



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,

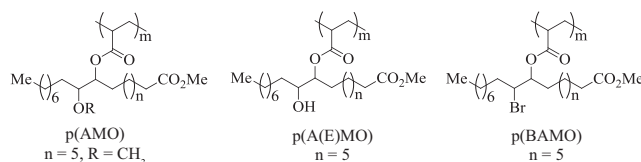


Fig. 1. Chemical structure of synthesized polymers based on methyl oleate.

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

attached to a glass plate using a 2 kg weight in 8–10 runs within a contact formation time of 4 min.

3. Results and discussion

The adhesive properties of a pressure sensitive adhesive are determined by various intrinsic bulk parameters such as polymer composition, average molecular weight (M_w), dispersity (\mathcal{D}), and crosslink density. Furthermore, substrate properties such as surface energy or roughness (R_a , defined as the average deviation from the mean surface plane: $R_a = \frac{1}{N} \sum_{n=1}^N |Z_n - Z|$), as well as external parameters such as humidity or temperature play an important role. Here, we will discuss the effect of polymer composition, molecular weight and degree of crosslinking on rheological and adhesive properties. The degree of crosslinking was varied upon storage of the ready-to-test films for different periods of time at 120 °C. Furthermore, first results regarding adhesion to low energy substrates and resistance to water uptake will be presented.

3.1. Influence of molecular weight on tack and peel

Tack and 90° peel tests were performed on p(AMO) homopolymers (see Fig. 1) of different molecular weight. The obtained results are shown in Fig. 3.

Note that, due to limited synthesis capacity, tack and peel experiments could not be performed with the same samples, instead different batches had to be used. The M_w values of the

samples used in tack experiments varied between 66 kDa and 690 kDa, those for the peel test samples between 370 kDa and 1180 kDa. Fig. 3 also includes the respective dispersity values \mathcal{D} , indicating that all samples had a broad molecular weight distribution as typical for free radical polymerization.

As expected, the work of adhesion W_{adh} as well as the peel strength strongly increase with increasing M_w . Similar results have been observed for various petro-chemical PSA polymers and this phenomenon is attributed to the increasing number of entanglements per chain [36–38].

Cavitation is a phenomenon well known to occur during the debonding step in tack experiments. The images of the polymer layer, taken at the maximum point of stress during debonding, clearly show that the number of cavities strongly increases from 34 to 51 and 93 with increasing M_w (Fig. 3a). This is in line with earlier findings for conventional polyacrylates [17] and a consequence of an increasing fraction of the substrate surface not wetted by the polymer during contact formation due to increased viscosity. In all these experiments, cohesive failure occurred indicating that these polymers exhibit a low degree of crosslinking or long-chain branching (gel content determined to <2%) [35].

3.2. Tailoring adhesion behavior via curing

The synthesized polymers are not crosslinked and almost completely soluble. Thus, they can be easily applied via solvent casting or slot-die coating. Curing of the already coated thin polymer layers results in crosslinking reactions and, depending on curing time, this can result in a non-soluble gel-like, but highly swellable material. This processing step can be used to tune the

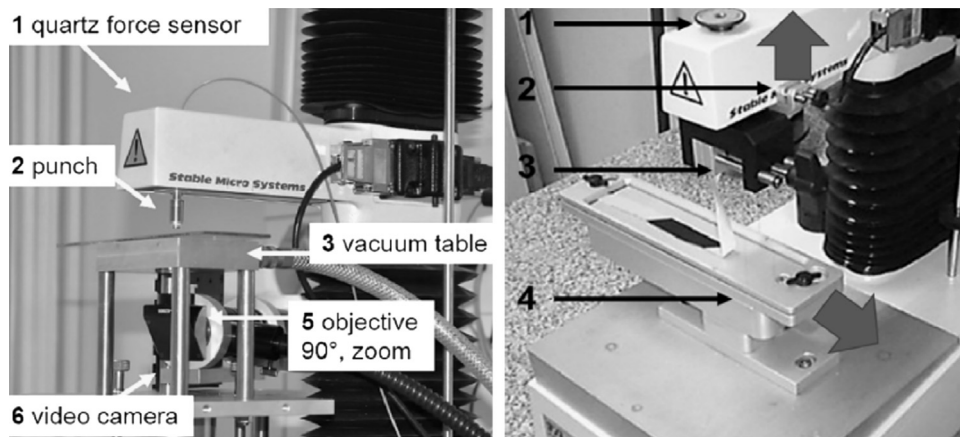


Fig. 2. Experimental set-up. Left: Tack measurements with video-optical observation: 1-quartz force sensor; 2-punch (probe/substrate); 3-vacuum table; 4-charge amplifier; 5-objective (90°); 6-video camera. Right: for peel measurements: 1-standard force sensor with calibration platform; 2-wire clamp; 3-strip holder/clamp; 4-slide table.

