

## Chapter 15

### Coextruded Multilayer Polymer Films and Sheets

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#### I. INTRODUCTION

Physical properties of polymers are modified and extended by several techniques, including copolymerization; formulation with plasticizers,

stabilizers, and fillers; rubber modification; and polymer blending. Sometimes all of these approaches are employed to tailor polymer properties to fit an end use application. These powerful tools for modifying polymers have broadened applications for plastics tremendously.

Frequently, however, no single polymer can satisfy all of the end use requirements economically, and the engineer then considers composites, such as laminations and coatings of different plastics to themselves or to other materials. The use of layered plastic composites for packaging and industrial uses developed rapidly in the 1950s. Each ply in the composite was chosen to provide a specific end-use characteristic to the product, for example, heat sealability, barrier, and chemical resistance.

In the early 1960s coextrusion emerged as a new fabrication method to make multilayer plastic film and sheet by direct simultaneous extrusion of two or more polymers through a single die. Coextrusion avoids many of the manufacturing steps required by conventional lamination and coating processes, such as making and handling of individual films, application of coatings and primers, and solvent drying. Because of these economic and technical advantages, the use of coextrusion is growing rapidly.

Both polymer blending and multilayer coextrusion are used to combine the properties of two or more polymers by melt fabrication to obtain desired end-use characteristics in a product. While polymer blending randomly mixes the components together, coextrusion has an advantage of yielding a layered morphology that can be an optimum "dispersion" geometry for many applications. Coextrusion shares many of the same technical considerations with polymer blending: adhesion (see Volume 1, Chapter 6), compatibility (see Volume 1, Chapters 1–5), mechanical interaction between phases (layers), (see Chapters 12–14), and rheology (see Volume 1, Chapter 7). Also, some early publications described extensive mixing of viscous fluids by deforming layers until they become "vanishingly thin" [1–4]. Coextruded films are being made that have individual layer thickness less than the wavelength of light and can approach molecular dimensions.

In this chapter we review coextrusion technology, some properties of multilayer films, and several applications that illustrate how coextrusion is being used to obtain composite properties economically.

## II. METHODS OF COEXTRUSION

Coextruded multilayer plastic films are being produced by two processes: (1) the tubular-blown film process, and (2) the flat-die chill-roll casting process. A variety of multilayer die designs can be used for both processes,

and we only review the more common methods, most of which are in commercial use.

#### A. Tubular Coextrusion Dies for Blown Film

The blown-film process is the most widely used method for manufacturing plastic film, and many of the early two- and three-layer coextrusions were produced by this process. A tubular die geometry is used, and the extrudate is inflated with air to stretch and cool the plastic bubble. Tubular die designs for coextrusion require the formation of uniform concentric layers in the die annulus.

Several dies for tubular coextrusion are illustrated in Figs. 1, 2, and 3. In Fig. 1 Polymers A and B are joined in an adaptor ahead of the single-manifold tubing die, and the concentric melt stream is pierced by the die mandrel to produce a two-layer annular extrudate [5]. The ratio of layer thickness is determined by the volumetric pumping rate of each extruder for each polymer.

A second tubular die design (Fig. 2) uses individual manifolds, which distribute the layers concentrically prior to final joining ahead of the die land [6]. The manifold for each layer must be designed carefully to obtain satisfactory layer uniformity.

A third design (Fig. 3) stacks toroidal distribution manifolds for the

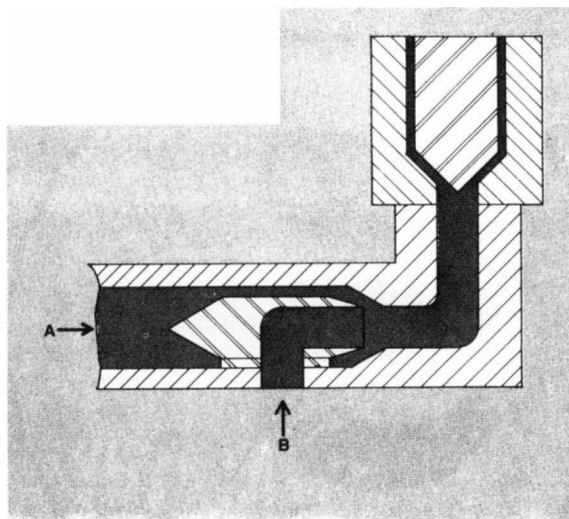


Fig. 1 Adaptor connected to single-manifold blown-film die that arranges Polymers A and B into a concentric melt stream. (Reprinted with permission from J. E. Johnson [6], *Plastics Technology* 22, 45, February 1976.)

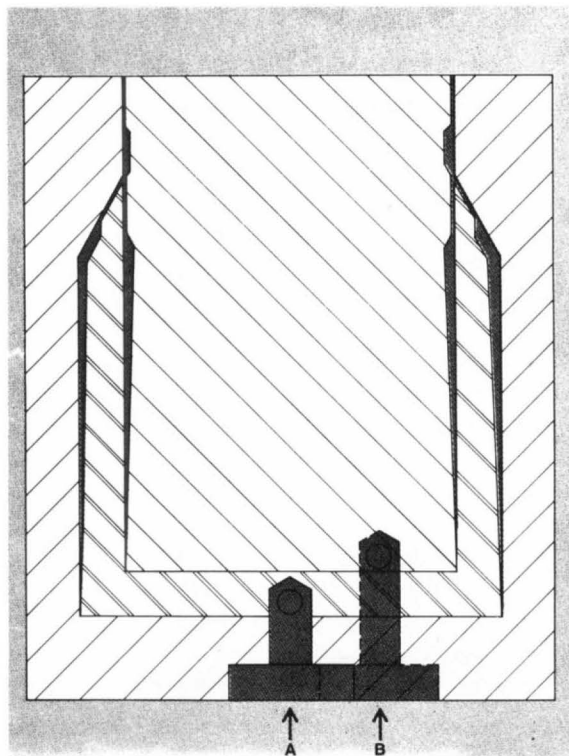


Fig. 2 Multimanifold blown-film die with individual annular channels for each layer that are joined before the final die land. (Reprinted with permission from J. E. Johnson [6], *Plastics Technology* 22, 45, February 1976.)

desired number of layers [7]. As the melt stream flows toward the die exit, layers are extruded on one another sequentially.

Such tubular die designs become quite complicated for coextrusions exceeding about three layers, but many two- and three-layer packaging films are produced by these blown-film dies.

A unique blown-film die has been developed that can generate a large number of layers of two or more polymers [8,9]. This tubular die system can make multilayer blown films having several hundred layers with individual layer thicknesses less than 1000 Å. A similar approach has been used to make multilayer bicomponent fibers [10]. The principle involves the generation of layers in an annular die having rotating elements. As shown in Fig. 4, the individual polymers are extruded through a feed port, which arranges them into alternating, radially extending layers in the die annulus. The layers then can be deformed into long, thin spirals by rotation of the annular die boundaries. Basically, four layer patterns, as shown in Fig. 5, can be generated, depending on the mode of die element rotation. Either the

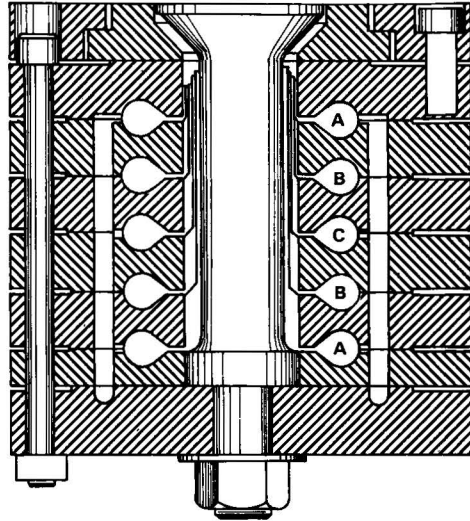


Fig. 3 Toroidal-distribution manifolds stacked to provide the desired number of layers by the sequential addition of polymers.

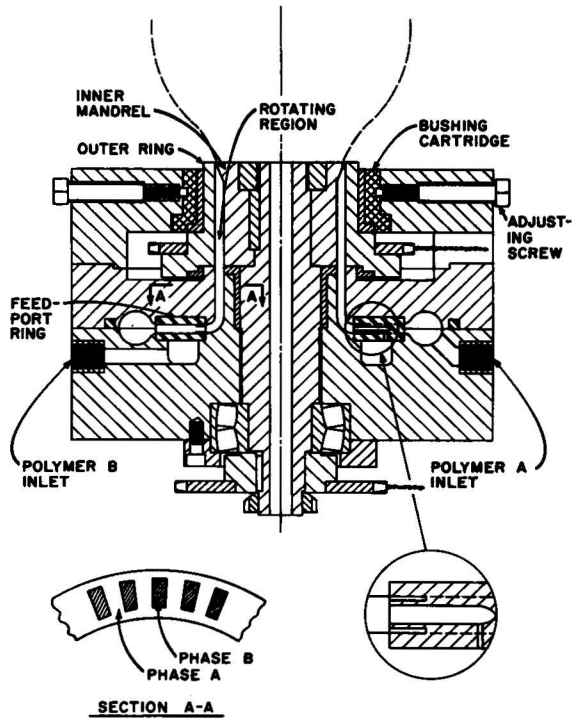


Fig. 4 Rotating annular die elements capable of generating large numbers of layers of Polymers A and B.

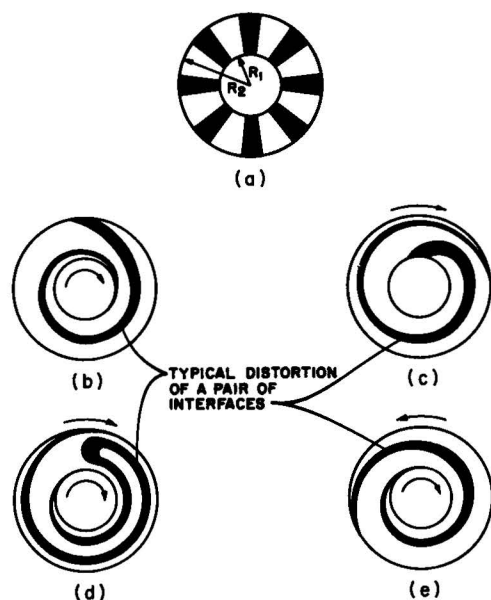


Fig. 5 Four modes of rotation of annular die boundaries can generate different layer patterns: (a) feed distribution entering annular die; (b) Case I; (c) Case II; (d) Case III; (e) Case IV. (From Schrenk and Alfrey [8].)

inner or outer annular die boundaries may be rotated individually, or simultaneously in the same direction or counterrotating. Each mode of die rotation will generate a different layer thickness distribution. The actual layer thickness will depend on the extrusion rate of each polymer, the rotational speed of the annular die elements relative to the feed ports, the length of the annular channel, and the radial location within the annulus.

