6.5. Acrylonitrile – Butadiene – Styrene (ABS) Polymers

6.5.1. Definition and Structure

ABS [*9003-56-9*] and HIPS (Chap. 6.1) represent the industrially most important thermoplastic two-phase systems with an amorphous structure. The ABS polymers are based on three monomers: acrylonitrile (A), butadiene (B), and styrene (S). The polymer components have different chemical compositions and coexist as two separate phases whose compatibility is controlled by their structure and chemical microstructure.

In all classical ABS molding compounds the continuous phase (matrix) consists of copolymers of styrene (or an alkylstyrene) and acrylonitrile. An elastomer based on butadiene forms the disperse phase that is distributed in the continuous phase and has a characteristic morphology (Fig. 11).

Figure 11. ABS graft polymer showing rubber particles embedded in a styrene – acrylonitrile (SAN) copolymer matrix

From a polymer physics point of view ABS polymers and analogous systems can be considered as "elastomer-modified thermoplastics".

6.5.1.1. Historical Aspects

The history of ABS polymers began in the mid 1940s. In attempts to produce bulletproof plastic sheets during the last years of World War II, polymer systems were developed from special butadiene – acrylonitrile copolymers and styrene – acrylonitrile copolymers with high molecular masses. These materials had a high impact resistance on account of their low thermoplastic flow, but could only be processed with extruders. Semifinished products (i.e., predominantly sheets, profiles, and pipes) were the first molded parts to be made from ABS polymers and had dull or matt surfaces.

A drastic increase in the flow of the material allowed processing by injection molding and thus opened up the way for the production of engineering plastics. Improved processibility was obtained by the use of graft polymerization. This technique allowed the production of molded parts with glossy or high-gloss surfaces.

Systematic research into ABS polymers has led to the development of other multiphase plastics with a chemically different make-up. These contain other monomer units in addition to or as a replacement for acrylonitrile, butadiene, or styrene.

Recent developments include modifications of the A, B, and S monomer units as well as complex blend systems, in which the ABS polymers are components of polymer mixtures with an extremely wide range of properties.

6.5.5. Properties

ABS polymers have a high toughness (even in the cold), satisfactory rigidity, and good resistance to heat, chemicals, and environmental stress cracking. Molded articles with high dimensional stability and good surface quality can be produced by simple processing techniques. Although each of these properties can be bettered by other thermoplastics, no other system displays such a good combination of technically important properties.

A deeper knowledge of structure – property relationships [79], [225], [226] allows producers to supply a range of commercial products with user-oriented property profiles. Table 10 gives an overview of some commercial grades [227].

The properties of ABS polymers are determined by molecular and morphological parameters. The matrix composition and molecular mass, the type of rubber, the volume ratio of the rubber to the continuous phase, the rubber particle size, the grafted rubber structure, and the additive content are also important.

Standard ABS systems are opaque because their two phases have different refractive indices. Opacity depends on the particle size of the grafted rubber phase and the difference between the refractive indices of the two phases (Mie's theory) [228]. If the particle diameter is small enough compared with the wavelength of visible light, the two phases can be considered as optically homogeneous, and they appear translucent. Completely transparent systems are obtained if the refractive indices are equal. This is achieved, for example, by using a MABS resin matrix [229] or by completely substituting methyl methacrylate for acrylonitrile [230] (see also Section 6.5.12.2). In bimodal graft rubber systems, depending on ratio of the graft base to the grafted polymer, opacity may be observed despite equal refractive indices. The same applies if grafted rubber particles accumulate to form clusters during processing or tempering because of an incompletely closed graft shell.

In all ABS polymers the continuous phase (SAN and/or AMS – AN copolymer) is responsible for most of the chemical properties. Since only C–C bonds are present in the polymer chains, hydrolysis reactions are unimportant. ABS polymers are therefore generally resistant to aqueous solutions of salts, acids, or bases. They can absorb up to 1.5 wt % water on storage in aqueous media due to residual emulsifier and the polarity of the nitrile side groups. Under normal conditions, dimensional or property changes are negligible.

Paraffinic hydrocarbons do not dissolve ABS polymers. A certain weight gain can be detected on storage in such media, and depends on the nature and quantity of the rubber phase. ABS polymers show equally good resistance to animal and vegetable fats and to a range of cosmetic creams.

