Investigation of the Influence of Different Filler Contents of Wine Pomace in PBS on Fracture Mechanics Properties

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Abstract: Biobased polybutylene succinate (PBS) represents a promising alternative to petrochemical-based polymers. The use of this biopolymeris limited in many areas by its low resilience against environmental influences. With the help of bio-based stabilizers the thermo-oxidative degradation process can be slowed down. Suitable stabilizing additives are natural antioxidants present in plant extracts with a high flavonoid content, which can be found in grapes, wine and wine by-products.

PBS was modified with two different bio-stabilizers based on wine grape pomace. The highest filler content tested was 20 wt.-%. In addition to improving stability, the additives also impact the polymer's mechanics. The influence of these functional fillers on the fracture mechanical properties was examined in a quasi-static test. The crack growth was recorded using integrated video monitoring. Based on the results, the corresponding crack resistance curve and tearing modulus were determined depending on filler type and content. Additional optical analysis was used to correlate fracture mechanics and structure.

The two bio-stabilizers based on red (RWP) and white wine pomace (WWP) differs distinctly in terms of their influence on fracture mechanical properties. The Influence of RWPon the fracture toughness is significantly higher than that of WWP. Especially at lower filler contents with RWP, there is a strong increase in the fracture mechanics parameter tearing modulus (T_J) and an increase in the slope of the R-curve. With 5 wt.% RWP DOM the T_J is 13.64 x 10^2, whereas with WWP Silv a value of only 6.39 x 10^2 can be achieved. This difference is also reflected in the increase in the R-curves. With 5 wt.% a slope of the fitted R-curve of 265.59 (RWP DOM) and 121.02 (WWP Silv) could be determined with the first derivative. In the optical analysis it was noticeable that the RWP particles were more homogeneously dispersed in the matrix while the WWP filler tended to agglomerate. The inhomogeneous distribution and strong agglomeration tendency can be attributed to a higher sugar content of WWP and a higher particle size distribution. The top cut (D97) of WWP Silv is 62.37 ± 0.05 µm and that of RWP DOM is 51.97 ± 0.09 µm.

Keywords: Fracture mechanic, tearing modulus, biopolymer, residues, biostabilizers, wine grape pomace, red wine pomace, white wine pomace.

1. INTRODUCTION

The use of biopolymersis often a huge challenge due to high material costs and the narrow application range of their property profile [1,2]. Various scientific studies have investigated the use of suitable natural bioadditives for a few years now. The aim of bioadditives is to improve or change the property profile of biopolymers. Most biopolymers are very brittle, have low UV resistance and/or poor antioxidant properties [3,4]. Thus, their use is not possible or only possible to a limited extent in certain applications.

A lot of studys focus on the utilization of various natural residues or plant raw materials [5-7]. Wine by-products are a very promising residual material [8,9]. During the industrial processing of grapes into juices or wine, large quantities of wine pomace (WP) are produced. After pressing the grapes, approx. 1/3 of the original weight remains as moist WP [10] .The pomace consists of a mix of skins, seeds and stems. Only very small amounts of the WP produced each year are reused, e.g. to produce animal feed, spirits such as grappa or extract grape seed oil [11-13] . However, a large amount ofWP remains unused. In addition to the high availability and low cost of this sustainable residue, wine by-products also contain bioactive chemical components, such as secondary plant substances like polyphenols, which can have functional antioxidant properties [14-16].

With the help of various processing methods, such as drying and grinding, the moist WP can be transformed into a homogeneous powder, which can then be added to the polymermatrix in a thermal processing step. The influence of the additives antioxidant properties on the polymer matrix was investigated by B. Hiller *et al.* [17].

The studies by B. Hiller *et al*. have shown that the use of wine pomace has a stabilizing effect on the bioplastic matrix PBS [17]. However, the influence of the fillers at lower filler amounts on the mechanical and, especially, fracture mechanical properties has not yet been analyzed in more detail. In most scientific studies investigating the mechanics, the wine pomace was used in very large quantities as a pure filler [18,19].

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The main aim of this study is to analyze the influence of the two functional reinforcing materials on the mechanical properties. The main objective here are the fracture mechanics. The fracture mechanics parameters will be used to compare the effects of both wine pomace in the biopolymer matrix.

