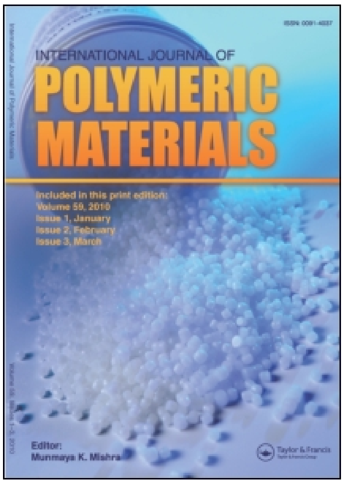

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Mechanical Fabrication of Thermoplastic Polymers

T. Alfrey[a]
[a] The Dow Chemical Company, Midland, Mich

To cite this Article Alfrey, T.(1973) 'Mechanical Fabrication of Thermoplastic Polymers', International Journal of Polymeric Materials, 2: 4, 361 — 366

To link to this Article: DOI: 10.1080/00914037308072368

URL: http://dx.doi.org/10.1080/00914037308072368

Intern. J. Polymeric Mater., 1973, Vol. 2, pp. 361–366

Printed in Reading, England

Mechanical Fabrication of Thermoplastic Polymers†

T. ALFREY

The Dow Chemical Company, Midland, Mich. 48640

(*Received August 1, 1973*)

The physical properties and performance of fabricated thermoplastic items depend upon the molecular structure (mainly established during polymerization) and the spatial arrangement of the polymer molecules (established during fabrication). The spatial arrangements can be favorably influenced by controlled molecular orientation (uniaxial, biaxial and "crossed") and by composites (fiber reinforcement, multi-layer films).

The mechanical fabrication of thermoplastic polymers embraces a wide range of operations. Some processes, such as extrusion and injection-molding, are carried out at high temperatures where the polymers behave as viscoelastic fluids. Other processes, such as bottle blowing and vacuum forming, entail only moderate deformations, and can be carried out at temperatures where the polymers behave as viscoelastic solids. Some thermoplastic polymers are capable of being fabricated at still lower temperatures (below the glass temperature for amorphous polymers; below the melting point for crystalline polymers), by processes similar to the rolling, forging, and drawing of metals. In some processes, a crystallizable polymer enters the fabrication zone in a metastable, supercooled amorphous state, and crystallization occurs during the mechanical deformation.

The primary purpose of any fabrication operation is, of course, the establishment of a desired geometrical shape. A less apparent, but most important, feature which is simultaneously established is the spatial arrangement of the polymer molecules within the fabricated article. This includes orientation in amorphous polymers, morphology and orientation in crystalline polymers, and phase geometry in multiphase systems such as composites and foams

---

†Lecture at the Scientific Symposium at the occasion of the Dedication of the Midland Macromolecular Institute, September 29, 1972.

The physical properties and performance of fabricated thermoplastic items depend upon the molecular structure (mainly established during polymerization) and the spatial arrangement of the polymer molecules (established during fabrication).

Consider first the influence of molecular orientation in amorphous thermoplastics, using atactic polystyrene as a specific example. At room temperature, unoriented polystyrene is a brittle, glassy, amorphous polymer. Uniaxially oriented polystyrene is highly *anisotropic*. In the direction of orientation it can have a high tensile strength and ductile extensibility, and resistance to environmental stress-crazing and cracking.[1] On the other hand, in the transverse direction it is even weaker and more susceptible to stress-cracking than unoriented polystyrene.[2] The tensile strength in the orientation direction increases monotonically with increasing level of orientation, while the elongation-to-break rises to a maximum and then decreases.

Molecular orientation occurs inevitably in most mechanical fabrication operations, the pattern of orientation in the part being governed by the process *kinematics*—the pattern of flow and deformation followed by the polymer during fabrication. The *effects* of orientation can be either favorable or unfavorable, depending on the directions of orientation relative to the stresses encountered in service. Planned, controlled molecular orientation can be a valuable aid in achieving optimum properties and performance Uncontrolled orientation will have beneficial effects only by accident; usually it is a source of weakness and failure. Controlled molecular orientation in fabricated polymeric articles can be classified as uniaxial, biaxial, and "crossed".

Fibers and monofilaments are subjected in service mainly to tensile and bending loads; and consequently, uniaxial orientation can provide satisfactory mechanical performance. Natural fibers, such as cotton and silk, exhibit molecular orientation, and most synthetic fibers are subjected to controlled uniaxial orientation during manufacture.

Apart from fibers and monofilaments, most thermoplastic articles are subjected to multiaxial stresses in service. In films, sheets, and thin-walled vessels, biaxial stresses are usual. Consequently, uniaxial orientation is often detrimental in such items, whereas biaxial orientation can often be employed to advantage. Biaxially oriented polystyrene sheets (e.g. stretched 3:1 in both directions at 110°C) are strong and tough in all directions in the plane. Tensile strength, impact strength, and resistance to stress-cracking agents are all strongly enhanced, compared with unoriented polystyrene.[3] Biaxially oriented high impact polystyrene exhibits improved strength, impact strength, and fatigue resistance.