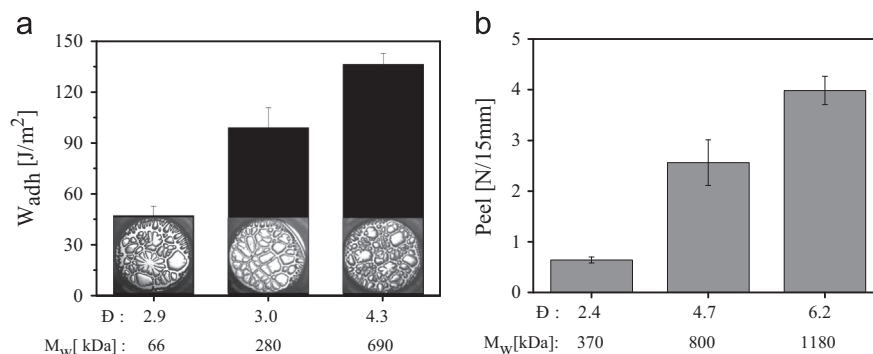


Fig. 3. Work of adhesion (a) and peel strength (b) of p(AMO) homopolymers with different average molecular weight M_w and dispersity \mathcal{D} . Tack experiments were performed using a steel probe with $R_a = 3$ nm, 1 mm/s debonding velocity and 1 s bonding time. Peel tests were performed on glass plates at a debonding velocity of 4 mm/s.

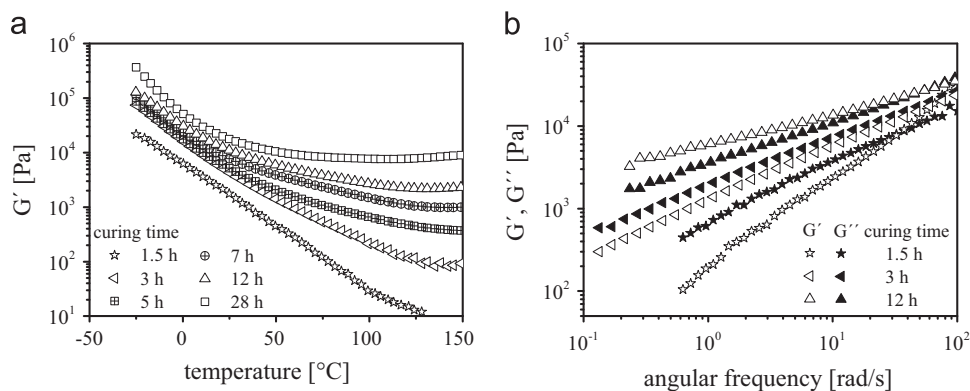


Fig. 4. Storage and loss modulus data of cured p(AMO) ($M_w=280$ kDa, $D=3$) by means of oscillatory shear measurements. (a) G' as function of temperature at different curing times measured at 1 Hz frequency and 0.01 strain. (b) G' and G'' as function of angular frequency measured at 20 °C.

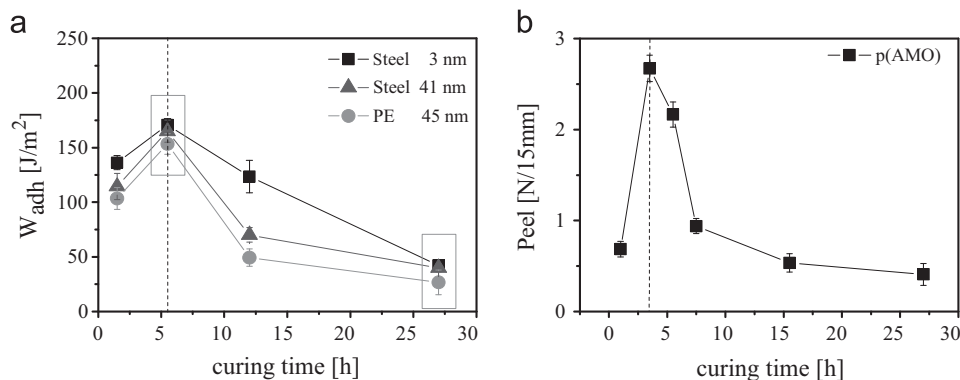


Fig. 5. Tack performance (a) and peel strength (b) of cured p(AMO) ($M_w=690$ kDa, $D=4.3$) on varying substrate types.

