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## INTERACTIONS IN POLYVINYL ACETATE – PAPER ADHESIVE JOINT AND INFLUENCE ON ITS ADHESION PARAMETERS

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**Abstract:** Adhesives have a wide range of applications in various industries. Water based emulsion adhesives being used in printing industry are most often based on polyvinyl acetate (PVAc) homopolymers, especially in bookbinding for short run book production and caseing in. Designing durable and quality short run products requires understanding the interactions between used materials in adhesive joint and the basic components of paper and adhesive. In this study, the adhesive parameters of PVAc adhesive on five paper samples containing different shares of inorganic fillers have been investigated. Paper samples were investigated in the terms of surface roughness, moisture, ash and CaCO<sub>3</sub> content. Besides the different paper properties, the varying amount of water (0%, 2.5%, 5%) in adhesive have been studied as well. PVAc adhesive was applied on all samples under the same conditions (23°C and 50% RH) and method. The analysis of the surface free energy (SFE) and its polar and dispersive components of paper and adhesive was performed by contact angle measurements. There was no large impact on SFE of hydrophilic adhesive samples due to added amount of water. According to the obtained results, the interfacial free energy between two phases and mechanical work of the adhesion was calculated.

**Keywords:** adhesion, PVAc adhesive, paper, inorganic fillers, surface free energy

### INTRODUCTION

The market for print products is constantly changing. Instead of high volume production runs, smaller volumes tailored to individual consumer requirements are in demand. Due to digital printing, highly personalized media – such as photo books, calendars, catalogues, planners or specialized journals and books are now economically feasible. According to Canon, in the year 2000, almost 40% of print products had volumes of over 10,000 copies. This share is expected to decline to 25% in 2020. As a result, more than half of the printing products will be in short runs between one and 2,000 copies; and, in 2010, the short run share already was 48%. Besides the constant print products volume reduction, 95% of active Croatian graphic companies have been qualified as small [6, 2, 15]. So, designing durable and quality on-demand or self-published single or short run products requires more attention in every aspect of production – prepress, press and frequently neglected postpress processes.

Unlike other, postpress or more often called finishing processes in graphic industry, include various types of bonding and adhesives. According to DIN 16 920, adhesives are non-metal materials which bond assembly parts by means of surface adhesion and internal strength. They are used to join two or more components together through attractive forces acting across the interfaces. The components being joined are commonly referred to as adherends or substrates. On the one hand substrates are bonded by means of the surface adhesion between the adhesive and substrates, i.e. adhesion, and on the other hand substrates are bonded by means of the internal strength of the adhesive material, i.e. the cohesion. Implicit in the formation of an acceptable adhesive bond is the ability of the adhesive to wet and spread on the adherends being joined. Attainment of such interfacial molecular contact is a necessary first step in the formation of strong and stable adhesive joints. Once wetting is achieved, intrinsic adhesive forces are generated across the interface through a number of mechanisms. The precise nature of these





mechanisms have been object of physical and chemical study since at least the 1960s, with the result that a number of theories of adhesion exist. The main mechanism of adhesion is explained by the adsorption theory, which states that substrates stick primarily because of intimate intermolecular contact. In adhesive joints this contact is attained by intermolecular or valence forces exerted by molecules in the surface layers of the adhesive and adherent. In addition to adsorption, four other mechanisms of adhesion have been proposed: mechanical interlocking, interdiffusion, adsorption and surface reaction – chemical reaction, and electronic or electrostatic attraction theory. In general, more than one of these mechanisms play a role in achieving the desired level of adhesion for various types of adhesive and adherend [4].

