ACRYLONITRILE–BUTADIENE–STYRENE (ABS) POLYMERS

1. Introduction

Acrylonitrile–butadiene–styrene (ABS) polymers [9003-56-9] are composed of elastomer dispersed as a grafted particulate phase in a thermoplastic matrix of styrene and acrylonitrile copolymer (SAN) [9003-54-7]. The presence of SAN grafted onto the elastomeric component, usually polybutadiene or a butadiene copolymer, compatabilizes the rubber with the SAN component. Property advantages provided by this graft terpolymer include excellent toughness, good dimensional stability, good processability, and chemical resistance. Property balances are controlled and optimized by adjusting elastomer particle size, morphology, microstructure, graft structure, and SAN composition and molecular weight. Therefore, although the polymer is a relatively low cost engineering thermoplastic the system is structurally complex. This complexity is advantageous in that altering these structural and compositional parameters allows considerable versatility in the tailoring of properties to meet specific product requirements. This versatility may be even further enhanced by adding various monomers to raise the heat deflection temperature, impart transparency, confer flame retardancy, and, through alloying with other polymers, obtain special product features. Consequently, research and development in ABS systems is active and continues to offer promise for achieving new product opportunities.

2. Physical Properties

The range of properties typically available for general purpose ABS is illustrated in Table 1 (1). Numerous grades of ABS are available including new alloys and specialty grades for high heat, plating, flaming-retardant, or static dissipative product requirements (1,2). Reference 1 discusses stress–strain behavior, creep, stress relaxation, and fatigue in ABS materials.

2.1. Impact Resistance. Toughness is a primary consideration in the selection of ABS for many applications. ABS is structured to dissipate the energy of an impact blow through shear and dilational modes of deformation. Upon impact, the particulate rubber phase promotes both the initiation and termination of crazes. Crazes are regions of considerable strength that contain both voids and polymer fibrils oriented in the stress direction. Crazes are terminated by mutual interference or are stopped by other rubber particles, thereby dissipating energy without the formation of a crack, which would lead to catastrophic

Table 1. **Material Properties of General Purpose and Heat Distortion Resistant ABS**[a]

Properties	ASTM Method	High impact	Medium impact	Heat resistant
notched Izod impact at RT, J/m[b]	D256	347–534	134–320	107–347
tensile strength, MPa[c]	D638	33–43	30–52	41–52
tensile modulus, GPa[d]	D638	1.7–2.3	2.1–2.8	2.1–2.6
flexural modulus, GPa[d]	D790	1.7–2.4	2.2–3.0	2.1–2.8
elongation to yield, %	D638	2.8–3.5	2.3–3.5	2.8–3.5
Rockwell hardness	D785	80–105	105–112	100–111
heat deflection[e], °C at 1820 kPa[f]	D648	96–102	93–104	104–116
heat deflection[e], °C at 455 kPaf	D648	99–107	102–107	110–118
Vicat softening pt, °C	D1525	91–106	94–107	104–118
coefficient of linear thermal expansion, $\times 10^5$ cm/cm·°C	D696	9.5–11.0	7.0–8.8	6.5–9.2
dielectric strength, kV/mm	D149	16–31	16–31	14–35
dielectric constant, $\times 10^6$ Hz	D150	2.4–3.8	2.4–3.8	2.4–3.8

[a] Ref. 1.

[b] To convert J/m to ft·lb/in. divide by 53.4.

[c] To convert MPa to psi multiply by 145.

[d] To convert GPa to psi multiply by 145,000.

[e] Annealed.

[f] To convert kPa to psi multiply by 0.145.

failure. Shear deformation also contributes to stress relaxation. The behavior of the rubber phase is understood from analyses of the stress distribution surrounding the particulate rubber phase. The rubber component may exist in a state of triaxial tension due to the higher rate of thermal contraction of the rubber compared to styrene–acrylonitrile copolymer upon cooling after molding. Crazes, in general, are initiated at local points of stress concentration. Mechanisms and the factors affecting fracture toughness have been discussed in detail in the literature (3–12).

The inherent ductility of the matrix phase depends on the composition of the SAN copolymer and is reported to increase with increasing acrylonitrile content (3). Controlling rubber particle size, distribution, and microstructure are important in optimizing impact strength. Good adhesion between the rubber and the matrix phase is also essential and is achieved by an optimized graft structure (3,8,10,13). Typically, toughness is increased by increasing the rubber content and the molecular weight of the ungrafted SAN.

2.2. Rheology. Effects of structure of ABS on viscosity functions can be distinguished by considering effects at lower shear rates ($<10/s$) vs higher shear rates. At higher shear rates melt viscosity is primarily determined by ungrafted SAN structure and the percentage of graft phase. The modulus curves correspond in their shape to that of the ungrafted SAN component, and the rubber particle type and concentration have little effect on the temperature dependence of the viscosity function (14). The extrudate swell, however, becomes smaller with increasing rubber concentration (15).

By contrast, the graft phase structure has a marked effect on viscosity at small deformation rates. The long time relaxation spectra are affected by rubber particle–particle interactions (16,17), which are strongly dependent on particle size, grafting, morphology, and rubber content. Depending on particle surface area, a minimum amount of graft is needed to prevent the formation of three-dimensional networks of associated rubber particles (17). Thus at low shear rates ABS can behave similarly to a cross-linked rubber; the network structure, however, is dissolved by shearing forces. Extensive studies on the viscoelastic properties of ABS in the molten state have been reported (14–21). Effects of lubricants and other nonpolymeric components have also been described (22).

2.3. Gloss. Surface gloss values can be achieved ranging from a very low matte finish at $<10\%$ (60° Gardner) to high gloss in excess of 95%. Gloss is dependent on the specific grade and the mold or polishing roll surface.

2.4. Electrical Properties. (See Table 1.) A new family of ABS products exhibiting electrostatic dissipative properties without the need for nonpolymeric additives or fillers (carbon black, metal) is now also commercially available (2).

2.5. Thermal Properties. ABS is also used as a base polymer in high performance alloys. Most common are ABS–polycarbonate alloys which extend the property balance achievable with ABS to offer even higher impact strength and heat resistance (2).

2.6. Color. ABS is sold as an unpigmented powder, unpigmented pellets, precolored pellets matched to exacting requirements, and “salt-and-pepper” blends of ABS and color concentrate. Color concentrates can also be used for online coloring during molding.

