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Interfacial Bonding Energies of Pressure Sensitive Adhesives to Substrates

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Abstract

The study reports the interfacial bonding energies of pressure-sensitive adhesives (PSAs). The materials include Acrylic, PVC-abro, Polyurethane and Epoxy as single PSAs and Hybrid PSAs from the single PSAs. The substrate material was a mild steel plate of 130mm x 130mm with 12mm thickness. The force/tack required to debond the PSA from the substrate was measured with a universal testing machine. For determination of interfacial bonding energies between the PSA and the substrate, the contact angle technique was used. This allowed for interfacial free energies calculation, hence the adhesive energies. The maximum forces (tack) at maximum machine deflection, was calculated also. Epoxy PSA appears to have the greatest tack with tack strength of 3.358E-05 N/m). This gave a stronger force required to debond or pull it out from the substrate. Acrylic PSA gives lowest tack strength of 0.854E-5N/m, hence not the best for tough adhesive determination. Hybrid PSAs gave higher tack than the single PSAs which is preferable for heavy-duty adhesive work. For both single and hybrid PSAs, an increase in work of adhesion was found to lead to an increase in the bonding strength or tack strength of the adhesive. Hybridization was found to increase the bonding strength of the resulting adhesive, on the average by about 19%. Thus valuable to those in carpentry, leather works or composites.

Keywords: Adhesion, cohesion, tack, hybrid, stress-deflection

1. Introduction

The process of holding two solid surfaces together using polymers as adhesive materials has wide industrial applications. Certain visco-elastic properties allow polymers to fulfil the requirement for their classification as adhesives (Creton, 2001; Carelli et al, 2007). For this purpose, the adhesive has to possess a good combination of two characteristic properties: adhesion and cohesion. Adhesion, or the adhesive's stickiness, is distinguished by low viscosity, compulsory for broad contact area and enhanced bond density. Cohesion forces represent the sufficient strength of the physical bonds between the polymer molecules to resist externally applied forces. Also, the cohesion of linear and branched polymer macromolecules is defined only by the partial valence bonds; whereas the adhesion is specified primarily by the secondary bonds (Aubrey and Ginosatis, 1999; Charles, 2003; Ahn et al, 2014). An important advantage of the adhesive joint is the uniform distribution of load over a large area avoiding localization of stress.

Design of adhesives is based on the oriented optimization of the adhesive connection and works successfully both for very small surfaces and for large areas of contact. Plenty of adhesive varieties exist for modification of the structure design to get the desired properties suitable for specified commercial applications (Pocius, 2002; Menyo et al, 200013). The adhesives differ not only by their chemical composition but also by the thermo-mechanical properties of the bonded joints, processing methods, as well as types of reactions during the bonding. One can categorize them as chemical reacting glues, reactive hot melts, and physical setting glues (Zosel and Barwich, 1995; Dailey et al, 2013).

Pressure Sensitive Adhesives (PSAs) represent a class of materials with the defining property of sticking to a variety of surfaces under low applied force (1-10 Pa) and short contact time (1-5 s) (Feldstein et al, 2015). This property of pressure sensitivity is called tack. In contrast to all other classes of adhesives, the adhesion process of PSAs occurs without any change of temperature or chemical reactions. Since neither solvent evaporation nor chemical reaction takes place, these materials are safe and easy to use. To have good tack properties, itisrequired to have low elastic modulus i.e. to be viscous enough for radial flow, to exhibit an ability to wet the adherent, and at the same time to have the cohesive strength to sustain a minimum level of strengthupon debonding (Sinebe et al, 2019 ; Okpe, 2020). Pressure-sensitive adhesives (PSA) are soft, viscoelastic solids, based mainly on polymers: acrylics, styrenic block copolymers and natural rubber. Pressure-sensitive adhesives can build a joint by the application of low pressure.

Understandably, the strength of the adhesives depends on the adhesive energy between the adhesive and the substrate. This adhesive energy can be determined through knowledge of the surface free energies of the contacting surfaces. Thus, this work studies the influence of interfacial energy on the bonding of different pressure-sensitive adhesives and compares it with tack and tack strength, which are the characteristic properties of PSAs required to perform this function (Toyama et al., 1993). It was noted that PSAs can adhere to surfaces without change of temperature or chemical reactions. This makes it safer and easier for users.

