Polyurethane chemistry improves adhesives

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Polyurethanes are a class of adhesive raw materials that, for nearly 50 years, have demonstrated tremendous reliability and high performance in many applications, including the footwear, plastics bonding, packaging, furniture assembly and automotive industries.

Properties of polyurethane adhesives can be customized to fit an application due to the variety of raw materials that can be used to formulate polyurethanes.

One polyurethane adhesive that has had great commercial significance over the years is based on hydroxyl polyurethanes that are dissolved in organic solvents. They are known for forming bonds with excellent green strength, plasticizer resistance and durability.

One- and two-component solvent-borne polyurethanes are also important for film-to-film laminating (packaging). As environmental legislation limits the further use of these solvent-based systems, there has been rapid growth in the demand for water-based polyurethanes.

Polyurethane dispersions consist of fully reacted urethane polymers dispersed in water. The polymer is usually modified with hydrophilic groups of cationic, anionic or nonionic nature—eliminating the use of external emulsifiers. These products have many of the same performance advantages of their solvent-based counterparts and even may exceed them in some areas.

Fig. 1. Formation of polyurethanes.

Fig. 2. Raw materials: Polyisocyanates and polyls.

Typical performance characteristics of aqueous polyurethane dispersions are:

- Easy processing via spray and roller coating;
- Good adhesion to difficult-to-bond substrates;
- High initial and final bond strength;
- Good resistance to moisture and plasticizers;
- Ability to blend with other aqueous systems;

- Good heat resistance; and
- Heat activation at low temperature.

These dispersions have found applications in the automotive industry for bonding interior trim, in the furniture/construction market for laminating vinyl to medium density fiberboard, in the shoe industry and in packaging applications (film-to-film, film-to-foil).

Fig. 3. Prepolymer mixing process.

Chemistry, manufacture of polyurethane dispersions

Raw materials

Polyurethane dispersions provide adhesive manufacturers with a variety of formulating options. These adhesive raw materials are available with a range of film properties—from hard to soft. The appropriate dispersion used depends on the end-use application.

Polyurethanes are produced by the reaction of polyisocyanates with compounds containing active hydrogen groups, such as hydroxyl or amine groups (Fig. 1). The typical building blocks for polyurethane dispersions are shown in Fig. 2.

Typical raw materials used for pre-polymerization bonding polyurethanes are generally similar to those used for solvent-borne or 100 percent solids polyurethanes, with the addition of raw materials that provide hydrophilic character to the polymer (ionic or nonionic groups). For example, if an application using a solvent-based adhesive is found to perform best using a highly crystalline polyester backbone, it is likely the waterborne system will benefit from similar chemistry in the polymer.

A number of factors, including performance, cost and manufacturing considerations, impact the choice of the monomeric isocyanate used in the dispersion. For most dispersion applications, aliphatic polyisocyanates are preferred. Typical aliphatic polyisocyanates are hexamethylene diisocyanate, isophorone diisocyanate and diisocyanylmethane diisocyanate.

Properties associated with aliphatic polyisocyanates include:

- Light stability, weather stability;
- Lower reactivity;
- Slower reaction with water—advantages for dispersing prepolymer;
- Longer prepolymer reaction time;
- Softer elastomer; and
- Slower reaction with water—advantages for activation applications, although they are more prone to oxidation. Products of this type have poor plasticizer resistance and are not prominent in heat-activation applications, although they are used in packaging.

In contrast to other types of dispersions, polyurethane dispersions most often contain only internal emulsifying groups (ionic or nonionic), meaning they are built into the polymer backbone. Other dispersions, e.g. polychloroprenes, are stabilized by the addition of external emulsifiers.

The most commonly used ionic groups are based on carboxylate ions and sulfonate groups. Sulfonate-stabilized dispersions have a pH value of approximately seven and...
are stable even at low pH values, which allows significant formulating flexibility when blending with other polymers. In contrast, carboxylate stabilized dispersions have a higher pH (>8). They are generally unstable at lower pH values, which limits formulating options.

Manufacturing processes

The most important production processes for preparing aqueous dispersions are the solution process and the prepolymer mixing process.

In the solution process, a prepolymer is formed by reacting a difunctional polyl with a diisocyanate. Further molecular weight is built into the solution by utilizing water miscible solvents, e.g., acetone, and chain extenders containing hydrophilic groups (carboxylates or sulfonates). This solution is then progressively diluted with water until a phase inversion occurs and a dispersion in water is formed. In the final step, the solvent is removed by distillation and a “solvent-free” dispersion of a polyurethane polymer is obtained.

The prepolymer mixing process (Fig. 3) avoids the use of large solvent volumes. A prepolymer containing hydrophilic groups is prepared first and then is dispersed in water under high shear action. The water may be pumped into a reactor of water with agitation (inverse process), or water may be pumped into the reactor containing the hydrophilic prepolymer (melt process).

The melt process has the disadvantage that a significant viscosity increase occurs as the water is added to the prepolymer prior to the phase inversion—when water becomes the continuous phase.

