

Effect of Different Skin Permeation Enhancers on Peel Strength of an Acrylic PSA

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ABSTRACT: Different amounts of two skin permeation enhancers, Oleic acid (OA) and Propylene glycol (PG), were mixed thoroughly with solution of a commercial acrylic pressure sensitive adhesive (Duro-Tak). Films with different adhesive layer thickness (30 and 60 μm) were prepared by casting of formulations with a film applicator on a PET 80- μm film and drying of solvents. Peel test was done on different formulations according to ASTM D3330. Surface study and thermal analysis were used for explaining the results. It was shown that the effect of interfacial work of adhesion on peel strength was too low to be considered. PG had no significant effect on peel strength, which was related to effect of hydrogen bonds between PG and copolymer

chains acting as crosslinks. OA decreased peel strength significantly, which is due to important changes in copolymer structure. These changes can be found by relatively sharp drop in T_g values. Adhesive-cohesive transition occurred in OA formulations as a result of OA crystals formation. OA migration to surface in concentrations of more than 10 (w/w %) was confirmed by results of DSC and surface study. In contrast with PG, doubling of thickness had no effect on peel strength. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2987–2991, 2003

Key words: adhesives; miscibility; glass transition

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are polymers that can adhere strongly to solid surfaces upon application of light contact pressure and short contact time. PSAs have numerous health care applications; one innovative use is in transdermal drug delivery systems.^{1,2} The transdermal route offer many advantages over conventional routes of drug administration (i.e., oral, injection etc.); the most important are avoidance of the first pass effect, ease of use and withdrawal (in case of side effects), and better patient compliance. The most common types of transdermal patches are reservoir, matrix, drug-in-adhesive, and multilaminate.³ Recently, drug-in-adhesive systems have been much favored because of their thin and flexible structure.⁴ Three main components of drug-in-adhesive patches are backing layer, PSA, and protective liner. Duro-Tak commercial PSAs are extensively used in drug-in-adhesive transdermal systems. Oleic acid (OA) and Propylene glycol (PG) are two important skin permeation enhancers that are often formulated with PSA.⁵

Three important performance tests of PSAs are peel strength, tack, and creep resistance.⁶ Peel strength data can give more information about the adhesive

character and its expected performance. Peel adhesion is dependent on viscoelastic properties of adhesives and surface properties of both adhesive and substrate.^{7–12} In this research work the effect of OA and PG on peel strength of DuroTak (87-2196) a copolymer containing vinyl acetate and acrylate monomers, is investigated.

EXPERIMENTAL

Materials and method

Duro-Tak 87-2196 (National Starch and Chemical Co., USA), 1,2-propylene glycol USP (Merck), oleic acid USP (Merck), and PET film with 80 μm thickness (generously prepared by Daroupat Shargh, IRAN) were used.

Duro-Tak was thoroughly mixed with OA and PG to prepare formulations containing 0 to 25 (w/w %) of mentioned enhancers in dry adhesive. Formulations were cast on PET films by a film applicator (BYK-Gardner, USA). After staying at room temperature for 10 min, drying was completed in 20 min in a 65°C oven.

Peel test

Peel tests were carried out according to the ASTM D3330 on adhesive-coated tapes with a 25-mm width. PSA tape/stainless steel joints were stored at room temperature for 24 h and peel force in 180°

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direction was measured at a peel rate of 300 mm/min at room temperature using an Instron machine (Model 6025, USA).

Thermal analysis

Glass transition temperature (T_g) of various formulations was measured with a differential scanning calorimeter (PL, UK) with a heating rate of 10°C/min. In all cases T_g was taken as the midpoint of the heat flow curve.

Contact angle measurement

To evaluate the surface free energy and to determine the thermodynamic work of adhesion (W_A) between different formulations and a stainless steel plate, contact angles were determined at room temperature for distilled water and diiodomethane after 45 s by a contact angle measuring system G10 (Kruss, Germany).

RESULTS AND DISCUSSION

Peel force vs. concentration curves for different thicknesses of adhesive layer are shown in Figure 1 for PG. It is obvious that increasing concentration of PG from 0 to 25 weight percentage has no significant effect on peel force. Similar curves for OA are shown in Figure 2. A large drop in peel force is evident specially when concentration changes from 5 to 10 (w/w %). On the other hand, in contrast with PG, there is no important difference between peel forces of different thicknesses. Also, there is transition from adhesive (region A) to cohesive (region B) failure. This transition occurs when OA concentration becomes more than 15 (w/w %) for 30 μm or 10 (w/w %) for 60 μm tapes.

