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The Effect of Poly(vinylpyrrolidone) Concentration on Peel Strength of Acrylic/PVP Pressure Sensitive Adhesive Blends

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ABSTRACT

The influence of poly(vinylpyrrolidone) (PVP) concentration on the peel strength of an acrylic pressure-sensitive adhesive (PSA) has been studied as a function of the adhesive thickness. Different amounts of PVP (2-30% w/w) were mixed thoroughly with an acrylic PSA. Films with different thicknesses (10, 40, and 70 μm) were prepared by casting the formulation on a poly(ethylene terephtalate) film. Peel tests were carried out by adhesive-coated tapes of 25 mm width on the stainless steel substrate at least for three samples. The samples were investigated by Fourier transmittance infrared (FTIR) spectroscopy technique and surface tension and viscoelastic properties measurements. The peel strength values are directly dependent on the thickness of adhesive. Also, results showed that due to the polar part of blend in 2 %w/w PVP, the peel strength has the maximum value. At higher concentrations of PVP, due to its surface migration, reduction in peel strength was more pronounced. The parallel investigations on the viscoelastic properties of blends showed that the storage modulus shifts to higher values at higher concentrations of PVP. Therefore, the bonding step becomes difficult and the peel strength decreases significantly.

Key Words:

PSA;
peel strength;
PVP;
FTIR;
surface energy.

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INTRODUCTION

Medical grade pressure-sensitive adhesives (PSAs) are widely used in wound dressing and development of transdermal patches. They have to be biologically inert, non-irritating, and non-sensitizing at skin level and should adhere strongly to the skin but can be easily removed with little or not trauma (adhesive properties) and adhesive residues (cohesion properties) [1,2]. Their excellent wetting kinetics and highly viscoelastic properties are the essential parameters for their attachment to soft tissues. Their adhesion and device function integrity are governed by the polymer chemistry, layer thickness, contents of additives (i.e., permeation enhancer and pharmaceutical

loading), and environmental conditions [3].

Three important performance tests on PSAs are peel strength, tack, and creep resistance measurements. Scientifically, there are two simplified advantages of the peel test compared to the other methods. It is the only method in which failure proceeds at a controlled rate and the peel force is a direct measure of the work of detachment [4-6]. When the patch is detached from the skin it must leave no visible residues, thus peel strength is a highly critical property of PSAs [7].

The performance of PSAs (e.g., peel, tack, and shear strengths) depends on the viscoelastic response of the bulk properties of the adhesive [8-10] as well as the surface energies of the adhesive and adherend. In addition, correlations of different peel failure modes with different rheological regions of PSAs have been established and reported by Aubrey et al. [11]. Bonding is a low rate process with low deformation that occurs when the PSA is brought into contact with a surface. While, debonding in a tack or peel test is a high rate process depending on the thickness of the adhesive.

PVP is usually used in many drugs because it inhibits crystallization of drugs in solid dispersions. PVP also plays a significant role in improving the solubility of the drugs in the transdermal drug delivery systems (TDSs) as well as adhesion properties [12-15]. Thus for designing a TDS, it is necessary to investigate the PVP effects on the adhesion properties of PSAs.

In our previous study the effects of miscibility of PVP and acrylic PSA in various concentrations of PVP/acrylic PSA binary blends were investigated on the tack [16]. In the best of our knowledge there is no published report about the PVP effect on the adhesion properties of PSAs. In this work, we have investigated the effects of different amounts of poly (vinylpyrrolidone) (PVP) on the peel strength of an acrylic PSA. The results are interpreted as the functions of viscoelastic properties, surface energies, and chemical interactions of the functional groups in PSA and PVP.

Table 1. Weight percentage of PVP in blends based on dried adhesive.

Sample	PVP (w/w %)
PVP2	2
PVP5	5
PVP10	10
PVP20	20
PVP30	30

EXPERIMENTAL

Materials and Method

Poly(vinylpyrrolidone) K 27/32 (Rahavard Tamin Co., Iran), Gelva 737(Solutia Inc., USA), and PET with thickness of 80 μm, (Daropat shargh Co., Iran) were used. Gelva (737) is an acrylic based adhesive copolymer containing acrylate comonomers including vinyl acetate-2-ethylhexyl acrylate, hydroxyethylacrylate, and glycidyl methacrylate.

