mil PET carrier layers, as described previously, in an effort to obtain information on neat EVAL film. The laminate thus contained 20 vol.% EVAL. The lower curve representing 12 vol.% EVAL was obtained from a coextruded film.

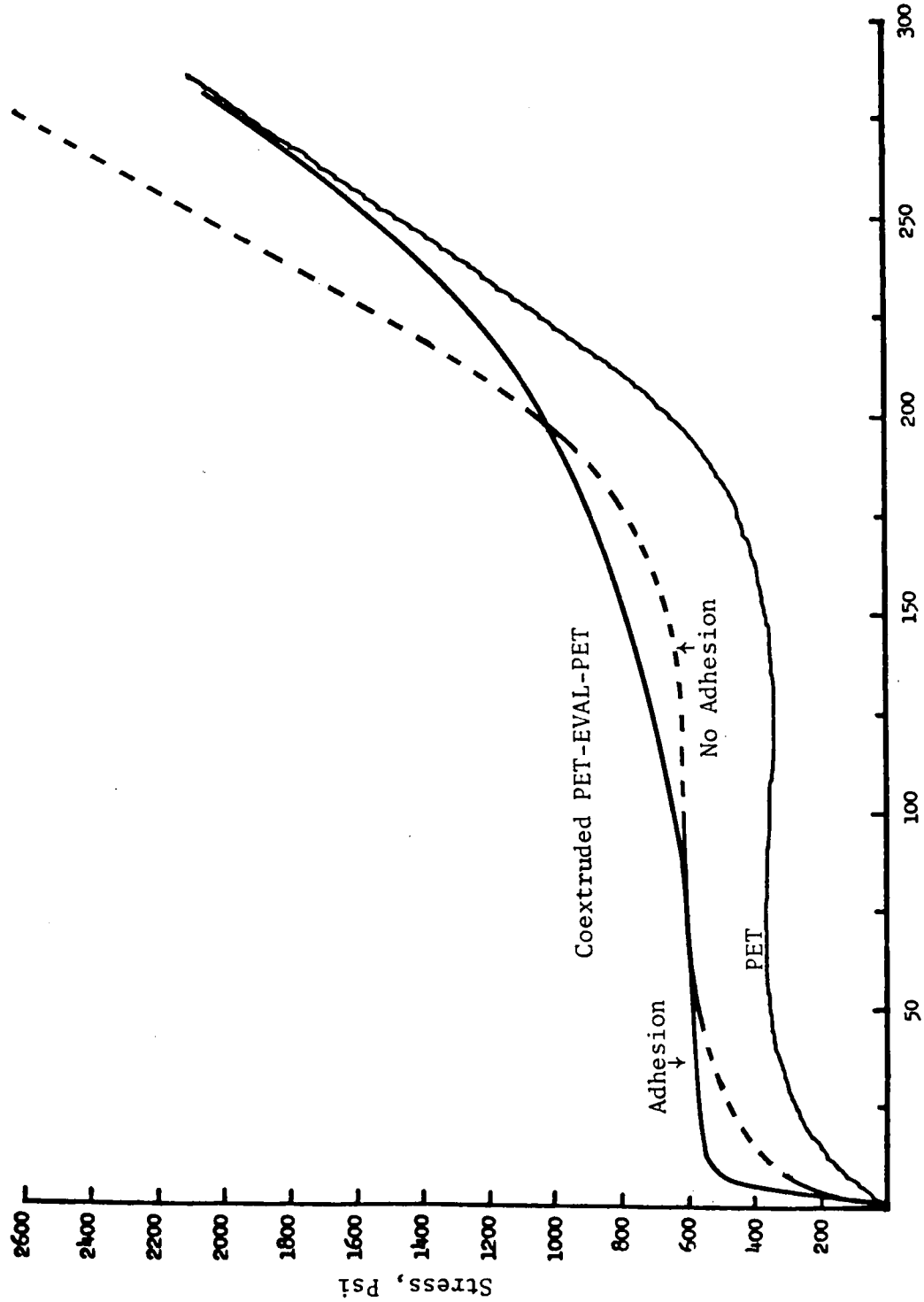


Figure 5. Behavior of Coextruded Films upon Stretching at 90°C.