2.0 Material and methods

2.1 Materials

The pressure-sensitive adhesives (PSAs) investigated include Acrylic sealant (mastic Acrylique) which is the model for the test manufactured in Turkey for Henkel South Africa Pty Limited. The second is PVC. PVC heavy-duty clear cement manufactured by Abro industries incorporation, South Bend IN 46624.CPSA, White Blanc. The third is EPOXY: Top Express Steel Epoxy manufactured by CHEMTOP P.O. Box 10479 Vorna Valley and the fourth is the Polyurethane Adhesive: which is manufactured by CHADHA corporation PVT LTD. All were sourced at Kenyatta and Ogbete Main Markets in Enugu, Enugu State. An eight number (8no) substrate material mild steel plates with a near smooth surface and an area of 130mm x 130mm with a thickness of 12mm were used for the test. A cleaning agent was poured on a white towel and was used to scrub off dirt and dust from the surfaces of the steel plates before experiments were started and after they were concluded. A computerized Universal testing machine that has facets for installing test material, screen for monitoring separation, recording meter for showing the breakup point of each adhesive was used for measuring the force at each point of PSA separation from the substrate.

2.2 Sample Preparation

The single PSAs selected were Acrylic (mode1 sample), PVC sealant, Epoxy and Polyurethane (Evostick). Hybrid PSAs, comprising of a 50-50 mixture of two PSAs, included Polyurethane/PVC-Abro, Acrylic/PVC-Abro, Epoxy/Acrylic, Epoxy/Polyurethane and Epoxy/PVC –Abro respectively, see table 1.

Table 1: Single and Hybrid PSAs

S/N	Single PSA	Hybrid PSA
1	Acrylic	Epoxy/Acrylic
2	PVC-Abro	Epoxy/Polyurethane
3	Epoxy	Epoxy/PVC-Abro
4	Polyurethane	Acrylic/PVC-Abro
		Acrylic/Polyurethane

Each sample of PSA was drawn from each container of PSA using a syringe of 25cm^3 volume. The drawn samples were deposited on the mild steel plate surface while the other half of the plate was carefully placed on top and allowed to stand for 7days under room temperature before testing commenced. For hybrid PSAs, each sample was also drawn from the container and poured into a dish, while the second was drawn from its container and also poured into the same dish and the 50-50 mixture was blended with the aid of a spatula. The samples for the tests were prepared as stated previously and left to stand for 7days under 23^{o}C room temperature before testing commenced. Each sample was properly labelled according to the mixture type. The plates (mild steel) were thoroughly cleaned with a clean white towel to remove dust and dried under the sun before the PSAs were applied.

2.3 Methods

The first set of experiments involved the determination of the force F required to pull apart two flat plates held together by the PSA. The PSA or the adhesive layer was sandwiched in between the two metal plates and mounted on the grip portion of the computerized Universal Testing Machine TUE-C-100 model. The force at which the plates began to separate was recorded as the tack or debonding force, F. This was done for single and for hybrid PSAs.

This force is a measure of the tack, which is expected to overcome the adhesiveness and better expressed as the tack strength. According to Wang, (2014);

$$\text{Tack strength} = \left(\frac{F}{b}\right) \quad (1)$$

Where; b is the width of the adhesive layer. This adhesive strength characterizes the tack force per width of the adhesive layer. The thickness of the adhesive layer is 12 mm and its width is 130mm.

The resulting stress-strain and stress-time responses of true stress and true strain of the PSA, recorded by the universal testing machine as the plates were pulled apart were used to calculate the PSA stress deflection ($\partial_{\max}$) on materials using the equation (Wang, 2014; Okpe, 2020):

$$(\partial_{max})N/mm^2 = \frac{F}{A}\left(1 + \frac{\Delta l}{l}\right) \quad (2)$$

Where A is the area of contact of the adhesive layer on the substrate, l is the length of adhesive.

The next experiment involved the measurement of contact angles of each PSA surface deposited on the mild steel plate. The contact angles so measured were used to calculate the works of adhesion and cohesion.

According to Krevelen & Nijenhuis, (2009), the specific free surface energy, also known as interfacial energy of a material is the excess energy per unit area due to the existence of the free surface; it is also the thermodynamic work to be done per unit area of surface extension. In PSAs, the specific free surface energy is also called the interfacial energy, since it is equivalent to a line tension acting in all directions parallel to the surface, is given as;

$$\gamma_s(mJ) = \frac{Work}{Area} \quad (3)$$

Where; W = Force x distannce

The work of adhesion is given by;

$$W_A(mJ/m^2) = \gamma_s + \gamma_L - \gamma_{SL} \quad (4)$$

When combined with Young's equation, gives;

$$W_A(mJ/m^2) = \Upsilon_L\,(1 + COS\,\theta) \quad (5)$$

According to Leger and Creton 2007 work done on a PSA is expressed as 0.001F which is constant.