Appropriate quantities of PVP (2-30 % w/w) were added to acrylic adhesive (Gelva 737) separately and treated overnight until PVP was completely dissolved in each of the blends and the appearence of the solutions became homogeneous. PSA Specimens were prepared by coating the blends of acrylic PSA/PVP with different thicknesses (10, 40, and 70 μm) onto PET films by using a film applicator (elcometer 3580, USA).

The samples were allowed to stand at room temperature for 20 min and then for complete solvent evaporation, the drying was performed in an oven at 50ºC for 45 min. Peel tests were carried out on a stainless steel substrate. The detailed information regarding the samples is shown in Table 1.

Peel Strength Measurement at Angle of 180°

Dried PSA tapes were pressed in stainless steel plates by 5 kg rubber roller passing two times over the samples. Peel tests were carried out according to the ASTM D 3330 on adhesive-coated tapes with 25 mm width. PSA Tape/stainless steel joints were stored at room temperature for 20 min and peel force at angle of 180° direction was measured for at least three samples at a peel rate of 30.5 cm/min using cheminstruments adhesive/release tester AR-1000 (Fair Field, Ohio, USA).

Contact Angle Measurement

To evaluate the surface energy, contact angles were

determined at room temperature using distilled water and diiodomethane by a contact angle measuring system Gio (Kruss, Germany). Dispersion and polar components of the surface energy, γ_A^d and γ_A^p were determined according to the improved Owens method.

FTIR

The FTIR spectra were taken using an Equinox 55 (Bruker, Germany). The treated adhesive samples were placed as thin films on KBr disks and dried in a oven at 50ºC for 8 h.

Rheological Studies

Viscoelastic properties were determined on a rheometer MCR-300(Anton Paar-Physica, Austria). The measurements were carried out by parallel plate method. Oscillation frequency was varied from 0.01 to 600 rad/s at different strains and the temperature 25ºC was selected to run each frequency sweep separately. G′ and G″ were plotted vs. frequency at room temperature.

RESULTS AND DISCUSSION

The peel force versus concentration of PVP for different thicknesses of adhesive layer are shown in Figure 1. There is a maximum of peel strength at PVP2 and then the peel strength is decreased by the addition of PVP. As the adhesive thickness is increased, a large volume of adhesive is subjected to deformation per unit area of detachment, therefore the related peel force is increased as shown in Figure 1.

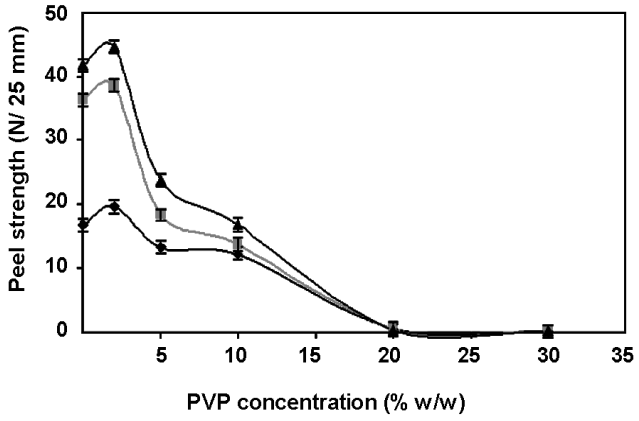
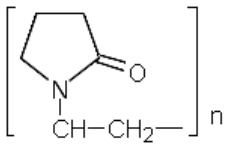


Figure 1. Plots of peel strength vs. PVP concentrations for 10 μm (◆), 40 μm (■), and 70 μm (▲) (n=3).



Scheme I. Molecular structure of PVP.

