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Extrusion Effects with Bactericidal Additives in Polymer Wood Composites

Wood polymer composite is an important material class for industries. Microbiological properties can be an important aspect to enlarge its application base. The biocidal properties of wood polymer composite (WPC) can be aggregated by incorporation of biocidal additives on its composition. But, an important aspect is the evaluation the influence of the fabrication process on its biocidal properties. In particular, the temperature and screw velocity are important parameters for extrusion processes, and the mass proportions of the compounds are important factors to define the WPC properties. Different combinations of process conditions and mass proportions of the composite can promote variation in the magnitude of the bactericidal effect. The bactericidal properties are aggregated in the composite by organic bactericidal additive and the high temperature and high shear rate during the extrusion process can affect the effectiveness of the bactericidal additive function. This paper investigates the effects of the extrusion process parameters associated with different percentages of bactericidal additives on the WPC. The results showed significant effects on the bactericidal properties that depended only on the bactericidal content.

1 Introduction

In the last two decades, many studies have been conducted on composites with polymeric matrix and wood residue elements. Some research has been carried out on the processing conditions of the composite (Balasurya et al., 2001 and Bhattacharyya et al., 2003), the mechanical properties and composition (Byskov et al., 2002; Coutinho et al., 1999; Elvy et al., 2001 and Ichazo et al., 1995) and the biodegradability and photo-degradability of WPC (Tascioglu et al., 2003; Geoge et al., 2005, Laurent et al., 2001).

WPC is a polymeric composite, where the wood mass substitutes for the polymeric resins, which generally have a relatively high cost, while the wood residue can be found at relatively low cost. Therefore, the production of this composite is an excellent way to utilize wood residues.

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WPC composite is an important material for the plastic industry. WPC composite is a combination of woody materials with thermoplastic polymers and is a material class attractive in the USA and Europe with a wide range of commercial products already available in the market (Gupta et al., 2007). WPC composites are used in a large number of applications in the automotive, civil construction, marine, electronic and aerospace industries (Schwarzinger et al., 2008). However, if the special properties of this class of material, in particular bactericidal properties, are enhanced, its application can be wide spread.

The utilization of WPC with bactericidal properties (BWPC – bactericidal wood polymer composite) can be relatively inexpensive. Technological growth in the last decade has led to a need for many special properties in materials. BWPC composites can be used in the manufacture of products for home use, public sanitation, laboratories, hospitals and various other industries. In powdered form, bactericidal composites can be used on chicken farms or in other animal surroundings as a cheap alternative for the prevention of bacterial diseases in animals.

BWPC composites can be obtained by the addition of the bactericidal compound during the production of WPC composites. These composites provide bactericidal effects that depend on the additive percentage and the ambient temperature (Fiori et al., 2008a). The extrusion processing parameters, i. e., temperature and screw velocity, can promote different rheological properties, influence composite degradation and affect the bactericidal properties of the composite. In addition, the processing conditions are an important factor in the production of BWPC in terms of defining the bactericidal effect.

Many products are manufactured with WPC composite by linear extrusion. This technique is traditional and very important in the production of many polymeric products. Thus, this work presents studies on the effects of the extrusion process and the additive percentage on the bactericidal properties of BWPC composite. These results are very relevant for the manufacture of BWPC products with bactericidal properties, because they demonstrate if the extrusion technical and additive percentage it influences on the biocidal properties of the composite.

2 Experimental

This work utilized polypropylene (PP) as the composite matrix and wood sample flour as the composite element for

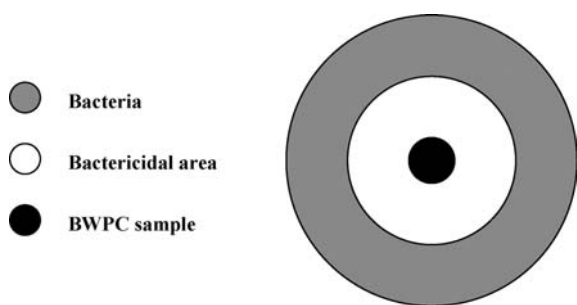


Fig. 1. Illustration of the bactericidal area and a bactericidal BWPC sample

BWPC. The wood sample (Pinus Elliot) had particle sizes between 28 to 100 mesh and after being dried for 100 min at 110 °C had water content on dry wood residues about 9.00 wt.%, determined by thermogravimetric analyses (TG).