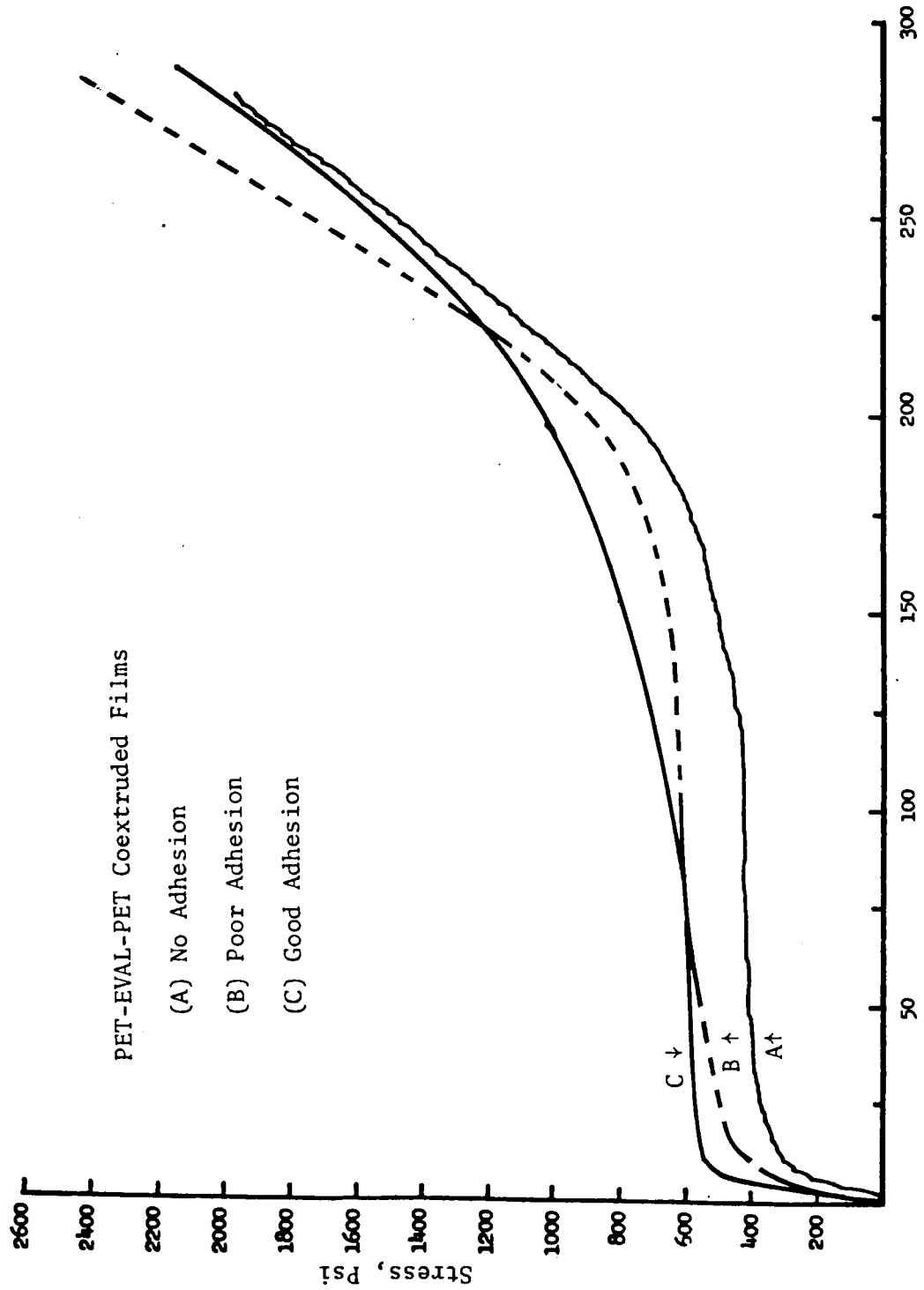


Figure 6. Contribution of Adhesion to Modulus of Films upon Stretching at 90°C.

