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# Characterization of self-adhesive structural tapes modified with polyvinyl acetal resins

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## ABSTRACT

Thermally curable self-adhesive structural tapes (SATs) based on epoxy resin/acrylate copolymer composition and modified with three types of polyvinyl acetal resins (i.e. polyvinyl butyral-*stat*-acetal and polyvinyl butyrals) were prepared. The influence of polyvinyl resins addition on reactivity and self-adhesive features of SATs as well as on mechanical resistance of aluminum-SAT-aluminum joints was investigated. It was revealed that polyacetal resin addition (0.5 wt. part/100 wt. parts of adhesive composition) increases the adhesion of SATs to a steel substrate and, moreover, improves the overlap shear strength of thermally cured joints. The type and content of applied polyvinyl acetals influence the enthalpy of the photocrosslinking process, crosslinking degree as well as the epoxy groups conversion of SATs matrix.

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## 1. Introduction

Self-adhesive structural tapes (SATs) are a new type of heavy duty structural adhesives in form of pressure-sensitive adhesive [1]. First SATs were developed in 1998 by 3M Company as structural bonding tapes (SBT) [2–4]. These materials were based on thick self-adhesive opaque films (> 0.5 mm) and exhibited relatively high shear strength after thermal curing. SBT tapes were designed to bond metallic elements in automotive and aircraft industries. Highly transparent epoxy-based thermosetting SATs have been developed by the authors team [1] and were characterized by thickness of 25–100 μm, good adhesion to steel, aluminum and glass, long pot-life at room temperature as well as high shear strength (after curing). Taking into consideration that relatively cheap polyvinyl acetal resins (polyacetals) exhibit high tensile strength, elongation at break, thermal resistance [5] and effectively improve adhesion of organic coatings and liquid adhesive to various substrates [6–8], these polymeric materials were tested as components of the SATs. Generally, hydroxyl functional polyacetals are produced by condensation of polyvinyl alcohol with *n*-butyraldehyde (polyvinyl butyral, PVB) and/or acetaldehyde (e.g. polyvinyl butyral-*stat*-acetal, PVBA) in the presence of an acid catalyst [6,9]. The mentioned hydrophobic polymers are also utilized as crosslinkable binders [6] and surface

shrinkage modifiers for organic compositions [10], but the main application of polyacetals is safety laminated glass production, particularly for automotive, aerospace and architectural purposes [6,11]. This paper presents influence of selected polyvinyl acetal resins (PVB, PVBA) on reactivity (epoxy group conversion, crosslinking degree), self-adhesive (adhesion to steel, cohesion) and mechanical (shear strength) properties of thermally curable pressure-sensitive structural adhesives.

## 2. Experimental

### 2.1. Materials

The following components were used for preparation of an acrylate copolymer for the self-adhesive structural tapes (SATs): *n*-butyl acrylate (BA), glycidyl methacrylate (GMA), 2-hydroxyethyl acrylate (HEA) (BASF, Germany), 4-acryloyloxy benzophenone (ABP; Chemitec, Germany), 2,2'-azobis(isobutyronitrile) (AIBN; Merck, Germany) and ethyl acetate (EA; POCh, Poland) as a solvent. Bisphenol-A type liquid epoxy resin with epoxy equivalent weight ca. 188 g/equiv. and viscosity 12,500 mPa s (Organika-Sarzyna, Poland) was used as an epoxy component of the SATs. Additionally, the Lewis acid adduct (Nacure Super Catalyst A 218; Worleé-Chemie, Germany) and modified polymethylalkylsiloxane (BYK 325; BYK-Chemie, Germany) were applied as latent curing agent and adhesion promoter, respectively. Polyvinyl butyral-*stat*-

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**Table 1**  
Specification of polyvinyl acetals [12].

Name	Symbol	Type	PVOH <sup>c</sup> block content (wt%)	PVAc <sup>d</sup> block content (wt%)	T <sub>g</sub> <sup>e</sup> (°C)	Average molecular weight (g/mole) <sup>f</sup>	Viscosity (mPa s) <sup>g</sup>
Pioloform BL16	P-BL16	PVBA <sup>a</sup>	16.0	2.5	84	20,000	19
Mowital B20 H	M-B20	PVB <sup>b</sup>	19.5	2.5	64	20,000	24
Mowital B30 HH	M-B30	PVB	12.0	2.5	63	30,000	29

<sup>a</sup> Polyvinyl butyral-*stat*-acetal;

<sup>b</sup> Polyvinyl butyral;

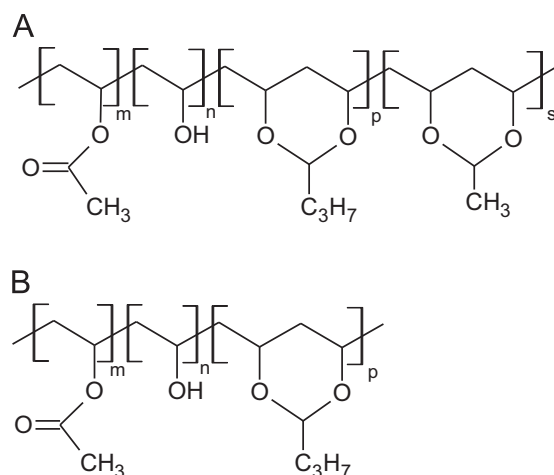
<sup>c</sup> Polyvinyl alcohol;

<sup>d</sup> Poly(vinyl acetate);

<sup>e</sup> Glass transition temperature (DSC technique, ISO 11357-1);

<sup>f</sup> Weight average molecular weight;

<sup>g</sup> For 10 wt% solution of a polyvinyl resin in ethanol/toluene equiweight mixture (20 °C, Brookfield method, 30 rpm).



