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2 **Nonlinear Oscillatory Shear Tests of Pressure Sensitive Adhesives (PSA) Designed for Transdermal Therapeutic**  
3 **Systems (TTS)**  
4

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16 **Abstract**

17 Transdermal Therapeutic Systems (TTS) based on pressure sensitive adhesives (PSA) allow for application of pharmaceutical  
18 substances via diffusion through the skin. Rheological performance of PSA is largely investigated within small amplitude  
19 oscillatory shear (typically up to 1 %), although the skin motions exceed strains beyond 40 %. In this paper, amine  
20 compatible (AC) and non-amine compatible (NAC) silicone based PSA compounds differing in the resin content were  
21 subjected to strain amplitude sweeps in a twin drive rheometer. Carreau-Yasuda-like fitting of storage and loss moduli curves  
22 intercept the substantial effect of resin content on both compounds; up to four-times higher moduli of AC compounds were  
23 determined in SAOS, and their higher molecular mass combined with enhanced interactions contributed to an earlier  
24 transition to nonlinear viscoelastic region. In the nonlinear range, elastic and viscous properties are affected by strains in a  
25 different manner with the trend favorable for the PSA application as TTS. The third relative higher harmonic from Fourier  
26 transformation  $I_{3/1}$  as well as intra-cycle strain stiffening and shear thickening ratios provide information relevant for an  
27 optimization of PSA subjected to large deformations.

28 **Keywords:** pressure sensitive adhesive; transdermal therapeutic system; viscoelastic behavior; non-linear coefficient; strain  
29 stiffening; shear thickening

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## 1 1. INTRODUCTION

2 Transdermal therapeutic systems (TTS) are patches which are used for medical treatments of e.g. Alzheimer's disease, severe  
3 pain and hormone therapy. They are applied directly on human skin and consist of a protective backing layer, an adhesive  
4 layer made of pressure sensitive adhesives (PSA) containing active pharmaceutical ingredients and a release liner.  
5 Application times vary from one to seven days (Minghetti et al. 2004, Schalaus et al. 2018). Their main purpose is to provide a  
6 continuous low concentrated flux of active medical ingredients through the human skin what requires good adhesion of the  
7 TTS during the application time (Venkatraman and Gale 1998).

8 PSAs are based on soft polymers (e.g. polyisobutylene, acrylates, silicones and their mixtures) ensuring a certain degree of  
9 contact and adhesion to human skin even under low pressure (Minghetti et al. 2004, Satas 1989). This short term and low  
10 contact pressure adhesion behavior is evaluated through a "tack" measurements such as rolling ball tack test, rotating drum  
11 tack test or toothed wheel tack test (Satas 1989). In the medical research, the standardized loop tack tests and probe tack tests  
12 are well established short term test methods for PSA/TTS. The long term adhesion behavior, relevant if the patches have to be  
13 removed from the skin after the application time, is determined by standardized (ISO 29863, ISO 29862) shear resistance and  
14 adhesion strength measurements under angles of either 90° or 180°. All above described methods were originally developed  
15 for technical bonding purposes mostly for metal substrates. Thus, these tests provide only limited information about the  
16 adhesion behavior of PSA/TTS on human skin (Schalaus et al. 2018, Venkatraman and Gale 1998), especially for a quality  
17 assurance as well as research and development to monitor changes of the PSA/TTS adhesion during application. In order to  
18 characterize the viscoelastic behavior, standardized oscillatory rheological measurements are carried out using small  
19 deformation amplitudes intercepting Small Amplitude Oscillatory Shear (SAOS) region.

20 Coblas et al. (2016) employed the frequency dependent moduli to correlate structural and performance properties of  
21 polydimethylsiloxane. Sweet and Ulmann (1997) and Chang (1997) correlated the PSA performance under shear and bonding  
22 conditions to frequency dependent rheological data in the range 0.01 and 0.1 rad/s, while debonding and peel were correlated  
23 to the frequencies around 100 rad/s, and tack behavior was correlated to frequencies between 1 and 10 rad/s.

24 Dahlquist (1969) proposed a criterion for adhesive properties and connected it to the storage modulus  $G'$  of 300 kPa. PSA  
25 moduli exceeding this value mean that the adhesive behaves contact-deficient, whereas below this value the adhesive is  
26 contact-efficient. Chang (1997) proposed another criterion, where storage and loss moduli ranging from  $10^3$  to  $10^6$  Pa are  
27 related to frequencies of 0.1 (bonding) and 100 rad/s (debonding) allowing for the classification of the PSA adhesion  
28 behavior in solid non-adhesive, high shear, removable and viscous state.

29 Silicone based PSA for medical applications usually consists of a mixture of viscous polymer and solid-like resin  
30 component, being slightly cross-linked via a polycondensation reaction in a "bodying process" (Schalaus et al. 2018, Benedek  
31 and Feldstein 2009, Merrill and Spa 1977, Cray et al. 2011). Structural correlations were achieved by analyzing PSA with  
32 different cross-linking densities in terms of frequency dependent storage modulus  $G'$  and loss modulus  $G''$  (Ho and Dodou  
33 2007, Schalaus et al. 2018). Webster (1997) found that higher cross-linking densities are more favorable due to a certain  
34 degree of cohesion which causes lower adhesion and rather trauma-less removal from human skin. Benedek and Feldstein  
35 (2009) and Lin et al. (2007) confirmed that the cross-linker concentration influences significantly the properties of a silicone  
36 based PSA. Rheological investigations in oscillatory shear show a viscous behavior of weakly cross-linked PSA with  $G' <$   
37  $G''$  (loss angle  $\tan(\delta) > 1$ ). Increasing resin contents leads to a gel or a solid-like behavior with  $G' > G''$  ( $\tan(\delta) < 1$ ) (Schalaus

1 et al. 2018, Cray et al. 2011, Benedek and Feldstein 2009, Merrill and Spa 1977, Webster 1997, Lin et al. 2007, Mezger  
2 2012).

3 Ho and Dodou (2007) found the limit of linear viscoelastic behavior of BIO-PSA<sup>®</sup> materials at the strain amplitude of  
4 2.5 %, which is often used for TTS. However, skin motions of daily life are exceeding strains beyond 40 % for knee motions,  
5 25 % for forearm motions and 15 % for shoulder (Wessendorf and Newman 2012, Maiti et al. 2016, Ge et al. 2017). Thus, a  
6 patch is subjected to strains being significantly beyond the SAOS region. This means that the nonlinear viscoelastic behavior  
7 of TTS is crucial for its performance during application.

8 Öhrlund (2018) showed that the deformation behavior of various cross-linked hyaluronic acid gels depends on the  
9 stretching capability of the molecular network. Hyun et al. (2006) correlated the deformation behavior of hard gels in the  
10 nonlinear region to the destruction of the layer interactions and the breakdown of initial microstructures. Other researchers  
11 (Khandavalli and Rothstein 2015, Du et al. 2018, Aliabadian et al. 2018, Kamkar 2020, Kádár et al. 2020) reported about  
12 interconnected filler networks or shear induced gelation at medium amplitudes being destroyed by higher amplitudes ( $\gamma_0 < 10$   
13 %) and resulting in oriented polymer chains and slippage of the particles or stretching of the network junctions, respectively.  
14 Nevertheless, a systematic study using oscillatory shear measurements of PSA/TTS from small strain amplitudes (< 0.1 %) to  
15 large strain amplitudes (10 % to 100 %) to characterize their deformation behavior under typical application conditions has  
16 not been performed yet. This study is focused on this aim for silicone-based amine PSA as well as non-amine compatible  
17 PSA having different resin concentrations. To the best of our knowledge this is the first time nonlinear rheological  
18 investigation of slightly cross-linked PSAs is reported. Thus, this survey can lead to a better insight into the microstructure  
19 and deformation related behavior, which might be used for TTS optimization as well as indications for other slightly cross-  
20 linked PSAs and rubbery systems. Furthermore, this study might lead to a new framework to characterize adhesives  
21 performance.

