The Effect of Alpha Hydroxy Acids on the Tack of Pressure-sensitive Adhesive

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A B S T R A C T

The adhesion and tackiness of cosmetic patches are very important factors, especially when the patches are applied to an area with sensitive skin, such as face. The objective of this work is to study the influence of varieties of alpha hydroxy acids concentration as ingredients of cosmetic patches on their tackiness. Different amounts of two cosmetic patch ingredients, glycolic acid(GA) and lactic acid(LA), were mixed thoroughly with solution of a acrylic pressure-sensitive adhesive(PSA). Films with 32 μm thickness were prepared by casting formulations on a polyethylene terephthalate film. Tack test was carried out on different formulations according to ASTM D3121-94. It was observed that tack value increases by increasing LA concentration up to 6 % (w/w). Tack value increase by increasing GA concentration up to 1 % (w/w), then it decreases by increasing GA concentration up to 3 % (w/w), and then increases again by increasing GA concentration above 6 % (w/w). These results are due to changes in entanglements, glass transition temperature, plateau modulus G^o of adhesive, and functional groups that exist in additives.

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INTRODUCTION

Pressure-sensitive adhesives (PSAs) are materials that adhere to a substrate by application of light force and leave no residue when they are removed [1].

Commercial use of PSAs cover a broad range of products such as labels, tapes, and cosmetics [2]. Several materials have PSAs properties, among them the major classes of these polymers are acrylics, silicones, and polyisobutylenes [3]. The acrylic PSAs have several desirable features, such as resistance to oxida-

tion and thermal degradation, and moderate cost. They are permeable to water vapour and oxygen and generally exhibit good tackiness. In addition, their properties can be easily modified by incorporating them different monomers during polymerization and penetration of enhancers and solubilitizers [4, 5].

Tack, 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 cosmetic patch ingredients on the tack of PSAs. In this research the effects of two cosmetic patch ingredients, lactic acid (LA) and glycolic acid (GA) on the tackiness of an acrylate-vinyl acetate copolymer are investigated.

EXPERIMENTAL

Materials
Poly(acrylate-*co*-vinyl acetate) with commercial grade Duro-tak 87-2196, was purchased from National Starch and Chemical Company, Bridgewater, NJ. Glycolic acid (99%) and lactic acid (*L*-lactic acid 85%) was supplied by Aldrich and PET films with 80 μm thickness (generously prepared by Daroupat Shargh, Iran) were used.

Matrix System Preparation
The solid content of adhesive is first determined by weighing a small amount of the adhesive solution in a pre-weighed Petri dish. The solvent is evaporated by drying in a vacuum oven maintained at 70ºC for 30 min and the percentage of solid content is determined on the basis of the weight of dried adhesive. The amount of adhesive in the solution was calculated by weight of the adhesive solution and the percent solid adhesive content. Appropriate quantities of glycolic acid and lactic acid (1-6 % w/w) are added to adhesive. The glass bottle is then tightly capped, sealed with Para film, and rotated overnight until all ingredients are completely dissolved and the solution is visually clear. The resulting solution was evenly applied on a PET film with a

thickness of 32 m by using a film applicator (BYK-Gardner, USA). The sample was allowed to stand at room temperature for 10 min and then further dried in an oven at 70ºC for 20 min. After solvent evaporation, backing PET film is then laminated on to this adhesive film on the opposite side of the release liner using a roller and kept in a 28ºC for further investigation.

Microscopic Observation
Phase separation and surface roughness of samples were investigated by using Optical Microscope (using Carl Zeiss Jenavert, Germany).

Tack test
Tack test was carried out for PSA coated tapes stored at room temperature for 24 h. The tapes with adhesive layer width of 22±2 mm and enough length were fixed on a glass plate from one end. An inclined trough made according to ASTM D3121 was put on the other end of the coated tape and pulled backward to make a completely stretched tape. A 1mm diameter steel ball was released from the top of the inclined trough. The reversed amount of the distance traveled by the ball was reported as tack value.