The relationship between these operating parameters has been analyzed mathematically [3] and was found to be in excellent agreement with experimental observations. The experimentally measured layer distribution as a function of position within a 1-mil film to the calculated distribution for a Case 2 layer pattern are compared in Fig. 6 [9].

The agreement between experiment and theory is even more remarkable when one considers that a Newtonian-flow model was used and that the calculations involved determination of the displaced layer position in the final film after leaving the die annulus [8].

Microlayer coextruded films made by this die system can approach layer dimensions of a few hundred angstroms. The films are, in a sense, polymer blends having a layered morphology of molecular dimensions. The process can reduce the layer thickness to a point where the layers become discontinuous, as illustrated in the electron photomicrograph in Fig. 7. In this

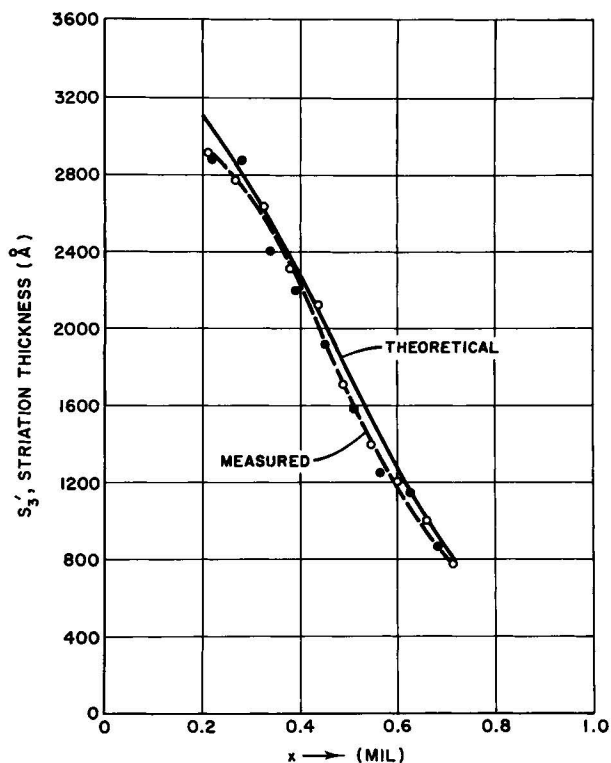


Fig. 6 Comparison of measured striation thickness with calculated values for a Case 2 layer pattern. Striation thickness is the thickness of a pair of adjacent A and B layers. (From Schrenk and Alfrey [9].)

coextruded film of polystyrene (PS) and polymethylmethacrylate (PMMA), the PMMA layers were thinned to where they break into spherical particles. Wherever "layer scission" has occurred, the ends are larger in diameter, presumably due to relaxation of the molecules. As these dumbbell-shaped layer segments are sheared further, ruptures continue until spherical particles are formed.

### B. Flat Die Coextrusion

Coextruded film and sheet is also being produced using flat die geometry, that is, where the multilayer melt is extruded through a wide narrow slit. The film can be drawn to varying thickness while still hot and then cooled below its solidification temperature on a large diameter chill roll.

The flat-die coextrusion geometry is used in:

1. chill-roll cast film process, which can run at high speeds since cooling is more rapid than air cooling by the blown film process;

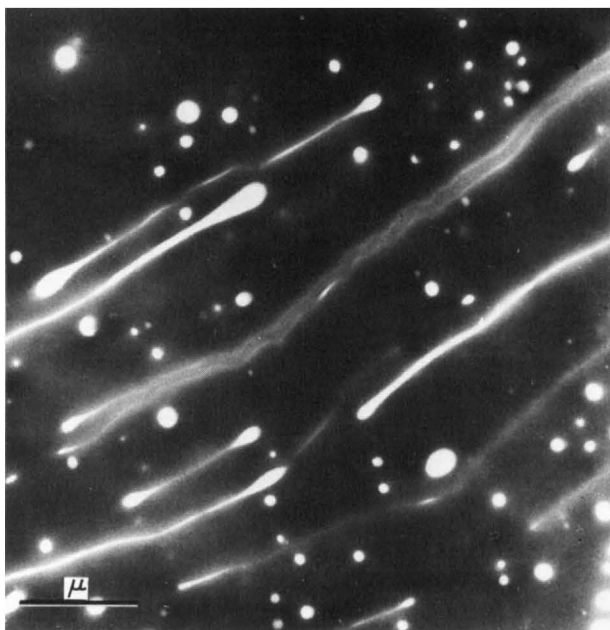


Fig. 7 Electron micrograph showing "layer scission" where PMMA layers become discontinuous. (From Schrenk and Alfrey [9].)

2. in-line coextrusion coating process in which a multilayer film is coextruded directly onto a nonextrudable substrate, such as paper or cellophane; and
3. coextrusion of thick film or sheet ( $>10$  mil) in which the tubular blown-film process is impractical.

Two flat-die coextrusion methods are used commercially. In early technology a multimanifold die is used, as illustrated in Fig. 8, with individual manifolds extending across the width of the die for each layer. The manifolds combine the melt streams just ahead of the die lips.

The newer and most widely used flat-die coextrusion method uses a conventional single-manifold die in conjunction with a feed block at the die inlet that introduces a prearranged multilayer melt stream into the die, as shown in Fig. 9. This coextrusion method involves deformation of the joined multilayer melt stream within the die by squeezing and spreading while maintaining layer integrity.

Each system has its advantages and disadvantages [11]. The major advantage of the multimanifold die is its ability to coextrude polymers of more widely different rheological properties. Each layer is independently extruded

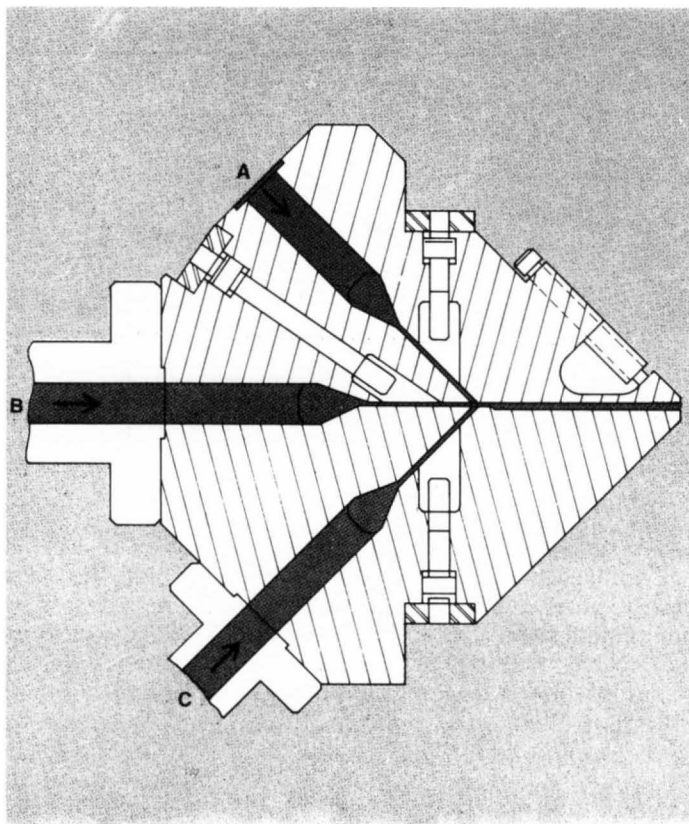


Fig. 8 Multimanifold flat die with individual manifolds for each layer that extend across the width of the die. The layers are joined ahead of the final die land. (Reprinted with permission from J. E. Johnson [6], *Plastics Technology* 22, 45, February 1976.)

to the width of the die prior to combining, in contrast to the feed-block method in which all layers must flow together, thus requiring more careful matching of viscosities. The major disadvantage of the multimanifold die system is its complexity, cost, and operating difficulties when used for more than three layers.

The feed-block method, while requiring a closer match of polymer viscosities to obtain uniform layers, has greater versatility since a single-manifold die can be used to make a wide variety of products having from two to as many as several hundred layers, including thermally degradable polymers.

Figure 10 is a schematic illustration of the feed-block method [12]. A feed port meters uniform layers of two or more polymers into a die channel. The feed port can subdivide and arrange the melt streams from each extruder

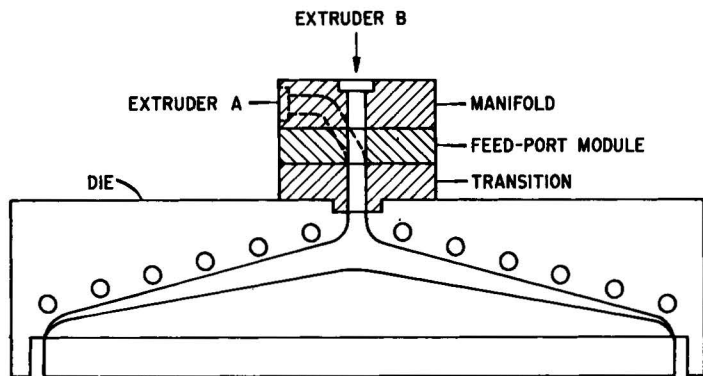


Fig. 9 Feed-block method of flat-die coextrusion using a conventional single-manifold die in conjunction with a feed block that arranges a multilayer melt stream ahead of the die inlet. (From Schrenk [13].)

into almost any layer distribution. It is frequently possible to change the layer arrangement by simply changing a feed-port module. Several layer arrangements are illustrated in Fig. 11. At the exit of the feedports the polymer streams combine into a multilayer melt stream, which flows through a die lamina-ly and decreases the layer thickness while spreading them to the width of the die.