Other organic liquids, such as halogenated hydrocarbons, aromatics, esters, and ketones dissolve the SAN phase. Oxidizing agents, especially inorganic acids, break up the chains and thus degrade the polymer. The resistance tables published by ABS producers only have limited meaning for practical applications. In order to answer specific questions, the running of a creep test under constant deformation, or, better, under constant tension is recommended. States of stress exist in each molded article as a result of its production. Additional stress is often produced by binding elements (e.g., rivets, screws, molded-in or enclosed metal parts) or on use of the article. Environmental stress cracking is low compared with polystyrene, but cannot always be excluded. Sensitivity towards stress cracking can be further lowered by increasing the acrylonitrile content and the molecular mass of the SAN phase, as well as by relaxation processes that are favored by the disperse rubber phase.

The double bonds in the elastic rubber phase (BR rubber) are responsible for the relatively high sensitivity of ABS polymers towards the long-term effects of heat, light, and weathering which result in yellowing and graying of the surface and a decrease in toughness [231]. Although satisfactory protection can be provided by using stabilizer combinations (phenolic antioxidant, a thiodipropionate ester, and/or a phosphite ester) during production and processing at 220 – 260 °C, long-term stabilization, particularly during simultaneous exposure to UV light and weathering, is difficult. Use of established stabilizer systems allows, however, repeated processing (e.g., recycling) without a serious decrease in toughness. For all indoor applications, ABS is aging-resistant. For outdoor use, adequate resistance to weathering is necessary. Three routes are currently used for this:

1) "Pigmenting" with soot (dark grey shades and black) to absorb UV radiation.
2) Coating semifinished or finished articles with barrier layers having a low oxygen permeability, with less sensitive materials, or with UV-protective paints.
3) Using grafted rubber systems with few or no double bonds. Although these systems do not contain the butadiene monomer unit they are nevertheless members of the ABS family because they have the same basic structure and morphology. They are SAN copolymers that are rendered impact-resistant by a dispersed elastomer phase.

At processing temperatures above 280 °C, ABS polymers lose their toughness because of damage of the rubber phase. Depolymerization begins above 300 °C. In the presence of atmospheric oxygen, decomposition can begin at ca. 280 °C.

6.5.9. Uses

ABS polymers are widely used as construction materials [241] – [243]. The main consumers are the automotive industry, the domestic appliances industry, the data technology and telecommunications area, and producers of refrigeration equipment, toys, sports articles, and semifinished articles. ABS polymers have a very favorable price – performance ratio. In the automotive industry ABS often competes with modified polypropylenes, but in other applications it also replaces industrial thermoplastics and thermoplastic blends. From 1995 to 2000, annual growth rates of 2 – 3 % (Europe, NAFTA, Japan) and 8 % (Asia excluding Japan) are expected [244].

Figure 23 shows the development of ABS consumption in Western Europe in 1975 – 1995. Consumption in Western Europe in 1995 was 560 000 t. This broke down as follows:

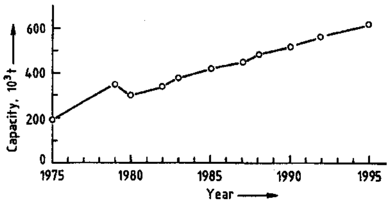

Figure 23. Market development of ABS polymers in Western Europe

Table 11. Product development of ABS in Western Europe, United States, and Japan (10^3 t)

Region	1982	1986	1990	1995
Western Europe	340	440	520	560
United States	300	477	527	555
Japan	290	390	473	470
Total	930	1307	1520	1585

Electrical/electronics	24 %
Domestic appliances	23 %
Automotive industry	22 %
Recreation	6 %
Extrusion	4 %
Miscellaneous	21 %

Trade names and producers of ABS polymers follow:

Western Europe and United States

Cycolac	GE Plastics
Magnum	Dow Chemical
Lustran, Novodur	Bayer
Ronfalin	DSM
Sinkral	Enimont
Terluran	BASF

Japan

Cevian	Daicel
Denka	Denki Kagaku
Shincolac	Mitsubishi Rayon
Stylac	Asahi Dow
Toyolac	Toray Industries