The mixture of polypropylene, dry wood flour and the bactericidal additive was made with a homogeneous system at ambient temperature. The homogenate process was realized in the cylindrical system within two helix coupled with velocity con-

trolled during one hour. The antimicrobial additive was a commercial additive that contained triclosan (Ciba Chemical). The BWPC composites were prepared with different ratios between the bactericidal additive, polypropylene and wood flour. All of the BWPC composites were processed utilizing an extrusion system, Oryzon-OZ-E-EX-L22, with an L/D (relationship between the length and the diameter of the screw) equal to 17 and screw diameter (D) 22 mm. There were four regions with controlled temperatures, and different screw velocities and temperatures were investigated.

The experiments were performed at processing temperatures with a minimum value of 160 °C, a mean value of 175 °C and a maximum value of 190 °C. The screw velocity ranged from 40 to 140 min⁻¹ with a mean value of 90 min⁻¹. The additive percentage ranged from 0.10 wt.% to 2.10 wt.% with a mean value of 1.10 wt.%. The polypropylene percentage ranged from 40.00 wt.% to 80.00 wt.%, with a mean value of 60.00 wt.%.

For the microbiological tests, four cylindrical samples of BWPC were made with a diameter of 0.50 cm and a height of 0.50 cm for each processing condition and composition. The samples underwent microbiological tests involving diffusion in agar using two types of bacteria: Escherichia Coli (EC-

	A wt. %	PP wt. %	T °C	V _{screw}	Bactericidal halo φ – cm				<φ> cm	E _{bac} cm ²	σ
1	0.10	40.00	160.0	40	2.8	3.0	3.1	3.2	3.0	7.2	0.1
2	2.10	40.00	160.0	140	4.9	4.9	5.3	5.1	5.0	20.0	0.2
3	0.10	80.00	160.0	140	3.7	3.3	4.0	3.5	3.6	10.2	0.3
4	2.10	80.00	160.0	40	6.2	6.5	5.6	5.5	5.9	27.7	0.5
5	0.10	40.00	190.0	140	2.8	2.9	2.8	2.4	2.8	5.9	0.2
6	2.10	40.00	190.0	40	5.4	5.4	5.3	5.3	5.4	22.5	0.1
7	0.10	80.00	190.0	40	3.3	3.6	3.3	3.3	3.4	8.9	0.1
8	2.10	80.00	190.0	140	5.5	5.3	5.2	5.2	5.3	21.8	0.2
9	1.10	60.00	175.0	90	4.7	4.8	4.8	5.1	4.8	18.3	0.2
10	1.10	60.00	175.0	90	5.1	4.9	4.8	4.7	4.9	18.7	0.2
11	1.10	60.00	175.0	90	5.8	5.8	5.2	4.8	5.4	22.7	0.5

A (wt.%) – additive percentage; PP (wt.%) – polypropylene percentage; T (°C) – machine temperature; V_{screw} – screw velocity; φ – bactericidal halo diameter and E_{bac} – bactericidal effect

Table 1. Microbiological results for different processing conditions and compositions of the BWPC – Staphylococcus Aureus