The present work focuses on the influence of WP powder as a functional bio-filler on the fracture mechanical properties by adding two different WPs in different amounts to the biopolymer matrix PBS.The wine pomace was compounded into the matrix and then processed into test specimens using the injection molding process. The notched samples were analyzed using a quasi-static fracture mechanics test. The tensile test was carried out at ambient temperature and recorded with a camera. The recorded images were used to analyze the different crack growth lengths at the respective test times. Based on the crack length (Δa), the fracture mechanics parameters (J-integral and tearing modulus) could be calculated.

2. MATERIALS AND METHODS

2.1. Materials and Functional Bio-Fillers

The PBS polymer used was BioPBS type FZ71PM from PTT MCC Biochem Co, Ltd (Bangkok, Thailand).The biopolyester has a density of 1.26 g/cm^3, a melting temperature of 115 °C and a MFR of 22 g/10 min (190°C, 2.16 kg).

The two WP types were provided by the winery Richard Dahms GmbH (Schweinfurt, Germany). A white WP of the Silvaner variety (WWP Silv) and a red WP of the Domina variety (RWP DOM) were used as functional bio-fillers. Both WPs were harvested in October 2021 and pressed on the same day. The fresh pomace was stored in sealed bags at -18 °C until the next processing step (mill-drying) occurred. The grinding of the WP was carried out by Mahltechnik Görgens GmbH (Dormagen, Germany) in a two-stage process. In the first step, mill-drying was carried out with a rotor speed of 94 m/s, an air flow of 2000 kg/h and a simultaneous drying process (air temperature of 220 °C). In the second grinding step, a rotor speed of 113 m/s and an air flow of 1800 kg/h were used.

An overview of the various processing and analysis steps is shown in Figure **1**.

2.3. Production of Biocompounds and Test Specimens

Compounding of the bio-fillers into the PBS matrix was carried out using a Labtech type LTE20-44 laboratory co-rotating twin-screw extruder with an L/D ratio of 44 and a screw diameter of 22 mm. The PBS was dried for 5 h at 80 °C before processing in accordance with the manufacturer's instructions. The WP was added via the side feeder using a gravimetric dosing system from Scholz Dosiertechnik GmbH (Großostheim, Germany). The temperature profile was set to 170 °C in the first seven heating zones and to 165 °C in zone 8 and 9, as well as in the nozzle area. Four different concentrations (5, 10, 15 and 20 wt.-%) were realized with each of the WP fillers. A screw speed of 260 rpm and a total throughput of 6.0-6.5 kg/h

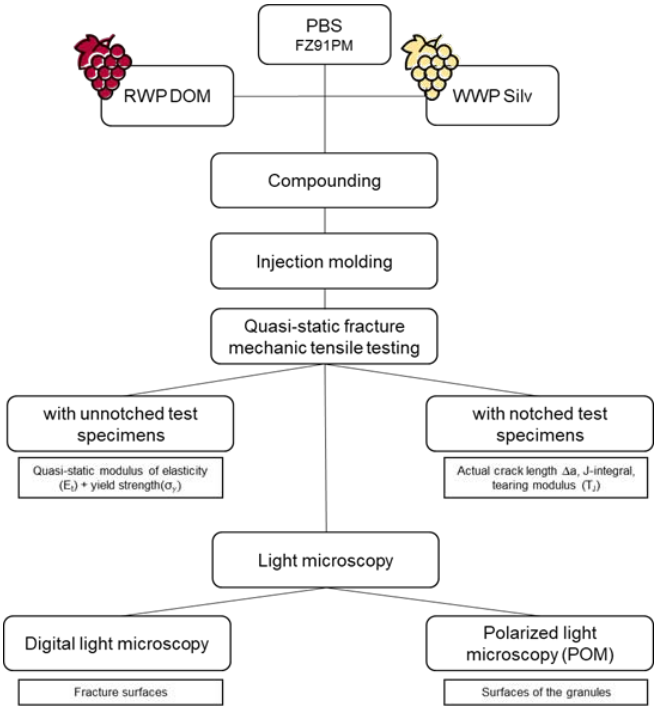

Figure 1: Overview of the various processing and analysis steps.

were used to produce the compounds. The extrudate was cooled directly in a water bath and then subsequently cold pelletized (granulator: Labtech type LZ-120/hp).

Before injection molding, all compounds were pre-dried at 80 °C for 5 h and then processed using a BOY XS injection molding machine (BOY Machines, Exton, PA, US) to produce type 1 test specimens in accordance with DIN EN ISO 179-1. The injection molding parameters used are listed in Table **1**.