The performance of PSAs depends on the surface energies of the adhesive and adherend as well as the viscoelastic response of the adhesive bulk [17,18]. A change in the nature of the adhesive may change the performance of adhesion which depends on the interfacial free energy. This is purely an interfacial effect, not necessarily connected with any change in the adhesive bulk, and therefore it is independent of the other factors. The results can be interpreted based on the interaction between PVP and acrylic PSA, surface energy, and viscoelastic properties at different amounts of PVP. This interaction was investigated by FTIR measurement. Gelva-737 contains acrylate comonomers such as vinyl acetate-2-ethylhexyl acrylate, hydroxyl ethyl acrylate, and glycidyl methacrylate. If molecular structure of PVP (Scheme I) is taken into account, it can be concluded that hydrogen bonding may take place between functional groups of adhesive and PVP molecular chains[19-21].

PVP is a well know hydrogen bond acceptor because it has not any acidic proton but only contains a basic carbonyl group capable of donating electrons [12]. Since, each vinylpyrrolidone unit has one effective hydrogen bond active site, PVP can form hydrogen bonds between carbonyl side groups of its repeat units and the terminal hydroxyl groups of the other comonomers functional groups [13].

Table 2. FTIR spectral data of the carbonyl stretching region of blends.

Sample	$\upsilon_{C=0}$ acrylate (cm^{-1})	$\upsilon_{C=0}$ PVP (cm^{-1})
PSA	1740	-
PVP 2	1738	1674
PVP 5	1734	1669
PVP 10	1729	1667
PVP 20	1728	1664
PVP 30	1726	1662
PVP	-	1659

The spectral data of the carbonyl stretching region are shown in Table 2. The vibration frequency of carbonyl group in pure PVP is observed at 1659 cm^{-1}. With the addition of adhesive, that has OH groups in its composition, nitrogen atoms in PVP donate their lone pairs to the hydrogens of OH groups, therefore they cannot participate in the resonance of carbonyl groups. Thus in the blends, the vibration frequency of carbonyl groups shift to higher frequencies (1662-1647 cm^{-1}).

However, by increasing PVP concentration in the blend due to enhancement of hydrogen bonding formation that has negative effect on force constant of double bond between carbon and oxygen atoms, the carbonyl stretching frequencies of adhesive shift to lower frequencies.

On the basis of FTIR results (Table 2) we can conclude that the chemical interaction is increased between PVP and acrylic PSA. This is due to relative reduction in the functionality of adhesive carbonyl groups that are involved in the interaction with amide groups of PVP. Also owing to its suitable hydrodynamic size, PVP molecules penetrate through the adhesive chains and thus decrease the hydrogen bondings between acrylic polymer chains themselves and cause reduction in the peel strength [22]. This fact is also observed in our results, that the frequency of carbonyl group of adhesive was shifted to the lower frequencies (1740 cm^{-1} net adhesive to 1726 cm^{-1} at 30 wt% PVP). As the PVP concentration increases, its molecules donate electrons from their nitrogen sites to different functional groups of the adhesive such as hydroxyl and carbonyl groups that have potential for accepting electrons. Consequently, the functionality of adhesive carbonyl groups decrease and the adhesive can no longer show a good contact with adherend and thus the peel strength of adhesive decreases [23].

The net decrease in the extent of interactions between acrylic adhesive polymer chains themselves, with the addition of PVP is clearly associated with the surface tension of adhesive blends. The surface tension of a system is governed by the usual thermodynamic variables and primarily by the chemical nature of the components present at the surface. Because of the presence of carbonyl groups in adhesive and PVP, they have the capability of H-bonding formation with the solvents and decreasing their surface tension similar to the other surface-active agents [24,25]. The surface activity phenomenon is qualitatively explained from its molecular stand point (i.e., the nature of monomeric unit and its orientation, etc.) and overall distribution in solvent medium as well as interaction with solvent molecules. Figure 2 shows the surface energy of blends as a function of PVP concentration. At low PVP concentration the surface energy is decreased drastically, and then the curve is flattened and continued to decrese slowly as the PVP concentration is increased. However, it is shown that decreasing trend is rather negligible at the higher concentration range.

