ACRYLONITRILE–BUTADIENE–STYRENE POLYMERS

Introduction

Acrylonitrile–butadiene–styrene (ABS) polymers [9003-56-9] comprise a versatile family of readily processable resins used for producing products exhibiting excellent toughness, good dimensional stability, and good chemical resistance. Special product features can also be obtained such as transparency, unique coloration effects, higher heat performance, and flame retardancy. ABS is comprised of particulate rubber, usually polybutadiene or a butadiene copolymer, dispersed in a thermoplastic matrix of styrene and acrylonitrile copolymer (SAN) [9003-54-7]. The presence of SAN chemically attached or “grafted” to the elastomeric particles compatibilizes the rubber with the SAN component. Altering structural and compositional parameters allows considerable versatility in the tailoring of properties to meet specific product requirements.

Physical Properties

Typical mechanical properties of some commercially available ABS materials are listed in Table 1. It is indicated that a wide range of mechanical and impact properties are achievable for ABS materials.

These property variations are obtained through comonomers, additives, or by making structural changes such as the following: rubber content, extent of rubber cross-linking, rubber particle size and distribution, grafted SAN level and composition, and the composition and molecular weight of the matrix. Depending on the polymerization technique, SAN can be controlled to varying levels as the continuous phase, as grafted polymer attached to the rubber particles, and as
Table 1. Material Properties of ABS Grades

<table>
<thead>
<tr>
<th>Properties</th>
<th>ASTM method</th>
<th>Medium impact</th>
<th>High impact</th>
<th>Heat resistant</th>
<th>Flame retardant</th>
<th>High modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Notched Izod impact at rt, J/m&lt;sup&gt;b&lt;/sup&gt;</td>
<td>D256</td>
<td>160–270</td>
<td>270–530</td>
<td>75–300</td>
<td>140–320</td>
<td>50–150</td>
</tr>
<tr>
<td>Tensile yield strength, MPa&lt;sup&gt;c&lt;/sup&gt;</td>
<td>D638</td>
<td>35–50</td>
<td>30–45</td>
<td>35–60</td>
<td>35–45</td>
<td>65–95</td>
</tr>
<tr>
<td>Flexural yield strength, MPa&lt;sup&gt;c&lt;/sup&gt;</td>
<td>D790</td>
<td>55–75</td>
<td>50–75</td>
<td>55–90</td>
<td>55–75</td>
<td>95–160</td>
</tr>
<tr>
<td>Flexural modulus, GPa&lt;sup&gt;d&lt;/sup&gt;</td>
<td>D790</td>
<td>2–3</td>
<td>1.5–2.5</td>
<td>2–3</td>
<td>2–2.5</td>
<td>4–9</td>
</tr>
<tr>
<td>Heat deflection&lt;sup&gt;e&lt;/sup&gt;, °C at 1825 kPa&lt;sup&gt;f&lt;/sup&gt;</td>
<td>D648</td>
<td>75–90</td>
<td>75–85</td>
<td>90–110</td>
<td>70–80</td>
<td>95–105</td>
</tr>
<tr>
<td>Vicat softening pt, °C</td>
<td>D1525</td>
<td>100–110</td>
<td>95–105</td>
<td>110–125</td>
<td>85–100</td>
<td>100–110</td>
</tr>
</tbody>
</table>

<sup>a</sup>Filled with ~10–30% glass.
<sup>b</sup>To convert J/m to ft·lbs/in., divide by 53.4.
<sup>c</sup>To convert MPa to psi, multiply by 145.
<sup>d</sup>To convert GPa to psi, multiply by 145,000.
<sup>e</sup>Unannealed at 6.35-mm thickness.
<sup>f</sup>To convert kPa to psi, multiply by 0.145.

occlusions contained within the rubber particles. Thus, both the rubber content and the “rubber phase” (defined as rubber that may contain occluded SAN) volume fraction at a given rubber weight fraction can be independently controlled. Because of the capability to vary such structural and compositional parameters for property enhancements, ABS is a versatile engineering thermoplastic that can be customized to provide a wide range of mechanical and flow properties.