3. Chemical Properties

The behavior of ABS may be inferred from consideration of the functional groups present within the polymer.

3.1. Chemical Resistance. The term chemical resistance is generally used in an applications context and refers to resistance to the action of solvents in causing swelling or stress cracking as well as to chemical reactivity. In ABS the polar character of the nitrile group reduces interaction of the polymer with hydrocarbon solvents, mineral and vegetable oils, waxes, and related household and commercial materials. Good chemical resistance provided by the presence of acrylonitrile as a comonomer combined with relatively low water absorptivity ($<1\%$) results in high resistance to staining agents (eg, coffee, grape juice, beef blood) typically encountered in household applications (23).

Like most polymers, ABS undergoes stress cracking when brought into contact with certain chemical agents under stress (23,24). Injection molding conditions can significantly affect chemical resistance, and this sensitivity varies with the ABS grade. Certain combinations of melt temperature, fill rate, and packing pressure can significantly reduce stress cracking resistance, and this effect is interactive in complex ways with the imposed stress level that the part is subjected to in service. Both polymer orientation and stress appear to be considerations; thus critical strains can be higher in the flow direction (25). Consequently, all media to be in contact with the ABS part during service should be evaluated under anticipated end-use conditions.

3.2. Processing Stability. Processing can influence resultant properties by chemical and physical means (26,27). Degradation of the rubber and matrix phases has been reported under very severe conditions (28). Morphological changes may become evident as agglomeration of dispersed rubber particles during injection molding at higher temperatures (28). Physical effects such as orientation and molded-in stress can have marked effects on mechanical properties. Thus the proper selection and control of process variables are important to maintain optimum performance in molded parts. Antioxidants (qv) added at the compounding step have been shown to help retention of physical properties upon processing (26).

Appearance changes evident under certain processing conditions include color development (26), changes in gloss (28), and splaying. Discoloration may be minimized by reducing stock temperatures during molding or extrusion. Splaying is the formation of surface imperfections elongated in the direction of flow and is typically caused by moisture, occluded air, or gaseous degradation products; proper drying conditions are essential to prevent moisture-induced splay.

Techniques for evaluating processing stability and mechanochemical effects include using a Brabender torque rheometer (29,30), injection molding (26,28), capillary rheometry (26,28), and measuring melt index as a function of residence time (26).

3.3. Thermal Oxidative Stability. ABS undergoes autoxidation and the kinetic features of the oxygen consumption reaction are consistent with an autocatalytic free-radical chain mechanism. Comparisons of the rate of oxidation of ABS with that of polybutadiene and styrene–acrylonitrile copolymer indicate that the polybutadiene component is significantly more sensitive to oxidation than the thermoplastic component (31–33). Oxidation of polybutadiene under these conditions results in embrittlement of the rubber because of cross-linking; such embrittlement of the elastomer in ABS results in the loss of impact resistance. Studies have also indicated that oxidation causes detachment of the grafted styrene–acrylonitrile copolymer from the elastomer which contributes to impact deterioration (34).

Examination of oven-aged samples has demonstrated that substantial degradation is limited to the outer surface (34), ie, the oxidation process is diffusion limited. Consistent with this conclusion is the observation that oxidation rates are dependent on sample thickness (32). Impact property measurements by high speed puncture tests have shown that the critical thickness of the degraded layer at which surface fracture changes from ductile to brittle is about 0.2 mm. Removal of the degraded layer restores ductility (34). Effects of embrittled surface thickness on impact have been studied using ABS coated with styrene–acrylonitrile copolymer (35).

Antioxidants have been shown to improve oxidative stability substantially (36,37). The use of rubber-bound stabilizers to permit concentration of the additive in the rubber phase has been reported (38–40). The partitioning behavior of various conventional stabilizers between the rubber and thermoplastic phases in model ABS systems has been described and shown to correlate with solubility parameter values (41). Pigments can adversely affect oxidative stability (32). Test methods for assessing thermal oxidative stability include oxygen absorption (31,32,42), thermal analysis (43,44), oven aging (34,45,46), and chemiluminescence (47,48).

3.4. Photooxidative Stability.

Unsaturation present as a structural feature in the polybutadiene component of ABS (also in high impact polystyrene, rubber-modified PVC, and butadiene-containing elastomers) also increases liability with regard to photooxidative degradation (49–51). Such degradation only occurs in the outermost layer (52,53), and impact loss upon irradiation can be attributed to embrittlement of the rubber and possibly to scission of the grafted styrene–acrylonitrile copolymer (49,54). Oxidative degradation induced by prior processing may affect photosensitivity (49,55). Appearance changes such as yellowing are also induced by irradiation and caused by chromophore formation in both the polybutadiene and styrene–acrylonitrile copolymer components (49,56). Comparative data on ABS with other acrylic-based plastics have been reported (57).

Applications involving extended outdoor exposure, especially in direct sunlight, require protective measures such as the use of stabilizing additives, pigments, and protective coatings and film. Light stabilizers provide some measure of protection (58,59) as illustrated by the very successful use of ABS in interior automotive trim. Effects of polymer-bound stabilizers have been described (60). Pigments can significantly enhance stability. Paints are also highly effective in minimizing weather degradation (61). A particularly effective technique for sheet products is the lamination during extrusion of an acrylic film to ABS. Test methods for assessing light stability include outdoor exposure (62) and accelerated testing (62,63). Reactivity toward singlet oxygen has been reported (64). The current trend in accelerated light-aging for ABS in automotive applications is the use of xenon arc testing.

3.5. Flammability. The general purpose grades are usually recognized as 94 HB according to the requirements of Underwriters' Laboratories UL94 and also meet the requirements, dependent on thickness, of the Motor Vehicle Safety Standard 302. Flame-retardant (FR) grades (V0, V1, and V2) are also available which meet Underwriters' UL 94/94 5V and Canadian Standards Association (CSA) requirements beginning at a minimum thickness of 1.57 mm. Flame retardancy is achieved by utilizing halogen in combination with antimony oxide or by alloys with PVC or PC. A new FR grade utilizing polymer-bound bromine has been developed to avoid additive bloom and toxicity (65).

