BUTYL ADHESIVES IN TAPE AND CONSTRUCTION APPLICATIONS

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Introduction

Butyl rubber is most often associated with the tire industry. It has shown itself to be an excellent replacement for natural rubber in some applications. It is harder and less porous than other elastomers, such as natural rubber or silicone. It also has excellent resistance to oxidation, which makes it the elastomer of choice for many outdoor applications. A low glass transition allows butyl rubber to maintain its flexibility at low temperatures. Butyl rubber’s resistance to moisture transmission and overall impermeability makes it the material of choice for use as a sealant in insulated glass window panes. The inherent vibration dampening characteristic of butyl rubber allows it to be used in sound abatement applications.

The low glass transition temperature, excellent environmental resistance, low permeability to gasses and moisture, and oxidation resistance would seem to make butyl rubber an excellent base for adhesive development. However, butyl rubber presents many challenges to the adhesive formulator in regards to processing, packaging, and application. If the processing and converting challenges can be overcome, an adhesive can be made using butyl rubber which exhibits its characteristic barrier, environmental resistance, and performance properties.

History

Butyl rubber was first produced by American chemists William Sparks and Robert Thomas at the Standard Oil Company, now ExxonMobil Corporation, in 1937. Continued improvements in the polymerization process eventually led to its adoption in applications requiring gas permeation resistance and oxidative stability.

Butyl rubber was one of the first synthetic rubbers ever produced. It was also the first low functionality elastomer. A low functionality elastomer is defined as a compound that has enough unsaturation so that flexible, low modulus, vulcanized networks can be produced. The very high percentage of the inert portions of the polymer chain contributes oxidative resistance. Cross linkable EPDM is also considered a low functionality elastomer. As the understanding of butyl rubber chemistry increased, halogenated versions were created. These halogenated versions lend themselves to being cross-linked and now account for the bulk of the butyl rubber sold worldwide. The majority of the butyl rubber produced in the world is used in the tire industry.

From a supply standpoint, there are few producers of butyl rubber, and supply can at times be problematic. Due to the low amount of producers, and the cyclic demand of the automotive industry, costs can be volatile. There are two primary producers of butyl rubber. Worldwide production of butyl rubber is in excess of one billion pounds annually.
Polymer Structure

Butyl rubber is produced by copolymerizing isobutylene in solution with low concentrations (1.5 to 4.5 percent) of isoprene. Both isoprene and isobutylene are usually obtained by the thermal cracking of natural gas or the lighter fractions of petroleum. The polymer repeating units have the following structures:

\[
\begin{align*}
\text{isobutylene} & \quad \text{isoprene} \\
\text{CH}_3 - \text{CH}_2 - \text{C} \quad \text{CH}_3 - \text{CH} - \text{CH}_2 - \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

**Figure 1.** Chemical Structures of Isobutylene and Isoprene

Butyl rubber contains approximately 98% isobutylene plus 2% isoprene. The higher the isoprene content, the easier it is to cross-link. Halogenated versions are easier to cross-link and are used predominantly in the tire industry.

The resulting polymer has a very low glass transition (Tg) temperature, around -60° C. It has no crystallinity and a tendency to flow under stress. This flow property is commonly known in the industry as “cold flow”. The molecular weight of the polymer controls hardness and strength.

As compared to the typical styrenic block copolymer (SBC) used to manufacture traditional pressure sensitive adhesives (PSAs), butyl rubbers are much higher in molecular weight and have a broader polydispersity. Butyl rubbers used in the adhesive industry have a molecular weight between 300,000 and 500,000 units, as compared to 100,000 to 250,000 units for SBCs. The polydispersity values of butyl rubbers range from 3 to 6, compared to 1 to 1.5 for SBCs. Butyl rubber also has about 50 times less unsaturation than a typical SIS or SBS block copolymer. This lack of unsaturation gives butyl rubber adhesives their characteristic oxidation, UV, and ozone resistance.

**Formulation**

As with other hot melt adhesives, butyl rubber based adhesives incorporate polymers, a tackification system, a diluent, and usually a filler.

Many formulations contain butyl rubber as the only polymer. The overall tack and resistance to creep can be improved by incorporating some SIS or SBS based polymers, however, using either an SIS or SBS polymer will negate the oxidative, UV, and ozone resistance inherent to butyl rubbers. A much better way to improve tack and inhibit cold flow is to add a hydrogenated block copolymer (HBC). The addition of an HBC allows the butyl rubber adhesive to maintain its characteristic environmental performance, in addition to having improved tack and cold flow resistance.
In order to further increase tack and improve heat resistance, a tackifier system can be added to butyl rubber based adhesives. Butyl rubbers are compatible with a variety of hydrocarbon based tackifiers. However, as with the addition of HBC polymers, the use of hydrogenated hydrocarbon (HHC) resins allows the butyl rubber adhesive to maintain its characteristic environmental performance.

The diluent used in butyl rubber formulations is typically a lower molecular weight polybutene. The lack of unsaturation in polybutene, similar to that of the HBC and HHC components, does not compromise butyl’s environmental resistance.

A filler is used to improve the stiffness, toughness and resistance to cold flow. The fillers of choice are typically calcium carbonate, talc, and fumed silica. Calcium carbonate is a low cost extender and can be used at relatively high concentrations. However, due to the high molecular weight of butyl rubber, the addition of a high filler level can lead to viscosities that are very difficult to process. Fumed silica is typically used to inhibit cold flow and can be used at relatively low levels, so as to not push the viscosity of the butyl formulation to extreme levels. As with any filler, particle size is extremely important.

