Introduction

During the early years of the pressure sensitive industry, formulation of a rubber elastomer together with a tackifying resin was the dominant adhesive technology. Building on years of experience and assisted by the development of new materials, skilled formulators have developed the technology to fill a wide variety of needs from removable to repositionable and permanent adhesives. They find application in numerous end uses. If one were to name the two outstanding properties of most rubber-resin adhesives these would be versatility in adhesion, particularly to low energy adherends such as polyolefins, and aggressive tack. They have excellent ‘thumb appeal’. While adhesion scientists may sometimes be tempted to discount the importance of this, it is undeniably a factor in consumer perception of performance. The Achilles heel of these products is generally their color and lack of long term durability due to oxidation and exposure to sunlight. Of course, wherever short term use is intended and color is not a factor, these deficiencies may be outweighed by the advantages of rubber-resins. While it is possible to formulate rubber-resin adhesives from low color, hydrogenated materials thus overcoming these problems, the excellent balance of adhesive properties is sacrificed.

Acrylic pressure sensitives are in many ways the complement to rubber-resin systems. First introduced to the merchant adhesive market in 1957, they have steadily replaced and overtaken the rubber-resin systems. The reason, of course, is performance and value in use. They produce colorless, optically clear films with outstanding resistance to environmental degradation. They adhere well to many substrates and have a good overall balance of adhesive properties. They are, however, generally weak in the areas of low surface energy adhesion and tack (unless a significant compromise in cohesive strength is made), i.e. precisely the areas in which rubber-resins stand out.

We shall now discuss approaches to resolving this dilemma which have led us to introduce an exciting hybrid polymer technology capable of giving us the most desirable features of the acrylics and the rubber formulations in a single material.

Tackification of acrylics

One answer to improving the tack and the low surface energy adhesion of acrylic polymers is the obvious one, namely to add a tackifying resin. Indeed, this is widely practiced, particularly with acrylic emulsions for paper label uses and the like. This method is also used to a much more limited extent in formulating solution acrylics for certain tape applications, for example. The following Figure and Table show some typical properties for an acrylic psa tackified with 40 parts of rosin ester on 100 parts of polymer.

Testing
The dry adhesive coating thickness was 2 mils on a 2 mil PET film backing. Peel adhesion was measured according to PSTC test method number 1 with wet out (dwell) time as indicated. The test panels were stainless steel (SS) and high density polyethylene (HDPE). Shear holding power was
measured following PSTC test method number 7 on stainless steel with 15 minutes wet out. Testing was performed at 72°F and 50% relative humidity. The Shear Adhesion Failure Temperature (SAFT) was obtained following ASTM D4498 with a 1 kg load on 1 square inch. Probe tack was measured with a Texture Analyzer® instrument, initially and after aging for 72 hours in a QUV® weatherometer equipped with UVB bulbs.

Figure 1: Peel strength of rosin ester tackified acrylic

![Peel Strength](image)

Table 1: Cohesive strength and tack of rosin ester tackified acrylic

<table>
<thead>
<tr>
<th>Substrate as function of wet-out time</th>
<th>No Tackifier</th>
<th>Tackified</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 20m</td>
<td>&gt;200</td>
<td>19</td>
</tr>
<tr>
<td>SS 7d</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>HDPE 20m</td>
<td>280</td>
<td>150</td>
</tr>
<tr>
<td>HDPE 7d</td>
<td>123</td>
<td>206</td>
</tr>
<tr>
<td>Probe tack (g), initial</td>
<td>117</td>
<td>159</td>
</tr>
<tr>
<td>Probe tack (g), 72h UV exposure</td>
<td>117</td>
<td>159</td>
</tr>
</tbody>
</table>

These data show that a large improvement in adhesion to a polyolefin can be achieved by this simple technique. However, the price of these gains is a substantial loss in cohesion and heat resistance and a sacrifice in the very properties for which acrylics are generally chosen, namely their superior aging characteristics.

The problem lies in the fact that the tackifying resins which are most compatible with acrylics are the rosin esters, which have rather poor aging properties. It is often observed that a loss of tack occurs on storage. This can be explained as a slow oxidation of the tackifier which then becomes immiscible with the polymer and results in phase segregation of this high Tg material at the surface. This phenomenon has been studied in a rosin ester / poly(ethylene-butylene) system by Paiva et al.¹ using atomic force microscopy. The miscibility and phase diagrams for acrylic polymers and tackifying resins have been studied in detail by Kim & Mizumachi.² Hydrogenation of the resin can help slow the process but is not a complete answer.