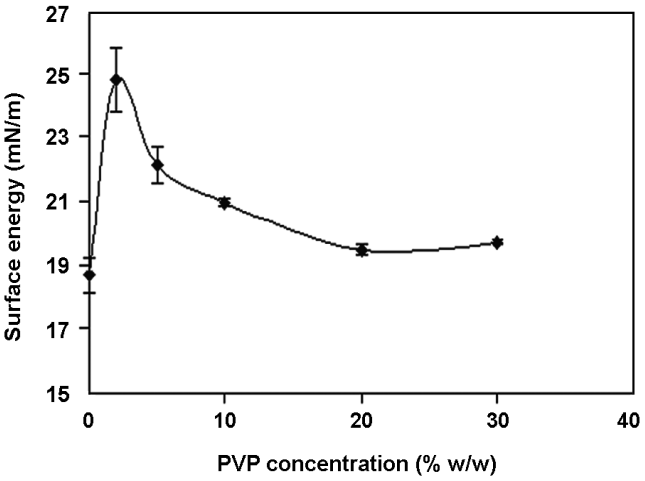


Figure 2. Surface energies of acrylic/PVP pressure sensitive adhesive blends as a function of PVP concentration (n=3).

Noskov and coworkers [26] have reported dynamic surface properties of PVP solutions in concentration range10^{-5} wt% up to about 1 wt% PVP [26]. They have observed that the surface energy changes slowly with time at low ($<10^{-4}$ wt%) and high concentration (>0.1 wt%). They have concluded that at low concentration there is a slow transport by diffusion of PVP molecules from the depth of the bulk phase to the surface. This is consistent with our data, since the pure adhesive and PVP2 have almost the same surface energies as PVP5 as shown in Figure 2. At low concentrations, PVP chains are unfolded and lie almost entirely in the proximal region of the surface layer. Noskov and coworkers concluded that at higher concentrations, impurity gradually displaces PVP chains from the surface and thus leads to slow equilibration of the system.

Table 3. Contact angles and surface energies of blends.

Sample	Contact angle (°)		γ (mN/m)	γ_A^d (mN/m)	γ_A^p (mN/m)
	Water	Diiodo methane			
PSA	110	77.7	18.68	18.68	0.28
PVP2	107.2	75.3	24.82	23.21	1.61
PVP5	107.5	71.8	22.11	21.85	0.26
PVP10	107.7	74.1	20.93	20.60	0.33
PVP20	105.7	77.7	19.48	18.69	0.79
PVP30	105.3	77.3	19.72	18.89	0.83
PVP	39.9	33.6	65.11	42.66	22.42

By measuring the interfacial tension between water and an alkane, the surface tension can be split into polar and dispersive components [27,28]. As the results show, there is a maximum value in the polar part of PVP2 and after that, polar part is decreased at PVP5 and then an increasing trend is observed (Table 3). On the other hand, the maximum of peel strength was observed at PVP2. From these results we can conclude that by the interaction between PVP and PSA a new species has been formed that has more polarity than the net adhesive and PVP alone. In PVP2, all of the PVP molecules are involved in the interaction with PSA comonomers. It seems that, with further addition of PVP, since available active sites of PSAs molecules are saturated, the free PVP are increased and because of their surface migration, the polarity of the blends also increases. The reduction of peel strength in spite of the increasing polarity of the blend can be attributed to the lower concentrations of adhesive on the surface.

The concentration dependence of peel strength also is associated with the viscoelastic properties of the blends. All PSAs are viscoelastic liquids (semi-solids). The moduli can be divided into in-phase (G′) and out-of phase (G″) components in conventional manner and plotted as a function of frequency ω (from 0.01 to 600 rads^{-1}). The dynamic mechanical properties (mostly G′ as a function of frequency, ω) have been correlated to adhesive properties [29].

Peel performance is dependent upon the efficiency of the bonding step as well as the separation resistance of the debonding step. The bonding efficiency can be correlated with the plateau modulus at the bonding frequency (0.01 rad/s). In other words, the lower the G′ value at 0.01 s^{-1}, the more favorable the bonding.