4. Manufacture

All manufacturing processes for ABS involve the polymerization of styrene and acrylonitrile monomers in the presence of an elastomer (typically polybutadiene or a butadiene copolymer) to produce SAN that has been chemically bonder or "grafted" to the rubber component termed the "substrate."

4.1. Rubber Chemistry. The rubber substrate is typically produced by the free-radical polymerization of butdiene. The radical source can be provided by either thermal decomposition or oxidation-reduction (redox) systems. The primary product is primarily 1,4-polybutadiene with some 1,2-polybutadiene, which contains a pendent vinyl group. Cross-linking of polymer occurs at high conversion through abstraction of reactive allylic sites or by copolymerization through double bonds (especially the double bonds in the more sterically accessibly pendent vinyl groups). Rubber cross-linking is controlled by the use of chain-transfer agents and the concentration and type of the initiator used; the reaction can also be affected by chain transfer to emulsifiers. For emulsion ABS, the rubber is typically both produced and subsequently used for grafting as a latex.

4.2. Graft Chemistry. Grafting of styrene and acrylonitrile onto a rubber substrate is the essence of the ABS process. Grafting is a free-radical process initiated by the abstraction of allylic hydrogens on the rubber substrate or by copolymerization through double bonds that are pendent or internal in the rubber substrate (66). Initiator level and type affects the extent of grafting (66–72) with oxyradicals yielding a higher degree of grafting than carbon radicals because of higher rates of abstraction from the rubber substrate. Chain-transfer agents are also used in controlling overall degree of grafting and grafting and graft molecular weight.

Ungrafted SAN is formed concurrently with grafted SAN, with the ratio controlled by factors that include temperature, chain-transfer agent, pendent vinyl content of rubber, initiator level, and initiator type (66–74). As previously described, occlusions of SAN can also form within the rubber particles with the mass process leading to significantly higher occulusion levels than the emulsion process (75,76). In the mass process, block copolymers of styrene and butadiene can be added to obtain unusual particle morphologies (eg, coil, rod, capsule, cellular) (75).

4.3. Emulsion Process. The emulsion process for making ABS has been commercially practiced since the early 1950s. Its advantage is the capability of producing ABS with a wide range of compositions, particularly higher rubber contents than are possible with other processes. Mixing and transfer of the heat of reaction in an emulsion polymerization is achieved more easily than in the mass polymerization process because of the low viscosity and good thermal properties of the water phase. The energy requirements for the emulsion process are generally higher because of the energy usage in the polymer recovery area. The emulsion polymerization process is typically a two-stage reaction process (77,78).

In the first stage, a rubber substrate, primarily composed of polybutadiene, is made using an emulsion polymerization process. The desired particle size of the rubber is either obtained by direct growth during polymerization or by an agglomeration process subsequent to polymerization. In a second-stage reaction, styrene and acrylonitrile are grafted onto the rubber substrate by emulsion polymerization. After the graft reaction is complete, the polymer can be recovered from the graft latex and compounded into a final pellet product (78–82).

4.4. Rubber Substrate Process. The rubber substrate can be made by a variety of different reaction processes including batch, semi-batch, and continuous (83). Butadiene monomer is primarily used in the substrate reaction, but comonomers such as styrene and acrylonitrile are common (81). The amount and type of comonomer employed will affect the glass transition of the rubber substrate and, thereby, influence the impact properties of the ABS polymer. Oxidation-reduction systems (eg, hydrogen peroxide and iron) or thermal initiators (eg, potassium persulfate or azobisisobutyronitrile) are used to initiate polymerization. Cross-link density is controlled by type and level of initiator, type and level of chain-transfer agent, reaction temperature, degree of conversion, or by the addition of comonomers. It is important to note that the graft process also can affect the cross-link density of the rubber. Various surfactant types can be employed to emulsify the monomer and stabilize the latex particles. Standard fatty acid soaps and derivatives are the most common emulsifiers employed; however, detergents such as sodium dobenzyl sulfonate and sodium lauryl sulfate can also be used. The use of nonionic surfactants has been reported (84). The “soap-free” emulsion polymerization of butadiene is possible using reactive surfactants (85), functional monomers such as acrylic acid (86), or high levels of potassium persulfate (87). The incorporation of surfactants into the polymer backbone provides the advantage of minimizing low molecular by-products in the final polymer that could result in mold buildup of juicing.

The incorporation of comonomers into the rubber substrate can be useful in achieving specialized performance of the final ABS polymer, such as adjusting the refractive index of the rubber phase to better match the continuous SAN phase to achieve a clear or more translucent ABS product (88). The incorporation of polymerizable antioxidants or uv stabilizers has also been reported (89). Typically, these modications increase the cost of ABS and are only employed for specialized applications.

Reactor productivity can be effected by various factors including initiator type, latex particle size, monomer purity, chain-transfer agents, and reaction temperature (83). As previously described, rubber particle size and distribution are important factors controlling the final properties of the ABS polymer. Large particles can be obtained by direct growth in the reactor, but much longer reaction times are needed. Comonomers such as AN can be added to speed the reaction rate and achieve relatively large particles in less time (90,91). Productivity can also be improved by the use of antifouling agents to minimize buildup of polymer on reactor heat-transfer surfaces (92–94). These antifouling agents improve heat transfer and minimize the time the reactor is down for cleaning.

4.5. Graft Process. Grafted SAN is critical to achieving effective dispersion of the rubber in the matrix phase, with key factors being SAN composition and rubber particle surface coverage. The composition of the grafted SAN depends on the monomer-feed composition and the monomer reactivity ratio. The composition of the polymer formed will equal the feed at the azeotropic composition, which occurs at ~3/1 mass ratio of styrene-to-acrylonitrile (76,84), and compositional drift will occur at monomer feed compositions other than the azeotropic concentration. Note that in aqueous systems, the difference in water phase solubility of acrylonitrile vs styrene can also perturb monomer concentrations at the reaction site and, thus, affect compositional drift. Polymerization techniques such as continuous vs batch processes and controlling pump rates can be used to control compositional drift (95–101). Surface coverage is controlled by rubber particle surface area and is effected by factors including initiator type, monomer feed to rubber level, and chain-transfer agents.

4.6. Resin Recovery Process. Typically, the polymer is recovered by the addition of coagulants which destabilize the ABS latex. Different coagulants are used depending on the surfactant. Thus, strong and weak acids work well with fatty acid soaps, and metal salts are used with acid stable soaps (102). The use of nonionic coagulants has also been reported (103,104). Acrylic latices have been used to control the coagulation process and obtain a narrow resin particle-size distribution (105).

