

BIO-COMPOSITES BASED ON POLY (VINYL) ALCOHOL (PVA) AND FOOD WASTES

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Abstract - This work is aimed to the production of new green composite materials based on a water soluble polymer, PVA, and different natural fillers. Two natural additives, such as shredded walnut shells and mixed food waste, were used to produce bio-composite systems. Both additives, deriving from food industry wastes, were added in a PVA/water solution, which allowed to produce samples by the use of a pressure free process. Rheological analysis was performed in order to study the evolution of the material viscosity during thermal treatment, aimed at water removal. Samples obtained were characterized by means of differential scanning calorimetry (DSC), showing an improvement of the glass transition temperature brought by the addition of walnut shells. Finally, flexural tests were carried out on samples obtained after the incorporation of the different additives in PVA and compared with the mechanical properties of the neat matrix. Results obtained indicate the potential improvement brought by the addition of walnut shells, which allow to increase the flexural modulus, at the expenses of a reduction of flexural strength.

Keywords - PVA, green-composites materials, mechanical properties

I. INTRODUCTION

Unlike other polymers, produced starting by their monomer, Polyvinyl alcohol (PVA) is obtained by the ester interchange with methanol of acetate groups in presence of anhydrous sodium methylate or aqueous sodium hydroxide[1]. Because of its non-toxic nature, PVA is employed in several industrial and scientific fields. Since the first years of 20th century PVA is used for food packaging and medical disposals[2], and due to its high biodegradability, it is often mixed with other biopolymers for the production of hydrophilic films or in order to improve the mechanical response of the material[3]. PVA is highly soluble, so it can be easily processed at low temperatures, through the addition of water, which brings a liquid solution, at relatively high concentrations of PVA, characterized by very low viscosity[4] and, in addition, very low cost and low gas permeability towards oxygen and carbon anhydride. Moreover, PVA can be added to fibre-reinforced composites in order to improve the fibre-matrix interfacial properties, through the development of strong bonds between its hydroxyl groups and the functionalized fillers[5][6].

On the other hand, PVA lacks adequate mechanical properties in different loading conditions[7]: therefore, many studies were carried out in order to improve its mechanical properties, through the addition of different fillers[8]. For instance, multiwall carbon nanotubes were added in different amounts to PVA, which allowed to increase stiffness and hardness of the polymer[9]. Other studies were focused on the addition of fully exfoliated graphene oxide (GO) sheets and multi-walled carbon nanotubes (CNTs), thus obtaining a significant improvement in

mechanical properties if compared to neat PVA films[10].

Alternatively, the production of bio-composites requires the addition of natural fillers or fibers, thus avoiding issues related to safety and toxicological impact, still preserving the excellent water solubility and biodegradability of PVA. Therefore, several studies were performed on the addition of naturally-derived reinforcements to PVA matrix.

Biodegradable cornstarch/PVA blends were prepared and characterized by many authors. The produced blends are characterized by a high hydrophilicity and poor mechanical properties, which, however, can be significantly improved by the methylation of cornstarch, as reported by Zhao Guohua et al.[11].

Addition of methylcellulose (MC) was shown to improve mechanical properties and impart to the material a more hydrophobic behavior[12], although many efforts should be carried out in order to improve the miscibility of the two components. Furthermore, PVA nanocomposites were produced by adding Bamboo Charcoal (BC) nanoparticles via solution casting. Authors found an increase of lamella size of PVA by the incorporation of BC, which in turn allowed for significant improvement in tensile strength. Also, the incorporation of BC nanoparticles was found to enhance the elastic moduli of both crystalline and amorphous phases of PVA[13].

On the other hand, the possibility to reinforce PVA by means of food wastes was not yet fully investigated. The food waste recycling for this application assumes a primary importance, since it

allows both the reinforcement of a matrix and the increase of the efficiency of waste management with the reduction of its negative effects on the environment and on population. This work was therefore focused on the improvement of PVA mechanical properties by the addition of natural fillers derived from selected or mixed solid urban waste. The PVA blends obtained, characterized by a very high loading of natural fillers, were analyzed in terms of mechanical and thermal properties.