Polyvinyl acetate (PVAc) adhesive is used for short run book production, casing in, or production of only a few pieces of some graphic product. Polyvinyl acetates are economically important products with many desirable features. Besides the graphic industry, they are used as adhesives for porous materials, particularly wood and cloth. They belong to the group of thermoplastic polymers that are capable of being reversibly deformed within a specific temperature range. They are obtained by vinyl acetate emulsion polymerization in presence of polyvinyl alcohol (PVA) as protective colloid and are well known as cold or white glues (Figure 1). White glue can be converted into gel glue or polyvinyl alcohol through a base induced hydrolysis reaction. These dispersions have a reactive solid content of 40–70% in order to tailor the product for the particular application and set through evaporation and diffusion of the water into the substrate and at the same time by coalescence of polymer particles. A pure PVAc emulsions without any plasticizer will become hard and brittle upon aging. However, the addition of the proper amount of plasticizer will soften it and eliminate embrittlement with age. All PVAc adhesives are affordable and cheap, very easy to handle and there are no problems of toxicity [1, 13, 16, 18].

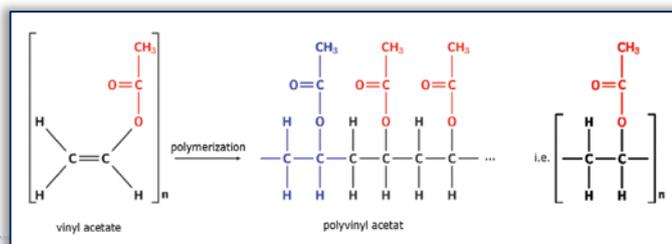


Figure 1: Vinyl acetate polymerization

For short run production and on demand printing office papers are often used. Due to their widespread use (photocopying, printing, writing and archiving) paper properties have to meet certain requirements, such as water resistance, dimensional and optical stability. That is why appropriate substances are added during paper production. Except for cellulose fibres (virgin or recovered by their origin), there are many organic and inorganic components added – fillers, adhesives, pigments, binders, etc. [14].

Designing quality graphic products requires understanding the interactions between used materials. In our case these are the interactions between paper and adhesive in adhesive joint, but also the interactions between the basic components inside these two materials.

It is widely recognized that surface free energy of paper is important parameter affecting their performance in terms of liquid penetration rate and adhesion with other polymeric materials. Finding a reliable measurement of the surface free energy of paper sheets is a challenge. Contact angle methods, including the sessile drop method, are considered the most convenient for determining the surface free energy of paper sheets. Determining the surface free energy of paper from contact angle data for various liquids is not straight forward and the results can sometimes be misleading. Errors may arise from rapid penetration of liquid probes into the sheet or factors associated with roughness of the sheet. The surfaces of paper sheets are far from ideal for contact angle measurements due to their topographical and chemical heterogeneity. Despite the fact that some of the sources of error are well known, contact angle methods are still favoured for determining the surface free energy of paper sheets [17].

After the calculation of the surface free energy of paper and adhesive by contact angle measurements, it is also possible to calculate the work of adhesion. The work of adhesion is the work which must be done to separate two phases in contact. Conversely, it is the energy which is released in the process of wetting. The work of adhesion is very useful parameter because it means that the optimal surface free energy of the adhesive can be calculated to create durable and quality products with sufficient strength of bonded joints. The quality of adhesive joints is highly complex issue as well as the theoretical relationship of the surface free energies of adhesive and substrate, but it certainly depends on the work of adhesion, which is therefore used to understand or predict in-process or end-use results of the particular adhesion [11].





## METHODS

### Materials

Four office papers of the same grammage (80 g/m<sup>2</sup>), all made from primary fibers but a different price range and from four different paper manufacturers reachable on Croatian market (Avery (A), Navigator Universal (B), IQ Premium (C), and Royal White (D)) were analysed. For better understanding the influence of inorganic fillers on PVAc – paper adhesion parameters, 5<sup>th</sup> analysed paper sample was filter paper (E) that does not contain any non-cellulosic components.

Used adhesive is Croatian company (Signoplast Ltd.) product and it's commercial name is Signokol L. It is water dispersion of vinyl acetate homopolymers with polyvinyl alcohol with the addition of plasticizer. This adhesive has 45±2% solid content. According to the Signokol L material safety data sheet, the varying amount of water (0% (S1), 2.5% (S2) and 5% (S3)) was added to the used adhesive. Water based polyvinyl acetate adhesive was applied on polyvinyl chloride (PVC) strips (100 x 15 mm) under the same conditions, application method (brushing), film thickness (66 µm±1) and set time (48 h).