**Structural and Compositional Effects.** Being a multiphase polymer blend, the effects of the compositional and structural features in ABS are complex and interdependent. However, to a first approximation, the rubber phase contributes toughness, the styrene component contributes rigidity and processability, and the acrylonitrile (AN) phase contributes chemical resistance.

**Effect of Dispersed Rubber Phase.** The impact toughness of ABS is one of many properties affected by the rubber phase volume fraction, particle size and size distribution, and structure. SAN alone is quite brittle—it is the presence of the uniformly distributed rubber phase (ranging in size from 50 to 2000 nm) that imparts the ductility observed in ABS resins. It is widely reported that rubber particles induce plastic deformation in the SAN phase on a microscopic scale in the form of crazing and shear yielding accompanied (in most cases) by rubber voiding (1–4). A maximum in impact energy seems to occur when the micro deformation process is dominated by shear yielding at the deformation rates involved. The impact strength of ABS increases with rubber phase content usually leveling off at ~30% rubber by weight. Most commercial ABS resins have a rubber content in the range of 10–35 wt%. The volume fraction of the rubber phase at a given rubber level can be much higher for products manufactured by the mass (or sometimes termed a “bulk ABS”) vs emulsion process because of the much higher level of occluded SAN produced in the mass process (see Figs. 1 and 2).
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. To convert J/m² to ft-lbf/in.², divide by 2100.

The rubber phase size and size distribution is also affected by the manufacturing process. Typically, the size of the rubber phase averages ~200–400 nm for resin produced by an emulsion process and ~1000–2000 nm for resin produced by mass polymerization. The size distribution of the rubber particles can be very broad, narrow monomodal, or bimodal. The dependence of the impact toughness of ABS on rubber phase particle size and size distribution can be of a complex nature because of the interactions with the graft interface. A maximum impact is reported (1) to occur for emulsion ABS at a mean rubber particle size of about 300 nm for a matrix SAN containing 25% AN.

It has been reported (5) that the elastic modulus of ABS resins prepared by either mass or emulsion polymerization can be represented by a single relationship with the dispersed phase volume fraction. This is in agreement with the theory that the modulus of a blend with dispersed spherical particles depends only on the volume fraction and the modulus ratio of particles to matrix phase. Since the modulus of rubber is almost 1000 times smaller than the modulus of the matrix SAN, the rubber particle volume fraction alone is the most important parameter controlling modulus values of ABS resins. Even for rubber particles containing a high occlusion level, as in ABS produced by mass polymerization, the modulus of the composite particle still remains unchanged from pure rubber, suggesting a unique relationship between modulus and dispersed phase volume fraction. Also, the modulus of a material is a small strain elastic property and is independent of particle size in ABS. The effects of rubber content on modulus and on tensile
Fig. 2. Transmission electron micrograph of ABS produced by a mass process. The rubber domains are typically larger in size and contain a higher concentration of occluded SAN than those produced by emulsion technology. To convert J/m to ft-lbf/in., divide by 53.4.

Fig. 3. Effect of rubber content on tensile and flexural modulus of emulsion ABS. The rubber particle volume fraction alone is the most important parameter controlling the modulus values of ABS. • Tensile mod and ■ flex mod.

and flexural yield stress are shown in Figures 3 and 4 for an emulsion produced ABS. As illustrated, the tensile and flexural yield stress values are also strongly affected by the rubber volume fraction, although—unlike modulus—the stress values are not independent of rubber particle size. It is known that tensile yield stress decreases at a given rubber volume fraction with an increase in particle
diameter; this behavior is explained on the basis of having an increased volume of matrix SAN under higher stress near rubber particles (6).

