Introduction
Clear thermoplastic elastomeric sealants based on styrene-ethylene-butene-styrene (SEBS) block copolymers are increasing in importance in the market. They are competitive with other technologies such as acrylics and silicones in critical performance criteria:

- Excellent transparency with no haze and water-white initial color
- Good resistance to degradation under UV light exposure—slight yellowing with time
- Adaptable to both hot melt and solvent application
- Good adhesion to common building substrates—glass and aluminum
- Attractive balance of cost vs. performance

A clear thermoplastic sealant can contain up to four classes of components: SEBS block copolymer rubber, hydrogenated hydrocarbon tackifiers, endblock modifying resins, and plasticizers. The formula will include one or more grades of SEBS block copolymer chosen for styrene content, molecular weight, and diblock/triblock structure ratio. Regalrez, Regalite, and Eastotac fully hydrogenated hydrocarbon resins modify the olefinic rubber midblock of SEBS block copolymers. These components produce the essential adhesion properties as well as viscosity control. Endex and Kristalex pure monomer resins modify the styrene phase of block copolymers and affect the cohesion, tensile strength, lap shear, and upper service temperature of the sealant. The plasticizers used are generally hydrocarbon oils that improve flexibility, decrease viscosity, and reduce the lower service temperature of the sealant.

Technical Discussion
Starting point formulations for solventborne and hot melt clear sealants are shown below in Table 1. The main difference between the two is in the lower level of tackifier and the absence of plasticizer in the solventborne system. Since the application viscosity of the solventborne system can be controlled by the solids level and solvent selection, it is possible to formulate without plasticizers. This gives a more durable and less tacky surface for the dried sealant as well as eliminating the use of plasticizers, which can volatilize and contribute to glass fogging. For the hot melt system, it is necessary to use a reduced level of triblock content in the SEBS rubber components, a higher level of tackifier, and some plasticizer in order to produce a system with a usable melt viscosity at application temperature.

Table 1: Clear Sealant Starting Point Formulations

<table>
<thead>
<tr>
<th>Sealant Component</th>
<th>Solventborne</th>
<th>Hot Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraton G1726 SEBS Block Copolymer</td>
<td>47</td>
<td>50</td>
</tr>
<tr>
<td>Kraton G1652 SEBS Block Copolymer</td>
<td>53</td>
<td>50</td>
</tr>
<tr>
<td>Endex 160 Hydrocarbon Resin</td>
<td>35</td>
<td>—</td>
</tr>
<tr>
<td>Kristalex 1120 Hydrocarbon Resin</td>
<td>—</td>
<td>30</td>
</tr>
<tr>
<td>Regalite R1100 Hydrocarbon Resin</td>
<td>80</td>
<td>130</td>
</tr>
<tr>
<td>Kaydol/ Mineral Oil</td>
<td>—</td>
<td>30</td>
</tr>
<tr>
<td>Solvent Composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VM&amp;P Naphtha</td>
<td>22</td>
<td>—</td>
</tr>
<tr>
<td>Propyl Acetate</td>
<td>58</td>
<td>—</td>
</tr>
<tr>
<td>Toluene</td>
<td>12</td>
<td>—</td>
</tr>
</tbody>
</table>

*aParts per hundred parts rubber—SEBS components add to 100, bKraton Polymers L.L.C., cEastman Chemical Company, dRegalrez 1094 or Eastotac H-100W can also be used, eWitco Chemical Co., fSolvent added to achieve 70% solids
UV Stability

A major concern for clear sealants is their resistance to yellowing with exposure to UV light. Figure 1 shows the results of a 1000-hour Xenon arc UV exposure test (ASTM Method C793 using Practice C1442 for Xenon Arc Exposure) with hot melt clear sealants applied on a 0.091 inch thick glass plate in a 0.125 inch thick layer. These were chosen as a worst-case scenario for testing because the tackifiers and plasticizers are the largest contributors to color and the hot melt formulas have the highest levels of these components. The study compares Regalrez 1094, Regalite R1100, and Eastotac H-100W hydrogenated hydrocarbon tackifiers at the same levels in the sealant formula. The results show that there is a difference between the three tackifiers in UV stability. The color of the blank specimen (0.091 inch glass plate covered with 1-mil polyester film) is also shown since this contributed about 5 Y1 units to the total color of each measurement. Regalrez 1094 shows the least color change as would be expected since these products are highly stable hydrogenated pure monomer resins. Regalite R1100 shows slightly more color change over time, but is a more economical product than the Regalrez types. Eastotac H-100W shows a higher color change, especially in the first 100 hours of exposure. Therefore, it significantly reduces the UV stability of the system, but would also be the lowest cost option of the three tackifiers evaluated.