Thermal Analysis
Dynamic mechanical thermal analysis (DMTA) carried out in the temperature range of -110 to +50ºC by Polymer Laboratory (PL-DMTA) instrument to determine any changes in the glass transition temperature (Tg) of samples and Gº. For this purpose the adhesives containing different amounts of AHAs were casted onto PET (approximateltly1mm thick) and placed in the vacuum oven at 70ºC for 24 h. The adhesive samples were cooled and held at -110ºC for three minutes before undergoing a temperature scan from -110ºC to +50ºC with scan rate of 2ºC per min under nitrogen atmosphere.

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 different samples. The measurements were done using a contact angle measuring system G10 (Kruss, Germany). Surface energy (γ), which is the sum of dispersion (γ_A^d) and polar components (γ_A^p), was determined according to improved Owens method [10].

RESULTS AND DISCUSSION

Figure 1 shows that increasing of GA and LA concentration causes PSA tack values change significantly. A maximum tack is observed for 6 % (w/w) concentration of GA and LA. It is observed that tack value increases initially, decreases between 1-3 % (w/w) and then increases above 3 % (w/w) GA. Also increasing of LA concentration up to 6 % (w/w) causes tack value to increase.

Miscibility

Miscibility of components of polymeric mixtures is effective on both of their surface and viscoelastic properties. Miscibility in the rubber/resin system depends on the solvent, the overall bulk resin concentration, the thickness of the film and the equilibration time after the film has dried [11]. Kim and his coworkers, by studying tack of acrylic copolymer/tackifier resin systems, have concluded that for immiscible blend systems the magnitude of fracture energy decreases with increasing the tackifier content [12]. Fujita and his coworkers have concluded that probe tack values of immiscible tackifier /natural rubber PSA systems are smaller than those of miscible ones [13].

Miscibility between additive and copolymer can be evaluated with macroscopic and microscopic observation as follows:

Macroscopic Observation
Phase separation and surface roughness of samples were investigated by using an optical microscope. Figure 2 shows that additives were completely dissolved in adhesive by continuous agitation after specific time. In
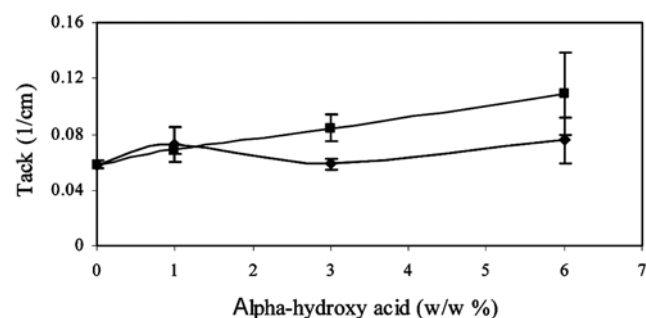
Figure 1. Plot of tack value against glycolic acid (GA) (◆) and lactic acid (LA) concentration (■) for 32 µm adhesive layer thickness.

miscible blends, the effect of alpha hydroxy acids can influence the adhesive properties via its effect on surface energy or via an effect on bulk viscoelastic properties of the adhesive, which results are evaluated in viscoelastic properties.

Microscopic Observation
In this study the microscopic miscibility between additive/adhesive was examined by dynamic mechanical thermal asnalysis (DMTA). The DMTA data (Figures 3, 4, 5, and 6) showed identical single T_g and no broadening in tan δ peak for additives up to 3 % (w/w) in comparison with the neat copolymer, which indicat that complete mixing was achieved. On the other hand, DMTA data have showed another curve in tan δ peak for copolymer with additives of 6 % (w/w) in comparison with the neat copolymer which indicates their immiscibility. In this case it is expected that tack value decreases. But tack value in this range increases. 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) [14]. M_e Maybe related to G′ with respect to the following equation [15]:

$$M_e = \rho RT/G_n^o \tag{1}$$

Where ρ is density of the polymer or blend, R is 8.31 J/mol K, T is absolute temperature, and, rubbery plateau modulus G_n^o, is determined from G′ at the onset of rubbery region.

It is observed in Table 1 that G^o value of samples (copolymer containing GA and LA) decrease significantly in 6 % (w/w) concentration and to cause that M_e in eqn (1) increase. This means that the adhesive can not be deformed easily and develop a good contact with substrate which leads to increasing tack value.

