

Effect of Different Skin Permeation Enhancers on Tack of a Pressure Sensitive Adhesive

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ABSTRACT: Solutions of an acrylic copolymer pressure sensitive adhesive with different concentrations of propylene glycol (PG) and oleic acid (OA) were cast on a PET film. A rolling ball tack test was carried out on the adhesive coated tapes with different thicknesses. The results were explained on the basis of the surface (energy and roughness) and viscoelastic properties of the copolymer, which were related to the glass-transition temperature. The 60- μm PG samples with an approximately equal glass-transition temperature and surface energy did not have a significantly different tack value. The tack value of the 30- μm tapes decreased with PG concentrations above 15% (w/w), which

was related to an increase in the surface roughness with a more prominent effect at the lower thickness. OA, which improved both the surface and viscoelastic properties, increased the tack value up to 15% (w/w). However, the tack value decreased above 15% (w/w). This was explained on the basis of OA large crystals, which can decrease viscoelastic energy dissipations and form a mechanically weak surface layer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1287–1291, 2005

Key words: glass transition; miscibility; adhesives; surfaces

INTRODUCTION

Pressure sensitive adhesives (PSAs) are commonly used in a variety of applications including transdermal drug delivery systems (TDDSs).^{1,2} The important advantages of TDDS are the avoidance of the first pass effect, ease of use and withdrawal (in case of side effects), and better patient compliance.³ However, the development of TDDSs is dependent on skin permeation enhancers.⁴ Acrylic PSAs are extensively used in skin contact applications because they have low irritating effects.⁵ They are inherently tacky without any additional compounding and their properties can be easily changed by combining different kind of monomers. Tack, which is the distinctive property of PSAs, is the ability of an adhesive to bond under conditions of light contact pressure and short contact time. It is a composite response of material surface (energy and roughness) and bulk (viscoelastic and thickness) properties.⁶ There are different tack test methods including rolling ball, probe, and peel-tack. The tack of some skin contact adhesives has been studied by the rolling ball method.^{7–9} However, nobody has investigated the effect of skin permeation enhancers on the tack of PSAs. In this research work the effect of two skin permeation enhancers, oleic acid (OA) and 1,2-pro-

pylene glycol (PG), and the adhesive thickness on the tack of an acrylate–vinyl acetate copolymer is investigated.

EXPERIMENTAL

Materials and methods

Duro-Tak 87-2196 (National Starch and Chemical Co.), PG USP (Merck), OA USP (Merck), and a poly(ethylene terephthalate) (PET) film (kindly prepared by Daroupat Shargh) were used.

Duro-Tak was thoroughly mixed with OA and PG to prepare formulations containing 5–25% (w/w) of the additives in the dry adhesive. Formulations were cast on PET films by a film applicator (BYK-Gardner). After staying at room temperature for about 10 min, drying was completed in a 65°C oven in a period of about 20 min.

Tack test

The tack test was carried out for PSA coated tapes stored at room temperature for 24 h. The tapes with an adhesive layer width of 22 ± 2 mm and sufficient length were fixed on a glass plate from one end. An inclined trough made similar to ASTM D3121 (Fig. 1) was put on the other end of the coated tape and pulled backward to make a completely stretched tape. A 1-mm diameter steel ball was released from the top of the inclined trough. The reversed amount of the dis-

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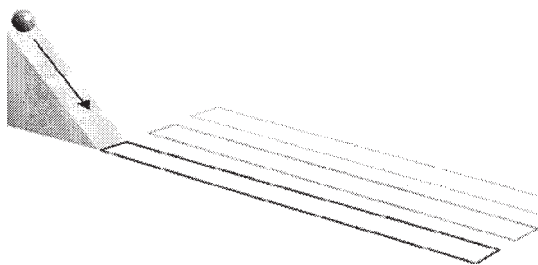


Figure 1 A schematic of the tack test method.

tance traveled by the ball was reported as the tack value.

Thermal analysis

The glass-transition temperature (T_g) of various formulations was measured with a differential scanning calorimeter (PL) at a heating rate of $10^\circ\text{C}/\text{min}$. In all cases the T_g was taken as the midpoint of the heat flow curve.

Contact angle measurement

In order to evaluate the surface energies, equilibrium contact angles were measured at room temperature for distilled water and diiodomethane on the surfaces of the samples. The measurements were done using a contact angle measuring system (G10, Kruss). The surface energy (γ), which is the sum of dispersion (γ_A^d) and polar components (γ_A^p), was determined according to the improved Owens method.¹⁰

Microscopy

The surface roughness of different PG samples was investigated using a Jenapol (Carl Zeiss) optical microscope.

