

## Types of adhesives used in the printing industry

Adhesives can be divided into many categories, such as origin, state, bonding mechanism, exploitation conditions and more. The main category division places adhesives into two major groups based on their origin: natural adhesives and synthetic adhesives. They can also be divided into organic and non-organic substances, and then subdivided further according to their raw materials. Adhesives can be also divided according to their state of matter: liquid or solid. The bonding mechanism of adhesive can be either physical or chemical. Physical bonding mechanisms work due to solvent (or water) evaporation or through setting of a melted adhesive. Chemical bonding mechanisms are bonds created by either polymerization, polycondensation or polyaddition. Adhesives can also be divided according to the conditions they are used in such as the operation temperature or setting temperature. [1]

This section describes adhesives based on their source of origin and explains their properties.

### **Natural adhesives (bioadhesives)**

Natural adhesives can be divided into adhesives of plant origin and of animal origin. Adhesives of plant origin are adhesives which come from plants such as: starch, dextrin, cellulose, vegetable protein, vegetable resin, gum (Gum arabic), and latex (natural latex).

**Starch based adhesives** are adhesives which are derived from plants rich in starch such as potatoes (which contain 20% of starch) and wheat (70% starch). Starch is created within green plants by means of photosynthesis. Carbon dioxide is deducted from the air and combined with water from the roots with sun energy powering the chloroplasts within plant cells. Starch is composed of large carbohydrate molecules which in turn are composed of small glucose units joined through 1,4-alpha glycosidic bonds (as opposed to cellulose which is glucose joined through 1,4-beta glycosidic bonds) and sometimes 1,6-alpha glycosidic bonds. Starch is composed of two types of substances: amylose and amylopectin. Amylose is composed of shorter linear polysaccharides while amylopectin contains longer branched chains. Although it largely depends on the plant producing the starch, usually mass content of amylopectin is three to four times larger than amylose. The amount of amylopectin has a direct impact on the adhesion strength and therefore some plants are better suited for adhesive production than others. For example wheat will be a better plant of origin than potatoes. Amylopectin is insoluble in

cold water, but forms a sticky dispersion in hot water. Starch adhesives are not very stable after being cooled down, as water is known to separate from the solution and the substance itself is prone to mold. Therefore it is advised for starch based adhesives to be used directly after being prepared. [1] For this reason, many bookbinding industries have produced such adhesives locally.

**Dextrin adhesives** are derived from starch through partial hydrolysis, therefore they have the same bonding structure as amylopectin, but are noticeably shorter. Two variants of dextrin adhesives are produced: white and yellow, where yellow dextrin undergoes further hydrolysis and has better adhesion properties. Nowadays dextrin adhesives are rarely used as they are replaced by synthetic adhesives. However, such adhesives can still be found in envelopes and postage stamps which are activated by wetting a dry dextrin layer. However, even this type of use is being replaced by pressure activated adhesives.

Apart from starch based adhesives, some can be derived from cellulose. For bookbinding purposes, water soluble cellulose esters are used to produce two popular substances: methyl cellulose and carboxymethyl cellulose.

**Methyl cellulose** is obtained through a reaction between alkali cellulose with chloromethane. Methyl cellulose is one of few polymers which are soluble in water. It has high viscosity at 6–8% solutions and possesses good adhesive properties for binding paper products. Methyl cellulose properties are highly correlated with the number of methyl groups replacing three available hydrogen atoms of the hydroxide groups. Methyl cellulose has the highest water solubility when, on average, 1.2–2.0 of three available hydroxide groups are replaced. More methyl groups reduce the hydrophilic character of the substance making it soluble only in non polar solutions. Although methyl cellulose is soluble in cold water, it gels when the water solution is heated to 40–70°C. As a water based solution, it is odorless and mildly acidic (pH 6–7).

Adhesives derived from methyl cellulose create a strong bond with an elastic, aging resistant, bondline. Due to its long setting time, the products can be corrected after contact which makes this adhesive useful for bonding the covering to the base case and spine board.