TABLE XI

Stretching Properties of Coextruded Films at 90°C

| | | | |
|---|---|---|---|
| Thickness, In. | 0.01490 | 0.01599 | 0.02000 |
| Temp, C | 90 | 90 | 90 |
| Ext Dir | X | X | X |
| X-Str | 4.00000 | 4.00000 | 4.00000 |
| Y-Str | 4.00000 | 4.00000 | 4.00000 |
| X Dial Setting | 1.00000 | 1.00000 | 1.00000 |
| X Range | 6.00000 | 6.00000 | 6.00000 |
| Y Dial Setting | 1.00000 | 1.00000 | 1.00000 |
| Y Range | 6.00000 | 6.00000 | 6.00000 |
| Material | PET | PET-EVAL-PET | PET-EVAL-PET |
| Tie-layer | No | No | Yes |
| Adhesion between Layers | No | No | Yes |
| Velocity, In./Sec | 2.07 | 2.10 | 2.07 |
| Total Stretch, In. | 11.45 | 10.42 | 11.48 |
| % Stretch | 286.29 | 260.71 | 287.02 |
| Actual Stretch Ratio | 3.86 | 3.60 | 3.87 |
| Modulus, Psi | 1417.73 | 2653.69 | 3904.71 |
| Harden Cof | 6.27 | 3.99 | 3.47 |
| Yield Cof | 1.08 | 1.07 | 0.92 |
| Yield Elong, % | 62.13 | 72.36 | 13.40 |
| Hard Elong, % | 118.65 | 124.50 | 71.14 |
| Final Elong, % | 286.29 | 260.71 | 287.02 |
| Yield Stress, Psi | 373.07 | 613.10 | 561.32 |
| Hard Stress, Psi | 343.81 | 572.22 | 607.65 |
| Final Stress, Psi | 2156.13 | 2287.20 | 2114.51 |
| 1000 Psi Elong, % | 220.75 | 195.16 | 193.21 |

TABLE XII

Contribution of Adhesion to Stretching Properties of Coextruded Films at 90°C

| | | | |
|---|---|---|---|
| Thickness, In. | 0.01149 | 0.01099 | 0.02000 |
| Temp, C | 90 | 90 | 90 |
| Ext Dir | X | X | X |
| X-Str | 4.00000 | 4.00000 | 4.00000 |
| Y-Str | 4.00000 | 4.00000 | 4.00000 |
| X Dial Setting | 1.00000 | 2.00000 | 1.00000 |
| X Range | 6.00000 | 6.00000 | 6.00000 |
| Y Dial Setting | 1.00000 | 2.00000 | 1.00000 |
| Y Range | 6.00000 | 6.00000 | 6.00000 |
| Material | PET-EVAL-PET | PET-EVAL-PET | PET-EVAL-PET |
| Tie-layer | No | Yes | Yes |
| Adhesion between Layers | None | Poor | Good |
| Velocity, In./Sec | 2.08 | 4.41 | 2.07 |
| Total Stretch, In. | 11.24 | 11.37 | 11.48 |
| % Stretch | 281.17 | 284.34 | 287.02 |
| Actual Stretch Ratio | 3.81 | 3.84 | 3.87 |
| Modulus, Psi | 2285.30 | 2555.06 | 3904.71 |
| Harden Cof | 4.53 | 3.74 | 3.47 |
| Yield Cof | 0.88 | 0.90 | 0.92 |
| Yield Elong, % | 28.26 | 72.85 | 13.40 |
| Hard Elong, % | 119.39 | 146.68 | 71.14 |
| Final Elong, % | 281.17 | 284.34 | 287.02 |
| Yield Stress, Psi | 386.22 | 594.52 | 561.32 |
| Hard Stress, Psi | 435.98 | 653.97 | 607.65 |
| Final Stress, Psi | 1978.50 | 2452.40 | 2114.51 |
| 1000 Psi Elong, % | 215.39 | 207.83 | 193.21 |