RESULTS AND DISCUSSION

The tack value of the $60\text{-}\mu\text{m}$ PG samples does not change significantly (Fig. 2). However, a significant drop in tack value is observed for $30\text{-}\mu\text{m}$ PG samples above 15% (w/w). It is observed in Figure 3 that the tack value increases sharply with the OA concentration up to 15% (w/w) and then it decreases.

Miscibility

The miscibility between the components of polymeric mixtures is effective on both their surface and viscoelastic properties. Miscibility in a rubber/resin system depends on the solvent, the overall bulk resin concentration, the thickness of the film, and the time

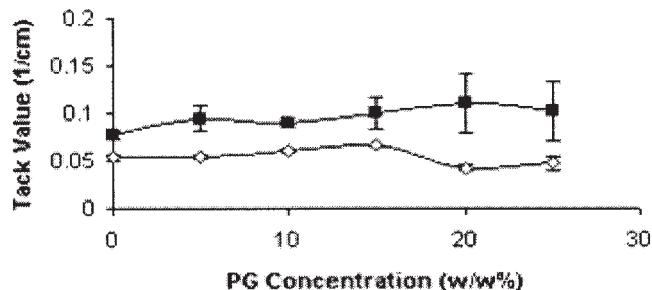


Figure 2 A plot of the tack value versus the PG concentration for (\diamond) $30\text{-}\mu\text{m}$ and (\blacksquare) $60\text{-}\mu\text{m}$ adhesive layer thicknesses.

for equilibration after the film has dried.¹¹ Kim and coworkers, who studied the tack of acrylic copolymer/tackifier resin systems, have concluded that for immiscible blend systems the magnitude of the fracture energy decreases with increasing tackifier content.¹² Fujita et al. have concluded that the probe tack values of immiscible tackifier/natural rubber PSA systems are smaller than those of miscible ones.¹³

Miscibility between PG and the neat copolymer can be concluded with respect to their similar DSC thermograms (Fig. 4). In regard to a large difference between the solubility parameter of PG (Table I) and the dry adhesive [$16(\text{cal}/\text{cm}^3)^{1/2}$], PG migration to the surface and surface energy increase is expected. However, the surface energy is approximately constant for different PG samples (Table II), which can be related to hydrogen bonding between the hydroxyl groups of PG and the carbonyl groups of the adhesive copolymer. The hydrogen bonds, acting as crosslinkers, withstand the plasticizing effect of PG, which leads to a constant T_g (Table III).

A broad T_g region for OA concentrations below 15% (w/w) in Figure 5 signifies a microheterogeneous microstructure [14]. However, exothermic peaks for concentrations more than 10% (w/w) are indicative of OA molecule crystallization. OA free crystals can easily migrate to the surface, which is confirmed by a sharp drop in surface energy from 22 to 16.2 (Table II). In addition, hydrogen bonding is possible between the

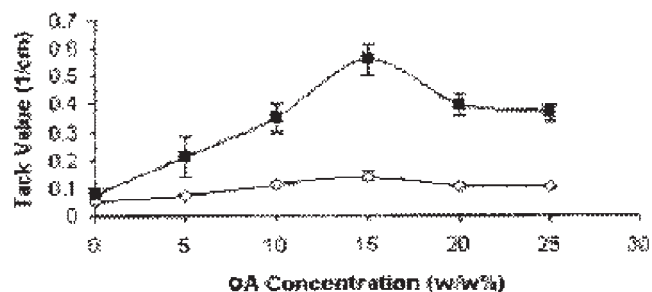


Figure 3 A plot of the tack value versus the OA concentration for (\diamond) $30\text{-}\mu\text{m}$ and (\blacksquare) $60\text{-}\mu\text{m}$ adhesive layer thicknesses.

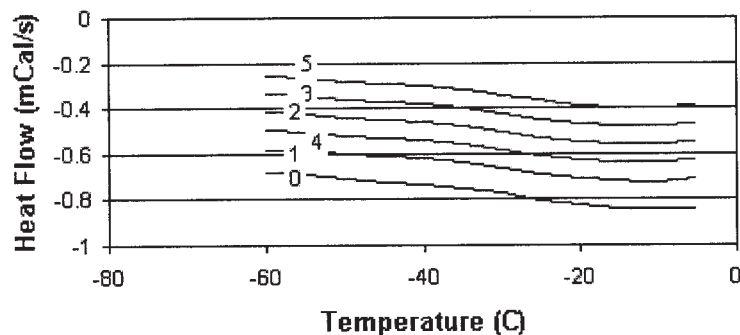


Figure 4 DSC thermograms of the copolymer containing (0) 0, (1) 5, (2) 10, (3) 15, (4) 20, and (5) 25 wt % PG.