**Carboxymethyl cellulose** is a cellulose carboxymethyl ester sodium salt dissolved in water. It is derived from an alkali cellulose reaction with chloroacetic acid sodium salt. As in the case of methyl cellulose, the physical properties of carboxymethyl cellulose depend on the number of hydroxide groups substituted by the carboxymethyl groups. The ideal mean number of substituted hydroxide groups for water solubility is 0.4–1.3 per ring. Carboxymethyl cellulose are very viscous at low concentrations, have a long bonding time and are relatively easy to distribute on a surface. Due to this property carboxymethyl cellulose is often used for attaching wallpapers and billboard advertisements. Lack of toxicity of the substance made it ideal for water based paint, washing powder, as a dispersion adhesive thickener, and some consumer products such as: ice cream, toothpaste, diet pills and more. [1]

Adhesives of animal origin are adhesives which gain their binding properties from animal proteins. Two major types of animal adhesives are gluten and casein.

**Gluten adhesives** are derived from degreased animal remains such as skin, tendons and bones. The main substance in such remains is collagen – main protein in connective tissue. Collagen has strong cohesion due to its hydrogen bonds. It is also insoluble in water. During long thermal treatment it undergoes hydrolysis and turns into gelatin. Lower grade gelatin is gluten which can be used as an adhesive. Gluten creates a colloidal solution (sol) with water at high temperatures and has the lowest viscosity at pH 5 as the amino acids of the protein reach an isoelectric point at this acidity. Bone glue is derived from bones and is sold as 3 to 8 mm pebbles, and skin glue is produced from tendons and skin.

**Casein adhesives** are adhesives with casein as their adhesive compound. Casein is a protein derived from milk. It is acidic in water and its isoelectricity is at pH 4.7. Apart from the main substance, casein adhesives contain other substances which alter the properties of the adhesive.

### **Synthetic adhesives**

The bonding substance of synthetic adhesives are large molecules such as polymers, copolymers and polycondensation resins. Synthetic adhesives are divided into three major groups: solvent based adhesives, dispersion adhesives (emulsion adhesives) and hot-melt adhesives.

**Solvent based adhesives** are composed of large molecules in organic solvents. Due to toxicity of most organic solvents in these adhesives, they became out of use in recent years.

**Dispersion adhesives** are widely used due to their low influence on the environment and human health. The main bonding substance in dispersion adhesives are solid polymer particles suspended in water. The size of polymer conglomerates ranges from 0.03 to 5  $\mu\text{m}$ . The polymer molecules are surrounded by a colloid which prevents the molecules from bonding into agglomerates.

Polymer dispersion is derived from an emulsion polymerization reaction. This process takes place in water where the emulsification of the monomer takes place with help of emulsification substances, stabilizers and polymerization initiators. The product of such polymerization is a polymer dispersion solution with dry matter percentage of 45–70%.

The viscosity of the adhesive is correlated with the dry matter percentage and the size of the dispersion grains. Low viscosity dispersion adhesives range from 100 to 3000 mPas, intermediate viscosity ranges are from 3000 to 10000 mPas, and dispersion adhesives with high viscosity are above 10000 mPas.

Dispersion adhesives are non Newtonian liquids with a thixotropic property which is greater for dispersions with higher viscosity.

The **most popular dispersions** used in adhesive production is the vinyl acetate (ethenylethanoate) homopolymer, acrylate ester polymers, vinyl acetate and acrylic acid based esters copolymers, and vinyl acetate and ethylene (ethene) copolymers (so called EVA copolymer).

Apart from the bonding substance, dispersion adhesives contain other substances which alter the characteristics of the adhesives such as the elasticity of the

bondline, bonding abilities, the dry matter percentage, viscosity, bonding time, and percolation.

The elasticity of the bondline is obtained by adding plasticizers to the adhesive. By adding plasticizers the dispersion grains swell and viscosity increases. Timing and mixing intensity are very important while adding plasticizers to the solution as to ensure good penetration of the dispersion grain. Inadequate mixing may cause the plasticizer to separate from the solution. Higher viscosity caused by plasticizers in the solution often requires additional substances which will bring this viscosity down. Some of the most popular chemicals that will reduce viscosity are vinyl alcohol, polyether alcohols, cellulose esters, polyacrylate acids or polyacrylate amides.

