A WOOD BIOPLASTIC COMPOSITE FROM SOY FLOUR AND SAWDUST: INFLUENCE OF PROCESS PARAMETERS AND COMPOSITION ON PHYSICAL AND MECHANICAL PROPERTIES

N.E. SUAREZ†, M.C. INALBON‡, C.I. MEYER†, S.A. REGENHARDT†, H.A. DUARTE†, M.A. ZANUTTINI‡ and A.J. MARCHI†

† *Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, CCT CONICET, Colectora Ruta Nacional 168, Km 0, Paraje El Pozo, (3000) Santa Fe, Argentina.*
amarchi@fiq.unl.edu.ar
‡ *Instituto de Tecnología Celulósica (ITC), FIQ-UNL, Santiago del Estero 2654, Santa Fe, Argentina.*

***Abstract*— The influence of the processing conditions and composition on the properties of biocomposites made of a bioplastic matrix from soybean protein, crosslinked with glutaraldehyde, reinforced with lignocellulosic material from wood sawdust (Wood Bio-Plastic Composite, WBPC) was investigated. The WBPCs were obtained by thermo-pressing applying a pressure of 70 bar at 100 and 120 °C for 30 or 60 minutes. Several test pieces were prepared varying the crosslinker/protein and protein/sawdust ratios. The samples obtained were characterized by scanning electron microscopy (SEM), flexural and hardness tests, and water absorption and swelling, according to international ASTM standards. The crosslinking of the protein improves the mechanical properties of the biocomposites, especially when contents of bioplastic matrix and crosslinker are low. It was also verified that the WBPCs prepared in this work recover their original shape and dimensions after immersion in water and subsequent drying. The results were explained considering crosslinker-protein and protein-sawdust interactions.**

***Keywords*— Bio-composites, bioplastic, soy protein, sawdust, thermo-pressing.**

I. INTRODUCTION

Currently, a wide variety of composite materials made of different types of polymeric matrices reinforced with glass fiber, carbon fiber or other synthetic or natural materials can be found. In this sense, wood is used in combination with thermosetting polymers to obtain composites such as plywood, particle board, oriented chipboard (OSB), wood cardboard (Hard-board) and medium-density fiberboard (MDF) (Stark et al., 2010). The most common uses of these composites are in sheathings, partition panels and furniture. For the manufacture of some of these composites, phenol-formaldehyde or urea-formaldehyde resins are used as adhesives agents of wood fibers, and to increase moisture resistance. In this regard, it is important to keep in mind that nowadays the use of formaldehyde is ruled by strict policies, since is considered a compound of high toxicity with carcinogenic properties (American Cancer Society, 2014).

Wood is also used in the form of sawdust (SD) or fines as reinforcing fiber of thermoplastic polymers, such as PE, PP, PET and PVC, in order to obtain WPCs (Wood Plastic Composites). In these cases, it is necessary to use additives to improve the adhesion between the hydrophilic wood fibers and the polymeric hydrophobic matrix (Schwarzkopf and Burnard, 2016; Rahman et al., 2013). WPCs are a homogeneous and intimate mixture of synthetic and biomass derived materials, where the encapsulation of the wood by the non-biodegradable polyolefin matrix leads to these composites to be non-recyclable (Chan et al., 2017).

All the matrices mentioned above are petroleum derived compounds, which implies not only the use of a non-renewable resource, but also contribute to the deepening of the environmental pollution. Besides, in general, the obtained composites cannot be reprocessed or recycled. Therefore, it becomes necessary to find alternative raw materials to produce WPC-like parts (Mitra, 2014; Netravali and Chabba; 2003). Nowadays, there is a great interest in developing green composites using sustainable, biodegradable, environment friendly and renewable fibers and resins, particularly derived from biomass. A wide variety of biodegradable matrices, such as starch, cellulose and proteins, mixed with natural fibers, such as flax, ramie, kenaf, jute, sisal and wood fines, have been used to fabricate green composites or biocomposites (Netravali and Chabba, 2003; Mitra, 2014). An attractive alternative are the ecocomposites where both the matrix and the reinforcement are obtained from renewable resources that are completely biodegradable, thus achieving environmental and ecological advantages over conventional composites (Mitra, 2014; Bogoeva-Gaceva et al., 2007). In this regard, wood fiber based ecocomposites or biocomposites, also known as WBPCs (Wood Bio-Plastic Composites), are of particular interest.