Once coagulated, the resulting slurry can then be filtered or centrifuged to recover wet ABS resin, which is then dried to a low moisture content. A variety of dryers can be used for ABS, including tray, fluid bed, and rotary kiln-type dryers. Other methods of recovery have been employed such as spray drying (106) and extruder dewatering (107). Spray drying allows for good control of the final particle size of the resin, but uses a significant amount of energy in the drying process. In extruder dewatering, the latex is either directly fed into the extruder or is first coagulated and then fed into the extruder. Extruder dewatering allows for more efficient stripping and recovery of unreacted monomer than standard drying process.

4.7. Air and Water Treatment. The emulsion process exerts a greater demand on wastewater treatment than other processes (suspension or mass) because of the quantity of water used, and air emissions may be higher because of the types of process equipment employed. Recent federal and state EPA regulations governing air emission from ABS facilities affect the level of styrene, acrylonitrile, butadiene, and other volatile organic compounds that can be emitted into the air or sent to wastewater treatment facilities. In some cases, effluent water can be recycled and reused, but ultimately the water must be discharged, requiring treatment of the water prior to discharge. Air emissions from an emulsion ABS process can be reduced by improving the conversion of the monomers (108), the installation of equipment to strip and recover monomers, or the installation of end-of-pipe controls. End-of-pipe controls such as regenerative catalytic oxidation, regenerative thermal oxidation, fixed and fluid bed carbon absorption, and biofiltration are viable means of addressing air emission issues (109).

4.8. Mass Polymerization Process. In the mass (110–118) ABS process, the polymerization is conducted in a monomer medium rather than in water, usually employing a series of two or more continuous reactors. The rubber used in this process is most commonly a solution polymerized linear polybutadiene (or copolymer containing sytrene), although some mass processes utilize emulsion-polymerized ABS with a high rubber content for the rubber component (119). If a linear rubber is used, a solution of the rubber in the monomers is prepared for feeding to the reactor system. If emulsion ABS is used as the source of rubber, a dispersion of the ABS in the monomers is usually prepared after the water has been removed from the ABS latex.

In the mass process (120) using linear rubber, the rubber initially dissolved in the monomer mixture will phase separate, forming discrete rubber particles as SAN polymerization procedes. This process is referred to as phase inversion since the continuous phase shifts from rubber to SAN during the course of polymerization. Special reactor designs are used to control to phase inversion portion of the reaction (111,113–116). By controlling the shear rate in the reactor, the rubber particle size can be modified to optimize properties. Grafting of some of the SAN onto the rubber particles occurs as in the emulsion process. Typically, the mass-produced rubber particles are larger than those of emulsion-based ABS and contain much larger internal occlusions of SAN. The reaction recipe can include polymerization initiators, chain-transfer agents, and other additives. Diluents are sometimes used to reduce the viscosity of the monomer and polymer mixture to facilitate processing at high conversion. The product from the reactor system is devolatilized to remove the unreacted monomers and is then pelletized. Equipment used for devolatilization includes single- and twin-screw extruders, and flash and thin film/strand evaporators. Unreacted monomers are recovered for recycled back to the reactors to improve the process yield.

The mass ABS process was originally adapted from the mass polystyrene process (121). Mass produced ABS typically has very good unpigmented color and is usually somewhat more translucent because of the large rubber phase particle size and low rubber content. Increased translucency can reduce the concentration of colorants required. The extent of rubber incorporation is limited to approximately 20% because of viscosity limitations in the process; however, the mass-produced grafted rubber can be more efficient (on an equal percent rubber basis) at impact modification than emulsion-grafted rubber because of the presence of high occlusion levels in the rubber phase. The surface gloss of the mass-produced ABS is generally lower than that of emulsion ABS because of the presence of the larger rubber particles, but recent advances provide additional flexibility to achieve higher gloss (111–115).

4.9. Suspension Process. The suspension process utilizes a mass (122) or emulsion reaction (123,124) to produce a partially converted mixture of polymer and monomer and then employs a suspension process (125) to complete the polymerization. When the conversion of the monomers is approximately 15–30% complete, the mixture of polymer and unreacted monomers is suspended in water with the introduction of a suspending agent. The reaction is continued until a high degree of monomer conversion is attained and then unreacted monomers are stripped from the product before the slurry is centrifuged and dried producing product in the form of small beads. The morphology and properties of the mass suspension product are similar to those of the mass-polymerized product. The suspension process retains some of the process advantages of the water-based emulsion process, such as lower viscosity in the reactor and good heat removal capability.

4.10. Compounding. ABS either is sold as an unpigmented product, in which case the customer may add pigments during the forming process, or it is colored by the manufacturer prior to sale. Much of the ABS produced by the mass process is sold unpigmented; however, precolored resins provide advantages in color consistency. If colorants, lubricants, fire retardants, glass fibers, stabilizers, or alloying resins are added to the product, a compounding operation is required. ABS can be compounded on a range of equipment, including batch and continuous melt mixers, and both single- and twin-screw extruders. The device must provide sufficient dispersive and distributive mixing dependent on formulation ingredients for successful compounding, and low work or low shear counterrotating twin-screw extruders as used in PVC are not recommended. In the compounding step, more than one type of ABS may be employed (ie, emulsion and mass-produced) to obtain an optimum balance of properties for a specific application. Products can also be made in the compounding process by combining emulsion ABS having a high rubber content with mass- or suspension-polymerized SAN.

5. Processing

Good thermal stability plus shear thinning allow wide flexibility in viscosity control for a variety of processing methods. ABS exhibits non-Newtonian viscosity behavior. For example, raising the shear rate one decade from 100/s to 1000/s (typical in-mold shear rates) reduces the viscosity by 75% on a general purpose injection molding grade. Viscosity can also be reduced by raising melt temperature; typically increasing the melt temperature 20 to 30°C within the allowable processing range reduces the melt viscosity by about 30%. ABS can be processed by all the techniques used for other thermoplastics: compression and injection molding, extrusion, calendering, and blow-molding (see PLASTICS PROCESSING). Clean, undegraded regrind can be reprocessed in most applications (plating excepted), usually at 20% with virgin ABS. Postprocessing operations include cold forming; thermoforming; metal plating; painting; hot stamping; ultrasonic, spin, and vibrational welding; and adhesive bonding.