2.3. Fracture Mechanics Investigations

The fracture mechanics tests were done usinga quasi-static tensile testing setup on a Zwick RetroLine Z2.5 with a 2.5kN Xforce P load cell (ZwickRoell GmbH und Co. KG, Ulm, Germany). To determine the quasi-static modulus of elasticity and the yield strength, 5 unnotched test specimens (type 1 DIN EN ISO 179-1) were tested in a tensile test. The test was carried out at ambient temperature, with a preload of 0.25 N and a clamping length of 35 mm. The test speed for determining the modulus (E_t) was 1 mm/min and 50 mm/min for determining the quasi-static yield strength (σ_γ). As there was no significant yield point for any of the samples, an alternative yield point was defined at 2 % ($\sigma_{\gamma 2.0}$).

For the quasi-static fracture mechanics test, the specimens were notched using a manual notch plane (ZwickRoell GmbH und Co. KG). The total notch depth was 4.5 mm, consisting of a 3.0 mm deep V-notch (notch radius r_N = 0.1 mm) and a razor blade notch with a depth of 1.5 mm. The tensile test was carried out at ambient temperature, a preload of 0.25 N, a clamping length of 35 mm and a test speed of 1 mm/min were set. The measurement was recorded by a camera, thus different crack growth lengths (∆a) could be measured and evaluated at their respective test times. A length scale was attached next to the sample to correlate the actual crack length ∆a. The schematic test setup is shown in Figure **2**.

For each measurement 12 - 13 images were analyzed and the corresponding ∆a value determined. It was a single specimen test. The measured ∆a values were used to determine the fracture mechanics parameters J-integral (Equ. 1) and tearing modulus (T_J) (Equ. 2) [20]

$$J = \frac{\eta\, A_G}{B\,(W-a)}\left[1 - \frac{(0{,}75\eta - 1)\Delta a}{(W-a)}\right] \; mit\; \eta = 2 \qquad (1)$$

A_G: energy of deformation [N mm]

B: thickness of the test specimen [mm]

W: width of the test specimen [mm]

a: notch depth [mm]

∆a: stable crack growth [mm]

η: dimensionless geometry factor that is a function of crack length to specimen width ratio

$$T_J = \frac{dJ}{d(\Delta a)}\frac{E_t}{\sigma_\gamma{}^2} \qquad (2)$$

J: J-Integral [N/mm]

∆a: stable crack growth [mm]

Table 1: Parameter Overview for Injection Molding

Temperatur profil	Injection pressure	Injections peed	Holding pressure	Holding time	Cooling time
Zone 1/hopper: 155 °C Zone 2: 160 °C Zone 3/nozzle: 170 °C	800 bar	3 cm^3/s	600 bar	2 s	20 s

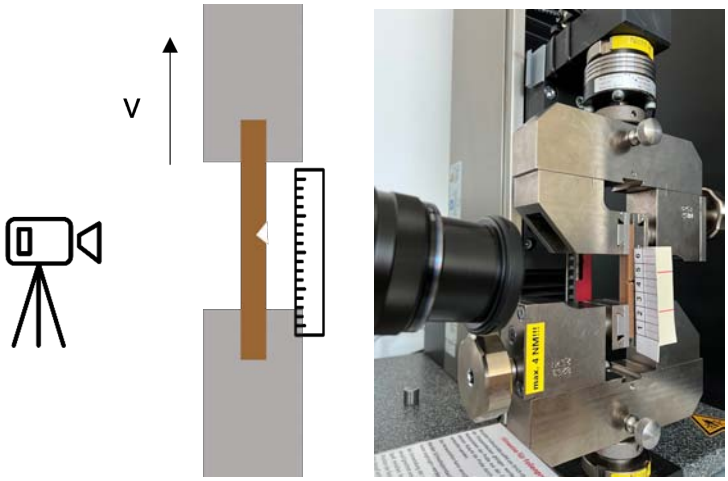

Figure 2: Quasi-static fracture mechanics test setup (left: schematic; right: actual test setup).

E_t : quasi-static modulus of elasticity [MPa]

σ_γ: quasi-static yield strength [MPa]

The J-Integral gives the amount of energy released per unit area of crack surface increase. It recognizes the polymer deformation area and progresses into the elastic area. This characteristic value can be used to determine the change in potential energy during crack propagation [21-23].