According to Song et al. (2011), soy protein isolate (SPI), a byproduct of soybean oil extraction, has a good biodegradability, biocompatibility and processability, making it a good candidate to replace synthetic polymers. However, its mechanical properties and water resistance are not good enough for most of its possible applications. One way in which these properties can be improved is by crosslinking. The most commonly used

crosslinkers are dialdehydes (Bai and Liu X, 2017; Wong and Jameson, 2012). In particular, glutaraldehyde (GTA) finds several applications as an SPI crosslinker to form better adhesives (Wang et al. 2006). The production of WBPCs from SD and SPI, coming from wood and bio-oil local industries, is investigated in this work. The aim of this work is to analyze and explain the influence of the process conditions and composite composition on the physical and mechanical properties of WBPC obtained from the mixture of a bioplastic (SPI), cellulosic fibers (SD) and a crosslinking agent (GTA), using thermo-pressing molding.

II. METHODS

A. Materials and Biocomposites preparation

Soy flour (SF) with 45% protein, 12.5% moisture and 1.2% ethereal extract was provided by "*La Agrícola Regional*" (Entre Ríos, Argentina). As reinforcement fiber, sawdust (SD) coming from the eucalyptus sawmill industry was used. A 50% GTA aqueous solution (GTA, Serquim) was used as crosslinker source.

The protein was extracted from the SF using NaOH (p.a., Cicarelli) and HCl (p.a., Cicarelli) aqueous solutions, following the procedure proposed by L'hocine et al. (2006). Initially, 100 g of SF were dispersed in hot water at a ratio 1:15. The extraction of the SF protein was carried out at 60 °C, keeping the pH at 9.0 with 2N NaOH aqueous solution, while stirring for 45 min. Then, the slurry was allowed to stand at room temperature for 15 min and then the liquid containing the protein extracted from the solid residue was filtered off. Subsequently, 2N $HCl_{(aq)}$ was added to the filtrate until reaching the isoelectric point of the proteins (pH ≅ 4.5), in order to achieve their precipitation. The suspension obtained was kept under stirring for other 45 min at room temperature. Afterwards, it was cooled down and maintained at 4 °C during 4h, and then brought to -15 °C for other 16 h. Finally, the suspension was unfreeze to recover the precipitated proteins by removing the supernatant. In this way, an isolated soy protein suspension with a concentration of 8% w/w was obtained.

WBPCs were prepared using a heated hydraulic press, maintaining a pressure of 70 bar, at 100 °C or 120 °C, during 30 or 60 minutes. The final temperature was always reached with a heating rate of 2.5 °C/min. The specimens were prepared with matrix/fiber ratios (SPI/SD) of 20/80, 35/65, 50/50 and 65/35, and varying the ratio of crosslinking agent to soy protein isolate (GTA/SPI) in the 0-1 g/g range.

B. Characterization methods

Flexural experiments were performed using the three-point test, according to the procedure described by ASTM D1037 (1999). Before the test, the specimens were conditioned at 23 °C and 50% relative humidity (RH). The flexural strength or modulus of rupture (MOR) and the modulus of elasticity (MOE) were determined by quadruplicate for specimens of rectangular sections, 50 mm width and 3-5 mm thickness, and a span 24 times the thickness of the specimen, using a universal Instron 1137 machine, at a speed of 5 mm/min, and a compression cell of 2000 kgf capacity.

A modified Janka method was applied to determine the hardness (H) of the 50 mm x 50 mm specimens, according to Standard ASTM D1037 (1999), using a universal INSTRON 1137 testing machine. The load was applied at a rate of 5 mm/min, using a spherical indenter with a diameter of 11.29 mm. The hardness value was expressed as the load applied to get the imprint to penetrate a depth equal to half its diameter.