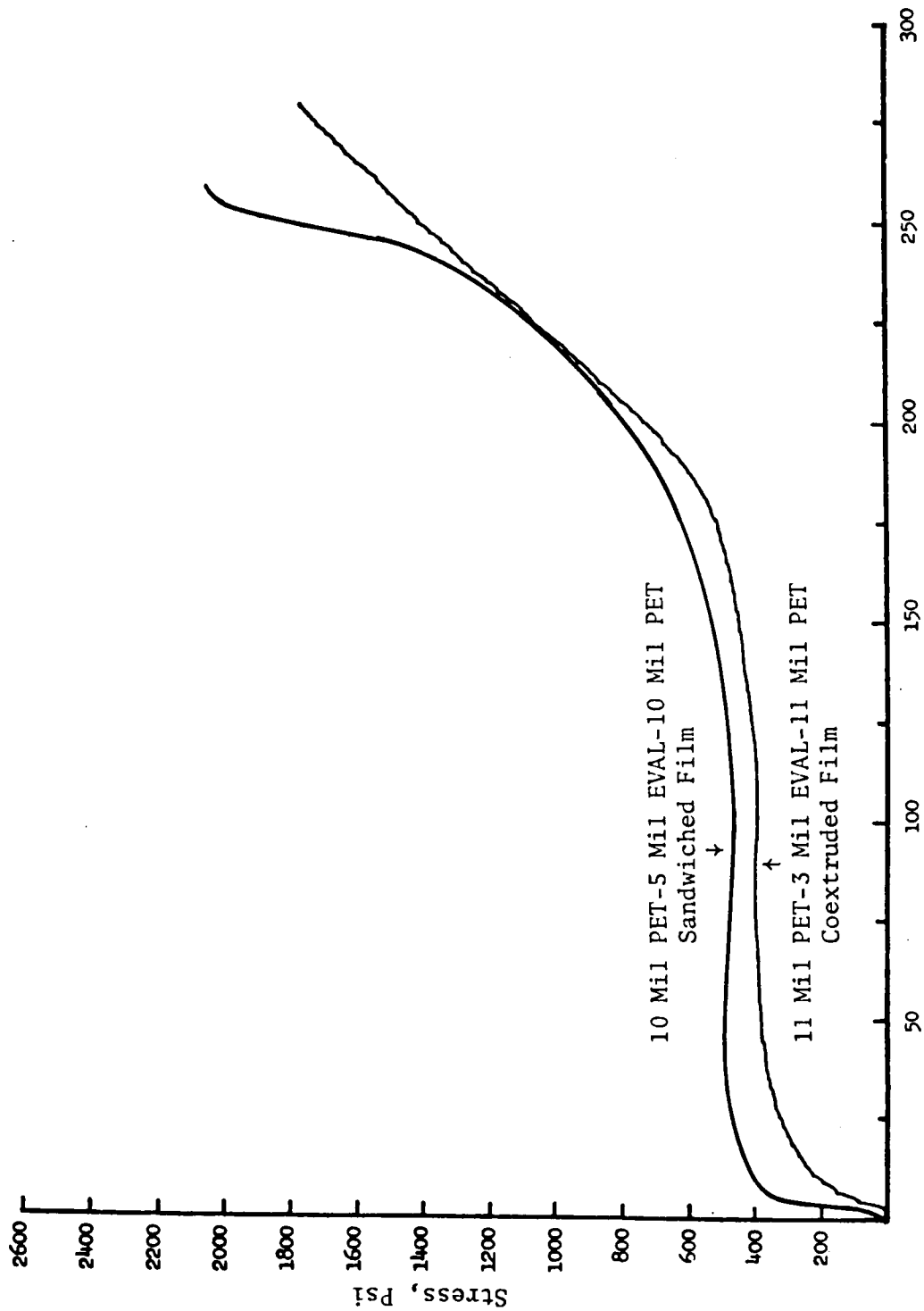


Figure 7. Contribution of EVAL to Modulus of Films upon Stretching at 90°C.

The 12% EVAL film exhibited a modulus of 1692 psi upon stretching at 90°C while the 20% EVAL film exhibited a modulus of 3515 psi, an increase of 49% over the previous laminate or an increase of 148% over PET (Table XI). Since the laminates possessed no adhesion between layers, an even greater increase in modulus upon the addition of EVAL would be expected with good adhesion existing.

# CHAPTER V

## SUMMARY AND CONCLUSIONS

The purpose of the project was to determine how the orientation behavior and properties of PET/EVAL copolymer laminates were related to the characteristics of the individual layers. Neat films of PET and EVAL were extruded. Laminates of PET/EVAL/PET were coextruded with and without tie-layers. The films were tested as-extruded and after heat-setting in both the machine and transverse directions. In addition, the neat films and the coextruded laminates were biaxially oriented. These films, as well as the substrate films separated from the oriented laminates were analyzed by the same methods used before orientation. Properties were related to those of the individual layers and used to predict properties of the laminates.

Film properties were found to be the same in the machine and transverse directions before and after heatsetting. Heatsetting crystallized the PET films and the laminates, thereby increasing tensile properties and reducing elongation. It had no significant effect on the properties of EVAL. The properties of EVAL were found not to be as reproducible as those of PET but tended to support the claims that it is sensitive to moisture and processing conditions. Properties of the laminates tended to be intermediate between those of PET and EVAL, depending upon the volume percent of each present and the degree of adhesion existing. One property of exception was tensile break strength which routinely was lower than that of either substrate.

Numerous polymers were evaluated as tie-layers for PET and EVAL; however, only a blend of Elvax 260 and EVAL exhibited good adhesion. Properties of the laminate were affected by the degree of adhesion and the mechanical properties of the tie-layer present.

