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The properties of glues in the graphic arts

Every subject matter when closely analyzed contains a set of attributes which are vital to understand the subject matter in question and to ensure that every individual uses a unified nomenclature. Adhesives can be described by a series of properties that are vital for understanding them, for example cohesion and adhesion. Other properties are important for ensuring a certain adhesive is proper for a specific use case scenario (bonding surface types, machine compatibility). This section defines and elaborates on some of the most important adhesive properties for bookbinding and packaging purposes, clarifies adhesive nomenclature and describes bond susceptibility types.

Adhesion

Adhesion is the main property of adhesives which defines their ability to attach to other materials. There are two types of adhesion; specific adhesion and mechanical adhesion.

Specific adhesion is the result of intermolecular van der Waals interactions and hydrogen bonds. Van der Waals forces can be subdivided into three categories:

– **Keesom forces** – Interaction between molecules with permanent dipoles;
– **Debye forces** – Interaction between a permanent dipole and a induced dipole caused by dipole forces of neighboring molecules;
– **London dispersion forces** – dispersion forces caused by atoms causing instantaneous induced dipoles. London forces are stronger as the atom in question is larger and the molecule the atom is attached to is smaller.

Hydrogen bonds, a uniquely strong type of dipole-dipole attraction which is not a van der Waals force due to its electrostatic nature, are caused by hydrogen atoms bound to a highly electronegative atom (such as nitrogen (N), oxygen (O) or fluorine (F)) being attracted by other nearby highly electronegative atoms within the same (intramolecular bonding) or other (intermolecular bonding) molecule.

Mechanical adhesion defines the attachment between two surfaces caused by intertwining of the adhesive within the uneven structure of the surface and absorption of the adhesive into the porous structure of a material.

Adhesion is the combined output of the specific and mechanic adhesion processes.

Cohesion

Cohesion is the intermolecular attraction between like-molecules. The forces acting on the molecules are the same forces as described in specific adhesion. Cohesion describes the interactions between the molecules within a substance while adhesion describes the interaction of molecules within a substance with the molecules of a surface the substance is placed on.

Both adhesion and cohesion are key ideas which explain some of the most important properties such as surface tension or capillary movement.

Wettability

Wettability is a characteristic defining the ability of a liquid to maintain contact with a solid surface. It is therefore dependent on the properties of the liquid, the solid, the surrounding fluid and the intermolecular interactions between them.
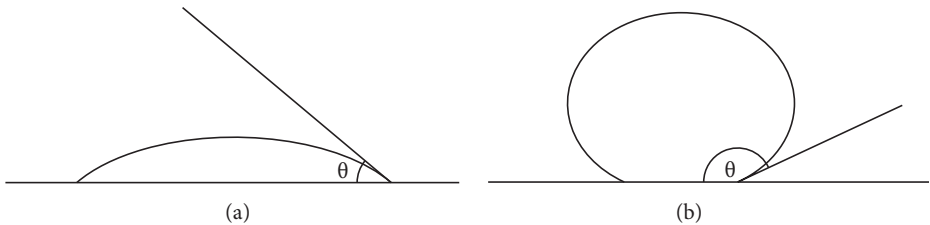

Fig. 1. Wettability of a surface by a liquid: good wettability
and poor wettability (source: own)

Wettability is one of the key properties in bonding of two materials, as good wettability of the surface by the adhesive is required for the adhesive to function. The degree of wettability (degree a surface can be wetted) is determined by the contact angle θ, which is the angle between the surface of the solid (also known as the baseline in wettability measurement) and the surface of the liquid at the point of their contact (called the triple point as it is the point where the solid, liquid and gas phases coincide with each other.[1] The greater the angle, the weaker the wettability, while a small angle corresponds to greater weattability (see Fig. 1). Good wettability enables the adhesive molecules to be closer to the material it is applied to. Surface tension has an impact on the wettability. The higher the surface tension of a liquid, the less wettability of that liquid. The surface tension of the adhesive should be less than the free surface energy or critical surface tension of the adherend.[2]

Surface free energy of a solid which characterizes the wettability of a solid material by a liquid can be described by the forces present in the state of equilibrium which are described by Young's formula:

$$\sigma_S = \gamma_{SL} + \sigma_L \cos \theta \tag{1}$$

Where σ_S is the surface free energy of the solid body surface, γ_{SL} is the interfacial energy of the solid body surface in contact with the liquid, and σ_L is the surface tension (or surface energy) of the liquid in equilibrium with the gas phase and θ is the contact angle.

