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Biocompatible Blends Based on Poly (Vinyl Alcohol) and Solid Organic Waste

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Abstract: This work is aimed at the development of new green composite materials through the incorporation of the solid organic waste (SOW) in a thermoplastic matrix. After being ground, the organic waste was exposed to a sterilization process, though an autoclave cycle, in order to obtain a complete removal of the bacterial activity. The SOW was found to have a high amount of water, about 65-70%, which made uneconomical its further treatment to reduce the water amount. Therefore, a water soluble polymer, poly (vinyl alcohol) (PVA) was chosen in order to produce SOW based blends. However, in order to reduce the viscosity of the PVA/SOW slurry, further amount of water was added. The very low viscosity attained by the water suspension allowed to process the PVA/SOW blends by a pressure-free process, for the production of samples, which were afterwards subjected to physical and mechanical characterization. Flexural tests showed the promising properties of the developed blends. In particular, the relevance of porosity was assessed. Increasing the water amount involved a signification increase of porosity, due to a faster water evaporation during processing. On the other hand, compared to neat PVA, addition of SOW allowed to significantly decrease the porosity of the produced samples. Despite this, the mechanical properties of the PVA/ SOW blends were shown to be lower than those of neat PVA processed analogously.

Keywords: Solid organic waste; PVA; evaporation; porosity; mechanical properties

1 Introduction

In recent years, different events, including the increase in the world population, the improvement of economic conditions and a sudden development of the industrial sector, led to a rapid growth in the production of waste.

The evolution and diversification of production processes caused a continuous change in the quantities and compositions of urban solid waste, thus generating several problems related to transport, storage and disposal. Therefore, the possibility to re-use the waste in a sustainable way assumes a primary importance, in order to improve the efficiency of waste management and reduce its negative effects on the environment and on population [1].

A particular kind of waste is the organic fraction of solid urban waste (SOW), or municipal solid waste, which represents about 40% by weight of municipal waste [1]. The high quantity of water contained in SOW promotes a rapid decomposition in presence of different kinds of bacteria, which can however be pathogens for humans and animals [2]. These features make SOW quite complex to be managed. It is therefore essential to develop processes which allow a decrease in the bacteriological content and a longer storage of the waste [3,4].

The aim of this work is the targeted recovery of organic waste by its transformation into a completely inert dry material, which can be used for several applications, such as insulating panels for the building sector or outdoor furniture.

The production of a green blend based on solid waste requires the incorporation of the organic waste into a matrix, which acts as a binder, thus reducing the danger of waste. Nowadays, the most widespread application involves the use of inorganic matrices such as cement, clay and lime [5,6]. Nevertheless, inorganic matrices have a series of disadvantages if used with organic waste. First, they can be attacked by acids, causing the release of the material [7]. Also, cements and additives highly increase the weight of the waste [8]. However, the main limitation is that the process is suitable only for the treatment of ashes deriving from the SOW combustion process (consisting essentially of inorganic materials), and it cannot be extended to materials rich of salts or organic components, since they can interfere with the setting and hardening processes, thus leading to the production of a very porous structure [9,10].

An alternative to inorganic matrices consists in the use of organic reagents, such as thermoplastic polymers; unlike the inorganic matrices, polymers do not chemically react with the waste, but carry out a process which allows insulating the SOW through its encapsulation in the matrix [11,12]. The main problem related to the use of thermoplastics lies in their high viscosities and processing temperatures [13,14].

On the other hand, PVA is a water-soluble thermoplastic polymer, which can be processed without heating to high temperatures [15]. Furthermore, PVA has a high biocompatibility, no toxicity and low costs [16]. Nevertheless, PVA lacks adequate mechanical properties in different loading conditions [17]; therefore, many studies were carried out in order to improve its mechanical response, through the addition of different fillers. A first route followed for improving PVA properties involved the production of nanocomposites through the addition of halloysite nanotubes (HNT) [16] and carbon nanotubes (CNT) [17,18]. An alternative way to reinforce PVA was found by the addition of natural fillers, such as corn-starch [19] and methylcellulose (MC) [20], which also allowed to preserve the biocompatibility and water solubility of PVA. PVA nanocomposites were also produced with the addition of cellulose nanofiber (CNF); however, a slower biodegradability was found for PVA/CNF compared to neat PVA [21].

In a previous work [22], the addition of different selected food wastes to PVA was found to improve some of the mechanical properties of the material; in particular, walnut shells could be used for increase of the materials modulus. On the other hand, addition of SOW in blend with PVA is expected to have some further advantages compared to selected food wastes: among these, transforming the poorest fraction of urban wastes into a valuable resource, avoiding the release of smells and percolates from SOW, and reducing the cost of items produced with PVA.

