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## Adhesion performance and optical properties of optically pressure-sensitive adhesives including an isosorbide

Seung-Woo Lee, Jong-Ho Back, Gyu-Sung Shim, Seong-Wook Jang, Hyun-Joong Kim\*

Laboratory of Adhesion &amp; Bio-Composites, Program in Environmental Materials Science, Research Institute for Agriculture &amp; Life Sciences, Seoul National University, Seoul, 151-921, Republic of Korea

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## ABSTRACT

Isosorbide is newly used as a cross-linking agent to replace petroleum-based cross-linking agents for optically clear pressure-sensitive adhesives (PSAs). To control and determine the optimal concentration of isosorbide, the relationship between the glass transition temperature ( $T_g$ ), referring to the viscoelastic characteristics of the organic polymeric materials as a key factor not only to synthesize the binders and but also to utilize the final products, and the concentration of isosorbide were investigated by measuring the optical properties, the adhesion performance via the peel strength, the probe tack, and the shear adhesion failure temperature. Consequently, it was found that the relationship provided by the linear plots between  $T_g$  and the other properties was strongly affected by the concentration of isosorbide due to the cross-linking density.

## 1. Introduction

A pressure-sensitive adhesive (PSA) is an adhesive that adheres instantly to a substrate by the application of light pressure. By pulling lightly, it also detaches easily and without residue [1,2]. Optical PSAs are increasingly used in areas, such as liquid crystal displays (LCDs), plasma display panels (PDPs) and organic light emitting diodes (OLEDs), due to the increased production of optical devices [3]. Optical PSAs should have high contrast, good clarity, a high refractive index and good reliability [4]. As optical PSAs, acrylic PSAs are widely used because they are inexpensive and exhibit properties such as self-adhesiveness and high resistance to weathering. Moreover, acrylic PSAs have several advantages, including excellent aging characteristics, resistance to elevated temperatures and plasticizers, exceptional optical clarity due to good compatibility with many polymers, resistance to yellowing, and the optimum balance of adhesion, and cohesion with excellent water resistance as well [5].

1,4:3,6-Dianhydrohexitols obtained from biomass-derived carbohydrates have attracted much attention owing to their potential applications to the creation of polymers, pharmaceuticals, and cosmetics [6–8]. They are divided into three stereoisomers corresponding to isosorbide, isomannide, and isoidide, prepared from glucose, mannose, and idose, respectively, via the reduction of the aldehyde group and subsequent

double dehydration [9]. Considering the carbon footprint and the depletion of petroleum reservoirs into account, isosorbide is one of the most commercially viable compounds for replacing petroleum-based compounds because its starting material, glucose, originates from the most abundant biomass resource on earth, as shown in Fig. 1. In addition, isosorbide is the only bio-based diol that improves resistance to heat, UV rays and chemicals, while also offering excellent optical and mechanical properties owing to its rigid structure. Hence, isosorbide has been applied as a monomer for transparent polymers such as polyester and polycarbonate [10–13].

The properties of PSAs synthesized by the co-polymerization of acrylic monomers and formulated in an organic solvent mixture are determined, to a large extent, by the type and amount of the cross-linking agent. Like the molecular mass, cross-linking also influences the bulk properties of the film and builds shear, heat and chemical resistance, while negatively impacting the tack and peel strength. It is necessary to achieve inter-chain cross-linking for heat resistance, as PSA polymers operate in the region above their glass transition temperatures. There, the polymer will readily flow under heat, losing its cohesive strength without cross-links [2].

The aim of this research is to synthesize acrylic PSAs using isosorbide as bio-based cross-linking agent. Optical acrylic binders based on a material with a high refractive index, 2-phenylethyl acrylate (2-PEA),

\* Corresponding author. Lab. of Adhesion & Bio-Composites, Program in Environmental Materials Science, 200-6204, Seoul National University, Seoul, 151-921, Republic of Korea.

E-mail address: [hjokim@snu.ac.kr](mailto:hjokim@snu.ac.kr) (H.-J. Kim).