"Crossed" molecular orientation was employed by Cleereman, who rotated the core of the mold during injection-molding of thin-walled polystyrene tumblers.[4] The direction of molecular orientation varied through the wall, in a fashion similar to cross-laminated plywood. This led to a threefold increase in hoop strength, and a 10,000-fold increase in time-to-fail in a stress-cracking test in which tumblers were filled with corn oil or motor oil and pressurized. Such tumblers with crossed molecular orientation can be used as parisons for a subsequent bottle-blowing operation, yielding blown bottles with superior performance.

Molecular orientation is also important in crystalline polymers, although the pattern of behavior does not exactly parallel that exhibited by glassy amorphous polymers. For example, Kresser[5] has reported that the tensile strength of polypropylene systematically increases (approximately fourfold) with increasing uniaxial orientation, while the elongation-to-break systematically decreases. In any particular application, the optimum level of orientation represents a compromise in which both strength and toughness must be given consideration. Furthermore, in crystalline polymers, orientation can be introduced in two fundamentally different fashions:

1) A crystallized specimen can be stretched at a temperature which is higher than the glass transition point but lower than the crystalline melting point. This requires extensive reorganization of the original crystal morphology.

2) Molten polymer can be oriented, followed by crystallization of the oriented melt. The crystal morphology so obtained, and the resulting physical properties, are different from those obtained by stretching already crystalline polymers.

Clark and Garber[6] have emphasized the effects of mechanical processing on the morphology and properties of crystalline polymers, in the cases of blown film, injection-molded specimens, and spun fibers. For example, blown polyoxymethylene film exhibits row-nucleated ("shish-kebab") morphology, and much higher elongation than *spherulitic* POM. Injection-molding of POM yields a skin-core structure: a skin layer formed from multiple nuclei under high shear stress, during filling; a continued growth inward of twisting lamellae after mold filling; and a spherulitic core nucleated and crystallized under quiescent conditions.

The manufacture of Saran film involves a biaxial orientation step carried out in a bubble, at a temperature below the crystalline melting point. Molten (but crystallizable) polymer is extruded as a tube, and rapidly quenched past the crystallization range, This metastable, supercooled, amorphous tube is passed between nip-rolls into a bubble zone of trapped air. Here the tube undergoes both machine-direction and circumferential stretching, which induces crystallization. The product, a biaxially oriented, crystalline, thin-walled tube, is passed through converging rolls and nip-rolls, and either slit or wound up as a flattened tube. Machine direction orientation can be made greater, equal, or less than the circumferential orientation by controlling mechanical variables in the bubble zone. Mechanical properties in the two directions, and shrinkage characteristics, can be made balanced or unbalanced, as called for in various specific end uses.[7]

Such bubble processes belong to a class of operations which are susceptible to complete mechanical analysis—namely those involving membranes of rotational symmetry.[16] This class includes both batch operations such as vacuum forming and continuous operations. In all these operations, whether batch or continuous, certain common features are encountered—namely, the geometry of rotationally symmetric surfaces, and the Equations of Equilibrium for membranes of rotational symmetry. The meridianal direction and the "hoop" direction, by symmetry, are also principal directions of stress and strain (as well as of curvature). The third principal direction is normal to the surface; and the stress in this direction can be taken as zero. The stress at any point is thus specified by two components: σ_{M} and σ_{H}. These principal stresses are everywhere non-negative in the processes under consideration. Since we usually are dealing with large deformations of a nearly incompressible material, it is usually convenient to define the state of deformation in terms of the two principal extension-ratios, λ_{M} and λ_{H}. If the material properties are simple, a complete predictive mechanical analysis can be made, by combining the laws of geometry, the equations of equilibrium and the material properties. In the Saran film process, where crystallization accompanies deformation, such a predictive analysis is impossible. Even so, a complete mechanical analysis can be made by setting the process into steady state operation, and then making the following measurements: (a) the air pressure in the bubble; (b) the machine tension; (c) the meridianal curve, $r(z)$; (d) the location of a moving particle along the meridian, as a function of time.

With this information, the Equations of Equilibrium can be used to calculate $\sigma_{\mathrm{M}}(z)$ and $\sigma_{\mathrm{H}}(z)$. The extension ratios, λ_{M} and λ_{H}, can be calculated for every point in the stretching zones. The trajectories on the biaxial stress plane and the biaxial extension-ratio plane can now be plotted, with the aim of correlating them with the directional physical properties of the product.

Some thermoplastic polymers can be fabricated at relatively low temperatures, by methods similar to those used in metal fabrication (crystalline polymers below their melting points; amorphous polymers below their glass temperatures). These low-temperature operations, such as cold rolling,[8] drawing,[9] and forging,[10] invariably introduce large orientations which strongly influence the mechanical performance of fabricated parts. In low-temperature forming, the polymer must yield in a ductile manner, rather than fracture. This eliminates many thermoplastic materials; but sometimes mechanical pretreatment can convert an unusable thermoplastic to a usable condition.