### Determination of paper properties

All paper samples were analysed in the terms of roughness (ISO 4287-1), moisture (T412 om-94), CaCO<sub>3</sub> and ash content. Measurements were performed according to standard methods.

For ash content determination crucibles with test specimen were placed into the muffle furnace at 900 ± 25°C. After reaching the set temperature, crucibles were left at 900°C for about an hour. When the specimen was completely combusted, crucibles were cooled, removed from furnace, placed in a desiccator to reach room temperature and weight. Percent of ash content was calculated based on the moisture-free weight of the paper test specimen as follows (Equation 1) (TAPPI T 413 om-93):

$$\text{Ash} = \frac{m_{(\text{ash})}}{m_{(\text{specimen})}} \times 100 [\%] \quad (1)$$

For determination of CaCO<sub>3</sub> content, five prepared paper samples were placed in an Erlenmeyer flask with 25 mL of distilled water and subjected to digestion in a known quantity of standardized hydrochloric acid (c<sub>HCl</sub>=0,1 mol/L, V<sub>HCl</sub>=20 mL). After heating up to the boiling point and cooling to a room temperature, back titration with standardized sodium hydroxide (c<sub>NaOH</sub>= 1 mol/L) was used to determine the amount of consumed hydrochloric acid, with phenolphthalein as indicator. The percentage of calcium carbonate was calculated based on the moisture-free weight of the paper test specimen, assumed that all of the alkaline material neutralized was calcium carbonate (Equation 2) (TAPPI T 553 pm-92):

$$\omega(\text{CaCO}_3) = \frac{(c_{\text{HCl}} \times V_{\text{HCl}} - c_{\text{NaOH}} \times V_{\text{NaOH}}) \times 0.05}{m_{(\text{speciment})}} \times 100 [\%] \quad (2)$$

Combustion of paper samples in muffle furnace leads to the decomposition of CaCO<sub>3</sub> to CaO and CO<sub>2</sub> according to the following reaction (Equation 3).



Due to above reaction, obtained results for CaCO<sub>3</sub> and ash content, after comparison the amounts of substances and calculating the mass of CaCO<sub>3</sub> and CaO, the share of CaO can be calculated (Equation 4). After determination of CaO amount it is very easy to calculate the amount of inorganic fillers residue too.

$$\omega(\text{CaO}) = \frac{m_{(\text{CaO})}}{m_{(\text{ash})}} \times 100 [\%] \quad (4)$$

### Determination of surface free energy and work of adhesion

The test specimens of five different papers were cut into strips (100 x 15 mm) for determination of surface free energy (SFE) using DataPhysics OCA 30 Goniometer, the Sessile Drop method. Stripes with PVAc adhesive were the same size. By measuring the contact angles (θ) between the solid surfaces and three different test liquids, with known surface tensions (demineralized water, diiodomethane and glycerol) (Table 1), free surface energies of analyzed paper and adhesive samples were evaluated via automatic calculation method integrated in the software (SCA20, Version 2.01). The volume of droplets was 1 µL. Contact angles were captured by CCD camera (Figure 2) and measured after the droplet has been in contact with the paper for about 1-2 s, immediately after the droplet was formed (TAPPI T 458cm-04).





Table 1: Surface tension ( $\gamma$ ) of test liquids, their dispersive ( $\gamma^d$ ) and polar components ( $\gamma^p$ )

TEST LIQUID	SURFACE TENSION [ $\text{mJ}/\text{m}^2$ ]		
	$\gamma$	$\gamma^d$	$\gamma^p$
Water	72.80	21.80	51.00
Diiodomethane	50.80	50.80	00.00
Glycerol	63.40	37.00	26.40