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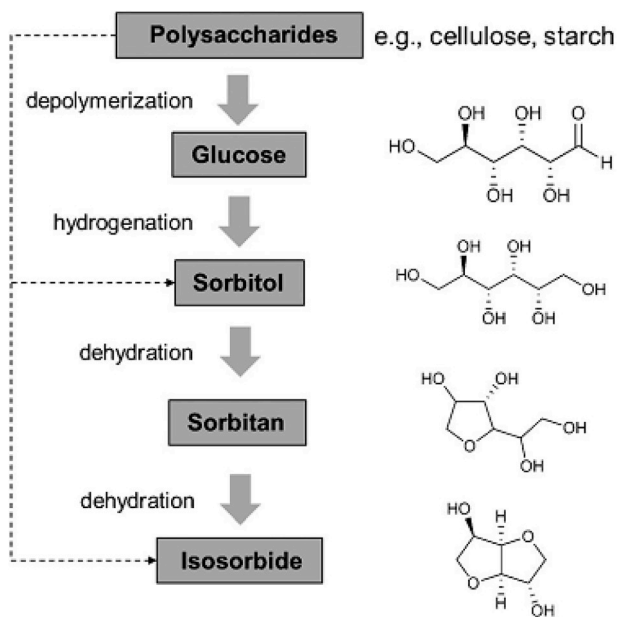


Fig. 1. Schematic reaction pathway for the production of isosorbide from biogenic polysaccharides [8].

were synthesized. Next, isosorbide was blended into the material by means of mechanical force. Various compositions of acrylic PSAs with isosorbide were prepared and their optical properties were measured using a UV–visible spectrometer and a prism coupler. Also, the curing behavior and adhesion performance were examined by assessing the gel fraction and peel strength, and the probe tack, and shear adhesion failure temperature (SAFT). Finally, the relationship between the glass transition temperature ( $T_g$ ) and the concentration of isosorbide as a cross-linking agent was investigated using plots in an effort to control the optimal concentration of isosorbide for optically clear acrylic PSAs.

## 2. Experimental

### 2.1. Materials

Acrylic binders were synthesized using 70 wt% 2-ethylhexyl acrylate (2-EHA, 99.0% purity, Samchun Pure Chemical Co., Ltd., Republic of Korea), 5 wt% acrylic acid (AA, 99.0% purity, Samchun Pure Chemical Co., Ltd., Republic of Korea) and 25 wt% 2-phenoxy ethyl acrylate (2-PEA, 90.0% purity, Tokyo Chemical Industry, Japan). Ethyl acetate was used as an organic solvent at a boiling point temperature of approximately 78 °C. 0.3 wt%. 2,2'-azobisisobutyronitrile (AIBN, Junsei Chemical, Japan) was used as the thermal initiator to start the radical polymerization process. Isosorbide (Dianhydro-D-glucitol, Sigma-Aldrich, USA) was used as the cross-linking agent and butylstannoic acid (FASCAT4100, Arkema Inc., USA) was used as a catalyst. Fig. 2 shows the chemical structure of the bio-based isosorbide, which has two hydroxyl groups which react with the carboxylic groups of acrylic acid.

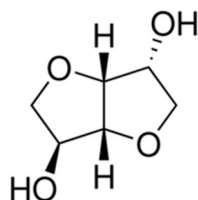


Fig. 2. Structure of the bio-based isosorbide.

### 2.2. Experimental

#### 2.2.1. Synthesis of binders

Acrylic binders were synthesized by means of solution polymerization, resulting in a solid content of approximately 40%. The mixture was placed into a 500 ml four-neck flask which was equipped with a stirrer, a condenser and a thermometer. The mixture was then heated to a temperature of approximately 80 °C with constant stirring. Towards the end of the exothermic reaction, the temperature was maintained for about 1 h, and a blend of ethyl acetate and AIBN was added. The reaction was allowed to proceed for 1 h and for 3 h. Finally, polymerization was terminated by cooling the mixture to room temperature.