For example, polystyrene is too brittle to cold-roll, but *oriented* polystyrene can be cold-rolled and further oriented.[8]

In multi-phase systems, such as composites and foams, another aspect of spatial arrangement is encountered. This is the geometrical disposition of the phases, which is established during fabrication.

The use of fibrous composites to achieve outstanding mechanical performance goes back to ancient times, and in recent years the role of fiber geometry has been the subject of intensive study.[12] In cross-plied laminates, the properties of a ply depend upon the mechanical properties of fiber and matrix material, and the geometrical arrangement within the ply; properties of the laminate depend upon the anisotropic properties of the individual plies and the geometry of their arrangement in the composite. The geometrical disposition of fibers in flexible composites, such as automobile tires, is as decisive a factor as in rigid structural composites.

Phase geometry is also important in laminar composites. Some swordmakers of early times hammered down alternate layers of hard and soft steel, obtaining blades which would take a fine cutting edge and yet were strong and tough.[13] Today, many multilayer thermoplastic film laminates are manufactured which exhibit combinations of properties which cannot be matched by any one of the constituent thermoplastic materials. For example, films containing alternating "hard" and "soft" layers can exhibit mutual interlayer mechanical reinforcement. Thin layers of a high modulus, low elongation material, sandwiched between thin adhering layers of a high elongation material, may be prevented from undergoing transverse fracture; and thereby forced to undergo large ductile deformations when the composite is stressed.[14] Such a layered composite has both a high modulus and a high elongation-to-break; it has a much higher work-to-break than any of the individual layers. It is possible to prepare multilayer plastic films containing up to hundreds of parallel layers, by co-extrusion from the melt. The geometrical arrangement of the phases in such a multilayer film is controlled by the flow-pattern developed during the mechanical fabrication operation. One method of developing such flow patterns has been described by Schrenk *et al.*[11] Different molten polymers are introduced as radial layers into an annular channel and pumped down the channel while the inner shaft, the outer cylindrical surface, or both are rotated. The molten polymer follows helical flowlines of varying pitch, and the initially thick radial layers are twisted into thin spiral laminae. The eventual layer distribution in the tubular film depends in a predictable manner upon the feed-port geometry, the volumetric rates of the various polymers, and the angular velocities of the two rotatable surfaces.

Finally, polymeric *foams* represent a broad class of multiphase systems whose properties depend upon phase geometry as well as upon the material properties of the bulk polymers. Expanded polymers range from elastomeric through semi-rigid (e.g., polyethylene) to rigid.[15] They can be high-density or low-density; open-celled or closed-celled; linear or cross-linked; amorphous or crystalline. They can be directly utilized as end-products, or incorporated into structures such as sandwich panels, which efficiently utilize their unique density-property characteristics.

Over the years, much progress has been made in the understanding of molecular structure of polymers, and in the controlled synthesis of desired molecular structures. Molecular weight distributions, degree of stereoregularity, copolymer sequence distributions, and related molecular features are most important in determining mechanical properties. But in many cases the supramolecular structure, subsequently established by mechanical means, is equally important in determining the performance of a fabricated item.

References

1. K. J. Cleereman, H. J. Karam and J. L. Williams, *Mod. Plast.* **30,** 119 (May, 1953).
2. L. J. Broutman and F. J. McGarry, *J. Appl. Polymer Sci.* **9,** 609 (1965).
3. L. S. Thomas and K. J. Cleereman, *SPE Journal* **28** (4), 2; (6), 9 (1972).
4. K. L. Cleereman, *SPE Journal* **23,** 43 (Oct., 1967); **25,** 56 (Jan., 1969).
5. T. O. Kresser, *Polypropylene*, Reinhold, New York (1960).
6. E. S. Clark and C. A. Garber, *AIChE Materials Eng. and Sci. Div.*, Biennial Conference (1970).
7. W. R. R. Park, *Plastics Film Technology*, Reinhold, New York (1969).
8. L. J. Broutman and R. S. Patil, *Poly. Eng. and Sci.* **11,** 165 (1971).
9. H. L. Li, P. J. Koch, D. C. Prevorsek and H. J. Oswald, *J. Macromol. Sci.-Phys.* **B4** (3), 687 (1970).
10. K. F. Wissbrun, *Poly. Eng. and Sci.* **11,** 28 (1971).
11. W. J. Schrenk and T. Alfrey, Jr., *ACS Symposium on Coextruded Plastic Films, Fibers, and Composites*, Boston, April, 1972.
12. J. E. Ashton and J. C. Halpin, *Primer on Composite Materials*, Technomic Publishing Company, Stamford (1969).
13. G. Slayter, *Sci. Am.* **206** (1), 124 (1962).
14. W. J. Schrenk and T. Alfrey, Jr., *Poly. Eng. and Sci.* **9,** 393 (1969).
15. R. E. Skochdopole, Cellular materials, *Encyclop. Poly. Sci. and Tech.* **3,** 80 (1965).
16. T. Alfrey, *Appl. Polymer Symposia* **17,** 3 (1971).