The work of cohesion of one substrate is expressed as

$$W_C(mJ/m^2) = \gamma_A + \gamma_A - 0 = 2\gamma_A \quad (6)$$

Eqs. (1) to (6) were used, together with experimental data to calculate the relevant quantities.

3.0 Results and Discussions

The maximum forces (tack) and hence using Eqs. (1) and (2), the tack strength at maximum stress deflection, at which the plates separated, for single PSAs are presented on table 2. Epoxy PSA appears to have the greatest tack strength (3.358E-05 N/m), which means that a stronger force will be required to debond it or pull it out from the substrate. Epoxy PSA also gives the maximum stress deflection of 4.907E-4 N/m^2. Acrylic PSA gives the lowest tack strength (0.854E-05 N/m) and so it is not the best where a tough adhesive is desired. It also gives the lowest stress deflection of 1.248 N/m^2.In PSA materials the maximum stress deflection and maximum tack strength are better achieved with Epoxy materials than in the other PSA materials; this infers superiority of Epoxy materials in adhesive bonding.

Table 2: Tack/Debonding Force at Maximum Stress Deflection and Calculated Tack Strength of Single PSAs.

Sample	Area, *A* m^2	Force, *F* (N)	Max. stress deflection (∂_{max})N/m^2	Calculated tack strength (F_{tack}) N/m
Acrylic	0.0169	0.00000111	0.000124793	8.53846E-06
Epoxy	0.0169	0.000004365	0.00049074	3.35769E-05
PVC- Abro	0.0169	0.000001715	0.000192811	1.31923E-05
Polyurethane	0.0169	0.000001745	0.000196183	1.34231E-05
Average	0.0169	0.000002234	0.0002511	0.1718E-05

The results for hybrid PSAs of Acrylic/Epoxy, Acrylic/Polyurethane and Epoxy/PVC –abro are presented on table 3. From table 3b, it can be seen that Epoxy/ PVC- Abro hybrid has the highest tack strength of 2.096 x 10^{-4} N/m. It also gives the maximum stress deflection of 3.0636 x $10^{-4}N/m^2$. The least tack strength and least stress deflection occurred with Acrylic/Polyurethane hybrid with the values of 1.361x10^{-5}N/m and 1.99 x 10^{-4} N/m^2, respectively.

Table 3a: Tack of Hybrid Acrylic with (PVC, Polyurethane and Epoxy)

Sample Mixture	Area, A (m^2)	Force, *F* (N)	Max. stress deflection (∂_{max}) (N/m^2)	Calculated tack strength (F_{tack}) (N/m)
Acrylic/ PVC -abro	0.0169	0.00000179	0.000201243	1.37692E-05
Acrylic/ Polyurethane	0.0169	0.00000177	0.000198994	1.36154E-05
Acrylic/Epoxy	0.0169	0.00000275	0.000228225	1.56154E-05

Table 3b: Tack of Hybrid Epoxy with (Acrylic, PVC and Polyurethane)

Sample Mixture	Area, A (m^2)	Force (N)	Max. stress deflection (∂_{max})(N/m^2)	Calculated tack strength (F_{tack}) (N/m)
Epoxy and Acrylic	0.0169	0.00000203	0.000228225	1.56154E-05
Epoxy and Polyurethane	0.0169	0.00000199	0.000223727	1.53077E-04
Epoxy and PVC- Abro	0.0169	0.000002725	0.000306362	2.09615E-04

Comparing the results of table 2 for single PSAs with those of table 3 for hybrid PSA shows that the pressure-sensitive materials have better tack strength when they are mixed (in hybrid). For the least strength PSAs, it is found that the tack strength of Acrylic/PVC-Abro is by a factor of 1.6 higher than the tack strength of single Acrylic PSA, and that of Acrylic/Polyurethane is 1.59 higher than that of single Acrylic PSA. For the high strength PSAs, the tack strength of Epoxy/PVC -Abrois by a factor of 6.2 higher than that of single Epoxy PSA and 15.89 higher than that of single PVC –Abro PSA. All these show that hybrid pressure-sensitive materials have better tack strength than the single PSAs and that hybrid Epoxy/Polyurethane PSA is most preferable from among those considered in this work.

The contact angle data are presented in tables 4 and 5 for single and hybrid PSAs and together with the works of adhesion and cohesion calculated using Eqs. (4) and (5).