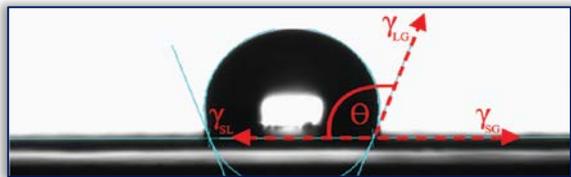


Figure 2: Wetting angle captured via CCD camera between B paper sample and water, forces of surface tensions

strength of the contact between two phases. It is the work which must be done to separate two adjacent phases. When one phase is wetted by another, the two previously existing surfaces disappear, as a result of which energy is released due to the respective surface free energies  $\gamma_1$  and  $\gamma_2$ . At the same time, work, which is referred to as surface free energy of interphase ( $\gamma_{12}$ ), must be done in order to form the interface. The work of adhesion is given by the following (Equation 6) [5, 3, 10].

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \quad (6)$$

The cohesion between two atoms and molecules which causes the surface free energy can be explained by different types of interactions. In particular, one can differentiate between dispersive and polar interactions. Interactions caused by temporary fluctuations of the charge distribution in the atoms/molecules are called dispersive interactions – van der Waals. Polar interactions comprised Coulomb interactions between permanent dipoles and between permanent and induced dipoles (e.g. hydrogen bonds). Because van der Waals interactions occur between all atoms and molecules there is no substance with a surface energy that solely consists of a polar part. On the other hand, there are substances which don't have any polar groups, such as alkanes that consist of hydrocarbon chains. Therefore, their surface energy is purely dispersive [7, 9].

## RESULTS

Average values for paper roughness, moisture, ash and  $\text{CaCO}_3$  content for all paper samples were calculated. Due to obtained results for ash and  $\text{CaCO}_3$  content, the share of CaO was calculated to determine the share of inorganic fillers residue in all paper samples (Table 2). Average values of ten drops on different places of the same sample were taken and presented as mean  $\pm$  SD (Table 3).

Table 2: Paper properties for analyzed paper samples

PAPER SAMPLE	PAPER PROPERTIES					
	Roughness [ $\mu\text{m}$ ]	Moisture [%]	Ash [%]	$\text{CaCO}_3$ [%]	CaO [%]	inorganic fillers residue [%]
A	$2.83 \pm 0.133$	4.66	11.39	17.85	10.76	0.63
B	$2.56 \pm 0.001$	4.78	13.67	20.55	13.33	0.34
C	$2.83 \pm 0.119$	5.10	11.51	20.27	11.16	0.35
D	$3.04 \pm 0.005$	4.40	16.63	30.01	16.60	0.03
E	$5.33 \pm 0.027$	5.11	00.00	00.00	00.00	0.00

Table 3: Contact angle ( $\theta$ ) measurements on paper and PVAc adhesive samples

SAMPLE	CONTACT ANGLE [ $^\circ$ ]			
	Water	Diiodomethane	Glycerol	
PAPER	A	$113.4 \pm 0.1$	$53.3 \pm 0.7$	$102.1 \pm 0.3$
	B	$110.9 \pm 0.2$	$44.0 \pm 0.5$	$89.0 \pm 0.4$
	C	$105.4 \pm 0.2$	$63.7 \pm 0.9$	$104.8 \pm 0.2$
	D	$112.2 \pm 0.1$	$42.5 \pm 0.6$	$94.3 \pm 0.6$
	E	$0.0 \pm 0.0$	$16.3 \pm 0.2$	$21.1 \pm 0.8$
PVAc	S1	$86.5 \pm 0.2$	$37.7 \pm 0.4$	$68.5 \pm 0.4$
	S2	$83.6 \pm 0.1$	$39.5 \pm 0.1$	$72.3 \pm 0.1$
	S3	$77.2 \pm 0.1$	$41.0 \pm 0.6$	$75.3 \pm 0.3$

According to the Young equation, the contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of the three interfacial tensions (Equation 5).

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta \quad (5)$$

In order to enable adhesion of two materials, it is necessary to bring the adhesive into close contact with substrate surface to achieve strong bonds. The viscosity has to be such that on the one hand it can create adequate bond strength and on the other should not destabilize substrate. This is normally adjusted by varying the water content of the PVAc adhesive, according to the technical data sheet (0–5% of water).