Commercially, the feed-block method has been used to make five- and six-layer film and sheet from as many as five different polymers (using five

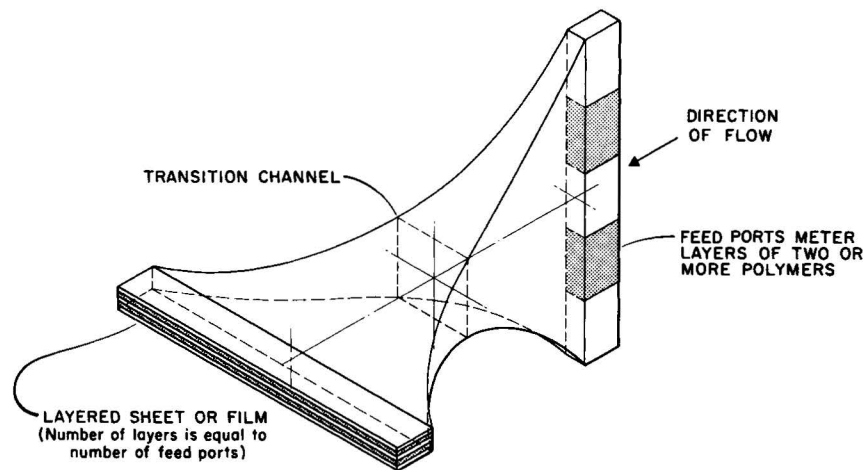


Fig. 10 Schematic illustration of the feed-block method. The feed ports arrange two or more polymers into the desired layer configuration, and the layers are subsequently thinned and spread during extrusion through a single-manifold die. (From Schrenk [13].)

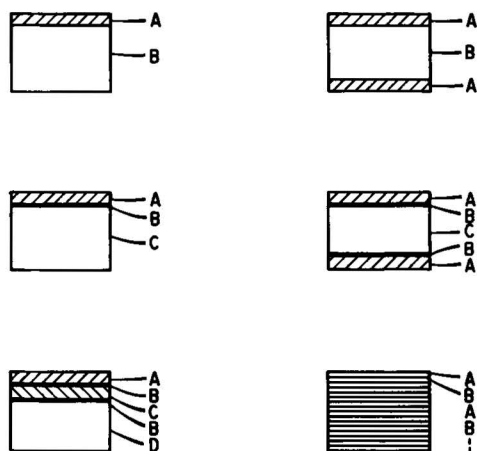


Fig. 11 Wide variety of layer arrangements obtainable by the feed-block method. Frequently the layer distribution can be changed quickly by inserting a different feed-port module, as shown in Fig. 9. (From Schrenk [13].)

extruders connected to the feed block) [13]. Also, unique films having over 100 layers of two polymers (using two extruders) are being made by this flat-die method. Figure 12 is a composite cross-sectional electron micrograph of a 249-layer film having alternating layers of PS and PMMA made by this method [14].

The feed block may be adapted to layer-multiplying devices to increase the number of layers further [15]. The principle of one such device, illustrated in Fig. 13, subdivides, stacks, and recombines the layered melt stream from the feed ports one or more times to increase the number of layers (and interfacial surface area) exponentially. Thus, it is possible to manufacture unique microlayer films containing many hundreds of layers by the flat-die coextrusion method. As in the case using the rotating, annular coextrusion die discussed previously, these microlayer films can approach a "layered polymer blend" of molecular dimensions.

### C. Polymer Selection for Coextrusion

Since coextrusion relies on laminar flow of a multilayer melt stream through a die, the proper selection of polymers is crucial. A variety of factors must be considered:

1. Obviously the polymers must be selected to provide the desired end-use properties for the intended application, for example, mechanical properties, permeability, heat sealability, and chemical or weathering

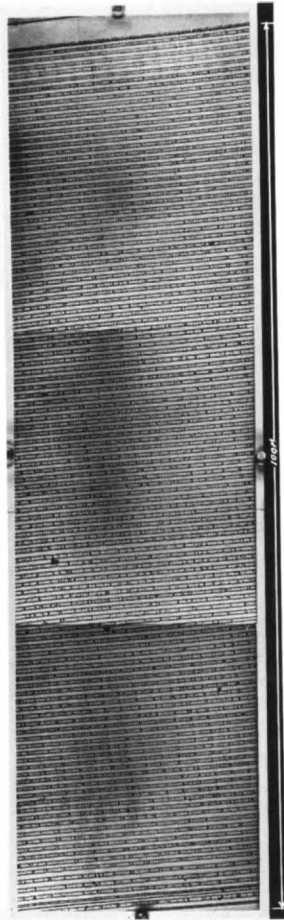


Fig. 12 Composite electron micrograph of 249-layer PS-PMMA film made by the feed-block method. Films with uniform layers as thin as  $300\text{\AA}$  have been made.

resistance. Also, postextrusion operations must be considered, for example, if the multilayer is to be thermoformed, it must have sufficient melt strength. Other properties, such as satisfactory surface characteristics, and coefficient of friction, must be specified for machinability on high-speed packaging machines.

2. Frequently, adequate adhesion must be obtained for the proposed end use. A "glue layer" polymer, which adheres to both of two other non-adhering polymers, may be coextruded as an intermediate layer. The degree of adhesion and the selection of glue layer polymers is discussed later.

3. Related to adhesion is the ability to recycle multilayer scrap, which is an important economic consideration. This also is discussed later.

4. A final important criterion for selection of polymers for coextrusion

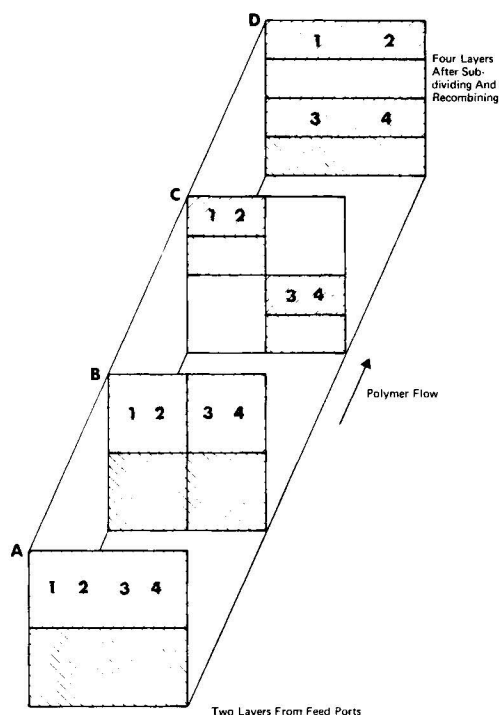


Fig. 13 Illustration of the principle of layer multiplication by using interfacial surface-generating devices.

is their rheological properties. It is particularly true when using the feed-block method of flat die coextrusion since the layers must spread uniformly in the die by laminar flow. This does not mean that all polymers must have identical viscosity; in fact, polymers with viscosity mismatches of three- or fourfold have been coextruded successfully [13]. Frequently, the melt temperature of the polymers entering the feed block may be adjusted to compensate partially for viscosity mismatch; however, this approach is limited since heat transfer takes place between layers. Also, the extrusion temperature of one polymer cannot exceed the short-term thermal degradation temperature of an adjacent layer.

Further, certain coextrusions can exhibit interfacial flow instability, which can cause layer nonuniformity, such as ripples and intermixing of layers. This type of flow instability is not unique to feed-block coextrusion; it can be observed in tubular die coextrusion and multimanifold, flat-die coextrusion as well.

The flow of non-Newtonian multilayer melts through a die is a complex

problem. The shear rate (and apparent viscosity) is a function of layer position within the die channel. Therefore, a mathematical model is desirable to assist in selecting the correct polymers for coextrusion.

### III. FLOW ANALYSIS OF NON-NEWTONIAN MULTILAYER COEXTRUSION

A mathematical analysis of multilayer flow has been done for simple geometric channels, such as concentric flow in pipes and annuli and parallel flow in wide rectangular slits. In these simple channels the analysis involves a one-dimensional flow problem. The analysis is useful in predicting pressure drop and shearing stresses for die design, and also for correlation of laboratory data in selecting polymers for large-scale production lines.

Figure 14 is an illustration of the velocity distribution in a multilayer fluid flowing through a slit die of gap  $x = h$ , which consists of roughly parabolic segments joined at interfaces  $a_{12}$ ,  $a_{23}$ , etc. (This is also a good approximation for narrow annular channels, such as tubular dies for blown film.) The boundary conditions are that the velocity is zero at the die walls, and adjacent fluid layers have equal velocity at their interface (no slippage). The shear stress is continuous across the interfaces.

The shearing stress  $\tau_{xz}$  (for brevity subscripts will be omitted hereafter) and the pressure gradient are related by Eq. (1):

$$-\partial p / \partial z + \partial \tau / \partial x = 0 \quad (1)$$

$$\tau = p'(x - c) \quad (2)$$

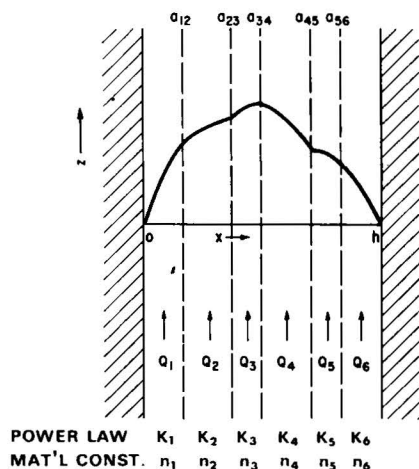


Fig. 14 Schematic velocity profile of a non-Newtonian multilayer flow through a wide, narrow slit, where  $dv/dx = K\tau^n$ .

where  $p'$  is the pressure gradient  $\partial p/\partial z$ , and  $c$  denotes the location where  $\tau = 0$ . (In the case of symmetrical multilayer flow,  $c = h/2$ .) If each fluid can be approximated by the power law model, then

$$\dot{\gamma}_i = K_i \tau^{n_i} \quad (3)$$

When negative shearing stresses are encountered, Eq. (3) should be written

$$|\dot{\gamma}_i| = K_i |\tau|^{n_i} \quad (4)$$

or more specifically

$$\dot{\gamma}_i = \text{sign}(\tau) K_i |\tau|^{n_i}, \quad \text{where} \quad \begin{aligned} \text{sign}(\tau) &= +1 & \text{for } \tau > 0, \\ \text{sign}(\tau) &= -1 & \text{for } \tau < 0 \end{aligned} \quad (5)$$

If  $v_i(x)$  is the velocity profile in the  $i$ th layer,

$$dv_i/dx = \dot{\gamma}_i = \text{sign}(p') \text{sign}(x - c) K_i |p'|^{n_i} |x - c|^{n_i} \quad (6)$$

Equation (6) can be integrated to yield  $v_M(x)$ , the velocity profile in the  $M$ th layer. (Total number of layers =  $N$ .)

$$\begin{aligned} v_M(x) = -\text{sign}(p') \left\{ \sum_{j=1}^{M-1} \frac{K_j |p'|^{n_j}}{n_j + 1} [a_{j-1,j} - c|^{n_j+1} - |a_{j,j+1} - c|^{n_j+1}] \right. \\ \left. + \frac{K_M |p'|^{n_M}}{n_M + 1} [a_{M-1,M} - c|^{n_M+1} - |x - c|^{n_M+1}] \right\} \quad (7) \end{aligned}$$