The Young-Dupre formula defines the work of adhesion obtained during wetting:

$$W_{ad} = \sigma_L + \sigma_L \cdot \cos \theta = \sigma_L \cdot (1 + \cos \theta) \qquad (2)$$

From formulas (1) and (2) the interfacial energy γ_{SL} between a solid body (S) and a liquid (L) is the sum of the surface tensions of the two phases ($\sigma_S + \sigma_L$), reduced by the disperse and the polar interactions at the phase border. These interactions are described as the doubled sum of the geometric mean values of the disperse $\sqrt{\sigma_S^D \cdot \sigma_L^D}$ and the polar $\sqrt{\sigma_S^P \cdot \sigma_L^P}$ tension components of the individual phases:

$$\gamma_{SL} = \sigma_S + \sigma_L - 2 \left(\sqrt{\sigma_S^D \cdot \sigma_L^D} + \sqrt{\sigma_S^P \cdot \sigma_L^P} \right) \qquad (3)$$

Substitution of γ_{SL} from the Young's formula (1) and rearrangement of formula (3) to the general form of a straight line

$$y = ax + b \qquad (4)$$

leads to the following formula:

$$\underbrace{\frac{(1 + \cos \theta) \cdot \sigma_L}{2\sqrt{\sigma_L^D}}}_{y} = \underbrace{\sigma_S^P}_{a} \cdot \underbrace{\frac{\sigma_L^P}{\sigma_L^D}}_{x} + \underbrace{\sigma_S^D}_{b} \qquad (5)$$

The square of the slope is the polar proportion of the solid body surface energy σ_S^P, the square of the ordinate intercept b is the disperse proportion σ_S^D. The sum of the two proportions is the total surface free energy of the solid body σ_S.

The solvent used in the adhesive has an impact on wettability. If the solvent of the adhesive has greater absorption abilities to a material than the bonding substance, the solvent may inhabit the pores of the material and reduce the adhesion. Therefore solvents used in the adhesives should be selected in away to reduce the possibility of them entering the material before the bonding substance.

Wettability is usually observed at room temperature as temperature is correlated with the degree of wettability. However, hot-melt adhesive contact angle is measured at the adhesive's operational temperature (usually between 140–180°C) due to its nature.

Viscosity

Viscosity is one of the basic adhesive properties which is related to wettability and the ability for the adhesive to fill surface imperfections.

Depending on the measurement method, there are three types of viscosity that can be measured: dynamic, kinematic and relative.

Dynamic (shear) viscosity η_d is the force needed to overcome the intermolecular friction required to move two consecutive layers of the liquid against each other. This type of viscosity in defined as the ratio of shear stress to shearing time for a given flow speed. The value of dynamic viscosity can be derived by Newton's law according to which the shearing time is proportional to the shearing stress applied to an ideal liquid:

$$F = \eta_d A \frac{dv}{dx} \qquad (6)$$

where F is the tangent force to two adjacent surfaces with a surface area of A, separated by dx, moving against each other with a speed of dv.

Hence, the resulting formula for dynamic (shear) viscosity is

$$\eta_d = \frac{F}{A} \frac{dx}{dv} \qquad (7)$$

with a unit of a Pascal second (Pas) or milliPascal second (mPas).[3]

Kinematic viscosity is the ratio of dynamic viscosity to the density of the adhesive measured at the same temperature. This concept is convenient when analyzing the Reynolds number, that expresses the ratio of the inertial forces to the viscous forces. However, for most purposes dynamic viscosity is preferably used.

Relative viscosity is a ratio between dynamic viscosity in relation to the viscosity of a control liquid – usually water.

For dispersion adhesives, viscosity should be measured directly after mixing due to their thixotropy. Measuring their viscosity without prior mixing will show higher results which will be unusable since adhesives are stressed inside machines. Viscosity is measured at a temperature of 23°C.

Viscosity can be measured by the use of Ford viscosity cup, Engler viscometer, Höppler viscometer or rotation viscometers.