The work of adhesion ( $W_{12}$ ) is a measure of the

strength of the contact between two phases. It is the work which must be done to separate two adjacent phases. When one phase is wetted by another, the two previously existing surfaces disappear, as a result of which energy is released due to the respective surface free energies  $\gamma_1$  and  $\gamma_2$ . At the same time, work, which is referred to as surface free energy of interphase ( $\gamma_{12}$ ), must be done in order to form the interface. The work of adhesion is given by the following (Equation 6) [5, 3, 10].

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Using two different calculation methods, Owens–Wendt & Kaelble (OW) and Wu's harmonic mean (WU), the surface free energies of analyzed samples were obtained (Table 4), along with their polar ( $\gamma^p$ ) – water attracting and dispersive ( $\gamma^d$ ) – water repellent share and dispersive index ( $x^d$ ).

After determination of surface free energies of paper and PVAc adhesive samples, interfacial free energies were determined using two above listed calculation methods (Table 5).





Table 4: Surface free energy of paper and PVAc adhesive according to OW and WU methods

SAMPLE	SURFACE FREE ENERGY [mJ/m <sup>2</sup> ] OWENS-WENDT & KAELEBLE (OW)				SURFACE FREE ENERGY [mJ/m <sup>2</sup> ] WU'S HARMONIC MEAN (WU)				
	γ	γ <sup>d</sup>	γ <sup>p</sup>	x <sup>d</sup> (γ <sup>d</sup> /γ) [%]	γ	γ <sup>d</sup>	γ <sup>p</sup>	x <sup>d</sup> (γ <sup>d</sup> /γ) [%]	
PAPER	A	30.04	29.51	0.54	98.23	33.41	33.41	0.0	100.00
	B	37.32	36.77	0.55	98.53	38.12	38.12	0.0	100.00
	C	21.94	21.84	0.09	99.54	26.95	26.95	0.0	100.00
	D	36.83	36.02	0.81	97.80	38.40	38.40	0.0	100.00
	E	72.94	42.11	30.83	57.73	75.01	41.87	33.12	55.82
PVAc	S1	39.12	36.87	2.25	94.25	42.67	37.67	4.99	88.28
	S2	39.12	36.87	2.25	94.25	44.05	39.56	4.49	89.81
	S3	37.95	33.67	4.27	88.72	42.01	35.37	6.65	84.19

OW model is an empirical model based on the assumption that the interfacial free energy is calculated based on the two surface free energies (γ<sub>1</sub> and γ<sub>2</sub>) and the similar interactions between the phases. These interactions are interpreted as the geometric mean of a disperse part (γ<sup>d</sup>) and a polar part (γ<sup>p</sup>) of the surface free energy (Equation 7):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2 \left( \sqrt{\gamma_1^d \times \gamma_2^d} + \sqrt{\gamma_1^p \times \gamma_2^p} \right) \quad (7)$$

The OW method is used when investigating the effect of polar and disperse interactions on wettability and adhesion.

Unlike OW model, WU model interpreted these interactions as the harmonic mean of a disperse part (γ<sup>d</sup>) and a polar part (γ<sup>p</sup>) of the surface free energy (Equation 8):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left( \frac{\gamma_1^d \times \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \times \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad (8)$$

The WU model is mostly used for polymers with low surface energy (up to 40 mJ/m<sup>2</sup>).

It must be emphasised that wetting performance and bonding strength depends on the interaction between adhesive and substrate. After the calculation of the surface free energies of paper and PVAc adhesive, work of adhesion and interfacial free energy for OW and WU methods were calculated too (Table 5).