Other additives can also be present such as waxes, flame retardants, and anti-oxidants. Their inclusion is dependent on the end use application. Carbon black is added to give the default black color associated with butyl rubber based adhesives.

As compared to standard hot melt PSAs, butyl rubber adhesives have much higher viscosities. These viscosities limit how the adhesives can be applied and packaged. Butyl rubber based adhesives are typically sold in drums and applied using extruders.

Compounding

Due to the tendency of butyl rubber to cold flow and aggregate, it is supplied in large bales ranging from 50 to 75 pounds. This severely limits the type of compounding equipment available to produce butyl based adhesives. Another challenge is the inherently high viscosity of butyl rubber, couple this with a high filler loading, and you can quickly produce formulated products in the hundreds of thousands or millions of centipoise.

Figure 2 shows a typical rheological curve of a SBC based PSA used in a flashing tape application. Figure 3 shows the G’ values of several butyl based adhesives. The use of butyl based polymers and fillers helps to raise the G’ values at elevated temperatures. However, this comes at the expense of making the butyl containing materials much more difficult to process.
Applications

Butyl rubber formulations have unique characteristics. Applications using butyl rubber do so primarily to take advantage of several of these unique characteristics:

- Low permeability to air, gases, and moisture
- Vibration damping
- Low glass transition temperature
- Self-healing or self-sealing properties
- Resistance to aging and to weathering from atmospheric exposure
- Broad range of durometer hardness and tensile strength properties

From a construction standpoint, hot melt butyl adhesives are used extensively in the insulated glass market place. Butyl’s low permeability to air, gases, and moisture, and its resistance to weathering and atmospheric exposure, makes butyl based adhesives the preferred sealant for this application.
Figure 3. Rheology curves for several butyl formulations

From a tape standpoint, two applications are road marking and flashing.

Road marking tapes take advantage of the vibration dampening characteristics, the environmental resistance and resistance to the various chemicals associated with this application. The vibration dampening associated with butyl rubber is important to prevent delamination of the tape due to exposure of the tape to repeated compression stress. A highly elastic adhesive may delaminate when exposed to these severe compression forces.

In flashing tape applications, a butyl-based adhesive offers inherent resistance to environmental forces, a low Tg to withstand cold environments, and a unique self-healing ability. Several tests require the adhesive in flashing applications to be able to seal around nails driven through the tape. The cold flow properties exhibited by butyl rubber make this an exceptionally effective adhesive for flashing tape applications.

The following pictures show the sequence of a test set-up for nail sealability. The specifics of this test are detailed under AAMA 711-13 Section 5.2. Figure 4 shows the initial preparation of the substrate where nails are driven through the membrane of interest, and then the heads of these nails are slightly lifted. Figure 5 below details the placement of a water filled can over the nail heads.
**Figure 4.** Preparation of the set-up for nail sealability testing

**Figure 5.** Set-up for nail sealability testing showing water filled container
Figure 6. Nail sealability test-setup underside

Figure 6 above shows the underside of the membrane construct. Any water leaking through the nail holes is considered a failure. The self-healing characteristics of butyl polymers can be improved through several formulation techniques. Reducing the filler level and/or decreasing the molecular weight of the butyl polymers improves this self-sealing capability.

As compared to asphalt based systems, butyl flashing tapes offer superior adhesion, aging performance, improved self-sealing characteristics, and are more environmentally friendly.

The table below details the characteristics of various adhesive technologies associated with flashing tapes.
Table 1. Comparison of different adhesives technologies and their applicable properties in flashing tapes

<table>
<thead>
<tr>
<th></th>
<th>Extruded butyl</th>
<th>SBC HMPSA</th>
<th>HM butyl/hybrid</th>
<th>Acrylic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion to OSB at RT (lbs/inch)</td>
<td>3.2</td>
<td>3.6</td>
<td>3.5</td>
<td>3.7</td>
</tr>
<tr>
<td>Nail Sealability</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Lower Application Temperature (°F)</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>Temperature Resistance</td>
<td>Class 3 (176°F)</td>
<td>Class 3 (176°F)</td>
<td>Class 3 (176°F)</td>
<td>Class 3 (176°F)</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.4</td>
<td>0.9-1.1</td>
<td>0.9-1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Cost</td>
<td>1x</td>
<td>1.5x</td>
<td>2x</td>
<td>4x</td>
</tr>
<tr>
<td>Coat weight (mils)</td>
<td>10-12</td>
<td>10-12</td>
<td>8-10</td>
<td>5</td>
</tr>
<tr>
<td>Coating/Application Requirements</td>
<td>Extruder, highly filled system</td>
<td>Drum unloader and slot die</td>
<td>Drum unloader and slot die</td>
<td>Water or solvent based applicator and dryer</td>
</tr>
</tbody>
</table>

As expected each technology has its advantages and disadvantages. The extruded butyl adhesives typically have the best overall performance but are the most difficult to apply. The SBC based adhesives are the easiest to apply but have the lowest environmental resistance. A skilled formulator can build a hybrid adhesive containing both SBC and butyl polymers which has better performance than a typical SBC based adhesive, but is much easier to convert than a filled butyl adhesive.

Summary and Conclusions

The skilled adhesive formulator should not neglect the unique advantages a butyl rubber based system can impart to their pressure sensitive applications. The use of hydrogenated polymers and tackifiers, in conjunction with the butyl rubber, will maintain the characteristic oxidative, UV and ozone resistance associated with the butyl compounds. If manufacturing and application obstacles can be overcome, butyl rubber based adhesives can offer improved performance over traditional SBC based pressure sensitive adhesives.