The water absorption and swelling of the WBPCs were determined by quadruplicate using the procedure established in ASTM D1037 (1999). The specimens of 50 mm x 50 mm were conditioned at 23 °C and 50% RH, and then were weighted for determining the initial mass (m_1). Next, the specimens were immersed in distilled water at 20 ± 1 °C during 2 h. Then, they were removed and the water excess eliminated. Finally, their mass was determined (m_2). This procedure was repeated to determine the final weight after 24 h (m_3). Water absorption (W_a) was calculated with Eq. 1, where i = 2 corresponds to the determination at 2 h and i = 3 at 24 h.

$$Wa = \frac{m_i - m_1}{m_1}.100 \quad (1)$$

In each of the water absorption measurements, the thickness of the specimens was also measured: before immersion (t_1), after 2 h immersion (t_2) and after 24 h immersion (t_3). To determine the residual swelling in the specimens after the absorption tests, they were reconditioned by drying in an oven at 105 °C for 24 h and cooling to room temperature in a desiccator. Then, the final thickness (t_4) was measured. The respective thickness swellings (TSw) were calculated with Eq. 2, where i= 2 corresponds to the measurement at 2 h, i= 3 at 24 h, i= 4 to the residual swelling.

$$TSw = \frac{t_i - t_1}{t_1}.100 \quad (2)$$

The average values estimated in the physical and mechanical characterization of the specimens were compared by applying ANOVA analysis, in order to determine whether they are significant different or not.

The compatibility and cohesion studies between the matrix and the fibers were carried out by scanning electron microscopy (SEM), in a PhenomWorld ProX model equipment operated at voltages between 5 and 15 kV. Since WBPCs samples are non-conductive, they were submitted to drying and subsequent surface coating with gold by sputtering, prior to microscopic observations.

III. RESULTS

A. Mechanical properties

The results obtained in the mechanical tests with WBPCs obtained at 100 °C and 120 °C, with different SPI/SD and GTA/SPI ratios, are shown in Fig. 1. It can be noticed that for samples without crosslinker, i.e. GTA/SPI = 0, at the same SPI/SD, the hardness (H) was lower when the thermo-pressing temperature was

120ºC. On the contrary, the modulus of rupture (MOR), for the same SPI/SD ratio, increases with temperature. One possibility to explain these results is that the temperature-induced denaturation of proteins is greater at 120 °C than 100 °C. In other words, the structure of proteins unfolds more at 120 °C than at 100 ºC, favoring the interaction and cross-linking between the denatured protein chains, specially, in the case of branched proteins containing secondary $–NH_2$, –C=O and –OH groups, which are rather active and, so, can react each other. These reactions are promoted by temperature to form crosslinked amino-carbonyl bonds (Wool and Sun, 2005). It is likely that similar interactions take place between the amino groups of proteins and carbonyl groups of cellulose molecules. This type of crosslinking results in a WBPC with greater MOR as the thermopressing temperature is raised. The hardness and stiffness become lower, probably due to the formation of an open network structure by the crosslinking between branched protein chains. For a given temperature, always for GTA/SPI = 0, the general trend is that the hardness and MOR decrease when the SPI/SD ratio increases from 20/80 to 35/65. This means that reducing the SD content in the biocomposite outcomes in less interaction between fibers and the proteins, resulting in a softer and less resistant WBPC.

It can be observed in Fig. 1 that WBPCs mechanical properties can be improved when the crosslinking agent was added (GTA/SPI = 0.375). For a given SPI/SD ratio and temperature, both the hardness and the MOR of the specimens prepared with GTA/SPI = 0.375 are similar or greater to those without crosslinking agent (GTA/SPI = 0). Thus, cross-linking of protein chains with GTA is essential to improve the mechanical properties of WBPCs. Furthermore, the cure rate will increase with temperature, and therefore the degree of crosslinking with GTA will be greater at 120 °C than 100 °C. This effect leads to an increase in hardness for SPI/SD = 20/80 and an increase in the MOR for SPI/SD = 35/65, when temperature was raised, indicating that the way in which protein chain crosslinking occurs depends on the SPI/SD ratio. In summary, the use of GTA and thermopressing at 120ºC allows to obtain WBPCs with greater hardness and rigidity, preserving the MOR obtained without GTA (Fig. 1). In agreement with our results, Wool and Sun (2005) established that it takes 10 min at 120 °C to reach the maximum curing resistance for soybean proteins, while at 150 °C only 3 min are needed. However, in our case, we observed excessive thermal degradation of the WBPCs when the temperature was kept at 130 °C for 20 minutes. Besides, no significant changes were observed in the mechanical properties of the WBPCs when 70 bar pressure was applied at 120 °C during 60 minutes. Therefore, we decided to use a maximum temperature of 120 °C for 30 minutes at 70 bar. It also stands out that specimens with a better surface finish are obtained when curing the specimens under these conditions.