One would like to use a synthetic hydrocarbon tackifier, which, even if not fully hydrogenated might be expected to age better than a rosin derivative. However, these are not generally compatible with acrylic copolymers. Typical rosin esters and acrylics have similar solubility parameters and both have moderate hydrogen bonding capability. In contrast, the hydrocarbons have somewhat lower solubility parameters and poor hydrogen bonding capability. Thus they are normally immiscible.
A new approach

One approach is to modify the acrylic polymer such that it becomes compatible with the preferred tackifiers. However, one cannot simply choose a new set of monomers from the typical acrylic ‘toolbox’ since the acrylic monomers and the usual vinyl comonomers which are useful for pressure sensitives all produce polymers with a similar solubility parameter. The solution to this problem is to create a block copolymer of an acrylic and another polymer which is compatible with the hydrocarbon tackifiers, i.e. a hydrocarbon polymer.

Block copolymers can be prepared by a number of methods. Most familiar in the pressure sensitive industry, particularly in hot melt adhesives, are the SIS and SBS polymers which are prepared by anionic polymerization. Manufacturers of acrylics have sought to adapt the well-established techniques of free radical polymerization to producing a block polymer architecture. Usually, the goal has been to incorporate domains of high Tg, such as polystyrene or poly(methyl methacrylate), with the intent to enhance the thermal and mechanical properties of the adhesive in a manner analogous to the use of SIS in hot melts. Two methods of achieving this are: a) with a high Tg macromer creating a comb polymer architecture,3,4 and b) via a multifunctional chain transfer agent and sequential low and high Tg monomer addition creating a radial block structure.5 Still a third method is to attach polymer side chains to the acrylic backbone in a second synthetic step. This method is practiced by National Starch for transdermal drug delivery applications where a change in solubility parameter may be desired for compatibility with a particular skin permeation enhancer or drug.6 Each method has advantages and limitations. The macromer approach is, perhaps, the easiest but is limited by the commercial availability of suitable macromers. Use of a saturated rubber macromer in psa’s was first demonstrated by Mallya and Smith.7 The challenge, which we address in this paper, was to turn this promising idea into a practical reality.

Polymer design

The primary considerations were: a) to achieve a balance of properties that brings value to customers, and b) to use a process which is compatible with safe and efficient manufacturing practices. A classic experimental design strategy was used to explore the compositional space. A typical, work-horse acrylic polymer is composed of the following elements:
- a low Tg monomer such as butyl acrylate, 2-ethylhexyl acrylate or isoctylacrylate to impart the pressure sensitive tack
- a higher Tg monomer such as methyl methacrylate, methyl acrylate or vinyl acetate to impart cohesive strength
- a functional monomer such as acrylic acid to impart specific adhesion, enhance cohesion and provide sites for crosslinking, if desired.

Superimposed on this design we have the rubber macromer, which in this case is a liquid ethylene-butylene polymer. Two series of polymers were prepared, A-E and F-J, each employing a different functional monomer but otherwise alike. Comparison is made with a pure acrylic polymer of typical composition.

The solutions were coated at 1 mil dry thickness on 2 mil PET film and tested as described above.
From these data one may conclude that the peel strength of the 'base' polymers is unexceptional. It can vary over a wide range but is not higher than a pure acrylic composition can achieve. However, the shear strength is very interesting (note the logarithmic scale) and somewhat unexpected, given the soft low Tg nature of the macromer. It suggests a reinforcing effect of the macromer, perhaps due to a microphase separation. This gives hope for substantial formulation latitude.
The viscoelastic properties were measured at a frequency of 10 radians/second. Two distinct Tg’s can be clearly discerned corresponding to the rubber and acrylic phases. Taken together with GPC data showing polymerization of the macromer and the absence of haze in the coated adhesive film, this is evidence of a block polymer architecture.

**Formulation**

Formulation parameters which were considered were:
- choice and level of tackifier
- crosslinking
- solvent selection

**Tackifier**
The choice and level of tackifier is dictated by compatibility (in this case we wanted to tackify the hydrocarbon polymer phase) and by the particular end use requirements. Incompatibility is associated with the onset of haze in the dried adhesive film and is easily detected by visual observation, or a haze meter can be used to quantify the effect. Where long term exterior exposure is anticipated one might choose a fully hydrogenated resin whereas in other applications a less costly resin might suffice. A number of hydrocarbon tackifiers of different types were screened for compatibility at high loading. Compositions E, H, I and J were found to have broad compatibility.

**Crosslinker**
As with acrylic adhesives, it is generally advantageous to use a crosslinker. While this could be a two-part system we prefer to use a self-cure technology in which the adhesive is supplied with a predetermined level of a metal chelate crosslinker. This simplifies use of the product and eliminates a potential source of error as well as reducing waste.

**Solvent selection**
The solvent blend is dictated, in part, by the requirements of polymerization and by the need to maintain solubility of the hybrid polymer and any formulating additives such as the tackifier. Consideration must also be given to the conditions required for drying, particularly for thick film applications. The result, then, is a solvent blend which is primarily a mixture of ethyl acetate and hydrocarbon solvents.