Ford viscosity cup is the simplest form of a viscometer which is composed of a cup with a funnel-like bottom with a hole of a specific diameter. A specific amount of the studied liquid is poured into the cup and its escape time is measured. This tool is best for adhesives of low viscosity and is ideal for quick relative tests in a production facility. The Engler viscometer is a variation of the Ford cup with additional features like a thermostat which enables better results.

Höppler viscometer is a falling ball visometer where a glass or a metal ball is being dropped through a tube filled with the studied liquid. The time it takes the ball to fall through the tube determines the dynamic viscosity of the liquid. All above viscometers are ideal for low viscosity adhesives with low thixotropy.

Viscosity of dispersion adhesives and hot-melt adhesives, which poses high thixotropy, is measured with rotation viscometers. Such tool is composed of a electric motor which spins a spindle submerged in the studied liquid while measuring the resistance of the spindle caused by that liquid. The rotation speed can be altered to measure the thixotropy effect. Additionally the spindle itself can be replaced by spindles of different sizes to measure vast viscosity ranges (from 100 to 500000 mPas). Another type of a rotation viscometer is the cone and plate viscometer which rotates a cone spindle of a very obtuse angle touching a flat plate with its tip. The resistance to the rotation of the cone produces a torque that is proportional to the shear stress in the fluid. The final reading of the torque is converted to absolute centipoise units mPas from precalculated range charts.

The cone and plate viscometer could be a better choice as it does not have some disadvantages which are typical for coaxial cylinder viscometer, such as shear

rate variation across the measuring annulus, limited range of operation, filling, cleaning, and centering difficulties.[3]

Dry weight percentage (dry matter percentage)

Dry matter is the content of dry matter inside the substance (in case of solvent and dispersion adhesives, as heat-melt adhesives have 100% of dry matter. To obtain the value of dry matter the substance must be dried at a given temperature until no more evaporation takes place. The percentage value of dry substance to the initial mass of the entire substance is the dry matter.

$$S = \frac{\alpha \cdot 100\%}{G} \tag{8}$$

where S is dry matter percentage, α is mass of dry matter and G is mass of substance.

pH

The pH is a measure of acidity or basicity of an aqueous solution. From a mathematical standpoint, pH is a negative common logarithm of the activity of the solvated hydronium ion or a common logarithm of the reciprocal of the hydrogen ion activity.

$$pH = -\log_{10}(a_{H^+}) = \log_{10}\left(\frac{1}{a_{H^+}}\right) \tag{9}$$

This definition is closely related to ion-selective electrodes which respond to activity and are used to measure pH. When pH is defined in terms of activity electrode potential is proportional to the pH. The electrode potential (E) for the hydrogen ion can be written in the form of the Nernst equation:

$$E = E^0 + \frac{RT}{F}\ln a_{H^+} = E^0 + \frac{2.303RT}{F}pH \tag{10}$$

where E is measured potential, E^0 is standard electrode potential, R is gas constant, T is temperature (K), and F is the Faraday constant.

The pH values range from 0 to 14. Asolution with a pH value of less than 7 is acidic, a solution with a pH greater than 7 is basic or alkaline and a solutions with a pH equal to 7 are neutral.

The acidity of an adhesive is an important parameter as in some cases high acidity or basicity can have a negative impact on machines that come in direct contact with the adhesive. In some cases the bonded materials can react with the adhesive. Basic solutions can cause yellowing of paper as well as cause it to become brittle. Adhesives should therefore not be highly acidic or basic. The ideal pH of adhesives falls between 6 and 7.

Adhesive absorption

Absorption is the ability of a dispersion to be absorbed by tissue paper. It is measured by vertically submerging 10 mm of three 7 mm by 200 mm tissue papers in a dispersion while a second set is submerged in distilled water. After thirty min-

utes the height both liquids were able to climb is recorded. Absorption is calculated with the following formula:

$$W = \frac{\overline{h}_1 \cdot 100\%}{\overline{h}_2} \qquad (11)$$

where W is Absorption, $\overline{h}_1$ is mean height of dispersion capillary climb and $\overline{h}_2$ is mean height of distilled water capillary climb.

In the past absorption was measured for every batch of produced adhesive due to high prices and low availability of absorption reducing agents such as poly-alcohol. Nowadays, due to wide availability and low cost, high absorption is less of an issue.