II. MATERIALS AND METHODS

PVA is Kuraray Poval 3-85, a partially saponified grade of polyvinyl alcohol, supplied as fine powder/granules with a bulk density of 0.4-0.6 gcm⁻³, a degree of hydrolysis of 84.2-86.2 mol% and a viscosity in a 4 % aqueous solution of 3.4 - 4.0 mPa*s at 20 °C. Walnut shells (WS) and mixed organic waste (MW) were obtained by the recycling of food industry.

PVA composite samples were obtained by mixing PVA and WS or MW in a ratio 1:1, in a water solution at 50% water. The mixtures, compositions reported in Table I, were realized by mixing for 10 min at 60 rpm in a Haake Rheocord mixer at room temperature. For comparison, mixtures with only PVA and water were also produced. After mechanical mixing, all the mixtures were poured in silicon molds and then kept in oven at 70°C until complete evaporation of the water.

Table I. Composition of mixtures

	Water (%)	PVA (%)	Walnut shells (WS) (%)	Mixed organic waste (MW) (%)
PVA	50	50	0	0
PVA_WS	50	25	25	0
PVA_MW	50	25	0	25

Rheological analyses were carried out on a Rheometrics Ares rheometer. Dynamic temperature ramp tests were performed on PVA samples, in order to analyze the water evaporation during heating scan from 25 °C to 70 °C at 3°C/min on a parallel plate geometry, with a gap of 0.3 mm, constant oscillatory amplitude (1%) and frequency (1 Hz).

DSC analysis, performed by Mettler Toledo 822 (Mettler Toledo, Greifensee, Switzerland) instrument under a nitrogen flux of 60 ml/min, applying heating scan from 20 to 180 °C, with heating rate of 10 °C/min.

Flexural tests were performed on 100x10x3mm, using a Lloyd LR5K and a crosshead speed of 1.5 mm/min. Before testing, samples were kept for 24h at 70°C in order to completely dry.

All the results are averaged on at least six samples.

III. RESULTS AND DISCUSSION

In order to evaluate the rheological properties of the blends, the analyses were performed on neat PVA samples with 50% of water and PVA/water samples with both additives, ranging between 20 and 70°C, as reported in Figure 1.

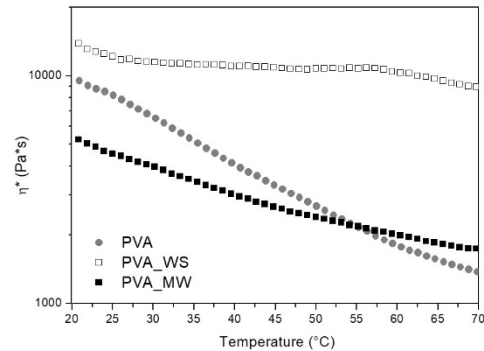


Figure 1: Rheological analyses on neat PVA and PVA mixed with walnut shells and mixed organic waste.

The viscosity evolution during heating was found to be significantly different for the different samples. Results reported in Figure 1 show that, at room temperature, the viscosity of PVA_WS is much higher than that of the two other systems, neat PVA and PVA_MW. This is attributed to the water absorption by PVA and PVA_MW, in contrast to PVA_WS, which absorbs much lower amounts of water.

Moreover, as reported in Figure 1, PVA shows a marked decrease of viscosity with increasing temperature; such decrease is mainly due to the viscosity decrease of water during heating. At higher temperatures (not shown in Figure 1) water evaporation causes a significant increase of the viscosity of PVA sample.

For PVA_MW, the slope of the viscosity curve is reduced, indicating that the effect of water viscosity decrease is counterbalanced by viscosity increase due to water evaporation. For PVA_WS, a further decrease of the slope of the curve indicates that in this sample water evaporation occurs at much lower temperatures compared to the other two samples.