viscoelastic and adhesive properties of the polymer in a wide range according to the demanded specifications in different applications. The effect of curing on linear viscoelastic and adhesive behavior has been investigated for different homopolymers synthesized using monomers deduced from fatty acid methyl ester based on native sunflower oil.

3.2.1. Effect of curing on shear modulus

The effect of curing on shear modulus $G^* = G' + iG''$ of p(AMO) is shown in Fig. 4. In Fig. 4a, the storage modulus G' determined after different times of curing is plotted as a function of the temperature, data were taken at a fixed frequency of $f=1$ Hz.

The modulus G' increases with increasing curing time and in the high temperature range ($T > 100$ °C) it reaches more than 1000-fold its initial value after 28 h of heat treatment. The modulus of the samples with short curing time steadily decreases with increasing temperature. After 5 h of curing, G' levels off at a constant value at temperatures $T > 100$ °C indicating the formation of a sample spanning network of crosslinks. Further curing then results in an increasing crosslink density as indicated by the higher level of G' in the high temperature range.

Fig. 4b displays the dependence of G' and G'' on frequency for three different curing times. After 1.5 h of heat treatment, G'' is still much higher than G' in the low frequency regime ($2\pi f = \omega < 10$ rad/s) and a crossover of G' and G'' occurs around $\omega = 40$ rad/s. This behavior is typical for flexible, non-crosslinked polymers. After 3 h of curing, G' and G'' are almost equal in their absolute values and exhibit a similar frequency dependence over an extended frequency range of more than three orders of magnitude. This is typical for the so-called sol–gel transition when the formation of a sample spanning network sets in [39]. For curing times larger than this critical value, G' exceeds G'' and reaches a

constant level at frequencies below $\omega = 0.1$ rad/s corresponding to the high temperature plateau value shown in Fig. 4a as expected for crosslinked, gel-like or rubbery materials.

3.2.2. Effect of curing on tack and peel

The effect of curing time on adhesion properties has been investigated for p(AMO), p(A(E)MO) and p(BAMO) homopolymers (see Fig. 1). Tack and peel strength data for p(AMO) obtained after different curing times are shown in Fig. 5. The work of adhesion, W_{adh} , in tack experiments was determined using different steel and PE probes. Peel tests were performed on a glass substrate.

Both tack and peel strength exhibit a pronounced maximum at a curing time of about 5 h, just above the sol–gel transition, and decrease monotonically for longer periods of heat treatment. Moreover, this maximum marks the transition from cohesive to adhesive failure. Representative images of the respective substrate surface visualizing the different debonding characteristics in tack as well as peel experiments are shown in Fig. 6

Tack and peel strength data for p(A(E)MO) and p(BAMO) homopolymers are shown in Fig. 7.

The p(A(E)MO) exhibits similar behavior as p(AMO) (c.f. Fig. 5) and a maximum in W_{adh} and peel strength is observed for a curing time of about 5 h, which again is accompanied by the transition from cohesive to adhesive failure.

In contrast, W_{adh} as well as peel strength remain constant within the experimental error irrespective of curing time for p(BAMO). Moreover, cohesive failure is observed for all p(BAMO) samples in tack as well as in peel experiments. Obviously, no or only little crosslinking takes place during curing. We attribute this to the bromo functionality of this polymer, which can act as retarder reducing the number of free radicals and thus suppressing