OA hydroxyl end group and the copolymer carbonyl group. As the OA concentration increases, the hydrogen bonding is limited by OA large molecules. Then, OA may exist as bounded and free molecules. The two crystallization peaks of the 20% (w/w) sample can be related to these two forms of OA. It can be supposed that at 25% (w/w), when increasing the polymer chain flexibility, the OA bounded molecules become too low to make a separate crystallization peak as for the 20% (w/w) sample. The second peak at the lower temperature can be related to OA free crystals. At 25% (w/w), the copolymer chains become more flexible and many hydrogen bonded OA molecules may be associated with OA free crystals. Then, the bounded molecules become too low to make a separate crystallization peak. The surface area of the crystallization peak for the 25% (w/w) sample is 20% less than that for the 20% (w/w) sample. This can be related to the increase of surface migration through the more flexible polymer chains in the 25% (w/w) sample. The surface migration is confirmed by a large decrease in the surface energy for the 25% (w/w) sample (Table II).

Viscoelastic properties

The tack test involves a bonding stage followed by a debonding stage. The bonding stage depends on the surface energy, surface roughness, and storage modulus of the adhesive. The debonding stage, which involves a peeling process, is related to polymer surface energy and viscoelastic energy dissipations (VEDs).¹⁵ We have shown that the thermodynamic

work of adhesion, which is the change in surface free energy when two materials are brought into contact, is 4 orders of magnitude smaller than the VEDs for peeling of different OA and PG samples from a stainless steel plate.¹⁶ Then, the surface energy has approximately no role in the debonding process. However, it is the major driving force toward bond formation. Strong bond formation has been observed for adhesives having a lower surface energy than the adherend.⁶ The storage modulus (G') is related to the T_g of the copolymer. It has been shown that the debonding process generally contains cavitation, lateral, and finally extensional growth of the cavity.¹⁷ Zosel has concluded that the debonding energy (related to G'') in a peel or tack test is proportional to the average mass between polymer chain entanglements (M_e).¹⁸ The M_e value can be related to G' with respect to the following equation¹⁴:

$$M_e = \rho RT / G_n^o \quad (1)$$

where ρ is the density of the polymer or blend; R is 8.31 J/mol K; T is the absolute temperature; and G_n^o is the rubbery plateau modulus, which is determined from G' at the onset of the rubbery region. Then, the viscoelastic properties changes can be studied using the T_g .

It is observed in Figure 2 that the tack value of the 60- μm PG samples does not change significantly. This can be explained on the basis of approximately equal T_g and surface energy for the different samples. However, a significant drop in tack value is observed for 30- μm PG samples above 15% (w/w). All factors af-

TABLE I
Physical Properties of Skin Permeation Enhancers

Material	Formula	MW (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

PG, propylene glycol; OA, oleic acid.

TABLE II
Contact Angles and Surface Energies of Different Samples

CA (°)	Samples										
	A0	OA5	OA10	OA15	OA20	OA25	PG5	PG10	PG15	PG20	PG25
Water	109.3	104.4	106.3	105.7	111.3	113.1	105.9	100.3	100.2	101.3	98.27
Diiodo	58.5	68.9	72.4	82.5	86.7	95.7	56.0	60.1	58.2	58.0	57.9
γ	33.0	23.9	22.0	16.2	14.2	10.4	33.6	29.1	30.4	30.8	30.3

A0, neat copolymer; CA, contact angle.

TABLE III
Glass-Transition Temperatures of Different Propylene Glycol and Oleic Acid Samples

T_g (°C)	Samples										
	A0	OA5	OA10	OA15	OA20	OA25	PG5	PG10	PG15	PG20	PG25
	-24.7	-36.9	-43.9	-60.3	-66.3	-71.7	-28.5	-30.7	-32.0	-32.0	-30.3

A0, neat copolymer.

fecting the bonding and debonding stage except surface roughness remain unchanged when the PG concentration exceeds 15% (w/w). Figure 6 shows that the number and height of the asperities is increased significantly above 15% (w/w). Increasing the surface roughness causes the tack value to decrease,⁶ which is partly related to the decrease of the real contact area between the rolling ball and the adhesive surface, although, even at large contact pressures, the tack of rough surfaces is much lower than smooth surfaces. This is related to the micromechanics of debonding. Zosel, who examined the tack of a poly(butyl acrylate) using stainless steel probes with different surface roughnesses, has concluded that the size of the initial cracks in the fibrillation process is larger for the rough surface.¹⁸ Another similar study has shown that cavities are formed at a lower level of stress for the rough surface.¹⁹ Then, increasing of the surface roughness decreases the fibrillation energy and tack value. With doubling of the thickness, not only the real contact area increases²⁰ but also more energy is dissipated for crack propagating. Then, the roughness effect is offset for the 60- μm samples.