The calculated J-integral plotted against the stable crack propagation (∆a) results in theR-curve. A lower (0.05 mm) and upper (0.55 mm) limit of validity parallel to the y-axis was defined for the ∆a measured value. One reason for the lower measurement limit is that very small crack growth values are rather difficult to measure, and measurement errors can often occur. The definition of the upper validity limit was based on astudy by E.Q. Clutton with the useof Equ.3 [21,24].

$$\Delta a_{max} = 0.1 \cdot (W - a) \quad (3)$$

Δa_{max} : upper Limit

W: width of the test specimen [mm]

a: notch depth [mm]

Values outside of the validity limits were not considered when creating the R-curve. The R-curve is fitted using a polynomial fit of the 2nd order. The tearing modulus (T_J) generally describes the material's resistance to stable crack propagation. With an increase in T_J the material reveals a higher resistance to crack initiation and propagation, whereas a decrease in this parameter results in a lower resistance to stable crack propagation [23].

Summary of Mathematical Calculations

- Determination J-Values
  1. measure the crack lengths (∆a) of the camera recordings at different test times
  2. determine the A_G value of the different test times
  3. calculate the J values at different test times using equation 1 and the corresponding ∆a and A_G values
- Determination T_J-Values
  1. determination of the quasi-static modulus of elasticity (E_t) and the quasi-static yield strength (σ_γ) using a tensile test with unnotched test specimens
  2. plot the R-curve (with a polynomial fit of the 2nd order)
  3. determine the slope of the crack resistance curve using the 1st derivative (slope is equal to the $\frac{dJ}{d(\Delta a)}$)
  4. calculate the T_J value using equation 2

2.4. Light microscopic investigations

The fracture surfaces of the samples were analyzed using a Keyence digital microscope type VHX-950F with a magnification of x50 and x150 (Keyence Deutschland GmbH; Neu-Isenburg Germany). The images were taken in reflected light mode, without the use of a polarizing filter.

In addition to the light microscopic images of the fracture surfaces, the surfaces of the granules were investigated using polarized light microscopy (POM). For this purpose, the granules were prepared using a SLEE CUT 5062 rotary microtome with a tungsten carbide blade. The prepared granulate cross-section should have a minimum thickness of 20 µm.

3. RESULTS AND DISCUSSION

3.1. Fracture Mechanics Analysis Results

The results of the quasi-static modulus of elasticity and yield strength are shown in Table **2**. For both fillers, the modulus of elasticity decreases slightly at low amounts (5 wt.-%) and increases with higher amounts. Overall, there is a higher increase for the filler RWP DOM, which indicates better bonding or interaction with the matrix. When looking at the yield strength, a similar behavior can be seen in comparison to the modulus of elasticity. First there is a slight decrease and then an increase. The influence of the functional bio-fillers on the yield strength is much smaller.

3.1.1. J-Integral and R-Curves as a Function of Filler Content of Red and White wine Pomace in PBS

The R-curves of the samples filled with RWP DOM or WWP Silv and the reference sample (neat PBS) are shown in Figure **3**. The corresponding slope values are Summerised in Table **3**. It is noticeable that the influence of RWP DOM is significantly higher than that of WWP Silv. The slope of the R-curves increases more strongly due to the addition of the RWP filler instead of using the WWP Silv filler. Based on this data, a reinforcing effect or an increase in the resistance of the material against crack propagation can be assumed. This effect is most evident in the samples with 5 wt.-% and 10 wt.-% of RWP DOM.

At a higher filler content (15 or 20 wt.-%) a flattening of the R-curves can be observed. One reason for this may be the smaller distances between particles,

Table 1: Results of the Influence of functional Bio-Filler Content on the Quasi-Static Modulus of Elasticity and Yield Strength

content [wt.-%]	RWP DOM		WWP Silv	
	E_t [MPa]	$\sigma_{\gamma 2.0}$ [MPa]	E_t [MPa]	$\sigma_{\gamma 2.0}$ [MPa]
0	543.75 ± 11.24	10.45 ± 0.11	543.75 ± 11.24	10.45 ± 0.11
5	522.35 ± 3.34	10.08 ± 0.05	510.53 ± 3.22	9.83 ± 0.07
10	548.59 ± 2.67	10.55 ± 0.05	526.58 ± 4.36	10.11 ± 0.08
15	571.37 ± 3.19	10.96 ± 0.04	546.24 ± 6.31	10.49 ± 0.08
20	602.29 ± 2.04	11.46 ± 0.05	566,20 ± 4.01	10.77 ± 0.06