Physical and mechanical properties of WBPCs obtained by pressing at 120 °C for 30 min, with different SPI/SD and GTA/SPI ratios, are summarized in Table 1. The average WBPC density, in all cases, was between 890 and 990 kg/m^3. These values are within the range of technical requirements specified for similar commercial products. Using ANOVA analysis, for a given SPI/SD ratio, it was determined that H is significant greater for WBPCs with GTA/SPI = 0.375 than for specimens with GTA/SPI= 0, while the corresponding densities are comparable. In contrast, for a given GTA/SPI, H, MOE and MOR tend to decrease as the SPI/SD ratio was raised, without significant differences in density average values. Finally, it was determined that the set with maximum values of H, MOE and MOR was obtained with GTA/SPI= 0.375 for SPI/SD between 20/80 and 35/65.

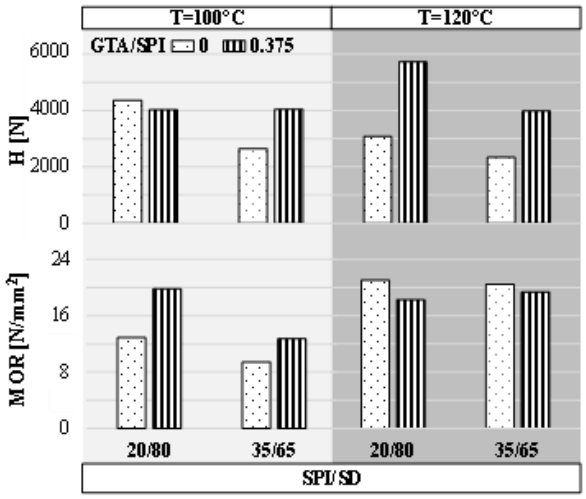

Figure 1: Mechanical properties of WBPCs, prepared at 70 bar and different molding temperatures. Compressing time: 30 min. SPI: soy protein isolate, SD: sawdust, GTA: glutaraldehyde (cross-linking agent).

In the absence of crosslinker (GTA/SPI=0), and considering that density average values are not significant different for SPI/SD between 20/80 and 65/35, the mechanical properties of WBPCs has been mainly attributed to adhesive strength reached from a combination of mechanical interlocking, penetration and interaction of the proteins with the cellulosic substrate. It has been suggested that small protein molecules can penetrate wood surface cells, staying at their lumen, generating a mechanical anchor between matrix and fiber components (Wool and Sun, 2005). Besides, it must be taking into account that the degree of crosslinking between protein chains, and also between proteins and cellulose molecules, can help to improve this adhesive strength. In the presence of GTA, new covalent bonds are formed, increasing the crosslinking of protein chains and, as a consequence, there is an increase in stiffness (MOE) and hardness (H) of the material (Table 1). In general, the MOR for WBPCs containing GTA is slightly lower than for specimens without GTA. It is likely that protein cross-linking with GTA reduces the number of the shortest protein chains that can get into the lumen of the wood surface cells, reducing thus the effect of the

Table 1. Physical and mechanical properties of WBPCs (Wood Bio-Plastic Composites) with different composition prepared by thermo-pressing at 70 bar and 120°C during 30 min.