## 22 2. MATERIALS AND METHODS

### 23 2.1. Materials

24 The two Amine-Compatible (AC) PSA, BIO PSA 7-4301 (high tack) and BIO PSA 7-4201 (medium tack) were blended to  
25 get five compounds having different volume resin contents ( $v_F$ ), and the two Non-Amine-Compatible (NAC) PSA, BIO-PSA  
26 7-4601 (high tack) and BIO PSA 7-4501 (medium tack) were blended to get three compounds having different resin contents.  
27 The four base polymers were supplied by DuPont and Dow Health Care Solutions (2016) and their chemical structure is  
28 shown in Fig. 1.

29 The eight compounds were manufactured in a coating box to form adhesive layers with a thickness of  $(150 \pm 15)$   $\mu\text{m}$   
30 between two release liners, Table 1. From the adhesive layers, four strips having a width of 20 mm were stacked to achieve a  
31 sample thickness around 600  $\mu\text{m}$ . Storage for minimum 12 hours at room temperature ensured molecular interpenetration  
32 between the layers.  
33  
34  
35  
36  
37

1 **Table 1:** Composition and thickness of PSA samples used

Amine compatible (AC)			Non-amine compatible (NAC)			Thicknesses of the samples	
ratio BIO PSA 4201:4301	Weight content (%)	Volume content (%)	ratio BIO PSA 4501:4601	Weight content (%)	Volume content (%)	AC ( $\mu\text{m}$ )	NAC ( $\mu\text{m}$ )
100:0	60.00	54.2	100:0	60.00	54.2	570	560
75:25	58.75	52.9	-	-	-	590	-
50:50	57.50	51.6	50:50	57.50	51.6	610	570
25:75	56.25	50.4	-	-	-	570	-
0:100	55.00	49.1	0:100	55.00	49.1	590	570

2

3 **2.2. Methods**

4 Rotational rheometer (MCR702 TwinDrive<sup>®</sup>, Anton Paar, Austria) was used to investigate the viscoelastic behavior of the  
 5 AC and NAC compounds. It was configured in the separate motor-transducer (strain-controlled) mode and equipped with a  
 6 convection oven (CTD450TD). Samples of 15 mm diameter and height of (590 $\pm$ 20)  $\mu\text{m}$  were taken out of the stripes together  
 7 with the release liners, and measured in a plate-plate geometry of 15 mm diameter. They were put on the upper plate of the  
 8 rheometer by removing the release liners, heated to 30  $^{\circ}\text{C}$  for 5 minutes to equilibrate temperature. The axial compression  
 9 force of 5 N was applied for 15 s to establish good contact without air bubbles. Prior to the start of the measurement the force  
 10 was removed, and the samples were allowed to relax for 600 s (compounds with  $\nu_F = 49.1$  and 50.4 %) or 900 s (higher  
 11 concentrated compounds). The measurements were performed using frequencies of 0.6, 1, 2 and 4 rad/s with at least 3 cycles  
 12 for each measured data point.

13

14 **2.3. Data evaluation**

15 In the SAOS region, a sinusoidal strain input excitation,  $\gamma(t) = \gamma_0 \sin(\omega t)$ , leads to a sinusoidal shear stress output  
 16 response,  $\sigma_{12} = \sigma_0 \sin(\omega t + \delta)$ , with phase shift  $\delta$ , strain amplitude  $\gamma_0$ , angular frequency  $\omega$  and shear stress amplitude  $\sigma_0$ ,  
 17 Fig. 2. The corresponding shear rate is  $\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t)$  with shear rate amplitude  $\dot{\gamma}_0 = \gamma_0 \omega$  (Barnes et al. 1989). With  
 18 increasing strain amplitudes a softening is expected which is to be described by an adapted Carreau-Yasuda-like fit for both  
 19 storage and loss moduli [similar to the Q-parameter fits in Lim et al. \(2013\) and Kádár et al. \(2020\)](#):

20 
$$G'(\gamma_0) = G'_0 \left(1 + (C_1 \gamma_0)^{C_2}\right)^{\frac{(C_3-1)}{C_2}} = G'_0 \left(1 + \left(\frac{\gamma_0}{\gamma_{0c}}\right)^{C_2}\right)^{\frac{(C_3-1)}{C_2}} \quad (1)$$

21

22 
$$G''(\gamma_0) = G''_0 \left(1 + (C_1 \gamma_0)^{C_2}\right)^{\frac{(C_3-1)}{C_2}} = G''_0 \left(1 + \left(\frac{\gamma_0}{\gamma_{0c}}\right)^{C_2}\right)^{\frac{(C_3-1)}{C_2}} \quad (2)$$

23

24 with storage modulus  $G'$  and loss modulus  $G''$  at the given strain amplitude  $\gamma_0$ .  $G'_0$  and  $G''_0$  are the initial storage and loss  
 25 moduli at low strain amplitudes, and correspond to those of SAOS measurements. The fitting parameter  $C_l$  represents the  
 26 gradual transition from the linear to the nonlinear viscoelastic region [also reported by Stadler et al. \(2008\) and related to the](#)

1 start of chain disentanglement for a similar Carreau-Yasuda-like model.  $C_2$  stands for the transition factor range of strain  
 2 amplitudes from the end of linear behavior to the beginning of the strain amplitude dependent decrease determined by  $C_3$ ,  
 3 which defines the strain amplitude dependency of  $G'$  and  $G''$  in the nonlinear range. It should be noted that from linear  
 4 viscoelastic point of view, the range of the linear viscoelastic regime is limited to the region where  $G'_0$  and  $G''_0$  are  
 5 independent of the strain amplitude  $\gamma_0$ , the angular frequency  $\omega$ , and therefore  $\gamma_{0c} < \frac{1}{C_1}$ . Stadler et al. (2008) correlated the  
 6 transition zone factor  $C_2$  to the polymer composition. A broad transition zone was connected to preferably branched  
 7 molecules and a narrow transition zone to linear molecules. Furthermore, the slope in the non-linear regime  $C_3$  was connected  
 8 to the disentanglement processes of the network.

9 The data were evaluated by Fourier transformation providing Fourier intensities of higher order if nonlinear behavior  
 10 occurs (Van Duschotten and Wilhelm 2001, Hyun et al. 2011, Ewoldt et al. 2008). In the SAOS region, the Fourier spectrum  
 11 consists only of the fundamental intensity  $I_1$  indicating that the imposed sinusoidal strain generates also a sinusoidal stress  
 12 response, Fig. 2. In the Medium Amplitude Oscillatory Shear (MAOS) and Large Amplitude Oscillatory Shear (LAOS)  
 13 regions the stress response is non-sinusoidal due to non-zero higher Fourier intensities (Cziep et al. 2016), Fig. 2. A basic  
 14 measure for the nonlinear behavior is therefore the ratio  $I_{3/1}$  of the 3<sup>rd</sup> harmonic  $I_3$  to the fundamental  $I_1$ , as the third  
 15 harmonic intensity contains the dominant nonlinear contribution in the spectra.

16 In the linear viscoelastic region, the ratio  $I_{3/1}$  is determined by the instrument noise generally shown as a scattered  
 17 decrease with increasing strain amplitude, generally following a scaling of  $I_{3/1} \propto \gamma_0^{-1}$ . This decrease is followed by an  
 18 increase of  $I_{3/1}$  (Kempf et al. 2013). As FT rheology provides increased S/N (signal/noise) ratios (Van Duschotten and  
 19 Wilhelm 2001), it is generally expected that nonlinearities would be detected at lower strain amplitudes than could be  
 20 evidenced from linear viscoelastic data. The section with increasing  $I_{3/1}$  shows often a quadratic scaling,  $I_{3/1} \propto \gamma_0^2$ , being  
 21 typical for the MAOS region (Hyun et al. 2011, Kempf et al. 2013, Hyun and Wilhelm 2009). This quadratic dependence can  
 22 be inferred theoretically considering the similitude between the Taylor series expansion of the shear viscosity and the  
 23 corresponding Fourier series, combined with symmetry arguments (Hyun and Wilhelm 2009). However, rather recently, this  
 24 has been shown not to be a universal scaling for numerous examples of material systems exhibiting non-quadratic scaling  
 25 behavior (Natalia et al. 2020), including polymer melts (Hyun et al. 2007) and filled polymer systems (Gaska and Kádár  
 26 2019, Kádár et al. 2017, 2020). It should be noted that based solely on  $I_{3/1}$  for non-quadratic scaling cases, it is rather  
 27 difficult to ascertain the noise-MAOS transition. For the cases described by Cziep et al. (2016), Kempf et al. (2013), Hyun  
 28 and Wilhelm (2009) and Song et al. (2017) the quadratic scaling of  $I_{3/1}$  in the MAOS region, Fig. 3, was defined by the  
 29 nonlinear coefficient  $Q(\gamma_0)$  as a measure for nonlinear behavior which achieves a plateau value there:

$$30 \quad Q(\gamma_0) = \frac{I_{3/1}(\gamma_0)}{\gamma_0^2} \underset{MAOS}{\cong} Q_0 \quad (3)$$

31 In the SAOS region,  $Q(\gamma_0)$  shows tremendous scatter, Fig. 3, due to the fact that both numerator and denominator are  
 32 small quantities. Deviations from the quadratic scaling for larger strain amplitudes indicate the transition to the LAOS region,  
 33 Fig. 3.