The debonding strength comes from two contributing terms, the cohesive strength which is indicated by the storage modulus, G′, and the energy of dissipation terms which is indicated by the loss modulus, G″, both measured at the debonding frequency (100 rad/s). Thus, the higher the debonding G′ and G″ values, the higher the debonding strength [27]. The diagonal tanδ=1 line is another important factor for investigating the PSA properties, as it separates regions where the elastic or storage modulus G′ is greater (i.e., tanδ <1) or smaller (tanδ >1) than the loss modulus G″. tanδ <1 indicates the more elastic region or better removability. Conversely, the closer tanδ to 1, the more viscous (or cohesive failure) the material [27].

In Figures 3a and 3b are shown the plots of (a) storage modulus and (b) loss modulus as functions of angular frequency (0.01-1000 rad/s), respectively. At bonding frequency (0.01 rad/s) by increasing PVP concentration, the storage modulus is increased. Also

Table 4. Tan δ of blends at 100 rad/s.

Sample	Tan δ
PSA	0.85
PVP2	0.83
PVP5	0.82
PVP10	0.76
PVP20	0.76
PVP30	0.71

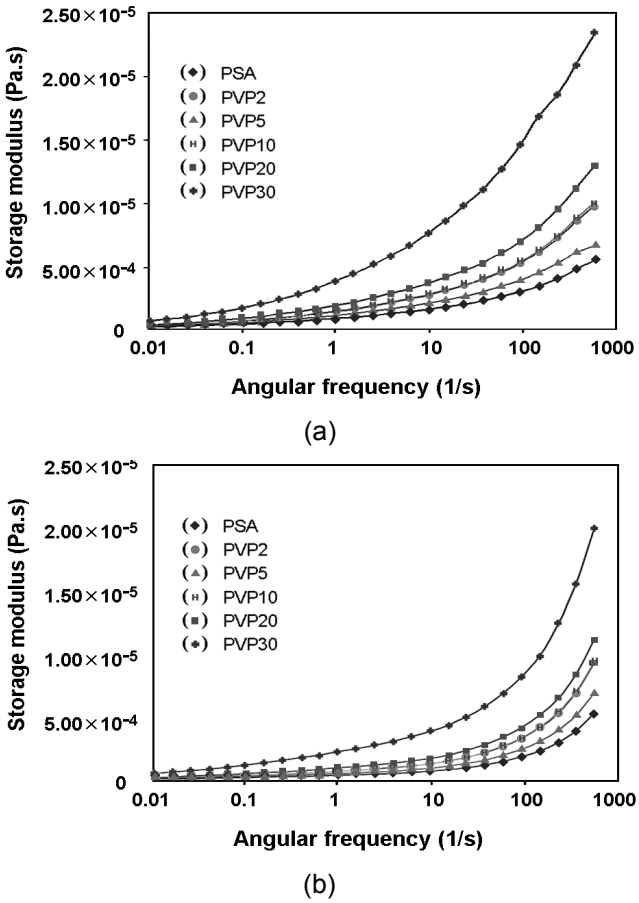


Figure 3. The plots of: (a) storage modulus and (b) loss modulus of blends as functions of angular frequency.

according to Table 4 by increasing PVP amount, the damping factor (tan δ) is gradually reduced. All these results showed that because of the highly elastic nature (lack of flow) of the blend, making the bonding step is unfavourable and the peel strength will be reduced.

CONCLUSION

PVP is commonly used in TDS as anti-nuleating agent and it also affects the adhesion properties of these systems. Our study showed that PVP to some extent improves peel strength although at higher concentrations of PVP it is reduced significantly .

Also, with increasing the thickness of adhesives the peel strength is increased. Hydrogen bonding and surface polarity have important effects on the peel strength of the blends. In this way, disruption of hydrogen bonding between polymer chains and migration of PVP molecules on the surface reduce the peel strength. Also, the storage modulus in bonding frequency and the damping factor have played a significant role in the peel strength of the systems in a manner that by increasing storage modulus the peel strength is shifted to lower values.

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