**Effect of Matrix SAN Composition and Molecular Weight.** At a given rubber content and grafted rubber particle size and distribution, the mechanical properties of ABS are also strongly affected by the molecular weight and composition of the SAN present as the continuous, matrix phase. Increasing the molecular weight of the matrix SAN increases impact toughness, an effect which tends to level off at molecular weights higher than a number-average molecular weight ($M_n$) of $\sim 60,000$. If the SAN $M_n$ is less than 25,000, no significant amount of crazing deformation is indicated, and therefore, no significant toughening takes place with rubber addition. Yield stress and modulus values of ABS appear to be independent of the molecular weight of the SAN, consistent with the observation that the craze initiation stress value for SAN is independent of molecular weight above an $M_n$ of $\sim 25,000$ (7). A similar relationship between craze initiation stress and molecular weight has been reported for polystyrene (8).

The AN content of SAN has a significant influence on the environmental stress-cracking resistance of ABS, and it is generally observed that increasing AN content increases the stress-cracking resistance of ABS. Most general-purpose ABS materials contain SAN with AN content of 20–30%, whereas improved chemical resistance ABS grades employ SAN with AN content of about 35%. It is also indicated that AN in SAN improves the crazing resistance of SAN, which can explain the increased ductility of ABS as compared to rubber-modified polystyrene (high impact polystyrene). Creep and fatigue performance also improve as the AN content of the SAN is increased. In addition to the AN content of SAN matrix, the AN content of the grafted SAN plays an important role in ABS materials prepared by the melt blending of grafted rubber with SAN pellets. If the difference between AN levels of matrix SAN and grafted SAN is over 5%, some immiscibility and partial phase separation can take place (9), which can cause rubber aggregation during compounding and processing steps. Surface gloss of final article may
be lowered although mechanical properties and impact toughness can be maintained with an AN mismatch of as high as 10% between the grafted SAN and matrix SAN. Surface appearance can also be affected if two different matrix SAN components having a differing AN content are mixed because of the surface of the molded part becoming enriched with the SAN of lower AN content (10).

**Effect of Grafted SAN.** The extent of grafting is a critical parameter as well. If the level of grafted SAN is lowered, a nonuniform dispersion of rubber may occur, affecting toughness and aesthetic properties (eg, gloss). Furthermore, the rubber aggregates will also have an increased tendency to undergo deformation during processing, resulting in the loss of toughness, mechanical, and aesthetic properties. In commercial ABS materials, SAN molecular weight and composition, graft amount, and rubber particle size and structure are properly balanced to achieve an optimal balance of mechanical properties, toughness, melt viscosity, and aesthetics.

**Rheology.** The ABS manufacturer controls rheological properties through structure variations which can have a complex effect dependent on shear rate. Effects of structural variations on viscosity functions are more evident at lower shear rates (<10/s) vs higher shear rates. At high shear rates, the melt viscosity is controlled primarily by the composition and molecular weight of the ungrafted SAN and by the percentage of the grafted rubber 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 (11). The extrudate swell, however, becomes smaller with increasing rubber concentration (12).

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 (13,14), 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 (14). At low shear rates, the associated rubber particles behave similar 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 (11–18). Effects of lubricants and other nonpolymeric components have also been described (19). Techniques for characterizing melt-flow differences include melt-flow rate, melt index, spiral flow, and capillary rheometry.

High shear rate viscosity (eg, 1000/s) is considered more relevant to injection-molding applications, and, in general, molding grades have lower melt viscosities than extrusion grades. Designers are striving to further reduce costs through thinwall design. ABS exhibits both low melt viscosity and good impact strength, key characteristics making ABS suitable for thinwall applications (20).

**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. Low gloss is achieved either through the use of large rubbery domains, aggregates of smaller rubber particles, or through the addition of dulling agents.

**Thermal Properties.** Higher heat ABS grades are achieved through copolymerization with monomers (eg, alpha methyl styrene or N-phenyl
maleimide) in the matrix phase or through the use of ABS 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 (21).