	A wt. %	PP wt. %	T °C	V _{screw}	Bactericidal halo φ – cm				<φ> cm	E _{bac} cm ²	σ
1	0.10	40.00	160.0	40	1.1	1.1	1.0	1.0	1.0	0.8	0.0
2	2.10	40.00	160.0	140	3.5	3.7	3.5	3.6	3.6	10.0	0.1
3	0.10	80.00	160.0	140	2.0	1.9	2.0	1.8	1.9	2.9	0.1
4	2.10	80.00	160.0	40	3.7	3.4	3.4	3.5	3.5	9.6	0.1
5	0.10	40.00	190.0	140	1.3	1.3	1.2	1.4	1.3	1.3	0.1
6	2.10	40.00	190.0	40	3.7	3.9	3.4	3.4	3.6	10.2	0.2
7	0.10	80.00	190.0	40	1.7	1.7	1.6	1.4	1.6	2.0	0.1
8	2.10	80.00	190.0	140	3.6	3.8	3.6	3.6	3.6	10.3	0.1
9	1.10	60.00	175.0	90	3.1	3.1	3.0	3.3	3.1	7.6	0.1
10	1.10	60.00	175.0	90	3.2	3.2	3.1	3.2	3.1	7.8	0.0
11	1.10	60.00	175.0	90	3.5	3.5	3.6	3.5	3.5	9.7	0.0

A (wt.%) – additive percentage; PP (wt.%) – polypropylene percentage; T (°C) – machine temperature; V_{screw} – screw velocity; φ – bactericidal halo diameter and E_{bac} – bactericidal effect

Table 2. Microbiological results for different processing conditions and compositions of the BWPC – Escherichia Coli

ATCC 25922) and Staphylococcus Aureus (SA-ATCC 25923). These bacteria type are many applied on microbiological tests and are sensitive to triclosan compound. When incorporated in the WPC compound it joins the bactericide properties (Fiori et al., 2008b).

For the evaluation of the bactericidal effects, a methodology was developed that defined the bactericidal area (Fiori et al., 2008b). An illustration of this method is presented in Fig. 1. In this way, many studies can be accomplished by associating the numeric values of this area with the bactericidal action and other interesting factors. This study considers the halo area for the bactericidal effect (E_{bac}) of the BWPC composites.

3 Results and Discussion

Table 1 and Table 2 show the microbiological effects values for different processing conditions for the BWPC composites with different temperatures, screw velocities, bactericidal addi-

tive percentages and polypropylene percentages in terms of Staphylococcus Aureus bacteria and Escherichia Coli bacteria activity. The results show the presence of bactericidal effects with low standard deviations and significant differences for the bactericidal response (E_{bac}), depending of the parameters combination.

The microbiological tests showed a large microbiological halo and an excellent bactericidal effect for the composites with the triclosan additive for both bacteria types. In both tests, large areas of death occurred for the bacteria and depend of bacterial type. However, for the Escherichia Coli bacteria, the microbiological halo was smaller, because this microorganism had a higher resistance to than the Staphylococcus Aureus bacteria. Microbiological studies indicate that Escherichia Coli are gram-negative bacteria, and Staphylococcus Aureus is gram-positive. Gram-negative bacteria have a cellular wall with a specific composition that offers higher resistance to bactericidal compounds than gram-positive bacteria (Denyer et al., 2002). This characteristic promotes a lower