The total volumetric flow rate of the  $M$ th layer can be obtained by integrating Eq. (7) between the two interfaces bounding that layer:

$$\begin{aligned} |Q_M| = \sum_{j=1}^{M-1} \frac{K_j |p'|^{n_j}}{n_j + 1} \{ |c - a_{j-1,j}|^{n_j+1} - |c - a_{j,j+1}|^{n_j+1} \} (a_{M,M+1} - a_{M-1,M}) \\ + K_M \frac{|p'|^{n_M}}{n_M + 1} \{ |c - a_{M-1,M}|^{n_M+1} \} (a_{M,M+1} - a_{M-1,M}) \\ + \frac{K_M |p'|^{n_M}}{(n_M + 1)(n_M + 2)} \{ \text{sign}(c - a_{M,M+1}) |c - a_{M,M+1}|^{n_M+2} \\ - \text{sign}(c - a_{M-1,M}) |c - a_{M-1,M}|^{n_M+2} \} \quad (8) \end{aligned}$$

If  $p'$ ,  $c$ ,  $a_{12}$ ,  $a_{23}$ , ...,  $a_{N-1,N}$  are known, these equations can be directly applied to yield the velocity profile and the volumetric rates of each layer. However, normally the problem is encountered in inverse form; the

volumetric rates  $Q_M$  are known (controlled), and we wish to calculate the pressure gradient  $p'$ , the location of the zero shear plane  $c$ , and the locations of the fluid interfaces ( $a_{12}$ , etc.). If a trial value is selected for  $p'$  and for  $c$ , Eq. (8) can be solved sequentially for  $a_{12}$ ,  $a_{23}$ , ...,  $a_{N,N+1}$ , and a velocity profile is obtained. The calculated value of  $a_{N,N+1}$  does not match the true location  $h$ , and the calculated velocity at this interface does not match the true value (zero). Iteration, with new trial values for  $p'$  and  $c$ , can remove these mismatches, and converge on the correct solution.

The problem is somewhat simpler with symmetrical multilayer systems, since the location of the zero-shear plane is known at the outset to be at the center of the channel ( $c = h/2$ ). A trial value of  $p'$  is selected, Eq. (8) is solved, and the correct value of  $p'$  determined by an iteration procedure that removes any mismatch with the boundary at  $x = h$ . The solution provides the complete velocity profile, locations of the fluid interfaces, and the shear stress at each interface.

#### IV. FLOW INSTABILITIES IN MULTILAYER COEXTRUSION

Several types of flow instabilities can occur in a multilayer melt stream while coextruding a plastic film or sheet. Nonuniform layer thickness may be caused by surging in the extruder output rates or by poor melt temperature uniformity within individual resin streams. Southern and Ballman [16] and others [17–19] have reported on another type of instability that occurs in layered melts of substantially different viscosities. The lower-viscosity resin migrates to the region of highest shear stress and will tend to encapsulate the higher-viscosity polymer if the viscosity difference and residence time are sufficient. This effect, which has been observed in capillaries and rectangular orifices, can lead to layer thickness variation and is discussed in greater detail by D. R. Paul in Chapter 16.

##### A. Interfacial Flow Instability in Multilayer Coextrusion

Another type of flow instability can occur at the interfaces of a multilayer stream, which in the extreme case can cause intermixing of the layers. Under stable flow conditions, the fluid interfaces within the die and the solid interfaces in the final multilayer film are smooth, flat, and parallel. As output rate is increased, a point is reached at which the outermost interface in the solid multilayer film exhibits a wavelike form. Beyond this point we do not have a quantitative understanding of the fluid velocity pattern within the die.

A low-amplitude waviness of the interface may not be noticeable to the eye, and may not interfere with the functionality of the multilayer film. At still higher output rates, the layer distortion becomes more severe. If a large-amplitude, transverse waveform develops in the flowing multilayer stream within the die, the velocity gradient can carry the crest forward and convert it into a fold. Multiple folding can result in an extremely jumbled interface, and a film with marbled appearance (which may be desirable for decorative applications). Figure 15 is a schematic illustration of a two-layer film with varying degrees of interfacial flow instability. In Fig. 16 two photomicrographs through the cross section of a three-layer coextruded sheet of acrylonitrile-butadiene-styrene copolymer (ABS) 213-Styron<sup>†</sup> 470-ABS 213 produced under conditions of stable coextrusion and severe instability are shown. The change from stable to unstable multilayer flow was obtained by changing melt and die temperatures. Higher temperatures (lower viscosities) were required to obtain the stable flow pattern.

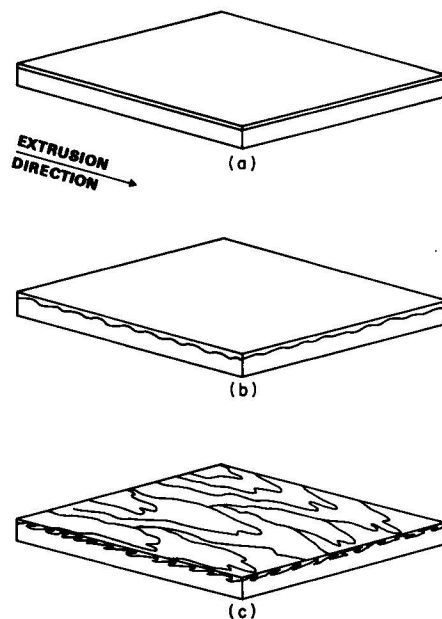


Fig. 15 Illustration of film or sheet appearance under (a) stable flow conditions, (b) incipient interfacial flow instability, and (c) severe instability.

<sup>†</sup> Trademark of The Dow Chemical Company.

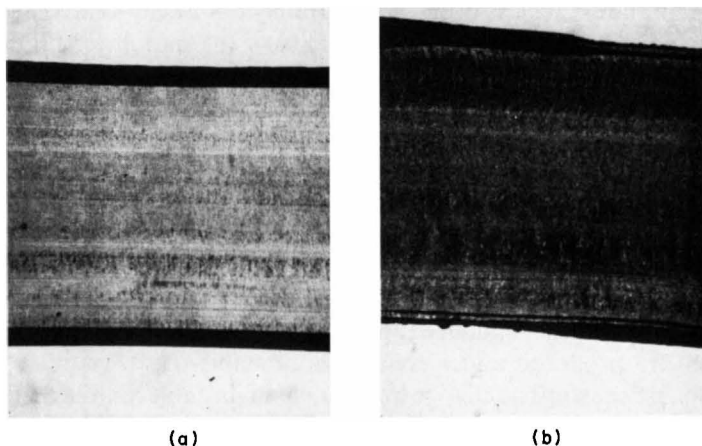


Fig. 16 Cross-sectional photomicrographs through a three-layer ABS-HIPS-ABS sheet made under (a) stable and (b) unstable coextrusion conditions. Thicknesses were 0.0013-in. ABS-0.0165-in. HIPS-0.0013-in. ABS.

### B. Location of Interfacial Flow Instability

To determine the source of instability, a small, single-manifold, flat-film die with a three-layer feed block was used to coextrude an ABS 213-Styron 470-ABS 213 sheet. Extruders deliver individual melts into the feed block, where they can be subdivided and combined into the desired layered structure. The combined melt stream then flows to the die, where the layers are spread and thinned to the final die land dimensions.

A set of coextrusion conditions were chosen in which incipient inter-layer instability was observed in the three layer sheet. At this point the extruders were stopped and the die orifice blocked to prevent drool. The die was allowed to cool, and was then disassembled. The solidified plastic was sectioned to study the interfaces throughout their flow path. It was found that the layer interfaces remained uniform and clearly defined at the exit of the feed block and up to the die land. Within the die land a wavelike distortion of the interfaces started to develop.

These findings, plus other observations, lead us to the hypothesis that there is a "critical interfacial shear stress" at which interfacial flow instability may occur in a given pair of polymers.

It is well known that melt fracture in a single polymer is related to a "critical" shear stress at the wall of a die. In polyethylene, melt fracture can occur at about  $10^6$  dyn/cm<sup>2</sup>. While many factors can affect melt fracture, the roughness of the extrudate is associated with a "stick-slip" instability

of the polymer velocity near the rigid die wall. In multilayer coextrusion, it appears that an interfacial flow instability can occur at an even lower “critical shear stress” than that required for melt fracture at the wall.

### C. Experiment

A fractional factorial experiment was designed to test the validity of our hypothesis that interfacial flow instability develops at a certain critical interfacial shear stress for a given pair of polymers. Again, we chose the three-layer coextrusion of ABS–HIPS–ABS. The first experiments were designed to ascertain which variables were most important. The independent variables considered were: (1) skin-layer temperature; (2) core-layer temperature; (3) die temperature; (4) ratio of skin-layer to core-layer thickness; (5) total extrusion rate; and (6) die gap. It was found that the most important variables were the skin-layer temperature and viscosity, the ratio of skin-to-core layer thickness, total extrusion rate, and die gap. The die temperature and core-layer temperature were only significant as they affected the skin-layer temperature (viscosity) through heat transfer.

### D. Determination of “Critical Interfacial Shear Stress”

The four most important variables (skin-layer viscosity, layer thickness ratio, total rate, and die gap) were varied independently over a range of shear stress that gave stable to unstable flow in the three-layer ABS 213–Styron 470–ABS 213 structure.

It was necessary that the point of incipient instability be determined by a rather arbitrary visual judgment. Six persons evaluated all the samples, where each variable spanned the range from stable to unstable flow while maintaining other conditions constant. The consensus of the judges on the occurrence of incipient instability was good.

The interfacial shear stress was calculated from the known coextrusion conditions at incipient instability for each variable and the two material constants,  $K$  and  $n$ , for each polymer as determined by Instron rheometer data. It was determined that interlayer melt fracture developed at an interfacial shear stress of approximately 500,000 dyn/cm<sup>2</sup>, regardless of which independent variable was varied.

These results support our hypothesis that interfacial flow instability is related to a “critical interfacial shear stress.”

The value of 500,000 dyn/cm<sup>2</sup> for the “critical interfacial shear stress” refers to the specific system studied (ABS 213–Styron 470–ABS 213). The transition to unstable flow may occur at a different stress level in other systems.

A sheet produced at the point of incipient instability would probably still be commercially acceptable, since very critical visual judgment was employed. Severe instability occurred at higher shear stresses. (The steady-state analysis used in this work of course cannot provide a meaningful value for shearing stress in the regime of severe instability.)