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

**Transparency.** Standard ABS grades are opaque because of the refractive index mismatch between the dispersed rubber phase and the continuous SAN matrix. However, ABS-type systems are available as transparent grades for clear applications, with transparency achieved by the matching of the refractive index of the rubber and matrix phases through the incorporation of comonomers. Typically, refractive index of the rubber phase is increased through the use of styrene–butadiene rubber and the matrix phase reduced and matched to the rubber phase through terpolymerization with methylmethacrylate.

**Chemical Properties**

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

**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. Environmental stress cracking can be assessed by applying a chemical to a prestressed sample and determining its stress-crack resistance over a specified period of time. As previously discussed, the presence of AN enhances environmental stress-cracking resistance. 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 AN 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 (22).

Similar to most polymers, ABS undergoes stress cracking when brought into contact with certain chemical agents under stress (22,23). 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 (24). Consequently, all media to be in contact with the ABS part during service should be evaluated under anticipated end-use conditions.

**Processing Stability.** Processing can influence resultant properties by chemical and physical means (25,26). Degradation of the rubber and matrix phases has been reported under very severe conditions (27). Morphological changes may become evident as agglomeration of dispersed rubber particles during injection
molding at higher temperatures (26). 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 added at the compounding step have been shown to help retention of physical properties upon processing (25).

Appearance changes evident under certain processing conditions include color development (25), changes in gloss (27), 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 (28,29), injection molding (26,28), capillary rheometry (26,28), and measuring melt index as a function of residence time (25).

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 SAN indicate that the polybutadiene component is significantly more sensitive to oxidation than the thermoplastic component (30–32). Oxidation of polybutadiene under these conditions results in embrittlement of the rubber because of cross-linking and the introduction of polar oxidized groups; such embrittlement of the elastomer in ABS results in the loss of impact strength. Studies have also indicated that oxidation causes detachment of the grafted SAN from the elastomer, which contributes to impact deterioration (33).

Examination of oven-aged samples has demonstrated that substantial degradation is limited to the outer surface (33), i.e., the oxidation process is diffusion limited. Consistent with this conclusion is the observation that oxidation rates are dependent on sample thickness (31). 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 (33). A demonstration of the effects of an embrittled surface on impact was achieved using ABS coated with SAN (34). Rates of oxidation can be significantly affected by additives such as colorants (31).

Test methods for assessing thermal oxidative stability include oxygen absorption (30,31,35), thermal analysis (36,37), oven aging (33,38,39), and chemiluminescence (40,41). Such techniques primarily reflect the reactivity of the rubber component in ABS with oxygen.

Antioxidants have been shown to improve oxidative stability substantially (42,43). Hindered phenols, thiodipropionates, and phosphites can be effective in improving processing or end-use stability (44). In multiphase systems like ABS, stabilizers can partition between the component phases. Thus, the additive concentration in each phase can differ significantly from the added or average concentration potentially influencing additive effectiveness. The use of rubber-bound stabilizers to permit concentration of the additive in the rubber phase has been reported (45–47). Scanning electron microscopy (SEM) using XEDS (energy dispersive x-ray analysis) has been used to determine the partitioning behavior of stabilizers in ABS. The partitioning of various conventional stabilizers between the rubber
and thermoplastic phases has been shown to correlate with solubility parameter values (48).

**Photo-oxidative Degradation.** Unsaturation present as a structural feature in the polybutadiene component of ABS (also in high impact polystyrene, rubber-modified PVC, and ABS–polycarbonate blends) increases lability with regard to photo-oxidative degradation (49–51), which can result in discoloration and loss of impact. Applications involving outdoor exposure require protective measures to maintain an optimum level of performance. Light stabilizers provide some measure of protection (52,53), as illustrated by the very successful use of ABS in interior automotive trim. Colorants have a significant effect on light stability and can either increase or decrease color fastness, depending on colorant type. For extended outdoor exposure, the best protection is provided by a protective coating which can be either paint or a cap layer of a weatherable polymer such as a thermoplastic acrylic, cast acrylic, or ASA (acrylonitrile–styrene–acrylate terpolymer). A cap layer of ASA vs acrylics (PMMA) minimizes brittle surface layer effects. The cap layer is applied by coextrusion over ABS, resulting in a laminate sheet which can be thermoformed into parts providing a favorable balance of cost and part performance that includes excellent weatherability.