Table 5: Adhesion parameters of paper and PVAc adhesive samples

SAMPLE	ADHESION PARAMETERS [mJ/m <sup>2</sup> ]			
	OW		WU	
	γ <sub>12</sub>	W <sub>12</sub>	γ <sub>12</sub>	W <sub>12</sub>
A + S1	0.98	68.18	5.26	70.82
B + S1	0.58	75.86	5.00	75.79
C + S1	3.41	57.65	6.78	62.84
D + S1	0.36	75.59	5.01	76.06
E + S1	16.60	95.46	21.01	96.67
A + S2	0.98	68.18	5.01	72.45
B + S2	0.58	75.86	4.52	77.65
C + S2	3.41	57.65	6.88	64.12
D + S2	0.36	75.59	4.51	77.94
E + S2	16.60	95.46	21.88	97.18
A + S3	1.91	66.08	6.70	68.72
B + S3	1.83	73.44	6.74	73.39
C + S3	4.42	55.47	7.78	61.18
D + S3	1.41	73.37	6.76	73.65
E + S3	12.63	98.26	18.17	98.85

## DISCUSSION

All investigated paper samples have similar paper roughness (2.56 – 3.04 μm), except sample E – filter paper (5.33 μm). Although, surface roughness is often one of the most important adhesion parameter, in this study may be excluded because of its similarity [14]. The highest share of CaCO<sub>3</sub> has sample D (30.01%), smallest sample A (17.85%), while paper samples B (20.55%) and C (20.27%) showed almost identical values. From Table 2 it can be observed that paper sample with highest CaCO<sub>3</sub> content contains the least amount of inorganic fillers residue (0.03%). Paper B (0.34%) and C (0.35%) have similar amounts. The highest amount has paper A (0.63). Of course, paper E does not contain any inorganic fillers. The moisture content in tested paper samples was similar, between 4.4 and 5.11%.

The contact angle indicates the wettability of a solid surface with selected liquid. The degree of wettability is determined by a force balance between adhesive and cohesive forces. Adhesive forces between a liquid and solid must be greater than cohesive forces within the liquid. Otherwise, the wetting will be low. High contact angles greater than 90° generally means that wetting of the surface is unfavourable, so the fluid will minimize contact with surface, form a compact liquid droplet and adhesion forces will be weak. Low contact angle less than 90° usually indicates that wetting of the surface is very favourable, and the fluid will spread over a large area of the surface. If contact angle is 0°, liquid will completely wet surface [3]. Obtained contact angles presented in Table 3 show low wettability of A–D paper samples with water, which means that those





papers have hydrophobic surfaces. While the hydrophobicity of samples A, B and D is almost same, sample C showed lowest hydrophobicity of these four samples. Water wets the sample E completely because polar interactions between water and cellulose fibers in sample E – filter paper. These polar interactions are hydrogen bonds between oxygen atoms from molecules of water and oxygen atoms from hydroxyl group in cellulose. Samples A–D showed high wettability with nonpolar liquid – diiodomethane, which confirmed hydrophobicity of those samples. From Table 3 it can be obtained that contact angles water – PVAc samples are lower than water – paper A–D samples. This means that PVAc is hydrophilic. Contact angles diiodomethane – PVAc are lower too. This can be explained by the existence of a hydrophobic phase in PVAc molecules which reduces the contact angle. By increasing the amount of water in PVAc adhesive its hydrophilic properties and diiodomethane – PVAc contact angle is also increasing. Based on obtained results, it can be concluded that paper samples A–D have hydrophobic coating on the surface.

Adhesion will be spontaneous only if surface free energy of the substrate is greater than surface tension of liquid. From Table 4, it is evident that samples A–D have low surface free energies (less than 40 mJ/m<sup>2</sup>), and that sample E is polymer with high surface energy (72.94 mJ/m<sup>2</sup>). Surface free energy of PVAc samples S1 – S3 is higher than surface free energy of paper samples A–D. Therefore, it can be expected that adhesion between PVAc and paper samples wouldn't be spontaneous, except for filter paper. According to OW method, S1 and S2 have same surface free energy despite the varying amount of water. Because highest amount of water, S3 has a lower surface free energy, more similar to B and D paper samples. Therefore, this paper samples should show good wettability with S3. It can be assumed that paper sample C is the worst sample for quality adhesive paper – PVAc joint, and that adhesive sample S3 should ensure the best adhesion joint with all paper samples.