Therefore, this work is aimed at studying the effect of the addition of SOW on the mechanical and physical properties of PVA. Compared to previous work [22] the PVA/SOW blends were obtained by varying the amount of water, as well as the PVA/SOW weight ratio. PVA/SOW blends produced by a pressure-free process were subjected to physical and mechanical characterization, showing the potential of the developed approach for the production of low environmental impact materials.

2 Materials and Methods

PVA used in this work is KurarayPoval 3-85, a partially saponified grade of polyvinyl alcohol, with a degree of hydrolysis 84.2-86.2% supplied as fine powder/granules with defined grain size and a viscosity of 3.4-4.0 mPa.s at 20°C.

The SOW used derived from the recycling of the urban solid waste. Once collected, SOW was ground by using Electrolux EGO23000x shredder. Then, SOW was put in the Steristeam 2 autoclave, in order to carry out a sterilization process which involved the elimination of the bacteria. The complete bacterial removal, confirmed by bacterial analyses, was achieved with an autoclave cycle at 121°C for 20 min, and a pressure of 1 bar.

A simultaneous thermal analyzer Netzsch STA 409 was used for thermogravimetric (TGA) characterization of SOW, heating samples from room temperature to 700°C at 10 °C/min in N_2 atmosphere. Ten replicates were performed in order to measure the water amount of SOW. For comparison purposes,

bigger scale tests were performed by drying a pre-weighted amount of SOW (about 5 Kg) at 80°C to constant mass (which about took 24 h). Even in this case, ten replicates were performed.

Infrared spectra were recorded in the wavelength range between 4,000 and 400 cm^{-1}, using a Fourier Transform Infrared spectrometer (FTIR) Jasco 6300 and KBr round crystal window. Each measurement was obtained with 128 scans and 4 cm^2 of resolution.

Rheological analyses were carried out on a Rheometrics Ares rheometer. Dynamic tests were performed on PVA samples, in order to analyze the effect of the water amount on the viscosity of the sample. A double plate geometry was used, setting a gap of 0.3 mm, constant oscillatory amplitude (1%) and frequency (1 Hz). Tests consisted in a temperature ramp from room temperature to 110°C.

A DINO-LITE digital microscope was used to observe PVA samples with increasing water content. Images of all samples were obtained with a 50x magnification; afterwards, the average diameter of the pores was calculated by using the DinoCapture software.

Different mixtures of PVA and SOW were produced, by dissolution in water. Addition of water is required in order to reduce material viscosity, and allow an efficient processing of the material in a pressure free process. On the other hand, water can be removed after processing by heating to a temperature at which the rate of water evaporation is high enough. In any case, the maximum temperature attained during processing is much lower than that required for processing of PVA by conventional thermoplastic processing, which requires heating above the melting of PVA (which is about 225°C). Processing at low temperatures is essential in order to avoid degradation of the SOW. However, the SOW itself is characterized by high amount of water, which contributes to the added water in order to reduce the viscosity of the suspension. Therefore, it is very important to point out the difference between the total amount of SOW added in the mixture, also including water, and the amount of dried SOW (dSOW) which remains in the sample after water evaporation. If w_{dSOW} is the required weight fraction of dSOW in the final mixture, the actual amount of SOW to add to the mixture, M_{SOW} also including water, can be estimated from:

$$w_{dSOW} = \frac{M_{dSOW}}{M_{tot}} = \frac{(1-w_{H2O,SOW})M_{SOW}}{M_{tot}} \tag{1}$$

where $w_{H2O,SOW}$ is the water content of SOW. Inversion of Eq. (1) yields the weight fraction of SOW to add to the mixture:

$$w_{SOW} = \frac{M_{SOW}}{M_{tot}} = \frac{w_{dSOW}}{(1-w_{H2O,SOW})} \tag{2}$$

On the other hand, the final weight fraction of water can be estimated as:

$$w_{H2O} = \frac{M_{H2O,SOW}+M_{H2O,added}}{M_{tot}} = \frac{w_{H2O,SOW}M_{SOW}+M_{H2O,added}}{M_{tot}} \tag{3}$$

where $M_{H2O,SOW}$ is the water amount in SOW and $M_{H2O,added}$ is the amount of added water. Inversion of Eq. (3) yields the weight fraction of added water:

$$w_{H2O,added} = \frac{M_{H2O,added}}{M_{tot}} = w_{H2O} - w_{H2O,SOW}w_{SOW} \tag{4}$$

Therefore, Eq. (2) and Eq. (4) were used for proper preparation of the different mixtures as reported in Tab. 1, where the composition of each sample is referred to the dried fraction of SOW, dSOW. The first four samples were obtained by varying the amount of water for a fixed 1:1 ratio between PVA and dSOW, whereas the other samples are characterized by a constant water amount, and varying proportions between PVA and dSOW.

