International Journal of Adhesion & Adhesives 49 (2014) 38–43

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

# Peel adhesion of acrylic pressure-sensitive adhesives on selected substrates versus their surface energies

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ARTICLE INFO

*Article history:*
Accepted 15 October 2013
Available online 10 December 2013

*Keywords:*
Peel adhesion
Surface free energy (SFE)
Acrylic pressure-sensitive adhesives
Aluminum acetylacetonate (AlACA)

ABSTRACT

This paper describes peel adhesion of solvent-borne acrylic pressure-sensitive adhesives (PSA) crosslinked using crosslinking agent aluminum acetylacetonate (AlACA). The peel adhesion of acrylic PSA crosslinked with AlACA was evaluated as a function of adhesive coating weight and kind of tested substrates characterized by various surface free energies (SFE). The diverse substrates tested were stainless steel, poly(methyl methacrylate) (PMMA), polycarbonate (PC), polyethylene (PE), polypropylene (PP) and polytetrafluoroethylene (PTFE) known as Teflon. For peel adhesion determination the most common method in the adhesive tape and PSA industries was used. In order to evaluate surface free energies (SFE) of materials used in tack measurements the Owens–Wendt (OW) and van Oss–Chaudhury–Good (vOCG) methods were employed. The conducted experiments have shown, that a clear relationship exists between SFE of the substrate and peel adhesion of model acrylic PSA. In general, an increase of the difference in SFE between the substrate and adhesive ($\Delta_{SFE}$) affects positive peel adhesion.

## 1. Introduction

Pressure sensitive adhesives (PSA's) are a class of materials that have ability to adhere quickly to any surface under a minimum pressure load. According to definition this category of adhesives are aggressively tacky in dried form and permanently adhere to any kind of surface. Generally speaking, polymer exhibits viscoelastic form and develops adhesion to material and cohesion resistant debonding. No chemical or physical reaction is needed to result in adhesive bonding [1]. To characterize pressure sensitive adhesive one should know three properties, which are adhesion, also known as peel adhesion, tack, and cohesion. Adhesion is a phenomena, which keeps two surfaces in contact. It is measured as a force needed to separate those two and in this manner is considered as peel adhesion. Tack is the ability to adhere instantly. The third – cohesion – is also known as shear strength and is the resistance to shearing forces. The last enables the adhesive to hold under tension [2].

The industrial development of pressure-sensitive adhesives has started in the thirties of the XX century, however an acceleration of research work from practice to a science begun in the fifties. Raw materials have been changing over the years and numbers of patents were granted in order to achieve material tailored on specific application characteristic. Different polymeric material are used as a pressures-sensitive adhesive raw material, however basic pressure sensitive adhesives formulations are acrylics, rubbers and silicones [3].

Acrylics as model polymers allow the exploration of the relative effects of surface and rheological behavior as a function of composition. Esters of acrylic acid with long alcohols may be used to form soft and tacky polymers of low transition temperature (Tg). The suitable monomers commonly reported in literature are alkyl acrylates and methacrylates of 4–17 carbon atoms, e.g. 2-ethylhexyl acrylate (2-EHA) with a *Tg* of $-70\,^{\circ}C$. Acrylic esters are usually copolymerized with other monomers having higher transition temperature *Tg* to result with wanted PSA's properties. This second monomer can be acrylic acid (AA) with *Tg* $106\,^{\circ}C$. Acrylic acid because of carboxyl groups in the structure is useful for crosslinking and for improvement of adsorption properties also. A typical acrylic PSA is composed of 50–90% major polymer, 10–40% modifying monomer and 2–20% of monomer with desired functional groups [4].

Acrylic pressure-sensitive adhesives have many widespread applications, from industry to common usage. They are applied in self-adhesive one-sided office tape (Scotch™) or carrier-free mounting tapes, sticky notes (Post-it™) splicing tapes, self-adhesive labels, protective films, sign and marking films, and double sided tapes used to assembly applications like bedding the window into the frame [5,6].

Adhesion is one of the most ubiquitous phenomena in nature and technology; it is complex, multifaceted, and governs processes

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http://dx.doi.org/10.1016/j.ijadhadh.2013.12.013

from cell adhesion to bio-fouling. The thermodynamic concept quantifying the adhesion on a fundamental molecular level is the work of adhesion. It combines all the fundamental interfacial forces responsible for adhesion of two different surfaces [7]. Many theoretical models explain forces occurring at the interface. Those models are described by adhesion theories which are known as mechanical interlocking, adsorption or thermodynamic, electrostatic, chemical bonding, diffusion, adhesive effect of thin liquid films and weak boundary layers [2]. Theories though are based on fracture mechanics, surface properties ( wetting and adsorption ), diffusion and electrostatic or chemical interaction.

Specific thermodynamic work of adhesion of two substances is equal to the sum of two surface tensions minus the interfacial tension; the dependence is known as the Duprè equation [8].