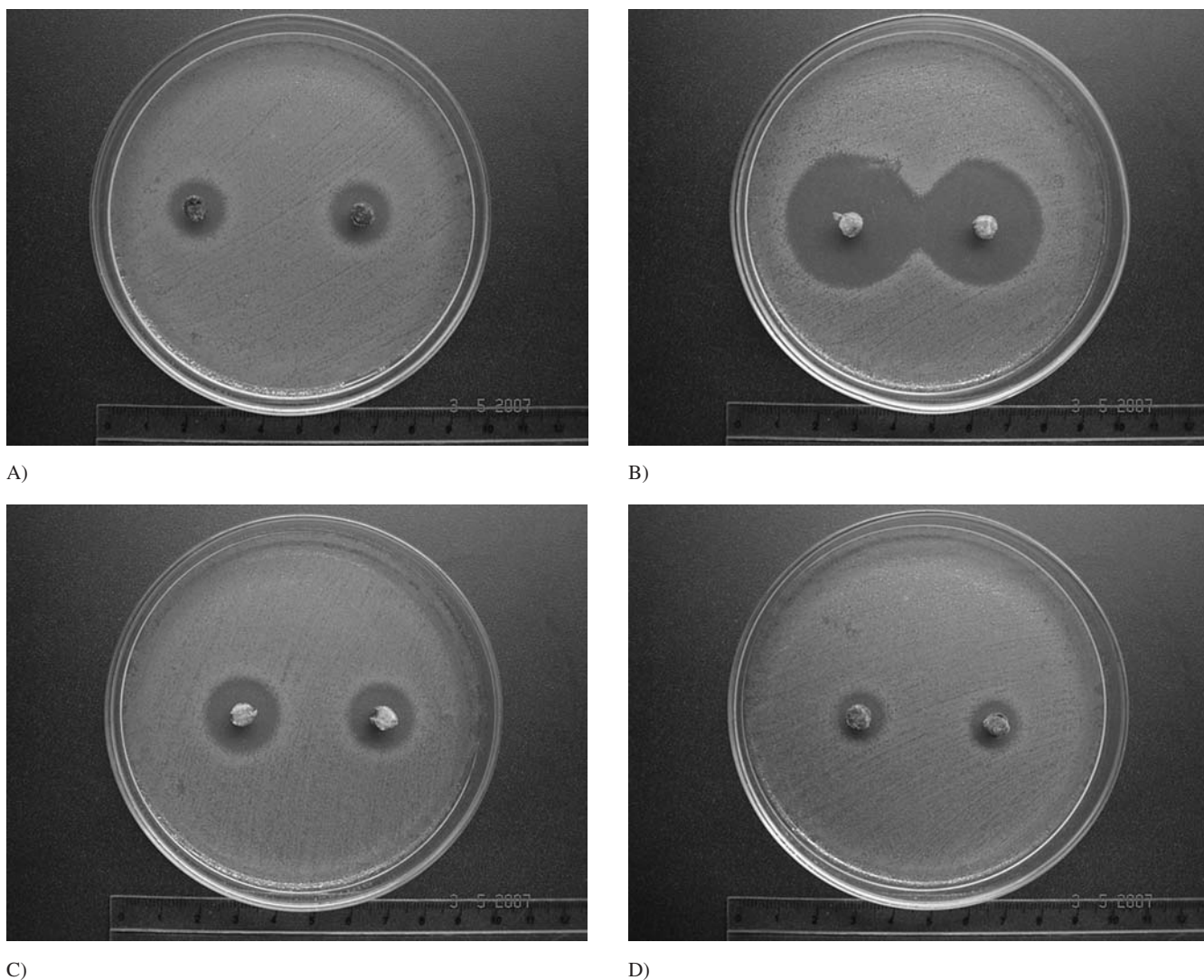


Fig. 2. Microbiological results with *Escherichia Coli* for different processing conditions and compositions of the BWPC: (A) test 1, (B) test 4, (C) test 3, and (D) test 5 – Table 2

diffusion halo with *Escherichia Coli* bacteria than that with *Staphylococcus Aureus*.

Fig. 2 shows the agar diffusion results for different processing conditions and compositions of the BWPC with *Escherichia Coli*. The presence of the halo indicates the bactericidal effect of the BWPC. The difference between halo diameters for different production conditions indicates the effect of the percentage additive or of the processing conditions on the antimicrobial action of the composite.

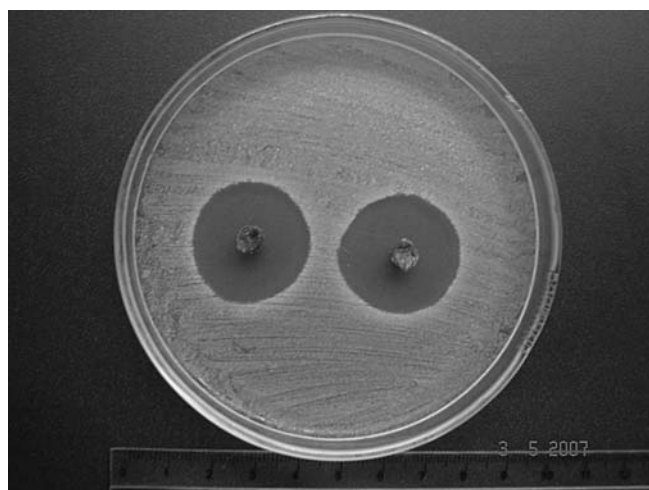
Figs. 2A and B correlate two different production conditions for BWPC with different additive percentages for the same processing condition. The results show the significant effect of the additive concentration on the bactericidal properties of the composite. The increase of the additive percentage promotes an increase in the bactericidal halo of around 1000.0% and indicates a significant modification of the BWPC bactericidal effects.