The photodegradation of ABS typically occurs in the outermost layer (54,55). Impact loss upon irradiation is due to embrittlement of the rubber and possibly scission of the grafted SAN (49,56). Appearance changes such as yellowing are caused by chromophore formation in both the polybutadiene and SAN components (49,57). Mechanisms describing the photo-oxidative degradation of ABS have been proposed (51,52,58). Oxidation studies with singlet oxygen have shown that initial attack on ABS occurs on the polybutadiene component (59). Weathering studies have been conducted using artificial (60,61) and outdoor exposure (60) conditions. Light wavelength dependence has been studied, and photodegradation of the polybutadiene component has been reported to be primarily initiated by wavelengths below 350 nm (62) but can extend into the visible region (63). For discoloration, photochemical yellowing is caused primarily by wavelengths between 300 and 360 nm, and maximum bleaching of yellow colored species is reported to occur in the 475- to 485-nm region (62). For the above reasons, any spectral difference between accelerated aging and actual exposure could lead to a lack of correlation, affecting predictive capability by accelerated techniques. Xenon arc is preferred vs other test methods (eg, carbon arc, HPUV) because of the closer simulation of the spectral distribution of sunlight by Xenon arc if the appropriate filter combination is used. Oxidative degradation induced by processing may also affect photosensitivity (49,64). A comparative study on the weathering of ABS and other acrylic-based plastics has shown that elastomer type and SAN phase composition are two key factors affecting both color and impact retention (65).

Test methods that have been used to determine the effects of light aging on embrittlement of ABS include Izod impact, Charpy impact, flexural tests, falling dart, and dynamic mechanical measurements. Because photodegradation occurs only on the outer surface and the interior of the sample remains essentially unaffected, a pendulum type of notched impact will not be sensitive to changes in surface embrittlement. Falling dart types of testing increase sensitivity to surface changes; the use of a high speed puncture test has been described for determining the effect of outdoor exposure on crack-initiation energy values for ABS (65).
Flammability. The general-purpose grades are usually recognized as 94 HB according to the requirements of Underwriters’ Laboratories UL94. Flame-retardant (FR) grades (V0, V1, and V2) are also available which meet Underwriters’ UL 94/94 V5 and Canadian Standards Association (CSA) requirements. Flame retardancy is typically achieved by utilizing halogenated additives in combination with antimony oxide or by alloys with PVC or PC (66–68). A wide variety of brominated flame retardants have been used in ABS with tetrabromobisphenol-A (TBBPA) and brominated epoxy oligomers (BEOs), currently in widespread use. Both are melt-blendable and can be well dispersed on most commercial equipment. TBBPA is very cost effective, providing excellent flame retardancy and good flow properties; however, products formulated with TBBPA generally have poorer light stability and a lower heat-deflection temperature. Although TBBPA exhibits low thermal stability, processing is usually not an issue if recommended guidelines are followed. Flame-retardant ABS grades formulated with BEOs are preferred if reduced color shift upon light exposure is required.

Polymerization

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 bonded or “grafted” to the rubber component termed the “substrate.”

Rubber Chemistry. The rubber substrate is typically produced by the free-radical polymerization of butadiene. 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 accessible 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.

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 pendant or internal in the rubber substrate, as illustrated in Figure 5 (69). Initiator level and type affects the extent of grafting (69–75) 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 graft molecular weight.