**Adhesive performance**

**Tackifier response**
Here we show the adhesive performance of Polymer E, formulated with an aliphatic hydrocarbon tackifier at a range of concentrations expressed in parts per hundred of base polymer. A fixed level of crosslinker was used. Testing was again performed at 1 mil as detailed above. A comparison is made with two commercially available rosin ester tackified acrylics. These are designated AC-1 and AC-2, and contain 15 and 40 pph tackifier, respectively.
As expected, the peel strength increases with tackifier loading and at 40 pph exceeds that of the tackified acrylics on stainless steel. On HDPE, which is the substrate of most interest, the peel is comparable to the acrylics at equal loading but does not exceed them. However, when one looks at the shear resistance one sees that at 40 pph the acrylic has minimal cohesion whereas the hybrid polymer still retains a very respectable level of shear strength. This is a consequence of their different polymer architectures.

We now look at a similar formulation of a hybrid polymer from the second functional monomer series.
Here the peel strength is significantly higher than the acrylic on both SS and HDPE when compared at 40 pph tackifier. At 55 oz/inch (15N/25mm) this is an excellent result for an initial peel measurement obtained with a 1 mil adhesive coating on a low energy substrate. Furthermore, the shear holding power is still at a useful level for many tape applications.

These examples serve to demonstrate the versatility of the technology. Polymer J with tackifier at 40 pph was selected for further evaluation.

**Performance profile**

The peel and shear strengths show a strong increase with coating thickness as expected. Again, the values on HDPE are particularly noteworthy. High loop tack was obtained and good heat resistance as demonstrated by the shear adhesion failure temperature. On balance, the adhesive has exceptional peel strength and tack combined with good cohesion and heat resistance.

**Table 2: Adhesive performance profile**

<table>
<thead>
<tr>
<th>Thickness, mils</th>
<th>SS</th>
<th>HDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Peel, oz/in.</td>
<td>94</td>
<td>140</td>
</tr>
<tr>
<td>Shear, hr</td>
<td>38</td>
<td>59</td>
</tr>
<tr>
<td>Loop tack, oz/in²</td>
<td>-</td>
<td>132</td>
</tr>
<tr>
<td>SAFT, °F</td>
<td>-</td>
<td>240</td>
</tr>
</tbody>
</table>

**Peel build**

Acrylic adhesives normally develop their full peel strength slowly after forming the bond whereas rubber-resins tend to have higher initial bond strength and exhibit little peel build with additional time. In this respect the hybrid adhesives behave like a typical rubber adhesive.
Figure 6: Peel strength buildup

![Peel strength buildup graph](image)

**Roll storage**
An interesting observation is that the measured initial peel strength increases during the first weeks following coating. Normally, laboratory prepared coatings are equilibrated at constant temperature and humidity for 24 hours and then tested. However, sometimes a longer period elapsed and it was found that the peel strength was higher than when first measured. Careful study has confirmed that this is a real phenomenon and not a testing artifact or a result of random experimental uncertainty.

Figure 7: Effect of roll storage on peel

![Effect of roll storage on peel graph](image)

Equilibrium for adhesion to HDPE is reached after about 2 weeks. For stainless steel no further increase is seen after one week. Ideally, an adhesive coating should remain perfectly stable once the cure is complete. In this case the cure is expected to be complete within a day or so and one must look elsewhere for an explanation. We hypothesize that the rubber phase becomes oriented towards the low energy interface with the release liner. Fortunately, the immediate adhesion is high and the effect only serves to *increase* it. This stands in marked contrast to situations with conventional tackified acrylics where a *loss* of tack occurs, as discussed above.

**Chemical resistance**

Hybrid psa formulations have excellent resistance to harsh chemical environments and improved hydrolysis resistance compared with a rosin ester tackified acrylic. Polyester backed test specimens bonded to stainless steel were immersed in the following liquids for 1 week: water, antifreeze, transmission fluid, one molar sulfuric acid and one molar caustic soda. All showed minimal to slight penetration of the bond line by the fluids. Similarly good results were obtained with the tackified acrylic excepting in caustic soda where the adhesive bond line was substantially penetrated.
Applications

Hybrid rubber-acrylic psa’s are expected to find use in a wide variety of tapes and transfer films, for example, in automotive applications, mounting and product assembly. They are particularly suited to applications in which an acrylic does not meet the requirements due to insufficient tack or adhesion to low energy surfaces. They show excellent adhesion to many foams, polyolefins, metals and engineering plastics and a very good balance between adhesion and cohesive strength. In addition, they exhibit a high degree of resistance to chemical and environmental degradation.

Future developments

This is a versatile technology which forms a foundation for a line of products to meet diverse needs. An initial development is targeted at applications requiring very high peel and tack without a major compromise in cohesion and heat resistance. It also has generally good resistance to UV and oxidative degradation, but is limited to applications where a slight yellow color can be tolerated. Future developments will offer a range of adhesives for higher heat resistance, long term resistance to oxidative and UV induced degradation, water clear bonds and other improvements.

References


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