34 For strain amplitudes above the instrumentation noise range, the nonlinear coefficient  $Q(\gamma_0)$  was fitted analogous to Lim  
 35 et al. (2013) and Kádár et al. (2020) using a sigmoidal equation similar to the Carreau-Yasuda-like model:

$$Q(\gamma_0) = Q_0(1 + (C_1\gamma_0)^{C_2})^{\frac{(C_3-1)}{C_2}} = Q_0\left(1 + \left(\frac{\gamma_0}{\gamma_{0C}}\right)^{C_2}\right)^{\frac{(C_3-1)}{C_2}} \quad (4)$$

with the initial nonlinear coefficient  $Q_0$  and the fitting parameters  $C_1$ ,  $C_2$  and  $C_3$ . Eq. 4 can be approximated for strain amplitudes  $\gamma_0 \geq 2.5 \gamma_{0C}$  by:

$$Q(\gamma_0) = Q_0 (C_1\gamma_0)^{(C_3-1)} = Q_0 \left(\frac{\gamma_0}{\gamma_{0C}}\right)^{(C_3-1)} \quad (5)$$

with an error less than 5 %. At these strain amplitudes the decrease of  $Q(\gamma_0)$  is only determined by the parameter  $C_3$ .

The strain dependent shear stress response signal can be represented in both elastic and viscous Lissajous-Bowditch (LB) diagrams, respectively, Fig. 4. For evaluation purposes one must distinguish between inter-cycle material behavior which reveals changes of material behavior due to the cycle number and increasing strain amplitudes (e.g.  $G'$  and  $G''$ ), and intra-cycle material behavior which describes material changes within a single oscillation (Rogers 2012). Thus, the intra-cycle nonlinear behavior can be used to quantify the nonlinear strain amplitude dependent behavior by defining elastic and viscous nonlinearity quantities (Ewold et al. 2008, Ewold and Bharadwaj 2013):

$$\text{Zero-strain modulus} \quad G'_M(\gamma) = \left. \frac{d\sigma}{d\gamma} \right|_{\gamma=0} \quad (6)$$

$$\text{Maximum-strain modulus} \quad G'_L(\gamma) = \left. \frac{\sigma}{\gamma} \right|_{\gamma=\pm\gamma_0} \quad (7)$$

$$\text{Zero-rate dynamic viscosity} \quad \eta'_M(\dot{\gamma}) = \left. \frac{d\sigma}{d\dot{\gamma}} \right|_{\dot{\gamma}=0} \quad (8)$$

$$\text{Maximum-rate dynamic viscosity} \quad \eta'_L(\dot{\gamma}) = \left. \frac{\sigma}{\dot{\gamma}} \right|_{\dot{\gamma}=\pm\dot{\gamma}_0} \quad (9)$$

where  $\sigma(t)$  is the time dependent shear stress response,  $\gamma(t)$  the time dependent strain,  $\gamma_0$  the strain amplitude,  $\dot{\gamma}(t)$  the time dependent shear rate and  $\dot{\gamma}_0$  the shear rate amplitude.

Ewoldt et al. (2008) used the quantities of Eqs. 6 to 9 to define characterizing ratios for the MAOS and LAOS regions:

$$\text{Strain stiffening ratio} \quad S(\gamma_0) \equiv \frac{G'_L(\gamma_0) - G'_M(0)}{G'_L(\gamma_0)} \quad (10)$$

$$\text{Shear thickening ratio} \quad T(\gamma_0) \equiv \frac{\eta'_L(\dot{\gamma}_0) - \eta'_M(0)}{\eta'_L(\dot{\gamma}_0)} \quad (11)$$

$S > 0$  indicates intra-cycle strain stiffening behavior and  $S < 0$  intra-cycle strain softening behavior,  $T > 0$  indicates intra-cycle shear thickening behavior and  $T < 0$  intra-cycle shear thinning behavior. If  $S = 0$  and  $T = 0$  the material behaves linearly.

### 3. RESULTS AND DISCUSSION

The fitting of the strain sweep tests with the Carreau-Yasuda-like model works fairly well for  $G'$  and  $G''$  with small standard deviations. Reasonable descriptions of the presented dynamic moduli are achieved, Fig. 5, although the curves for

1  $v_F = 49.1$  % flatten at the highest strain amplitudes due to other nonlinear contributions. The comparison of AC and NAC  
 2 compounds shows that AC compounds have higher moduli for the same volume content and that both transform from a  
 3 viscoelastic solid-like behavior ( $G' > G''$ ) to a viscoelastic liquid-like behavior ( $G' < G''$ ) in the range of the investigated  
 4 resin contents. Resin content dependent gel behavior ( $G' \approx G''$ ) is found around  $v_F = 51.6$  % at a frequency of 2 rad/s for the  
 5 AC compound and  $v_F = 54.2$  % at a frequency of 1 rad/s for the NAC compound. In the nonlinear region the decrease of  $G'$   
 6 is more pronounced than the decrease of  $G''$  for all resin contents and frequencies, Fig. 5. According to the rheological  
 7 interpretation of Sim et al. (2003), all curves of AC and NAC can be classified as Type I, representing a decreasing behavior  
 8 of  $G'$  and  $G''$  which is commonly reported for polymer melts or solutions.

9 The Carreau-Yasuda-like fitting of  $G'$  and  $G''$  curves shows that the resin content has tremendous effect on the properties  
 10 of both compounds (see Online Resource). For the AC compounds:

- 11 •  $G'_0$  values between  $v_F = 54.2$  % and  $49.1$  % decrease a factor 35 at a frequency of 0.6 rad/s and a factor 20 at a  
 12 frequency of 4 rad/s
- 13 •  $G''_0$  values between  $v_F = 54.2$  % and  $49.1$  % decrease a factor 13 at a frequency of 0.6 rad/s and a factor 7 at a  
 14 frequency of 4 rad/s
- 15 •  $\gamma_{0C}$  values increase a factor 3 to 4 for decreasing resin contents and decrease 10 % to 20 % within the frequency range  
 16 0.6 to 4 rad/s. Furthermore, the  $\gamma_{0C}$  values determined from  $G''$  curves exceed those from  $G'$  curves a factor 1.7  
 17 typically
- 18 •  $\frac{G'(\gamma_0)}{G'_0}$  ratios increase from  $0.70 \pm 0.04$  for  $v_F = 54.2$  % to  $0.88 \pm 0.03$  for  $v_F = 49.1$  % but do not depend on frequency
- 19 •  $\frac{G''(\gamma_0)}{G''_0}$  ratios increase from  $0.80 \pm 0.04$  for  $v_F = 54.2$  % to  $0.87 \pm 0.03$  for  $v_F = 49.1$  % but do not depend on frequency
- 20 • parameters  $C_2$  are close to “2” with slightly larger mean values for  $G'$  ( $C_2 = 2.14 \pm 0.19$ ) than  
 21 for  $G''$  ( $C_2 = 2.03 \pm 0.16$ )
- 22 • parameters  $C_3$  range from -0.2 to 0.7 for  $G'$  and from 0.2 to 0.7 for  $G''$ . They are smaller than “1” what affirms  
 23 decreasing moduli in the range of nonlinear behavior. The  $C_3$  values increase with decreasing resin content, and there  
 24 seems to be slight decrease for increasing frequencies. According to Stadler et al. (2008) this indicates that PSAs with  
 25 lower resin contents disentangle easier than PSAs with higher resin contents.