5.1. Material Handling and Drying. Although uncompounded powders are available from some suppliers, most ABS is sold in compounded pellet form. The pellets are either precolored or natural to be used for in-house coloring using dry or liquid colorants or color concentrates. These pellets have a variety of shapes including diced cubes, square and cylindrical strands, and spheroids. The shape and size affect several aspects of material handling such as bulk density, feeding of screws, and drying (qv). Very small particles called fines can be present as a carryover from the pelletizing step or transferring operations; these tend to congregate at points of static charge build up. Certain additives can be used to control static charges on pellets (126).

ABS is mildly hygroscopic. The moisture diffuses into the pellet and moisture content is a reversible function of relative humidity. At 50% relative humidity typical equilibrium moisture levels can be between 0.3 and 0.6% depending on the particular grade of ABS. In very humid situations moisture content can be double this value. Although there is no evidence that this moisture causes degradation during processing, drying is required to prevent voids and splay (127) and achieve optimum surface appearance. Drying down to 0.1% is usually sufficient for general purpose injection molding and 0.05% for critical applications such as plating. For nonvented extrusion and blow-molding operations a maximum of 0.02% is required for optimum surface appearance.

Desiccant hot air hopper dryers are recommended, preferably mounted on the processing equipment. Tray driers are not recommended, but if used the pellet bed should be no more than 5 cm deep. Many variables affect drying rates (128,129); the pellet temperature has a stronger effect than the dew point. Most pellet drying problems can be a result of actual pellet temperatures being too low in the hopper. Large particles dry much more slowly than pellets, thus regrind should be protected from moisture regain. Supplier data sheets should be consulted for specific drying conditions. Several devices are available commercially for analytically determining moisture contents in ABS pellets (130–132). Alternatives to pellet drying are vented injection molding (133) and cavity-air pressurization (counterpressure) (134).

5.2. Injection Molding. *Equipment.* Although plunger machines can be used, the better choice is the reciprocating screw injection machine because of better melt homogeneity. Screws with length-to-diameter ratios of 20:1 and a compression ratio of 2–3:1 are recommended. General purpose screws vary significantly in number and depth of the metering flights; long and shallow metering zones can create melt temperature override which is particularly undesirable with flame-retardent (FR) grades of ABS. Screws with a generous transition length perform best because of better melting rate control (135). Good results have been realized with a long transition “zero-meter” screw design (136). Some comments on the performance of general purpose and two-stage vented screws used for coloring with concentrates is given in reference 137. Guidelines for nozzle and nonreturn valve selection as well as metallurgy are given in references 138 and 139. Gas-nitrided components should be avoided; ion-nitrided parts are acceptable.

A variety of mold types can be used: two plate, three plate, stack, or runnerless. Insulated runner molds are not recommended. If heated torpedoes are used with hot manifold molds, they should be made from a good grade of stainless steel and not from beryllium copper. Molds are typically made from P-20, H-13, S-7, or 420 stainless; chrome or electroless plating is recommended for use with FR grades of ABS. Mold cavities should be well vented (0.05 mm deep) to prevent gas burns. Polished, full round, or trapezoidal runners are recommended; half or quarter round runners are not. Most conventional gating techniques are acceptable (138,139). On polished molds a draft angle of 0.5° is suggested to ease part ejection; side wall texturing requires an additional 1° per 0.025 mm of texture depth. Mold shrinkage is typically in the range of 0.5 to 0.9% (0.005

to 0.009 cm/cm) depending on grade, and the shrinkage value for a given grade can vary much more widely than this because of the design of parts and molding conditions.

Processing Conditions. Certain variables should be monitored, measured, and recorded to aid in reproducibility of the desired balance of properties and appearance. The individual ABS suppliers provide data sheets and brochures specifying the range of conditions that can be used for each product. Relying on machine settings is not adequate. Identical cylinder heater settings on two machines can result in much different melt temperatures. Therefore, melt temperatures should be measured with a fast response hand pyrometer on an air shot recovered under normal screw rpm and back-pressure. Melt temperatures range from 218 to 268°C depending on the grade. Generally, the allowable melt temperature range within a grade is at least 28°C. Excessive melt temperatures cause color shift, poor gloss control, and loss of properties. Similarly, a fill rate setting of 1 cm/s ram travel will not yield the same mold filling time on two machines of different barrel size. Fill time should be measured and adjusted to meet the requirements of getting a full part, and to take advantage of shear thinning without undue shear heating and gas burns. Injection pressure should be adjusted to get a full part free of sinks and good definition of gloss or texture. Hydraulic pressures of less than 13 MPa (1900 psi) usually suffice for most molding. Excessive pressure causes flash and can result in loss of some properties. Mold temperatures for ABS range from 27 to 66°C (60 to 82°C for high heat grades). The final properties of a molded part can be influenced as much by the molding as by the grade of ABS selected for the application (140). The factors in approximate descending order of importance are polymer orientation, heat history, free volume, and molded-in stress. Izod impact strength can vary severalfold as a function of melt temperature and fill rate because of orientation effects, and the response curve is ABS grade dependent (141). The effect on tensile strength is qualitatively the same, but the magnitude is in the range of 5 to 10%. Modulus effects are minimal. Orientation distribution in the part is very sensitive to the flow rate in the mold; therefore, fill rate and velocity-to-pressure transfer point are important variables to control (142). Dart impact is also sensitive to molding variables, and orientation and thermal history can also be key factors (143). Heat deflection temperature can be influenced by packing pressure (144) because of free volume considerations (145). The orientation on the very surface of the part results from an extensionally stretching melt front and can have deleterious effects on electro-plate adhesion and paintability. A phenomenon called the mold-surface-effect, which involves grooving the nonappearance half of the mold, can be employed to reduce unwanted surface orientation on the noncorresponding part surface (146–148). Other information regarding the influence of processing conditions on part quality are given in references 149–153.

