Thermoplastic Rubber (A-B-A Block Copolymers) in Adhesives

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WHAT IS THERMOPLASTIC RUBBER?

Thermoplastic rubber is truly a useful and versatile class of polymer. It has the solubility and thermoplasticity of polystyrene, while at ambient temperatures it has the toughness and resilience of vulcanized natural rubber or polybutadiene. This characteristic results from its unique molecular structure. Visualize the simplest thermoplastic rubber molecule: a rubbery midblock with two plastic endblocks. This situation is pictured schematically in Fig. 1 where the diamonds represent monomer units in the plastic endblocks and the circles represent monomer units in the rubbery midblock. Such a molecule is called a block copolymer.

Patent and scientific literature describes numerous molecular variations: the structure pictured in Fig. 1 (A-B-A), more than two monomers (A-B-C), branched or radial configurations (A-B-A), repeating segments (A-B-A-B-A), and so forth. The key requirement is that the thermoplastic rubber molecules terminate with hard, glasslike endblocks which are incompatible with the rubbery midblocks. All such polymers consequently consist of two phases in the solid state—a continuous rubber phase and a basically discontinuous plastic phase which “locks” the rubbery molecules in place.

The principles which apply to the simplest version shown in Fig. 1 also apply generally to other configurations. For simplicity, discussions in this chapter will be focused on the sim-
plest version, yet will apply broadly to other structures as well. Discussion will also be focused on two basic classes of thermoplastic rubber. One class consists of block polymers in which the rubbery midblocks of the molecule is an unsaturated rubber. The two types of polymers in this class are the polystyrene-polybutadiene-polystyrene (S–B–S) polymers and the polystyrene-polyisoprene-polystyrene (S–I–S) polymers. The second class of thermoplastic rubber consists of block polymers in which the elastomeric midblock is a saturated olefin rubber. The polymers in this class are the polystyrene-poly(ethylene/butylene)-polystyrene (S–EB–S) polymers and the polystyrene-poly(ethylene/propylene) (S–EP) polymers.

When many A–B–A molecules are combined in the solid phase, a two-phase structure is formed by the clustering of endblocks. An idealized and simplified representation of this is shown in Fig. 2.

The plastic endblocks phase regions, called “domains”, are shown in sphere-like form. Other forms are discussed later. These domains act as crosslinks between the ends of the rubber chains, serving to lock the rubber chains and their inherent entanglements in place. The system acts like a conventionally vulcanized rubber that contains dispersed reactive filler particles.

This physically crosslinked matrix exhibits typical physical properties shown in Table 1. The data represent various neat S–B–S and S–I–S thermoplastic rubber samples cast from toluene solutions.

Table 1. Typical Physical Properties of S–B–S and S–I–S Thermoplastic Rubber at 23°C.

<table>
<thead>
<tr>
<th>Property</th>
<th>S–B–S</th>
<th>S–I–S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength at break (TB), psi</td>
<td>3000–5000</td>
<td></td>
</tr>
<tr>
<td>300% Modulus (M300), psi</td>
<td>100–400</td>
<td></td>
</tr>
<tr>
<td>Elongation at break (E_B), %</td>
<td>800–1300</td>
<td></td>
</tr>
<tr>
<td>Hardness, Shore A</td>
<td>30–80</td>
<td></td>
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</tbody>
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The same range of properties may also be obtained on casting these polymers from a melt. In neither case is chemical vulcanization required. That thermoplastic rubber really is a new class of polymer is depicted in Fig. 3.

Thermoplastic rubber as defined above was first marketed commercially in 1965 by Shell Chemical Company. A list of the trade names, manufacturers, and types of thermoplastic polymers produced is presented in Table 2.

Thermoplastic rubber polymers act as high strength film-formers when used alone or act to increase the cohesive strength or viscosity of systems to which they are added. They dissolve rapidly, without premastication, in a range of low-cost solvents to give useful high solids, low viscosity solutions. They can be mixed readily with many compounding ingredients, and the resulting formulations may be applied to substrates either by solution or by hot-melt techniques. High-tack pressure-sensitive adhesives or nonblocking assembly adhesives may be formulated by varying the types of resins and plasticizers used.

Thermoplastic rubber polymers are resistant to attack by most aqueous reagents, normally have good electrical insulating properties, and

Fig. 2. Idealized two-phase network of thermoplastic rubber molecules.

Fig. 3. Polymer classification.