Report Abstract

ABS Resins
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ABS Resins

1 INDUSTRY DEVELOPMENTS

Styrenics producers have been under considerable pressure in recent years due to high and volatile feedstock costs and global overcapacity. Additional negative factors for downstream styrenics operations are stiff competition from other polymers, such as polypropylene and polyvinyl chloride, and the movement of margins upstream to crackers and benzene facilities. In this context, BASF has put selected styrenics assets up for sale, including plants in Belgium, Mexico, Brazil, South Korea, and India. BASF stated that it had received an initial offer for its styrene monomer, polystyrene, styrene butadiene copolymer, and ABS activities and that negotiations had begun. Consolidation in the downstream sector has already taken the form of joint ventures involving the assets of NOVA Chemicals in one instance and those of Innovene/INEOS in another instance.

INEOS agreed in June 2007 to acquire the Lustran ABS business from Lanxess. As part of INEOS, the ABS business will benefit from back-integration into the three key raw materials (acrylonitrile, butadiene, and styrene). INEOS also is involved in a polystyrene joint venture with NOVA. INEOS has been consolidating its global position in petrochemicals following the acquisition of Innovene refining and petrochemicals assets from BP. SABIC and Basell would benefit from further integration of their respective upstream styrene and benzene positions. SABIC made a successful bid for GE Plastics in May 2007, giving it a considerable presence in downstream engineering plastics, but only a relatively small plant producing ABS in Europe. SABIC has access to benzene in Europe from its (former Huntsman) plants in the U.K. bought in January 2007 and from crackers bought from DSM in 2002. Basell’s purchase of Lyondell Chemical in July 2007 gives it access to large quantities of styrene monomer from Lyondell’s propylene oxide/styrene monomer plants in Europe.

2 CHEMISTRY

ABS polymers are composed of elastomer dispersed as a grafted particulate phase in a thermoplastic matrix of styrene and acrylonitrile copolymer (SAN). Grafting SAN on the elastomer, which is usually polybutadiene, compatibilizes the rubber and SAN components and imparts excellent toughness, good dimensional stability, good processability, and chemical resistance.

High purity monomers are required in making ABS. Property balances are optimized by adjusting SAN composition, molecular weight, elastomer particle size, morphology, microstructure, and graft structure. The ABS polymer system, though structurally complex, offers unique advantages in tailoring properties to meet specific product requirements. Altering basic structural and compositional parameters allows a wide range of versatility, and the introduction of other monomers can raise heat deflection temperature, impart transparency, or confer flame retardancy. ABS can also be alloyed with other polymers such as polycarbonate to further broaden the application envelope.
A chemical connection between elastomer molecules and the styrene-acrylonitrile copolymer is created by polymerizing styrene and acrylonitrile in the presence of polymerized elastomer. The resulting grafts, as shown in the following diagram, serve to compatibilize the rubber and SAN copolymer phases:

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----B----B----B----B----B----B----B----
    ^                ^                
    |                |                |
    S----S----S----S----S----S----S----
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To maximize the creation of internal surface area during strain, and hence the degree of energy absorption, it is desirable to increase specific surface (surface area per unit volume). At constant rubber content in the polymer, this can be done by dispersing the rubber as smaller sized particles. However, very small particles can apparently act as stress concentration points and lead to brittle behavior; therefore 0.2 microns is typically the smallest rubber particle diameter used. Brittleness can also result from excessive grafting, which raises the modulus of the rubber particle until it begins to resemble the rigid SAN phase and can no longer absorb energy effectively. Increasing impact strength by raising the elastomer content in the formulation has the disadvantages of reducing tensile strength, tensile modulus, and flexural modulus.

3 PROCESS TECHNOLOGY

The first commercial grades of acrylonitrile butadiene styrene (ABS) polymer, originally introduced in 1948, were simply mechanical blends of rubber with styrene acrylonitrile (SAN) polymer. These blends reportedly used nitrile rubber since it was found to be more compatible with the SAN resin than was polybutadiene rubber. Although these early ABS polymers were superior to impact polystyrenes then on the market, it was recognized that the properties were inferior to graft copolymers where there is an actual chemical linkage between the continuous and elastomeric phases.

Today, ABS is produced by the emulsion, suspension, mass (or bulk), or emulsion/mass hybrid polymerization of three monomers: acrylonitrile, butadiene, and styrene. Material properties may be varied by adjusting the concentrations of the constituents, the degree to which the butadiene grafts to the styrene acrylonitrile portion, or by adding an additional monomer such as methyl methacrylate or alpha-methylstyrene. ABS polymers are tough and thermally resistant. The butadiene contributes toughness and low temperature impact strength, whereas acrylonitrile improves thermal stability and chemical resistance. The styrene portion of the polymer lends stiffness to the composition. Most ABS polymers are glossy, but low gloss or matte versions are being developed for selected uses.