All the mixtures were poured in silicon molds and put in a static oven at 65°C for the time necessary to complete the water evaporation. For comparison, mixtures with only PVA and water were also produced. Also, two sets of 5 samples (with and without SOW) were pressed by using a CAMPANA hot press, in order to obtain thick specimens without porosity. For this purpose, samples were placed in a 0.5 thick mold and heated up to 200°C in a forced convection oven, followed by pressing in a hot press (Campana, Italy) under 20 tons force.

Table 1: Composition of mixtures

Formulation	Water (%)	PVA (%)	dSOW (%)
W66_P17_dSOW17	66	17	17
W60_P20_dSOW20	60	20	20
W56_P22_dSOW22	56	22	22
W50_P25_dSOW25	50	25	25
W50_P50	50	50	0
W50_P33_dSOW17	50	33	17
W50_P30_dSOW20	50	30	20
W50_P20_dSOW30	50	20	30

Flexural tests were performed on samples obtained after inertisation, using a LloydLR5K and a crosshead speed of 1.5 mm/min.

3 Experimental Results

Fig. 1 shows a typical TGA curve for SOW. As it can be observed, the SOW shows a first weight loss at temperatures up to 150°C, which is due to water evaporation. A second weight loss observed between 250°C and 650°C is due to degradation of the organic fraction of the SOW. The weight loss corresponding to water evaporation was estimated to be $65 \pm 6\%$, whereas the weight loss of the second degradation step leaves about 8% of solid residue at temperatures higher than 700°C. Referring to Eq. (4), the value of $w_{H2O,SOW}$ is also highlighted in Fig. 1. Also, the results of Fig. 1 highlight the relevance of low processing temperatures. In facts, as SOW is mixed with PVA, processing by conventional thermoplastic routes would require heating to temperatures higher than 230-240°C, which in turn could result in SOW degradation.
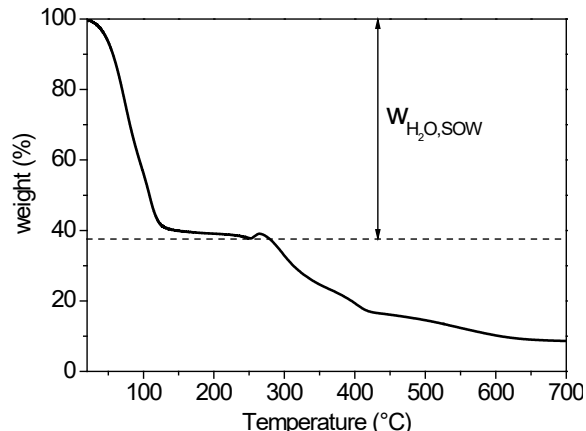
Figure 1: TGA curve of SOW

Bacterial analyses were carried out on SOW before and after autoclave treatment, by spotting the samples on an L agar slab and incubating at 37°C overnight. Results, shown Fig. 2, indicates a complete removal of the bacterial load with autoclave sterilization.
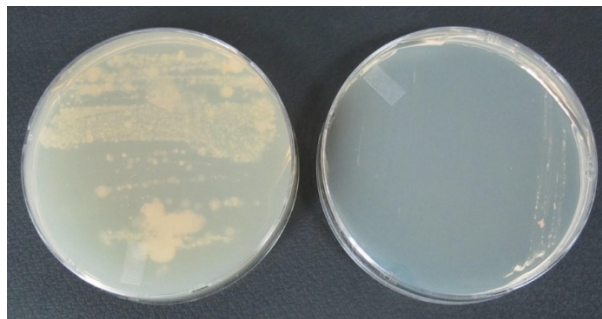
Figure 2: Bacterial analyses on SOW before and after autoclave treatment

FTIR analyses carried out on SOW before and after the autoclave cycle are reported in Fig. 3, showing that the autoclave treatment involves the complete sterilization of the SOW without any significant modification in its chemical composition. In fact, besides a light decrease of the intensity, all the typical peaks of the SOW are visible at the same wavenumber.

In particular, the two peaks related to the C=O and C=C stretching are well visible in 1900-1400 cm^{-1} region for the SOW after autoclave cycle. For the SOW before autoclave cycle, the C=O stretching peak at 1730 cm^{-1} is partially covered by the C=C stretching 1640 cm^{-1}.
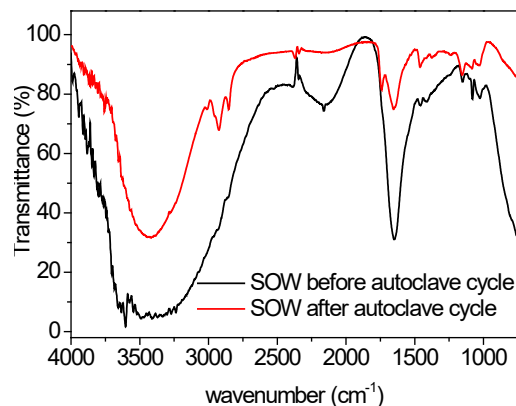