#### 2.2.2. Preparation of cured acrylic PSAs

Various composition of acrylic PSAs were prepared by blending the polymerized binders and isosorbide, as shown in Table 1. The mixture was stirred for 30 m using a mechanical stirrer at 50 °C. Butylstannoic acid (FASCAT4100, Arkema Inc., USA) was used as a catalyst to catalyze polymerization and prevent a transesterification reaction during the polymerization. Cured polymers were coated onto the polyester films (PET, 50 $\mu$ m thick, SKC, South Korea) using a bar coater (No. 18, wet thickness: 41.1 $\mu$ m), after which drying took place at 80 °C for 20 min. By blending in isosorbide, the acrylic PSAs could be cross-linked due to the reaction between the two OH groups in the isosorbide and the COOH groups in the synthesized acrylic binders, as shown in Fig. 3.

#### 2.2.3. Optical properties

**2.2.3.1. UV–visible spectroscopy.** UV–visible spectroscopy (Cary 100, Agilent Technologies, USA) was used to examine the transmittance of the cured acrylic PSAs. Bare PET as a control and an acrylic PSA sample which was coated onto the PET film, were placed on the instrument. The transmittance was determined to be in the visible range of 400–700 nm.

**2.2.3.2. Prism coupler.** The refractive index of the acrylic PSAs which were coated onto the PET film was detected using a prism coupler 2010/M (Metricron, USA). For reference, a bare PET film was used. The prism and film were joined and the incidence angle of the laser beam was varied. Therefore, the refractive index in both the thickness and plane directions could be determined.

#### 2.2.4. Gel fraction

The gel fraction can be used to determine the degree of cross-linking. First, the weight of the samples was measured. Then, for 24 h the samples were immersed in toluene at room temperature, after which the insoluble polymers were removed by filtration through a 200 mesh wire net. The samples were then dried at 70 °C until they reached a constant weight. The gel content was calculated using the following equation:

Table 1

Monomer compositions of the acrylic PSAs.

	Binder compositions (wt.%)			Cross-linking agent (phr in the binder)	$T_g$ (°C by DSC)
	2-EHA	AA	2-PEA		
PSA-1	70	5	25	0	-38.4
PSA-2	70	5	25	0.5	-19.5
PSA-3	70	5	25	1	10.2
PSA-4	70	5	25	2	26.8
PSA-5	70	5	25	5	32.4

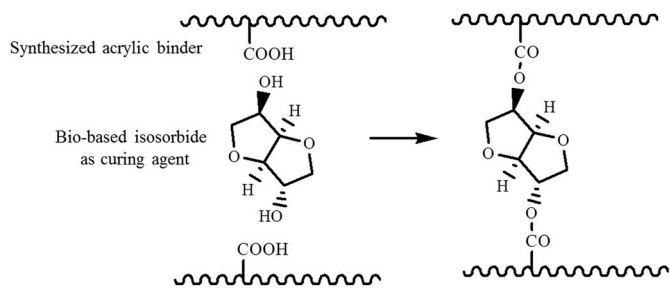


Fig. 3. Scheme of cross-linking between two OH groups in the isosorbide and COOH groups in the synthesized acrylic binders.

$$\text{Gel content (\%)} = W_1 / W_0 \times 100$$

where,  $W_0$  denotes the weight before immersion, and  $W_1$  is the weight after immersion.

### 2.2.5. Adhesion performance

**2.2.5.1. Peel strength.** The peel strength was also measured using a Texture Analyzer. Samples were prepared with widths of 1 in. The specimens were pressed onto the stainless steel substrate by two passes of 2 kg of rubber, after which it was stored for more than 12 h at room temperature. The peel strength was determined at an angle of  $180^\circ$  with a crosshead speed of 300 mm/m at  $20^\circ$  based on ASTM D3330. The peel strength is the average force during the debonding process. For 10 different runs, the force was recorded in GF units. The average force was reported in GF/in.