Chain extension to build molecular weight is carried out in the aqueous phase using diamines. A controlling factor in the prepolymer manufacturing process is the viscosity of the prepolymer, since excessively high viscosities will cause difficulties in the dispersion step.

The addition of a solvent (e.g., toluene, n-methyl pyrrolidone) can aid in improving the efficiency of the dispersing operation and help film coalescence.

Typical properties

For many adhesive applications, anionic polyester polyurethanes based on aromatic isocyanates are the preferred materials, since they offer more favorable adhesion characteristics and freedom from discoloration.

But dispersions based on aromatic diisocyanates or mixtures of aromatic and aliphatic polyisocyanates also are commercially available. The polymer backbone also may be based on polyether or polyurea, depending on the application.

Commercially available dispersions usually are specified by solids content, pH and viscosity. Typical property ranges for commercial products from various sources are listed in Table I. Products are available with and without co-solvent, depending on the manufacturer. Typical solvents found in adhesive dispersions include acetone and NMP. Co-solvents in the dispersions may be present to improve film formation or act as a wetting aid or may exist in trace quantities as a residue from the manufacturing process.

Polymers have been designed with a wide range of film properties to meet the requirements of target applications. The range of polymer properties available is illustrated in Table II, with values taken from published supplier literature. As can be seen in the table, the physical properties of free films can vary widely due to the inherent flexibility of polyurethane chemistry. This allows the development chemist to tailor products for a wide range of applications to meet requirements of high strength, flexibility and softness, transparency in appearance, discoloration resistance or heat sealability.

The dispersions highlighted in the next section are typical products made for wet bonding and heat-reactivation applications (Fig. 4). These dispersions were manufactured by the solution process and have anionic stabilization. They are each based on aliphatic polyisocyanates and polyester polyols.

Generally, the products have good storage life (a minimum of six months), very good mechanical stability, are film-forming at ambient conditions and exhibit good compatibility with other dispersions (e.g., VAE, acrylic).

Application conditions

Polyurethane dispersions are used in two main types of applications—a wet bonding process and the heat-activation bonding process.

The use of the wet bonding process requires that at least one substrate be porous to allow water to evaporate and requires a longer fixation time to allow bond strength to develop. With the heat-activation bonding process (Fig. 5), the adhesive is applied to a substrate, and the water is evaporated in a drying tunnel. At this point, the adhesive surface is warm and tacky, and the substrates to be bonded are mated. Pressure is applied to the bond over a short period of time via a fixture or a vacuum operation to produce the finished part. During the heat-activation bonding process, a number of polymer physical changes occur as temperature changes. Fig. 6 shows a typical curve generated from a thermomechanical analysis for a crystalline polyurethane dispersion. It indicates that at a temperature of about 50°C, the polymer softens significantly due to a melting transition of a crystalline polyester segment in the polymer backbone.

The graph on the right refers to adhesive tack. If the tack of the adhesive film is measured at various temperatures, it is observed that at room temperature or below, many polyurethanes form a non-tacky film similar to a coating.

But at the same temperature of about 50°C, it is observed that the tack property significantly increases. This means that the adhesive film needs to be warmed to about 50°C to allow tack to develop and thus enable a good bond to form. If the film is overheated, the tack value decreases due to a further softening of the polymer.

In Fig. 7, the heat-activation bonding process is explained in more detail. The graph charts polymer modulus against time after a bond has been formed. Before the heat-activation process is initiated, the adhesive polymer is a dry, non-tacky film.

After heat activation, the flexible crystalline segments of the polyester polyurethane melt (decrystallize), and the film becomes tacky and capable of forming a bond. The two substrates are joined at this point under low to moderate pressure. The viscosity of the polymer is still high enough, though, to prevent the adhesive from flowing and excessively wetting the substrates.

In the period immediately following bonding (phase 1), the bond line starts to cool down. At this point the polymer is...
Adhesives

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increases in modulus, and there is a jump in bond strength. This happens in a period of seconds.

In a matter of minutes (phase 2), the polyester segments begin to recrystallize, and the adhesive develops its high initial bond strength. If this polyurethane adhesive contains a polysocyanate crosslinker, over a period of days (phase 3) the polymer modulus will increase further to produce a cross-linked polymer with improved heat and hydrolysis resistance.

Adhesion performance

The excellent adhesion characteristics typical for hydroxyl-terminated solvent-borne polyurethanes also were found in aqueous dispersions yielding good adhesion to substrates, such as PVC, ABS, polyurethanes, nylon, leather, fabrics and wood.

One piece of “conventional wisdom” for many in the adhesive field was that water-based adhesives could not attain the level of performance of the traditionally used solvent-based adhesives. The tack and initial peel strength performance of solvent-borne systems, in particular, were believed to be difficult to duplicate in environmentally friendly water-borne products.

Fig. 5 compares the peel strength of a typical high-performance polyurethane solvent-based adhesive (Solv HP) with several dispersions. The substrate was PVC containing 30 percent dioctyl phthalate plasticizer. It can be seen that dispersions are available, in particular PUD 2 and PUD 4, which yield the same good adhesion values as solvent systems. The polyurethane dispersions differ in their initial strength values and in the rate of strength development. PUD 2 develops strength the fastest and ultimately shows the same high level of performance as Solv HP.