Interfacial energies

Separation of an adhesive tape from a substrate is a process in which both the thermodynamic work of adhesion and dissipation factors are involved.⁶ In the other words, the total work of peeling may be expressed in the form:

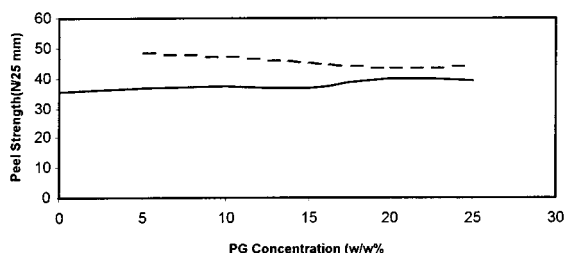


Figure 1 Plot of peel strength against PG concentration for 30 μm (solid line) and 60 μm (dashed line) adhesive layer thicknesses.

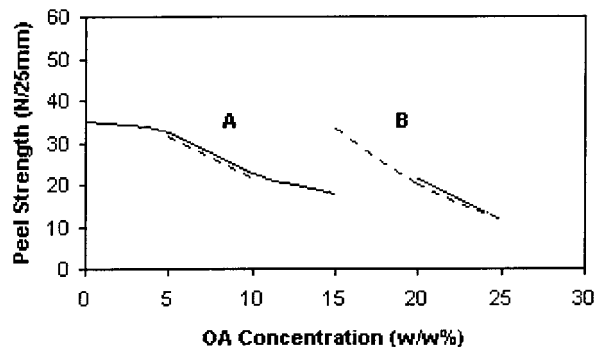


Figure 2 Plot of peel strength against OA concentration for 30 μm (solid line) and 60 μm (dashed line) adhesive layer thicknesses in adhesive failure (A) and cohesive failure (B) regions.

$$W_T = W_A + W_A \Phi \quad (1)$$

where W_A and W_T are the thermodynamic and total work of adhesion, respectively, and Φ is a dissipation factor. Thermodynamic or reversible work of adhesion, W_A , is the change in free energy when the materials are brought into contact, and it is the same as the amount of work expended under reversible or equilibrium conditions to disrupt the interface. W_A is related to surface-free energies or surface tensions by the Dupré equation. If the phases are separated in dry air, the following equations result:¹³

$$W_A = \gamma_A + \gamma_S - \gamma_{AS} \text{ (Dupré eq)} \quad (2)$$

As

$$\gamma_{AS} = \gamma_A + \gamma_S - 2(\gamma_A^d \gamma_S^d)^{1/2} - 2(\gamma_A^p \gamma_S^p)^{1/2} \text{ (Fowkes eq)} \quad (3)$$

Then

$$W_A = 2[(\gamma_A^d \gamma_S^d)^{1/2} + (\gamma_A^p \gamma_S^p)^{1/2}] \quad (4)$$

where γ_A^d , γ_S^d , γ_A^p , and γ_S^p are disperse and polar parts of adhesive and substrate. These parameters calculated by contact angles in addition with W_A , W_T and W_T/W_A are shown in Table I. W_T has been calculated using the following equation:¹⁴

$$W_T = F/b (1 - \cos\Theta) \quad (5)$$

where F , b , and Θ are peel force, tape width, and peel angle, respectively. As W_A amounts are very small compared to W_T , W_T/W_A is approximately equal, with Φ (viscoelastic dissipation factor). It is observed in Table I where W_A is approximately constant for PG formulations. This can be the result of a chemical interaction between PG and copolymer. W_A is smaller