**2.2.5.2. Probe tack.** The probe tack was measured at room temperature using a Texture Analyzer (Micro Stable Systems, TA-XT2i) with a stainless steel cylinder probe which had a diameter of 5 mm. The standard probe tack test was divided into the following three stages: approach the surface of the PSAs, contact, and detachment from the surface of the PSAs. The speed of the probe while approaching the surface of the PSAs was 0.5 mm/s, the contact time on the PSAs surface was 1 s under a constant force of 100 g/cm<sup>2</sup> and the separation rate was 10 mm/s. During the debonding process, the probe tack was obtained at the maximum debonding force.

**2.2.5.3. Shear adhesion failure temperature (SAFT).** The shear adhesion failure temperature (SAFT) was measured using a sample with a size of 1 x 1 that was attached to a stainless steel substrate by rolling with a 2 kg rubber roller twice. The samples were then stored at room temperature for 24 h. After loading with a 1 kg weight, the samples were held in an oven at a heating rate of 0.4 °C/m until the temperature reached 200 °C. The temperature when shear failure occurred was also recorded.

## 3. Results and discussion

### 3.1. Optical properties

#### 3.1.1. Prism coupler

Optical properties play an important role in optically clear adhesives in relation to industrial applications. They also depend on the brightness as well as the contrast ratio in optical displays [4]. Fig. 4 shows the refractive index of the acrylic PSAs. The influence of different cross-linking densities on the refractive index was noted. The amount of isosorbide as the cross-linking agent corresponds to the refractive index in the visible wavelength. The refractive index was increased slightly by increasing the isosorbide content. In particular, the refractive index of PSA-5 is much higher than that of any other sample due to highly cross-linked structures. This indicates that the glass transition temperature ( $T_g$ ) in the acrylic PSA is very closely related with the refractive index of the polymer, and contrast ratio in display devices would be

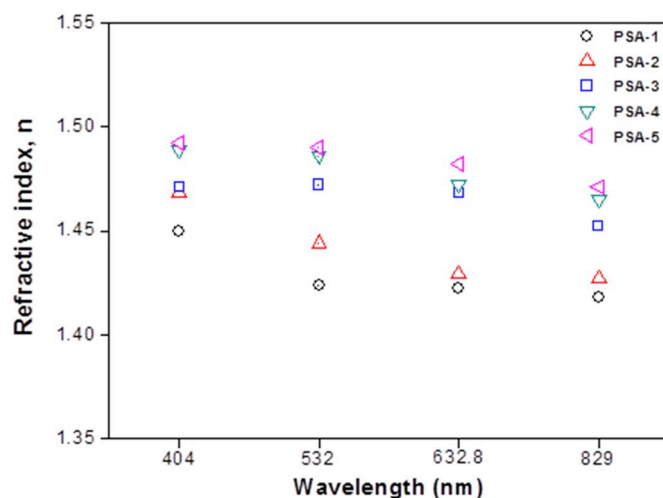


Fig. 4. Refractive index of the synthesized acrylic PSAs.

affected by the glass transition temperature ( $T_g$ ) of the acrylic PSAs.

#### 3.1.2. UV-visible spectroscopy

Fig. 5 shows the transmittance of the acrylic PSAs. As noted earlier, the brightness is most important factor with regard to the optical properties of optically clear PSAs. The transmittance in the visible area can be obtained during the curing process and by determining the cross-linking density [14]. Generally, acrylic PSAs in a display should show high transmittance (>95%) [15]. The transmittance can be increased slightly by increasing the isosorbide contents, indicating that the relationship between the glass transition temperature ( $T_g$ ) of acrylic PSAs and the transmittance can be understood in terms of the cross-linking density.