The PET and PET-EVAL-PET laminates oriented biaxially up to 300% without difficulty, whereas, the EVAL films would orient only to 200% at thicknesses $\leq$ 10 mils. Orientation significantly increased the strength characteristics of the materials, while decreasing elongation to break. Heatsetting the oriented films offered little improvement in properties. The presence of a tie-layer was not necessary for the oriented laminates and may be detrimental to the overall mechanical properties.

The equations of Schrenk and Alfrey, and Guillotte were useful in predicting the properties of the laminates. In the absence of a tie-layer, the properties were additive. In the presence of a tie-layer, the properties were dependent upon whether or not adhesion existed but could be predicted knowing the properties of the tie-layer, the volume percent present, and the presence of adhesion. When good adhesion was present, however, properties of the laminate could not be predicted with the additive equations.

The actual stretching of the films was found to differ markedly with the substrate. PET oriented easily under all conditions attempted but EVAL would only orient at a slow rate, at thicknesses $\leq$ 10 mils, and with the aid of PET supports to prevent stress concentrations. This was attributed to the crystalline nature of EVAL and its high modulus at 90°C.

Ease of stretching the coextruded films depended upon the adhesion existing and the amount of EVAL present, since the modulus of the EVAL component at 90°C was the controlling factor in the orientation experiments.

Based on the cost of EVAL, its processing sensitivity and resulting effects on mechanical properties, and the problems associated with its orientation, the minimum amount needed to impart acceptable barrier characteristics should be used in PET/EVAL laminates.

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# APPENDIXES

# APPENDIX A

## PROPERTIES PUBLISHED ON FILMS MADE FROM TENITE® PET THERMOPLASTIC POLYESTER 6857

### Properties of Amorphous Films or Coatings of *TENITE* PET Polyester 6857

| Property, Units | Value |
|---|---|
| Crystallinity, % | ~2 |
| Density, g/cm$^3$ | 1.33 |
| Basis Weight (1 mil [0.025 mm]), lb/ream (g/m$^2$) | 20.8 (29.3) |
| Temperature Characteristics, °C | |
| Glass Transition Temperature, $T_g$ | 81 |
| Crystallization Temperature on Heating, $T_{ch}$ | ~145 |
| Crystalline Melt Temperature, $T_m$ | ~255 |
| Crystallization Temperature on Cooling, $T_{cc}$ | ~190 |
| Heat of Crystallization, | |
| On Heating, cal/g (J/g) | 7.1 (30) |
| On Cooling, cal/g (J/g) | 9.2 (39) |
| Thermal Conductivity, cal/cm·°C·s (W/m·K) | 5.2 x 10$^{-4}$ (0.22) |
| Heat of Fusion, cal/g (J/kg) | 10 (42 x 10$^3$) |
| Specific Heat, (cal/g)/°C (J/kg·K) | |
| @ 50°C | 0.27 (1130) |
| @ 100°C | 0.36 (1510) |
| @ 200°C | 0.39 (1630) |
| @ 275°C | 0.43 (1800) |
| @ 300°C | 0.45 (1880) |
| @ 330°C | 0.47 (1970) |

### Tentative Properties of 1.25-Mil (0.032-mm) Film Extruded from *TENITE* PET Polyester 6857

| Property, Units | | ASTM Method | PET 6857 |
|---|---|---|---|
| Thickness, mils (mm) | | | |
| Minimum | | | 1.2 (0.030) |
| Maximum | | | 1.3 (0.033) |
| Pellet Inherent Viscosity | | D 1238-E | 0.69 |
| Film Inherent Viscosity | | D 1238-E | 0.67 |
| Film Density, g/cm$^3$ | | D 1505 | 1.33 |
| Haze, % | | D 1003 | 1.0 |
| Gloss at 45°, Gardner Rating | | D 2457 | 105 |
| Transparency, % | | D 1746 | 85 |
| Elmendorf Tear | M.D. | D 1922 | 35 |
| Strength, grams | T.D. | D 1922 | 35 |
| Tensile Strength at Fracture, | M.D. | D 882 | 7000 (48) |
| psi (MPa) | T.D. | D 882 | 6900 (48) |
| Ultimate Elongation, % | M.D. | D 882 | 5 |
| | T.D. | D 882 | 5 |
| Tensile Modulus of Elasticity, | M.D. | D 882 | 309,000 (2130) |
| psi (MPa) | T.D. | D 882 | 296,000 (2040) |
| Coefficient of Friction at 6 in./min (150 mm/min) | | D 1894 | >1 |
| Water Vapor Transmission Rate, (g/24 h)/100 sq. in. ([g/24 h]/m$^2$) | | E 96-E | 3.3 (51) |
| Gas Transmission Rate, | $CO_2$ | D 1434 | 720 (18) |
| cm$^3$·mil/m$^2$·24 h·atm | $O_2$ | D 1434 | 130 (3.3) |
| cm$^3$·mm/m$^2$·24 h·atm | $N_2$ | D 1434 | 45 (1.1) |
| Impact Strength, 1/2-in. Dart at 26 in. (12.7 mm Dart at 660 mm), grams | 73°F | D 1709 | 85 |