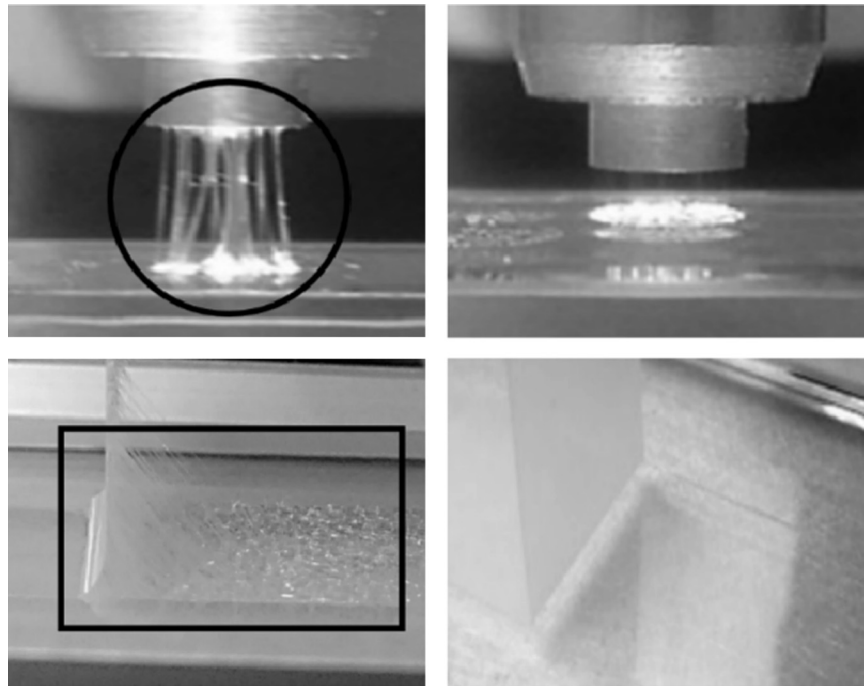


Fig. 6. Cohesive (left) and adhesive failure (right) in tack and peel measurements of cured p(AMO) ($M_w=690$ kDa, $D=4.3$) cured for 1.5 h (left) and 27.5 h (right).

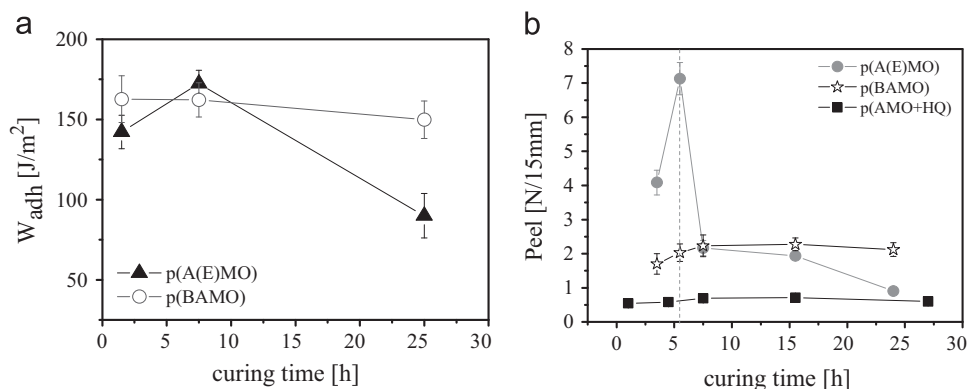


Fig. 7. Tack values (a) and peel strength (b) of cured p(A(E)MO) ($M_w=290$ kDa, $D=2.2$) and cured p(BAMO) ($M_w=250$ kDa, $D=3.5$). Tack tests were done using a steel probe with $R_a=41$ nm. Peel tests were also performed for a mixture of p(AMO)+HQ ($M_w=550$ kDa, $D=5.1$).

gel formation. This hypothesis is further supported by the peel results obtained for p(AMO) with added hydroquinone (HQ 1 w%) as radical quencher shown in Fig. 7b together with data for p(A(E)MO) and p(BAMO). While p(A(E)MO) exhibits a pronounced maximum similar to the one observed in the tack experiments, the peel strength of p(BAMO) and p(AMO+HQ) remain on a low level independent of curing time and failure is always cohesive, indicating that crosslinking is suppressed. During heat treatment, radicals may be formed from remaining initiator and/or monomer. HQ is known to serve as a polymerization inhibitor, able to prevent occurring radical crosslinking reactions [40,41]. The results thus strongly suggest that the observed curing proceeds via a radical mechanism.