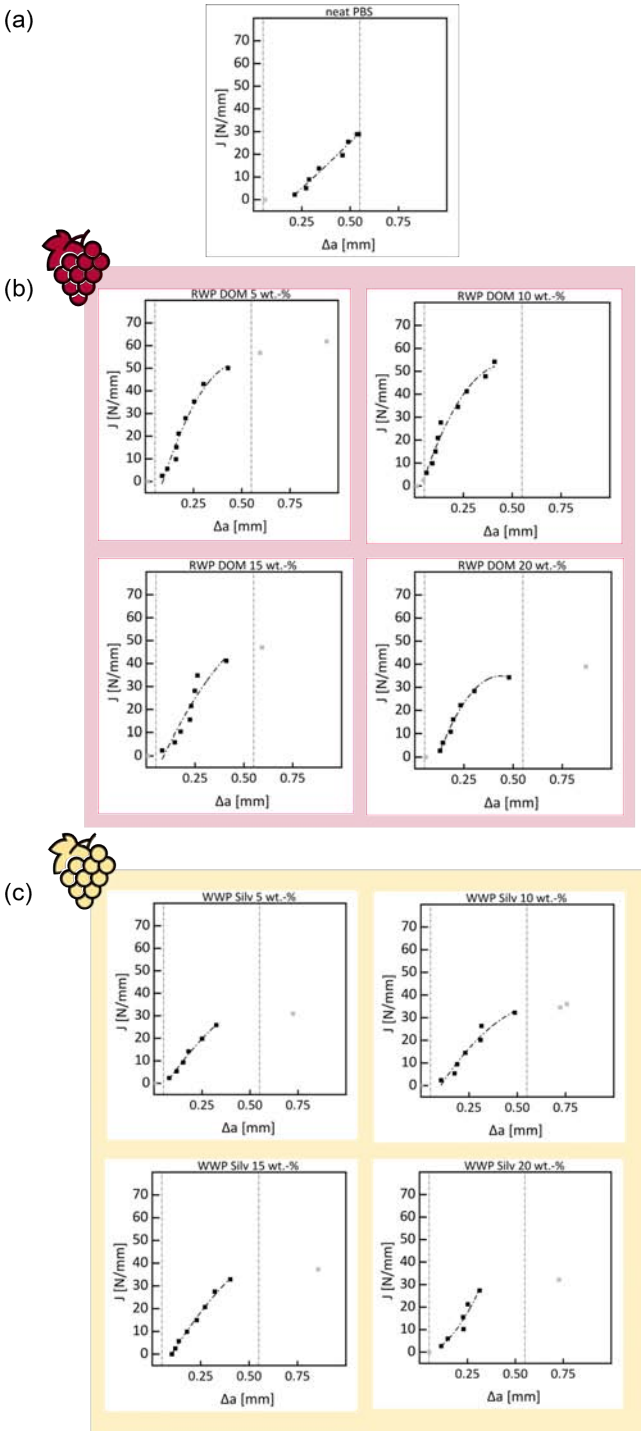

Figure 3: R-curves of the neat PBS (**a**) and the filled samples with RWP DOM (**b**) and WWP Silv (**c**).

caused by increasing filler content [25]. A crack can therefore propagate more easily through the material. The effect of decreasing energy absorption with increasing filler content has already been demonstrated in a PP/$CaCO_3$ composite by D. Li *et al.* [26].

When using WWP Silv, a lower improvement or reinforcement effect can be seen compared to RWP DOM. The influence of the different filler amounts is also significantly lower. This suggests that WWP Silv is distributed differently in the matrix or shows poorer interaction with it in contrast to RWP DOM.

3.1.2. Tearing Modulusin Dependence on Filler Content of Red and White Wine Pomace in PBS

The results of the tearing modulus (T_J) are shown in Table **4** and Figure **4**.

Similar to the results of the R-curves, the use of RWP DOM leads to a significantly higher increase of T_J. If the filler content is further increased, this effect levels off. The highest reinforcing effect can be seen with a filler content of 5 wt.-% RWP DOM. For all four filler contents the achieved T_J is higher than that of neat PBS, which means that the addition of RWP DOM improves the fracture toughness. A possible reason for this increase is a sufficiently good interfacial adhesion between the filler and the matrix. This enables good load and stress transfer between the two components. Based on good interfacial adhesion, resistance to crack propagation can be improved by mechanisms such as crack deformation/deflection or crack bridging, which contribute to a higher energy absorption of the material [27].

The assumption that a nucleation effect could be the reason for the increase in fracture toughness does not apply here. *B. Hiller et al.* [17] proved with thermal investigations via DSC that the degree of crystallization (χ_c) does not significantly change with addition of the two wine pomace fillers. The increase or variation of the degree of crystallization is in the range of 0.3–1.6 %. Thus, both WPs do not act as nucleating agents.