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \tag{1}$$

where $W_A$ is the work of adhesion, $\gamma_1$ and $\gamma_2$ are the surface energies of 1 and 2 substrates and $\gamma_{12}$ is the energy of the interface. From the equation it is clear that surface tensions are involved in adhesion phenomena understanding. In formal treatments the distinction between surface tension and surface energy is drawn. In technology the complex solid surfaces are usually of interest, and it is common to refer to both as surface energies. To enable the equation possible to use, first the surface tensions-energies have to be known. Surface energies of liquids are relatively simple to measure, e.g. the Wilhelmy plate or the Nouy ring. Tests employed to obtain surface energy of solids are based on measuring the contact angles of liquids on solids. These methods are in fact based on Young's equation, which provides the relationship between surface energy, interface energy and contact angle [9].

$$\gamma s = \gamma sl + \gamma l \cos \Theta \tag{2}$$

where $\gamma s$ is surface free energy, $\gamma sl$ means energy of solid–liquid interface, $\gamma l$ is the liquid surface free energy (surface tension) and $\cos \Theta$ is a contact angle of liquid on solid. To solve the equation one needs an assumption regarding relationship between $\gamma s$, $\gamma sl$ and $\gamma l$. Berthelot assumed work of interfacial adhesion ($Wsl$) is equal to geometric average of cohesion work of surface (Wss) and measured liquid (Wll)

$$Wsl = (WssWll)^{0,5} \tag{3}$$

and combining with the Duprè equation Berthelot hypothesis was found to be

$$\gamma sl = \gamma s + \gamma l - 2(\gamma s \gamma l)^{0,5} \tag{4}$$

Surface free energy is considered to consist of different kind of interactions, Fowkes proposed that surface tension can be broken down into its separate components:

$$\gamma s = \gamma s^d + \gamma s^p + \gamma s^i + \gamma s^h + \gamma s^{ab} + \gamma s^0 \tag{5}$$

where $d$ stands for dispersion, $p$ for polarity, $i$ for induction, $h$ for H-bonding, $ab$ for acid–base, 0 for any other interaction affecting surface free energy. Owens and Wendt proposed that interfacial interactions can be distinguished to only two types forces, which are dispersion and polar. These result in:

$$\gamma sl = \gamma s + \gamma l - 2(\gamma s^d \gamma l^d)^{0,5} - 2(\gamma s^p \gamma l^p)^{0,5}, \tag{6}$$

where $d$ and $p$ indexes stand for dispersion and polar, respectively. From Eqs. (2) and (6) the method of Owens–Wendt of surface energy estimation by contact angle measurement is derived, described by

$$(\gamma s^d \gamma l^d)^{0,5} + (\gamma s^p \gamma l^p)^{0,5} = 0,5\gamma l(1 + \cos \Theta) \tag{7}$$

Since two values are unknown, $\gamma s^d$ and $\gamma s^p$, measurements of contact angle for two liquids are essential. First of the measurement liquids is chosen to be polar and the second apolar – dispersive.

The most recent method of surface examination, including surface energies estimation is known as van Oss–Chaudhury–Goods method. It is considered that in many materials forces of Liftshits–van der Waals and polar interactions of the hydrogen-bonding type occur. Liftshits–van der Waals forces are regarded as relatively long-distance and include randomly orienting dipole–dipole interactions (Keesom), randomly orienting dipole-induced dipole interactions (Debye) and fluctuating dipole-induced dipole (or dispersion) interactions (London). The hydrogen-bonding type interaction is the all possible electron acceptor–donor type and is considered due to Lewis acid–base theory. The electron acceptor–donor interaction is asymmetrical which strictly highlights the need of considering it by this manner. Consequently, the electron acceptor parameter is expressed by $\gamma^+$ and the electron donor parameter by $\gamma^-$. Starting with this approach surface energy can be calculated by determination of contact angles of three liquids with known $\gamma l^{LW}$, $\gamma l^+$, $\gamma l^-$ parameters. At least two of the liquids must be polar and have high energies and $\gamma l^+$, $\gamma l^-$ values. The acid–base component is a geometrical average of base and acid components, $\gamma l^{AB} = 2(\gamma^+ \gamma^-)^{0,5}$. The third is apolar and is used to determine $\gamma s^{LW}$.

The term adhesion can be understood in two different approaches. The first outlined above has strictly theoretical expansion and the second called practical adhesion means in fact the force necessary to break the adhesive bond, to separate two surfaces being in contact. As the first consists of many interfacial interactions the latter is the sum of these interactions and dissipative energy losses related to mechanical response of interface, its rheology especially. This value is determined in technology and the most common is peel test. Through the years a number of experimental tests have been standardized (ASTM, PSTC, ISO, AFERA) [10–12].

## 2. Experimental

### 2.1. Surface free energy determination

The contact angles measurements were performed by optical goniometer (Cobrabid Optica (Warsaw) with digital camera assembled in the lens axis. Measurement droplets of 10 μl volume were applied on tested surfaces using micropipette. Examined materials were held on goniometry stand. Temperature was 22 ± 1 °C. Angle values were determined by geometrical analysis of droplet picture with the usage of original software based on Young's equation.

Materials chosen to tests were polytetrafluoroethylene (PTFE), polyethylene (PE), polypropylene (PP), polycarbonate (PC), poly(methyl methacrylate) (PMMA) and stainless steel (steel).

On each material 11 droplets were put and picture was taken. Angles value were determined, two most deviated results were rejected and the arithmetical average calculated. Results are shown in Table 1. Liquids used in measurement were water, formamide and diiodomethane. To calculate surface energies two models were applied: Owens–Wendt and van Oss–Goods.

Surfaces free energies values and their polar and dispersion components calculated from Owens–Wendt method show Table 2. Table 3 consist values of surfaces energies and their Liftshitz–van der Waals, acid–base, acid, and base components derived by van Oss–Goods model.

### 2.2. Synthesis of investigated acrylic PSAs

The solvent-borne pressure sensitive adhesive to be investigated was obtained from Poly-Chem (Germany). It was synthesized in ethyl acetate from a mixture consisting 55 wt.% butyl