Interfacial flow instability can be reduced or eliminated by increasing the skin-layer thickness, increasing the die gap, reducing the total extrusion rate, or decreasing the viscosity of the skin-layer polymer. (The last remedy for the interfacial instability problem, in some cases, may introduce a systematic nonuniform layer distribution because of viscosity mismatch, as described earlier.)

## V. ADHESION IN COEXTRUSION

### A. Interfacial Adhesion

When a coextruded sheet or film is cooled, and the fluid layers solidify (by crystallization or by vitrification), the solidified layers may hold together tenaciously, or they may peel apart easily. Some pairs of polymers exhibit strong interfacial adhesion; other pairs exhibit weak interfacial adhesion. Accumulated experience provides a reservoir of knowledge regarding the degree of adhesion between various thermoplastic materials, but the reasons behind these facts are only partially understood, and predictability of new systems is low (see Volume 1, Chapter 6).

When two molten polymer streams join, a fluid interface is created and is transported for some distance under pressure before leaving the die. These conditions favor the establishment of complete and intimate interfacial contact of the two fluids. This is accompanied by some molecular interpenetration, as polymer segments of one phase diffuse across the interface into the other phase. However, since dissimilar polymers are usually thermodynamically immiscible, this interpenetration is limited in extent. The localized variation in composition in the vicinity of the interface is indicated in Fig. 17. The thickness of the "interphase" increases with time of contact, approaching a limiting equilibrium thickness. The limiting thickness is presumably greater with polymers that are nearly compatible, and smaller with highly incompatible polymers.

The extent of molecular interpenetration of the molten polymer streams must be one of the factors that determine the interlayer adhesion of the final product, but the solidification processes are probably also involved. Two adjacent layers may solidify at different temperatures, at different times,

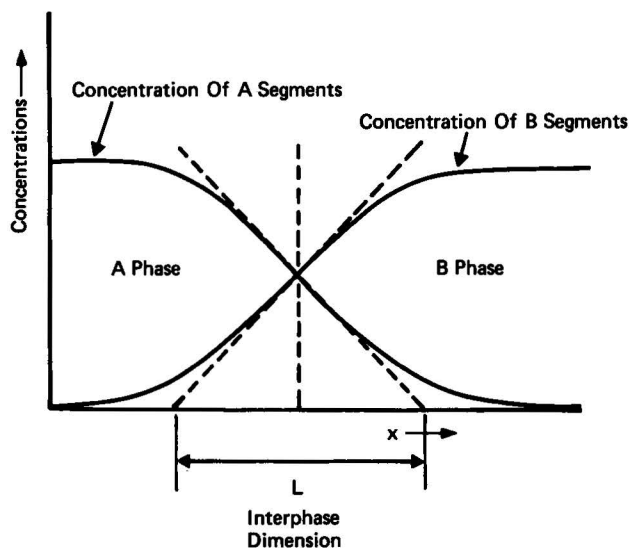


Fig. 17 Concentration of Polymer Segments A and B in the "interphase" region at the interface of A and B.

and by different mechanisms, thereby affecting the structure and properties of the interface. For example, if layer *A* crystallizes while layer *B* is still a viscoelastic fluid, penetrating segments of *A* chains might be drawn back from the "interphase" in the *A* layer.

Yamakawa [20] has studied the closely related problem of hot-melt adhesive bonding of polyethylene with ethylene copolymers. The observation of cross sections of bonded joints with an interference microscope showed the presence of an interfacial boundary layer and a mixed layer of polyethylene and the copolymer. The relation between peel strength and the character of the two layers was discussed.

Another closely related problem is the interpenetration of polymer chains across a weld line, to develop a bond between two converging streams of the same molten polymer [21]. If adjacent layers of general-purpose polystyrene and rubber-reinforced polystyrene are coextruded, the interfacial bonding is similar to that of a polystyrene weld line. The continuous phase in the HIPS layer is polystyrene. Molecular interpenetration across the fluid interface is thermodynamically allowed. The two layers solidify together, by vitrification, at nearly the same temperature, so that the solidification process should not destroy the bond. In practice, this simple system behaves as expected. In the general case of the coextrusion interface between two arbitrarily chosen polymers, however, we do not know of any

quantitative theory that can predict the degree of interfacial adhesion in the final solidified film.

### B. Use of "Glue Layer" Polymers in Coextrusion

It sometimes develops that a desired multilayer arrangement in sheet or film exhibits poor adhesion between a pair of adjacent layers, with consequent delamination. This weakness can be remedied by introducing a thin layer of a third polymer that shows good adhesion to both of the materials in question ("glue layer").

An obvious candidate for a glue layer between nonadhering Polymer A and Polymer B would be an AB block copolymer, which could penetrate strongly into both phases (see Chapter 12). However, in most cases this is only a hypothetical solution, since the indicated block copolymers are not available. In practice, the choice of a glue layer polymer depends upon the accumulated experience regarding the interlayer adhesion referred to above. Table I is a qualitative guide to the degree of adhesion that can be obtained in coextrusion of several different polymers [6].

### C. Polymer Blends for Adhesion

Occasionally polymer blends are used as coextruded glue layers between dissimilar, nonadhering layers. Blends are used for:

1. optimizing adhesion by combining the molecular functionality of two polymers,
2. improving coextrudability of some glue-layer polymers by incorporating a polymeric "extrusion aid" to adjust viscosity, and
3. obtaining "mechanical" adhesion by a glue-layer blend of incompatible polymers.

Frequently adhesion between two layers can be optimized by a glue-layer blend of two generally compatible polymers. For example, styrene-butadiene block copolymer adheres well to polystyrene and its copolymers, but its adhesion is borderline with polyethylene. A blend of styrene-butadiene with ethylene-vinyl acetate can be an effective glue layer to adhere a polystyrene layer to a polyethylene layer [22]. Also, a blend of ethylene-acrylic acid copolymer with ethylene-vinyl acetate copolymer can adhere nylon to poly(vinyl chloride) and vinylidene chloride-vinyl chloride copolymers [23].

Similar blends are used to improve coextrudability, especially where viscosity must be adjusted to obtain satisfactory layer uniformity. Some glue-layer polymers are thermally degradable, and blends are used as polymeric lubricants or "extrusion aids" to improve extrudability.

Table I  
Qualitative Degree of Adhesion between Resins<sup>a</sup>

|           |                                              | Olefins | Styrenes |    |               |                  |                | Vinyl      | Misc.            |     |           |              | Adhesives                                    |               |              |         |          |         |     |     |          |                  |     |   |
|-----------|----------------------------------------------|---------|----------|----|---------------|------------------|----------------|------------|------------------|-----|-----------|--------------|----------------------------------------------|---------------|--------------|---------|----------|---------|-----|-----|----------|------------------|-----|---|
| Material: |                                              | LDPE    | HDPE     | PP | Low-impact PS | Medium-impact PS | High-impact PS | Crystal PS | ABS <sup>b</sup> | ABS | Rigid PVC | Flexible PVC | Vinylidene chloride-vinyl chloride copolymer | Polycarbonate | Polyurethane | Acrylic | Nitriles | Nylon 6 | EAA | EVA | Ionomers | SBS <sup>c</sup> | CPE |   |
| Olefins   | LDPE                                         | G       | G        | P  | P             | P                | P              | P          | P                | P   | P         | P            | P                                            | P             | F            | P       | P        | P       | P   | G   | G        | G                | F   | G |
|           | HDPE                                         | G       | G        | P  | P             | P                | P              | P          | P                | P   | P         | P            | P                                            | P             | F            | P       | P        | P       | P   | G   | G        | G                | F   | G |
|           | PP                                           | P       | P        | G  | P             | P                | P              | P          | P                | P   | P         | P            | P                                            | P             | P            | F       | P        | P       | P   | F   | G        | P                | G   | G |
| Styrenes  | Low-impact PS                                | P       | P        | P  | G             | G                | G              | G          | P                | P   | P         | P            | P                                            | P             | F            | P       | P        | P       | P   | P   | G        | P                | G   | F |
|           | Medium-impact PS                             | P       | P        | P  | G             | G                | G              | G          | P                | P   | P         | P            | P                                            | P             | ?            | F       | P        | P       | P   | P   | G        | P                | G   | F |
|           | High-impact PS                               | P       | P        | P  | G             | G                | G              | G          | P                | P   | P         | P            | P                                            | P             | ?            | F       | P        | P       | P   | P   | G        | P                | G   | F |
|           | Crystal PS                                   | P       | P        | P  | G             | G                | G              | G          | P                | P   | P         | P            | P                                            | P             | ?            | F       | P        | P       | P   | P   | G        | P                | G   | F |
|           | ABS <sup>b</sup>                             | P       | P        | P  | G             | G                | G              | G          | G                | G   | G         | G            | G                                            | G             | ?            | F       | G        | P       | P   | P   | G        | P                | G   | G |
|           | ABS                                          | P       | P        | P  | P             | P                | P              | P          | G                | G   | G         | G            | G                                            | G             | ?            | F       | G        | P       | P   | P   | G        | P                | G   | G |
| Vinyl     | Rigid PVC                                    | P       | P        | P  | P             | P                | P              | P          | G                | G   | G         | G            | F                                            | U             | G            | G       | P        | U       | P   | G   | P        | G                | G   |   |
|           | Flexible PVC                                 | P       | P        | P  | P             | P                | P              | P          | G                | G   | G         | G            | F                                            | U             | G            | G       | P        | U       | P   | G   | P        | G                | G   |   |
|           | Vinylidene Chloride-Vinyl Chloride copolymer | P       | P        | P  | P             | P                | P              | P          | G                | G   | F         | F            | G                                            | U             | G            | G       | ?        | P       | P   | G   | P        | G                | G   |   |
| Misc.     | Polycarbonate                                | P       | P        | P  | P             | ?                | ?              | ?          | ?                | ?   | U         | U            | U                                            | G             | ?            | G       | P        | ?       | ?   | ?   | ?        | ?                | ?   |   |
|           | Polyurethane                                 | F       | F        | F  | F             | F                | F              | F          | F                | F   | G         | G            | G                                            | ?             | G            | ?       | P        | ?       | F   | G   | ?        | F                | G   |   |
|           | Acrylic                                      | P       | P        | P  | P             | P                | P              | P          | G                | G   | G         | G            | G                                            | G             | ?            | G       | P        | ?       | ?   | ?   | ?        | ?                | F   |   |
|           | Nitriles                                     | P       | P        | P  | P             | P                | P              | P          | P                | P   | P         | P            | ?                                            | P             | P            | P       | G        | P       | P   | F   | ?        | F                | ?   |   |
|           | Nylon 6                                      | P       | P        | P  | P             | P                | P              | P          | P                | P   | U         | U            | P                                            | ?             | ?            | ?       | P        | G       | G   | P   | G        | P                | ?   |   |
| Adhesives | EAA                                          | G       | G        | F  | P             | P                | P              | P          | P                | P   | P         | P            | P                                            | ?             | F            | ?       | P        | G       | G   | G   | G        | F                | G   |   |
|           | EVA (ethylene-vinyl acetate)                 | G       | G        | G  | G             | G                | G              | G          | G                | G   | G         | G            | G                                            | ?             | G            | ?       | F        | P       | G   | G   | ?        | G                | G   |   |
|           | Ionomers                                     | G       | G        | P  | P             | P                | P              | P          | P                | P   | P         | P            | P                                            | ?             | ?            | ?       | ?        | G       | G   | ?   | G        | ?                | G   |   |
|           | SBS <sup>c</sup>                             | F       | F        | G  | G             | G                | G              | G          | G                | G   | G         | G            | G                                            | ?             | F            | ?       | F        | P       | F   | G   | ?        | G                | G   |   |
|           | CPE (chlorinated polyethylene)               | G       | G        | G  | F             | F                | F              | F          | G                | G   | G         | G            | G                                            | ?             | G            | F       | ?        | ?       | G   | G   | G        | G                | G   |   |

<sup>a</sup> G = good, F = fair, P = poor, ? = unknown, U = undesirable for coextrusion. (Reprinted with permission from J. E. Johnson [6], *Plastics Technology* 22, 45, February 1976.)