However, according to the two-component model, the interfacial tension depends on whether polar and dispersive parts can form interactions with corresponding parts of the adjacent phase. Considering that and OW method results, it can be noticed that S3 adhesive will not be the best choice for all paper samples. By comparison of dispersion and polar forces, or dispersion index, it is notable that sample S3 has the lowest index (88.72) due to polar interactions – hydrogen bonds between hydrogen atoms from water molecules, oxygen atoms from carbonyl group and oxygen atoms from the ester bond in PVAc structure. Dispersion index S1 and S2 adhesive is similar (94.25). If we take a look on dispersion indexes of paper samples, sample E has a lowest (57.73) due to its hydrogen bonds in cellulose chains, then sample D (97.80), sample B (98.53), sample A (98.23) and at the end is sample C (99.54). Comparing the ratio between the dispersive and the polar part of the surface free energy for two phases allows for a

prediction of the adhesion between these two phases (Figure 3). The closer ratios match the more interactions are possible between the phases and the higher the adhesion is to be expected. A high potential for interactions between two phases also leads to a small interfacial energy [9, 10].

To ensure optimum adhesion, the work of adhesion must be as large as possible, i.e. maximum and interfacial free energy must be as close as possible to zero, i.e. minimum. From Table 5 it can be observed that work of adhesion is highest for samples E, B and D, as

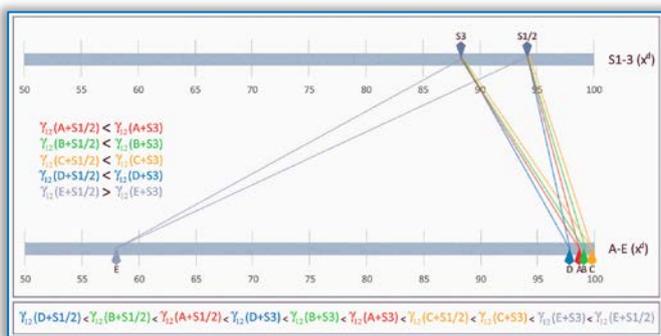


Figure 3: Comparison of interfacial energies ( $\gamma_{12}$ ) based and dispersion index ( $x^d$ ) – paper and PVAc samples

expected due to their larger SFE. The lowest work of adhesion was obtained for sample C, regardless of used adhesive sample. The lowest interfacial energy is: D, B, A, C and E.

Figures 4 and 5 show the impact of all observed parameters on adhesion efficient (roughness, CaCO<sub>3</sub> content, SFE,  $W_{12}$  and  $\gamma_{12}$ ). Figure 4 refers to the quality of the adhesion between all tested paper samples (A–E) with PVAc adhesive samples S1 and S2. Figure 5 refers to the quality of the adhesion between all tested paper samples (A–E) with PVAc adhesive sample S3. By comparing the area of obtained polygon shapes (pentagons), it is possible to determine which paper sample will give the best adhesion results with selected adhesive. For all adhesives filter paper should be the best. Due to the fact that filter paper does not belong to the same category as the rest of the tested samples, more interesting is the order of the office paper group: D, B, A and C.



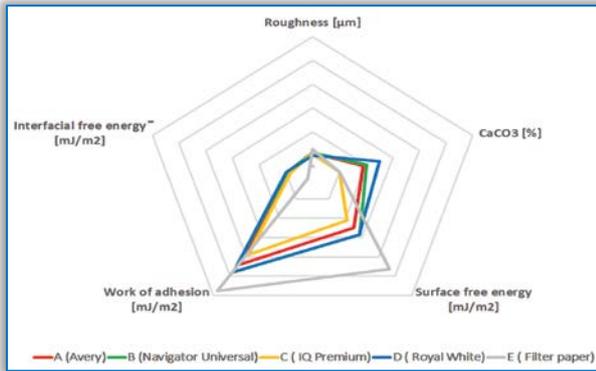


Figure 4: Comparison of adhesive joint strength – all paper samples (A–E) with S1/2 adhesive (OW method)