The results with WWP Silv also show an increase in T_J compared to neat PBS. This increase is significantly lower than that with RWP DOM filler. Similar to the R-curves of Figure **3**, only a very small difference in the results with filler weights of 5 - 15 wt.-% can be seen. Only at 20 wt.-% WWP Silv the modulus does drop decrease more strongly and even falls below the initial value of neat PBS. The reasons for a lower improvement in fracture toughness may be a high tendency towards agglomeration, larger particle sizes and/or super saturation, which increases the stress concentration points at the interface between filler and the polymer matrix. The crack can propagate through the material with less resistance.

The studies by B. Hiller *et al.* showed that the particle size distribution of WWP Silv is larger than that of RWP DOM filler [17]. The top cut (D_{97}) of WWP Silvis 62.37 ± 0.05 µm and of RWP DOM is 51.97 ± 0.09 µm. The difference in size can also be seen in the median particle size (D_{50}) with 19.45 ± 0.09 µm (WWP Silv) and

Table 3: Results of the Slopes of the R-Curves

Content [wt.-%]	Slope of the R-curve [N/mm^2]	
	RWP DOM	WWP Silv
0	77.76	
5	265.59	121.02
10	232.47	128.24
15	177.79	134.98
20	209.83	70.04

Table 4: Results of the Tearing Modulus

Content [wt.-%]	T_J x 10^2 [-]	
	RWP DOM	WWP Silv
0	3.87	
5	13.64	6.39
10	11.46	6.60
15	8.45	6.70
20	9.63	3.42

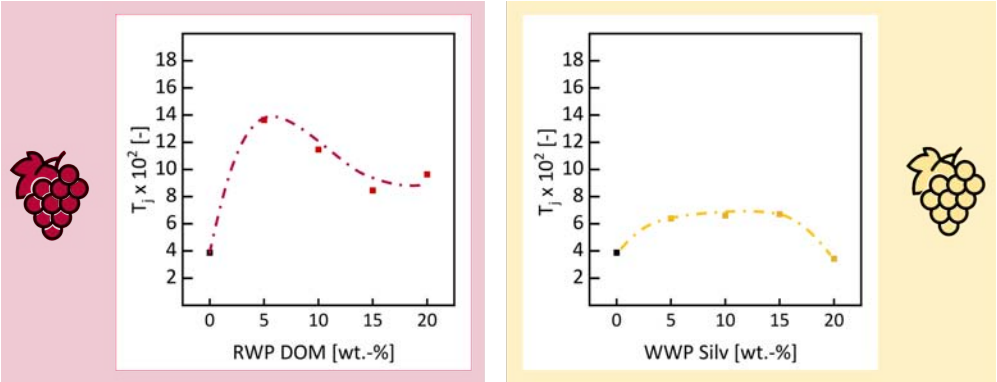

Figure 4: Tearing modulus of the filled samples.

12.75 ± 0.12 µm (RWP DOM) [17]. The larger particle size distribution of WWP Silv may be a reason for the lower improvement in fracture toughness.

The results of the T_J values of both additives were statistically analyzed using the Wilcoxon test. A very strong negative effect (effect size r = -0.91) between the two groups or fillers was shown. The difference between the two groups is very significant. This is reflected in the p value (p = 0.05). The differences at a significance level of 0.05 can be regarded as statistically significant. The observed effect when compared to random noise is very large.

3.2. Optical Analysis Results

The different modes of action of the WP fillers regarding the fracture mechanics parameters from section 3.1 are also reflected in the light microscope images of the fracture surfaces shown in Figure **5**. RWP DOM is largely homogeneously dispersed in the matrix, while the use of WWP Silv shows a strong tendency to agglomerate and form holes even at low quantities. This heterogeneous distribution of the fillers maybe the reason for a highly inhomogeneous stress distribution in the matrix. As previously mentioned in the section above, the tendency towards agglomeration can be a reason why the fracture toughness is negatively influenced through the formation of stress concentration points. The highest tendency towards agglomeration can be seen at 20 wt.-% WWP Silv, which is also shown by the strong decrease of T_J in Figure **4**. On the fracture surfaces of the RWP DOM samples, a lower tendency toward agglomeration formation is recognizable, while a clear visual difference between the varying filler contents is still noticeable. The fracture surfaces of the samples with 15 wt.-% and 20 wt.-% RWP DOM appear to be very highly filled.