Source: Materials Bulletin MB-79A, Eastman Chemicals Products, Inc., Kingsport, Tennessee.

# APPENDIX B

## PROPERTIES PUBLISHED ON KURARAY EVAL FILM

## IN COMPARISON WITH OTHER FILM

| Property | | Unit | Condition of Measuring | KURARAY EVAL FILM EF-F | Polyester (PET) | Orientated Nylon (ON) |
|---|---|---|---|---|---|---|
| Thickness | | μ | | 15 | 12 | 15 |
| Tensile Strength | MD | kg/mm² | 20°C 65% RH | 8.2 | 17.7 | 21.8 |
| Tensile Strength | TD | | | 5.3 | 14.4 | 17.9 |
| Elongation | MD | % | 20°C 65% RH | 160 | 101 | 64 |
| Elongation | TD | | | 200 | 58 | 61 |
| Tear Strength | MD | g | 20°C 65% RH | 250 | 121 | 400 |
| Tear Strength | TD | | | 380 | 151 | – |
| Impact Strength | | kg·cm | 20°C 65% RH | 3.0 | 5.0 | 10.5 |
| | | | 20°C 80% RH | 6.0 | – | – |
| Bursting Strength | | kg/cm² | 20°C 65% RH | 1.0 | 6.0 | – |
| Young's Modulus | MD | kg/mm² | 20°C 65% RH | 200 | 220 | 164 |
| Young's Modulus | TD | | | 190 | 192 | 208 |
| Dimensional Stability when heated | MD | % | 140°C 1 hr | −2.0 | −0.9 | – |
| Dimensional Stability when heated | TD | | | −0.5 | 0.2 | – |
| Moisture Permeability | | g/m² · 24 hrs 30μ | 40°C 90% RH | 50 | 22.1 | 134 |
| Water Absorption | | % | 30°C 24 hrs | 6.5 | 0.2 | 8.9 |
| Moisture Absorption | | % | 20°C 65% RH | 3.8 | <0.1 | – |
| Oxygen Permeability Coefficient | | cc·cm/cm²·sec·cmHg×10¹² | 35°C Dry | 0.02 | 2.4 | 3.8 |
| Electrification | | V | 30°C 40–45% RH | 16 | 143 | – |
| Oil Resistance | | hr | JIS-Z1515 | ∞ | ∞ | – |
| Melting Point | | °C | | 180 | 260 | 223 |
| Haze | | % | | 1.8 | 2.5 | 2.0 |
| Slipping Property | | Static Friction Coefficient | 20°C 65% RH | 0.4 | 0.44 | – |
| Density | | g/cm³ | 25°C 65%RH | 1.19 | | |

Source: Publication 1980-6 and publication entitled "Duraray EVAL® Resin," Kuraray Co., Ltd., Osaka, Japan.

# VITA

James Clyde Weaver was born in Abingdon, Virginia, on June 21, 1944. He attended elementary school in Meadowview, Virginia, and graduated from Patrick Henry High School, Emory, Virginia, in May 1961. He entered Emory and Henry College, Emory, Virginia, in September 1961 and graduated with a Bachelor of Science degree with majors in Chemistry and Mathematics in May 1965. He was employed by Tennessee Eastman Company immediately following graduation as a laboratory technician, research, and has held the positions of chemist and research chemist in the Tennessee Eastman Research Laboratories. He has done graduate work in Chemistry at East Tennessee State University.

He entered the Graduate School at The University of Tennessee, Kingsport University Center, in September 1977 and received the Master of Science degree with a major in Polymer Engineering in December 1981.

He married the former Susan Benson of Marshalltown, Iowa, in August 1973, and they have two children, Christopher and Todd and reside in Kingsport, Tennessee.