Figure 3: DSC analysis on SOW before and after autoclave cycle

The typical evolution of the viscosity of PVA dissolved in water during thermal treatment up to 105°C is reported in Fig. 4 for two different amounts of water, 50% and 66%. As it can be observed, for the sample characterized by the lower water amount, the viscosity initially decreases, as a consequence of the viscosity decrease of water. After reaching a minimum value, viscosity increases due to water evaporation, which, at 105°C, is almost complete. Therefore, PVA/SOW blends can be processed, upon addition of water, at much lower temperatures than those required for standard thermoplastic processing. In addition, comparison with the TGA results of Fig. 1 indicates that processing of PVA/SOW/water suspensions can be done at temperatures much lower than the degradation temperatures of SOW.

The room temperature viscosity of water/PVA solution decreases as the water content is increased to 66%, as clearly observed in Fig. 4. On the other hand, as temperature increases, the viscosity reduction is less evident compared to the sample with 50% of water. This is attributed to the faster evaporation of water, which yields a viscosity increase, and counterbalances the viscosity reduction of water. This effect if also highlighted by the sharp increase in slope for W66_P34, indicating a faster water evaporation if compared to W50_P50 sample.
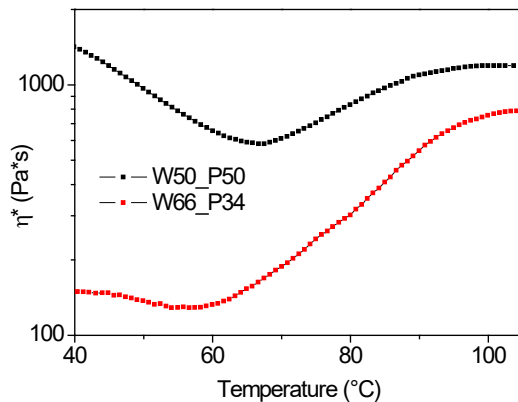
Figure 4: Rheological analyses on PVA samples with different water amounts

The amount of water added during mixing of PVA and SOW also has a significant influence on the morphology of the produced samples after water evaporation. This is highlighted in Figs. 5(a)-5(d), which shows the optical microscopies of neat PVA samples with different water contents. As water evaporates, voids are formed inside the bulk of the polymer. A faster evaporation of the water, resulting from a higher initial content of water, as highlighted from the results of Fig. 4, involves the formation of bigger pores, as shown by comparison between Figs. 5 (a)-5(d) and the corresponding average pore dimension, reported in Tab. 2.
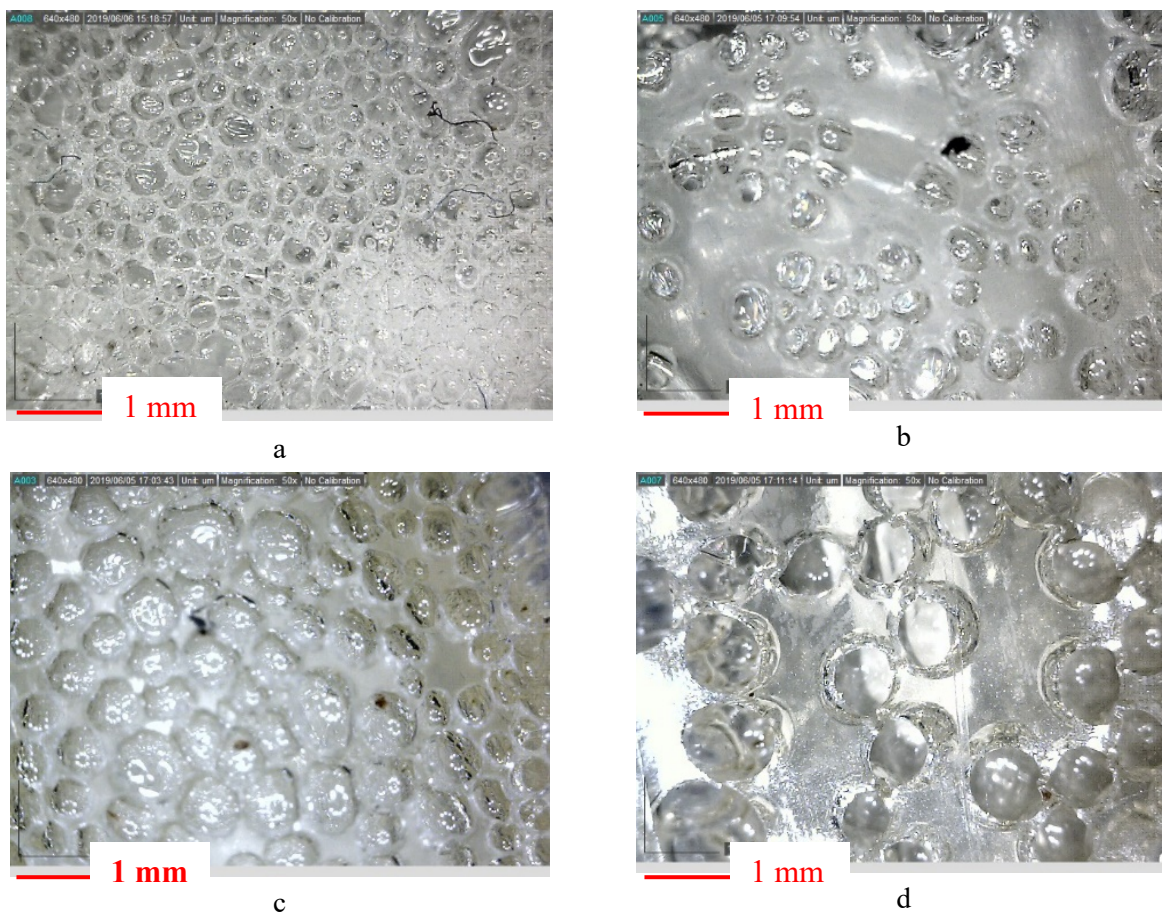