SPI/SD	**20/80**		**35/65**		**50/50**		**65/35**		CS[d]
GTA/SPI	0	0.375	0	0.375	0	0.375	0	0.375	
Density [kg/m^3]	890±6	930±11	860±16	940±2	870±23	990±14	940±23	950±23	790
H[a] [N]	3072±72	5720±330	2331±173	3985±710	1384±180	2664±108	1287±140	1647±114	5150
MOE[b] [N/mm^2]	2059±187	2552±162	1865±139	2473±170	1588±129	2315±123	1653±150	1640±76	2816
MOR[c] [N/mm^2]	21.0±0.6	18.3±1.0	20.5±0.8	19.3±0.9	15.1±1.2	14.1±1.2	16.3±0.7	13.9±0.5	30

SPI: soy protein isolate, SD: sawdust, GTA: glutaraldehyde.
[a]Janka Hardness, [b] Modulus of elasticity and [c] Modulus of rupture determined according ASTM D1037-99.
[d] Commercial sample based on urea-formaldehyde resins for comparison.

adhesion mechanism and so its resistance to rupture by bending stress.

In summary, the WBPCs with the best mechanical properties obtained so far are those with SPI/SD = 20/80 and 35/65, especially those in which SPI is cross-linked with GTA (GTA/SPI = 0.375). Although these samples have a MOR 30% lower than those determined for some commercial boards, they show good values of density, hardness and stiffness (Table 1). The rupture module could be improved by varying the temperature and pressing time, what can allow to control the degree of proteins crosslinking and, as a consequence, the hardness, stiffness and bending strength. This would lead to WBPCs with lower hardness and stiffness, but with greater resistance to rupture by bending stress.

For samples without crosslinker (GTA/SPI = 0), it was observed by SEM that the coating of SD particles with bioplastic depends on SPI/SD ratio (Figs. 2.A and 2.C). For example, a discontinuous coating of the fibers was observed for SPI/SD= 20/80 (Fig. 2.A), while a higher and more continuous coverage was determined when SPI/SD= 65/35 (Fig. 2.C). In both cases, the protein acts as an adhesive between the reinforcing fibers, and the WBPCs have a heterogeneous texture, formed by protein aggregates and holes. For the same SPI/SD ratios but with GTA/SPI = 0.375, a more continuous and smoothed formation of the bioplastic matrix was observed, probably as a result of the mayor crosslinking between the protein chains with GTA molecules (Figs 2.B and 2.D). This is in accordance with the highest hardness and stiffness observed for GTA/SPI = 0.375 with respect to the sample without GTA. In all cases, surface microfissures were detected. These microfissures are smaller and the amount of them per surface unit diminishes when the bioplastic is crosslinked (Figs. 2.B and 2.D).

The mechanical properties as a function of the GTA/SPI ratios, for SPI/SD = 20/80, are represented in Fig. 3. It is observed that both the hardness (H) and the modulus of elasticity (MOE), reached their maximum values for GTA/SPI between 0.1875 and 0.375. This indicates that, for a high percentage of fibers, an intermediate content of GTA contribute to reach an optimum degree of crosslinking, what allows to obtain the maximum values of H and MOE. On the other hand, it can be observed that the MOR decrease slightly from GTA/SPI = 0 to GTA/SPI = 0.375 and then drops drastically for GTA/SPI ≥ 0.5.

The decrease in H, MOE and MOR observed for GTA/SPI ≥ 0.5 could be accounted from the excess of crosslinker that did not react with the amino groups of the proteins, what give place to two possibilities, that are not mutually exclusive: a) only one of the two carbonyl groups (– C=O) of the GTA molecules can react with the amino groups (– NH_2) of the proteins, giving place to branched polymer chains instead of a network;