Figs. 2C and D correlate the microbiological results for the BWPCs processed with different machine temperature condi-

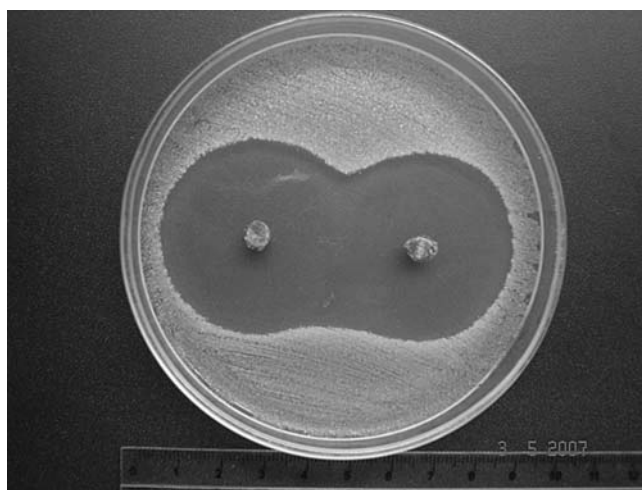
tions and the same screw velocity and same bactericidal additive percentage. The microbiological test shows low variability for the bactericidal halo with the BWPC processed at 160.0 °C (Fig. 2C) and 190.0 °C (Fig. 2D).

Fig. 3 shows microbiological results with *Staphylococcus Aureus* bacteria for the BWPC processed with different processing temperatures and different compositions. Fig. 3A and B show the microbiological results for the BWPC samples processed with different additive percentages at the same processing temperature. The results indicate the significant effect of the additive percentage on the bactericidal properties of the composite. The increase in the additive percentage promoted an increase of around 300.0% of the bactericidal halo (bactericidal effect) of the BWPC.

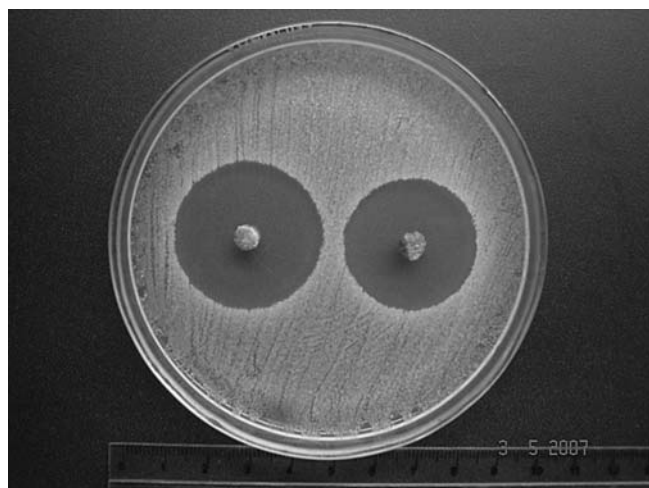
Figs. 3C and D show the microbiological results for BWPC samples processed with different processing temperatures and the same bactericidal additive percentage. The microbiological test shows the low variability of the bactericidal halo for the BWPC processed at 160.0 °C (Fig. 3C) and 190.0 °C (3D).