One reason for the very different interaction of the two fillers in the PBS matrix may be their different chemical composition. For example, some studies have already shown that the soluble sugar content in wine pomace varies significantly between RWP and WWP because of the production process [28,29]. White grapes are pressed immediately after harvesting before fermentation can take place, whereas red grapes are fermented for several days before pressing [30]. *Q. Deng et al.* [29] were able to prove that the

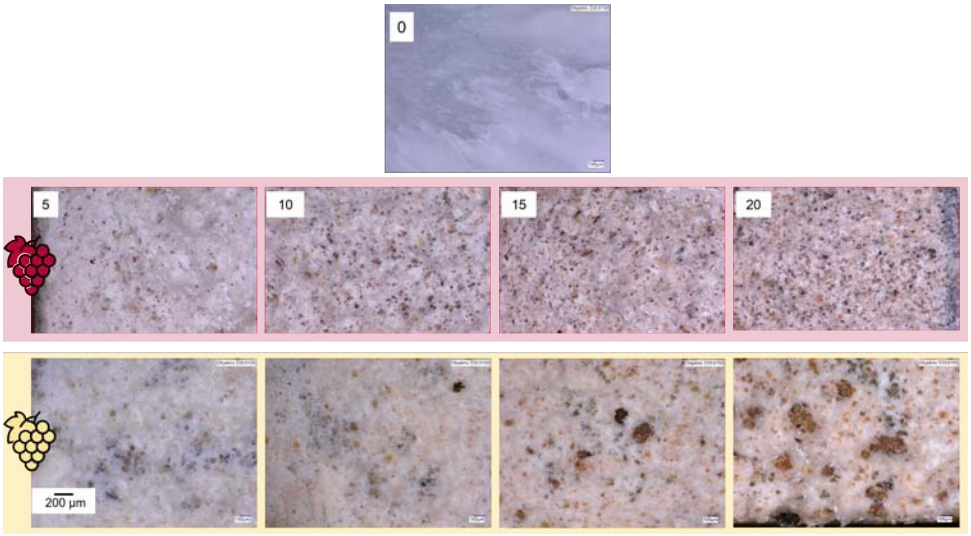

Figure 5: light microscope images of the fracture surfaces of the samples with PBS (top), RWP DOM (middle) and WWP Silv (bottom) with different filler content in wt.-%.