Viscoelastic Properties

Viscoelastic properties and glass transition temperature of the adhesive play an important role in tack and wear performance.In a good pressure-sensitive adhesive viscoelastic properties must balance each other. This balance would include sufficient flow enabling the adhesive to form a bond with substrate [16]. The small molecules adjust the glass transition temperature of the blend in a range that is giving high dissipation at room
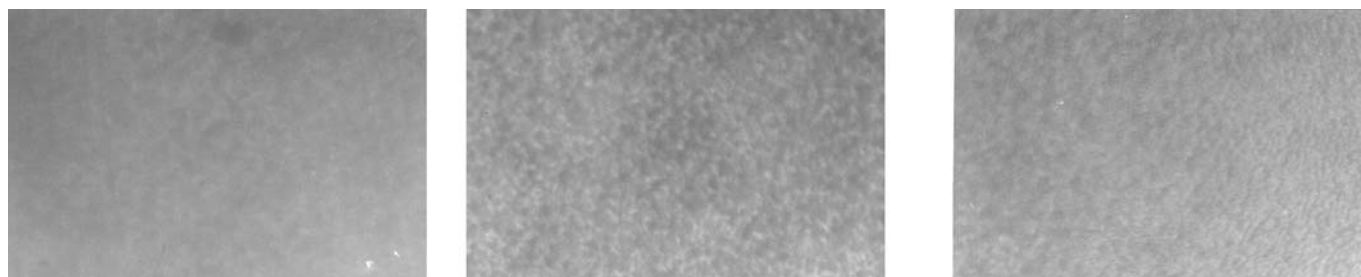
Figure 2. Optical microscopic observation show that additives were completly dissolved in adhesive:(I)PSA containing 3 % (w/w) glycolic acid, (II) PSA containing 6 % (w/w) glycolic acid, and (III) PSA containing 6%(w/w) lactic acid (magnification x 200).

temperature and therefore weaken the entanglements.

The addition of glycolic and lactic acid up to 3 %(w/w) reduced the T_g. In this case additions of glycolic and lactic acid have an effect similar to the effect of plasticizer addition. Plasticizers have little effect on the free volume of the adhesive as it lower the T_g and the modulus by acting as compounding agent with a lower T_g.

Plasticizers allow the adhesive film to flow more easily and are responsible for more rapid wetting of the adherent [5]. Therefore, the tack value was increased due to increasing real contact area between the rolling ball and adhesive. Perhaps low changes in T_g value related to hydrogen bondings that take place between hydroxy groups of AHAs (Alpha Hydroxy Acids) and carbonyl groups of the adhesive copolymer. Therefore hydrogen bonds, acting as cross-linkers, withstand the plasticizing effect of AHAs which leads to low change in T_g (Table 1) [17].

But tack test involves a boding stage followed by a debonding stage. The bonding stage depends on 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 (V.E.D.)[18]. Tse [19] pointed out that PSA tackiness (T) is expressed by considering the bonding and debonding processes of adhesive, as follows.

$$T = W_a . B . D \qquad (2)$$

Table 1. Glass transition temperature and G° of neat copolymer (pressure-sensitive adhesive) and copolymer containing glycolic acid and lactic acid (GA, LA).

Materials	Da (g/cm³)	Log G° (Pa)	T(abs) (K)	Tan δ	Log G' (Pa)	Log G" (Pa)	T_g (K)
					T = 298 (K)		
Duro-tak (87,2196)	0.88	9.16	275.75	0.110	9.1854	1.019	-16.22
Glycolic acid	1.250	-	-				-
C₂H₄O₃(wt=76.03)							
PSA containing GA 1 % (w/w)		9.38	280.58	0.120	9.2874	1.114	-17.52
PSA containing GA3 % (w/w)		9.48	277.13	0.108	9.3908	1.014	-20.42
PSA containing GA 6 % (w/w)		9.29	279.89	0.106	9.2752	0.986	-15.68
Lactic acid	1.206	-	-				-
C₃H₆O₃(wt=90.08)							
PSA containing LA 1 % (w/w)		9.38	275.75	0.103	9.2303	0.9562	-18
PSA containing LA 3 % (w/w)		9.48	273.46	0.116	9.3908	1.051	-20.22
PSA containing LA 6 % (w/w)		9.38	276.1	0.118	9.2643	1.903	-18.30
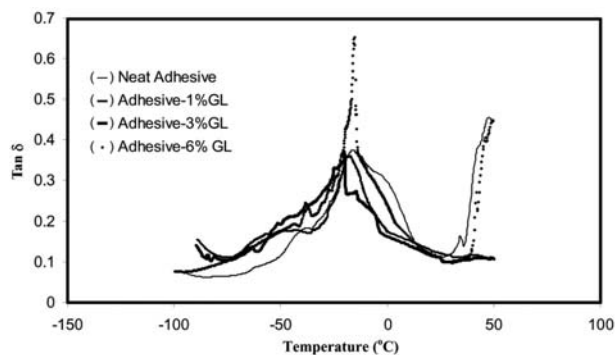
Figure 3. Master curves of tan δ as a function of temperature for the neat adhesive and adhesive-additive with three different weight percentages of glycolic acids.