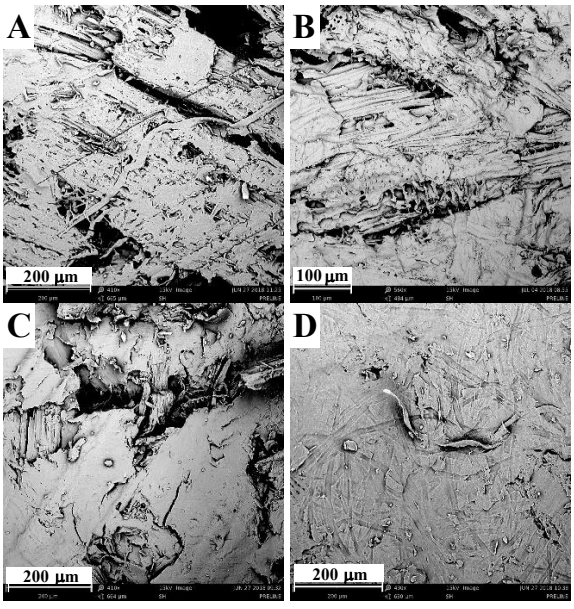

Figure 2: SEM images of WBPCs with different SPI/SD and GTA/SPI ratios. A) SPI/SD = 20/80, GTA/SPI = 0; B) SPI/SD = 20/80, GTA/SPI = 0.375; C) SPI/SD = 65/35, GTA/SPI = 0; D) SPI/SD = 65/35, GTA/SPI = 0.375. SPI: soy protein isolate, SD: sawdust, GTA: glutaraldehyde.

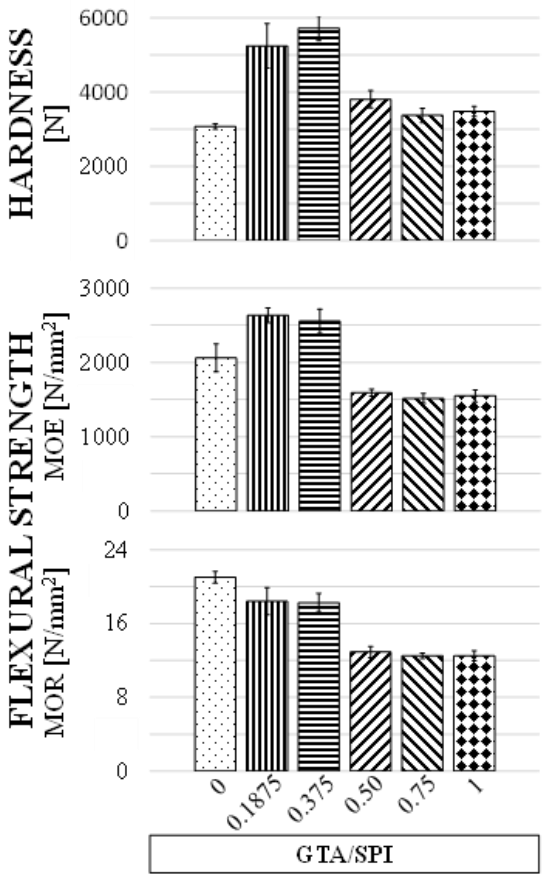

Figure 3: Mechanical properties of WBPCs for SPI/SD=20/80 and different GTA/SPI ratios. SPI: soy protein isolate, SD: sawdust, GTA: glutaraldehyde.

b) none of the two carbonyl groups react with the amino groups of protein chains and the free GTA molecules act as a plasticizer. In both case, crosslinked network is formed in lower degree than when GTA/SPI < 0.5 and, as a consequence, the mechanical resistance and the hardness of the bioplastic diminish.

B. Water absorption and swelling

The water absorption rate in the first 2 h was almost double in crosslinked WBPCs than in those without GTA (Fig. 4.A, full lines). The opposite behavior was observed after the following 22 h in water, i.e., specimens without GTA adsorbed much more water than those cross-linked with GTA (Fig. 4.A, dashed lines). It is likely that, in absence of GTA, the smallest protein molecules penetrate into the lumen of wood surface cells and partially block the capillary porous structure (Wool and Sun, 2005; Stark et al, 2010), hindering thus the diffusion of water molecules. Instead, crosslinked networks, which include the shorter protein chains, are formed when GTA is added. These networks are too large as to get into the lumen of the wood surface cells and, thus, the partial blockage of them is much lower than in WBPCs without GTA. Therefore, water molecules can diffuse more easily through the capillary porous structure and this explain why WBPCs containing GTA absorb water more rapid than those without GTA. The diminution of the water amount absorbed with the increase in SPI/SD ratio, for a given GTA/SPI (Fig. 4.A), is explained in a similar way, since the increase in the amount of SPI rises the probability of filling the lumen of wood cells with short protein chains.