In some cases the plasticizers are not used, as some materials do not tolerate them. Plasticizers have a tendency of migrating into other materials over time until they reach a density equilibrium. During polymerization ethylene is added with the vinyl acetate to eliminate the need of plasticizers. Although this makes the dispersion suitable for some uses, it makes the bondline soft and less durable. This eliminates adhesives without plasticizers for some uses as, for example, threadless book-binding.[2]

Percolation of the adhesive is another important property of dispersion adhesives, which is the ability of water to pass into the pores and capillaries of the material the adhesive is applied to. High percolation causes the pores and capillaries of the material to fill up with water blocking the dispersion from interlocking with the surface. Additionally, the dispersion coagulates near the surface due to the rapid loss of water which reduces the adhesive properties of the dispersion. Percolation also depends from the grain size of the dispersion. Large grains have a difficult time in penetrating the pores of the material especially when the molecules are nearly the size of the pores they are expected to fill. Substances with large molecules are used to lower the degree of percolation such as: polyvinyl alcohol, polyacrylate amides, polyvinylpyrrolidoneect.

It is normal for some water to enter the bonded material, as this enables the adhesive to initiate the bonding process. This process is only detrimental to the bondline if the bonded material takes up too much water too fast.[2] Paper sizing has a large effect on adhesive percolation. Papers without sizing are more vulnerable to negative percolation effects while papers with sizing are not influenced by this effect.

**Hot-melt adhesives** are entirely solid. This means that the dry matter percentage of such adhesives is equal to 100%. This type of adhesives acquire their bonding properties when melted above their melting point. At their operation temperatures, these types of adhesives have great wettability properties and their bonding time is very short – bonding takes place instantly after contact.

One of the greatest advantages of this type of adhesive beside its bonding time is short drying time, which eliminates the need for special drying tunnels. As hot-melt adhesives do not contain any solvents, their bondline does not reduce in size while congealing. Full bondline strength is reached in a very short time after

being applied. This enables the bonded materials to enter subsequent production steps relatively quickly.

The bondline of hot-melt adhesives is strong and elastic. It is however subject to degradation over time due to oxidation and crystallization of waxes and thermoplastic polymers. Oxidation and crystallization has a large impact on the elasticity of the bondline which in turn causes it to break when flexed.

This type of adhesives are solids which receive their wettability and adhesive properties while melted and kept at temperatures above their melting points (which depends on the chemical makeup of the substances).

The molten viscosity of a polymer in a given system is proportional to its molecular weight. A hot-melt adhesive could be entirely composed of a polymer, but this would cause reduced adhesion and elimination of properties such as tack, range, and wettability.

Polymers with low molecular mass produce low viscosity, low strength, and poor mechanical properties in a hot-melt adhesive. Analogically, high molecular mass of polymers in a hot-melt adhesive produces high viscosity, high strength and good mechanical properties. Because the properties of the polymer have great impact on the final hot-melt adhesive properties, high-molecular-weight polymers are more desirable.

The second component of hot-melt adhesives is the diluents system which aids or alters the properties of the polymer. Some of the effects which can be obtained through a diluents system include: lowering the viscosity of the hot-melt adhesive, enhancing the wettability and adhesive strength, providing molten tack and tack range, contributing barrier properties and gloss, and aiding polymer rigidity or flexibility. [3]

In general, although a hot-melt adhesive can be composed of a polymer alone, it usually has an array of additional ingredients in its diluents system such as: tackifier, plasticizer, wax, extender, and antioxidant (stabilizer).

Polymers (ethylene-vinyl acetate copolymers, polyvinyl acetates, polyethylene, polypropylene, polyamides) provide strength, adhesion, and mechanical properties. Tackifier (rosin, modified rosin, tacky polymers, terpenes, modified terpenes, hydrocarbons, and chlorinated hydrocarbon) promotes wettability and adhesion, contributes tack and flexibility. Plasticizer (phthalates, glycolates, polybutenes, mineral oil) promotes flexibility and wettability. Wax (paraffin, microcrystalline, vegetable, synthetic wax) is a diluent, nonblack and rigidifying agent which promotes wettability and controls setting speed. Extender (talc, barites, clay) is a filler that reduces cost, controls in melt flow and impacts the solid color. Antioxidant (hindered phenols) maintains viscosity, color, odor and prevents from adhesive degradation over time.

