NOVEL PRESSURE-SENSITIVE ADHESIVES FOR VINYL FACESTOCKS

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ABSTRACT

The flexibility of Polyvinylchloride (PVC) film makes it ideal for many industrial tape and label applications. Unfortunately, PVC film can be difficult for many adhesives to bond to and transfer failure is common. This can lead to longterm debonding as well as reduced holding power and chemical resistance. This paper will provide an in-depth look at PVC adhesion and describe a solventborne adhesive with superior anchorage to PVC films as well as improved heat-resistance.

INTRODUCTION

The use of thermoplastic materials as films for tape, label, or sign applications has become quite common. The majority of pressure-sensitive label material has historically been made with paper stock due to the relative cost difference. However, in recent years appearance and performance have begun to dictate the types of materials used in many applications. Thermoplastic materials offer many benefits over paper such as weather and chemical resistance, durability, flexibility, graphic appeal, and transparency. As a result of these benefits the growth rate of thermoplastic pressure-sensitive films has consistently outpaced that of paper. According to a 1998 study conducted by the European Pressure Sensitive Manufacturers Association the use of film materials in pressure-sensitive products over a seven year period from 1991 to 1997 grew at an annual average rate of 21.6%. This dwarfs the 6.5% annual average rate of growth shown by pressure-sensitive materials using paper during the same period. [1], [2]

Some of the most common thermoplastic materials currently in use are polyethylene, polypropylene, polyethylene terephthalate, and polyvinyl chloride. Among the family of thermoplastic film materials PVC has many properties that make it ideal for pressure-sensitive products. It has great resistance to environmental conditions and is suitable for exterior advertising and fleetmarking. When plasticized it has terrific flexibility and is able to conform well to odd-shaped surfaces. It offers a reasonably high surface tension for ease of printability and may be made in virtually any color. It has good electrical properties and resistance to chemical oils and greases. Since its introduction to the converting market in the 1950's, PVC has found its way into several applications such as capacitor tape for electrical work, shelf marking labels for supermarkets, and most recently colorful floor graphic advertisements for retail centers.

FACESTOCK DEBONDING

While thermoplastic films offer many advantages to the converter they can also cause some problems. Thermoplastic films are generally much smoother and less porous than paper. This can make wetting of the film with an ink or adhesive difficult to accomplish. With PVC film there is the additional problem of plasticizer or stabilizer migration into the adhesive layer. This can drastically affect the adhesive's performance and ability to anchor onto the facestock, which may lead to transfer failure.

Transfer failure or debonding from a facestock occurs when the adhesive has a greater affinity for the substrate than it does to the facestock (see Figure I). When the adhesive of a pressure-sensitive construction has a tendency to transfer from its facestock the product is subject to a myriad of problems. Longterm delamination can lead to flagging and ultimate failure of the tape or label. The tendency of the adhesive to remove itself from the film can also lead to reduced holding power and lower shear. The adhesive film will be much more mobile and subject to bleeding or oozing, which can lead to machine buildup during cutting or sheeting. Finally, with poor facestock bonding the adhesive is more prone to failure when exposed to water and other chemicals.
Anchorage onto a polymer facestock can be improved in a number of ways. Perhaps the simplest way which involves no additional process steps is to coat the adhesive directly onto the film. This allows the adhesive to be applied in a molten state, thereby improving initial wetout for a stronger and deeper bond after drying, cooling, or crosslinking. Another simple method of treating a film is by physical etching or scoring. While this doesn’t improve the strength of the bond it does increase the surface area, which imparts a marginal improvement.

Some of the more effective and more common methods of surface preparation involve oxidation of the polymer surface. By oxidizing the surface of a polymer new chemical groups are introduced which improve the polarity of the film and make it easier to adhere to. Examples of oxidative processes include chemical etching, corona, flame, and plasma treatment. Another effective means of improving anchorage is to apply some kind of primer to the surface. A primer is an extremely thin interfacial layer that bonds to the film and presents the adhesive with a whole new surface to adhere to. [3]

Anchorage to a PVC facestock is made even more difficult by two factors. First, plasticizers or stabilizers can migrate into the adhesive layer over time and destroy its properties. Second, the surface of PVC is slightly different than other thermoplastic polymers (see Figure II). The chlorine atoms on the alternating carbons are highly electronegative, which imparts a dipole onto the molecule and leaves the surface very electron-poor. This presents a problem for many adhesives that are not designed to bond to an acidic surface for an extended period of time, especially when exposed to weather or migrating additives. Furthermore, this condition cannot be improved by oxidative pretreatments commonly used with other popular thermoplastic films.

SPECIFIC INTERACTIONS

One solution to the PVC anchorage problem is to create specific interactions between the adhesive and the PVC surface. Since we cannot effectively change the PVC surface by oxidative process it is essential that we focus on the adhesive and how we can make it complement the PVC surface. By incorporating the monomer shown in Figure III the adhesive can be made to better accept the acidic surface. The π-bond on the oxygen is easily delocalized, forming the resonance structure shown in Figure IV. The free electron pair on the nitrogen is actually distributed across the molecule, creating a dipole. This electron-rich molecule will readily accept the surface of the vinyl.
DATA ON VINYL

The data shown in Table I compares a commercially-used graphic films grade solution acrylic adhesive to an adhesive utilizing the monomer described previously. Because the commercially-used adhesive was specifically designed for use on plasticized PVC facestocks and rarely transfers only one vinyl was chosen for this comparison. This vinyl is a soft 100g/m² clear film used for both indoor and outdoor applications and represents a difficult application that is more likely to induce transfer failure. All samples were coated at a coatweight of 25g/m².