The above also explains why water absorption in the next 22 h is much smaller for WBPCs prepared with GTA than for WBPCs without GTA. In the former case, the filling of the most accessible wood cells occurs rapidly in the first 2 h. Then, in the next 22 h, water fill the less accessible cells of cellulosic fibers. Instead, in samples without GTA, as the access and diffusion of water to the partially block cells is more difficult, water molecules diffuse very slowly and fill cells just after the subsequent 22 hours. As these cells are partially occupied by the shortest protein chains, the final amount of absorbed water is lower in sample with GTA/SPI= 0 than the one in samples containing GTA.

In general, the swelling of these WBPCs is proportional to the amount of water absorbed (Fig. 4.B). These values are lower than those established in technical requirements (Akgul, 2012): 35% maximum for commercial samples of similar characteristics. It is also worth to mention that, after drying, the shape and thickness of these WBPCs were practically recovered, the residual swelling being less than 6% in all samples (Fig. 5). Instead, water absorption tests with some commercial composites based on urea-formaldehyde resins, and their subsequent drying, showed that they suffer irreversibly swelling and deformation.

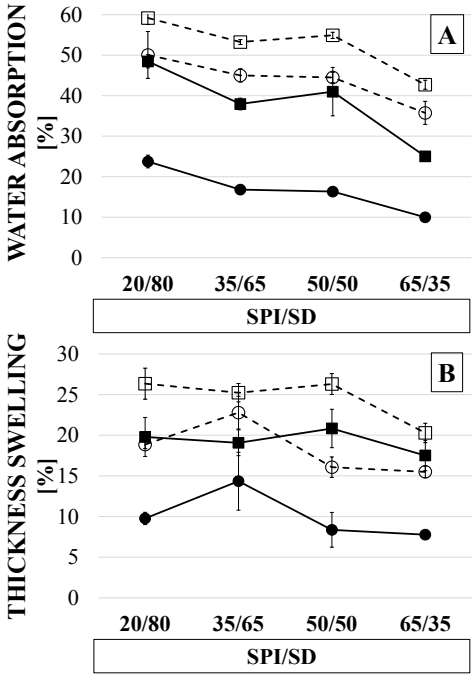

Figure 4: Water absorption and thickness swelling of WBPCs with different SPI/SD and GTA/SPI ratios (●○ GTA/SPI=0; ■□ GTA/SPI= 0,375). Full line: 2 h, dashed line: 24 h. SPI: soy protein isolate, SD: sawdust, GTA: glutaraldehyde.

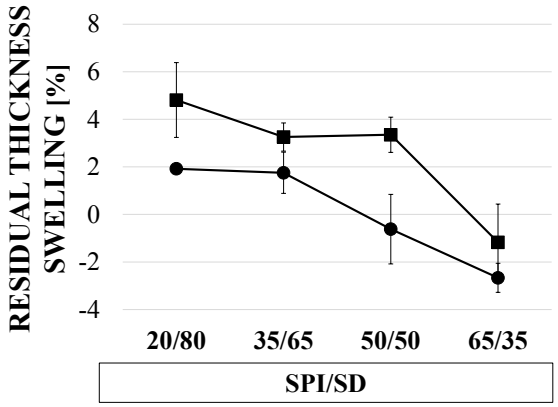

Figure 5: Residual swelling of WBPCs with different SPI/SD and GTA/SPI ratios (● GTA/SPI=0, ■ GTA/SPI= 0,375).

The trends observed for the residual swelling as a function of SPI/SD (Fig. 5) are similar to those for water absorption and swelling of WBPCs (Fig. 4.A and 4.B), which suggests the reversibility of the process.