<sup>b</sup> Less than 20% acrylonitrile content.

<sup>c</sup> Styrene-butadiene-styrene.

Finally, blends of two incompatible polymers have been used as an intermediate glue layer between layers of the same incompatible polymers [24]. While this approach provides a convenient place for recycle of scrap, the adhesion is usually poorer than that possible with other glue-layer polymers. Delamination at the interface usually exhibits a fibrillar appearance where portions of the mechanically interlocked blended phases adhere to their homogeneous-layered counterparts and are elongated during delamination. In some cases this degree of "mechanical" adhesion is satisfactory.

It is certain that the use of polymer blends will play an increasing role in obtaining adhesion in coextruded products.

## VI. PROPERTIES OF MULTILAYER FILMS

### A. Permeability of Multilayer Films

The permeation of gases and water vapor through a homogeneous polymer film depends upon the permeability of the polymer and the thickness of the film (see Volume 1, Chapter 10):

$$\text{Flux (steady state)} = P(p_1 - p_2)/l \quad (9)$$

or

$$\text{film permeance} = P/l \quad (10)$$

where  $P$  is permeability,  $l$  thickness, and  $p_1$  and  $p_2$  the partial pressures of the diffusing gas on the two sides of the film. The permeability, in turn, is the product of a solubility coefficient  $S$  and a diffusion coefficient  $D$ :

$$P = DS \quad (11)$$

In a multilayer film, each polymer exhibits its own values of  $S$ ,  $D$ , and  $P$ . The permeance of the composite film is calculated by treating it as a series of resistances, with each ply contributing to the barrier:

$$1/\text{Permeance} = l_1/P_1 + l_2/P_2 + l_3/P_3 + \cdots + l_N/P_N \quad (12)$$

In the steady state, the diffusion flux is uniform through the film, but the concentration of diffusing gas exhibits a discontinuity at each interface.

Actually, the permeability of a given polymer can depend upon the degree of crystallization, and the crystalline morphology. Very thin layers, unable to accommodate the normal morphology, might be expected to exhibit different values of permeability from thick specimens of the same polymer. However, multilayer films and polystyrene-polyethylene and

polystyrene–polypropylene containing layers a few hundred angstroms thick have been reported to follow Eq. (12) [25].

Films containing multiple-barrier layers can retain their barrier properties after severe crumpling. Randomizing of flaws in multiple, sandwiched, barrier layers forces the permeating gas through a tortuous path. For example, a film containing multiple layers of Saran<sup>†</sup> can retain barrier properties after severe crumpling at low temperature [26a]. Because of low-temperature brittleness, a single Saran layer of equivalent thickness may show a catastrophic loss of barrier properties.

Also, the water vapor transmission rates through 125-layer PE–PS and PP–PS films were measured before and after crumpling. It was found that crumpling did not appreciably change the water vapor permeation rate [25].

Many applications for coextruded plastic film and sheet are designed to give gas- and moisture-barrier properties to the layered product. The permeability coefficients for oxygen transmission through several different polymers is given in Table II.

High-barrier Saran, hydrolyzed ethylene–vinyl acetate copolymers, high nitrile copolymers, rigid PVC, nylon, and polyesters all have relatively good oxygen barrier properties compared to polyethylene (PE), polypropylene (PP), polystyrene (PS), etc. One mil of Saran provides a barrier equivalent to about 4–5 mils of nitrile barrier resins, 10 mils of nylon, 40 mils of rigid PVC, and over 1000 mils (1 in.) of PS, PE, or PP. Thin layers of the high-barrier

Table II  
Approximate Oxygen Transmission Rates  
through Several Plastics

| Resin                             | Permeability<br>(cm <sup>3</sup> -mil/100 in. <sup>2</sup> -day-atm)<br>(at 23°C) |
|-----------------------------------|-----------------------------------------------------------------------------------|
| Hydrolyzed ethylene–vinyl acetate | <0.02 dry gas<br>0.08 moist gas                                                   |
| High-barrier Saran                | <0.2                                                                              |
| Nitrile-barrier resin             | 0.6                                                                               |
| Nylon                             | 2.6                                                                               |
| Polyester                         | 7                                                                                 |
| Rigid PVC                         | 14                                                                                |
| Polypropylene                     | 150                                                                               |
| HDPE                              | 150                                                                               |
| PS                                | 260                                                                               |
| LDPE                              | 420                                                                               |

<sup>†</sup> Trademark of The Dow Chemical Company.

resins are frequently coextruded with thick layers of PE or PS to provide gas barrier properties in films or sheets of these polymers.

The water vapor transmission rate through a 1-mil ply of the same polymers is shown in Table III. With the exception of Saran, the ranking for water vapor barrier properties changes significantly. Hydroscopic materials, such as nitriles, hydrolyzed ethylene vinyl acetate, and nylon, are poor barriers to water vapor. Polyethylene and PP are good barriers to water vapor. Saran is the only commercially available extrusion resin that has excellent barrier properties to both gases and water vapor.

### B. Mechanical Properties of Multilayer Films

A polymer layer in a multilayer sheet or film can exhibit different mechanical behavior from a free film of the same material. Particularly striking effects can be observed in laminar composites containing a "hard" component and a "soft" component, or a "brittle" component and a "tough" component. Sword makers of early times hammered down alternate layers of hard and soft steel, obtaining blades that would take a fine cutting edge and yet were strong and tough. Similar effects can be observed with coextruded multilayer polymer systems.

Consider a laminar composite containing a layer of high-modulus, low-elongation polymer sandwiched (with good adhesion) between layers of a high-elongation material. When the composite is tested to failure in tension, the adhering high-elongation layers may act to prevent transverse crack

Table III  
Approximate Water Vapor Transmission Rates  
through Several Plastics

| Resin                             | Water vapor transmission rate<br>(gm-mil/100 in. <sup>2</sup> /24 hr)<br>(100°F, 90%RH) |
|-----------------------------------|-----------------------------------------------------------------------------------------|
| High-barrier Saran                | 0.05                                                                                    |
| Nylon                             | 0.6                                                                                     |
| PP                                | 0.7                                                                                     |
| HDPE                              | 0.7                                                                                     |
| LDPE                              | 1.2                                                                                     |
| Polyester                         | 1.8                                                                                     |
| Rigid PVC                         | 3                                                                                       |
| Nitrile                           | 5                                                                                       |
| PS                                | 7                                                                                       |
| Hydrolyzed ethylene-vinyl acetate | 45                                                                                      |

propagation in the hard layer. With crack propagation so blocked, the hard layer may reach its ductile yield stress, and the entire composite stretch in a ductile manner to high elongation. This toughening effect may be termed “mutual interlayer reinforcement” and is indicated schematically in Fig. 18.

Interlayer interaction can sometimes result in the opposite result; a normally tough polymer may act in a brittle manner in a laminar composite.<sup>†</sup> In this case the high-elongation material is not able to block crack propagation in the brittle layer; a crack forms in the brittle layer, and continues into and through the tough layer, causing a localized failure at low overall elongation. For example, a skin of general-purpose polystyrene on a core of high-impact polystyrene can force the entire composite to undergo brittle failure on bending. This behavior has been called “mutual interlayer destruction” [25].

Such interlayer interactions, whether of a beneficial or a deleterious nature, require some degree of adhesion at the interfaces. However, the thinner the layers, the lower will be the degree of adhesion required in

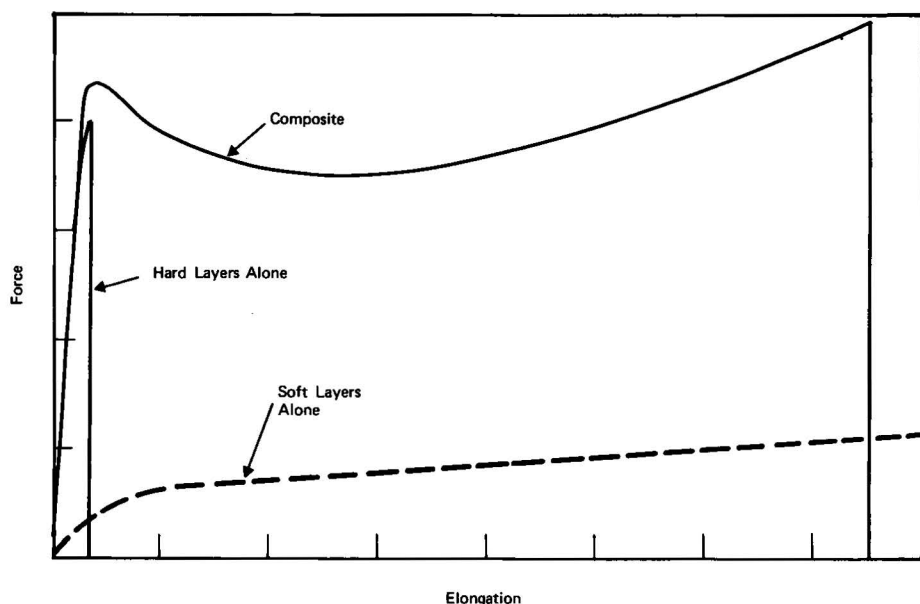


Fig. 18 Schematic illustration of “mutual interlayer reinforcement” obtained when “soft” layers block crack propagation in normally brittle “hard” layers.