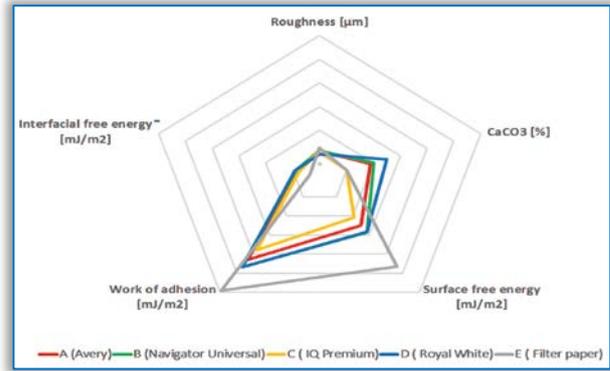


Figure 5: Comparison of adhesive joint strength – all paper samples (A–E) with S3 adhesive (OW method)

## CONCLUSIONS

In response to environmental regulations, adhesives based on water emulsions and dispersion are becoming increasingly important. This trend has been driven by restrictions on the use of volatile organic compounds (VOC), which include solvents that are realised into atmosphere and contribute to the depletion of ozone. In this study, the influence of several parameters on adhesion between polyvinyl acetate and office paper samples were investigated. The main aim of investigation was influence of surface free energy, the work of adhesion and interfacial free energy between phases. Also, influence of inorganic fillers, especially  $\text{CaCO}_3$  in paper samples A–D on adhesion was investigated too.

Although obtained results for above listed parameters (Tables 4–5), for OW and WU methods were almost identical, analysis of the results was made according the OW method, which is used when investigating the effect of polar and dispersive interactions on adhesion.

In the formation of an adhesive bond, a transitional zone arises in the interface between adherend and adhesive – the interphase. In this zone, chemical and physical properties of the adhesive may be considerably different from those in the noncontact portions.

Despite the order based on work of adhesion (E, B, D, A, C), considering dispersion index and interfacial energy it can be concluded that filter paper with PVAc S3 (5% water amount) would make best adhesive joint. Also, it can be predicted that paper sample D with adhesive S1 or S2 would make best adhesive joint comparing it to the tested office paper samples. Next is sample B, then A and at least C, all three with adhesive S1 or S2. S1 and S2 proved to be better adhesives for office papers (A–D) because of its dispersion index which is numerically closer to dispersion indexes of paper samples A–D (Figure 3). S3 is numerically closer to filter paper dispersion index i.e. to papers with higher amount of cellulose fibres and without any inorganic fillers. Thus influence of the ratio between polar and dispersive part on decreasing or increasing interphase free energy has been proven. Interphase energy controls the durability and strength of an adhesive joint and is primarily responsible for the transference of the stress from one adherent to another. Analysing the amount of calcium carbonate and other inorganic fillers in tested paper samples, it can be assumed that the increase of the amount of the  $\text{CaCO}_3$  in paper can reduce interfacial energy between these two phases, due to ion–dipole interactions. To reduce the consumption of PVAc adhesive, small amount of water can be added to the dispersion (about 2.5%), without reducing the strength of the PVAc – office paper adhesion joint.

The strength of adhesive joints is usually determined by destructive tests which measure the stresses set up at the point of line of fracture of the test piece (peel, tensile lap shear cleavage). An alternative method that was used in this study was characterization of adhesive joints by determining the energy expended in cleaving apart the unit area of the interphase. Although, the conclusion derived from such energy calculations are, in principle, completely equivalent to those derived from stress analysis, plans for further research are attached to expanding this study with peel strength test – to be completely sure in obtained results and derived conclusions.

The quality of adhesive joints is generally highly complex issue. Speaking of PVAc – paper adhesive joint there is a lot of interactions, a lot of interdependences between examined parameters and several disadvantages associated with the used methods, so it is not easy to make a simple and an unambiguous interpretation of obtained results. Also, paper samples A–D, besides the cellulose and calcium carbonate, are containing different amounts of various binders, fillers and pigments that cannot be precisely defined. Plans for further research of this topic, with this preliminary research and above-mentioned





destructive tests, certainly include the determination of cellulose content in already tested samples and production of laboratory hand-sheet paper containing only cellulose with different amounts of calcium carbonate.

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