Part Design. For optimum economics and production cycle time, wall thicknesses for ABS parts should be the minimum necessary to satisfy service strength requirements. The typical design range is 0.08 to 0.32 cm, although parts outside this range have been successfully molded. A key principle that guides design is avoiding stress concentrators such as notches and sharp edges. Changes in wall thickness should be gradual, sharp corners should be avoided, and generous radii (25% of the wall thickness) used at wall intersections with ribs and bosses. To avoid sinks, rib thickness should be between 50 and 75% of the nominal wall. Part-strength at weld lines can be diminished; thus welds should be avoided if possible or at least placed in noncritical areas of the part (154). Because of polymer orientation, properties such as impact strength vary from point to point on the same part and with respect to the flow direction (140). Locations of highest Izod impact strength can be points of lowest dart impact strength because of the degree and direction of orientation. ABS suppliers can provide assistance with design of parts upon inquiry and through design manuals (155). There are a number of special considerations when designing parts for metal plating to optimize the plating process, plate deposition uniformity, and final part quality (156). ABS parts can be also designed for solid–solid or solid–foam co-injection molding (157) and for gas-assisted-injection molding (158).

5.3. Extrusion. *Equipment.* Since moisture removal is even more critical with extrusion than injection molding, desiccant hot-air hopper drying of the pellets to 0.02% moisture is essential for optimum properties and appearance. The extruder requirements are essentially the same for pipe, profile, or sheet. Two-stage vented extruders are preferred since the improved melting control and volatile removal can provide higher rates and better surface appearance. Barrels are typically 24:1 minimum L/D for single-stage units and 24 or 36:1 for two-stage vented units. The screws are typically 2:1 to 2.5:1 compression ratio and single lead, full flighted with a 17.7° helix angle. Screen packs ($20 - 40$ mesh $= 840 - 420$ μm) are recommended.

For sheet, streamlined coat-hanger type dies are preferred over the straight manifold type. Typically, three highly polished and temperature controlled rolls are used to provide a smooth sheet surface and control thickness (159). Special embossing rolls can be substituted as the middle roll to impart a pattern to the upper surface of the sheet. ABS and non-ABS films can be fed into the polishing rolls to provide laminates for special applications, eg, for improved weatherability, chemical resistance, or as decoration. Two rubber pull rolls, speed synchronzied with the polishing rolls, are located far enough downstream to allow sufficient cooling of the sheet; finally, the sheet goes into a shear for cutting into lengths for shipping.

Pipe can be sized using internal mandrels with air pressure contained by a downstream plug or externally using a vacuum bushing and tank. Cooling can be done by immersion, cascade, or mist. Water temperatures of 41 to 49°C at the sizing zone reduce stresses. Foamcore pipe has increased in market acceptance significantly over the last few years, and cooling unit lengths must be longer than for solid pipe. Drawdown should not exceed 10 to 15%.

Profile dies can be flat plates or the streamline type. Flat plate dies are easy to build and inexpensive but can have dead spots that cause hang-up, polymer degradation, and shutdowns for cleaning. Streamlined, chrome-plated dies are more expensive and complicated to build but provide for higher rates and long runs. The land length choice represents a tradeoff; long lands give better quality profile and shape retention but have high pressure drops that affect throughput. Land length to wall thickness ratios are typically 10:1. Drawdown can be used to compensate for die swell but should not exceed 25% to minimize orientation.

Sizing jigs vary in complexity depending on profile design; water mist, fog, or air cooling can be used. The latter gives more precise sizing. Also, water immersion vacuum sizing can be used. Accurate, infinitely adjustable speed control is important to the takeoff end equipment to guarantee dimensional control of the profile.

With sheet or pipe, multilayer coextrusion can be used. Solid outer-solid core coextrusion can place an ABS grade on the outside that has special attributes such as color, dullness, chemical resistance, static dissipation, or fire-retardancy over a core ABS that is less expensive or even regrind. Composites can be created in which the core optimizes desired physical properties such as modulus, whereas the outer layer optimizes surface considerations not inherent in the core material. Solid outer–foam core can provide composites with significant reductions in specific gravity (0.7). Dry blowing agents can be “dusted” onto the pellets or liquid agents injected into the first transition section of the extruder.

Extrusion processing conditions vary depending on the ABS grade and application; vendor bulletins should be consulted for details. Information for assistance in troubleshooting extrusion problems can be found in Reference 160.

5.4. Calendering. The rheological characteristics of the sheet extrusion grades of ABS easily adapt them to calendering to produce film from 0.12 to 0.8 mm thick for vacuum forming or as laminates for sheet. The advantages of this process over extrusion are the capability for thinner gauge product and quick turnaround for short runs.

5.5. Blow Molding. Although ABS has been blow molded for over 20 years, this processing method has been gaining popularity recently for a variety of applications (161). Better blow-molding grades of ABS are being provided by tailoring the composition and rheological characteristics specifically to the process. Whereas existing polyolefin equipment can often be easily modified and adjusted to mold ABS, there are some key requirements that require attention.

Pellet predrying is required down to 0.02 to 0.03% moisture. High shear polyolefin screws must be replaced with low shear 2.0:1 to 2.5:1 screws with L/D ratios of 20:1 to 24:1 to keep the melt temperature in the 193 to 221°C optimum range. The land length of the tooling can be reduced to 3:1–5:1 because ABS shows less die swell; this also helps to reduce the melt pressure resulting from the higher viscosity. The accumulator tooling should be streamlined to reduce hang-up and improve re-knit, and be capable of handling the higher pressures required with large programmed parisons. Mold temperatures of 77 to 88°C provide good surface finish. It is recommended that the material vendor be consulted to confirm equipment capability and provide safety and processing information (162).

5.6. Secondary Operations. *Thermoforming.* ABS is a versatile thermoforming material. Forming techniques in use are positive and negative mold vacuum forming, bubble and plug assist, snapback and single- or twin-sheet pressure forming (163). It is easy to thermoform ABS over the wide temperature range of 120 to 190°C. As-extruded sheet should be wrapped to prevent scuffing and moisture pickup. Predrying sheet that has been exposed to humid air prevents surface defects; usually 1 to 3 h at 70–80°C suffices. Thick sheet should be heated slowly to prevent surface degradation and provide time for the core temperature to reach the value needed for good formability. Relatively inexpensive tooling can be made from wood, plaster, epoxies, thermoset materials, or metals. Tools should have a draft angle of 2° to 3° on male molds and ½° to 1° on female molds. More draft may be needed on textured molds. Vacuum hole diameters should not exceed 50% of the sheet thickness. Mold design should allow for 0.003 to 0.008 cm/cm mold shrinkage; exact values depend on mold configuration, the material grade, and forming conditions. Maximum depth of draw is usually limited to part width in simple forming, but more sophisticated forming techniques or relaxed wall uniformity requirements can allow greater draw ratios. Some definitions for draw ratios are given in Reference 164. Pressure forming, with well-designed tools, can make parts approaching the appearance and detailing obtained by injection molding. Additional information on pressure forming is given in Reference 165.