<sup>†</sup> Djiauw and Fesko [26b] describe in detail the analogous behavior of elastomeric substrates coated with thin paint films. [—EDITORS]

order for one layer to influence the response of its neighbor. Thus, in micro-layer film, with hundreds of very thin layers, interlayer interactions can be anticipated even with very poorly adhering components.

The mechanical properties of a homogeneous polymer sheet or film depend strongly upon the pattern of molecular orientation. A unidirectionally oriented crystalline polymer, such as polyethylene or polypropylene, can exhibit a tensile strength (in the orientation direction) higher by an order of magnitude than that of the same polymer when unoriented. Strength in the transverse direction is low [27]. Polystyrene, a glassy amorphous polymer, can be made strong, tough, and craze resistant in one direction by uniaxial orientation, while being made extremely weak and brittle in the transverse direction [28]. Biaxial orientation of a sheet or film can impart desirable mechanical properties in all direction in the plane, and is commonly employed in the manufacture of plastic films of both the crystalline and the glassy amorphous types [29].

The mechanical properties of coextruded multilayer sheets and films also depend upon the degree of molecular orientation. An appropriate level of orientation can optimize the properties of the individual layers, and thereby the likelihood and the extent of interlayer reinforcement. For example,

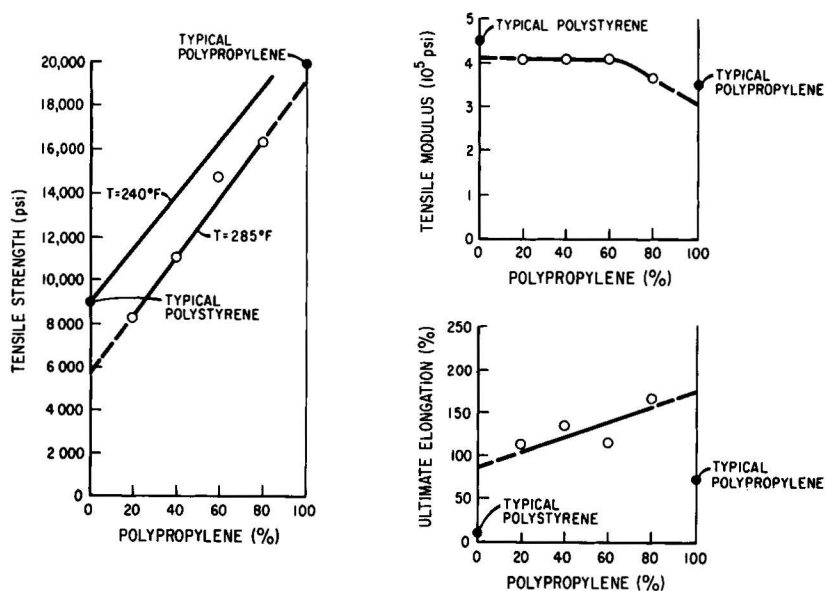


Fig. 19 Mechanical properties of biaxially oriented 125-layer films of PP and PS of different composition. Ultimate tensile strength can depend on the orientation temperature (240 versus 285°). (From Schrenk and Alfrey [25].)

biaxially oriented 125-layer films of polypropylene and polystyrene have been reported to exhibit high tensile strengths and ultimate elongations, over a composition range from 80/20 to 20/80 [25]. The reported tensile properties of these films are shown in Fig. 19.

### C. Optical Properties of Multilayer Films

A multilayer film made up of alternating layers of two transparent polymers of differing refractive indexes can exhibit vivid optical effects. Some wavelengths of light are strongly reflected; others are transmitted through the film [30a].

Figure 20 is a schematic drawing of a 125-layer film in which the odd layers have a refractive index of 1.6, and the even layers a refractive index of 1.5. When a beam of light of wavelength  $\lambda$  shines upon the film, partial reflection occurs at each of the many interfaces. The reflections at the interfaces of increasing refractive index suffer a phase reversal. Since the layers differ only by 0.1 in refractive index, the individual reflections are weak. However, if reflections from the different interfaces all leave the film in phase with each other, the constructive interference yields a high-intensity reflection.

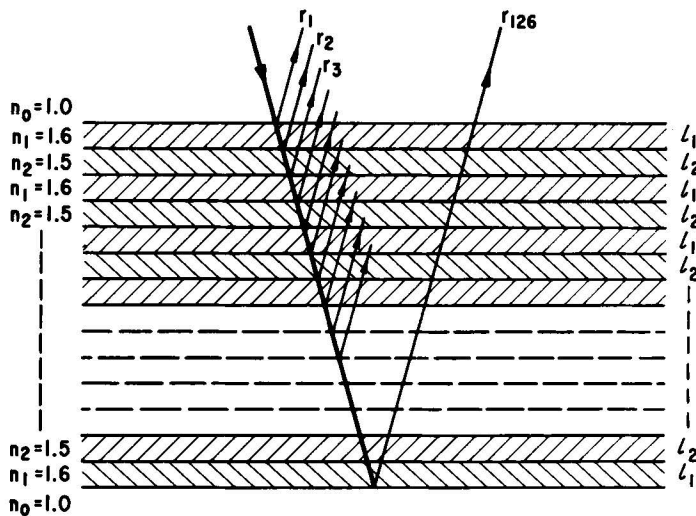


Fig. 20 Reflection of incident light from the many interfaces between polymers of different refractive index, which yields intense iridescent colors. The remaining light is transmitted through the film and is the complementary color to the reflected light. (From Schrenk and Alfrey [30a].)

The wavelength of the first-order reflection (for normal incidence) is given by

$$\lambda_1 = 2(n_{\text{odd}}l_{\text{odd}} + n_{\text{even}}l_{\text{even}}) \quad (13)$$

For example, if the thicknesses of the odd and even layers are set at 700 and 746.5 Å, respectively,

$$n_{\text{odd}}l_{\text{odd}} = 1.6 \times 700 = 1120$$

$$n_{\text{even}}l_{\text{even}} = 1.5 \times 746.5 = 1120$$

$$\lambda_1 = 2(1120 + 1120) = 4480 \text{ Å}$$

In addition to the first-order reflection  $\lambda_1$ , higher-order reflections occur at wavelengths  $\lambda_{\text{II}}$ ,  $\lambda_{\text{III}}$ , etc.:

$$\lambda_{\text{II}} = (2/2)(n_{\text{odd}}l_{\text{odd}} + n_{\text{even}}l_{\text{even}}) \quad (14)$$

$$\lambda_{\text{III}} = (2/3)(n_{\text{odd}}l_{\text{odd}} + n_{\text{even}}l_{\text{even}}) \quad (15)$$

$$\lambda_M = (2/M)(n_{\text{odd}}l_{\text{odd}} + n_{\text{even}}l_{\text{even}}) \quad (16)$$

The relative intensities of these higher-order reflections depend upon the ratio of optical thicknesses of the two kinds of layer. For example, if the odd and even layers have equal optical thickness, the second-order and fourth-order reflections are suppressed. On the other hand, if  $n_{\text{odd}}l_{\text{odd}} = 2n_{\text{even}}l_{\text{even}}$ , the third-order reflection is suppressed.

Finally, the breadth of the reflection spectrum is related to the layer thickness gradient through the film. Uniform layers through the film yield a relatively narrow reflection band, while a layer thickness gradient reflects a wider portion of the spectrum.

An experimental study of iridescent coextruded multilayer films of polystyrene-PMMA has been reported [14]. Dimensions corresponding to

Table IV

Typical Reflecting Wavelengths and Layer Thicknesses for 231-Layer Films of Polystyrene and Poly(methyl methacrylate) (Equal-Thickness Layers)

| Light type            | Reflecting wavelength |       | Single-layer thickness |        |                       | Total film thickness |       |
|-----------------------|-----------------------|-------|------------------------|--------|-----------------------|----------------------|-------|
|                       | Å                     | μm    | Å                      | μm     | mils                  | μm                   | mils  |
| Ultraviolet           | <3800                 | <0.38 | <617                   | <0.062 | $<2.4 \times 10^{-3}$ | <14.3                | <0.56 |
| Visible "pure" blue   | 4730 <sup>a</sup>     | 0.473 | 768                    | .077   | $3.0 \times 10^{-3}$  | 17.7                 | 0.70  |
| Visible "pure" green  | 5130 <sup>a</sup>     | 0.513 | 833                    | .083   | $3.3 \times 10^{-3}$  | 19.2                 | 0.76  |
| Visible "pure" yellow | 5770 <sup>a</sup>     | 0.577 | 937                    | .094   | $3.7 \times 10^{-3}$  | 21.6                 | 0.85  |
| Infrared              | >7600                 | >0.76 | >1234                  | >0.123 | $>4.9 \times 10^{-3}$ | >28.5                | >1.12 |

<sup>a</sup> From Burnham *et al.* [30b].

various colors are shown in Table IV. Observed reflectance spectra correlated well with measured layer thickness distributions.

In addition to reflecting wavelengths in the visible range of the spectrum to give iridescent colors, similar coextruded films can be designed that reflect in the near infrared or the ultraviolet portion of the spectrum. Films have been tested that can effectively reflect a high percentage of incident solar infrared radiation.

## VII. APPLICATIONS

Having reviewed the technology of coextrusion and some of the properties of coextruded film and sheet, a discussion of several commercial applications and development activities will illustrate how coextrusion is currently used to obtain desired end-use characteristics in products more economically than other laminating and coating processes.

One of the early coextrusions was a three-layer film of polyethylene–polypropylene–polyethylene (PE–PP–PE) for wrapping bread. Polyethylene provided heat sealability on high-speed packaging lines, while the polypropylene core added stiffness and toughness, and, because of its higher melting point, prevented burnthrough during heat sealing to broaden the effective heat-sealing range of the film. While the adhesion of PE to PP is generally poor, in thin films it was adequate for packaging low specific gravity products such as bread. Where better adhesion and stronger heat seals are desired, ethylene–vinyl acetate copolymers can be used.

Other early applications, using blown, coextruded films of low-density polyethylene–poly [ethylene-*co*-(vinyl acetate)] (LDPE–EVA), chlorinated polyethylene–low-density polyethylene (CPE–LDPE), and LDPE–HDPE, were for heavy-duty shipping bags for fertilizers, chemicals, salt pellets, etc. These combinations were designed to provide heat sealability, toughness, and chemical resistance. Also, a nonslip outer layer having a high coefficient of friction, such as CPE, could be used to improve stacking of bags on a pallet. Another early application in Europe was a two-color LDPE milk pouch film consisting of a white outer layer and a black inner layer to provide protection to the milk from light. Also, ionomer–LDPE coextrusions are used for sterilized medical product packaging, and applications are being found for EVA–HDPE films in snack food and cereal packaging.