**Fig. 1.** Chemical structure of tested PVBA (A) and PVB (B).

acetal Pioloform BL16 (P-BL16) as well as polyvinyl butyrals Mowital B20 H (M-B20) and Mowital B30 HH (M-B30) (Kuraray Europe, Germany) were used as polymeric modifiers of the SAT composition. Characteristics and chemical structures of the applied polyvinyl resins are presented in Table 1 and Fig. 1, respectively.

## 2.2. Preparation and characterization of the acrylate copolymer

The acrylate copolymer was synthesized via free radical copolymerization of BA (61 wt%), GMA (25 wt%), HEA (14 wt%) and ABP (1.0 wt%) in EA containing AIBN (0.1 wt. part/100 wt. parts of monomers). The copolymerization process was carried out for 5 h at 78 °C in a glass reactor equipped with a mechanical stirrer and oil bath. Monomers and initiator were applied without their purification.

## 2.3. Preparation of SATs

The structural adhesives tapes were compounded using the acrylate copolymer (50 wt. parts), epoxy resin (50 wt. parts), latent curing agent (1 wt. part) as well as silicone adhesion promoter (0.5 wt. part) and polyvinyl acetal resin (0.1–5.0 wt. parts). The adhesive compositions were applied onto a silicone paper or polyester film (samples for self-adhesive tests), dried for 10 min at 105 °C and then UV-C irradiated using the medium pressure mercury lamp (Hönle UV-Technology, Germany). The UV exposition was controlled with the integrated radiometer (Dynachem 500, Dynachem Corp., USA); a single UV dose was 50 mJ/cm<sup>2</sup>. Base weight and thickness of the UV-photocrosslinked adhesive layers were 120 g/m<sup>2</sup> and 100 μm, respectively. Description of the prepared structural adhesive tapes is shown in Table 2.

## 2.4. Self-adhesive tests of SATs

Self-adhesive properties of the prepared SATs were tested according to AFERA standards (Association des Fabricants Européens de Rubans Auto-Adhésifs), i.e. AFERA 4001 (adhesion to a steel substrate) and AFERA 4012 (cohesion). These parameters were evaluated using three samples of each SAT. Adhesion is defined as a force value required to remove a pressure sensitive material from stainless steel plate; the removal is proceed at the angle of 180° with speed of 300 mm/min [13]. Cohesion (static shear adhesion) describes the time needed to shear off the adhesive tape sample (under load of 1 kg) from defined steel surface.

## 2.5. Thermal analysis of SATs and characterization of prepared joints

Differential scanning calorimeter (DSC Q100, TA Instruments, USA) was used for determination of glass transition temperature ( $T_g$ ) of SATs as well as enthalpy of their curing process ( $\Delta H$ ), onset temperature of curing reaction ( $T_i$ ) and maximum/peak temperature of curing reaction ( $T_p$ ). Standard aluminum DSC pans were used and samples (ca. 10 mg) were analyzed from –90 °C to 300 °C (with heating rate of 10 °C/min). Two DSC measurements for each composition were carried out. The overlap shear strength of aluminum-SAT-aluminum joints, prepared using degreased 2024 aluminum panels (100 × 25 × 2 mm<sup>3</sup>) and cured at 160 °C for 40 min, was measured according to PN-ISO 4587 standard (ten samples of each system) at room temperature by means of Zwick/Roell Z010 machine (Zwick, Germany). Thermally cured SATs were also analyzed with the Fourier transform infrared spectroscopy equipped with attenuated total reflectance (ATR) accessories (Nexus FT-IR, Thermo Nicolet, USA); variation of absorbance values at 915 cm<sup>-1</sup> (oxirane groups) had been recorded and epoxy groups conversion (EGC) was calculated according to the equation [14]:

$$EGC = \left(1 - \frac{A(t)}{A(0)}\right) \cdot 100 (\%) \quad (1)$$

where:  $A(0)$  – the initial intensity of the peak at 915 cm<sup>-1</sup>;  $A(t)$  – the intensity of the peak at 915 cm<sup>-1</sup> after thermal curing. The mentioned peaks were normalized in relation to the reference peaks at 1182 cm<sup>-1</sup> (C–O–Ar bonds of bisphenol glycidyl ethers [15]).

Additionally, the crosslinking degree ( $\alpha$ ) of thermally cured SATs was calculated using DSC data according to the following equation [16]:

$$\alpha = \left(\frac{\Delta H_T - \Delta H_{res}}{\Delta H_T}\right) \quad (2)$$

where:  $\Delta H_T$  – total enthalpy of SAT curing process (J/g);  $\Delta H_{res}$  – enthalpy of post-curing process of the thermally cured SAT (in Al-SAT-Al joint).

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