The results of Figure 1 can be correlated to the affinity between the material and water; for neat PVA, which is water soluble, a complete water adsorption causes a better retention of water during heating. Therefore, water evaporation occurs at much higher temperatures. Upon addition of MW, which is not completely water soluble, but absorbs some water, water release occurs, quite slowly, during heating. For WS, which does not absorb water, water release occurs much faster during the heating stage.

DSC analyses were carried out on neat PVA and PVA_WS and PVA_MW samples, in order to

evaluate the glass transition temperature (T_g) of the mixture. The T_g values are reported in Table II.

Table II. Glass transition temperature for neat PVA and PVA composites.

	Onset (°C)	Midpoint(°C)	Endset (°C)
PVA	45.18	49.41	53.55
PVA_WS	53.20	61.73	72.07
PVA_MW	49.27	53.41	61.94

As shown in Table II, an increase in T_g from about 49°C to about 61°C was obtained with the addition of walnut shells to PVA. In contrast, no significant change in the glass transition was observed upon addition of MW to PVA.

The development of a pressure-free process for the production of such components poses severe issues related to the void amount in the produced samples. To this purpose, density measurements were performed by using a pycnometer, in order to evaluate the density ρ of the component; afterwards, the theoretical density ρ_T of each mixture was calculated by using:

$$\rho_T = \rho_{PVA} v_{PVA} + \rho_f v_f \quad (1)$$

where:

- ρ_f and ρ_{PVA} are the density of the filler (measured to be 0.99 g/cm³ for the solid waste and 1.50 g/cm³ for the walnut shells) and PVA (1.19 g/cm³ from the materials technical data sheet), respectively;
- v_{PVA} and v_f are the volume fraction of PVA and fillers, respectively.

Once the theoretical density was calculated, the void fraction v_v was estimated as:

$$v_v = 1 - \frac{\rho}{\rho_T} \quad (2)$$

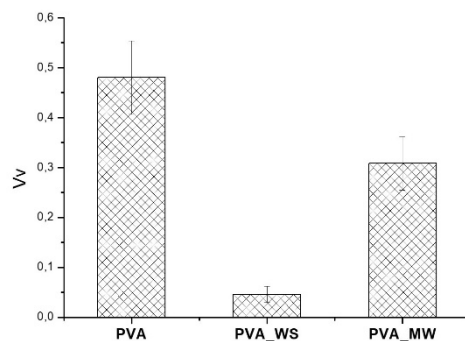


Figure 2. Void fraction (v_v) for PVA samples composites

where ρ is the measured density of the different samples, obtained as the average of ten measurements. The void fraction for the produced

PVA samples obtained by the use of (2) is reported in Figure 2.

By considering the graph reported in Figure 2, the addition of walnut shells, in particular, allows an evident reduction of the voids compared to neat PVA based samples. This result confirms that the free-pressure process is efficient in order to realize a composite with higher consistence.

Flexural tests were carried out on samples with and without filler addition.

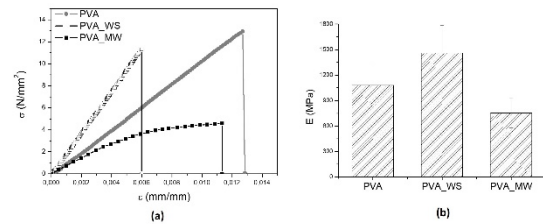


Figure 3: stress strain curves (a) and flexural modulus (a) of PVA samples with different filler.

By considering the stress/strain curves reported in Figure 3 (a), it is possible to note that the addition of different kinds of additive brings different mechanical properties to the system. In fact, by adding walnut shells to PVA, a modulus increase, and a strain at break reduction, is observed. The strength shows a negligible reduction. On the other hand, addition of MW involves a decrease of the flexural modulus and strength compared to neat PVA, but the strain at break is not significantly modified.

In view of the results reported in Figure 3 (b), the flexural modulus was plotted as a function of the void fraction calculated according to (2) and the results are reported in Figure 4, where, the strong correlation between modulus and void fraction can be observed.