The tack value increases sharply with the OA concentration up to 15% (w/w), which is presented in Figure 3. OA causes a large drop in the T_g , which promotes wetting area and M_e . In addition, it decreases the surface energy of the copolymer (Table II), which leads to a stronger driving force toward bond formation. Then, addition of OA up to 15% (w/w) improves both the bonding and debonding stages. However, above 15% (w/w) the tack value decreases with a concentration increase. It is observed in Figure 5 that the OA crystals become significantly larger above 15% (w/w). These large crystals cause polymer chains to be dissociated mainly. Then, the chain entanglements become so weak that they cannot be extended significantly during contact with the rolling

ball. In the other words, the fibrillation is limited. According to the previous discussions, the crystal size must be equal for the 20 and 25% (w/w) OA samples, which accounts for their equal tack values. The decrease in tack value can also be related to the transfer of migrated OA to the ball surface or formation of a mechanically weak surface layer,²¹ which reinforces the bulk effect of the crystals. This decreasing mechanism for tack must be more effective for a 25% (w/w) OA sample having a high surface migration level. A large difference between the tack value of 60- and 30- μm OA samples can be related to the lower surface concentration of OA in the 60- μm sample as described below.

As discussed before, OA is partially or completely immiscible with the dry adhesive but its large molecules can be better solved in the adhesive solvents. It can be concluded that during the evaporation process OA moves toward the surface with the solvents and diffuses back into the bulk as a result of the concentration gradient. The longer drying time for the higher thickness leads to more back-diffusion and a lower surface concentration of OA.

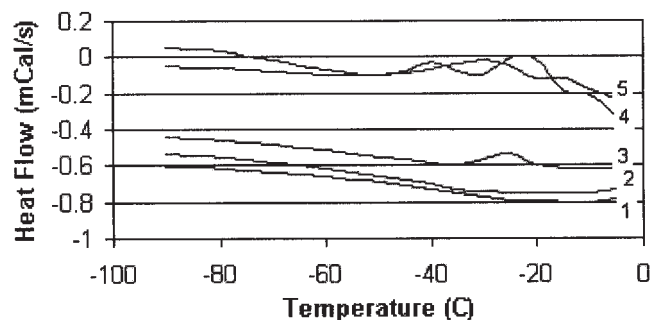


Figure 5 DSC thermograms of the copolymer containing (1) 5, (2) 10, (3) 15, (4) 20, and (5) 25 wt % OA.

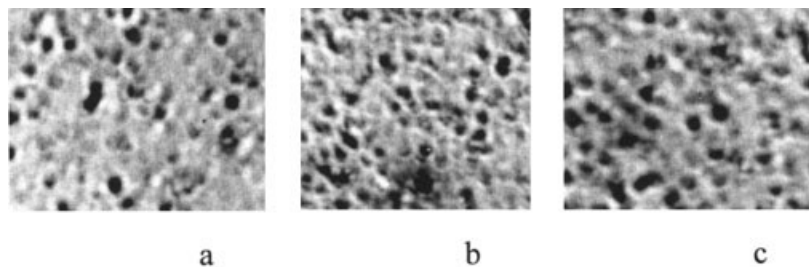


Figure 6 Optical micrographs (original magnification $\times 200$) of samples containing (a) 15, (b) 20, and (c) 25 wt % PG.

CONCLUSIONS

The effects of PG and OA on the tack of an acrylic adhesive copolymer with different thicknesses was investigated. PG has no significant effect on the tack value of 60- μm tapes. This was explained on the basis of an approximately constant M_e and surface energy. However, it decreases the tack value of the 30- μm tapes above 15% (w/w), which is due to a significant increase in the surface roughness. The difference between the 30- and 60- μm tapes was related to the real contact area and viscoelastic energy dissipations increase for the higher thickness. The tack value increases rapidly with OA concentration up to 15% (w/w). This is explained on the basis of a decrease of the T_g and surface energy. Decreasing of the tack value above 15% (w/w) was related to OA large crystals, which limit the fibrillation level, and OA migration to the surface.

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