Ungrafted SAN is formed concurrently with grafted SAN, with the ratio controlled by factors that include temperature, chain-transfer agent, pendant vinyl content of rubber, initiator level, and initiator type (69–77). As previously described, occlusions of SAN can also form within the rubber particles with the mass process leading to significantly higher occlusion levels than the emulsion
process (78,79). In the mass process, block copolymers of styrene and butadiene can be added to obtain unusual particle morphologies (e.g., coil, rod, capsule, cellular) (78).

**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 (80,81), as illustrated in Figure 6.

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 (81–86).

**Rubber Substrate Process.** The rubber substrate can be made by a variety of different reaction processes including batch, semi-batch, and continuous (87). Butadiene monomer is primarily used in the substrate reaction, but comonomers such as styrene and acrylonitrile are common (84,85). The amount

<table>
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<tr>
<th>Graft Initiation</th>
<th>1,4-polybutadiene (cis &amp; trans)</th>
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|                  | \([\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{]}_n\) | \(\text{Via} \)
| free radical     | polybutadiene                   | \('\text{cis-double bond} \) \('\text{trans-double bond} \)
| polybutadiene radical | polybutadiene (vinyl) | \('\text{vinyl double bond} \) \('\text{allylic hydrogen abstraction} \)

**Graft Propagation**

Styrene and Acrylonitrile can be copolymerized to form random copolymer.
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 (e.g., hydrogen peroxide and iron) or thermal initiators (e.g., 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 (88). The “soap-free” emulsion polymerization of butadiene is possible using reactive surfactants (89), functional monomers such as acrylic acid (90), or high levels of potassium persulfate (91). 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 or 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 (92). The incorporation of polymerizable antioxidants or uv stabilizers has also been reported (93). Typically, these modifications 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 (87). 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 (94,95). Productivity can also be improved by the use of antifouling agents to minimize buildup of polymer on reactor heat-transfer surfaces (96–98). These antifouling agents improve heat transfer and minimize the time the reactor is down for cleaning.

**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 (80,88), 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 (99–105). 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.

**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 (106). The use of nonionic coagulants has also been reported (107,108). Acrylic latices have been
used to control the coagulation process and obtain a narrow resin particle-size distribution (109).

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 (110) and extruder dewatering (111). 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 processes.

**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 (112), 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 (113).

**Mass Polymerization Process.** In the mass (114–122) 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 styrene), although some mass processes utilize emulsion-polymerized ABS with a high rubber content for the rubber component (123). 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 (124) using linear rubber, the rubber initially dissolved in the monomer mixture will phase separate, forming discrete rubber particles as SAN polymerization proceeds. 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 the phase inversion portion of the reaction (115,117–120). 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 de-
volatilized 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 and recycled
back to the reactors to improve the process yield.

The mass ABS process was originally adapted from the mass polystyrene
process (125). 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 approxi-
mately 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 (115–119).

**Suspension Process.** The suspension process utilizes a mass (126) or
emulsion reaction (127,128) to produce a partially converted mixture of polymer
and monomer and then employs a batch suspension process (129) 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.

**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 consis-
tency. If colorants, lubricants, fire retarding, 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 suffi-
cient 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 ob-
tain 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.

**Analysis.** Analytical investigations may be undertaken to identify the
presence of an ABS polymer, characterize the polymer, or identify nonpolymeric
Fourier transform infrared (FTIR) spectroscopy is the method of choice to identify the presence of an ABS polymer and determine the ABS ratio of the composite polymer (130,131). 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 by pyrolysis gas chromatography (132) and DSC (133) 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 (134,135), 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] (135,136), potassium permanganate [7722-64-7] (137), or osmium tetroxide [20816-12-0] (138). Chromatographic and spectroscopic analyses of the isolated fractions provide structural data on the grafted and ungrafted SAN components (139). Information on the microstructure of the rubber is provided by analysis of the cleavage products derived from the substrate (135,137). The extraction of ungrafted rubber has also been reported (140). Additional information on elastomer and SAN microstructure is provided by $^{13}$C NMR analysis (141). 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 (142) is indicative of the ABS manufacturing process (78) (see Fig. 1).