<table>
<thead>
<tr>
<th>Heat/Humidity Conditioning</th>
<th>Test</th>
<th>Graphic Films Adhesive</th>
<th>Modified Adhesive</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>24 hours at 25°C</td>
<td>24.4</td>
<td>28.2</td>
</tr>
<tr>
<td>none</td>
<td>1 week at 25°C</td>
<td>27.1, 20% transfer</td>
<td>33.3</td>
</tr>
<tr>
<td>24 hours at 72°C on panel</td>
<td>1 hour at 25°C</td>
<td>26.3, 20% transfer</td>
<td>33.4</td>
</tr>
<tr>
<td>1 week at 72°C on panel</td>
<td>1 hour at 25°C</td>
<td>29.2, 20% transfer</td>
<td>35.3</td>
</tr>
<tr>
<td>24 hours at 38°C, 100% rh on panel</td>
<td>1 hour at 25°C</td>
<td>28.8, 30% transfer</td>
<td>31.8</td>
</tr>
<tr>
<td>1 week at 38°C, 100% rh on panel</td>
<td>1 hour at 25°C</td>
<td>29.6, 40% transfer</td>
<td>17.7</td>
</tr>
</tbody>
</table>

As you can see from the data the inclusion of the monomer greatly assisted the adhesive in maintaining anchorage to the vinyl. Although the transfer-inducing tests under high heat and humidity did somewhat affect the peel strength of the adhesive they did not promote failure of the bond.

ADDITIONAL BENEFITS

In addition to improved PVC anchorage benefits in high temperature performance can also be obtained. A pressure-sensitive polymer must be soft and mobile enough to provide tack, yet also must have the cohesive strength necessary to hold onto the surface it wets out. Since these two properties contradict each other it can be a struggle to find the right rheological balance in an adhesive product. Most conventional solution acrylic adhesives consist of soft polymers of low to moderate molecular weight with a small amount of carboxylic functionality. These polymers can be crosslinked with a post-added metal chelate, which hinders the mobility of the polymer somewhat while increasing the cohesive strength.

When trying to achieve a product with high shear or heat-resistance some barriers can materialize with this approach. One way to achieve improved cohesion is simply by increasing the amount of post-added chelate. Unfortunately, the more crosslinker one adds to the system the greater the drop in mobility and tack. A better way to increase the cohesion of an adhesive is to increase the molecular weight of the uncrosslinked polymer. This will increase the degree of molecular entanglement that occurs in the polymer and when used in combination with standard chelate-induced crosslinking increases cohesion without causing as great a loss in tack. This is a common method used to produce industrial-grade solution acrylics.
But how can one further improve the heat-resistance of a crosslinked high molecular weight system? Because the inclusion of additional carboxylic functionality can cause problems with synthesis and product stability the amount of acid incorporated on the polymer must be kept at a modest level. What is needed is a secondary bonding method to complement the one already implemented. This extra bonding is provided by the inclusion of the monomer described previously.

As shown in Figure V utilization of this monomer will also assist in crosslinking. It easily bonds to the carboxylic groups via simple acid-base interactions to provide additional crosslinking sites that further boost the cohesive strength and heat-resistance of the polymer. This is similar to the effect described by Vanhoye et al. [4]

![Figure V: Additional crosslinking achieved without the addition of post-added chelating material (note the distribution of the electrons across the molecule between the nitrogen and oxygen)](image)

**DATA ON HEAT-RESISTANCE**

In Table II data is shown comparing a commercially-used high molecular weight industrial grade solution acrylic to a high molecular weight version of the modified acrylic product. The products were coated 50 g/m² thick on 50g/m² polyester film. Of specific interest is the lack of peel build when heat-aged on the test panel. The commercial product softens more under heat and further wets out the surface. This is seen as an increase in peel when the heat-aged sample is returned to room temperature. However, when tested at an elevated temperature one can truly see that it softens more than the modified product (note: 82°C was chosen for this test because it is the highest temperature our peel tester would tolerate).

**Table II: Comparison to industrial grade solution acrylic on 50g/m² PET film**

(All peels in N/25mm from stainless steel)

<table>
<thead>
<tr>
<th>Heat Conditioning</th>
<th>Test</th>
<th>Industrial Adhesive</th>
<th>High MW Modified Adhesive</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>24 hour at 25°C</td>
<td>22.5</td>
<td>20.7</td>
</tr>
<tr>
<td>none</td>
<td>1 week at 25°C</td>
<td>25.6</td>
<td>24.7</td>
</tr>
<tr>
<td>24 hour at 72°C on panel</td>
<td>1 hour at 25°C</td>
<td>34.1</td>
<td>27.0</td>
</tr>
<tr>
<td>1 week at 72°C on panel</td>
<td>1 hour at 25°C</td>
<td>35.5, 10% transfer</td>
<td>27.1</td>
</tr>
<tr>
<td>none</td>
<td>1 hour at 82°C</td>
<td>8.4</td>
<td>10.4</td>
</tr>
<tr>
<td>none</td>
<td>2kg shear at 25°C</td>
<td>100+ hours</td>
<td>100+ hours</td>
</tr>
<tr>
<td>none</td>
<td>1kg shear at 121°C</td>
<td>21 hours</td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSIONS

The use of special monomers in solution acrylics can provide both specific adhesion and performance advantages in a variety of ways. Creative polymer compositions allow formulators to move past existing barriers and continue to create new products. As applications become more and more demanding adhesive formulators must rise to the challenge and use every tool available to assist them in constructing their product. Creativity and an open mind are the keys to pushing the performance bar higher one small notch at a time.

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REFERENCES