### 3.2. Gel fraction

The crosslinking efficiency with the cross-linking agents is indirectly measured by the gel fraction. The amount of gel phase that is obtained is defined as the amount of cross-linked molecules both as highly entangled and as coiled polymer molecules. In the latter case, cross-linking occurs only through entanglement. Also, it is not truly a polymeric network, which usually consists of interconnected polymeric molecules [16–19]. The gel fraction increases by increasing the amount of isosorbide as a cross-linking agent, as shown in Fig. 6(a). As noted above,

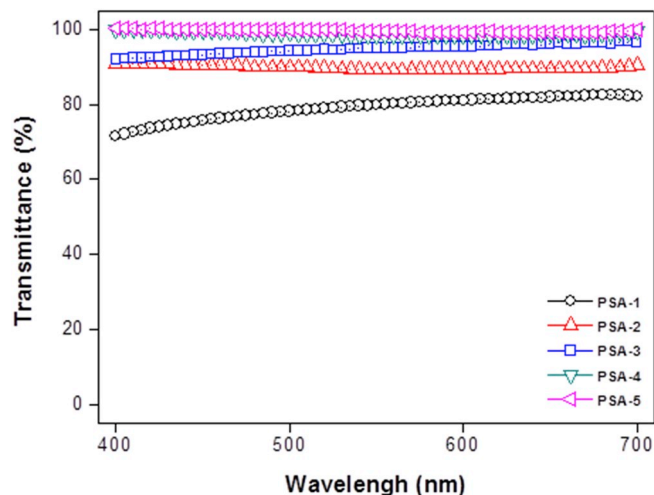


Fig. 5. Transmittance of the synthesized acrylic PSAs.

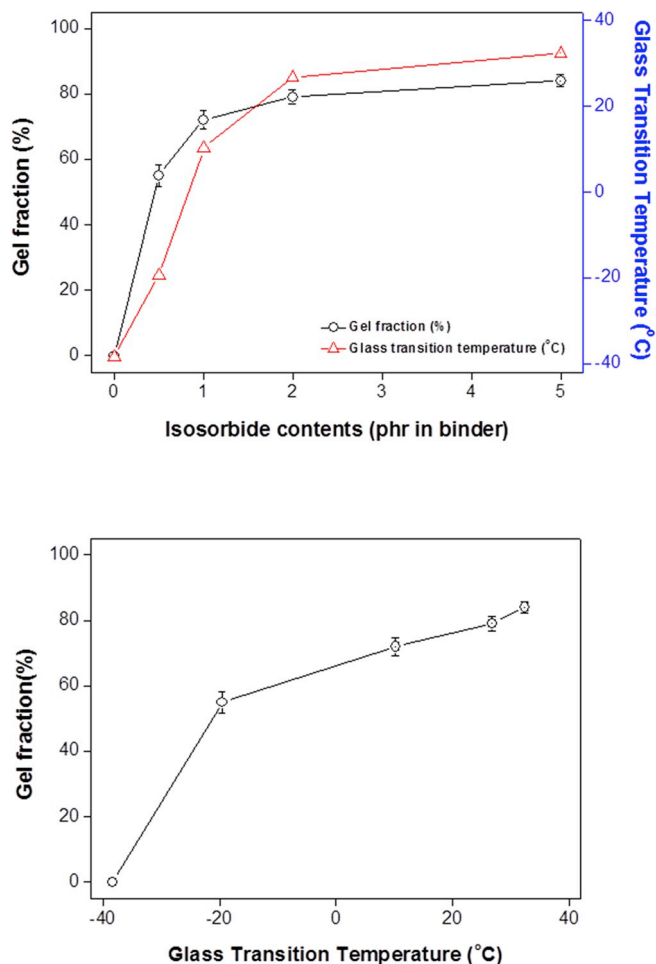


Fig. 6. Gel fraction with different amounts of isosorbide (a) and  $T_g$  (b).

the glass transition temperature of the acrylic PSAs can be increased by increasing the isosorbide content due to the cross-linking density, which clearly affects the gel fraction. Thus, more efficient cross-linking is obtained when using more than 1 phr of isosorbide content as a cross-linking agent. Fig. 6(b) indicates the relationship between the glass transition temperature and the gel fraction. The gel fraction increases rapidly when the glass transition temperature increases from approximately  $-40^\circ\text{C}$  to  $-30^\circ\text{C}$  for the samples, but the slope then slowly increases due to the presence of more activated cross-linking during the initial curing process. Despite this result, it appears that there is a linear relationship between the glass transition temperature and the gel fraction of acrylic PSAs.