26 For the NAC compounds:

- 27 •  $G'_0$  values between  $v_F = 54.2$  % and  $49.1$  % decrease a factor 18 at a frequency of 0.6 rad/s and a factor 15 at a  
 28 frequency of 4 rad/s
- 29 •  $G''_0$  values between  $v_F = 54.2$  % and  $49.1$  % decrease a factor 16 at a frequency of 0.6 rad/s and a factor 10 at a  
 30 frequency of 4 rad/s
- 31 •  $\gamma_{0C}$  values increase a factor of roughly 20 but partly with large standard deviations for decreasing resin contents.  
 32 Furthermore, in the frequency range 0.6 to 4 rad/s the  $\gamma_{0C}$  values decrease more than 30% for  $v_F = 54.2$  % to less than  
 33 10% for  $v_F = 49.1$  %. The  $\gamma_{0C}$  values determined from  $G''$  curves still exceed those from  $G'$  curves a factor 1.3 for  
 34  $v_F = 54.2$  % and  $49.1$  %, respectively, but becomes almost “1” for  $v_F = 51.6$  %
- 35 •  $\frac{G'(\gamma_0)}{G'_0}$  ratios increase from  $0.73 \pm 0.02$  for  $v_F = 54.2$  % to  $0.89 \pm 0.04$  for  $v_F = 49.1$  % and do not depend on frequency

- 1 •  $\frac{G''(\gamma_0)}{G''_0}$  ratios increase from  $0.81 \pm 0.01$  for  $\nu_F=54.2\%$  to  $0.90 \pm 0.04$  for  $\nu_F=49.1\%$  and do not depend on frequency
- 2 • parameters  $C_2$  are close to “2” with slightly larger mean values for  $G'$  ( $C_2 = 1.88 \pm 0.14$ ) than for  $G''$  ( $C_2 = 1.92 \pm$   
3  $0.18$ ).
- 4 • parameters  $C_3$  range from 0.0 to 0.7 for  $G'$  and from 0.4 to 0.8 for  $G''$  what affirms decreasing moduli in the range of  
5 nonlinear behavior. The  $C_3$  values increase with decreasing resin content, and there seems to be a slight decrease for  
6 increasing frequencies. The  $C_3$  values of the NAC compounds exceed the  $C_3$  values of the AC compounds for all given  
7 resin contents.

8 Depending on frequency, storage and loss moduli of the AC compounds are twice to four-times higher than those of the  
9 NAC compounds. This difference can be attributed to higher interactions as the -OH end groups of the NAC compounds were  
10 substituted by -CH<sub>3</sub> end groups of the AC compounds during polycondensation, which increases their molecular mass, and as  
11 a consequence it might affect a chain length. The larger end groups may also form steric hindrances if the polymer chains are  
12 strained. Hyun et al. (2006) explained the drop of moduli of a hard gel in MAOS as the result of the destruction of physical  
13 layer interactions and the breakdown of microstructure, whereas Öhrlund (2018) explained the same behavior of a hyaluronic  
14 acid gel in MAOS as the result of a straining of a covalently crosslinked molecular network.

15 The smaller interaction forces combined with lower molecular mass of the NAC compounds reduce internal frictions and  
16 lead to an increased linear viscoelastic range in  $G'$  and  $G''$  to higher strain amplitudes for identical resin contents. The resin  
17 content mainly determines the crosslinking density of the compounds and as a consequence the range of strain amplitudes in  
18 which linear viscoelastic behavior can occur. The large increase of storage and loss moduli as well as the large decrease of  
19 critical strains with increasing resin contents show that both AC and NAC compounds have their gel points and/or glass  
20 transitions between  $\nu_F=49.1\%$  and  $54.2\%$ .

21 The fitting parameter  $C_2$  is a measure of the strain amplitude range in which linear deformation behavior turns into a  
22 nonlinear one. The  $C_2$  means over the fits of AC compounds and NAC compounds, respectively, are close to “2” with respect  
23 to the standard deviations. This is surprising as it is comparable to the  $C_2$  values which were defined in the original Bird-  
24 Carreau model to describe the shear rate dependent melt viscosity of polymers (Osswald and Menges 2012). However, the  
25  $C_2$  means of the AC compounds exceed slightly those of the NAC compounds indicating that  $C_2$  is sensitive to the chemically  
26 modified interactions of the polymer chains and the corresponding internal cohesions of the compounds. This is in  
27 accordance with Carreau-Yasuda fits of shear rate dependent viscosities showing that the  $C_2$  values also vary for different  
28 polymers due to effects of molecular weight and chain conformation (García-Franco 2013) or due to effects of polymer filler  
29 interactions (Zare et al. 2019). Furthermore, according to Stadler et al. (2008) the lower mean values of  $C_2$  for NAC show that  
30 this PSA has a broader transition zone leading to the assumption that NAC molecules may have a higher degree of branching  
31 than AC. Due to the aforementioned further polycondensation step for AC, a more internal coherent molecule due to higher  
32 amounts of cross-links and molecular masses is expected, which could lead to a less branched PSA. We note, however, that  
33 sigmoidal Carreau-Yasuda-like fits are purely empirical.

34 The fitting parameters  $C_3$  is a measure of the strain amplitude dependent softening of  $G'$  and  $G''$  if  $C_3 < 1$ . The closer the  
35  $C_3$  values approach to “1”, the less pronounced is the softening behavior. Thus, lower resin contents lead to a more elastic  
36 behavior and larger  $C_3$  values. This can only be understood in terms rubber elasticity as both AC and NAC compounds  
37 become more liquid or gel-like with decreasing resin content. Interestingly, the range of  $C_3$  values determined by  $G'$  is double



1 that of  $G''$ . Furthermore, the strain amplitude dependent  $G'$  and  $G''$  functions of all AC and NAC compounds with  $G'_0 > G''_0$   
2 exhibit crossover points located between the strain amplitudes  $\gamma_{0C}(G')$  and  $\gamma_{0C}(G'')$ , respectively, Fig. 5. This indicates that  
3 the inter-cycle softening in the nonlinear range affects the elastic behavior stronger than the viscous one.

4 Disregarding the possibility of a non-quadratic scaling behavior in  $I_{3/1}$ , the nonlinear coefficient  $Q(\gamma_0)$  can be fitted using  
5 Eq.4 (see [Online Resource](#)). For strain amplitudes  $\gamma_0 > \gamma_{0C}$  the nonlinear coefficients  $Q(\gamma_0)$  decrease for all compounds with  
6 strain amplitude  $\gamma_0$ . This decrease is unexpected as according to Hyun et al. (2013) and Hyun and Wilhelm (2009), the  
7 nonlinear coefficient  $Q(\gamma_0)$  is to reflect a nonlinear mechanical material property, and therefore it should increase with strain  
8 amplitude. The nonlinear coefficient  $Q(\gamma_0)$  also increases strongly with resin content indicating that higher resin contents  
9 enhance the nonlinear viscoelastic behavior.

10 The fitting parameters of the AC compounds differ significantly from those of the NAC compounds (see [Online Resource](#)).  
11 For the AC compounds:

- 12 •  $Q_0$  parameters decrease with decreasing resin content. However, this decrease is frequency dependent; by a factor of 50  
13 for  $\omega = 0.6$  rad/s and a factor of 1.2 for  $\omega = 4$  rad/s
- 14 •  $C_1$  parameters decrease with decreasing resin content but this decrease is not very pronounced if standard deviations are  
15 taken into account. Correspondingly the  $\gamma_{0C}$  values increase with decreasing resin content but this increase is less  
16 pronounced compared to the  $\gamma_{0C}$  values determined from  $G'$  and  $G''$  fits
- 17 •  $C_2$  parameters decrease with decreasing resin content with no clear frequency dependent manner and with much larger  
18 standard deviations compared to those determined from  $G'$  and  $G''$  fits
- 19 •  $C_3$  parameters decrease with decreasing resin content in contrast to those determined from  $G'$  and  $G''$  fits.