The isolation and/or identification of nonpolymerics has been described, including analyses for residual monomers (131,143,144) and additives (131,145–147). The determination of localized concentrations of additives within the phases of ABS has been reported; the partitioning of various additives between the elastomeric and thermoplastic phases of ABS has been shown to correlate with solubility parameter values (48).

**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 20–30°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. Clean, undegraded regrind can be reprocessed in most applications (plating excepted), usually at 20% with
virgin ABS. Post-processing operations include cold forming; thermoforming; metal plating; painting; hot stamping; ultrasonic, spin, and vibrational welding; and adhesive bonding.

**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. 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 buildup. Certain additives can be used to control static charges on pellets (148).

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 (149) 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 (150,151); 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 (152–154). Alternatives to pellet drying are vented injection molding (155) and cavity-air pressurization (counterpressure) (156).

**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 FR grades of ABS. Screws with a generous transition length perform best because of better melting rate control (157). Good results have been realized with a long transition “zero-meter” screw design (158). Some comments on the performance of general-purpose and two-stage vented screws used for coloring with concentrates is given in Reference 159. Guidelines for nozzle and nonreturn valve selection as well as metallurgy are given in References 160 and 161. Gas-nitrided components should be avoided; ion-nitried 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 (160,161). 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 0.5–0.9% (0.005–0.009 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 moldings. Excessive pressure causes flash and can result in loss of some properties. Mold temperatures for ABS range from 27 to 66°C (60–82°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 (162). 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 (163). The effect on tensile strength is qualitatively the same, but the magnitude is in the range of 5–10%. 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 (164). Dart impact is also sensitive to molding variables, and orientation and thermal history can also be key factors (165). Heat-deflection temperature can be influenced by packing pressure (166) because of free volume considerations (167). 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 (168–170). Other information regarding the influence of processing conditions on part quality are given in References 171–175.

**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 0.08–0.32 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 (176). 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 (162). 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 (177). 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 (178). ABS parts can also be designed for solid–solid or solid–foam co-injection molding (179) and for gas-assisted-injection molding (180) (see Injection Molding).

**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 \( \approx 840–420 \mu m \)) 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 (181). 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 synchronized 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 41–49°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 10–15%.
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 182 (see EXTRUSION).

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.

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 (183). Better blow-molding grades of ABS are being provided by tailoring the composition and rheological characteristics specifically to the process. While 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 0.02–0.03% 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 193–221°C optimum range. The land length of the tooling can be reduced to 3:1 to 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 77–88°C provide good surface finish. It is recommended that the material vendor be consulted to confirm equipment capability and provide safety and processing information (184) (see BLOW MOLDING).
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 (185). It is easy to thermoform ABS over the wide temperature range of 120–190°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 1–3 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, thermostet materials, or metals. Tools should have a draft angle of 2° to 3° on male molds and 0.5° 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 0.003–0.008 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 186. 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 187 (see THERMOFORMING).

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 188.

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 169 and 178.

Fastening, Bonding, and Joining. Often parts can be molded with various snap-fit designs (189) and bosses to receive rivets or self-tapping screws. Thermal-welding techniques that are easily adaptable to ABS are spin welding (190), hot plate welding, hot gas welding, induction welding, ultrasonic welding, and vibrational welding (191,192). 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 193.
Applications

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. Table 2 summarizes estimates for 1999 regional consumption of ABS resins by major use (194). In 1999 the single largest market for ABS resins worldwide was transportation. 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. Appliances were the second largest market segment for ABS. The majority of this consumption was for major appliances; extruded/thermoformed door and tank liners lead the way. Other applications in the appliance market include injection-molded housings for kitchen appliances, power tools, vacuum sweepers, sewing machines, and hair dryers. Transparent ABS grades are commonly used in refrigerator crisper trays, vacuum sweeper dirt cups, and other applications requiring premium aesthetics.