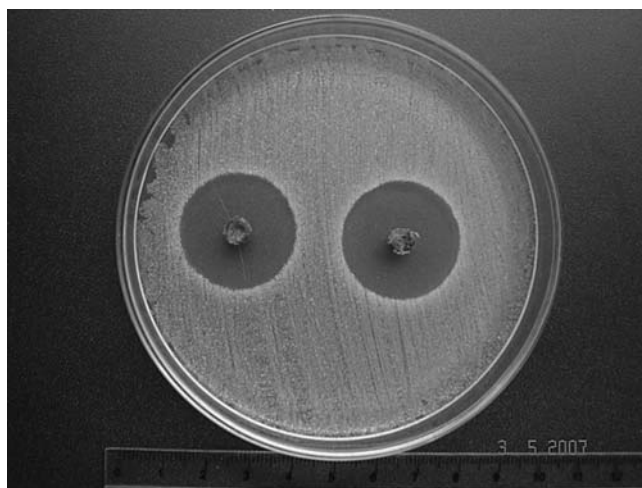
A)



B)



C)



D)

Fig. 3. Microbiological results with *Staphylococcus Aureus* for different processing conditions and compositions of the BWPC: (A) test 1, (B) test 4, (C) test 3, and (D) test 5 – Table 1

The variability of the bactericidal halo is low for the BWPC processed with the same bactericidal additive percentage and different processing temperatures for both bacteria types. So, the low difference between results not permits to define the significance for the microbiological results. The significant effect of the processing temperature depends on statistical analysis to reach a conclusion.

Table 3 shows the variance analysis, and Table 4 gives the estimated statistical effects for the microbiological results with *Staphylococcus Aureus* for BWPC samples processed with different temperatures and compositions. The statistical results indicate significant differences only for the additive percentage variable with positive estimate effects of (16.02 ± 3.26) % and a statistical coefficient of 8.01 ± 1.63 .

ANOVA – <i>Staphylococcus Aureus</i> bacteria – $R^2 = 0.8135$					
	SS	Df	MS	F	P
*A (%)	*513.4192	*1.0000	*513.4192	*24.1269	*0.0390
PP (%)	45.9815	1.0000	45.9815	2.1608	0.2794
T (°C)	2.6298	1.0000	2.6298	0.1236	0.7588
V_{screw} (min ⁻¹)	8.5659	1.0000	8.5659	0.4025	0.5907
Lack of fit	89.0721	4.0000	22.2680	1.0464	0.5421
Pure error	42.5599	2.0000	21.2800		
Total SS	702.2284	10.0000			

* – significant variable. A (wt.%) – additive percentage; PP (wt.%) – polypropylene percentage; T (°C) – machine temperature; V_{screw} – screw velocity; ϕ – bactericidal halo diameter and E_{bac} – bactericidal effect

Table 3. Variance analysis (ANOVA) for microbiological results with *Staphylococcus aureus* for BWPC samples processed with different temperatures and compositions

Estimated statistical effects – <i>StaphylococcusAureus</i> bacteria – $R^2 = 0.8135$								
	Effect	Std.Err.	t(6)	P	-95 % Cnf.Limit	+95 % Cnf.Limit	Coeff.	Std. Err. Coeff.
*Mean	*17.41	*1.39	*12.52	*0.01	*11.43	*23.40	*17.41	*1.39
*A (%)	*16.02	*3.26	*4.91	*0.04	*1.99	*30.06	*8.01	*1.63
PP (%)	4.79	3.26	1.47	0.28	-9.24	18.83	2.40	1.63
T (°C)	-1.15	3.26	-0.35	0.76	-15.18	12.89	-0.57	1.63
V_{screw} (min ⁻¹)	-2.07	3.26	-0.63	0.59	-16.10	11.97	-1.03	1.63

* – significant variable. A (wt.%) – additive percentage; PP (wt.%) – polypropylene percentage; T (°C) – machine temperature; V_{screw} – screw velocity; ϕ – bactericidal halo diameter and E_{bac} – bactericidal effect

Table 4. Estimated statistical effects for microbiological results with *Staphylococcus aureus* for BWPC samples processed with different temperatures and compositions