Figure 5: 50X magnification on PVA samples with a) 50% of water, b) 56% of water, c) 60% of water, d) 66% of water

Table 2: Average pore diameter of PVA samples at different water contents

Sample	W50_P50	W56_P44	W60_P40	W66_P34
Average pore diameter (mm)	0.39 ± 0.06	0.50 ± 0.08	0.71 ± 0.08	1.15 ± 0.12

The typical stress-strain curves for samples with different amounts of water and a fixed 1:1 ratio between PVA and dSOW, are reported in Fig. 6.
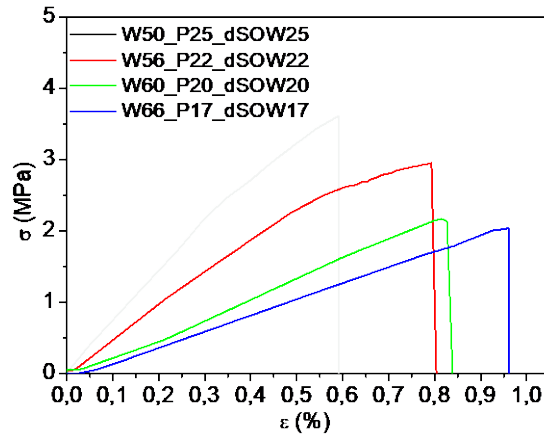
Figure 6: Stress strain curves of PVA-dSOW blends with different amount of water

The mechanical properties of PVA/dSOW blends are reported Fig. 7.

Also in view of the relatively wide error bars associated to measurement, one-way analysis of variance (ANOVA) was performed in order to better highlight the effect of the water amount on each mechanical characteristic.

The significance of water amount was tested by calculating the *F* value, as the ratio of the variance between the means to the variance of the experimental error. The F value was then used in order to calculate the corresponding p value, which was then compared with the confidence level, $\alpha = 0.05$. According to ANOVA, $p > \alpha$, corresponds to the null hypothesis (equivalence of the means), whereas $p < \alpha$ indicates that the population means are significantly different [23].

The p value calculated for the flexural modulus, strength and strain at break are $p < 1*10^{-5}$, $p = 0.0193$ and $p = 0.0005$, in any case much lower than the confidence value, indicating the statistically relevant effect of the amount of water on each of the flexural property of the material.