20 For the NAC compounds the

- 21 •  $Q_0$  parameters decrease with decreasing resin content in a pronounced manner; by a factor of 150 for  $\omega = 0.6$  rad/s and a  
22 factor of 15 for  $\omega = 4$  rad/s. With increasing frequency a decrease is found for  $v_F = 54.2$  %, but an increase for  $v_F =$   
23 49.1 %
- 24 •  $C_1$  parameters decrease with decreasing resin content but there is no clear dependency on frequency. Correspondingly  
25 the  $\gamma_{0C}$  values increase with decreasing resin content
- 26 •  $C_2$  parameters can be considered to be around “2” but partly with large standard deviations
- 27 •  $C_3$  parameters exhibit an arbitrary dependency on resin content and frequency.

28 In general, it is found that the standard deviations of the nonlinear parameter are significantly higher. Whereas  $G'_0$  and  $G''_0$   
29 have a physical meaning as initial storage and loss moduli, respectively, only the mathematical meaning of  $Q_0$  is clear. It  
30 represents the “zero-strain  $Q$ -parameter” (Kádár et al. 2020). The definition of the nonlinear coefficient  $Q(\gamma_0)$  is based on the  
31 existence of a MAOS region having a quadratic strain amplitude dependency of  $I_{3/1}$  generating a constant value  $Q_0$   
32 corresponding to Eq.3. As already mentioned, the determined nonlinear coefficients  $Q(\gamma_0)$  decreased with strain amplitude  
33 for all AC and NAC compounds without exhibiting a plateau at low strain amplitudes, and a strong dependency of  $Q_0$  on the  
34 resin content was found. Especially the decrease of  $Q(\gamma_0)$  with strain amplitude violates the idea of a nonlinear coefficient  
35 enhancement with strain amplitudes. Because  $\gamma_{0C}$  is an overestimation of the linear viscoelastic limit based on linear  
36 viscoelastic data, the measurable nonlinear region from FT rheology should occur at strain amplitudes below  $\gamma_{0C}$ . However,  
37 the frequency dependency of the  $Q_0$  values shows a contradictive behavior for the AC and NAC compounds as it provides

1 large and decreasing  $Q_0$  values for  $v_F = 54.2$  % and small and increasing values for  $v_F = 49.1$  %. Thus, the parameter  $Q_0$  does  
 2 not characterize the resin content dependent effects on the nonlinear material behavior consistently. However, the AC and  
 3 NAC compounds do not exhibit at all a quadratic strain amplitude dependency of  $I_{3/1}$ , similar to results reported in several  
 4 recent works (Jana et al. 2020, Natalia et al. 2020, Kádár et al. 2020). Therefore, difficulties in interpreting  $Q_0$  could be  
 5 attributed to the absence of a quadratic scaling behavior in  $I_{3/1}$  which in turn induce unknown errors in extrapolating  $Q_0$ .

6 The raw  $I_{3/1}$  curves, showing the influence of the applied angular frequencies and different resin contents, are presented in  
 7 Fig. 6. The reference (-1) scaling corresponding to the instrumentation noise region (Cziep et al. 2016) and the theoretically  
 8 expected quadratic scaling for MAOS are also included (dotted lines). Previously, the following anomalous behaviors, i.e.  
 9 nonlinear ‘oddities’, have been observed in polymeric systems: (i) angular frequency dependent  $I_{3/1}$  and (ii)  $I_{3/1}$  scaling  
 10 exponents  $n \in [0, 2]$  where  $I_{3/1} \propto \gamma_0^n$ . The two types of ‘oddities’, (i), (ii) were reported to occur simultaneously as well,  
 11 particularly around the percolation threshold of polymer nanocomposites (Kádár et al. 2020). The scaling exponents  $n < 2$   
 12 have generally been shown to be a function of the applied angular frequency, with a typical behavior being that an increasing  
 13 applied angular frequency would revert to the quadratic scaling (Kádár et al. 2020). Scaling exponents of approximately zero  
 14 were reported for consolidate percolated networks (Gaska and Kádár 2019). All data share common features including scaling  
 15 exponents  $\neq 2$ ,  $I_{3/1}$  dependence on  $\omega$  and multiple scaling exponents in the measurable strain amplitude range below LAOS.  
 16 Since for angular frequency dependent  $I_{3/1}$  data we expect a general trend between the minimum and maximum applied  
 17 angular frequency, we discuss our findings by comparing the nonlinear behavior of 0.6 and 4 rad/s, and for strain amplitudes  
 18 below the LAOS limit. For the AC compounds the main findings are:

- 19 • for  $v_F = 49.1$  % a slope of -1 for the noise region could be generally inferred for approximately  $\gamma_0 \leq 0.2$  %. It should  
 20 be noted that between  $\gamma_0 \cong 0.2$  % and the detection of a clearly positive scaling exponent the data is unclear, with a  
 21 potential local maxima (e.g. see 4 rad/s and compare to e.g. NAC  $v_F = 51.6$  %):
  - 22 ○ for  $\omega = 0.6$  rad/s:  $n \cong 2.1$  for  $\gamma_0 \in [2, 14]$  %
  - 23 ○ for  $\omega = 4$  rad/s:  $n \cong 1.6$  for  $\gamma_0 \in [1, 11]$  %
- 24 • for  $v_F = 51.6$  % a slope of -1 for the noise region is detected for approximately  $\gamma_0 \leq 0.36$  %:
  - 25 ○ for  $\omega = 0.6$  rad/s:  $n \cong 0$  for  $\gamma_0 \in [0.3, 0.6]$  %;  $n \cong 1.5$  for  $\gamma_0 \in [0.6, 3.6]$  %
  - 26 ○ for  $\omega = 4$  rad/s:  $n \cong 1.7$  for  $\gamma_0 \in [0.7, 4.5]$  %
- 27 • for  $v_F = 54.2$  % a slope of -1 for the noise region is detected for approximately  $\gamma_0 \leq 0.15$  %:
  - 28 ○ for  $\omega = 0.6$  rad/s: a local maxima,  $dI_{3/1}/dt = 0$ , could be inferred for  $\gamma_0 \in [0.2, 0.6]$  %;  $n \cong 3.8$  for  
 29  $\gamma_0 \in [0.6, 1.3]$  %;  $n \cong 1.6$  for  $\gamma_0 \in [1.3, 4]$  %,
  - 30 ○ for  $\omega = 4$  rad/s:  $n \cong 1.3$  for  $\gamma_0 \in [0.16, 0.3]$  %;  $n \cong 0$  for  $\gamma_0 \in [0.4, 0.8]$  %;  $n \cong 2$  for  $\gamma_0 \in [1, 3.6]$  %.

31 For comparison, the NAC compounds have:

- 32 • for  $v_F = 49.1$  % a slope of -1 for the noise region could be generally inferred for approximately  $\gamma_0 \leq 0.2$  %. It should  
 33 be noted that between  $\gamma_0 \cong 0.2$  % and the detection of a clear positive scaling exponent the data is unclear:
  - 34 ○ for  $\omega = 0.6$  rad/s:  $n \cong 2.3$  for  $\gamma_0 \in [6, 19]$  %
  - 35 ○ for  $\omega = 4$  rad/s:  $n \cong 1.6$  for  $\gamma_0 \in [3.4, 18.5]$  %
- 36 • for  $v_F = 51.6$  % a slope of -1 for the noise region could be generally inferred for  $\gamma_0 \leq 0.2$  %

- 1           ○ for  $\omega = 0.6$  rad/s: a pronounced local maxima,  $dI_{3/1}/dt = 0$ , is apparent in the transition region  $\gamma_0 \in$
- 2           [0.3, 1.3] %, with similar maxima recorded for all  $\omega < 4$ ;  $n \cong 1.7$  for  $\gamma_0 \in [2.2, 6]$  %
- 3           ○ for  $\omega = 4$  rad/s:  $n \cong 1.6$  for  $\gamma_0 \in [0.8, 6]$  %
- 4       • for  $v_F = 54.2$  % a slope of -1 for the noise region is detected for  $\gamma_0 \leq 1$  for  $\omega = 1$  while a slope of -1 for the noise
- 5       region is not detected in the applied strain amplitude range
- 6           ○ for  $\omega = 0.6$  rad/s: a pronounced local maxima,  $dI_{3/1}/dt = 0$ , is apparent in the transition region  $\gamma_0 \in$
- 7           [0.36, 1] %. This can also be interpreted as having  $n \cong 2.8$  followed by  $n \cong 0$ . Similar maxima can be
- 8           recorded for all  $\omega < 4$ ;  $n \cong 1.5$  for  $\gamma_0 \in [1.3, 6]$  %
- 9           ○ for  $\omega = 4$  rad/s: a local maxima could be inferred but is not evident, leaving an apparent two-region
- 10          scaling;  $n \cong 2$  for  $\gamma_0 \in [0.28, 0.8]$  %;  $n \cong 1.5$  for  $\gamma_0 \in [1.3, 6]$  %.