Cold Forming. Some ABS grades have ductility and toughness such that sheet can be cold formed from blanks 0.13–6.4 mm thick using standard metalworking techniques. Up to 45% diameter reduction is possible on the first draw; subsequent redraws can yield 35%. Either aqueous or nonaqueous lubrication is required. More details are available in Reference 166.

5.7. Other Operations. *Metallizing.* ABS can be metallized by electroplating, vacuum deposition, and sputtering. Electroplating (qv) produces the most robust coating; progress is being made on some of the environmental concerns associated with the chemicals involved by the development of a modified chemistry. An advantage to sputtering is that any metal can be used, but wear resistance is not as good as with electroplating. Attention must be paid to the molding and handling of the ABS parts since contamination can affect plate adhesion, and surface defects are magnified after plating. Also, certain aspects of part design become more important with plating; these are covered in References 147 and 156 (see also ELECTROLESS PLATING; METALLIC COATINGS).

Fastening, Bonding, and Joining. Often parts can be molded with various snap-fit designs (167) and bosses to receive rivets or self-tapping screws. Thermal-welding techniques that are easily adaptable to ABS are spin welding (168), hot plate welding, hot gas welding, induction welding, ultrasonic welding, and vibrational welding (169,170). ABS can also be nailed, stapled, and riveted. There are a variety of adhesives and solvent cements for bonding ABS to itself or other materials such as wood, glass, and metals; for more information, contact the material or adhesives suppliers. Joining ABS with materials of different coefficients of thermal expansion requires special considerations when wide temperature extremes are encountered. An excellent review of joining methods for plastics is given in Reference 171.

6. Economic Aspects

6.1. Capacity. Estimated ABS capacity worldwide in 2000 is given in Table 2 (172). Accurate ABS capacity figures are difficult to obtain because significant production capability is considered “swing” and can be used to manufacture polystyrene or SAN as well as ABS. From a regional standpoint, Asia-Pacific has the largest ABS nameplate production capability at 3977 t. The United States has approximately 17% of the world’s capacity at 1068 t. Most suppliers

Table 2. **Worldwide Capacity for ABS Plastics 1994–2000 by Region, 10^3 t**

Region	1994	1995	1996	1997	1998	1999	2000
Western Europe	841	838	865	882	1000	1000	990
Eastern Europe	80	80	81	81	82	82	82
Africa	0	0	0	0	0	0	0
North America	931	894	894	934	1083	1098	1098
Latin America	128	115	127	129	126	230	267
Middle East	0	0	0	0	0	0	0
Asia-Pacific	2130	2535	3158	3292	3712	3857	3977
Total	*4110*	*4462*	*5125*	*5318*	*6003*	*6267*	*6414*

have multiple facilities with the largest producers regionally being GE in North America, Bayer in Europe, and Chi Mei in the Pacific. As shown in Table 3, these three producers account for almost 50% of the world's capacity (172).

Table 4 lists the current U.S. producers of ABS and their capacities. The ABS resin is produced by either continuous mass (or bulk) suspension or emulsion polymerization. ABS contains over 50% styrene and varying amounts of butadiene and acrylonitrile. Some production is from swing capacity. ABS is the largest volume engineering thermoplastic. High impact polystyrene has become almost as expensive as ABS so some manufacturers have changed back to ABS resins (173).

ABS growth in 2002 was 2–4% due in part to new applications in recreational vehicles, solid automotive and appliance business, and increased activity in building and construction. The rise in the price of oil has impacted the

Table 3. **World Capacity of Leading ABS Producers**

Producer	2000 Capacity, 10^3 t	Largest producer in
GE Plastics	855	North America
Bayer	766	Europe
Chi Mei Industrial	1120	Pacific

Table 4. **Producers of ABS Resins and their Capacities**[a] **$\times 10^6$ kg ($\times 10^6$ lb)**

Producer	Capacity
Bayer, Addyston, Ohio	209 (450)
Diamond Polymers, Akron, Ohio	23 (50)
Dow, Allyn's Point, Conn.	25 (55)
Dow, Hanging Rock, Ohio	64 (140)
Dow, Midland, Mich.	88 (195)
GE Plastics, Bay St. Louis, Miss.	177 (280)
GE Plastics, Ottawa, Ill.	215 (475)
GE Plastics, Washington, W.Va.	73 (160)
Total	*819 (1805)*

[a] Ref. 174.

feedstock costs. The market has evolved into general purpose ABS and higher engineered products. Growth is expected at the rate of 2.4% annually.

Demand in 2001 was 0.58×10^9 kg (1.27×10^9 lb). Projected demand for 2005 is 0.63×10^9 kg (1.40×10^9 lb). In recent years U.S. exports have declined as new production in the Far East came on line. The Far East represents 70% of consumption, North America, 15% (173). Demand is expected to grow at an annual rate of 15% from 2000–2005 (174).

6.2. Price. Price history for 1996–2001: \$0.31–0.50/kg (\$0.69–\$1.04/lb) tl, delvd, market high impact injection molding grade. Current \$0.33–0.39/kg (\$0.72–0.85/lb same basis) (173).

7. Analytical Methods

Analytical investigations may be undertaken to identify the presence of an ABS polymer, characterize the polymer, or identify nonpolymeric ingredients. Fourier transform infrared (ftir) spectroscopy is the method of choice to identify the presence of an ABS polymer and determine the acrylonitrile–butadiene–styrene ratio of the composite polymer (175,176). Confirmation of the presence of rubber domains is achieved by electron microscopy. Comparison with available physical property data serves to increase confidence in the identification or indicate the presence of unexpected structural features. Identification of ABS via pyrolysis gas chromatography (177) and dsc (178) has also been reported.