Therefore, in any case, for all the produced samples, flexural modulus (Fig. 7(a)), strength (Fig. 7(b)) and strain at break (Fig. 7(c)) decrease with increasing water amount.
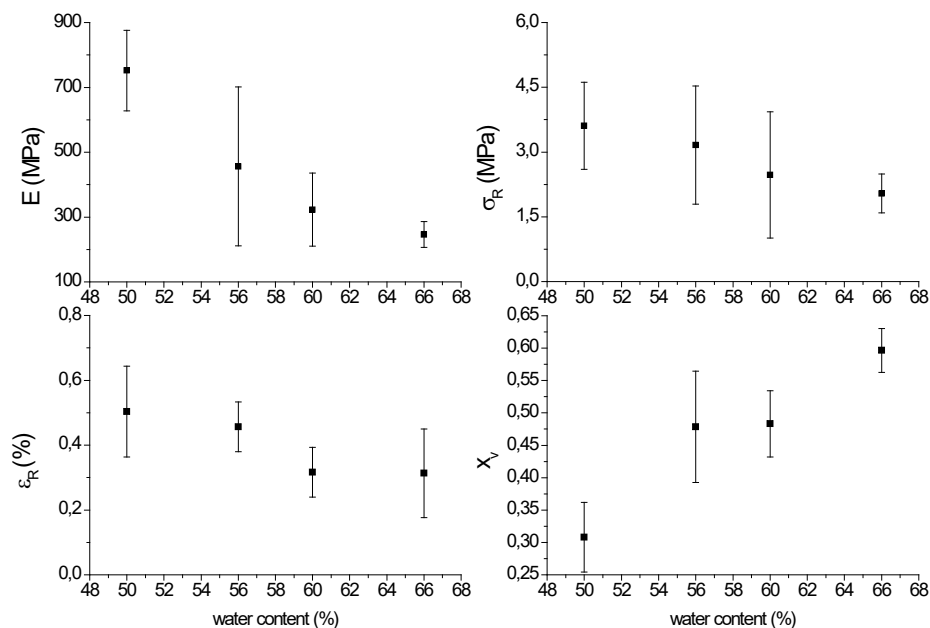
Figure 7: Mechanical and physical properties of PVA/dSOW blends with different amount of water

The decrease of the mechanical properties can be explained by considering the results for the void fraction, which was estimated as:

$$x_v = 1 - \frac{\rho}{\rho_T} \tag{5}$$

where ρ is the measured density, and ρ_T the theoretical density, estimated from the rule of mixtures, by considering a PVA density of 1.26 g/cm^3, from the materials technical data sheet, and a measured density for dSOW of 0.99 g/cm^3. The results reported in Fig. 7(d) clearly show that the void fraction increases as the water amount increases. This can be explained by considering the higher amount of water released during evaporation, which remains partially entrapped in the polymer matrix. Besides this, increasing the water content involves a significant increase of the pore dimension, as reported in Fig. 5. Both the increase of the void fraction, and the increase of the pore dimensions, which are observed as the water amount increases, are responsible of the decrease of the mechanical properties reported in Fig. 7 .

For comparison purposes, samples were produced by compression molding of PVA and PVA/dSOW with a ratio 1:1 and 50% of water. Results reported in Fig. 8 and Tab. 3 show that neat PVA is characterized by a flexural modulus comparable to values typically reported in literature for thin films [24]; on the other hand, the lower values for flexural strength and strain at break are due to the incomplete densification of PVA during the compression molding; in facts, as observed in Tab. 3, the density attained at the end of the process is lower than the theoretical value for PVA, which is 1.26 g/cm^3, and allows to estimate a void fraction of 0.18 for W50_P50. The flexural modulus of compression molded samples is not significantly modified upon addition of dSOW, as evidenced by the results of Fig. 8 and Tab. 3; on the other hand, the flexural strength and strain at break are significantly reduced compared to neat PVA. However, density data reported in Table show that addition of SOW allows to significantly increase the density of PVA; from Eq. (5) and the rule of mixture, the void fraction of sample W50_P25_dSOW25 approaches zero. In a previous work [22] this was shown to depend on the different rate of water release for neat PVA and PVA_dSOW. In the case of neat PVA, water is absorbed in the hydrosoluble PVA molecules, and therefore released very fast at high temperatures, which causes high amounts of steam to be entrapped in the bulk of the polymer. Addition of SOW reduces the temperature of water evaporation, which occurs more slowly already during the heating stage, thus allowing for a more efficient stem removal. Therefore, the results obtained on compression molded samples indicate that SOW is able to reduce the void fraction of PVA samples; despite this, its addition involves, a reduction of the mechanical properties. However, the mechanical properties of

the PVA/SOW blends are better than those reported for our PVA based blends, as for example PVA/ chitosan, which was shown to reduce the strength by a factor of 50%, the strain at break by a factor of almost 90% [25]. Addition of poly(ethylene glycole) (PEG) in lower amounts (15%) than those used in this work for SOW was also found to reduce the strength and strain at break by a higher extent than the values reported in Tab. 3 [26].
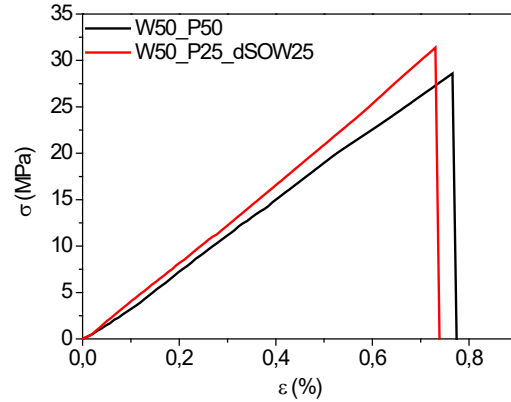