ABS is readily processable by most thermoplastic fabrication techniques. Extrusion is used to produce pipe and electrical conduit, which compete with polyvinyl chloride (PVC). Extruded sheet is commonly thermoformed into luggage, sanitary ware, and transportation panels. Thermoformed refrigerator liners made of ABS are undergoing competition from high impact polystyrene and polypropylene. Injection molding is used to produce telephone housings, plumbing fittings, and a variety of other consumer and industrial goods.
ABS Resins

ABS is available in a wide variety of grades tailored for particular end uses. Reinforcing agents and fillers, such as glass fiber and minerals, improve the polymer’s tensile strength and stiffness. Heat resistance is imparted by using alpha-methylstyrene as a fourth monomer. Although most ABS grades are opaque, transparent grades may be produced by including methyl methacrylate as a monomer. Plateable grades were developed principally for plumbing and automotive uses; structural foam grades find application in business machine enclosures. Flame retardant grades can be produced through the inclusion of additives or by blending with PVC. Antistatic grades that incorporate conductive fillers have also been developed.

ABS may be alloyed and blended with other polymers. Compared to straight polycarbonate, ABS/polycarbonate alloys reduce cost and improve processability. The materials compete with polycarbonate and modified polyphenylene oxide, primarily in business machine housings. ABS/PVC blends provide the flame retardancy of PVC with the easy processing of ABS.

The mass or bulk process for ABS production is based on the polymerization of styrene-acrylonitrile mixtures in the presence of a rubber substrate dissolved in this monomer phase. This is in contrast to the emulsion process that takes place in an aqueous phase affording lower viscosity of the reaction medium and better heat transfer. Rubber is usually introduced to the process in large bales or slabs that are ground into small particles and dissolved in a mixture of styrene and acrylonitrile monomers. Since no preformed rubber particles are present at the beginning of the grafting reaction as in the emulsion process, a different distribution of elastomer phase in the SAN matrix results from the mass process.

As the name implies, the hybrid emulsion/mass process combines features of the emulsion process, which forms polybutadiene latex and grafts styrene and acrylonitrile, and the mass process, which makes the SAN component. The recovered graft rubber and SAN are compounded together to give the final ABS product, an approach that permits the production of a wide range of ABS products using two or three basic SAN polymers and a similar number of high rubber ABS graft resins and compounding them together in various combinations and proportions. Chi Mei, a large ABS producer based in Taiwan, has had notable commercial success with materials made in a hybrid process.

4 ECONOMICS

Cost of production estimates for the following ABS processes are included in the report:

- Emulsion Process (USGC @ 100,000 metric tons/yr)
- Bulk Mass Process (USGC @ 100,000 metric tons/yr)
- Hybrid Process (USGC @ 100,000 metric tons/yr)

5 COMMERCIAL ANALYSIS

The major uses for ABS include automotive parts (instrument panels, consoles, door post covers, radiator grilles, headlight housings and interior trim parts); appliance parts (extruded/thermoformed doors and tank liners, crisper trays, injection-molded housings); and business machine casings (including fire-retardant applications such as computer housings and consoles). Other uses of ABS are for sports goods, luggage, pipes and fittings, and toys. ABS also enjoys a unique position as a “bridge” polymer between commodity plastics and other higher performance engineering thermoplastics.
With variations in composition and structure, ABS can exhibit a wide range of properties, allowing its use in diverse applications. These applications include appliances, transportation, piping, electrical/electronic components, blends with other polymers, medical uses, and miscellaneous applications (comprising toys, luggage, shower stalls, furniture trim, and lawn and garden products). New applications frequently involve the replacement of painted parts.

Figure 1 shows an overview of global ABS demand.

![Figure 1 Global ABS End Use Distribution](Q307_00101.007.4116-Charts.xls:F5.1)

To tailor properties and costs to application requirements, ABS is also used in polymer blends, particularly with polycarbonate. ABS/polycarbonate blends offer heat resistance coupled with low-temperature impact strength and find application in automotive instrument panels and wheel covers, as well as safety and leisure products (helmets, etc.). ABS/polyvinyl chloride offers good impact strength, toughness, and flame retardation. These attributes are beneficial in electrical components, machine enclosures, and appliances.
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