The rate of crystallization of the dispersions correlates well with the rate of strength development. Relative crystallization rates were determined by heating films of the polyurethanes at 80°C to decrystallize the polymer backbone and measuring the hardness of the films as they cooled at room temperature. If the ambient temperature is higher, the recrystallization will take place at a slower rate. This would have the practical consequence that the adhesive bond may not develop strength fast enough, and bond failures may occur.

Tack as a function of the adhesive film temperature

A typical high-performance polyurethane adhesive has been shown to be a good predictor of initial bond strength. By varying the chemical backbone of the polyurethane, it is possible to change the tack behavior of these adhesive raw materials in a controlled fashion.

A typical heat-activatable adhesive shows the highest tack values in the temperature range from 45°C to 55°C, which indicates that the adhesive is fairly activated. This film temperature is achieved in practice by heating the adhesive film for a few seconds under a high-intensity infrared lamp. The substrate itself is only very minimally heated. This method is called flash or shock activation.

At higher adhesive film temperatures, the tack values decrease due to the lower cohesive strength of the adhesive at these temperatures. This behavior of heat-activatable adhesives has to be taken into consideration when defining the final application parameters.

There is always an ideal “temperature and processing window” in which the adhesive shows its optimal tack behavior. It is possible to adjust this processing window to the demands of the bonding process by altering the chemical structure of the polyurethane or by adjusting the raw materials used to formulate the finished adhesive.

The rate of crystallization of polyurethane dispersions can be measured by tack experiments. Measurements of tack as a function of time after a single activation of the adhesive film allow conclusions to be made regarding the so-called “hot tack life.”

Fig. 9 shows the crystallizing behavior of two polyurethane systems. PUD 3 is fast crystallizing while PU HTL crystallizes at a slower rate and thus retains a higher tack level for a longer period of time. System PU HTL has a much longer hot tack life than system PUD 3. Polyurethane dispersions can be produced with optimum tack value at various temperatures. The activation temperature needs to be matched with the thermal properties of the substrates being bonded and the limitations of the application process (Fig. 10). PUD 3 loses its tack performance at a temperature above 80°C due to the loss of cohesive strength. This is a result of the chemical and molecular structure of the polymer. Even at this high temperature, product PUD 6 retains its strength, which can be seen by the higher tack values, compared with PUD 3. For that reason, PUD 6 is the product of choice for high-temperature lamination processes.

PUD 7 has a very special advantage over common polyurethanes (PUD 3) for processes in which a low temperature for activation of the adhesive is required. One targeted application area for such a product could be a lamination...
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The performance of polyurethane dispersions can be tailor-made based on:
- The variety of backbones available in polyurethane chemistry;
- The segmented structure of polyurethanes; and
- The molecular design.

The elevated temperature performance and environmental performance of polyurethane dispersions can be varied over a wide range. Thermomechanical analysis is a more commonly available technique that can also be used to differentiate the thermal properties of polyurethane dispersions. The results from this technique complement those obtained from the tack experiments.

Conclusions

Polyurethane adhesives can furnish excellent bonding performance with respect to peel strength, heat resistance and activation behavior.

From a practical standpoint, in order to make a water-based adhesive system perform, the polymer must have the required bonding performance, must be able to be applied according to the needs of the application and has to have the proper cost-performance ratio.

One of the strong points of polyurethane dispersions is their compatibility with other polymer dispersions (e.g., acrylic and vinylacetate-ethylene copolymer dispersions). This enables the compounder to create combinations that are not possible with solvent systems due to insolubility or incompatibility problems and allows cost and performance to be optimized.

Thermoactivatable polyurethanes, proven for a long time as solvent-borne systems, exhibit exceptional importance in the field of adhesive raw materials. With this group of adhesives, durable and reliable adhesive bonds can be achieved in an economical way.

Consequently, thermoactivatable polyurethanes are the raw materials of choice for many industrial applications, especially when working with difficult-to-bond-to substrates such as plasticized PVC.

As environmental pressures to remove solvent from the workplace have increased, environmentally friendly alternatives based on aqueous polyurethane dispersions are being offered by producers of adhesive raw materials.

The data show that these water-borne products can be used to formulate high-performance adhesives.

The ultimate success of an adhesive in an application depends not only on the adhesive raw material but also on the substrate supplier, the manufacturer that uses the adhesive, and the environment that is present at the time of application.

Through the continued cooperation of adhesive manufacturers, raw material suppliers and adhesive end-users, new adhesives with optimum performance levels will continue to be developed.

References


Abbreviations in text and graphs

PUD 1: Dispercoll U 42
PUD 2: Dispercoll U 53
PUD 3: Dispercoll U 54
PUD 4: Experimental polyurethane dispersion
PUD 5: Experimental polyurethane dispersion
PUHTL: Experimental polyurethane dispersion

Successful polyurethane adhesives can be tailored to exhibit the desired tack life.

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