Open time

Open drying time or open time is the maximum time an adhesive will sustain its adhesive properties and be usable after being applied to the first surface. Some companies use the term "maximum open time".

The meaning of the term is not very specific. In laboratories open time is measured by heating the adhesive to the operation temperature (if needed) and applying a layer of 0.7 mm to a surface. The open time greatly depends on adhesive temperature, surface type and the thickness of the layer applied.

Thixotropy

Dispersion and hot-melt adhesives are non-Newtonian fluids which are thixotropic, which means they show a time-dependent decrease in viscosity under shear stress. A thixotropic fluid is a fluid which takes finite time to reach equilibrium viscosity while under shearing. Shear stress can be introduced by shaking or stirring of the liquid.

Bondline

Bondline is the layer of glue which remains after the surfaces are attached and the glue is fixed. There are various properties of the bondline such as the elasticity of the seam, resistance to temperature, solvents and air, visual properties as color, translucency and other visual properties, temperature, solvent, and air resistance.

Bonding susceptibility

As adhesion depends on both the adhesive and the bonded material, new materials should undergo a bonding susceptibility test. To perform the test, a 150 mm by 15 mm material with an adhesive layer is bonded with a class three offset paper with $80 g/m^2$ density of the same size as the sample. After the adhesive has set, the two strips are pulled a part. If the joint failure occurs in the paper layer, the material adhesion is said to be good. If the join failure occurs in the adhesive (adhesive or cohesive joint fracture) or in the studied material, the adhesion is said to be inadequate. It is important that bonding susceptibility refers to bonding susceptibility of a material via a specific adhesive.[4]
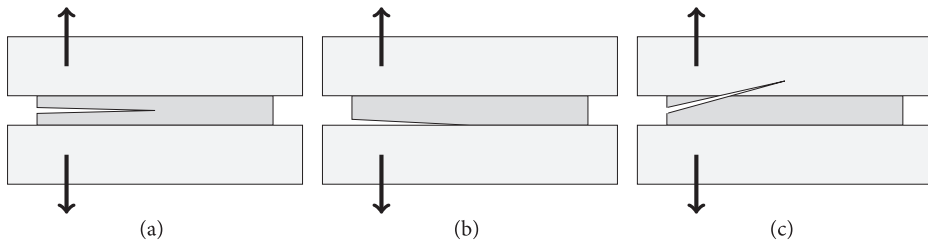
Fig. 2. Different types of adhesive joint fractures: (a) cohesive fracture (CF) – signifies a strong bond and in most common when the bonded material is physically stronger, (b) adhesive fracture (AF) – signifies weak bond and poor wettability of the bonded surface, (c) fracture occurring in the adherend (SF) – signifies a strong bond when the bonded material is physically stronger than the adhesive, which is typical in joining of paper products (source: own)

On a short-time basis and in the absence of environmental exposure, a good bond will usually fail cohesively. However this is only true when two bonded surfaces are by nature stronger than the adhesive. In case of graphic design, where bonded materials are cellulose derivatives, the failure should occur inside the material, not in the bondline, thus making it a surface fracture (SF) – where the adherend is damaged (ripped) while peeling, or a cohesive surface fracture (CSF) – where the adherend internal structure comes a part.

A weak bond usually fractures adhesively where the bondline detaches from the adherend without any cohesive adhesive or cohesive adherend fractures. This does not mean that the adhesive itself is bad, it may be either inadequate for the adherend used, or the adherend-adhesive selection was proper, but the adherend surface preparation was not. Additionally, not all bondlines are required nor expected to fracture cohesively or through material damage. For example, an adhesive applied to sticky notes is expected to come off adhesively from one side and remain entirely on the pulled leaf. Some art notebooks are expected to hold the notebook while drawing and fail adhesively when the paper is pulled from the notebook, so the paper, and more importantly the artwork, is not damaged.

As the world is not ideal, so are the fractures. Some of adhesive fractures will be a combination of cohesive surface fractures, (bondline) cohesive fractures and adhesive fractures, some of the fractures will be of an adhesive-cohesive fracture with peeling (ACFP) variety, while other could even be oscillating fractures where adhesive and cohesive fractures alternate throughout the fracture.[5]

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Streszczenie

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