Table 4: Contact Angle data and works of adhesion and cohesion for single PSAs

Sample	θ (deg)	$\gamma_L = W/A$ (N/m)x10^{-3}	W_A(mJ/m^2)x10^{-3}	W_C (mJ/m^2)x10^{-3}
Acrylic	86.6	0.1263	0.0695	0.132
Epoxy	89.1	0.4967	0.262	0.517
PVC- Abro	87.8	0.1952	0.105	0.203
Polyurethane	87.8	0.1986	0.107	0.207

The highest value of the angle of contact occurred for Epoxy with a value of 89.1^0. The work of adhesion was calculated to be 2.62x10^{-3}mJ/m^2 and that of work of cohesion is 0.517x10^{-3}mJ/m^2. Acrylic PSA was least with a contact angle of 86.6^0 with the work of adhesion as 0.0695x10^{-3}mJ/m^2 and work of cohesion as 0.132x10^{-3}mJ/m^2. These results show that the works of adhesion and cohesion are increased with increases in contact angles of the PSAs. It is instructive to know that Epoxy PSA also had the highest tack strength (see table 2). Thus, the higher the tack strength, the higher the contact angle and the works of adhesion and cohesion.

Table 5: Works of Adhesion and Cohesion Calculated from Contact Angles

Sample Mixtures	θ(^{0})	Work of adhesion x10^{-4}(mJ/m^2)	Work of cohesion x10^{-4} (mJ/m^2)
Epoxy and Acrylic	88.2	1.239	2.402
Epoxy and Polyurethane	88.1	1.216	2.355
Epoxy and PVC- Abro	88.93	1.642	3.225
Acrylic/ PVC – Abro	87.92	1.1	2.118
Acrylic/ Polyurethane	87.89	1.085	2.095
Acrylic/Epoxy	88.2	1.24	2.402

It was observed from table 5 for hybrid PSAs that the highest contact angle of 88.93^o was obtained for Epoxy/PVC-Abro which also gave the highest works of adhesion and cohesion. Acrylic/Polyurethane with the lowest contact angle gave the lowest works of adhesion and cohesion. Thus, the higher the contact angle, the higher the bond existing between the PSA and the substrate and within the PSA itself as was also observed for single PSAs.

These results show that for stronger bonding, the adhesive materials should be more hydrophobic. This is consistent with the finding in fibre-reinforced polymer composite study where the requirement for enhanced fibre/matrix adhesive bond (Sinebe, 2019; Bledzki, et. al., 2008) is that the fibre is rendered hydrophobic.

The tack strength (N/m) and the work of adhesion (mJ/m^2), are compared in figure (1a) for single PSAs and figure (1b) for hybrid PSAs.

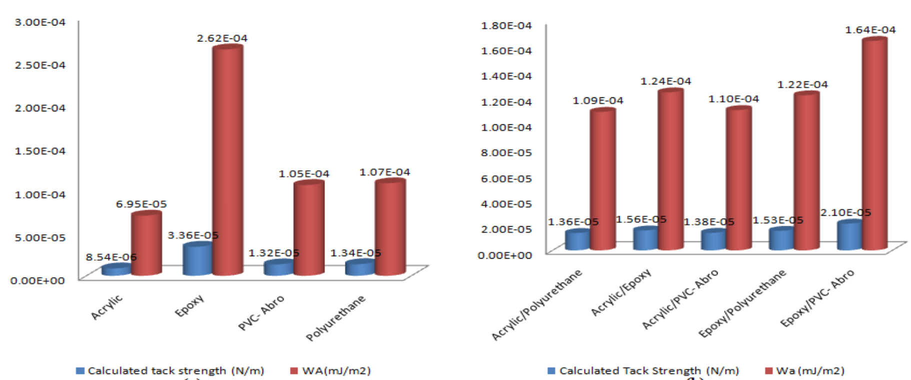

Figure 1: Tack strength and work of adhesion for (a) single PSAs (b) hybrid PSAs

As shown in figure (1) in this study, the average value of tack strength was 0.1718E-5N/m and the work of adhesion was 0.1359E-3mJ/m^2 for single PSAs. This is in line with the dominant contribution to the tack resistance force as noted by Benedek and Feldstain(2009).

To check the proper trends in these relationships, these data are plotted on figure (2). For single PSAs (figure 2a), it is obvious that increase in work of adhesion also leads to increase in tack strength (i.e., on the bonding strength of the adhesive).