Figure 8: Stress-strain curves of compression molded PVA and PVA_dSOW

Table 3: Mechanical properties of compression molded PVA and dSOW

	E (MPa)	σ_R (MPa)	ε_R (%)	ρ (g/cm³)
W50_P50_	4025 ± 292	35 ± 8.99	8.66E-1 $\pm$ 2.51E-1	1.04 ± 0.04
W50_P25_dSOW25	4201 ± 298	28.2 ± 4.5	7.79E-1 $\pm$ 5.60E-2	1.16 ± 0.07

The mechanical properties of sample W50_P25_dSOW25 produced by compression molding are much higher than the corresponding properties of the same sample produced by pressure-free process, as highlighted from the results reported in Fig. 9. In any case, the difference in the mechanical properties can be explained by considering the high void fraction of the sample obtained by pressure free process.
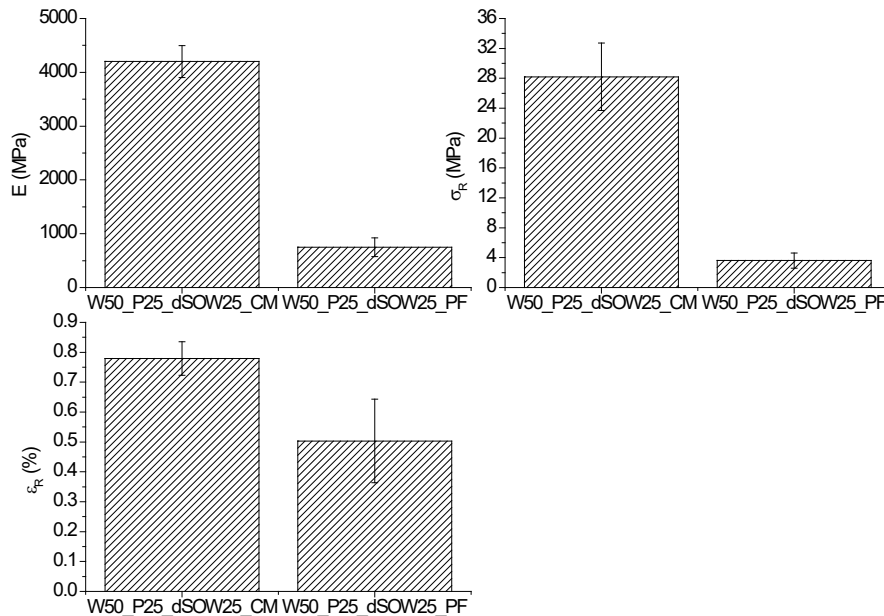

Figure 9: Comparison in mechanical properties of sample W50_P25_dSOW25 produced by compression molding (W50_P25_dSOW25_CM) and pressure-free process (sample W50_P25_dSOW_PF)

On the other hand, it was not possible to process by pressure-free technologies the PVA/dSOW blends at amounts of water than lower than 50%. Therefore, 50% of water was chosen as good compromise between mechanical properties and processability. In the following analysis, samples were produced by varying the amount of dSOW compared to PVA. Typical stress-strain curves are reported in Fig. 10 and resulting mechanical properties are reported in Fig. 11. For comparison purposes, a sample, labeled as W50_P50, obtained without addition of dSOW, was also produced.
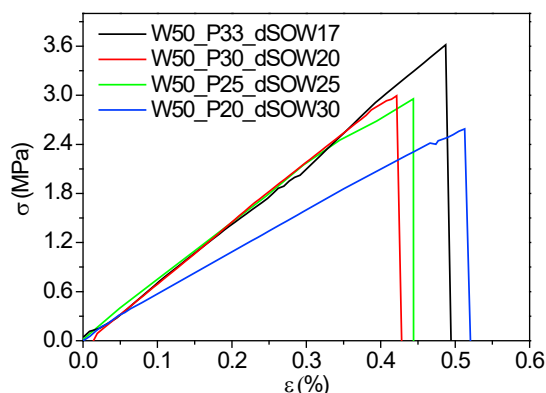