### 3.3. Adhesion performance

#### 3.3.1. Peel strength

The relationship between the concentration of isosorbide and the peel strength is measured by a  $180^\circ$  angle peel test at room temperature, as shown in Fig. 7(a). The dependence cannot be attributed to the crystalline aggregate of the long alkyl side group [20]. The peel strength of the acrylic PSAs cross-linked by isosorbide rapidly decreases by increasing the concentration of isosorbide up to 2 phr in the binder, after which it levels off. As noted earlier, the reduced peel strength can be attributed to the increased polymer cross-linking. Cross-linking improves the cohesive strength of the adhesive, which influences the degree of deformation and hence makes easier for debonding process. It is known that the formation of a cross-linked polymer structure affects the peel strength of an adhesive [18,21,22]. With more isosorbide, most

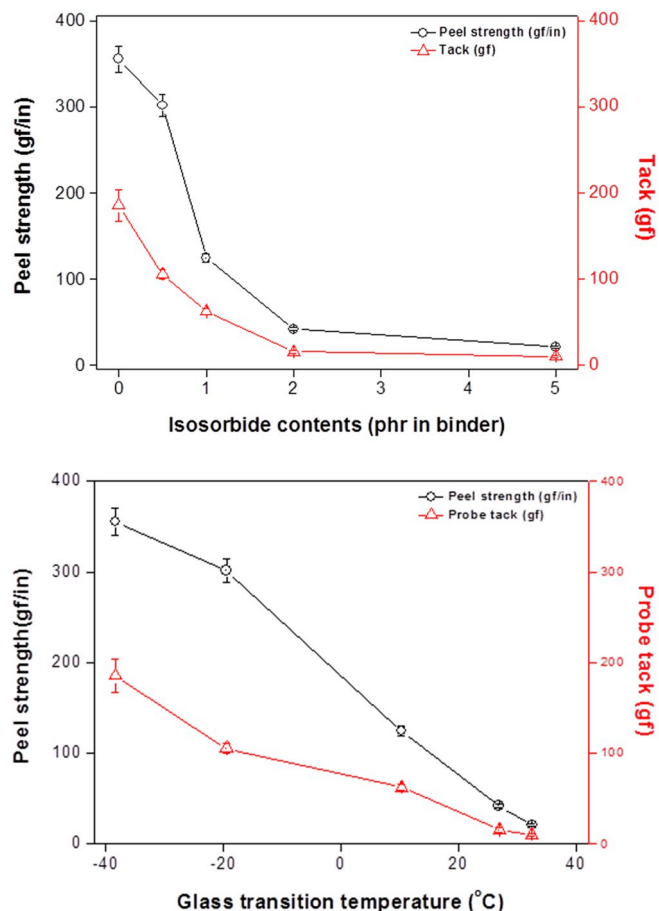


Fig. 7. Peel strength and probe tack with different amounts of isosorbide (a) and  $T_g$  (b).

acrylic PSAs lose their adhesion properties because their rubbery characteristics become glassy with an increase in  $T_g$ , as shown in Fig. 7(b).

#### 3.3.2. Probe tack

The probe tack values against the amounts of the isosorbide are also shown in Fig. 7(a). Tack refers to the initial adhesion performance, meaning the ability to stick to a substrate in a short time and at a low pressure. It is closely related to the degree of polymer mobility. A decrease can be attributed to the presence of cross-linked structures, which limits the optimal wetting characteristics of the stainless steel probe and the contact area between the adhesives and substrates [23]. Accordingly, the tack decreases with a higher concentration of isosorbide, like the peel strength, especially, when as much as 2 phr is used in the binder. Not only the peel strength but also the probe tack clearly has a linear relationship with the glass transition temperature ( $T_g$ ), as shown in Fig. 7(b), due to the polymer mobility.