One of the greatest hot-melt adhesive limitation is its limited toughness at usable viscosities. As polymers are organic materials subject to thermal degradation, the ability of heating it with higher temperatures to obtain lower viscosity is limited. Additionally, even with the use of thermal stabilizers viscosity reaches a limit asymptotically. As stated previously, reducing the viscosity by

using lower atomic mass polymers decreases the strength of the adhesive. This means that viscosity and key adhesive properties will always be a trade-off to some extent.

### **Adhesives used in bookbinding and packaging**

Although adhesives for packaging and bookbinding purposes are not viewed as a separate category, automation of bookbinding production has introduced a need for an array of various adhesives for specific production purposes and machine types. Even today, new technologies require new adhesive types.

Adhesives can be divided into categories describing which part of a bookbinding process they are used in: cover joining, endpaper joining, block spine joining, binding gauze and backing strip joining, and threadless binding adhesives. The most popular adhesives used in bookbinding and packaging include: gluten adhesives, dispersion adhesives, and hot-melt adhesives.

### **Gluten adhesives**

As described in the previous section, gluten adhesives originate from animal remains. Currently gluten adhesives derived directly from bone and skin is not used. Instead compounds containing gluten are used. Gluten adhesives have a high dry matter percentage ranging from 50–70%. These type of adhesives require biological inhibitors lowering its degradation due to protein causing molding, fungus and bacteria. [4]

Addition of plasticizers is also needed as gluten based bondline is brittle. For bone adhesives alcohols with high boiling points, such as glycerin or glycols, are good plasticizers. Other compounds such as kaolin, talc, silica or other fine grained fillers are used. This reduces the cost of the adhesive and brightens its color.

Wettability and flow of the gluten adhesives is enhanced by adding polyether alcohols such as ethylene oxide and propylene oxide which additionally act as plasticizers.

Gluten adhesives possess a very strong ability to bond to cellulose based materials which make them ideal for bookbinding. One of the best features of these adhesives is short bonding time which takes place instantly after contact. This makes this glue ideal for bonding book covers to book blocks as well as flexible materials. Gluten adhesives should be applied at temperature of 45–70°C. Temperatures above 70°C causes forming of additional cross-links (bridges) which destroy the adhesive. At the operation temperature gluten based adhesives are a sol which turns to a gel at around 30°C. The initial gel has very good bonding characteristics which reach their maximum when all water has evaporated from the bondline. [4]

One of the main weaknesses of gluten adhesives is their ability to go bad in a biological sense. The bondline is susceptible to losing its flexibility with time due to migration of plasticizers into the bonded material. This causes the bondline to become brittle. Brittle bondlines can damage the materials which were meant to be bonded. [6]

### Dispersion adhesives

Dispersion adhesives are currently one of the most used adhesives in book-binding and packaging. The main benefits of these adhesives are: good wettability of surfaces, high adhesion, high elasticity and bondline strength, resistance to aging, low toxicity and no repulsive scent. [5]

Dispersion adhesives with higher dry matter percentage have higher bonding strengths and shorter bonding time. Short bonding time can be enhanced even further via high frequency wave drying machines.

Dispersion adhesives are available in a wide range of viscosity (300–5000 mPas) and thus can be used in a wide array of machines. The most popular dispersion adhesive is based on the vinyl acetate homopolymer which is used in threadless binding and joining of the bookblock with a cover. To ensure proper bonding the adhesive layer applied to a material should range from 500 to 600 g/m<sup>2</sup> (0.5–0.7 mm). Applying more adhesive not only does not improve the strength of the bond, but also extends the drying time. Dispersion adhesives work at temperatures between 5–35°C. [6]