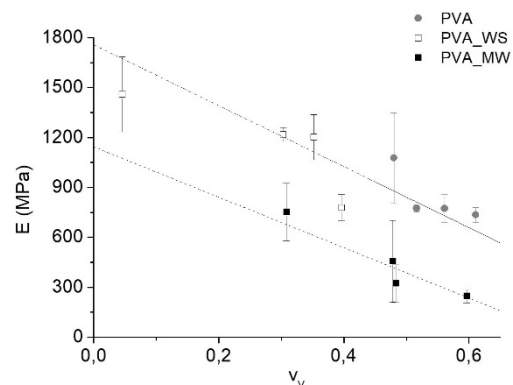


Figure 4: Flexural modulus as a function of void fraction

Based on the correlation between flexural modulus and void fraction reported in Figure 4, it seems that there is no direct dependence of the flexural modulus on the addition of WS; instead, addition of WS allows to reduce the void fraction, which in turn involves an increase of the modulus. This means, according to the

results of Figure 4, that, for the same value of the void fraction, there is no significant difference between the samples PVA and PVA_WS, whose data fall on a single master curve.

The situation when considering the PVA_MW is different; in this case, the data do not fall on a single master curve, and therefore the evolution of the flexural modulus can only be explained by considering that for the same void fraction, the modulus of PVA_MW is lower than that of PVA and PVA_WS.

The situation is quite different when considering the curves for flexural strength vs void fraction, reported in Figure 5.

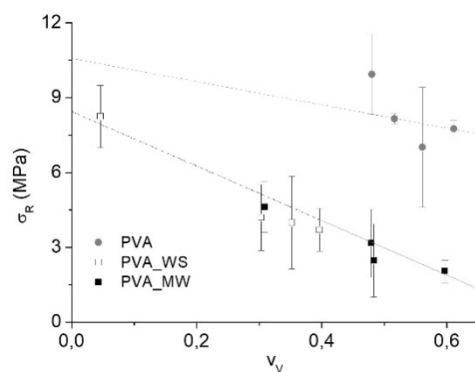


Figure 5 Flexural strength as a function of void fraction

In this case, the data for PVA_WS and PVA_MW fall on a single master curve. This indicates that the effect of adding WS of MW has no direct influence on the flexural strength; instead, different additives have a different effect on the void fraction, which in turn involves a change in the flexural strength. Therefore, for the same value of the void fraction, the flexural strength of samples PVA_WS and PVA_MW is not significantly different. In this case, the data of neat PVA do not fall on the same master curve, so for the same void fraction, the flexural strength of PVA is higher than that of PVA_WS and PVA_MW.

CONCLUSIONS

This work was focused on the reinforcement of PVA by the addition of natural fillers, derived from food industry wastes. In particular, the effect of a selected waste (walnut shells) and of a mixed waste on PVA properties was explored. PVA samples, with and without filler addition, were produced by the use of a pressure free process, taking advantage of the water solubility of PVA.

The evolution of viscosity was then studied by rheological analysis. Although a decrease in viscosity with the increase in water content was found for all the samples, higher viscosities were achieved with PVA with walnut shells, due to its lower absorption

of water. This in turn caused water release during the heating stage to occur at much lower temperatures. The release rate of water was found to deeply affect the porosity of the sample. In fact, a lower adsorption of water, causing water evaporation at lower temperatures, was found to have a beneficial effect on the reduction of porosity. Therefore, addition of food wastes caused a decrease of void fraction compared to neat PVA; however, the effect was more relevant for WS compared to MW.

The presence of voids significantly affected the mechanical response of the material. Due to the lower amount of voids, PVA_WS showed an increase in stiffness compared to neat PVA. In contrast, addition of MW caused a stiffness decrease compared to neat PVA. On the other hand, both additives caused a significant decrease of flexural strength compared to neat PVA. The experimental results obtained for PVA_WS show the potential of the developed approach for the production of PVA samples characterized by higher stiffness compared to neat PVA, as well a cost reduction and increase of the efficiency of waste management, with the reduction of its negative effects on the environment and on population.

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