Figure 5. Temperature dependence of storage modulus of neat PSA, PSA containing 1 % (w/w), 3 % (w/w), and 6 % (w/w) of glycolic acid, respectively.
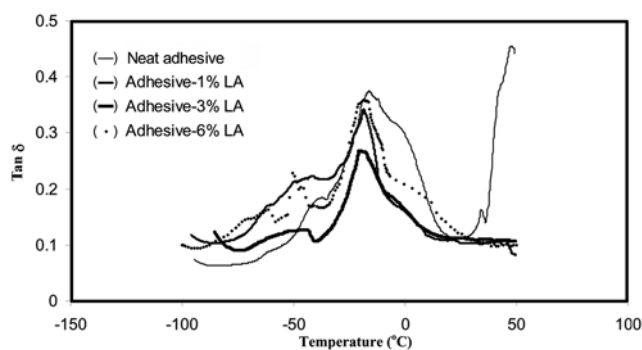
Where W_a is the work of adhesion between adhesive and adherent. The parameter W_a is calculated by the following equation.
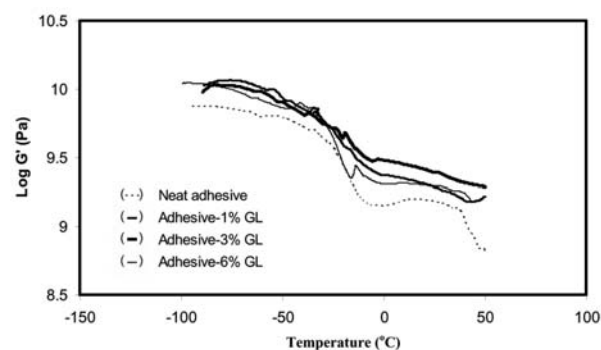
$$W_a = \gamma_S + \gamma_A - \gamma_{SA} \tag{3}$$

Where γ_S is the substrat s surface energy, γ_A is adhesive s surface energy, and γ_{SA} is the substrate - adhesive interfacial surface energy. We have shown in Table 2 that surface energy values are approximately constant for all samples. Therefore, W_a value in this equation is constant and has no role in the tackiness. Parameter D in eqn (2) correlates with debonding process and increase with increasing loss modulus G'' of adhesive. G'' is calculated by the following equation.

$$G'' = (\tan\ \delta).\ G' \tag{4}$$

In this study tan δ and G' are obtained from Figures 3, 4, 5, and 6 at 24°C. It is observed in Table 1 that for all
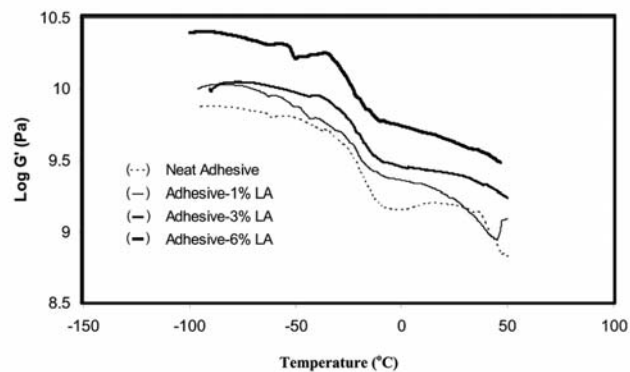
samples G'' does not change significantly. If the G'' value is approaching constant, eqn (2) can be simplified as follows:

$$T = (\text{constant}) . B \tag{5}$$

B is the function of bonding process and depends on the plateau modulus G^o of adhesive. By eqn (5) the PSA tackiness is correlated with the only G^o.