TABLE I
Contact Angles, Surface Energies, and Works of Adhesion

Sample	CA (deg)		γ (mJ/m ²)		W (mJ/m ²)		
	Water	Diiodomethane	γ^d	γ^p	W_A	W_T	W_T/W_A
A0	109.3	58.5	32.5	0.5	64.1	2.8 ⁶	4.4 ⁴
OA5	104.4	68.9	23.8	0.1	52.3	2.6	5.0
OA10	106.3	72.4	21.9	0.1	50.3	1.8	3.6
OA15	105.7	82.5	15.3	0.9	48.2	1.4	3.0
OA20	111.3	86.7	13.8	0.4	43.3	1.7	4.0
OA25	113.1	95.7	9.5	0.9	39.8	0.9	2.2
PG5	105.9	56.0	33.4	0.2	62.6	2.9	4.7
PG10	100.3	60.1	29	0.1	57.4	3.0	5.2
PG15	100.2	58.2	30.3	0.1	58.6	2.9	5.0
PG20	101.3	58.0	30.8	0.0	56.3	3.2	5.6
PG25	98.2	57.9	30.1	0.2	59.6	3.1	5.2
Steel	56.3	48.7	25.7	20.2	—	—	—

in OA formulations and decreases when concentration increases. W_T/W_A amounts for different formulations of PG and OA change from 22,000 to 56,000. Then W_A has approximately no role in peel strength.

T_g and miscibility

Glass transition temperature, T_g , relates to the onset of viscoelastic energy dissipation, and is an important molecular parameter affecting PSA properties. Aubrey has shown that increasing T_g (by addition of tackifier resins) raises the peel force in the rubbery region and causes a rubbery state peeling to occur in lower peeling rates.¹⁵ Aubrey and Sherriff have shown that there is a good correlation between peel force and elastic modulus (G') curves at the region change over from viscous to rubbery peeling.¹⁶ Cantor has shown that there is a relationship between T_g and peel force for a commercial PSA.¹⁷ The following equation can be used for prediction of formulations T_g :

$$W_1/T_{g1} + W_2/T_{g2} = W/T_g \text{ (Fox eq)} \quad (6)$$

where W_1 and W_2 are formulation components weight percentages. Measured and calculated amounts of T_g by eq. (6) are shown in Table II. The general effect of the plasticizer is increasing spaces between entanglements and free volume and then decreasing cohesive strength and T_g of polymer. Positive deviations for PG and negative deviations for OA formulations from eq.

(6) are observed. These deviations are dependent on specific interactions between polymer and plasticizer. Feldstein and his coworkers¹⁸ have studied plasticization of polyvinyl pyrrolidone by polyethylene glycol (PEG). They have shown that PEG400 with a two functional structure, like PG, leads to formation of hydrogen bonds. However, relatively long and flexible chains of PEG400 leads to plasticization, which is not the expected effect of hydrogen bonding. Some physical properties and chemical formula of OA and PG are shown in Table III. DuroTak commercial copolymer contains acrylate and vinyl acetate components. Both acrylate and vinyl acetate have carbonyl groups in their structure and the probability of formation of hydrogen bonds between two OH groups of PG and CO groups of copolymer is very high. These short hydrogen bonds act as crosslinking agents that have more effect on T_g than free volume increasing and cause a positive deviation from eq. (6) to occur. On the other hand, formation of intermolecular interactions (especially initial hydrogen bonds between polymer chains) and entanglements is extensively inhibited by large molecules of OA. This significant structural change makes such a weak polymer where its T_g has a large negative deviation from eq. (6).

The effect of miscibility of acrylic copolymers with tackifiers on PSA performance have been studied.¹⁹ Hayashi has resulted that in the case of miscible blend systems, the dynamic mechanical properties of PSA

TABLE II
Measured and Calculated T_g Amounts of Different Formulations

Sample	A0	OA5	OA10	OA15	OA20	OA25	PG5	PG10	PG15	PG20	PG25
T_g (°C)	-24.7	-36.9	-43.9	-60.3	-66.3	-71.7	-28.5	-30.7	-32.0	-32.0	-30.3
Calculated T_g (°C)	—	-26.1	-27.5	-28.8	-30.2	-31.5	-29.9	-35.0	-39.8	-44.5	-48.9
Deviation	—	-10.8	-16.4	-31.5	-36.1	-40.2	+1.4	+4.3	+7.8	+12.5	+18.6