ANOVA – <i>Escherichia coli</i> bacteria – $R^2 = 0.9008$					
	SS	Df	MS	F	P
*A (%)	*141.2470	*1.0000	*141.2470	*120.4461	*0.0082
PP (%)	1.7033	1.0000	1.7033	1.4524	0.3514
T (°C)	0.0005	1.0000	0.0005	0.0004	0.9855
V_{screw} (min ⁻¹)	0.0259	1.0000	0.0259	0.0221	0.8954
Lack of fit	13.3963	4.0000	3.3491	2.8559	0.2758
Pure error	2.3454	2.0000	1.1727		
Total SS	158.7185	10.0000			

* – significant variable. A (wt.%) – additive percentage; PP (wt.%) – polypropylene percentage; T (°C) – machine temperature; V_{screw} – screw velocity; ϕ – bactericidal halo diameter and E_{bac} – bactericidal effect

Table 5. Variance analysis (ANOVA) for microbiological results with *Escherichia Coli* for BWPC samples processed with different temperatures and compositions

Estimated statistical effects – Escherichia Coli bacteria – $R^2 = 0.9008$								
	Effect	Std.Err.	t(6)	p	-95 % Cnf.Limit	+95 % Cnf.Limit	Coeff.	Std. Err. Coeff.
*Mean	*6.75	*0.33	*20.66	*0.00	*5.34	*8.15	*6.75	*0.33
*A (%)	*8.40	*0.77	*10.97	*0.01	*5.11	*11.70	*4.20	*0.38
PP (%)	0.92	0.77	1.21	0.35	-2.37	4.22	0.46	0.38
T (°C)	0.02	0.77	0.02	0.99	-3.28	3.31	0.01	0.38
V_{screw} (min^{-1})	-0.11	0.77	-0.15	0.90	-3.41	3.18	-0.06	0.38

* – significant variable. A (wt.%) – additive percentage; PP (wt.%) – polypropylene percentage; T (°C) – machine temperature; V_{screw} – screw velocity; ϕ – bactericidal halo diameter and E_{bac} – bactericidal effect

Table 6. Estimated statistical effects for microbiological results with Escherichia Coli for BWPC samples processed with different temperatures and compositions

Table 5 shows the variance analysis and Table 6 gives the estimates statistical effects for the microbiological results with Escherichia Coli for BWPC samples processed with different temperature conditions and different compositions. The statistical results indicate significance values only for the additive percentage variable with positive estimate effects of 8.40 ± 0.77 and a statistical coefficient of 4.20 ± 0.38 .

The positive estimated effects for both types of bacteria indicate the positive effect of the additive percentage factor on the bactericidal properties of the BWPC. An increase in the percentage of bactericidal additive promotes an increase in the bactericidal effects of the BWPC composite.

For both bacteria types, the processing temperature and screw velocity did not have significant statistical effects on the microbiological response of the BWPC. The statistical analysis showed that the microbiological response of the BWPC does not depend on the processing conditions for the range of screw velocities and temperatures applied. Recent work has shown that the microbiological response of the BWPC depends on the length of time the composite is exposed to different temperatures. The work of Fiori et al. showed that after exposing the BWPC for several days at 110°C , thermo-degradation of the triclosan compound occurred and consequently the bactericidal effect of the composite decreased (Fiori et al., 2008a).

The estimated effects shown in Tables 4 and 6 were obtained with statistical equations that correlate the bactericidal effect with the significant variable studied. Eqs. 1 and 2 present a linear relation between the bactericidal effect and percentage bactericidal additive. These equations can be utilized by industries before BWPC production to define the additive percentage values associated with the magnitude of the bactericidal effect.

$$E_b(A) = 17.41 (\pm 1.39) + 8.01 (\pm 1.63)A, \quad (1)$$

$$E_b(A) = 6.,75 (\pm 0.33) + 4,20 (\pm 0.38)A, \quad (2)$$

where the E_b is the BWPC bactericidal effect, and A is the percentage of the triclosan additive in the composite.