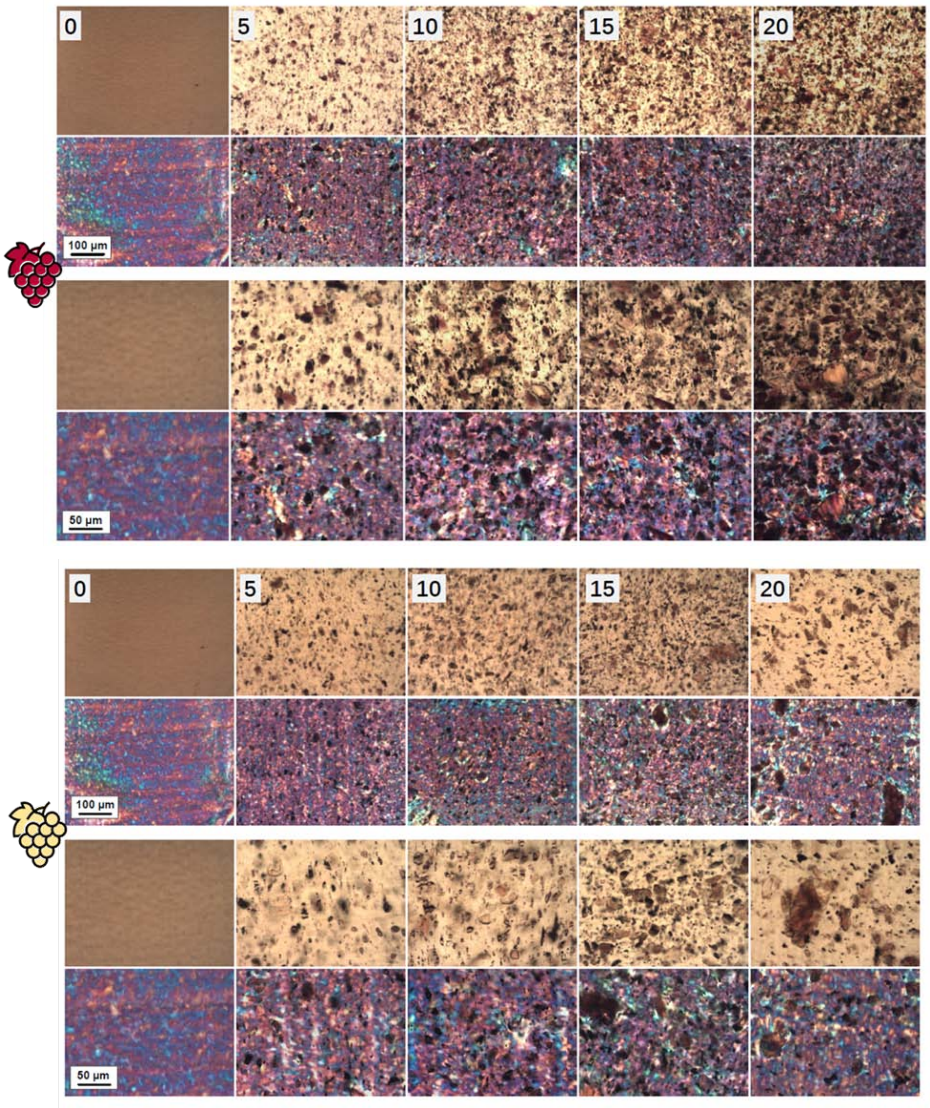

Figure 6: POM images of the granulate cross-sections of the filled PBS samples with RWP DOM (top) and WWP Silv (bottom) with different filler content in wt.-%.

WWP varieties Mueller Thurgau (55.77±2.12 %) and Morio Muscat (77.53±1.01 %) have a significantly higher sugar content than the RWP varieties Cabernet Sauvignon (1.71±0.49 %), Merlot (1.34±0.92 %) or Pinot Noir (1.38±0.93 %). Since the sugar degrades or caramelizes at lower temperatures, relative to the processing temperature, the production of these degradation products may cause the greater agglomeration tendency of WWP Silv.

Similar to the light microscopic images of the fracture surfaces, the POM images also show differences depending on the filler type and content (Figure **6**). WWP Silv shows a greater tendency to agglomerate, whereas RWP DOM tends to be better dispersed. However, at a filler content of 15 wt.-% or 20 wt.-% RWP DOM, a strong oversaturation can be recognized.

The results of the light microscopy and POM images are reflected in the R-curves in Figure **3**. It can be assumed that the strong tendency of WWP Silv to agglomerate and its lower interaction with the matrix compared to RWP DOM leads to a lower reinforcing effect.

4. CONCLUSION

Fillers from wine pomace can be successfully added to PBS. However, the effect of fillers obtained from red and white wine pomace differs greatly in terms of their influence on fracture mechanical properties. RWP DOM causes a larger improvement in fracture toughness, especially at lower filler contents (5–10 wt.-%), which is reflected by a strong increase in T_J and an increase of the slope of the R-curve. With a further increase in filler content, a decrease of both characteristic values can be seen. However, compared to pure PBS, there is still an overall increase in fracture toughness.

The use of WWP Silv results in a significantly lower increase in T_J and the R-curve is also less affected. It is

notable that the influence of filler contents between 5–15 wt.-% is very similar. Only a content of 20 wt.-% WWP Silv leads to a drastic decrease in fracture toughness with a value below that of pure PBS.

A different interaction of the fillers with the matrix was also demonstrated in the optical analysis of this study. It was noticeable that the RWP DOM particles were more homogeneously dispersed in the matrix while the WWP Silv filler tended to agglomerate more. In addition to the agglomerations, significant hole formation could be observed on the fracture surfaces of WWP Silv samples. In accordance with the fracture mechanics results, a super saturation of the matrix was recognized at a filler content of 20 wt.-% for both WPs.

The different modes of interaction with the polymer matrix can be attributed to different particle size distributions and chemical compositions. With regard to the particle size distribution, B. Hiller *et al.* have shown that the distribution of WWP Silv is skewed toward larger particle sizes when compared to that of RWP DOM [17]. In addition to their particle size, WWP and RWP also vary in their chemical composition, e.g. sugar content [29]. WWP has a much higher sugar content, which can result in more degradation products during thermal processing, increasing agglomeration tendency.

In summary, both WP fillers have a positive influence on the fracture toughness of PBS, however, RWP DOM yields to better results. In addition, the influence of lower filler quantities is more significant, while higher quantities offer no additional improvement and may also be detrimental to fracture toughness.

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