Technically, dispersion adhesives should be stored for up to a year in airtight containers with temperatures above 5°C and minimal temperature variation. In practice however, it is known for dispersion adhesives to withstand longer periods of time without losing its adhesive properties if stored correctly. Temperature variation within the 5–35°C range might cause some of the water to escape the dispersion and to condensate on the lid and return to the surface. In this case, the adhesive can be used after mixing. Temperatures below 5°C make the adhesive swell and render it completely unusable. [2]

According to calculations performed by German Book Production Association (Fachverband der Buchherstellung) dispersive adhesives constitute for 30% of all adhesives used in bookbinding. [2]

### Hot-melt adhesives

Hot-melt adhesives are currently popular in threadless binding. Although this type of adhesive is weaker than dispersion adhesives it has a very important advantage in shorter drying time that eliminates the need for additional dryers in the book binding workflow. However new equipment paired with evolving technology enables hot-melt adhesives to reach the durability found in dispersion adhesives. [5]

Regular hot-melt adhesives are a combination of three main substances: wax, modified natural or synthetic resins and vinyl acetate with ethylene copolymers (EVA). Each substance has an effect on the adhesive. High concentration of wax causes thinning of the adhesive and shortens its open time. It also causes the bondline to become brittle making it useless for threadless bookbinding. High modified natural or synthetic resin content has impact on higher bonding strength. The EVA copolymer is the main bonding compound in the adhesive which adds stability to the final bondline. High amounts of EVA increases the elasticity of the bondline and resist breaking and stretching. Additionally EVA makes the bondline

more resistant to low temperatures. However, high concentrations of the copolymer makes the bondline compress which can make the book unable to lay flat. [7]

Most important features of the adhesive such as bonding time, operating temperature, and adhesion strength is dependent on resins which were used in the adhesive. Some of the resins include rosin derivatives (usually in hydrogenated form), methylstyrene copolymers with maleic anhydride or vinyl toluene as well as coumarone (benzofuran)-indene-styrene resins.

To increase the elasticity of the bondline and wettability during the bonding process, liquid plasticizers are sometimes included in hot-melt adhesives. The plasticizers often used are phthalic acid esters and trimellitic acid esters. However plasticizers within hot-melt adhesives can have negative effects on bonding strength, weaker cohesion, and plasticizer migration to the bonded surfaces.

The quality of the final bookbinding product largely depends on the correct use of the adhesive during the production process. It is important to obey the rules and restrictions of the adhesive provided by the manufacturer to ensure top performance. Some of the parameters included by the manufacturer include: adhesive operation temperature, operation temperature viscosity, open time, and machine types the adhesive can be used on.

The operating temperature for most hot-melt adhesives designed for bookbinding purposes falls between 150 and 180°C. The proposed operating temperature must be obeyed by the user, as lower temperatures increase the viscosity of the adhesive and make it harder to apply to a surface, which in turn results in a weak bondline. Temperatures above the operating temperature result in oxidation and destruction of intermolecular bonds. If the adhesive is overheated for extended periods of time it will become too viscous or might completely gel. It is important that the operating temperature is the temperature at which the adhesive should be applied to a material, and thus this temperature should be equal to the roller temperature, which apply the adhesive, and not the fountain temperature. In most cases the temperature of hot-melt adhesives used in bookbinding does not go over 180°C which is roughly equivalent to viscosity from 3000 to 7000 mPas depending on adhesive type. [7]

Another important technical parameter is the open time of the adhesive. Usually the longer the open time is, the slower a machine applying the adhesive is. Shorter open time adhesives should be used on faster machines.

In general the thickness of the hot-melt adhesive applied to the block spine should be from 0.5 to 1.0 mm (500–1000 g/m<sup>2</sup>). Application of hot-melt adhesives is usually performed via a set of rollers – usually two or three. In a three roller system the first roller is in contact with the block spine while the knife roller delivers an adhesive layer of 0.5 to 1.0 mm. The second roller is set one millimeter away from the block spine and delivers a layer 1.0 to 2.5 mm thick. The third roller is responsible for the transfer of the adhesives onto the first two rollers. It rotates in the opposite direction to the first two rollers and is heated to temperatures above the temperature the adhesive is applied. Apart from transferring the adhesive layer, the third roller smooths out the adhesive layer and eliminates air



bubbles from the liquid. In the two roller system the third roller described above is not included, while the first two rotate not with, but against the direction of the blocks.