A large “value-added” market for ABS is business machines and other electrical and electronic equipment. Although general-purpose injection-molding grades meet the needs of applications such as telephones and ink jet printer covers, significant growth exists in more demanding FR applications such as computer housings and displays.

An emerging application base for ABS products has been in consumer applications requiring differentiation through aesthetic appeal vs mechanical performance. A wide range of options featuring inherent aesthetic looks such as metallic, sparkle, metamerism, or even thermochromatic color change can be found in products ranging from computers to telephones.

Pipe and fittings remain a significant market for ABS, particularly in North America. ABS foam core technology allows ABS resin to compete effectively with PVC in the primary drain-waste and vent pipe market.
Table 3. Worldwide Capacity for ABS Plastics 1994–2000 by Region, $10^3$ t

<table>
<thead>
<tr>
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<tr>
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<td>841</td>
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<td>865</td>
<td>882</td>
<td>1000</td>
<td>1000</td>
<td>990</td>
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<tr>
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<td>82</td>
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<tr>
<td>North America</td>
<td>931</td>
<td>894</td>
<td>894</td>
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<td>1083</td>
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<td>Asia-Pacific</td>
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<td>3158</td>
<td>3292</td>
<td>3712</td>
<td>3857</td>
<td>3977</td>
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<tr>
<td><strong>Total</strong></td>
<td>4110</td>
<td>4462</td>
<td>5125</td>
<td>5318</td>
<td>6003</td>
<td>6267</td>
<td>6414</td>
</tr>
</tbody>
</table>

Table 4. World Capacity of Leading ABS Producers

<table>
<thead>
<tr>
<th>Producer</th>
<th>2000 Capacity, $10^3$ t</th>
<th>Largest producer in</th>
</tr>
</thead>
<tbody>
<tr>
<td>GE Plastics</td>
<td>855</td>
<td>North America</td>
</tr>
<tr>
<td>Bayer</td>
<td>766</td>
<td>Europe</td>
</tr>
<tr>
<td>Chi Mei Industrial</td>
<td>1120</td>
<td>Pacific</td>
</tr>
</tbody>
</table>

Other uses of ABS include consumer and industrial applications such as luggage, toys, medical devices, furniture, shower stalls, and bathroom fixtures.

Economic Aspects

Capacity. Estimated ABS capacity worldwide in 2000 is given in Table 3 (195). 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 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 4, these three producers account for almost 50% of the world’s capacity (195).

Table 5. U.S. Unit Sales Values for ABS Resins

<table>
<thead>
<tr>
<th>Year</th>
<th>Value, $/kg</th>
<th>Year</th>
<th>Value, $/kg</th>
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<tbody>
<tr>
<td>1986</td>
<td>1.56</td>
<td>1993</td>
<td>1.83</td>
</tr>
<tr>
<td>1987</td>
<td>1.68</td>
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<td>1.87</td>
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<tr>
<td>1988</td>
<td>1.93</td>
<td>1995</td>
<td>2.03</td>
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<tr>
<td>1989</td>
<td>2.03</td>
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<tr>
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<td>1997</td>
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<tr>
<td>1991</td>
<td>1.92</td>
<td>1998</td>
<td>1.48</td>
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<tr>
<td>1992</td>
<td>1.86</td>
<td>1999</td>
<td>1.76 * est.</td>
</tr>
</tbody>
</table>
Price. The price history of ABS in the United States is presented in Table 5 for the period from 1986 to 1998 (196). The cyclical nature of prices during this period reflects both the cyclical nature of key feedstocks (197–199) and the increased global capacity available. The change also represents the changing mix of ABS resins and blends toward higher value, higher performance applications. Since late 1999, prices have risen appreciably because of dramatic increases in raw material feedstocks and stronger global demand.

Although ABS resins have a long history by industry standards, the products are anything but mature. ABS resins and blends are, and are expected to remain, the engineering thermoplastics of choice for a wide array of markets.

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