Figure10: Stress strain curves of PVA/dSOW blends with different ratios between solid fractions
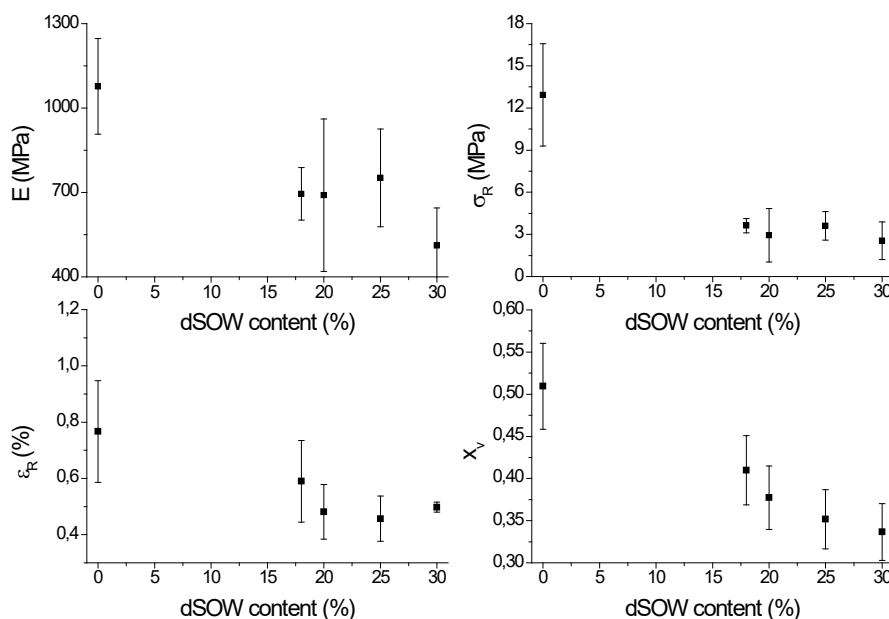

Figure 11: Mechanical properties and density of PVA-dSOW blends in different amounts

As it can be observed, each of the flexural properties of PVA/dSOW is lower than the corresponding value for neat PVA. In facts, ANOVA provided for the flexural modulus, strength and strain at break $p = 0.0014$, $p < 1*10^{-5}$ and $p = 0.0029$ respectively, which indicates the statistically relevant effect of the addition of SOW on the mechanical properties of PVA.

However, there is no significant difference between the flexural properties of the samples obtained at different amounts of dSOW. In facts, one-way ANOVA performed excluding the sample at 0% dSOW, and therefore with four different levels, corresponding to the four different amounts of dSOW, provides $p = 0.21$, $p = 0.47$, and $p = 0.18$ for the flexural modulus, strength and strain at break. Therefore, in each case

the p value is higher than the confidence level $p = 0.05$, indicating that the difference between the samples obtained at different amounts of dSOW is not statistically significant. In contrast, the effect of the amount of dSOW on the void fraction (xv) of PVA samples is highlighted in Fig. 11(d). Addition of dSOW involves a significant decrease of the void fraction of PVA_ dSOW blends; this is attributed to the aforementioned effect of dSOW, which is able to reduce the temperature of water evaporation, thus allowing for a slower steam release in the bulk of the polymer. Therefore, despite a decrease of the void fraction, addition of dSOW involves a decrease of the flexural properties of PVA; this is in agreement with the results obtained on compression molded samples, reported in Tab. 3. This is due to the lower mechanical properties of dSOW compared to neat PVA.

4 Conclusions

This work was focused on the production of blends between PVA and organic fraction of the municipal solid waste, aimed at stabilization of municipal solid waste for reduction of odors and percolate. Among other polymers, PVA was chosen as matrix, due to its water solubility, which allows blending with SOW without any drying, energy consuming process. On the other hand, further addition of water to the blends allows processing by pressure free process at room temperature, which does not involve any degradation of SOW.

Before blending with PVA, SOW was subjected to an autoclave cycle, which allowed obtaining a complete bacterial removal. Then, SOW was blended with PVA, by varying both water and SOW amounts, and processed by a pressure free process.

Viscosity tests showed that during thermal treatment, water evaporation involves a viscosity increase, finally leading to setting of the blends. As the water amount is increased, water evaporation occurs at lower temperatures, leading to more porous structures, characterized by bigger pores.

Flexural tests highlighted the relevance of porosity on the evolution of the mechanical properties of the blends. In general, mechanical properties decreased upon increasing of water content, which was attributed to the higher porosity of the produced samples. However, once the amount of water remains constant, the mechanical properties of the blends were poorly dependent on the relative proportion between PVA and dSOW. In particular, addition of SOW, even in small amount, causes a significant decrease of the flexural strength. The flexural modulus and strain at break show a reduction by a factor of about 20-25%. On the other hand, there is no further reduction of the properties when the amount of SOW is increased to values up to 50%. Therefore, despite the decrease of the mechanical properties, the proposed approach allows to transform the poorest fraction of the solid urban waste into a valuable material, contemporarily eliminating the problems associated to smell and percolate release, and also allowing to reduce the costs of PVA.

Therefore, by properly tailoring the porosity of the material, and its mechanical properties, the developed PVA/SOW blends could find use in different industrial applications. Materials characterized by higher porosity, and therefore lower mechanical properties, could find used as insulating panels, whereas materials characterized by lower porosity, and therefore higher mechanical properties, could be used for the production of garden furniture.

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