IV. CONCLUSIONS

In this work, the processing conditions and the optimal ratios of crosslinker, biopolymer and reinforcement fibers to obtain WBPC, with physical and mechanical properties similar to those of some commercial products, are determined. These WBPCs can be manufactured from industrial residues and surpluses by applying molding pressures lower than those employed in some previous works and avoiding the use of high toxicity reagents. The WBPCs with the best mechanical properties were obtained at 120°C and 70 bar, with SPI/SD between 20/80 and 35/65, and GTA/SPI in the range of 0.18 to 0.38. An excess of SPI and/or GTA acts in detriment of the mechanical properties of the WBPCs.

The improved physical and mechanical properties of these WBPCs are explained on the basis of interactions between protein chains, and interactions of biopolymer chains with the cellulose fibers and the crosslinker. For the optimum SPI/SD and GTA/SPI ratios, these interactions lead to the increase of hardness (H), modulus of elasticity (MOE) and modulus of rupture (MOR).

In summary, the addition of sawdust and crosslinker to the bioplastic matrix produces an increase of the stiffness, hardness and bending strength of these WBPCs, but it also augments water absorption and swelling of these materials. However, WBPCs are able to recover the original dimensions after the drying in an oven.

REFERENCES

Akgul, M., N. Ayrilmis, O.Çamlıbel and S. Korkut, "Potential utilization of burned wood in manufacture of medium density fiberboard," *J. Mater. Cycles Waste Manag.,* **15**(2), 195-201 (2013).

American Cancer Society, "Formaldehyde". Recovered from https://www.cancer.org/cancer/cancer-causes/formaldehyde.html (2014)

ASTM Standard D1037. "Standard test methods for evaluating properties of wood-base fiber and particle panel materials." ASTM International,West Conshohocken (1999).

Bai, H. and X. Liu, "Soy protein isolate-based films: preparation, properties, and applications," In: *Soy-based Bioplastics*, Smithers Rapra Technology, Shrewsbury (2017).

Bogoeva-Gaceva, G., M. Avella, M. Malinconico, A. Buzarovska, A. Grozdanov, G. Gentile and M.E. Errico, "Natural fiber eco-composites," *Polym. Compos.,* **28**, 98-107 (2007).

Chan, C.M., L-J. Vandi, S. Pratt, P. Halley, D. Richardson, A. Werker and B. Laycock, "Composites of wood and biodegradable thermoplastics: a review," *Polymer Rev.,* **58**(3), 444-494 (2017).

L'hocine, L., J.I. Boye and Y. Arcand. "Composition and functional properties of soy protein isolates prepared using alternative defatting and extraction procedures," *J. Food. Sci.,* **71**(3), 137-145 (2006).

Mitra, B.C., "Environment friendly composite materials: biocomposites and green composites," *Def. Sci. J.,***64**(3), 244-261 (2014).

Netravali, A.N. and S. Chabba, "Composites get greener," *Mater. Today*,**6**(4), 22-29 (2003).

Rahman, K.S., N. Islam, M. Rahman, O. Hannan, R. Dungani and A. Khalil, "Flat-pressed wood plastic composites from sawdust and recycled polyethylene terephthalate (PET): physical and mechanical properties," *SpringerPlus***2**, 629-636 (2013).

Schwarzkopf, M.J., M.D. Burnard. "Wood-plastic composites - Performance and environmental impacts," In: *Environmental impacts of traditional and innovative forest-based bioproducts*,Springer, Singapore (2016).

Song, F., D. Tang, X. Wang and Y. Wang, "Biodegradable soy protein isolate-based materials: a review," *Biomacromolecules*,**12**, 3369-3380 (2011).

Stark, N.M., Z. Cai, C. Carll, "Wood-based composite materials panel products, glued-laminated timber, structural composite lumber, and wood–nonwood composite materials," In: *Wood handbook: wood as an engineering material*, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison (2010).

Wang, Y., X. Mo, X. Sun and D. Wang, "Soy protein adhesion enhanced by glutaraldehyde crosslink," *J. Appl. Polym. Sci.*, **104**, 130-136 (2007).

Wool, R.P and X. Sun, *Bio-based polymers and composites*. Elsevier Academic Press, Burlington (2005).

Wong S.S., D.M. Jameson, *Chemistry of protein and nucleic acid cross-linking and conjugation*. Taylor & Francis Group, Boca Raton (2012).