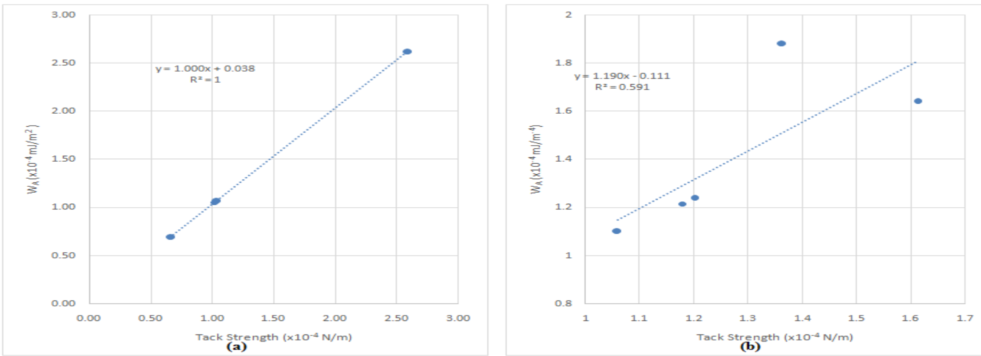

Figure 2: Relationship between tack strength and work of adhesion for (a) single PSAs (b) hybrid PSAs

Figure (2), show clearly the relationships between work of adhesion and tack strength for both single and hybrid PSAs. As the work of adhesion is increased, tack strength also increases in both cases. The adhesive bond which holds the PSA to the substrate increases as the tack strength is increased. In the design of adhesives therefore, it is necessary to choose the treatment that will give higher adhesive bond if strong adhesives are desired. The fact that the slope (1.1902) of the graph of figure (2b) for the hybrid PSAs is higher than the slope (1.0004) of figure (2a) for single PSAs (a difference of about 19%) shows that hybridization increases the bonding strength of the resulting adhesive as observed in tack strength consideration only.

4.0. Conclusion

A study on the interfacial bonding energies of pressure-sensitive adhesives (PSAs) was carried out. The Acrylic, PVC-Abro, Polyurethane and Epoxy were materials used as single PSAs. Hybrid PSAs comprised of a 50-50 mixture of two PSAs. From which thereof, Polyurethane/PVC-Abro, Acrylic/PVC-Abro, Epoxy/Acrylic, Epoxy/Polyurethane and Epoxy/PVC-Abro were hybridized. The substrate material was a mild steel plate of 130mm x 130mm with 12mm thickness. The force (tack) and tack strength were applied for deboning of the PSA from the substrate, using universal testing machine TUE-C-100 model. Also contact angle technique was used for determination of interfacial bonding energies between the PSA and the substrate.

In addition, the contact angle measured on surfaces of PSA was used for evaluation of interfacial free energies that was used for calculation of adhesive energies. From the results obtained, it was deduced that the higher the angle of contact, the higher the works of adhesion and cohesion. This was seen at the highest contact angle of 88.93^o from Epoxy/PVC -Abro, at which the highest works of adhesion and cohesion occurred.
Inversely, the Acrylic/Polyurethane with the lowest contact angle gave the lowest works of adhesion and cohesion. The calculated maximum forces (tack) at maximum deflection for single Epoxy PSA appeared to have the greatest tack strength of 2.621E-04 N/m. This infers that a stronger force needed to be applied to make debonding .However, the Acrylic PSA gave the lowest tack of 0.6953E-04 N/m., suggesting that it is not the best adhesive desired. Besides, the hybrid PSAs gave higher tack when compared to single PSAs counterparts, making them preferable for heavy-duty adhesive work. Comparatively, in both single and hybrid PSAs, an increase in work of adhesion was found. All led to an increase in tack strength on the bonding strength of the adhesive.

In the design of adhesives, therefore, it is necessary to choose the treatment that will give higher adhesive bond if strong adhesives are desired. Hybridization was found to increase the bonding strength of the resulting adhesive. Conclusively, this is on the average of 19% making it valuable to those in carpentry, leather works or composites.

5.0 Recommendation

Further study on the influence of surface energetic on the Tack of acrylic pressure sensitive adhesive is required. Locally made pressure adhesives ought to be tried to reduce cost. More statistical tool should be applied to do more comparative study

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Nomenclatures

δ_{max}	=	maximum stress deflection	(N/mm^2)
γ_s	=	surface free energy	(mJ)
W_A	=	work of Adhesion	(mJ/m^2)
W_C	=	work of cohesion	(mJ/m^2)

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