11       For the equivalent concentrations the two adhesive formulations share nonlinear scaling similarities but also striking

12       differences. For  $v_F = 49.1$  %, both AC and NAC share a similar scaling behavior with  $I_{3/1} \propto \omega^{-1}$  and one scaling exponent

13       characterizing the MAOS region, with  $n \propto \omega^{-1}$  ranging from 2.3 to 1.6. To our knowledge, scaling exponents  $n > 2$  have

14       not been previously reported, and thus any implications remain unclear. Taking the linear viscoelastic moduli as evidence that

15        $v_F = 49.1\%$  is below a gelation concentration for the parameters investigated, the nonlinear material properties results can be

16       considered to reflect that. Thus,  $n(\omega)$  could be considered as an early evidence of gelation behavior. Such angular frequency

17       scaling dependencies have been previously associated to percolation behavior as well as gelation in suspensions (Kádár et al.

18       2020). As the strain amplitude characteristic of the measurement range is inducing a nonlinear material behavior, the large

19       deformation could access partially gelled network domains, whose contribution to the material response would not be

20       accessible through linear means. It should be also noted that the concentration differences investigated are not that large.

21       Comparatively, a striking difference is recorded at  $v_F = 51.6$  % both compared to the lower concentration and between AC

22       and NAC. The most pronounced difference is recorded at the linear-nonlinear transition for AC appearing to have generally a

23       two-region scaling ranging from  $n = 0$  for  $\omega < 4$  rad/s at  $\gamma_0 \in [0.3, 0.6]$  %. For  $\gamma_0 > 0.6$  % a moderate variation in  $I_{3/1}$

24       scaling between  $n = 1.5$  and 1.7 was recorded for all imposed  $\omega$ . A possible local maximum could be assumed around 1 %.

25       In a clear contrast, NAC shows a pronounced local maximum at the noise-nonlinear transition,  $dI_{3/1}/dt = 0$ , for  $\omega < 4$  rad/s

26       at  $\gamma_0 \in [0.36, 1]$ . Scaling laws  $n \approx 0$  have previously been associated to consolidated percolated or gelled networks (Kádár et

27       al. 2020). The local maximum at the noise-nonlinear transition has not been previously reported in the literature and based on

28       the evaluating the higher concentrations investigated it could be related to the occurrence of a three-region scaling behavior in

29        $I_{3/1}$ . Considering the linear  $G'$ ,  $G''$  data as an evidence for the buildup of a gelled network between  $v_F = 49.1$  % and  $v_F = 51.6$

30       %, this would correspond to a pronounced change in nonlinear behavior in the third relative higher harmonic, while  $v_F = 54.2$

31       % is similar to the preceding concentration for both compositions. For AC, the apparent  $n \approx 0$  scaling becomes more

32       pronounced for higher  $\omega$ , however, it increases to positive values (albeit still strongly dependent on  $\omega$ ). For NAC, the local

33       maximum continued to be present and a three-region scaling behavior can be readily envisioned. Overall, correlating  $I_{3/1}$  to

34       the microstructure in a causal manner is not straightforward but the results point towards unique sequences of physical

35       processes corresponding to the nonlinear behavior of the compounds. Such effects are not apparent in the linear data. In this

36       respect, the nonlinear scaling behavior in  $I_{3/1}$  could be the result of buildup and consolidation of the gelled network domains

1 with increasing concentration, in relation to the molecular stretching between tie chains and to the release of physical  
2 crosslinks with increasing strain amplitude.

3 The Dahlquist (1969) and Chang (1997) representations show that the resin content and frequency dependent ( $G''$ ,  $G'$ ) data  
4 pairs of AC and NAC compounds lay on “master curves” starting in the liquid phase (data points below the  $\tan(\delta) = 1$  line) at  
5 low resin contents in a progressive manner ending in the solid state (data points above the  $\tan(\delta) = 1$  line) at large resin  
6 contents. Both compounds show the liquid solid transition if  $G'$  coincides with the Dahlquist criterion (300 kPa) being at  $v_F =$   
7 51.6 % for the AC compounds and between  $v_F = 51.6$  % and 54.2 % for the NAC compounds, Fig. 7. It is also obvious that  
8 the slopes of the AC master curve exceed those of the NAC curve. This indicates that the viscoelastic properties of the AC  
9 compounds vary more than those of the NAC compounds. In that respect the Dahlquist&Chang representation is able to  
10 compare and to distinguish the resin content and frequency dependent behavior of PSA for materials selection purposes.  
11 Furthermore, as can be seen in Fig. 7, the Dahlquist criterion line is a pragmatic estimate for the gel point as the master  
12 curves of both compounds cross the Dahlquist criterion line and the  $\tan(\delta) = 1$  line in the same moduli range.

13 Insights in the nonlinear material response of the AC and NAC compounds are gained through monitoring the shape  
14 change of the normalized elastic and viscous Lissajous-Bowditch curves with strain amplitude and shear rate amplitude (see  
15 Fig. 4 and also [Online Resource](#)). Their evaluations quantify the nonlinear elastic and viscous intra-cycle material behavior in  
16 terms of strain stiffening ratio or shear thinning ratio, respectively. The strain stiffening and shear thickening ratios are  
17 approximately  $S = T = 0$  for all AC and NAC compounds, as large strain moduli and minimum strain moduli coincide for  
18 linear viscoelastic behavior, Fig. 8 - 9. We note that the onset of nonlinear behavior for  $S, T \neq 0$  occurs at strain amplitudes  
19 typically higher than the limit of the linear viscoelastic regime as determined from  $G', G'' \neq f(\gamma_0)$ , but is lower than could be  
20 inferred from  $I_{3/1}$  data. The differences in detecting the onset of nonlinear behavior pertain to the sensitivities of the different  
21 methods. Interestingly, but not surprisingly,  $1/C_1$  from the Carreau-Yasuda-like fits does not appear to capture any of the  
22 critical onsets for nonlinear behavior from the different methods. For the discussion below, it should be noted that the strain  
23 amplitudes, which characterize the nonlinear behavior, are typically higher than those corresponding to the ‘oddities’ detected  
24 at the noise-nonlinear transition in the third relative higher harmonic.