TABLE III
Some Physical Properties of Enhancers

Solvent	Formula	M_w (g/mol)	V (cm ³ /mol)	T_g (°C)	bp ₁₀₀ (°C)	δ (cal/cm ³) ^{1/2}
PG	C ₃ H ₈ O ₂	76.10	73.6	-100	132	25.8
OA	C ₁₈ H ₃₄ O ₂	282.47	320	-50	286	17.38

bulk, and also the performance of it are systematically modified by incorporation of tackifiers. But in immiscible systems the mechanical properties of the matrix phase in PSA are not modified.²⁰ DSC curves for PG and OA formulations are shown in Figures 3 and 4, respectively. A broad T_g region for concentrations of 5 and 10 (w/w %) of OA, in contrast with PG formulations, signifies microheterogeneous microstructure. However, exothermic peaks for more than 10 (w/w %) concentrations of OA is related to free (unbound to polymer chains) OA molecules crystallization and indicates macroscopic immiscibility. This immiscibility and probably migration of OA to the surface is in accordance with a sharp drop in surface energy from 22.0 to 16.2 (Table I). The sharp drop in peel force observed in Figure 2 is not accounted for by T_g . This can be related to entanglement molecular weight (M_e), which influences elastic modulus. Zosel has shown that high M_e values are needed for PSA films to undergo fibrillation during the peeling process, which significantly increases peel energy.²¹ However, it seems logical to consider the entanglements strength. Although addition of OA, as mentioned before, increases the spaces between entanglements (M_e), it causes entanglements to be weak. It can be concluded that increasing OA concentration from 5 to 10 (w/w %) has formed such weak entanglements that polymer chain extensions or fibrillation become very low. On the other hand, no significant change in T_g and surface energy of PG formulations is in accordance with an approximately constant peel force in Figure 1.

Thickness effect

The relationship between peel strength and PSA thickness has been investigated by some researchers.^{14,22} As the adhesive thickness increases, a larger volume

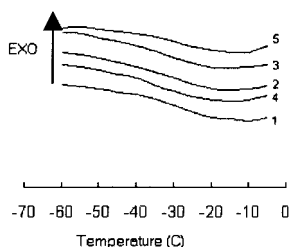


Figure 3 DSC thermogram measured in heating mode for DuroTak-PG formulations containing: (1) 5, (2) 10, (3) 15, (4) 20, and (5) 25 wt % PG.

of adhesive is subjected to deformation per unit area of detachment, so that the total work expended and peel force increases. This increase in peel force is observed in Figure 1 for PG formulations. On the other hand, lower T_g amounts of OA formulations means higher viscous response of adhesive. Then peel force does not transfer in overall thickness of adhesive, and dissipation process occurred in a relatively small portion of the thickness. This is the answer to why doubling of the thickness, in Figure 2, has caused no significant effect on peel strength of OA formulations.

Adhesive-cohesive transition

The transition from adhesive to cohesive failure mechanism is observed in Figure 2 for OA formulations. As mentioned earlier, free crystal formation occurred in concentrations more than 10 (w/w %). These crystals act as stress concentrators and decrease cohesive strength sharply. The adhesive-cohesive transition for 30 μ m occurs in higher concentrations than 60 μ m tapes. In thicker adhesive layers the acting moment arm is larger, and the peel force is inversely proportional to the acting moment arm.

CONCLUSIONS

The effect of PG and OA on peel strength was investigated, and the results were explained by surface properties and thermal analysis of different formulations. It was shown that interfacial work in comparison with total work of adhesion is so small that can be ignored. PG has no significant effect on peel strength, which was related to the effect of hydrogen bonds between PG and polymer chains making a crosslinked structure. DSC curves do not show immiscibility in

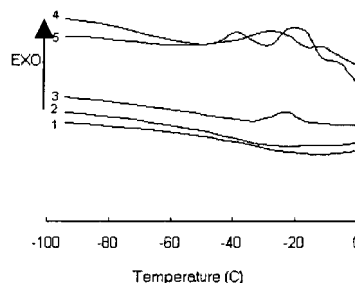


Figure 4 DSC thermograms measured in the heating mode for DuroTak-OA formulations containing: (1) 5, (2) 10, (3) 15 (4) 20, and (5) wt % OA.

any PG concentration. However, a positive deviation from the Fox equation was related to hydrogen bonding. OA decreases peel strength significantly, which was explained by an important change in polymer structure and T_g drop. A sharp drop in peel force between 5 and 10 (w/w %) was related to a significant decrease in M_e . Doubling of the adhesive layer thickness has no effect on peel force of OA formulations. Adhesive-cohesive failure mechanism transition occurred due to the effect of free OA crystals as stress concentrators. OA migration to surface in concentrations more than 10 (w/w %) was confirmed by the results of thermal analysis and surface properties. A large negative deviation of T_g from the Fox equation was related to the effect of large OA molecules on the cohesion strength depression.

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