Another pioneering application for coextrusion is a chill-roll-cast five-layer film of PE–EVA–Saran–EVA–PE (Saranex<sup>†</sup>) in which the Saran core

<sup>†</sup> Trademark of The Dow Chemical Company.

layer provides an excellent gas barrier, while the PE skin layers contribute good heat sealability [31]. The EVA layers bond the Saran and PE layers. These films find application in food packaging requiring excellent gas-barrier properties (meat, cheese, nuts and condiments, snack foods, fruit drinks, etc.) and certain medical applications.

Recently, The Mearl Corporation has commercialized the first microlayer film that consists of over 100 layers, each less than 1000 Å thick. The film is coextruded from two polymers having different refractive indexes, which gives the film striking iridescent color effects. The physical optics of these unique films have been discussed earlier. Applications for iridescent film include lamination to paper and other plastics for decorative uses [32].

Rasmussen [33] has developed a coextrusion process to manufacture bicomponent fibers by generating many multiple layers of three polymers in the sequence ABCABC..., where B adheres to A and C but A and C can delaminate at their interfaces. The multilayer stream is extruded through orifices, drawn into thin ribbons, and subsequently delaminated mechanically at a high rate of production to give a tow with a large number of very thin bicomponent fibers, each consisting of components A and C held together by the adhesive B.

Continued growth in coextrusion coating is forecast in which a multilayer film is extruded through a flat die directly onto a substrate, such as paper, plastic foam, or cellophane. More recently coextrusion is being used to manufacture thick (greater than 0.010 in.) sheet. The major current use includes simple two- and three-layer structures for packaging. A thin layer of general purpose polystyrene (GPPS) is coextruded over a colored layer of high-impact polystyrene to impart high gloss for marketing appeal. It is desirable to keep the GPPS layer as thin as possible since it tends to embrittle the sheet by crack initiation and propagation through the rubber-modified layer (mutual interlayer destruction).

Two-color sheets, usually made as a three-layer sheet with the mixed colored scrap buried as a core layer, is also used for marketing appeal and improved economics since the scrap can be reused without color matching. In addition to packaging, a similar approach is being used for interior vinyl automobile trim. Before the advent of coextrusion, the scrap from each color of interior trim had to be carefully segregated and color matched for recycle. With coextrusion all of the mixed colored scrap can be collected at one place and coextruded with a surface layer of virgin vinyl of the desired color. The economic advantage of this approach is obvious.

In Europe the use of coextruded sheet for thermoformed packages is highly advanced, and multilayer sheet containing as many as five or six layers is being produced for applications requiring good thermoformability, heat sealability, stress crack resistance, barrier to gases and water vapor,

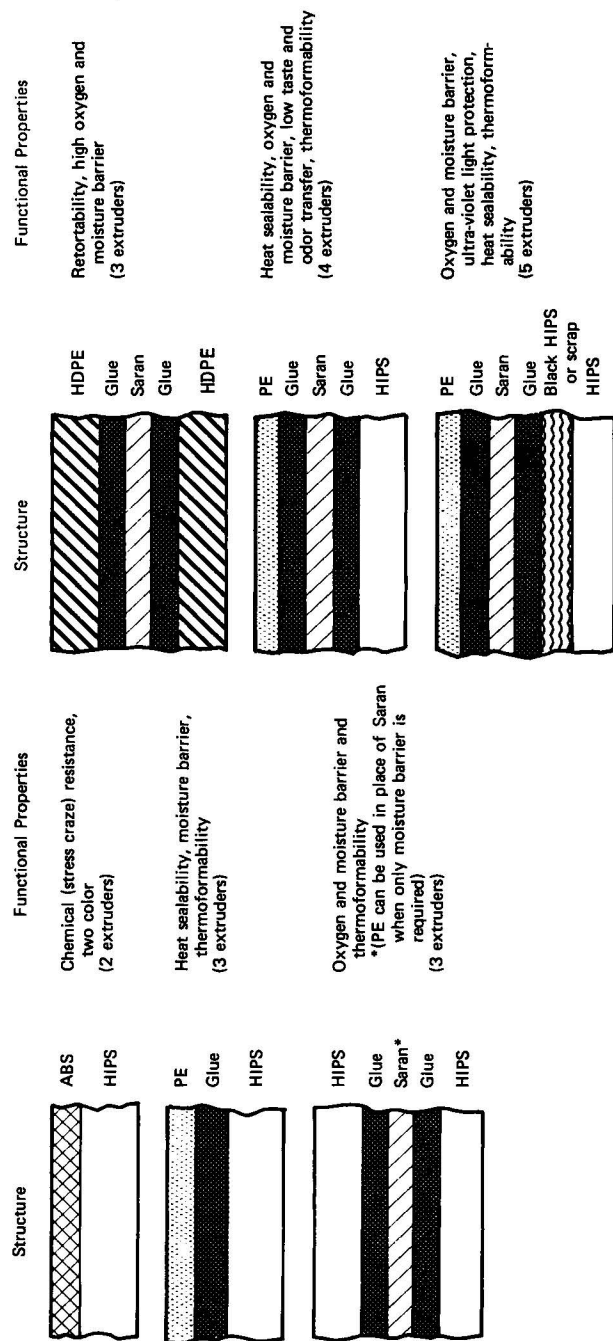


Fig. 21 Schematic illustration of several coextruded sheet structures used in packaging in which each layer provides a specific functional characteristic to the product.

and low taste and odor transfer. Some of the multilayer constructions and functional properties of these sophisticated structures are illustrated in Fig. 21. They are being used to package margarine, fruit drinks, cheese, puddings, sterilized milk, cakes, pickles, mayonnaise salads, and other items [22].

Developmental work has demonstrated the potential of manufacturing plastic cans that can withstand retorting at 250°F for 90 min [34]. A five-layer coextrusion of HDPE-EVA-Saran-EVA-HDPE can be formed into a can and hermetically sealed by double-seaming an aluminum lid to the plastic can body. The Saran layer provides a gas barrier, and HDPE layers give the can thermal stability during autoclaving.

While most of the early commercialization of coextrusion has been in film and sheet for packaging, its use for durable goods is increasing. Appliance manufacturers are developing refrigerator door liners and food boxes that may consist of a thin layer of ABS on HIPS to replace the all-ABS sheet currently used, at considerable cost saving in raw materials [35]. A modified polyethylene layer may also be coextruded on the other surface to act as a barrier to the polyurethane foam-fluorocarbon blowing gases, which tend to craze ABS and HIPS.

Coextrusion is being used in outdoor applications, such as in the fabrication of window shutters, house trim, and recreational vehicles. In these applications a thin layer of pigmented acrylic is coextruded over ABS or HIPS to provide weatherability by protecting the styrenics from ultraviolet exposure.

Other applications include coextrusions of a surface layer having a high coefficient of friction for shower mats. Also, decorative signs, luggage, boat hulls, and bath units are being made from coextruded sheets.

The ability to coextrude multilayer films and sheets economically from a wide variety of polymers, each adding a desired property to the end use characteristics of the product, has made coextrusion a major, growing fabrication process.

## VIII. SCRAP RECYCLE

The reuse of scrap from coextrusion is an important economic consideration. The recycling of scrap from compatible polymer combinations is fairly straightforward as long as the amount of scrap recycle is controlled to maintain consistent physical properties. For example, in a coextruded sheet of GPPS and HIPS, or styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene copolymer (ABS), the scrap may be extruded

back into the rubber-modified layer as a mixed polymer blend. The dilution of the rubber-modified phase with unmodified skin-layer polymer may cause some loss in impact strength, but is acceptable if the skins are thin and the amount of recycle remains consistent.

The recycling of dissimilar (incompatible) polymers poses a more difficult problem since the mixed blend can cause severe loss of mechanical properties in some cases. This is an important area of continuing research. Frequently the glue layers used in coextrusion of nonadhering polymers can act as compatibilizers in the mixed recycle blend.

The recycling of incompatible polymers, usually as a buried core layer, has been demonstrated for certain polymer combinations, such as ABS and HIPS; PS, EVA, and PE; PS, styrene-butadiene, and SARAN; and HDPE, EVA, and Saran. It is difficult, however, and must be approached carefully. The loss of properties due to a buried core layer of incompatible polymers is reduced when tough, virgin skin layers are used because of mutual interlayer reinforcement.

Approaches being taken to improve the compatibility of multilayer scrap recycle include:

1. polymer modification to improve compatibility, including copolymers with a minor amount of a comonomer to achieve bonding;
2. compatibilizers, such as CPE and other glue-layer polymers, as an intermediate phase to promote bonding; and
3. mixing, as there is evidence that the loss of properties is reduced by intensive mixing of the blended scrap.

The technology developed for polymer blends will undoubtedly be used in coextrusion to solve the important economic problem of scrap recycling. Meanwhile, coextrusion can still show economic advantages over other processes for many film and sheet products even when total loss of scrap is considered.

## IX. NEW DEVELOPMENTS

Brief mention should be made regarding some new developments in coextrusion.

Foamed plastics are being coextruded with one or two solid polymer skins to obtain lightweight, rigid-sheet structures. With present flat-die coextrusion technology, foam layer densities of about  $0.5 \text{ gm/cm}^3$  are possible. Limitations on foam density achieved in flat-die coextrusion include corrugations in the sheet due to lateral expansion of the foam, and collapse of the foam cells in

thick-sheet coextrusion because of insufficient cooling rate. Tubular coextrusion of thinner, lower-density, multilayer solid-skin-foam composites is being developed. The tubular coextrusion is expanded circumferentially over a cooling mandrel to permit foam expansion in all three directions. The potential for savings of raw material by using a lightweight foam core in combination with solid skins to obtain rigidity will stimulate applications in packaging and durable goods. One problem is that some foam composites tend to be brittle. Improved reinforcement of the foam layer by the skin layers or internal reinforcement of the foam core by including thin ductile layers within the foamed core are possible solutions.

Multilayer injection molding of finished objects by simultaneous injection of two polymers into a mold has been demonstrated [36, 37]. This technology is still new, and applications are being developed.

Squeeze tubes and blow-molded bottles, using a tubular coextrusion die to produce a multilayer parison, have been made and are undergoing development for several applications.

Finally, a new solid-phase forming process is being commercialized that can form multilayer containers and similar objects without the trim scrap normally associated with conventional thermoforming [38]. The scrapless feature of this new process will undoubtedly expand the use of coextruded sheets.

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