25 The intra-cycle elastic nonlinear behavior is summarized Fig. 8. Interestingly, while polymeric systems are found to  
26 exhibit a strain stiffening behavior,  $S > 0$ , with a relatively trivial monotonic behavior with weak dependence on the angular  
27 frequency (Gaska and Kádár 2019, Kádár et al. 2020), we observed significant differences between compositions and  
28 concentrations. Specifically, the intra-cycle strain stiffening ratio seems not to be a monotonically increasing function.  
29 Especially the AC compounds show a frequency dependent nonlinear behavior, with a wave-like response apparent for  $v_F =$   
30 49.1 %. The AC compound with  $v_F = 49.1$  % reveals a maximum in the order of  $S \approx +0.3$  for 4 rad/s at strain amplitudes  
31 between 20 % and 30 %. The maxima of  $S$  ratios are shifted to lower strain amplitudes with increasing resin contents and  
32 decreasing frequencies, Fig. 8. Thus, one may assume that the AC compounds with  $v_F = 51.6$  % and 54.2 % have their  
33 maxima between strain amplitudes of 10 % and 20 %, outside of the measured range. Furthermore, after reaching minima of  
34  $S$  ratios at strain amplitudes between 60 % and 80 %, a second increase is observed. This strain amplitude dependent intra-  
35 cycle strain stiffening indicates that the strain stiffening appears to be determined by different sequence of physical processes  
36 within this compound. As the other AC compounds were only strained to maximum strain amplitudes of 10 %, further  
37 maxima of  $S$  ratios are only observed for  $v_F = 54.2$

1 % . Surprisingly, at the higher frequencies, the AC compound with  $v_F= 54.2$  % displayed slightly negative  $S$  values in a  
2 narrow strain amplitude range, indicating a temporary strain softening behavior before reverting to  $S >0$ .

3 The NAC compounds show intra-cycle strain stiffening, however, maxima of  $S$  ratios are not observed probably because  
4 the maximum strain amplitudes applied were too small. Nevertheless, it seems that the (nonlinear) intra-cycle strain stiffening  
5 behavior is shifted to smaller strain amplitudes with increasing frequency, Fig. 8. Similar filler concentration dependent  
6 behavior of  $S$  has been observed by Du et al. (2018), Gaska and Kádár (2019), Kamkar et. al. (2018) and Kádár et al. (2020).  
7 Kamkar et al. (2018) explained the high  $S$  values of the sample with the highest filler concentration in the region of 20 and  
8 100 % strain amplitude due to low chain mobility leading to more homogenous filler distribution. Khandavalli and Rothstein  
9 (2015) related high  $S$  values to the yielding of the microstructures in polyethylenoxide dispersions with hydrophobic fumed  
10 silica particles. However, Kamkar (2020) explained positive  $S$  values of gelatin methacryloyl hydrogel at the highest strain  
11 amplitude with the stretching of the chains between two polymer junctions, which would react stiffer if the chains were  
12 already stretched to large deformations.

13 The intra-cycle viscous nonlinear behavior is summarized Fig. 9. Both AC and NAC exhibit a concentration and angular  
14 frequency dependent behavior in  $T$ . The AC compound with  $v_F= 49.1$  % and NAC compounds with  $v_F= 49.1$  % exhibit intra-  
15 cycle shear thinning behavior ( $T <0$ ), in contrast to the higher concentrations. The AC compound discloses a dependence on  
16 the imposed angular frequency, with a small region of strain amplitudes exhibiting intra-cycle shear thickening nonlinear  
17 behavior ( $T >0$  for  $\gamma_0 \in [3, 15]$  % ). Considering that at this concentration we are below the apparent gel point identified from  
18 linear viscoelastic dynamic moduli data, the results stand in contrast to nonlinear data below the percolation thresholds in  
19 nanocomposites (Kádár et al. 2020). This could be attributed to the particular molecular structure of the adhesive compounds  
20 compared to thermoplastic polymer melts. While physical intermolecular forces and chain entanglements govern properties of  
21 a thermoplastic polymer melt (e.g. PE (Ramos et al. 2015)), in the adhesives it is the complex molecular structure of the resin  
22 and chemical crosslinks between resin and silicone polymer (Benedek and Feldstein 2009), which lead to a broad network  
23 that dominates the material behavior. With increasing resin contents the  $T$  ratios show a more complex behavior. AC and  
24 NAC compounds with  $v_F= 51.6$  % and 54.2 %, respectively exhibit strongly angular frequency dependent intra-cycle shear  
25 thickening,  $T >0$ . Both AC compounds and the NAC compound with  $v_F= 54.2\%$  reveal a local maximum of  $T$  for  $\omega \leq 2$  rad/s  
26 implying a transition to  $T <0$  at higher strain amplitudes. The maxima are shifted to lower strain amplitudes with increasing  
27 resin contents and decreasing frequencies, Fig. 9. One may assume that the maxima are attributed to an initial shear  
28 thickening behavior, which decreases apparently leading to a shear thinning behavior for sufficiently high strain amplitudes.  
29 This is already indicated by the 4 rad/s curve of the AC compound with  $v_F= 49.1$  % . Similar cross-linking dependent findings  
30 were reported by Kamkar (2020) for a gelatin methacryloyl hydrogel, and explained intermediate shear thickening ( $T >0$ )  
31 followed with shear thinning behavior ( $T <0$ ) at higher amplitudes by shear induced gelation processes through physical cross-  
32 links being destroyed by increasing amplitudes. Du et al. (2018) found a filler dependent behavior for  $T$  showing a transition  
33 from intra-cycle shear thickening ( $T >0$ ) to intra-cycle ( $T <0$ ) shear thinning with increasing filler content for  
34 polydimethylsiloxane nanocomposites and Kádár et al. (2020) for 3D hierarchical graphene nanocomposites; both attributed  
35 this effect to the destruction of a weakly interconnected filler network, or (given the high strain amplitudes) to the distortion  
36 of partially interconnected filler network patches. Comparable findings were also reported by Aliabadian et al. (2018) for  
37 partially hydrolysed polyacrylamide solutions filled with fumed silica nanoparticles. There the increase of  $T$  ratio was

1 explained due to a flow-enhanced network formation up to a certain point, and the subsequent decrease of the  $T$  ratio to  
2 negative values was attributed to a breakup of the nanoparticle flocculated structures, orientation of the polymer chains and  
3 slippage of at the nanoparticle/polymer interface. Interestingly, similarly to  $S$ ,  $T$  ratios depend strongly on the applied  
4 frequency for 51.6 % and 54.2 %. At low frequencies, the intra-cycle shear thickening is less pronounced. This fact is also  
5 confirmed in Du et al. (2018), Kamkar et al. (2018), and Aliabadian et al. (2018).

6 Furthermore, with increasing strain amplitudes in shear modulus measurements one starts to deal with the problem that  
7 tensile strains become more and more dominant. Estimating the tensile strain via the ratio of lateral shear strain amplitude to  
8 height of the sample one gets  $\varepsilon = 0.5$  % for  $\gamma_0 = 10$  %,  $\varepsilon = 4.4$  % for  $\gamma_0 = 30$  %, and  $\varepsilon = 41$  % for  $\gamma_0 = 100$  %. This shows that  
9 the strain state experienced by the sample changes from shear to tensile if the strain amplitudes exceed 30 %. However, it  
10 should be noted that with plate-plate geometry the material experiences the distribution of strain amplitudes in the radial  
11 direction, and thus such contribution would occur gradually throughout the flow domain until they become dominant. Thus,  
12 one may assume that the observed minimum of the  $S$  ratio and the plateau of the  $T$  ratio indicate this change of the  
13 dominating load case.

14 A synopsis of all rheological parameters, their structural meanings and physical interpretations are listed in Table 2. The  
15 SAOS evaluation by Carreau-Yasuda-like (CY) fitting and Chang (1997) showed that the investigated PSAs are in the range  
16 of the gel point. Furthermore, the Carreau-Yasuda-like fitting revealed increasing moduli with increasing resin contents  
17 which is attributed to higher crosslinking densities (Benedek and Feldstein (2009) and Schalaus et al. (2018)). Moreover, the  
18 higher moduli of AC can be related to the substitution of the polymers end-groups (Benedek and Feldstein 2009, Schalaus et al.  
19 2018) due to polycondensation that might affect the chain length and cause a denser network. This fits to the results from  
20 Chang's evaluation (1997) showing a higher slope for the ACs master curve that indicates more pronounced viscoelastic  
21 property changes for AC compared to NAC. Additionally, by using the interpretation of  $C_2$  and  $C_3$  fitting parameters  
22 suggested by Stadler et al. (2008), AC is expected to be more homogeneous with less disentanglements than more branched  
23 NAC.