3.3. Adhesion to low energy substrates

Early studies on the adhesion of model PSAs to low energy surfaces date back to the 1970 s [42]. Recently, the interest in this topic recurred and in the majority of cases two types of substrates were investigated, namely stainless steel and polyolefins, such as PE [43,44]. Accordingly, the tack of the highly hydrophobic

homopolymer p(AMO) as well as the copolymer p(AMO/MMA) on steel (surface energy $\gamma=43$ mJ/m²) and PE ($\gamma=30$ mJ/m²) substrates of similar roughness was investigated and compared to conventional petroleum-based PSAs. First, the linear viscoelastic properties of the investigated polymers are discussed. Fig. 8 displays the storage modulus G' as a function of temperature for the investigated samples, namely a commercial acrylate copolymer from emulsion polymerization (Acronal V212) widely used in PSA applications, a linear p(BA/MMA) copolymer synthesized in solution polymerization ($M_w=192$ kDa, $D=6.4$) [17] and two homopolymers p(AMO) with $M_w=280$ kDa and $D=3$ differing in curing time, as well as a non-cured copolymer composed of AMO and methyl methacrylate (MMA) with a molar ratio of 80:20 ($M_w=341$ kDa, $D=2.0$).

The cured p(AMO) polymers clearly exhibit a plateau in G' at temperatures $T > 100$ °C as already mentioned. The sample cured for 27 h shows absolute modulus values close to that of Acronal V212 throughout the investigated temperature range. In contrast, the modulus of the non-crosslinked p(AMO/MMA) copolymer decreases monotonically with increasing temperature, but the absolute values are similar to that of p(AMO) homopolymer cured

for 5.5 h and are about two orders of magnitude lower than that of the Acronal V212 and the long cured p(AMO) in the high temperature range ($T > 100\text{ }^\circ\text{C}$). The solution polymerized p(BA/MA) exhibits a temperature dependence similar to that of the non-cured p(AMO/MMA).

In order to get a first insight into the adhesive performance of hydrophobic plant-oil based PSAs on low energy substrates, we have compared the adhesion to a PE probe with a surface roughness of $R_a = 45\text{ nm}$ and to a steel probe with similar roughness of $R_a = 41\text{ nm}$. Fig. 9 shows the ratio of the resulting work of adhesion W_{adh} values obtained on PE and steel for the samples described above. Tack data for the solution-based copolymer were taken from Peykova et al. [45] obtained at a debonding velocity of only 0.1 mm/s but otherwise similar test conditions. Adhesive failure was observed in all cases, except for the p(BA/MA).

Fig. 9 clearly demonstrates that the reduction in W_{adh} on the surface of the PE compared to the steel probe is much less pronounced for the p(AMO) polymers than for the commercial acrylate adhesives from emulsion and solution polymerization. The p(BA/MA) exhibits at tack ratio of about 0.5 and for the Acronal V212 it is close to 0.3. The latter very low ratio may be attributed to the surfactants included in this emulsion polymer generally known to deteriorate adhesion. The weakly or not crosslinked

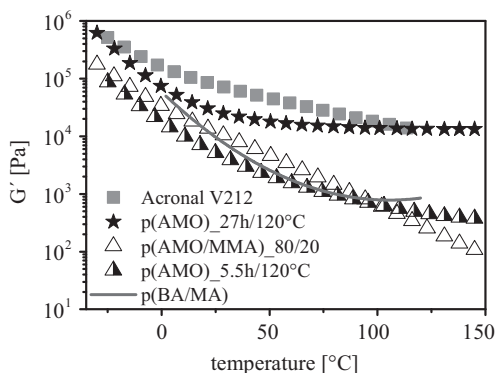


Fig. 8. Storage modulus as a function of temperature at 1 Hz and 0.01 strain for a model copolymer dispersion Acronal V212 compared to a synthesized cured homopolymer p(AMO) ($M_w = 280\text{ kDa}$, $D = 3$) and a non-cured copolymer p(AMO-MMA) in a molar ratio of 80/20 ($M_w = 341\text{ kDa}$, $D = 2.0$). Values for p(BA/MA) calculated from $G'(w)$ data shown in Peykova et al. [17].