Adhesive Properties

Results of adhesive testing for the clear sealant formulas are shown in Figure 2. For the solventborne formula, all three tackifiers produced nearly equal adhesion to aluminum. The hot melt formulas all developed outstanding adhesion to aluminum with over 500 lbs/inch force observed. For adhesion to glass, Eastotac H-100W was significantly better than either Regalite R1100 or Regalrez 1094 in the solventborne formulas. In the hot melt formulas, all three tackifiers produced over 100 lbs/inch of adhesion to glass with no significant difference between the three resins tested. The lap shear tests produced highly variable results. Regardless of resin used, both the solventborne and the hot melt formulas can withstand over 100 psi of shear force to wood at room temperature.

Endblock Modification

Another important component of a sealant using block copolymers is the inclusion of a styrenic endblock modifying resin. An aromatic pure monomer resin associates only with the styrene phase of the rubber, which effectively increases the physical crosslink density of the system. This would be expected to increase tensile strength, hardness, SAFT, softening point, and melt viscosity of the system, as well as reducing the surface tack.

Figure 3 shows the effects of adding an endblock reinforcing resin to the sealant formula from Table 1. Shown here are three versions: one without endblock modifying...
Clear Thermoplastic Sealants Using Eastman Hydrocarbon Resins (TT-84)

resin; one containing 100 parts of Kristalex 1120 (calculated based on the styrene content of the rubber); and another containing 100 parts of Endex 160. Addition of Endex 160 to the adhesive formulation increases tensile strength from 370 to 480 psi and increases the softening point by 10°C compared to the control with no pure monomer resin added. Melt viscosity of the sealant increases from 8500 cps to 15000 cps at 177°C when Endex 160 is used, so its use may be limited to solvent systems if application equipment cannot handle the higher viscosity. As seen in Figure 3, Kristalex 1120 does not have a significant effect on any of the displayed properties, however, it does increase the Shore A hardness of the system from 8 to 14.

Figure 3: Effect of Endblock Modifying Resin on Sealant Properties

Kristalex 1120 would be preferred in a hot melt system as a hardener to reduce the surface tack, which can reduce dirt pickup tendencies without increasing the application viscosity.

Conclusion

Thermoplastic SEBS-based clear sealants are an option in applications where transparency, durability, and adhesion are required and a lower cost option to silicone is sought. These are typically composed of two or more grades of SEBS chosen for the diblock/triblock ratio and styrene content to provide a balance of cohesion, hardness, and viscosity. The SEBS rubber is tackified with a hydrogenated hydrocarbon resin to develop the required adhesion characteristics, as well as to reduce viscosity. A plasticizer is typically included to reduce melt viscosity. An aromatic pure monomer resin is included as well, to increase the cohesion and SAFT of the system.

Solventborne sealants are typically made at 70% solids using solvents with medium evaporation rates (0.8–3.0 on the n-butyl acetate scale). Depending on local VOC regulations, a low to zero VOC sealant can be made by using tert-butyl acetate. Solventborne sealants are typically used in construction site and DIY applications where hot melt application equipment is not available.

Hot melt clear sealants are used most frequently in applications where application speed is needed and the hot melt dispensing equipment is available. Hot melts use a high level of hydrogenated hydrocarbon tackifiers and plasticizer to achieve the required low application viscosity. Care must be taken to avoid use of volatile plasticizers that cause fogging over time. Hot melt sealants will have higher adhesion than solventborne, but will also have greater tack leading to dirt pickup.

The examples presented here demonstrate that formulation of clear thermoplastic sealants is quite flexible. Hydrocarbon resins from Eastman Chemical Company are a critical component in these applications since a typical clear sealant composition will contain more than 50% hydrocarbon resin. Contact Eastman to learn more about how our Eastotac, Endex, Kristalex, Regalite, and Regalrez brands of hydrocarbon resins can help with your clear thermoplastic sealant applications.
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