Polyurethane hot-melt adhesives are a special type of hot-melt adhesives developed in the mid 1980's which sets due to a reaction with water vapor from the air. The main compound in this adhesive is a prepolymer containing isocyanate groups which create bridges when in contact with water vapor. Heating the adhesive creates some bridges, but this does not have a vast impact on the substance, as even five or six hour heating sessions do not create a number of bridges that would render the adhesive unusable. Polyurethane adhesives have a lower operation temperature than regular hot-melt adhesives of around 120 to 130°C. The strength of the bond at 100°C is roughly equal to the strength of regular hot-melt adhesives at room temperature.

The elasticity of the bondline depends on the amount of isocyanate groups in the adhesive. Too many groups will result in a large amount of bonds which can cause the bondline to become harder. This allows the final elasticity of the adhesive to be adjusted by setting correct proportions of raw materials.

Bonding of polyurethane adhesives is a two step process. The initial bonding takes place during cool down as the adhesive solidifies. This process is similar to regular hot-melt adhesives. The second step takes up to 72 hours while the adhesive creates additional bonds due to the reaction with water vapor. The initial bonding process is so quick, that books can withstand later processes within two minutes after the adhesive has been applied. The second part of the bonding process takes place in the finished product.

A thickness of only 0.2 mm is enough to create a lasting bond on the block spine, but a layer of 0.3 to 0.4 mm is used to ensure its durability. This is noticeably less than what is used in regular hot-melt adhesives.

Other benefits of polyurethane adhesives are good wettability, fast bonding speed, good adhesion even to materials difficult to bond, high elasticity of the bondline, good resistance to aging and low temperatures up to -30°C.

There are some drawbacks to consider while using polyurethane adhesives. High reactivity of the adhesive is a problem, as once the adhesive is brought to its operating temperature and has cooled to room temperature it can no longer be reused. As the adhesive reacts with water vapor in the air, it is packaged and distributed in a hermetic enclosure. This also means that once the package is open, the adhesive must be used immediately.

Polyurethane adhesives are also four to five times more expensive than regular hot-melt adhesives. Bookbinding machines designed for polyurethane hot-melt adhesives are also quite expensive. Additionally, emission of harmful gases during heating is a problem.

According to calculations performed by German Book Production Association (Fachverband der Buchherstellung) hot-melt adhesives constitute for 70% of all adhesives used in bookbinding. [2]

### Bibliography

1. Szczęsny R., *Materiałoznawstwo introligatorskie*. Ed. by M. Piechowska. Warszawa 1983.
2. Schulz-Wachler J., *Kleje Introligatorskie – właściwości i zastosowanie*. In: *Eukalin Spezial-Klebstoff Fabrik GmbH*. Eschweiler (undate).
3. Cagle Ch. V., *Handbook of Adhesive Bonding*. Chicago 1973.
4. Pizzi A., Mittal K. L., *Handbook of Adhesive Technology*. New York 2003.
5. Tedesco T. J., Clossey D., Hershey J.-M., *Binding, Finishing, and Mailing: The Final Word*. Warrendale (U.S.) 2005.
6. Busz W., *Kleje. Część II*. „Świat Druku” 2/2006, p. 54–56.
7. Busz W., *Kleje. Część IV. Kleje topliwe w introligatorstwie przemysłowym*. „Świat Druku” 12/2006, p. 46–48.

### Streszczenie

#### *Rodzaje klejów wykorzystywanych w poligrafii*

Istnieje wiele rodzajów klejów stosowanych w poligrafii od klejów PUR, przed wodne dyspersje poli- oraz copolimerowe, aż po kleje roślinne i zwierzęce. Wszystkie można podzielić na kategorie uwzględniając ich różne atrybuty takie jak: pochodzenie, stan skupienia, mechanizm spajania i inne. Co więcej, wymienione kategorie mogą być dalej dzielone na podkategorie. W artykule wymienione zostały kleje stosowane w poligrafii przy zastosowaniu najpopularniejszego podziału na kleje naturalne i kleje syntetyczne.