#### 3.3.3. Shear adhesion failure temperature (SAFT)

The shear adhesion failure temperatures (SAFT) of the acrylics PSAs are shown in Fig. 8(a). As shown in the figure, the shear adhesion failure temperature provides information not only about the cohesion force but also about the thermal resistance against the substrate. In a display, the thermal resistance is considered to be crucial because the device may shut down at a high temperature. Thus, optical acrylic PSAs as a component in a display device must a certain level of thermal resistance. The SAFT increases more sharply up to  $120^\circ\text{C}$  by increasing the concentration of isosorbide, but it levels off when the isosorbide amount exceeds 2 phr. With regard to the relationship between  $T_g$  and the SAFT, the SAFT is gradually increased by increasing  $T_g$ , displaying a linear

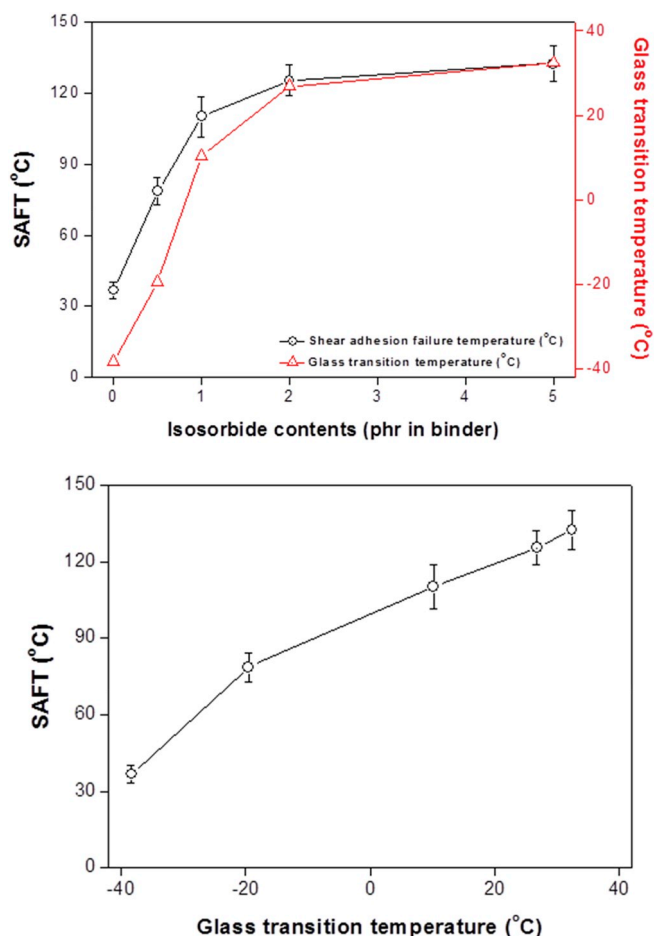


Fig. 8. Shear adhesion failure temperature (SAFT) with different amounts of isororbide (a) and  $T_g$  (b).

relationship as shown in Fig. 8(b).

#### 4. Conclusions

Optical properties, curing behaviors and adhesion performance of

optically clear acrylic PSAs are investigated. Also, the bio-based isororbide is used as cross-linking agent. The emphasis on this study has been investigated on relationship between glass transition temperature ( $T_g$ ) and the concentration of the isororbide in the optical properties, the gel fraction, the adhesion performance, respectively.  $T_g$  is a fundamental property in viscoelastic polymer such as pressure-sensitive adhesives (PSA) and affected cross-linking by an external cross-linking agent. Based on the above results, it can be affordable to determine the optimal concentration of the isororbide as a cross-linking agent. Furthermore, it is helpful to control and handle the optical properties, curing behaviors, and adhesion performance by providing the plots based on the relationship between  $T_g$  and the concentration of the isororbide regarding as an industrial aspect.

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