4 Conclusion

This study showed that the bactericidal properties of BWPC composites produced with triclosan additive are influenced

by the additive percentage and the effects of the extrusion parameters, i.e., temperature and screw velocity, are not significant. These results are very important for several industries. They indicate that the traditional extrusion process and the process parameters, the temperature and screw velocity, do not prejudice the microbiological properties of BWPC composites.

References

- Balasurya, P. W., et al., "Mechanical Properties of Wood Flake – Polyethylene Composites. Part I: Effect of Processing Methods and Matrix Melt Flow Behavior". *Composites Part A*, **32**, 619–629 (2001) DOI:10.1016/S1359-835X(00)00160-3
- Bhattacharyya, D., et al., "Thermoforming Wood Fibre-Polypropylene Composite Sheets". *Compos. Sci. Technol.*, **63**, 353–365 (2003) DOI:10.1016/S0266-3538(02)00214-2
- Byskov, E., et al., "Kinkband Formation in Wood and Fiber Composites – Morphology and Analysis". *Int. J. Solids Struct.*, **39**, 3649–3673 (2002) DOI:10.1016/S0020-7683(02)00174-9
- Coutinho, F. M. B., Costa, T. H. S., "Performance of Polypropylene – Wood Fiber Composites". *Polym. Test.*, **18**, 581–587 (1999) DOI:10.1016/S0142-9418(98)00056-7
- Denyer, S. P., Maillard, J. Y., "Cellular Impermeability and Uptake of Biocides and Antibiotics in Gram-negative Bacteria". *J. Appl. Microbiol.*, **92**, 35–45 (2002). DOI:10.1046/j.1365-2672.92.5s1.19.x
- Elvy, S. B., et al., "Effects of Coupling Agents on the Physical Properties of Wood – Polymer Composites". *J. Mater. Process. Technol.*, **48**, 365–372 (1995) DOI:10.1016/0924-0136(94)01670-V
- Fiori, M. A., et al., "Effect of the Temperature in the Antimicrobial Action of the Bactericidal Wood Polymer Composite – BWPC". *Mater. Sci. Forum*, 591–593, 362–367 (2008a) DOI:10.4028/www.scientific.net/MSF.591-593.362
- Fiori, M. A., et al., "Bactericide Effect of Powder Glasses Submitted to Na+/Ag+ Ionic Exchange in Ionic Media Containing Different Concentration of AgNO₃". *Mater. Sci. Forum*, 591–593, 849–85 (2008b) DOI:10.4028/www.scientific.net/MSF.591-593.849
- Geoge, B., et al., "Photodegradation and Photostabilisation of Wood – The State of the Art". *Polym. Degrad. Stab.*, **88**, 268–274 (2005) DOI:10.1016/j.polymdegradstab.2004.10.018
- Gupta, B. S., et al., "Surface Properties and Adhesion of Wood Fiber Reinforced Thermoplastic Composites". *Colloids Surf., A*, **302** (1–3), 388–395 (2007) DOI:10.1016/j.colsurfa.2007.03.002
- Ichazo, M. N., et al., "Polypropylene/Wood Flour Composites: Treatments and Properties". *Compos. Struct.*, **54**, 207–214 (2001) DOI:10.1016/S0263-8223(01)00089-7
- Laurent, M. M., et al., "Photoaging and Stabilization of Rigid PVC/Wood-Fiber Composites". *J. Appl. Polym. Sci.*, **80**, 1943–1950 (2001) DOI:10.1002/app.1292

Schwarzinger, C., et al., "Analysis of Wood Polymer Composites by Two-stage Pyrolysis-GC/MS". *J. Anal. Appl. Pyrolysis*, **83**, 213–219 (2008) DOI:10.1016/j.jaap.2008.09.008

Tascioglu, C., et al., "Monitoring Fungal Degradation of E-Glass/Phenolic Fiber Reinforced Polymer (FRP) Composites Used in Wood Reinforcement", *Int. Biodeterior. Biodegrad.*, **51**, 157–165 (2003) DOI:10.1016/S0964-8305(02)00100-2

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Bibliography
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