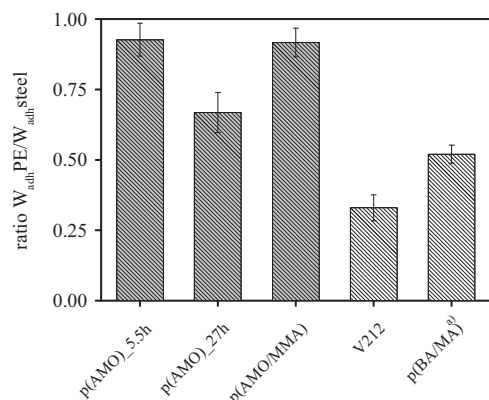


Fig. 9. Ratio of W_{adh} measured on PE ($R_a = 45\text{ nm}$) and on steel ($R_a = 41\text{ nm}$) of a cured homopolymer p(AMO) 5.5 h and p(AMO) 27 h ($M_w = 690\text{ kDa}$, $D = 4$) and a non-cured copolymer p(AMO-MMA) in a molar ratio of 80/20 ($M_w = 341\text{ kDa}$, $D = 2.0$) compared to acrylate copolymer dispersion Acronal V212 and model solution-based copolymer p(BA/MA) ($M_w = 192\text{ kDa}$, $D = 6.4$) at a debonding velocity of 1 mm/s. ^{a)}Tack data of copolymer p(BA/MA) taken from Peykova et al. [45]. Note that respective measurements were performed at a debonding velocity of only 0.1 mm/s.

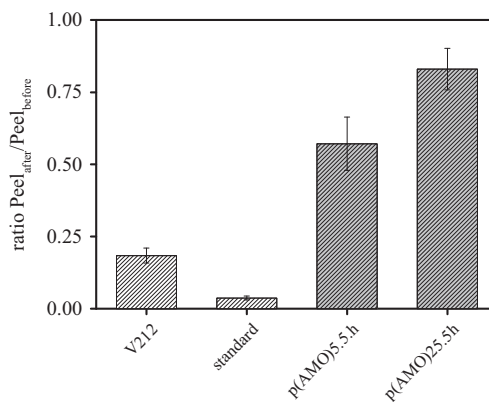


Fig. 10. Remaining peel strength after 24 h water immersion of acrylate copolymer Acronal V212, a standard office tape (tesa SE product) and cured p(AMO) after 5.5 h and 25.5 h of curing time ($M_w = 480\text{ kDa}$, $D = 4$).

hydrophobic p(AMO) and p(AMO/MMA) show tack ratios between 0.9 and 1.0, demonstrating their high potential for adhesion applications on low energy substrates. A tack ratio of about 2/3 is found for the densely crosslinked p(AMO). This may be attributed to the poor wetting of the rough low energy substrate.

3.4. Water resistance

Performance of PSAs under conditions of high humidity or in an aqueous environment is another feature of significant technical relevance. In general, the adhesive properties of dispersion-based PSAs suffer from contact with water due to the presence of hydrophilic components such as co-monomers or surfactants needed in the emulsion polymerization process. In order to get a first insight into the behavior of plant oil based PSAs from solution polymerization we have compared the loss of peel strength after immersion in water for 24 h for a commercial acrylate type office tape (tesa SE), the Acronal V212 from emulsion polymerization and two p(AMO) homopolymers differing in curing time. Corresponding data are shown in Fig. 10.

Obviously, the reduction in peel strength is much less pronounced for the p(AMO) polymers than for the commercial acrylate adhesives, the latter loose more than 80% of their original peel strength, while the p(AMO) retains about 3/4 of their initial strength even after 24 h storage in water. The strong loss in adhesion of the Acronal V212 comes along with a strong moisture-whitening, which itself is an important quality attribute, especially for consumer applications. In contrast, the p(AMO) polymers remain absolutely clear even after this extended immersion in water.

We attribute these findings to the pronounced hydrophobicity of the AMO monomer (solubility in water $< 10^{-7}$) [28,46]. This is typical for monomers deduced from plant oils and demonstrates the high potential of corresponding PSAs for such generally challenging applications.

4. Conclusions

Plant derived homopolymers and a copolymer were characterized in terms of their viscoelastic and adhesive properties. It was shown that p(AMO) as well as p(A(E)MO) homopolymers are easily tunable in their viscoelastic and adhesive performance by curing at an elevated temperature due to crosslinking and network formation. At a critical curing time tack as well as peel strength exhibit a pronounced maximum and debonding changes from cohesive to adhesive failure. Accordingly, adhesive properties can

be adjusted in a wide range meeting the demands of different PSA applications. Beyond that, the p(AMO) polymers show improved adhesion to low energy substrates as well as a good water resistance without any whitening effect, thereby demonstrating an attractive alternative with superior adhesion performance compared to common petroleum based PSAs. These specific features are attributed to the highly hydrophobic nature of the base monomer.

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