24 From LAOS evaluation a slope  $n$  of "0" for  $I_{3/1}$  is reported by Kádár et al. (2020) as an early evidence for percolation  
25 concentration or gelation in suspensions and fits to the previously reported findings from SAOS evaluation. In addition,  $S$  and  
26  $T$  analyses gave a deeper insight into the behavior of molecular segments of the PSAs by comparing them with findings from  
27 literature for gelled networks or particle filled systems. Firstly, the onset of the inter-cycle nonlinearity of  $S$  and  $T$  decreases  
28 with increasing resin content due to a lower chain mobility, which was also found by Du et al. (2018), Kamkar et al. (2018),  
29 Kamkar (2020), Gaska and Kádár (2019), Goudoulas and Germann (2018), Kádár et al. (2020) and Aliabadian et al. (2018).  
30 Secondly, the occurring strain stiffening behavior might be attributed to stretching and yielding of the network as reported by  
31 Kamkar (2020), Aliabadian et al. (2018) and Khandavalli and Rothstein (2015). Thirdly,  $T$  shows an intra-cycle transition from  
32 shear thickening ( $T > 0$ ) at moderate strain amplitudes to intra-cycle shear thinning ( $T < 0$ ) at higher strain amplitudes for lower  
33 resin contents. A similar behavior can be expected at strain amplitudes exceeding the investigated range for higher resin  
34 contents. Comparable findings were reported with increasing polymer concentrations or filler contents by Aliabadian et al.  
35 (2018), Goudoulas and Germann (2018), Du et al. (2018) and Kamkar (2020). These observations were explained by the  
36 destruction of a shear induced filler network or gelation due to particle-particle interactions or physical cross-links at  
37 moderate strain amplitudes followed by orientation of the polymer chains or stretching of the network at high strain  
38 amplitudes, respectively.

By referring all results and structural related findings from literature to the PSAs, this study deepens the knowledge into the rheological and structural behavior of PSAs for intra-cycle loading within SAOS and LAOS region. All investigated PSAs are in the range of the gel points. However, the chemical modification of AC leads to a more homogeneous and condensed network being less entangled than the probably more branched NAC. First, increasing strain amplitudes lead to shear thickening and strain stiffening behavior due to the formation of shear induced structures or gelation. Then, these structures are destroyed with the further increase of the strain amplitudes as stretching and yielding occur in the network.

**Table 2** Synopsis of the rheological parameters and their structural meaning/physical interpretation from SAOS and LAOS regions

Parameter	Results for AC/NAC PSAs	Structural Meaning/Physical Interpretation
SAOS	$G'_0, G''_0$ increasing with increasing $v_F$	higher crosslinking density
CY-fitting $G'; G''(\gamma_0)$	$G'_0, G''_0$ of AC $\gg$ $G'_0, G''_0$ of NAC	polycondensation affecting chain length and causing denser network
	$C_2$ (AC) $>$ $C_2$ (NAC)	NAC more branched
	$C_3$ (AC) $<$ $C_3$ (NAC)	AC expected to disentangle less
	$\gamma_{0c}$ decreasing with increasing $v_F$	start of a nonlinear behavior shifts to lower amplitudes
SAOS Chang, Dahlquist	slope of master curve for AC $>$ NAC	more pronounced changes in viscoelastic properties of AC
	crossing of $\tan(\delta)=1$ line $\approx$ Dahlquist (300 kPa)	liquid to solid transition $\tan(\delta)=1$ means gelation
LAOS $Q(\gamma_0)$	$Q(\gamma_0)$ increasing with increasing $v_F$ ( $\omega$ -dependent for AC, non $\omega$ -dependent for NAC)	nonconsistent $v_F$ related characterization
	$C_2, C_3$ decrease with decreasing $v_F$	in contrast to SAOS results (CY-fitting)
LAOS $I_{3/1} \propto \gamma_0^n$	$n$ ranging from -1 to $>2$ for AC and NAC	$n = -1$ instrument noise $n = 0$ indication for consolidated percolated network or gelled network $n = 2$ theoretical value $n > 2$ firstly reported here – no interpretation available
LAOS $S, T$	onset of $S, T \neq 0$ decreasing with increasing $v_F$	nonlinear behavior reached at smaller strain amplitudes due to a lower chain mobility
	( $S > 0$ ) wave-like response for 49.1 % AC	strain stiffening behavior; $S$ determined by different sequences of physical processes
	$S$ increases for AC, NAC with increasing $v_F$	less chain mobility/yielding of microstructure
	positive $T$ values at intermediate moderate strains	shear thickening behavior due to shear induced physical network creation
	negative $T$ values at high shear rates	shear thinning starts due to the destruction of the flow
	$T$ increases with increasing $v_F$	enhanced network and stretching of the chains

#### 4. CONCLUSION

Pressure Sensitive Adhesives (PSA) for Transdermal Therapeutic Systems (TTS) are subjected to periodically occurring small and large deformations during application, wearing and removal. Thus, their viscoelastic behavior should be investigated over a wide range of strain amplitudes to gain an insight to the occurring mechanical deformation processes, and their temporal evolutions for further optimization. The strain amplitude sweeps in oscillatory shearing using a rheometer with a plate-plate arrangement turned out to be a good method for a precise characterization of both the linear (storage and loss



1 moduli) and the nonlinear viscoelastic (critical strain amplitude, inter-cycle softening, Fourier intensity ratio  $I_{3/1}$ , intra-cycle  
2 strain softening ratio  $S$  and intra-cycle shear thickening ratio  $T$ ) behavior.

3 Data evaluation of the investigated amine (AC) as well as non-amine (NAC) compatible silicone PSA compounds with the  
4 Carreau-Yasuda-like approach revealed that the  $G'(\gamma_0)$  and  $G''(\gamma_0)$  functions as well as the nonlinear coefficient  $Q(\gamma_0)$   
5 depend largely on the resin content and strain amplitude. Especially, the dependency of  $G'_0$  and  $G''_0$  on the resin content  
6 confirms that all compounds are close to the glass transition allowing to adjust the properties with respect to the application  
7 requirements.

8 However, the fitting parameters of the nonlinear coefficient  $Q(\gamma_0)$  exhibited inconsistencies, which **make it inappropriate**  
9 **to quantify the nonlinear viscoelastic behavior of the PSA compounds due to the decreasing behavior of the nonlinear**  
10 **characterizing parameter  $Q(\gamma_0)$  with increasing strain amplitude.** There is no region having a quadratic strain amplitude  
11 dependency. This confirms the  $I_{3/1}$  ratio revealing the frequency and resin content dependent scaling exponents of unreported  
12 values after the linear/nonlinear transition region. Within the linear/nonlinear transition region, the zero scaling for  $I_{3/1}$  might  
13 indicate a building up and consolidation of gelled network domains, which will be stretched/released with increasing strain  
14 amplitude.

15 Dahlquist&Chang criteria, well established to distinguish resin content dependent and frequency dependent behavior of  
16 PSA for materials selection purposes, revealed enhanced dependency of the viscoelastic properties of the AC compounds.

17 With the help of Carreau-Yasuda approach applied to nonlinear region it was found that both compounds exhibit inter-  
18 cycle strain softening, which is less pronounced for  $G''(\gamma_0)$  compared to  $G'(\gamma_0)$ . Thus, elastic and viscous properties are  
19 affected in a different manner by strains in the nonlinear range. In practice this means that the effective modulus becomes  
20 small in case of large strain amplitudes what eases removal of PSA from skin, and viscous properties remain rather stable  
21 giving PSA enough time to establish good wetting.

22 Finally, the intra-cycle viscoelastic behavior within complete single load oscillations investigated by analyzing Lissajous-  
23 Bowditch diagrams may support the assumption from  $I_{3/1}$  ratio of a consolidating gelled network being stretched and  
24 released by increasing strain amplitudes in the nonlinear range. Furthermore, with respect to both frequency and strain  
25 amplitude dependency, especially  $T$  ratios play an important role in the optimization of PSA subjected to large deformations.  
26

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36

## 37 **Data Availability**



1 The datasets generated during and/or analysed during the current study are available in the Zenodo open repository  
2 maintained by CERN [https://doi.org/ 10.5281/zenodo.4456643](https://doi.org/10.5281/zenodo.4456643).

#### 3 4 **Compliance with ethical standards**

5 **Conflict of interest** The authors declare that they have no competing interests.

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29

30