



Unique adhesive properties of pressure sensitive adhesives from plant oils



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ABSTRACT

We report novel insights into the adhesive performance of bio-based pressure sensitive adhesives (PSAs). Three different homopolymers based on renewable fatty acid methyl esters were characterized in terms of their mechanical and adhesive properties. The polymers display the typical dependence of adhesive properties on molecular weight and degree of crosslinking, as quantified by shear modulus, tack and peel measurements. The absolute values of characteristic adhesion parameters are in the range of commercially available petrochemical PSAs. Curing of applied PSA films at elevated temperature results in a pronounced maximum in tack and peel strength at a critical curing time, which corresponds to a change from cohesive to adhesive failure. Thus, demand-oriented tailoring of adhesive properties can be achieved via an appropriate choice of curing time. Moreover, these bio-based adhesives offer improved adhesion on hydrophobic substrates and high water-resistance without any whitening, thus rendering them an attractive alternative to conventional petroleum-based products. These peculiar features are attributed to the high hydrophobicity of the used monomers.

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1. Introduction

Renewable feedstocks that have the potential to replace fossil resources in industrial production processes receive increasing attention in research and technology. The diversity in renewable feedstock offers a vast number of opportunities for industrial applications, since potential renewable materials are capable of fulfilling highly challenging tasks. Especially plant oils bear a large potential for the substitution of currently used petrochemicals [1–5]. Within this contribution, we focus on adhesives obtained from plant oils. Generally, the demand of adhesives has increased more than 25% over the last 10 years and they play an important role in industrial applications and consumer products [6]. In particular, the increasing demand of pressure sensitive adhesives (PSAs) has contributed to this strong growth.

A PSA is a polymeric system that allows an instantaneous adhesion to a variety of surfaces within short contact time and low contact pressure without any phase transition or chemical reaction due to its specific viscoelastic properties [7]. Major materials used in PSA formulation are natural rubber, petroleum-based styrene-butadiene-styrene (SBS), polyisobutylene (PIB), nitrile rubber

(NBR), polyurethanes, and polyacrylates. Polyacrylates are widely used due to their good stability over a large temperature range, high flexibility and good resistance towards degradation. Commonly used acrylate monomers are *n*-butyl acrylate, methyl acrylate, or 2-ethylhexyl acrylate, usually copolymerized to tune the adhesive behavior by controlling the glass transition temperature T_g . Common PSAs are specifically formulated to achieve optimum tack as well as peel strength and can be tailored in a wide range according to the desired application. A high cohesion is needed to sustain loads and to enable a clean removal. However, a sufficiently low viscosity is required to wet the surface of the substrate and to create an intimate contact. These conflicting demands are balanced adjusting T_g and molecular weight distribution, as well as degree of crosslinking and branching of the respective copolymers [8–14]. The nature of the substrate, including its roughness and its polarity, i.e. surface energy, is another crucial factor [15–18]. Generally, PSAs stick very well to polar substrates such as steel, glass or aluminum. The adhesive itself has usually a lower free surface energy than the adherend [19]. Especially polyethylene, polypropylene and other commonly used polyolefins exhibit a similarly low surface energy and adhesion of PSAs to such substrates is still a challenge. Furthermore, PSA formulation addresses environmental resistance including the design of special compositions with resistance to humidity or water [20]. Water resistance of polymers depends on their polarity and structure. Usually, water-insoluble, solvent-based adhesives

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are used for water-resistant applications. It can be benchmarked as the change in adhesion after a 24 h immersion in water by performing a peel strength test [21]. The water resistance of dispersion-based PSAs is strongly affected by their water-soluble additives [22], e.g. the type of surfactant used as stabilizer [23]. In general, PSAs suffer water whitening and loss of transparency of the PSA film after immersion.

Triglycerides and polyols derived from vegetable and/or animal fats and oils, along with lactides and lactones (derived from carbohydrates), have been used to synthesize renewable PSAs [1,24]. Ongoing research not only addresses the replacement of petrochemical adhesives by products from renewable resources, but also the development of materials with improved adhesive performance. Moreover, copolymer networks of epoxidized soybean oil (ESO) with lactic acid oligomers for pressure-sensitive adhesives have been discussed recently [25]. In addition, hydroxyl-containing polyesters were obtained via step-growth polymerization of epoxidized oleic acid and showed adequate adhesion but low molecular weights [26]. Wool et al. developed PSAs from acrylated methyl oleate using emulsion and miniemulsion polymerization techniques [27,28]. In addition, copolymerization with both methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) was shown to improve PSA performance [29]. Sun et al. explored a concept for novel bio-based PSAs derived from soybean oil with the aim to raise thermal stability, transparency, and peel strength for use in opto-electronic applications [30]. A solvent-free PSA based on acrylated ESO was prepared via UV initiated free-radical polymerization, resulting in a high shear strength product [31].