Detailed compositional and molecular weight analyses involve: determining the percentage of grafted rubber; determining the molecular weight and distribution of the grafted SAN and the ungrafted SAN; and determining compositional data on the grafted rubber, the grafted SAN, and the ungrafted SAN. This information is provided by a combination of phase-separation and instrumental techniques. Separation of the ungrafted SAN from the graft rubber is accomplished by ultracentrifugation of ABS dispersions (179,180) which causes sedimentation of the grafted rubber. Cleavage of the grafted SAN from the elastomer is achieved using oxidizing agents such as ozone [10028-15-6] (180,181), potassium permanganate [7722-64-7] (182), or osmium tetroxide [20816-12-0] with *tert*-butylhydroperoxide [75-91-2] (183). Chromatographic and spectroscopic analyses of the isolated fractions provide structural data on the grafted and ungrafted SAN components (184). Information on the microstructure of the rubber is provided by analysis of the cleavage products derived from the substrate (94,96). The extraction of ungrafted rubber has also been reported (185).

Additional information on elastomer and SAN microstructure is provided by ^{13}C-nmr analysis (186). Rubber particle composition may be inferred from glass-transition data provided by thermal or mechanochemical analysis. Rubber particle morphology as obtained by transmission or scanning electron microscopy (187) is indicative of the ABS manufacturing process (77). (See Figs. 1 and 2.)

The isolation and/or identification of nonpolymerics has been described, including analyses for residual monomers (176,188,189) and additives (176,190–192). The determination of localized concentrations of additives within the phases of ABS has been reported; the partitioning of various additives

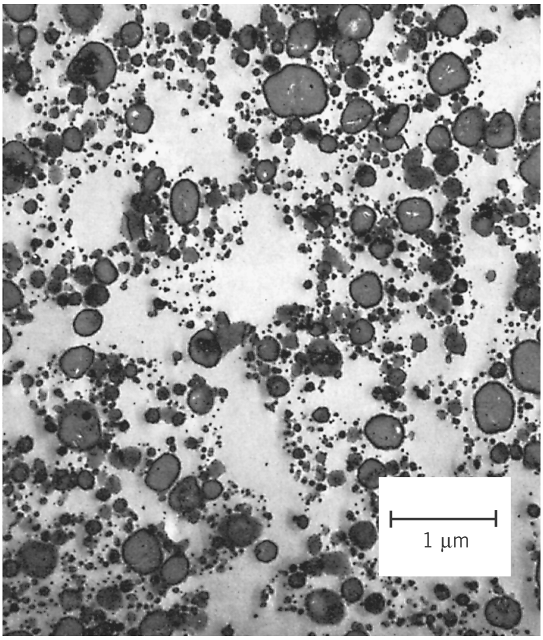

Fig. 1. Transmission electron micrograph of ABS produced by an emulsion process. Staining of the rubber bonds with osmium tetroxide provides contrast with the surrounding SAN matrix phase.

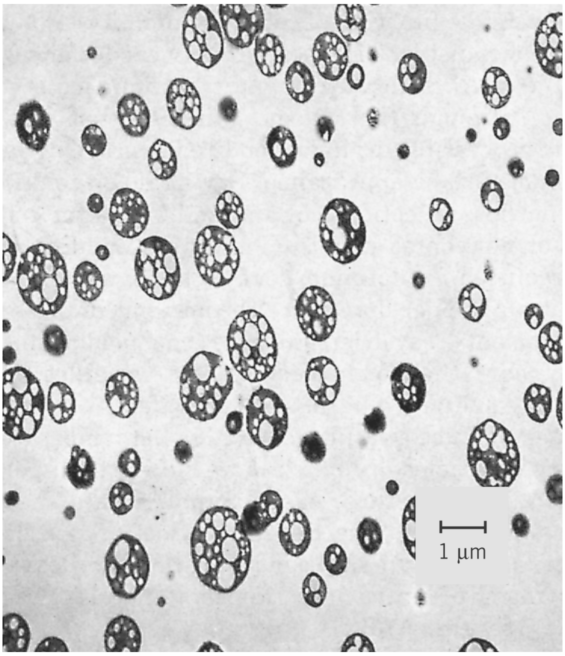

Fig. 2. Transmission electron micrograph of ABS produced by a mass process. The rubber domains are typically larger in size and contain higher concentrations of occluded SAN than those produced by emulsion technology.

between the elastomeric and thermoplastic phases of ABS has been shown to correlate with solubility parameter values (41).

8. Health and Safety Aspects

ABS is a questionable carcinogen. When heated to decomposition, it emits toxic vapors of nitrogen oxide and CN. These products are highly toxic when inhaled (193).

9. Uses

Its broad property balance and wide processing window has allowed ABS to become the largest selling engineering thermoplastic. ABS enjoys a unique position as a "bridge" polymer between commodity plastics and other higher performance engineering thermoplastics.

In 2002 the largest market for ABS resins worldwide was for appliances (23%). The majority of this consumption was for major appliances; extruded/thermoformed door and tank liners lead the way. Transparent ABS grades are also used in refrigerator crisper trays. Other applications in the appliance market include injection-molded housings for kitchen appliances, power tools, vacuum sweepers, sewing machines, and hair dryers. Transportation was the second largest market (21%). Uses are numerous and include both interior and exterior applications. Interior injection-molded applications account for the greatest volume. General purpose and high heat grades have been developed for automotive instrument panels, consoles, door post covers, and other interior trim parts. ABS resins are considered by many the preferred material for components situated above the "waistline" of the car. Exterior applications include radiator grilles, headlight housings, and extruded/thermoformed fascias for large trucks. ABS plating grades also account for significant ABS sales and include applications such as knobs, light bezels, mirror housings, grilles, and decorative trim. ABS in disks for brakes has been reported (194).

Pipe and fittings remain a significant market for ABS at 13%, particularly in North America. ABS foam core technology allows ABS resin to compete effectively with PVC in the primary drain-waste and vent (DWV) pipe market.

A large "value-added" market for ABS is business machines and other electrical and electronic equipment at 11%. Although general purpose injection-molding grades meet the needs of applications such as telephones and micro floppy disk covers, significant growth exists in more demanding flame-retardant applications such as computer housings and consoles.

The use of recycled ABS resin in electric and electronic applications has been reported (195).

Medical application accounted for 4% of use. Miscellaneous applications included toys, luggage, lawn and garden products, shower stalls, furniture and ABS resin blends with other polymers. Miscellaneous uses accounted for 28% of consumption (174).

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