In this study G^o is determined from G' at the onset of rubbery region. As shown in Table 1, G^o increases with increasing of LA and GA concentration from 1 to 3 % (w/w) and then decreases. According to eqn (1), high-plateau modulus leads to low values of M_e, and this means that the adhesive cannot be deformed easily and develop a good contact with substrate, which leads to decreasing of tack value.

Figure 1 shows that tack value for copolymer containing 3 % (w/w) of GA decreases but increases for copolymer containing 3 % (w/w) of LA. Increasing of GA con-

Figure 4. Master curves of tan δ as a function of temperature for the neat adhesive and adhesive-additive with three different weight percentages of lactic acids.

Figure 6. Temperature dependence of storage modulus of neat PSA, PSA containing 1 % (w/w), 3 % (w/w), and 6 % (w/w) of lactic acid, respectively.

Table 2. Contact angles and surface energies of different samples (As: Adhesive without additive, GA1: Adhesive with 1 % glycolic acid, GA3: Adhesive with 3% glycolic acid, GA6: Adhesive with 6% glycolic acid, LA1: Adhesive with 1% lactic acid, LA3: Adhesive with 3% lactic acid, LA6: Adhesive with 6% lactic acid).

Sample	As[†]	GA1	GA3	GA6	LA1	LA3	LA6
Water CA[‡] (o)_	109.2	107.0	107.8	109.0	107.0	108.3	109.3
Diiodo	57.2	53.9	56	53.2	55	58.8	55.9
γ (mN/m)	33.9	35.7	33.7	35.2	34.9	32.4	35.2

† Neat copolymer; ‡ contact angle.

centration up to 3 % (w/w) causes G^o increases, and M_e decreases, thus the debonding stage becomes weak.

Increasing of LA not only causes increasing of G^o but also leads to decreasing of T_g. When T_g decreases, the adhesive film flows which causes the adherent to wet more easily. Then the tack value increases.

In Figure 1, beyond concentration of 3 % (w/w) of glycolic and lactic acid, G^o decreases and M_e increases, which causes the adhesive to be deformed more easily. This makes a good contact with the substrate which leads to increasing of tack value.

In all concentrations, the increasing effect of LA on tack value is more than GA. The reason is that, carboxylic acids are among the most polar organic compounds because their functional groups consists of two polar groups: a hydroxyl (-OH) group and a carbonyl (C=O) group. Therefore, carboxylic acids form hydrogen bonds with other carboxylic acid molecules and carbonyl groups of the copolymer. This ability to form hydrogen bonds has a major influence on tack value.

Due to the fact that lactic acid is a weaker acid than glycolic acid. it is possible that lactic acid dimmers more which in turn results in less hydrogen bonds development in polymer back bone. But, however glycolic acid develops more hydrogen bonds in polymer backbone. This increase in tack value for lactic acid is attributed to lower hydrogen bond in polymer back bone.

CONCLUSION

Glass transition temperature (T_g) and entanglement molecular weight M_e are significant molecular parameters affecting PSA adhesive properties [20]. While T_g is related to the onset of viscoelastic energy dissipation, M_e influences the elastic modulus. The T_g, on the other hand, is strongly depended on the miscibility of the components in the PSA [21]. In this study, the effects of GA and LA on the tack value of an acrylic adhesive copolymer with a constant thickness was investigated. All factors affecting debonding stage except surface roughness which remains unchanged, when increasing LA and GA concentration up to 6 % (w/w). The tack value first increases rapidly as GA concentration increases up to 1 % (w/w) and then decrease up to 3 % (w/w) of GA and then increase above this concentration. Decreasing of the tack value in 1-3 % (w/w) of GA was related to the basis of the plateau modulus G^o of adhesive that influences bonding stages and M_e, and probably also to the migration of GA to the surface. Increasing tack value above 3 % (w/w) GA explained on the basis of viscoelastic behaviour such as G^o value that influence bonding stages and M_e. Increasing of the tack value in concentrations of 1-6 % (w/w) of LA was related firstly to decrease of T_g in the 1-3 % (w/w) and then decrease of G^o above 3 % (w/w) that influence bonding stages and M_e. Therefore, both G^o and T_g are two important parameters that can control the tack value.

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