Here, we report a detailed evaluation of bio-based pressure sensitive adhesives regarding control of cohesion and adhesion. Adhesion to low energy substrates and resistance to water uptake are especially addressed. This is based on an application relevant characterization of the synthesized polymers in terms of their viscoelastic and adhesive properties. Monomers were obtained from vegetable oil derived fatty acids and proceeded via a one-step, a two-step or a three-step synthesis route [32–34]. These monomers were polymerized *via* free radical polymerization in bulk resulting in high molecular weight polymers with sticky, adhesive behavior, as recently described [35].

Adhesive properties of the synthesized homopolymers were investigated performing small amplitude oscillatory shear, tack and peel tests on samples with different molecular weight and degree of crosslinking. The influence of the substrate type and the resistance to water uptake was also addressed. The described polymers generally show PSA performance similar to common industrial standards. The balance of adhesive and cohesive properties can be tailored in a wide range by curing the applied polymer films at elevated temperature. Promising results regarding adhesion to low energy substrates and high resistance to water uptake were obtained.

2. Experimental section

2.1. Materials

Polymers were prepared as described above [35]. Their structure is given in Fig. 1.

2.2. Methods

The experimental set-up used for the tack measurements has been thoroughly described previously [17]. It is based on a commercial device Texture Analyzer TA.XTplus (Stable Micro Systems, UK) modified with a quartz force sensor (Kistler Instruments,

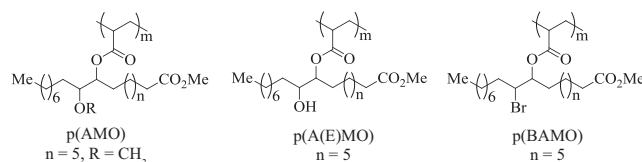


Fig. 1. Chemical structure of synthesized polymers based on methyl oleate.

GmbH, Germany) covering a force range of ± 500 N with a threshold of 1 mN. The Texture Analyzer TA.XTplus was also equipped with a high-speed camera KL MB-Kit 1M1 (Mikrotron GmbH, Germany) used in combination with a zoom objective 90° KL-Z6 and a cold light source KL3000B. The camera was attached under an adjustable vacuum table, where a transparent glass plate with the coated sample was positioned in order to take images of the contact area during contact formation and debonding (see Fig. 2).

The camera allowed to record 124 frames/s at maximum resolution of 1280×1024 pixels. The true contact area was obtained in each test by analyzing the images using Visiometrics Image Processing System (IPS) software, developed by Prof. Dr. Stephan Naser (University Darmstadt). Tack tests were performed at 21 °C using three different cylindrical punch substrates, steel probes with average roughness $R_a=3$ nm and 41 nm as well as a polyethylene (PE) probe with $R_a=45$ nm. The probe velocity for bonding was set to 1 mm/s, a contact force of 10 N was selected and a contact time of 1.0 s was chosen. Detachment followed at a release rate of 1.0 mm/s. The work of adhesion W_{adh} , often also termed tack, was calculated using the area under the nominal stress vs. strain curve as described by Peykova et. al. [17].

For peel tests, a 90° peel device (FINAT No. 2) was used in combination with the TA.XTplus Analyzer. In each test, a 15 mm wide carrier foil (coated with the given polymer) was peeled at a constant speed of 4.0 mm/s from a fixed glass plate in a 90° angle. The peel force was determined as the average force value obtained during a debonding length of 80 mm.

Storage and loss moduli (G' , G'') were determined using a Physica MCR-501 (Anton Paar, Austria, Graz) equipped with a plate/plate fixture (diameter $d=8.0$ mm, gap height $h=1$ mm). Moduli were measured at a given frequency of 1.0 Hz and a deformation of $\gamma=0.01$ at temperatures ranging from -30 °C to 150 °C with a heating rate of 5 K/min.

2.2.1. Preparation of polymer test samples

Adhesive polymer films were prepared with an average film thickness of 50 ± 5 μm for tack tests and 15 ± 2 μm for peel tests.

For tack experiments, this was achieved by coating a polymer methyl ethyl ketone (MEK) solution (60–80% solid content) onto a glass slide using doctor blades with a defined gap size (0.075–0.15 mm) mounted onto an automatic film applicator ZAA 2300 (Zehntner GmbH, Switzerland). The coating speed of the film applicator was kept constant at 20 mm/s. Gap size and/or polymer concentration were varied to reach the desired polymer film thickness. Freshly prepared films were first stored at room temperature overnight, followed by treatment at 120 °C for 1.5 h to remove the remaining solvent and to achieve a smooth polymer surface.

For peel tests, a 36 μm etched PET foil (provided by tesa SE) was coated with each polymer solution (60–80% solid content) using a doctor blade at constant coating speed of 10 mm/s to gain a film thickness of 15 ± 2 μm . The prepared polymer films were directly dried at 120 °C for 1 h. The prepared samples were cut to a width of 15 mm. Prior to any measurement, each sample was cooled down to room temperature (21 °C). Each polymer film was then

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